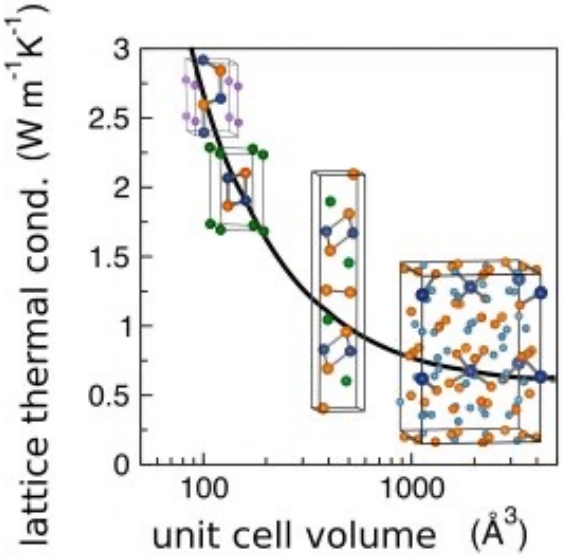
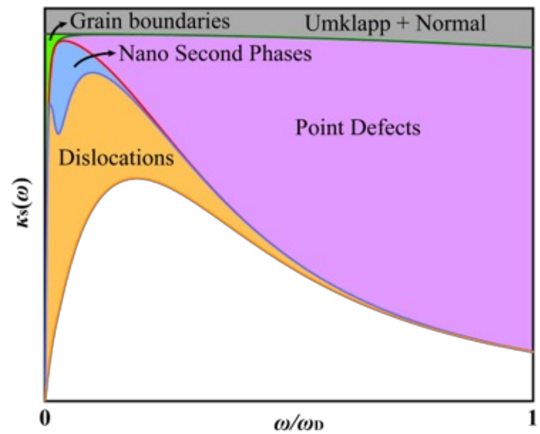
Phonon Engineering of Thermal Conductivity in Complex Materials

G. Jeffrey Snyder

Northwestern University

http://thermoelectrics.matsci.northwestern.edu/thermoelectrics/index.html#thermal





Link to Slides

Thermoelectrics

Northwestern Materials Science and Engineering

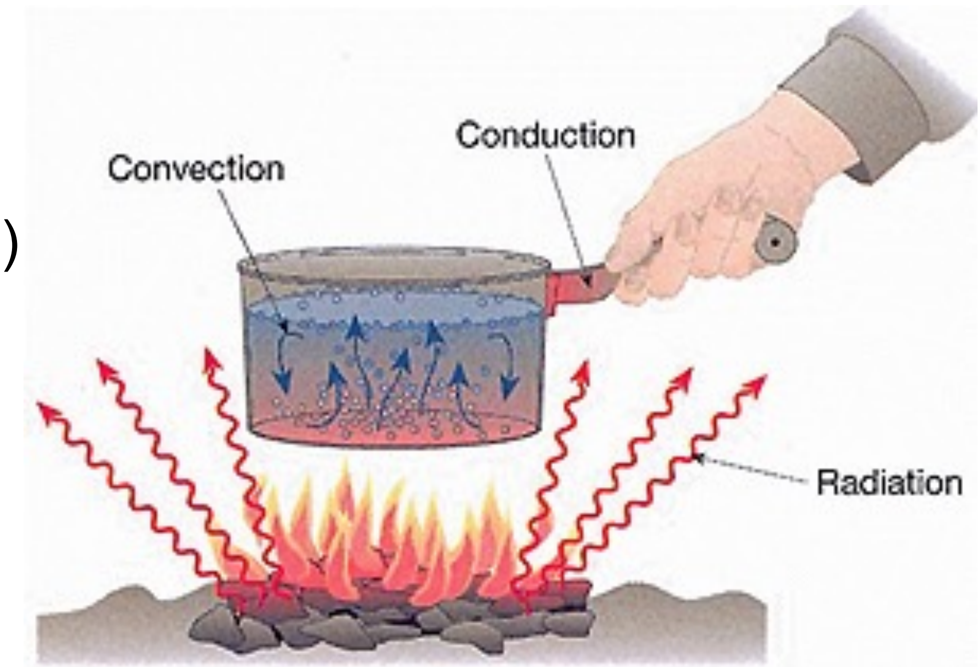
Toberer, Zevalkink, Snyder *J. Mat. Chem.*, **21,** 15843 (2011)

Hanus, Snyder et al, *Applied Physics Reviews* 8, 031311 (2021)

Mechanisms of Thermal Conductivity

Heat can be transported by

- Convection = Mass Flow
- Radiation (Infra-red (IR) light)
- Conduction = heat diffusion (in solid)



$$\kappa = \kappa_e + \kappa_l$$

$$\kappa_e = L\sigma T$$

$$\frac{L}{10^{-8}\mathrm{W\Omega K^{-2}}} = 1.5 + exp\left[\frac{-|S|}{116\mu\mathrm{V/K}}\right]$$

Conduction of heat by electrons or lattice vibrations (phonons)

Conduction of heat by electrons

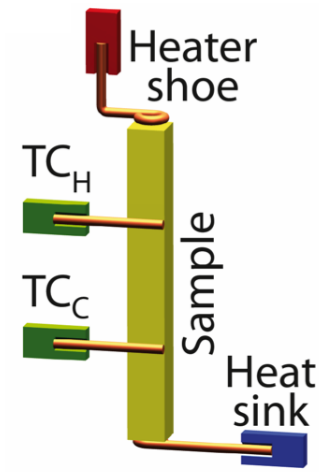
- Proportional to Electrical Conductivity σ

H-S Kim, Snyder et. al. *APL Materials*, **3**, 041506 (2015)

Thermal Diffusivity

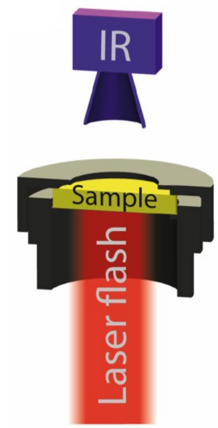
Thermal Conductivity from Thermal Diffusivity Measurements

less problem with radiative losses than direct measurement



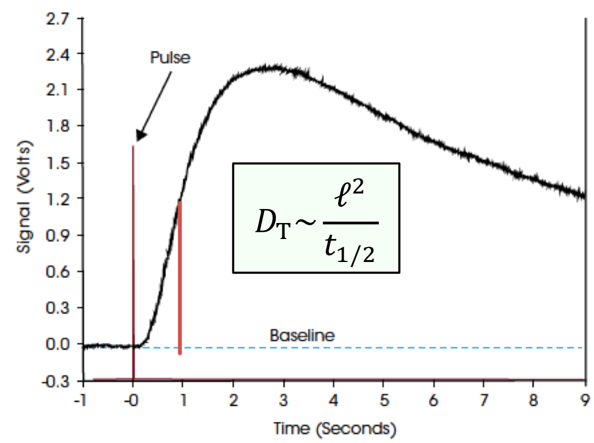
Thermal Conductivity
Steady-State Method

$$\kappa = \rho c_{\mathrm{p}} D_{\mathrm{T}}$$



Thermal Diffusivity
Flash Method

κ = [W/mK]
D_{T} = [m^2/s]
$\rho\, c_p$ = [J/m^3]
geometric density
not Archimedes



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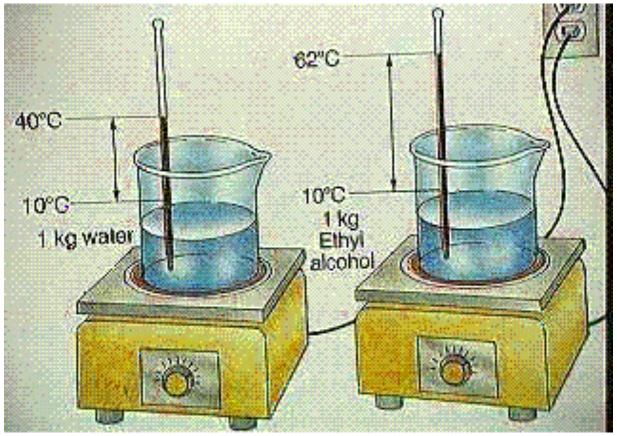
Borup, Snyder, et al., *Energy. Env. Sci.*, **8**, 423 (2015)

Specific Heat – Heat Capacity

Heat Capacity = Thermal Energy (Heat Q [J]) required to raise temperature

depends on size of sample



$$C = \frac{dU}{dT} = \frac{Q}{\Delta T}$$

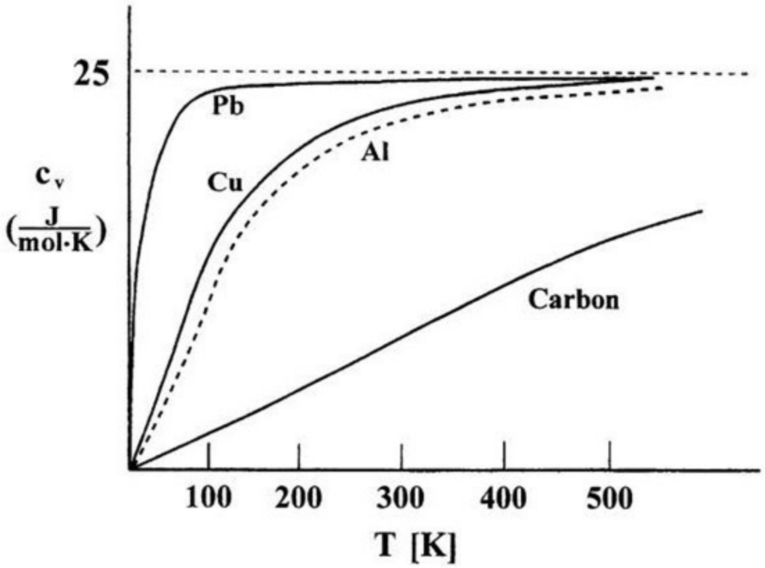
$$[c] = \frac{J}{kg \cdot K} \qquad [c] = \frac{J}{m^3 \cdot K}$$

Specific Heat (capacity) = heat capacity per unit mass or volume

material property

High Temperature Specific Heat of solid

$$\boxed{c = 3k_B / atom}$$



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Dulong-Petit Specific Heat

Equipartition of Energy in Classical Systems

in thermal equilibrium, energy is shared equally among all of its various forms: ½ $k_B T$ for each dimension of KE and PE

Monoatomic Gas $KE = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{3}{2}k_B T$ $\quad C = \frac{3}{2}k_B$

Atoms in Solid

$$KE = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{3}{2}k_B T$$

$$PE = \frac{1}{2}\beta\Delta x^2 + \frac{1}{2}\beta\Delta y^2 + \frac{1}{2}\beta\Delta z^2 = \frac{3}{2}k_B T$$

$$\boxed{C = 3k_B}$$

Dulong-Petit Heat Capacity per atom

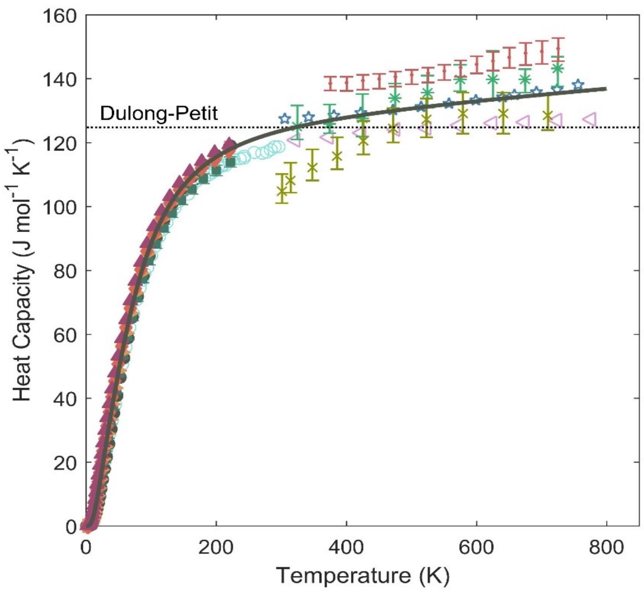
Heat Capacity (per atom)

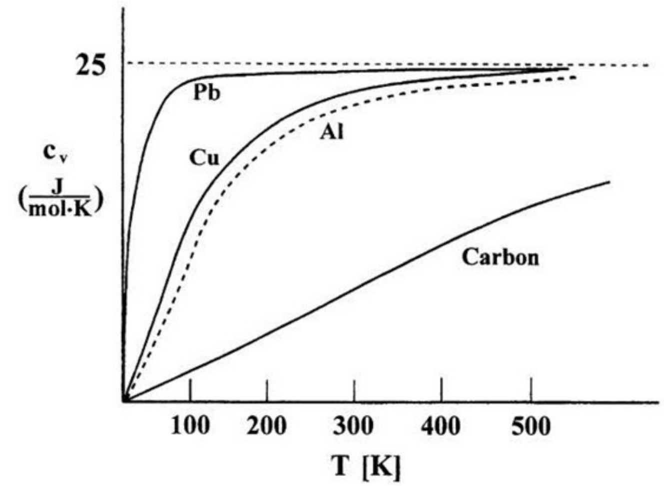
$$C = \frac{d(KE + PE)}{dT}$$

Table 4.5 Debye temperatures T_D, heat capacities, and thermal conductivities of selected elements

	Crystal								
	Ag	**Be**	**Cu**	**Diamond**	**Ge**	**Hg**	**Si**	**W**	**Dulong-Petit**
T_D (K)*	215	1000	315	1860	360	100	625	310	
C_m (J K^{-1} mol^{-1})†	25.6	16.46	24.5	6.48	23.38	27.68	19.74	24.45	**25**
c_s (J K^{-1} g^{-1})†	0.237	1.825	0.385	0.540	0.322	0.138	0.703	0.133	
κ (W m^{-1} K^{-1})†	429	183	385	1000	60	8.65	148	173	

General Heat Capacity Equation





$$c_{\mathrm{p}}[\mathrm{J\ g^{-1}K^{-1}}] \approx \frac{3NR}{M_{\mathrm{W}}}\left[1+\frac{1}{10^4}\left(\frac{T}{\theta_{\mathrm{D}}}\right)-\frac{1}{20}\left(\frac{T}{\theta_{\mathrm{D}}}\right)^{-2}\right]+A\left(\frac{T}{\theta_{\mathrm{D}}}\right)$$

$3NR$ = 124.7 Jmol^{-1}K^{-1}

M_W is the molecular weight [g mol^{-1}]

θ_D is Debye Temperature

α_V is volumetric thermal expansion coefficient

B is the isothermal bulk modulus

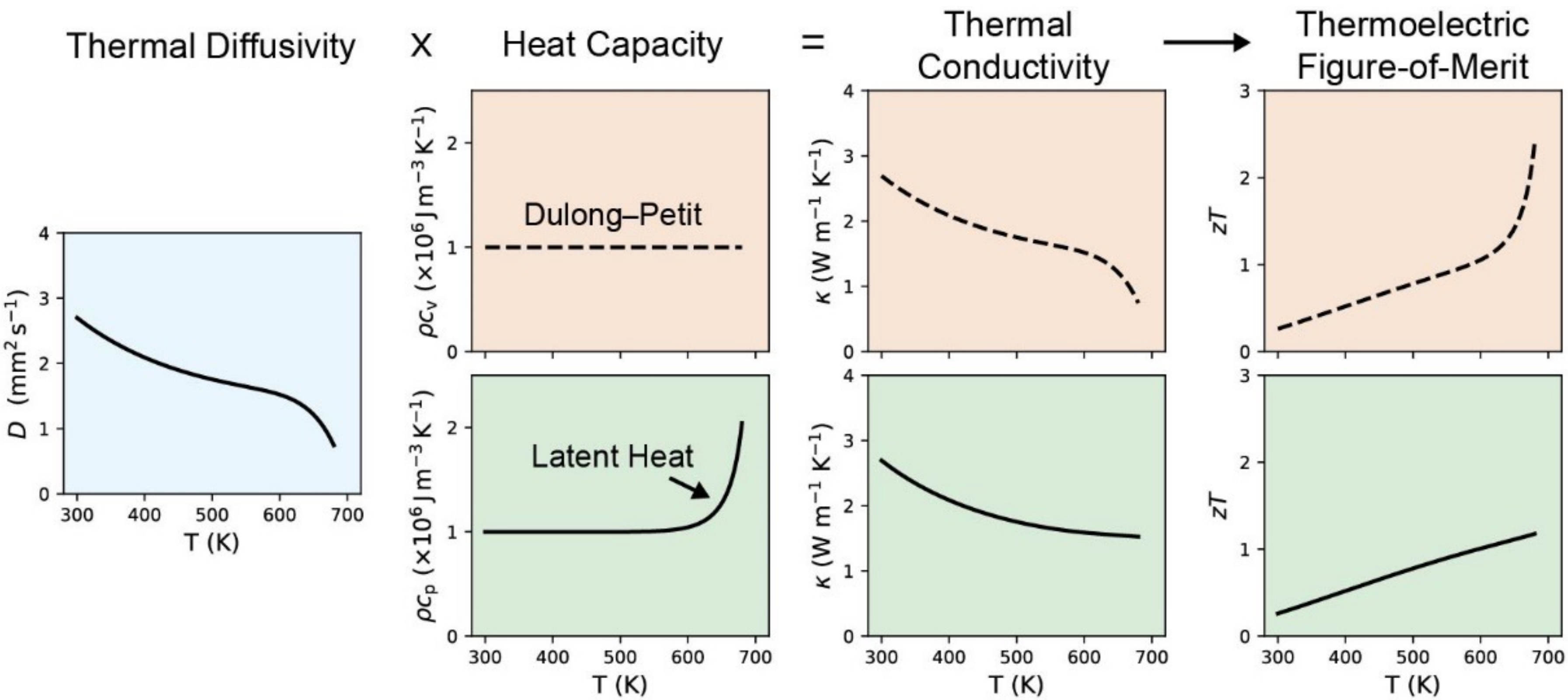
γ is Gruneisen parameter

$$A = BV_{\mathrm{m}}\alpha_V^2\theta_{\mathrm{D}}/M_{\mathrm{W}}$$

$$\gamma = B\alpha_V/C_{\mathrm{v}}$$

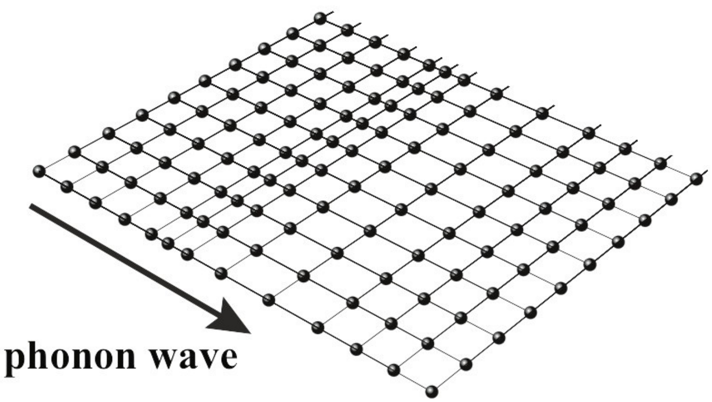
Agne, et al *Materials Today Physics* 6, 83 (2018)

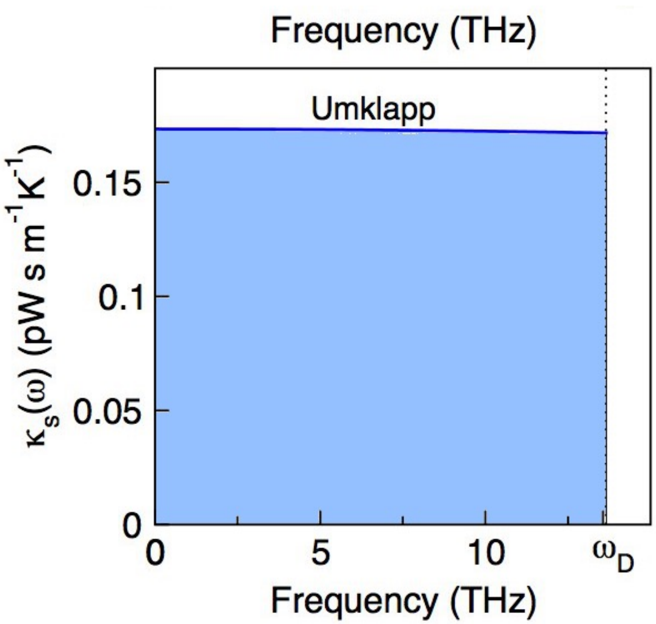
Low Diffusivity near Phase Transformation



M.T. Agne, Snyder. *Advanced Materials* 1902980 (**2019**)

Thermal Conductivity Spectrum





Toberer, Zevalkink, Snyder *J. Mat. Chem.*, **21,** 15843 (2011)

Phonon Heat Transport

$$\kappa_L = \frac{1}{3}\int_0^{\omega_{max}} C(\omega)\, v_g^2(\omega)\tau(\omega)d\omega$$

Spectral heat capacity: | Phonon Velocity: | Relaxation Time:

