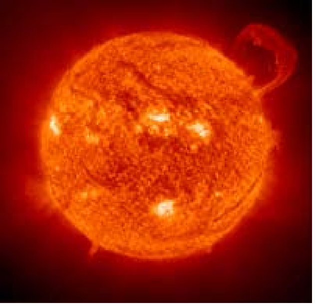
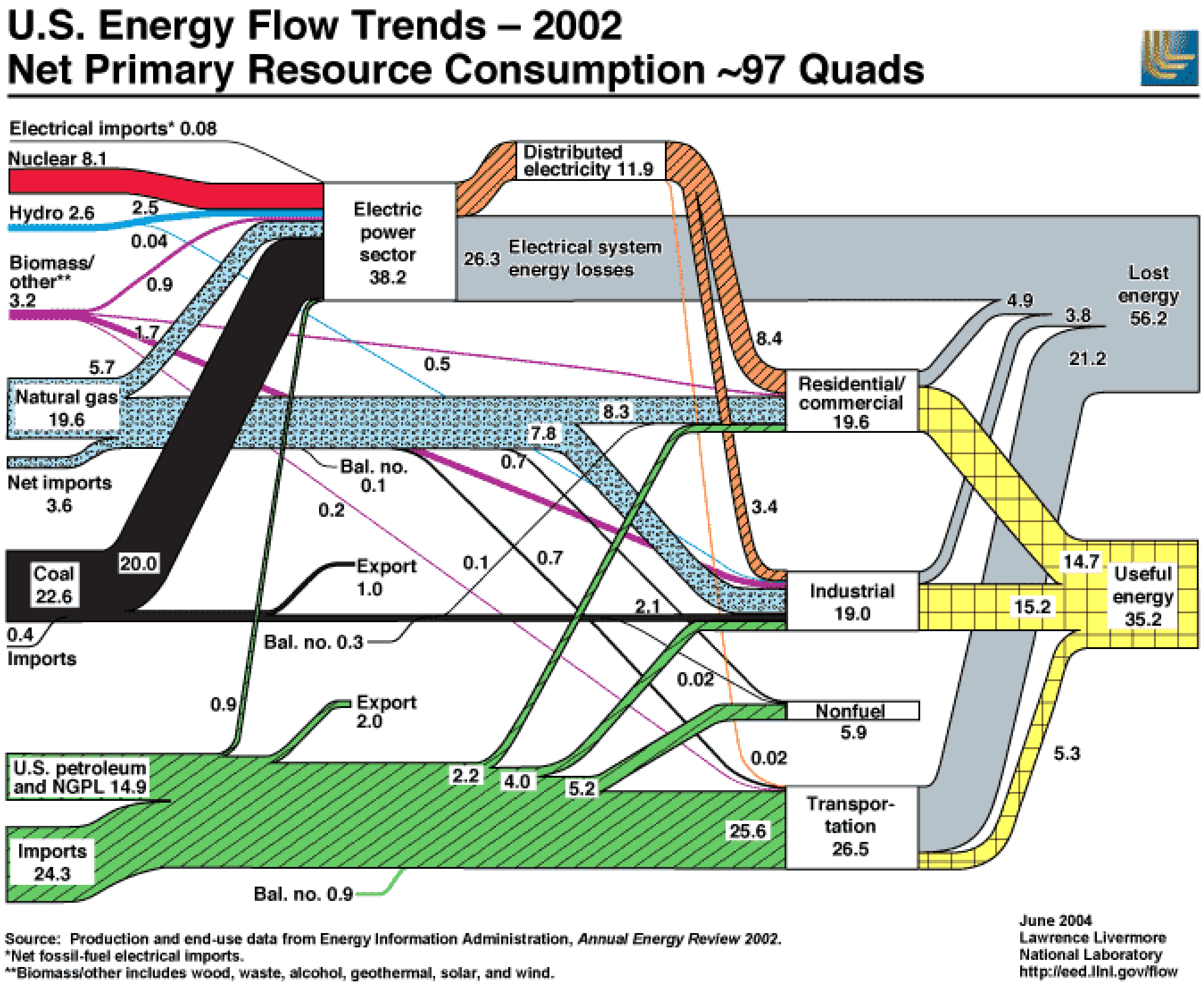
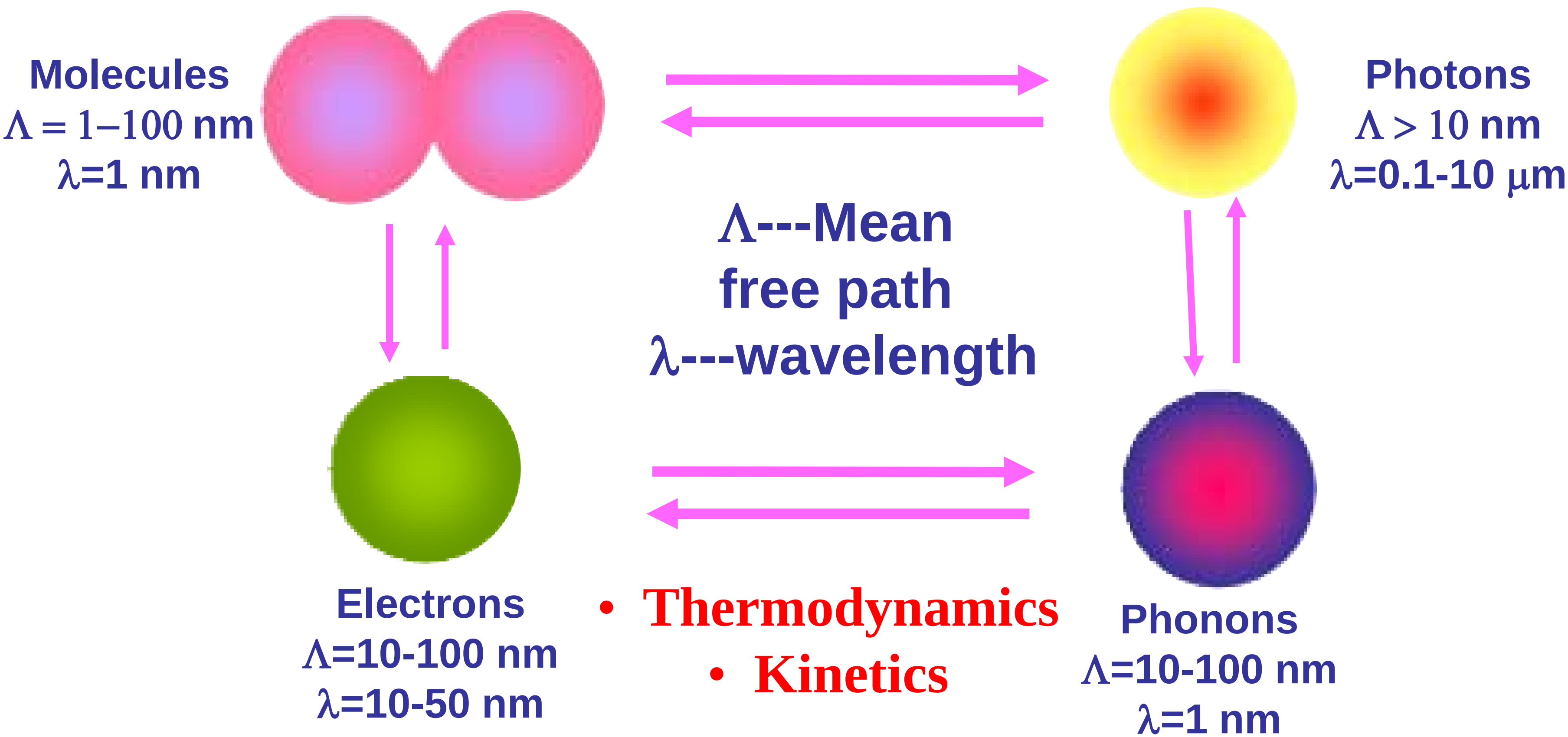


Importance of Heat



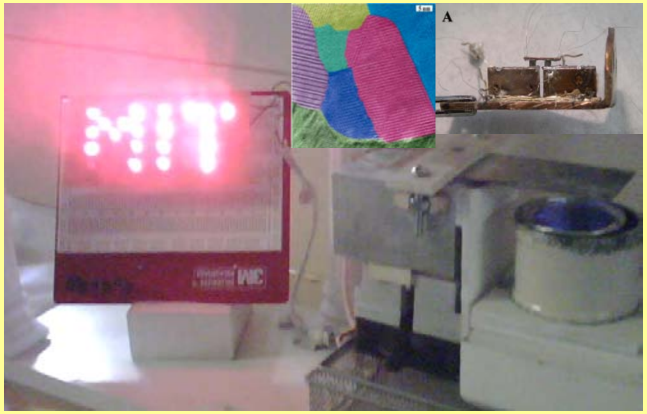
Nano for Energy

- Increased surface area
- Interface and size effects

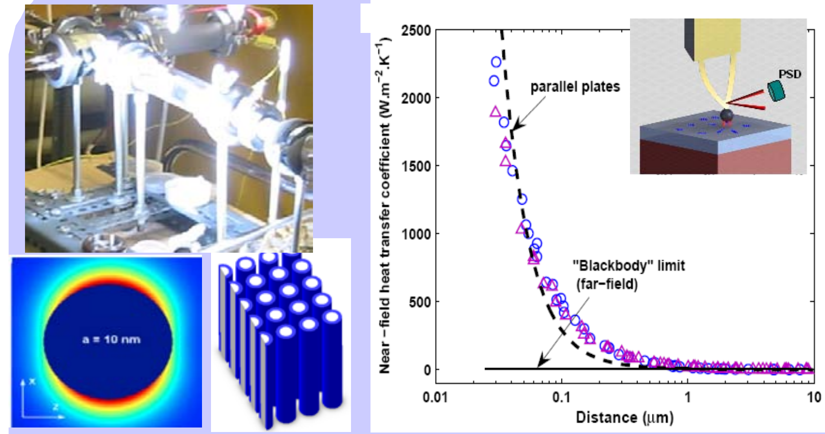


Nanoengineering Group

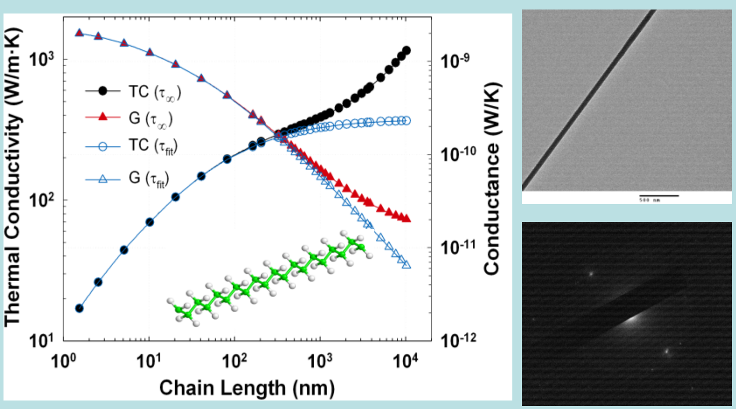
Nano : Heat : Energy



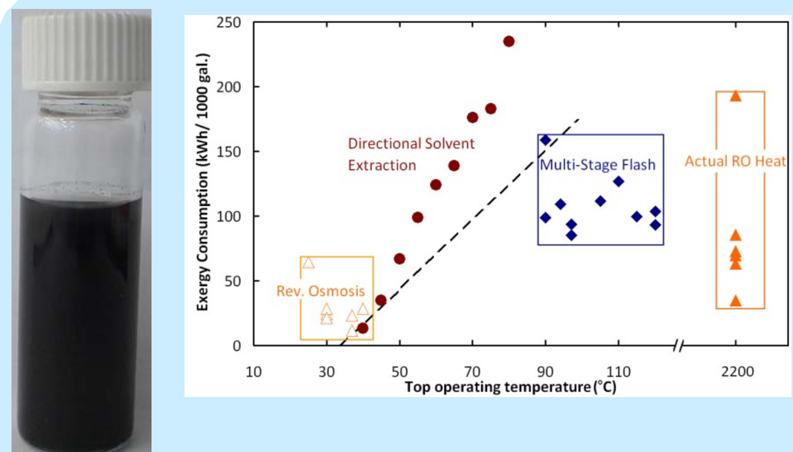
Nanostructured Thermoelectric Materials, Thermoelectric Power Generators and Refrigerators



Photon Control, Thermal and Solar Photovoltaics, Solar Thermal



High Thermal Conductivity Polymers



High Thermal Conductivity Liquids, Desalination

Thermoelectric Energy Conversion: Transport, Materials, and Systems

Gang Chen

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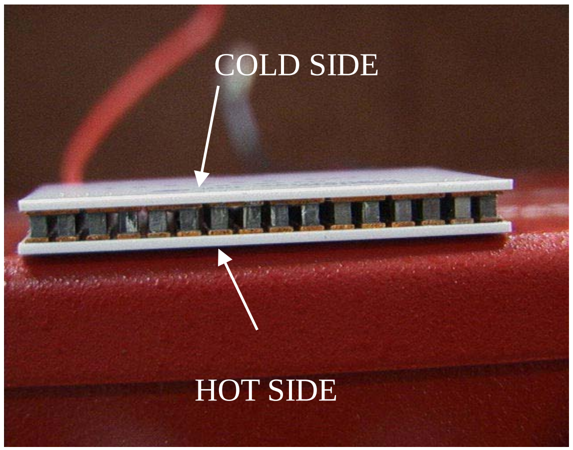
Email: gchen2@mit.edu
http://web.mit.edu/nanoengineering

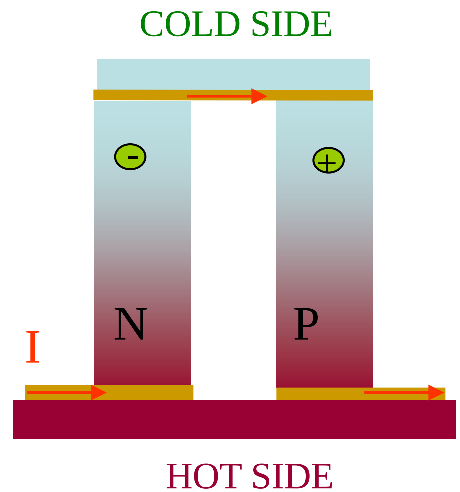
Hawkins Memmorial Lecture, 2012
School of Mechanical Engineering
Purdue University

Outline

- Thermoelectrics and materials
- Phonon and electron engineering
- Solar thermoelectric energy conversion

Thermoelectric Energy Conversion





Nondimensional Figure of Merit

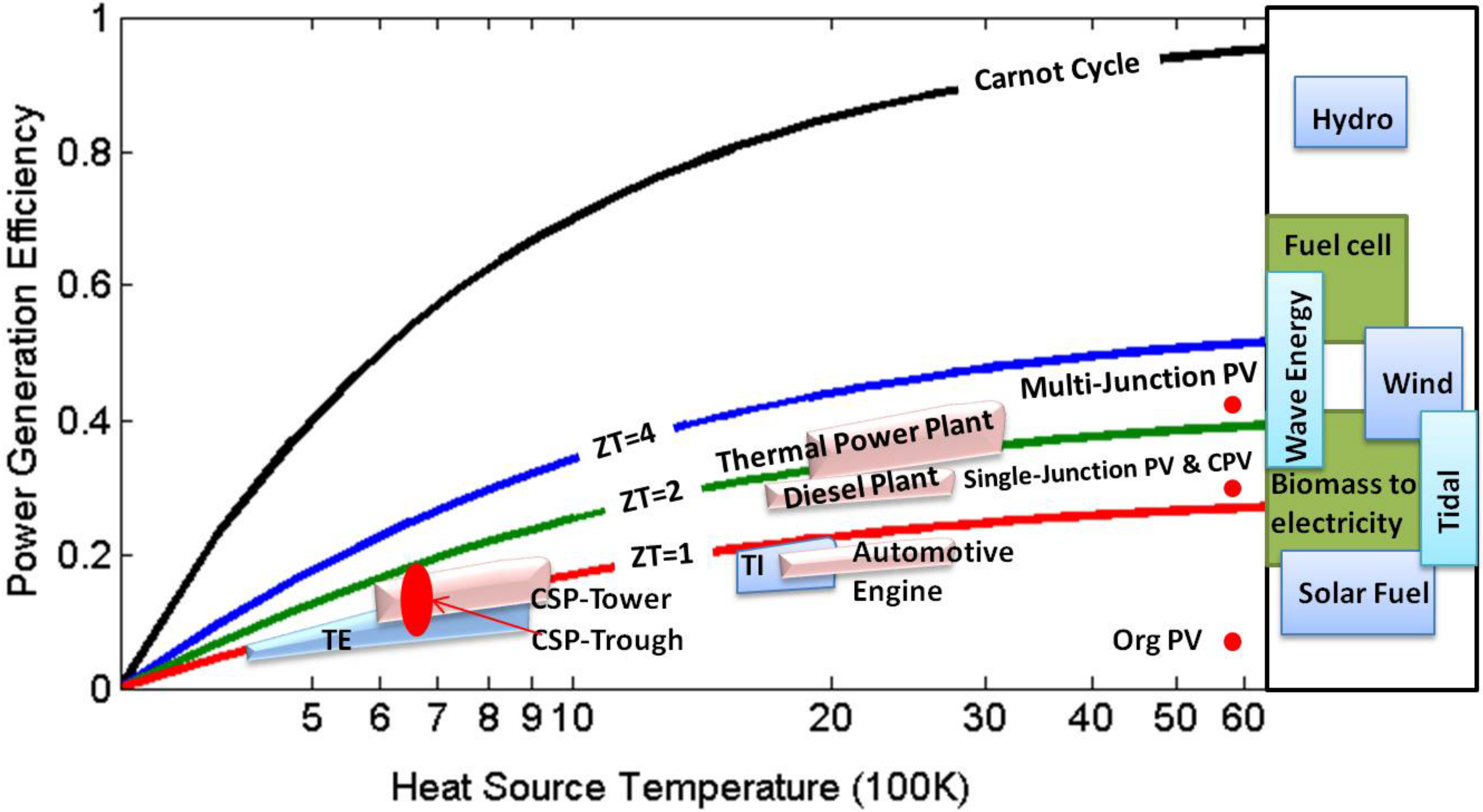
Joule Heating

Seebeck Coeff. Electron Cooling

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

Reverse Heat Leakage Through Heat Conduction

Device Efficiency



Zebarjadi et al., Energy & Env. Sci., 5, 5147, 2012.

