Research on New Thermoelectric Materials: From Seeds to Saplings

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Impacting Energy Use in the Near-Term: Increasing Energy Efficiency

Efficiency = Usable Energy Output/Energy Input

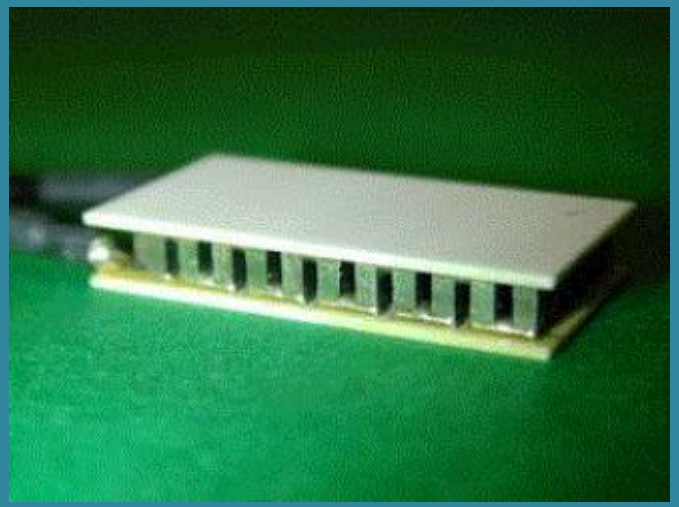
Where can we improve efficiency?

- power generation (combined cycle, cogeneration)
- lighting (LED's, OLED's, fluorescent lighting)
- automotive power conversion (diesel, hybrid gas/electric)
- indoor climate conditioning (30 % of total electricity usage in US)
- waste heat recovery

One approach: Thermoelectric Energy Conversion

Uses of Thermoelectrics

- **A Thermoelectric Device Can Do Two Things:**
  - absorb/liberate heat under electrical excitation (solid state heat pump)
  - convert thermal energy to electrical energy



- **Current Applications**
  - heating/cooling
    - » cooling for infrared detectors, laser diodes
    - » temperature control of medical specimens
    - » portable picnic coolers
  - power generation
    - » radioisotope thermoelectric generators for interplanetary probes
    - » auxiliary generators for battlefield use

- **Future Applications**
  - solid state climate control on a large scale: residential, automotive, etc.
  - power generation from waste heat in industry, transportation

Power Generation from Waste Heat

- **Typical Engine: 100 horsepower = 75 kW**

  Σ (shaft work) + (power loss in exhaust) + (power loss in coolant)

- **Power Dissipated in Exhaust Gas**

$$P_{exhaust} = mc_p(T_{gas} - T_{ambient})$$

$$P_{exhaust} = 23kW$$

m = mass flow rate ≈ 0.025 kg s^{-1}
c_p = exhaust gas specific heat ≈ 1150 J kg^{-1} K^{-1}
T_{gas} = 1100 K
T_{air} = 300 K

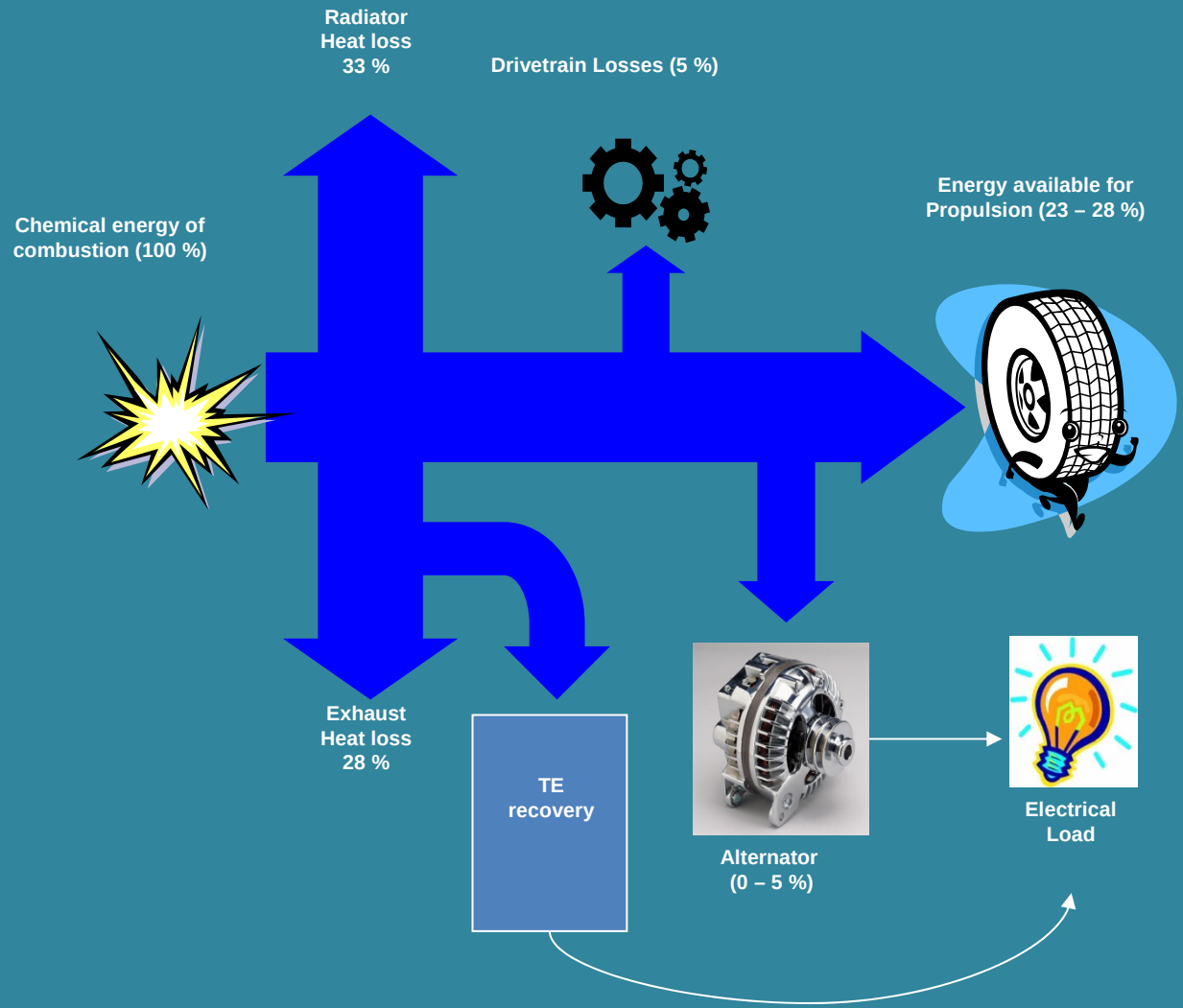
- **Power Dissipated in Engine Coolant**

$$P_{coolant} = mc_p(T_{in} - T_{out})$$

$$P_{coolant} = 22kW$$

m = mass flow rate ≈ 0.7 kg s^{-1}
c_p = coolant specific heat ≈ 3900 J kg^{-1} K^{-1}
T_{in} = 368 K
T_{out} = 360 K

2/3 of Engine Power is Lost in Heat!


Radiator
Heat loss
33 %
Drivetrain Losses (5 %)
Chemical energy of
combustion (100 %)
Energy available for
Propulsion (23 – 28 %)
Exhaust
Heat loss
28 %
TE
recovery
Alternator
(0 – 5 %)
Electrical
Load

Brief History of Refrigeration

- **Pre-1930**
  - – CO_2
  - – ammonia
  - – hazardous, not very efficient

- **1930's: Disovery of hydrofluorocarbons**
  - – efficient, safe refrigerants: Freon

- **1971: Ozone Depletion**
  - – attributed to freon and other HFC's
  - – Montreal Protocol (1981) places restriction on HFC's
  - – R-134a (non chlorine containing FC) developed as replacement

- **1990's: Global Warming**
  - – Kyoto Accord identifies six GW gases, including R-134a

- **Potential future ban on all refrigerants?**

- **Other refrigeration technologies must be developed**

Thermoelectric Energy Conversion

• **Power Generation from Waste Heat**

$$\varepsilon = \frac{\Delta T}{T_H} \frac{\sqrt{1+ZT_{ave}}-1}{\sqrt{1+ZT_{ave}}+T_C/T_H}$$

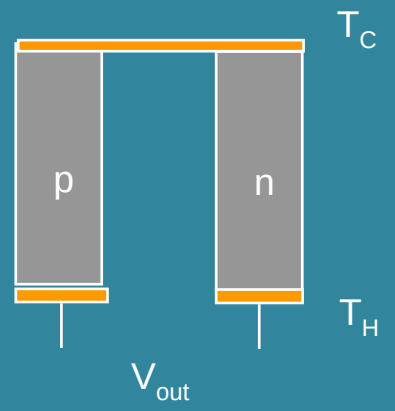
with

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

S = Seebeck coefficient

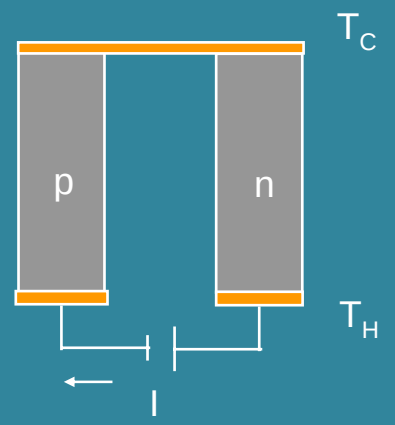
κ = thermal conductivity

σ = electrical conductivity



• **Solid State Heating and Cooling**

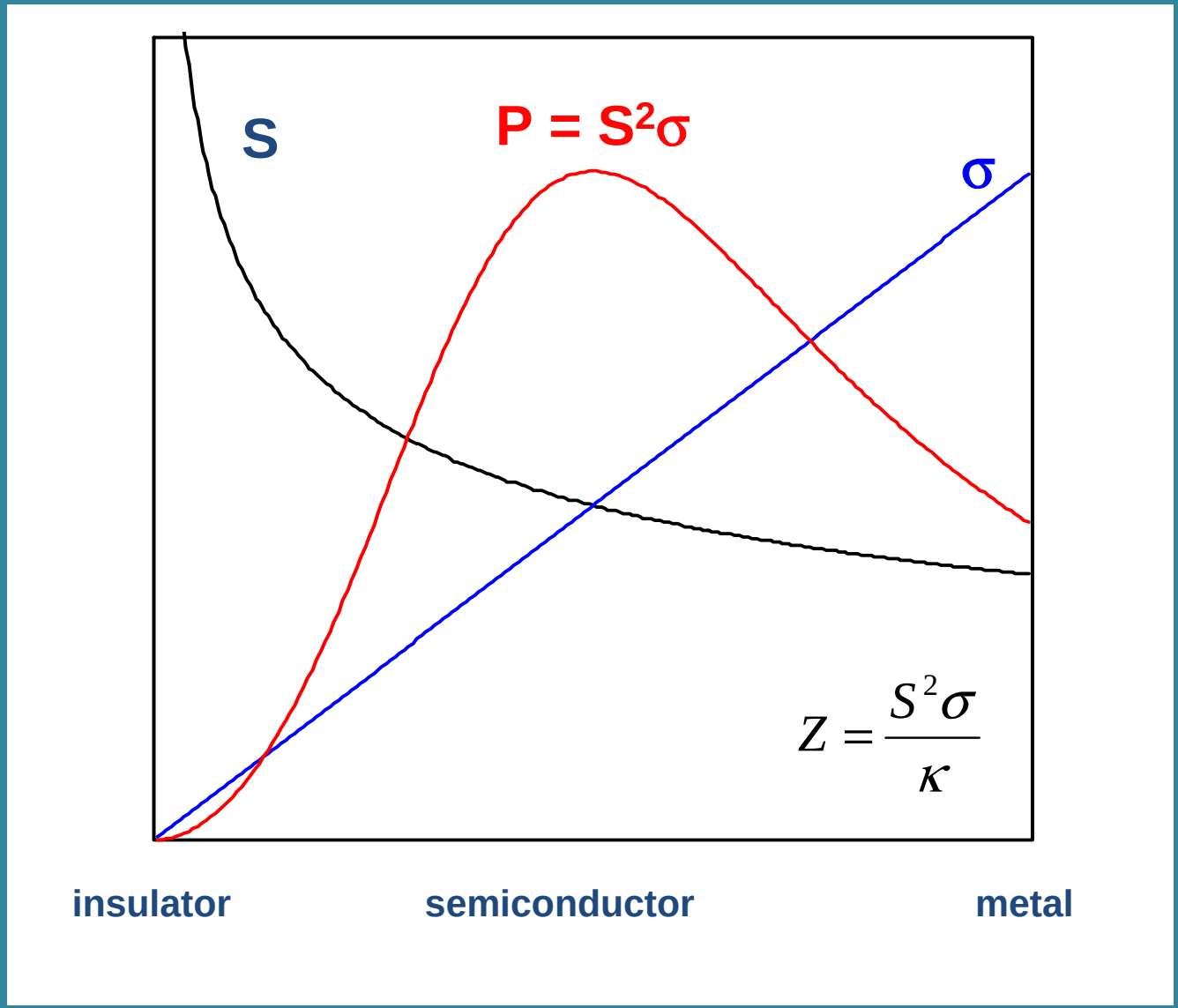
$$COP_{\max} = \frac{T_{av}(\sqrt{1+ZT_{av}}-1)}{\Delta T(\sqrt{1+ZT_{av}}+1)} - \frac{1}{2}$$



ZT is dimensionless = “Figure of Merit”