Phonon dispersion & Debye Model

Near linear dispersion

like massless photons, unlike electrons

$$E = \hbar\omega = \hbar v_p k$$

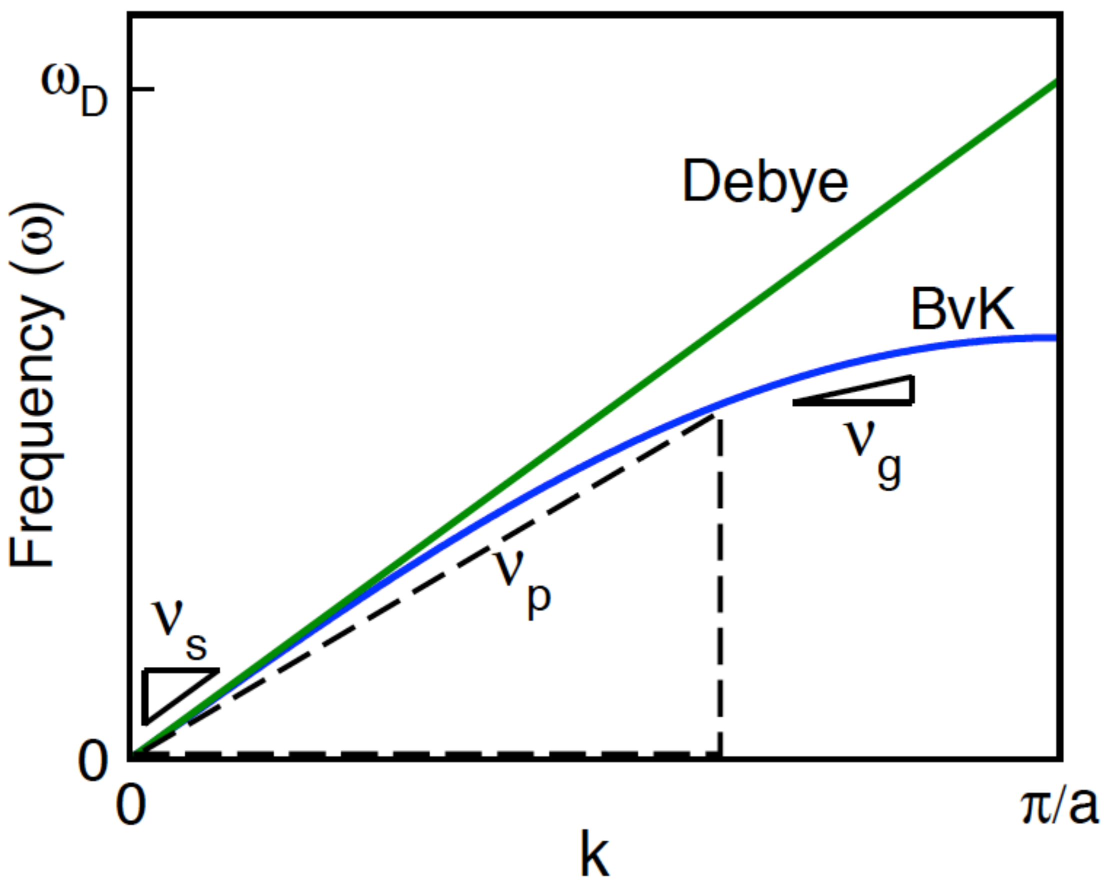
Debye Model

$$v_p = v_g = v_s$$

up to Debye Frequency

defines Debye Temperature

$$\hbar\omega_D = k_B\theta_D$$



v_s - average speed of sound
v_L - longitudinal speed of sound
v_T - transverse speed of sound
θ_D- Debye temperature
B - bulk modulus
G - shear modulus
ρ - density
V - volume/atom
(all phonon Debye model)
V - volume of primitive cell
(acoustic only Debye model)

$$v_p = \frac{\omega}{k} \qquad v_g = \frac{d\omega}{dk}$$

$$\hbar\omega_D = k_B\theta_D = \hbar\left(\frac{6\pi^2}{V}\right)^{1/3} v_s$$

$$v_s = \left(\frac{1}{3}\left[\frac{1}{v_L^3} + \frac{2}{v_T^3}\right]\right)^{-1/3}$$

$$v_L = \sqrt{\frac{B + \frac{4}{3}G}{\rho}} \qquad v_T = \sqrt{\frac{G}{\rho}}$$

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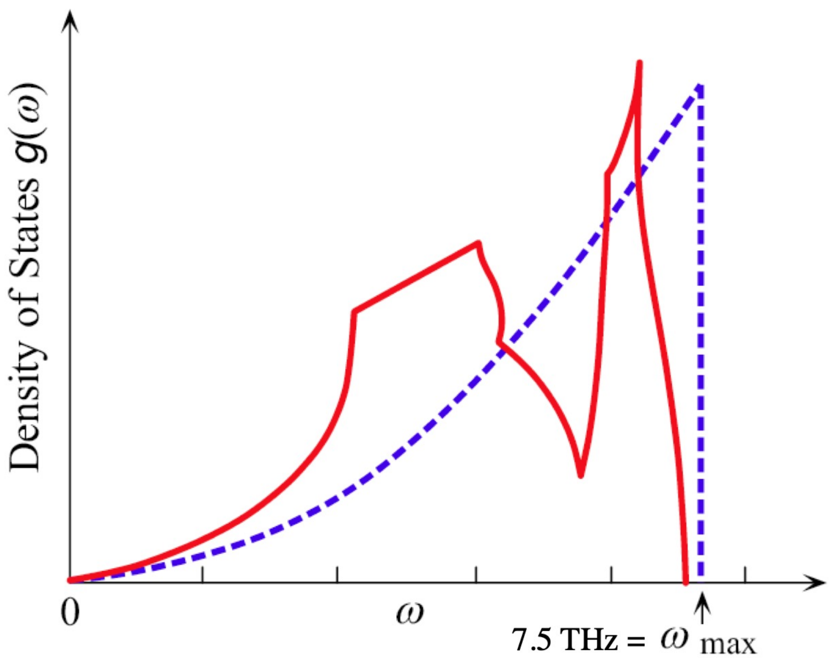
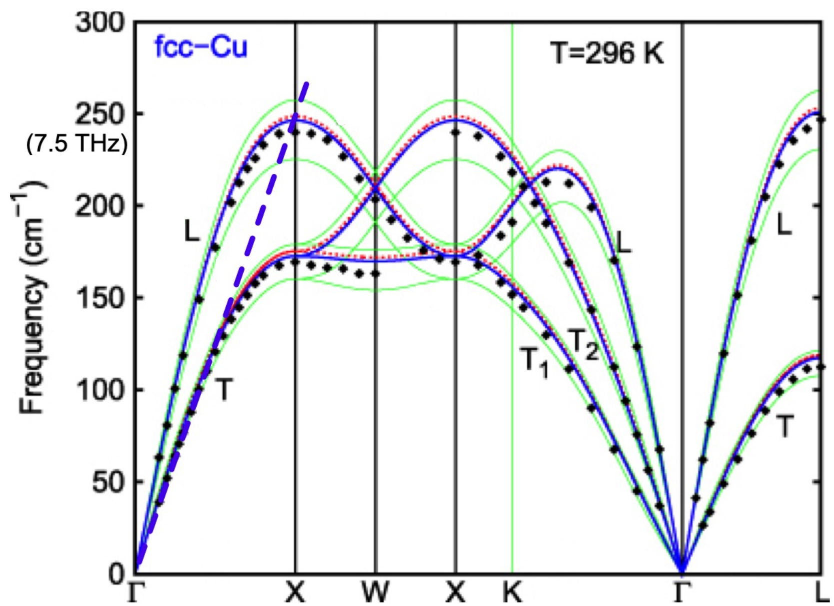
Debye Approximation

Acoustic Phonons in Copper





Debye density of states

$$c_s/k_B = g(\omega) = \frac{3}{2\pi^2}\frac{\omega^2}{v_s^3}$$

Debye dispersion

$$\frac{d\omega}{dk} \approx v_s$$

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From Principles of Electronic Materials and Devices, Third Edition, S.O. Kasap (© McGraw-Hill, 2005)

Phonon Heat Transport

$$\kappa_l = \frac{1}{3}\int C_s(\omega) v_g^2(\omega)\tau(\omega)d\omega$$

$$C_s = \frac{3k_B}{2\pi^2}\frac{\omega^2}{v_g v_p^2}$$

$$v_g = \frac{d\omega}{dk}$$

$$\tau$$

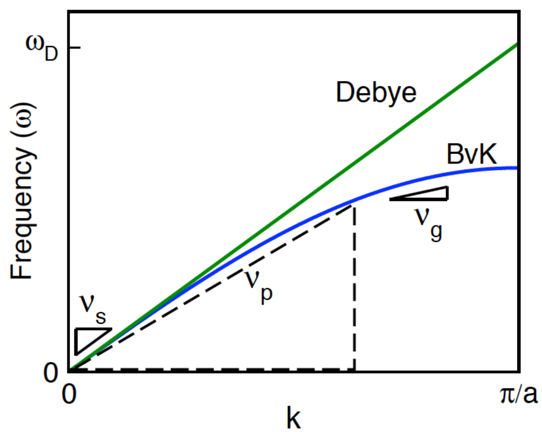
Spectral Heat Capacity

Related to Phonon DOS

$$C = \int C_s(\omega)d\omega = 3k_B$$

High Temperature Approx.

Phonon Group Velocity



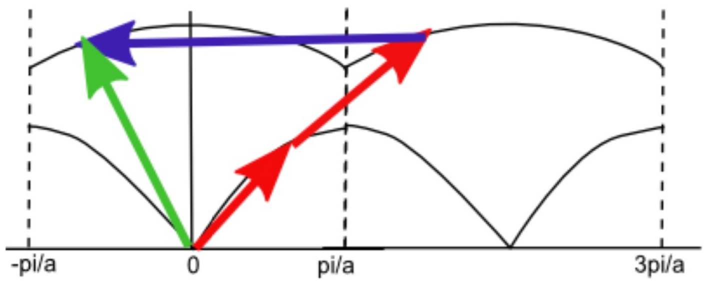
$v_g \approx$ Speed of Sound

Phonon Relaxation Time

$$\tau^{-1} = \tau_U^{-1} + \tau_{PD}^{-1} + \tau_{PD}^{-1} + \ldots$$

Phonon Scattering Rate

Thermal Conductivity Spectrum



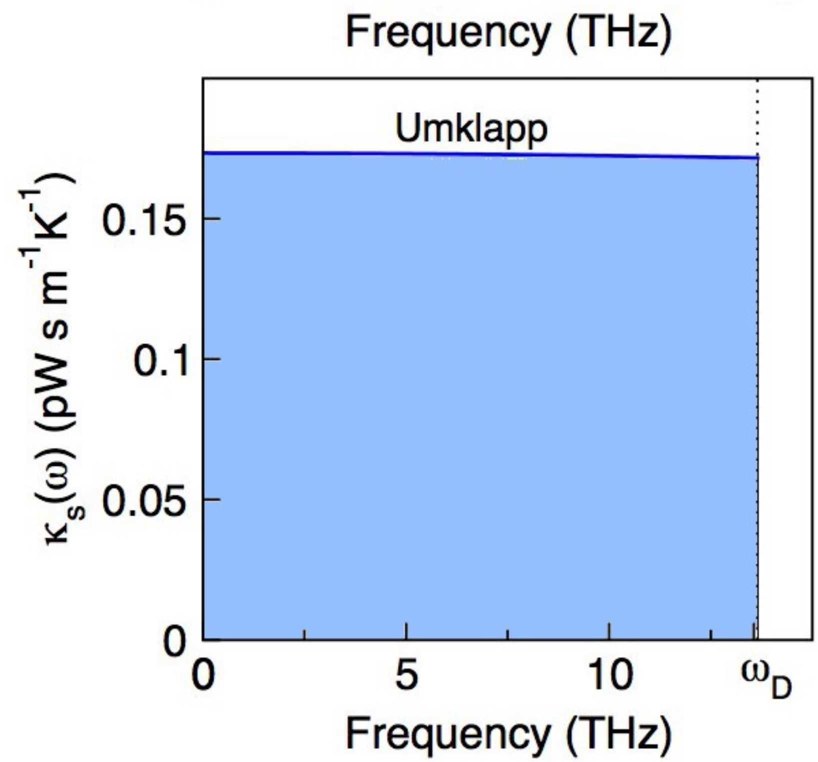
Phonon–Phonon Umklapp Scattering

$$\tau_u^{-1} \propto g(\omega) \propto c_s(\omega)$$

$$\kappa_s(\omega) = \frac{1}{3} c_s(\omega) v_g^2(\omega) \tau(\omega)$$

$$\kappa_L = \int_0^{\omega_D} \kappa_s(\omega) d\omega$$

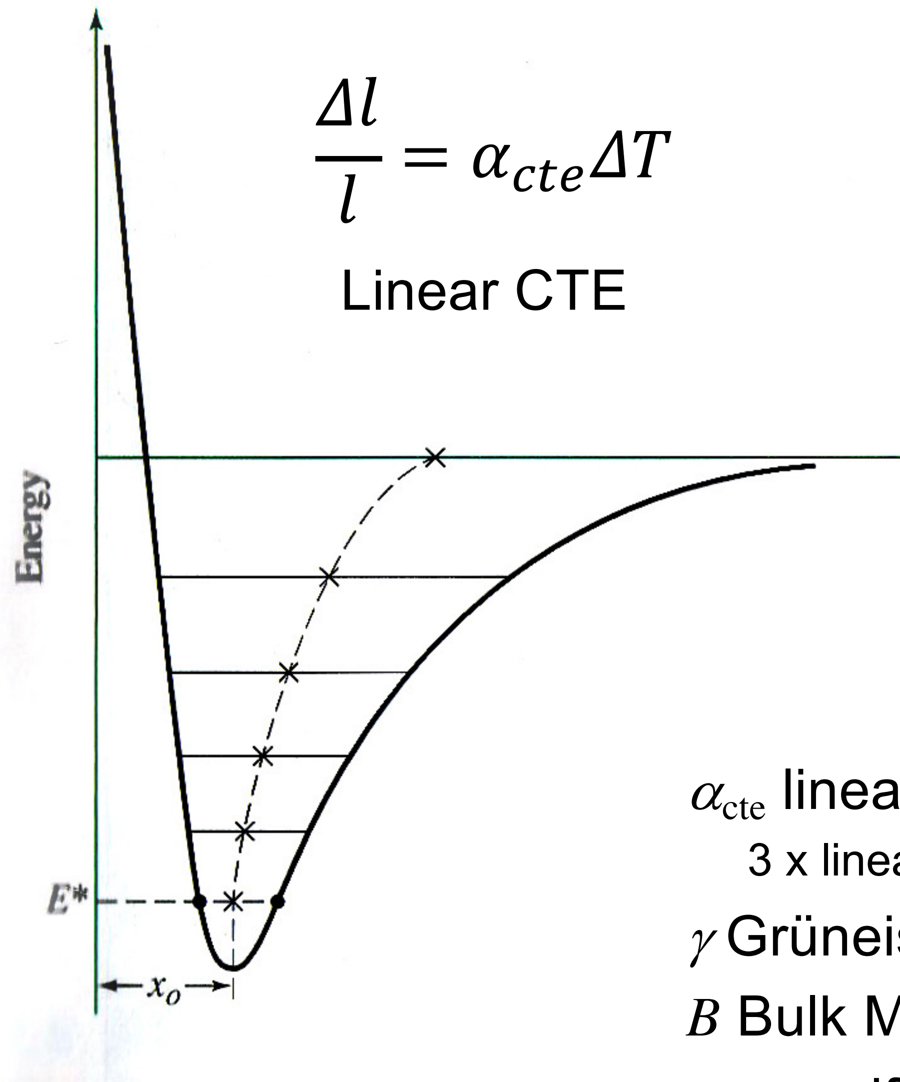
avg. speed of sound v_s
Grüneisen parameter γ
avg. atomic mass M, volume V



$$\kappa_U \sim 0.385 \frac{\bar{M}}{TV^{\frac{2}{3}}} \frac{v_s^3}{\gamma^2}$$

Toberer, Zevalkink, Snyder *J. Mat. Chem.*, **21,** 15843 (2011)

Grüneisen and Thermal Expansion



$$\frac{\Delta l}{l} = \alpha_{cte} \Delta T$$

Linear CTE

Thermal Expansion due to anharmonicity of potential well

$$\gamma = \frac{3\alpha_{cte} B}{c_V}$$

α_{cte} linear Coeff. Thermal Expansion

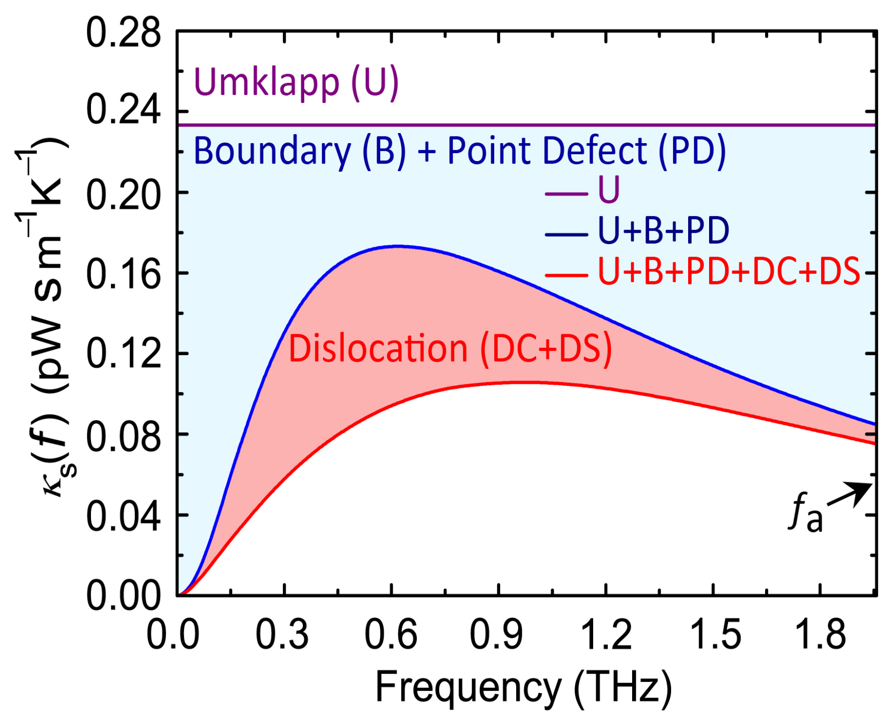
3 x linear CTE = volume CTE

γ Grüneisen parameter

B Bulk Modulus

c_V specific heat (per volume)

Full Spectrum Phonon Scattering

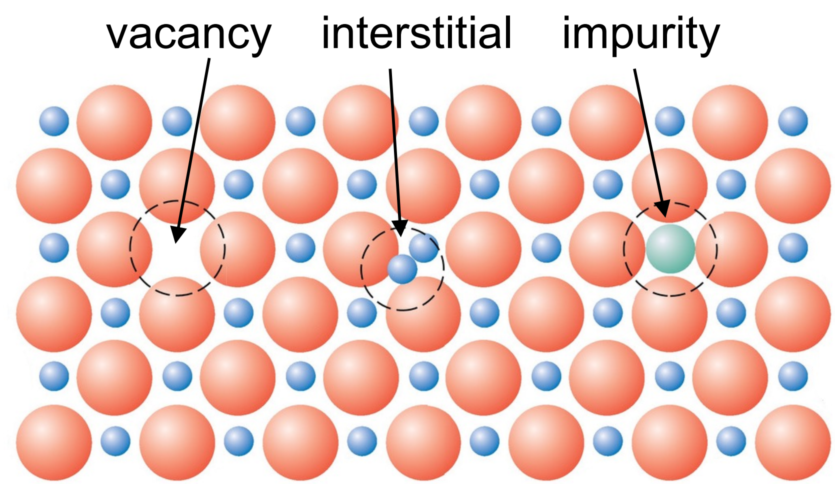


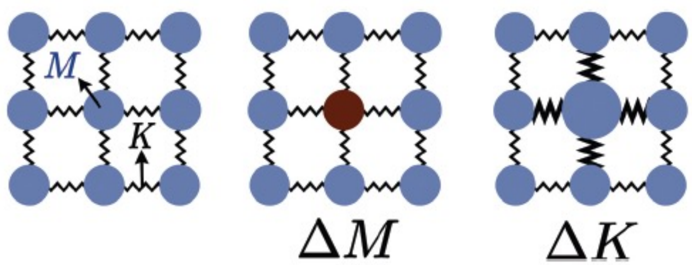
Toberer, Zevalkink, Snyder ***J. Mat. Chem., 21,*** 15843 (2011)

Point Defect Scattering

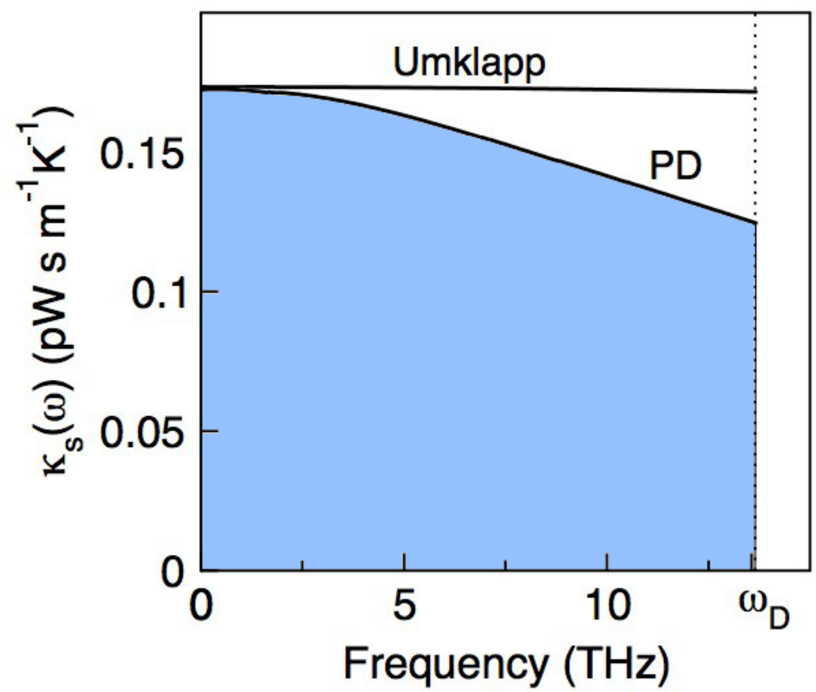
Impurities and point defects scatter phonons with wavelengths similar in size to the defect.