Contra Properties

Electrical Conductivity

Seebeck Coefficient

$$ZT = \frac{\sigma S^2 T}{k_e + k_p}$$

Electronic Thermal Conductivity

Phononic Thermal Conductivity

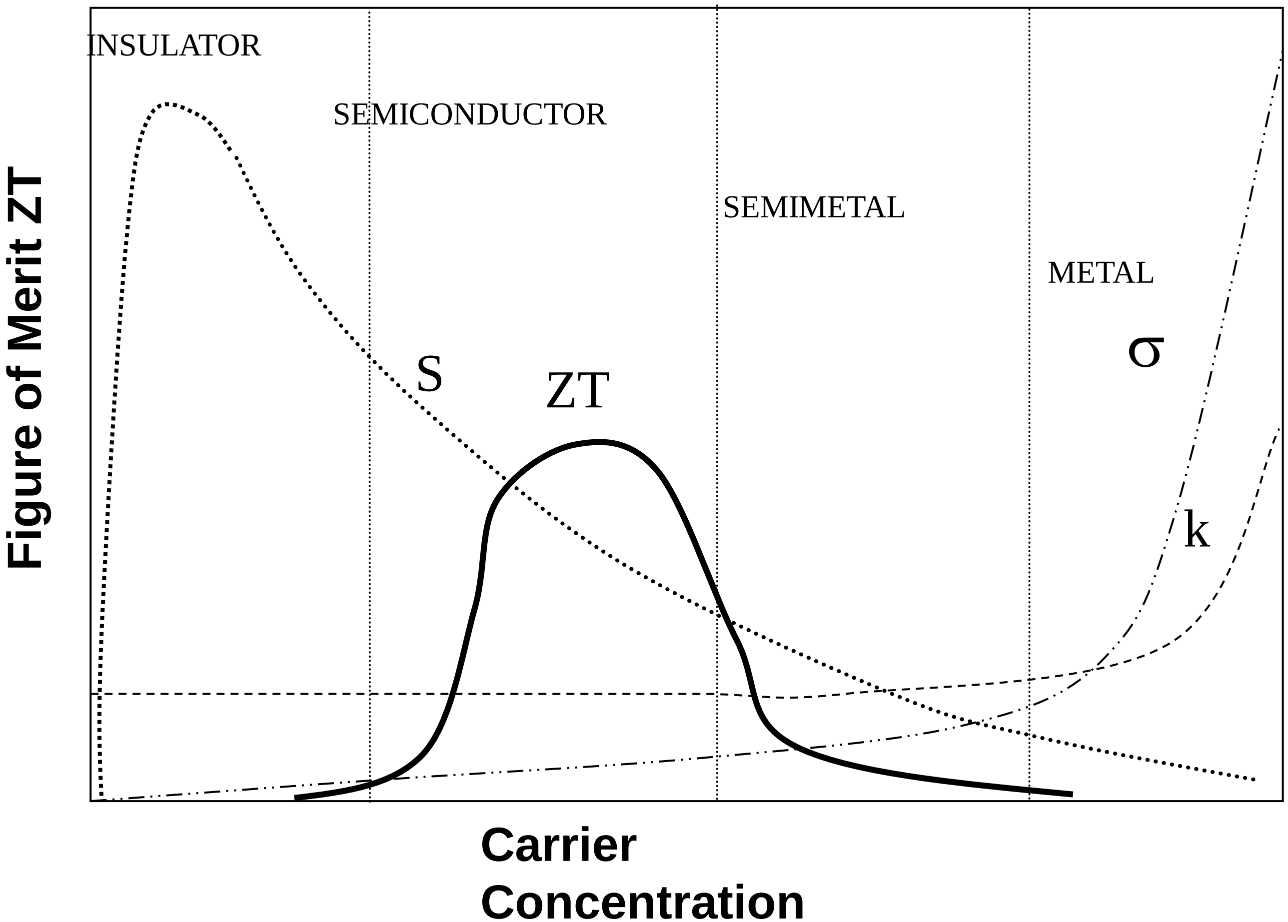
Wiedemann-Franz Law

$$\frac{k_e}{\sigma T} = L(n)$$

Lorenz Number:

In Metal: L =2.44 x 10-8 $W\Omega^{-1}K^{-2}$
In semiconductor: depends on n

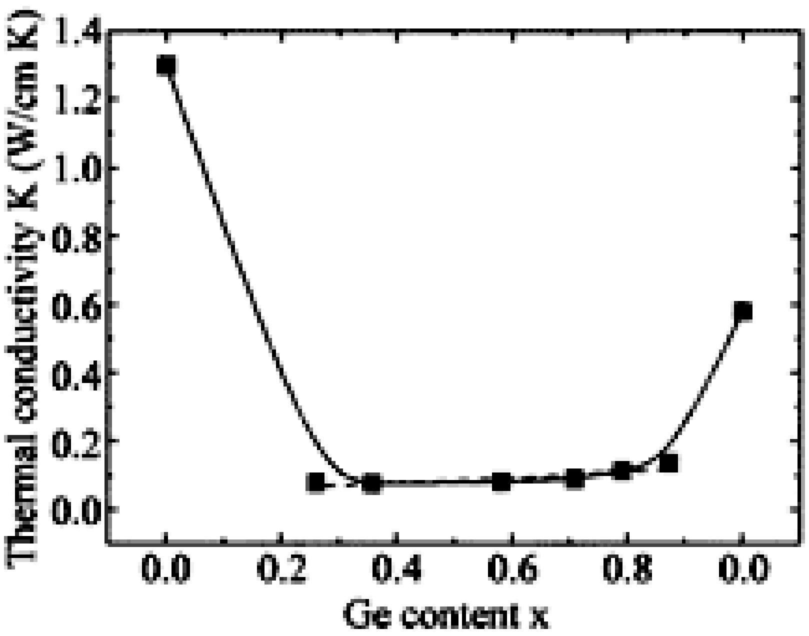
ZT Dilemma

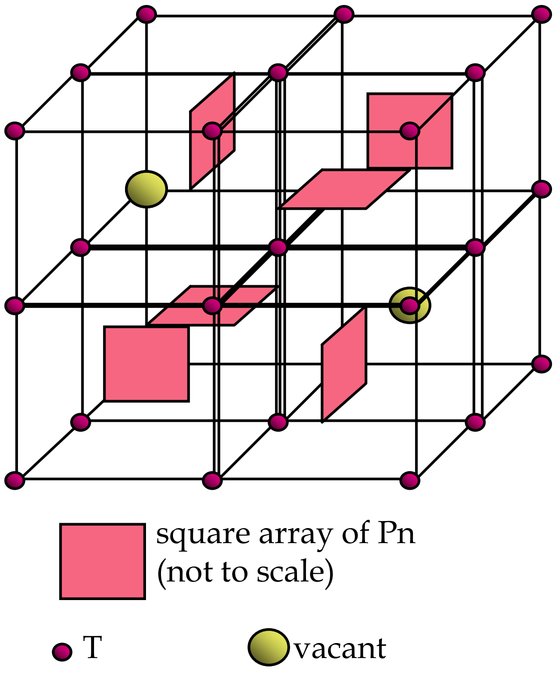


Wanted: Phonon Glass / Electron Crystal

Phonon Engineering

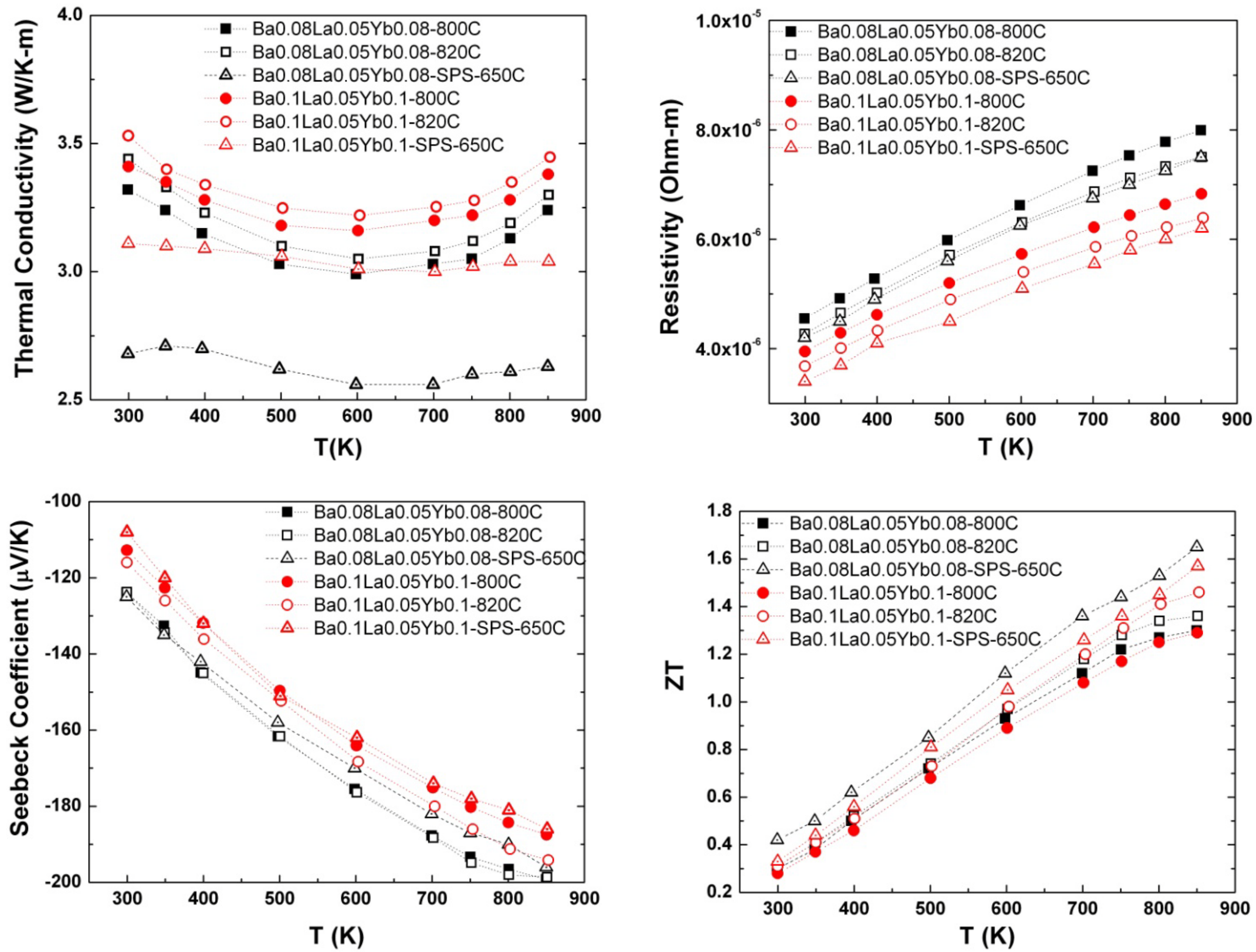
Methods of Reducing k_p In Bulk Materials:





- Alloy, 1950s (Ioffe)
- Rattlers, 1990 (Slack)

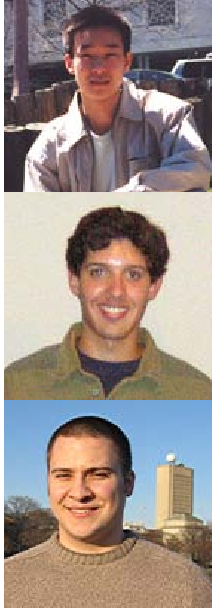
Triple Filled n-type Skutterudites



Triangles: the literature data.

From Z.F. Ren

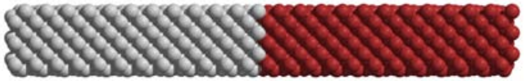
Benefits of Nanostructures

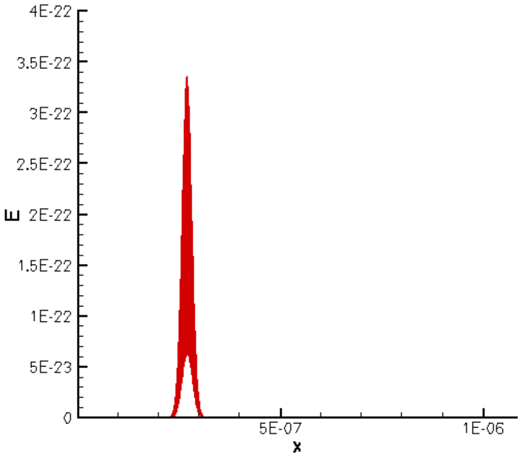


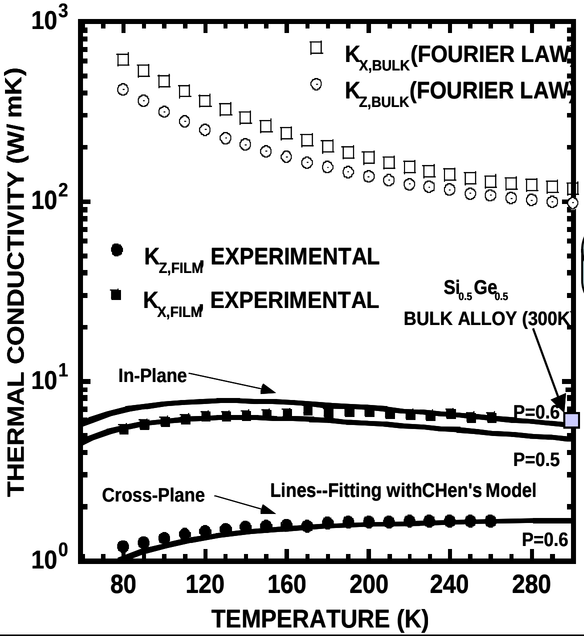
Interfaces that Scatter Phonons but not Electrons

