Chaire de Physique de la Matière Condensée

III.1 Effets thermoélectriques: Introduction

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Cycle 2014-2015

1er juin 2015 – III.1

Séance du 1er juin 2015

- Effets thermoélectriques: introduction, réponse linéaire, thermodynamique
- Expression des coefficients de réponse pour un système mésoscopique et exemples
- Observation d'effets thermo`électriques' dans les gaz atomiques froids.

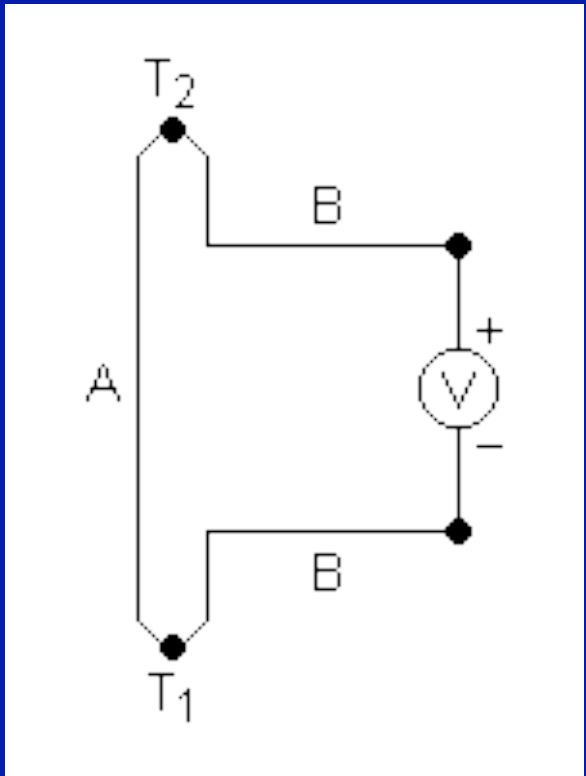
Pour (bien) plus de détails, consulter le site web
du Collège de France.
Les cycles de cours 2012-2013 et 2013-2014
sont consacres a la thermoélectricité.
Cours et séminaires invités disponibles en ligne.

En mémoire de
Roger Maynard

Two Basic Thermoelectric Effects: Seebeck and Peltier

The Seebeck effect (1821)

A thermal gradient applied at the ends of an open circuit induces a finite voltage difference

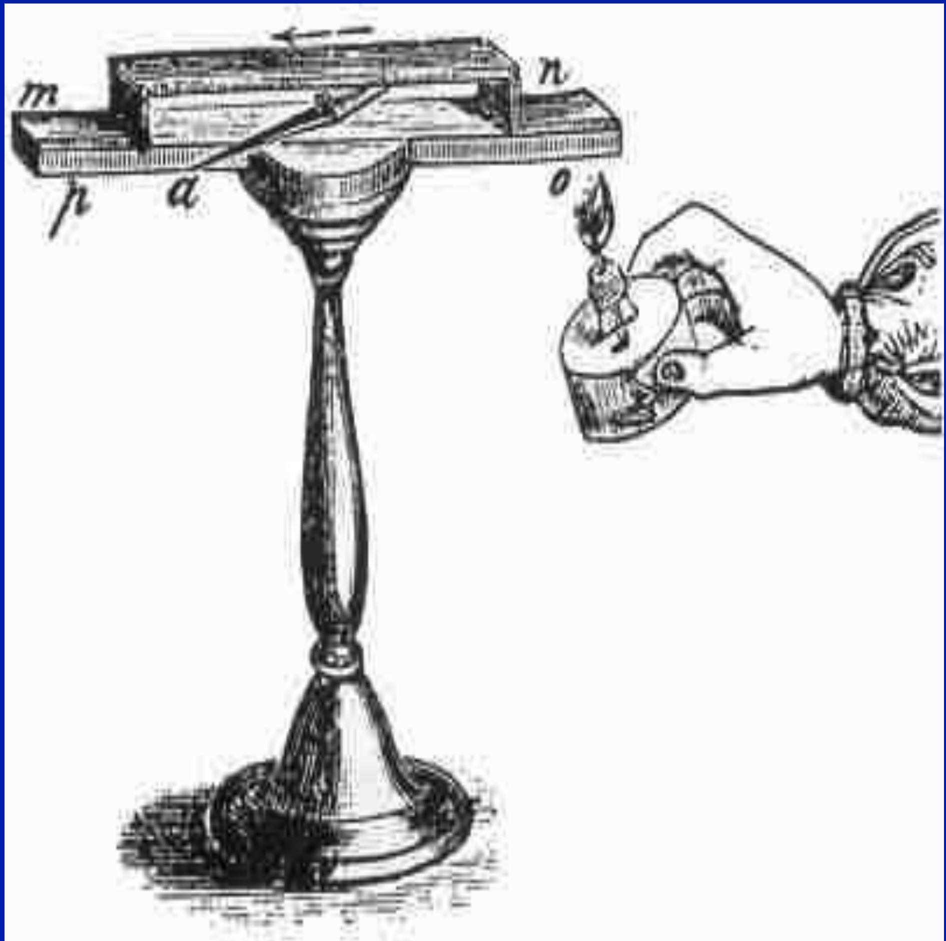


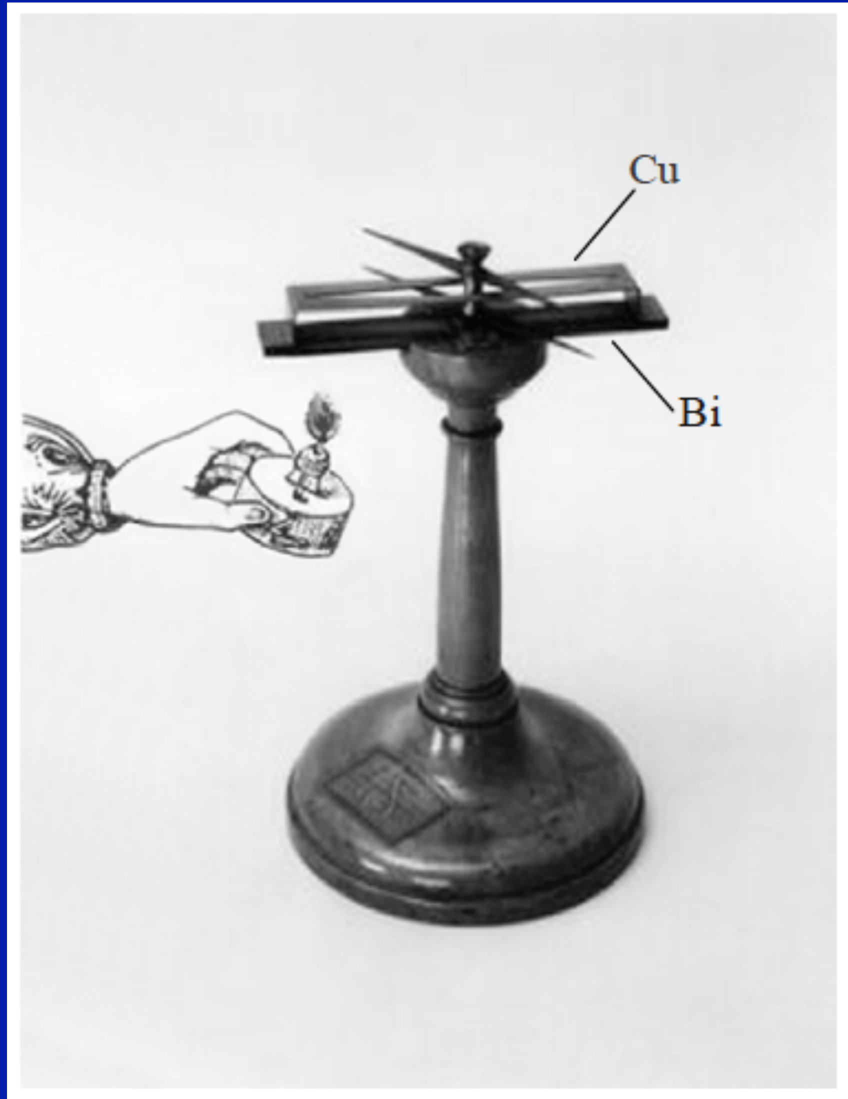
$$\Delta V = -\alpha\,\Delta T$$

α: Seebeck coefficient (thermopower)

Actual observation: junction between two metals, voltage drop:

$$V = (\alpha_B - \alpha_A)\,(T_2 - T_1)$$





Seebeck's original instrument: deflection of a compass needle
Heated junction of two metals (o,n)

Thomas Johann Seebeck

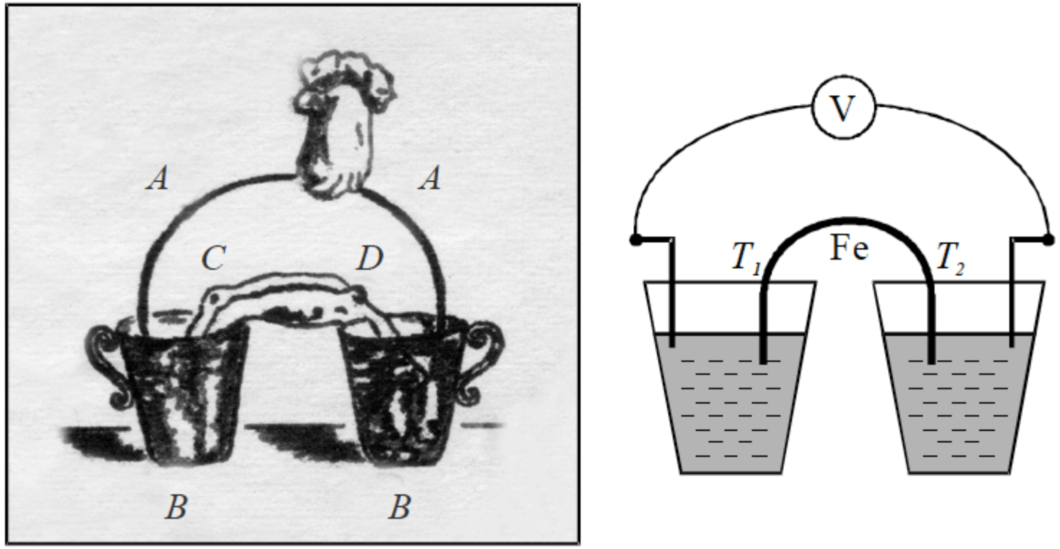
(Tallinn 1770 - Berlin 1831)

- **Thomas Johann Seebeck:**

- Discoverer of the Seebeck thermoelectric effect
- Apparently always refused to consider the Seebeck effect as the manifestation of an electrical phenomenon…
- Rather: magnetism. Proposed this as a mechanism for the earth magnetic field (!)
- Discovered the sensitivity of silver chloride to light → `precursor of photography'
- Magnetic properties of nickel and cobalt (1810)

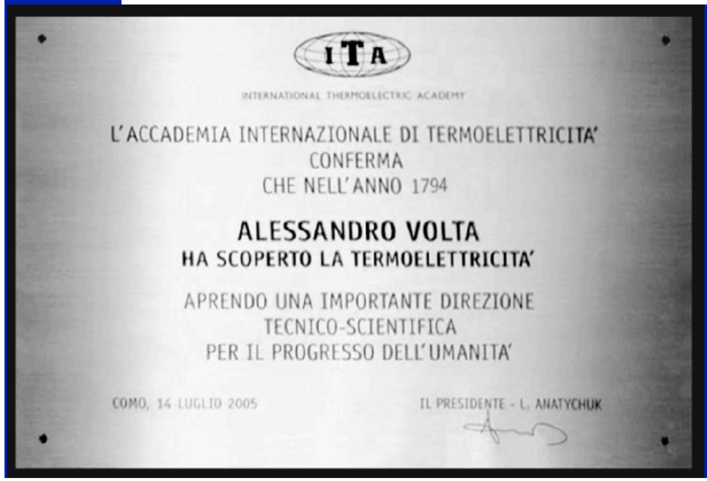
Source: mostly wikipedia

Alessandro Volta discovered it before in 1794…




Alessandro Volta

Fig. 3. Discovery of thermoelectricity by Volta on February 10, 1794.

