The Abdus Salam
International Centre
for Theoretical Physics

**2371-9**

**Advanced Workshop on Energy Transport in Low-Dimensional Systems: Achievements and Mysteries**

***15 - 24 October 2012***

# Nanostructured Materials for Thermoelectric Energy Conversion

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# Nanostructured materials for thermoelectric energy conversion

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Acknowledgement: **DOE/EFRC (CEEM Center), DARPA, ONR, AFOSR, NSF, SRC-IFC, CEA, Intel, Wyle Lab**

Advanced Workshop on Energy Transport in Low Dimensional Systems
16 October 2012

# $CO_2$ Emission Goals (2000-2100)

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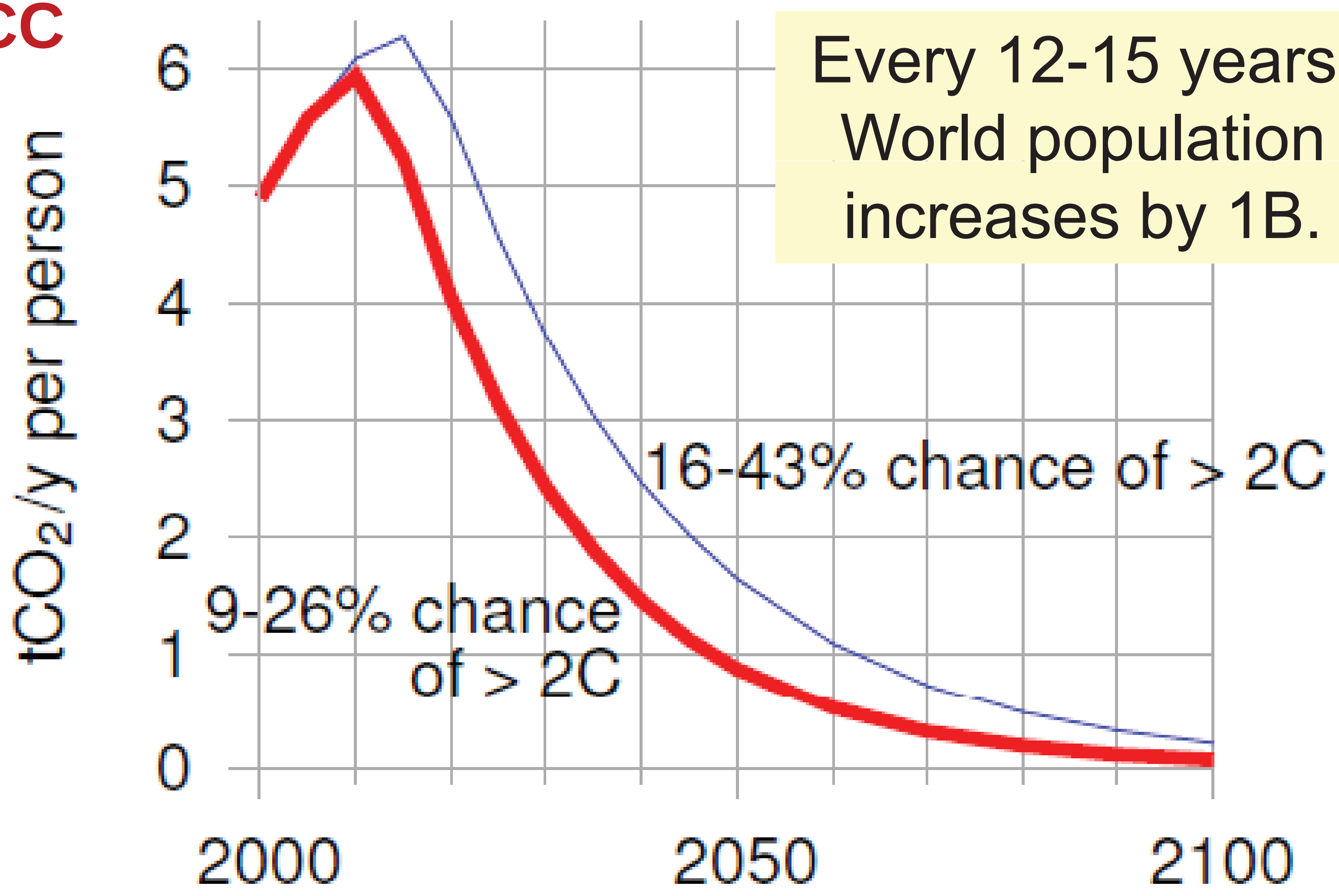
**IPCC**




Every 12-15 years, World population increases by 1B.

David McKay, Sustainable Energy -Without the Hot Air



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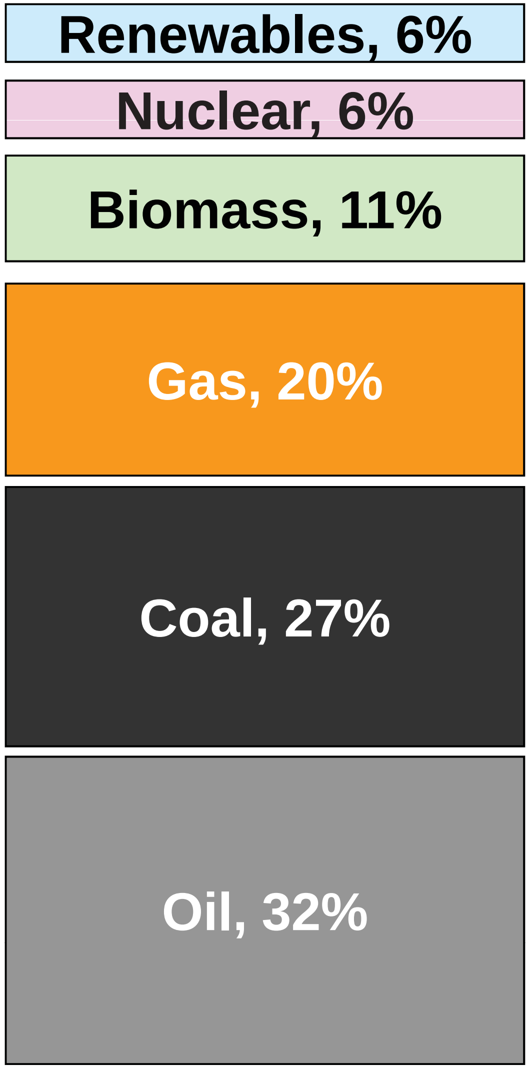
# World Energy Use in 2005 (15TW)

## Energy Sources

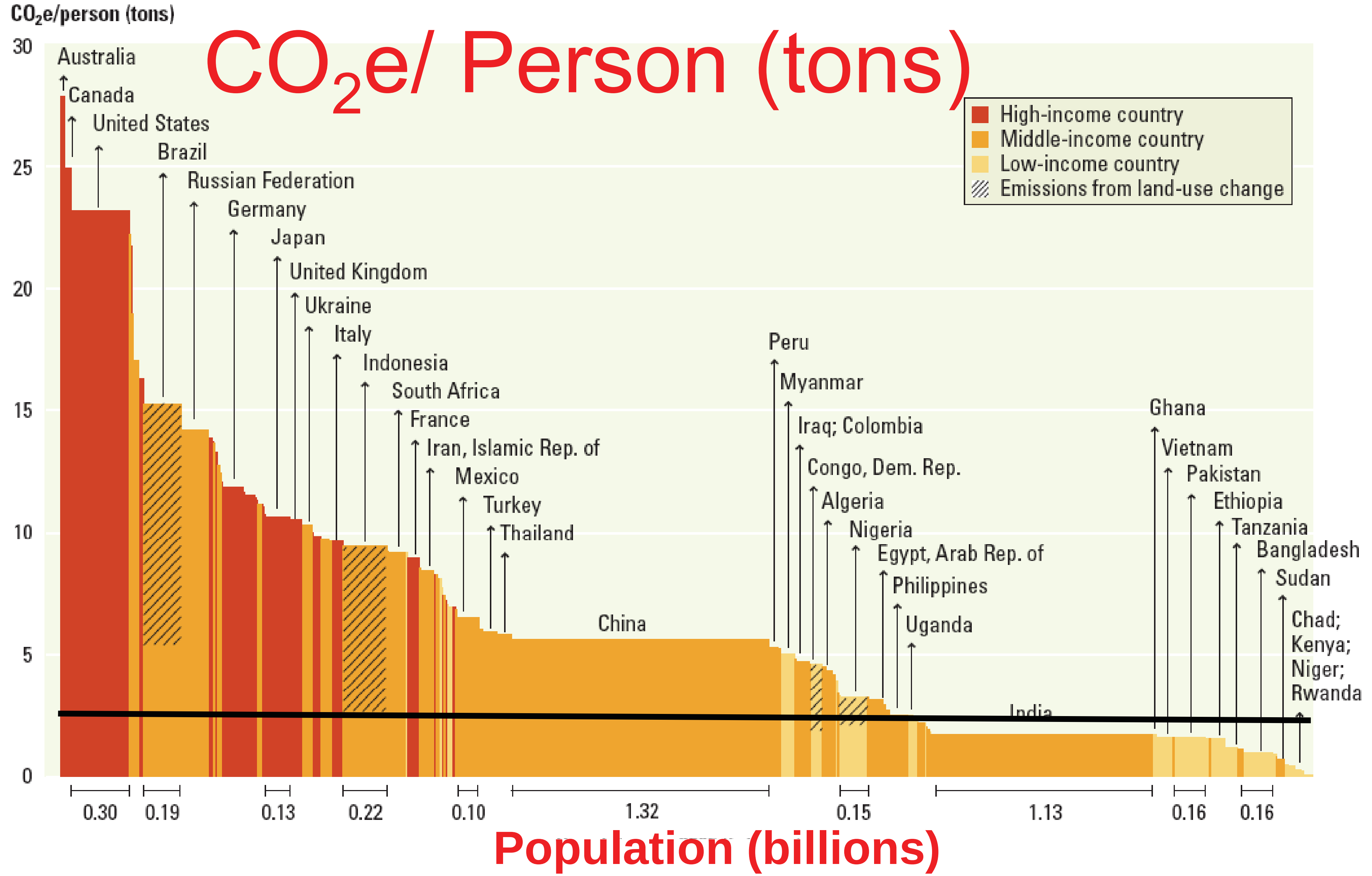



- More than 90% of primary energy is first converted to heat.
- Overall end-use exergy (12% of sources):
  - Motion 0.95 TW
  - Heat 0.73 TW
  - Cooling/Light/Sound 0.06 TW

A. S. 15 August 2012

Adapted from Cullen and Allwood, *Energy*, 2010

**Figure 1.1 Individuals' emissions in high-income countries overwhelm those in developing countries**




*Sources*: Emissions of greenhouse gases in 2005 from WRI 2008, augmented with land-use change emissions from Houghton 2009; population from World Bank 2009c.

*Note*: The width of each column depicts population and the height depicts per capita emissions, so the area represents total emissions. Per capita emissions of Qatar (55.5 tons of carbon dioxide equivalent per capita), UAE (38.8), and Bahrain (25.4)—greater than the height of the y-axis—are not shown. Among the larger countries, Brazil, Indonesia, the Democratic Republic of Congo, and Nigeria have low energy-related emissions but significant emissions from land-use change; therefore, the share from land-use change is indicated by the hatching.

# Individual Emissions (2030)

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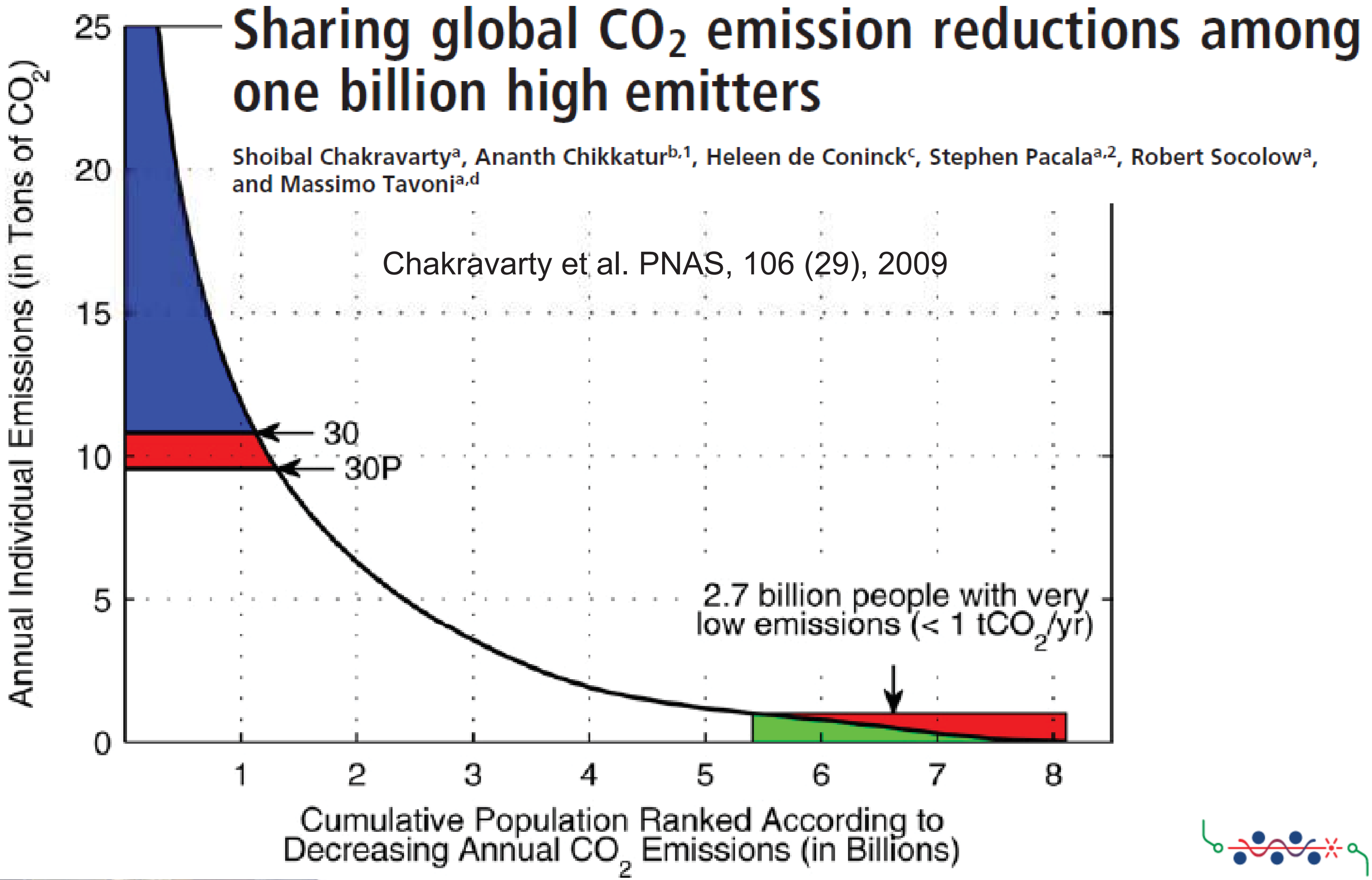




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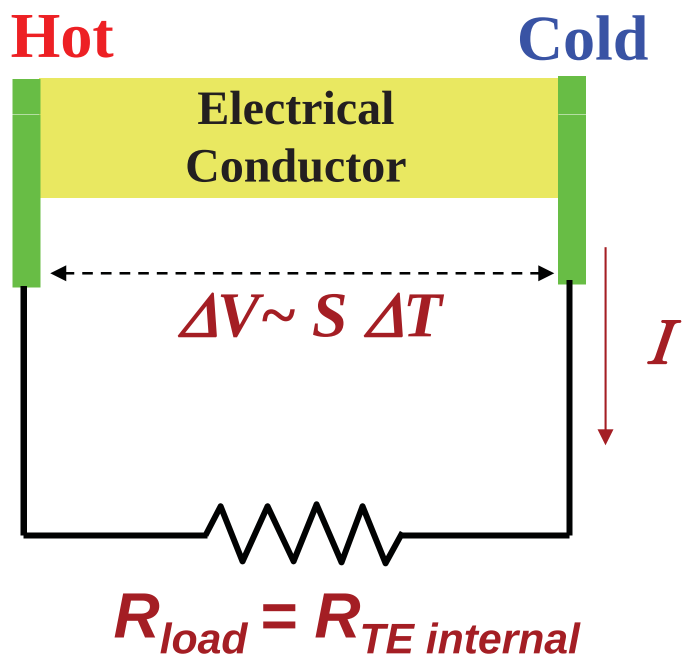
# Direct Conversion of Heat into Electricity



Seebeck coefficient (1821)

$$S = \frac{\Delta V}{\Delta T}$$




Efficiency function of thermoelectric figure-of-merit (Z)

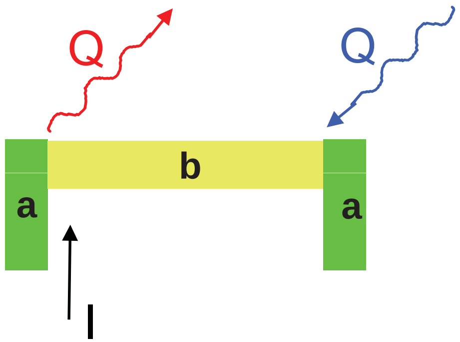
$$Z = \frac{S^2 \sigma}{k}$$

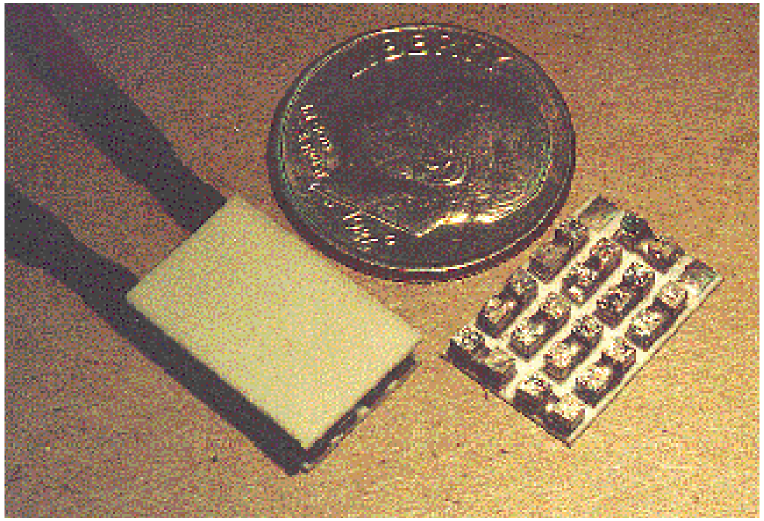
$$Z = \frac{(Seebeck)^2 (electrical \quad conductivity)}{(thermal \quad conductivity)}$$

# Peltier Effect (1834)



Peltier: $$\pi_{ab} = \pi_a - \pi_b = \frac{Q}{I}$$



**Commercial TE Module**

- ΔT=72C (no heat load)
- Individually Fabricated, Big
- Cooling density <10W/cm$^2$
- Efficiency 6-8% of Carnot

When the current flows from material (a) into material (b) and then back to material (a), it heats the first junction and cools the second one (or vice versa). Thus, heat is <u>transferred</u> from one junction to the other one.