- ω^4 like Raleigh Scattering
- due to strain (radius) r
- and mass m fluctuation





$$\tau_{PD}^{-1} = \frac{V}{4\pi}\frac{\omega^4}{v_g v_p^2}\left(\sum f_i\left(\frac{\Delta m_i}{m}\right)^2 + \varepsilon\sum f_i\left(\frac{\Delta r_i}{r}\right)^2\right)$$



vacancy or interstitial

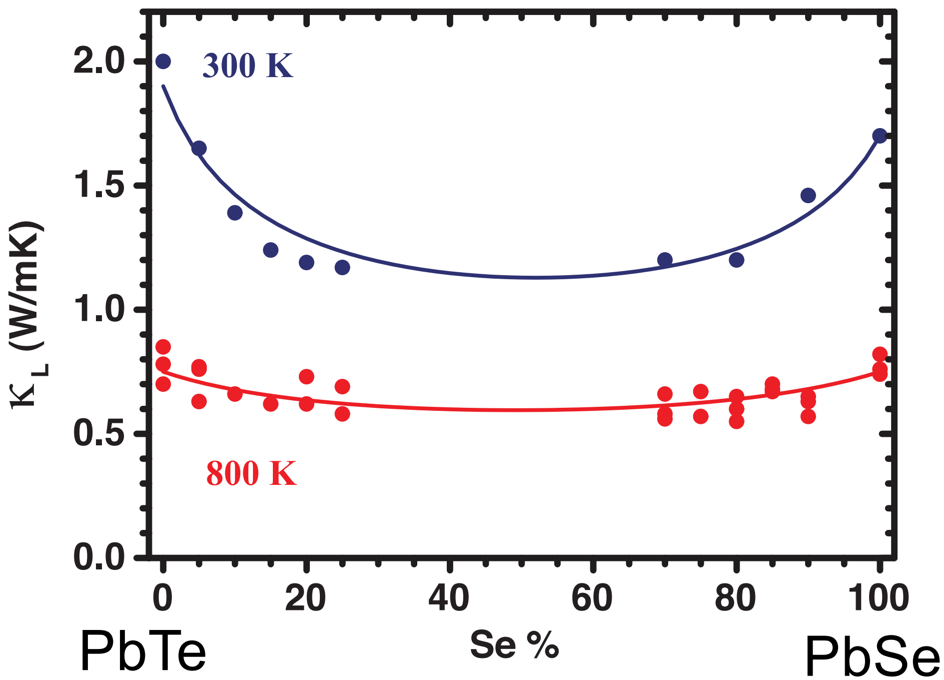
$$\Delta m_i = m_i + 2m$$

can be 10× stronger than impurity

Gurunathan, et al. *Materials Horizons*.,**7,** 1452 (2020)

Alloying affects Phonons *and* Electrons

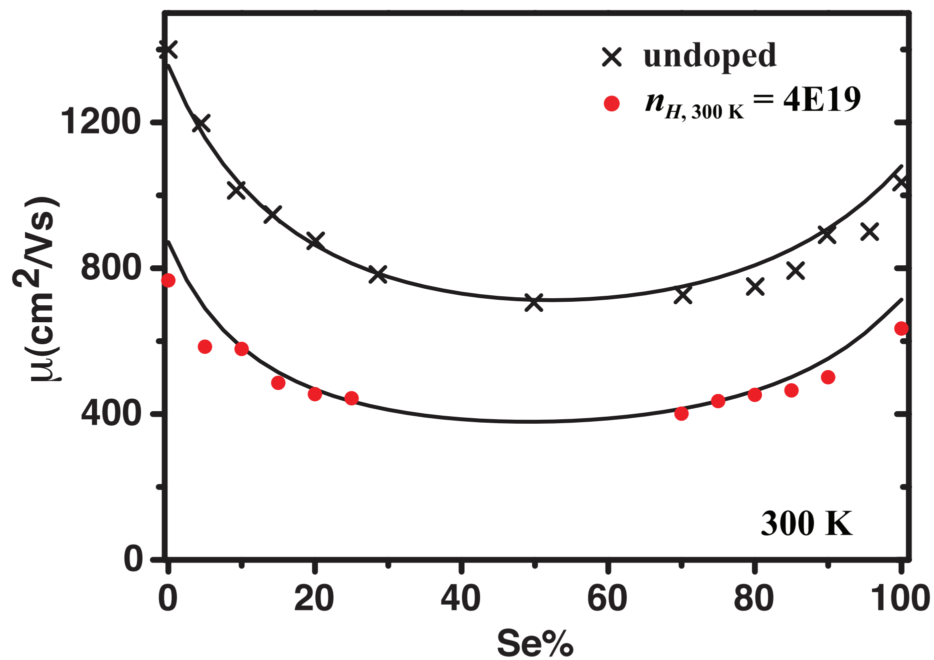
Disorder reduces thermal conductivity



ΔM = mass difference

Δr = strain

But also reduces electronic mobility



- U = alloy scattering potential

$$\frac{\kappa_L}{\kappa_0} = \frac{\tan^{-1} u}{u}, \quad u^2 = \frac{(6\pi^5 V^2)^{1/3}}{2 k_B v_s} \kappa_0 \Gamma. \quad \Gamma_M = \frac{\langle \overline{\Delta M^2} \rangle}{\langle \overline{M} \rangle^2}.$$

$$zT \propto B \approx \frac{\mu_w}{\kappa_l}$$

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Gurunathan, *Materials Horizons.*,**7,** DOI:10.1039/c9mh01990a (2020)
Wang, Snyder, et al, *Adv. Funct. Mat.*,**23,** 1586 (2013)

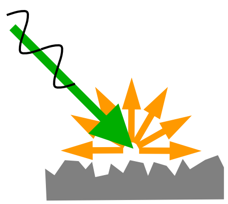
Standard Boundary Scattering

Boundaries limit mean free path

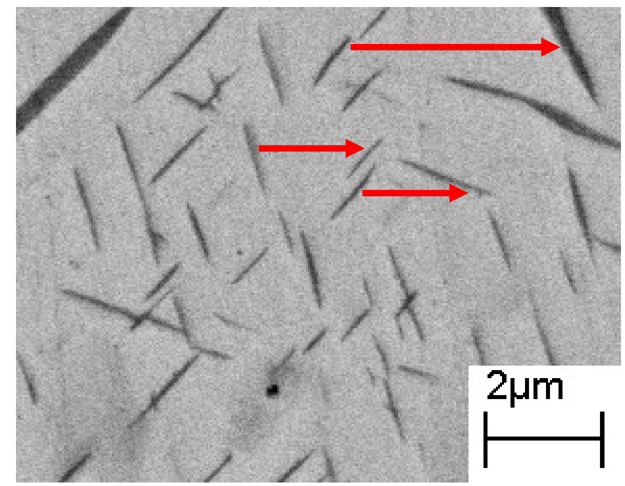
nanowires, grain size

$$\text{mean free path} \quad l = v_g \tau$$

Phonon transporting heat



Diffuse Scattering at Interfaces

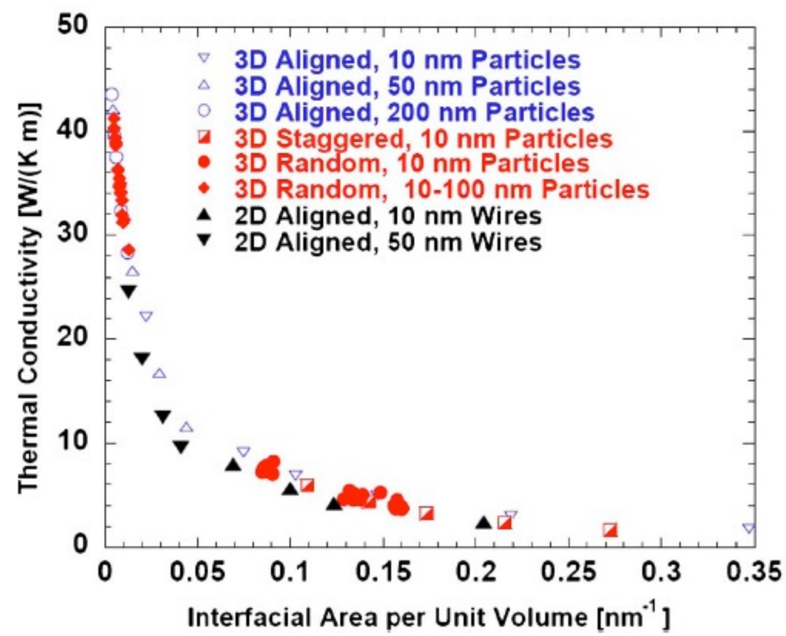


Mean distance between boundaries

grain size or nanowire diameter

not size of precipitates

Characterized by Interface area/volume



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G. Chen, C. Dames, R-G Yang et al. *J Heat Transfer* **130**, 42410 (2008)

Klemens & Callaway models

Klemens & Callaway models

Spectral κ and Matthiessen's Rule

$$\kappa_l = \frac{1}{3}\int C_s(\omega) v_g^2(\omega)\tau(\omega)d\omega$$

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_U} + \frac{1}{\tau_{PD}}$$

Boundary $\tau \sim \omega^{-0}$

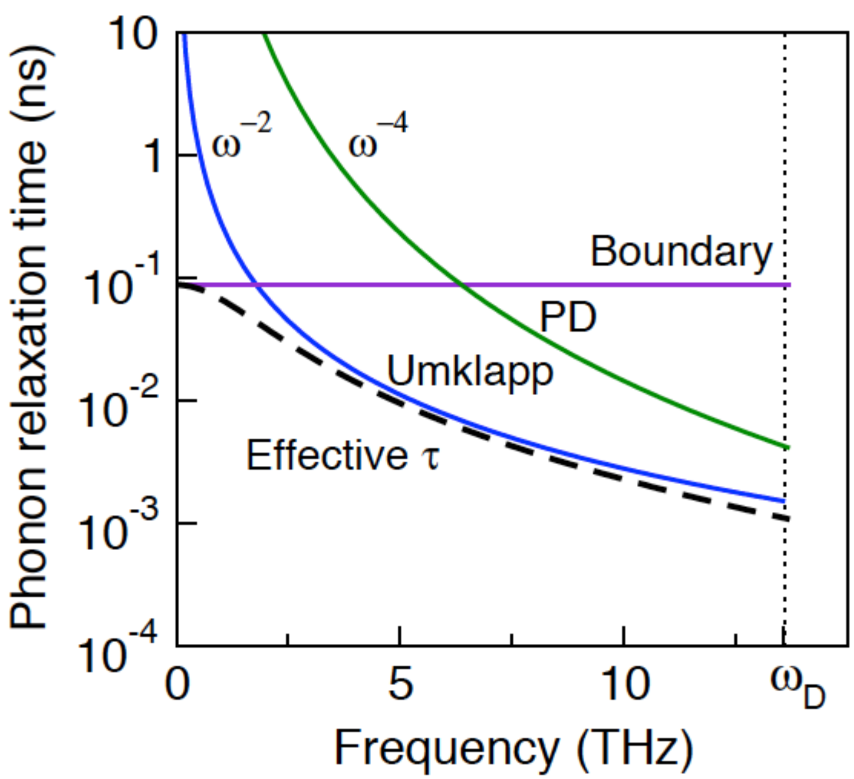
Umklapp $\tau \sim \omega^{-2}$

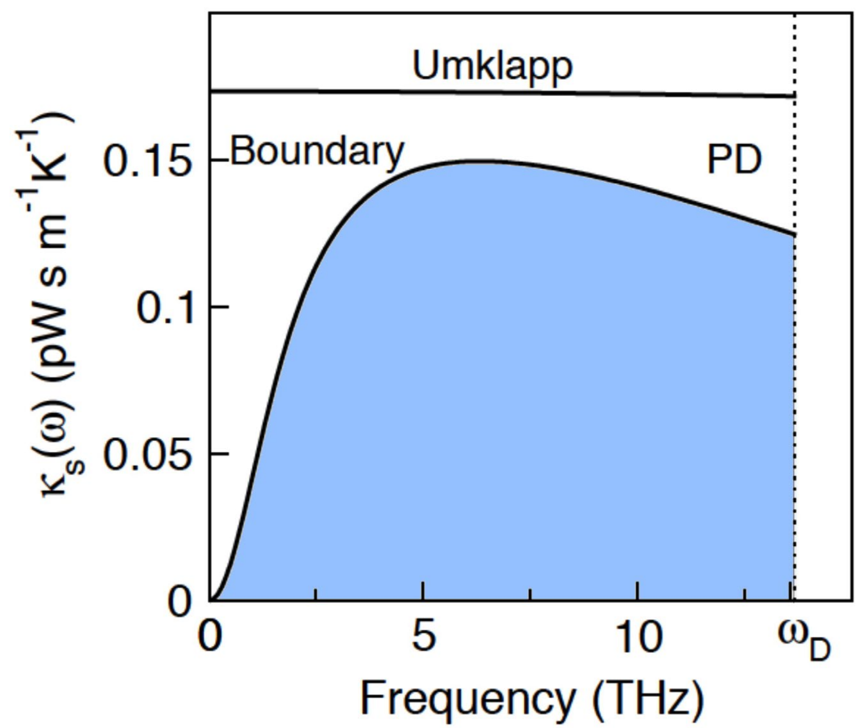
Point defect $\tau \sim \omega^{-4}$

Dislocation

Strain $\tau \sim \omega^{-1}$

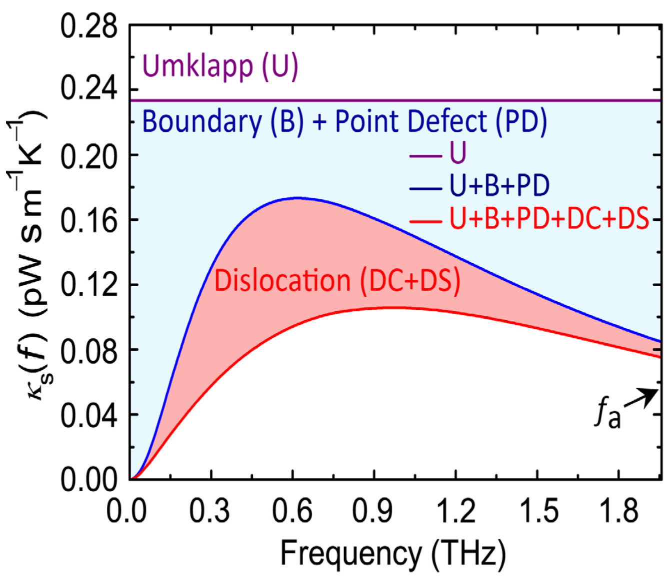
Core $\tau \sim \omega^{-3}$

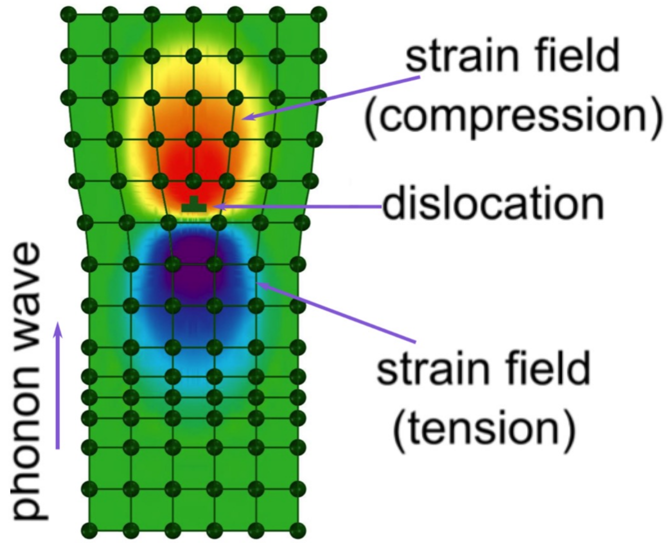


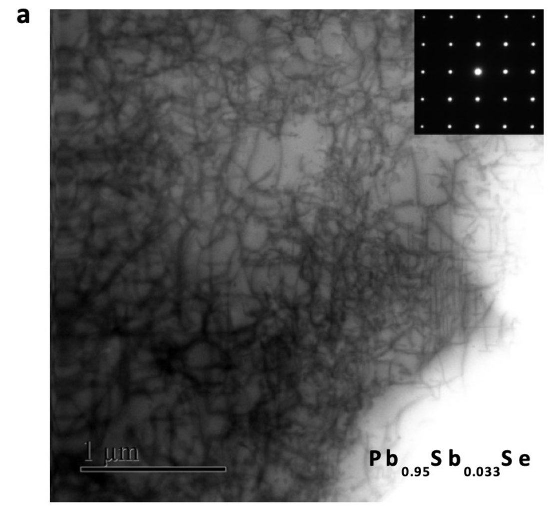


Dislocation Strain Scattering

$$\kappa = \int \kappa_s \, d\omega = \int \tfrac{1}{3} c_v(\omega) v_g^2(\omega) \tau(\omega) d\omega$$







Kim et al, *Science.*, **348,** 109 (2015)

Pei, *Nat. Comm.*, ***8,*** 13828 (2017)

$$\tau^{-1} = \frac{v}{d} + C_{DS} N_D B_D^2 \omega + C_U T \gamma^2 \omega^2 + C_{PD} \omega^4$$

boundary? — dislocation strain — phonon-phonon (Umklapp) — point defect

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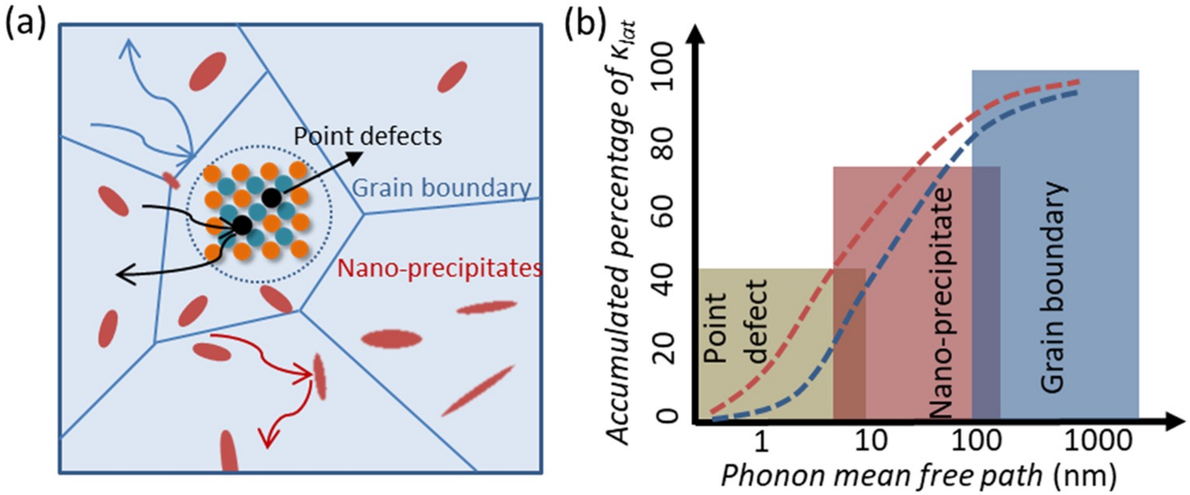
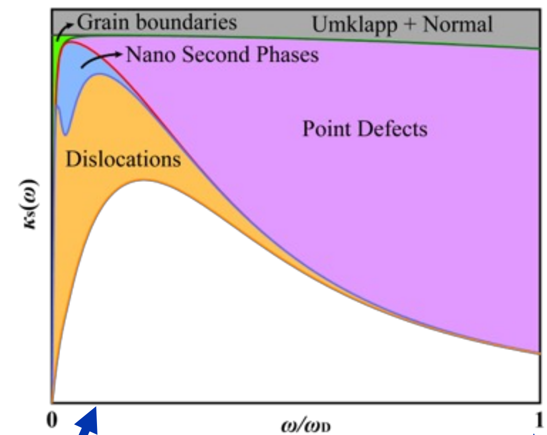
HS Kim et al, *Mat. Horizons.*, **3,** 234 (2016)
Hanus, Snyder. et al. *Communications Physics*, **1,** 78 (2018)