For both cases, efficiency increases with increasing ZT

Good Thermoelectrics are (Almost) Always Semiconductors



Good Thermoelectrics Have Low Thermal Conductivity

Thermal conductivity is dominated by lattice component

$$\kappa = \frac{const \circ M \delta \gamma^2 \theta^3}{n^{2/3} \circ T}$$

M = average atom mass δ^3 = volume/atom

γ = Gruneisen parameter θ = Debye temperature

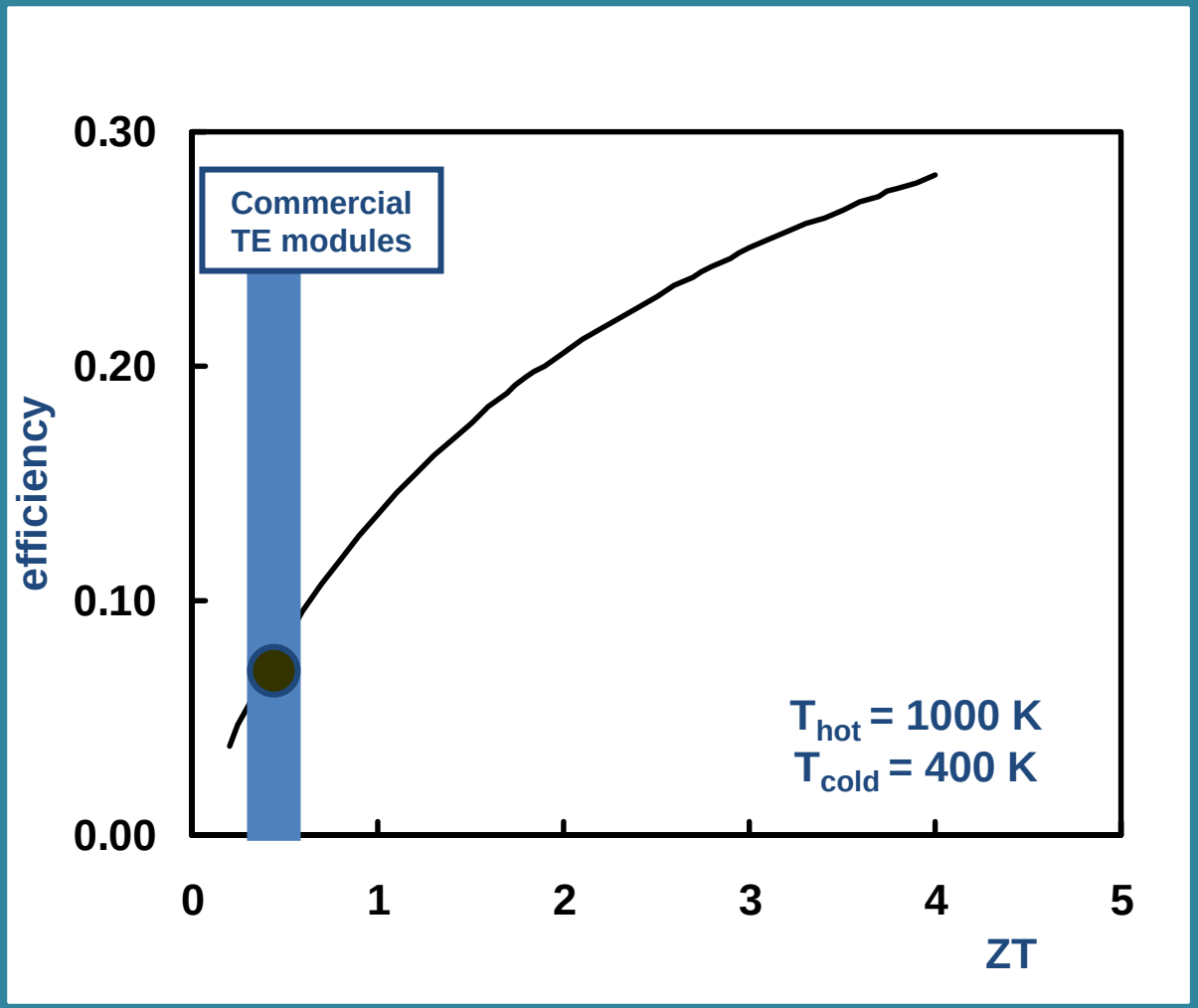
n = number atoms in crystalline repeat unit

The best thermoelectric materials are compound semiconductors comprised of elements from the lower portion of the periodic table

Fundamental Physical Requirements

- complex atomic lattice
- heavy atom masses

How Big Must ZT Be For Power Generation?



- For current modules with ZT = 0.5, efficiency is ~ 5 %

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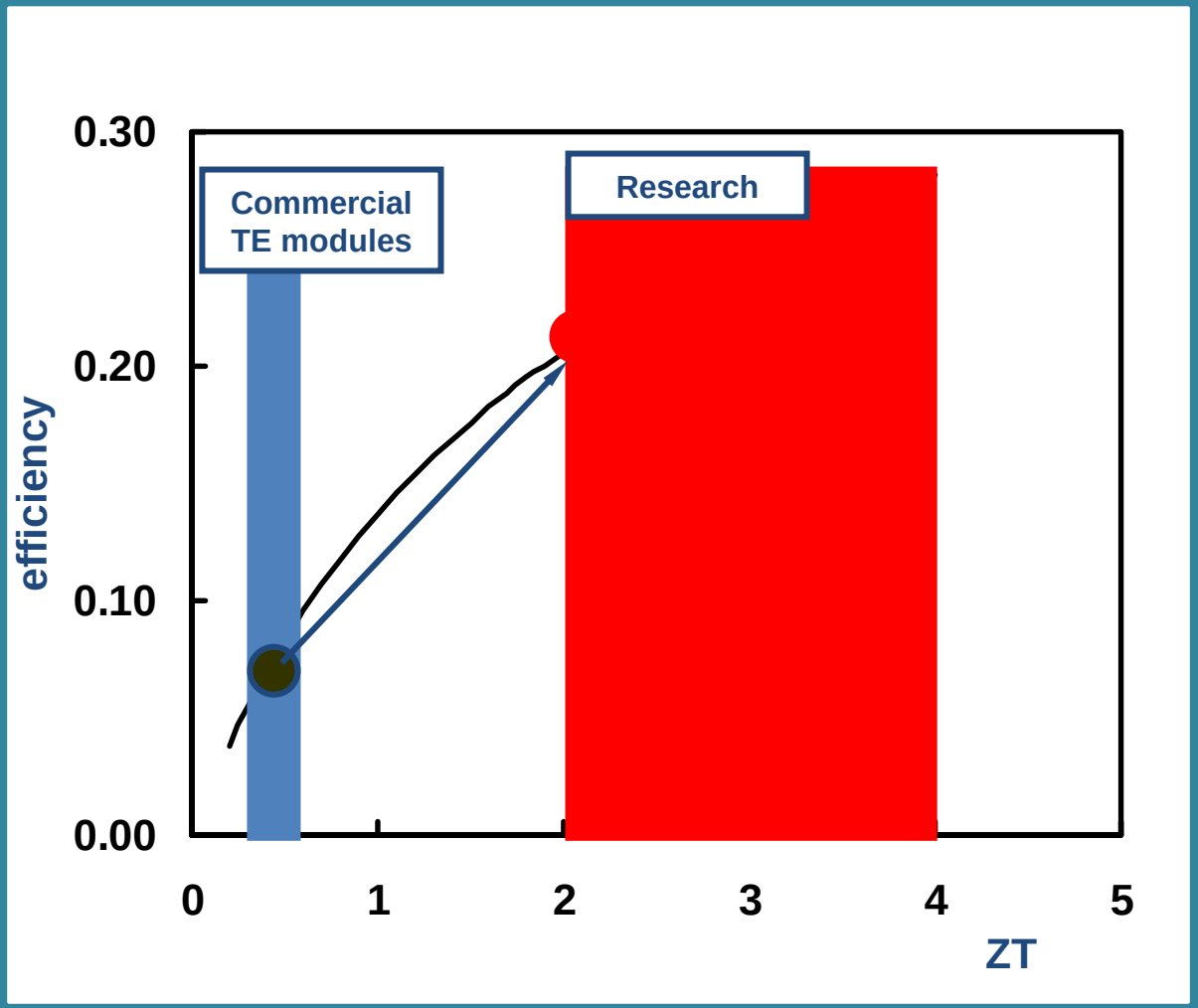
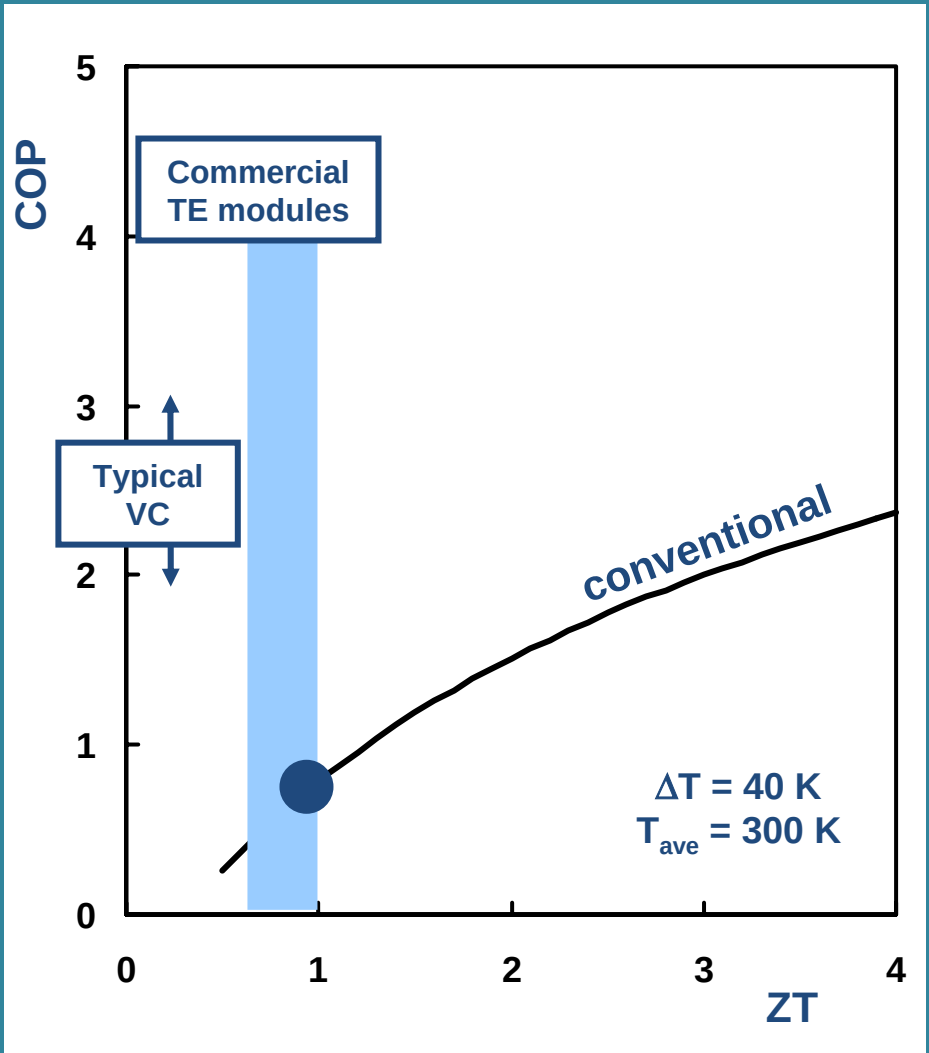


- For current modules with ZT = 0.5, efficiency is ~ 5 %
- For ZT ≥ 2 efficiency increases to > 20 %

Research Goal: ZT ≥ 2

How Big Must ZT Be for Climate Control?



- Current modules with ZT = 1 and conventional isothermal design are *far less efficient* than typical vapor compression (VC) systems

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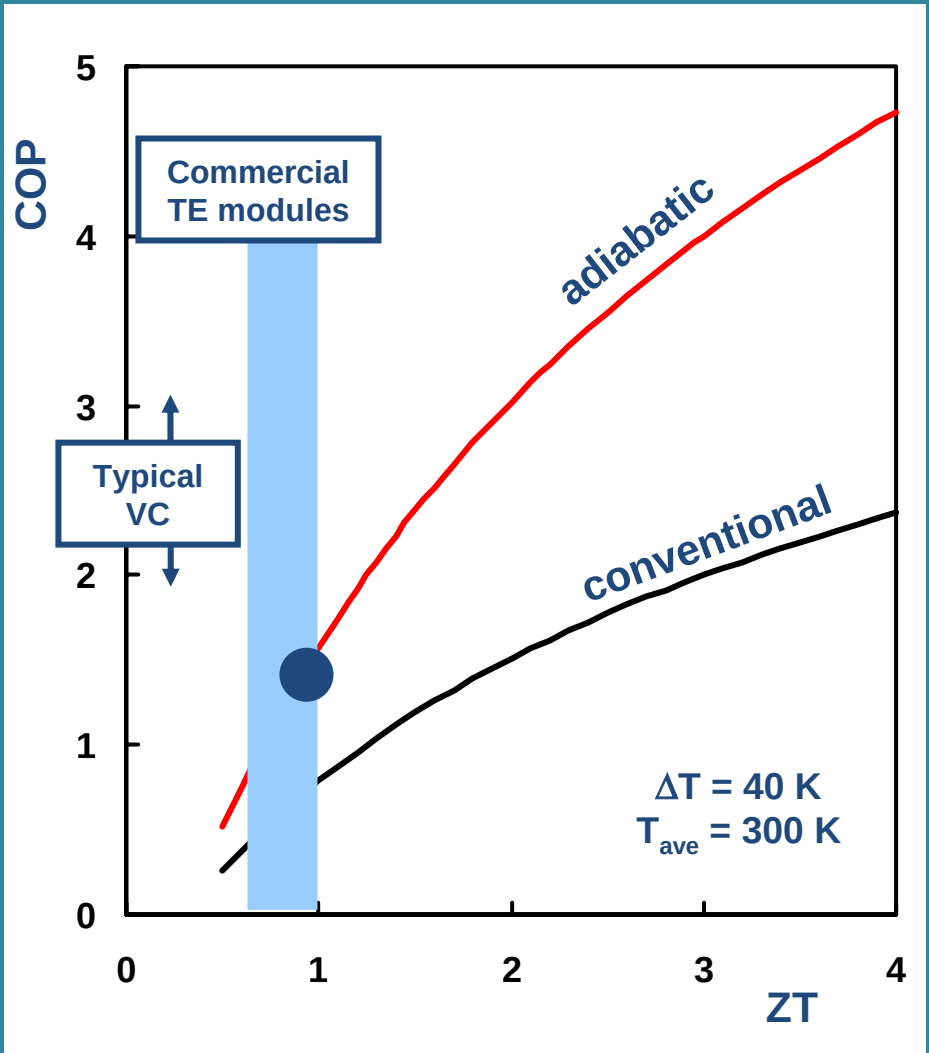

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- New adiabatic cross-flow module design (Bell, ICT 2001) could provide 2x increase in COP relative to conventional design

