TECHNICAL OPERATIONS SUPPORT III (TOPS III)
Task Order 0061: Fundamental Theory Based Assessment of
Thermoelectric Merit Factor for Heusler Alloys

Alper Kinaci, Shiv Meka, Cem Sevik, and Tahir Cagin
Texas A&M University

OCTOBER 2010
FINAL REPORT

Approved for public release; distribution is unlimited.

See additional restrictions described on inside pages.

STINFO COPY

AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE
NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the USAF 88th Air Base Wing (88 ABW) Public Affairs Office and is available to the general public, including foreign nationals. Copies may be obtained from the Defense Technical Information Center (DTIC) (http://www.dtic.mil).

AFRL-RX-WP-TR-2011-4133 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

*//SIGNATURE//
DOUGLAS DUDIS, Program Manager
Thermal Sciences and Materials Branch
Nonmetallic Materials Division

*//SIGNATURE//
NADER HENDIZADEH, Chief
Thermal Sciences and Materials Branch
Nonmetallic Materials Division

*//SIGNATURE//
SHASHI K. SHARMA, Deputy Chief
Nonmetallic Materials Division
Materials and Manufacturing Directorate

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government’s approval or disapproval of its ideas or findings.

*Disseminated copies will show “//signature//” stamped or typed above the signature blocks.
### REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Defense, Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