Full Spectrum Phonon Scattering



$(Bi,Sb)_2Te_3$



λ ~ 3 nm
long wavelengths for thermal transport

λ ~ 0.3 nm
interatomic distance

"Hierarchical Complexity"

Size ↔ Wavelength λ

Spacing ↔ Mean Free Path l

$$\tau^{-1} = \frac{v}{d} + C_{DS} N_D B_D^2 \omega + C_U T \gamma^2 \omega^2 + C_{PD} \omega^4$$

boundary? — dislocation strain — phonon-phonon (Umklapp) — point defect

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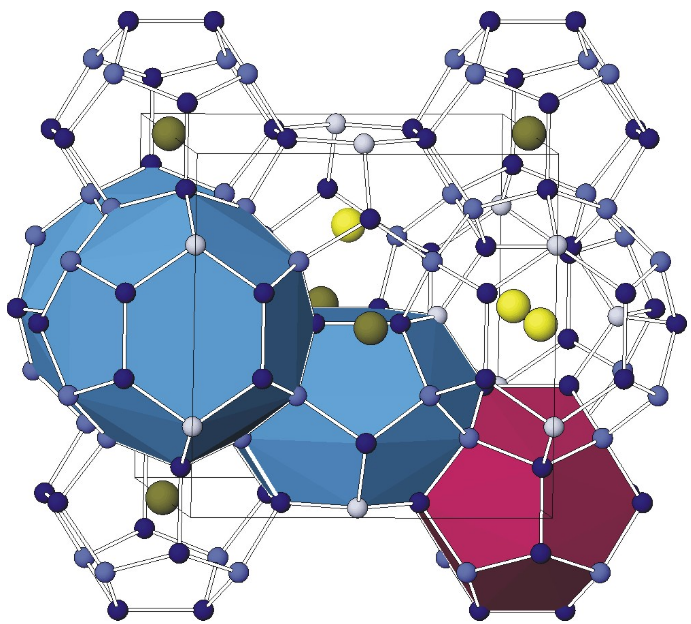
Snyder and Toberer, *Nature Materials* (2008)
Yu Xiao, LD Zhao, *npj Quant. Mater.* 3, 55 (2018); Zhuang, J. F. Li, (2020)

Thermal Conductivity of Complex Unit Cells



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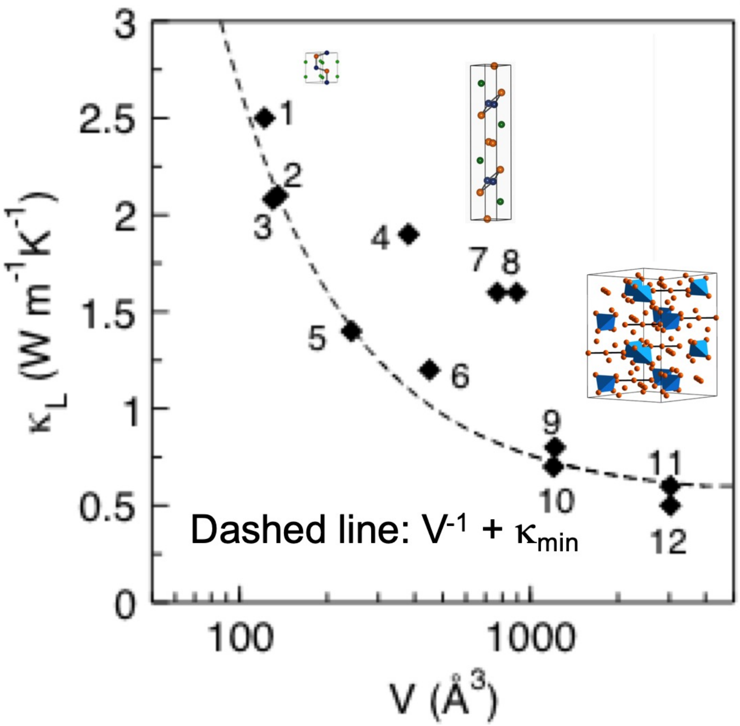
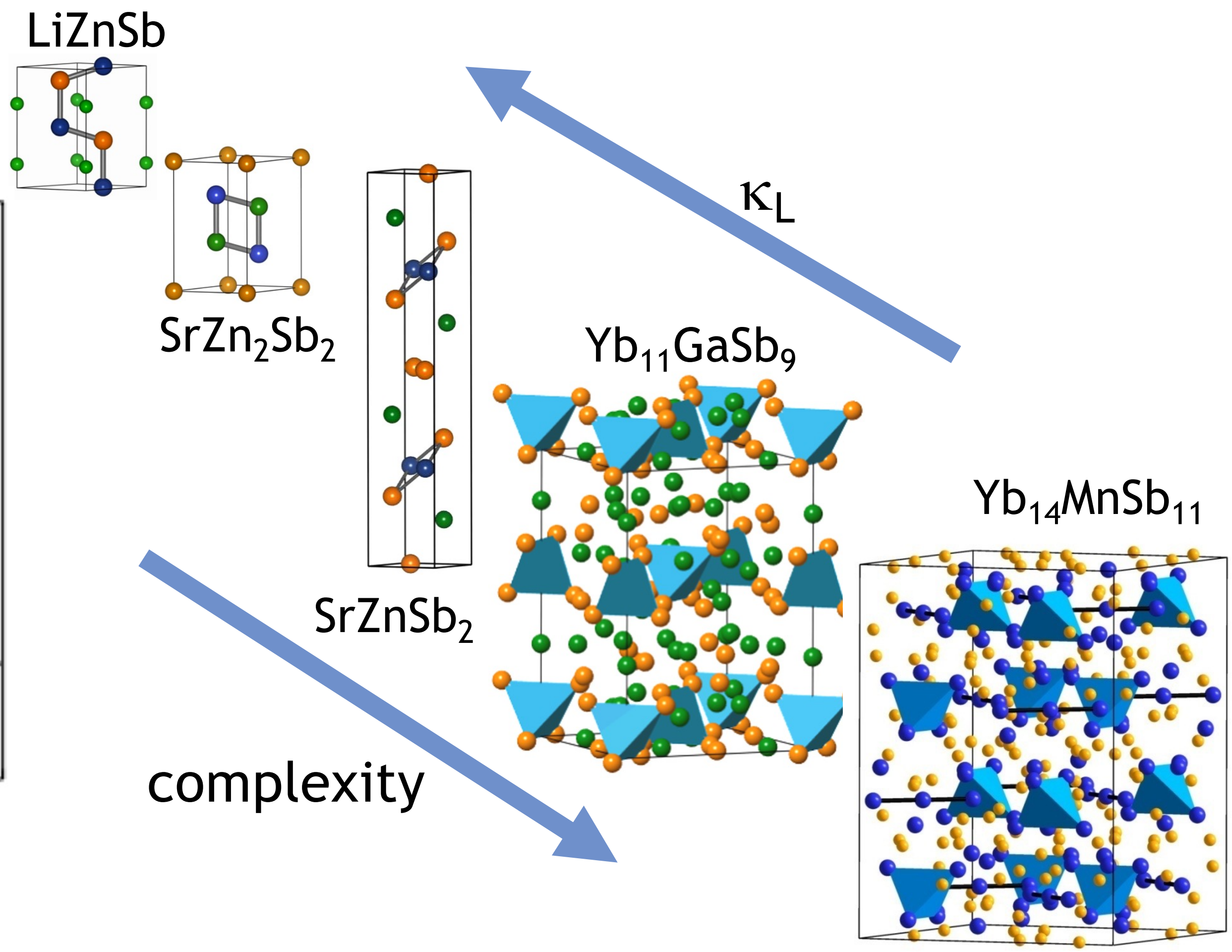
Complex Structures with low κ_L

Primitive unit cell volume is a good indicator for κ_L (when constituent atoms are similar).





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Toberer, May, Snyder ***Chem. Mat.*, 22**, p. 624 (2010)

Acoustic vs. Optical Phonons

Acoustic Phonons

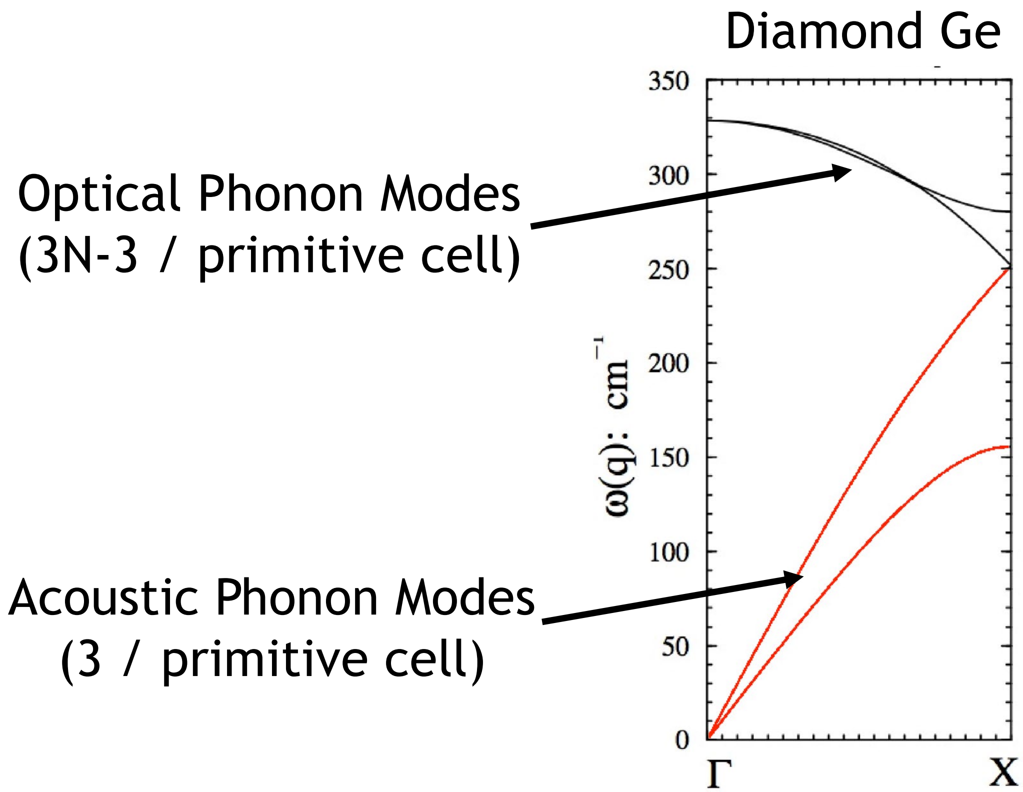
- Have high group velocity ($v_g = d\omega/dk$ ~ speed of sound)
- only 3 modes per primitive cell
- Conduct most of the heat

Optical Phonons

- Have low group velocity ($v_g = d\omega/dk$ ~ small)
- Large cells have many optic modes
  - ($3N$-3 per primitive cell)
- Conduct little heat

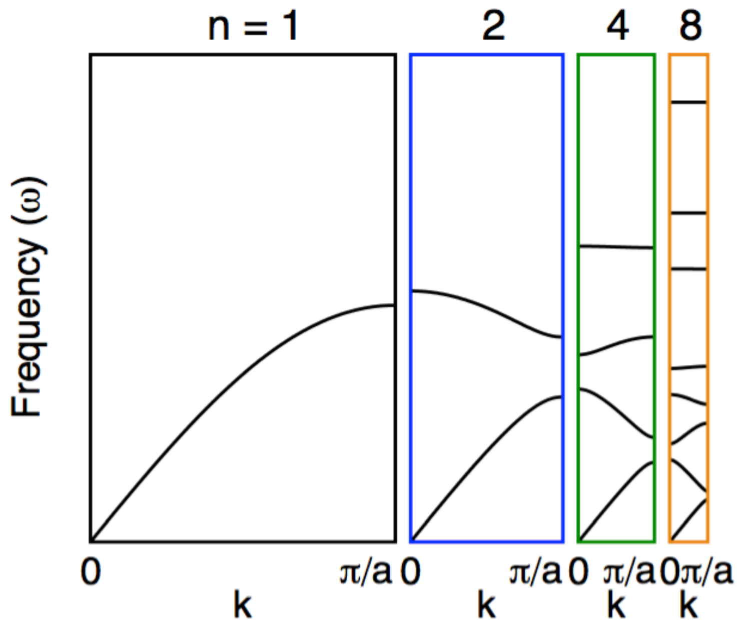
C - heat capacity
v - speed of sound
τ - phonon relaxation time
N - atoms per cell
V - volume of cell

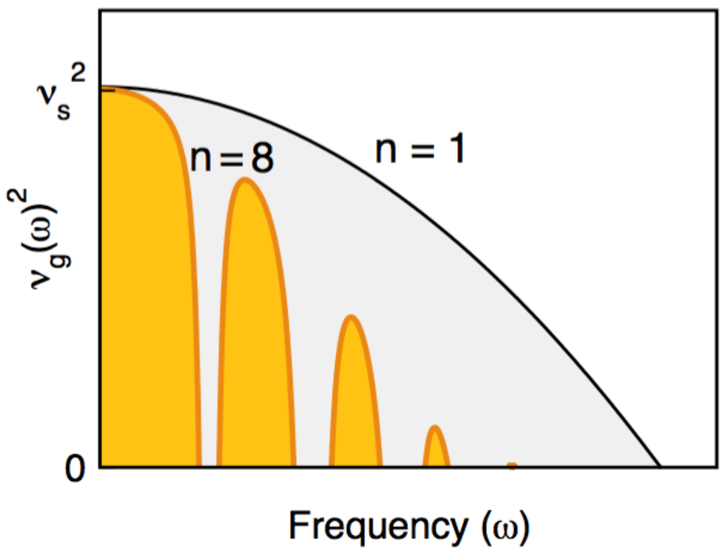
$$\kappa_l = \frac{1}{3}\int C_s(\omega)v_g^2(\omega)\tau(\omega)d\omega$$



Dong et al, Phys. Rev. Lett. 2001

Large Cells = many optical phonons



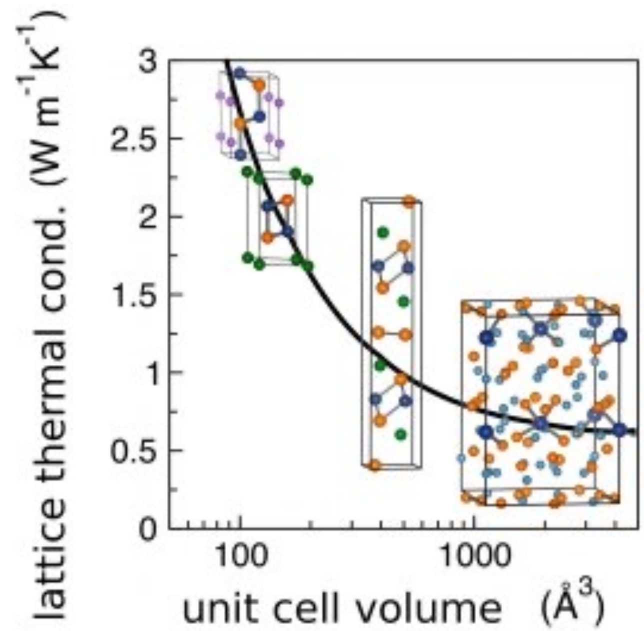


$$\kappa_l = \frac{1}{3}\int C_s(\omega) v_g^2(\omega)\tau(\omega)\, d\omega$$

$$v_g = \frac{d\omega}{dk}$$

Many atoms in unit cell (N)

decreases average phonon v_g and κ



Toberer, Zevalkink, Snyder *J. Mat. Chem.*, **21,** 15843 (2011)

Large Cells with low thermal cond.

Heat primarily carried by acoustic modes

But only 3 acoustic modes in a Large cell

Low lattice thermal conductivity

for large primitive unit cell volume (V)

should decrease with V

- for materials with same chemistry

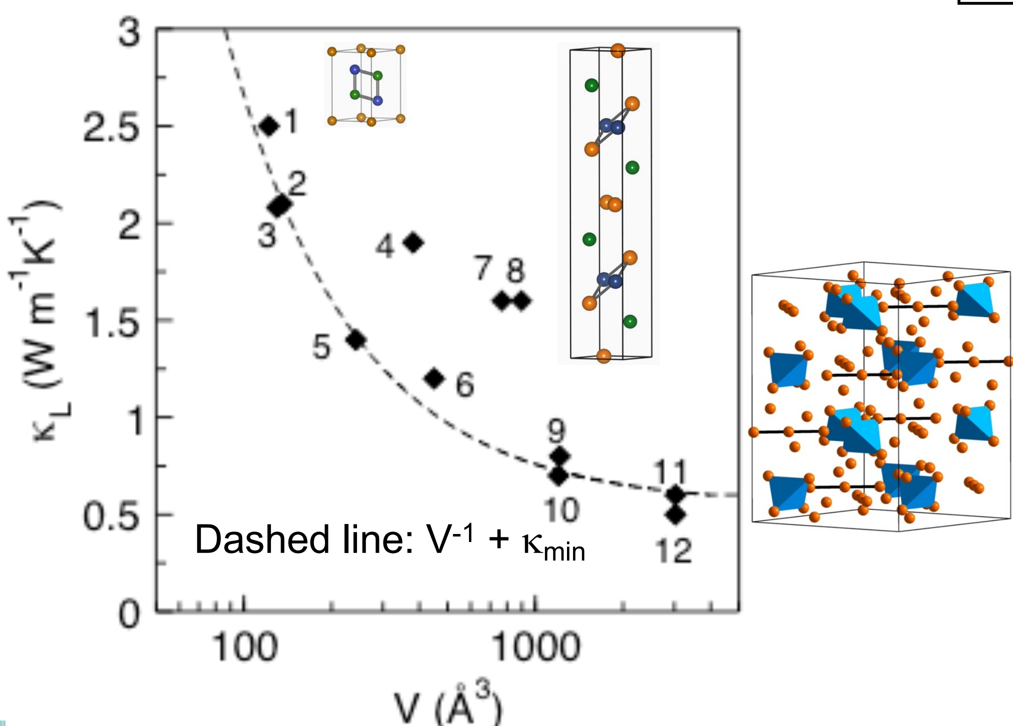
$$\kappa_{lattice} = \frac{1}{3} C v l$$

$$\text{acoustic} \quad C = \frac{3k_B}{V}$$

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

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

Antimonide Zintl Phases



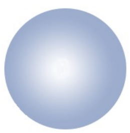
Does l change with V ?!

