Struggling Experimentalists' Perspective

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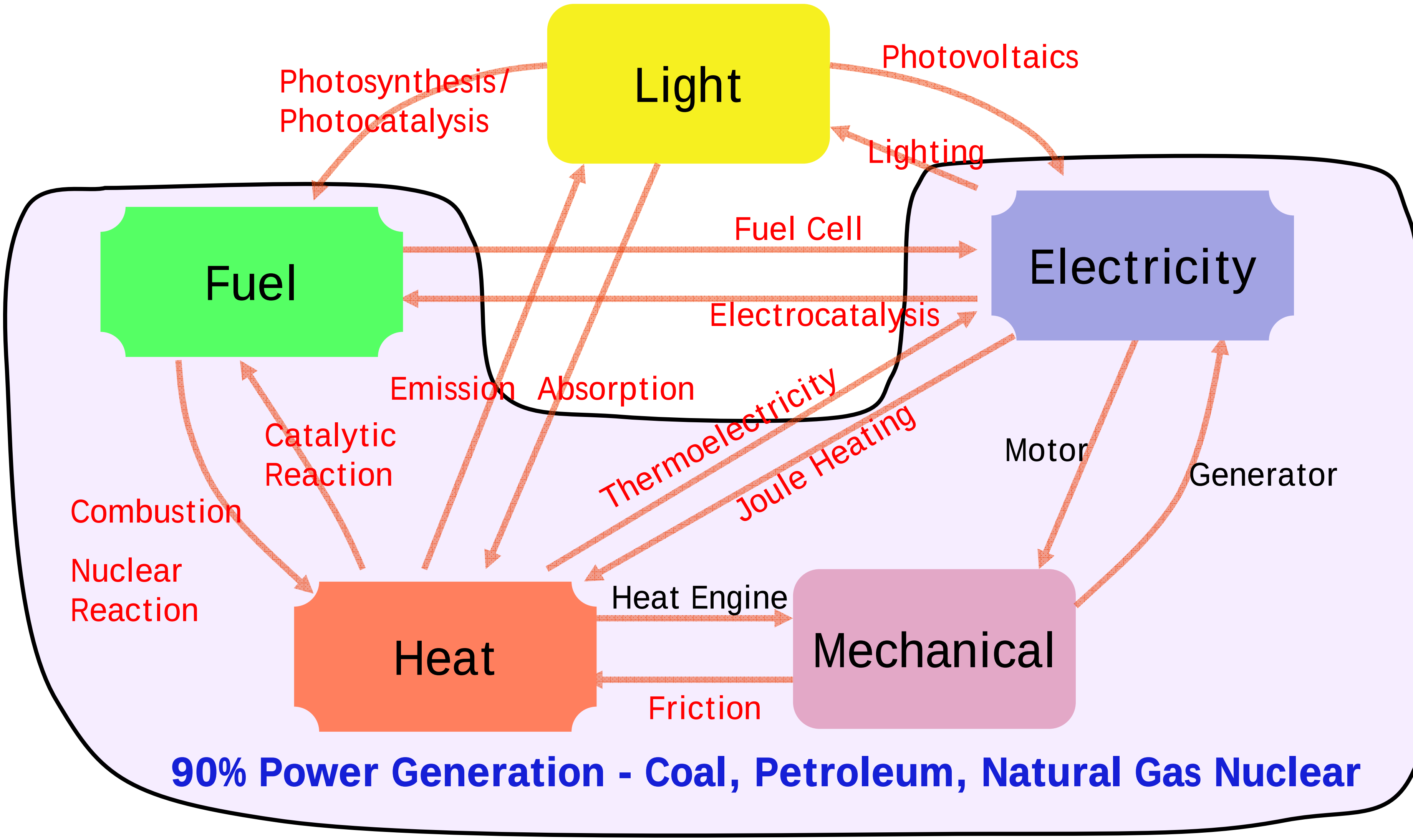
Energy Conversion



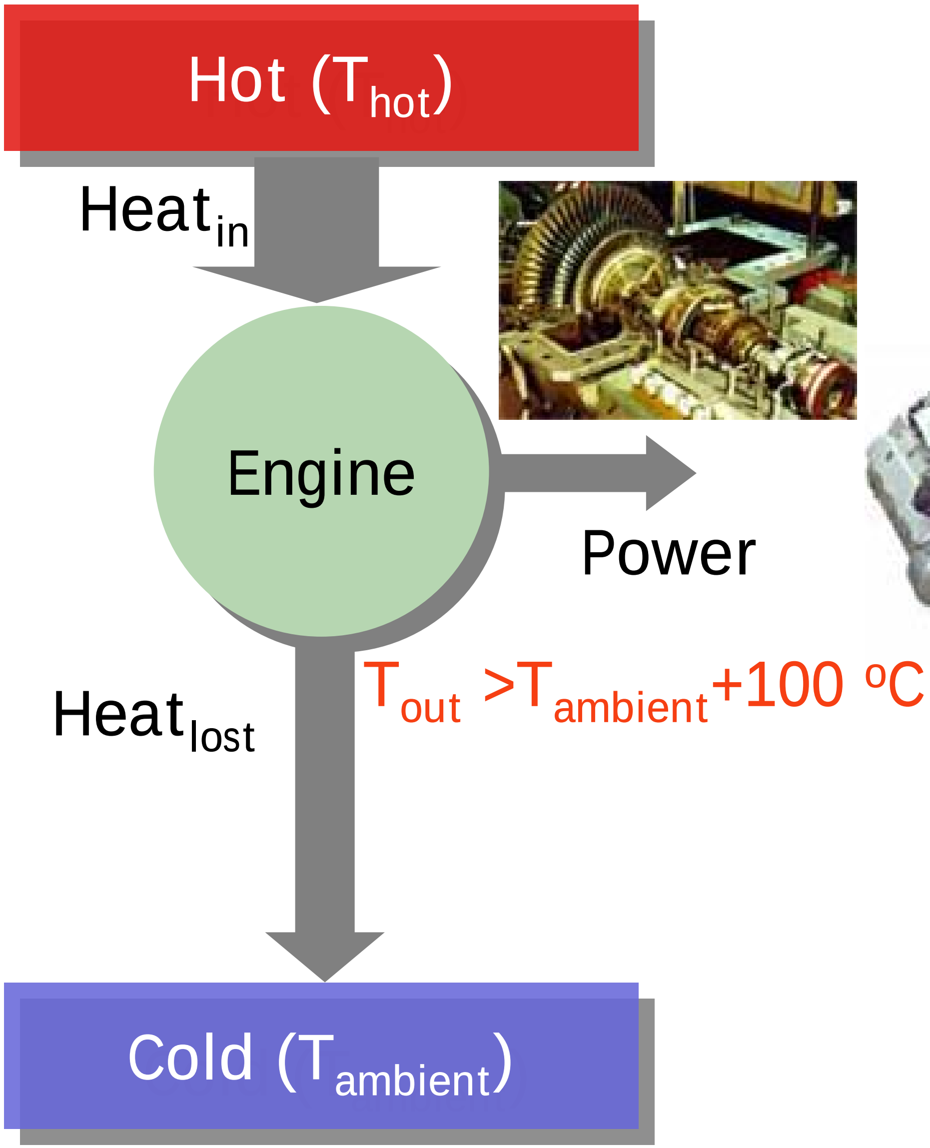
Power Generation

Power = 10 TrillionWatts

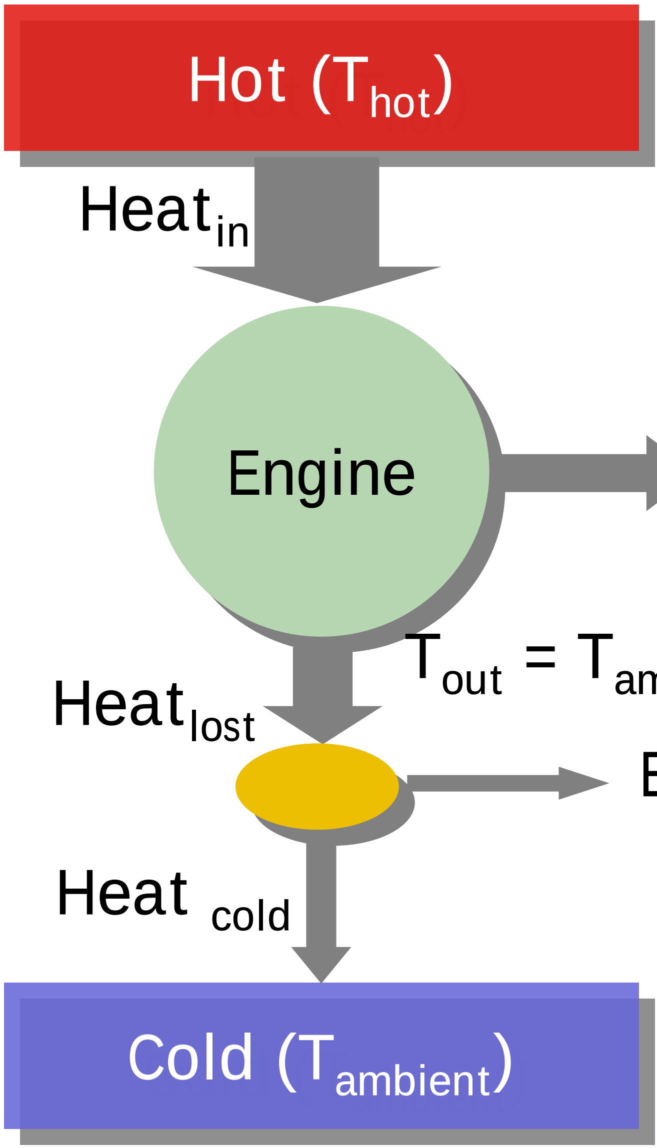
Efficiency = Power / $Heat_{in}$ ~ 40%

$Heat_{in}$ = 25 TW

$Heat_{lost}$ = 15 TW



Power Co-Generation

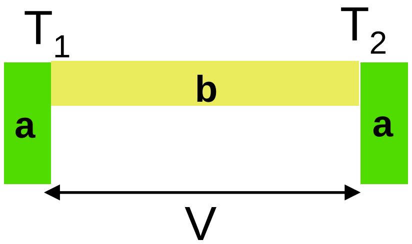


Power = 10 TrillionWatts
Efficiency = Power / $Heat_{in}$ ~ 40%
$Heat_{in}$ = 25 TW
$Heat_{lost}$ = 15 TW

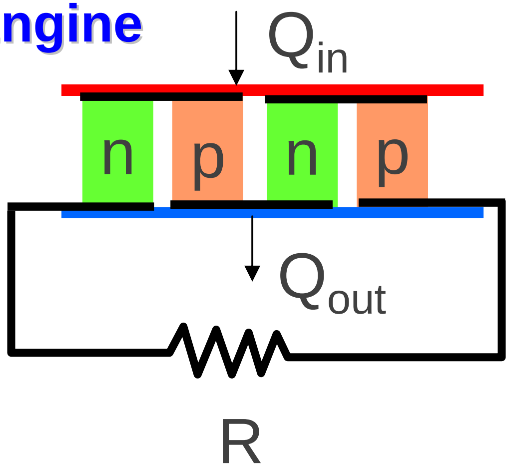
Efficiency ~ 3 %
Extra Power = 0.45 TW
US Electrical Capacity = 1 TW (2005)

