Short Course on the ABCs of Thermoelectrics

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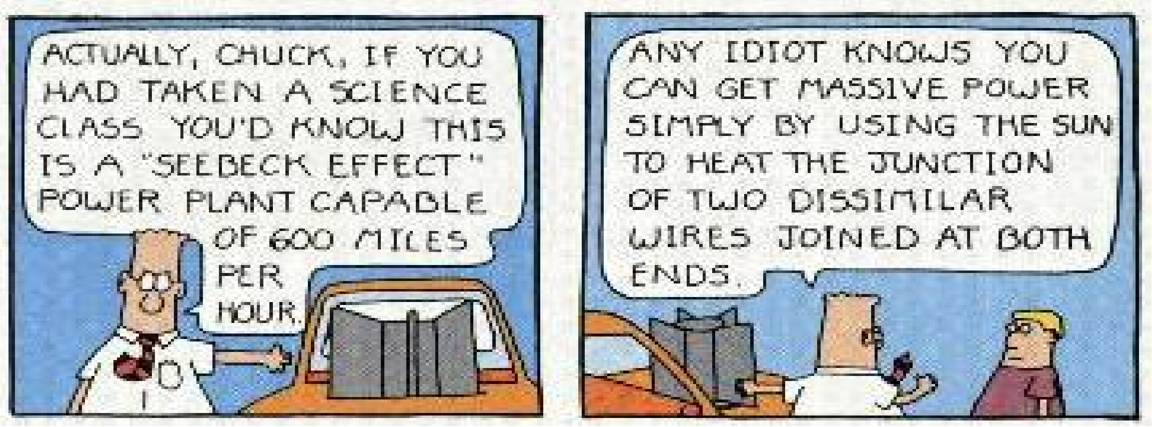


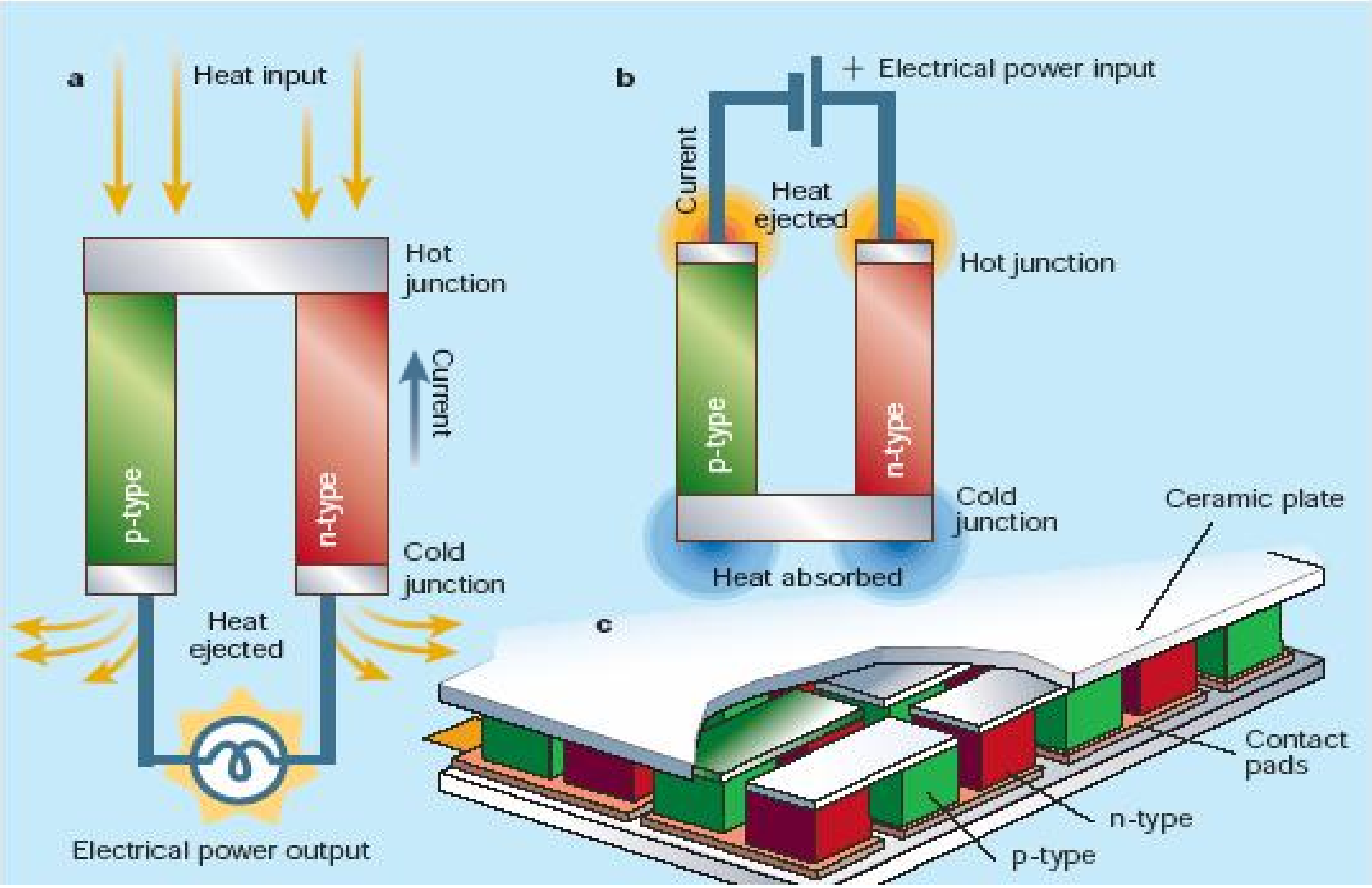
Dilbert 10-10-1993

Outline

Introduction to Thermoelectricity

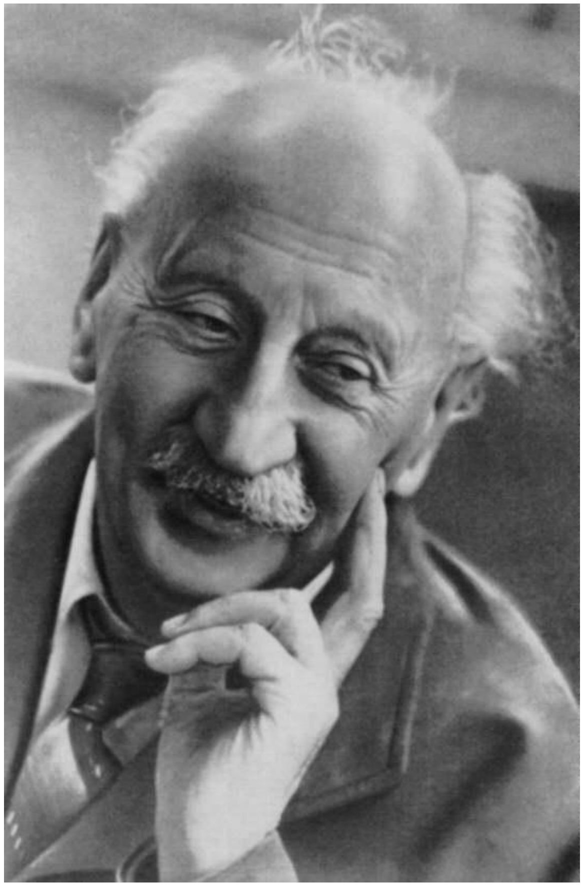
Very Basic Thermoelectrics

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.

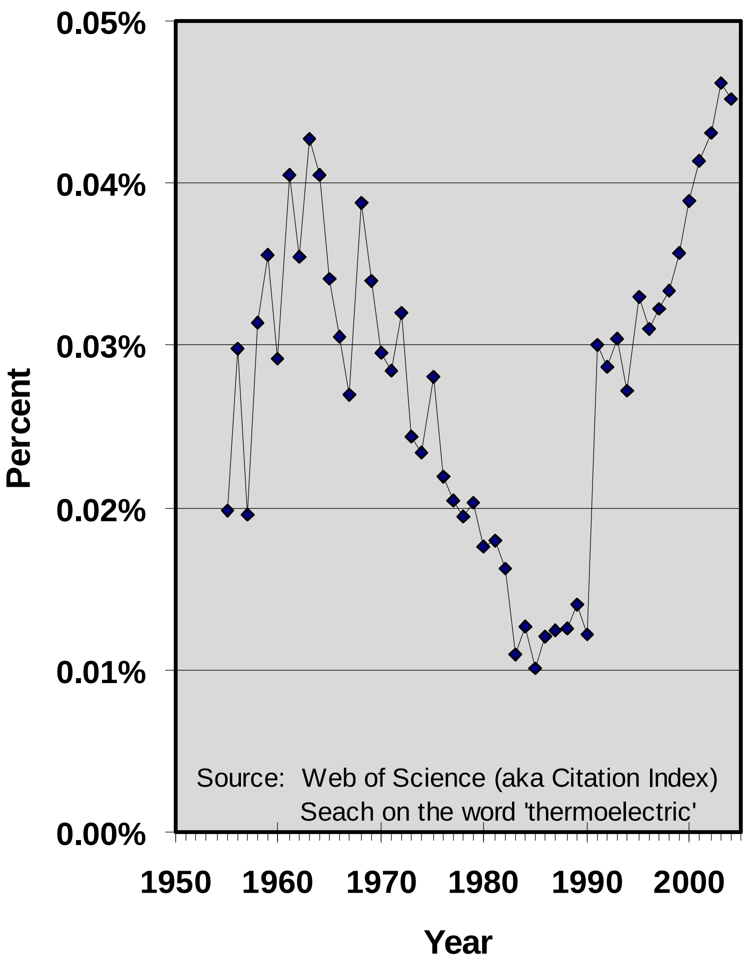
Three categories of Thermoelectric Applications

- Power generation
  - Space power
    - Outer planetary exploration, certain lunar & Mars missions, etc.
  - Remote power
    - oil & gas pipelines, remote telecom stations
  - Waste heat recovery (R&D only)
    - Vehicles, industrial waste heat
  - Microdevices
    - Body-heat powered wrist watches (!)
- Cooling
  - Car seat cooling
  - IR detector cooling (missile guidance, night vision)
  - Fiber optic (mainly temperature control)
  - Semiconductor/Industrial process temperature control
  - Consumer products (aka beer coolers)
- Metrology
  - Temperature measurement
  - Nano-calorimeters
  - Won’t discuss these further in this short course, but be aware that metrology is by far the most widespread use of thermoelectrics

Reliable, Reliable, Reliable

- The all solid-state nature of thermoelectric technology is usually its greatest appeal
- Attractive for a wide variety of applications
  - None of which can be described as a major industry
- It is sometimes said you choose thermoelectrics not so much because you want to, but because nothing else will do the job
- Efficiency has never been its strength

TE R&D Resurgence

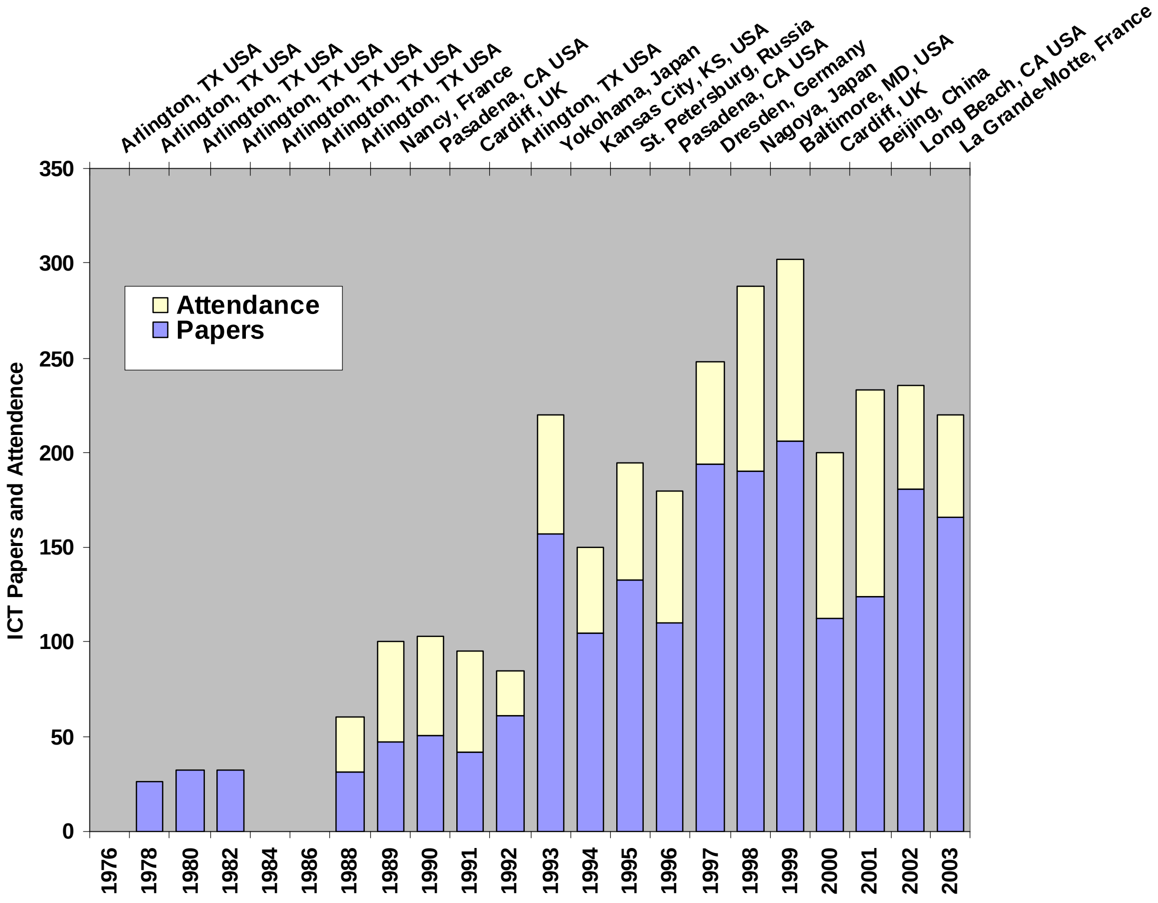


Source: Web of Science (aka Citation Index) Seach on the word 'thermoelectric'

- 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

International Thermoelectric Society

- ITS founded in 1988
- Has become an important forum for thermoelectric science & technology



Role of Dr. Rudy Buser

Director, US Army Night Vision Labs through ~ 1993

- Through the 1980's the Night Vision Lab supported work at Marlow Industries to push the low temperature limit of thermoelectric coolers.
- By late 1989 Dr Buser was frustrated by the slow progress and asked Ray Marlow why TE coolers couldn't go to cryogenic temperatures
  - Marlow replied that it was a limitation of the materials, but Buser persisted: "Why is that?"
  - Ray Marlow said he didn't know, but promised to find out
- Marlow brought in consultants (including me), put together a story & went on the road to every funding agency that would listen
- About the same time, Buser put a note in an Army Newsletter speculating that maybe there was something new could be done in thermoelectric materials
  - Ted Harman at MIT saw Buser's remarks and began his work on PbTe superlattices
- Quite independently, Dr. Dresselhaus at MIT began thinking about thermoelectrics, inspired by a dinner in France with two people (Stockholm & Issi) who had recently returned from an International Conference on Thermoelectrics
- It seems the time was right for some new ideas.

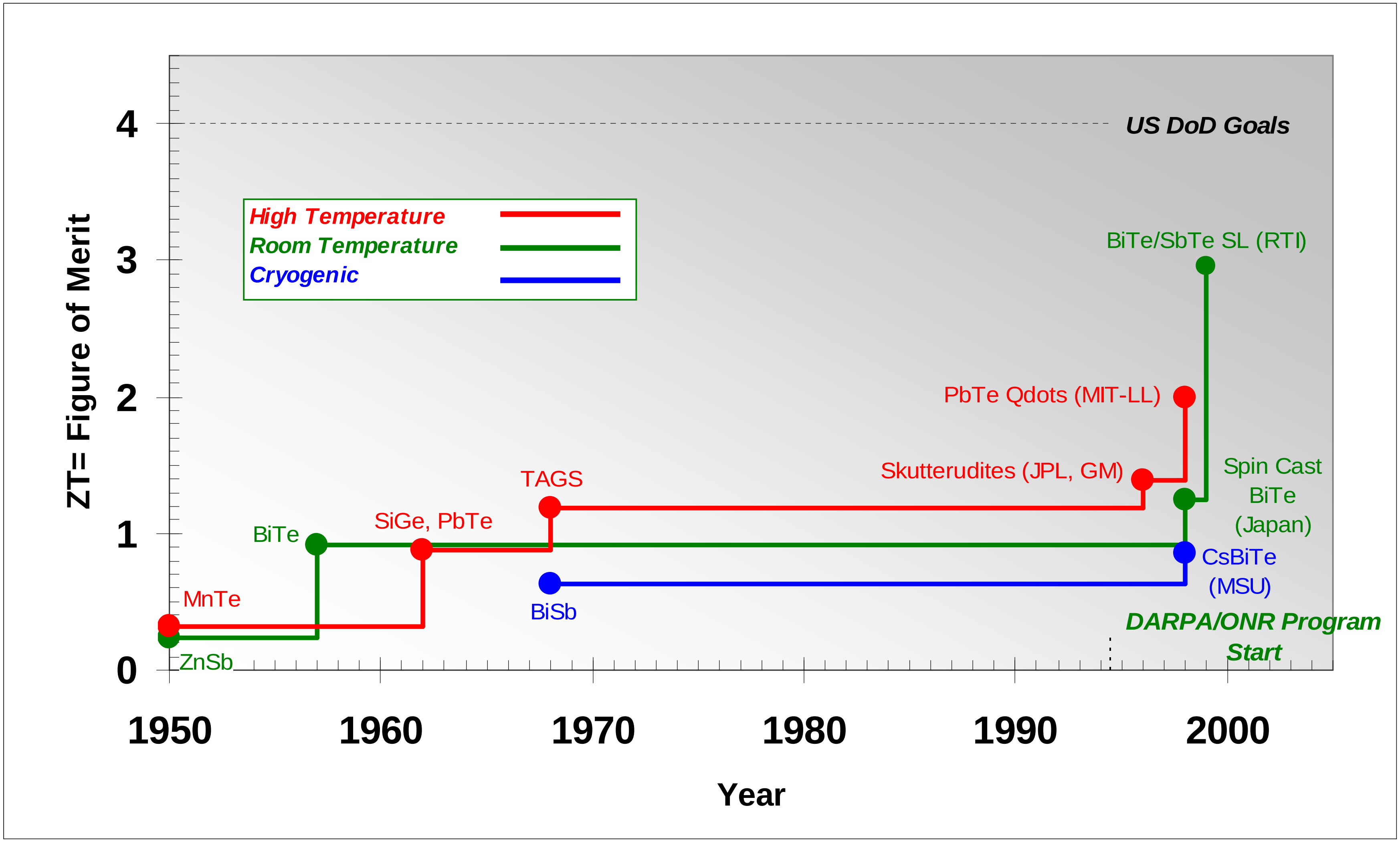
1st National Thermogenic Cooler Conference