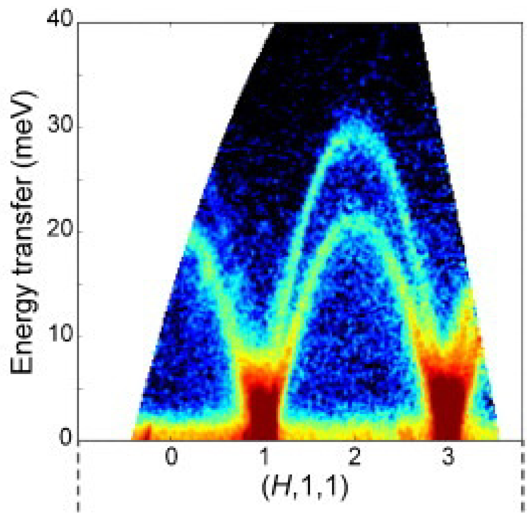
1 - LiZnSb
2 - $SrZn_2Sb_2$
3 - Mg_3Sb_2
4 $CeFe_4Sb_{12}$
5 - $BaZn_2Sb_2$
6 - $SrZnSb_2$
7 - $Yb_5In_2Sb_6$
8- $Ba_4In_8Sb_{16}$
9 - $Yb_{11}Sb_{10}$
10 - $Yb_{11}GaSb_9$
11 - $Yb_{14}AlSb_{11}$
12 - $Yb_{14}MnSb_{11}$

Toberer, May, Snyder ***Chem. Mat., 22,*** p. 624 (2010)

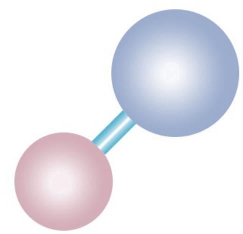
Phonons in Large Unit Cell Crystals

Cu
1 atom per
primitive cell

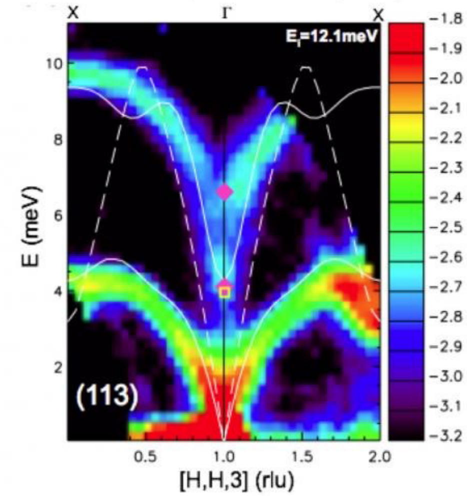




PbTe
2 atoms per
primitive cell

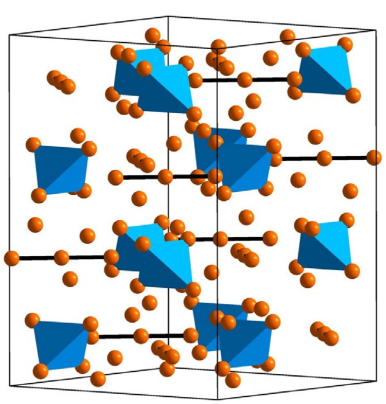


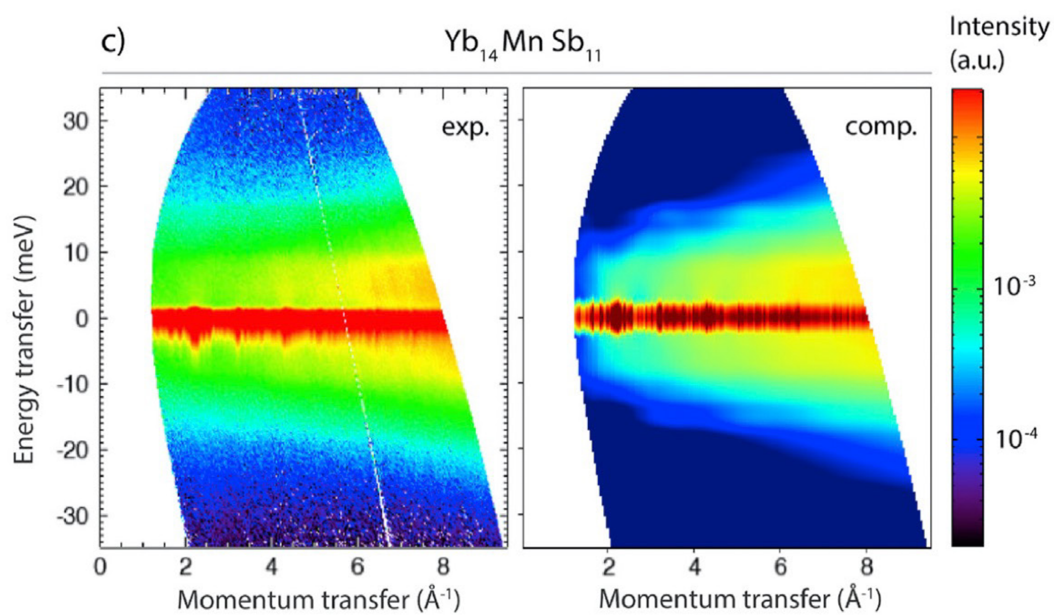
PbTe experiment (INS)

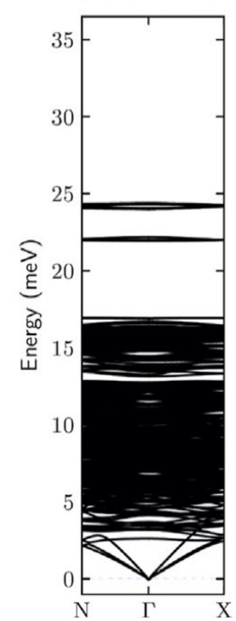


Delaire *et al.*, N

$Yb_{14}MnSb_{11}$
104 atoms/primitive cell







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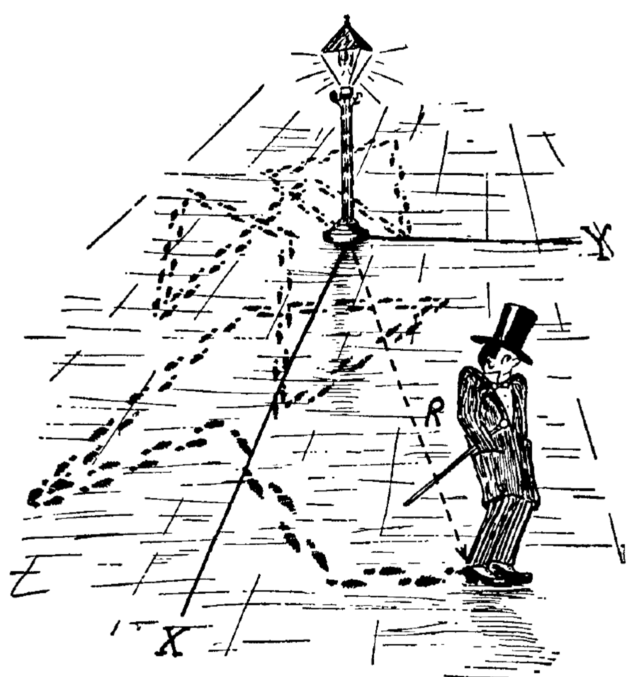
Northwestern Materials Science and Engineering

Hanus, Snyder *Materials Today Physics*, ***18***, 100344 (2021)

Minimum Thermal Conductivity by Diffusive Heat Transport



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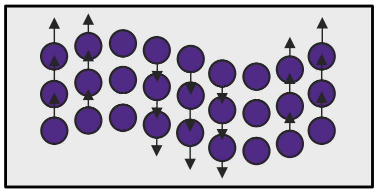
Propagons vs Diffusons

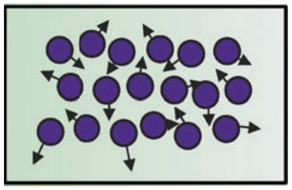
Propagon Phonons



Ballistic Transport

heat pulse travels as vt

Diffusons



Diffusive Transport

heat pulse travels as $\sqrt{Dt}$

PB Allen, et al. *Philos. Mag. B* **79**, 1715-1731 (1999).
F DeAngelis, O Henry, et al. Nano. Micro. Thermophys. Eng. (2018)

Generalized Atom Vibrations

Phonons = Eigenmodes of atom vibrations

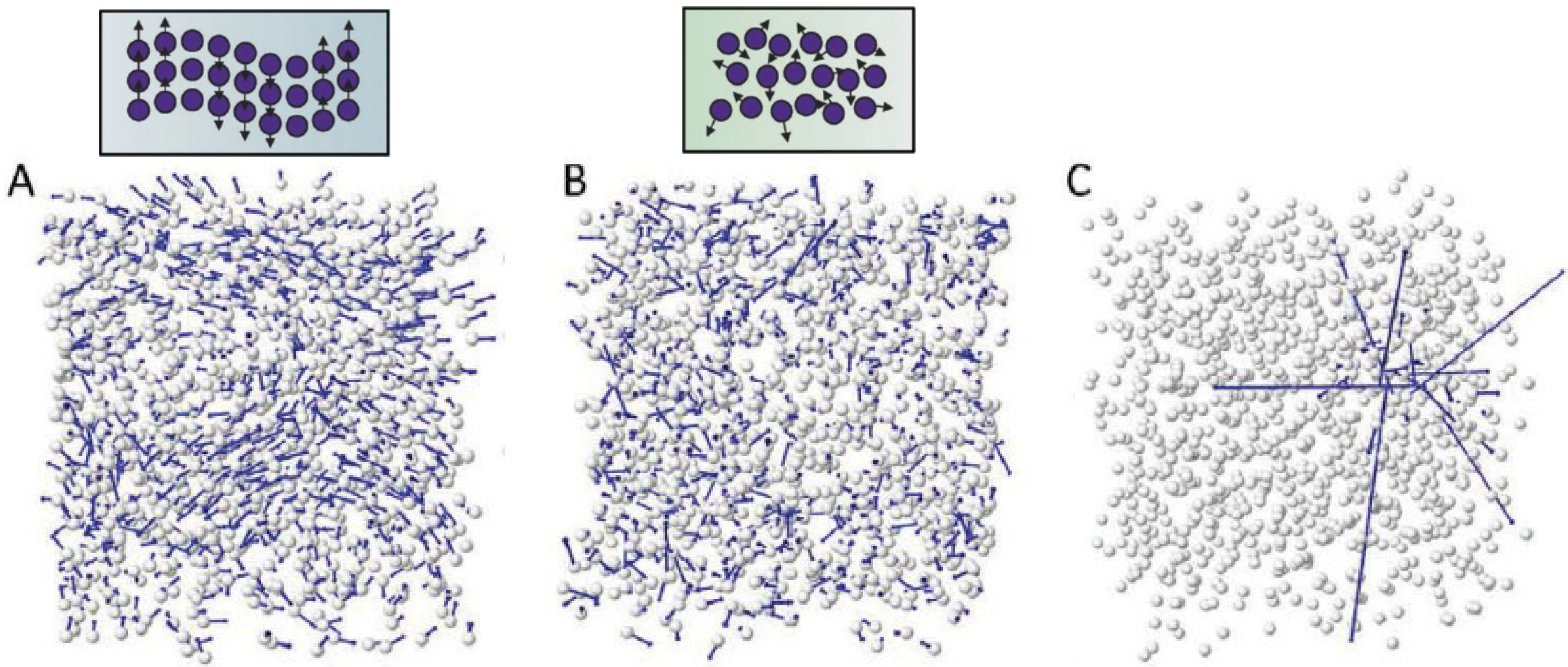
Propagons = Classical wave-like phonon modes. Acoustic waves in anything

transport energy linear with time $v_g t$

Diffusons = Eigenmodes with no apparent periodicity not localized

transport energy square-root with time $\sqrt{t}$

Locons = localized vibrational modes – do not transport heat effectively



Propagon Diffuson Locon

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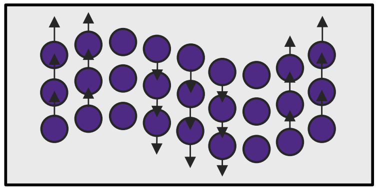
PB Allen, et al. *Philos. Mag. B* **79**, 1715-1731 (1999).
F DeAngelis, O Henry, et al. Nano. Micro. Thermophys. Eng. (2018)

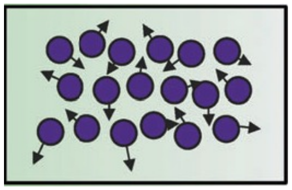
Diffusons in Complex Materials

Classical Phonons are good description in simple crystals

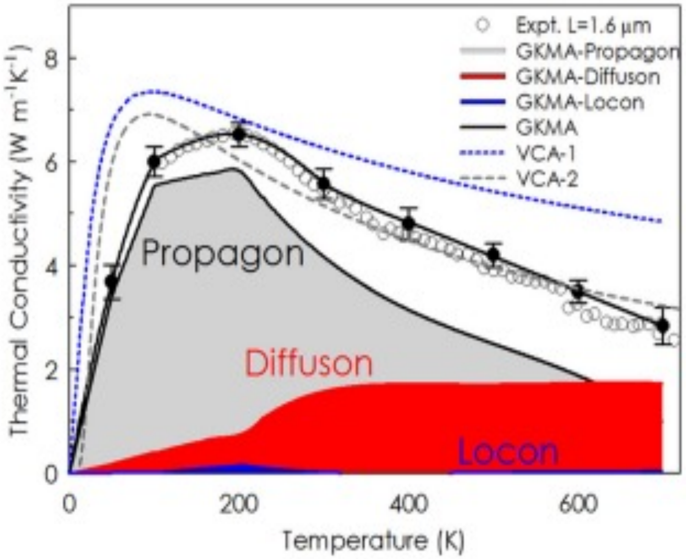
Diffusons dominate in Complex Materials

- amorphous, non crystalline materials
- disordered materials
- complex crystal structures
- high temperature
- strong phonon interactions

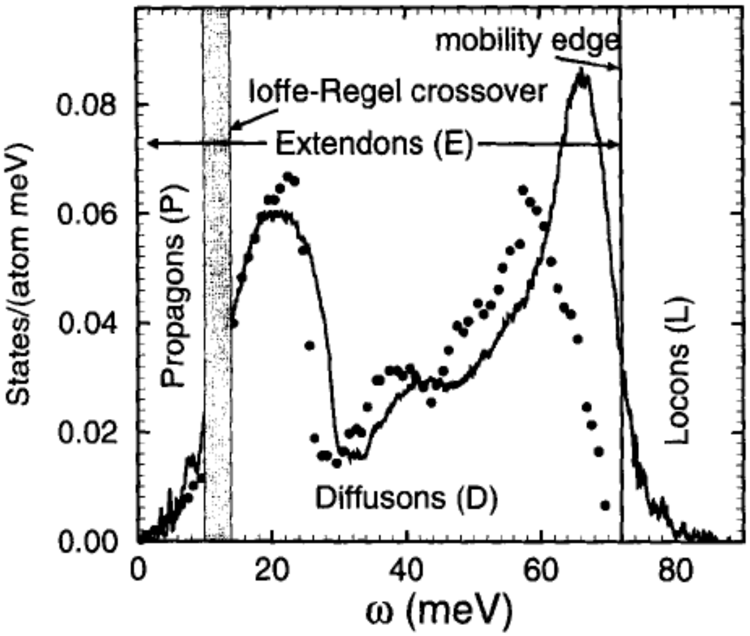




$In_{0.53}Ga_{0.47}As$



amorphous Si vibrational states



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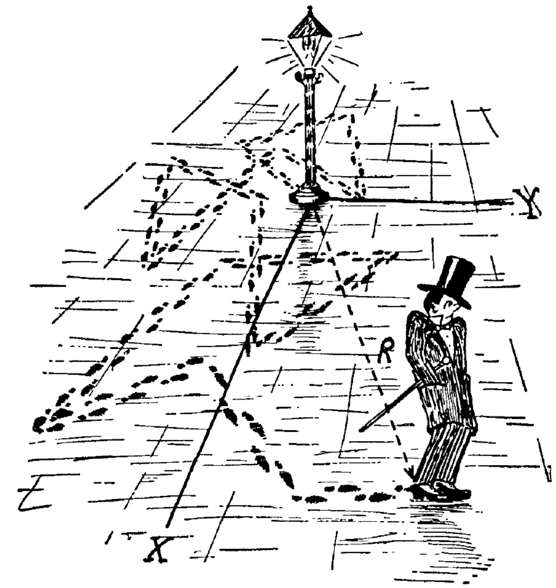
PB Allen, et al. *Philos. Mag. B* **79**, 1715-1731 (1999).
F DeAngelis, O Henry, et al. Nano. Micro. Thermophys. Eng. (2018)

Diffusive Thermal Conduction

$$\kappa = \tfrac{1}{3} c v \ell = \tfrac{1}{3} c f a^2$$



Minimum Phonon transport (Cahill)

min. mean free path $l(\omega) = \lambda/2$ wavelength/2

$$\kappa_{\mathrm{Cahill}} = 1.21\, n^{2/3}\, k_B \tfrac{1}{3}(2v_T + v_L)$$

Diffusive Heat Transport (Diffuson)

Random walk of heat energy

step length $a = l$ mean free path

attempt frequency $f = v/l$

$$\kappa_{\mathrm{Diff}} = 0.76\, n^{2/3} k_B \tfrac{1}{3}(2v_T + v_L)$$

c - heat capacity
v - speed of sound
τ - phonon relaxation time
$l = v\tau$ - mean free path
a = interatomic distance
n = number density of atoms
$V = a^3$ - volume per atom

Thermoelectrics
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Einstein (1911); Cahill, et al *Phys. Rev. B.*, **46** 6131 (1992)
Agne, *Energy Environ. Sci.* **11**, 609 (2018)

Thermal Conductivity model

$$\kappa_L = \kappa_U + \kappa_{optic}$$
$$= \frac{A}{T} + B$$

Acoustic phonons

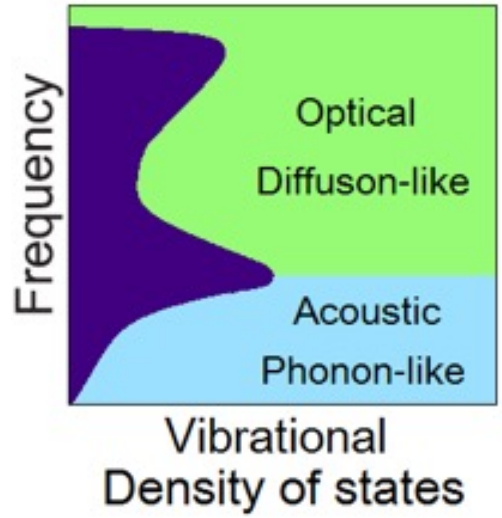
Umklapp Scattering

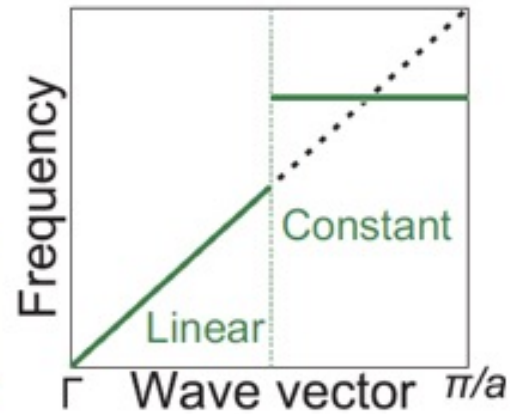
$$\kappa_U \sim 0.385 \frac{\bar{M} v_s^3}{T V^{\frac{2}{3}} \gamma^2} N^{\frac{-1}{3}}$$

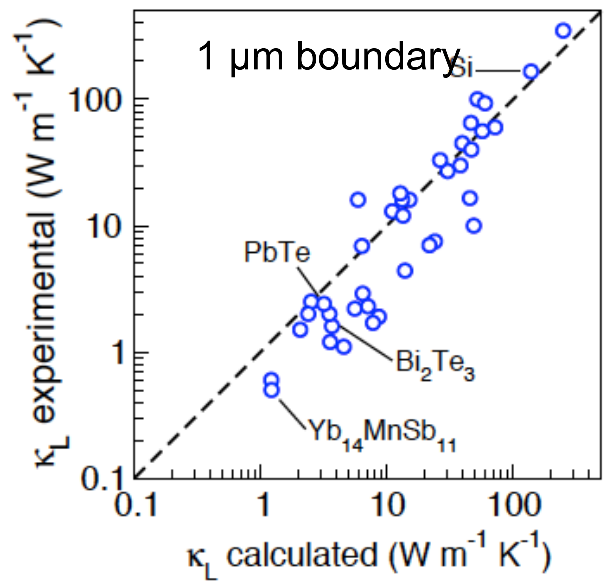
Optical phonons at κ_{min}

Diffuson or Cahill model

$$\kappa_{optic} \sim 1.2 \frac{k_B v_s}{V^{\frac{2}{3}}} \left(1 - N^{\frac{-2}{3}}\right)$$



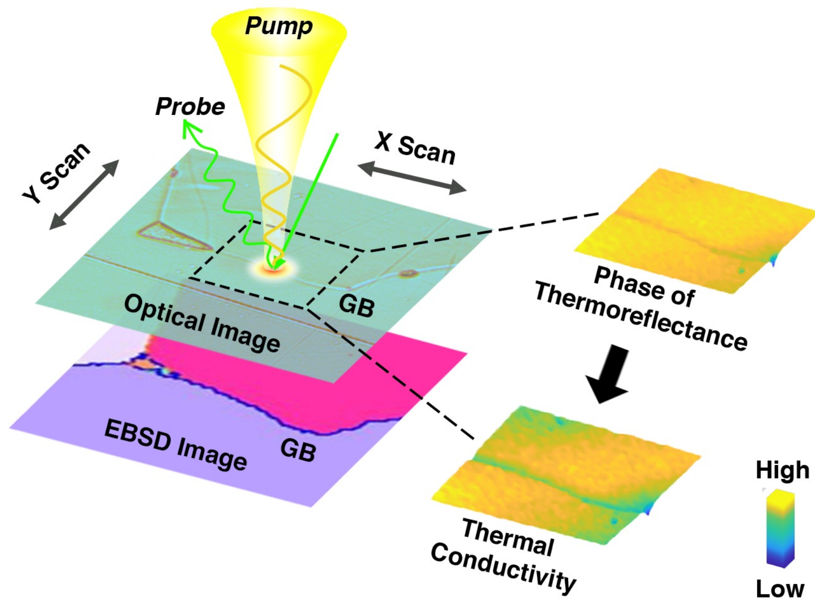


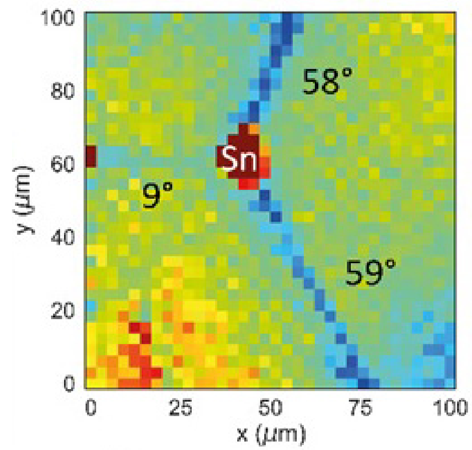


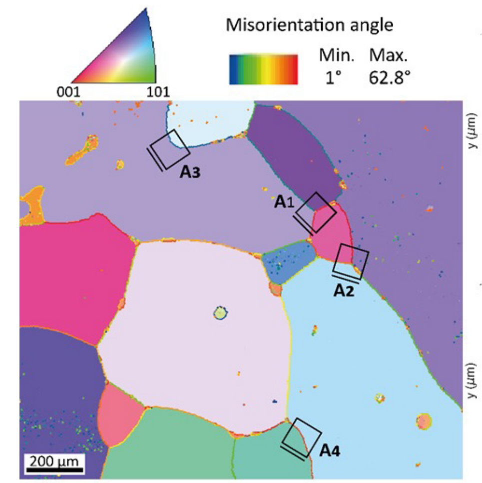
Toberer, GJS *J. Mat. Chem.*, **21,** 15843 (2011); *National Sci. Rev.*, **6**, 380 (2019)

