The effect of extended strain fields on point defect scattering

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Extended Strain Fields and Point-Defect Phonon Scattering

Brenden Ortiz, Haowei Peng, Armando Lopez, Phillip Parilla, Stephan Lany, Eric Toberer

Colorado School of Mines, Golden, CO

National Renewable Energy Laboratory, Golden, CO

ECI Non-Stoichiometric Compounds (Santa Fe 2016)
Thermoelectrics as an Optimization Problem

\[ zT(\kappa, S, \sigma, T) = \frac{S^2 \sigma}{\kappa} T \]

\[ zT = zT(\eta, m^*, \tau, E_g, \ldots) \]

Each transport phenomenon also has \( T \) dependence
Thermoelectrics as an Optimization Problem

\[ zT(\kappa, S, \sigma, T) = \frac{S^2 \sigma}{\kappa} T \]

\[ zT = zT(\eta, m^*, \tau, E_g, \ldots) \]

The thermal conductivity, \( \kappa \), is commonly targeted for optimization.

Each transport phenomenon \textbf{also} has \( T \) dependence.
Thermoelectrics as an Optimization Problem

\[ zT(\kappa, S, \sigma, T) = \frac{S^2\sigma}{\kappa} T \]

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Alloys as a source of point defect scattering

Mass contrast simple, but role of strain field not obvious in complex crystals
Chemical degrees of freedom can slow down experimental searches
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Mission Statement

Can we find a way to accelerate the discovery of effective alloys using simple, intuitive computational models?
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Experiment / Modeling

Ab Initio Computation
Mission Statement

Can we find a way to accelerate the discovery of effective alloys using simple, intuitive computational models?

Experiment / Modeling
- Model System
  - Classical Alloy Models
  - Experimental Results

Ab Initio Computation
- Toy Models for Strain
  - Computational Methods
  - Computational Results
Mission Statement

Can we find a way to accelerate the discovery of effective alloys using simple, intuitive computational models?

Experiment / Modeling
- Model System
  - Classical Alloy Models
  - Experimental Results

Ab Initio Computation
- Toy Models for Strain
  - Computational Methods
  - Computational Results

Effective Proxy?
Experiment – Model System

**SnSe** (Pnma) + one of Sr, Ba, S, Se, Te
(e.g. Sn$_{1-x}$Ba$_x$Se)

Distorted-rock salt structure
+ Rock-salt and non rock-salt endpoints

BaSe, SrSe, SnTe: Rock-salt

SnS, GeSe: Layered Pnma (distorted-RS)
Experiment – Model System

\[
\text{SnSe (Pnma) + one of Sr, Ba, S, Se, Te} \\
\text{(e.g. Sn}_{1-x}\text{Ba}_x\text{Se)}
\]

Synthesis (e.g. SnSe + SnSe}_2 + Ba) \\
+ Ball-milling and inductive hot-pressing
Experiment – Model System

**SnSe** (Pnma) + one of Sr, Ba, S, Se, Te
(e.g. Sn$_{1-x}$Ba$_x$Se)

X-ray Diffraction, Rietveld Refinement
+ Vegard’s Law

![Graph showing the cell volume vs. nominal composition for different elements: S, Ge, Te, Sr, Ba. The graph includes error bars and shows a linear trend for each element.](image-url)
Note large spread in the thermal conductivity w/alloying species.

Depressions range from slight (e.g. Sulfur) to severe (e.g. Ba)

Need to model to understand role of chemistry on scattering.

Abeles Model for Alloy Scattering \(^1\)

---

Abeles model for composition dependent thermal conductivity

Thermal Conductivity of Alloy ($\kappa_{\text{alloy}}$) ...

$$\kappa_{\text{alloy}} = \kappa_0 \left( \frac{\tan^{-1}(u)}{u} \right)$$
Abeles model for composition dependent thermal conductivity

Thermal Conductivity of Alloy ($\kappa_{\text{alloy}}$) ...

Disorder Scaling Parameter ($u$) ...

\[
\kappa_{\text{alloy}} = \kappa_0 \left( \frac{\tan^{-1}(u)}{u} \right)
\]

\[
u = \left( \frac{\pi^2 \Theta \Omega}{h\nu_s^2} \kappa_0 \Gamma_{\text{tot}} \right)^{1/2}
\]
Abeles model for composition dependent thermal conductivity

Thermal Conductivity of Alloy ($\kappa_{\text{alloy}}$) ...

