Guest Lecture

Nanomaterials for Thermoelectric Conversion

Dr. Sunmi Shin
(mpeshin@nus.edu.sg)
Department of Mechanical Engineering
National University of Singapore

Lecture on Oct 13, 2022

Agenda

- Nanotechnology in Thermal Engineering
- State-of-the-art Technology
- Application for Thermo-Electric Energy Conversion

Range of *THERMAL* Conductivity (κ)

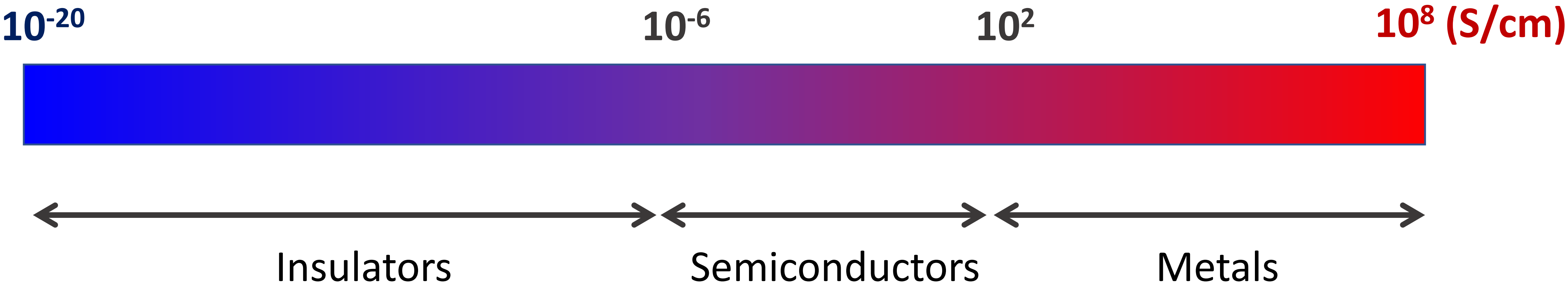
Range of *THERMAL* Conductivity (κ)

Insulators ← → Conductors

10^{-2} **10^{3} (W/m-K)**

Aerogels	Air	Wood / Nylon	Glass	Si	Al	Cu	Diamond	Graphene
(<0.02)	(0.02)	(0.25)	(1.4)	(130)	(200)	(400)	(2000)	(~5000)

Range of *ELECTRICAL* Conductivity (σ)



Clearly….

Hard to control heat!

$10^{-2} < \kappa < 10^{3}$

$10^{-20} < \sigma < 10^{8}$

Stay hot up to 5 hours

What are the parameters to determine κ?

Insulators ← → Conductors

10^{-2} **10^{3} (W/m-K)**

Aerogels (<0.02) | Air (0.02) | Wood Nylon (0.25) | Glass (1.4) | Si (130) | Al (200) | Cu (400) | Diamond (2000) | Graphene (~5000)

What are the parameters to determine κ?

Insulators

Conductors

10^{-2}

10^{3} (W/m-K)

Aerogels (<0.02)

Air (0.02)

Wood Nylon (0.25)

Glass (1.4)

Si (130)

Al (200)

Cu (400)

Diamond (2000)

Graphene (~5000)

Related to Electrical Property?

What are the parameters to determine κ?

Insulators ← → Conductors

10^{-2} — **10^{3} (W/m-K)**

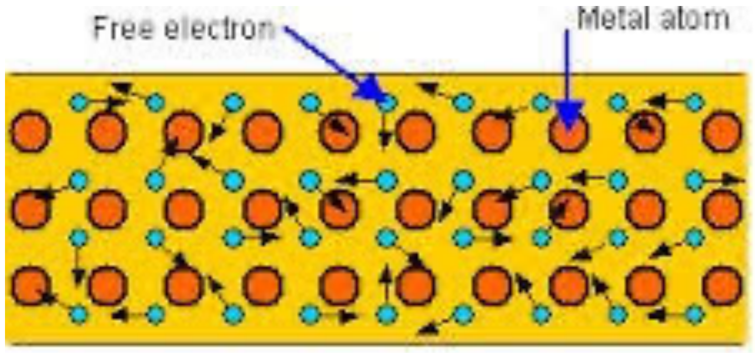
Aerogels	Air	Wood / Nylon	**Glass**	Si	Al	Cu	**Diamond**	Graphene
(<0.02)	(0.02)	(0.25)	**(1.4)**	(130)	(200)	(400)	**(2000)**	(~5000)

Related to Electrical Property?

Mechanical Property?

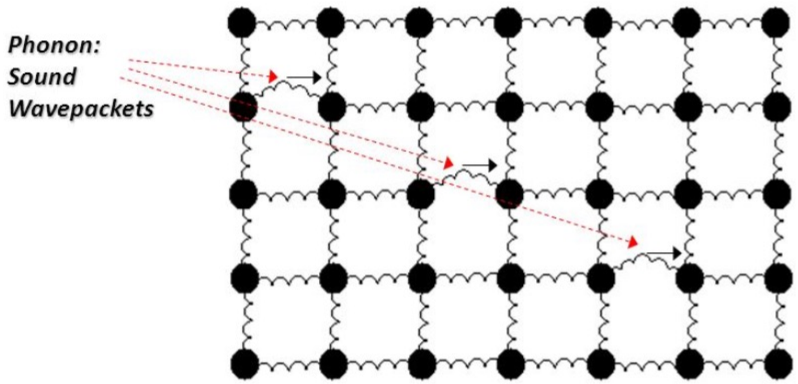
Thermal Energy Carriers

Electrons



ex) Metals (Cu, Au…)

Phonons (Lattice)



ex) Dielectrics (Glass, diamond…)

Total thermal conductivity, $K_t = K_e + K_L$

Reducing the Thermal Conductivity

Total thermal conductivity, $K_t = K_e + K_L$

Wiedemann–Franz law: $K_e = \sigma L T$

σ: Electrical conductivity
L: Lorentz number
T: Temperature

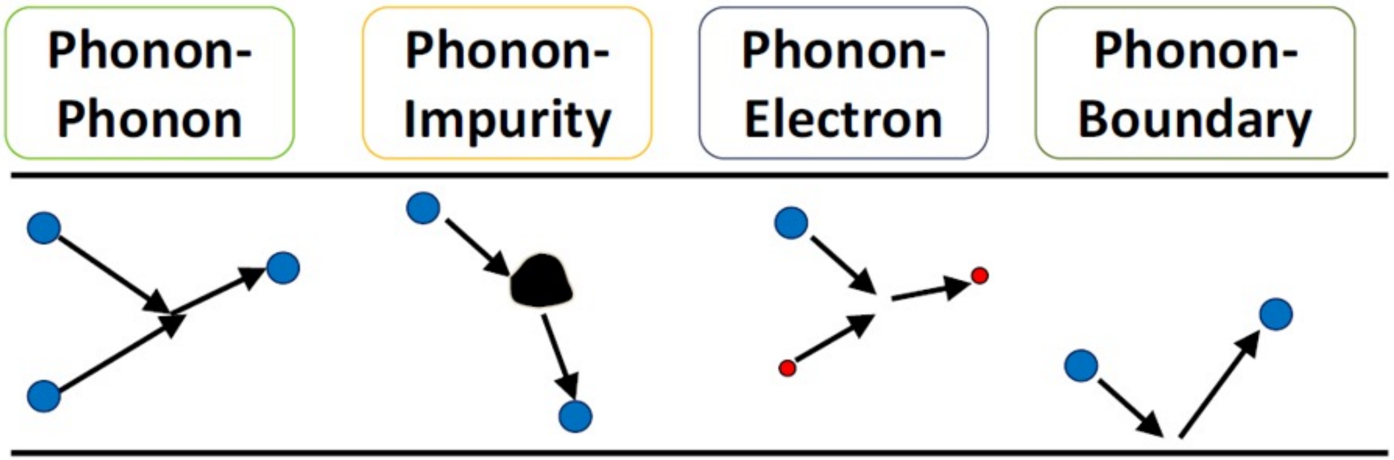
Reducing the Lattice Thermal Conductivity

Lattice Thermal Conductivity

Lattice thermal conductivity $$\kappa_L = \frac{1}{3} C v l$$

C: Specific heat
v: phonon velocity
l: phonon mean free path

Phonon mean free path: Average distance between two successive particle scattering events. Interactions to consider include:



Lattice Thermal Conductivity

Lattice thermal conductivity

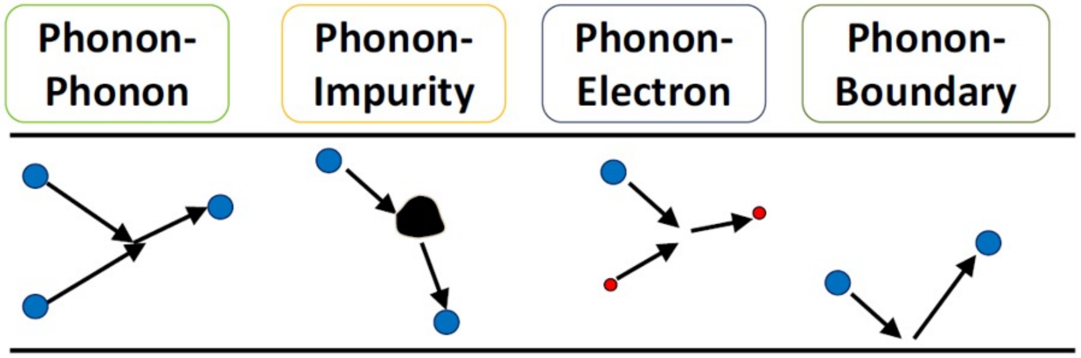
$$\kappa_L = \frac{1}{3} C v l$$

C: Specific heat
v: phonon velocity
l: phonon mean free path

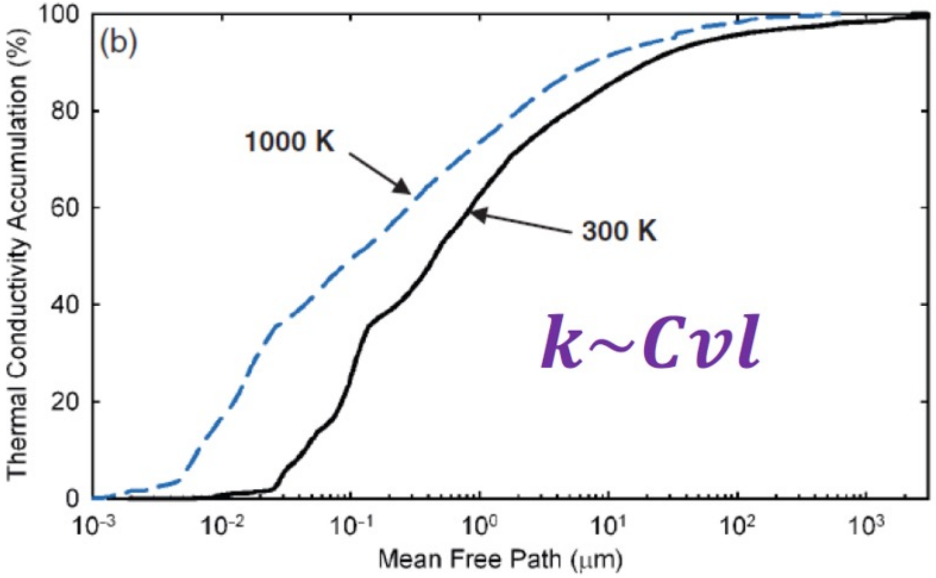
Matthiessen Rule:

$$\frac{1}{l} = \frac{1}{l_U} + \frac{1}{l_I} + \frac{1}{l_B} + \frac{1}{l_{ph-e}}$$

l_U: (phonon-phonon) Umklapp scattering
l_I: Impurity scattering
l_B: Boundary scattering
$l_{ph\text{-}e}$: phonon-electron scattering



