Investigation of High Temperature Thermoelectric Materials

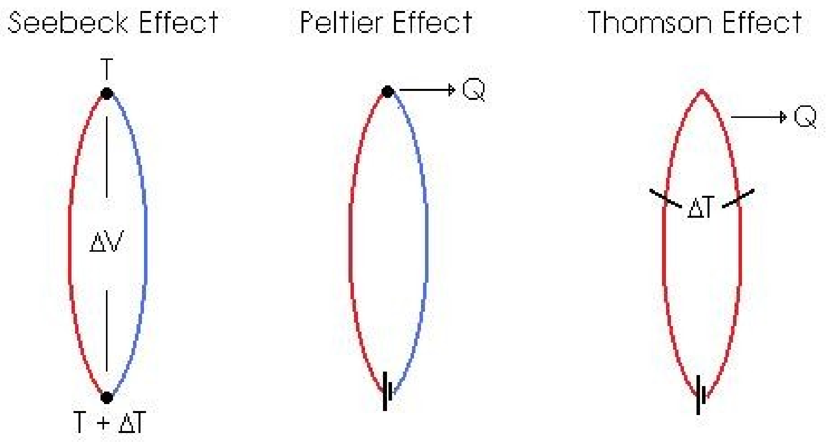
Research Progress and Prospects for Completion

Jack Simonson

Outline

- Review of Themoelectricity
- XNiSn-type Half-Heusler Dopant Electronic Structure Investigation
- Rare Earth Telluride high-temperature thermoelectrics

Thermoelectricity



- Seebeck:

$$S = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}$$

- Peltier:

$$\pi = \frac{Q}{I} = S \cdot T$$

- Thomson:

$$\gamma = \lim_{\Delta T \to 0} \frac{\Delta Q}{I \Delta T} = T \frac{dS}{dT}$$

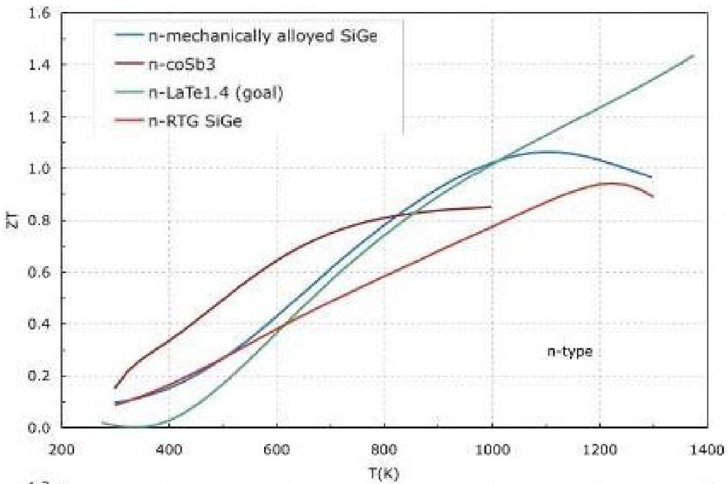
Thermoelectric Efficiency for Power Generation

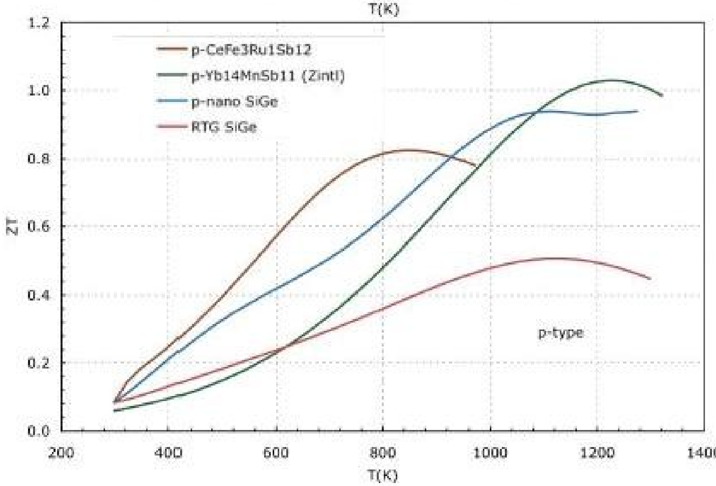
- Dimensionless Figure of Merit:

$$ZT = \frac{S^2 T}{\rho\kappa}$$

- ZT is a measure of efficiency. A ZT of zero indicates no power generation, and a ZT of infinity is Carnot Efficiency.

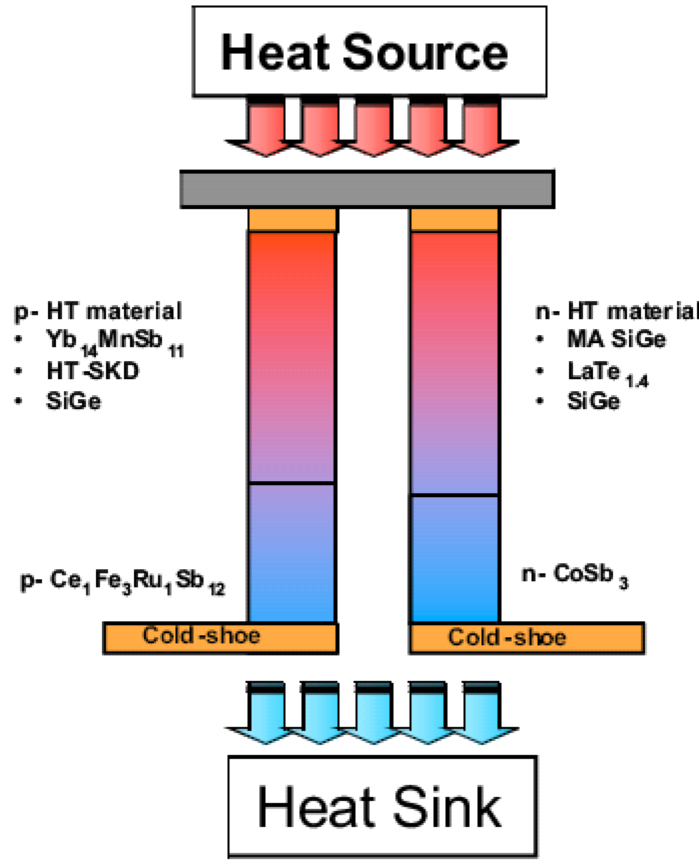
$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_C}{T_H}}$$





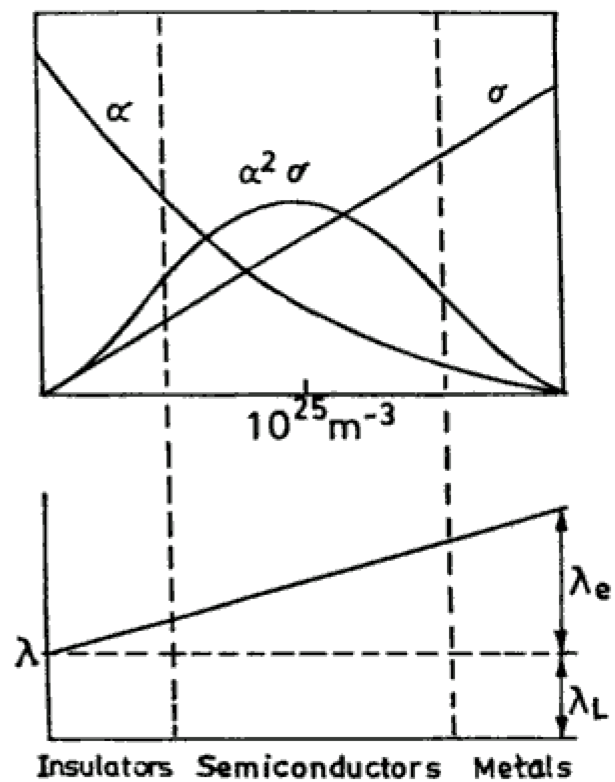
Thermoelectric Devices Power Generation

- P-type leg and n-type leg
- Segmented for greater efficiency.
- Compatible currents