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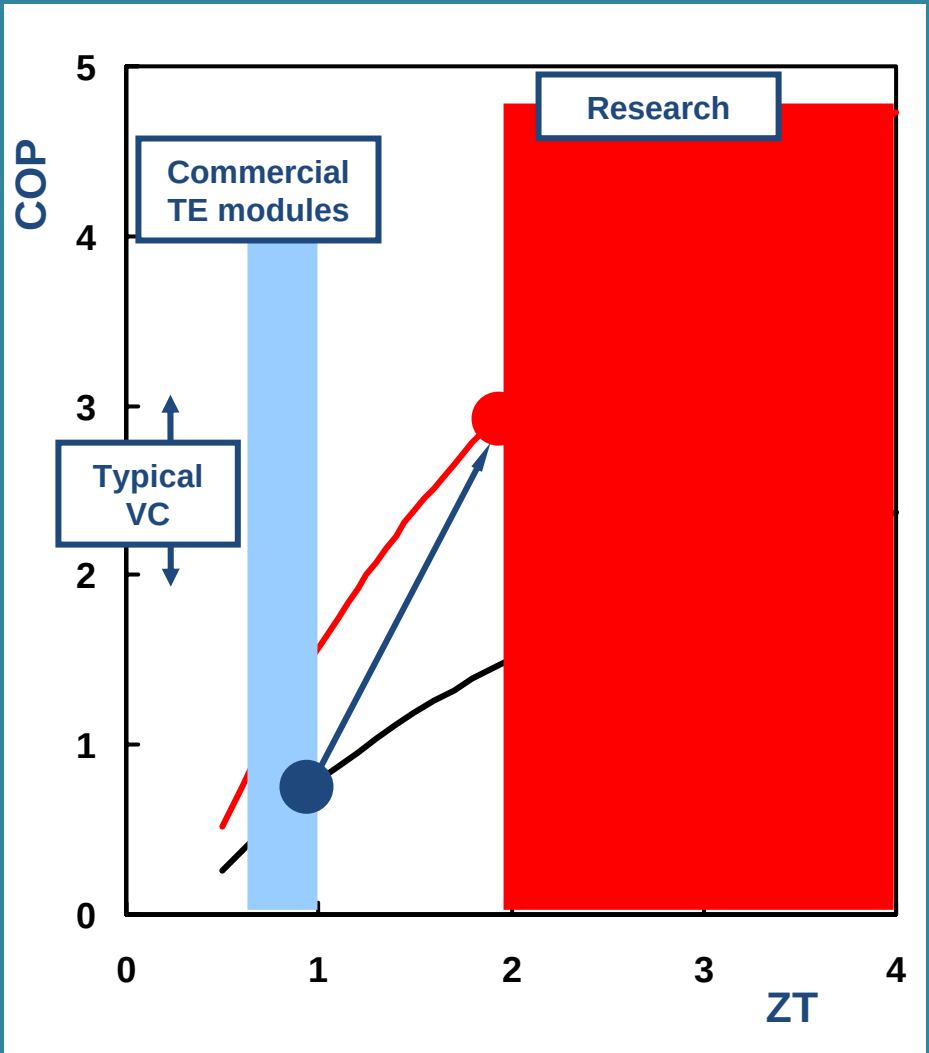
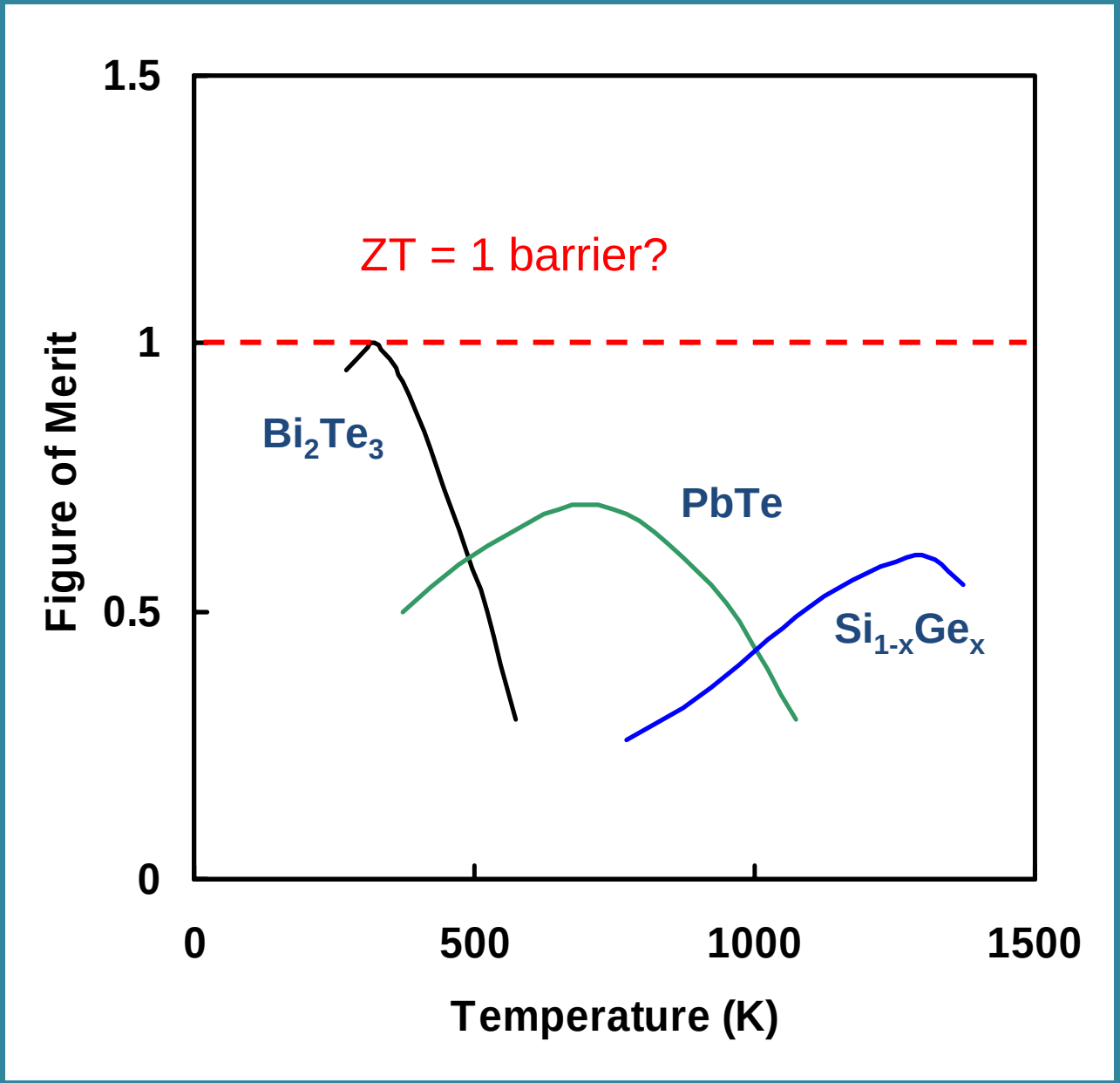


- Current modules with ZT = 1 and conventional isothermal design are *far less efficient* than typical vapor compression (VC) systems
- New adiabatic cross-flow module design (Bell, ICT 2001) could provide 2x increase in COP relative to conventional design
- New materials with ZT ≥ 2 combined with new design would provide modules that are *more efficient* than current VC systems

Research Goal: ZT ≥ 2

State of the Art Thermoelectric Materials (1995)



How to Increase Z?

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

“electrical” part (power factor)

“thermal” part (lattice κ)

Reducing the lattice thermal conductivity

- crystalline solids with intrinsically low thermal conductivity
- unusual phonon scattering mechanisms
- nanotechnology

Mechanisms of reducing the lattice thermal conductivity of crystalline solids

I. Intrinsically low thermal conductivity

$$\kappa = \frac{const \circ M \delta \gamma^2 \theta^3}{n^{2/3} \circ T}$$

Classification of Solids by their Compexity

Classify solids by number of atoms in the unit cell:

n = 1 (simple cubic structure)
- noble gases (He, Ne, Ar, Kr, etc….)
- solids only at very low temperature – not of interest to us here

n = 2 (zincblende, diamond structure, and rocksalt structure compounds)
- diamond, Si, Ge, III-V semiconductors

n = 3 (fluorite and antifluorite structure compounds)
- calcium fluoride, lithium oxide, etc.

n = 4 (wurtzite structure compounds)
- aluminum nitride, beryllium oxide, silicon carbide, etc…

AND SO ON…..

e.g. alumina (n = 10), spinel (n = 14), garnets (n = 80)…polymer (n ~ thousands)

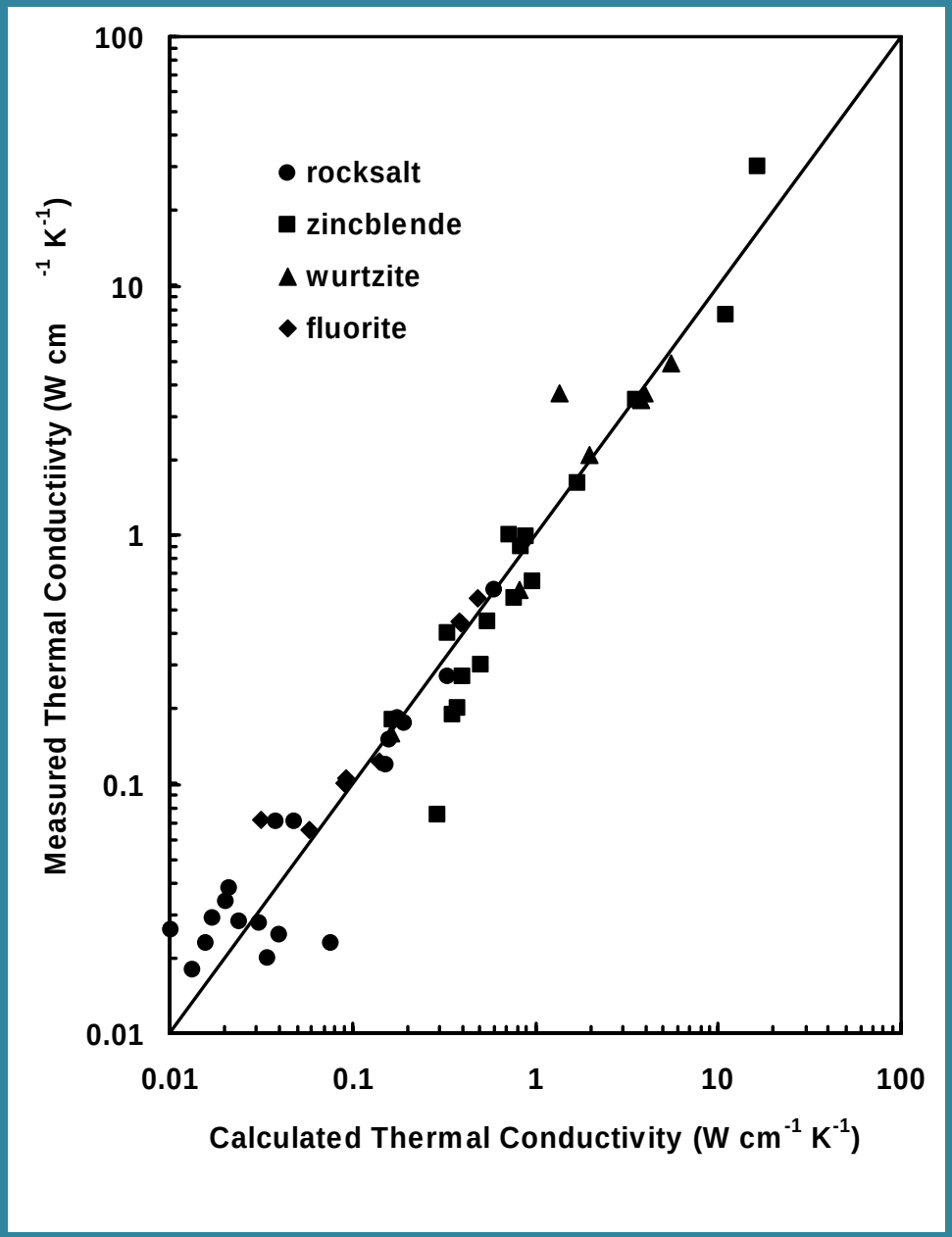
D.T. Morelli and G.A. Slack, in *High Thermal Conductivity Materials* (Springer, 2006)

Diamond and Zincblende Structure Compounds (n = 2)

Element/ Compound	θ_a (K)	γ	δ (Å)	M (amu)	κ_{calc} (W cm^{-1} K^{-1})	κ_{exp} (W cm^{-1} K^{-1})
C	1450	0.75	1.78	12.01	16.4	30
Si	395	1.06	2.71	28.08	1.71	1.66
Ge	235	1.06	2.82	72.59	0.97	0.65
BN	1200	0.7	1.81	12.41	11.05	7.6
BP	670	0.75	2.27	20.89	3.59	3.5
BAs	404	0.75	2.39	42.87	1.70	
AlP	381	0.75	2.73	28.98	1.10	
AlAs	270	0.66	2.83	50.95	0.89	0.98
AlSb	210	0.6	3.07	74.37	0.77	0.56
GaP	275	0.75	2.73	50.35	0.72	1.00
GaAs	220	0.75	2.83	72.32	0.55	0.45
GaSb	165	0.75	3.05	95.73	0.33	0.4
InP	220	0.6	2.94	72.90	0.83	0.93
InAs	165	0.57	3.03	94.87	0.51	0.3
InSb	135	0.56	3.24	118.29	0.38	0.2
ZnS	230	0.75	2.71	48.72	0.40	0.27
ZnSe	190	0.75	2.84	72.17	0.35	0.19
ZnTe	155	0.97	3.05	96.49	0.17	0.18
CdSe	130	0.6	3.06	95.68	0.23	
CdTe	120	0.52	3.23	120.00	0.296	0.075

Rocksalt Structure Compounds (n = 2)

Compound	θ_a (K)	γ	δ (Å)	M (amu)	κ_{calc} (W cm^{-1} K^{-1})	κ_{exp} (W cm^{-1} K^{-1})
LiH	615	1.28	2.04	3.97	0.159	0.15
LiF	500	1.5	2.00	12.97	0.194	0.176
NaF	395	1.5	2.31	21.00	0.179	0.184
NaCl	220	1.56	2.81	29.22	0.048	0.071
NaBr	150	1.5	2.98	51.45	0.031	0.028
NaI	100	1.56	3.23	74.95	0.013	0.018
KF	235	1.52	2.66	2.05	0.058	
KCl	172	1.45	3.14	37.27	0.038	0.071
KBr	117	1.45	3.30	59.50	0.020	0.034
KI	87	1.45	3.52	68.00	0.010	0.026
RbCl	124	1.45	3.27	60.46	0.024	0.028
RbBr	105	1.45	3.42	82.69	0.021	0.038
RbI	84	1.41	3.66	106.10	0.015	0.023
MgO	600	1.44	2.11	20.00	0.596	0.6
CaO	450	1.57	2.4	28.04	0.332	0.27
SrO	270	1.52	2.57	51.81	0.152	0.12
BaO	183	1.5	2.7	76.66	0.076	.023
PbS	115	2	2.97	119.60	0.017	.029
PbSe	100	1.5	3.06	143.08	0.035	.020
PbTe	90	1.45	3.23	167.4	0.030	0.025

