``Enseigner la recherche en train de se faire''

COLLÈGE DE FRANCE 1530

Chaire de
Physique de la Matière Condensée

THERMOELECTRICITE: CONCEPTS, MATERIAUX ET ENJEUX ENERGETIQUES

Antoine Georges

Cycle 2012-2013

Première séance - 20 mars 2013

- Perspectives générales / Overview
- Historique / Historical aspects
- Principaux effets thermoélectriques / Main thermoelectric effects
- Coefficients et équations de transport Transport equations: linear response, transport coefficients

→ *Today: A general, non-technical introduction*

Séminaire – 20 mars 2013

- Séminaire : 11h15 -

Thierry CAILLAT, *Jet Propulsion Laboratory, CALTECH*

Thermoelectrics: From Space to Terrestrial Applications - Successes, Challenges and Prospects

Excerpt from abstract:

A review of the various prospective applications including automobile and industrial waste heat recovery is provided and the technical and economical challenges are highlighted. One of the key-enabling technologies for these applications is high-temperature, high-efficiency thermoelectric materials and converters. A review of state-of practice and state-of-the art high-temperature thermoelectric materials and converters is presented including recent development at the Jet Propulsion Laboratory (JPL). Key challenges are summarized and future prospects for large-scale application of thermoelectrics are discussed.

Outline of future lectures:

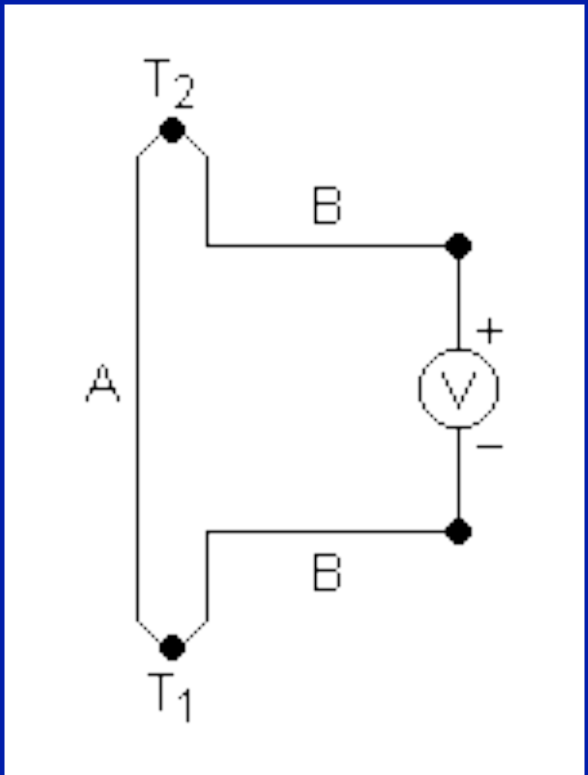
- March 27: : Thermodynamics of thermoelectricity (seminar: K.Behnia)
- No lecture on April, 3
- April 10: Theory for Seebeck coefficient, Oxide Materials (seminar: S.Hebert)
- April 17: Theory (cont'd). Seminar: F.Gascoin
- April 24: Two lectures (subject to be announced)
- May 22 (or 15 ?): 3 seminars on thermal transport and nanostructuration
- Fall 2013: Continuation (mesoscopics, etc.)

I gratefully acknowledge help and input from:

- S. Hebert and A. Maignan (CRISMAT Caen)
- J-L Pichard (SPEC-CEA Saclay)
- K.Behnia (ESPCI)
- C. Goupil (CRISMAT Caen)
- C.Grenier, J.Mravlje, A.Subedi (Ecole Polytechnique and Collège de France)

TWO KEY THERMOELECTRIC EFFECTS :
1. The Seebeck effect (1821)

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

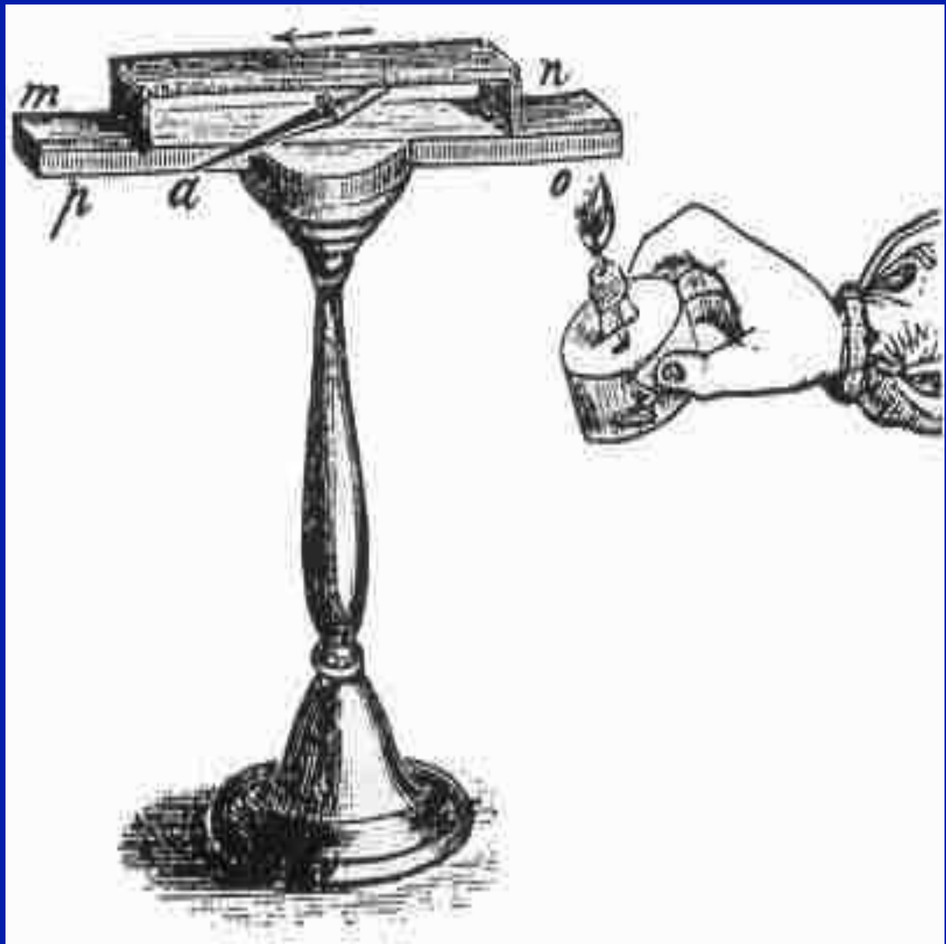


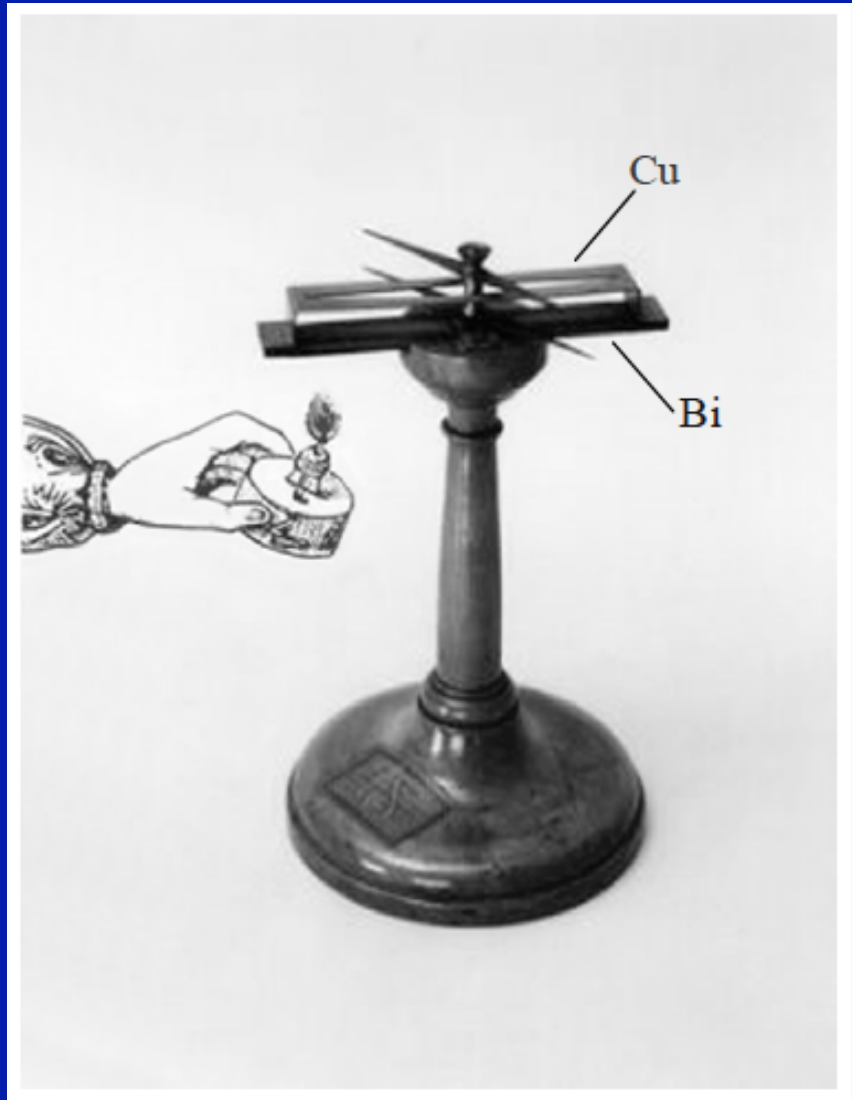
$$\Delta V = -\alpha \, \Delta T$$

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 magetic field
- Discovered the sensitivity of silver chloride to light → `precursor of colour photography’
- Magnetic properties of nickel and cobalt (1810)