<table>
<thead>
<tr>
<th>1. REPORT DATE (DD-MM-YYYY)</th>
<th>October 2010</th>
<th>2. REPORT TYPE</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. DATES COVERED (From – To)</td>
<td>19 December 2008 – 18 December 2010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. TITLE AND SUBTITLE</td>
<td>TECHNICAL OPERATIONS SUPPORT III (TOPS III) Task Order 0061: Fundamental Theory Based Assessment of Thermoelectric Merit Factor for Heusler Alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5a. CONTRACT NUMBER</td>
<td>FA8650-05-D-5807-0061</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5b. GRANT NUMBER</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5c. PROGRAM ELEMENT NUMBER</td>
<td>62102F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5d. PROJECT NUMBER</td>
<td>4084</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5e. TASK NUMBER</td>
<td>1P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5f. WORK UNIT NUMBER</td>
<td>BT103100-A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. AUTHOR(S)</td>
<td>Alper Kinaci, Shiv Meka, Cem Sevik, and Tahir Cagin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</td>
<td>Texas A&amp;M University College Station, TX 77843-3122 For Universal Technology Corporation 1270 N. Fairfield Road Dayton, OH 45432-2600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. PERFORMING ORGANIZATION REPORT NUMBER</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</td>
<td>Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. SPONSOR/MONITOR’S ACRONYM(S)</td>
<td>AFRL/RXBTC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. SPONSOR/MONITOR’S REPORT NUMBER(S)</td>
<td>AFRL-RX-WP-TR-2011-4133</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. DISTRIBUTION / AVAILABILITY STATEMENT</td>
<td>Approved for public release; distribution is unlimited.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. SUPPLEMENTARY NOTES</td>
<td>Report contains color. PAO Case Number: 88ABW-2011-3204; Clearance Date: 06 Jun 2011.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. ABSTRACT</td>
<td>Intensive previous work (1950-1970) led to discovery of bulk Bi\textsubscript{2}Te\textsubscript{3} and Sb\textsubscript{2}Te\textsubscript{3} type heavy metal, low temperature thermoelectrics having dimensionless figure of merits (ZT’s) in the vicinity of 1. Nonetheless, no material having marginally higher performance over Bi-Te and Sb-Te thermoelectrics can yet be commercialized. Moreover, these materials are not very practical due to scarcity of the elements, toxicity and decomposition-evaporation problems at elevated temperatures. Today, there are a number of promising ideas eliminate that can be realized through advanced synthesizing techniques, to increase ZT of more commonplace compounds such as clathrates, skutterudites, disordered heavy metal compounds, Half-Heusler allows and complex oxides.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15. SUBJECT TERMS</td>
<td>Half-Heusler alloys, thermoelectrics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16. SECURITY CLASSIFICATION OF:</td>
<td>a. REPORT UNCLASSIFIED b. ABSTRACT UNCLASSIFIED c. THIS PAGE UNCLASSIFIED</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17. LIMITATION OF ABSTRACT</td>
<td>SAR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18. NUMBER OF PAGES</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19a. NAME OF RESPONSIBLE PERSON</td>
<td>Douglas Dudis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19b. TELEPHONE NUMBER (include area code)</td>
<td>(937) 255-9728</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Approved for public release; distribution unlimited.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>ii</td>
</tr>
<tr>
<td>1.0 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2.0 THEORY</td>
<td>3</td>
</tr>
<tr>
<td>2.1 Electronic Contribution</td>
<td>3</td>
</tr>
<tr>
<td>3.0 RESULTS</td>
<td>5</td>
</tr>
<tr>
<td>4.0 HALF-HEUSLERS</td>
<td>12</td>
</tr>
<tr>
<td>5.0 REFERENCES</td>
<td>22</td>
</tr>
<tr>
<td>LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS</td>
<td>24</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ni$_3$Sn (Hexagonal)</td>
<td>5</td>
</tr>
<tr>
<td>2. Ni$_3$Sn Performance Data</td>
<td>6</td>
</tr>
<tr>
<td>3. NiZr (Orthorhombic)</td>
<td>7</td>
</tr>
<tr>
<td>4. NiZr Performance Data</td>
<td>8</td>
</tr>
<tr>
<td>5. Zr$_5$Sn$_3$ (Hexagonal)</td>
<td>9</td>
</tr>
<tr>
<td>6. Zr$_5$Sn$_3$ Performance Data</td>
<td>10</td>
</tr>
<tr>
<td>7. NiSrZn</td>
<td>11</td>
</tr>
<tr>
<td>8. Summary of Lattice Parameters, Computational Parameters, and Band Gaps in HH</td>
<td>14</td>
</tr>
<tr>
<td>9. DOS, Experimental Fits to Compute Relaxation Time and $zT$</td>
<td>15</td>
</tr>
<tr>
<td>10. (Clockwise) i) Total-DOS of NiSnZr Calculated with the Two Methods - L(S)DA+U (U=7.5, J=0.65) and LDA. Basic Implementation of LDA Fails to Correctly Treat Correlation Effects in Highly Correlated Systems. Figure Also Compares Projected pDOS of Nickel in ii) $t_2g$ and iii) $eg$ States Using Both Methods</td>
<td>16</td>
</tr>
<tr>
<td>11. Seebeck Coefficient, Power Factor and ZT Plots of NiSnZr</td>
<td>17</td>
</tr>
<tr>
<td>12. DOS, Seebeck Coefficient, Power Factor and ZT Plots of LiAlSi</td>
<td>18</td>
</tr>
<tr>
<td>13. DOS, Seebeck Coefficient, Power Factor and ZT Plots of MbFeSb</td>
<td>19</td>
</tr>
</tbody>
</table>
1.0 INTRODUCTION

The intensive work in 1950-1970 period had led to discovery of bulk Bi$_2$Te$_3$ and Sb$_2$Te$_3$ type heavy metal, low temperature thermoelectrics having dimensionless figure of merits (ZT’s) in the vicinity of 1. Nonetheless, no material having marginally higher performance over Bi-Te and Sb-Te thermoelectrics can be commercialized yet. Moreover, these materials are not very practical due to scarcity of the elements, toxicity and decomposition-evaporation problems at elevated temperatures [1]. Today, there are a number of promising ideas eliminate that can be realized through advanced synthesizing techniques, to increase ZT of more commonplace compounds such as clathrates [2], skutterudites [3], disordered heavy metal compounds [4], Half-Heusler alloys [5] and complex oxides [6].