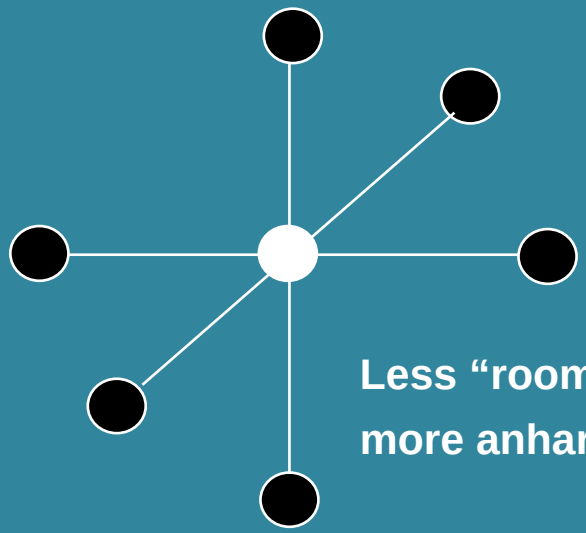

100
10
1
0.1
0.01
0.01
0.1
1
10
100
rocksalt
zincblende
wurtzite
fluorite
Measured Thermal Conductiivty (W cm -1 K-1)
Calculated Thermal Conductivity (W cm-1 K-1)

Some General Observations

- **Magnitude of κ_L is determined predominantly by the Debye temperature**

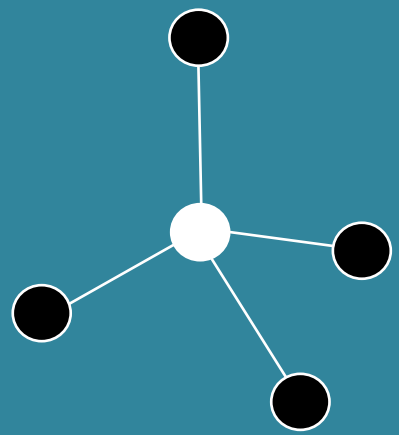
- **Grüneisen parameter also affects the conductivity**
  - rocksalt and fluorite structure compounds have $\gamma \sim 2$ ⟶ favors low κ
  - diamond, zincblende, and wurtzite structure compounds have $\gamma < 1$ ⟶ favors high κ

rocksalt/fluorite: octahedral coordination



Less "room" to vibrate: more anharmonic

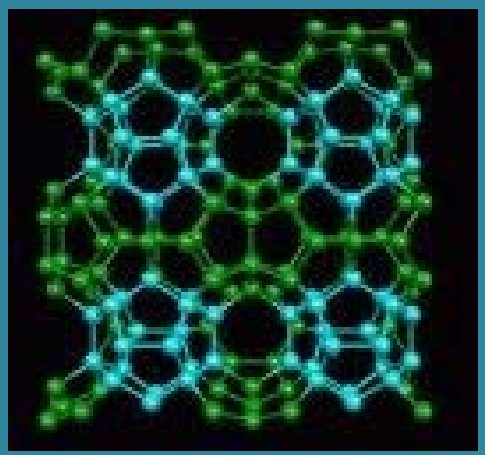
diamond, et al.: tetrahedral coordination



Materials with large Grüneisen parameters may make good thermoelectrics [e.g., $AgSbTe_2$ (Morelli, *et al.*, in preparation).

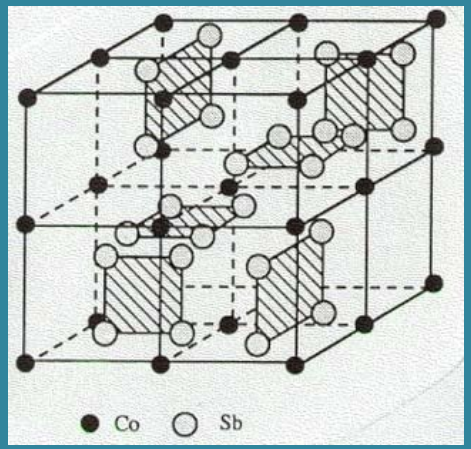
Mechanisms of reducing the lattice thermal conductivity of crystalline solids

II. Phonon Glass Electron Crystal (PGEC)



Skutterudites: Background

- Early work of Dudkin, Zobrina, and Abrikosov (1959-1963)
  - identified AB_3 compounds as potentially good thermoelectric materials
  - covalent bonding, high mobility (up to $10^4 cm^2 V^{-1} s^{-1}$ for p-type)
  - heavy atom masses, complex unit cell



AB_3 with

A = Co, Rh, or Ir

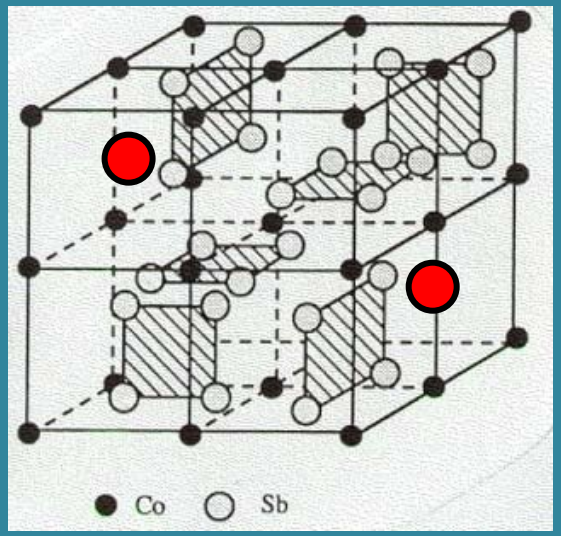
B = P, As, or Sb

  - $CoSb_3$ can be doped n-type with Te and p-type with Sn on the anion site
  - thermal conductivity only moderately low

This was apparently the end of the story of skutterudites!

The Discovery of Filled Skutterudite Compounds

- Structural Studies of Jeitschko (ca. 1975)
  - structure can be “filled” with rare earth atom by concomitantly replacing metal atom with element one column to the right e.g., $CoSb_3 \longrightarrow CeFe_4Sb_{12}$



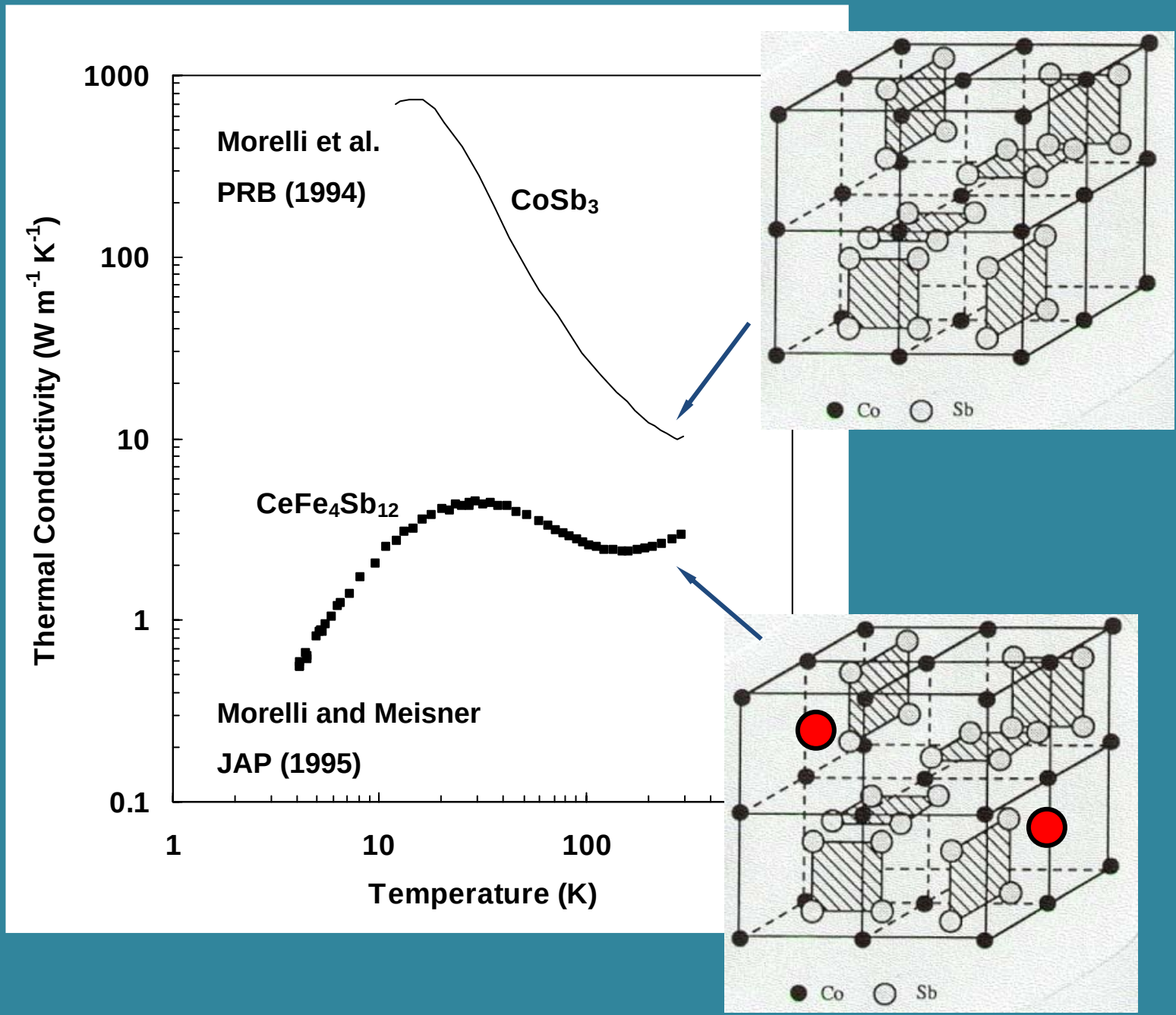
  - filling ion is either trivalent or tetravalent and modifies electronic properties
  - filling ion exhibits large X-ray thermal parameter: “rattling”

Phonon-Glass Electron-Crystal

- **Minimum Lattice Thermal Conductivity**
  - phonon mean free path approaches interatomic distances
  - exhibited in amorphous and highly disordered solids
  - also found in certain solids with long range order, e.g.,
    - » KBr-KCN (rotational degree of freedom of CN- molecule)
    - » YB_{66} (tunneling of Y between two cavities)
    - » insulators
- **What about a crystal with long range order containing electrons?**
  - glasslike behavior for phonon transport
  - pure crystal behavior for electron transport
  - Phonon Glass/Electron Crystal: PGEC (Slack 1994)

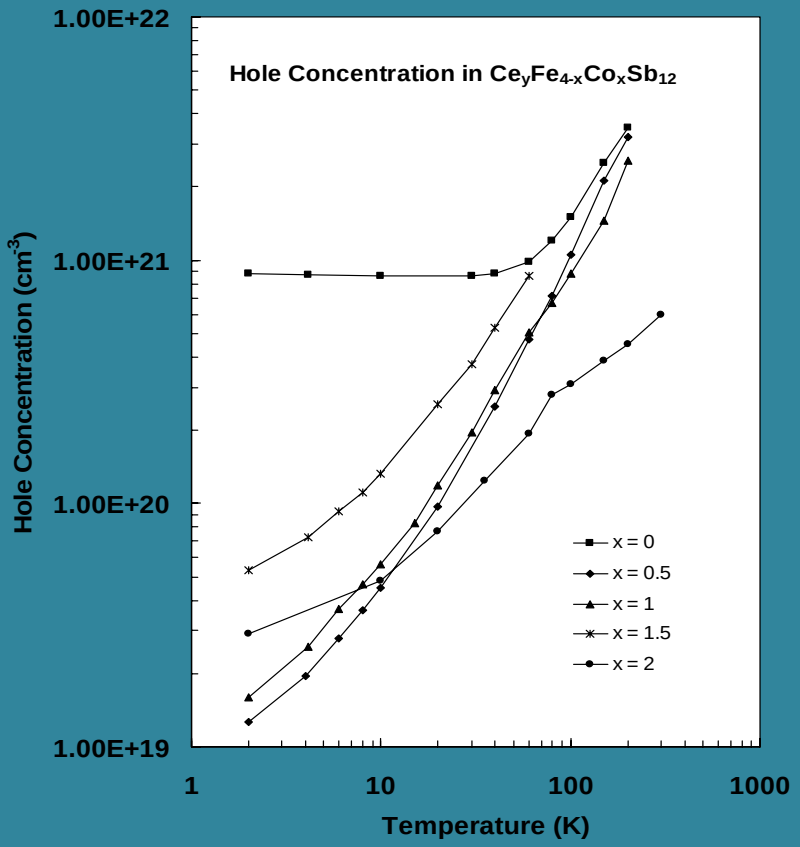
Such a material would be the ideal thermoelectric because it maximizes σ/κ!

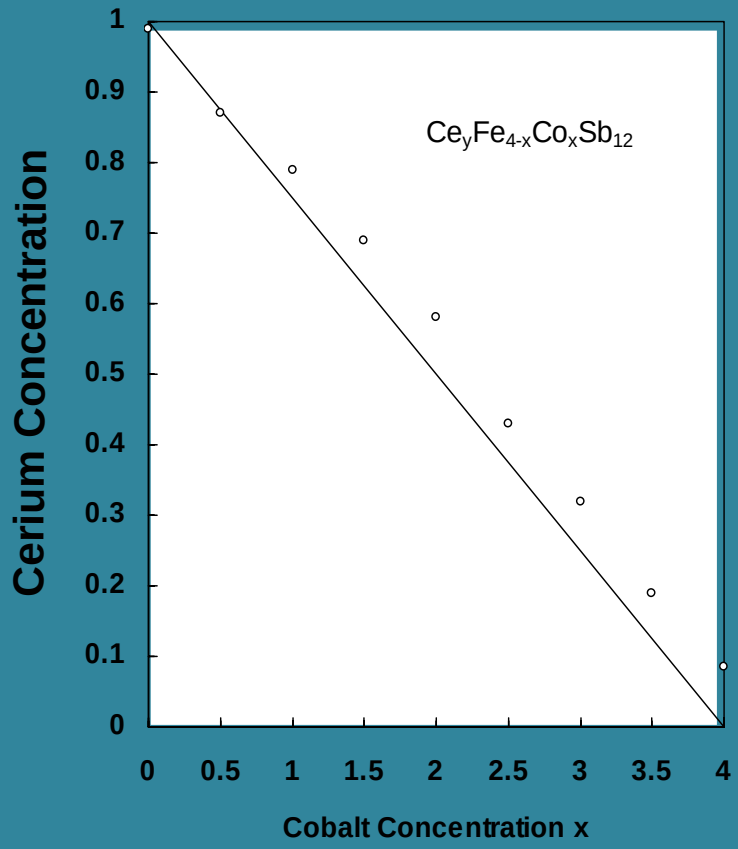
PGEC-Like Behavior in Filled Skutterudites



