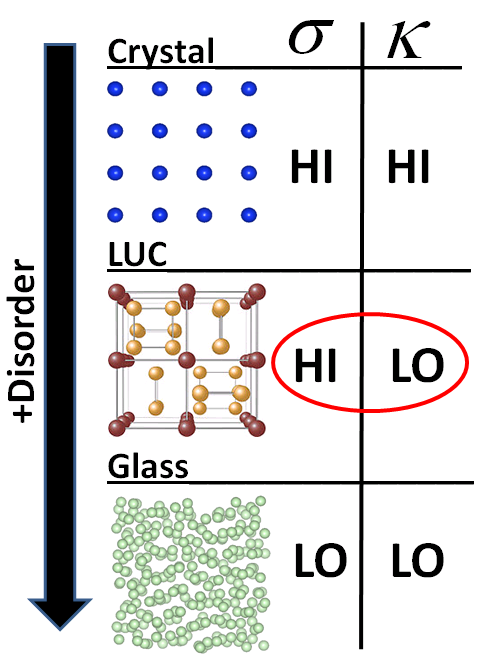
Project Title: Atomistic Modeling of Thermal Transport in Large Unit Cell Crystals for Thermoelectric Application

Research Team:

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**Project Description**

Thermoelectric energy generation - the transformation of wasteheat into useful electricity - is a promising method for energy sustainability []. In this method, thermoelectric materials directly convert wasted heat into electricity because of intrinsic material properties. The main obstacle for thermoelectric efficiency of materials is maximizing the thermoelectric figure of merit defined as: **ZT =** , where T is the average device temperature, S is the seebeck coefficient (a ratio of the induced voltage for an applied temperature difference), is the electrical conductivity, and is the thermal conductivity. For thermoelectric devices to be efficient and competitive with other power generation requires ZT>3, depending on the application[cite]. Since the 1960s [cite], no progress was made on improving ZT, until the mid 1990s when Quantum confinement and dimensional effects were theorized to potentially increase ZT>3 [cite]. This hasn’t been realized yet [cite], and major progress on increasing ZT since then has focused on reducing the of thermoelectric materials [cite]. Introducing disorder has been particularly effective at reducing [cite]. The key is to reduce without reducing , which tend to both be large in crystalline (ordered) materials and produce very low ZT [cite]. The ideal thermoelectric can be thought of as an “electron-crystal/ phonon-glass” [cite] (see Figure 1).

Figure 1: LUC crystals can maximize ZT. ZT.

Large Unit Cell (LUC) materials have a crystalline (ordered) structure, but the basic building block (unit cell) of the crystal has a large number of distinct atoms [cite]. This makes them effectively disordered over length scales on the order of the atomic distances, and as such, their thermal conductivities can be as low as a glass, which is completely disordered [cite]. The key difference with LUC materials is that they are still ordered for electron transport, which results in a large and ZT. Thus, LUC crystals are “electron-crystals/phonon-glasses”. For current LUC materials, ZT<3, but progress has been steady [cite].

Improving the ZT of LUC materials requires a detailed analysis of the atomistic behavior of these LUC crystals. The atomistic computational tools available to the Nanoscale Transport Phenomena Laboratory (NTPL) can provide the required anaylsis (maybe talk about equipment?). First, classical simulations using Molecular and Lattice Dynamics (MD and LD) will be performed [cite]. These methods are referred to as “classical” since they do not include quantum mechanical effects explicitly [cite]. These classical simulation results will then be used to design Ab-initio (from first principles) simulations. Ab-initio simulations include the effects of quantum mechanics explicitly, and so have very high accuracy []. The ab-initio simulation results can then be directly compared to experiment to more efficiently search the LUC crystal design space. *The objective of this project is to build a robust, accurate, and efficient computational framework for predicting the thermal conductivity of LUC crystalline solids to improve the thermoelectric figure of merit ZT.*