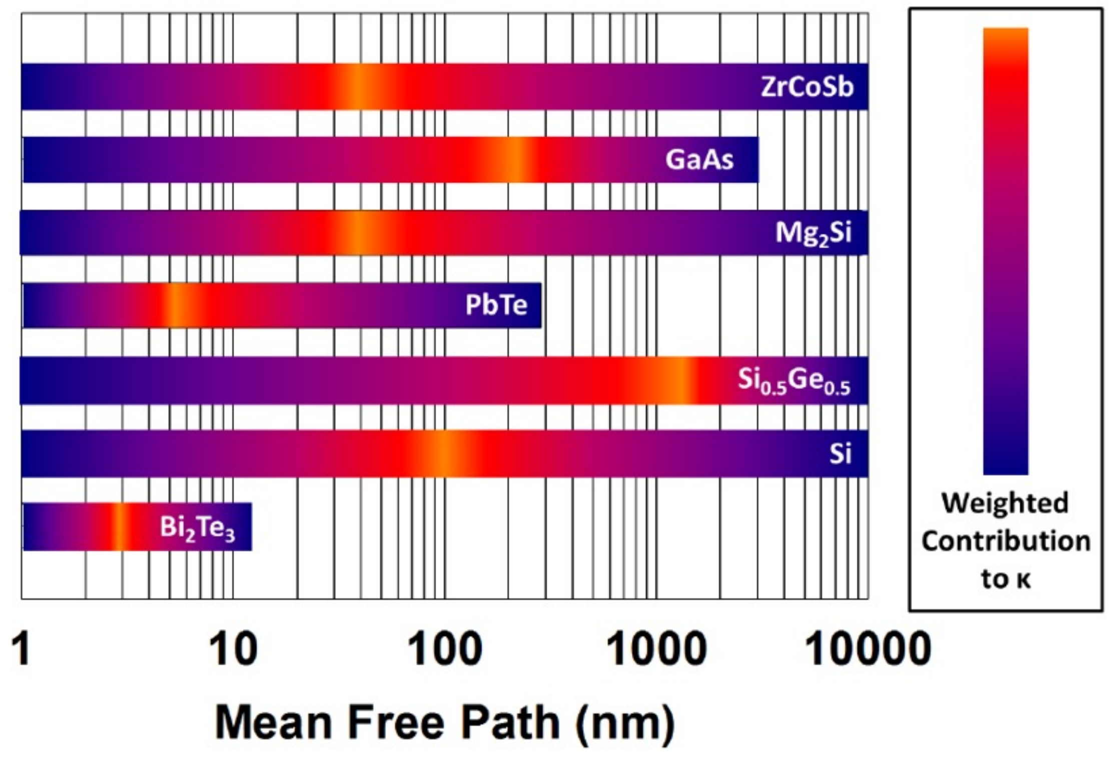
Phonon MFP Contribution to Thermal Conductivity



Majority (~80%) of thermal conductivity contribution in Si from phonons with MFP < 10 µm.

Theory: A. Henry and G. Chen, J. Comput Theor. Nanosci., **5**, 1-12 (2008)
Exp: J.A. Malen *et al*., Nature Communications **4**, 1640 (2013)

Phonon MFP Spectra of Selected TE Materials

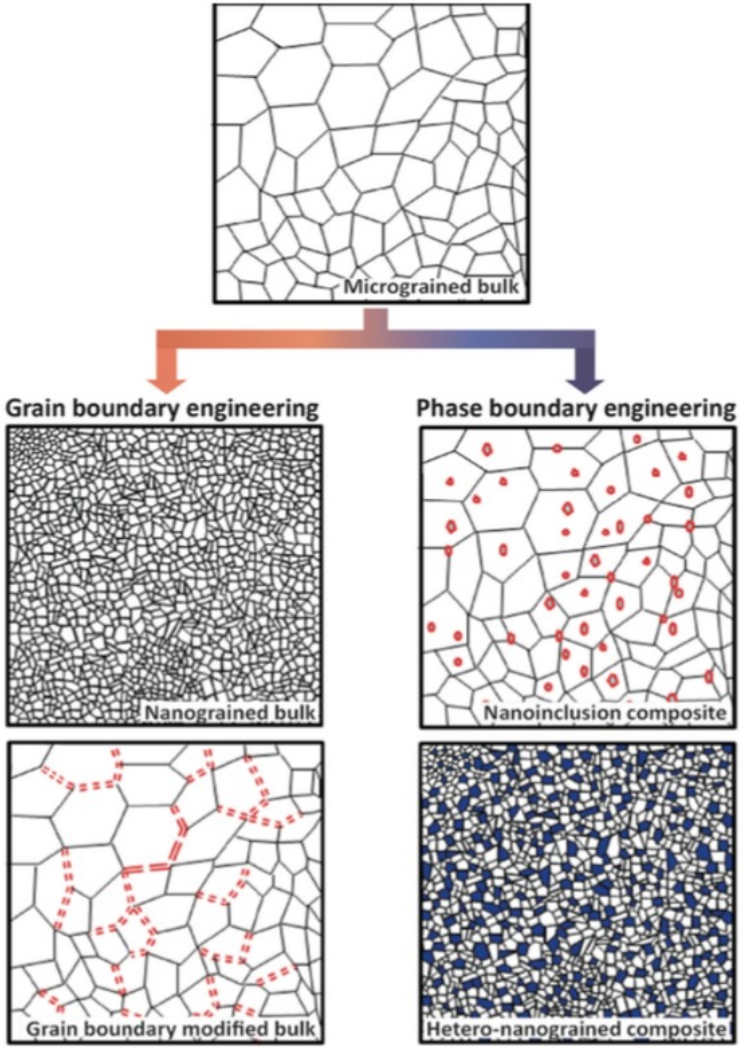


Dechaumphai et al., “Phononic and Electronic Engineering in Nanowires for Enhanced Thermoelectric Performance”, book chapter in “Semiconductor Nanowires”

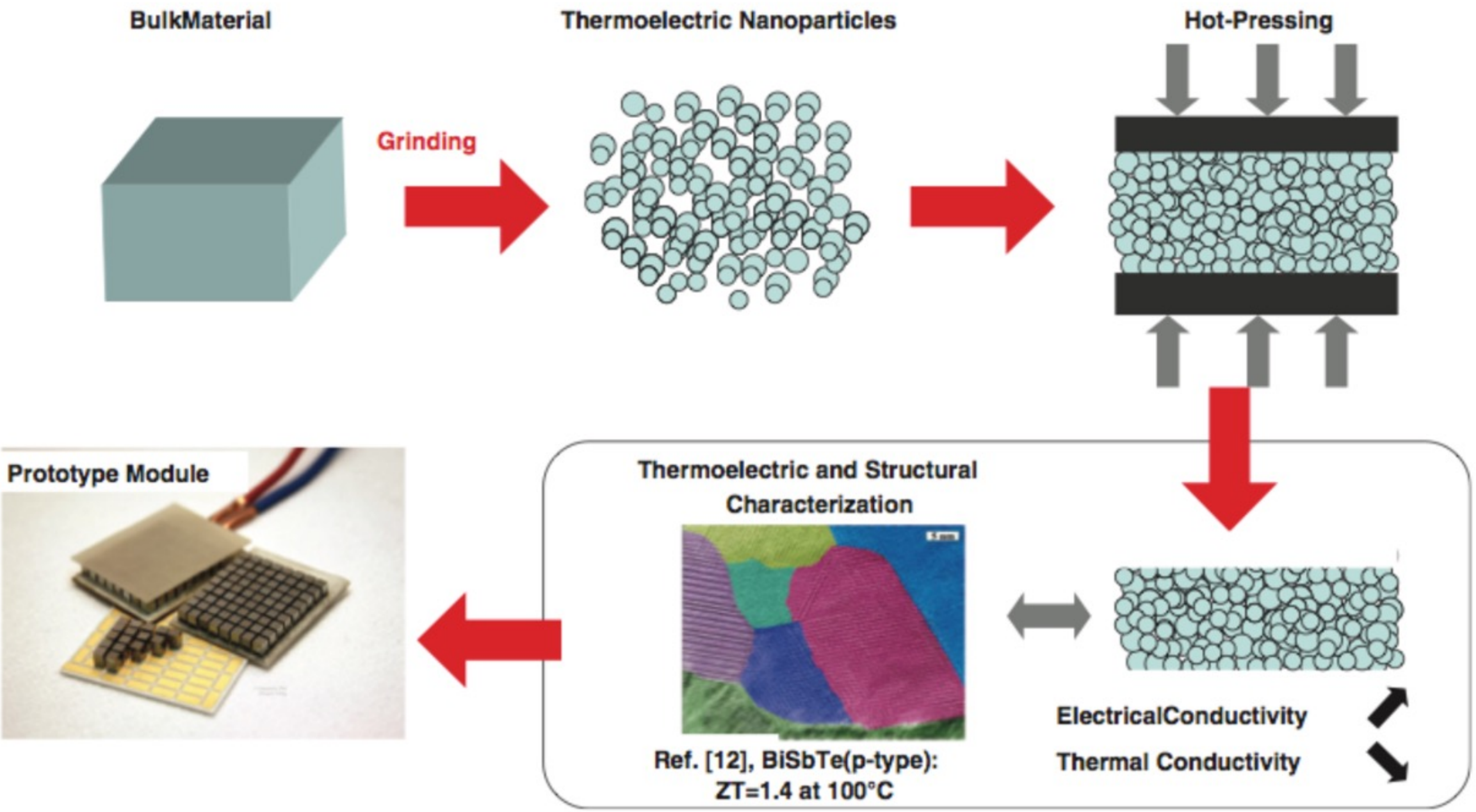
Boundary Engineering for the Thermoelectric Performance of Bulk Alloys Based on Bismuth Telluride

Hyeona Mun,[a, b] Soon-Mok Choi,[c] Kyu Hyoung Lee,*[d] and Sung Wng Kim*[a, b]

