Thermocouples: Boltzmann, Beer and Jupiter

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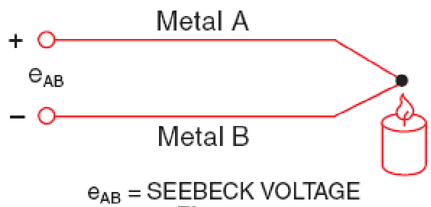
Abstract

- The familiar thermocouple is a simple, reliable temperature sensor. The underlying principles caught the attention of Boltzmann and Kelvin and sorting out the physics led to a Nobel Prize (Onsager, 1968). Further principles established in the 1950s and 1960s, notably by Ioffe in Russia as well as in the US, enabled these ‘sensors’ to do work in their own right, from cooling beer to powering spacecraft such as Voyager and Galileo. The past decade has witnessed a new generation of scientific ideas, some of which may extend their utility to mainstream applications. This presentation will briefly outline historical developments and how they connect to more recent developments

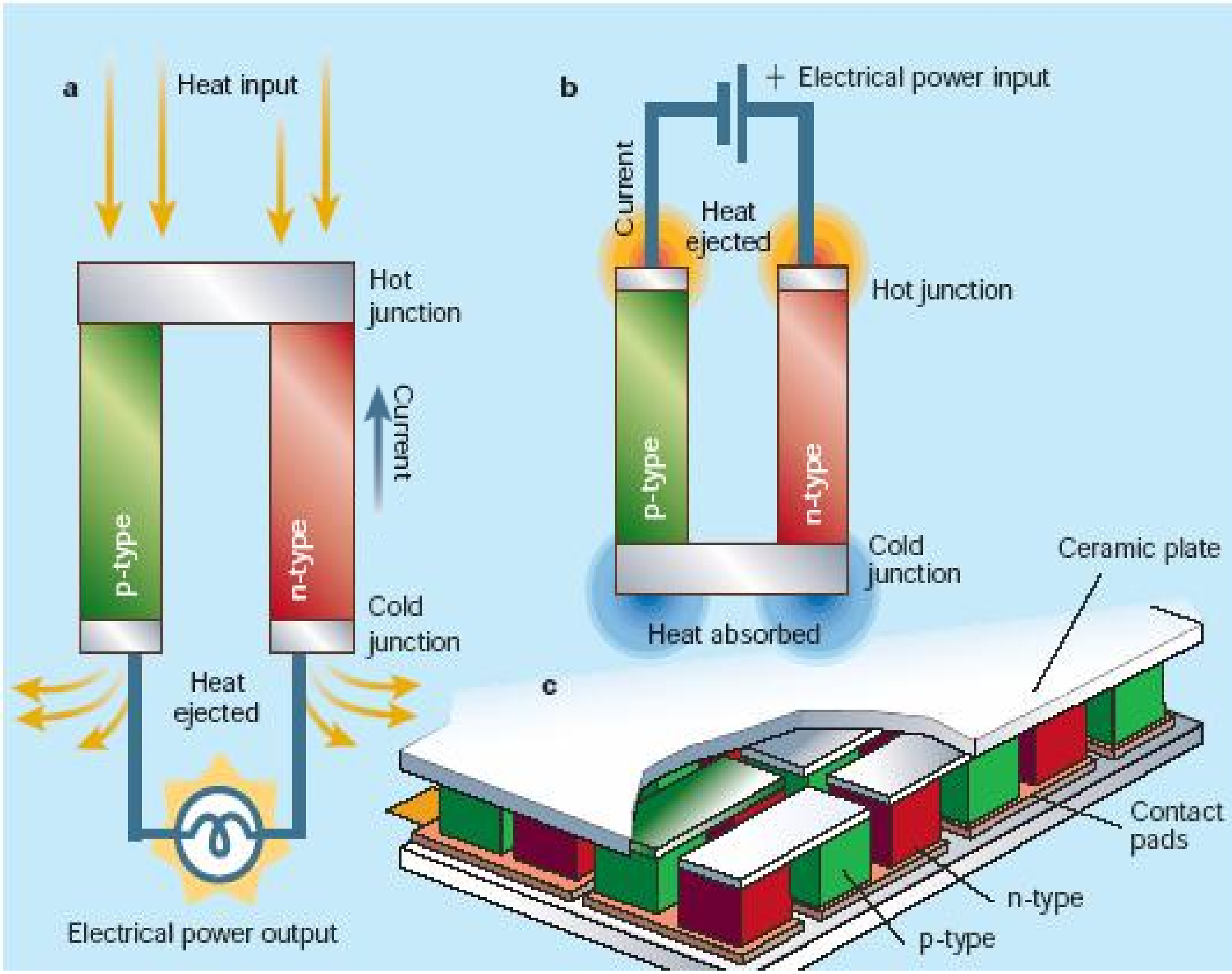
Outline

- Introduction
- Applications
  - Power Generation: Jupiter (and it’s moons)
  - Cooling: Beer and your Backside
- Early Ideas
  - Kelvin, Boltmann & Onsager
  - Ioffe
- Modern Ideas
  - New Materials
  - Nano-scale



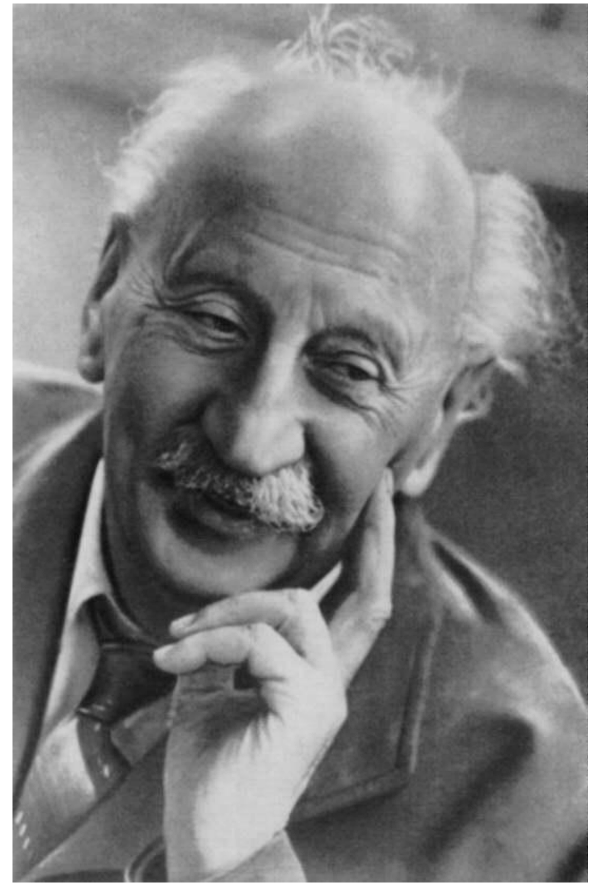
Basic Thermoelectrics

a) Power Generator, b) Cooler, c) 'Module'



Early Thermoelectricity

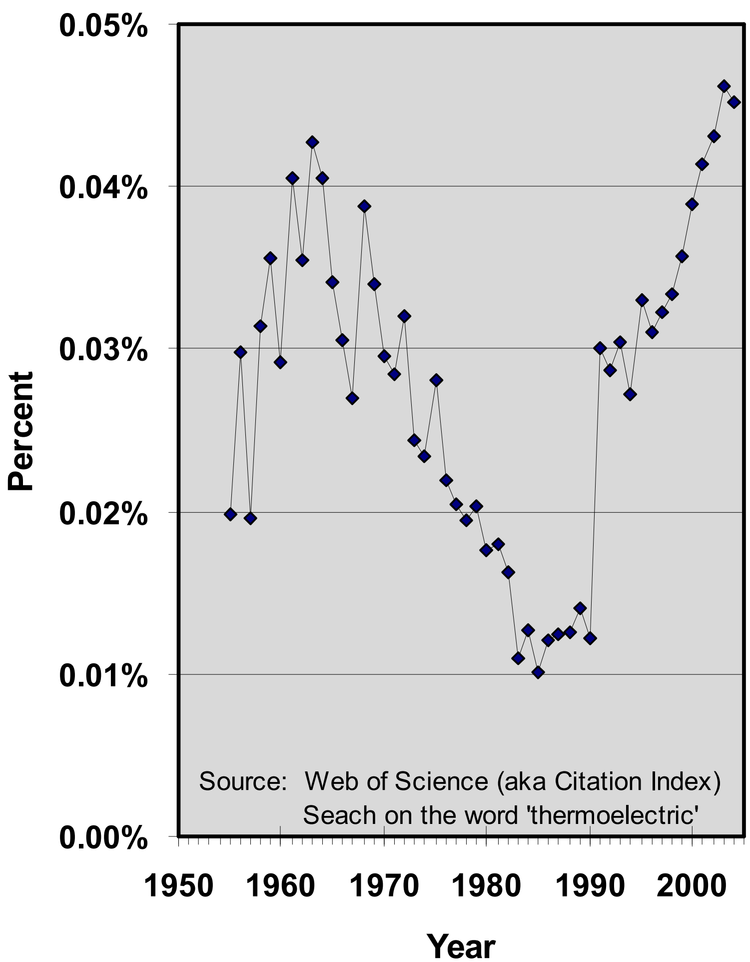
- Discoveries by Seebeck (1822-23), Peltier (1834), Thomson (1854)
  - Compare to Watt & Boulton steam engine (1770s-80s)
- First practical devices USSR during WWII
  - Tens of thousands built, to power radios from any available heat source.
- Ioffe's 1957 book describes 80-85% of the important principles
  - It is still a valuable reference today
- 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