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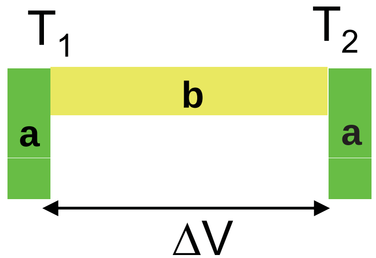
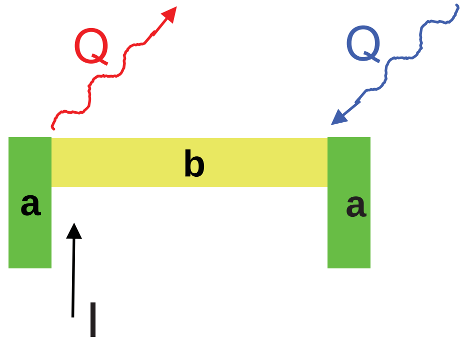
## Seebeck:

$$S = \frac{\Delta V}{\Delta T}$$




## Peltier:

$$\pi_{ab} = \pi_a - \pi_b = \frac{Q}{I}$$

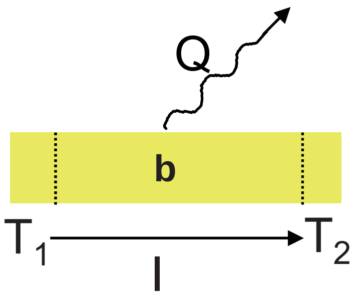



Thermodynamics (Lord Kelvin):

$$\begin{cases} \pi = S \cdot T \\ \dfrac{dS}{dT} = \dfrac{\gamma}{T} \end{cases}$$

## Thomson:

$$\gamma = \frac{\Delta Q}{I \cdot \Delta T}$$



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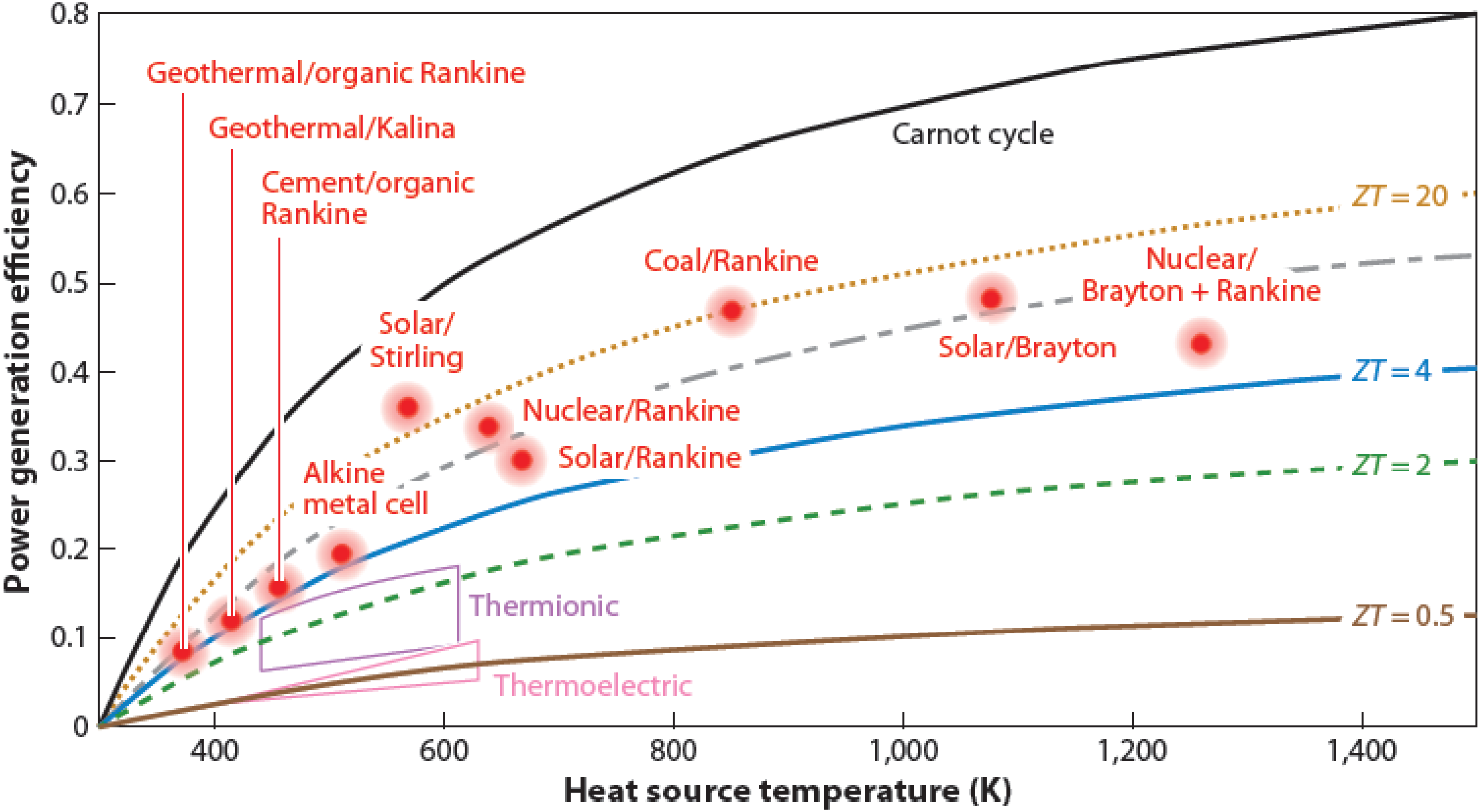
# Power Generation Efficiencies






**K. Yazawa and A. Shakouri, J. Appl. Phys. 111, 024509 (2012)**

Adapted from Cronin Vining, Nature Materials 2009

# TE vs. conventional refrigerator

If we could create 1st order phase transition (latent heat) in "transported" electron gas, the efficiency of thermoelectric energy conversion could be significantly increased.

**C. Vining, "Thermo-electric Process", MRS Spring 1997 (Vol. 478, p.3)**

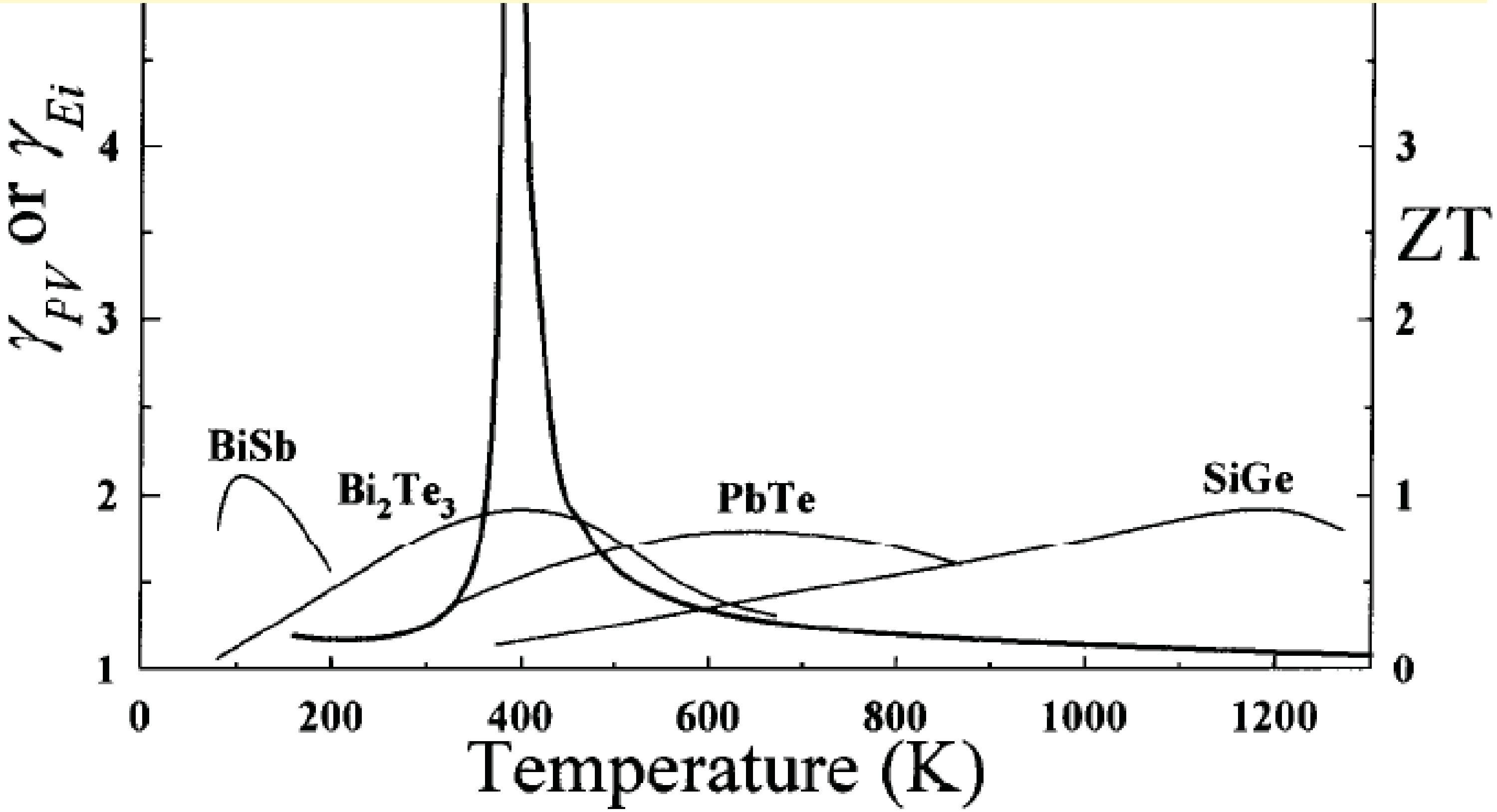
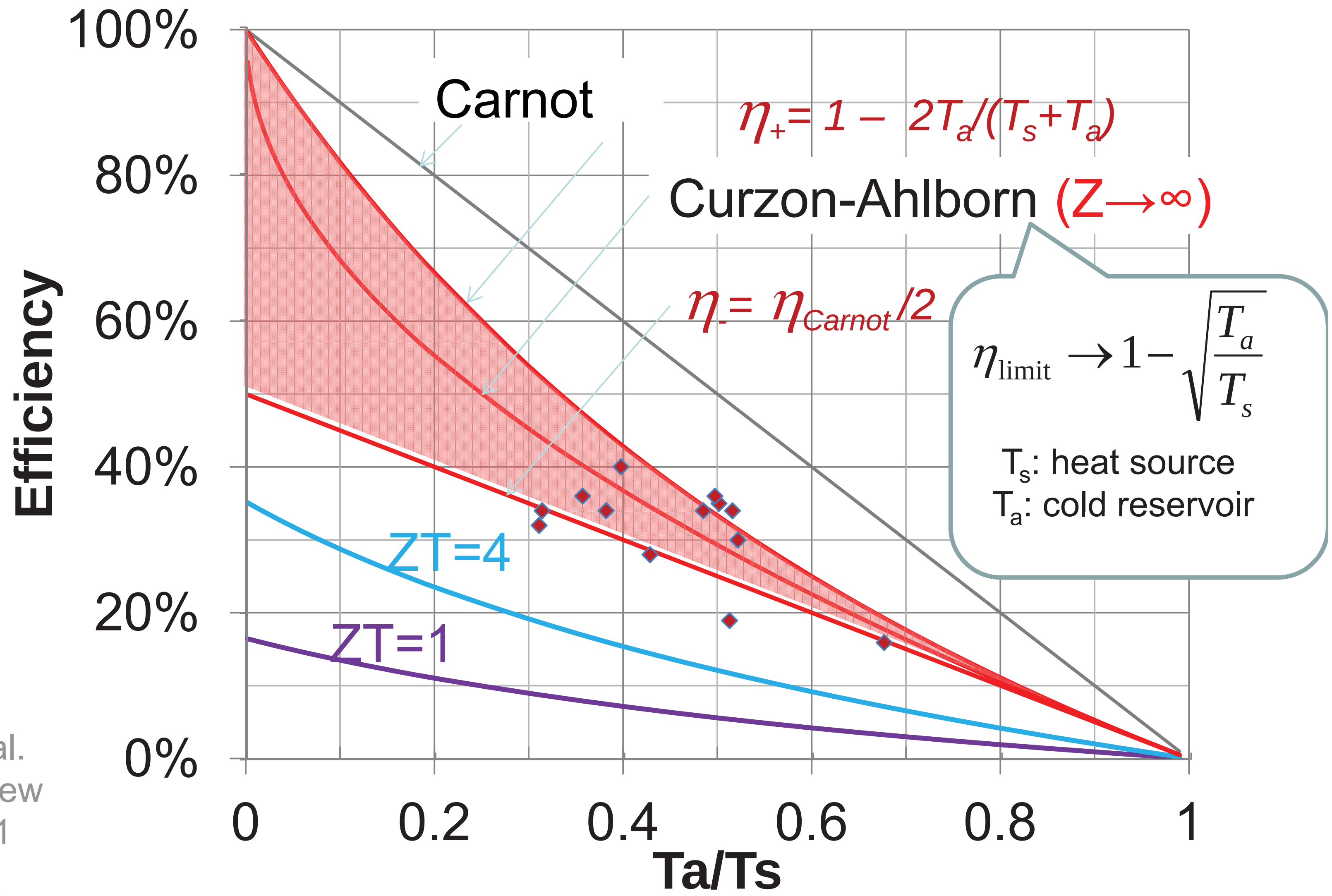



Fig. 4: Specific heat ratios, $\gamma_{PV}$ for a *PV* system (Freon 12) and thermal conductivity ratios, $\gamma_{Ei}$=1+ZT, for selected n-type semiconductor alloys as a function of temperature.

# Efficiency at maximum output power



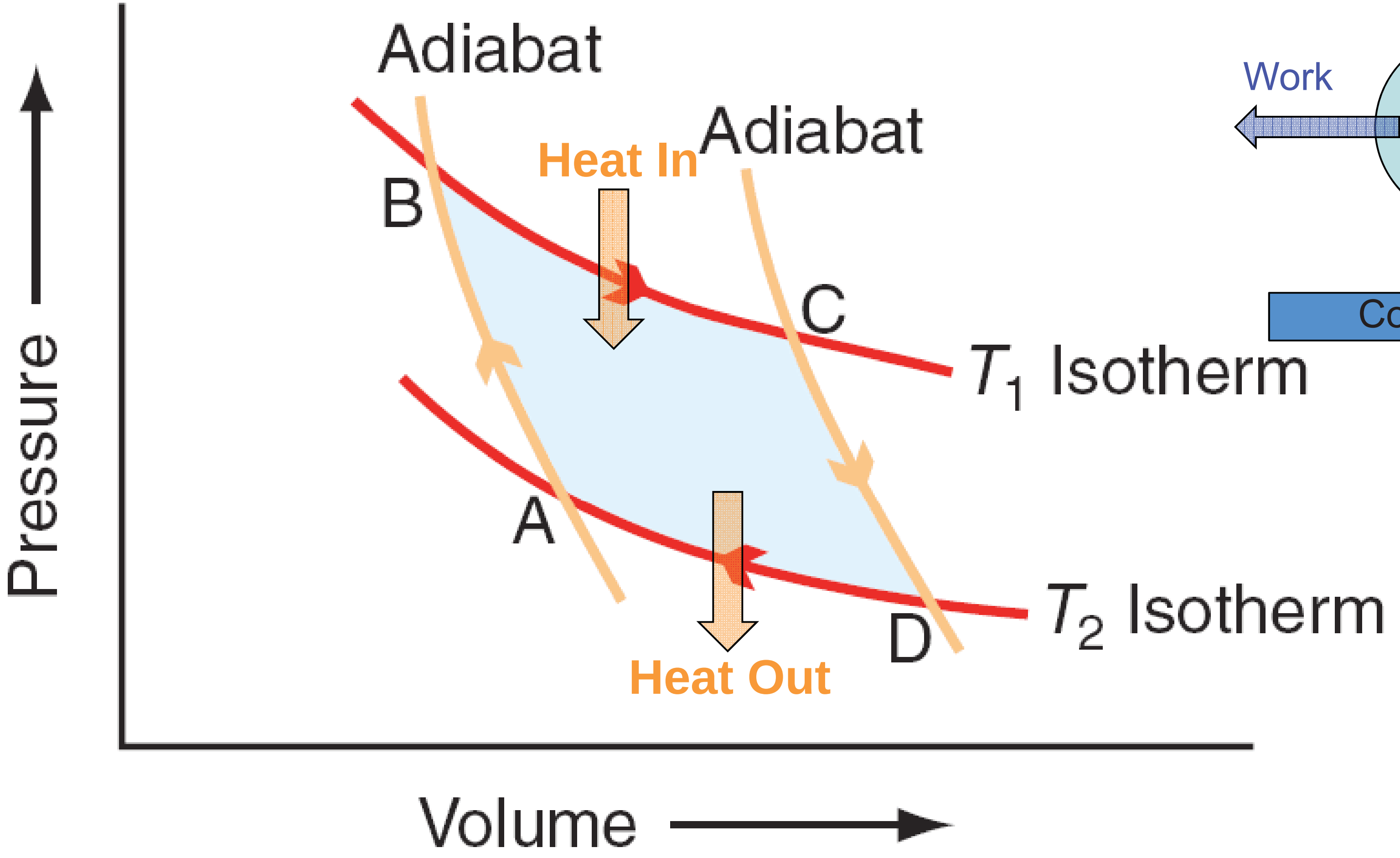


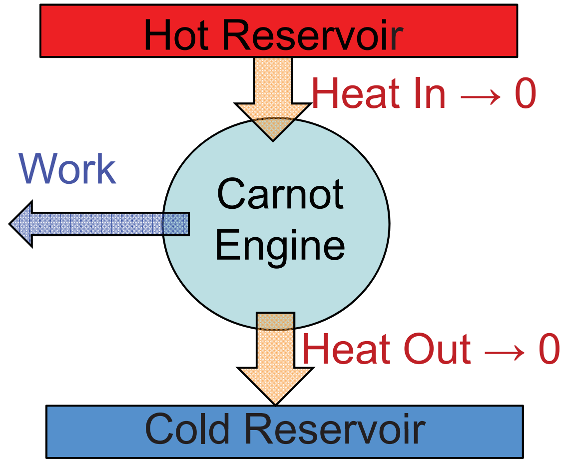

Esposito et al. Physical Review Letters 2011

**K. Yazawa and A. Shakouri, J. Appl. Phys. 111, 024509 (2012)**

# Carnot Cycle (reversible)

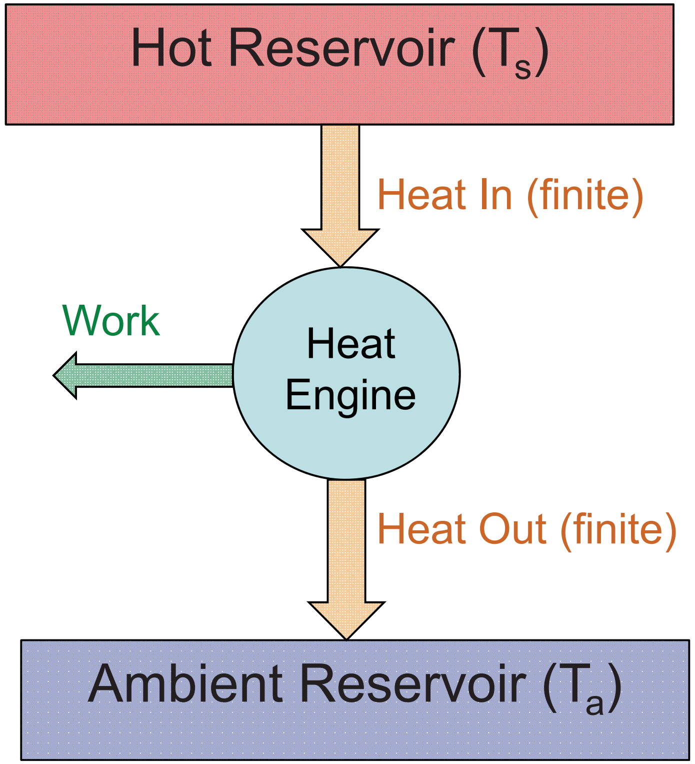




# Curzon-Ahlborn Limit






F.L. Curzon and B. Ahlborn, *Am. J. Phys*. **43**, 22 (1975)

