Electron Transport

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MSE485/385 Electronic and Thermal properties of materials

Thermoelectrics
Northwestern Materials Science and Engineering

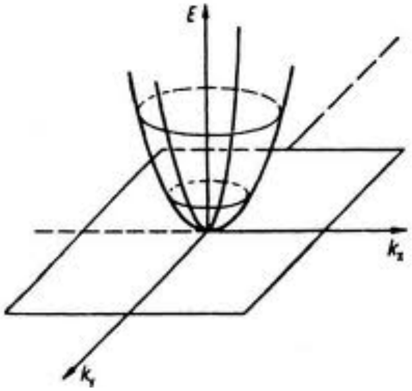
Mott and Jones *The Theory and Properties of Metals and Alloys* (1936)
Mott and Davis *Electronic Processes in Noncrystalline Materials* (1971)

Free Electron – Effective Mass

with Free electron-like (single parabolic) band (SPB)

mass has analogy to classical mechanics

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m^*}$$



and is commonly used for

electrical conductivity DOS, n, cyclotron

$$\sigma = \frac{ne^2\tau}{m^*} \qquad \mu = \frac{e\tau}{m^*}$$

a common definition is effective mass tensor

$$\frac{1}{m^*_{ij}} = \frac{\partial^2 E}{\hbar^2 \partial k_i \partial k_j}$$

but how is it related to measurements ?

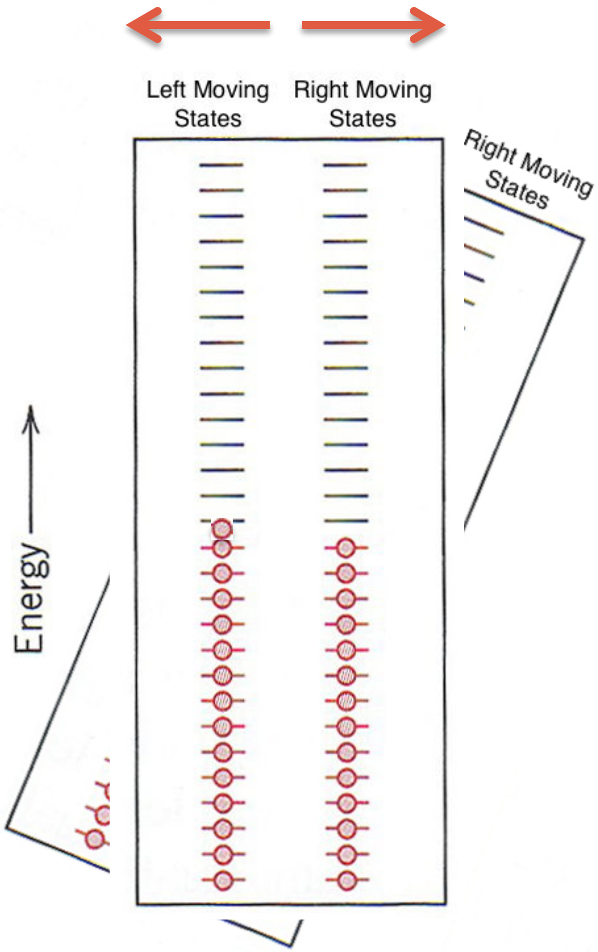
σ = conductivity
f = Fermi function
ζ = chemical potential
g = DOS
v = velocity
τ = relaxation time
E = energy
T = temperature

Wilson *The Theory of Metals* (1954)

Electric Conduction in Bands

Electric Field

- Energy increased for electrons moving opposite to Electric Field
- Shifting Electron population creates net electrical current
- In a Metal the smallest Electric Field is enough to shift electrons



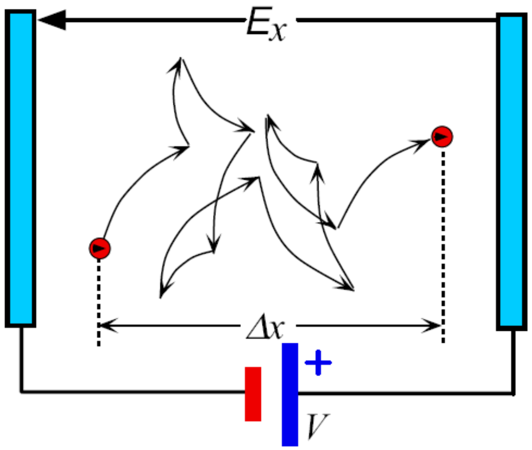
Drude Model

Based on a average Drift Velocity of electrons

$$v_d = \frac{e\vec{E}}{m}\tau$$

$$v_d = a\tau$$

$$F = ma = e\vec{E}$$



Then Conductivity is

$$\sigma = \frac{ne^2\tau}{m} = ne\mu$$

$$J = \sigma\vec{E}$$

$$J = nev_d$$

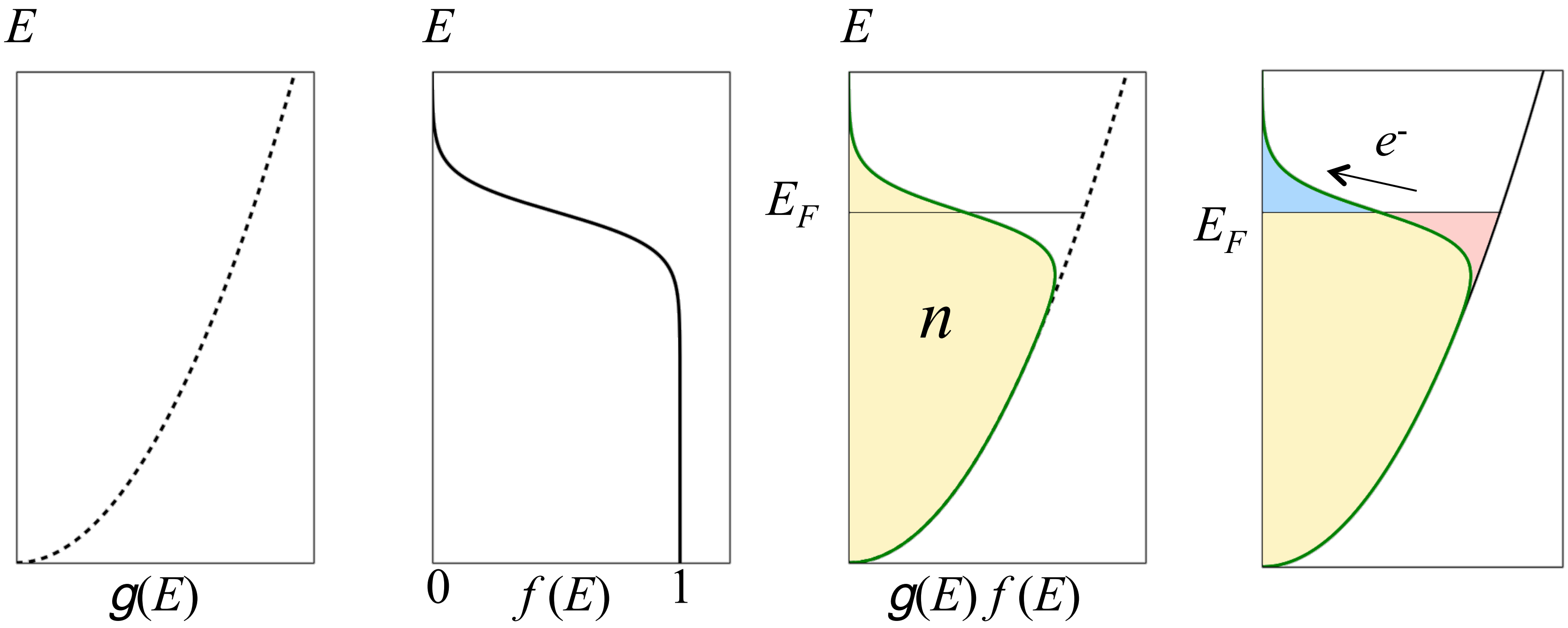
$$\mu = \frac{e\tau}{m}$$

For mean free path use *speed* of electron

$$l = v_{total-speed}\tau$$

Fermi Function & Sommerfeld model

$$\sigma = \frac{ne^2\tau}{m} \qquad \text{speed} = v_F \qquad \ell = v_F\tau$$



Conductivity Tensor

Ohm's Law

$$\vec{j} = \vec{\sigma}\vec{E} \qquad V = IR$$

$$j_j = \sigma_{ji}\vec{E}_i$$

$$\begin{pmatrix} j_x \\ j_y \\ j_z \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

Nonlinear terms not considered here

E^2, E^3, EB, EM, ...

Electric Field $\vec{E} = -\nabla V$

(E on this slide is not Energy!)

Conductivity (and Seebeck) Tensor is symmetric (Onsager) $\sigma_{ij} = \sigma_{ji}$

and therefore can be represented as an ellipse with three principle directions.

$$\begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}$$

i.e. in these principle directions it can be represented as a diagonal matrix.

in orthorhombic, tetragonal crystals these principle directions are along a, b, c

in cubic crystals σ, α, κ is isotropic

Boltzmann Relaxation Time

Force displaces Fermi surface

- only states near Fermi surface contribute

$$F = ma = \frac{dp}{dt} = \hbar \frac{dk}{dt} \qquad F = -\nabla U \qquad \hbar v = \nabla_k E \approx \frac{dE}{dk}$$

Relaxation Time approximation for non-equilibrium dist. function f`

$$\Delta f = \tau \frac{df}{dt} = \tau \frac{df}{dE}\frac{dE}{dk}\frac{dk}{dt} \qquad f' = f^0 - e\tau \vec{E} \bullet v \frac{-\partial f}{\partial E}$$

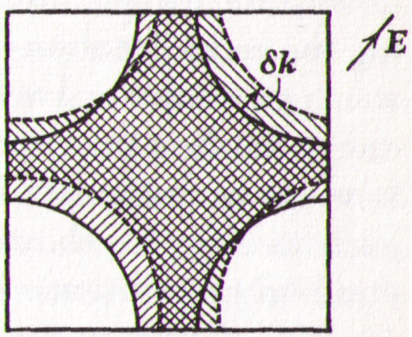


FIG. 80. Effect of field on distribution function and Fermi surface.

Ziman (1960)

relaxation time establishes steady state

Current density is

$$j = -e \iiint vf \, dV \qquad j_j = \sigma_{ij} \vec{\mathrm{E}}_i$$

$$\sigma_{ij} = \frac{e^2}{4\pi^3} \iiint v_i v_j \tau \frac{-\partial f}{\partial E} dV$$

σ = conductivity

f = Fermi function

ζ = chemical potential

g = DOS

v = velocity

τ = relaxation time

E = energy

T = temperature

Ashcroft and Mermin *Solid State Physics* chapter 13 (1976)

Transport Function σ_E

States near Fermi surface have the most effect

– reformulate from k to E to focus of Fermi Surface

$$\sigma_{ij} = \frac{e^2}{4\pi^3}\iiint v_i v_j \tau \frac{-\partial f}{\partial E}\, dV$$

3-D $k_x k_y k_z$ to 2-D Fermi Surface and 1-D Energy

$$dV = dS \bullet \frac{dk}{dE} dE \qquad \sigma = \int \sigma_E \frac{-\partial f}{\partial E}\, dE$$

$$\sigma_E = \frac{e^2}{4\pi^3}\oint_E v_i v_j \tau \frac{dS}{\nabla_k E} \approx \frac{2e^2}{3} v^2 \tau g$$

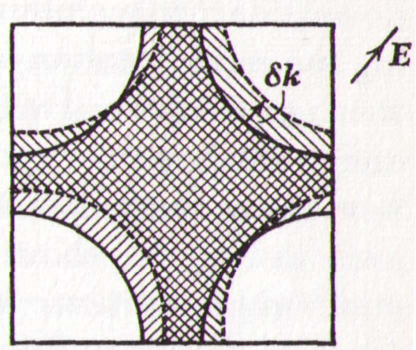


FIG. 80. Effect of field on distribution function and Fermi surface.

Ziman (1960)

- Conductivity derived from Kubo-Greenwood is same as Boltzmann
- Assumes distribution function and rigid band
  - σ_E is independent of Fermi Level, property of bands only
- σ_E also exists for hopping conduction
  - (Cutler Mott 1969)

$$\text{hopping } \sigma_E = e^2 p l^2 g$$

σ = conductivity
f = Fermi function
E_F = chemical potential
g = DOS
v = velocity
τ = relaxation time
E = energy
T = temperature

Ashcroft and Mermin *Solid State Physics* (1976)
Cutler and Mott, *Phys. Rev.* 1811336 (1969).

Seebeck from σ_E

See Datta L1.4

$$\boxed{\alpha\sigma = \frac{1}{eT}\int \sigma_E \left(E - E_F\right)\frac{-\partial f}{\partial E}\, dE}$$

Boltzmann Transport Derivation is similar...

$$\Delta f = \tau\frac{df}{dt} = \tau\frac{df}{dE}\frac{dE}{dk}\frac{dk}{dt} + \tau\frac{df}{dT}\frac{dT}{dx}\frac{dx}{dt}$$

$$v = \frac{dx}{dt}$$

$$f' = f^0 + \left(e\nabla V - \left.\frac{\partial E_F}{\partial x}\right|_T - \left(\frac{E - E_F}{T}\right)\nabla T\right)\bullet v\tau\frac{-\partial f}{\partial E}$$

$$j_j = \sigma_{ij}\vec{\mathrm{E}}_i$$

$$\vec{\mathrm{E}}_i = -\nabla_i V + \alpha_{ij}\nabla_j T$$

$$j_i = -\sigma_{ij}\nabla_j V + \sigma_{ij}\alpha_{jk}\nabla_k T$$

$$j = -e\iiint vf\, d\vec{k}$$

$$\sigma = \int \sigma_E \frac{-\partial f}{\partial E}\, dE$$

$$\vec{j} = \int \sigma_E \frac{-\partial f}{\partial E}\left(-\nabla V + \left(\frac{E - E_F}{eT}\right)\nabla T\right) dE$$

$$f = \frac{1}{1 + e^z} \qquad z = \frac{E - E_F}{k_B T}$$

$$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial E}\frac{\partial E}{\partial z}\frac{\partial z}{\partial T}$$

$$\frac{\partial E}{\partial z}\frac{\partial z}{\partial T} = k_B T\frac{-(E - E_F)}{k_B T^2}$$

Uniform Material

$$\left.\frac{\partial E_F}{\partial x}\right|_T = 0$$

σ = conductivity

f = Fermi function

E_F = chemical potential

g = DOS

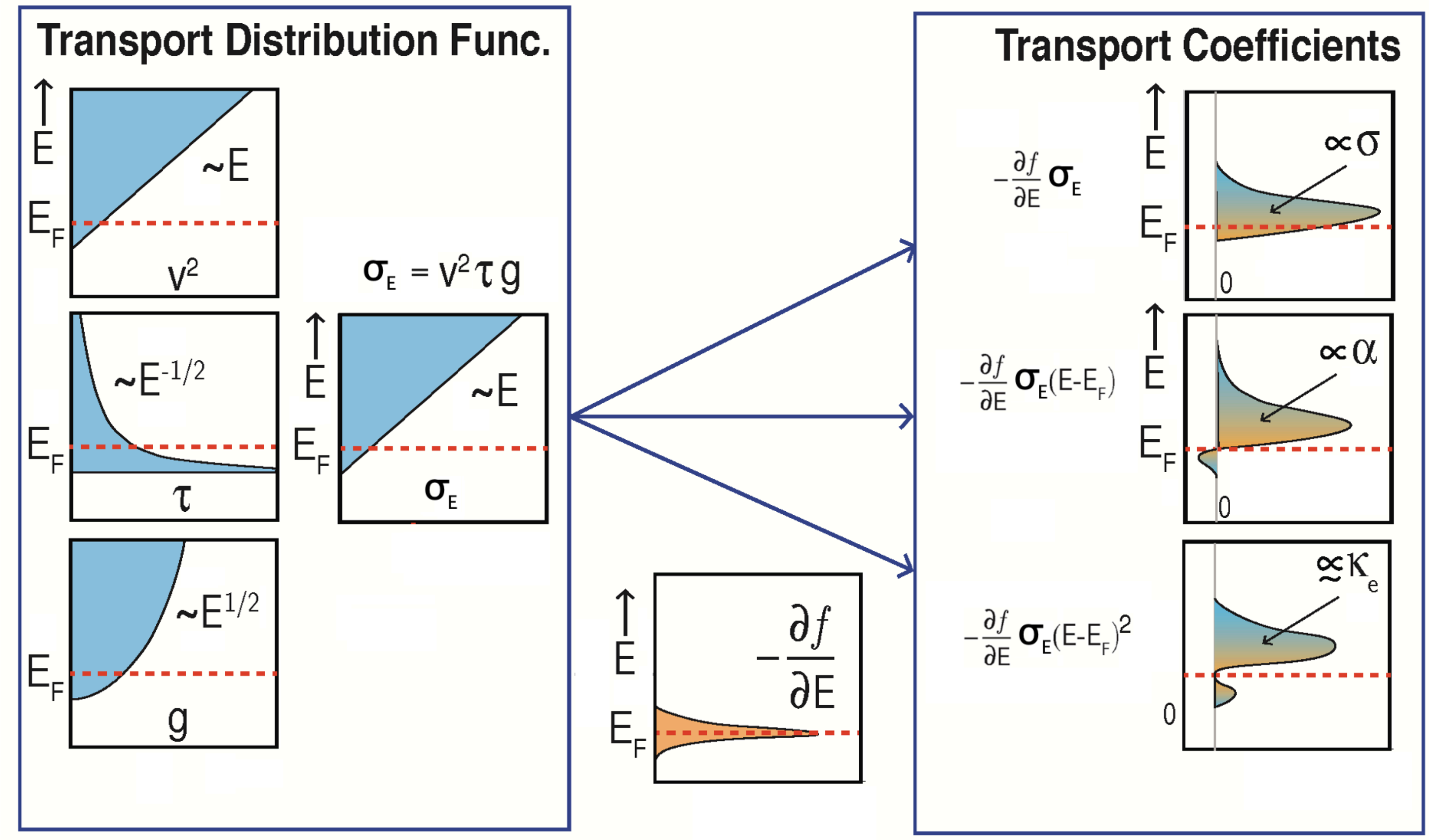
v = velocity

τ = relaxation time

E = energy

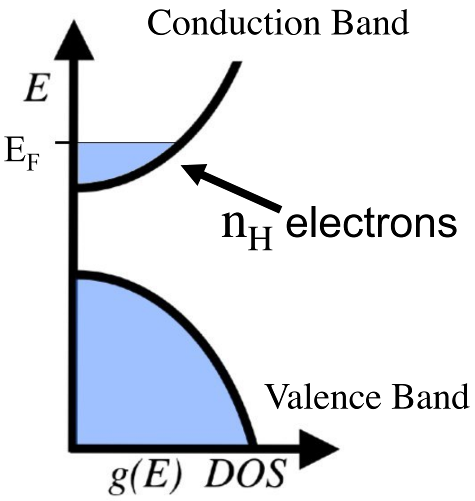
T = temperature

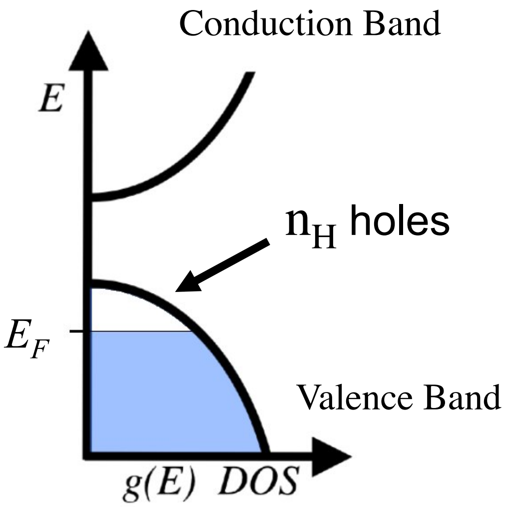
σ , α and ~κ_e as Components of σ_E



Thermoelectric Electron Filter

Semiconductors act as filter allowing only high energy electrons or holes





n-type
E_F near conduction band edge
filters out holes

p-type
E_F near valence band edge
filters out electrons

Mott-Equation

$$\sigma = \int \sigma_E \frac{-\partial f}{\partial E} dE \qquad \alpha\sigma = \frac{1}{eT}\int \sigma_E \left(E - E_F\right)\frac{-\partial f}{\partial E} dE$$

Assumptions: rigid band, Fermi liquid

First non-zero terms of
Sommerfeld expansion

$$\boxed{\sigma \approx \sigma_E\Big|_{E=E_F}} + \frac{\pi^2}{6}k_B^2T^2\frac{\partial^2\sigma_E}{\partial E^2}\Bigg|_{E=E_F} + \ldots \qquad \boxed{\alpha\sigma \approx \frac{\pi^2}{3}\frac{k_B}{e}k_BT\frac{\partial\sigma_E}{\partial E}\Bigg|_{E=E_F}} + \frac{7\pi^4}{90}\frac{k_B}{e}k_B^3T^3\frac{\partial^3\sigma_E}{\partial E^3}\Bigg|_{E=E_F} + \ldots$$

Assumptions: $k_B^nT^n\frac{\partial^n\sigma_E}{\partial E^n}\Bigg|_{E=E_F} << 1$

$$\boxed{\alpha \approx \frac{\pi^2}{3}\frac{k_B^2T}{e}\frac{\partial\sigma_E}{\sigma_E\partial E}\Bigg|_{E=E_F}}$$

$k_BT << E_F$??