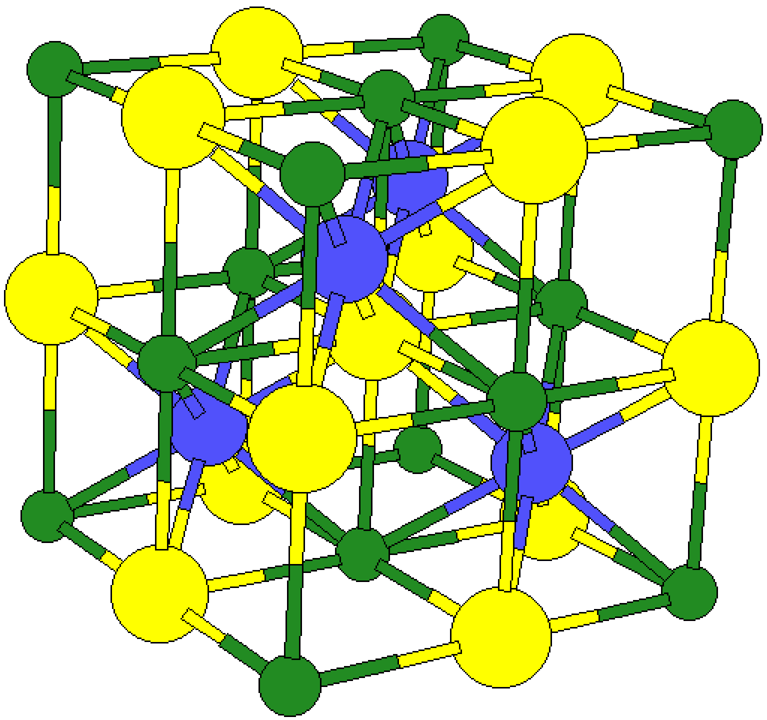


Semiconductors as Thermoelectrics

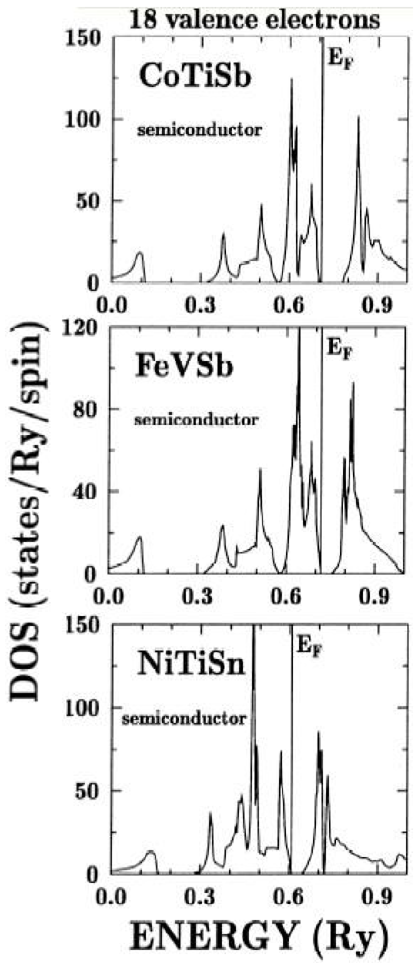
- The best thermoelectric materials are semiconductors.
- Gap at Fermi energy allows preferential flow of one carrier type.
- N-type: electron flow in conduction band
- P-type: hole flow on valence band.
- A sharp gap gives the best results.



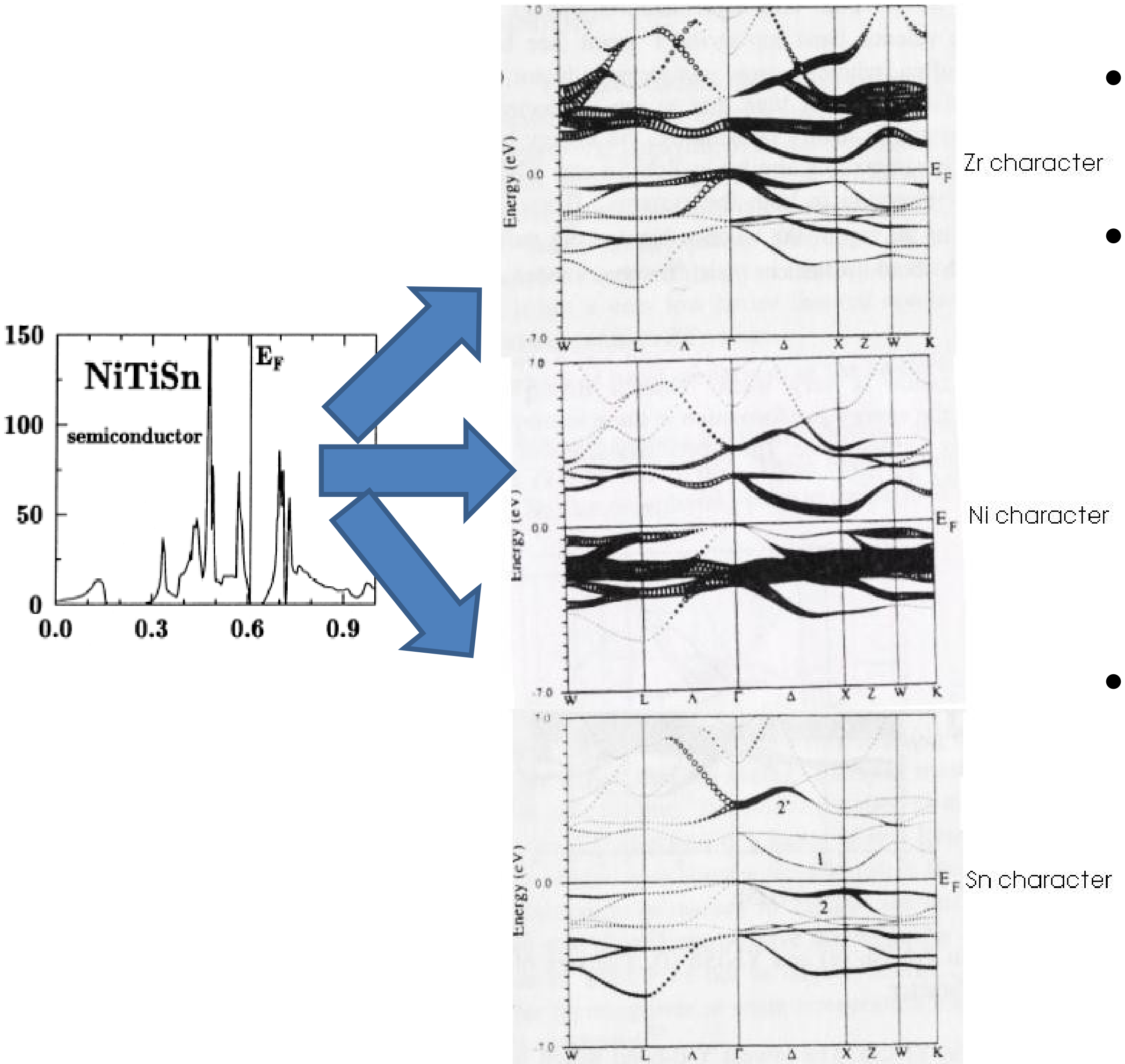
Why half-Heusler?