DOI: 10.1002/cssc.201403485

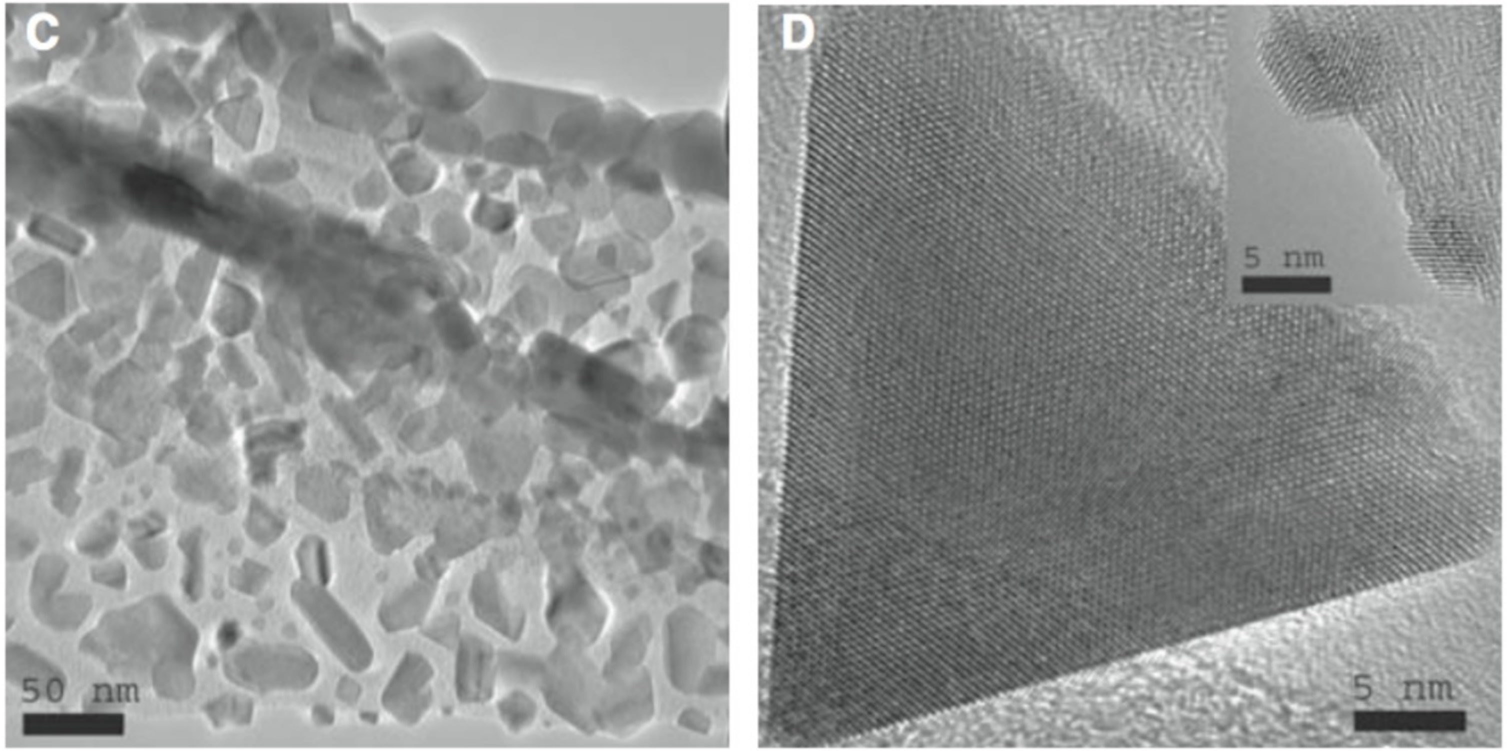


Nanocomposite



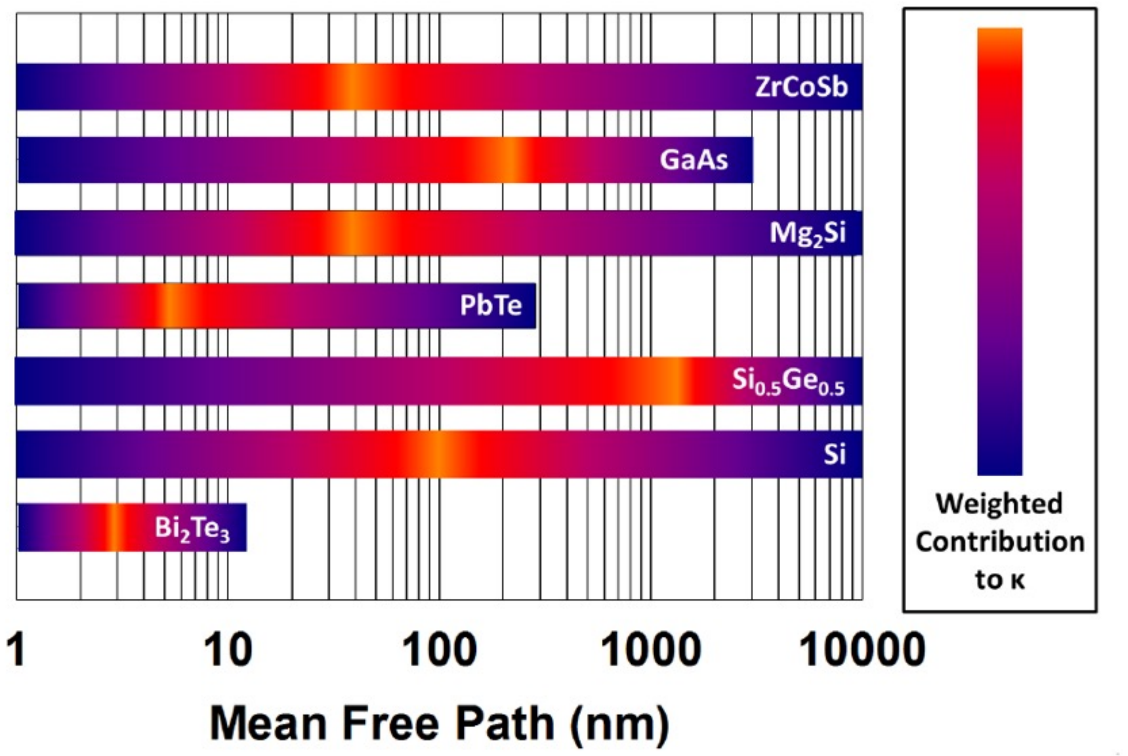
Nielsch et al., Adv. Energy. Mater., 2011

Grain Boundary Scattering



G. Chen et al., "High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys". Science, 2008

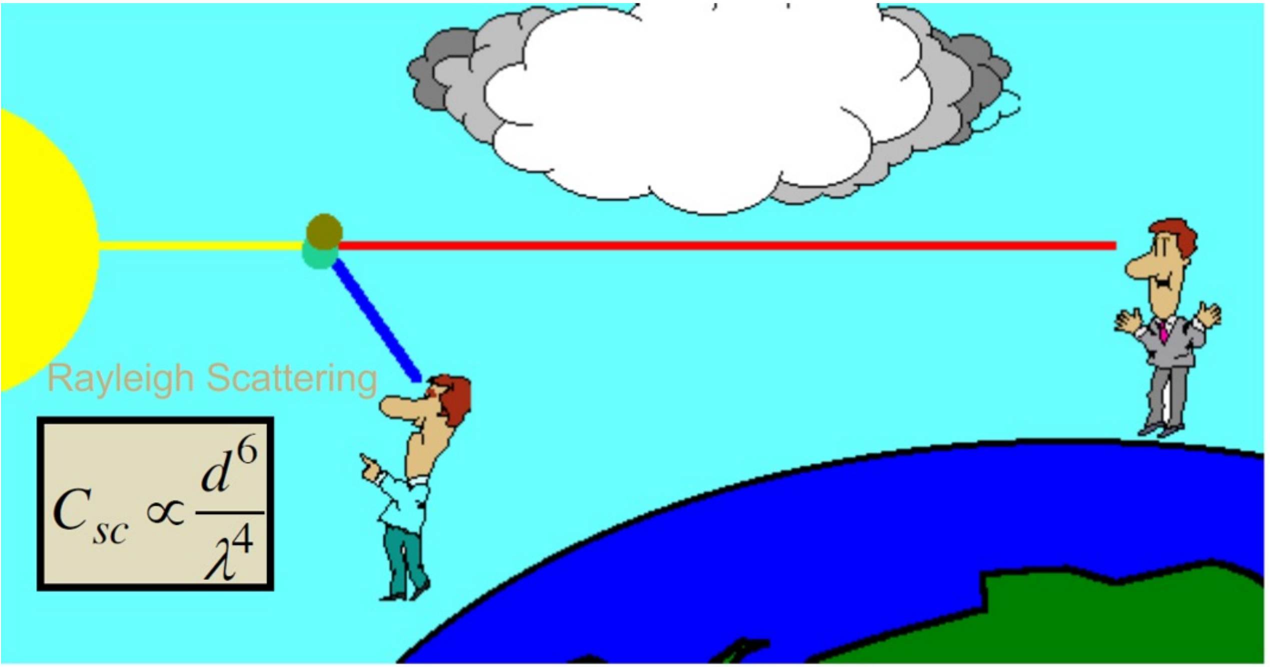
Phonon MFP Spectra of Selected TE Materials



Dechaumphai et al., “Phononic and Electronic Engineering in Nanowires for Enhanced Thermoelectric Performance”, book chapter in “Semiconductor Nanowires”

Impurity Scattering

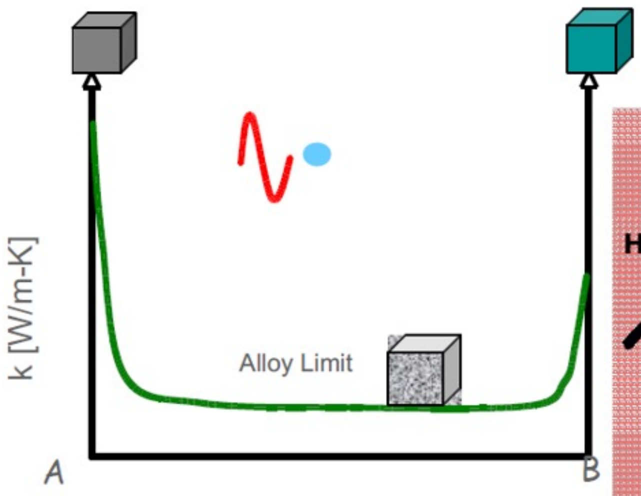
Why the sky is blue?

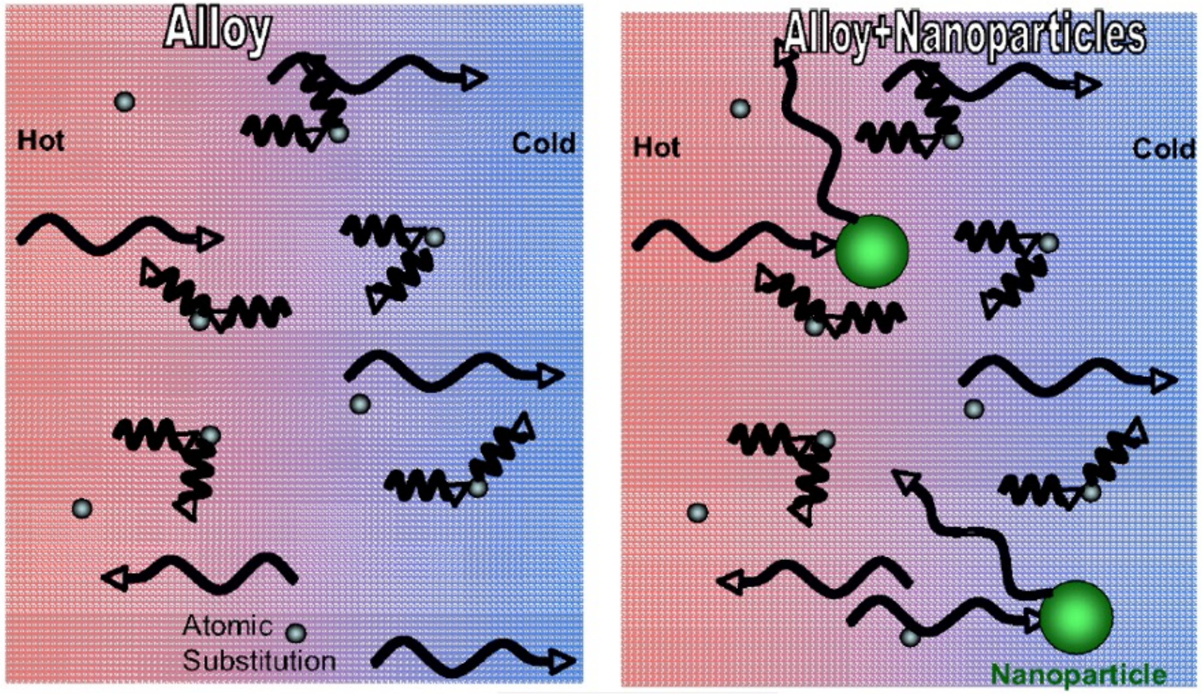


Particles scatter (shorter wavelength) blue light more strongly than they scatter red light.