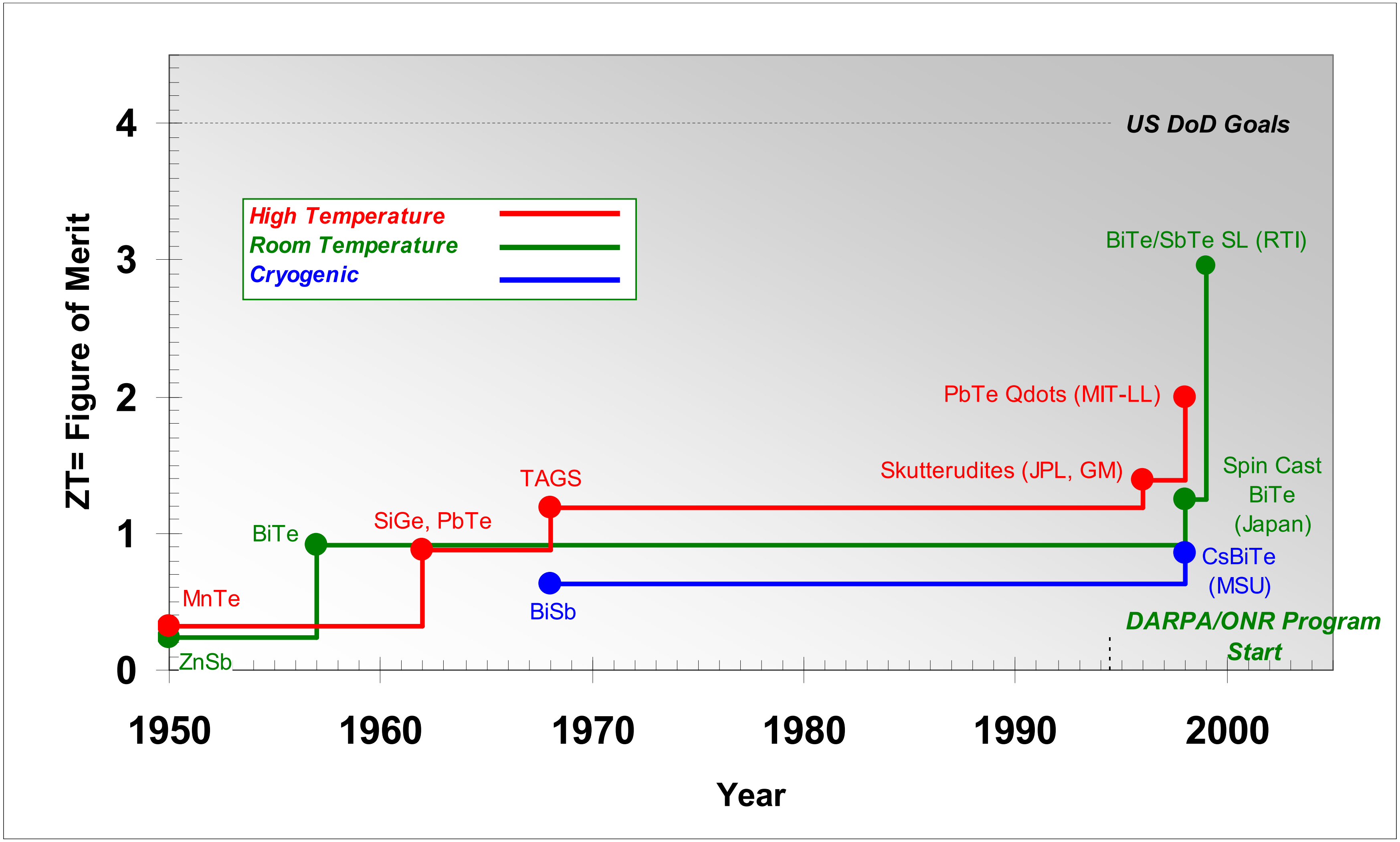
Ioffe, A. F. (1957). Semiconductor Thermoelements and Thermoelectric Cooling. London, Infosearch Limited.

TE R&D Resurgence



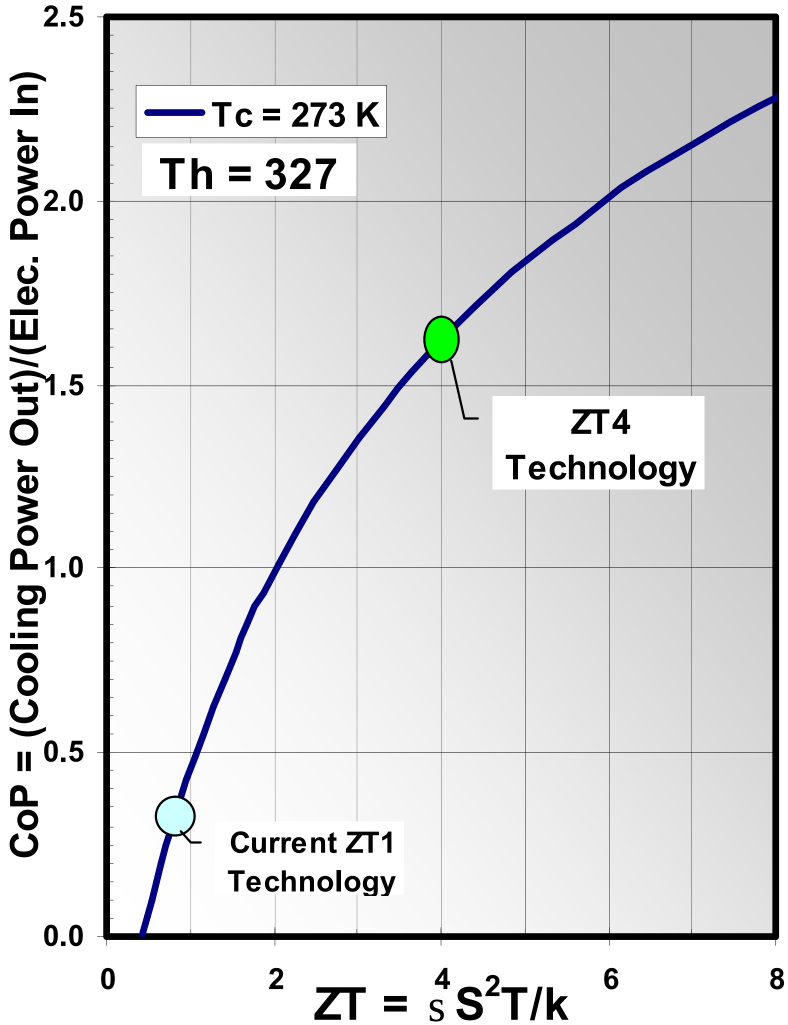
- Most of the 1950s-60s era work was funded by the US Navy, for possible use in the nuclear Navy
  - Hint: didn't happen
- What NASA needed then had largely been demonstrated as feasible by the Navy projects
  - Virtually all the key basic research was Navy funded
  - NASA's use of RTGs in the 1960's-1970's could not halt the general decline in R&D
- After years in decline, papers published on Thermoelectrics increased dramatically since the introduction of 'Quantum Well' and 'Superlattice' concepts in the early 1990's
- New funding from DARPA/ ONR in US & NEDO in Japan & spurred growth in the 1990's
  - ONR was interested in silent air conditioning for nuclear submarines but has supported a lot of basic science
  - NEDO in Japan has emphasized waste heat recovery more than basic science

History of the Thermoelectric Figure of Merit



Inspired by Dubios, ICT, 1999

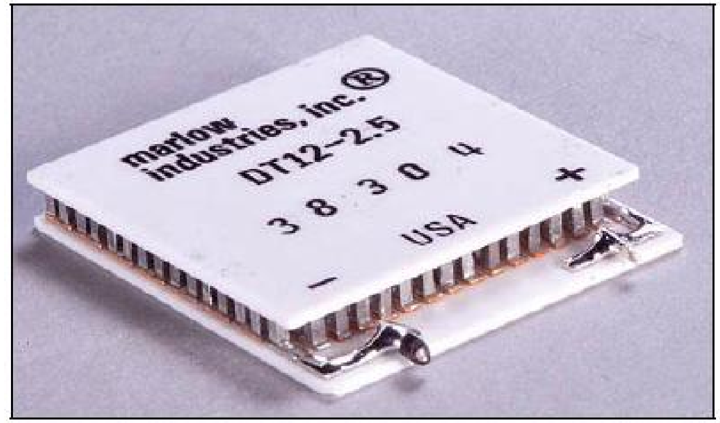
TE Coefficient of Performance

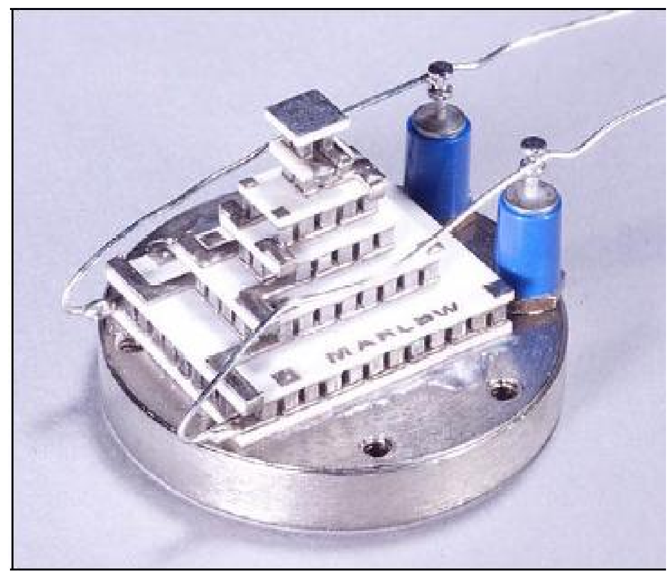


- ZT values near 1 are in production today
- Dramatic CoP improvement with ZT
- ZT ~ 2 to 3 demonstrated in lab
  - Several entirely different approaches: quantum dots, superlattices & new bulk materials

Typical Commercial TE Cooler Modules

- Single stage TE coolers typically achieve ΔT_{max} = 66-75 K (ideal, no load)
- Multistage coolers might achieve ΔT_{max} = 150 K (ideal, no load)
- Several manufacturers available in US, China, Japan, Russia & Ukraine
- Prices from Chinese manufacturers have been quoted as low as $3/module





CONSUMER APPLICATIONS

BEER COOLER

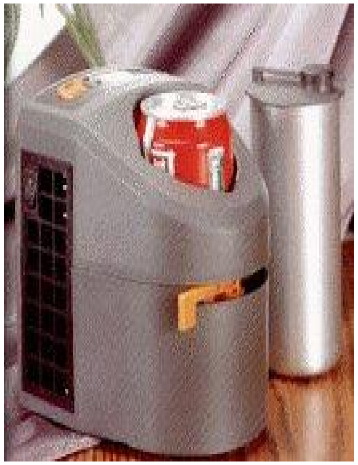
TE FRIDGE

CHOCOLATE COOLER

AUTOMOBILE APPLICATIONS

- An important emerging application is in car seats as a local cooler, warmer
  - Provides comfort where it is needed
  - 140,000 installed in cars last quarter
  - Predicted to be the largest application for TE coolers by this year
  - Costs coming down with volume production will likely lead to further applications
- Major auto makers keep an eye on TE cooling as ‘insurance’ against possible bans against all present compressor technologies