Finite thermal resistances with hot and cold reservoirs

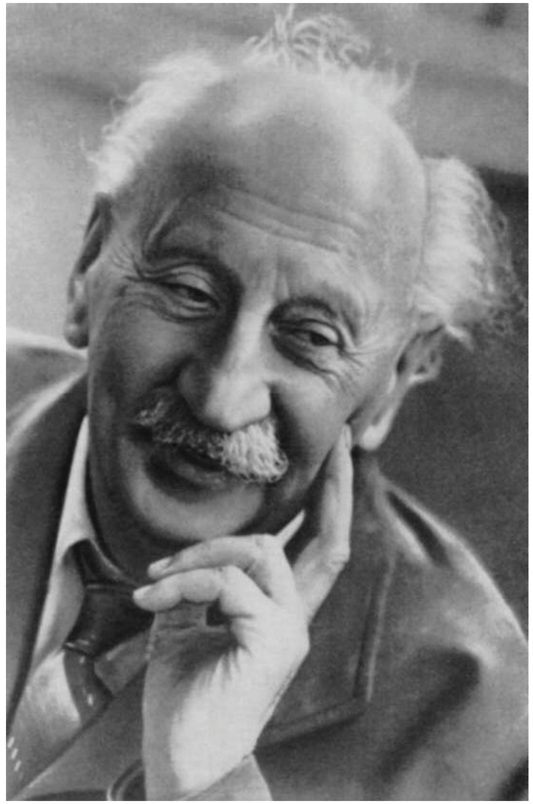
$\Rightarrow$ Finite output power

$\Rightarrow$ Curzon-Ahlborn efficiency at maximum output power:

$$\eta_{\text{limit}} \rightarrow 1 - \sqrt{\frac{T_a}{T_s}}$$

# Early Thermoelectricity

- First practical devices USSR during WWII
  - Tens of thousands built, to power radios from any available heat source.
- In the 1950s-60s many in the US & USSR felt semiconductor thermoelectrics could replace mechanical engines, much as semiconductor electronics were replacing vacuum tube technology.
  - Hint: it didn't happen!



Abram F. Ioffe 1880-1960

Ioffe, A. F. (1957). Semiconductor Thermoelements and Thermoelectric Cooling. London, Infosearch Limited.

Cronin Vining, ZT Services

# Radioisotope Thermoelectric Generators (Voyager, Galileo, Cassini, …)

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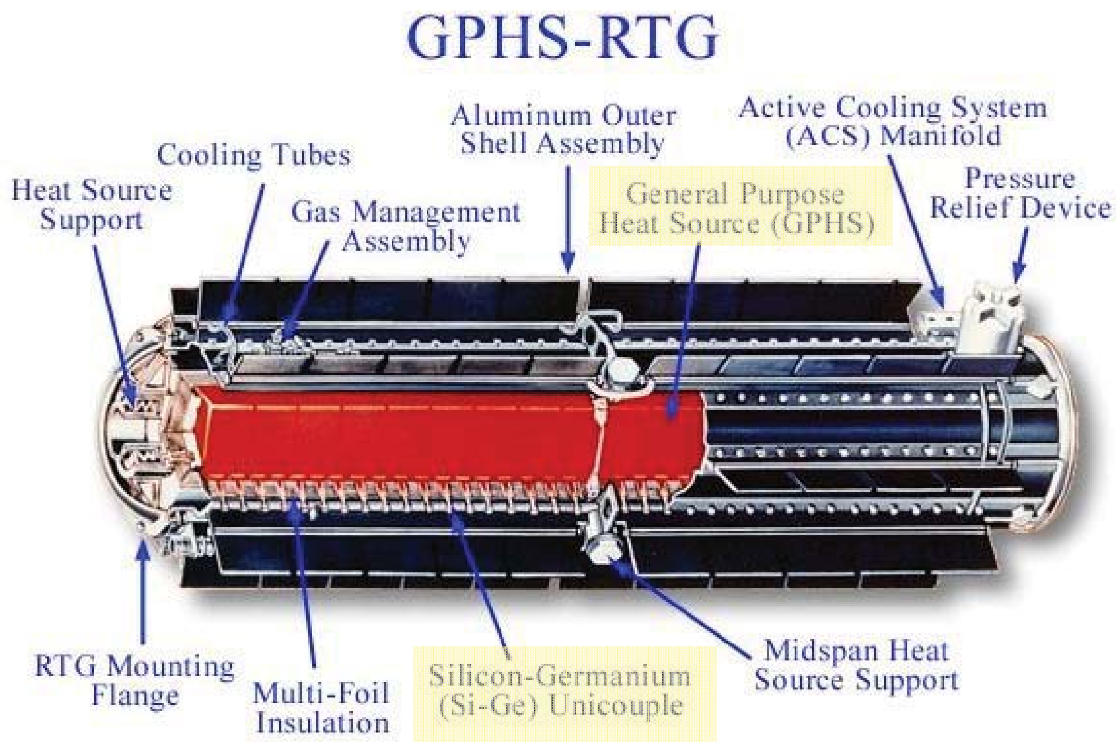
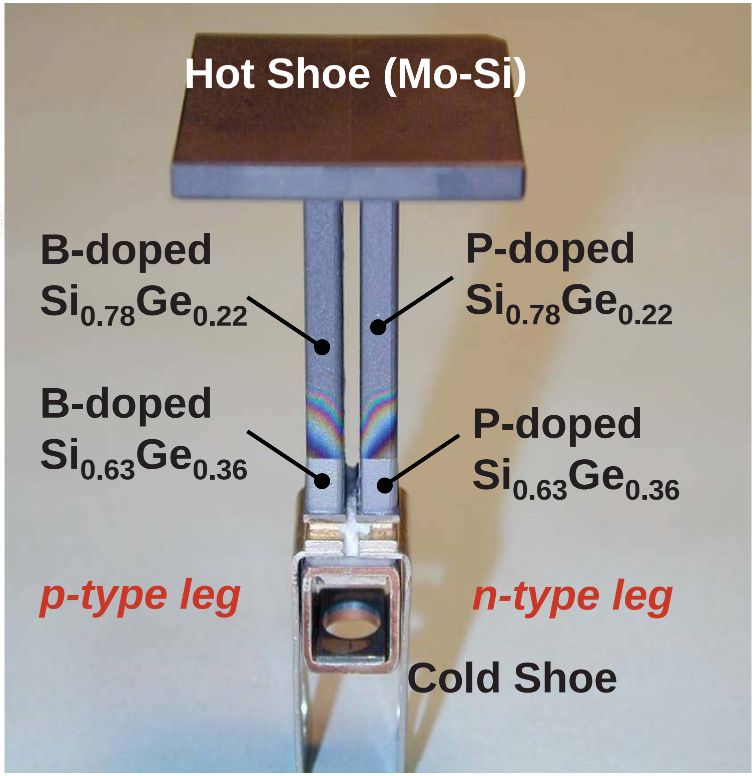
- 55 kg, 300 $W_e$, ‘only’ 7 % conversion efficiency
- But > 1,000,000,000,000 device hours without a single failure




SiGe unicouple

**Cronin Vining, ZT Services**



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# TEs for Telecom Cooling

- Melcor, Marlow and many other TE manufacturers provide coolers specifically designed for Telecom laser-cooling applications

**Typical Distributed Feedback Laser:**

**$\Delta\lambda/\Delta T$= 0.1 nm/°C**

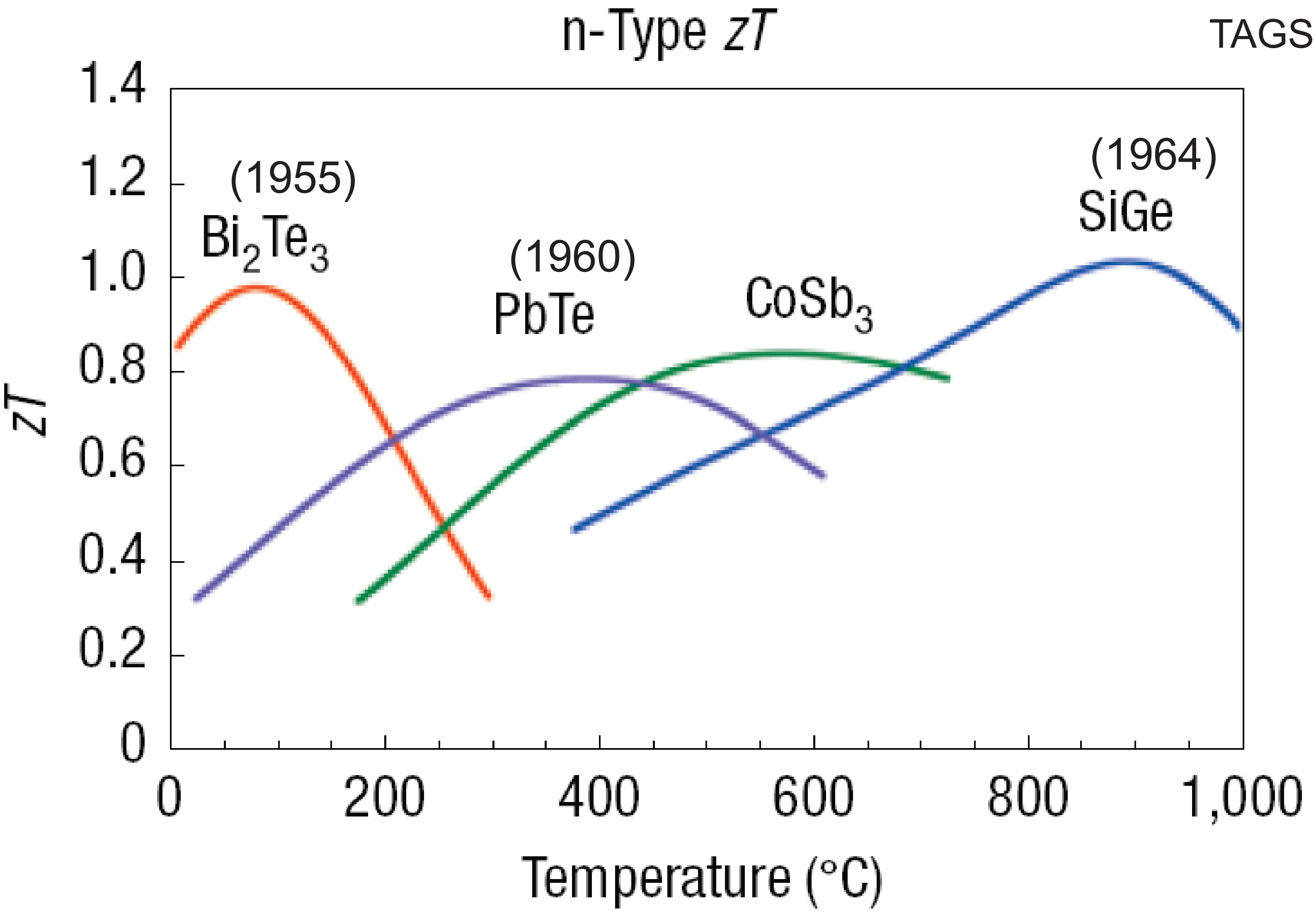
**Heat generation kW/cm²**

**Cronin Vining, ZT Services**

# Classical thermoelectric materials



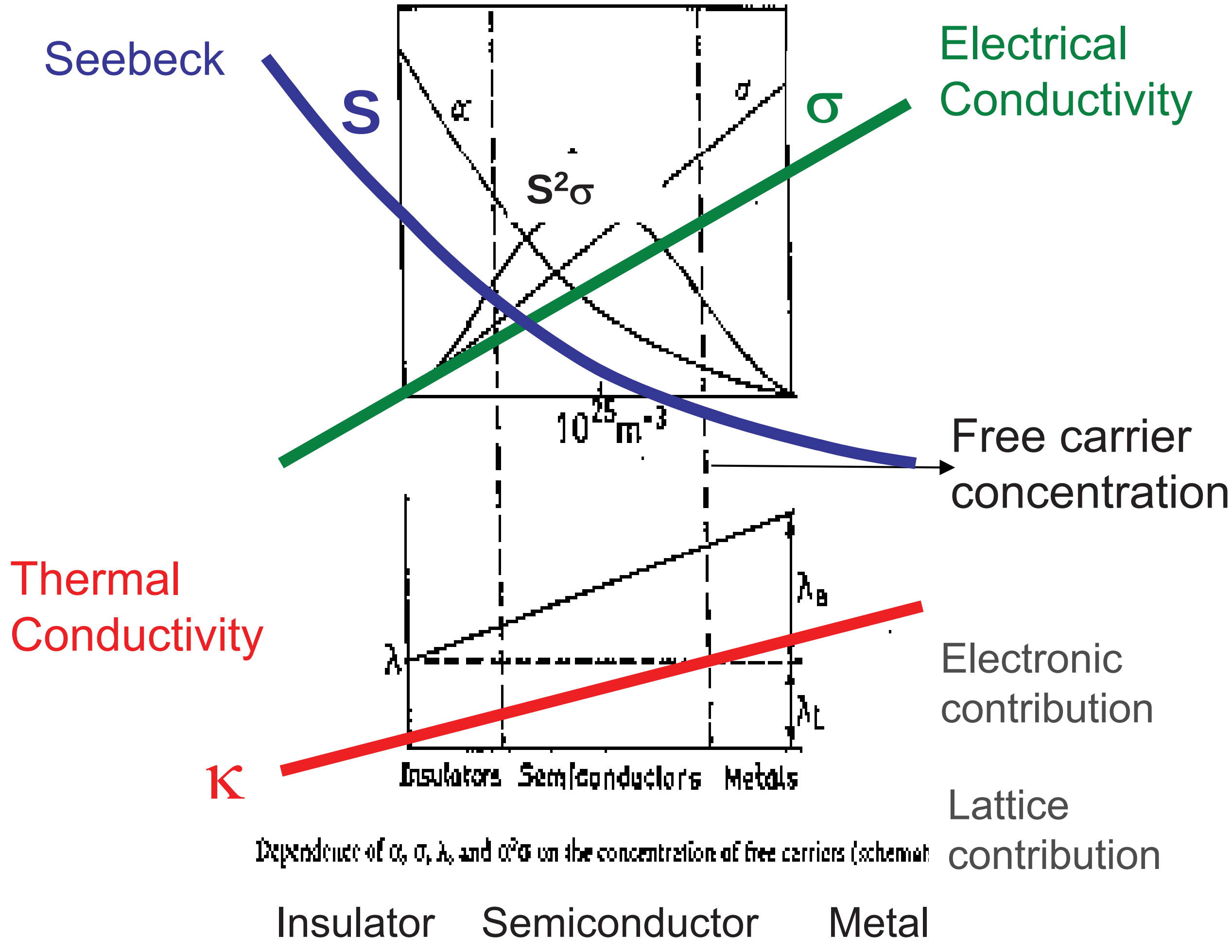
TAGS 1961




Current thermoelectric technology based on the above materials.

# Thermoelectric Figure-of-Merit (Z)

$$Z = (S^2\sigma)/(\kappa_e+\kappa_L)$$




For almost all materials: $S \leftrightarrow 1/\sigma$. Similarly $\sigma \leftrightarrow \kappa_e$ (Lorenz #) and $\sigma \leftrightarrow \kappa_L$ (electron vs. phonon transport)

# Microscopic Origin of Thermoelectric Cooling

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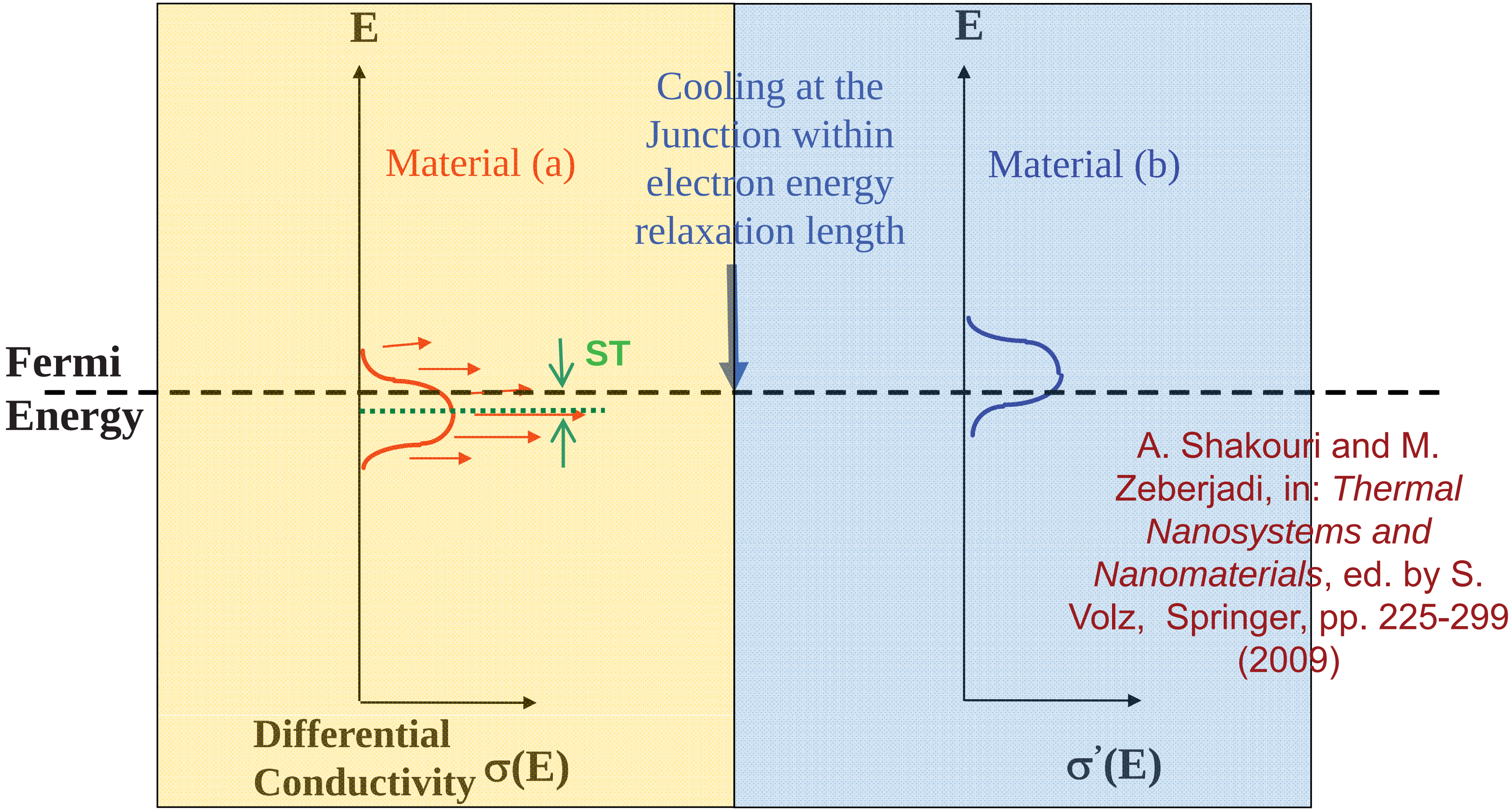


Peltier cooling/heating is due to the change in <u>average transport energy</u> of carriers (Peltier Coef.) as they move from one material into another one.