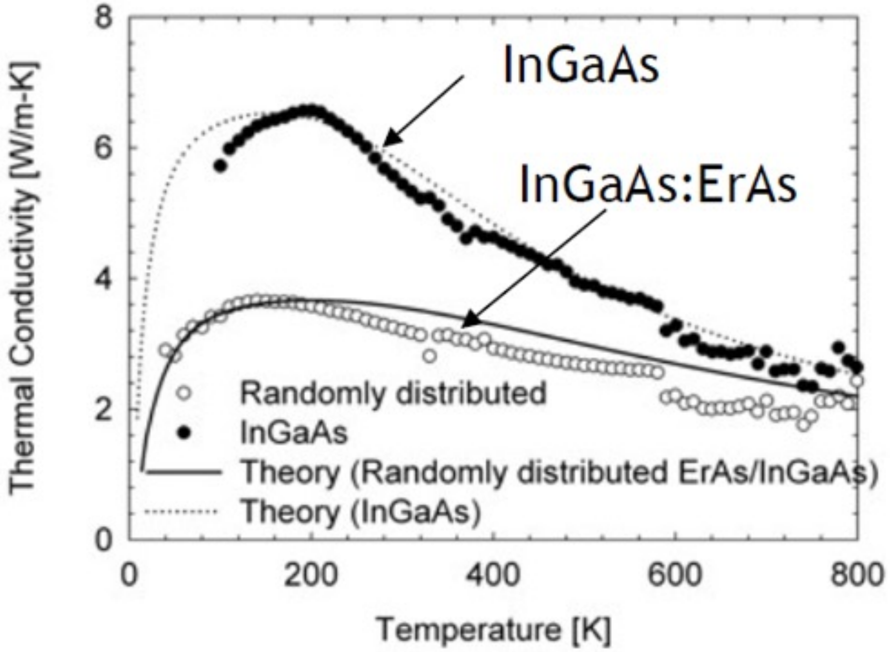
http://math.ucr.edu/home/baez/physics/General/BlueSky/blu_sky.html

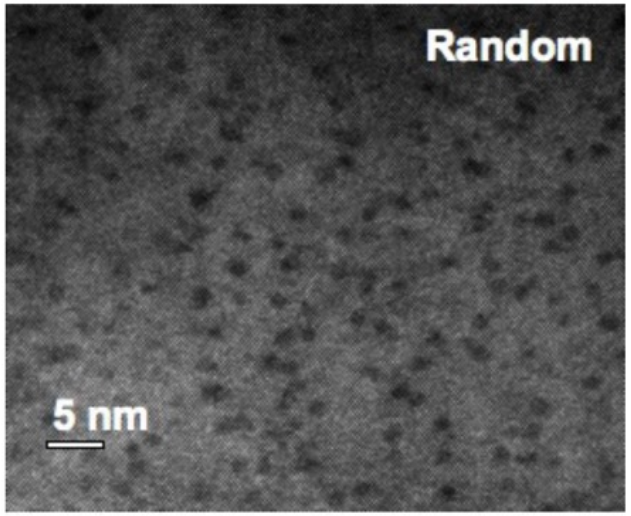
Beating the Alloy Limit

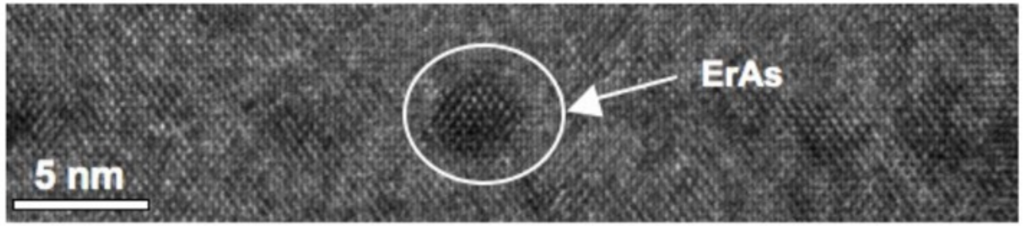




Inserting Impurity





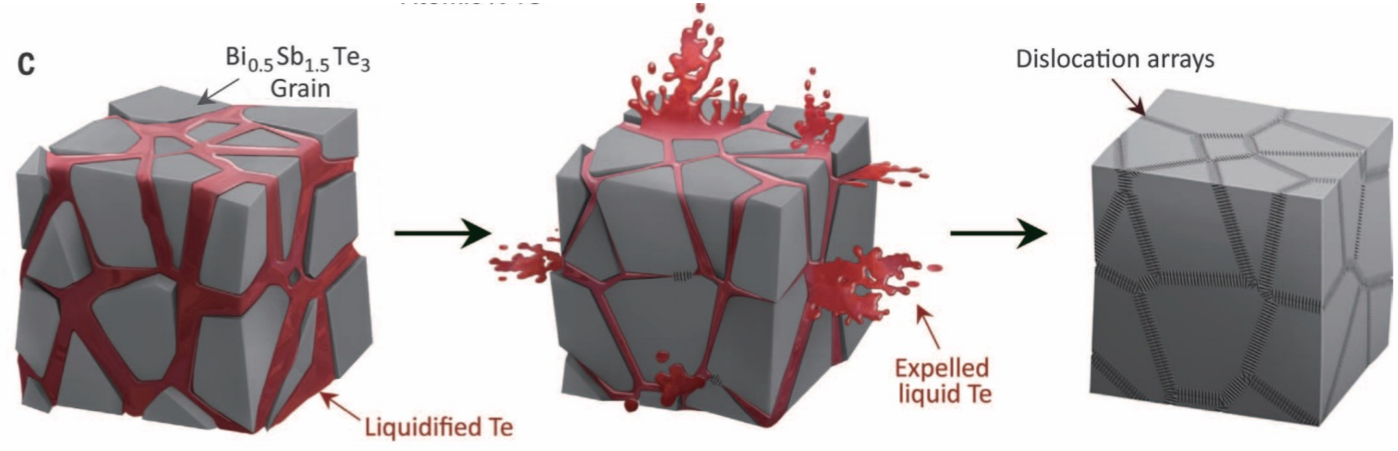


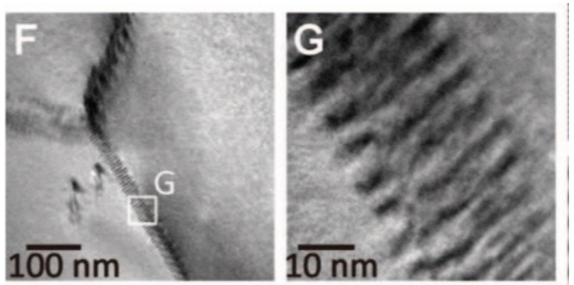
Kim, Zide, Gossard, Klenov, Stemmer, Shakouri, Majumdar, Phys. Rev. Lett. (2006)

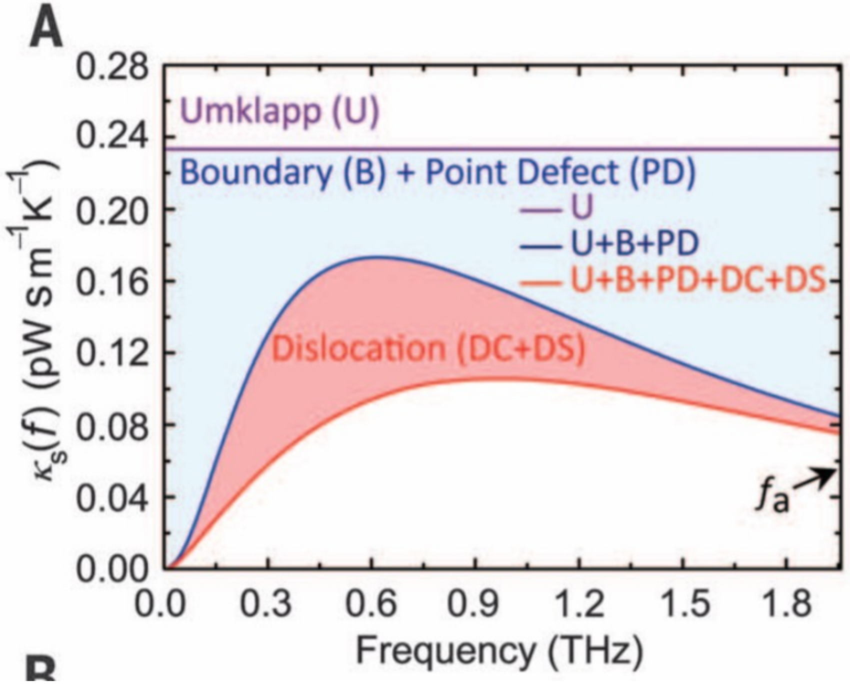
All-scale hierarchical architectures

THERMOELECTRICS

Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics







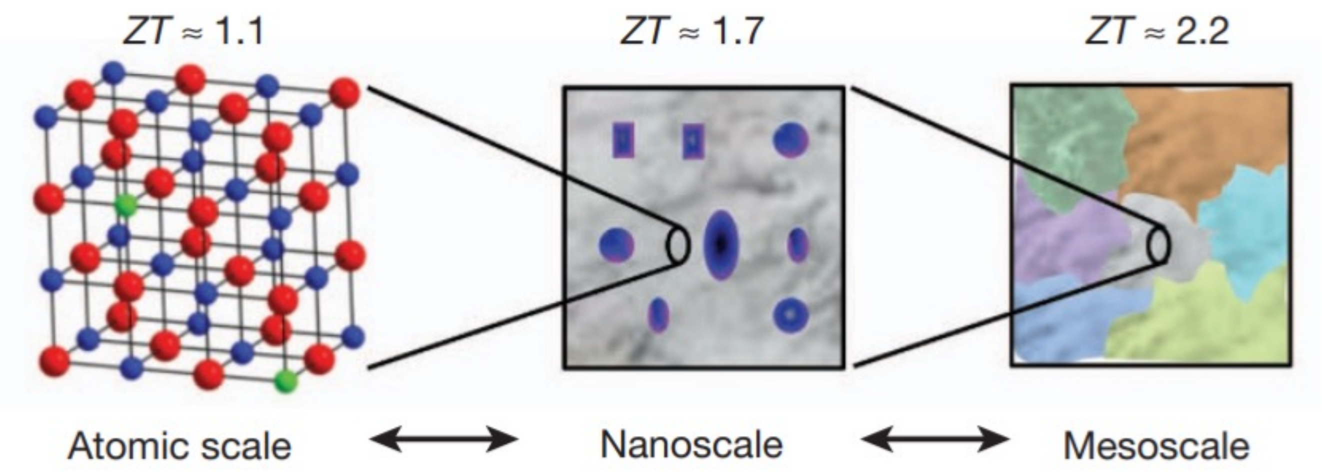
S. I. Kim et al., Science, **348**, 6230 (2015)