- Although there never was a 2nd conference, this meeting was critical to setting off the modern resurgence of interest in thermoelectrics.
- Organized by the Center for Night Vision and Electro-Optics, Fort Belvoir, MD, 17 Sept. 1992
- First (or nearly first) public discussion of:
  - Skutterudites – Fluerial (JPL), Slack (GE)
  - Quantum Wells – Hicks & Dresselhaus (MIT)
  - PbTe Superlattices – Harman (MIT/Lincoln Labs)
  - Bi_2Te_3-based superlattices – Venkatasubramanian (RTI)
- Following this conference the Army Night Vision Lab issued a Call for Proposals
  - Generated many proposals, but no funding was forthcoming
  - Nevertheless, the material in those proposals became available to the Office of Naval Research and DARPA and helped persuade them that there were promising ideas to pursue in thermoelectrics
  - DARPA & ONR went on to fund a significant level effort in the basic science of thermoelectric materials since about 1994

Recent Progress in TE

- New ideas emerged in early 1990s
  - Novel materials, especially the ‘skutterudites’
  - Quantum Wells, Quantum wires & superlattices first proposed
- New funding emerged in US by 1994-5
  - Mainly DARPA (Defense Advanced Research Projects Agency) and ONR (Office of Naval Research)
- Late 1990s see first significant progress in ZT since 1960s
  - Skutterudites (Slack, JPL), superlattices and most recently a new PbTe alloy
  - Most notable progress is so far more appropriate for cooling than power generation
- More efforts now focusing on reducing these advances to practical devices

History of the Thermoelectric Figure of Merit

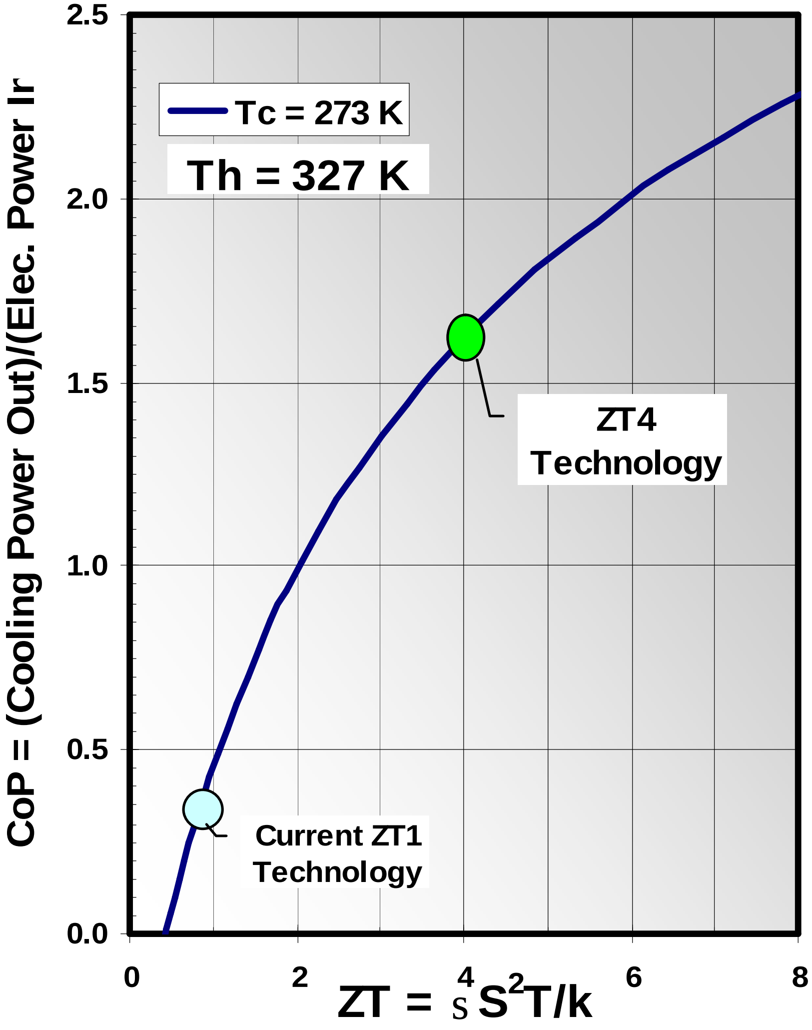


Inspired by Dubios, ICT, 1999

TE Cooling Applications

Significant to space power to the extent that potential cooling applications are driving the technology development

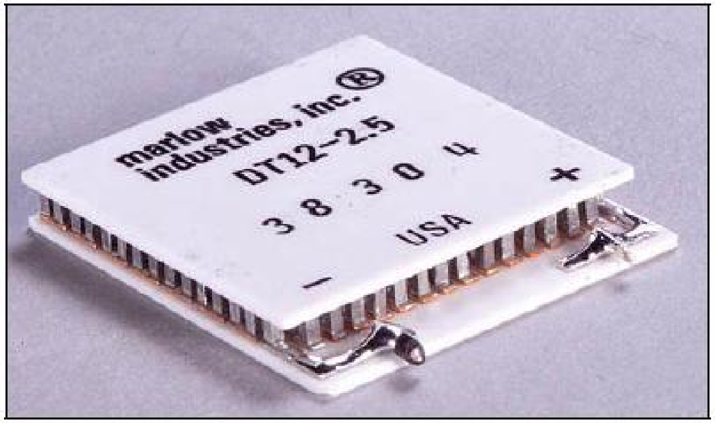
TE Coefficient of Performance

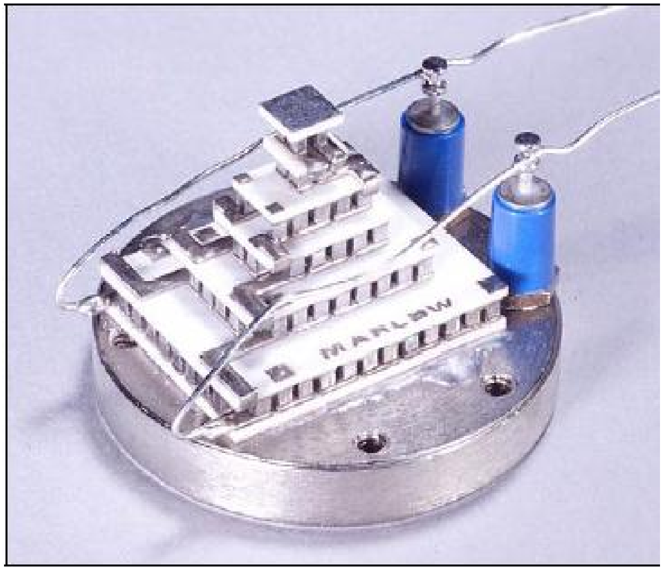


- ZT values near 1 are in production today
- Dramatic CoP improvement with ZT
- ZT ~ 2 to 3 demonstrated in lab
  - Three entirely different approaches: quantum dots, superlattices & new bulk alloy

Typical Commercial TE Cooler Modules

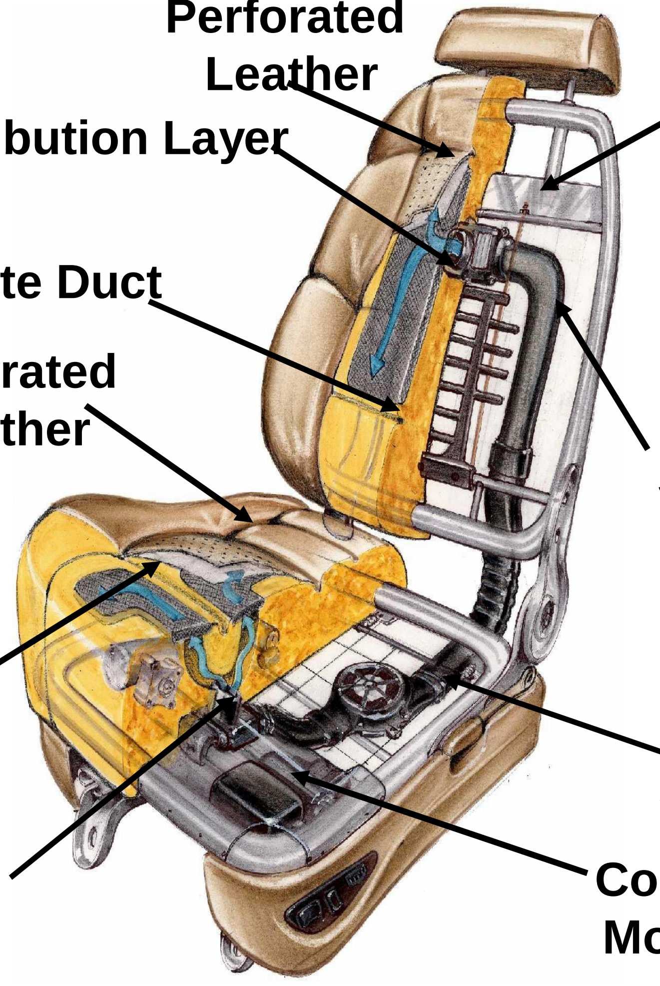
- Single stage TE coolers typically achieve ΔT_{max} = 66-75 K (ideal, no load)
- Multistage coolers might achieve ΔT_{max} = 150 K (ideal, no load)
- Several manufacturers available in US, China, Japan, Russia & Ukraine
- Prices from Chinese manufacturers have been quoted as low as $3/module





Case Study: http://www.amerigon.com Climate Control Seat™ (CCS™) System Vehicle Application

Production CCS Assembly



Perforated Leather

Distribution Layer

Waste Duct

Perforated Leather

Distribution Layer

Cushion TED

Back TED

Supply Duct

Blower Assembly

Control Module

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

Typical TE-Telecom Applications:

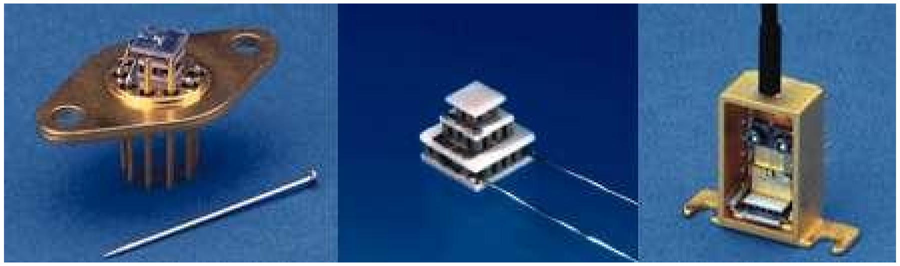
Temperature Control and Stabilization

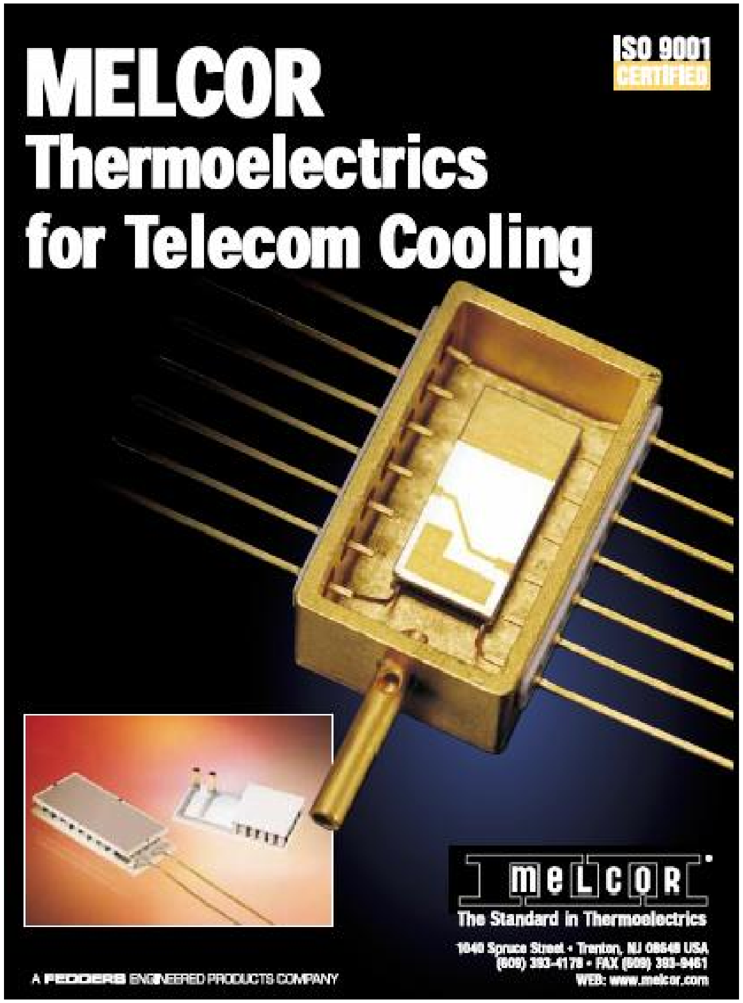
- **Controlling lasers to tight temperature tolerances with TECs**
  - **1300-1550nm distributed feedback Laser Diodes**
  - **Increased number of optical channels per fiber (and bandwidth)**
  - **Dense Wavelength Division Multiplexing (DWDM) Optical transmitters required for applications**
- **"Passive" Components for the "All Optical Network"**
  - **TECs stabilize critical temperature sensitive components**
    - **Arrayed Wave Guides (AWGs), Optical Multiplexers (MUX and DeMux), Optical Switches and Variable Optical Attenuators (VOAs)**
- **Temperature tune the pump laser wavelength**
  - **Typically 980nm and 1480nm**
  - **Match the absorption wavelength of the media being optically pumped (EDFA Optical Amplifiers, Diode Pumped Lasers)**

- Source: Marlow Industries, http://www.marlow.com

TEs for Telecom Cooling

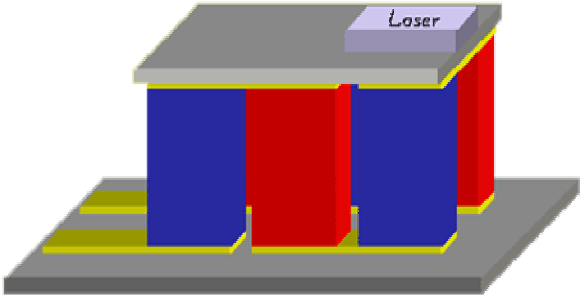
- Melcor, Marlow and many other TE manufacturers provide coolers specifically designed for Telecom laser-cooling applications

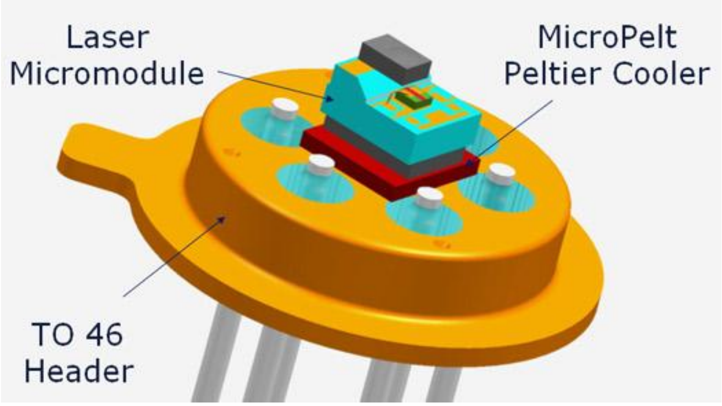




From Melcor, http://www.melcor.com

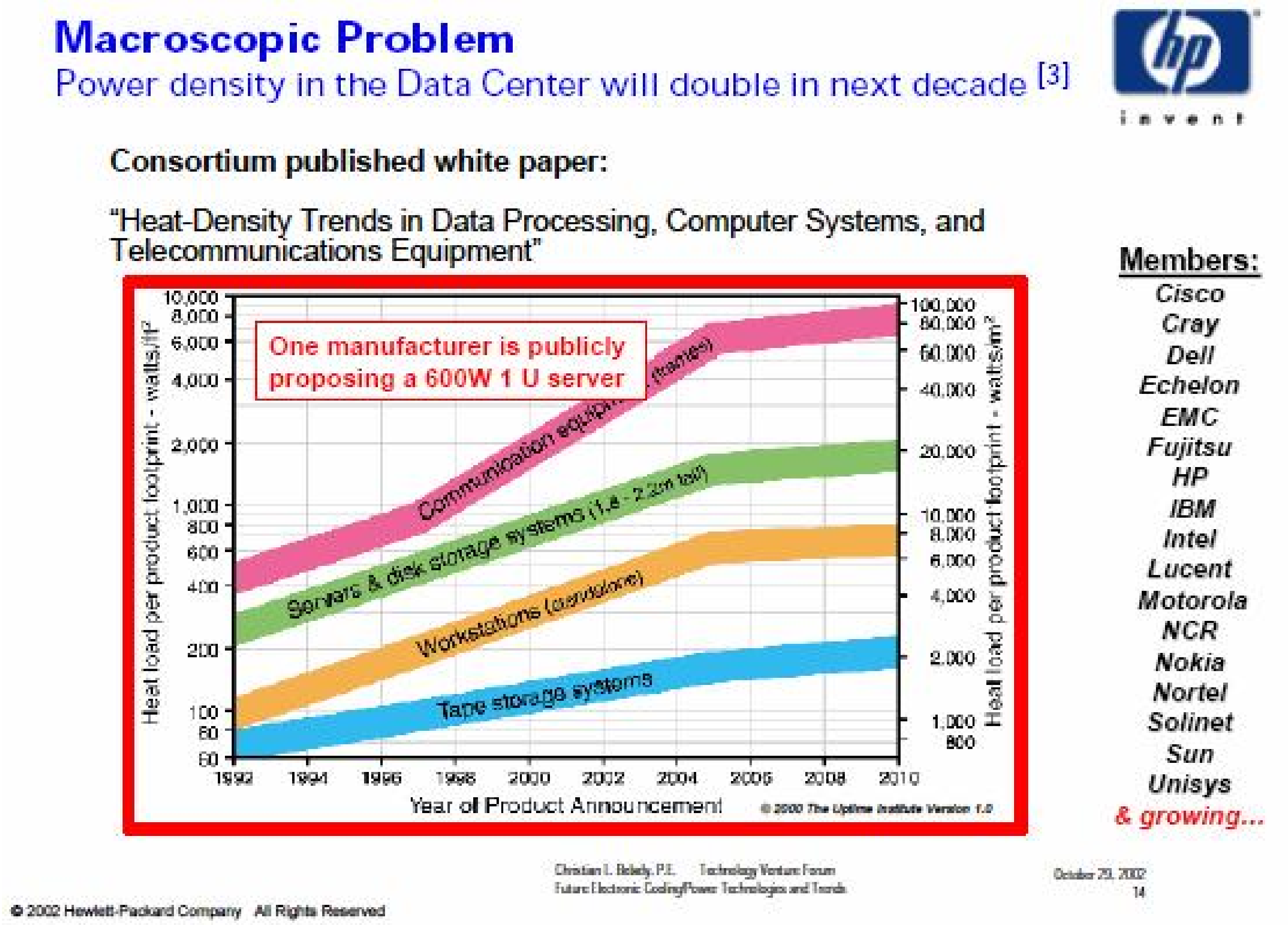
Temperature Control for Telecommunications Lasers





- From MicroPelt
  - German startup, http://www.micropelt.com
  - Partnered with Infineon
  - ‘Cooler-on-a-chip’ approach
- Emission wavelength stabilization for fiber-optics
- Small cooling area < 1 mm^2
- Fast control time to 10 milliseconds

Data Center Thermal Management



Macroscopic Problem

Power density in the Data Center will double in next decade [3]

Consortium published white paper:

"Heat-Density Trends in Data Processing, Computer Systems, and Telecommunications Equipment"

One manufacturer is publicly proposing a 600W 1 U server

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Members:

Cisco
Cray
Dell
Echelon
EMC
Fujitsu
HP
IBM
Intel
Lucent
Motorola
NCR
Nokia
Nortel
Solinet
Sun
Unisys
& growing...