Thermoelectricity & Energy Conversion

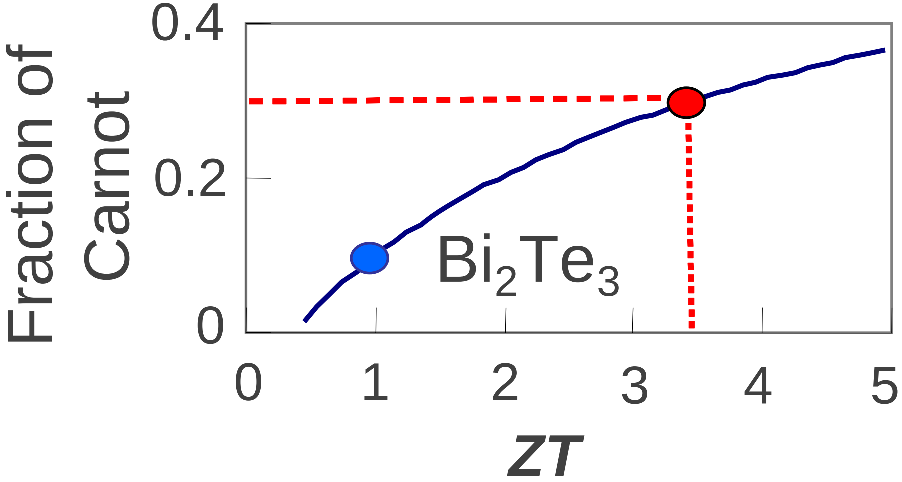
Seebeck Coefficient, S = V/ΔT



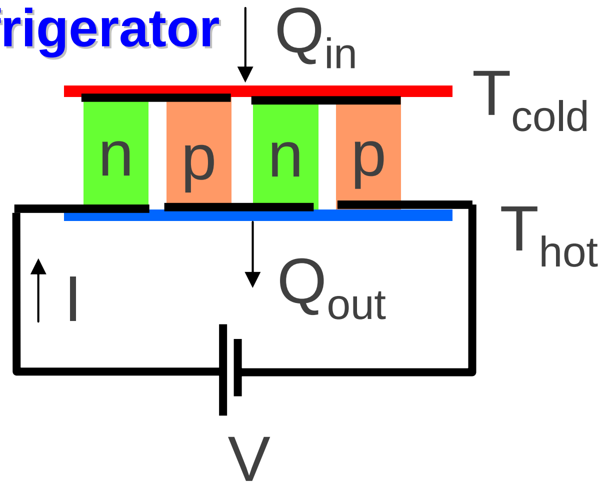
Engine



$$ZT = \frac{S^2 \sigma T}{k}$$

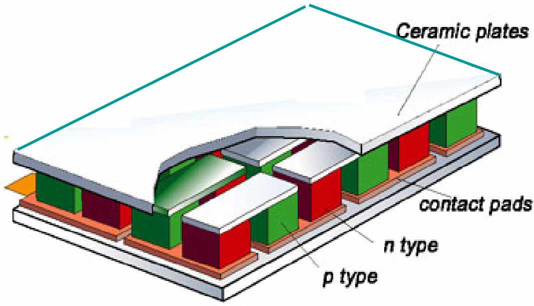


Refrigerator

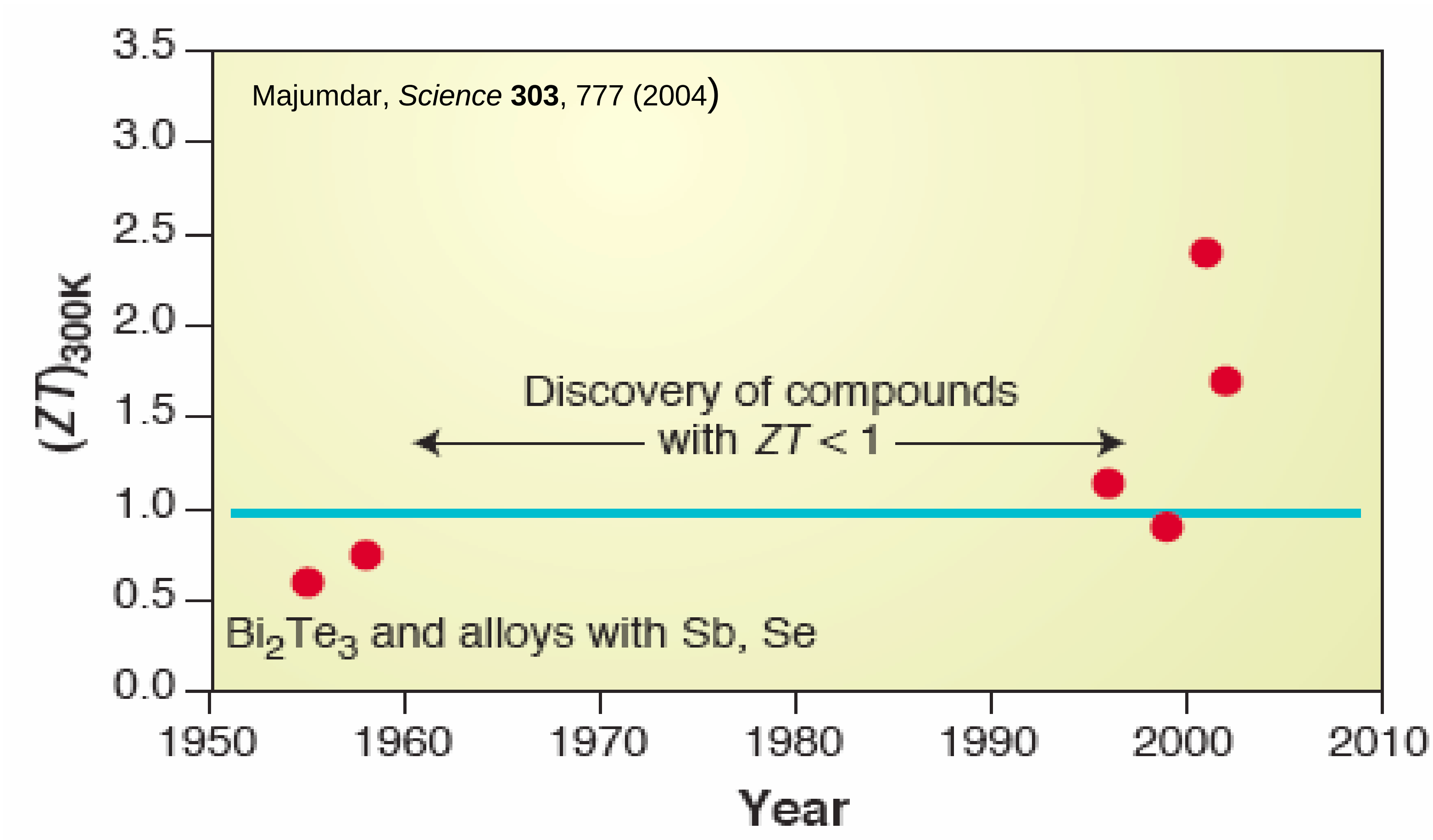


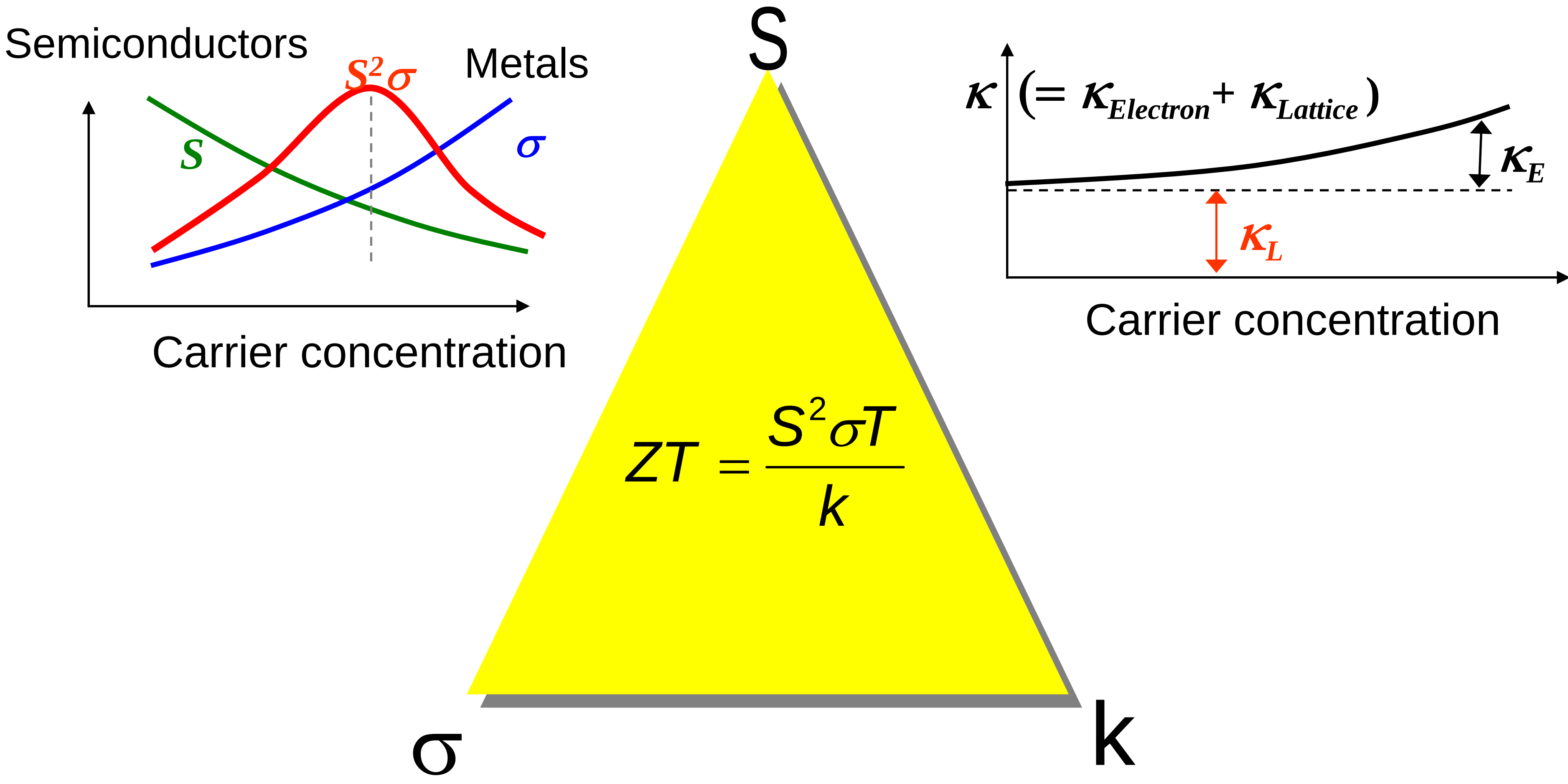
Bismuth Telluride

(low efficiency, expensive)