The performance of a device for such an application is generally defined by its figure of merit $Z$.

$$Z = \frac{\sigma S^2}{\kappa}$$

where $\sigma$ is electrical conductivity, $\kappa$ is thermal conductivity and $S$ is the Seebeck coefficient (thermo-electromotive force – voltage gradient produced in a material due to temperature gradient when electrical current is zero). By multiplying with average temperature, $ZT$ (dimensionless figure of merit) is obtained. It is customary to seek a $ZT$ larger than 0.5 in a material order to consider it as thermoelectric. However, it is stated that a magnitude 3 or higher should be obtained to replace existing commercial appliances, such as compressor based refrigerators, with thermoelectric based systems [7].

As it is seen from the Eq. (1), a high $ZT$ is associated with, low internal resistance to electric flow i.e. high electrical conductivity ($\sigma$), low thermal conductivity ($\kappa$), which produces a large temperature difference between the ends and a large thermopower ($S$), that is required to obtain high voltage. The main problem with the thermoelectric performance is the inter-dependence of $\sigma$, $\kappa$ and $S$. This dependence is basically through carrier concentration. Thermal and electrical conductivity increases while Seebeck coefficient decreases with increasing carrier concentration.

Luckily, recent developments in material synthesizing and device production methods can realize several ideas for increasing thermoelectric performance. Optimizing carrier density and band gap width (at least 10 kT [8]) is one route. This is achievable through doping and alloying. On the other hand, thermal conductivity has an additional contribution from lattice conduction which must also be minimized. Over the years, several empirical rules were obtained for low thermal conductivity such as, the necessity of high average coordination numbers, large number of atoms in unit cell and high atomic masses in materials. In addition to these, there are also two relatively new and promising ideas exist to produce materials with low lattice thermal conductivity. One of them is the cake-like structures where a weakly bonded atom or molecule in the unit cell creates localized vibrational and rotational modes. This controlled disorder is believed to posses the phonon behavior of a glass and electronic conduction of a crystal. The interest in Half-Heusler alloys is resulted from this design. Secondly, low dimensional structures such as ultra-thin films, nanowires, superlattices etc. should have reduced $\kappa_{\text{lattice}}$ due to increased phonon scattering from interfaces depending on the phonon mean free path. However, it is shown that [9, 10] miniaturizing below some critical length also modifies electronic band structure which results in high ZT’s [11].

1

Approved for public release; distribution is unlimited.
The figure of merit measurement is not a hard task for a large sized bulk sample, yet, it can get quite complicated for extremely small structural features. In order to understand partial contribution of each constituent in ZT and the physical reasoning behind it for a specific configuration, theoretical evaluation is necessary. Then again, calculation of ZT is a formidable task and generally necessitates several approaches to be employed at the same time. Here, it is convenient to state some of these methods in two general headings, electronic and lattice contribution.
2.0 THEORY

2.1 Electronic Contribution

Several qualitative methods are presented in literature [4, 12-18]. The approximations in these studies are similar, if not same, when calculating figure of merit. Restraining ourselves to derivation of Scheidemantal et al.’s [12] work, the transport coefficients for an isotropic solid in the presence of electric field and thermal gradient are given in equations

\[ \vec{J} = \sigma \vec{E} - \nabla \vec{T} \]  
(2)

\[ \vec{J}_\theta = T \nabla \vec{E} - \kappa_0 \nabla \vec{T} \]  
(3)

where \( \vec{J}, \vec{J}_\theta, \vec{E}, \sigma, \nabla \vec{T}, T \) are electric current density, heat current density, electric field, electrical conductivity, temperature gradient and absolute temperature respectively. Underscore (~) symbol represents tensorial quantities. From the definition of the Seebeck coefficient, the following equation can be extracted for single components as

\[ S = \frac{N}{\sigma} \]  
(4)

Electronic contribution to thermal conductivity (\( \kappa_{el} \)) can be defined as the heat current produced per unit temperature gradient when electrical current is zero, thus

\[ \kappa_{el} = \kappa_0 - T \sigma S^2 \]  
(5)

The electrical current can be defined by the group velocity approximation as below

\[ \vec{J} = e \sum_k f_k \vec{v}_k \]  
(6)