Source: mostly wikipedia

Or, actually, Alessandro Volta in 1794…

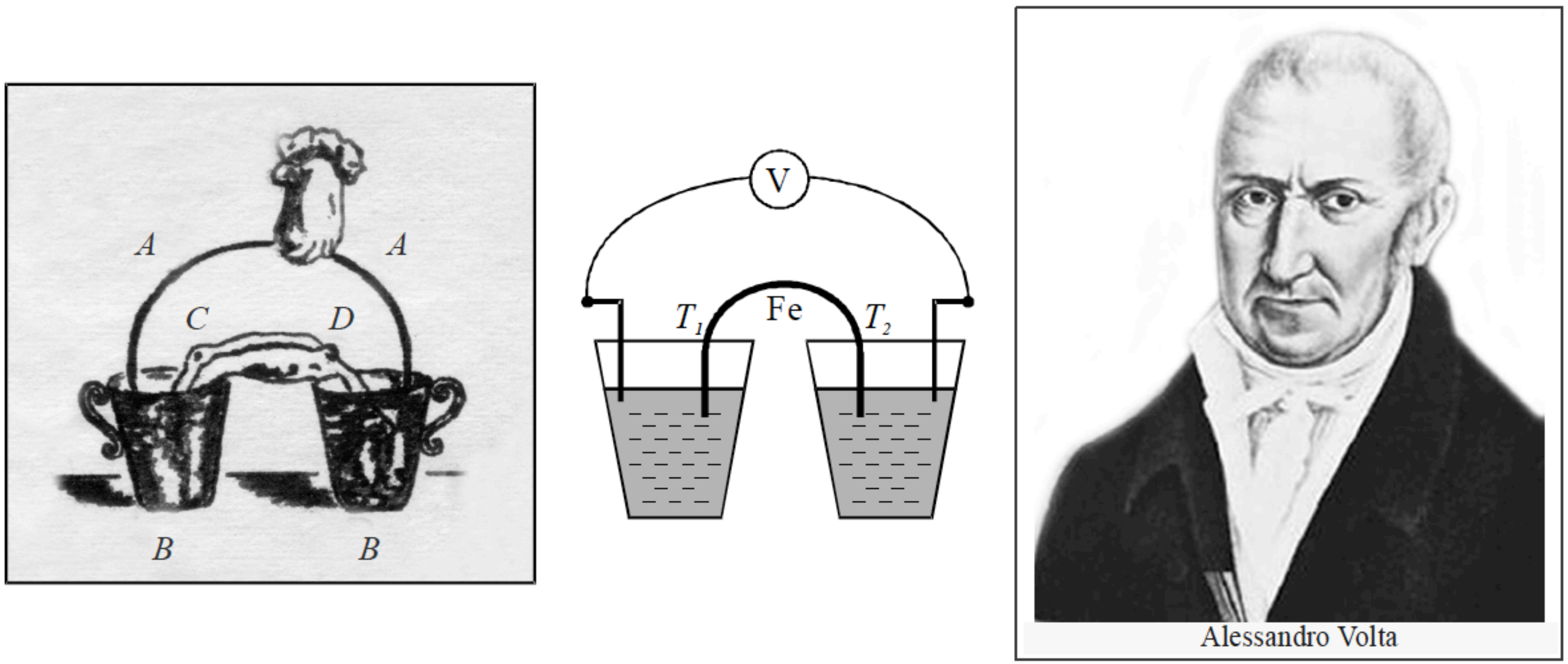
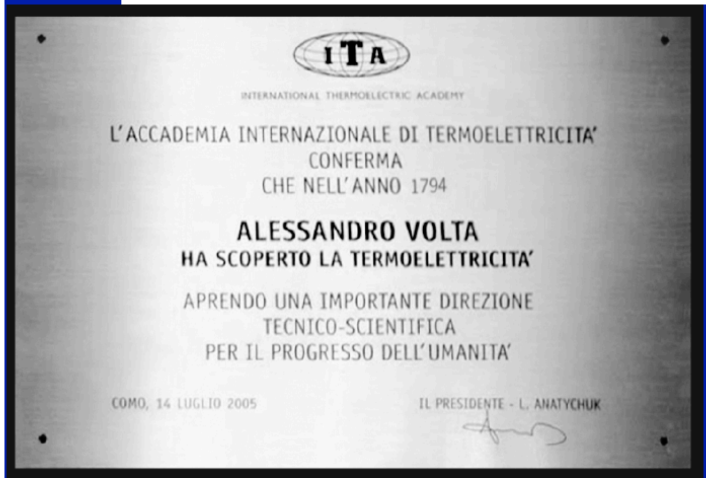


Fig. 3. Discovery of thermoelectricity by Volta on February 10, 1794.

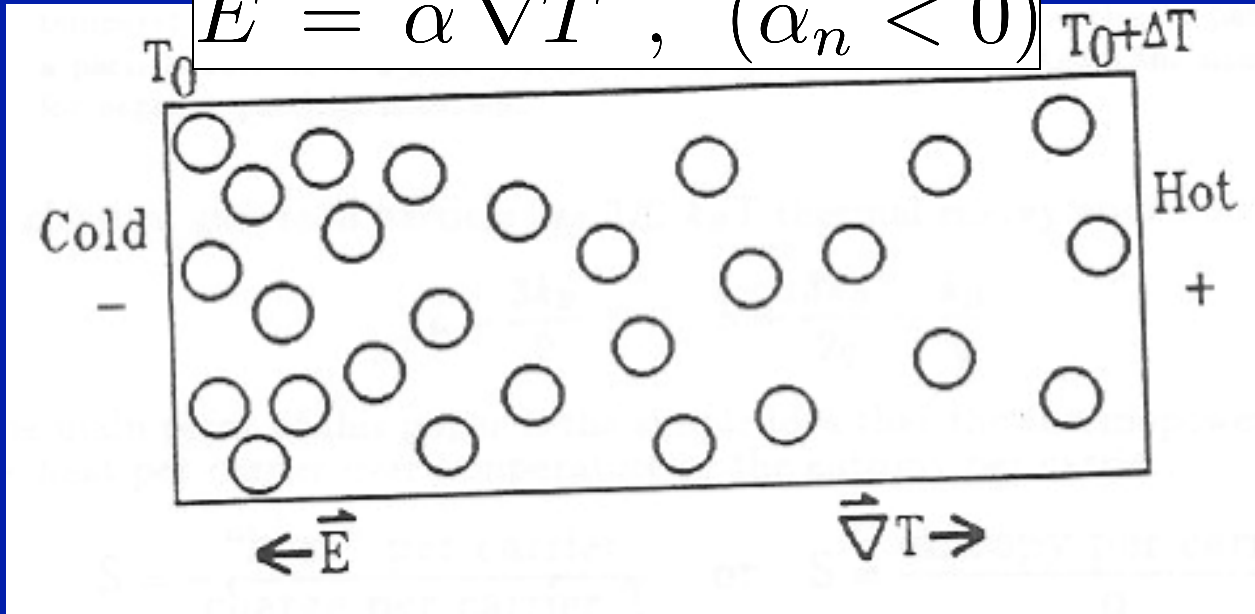


cf. e.g. LI Anatychuk,
Journal of Thermoelectricity, 1994
G.Pastorino, ibid., 2009

Qualitative picture:

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

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

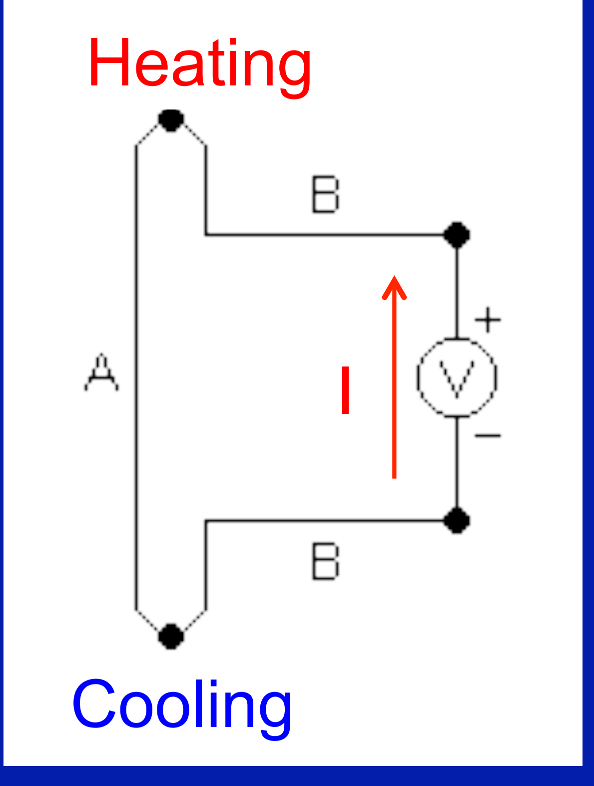


- Higher density of carriers on the cold side, lower on hot side
- → an electric field is established
- In this cartoon: carriers are negatively charged, hence field is <u>opposite</u> to thermaal gradient
- Electron-like (hole-like) carriers correspond to negative (positive) Seebeck coefficient → Seebeck useful probe of nature of carriers

TWO KEY THERMOELECTRIC EFFECTS :
2. 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):

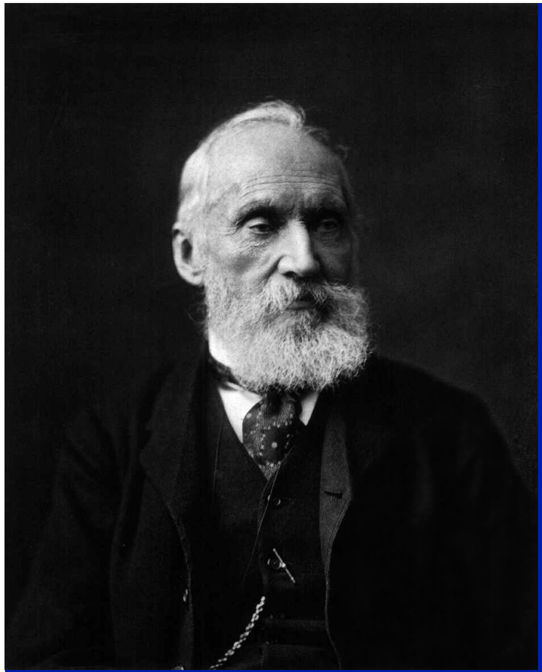
$$\Pi = T\,\alpha$$

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

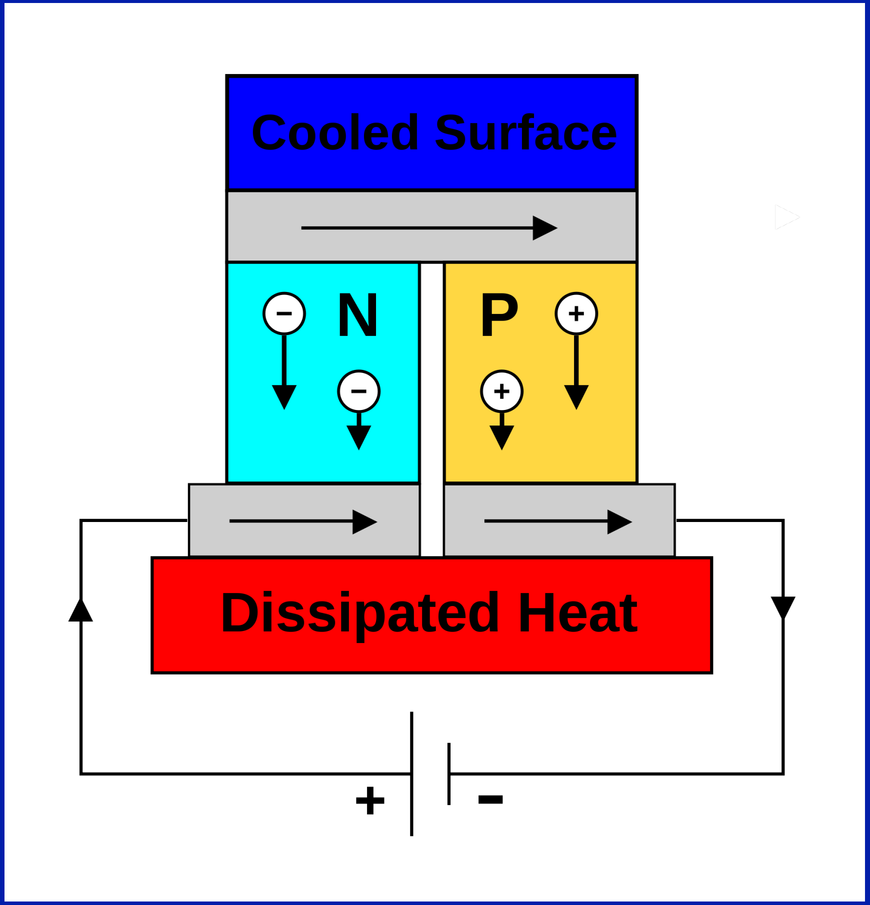


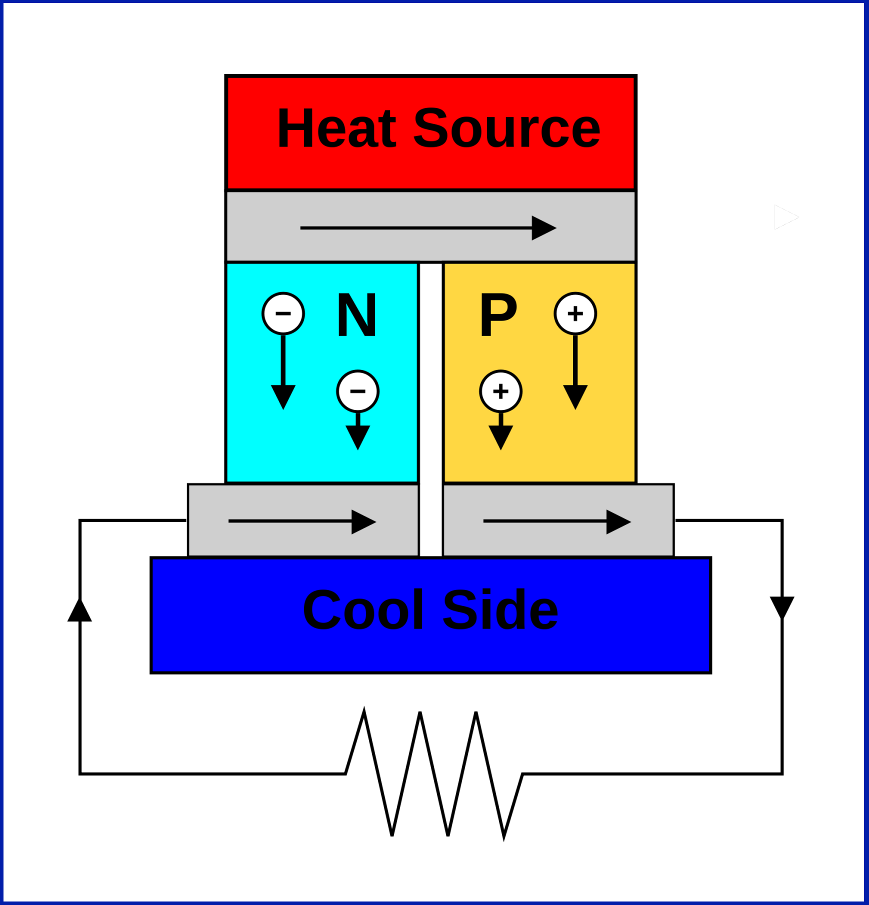
Thermodynamics of thermoelectricity: William Thomson (Lord Kelvin)

