Functional properties

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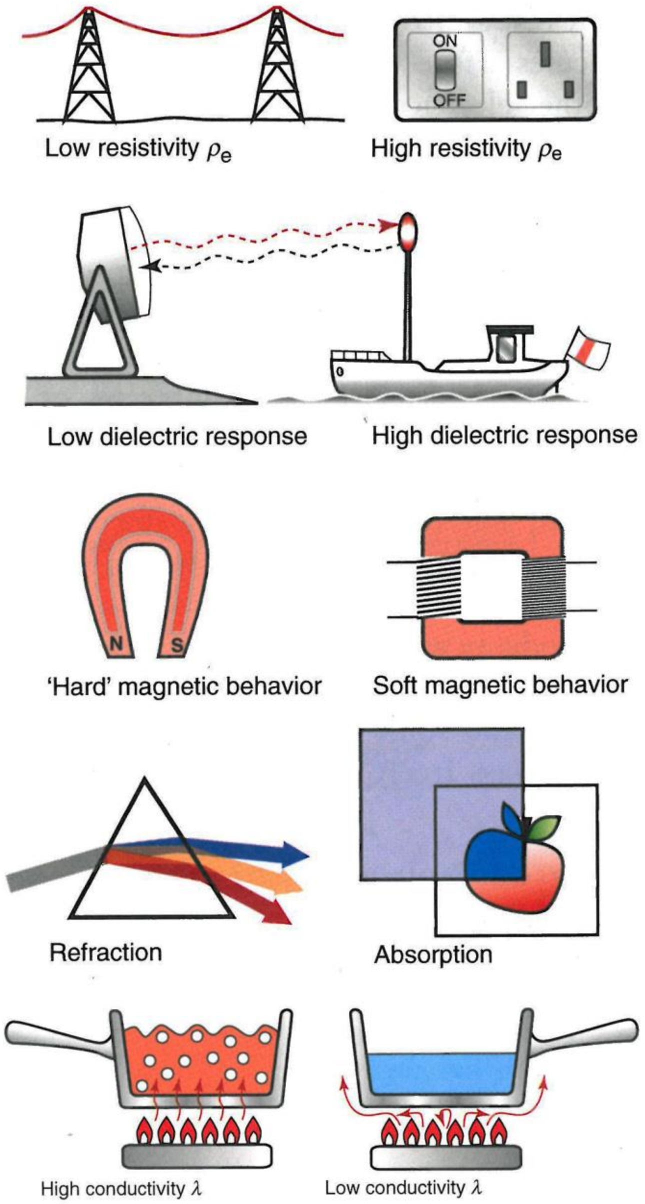
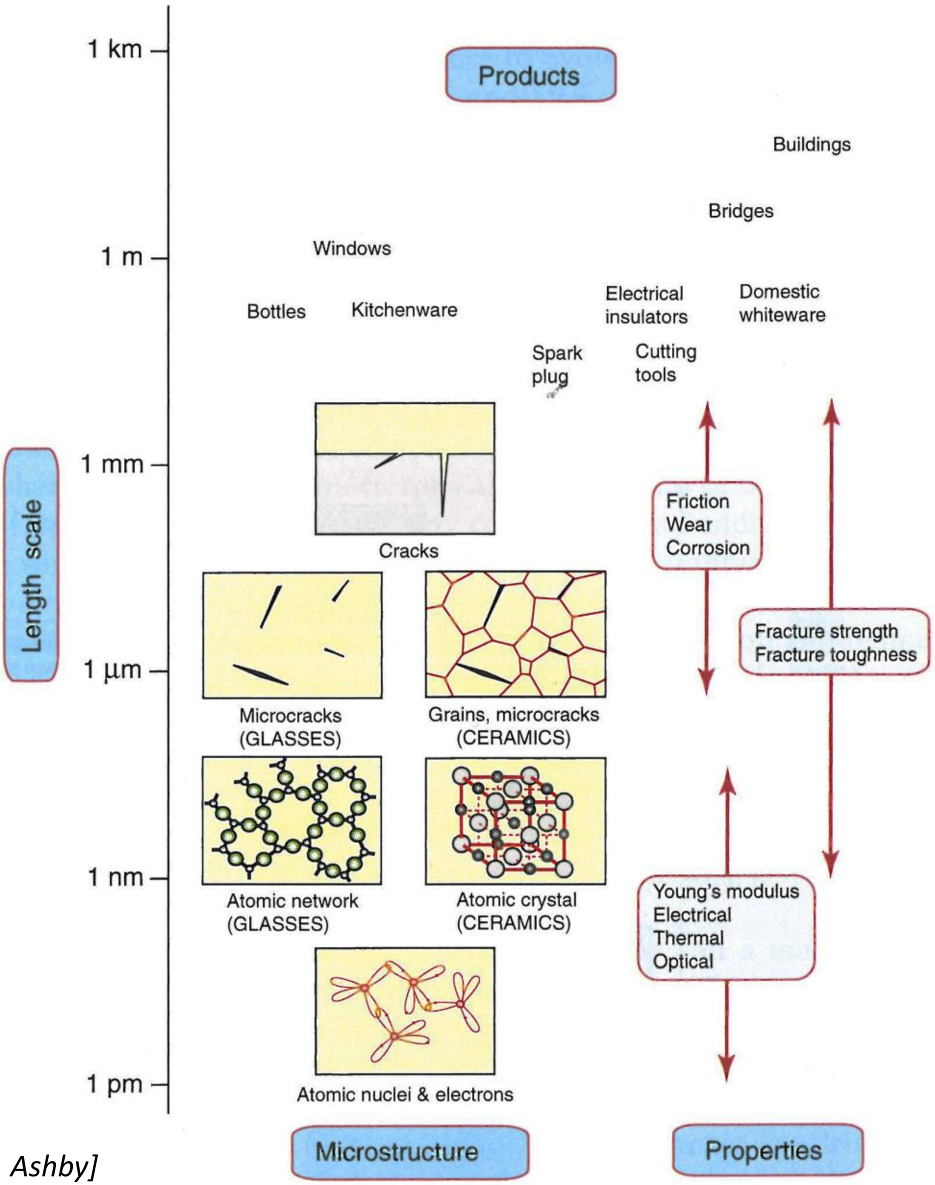
Action Nationale de Formation en Métallurgie

22-25/10/2012 - Aussois

Functional properties and microstructural features in ceramics

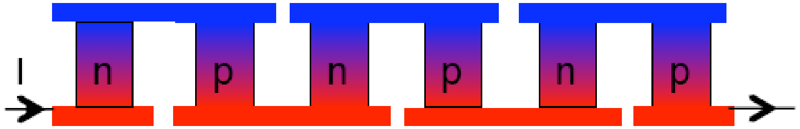




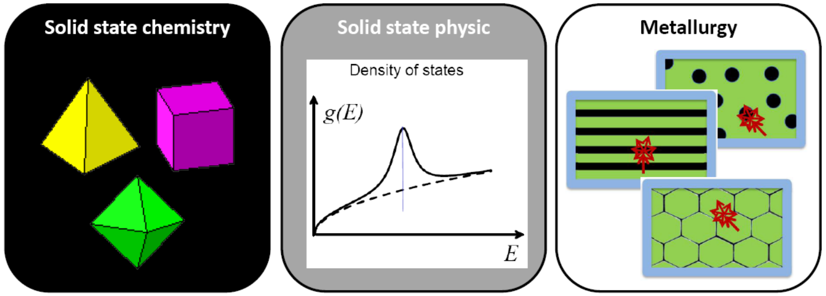
[from M. Ashby]

Plan

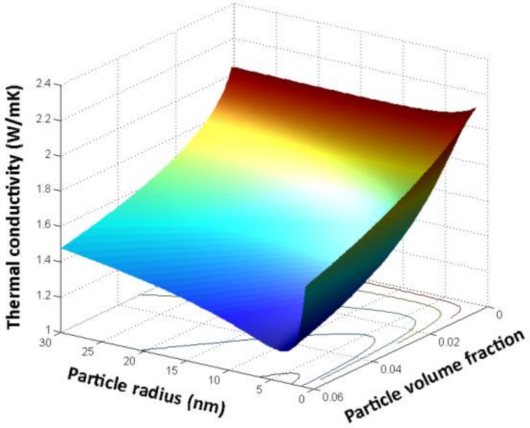
❶ Thermoelectricity : applications, principle & materials



❷ How to tune transport properties ?

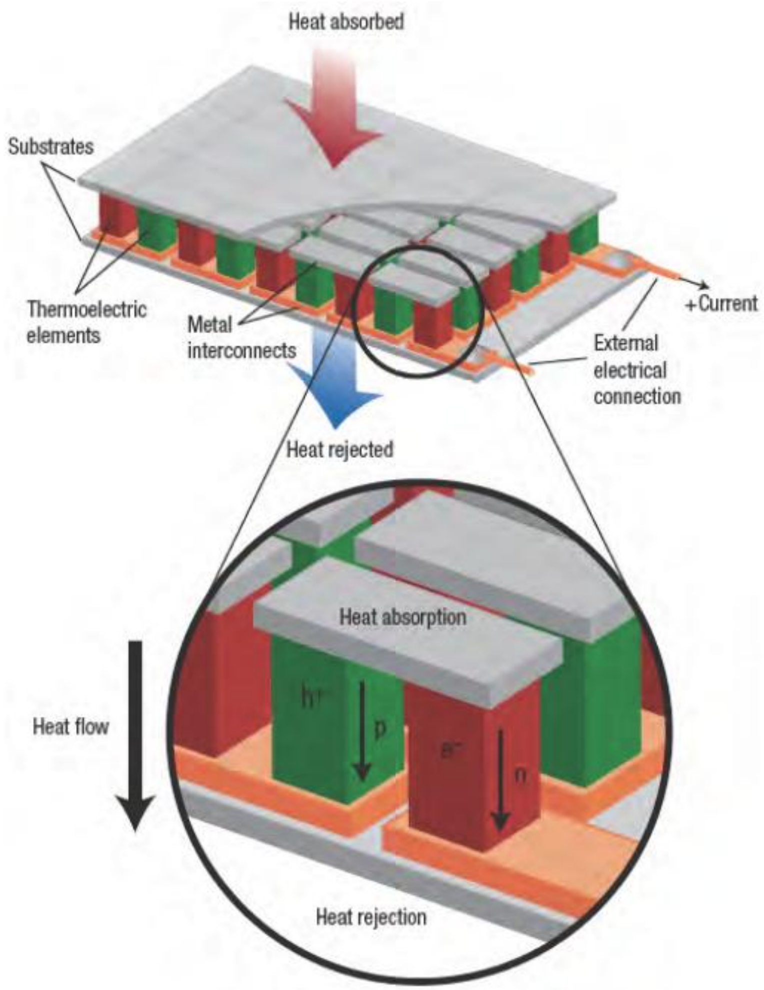


❸ TE materials by design (microstructure engineering)