(degenerate carriers)

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Mott and Jones *The Theory and Properties of Metals and Alloys* (1936)

DOS version of Mott equation

$$\sigma_E\Big|_{E=E_F} = \oint_{E=E_F} v^2(\mathbf{k})\tau(\mathbf{k})\frac{dS}{\nabla_k E}(\mathbf{k})$$

$$g(E) = \oint_E \frac{dS}{\nabla_k E}(\mathbf{k})$$

Integrating over Fermi Surface

pull out v and τ from integral

Assumptions: isotropic $v(E)$, $\tau(E)$

All bands degenerate

$$\boxed{\sigma_E(E) \approx v^2(E)\tau(E)g(E)}$$

$$\boxed{\alpha^{M1} = \frac{\pi^2}{3}\frac{k_B^2 T}{e}\frac{\partial \sigma_E}{\sigma_E \partial E}\bigg|_{E=E_F}}$$

$$\boxed{\alpha^{M} \approx \frac{\pi^2}{3}\frac{k_B^2 T}{e}\left(\frac{2\partial v}{v\partial E} + \frac{\partial \tau}{\tau \partial E} + \frac{\partial g}{g\partial E}\right)\bigg|_{E=E_F}}$$

σ = conductivity

f = Fermi function

E_F = chemical potential

g = DOS

v = velocity

τ = relaxation time

E = energy

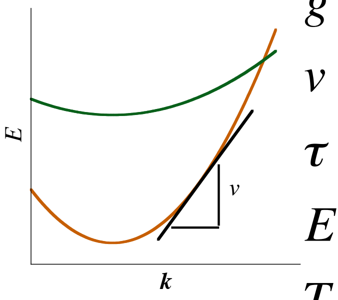
T = temperature

Density of States $g(E)$ now apparent

assume all e^- at E_F have same v and τ

Not strictly valid for multiple bands

- Non-parabolic band OK - *for this version*



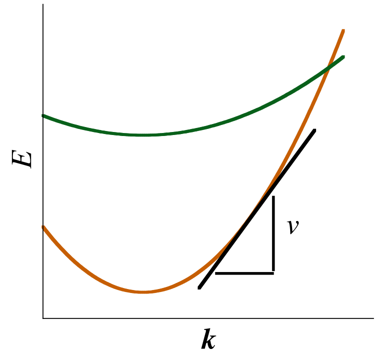
Wilson *The Theory of Metals* (1954)

Linear or Parabolic

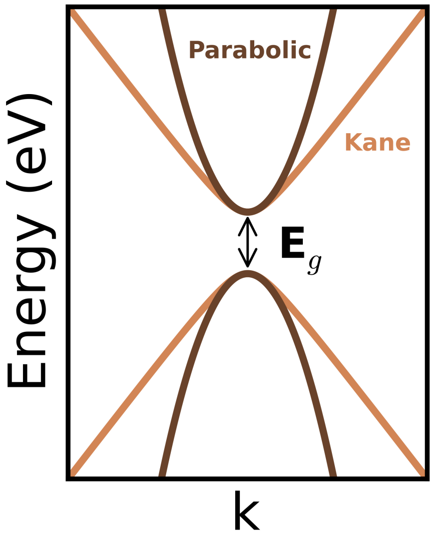
For r = 0, τ and DOS (g) cancel each other

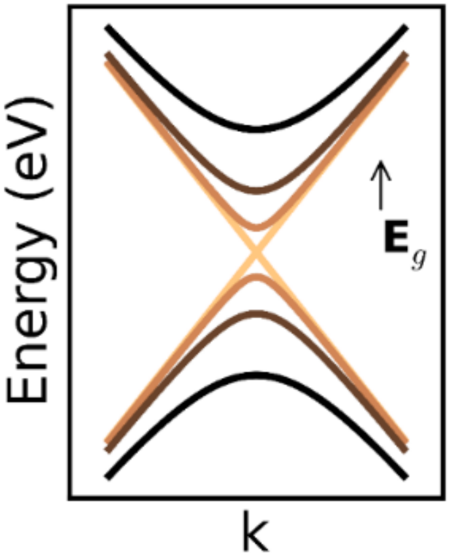
$$\alpha = \frac{\pi^2}{3}\frac{k_B^2 T}{e}\left(\frac{2\partial v}{v\partial E} + \cancel{\frac{\partial \tau}{\tau\partial E}} + \cancel{\frac{\partial g}{g\partial E}}\right)$$

$$v \equiv \frac{dE}{\hbar dk}$$



so S depends only on dv/dE





$$m_0{}^* = \frac{\hbar^2 E_g}{4P^2}$$

Constant m_0*

parabolic is definitely better

Constant Kane P

smaller E_g leads to lighter mass

which has higher velocity

Mott with m* parabolic Band

with Free electron-like band with mass m* (SPB)

and energy dependent (but otherwise isotropic) relaxation time

$$\tau = \tau_0 E^{\lambda - \frac{1}{2}} \qquad E = \frac{mv^2}{2} \qquad g(E) = 8\pi\sqrt{2}\frac{\left(m^*\right)^{3/2}}{h^3}E^{1/2}$$

$$\alpha^M \approx \frac{\pi^2}{3}\frac{k_B^2 T}{e}\left(\frac{2\partial v}{v\partial E} + \frac{\partial \tau}{\tau \partial E} + \frac{\partial g}{g \partial E}\right)\Bigg|_{E=E_F}$$

$$E_F = \left(\frac{h^2}{8m}\right)\left(\frac{3n}{\pi}\right)^{2/3}$$

$$\boxed{\alpha^M \approx \frac{8\pi^2}{3}\frac{k_B^2 T}{e}\frac{m^*}{h^2}\left(\frac{\pi}{3n}\right)^{2/3}(1+\lambda)}$$

$$\alpha \approx \frac{\pi^2}{3}\frac{k_B^2 T}{e}\frac{1}{E_F}$$

Degenerate SPB with scattering parameter λ

not valid in non-degenerate region n < 10^{20}/cm^3

Mott Relation Is Degenerate Approximation

$$\mu_E = \frac{e\tau}{m^*} \qquad \sigma_E = e^2\tau\int\frac{gfdE}{m^*_{ij}} \approx \frac{ne^2\tau}{m^*}$$

σ = conductivity

f = Fermi function

E_F = chemical potential

g = DOS

v = velocity

τ = relaxation time

E = energy

T = temperature

Wilson *The Theory of Metals* (1954)

Narrow Band Seebeck

Common form of Seebeck for insulators

Assume conducting band is narrower than $k_B T$

Band at energy E_b that has total of n_c states $\quad n_c = \int g\,dE$

narrow band means f is a constant along with $\quad \dfrac{-\partial f}{\partial E} = f(1-f)$

(regardless of relative position of E_b and E_F)

$$n = \int gf\,dE = f(E_b)\int g\,dE = f(E_b)n_c$$

$$c = \frac{n}{n_c} = f(E_b)$$

in terms of narrow band filling fraction

gives conductivity

$$\sigma = \int \sigma_E \frac{-\partial f}{\partial E} dE = c(1-c)\int \sigma_E dE$$

and Seebeck $\quad \alpha\sigma = \dfrac{1}{eT}\displaystyle\int \sigma_E \left(E - E_F\right)\dfrac{-\partial f}{\partial E} dE = \dfrac{E_b - E_F}{eT} c(1-c)\int \sigma_E dE$

Narrow Band Seebeck Formula $\quad \boxed{\alpha = \dfrac{E_b - E_F}{eT}}$

Narrow Band Heikes Formula

Common form of Seebeck for oxides

Assume conducting band is narrower than $k_B T$

Band at energy E_b that has total of n_c states $$n_c = \int g\, dE$$

Fermi Level determined by c $$c = \frac{n}{n_c} = f(E_b)$$

$$f(E_b) = \frac{1}{1 + Exp\left(\frac{E_b - E_F}{k_B T}\right)} \qquad \frac{E_b - E_F}{k_B T} = \ln\left(\frac{1-c}{c}\right)$$

gives conductivity $$\sigma = \int \sigma_E \frac{-\partial f}{\partial E} dE = c(1-c)\int \sigma_E dE$$

and Seebeck $$\alpha = \frac{E_b - E_F}{eT}$$

Heikes Formula $$\boxed{\alpha = \frac{k_B}{e} \ln\left(\frac{1-c}{c}\right)}$$

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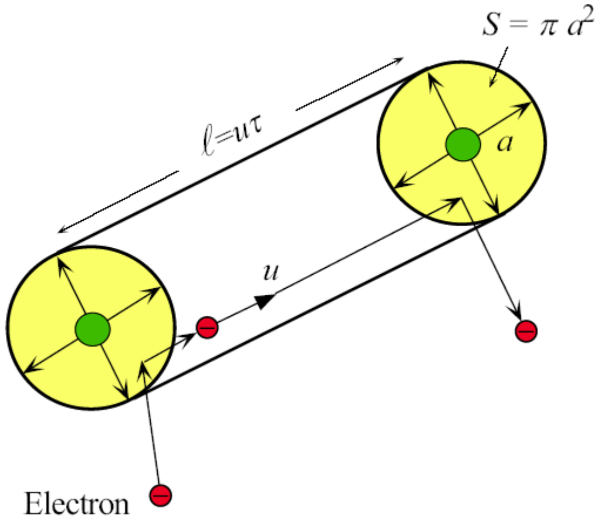
Scattering of Electrons by Atom Motion



$$\tau = \frac{1}{SuN_s}$$

$$\mu = \frac{ne^2\tau}{m^*}$$

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

From equipartition theorem the a^2 potential energy of atom is proportional to $k_B T$

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

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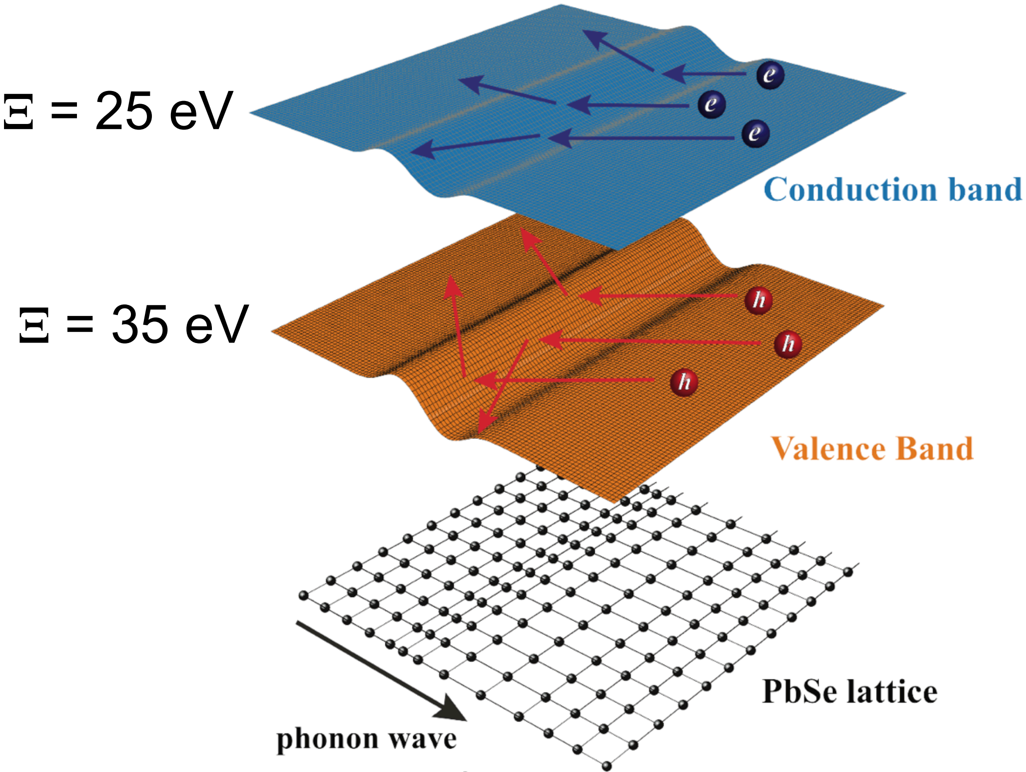
τ = mean time between scattering, u = mean speed of the electron, N_s = concentration of scatterers, S = scattering cross-sectional area

Deformation Potential

n-type vs p-type PbTe, PbSe

Same effective mass *m**

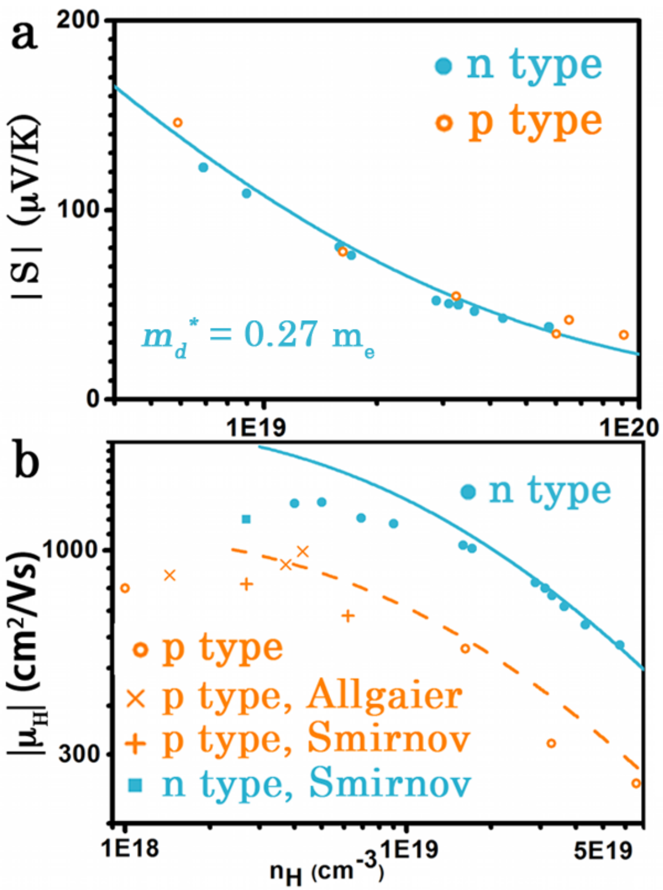
- Symmetric Kane band at L



Higher mobility for n-type

- lower deformation potential

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



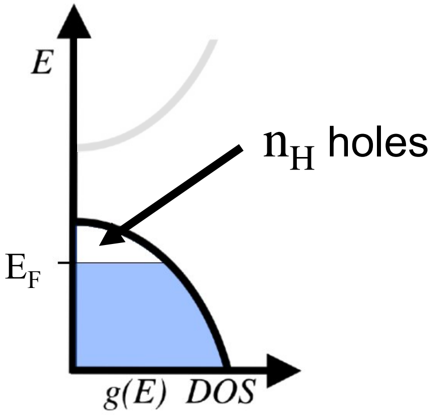
$$\mu_0 \sim \frac{e}{(k_B T)^{3/2}} \frac{C_l}{m_I^* m_b^{*3/2} \Xi^2}$$

Wang, Pei, Snyder, et al, PNAS **109**, 9705 (2012)

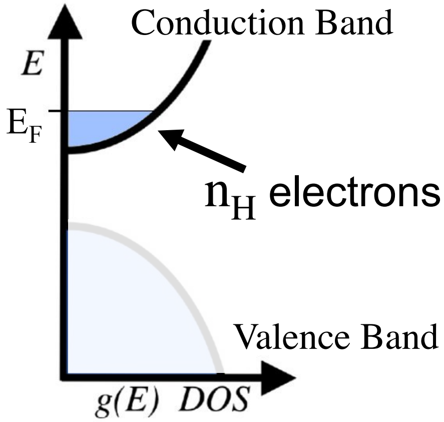
Effective Mass Model

Single Parabolic Band (SPB) Modeling

p-type
Thermoelectric

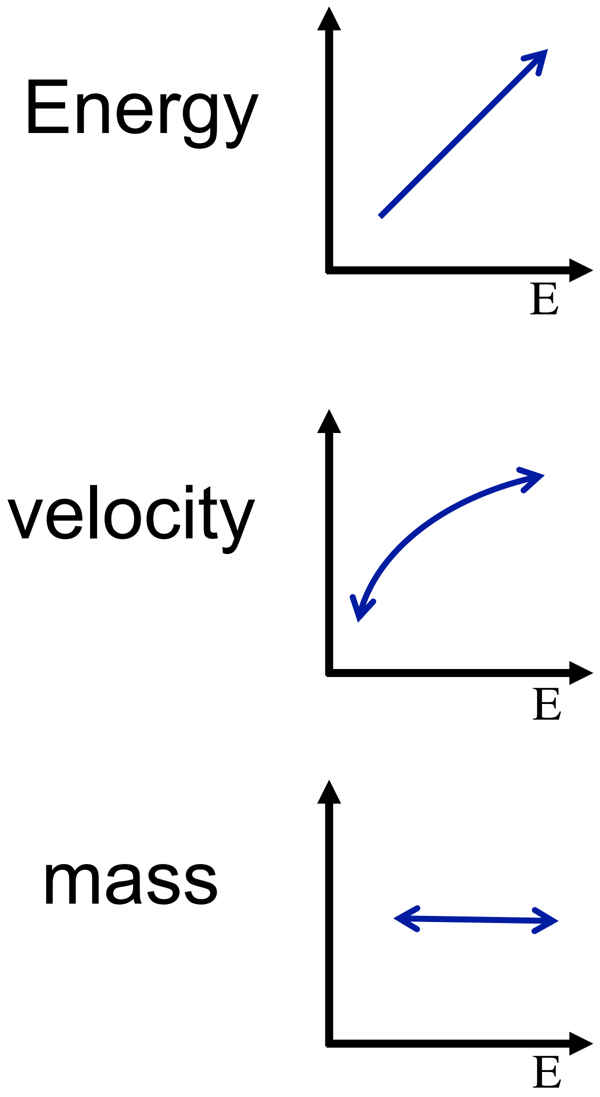


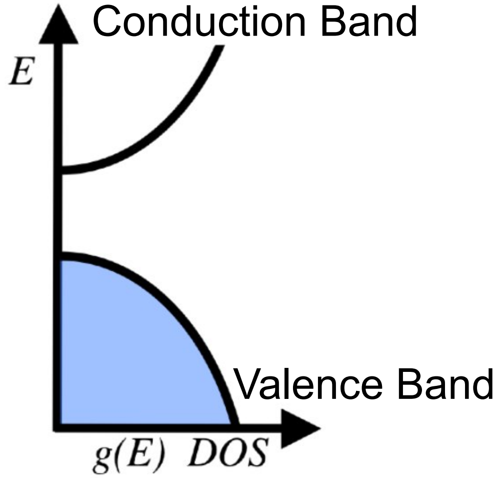
n-type
Thermoelectric



May, Snyder **Thermoelectrics Handbook,** CRC Press (2005)
May, Snyder Phys. Rev. B **80** 125205 (2005)

m^* best characterizes a band



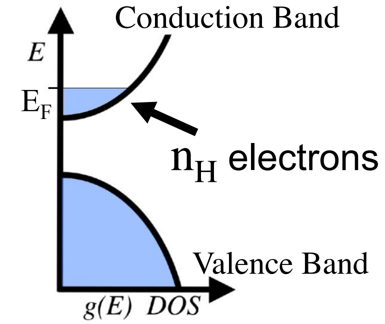


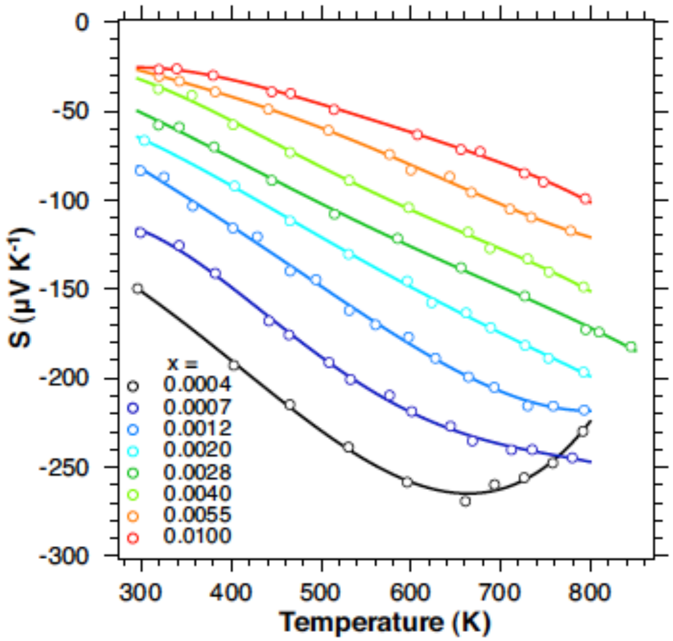
m^* is best (most constant) descriptor for band shape

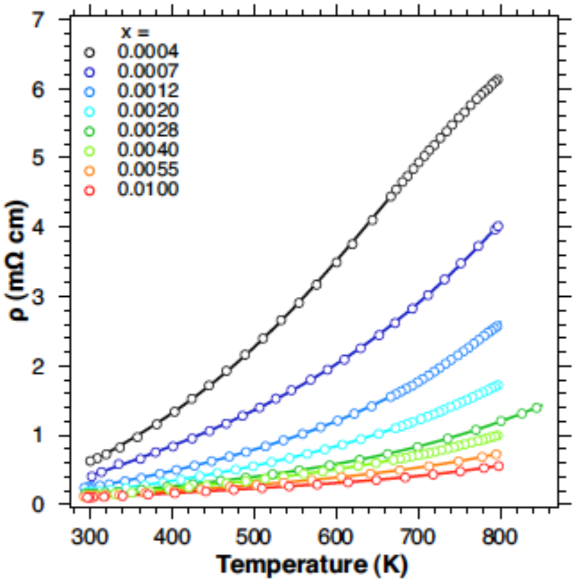
Degenerate Semiconductor Behavior

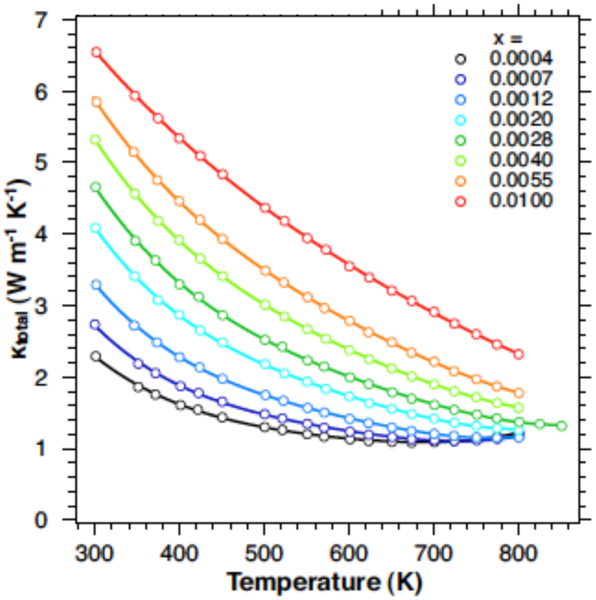
1. linear Seebeck
2. Linear Resistivity
3. 1/T + Constant thermal conductivity

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









Non-Degenerate Resistivity
(Intrinsic Semiconductor)

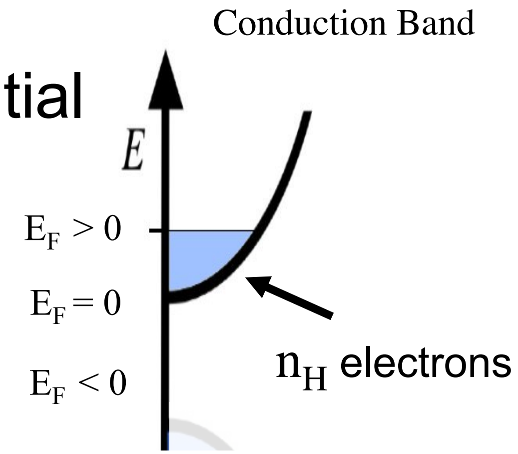
$$\ln\left(\frac{1}{\rho}\right) = \frac{-E_g}{2k_BT}$$

Electron Chemical Potential and E_F

‘Fermi Level’ and ‘electron chemical potential’

Used differently in Physics, Electrochemistry and E.E.