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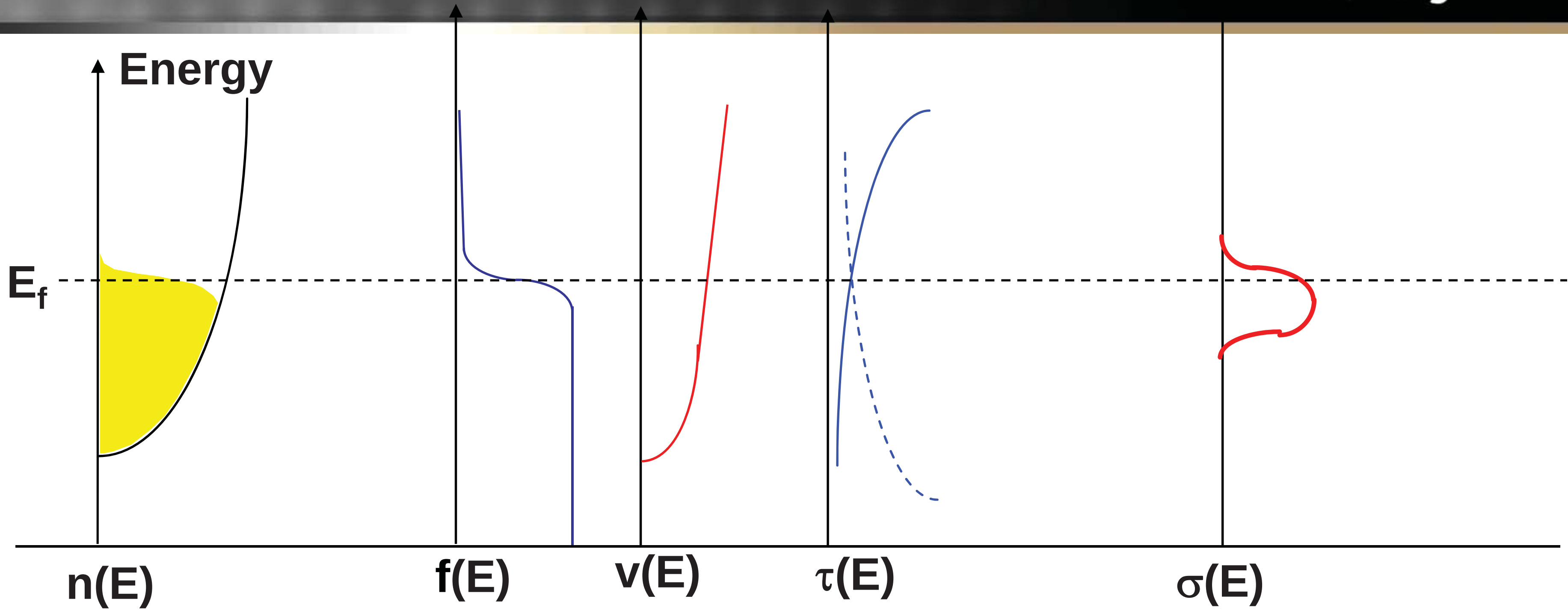
# Intuitive Picture




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

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

$$\sigma(E) \cong e^2 \tau(E) \bar{v}_x^2(E) \bar{n}(E) \left(-\frac{\partial f_{eq}}{\partial E}\right)$$

Differential Conductivity

$\tau$ = relaxation time
$\bar{v}_x$ = average velocity
$\bar{n}$ = density-of-states
$f_{eq}$ = Fermi-Dirac distribution

# Low Dimensional Thermoelectrics

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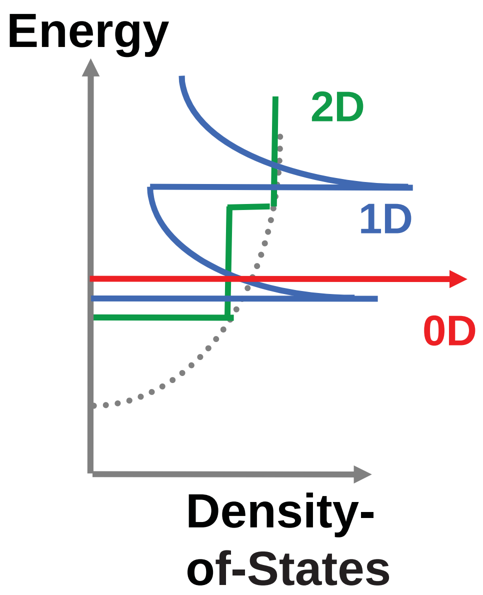


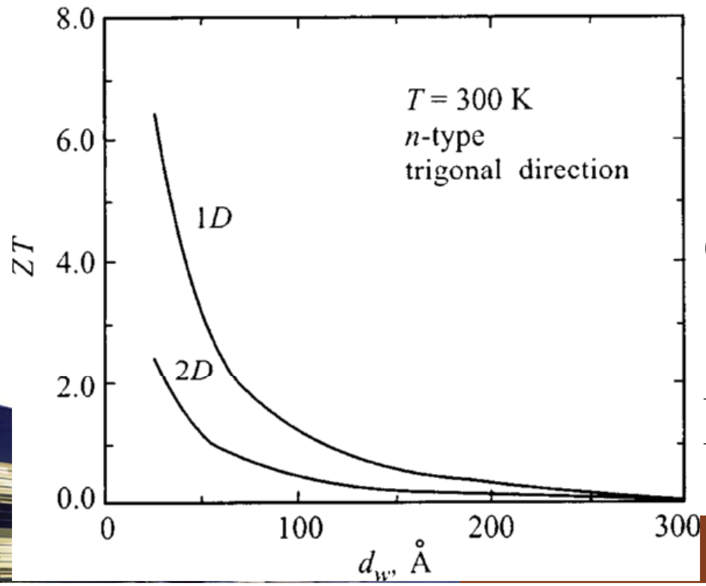


- Sharp features in Density-of-States can enhance the asymmetry in differential conductivity ⇒ ZT>4-5
  - Dresselhaus et al. 1993
- Difficulty
  - Non-active barrier layers: Broido and Reinecke PRB '01, Mahan, etc.
  - "Number of conduction channels": Minimum fill factor needed - Kim et Lundstrom J. Appl. Phys. 105, 034506 (2009)
  - Requires size uniformity
  - Original theory does not apply to 0D

Calculated ZT of **Bi** quantum well and quantum wire

Dresselhaus, MS; Dresselhaus, G; Sun, X; Zhang, Z; Cronin, SB; Koga, T; Ying, JY; Chen, G; Microscale Thermophysical Engineering, 1999, V3:89-100.



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# Historical Perspective

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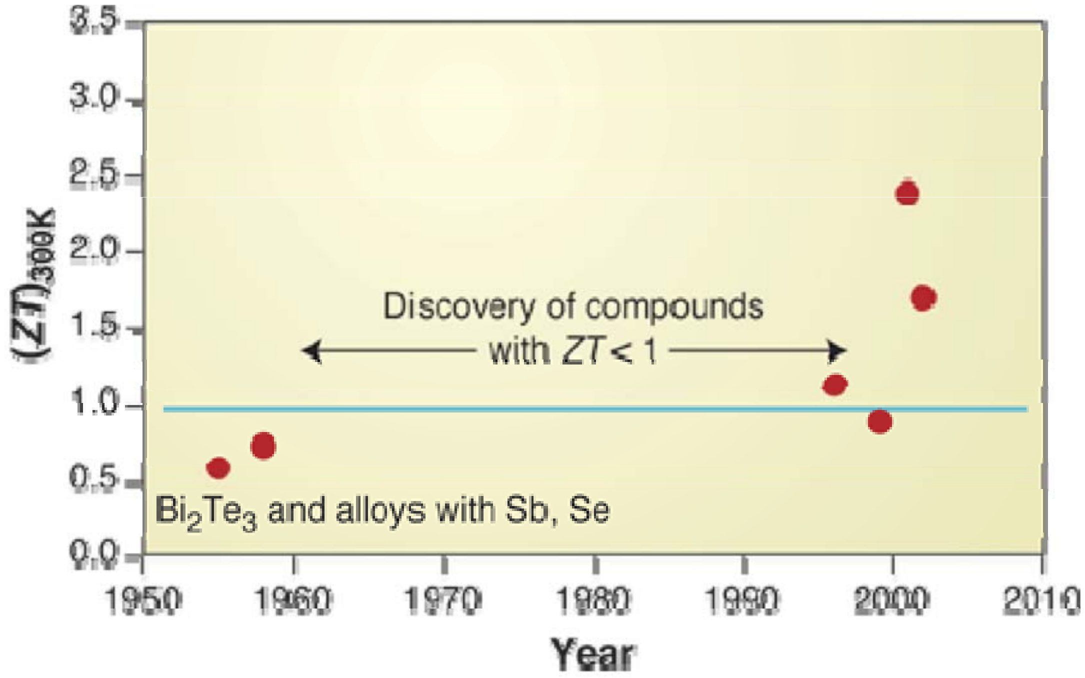


- Recent studies in nanostructured thermoelectric materials led to a sudden increase in $(ZT)_{300K} > 1$
- Higher ZT reported experimentally at higher T.

A. Majumdar, *Science* **303**, 777 (2004)



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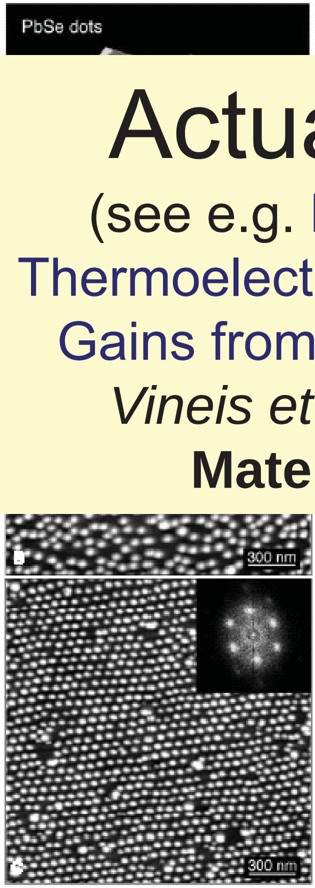
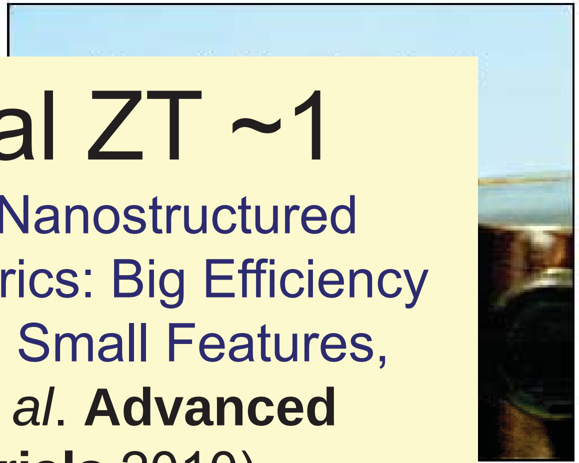
# Superlattices/ Quantum Dot Thermoelectrics

*T. C. Harman (2002) and R. Venkatasubramanian (2001)*



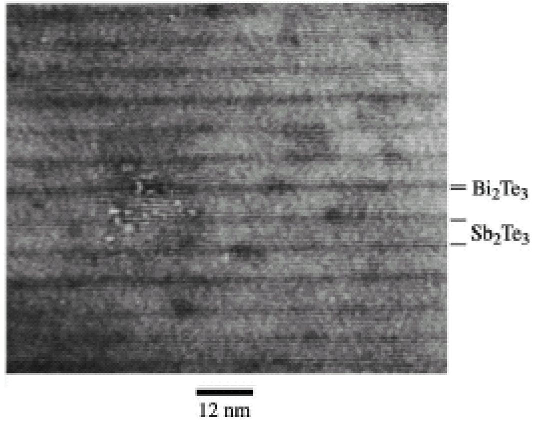
## Actual ZT ~1

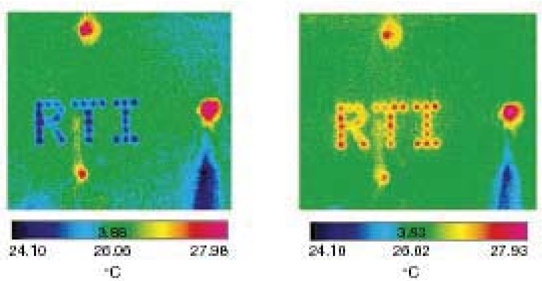
(see e.g. Nanostructured Thermoelectrics: Big Efficiency Gains from Small Features, *Vineis et al*. **Advanced Materials** 2010)

**PbTe/PbTeSe Quantum Dot Superlattices**

**Quaternary: ZT=2**
**ΔT=43.7 K**

**T.C. Harman, Science, 2002**




**ΔT=32.2 K, ZT ~2-2.4**
**R. Venkatasubramanian, Nature, 2001**

| PbTe/PbSeTe | Nanostructure | Bulk |
|---|---|---|
| Power Factor ($\mu W/cmK^2$) | 25.5 | 28 |
| Thermal Conductivity (W/mK) | 0.5 | 2.0 |

In-plane geometry

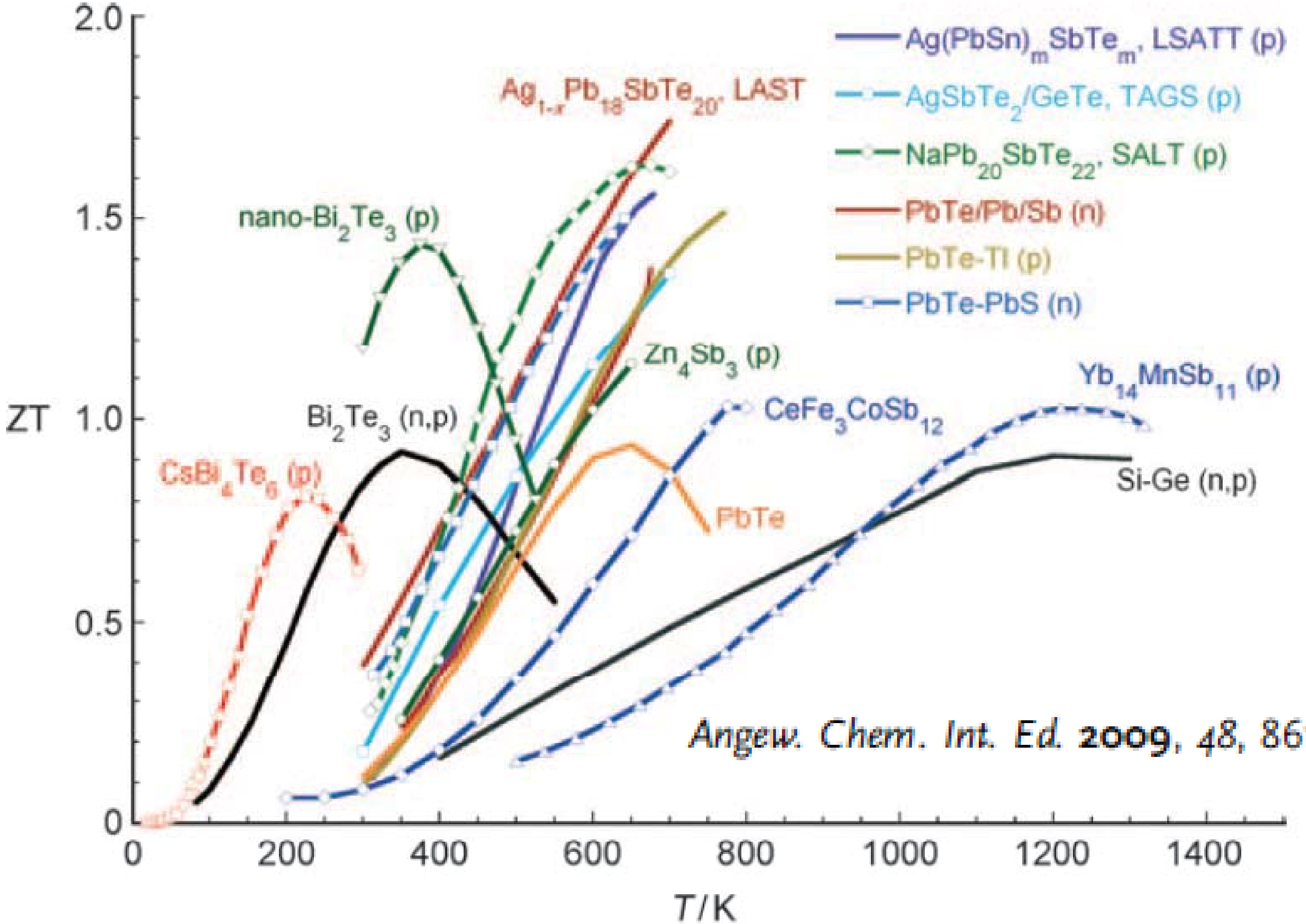
| $Bi_2Te_3/Sb_2Te_3$ | Superlattice | Bulk |
|---|---|---|
| | 40 | 50.9 |
| | 0.5 | 1.26 |