(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

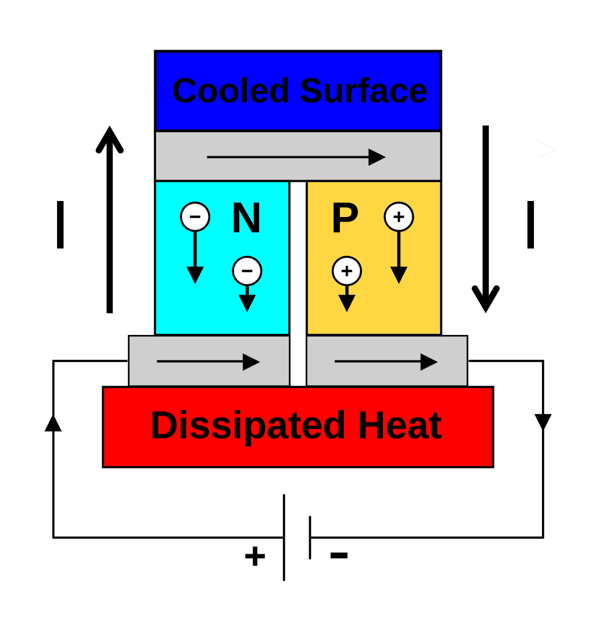




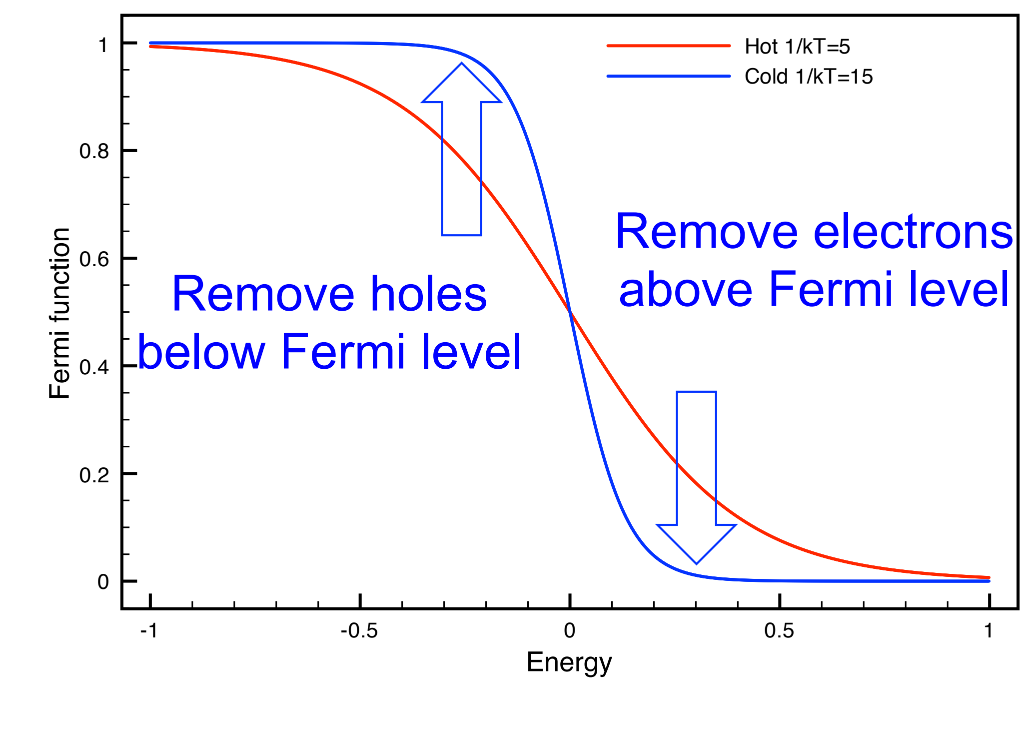
Cooling module [Peltier]

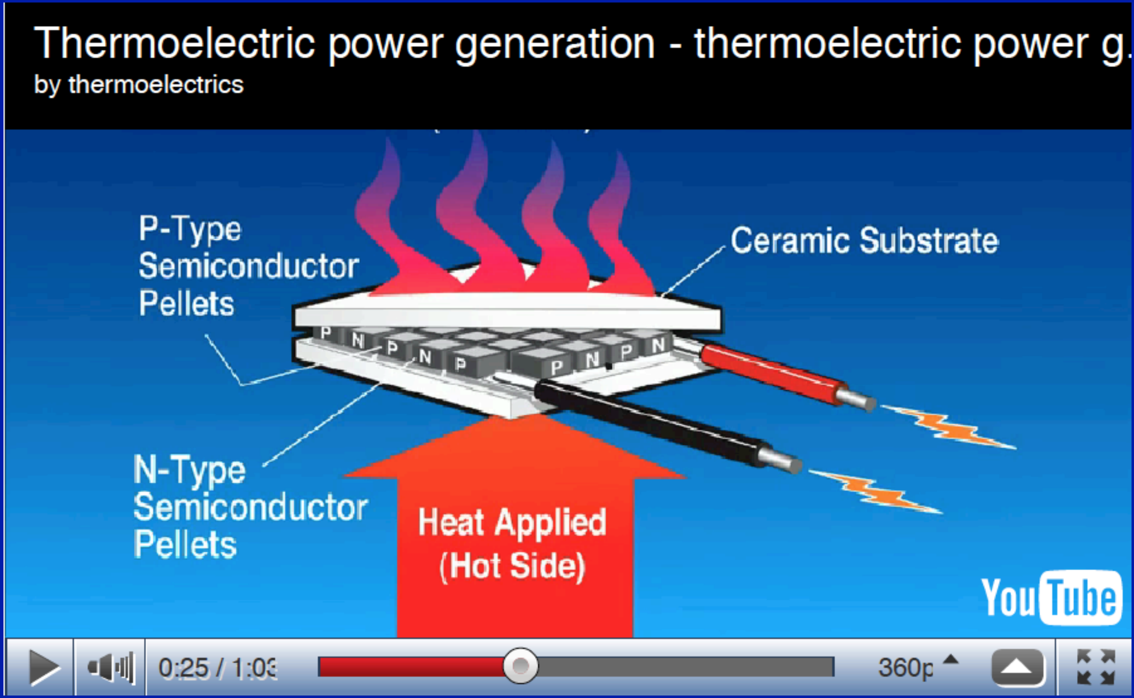
Power generation module [Seebeck]

Simple intuition about thermoelectric cooling



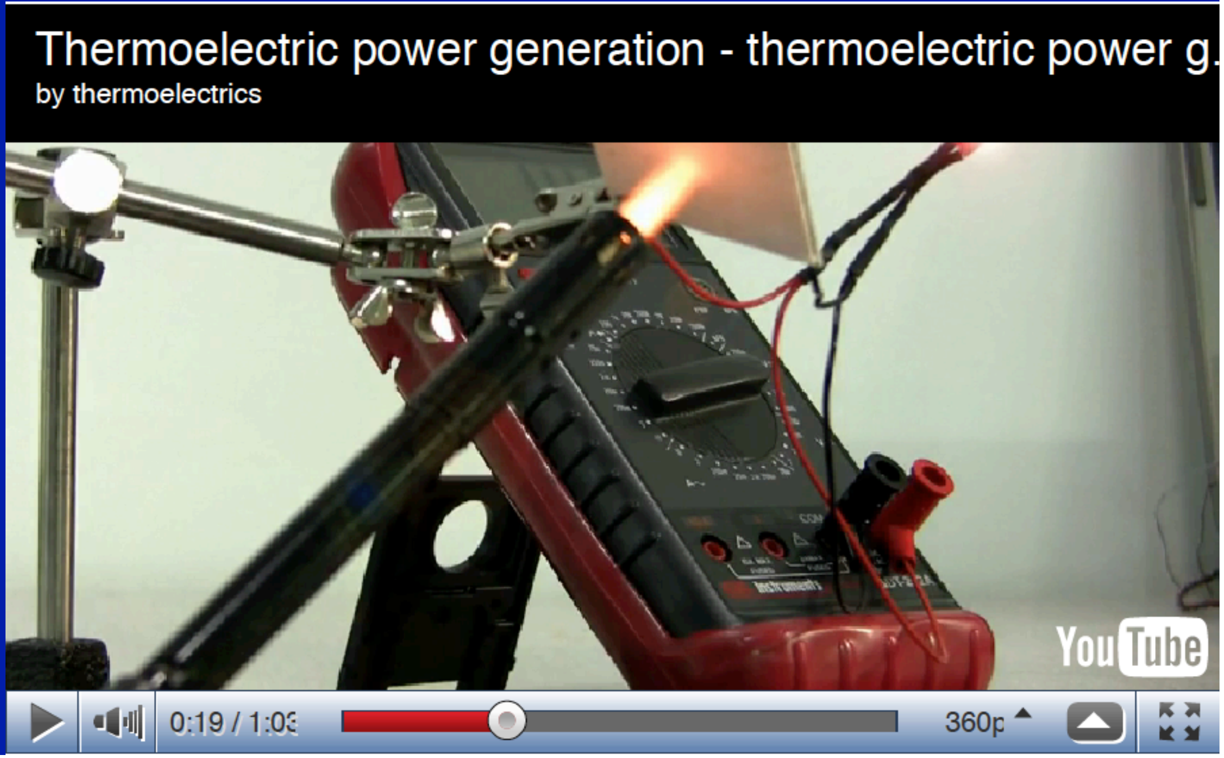
- Electrons move against current
- Holes move along current
- BOTH electrons and holes leave cold end to reach hot end
- BOTH processes correspond to lowering of entropy of cold end



