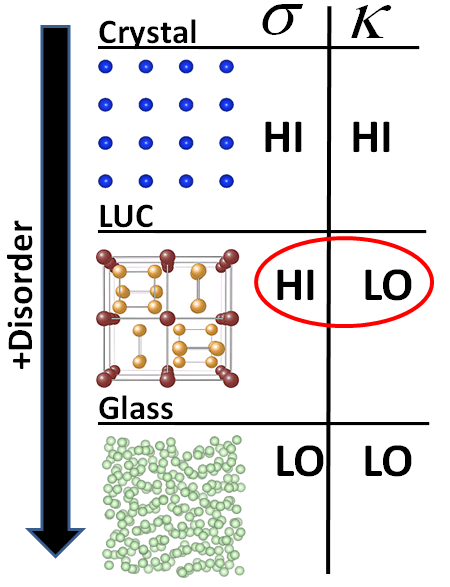
**Project Title:** Atomistic Modeling of Thermal Transport in Large Unit Cell Crystals for Thermoelectric Application

**Research Team:**

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Faculty Advisor: Associate Professor Alan McGaughey, Mechanical Engineering  
Affiliated Faculty: Visiting Professor Wissam Al-Saidi, Department of Chemical and Petroleum Engineering, University of Pittsburgh

**Project Description**

*The objective of this project is to build a robust, accurate, and efficient computational framework for predicting the thermal conductivity of large unit cell crystalline solids for improving the efficiency of thermoelectric energy generation.*

Thermoelectric energy generation - the transformation of waste heat into useful electricity - is a promising source of sustainable energy [cite]. Thermoelectric materials directly convert temperature differences into electric voltage as a result of their intrinsic (atomic-level) electronic and thermal properties. The performance of a thermoelectric device can be quantified through the *thermoelectric figure of merit*, ***ZT* =** , where *T* is the average device temperature, *S* is the Seebeck coefficient (the ratio of the induced thermoelectric voltage to the applied temperature difference), is the electrical conductivity, and is the thermal conductivity. For thermoelectric devices to be competitive with traditional power generation cycles requires *ZT* > 3 [cite]. Achieving this performance is challenging because the electrical and thermal properties in *ZT* are coupled in the majority of materials [cite]. The ideal thermoelectric can be thought of as an “electron-crystal/ phonon-glass” (high , low ) [cite] (see Figure 1). Reducing has become a primary strategy in the design of new thermoelectric materials [cite]. Using nanostructuring to reduce while maintaining good electrical properties has been identified as one possible strategy [], but such materials are costly [cite]. An emerging area of study is the use of large unit cell (LUC) crystals [cite].

Figure 1: LUC crystals can maximize ZT. ZT.

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Large Unit Cell crystals have an ordered (crystalline) structure, but the basic building block (unit cell) of the crystal has a large number of distinct atoms (Figure 1) [cite]. They are thus effectively disordered over length scales on the order of the atomic spacing and their thermal conductivities can be as low as a glass [cite]. The key advantage of LUC materials is that they are still ordered from the standpoint of electrons, which results in large and *ZT*. Thus, LUC crystals are “electron-crystals/phonon-glasses.” Current LUC crystals have ZT<3 [cite] and more research is required to improve their thermoelectric performance.

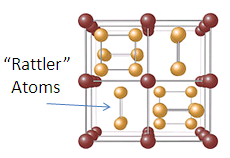
The LUC crystals to be studied are skutterudites [cite] and Zintl compounds [Skutt,Zintl] (Figure 2). Both LUC crystals have rather low , but experiments show potential for improved thermoelectric efficiency [Yang1, Yang2]. Identifying design strategies for improving their *ZT* requires detailed atomistic analyses. The necessary computational tools and resources available in my research group, the Nanoscale Transport Phenomena Laboratory (NTPL) [cite]. Classical molecular and Lattice Dynamics (MD and LD) calculations will be used in preliminary testing in order to study the structural features of LUC crystals that lead to low thermal conductivity [Yang1]. The less-accurate classical simulation results will then be used to efficiently design computationally-intensive *ab initio* (quantum mechanical) simulations, which have high accuracy [cite]. From these ab initio simulations, structural features that lead to low thermal conductivity will be identified with high accuracy to improve *ZT*. The simulation results will be validated against limited experimental data [Skutt,Zintl], and used to provide guidance to the experimental community working on these materials.

Figure 2: large unit cell skutterudite compound [cite].

**Research Plan**

***Objective 1****: Use Molecular and Lattice Dynamics to explore LUC crystal design concepts.*

As the name suggests, LUC materials require a large number of atoms to model accurately. Size effects will be initially tested to ensure converged results, as in [Galli]. Preliminary tests will be conducted to vary structural features that lead to low thermal conductivity. In particular, the influence of “rattler” atom mass and bonding will be explored (Figure 2). These simulations will identify important trends in varying LUC crystal properties. These test results will be valuable when designing time-efficient *ab initio* simulations.

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

*Ab initio* simulations have high accuracy, but are very computationally expensive [cite]. This makes it important to test size effects using computationally inexpensive methods developed by the NTPL group (*Objective 1*). *Ab-initio* simulations of sutterudites and Zintl compounds will be run on the extensive resources NTPL has at the ERDC (see below). In particular, Density Functional Theory (DFT) [cite] and Density Functional Perturbation Theory (DFPT) [cite] simulations will be efficiently designed using the size effect studies from *Objective 1*. The atomistic mechanisms that reduce thermal conductivity in skutterudites and Zintl compounds will be identified with high accuracy to compare with experiment.

. This will allow us to design efficient ab-initio simulations to run on the ERDC supercomputing resources (see below).

***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. ***Ab-initio simulations can predict large unit cell materials with even lower thermal conductivities, and thus increase ZT>3.*** For example, modifying large unit cell crystals with heavy atoms and/or bonding disorder has been shown to be promising mechanisms for reducing thermal conductivity [cite].

**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.

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Just listing out the references I have so far that are applicable.

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