Christian L. Belady, P.E. Technology Venture Forum
Future Electronic Cooling/Power Technologies and Trends

October 23, 2002
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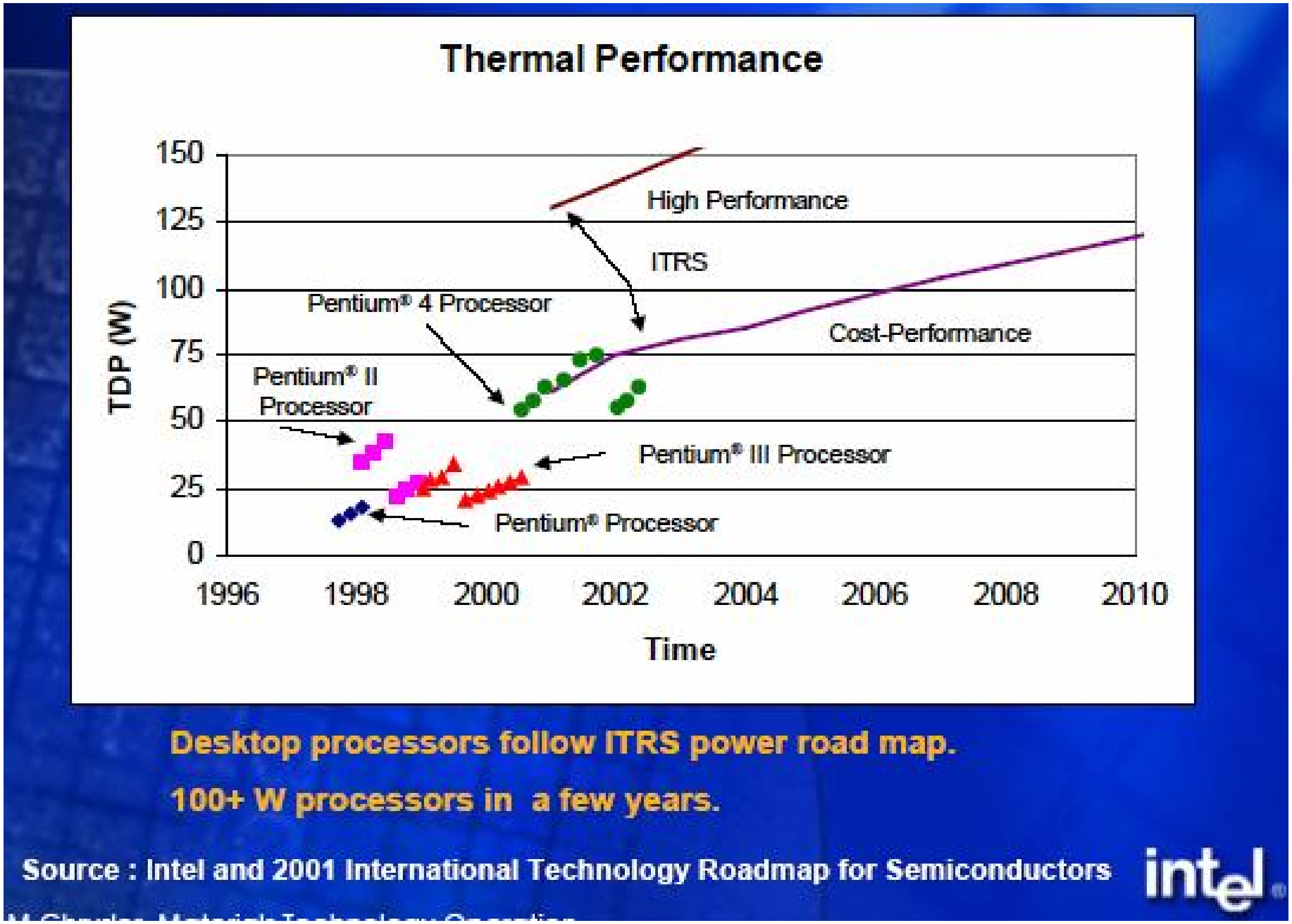
Moore’s Law = Greater Heat Burden



Desktop processors follow ITRS power road map.

100+ W processors in a few years.

Source : Intel and 2001 International Technology Roadmap for Semiconductors

- Chyrsler, G. M. (2002). Building Blocks for Thermal Management of Electronics. Next-Generation Thermal Management Materials and Systems. Dallas/Fort Worth, Texas, Research Triangle Institute.

Commodity Industry vs. Proprietary Technology

Barriers and Opportunities

Heat fluxes are increasing in the semiconductor package

- **New packaging technologies**
  - Liquid cooling
  - Spray cooling
  - High conductivity material – ie diamond/graphite
  - Refrigeration
  - Thermoelectrics and Thermionics
  - etc
- **Interface advancement**
  - Metal pastes
  - solders
  - etc

All of these technologies exists today…why are they all still boutique industries?

It's not a technical issue…it's a business issue, you're in a commodity industry selling proprietary stuff.

Christian L. Belady, P.E. Technology Venture Forum
Future Electronic Cooling/Power Technologies and Trends

October 29, 2002
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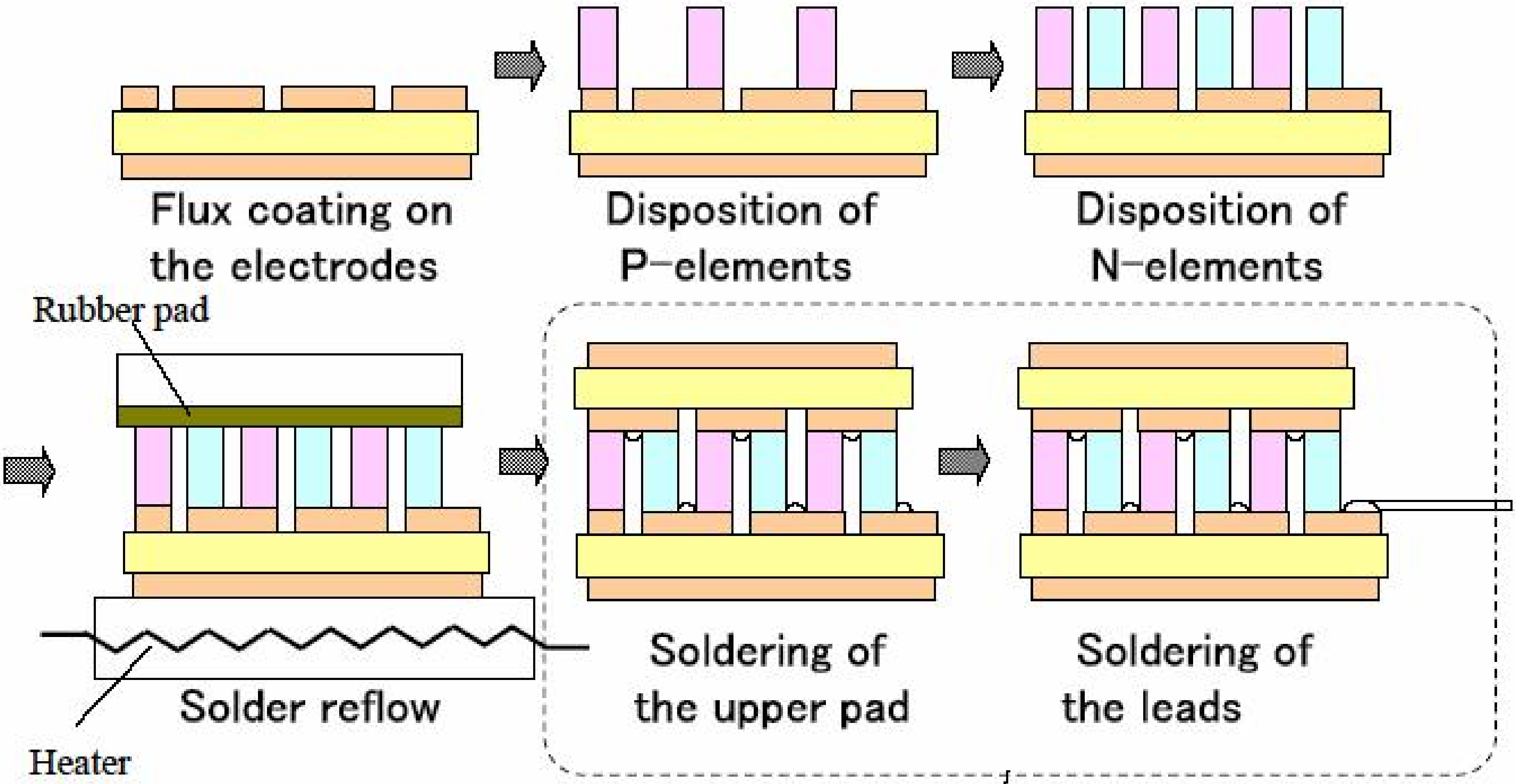
- Source: Belady, C. (2002). Future Electronic Cooling/Power. Next-Generation Thermal Management Materials and Systems. Dallas/Fort Worth, Texas, Research Triangle Institute.

Robotic Assembly of Telecom TECs



Flux coating on the electrodes

Disposition of P-elements

Disposition of N-elements

Solder reflow

Soldering of the upper pad

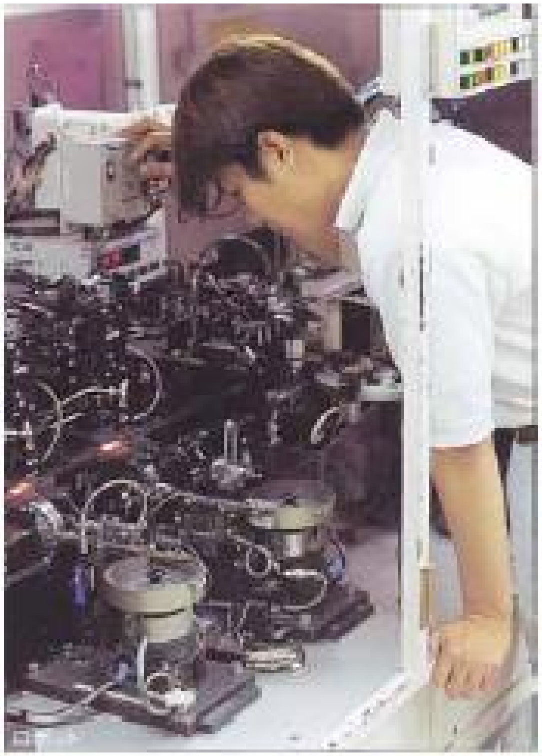
Soldering of the leads

The processes in the dotted line are not always subjected to automation.

KOMATSU
Komatsu Electronics Inc.

Robotic assembly of telecom TECs in Komatsu Electronics Inc.

Close up of element feeder →



Assembly shop in 2000

Komatsu TE Assembly Robots

30,000 18-couple modules/month/robot

Two Robots in the Assembly Line of Telecom TECs

CONSUMER APPLICATIONS

BEER COOLER

TE FRIDGE

CHOCOLATE COOLER

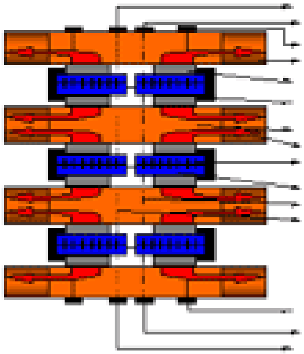
INDUSTRIAL APPLICATIONS

Electronic Cooler

TE Dehumidifier

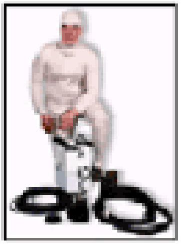
MILITARY AND SPACE APPLICATIONS

Multi-Module Chips



Thermal Management of IR Imaging

Individual Soldier Climate Control

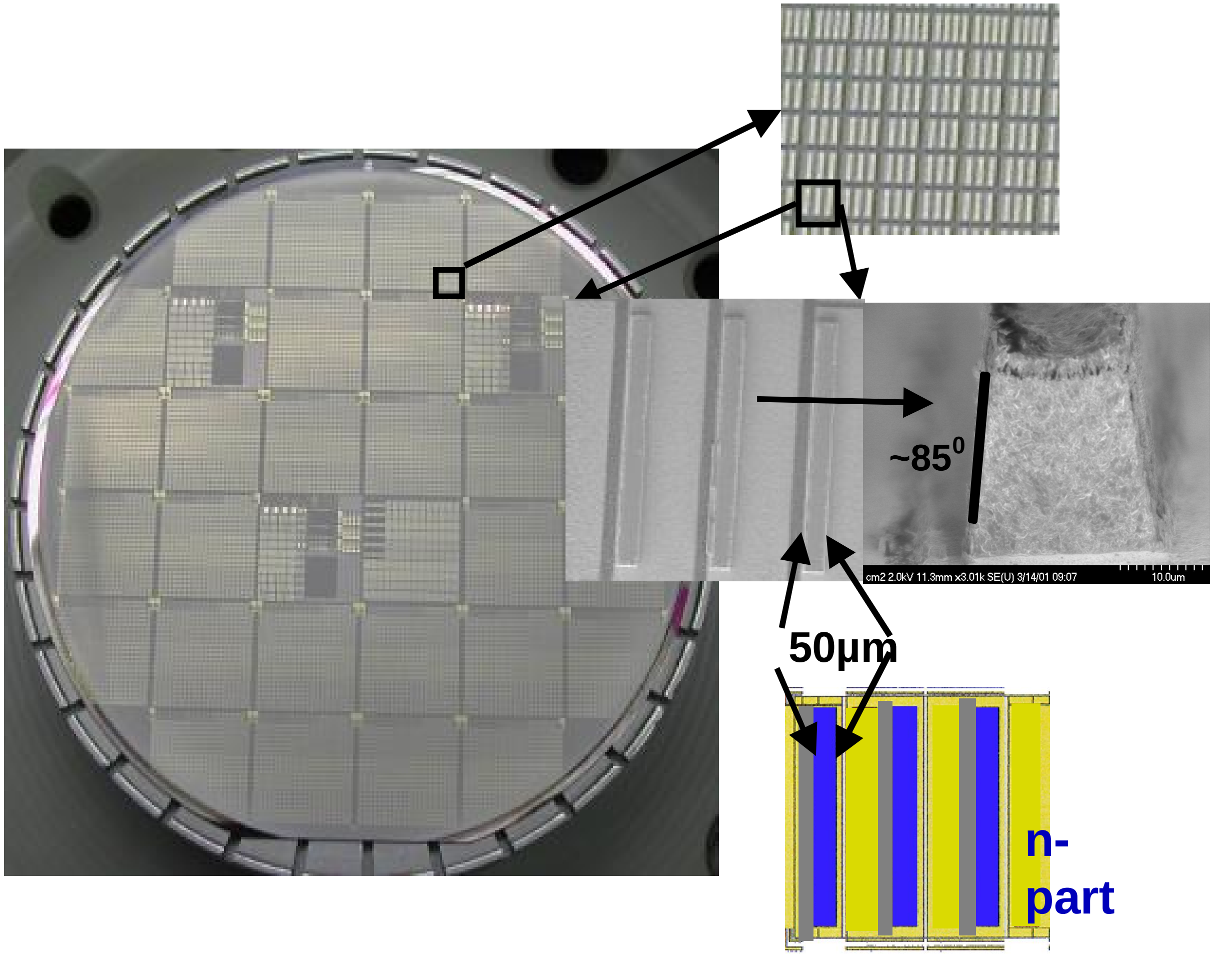


Navy Propulsion Using Superconductor Motors

NIGHT VISION

TE Cooler-on-a-Chip

http://www.micropelt.com



Bi_2Te_3-based thermopiles fabricated on a chip using methods well suited for mass production

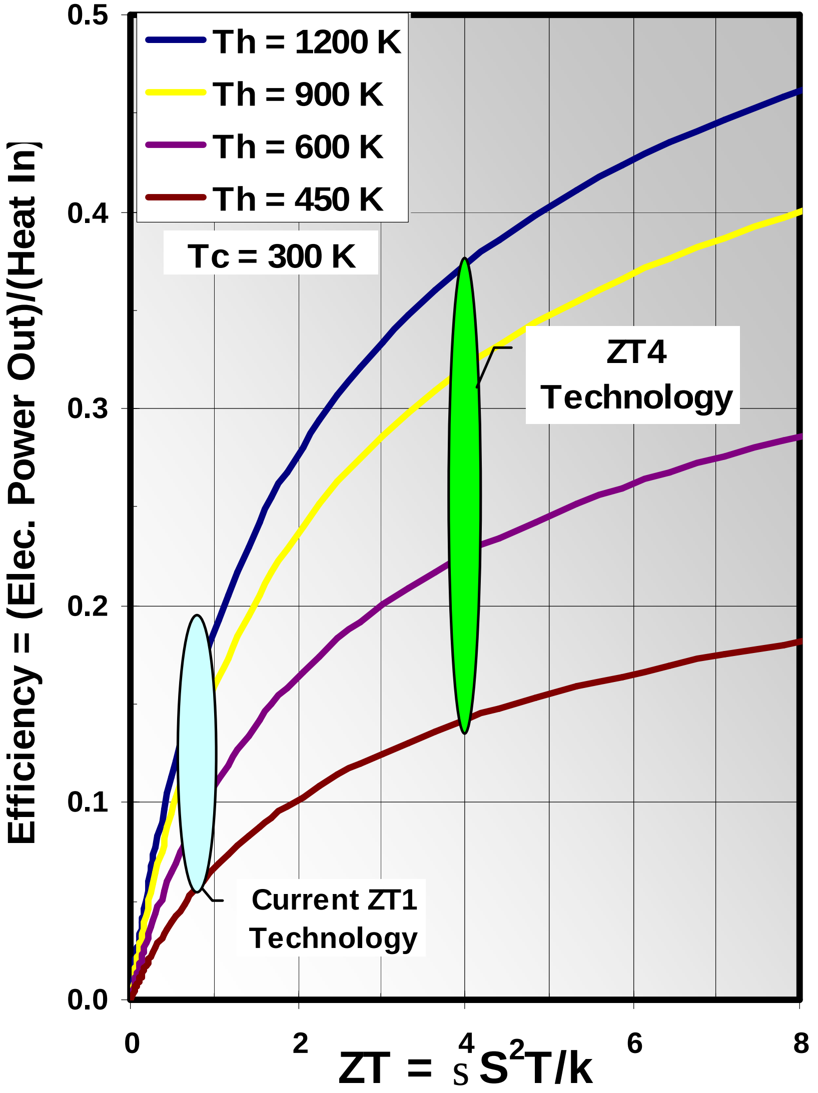
Also suitable to micro scale power generation