- High symmetry: low resistivity, degenerate bands
- Three sites: options for doping & isoelectronic substitution.
- Three semiconducting compounds
- The downside: high thermal conductivity.

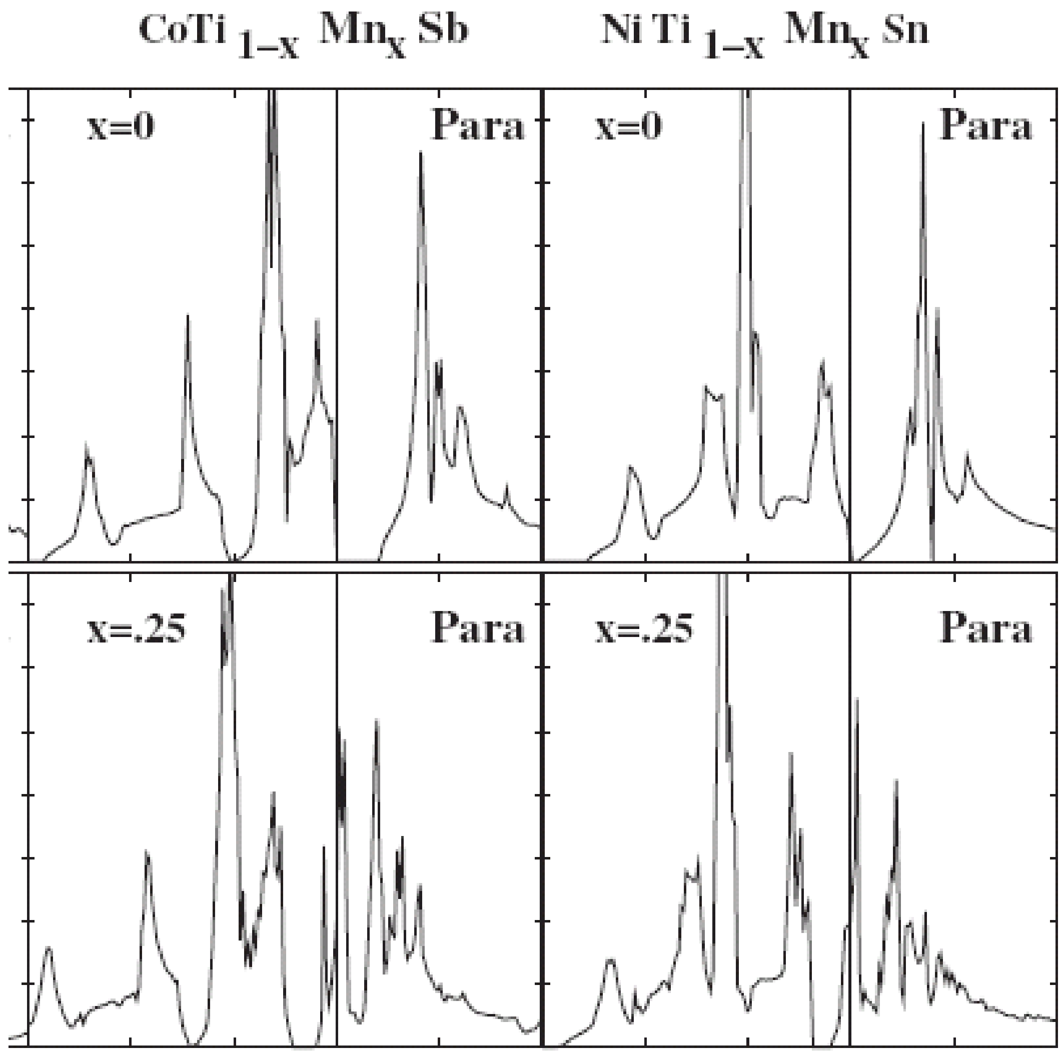


Electronic Structure of MNiSn



- For ZrNiSn: Zr and Ni bands form the gap
- Sn bands have nothing to do with gap formation – Sn site can be doped without interfering with the gap.
- The same is true for MCoSb-type and VFeSb-type materials.

KKR-CPA-LDA Calculations



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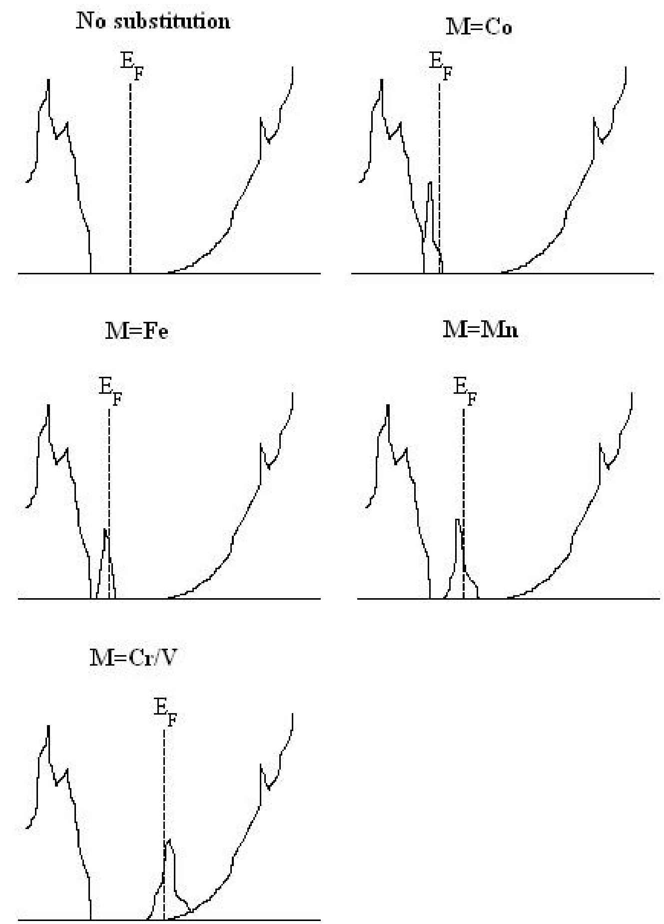
Cartoon Model of Dopant Effects on XNiSn Bandstructure