Scanning Thermal Images

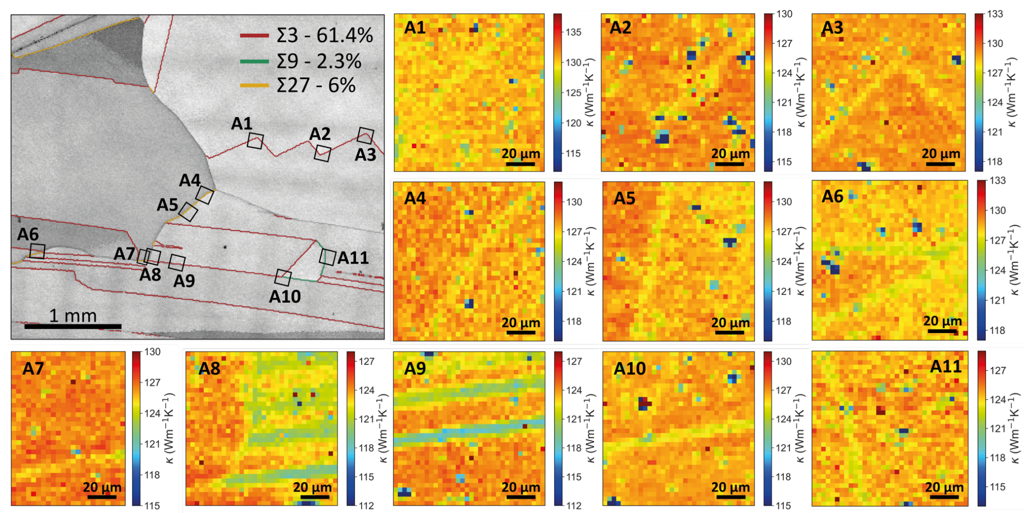
SnTe







Si



Spatially-resolved frequency domain thermoreflectance (FDTR)

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Northwestern Materials Science and Engineering

Isotta, GJS, et al, *Adv. Mater.* 2302777 (2023)
Isotta, GJS, et al, *Adv. Functinal Mater*. in press (2024)

Homogeneous Assumption

Homogeneous Models

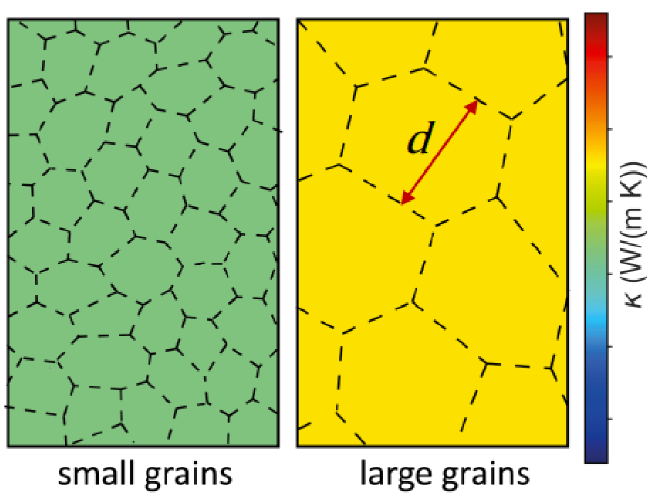
Klemens-Callaway

$$\kappa_l = \frac{1}{3}\int C_s(\omega) v_g^2(\omega)\tau(\omega)\, d\omega$$

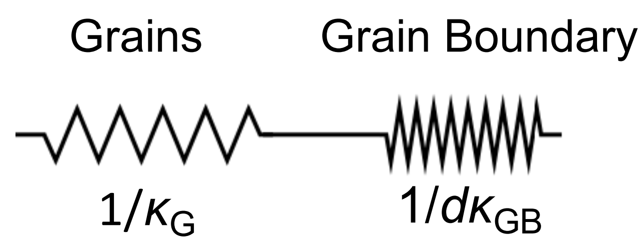
Lattice or Phonon thermal conductivity

$$\tau^{-1} = \frac{v}{d} + C_{DS}N_D B_D^2\omega + C_U T\gamma^2\omega^2 + C_{PD}\omega^4$$

boundary ($\frac{v}{d}$), dislocation ($C_{DS}N_D B_D^2\omega$), Umklapp ($C_U T\gamma^2\omega^2$), point defect ($C_{PD}\omega^4$)

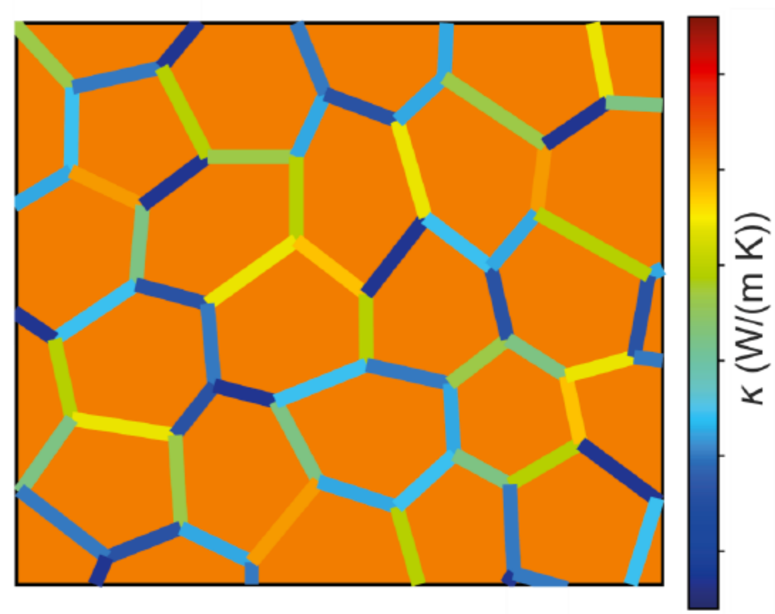


InHomogeneous Model



Series Circuit Model for Thermal Resistivity

Actual local κ



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Isotta, GJS, et al, *Adv. Mater.* 2302777 (2023)
Isotta, GJS, et al, *Adv. Functional Mater.* in press (2024)

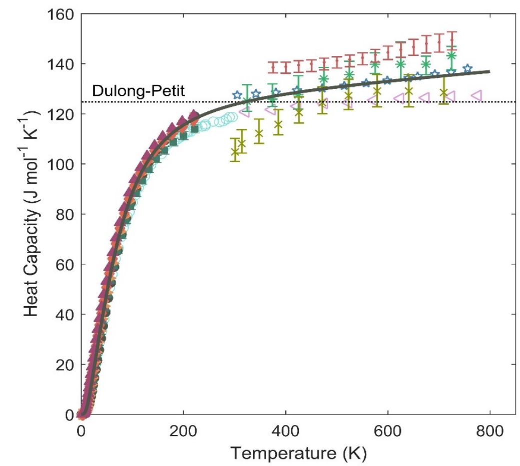
Summary

Heat Capacity – Specific Heat

Dulong Petit $3k_B$/atom above $\Theta_D/2$

Thermal expansion adds a linear *T* term

Watch out for phase transformations



Thermal Conductivity

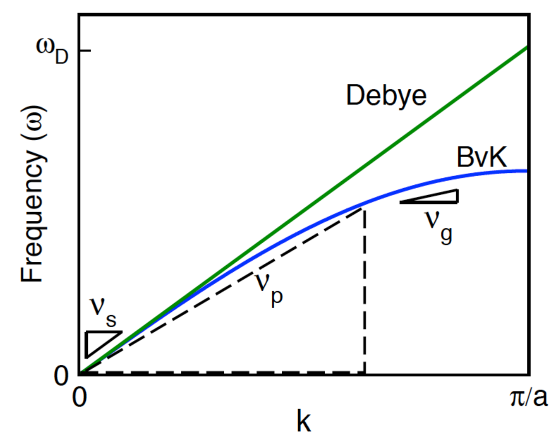
κ = A/T + B

A from classical phonon transport

$$C_s = \frac{3k_B}{2\pi^2}\frac{\omega^2}{v_g v_p^2}$$

- Mostly Acoustic Phonons
- $v_s = v_g = v_p$ speed of sound
- Grüneisen γ from thermal expansion
- τ_{PD} from mass (+strain) disorder

$$\gamma = \frac{3\alpha_{cte}B}{c_V}$$



B from diffuson heat transport

$$\kappa_{\text{Diff}} = 0.76\, n^{2/3} k_B \tfrac{1}{3}(2v_T + v_L)$$

$$\kappa_l = \frac{1}{3}\int C_s(\omega) v_g^2(\omega)\tau(\omega)d\omega$$

Excess Interface Resistance

- instead of boundary term
- adds $1/d\kappa_{GB}$ in series

$$\tau^{-1} = \frac{v}{d} + C_{DS}N_D B_D^2\omega + C_U T\gamma^2\omega^2 + C_{PD}\omega^4$$

boundary?
dislocation strain
phonon-phonon (Umklapp)
point defect

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Electronic Properties of Complex Semiconductors

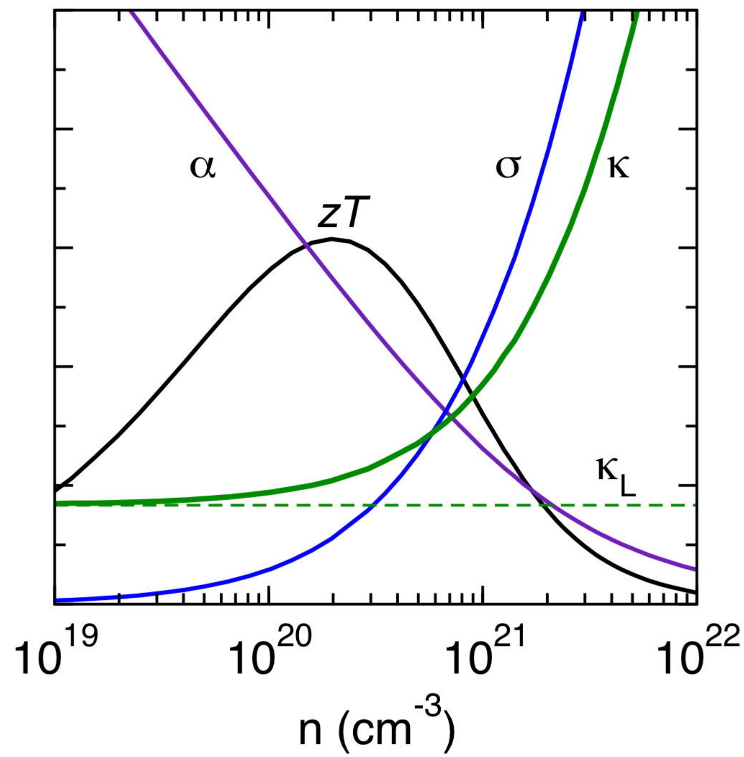
G. Jeffrey Snyder
Northwestern University
http://thermoelectrics.matsci.northwestern.edu/thermoelectrics/index.html#electronic

Thermoelectric Quality Factor

$$B \sim \frac{\mu_W}{\kappa_L}$$

Weighted Mobility (μ_W)

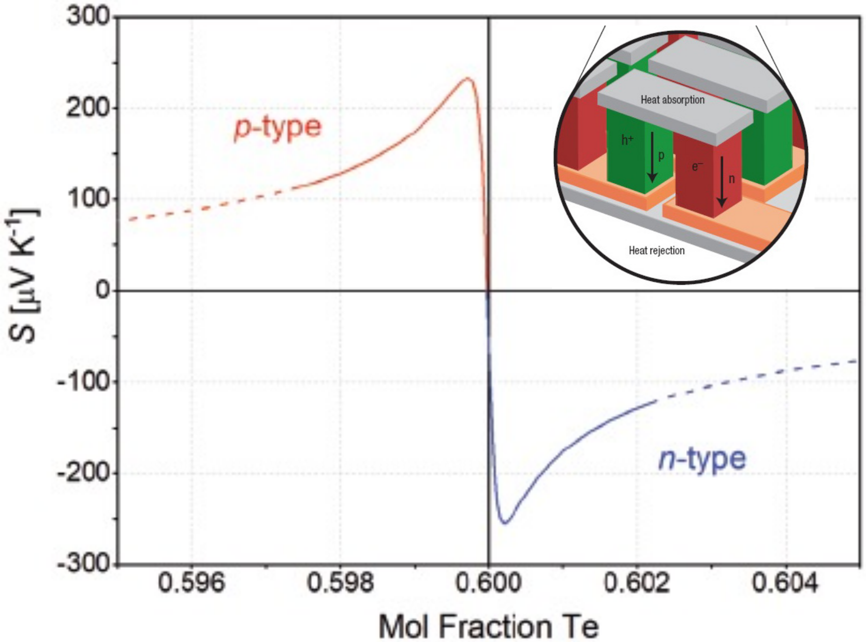
Lattice Thermal Conductivity (κ_L)

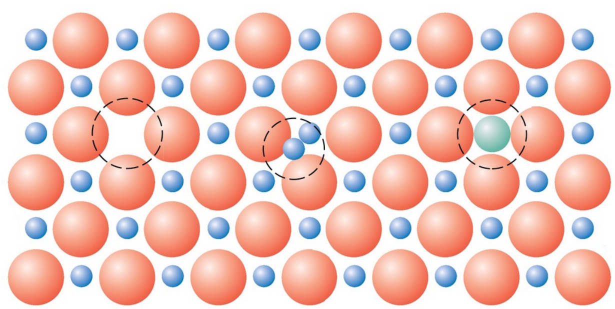


Pei, Wang, Snyder Advanced Materials **24**, 6125 (2012).

Thermoelectric Semiconductor

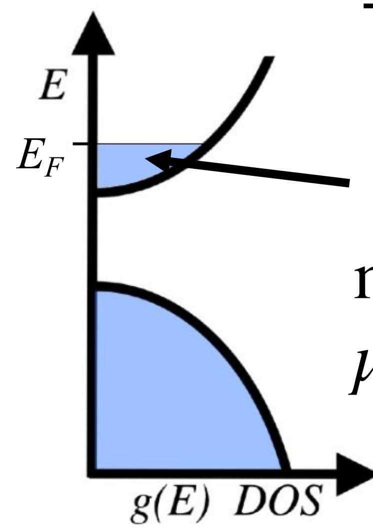
Bi_2Te_3





Doping from Charged Defects

n-type Thermoelectric

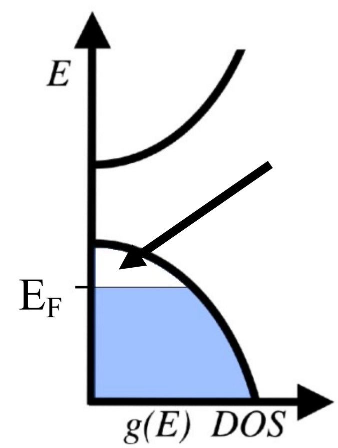


n electrons in conduction band

m_e^* effective mass

μ_e mobility

p-type Thermoelectric



n holes in valence band

m_h^* effective mass

μ_h mobility

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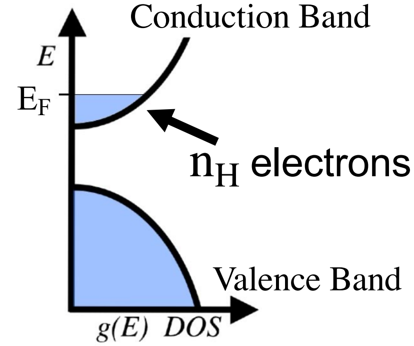
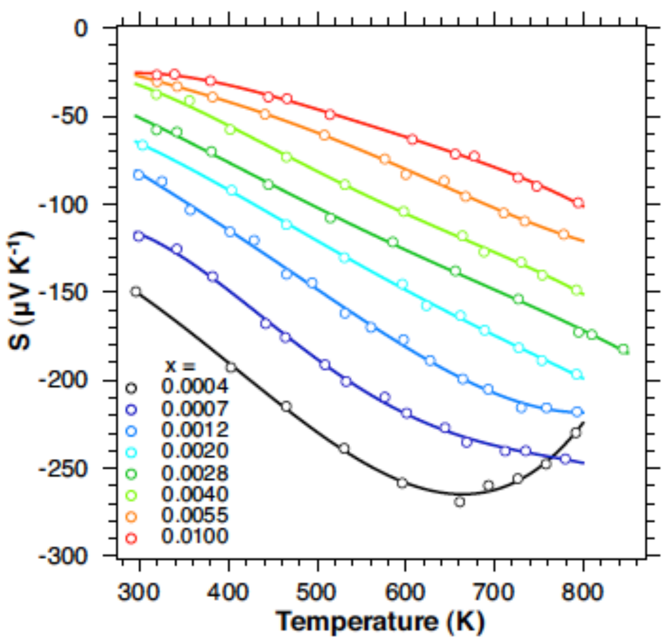
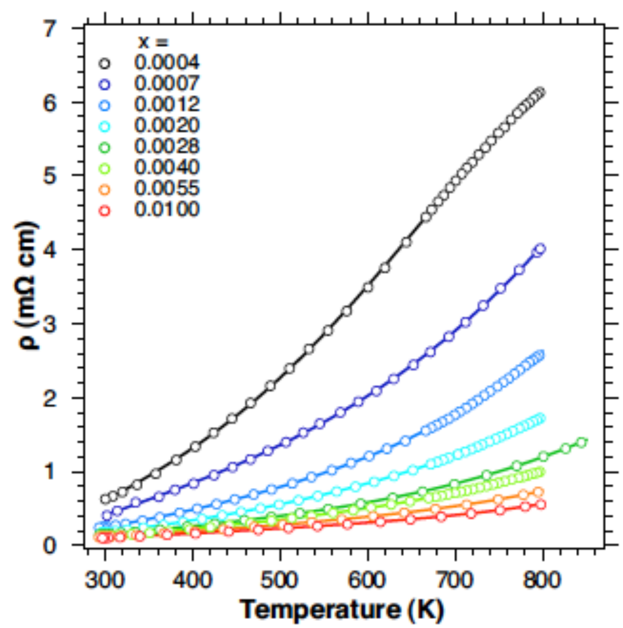
Toberer, May, Snyder *Chem. Mat.*, **22**, p. 624 (2010)
Zeier, Snyder, et al. *Angew. Chem. Int. Ed.* **55,** 6826 (2016)

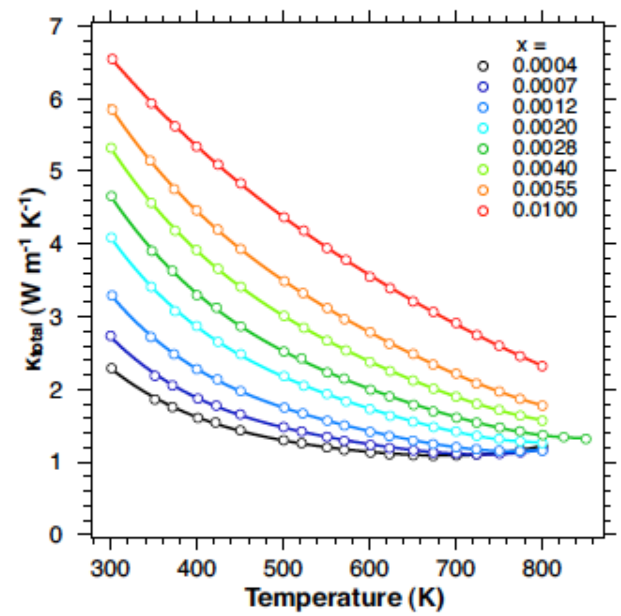
Degenerate Semiconductor Behavior

1. Linear Thermopower |S| or |α|
2. Increasing, ~linear, Resistivity $\rho = 1/\sigma$
3. $1/T + C + L\sigma T$ Thermal Conductivity









