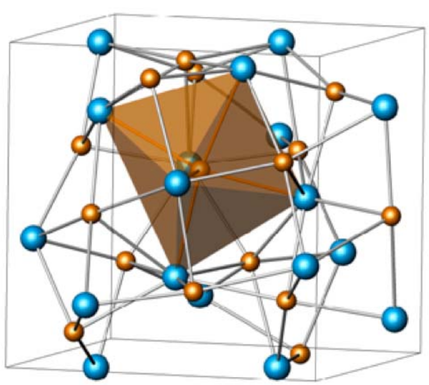
Challenges and Opportunities for Condensed Matter Physics of Thermoelectric Materials

G. Jeffrey Snyder

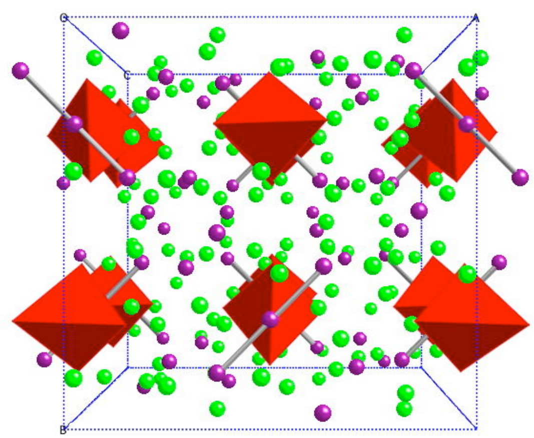
California Institute of Technology

Pasadena, California, USA

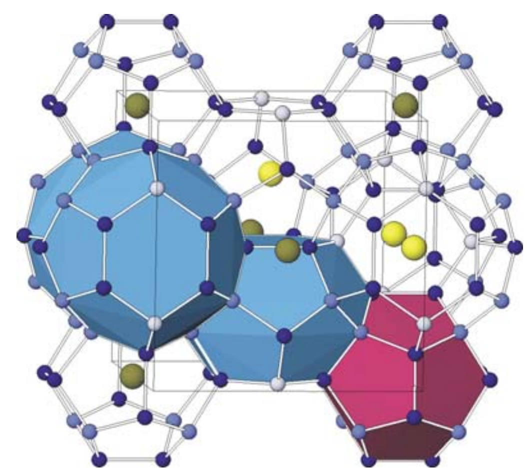
http://thermoelectrics.caltech.edu



La_3Te_4



$Yb_{14}MnSb_{11}$



$Ba_8Ga_{16}Ge_{30}$
Type I Clathrate

THERMOELECTRICS

Toberer, May, Snyder ***Chem. Mat.,*** (DOI: 10.1021/cm901956r)

Thermoelectric Generator

Thermoelectrics

Convert Heat into Electricity

Heat Flow drives free
electrons and holes
from hot to cold

Voltage Produced

Seebeck effect

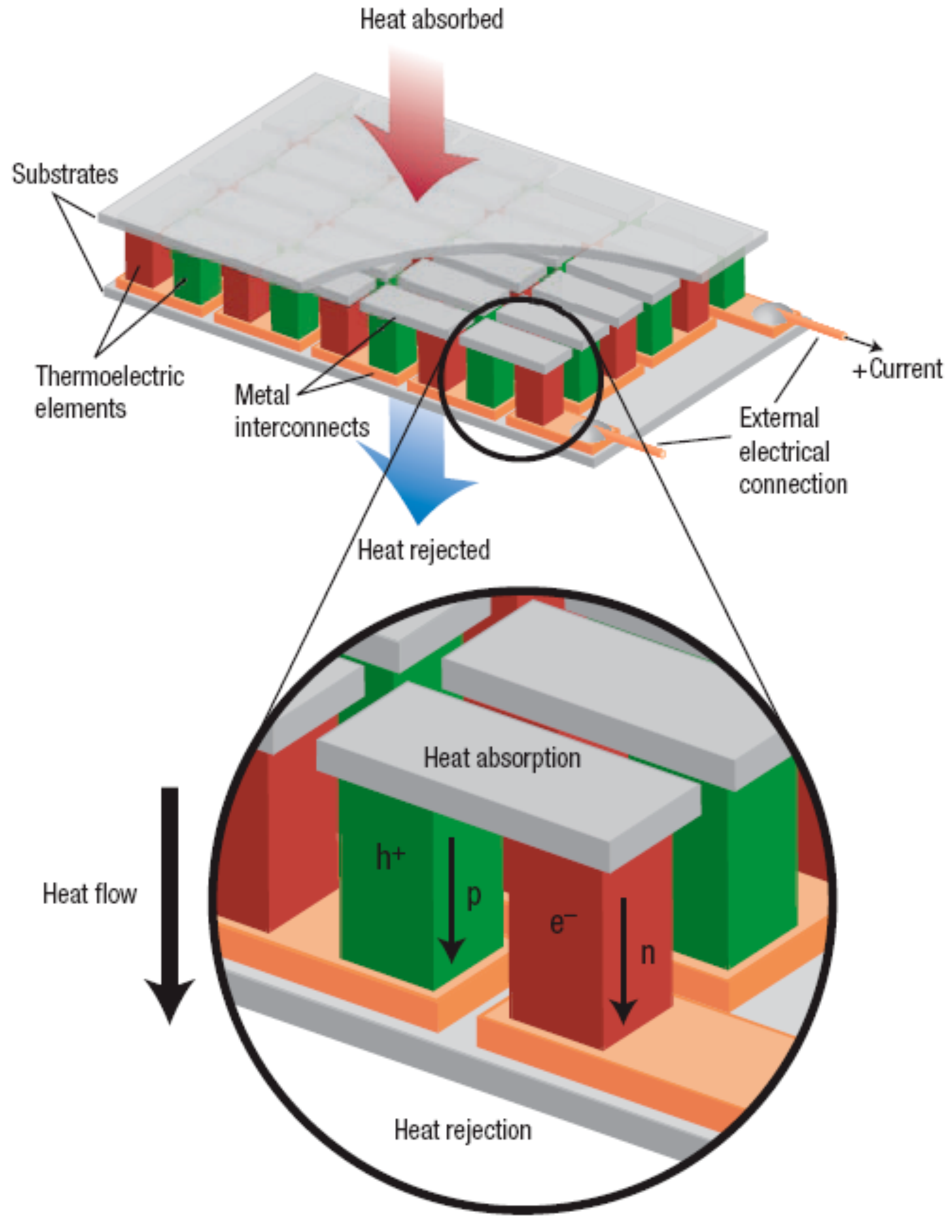
or Thermoelectric Power

$$V = \alpha \Delta T$$

Seebeck Coefficient α

Efficiency ~ zT

$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$



THERMOELECTRICS

Snyder, Toberer *Nature Materials* **7,** 105 (2008)

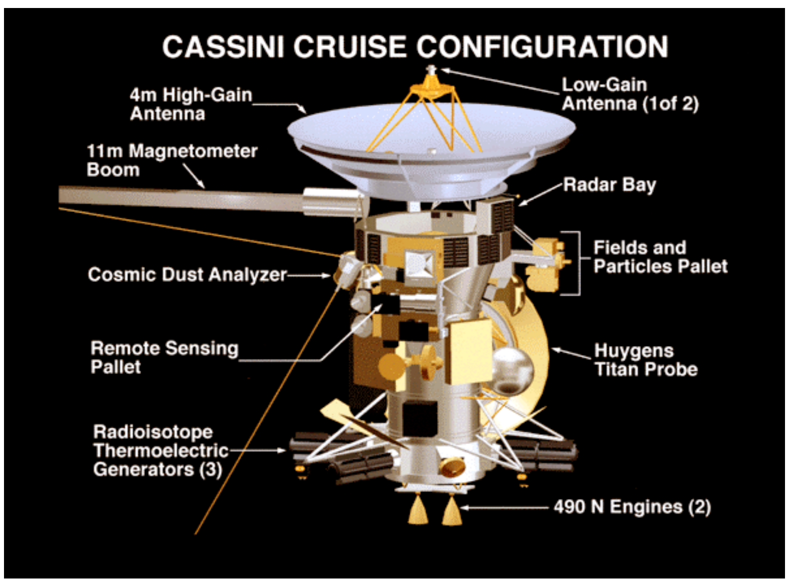
Thermoelectric Applications

Solid State Advantage

- No moving parts
- No maintenance
- Long life
- Scalability

Power Generation (heat to electricity)

- Spacecrafts
  - Voyager over 30 years!
- Remote power sources



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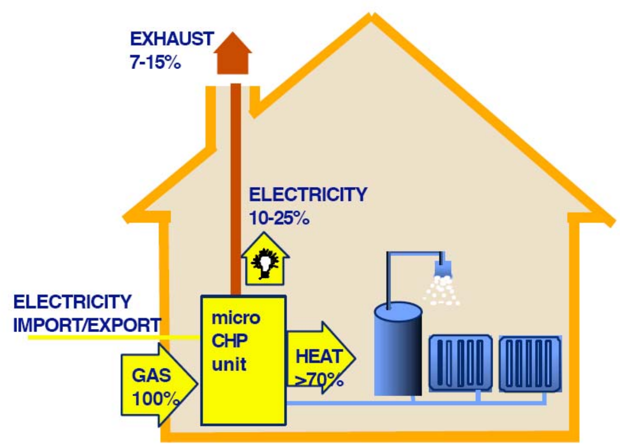
Cooling - Thermal Management

- Small Refrigerators
- Optoelectronics
- Detectors

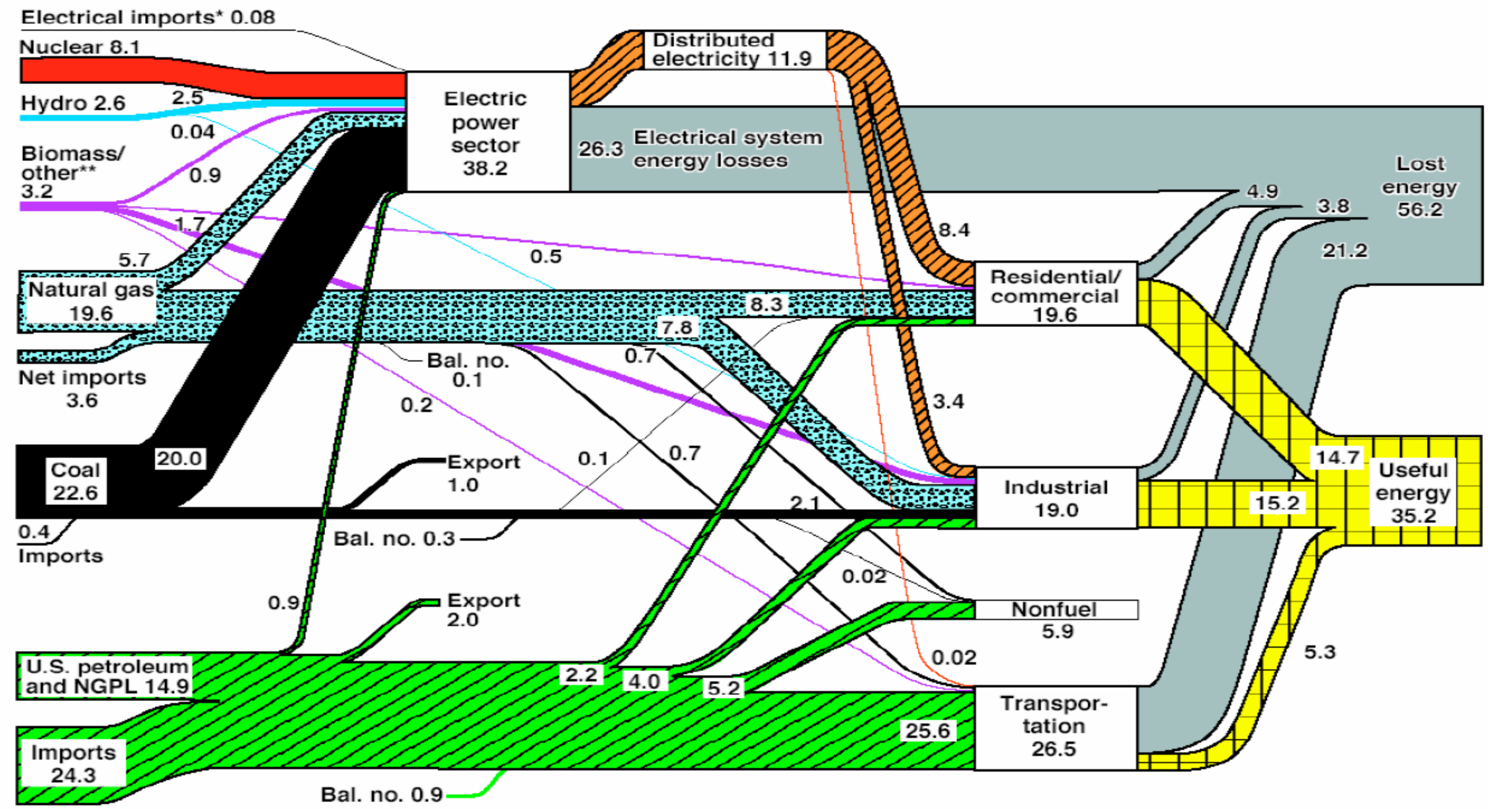
Future Possibilities

- Waste Heat Recovery
  - Automobiles
- CoGeneration
- Distributed Thermal Management



Heat in Energy Use

USA



As in End Product

Home, Business heating systems

As waste by product

In production of useful energy

In consumption of useful energy

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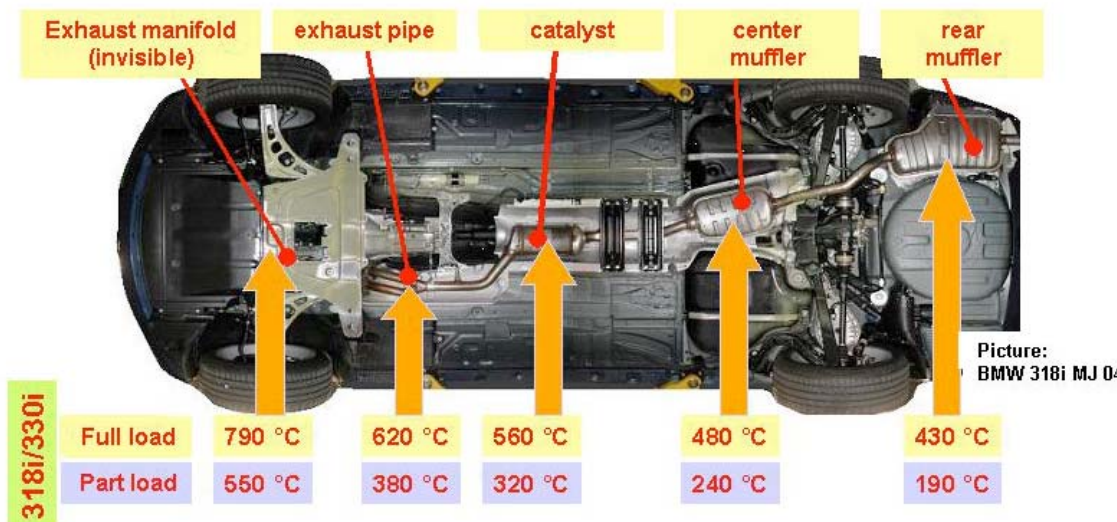
Automotive TE Generator

Convert Exhaust heat to electricity

- Replace alternator
- Improve fuel economy by 10%,



BSST
innovative solutions in temperature control

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KITP Outline

Transport Physics of Complex Thermoelectric Materials

Semi-empirical Approach

Solid-State Chemistry Inspired

- Single Parabolic Band
- Rigid Bands
- Acoustic Phonon Scattering

Successful examples of approach

- Predict trends in
  - Seebeck
  - mobility
  - zT
- Optimize material
- Simplify the physics

Challenges - Opportunities

Band Structure Calculations

- Band Gap (within ~0.05eV)
- Band Edge Energy (within ~0.01eV)
- Effective Mass (within ~0.1m_e)

Disorder

- Doping at ~1%
- Alloying ~10%
- Vacancies
- Anti-Site Defects
- Interstitial atoms

Transport Calculations

- Relaxation Time Approximation
- Constant RTA (?)
- Thermal Transport

Exotic TE Materials

- Resonant States
- Nano-structures/e- filtering
- Heavy Fermion
- Kondo
- Correlated Electron Systems

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Ideal Thermoelectric Material

Desire High *zT* Figure of Merit

$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

"Electron Crystal - Phonon Glass"

α Seebeck Coefficient

High in Crystalline Semiconductor

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

σ Electrical Conductivity

High In Crystalline Metal

$$\sigma = ne\mu$$

κ Thermal Conductivity

Low for Glass

$$\kappa \approx \kappa_l + L\sigma T$$

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Carrier Concentration

Desire High *zT* Figure of Merit

$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

Conflicting Materials Requirements

α Seebeck Coefficient

Need small *n*, large *m**

- Semiconductor (Valence compound)

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

σ Electrical Conductivity

Need large *n*, high *μ*

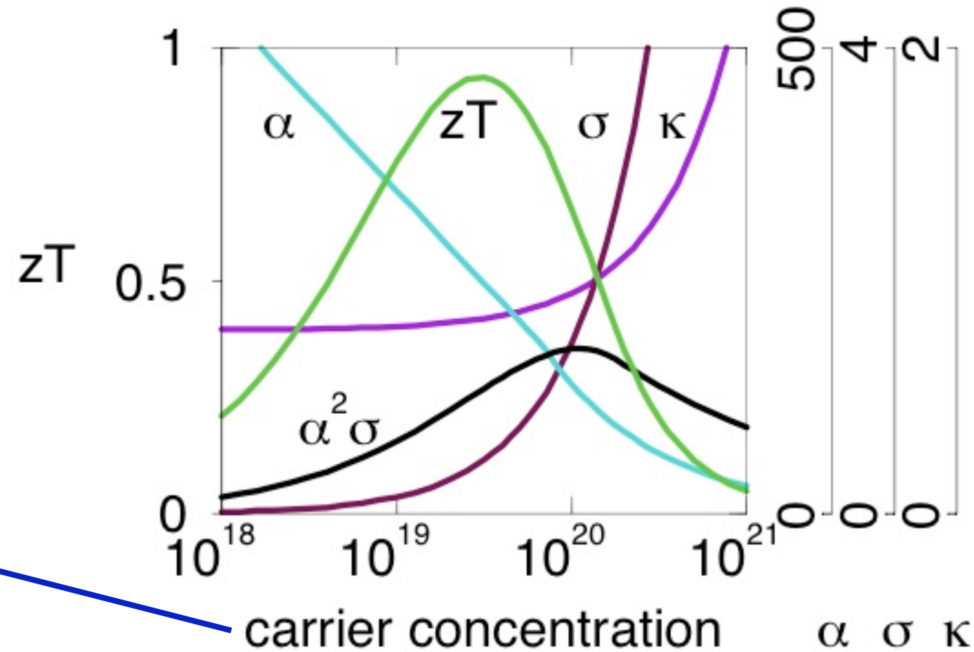
- Metal

$$\sigma = ne\mu$$

κ Thermal Conductivity

Desire small κ_l, small *n*

$$\kappa \approx \kappa_l + LTne\mu$$



"Electron Crystal - Phonon Glass"