**Research Plan**

***Objective 1****: Use Molecular and Lattice Dynamics to explore LUC/disordered crystal design space.*

As the name might suggest, Large Unit Cell materials require a large collection of atoms to model accurately. Size effects of the LUC simulation cell will be initially tested to ensure converged results, as in [Galli]. These test results will be valuable when designing time-efficient ab-initio simulations.While these simulations can make experimentally accurate predictions, they are very computationally expensive [cite]. Simulations are limited by the computational density of the resources available, but typically simulations can allow for 100s-1000s of atoms. This makes it important to test size effects using computationally inexpensive methods developed by the NTPL group. This will allow us to design efficient ab-initio simulations to run on the ERDC supercomputing resources (keep?).

***Objective 2:*** *Design ab-initio simulations to predict the thermal properties of realistic LUC crystals.*

Ab-initio simulations will be run on the extensive resources NTPL has at the ERDC (keep?). In particular, Density Functional Theory (DFT) and Density Functional Perturbation Thoery (DFPT) will be used to make analyze the vibrational properties of LUC crystals []. Previous measurements suggest that system crystal sizes of roughly 1000 atoms can give accurate results [Galli]. This is well within the capabilities of the ERDC resources, whose number of processors is roughly 15,000 (eh, keep?).

***Objective 3:*** *Report ab-initio simulation results to publishing journal(s) and experiments to improve ZT over existing LUC/disordered materials.*

These above objectives can be used iteratively, with data from real experiments, to efficiently search the Large Unit Cell design space. New ab-initio simulations can be run to predict LUC materials with even lower thermal conductivities. Colloboration with NTPL’s adjacent lab group Thermal Energy Engineering Laboratory led by Jon Malen will allow the comparison of our ab-initio simulation with real experimental results.

**Relationship to CIT/ICES Strategic Focus**

Atomistic simulation of LUC materials fits directly into CIT’s nanotechnology initiative. This project is aligned with ICES’s Center for Multiscale Modeling for Engineering Materials (CM2EM) and Center for Nano-enabled Device and Energy Technologies (CNXT), both of which McGaughey is affiliated with. The work provides a compelling example of multi-scale modeling by demonstrating how classical-level (Molecular and Lattice Dynamics) simulations can inform quantum-level (ab-initio) simulations, maximizing the impact of both.

**Present and Future Funding**

Preliminary funding for this project was through the PITA grant “Multi-scale modeling of phase change materials,” with Jason Larkin as the supported graduate student. He does not have support in place for the 2010-2011 academic year.

The Dowd fellowship will enable the team to complete the development of interatomic potentials for a wide range of Ge-Sb-Te materials. With these interatomic potentials in hand, the team will be competitive for funding from NSF’s Thermal Transport Processes (ENG-CBET) and Electronics, Photonics & Device Technologies (ENG-ECCS) programs, SRC’s Device Sciences – Modeling and Simulation program (a call will open in Spring 2011), and CMU’s DSSC. The team will collaborate with CMU’s Jim Bain (ECE, DSSC), who does experimental work on PCM materials and devices and Jon Malen (ME), who thermally characterizes micro- and nanoscale materials and devices. Together, they will apply for funding from NSF’s Interdisciplinary Research (IDR) program.

Our approach first uses dispersion-corrected density functional theory (DFT) calculations to

determine atomic force constants. The force constants are then used in harmonic and anharmonic

lattice dynamics calculations to predict the properties (e.g., specific heats, velocities, relaxation

times) of the full spectrum of phonons and other vibrational entities. The vibrational properties

are then used in thermal transport frameworks (e.g., the phonon Boltzmann transport equation)

to predict specific heat and thermal conductivity. The use of lattice dynamics calculations instead

of molecular dynamics (MD) simulations allows for the natural inclusion of quantum effects. The

accuracy of the underlying DFT calculations, as opposed to using empirical force fields to obtain

the force constants, will make the predictions directly comparable to experimental measurements.