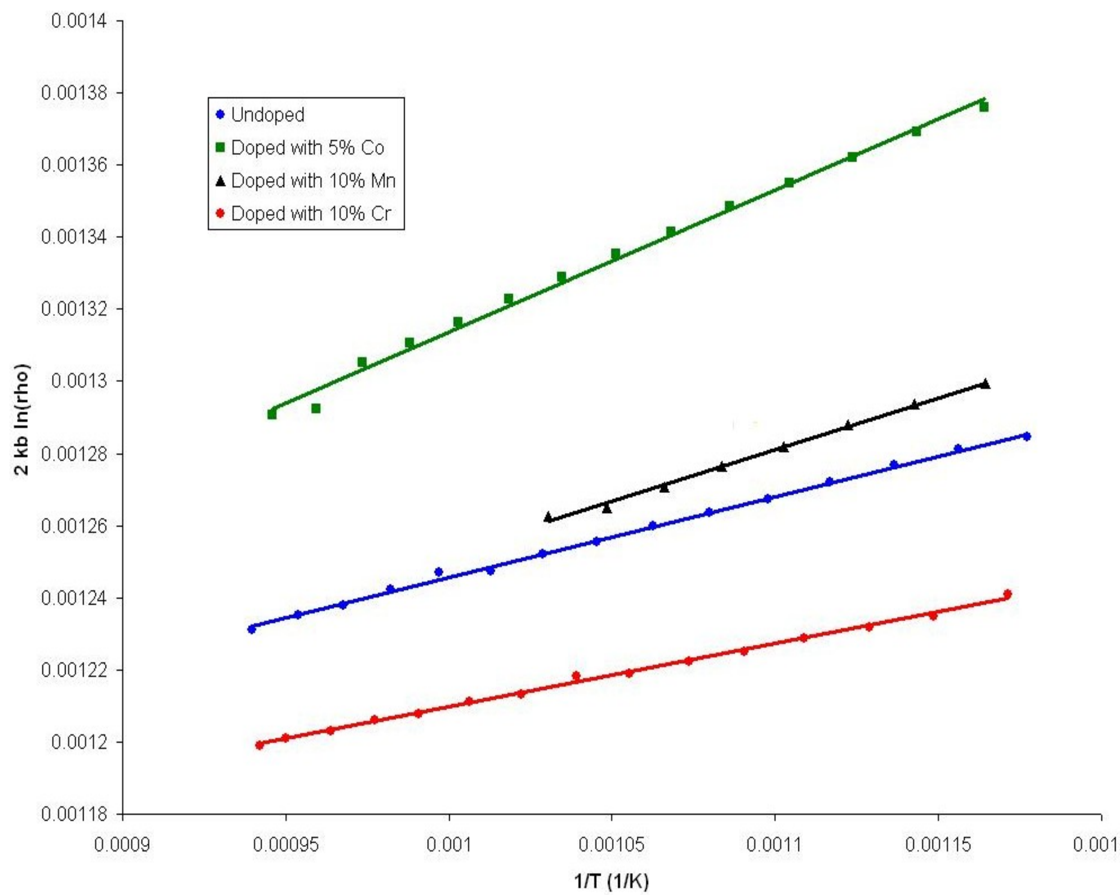
- Transition metal dopants: V, Cr, Mn, Fe, Co, Ni, Cu on either the Hf/Zr or Ni site.
- Result: creation of dopant band in gap.
- Location determined by high-temperature electrical resistivity



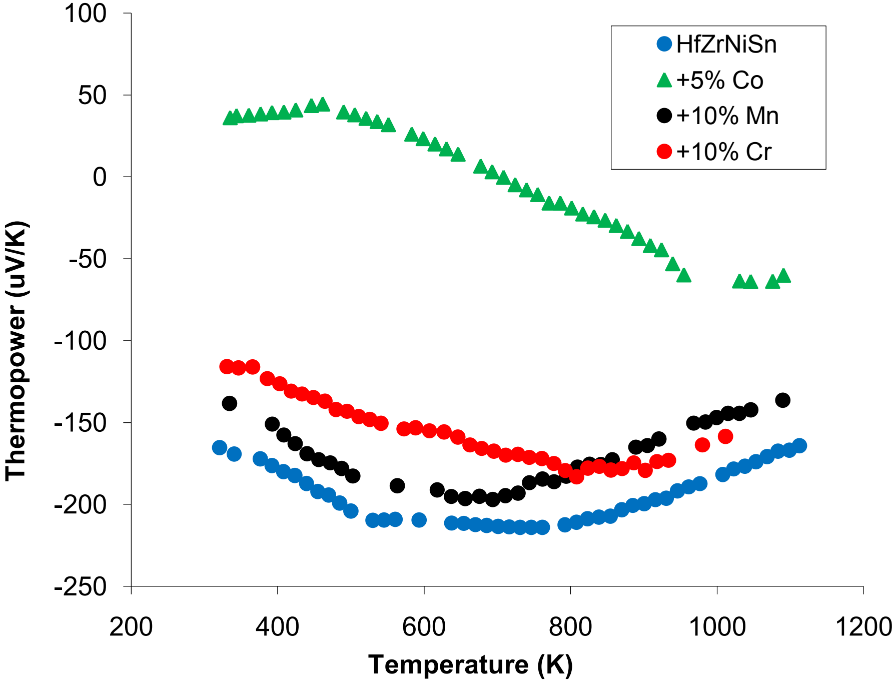
High Temperature Electrical Resistivity Curve Fitting

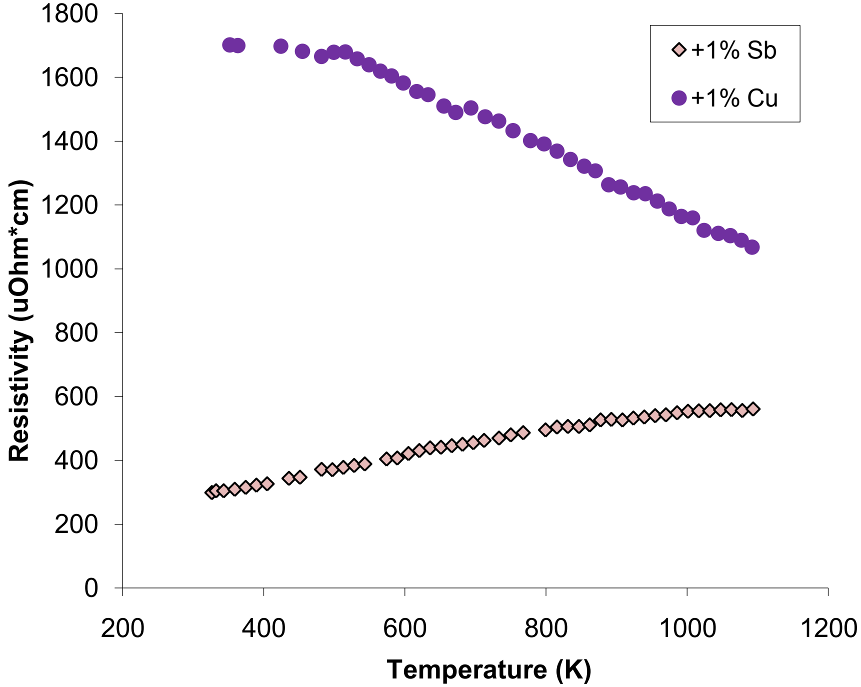
Composition	Gap Size (eV)
ZrNiSn (theoretical)	0.50-0.51
HfNiSn (theoretical)	0.48
$Hf_{0.75}Zr_{0.25}NiSn$	0.23
$Hf_{0.75}Zr_{0.25}Co_{0.05}Ni_{0.95}Sn$	0.40
$(Hf_{0.75}Zr_{0.25})_{0.95}Co_{0.05}NiSn$	0.47
$Hf_{0.75}Zr_{0.25}Fe_{0.05}Ni_{0.95}Sn$	0.27
$Hf_{0.75}Zr_{0.25}Mn_{0.1}Ni_{0.9}Sn$	0.27
$(Hf_{0.75}Zr_{0.25})_{0.9}Mn_{0.1}NiSn$	0.27
$(Hf_{0.75}Zr_{0.25})_{0.9}Mn_{0.2}Ni_{0.9}Sn$	0.33
$Hf_{0.75}Zr_{0.25}Cr_{0.1}Ni_{0.9}Sn$	0.18
$Hf_{0.75}Zr_{0.25}V_{0.1}Ni_{0.9}Sn$	0.19