GJS & Wikipedia recommendation:



$E_F(T)$ “Fermi Level” = Electron Chemical Potential

Energy where Fermi function is ½

SC: measured from band edge

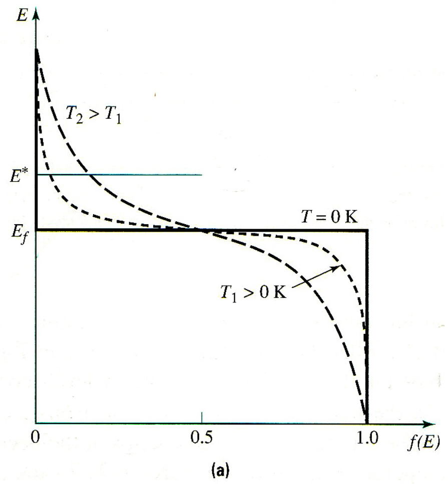
- >0 inside band (metal, “degenerate” SC)
- <0 in band gap (“nondegenerate” SC)

Moves toward middle of gap at high T

“Fermi Energy” as used in physics ≠ E_{F0}

$$E_{F_0} = \frac{Limit}{T \rightarrow 0} E_F$$

intrinsic E_{F0} at middle of gap not valence band edge



Reduced Fermi Level

$$\eta = \frac{E_F(T)}{k_B T}$$

Transport Function for m^* model

$$\sigma_E = \frac{e^2}{4\pi^3}\oint_E v_i v_j \tau \frac{dS}{\nabla_k E} \approx \frac{2e^2}{3} v^2(E)\tau(E)g(E)$$

$$E = \tfrac{1}{2} m^* v^2$$

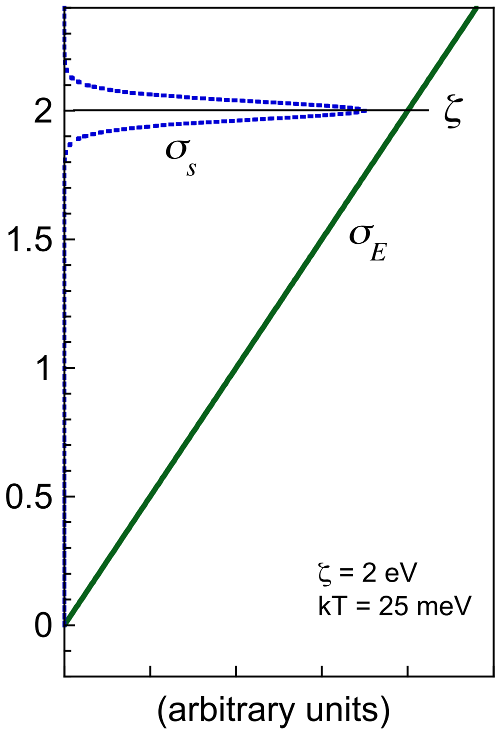
(E - band bottom $E_b = 0$)

$$g(E) = 8\pi\sqrt{2}\frac{\left(m^*\right)^{3/2}}{h^3}E^{1/2}$$

$$\sigma_E = \sigma_{E_0}\frac{E}{k_B T}$$

$$\sigma_{E_0} = \frac{8\pi e(2m_e k_B T)^{3/2}}{3h^3}\mu_0\left(\frac{m^*}{m_e}\right)^{3/2}$$

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



$$\tau = \frac{1}{S\,|v|\,N_s}$$

$$S = \pi a^2 \propto kT$$

$$\tau \propto \frac{1}{k_B T\sqrt{2E/m}}$$

$$\tau = \tau_0\left(\frac{E}{k_B T}\right)^{-1/2}$$

$$\mu_0 = \frac{e\tau_0}{m^*}$$

Conductivity using Fermi Integrals

$$\sigma = \int_0^\infty \sigma_E \frac{-\partial f}{\partial E} dE$$

$$\sigma = \int_0^\infty \sigma_{E_0} \varepsilon d(-f)$$

$$\sigma = \sigma_{E_0} \left[\left(-\varepsilon f\right)\Big|_0^\infty - \int_0^\infty -f \, d\varepsilon \right]$$

$$\sigma = \sigma_{E_0} \int_0^\infty f \, d\varepsilon$$

$$\boxed{\sigma = \sigma_{E_0} F_0\left(\frac{E_F}{k_B T}\right)}$$

reduced variables

$$\eta = \frac{E_F}{k_B T} \qquad \varepsilon = \frac{E}{k_B T} \qquad f = \frac{1}{1+e^{\varepsilon-\eta}}$$

transport function

$$\sigma_E = \sigma_{E_0} \varepsilon \qquad \sigma_{E_0} = \frac{8\pi e(2m_e k_B T)^{3/2}}{3h^3} \mu_0 \left(\frac{m^*}{m_e}\right)^{3/2}$$

integration by parts

$$\int u \, dv = uv - \int v \, du$$

Fermi Integrals

$$F_j(\eta) = \int_0^\infty f \varepsilon^j \, d\varepsilon = \int_0^\infty \frac{\varepsilon^j}{1+e^{\varepsilon-\eta}} d\varepsilon$$

Seebeck using Fermi Integrals

$$\alpha\sigma = \frac{1}{eT}\int \sigma_E\left(E-E_F\right)\frac{-\partial f}{\partial E}\,dE$$

$$\alpha\sigma = \frac{k_B}{e}\int \sigma_{E_0}\varepsilon\left(\varepsilon-\eta\right)\frac{-\partial f}{\partial E}\,dE$$

$$\alpha\sigma = \frac{k_B}{e}\sigma_{E_0}\left(-\varepsilon\left(\varepsilon-\eta\right)f\Big|_0^\infty - \int_0^\infty -f\,d\left(\varepsilon(\varepsilon-\eta)\right)\right)$$

$$\alpha\sigma = \frac{k_B}{e}\sigma_{E_0}\int_0^\infty f\left(2\varepsilon-\eta\right)d\varepsilon$$

$$\alpha\sigma = \frac{k_B}{e}\sigma_{E_0}\left(2F_1-\eta F_0\right)$$

$$\boxed{\alpha = \frac{k_B}{e}\left(\frac{2F_1(\eta)}{F_0(\eta)}-\eta\right)} \qquad \boxed{\sigma = \sigma_{E_0}F_0(\eta)}$$

transport function

$$\sigma_E = \sigma_{E_0}\varepsilon \qquad \sigma_{E_0} = \frac{8\pi e(2m_e k_B T)^{3/2}}{3h^3}\mu_0\left(\frac{m^*}{m_e}\right)^{3/2}$$

reduced variables

$$\eta = \frac{E_F}{k_B T} \qquad \varepsilon = \frac{E}{k_B T} \qquad f = \frac{1}{1+e^{\varepsilon-\eta}}$$

integration by parts

$$\int u\,dv = uv - \int v\,du$$

Fermi Integrals

$$F_j(\eta) = \int_0^\infty f\varepsilon^j\,d\varepsilon = \int_0^\infty \frac{\varepsilon^j}{1+e^{\varepsilon-\eta}}\,d\varepsilon$$

Lorenz Factor using Fermi Integrals

$$\dot{q}_j = \iiint (E - E_F) v_j f \, d\vec{k}$$

$$f' = f^0 + \left(e\nabla V - \left.\frac{\partial E_F}{\partial x}\right|_T - \left(\frac{E - E_F}{T} \right) \nabla T \right) \bullet v\tau \frac{-\partial f}{\partial E}$$

$$\dot{q} = T\alpha j + \kappa_e \nabla T$$

$$\kappa_e = \kappa_{SC} - T\alpha^2\sigma$$

$$\kappa_{SC} = \frac{k_B^2}{e^2} \sigma_{E_0} \int \varepsilon (\varepsilon - \eta)^2 \frac{-\partial f}{\partial E} dE$$

$$\kappa_{SC} = \frac{k_B^2}{e^2} \sigma_{E_0} \left(3F_2 - 4\eta F_1 + \eta^2 F_0 \right)$$

$$\kappa_e = L\sigma T$$

$$\boxed{L = \frac{k_B^2}{e^2} \left(\frac{3F_0 F_2 - 4F_1^2}{F_0^2} \right)}$$

transport function

$$\sigma_E = \sigma_{E_0} \varepsilon \qquad \sigma_{E_0} = \frac{8\pi e (2 m_e k_B T)^{3/2}}{3h^3} \mu_0 \left(\frac{m^*}{m_e} \right)^{3/2}$$

reduced variables

$$\eta = \frac{E_F}{k_B T} \qquad \varepsilon = \frac{E}{k_B T} \qquad f = \frac{1}{1 + e^{\varepsilon - \eta}}$$

integration by parts

$$\int u \, dv = uv - \int v \, du$$

Fermi Integrals

$$F_j(\eta) = \int_0^\infty f \varepsilon^j \, d\varepsilon = \int_0^\infty \frac{\varepsilon^j}{1 + e^{\varepsilon - \eta}} d\varepsilon$$

More Fermi Integrals

$$n = 4\pi \left(\frac{2m^* kT}{h^2} \right)^{3/2} F_{1/2}$$

$$n_H = n \frac{4F_0^2}{3F_{1/2}F_{-1/2}}$$

$$\mu_H = \mu_0 \frac{F_{-1/2}}{2F_0}$$

May, Snyder CRC Handbook (2012)

Fermi Integrals

$$F_j(\eta) = \int_0^\infty f \epsilon^j d\epsilon = \int_0^\infty \frac{\epsilon^j \, d\epsilon}{1 + Exp[\epsilon - \eta]}$$

Table of Integrals for use in Excel Spreadsheet

η (kT)	α $(\mu\mathrm{V\ K^{-1}})$	L $(10^{-8}\,\mathrm{W\Omega K^{-2}})$	n $(10^{19}\mathrm{cm^{-3}})$	r_H (-)	$\frac{F_{-1/2}}{2F_0}$ (-)	ψ $(\mathrm{C\ K^{-3/2}\ m^{-3}})$
-3	433	1.49	0.123	1.17	0.877	28.3
-2	350	1.51	0.324	1.17	0.863	73.9
-1	272	1.54	0.823	1.16	0.832	182
0	205	1.61	1.92	1.13	0.773	403
1	151	1.72	3.95	1.11	0.693	764
2	112	1.86	7.09	1.08	0.610	1240
3	86.1	1.99	11.3	1.05	0.539	1770
4	68.2	2.09	16.3	1.04	0.482	2340
6	46.9	2.24	28.7	1.02	0.403	3490
8	35.4	2.32	43.6	1.01	0.351	4660
10	28.3	2.36	60.4	1.01	0.315	5820

May, Snyder CRC Handbook (2012)

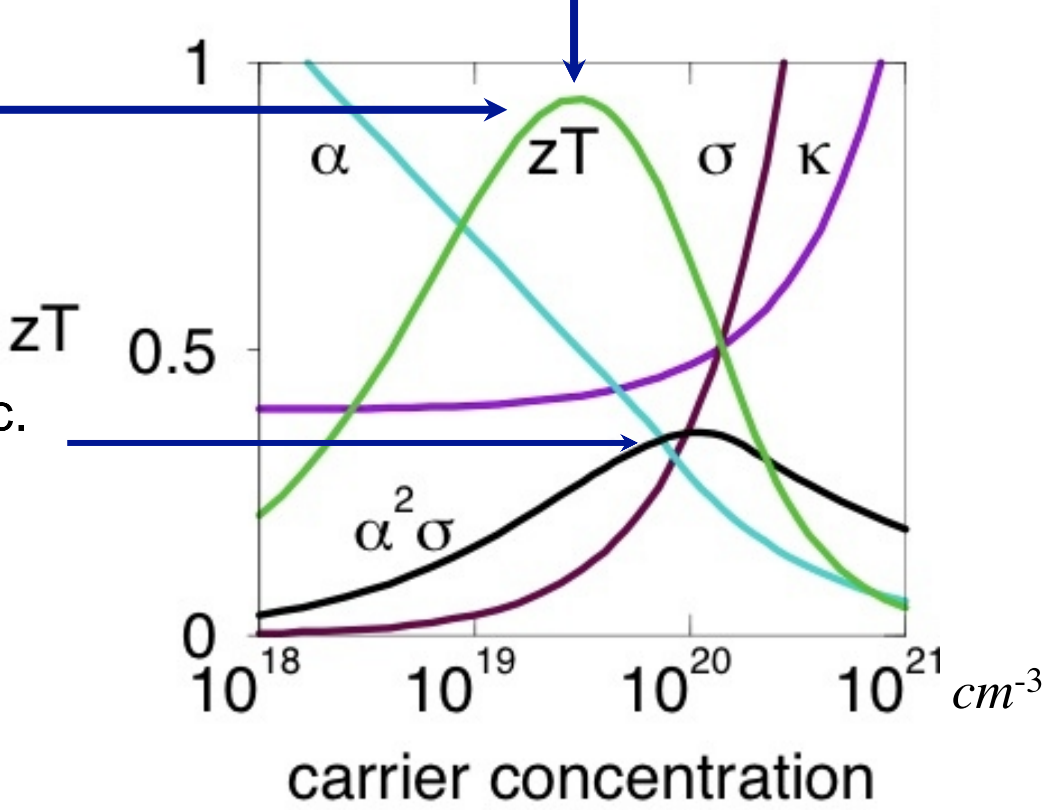
Optimum Carrier Concentration

Optimized
carrier concentration
$n \sim m^* T^{3/2}$

Maximum zT depends on
Quality Factor

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

Power factor $\alpha^2\sigma$
optimizes at a different carrier conc.
tends to overemphasize metals



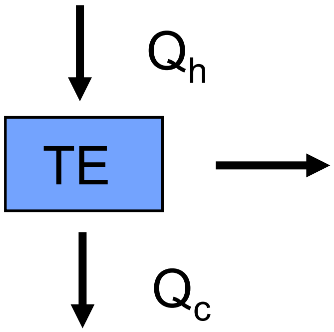
ZT for maximum Power

Typical TE Power Equation $P = \alpha^2 \sigma \frac{A}{l} \Delta T^2 \frac{R_L / R_{TE}}{\left(1 + R_L / R_{TE}\right)}$

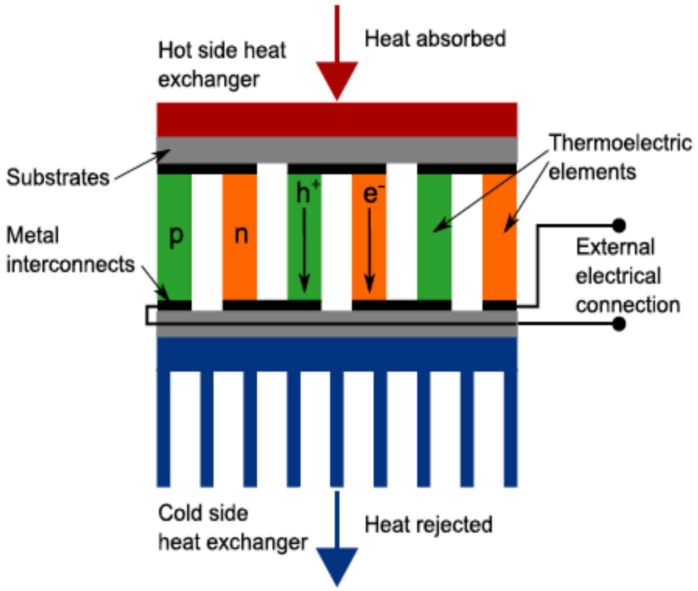
shows power factor but not zT ! is $\alpha^2\sigma$ the real figure of merit?