Cross-plane geometry

*(From M. S. Dresselhaus, Rohsenow Symposium, 2003)*

# New and Old Concepts in Thermoelectric Materials

*Joseph R. Sootsman, Duck Young Chung, and Mercouri G. Kanatzidis**

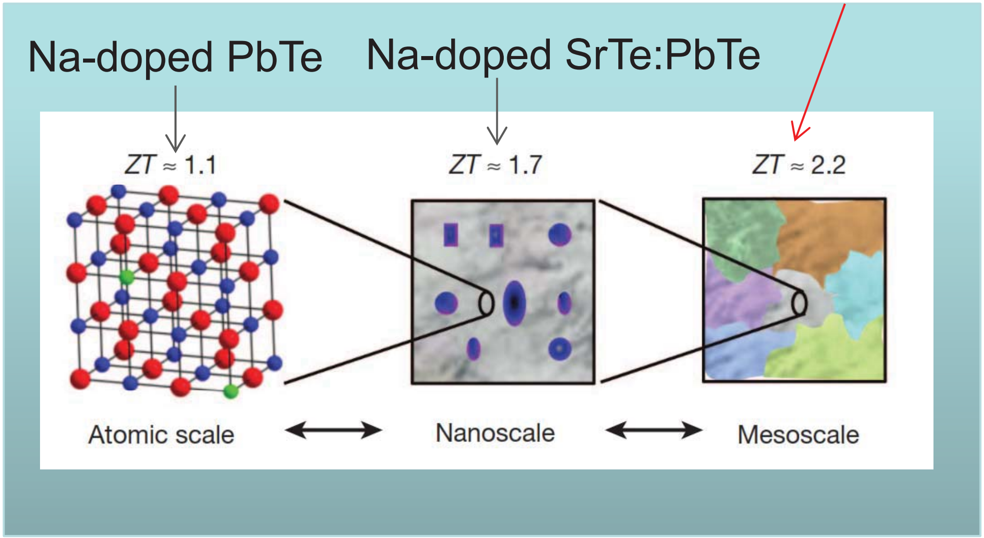


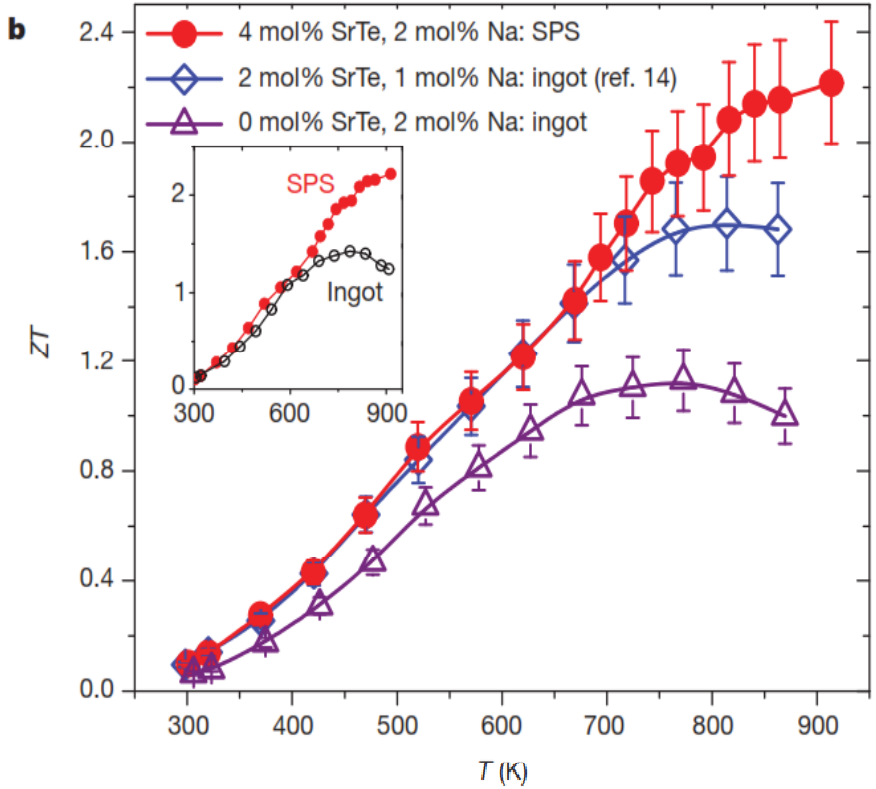

*Angew. Chem. Int. Ed.* **2009**, *48*, 8616–8639

# Latest results ZT~2.2 at 900K

[Biswas et al.(Kanatzidis group), *Nature* 489, 414 (2012)]
Spark-plasma-sintered Na(2%)-doped PbTe:SrTe(4%)

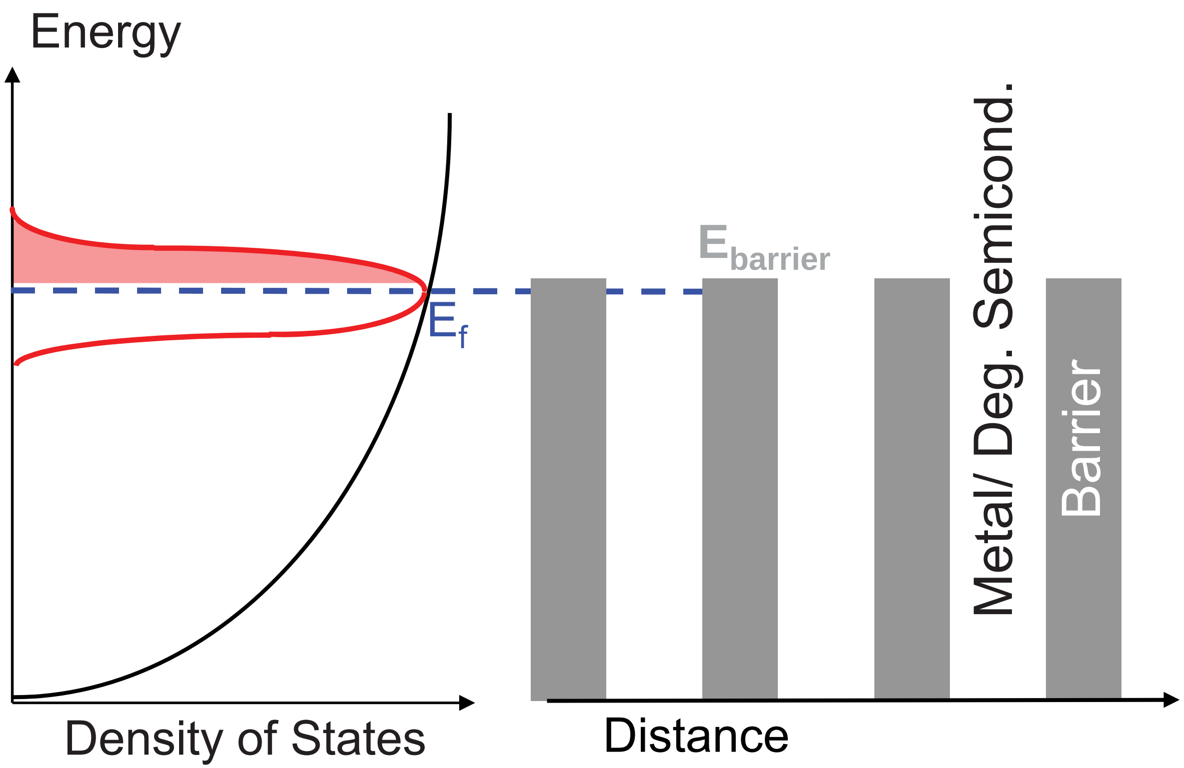
Na-doped SPS SrTe:PbTe




# Seebeck –Conductivity Trade off






**Deg. Semiconductor/Metal + Energy Filter (Thermionic emission)**

Symmetry of DOS near Fermi energy is the main factor determining Seebeck coefficient.

A. Shakouri, "TE, thermionic and thermophotovolt. energy conversion", ICT 2005

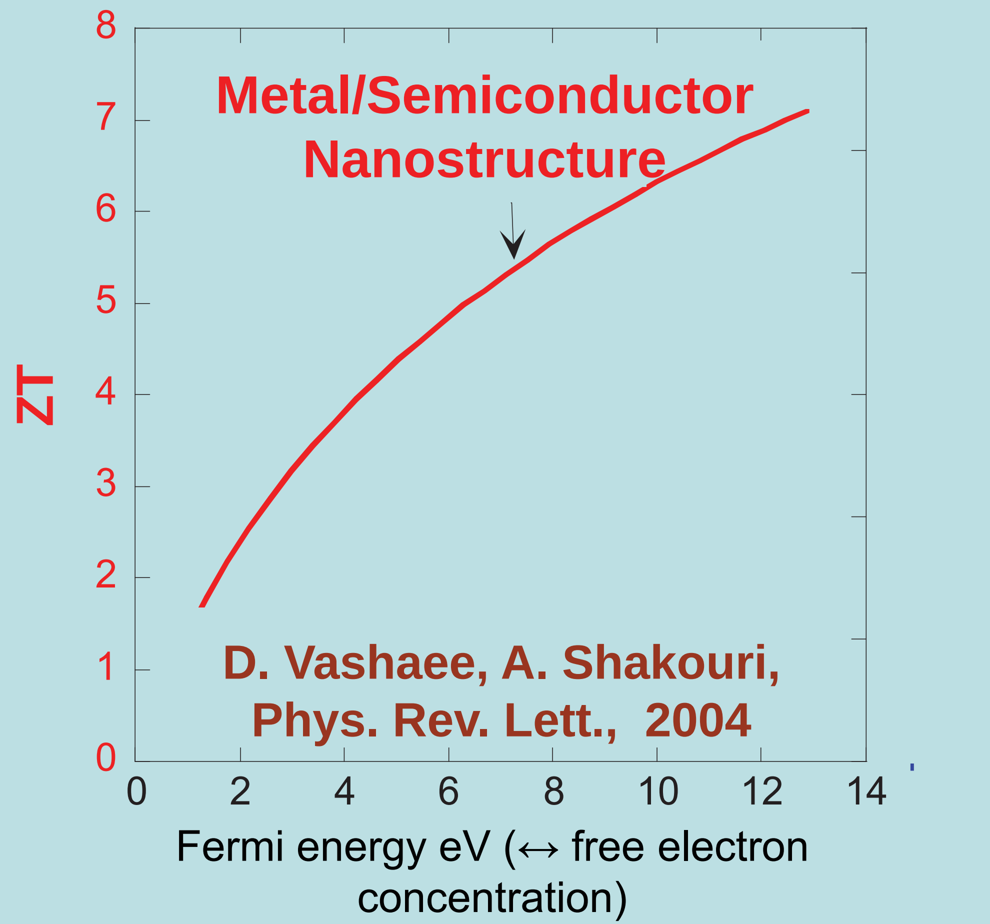
# Thermionic Energy Conversion Center

Ali Shakouri, Director

- **Engineering current and heat flow in metal/semiconductor nanostructures**

- **Goal: efficiency > 20-30% (ZT>2.5)**

Assume: $\kappa_{lattice}$=1W/mK, mobility ~10 cm$^2$/Vs

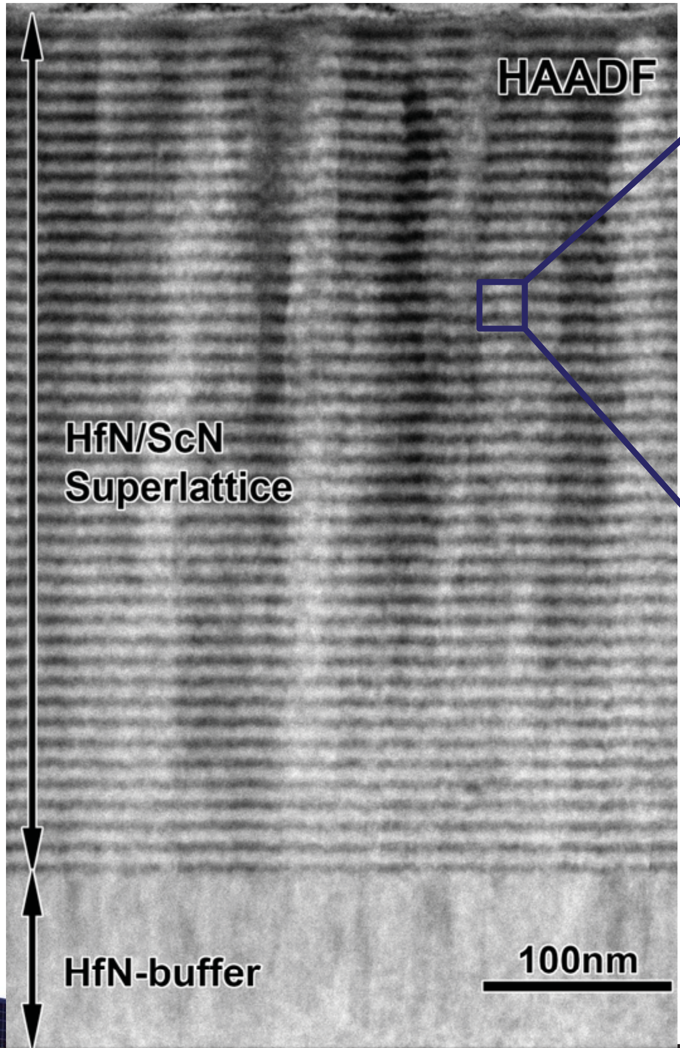


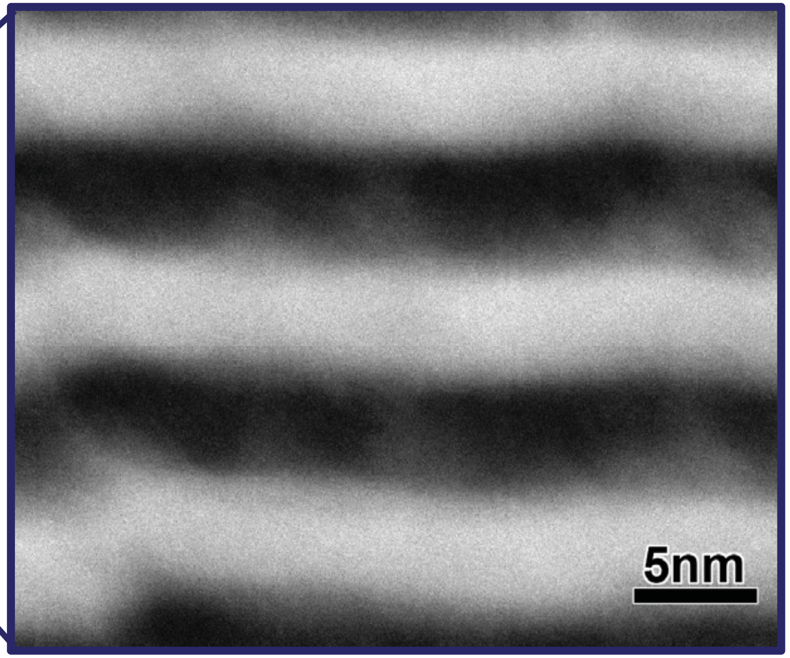

**UCSC** (Bian, Kobayashi), **Berkeley** (Majumdar), **BSST Inc.** (Bell), **Delaware** (Zide), **Harvard** (Narayanamurti), **MIT** (Ram), **Purdue** (Sands), **UCSB** (Bowers, Gossard)

**ONR (2003-2010), DARPA (2008-2012)**

# Metal/ Semiconductor Multilayers for TEs

Rough coherent interfaces



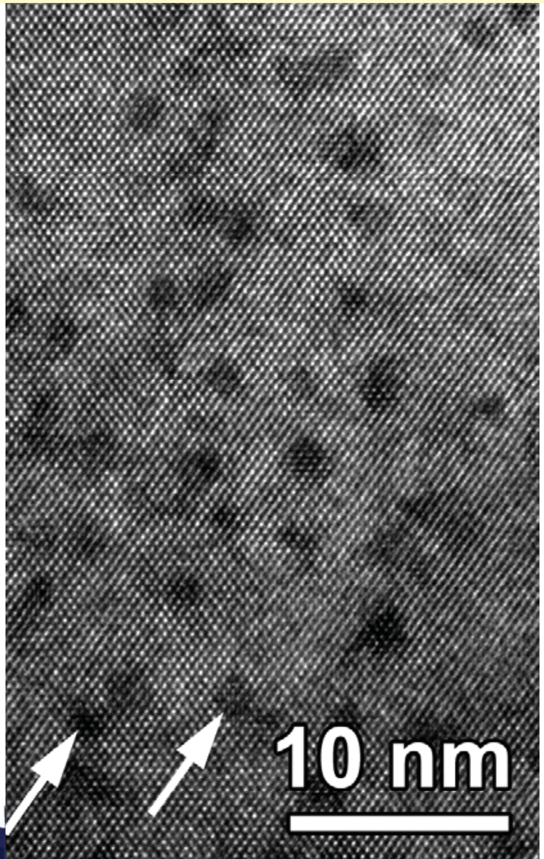

HfN/ScN

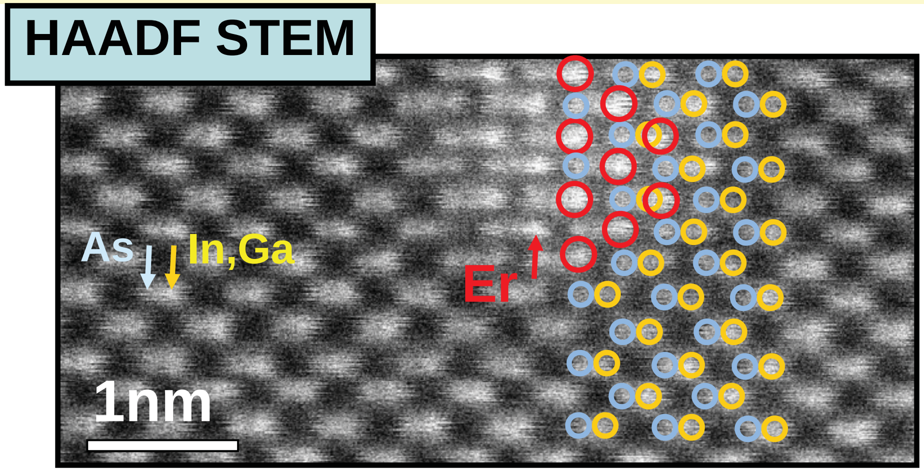
**Purdue** (Sands)

# ErAs Semi-metal Nanoparticles embedded in InGa(Al)As Semiconductor Matrix

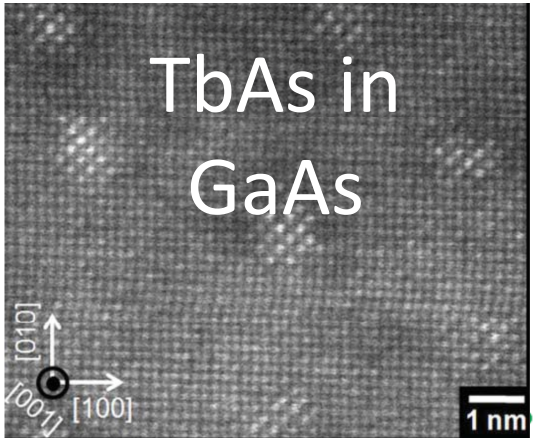


- Erbium is co-deposited at a growth rate which is a fixed fraction of the InGaAlAs growth rate (MBE growth)
- Solubility limit is exceeded → islands are formed (2-3nm ErAs)