This undertaking is possible due to our team’s expertise in atomistic thermal transport, electronic

structure calculations, and high-performance computing.

At the carrier-level, thermal storage and transport

in non-metallic crystals is dominated by phonons, quanta of energy associated with atomic vibrations.

1, 14–16 One can think of a phonon as an energy wave that propagates through a periodic

system. Finite thermal conductivity exists because phonons scatter with other phonons, defects,

and system boundaries. The specific heats and thermal conductivities measured in an experiment

are a collective effect of the full spectrum of phonon modes in a material.

In thermoelectric energy generation, waste heat (e.g., from engine exhaust) is used to generate

electricity.10–12 To maximize the thermoelectric figure a merit, thermal conductivity

should be minimized, while electrical conductivity and the Seebeck coefficient should be

maximized. Large, complex unit cell crystals such as clathrates, skutterudites, and Zintl

compounds, Fig*:* 1(c), can have thermal conductivities lower than 1 W/m-K.11 ***Using theory***

***to identify the underlying thermal transport mechanisms will accelerate the design of new***

***thermoelectric materials with even lower thermal conductivities***.

which ***we hypothesize to be related to sub-unit cell level effects that cannot be***

***captured by standard phonon transport theory*.** We imagine a combination of sub-unit cell level

transport typical of a disorder phase, where thermal energy moves between atoms, coupled with

phonon-like transport between unit cells.

**Approach and Methodology**

The current paradigm for predicting specific heat and thermal conductivity is to use empirical

force fields in classical molecular dynamics (MD) simulations.20–23 This approach is limited by: (i)

a lack of force fields for many material systems, (ii) errors introduced by the inability of theforce fields to accurately describe atomic interactions, (iii) the large computation time needed to

perform MD simulations, and (iv) the neglect of quantum effects. Our proposed first-principles

approach uses quantum mechanics-based electronic structure (specifically dispersion-corrected

DFT) calculations and lattice dynamics calculations to directly predict phonon properties, and

from these, specific heat and thermal conductivity.29–34 All materials of interest can be modeled

within the same framework. In general, DFT provides a better description of phonons than do

force-field approaches, which translates to more accurate thermal property predictions. Although

DFT calculations are computationally demanding, the time can be considerably reduced by using

efficiently-parallelized codes.

The procedure for making a lattice dynamics-based thermal conductivity prediction is shown

in Fig*:* 3. Harmonic, cubic, and quartic atomic force constants are first calculated from an empirical

force field or using DFT.29, 31 Ignoring the higher-order force constants is expected to be valid up

to half of the melting temperature.32 The force constants are then used in lattice dynamics calculations

to predict the properties of the vibrational modes (phonons in crystals, other entities such as

diffusons in disordered materials).16, 30, 32, 35–37 These properties are then used in a thermal transport

framework (e.g., the phonon Boltzmann transport equation for crystals38–40 or Allen-Feldman

theory41, 42 for disordered solids) to predict thermal conductivity. The majority of previous efforts

have focused on one part of this procedure. ***We will build an integrated computational framework***

***that starts from DFT and ends with a true first-principles thermal conductivity.***

**Silicon Thermal Conductivity Over-Predicted using Classical MD**

Based on these results,

we should not expect the silicon thermal conductivity calculated using the SW force field to agree

with the experimental value, which it does not (62 W/m-K at a temperature of 1000 K from MD

simulation20 compared to the experimental value of 31 W/m-K39). In fact, no available silicon force field, used in either MD simulation or lattice-dynamics based methods, successfully predicts its thermal conductivity.43

With advances in electronic structure methodologies [e.g., density functional perturbation theory

(DFPT)] and increases in computational power, force constants of periodic systems can now be

obtained from electronic structure calculations.29, 31, 46, 47

Previous efforts in this area41, 42, 108 have (i) used empircal force-fields to obtain the force constants,

and (ii) not simultaneously considered propagating and non-propagating thermal energy transport

mechanisms.*{* ***As such, thermal transport in amorphous materials at room temperature is***

***still poorly understood.***

No study to date has examined all the vibrational entities in the same system. Diffusons are

typically assumed to dominate in amorphous materials, in large part because they can be easily

modeled under the harmonic approximation. It has been found, however, that diffusions alone

cannot account for all the thermal transport in amorphous materials.42 Our lattice dynamics calculation

framework presents an ideal framework for studying the combined and coupled roles of

propagons, diffusons, and locons.

