Nanocomposite Design of Thermoelectric Materials Introductory Report

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***Abstract*—Thermoelectrics are a promising area of materials research recently revitalised by the introduction of nanocomposites. In this project, we aim to derive a theoretical mechanism, through which new, high efficiency thermoelectric materials can be designed. This will involve a detailed understanding of the fundamental theories of solid-state physics, of which the phonon model plays a critical role. This theoretical project aims to guide expierment, keeping within practical limits and computationally modelling potential designs.**

I. Introduction

From its discovery in 1821, thermoelectricity has seen constant attention by the scientific community. Its source lies deep in the fundamental nature of solid state materials. Through understanding thermoelectricity we combine all the concepts underpinning solid-state physics.

Thermoelectricity is not only a central area of research for solid-state physics, but also has enormous practical significance. A key quantity in thermoelectrics is the figure of merit ZT, which is proportional to the total efficiency of thermoelectric conversion. Current bulk thermoelectrics achieve ZT up to one, which results in a practical thermal efficiency (heat to work) of just 4% [2], six times less than modern internal combustion engines [3].

Despite this low figure, thermoelectrics still see niche use in refrigeration and space exploration due primarily to their exceptional reliability. By increasing ZT up to three, new applications in heat recovery systems and solar thermal generators emerge, improving the thermal efficiency of current power generation methods. Theoretically, there is no upper limit to ZT, and as it approaches infinity, efficiencies at the Carnot limit can be obtained. If we achieve $ZT \to \infty$, all heat gradients will be maximally exploitable for high value electrical energy.

II. Background Theory

A. Thermoelectricity

In 1821, Thomas Seebeck discovered that a circuit made from two dissimilar metals, with junctions at different temperatures would deflect a compass magnet (Fig. 1), he had discovered thermoelectricity. The temperature gradient ∇T between the junctions generates an electromotive force:

$$\mathbf{E_{emf}} = -S\nabla T \tag{1}$$

where S is the Seebeck coefficient, defined as the induced voltage per unit temperature difference, mathematically $\Delta S = \frac{\Delta V}{\Delta T}$ [6]. This coefficient is not only material dependent, but also temperature dependent, i.e., a temperature gradient produces an electromotive force gradient. This electromotive force gradient produces a current density gradient described macroscopically by a modified Ohm's law [7]:

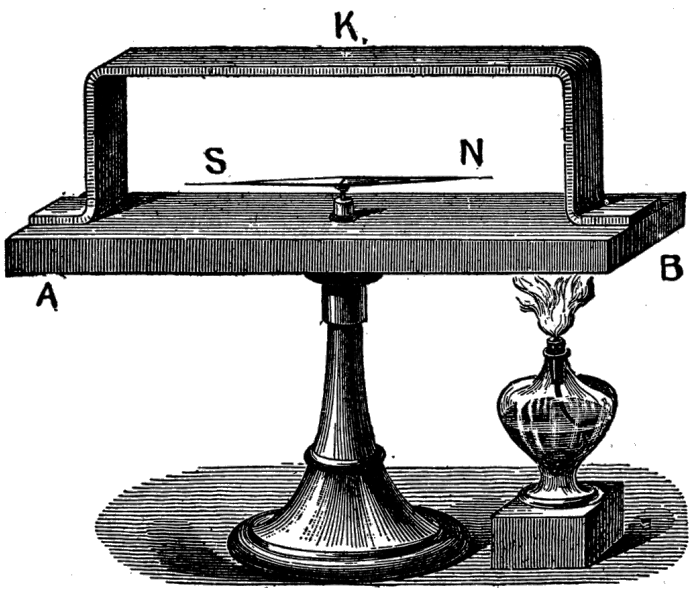

Fig. 1. Thomas Seebeck's original thermoelectricity experiment diagram [4]. A compass needle lies on top of one metal, underneath a bridge of a different metal (K), connected by two junctions and heated at one of these junctions.

$$\mathbf{J} = \sigma(-\nabla V - S\nabla T) \tag{2}$$

where $\mathbf{J}$ and σ are the current density $\frac{I}{A}$ and electrical conductivity at a given location in the material and ∇T and ∇V are the temperature and resultant voltage gradients across the material. If we were to repeat the experiment conducted by Seebeck (Fig. 1), using a probe to measure V between junctions and σ at each junction for one of the metals, assuming steady state, i.e., $I = 0$ so $\mathbf{J} = 0$, the metal's Seebeck coefficient can be determined.