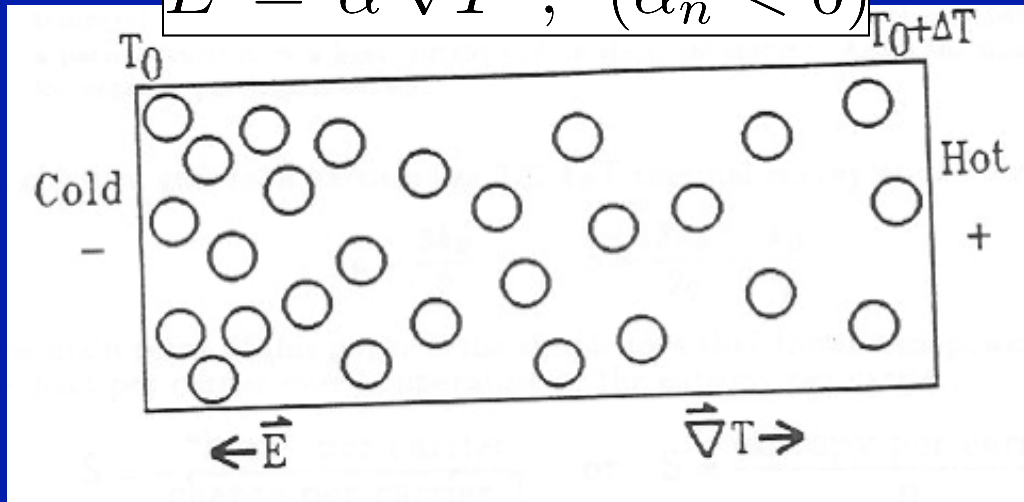


cf. e.g. LI Anatychuk,
Journal of Thermoelectricity, 1994
G.Pastorino, ibid., 2009

Qualitative picture:

cf: *PM Chaikin, An introduction to thermopower for those who might want to use it…in `Organic superconductors', 1990*

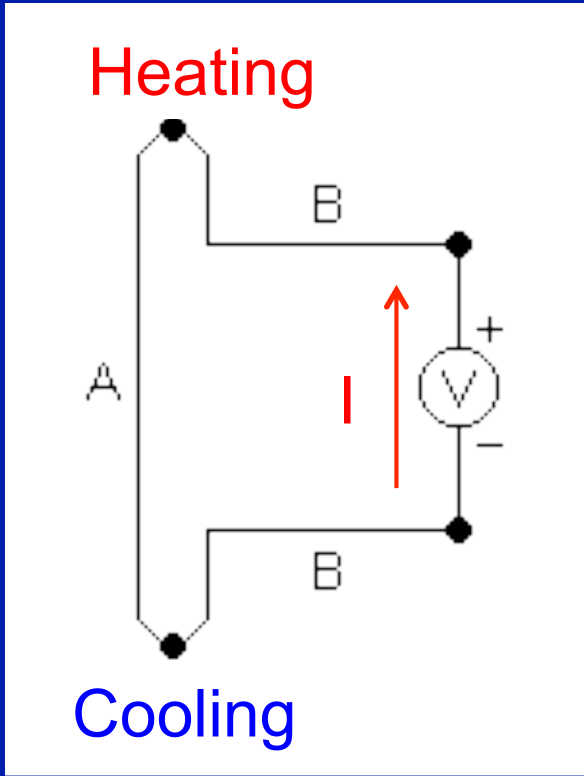
$$\vec{E} = \alpha \vec{\nabla} T \ , \ (\alpha_n < 0)$$



- Higher density of carriers on the cold side, lower on hot side
- → an electric field is established
- `Stopping condition': balance electric field and thermal gradient to get zero particle flow.
- In this cartoon: carriers are negatively charged, hence field is <u>opposite</u> to thermal gradient
- Electron-like (hole-like) carriers correspond to negative (positive) Seebeck coefficient → Seebeck useful probe of nature of carriers

The Peltier effect (1834)

Heat production at the junction of two conductors
in which a current is circulated.
***Reversible**: heating or cooling as orientation of current is reversed.*



Heating rate: Π: Peltier coefficient

$$\dot{Q} = \Pi_{AB}\, I$$

2nd Kelvin relation (Onsager):

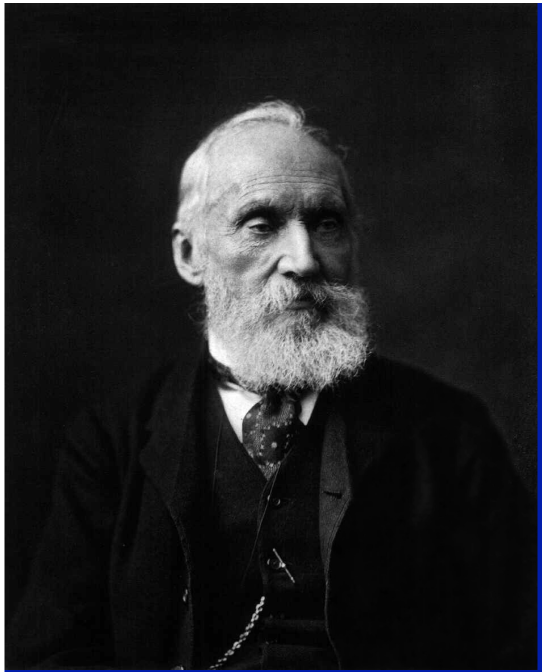
$$\Pi = T\,\alpha$$

Note: thermoelectric coefficients are actually intrinsic to a single conductor (ex: B is a superconductor)

Jean Charles Athanase Peltier
(Ham, 1785 – Paris, 1845)

Jean-Charles-Athanase Peltier
(1785-1845)

- Watchmaker until he retired at age ~ 30
- Then a physicist by vocation
- Also known for determining the temperature of calefacting water



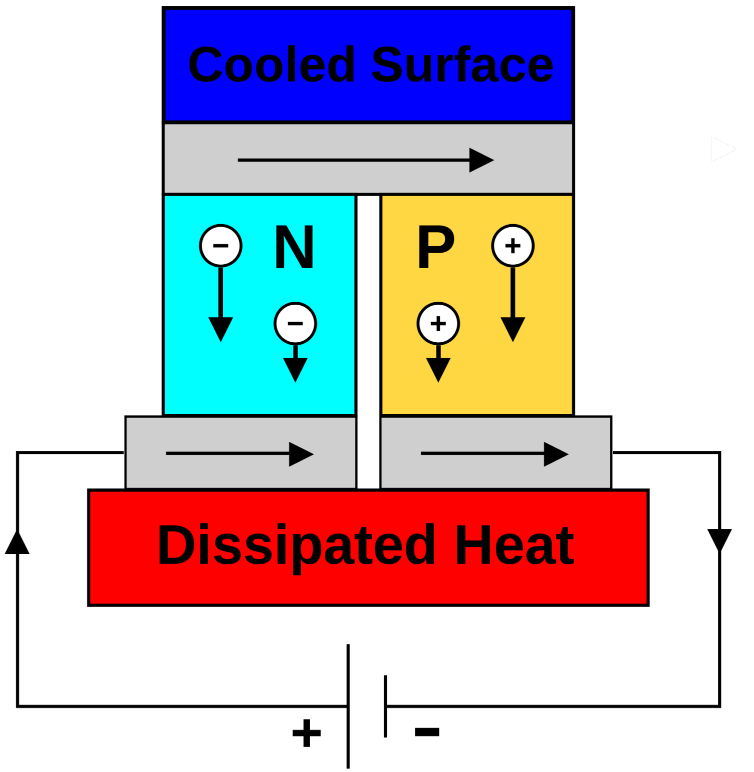
Thermodynamics of thermoelectricity: William Thomson (Lord Kelvin)

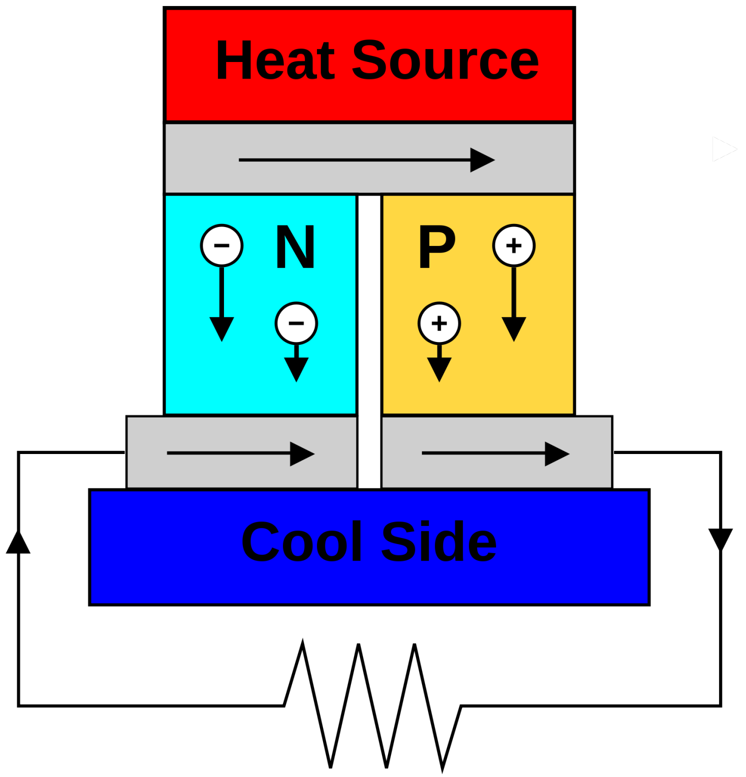
(1827 – 1907)

- Multi-talented Belfast-born British physicist and engineer
- Key role in formalizing thermodynamics, especially Carnot's ideas, in a long discussion/controversy with Joule. Determined absolute zero (Kelvin temperature scale).
- First gave firm foundations to thermodynamics of thermoelectricity: the two Kelvin relations (anticipating Onsager's)
- Knighted (Baron Kelvin) for his contribution to laying the 1st transatlantic telegraph cable
- Proponent of the vortex theory of atoms, now forgotten…

Two basic applications of the Peltier and Seebeck effects: Coolers and Generators

Modules in series electrically, in parallel thermally

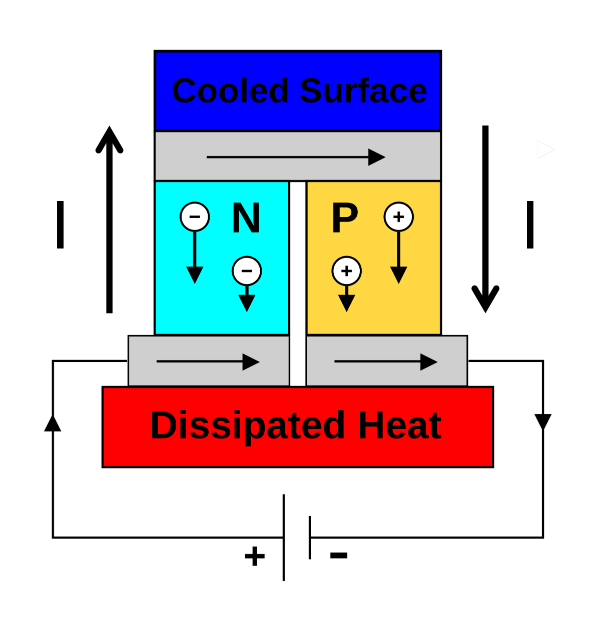




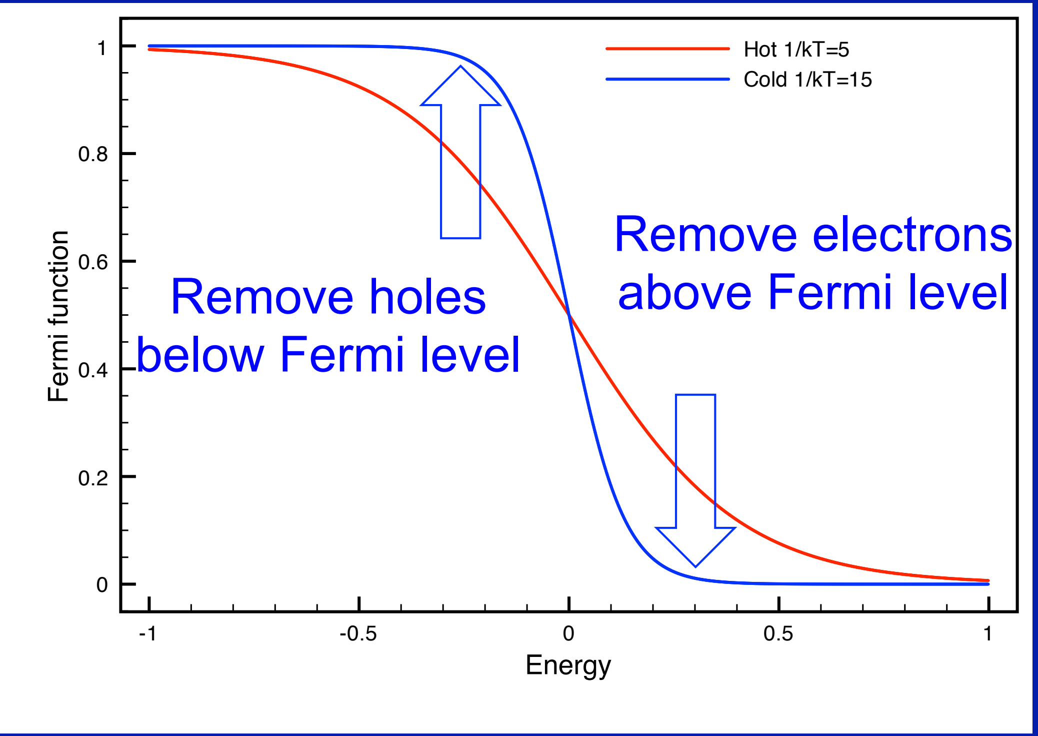
Cooling module [Peltier]

Power generation module [Seebeck]

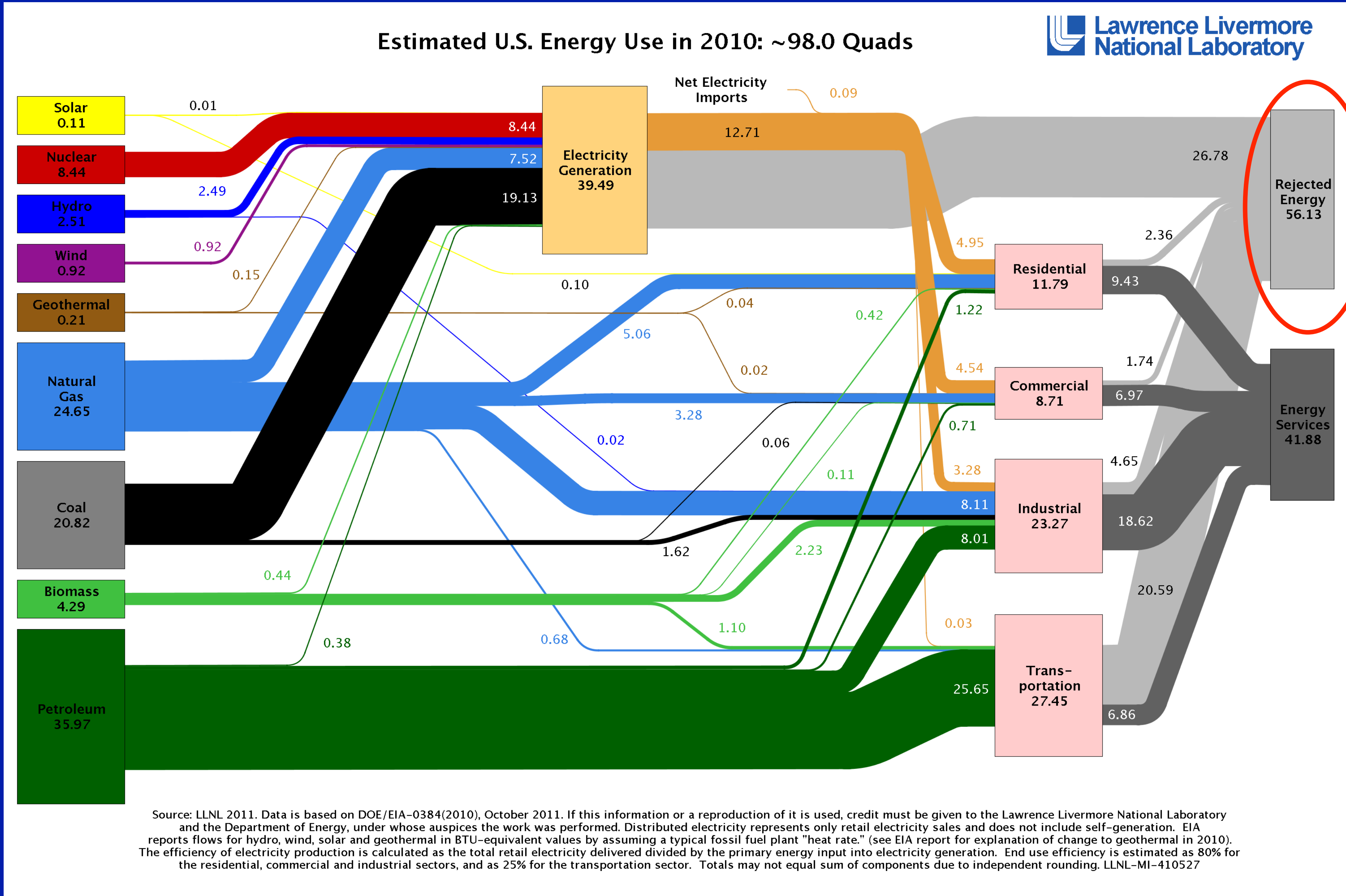
Simple intuition about thermoelectric cooling