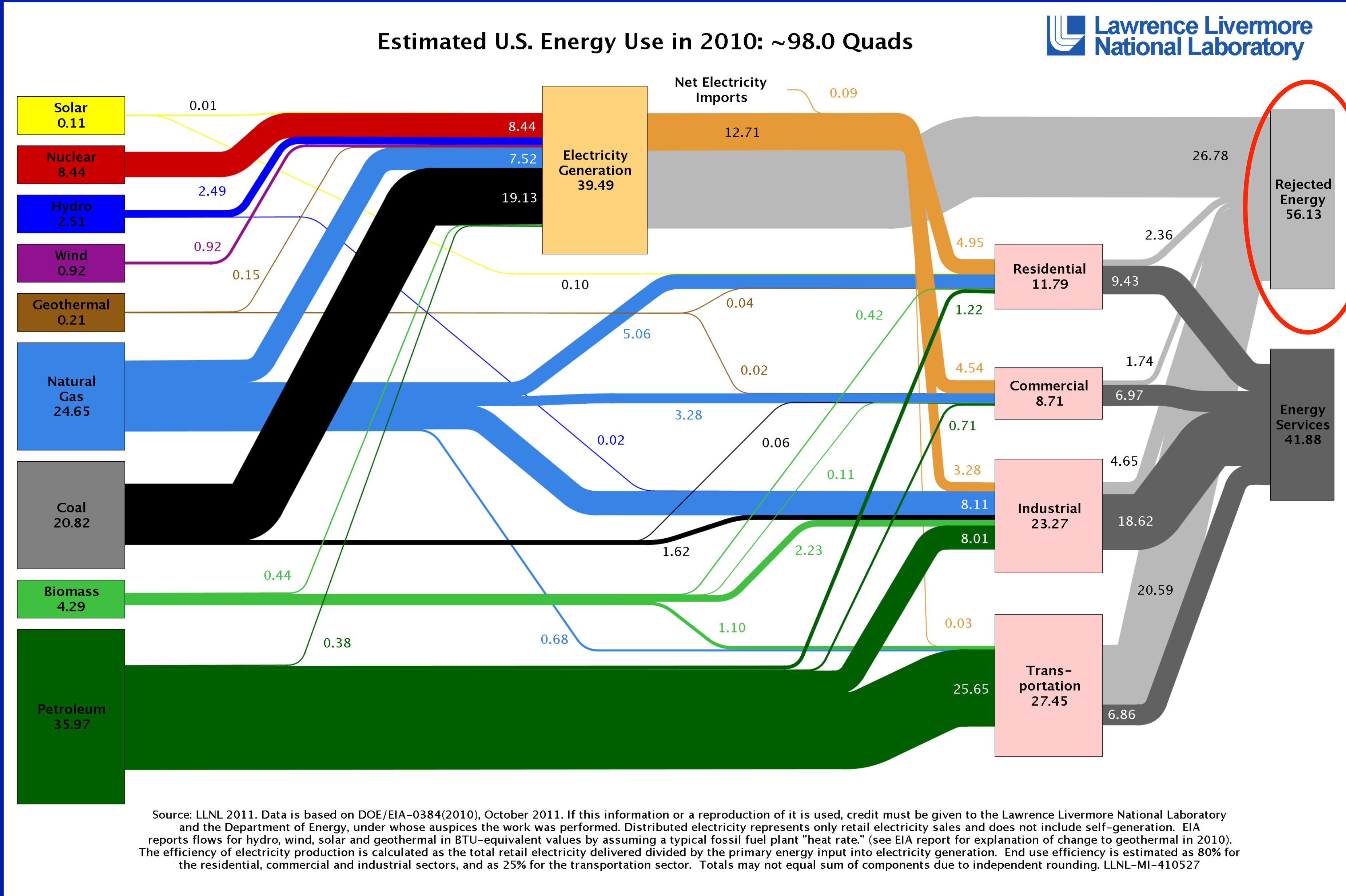


A real module

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

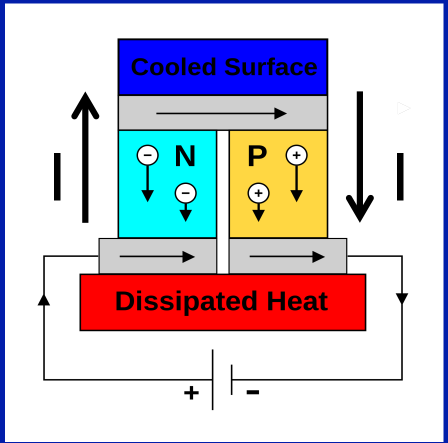


Waste heat recovery: about 55% of energy in the US rejected as waste…



Cooling efficiency: the `Figure of Merit'

$$\alpha \equiv \alpha_p - \alpha_n \;, \quad R \equiv R_p + R_n \;, \quad K = K_p + K_n \;, \quad \Delta T \equiv T_H - T_C$$



Heat production rate at cold side:

$$\dot{Q}_c = \alpha T_C I - K \Delta T - \frac{1}{2} R I^2$$

Peltier heat

<u>Loss</u> from heat conduction from hot to cold side

<u>Loss</u> by Joule heating

Heat absorption rate at hot side:

$$\dot{Q}_H = \alpha T_H I - K \Delta T + \frac{1}{2} R I^2$$

Cost of operation (power provided by generator):

$$\dot{W} = \dot{Q}_H - \dot{Q}_C = \alpha \Delta T I + R I^2$$

V.I : power to sustain Peltier voltage

Joule

Cooling efficiency (`coefficient of performance' COP):

x: dimensionless voltage ratio

$$\phi \equiv \frac{\dot{Q}_C}{\dot{W}} = \frac{-x^2/2 + (T_c/\Delta T)x - 1/(Z\Delta T)}{x(1+x)} \quad , \quad x \equiv \frac{RI}{\alpha \Delta T}$$

$$\boxed{Z \equiv \frac{\alpha^2}{KR}}$$

`Figure of merit'
(Note:
Z.T dimensionless)

$$\dot{Q}_C = \frac{\alpha^2}{R} (\Delta T)^2 \times (\text{numerator})$$

$$\boxed{\alpha^2/R}$$

`Power factor'

Largest cooling: $\frac{\Delta T_{\max}}{T_C} = \frac{1}{2} Z T_C$

Study x-dependence → Two important values:

Maximum COP (cooling):

$$\phi_{\max} = \frac{1}{1 - T_C/T_H} \frac{\sqrt{1+\overline{Z}} - T_C/T_H}{\sqrt{1+\overline{Z}} + 1} \quad , \quad \overline{Z} \equiv Z \frac{T_C + T_H}{2}$$

Similar calculation for efficiency of Seebeck generator:

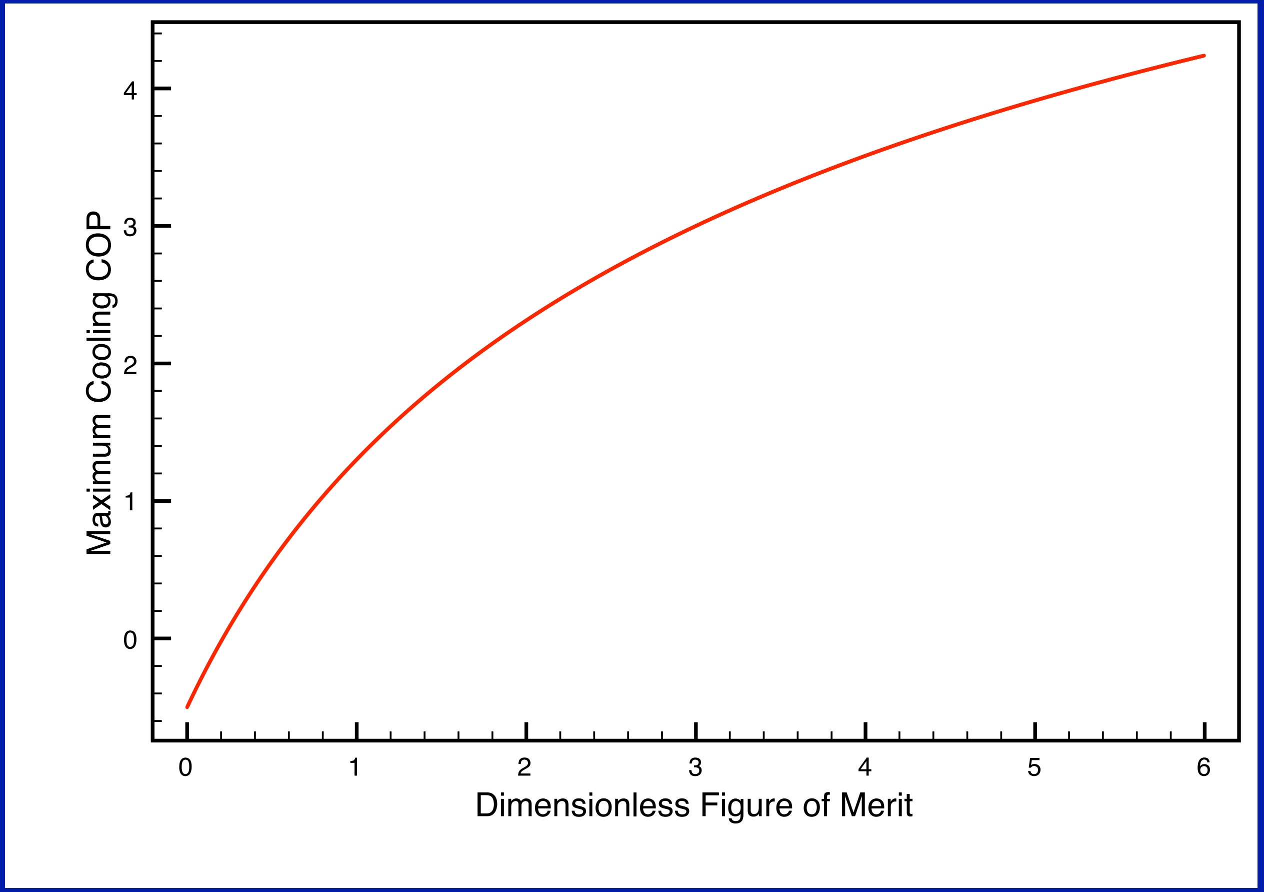
$$\eta_{\max} = \left[1 - \frac{T_C}{T_H}\right] \frac{\sqrt{1+\overline{Z}} - 1}{\sqrt{1+\overline{Z}} + T_C/T_H}$$