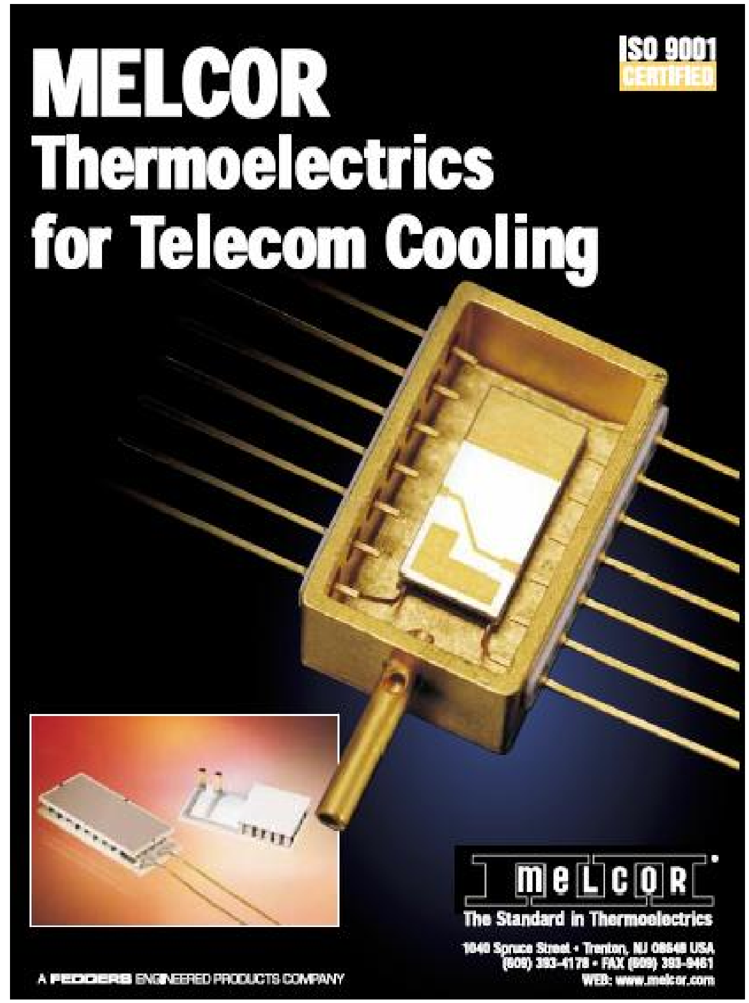
Seat Cooler/Warmer



Beverage Cooler

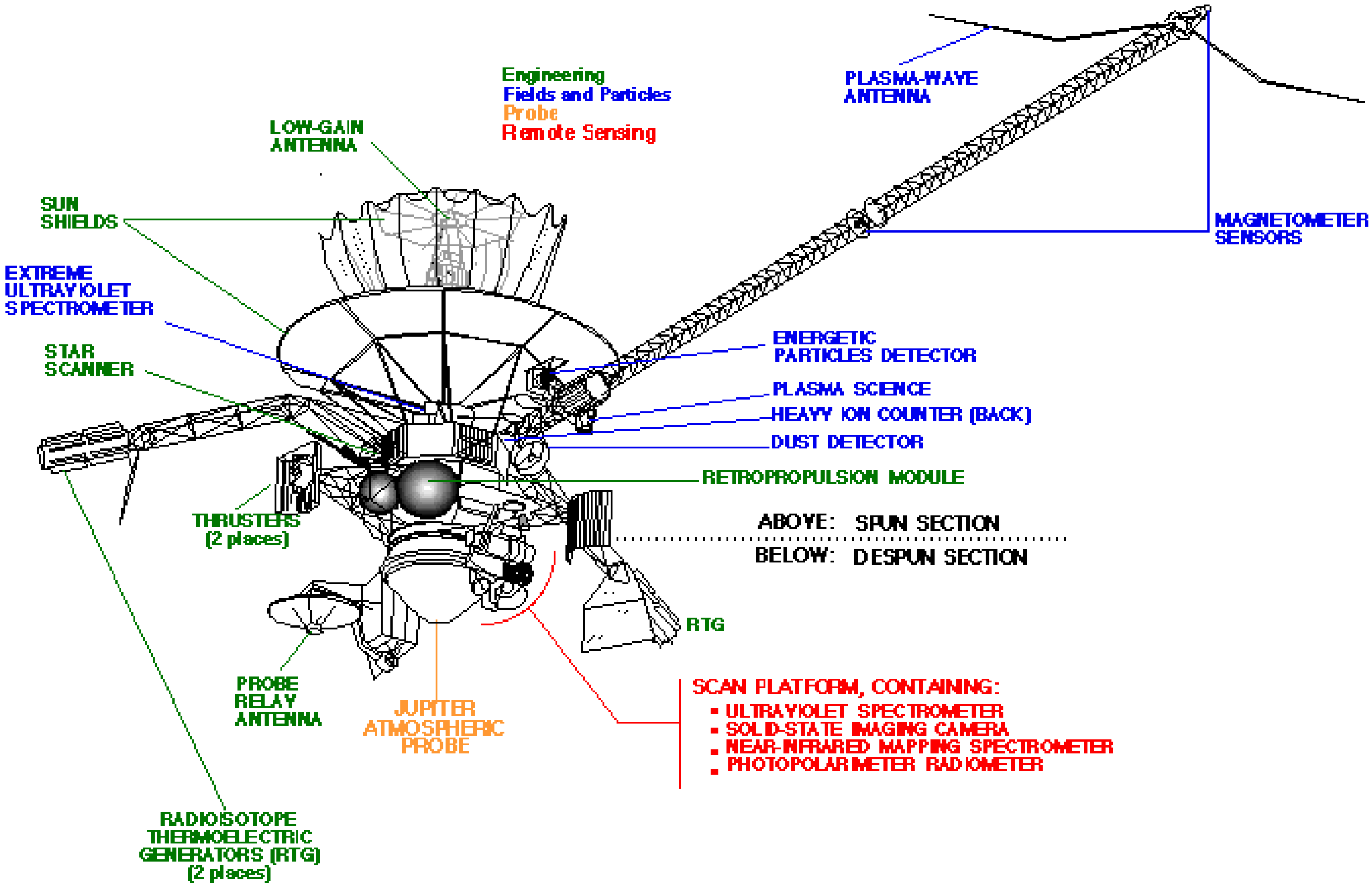
TEs for Telecom Cooling

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



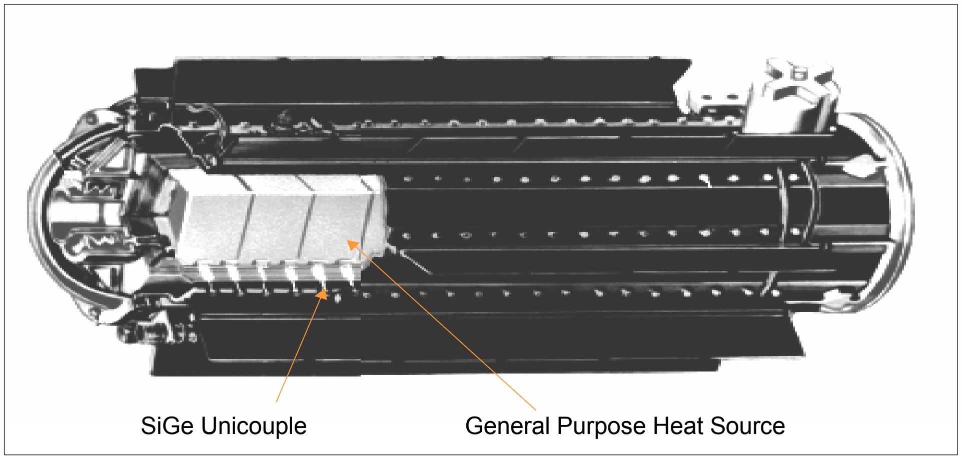
From Melcor, http://www.melcor.com

Galileo Spacecraft with 2 Radioisotope Thermoelectric Generators (RTGs)