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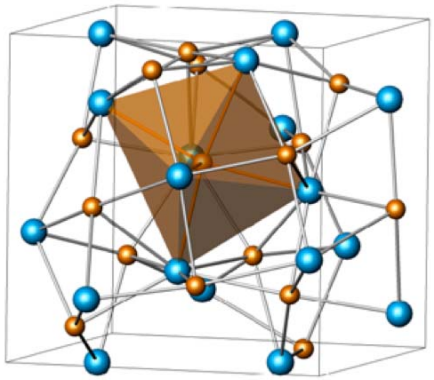
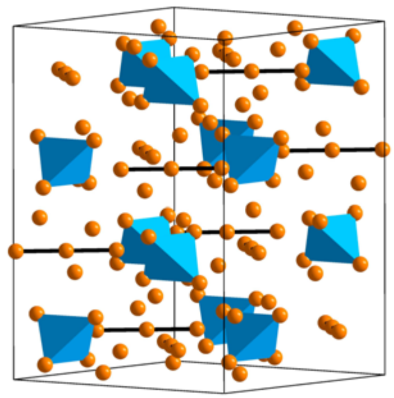
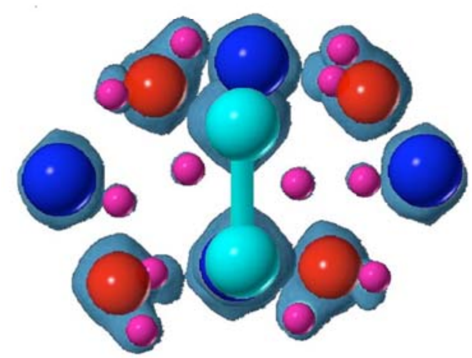
Good Thermoelectric Materials

La_3Te_4	$Yb_{14}MnSb_{11}$	Zn_4Sb_3
		
Ionic	Zintl	Intermetallic

Very different materials but with some common features

- Structural complexity - good for low thermal cond.
- Structurally related to intrinsic semiconductors
  near valence balanced compounds using Zintl concepts
- Transport properties of metals

Are Thermoelectric Materials Semiconductors or Metals ?

THERMOELECTRICS

Snyder, Toberer ***Nature Materials, 7***, p. 105, (2008)

Semiconductors vs. Metals

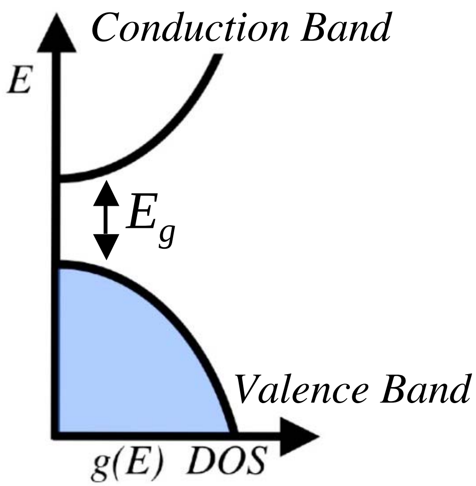
Semiconductors

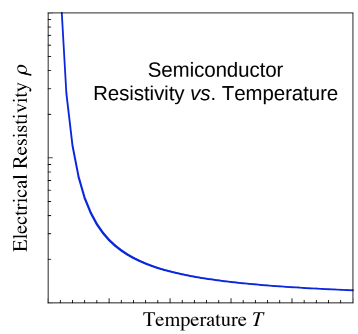
Filled Valence Band & Empty Conduction band Separated by Band Gap E_g

- Elec. resistivity ρ, *decreases* as Temperature increases

  $\rho \to \infty$ as $T \to 0$ K

- charge carriers n_H increase with Temperature

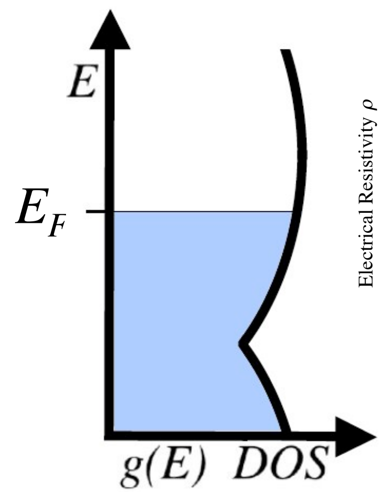


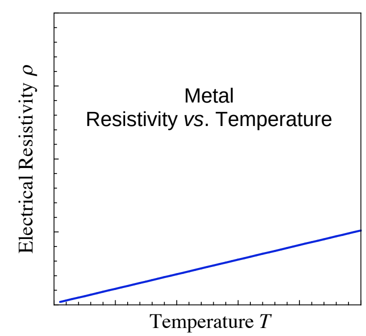


Metals

no band edges near Fermi Level E_F

- Elec. resistivity ρ, *increases* as Temperature increases
- charge carriers n_H constant with Temperature





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Valence Semiconductors

Semiconductors

Filled Valence Band & Empty Conduction band Separated by Band Gap E_g

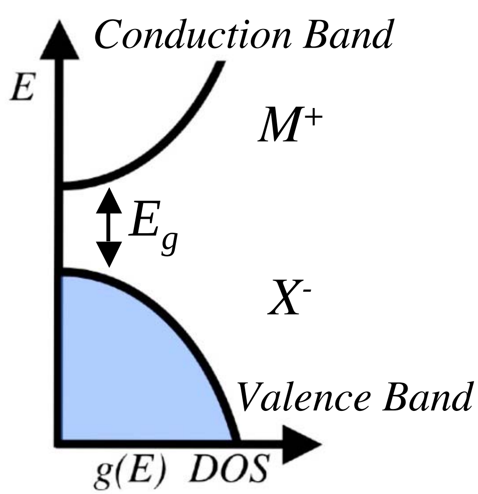
Valence Compounds

Stoichiometric balance of valences $\Rightarrow$ Semiconductor

- Ionic Compound: Valence Band = filled anion states; Conduction = cation states
- Covalent Compound: Valence Band = filled bonding states; Conduction = antibonding states

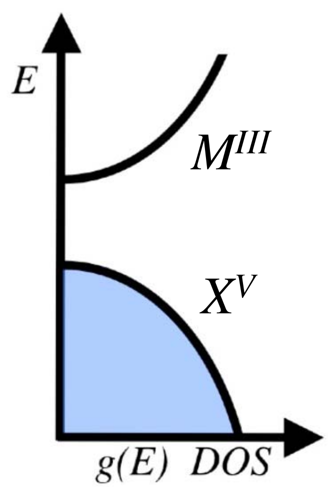
Ionic MX

$La^{3+}{}_2Te^{2-}{}_3$



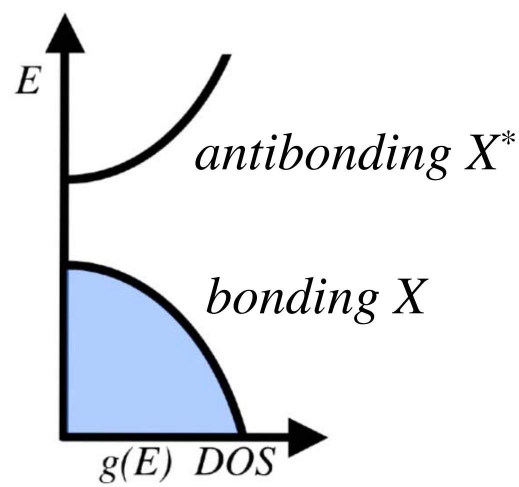
Polar SC MX

InSb $E_g \sim 0.2$ eV



Semicond. X

Ge^0 $E_g \sim 0.7$ eV



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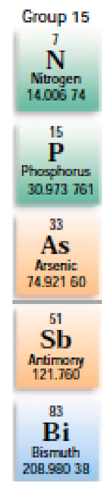
Zintl Electron Counting

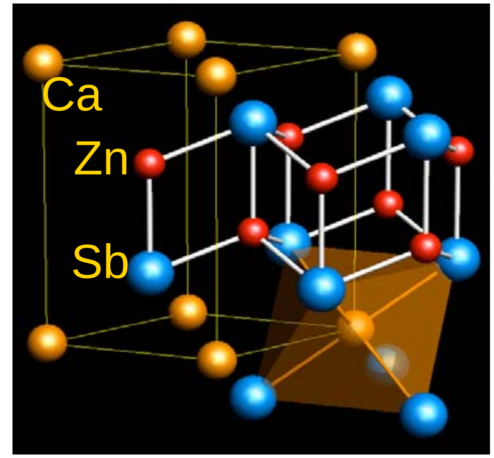
Sb Zintl Electron Counting

- Sb^{3-} discrete ions = Same as N^{3-}
  - $CaZn_2Sb_2$ closest Sb-Sb is 4.4 Å

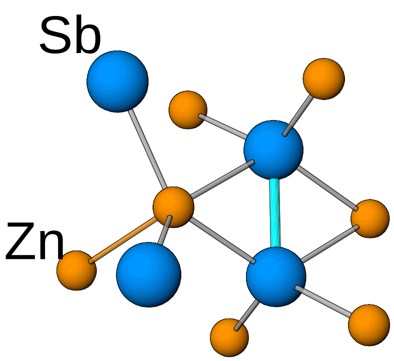
Each bond (~2.9Å) reduces valence by 1

- Sb^{2-} dimer = one bond
  - ZnSb Sb-Sb is 2.84Å
- Sb^{1-} chain or ring = two bonds
  - $SrZnSb_2$ Sb^{1-} chains
  - $CoSb_3$ Sb^{1-} square ring
- Sb^{0} sheet = three bonds
  - Elemental Sb (α-Sb) Sb^{0} sheet

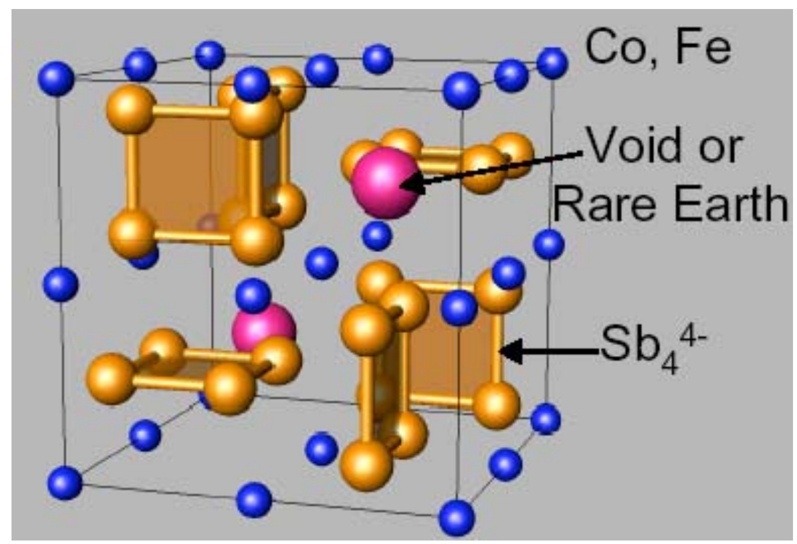




$CaZn_2Sb_2$: Sb^{-3}
No Sb-Sb bonds



ZnSb: Sb^{-2}-Sb^{-2} dimers



Skutterudite: Sb^{-1} two bonded rings

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"Zintl Metals"

"Zintl Phases" = Semiconductors (G. Miller in *Chemistry, Structure, and Bonding of Zintl Phases and Ions* S. Kauzlarich ed.)

"Metallic Zintl Phases" (J. Corbett in *Chemistry, Structure, and Bonding of Zintl Phases and Ions* S. Kauzlarich ed.)

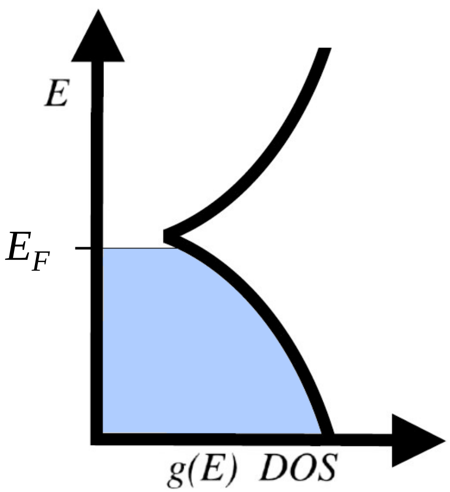
Semi-Metallic Zintl Phases

- Valence Precise according to Zintl electron counting
- but Band Gap $E_g < 0$

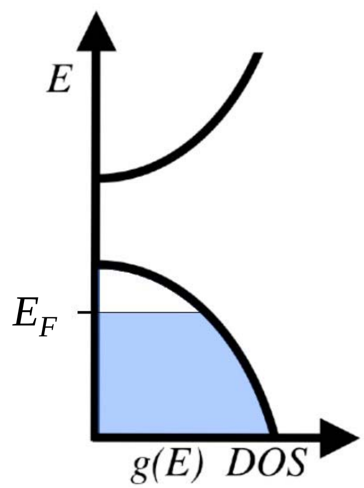
Valence Imbalanced Zintl-like Phases (~1e^-/Formula)

- Zintl valence count is slightly off
- giving electron-rich or electron-poor phases that are metallic (heavily doped semicondutor)

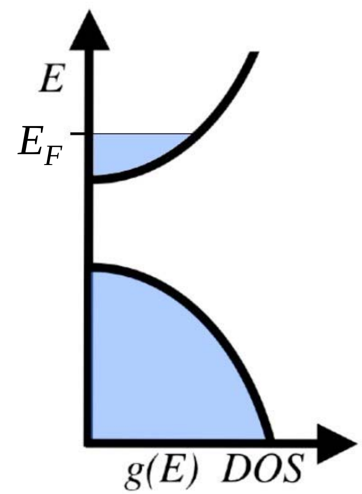
Valence Balanced
Semi-Metal



Valence Imbalanced
Metal with band gap
(heavily doped semiconductor)



Electron Poor



Electron Rich

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Valence Metals with Band Gap

Thermoelectric materials are (postulate ?)

Off Valence Balance compounds

Where ***concentration of valence imbalance = free carrier concentration***

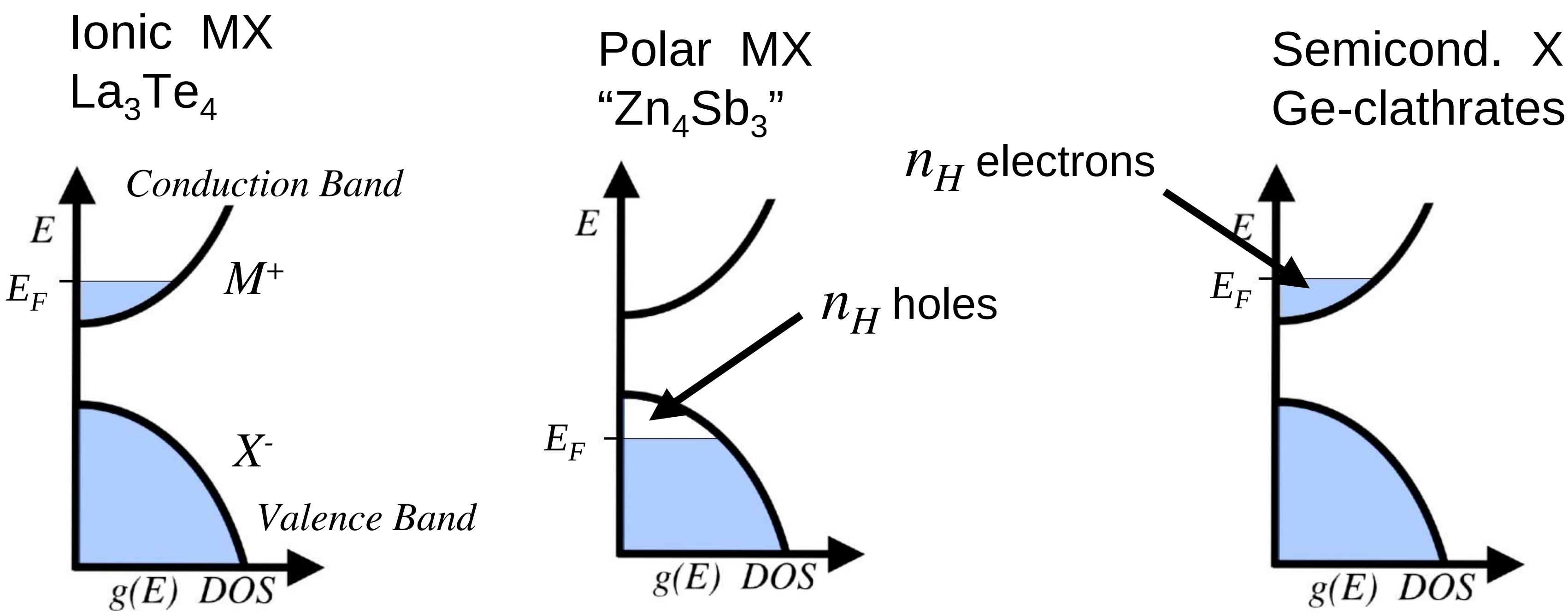
- free Carrier Concentration measured by Hall Effect n_H