In this equation \( e, f_k, \vec{v}_k \) are the charge of the carriers, population of the quantum state at \( k \) and the group velocity associated with that state. Group velocity can be represented as the gradient of band structure in reciprocal space, so

\[ \vec{v}_k = \frac{1}{\hbar} \frac{\partial \epsilon_k}{\partial k} \]  
(7)

Another approach can be constructed by relating group velocity to momentum

\[ \vec{v}_k = \frac{1}{m} \vec{p}_k = \frac{1}{m} \langle \psi_k | p | \psi_k \rangle \]  
(8)

It is shown that both methods can be implemented in DFT successfully to obtain group velocity [12, 13]. Finally, a model is needed to bridge between transport coefficients and group velocity. Here, Boltzmann transport equation is introduced

\[ \frac{df_k}{dt}_{\text{scattering}} = \frac{\partial f_k}{\partial t} + \vec{v}_k \cdot \frac{\partial f_k}{\partial \vec{r}} + \frac{e}{\hbar} \left( \vec{E} + \frac{1}{c} \vec{v}_k \times \vec{H} \right) \cdot \frac{\partial f_k}{\partial k} \]  
(9)
The terms on the right hand side are the drift terms in time, spatial and momentum space. The term on the left hand side is the change of population due to scattering events. Due to complexity of such events relaxation time approximation can be used

\[
\frac{df_k}{dt}_{\text{scattering}} = -\frac{f_k - f_0}{\tau}
\]  

(10)

where \(\tau\) is the relaxation time. \(f_0(\varepsilon_k)\) is the Fermi distribution function for fermions in the absence of fields and \(\varepsilon_k\) represent state energies. Replacing the scattering term and assuming no magnetic field and temperature gradient (diffusional dependence), the population is given as

\[
f_k = f_0(\varepsilon_k) + e\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\tau_k \vec{v}_k \cdot \vec{E}
\]  

(11)

Using Eq. 2, 6 and 11 together, and noting that the population \(f_0(\varepsilon_k)\) is same for \(k\) and \(-k\), leading to cancellation in the summation and zero net current flow, electrical conductivity can be written as

\[
\sigma = e^2 \sum_k \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \vec{v}_k \cdot \vec{E} \tau_k
\]  

(12)

Let \(\xi\) be defined as the transport distribution such that

\[
\xi = \sum_k \vec{v}_k \cdot \vec{E} \tau_k
\]  

(13)

Then, by using scalar components of coefficients electrical conductivity, Seebeck coefficient and thermal conductivity can be written as

\[
\sigma = e^2 \int \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \xi(\varepsilon) d\varepsilon
\]  

(14)

\[
S = \frac{ek_B}{\sigma} \int \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \xi(\varepsilon) \frac{\varepsilon - \mu}{k_B T} d\varepsilon
\]  

(15)

\[
\kappa = k_B T \int \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \xi(\varepsilon) \left[\frac{\varepsilon - \mu}{k_B T}\right]^2 d\varepsilon
\]  

(16)

The equations written above are for single band only, so additional band index \(n\) should be added next to \(k\) index.
3.0 RESULTS

The following are the cell structures and transport data (obtained from the theory mentioned above) for the three selected binary alloys (Ni₃Sn, NiZr and Zr₅Sn₃) between Ni-Sn, Ni-Zr and Sn-Zr. All have metallic properties conduction properties. In addition, we also present ternary NiSrZr (which comes out to be a semiconductor) transport data.

Figure 1. Ni₃Sn (Hexagonal)
Figure 2. Ni3Sn Performance Data
Figure 3. NiZr (Orthorhombic)
Figure 4. NiZr Performance Data
Figure 5. Zr5Sn3 (Hexagonal)
Figure 6. Zr5Sn3 Performance Data
Equilibrium structure of NiSrZn is found from equation of state. Secondly, the effect of hydrostatic pressure (volume contraction) on transport properties is shown.