$$\rho \sim e^{\frac{\varepsilon_g}{2k_B T}}$$



Thermoelectric, Resistivity, and Hall Measurements





Composition	Thermopower (μV/K)	Resistivity (μΩ·cm)	Carrier Type	Carrier Concentration (cm^{-3})
$Hf_{0.75}Zr_{0.25}NiSn$	-213	6800	Electrons	5.5×10^{19}
$Hf_{0.75}Zr_{0.25}Ni_{0.99}Cu_{0.01}Sn$	-71	1700	Electrons	2.2×10^{20}
$(Hf_{0.75}Zr_{0.25})_{0.99}Cu_{0.01}NiSn$	-171	1480		
$Hf_{0.75}Zr_{0.25}Co_{0.05}Ni_{0.95}Sn$	36	6700	Holes	3.1×10^{20}
$Hf_{0.75}Zr_{0.25}Co_{0.15}Ni_{0.85}Sn$	56	3800	Holes	7.3×10^{20}
$(Hf_{0.75}Zr_{0.25})_{0.97}Co_{0.18}Ni_{0.85}Sn$	25	4420		
$Hf_{0.75}Zr_{0.25}Fe_{0.05}Ni_{0.95}Sn$	-86	6750	Electrons	Obscured by magnetic effects
$Hf_{0.75}Zr_{0.25}Mn_{0.1}Ni_{0.9}Sn$	-172	7050	Electrons	5.4×10^{19}
$(Hf_{0.75}Zr_{0.25})_{0.9}Mn_{0.1}NiSn$	-201	8000	Electrons	4.1×10^{19}
$(Hf_{0.75}Zr_{0.25})_{0.9}Mn_{0.2}Ni_{0.9}Sn$	-195	4000		
$Hf_{0.75}Zr_{0.25}Cr_{0.1}Ni_{0.9}Sn$	-100	2645		
$Hf_{0.75}Zr_{0.25}V_{0.1}Ni_{0.9}Sn$	-129	2370	Electrons	2.6×10^{20}
$(Hf_{0.75}Zr_{0.25})_{0.9}V_{0.1}NiSn$	-161	4900		
$(Hf_{0.75}Zr_{0.25})_{0.9}Ce_{0.1}NiSn$	-36	2300		

Transition Metal Doping in XNiSn: Analysis

- Transition metal doping on the X or Ni site has two effects:

1: Lowers thermopower by placing the Fermi energy in a partially unfilled DOS location.

2: Dopes inefficiently. The dopant bands are not fully part of the conduction band.

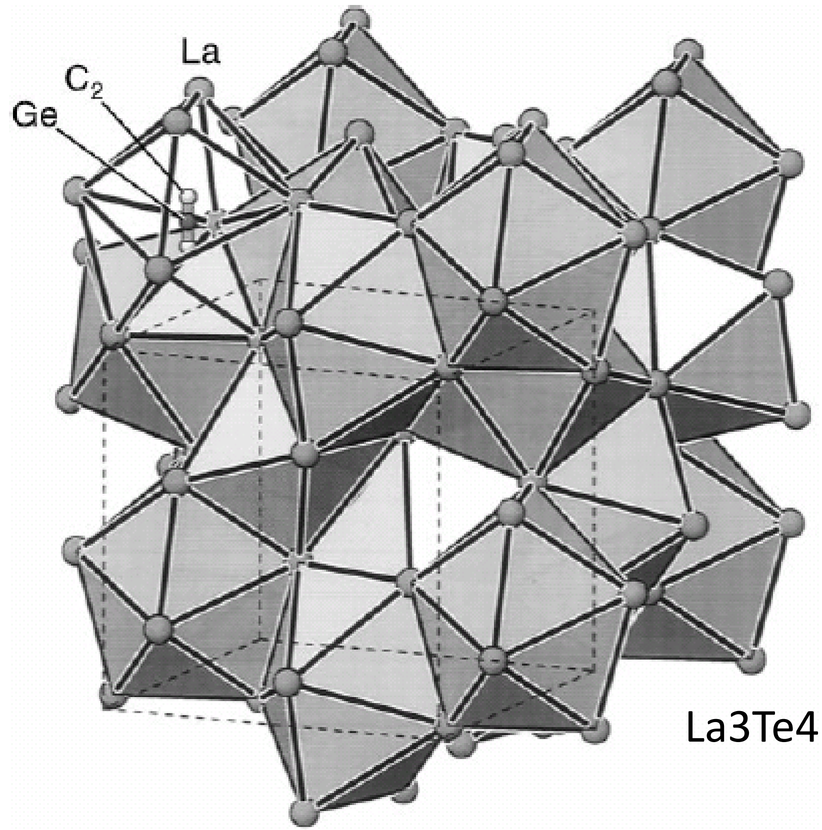
- Transition metal doping is detrimental to high ZT. Lesson learned: future doping efforts must be sp-type only.

Why Rare Earth Sesquichalcogenides?

- Semiconducting
- High melting points
- Self-doping and highly sensitive
- Low thermal conductivities
- Good results (ZT=1.5) reported by JPL in 1980s.

Why $La_{3-x}Te_4$? (Or $LaTe_y$)

- Continuous series of solid solutions for $1.33 < y < 1.50$
- All have Th_3P_4 structure
- Wide range of carrier concentration from 0 to 4.5 x 10^{21} /cm^3
- Low sublimation rate
- Coefficient of thermal expansion matches p-type Zintl $Yb_{14}MnSb_{11}$