Transport properties are metallic

- Heavily doped, degenerate semiconductors

Zintl electron counting rules apply

- Poly anions, Metal-Metal bonding



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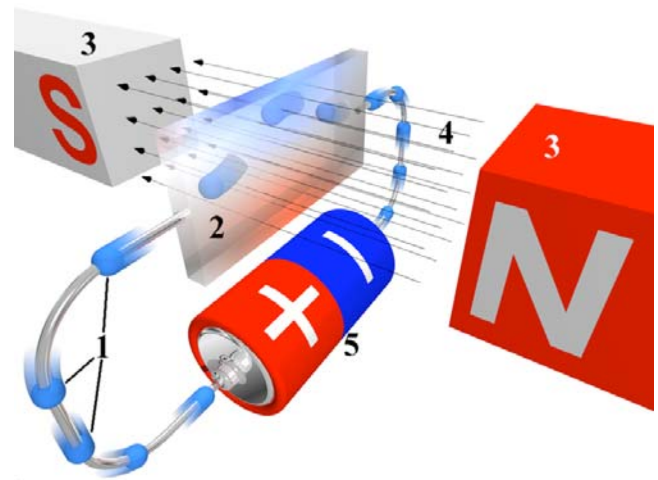
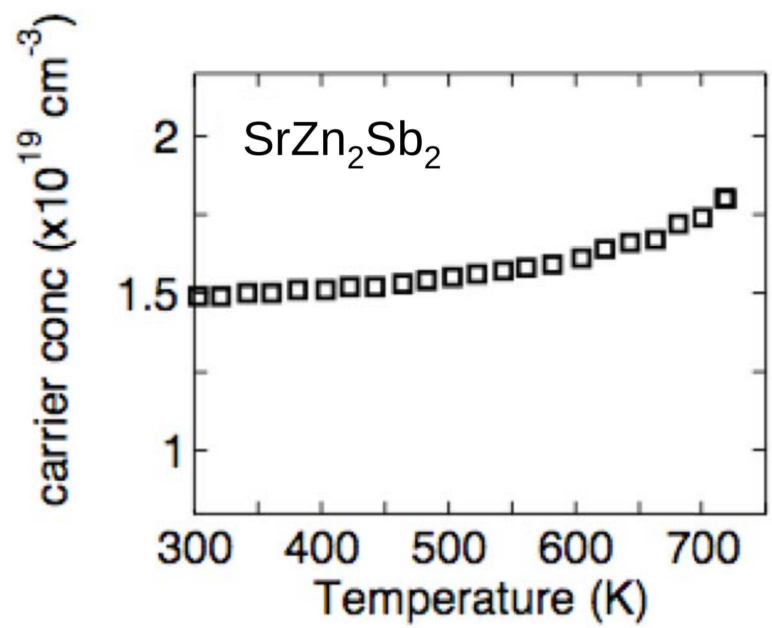
Hall Effect

- Hall Effect
  - Magnetic Field deflects mobile charges
- Hall Effect measurements give:
  - Sign of Charge Carrier
    - n (electron) or p (hole) type
  - Carrier concentration
    - $n_H = 1/R_H e$
  - Mobility
    - $\mu_H = \sigma / n_H e$

- Hall Effect of Extrinsic Semicond.
  - Constant n_H at low temp
    - n_H = dopant concentration
  - Rises at high temp
    - minority carriers activated across Band Gap





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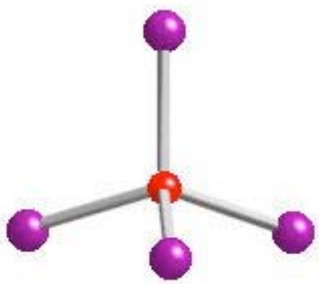
$Yb_{14}AlSb_{11}$

Complex structure

Contains variety of structural elements

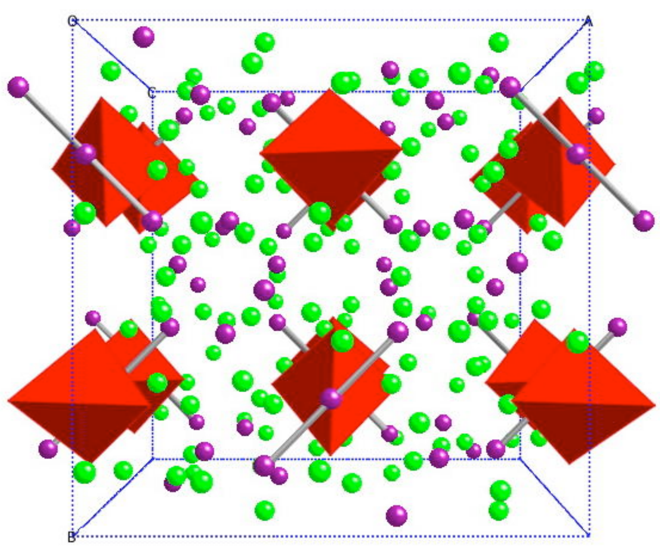


1 $[Al^{+3}Sb_4]^{-9}$

1 $[Sb_3]^{-7}$

14 Yb^{+2}

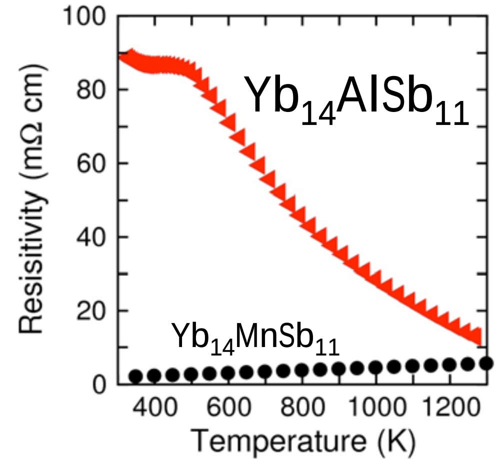
4 Sb^{-3}

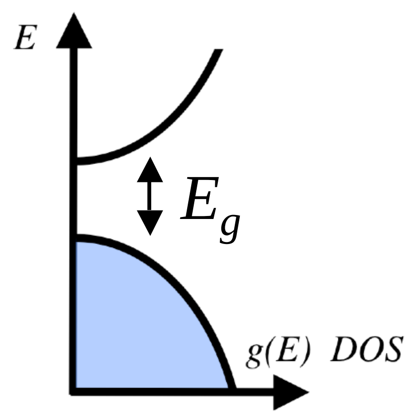


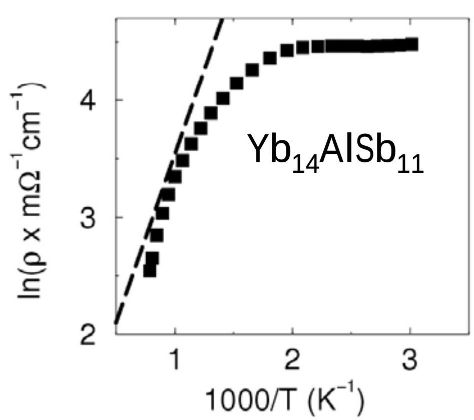
Valence Balance

Semiconductor

Band Gap ~ 0.5 eV







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Cation doping $Yb_{14}MnSb_{11}$

Mn^{+2} (for Al^{+3}) gives 1h^+ per $Yb_{14}MnSb_{11}$

- delocalized hole $n \sim 1.3 \times 10^{21}$/cc

Linear resistivity with T

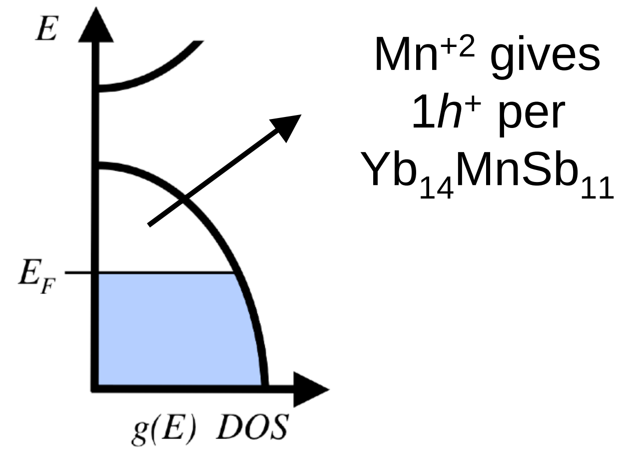
- Metal (Heavily doped semiconductor)

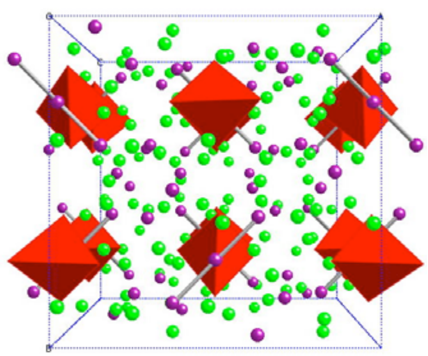
Linear p-type Seebeck with T

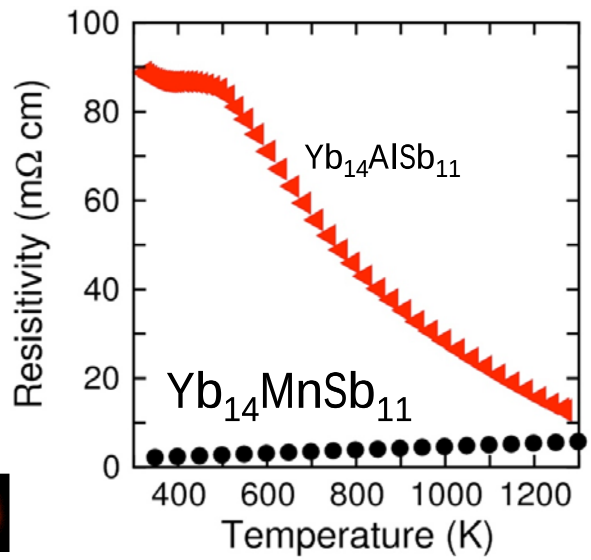
- $m^* \sim 3\ m_e$, $\mu \sim 3$ cm²/Vs, $E_g \sim 0.5$ eV

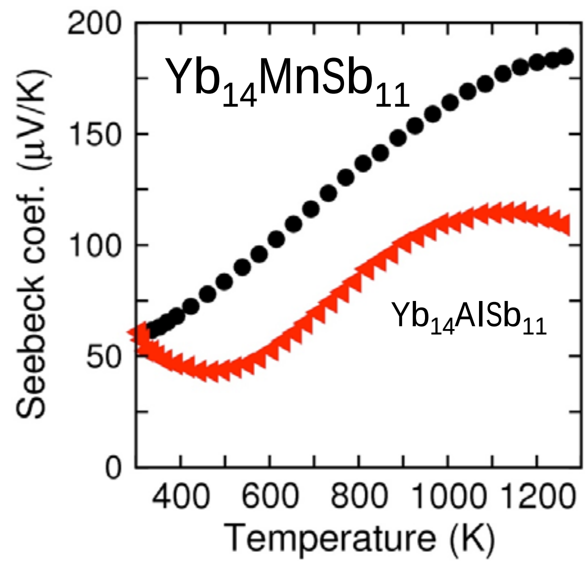
Mn^{2+} (h.s. d^5) + spin paired hole (anti-ferro.)

- net spin = 5/2 - 1/2 = 2
- Under-screened Kondo lattice
- Sales, et al. *PRB* **72** 205207 (2005)









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Thermoelectric $Yb_{14}MnSb_{11}$

High Efficiency, *zT*

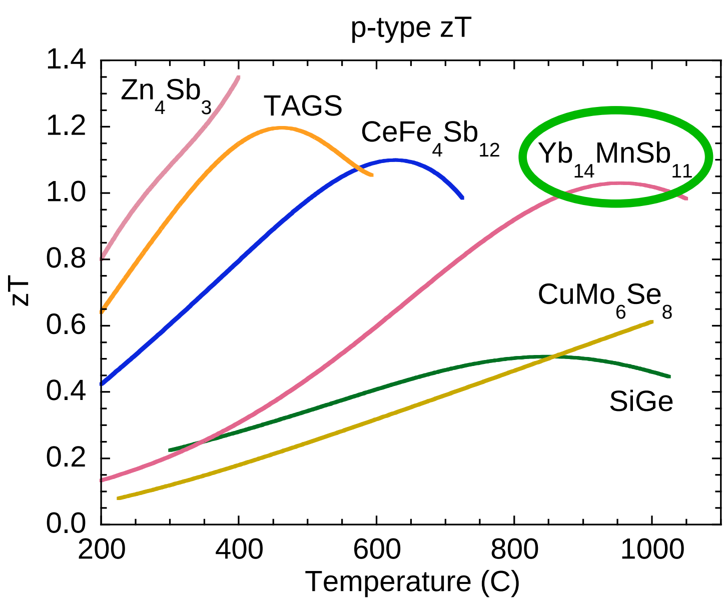
zT maximum > 1.0

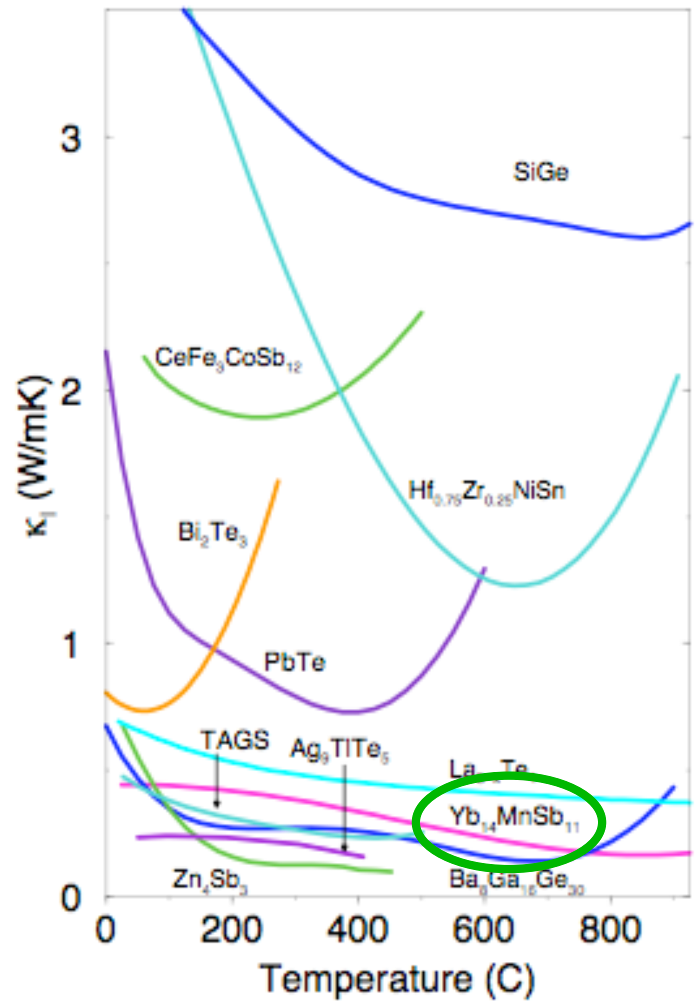
Avg *zT* 0.95

- for 700 < T < 1000 C
- 2 x better than SiGe
- Due to low lattice thermal conductivity
  - Complex structure ?

Currently being developed by NASA

- Next generation RTG





Snyder, *Nature Materials* **7,** 105 (2008)

THERMOELECTRICS

Brown, Kauzlarich, Gascoin, Snyder, *Chem. Materials* **18,** 873 (2006)

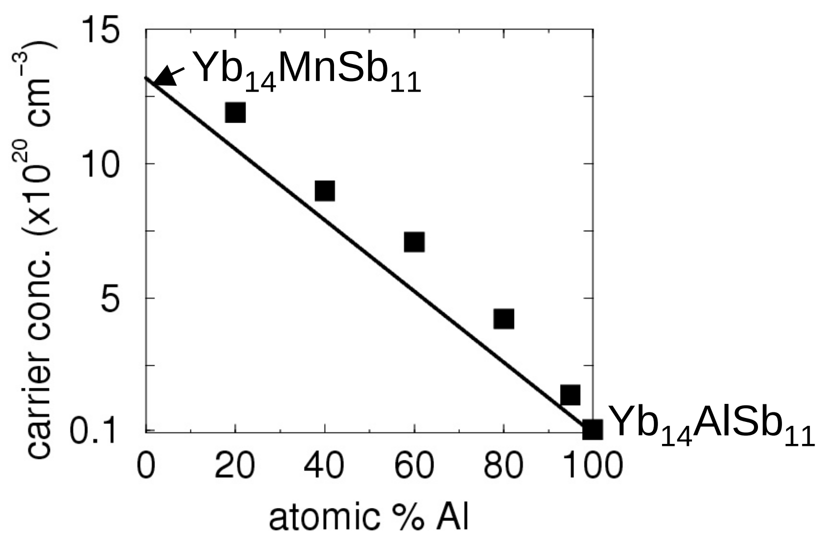
Carrier Concentration Tuning

zT maximizes at optimum free carrier concentration

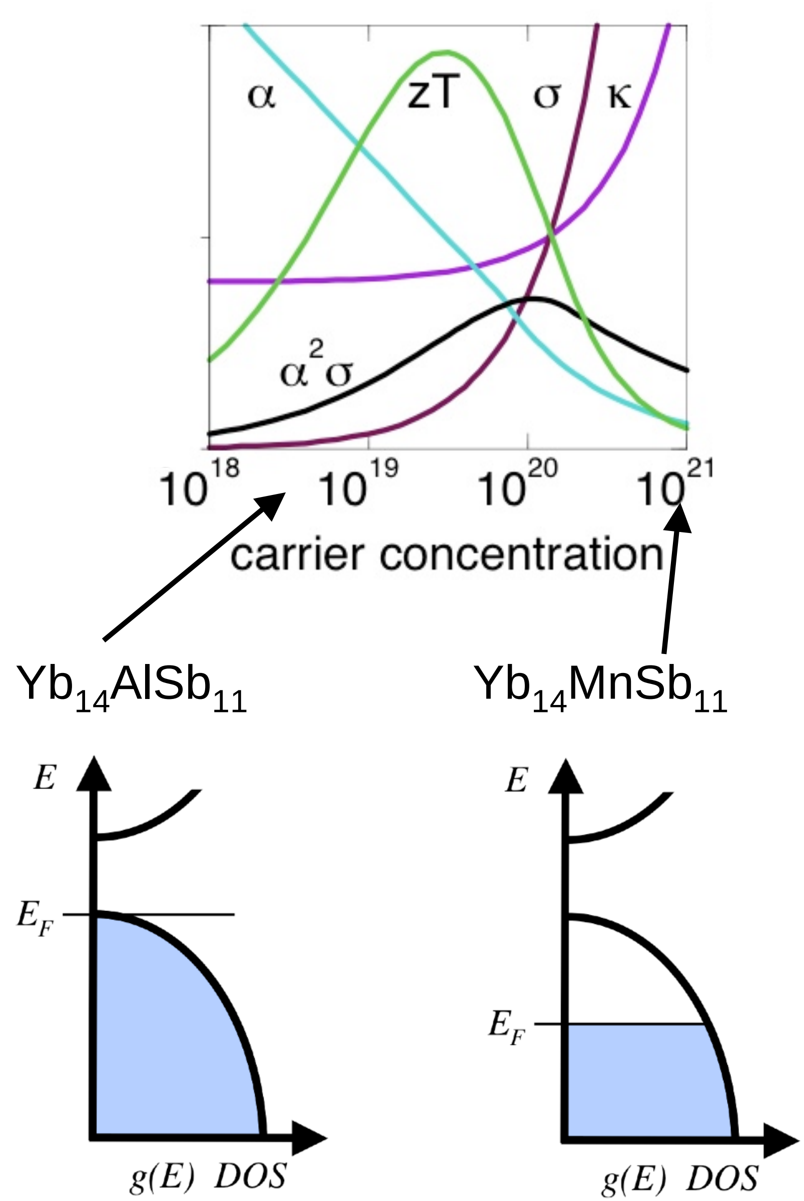
$Yb_{14}Mn_{1-x}Al_xSb_{11}$

Al^{3+} for Mn^{2+} + h^{+}

- reduces hole concentration



From Room Temperature Hall Effect



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Rigid Bands in $Yb_{14}Mn_{1-x}Al_xSb_{11}$