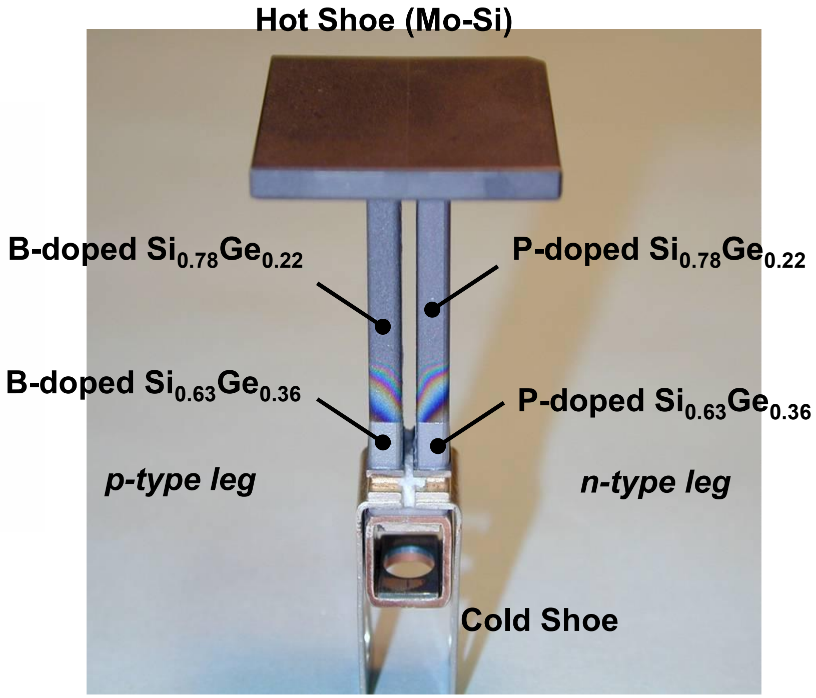


Galileo/Ulysses/Cassini-class RTG

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



Radioisotope Thermoelectric Generator



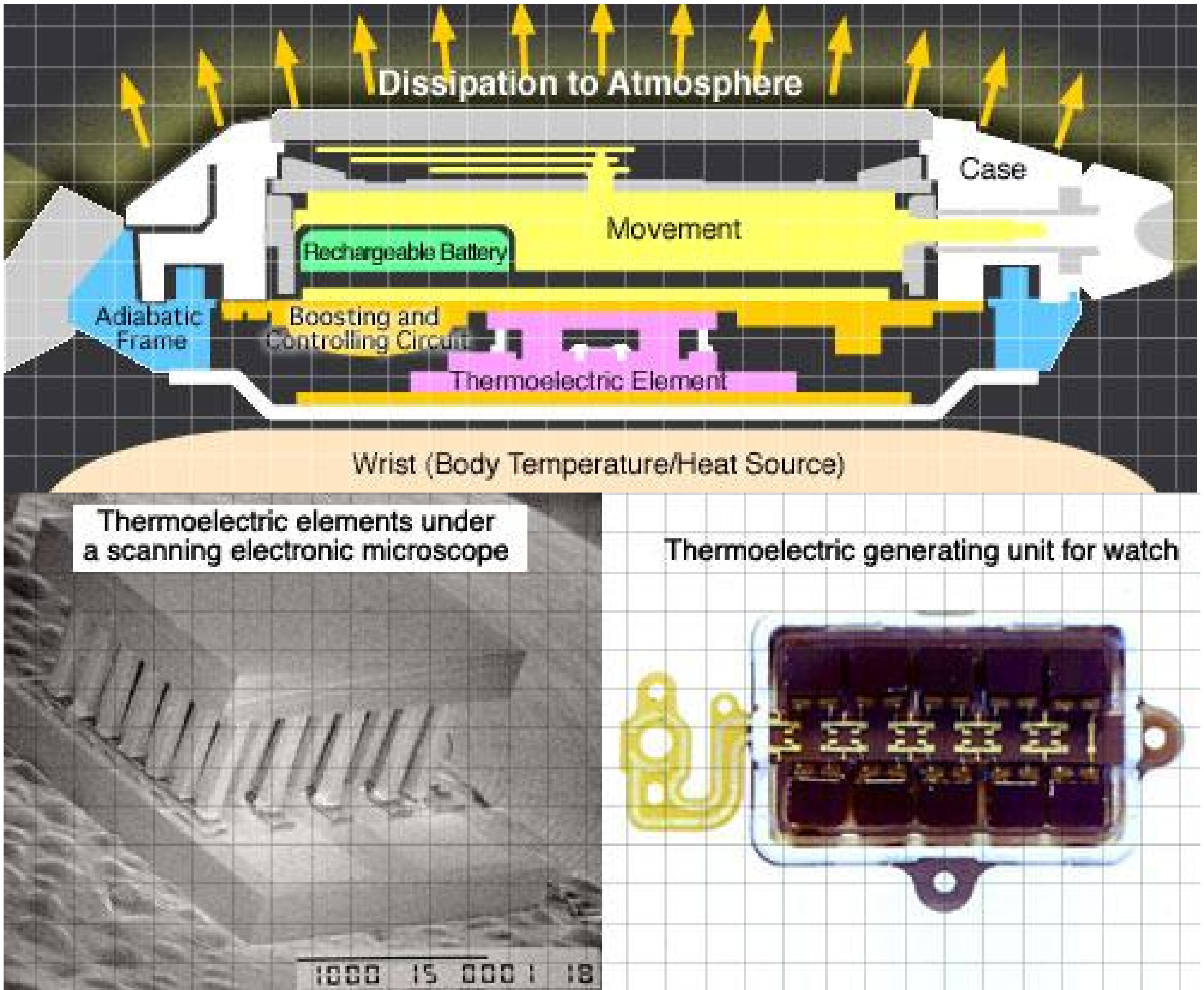
SiGe unicouple

NASA: Next Generation

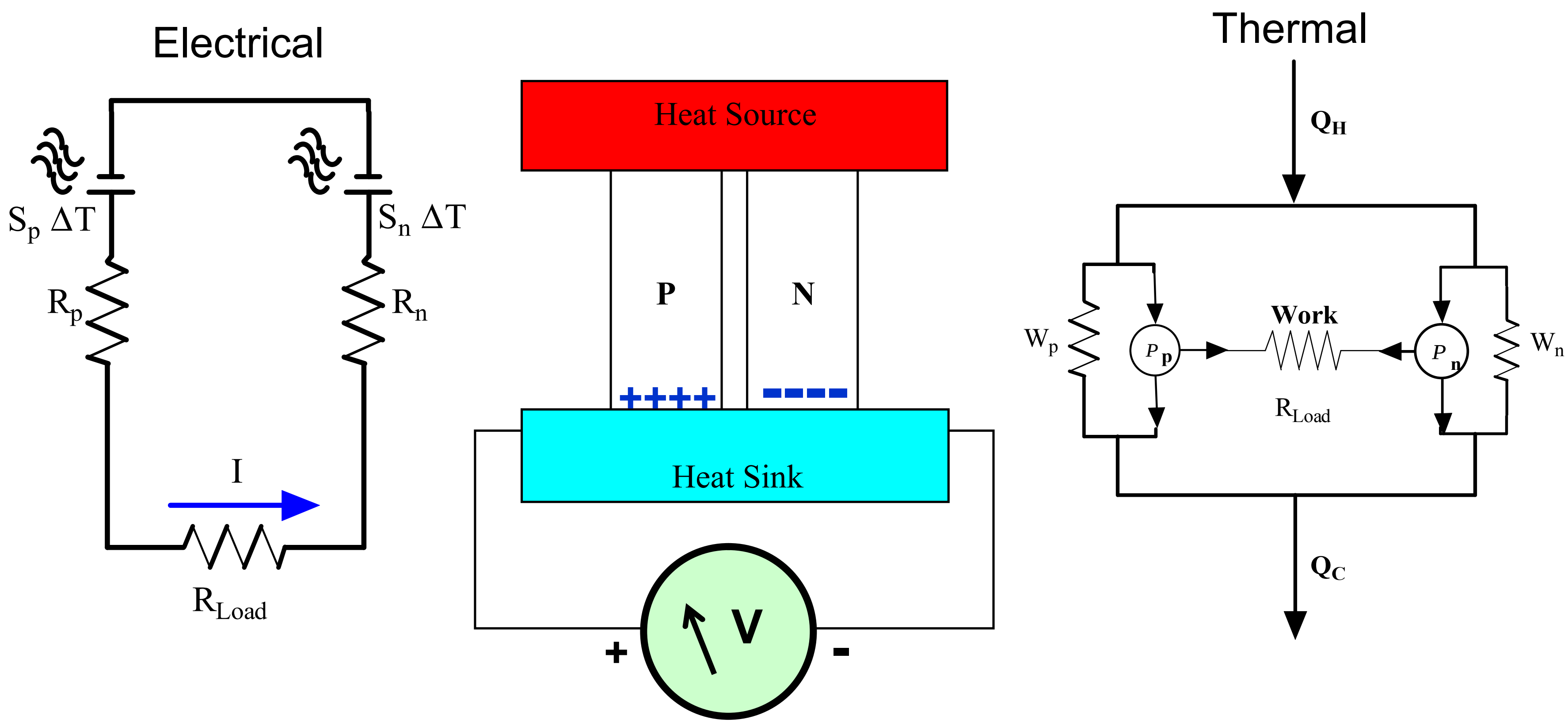
- Jupiter Icy Moons Orbiter (?)
- Nuclear Fission Reactor – 100 kW_{elec}
- Electric Powered – Ion Propulsion
- Launch Target: 10 years
- Cost: Billions & Billions! (mostly for nuclear safety)

Seiko's 'THERMIC' TE Wristwatch

104 elements, 80 μm by 600 μm, 2 mm x 2 mm/module, 10 modules/watch

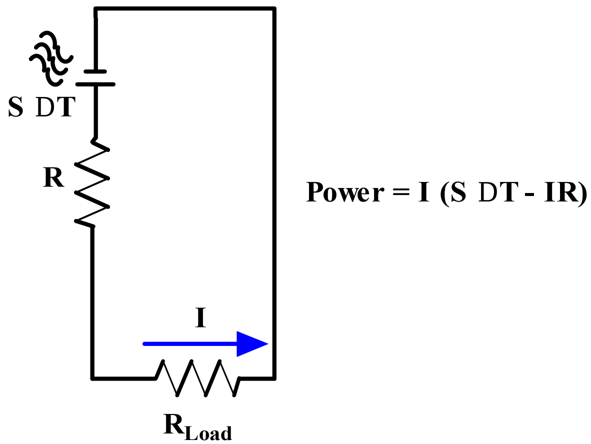


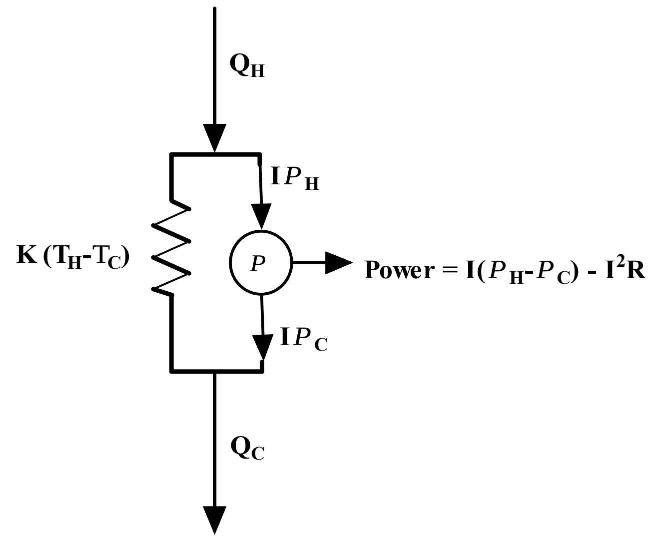
Electrical and Thermal Models



- Note the electrical circuit contains a thermal term
- And thermal circuit contains an electrical term

Work and Kelvin's Relation





- Derive power from electrical analysis & separately from thermal. Compare…
- Kelvin (1854) proposed: $ST=\Pi$

Efficiency

- Adjust current (i.e. by varying the load) to find the maximum efficiency
- *'Z'* here is a device parameter, involving
  - Averages of thermoelectric properties
  - Geometry factors
- One more generic optimization is possible

$$
\begin{aligned}
h &\equiv Efficiency \\
&\equiv \frac{\text{Electrical Power Out}}{\text{Heat In}} \\
&= \frac{IV}{Q_h} \\
&= \frac{I(S\Delta T - IR)}{IST_h + K\Delta T - \frac{1}{2}I^2 R}
\end{aligned}
$$

$$I_{opt} = \frac{S\Delta T}{R}\frac{1}{1+\sqrt{1+ZT_{ave}}}$$

$$\left(\frac{R_L}{R}\right)_{opt} = \sqrt{1+ZT_{ave}}$$

$$V_{opt} = S\Delta T\frac{\sqrt{1+ZT_{ave}}}{1+\sqrt{1+ZT_{ave}}}$$

$$ZT_{ave} \equiv \frac{S^2}{RK}\frac{T_h+T_c}{2}$$

$$h_{opt} = \frac{\Delta T}{T_h}\frac{\sqrt{1+ZT_{ave}}-1}{\sqrt{1+ZT_{ave}}+\frac{T_c}{T_h}}$$

ST=Π: Kelvin (1854) …

had to make one additional assumption, namely: "*The electromotive forces produced by inequalities of temperature in a circuit of different metals, and the thermal effects of electric current circulating in it, are subject to the laws which would follow from the general principles of the thermodynamic theory of heat if there were no conduction of heat from one part of the circuit to another.*" Thom-

Onsager quoting Kelvin (1931)

- Kelvin's assumption is equivalent to using Maxwell's relations from thermodynamics

Linear Response

Transport

$$\vec{i} = s_T\left(\vec{E} - a\vec{\nabla}T\right)$$

$$\vec{q} = T\vec{s}$$

$$= \Pi\vec{i} - l_i\vec{\nabla}T$$

Thermodynamics

$$dN = \left.\frac{\P N}{\P m}\right|_T dm + \left.\frac{\P N}{\P T}\right|_m dT$$

$$dQ = TdS$$

$$= \left(\left.\frac{\P U}{\P N}\right|_T - m\right)dN + \left.\frac{\P U}{\P T}\right|_N dT$$

$$\begin{pmatrix}\vec{i}\\ \vec{s}\end{pmatrix} = L\begin{pmatrix}\vec{E}\\ -\vec{\nabla}T\end{pmatrix}$$

$$\begin{pmatrix}dN\\ dS\end{pmatrix} = C\begin{pmatrix}dm\\ dT\end{pmatrix}$$

$$L = \begin{pmatrix} s_T & s_T a \\ s_T\Pi/T & l_E/T \end{pmatrix}$$

$$C = \begin{pmatrix} \left.\frac{\P N}{\P m}\right|_T & \left.\frac{\P N}{\P T}\right|_m \\ \frac{1}{T}\left.\frac{\P N}{\P m}\right|_T\left(\left.\frac{\P U}{\P N}\right|_T - m\right) & \frac{1}{T}\left[\left.\frac{\P U}{\P T}\right|_N + \left.\frac{\P N}{\P T}\right|_m\left(\left.\frac{\P U}{\P N}\right|_T - m\right)\right] \end{pmatrix}$$

- That $C_{12}=C_{21}$ is a Maxwell Relation (thermodynamics)
- Kelvin (1854) suggested, but could not prove, $L_{12}=L_{21}$