NB: Eqn has no maximum if TE leg length l can vary

For a given heat input and ΔT power is given by:



$$P = \eta \dot{Q}_h$$



Thus TE device should be optimized for maximum efficiency (device ZT)

Baranowski, Snyder et al, *J Applied Phys.* 115, 126102, (2014)
Baranowski, Snyder et al, *J Applied Phys.* 113, 204904, (2013)

TE Quality Factor

Maximum zT depends on Quality Factor

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

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

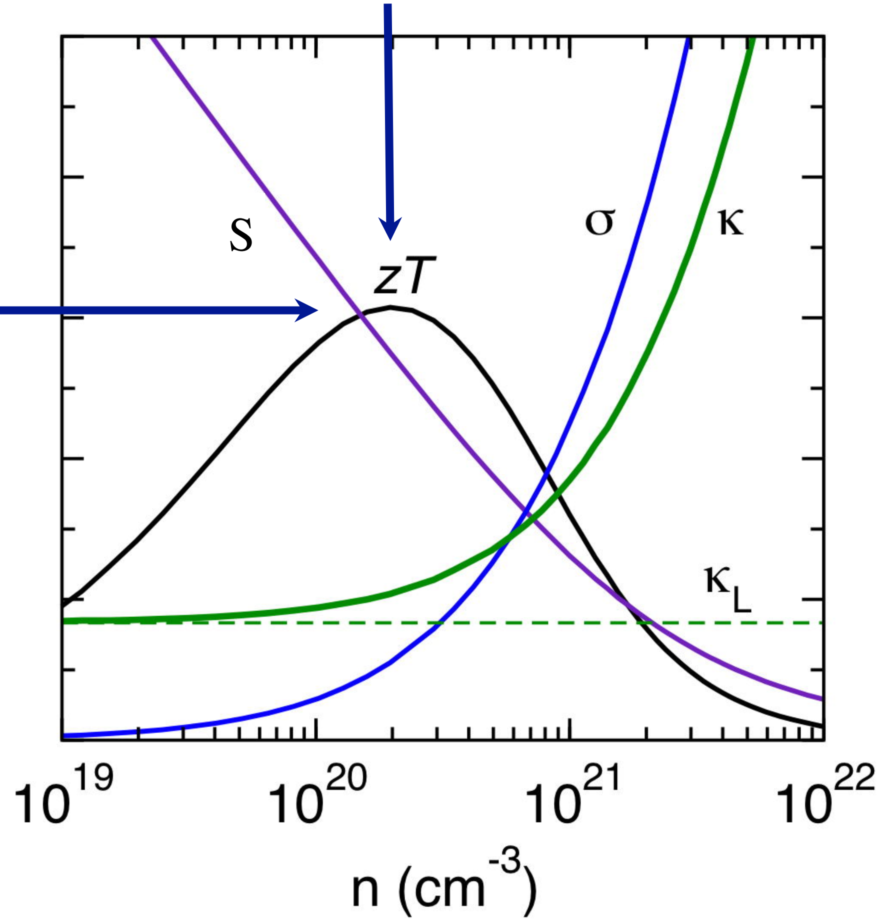
Weighted Mobility

$$\boxed{\mu_w = \mu\left(\frac{m^*_{DOS}}{m^*_e}\right)^{3/2}}$$

Lattice Thermal Conductivity

$$\boxed{\kappa_L}$$

Optimized carrier concentration



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

1. Scattering Mechanism

1. Scattering Mechanism

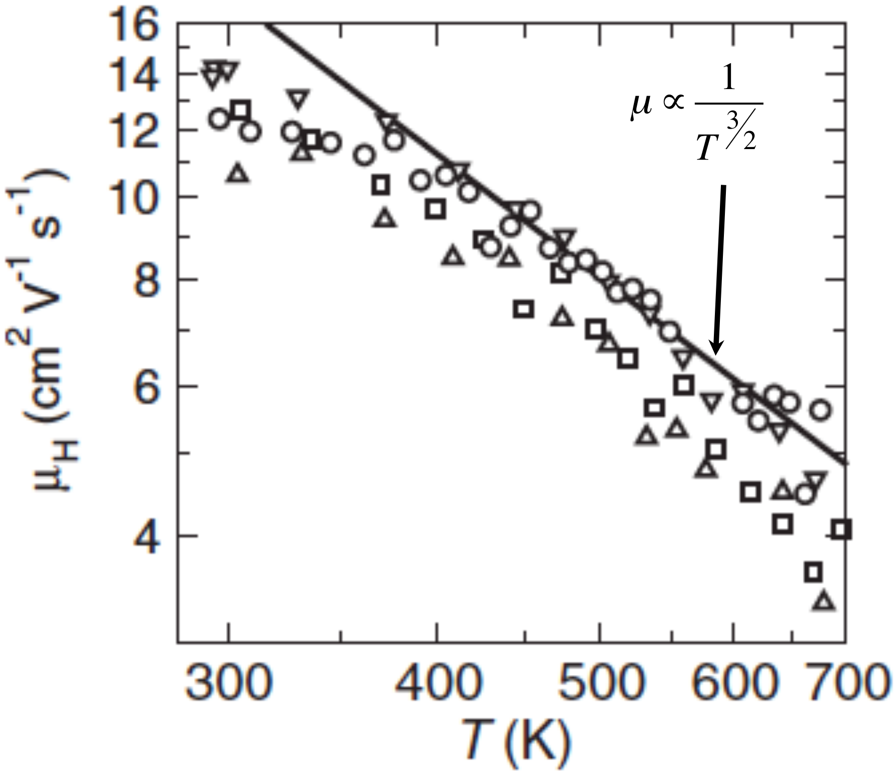
Acoustic Phonon Scattering at High Temperatures

$$\tau = \tau_0 \epsilon^{\lambda - 1/2}$$

$$\epsilon = E/kT$$

$$\lambda = 0$$

$$\frac{1}{\rho} = \sigma = ne\mu$$



Degenerate (Metals)

$$\mu \propto \frac{1}{T}$$

Non Degenerate (Semiconductors)

$$\mu \propto \frac{1}{T^{3/2}}$$

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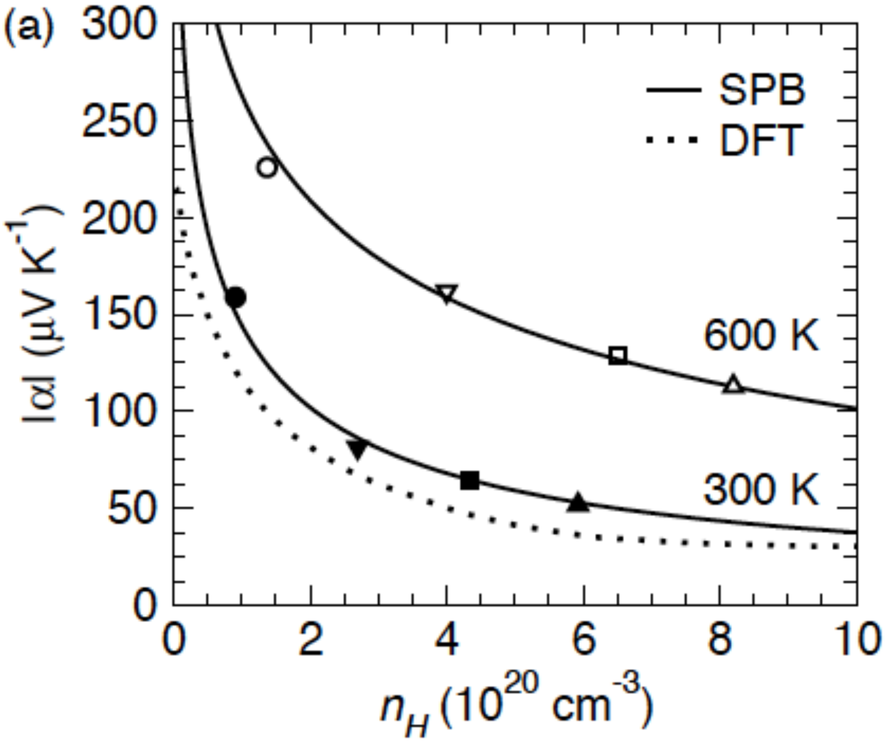
2. Effective Mass

2. Effective Mass (e.g. at 300K)

Pisarenko Plot of Seebeck vs Carrier Concentration indicates quality of band model

- parabolic, Kane (linear), multiple bands

$$\alpha = \frac{k_B}{e}\left(\frac{2F_1}{F_0} - \eta\right)$$



$$n = 4\pi\left(\frac{2m^* k_B T}{h^2}\right)^{3/2} F_{1/2}$$

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

Degenerate (Metals, |α|<75μV/K)

$$m_S^* \approx \frac{3h^2}{8\pi^2 k_B T} \frac{|S|}{(k_B/e)} \left(\frac{3n_H}{\pi}\right)^{2/3}$$

Non Degenerate (|α|>75μV/K)

$$m_S^* \approx \frac{h^2}{2k_B T}\left\{n_H \cdot \frac{3}{16\sqrt{\pi}}\left(1 - \exp\left[\frac{-|S|}{(k_B/e)}\right]\right)\right\}^{2/3}$$

3. Mobility Parameter μ_0

3. Mobility parameter μ_0 (near temp of max zT)

Plot of Mobility vs Carrier Concentration (Toberenko)

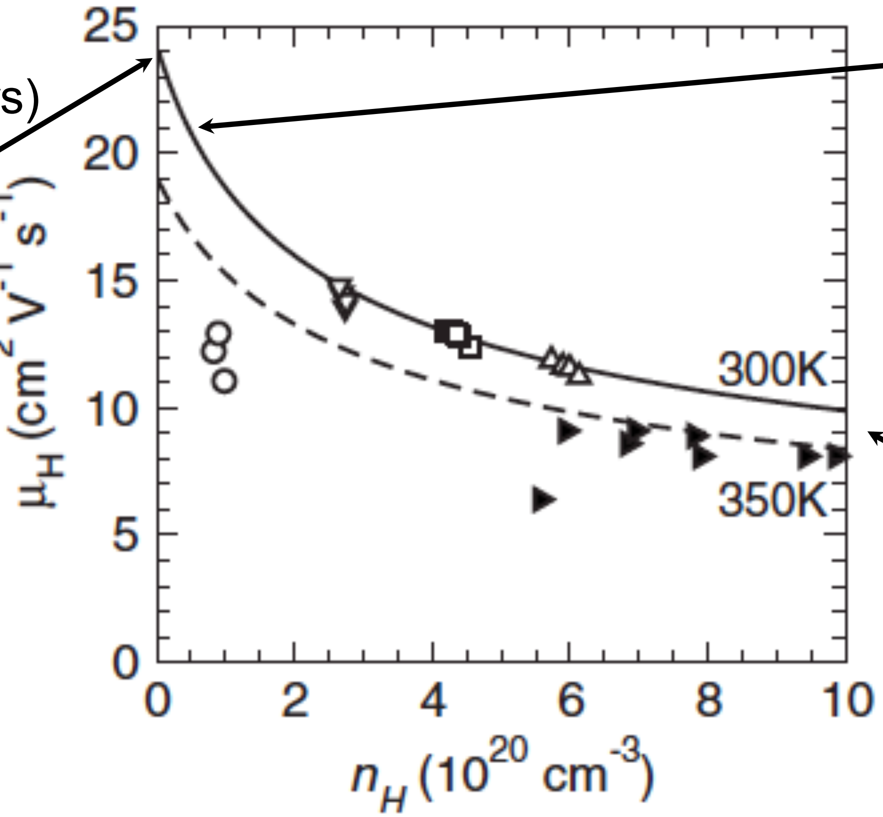
also indicates quality of band model

- parabolic, Kane (linear), multiple bands

$$\mu_H = \mu_0 \frac{F_{-1/2}}{2F_0}$$

Non Degenerate limit
(small n semiconductors)

$$\mu_{H,0} = \frac{\sqrt{\pi}}{2}\mu_0$$



non-degenerate
(Intrinsic SC - APS)

$$\mu_0 \sim \frac{e}{(k_B T)^{3/2}} \frac{C_l}{m_I^* m_b^{*3/2} \Xi^2}$$

Degenerate
(Metals)

$$\mu \propto \frac{\mu_0}{m^{*2} T n^{1/3}}$$

4. Electronic Thermal Conductivity

4. Lorenz factor from Seebeck only

$$L = \frac{k_B^2}{e^2}\left(\frac{3F_0F_2 - 4F_1^2}{F_0^2}\right)$$

independent of carrier concentration or Temperature

subtract to get lattice thermal conductvity

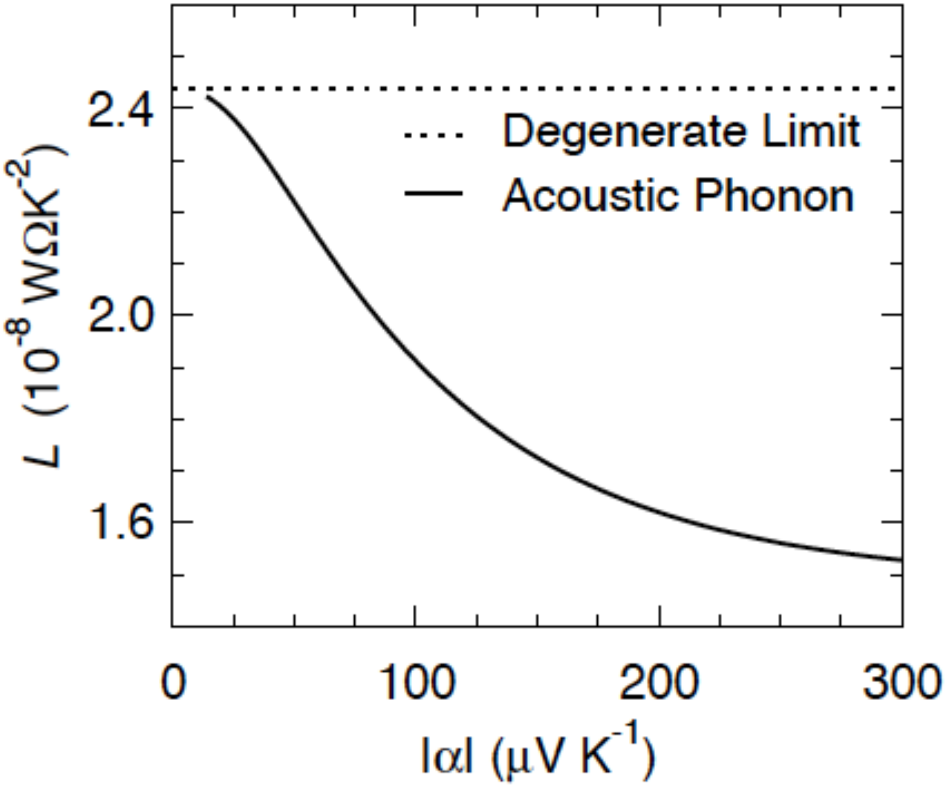
$$\kappa_e = L\sigma T \qquad \kappa = \kappa_e + \kappa_l$$

Degenerate (Metals)

$$L = \frac{\pi^2 k_B^2}{3e^2} = 2.45\times10^{-8}\,\mathrm{W\Omega K^{-2}}$$

$$L = 1.5 + Exp\left[-\frac{|S|}{116}\right]$$

$$\times10^{-8}\,\mathrm{W\Omega K^{-2}}$$



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

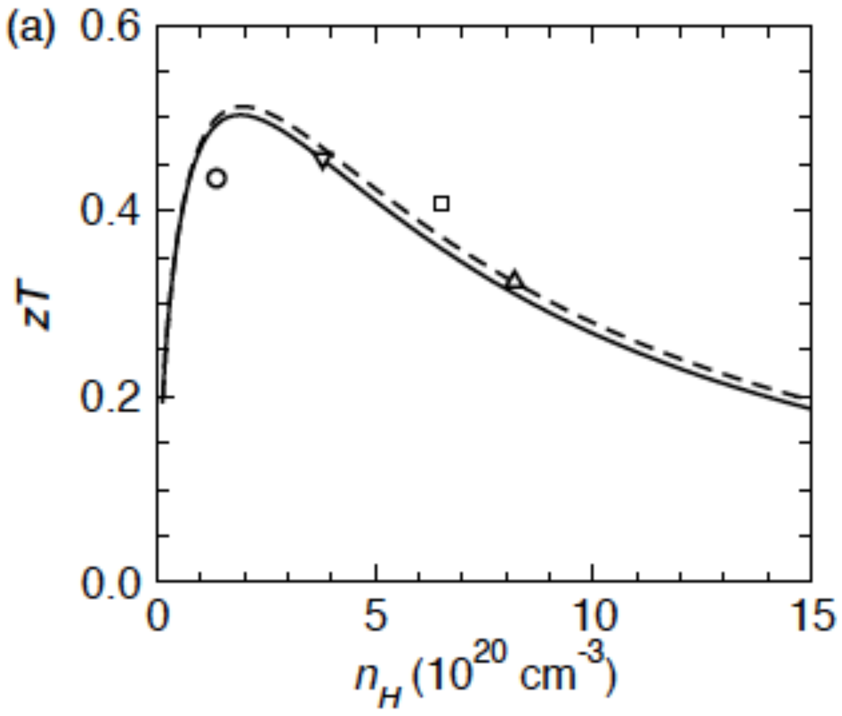
5. Predict *zT* and Doping

5. *zT* as function of doping

Predicts peak *zT*

predicts optimum carrier concentration

$$zT = \frac{\alpha^2}{L + (\psi\beta)^{-1}}$$



$$\beta = \frac{\mu_0 \left(\frac{m^*}{m_e}\right)^{3/2}}{\kappa_l} T^{5/2}$$

Quality factor parameter

$$\psi = \frac{8\pi e}{3}\left(\frac{2m_e k_B}{h^2}\right)^{3/2} F_0$$

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Weighted mobility without Hall Data

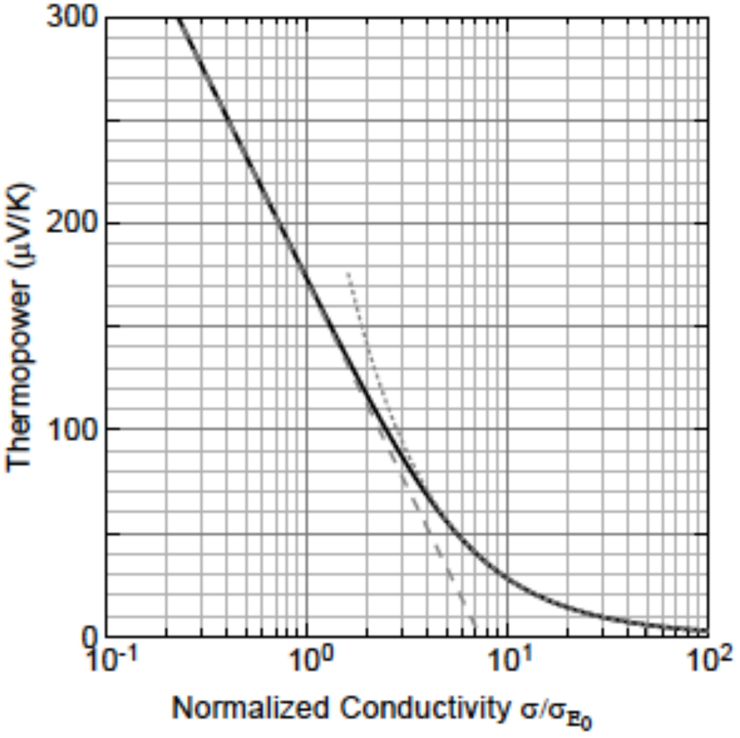
Quality factor without Hall data

$$S = \alpha = \frac{k_B}{e}\left(\frac{2F_1}{F_0} - \eta\right)$$

$$\sigma = \sigma_{E_0} F_0$$

$$\sigma_{E_0} = \frac{8\pi e (2 m_e k_B T)^{3/2}}{3h^3} \mu_0 \left(\frac{m^*}{m_e}\right)^{3/2}$$

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



when is $|S|$ is large (within 5% when $|S| > 120\ \mu\mathrm{V/K}$):

$$\sigma_{\mathrm{E}_0} = \sigma \cdot \exp\left[\frac{|S|}{k_\mathrm{B}/e} - 2\right], \tag{3}$$

or small (within 5% when $|S| < 75\ \mu\mathrm{V/K}$):

$$\sigma_{\mathrm{E}_0} = \sigma \cdot \frac{3}{\pi^2}\frac{|S|}{k_\mathrm{B}/e}. \tag{4}$$

Weighted mobility without Hall Data

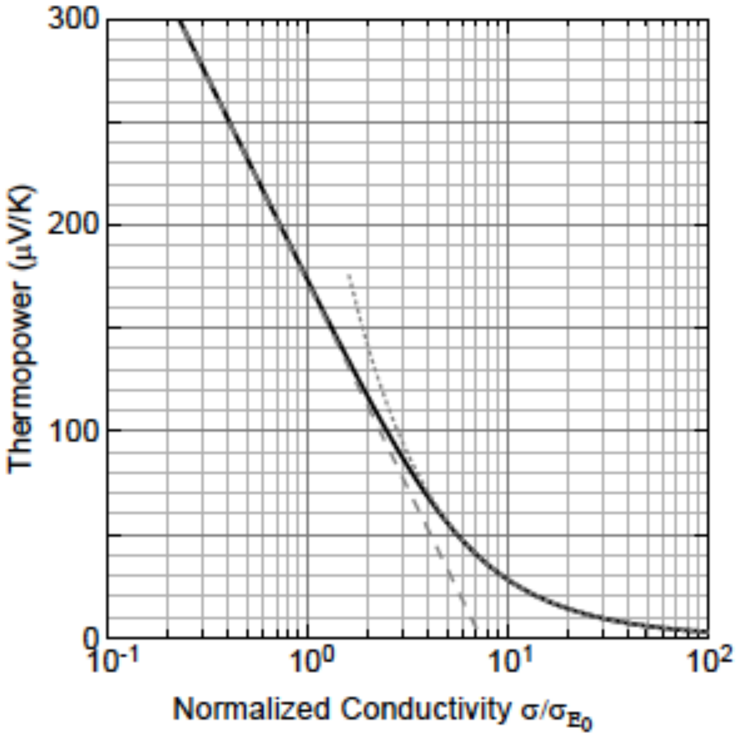
$$\mu_w = 331\frac{cm^2}{Vs}\times\left(\frac{m\Omega cm}{\rho}\right)\times\left(\frac{T}{300K}\right)^{-3/2}\times\exp\left[\frac{|S|}{86.3\mu V/K}-2\right] \qquad |S|>120\mu V/K$$

$$\mu_w = 331\frac{cm^2}{Vs}\times\left(\frac{m\Omega cm}{\rho}\right)\times\left(\frac{T}{300K}\right)^{-3/2}\times\frac{|S|}{284\mu V/K} \qquad |S|<75\mu V/K$$

What is μ_w for Bi_2Te_3 with 300K

S = 173 μV/K

$\rho = 1/\sigma = 1 m\Omega$ cm



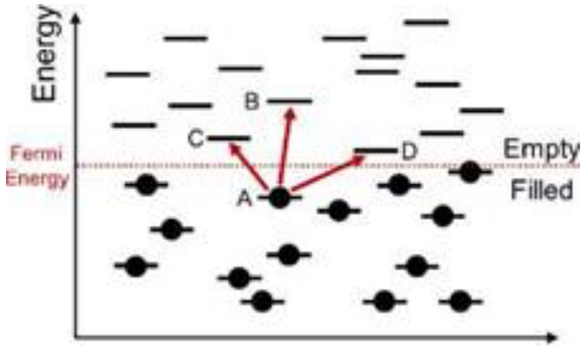
Transport Function σ_E

Generalized Boltzmann Transport Equation

Can be derived from Kubo formula, fluctuation-dissipation theorm

Conductivity σ can be described by a Transport Function σ_E

$$\sigma = \int \sigma_E \frac{-\partial f}{\partial E} dE$$



$f(E)$ is distribution function (Fermi function)