Fractional Filling

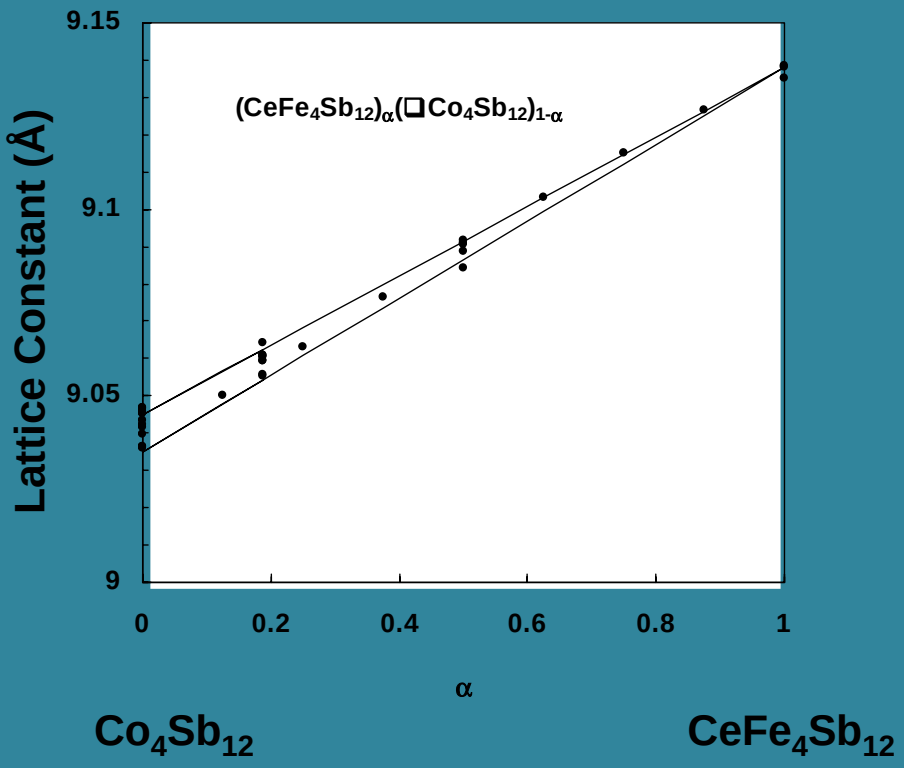
- Cerium-filled antimonide skutterudites are metallic
  - 3 electrons from the rare earth, 4 holes from replacing Co with Fe
  - one unfilled hole in the valence band
- Try to compensate by reintroduction of Co
- Degree of Rare Earth Filling is Tied to Co/Fe ratio!

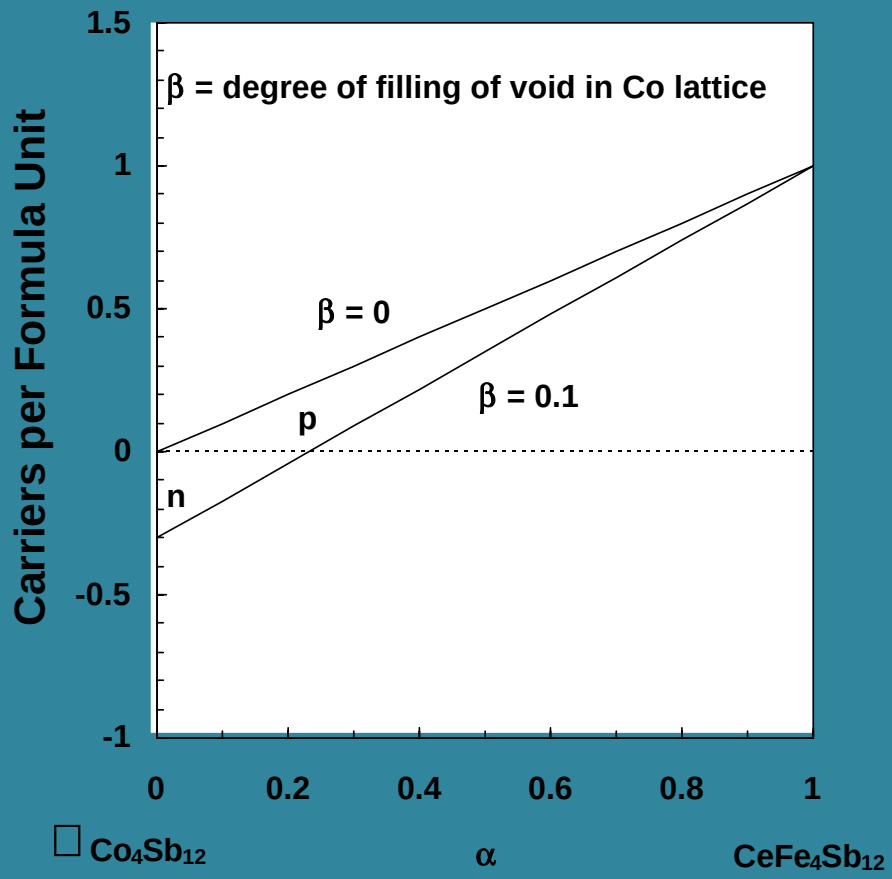




Chen et al. PRB (1997)

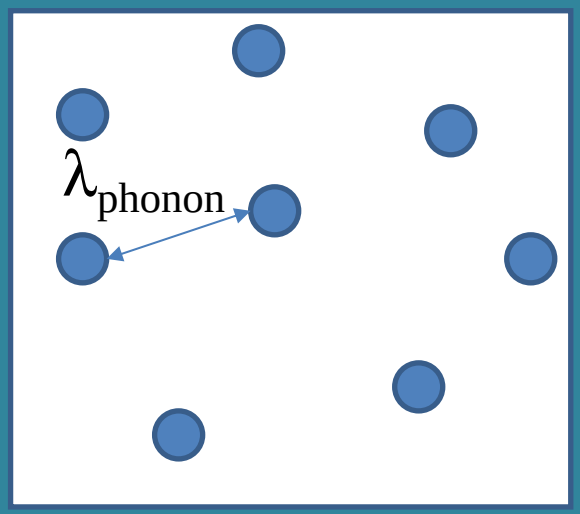
N- and P-Type Filled Skutterudites





Mechanisms of reducing the lattice thermal conductivity of crystalline solids

III. Nanostructural Effects



Phonon Scattering From Nanoscale Inclusions

Some examples, old and new:

- Slack (1957): $CaCl_2$ precipitates in KCl:
  - Platelets 10 nm in diameter, 1.5 nm thick

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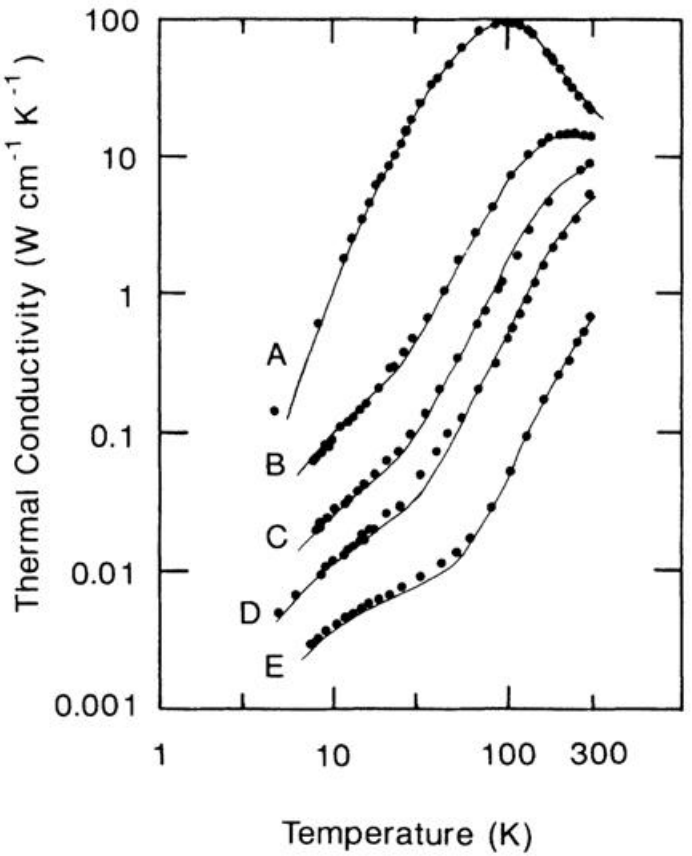
- Morelli *et al*. (1991): irradiated diamond
  - Regions of non-diamond carbon 2nm in diameter

$$\tau_{prec.}^{-1} = \frac{\rho v \pi a^2}{4} \qquad \lambda < 2\pi a$$

$$= C\omega^4 \qquad \lambda > 2\pi a$$

ρ = precipitate concentration
a = precipitate diameter
λ = phonon wavelength

By measuring the temperature dependence of thermal conductivity one can determine both precipitate SIZE and CONCENTRATION



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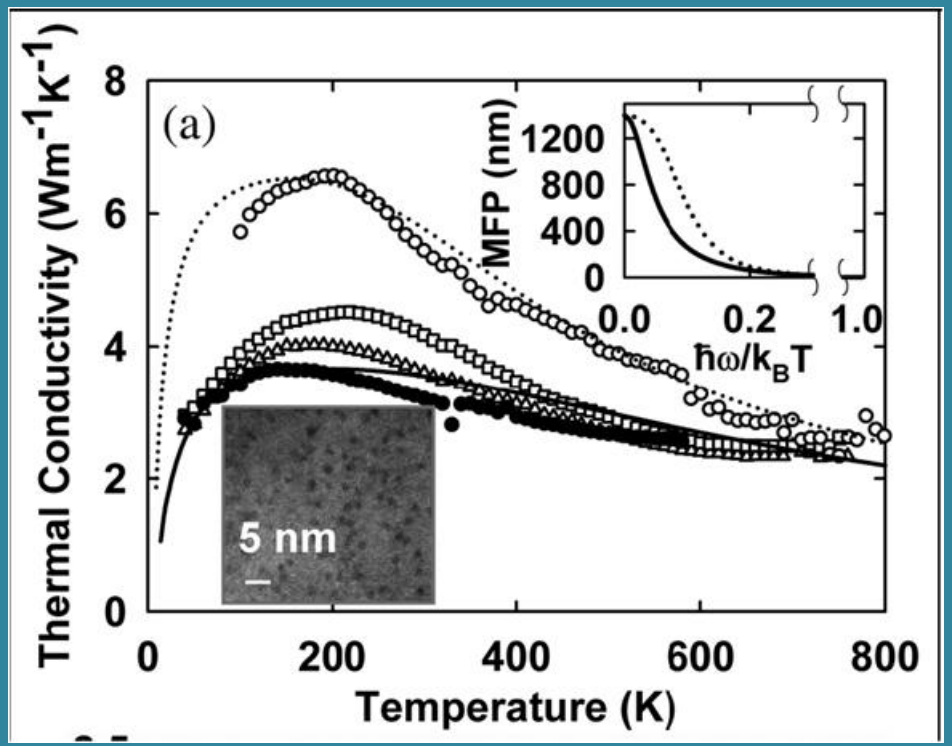
- Majumdar, et al. (2006) ErAs nanoparticles in InGaAs

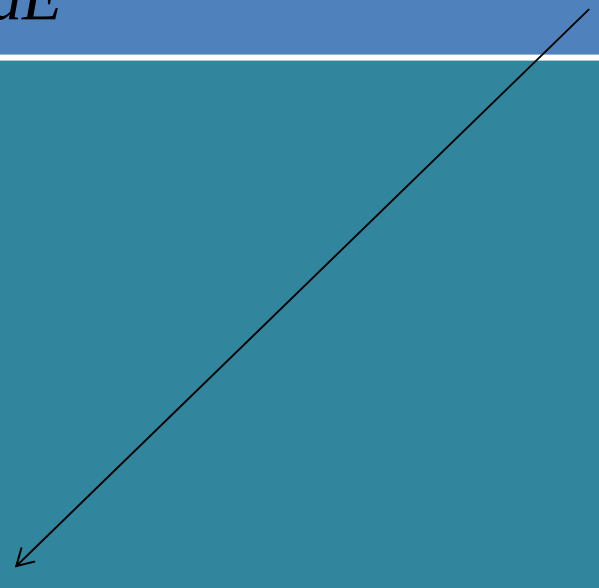


$$\tau_{prec.}^{-1} = v\rho \frac{\int_0^\infty \sigma(\omega, a)\phi(a)da}{\int_0^\infty \phi(a)da}$$

σ = scattering crossection
ϕ = size distribution

Increasing the power factor

$$S \propto \frac{d}{dE}\ln(\sigma) \qquad \sigma \propto N(E)\tau(E)$$



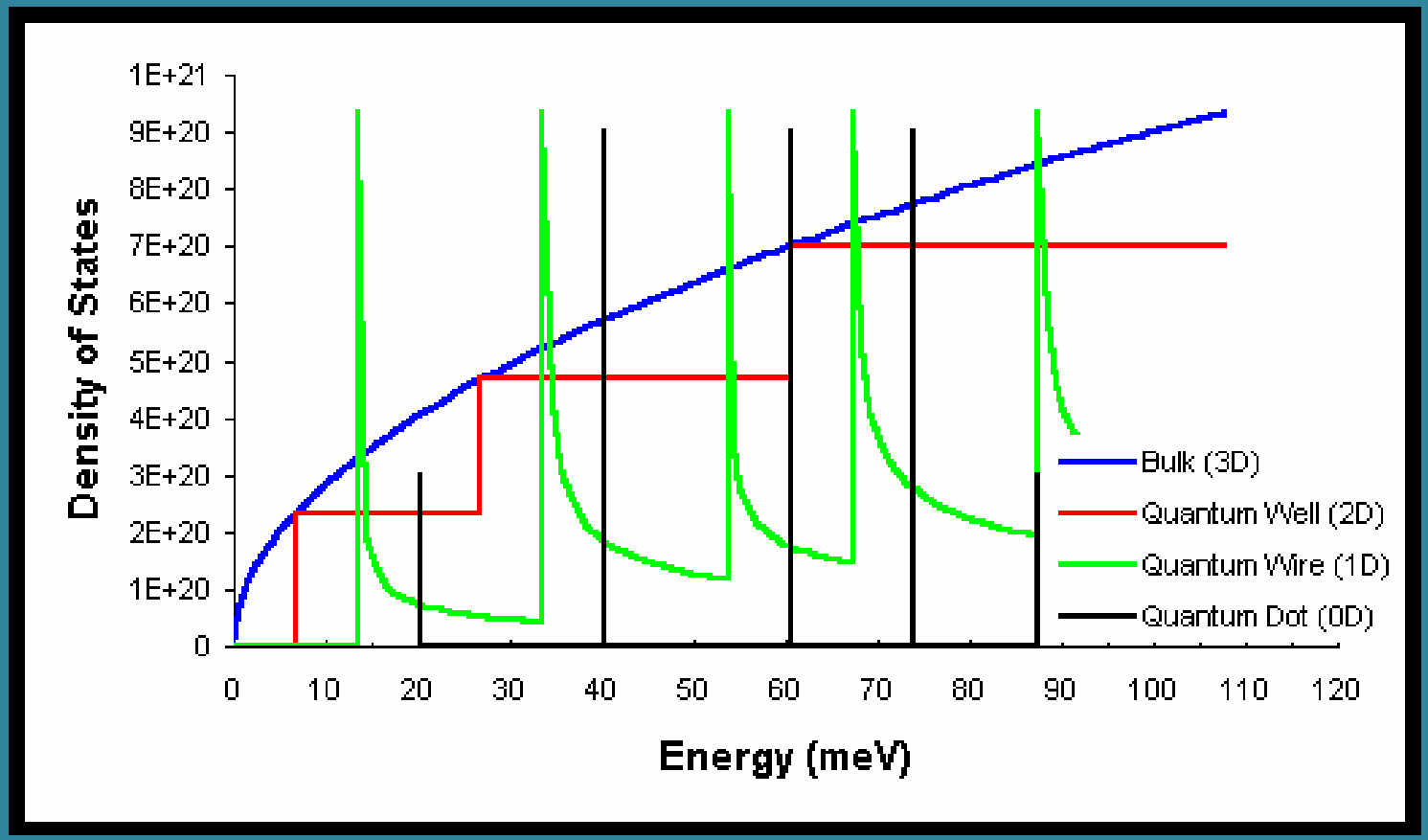
Alter the energy dependence of the density of states