Boltzmann

- Aware of Kelvin's assumptions, Boltzmann (1887) tried again and showed thermodynamics assures only the much weaker condition:

$$1 > \frac{1}{4}\frac{T}{l\,r}\left(S - \frac{\Pi}{T}\right)^2$$

- Compare:

$$ZT \equiv \frac{S^2 T}{l\,r}$$

Onsager's Reciprocal Relations

$$\Pi = ST$$

- Onsager was interested in all sorts of coupled flow problems
  - Thermoelectricity was his first example, but discusses electrolyte problems, chemical reaction problems and others
  - Ex: exchange of ions (Na+, K+, etc.) through a cell membrane is a coupled flow problem, with efficiency expressions analogous to thermoelectric ones (i.e., not very efficient).
- Onsager (1931) used a statistical mechanics argument:
  - "Kinetic theory requires that every type of [microscopic] motion must occur just as often as its reverse"
  - Reciprocal relations are a consequence of this 'microscopic reversibility' and are of profound generality for that reason.
  - Kelvin's Relations are special cases of very general 'reciprocal' relations, relating 'Cross' phenomena of which the interaction between heat and electricity perhaps the simplest.
  - Won the Nobel Prize in Chemistry in 1968
    - "for the discovery of the reciprocal relations bearing his name, which are fundamental for the thermodynamics of irreversible processes"

Noise: Fluctuation/Dissipation Connection

- Nyquist-Johnson noise (ΔB=bandwidth)
  - Isothermal!
- Do measurement adiabatically
- Analogous thermal measurement (i=0)
- Short circuit (ΔV=0)

$$\left\langle \left(\Delta V \right)^2 \right\rangle = 4 k_B T R \Delta B$$

$$\left\langle \left(\Delta V \right)^2 \right\rangle = 4 k_B T R \left(1 + ZT \right) \Delta B$$

$$\left\langle \left(\Delta T \right)^2 \right\rangle = 4 k_B T^2 W \Delta B$$

$$\left\langle \left(\Delta T \right)^2 \right\rangle = 4 k_B T^2 \frac{W}{1 + ZT} \Delta B$$

- Connects transport properties to equilibrium fluctuations
- The recent advent of large ZT allows tests of these basic concepts not previously possible.

Thermoelectric Materials

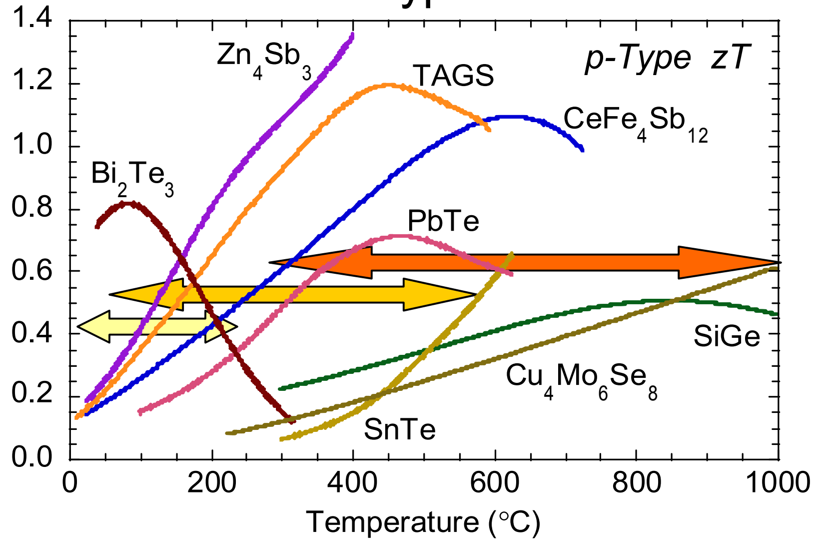
The Ioffe Era

1950s-1970s

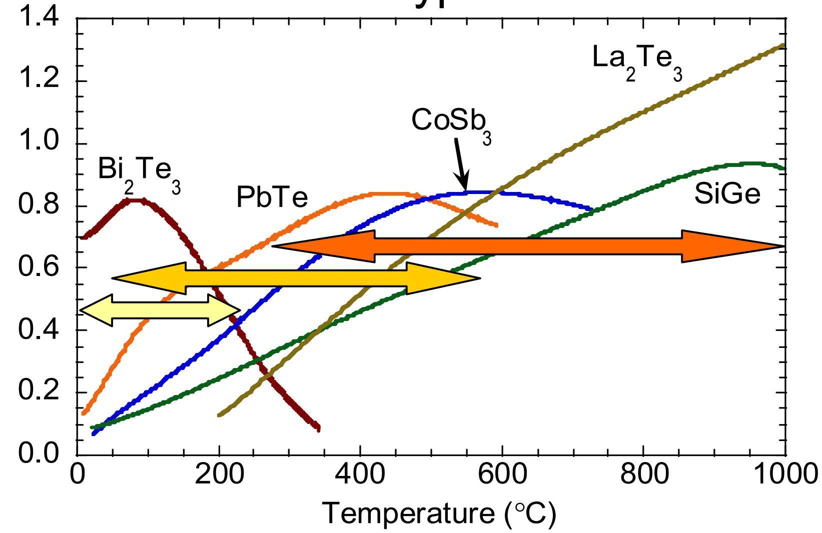
ZT for Some Known Materials

ZT~ 1 available from 300 – 1000 ^{o}C

P-Type



N-Type



- Three main operating ranges for proven materials:
  - "Low Grade Heat": 30 ^{o}C – 250 ^{o}C, Bi_2Te_3 – based materials
  - "Intermediate": 50 ^{o}C – 600 ^{o}C, PbTe –based materials
  - "High Temperature (ex: Space): 300 ^{o}C – 1000 ^{o}C, SiGe
- Device technology not yet available for $CoSb_3$, $CeFe_4Sb_{12}$, Zn_4Sb_3 or La_2Te_3

(Original Figures: Snyder, 2004, http://www.its.caltech.edu/~jsnyder/thermoelectrics/science_page.htm)

The ZT Question

- Transport properties (ρ particularly) can vary by 20 orders of magnitude
- ZT is a transport property
  - Or a combination of transport properties, as you like
- WHY are there no materials with ZT=10? or 50?
- There is no rigorous answer
- But there are some excellent guidelines

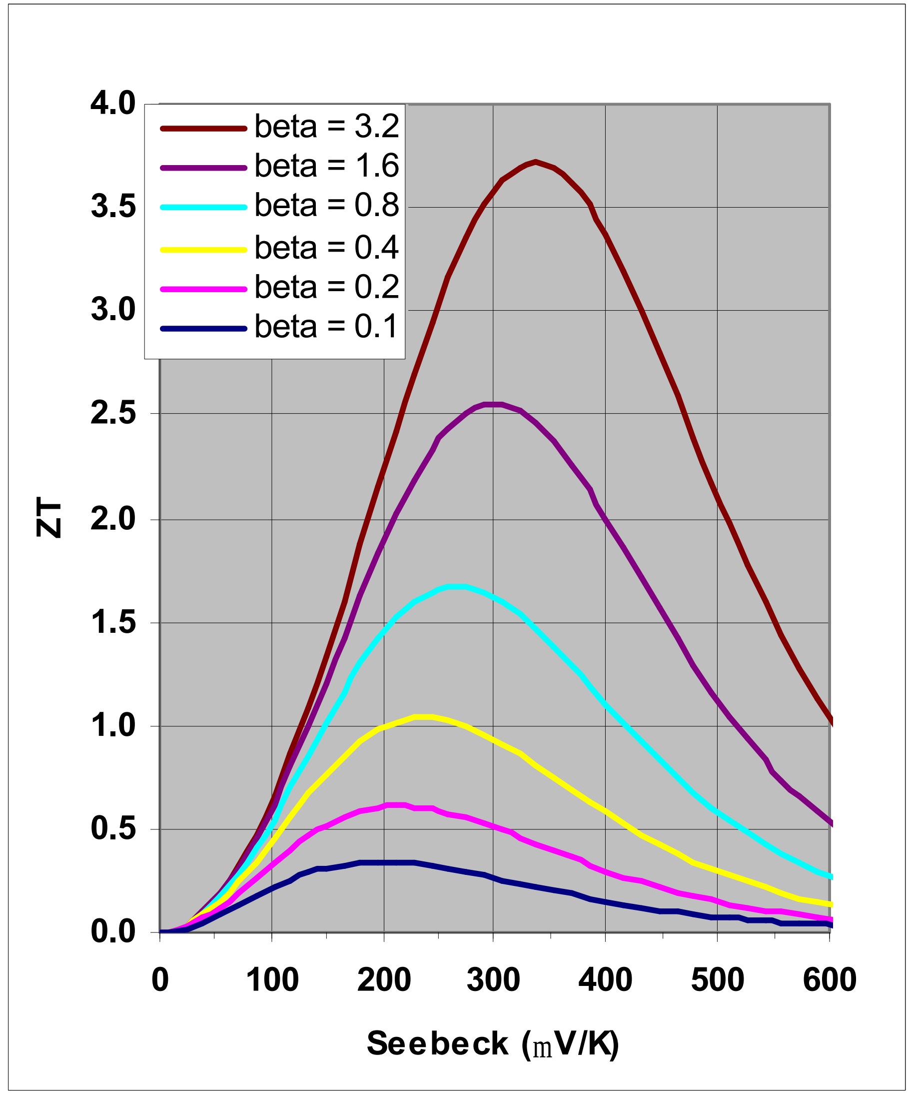
Optimize the Carrier Concentration

- Perhaps simplest to plot ZT vs. S
- For known materials, the optimum S is ~ 200-250 μV/K
- You want bigger β:
  - Higher μ for better electrical conductivity
  - Larger m_{eff}, gives higher S for the same doping
  - Smaller λ_p to reduce heat carried by phonons

$$S = \frac{k_B}{e}\left(2 - \ln(x)\right)$$

$$ZT = \frac{S^2 \sigma T}{\lambda} = \frac{x\left(2 - \ln(x)\right)^2}{2x + \frac{1}{\beta}}$$

$$\beta = 9x10^{-6}\frac{\mu m_{eff}^{1.5}}{\lambda_p} T^{2.5}$$



Classical Relation for λ_p

$$l_p = \frac{1}{3} C_p v_p l_p = \frac{1}{3} C_p v_p^2 t_p$$

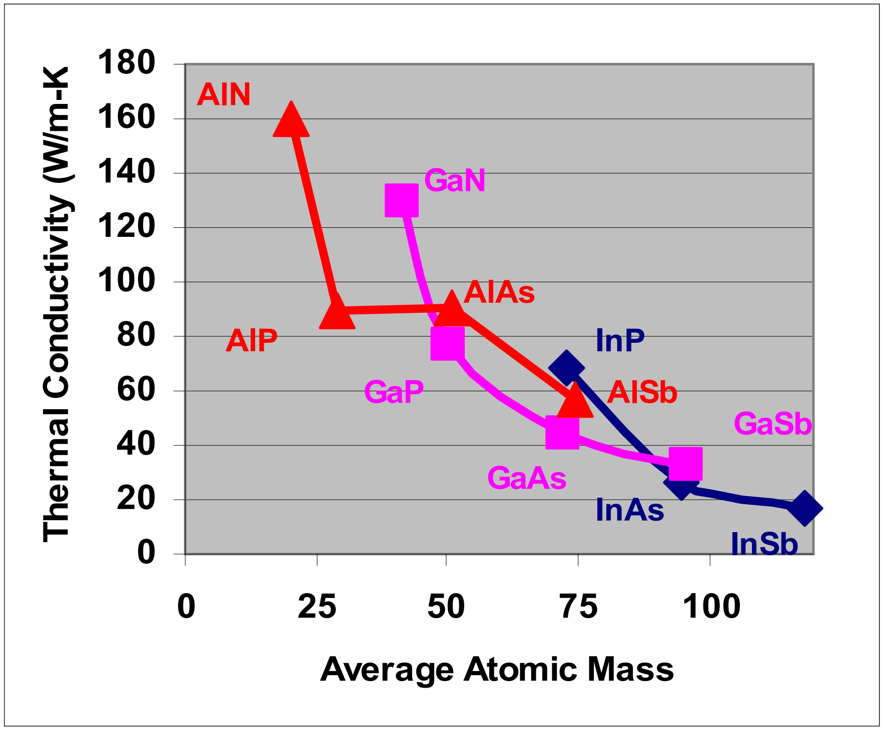
- Phonon Heat Capacity
- Speed of Sound
- Phonon mean free path
- Phonon relaxation time (1/scattering rate)

$$C_p \cong 3R, \text{similar for all solids}$$

- To reduce thermal conductivity
  - Pick heavy atoms, complex crystal structure
    - Lower speed of sound
  - Introduce as much phonon scattering as possible
    - Without screwing up electrical properties (that’s the trick)