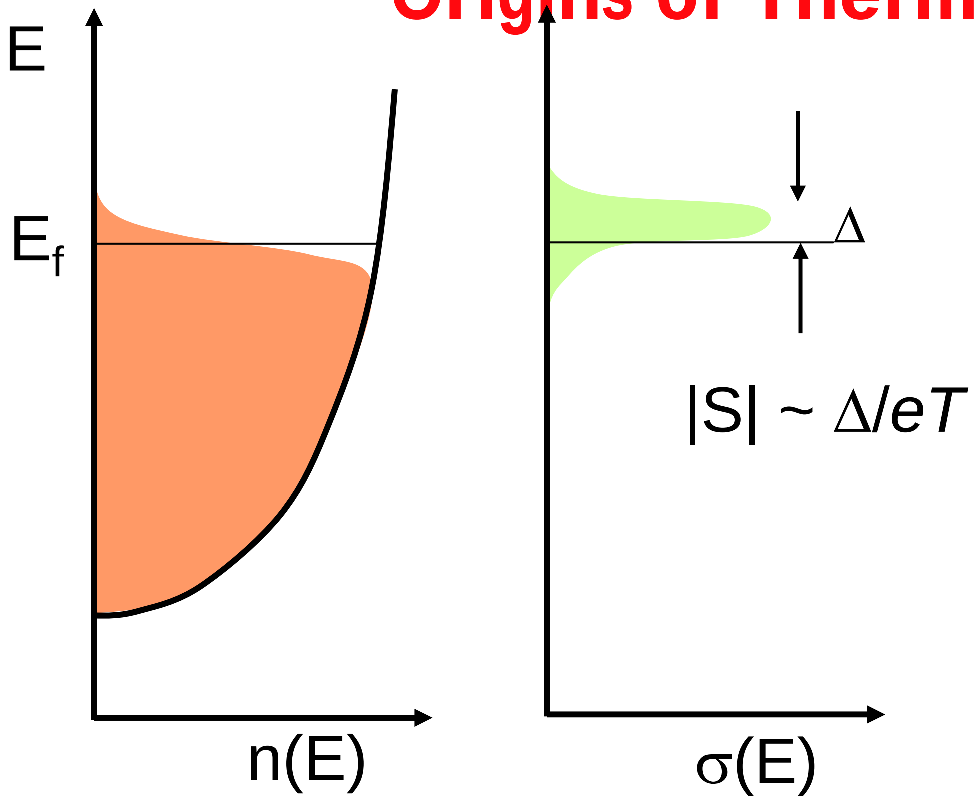


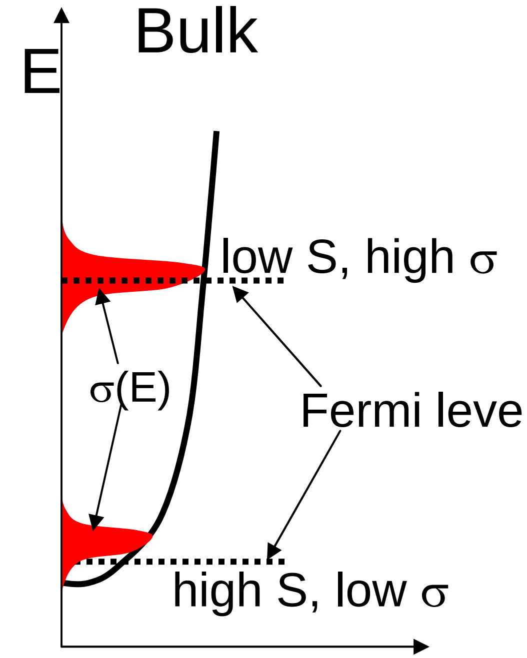
History


Majumdar, *Science* **303**, 777 (2004)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
$(ZT)_{300K}$
Discovery of compounds with $ZT < 1$
Bi_2Te_3 and alloys with Sb, Se
1950
1960
1970
1980
1990
2000
2010
Year


Semiconductors
S2σ
Metals
S
σ
Carrier concentration
S
ZT = S2σT / k
σ
k
κ (= κElectron + κLattice)
κE
κL
Carrier concentration

Origins of Thermoelectricity



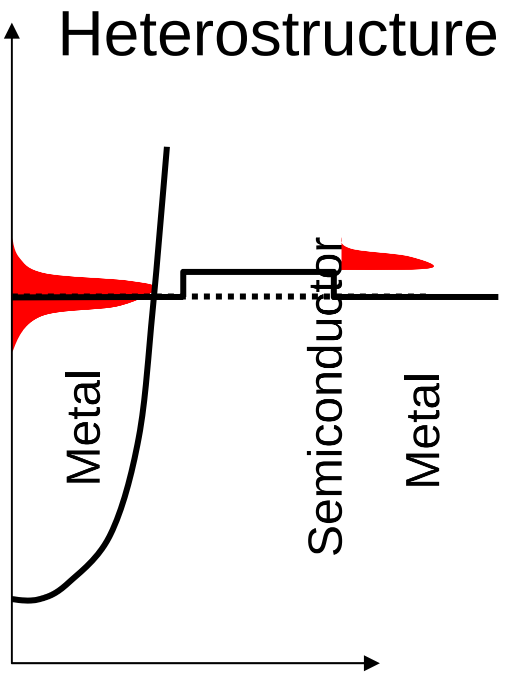


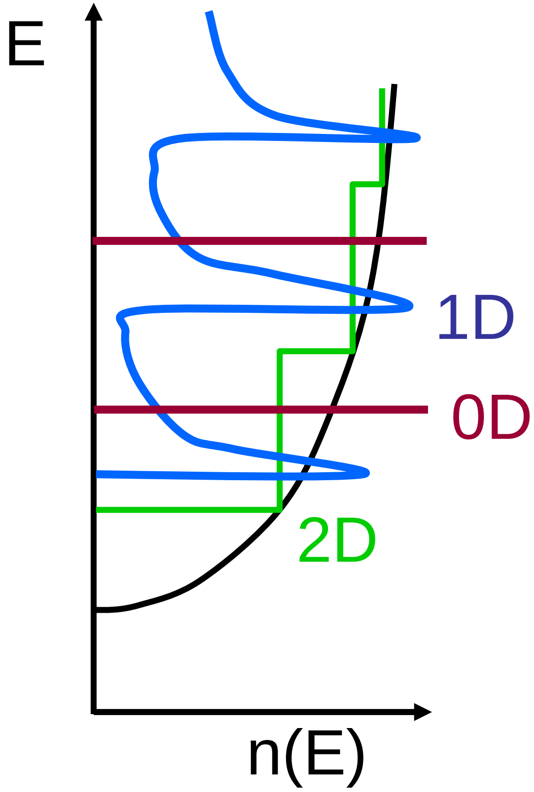
$$\sigma(E) = q^2 \tau(E) v^2(E) n(E) \left(-\frac{\partial f_{eq}}{\partial E} \right)$$

$$\sigma = \int \sigma(E) dE$$

$$S = \frac{1}{eT} \frac{\int \sigma(E)(E - E_f) dE}{\int \sigma(E) dE}$$

How do we increase $S^2\sigma$

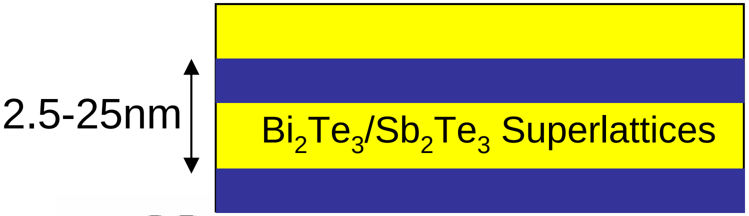




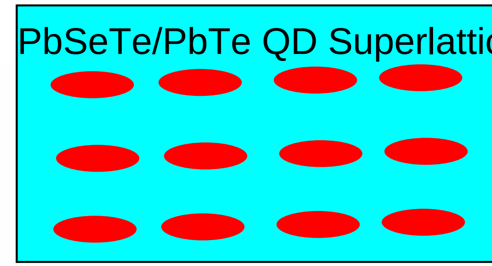
Quantum Confinement

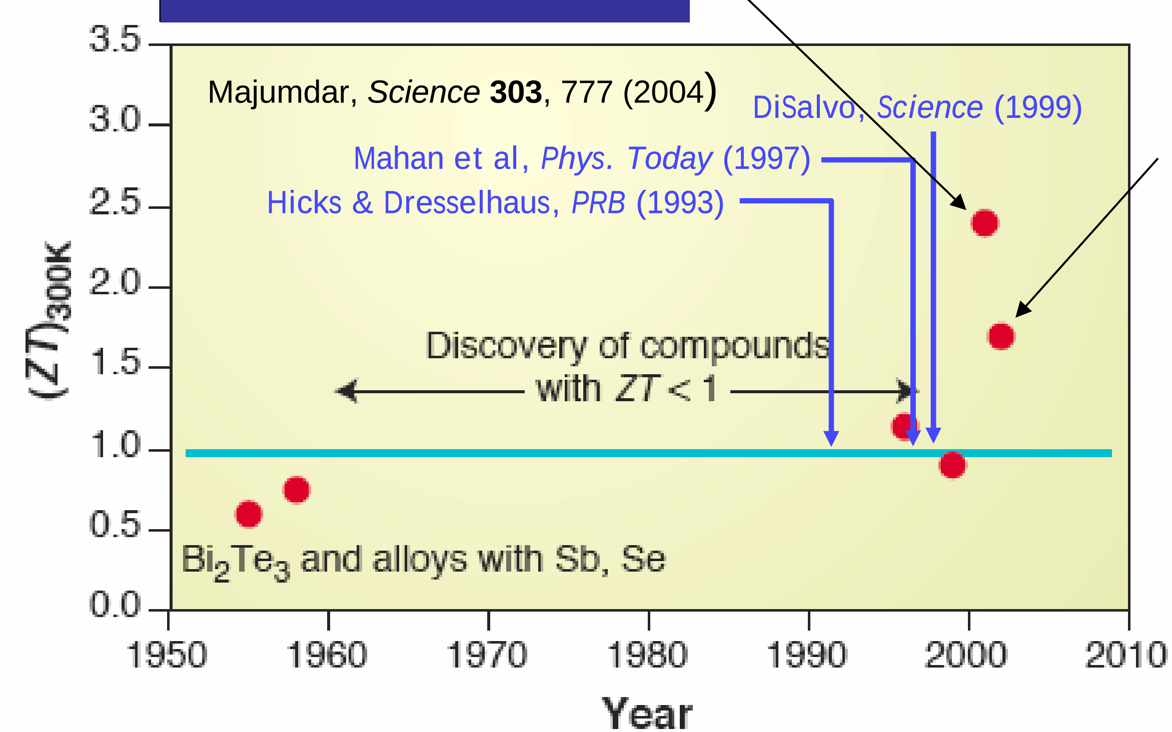
History

Venkatasubramanian et al. *Nature* **413**, 597 (2001)