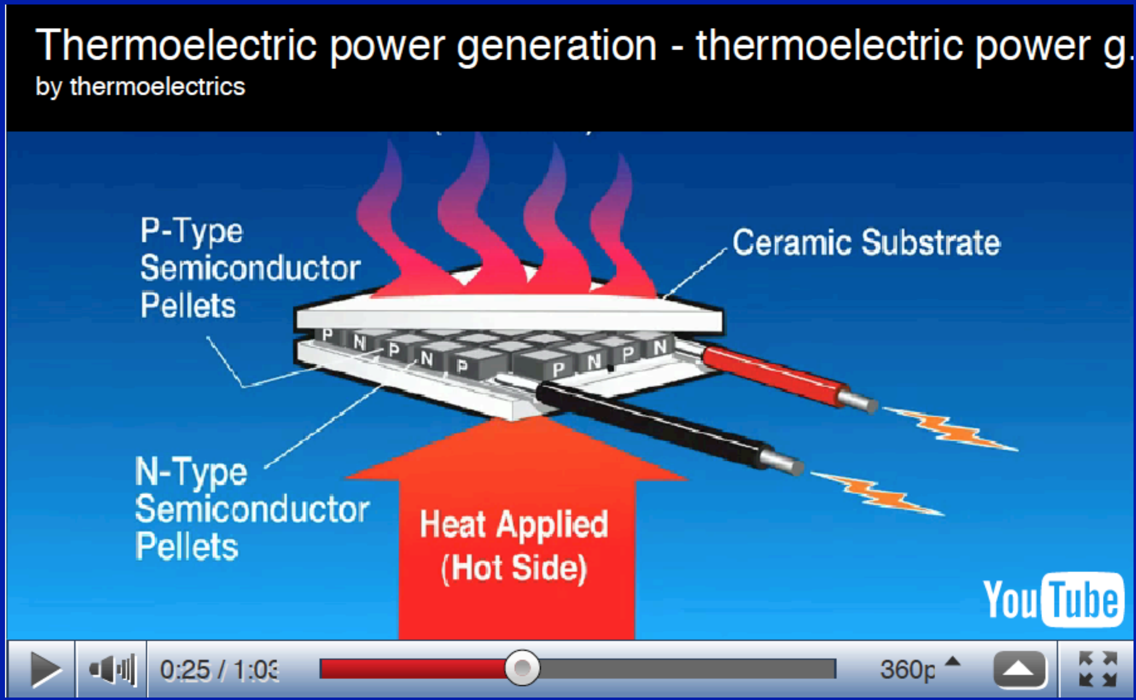


- Electrons move against current
- Holes move along current
- BOTH electrons and holes leave cold end to reach hot end
- BOTH processes correspond to lowering of entropy of cold end



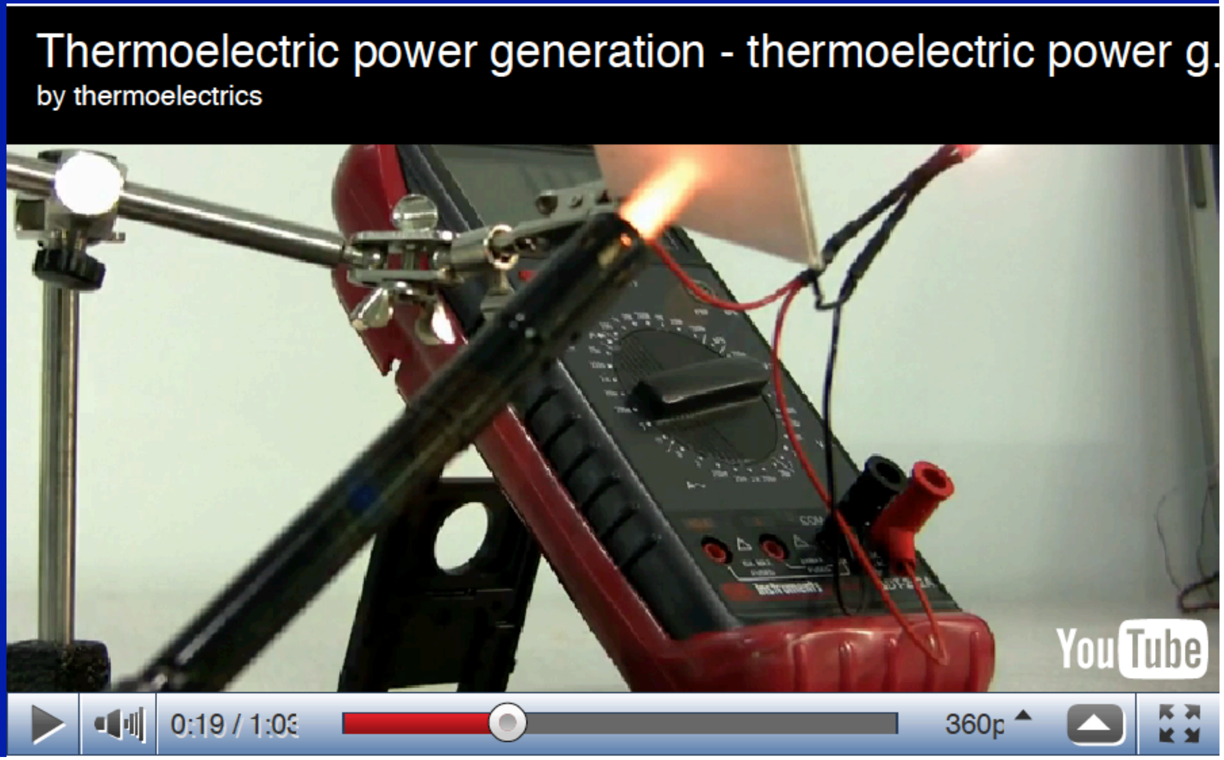
Waste heat recovery: about 55% of energy in the US rejected as waste…





A real module

(e.g. tellurex.com
– videos on youtube)



Linear-Response Theory: Onsager Transport Coefficients

Transport equations (linear response) :

Grand-canonical potential (per unit volume):

$$\Omega(T,\mu) = -k_B T \ln Z_G$$

Particle-number and Entropy (densities):

$$s = -\frac{\partial \Omega}{\partial T}\Big|_{\mu} \;\;,\;\; n = -\frac{\partial \Omega}{\partial \mu}\Big|_{T}$$

Particle and entropy currents: linear response

$$j_n \;=\; -L_{11}\nabla\mu - L_{12}\nabla T$$
$$j_s \;=\; -L_{21}\nabla\mu - L_{22}\nabla T$$

Chemical potential: in fact `electrochemical’ potential’

Note: electrochemical potential. Consider a system with a local electrostatic potential, conjugate to the local charge density $n_q(\boldsymbol{r})$ and a local chemical potential, conjugate to the local particle density $n(\boldsymbol{r})$. For carriers of charge q ($= -e$ the electron charge with $e > 0$), we have $n_q(\boldsymbol{r}) = qn(\boldsymbol{r})$. The scalar potential $V(\boldsymbol{r})$ and chemical potential $\mu(\boldsymbol{r})$ thus cannot be independently observed, and only the following combinations are relevant:

$$\overline{\mu}(\boldsymbol{r}) = \mu(\boldsymbol{r}) + qV(\boldsymbol{r}) \;,\; \overline{V}(\boldsymbol{r}) = V(\boldsymbol{r}) + \frac{1}{q}\mu(\boldsymbol{r}) \tag{5}$$

$\overline{\mu}$ is called the *electrochemical potential.* In any experiment, only the total voltage drop arising from $\overline{V}(\boldsymbol{r})$ can be measured, not separately $\boldsymbol{\nabla} V$ and $\boldsymbol{\nabla}\mu$. The energy we need to give to the system to add one particle is μ, the electrostatic energy to add one extra charge q is qV. Hence, it is actually convenient to forget about the scalar potential $V(\boldsymbol{r})$, and consider only $\overline{\mu}(\boldsymbol{r})$. This is what is done in these notes: the ‘chemical potential’ is actually the electrochemical potential *but the bar is dropped everywhere for simplicity* and it is simply denoted μ. The measured electric field can be obtained as:

$$\mathcal{E} \equiv -\boldsymbol{\nabla}\overline{V}(\boldsymbol{r}) = -\frac{1}{q}\boldsymbol{\nabla}\overline{\mu} = \frac{1}{e}\boldsymbol{\nabla}\overline{\mu} = -\boldsymbol{\nabla}V - \frac{1}{q}\boldsymbol{\nabla}\mu \tag{6}$$

In the following all overbars are dropped and the electric field is simply called $\boldsymbol{E}$.

In practice, electric field: $\boxed{\vec{E} = \frac{1}{e}\vec{\nabla}\mu}$

Electrical and heat currents:

$$\vec{j}_e = q\vec{j}_n \ (q = -e)$$

Heat : $\delta Q = T\,ds \Rightarrow j_Q = T\,j_s$

$$\vec{j}_e \ = \ q^2\,L_{11}\vec{E} - q\,L_{12}\nabla T$$

$$\vec{j}_Q = T j_s \ = \ Tq\,L_{21}\vec{E} - T\,L_{22}\nabla T$$

Electrical conductivity: $\nabla T = 0 \Rightarrow \sigma = q^2\,L_{11}$

Thermal conductivity:
(no particle current)

$$j_n = 0 \Rightarrow j_Q = \kappa(-\nabla T)$$

$$\kappa = T\left[L_{22} - \frac{L_{12}L_{21}}{L_{11}}\right]$$

Seebeck and Peltier coefficients:

1. Seebeck effect: thermal gradient induces a voltage drop between the two ends of a conductor

$$j_e = 0 \Rightarrow \vec{E} = \alpha \vec{\nabla} T \quad , \quad \alpha \equiv \frac{L_{12}}{q L_{11}}$$

2. Peltier effect: electrical current induces heat current

$$\nabla T = 0 \Rightarrow j_Q = \Pi \, j_e \quad , \quad \Pi \equiv T \frac{L_{21}}{q L_{11}}$$

Kelvin's relation (consequence of Onsager's reciprocity): $\Pi = T \alpha$

<u>The Seebeck coefficient measures the ratio of entropy flow to carrier current</u> (once the irreversible Fourier thermal diffusion current is substracted):

$$j_s = \alpha \, j_e - \frac{\kappa}{T} \nabla T$$

(eliminating μ)

Dimensions. The current density j_X associated with a quantity X is such that $dX/dt = I_X = \int d^2 l j_X$ is given by the flux traversed by j_X, hence $[j_X] = [X]/[time][length]^2$. Hence:

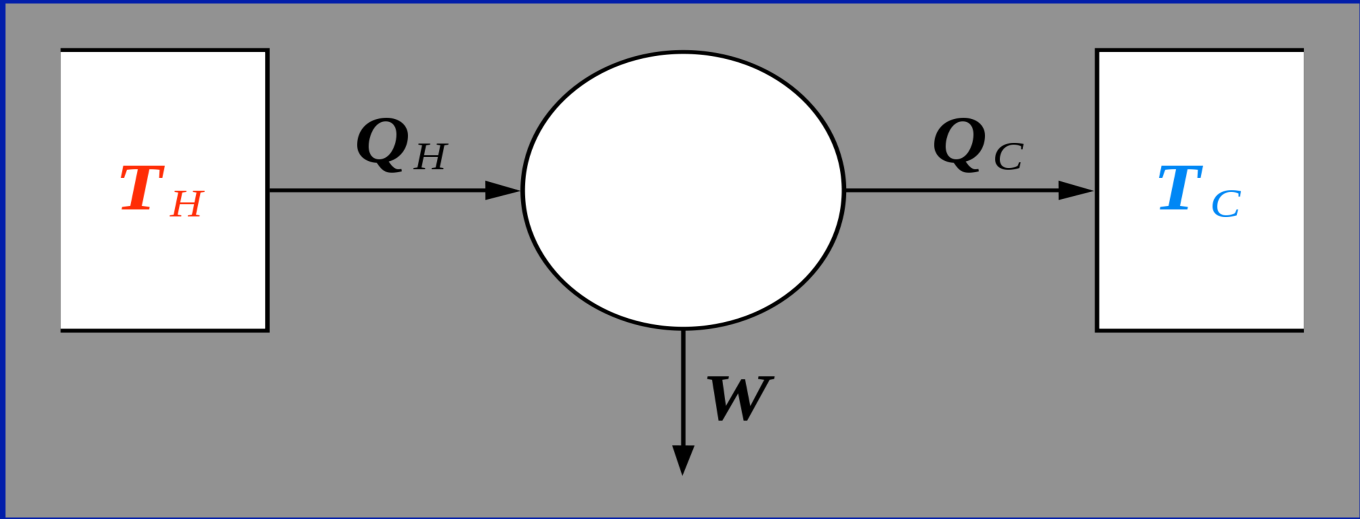
- Conductivity σ has dimension $\Omega^{-1}m^{-1}$. A good metal has a resistivity of order $1\mu\Omega$cm, diamond has $10^{20}\mu\Omega$cm
- Seebeck has dimension $Field.Length/Temperature = Energy/Temperature$, hence the unit of k_B/e. We note that:

$$\boxed{\frac{k_B}{e} = 86.3\mu V K^{-1}} \tag{18}$$

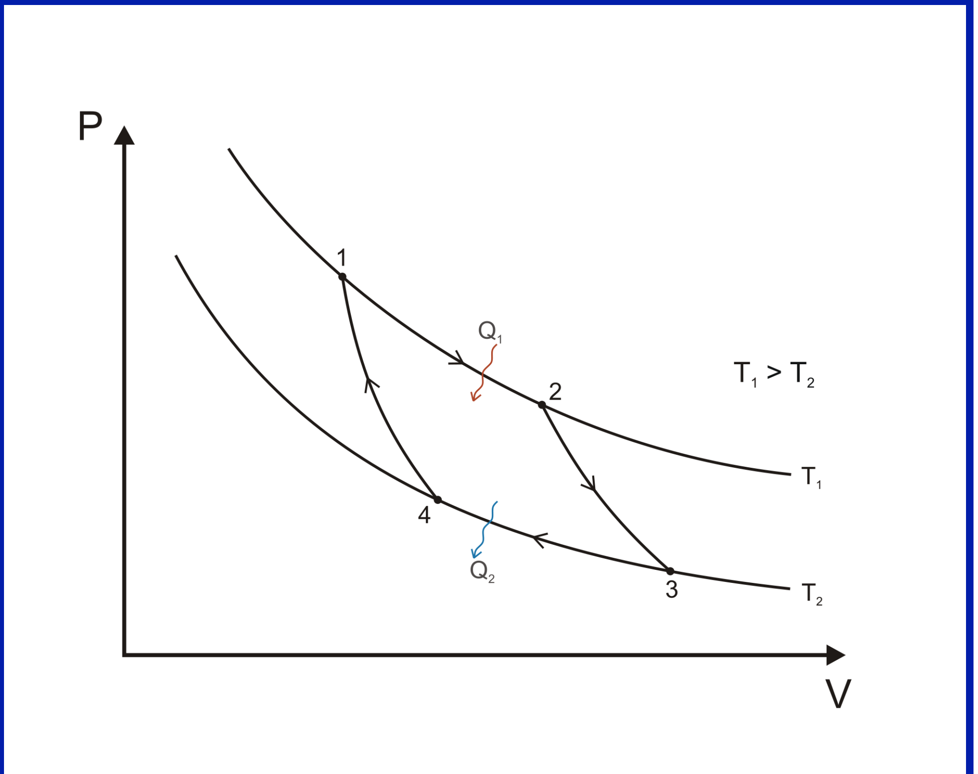
- Thermal conductivity has dimension $Energy/[Length^2 \times Time] \times [Length/Temperature] = [Power]/[Length \times Temperature]$. Unit is hence $W.m^{-1}K^{-1}$. Diamond, one of the best thermal conductors has $\kappa \sim 10^3 W.m^{-1}K^{-1}$ while silicon aerogels, excellent thermal insulators, have κ of order $10^{-2} - 10^{-3}$. Glass is $O(1)$.

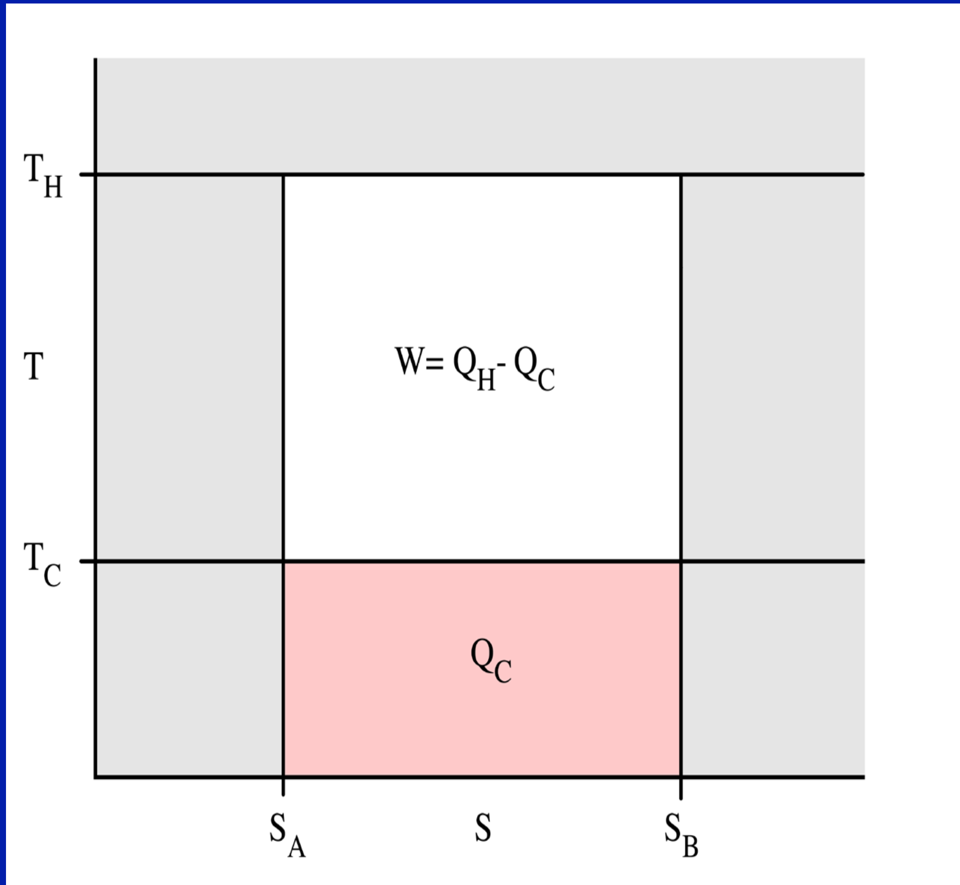
EFFICIENCY OF ENERGY CONVERSION

General considerations and application to the thermodynamics of thermoelectrics -



Carnot cycle :





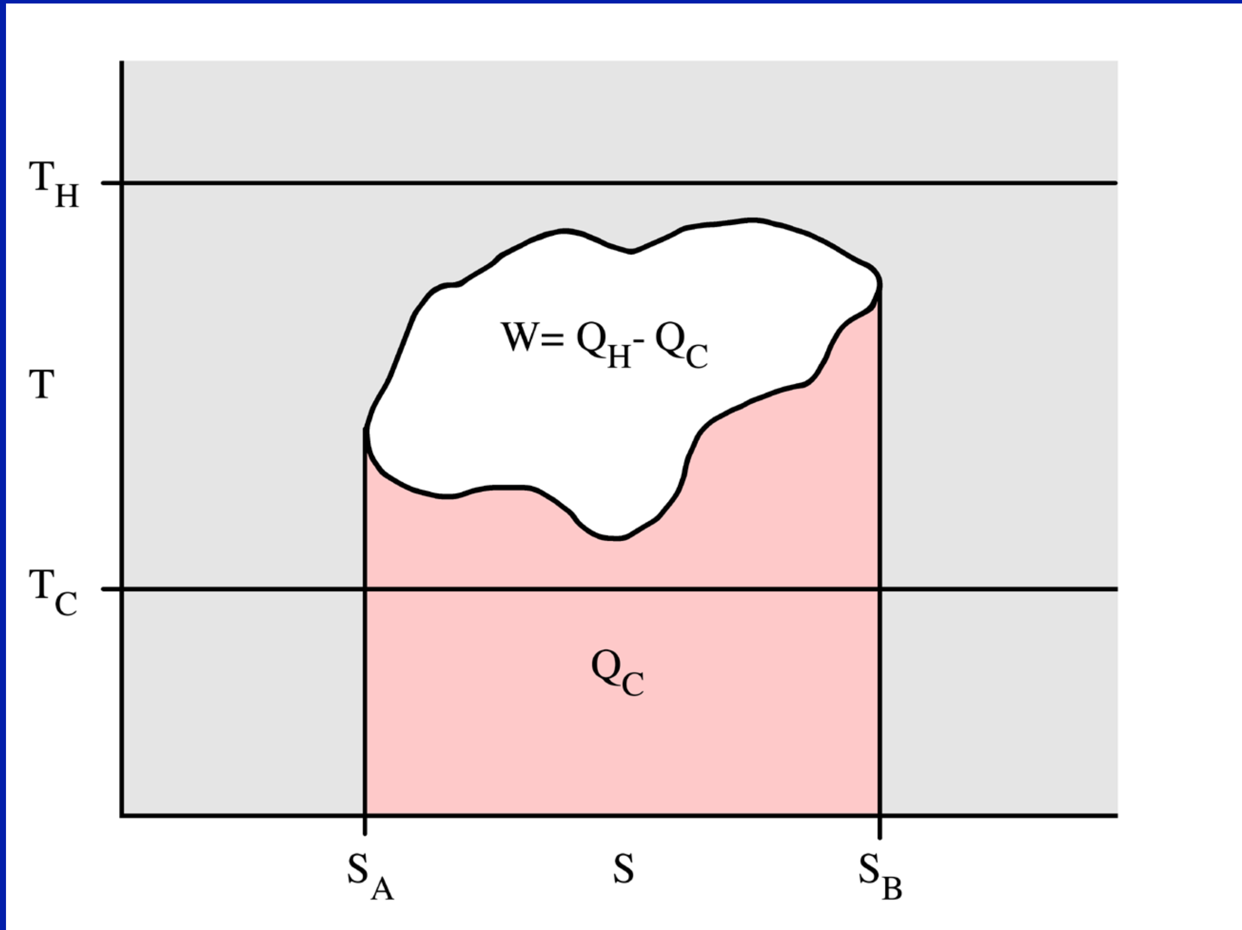
Maximum theoretical efficiency: the Carnot reversible engine

Carnot efficiency:

$$\eta_C = 1 - \frac{T_C}{T_H}$$

Since it corresponds to a reversible,
quasi-static and hence infinitely slow process,
a Carnot engine delivers ZERO POWER !

A Carnot cycle maximizes efficiency… but delivers zero power !



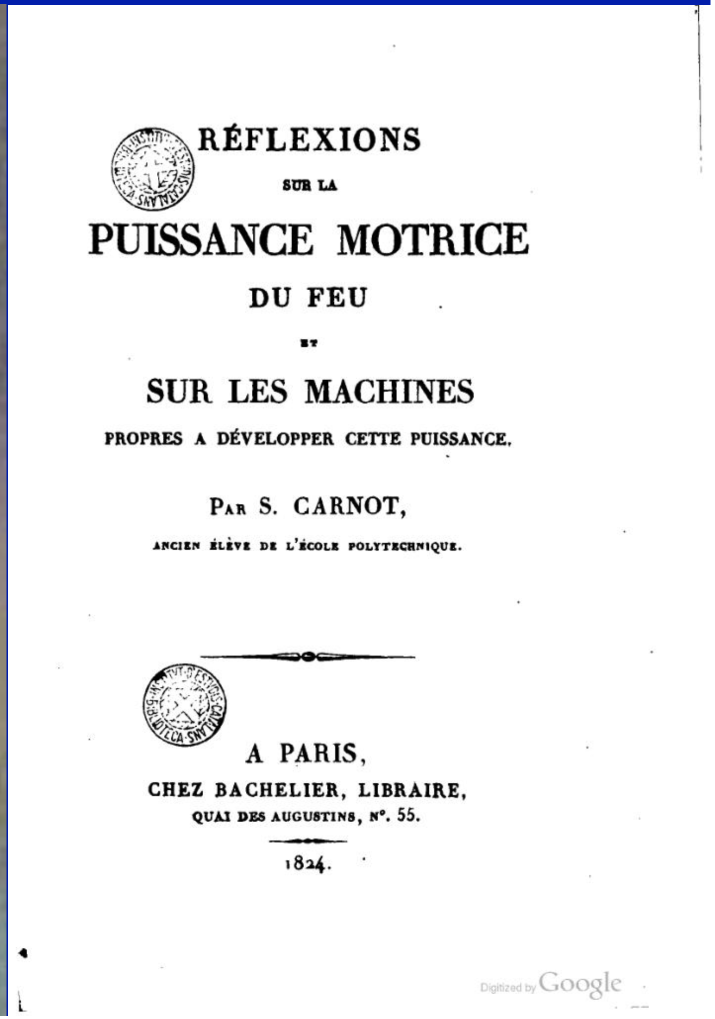
A general cycle (non-Carnot): Carnot maximizes the ratio of the white to total area, subject to the constraints of the 2nd principle.

Sadi Carnot (1796-1832)

- Officer and Physicist/Engineer -

[Not to be confused with President Sadi Carnot (1837- 1894)]
Both are descendents of Lazare Carnot, great revolutionary, statesman, also a mathematician and physicist, and one of the founders of Ecole Polytechnique1753-1823

Sadi Carnot, then a student at Ecole Polytechnique (painting by Louis Leoplod Boilly [Wikipedia])



RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, N°. 55.
1824.