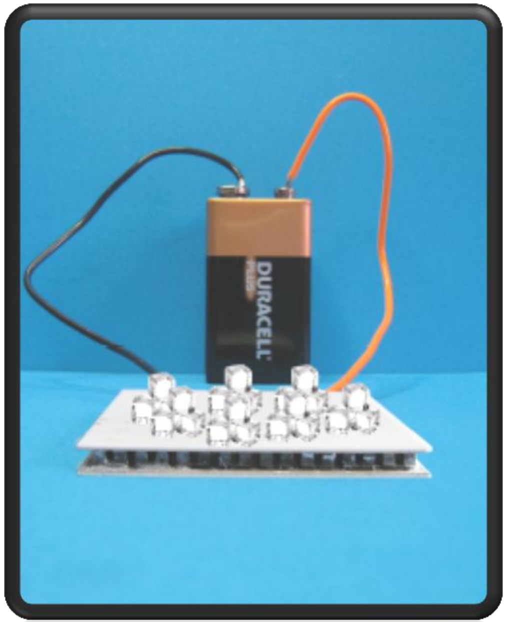


① **Thermoelectricity -** Applications, principle & materials

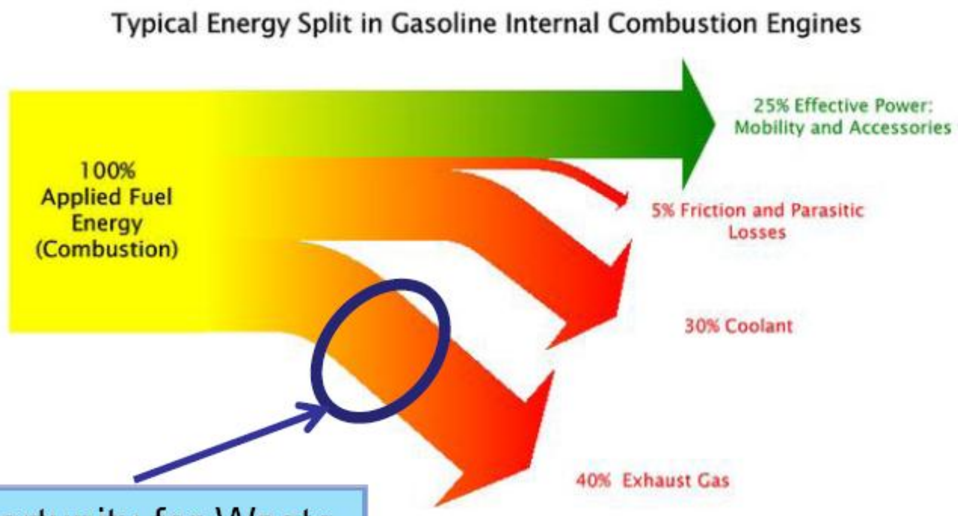
Power generation



Cooling



① **Thermoelectricity -** Applications, principle & materials

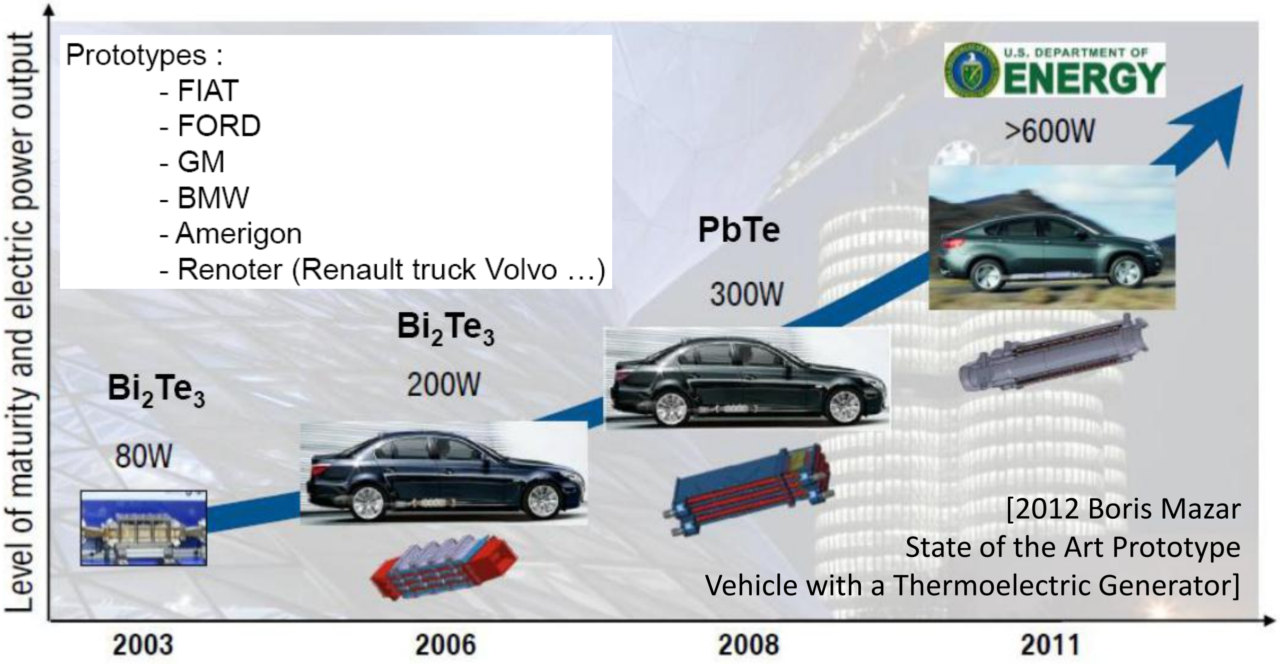


Opportunity for Waste Heat Recovery with Thermoelectrics

Thermal power from exhaust = 10 kW

5% efficiency → 500 W_{el}

Reduction of 7 g/km CO_2

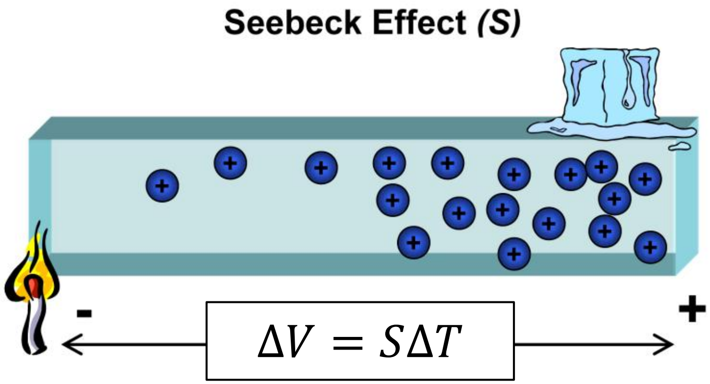


Prototypes :
- FIAT
- FORD
- GM
- BMW
- Amerigon
- Renoter (Renault truck Volvo …)

[2012 Boris Mazar
State of the Art Prototype
Vehicle with a Thermoelectric Generator]

① **Thermoelectricity -** Applications, principle & materials

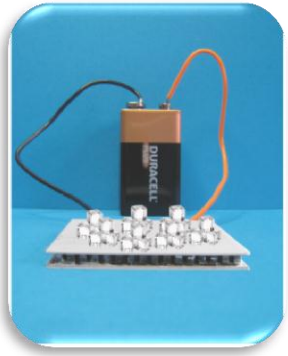
Thomas J. Seebeck (1770-1831)

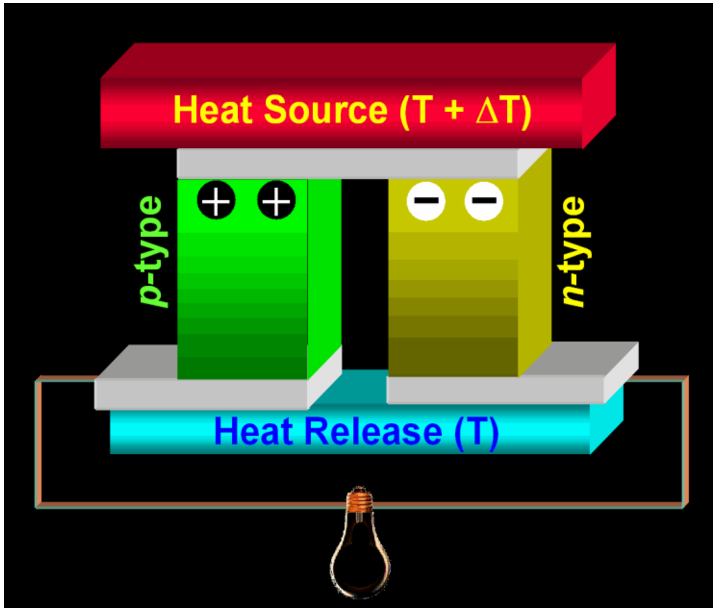


Seebeck Effect *(S)*

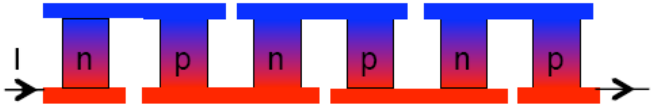
$$\Delta V = S\Delta T$$

J.C. Athanase Peltier (1785-1854)