– only states near Fermi Level contribute

$$\sigma_E = \tfrac{2e^2}{3} v^2 \tau g$$

Free Electron Metals (Drude model)

v velocity, τ scattering time, g Density of States

Hopping Model

$v\tau$ jump distance, τ^{-1} jump frequency, g Density of States

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Cutler and Mott *Physical Review* **181**, 1336 (1969)

Power law form of σ_E

$$\sigma_E = \tfrac{2e^2}{3} v^2 \tau g$$

for Metals and Semiconductors:

Energy is measured from E_t

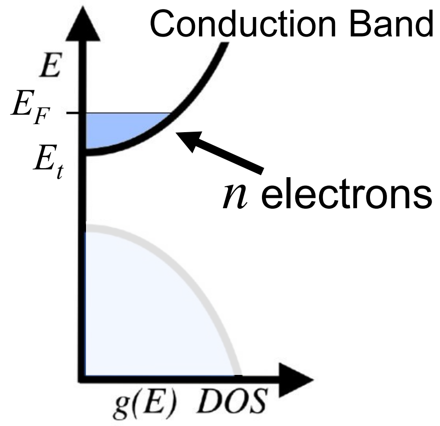
$$\tfrac{1}{2} m^* v^2 = E - E_t$$

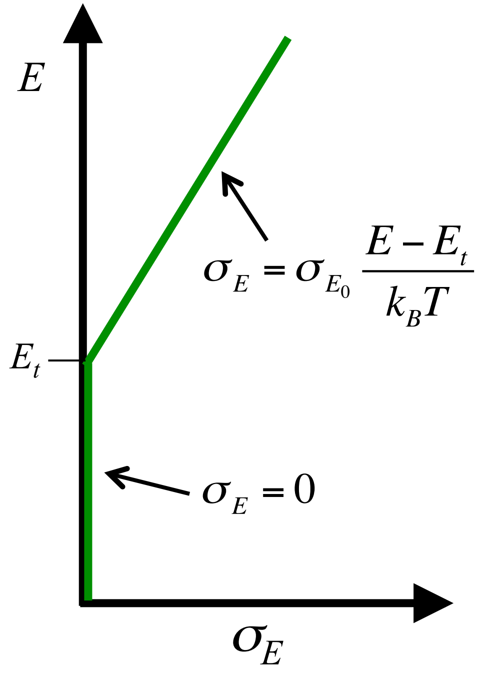
$$g(E) = \tfrac{8\pi\sqrt{2}}{h^3} m^{*3/2} \sqrt{E - E_t}$$

relaxation time ~ Energy and DOS

e.g. phonon scattering

$$\tau(E) = \tau_0 / g(E)$$





Transport Parameter: s **Characteristic of the Transport Mechanism**

s = 1 for parabolic band, acoustic phonon scattering

s = 3 ionized impurity scattering

$$\sigma_E(E,T) = \sigma_{E_0}(T) \times \left(\frac{E - E_t}{k_B T} \right)^s \qquad (E > E_t)$$

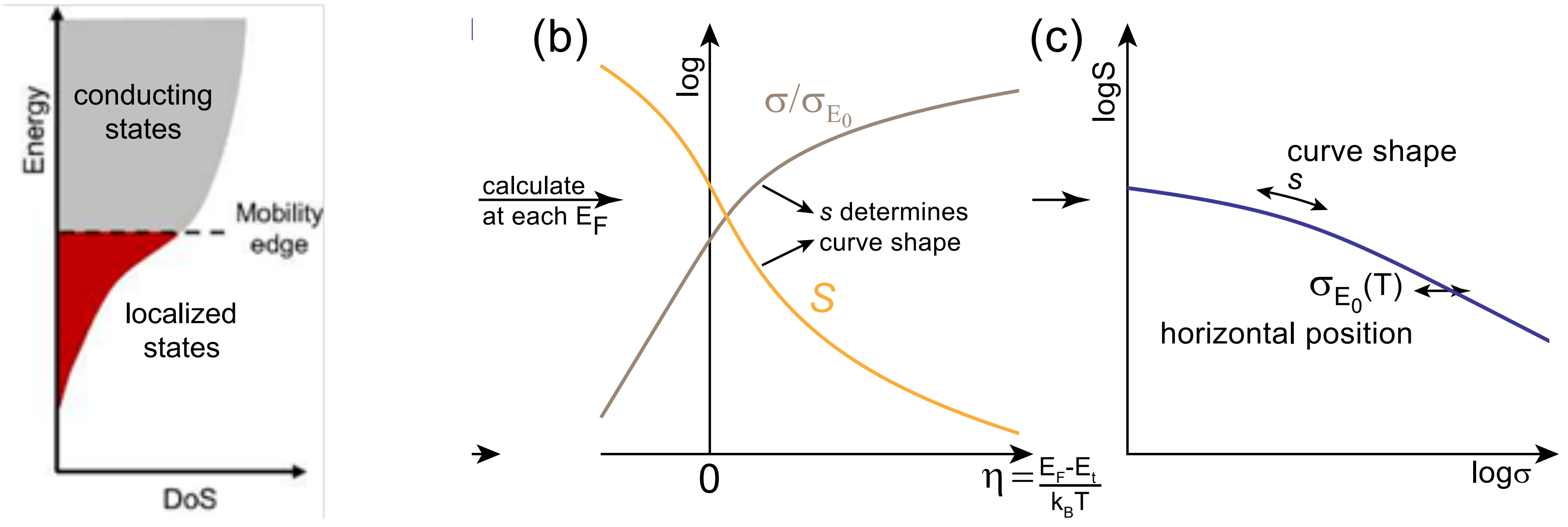
$$\sigma_E(E,T) = 0 \qquad (E < E_t)$$

Transport Mechanism from S and σ

Two simple Parameters: s and σ_{E_0}

s from mechanism – shape of Seebeck vs conductivity

σ_{E_0} gives magnitude – acts like weighted mobility



Transport Model σ_E

Determines S and σ at each E_F (doping)

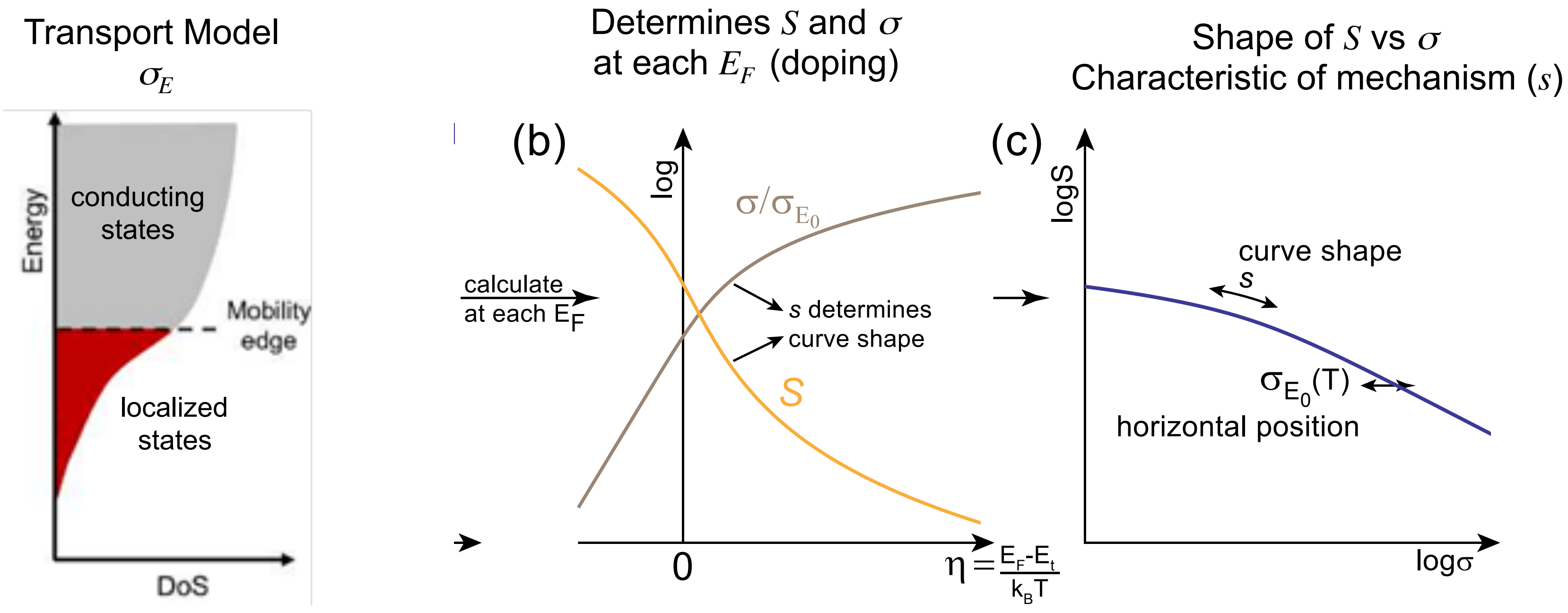
Shape of S vs σ Characteristic of mechanism (s)

Transport Mechanism from S and σ

Two simple Parameters: s and σ_{E_0}

s from mechanism – shape of Seebeck vs conductivity

σ_{E_0} gives magnitude – acts like weighted mobility

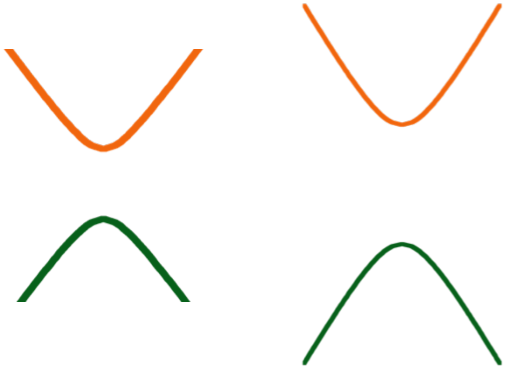


Transport Model σ_E

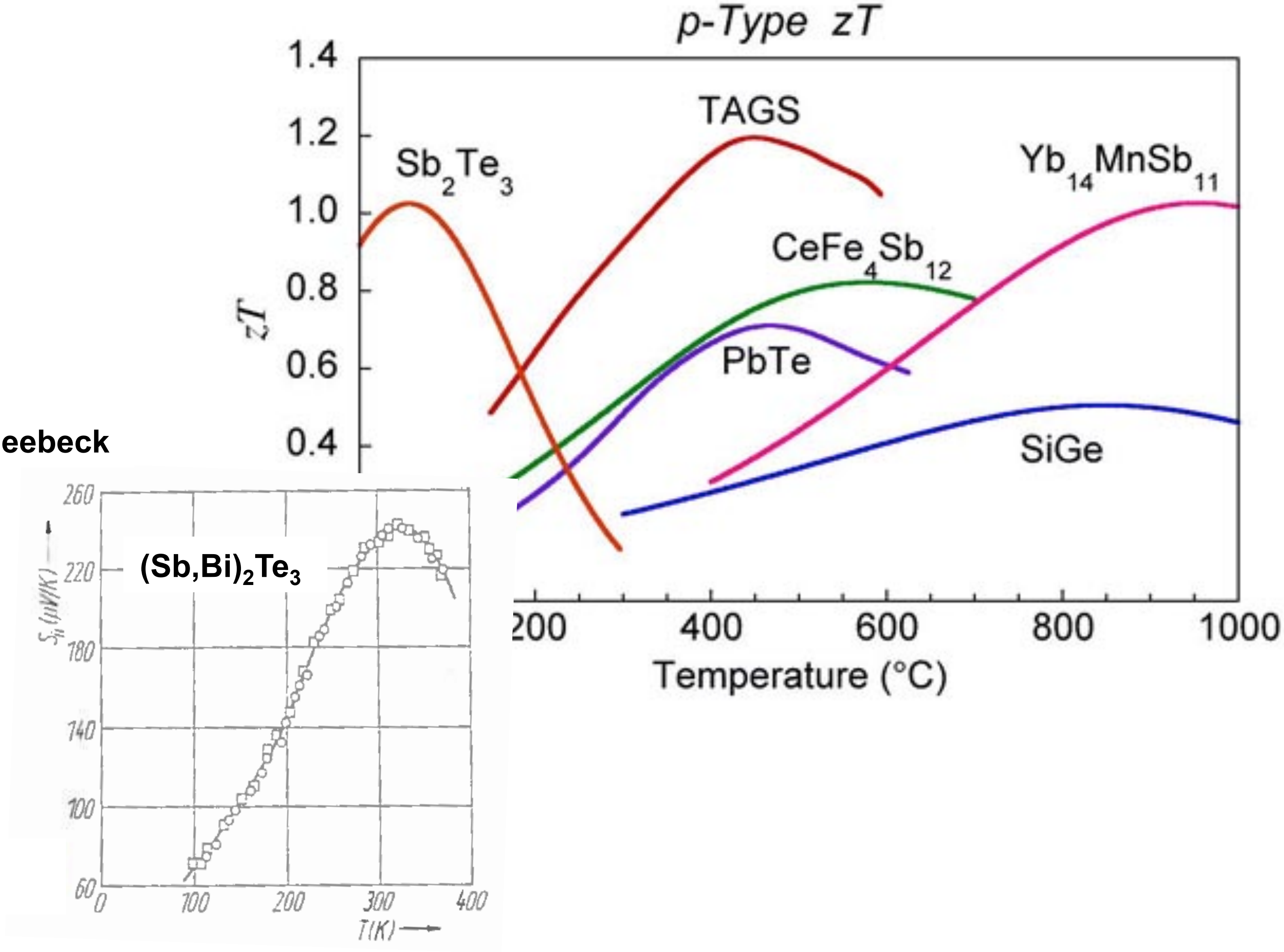
Determines S and σ at each E_F (doping)

Shape of S vs σ Characteristic of mechanism (s)

Band Gap



Thermopower peak = zT peak



H. J. Goldsmid and J. W. Sharp, J. Electron. Mater. **28**, 869 (1999)

M. Stordeur and W. Kuhnberger, Phys. Stat. Sol. (b) **69**, 377 (1975)

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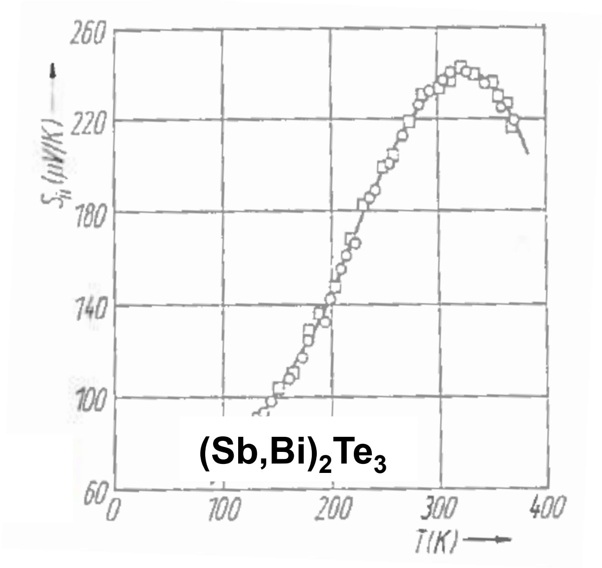
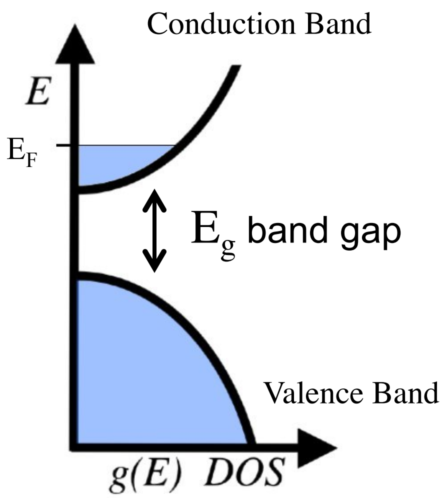
Bipolar effect

Seebeck





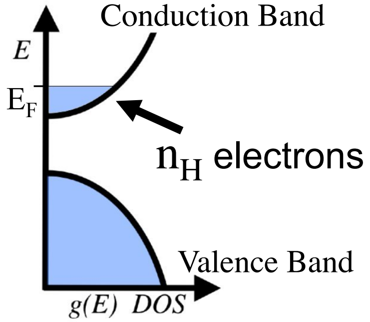
$$S_{total} = \frac{\sigma_{major} S_{major} - \sigma_{minor} S_{minor}}{\sigma_{major} + \sigma_{minor}}$$

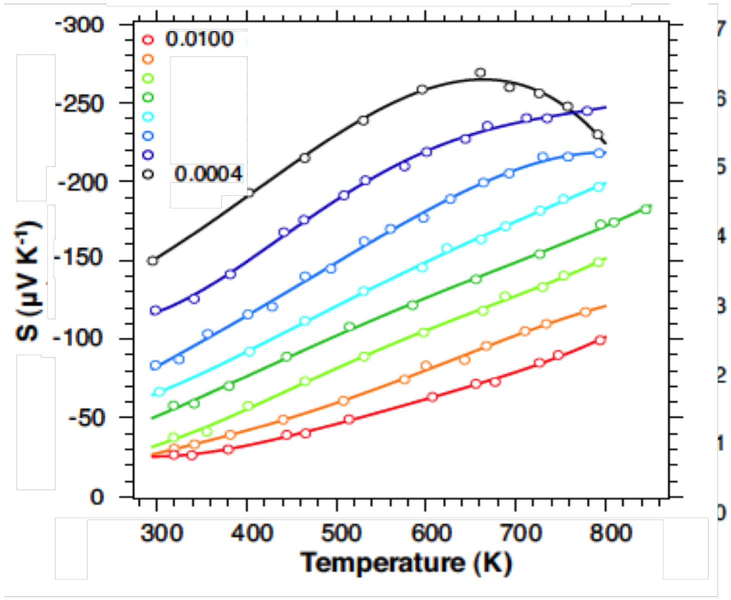
M. Stordeur and W. Kuhnberger, Phys. Stat. Sol. (b) **69**, 377 (1975)

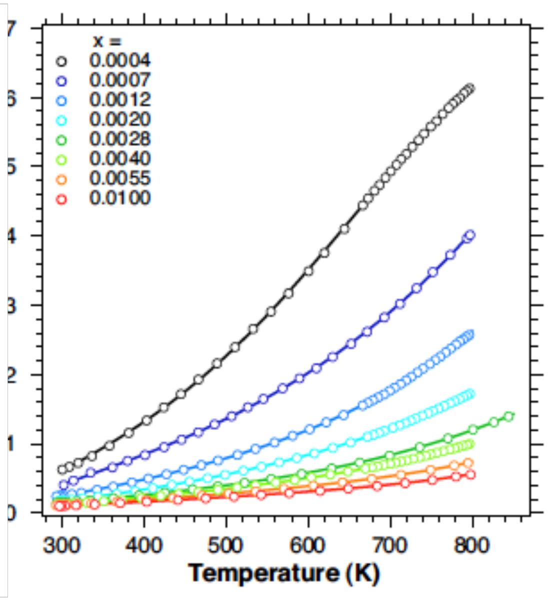
Degenerate Semiconductor Behavior

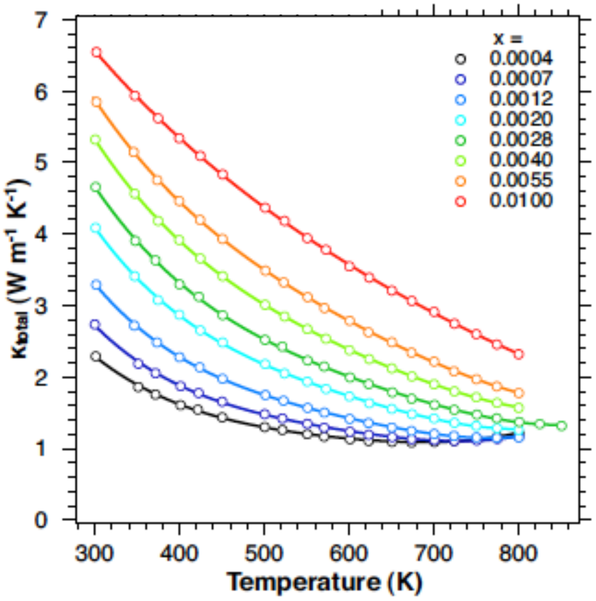
1. linear Seebeck
2. Linear Resistivity
3. 1/T + Constant thermal conductivity

