A Project to Study Maximising the Thermoelectric Figure of Merit

Andrew Morris

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This paper will aim to introduce a qualitative background understanding of the thermoelectric effect. This will cover basic phenomena along with a theoretical explanation. The Figure of Merit, ZT, will be introduced along with an explanation of why it is an important concept. This will include methods to model both electrons and phonons and how these particles contribute to ZT in thermoelectric materials.

1 Introduction

The thermoelectric effect is classified by three fundamental phenomenae. The Seebeck effect describes the potential difference produced across a thermoelectric in response to a thermal gradient. The Peltier effect describes the thermal gradient generated at the interface between two thermoelectrics when driven by a current. The Joule Heating process is a continuous form of the Peltier effect and describes the thermal gradient generated across a thermoelectric when driven by a current. The Joule heating process can be thought of as the inverse of the Seebeck effect. One driven by a thermal gradient, generating a potential difference. The other driven by a current, generating a thermal gradient.

The applications of these effects have huge potential in energy conservation. The Seebeck effect allows any thermal gradient to generate electrical power. This could range from more efficient solar panels to energy harvesting radiators. Thermoelectrics could be applied to practically any existing technology which currently wastes heat. Thermoelectric generators also have no theoretical upper limit of efficiency. That is to say that theoretically the only limit is the thermodynamic Carnot limit itself.

The Peltier effect also has huge potential to create both efficient electric heat pumps and electric refrigerators. Current refrigerating technologies rely on primitive gas compressors to remove heat from the system. The main problem with this is that many of the gases used (Freon-12 as an example) are harmful to the environment and the ozone layer. Thus research into thermoelectrics could potentially hugely improve the 'green credentials' of such devices.

2 Basic Theory

The Seebeck effect can be explained by considering a uniform bar held between two different temperature reservoirs. Due to the increased kinetic energy of the charge carriers imposed by the higher temperature we expect a net diffusion of charge carriers from the hotter towards the colder temperature. This flow of charge will create a potential difference across our system. We define the potential difference required to effectively balance this diffusion as the Seebeck voltage. If we were then to connect our system into a circuit it would produce a current effectively acting as a battery. The Seebeck coefficient S is important as a measure of the magnitude of this effect and is defined as the voltage generated per unit temperature

gradient.

The Peltier effect can be explained by describing the thermal energy carried by a charge carrier in a particular material (The Peltier coefficient). When two materials displaying two different Peltier coefficients are connected in series the interface will either have to absorb or supply heat to accommodate this change in thermal energy per charge carrier. This is effective as charge must conserved across the interface. This idea can be extended to explain the phenomena of joule heating. Instead of describing a step in the thermal energy per charge carrier we can imagine a continuous form of the Peltier coefficient . As charge is driven up or down this potential a continuous flow of heat must be produced.

3 Introducing ZT

The concept of a dimensionless figure of merit can be introduced as a way of ranking thermoelectric materials. The origin of ZT is from the derivation of the efficiency of a thermoelectric generator. The result of this is shown in equation (1).

$$\eta_{max} = \frac{\Delta T}{T_h} \frac{(1+ZT)^{\frac{1}{2}} - 1}{(1+ZT)^{\frac{1}{2}} + 1} \tag{1}$$

From (1) it can be seen that the efficiency of a thermoelectric is directly related to ZT. It is also worth noting that as ZT tends towards infinity the efficiency will tend towards the carnot limit. While theoretically there is no upper limit on ZT a realistic goal of $ZT >= 3$ has been introduced. If this can be achieved thermoelectrics will become commercially viable and will out perform existing energy harvesting technologies.

To continue the functional form of ZT will be introduced in equation (2).

$$ZT = \frac{S^2\sigma}{k}T \tag{2}$$

From (2) it can be seen that an increase in ZT can be produced by either increasing the power factor $S^2\sigma$ or decreasing the thermal conductivity k. There are three contributors to the thermal conductivity k. k_{phonon}, $k_{chargecarrier}$ and $k_{bipolar}$ (not covered here). Due to the Weidemann-Franz law (equation (3)) $k_{chargecarrier}$ is directly related to σ. As such once σ has been chosen to maximise the power factor $k_{chargecarrier}$ is fixed. k_{phonon} however is largely independent of other variables and can be modified freely. The phonon glass electron crystal (PGEC) concept can be introduced as a way of describing the perfect thermoelectric (covered later). This material should behave as a conductor for charge carriers maximising the power factor while simultaneously acting as an insulator for phonons minimising k_{phonon}.

$$\frac{k_{cc}}{\sigma} = LT \tag{3}$$

4 Experimental data ZT

As ZT contains purely measurable properties it can be directly measured through experiment. Below is a graph providing information on current experimental efforts to maximise ZT:

Figure 1: Experimental Data On Thermoelectrics [1]

It can be seen that there are currently three stand out alloys in three temperature regimes:

It can be seen that each of these alloys can display improved ZT through the use of nanocompositing. This technique allows the manufacture of artificial ordered alloys. The precise width of the layers of each element can be engineered on the nano-scale. The concept of nanocomposites becomes important for achieving a PGEC. Currently however techniques for engineering quality nanacomposites are very expensive making experiment in this field slow moving. This in turn makes the theory behind why and how they achieve improved ZT very important.