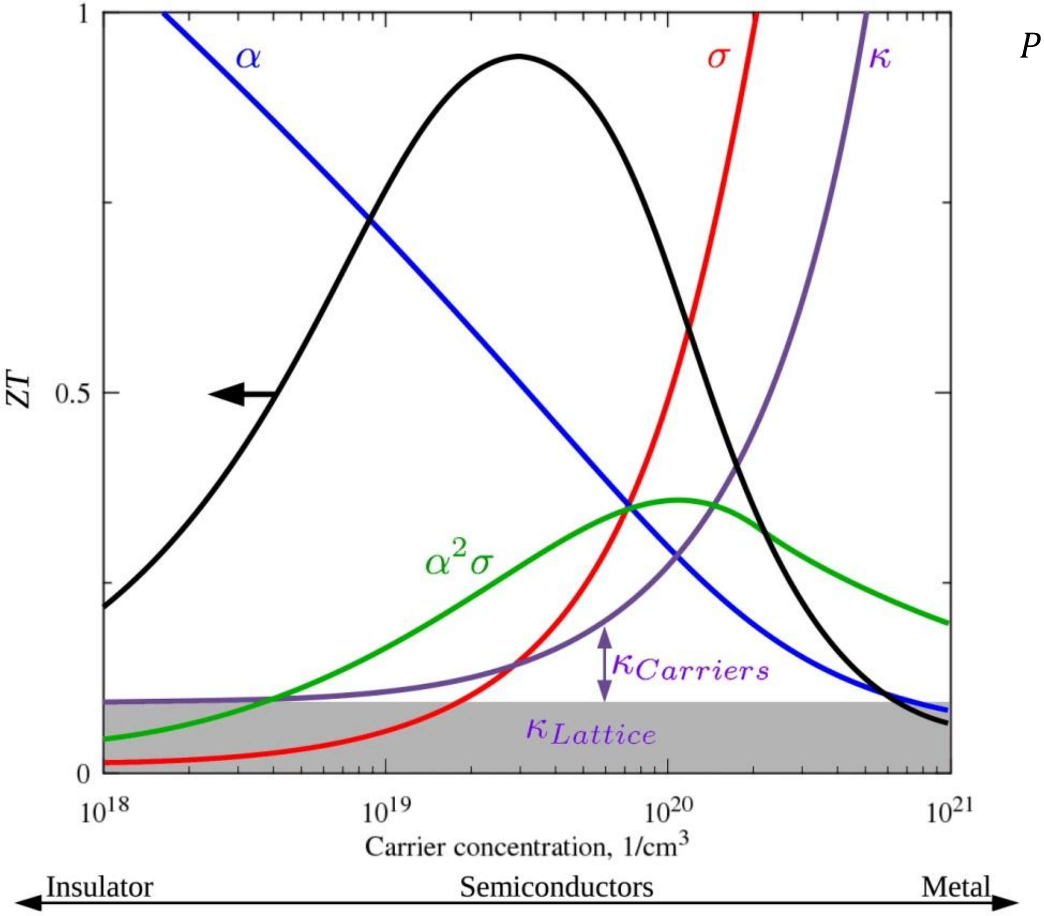
Series-Parallel Arrangement

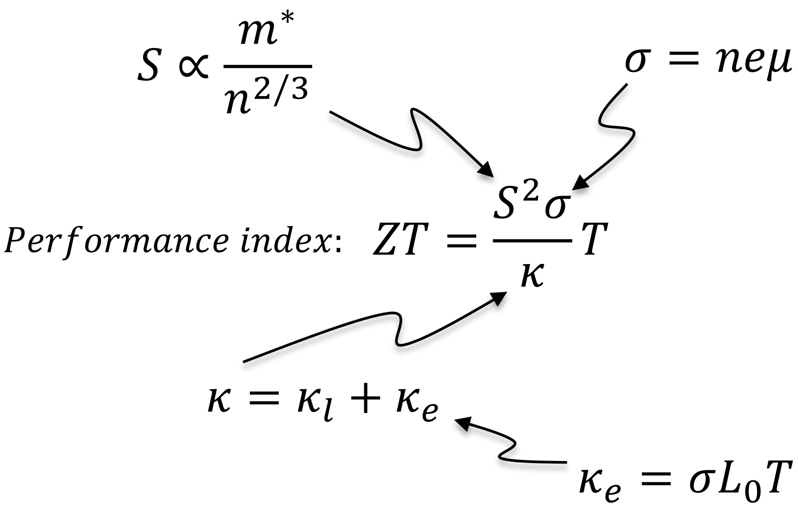


$$U \propto NS\Delta T \qquad P \propto N\sigma S^2\Delta T^2$$

$$\eta_{max} = \frac{T_c - T_f}{T_c}\,\frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + \frac{T_c}{T_f}}$$

Squaring a circle





$$S \propto \frac{m^*}{n^{2/3}}$$

$$\sigma = ne\mu$$

$$Performance\ index:\ \ ZT = \frac{S^2\sigma}{\kappa}T$$

$$\kappa = \kappa_l + \kappa_e$$

$$\kappa_e = \sigma L_0 T$$

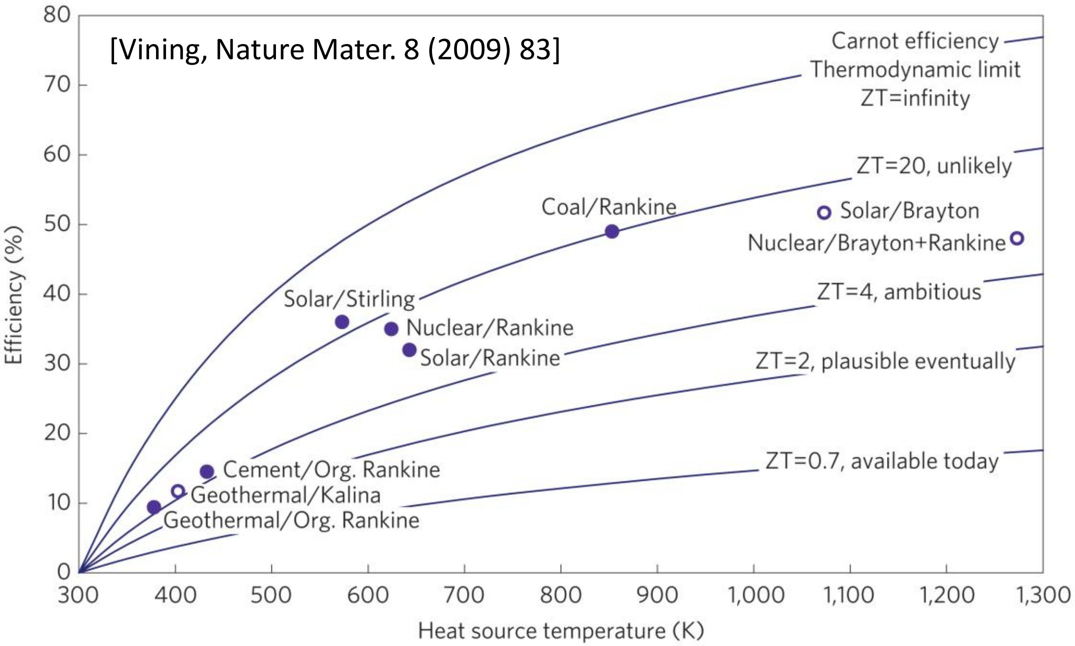
<u>Ideal material:</u>

high S, high σ and low κ
but when S increases ➔ σ decreases
and when σ increases ➔ S decreases
κ increases

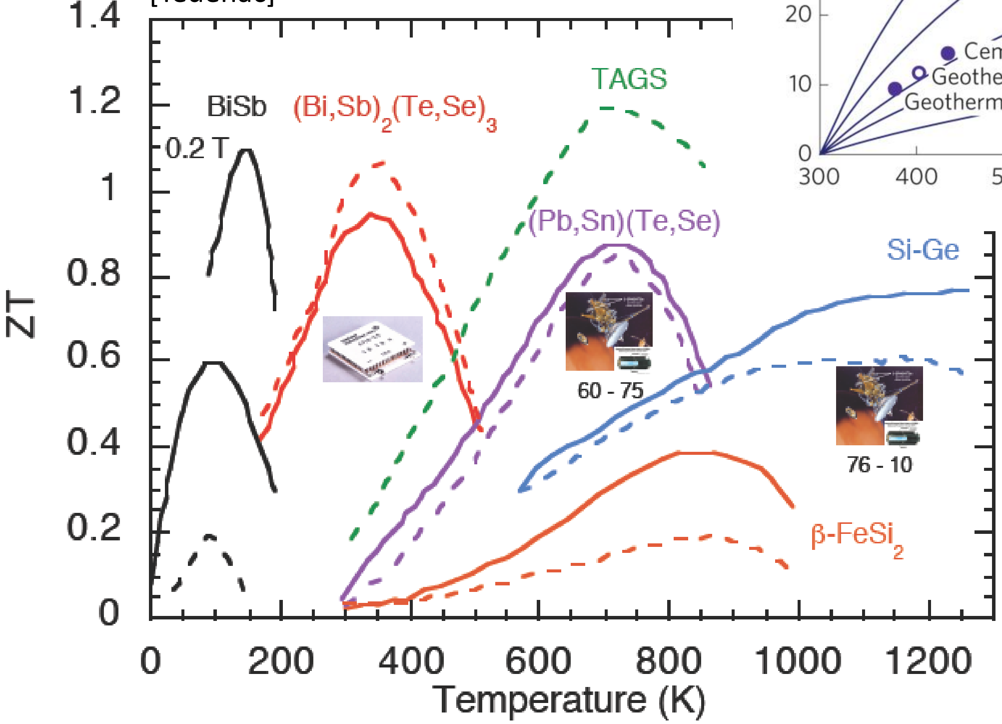
Best compromise:
semiconductors with high mobility and high effective mass of the carrier, and low lattice thermal conductivity