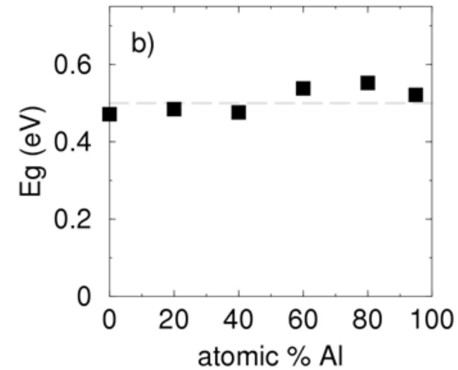
Properties Follow simple rigid, parabolic-band model as Fermi Level changes

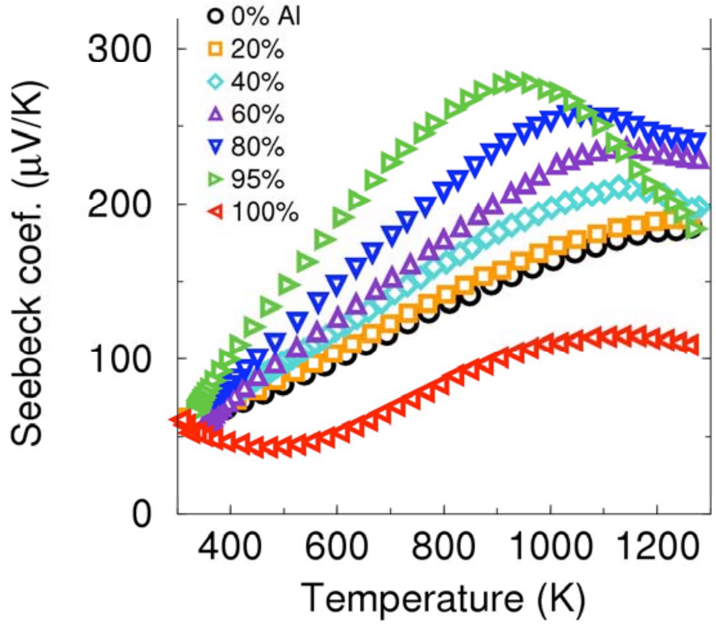
$E_g \sim 2e\alpha_{max}T_{max}$

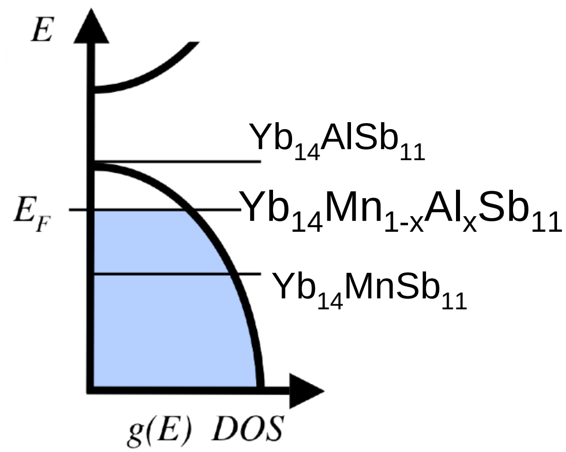
- Constant effective band gap
  - From peak in Thermopower

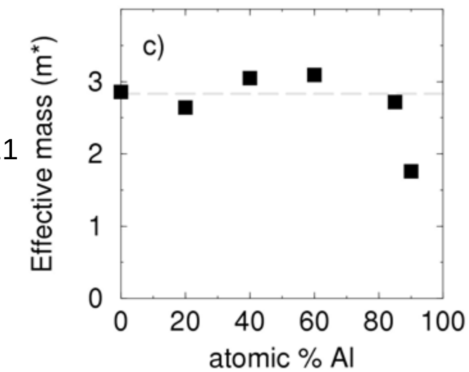
    Sharp, et al., *J. Elec. Mater.* **28** 869 (1999)

    – additional h^+ and e^- reduce thermopower
- Constant effective mass
  - From $d\alpha/dT$ in linear region









$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

THERMOELECTRICS

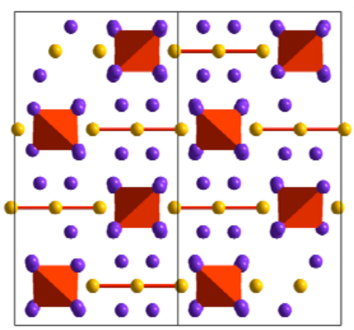
Complex Crystal Structures

Low Lattice Thermal Conductivity

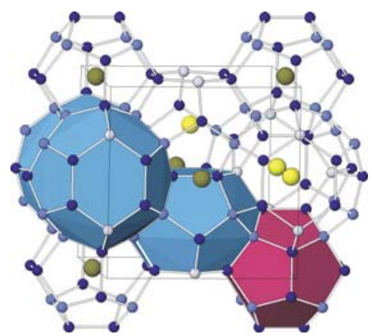
From complex structure

- $Yb_{14}MnSb_{11}$
- Clathrate $Ba_8Ga_{16}Ge_{30}$
- Zn_4Sb_3

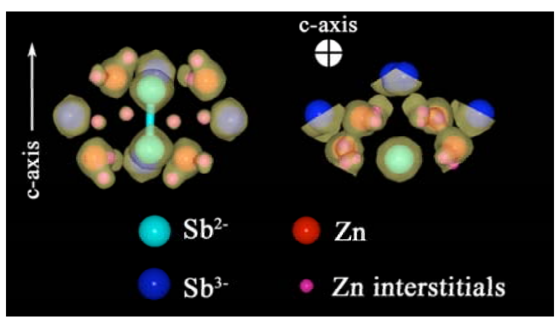
$Yb_{14}MnSb_{11}$

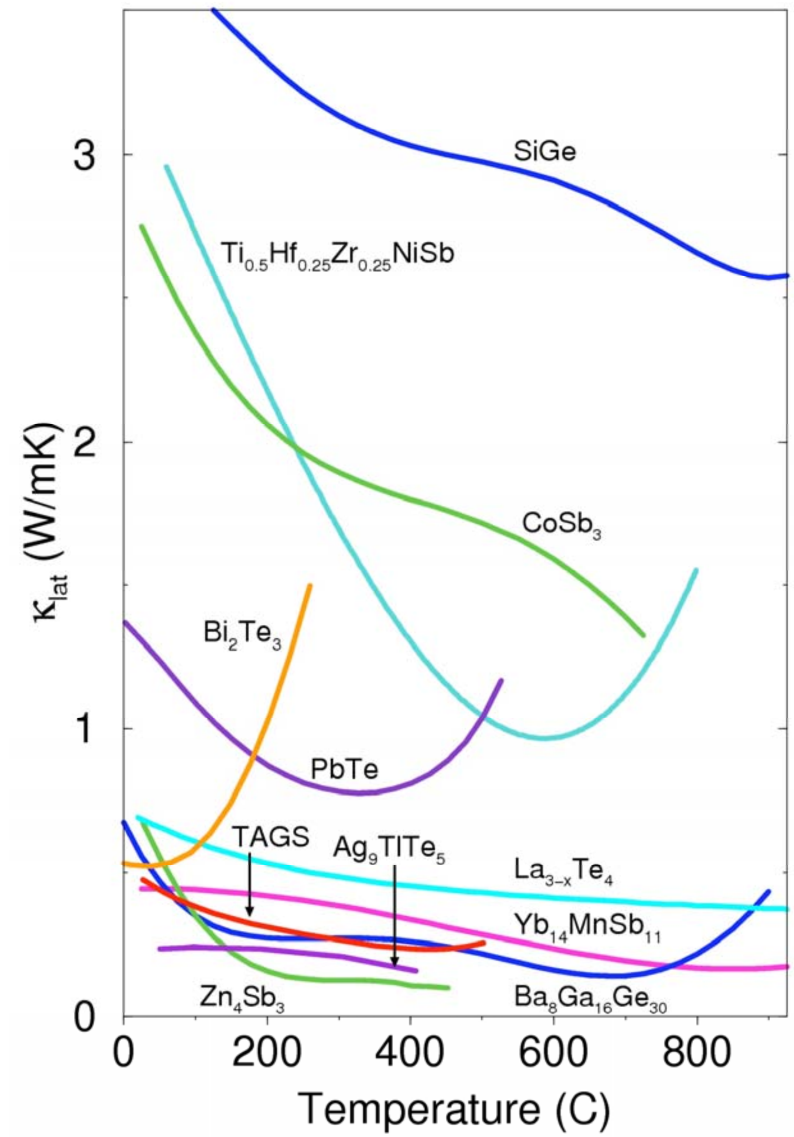


$Ba_8Ga_{16}Ge_{30}$



Zn_4Sb_3





THERMOELECTRICS

Large Cells with low thermal cond.

Heat primarily carried by acoustic modes

$$\kappa_{lattice} = \frac{1}{3} C v l$$

C - heat capacity
v - speed of sound
l - phonon mean free path
N - atoms per cell
V - volume of cell

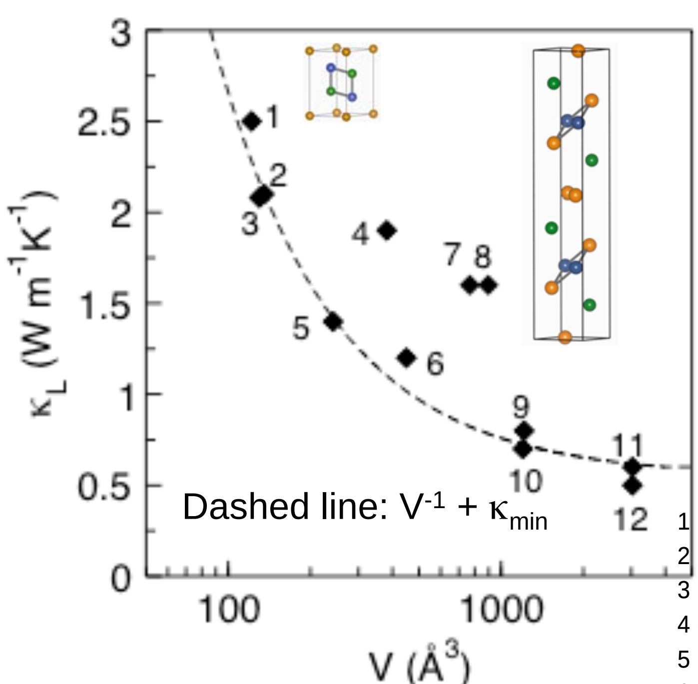
Large cells have many more optic modes than acoustic

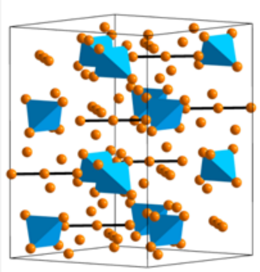
$$\text{acoustic } C = \frac{3k_B}{cell} = \frac{3k_B}{V} \qquad \text{optic } C = \frac{3(N-1)k_B}{cell} = \frac{3(N-1)k_B}{V}$$

Low lattice thermal conductivity

for large primitive unit cell volume (V)

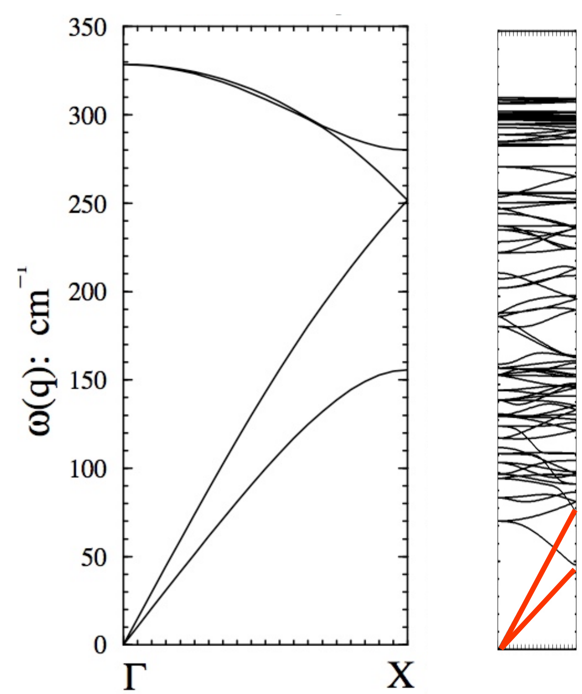
$$\kappa_l \approx \frac{k_B v l}{V}$$





1 - LiZnSb
2 - $SrZn_2Sb_2$
3 - Mg_3Sb_2
4 $CeFe_4Sb_{12}$
5 - $BaZn_2Sb_2$
6 - $SrZnSb_2$
7 - $Yb_5In_2Sb_6$
8- $Ba_4In_8Sb_{16}$
9 - $Yb_{11}Sb_{10}$
10 - $Yb_{11}GaSb_9$
11 - $Yb_{14}AlSb_{11}$
12 - $Yb_{14}MnSb_{11}$

Diamond Ge_2 | Empty clathrate Ge_{46}



Dong et al, Phys. Rev. Lett. 2001

THERMOELECTRICS

Toberer, May, Snyder ***Chem. Mat.***, (DOI: 10.1021/cm901956r)

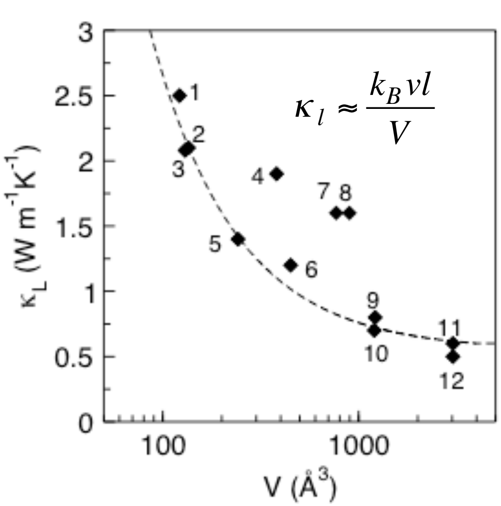
Clathrates

Large Unit Cell

- expect low κ_l

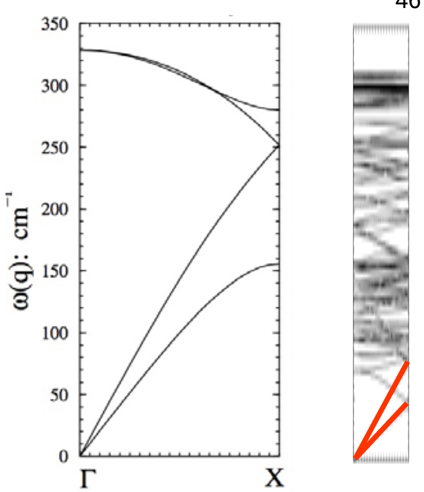
Covalent bonding

- high m^* and μ like elemental Si or Ge?
- can we modify n ?