Major Trends in TE Cooling

- Move improved efficiency (ZT) from lab to devices
  - Research Triangle Institute is making prototype modules from next-generation ‘superlattice’ TE materials
- New applications through cost reduction (ex: car seats)
- Cost reduction through robotics
  - Much assembly is still ‘by hand’, but increasingly semiconductor industry fabrication techniques are being adopted
- ‘On-A-Chip’ device fabrication technology
- Novel heat transfer technologies

Power Generation

TE Efficiency – Power Generation

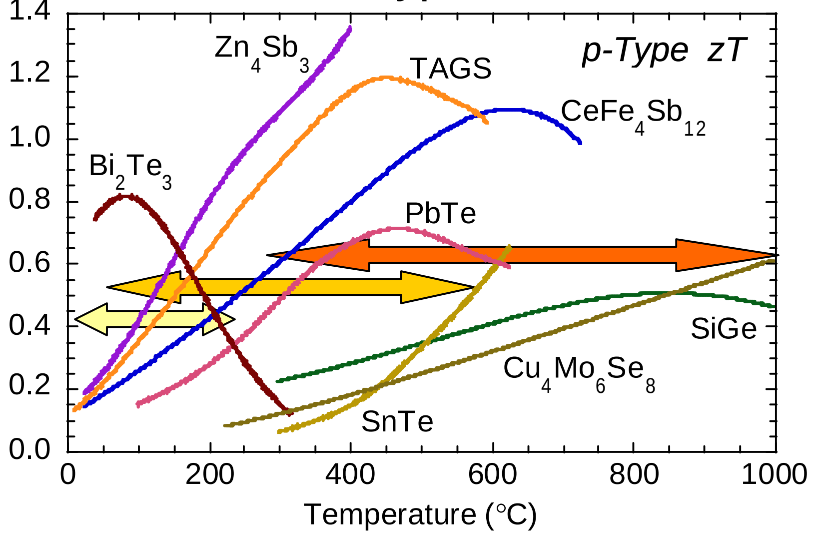


- Can operate over large temperature differences
  - Large fraction of Carnot Efficiency
- Average ZT values near 1 available today
- ZT = 2-3 in labs to about 600 K

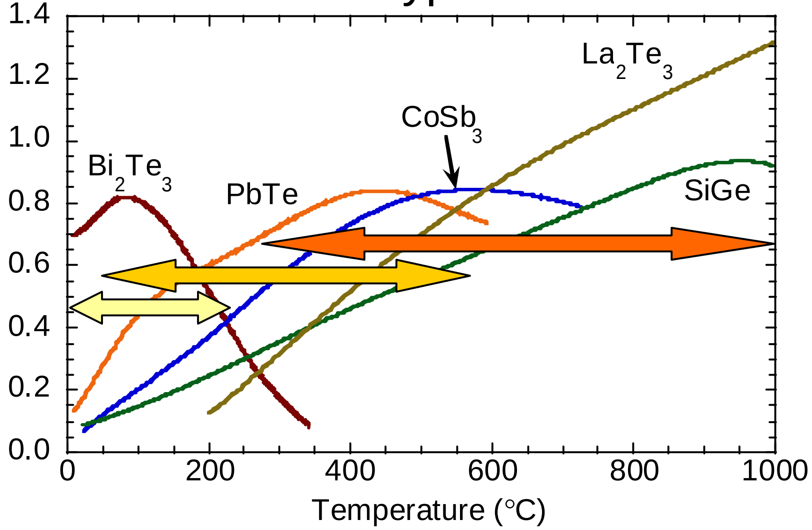
ZT for Some Known Materials

ZT~ 1 available from 300 – 1000 °C

P-Type



N-Type



- Three main operating ranges for proven materials:
  - “Low Grade Heat”: 30 °C – 250 °C, Bi_2Te_3 – based materials
  - “Intermediate”: 50 °C – 600 °C, PbTe –based materials
  - “High Temperature (ex: Space): 300 °C – 1000 °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)

Available TE Generator (TEG) Technologies

- The 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, & TAGS
  - “High Temperature (ex: Space): 300 ^{o}C – 1000 ^{o}C, SiGe
- Mature device and system technologies are available for each of these materials systems.
  - The limited markets for TEGs means there are relatively few suppliers.
  - TE coolers are all based on Bi_2Te_3 but only a few commercial modules have been designed to operate above room temperature as required for power generation
  - SiGe, in particular, appears to have no terrestrial applications, although some R&D in Japan has examined the possibility of using SiGe in certain vehicle waste heat applications
- Almost all semiconductors ever discovered with attractive ZT values have been successfully reduced to practice
  - Historically, the hard part has usually been the development of high ZT values
  - Developing appropriate device technology (i.e. bonding, electrical interconnects, electrical insulators, etc.) is always a challenge, but generally a solvable engineering problem

TE Generator Applications

Using available technology

Today

- Space Nuclear Power
  - – Up to a few kW_{elec}
- Remote power
  - – Generally a few to several hundred Watts
  - – Can be up to a few KW
- Corrosion Protection

In Development

- Waste Heat
  - – Municipal Incinerators (Japan)
  - – Alternators in cars & trucks (US, Japan, Europe)
- Space Reactors (US)
  - – 100 kW_{elec} and up
- Micro-devices

TE Power Generation

Applications Remarks

- Presently used only for niche applications (ex: space, remote power) where reliability supercedes efficiency & cost issues
- Recent, basic R&D in the US has focused mostly on ZT for cooling
  - Space power funding halted for TE about 1992-3, until recently
  - Present terrestrial power markets too small to justify R&D costs
- Chicken-and-Egg problem – no R&D means performance and costs problems haven't been worked much for power generation
- Waste heat recovery has the potential to break the cycle
  - TEGs are nearly cost-competitive now in either vehicle or industrial waste heat recovery. Once the threshold is crossed, market forces can begin driving down manufacturing costs for generators
- US Space Power programs can be expected to push the technology base
  - In particular, new skutterudite materials are entering device testing phase
  - But space power is not particularly sensitive to device-cost

Space Power

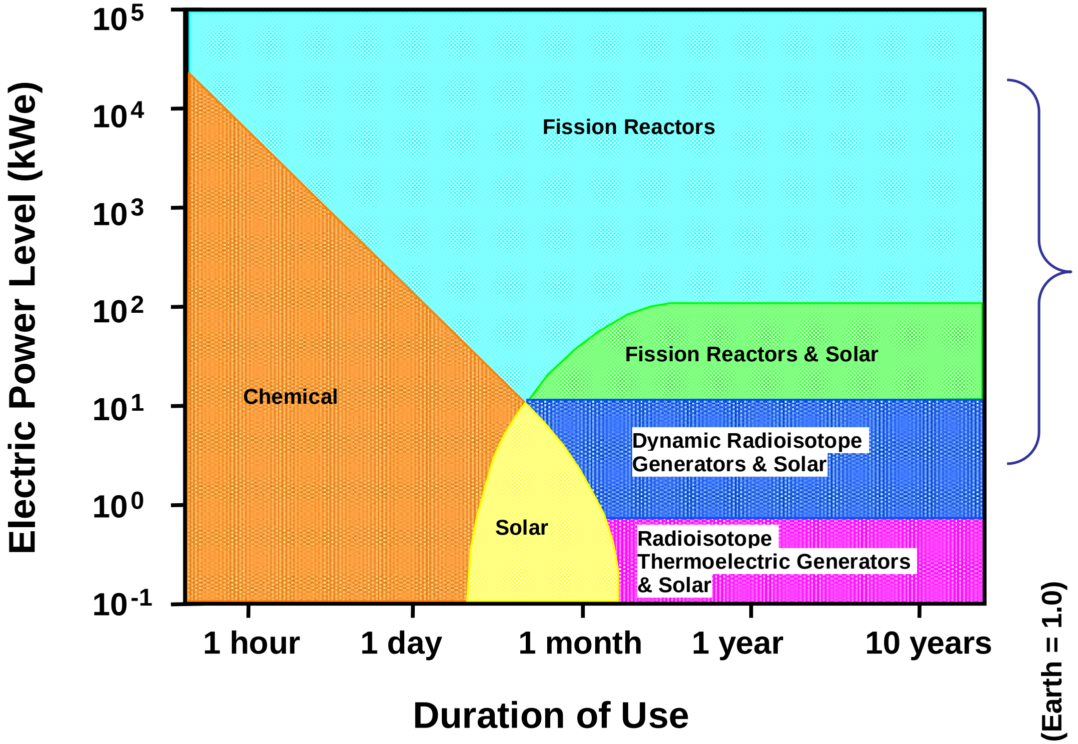
- Space power systems have demanding requirements for various missions
- Long life: 7 years and more
  - Batteries generally insufficient and/or heavy
- Too far from the sun for solar
- Radioisotopes provide heat
  - In future, nuclear reactors will be used for higher power levels
- To date, only thermoelectrics have proven reliable for heat-to-electric conversion
  - Several alternatives are under consideration, but none has yet been used in space

Space Power

- Drives technology
  - Space funds the heavy device-development costs
- For the first time in years space is making a major, long term investment in TE Technology
  - Billions of US$ expected to be invested over the next decade
- Improved efficiency = more power, less mass
  - Note that space power ***systems*** are optimized for maximum specific power (Watts per kg), not maximum efficiency
  - Heat rejection is by radiators, which are lighter when run hot
  - But ***TE efficiency*** is still the single most important spec.
- New TE materials & device designs need to be reduced to practice
  - Skutterudites, segmented thermocouples hope to double efficiency and produce more than 100 times the power
  - Eventually these technologies could become available for terrestrial applications, as has been the case in the past

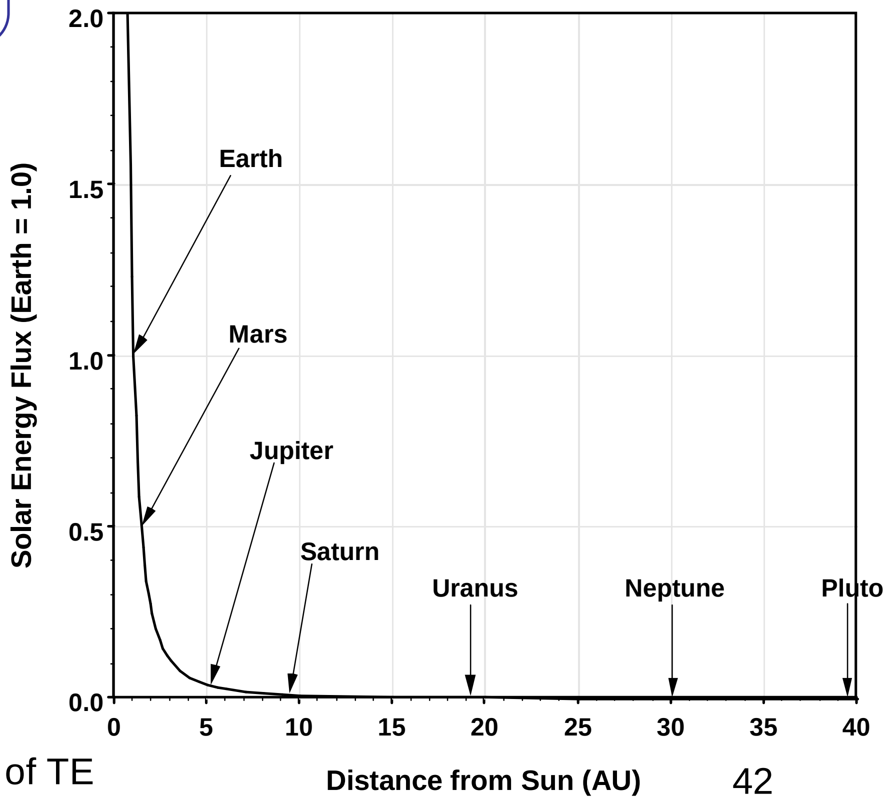
Why Use Nuclear Systems in Space?

(From Burdick, JPL, 2002)



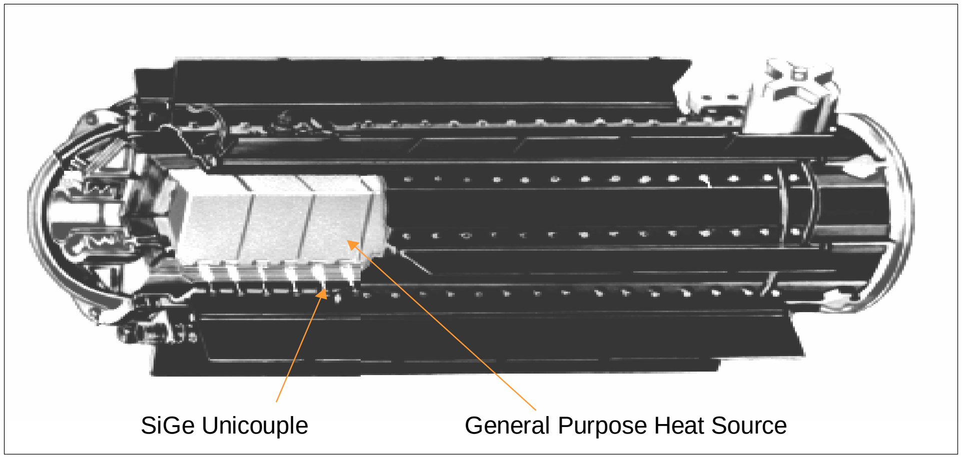
- **Long-duration operations (> 1 week)**
- **High sustained power (> 10-100 kWe)**

- **Distances where solar power density is too low (> ~1.5 AU)**
- **Locations where solar power not readily or continuously available (lunar polar craters, high Martian latitudes)**

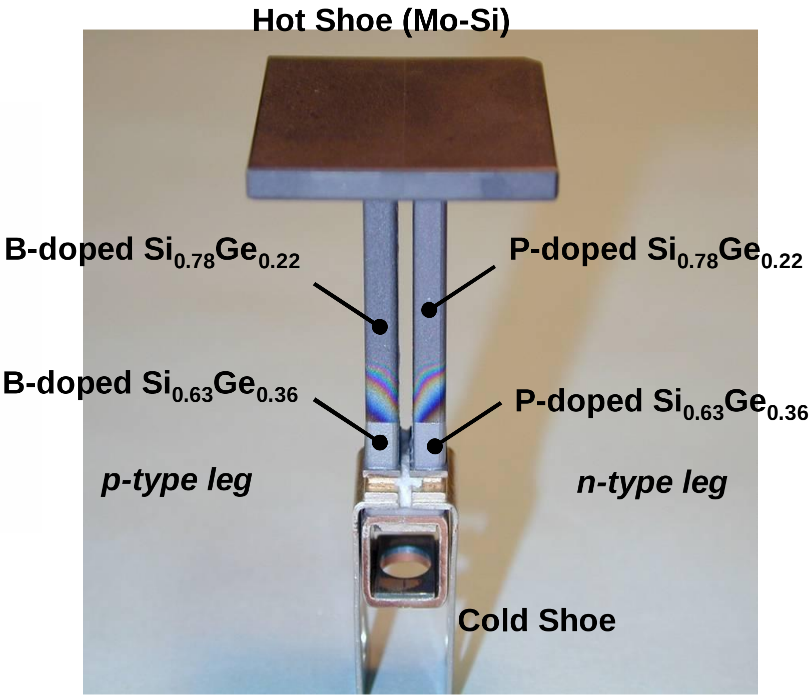


Galileo/Ulysses/Cassini-class RTG

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

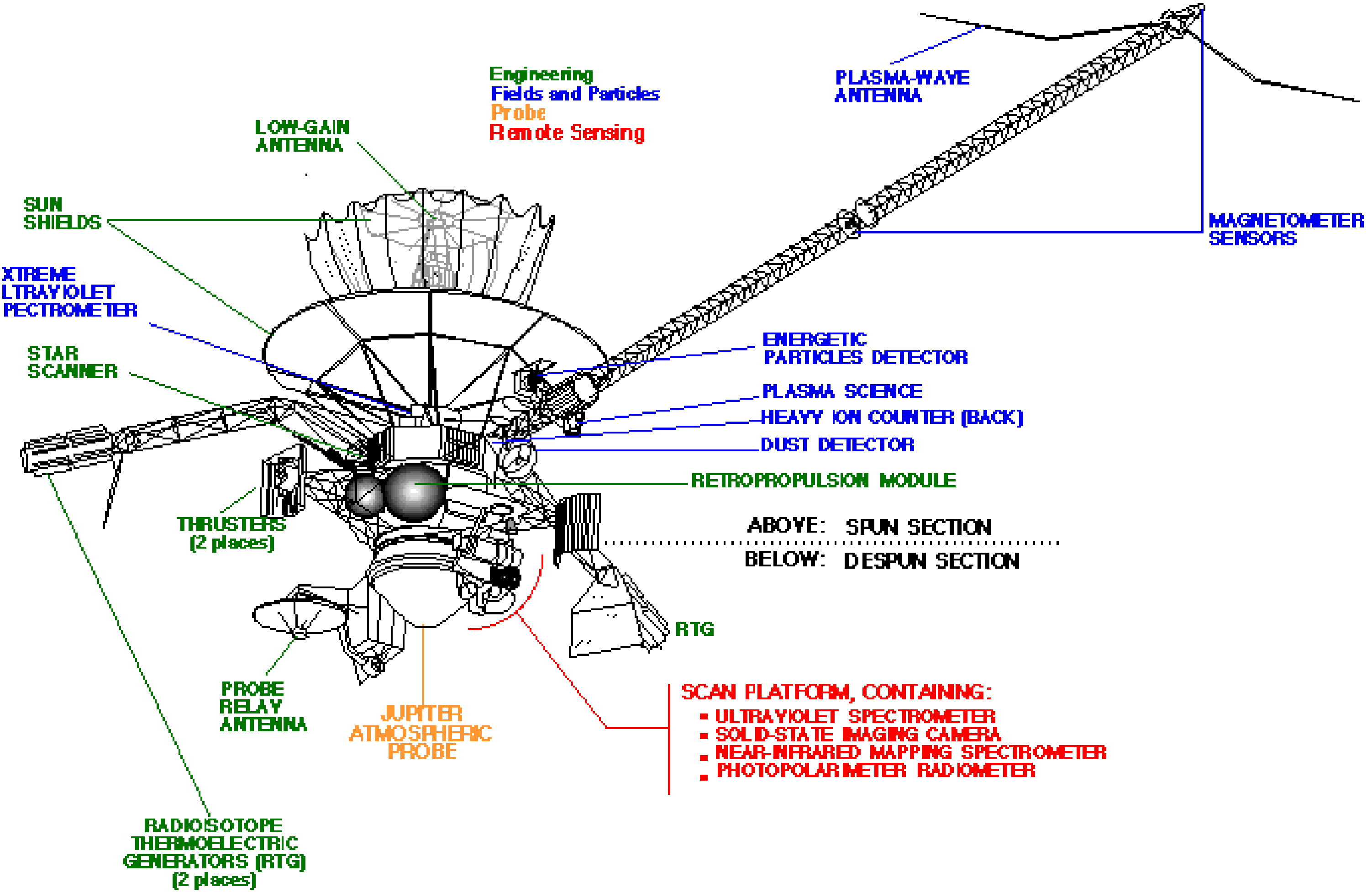


Radioisotope Thermoelectric Generator



SiGe unicouple

Galileo Spacecraft with 2 Radioisotope Thermoelectric Generators (RTGs)