Thermoelectricity, its uses and current nanocomposite research are well summarised by J. W. Bos [5] and A. J. Minnich et al. [2].

B. Statistical Mechanics

Using the kinetic theory, with relevant assumptions defined in Section III, the charge density **J** of an arbitrary charge carrier can be described microscopically [8]:

$$\mathbf{J} = \frac{nq^2\mathbf{E}\tau}{m} \tag{3}$$

where n is free charge carrier density, q is the charge of the carrier, **E** is the electric field accelerating the carrier, τ is the mean time between carrier collisions and m is carrier mass. Applying this to solid-state electrical conductivity $\sigma = \frac{ne^2\tau}{m^*}$ it can be shown that [7]:

$$\sigma = \frac{e^2}{m^*}\sum_{\text{spin}}\sum_{\mathbf{k}} n(\mathbf{k})\tau(\mathbf{k}) \tag{4}$$

where e is electron charge, m^* is the electron effective mass, spin refers to electron spin and **k** is the electron wavevector over the Brillouin zone. These new concepts are all derived from the nearly free electron model, as described in Kittel [8]. The Boltzmann transport equation "describes the statistical behaviour of a thermodynamic system not in thermodynamic equilibrium" [9] and its general definition is:

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\text{force}} + \left(\frac{\partial f}{\partial t}\right)_{\text{diff}} + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \tag{5}$$

where $\frac{\partial f}{\partial t}$ is time dependence of a system of particles f, the "force" term represents external forces on the particles, the "diff" term is the diffusion of particles through the system and the "coll" term represents forces acting between particles in collisions.

A phonon is the quantisation of vibrational motion of a lattice of atoms at a single frequency, known as a normal mode [8]. These phonons are quasiparticles, free to move around the lattice and they are distributed according to the Bose-Einstein distribution [8]:

$$\bar{n} = \frac{1}{e^{(\hbar\omega)/kT} - 1} \tag{6}$$

where $\bar{n}$ is the probability of a phonon existing with energy $\hbar\omega$.

Electrons can be modelled as quasiparticles in a similar way, with a wavevector and effective mass as in equation (4), leading to the Fermi-Dirac distribution [8]:

$$\bar{f} = \frac{1}{e^{(E-E_f)/kT} + 1} \tag{7}$$

where $\bar{f}$ is the probability of an electron existing with energy E and E_f is the Fermi level.

In the presence of an external fields, phonon and electron distributions ((6) & (7)) both satisfy the Boltzmann transport equation (5) with [7]:

$$\left.\frac{df}{dt}\right|_{field} + \left.\frac{df}{dt}\right|_{collisions} = 0 \tag{8}$$

where function f is $f = \bar{n}$ or $f = \bar{f}$, the Bose-Einstein and Fermi-Dirac distribution functions.

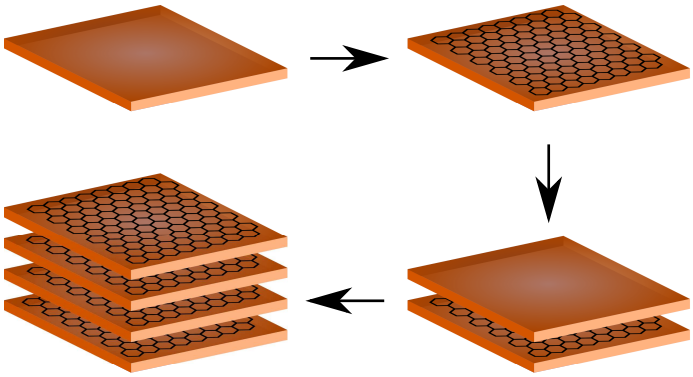

Fig. 2. Superlattice of graphene and copper. Alternate layers of nanoscale copper and graphene are sandwiched together.