**5.3 Task B2: Large Unit Cell Crystals**

We hypothesize that not all the vibrational modes in a large unit cell crystal are effective at

propagating [i.e., Eq. (9) is not appropriate for some modes] and that energy transport mechanisms

at length scales smaller that the lattice constant are important. This hypothesis is consistent

with the experimental data shown in Fig*:* 2(b) and MD-predicted thermal conductivities of

zeolites,9 methane hydrate,52 and metal-organic frameworks,112 which show weak temperaturedependence.

Thermal transport within the unit cell may be affected by local distortions of the

unit cell or the presence of non-framework species (e.g., caged gas molecules in a hydrate, the

cations required to maintain charge neutrality in aluminum-silicon zeolites, and adsorbed gas

molecules in a zeolite or metal organic framework). Also of interest is the role played by optical

phonons. Large unit cell crystals have many optical phonon branches that can: (i) scatter the acoustic phonons that are generally assumed to dominate thermal transport, but (ii) carry a

significant amount of thermal energy due to their shear numbers.60

Using the analysis tools for ordered and disordered materials discussed in Sections 3 and 5.2,

we will analyze thermal transport in gas hydrates, zeolites, and Zintl compounds. These material

systems, in addition to covering a range of energy-related applications, are also distinct in their

structures. Gas hydrates are built from weakly-bonded, closed cages. Zeolites are rigidly-bonded

structures containing Angstrom-sized pores and channels. Zintl compounds are not porous.

**Zintl Compounds**

The ideal thermoelectric material is a phonon-glass, electron-crystal (PGEC).11 In a PGEC,

electrons have high mobility, while phonons are quickly scattered, leading to a large thermoelectric

figure of merit. Recent efforts in thermoelectric material development have focused on

lowering thermal conductivity. Significant work has been done related to nanostructuring (e.g.,

semiconductor superlattices,136–138 dispersing nanoparticles in a bulk material,139 or ball-milled

alloys140, 141). An alternative approach is to use complex unit cells.11 In clathrates and skutterudites,

rattler atoms in the unit cell cages can scatter phonons. In Zintl compounds, which we will

study here, sub unit cell structures allow for the decoupling of the phonon and electron transport.

A Zintl compound (e.g., Ca*x*Yb1*􀀀x*Zn2Sb2, Yb14Al*x*Mn1*􀀀x*Sb11) is a small bandgap semiconductor

whose elements have a large different in electronegativity. The unit cell typically consists

of a few hundred atoms and contains distinct structural features. In Yb14MnSb11, see Fig*:* 1(c), the

208 atom unit cell contains [MnSb4]9*􀀀* tetraherdra, polyatomic [Sb3]7*􀀀* cations, and isolated Sb3*􀀀*

and Yb2+ cations.13 The larger structures are covalently bonded, leading to a continuous region

of high electron mobility. Doping the ionic substructure leads to high rates of phonon scattering

without disrupting the electronic transport. Zintl compounds have been found to have thermal

conductivity as low as 0.4 W/m-K (about half of which is related to phonons), making them candidates

to replace the SiGe alloys that have dominated high-temperature thermoelectrics for many

decades.11, 13, 142, 143

***We are not aware of any atomic-level modeling work on thermal transport in Zintl compounds.***

Our objective in this part of the proposed work is to predict their phonon properties, so

that the specific reasons why these materials have such low thermal conductivities can be elucidated.