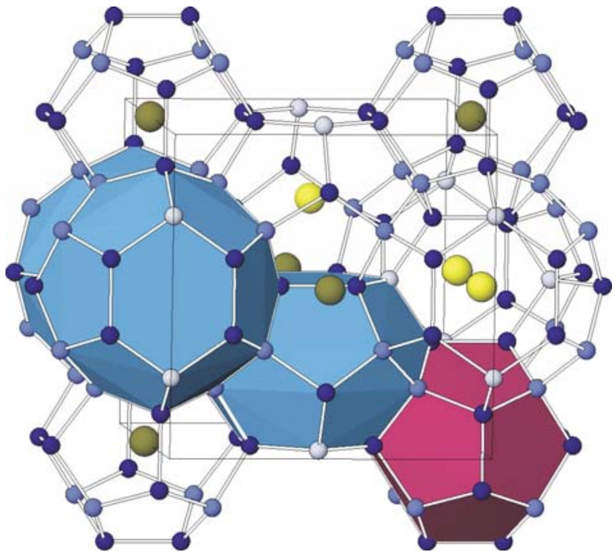
Diamond Ge_2

Empty clathrate Ge_{46}



Dong et al, Phys. Rev. Lett. 2001

$Ba_8Ga_{16}Ge_{30}$
Type I Clathrate



Toberer, May, Snyder ***Chem. Mat.,*** (DOI: 10.1021/cm901956r)

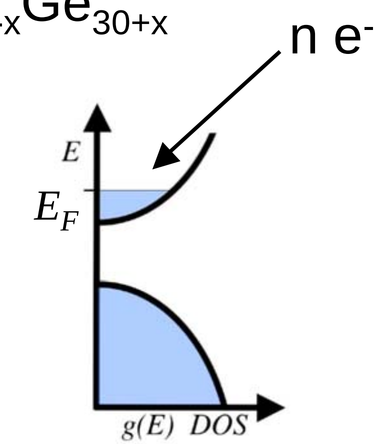
Thermoelectric $Ba_8Ga_{16-x}Ge_{30+x}$

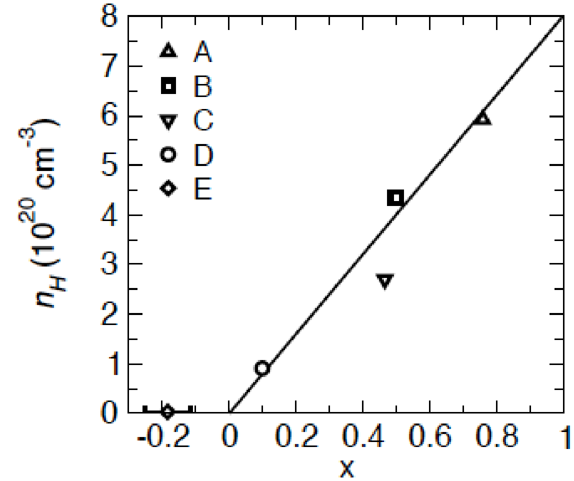
Zintl Electron Counting for $Ba_8Ga_{16-x}Ge_{30+x}$

no vacancies for $x < 3$

$n = 2 \times [Ba^{2+}] - 1 \times [4b\text{-}Ga^{-1}]$

$n/FU = 16 - (16 - x) = x$

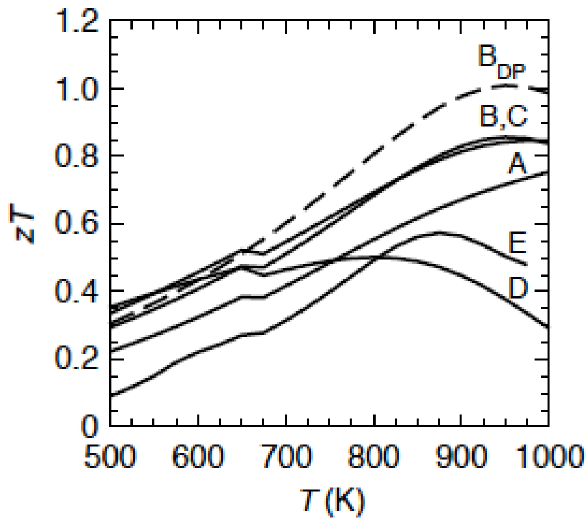


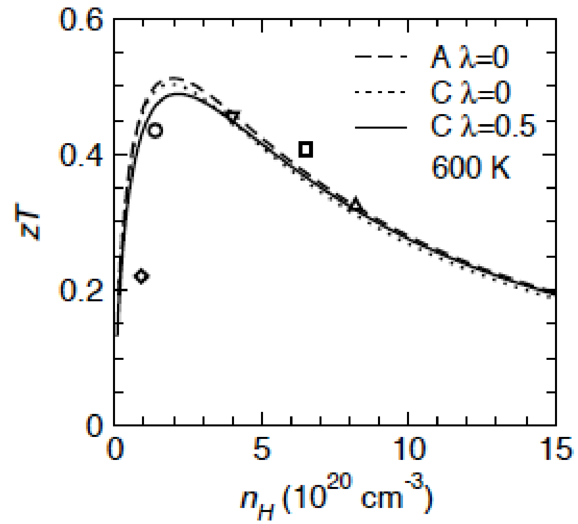


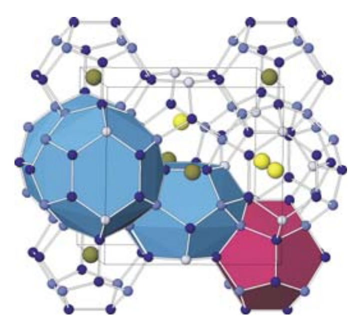
Observed n_{Hall} = valence imbalance

zT optimized by tuning n

Transport fits Single Parabolic Band model





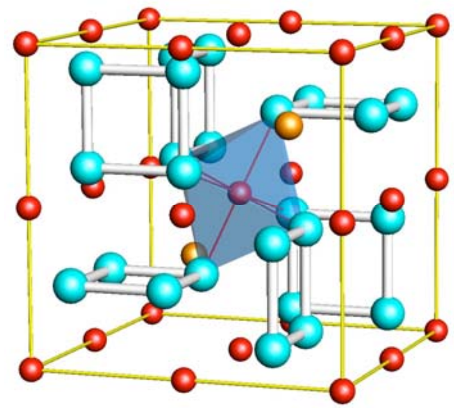


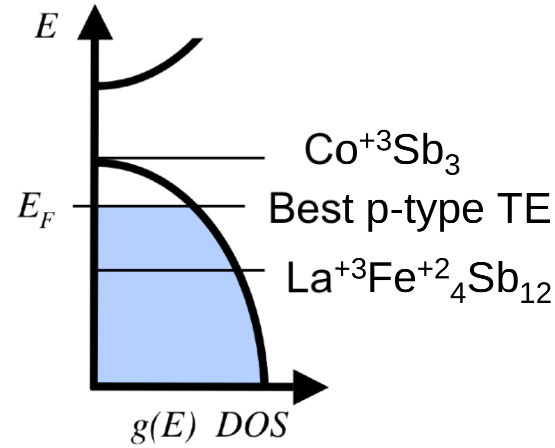
May et. al. *Phys. Rev. B,* **80,** 125205 (2009)

Other Thermoelectric Zintl Metals

Filled Skutterudites

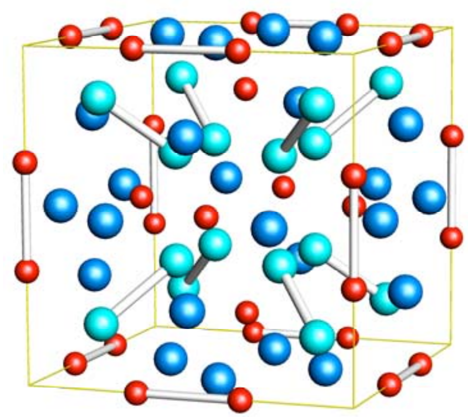
- Sb square rings 2b-Sb^{-1}
- $Co^{+3}Sb_3$ valence semicond.
- $La^{+3}Fe_4^{+2}Sb_{12}$ Zintl Metal
  - 1 hole/fu

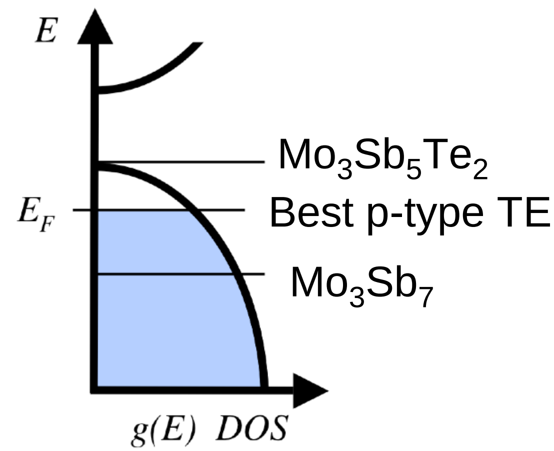




Mo_3Sb_7

- 4x Sb dimers 1b-Sb^{-2}
- 3x Sb isolated 0b-Sb^{-3}
- Mo-Mo dimer 1b-Mo^{+5}
- 2 holes/FU = metal
  - $Mo_3Sb_5Te_2$ for SC



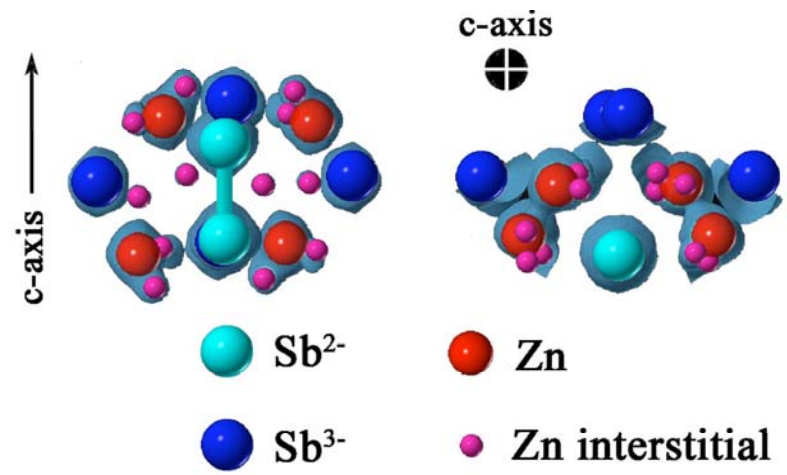


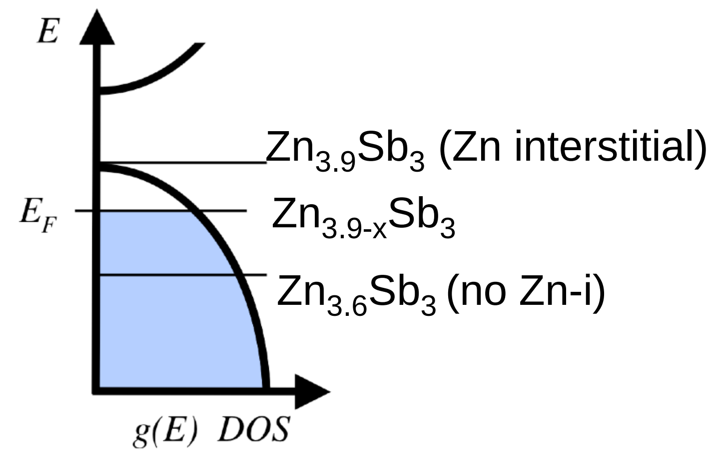
THERMOELECTRICS

Gascoin, et al *J. Alloys. Compounds* **427,** 324 (2007)
Kauzlarich, Snyder et al, *Dalton Trans.* p. 2099 (2007)

Zn_4Sb_3

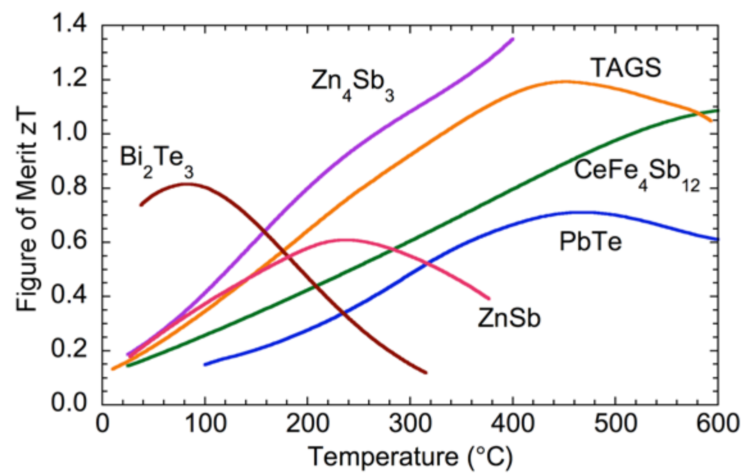
Extra Zn found in interstitial sites





Zn-i adds $2e^-$ (Zn^{2+})

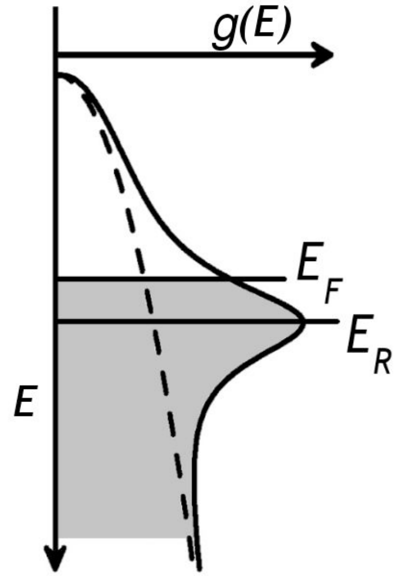
- Moves Ef up in valence band
  - rigid band model
  - $Zn_{3.9}Sb_3$ should be Semiconducting
- Does not add new states



THERMOELECTRICS

Snyder et al, *Nature Materials* **3**, 458 (2004)
See Haüsserman et al, *Chem. Eur. J.,* **11,** 4912 (2005)

High Efficiency
from
Band Structure Engineering



THERMOELECTRICS

Enhancing Thermopower

Mott Equation

Thermopower of metals depends on

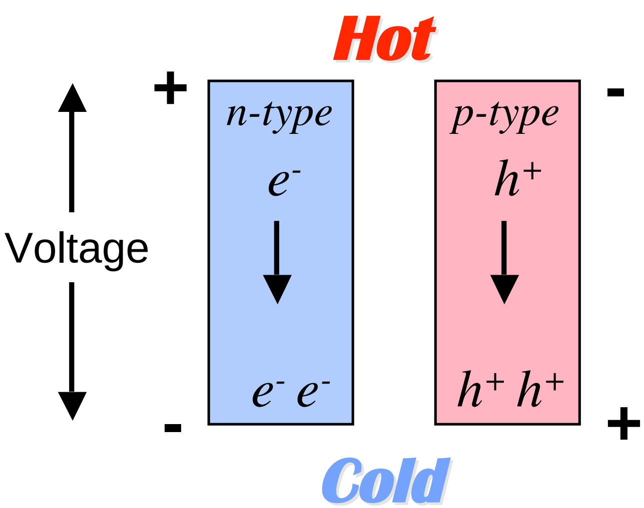
Energy dependent Conductivity

- $\sigma(E)$ is conductivity σ when $E = E_F$

$$\alpha = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{d\left[\ln(\sigma(E))\right]}{dE}\right\}_{E=E_F}$$

- if $\sigma(E_{hot}) \neq \sigma(E_{cold})$ then

charge will build up at the cold end



$$\alpha = \frac{\pi^2 k_b^2 T}{3q}\left(\frac{d\ln N(E)}{dE} + \frac{d\ln\tau(E)v(E)^2}{dE}\right)_{E=E_F}$$

Large Thermopower from

rapidly changing density of states

$$\frac{dN(E)}{dE}$$

or Scattering

- relaxation time τ
- group velocity v
- effective mass m^*
- mobility μ
- mean free path $\lambda \propto \tau$
- carrier concentration n

$$\mu = \frac{e\tau}{m^*}$$

$$\sigma = ne\mu$$

La_2Te_3

Ionic $La_2Te_3 = La^{+3}{}_2Te^{-2}{}_3$

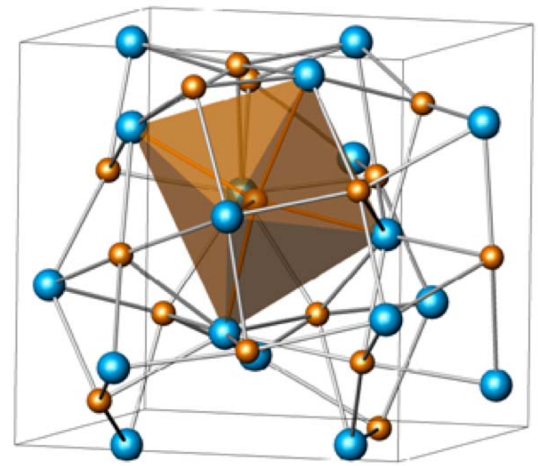
valence balanced insulator

$E_g \sim 1.0$ eV

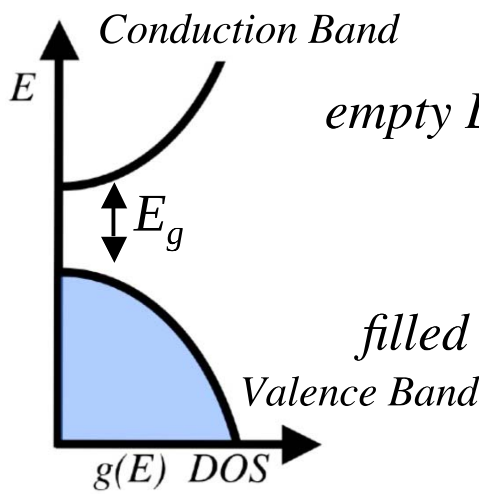
Defect Th_3P_4 structure type

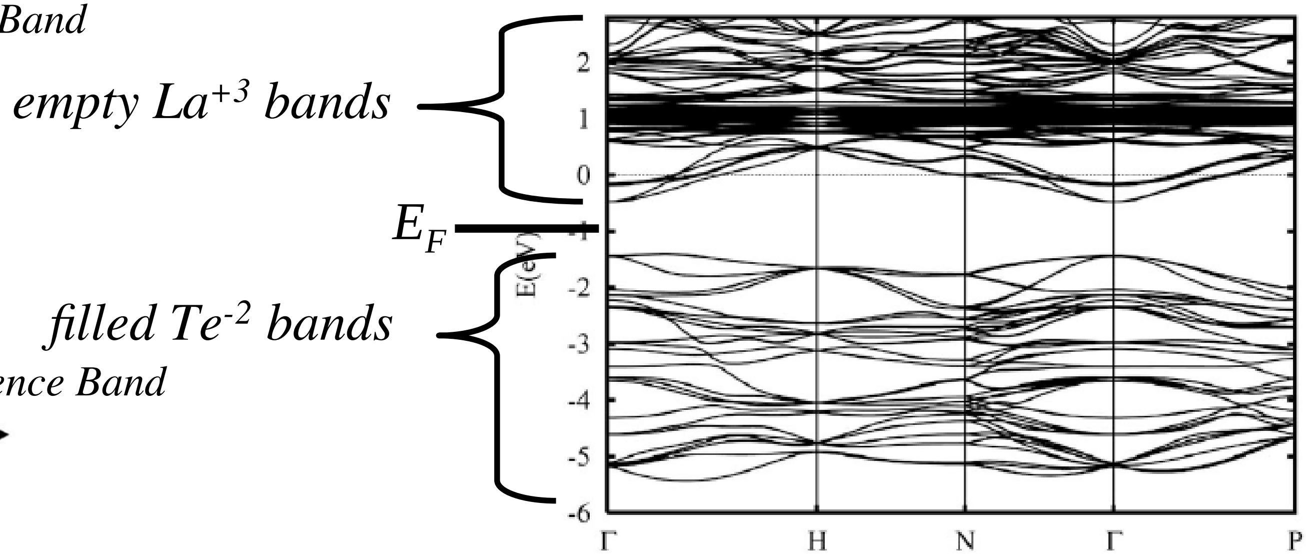
- $La_{3-x}Te_4$
- La vacancies: x = 1/3 for La_2Te_3

