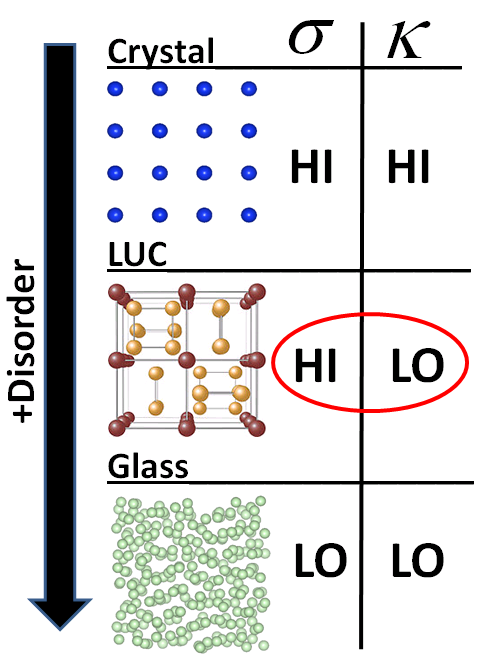
**Project Title:** Atomistic Modeling of Thermal Transport in Large Unit Cell Crystals for Thermoelectric Application

**Research Team:**

Graduate Student: Jason Larkin, Mechanical Engineering  
Faculty Advisor: Assistant Professor Alan McGaughey, Mechanical Engineering  
Co-PI: Professor Kenneth D. Jordan, Department of Chemistry, University of Pittsburgh Co-PI: Visiting Professor Wissam Al-Saidi, Department of Chemical and Petroleum Engineering, University of Pittsburgh

**Project Description**

Thermoelectric energy generation - the transformation of wasteheat into useful electricity - is a promising source of sustainable energy [cite]. Thermoelectric materials directly convert temperature differences into electric voltage because of intrinsic (atomic-level) material properties. The challenge is to optimize these atomic-level thermoelectric properties, which can be combined into an expression called 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 thermoelectric 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]). This is challenging because the atomic-level material properties in the expression for ZT are interdependent. The key to improving ZT is reducing without reducing (or changing) , both which tend be large in crystalline (ordered) materials and produce very low ZT [cite]. In glassy (disordered) materials, both and are small which also leads to a small ZT. 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) 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]. This makes them effectively disordered over length scales on the order of the atomic spacing, and as such, their thermal conductivities can be as low as a glass [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”. Current LUC crystals have ZT<3 [cite], so more research is required to improve their thermoelectric efficiency.

Improving the ZT (reducing the thermal conductivity ) of LUC crystals requires a detailed analysis of their atomistic behavior. The atomistic computational tools available to the Nanoscale Transport Phenomena Laboratory (NTPL) can provide the required analysis (talk about equipment?) [cite]. 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 [cite]. 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 [cite]. 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 analyze the vibrational properties of LUC crystals []. From these vibrational properties the thermal properties of LUC crystals can be predicted, including the thermal conductivity [cite]. 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 LUC design space. ***Ab-initio simulations can predict LUC materials with even lower thermal conductivities.*** For example, modifying LUC crystals with heavy atoms and/or bonding disorder has been shown to be promising mechanisms for reducing thermal conductivity [cite]. 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, each method assisting the other.

**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.

**References**

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

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

[Galli] Y. He, D. Donadio, G. Galli, “Heat Transport in Amorphous Silicon: Interplay between morphology and disorder”, Appl. Phys. Lett. **98** (2011) 144101.

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

[Chen] 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: current research and future prospects.” *Energy and Environmental Sciences* **2** (2009)

466–479.

[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.