Figure 7. NiSrZn
4.0 HALF-HEUSLERS

Half-heuslers (HH) are Heusler-like structures with half the atoms missing. Valence electron count (VEC) determines the electronic structure of Heusler\textsuperscript{19} and HH structures\textsuperscript{20}. VEC count of 18 implies existence of bandgap in HH\textsuperscript{21}. HH are usually narrow bandgap semiconductors\textsuperscript{8} that have moderate zT at high temperatures\textsuperscript{22}. The important contributing factor to this “moderateness” is the thermal-conductivity (for eg. NiSnZr has $k$ close to 10 W/m·K). But, their thermal conductivities are obviously lower than their Heusler counterparts. Tailoring the crystal could improve the thermal conductivity. For eg. in NiSnZr, Zr is replaced by a heavier Hf\textsuperscript{23} and the thermoelectric conductivity was halved. The maximum zT in NiSnZr was found to be 0.7 (fig.2.3) which also happens to be an experimental prediction\textsuperscript{23}. Most HH are n-type. It is still a challenge to find their intrinsic p-type and Si-Ge like alter ego. Asymmetry in the position of the Fermi level in the case of LaAlSi and CoSbTi implies they are a natural p-type alloys. In this study, four HH alloys were studied: i) CoSbTi ii) NiSnZr iii) LaAlSi and iv) NbFeSb

An ideal thermoelectric not only has a high zT. While three of the four observed structures performed well at 200 K (with $zT \sim 0.75$), counter intuitive to the generalized perception of zT in HH, NbFeSb has a high zT and behaves as a good thermoelectric over a wide temperature range and for a given doping concentration.

CoSbTi

From the functional form of the Seebeck coefficient, it is apparent that sharp DOS would lead to high S. These ternary inter-metallic structures resemble the MgAgAs cubic types. The transport coefficients of CoSbTi are fit to experiments (fig.2.1).

The doping concentration is estimated as 1.03E20 /cm$^3$. The bandgap was found to be: 0.98 eV (exp.:0.95). PBE functional was used for both exchange and correlation. The lattice parameters are almost the same as the experiment (deviation of 0.002%).

NiSnZr

NiSnZr is our first case where the use of LDA along with a fudge-factor “U” is necessary to prevent Mott-insulator\textsuperscript{24,25} behavior. The approximate exchange-correlation functional, no doubt, gives reasonable results for ground state energies, but fails in spelling out the proper electronic structure. Metallic behavior of the Half-filled d-shells is the prime reason for such an observation. In such cases, d-d Coulombic energies have to be taken into account and if one adds such a correction, the metallic behavior disappears. Is there a reasonable value of U to be added? Yes! “U”, obviously depends on the orbital occupancy which means that the half-filled orbitals have less magnitude of U than the quarter-filled ones. One could make an educated guess and

\textsuperscript{a} Take the case of NiSnZr, the bandgap is thanks to the hybridization of the d-shell electrons of Ni and p-electrons of Sn, and also contribution due to exchange splitting.
sweep $U$ to match the lattice parameters or the electronic bandgap, OR a single-shot calculation needs the value of $U$ be obtained from XPS\textsuperscript{b,c,d}. It is apparent from fig. 2.3 that NiSnZr has a satisfactory $\max\{zT\}$ of 0.7 which agrees with the experimental prediction\textsuperscript{23}.

**Computational details**

The L(S)DAU parameters used are: $U=7.52$ and $J=0.65$. MHP grid of $26^3$ was used. The deviation from experimental lattice parameters was close to 1%.

**LaAlSi**

Both the power factor and $zT$ are to be kept in mind while deciding the overall performance of a dielectric. Since, Seebeck coefficients occurs as a squared value, one cannot rule out a possibility of a very high Seebeck and very low power factor exists. LaAlSi is a reasonably good thermoelectric for below 200 K applications (fig. 2.4). This is apparent from the mean positions of the various Gaussian like $zT$ vs $T$ curves. At higher $T$s, the electrons get thermally excited and nullify any voltage drop (because of narrow bandgap).