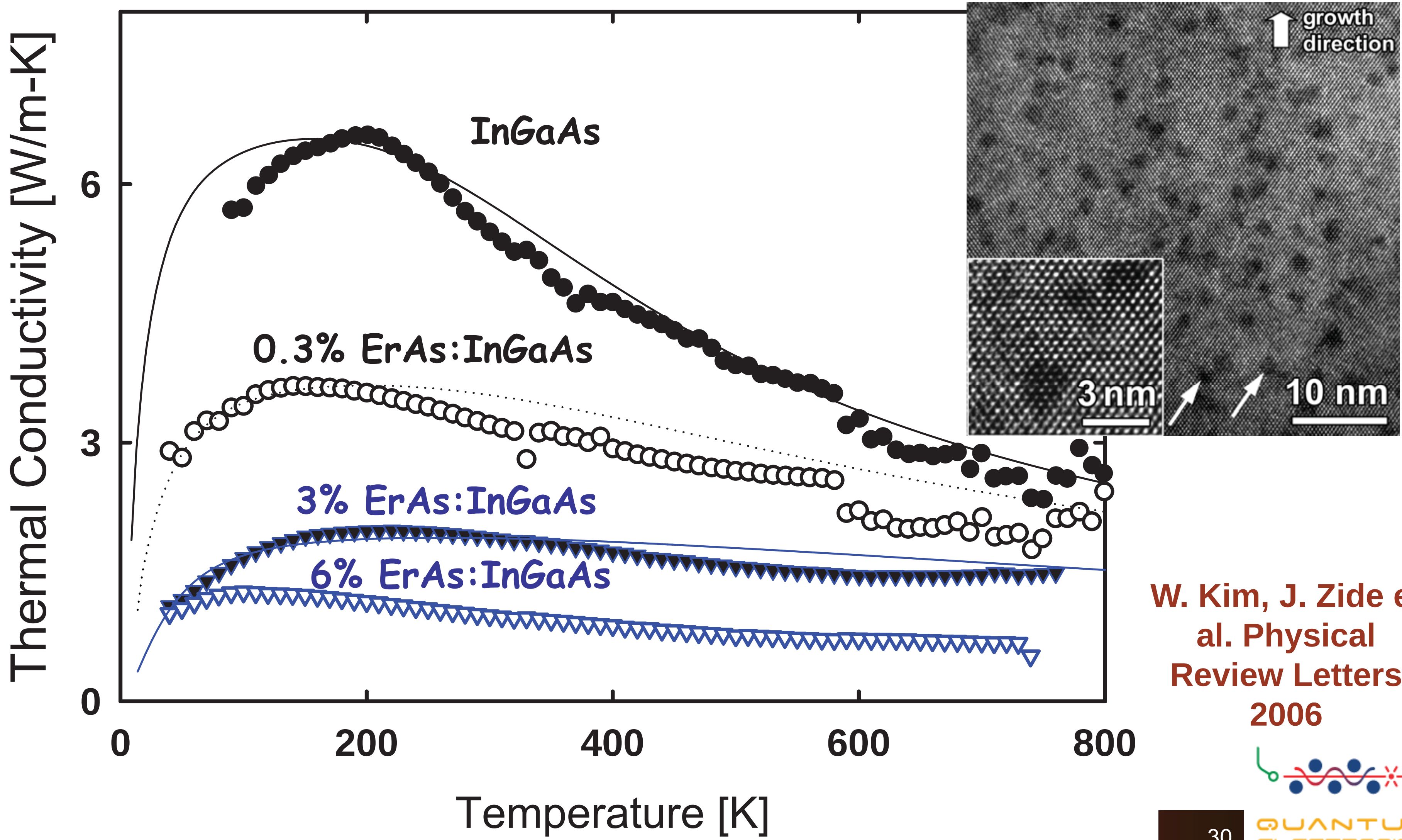




Josh Zide, Art Gossard, Susan Stemmer and Chris Palmstrøm (UCSB and Delaware)



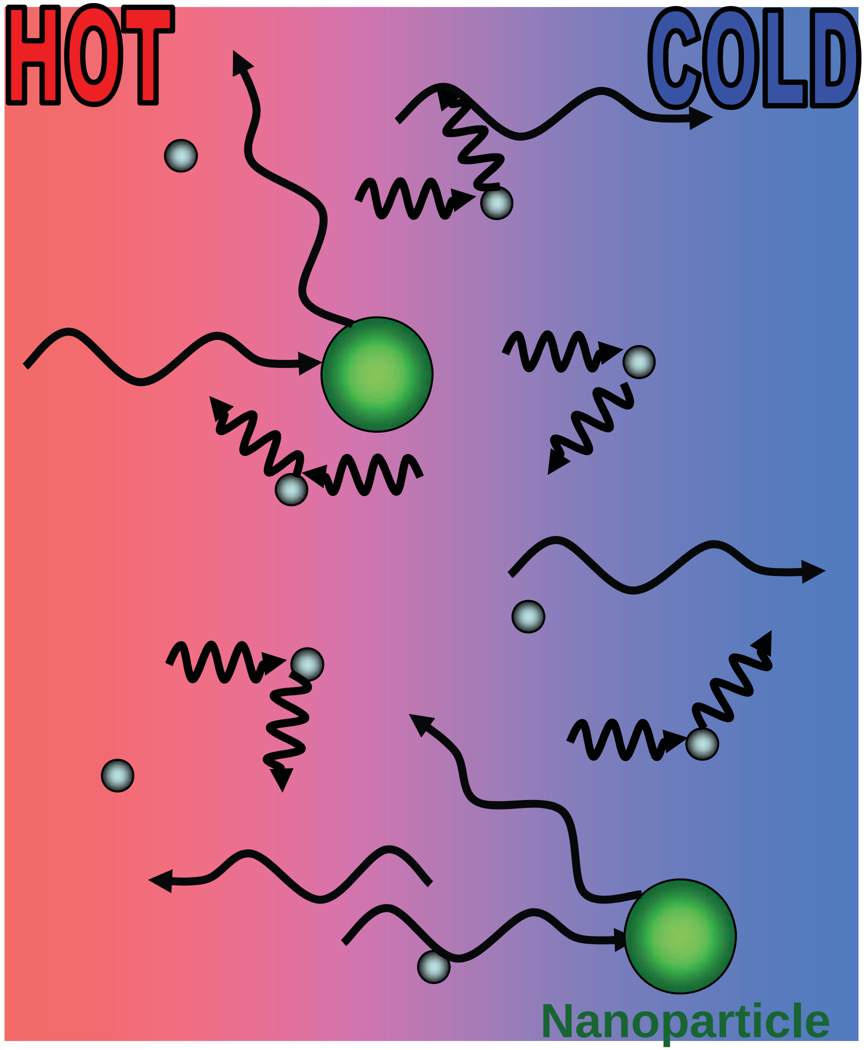
**Long *and* Short Wavelength Phonon Scattering**

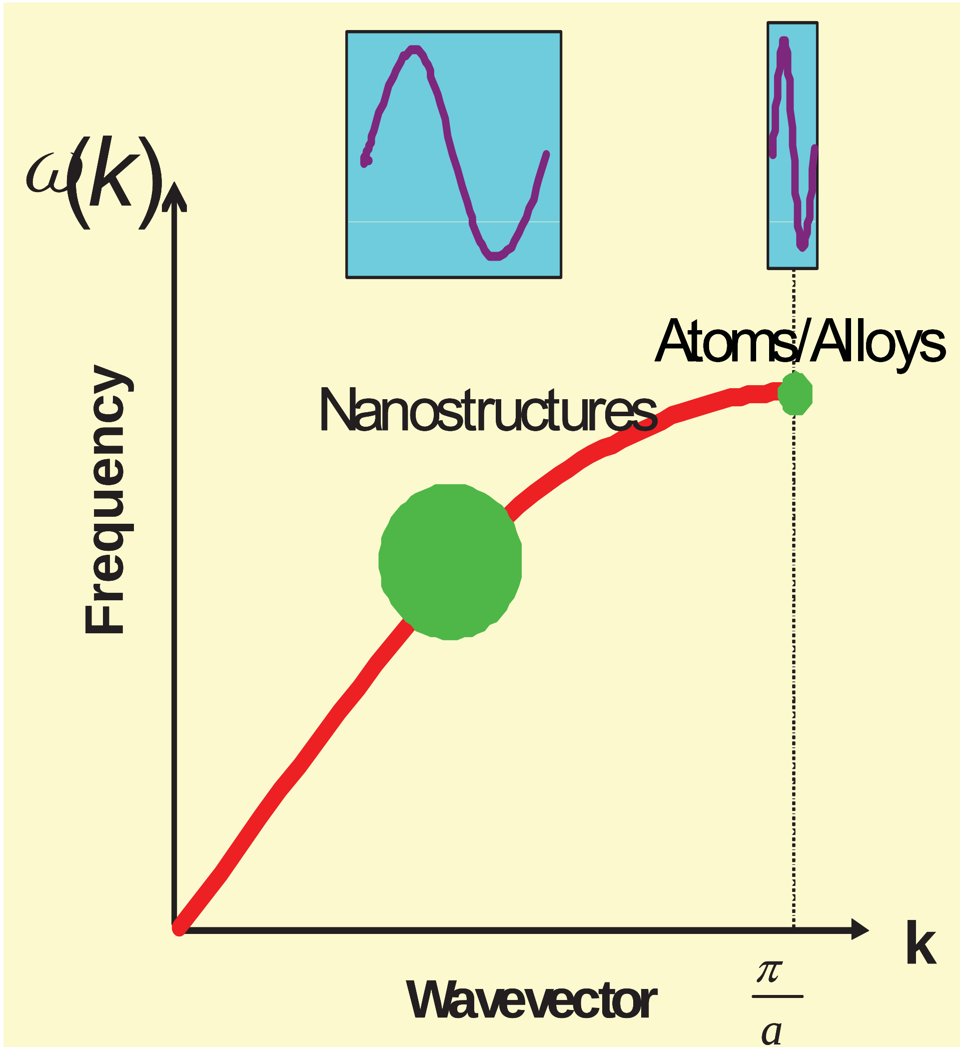
**➤ Thermal Conductivity Reduction**




**W. Kim, J. Zide et al. Physical Review Letters 2006**

# Thermal conductivity reduction




W. Kim, et al. Physical Review Letters 2006

# Thermoelectric figure-of-merit

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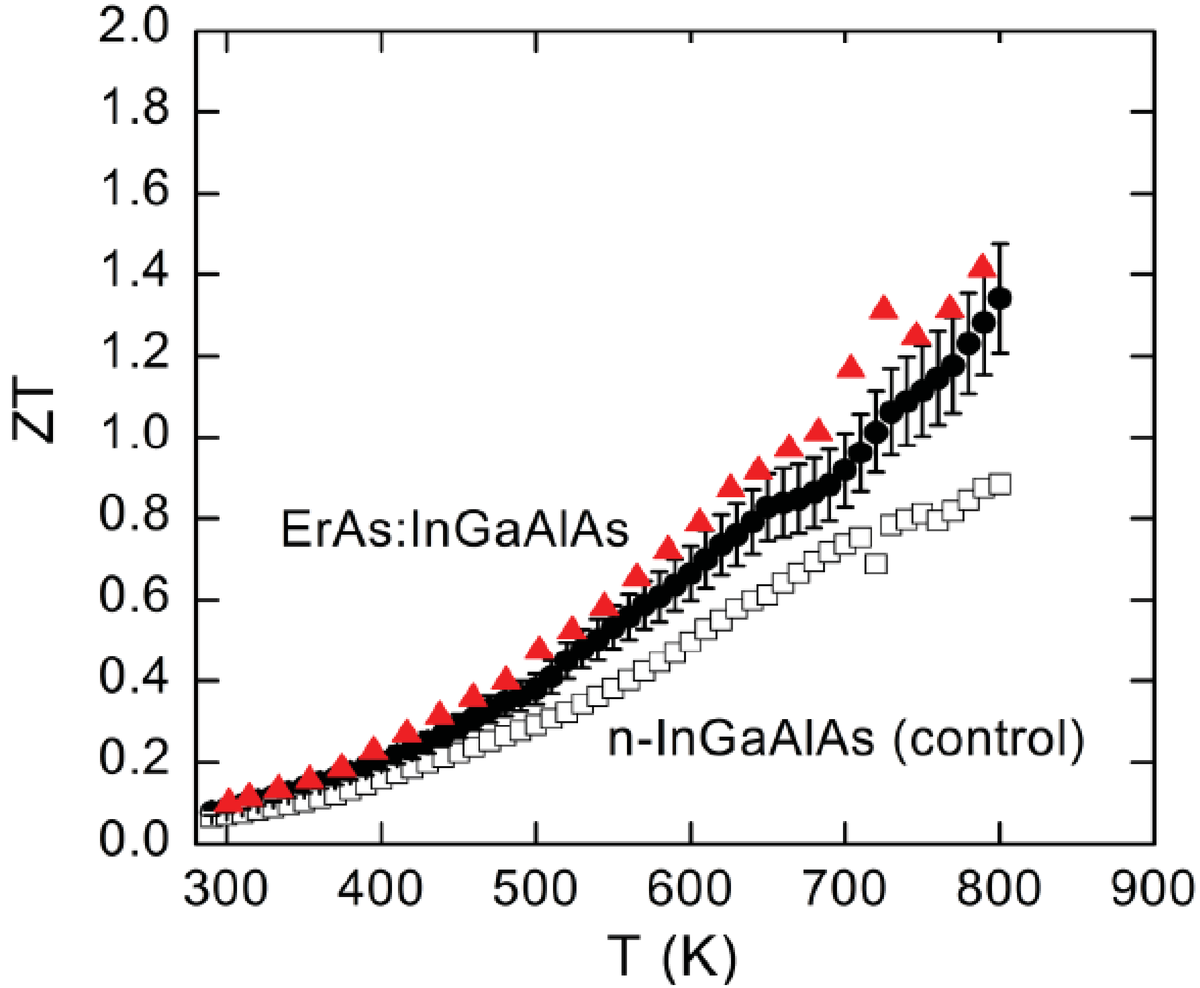


**Zide et al. J. of Applied Physics (2010); Burke, Bahk, et al. to be published (2012)**

The majority of ZT enhancement is from thermal conductivity reduction.
5% power factor enhancement at 800K.



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# Cross-plane and in-plane Seebeck in thick barrier superlattices InGaAs:ErAs/InGaAlAs

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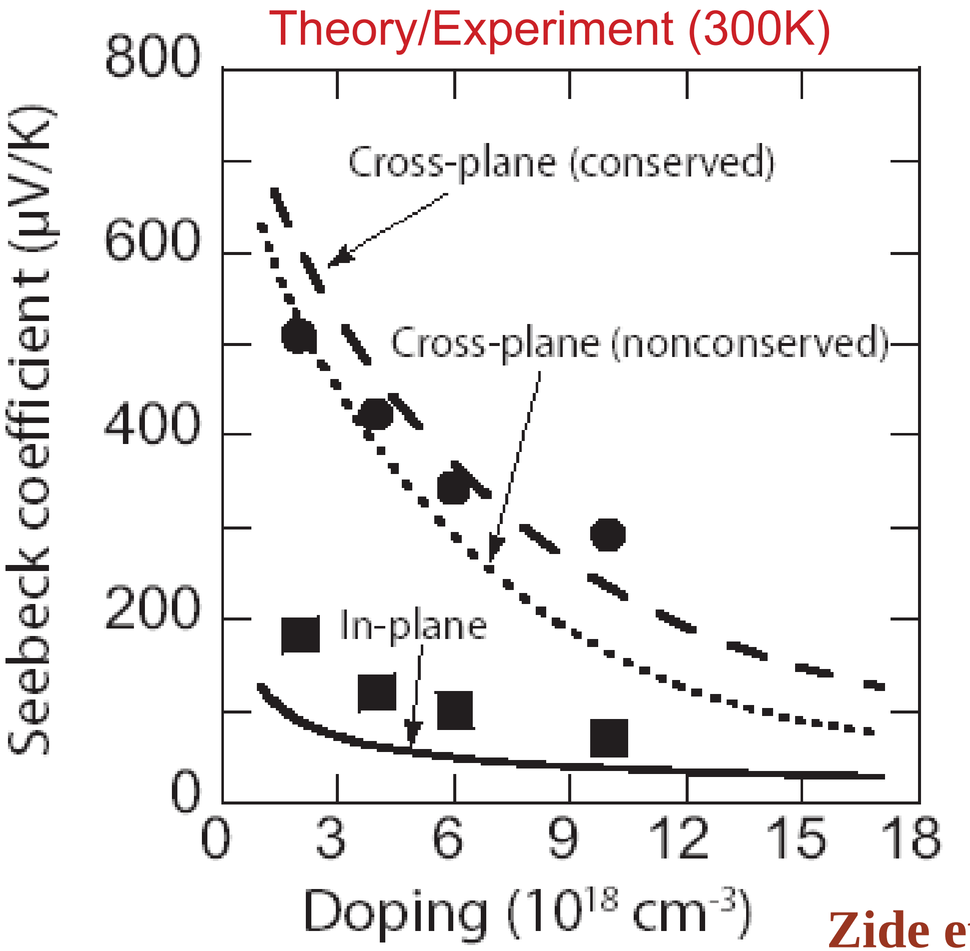
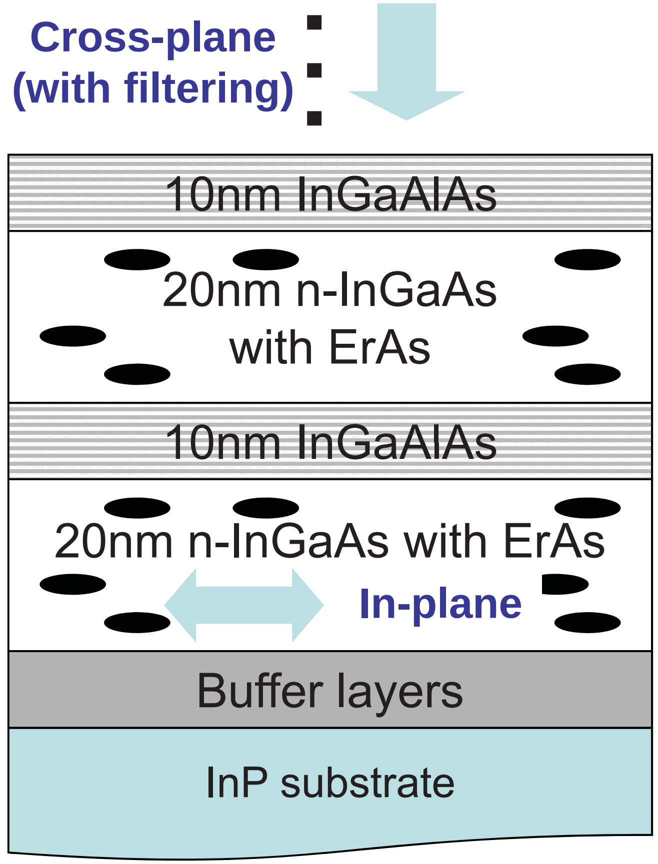
- Enhance energy filtering by inserting InGa**Al**As barriers inside ErAs:InGaAs can enhance cross-plane Seebeck by a factor of 3