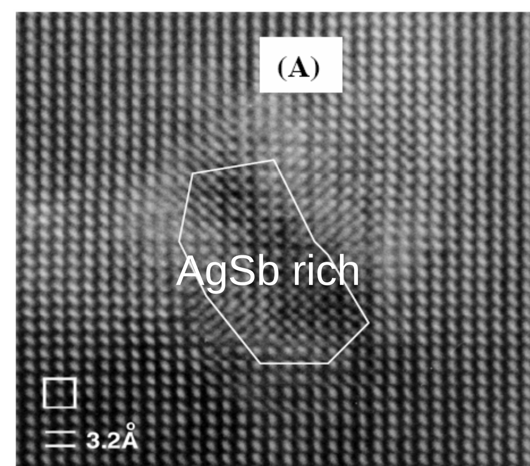
Harman et al., *Science* **297**, 2229 (2002)





$$ZT = \frac{S^2 \sigma T}{k \downarrow}$$

Hsu et al., *Science* **303**, 818 (2004)



$AgPb_{18}SbTe_{20}$
ZT = 2 @ 800K

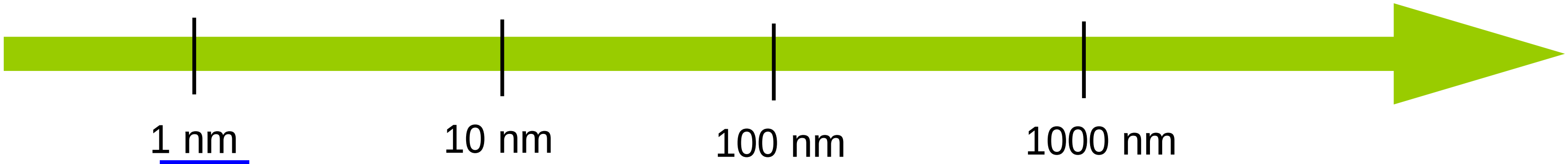
Transport Length Scales for Si @ 300 K

Ju, Goodson (1999)

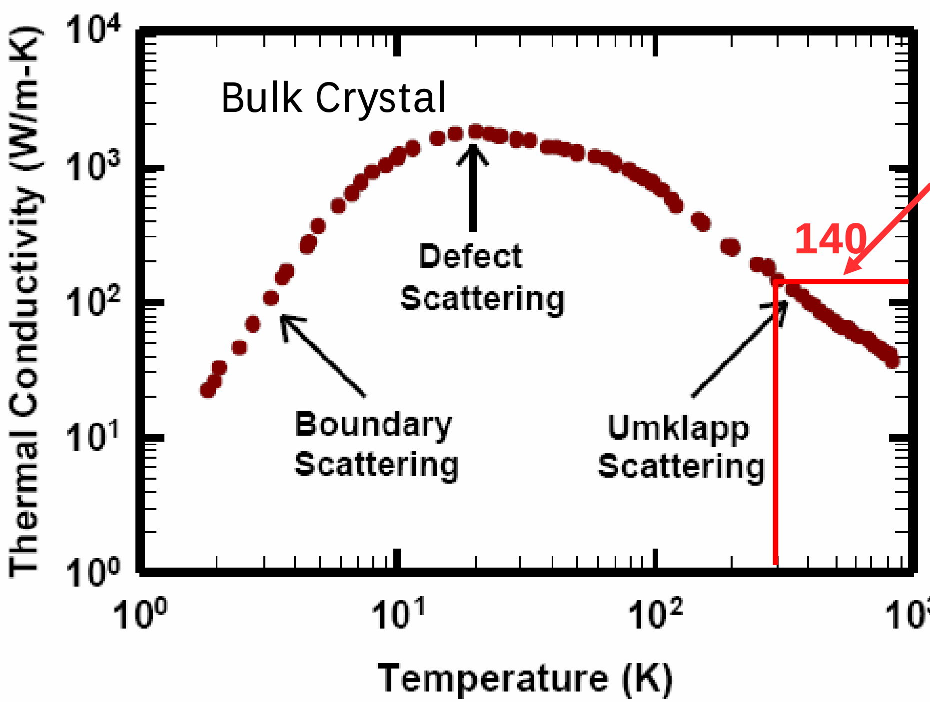
Mean Free Path

Electrons $\sigma = \dfrac{\eta e^2 \ell_e}{m v_{therm}}$

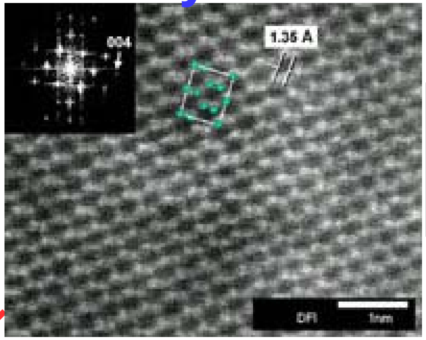
Phonons $k = \dfrac{1}{3} C v_s \ell_{ph}$



Wavelength



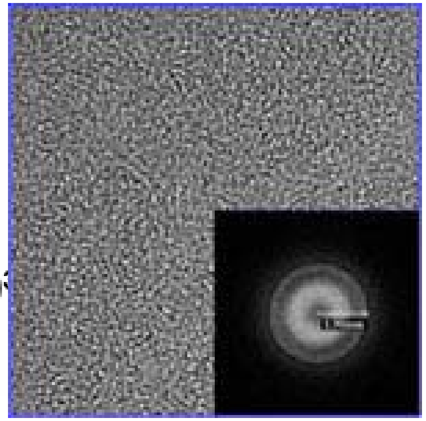
Crystal



k_{max} = 140 W/m-K

$$ZT_{Bulk,Crys} = \frac{S^2 \sigma T}{k} \approx 0.008$$

Amorphous



$$\ell_e, \ell_{ph} \leq 1\, nm$$

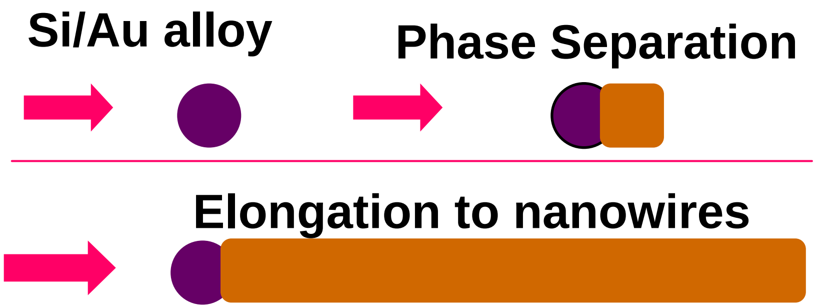
k_{min} = 1 W/m-K

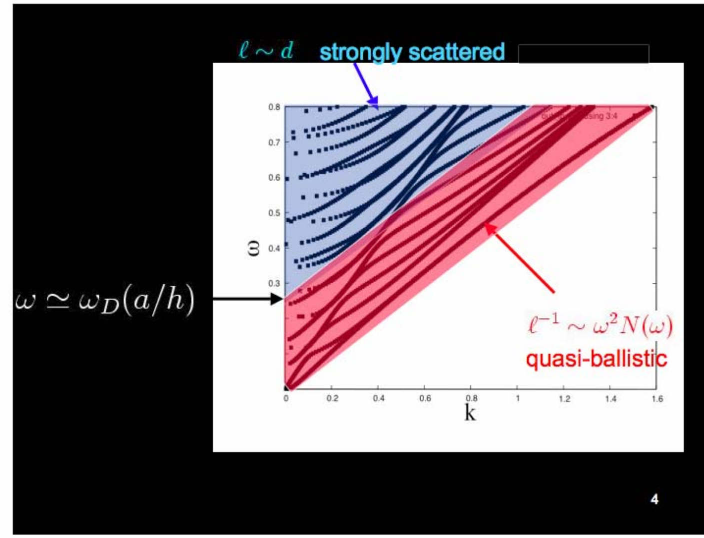
σ ↓

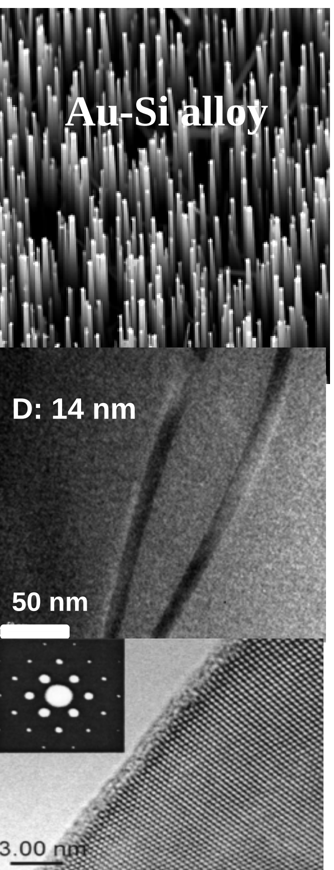
$$ZT_{Bulk,Amorp} \approx 0.08$$

Vapor-Liquid-Solid (VLS) Si Nanowires

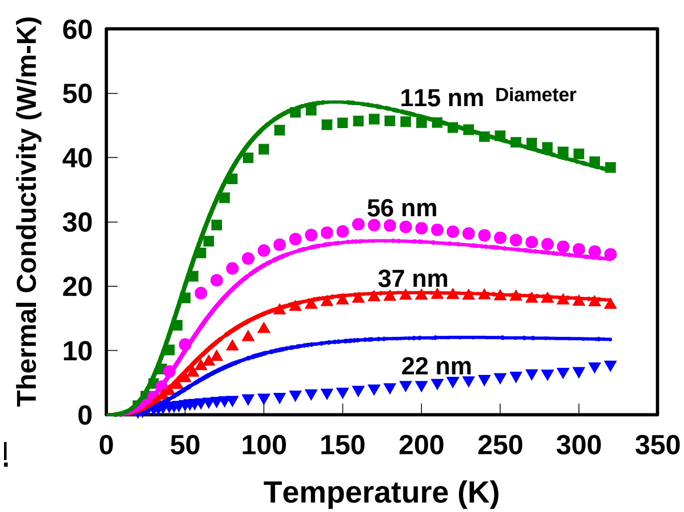
Vapor-Liquid-Solid (VLS) Technique



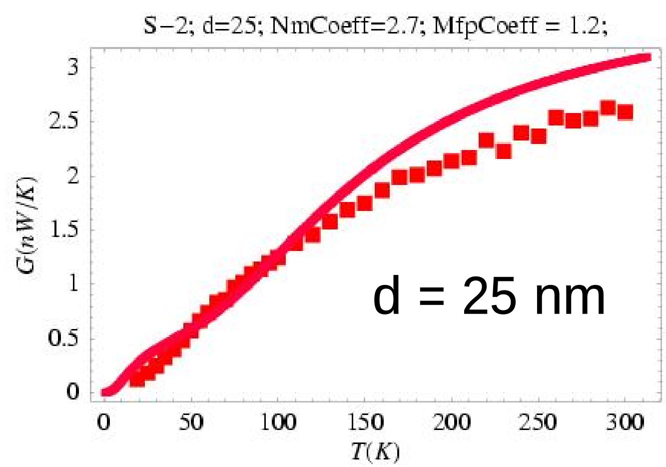




Li, Wu, Kim, Shi, Yang, Majumdar, APL (2003)