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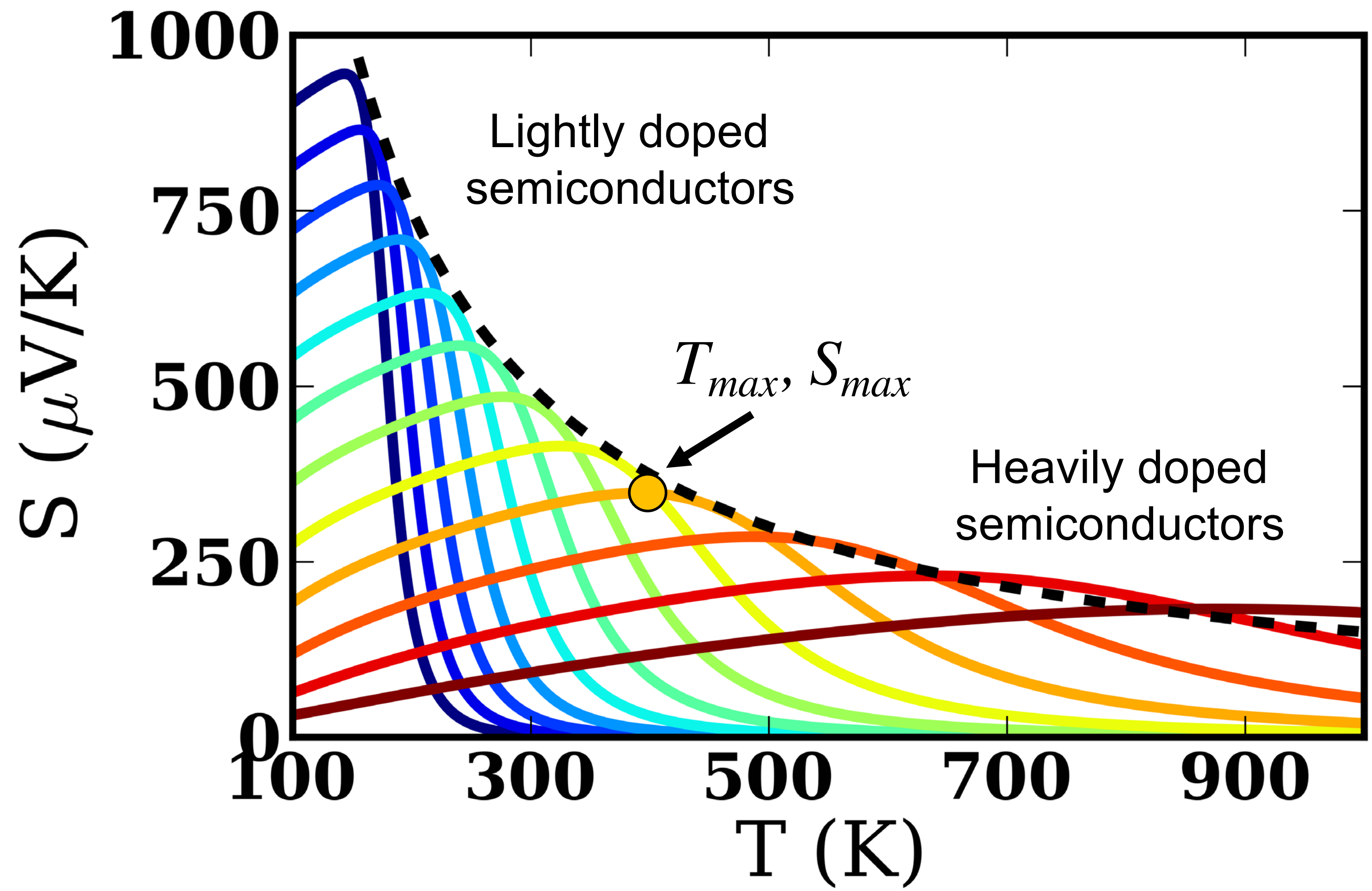
Goldsmid-Sharp Maximum Seebeck

Doping changes S vs T

But peak S is limited by E_g

$$E_g = 2eS_{max}T_{max}$$



H. J. Goldsmid and J. W. Sharp, J. Electron. Mater. **28**, 869 (1999)
Gibbs, H-S Kim, GJS *Appl. Phys. Lett.* **106**, 022112 (2015)

TE Quality Factor

Maximum zT depends on Quality Factor

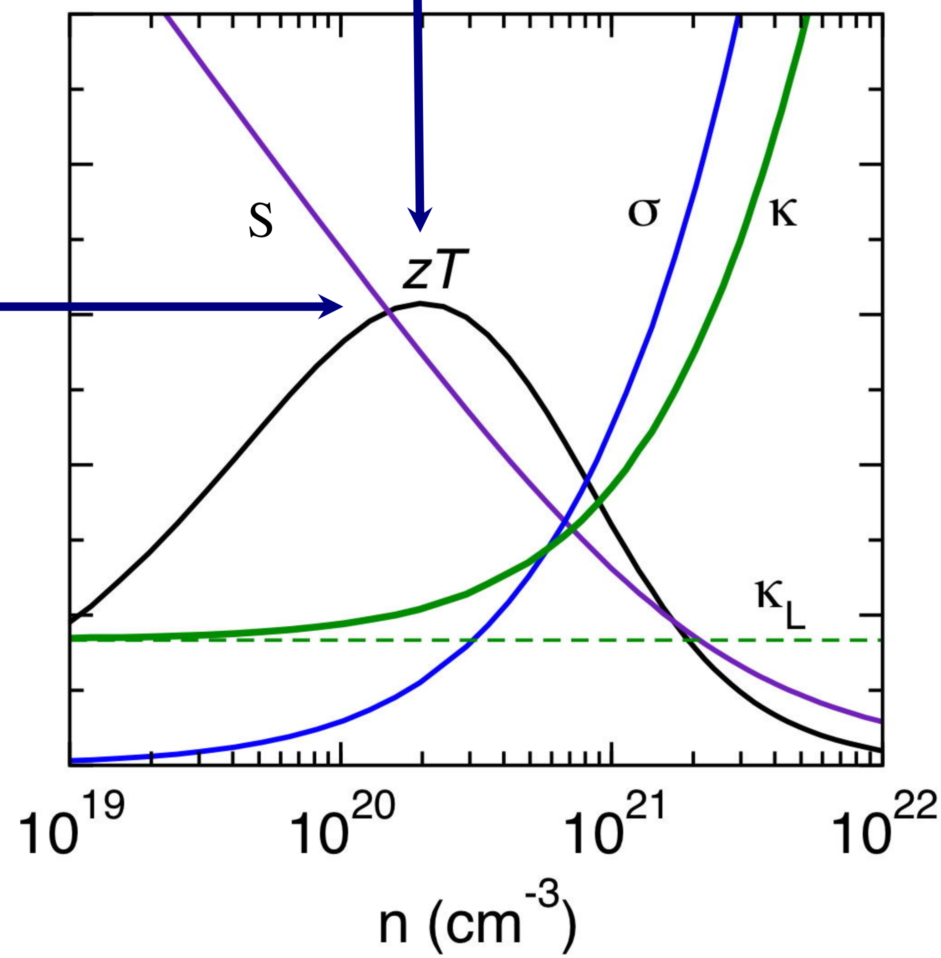
$$B = \frac{\mu m^{*3/2}_{DOS}}{\kappa_L}$$

Weighted Mobility μ_w

Density of States
effective mass m^*_{DOS}

κ_L Lattice Thermal Conductivity

Optimized carrier concentration



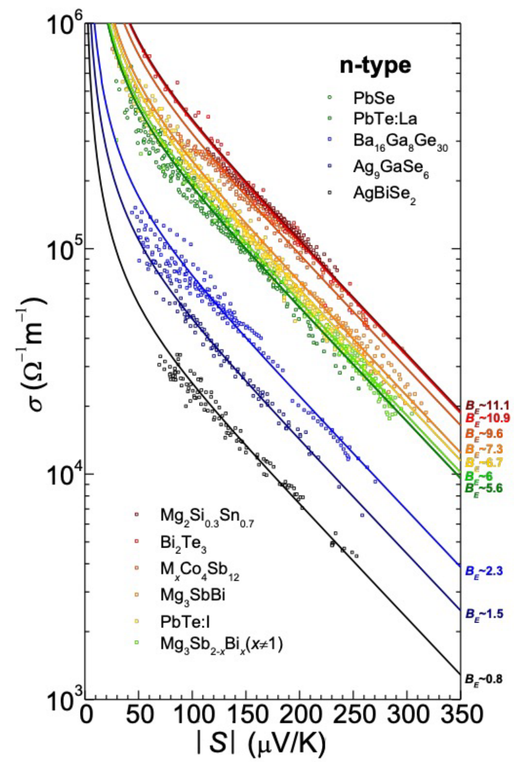
Pei, Wang, Snyder Advanced Materials **24**, 6125 (2012)

Weighted Mobility

Single parameter for *S* vs σ curves

$$\mu_w = \mu_0 \left(\frac{m^*_{DOS}}{m_e}\right)^{3/2}$$

Density of States



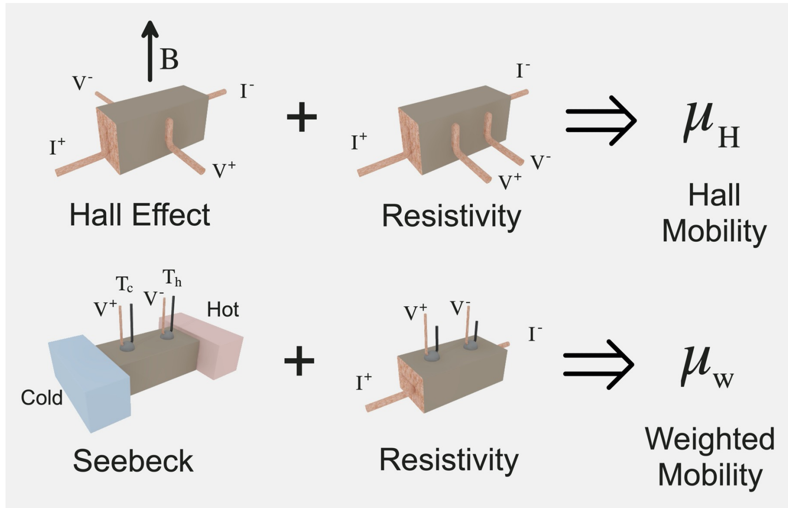
Define weighted mobility as simply a function of $|S|$ and σ

$$\mu_w \equiv 331\frac{\mathrm{cm}^2}{\mathrm{Vs}}\left(\frac{m\Omega\mathrm{cm}}{\boldsymbol{\rho}}\right)\left(\frac{T}{300\mathrm{K}}\right)^{-3/2}\left[\frac{exp\left[\frac{|S|}{k_B/e}-2\right]}{1+exp\left[-5\left(\frac{|S|}{k_B/e}-1\right)\right]}+\frac{\frac{3}{\pi^2}\frac{|S|}{k_B/e}}{1+exp\left[5\left(\frac{|S|}{k_B/e}-1\right)\right]}\right]$$

$k_B/e = 86\,\frac{\mu\mathrm{V}}{\mathrm{K}}$ $\qquad \varrho = 1/\sigma$

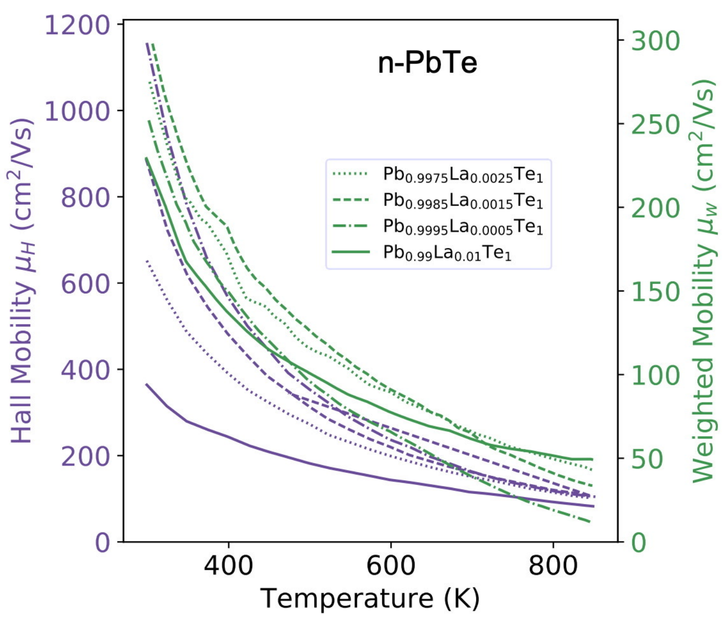
Snyder et. al. *Advanced Materials*, **32**, 2001537 (2020)

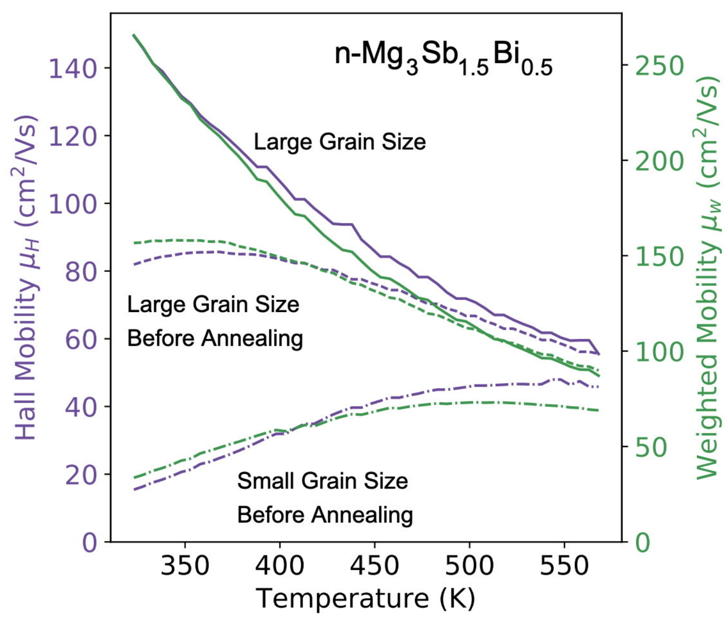
Hall and Weighted Mobility



$$\mu_{\mathrm{H}} = \sigma R_{\mathrm{H}}$$

$$\mu_{\mathrm{w}} = \mu_0 \left(\frac{m^*_{DOS}}{m_e}\right)^{3/2}$$





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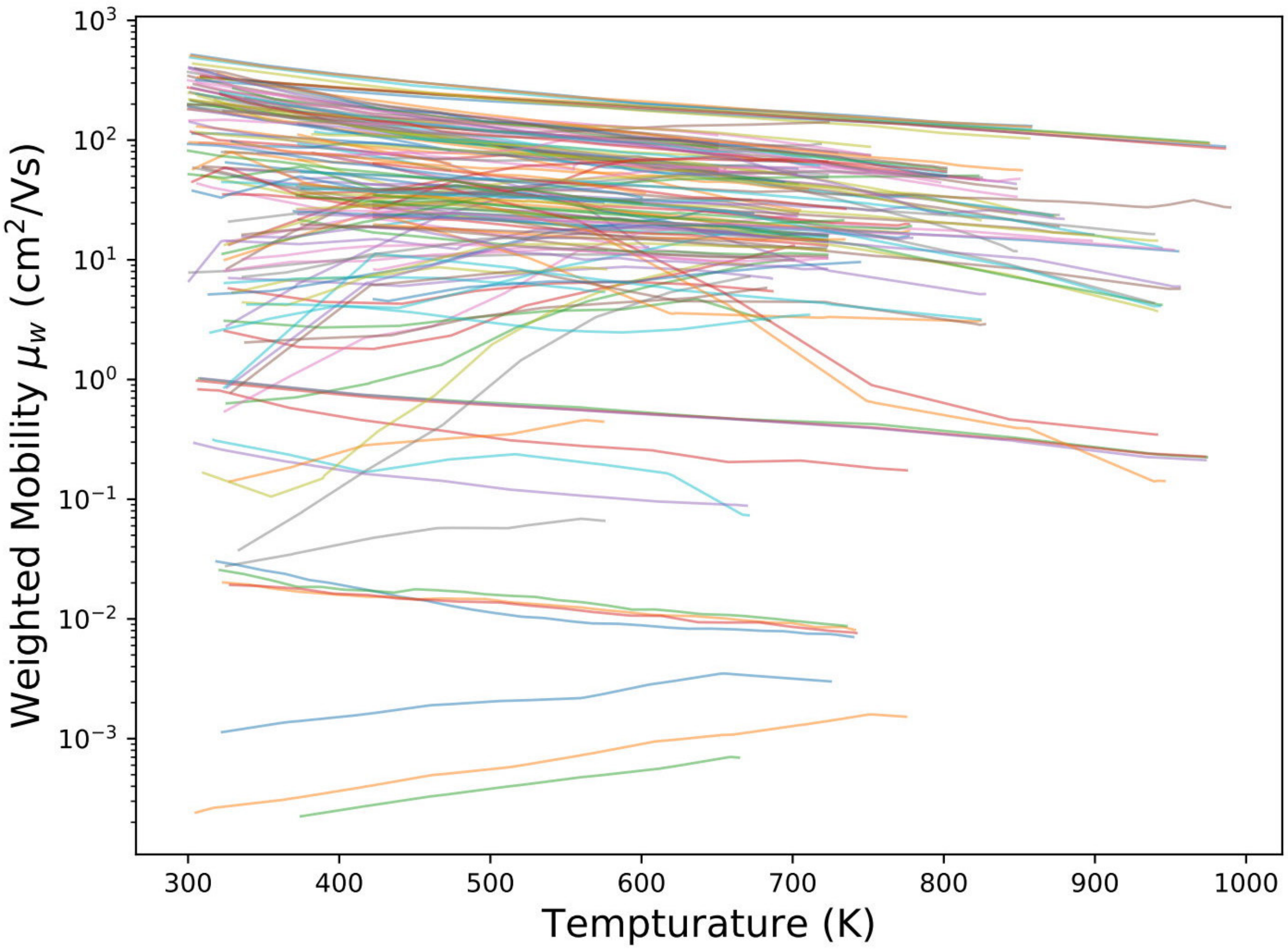
Snyder et. al. *Advanced Materials*, **32**, 2001537 (2020)

Weighed mobility for other materials

Typical Thermoelectric semiconductors



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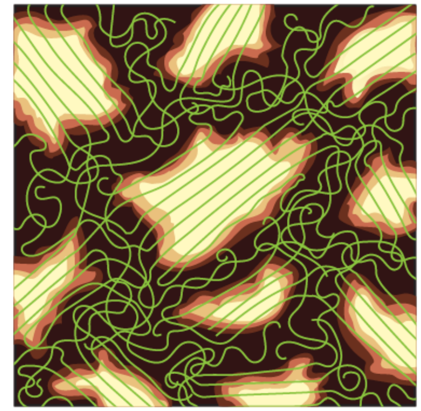
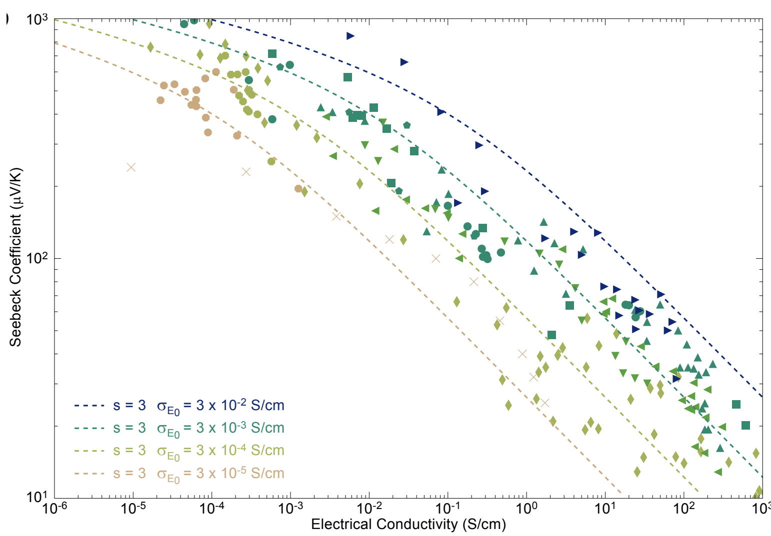
StarryData in *Advanced Materials*, **32**, 2001537 (2020)

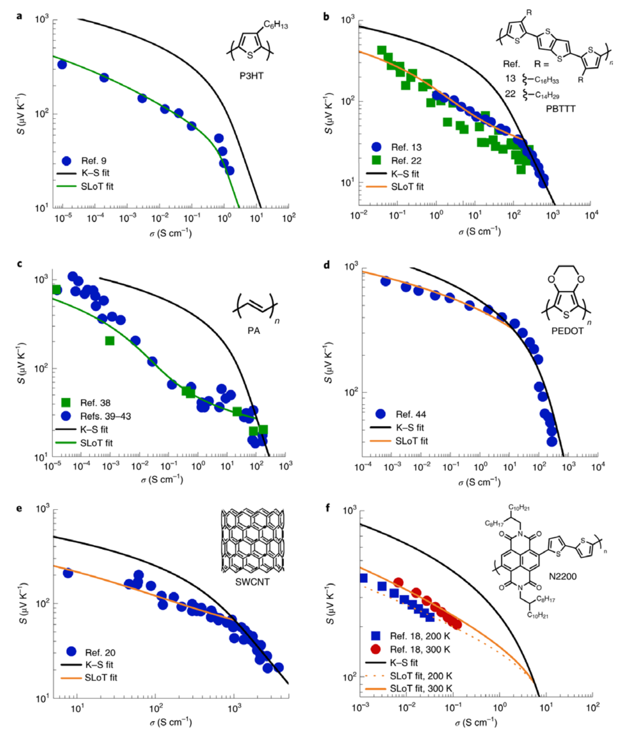
μ_W for Conducting Polymers

- Model how properties change with doping
- Helps identify transport mechanism
- Quantify Localization
- Predicts peak S²σ