C. Nanocomposites

Composite materials are combinations of two or more materials, forming a new structure with significantly different physical or chemical properties than its constituent parts. In a similar way, nanocomposites are the structuring of multiple materials, but at the nanoscale. As our nanocomposites are at a comparable size to the crystal lattices of their constituent materials, we can view nanocomposites as artificial defects in a larger crystal lattice. A simple example of a 2D nanocomposite, a copper-graphene superlattice, is pictured in Fig. **??**. Examining one layer of the superlattice, the material in bulk form would be a 3D crystal structure, but by constraining the layer thickness we have introduced a boundary defect. The periodic array of these boundary defects forms a new 3D artificial crystal, which we define as a superlattice, a nanocomposite.

III. Project Theory Discussion

A. Assumptions

For our project we will be using the phonon and nearly free electron models, which bring with them a multitude of assumptions. For the phonon model, our main assumption is that our system consists of at least 50 atomic oscillators [8]; this means we are limited to a $50\mathring{A} = 5\text{nm}$ fabrication size. Current fabrication methods are at best 25nm [2], so our 50 oscillator assumption is well met. For both the phonon and the nearly free electron model, we assume an ideal gas, i.e., particles do not interact with each other and can move freely around the lattice, affected only by lattice perturbations. This is known to be a good assumption for the low temperatures found in solid-state physics [8].

Based on this limited initial analysis, we believe these assumptions should be valid. If it transpires that these assumptions cannot be met, we will seek alternative models.

B. Thermoelectric Efficiency

The thermoelectric efficiency is best expressed in the dimensionless parameter ZT with thermal efficiency η which is a function of (ZT, T_h, T_c), where Z is the figure of merit,

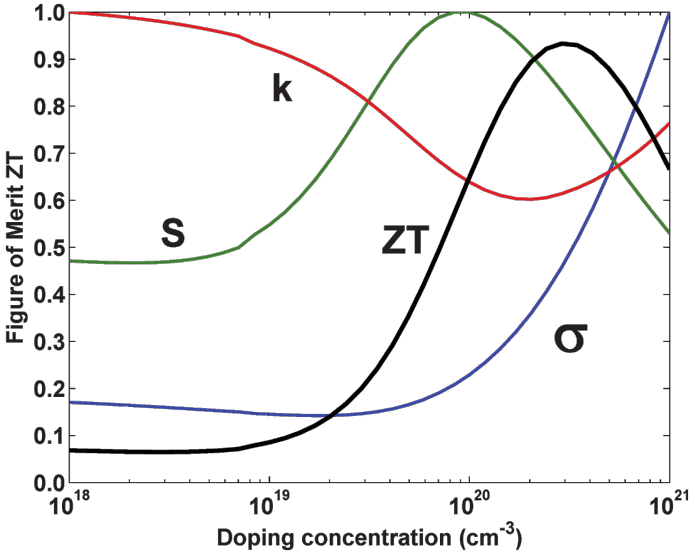

Fig. 3. Graph of doping concentration (electron density) against ZT. Insulators are seen up to 10^{19} with semi-conductors occupying the rest of the range. A compromise between variables σ, κ, S^2, results in heavily doped semi-conductors at the ZT peak [2].