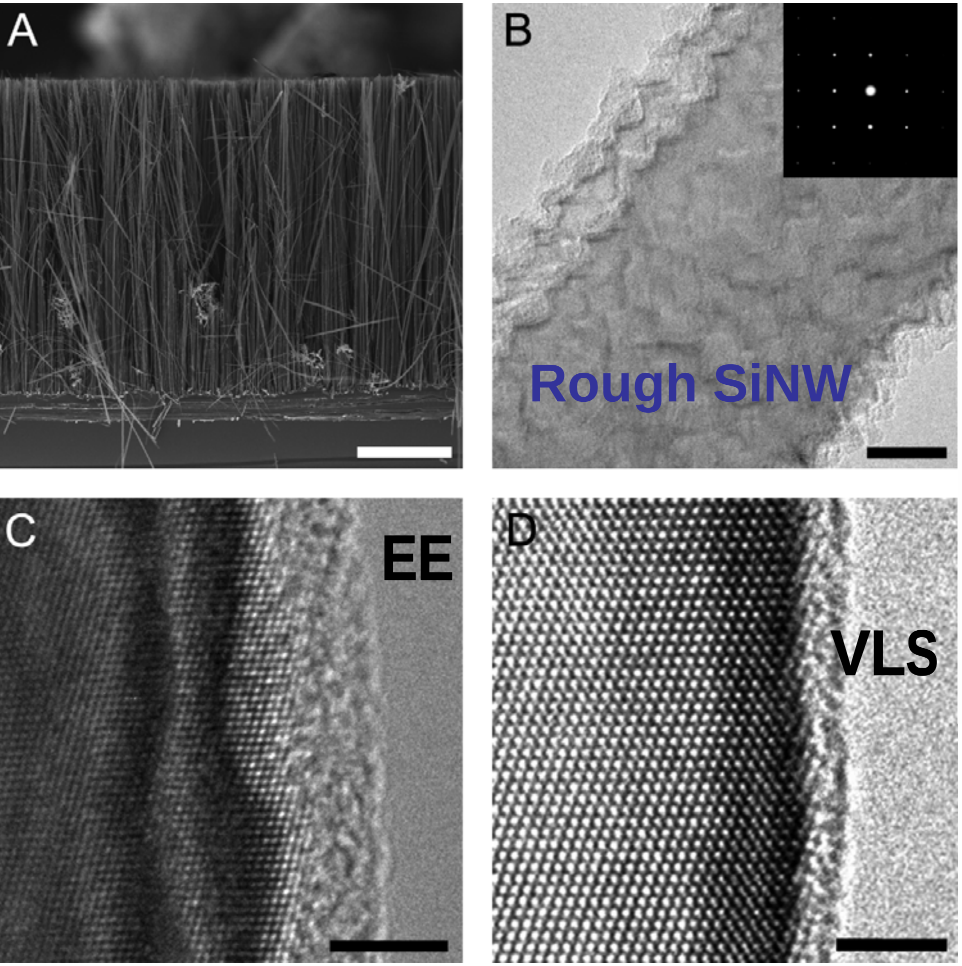


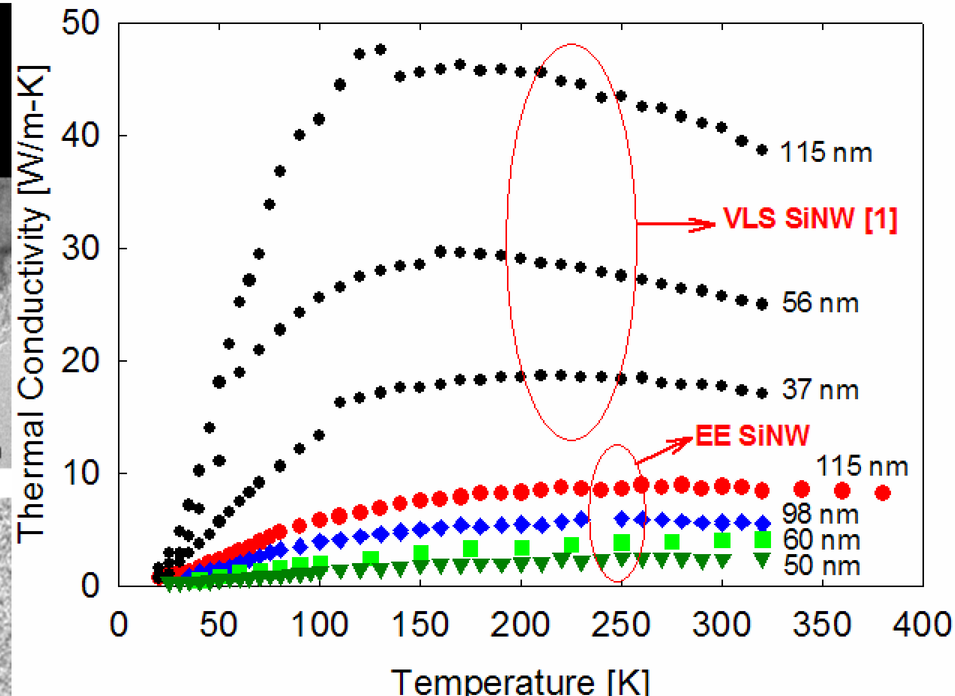
Peidong Yang (UCB)

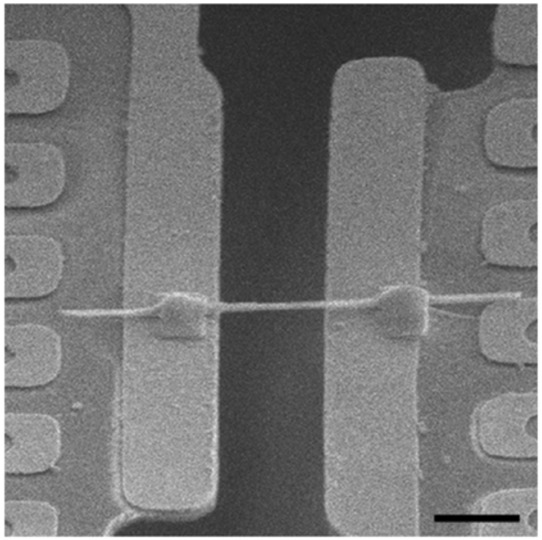


Padraig Murphy, **Joel Moore** (UCB)

Electroless Etched Si Nanowires



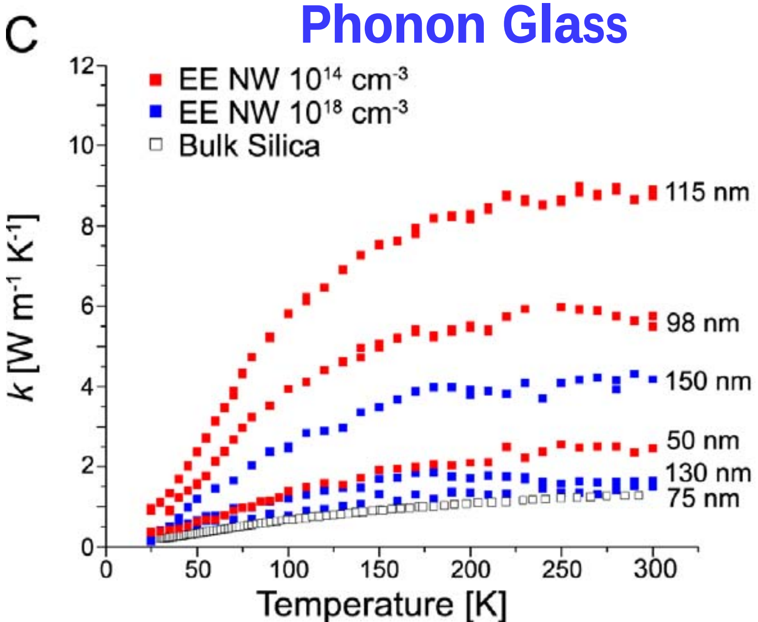


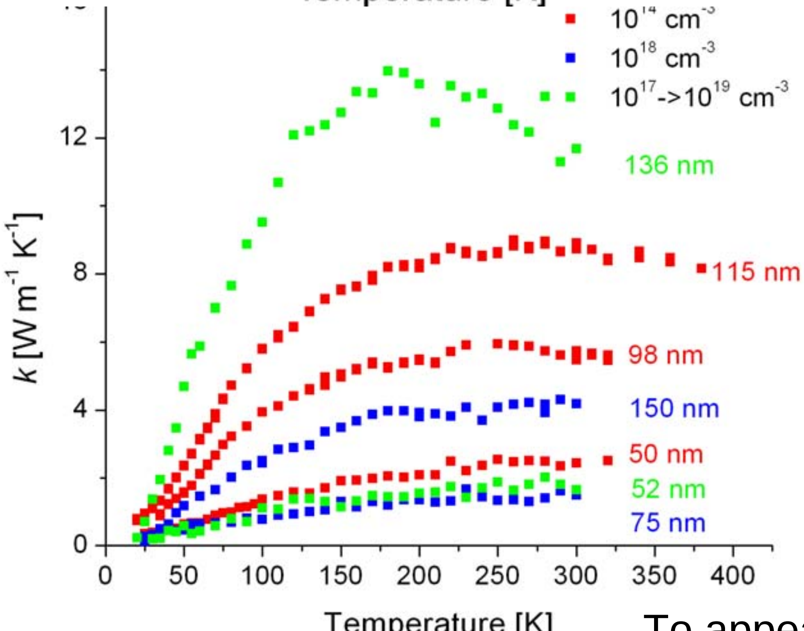


Allon Hochbaum, Renkun Chen,
Peidong Yang (UCB)