Note: Carnot efficiency reached as $\overline{Z} \to \infty$ (cf. future lecture)

COP at maximum cooling power :

$$\phi[\dot{Q}_C^{max}] = \frac{ZT_C/2 + 1 - T_H/T_C}{ZT_H}$$

Max. COP vs. Dimensionles Figure of Merit for $(T_C,T_H)=(0,30)$ °Celsius :



Current conventional commercial refrigerators have COP ~ 3-4
→ Need to achieve ZT ~ 3-4 in a cost-efficient way… !!!!

Note:

Here we have seen the
dimensionless figure of merit ZT
appearing everywhere,
but we have not really understood
WHY…

→ see subsequent lecture
(# 2-3)

(in fact, a very general thermodynamic property
relevant to many different fields)

Actually, coupling constant is : $\boxed{\dfrac{\overline{Z}}{\overline{Z}+1}}$

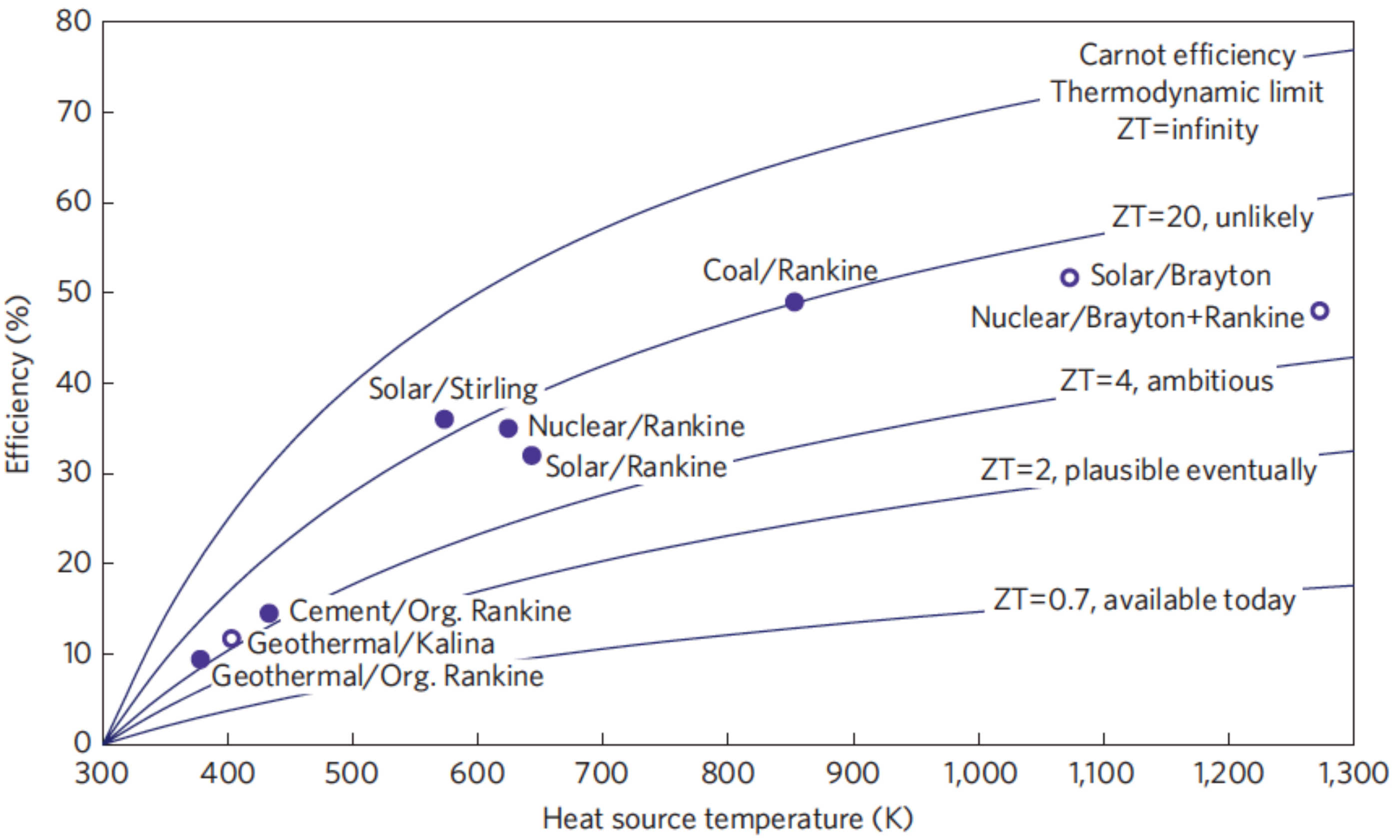


Figure 2 | Assessing thermoelectrics. Efficiency of 'best practice' mechanical heat engines compared with an optimistic thermoelectric estimate (see main text for description).

For a (perhaps overly) critical view of the use and future of thermoelectrics, see:
C.B. Vining, Nature Materials 8 (2009) 85

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 are much better…

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

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

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

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

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

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

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

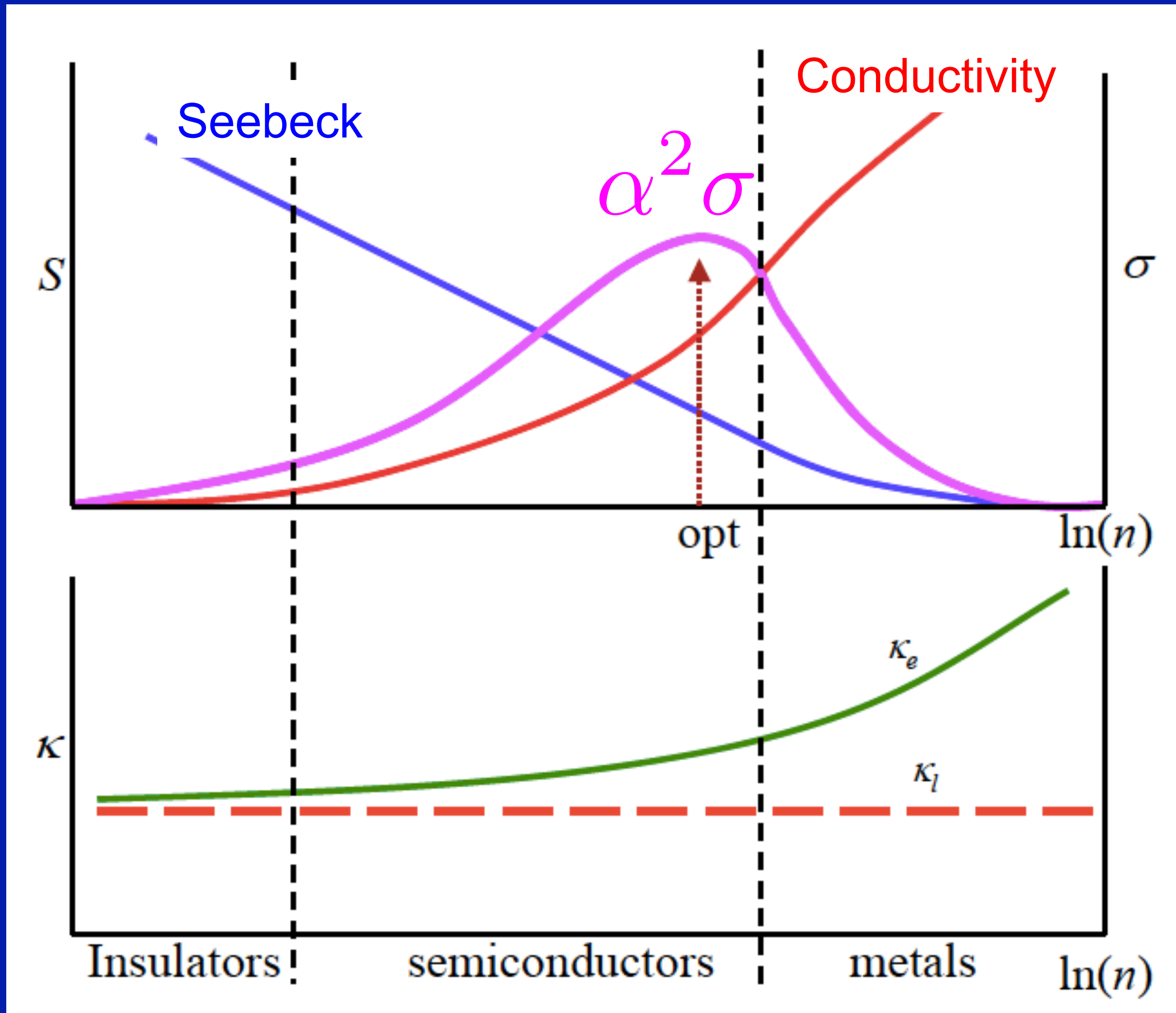
Need ~ a single type of carriers (e.g. very different mobilities)