Efficiency at maximum power of an `endoreversible' engine: the Chambadal-Novikov (Curzon-Ahlborn) efficiency

$$\eta_{CN} = 1 - \sqrt{\frac{T_C}{T_H}}$$

P. Chambadal *Les centrales nucléaires*, Armand-Colin 1957
I.I. Novikov *The efficiency of atomic power stations*
J. Nuclear Energy II 7 (1958) 125
FL Curzon and B.Ahlborn *Efficiency of a Carnot engine at maximum power output* Am J Phys 43, 22 (1975)

In the limit of infinitesimal gradients :

$$\eta_C \sim -\frac{\nabla T}{T} \quad , \quad \eta_{CN} \simeq \frac{1}{2}\eta_C$$

In the following, we shall follow an approach based on:

- Local entropy vs. work balance
- For infinitesimal gradients

Efficiency relative to a Carnot reversible device:

$$\eta_r \equiv \frac{\eta}{\eta_C} \simeq \frac{T}{\nabla T}\eta$$

Entropy and heat production rates

$$T\left[\frac{\partial s}{\partial t} + \boldsymbol{\nabla}\cdot \boldsymbol{j}_s\right] = \boldsymbol{j}_s \cdot (-\boldsymbol{\nabla} T) + \boldsymbol{j}_n \cdot (-\boldsymbol{\nabla}\mu)$$

$$\frac{\partial s}{\partial t}\Big|_{prod} \equiv \frac{\partial s}{\partial s} + \boldsymbol{\nabla}\cdot \boldsymbol{j}_s = \frac{1}{T}\boldsymbol{G}\cdot \underline{L}\boldsymbol{G}$$

$$\boldsymbol{G} \equiv \begin{pmatrix} -\boldsymbol{\nabla}\mu \\ -\boldsymbol{\nabla} T \end{pmatrix}$$

$$\frac{\partial Q}{\partial t}\Big|_{irr} \equiv_{\mathrm{T}} \left[\frac{\partial s}{\partial t} + \boldsymbol{\nabla}\cdot \boldsymbol{j}_s\right] = \rho \boldsymbol{j}_e^2 + \frac{\kappa}{T}(\boldsymbol{\nabla} T)^2$$

Note: Seebeck coefficient does not enter ! (reversible)

Positivity of entropy production (2nd principle of thermo.) implies that L is a <u>positive semi-definite matrix</u>

This is equivalent to:

$$L_{11} \geq 0 \quad , \quad L_{22} \geq 0 \quad , \quad \det L \geq 0$$

Onsager's reciprocity relation (in the absence of an applied magnetic field):

$$L_{12} = L_{21}$$

Currents and conjugate forces:

$$\frac{\partial S}{\partial t}\Big|_{\rm irr} = \sum_A J_A . X_A$$

$$A = N, S \;\Rightarrow\; X_N = -\frac{1}{T}\nabla\mu \;\;,\;\; X_S = -\frac{1}{T}\nabla T$$

Linear response: $J_A = \sum_B L_{AB}\, X_B$

$$L_{AB} = -\frac{1}{\beta}\int_0^\infty dt e^{-st}\int_0^\beta d\tau\, \mathrm{Tr}\left[\hat{\rho}_0\, j_A(-t-i\tau) j_B(0)\right]$$

$$L_{AB} = \pi \sum_{nm} e^{-\beta E_n} \langle n|j_A|m\rangle \langle m|j_B|n\rangle\, \delta(E_n - E_m)$$

Onsager symmetry is manifest on this form

$$T\left[\frac{\partial s}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_s\right] = \boldsymbol{j}_s \cdot (-\boldsymbol{\nabla} T) + \boldsymbol{j}_n \cdot (-\boldsymbol{\nabla} \mu)$$

$j_n.(-\nabla\mu) = j_e.E$: power generated by carrier flow

$j_Q = Tj_s = (T/\nabla T)(j_s \nabla T)$ power delivered by the heat source

(Instantaneous) efficiency relative to Carnot: (=$\nabla T/T$)

$$\eta_r \equiv \frac{-\boldsymbol{j}_n \cdot \boldsymbol{\nabla}\mu}{\boldsymbol{j}_s \cdot \boldsymbol{\nabla} T} = \frac{\boldsymbol{j}_e \cdot \boldsymbol{E}}{\boldsymbol{j}_s \cdot \boldsymbol{\nabla} T}$$

Conductivity matrix:

$$\begin{pmatrix} \boldsymbol{j}_e \\ \boldsymbol{j}_Q \end{pmatrix} = \underline{\sigma} \begin{pmatrix} \boldsymbol{E} \\ -\boldsymbol{\nabla} T \end{pmatrix} \quad , \quad \underline{\sigma} = \begin{pmatrix} \sigma & \alpha\sigma \\ T\alpha\sigma & \kappa(1+\overline{z}) \end{pmatrix}$$

Dimensionless `figure of merit':

$$\boxed{\overline{z} \equiv T\frac{\alpha^2\sigma}{\kappa}}$$

Note: $\det \underline{\sigma} = \sigma\kappa$

Coupling constant characterizing energy conversion :

$$g \equiv \frac{L_{12}}{\sqrt{L_{11}L_{22}}} \ , \ g^2 = \frac{\overline{z}}{1+\overline{z}}$$

$$\det \underline{L} \geq 0 \quad \Rightarrow \quad -1 \leq g \leq +1$$

Using the linear-response equations, one obtains:

$$\boxed{\eta_r = \frac{x(x-1)}{x-1/g^2}}$$

$$x \equiv \frac{E}{\alpha\,\nabla T} = \frac{E}{E_{stop}}$$ control/optimization parameter

$$P = 4x(1-x)\,P_{max}$$ Power

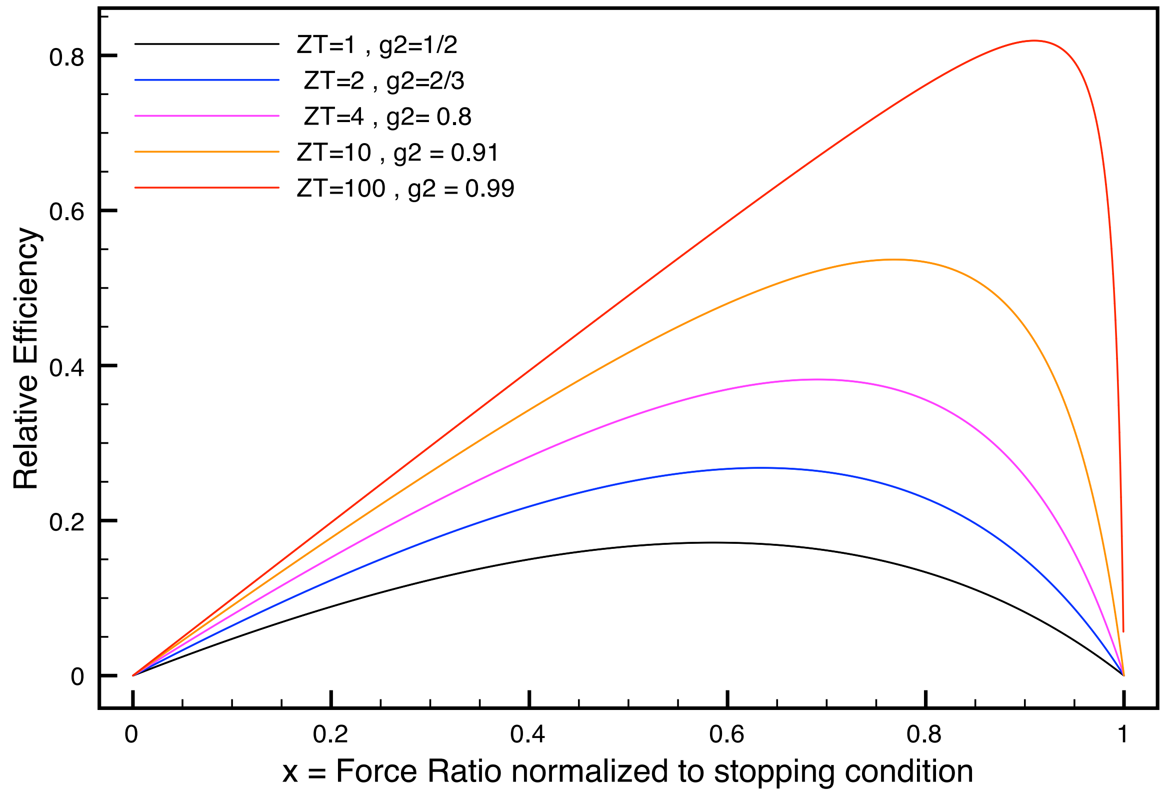
$$P_{max} = \frac{1}{4}\alpha^2\sigma\,(\nabla T)^2$$ Maximum power always reached at x=1/2 !
Power factor: $\alpha^2\sigma$

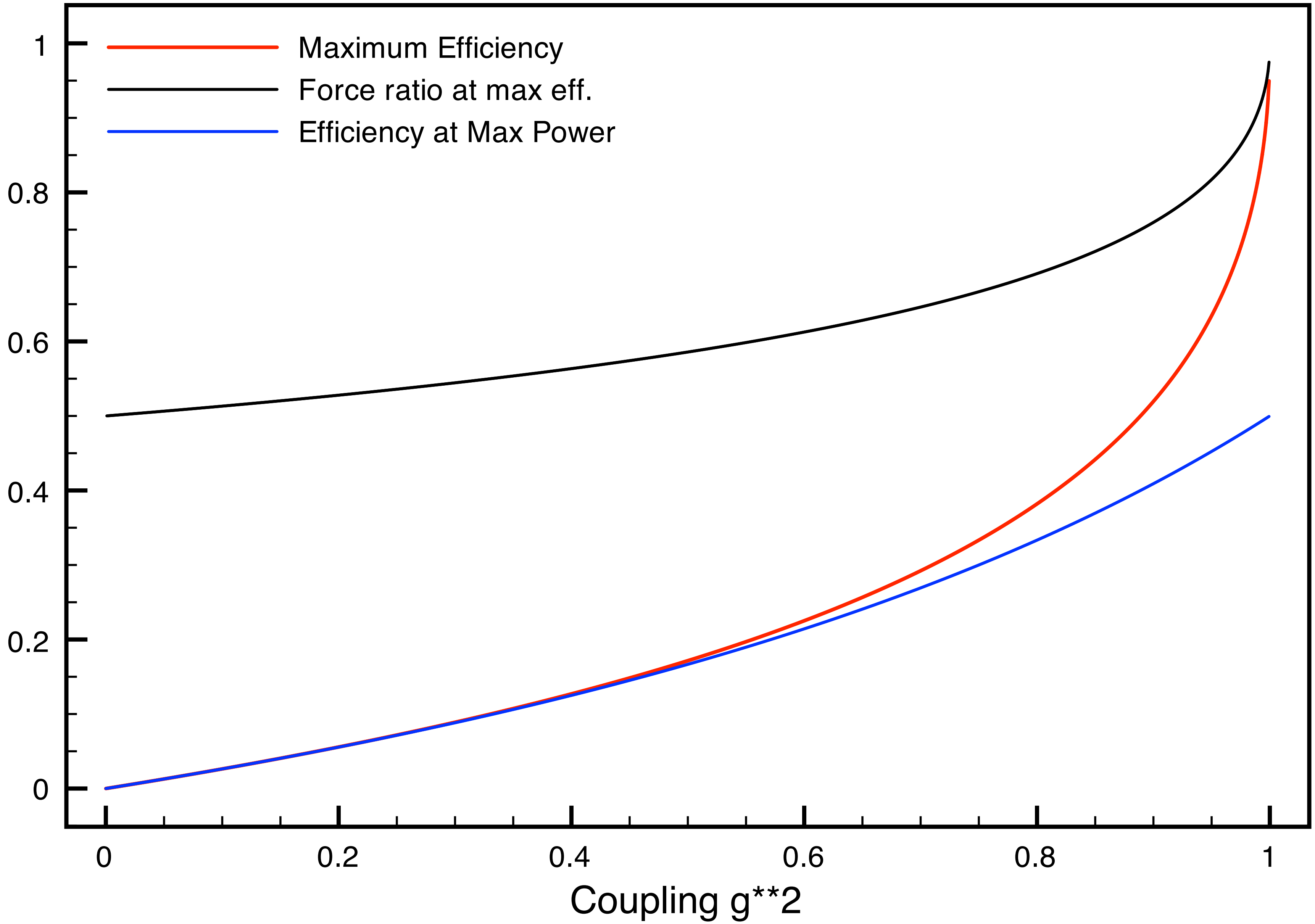
Maximum efficiency:

$$\eta_r^{max} = \frac{\sqrt{\overline{z}+1}-1}{\sqrt{\overline{z}+1}+1} = \frac{1-\sqrt{1-g^2}}{1+\sqrt{1+g^2}} \quad , \quad x_{max} = \frac{1}{\overline{z}}\left[\overline{z}+1-\sqrt{\overline{z}+1}\right] = \frac{1-\sqrt{1-g^2}}{g^2}$$

Efficiency at maximum power (@x=1/2):

$$\eta_r(p_{max}) = \frac{\overline{z}}{2(2+\overline{z})} = \frac{g^2}{2(2-g^2)}$$





Maximum Efficiency
Force ratio at max eff.
Efficiency at Max Power
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
Coupling g**2

Eliminating x in favour of P/P_{max}

Finally, we can also eliminate the force ratio, and establish an efficiency vs. power plot. We define the power normalized to its maximum value:

$$\overline{p} \equiv \frac{p}{p_{max}} = 4x(1-x) \tag{57}$$

and invert:

$$x = \frac{1}{2}\left[1 \pm \sqrt{1-\overline{p}}\right] \tag{58}$$

with the upper (+) sign for $x \geq 1/2$ and the lower (−) one for $x \leq 1/2$. Inserting this into the expression of η_r, we obtain two branches:

$$\eta_r = \frac{\overline{p}}{2 + 4/\overline{z} \pm 2\sqrt{1-\overline{p}}} \;, \quad (+ : x \leq 1/2 \;, \; - : x \geq 1/2) \tag{59}$$