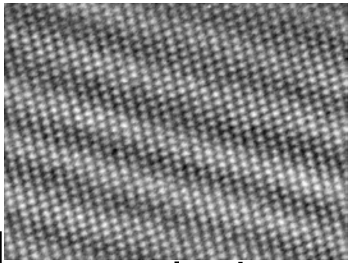
Electrons
Λ=10-100 nm
λ=10-50 nm

Phonons
Λ=10-100 nm
λ=1 nm

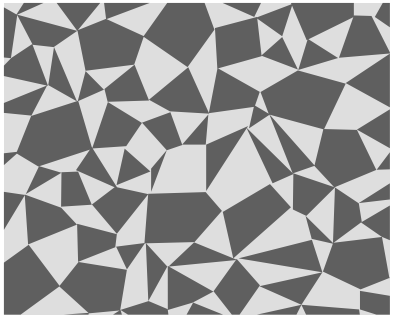






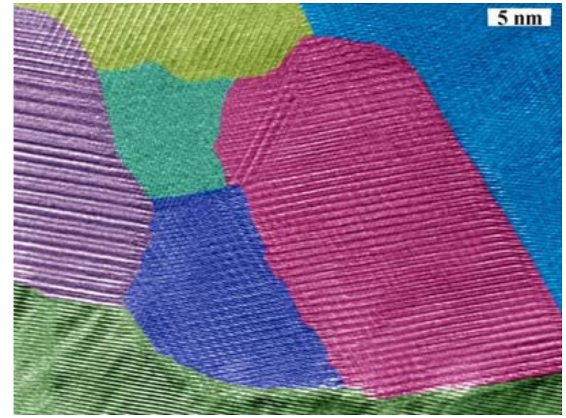


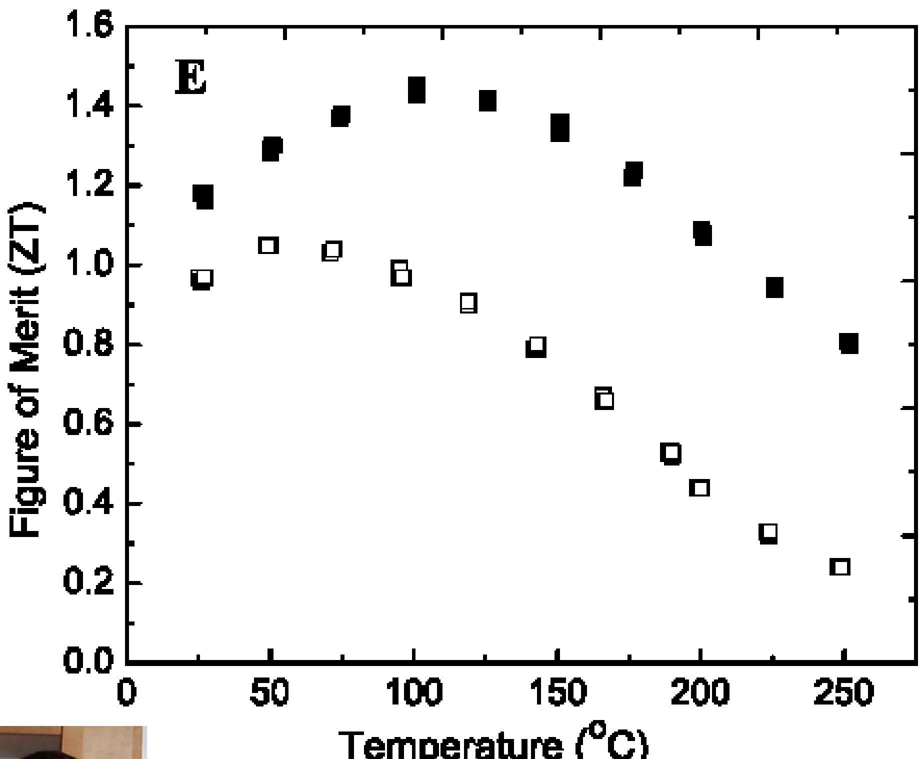
Superlattices

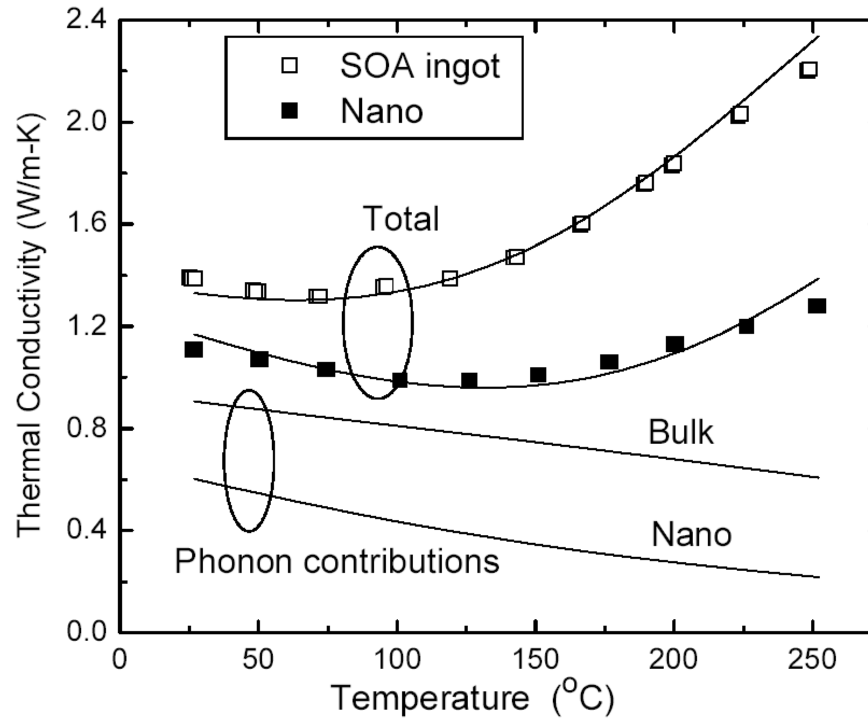


Nanocomposites

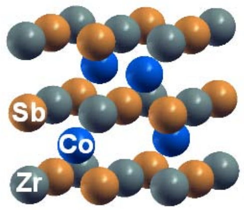
Nanostructured Thermoelectric Materials



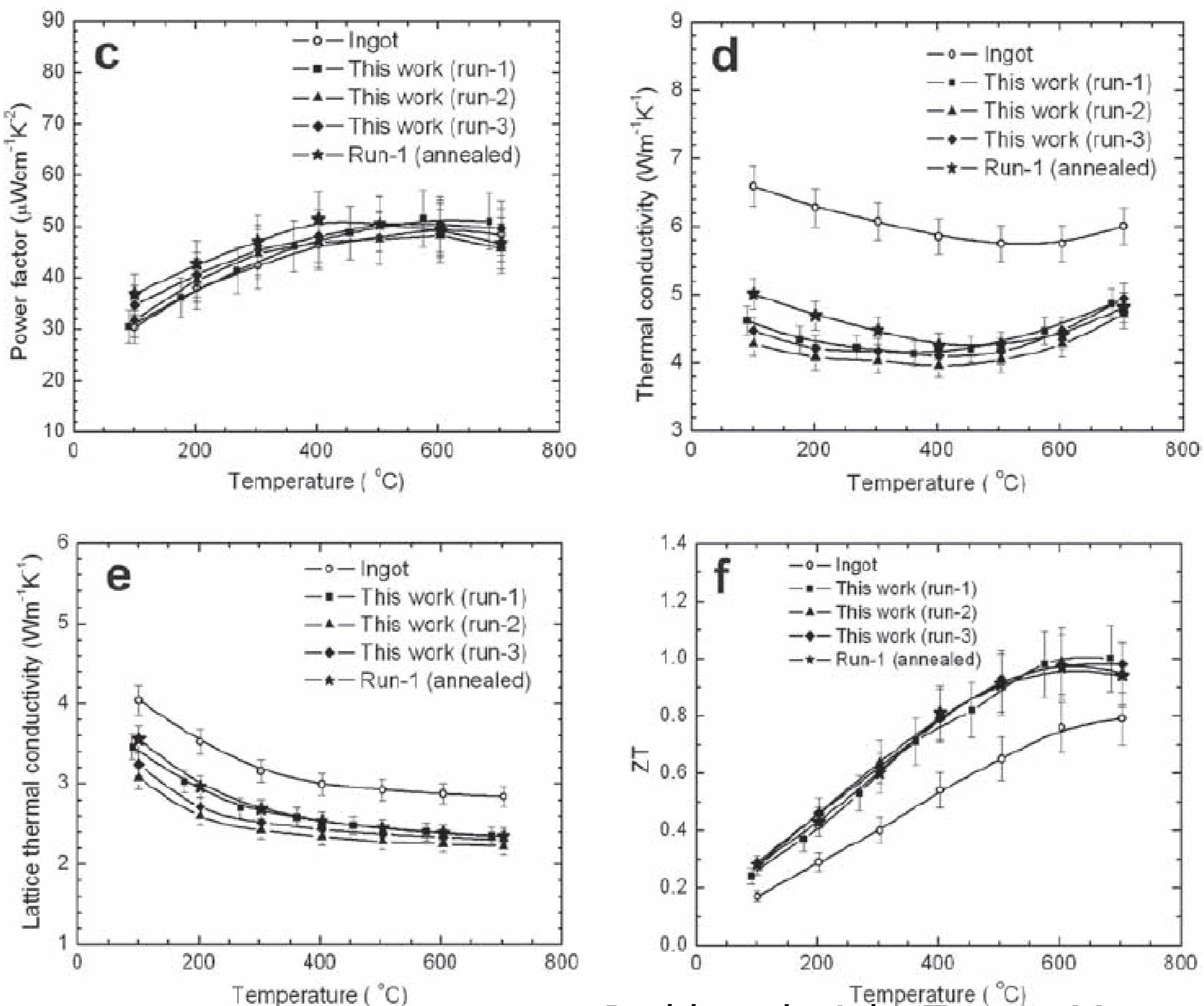




Poudel et al. Science, v. 320, p. 634, 2008

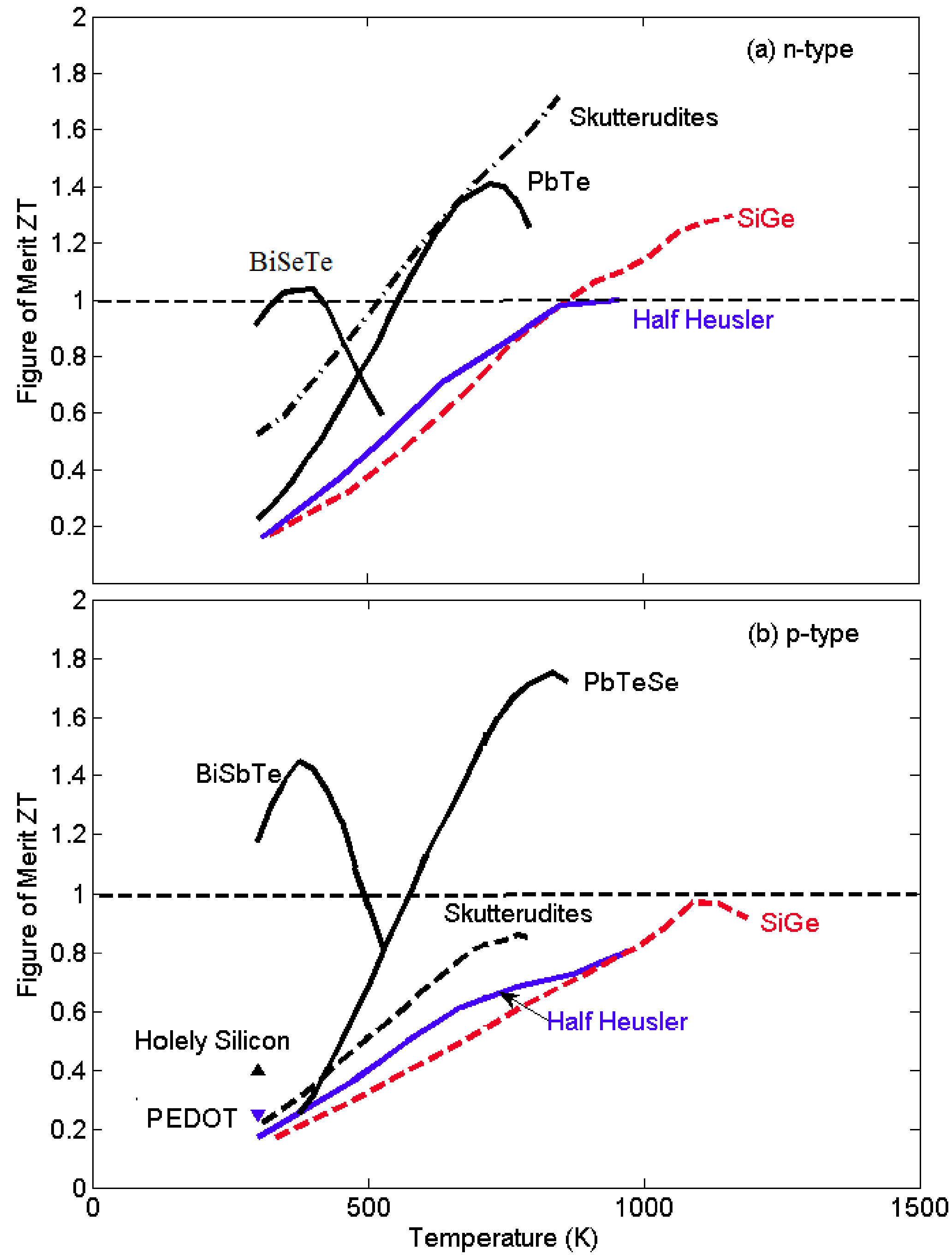


Half-Heuslers



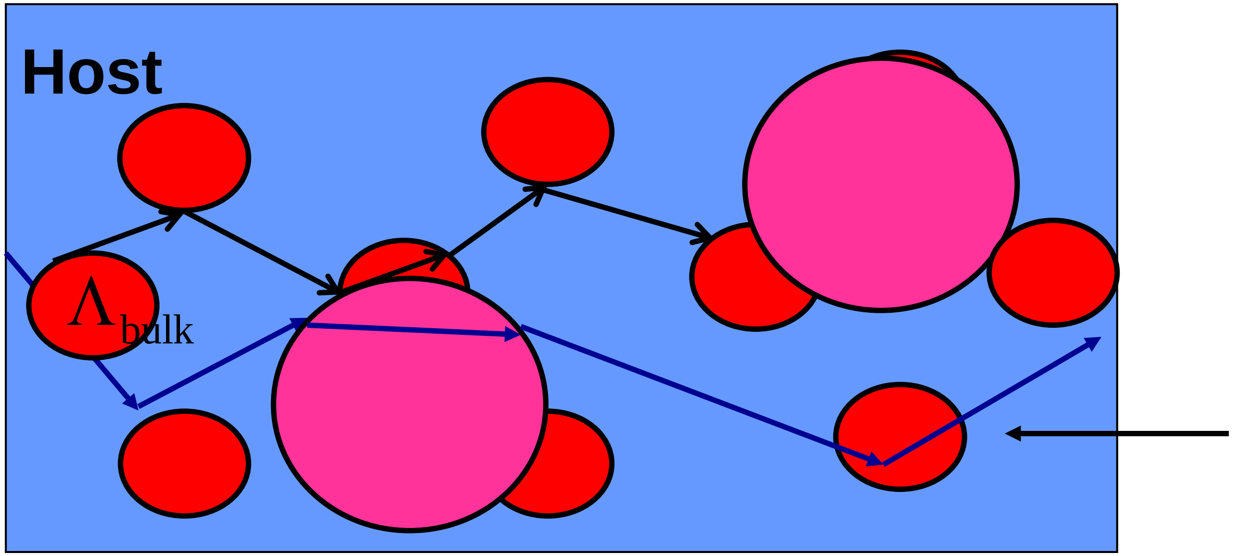
Joshi et al., Adv. Energy Mater., 1, 643, 2011.

Recent Progress in ZT



Zebarjadi et al., Energy & Env. Sci., 5, 5147, 2012

Phonon Engineering



$$\Lambda_{nano} < \Lambda_{bulk}$$

Thermal Conductivity $$k = \frac{1}{3}\int C_\omega \mathrm{v}_\omega \Lambda_\omega d\omega = \frac{1}{3} C \mathrm{v} \Lambda$$

Specific Heat → C

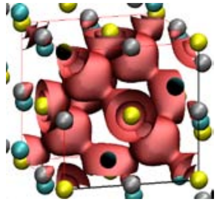
Speed of Sound → v

Mean Free Path → Λ

First-Principles Simulation

First Principle (DFT)calculations

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi$$



→ e-band, e-DOS → Seebeck, e-conductivity

→ ph-band, ph-DOS

- Density functional perturbation theory
- **<u>Real space approach</u>**

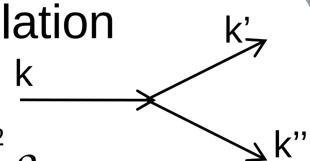
Broido et al., APL, 91, 231922, 2007;

Esfarjani et al., Physical Review B **84**, 085204, 2011.

Anharmonic Interatomic force

$$V = V_0 + \sum_i \Pi_i u_i + \frac{1}{2!}\sum_{ij} \Phi_{ij} u_i u_j + \frac{1}{3!}\sum_{ijk} \Psi_{ijk} u_i u_j u_k + \frac{1}{4!}\sum_{ijkl} X_{ijkl} u_i u_j u_k u_l$$

Scattering calculation



$$W_{i \to f} = \frac{2\pi}{\hbar} \left| \langle f | V | i \rangle \right|^2 \rho$$

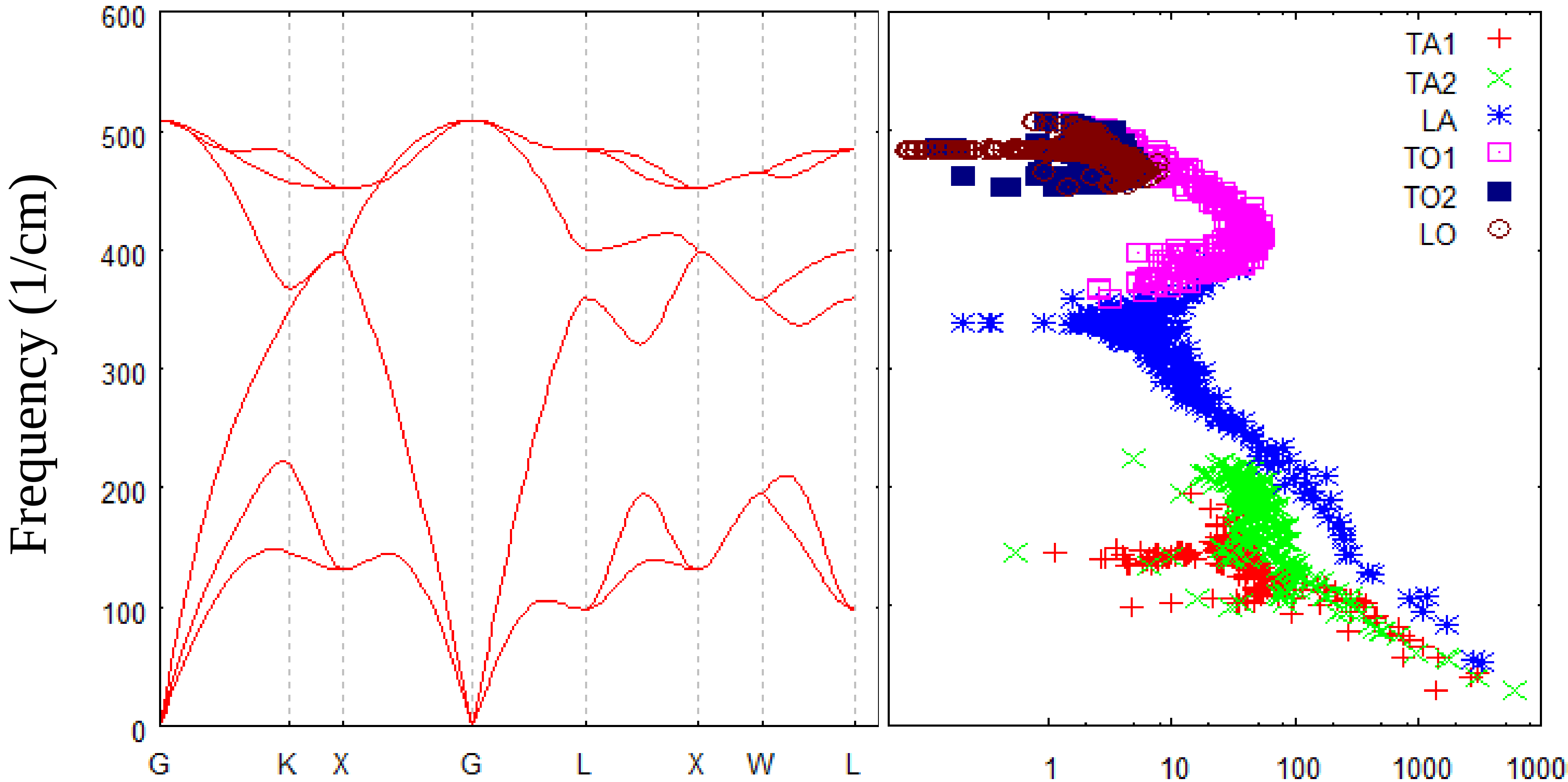
Molecular dynamics simulations

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla V$$

Alloy effects

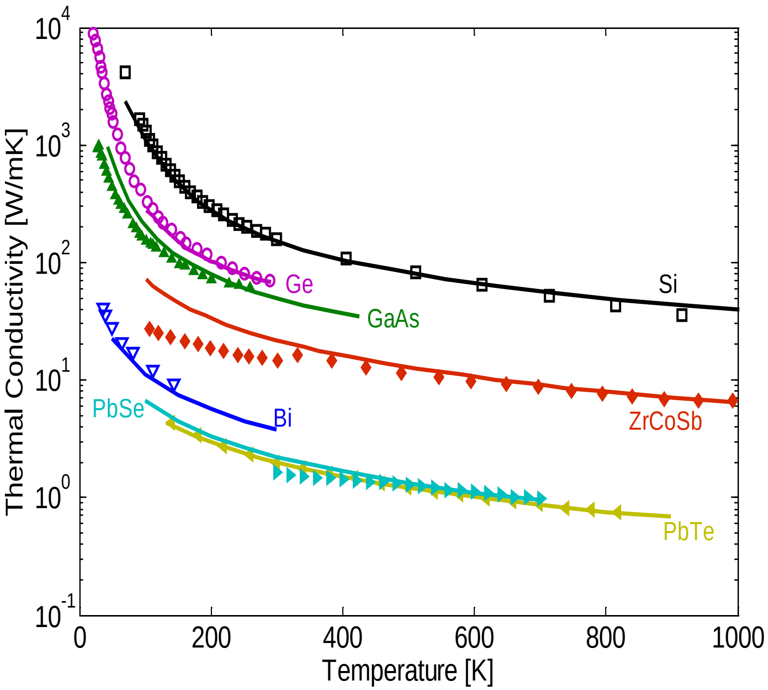
Thermal conductivity + mean free path (mode-dependent)

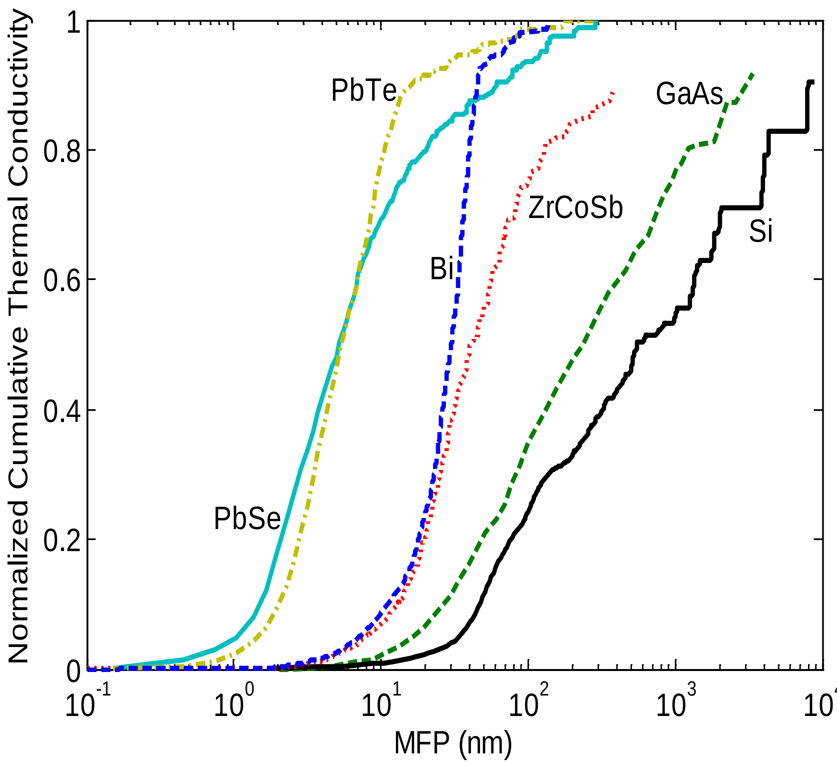
Phonon Mean Free Path in Si at 300 K



Esfarjani et al., Physical Review B **84**, 085204 (2011).