La3Te4

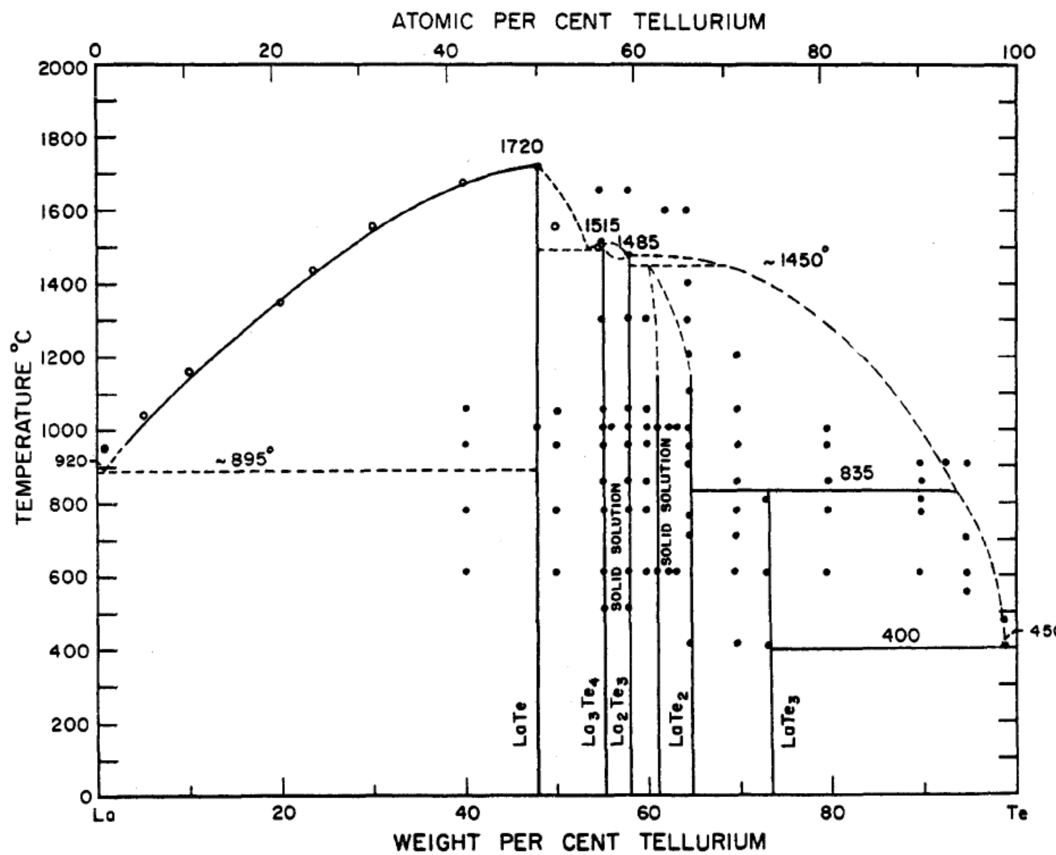
LaTe$_y$ Self-doping

- $La_{3-x}Te_4$ is n-type material =>

  $(La^{+3})_{3-x}V_xTe^{-2}{}_4e^{-1}{}_{1-3x}$

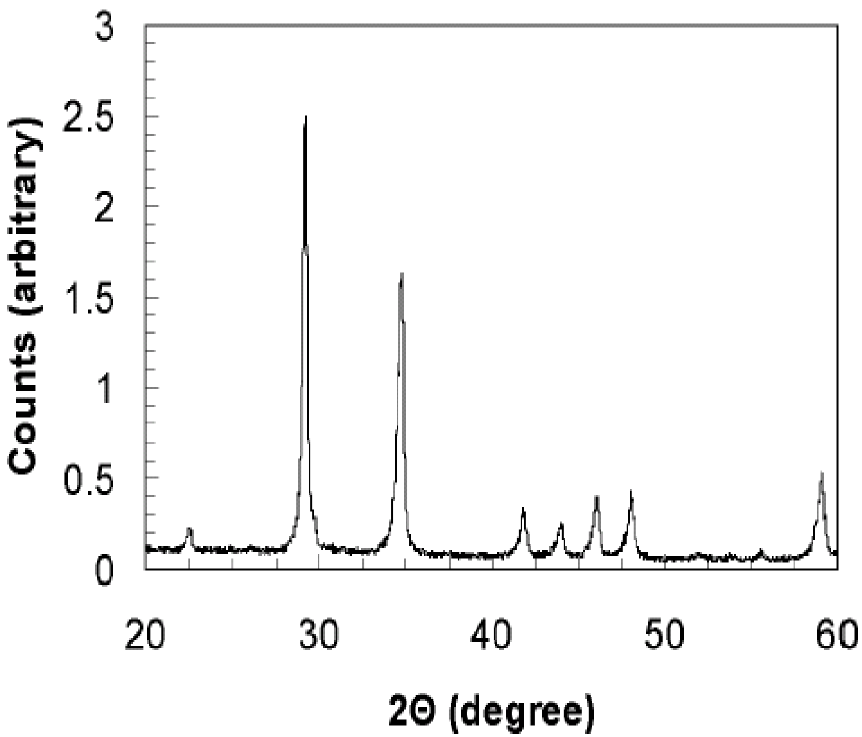
- When x=0, one free electron/F.U.
- When x =1/3, no free electrons.
- $La_{3-1/3}Te_4$=$La_{2/3}Te_4$=La_2Te_3

- Carrier concentration: $n=n_{max}(1-3x)$

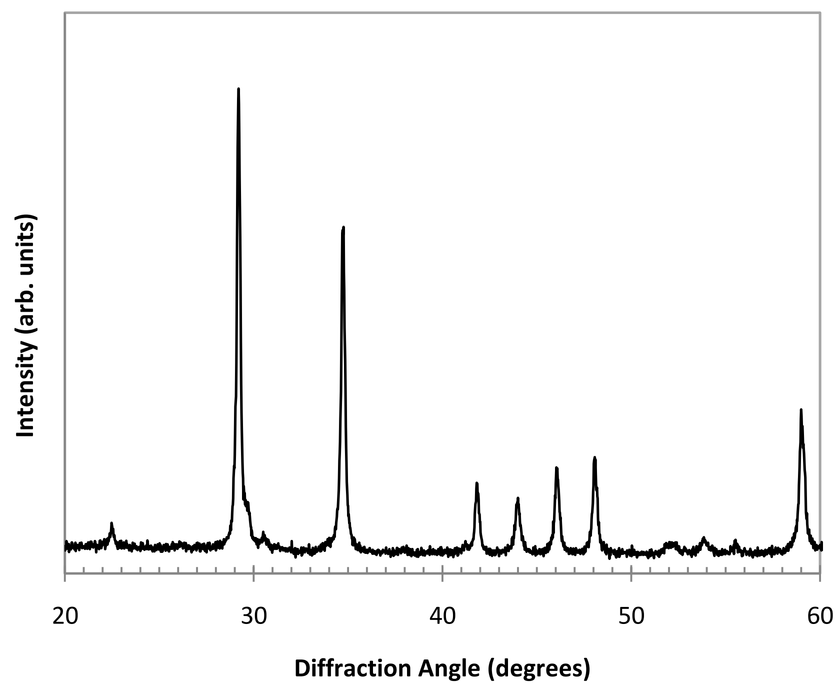


Comparison: Recent JPL data and our data

Caltech/JPL



Uva



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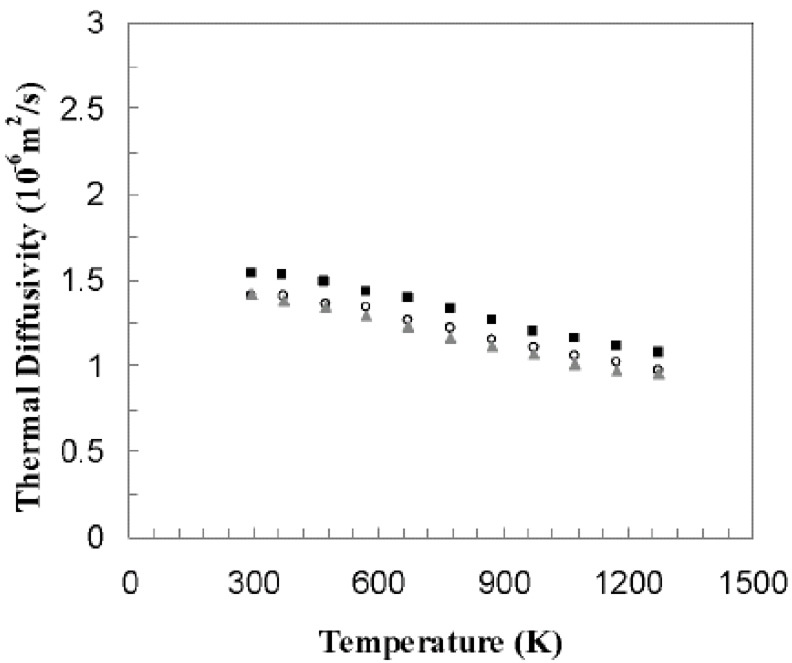