Zide et al, PRB 74, 205335, 2006



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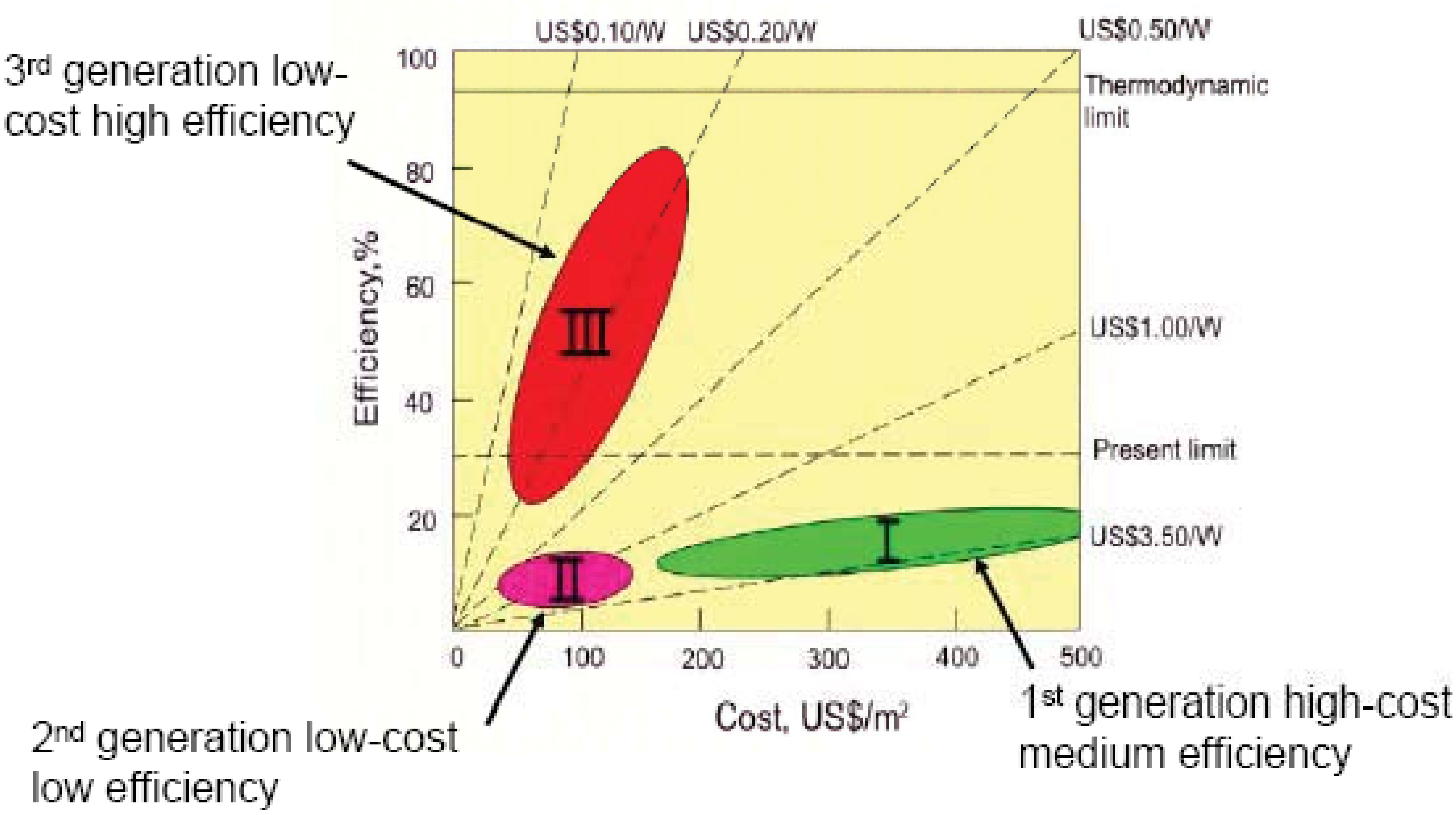
# Solar Cells

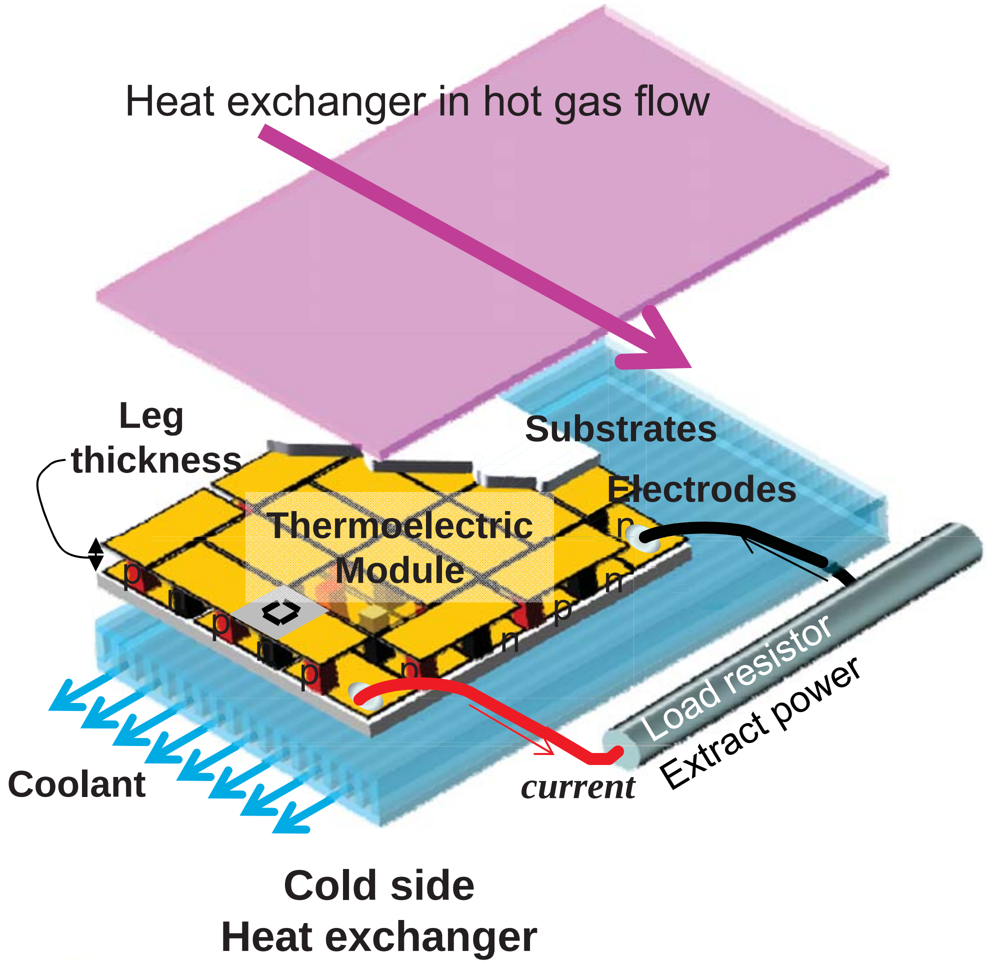
## (Efficiency+ Cost → $/W)

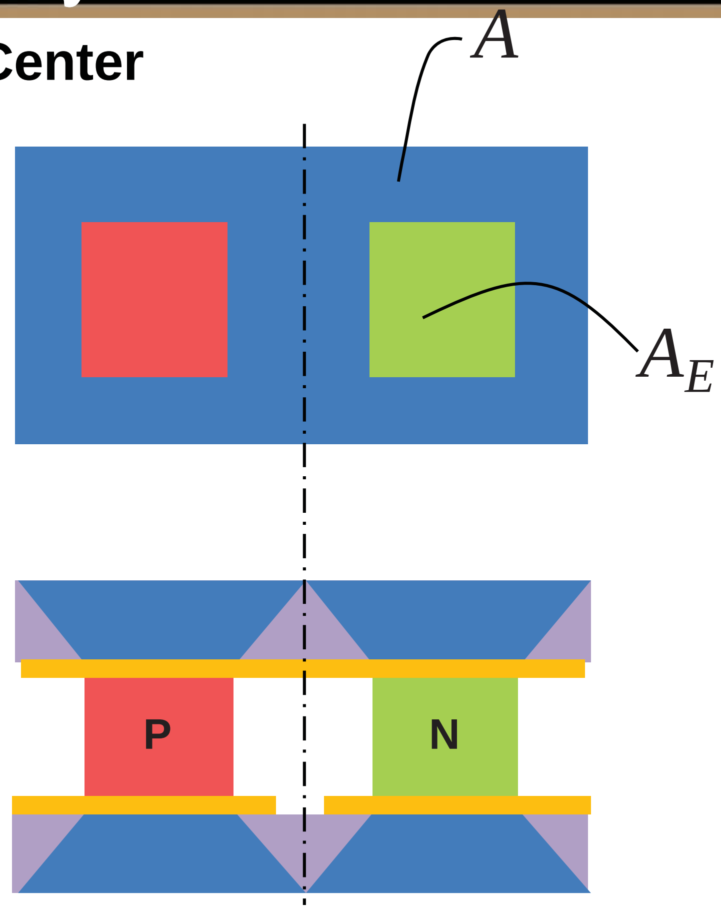


# Model of TE module + heat exchanger for cost/efficiency trade off analysis

PURDUE UNIVERSITY Discovery Park

**DOE/EFRC CEEM Center**




Fractional area coverage

$F = A_E/A$

K. Yazawa and A. Shakouri, Env. Science and Technology (July 2011)



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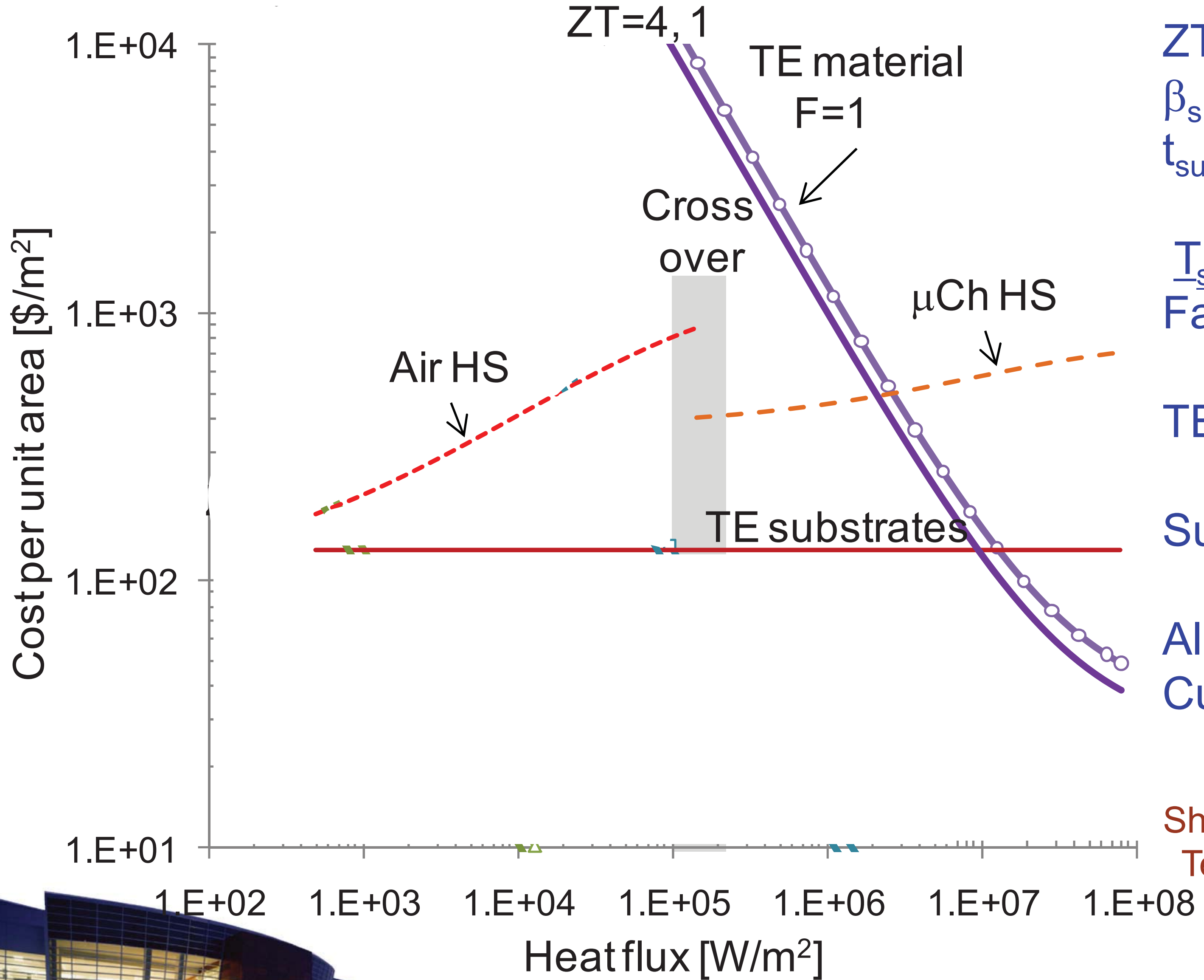
# Components of TE system (cost per unit area)




ZT=1, $\beta$=1.5 W/mK
$\beta_{sub}$=100 W/mK
$t_{sub}$=0.2mm

$T_s$=600K, $T_a$=300K
Fan efficiency 30%

TE (BiTe or PbTe): $500/kg
Substrate-AlN: $100/kg
Al: $8/kg
Cu: $20/kg

K. Yazawa and A. Shakouri, Env. Science & Technology (July 2011)

# TE Module Material cost per Watt

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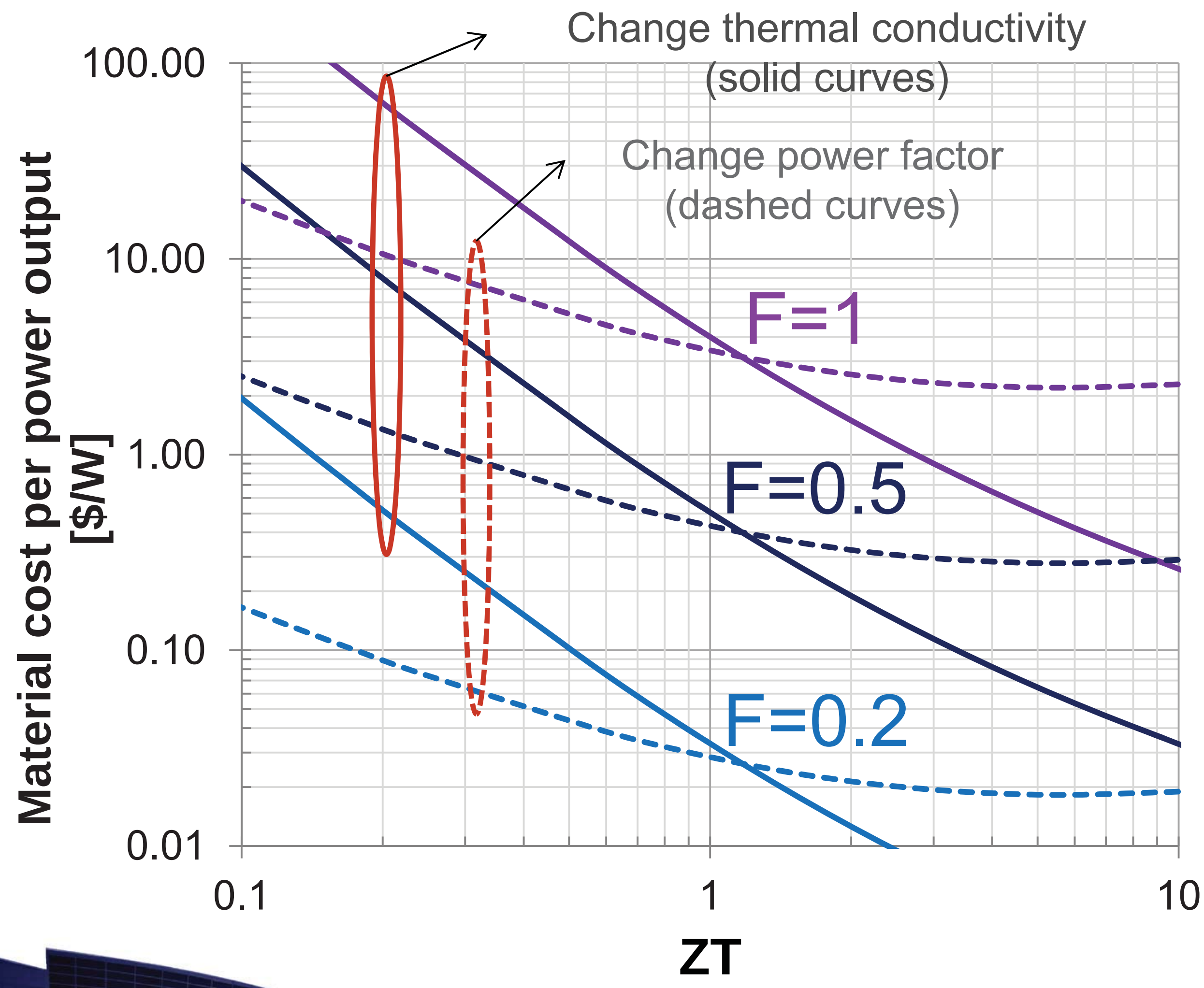



ZT=1, β=1.5 W/mK, $\beta_{sub}$=23 W/mK, $t_{sub}$=0.2mm,

Ts=900K, Ta=330K, Pump efficiency 30%

TE: $500/kg,
Alumina substrate: $ 5/kg,
Copper heat sink: $ 20/kg

$U_h$=4.6x10$^2$W/m$^2$K
$U_c$=1.5x10$^3$W/m$^2$K ($U_c/U_h$=0.3)