Alter the energy dependence of the electron scattering

N(E) in nanostructures

$$S \propto \frac{dN}{dE}$$

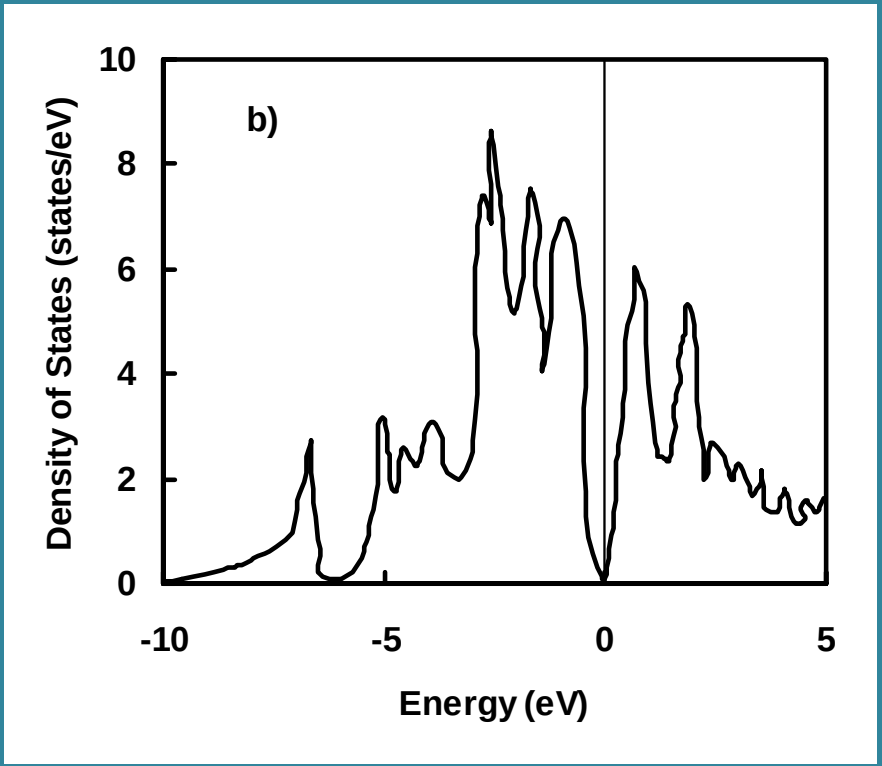
enhanced by sharp features



Quantum Confinement : Hicks and Dresselhaus, PRB (1994)

N(E) in bulk materials

Hybridization “gaps” and “wells” in intermetallic alloys

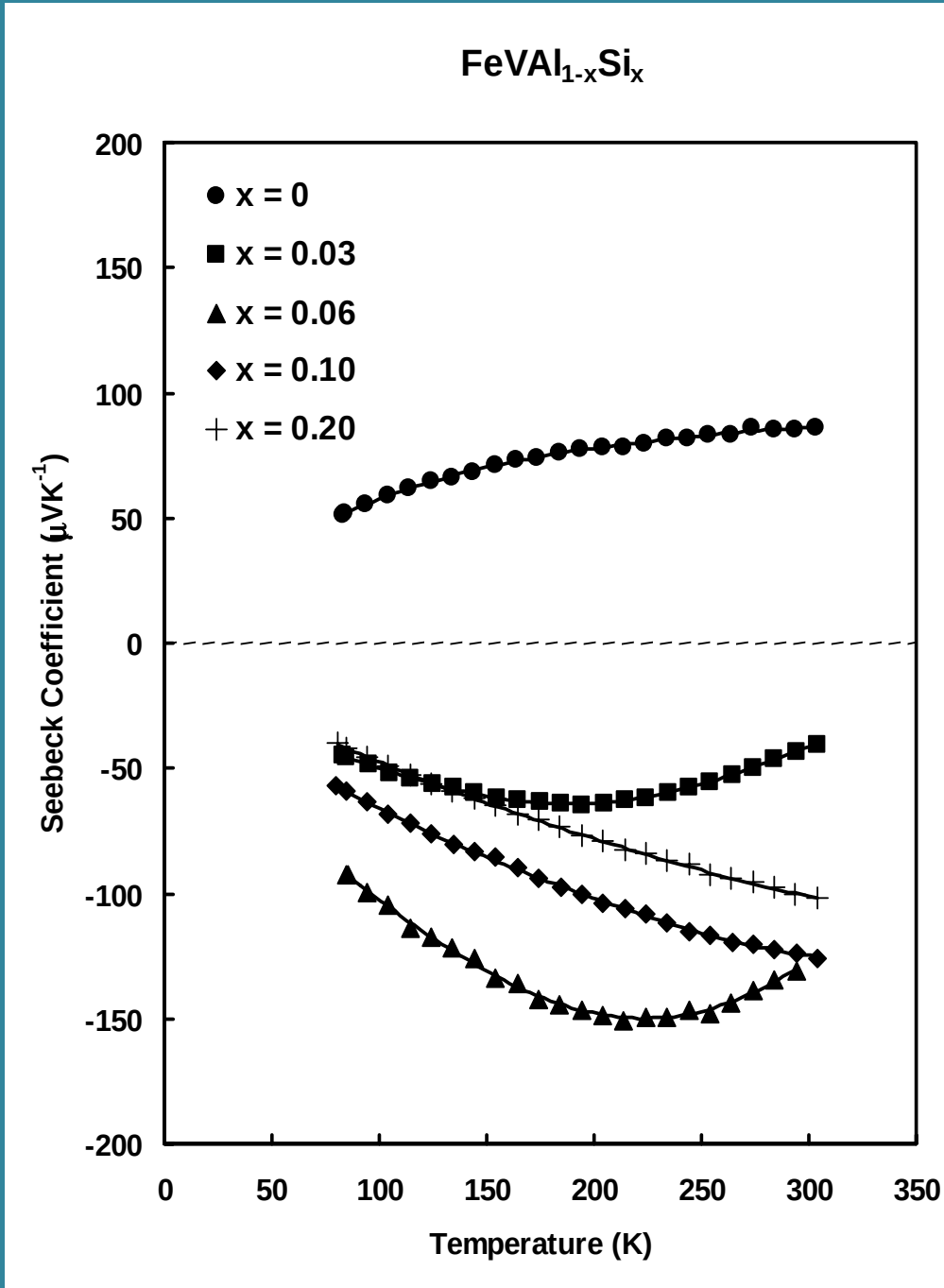


Calculated DOS of Fe_2VAl (Watson, et al)

Thermoelectric Properties of Fe_2VAl-Based Compounds

- Member of family of intermetallic compounds called Heusler alloys
  - general formula X_2YZ X = Fe, Co, Ni,Cu
    Y = V, Cr, Mn, Nb
    Z = Al, Si, Ga, Ge, Sn
- Most are metallic and exhibit interesting magnetic properties
  - shape memory (Ni_2MnGa)
  - spintronics (Co_2MnSi)
- Some Heusler alloys with Z = Al are semiconductor-like

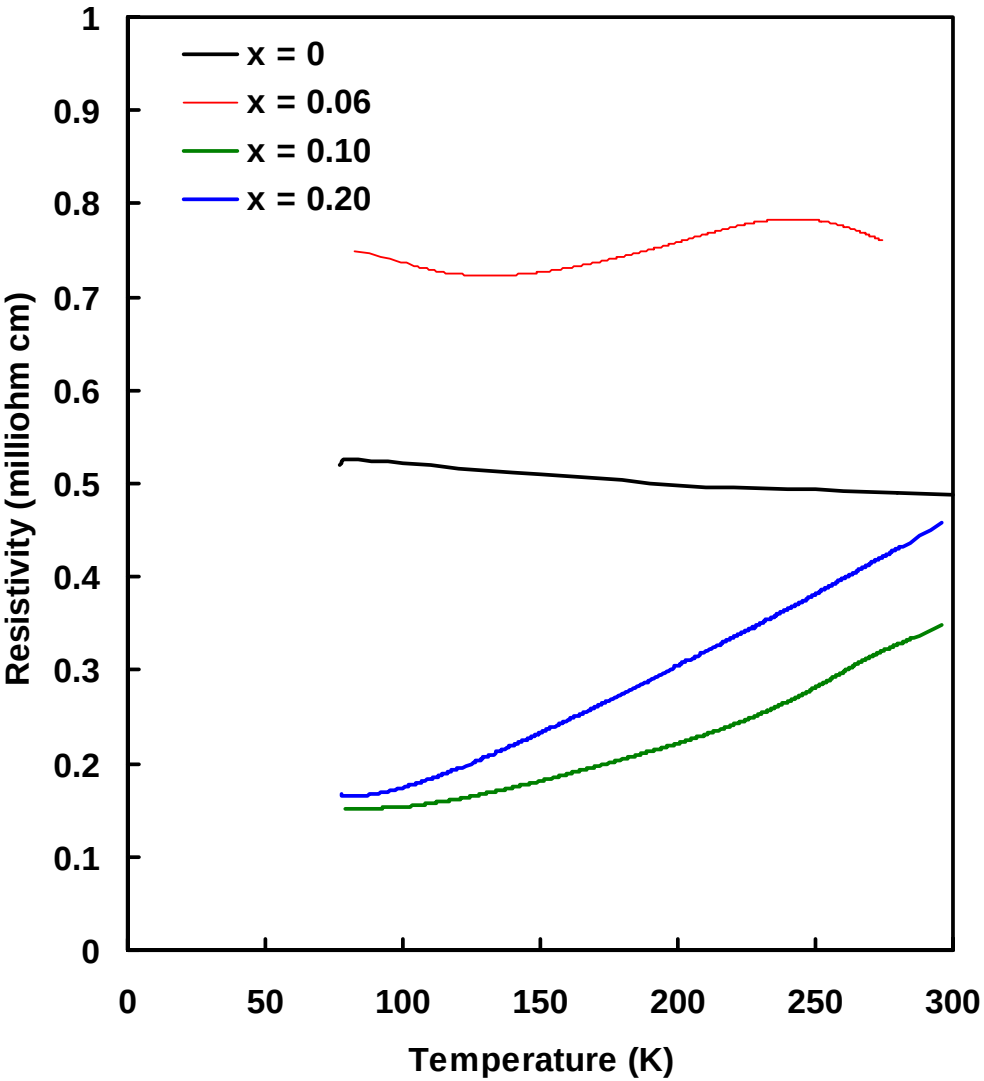
Thermoelectric Properties of $Fe_2VAl_{1-x}Si_x$



- x = 0: S > 0
- x = 0.03 and 0.06: negative minimum where R_H changes sign
- x = 0.10 and 0.2: S increases monotonically

Consistent with semimetallic band structure with Fermi level moved up into conduction band with Si-doping

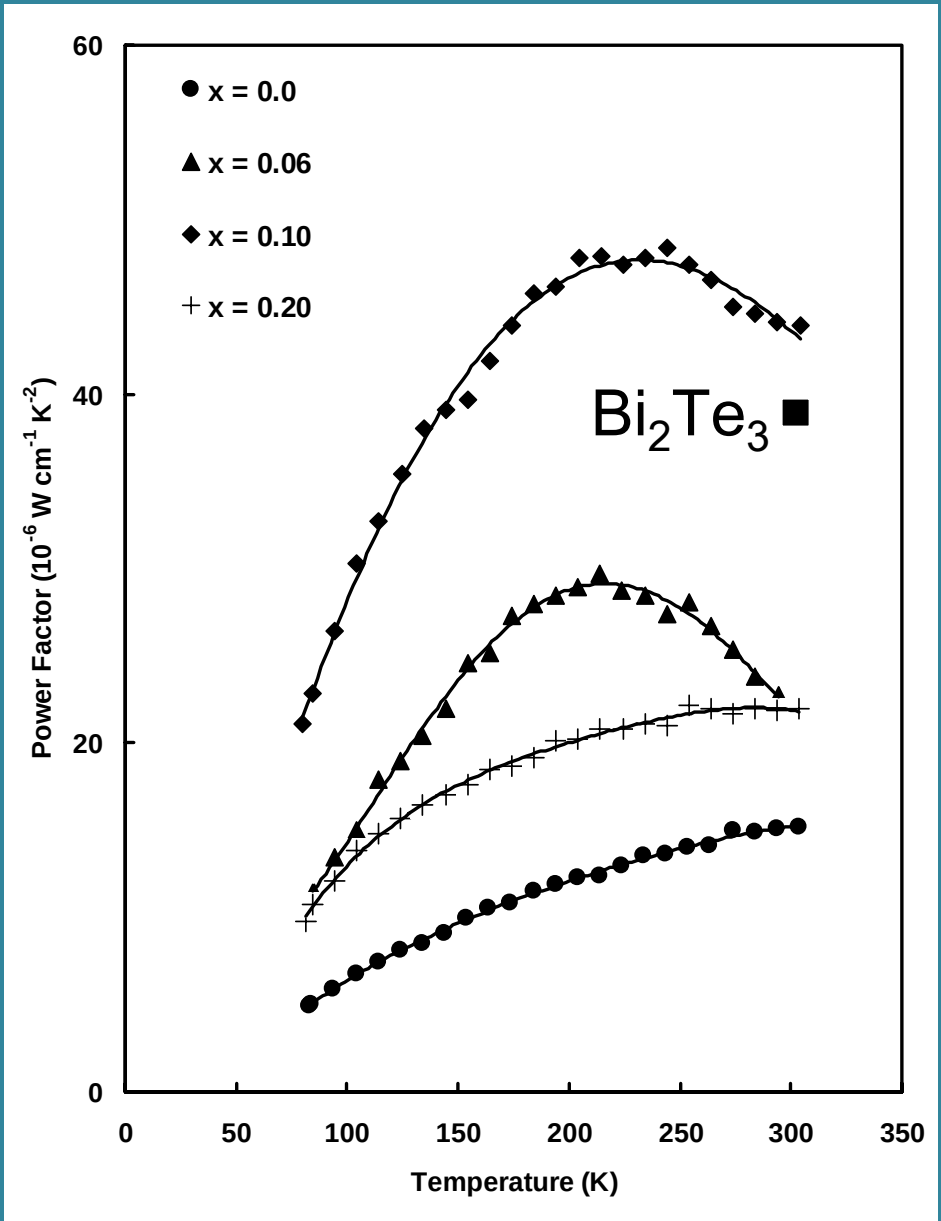
Thermoelectric Properties of $Fe_2VAl_{1-x}Si_x$



- x = 0: semiconductor-like resistivity
- progressively becomes more metallic with increasing x (degenerate semiconductor)

Consistent with semimetallic band structure with Fermi level moved up into conduction band with Si-doping

Thermoelectric Properties of $Fe_2VAl_{1-x}Si_x$



- power factor optimized near x = 0.06
- exceeds Bi_2Te_3 at 300 K

Very promising result!