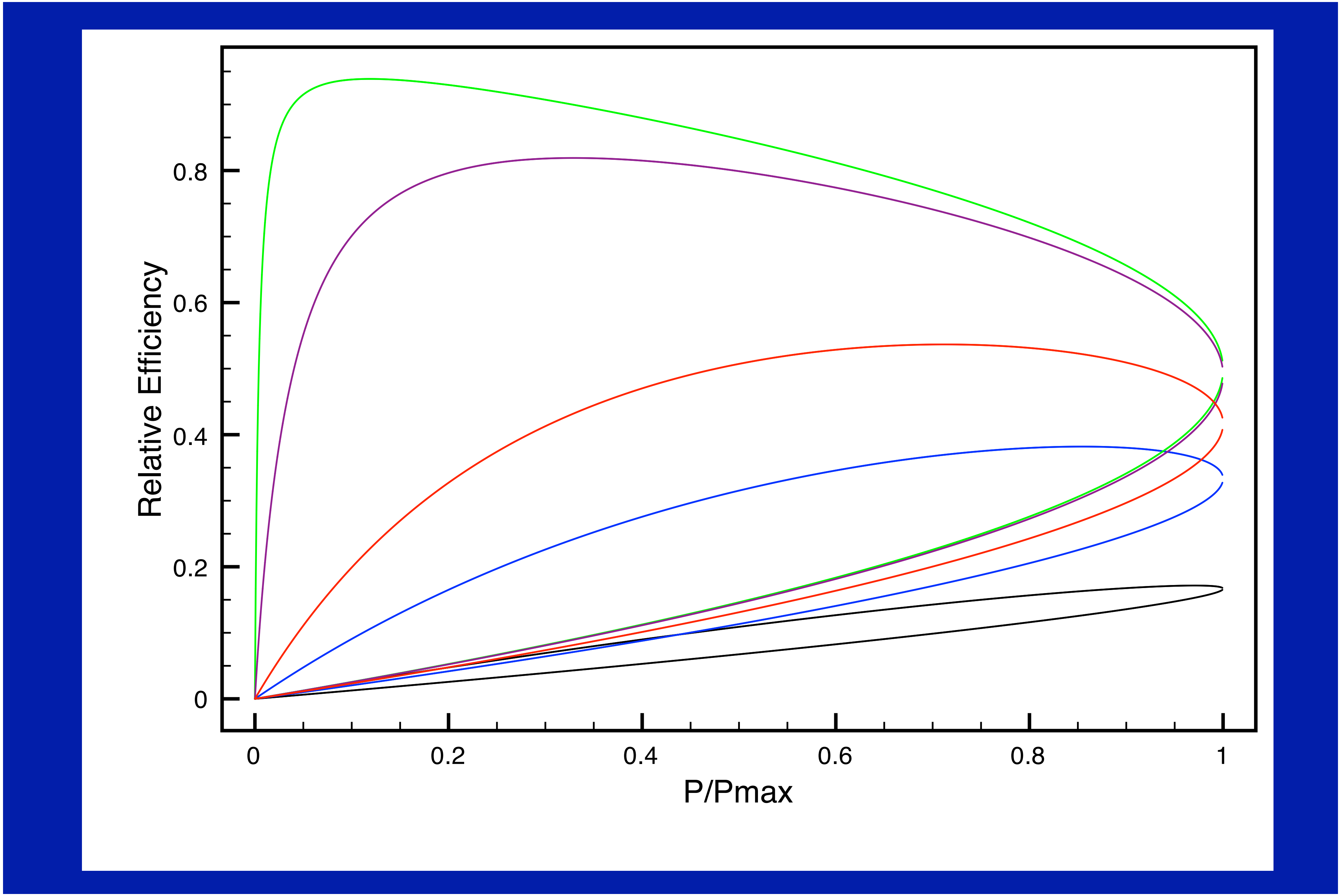


FIG. 4: Relative efficiency vs. power normalized to its maximum value, for (bottom to top): $\overline{z} = 1, 4, 10, 100, 1000$. The upper (resp. lower) branches correspond to a force ratio $x \geq 1/2$ (resp. $x \leq 1/2$). Maximum efficiency is realized on the upper branch.

Take-home Message

- Energy conversion efficiency is controlled by the dimensionless figure of merit/coupling:

$$\overline{z} = T\frac{\alpha^2\sigma}{\kappa}\ ,\ g = \frac{L_{12}}{\sqrt{L_{11}L_{22}}}\ ,\ g^2 = \frac{\overline{z}}{1+\overline{z}}$$

- Useful thermoelectric materials must have:
- Large power factor
- (Often summarized as large Seebeck, low resistivity – such as to minimize Joule losses)
- Low thermal conductivity (such as to sustain the thermal gradient)
- → A materials science challenge !

Concluding paragraph of Goldsmid, 1954:

Finally attention is drawn to the fact that the same figure of merit, which applies to thermoelectric refrigerators, also applies to thermoelectric generators, and the latter might well have an important place in the future, notably in connexion with the utilization of solar energy.[13]

GOOD METALS are bad thermoelectrics…

Thermopower measures *entropy per charge carriers*

In a metal (quantum degenerate regime), entropy ~ $k_B \dfrac{k_B T}{\epsilon_F}$

$$\alpha \sim \pm \frac{k_B}{e} \frac{k_B T}{\epsilon_F} \ , \quad k_B T << \epsilon_F$$

Very low !

$$\boxed{\frac{k_B}{e} \simeq 86.3 \, \mu \mathrm{V.K}^{-1}}$$

Note: $\overline{Z} = \alpha^2 \dfrac{\sigma}{\kappa / T} = \dfrac{\alpha^2}{\mathcal{L} + \kappa_l / \kappa_e}$

→ Need to beat Wiedemann-Franz law

Semiconductors have a much better Seebeck …

Simple-minded calculation: two energy levels separated by a gap Δ, non-degenerate (~ classical Boltzmann) regime kT<<Δ :

$$p_c = \frac{e^{-\beta\Delta/2}}{e^{\beta\Delta/2} + e^{-\beta\Delta/2}} \simeq e^{-\beta\Delta}$$

$$p_v \simeq 1 - e^{-\beta\Delta}$$

$$S_c/k_B = -p_c \ln p_c - (1-p_c)\ln(1-p_c) \simeq \beta\Delta e^{-\beta\Delta}$$

$$n_c = p_c \simeq e^{-\beta\Delta}$$

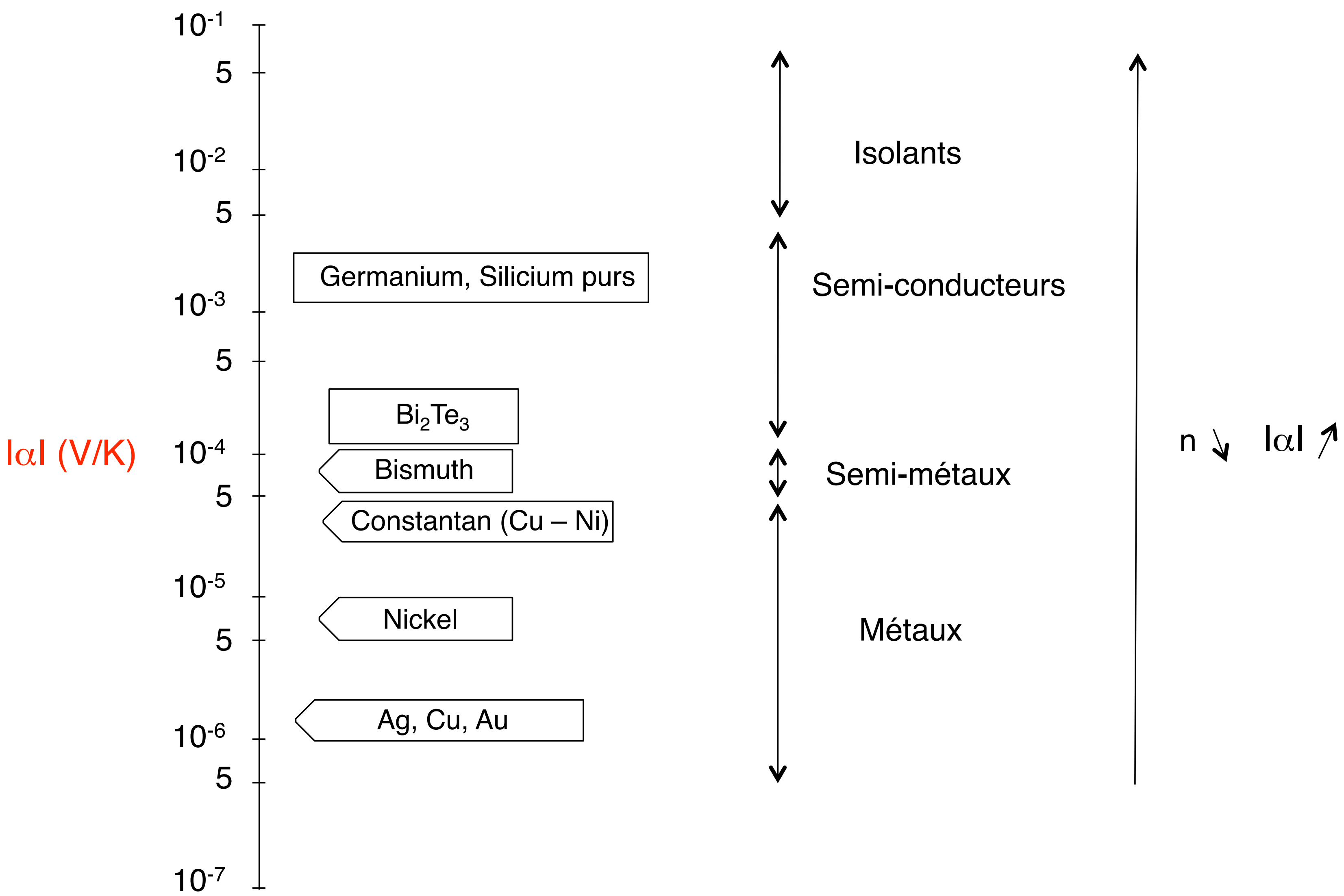
$$\boxed{\alpha_{\max} \sim \pm \frac{k_B}{e}\frac{\Delta}{k_B T}}$$

$$\alpha \simeq \frac{\alpha_n\mu_n + \alpha_p\mu_p}{\mu_n + \mu_p}$$

Need ~ a single type of carriers (e.g. very different mobilities)

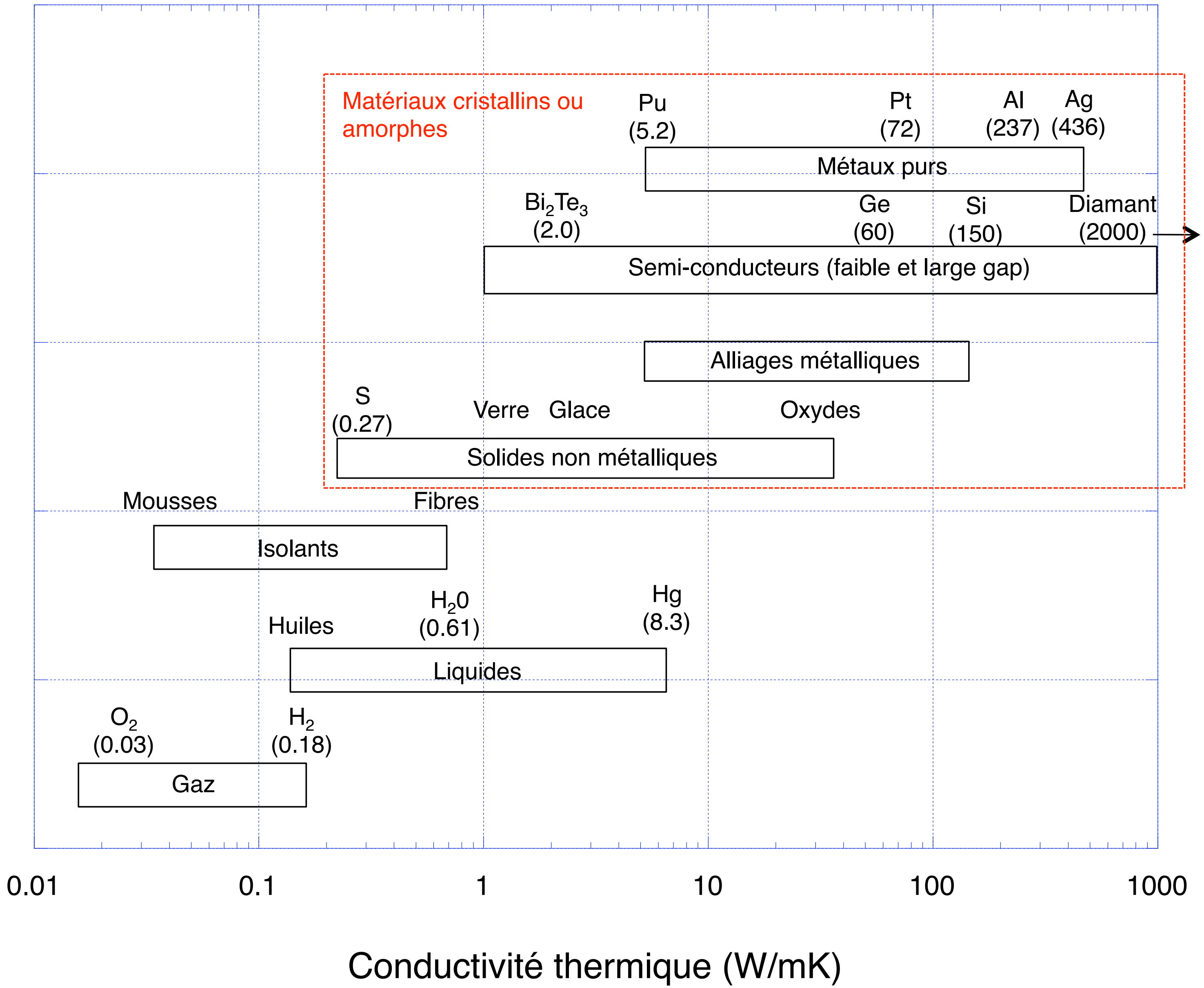
… but a too large gap spoils the conductivity