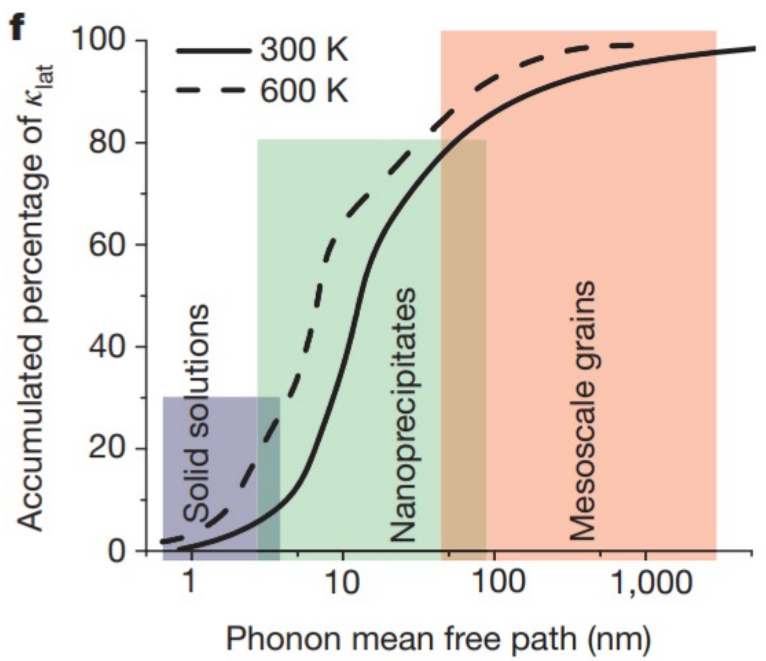
All-scale hierarchical architectures

LETTER

doi:10.1038/nature11439

High-performance bulk thermoelectrics with all-scale hierarchical architectures





K. Biswas *et al.*, Nature, 489, p414 (2012)

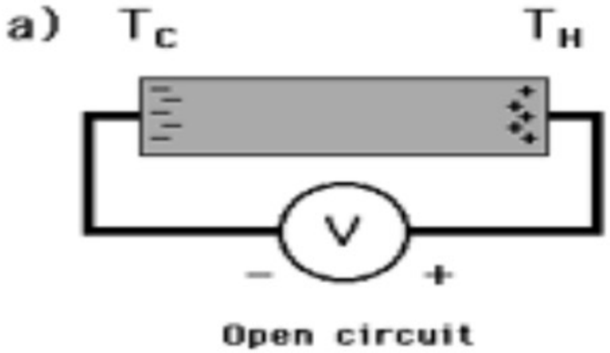
Thermoelectric Effect

The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice-versa in solid state semiconductors.

1. Seebeck Effect
2. Peltier Effect

Seebeck Effect

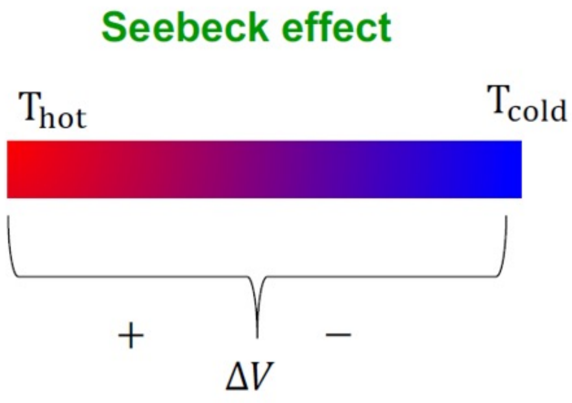
In 1821, Thomas Seebeck found that an electric current would flow continuously in a closed circuit made up of two dissimilar metals, if the junctions of the metals were maintained at two different temperatures.



$$S = -\frac{dV}{dT}$$

S: Seebeck Coefficient [V/K]

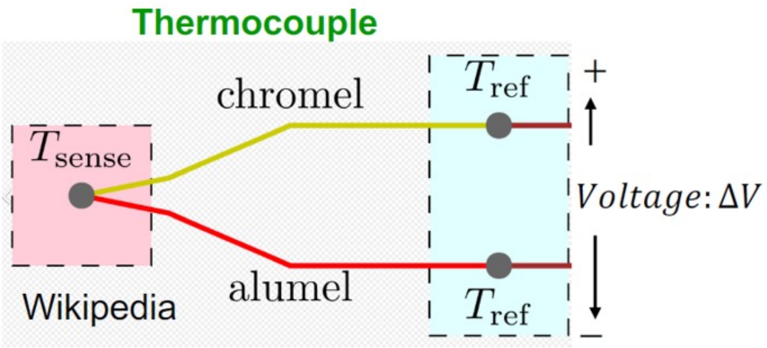
Seebeck Effect and Thermocouple



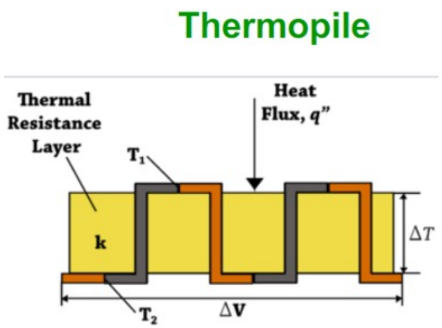
$$\Delta V = -S(T_{hot} - T_{cold})$$

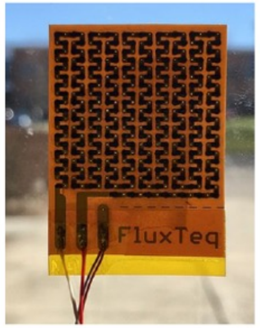
S is positive for p-type conductor (hole as the majority carrier);

S is negative for n-type conductor (electron as the majority carrier).



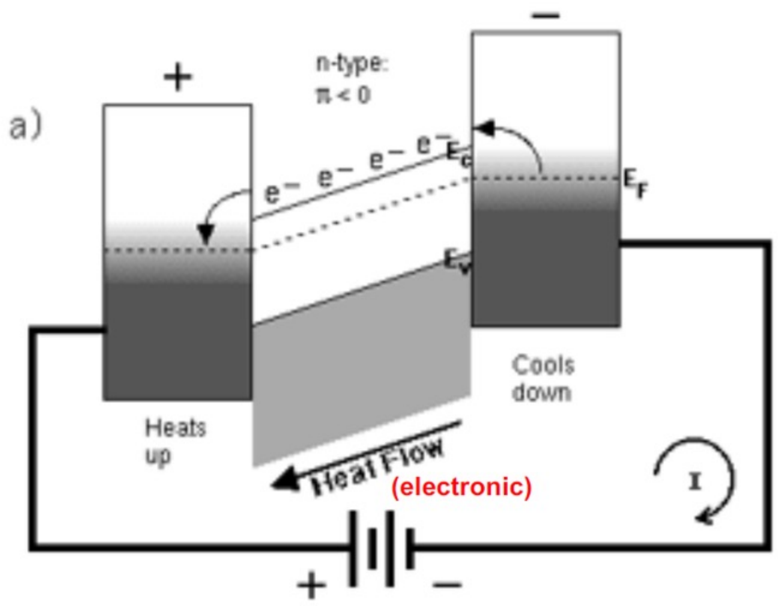
$$\begin{aligned}\Delta V &= \Delta V_{chromel} + \Delta V_{alumel}\\ &= -S_A\left(T_{ref} - T_{sense}\right) + \left[-S_B\left(T_{sense} - T_{ref}\right)\right]\\ &= \left(S_A - S_B\right)\left(T_{sense} - T_{ref}\right)\end{aligned}$$





Peltier Effect

In 1834, Jean Peltier found that an electrical current would produce a temperature gradient at the junction of two dissimilar metals.



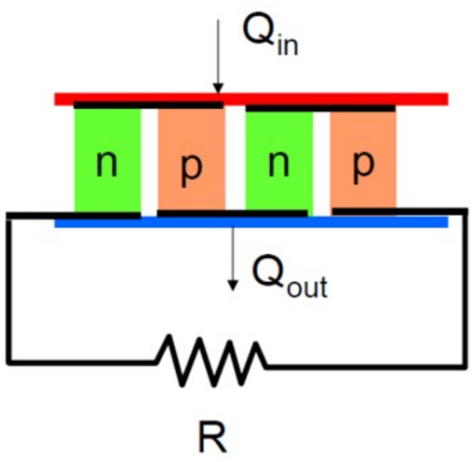
Jean-Charles-Athanase Peltier
(1785-1845)

$$\boldsymbol{Q = \Pi \cdot I}$$

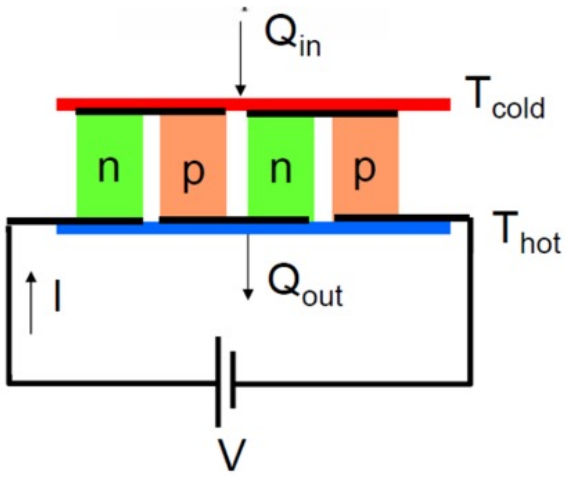
Q: Thermal current (Heat Flux)
I: Electrical current
Π: Peltier coefficient [V]