→ More accurate calculation in a subsequent lecture…

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

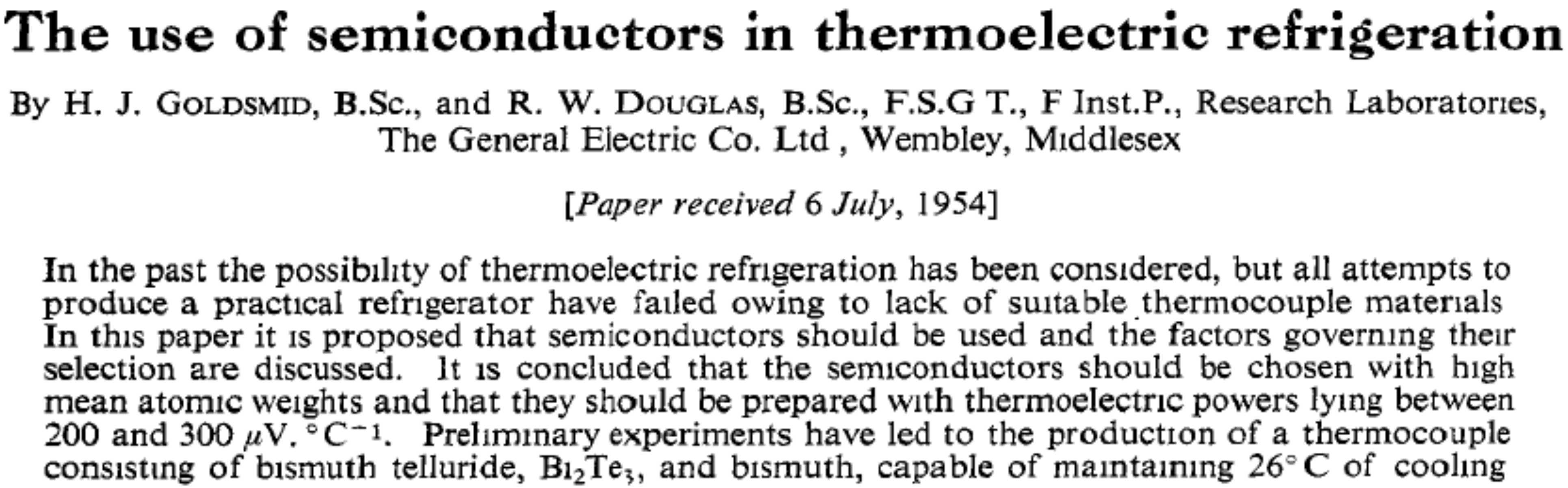
- Author of books `Semiconductor thermoelements' and `Thermoelectric cooling' (1957)

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

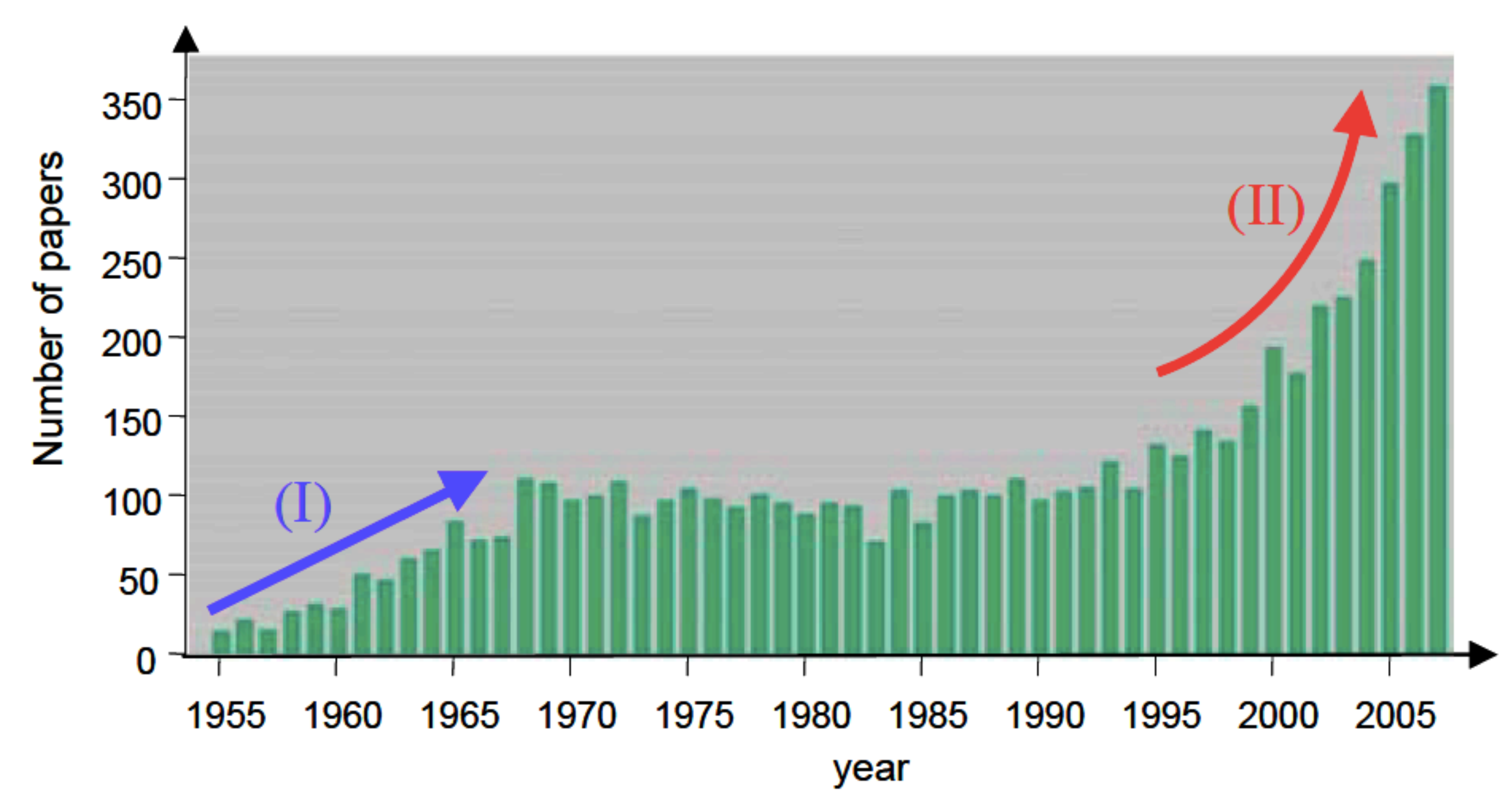
Concluding paragraph of Goldsmid, 1954:

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]

~ 1995 → …

A new Golden Age
of Thermoelectricity ?

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 this cycle.