Effet Seebeck : ordre de grandeur à 300 K



From: B.Lenoir, GDR Thermoelectricite summer school 2012

Conductivité thermique : ordre de grandeur à T = 300 K

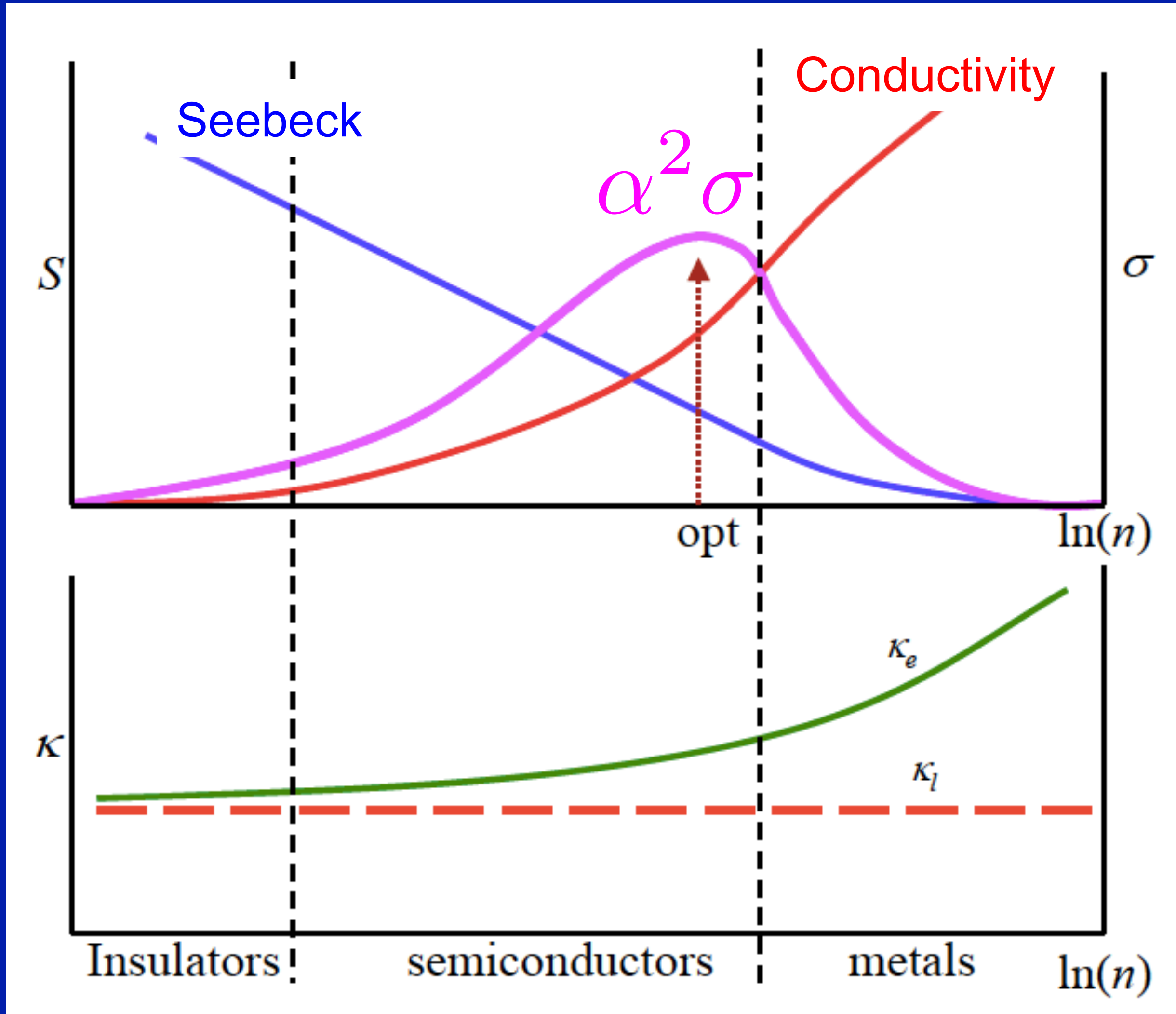


From: B.Lenoir, GDR Thermoelectricite summer school 2012

Table I. Comparison of thermoelectric properties of metals, semiconductors and insulators at 300K. (after ref. [2])

Property	Metals	Semiconductors	Insulators
S (μVK^{-1})	~ 5	~ 200	~ 1000
σ ($\Omega^{-1}cm^{-1}$)	~ 10^{6}	~ 10^{3}	~ 10^{-12}
Z (K^{-1})	~3×10^{-6}	~2×10^{-3}	~5×10^{-17}

Semiconductors and the first golden age of thermoelectricity: 1950 → ~ 1965



→ Optimal range of carrier concentration (~ 10^{19}-10^{20} /cm^3)

Abram Ioffe (1880-1960)

- Prominent physicist, Soviet Union
- Pioneer of semiconductor physics, use of semiconductors as thermoelectrics, and much more…
- Also the author of the `Ioffe-Regel – Mott' criterion
- Directed PhD's of Aleksandrov, Davydov, Frenkel, Kapitsa, Kurchatov, etc…
- Ioffe Physico-Technical Institute in St Petersburg bears his name
- Stalin Prize, Lenin prize, Hero of Socialist Labor

- Author of books `Semiconductor thermoelements' and `Thermoelectric cooling' (1957)

From Abram Ioffe’s book: how to operate a few W
radio receiver with a kerosene-burning lamp… (USSR, ca. 1955)

H.J. Goldsmid (U. of New South Wales, Australia): Bi_2Te_3 and thermoelectric cooling (1954)

Author of several books, especially: `Introduction to Thermoelectricity' (Springer, 2010)
– Recommended reading

(British J. Appl. Phys. 5 (1954) 386)

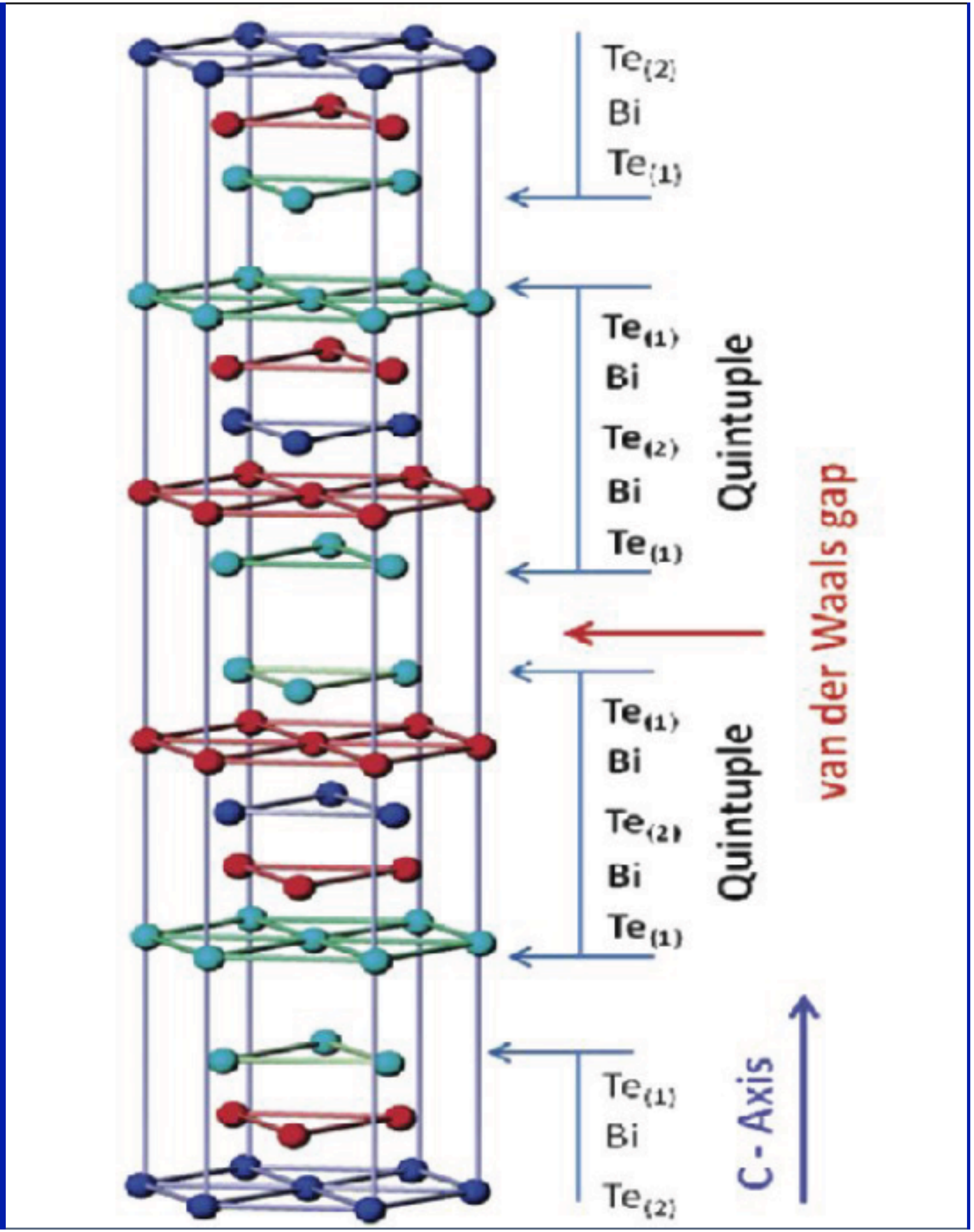
The use of semiconductors in thermoelectric refrigeration

By H. J. Goldsmid, B.Sc., and R. W. Douglas, B.Sc., F.S.G T., F Inst.P., Research Laboratories, The General Electric Co. Ltd , Wembley, Middlesex

[*Paper received* 6 *July*, 1954]

In the past the possibility of thermoelectric refrigeration has been considered, but all attempts to produce a practical refrigerator have failed owing to lack of suitable thermocouple materials In this paper it is proposed that semiconductors should be used and the factors governing their selection are discussed. It is concluded that the semiconductors should be chosen with high mean atomic weights and that they should be prepared with thermoelectric powers lying between 200 and 300 $\mu V.{}^{\circ}C^{-1}$. Preliminary experiments have led to the production of a thermocouple consisting of bismuth telluride, Bi_2Te_3, and bismuth, capable of maintaining 26° C of cooling

Bi_2Te_3

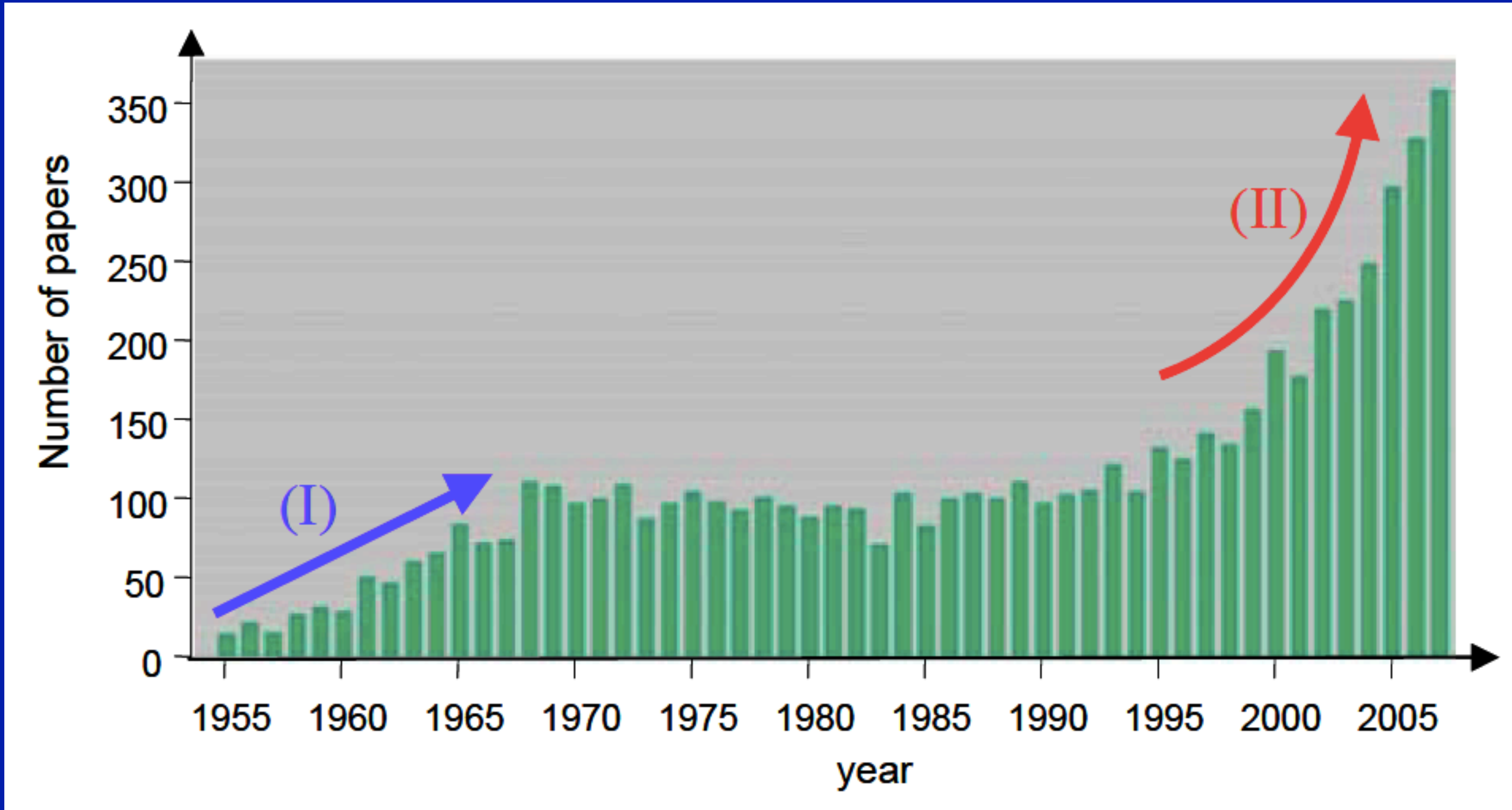

Te(2)
Bi
Te(1)
Te(1)
Bi
Te(2)
Bi
Te(1)
Quintuple
van der Waals gap
Te(1)
Bi
Te(2)
Bi
Te(1)
Quintuple
Te(1)
Bi
Te(2)
C - Axis

Basic electronic properties

- Energy gap: about 0.13 eV
- Multivalley (6 in c-band, 6 in v-band)
- Relatively low effective masses in each valley
- But because of multivalley: d.o.s effective mass sizeable (0.5 m_e → 1.5 m_e)
- Scattering exponent r = -1/2 observed
- Lattice thermal cond. of order 1W/m/K @ 300K (anisotropic, see below)

~ 1995 → …
A new Golden Age of Research on Thermoelectrics

Number of articles on Thermoelectrics:



JC Zheng
Front. Phys. China
3 (2008) 269

Data obtained from database of "ISI Web of Knowledge" with search option of "thermoelectric or thermoelectrics" in Title only. http://www.isiwebofknowledge.com/ (accessed March 19, 2008).