Many RE_2X_3 chalcogenides have related structure



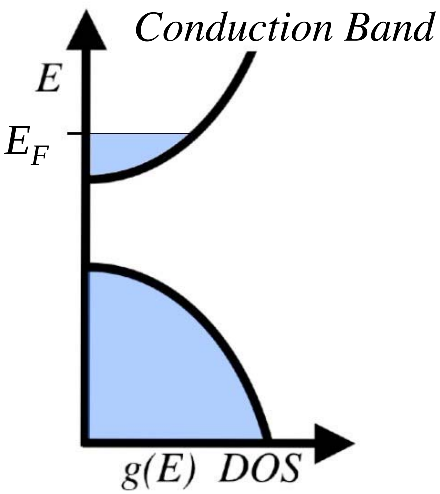
La_3Te_4 distorted octahedron around Te

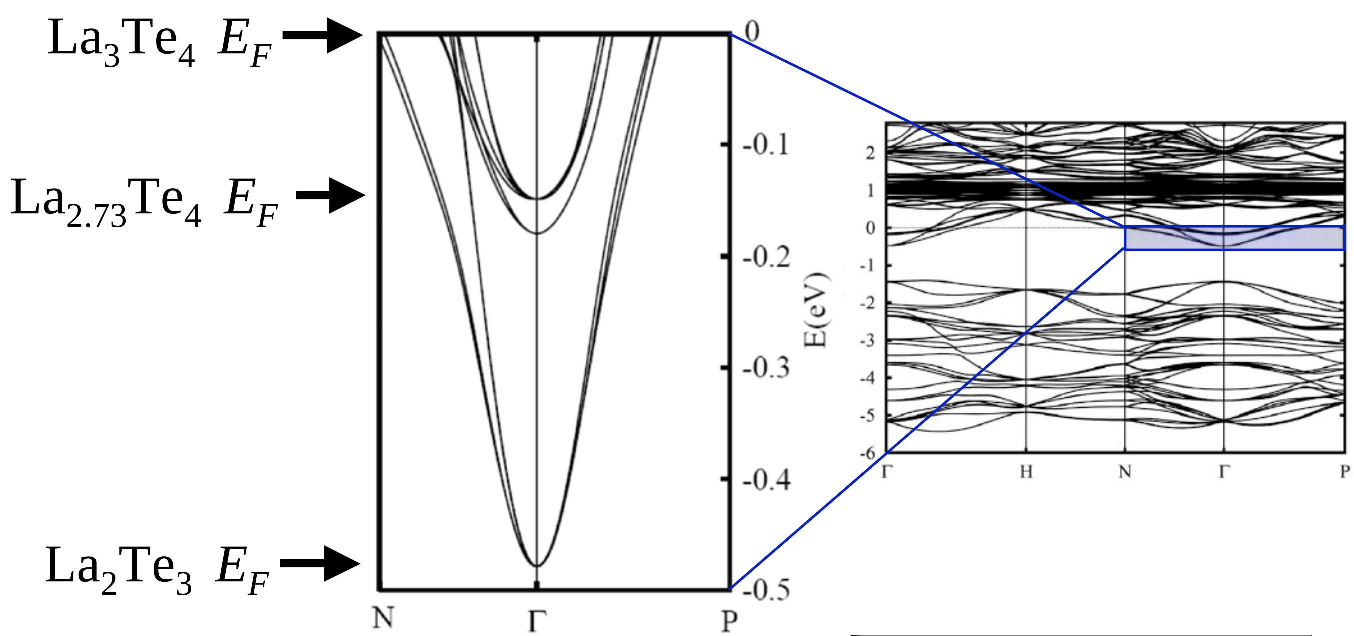




THERMOELECTRICS

$La_{3-x}Te_4$





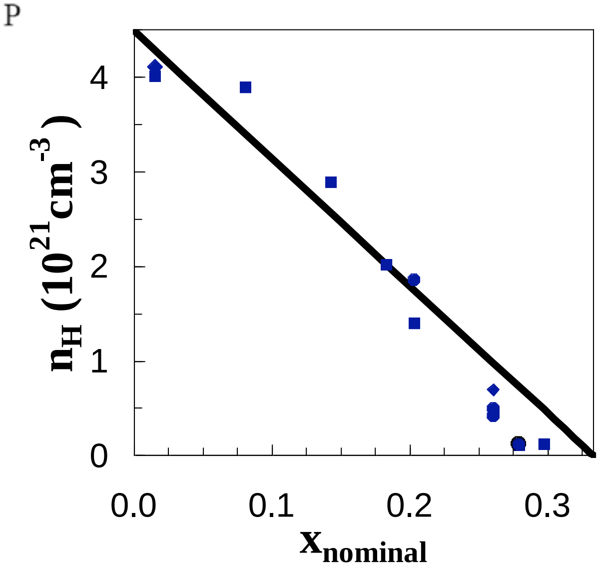
Valence-Imbalanced Metal $La_{3-x}Te_4$ (Ionic)

electron concentration = valence imbalance

$n = n_H = 3\ [La^{3+}] - 2\ [Te^{2-}]$

removing La removes e^- (E_F drops)

- not available states
- states determined by unit cell



THERMOELECTRICS

May et. al. *Phys. Rev. B*, **79**, p. 153101, (2009)

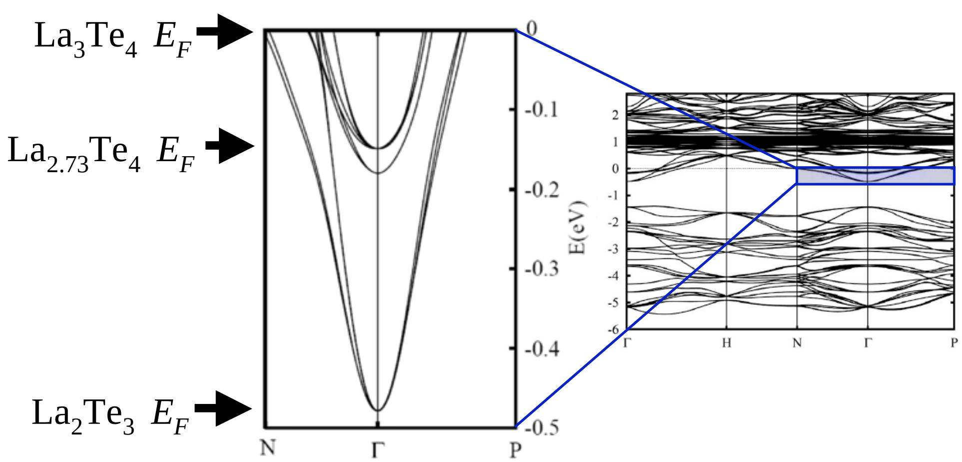
Ab initio vs Semi-Emperical

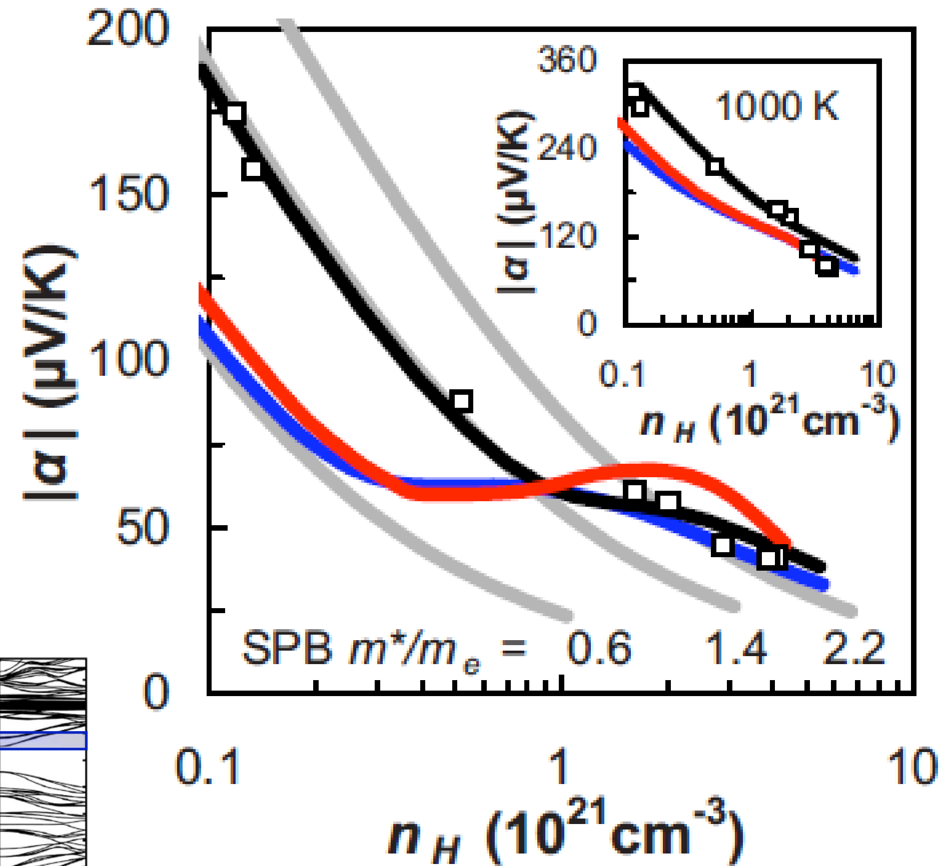
Ab Initio calculations

- Explain qualitative trends
  - D. Singh, Oak Ridge NL

Semi-emperical

- assume parabolic bands
- provides better fit



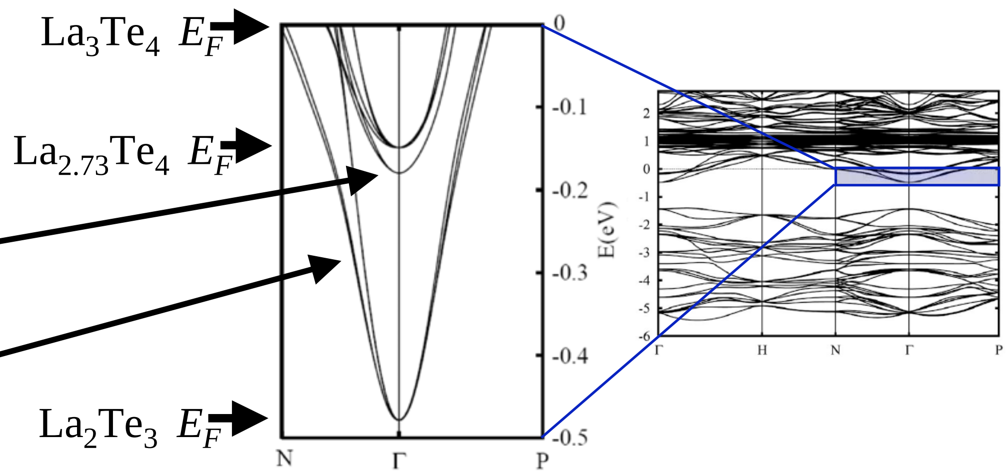


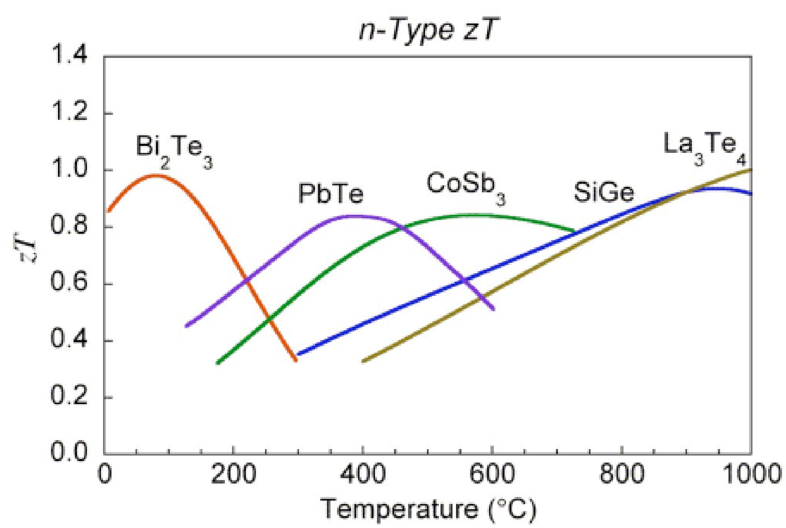
THERMOELECTRICS

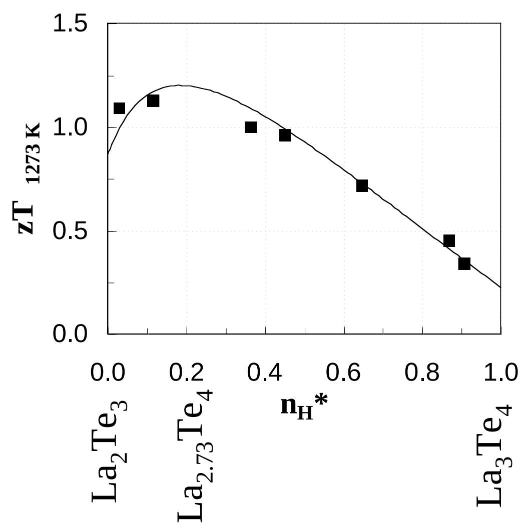
May et. al. *Phys. Rev. B*, **79**, p. 153101, (2009)

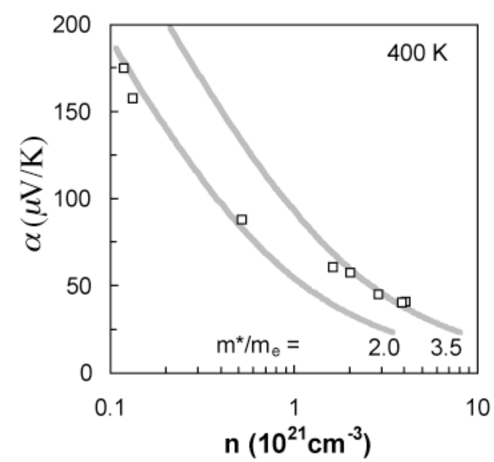
Thermoelectric $La_{3-x}Te_4$

- $La_{3-x}Te_4$ has high zT at high T
  - Higher than SiGe used by NASA
- Highest zT for $La_{2.73}Te_4$
  - E_F at edge of heavy band
    - $m^* \sim 3.5\, m_e$
  - E_F deep inside light band
    - $m^* \sim 2\, m_e$







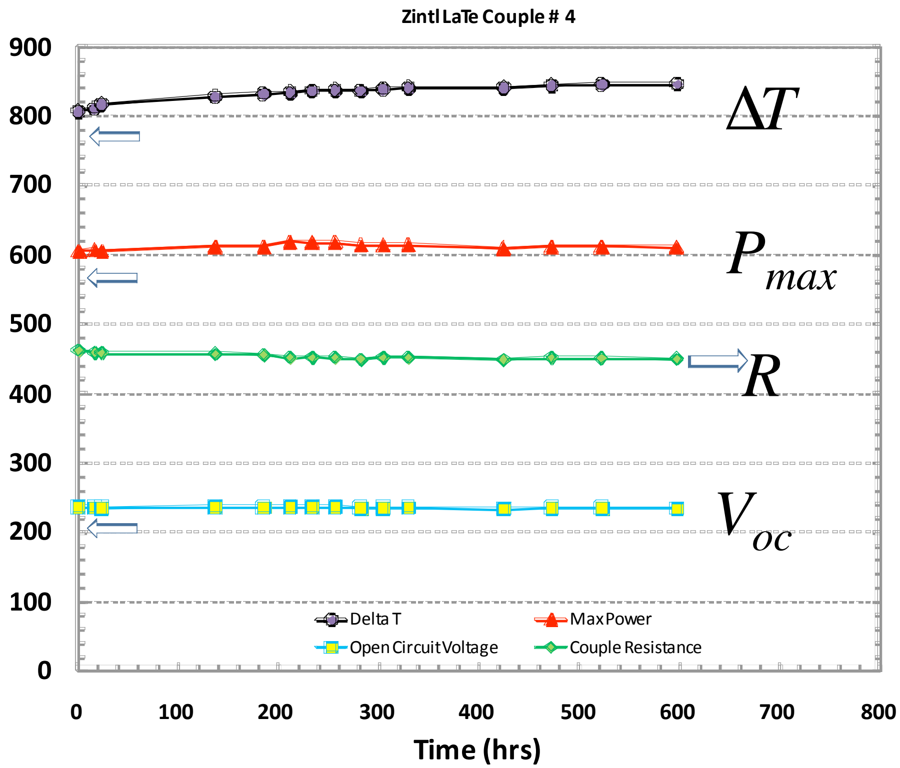


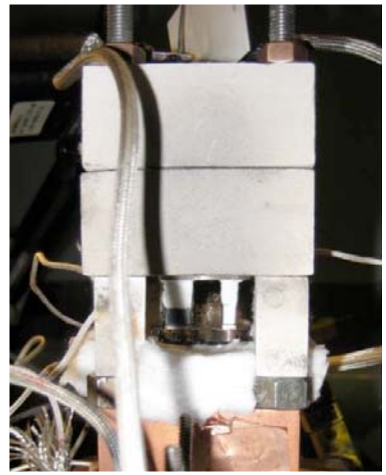
THERMOELECTRICS

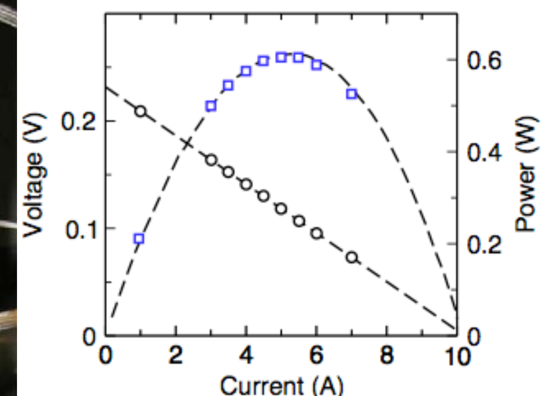
May et. al. *Phys. Rev. B*, **78**, p. 125205, (2008)
May et. al. *Phys. Rev. B*, **79**, p. 153101, (2009)