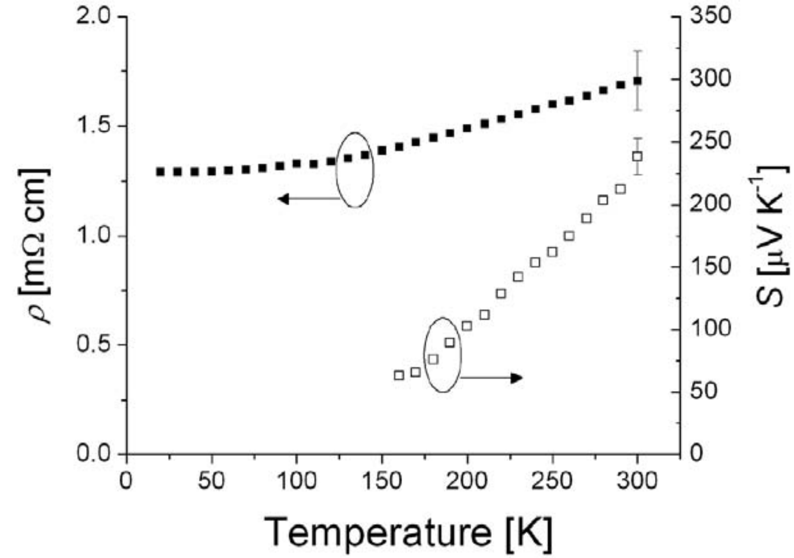
Electroless Etched Si Nanowires

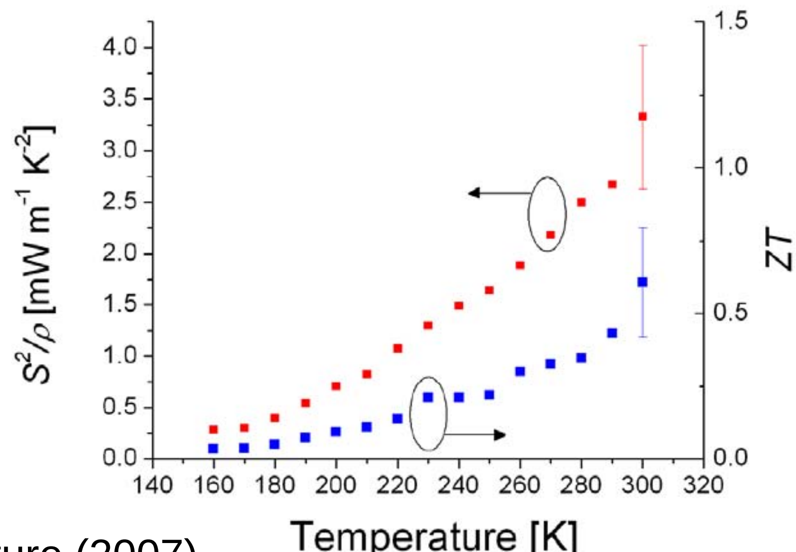
Phonon Glass





Electronic Crystal





To appear in Nature (2007)

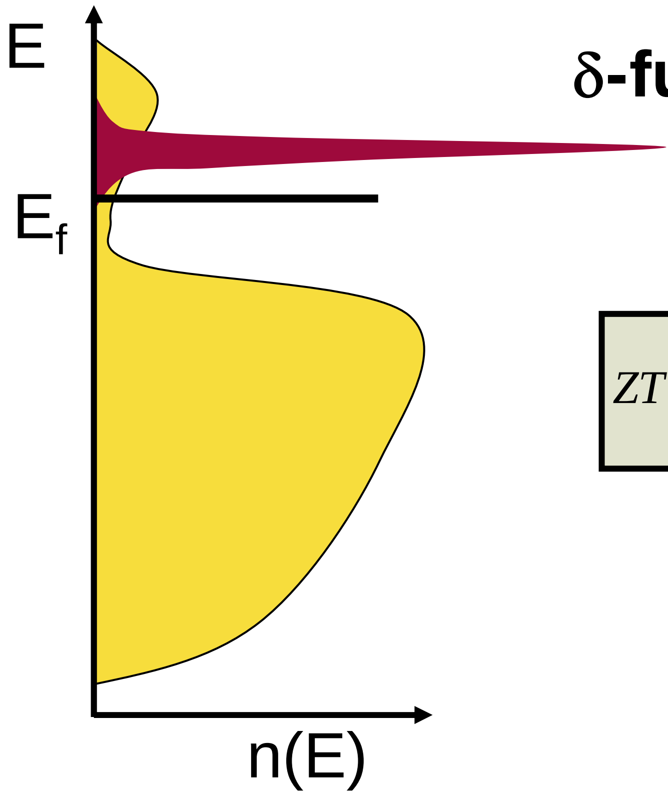
Heat Flow in Solids

$$k = \frac{1}{3}Cvl = \frac{1}{3}\int C(\varepsilon)v(\varepsilon)^2\,\tau(\varepsilon)D(\varepsilon)d\varepsilon$$

We do not understand the wave effects in phonon transport and we don’t have simple experimental tools to perform phonon spectroscopy.

We need help from theory!

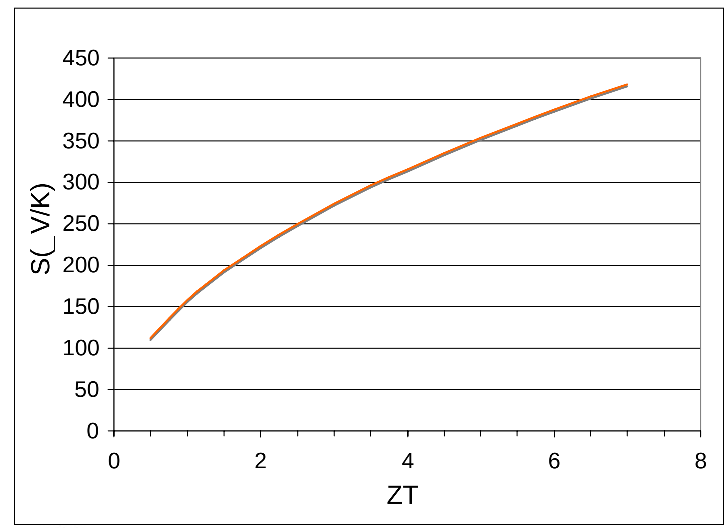
Best Thermoelectric



δ-function/Lorenztian

$YbAl_3$ has highest $S^2\sigma$ due to f-electron resonance state

$$ZT = \frac{S^2\sigma T}{k} = S^2\left(\frac{\sigma T}{k}\right) = \frac{S^2}{L_o} \approx 40\left[S\left(mV\right)\right]^2$$



Proc. Natl. Acad. Sci. USA
Vol. 93, pp. 7436–7439, July 1996
Applied Physical Sciences

This contribution is part of a special series of Inaugural Articles by members of the National Academy of Sciences elected on April 25, 1995.

The best thermoelectric

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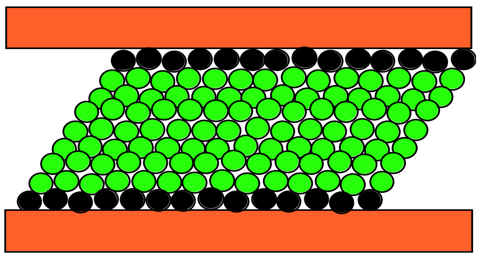
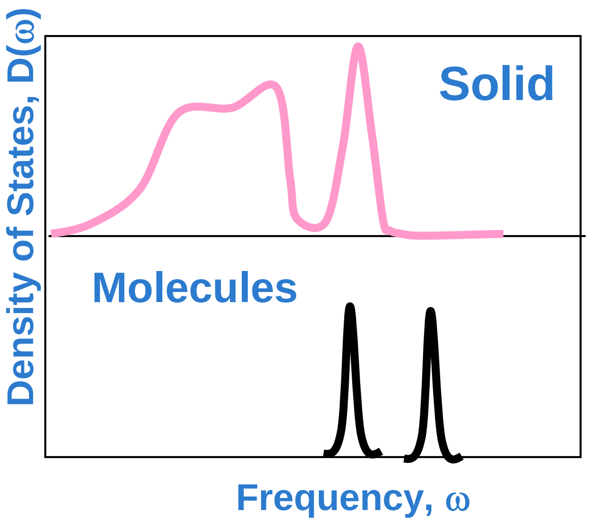
Why Molecular Thermoelectrics?

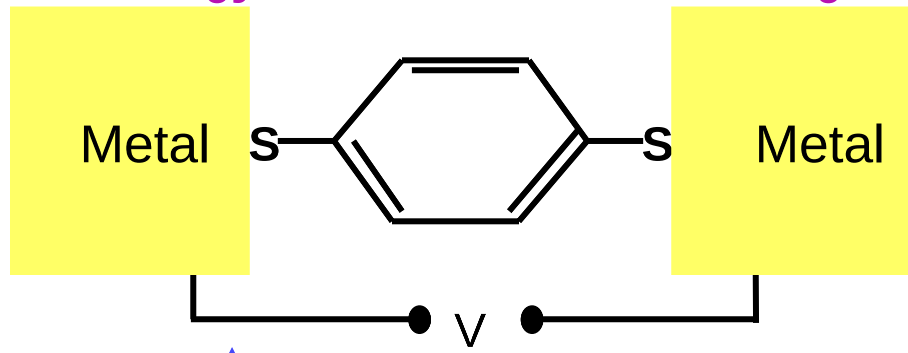
Large Thermal Impedance By Phonon Filtering

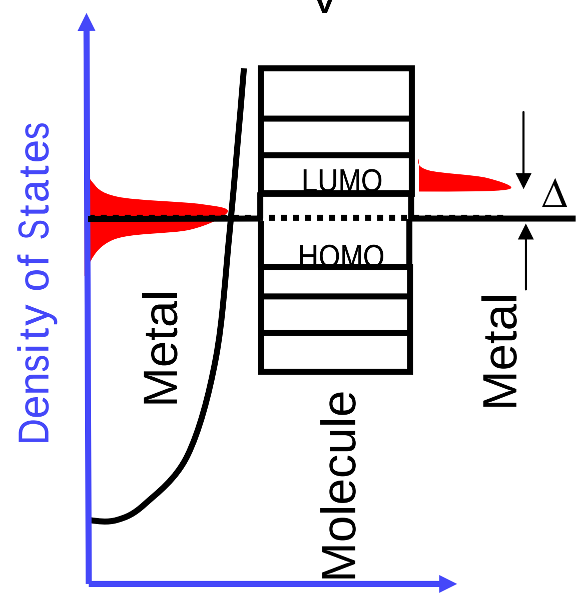
Molecular Heterostructures





Potentially High Power Factor by Energy-Based Carrier Filtering

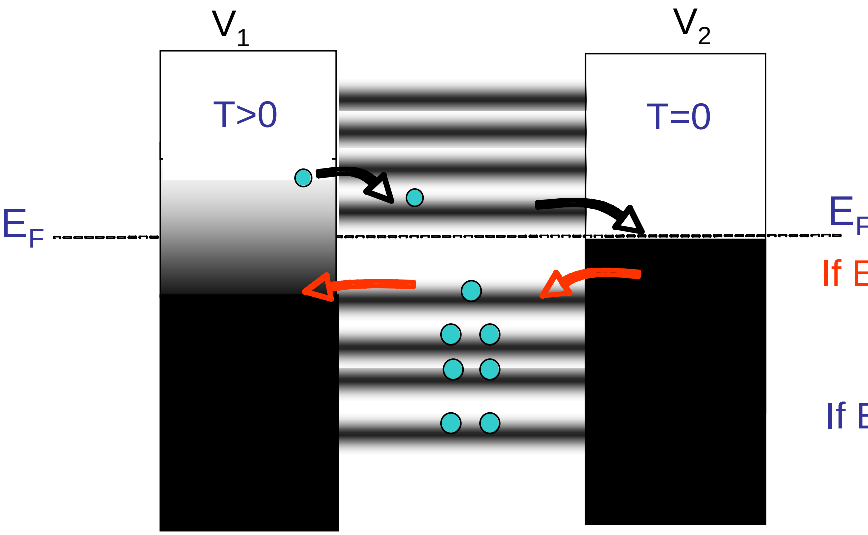




Pramod Reddy, Sung-Yeon Jang, Kaal Baheti,
Jon Malen, Peter Doak, **Don Tilley, Rachel Segalman**