Key advances :

- Nanostructuration → lowering of thermal conductivity
- New materials with good Seebeck and/or low thermal conductivity :
- Oxides
- Skutterudites, Clathrates, Zintl phases,…

cf. review by GJ Snyder and ES Toberer, Nat Mat 7 (2008) 105

- → See seminars by S.Hebert and by F.Gascoin,

as well as other seminars in the 2012-2013 cycle.

Cobalt oxides: Na_xCoO_2

Terasaki et al. PRB 56 (1997) R12685 ~ 1280 citations…

`Misfit' cobaltates in CRISMAT-Caen

Na ions in between layers →

Triangular CoO_2-layers →

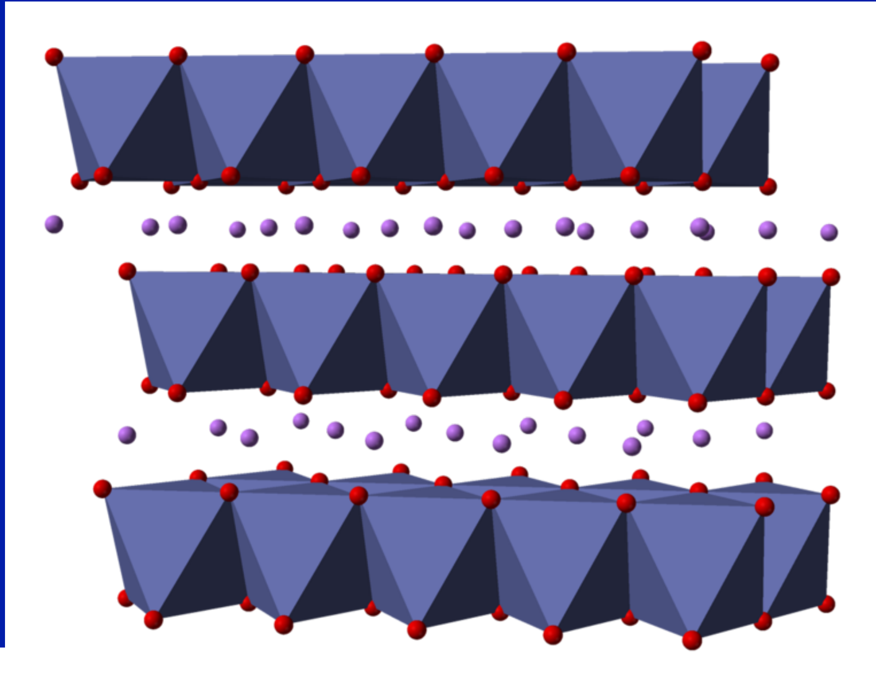
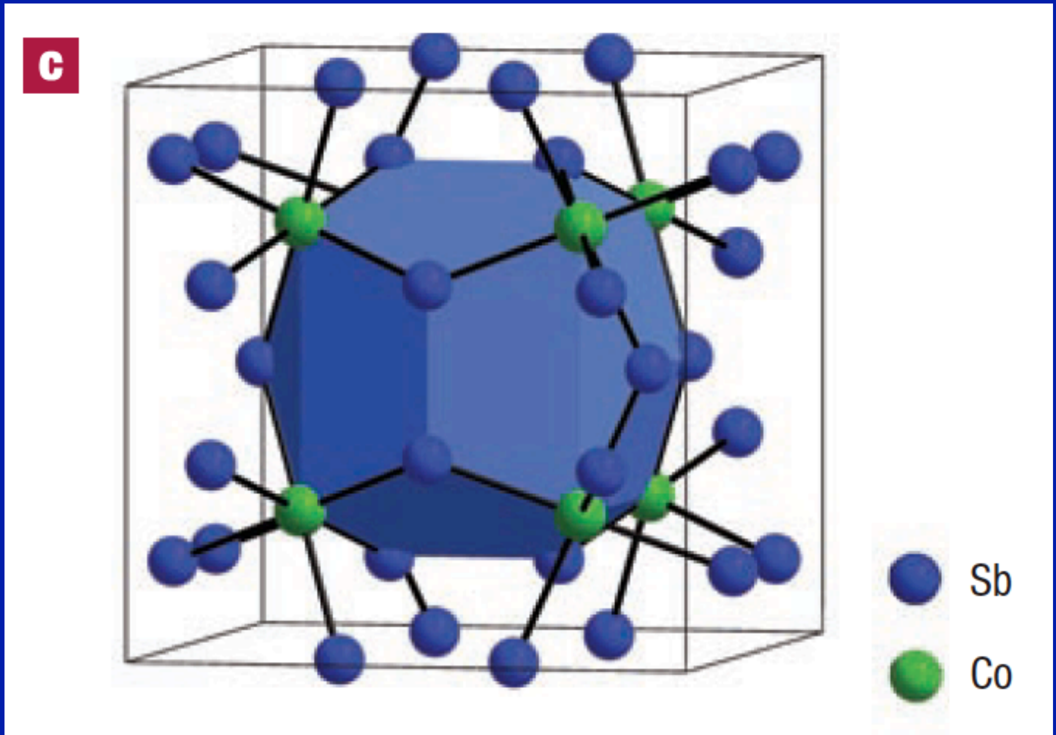


TABLE I. Various physical parameters for $NaCo_2O_4$ and Bi_2Te_3 (Ref. 6) at 300 K. ρ, S, and μ are resistivity, thermoelectric power, and mobility, respectively. Note that ρ and S of $NaCo_2O_4$ are the in-plane data.

Parameters	Unit	$NaCo_2O_4$	Bi_2Te_3
ρ	mΩ cm	0.2	1
$\lvert S \rvert$	μV/K	100	200
S^2/ρ	μW/K^2 cm	50	40
μ	cm^2/V s	13	150

Note similarities to $LiCoO_2$ batteries

Skutterudites, Clathrates:
`Rattling' atoms in cages scatter phonons
`Phonon glass, electron crystal'



Skutterudite $CoSb_3$: the tilted $CoSb_6$ leave a large cage
In which `rattler' atoms can be inserted.

Cf. review by Nolas et al. Ann. Rev. Mat Sci.

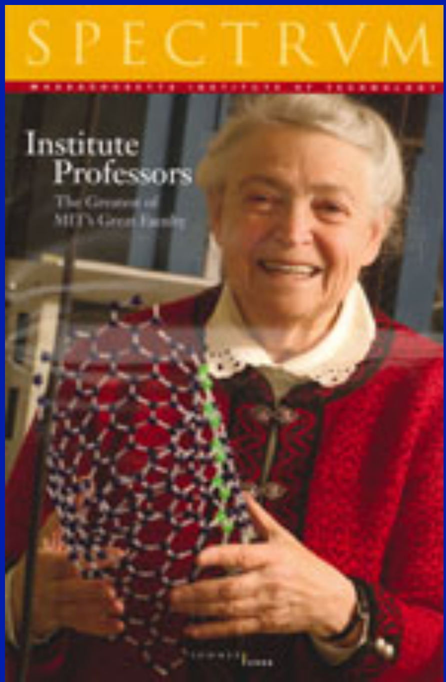
PHYSICAL REVIEW B VOLUME 47, NUMBER 19 15 MAY 1993-I

Effect of quantum-well structures on the thermoelectric figure of merit

L. D. Hicks
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

M. S. Dresselhaus
Department of Electrical Engineering and Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 3 December 1992)

> 1100 citations



Mildred Dresselhaus, MIT

Originally envisioned as improvement of Electronic properties, but turned out to be especially efficient for lowering thermal conductivity !

Reports of ZT > 2

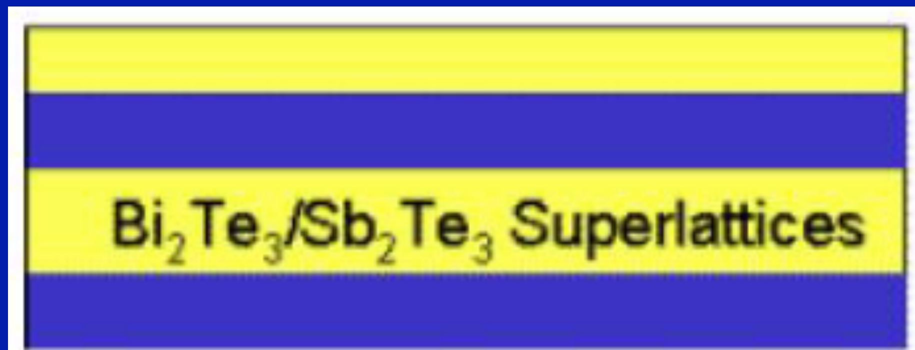
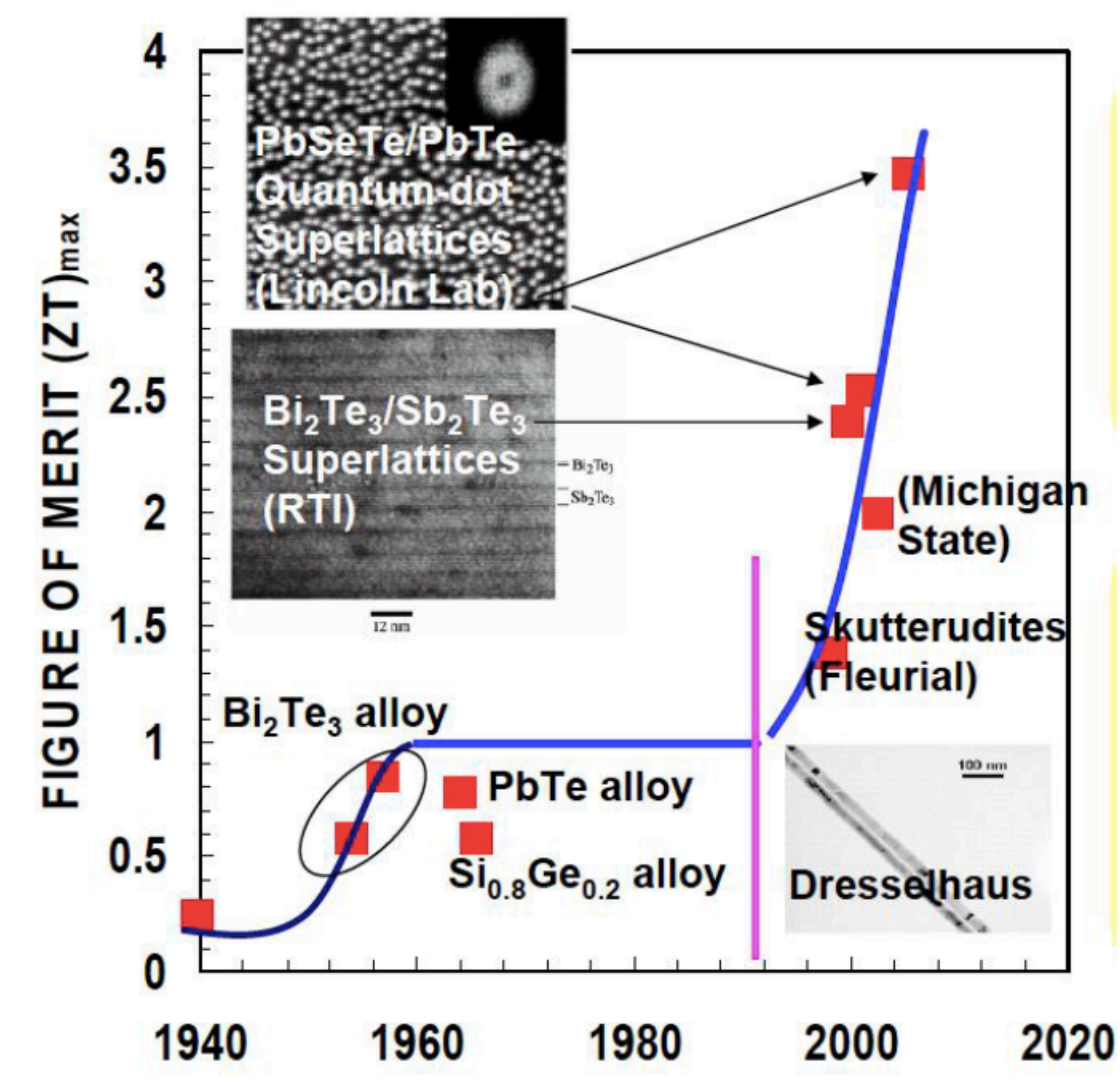


Figure of merit vs. time ?

From S.Volz Talk@Cargese, 2012



`One should be encouraged by results of ZT>1 but wary of the uncertainties involved to avoid pathological optimism
`G.Snyder, Nat Mat'

A thermomagnetic mechanism for self-cooling cables

Luca de' Medici[1,2]

[1] *European Synchrotron Radiation Facility, 71 Av. des Martyrs, Grenoble, France*
[2] *Laboratoire de Physique et Etude des Matériaux, UMR8213 CNRS/ESPCI/UPMC, Paris, France*

(Dated: May 22, 2015)

A solid state mechanism for cooling high-power cables is proposed based on the Ettingshausen effect, i.e. the transverse thermoelectric cooling generated in high magnetic fields. A small current running through a layer of a strong "thermomagnetic" material coating the conducting cable core can exploit the magnetic field generated by the high current transported in the core itself in order to create a temperature gradient between the inside of the cable and the external environment. Both analytical calculations and realistic numerical simulations for Bismuth coatings in typical magnetic fields are presented. The latter yield temperature drops $\simeq$60K and >100K for a single- and double-layer coating respectively. These encouraging results should stimulate the search for better thermomagnetic materials, in view of applications such as self-cooled superconducting cables working at room temperature.