**NbFeSb**

Surprisingly, NbFeSb shows a good thermoelectric behavior for temperatures below 600K. There was minimal deviation in the calculated structural parameters when compared to the experimental ones obtained from ICSD. The bandgap was found to be 0.075 eV. A maximum $zT$ was found to be 1.14. Carriers at the valence band have a small effective mass and thus making it possible for even the faintest of temperature gradients to populate the conduction band (which has a sharp band edge). Since the conduction band electrons are massive (from the DOS) and delocalized, possibility is that it develops reasonable potential (associated with the effective mass) and also has high-conductivity.

**Computational details**

There was minimal deviation between the experimental and the computed lattice parameters. LDA was used for both the exchange and correlation functional. $18^3$ MHP grid was used from an SCF calculation which followed a $8^3$ MHP relaxation\textsuperscript{e}.

Statement without proof: The difference between computed lattice parameters and the experimental values is minimal if one uses a primitive cell representation instead of the supercell.

\textsuperscript{b} This exercise doesn’t guarantee of exact lattice parameters as there are other shells that suffer from the lack of a better exchange-correlation functional.

\textsuperscript{c} Ref. [31] deals with the extraction of $U$ from XPS binding energies. In general, it is the effective ($U-J$) that needs to be corrected, $J$ being the exchange correction which also depends on the occupancy since the exchange and correlation are a lumped unit in GGA/LDA.

\textsuperscript{d} Occupancies needn’t always be whole numbers as it would be shown in Chapter 3, the electron occupancies may even assume fractional values owing to hybridization of a particular state.

\textsuperscript{e} Prior to calculating the SCF data values, it was made sure that all the systems saw through 1meV convergence both on k-points and the energies.
Figure 8. Summary of Lattice Parameters, Computational Parameters, and Band Gaps in HH
Figure 9. DOS, Experimental Fits to Compute Relaxation Time and $zT$
Figure 10. (Clockwise) i) Total-DOS of NiSnZr Calculated with the Two Methods - L(S)DA+U (U=7.5, J=0.65) and LDA. Basic Implementation of LDA Fails to Correctly Treat Correlation Effects in Highly Correlated Systems. Figure Also Compares Projected pDOS of Nickel in ii) t_{2g} and iii) e_{g} States Using Both Methods
Figure 11. Seebeck Coefficient, Power Factor and ZT Plots of NiSnZr
Figure 12. DOS, Seebeck Coefficient, Power Factor and ZT Plots of LiAlSi
Figure 13. DOS, Seebeck Coefficient, Power Factor and ZT Plots of NbFeSb
The demand for energy is for sustainable development is increasing. One way to go about the problem is to *squeeze the fruit till the last drop*. Thermoelectrics do just this! They perform the last rites by scavenging waste heat. Car exhausts, geothermal energy, home heating, industries and microchips are sources where the systems get thermally equilibrated before being put to good use. Scavenger engineering has been one of the challenges of the recent past. A plethora of materials and alloys leads to confusion on rounding in on a material to be used as a thermoelectric. A rational approach would be to observe patterns of behavior of different classes of heat-scavengers and capture the physics to understand the rationale behind the working of these devices. Also, the quality of thermoelectric conversion has to be expressed in numbers so that one would be able to compare between two given samples, observe empirical patterns that could even help on improving the efficiency. Mathematically, the figure of merits (zT) sums it all: 

$$zT = S^2 \sigma T/k$$

where $S$ is the Seebeck coefficient which tells how much electrical work does a temperature gradient does, $\sigma$ is the conductivity, $T$, the temperature and $k$: the thermal conductivity. While $S$ is directly proportional to the open circuit voltage (developed across the structure that has just a temperature gradient without any external electric field ($\Delta V/\Delta T$)), the power factor (pf$\sigma$) is the closed circuit current and depends on the conductivity. In order to maximize the function $zT$, one needs to have both Seebeck coefficient and the electrical conductivity high, and $k$ low. But this is contradicting. How can something develop a high *emf* and even pump current? The subtlety is: the overall product is what matters. But, it is a reasonable assumption since one needs not just a voltage difference developed, but the circuit ought to be closed or there could be charge buildup finally breaking the dielectric (joule heating). Beginning with thermocouples, thermoelectrics have a very long history. Thermoelectrics of the 70’s aren’t any better. Recent trends in nanostructured materials improved efficiency 4 folds.