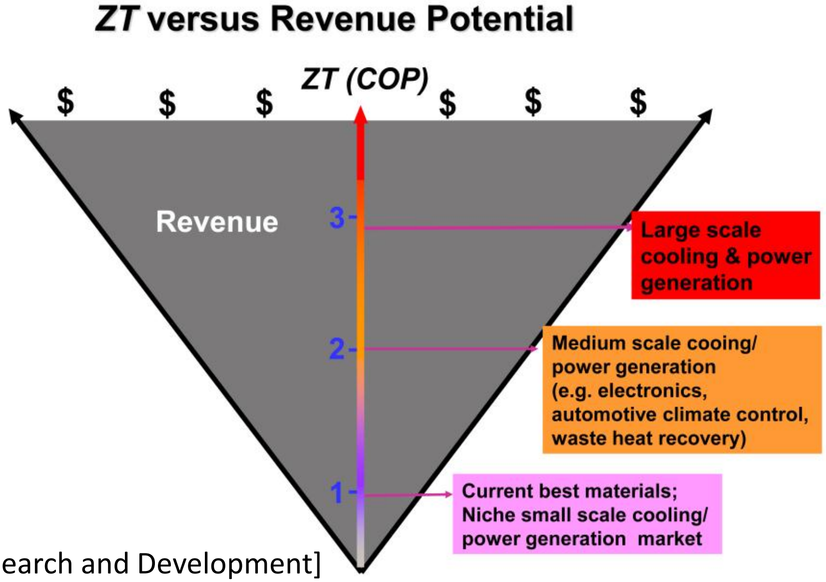
① Thermoelectricity - Applications, principle & materials

From 1950 to 1990 : conventional TE materials


[Vining, Nature Mater. 8 (2009) 83]

[Tedenac]




***ZT* versus Revenue Potential**

Large scale cooling & power generation

Medium scale cooing/ power generation (e.g. electronics, automotive climate control, waste heat recovery)

Current best materials; Niche small scale cooling/ power generation market

[M. Subramanian,
DuPont Central Research and Development]

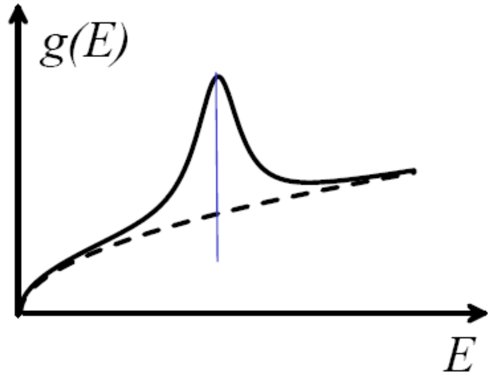
② Main strategies to tune transport properties

$$ZT = \frac{S^2\sigma}{\kappa}T = \frac{S^2}{L_0}\left(1+\frac{\kappa_{ph}}{\kappa_{el}}\right)^{-1}$$

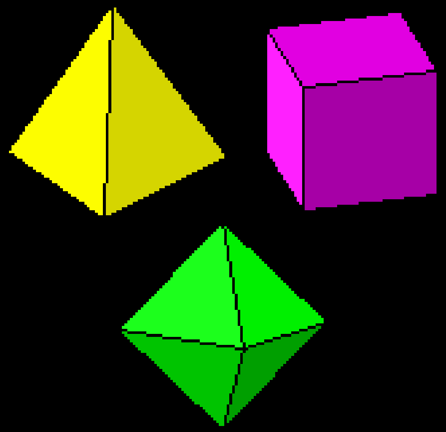
$$\kappa_l = \tfrac{1}{3}C\upsilon\,\lambda_{\mathrm{ph}} = \tfrac{1}{3}C\upsilon^2\tau_{ph}$$

Solid state physics

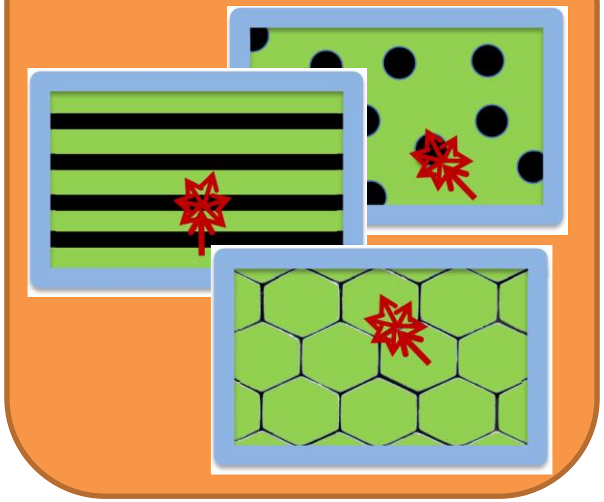
Density of states



Solid state chemistry



Metallurgy

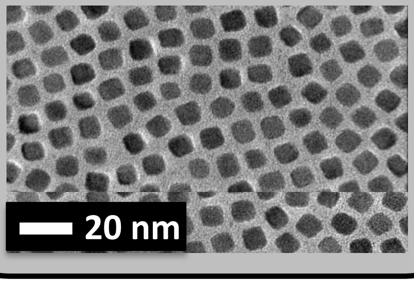


Materials science

(Bottom-up app.)

Colloidal nanocrystals

↳ Nanocomposites

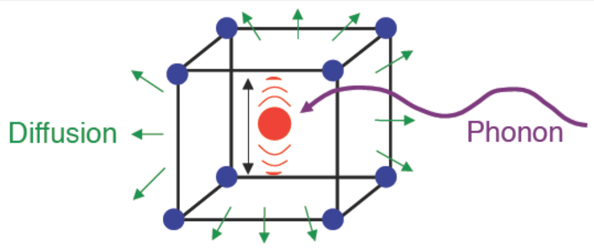


② Solid state chemistry → phonon glass electron crystal

Phonon Glass Electron Crystal

[G. Slack, 1994]

Nanocages and Rattlers

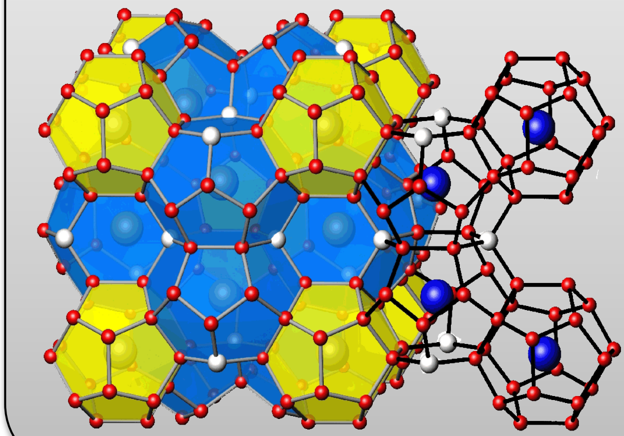


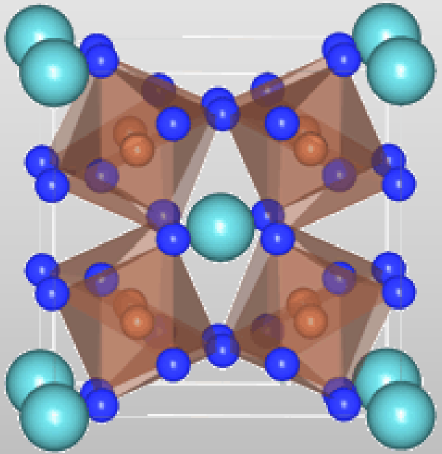
Large unit cell and structural complexity

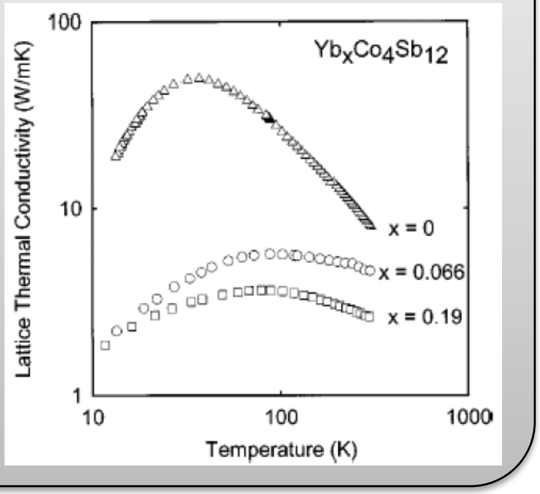
$$\kappa_l = \frac{k_B \upsilon \lambda_{\mathrm{ph}}}{V}$$

Clathrates, $X_2Y_6E_{46}$ (X & Y guest atoms encapsulated in polyhedra of E = Si, Ge or Sn)

Filled skutterudites, $\square_2T_8X_{24}$ (guest atom inside a 12-coordinated cage surrounded by 8 TX_6 octahedra)