5 The Phonon Glass Electron Crystal Concept

The PGEC concept will be key to maximising ZT. The aim is to design a material which appears amor-

Table 1: Table of Thermoelectric Alloys

Alloy	Temperature Regime (Kelvin)
BiSbTe	0-200
PbTe	200-500
SiGe	500-1000

phous to phonons whilst appearing crystalline to charge carriers. This can be achieved by exploiting the fact that the average phonon wavelength is much less than the average electron wavelength. A material can be designed to appear periodic on the scale of electron mean wavelength conserving the concept of electron crystal. Simultaneously a material can be designed to appear amorphous on the scale of phonon mean wavelengths conserving the phonon glass concept. Nano composite super lattices become an easy way to visualise this concept, see diagram below:

Figure 2: Super Lattice Diagram showing changes in energy levels

Due to the larger wavelength of charge carriers propagating through our superlattice they only 'see' an ordered structure. The super lattice can be engineered so that the interfaces between neighbouring 'layers' are highly Amorphous. As these interfaces are thin enough to be 'seen' by phonons but not by electrons they effectively act to increase phonon scattering.

Nanocomposites come in all shapes and sizes. These range through quantum dots (0D), nanowires (1D), superlattices (2D) and Bulk Nanocomposites (3D). The theory behind nanocomposites should prove invaluable in achieving the PGEC concept and maximising ZT.

6 Modelling the Electronic contribution to the thermoelectric effect

In order to model the thermoelectric effect accurately the theory behind charge carrier propagation must be understood. To begin the kinetic method can be studied. This provides a way to classically model the charge carriers within a material. We approximate the force due to an electric field on the charge carrier as causing an associated acceleration. We introduce the idea of a relaxation time. This is the mean time the charge carrier will accelerate for before it interacts with something. The average velocity between o and an interaction is defined as the drift velocity. In practise this is all we need to know to define $k_{chargecarrier}$ in the classical model. This is interesting as the thermal conduction due to charge carriers can be described classically by the transfer of momentum to the lattice through interactions. These concepts are important for describing the rate at which current and heat flows through a material.

As charge carriers are Fermions they can be modelled as a Fermi gas or nearly free electron gas. The distribution of charge carriers is described through Fermi-dirac statistics:

$$\bar{n_i} = \frac{1}{e^{(\epsilon_i - \mu)/KT} + 1} \tag{4}$$

Due to this research being focussed on dynamic equilibriums it becomes necessary to modify this distribution according to the Boltzmann transport equation.

As electrons are momentum carrying particles with a rest mass they have a wavelength associated with their momentum through the de Broglie relation. Accordingly a dispersion relation $E(k)$ can be derived

from the form of the electron kinetic energy. This can be seen in the diagram below:

Figure 3: Electron Dispersion Relation

This can be combined with the band theory concept of a semiconductor. This can be seen in the diagram below:

Figure 4: Band Theory Diagram

In order for an electron to contribute to conduction it must acquire enough energy to bridge the band gap. This will effectively place an electron from the valence band into the conduction band. This leaves an effective lack of charge in the valence band. We call this lack of charge a hole and it acts as a positive charge carrier. This can be thought of as a sort of pair production, each conducting electron is paired with a corresponding conducting hole. If the electron returns to the valence band the corresponding hole will also return to the conduction band.

The Fermi energy describes a hypothetical energy state which will have a 0.5 chance of being occupied at 0k. The Fermi level describes the Fermi energy at a temperature T and is described by the equation below:

$$\epsilon_{fi} = \frac{1}{2}(\epsilon_v + \epsilon_c) + KTln(\frac{m_p*}{m_n*})^{\frac{3}{4}} \tag{5}$$

If the temperature is large enough that the Fermi level bridges the band gap we can expect to see electrons in the conduction band. For our research it is important that this is not achieved as past this point an extrinsic semi conductor will start to behave intrinsicly. This in turn alters the mathematics and provides additional difficulties. The Fermi level becomes an important concept for deriving both the Seebeck and Peltier coefficients. It can be realised that the difference in Peltier coefficients between two materials is really due to the difference in their Fermi levels. For our first approximation we assume both the effective mass of electrons and holes to be constant with temperature. This means that over a temperature gradient we expect a linear change in the Fermi level. This Fermi level gradient can be thought of as a potential difference. This allows us to define the Seebeck coefficient as the voltage generated over a temperature gradient.