Results from First-Principles Simulation

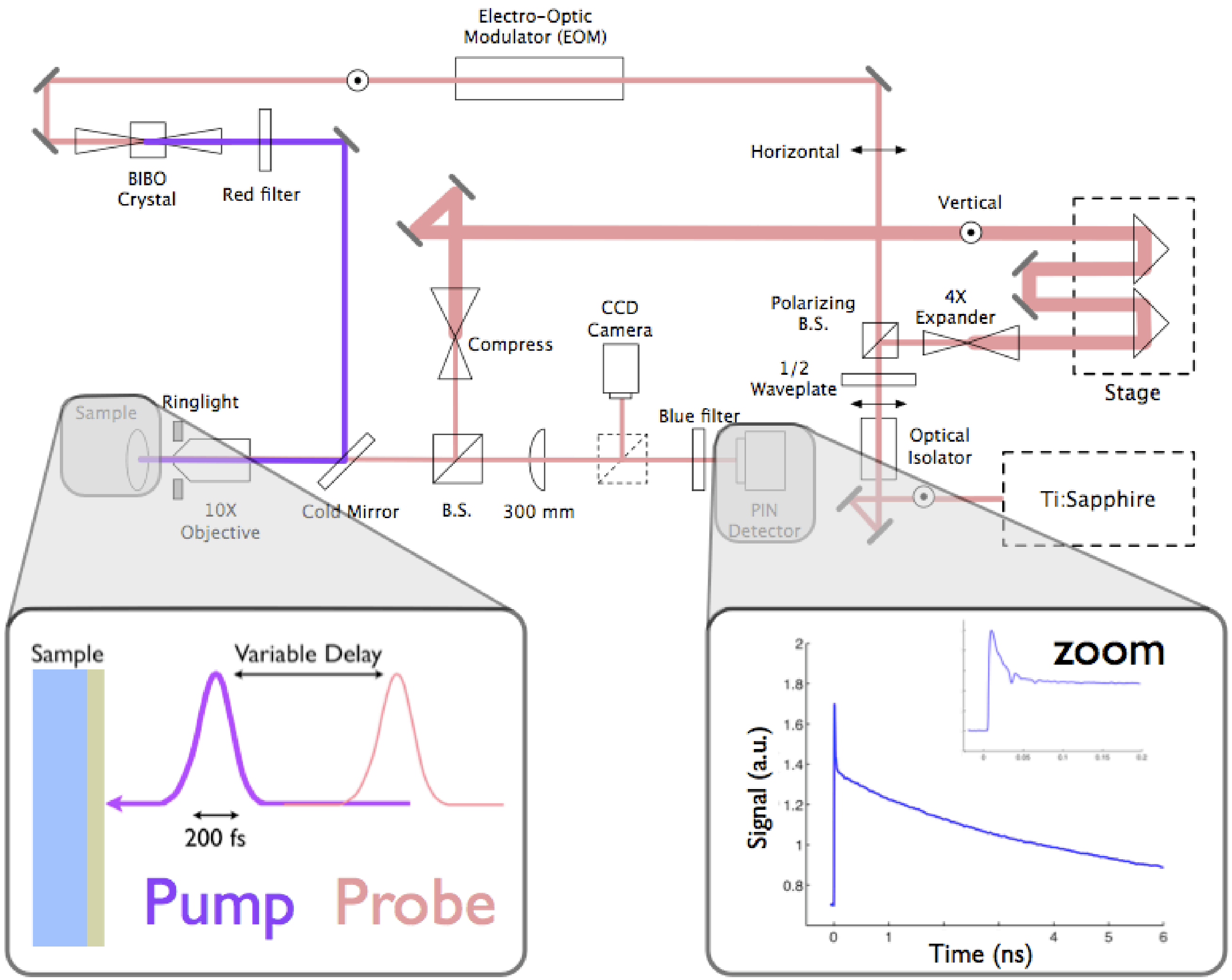


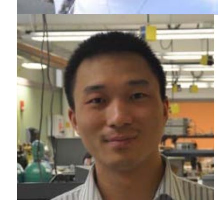


Esfarjani et al., Phys. Rev. B 84, 085204 (2011).
Shiomi et al., Phys. Rev. B 84, 104302 (2011).
Takuma et al., Phys. Rev. B 85, 155203 (2012).
Tian et al., Phys. Rev. B 85, 184303 (2012).
Zebarjadi et al., Energy & Env. Sci, 5, 5047 (2012)

Group

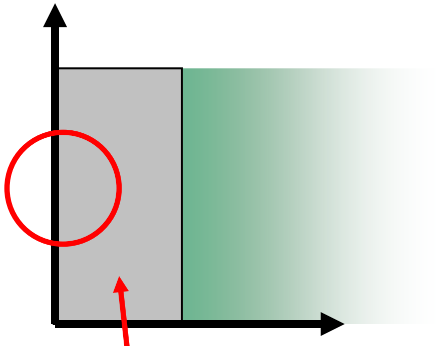
Thermal Conductivity Spectroscopy

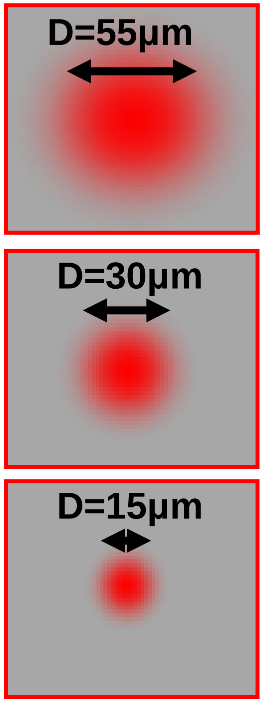


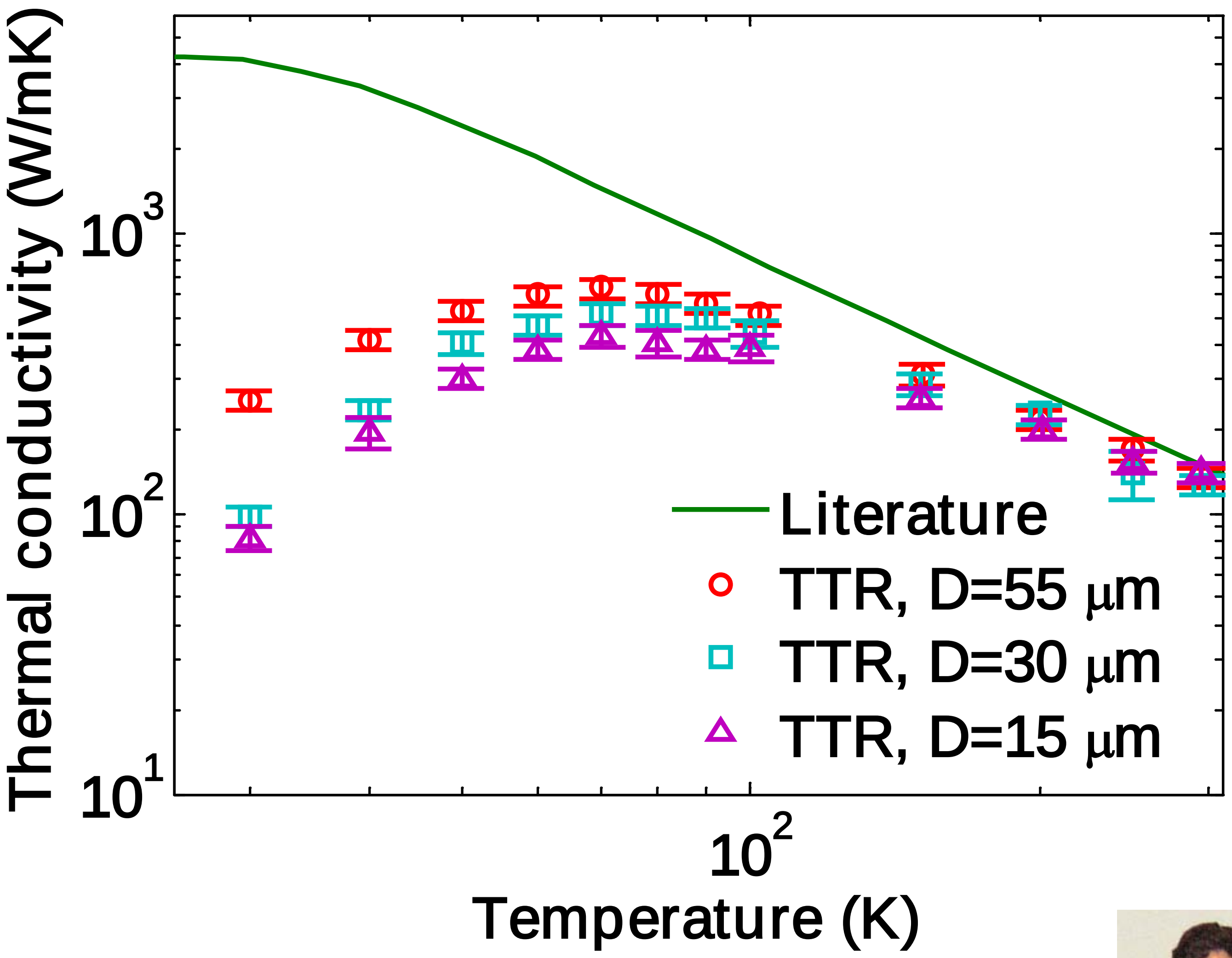


Schmidt et al. Review of Scientific Instruments, 79, 114902, 2008.

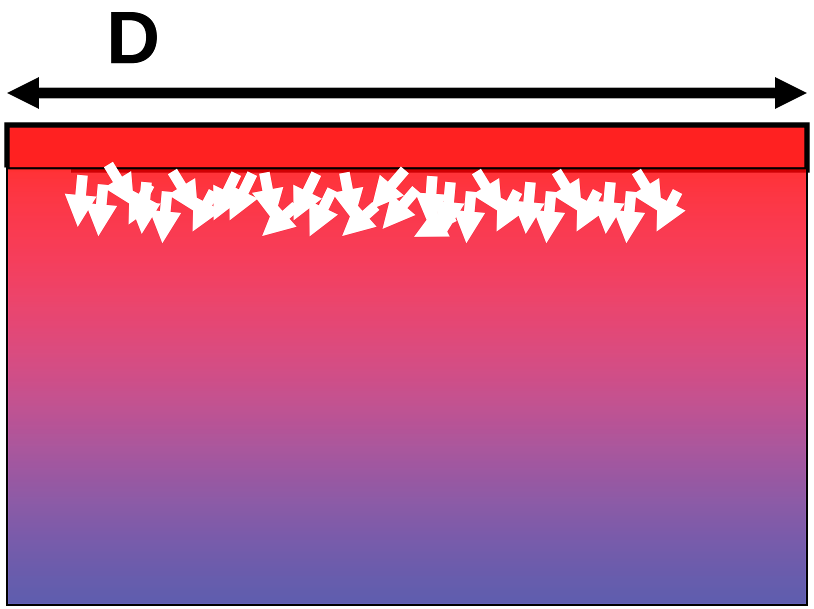
Experimental Results on Si

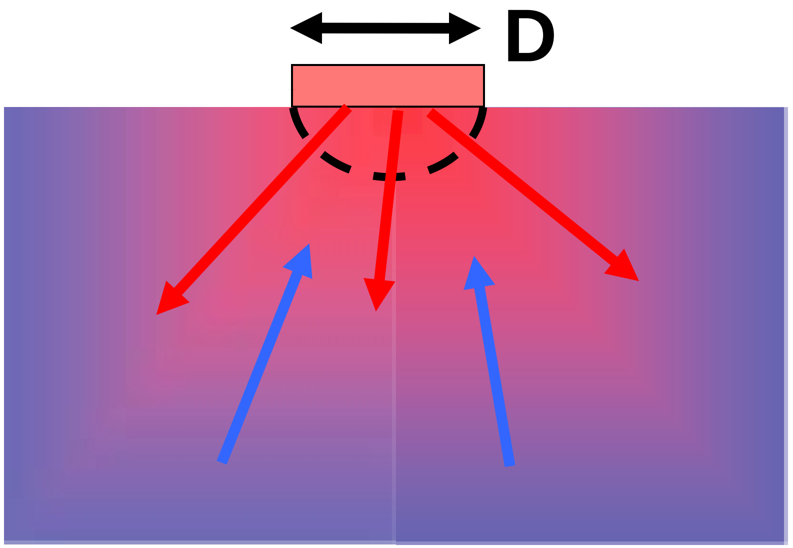






Effect of Quasi-ballistic Transport





Diffusive → **Ballistic**

Fourier's Law → **Phonon radiation**

$$\frac{q_{B\omega}}{q_{D\omega}} \sim \frac{D}{\Lambda_\omega}$$

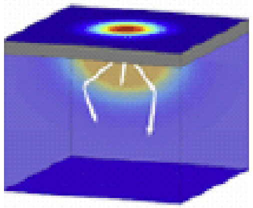
Ballistic heat flux is less than Fourier law prediction

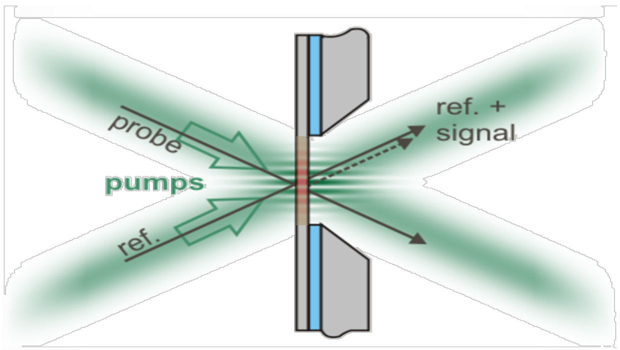
Chen, J. Heat Transfer, 118, 539, 1996

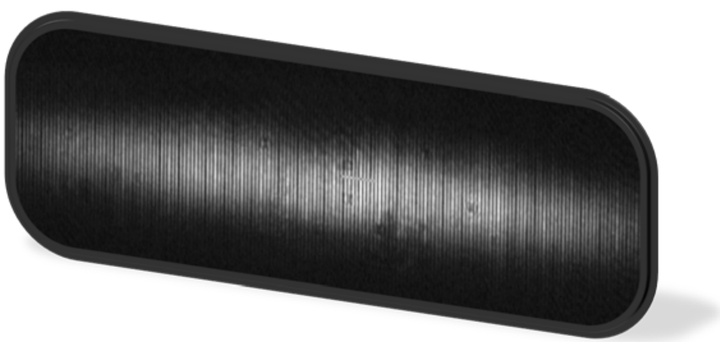
Physics: Measuring how far vibrations travel