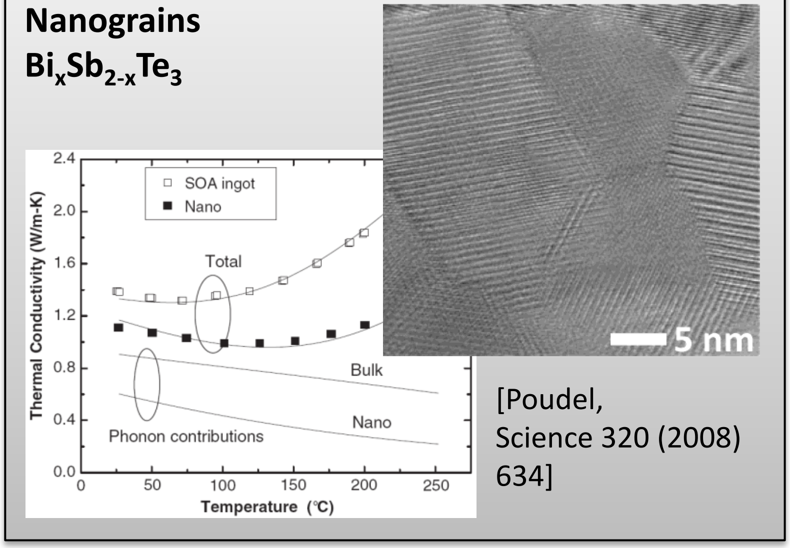






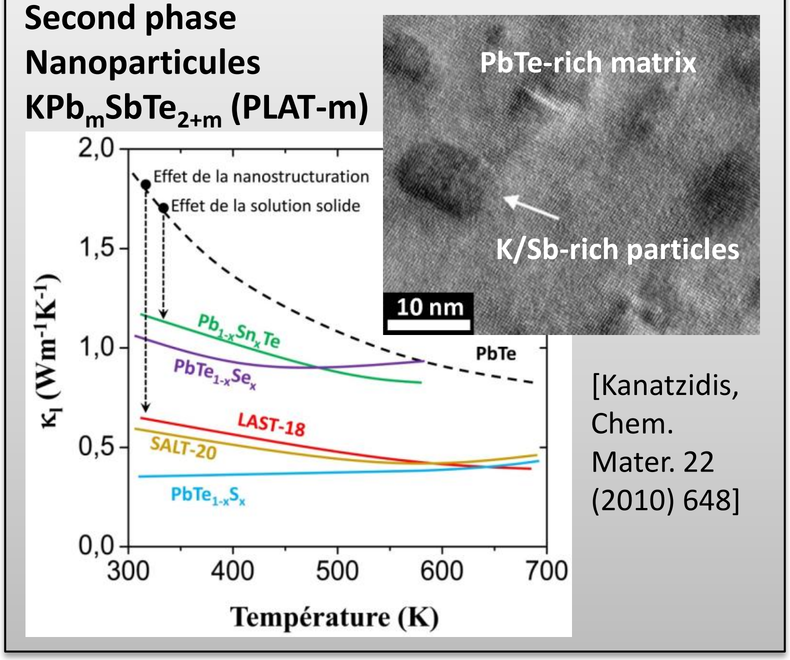
② Metallurgy → nano to mesoscale engineering

Nanograins
$Bi_xSb_{2-x}Te_3$

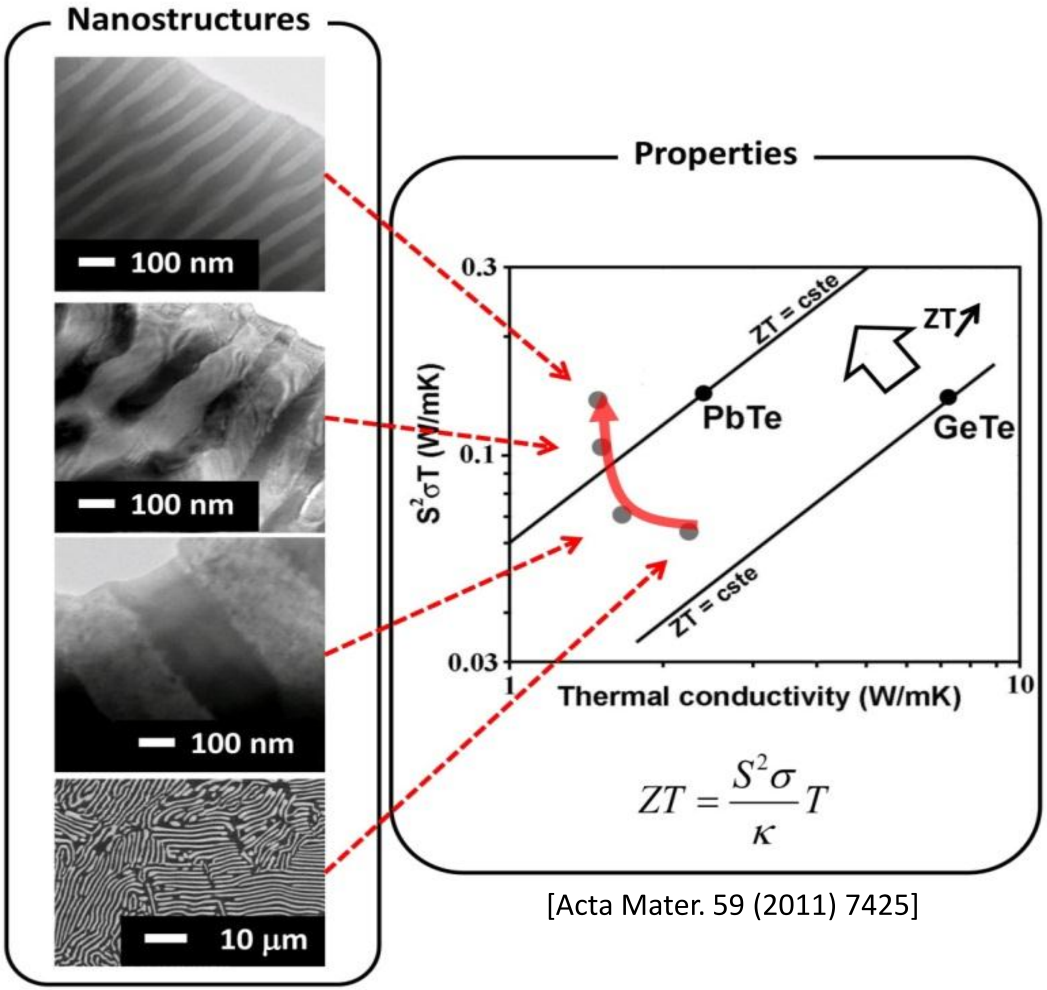


[Poudel, Science 320 (2008) 634]

Second phase
Nanoparticules
KPb_mSbTe_{2+m} (PLAT-m)



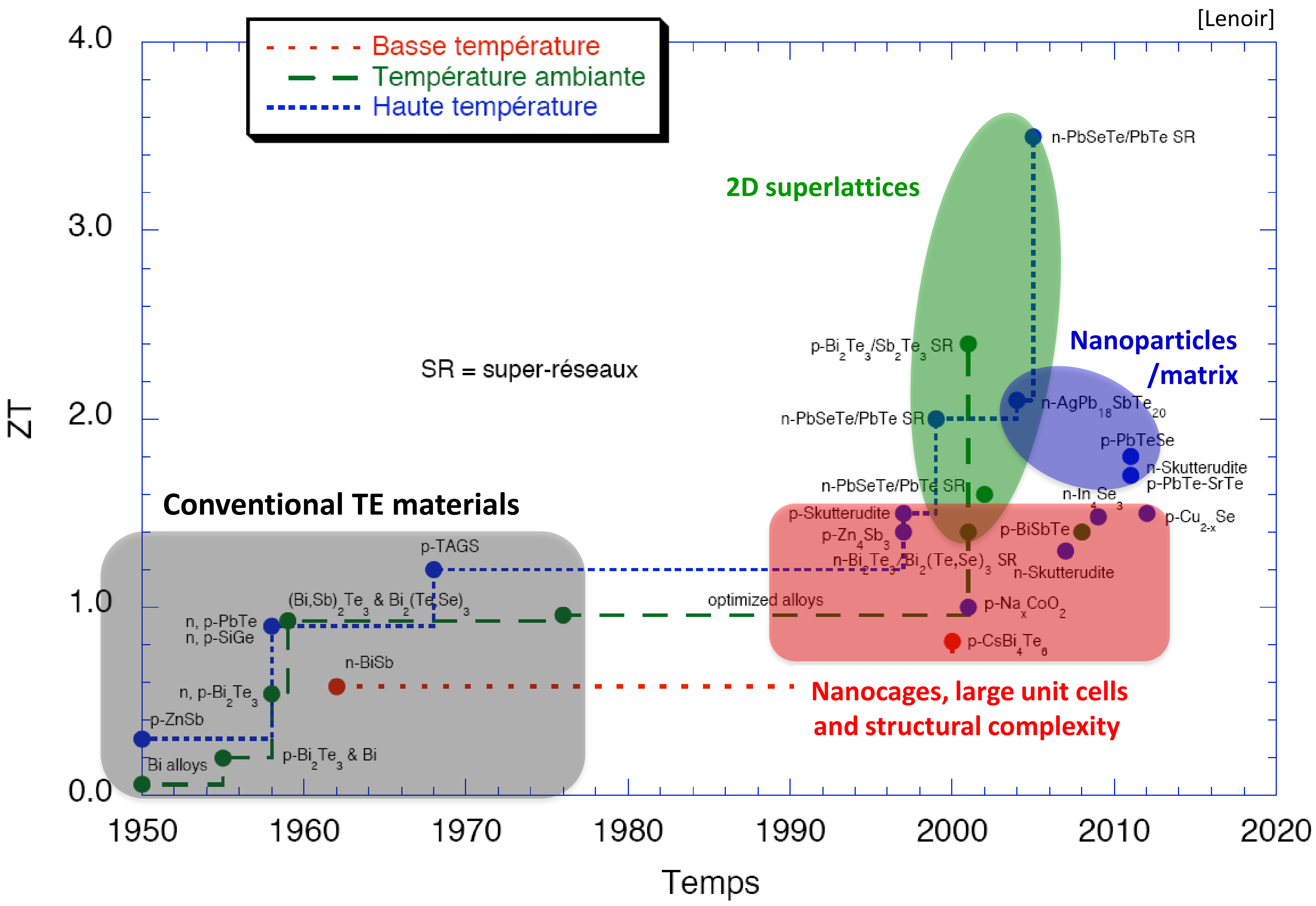
[Kanatzidis, Chem. Mater. 22 (2010) 648]