NASA Missions That Have Used RTGs

(From Burdick, JPL, 2002)

Missions		Launch Year	Type of RTG	Power Level Per Unit (We)	Thermoelectrics Used
NIMBUS	B-1	1968 (Aborted)	--	--	--
	III	1969	SNAP 19 (1)	~28	PbTe
APOLLO	11	1969	Heater Units	--	--
	12	1969	SNAP 27 (1)	~73	PbTe
	13	1970 (Aborted)	--	--	--
	14	1971	SNAP 27 (1)	~73	PbTe
	15	1971	"	"	"
	16	1972	"	"	"
	17	1972	"	"	"
PIONEER	10	1972	SNAP 19 (4)	~40	PbTe/TAGS
	11	1973	"	"	"
VIKING	1	1975	SNAP 19 (2)	~35	PbTe/TAGS
	2	1975	"	"	"
VOYAGER	1	1977	MHW (3)	~150	SiGe
	2	1977	"	"	"
GALILEO		1989	GPHS-RTG (2)	~285	SiGe
ULYSSES		1990	GPHS-RTG (2)	~285	SiGe
CASSINI		1997	GPHS-RTG (3)	~285	SiGe

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)

Remote Power

- Principal applications for thermoelectric generators
  - Natural gas well and pipeline cathodic corrosion protection
  - Remote power for instrumentation
    - Power remote telemetry units, gas analyzers and metering equipment, routine operating functions and emergency shutdown
  - Automation and telecommunication systems
  - Offshore Operations
    - Primary power for unmanned platforms and backup power on manned platforms for critical communications and emergency shutdown systems
    - Ultimate test in the harsh and highly corrosive offshore environment
- Some Players (very few):
  - Global Thermoelectric, http://www.globalte.com
    - Estimated Annual TE Generator Sales: US$20M
  - Teledyne Energy Systems, http://www.teledyneenergysystems.com/news.asp
    - Also space power
  - Ferrotec USA, http://www.ferrotec.com/usa/
  - There are a few others, including some in Russia, Ukraine and/or China
    - Xiamen Taihuaxing Trading Co., (China). , http://www.sitechina.com/thermoelectric/
    - Institute of Thermoelectricity (Ukraine), http://ite.cv.ukrtel.net/

Remote Power

- **Navigational aids:**
  100 watt system
  operating since 1985
  - Yukon, Canada

- **Pipeline:**
  5000 watts for SCADA,
  communications and
  cathodic protection of
  gas pipeline
  - India

- From Global TE, http://www.globalte.com

Waste Heat

- Electrical power from otherwise wasted heat
  - Low operating expenses
  - Higher ZT means much lower capital investment
- Automotive/Vehicle Applications
  - Replace/supplement alternator
  - Increase fuel efficiency
  - Payback times have been estimated as short as 18 months
- Municipal Incinerators
  - Major, multiyear effort in Japan
  - Japan's conditions may be more acute than elsewhere
  - Energy costs & availability, landfill space, environmental factors all make energy a high priority in Japan
- Not yet in field service, but under aggressive development

- Selected Players
  - Hi-Z Technology, http://www.hi-z.com
  - Japan: Ministry of Economic, Trade and Industry (METI) & New Energy and Industrial Development Organization (NEDO)
    - Nissan, Honda, Sanyo, Mitsubishi, Komatsu, Tokyo Gas, Nagoya U., Osaka U.,
    - Many more R&D groups in Japan
  - Univ. Wales (funded largely by Japan)
  - Monash U., Australia

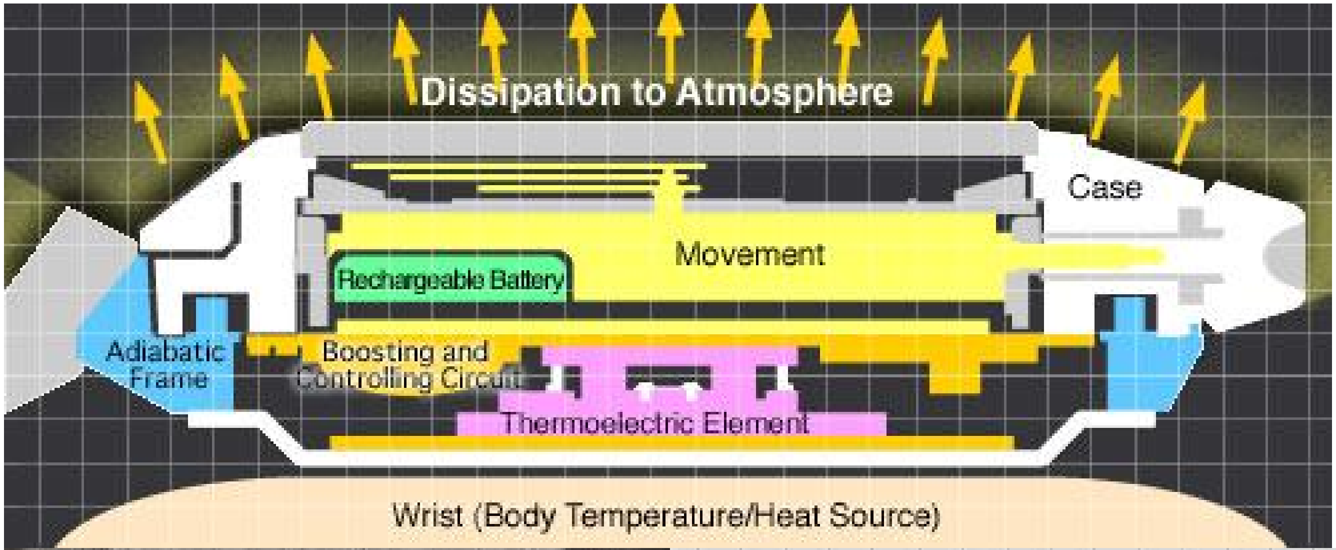
Microgenerators (& microcoolers)

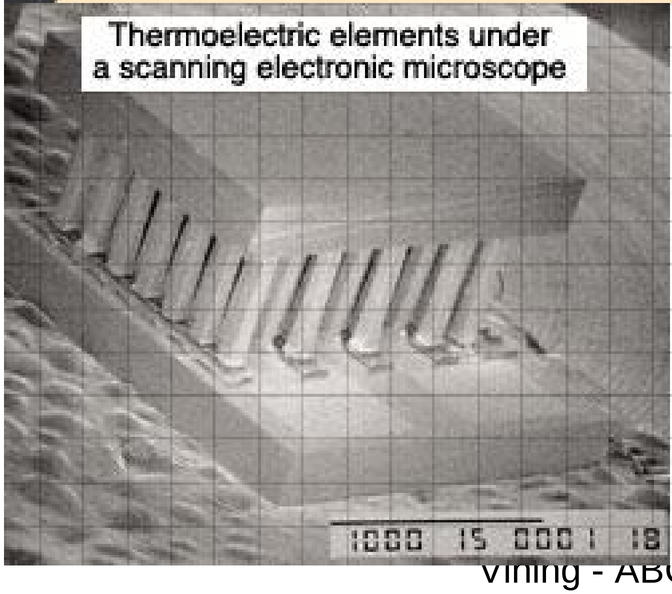
- Emerging capabilities promise small, inexpensive, mass produced power supplies
- Operate off very small $\Delta T = 1\text{-}100$ K
- Typically micro- to milli-Watt power generation
- Can provide small amounts ‘wireless’ power, taping local heat sources.
- Not contingent on higher ZT values, but would generate that much more electrical power

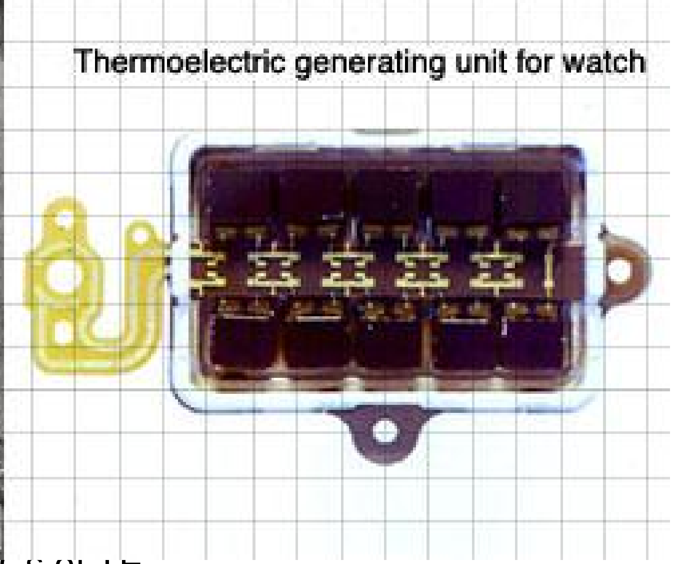
- Some Players
  - Seiko, http://www.sii.co.jp/info/eg/thermic_main.html
  - Micropelt, http://www.micropelt.com
  - D.T.S (Germany), http://www.dts-generator.com/
  - RTI (USA), http://www.rti.org/page.cfm?nav=450
  - JPL, http://www.its.caltech.edu/~jsnyder/thermoelectrics/

Seiko’s ‘THERMIC’ TE Wristwatch

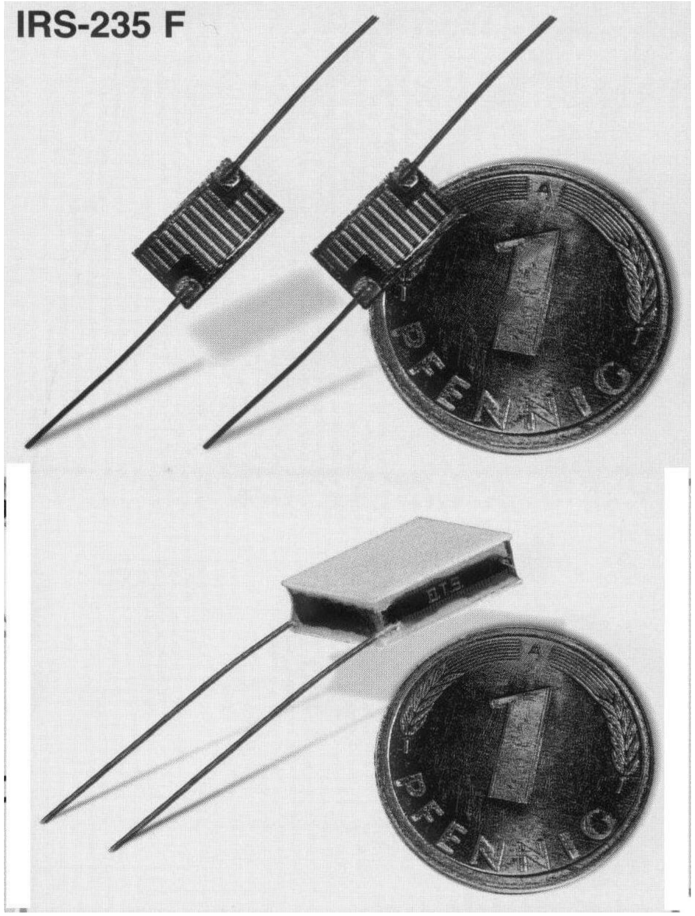
104 elements, 80 µm by 600 µm, 2 mm x 2 mm/module, 10 modules/watch




Thermoelectric elements under a scanning electronic microscope


Thermoelectric generating unit for watch

Thermopile Sensors & Microgenerators



D.T.S. (Germany) manufactures miniature thermopile-based infrared sensors (above) and power generation modules (below).

Devices are based on Bi_2Te_3 deposited on low thermal conductivity polyamide substrates.

Possible Future TE Generator Trends

- Microgenerators
  - Possible ‘early adaptor’ of emerging high ZT materials for high-value-added applications
  - Well suited to semiconductor industry-style manufacturing techniques, which are just beginning to be applied to thermoelectrics
- Higher ZT materials (skutterudites & Zn_4Sb_3) will gradually migrate from US Space Power to remote power & waste heat applications
- Japanese national waste heat project should have pilot plants under test in near future
  - Critical to driving down costs is developing high volume fabrication techniques

Basic Thermoelectric Generator Design Principles

Here we concentrate on the thermopile itself

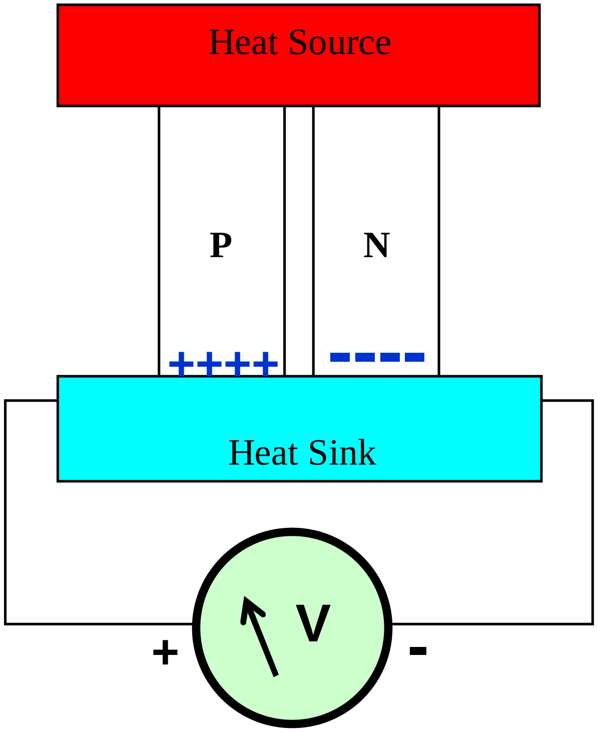
Physical Origin of ZT

- *Any* efficiency calculation will involve the same factors shown here
  - This approach only gets the units right!
- S, ρ and λ *always* occur together in the end
- ZT (not just Z) is the preferred quantity
  - this is the *only* unitless combination of S, ρ and λ.
  - ZT also occurs in thermodynamics

$$
\begin{aligned}
Efficiency &\equiv \frac{\text{Power Out}}{\text{Heat In}} \\
&\sim \frac{V^2 / R}{Q} \\
&\sim \frac{S^2 \left(\Delta T\right)^2 / R}{K \Delta T} \\
&\sim \frac{S^2}{RK} \Delta T \\
&\sim \frac{S^2 T}{r\, l} \frac{\Delta T}{T} \\
&\sim ZT \frac{\Delta T}{T}
\end{aligned}
$$

Open Circuit Voltage

- How to get the Sign right
  - Particles tend to ‘fall’ from hot to cold
  - In open circuit, a voltage builds up which is just enough to stop the charges from ‘falling’ to the cold end
    - Carriers of both signs are driven from the hot side to the cold side
  - “P-type” semiconductors have positive charges which can move
    - “+” charge accumulates on cold end
  - “N-type” semiconductors have negative charges which can move
    - “-” charge accumulates on cold end



Open Circuit Voltage

- Average Seebeck Coefficient

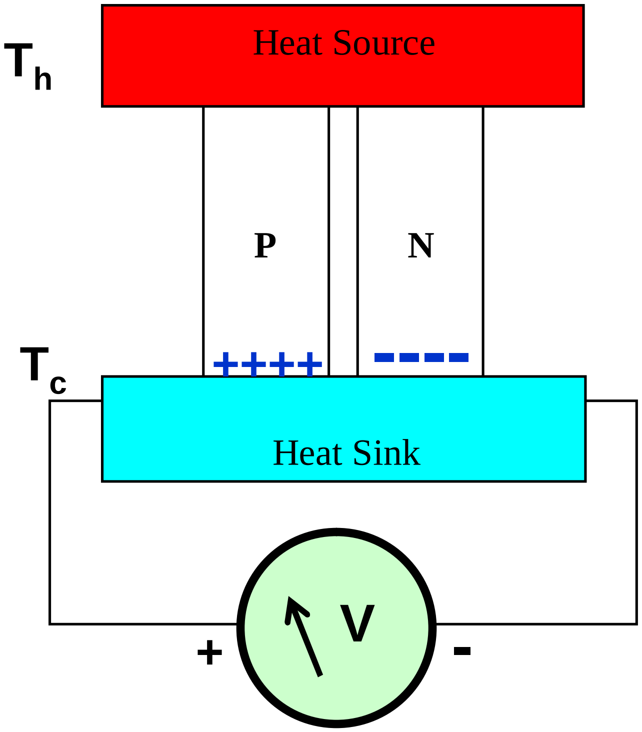
$$S_{average}(T_2 - T_1) \equiv \int_{x=0}^{x=L} S\nabla T dx \equiv \int_{T=T_1}^{T=T_2} S dT$$

or

$$S_{average} \equiv \frac{\int_{T=T_1}^{T=T_2} S dT}{(T_2 - T_1)}$$

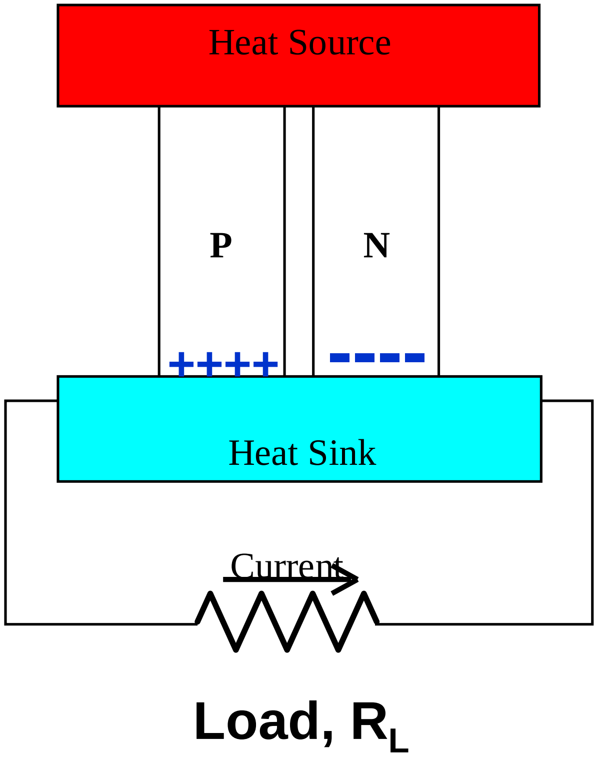
$$V_{\text{Open Circuit}} = (S_P - S_N)(T_h - T_c) \equiv (S_P - S_N)\Delta T$$