Disorder Scaling Parameter ($u$) ...

Net Scattering Factor ($\Gamma_{\text{tot}}$) ...

\[ \kappa_{\text{alloy}} = \kappa_0 \left( \frac{\tan^{-1}(u)}{u} \right) \]

\[ u = \left( \frac{\pi^2 \Theta \Omega}{h \nu_s^2} \kappa_0 \Gamma_{\text{tot}} \right)^{1/2} \]

\[ \Gamma_{\text{tot}}' = \Gamma_{m}' + \Gamma_{s}' \]
\[ \Gamma_{\text{tot}}' = \Gamma_m' + \Gamma_s' \]

\[ \Gamma_m' = x(1 - x) \frac{a}{a + b} \left( \frac{\Delta M_{\text{Sn,X}}}{M_{\text{Sn,X}}} \right)^2 \]

\[ \Gamma_s' = x(1 - x) \epsilon \frac{a}{a + b} \left( \frac{\Delta r_{\text{Sn,X}}}{r_{\text{Sn,X}}} \right)^2 \]
\[ \Gamma'_{\text{tot}} = \Gamma'_m + \Gamma'_s \]

\[ \Gamma'_m = x(1-x) \frac{a}{a+b} \left( \frac{\Delta M_{\text{Sn,X}}}{M_{\text{Sn,X}}} \right)^2 \]

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Experiment – Transport and Modeling

\[ \Gamma'_\text{tot} = \Gamma'_m + \Gamma'_s \]

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- **Mass Contrast**
  - \[ \left( \frac{\Delta M_{\text{Sn},X}}{M_{\text{Sn},X}} \right)^2 \]
- **Radii Contrast**
  - \[ \left( \frac{\Delta r_{\text{Sn},X}}{r_{\text{Sn},X}} \right)^2 \]
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Mass Contrast

Free parameter

Radii Contrast
Experiment – Transport and Modeling

\[ \Gamma'_\text{tot} = \Gamma'_m + \Gamma'_s \]

\[ \Gamma'_m = x(1-x) \frac{a}{a+b} \left( \frac{\Delta M_{\text{Sn},X}}{M_{\text{Sn},X}} \right)^2 \]

\[ \Gamma'_s = x(1-x) \varepsilon \frac{a}{a+b} \left( \frac{\Delta r_{\text{Sn},X}}{r_{\text{Sn},X}} \right)^2 \]

\[ \kappa_{\text{alloy}} \left( \kappa_0, v_s, x, \varepsilon, r_\alpha \ldots, m_\alpha \ldots \right) \]
Experimental Summary

\[ \kappa_{\text{alloy}}(k_0, \nu_s, x, \varepsilon, r_\alpha \ldots, m_\alpha \ldots) \]

Increasing Strain Contribution

+ Decreasing Thermal Conductivity

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(\frac{\Gamma_s}{\Gamma_m})</th>
<th>(\Gamma_s')</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ge</td>
<td>1.73</td>
<td>0.0063</td>
</tr>
<tr>
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<tr>
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Computational Toy Models

Mass Contrast:
\[ m \neq m' \]

Registry Loss:
\[ \neq \]

Bond Strain:
\[ \neq \]
Computational Methods

**Approach 1: Pair-Distribution Function (Supercell)**

32-atom special quasi-random structures (SQS) to mimic 25% alloy PDF’s
Computational Methods

Approach 1: Pair-Distribution Function (Supercell)

32-atom special quasi-random structures (SQS) to mimic 25% alloy PDF’s
Computational Methods

Approach 1: Pair-Distribution Function (Supercell)

32-atom special quasi-random structures (SQS) to mimic 25% alloy PDF’s
Computational Methods – Pair Distribution Fn

SnSe

\[ \Delta_{PDF} = 1.62 \]

Sn\textsubscript{0.75}Ge\textsubscript{0.25}Se

\[ \Delta_{PDF} = 2.69 \]

Sn\textsubscript{0.75}Te\textsubscript{0.25}

\[ \Delta_{PDF} = 2.89 \]