The concept of an effective mass can be introduced to simplify the mathematics when modelling charge carriers. This concept allows us to model our nearly free electron gas as a free electron gas under the modification that m goes to $m*$. This effective mass contains the effect of all the potentials effecting the charge carrier. As our dispersion relation for an electron describes the change of potential against kinetic energy the effective mass describes the rate of change of gradient of the parabolic charge carrier potential. Theoretically the effective mass can range between $\pm\infty$. It becomes necessary to model an electron of negative effective mass as a positive 'hole' of positive mass. The form of the effective mass for both electrons and holes becomes incredibly important for truly understanding the movement of the Fermi level with temperature.

7 Modelling the Phonon Contribution to the Thermoelectric Effect

In order to model the thermoelectric effect accurately the theory behind the phonon contribution to the thermal conductivity must be understood. Phonons are collective excitations of the normal modes of oscillation of vibrating atoms within the lattice. That is to say that in analogy to photons a phonon is a propagating wave packet described by the superposition of the fundamental modes of oscillation. An electron has a preferred frequency of oscillation and therefore energy of photon it wants to absorb. In analogy atoms within the lattice also have a preferred frequency of oscillation. It can be pictured that our large phonon contains many small phonons of varying frequency just as white light contains many photons. When this large phonon interacts the oscillating atom will essentially absorb small constituent phonons of it's preferred frequency. This effectively transfers energy to the lattice and is responsible for the propa-

gation of heat through the system. Again in analogy to an excited electron this oscillating atom will re-emit small phonons in a random direction. Due to this random re-emition process phonon scattering is essential for disrupting the flow of heat through a material, decreasing k_{phonon}.

As phonons are bosons they are distributed amongst quantum states according to the Bose-Einstein Distribution:

$$\bar{n_i} = \frac{g_i}{e^{(\epsilon_i - \mu)/KT} - 1} \tag{6}$$

Again due to this research being focussed on dynamic equilibriums it becomes necessary to modify this distribution according to the Boltzmann transport equation.

Just as the kinetic method is used to describe electron propagation the kinetic method for phonon propagation can be introduced. This provides a classical model to determine the mean time and distance between phonon-atom interactions. The concept of a phonon relaxation time can be introduced describing the mean time a phonon will propagate for before interacting. The analogy between the kinetic methods breaks down due to phonons not accelerating. Phonons propagate at a fixed velocity depending on their effective group velocity. That is to say that a phonon spawned due to a specific frequency of oscillation will always propagate at the same velocity. It can be seen from the Bose-Einstein distribution that as the temperature of the system increases so does the average energy of propagating phonons.

So the research must focus on maximising propagating phonon scattering, minimising their effective mobility and therefore k_{phonon}. One method would be to introduce atoms of a different mass. These atoms would have a different preferred frequency and would therefore interact with different phonons. It can be seen that this method would prove most effective if these two preferred frequencies of oscillation were as different as possible while remaining in the range of propagating phonons. This is achieved through a large difference in mass between the two atoms contained within an alloy. Another method is to introduce complex structures on the scale of propagating phonon wavelengths. These structures would effectively act to enhance the chance of a phonon interacting with an atom. Once the phonon dispersion relation is known the specific velocities of propogation for phonons of varying wavelengths is known. Small wavelength phonons are easily scattered. Phonons with a large velocity of propogation contribute the most to the transfer of heat. This research will need to focus on scattering phonons with the largest velocities of propogation in order to minimize k_{phonon}.

8 Summary

The thermoelectric effect is defined by the propogation of charge carriers and phonons through a material. Electrons will be modelling using the nearly free electron modelling obeying Fermi-Dirac statistics. Phonons will be modelled as a gas of bosons obeying Bose-Einstein statistics. Both of these distributions will be modified according to the Boltzmann transport equation due to this research being focussed on dynamic equilibriums. Further research will focus on turning this qualitative understanding into something more quantitative. Further research into modelling phonons is required to understand heat propogation. Understanding how phonons interact with charge carriers will be important to understand basic phenomena. Research into nanocomposites and the effective mass concept will provide insight into how nanocomposite display increased ZT.

A list of the symbols used is given below:

References

[1] A. J. Minnich, M. S. Dresselhaus, Z. F. Ren and G. Chen, *Bulk nanostructured thermoelectric materials: current research and future prospects*

Table 2: Table of symbols

Symbol	Meaning
ZT	Figure of Merit
T	Absolute Temperature
k	Thermal Conductivity
ϵ	An Energy State (Fermi or specific)
σ	Electrical Conductivity
η	Efficiency
$\bar{n_i}$	State Occupancy
g_i	Degeneracy
S	Seebeck Coefficient