Effect of Atomic Mass on Thermal Conductivity

- Other factors enter, but the mass of the atoms is a huge effect
  - Heavy mass means low speed of sound
- This is why you see a lot of Sb, Bi, Pb, & Te
  - They are all heavy
- Large unit cell size is also a plus
  - Large, complex unit cells means some of the vibration modes are more localized & don't carry heat well
  - Ex: Skutterudites, Clathrates, Chevrel Phase & others



Mass Alloy Scattering in SiGe/GaP

$$\frac{1}{l_{ph}} \propto \frac{1}{\overline{M}^2}\sum_i y_i\left(M_i - \overline{M}\right)^2$$

$$y_i = \text{concentration of atomic mass } M_i$$

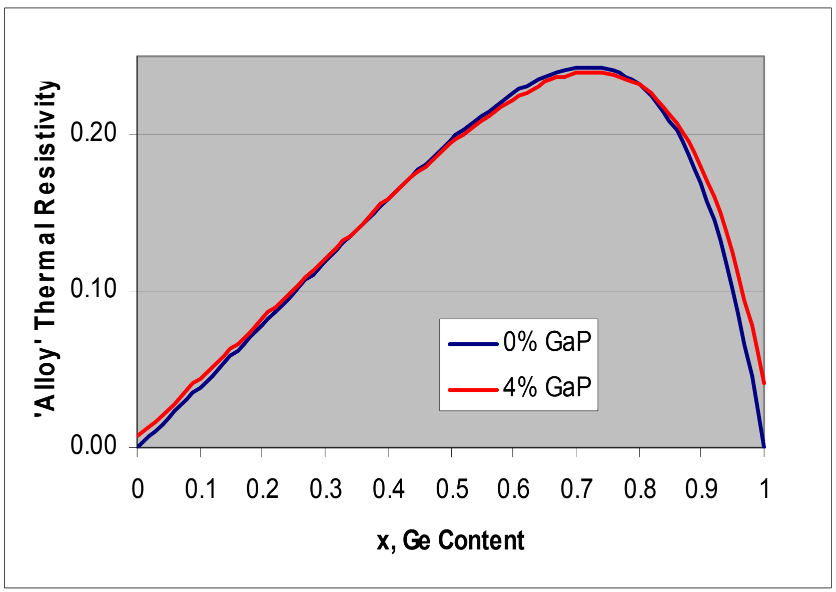
$$\overline{M} = \sum_i y_i M_i = \text{Average Atomic Mass}$$

$M_{Si} < M_P < M_{Ga} < M_{Ge}$

28 < 31 < 70 < 73

Over the main range of interest GaP should slightly *increase* λ

Theory (left) works well for SiGe (right) & predicts no benefit to GaP



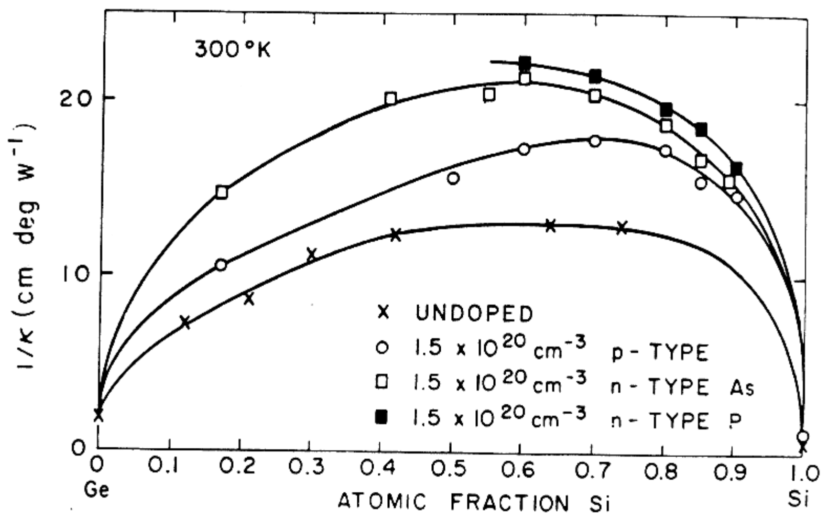
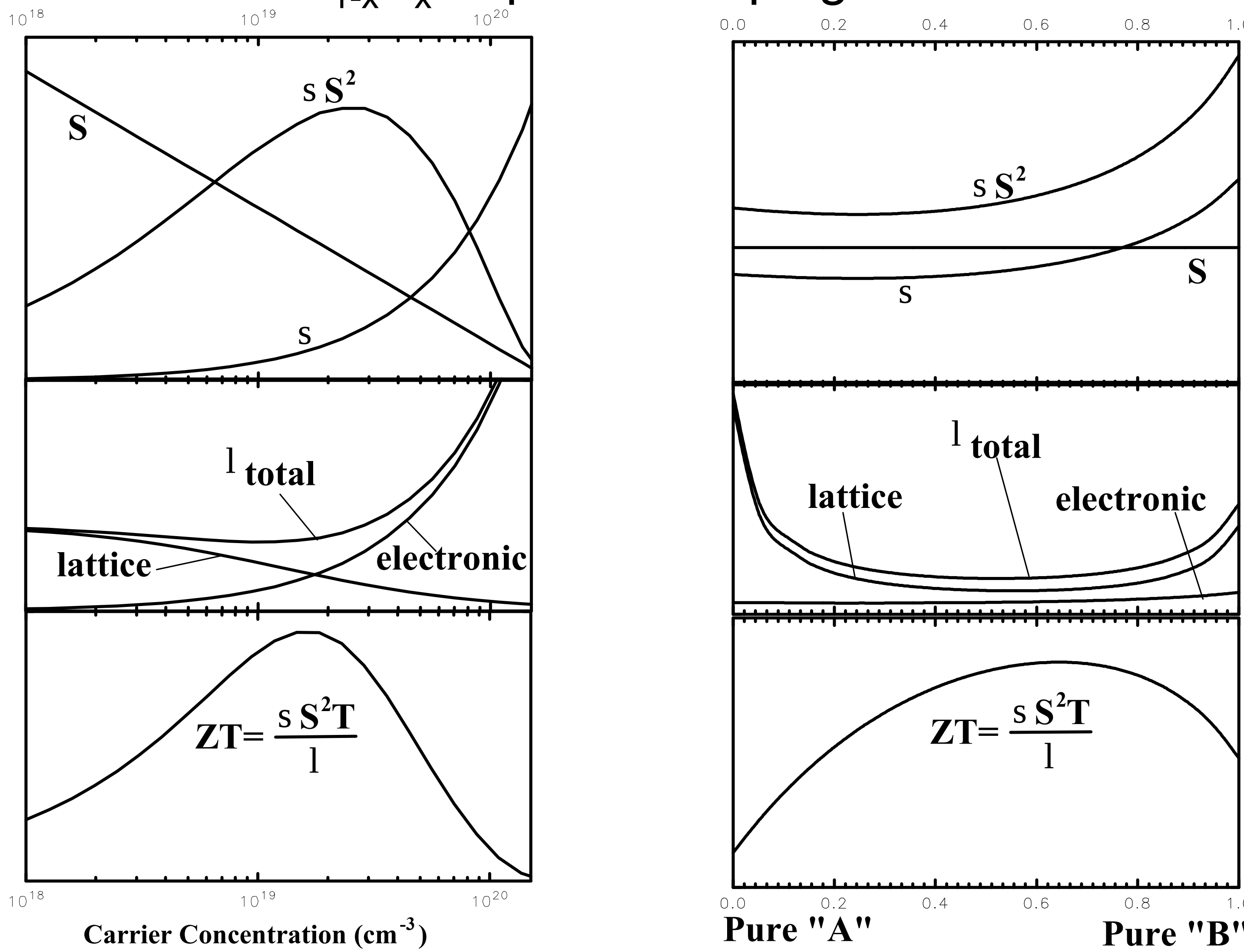


Fig. 44. The thermal resistivity of undoped and doped, p–and n–type Ge–Si alloys as a function of alloy composition at 300 °K.

Dismukes, 1964

Conclusion: Doping, Heavy Masses, and Alloying
$A_{1-x}B_x$: optimize doping & 'x'



Modern Era

- In the 1990s DARPA & the Office of Naval Research initiated support for basic R&D
- Some of the key new ideas:
  - New bulk materials: skutterudites ($IrSb_3$)
  - Slack's "Phonon Glass – Electron Crystal"
  - Hicks & Dresselhaus Quantum Wells

Slack's PGEC- Simple & Effective

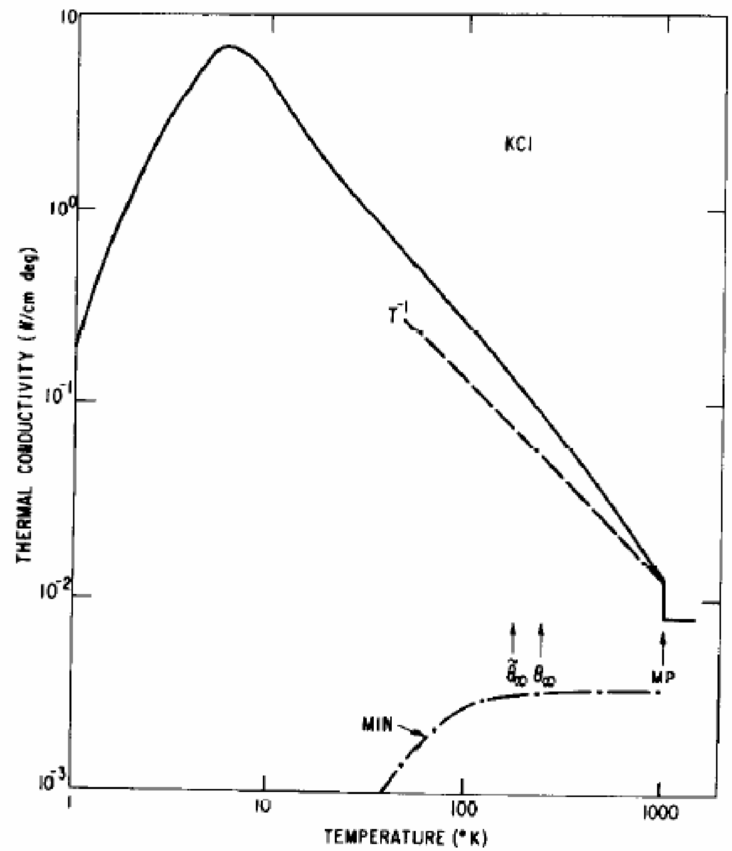
Phonon Glass - Electron Crystal

- Look for complex crystals of heavy atoms (for low λ) with small electronegativity differences (for high mobility)