From theses results, we will be able to suggest design strategies for further reduction and

establish a lower limit to thermal conductivity. We will focus the initial attention on Yb14MnSb11,

for which experimental thermal conductivity measurements are available between temperatures

of 300 and 1200 K.13, 143 Once we have uncovered the mechanisms of thermal transport, we will

consider this structure but with Al in place of some of the Mn atoms (i.e.,Yb14Al*x*Mn1*􀀀x*Sb11),

to determine how the phonon properties and thermal conductivity are affected by small perturbations

in the unit cell. The analysis will be performed in a similar manner to the protondisorder

studies in the gas hydrates, whereby multiple configurations will be considered and then

Boltzmann-averaged to give a result typical of a bulk experimental system.

**Relationship to CIT/ICES Strategic Focus**

Atomistic simulation of PCM materials fits directly into CIT’s nanotechnology initiative and is a focus of the Data Storage Systems Center (DSSC). This project is also aligned with ICES’s Center for Multiscale Modeling for Engineering Materials (CM2EM) and Center for Nano-enabled Device and Energy Technologies (CNXT), both of which McGaughey is affiliated with. The work will provide a compelling example of multi-scale modeling by demonstrating how high-level (quantum) computational techniques can feed into and drive classical-level methods.

**Present and Future Funding**

Preliminary funding for this project was through the PITA grant “Multi-scale modeling of phase change materials,” with Jason Larkin as the supported graduate student. Jason initiated the collaboration with Dr. Juarez Da Silva from the Sao Paulo Institute of Physics, which been fruitful to date. He does not have support in place for the 2010-2011 academic year.

The Dowd fellowship will enable the team to complete the development of interatomic potentials for a wide range of Ge-Sb-Te materials. With these interatomic potentials in hand, the team will be competitive for funding from NSF’s Thermal Transport Processes (ENG-CBET) and Electronics, Photonics & Device Technologies (ENG-ECCS) programs, SRC’s Device Sciences – Modeling and Simulation program (a call will open in Spring 2011), and CMU’s DSSC. The team will collaborate with CMU’s Jim Bain (ECE, DSSC), who does experimental work on PCM materials and devices and Jon Malen (ME), who thermally characterizes micro- and nanoscale materials and devices. Together, they will apply for funding from NSF’s Interdisciplinary Research (IDR) program.

[] J. Larkin, A.J.H. McGaughey, “Predicting Phonon Properties of Defected Systems using Spectral Energy Density”

[1] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*. Saunders, Fort Worth (1976).

[10] G. Chen, M. S. Dresselhaus, G. Dresselhaus, J.-P. Fleurial, and T. Caillat, “Recent developments

in thermoelectric materials.” *International Materials Reviews* **48** (2003) 45–66.

[11] G. J. Snyder and E. S. Toberer, “Complex thermoelectric materials.” *Nature Materials* **7** (2008)

105–114.

[12] A. J. Minnich, M. S. Dresselhaus, F. Ren, and G. Chen, “Bulk nanostructured thermoelectric

materials:

[14] J. M. Ziman, *Electrons and Phonons*. Oxford, New York (2001).

[15] G. P. Srivastava, *The Physics of Phonons*. Adam Hilger, Bristol (1990).

[16] M. T. Dove, *Introduction to Lattice Dynamics*. Cambridge, Cambridge (1993).

[20] P. K. Schelling, S. R. Phillpot, and P. Keblinski, “Comparison of atomic-level simulation

methods for computing thermal conductivity.” *Physical Review B* **65** (2002) 144306.

[21] A. J. H. McGaughey and M. Kaviany, “Quantitative validation of the Boltzmann transport

equation phonon thermal conductivity model under the single-mode relaxation time approximation.”

*Physical Review B* **69** (2004) 094303.