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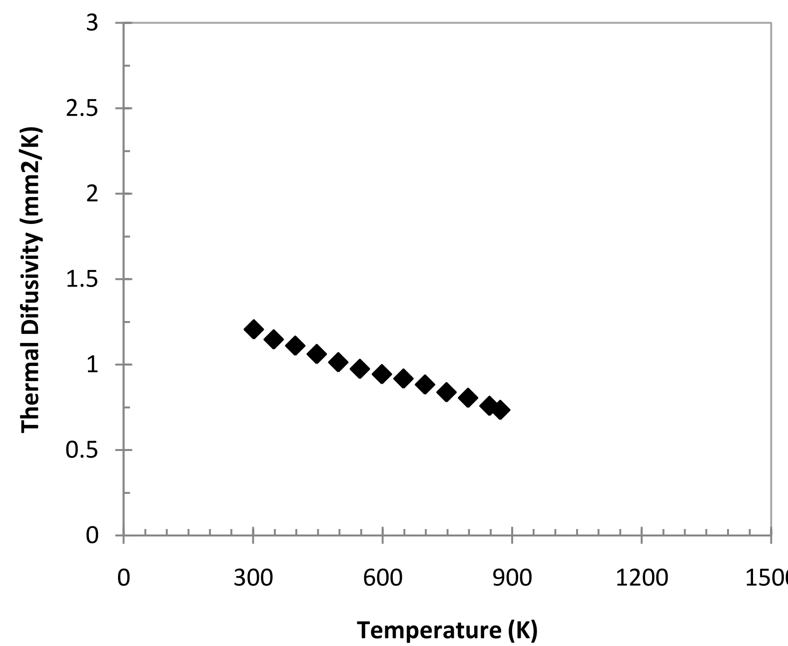

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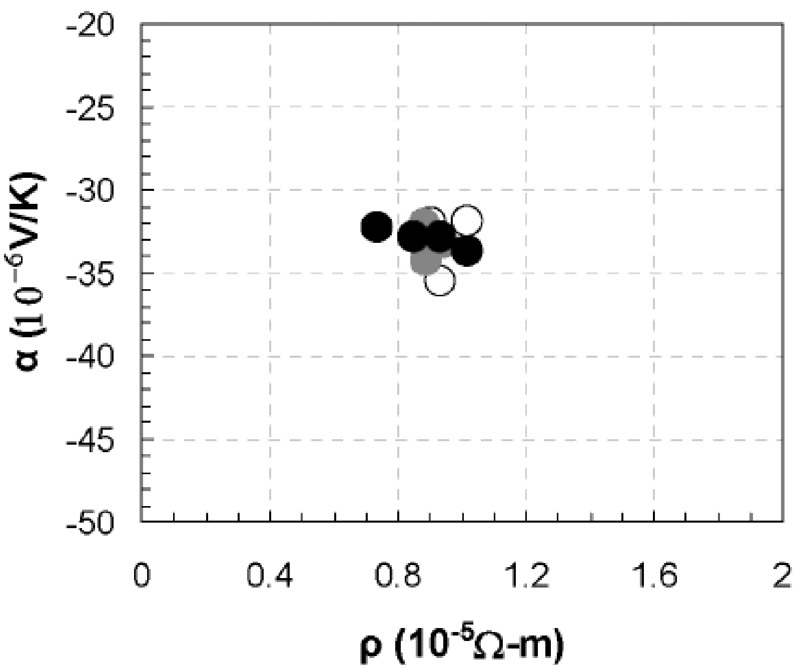

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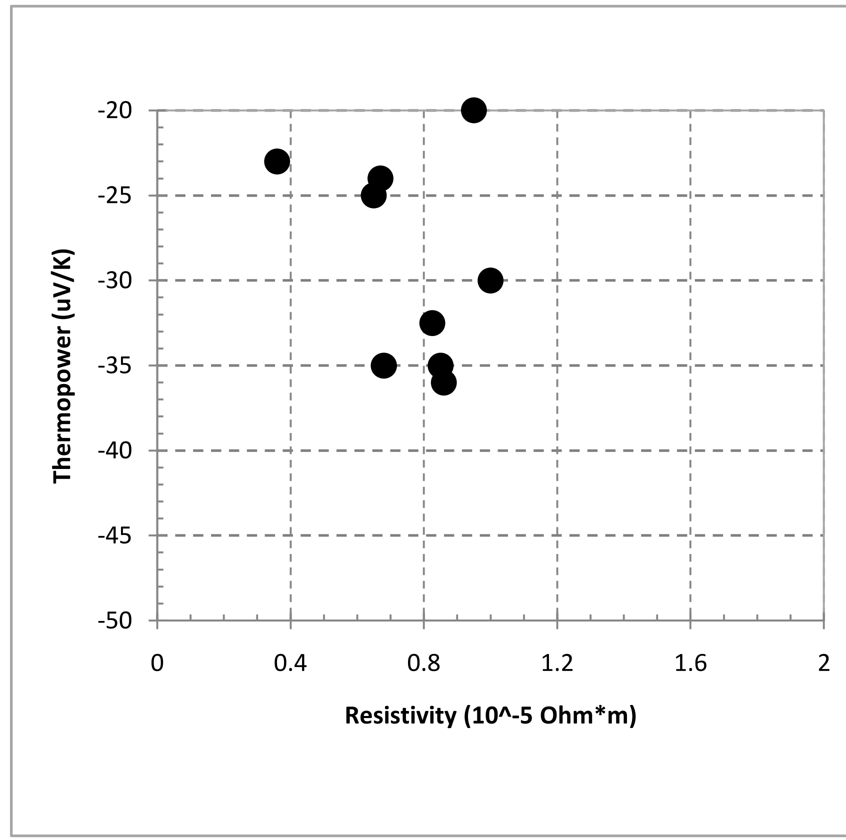
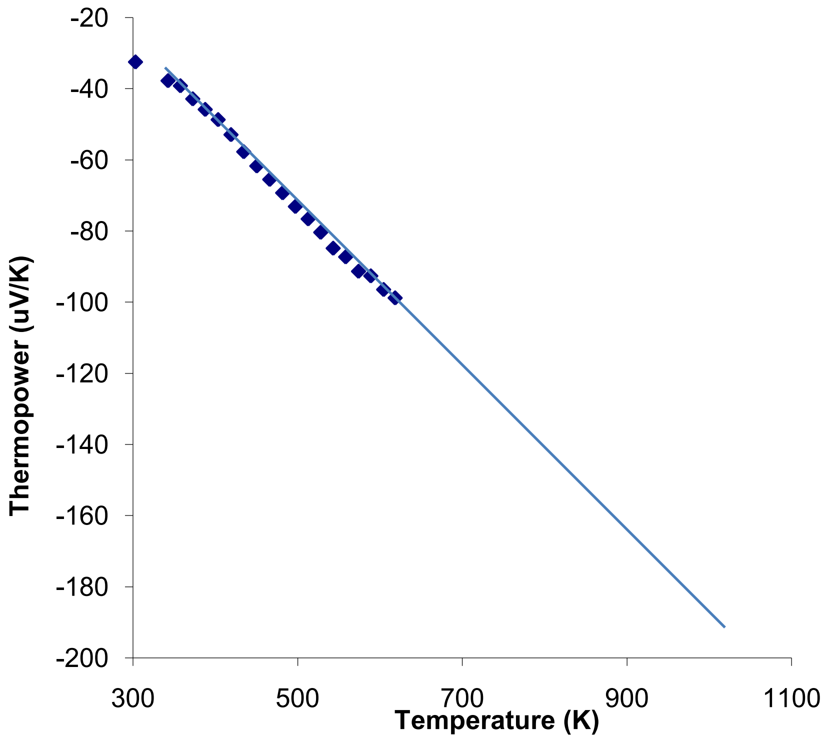
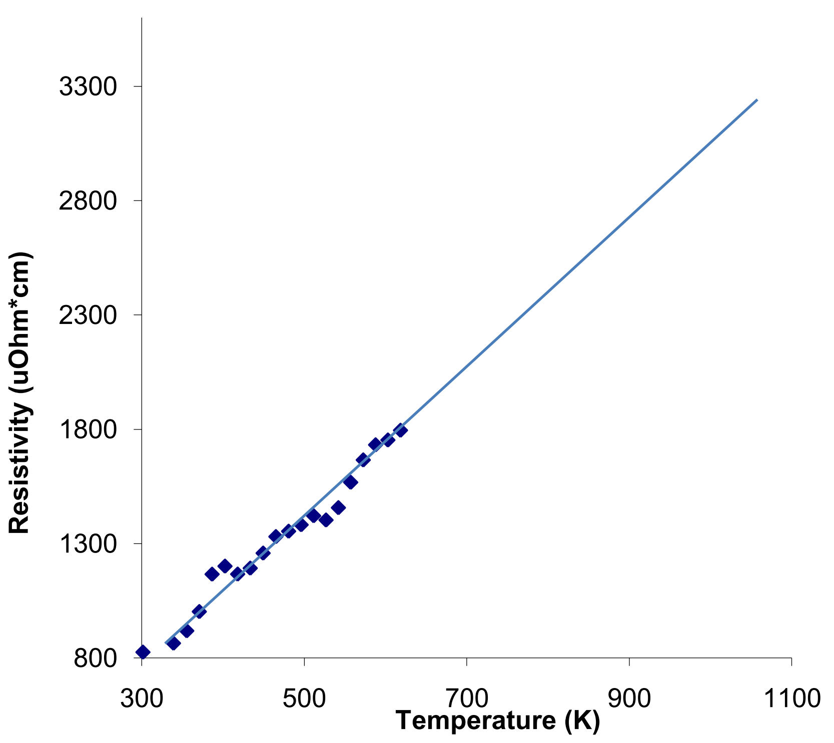