- Independent of Geometry
- Independent of Temperature Profile (only T_h & T_c)



Internal Resistance & Load

- Neglect Contacts & Leads
- Integrate over length of each leg
- Typically legs are the same length, but different cross-sectional areas
- Depends on geometry, temperature(s) AND temperature profile
- For greatest precision, do numerically



Load, R_L

$$R \equiv \frac{\int_{x=0}^{x=L} r\,dx}{A} \equiv r_{average}\,\frac{L}{A},$$

$$R_{Total} = R_P + R_N + R_L$$

$$= \left(\frac{r_P}{A_P} + \frac{r_N}{A_N}\right)L + R_L$$

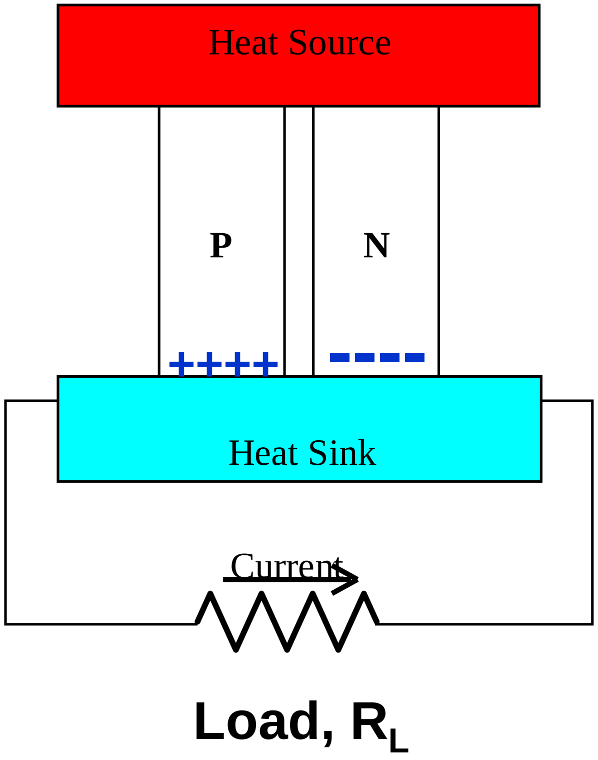
Voltage & Current to Load

- Similar analysis as for a battery
  - Internal resistance from N-Leg + P-Leg
  - EMF is thermal, instead of electrical

$$V = (S_P - S_N)\Delta T - I(R_P + R_N)$$
$$= IR_L$$

so

$$I = \frac{(S_P - S_N)\Delta T}{R_P + R_N + R_L}$$



Load, R_L

Power To Load

In terms of Load Resistance

$$I = \frac{V_{Open\ \ Circuit}}{R}$$

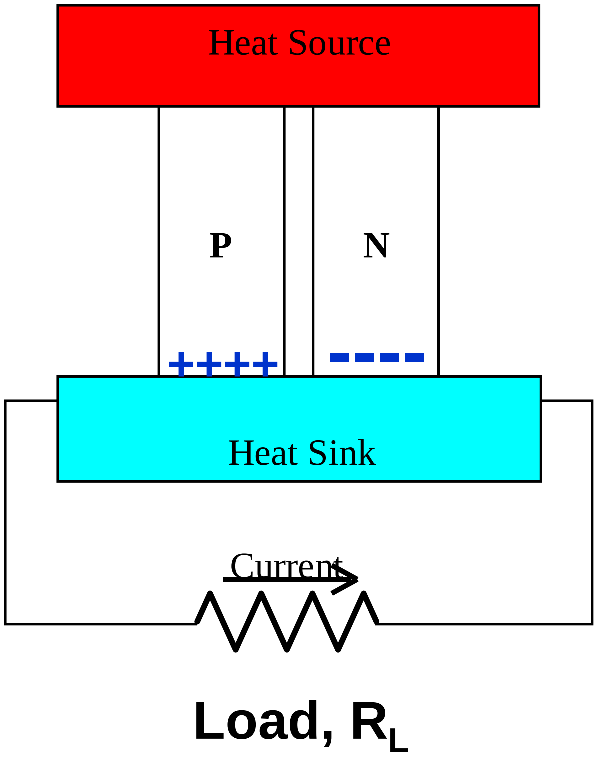
$$= \frac{(S_P - S_N)}{R_P + R_N + R_L} \Delta T,$$

$$P = I^2 R_L$$

$$= \frac{(S_P - S_N)^2}{(R_P + R_N)} \Delta T^2 \frac{x}{(1 + x)^2}$$

where

$$x = \frac{R_L}{R_P + R_N}$$



Load, R_L

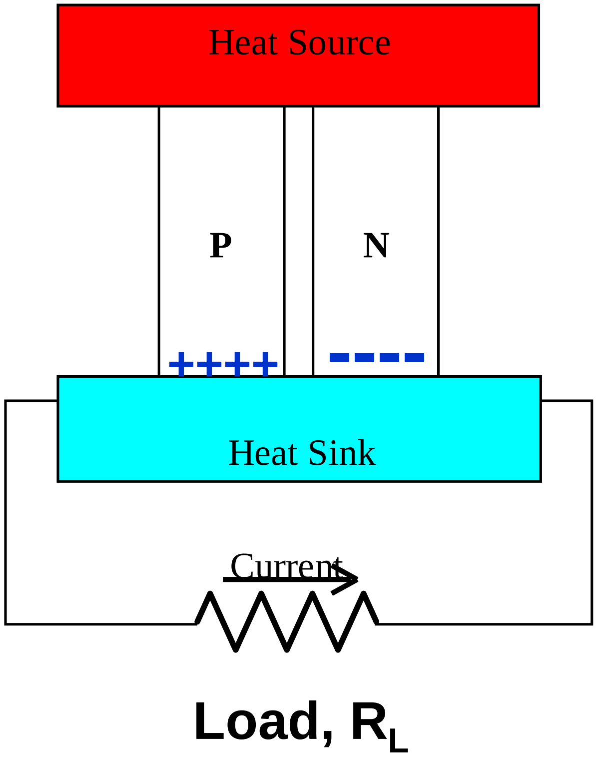
Power To Load

In Terms of Current

$$V = (S_P - S_N)\Delta T - I(R_P + R_N)$$

$$P = IV$$

$$= I((S_P - S_N)\Delta T - I(R_P + R_N))$$



Maximizing Things

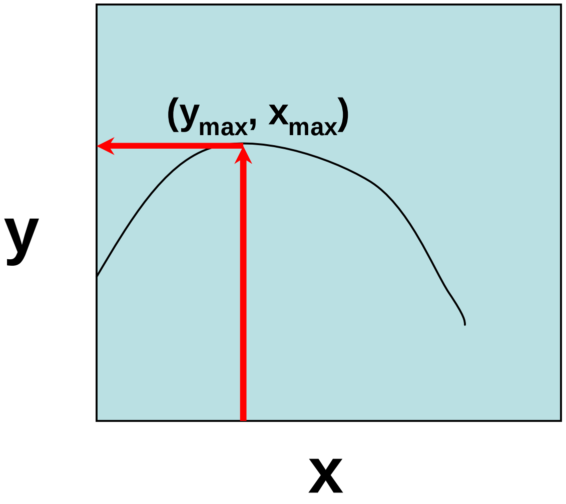
- Some Function ‘y’
- Depends on some variable ‘x’
- Find the value of x which maximizes y
  - Set dy/dx=0
  - Solve for x_{max}
  - Substitute x_{max} back in y to get y_{max}
  - Verify that it is a maximum (not a minimum or inflection point)
- Trivial example:

$$y = a + bx - cx^2$$

$$\frac{dy}{dx} = b - 2cx = 0 \quad \text{yields}$$

$$x_{\max} = \frac{b}{2c}$$

$$y_{\max} = a + \frac{1}{4}\frac{b^2}{c}$$



Maximum Power To Load

- Current Method:

$$P = I\left(\left(S_P - S_N\right)\Delta T - I\left(R_P + R_N\right)\right), \text{ maximize with respect to I:}$$

$$I_{\max} = \frac{1}{2}\frac{\left(S_P - S_N\right)\Delta T}{R_P + R_N}$$

$$P_{\max} = \frac{1}{4}\frac{\left(S_P - S_N\right)^2}{R_P + R_N}\Delta T^2$$

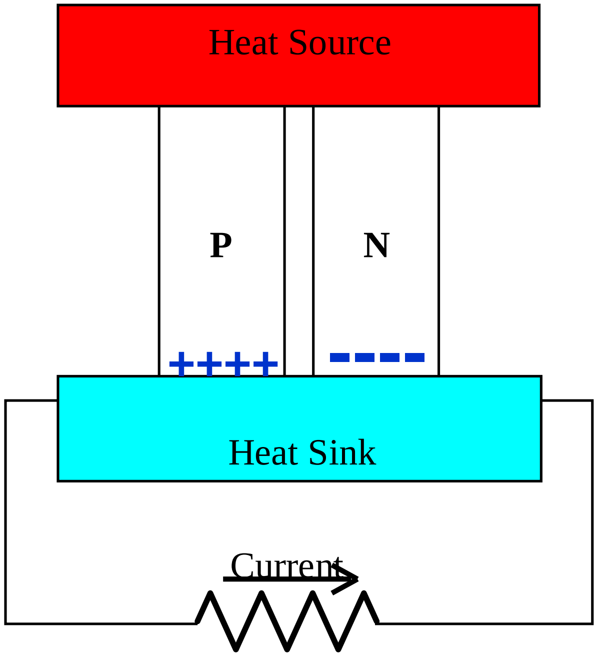
- Load Method:

$$P = \frac{\left(S_P - S_N\right)^2}{\left(R_P + R_N\right)}\Delta T^2 \frac{x}{(1+x)^2}, \text{ maximize with respect to load:}$$

where

$$x_{opt} = \frac{R_L}{R_P + R_N} = 1$$

$$P_{\max} = \frac{1}{4}\frac{\left(S_P - S_N\right)^2}{\left(R_P + R_N\right)}\Delta T^2$$



- Optimum Load For Power Out
  - x=1
  - Matched load gives most power out
- Optimum Load for Efficiency Comes Later
  - Sacrifice some power for efficiency, as usual!

Heat Flow & Heat Balance

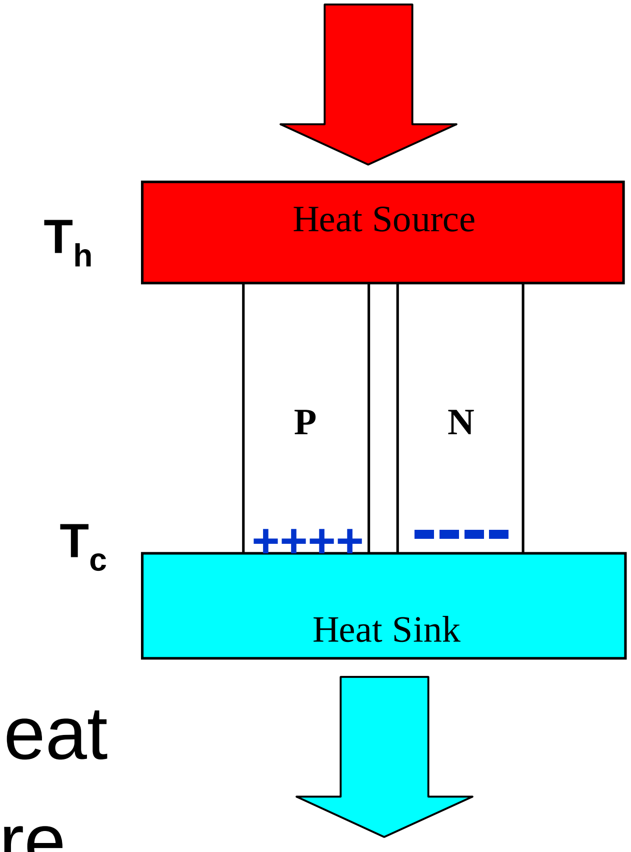
- There are two distinct contributions to Heat Flow in thermoelectrics
  - Conduction, proportional to temperature difference
  - Peltier Heat Flow, proportional to electrical current
- In steady state the flow in & out of a region must balance with the joule heating
  - An additional contribution, called the ‘Thomson Effect’ is
    1. Typically a second order effect
    2. Safely neglected in rough-order-of-magnitude estimates
    3. Handled ‘automatically’, with good heat balance technique

Thermal Conduction

- Heat conducts in parallel
- Open circuit only (no electrical current):

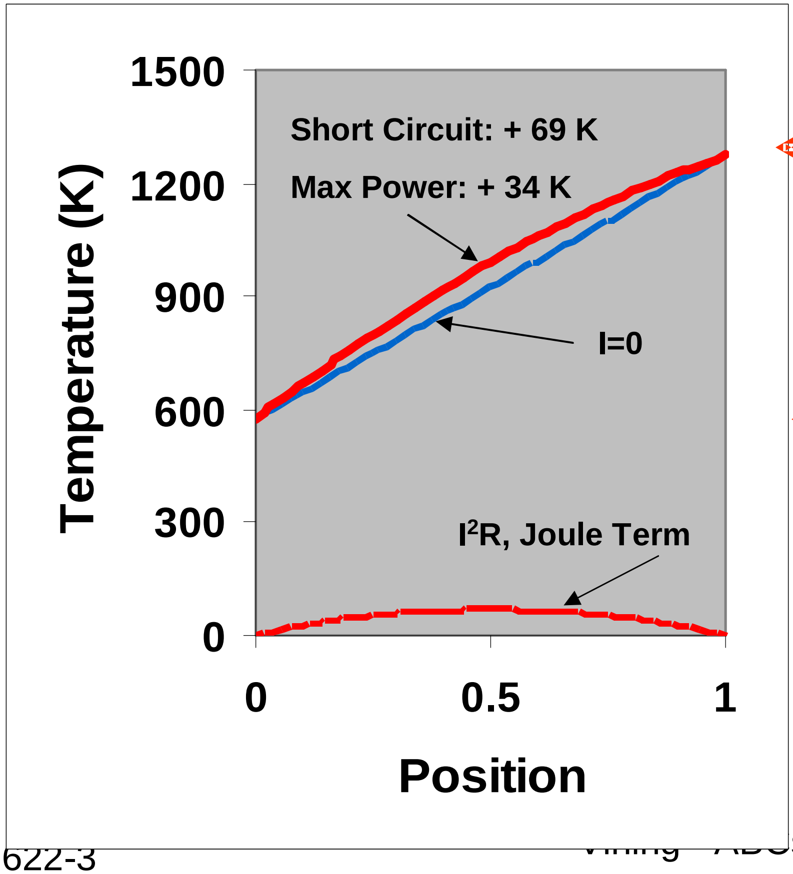
$$
\begin{aligned}
Q &= K\Delta T \\
&= (K_P + K_N)\Delta T \\
&= (l_P A_P + l_N A_N)\frac{\Delta T}{L}
\end{aligned}
$$

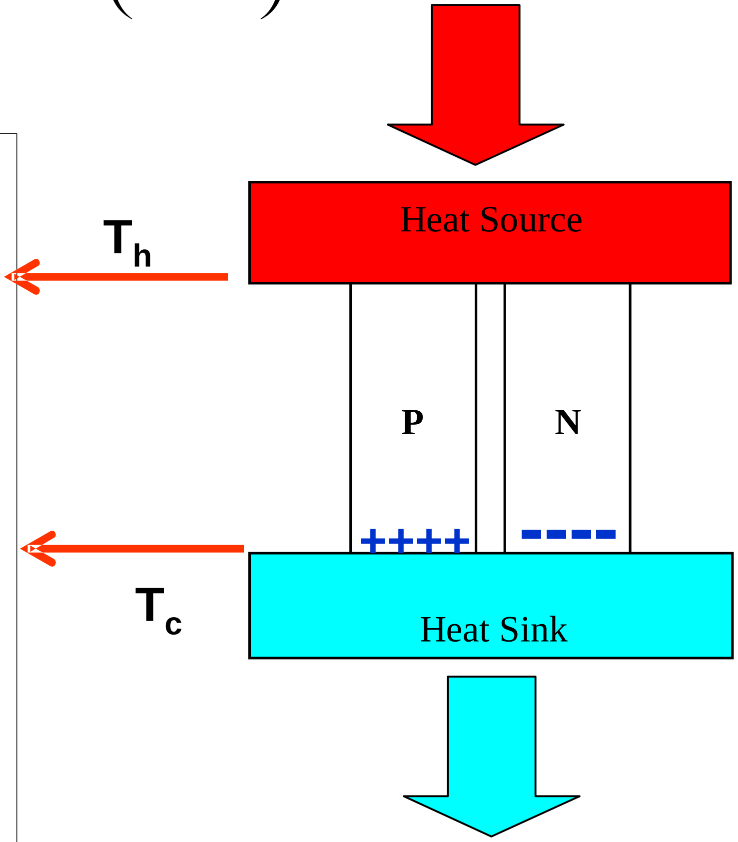
- Need to account for Joule Heat
- Need to estimate temperature profile



Joule Heat Modifies Temperature Profile

$$T(x) = T_c + \Delta T \frac{x}{L} + \frac{1}{2}\frac{I^2 R}{K}\frac{x}{L}\left(1 - \frac{x}{L}\right)$$