Jeff Neaton, Joel Moore

Thermopower of Molecular Junctions

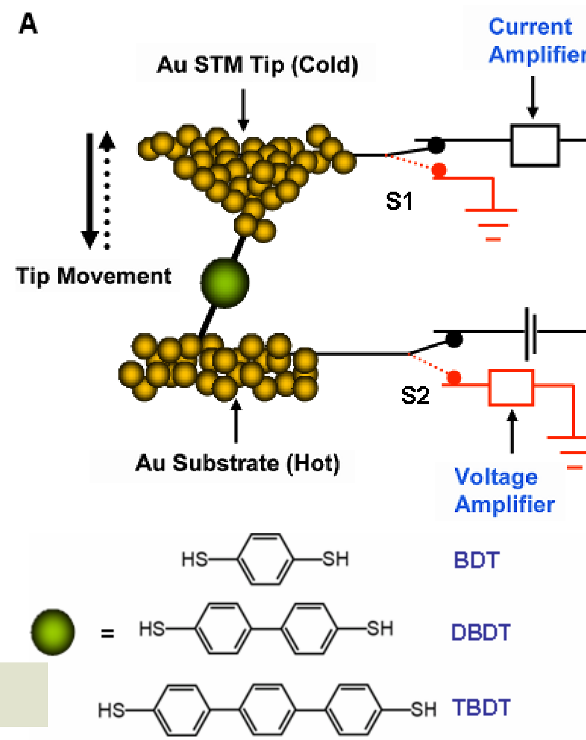


If E_F close to LUMO

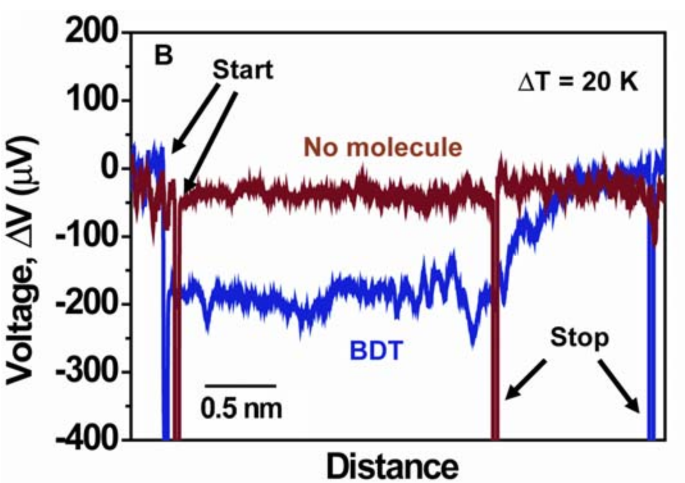
$V_1 > V_2$

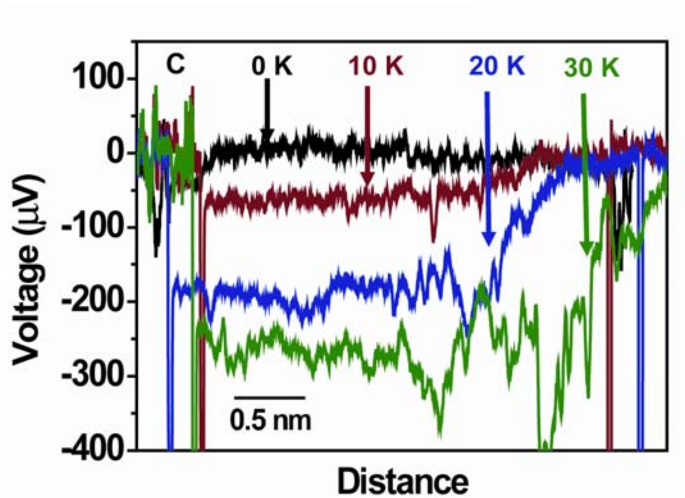
If E_F close to HOMO

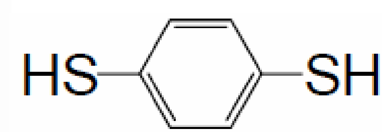
$V_1 < V_2$



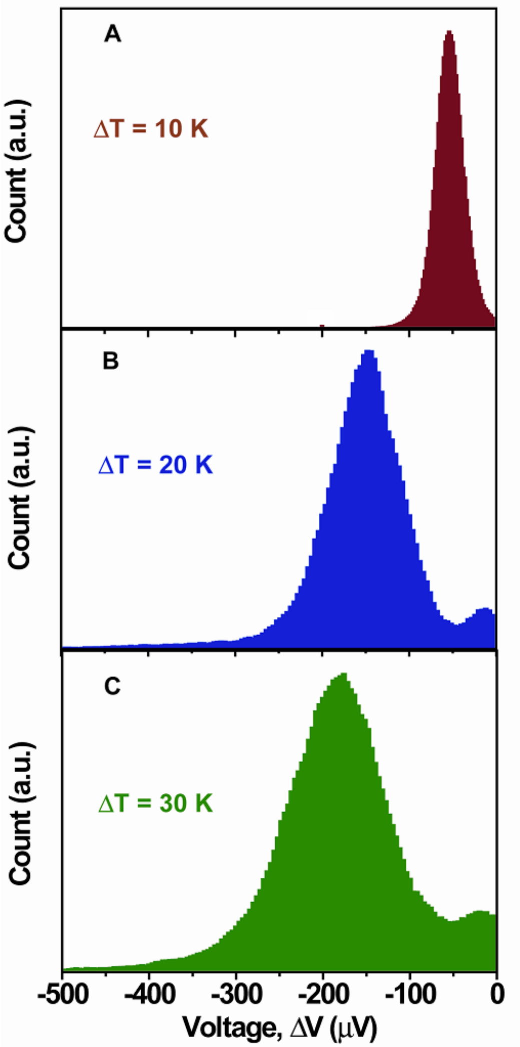
Reddy, Jang, Segalman, Majumdar, *Science* (2007)