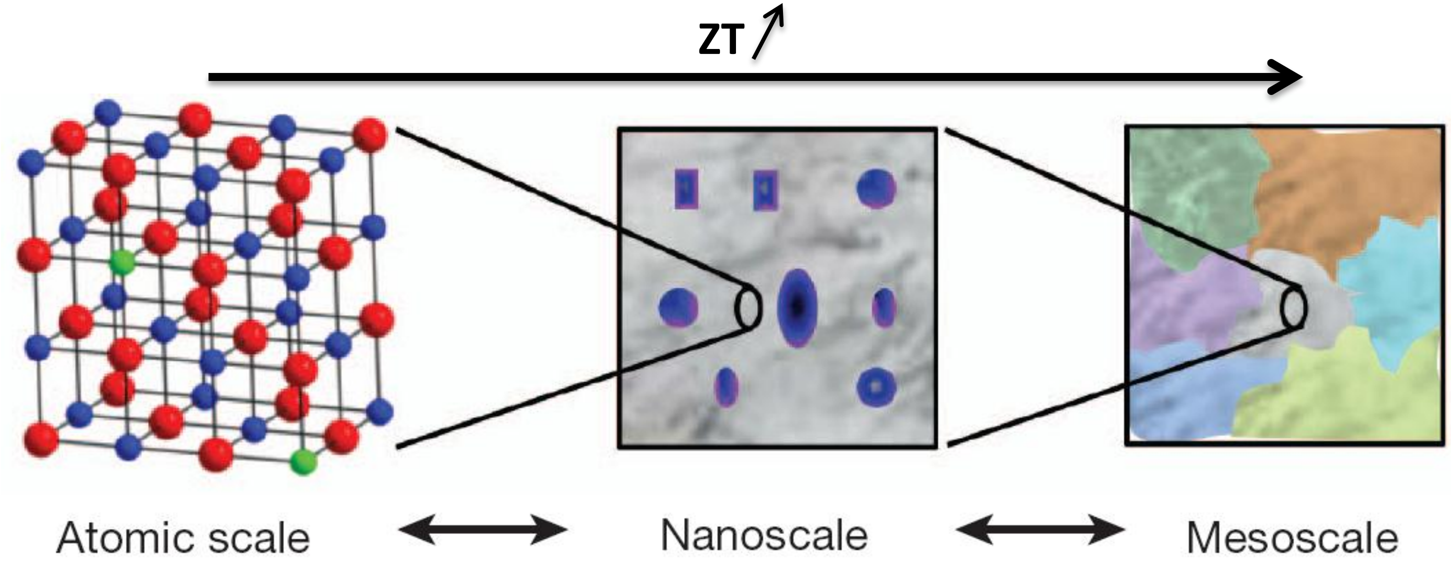
$$ZT = \frac{S^2\sigma}{\kappa}T$$

[Acta Mater. 59 (2011) 7425]

② Main strategies to tune transport properties



③ Toward a "material by design" approach

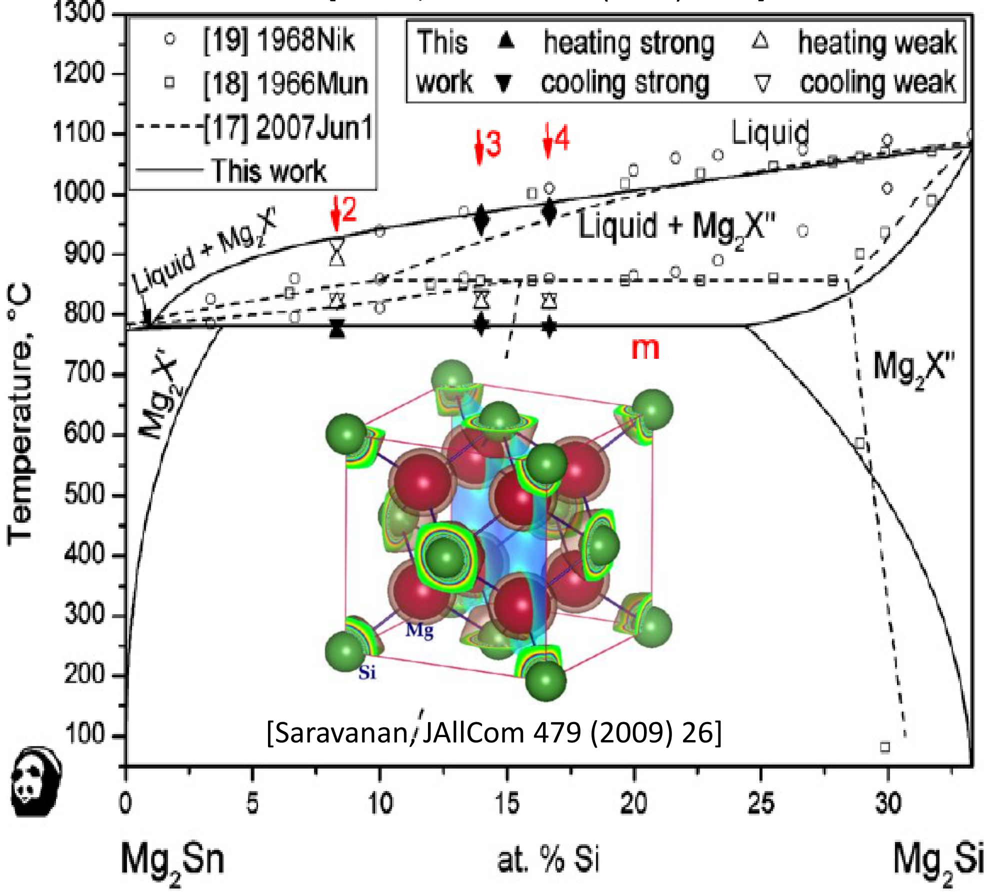


[Figure from Biswas, Nature 489 (2012) 414]

Need a predictive tool that couples
a description of the microstructure genesis and evolution
to the various contributions to ZT

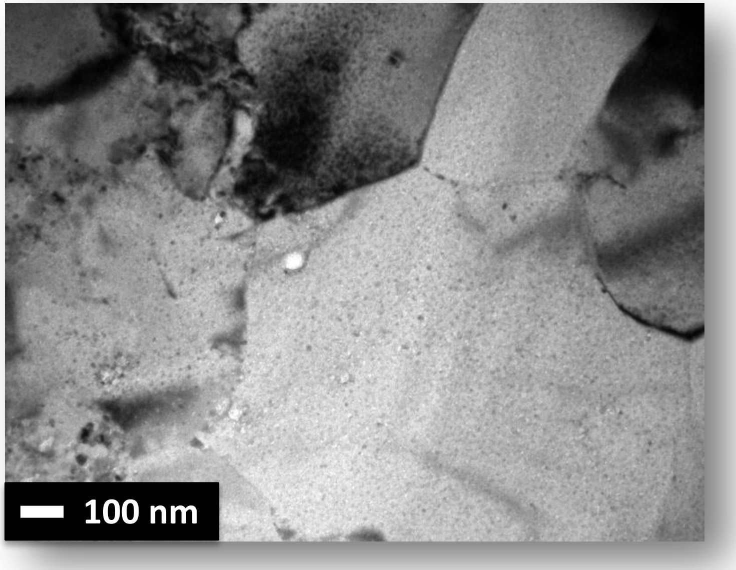
③ Toward a "material by design" approach

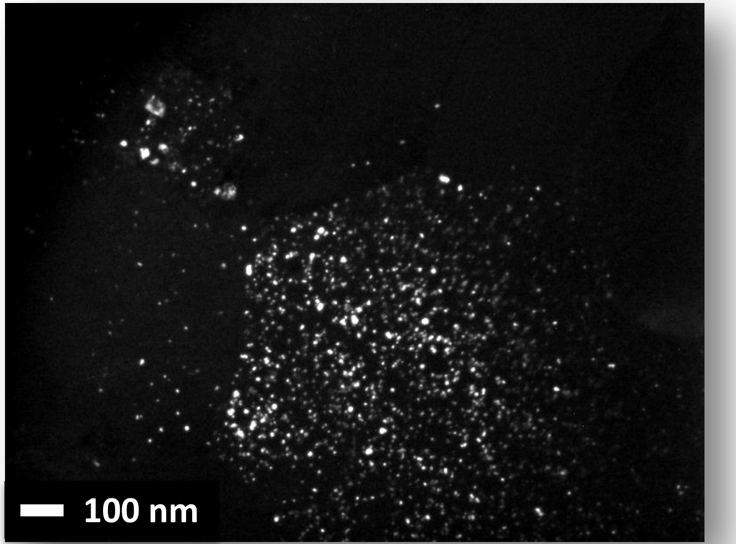
[Kozlov, JAllCom 509 (2011) 3326]



[Saravanan, JAllCom 479 (2009) 26]