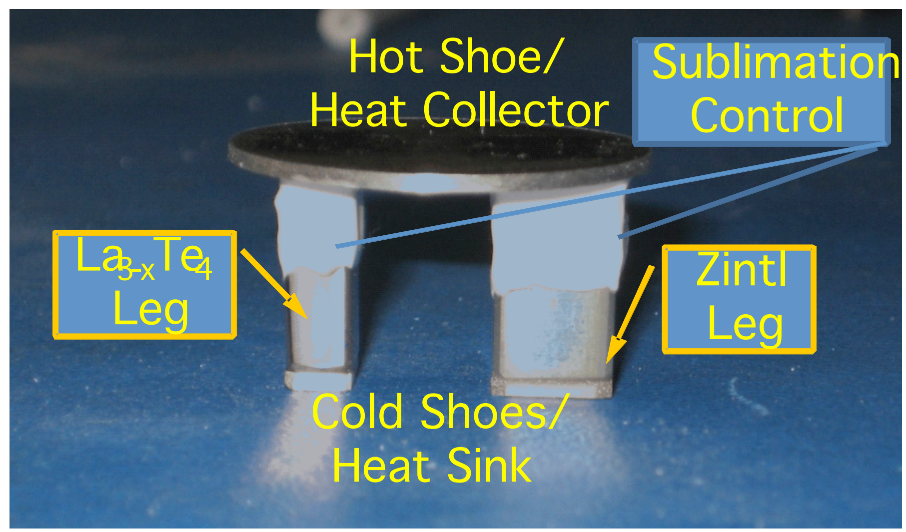
$Yb_{14}MnSb_{11}$ - $La_{3-x}Te_4$ Couple Testing

10% efficiency with 750ºC ΔT (200ºC - 950ºC)
2 month lifetime test successful, 1 year underway









Jean-Pierre Fleurial (JPL)

THERMOELECTRICS

Resonant States

Goal:

Increase Density of States (DOS)

Without ruining mobility

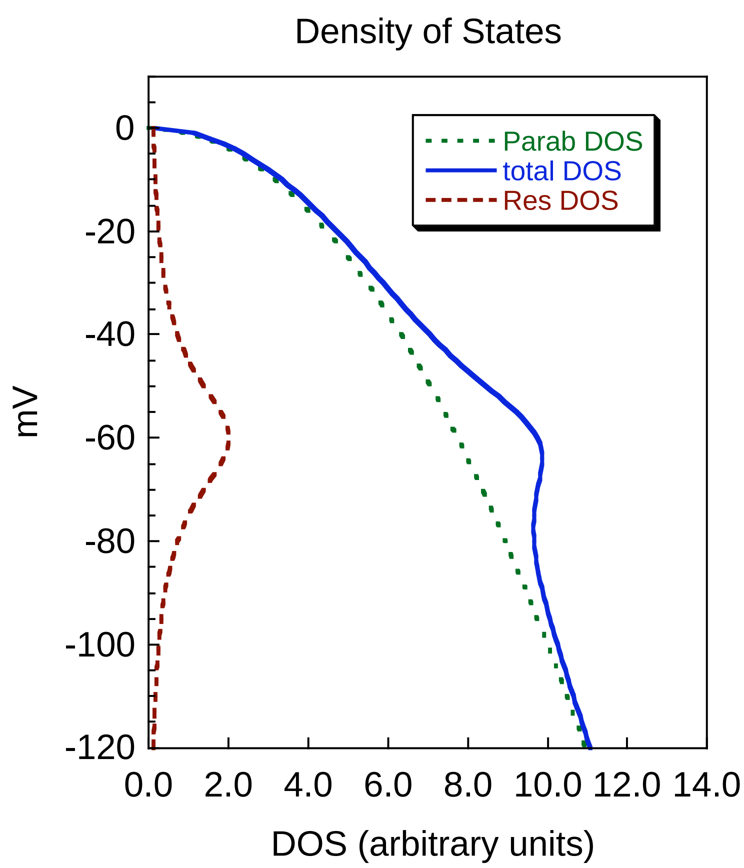
Isolated impurity state

adds delta function in DOS

but hopping conduction

Resonant Impurity State

Adds DOS to existing bands



THERMOELECTRICS

Tl Resonant States in PbTe

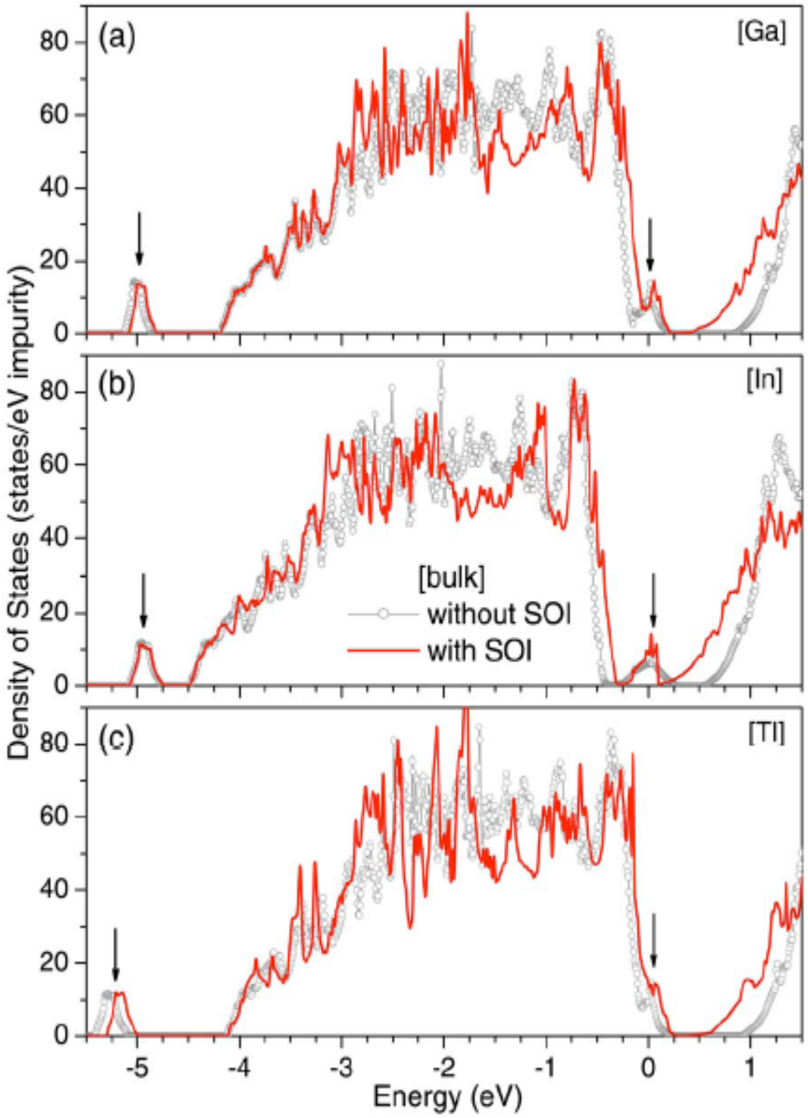
Tl impurity in PbTe

add DOS to top of valence band

- Ga and In states are in the gap
  - *Huang, Mahanti and Jena, PRB **76** 115432 (2007)*

Increased DOS of holes observed

- larger electronic heat capacity
- superconducting T_c
  - *Y. Matsushita, et al., Phys. Rev. B **74** 134512 (2006)*



THERMOELECTRICS

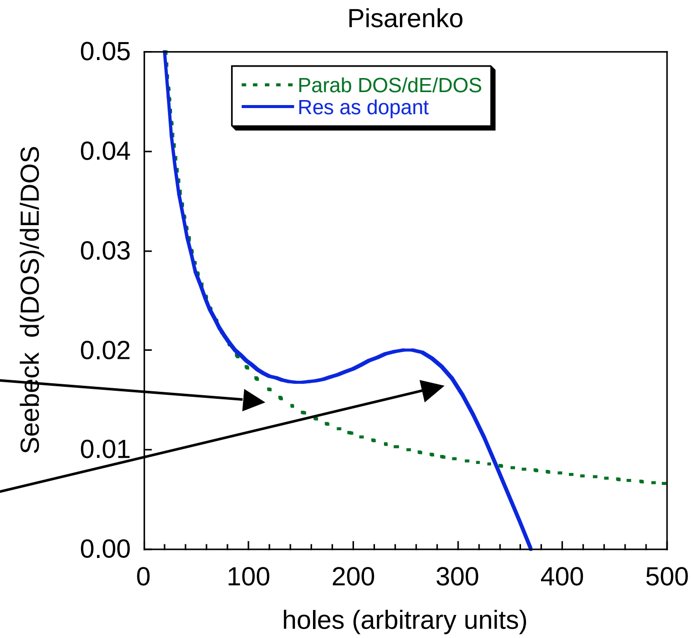
*Huang, Mahanti and Jena, PRB **76** 115432 (2007)*

PbTe:Tl Pisarenko Plot

Thermopower depends on carrier concentration

parabolic band metal $\alpha \propto n^{-2/3}$

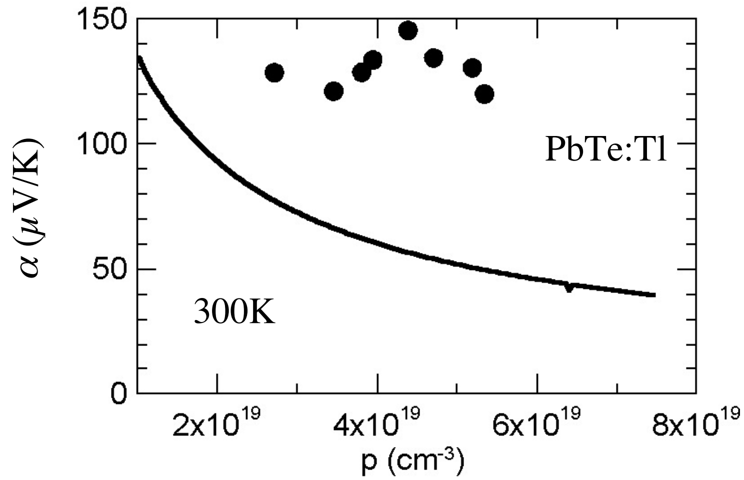
$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$



Resonant state should alter thermopower from increased DOS

PbTe:Tl shows higher thermopower than other p-type dopants

J. P. Heremans, et al.. *Science* **321**, p 554 (2008).



Improved zT from impurity states

PbTe:Tl shows higher thermopower than p-type Na-doped at same carrier concentration

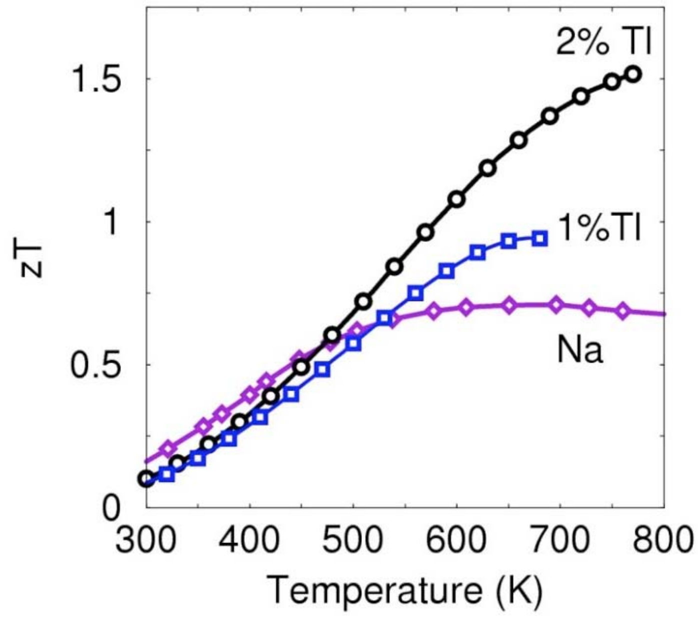
Results in a higher zT

about twice that of PbTe:Na

Mobility and effective mass are also different but net effect is positive

Thermal conductivity is about the same

Would benefit from reduction in lattice thermal conductivity using other methods



J. P. Heremans, et al.. *Science* **321**, p 554 (2008).

Theory Challenges = **Opportunities**

Band Structure Calculations

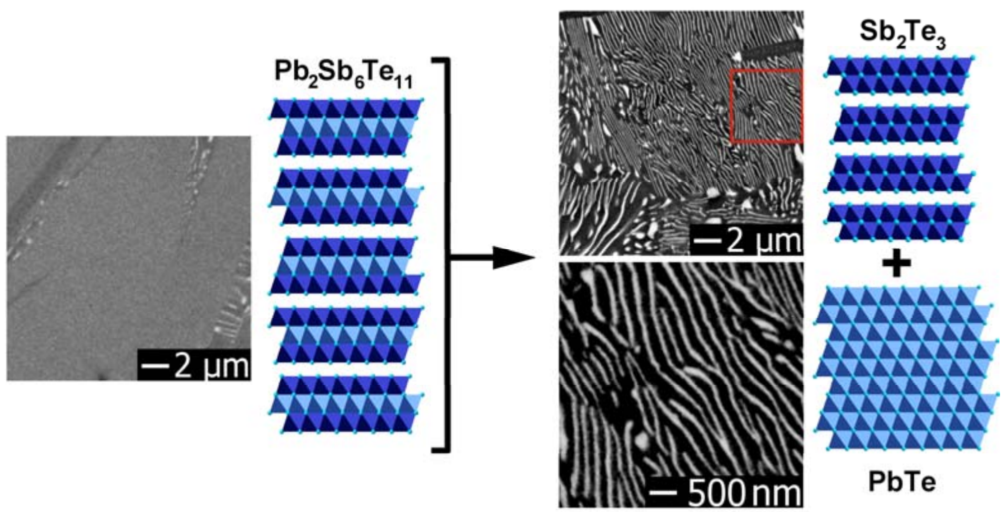
- **Need Accuracy near E_F**
- **Transport is derivative property**
  - **Band Gap (within ~0.05eV)**
  - **Band Edge Energy (within ~0.01eV)**
    - **location of resonant states, other bands**
  - **Effective Mass (within ~0.1me)**
- **Imperfect crystals = Disorder**
  - **Doping at ~1%**
  - **Alloying ~10%**
  - **Vacancies**
  - **Anti-Site Defects**
  - **Interstitial atoms**

Transport Calculations

- **Relaxation Time Approximation**
  - $\tau \sim E^{\lambda}$
- Constant RTA (?)
- **Thermal Transport**
  - diamond structure is 2009
- Exotic TE Materials
  - **Resonant States**
  - e- filtering
  - **Heavy Fermion**
  - **Kondo**
  - **Correlated Electron Systems**
- Nano-structures
  - nanowires
  - superlattices
  - **composites**
  - **interfaces**

THERMOELECTRICS

Complex Thermoelectrics from Nanosized Microstructures

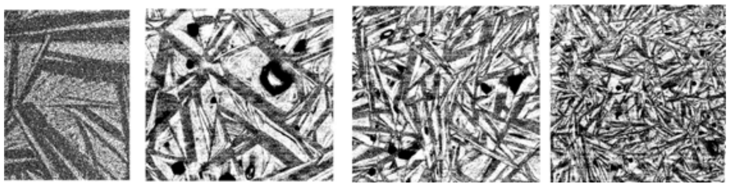


PbTe - Sb_2Te_3 Composites

1) Crystallization from liquid

fast diffusion in liquid

control by cooling rate

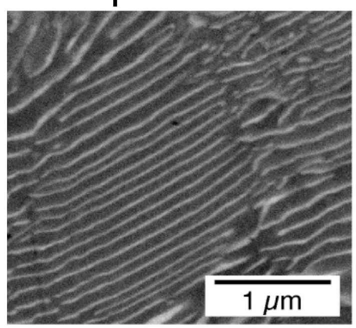


2) Solid-to-Solid eutectoid decomposition

slow diffusion in solid

control by quench

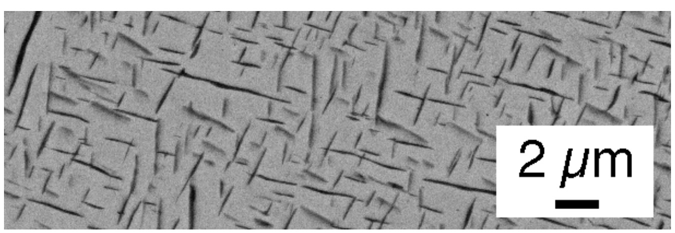
and anneal



3) Solid-state Precipitation

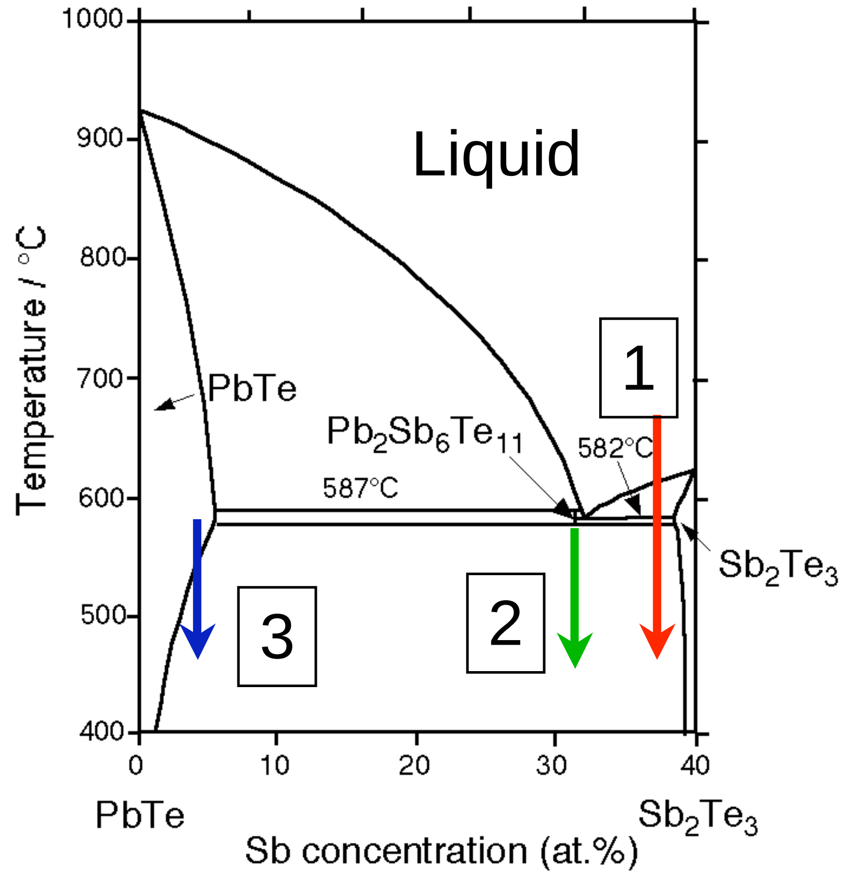
slow diffusion in solid

control by composition and anneal



Three Methods to Create Microstructure

in Sb_2Te_3 - PbTe System



THERMOELECTRICS

Ikeda, Snyder, Ch. 4.2 in "Handbook of Thermoelectric Conversion Technology"