Sn\textsubscript{0.75}Sr\textsubscript{0.25}Se

\[ \Delta_{PDF} = 3.74 \]

Sn\textsubscript{0.75}Ba\textsubscript{0.25}Se

\[ \Delta_{PDF} = 4.14 \]
Computational Methods – Pair Distribution Fn

\[ \Delta_{PDF} = \int_{0}^{r_{\text{max}}} |PDF_{\text{SnSe}}(r) - PDF_{\text{Alloy}}(r)| \, dr \]
\[ \Delta_{PDF} = \int_0^{r_{\text{max}}} |PDF_{SnSe}(r) - PDF_{Alloy}(r)| \, dr \]
Computational Methods – Pair Distribution Function

\[ \Delta_{PDF} = \int_{0}^{r_{\text{max}}} |PDF_{\text{SnSe}}(r) - PDF_{\text{Alloy}}(r)| \, dr \]

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Computational Methods

**Approach 2: Single Atom Distortion (Supercell)**

256-atom supercell with singular atom replaced by alloying species
Computational Methods

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Approach 2: Single Atom Distortion (Supercell)

256-atom supercell with singular atom replaced by alloying species

Change in local coordination around species...

How far from source atom does it extend?

How large of a distortion?

Relation with chemistry?
Computational Methods – Single Atom Distortion

Sulfur

$\Delta_{\text{SAD}} = 0.38$

Germanium

$\Delta_{\text{SAD}} = 0.54$

Tellurium

$\Delta_{\text{SAD}} = 0.92$

Strontium

$\Delta_{\text{SAD}} = 1.86$

Barium

$\Delta_{\text{SAD}} = 2.96$

Atomic Displacement

- > 0.10Å
- Thermal Cutoff
- < 0.01Å
\[ \Delta_{SAD} = \sum_{i=1}^{N} |\vec{r}_{\text{Alloy},i} - \vec{r}_{\text{SnSe},i}| \]

Atomic Displacement

\begin{tabular}{c|c|c}
 & > 0.10Å & < 0.01Å \\
\hline
Thermal Cutoff & & \\
\end{tabular}

Tellurium: \( \Delta_{SAD} = 0.92 \)

Strontium: \( \Delta_{SAD} = 1.86 \)

Barium: \( \Delta_{SAD} = 2.96 \)
Computational Methods – Single Atom Distortion

\[ \Delta_{\text{SAD}} = \sum_{i=1}^{N} \left| \vec{r}_{\text{Alloy},i} - \vec{r}_{\text{SnSe},i} \right| \]

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Computational Summary

**Approach 3: Bulk Modulus (Supercell)**

Standard calculation of total energy in DFT (LDA) as a function of cell volume...

Fitting of the Murnaghan equation of state to $E(\Omega)$

$$E(\Omega) = E_0 + \frac{B_0 \Omega}{B'_0} \left( \frac{(\Omega_0/\Omega)^{B'_0/B'_0}}{B'_0 - 1} + 1 \right) - \frac{B_0 \Omega_0}{B'_0 - 1}$$

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<tr>
<td>SnSe</td>
<td>42.2</td>
</tr>
<tr>
<td>S</td>
<td>40.8</td>
</tr>
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<td>Ge</td>
<td>39.9</td>
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Hybridization of Experimental and Computation

Do experiment and computation agree?

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Do experiment and computation agree?

![Graph showing data points for different elements]

- Red: S
- Orange: Ge
- Green: Te
- Blue: Sr
- Purple: Ba
Hybridization of Experimental and Computation

Do experiment and computation agree?

Only determined by experiment

Only determined by computation

\[ \Delta_{SAD} \text{ (Å)} \]

\[ \text{Bulk Modulus (GPa)} \]

\[ \Delta_{PDF} \text{ (Å)} \]
Hybridization of Experimental and Computation

Do experiment and computation agree?

Only determined by experiment

Only determined by computation

Yes!
Computation successfully ranks relative changes in strain and transport by proxy.
Conclusion

Presented inexpensive, conceptually transparent methods to visualize alloying in SnSe.

Strain effects can be observed far from host lattice site.

Computational ranking successful as proxy for experiment.

Possible down-selection of effective alloying agents.