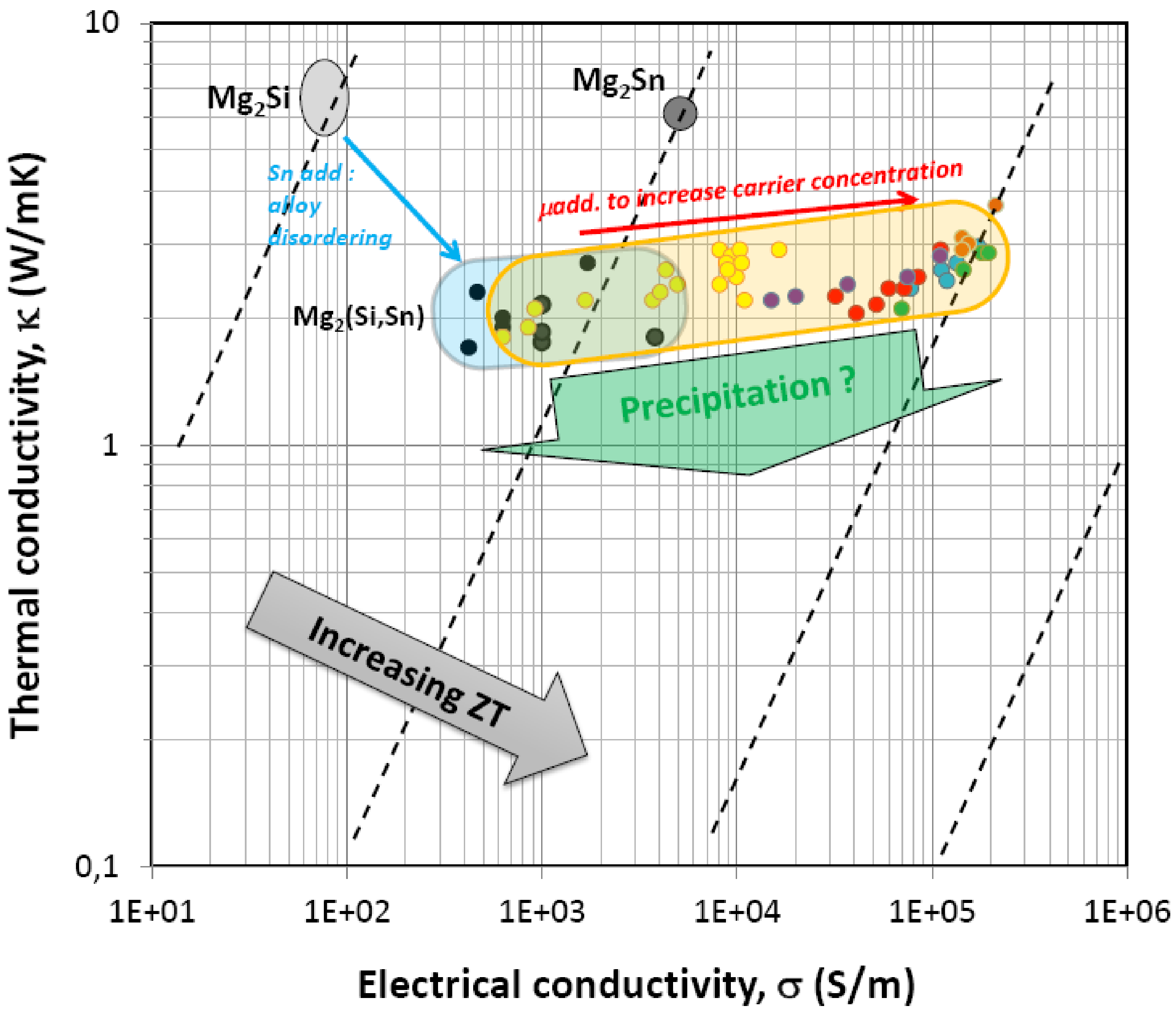
$Mg_2Si(Sn)^{SSSS} \rightarrow Mg_2Si(Sn)^{matrix} + Mg_2Sn(Si)^{precip.}$





[P. Bellanger's Thesis (ICMCB), collab. Redjaimia]

③ Toward a "material by design" approach



③ Toward a "material by design" approach

- **Model development**

Development of Microstructure

We need the knowledge of

- Grain size, d
- Second phase particle size, Rp
- Particle density, Np
- Amount of solute in solution, Xsol

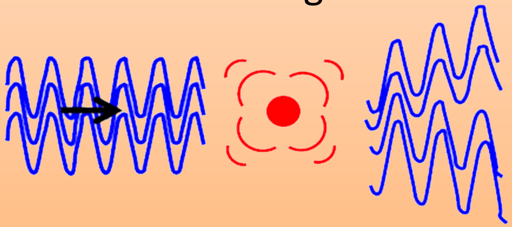
Need to develop a simple precipitation model

➔ Monitor : R_p, N_p, X_{sol}

Lattice thermal conductivity contributions

Evaluate contributions to phonon scattering :

- Intrinsec lattice resistance
- Alloy disordering
- Grain boundary resistance
- Particule scattering



❸ "Material by design" : μstructure modeling

- **Model development – Microstructural genesis and evolution**

Continuous precipitation of Mg_2Si from the supersaturated $Mg_2(Si,Sn)$ solid solution

Thermodynamic assessment

(sub-lattices)

$$G_m^{\phi} = {}^{ref}G_m^{\phi} + RT\left(\sum x_i ln x_i\right) + {}^{ex}G_m^{\phi}$$

$${}^{ref}G_m^{\phi} = \sum x_i\ {}^{0}G_i^{\phi}$$

$${}^{ex}G_m^{\phi} = \sum_i \sum_{j>i} x_i x_j \sum_{\nu=0}^{n}\left({}^{\nu}L_{i,j}^{\phi}\left(x_i - x_j\right)^{\nu}\right)$$

$$G_m^{A_aB_b} = a\ {}^{0}G_A^{ref} + b\ {}^{0}G_B^{ref} + \Delta H_f^{A_aB_b} - T\Delta S_f^{A_aB_b}$$

Diffusion coefficients

Classical nucleation Theory

[Gibbs 1928, Becker 1935, Zeldovich 1943]

$$\left.\frac{dN}{dt}\right|_{N+G} = N_0 Z\beta^{*} exp\left(-\frac{\Delta G^{*}}{kT}\right) exp\left(-\frac{\tau}{t}\right)$$

$$\left.\frac{d\bar{R}}{dt}\right|_{N+G} = \frac{D_s}{\bar{R}}\frac{X_s^{\beta} - X_{eq}^{R}}{X_s^{\beta} - X_{eq}^{R}} - \frac{1}{N}\frac{dN}{dt}(1{,}05R^{*} - R^{*})$$

$$\left.\frac{dN}{dt}\right|_{co} = \frac{4}{27}\frac{D_s}{\bar{R}^2}\frac{2\gamma\nu_{at}}{kT}\frac{X_s^{\alpha}}{X_s^{\beta} - X_s^{\alpha}}\left[\frac{2\gamma\nu_{at}}{kT}\frac{X_s^{\alpha}}{X_s^{\beta} - X_s^{\alpha}}\left(\frac{3}{4\pi\bar{R}^3} - N\right) - 3N\right]$$

$$\left.\frac{d\bar{R}}{dt}\right|_{co} = \frac{4}{27}\frac{D_s}{\bar{R}^2}\frac{2\gamma\nu_{at}}{kT}\frac{X_s^{\alpha}}{X_s^{\beta} - X_s^{\alpha}}$$

[Deschamps and Bréchet, Acta Mater. 47 (1999) 293]

③ "Material by design" : prop. modeling

Model development – Lattice thermal conductivity

Debye phonon spectrum
- acoustic branch
- Velocity, v=cst
- Highest frequency ω_D

Phonon scattering characterized by phonon life time.

$$\kappa_l = \frac{1}{3} C_V v \lambda = \frac{1}{3} C_V v^2 \tau$$

Phonon life time

Speed of sound

Heat capacity

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V$$

$$g(\omega) = 3\,\frac{\omega^2}{2\pi^2 v^3}$$

Debye frequency

Phonon density of states

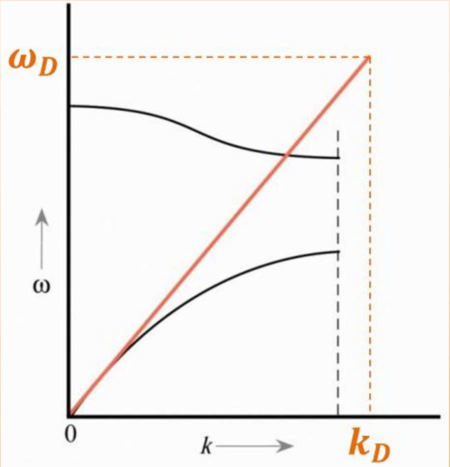
$$U = \int_0^{\omega_D} \hbar\omega\, n(\omega)\, d\omega = \int_0^{\omega_D} \hbar\omega \frac{g(\omega)}{exp(\hbar\omega/k_B T) - 1}\, d\omega$$

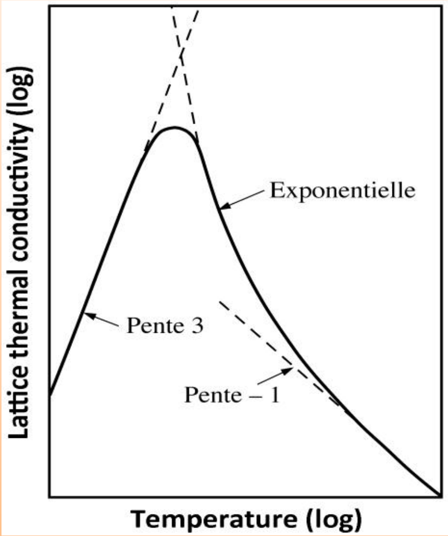
Phonon energy

Phonon distribution

Bose-Einstein distribution function

Debye model : $\omega = vk$





③ "Material by design" : prop. modeling

Phonon life time (Mathiessen’s rule) :

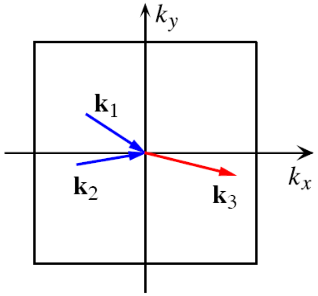
$$\tau^{-1} = \tau_a^{-1} + \tau_{ss}^{-1} + \tau_p^{-1} + \tau_{GB}^{-1} + \tau_D^{-1}$$

Anharmonic contribution

[Mingo, PRB 68 (2003) 113308]