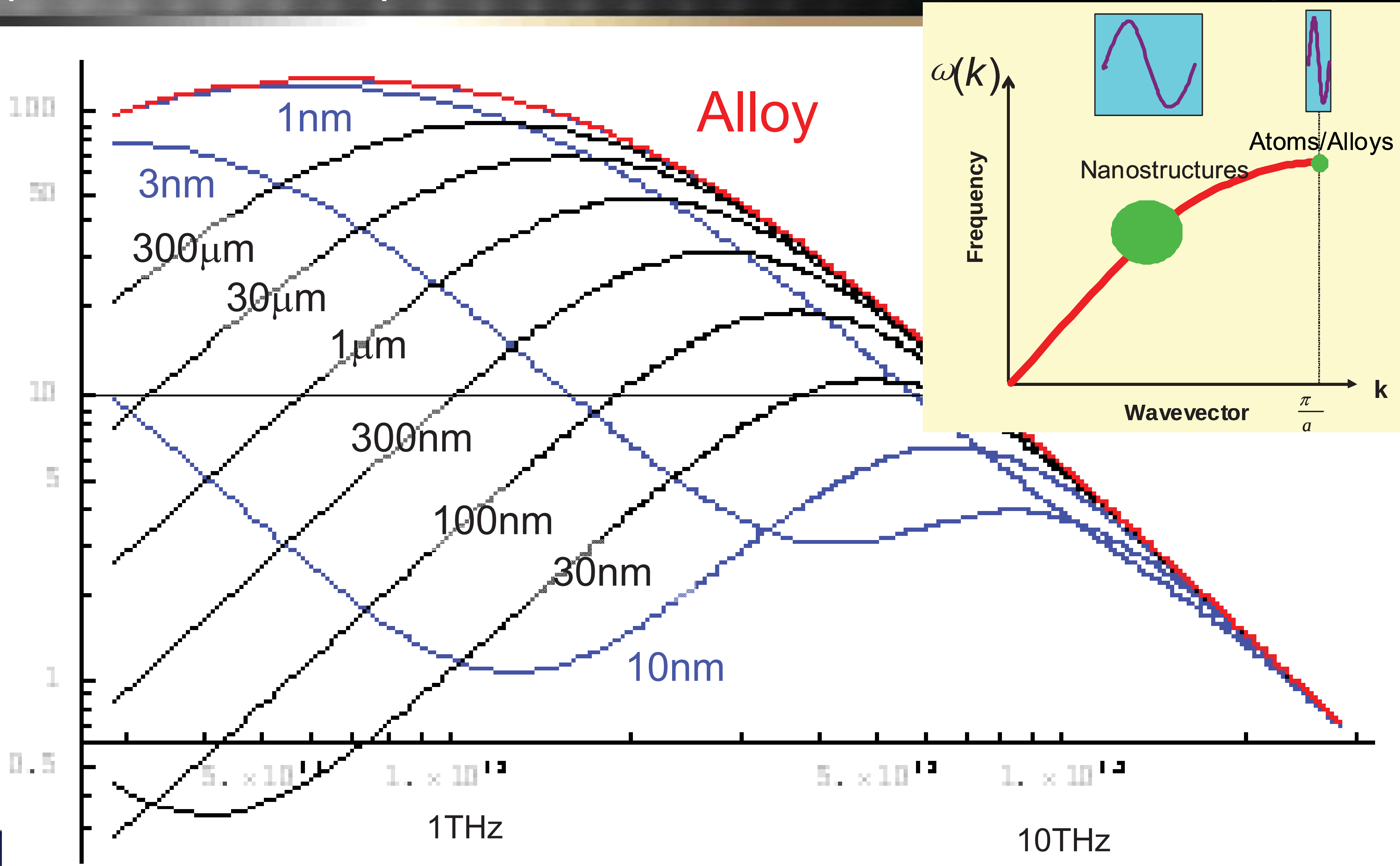
**Yazawa & Shakouri; Journal of Material Research 2012**



QUANTUM ELECTRONICS

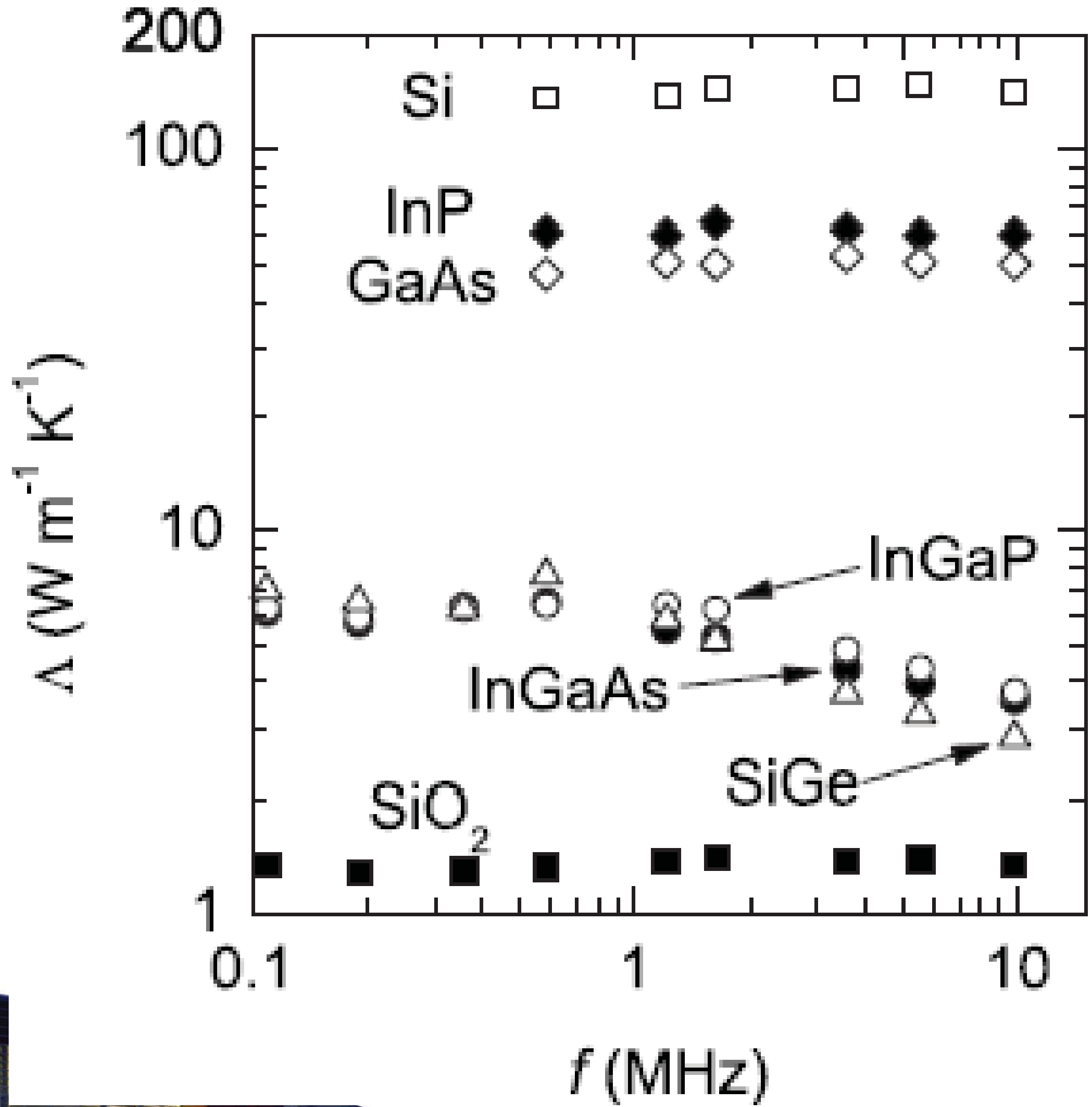
# Phonon contributions to thermal conductivity in presence of nanoparticles in SiGe at 300K






**Natalio Mingo**, CEA, 2009 (unpublished)

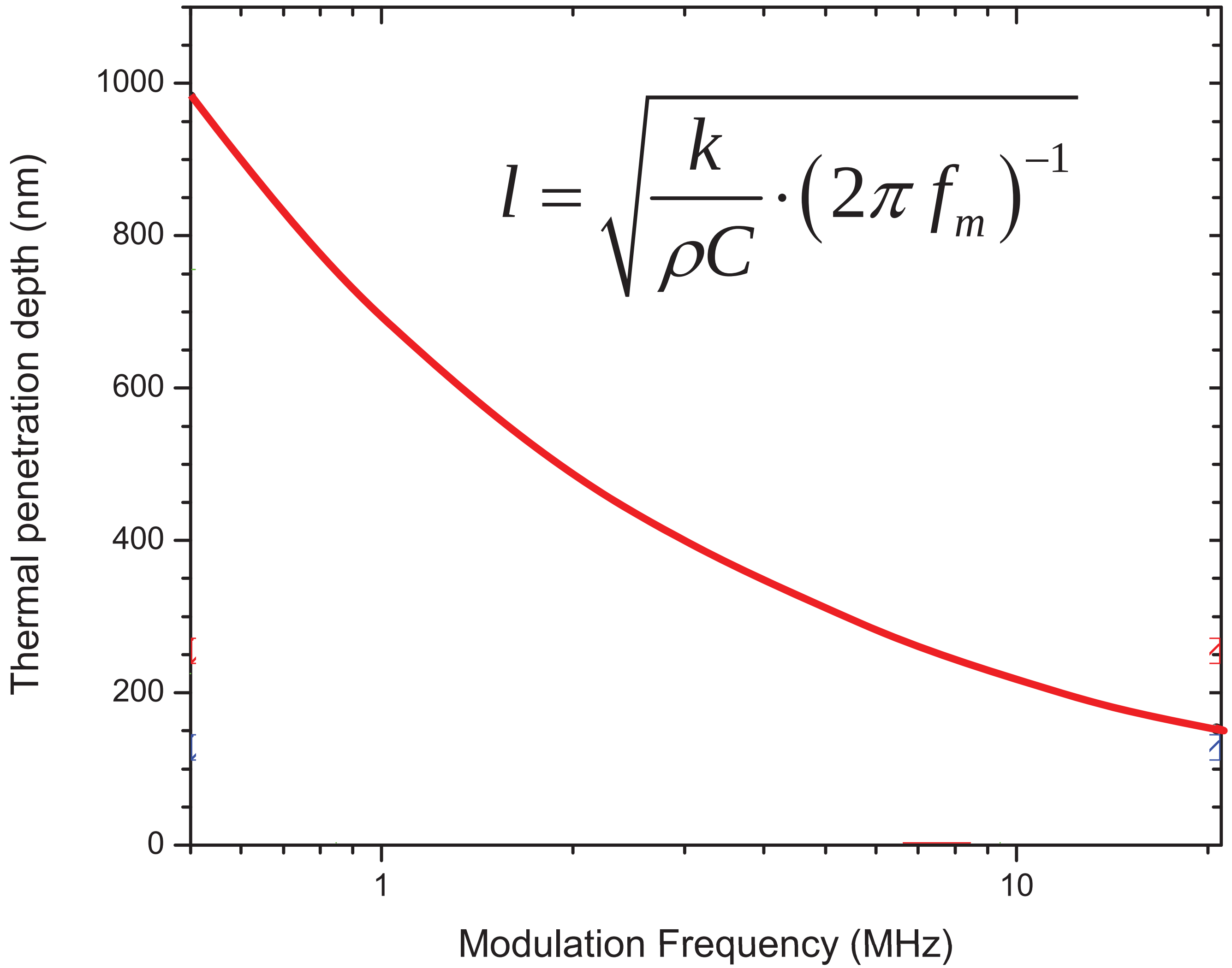
# Frequency-Dependent Thermal Conductivity




Koh and Cahill, PHYSICAL REVIEW B 76, 075207 (2007)

# Thermal penetration length

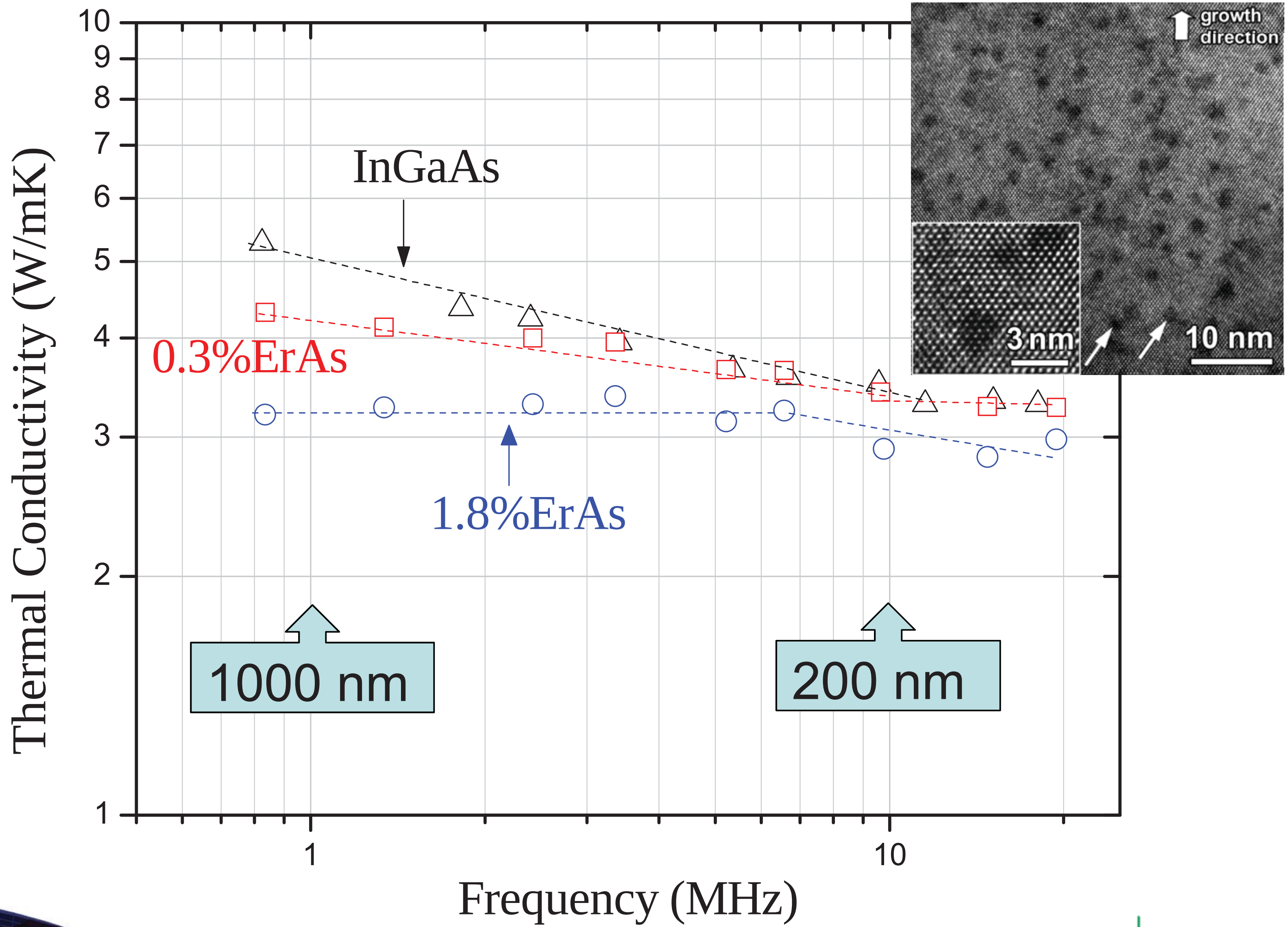





Gilles Pernot (UCSC)

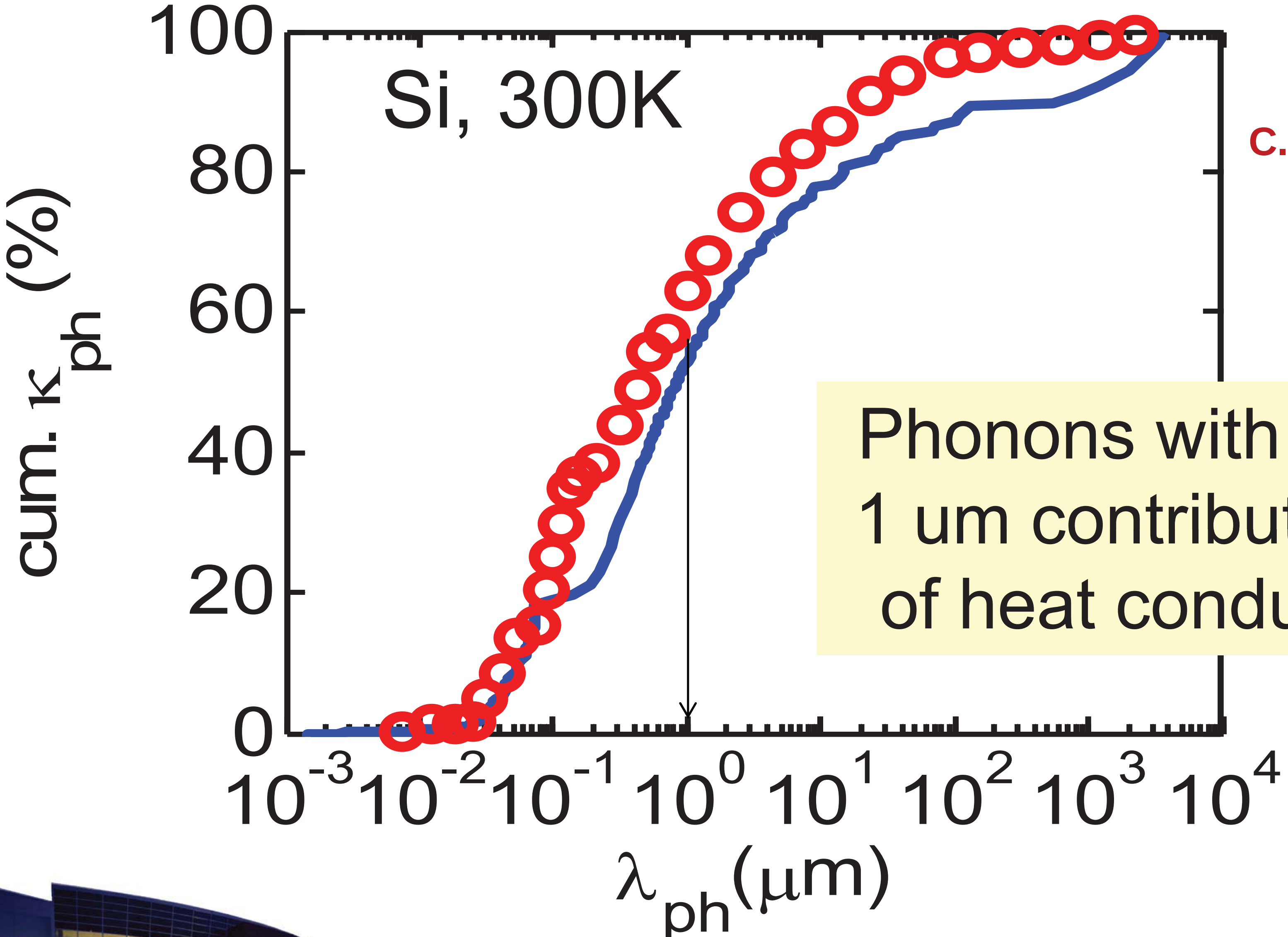
# Frequency-dependent Thermal Conductivity






Gilles Pernot, H. Lu, P. Burke et al., MRS 2012

# Cummulative $\kappa_{ph}$ vs. mfp at 300K




C. Jeong and M. Lundstrom (Purdue)

Phonons with mfp > 1 um contribute 50% of heat conduction.

# Summary

- Energy challenge: Role of solid-state thermoelectrics in direct conversion of heat into electricity
- Metal/semiconductor nanocomposites (e.g. ErAs: InGaAs)
  - Hot electron filtering (increases electrical conductivity times Seebeck coefficient square)
  - Embedded nanoparticles scatter mid/long wavelength phonons (reduce thermal conductivity)
- Heat transport in thin films (=> frequency-dependent thermal conductivity in 1-10MHz range)
- Cost/efficiency trade off for thermoelectrics
- Open issues (efficiency at maximum output power, non-equilibrium heat engines, phase change)

A. Shakouri, *Annual Review of Materials Research,* July 2011

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