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





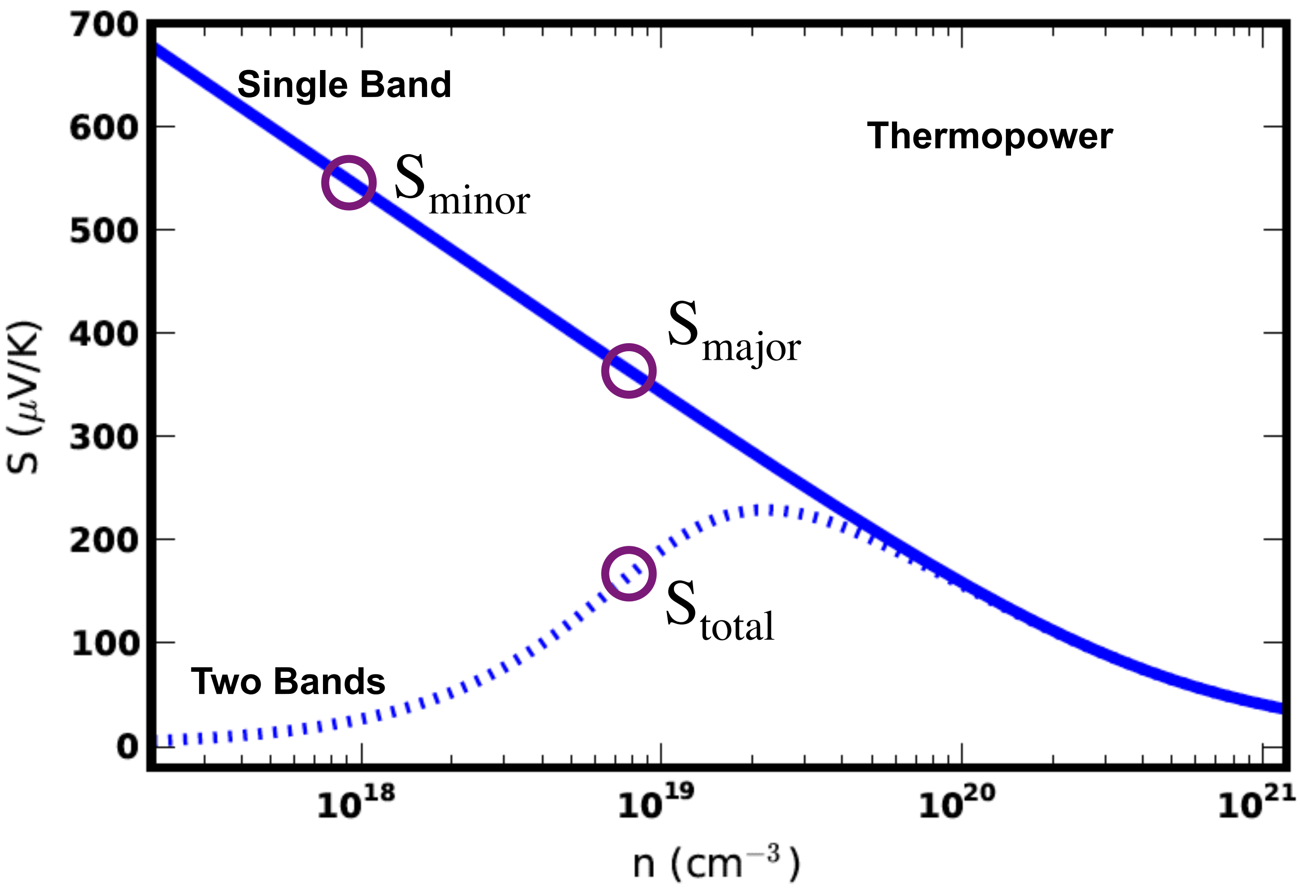




Non-Degenerate Resistivity
(Intrinsic Semiconductor)

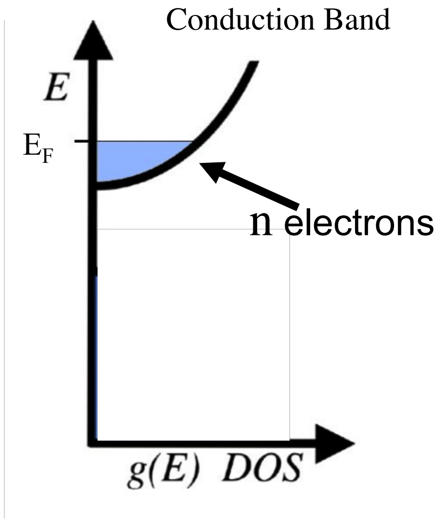
$$\ln\left(\frac{1}{\rho}\right) = \frac{-E_g}{2k_BT}$$

Bipolar Thermopower

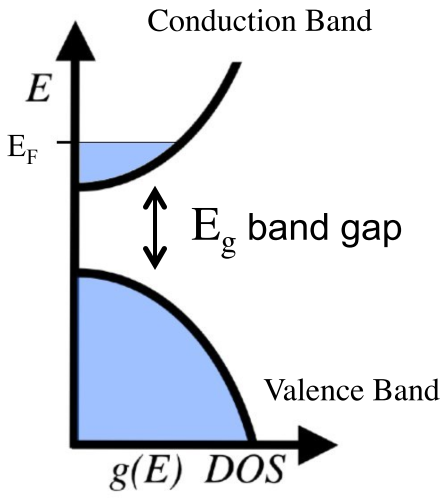


$$S_{total} = \frac{\sigma_{major} S_{major} - \sigma_{minor} S_{minor}}{\sigma_{major} + \sigma_{minor}}$$

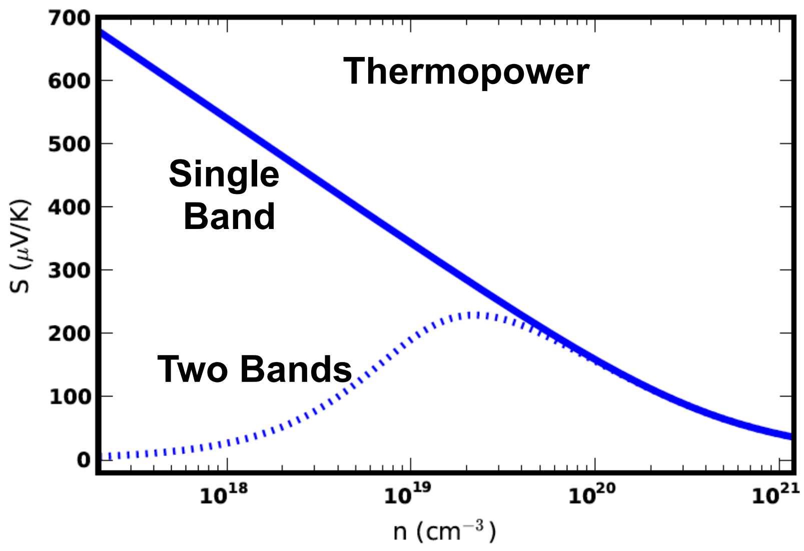
Single Band

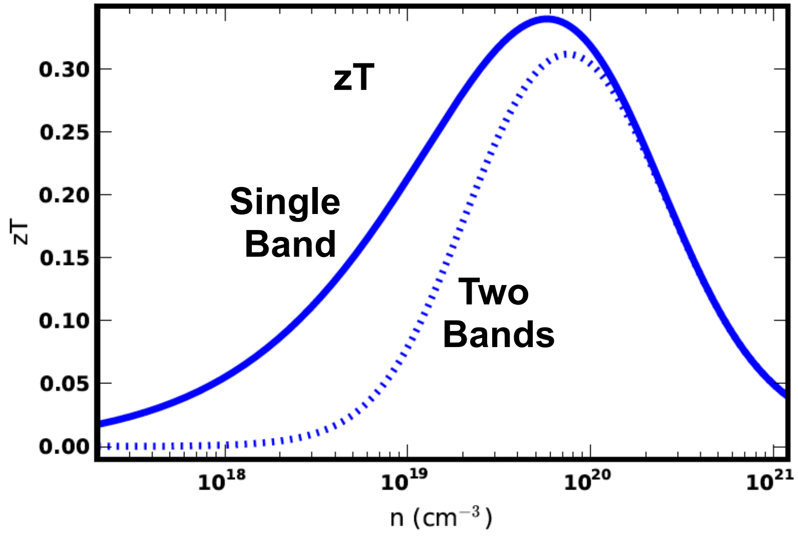


Two Bands

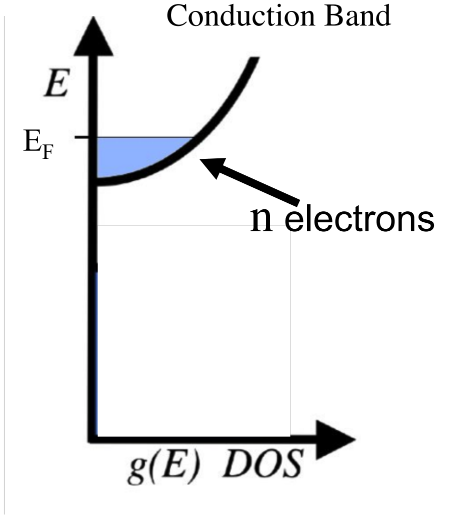


zT Peak

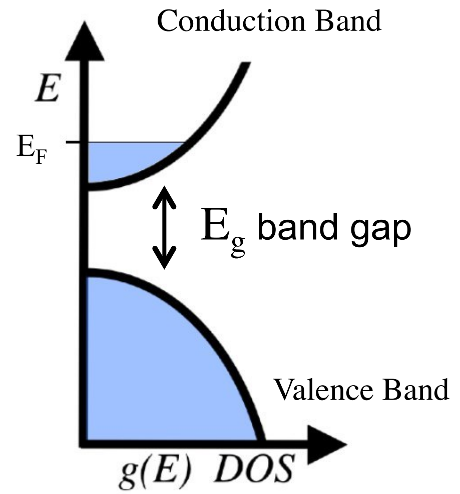




Single Band



Two Bands

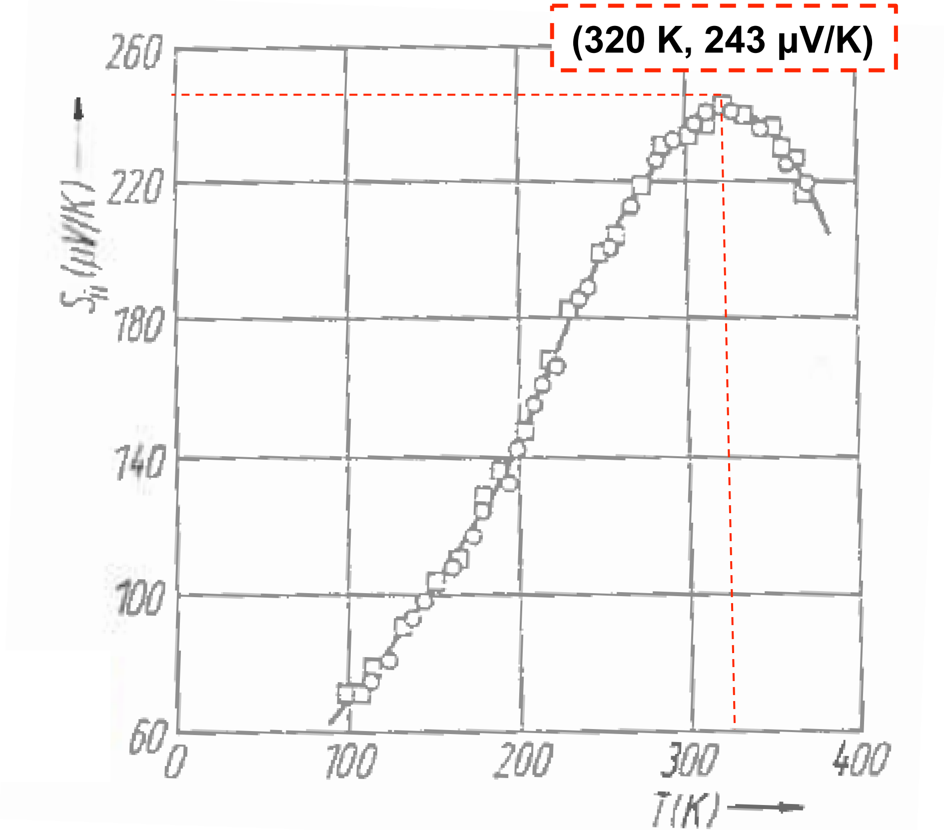


Goldsmid-Sharp Formula

H. J. Goldsmid

Jeff Sharp

Goldsmid-Sharp $$E_g = 2eS_{\max}T_{\max}$$



$(Sb,Bi)_2Te_3$

$$E_g = 2eS_{\max}T_{\max} = 0.156eV$$

Optical Gap

$$0.14eV$$

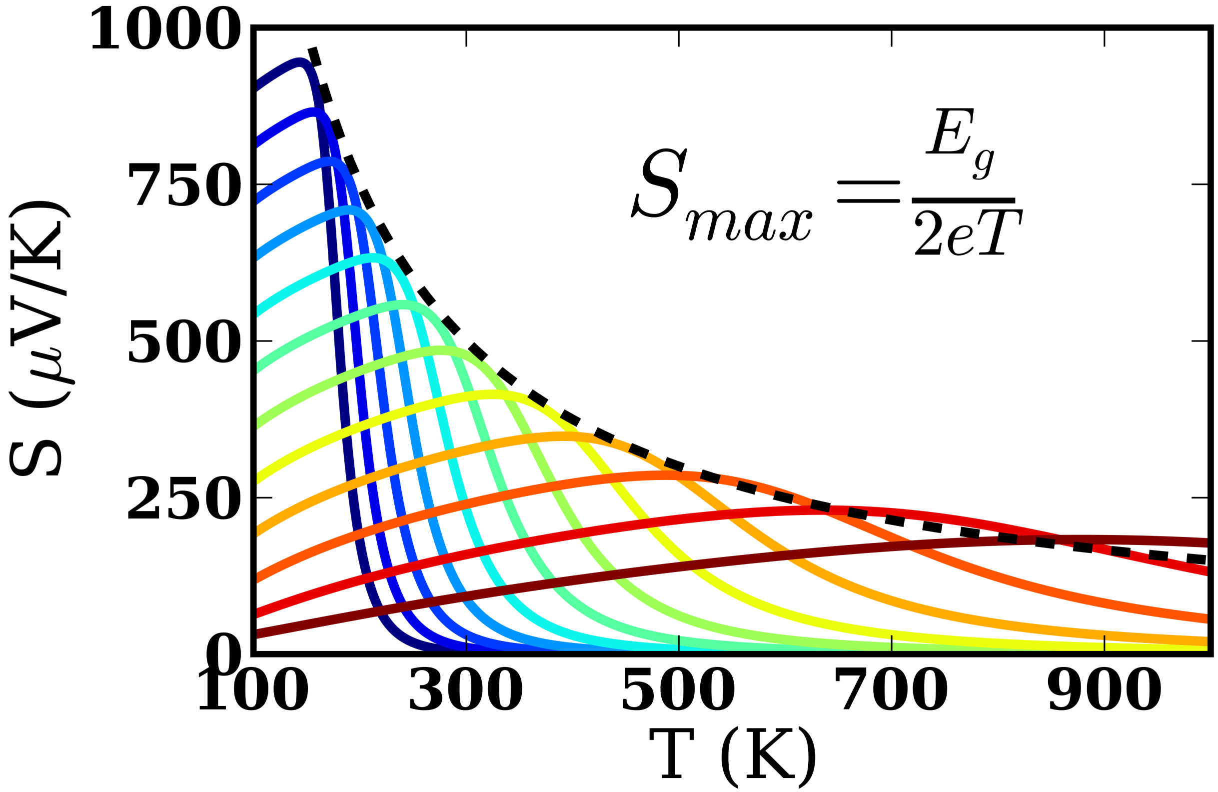
H. J. Goldsmid and J. W. Sharp, J. Electron. Mater. **28**, 869 (1999)
M. Stordeur and W. Kuhnberger, Phys. Stat. Sol. (b) **69**, 377 (1975)
O. Madelung, Semiconductors: Data Handbook (2003)

Goldsmid-Sharp Maximum Seebeck

Doping changes S vs T

But peak S is limited by E_g

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



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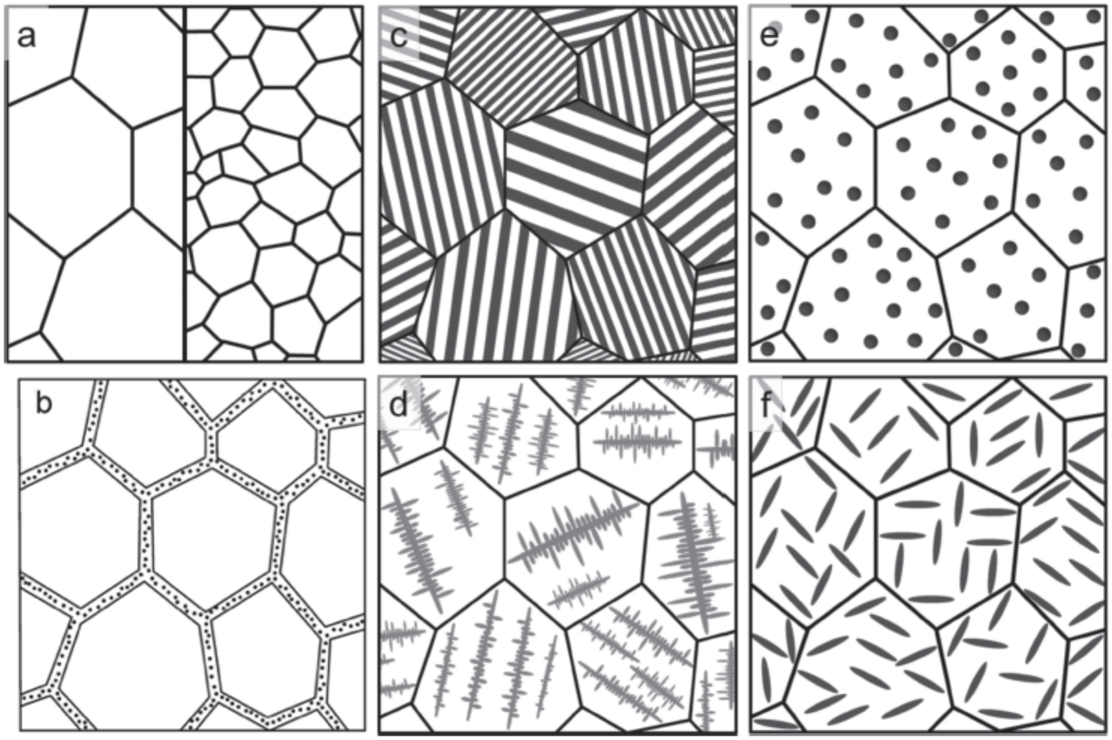
H. J. Goldsmid and J. W. Sharp, J. Electron. Mater. **28**, 869 (1999)
Gibbs, H-S Kim, GJS unpublished

Electron Scattering from Interfaces



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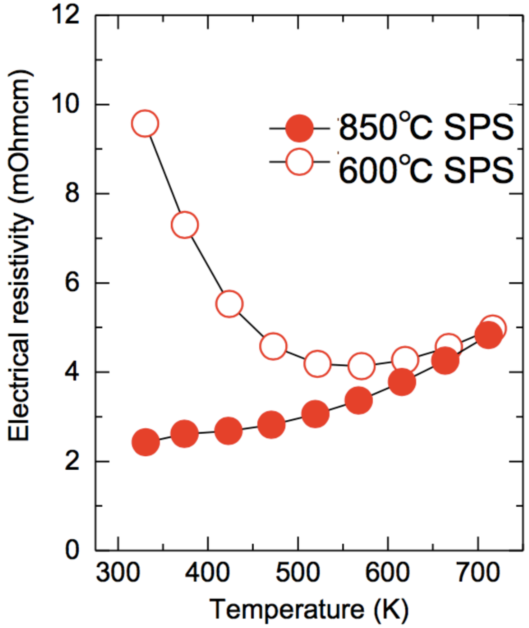
Heinz, Snyder et al, Adv. Functional Mat. **24**, 2135 (2014)

Grain Size Dependence

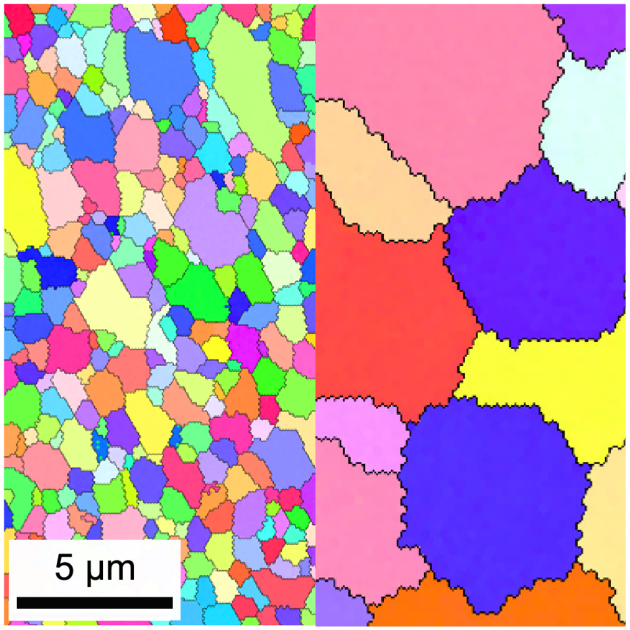
Experimentally, the thermally activated behavior can be reduced by increasing the grain size