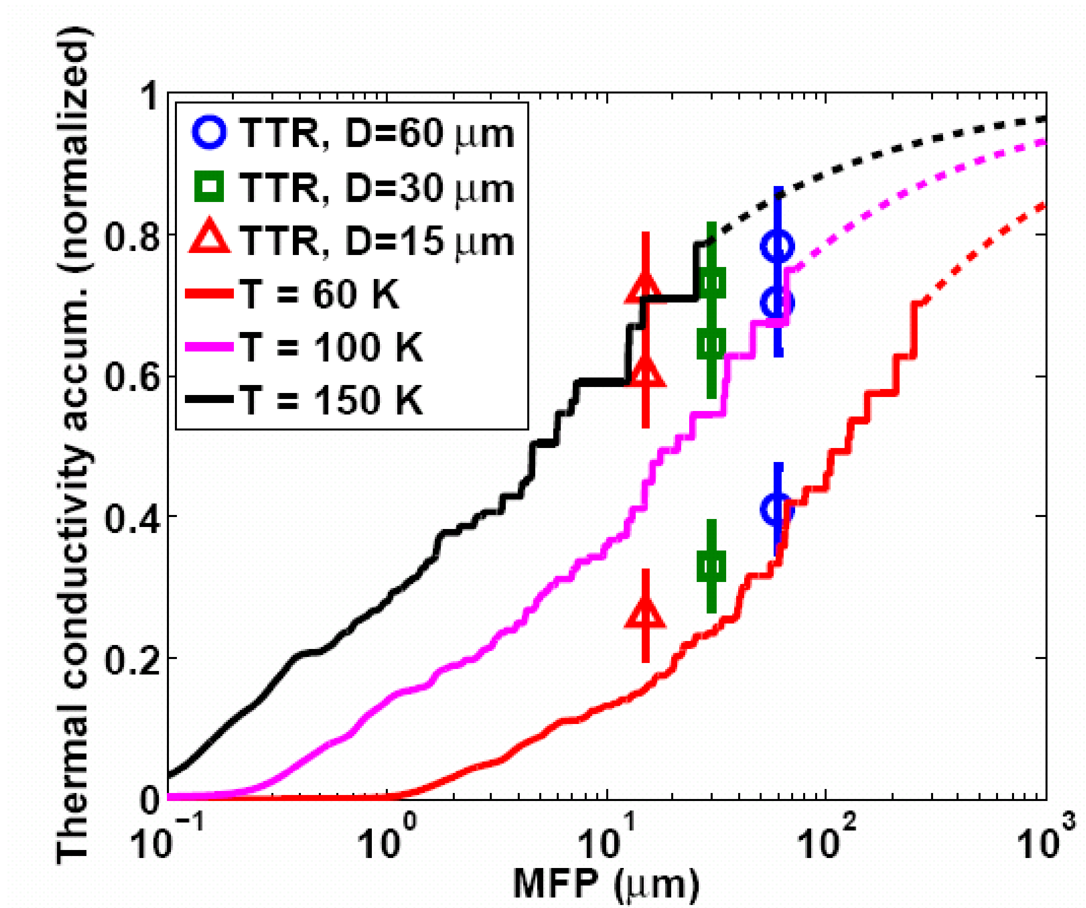
August 25, 2011

Thermal Conductivity Spectroscopy on Phonon MFP Distribution



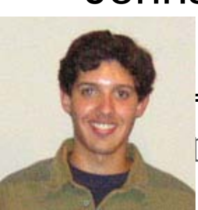




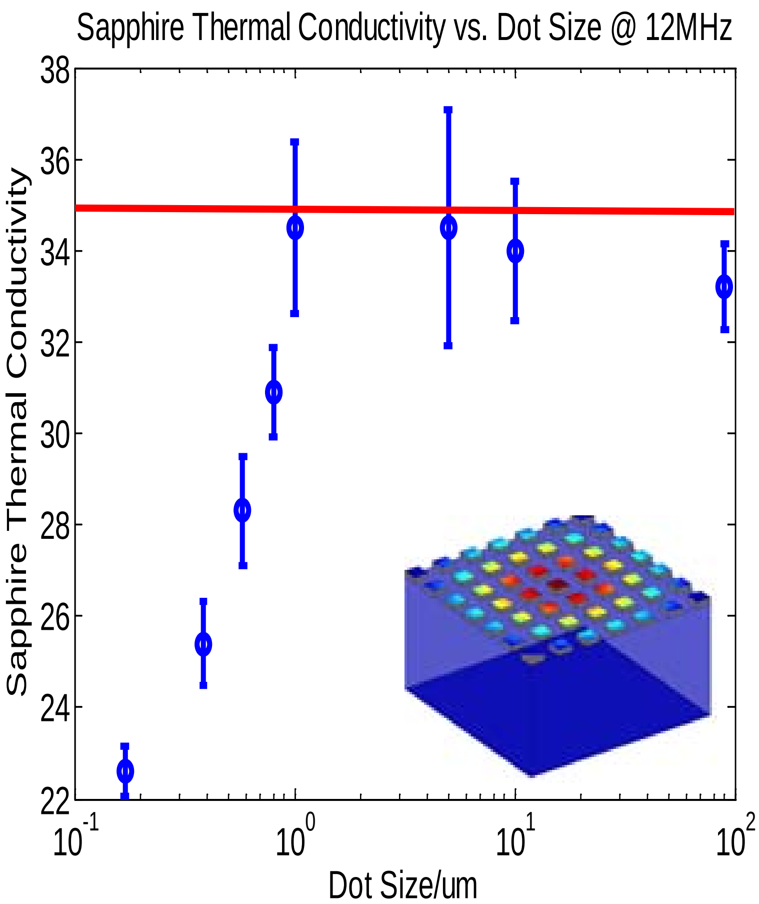


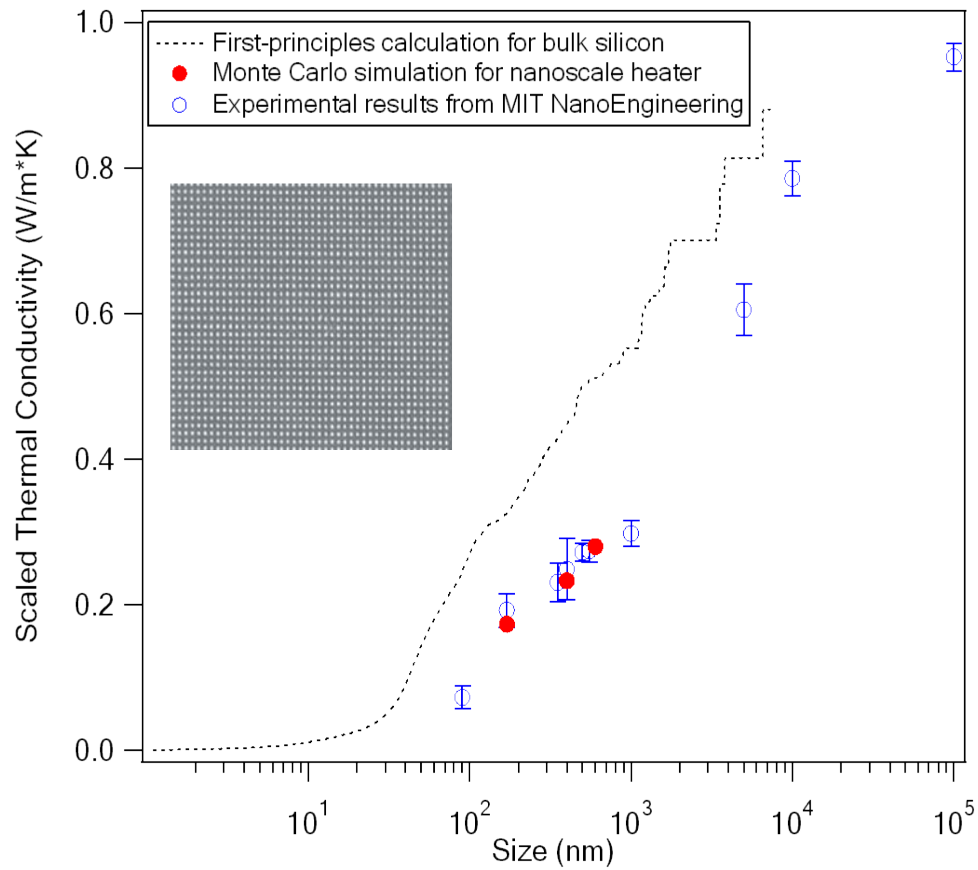
Johnson et al., submitted

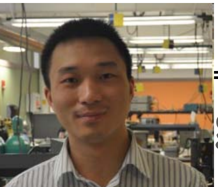
Minnich et al., PRL, 107, 095901, 2011



Pushing Down to Nanometer





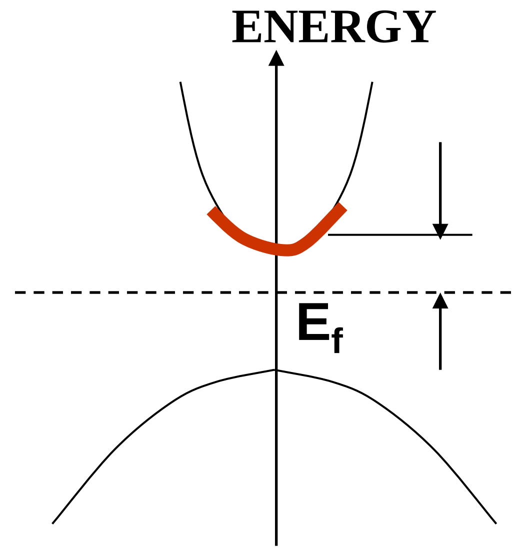


Electron Transport

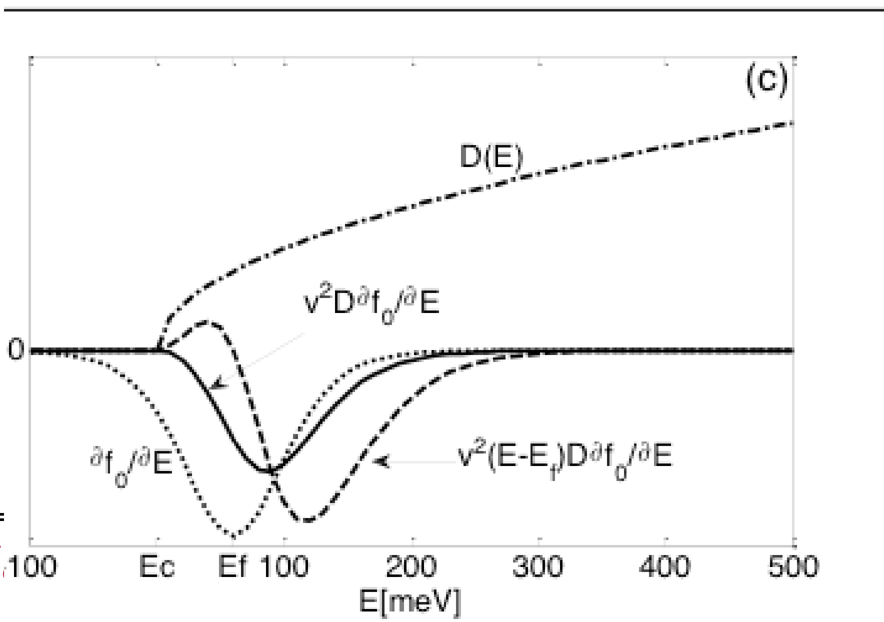
$$S == \frac{1}{\mathrm{q}}\frac{\int (E-E_F)\sigma dE}{\int \sigma(E)dE} \propto \langle E-E_f \rangle$$

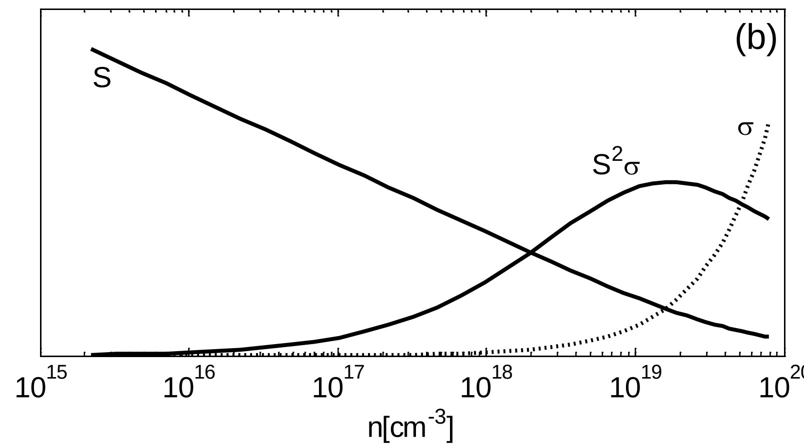
$$\sigma = \frac{q^2}{3}\int \tau \mathbf{v}^2 \mathrm{D(E)}(-\partial f_{eq}/\partial \mathrm{E})\mathrm{dE}$$

Relaxation Time **Density of States** **Fermi-Dirac Distribution**



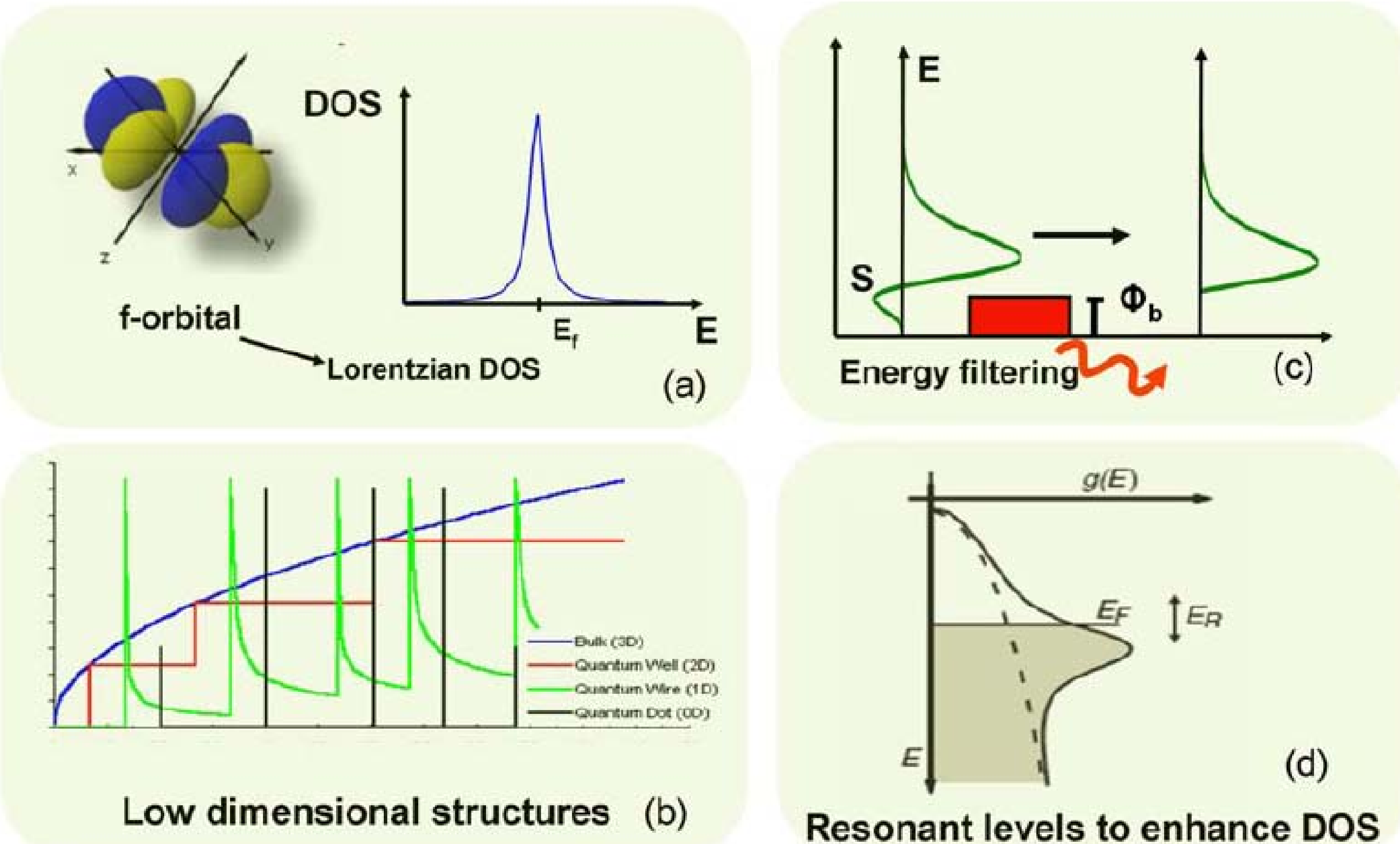
Fermi Level Controlled By Doping





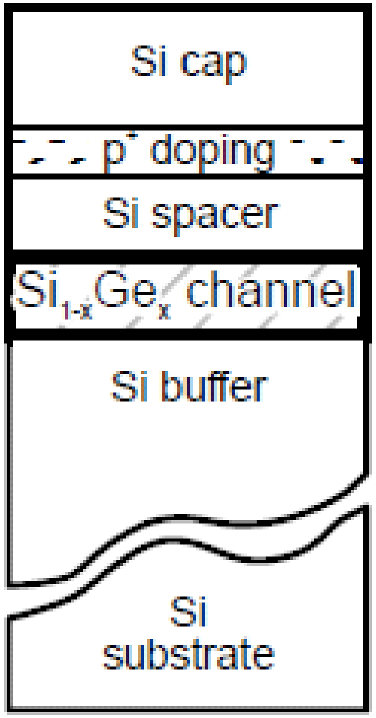
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Electron Engineering



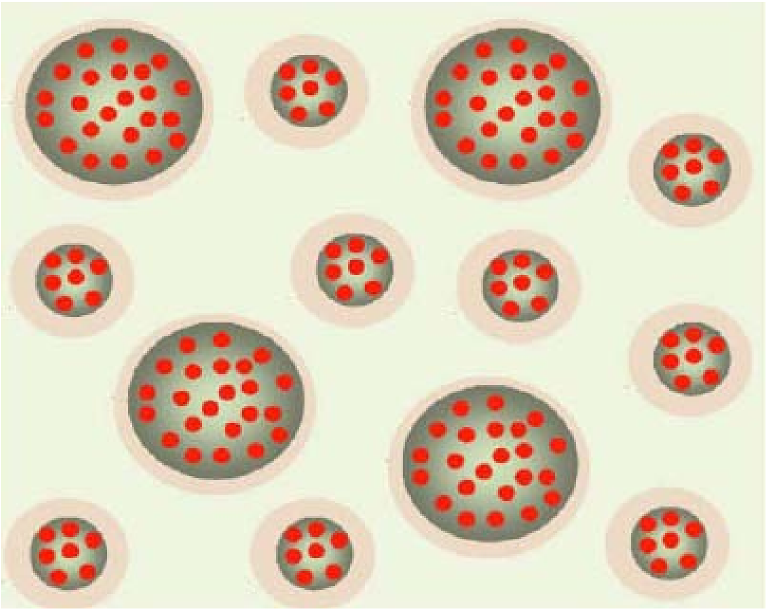
Modulation Doping

2D Thin-Films



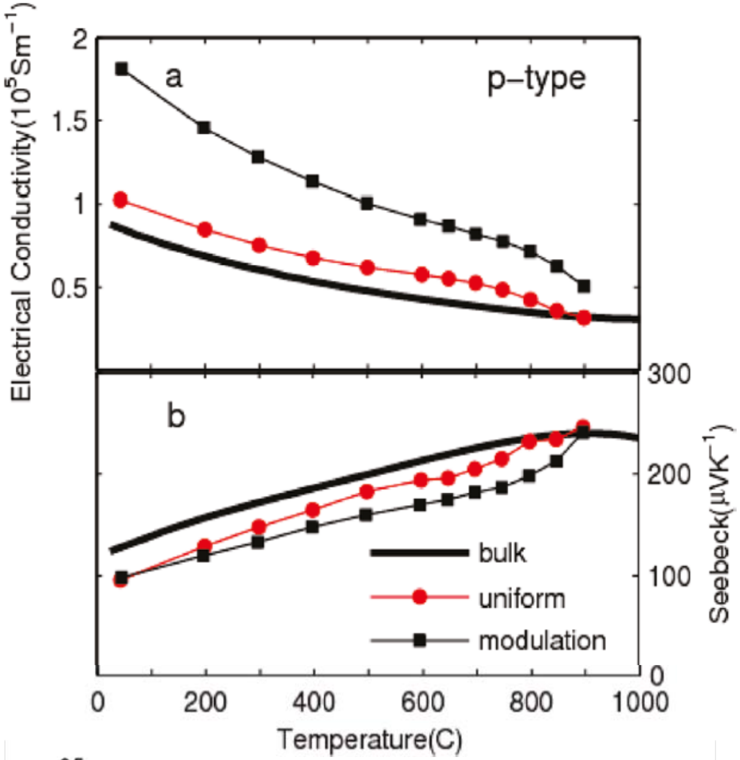
Schaffler, Semicond. Sci. Tech. 12 1997

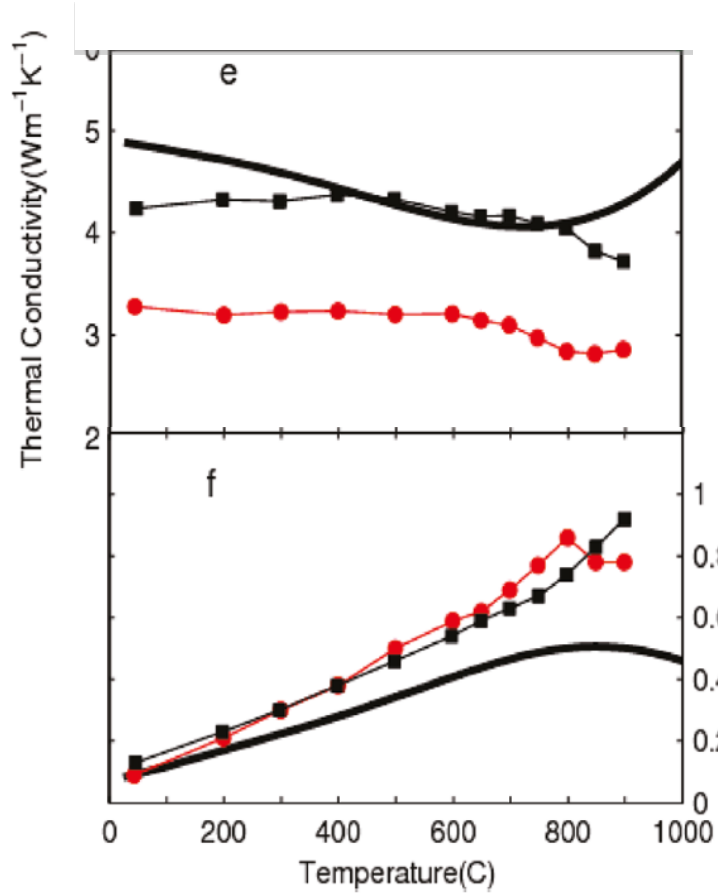
3D Bulk Nanostructures

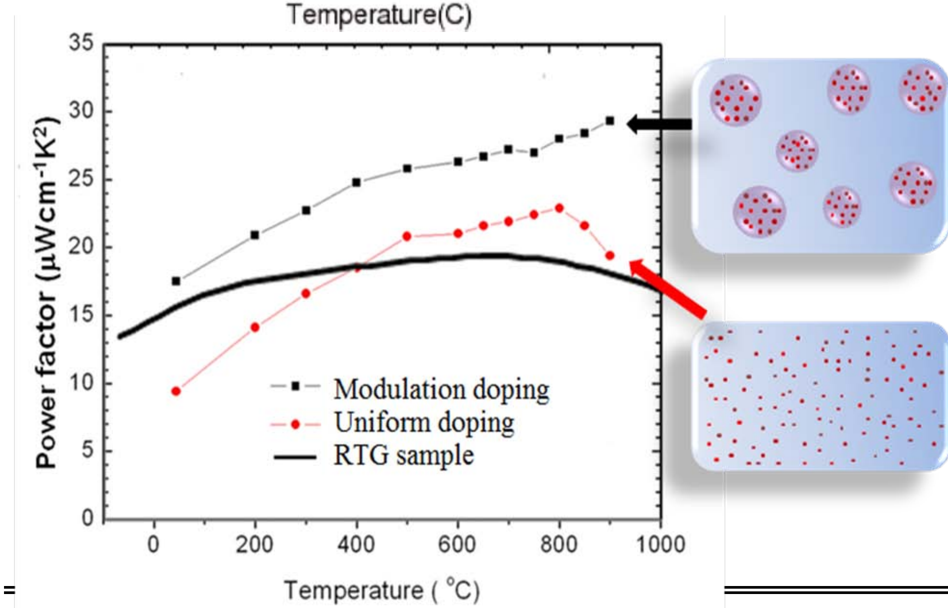


Zebarjadi et al., Nano Letters, 11, 2225, 2011.