$$\Pi = S \cdot T$$

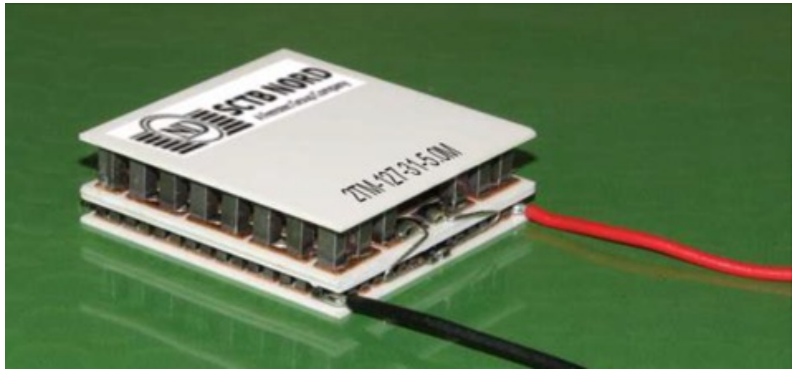
Thermoelectric Energy Conversion



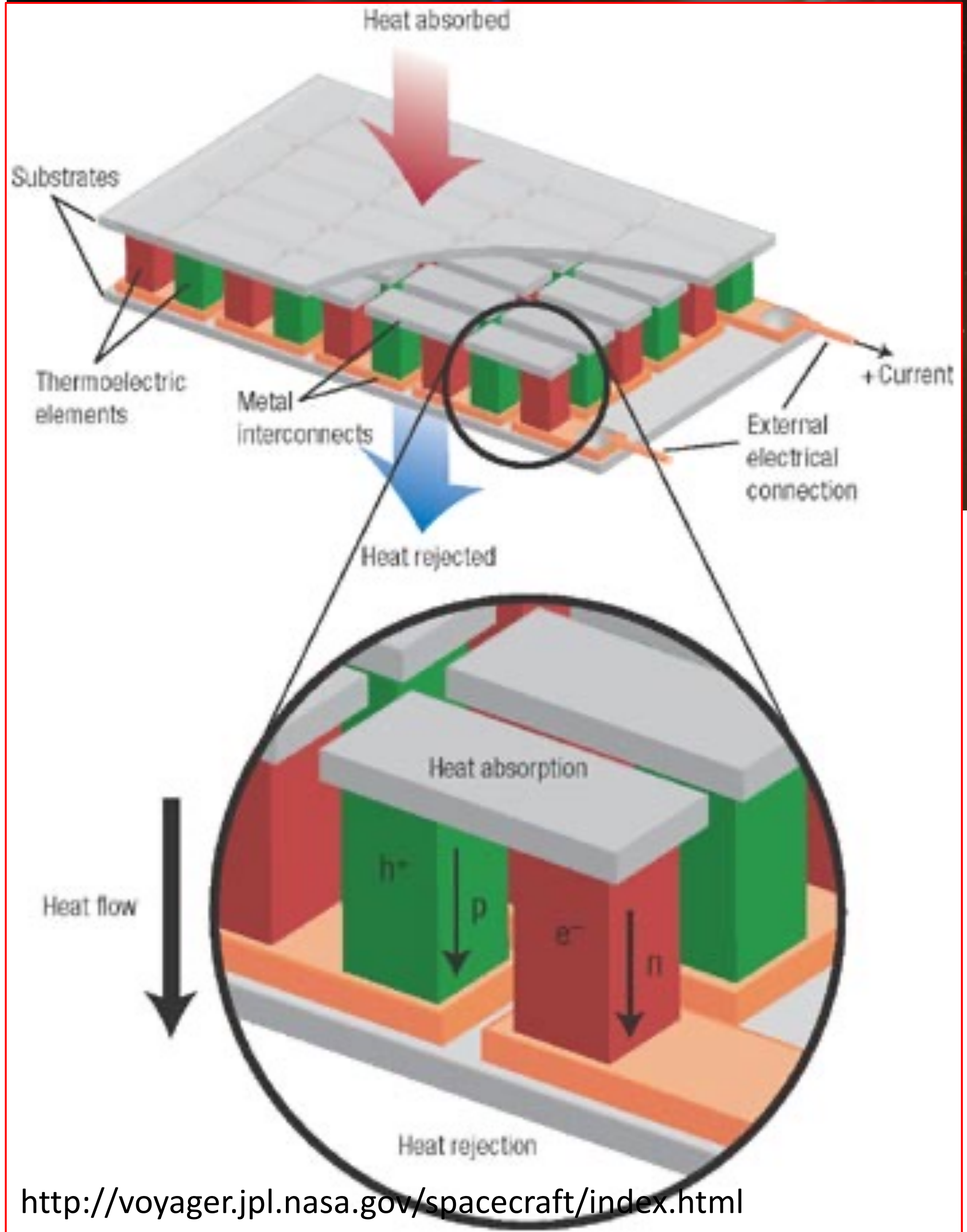
Power Generation



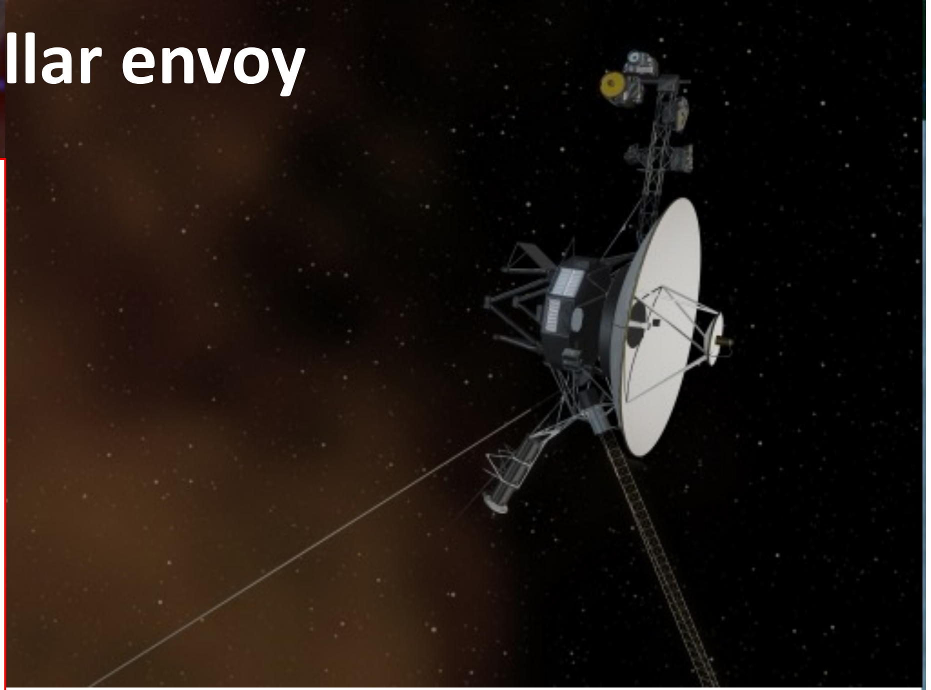
Refrigeration

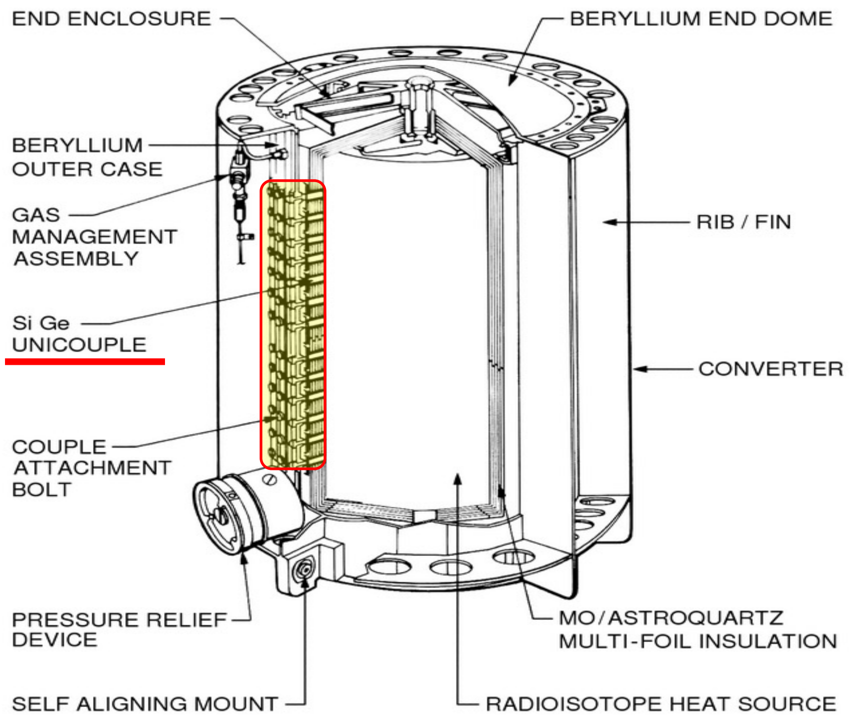


Voyager, human's first interstellar envoy



http://voyager.jpl.nasa.gov/spacecraft/index.html



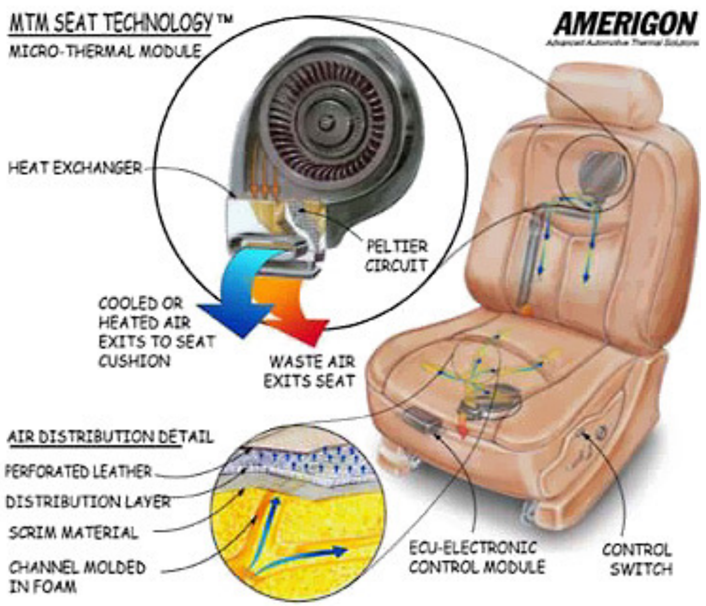


Applications

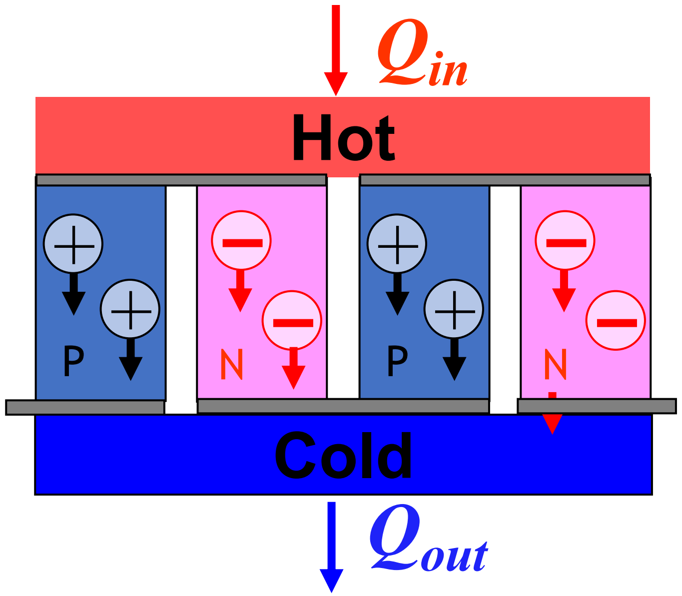
Wood Stove

Wine Cooler

Climate-controlled seat made by Amerigon for several auto makers



Efficiency and Figure of Merit (ZT)