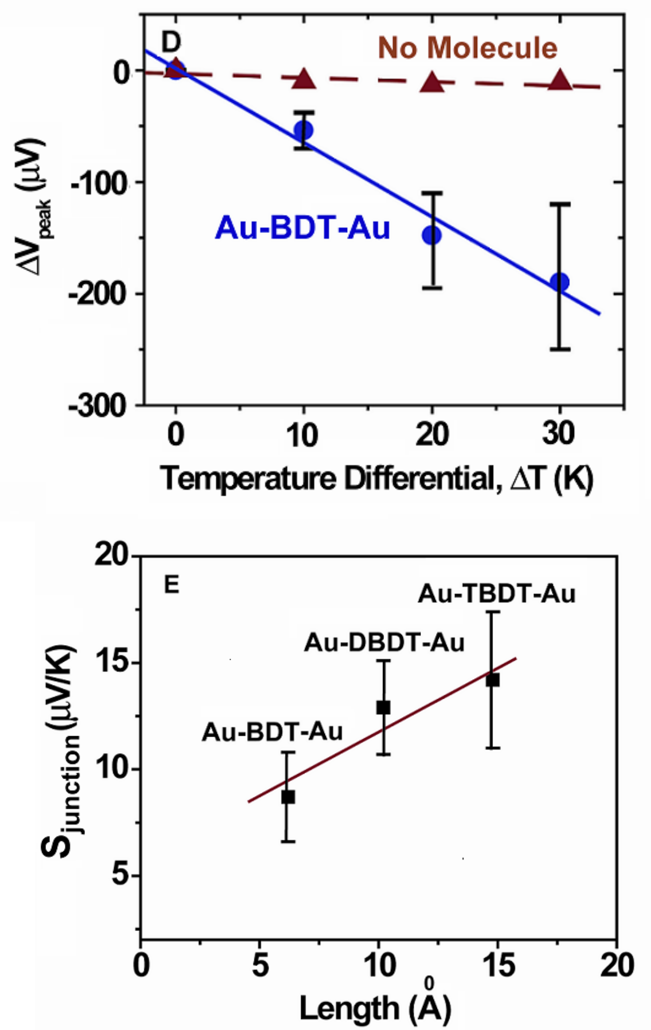




Thermopower of Molecular Junctions

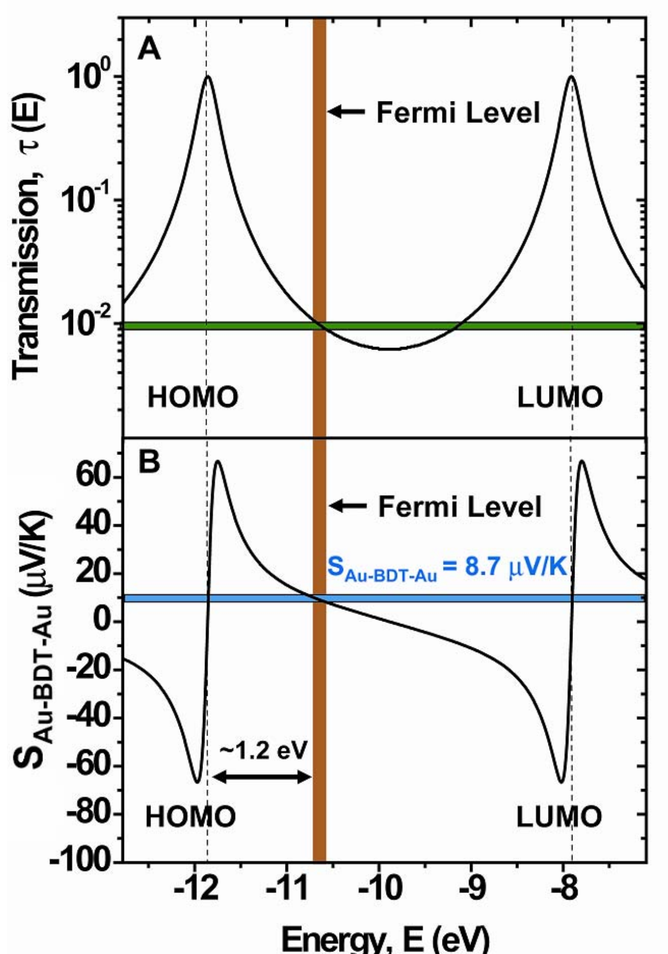


From >2000 consecutive measurements



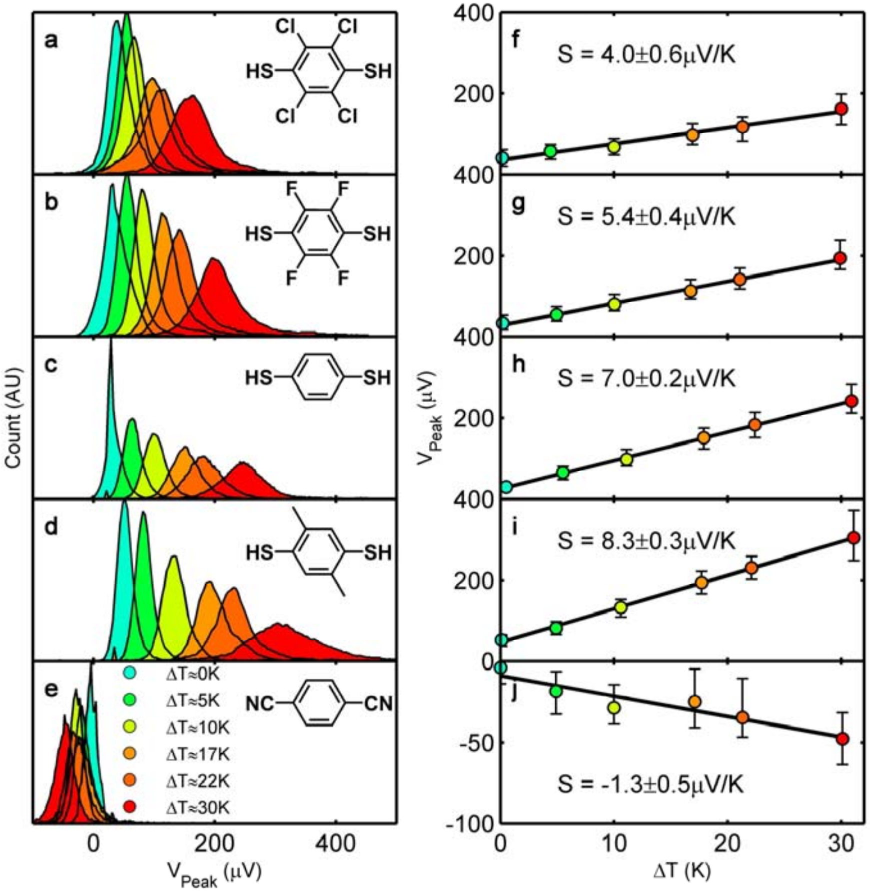
Reddy, Jang, Segalman, Majumdar, *Science* (2007)

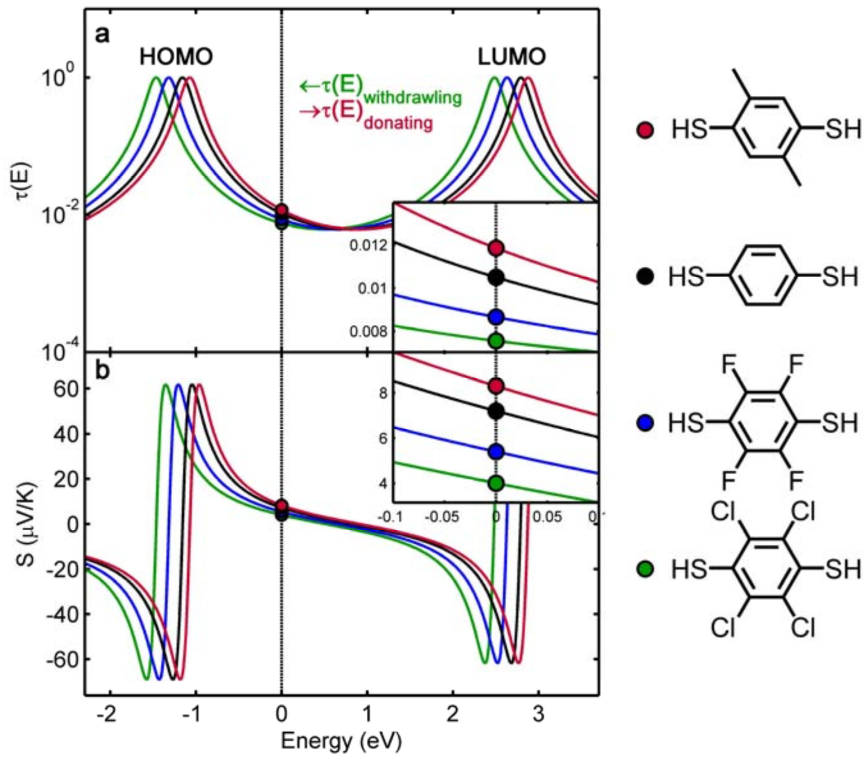
$$S = \frac{V}{\Delta T} = -\frac{\pi^2 \kappa_B^2 T}{3e}\left(\frac{1}{\tau(E)}\frac{\partial \tau(E)}{\partial E}\right)_{E=E_f}$$

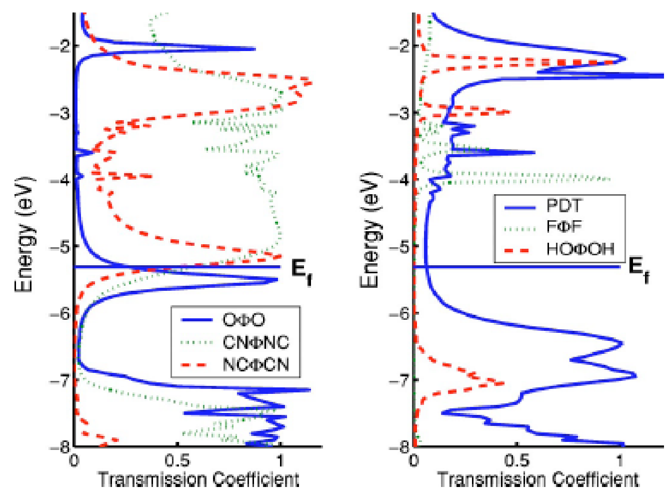


Paulsson & Datta, *PRB* (2003)

Role of Chemistry





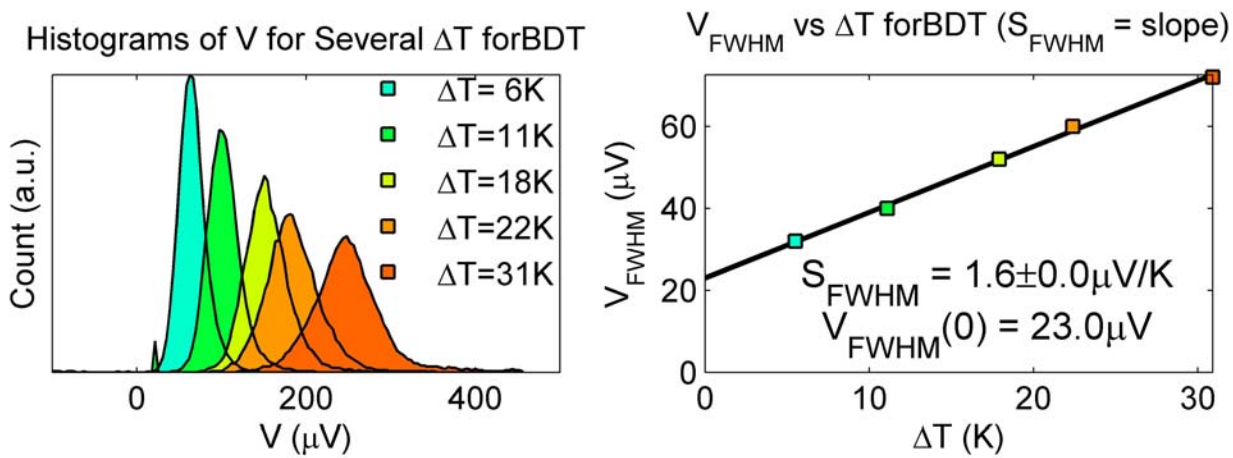


Transmission for BDT (PDT) & BDCN (CNΦCN) [2]

[1] Xue & Ratner PRB (2003)

[2] Xue & Ratner PRB (2004)

Role of Fluctuations



Lorentzian

$$\tau(E) = \sum_{i=1}^{2} \frac{\Gamma_1 \Gamma_2}{(E - E_i)^2 + (\Gamma_1 + \Gamma_2)^2 / 4}$$

$$\frac{\Delta E}{(E_F - E_{HOMO})} \approx 0.2 - 0.5!!$$

$$\frac{\Delta V_{1-2}}{(T_1 - T_2)} = \frac{\Delta E S_{HOMO}}{(E_f - E_{HOMO})}$$

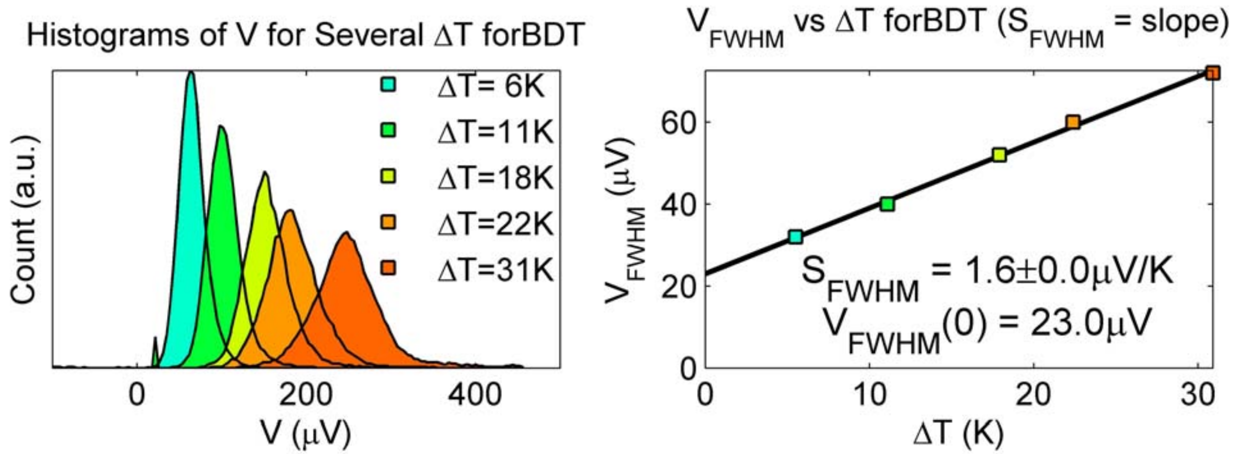
Transport in Molecular Heterojunctions

How do we design molecular junctions to obtain a property or combination of properties?

Role of:

- **Contacts**
- **Chemistry**
- **Fluctuations**

Role of Fluctuations



Lorentzian

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Discussion