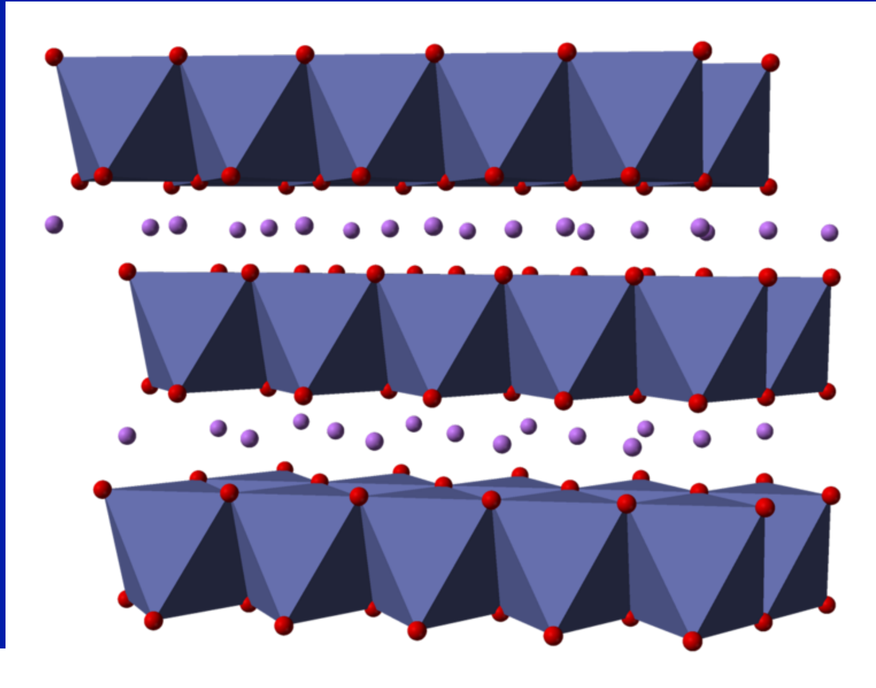
Cobalt oxides: Na_xCoO_2

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

`Misfit' cobaltates in CRISMAT-Caen

Na ions in between layers →

Triangular CoO_2-layers →

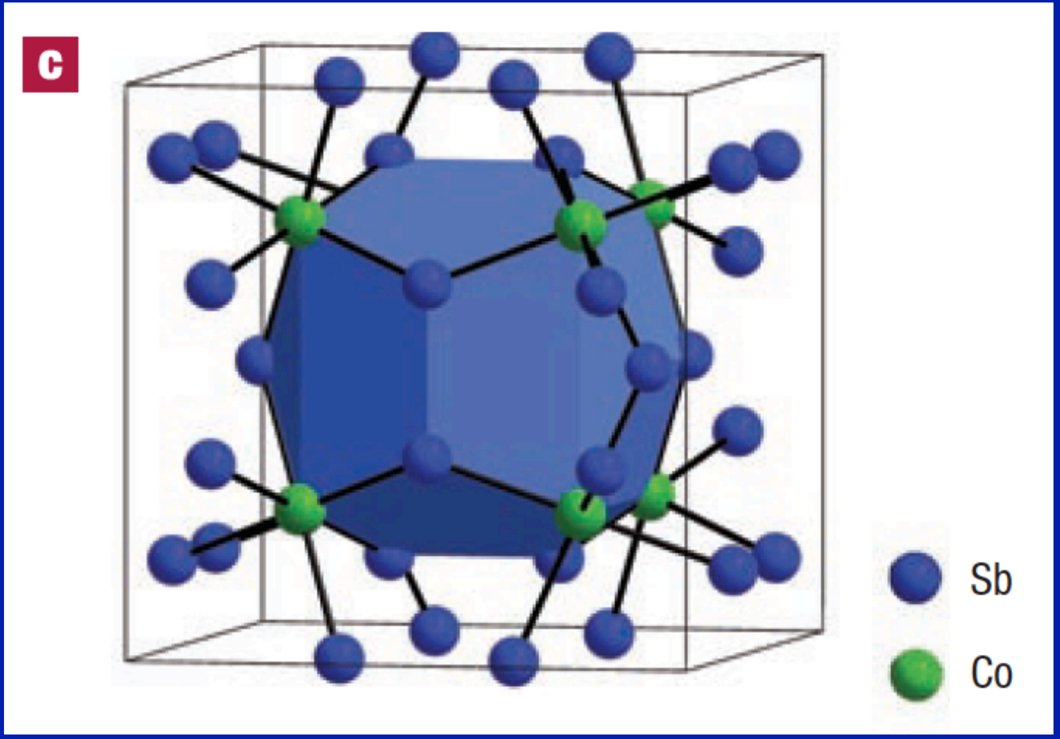


Note similarities to $LiCoO_2$ batteries

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
$\vert S\vert$	μV/K	100	200
S^2/ρ	$\mu W/K^2$ cm	50	40
μ	cm^2/V s	13	150

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

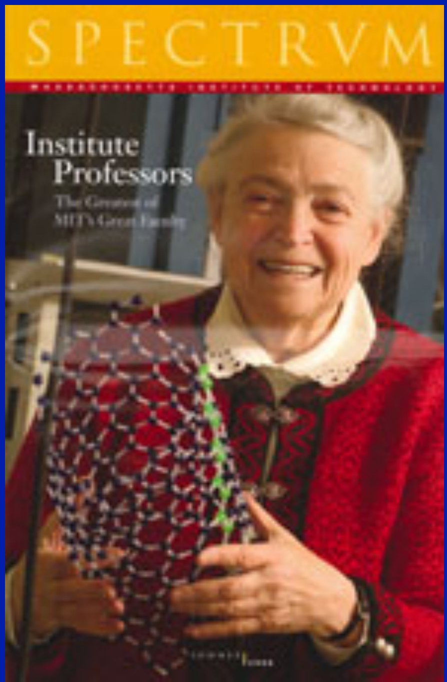
Effect of quantum-well structures on the thermoelectric figure of merit

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)

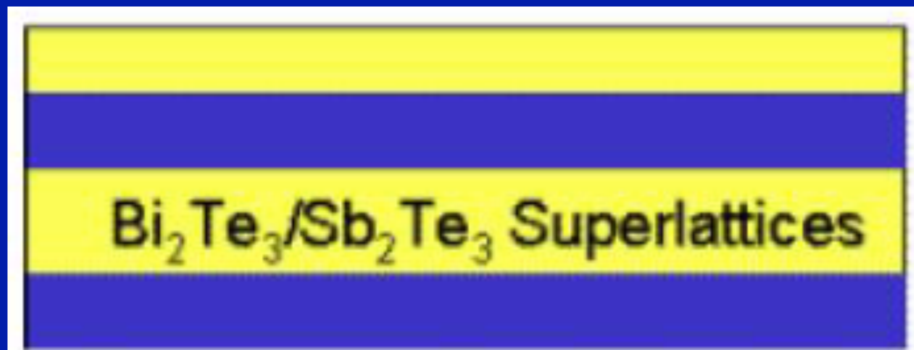
> 1100 citations



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

Mildred Dresselhaus, MIT

Reports of ZT > 2

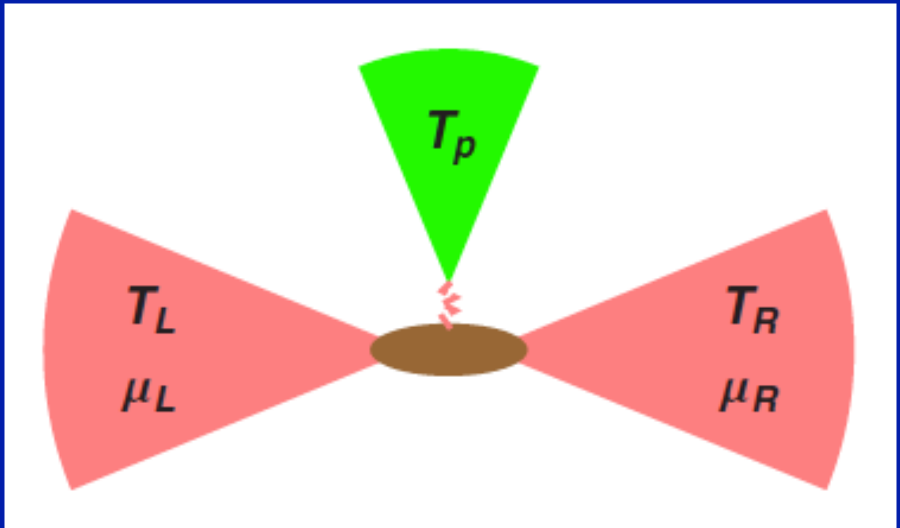


Recent interest in thermoelectric effects in mesoscopic systems and nanoconductors

See for example presentations at workshop:

http://iramis.cea.fr/meetings/nanoctm/

For example:
3-terminal setup
Entin-Wohlman et al.
PRB 82 (2010) 115314



… and even in ultra-cold atomic gases
[C.Grenier et al. arXiv:1209.3942
And work in progress w/ ETH group]