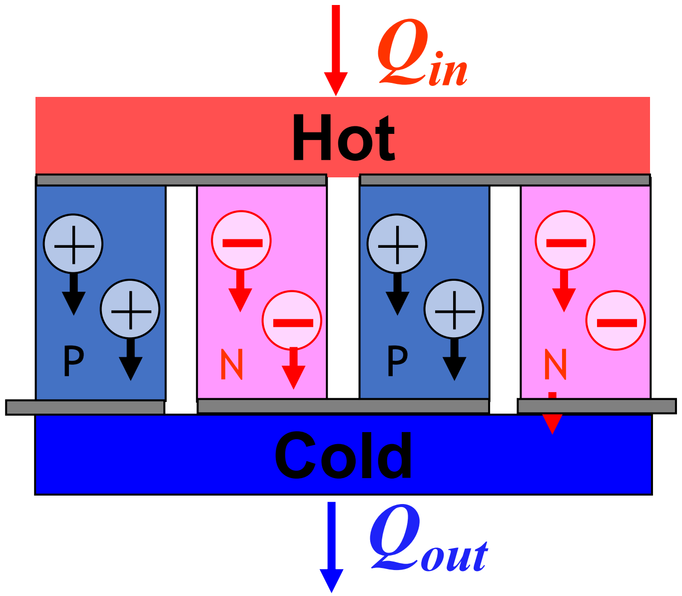
$$ZT = \frac{S^2 \sigma T}{k}$$

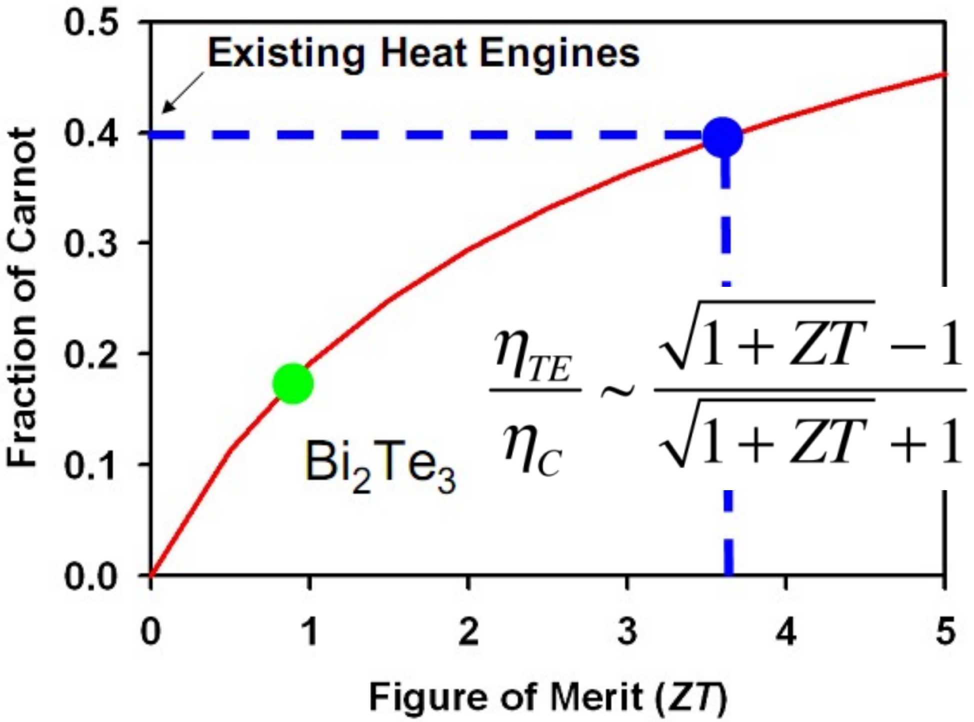
S: Seebeck (V/K)
σ: Electrical conductivity (S/m)
k: thermal conductivity (W/m-K)

$$k = k_e + k_L$$

T: Absolute Temperature (K)

Efficiency and Figure of Merit (ZT)





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

S: Seebeck (V/K)

σ: Electrical conductivity (S/m)

k: thermal conductivity (W/m-K)

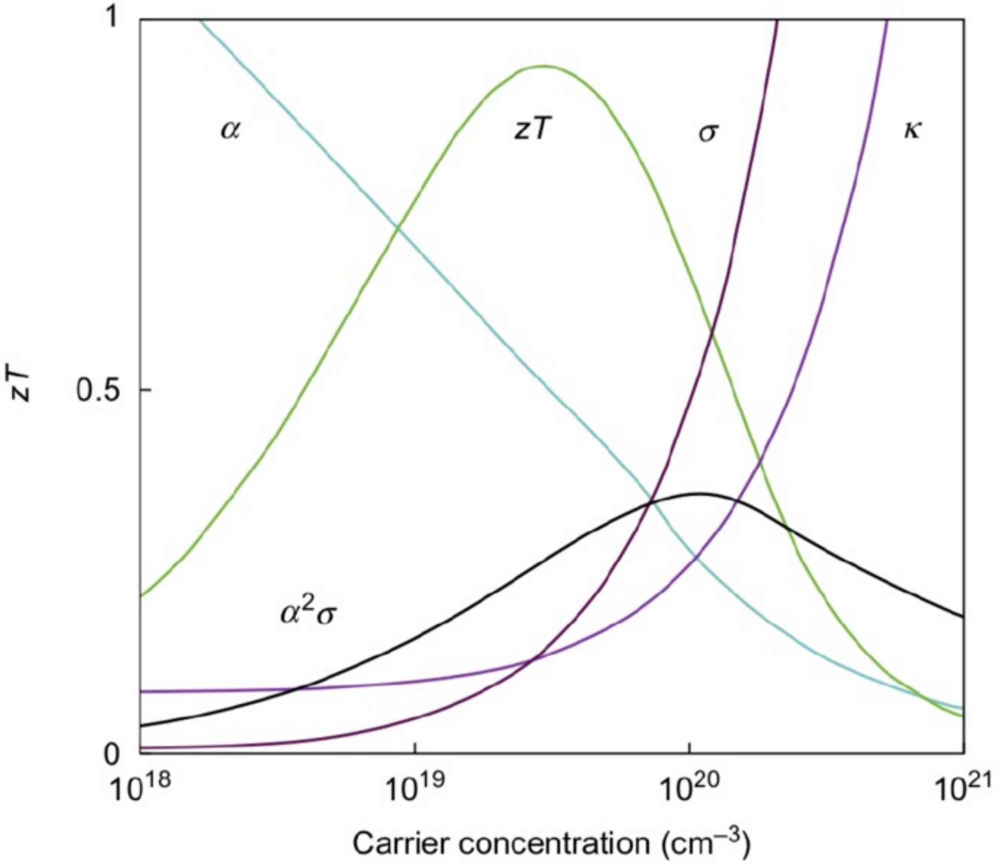
$$k = k_e + k_L$$

T: Absolute Temperature (K)

Commercial TE Materials:

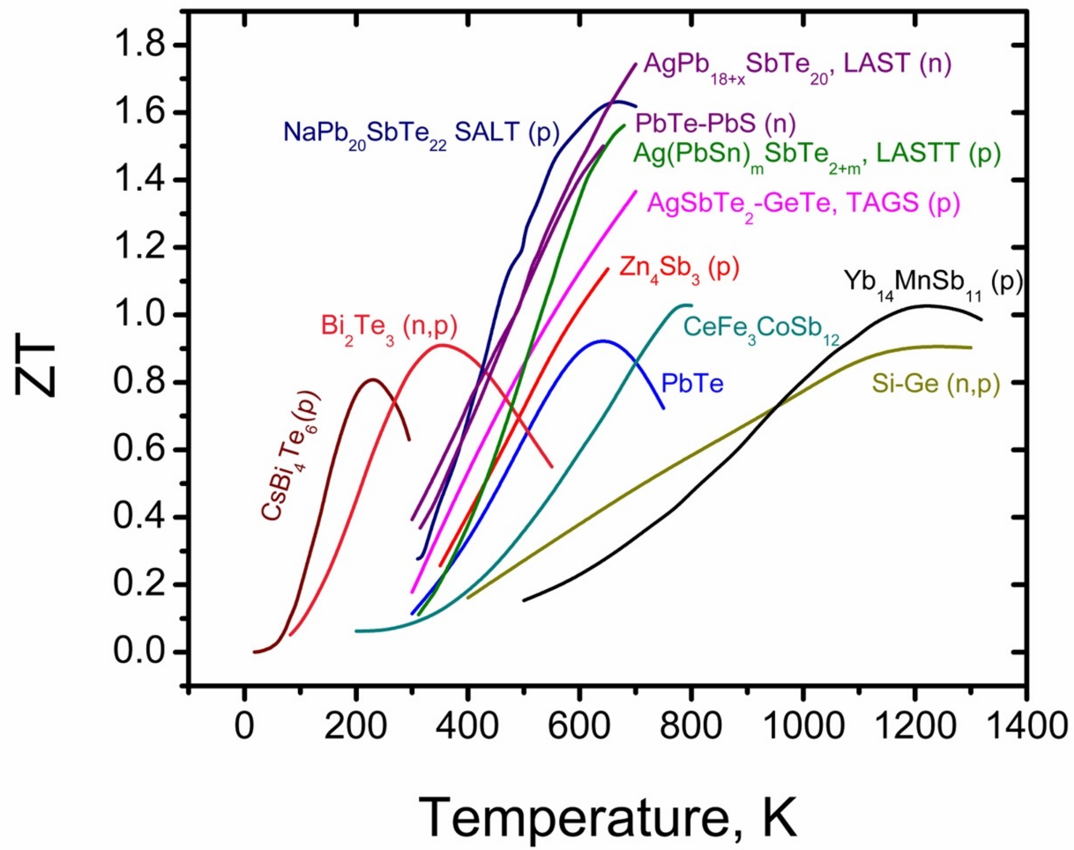
Bi_2Te_3, PbTe, SiGe, with ZT ~ 1

Optimal Carrier Concentration



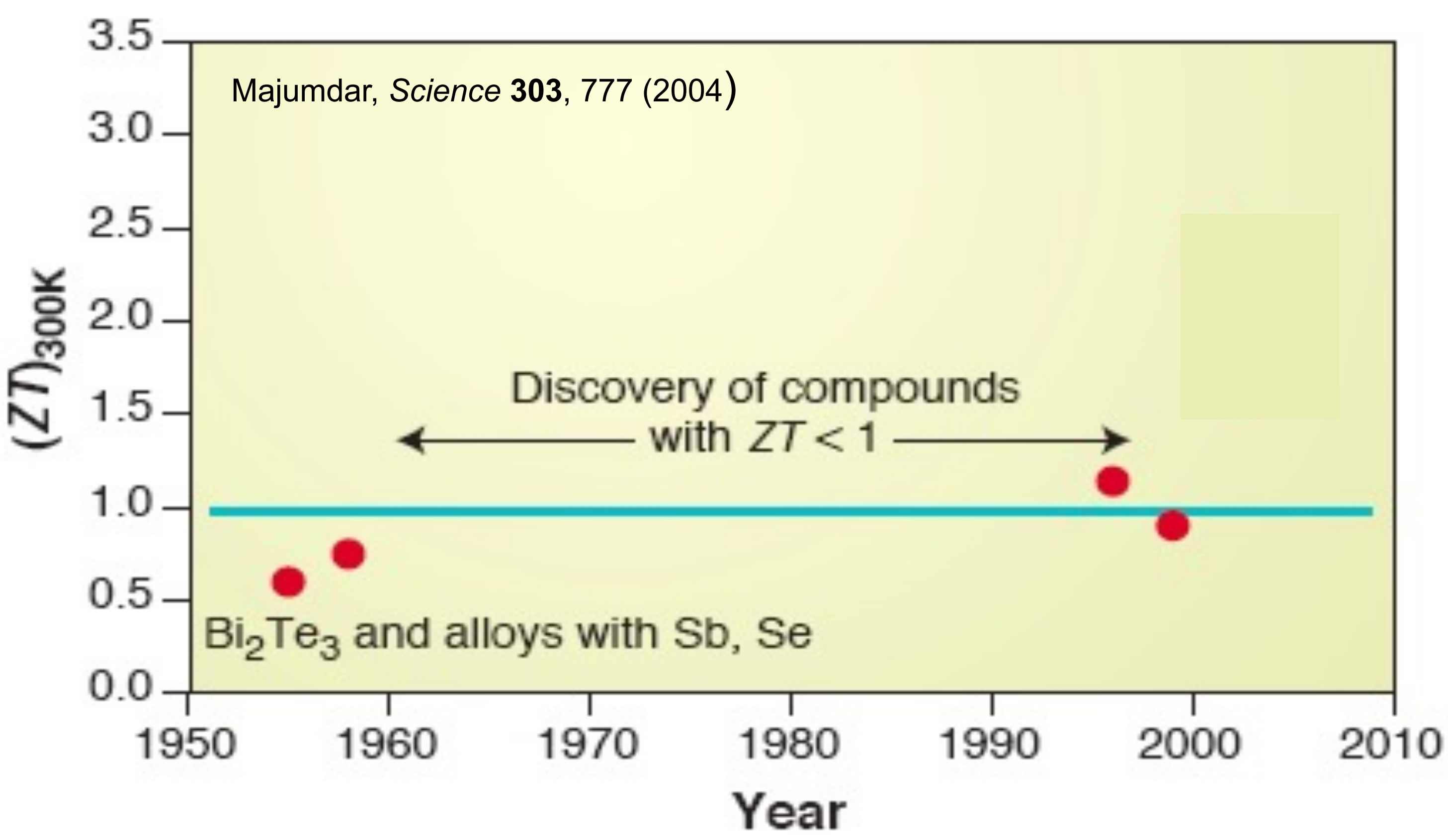
G.J. Snyder *et al*., Complex thermoelectric materials, Nat. Mater. 7(2), 105-114 (2008)