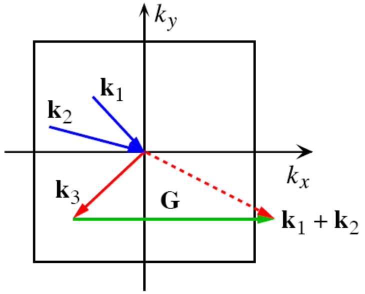
Normal phonon-phonon scattering

$$\tau_n^{-1} = \mathcal{B}_n T \omega^a T^b$$



Umklapp scattering

$$\tau_u^{-1} = \mathcal{B}_u T \omega^2 exp(-C/T)$$

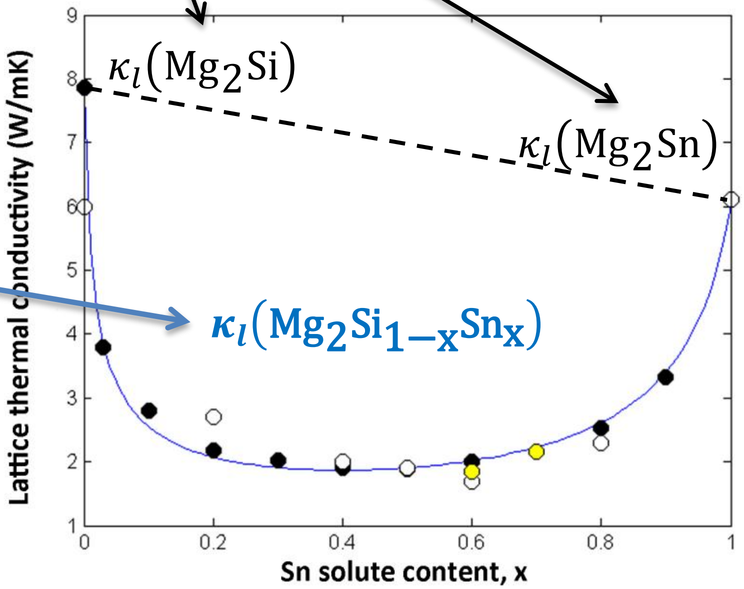


- **Results – Phonon scattering by solute atoms**

$$\tau_{ss}^{-1} = x(1-x)\mathrm{A}\omega^4$$

$$\mathrm{A}_{AB} = \frac{\{[(M_A - M_B)/M_{AB}]^2 + 2[(K_A - K_B)/K_{AB}]^2\}\delta^3}{4\pi v^3}$$

[Abeles, PRB 131 (1963) 1906]



❸ **"Material by design"** : prop. modeling

- **Results – Second phase particle scattering**

$$\tau_p^{-1} = v\left(\underbrace{\sigma_s^{-1}+\sigma_l^{-1}}_{\text{Short and long wavelength cross sections}}\right)^{-1}\rho$$

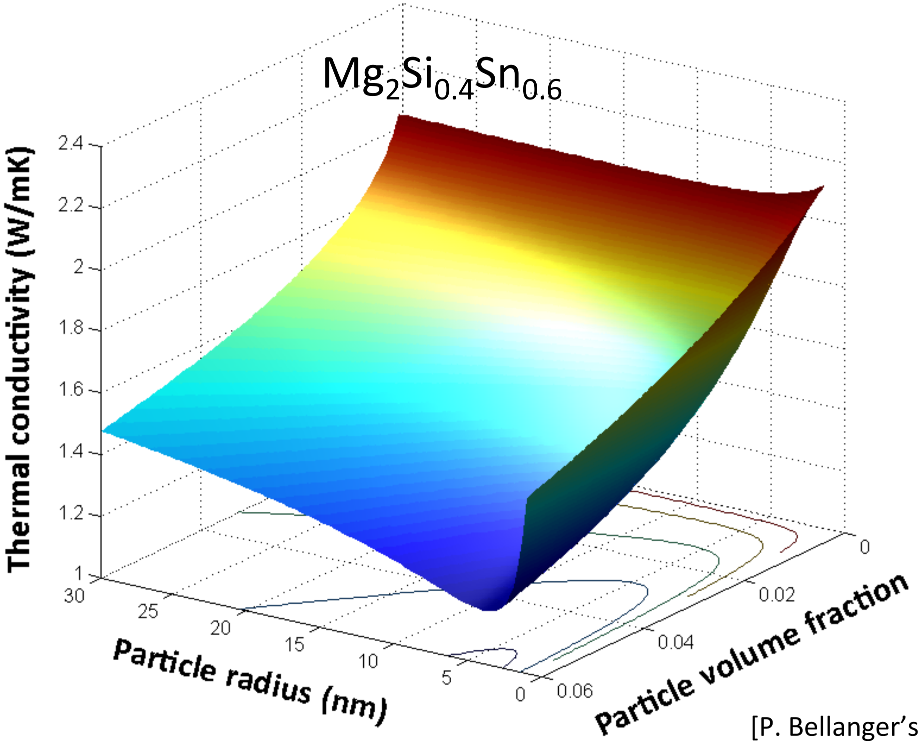
[Kim & Majumdar, JAP 99 (2006) 084306]

Particles size comparable to the wavelength

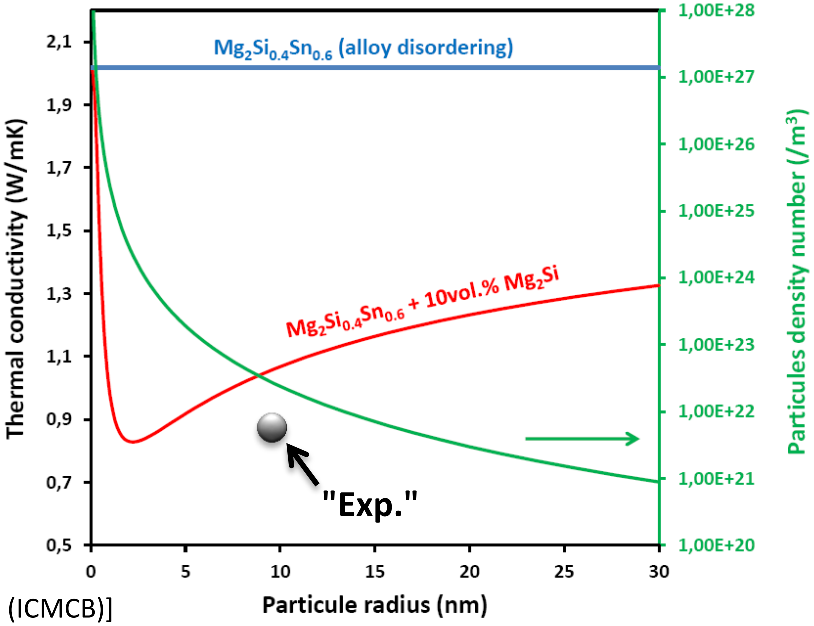
$$\sigma_s = 2\pi R^2$$

Combination of scattering due to difference in mass and force constant of a spherical nanoparticle in the Rayleigh regime (particles much smaller than the wavelength)

$$\sigma_l = \frac{4\pi R^2}{9}\left(\frac{\omega R}{v}\right)^4\left[\left(\frac{\Delta D}{D}\right)^2 + 3\left(\frac{\Delta K}{K}\right)^2\right]$$

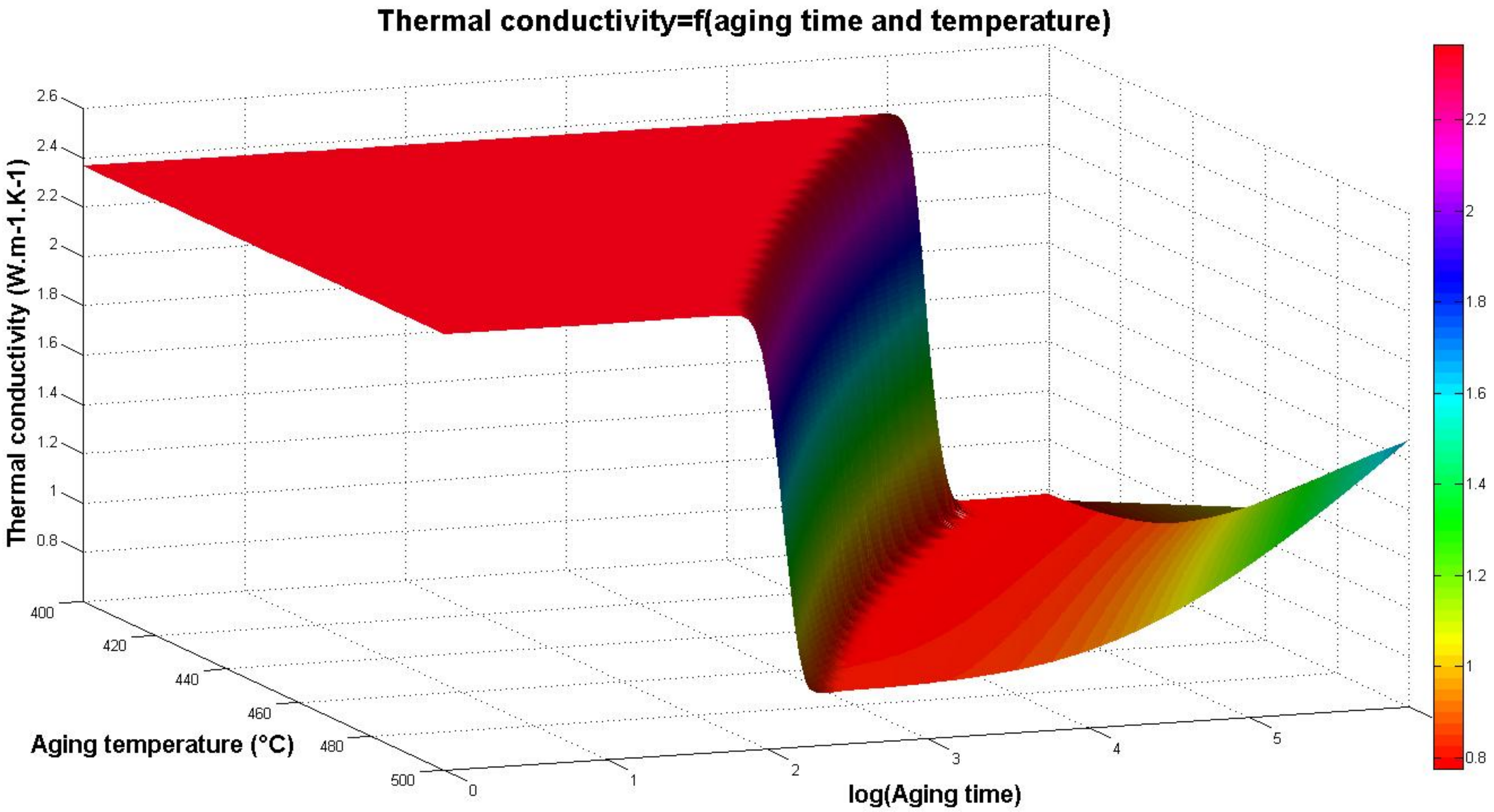


[P. Bellanger's Thesis (ICMCB)]



❸ "Material by design" : μstructure – prop. coupling

- **Results – From the property to the process conditions**



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