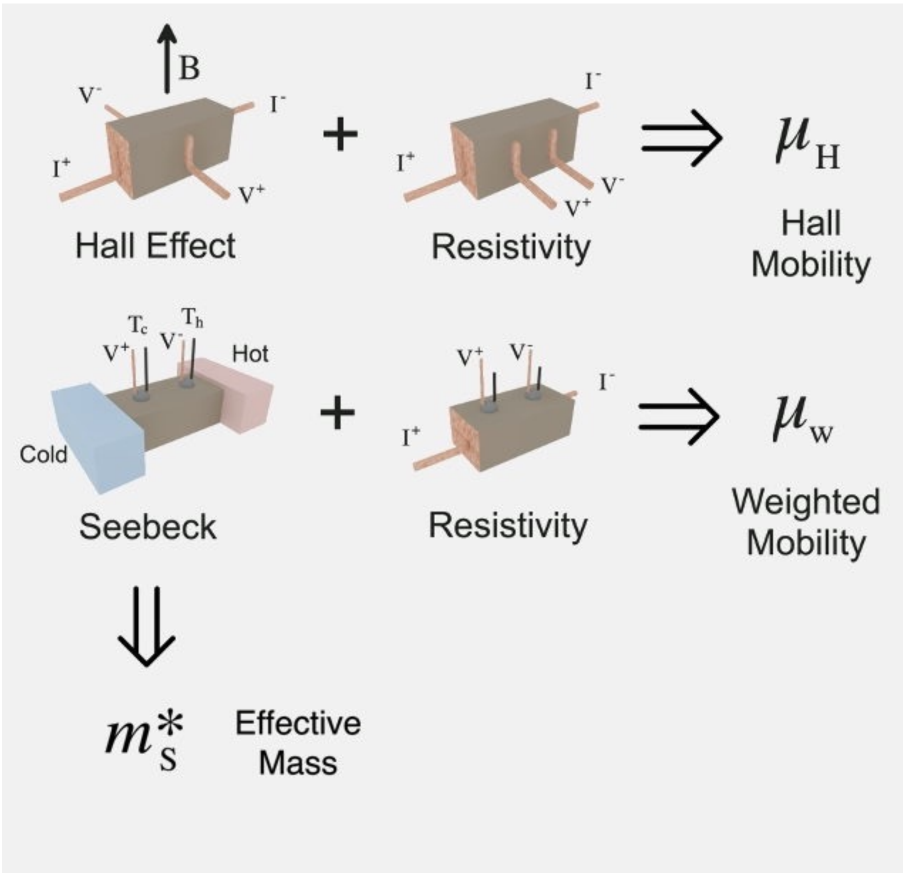


polyacetylene (◆); PBTTT (■◀); P2TDC17-FT4 (⬟)
P3HT (●▲); PDPP3T (▶); PSBTBT (▼); P3HTT (⬣)



S. Kang and Snyder, *Nature Materials* **16**, 252 (2017)
S. Gregory et al, Nature Materials **20**, 1414 (2021)

Effective Mass from Seebeck



DOS Effective Mass

$$DOS \propto (m^*_{DOS})^{3/2}$$

Historically from low temperature (1-10K) heat capacity $C_P = \gamma T$

From Seebeck and Hall (10K-1500K)

$$\mu_w = \mu_0 \left(\frac{m^*_{DOS}}{m_e}\right)^{3/2}$$

Weighted Mobility

$$\mu_H = \mu_d r_H$$

Hall Mobility

$$\frac{m_S^*}{m_e} \equiv 0.924\left(\frac{300\text{K}}{T}\right)\left(\frac{n_H}{10^{20}cm^{-3}}\right)^{2/3}\left[\frac{3\left(exp\left[\frac{|S|}{k_B/e}-2\right]-0.17\right)^{2/3}}{1+exp\left[-5\left(\frac{|S|}{k_B/e}-\frac{k_B/e}{|S|}\right)\right]}+\frac{\frac{|S|}{k_B/e}}{1+exp\left[5\left(\frac{|S|}{k_B/e}-\frac{k_B/e}{|S|}\right)\right]}\right]$$

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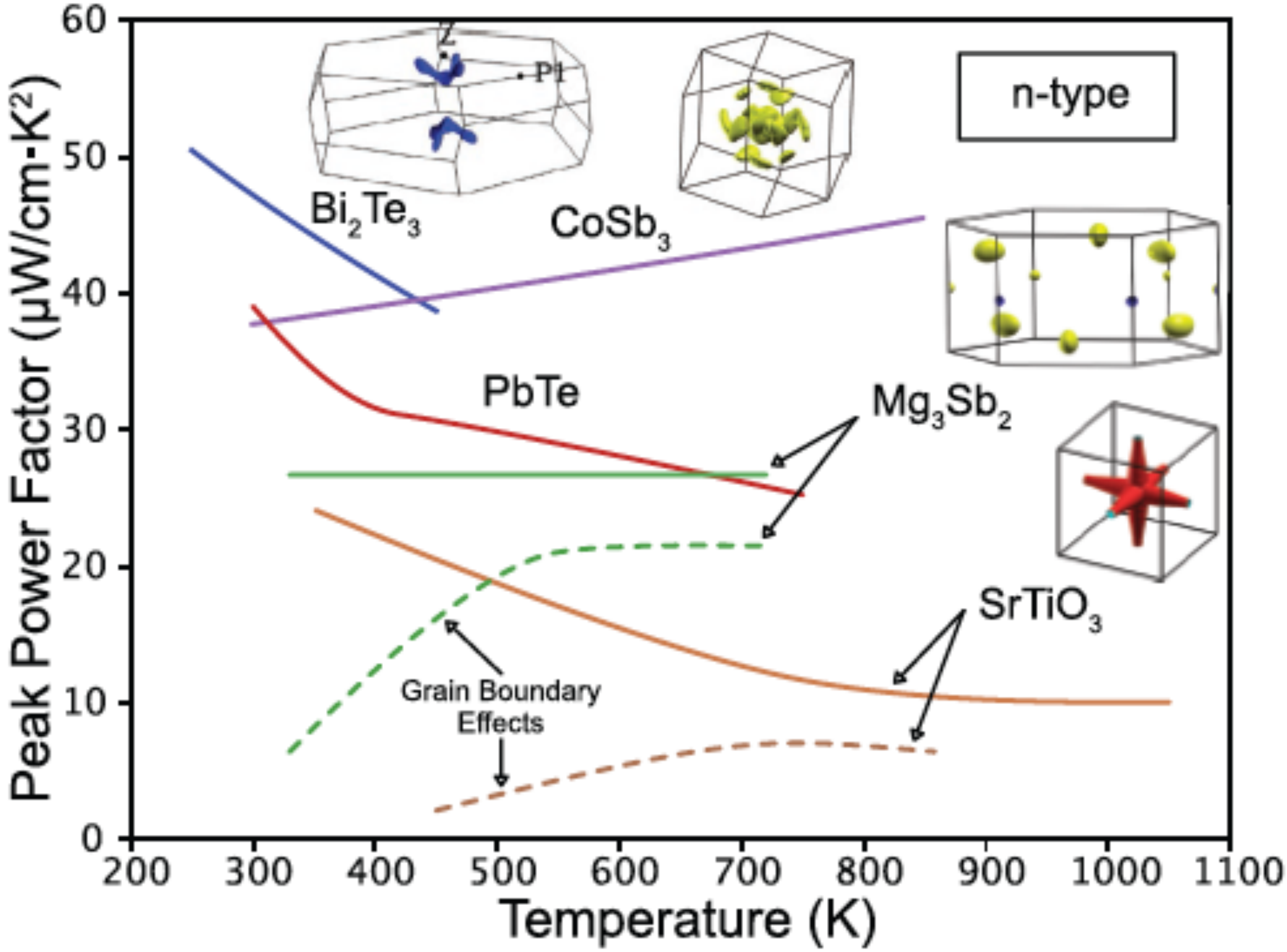
Snyder et. al. *Advanced Functional Materials*, 202112772 (2022)

High DOS Complex Fermi Surfaces

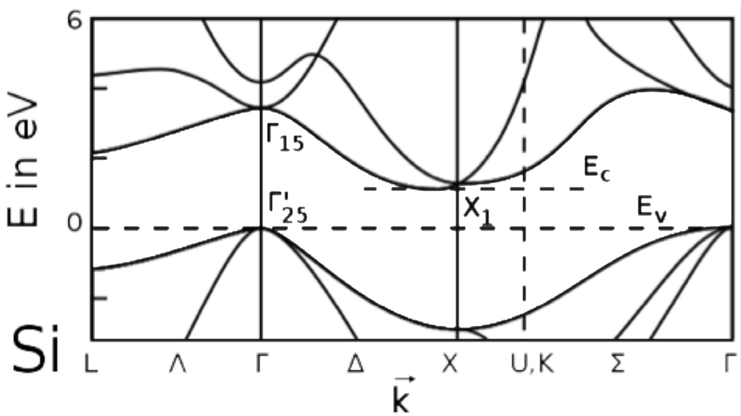


DOS and Valley Degeneracy N_V

N_V is number of carrier pockets (valleys)

Spherical Fermi Surface

- free-electron model

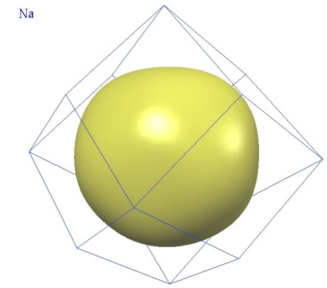


Multiple valley when:

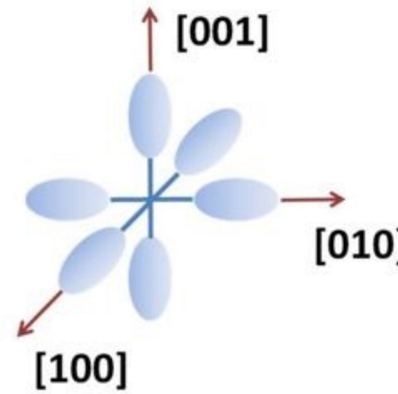
- Symmetrically equivalent (not at Γ)
- Different bands at band gap (orbital degeneracy)

Fermi Surfaces

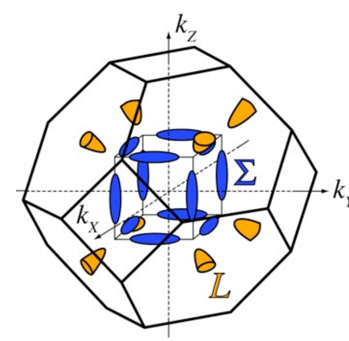
Na
$N_v = 1$



Si
$N_v = 6$

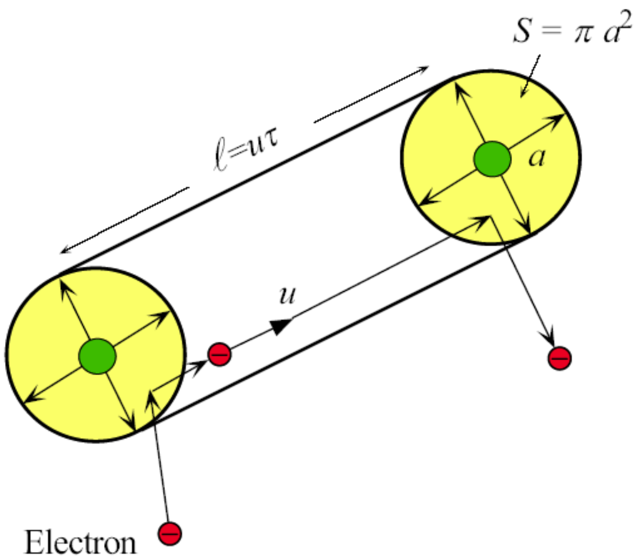


PbTe
v: $N_v = 4, 12$
c: $N_v = 4$



Phonon Scattering of Electrons

Atom Vibrations (phonons)



$$\tau = \frac{1}{S v N_s} \qquad \mu = \frac{e\tau}{m^*}$$

Metal	Semiconductor
$v_F = \text{constant}$	$\frac{1}{2} m v_{th}^2 = k_B T$
$\mu_L \propto \frac{1}{T}$	$\mu_L \propto \frac{1}{T^{3/2}}$

Scattering Cross-section

$$S = \pi a^2 \propto k_B T$$

From equi-partition theorem
a^2 potential energy of atom
is proportional to $k_B T$

Resistivity $\rho = \frac{1}{ne\mu} \sim T^p$

$1 < p < 1.5$

not just acoustic phonon scattering

τ = mean time between scattering, v = mean speed of the electron,
N_s = concentration of scatterers, μ = mobility, n = charge carrier concentration

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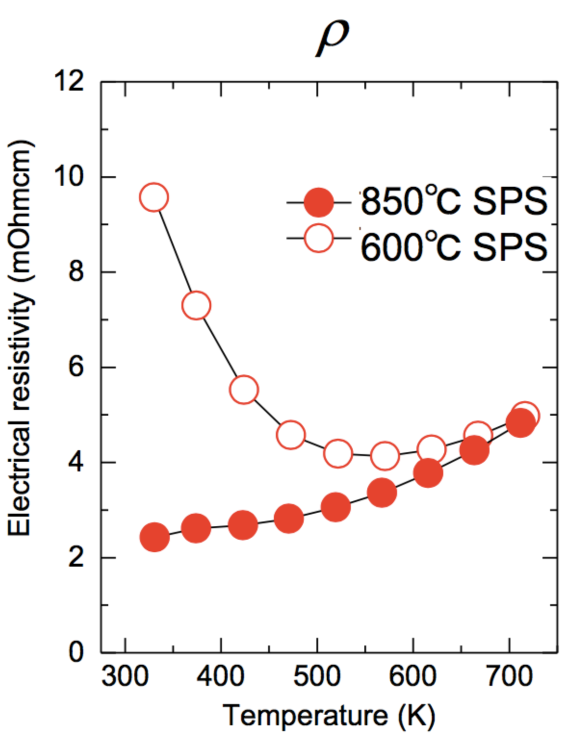
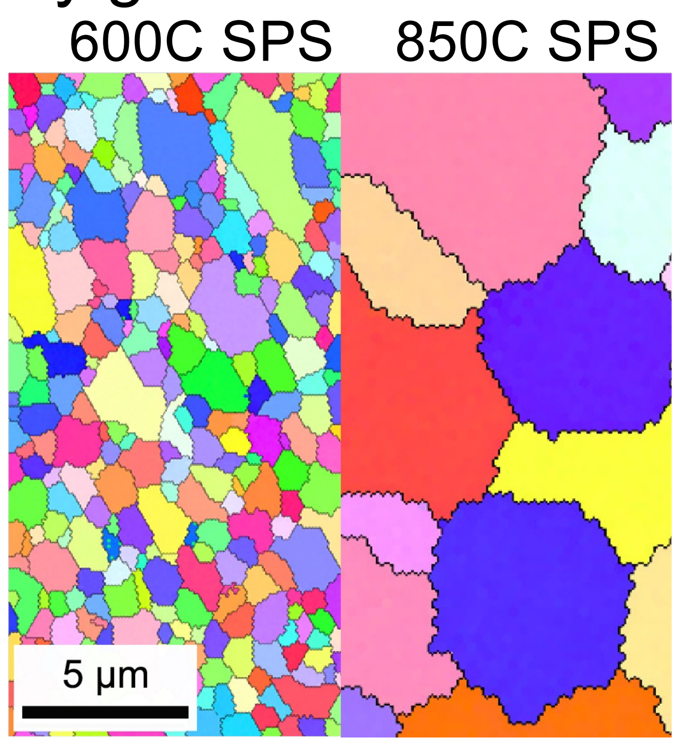
Grain Boundary Electrical Resistance

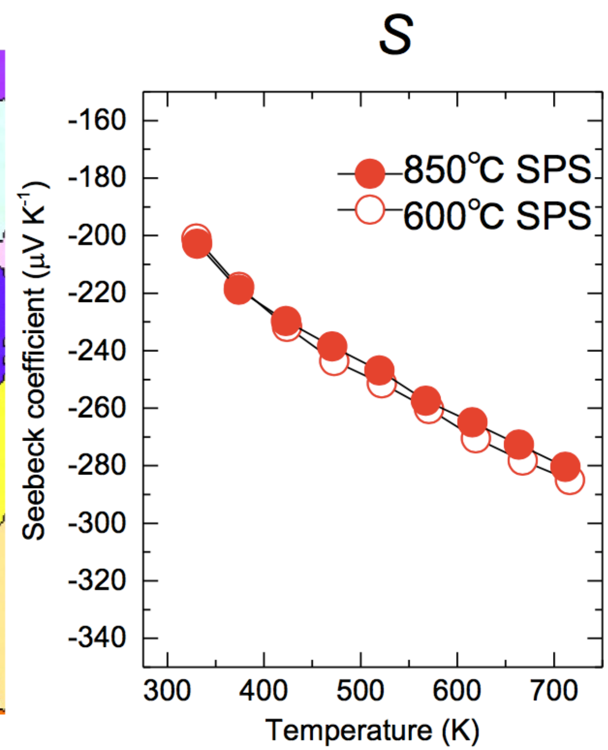
Thermally activated resistivity reduced by increasing the grain size

Seebeck unaffected by grain size





EBSD crystal-orientation maps



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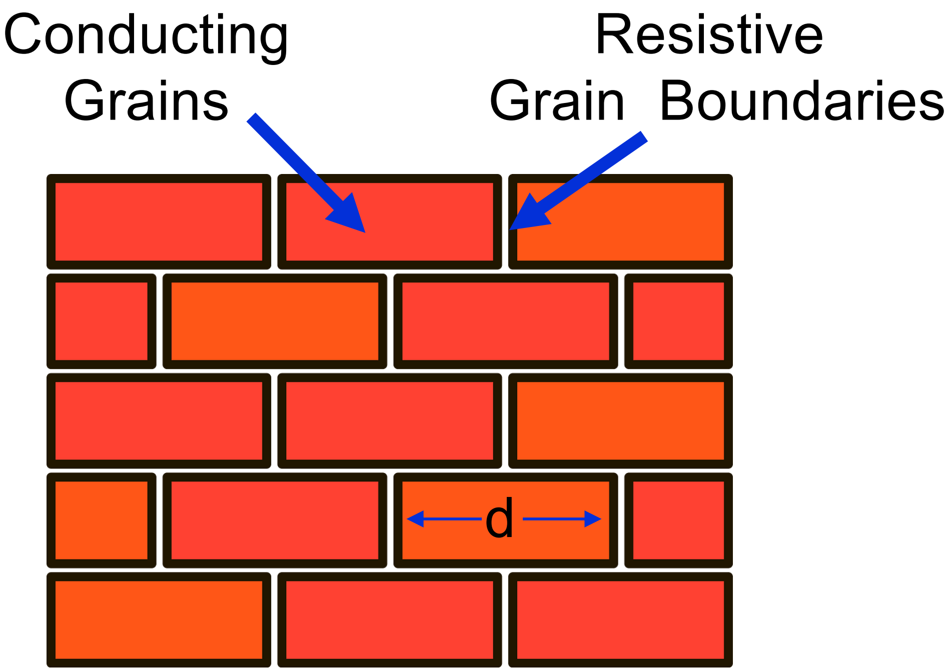
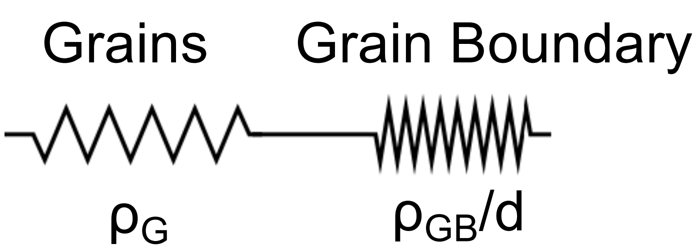
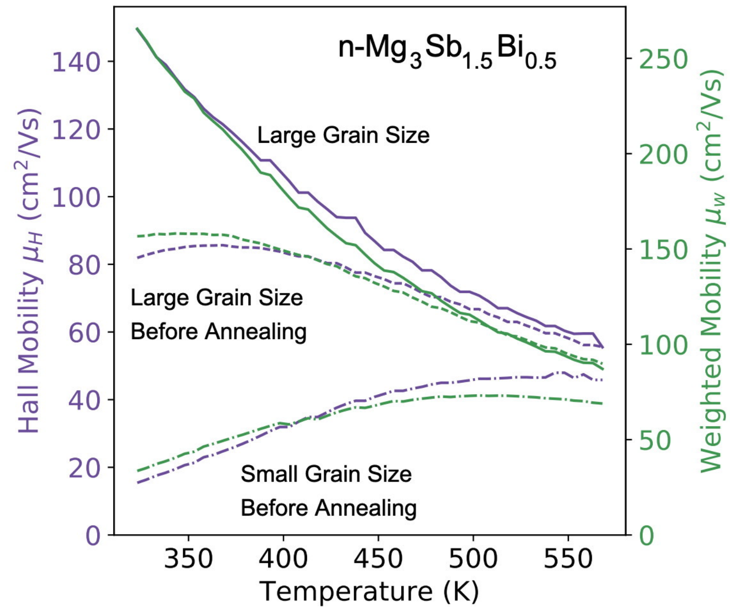
Kanno et. al., Appl. Phys. Lett. **112**, 033903 (2018)

Bricklayer Model





Series Circuit Model
For effective resistivity



Grain Boundary Resistance seen as thermally activated electron mobility

J.J. Kuo, M. Wood, et al. Energy Environ. Sci. **13**, 1250 (2020)