[22] A. J. H. McGaughey and M. Kaviany, “Phonon transport in molecular dynamics simulations:

Formulation and thermal conductivity prediction.” In G. A. Greene, Y. I. Cho, J. P. Hartnett,

and A. Bar-Cohen (eds.), “Advances in Heat Transfer, Volume 39,” Elsevier (2006) 169–255.

[23] D. P. Sellan, E. S. Landry, J. E. Turney, A. J. H. McGaughey, and C. H. Amon, “Size effects in

molecular dynamics thermal conductivity predictions.” *Physical Review B* **81** (2010) 214305.

[29] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, “Phonons and related crystal

properties from density-functional perturbation theory.” *Reviews of Modern Physics* **73** (2001)

515–562.

[30] D. A. Broido, M. Maloney, G. Birner, N. Mingo, and D. Stewart, “Intrinsic lattice thermal conductivity

of semiconductors from first principles.” *Applied Physics Letters* **91** (2007) 231922.

[31] K. Esfarjani and H. T. Stokes, “Method to extract anharmonic force constants from first principles

calculations.” *Physical Review B* **77** (2008) 144112.

[32] J. E. Turney, E. S. Landry, A. J. H. McGaughey, and C. H. Amon, “Predicting phonon properties

and thermal conductivity from anharmonic lattice dynamics calculations and molecular

dynamics simulations.” *Physical Review B* **79** (2009) 064301.

[33] J. E. Turney, A. J. H. McGaughey, and C. H. Amon, “Assessing the applicability of quantum

corrections to classical thermal conductivity predictions.” *Physical Review B* **79** (2009) 224305.

[34] J. E. Turney, A. J. H. McGaughey, and C. H. Amon, “In-plane phonon transport in thin films.”

*Journal of Applied Physics* **107** (2010) 024317.

[35] A. J. C. Ladd, B. Moran, and W. G. Hoover, “Lattice thermal conductivity: A comparison

of molecular dynamics and anharmonic lattice dynamics.” *Physical Review B* **34** (1986) 5058–

5064.

[36] A. J. H. McGaughey, M. I. Hussein, E. S. Landry, M. Kaviany, and G. M. Hulbert, “Phonon

band structure and thermal transport correlation in a layered diatomic crystal.” *Physical*

*Review B* **74** (2006) 104304.

[37] A.Ward, D. A. Broido, D. A. Stewart, and G. Deinzer, “Ab initio theory of the lattice thermal

conductivity in diamond.” *Physical Review B* **80** (2009) 125203.

[38] J. Callaway, “Model for lattice thermal conductivity at low temperatures.” *Physical Review*

**113** (1959) 1046.

[39] M. G. Holland, “Analysis of lattice thermal conductivity.” *Physical Review* **132** (1963) 2461.

[40] M. Omini and A. Sparavigna, “Beyond the isotropic assumption in the theory of thermal

conductivity.” *Physical Review B* **53** (1996) 9064–9073.

[41] P. B. Allen and J. L. Feldman, “Thermal conductivity of disordered harmonic solids.” *Physical*

*Review B* **48** (1993) 12581–12588.

[42] S. Shenogin, A. Bodapati, P. Keblinski, and A. J. H. McGaughey, “Predicting the thermal conductivity

of inorganic and polymeric glasses: The role of anharmonicity.” *Journal of Applied*

*Physics* **105** (2009) 034906.

[43] D. A. Broido, A.Ward, and N. Mingo, “Lattice thermal conductivity of silicon from empirical

interatomic potentials.” *Physical Review B* **72** (2005) 014308.

[46] W. Frank, C. Els¨asser, and M. F¨ahnle, “Ab initio force-constant method for phonon dispersions

in alkali metals.” *Physical Review Letters* **74** (1995) 1791–1794.

[47] P. Pavone, “Old and new aspects in lattice-dynamical theory.” *Journal of Physics: Condensed*

*Matter* **13** (2001) 7593–7610.