$LaTe_y$ at Intermediate Temperature

Thermopower



Resistivity



$LaTe_y$ Challenges

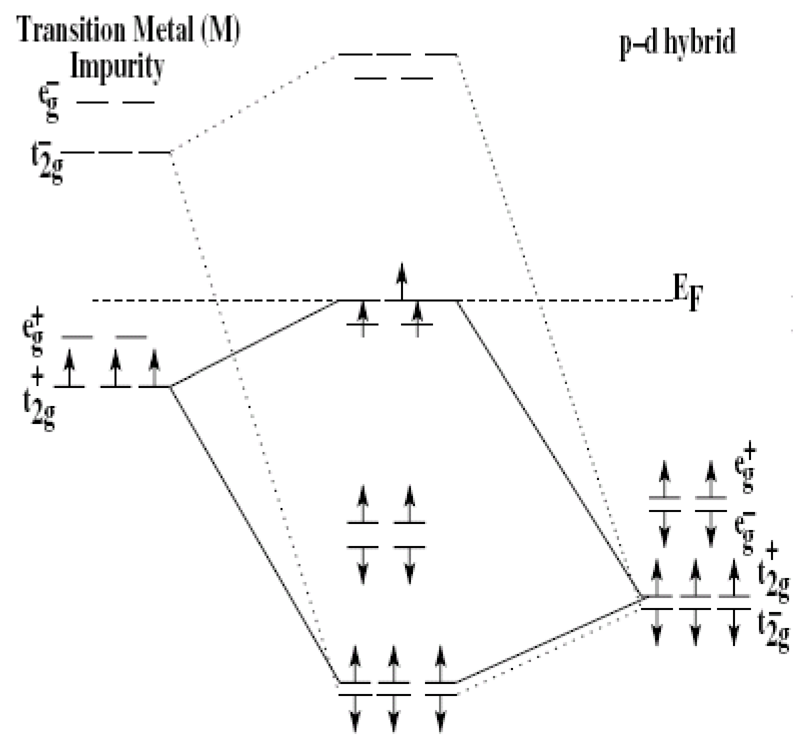
- $LaTe_y$ has significant Te evaporation during melting. Sample stoichiometry must be improved.
- Oxidation occurs during initial reaction and ball milling.
- Obtaining a solid sample challenging. $LaTe_y$ reaction is exothermic.
- Find better method for High Temperature measurement.

Future Work

- Suction casting to constrain $LaTe_y$ and form solid samples – will improve resistivity.
- Begin looking at dopants/substitutions to minimize thermal conductivity, possibly improve electronic properties.

Dopant band formation: $Ti_{1-x}Mn_xNiSn$

- Ti vacancy depletes 4 electrons, Mn adds 7.
- Ti levels tend to be above gap, Ni tend to be below. Larger nuclei pull electrons to lower energy.



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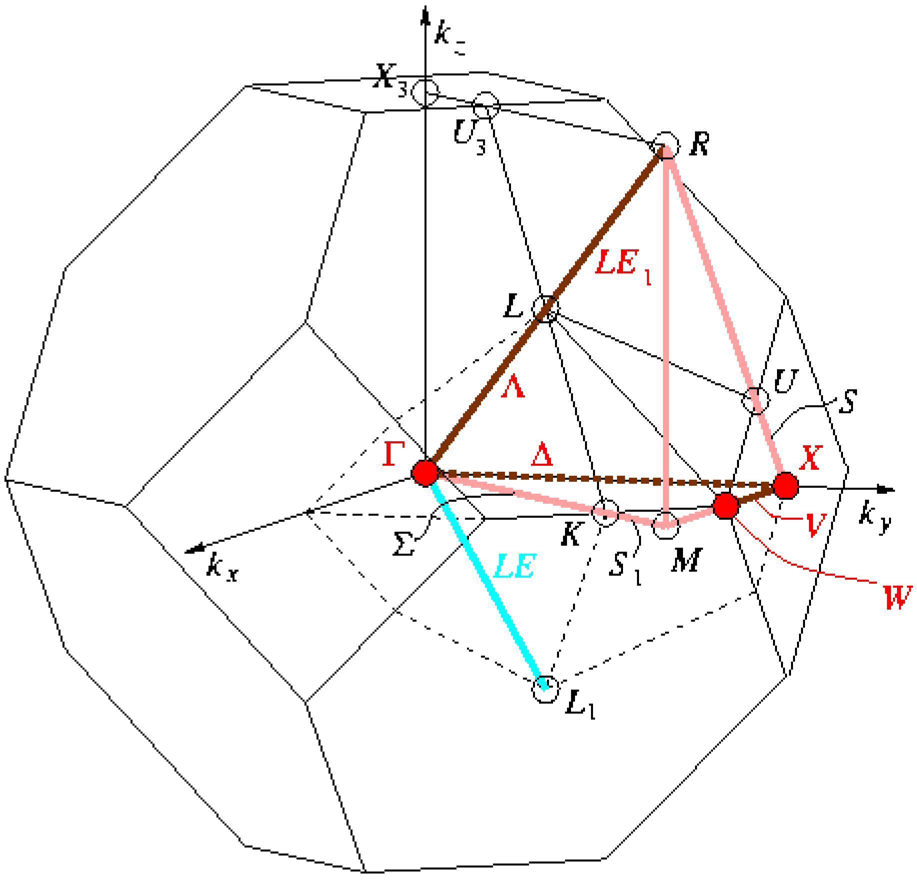
High-Symmetry Points for F-43m



Electronic Structure of TiCoSb