- Slack introduced the PGEC concept for the 'ideal' thermoelectric
  - Conducts heat like a glass
  - Conducts electricity like a perfect crystal
- The PGEC concept has proved a powerful motivation for experimentalists and theorists alike
  - Simple enough to guide day-to-day choices
  - Captures the right physics for high ZT
- Slack has estimated ZT ~ 3-4 may be possible in bulk materials
- Higher values (if possible) likely require 'Quantum' effects

Slack's Minimum Lattice Thermal Conductivity

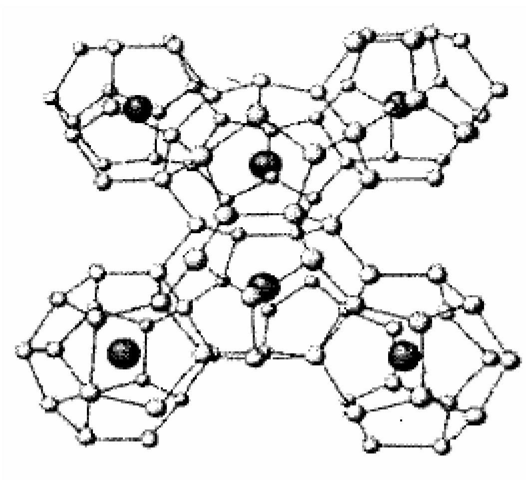
- Slack introduced the idea that all solids must conduct a minimum amount of heat
  - Heat is a wave
  - Imagine each wave travels one wavelength & then scatters
  - This is the most amount of scattering you can have, and still have a wave
  - With that simple assumption, you can estimate λ_{min}
  - 'Glasses' & amorphous materials have very low λ, often close to this minimum
- No known solid has λ less than this estimated minimum
- By systematically introducing different scattering mechanisms, often one can approach λ_{min}

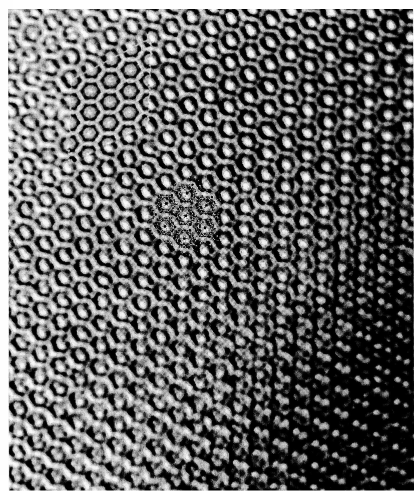


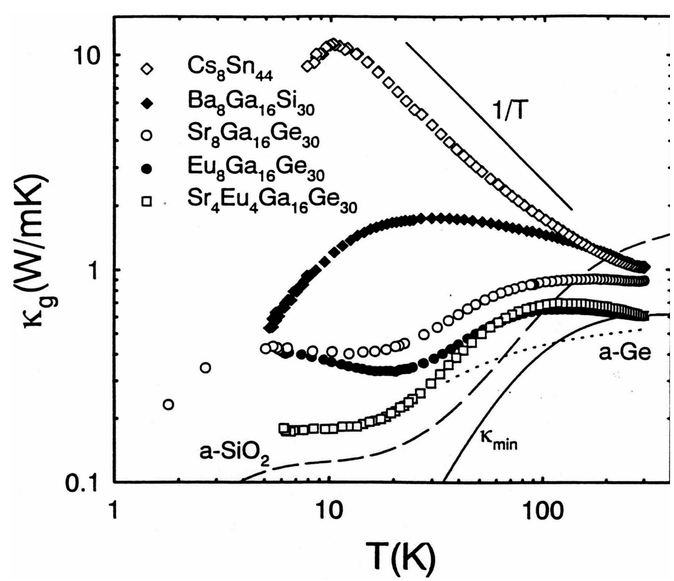
Slack, G. A. (1979). "The thermal conductivity of nonmetallic crystals." Solid State Physics **34**: 1-71.

Clathrates

- Another idea from Slack
- Cage-like crystal structure
  - With room in the polyhedra for a “guest” atom to sit loosely bound & ‘rattle’ phonons
- Examples:
  - $X_8Ga_{16}Ge_{30}$ (where X = Eu, Sr, Ba)
  - Na_8Si4_6
  - Na_xSi_{136}
  - & very recently, a new form of silicon: Si_{136} (Nolas, 2003)







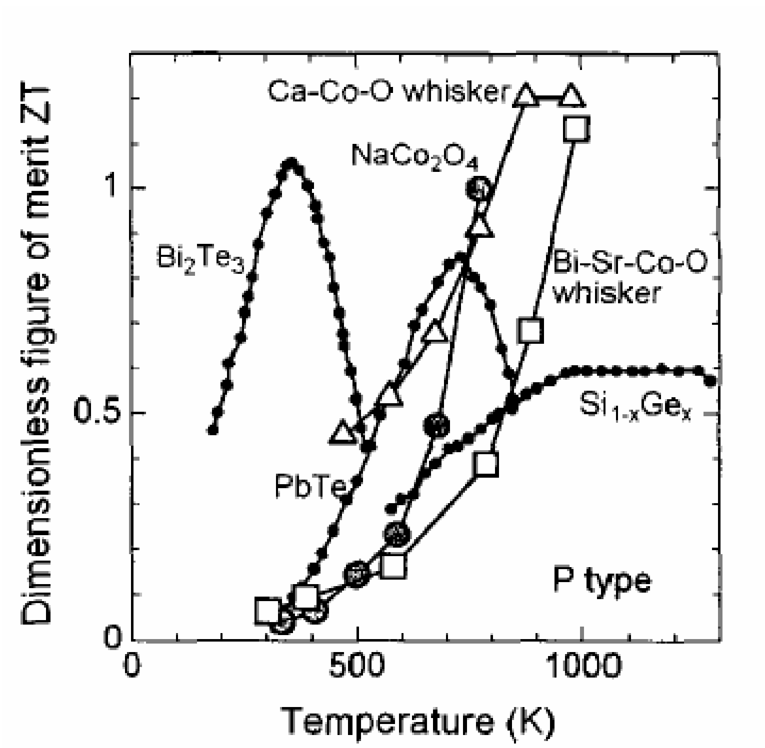
Selected High Temperature Materials Examined at JPL

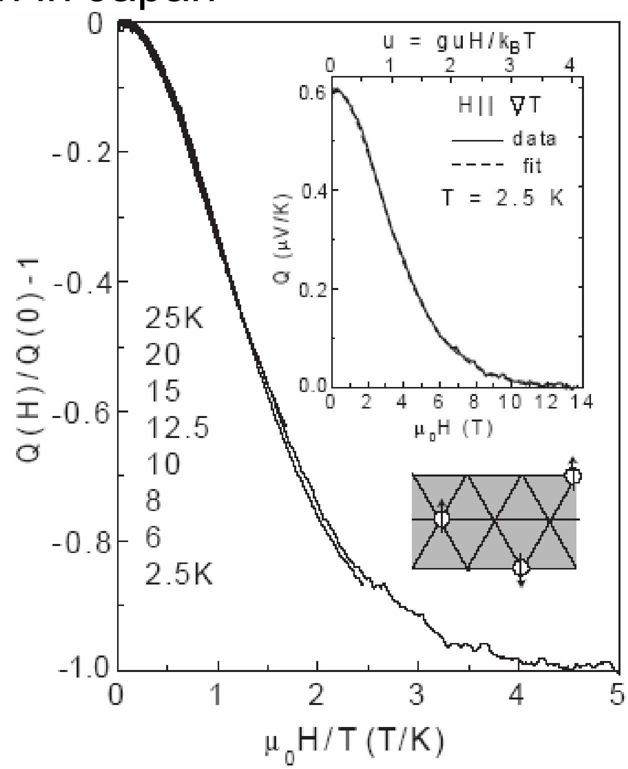
- Since the 1980s JPL has maintained an active new thermoelectric materials effort
- Skutterudites ($CeFe_4Sb_{12}$) and some others may be approaching application in space
- Many more have been investigated, including those below
- With respect to high temperature applications, the breadth of materials examined has no match

	ZT_{max}	
Re_2Te_5	Doping limited	Caillat, ICT,1998
Ge_xNbTe_2	-	Snyder, ICT, 1999
$Ga_xCu_{1-x}Cr_2Se_4$ $Zn_xCu_{1-x}Cr_2Se_4$	0.17 @ 700 K	Snyder, MRS, 2000
$Fe_xCr_{3-x}Se_4$	0.15 @ 525 K	Snyder, PRB, 2000
$PbBi_4Te_7$	0.55 @ 400 K	Caillat, ICT, 2000
$Co_{1-x}Ni_xP_3$ $CoAs_{3-x}P_x$	various	Shields, ICT, 2002
$CaZn_2Sb_2$	0.52 @ 773 K	Snyder, ICT 2002
$Nb_3Sb_xTe_{7-x}$	Doping limited	Wang, ICT, 2002

‘Spin’ contribution to Seebeck

- Wang (2003) has shown the Seebeck coefficient strongly depends on magnetic field
  - Means the ‘spin’ of the charge carrier is important
  - Never before seen with high ZT
- This is presumably the origin of high ZT
  - ZT~1.2 @ 900 K has been reported for $NaCo_2O_4$ (Terasaki, 2003)
- Most of the work on these oxides has been in Japan





Hicks & Dresselhaus: ZT>7?