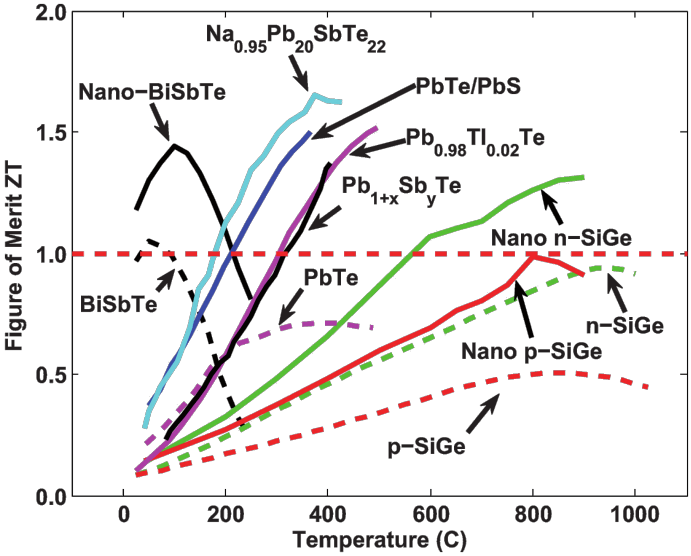

Fig. 4. Graph of thermoelectric figure of merit ZT against temperature. The dashed line represents bulk thermoelectric materials, above the dashed line shows current generation nanocomposites [2].

$T = \frac{1}{2}(T_h + T_c)$, T_h is the temperature at the hot junction and T_c is the temperature at the cold junction. ZT:

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_{ph}} \tag{9}$$

where S is the Seebeck coefficient from equation (1) & (2), σ is electrical conductivity, κ_e and κ_{ph} are the thermal conductivity due to electrons and phonons respectively. This is derived in D. M. Rowe's Modern Thermoelectrics [10]. Important points to note about ZT are that it is proportional to thermal efficiency η, is increased by a reduction in thermal conductivity and it depends on the square of the Seebeck coefficient. Figure Fig. 3 demonstrates the comprimise between the variables in equation (9). ZT values of current generation thermoelectric materials have been plotted in figure Fig. 4.

C. Phonon Glass Electron Crystal

A core concept for for our project is the idea of phonon glass electron crystal (PGEC) first proposed by G. A. Slack [1]. Slack proposes that developing a material with the properties of both phonon scattering glasses and electron transmissive crystals, will achieve the desired $ZT > 3$. It is thought that the low dimensional systems of nanocomposites introduce the short range disorder of crystal structures common to glasses, yet they maintain the long range order common to electron crystals common [1]. Some key questions for our project are; How can we achieve PGEC? What are its constraints? How effective is it at increasing ZT?

IV. Project Aims

Thermoelectric theory provides a good basis from which we can understand solid-state physics. Using phonon and nearly free electron models together with the Boltzmann transport equation (5) we aim to develop a PGEC inspired mechanism through which ZT can be increased. If such a mechanism is found we will design novel structures and model them computationally. In pursuit of this aim, it is likely that we utilise nanocomposite material design for the introduction of multiple boundary defects.

References

[1] G. A. Slack, *CRC Handbook of Thermoelectrics*. Ed D. M. Rowe, CRC Press, 1995

[2] A. J. Minnich et al. *Bulk nanostructured thermoelectric materials: current research and future prospects*. Energy Environ. Sci., 2009, 2, 466-479. DOI: 10.1039/B822664B

[3] L. M. Baglione, *Development of System Analysis Methodologies and Tools for Modeling and Optimizing Vehicle System Efficiency* University of Michigan, 2009, . pp. 5254.

[4] etc.usf.edu/clipart/35600/35659/seebeck_35659_lg.gif 24 November 2013

[5] J. W. Bos, *Thermoelectric materials: efficiencies found in nanocomposites*. Education in Chemistry, March 2012. Available from: http://www.rsc.org/images/Thermoelectric-materials_tcm18-214041.pdf 24 November 2013

[6] N. Auparay, *Room Temperature Seebeck Coefficient Measurement of Metals and Semiconductors*. Available from: http://www.physics.oregonstate.edu/~tate/TateLabWiki/lib/exe/fetch.php?media=theses:auparay_bs_2013.pdf 20 November 2013

[7] J. M. Ziman, *Electrons and Phonons: The Theory of Transport Phenomena in Solids*. 1960, ISBN: 978-0-19-850779-6

[8] C. Kittel, *Introduction to Solid State Physics, 8th ed*. November 2004, ISBN: 978-0471415268

[9] http://en.wikipedia.org/wiki/Boltzmann_equation 18 November 2013

[10] D. M. Rowe, *Modern Thermoelectrics*. Reston Pub Co, September 1983. ISBN: 978-0835945936