**Doping:**

Type of carriers involved in the transport plays a crucial role in determining the efficiency of a thermoelectric. In general, it is advised to have higher concentration of carriers of one type. Bipolar carrier recombination adds to $k$ which degrades the performance of the thermoelectric. And, therefore, one carrier type must dominate in order to have maximum $S$. Mixed conduction cancels out the net effect of charge flow as one carrier moves to the hot end and the other to the cold.

**kappa “k”**

According to Wiedemann-Franz law: 

$$k = k_e + k_l$$

where $k_e$ is the electronic contribution (Lorentz factor $L = 2.4 \times 10^{-8} J^2 K^{-2} C^{-2}$) because of charge carriers transporting heat and $k_l$ is the thermal conductivity due to phonons. For most systems, $k_l$ has an above 75% contribution to the total $k$, and is mostly constant with concentration. Glasses are known for low $k_l$, But, electrons in glasses are scattered making them poor thermoelectrics.

**Low or High $m^*$?**

From simple Drude’s model, large $m^*$ means good $S$ but a bad $\sigma$. So, mobility is an important deciding factor in thermoelectric design. $m^*$ is directly proportional to the density of states. Flat bands (large $m^*$) mean localized electrons and have a high $S$. Dephasing issues and lattice thermal conductivity, scattering, and anisotropy are a summed up contribution in the overall performance. Large $m^*$ with low conductivity (for eg.:chalcogenides) are a result of small
electronegativity differences while small m* and large conductivity are a result of large electronegativity differences, but both have a good zT.

**Final Verdict**

One needs a “phonon-glass and an electron crystal”\(^1\) to realize a close to ideal thermoelectric. Glass like properties are achieved by scattering phonons, engineering scattering centers and making solid-solutions. Clathrates, filled skutterudites, Quantum dot super-lattices (QDSLs), Zintl phases have so far been identified as potential candidates in the high-zT region of thermoelectric operation. Nanostructuring and organic-inorganic hybrid structures may present other avenues to achieve goal of high ZT.
5.0 REFERENCES


# LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFRL</td>
<td>Air Force Research Laboratory</td>
</tr>
<tr>
<td>DOD</td>
<td>Department of Defense</td>
</tr>
<tr>
<td>DTIC</td>
<td>Defense Technical Information Center</td>
</tr>
<tr>
<td>EAR</td>
<td>Export Administration Regulation</td>
</tr>
<tr>
<td>HH</td>
<td>Half-Heuslers</td>
</tr>
<tr>
<td>ITAR</td>
<td>International Traffic in Arms Regulation</td>
</tr>
<tr>
<td>LaAlSi</td>
<td>Lanthanum Aluminum Silicide</td>
</tr>
<tr>
<td>NbFeSb</td>
<td>Niobium Ferrous Antimonide</td>
</tr>
<tr>
<td>QDSLs</td>
<td>Quantum Dot Super-Lattices</td>
</tr>
<tr>
<td>RX</td>
<td>Materials</td>
</tr>
<tr>
<td>RXB</td>
<td>Nonmetallic Materials Division</td>
</tr>
<tr>
<td>RXBTC</td>
<td>Active Thermal Control Section</td>
</tr>
<tr>
<td>TOPS</td>
<td>Technical Operations Support</td>
</tr>
<tr>
<td>USAF</td>
<td>United States Air Force</td>
</tr>
<tr>
<td>VEC</td>
<td>Valence Electron Count</td>
</tr>
<tr>
<td>WPAFB</td>
<td>Wright-Patterson Air Force Base</td>
</tr>
<tr>
<td>ZT’s</td>
<td>Figure of Merits</td>
</tr>
</tbody>
</table>