Seebeck unaffected by grain size

ρ

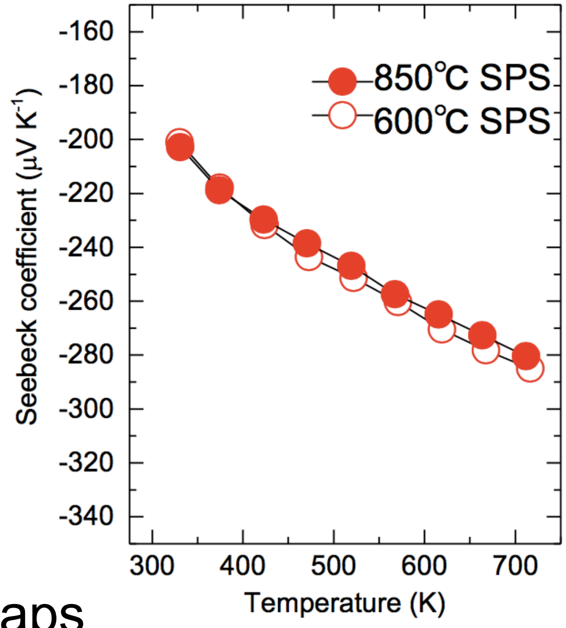


600C SPS 850C SPS



EBSD crystal-orientation maps

S

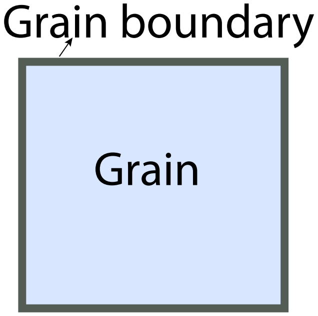


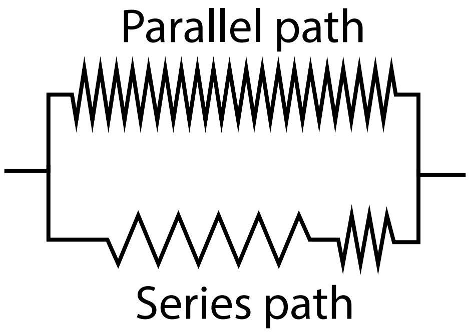
Interface Resistance Model

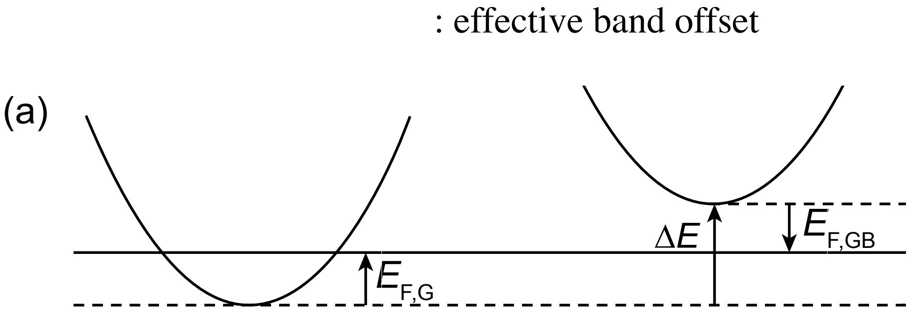
Assume separate resistance for Grain and Grain Boundary

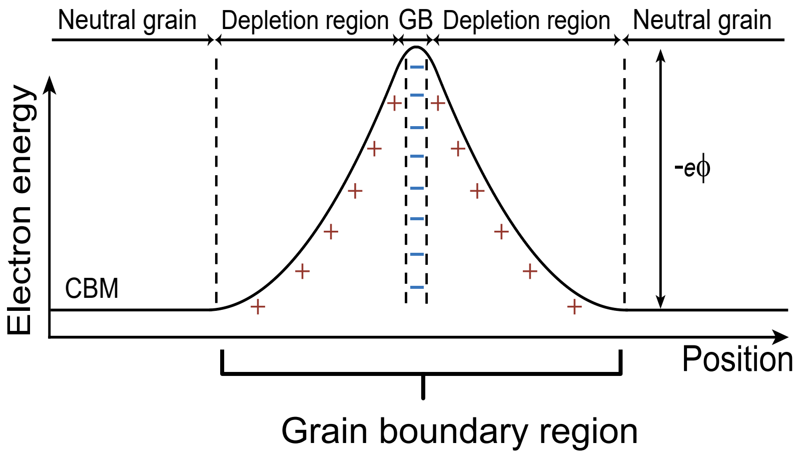
equivalent to effective medium theory

charged interfacial layer may provide band offset









$$\sigma \propto \exp\left(\frac{-\Delta E}{k_B T}\right)$$

DJ. Bergman et. al., *Journal of Applied physics* 85.12 (1999): 8205

Band Engineering of Thermoelectric Materials

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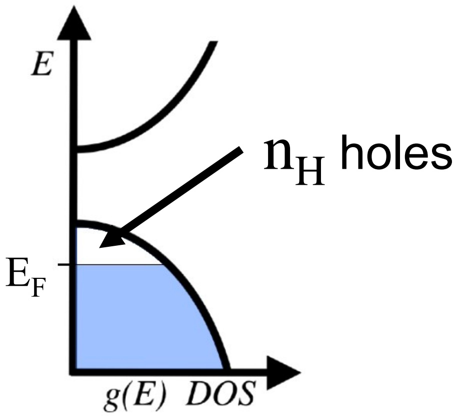
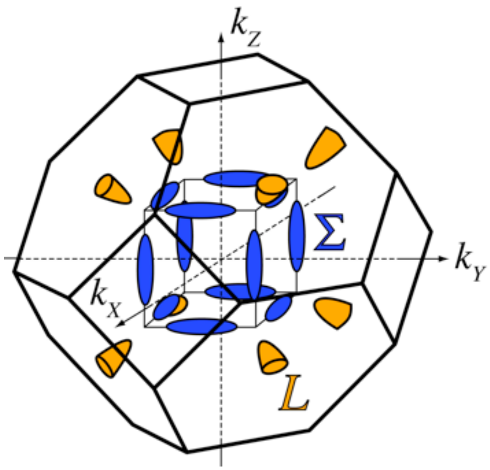
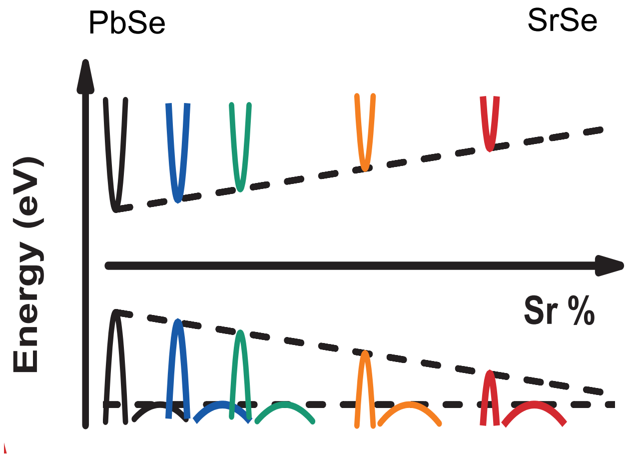
http://thermoelectrics.matsci.northwestern.edu







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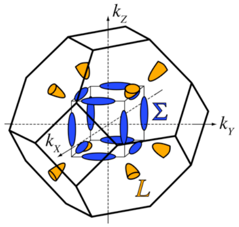
Pei, Snyder, **Advanced Materials, 24**, 6125 (2012)

Quality Factor

Multi Valley Fermi Surface with Valley Degeneracy N_v

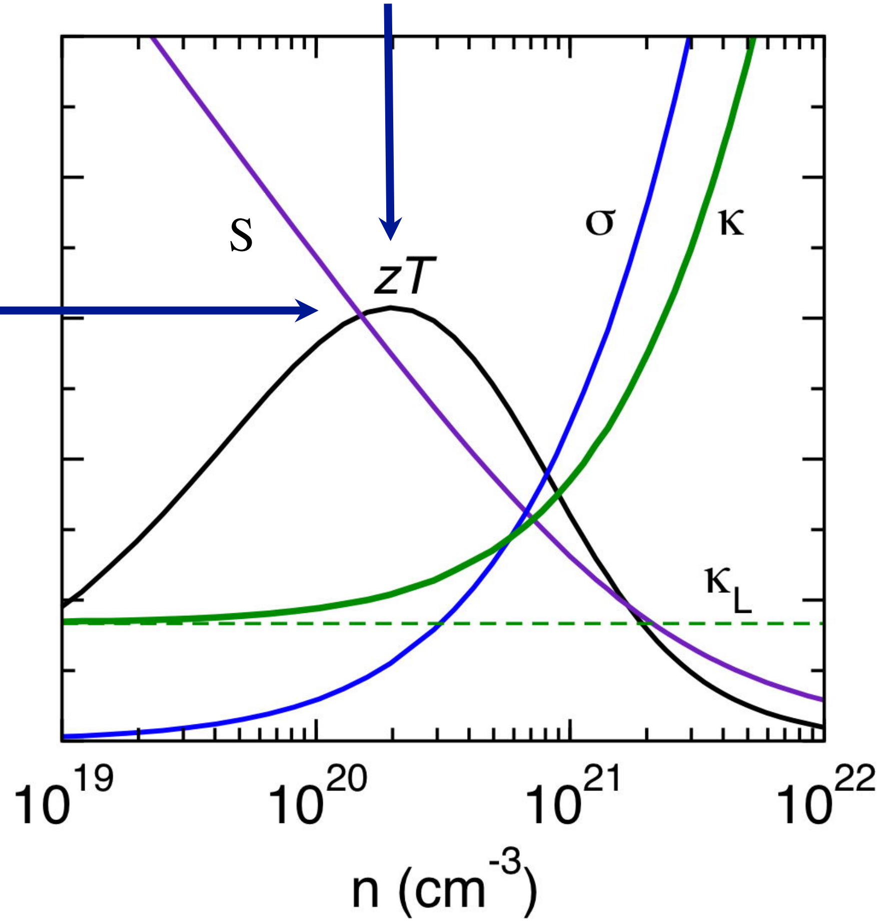
$$m^* = m_b^* N_V^{2/3}$$



Optimized
carrier concentration
$n \sim N_v (m_b^* T)^{3/2}$

Maximum zT depends on Quality Factor

$$B \sim \frac{\mu N_v m_b^{*3/2}}{\kappa_L}$$



But μ decreases with m*

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

Acoustic Phonon Scattering

$$\tau \propto \frac{1}{m_b^{*3/2}}$$

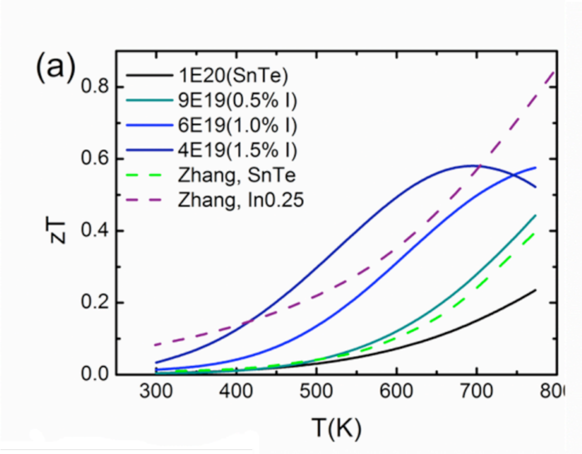
$$\boxed{B \sim \frac{N_V}{m_I^* \kappa_L}}$$

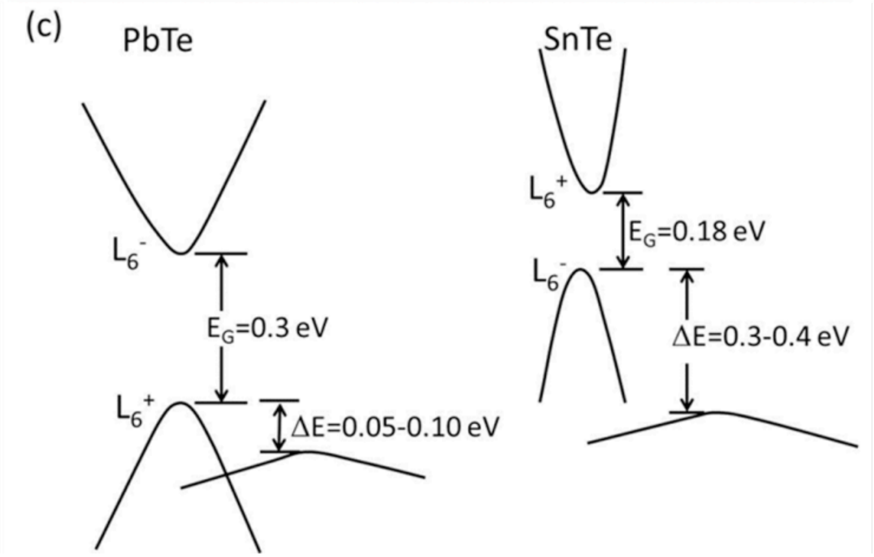
Pei, Wang, Snyder Advanced Materials **24**, 6125 (2012).

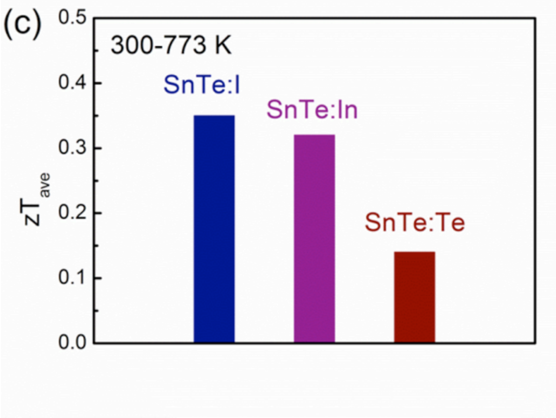
SnTe Small Effective Mass

Light band 0.14me in SnTe

better than high Nv band







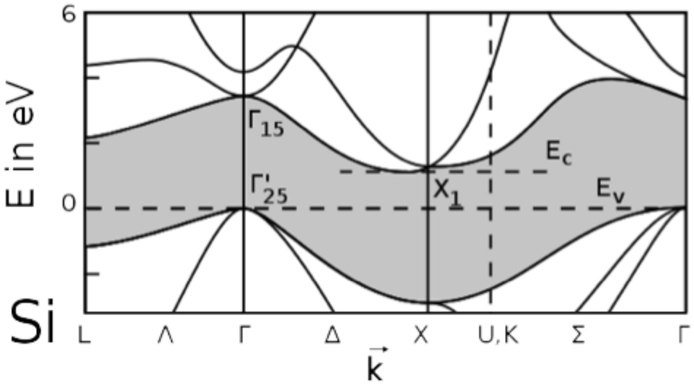
Zhou, Snyder, et al, Phys. Chem. Chem. Phys. 16, 20741 (2014)

Valley Degeneracy N_v

N_v is number of carrier pockets (valleys)

Spherical Fermi Surface

- free-electron model



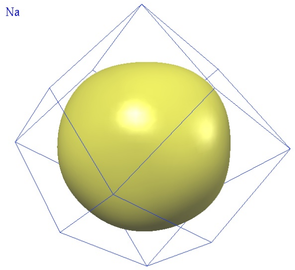
Multiple valley when:

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

Fermi Surfaces

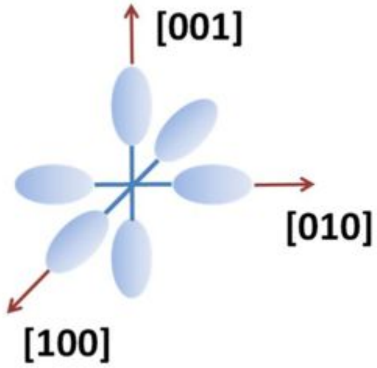
Na

$N_v = 1$

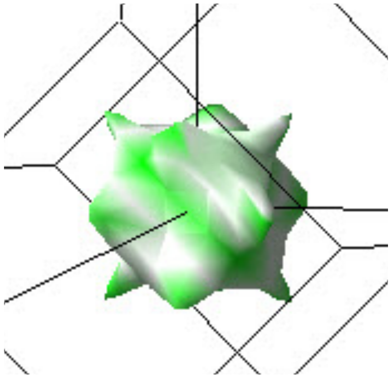


Si

c: $N_v = 6$



v: $N_v = 3$



High N_V in PbTe

Valence Band Maximum is at *L* point

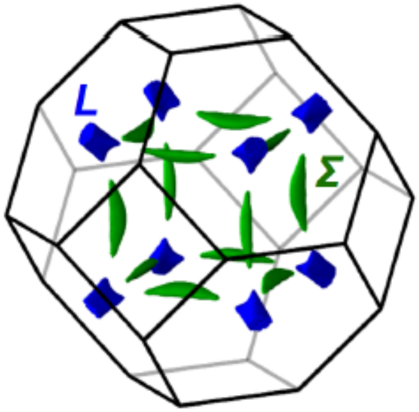
- "Light Band" $N_V = 4, \quad m_b^* = 0.14\, m_e$

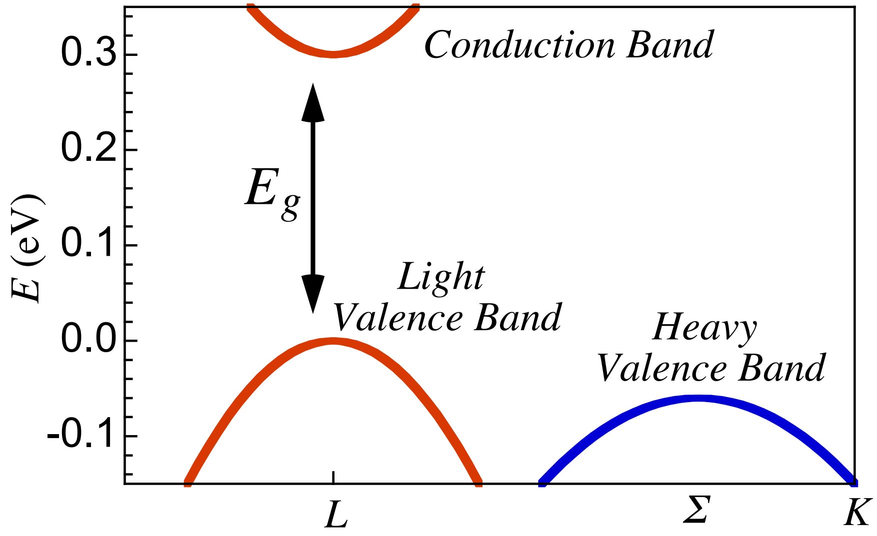
Second valence band occurs at Σ line

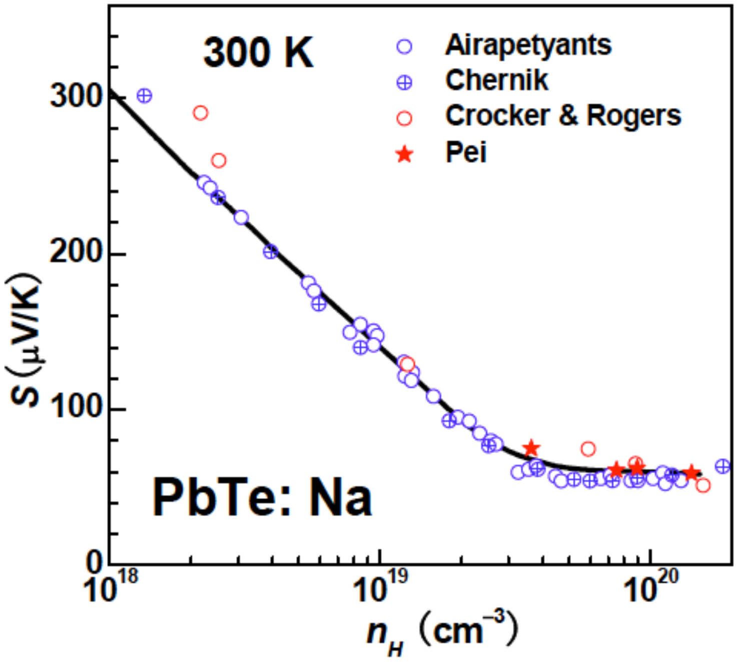
- "Heavy Band" $N_V = 12\ , \quad m_b^* = 0.28\, m_e$

$$m^* = m^*_{band} N_V^{2/3}$$

Transition from single to multiple band occurs at $n_H \sim 3 \times 10^{19}$ holes/cm^3