熱電変換技術ハンドブック

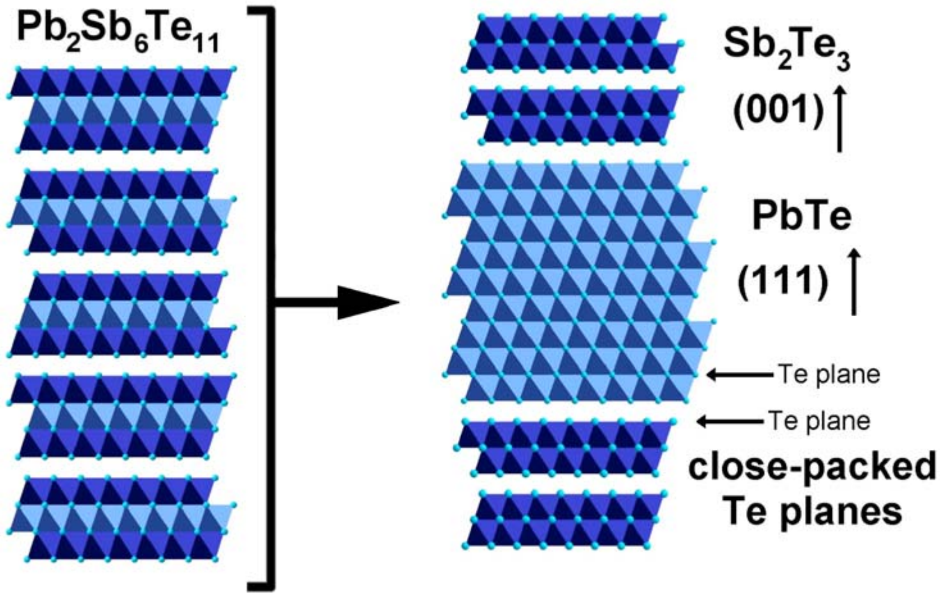
Epitaxy-like Orientation

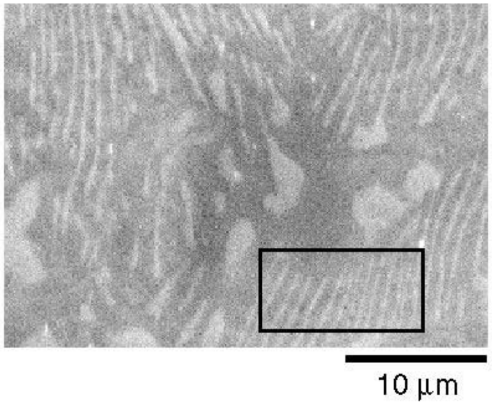
Sb_2Te_3 (001) aligned with PbTe (111)

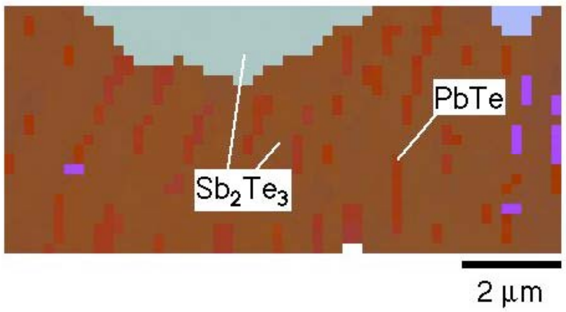
- SEM Electron Backscatter Diffraction (EBSD)
- close packed Te plane

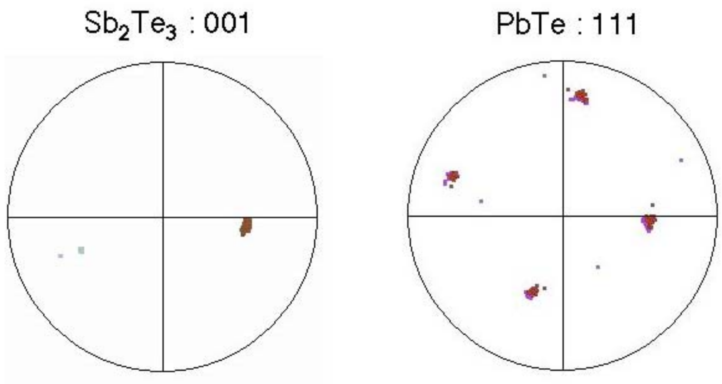
Forms epitaxy-like interface

- *May be critical for High zT*
  - Allow high e^- mobility
  - Disrupt phonon at interface









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Semi-coherent interfaces

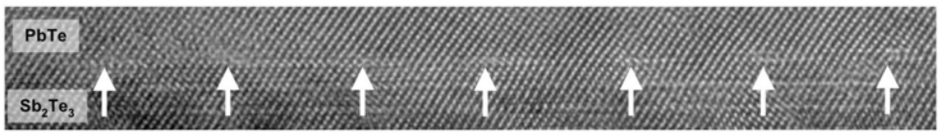
Transmission Electron Microscopy (TEM)

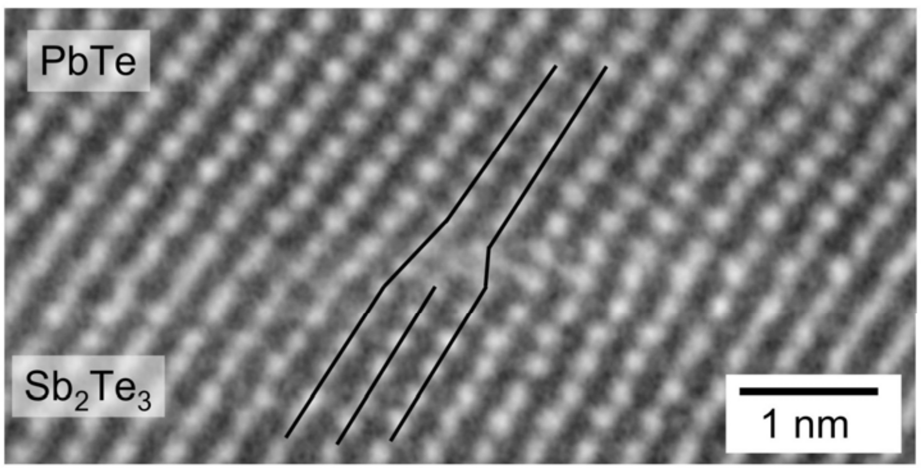
Reveals Crystal orientation

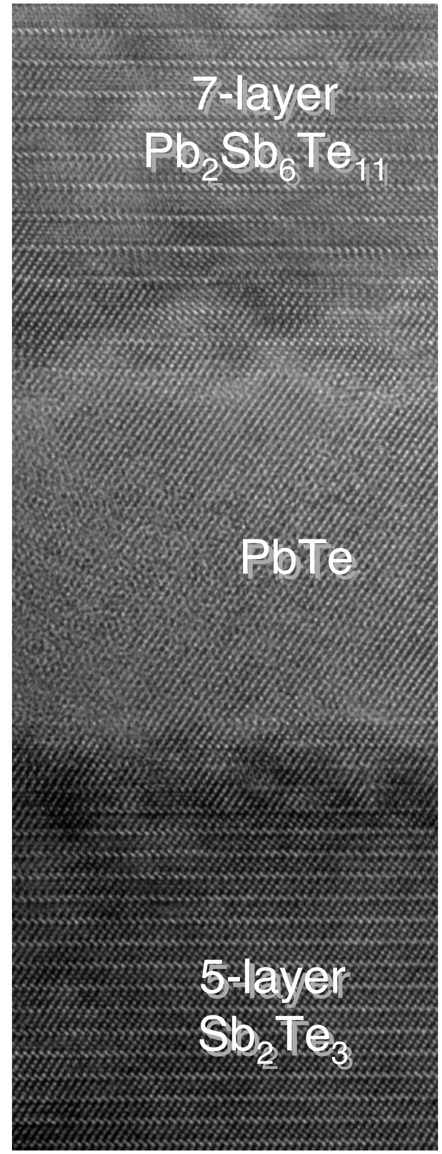
Sb_2Te_3 (001) aligned with PbTe (111)

6% lattice mismatch

Accommodated by periodic dislocations at surface



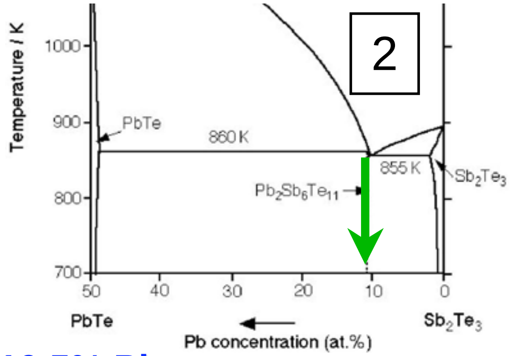




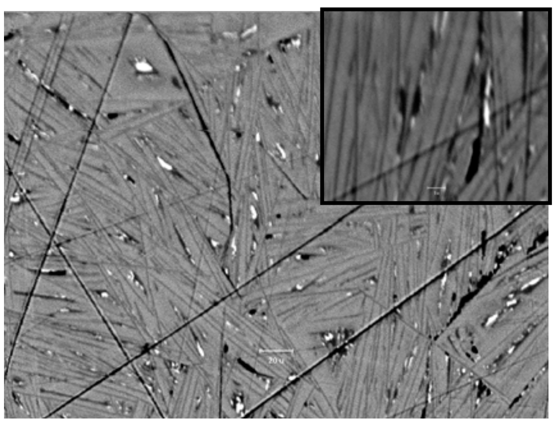
THERMOELECTRICS

Doug Medlin, Sandia Labs CA

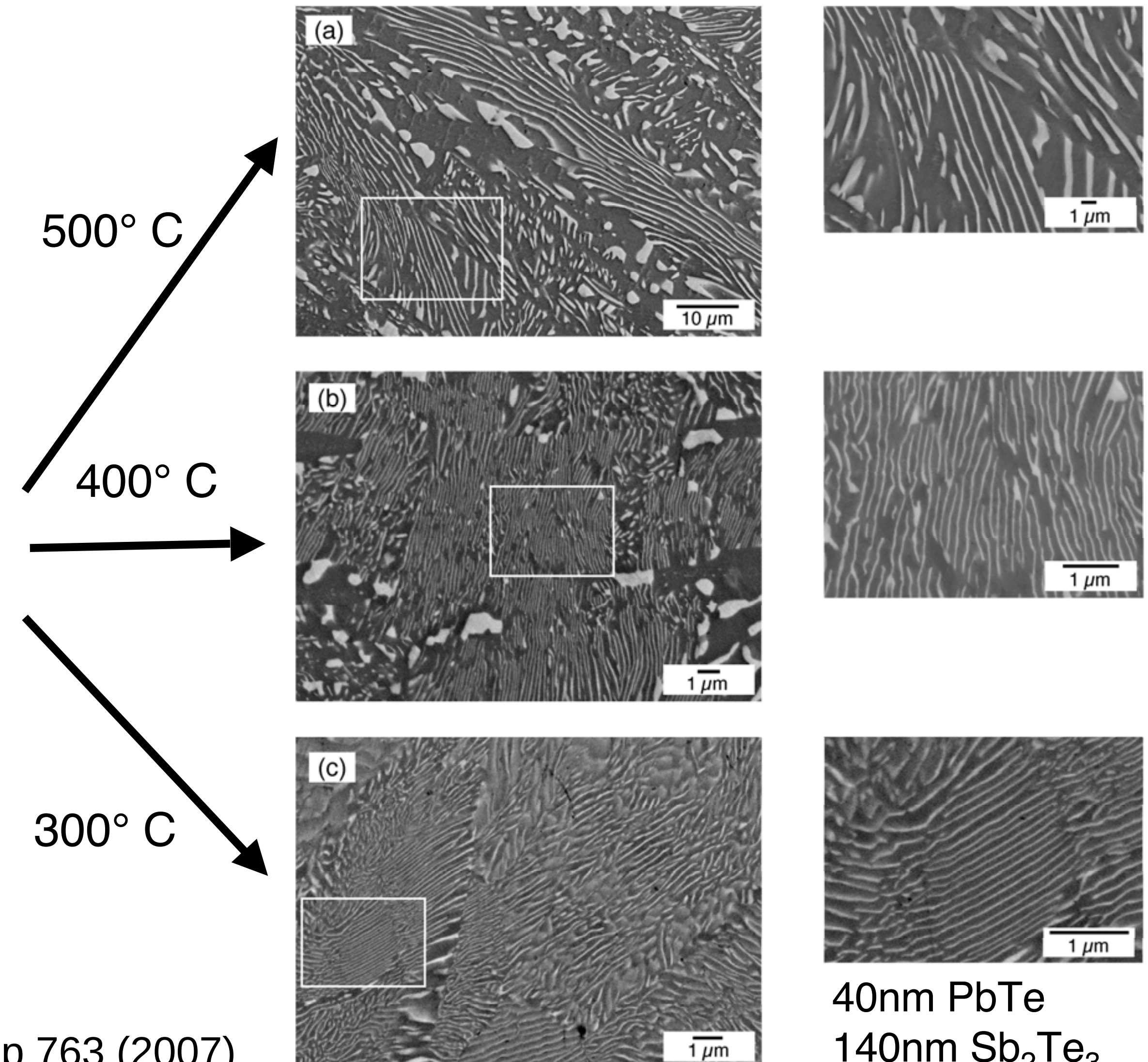
PbTe - Sb_2Te_3 nano-lamellae



10.5% Pb



20 μm



40nm PbTe
140nm Sb_2Te_3

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THERMOELECTRICS

Control of Lamellae size

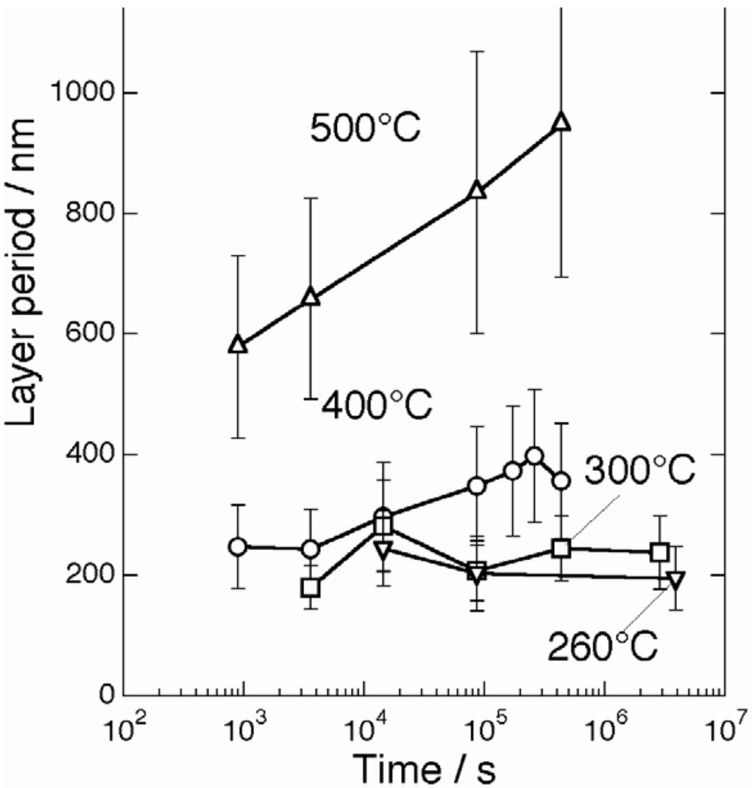
Control by time (*t*) and Temperature (*T*)

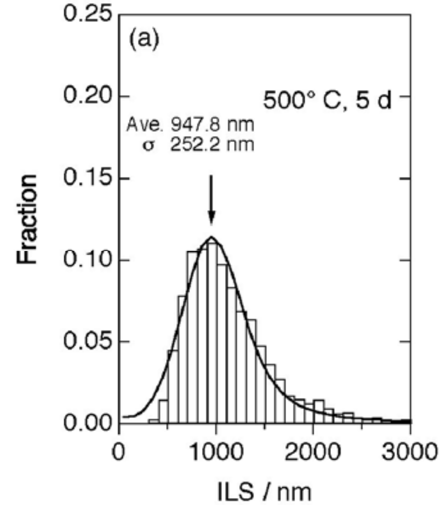
Solid-State transformation

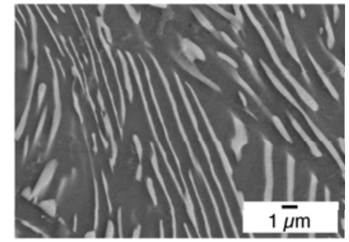
Slow diffusion = Fine microstructure

$$\lambda - \lambda_0 = \frac{KD(T)t}{T}$$

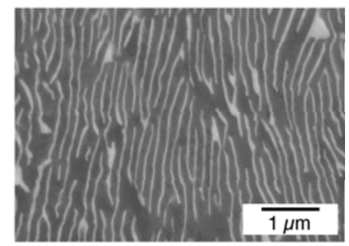
$$\lambda_0 = \frac{4\gamma T_E V_m}{\Delta H \Delta T}$$



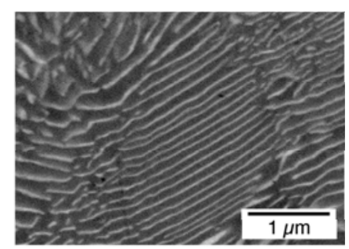




500° C



400° C



300° C

THERMOELECTRICS

Summary

Most Thermoelectrics are Heavily Doped SC

- Near Valence Balance using Zintl Rules
  - needed for Band Gap
- Slight Valence Imbalance
  - provides metallic carriers

Electronic Transport of Complex Materials

- Semi-Emperical approach successful
- *Ab initio* is not accurate to be quantitative and difficulty including disorder

Opportunities for theory

- Thermal transport
- Exotic electronic states
  - resonant, Kondo, correlations
- Nanostructures
  - composites