Modulation Doping

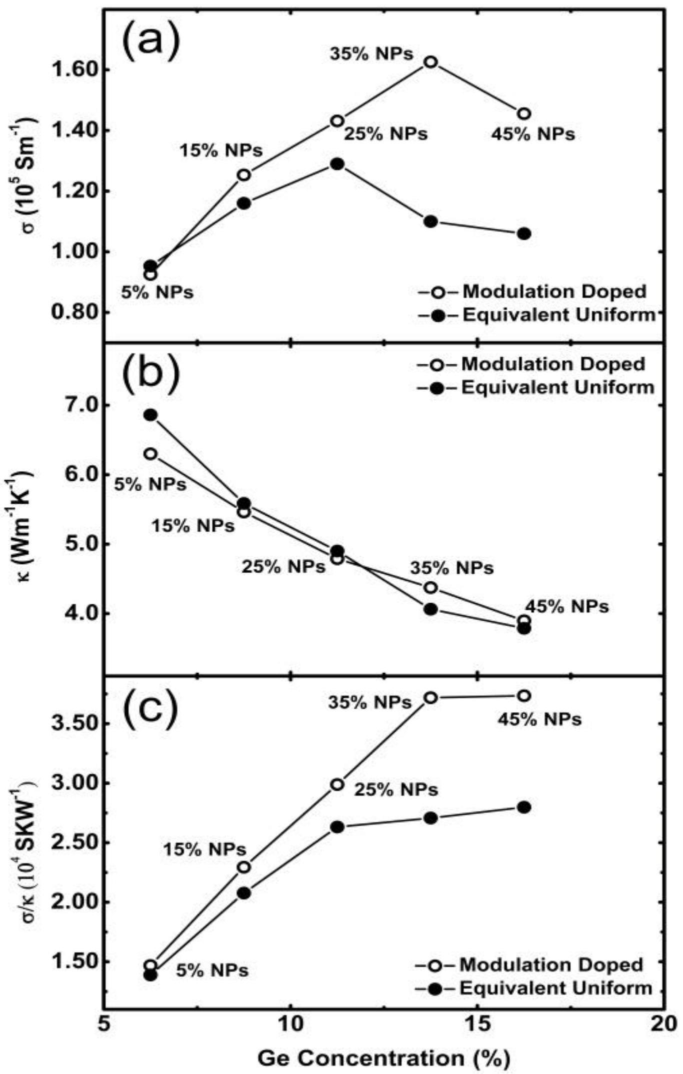


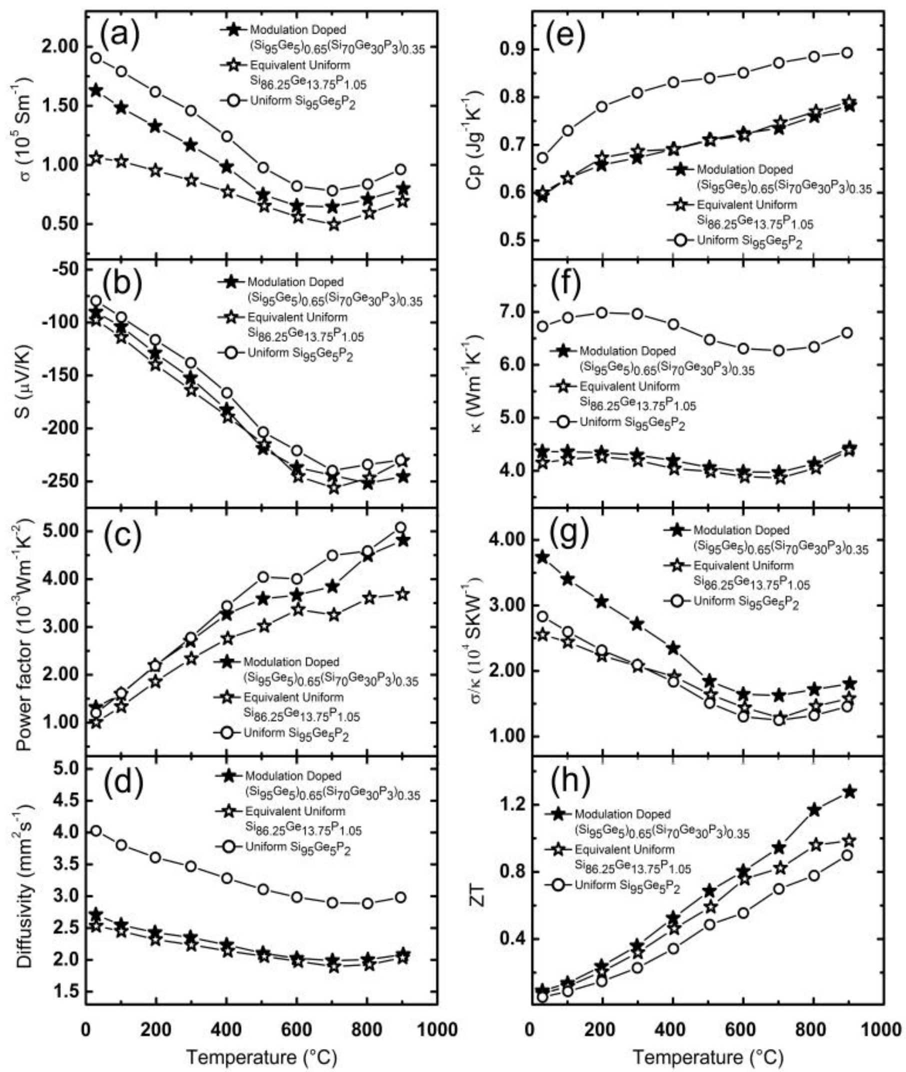




Zebarjadi et al., Nano Lett **11**, 2225-2230 (2011)

Concurrent Electron and Phonon Engineering

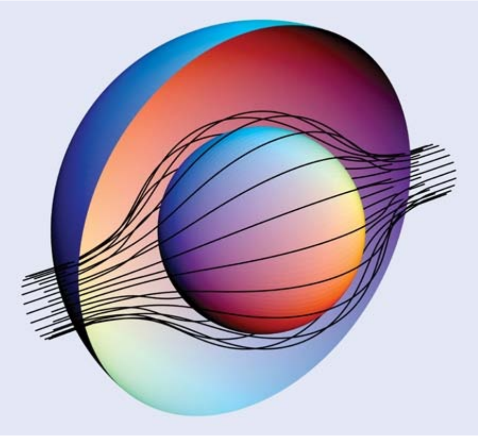




Yu et al., Nano Letters, 12, 2077 (2012).

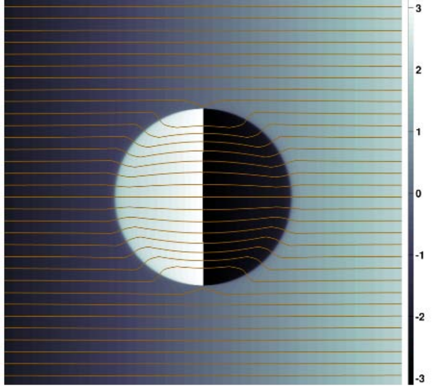
Invisible Cloak

en.wikipedia.org



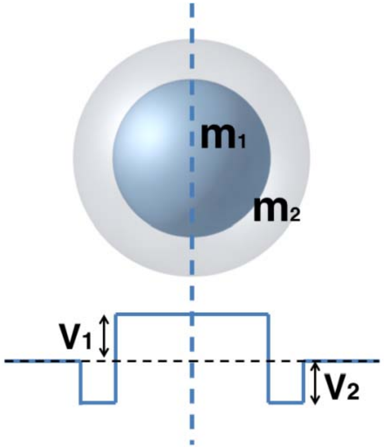
physicsworld.com

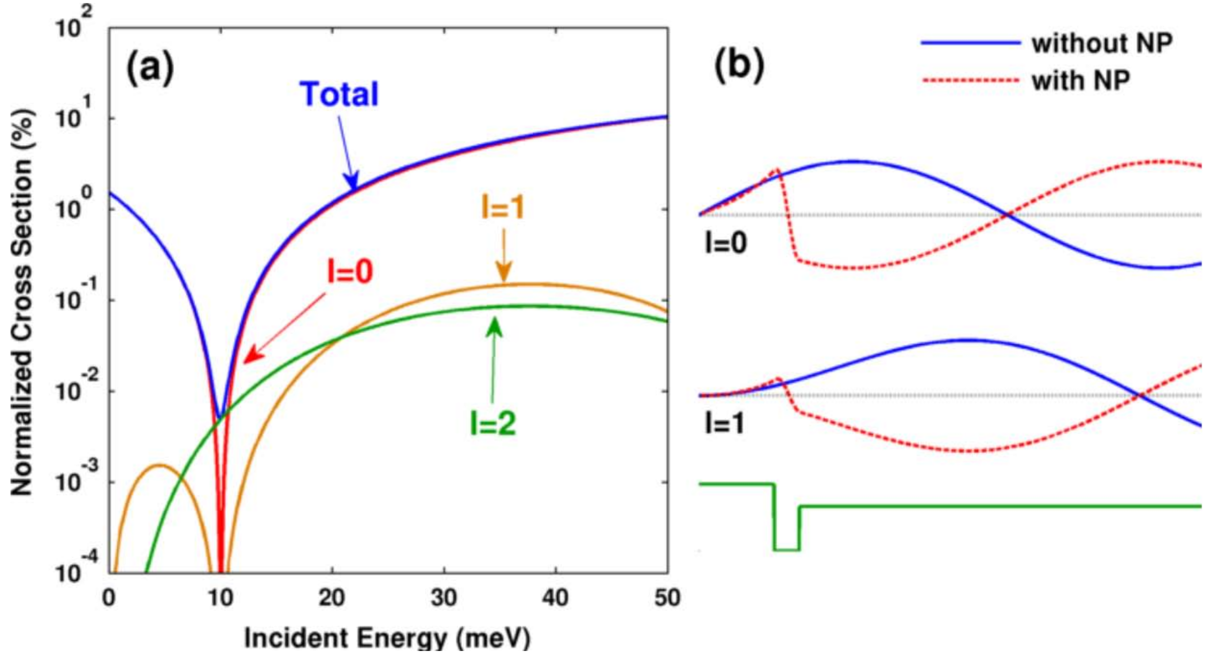
Invisible Particles



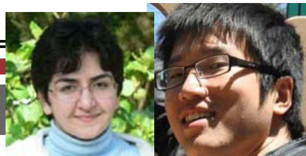
- **Mott formula for the Seebeck coefficient:**

$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{1}{D}\frac{dD(E)}{dE} + \frac{1}{\mu}\frac{d\mu(E)}{dE}\right\}\Bigg|_{E=E_F}$$





B. Liao et al., Phys. Rev. Lett., 109, 126806, 2012



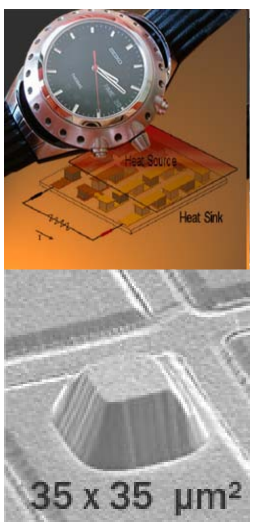
Application: From Micro Watts to Giga Watts

Vehicles

Power Plants

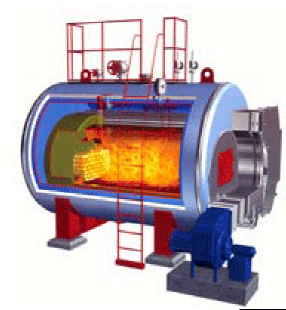
μW — W — kW — MW — GW

Sensors



Stove

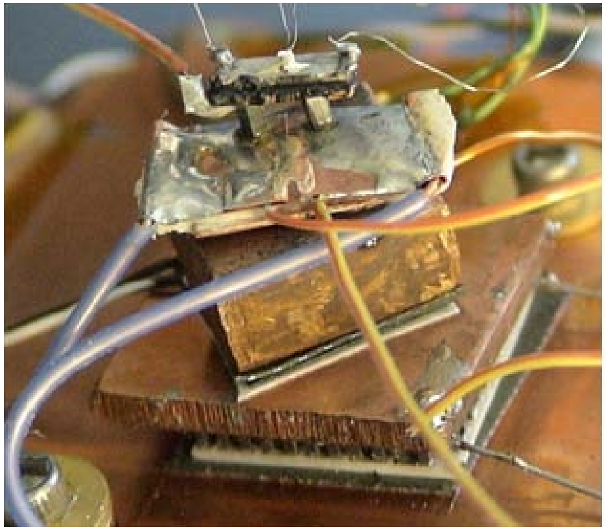
Furnace

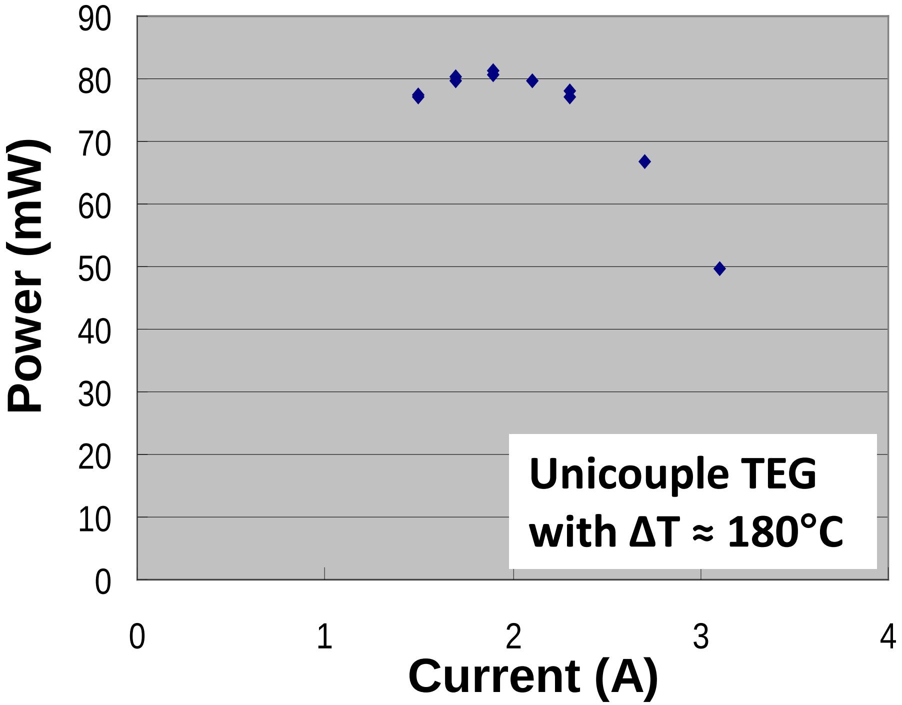


Solar

Industrial Waste Heat

Power and Cost Example

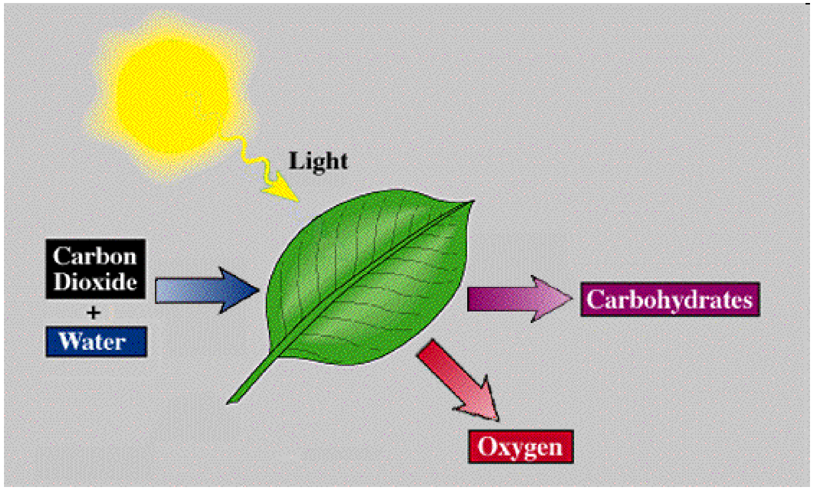




- Dimensions of TE elements: 1.5mm x 1.5 mm x 1.6 mm
- Material cost per power output ≈ 0.1 $/Watt
- Cost of TE material can be small relative to total system cost!

Solar Energy Utilization

Solar Fuel



http://www.phschool.com/science/biology_place/biocoach/photosynth/overview.html

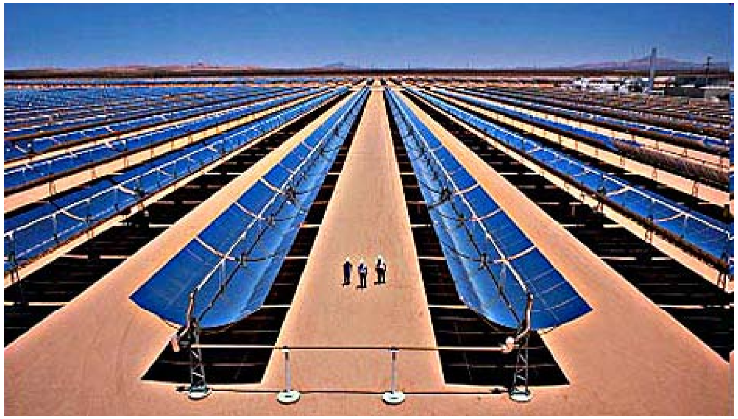
Solar Electricity: PV

homesolarpvpanels.com

Solar Heating

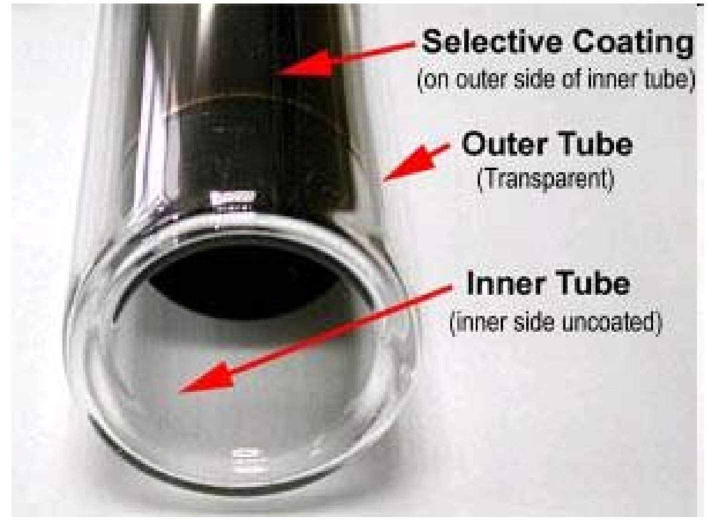
http://www.global-greenhouse-warming.com/solar-hot-water.html