- Hicks PhD Thesis ~1992
  - Curious about effect of low dimension materials on ZT
- A ‘Quantum Well’ is a semiconductor so thin that the charge carriers move only in the plane of the film
- Need to be ‘quantum’ thin to see effect
- All properties can be effected
- Initial expectation:
  - Seebeck enhancement

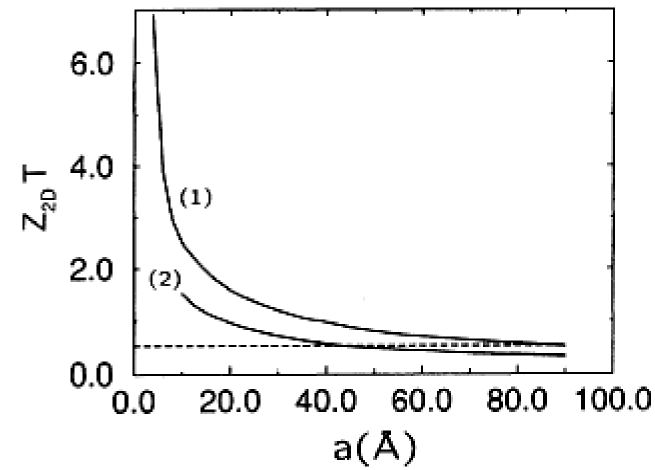
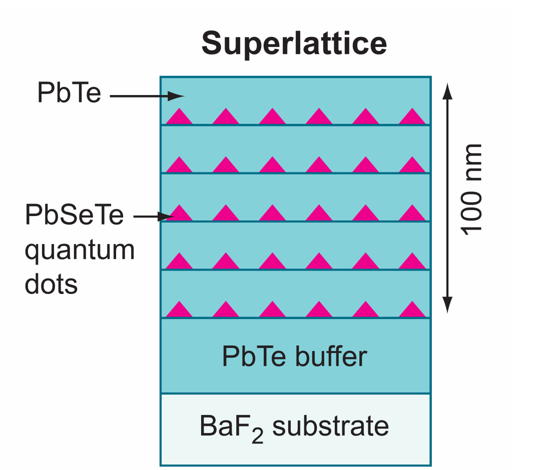


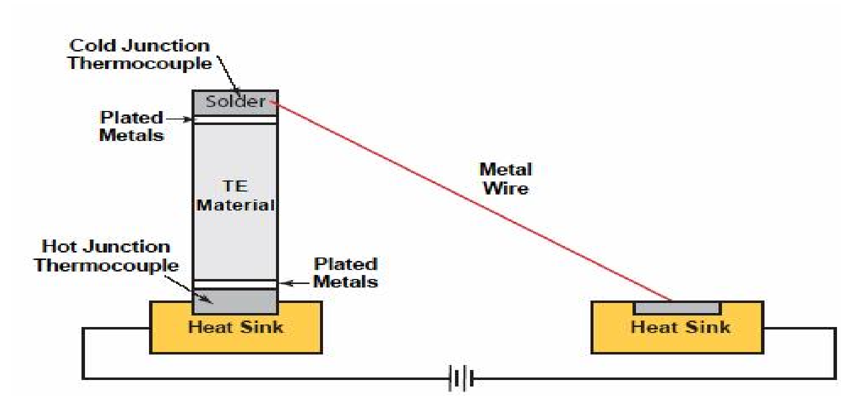
FIG. 5. Plot of $Z_{2D}T(\zeta^*_{opt})$ vs layer thickness a for (1) a_0-b_0 plane layers and (2) a_0-c_0 plane layers. The dashed line indicates the best ZT for 3D bulk Bi_2Te_3.

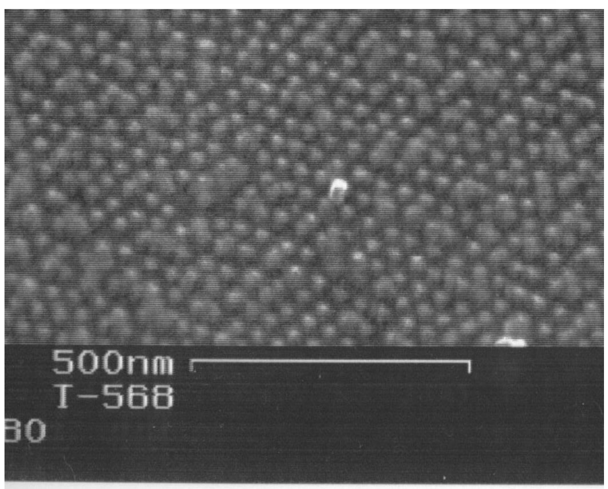
Hicks, L. D. and M. S. Dresselhaus (1993). "Effect of quantum-well structures on the thermoelectric figure of merit." Phys. Rev. B **47**(19): 12727-12731.

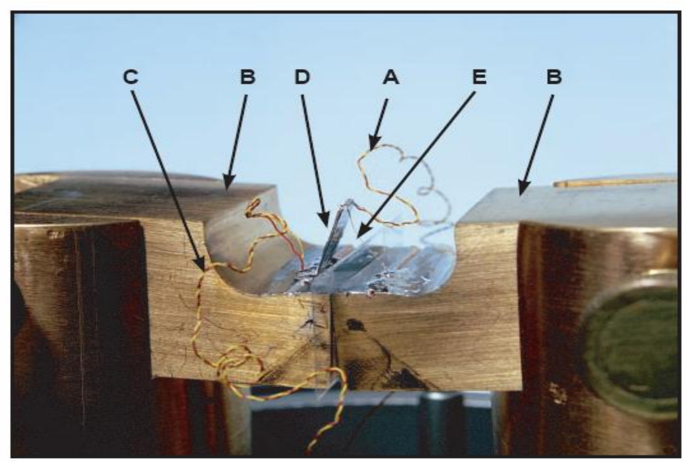
ZT~1.6 @ 300 K in a PbTe QDSL Device

An actual Quantum-Dot device, Harman, et. al., Science, (2002)

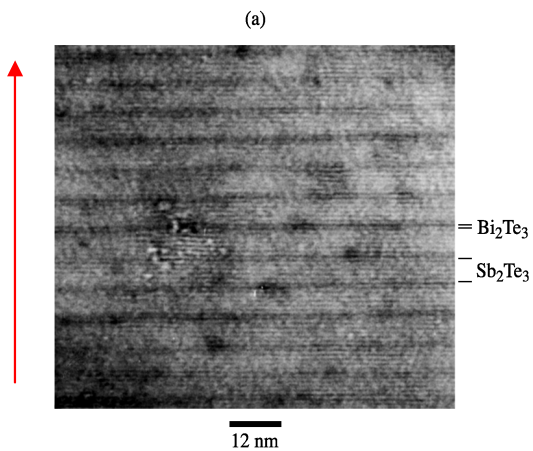


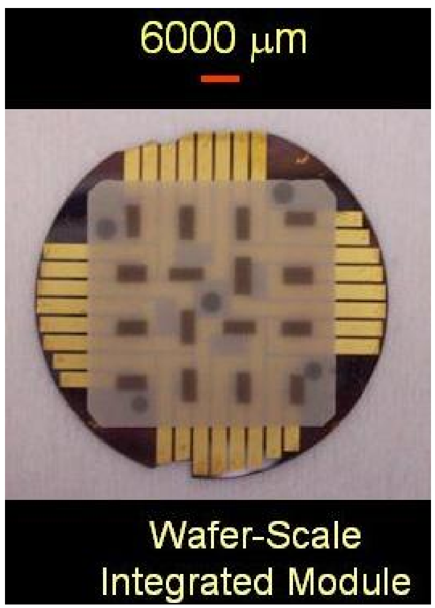




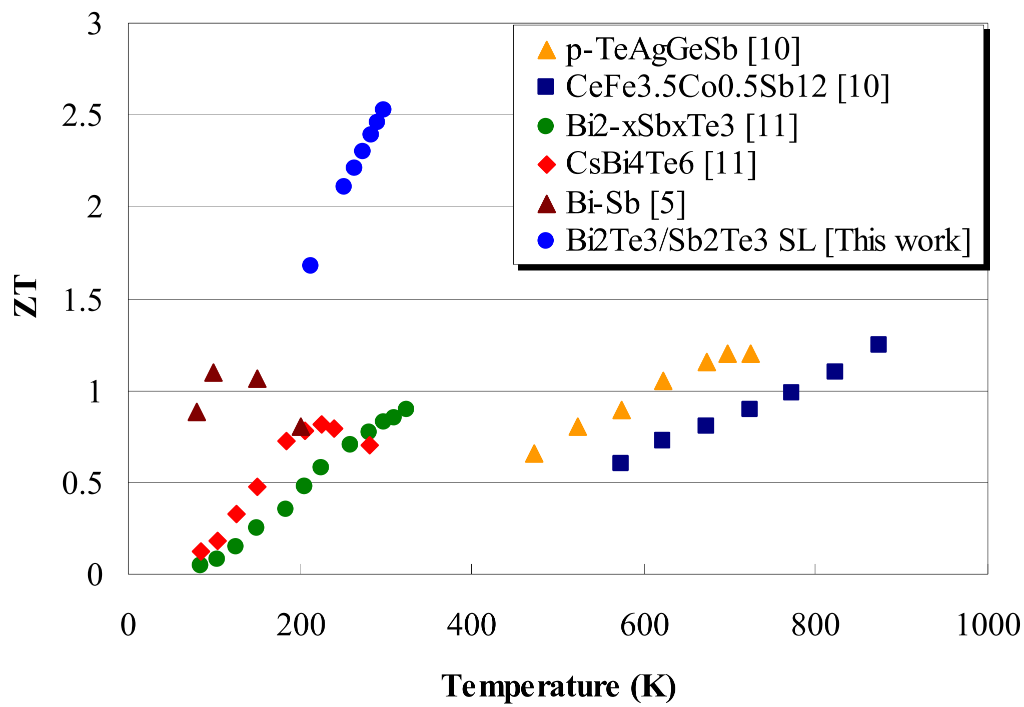


RTI's Nano-structured Superlattice Material





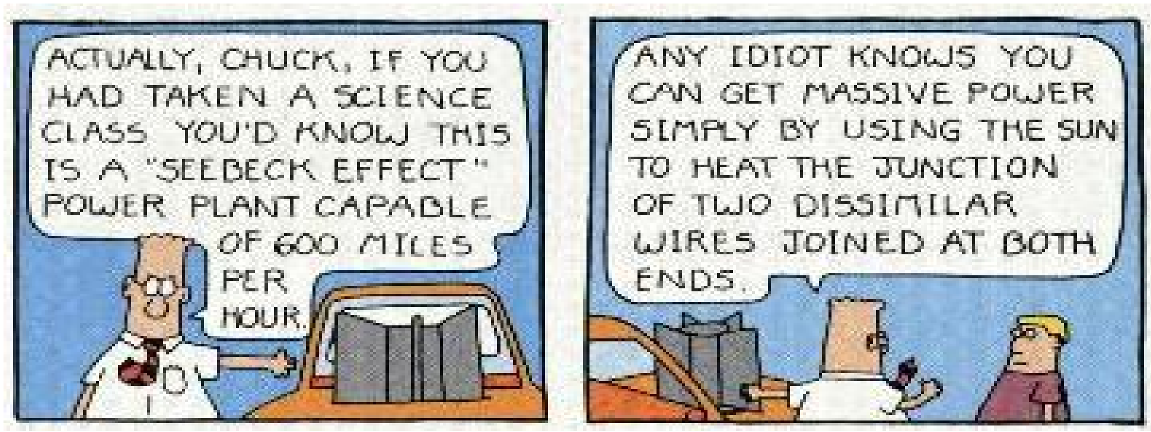
- Venkatasubramanian (Rama) at Research Triangle Institute, Nature (2001)
- Heat/Current ***perpendicular*** to planes



Applied Physics Letters, 75, 1104 (1999)

Summary

- Study of relationships between transport coefficients, of which thermoelectricity may be the canonical example, has a history of producing some profound ideas
  - Perhaps it can do so again
- In the mean time we'll content ourselves with exploring new materials ideas, keeping our beer (and backsides) cool while we watch pictures from Jupiter.



Dilbert 10-10-1993