τ(E) in Nanostructures

$$S \propto \frac{d\tau(E)}{dE}$$

τ(E) = electron scattering time

Altering the energy dependence of electron scattering should alter the Seebeck coefficient

$$\tau(E) = \tau_o E^{\lambda - 1/2}$$

λ is determined by the scattering process:

phonon scattering $\lambda = 0$

defect scattering $\lambda > 0$

New Concept

- Scattering of electrons by use of nanometer-scale particles increases S

Measure electron MFP ~ 30 nm

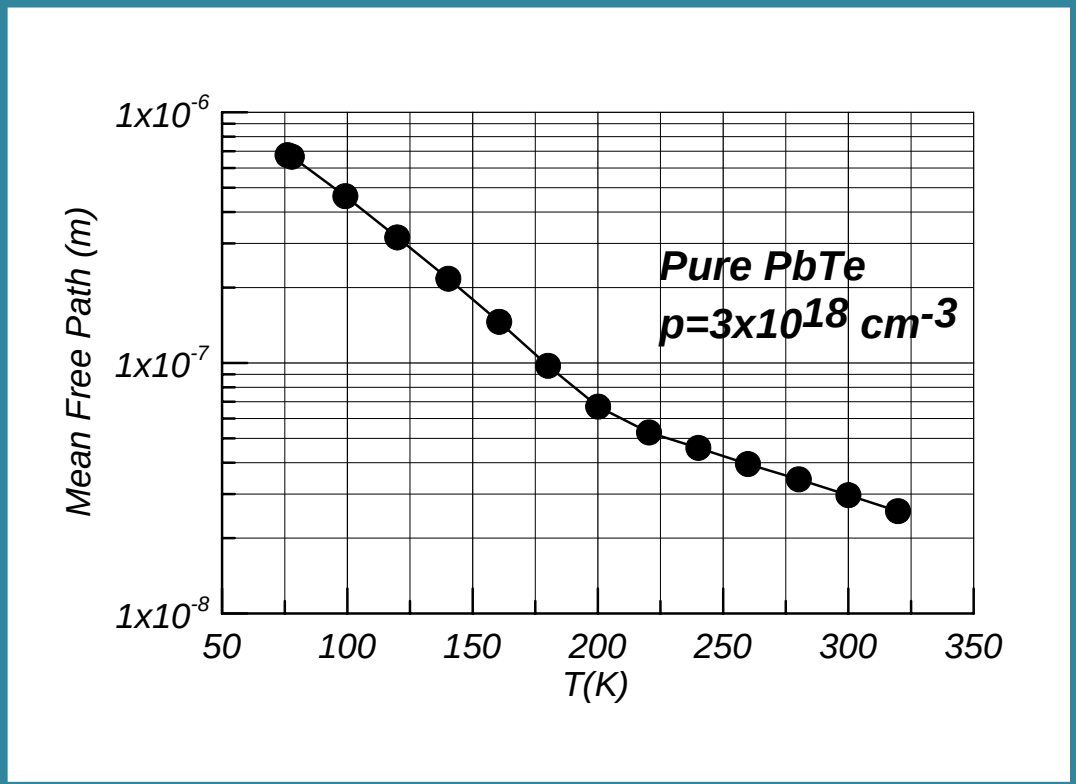
Ball-mill material into grains so that

Grain size ~ MFP

OR

Add small particles so that

Distance between particles ~ MFP

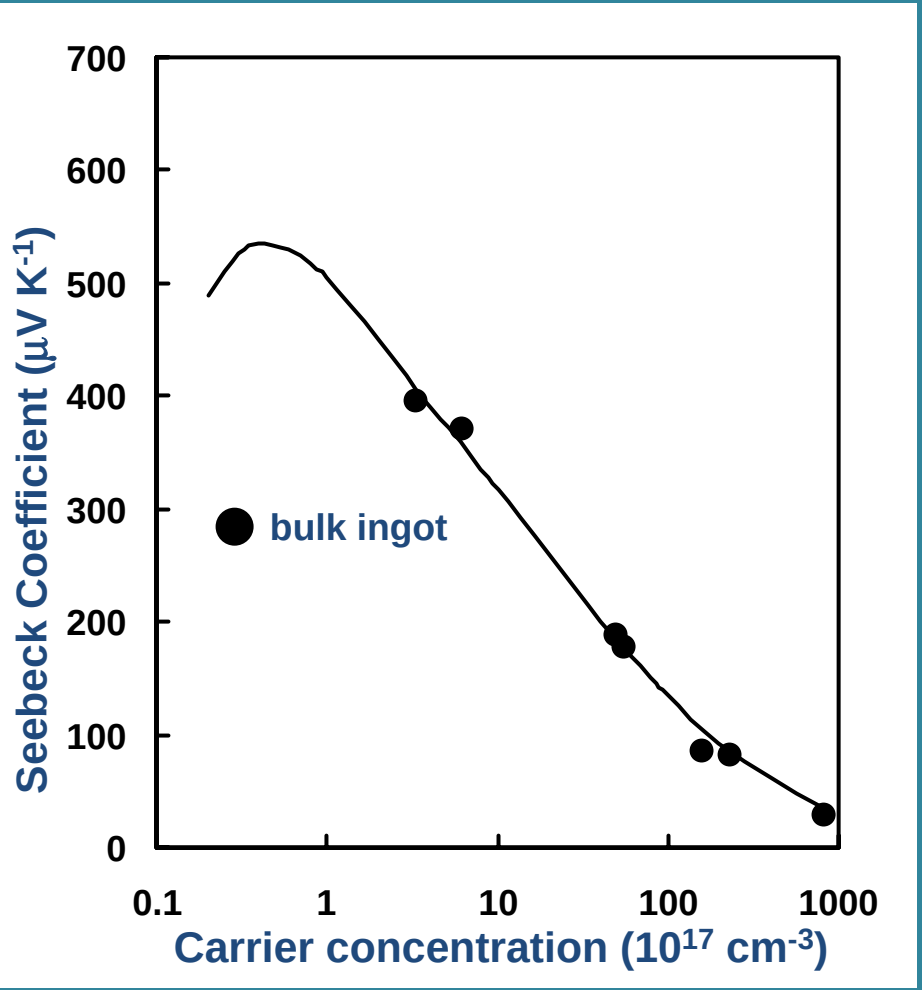


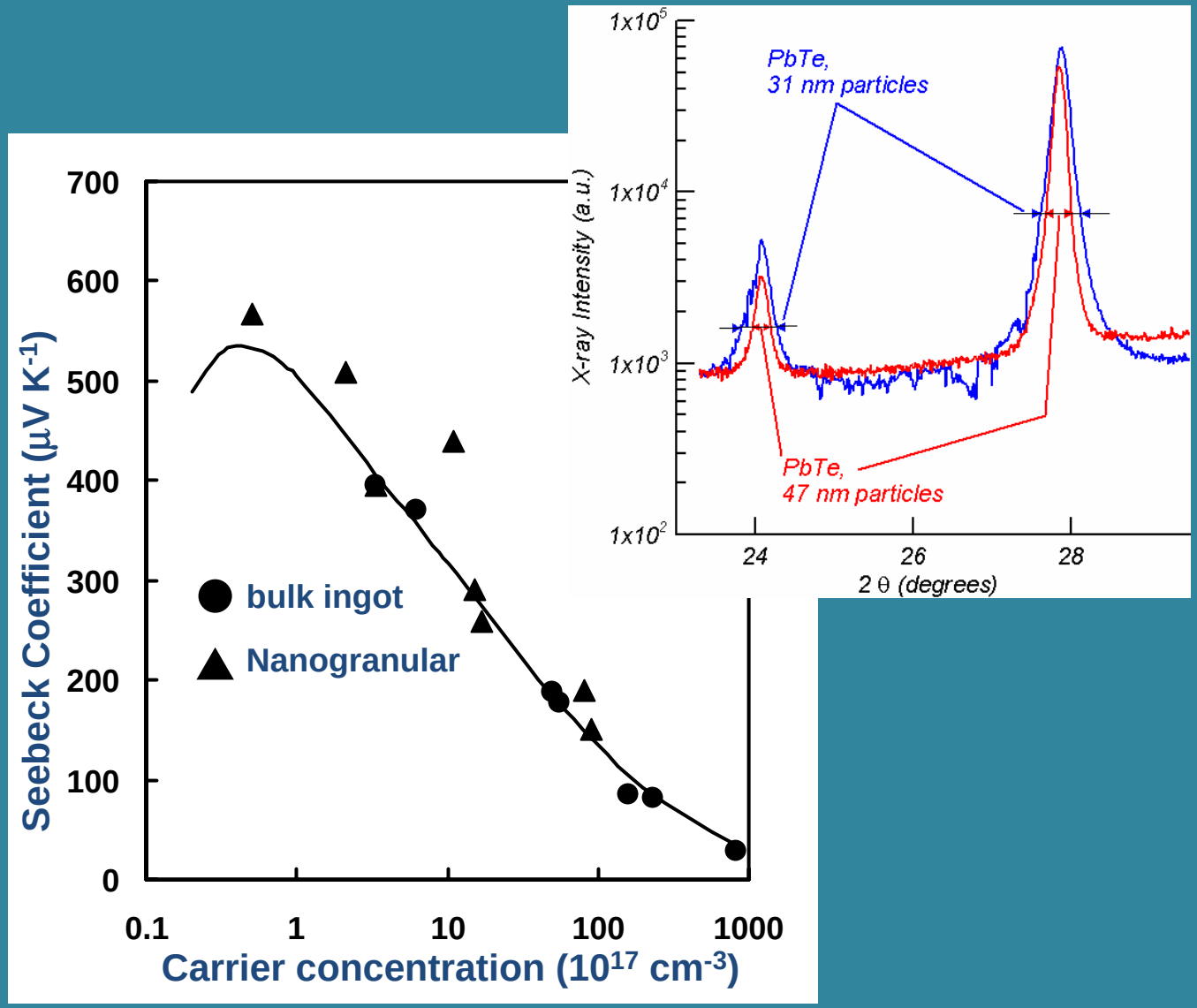
$$S \propto \left[\frac{const. + \lambda}{n^{2/3}} \right]$$