Solar Electricity: Thermal-Mechanical

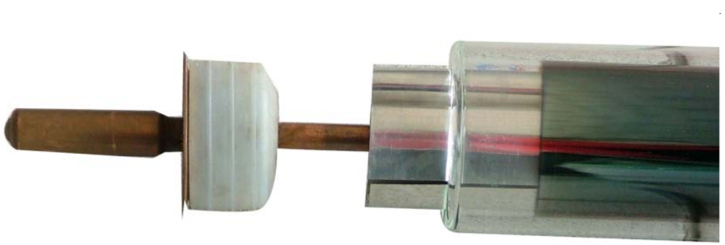


http://www.treehugger.com/Solar-Thermal-Plant-photo.jpg

Solar Hot Water Systems

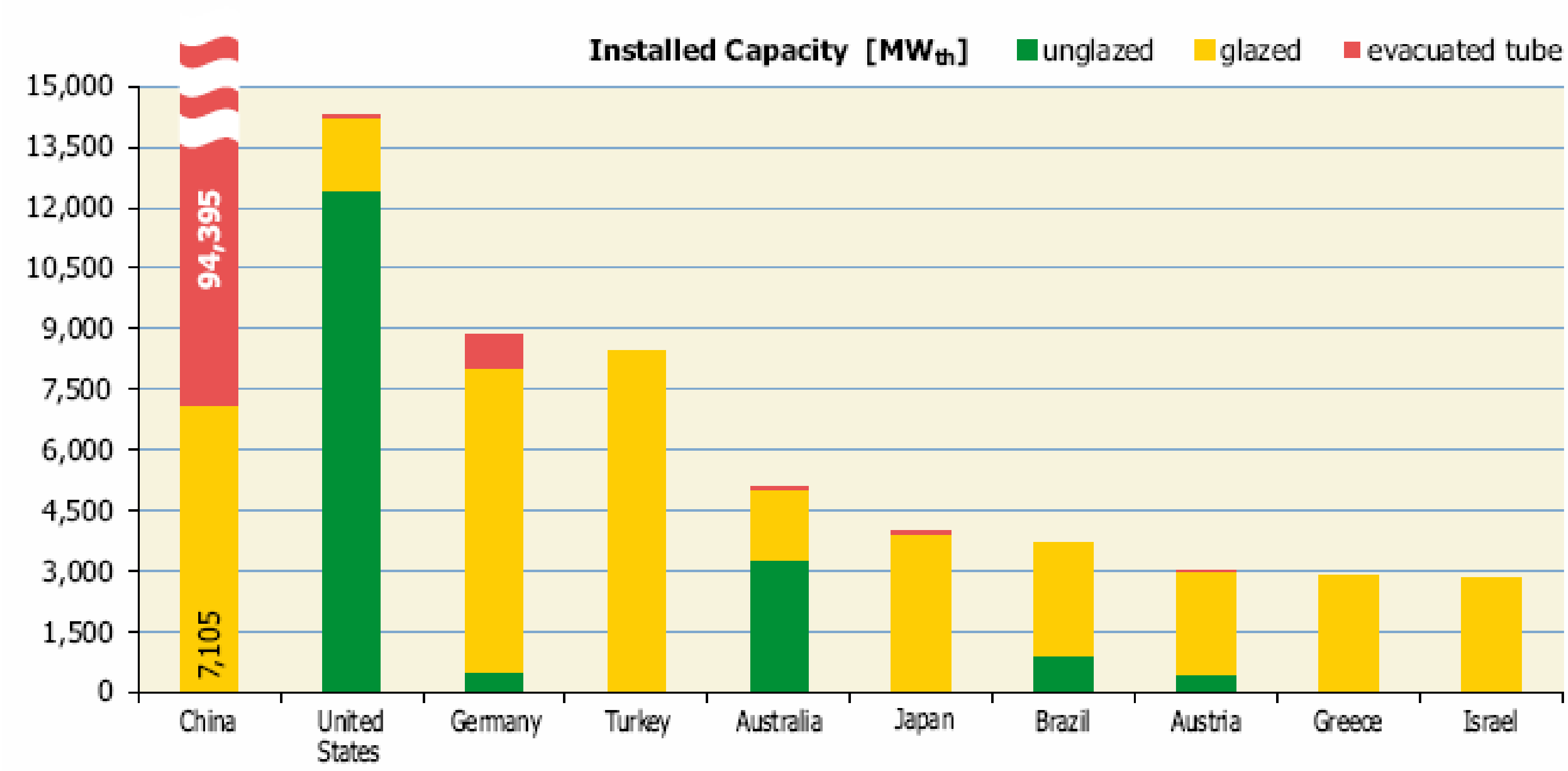


http://www.freewebs.com/solarwyse/solar_tubesspecs.html



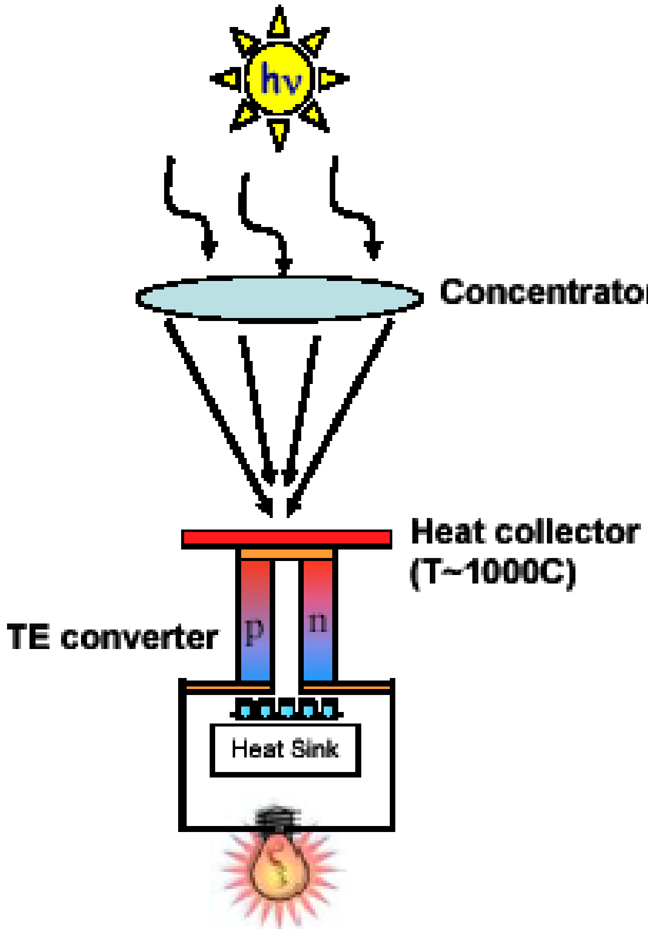
http://www.made-in-china.com

Solar Thermal Installed Capacity, 2009

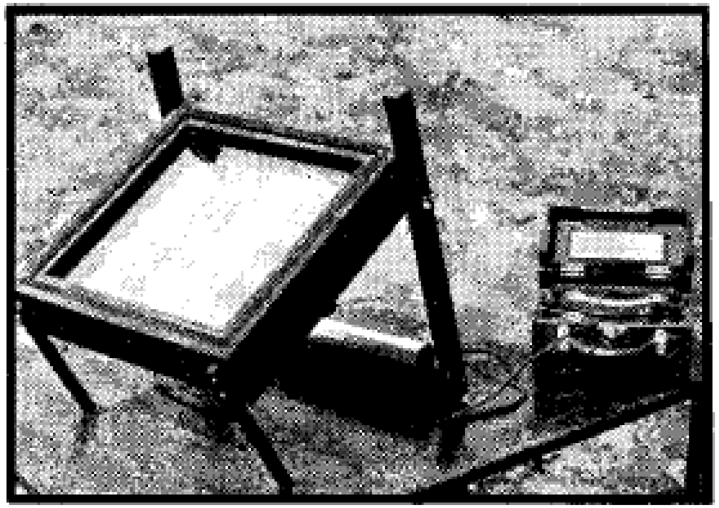


China in 2009, total of 134 Million m^2 Evacuated Tubes

Solar Thermoelectric Energy Conversion



- US Patent No. 389124: E. Weston in 1888
- M. Telkes, JAP, 765, 1954



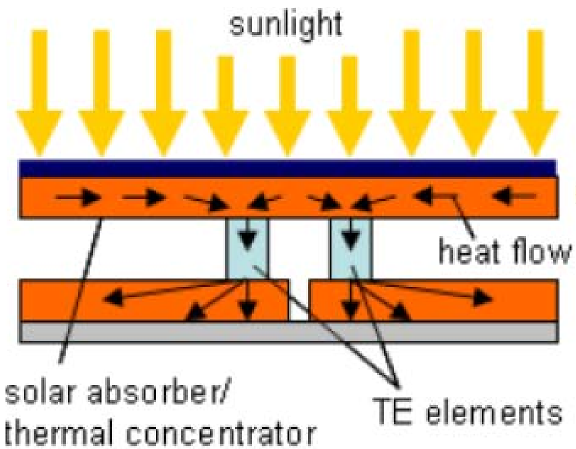
Efficiency: 0.63%

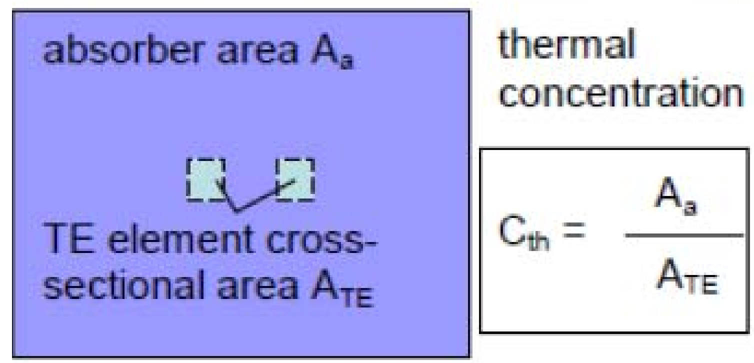
Heat Flux Consideration

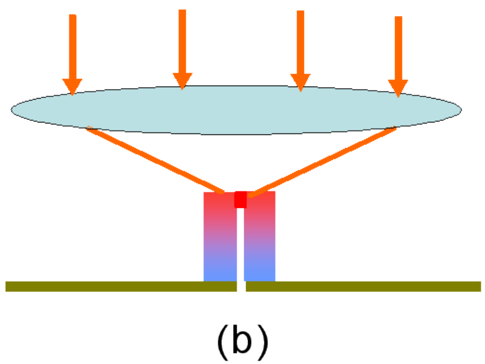
$$q = k\frac{\Delta T}{L} \approx 1\frac{\mathrm{W}}{\mathrm{m}*\mathrm{K}}\frac{100\,\mathrm{K}}{\mathrm{L}}$$

q=1000 W/m^2 (1 Sun); L=100 mm
q=100,000 W/m^2 (100 Sun); L=1 mm

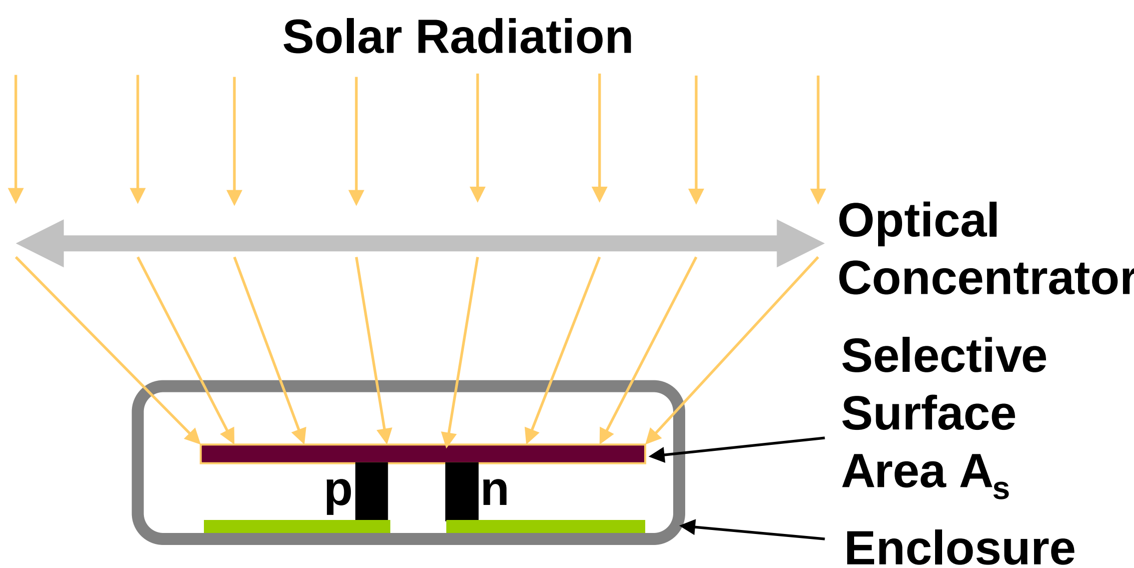
Possible Configurations



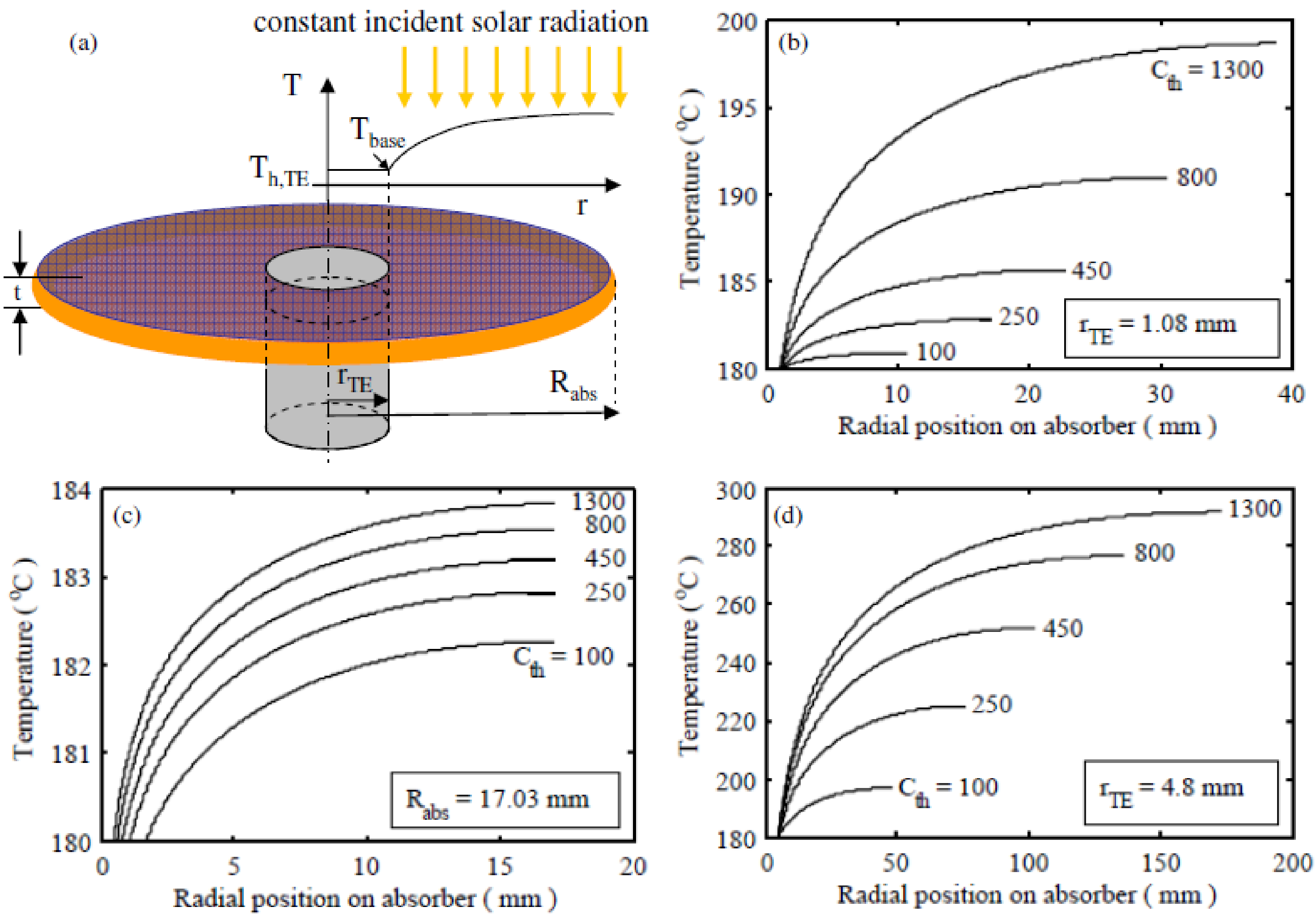




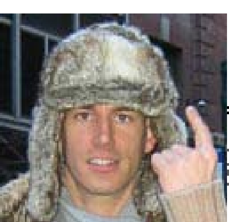
Optical Concentration



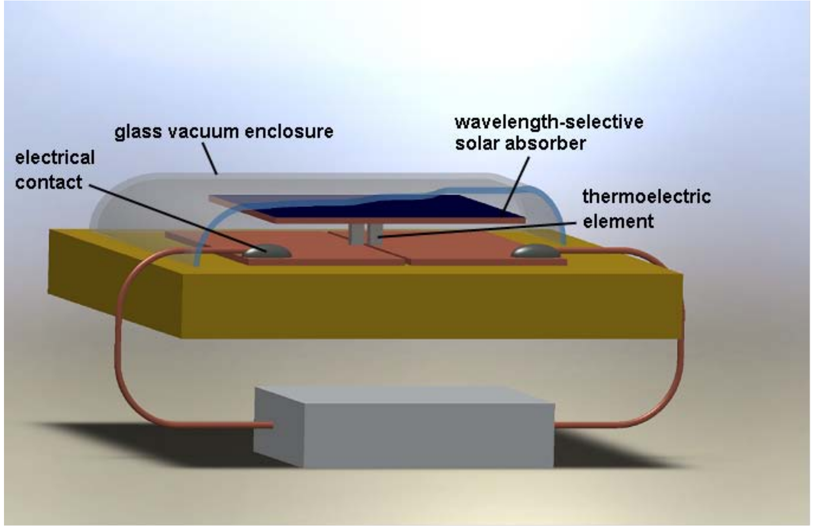
Thermal Concentration

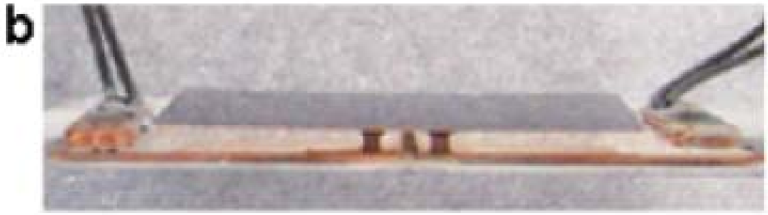


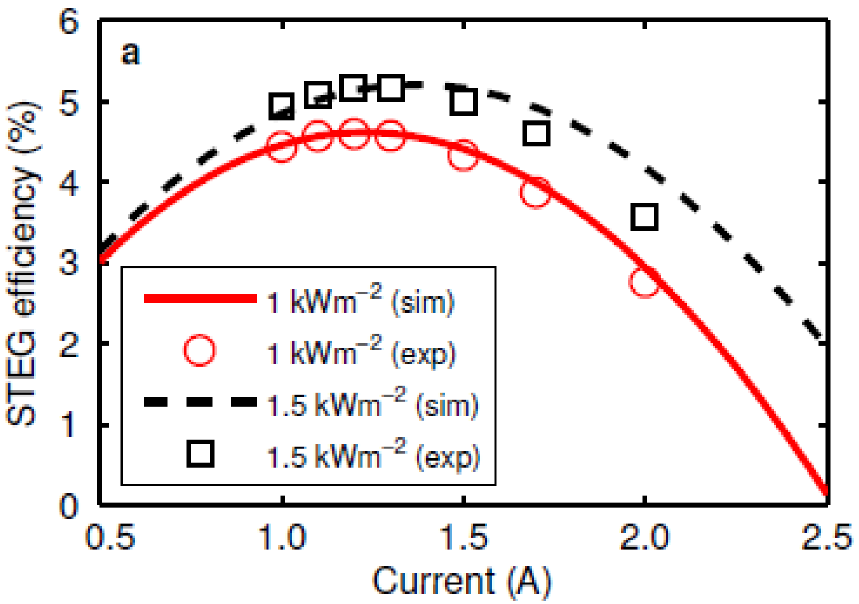
Kraemer et al., Solar Energy, 86, 1338, 2012.