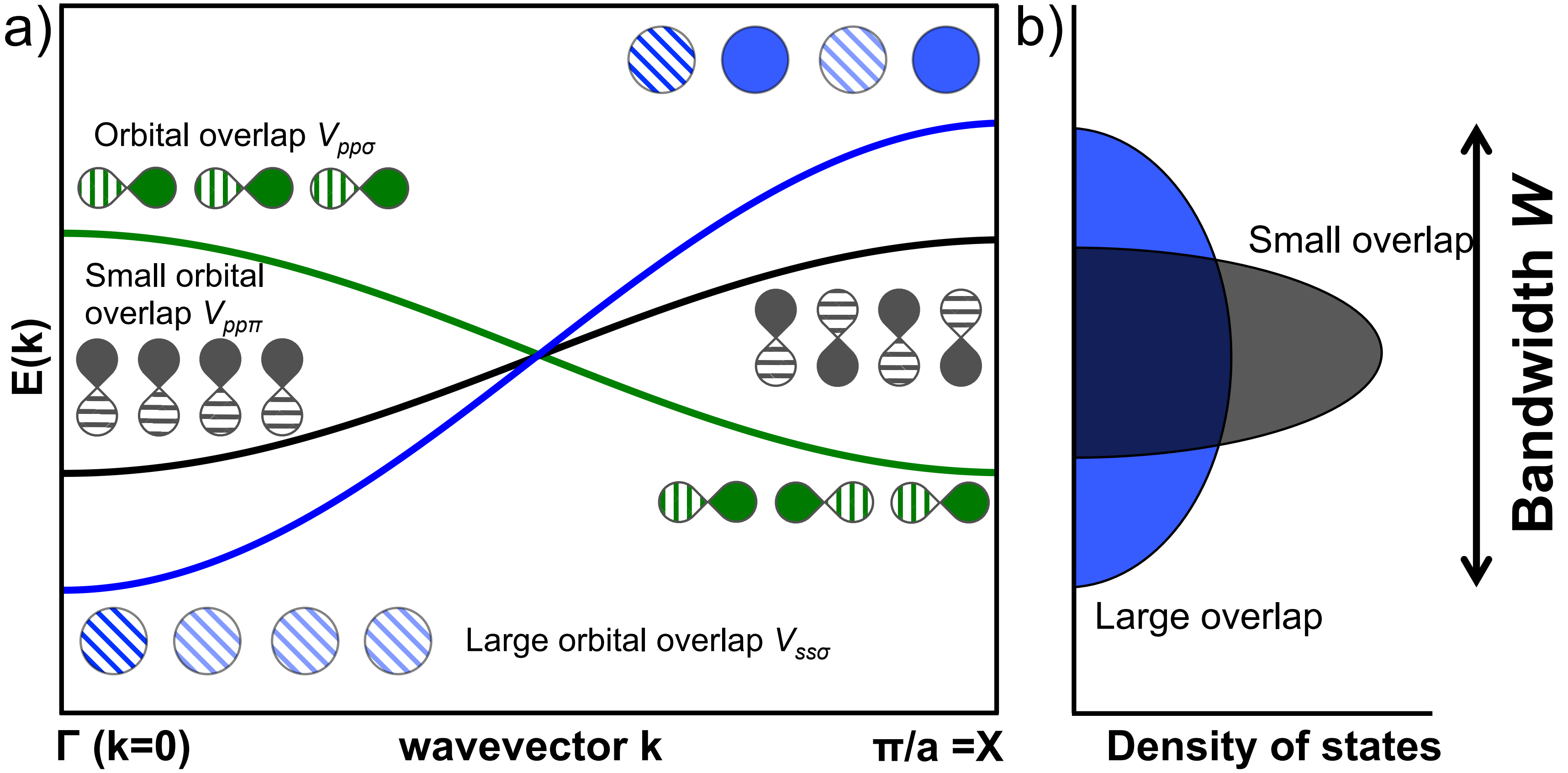






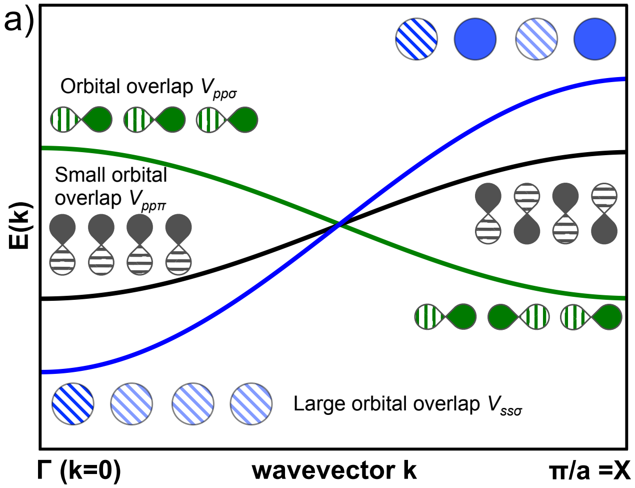
Pei, Snyder, et al.. Energy Environ. Sci. **4**, 2085 (2011).

Mass, Bandwidth and DOS



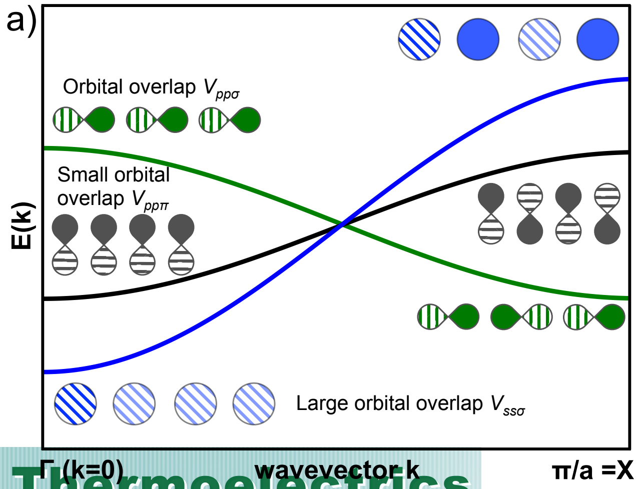
Achieving High Degeneracy

higher valley degeneracy when bands are *off* Γ



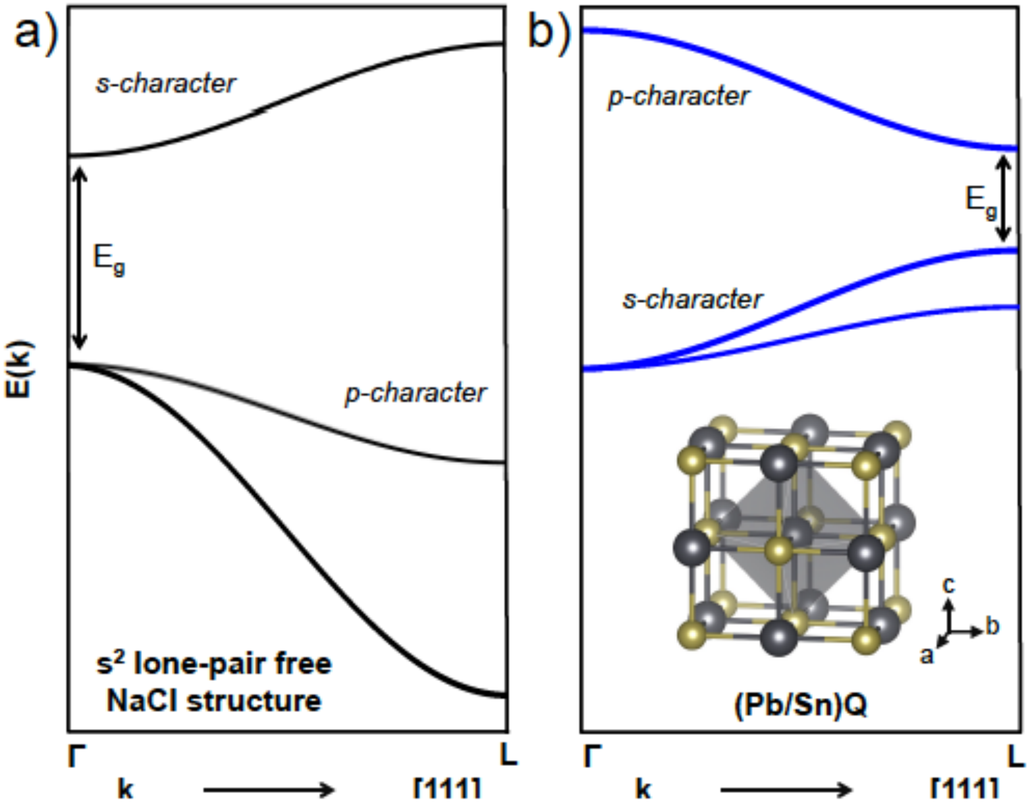
Want
P-like conduction band

band gap



Want
S-like valence bands

Lone Pair PbX band structure



Typical NaCl

has Γ band gap

PbTe has unfilled Pb-p

conduction band

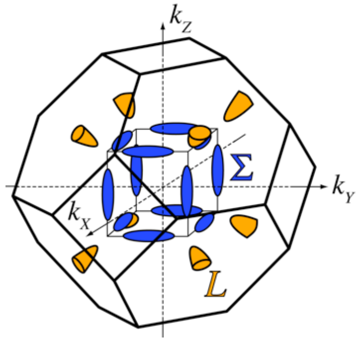
PbTe has filled Pb-s

lone pair

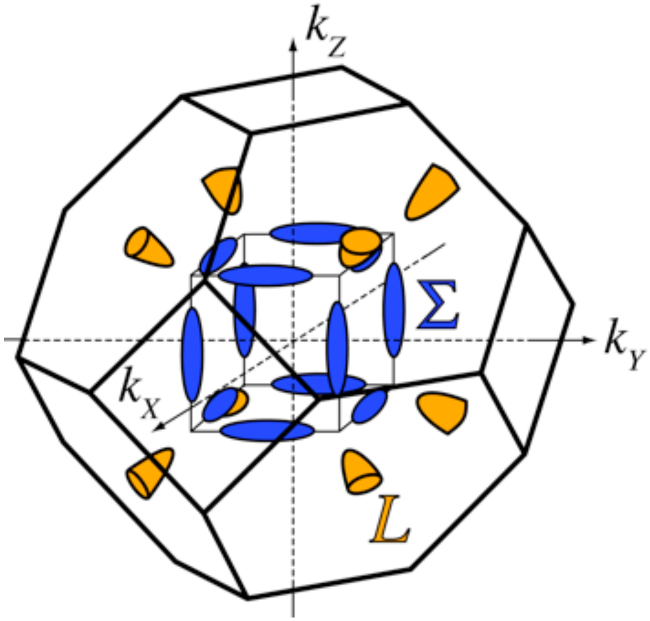
valence band

makes band gap at L

not Γ



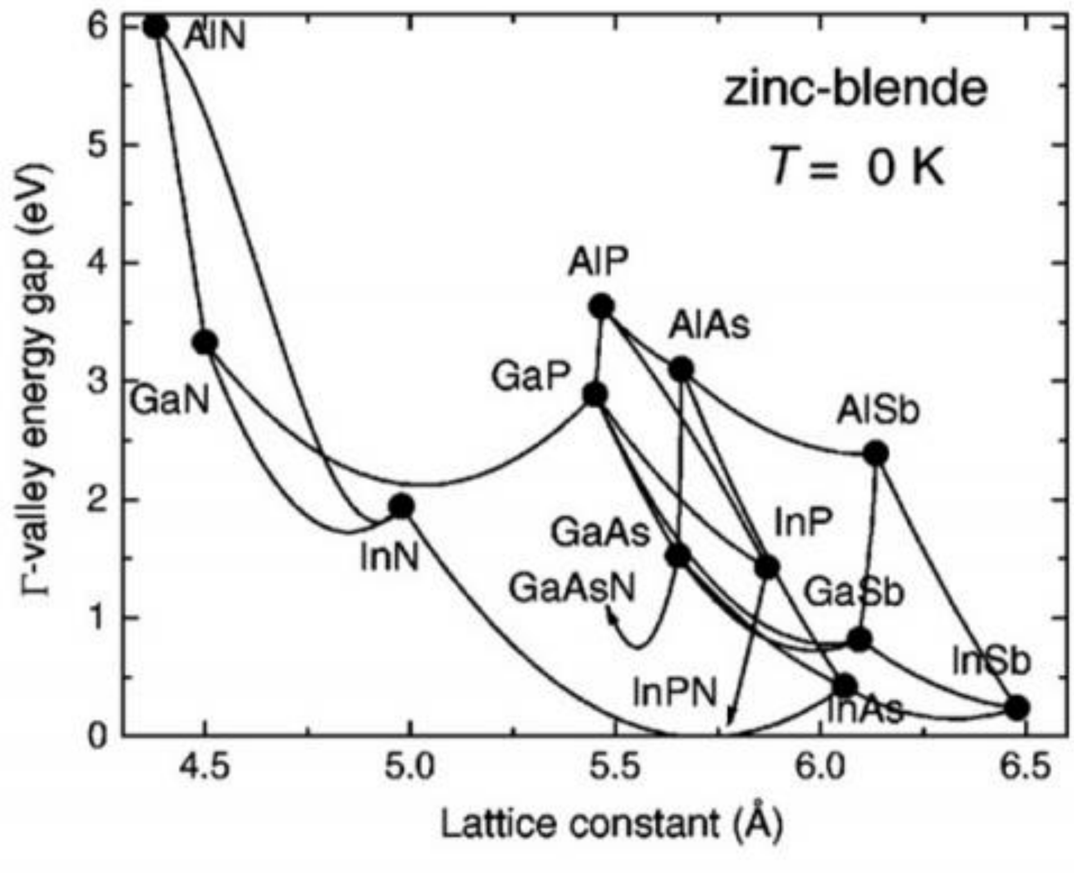
Band Engineering with Alloys



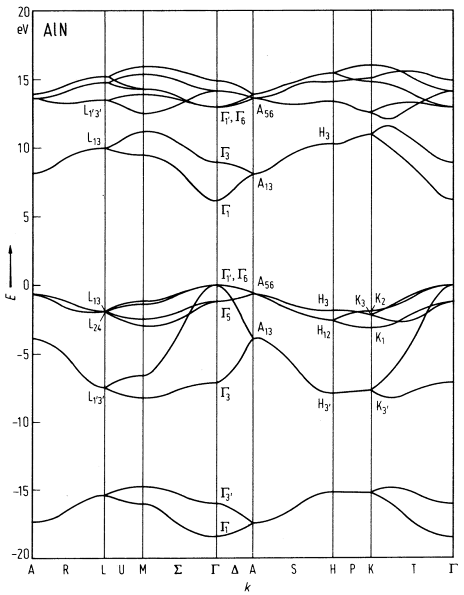
Vegard’s other law

Band Energy ~ linear function of alloy composition

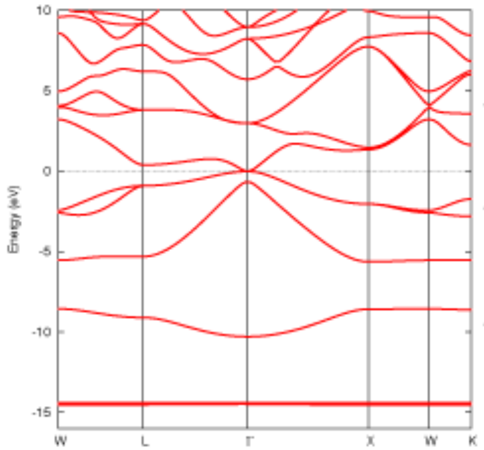
Band Gap vs lattice parameter



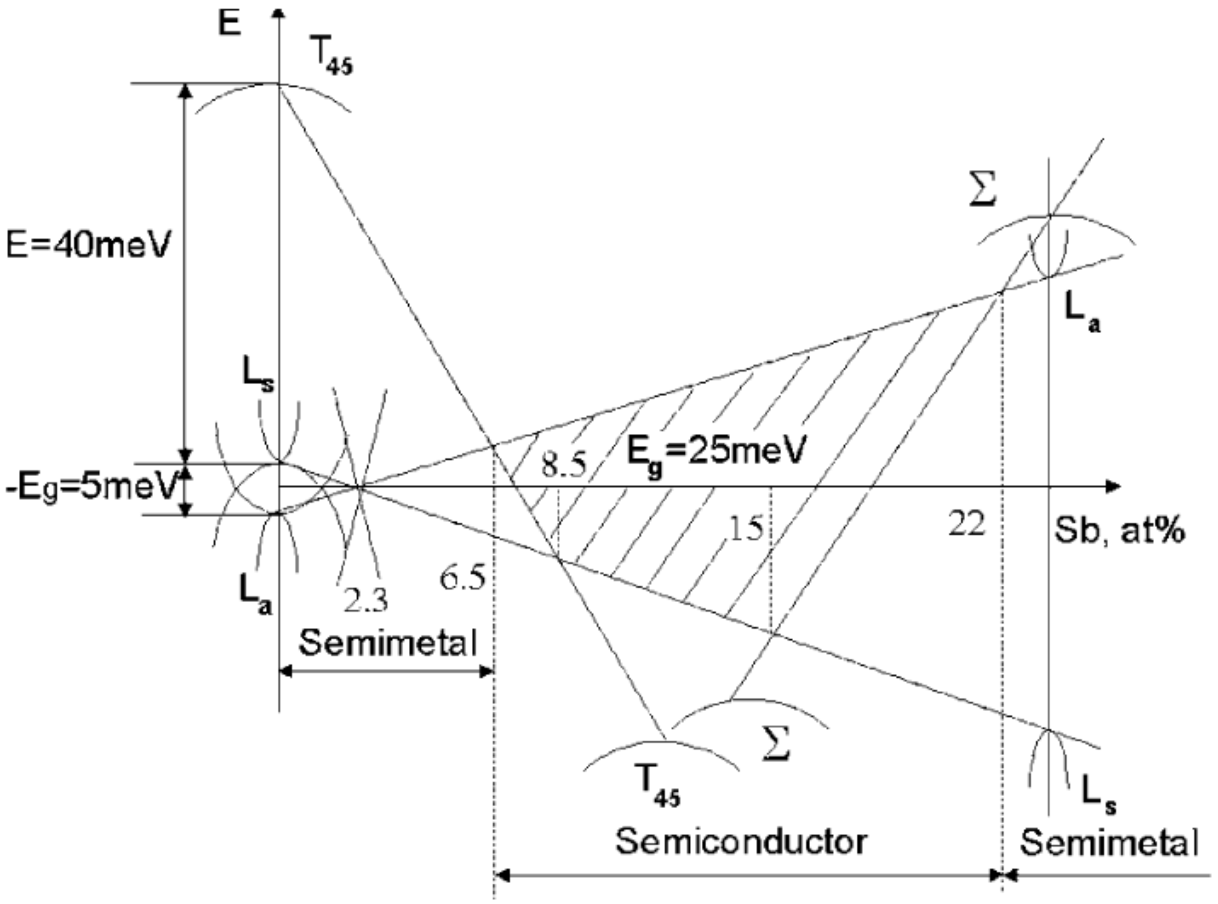
AlN



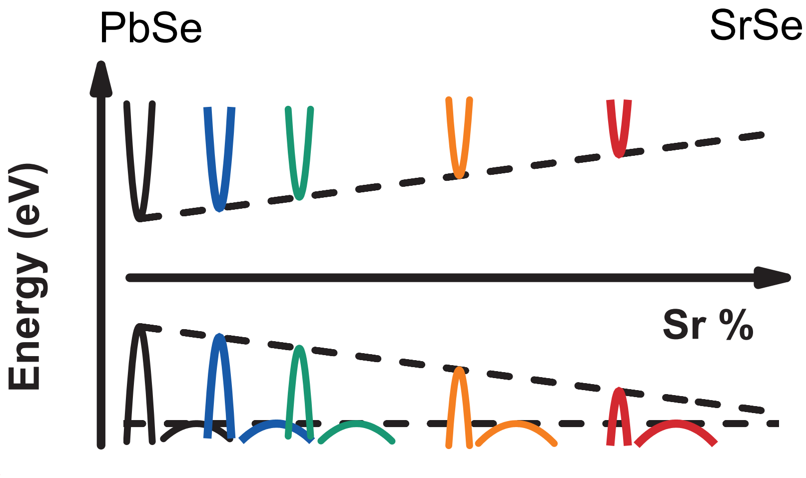
InSb



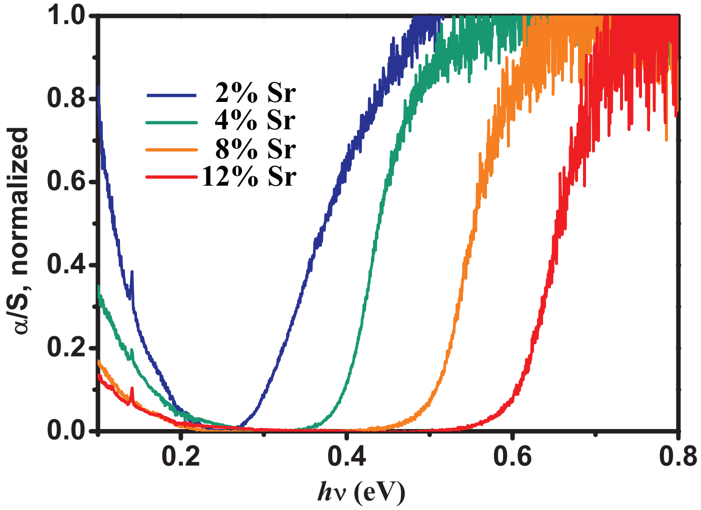
Bi-Sb band diagram

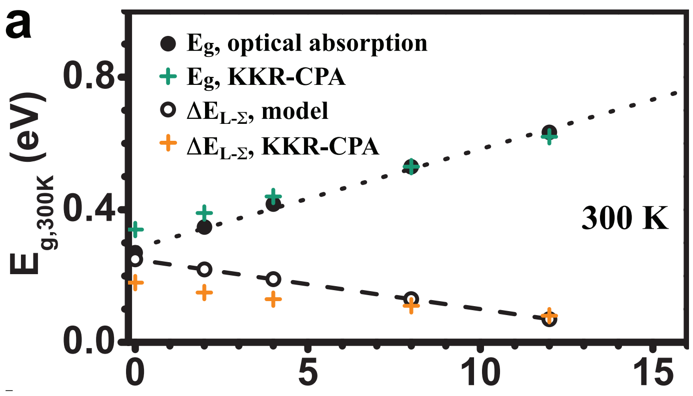


Band Tuning with Alloying



Optical Band Gap





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Wang, Gibbs, Snyder et. al. *Energy Env. Sci.* **7**, 804 (2014)