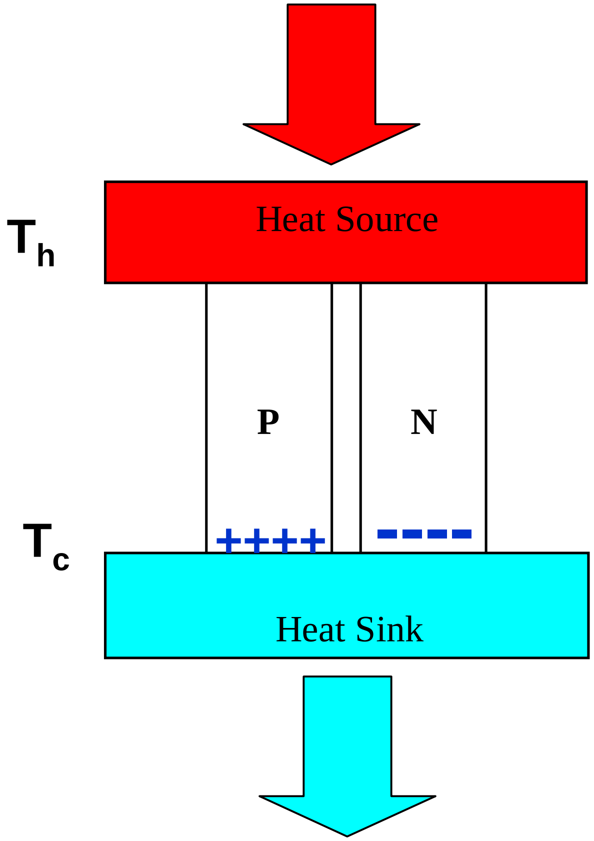




Thermal Conduction + Joule Heat

$$Q_h = (K_P + K_N)\Delta T - \frac{1}{2} I^2 (R_P + R_N)$$

$$Q_c = (K_P + K_N)\Delta T + \frac{1}{2} I^2 (R_P + R_N)$$



- One more term missing
  - Peltier ‘cooling’ term

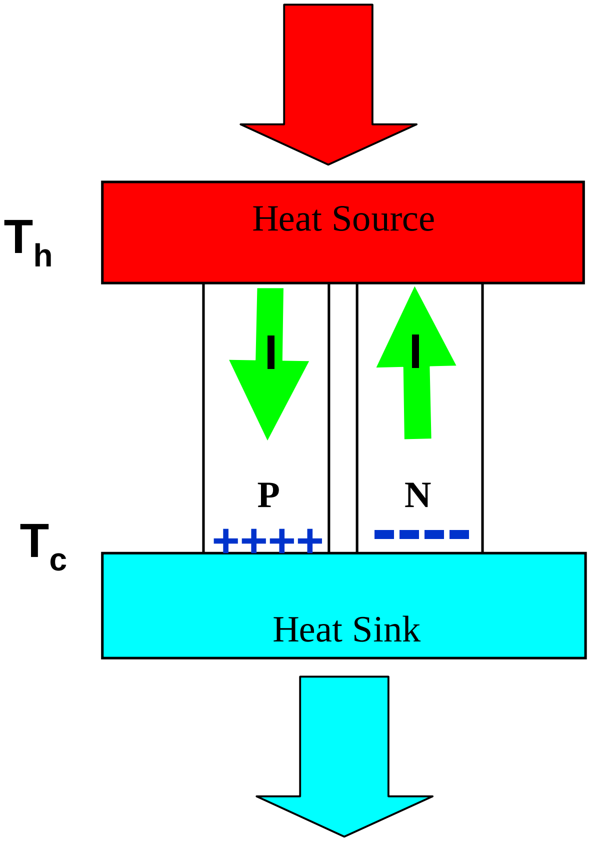
Peltier ‘Cooling’ Term

$$Q_{Peltier} = \Pi I$$

- A heat flow proportional to the electrical current
- Very much like a ‘convection’ term in fluid flow
  - A moving fluid carries heat with it
- Π is a material property
  - Different for N- & P-Type
- Depends on temperature (and position)

$$Q_h = \left(\Pi_{h,P} - \Pi_{h,N}\right)I + \left(K_P + K_N\right)\Delta T - \frac{1}{2}I^2\left(R_P + R_N\right)$$

$$Q_c = \left(\Pi_{c,P} - \Pi_{c,N}\right)I + \left(K_P + K_N\right)\Delta T + \frac{1}{2}I^2\left(R_P + R_N\right)$$



Simple Heat Balance

$$Q_h = I\Pi_h + K\Delta T - \frac{1}{2}I^2R$$

$$Q_c = I\Pi_c + K\Delta T + \frac{1}{2}I^2R$$

Heat Balance:

$$Q_h - Q_c = I(\Pi_h - \Pi_c) - I^2R$$

$$\text{Electrical Power Out} = IV$$

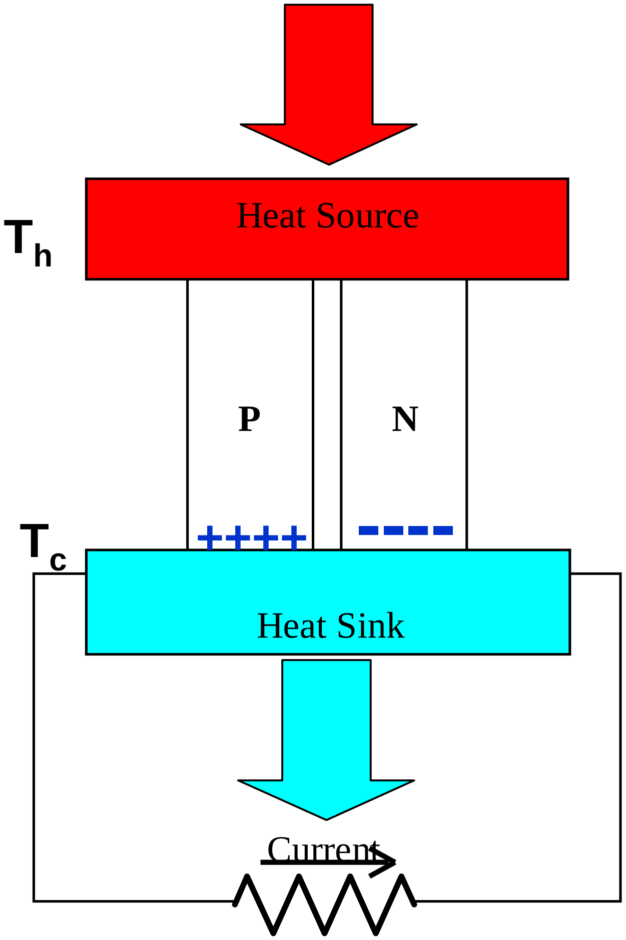
$$= I(S\Delta T - IR)$$

$$= IS\Delta T - I^2R$$

So, from Conservation of Energy:

$$Q_h - Q_c = IV \text{ and}$$

$$(\Pi_h - \Pi_c) = S\Delta T$$



Toward's Kelvin's First Relation

$$\left(\Pi_h - \Pi_c\right) = S\Delta T$$

- There are no significant approximations in arriving at this expression
  - Thermodynamically correct
  - Follows from conservation of energy
  - All quantities can be experimentally measured independently (although they rarely are!)
- 'S' is an average material property, over the entire temperature span
- Each 'Π' is a material property measured at a given temperature
- Is there a more general expression?

Kelvin’s ‘Second’ Relation

$$\Pi = ST$$

- Thomson (aka Lord Kelvin, 1855) first derived this expression based on thermodynamic arguments, similar to the previous slide
- But Kelvin’s derivation was not strictly correct (even though the result is correct)
- Boltzmann (1877) was able to place rigorous bounds on the relation between ‘Π’ and S, but could not prove the equality
  - If ‘Π’ were very different from *ST* SOME thermoelectric devices could exceed Carnot Efficiency!
- Not until Onsager (1931) was Kelvin’s Second Relation proved
  - used statistical mechanics arguments
  - Showed Kelvin’s Relations are special cases of very general ‘reciprocal’ relations, relating what I call ‘Cross’ phenomena such as interactions between heat and electricity
  - 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"

Simple Heat Balance

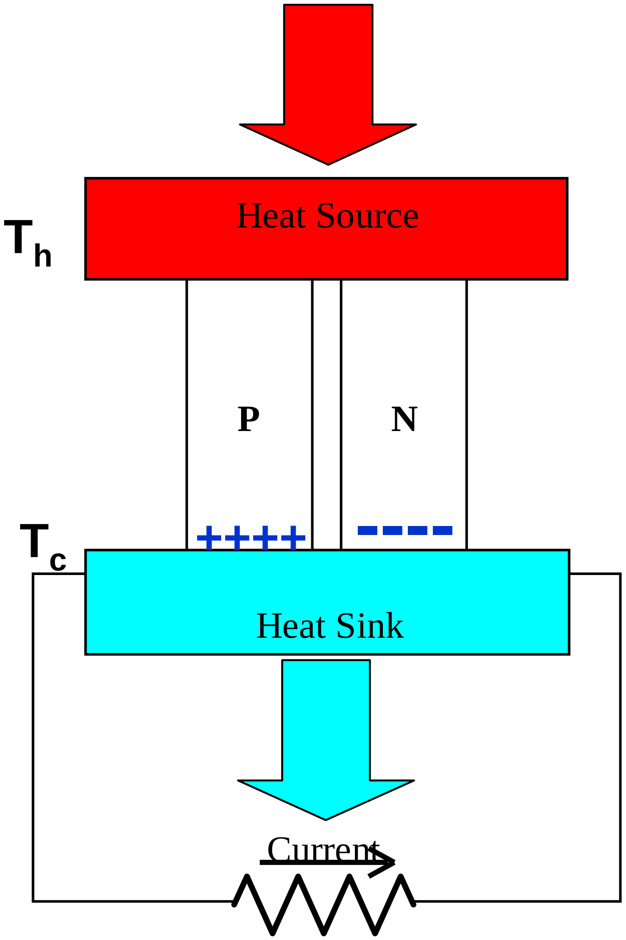
Using Kelvin's Second Relation: Π=ST

$$Q_h = I\Pi_h + K\Delta T - \frac{1}{2}I^2R$$

$$= IST_h + K\Delta T - \frac{1}{2}I^2R$$

$$Q_c = I\Pi_c + K\Delta T + \frac{1}{2}I^2R$$

$$= IST_c + K\Delta T + \frac{1}{2}I^2R$$



- It is important to use here the average value for '*S*', not the value at the hot side (S_h)
- Using the wrong value for '*S*' will violate energy conservation!
  - See the discussion of the Thomson effect

Thomson Effect
The Third Thermoelectric Effect

$$q(x) = iS(T)T(x) - l(T)\nabla T(x)$$

Conservation of Energy:

$$\nabla \cdot q(x) = E \cdot i$$

Yields the Heat Equation:

$$-\frac{\partial l(T)}{\partial T}\nabla T^{2} - l(T)\nabla^{2} T = i^{2} r(T) - \left[T(x)\frac{\partial S(T)}{\partial T}\right] i \cdot \nabla T$$

- Consider the heat flow as a function of position through the leg
- The last term [in brackets] is the Thomson Effect
- Heat is absorbed (rejected) from the material depending on
    1. Current in the same (opposite) direction as temperature gradient
    2. The temperature dependence of the Seebeck coefficient
- It is often entirely adequate to use ‘averaged’ properties in the heat balance, which implicitly accounts for the Thomson Effect
- If more precise design is needed, solve for the temperature profile numerically and use a heat balance at each ‘node’
- Do not mix approaches: you may double count (or zero) the Thomson Effect & violate energy conservation!

Alternative Heat Balance

Schock's Method to explicitly include 'Thomson Effect'

- Using Average Seebeck Value (Thomson Effect is implicit)

$$Q_h = IST_h + K\Delta T - \frac{1}{2}I^2R$$

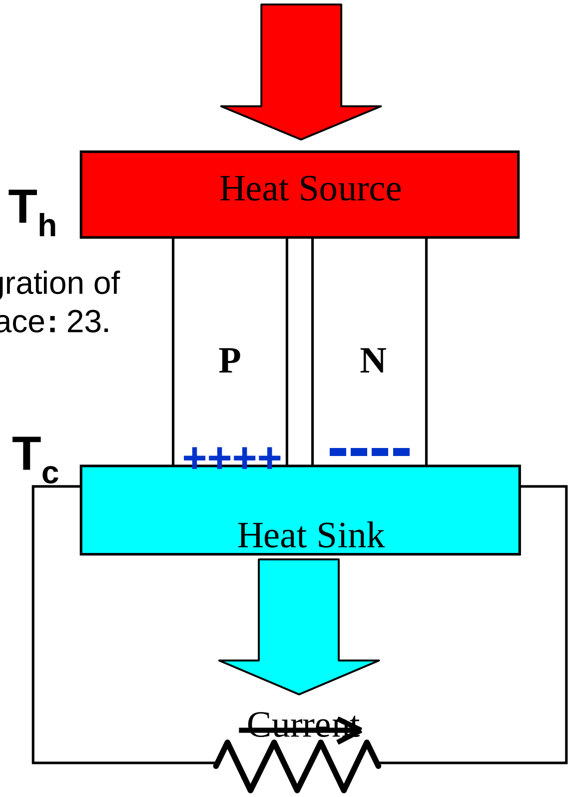
$$Q_c = IST_c + K\Delta T + \frac{1}{2}I^2R$$

- Include Thomson Effect explicitly
  - Schock, A., T. Or, et al. (1991). Design, Analysis, and Spacecraft Integration of RTGs for CRAF and Cassini Missions. Germantown, MD, Fairchild Space: 23.

$$Q_h = IS_hT_h + K\Delta T - \frac{1}{2}I^2R - \frac{1}{2}I\left(S_hT_h - S_cT_c - S\Delta T\right)$$

$$Q_c = IS_cT_c + K\Delta T + \frac{1}{2}I^2R + \frac{1}{2}I\left(S_hT_h - S_cT_c - S\Delta T\right)$$

- Amounts to about 2-3% error in the Peltier contribution to the heat



Efficiency (At Last!)

- 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

$$h \equiv Efficiency$$

$$\equiv \frac{\text{Electrical Power Out}}{\text{Heat In}}$$

$$= \frac{IV}{Q_h}$$

$$= \frac{I\left(S\Delta T - IR\right)}{IST_h + K\Delta T - \frac{1}{2} I^2 R}$$

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

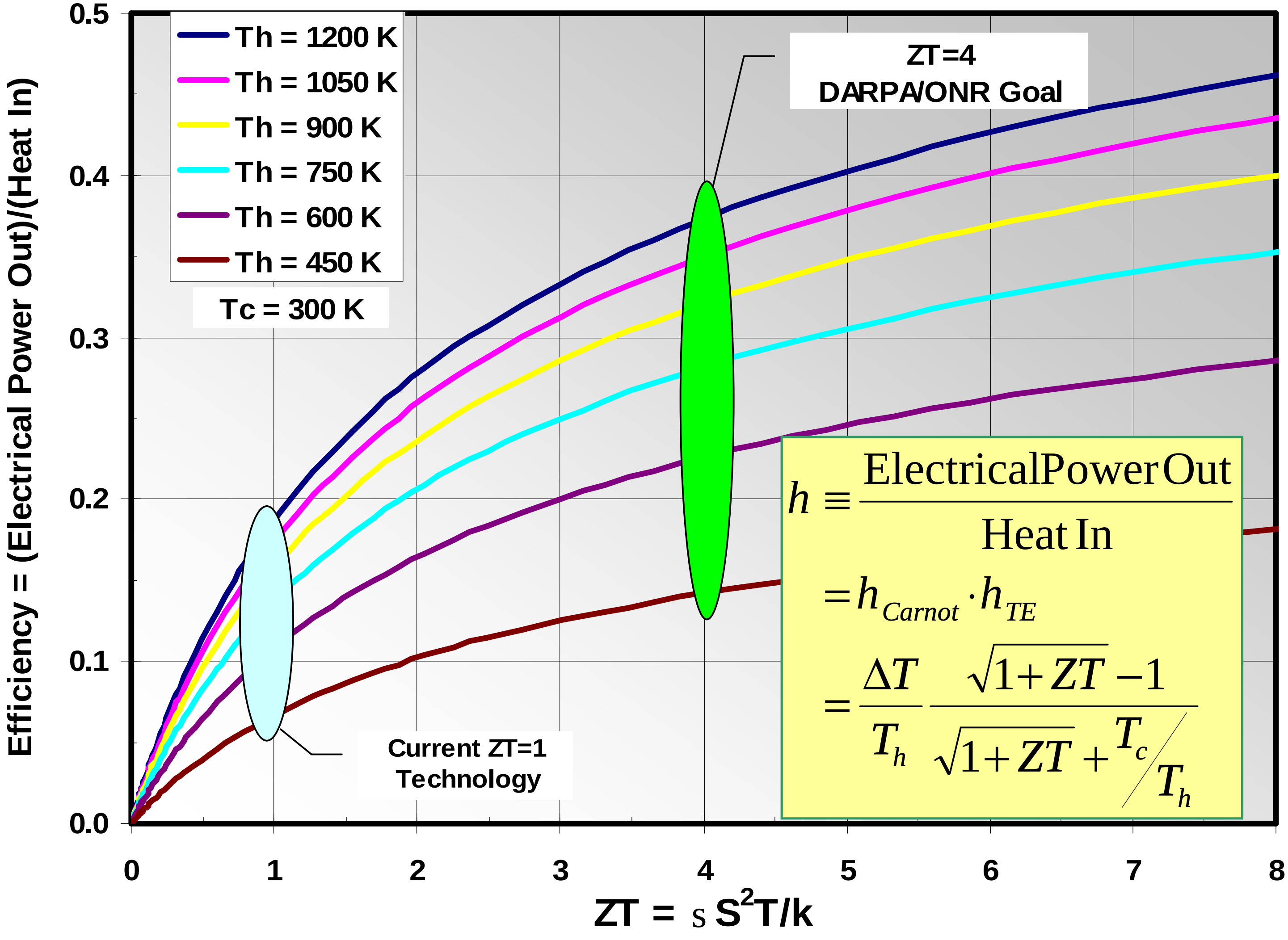
$$\left(\frac{R_L}{R}\right)_{opt} = \sqrt{1+ZT_{ave}}$$

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

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

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

TE Generator Efficiency



$$h \equiv \frac{\text{Electrical Power Out}}{\text{Heat In}}$$

$$= h_{Carnot} \cdot h_{TE}$$

$$= \frac{\Delta T}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+{T_c}/{T_h}}$$