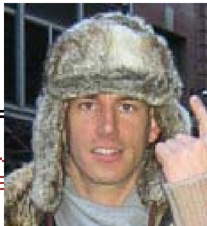
Solar Thermoelectric Power Conversion

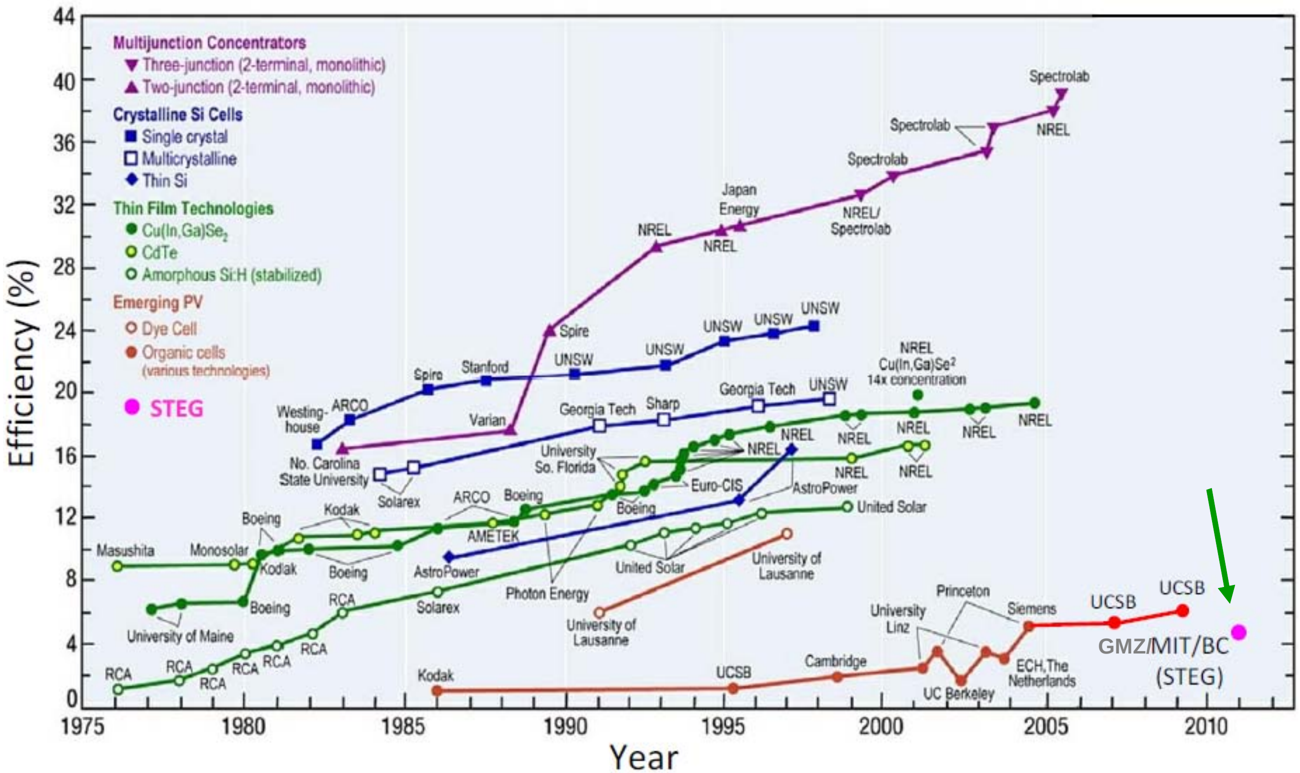


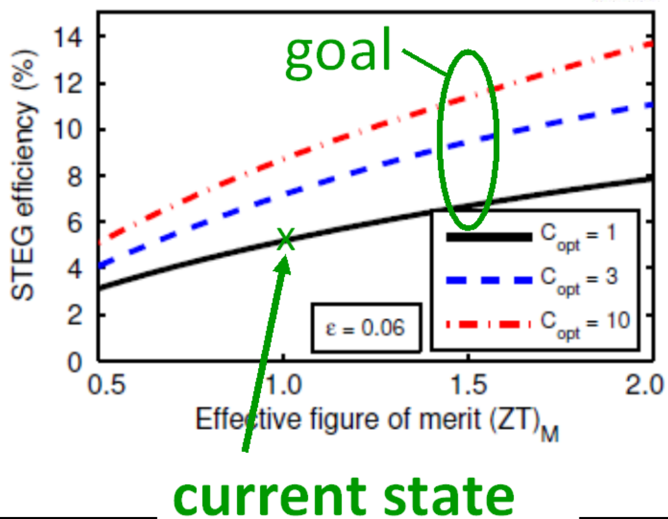


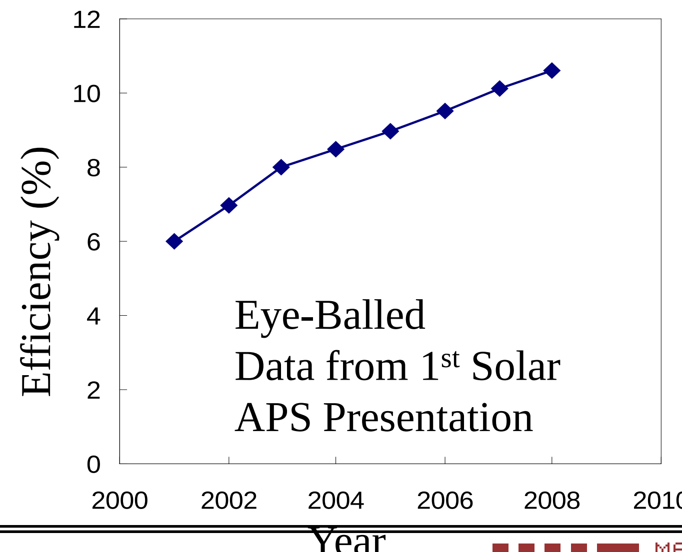


Kraemer et al., Nature Materials, 10, 523, 2011

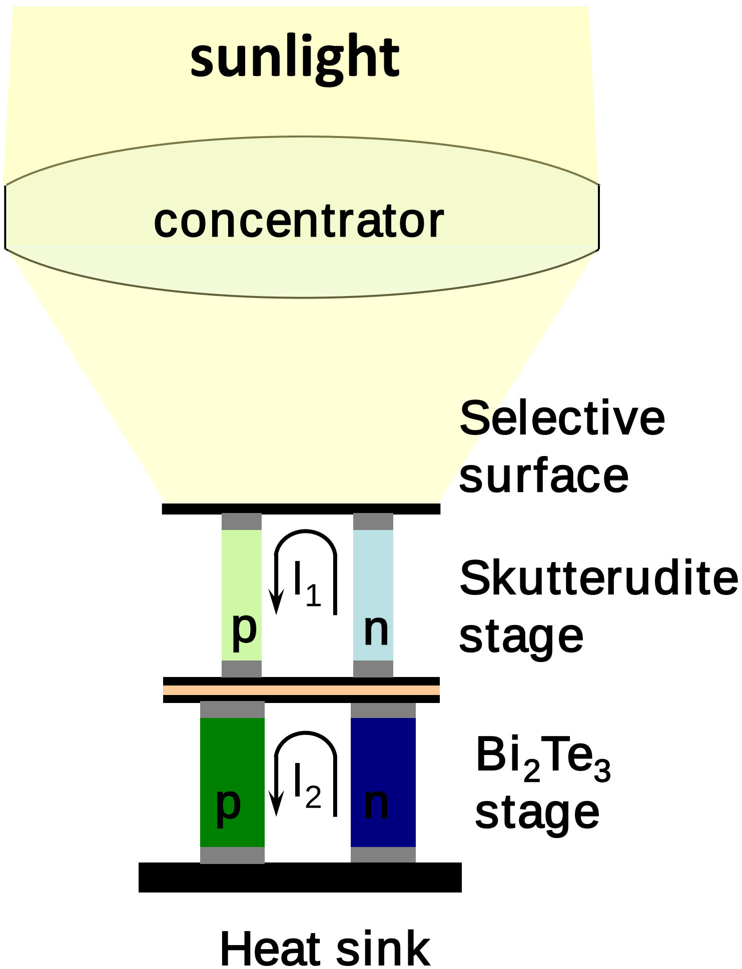


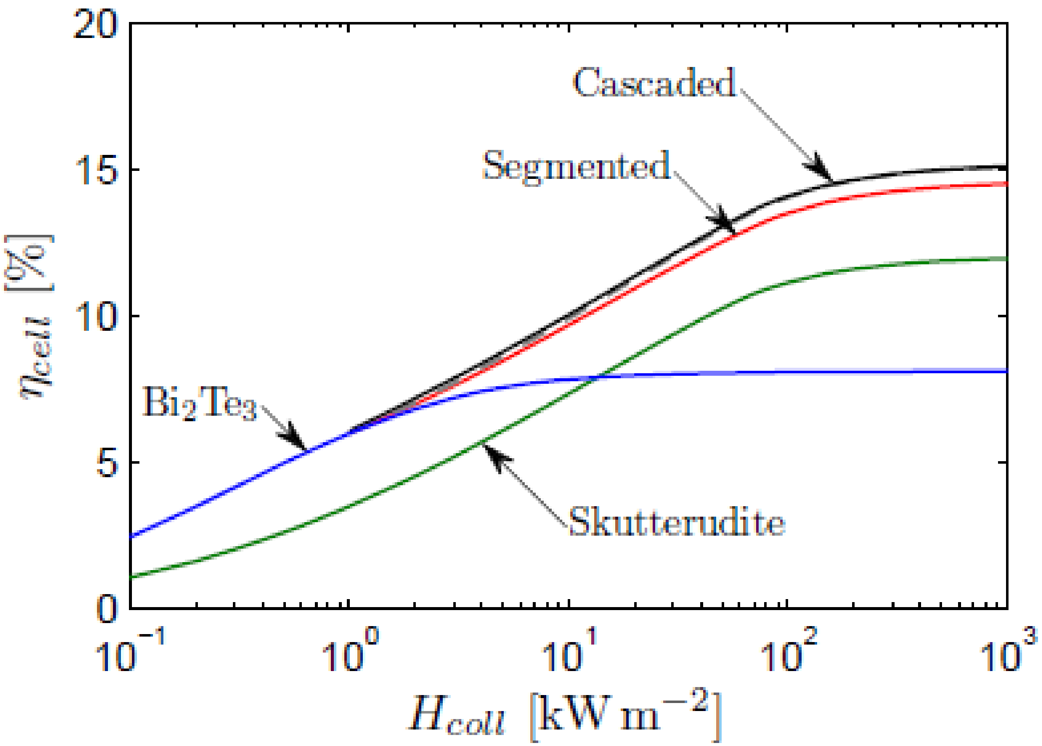

Multijunction Concentrators
Three-junction (2-terminal, monolithic)
Two-junction (2-terminal, monolithic)
Crystalline Si Cells
Single crystal
Multicrystalline
Thin Si
Thin Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Emerging PV
Dye Cell
Organic cells
(various technologies)
STEG
Spectrolab
NREL
Japan Energy
NREL/ Spectrolab
Spire
Varian
UNSW
Stanford
ARCO
Westing-house
Georgia Tech
Sharp
NREL Cu(In,Ga)Se2 14x concentration
No. Carolina State University
Solarex
University So. Florida
Euro-CIS
AstroPower
United Solar
Boeing
Kodak
Masushita
Monosolar
AMETEK
Photon Energy
University of Maine
RCA
University of Lausanne
Princeton
University Linz
Siemens
Cambridge
UCSB
UC Berkeley
ECN, The Netherlands
GMZ/MIT/BC (STEG)
Efficiency (%)
Year
1975 1980 1985 1990 1995 2000 2005 2010
0 4 8 12 16 20 24 28 32 36 40 44


goal
current state
STEG efficiency (%)
Effective figure of merit (ZT)M
ε = 0.06
Copt = 1
Copt = 3
Copt = 10
0 2 4 6 8 10 12 14
0.5 1.0 1.5 2.0


Efficiency (%)
Year
Eye-Balled
Data from 1st Solar
APS Presentation
0 2 4 6 8 10 12
2000 2002 2004 2006 2008 2010

Cascaded/Segmented STEGs

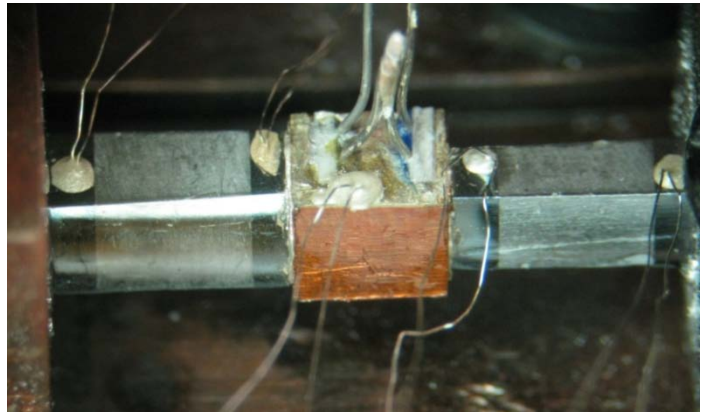




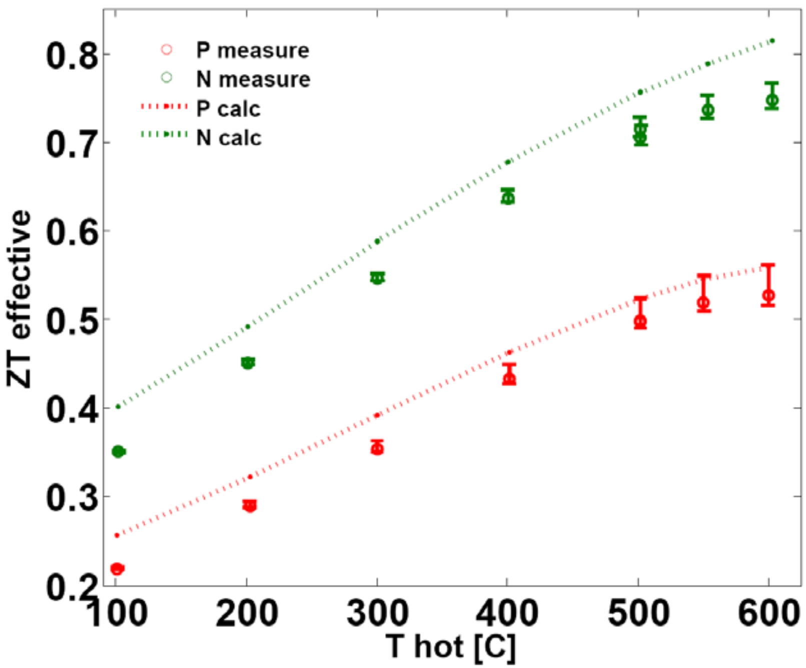
McEnaney, J. Appl. Phys., 110, 074502, 2011.

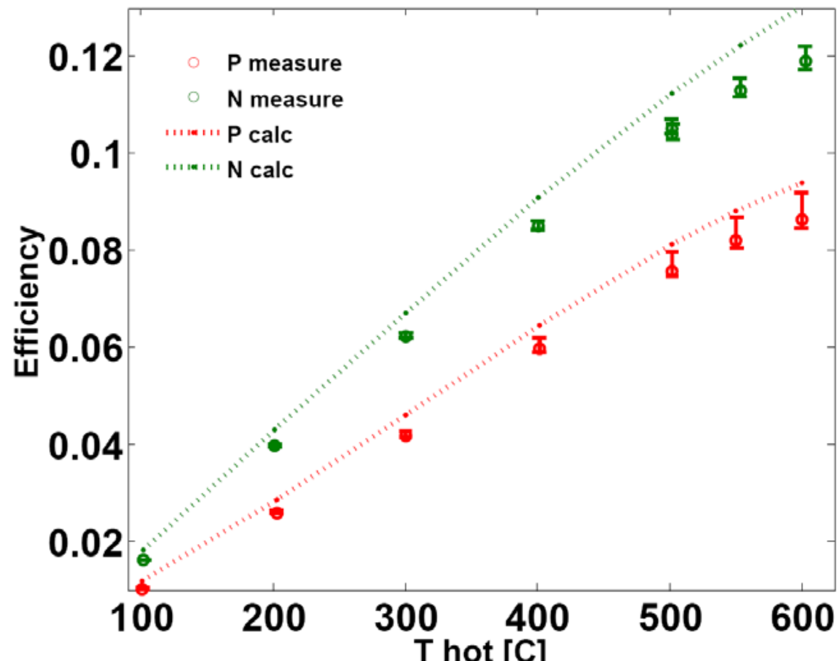
Skutterudites

N-type: ZT_{eff} =.75
P-type: ZT_{eff} =.5



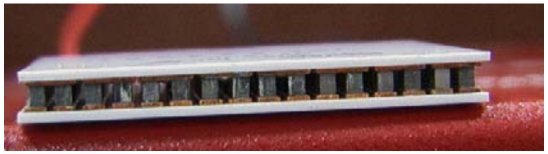
N-type: 12%
P-type: 8.5%
Pair: 9.1%

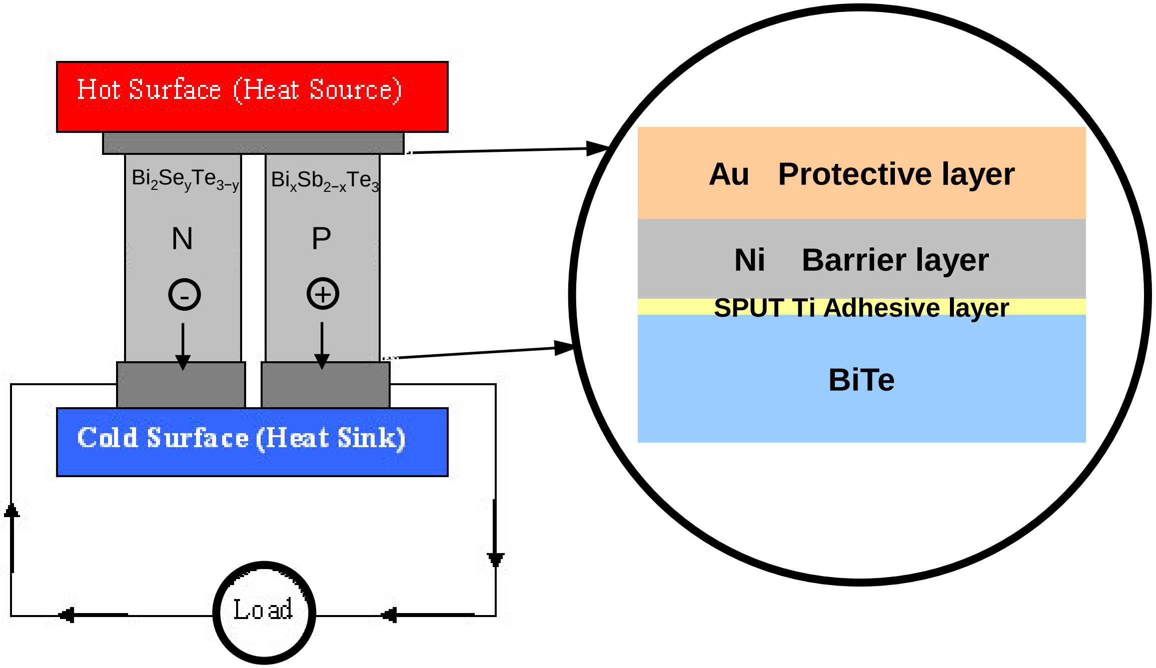




Muto et. al., Adv. Energy Materials, September, 2012.

Key Challenges in Devices





- Diffusion barriers
- Bonding strength
- Thermal stress
- Electrical contact resistance
- Thermal contact resistance

Summary

- Contra-properties in ZT: great challenges in understanding electron and phonon transport,
- Nanostructures provide new knobs to improve ZT, and significant progresses have been made in materials,
- Thermoelectric devices raise new challenges: thermal, mechanical, and electrical coupling,
- Ample room in system innovation, taking existing materials into real world.

Acknowledgments

All S3TEC Members

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MITEI
MIT-CCWC
DOE Sunshot

Olivier Delaire
Gene Fitzgerald Group
Keith Nelson Group
David Singh Group

SOLID-STATE SOLAR-THERMAL ENERGY CONVERSION CENTER

U.S. DEPARTMENT OF ENERGY

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