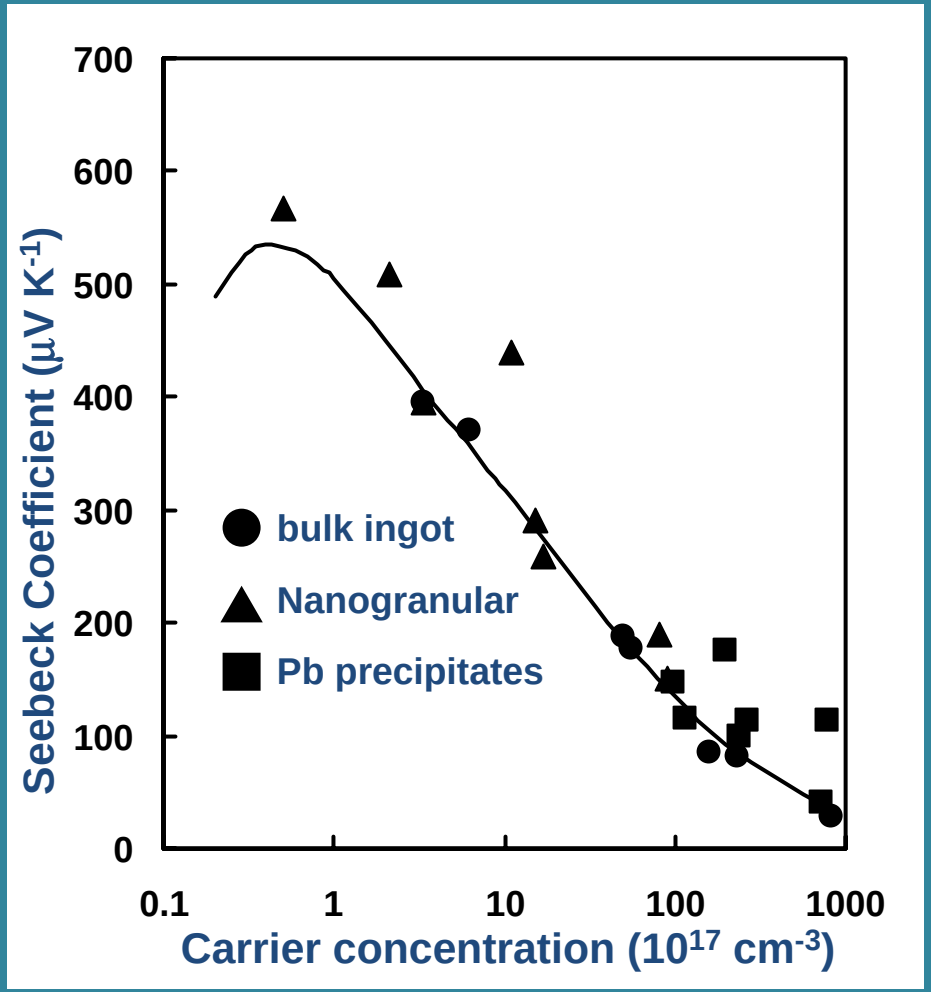
λ = electron scattering parameter

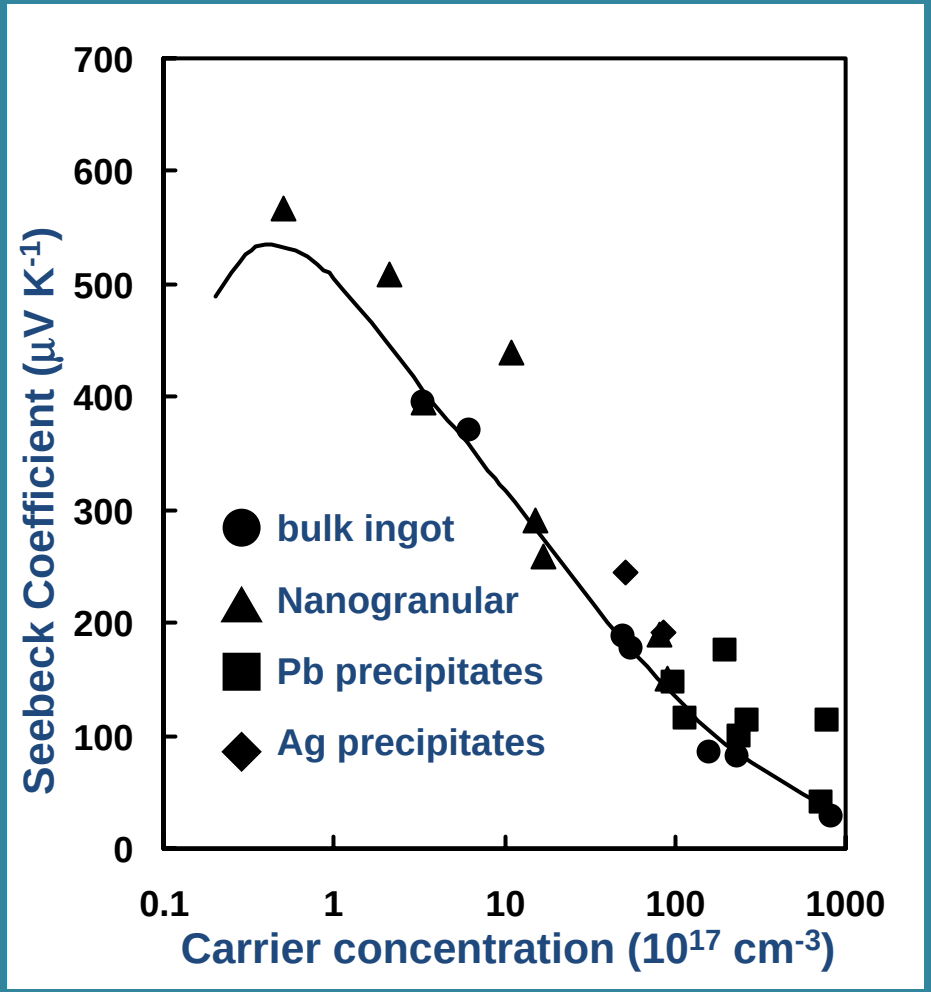
$$\tau = \tau_o E^{\lambda - 1/2}$$

λ= 0 for scattering of electrons by acoustic phonons




Seebeck Coefficient (μV K-1)
700
600
500
400
300
200
100
0
0.1
1
10
100
1000
Carrier concentration (10^17 cm^-3)
bulk ingot
Nanogranular
X-ray Intensity (a.u.)
1x10^5
1x10^4
1x10^3
1x10^2
PbTe,
31 nm particles
PbTe,
47 nm particles
24
26
28
2 θ (degrees)


700
600
500
400
300
200
100
0
Seebeck Coefficient (μV K-1)
bulk ingot
Nanogranular
Pb precipitates
0.1
1
10
100
1000
Carrier concentration (10^17 cm^-3)


700
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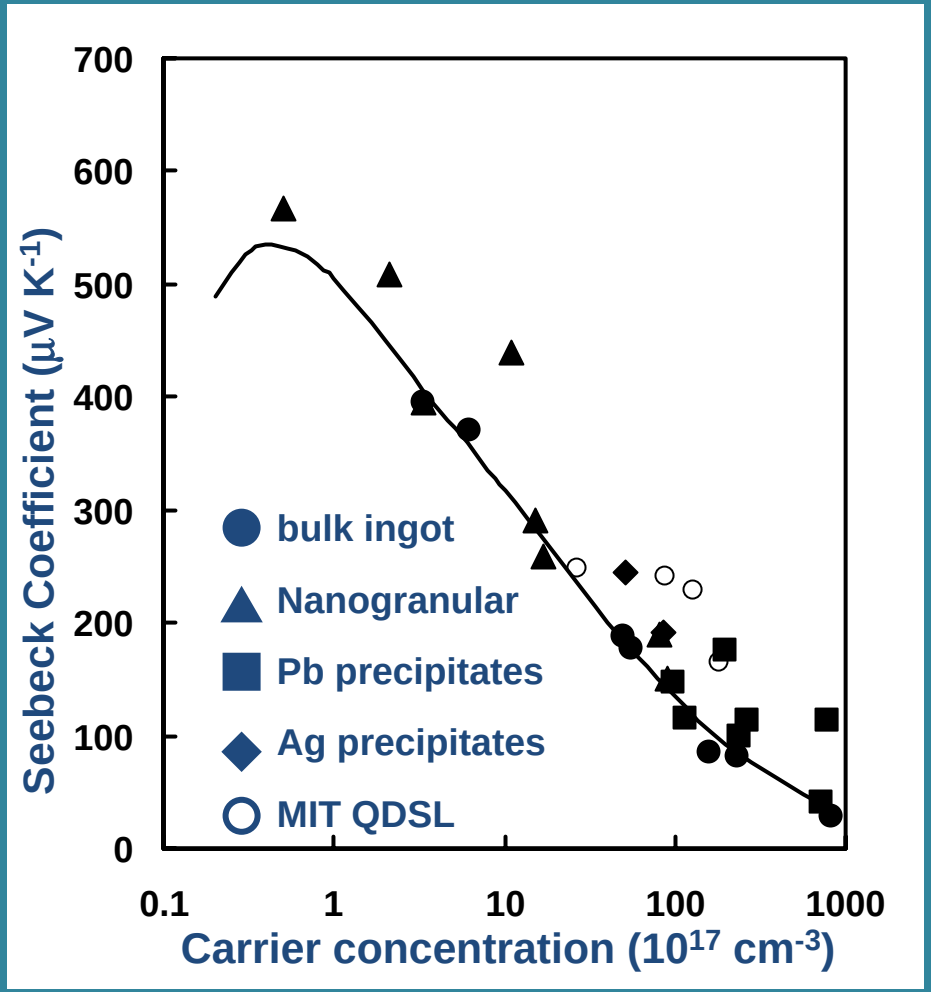
Seebeck Coefficient (μV K-1)
0.1
1
10
100
1000
Carrier concentration (10^17 cm^-3)
bulk ingot
Nanogranular
Pb precipitates
Ag precipitates


700
600
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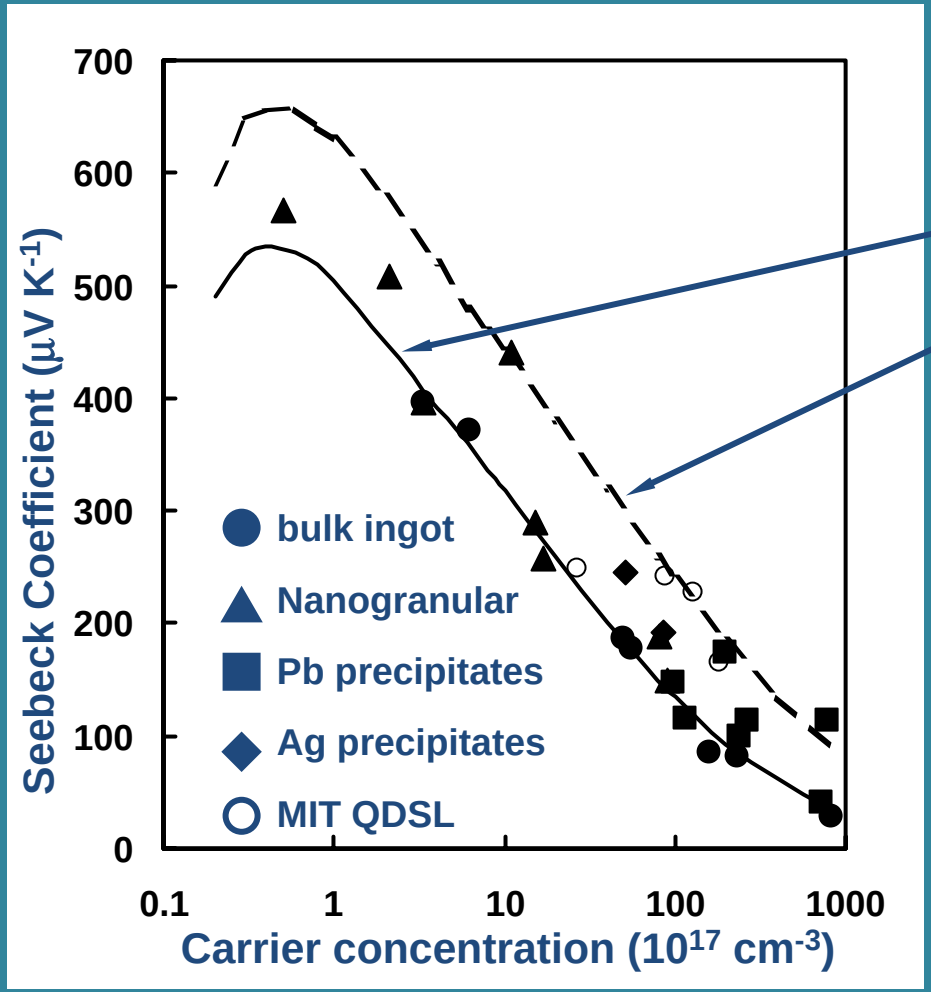
200
100
0
Seebeck Coefficient (μV K-1)
bulk ingot
Nanogranular
Pb precipitates
Ag precipitates
MIT QDSL
0.1
1
10
100
1000
Carrier concentration (10^17 cm^-3)

$$S \propto \left[\frac{const. + \lambda}{n^{2/3}} \right]$$



λ = 0

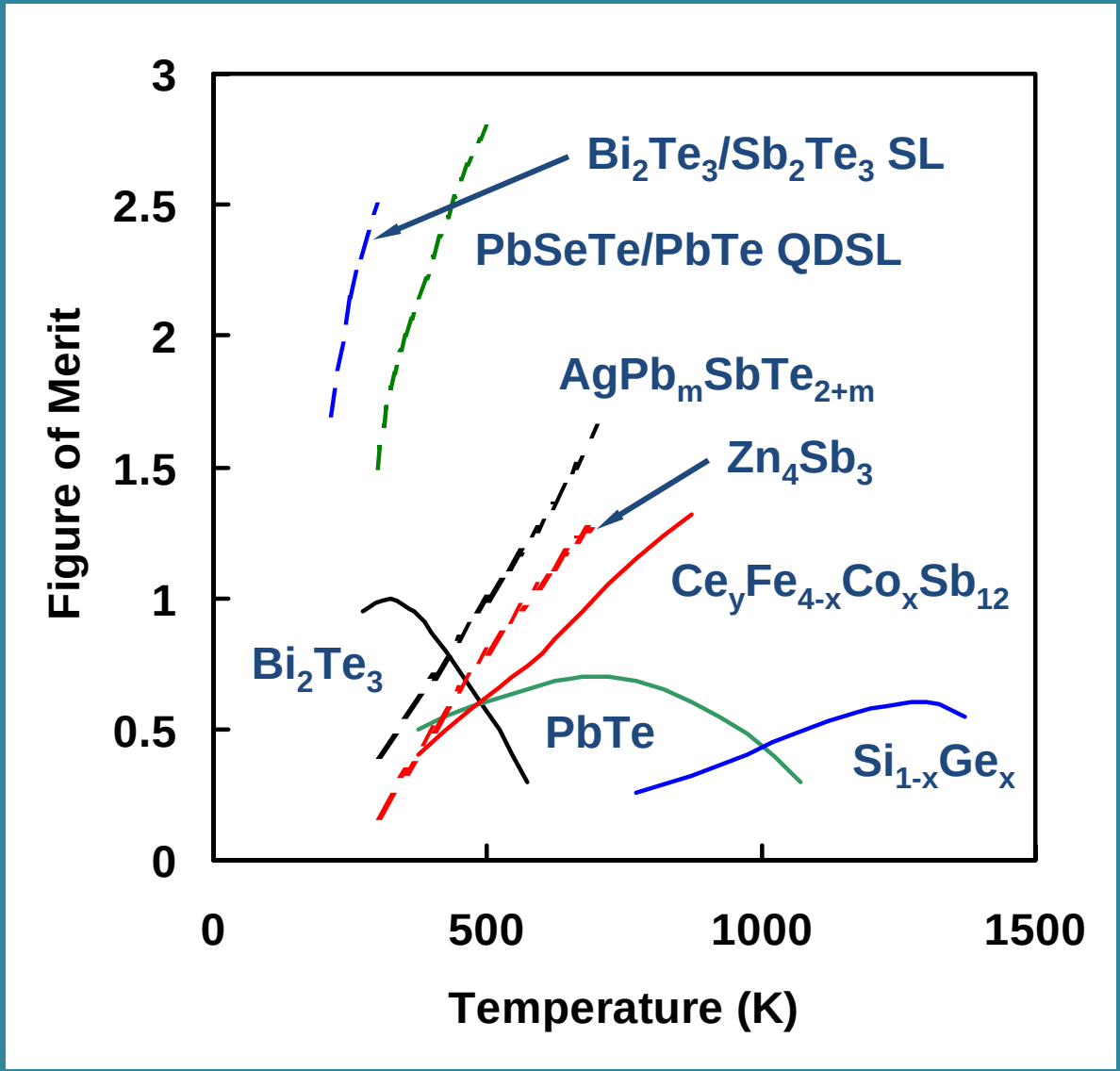
λ= 1.5

Indicates a change in the electron scattering mechanism

Verified by Nernst effect data that measure λ directly!

Heremans, Thrush, and Morelli (2005)

State of the Art Thermoelectric Materials (2005)



These and other novel approaches have helped push up Z!

Summary and Future

- TE materials can increase the efficiency of energy processes but better materials are needed

- New ideas and concepts in the fields of transport, thermoelectricity, and nanotechnology are providing guidance (the SEEDS)

- Experimental studies are paying off in enhanced values of Z (the SAPLINGS)

- More work is needed but the future is very promising (TOWERING TREES are just around the corner)!

Acknowledgments

- GM Research: Greg Meisner and Jihui Yang
- Jet Propulsion Lab/Caltech: Jean-Pierre Fleurial and Thierry Caillat
- University of Michigan: Ctirad Uher
- Delphi Research Labs: Joseph Heremans (OSU) and Chris Thrush
- DOE, ONR, DARPA

Thanks for listening!