TE Materials at a Glance

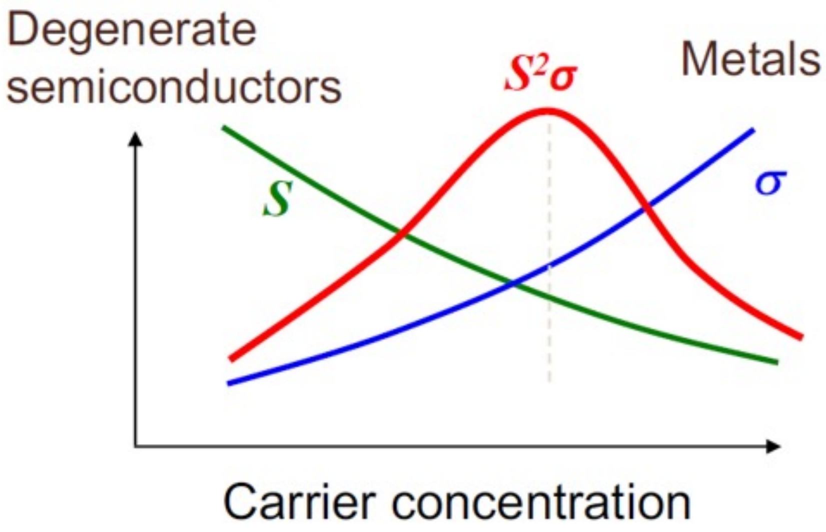


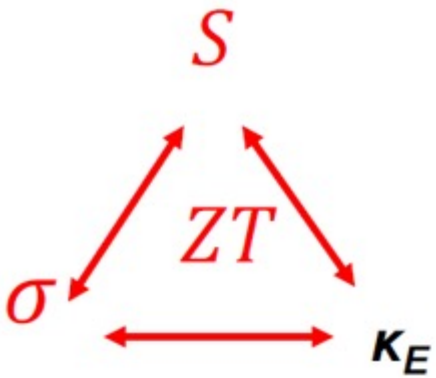
- **ZT < 2**
- **Mostly based on rare, expensive, or toxic elements.**
  e.g.: Te, Pb, Co...
- **Commercial TE module:**
  ~ 20$/Watt
  (Bi_2Te_3: ~ 1000 $/kg)

History


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

Optimize Each Parameters for High ZT



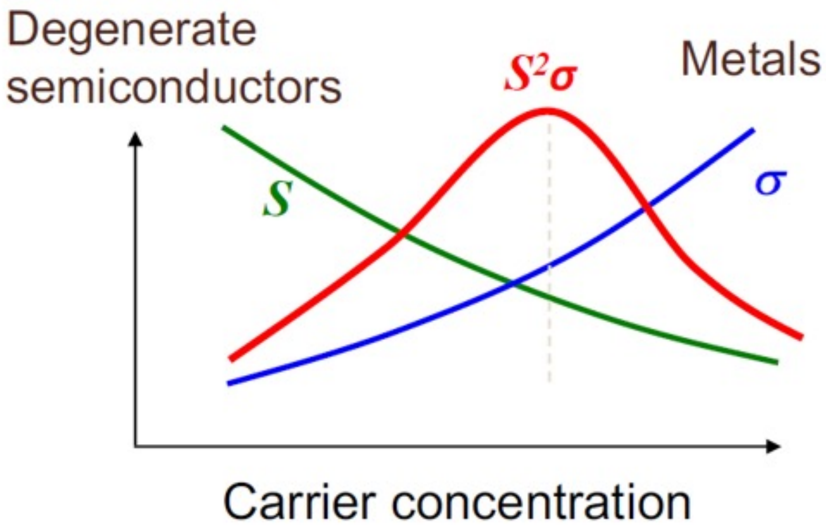


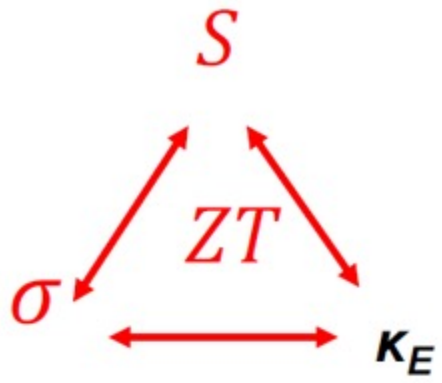
From Wiedermann-Franz Law,

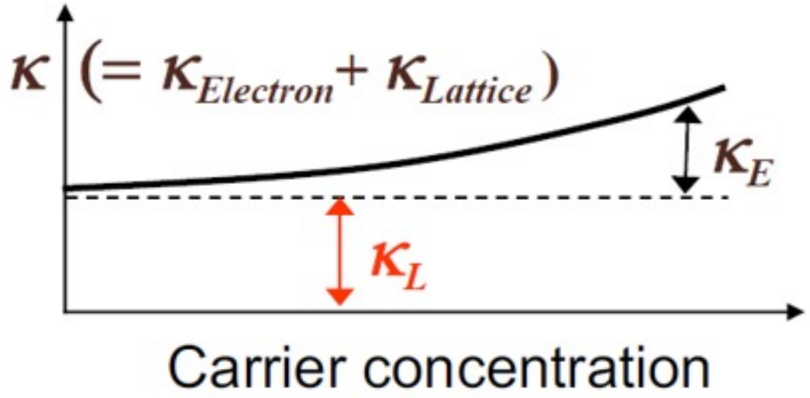
$$\kappa_e = L\sigma T$$

D.M. Rowe, Thermoelectrics Handbook:Macro to Nano, Chapter 1 (2006)

Optimize Each Parameters for High ZT







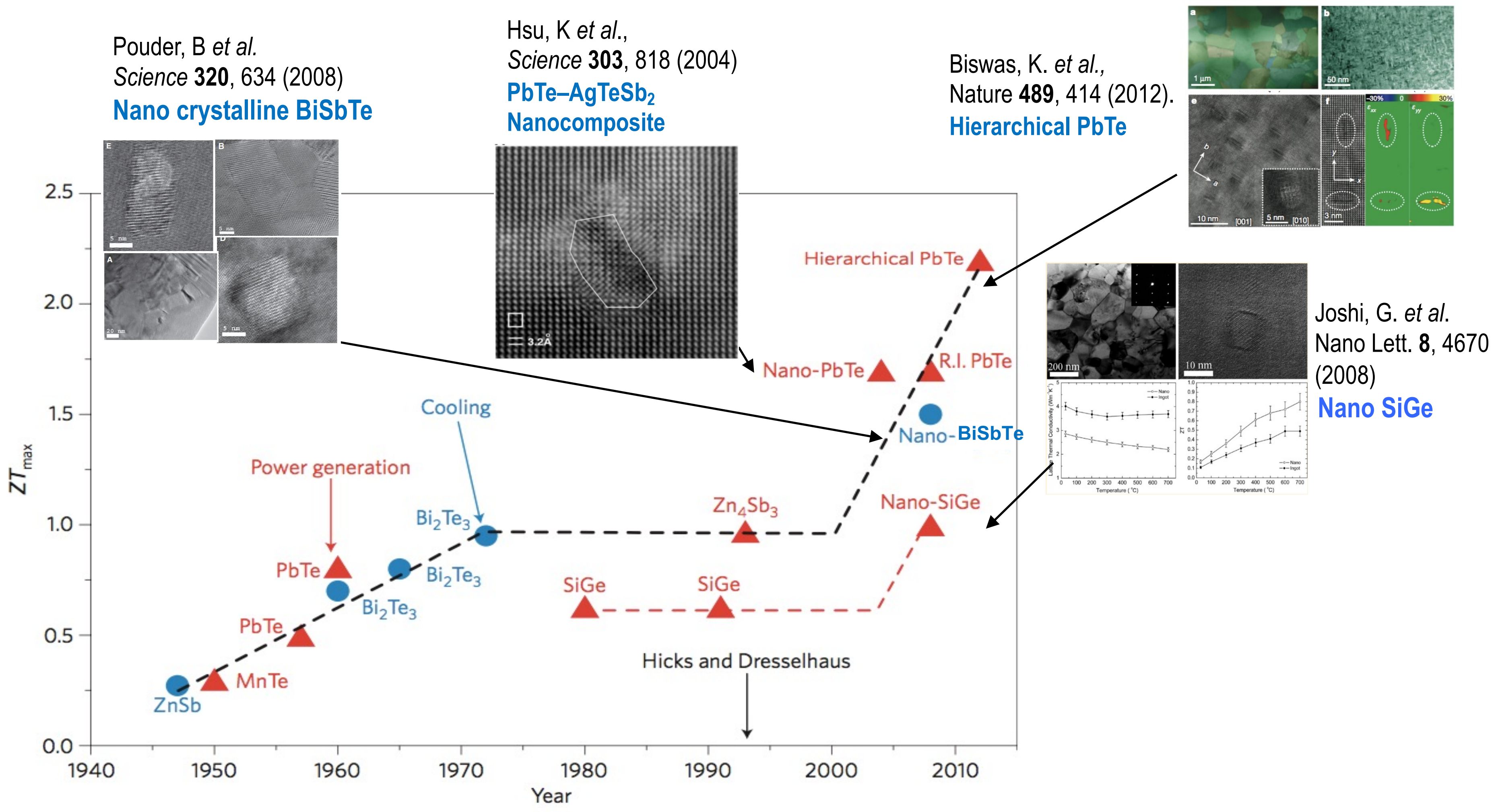
From Wiedermann-Franz Law,

$$\kappa_e = L\sigma T$$

Lattice conductivity (κ_L) is the only "independent" parameter.

D.M. Rowe, Thermoelectrics Handbook:Macro to Nano, Chapter 1 (2006)

Recent ZT Trends in TE Materials



- Significant improvement in ZT has been obtained in recent years.
- Most of high ZT reports were achieved by reducing the lattice thermal conductivity.

J.P. Heremans, et al., Nature Nanotechnology **8,** 471 (2013)

Localized Thermal Control

HEALTH

Why your office is so cold, and how to deal with it

The summer freeze is upon us.

The big chill is here. *DepositPhotos*

https://www.popsci.com/office-summer-cold/

Wearable Cooling Devices

WEARABLES

Sony is crowdfunding a wearable air conditioner for personal climate control

https://newatlas.com/sony-reon-pocket-air-conditioner/60797/

HEAT

Summary

- Nanostructures have been shown to be effective in reducing lattice thermal conductivity, owing to the broad mean free path spectra of phonons in semiconductors.

- The synergistic effect of impurity scattering and boundary scattering lowers the thermal conductivity below the alloy limit.

- Significant improvement in the thermoelectric figure of merit ZT, most notably in nanostructured materials, during the past 15 years. The field is moving steadily forward in the foreseeable future, and the implementation of material development into the device applications seems to be a key factor.

Questions?

Dr. Sunmi Shin
(mpeshin@nus.edu.sg)

Shin *et al*., “Chapter 14.3 Low dimensional thermoelectric materials”,
Book chapter in Advanced Thermoelectrics: Materials, Contacts, Modules, and Systems.