ZT = s S^{2}T/k

Optimum Efficiency vs. Efficiency at Maximum Power

- Adjust current (i.e. by varying the load) to find the maximum power

$$h = \frac{I\left(S\Delta T - IR\right)}{IST_h + K\Delta T - \frac{1}{2} I^2 R}$$

$$I_{\max P} = \frac{1}{2}\frac{S\Delta T}{R}$$

$$\left(\frac{R_L}{R}\right)_{\max P} = 1$$

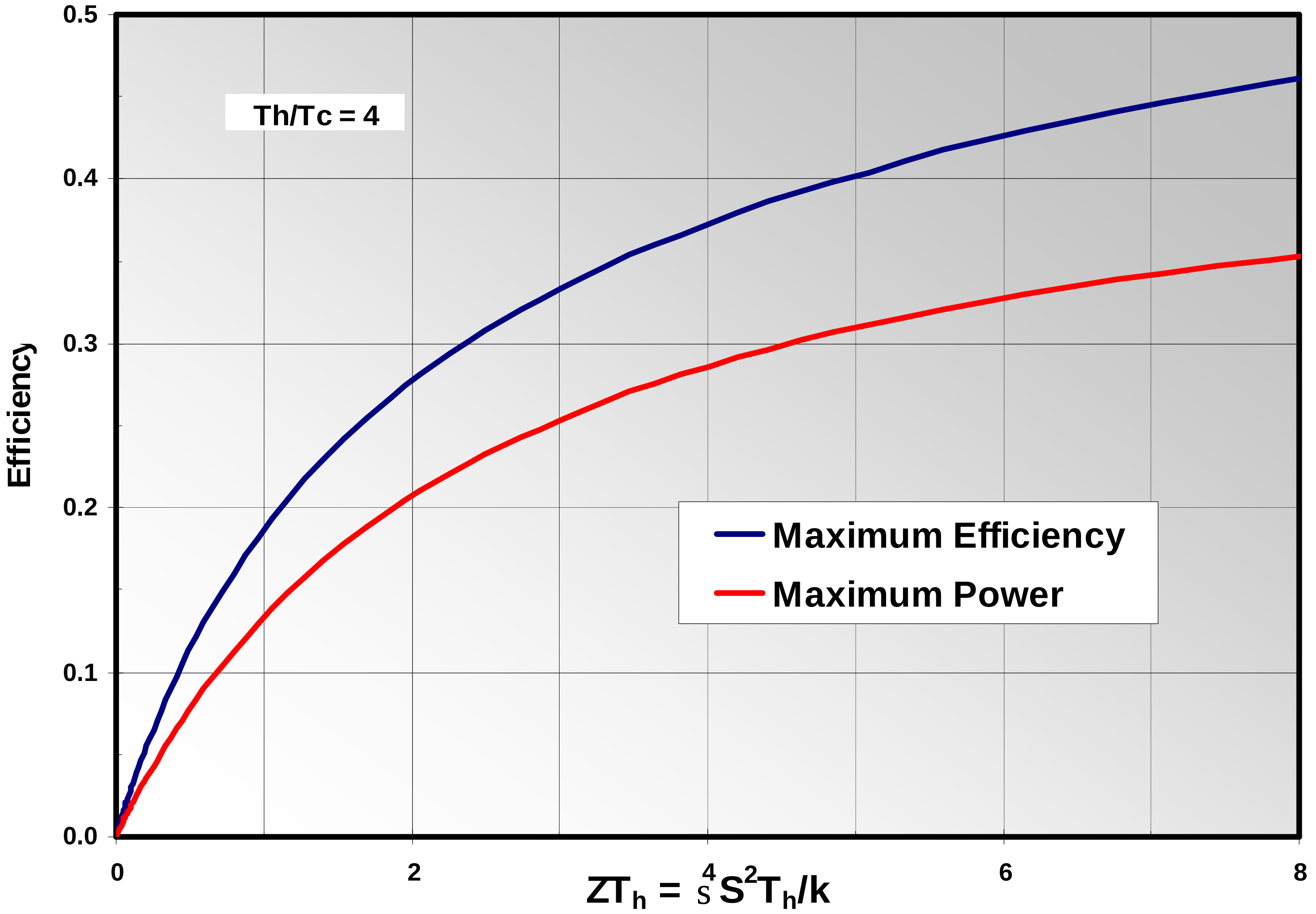
$$V_{\max P} = \frac{S\Delta T}{2}$$

$$h_{\max P} = \frac{\Delta T}{T_h}\frac{1}{2 - \frac{1}{2}\frac{\Delta T}{T_h} + \frac{4}{ZT_h}}$$

Compare to:

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

Maximum Efficiency vs. Maximum Power



Electrical/Thermal Impedance Matching

$$RK = (R_P + R_N)(K_P + K_N)$$

$$= \left(r_P \frac{L}{A_P} + r_N \frac{L}{A_N} \right)\left(l_P \frac{A_P}{L} + l_N \frac{A_N}{L} \right)$$

$$= r_P l_P + r_P l_N \frac{A_N}{A_P} + r_N l_P \frac{A_P}{A_N} + r_N l_N$$

minimize by choosing the optimum ratio of areas

$$\left(\frac{A_N}{A_P} \right)_{opt} = \sqrt{\frac{r_N l_P}{r_P l_N}}$$

$$(RK)_{opt} = \left(\sqrt{r_P l_P} + \sqrt{r_N l_N} \right)^2$$

$$Z_{opt} T_{ave} = \frac{(S_P - S_N)^2}{\left(\sqrt{r_P l_P} + \sqrt{r_N l_N} \right)^2} \frac{T_h + T_c}{2}$$

- We want largest ZT value possible
- Heat flows parallel through legs
- Electricity flows in series
- ***So the optimum ZT and efficiency do not depend on geometry at all!***

Rough Order of Magnitude Design

- Assume we want to design an RTG using tried-&-true SiGe
  - This is a little bit circular of course, since we know the answers!
- Targets:
  - About 300 W_e
  - 30 Volt system output
  - T_h ~ 1275 K, typical margin for heat source
  - T_c ~ 575 K
    - ultimately a system tradeoff for mass

Voyager-Cassini Era $Si_{0.78}Ge_{0.22}$

Averages between 300-1000 °C

As prepared data from GE

	Units	P-Type	N-Type	Combined
Electrical Resistivity	milliΩ-cm	2.270	2.057	8.653
Seebeck Coefficient	μV/K	214.9	-242.5	457.4
Thermal Conductivity	W/cm-K	0.0452	0.0409	0.0431
$ZT_{average}$		0.423	0.659	0.518

$$\text{Optimum ratio of N-leg area to P-leg area}: \left(\frac{A_N}{A_P}\right)_{optimum} = 1.0001$$

How much heat do we need?

- First, estimate the efficiency:

$$
\begin{aligned}
Z_{opt}T_{ave} &= \frac{\left(S_P - S_N\right)^2}{\left(\sqrt{r_P\, l_P} + \sqrt{r_N\, l_N}\right)^2}\,\frac{T_h + T_c}{2} \\
&= \frac{\left(242.5-(-214.9)\right)^2\left(10^{-6}\,\frac{V}{K}\right)^2}{\left(\sqrt{2.27\cdot 0.0452}+\sqrt{2.06\cdot 0.0409}\right)^2\left(10^{-3}\,\Omega - cm\,\frac{W}{cm-K}\right)}\,\frac{1273K + 573K}{2} \\
&= 0.518
\end{aligned}
$$

$$
\begin{aligned}
h_{opt} &= \frac{\Delta T}{T_h}\,\frac{\sqrt{1+ZT_{ave}}-1}{\sqrt{1+ZT_{ave}}+\frac{T_c}{T_h}} \\
&= \frac{1273-573}{1273}\,\frac{\sqrt{1+0.518}-1}{\sqrt{1+0.518}+\frac{573}{1273}} \\
&= (0.550)\frac{1.232-1}{1.232+0.450} \\
&= 0.0759 \ \text{ or } \ 7.59\%
\end{aligned}
$$

How much heat do we need?

- To get 300 W_e we need:
- Each GPHS thermal power source module provides 245 Watts:
- 16 GPHS @ 7.59%

$$Q_h = \frac{P}{h} = \frac{300\,\mathrm{W}}{0.0759} = 3954\,\mathrm{W}$$

$$\#GPHS = \frac{3954}{245} = 16.1 \sim 16$$

$$P = h \cdot Q_h = h \cdot 16 \cdot 245$$

$$= 0.0759 \cdot 3920 = 297\ \mathrm{W_e}$$

What are the voltages?

- Target operating voltage: 30 V
- Optimum Load (compared to couple internal resistance):
- To get 30 V need N in series:
- System Voltage:

$$\left(\frac{R_L}{R}\right)_{opt} = \sqrt{1+ZT_{ave}} = 1.232$$

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

$$= V_{open\,circuit} \frac{\sqrt{1+ZT_{ave}}}{1+\sqrt{1+ZT_{ave}}}$$

$$= (0.320\ \mathrm{V})\frac{1.232}{1+1.232} = 0.177\ \mathrm{V}$$

$$N = \frac{30\,\mathrm{V}}{0.177\,\mathrm{V/couple}} = 169.8 \sim 170$$

$$V_{system} = N \cdot V_{opt} = 170 \cdot 0.177 = 30.04\ \mathrm{V}$$

What are the currents?

- Total Current:
- You could have one or more parallel ‘branches’ (B) of thermocouple strings
- Lets assume B=4 branches, or 4x170=680 total couples:

$$I_{system} = \frac{P}{V_{system}} = \frac{297.4\,\mathrm{W}}{30.04\,\mathrm{V}} = 9.90\,\mathrm{A}$$

$$I_{couple} = \frac{I_{system}}{B} = \frac{9.90}{4} = 2.47\,\mathrm{A}$$

$$P_{couple} = I_{couple} V_{couple} = 2.47 \cdot 0.320 = 0.437\,\mathrm{W}$$

Notice that we know a lot about the couple, but as yet nothing about its geometry!

Couple Resistance and A/L Ratio

- Couple Resistance:
- Couple Resistivity:

$$V_{couple} = S\Delta T - IR$$

$$R = \frac{S\Delta T - V_{couple}}{I} = \frac{0.320 - 0.177}{2.47} = 0.0580\,\Omega$$

$$R = R_P + R_N$$

$$= \frac{L}{A_P} r_P + \frac{L}{A_N} r_N$$

$$= \frac{L}{A}\left(\left(1 + \frac{A_N}{A_P}\right) r_P + \left(1 + \frac{A_P}{A_N}\right) r_N\right)$$

$$= \frac{L}{A}\left((1 + 1.0001)2.270 + \left(1 + \frac{1}{1.0001}\right)2.057\right)$$

$$= \frac{L}{A} \cdot 8.653\,\mathrm{milli}\Omega - cm$$

- A/L Ratio:

$$\frac{A}{L} = \frac{\mathrm{Couple\,Resistivity}}{\mathrm{Couple\,Resistance}} = \frac{8.653\,\mathrm{milli}\Omega\text{-}\mathrm{cm}}{0.0580\,\Omega} = 0.149\,\mathrm{cm}$$

Couple Resistance and A/L Ratio

Alternate Method

- Directly from the inputs:
  - Temperatures
  - Material Properties
  - System Power, Voltage
  - Number of parallel branches
  - Just a bit of algebra yields:

$$\frac{A}{L} = \frac{1}{B}\frac{P}{V_{system}}\frac{1+\sqrt{1+ZT_{ave}}}{S\Delta T}\left(\left(1+\frac{A_N}{A_P}\right)r_P + \left(1+\frac{A_P}{A_N}\right)r_N\right)$$

$$= \frac{1}{4}\frac{300}{30}\frac{1+1.232}{457.4x10^{-6}\cdot 700}\left((1+1.0001)2.270+\left(1+\frac{1}{1.0001}\right)2.057\right)$$

$$= 0.151\text{cm}$$

Heat Through a Couple

- Joule heating is 0.178/5.76=3% of the heat in
- Only 4.50/5.76=78% of the heat is carried away from the hot junction by thermal conduction
- Thermal design will not even be close if Peltier effect were neglected
- You can't turn off radioisotopes, so if the RTG goes open circuit, everything heats up
  - Peltier cooling of hot junction would stop

$$Q_{h,couple} = \frac{Q_h}{\#\,\text{couples}} = \frac{3920}{680} = 5.76\,\text{W}$$

$$Q_h = IST_h + K\Delta T - \frac{1}{2} I^2 R$$

$$K = \frac{Q_h - IST_h + \frac{1}{2} I^2 R}{\Delta T}$$

$$= \frac{5.76 - 2.48 \bullet 0.0004574 \bullet 1273 + 0.5 \cdot 2.48^2 \cdot 0.0580}{1273 - 573}$$

$$= \frac{5.76 - 1.44 + 0.178}{1273 - 573} = \frac{4.50}{700} = 0.0643\,\tfrac{W}{K}$$

A/L Ratio from the Heat

- Estimate the combined thermal conductivity of the couple:

$$K = K_P + K_N$$

$$= \frac{A}{L}\left(\frac{l_P}{\left(1+\frac{A_N}{A_P}\right)} + \frac{l_N}{\left(1+\frac{A_P}{A_N}\right)}\right)$$

$$= \frac{A}{L}\left(\frac{0.0452}{(1+0.9999)} + \frac{0.0409}{\left(1+\frac{1}{0.9999}\right)}\right)$$

$$= \frac{A}{L}\cdot\left(0.0431\,\tfrac{\text{W}}{\text{cm-K}}\right)$$

- In previous slide we estimated thermal conductance of the couple, so divide to get A/L:

$$\frac{A}{L} = \frac{K}{\text{combined thermal conductivity}}$$

$$= \frac{0.00643\,\frac{\text{W}}{\text{K}}}{0.0431\,\frac{\text{W}}{\text{cm-K}}} = 0.149$$

- Whew! Same answer.

How did we do so far?

	units	CRAF/Cassini Schock, 1991	ROM
Q_h	Watts	4410	3920
T_h	K	1280-1315	1273
T_c	K	549-575	573
Material Efficiency	%	7.90	7.59
Eff. /w contact resistances	%	7.55	N/A
Eff. /w heat losses	%	7.01	N/A
Power Out	Watts	309	297
System Voltage	V	30	30.04
Voltage/Couple	V	0.197-0.215	0.177
# in series		144	170
# Parallel Strings		4	4
# Couples		576	680
System Current	A	10.3	9.90
Couple Current	A	2.57-2.58	2.47
Couple Resistance	ohms	N/R	0.0580
A/L	cm	N/R	0.149

Estimate Temperature Change due to Open Circuit

- Radiator heats up some, because all the heat from the heat source must go through the radiator
  - Cold side heats up ~ 12 K
- Hot side heats up more, due to loss of Peltier Cooling effect
  - Hot side heats up ~ 200 K

$$T_{c,\,final}^4 = T_{c,\,initial}^4 \frac{\mathrm{Q_{c,\,final}}}{\mathrm{Q_{c,\,initial}}} = 573^4 \frac{3290}{3920-297}$$

$$T_{c,\,final} = 585\,\mathrm{K}$$

$$Q_h = IST_h + K\Delta T - \frac{1}{2} I^2 R$$

$$K = \frac{Q_h - IST_h + \frac{1}{2} I^2 R}{\Delta T}$$

$$= \frac{5.76 - 1.44 + 0.178}{1273-573} = \frac{4.50}{700} = 0.0643 \tfrac{W}{K}$$

$$\text{with I} = 0\text{, what is } \Delta\text{T?}$$

$$\Delta T = \frac{Q_h}{K} = \frac{5.76}{0.0643} = 897\,\mathrm{K}$$

radiator will heat up

$$T_{h,\,final} = T_{c,\,final} + \Delta T = 585\,\mathrm{K} + 897\,\mathrm{K} = 1481\,\mathrm{K!}$$

$$T_{h,\,final} - T_{h,\,initial} = 1481 - 1273 = 208\,\mathrm{K}$$

Important Losses

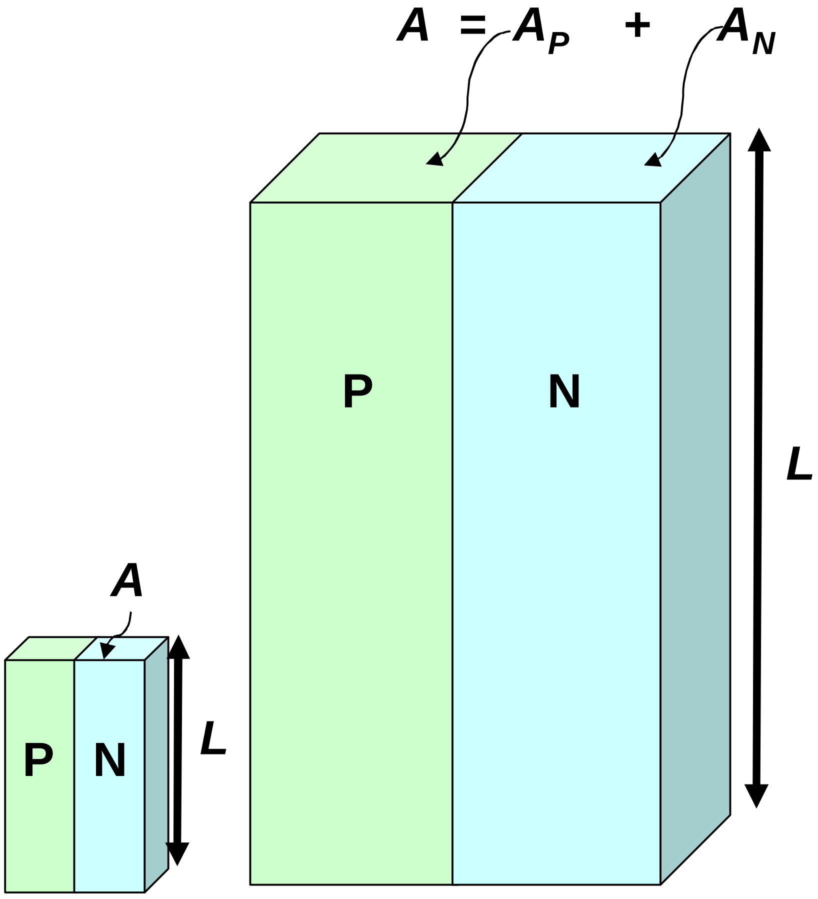
won’t cover these in any great detail

- Without Losses: η~7.90 % (Schock, 1991)
- Electrical Losses
  - Electrical contact resistances
  - Electrode & interconnect resistances
  - Reduces efficiency to η~7.55 %
- Thermal losses
  - Temperature drop between heat source and upper end of thermocouple
    - Radiation, compliant pad, heat pipe, etc.
  - Thermal resistance of Electrode
  - Heat leak through thermal insulation
  - Heat leak through structural supports
- Reduces efficiency to η~7.01 %
  - Roughly equivalent to reducing ZT by 14%

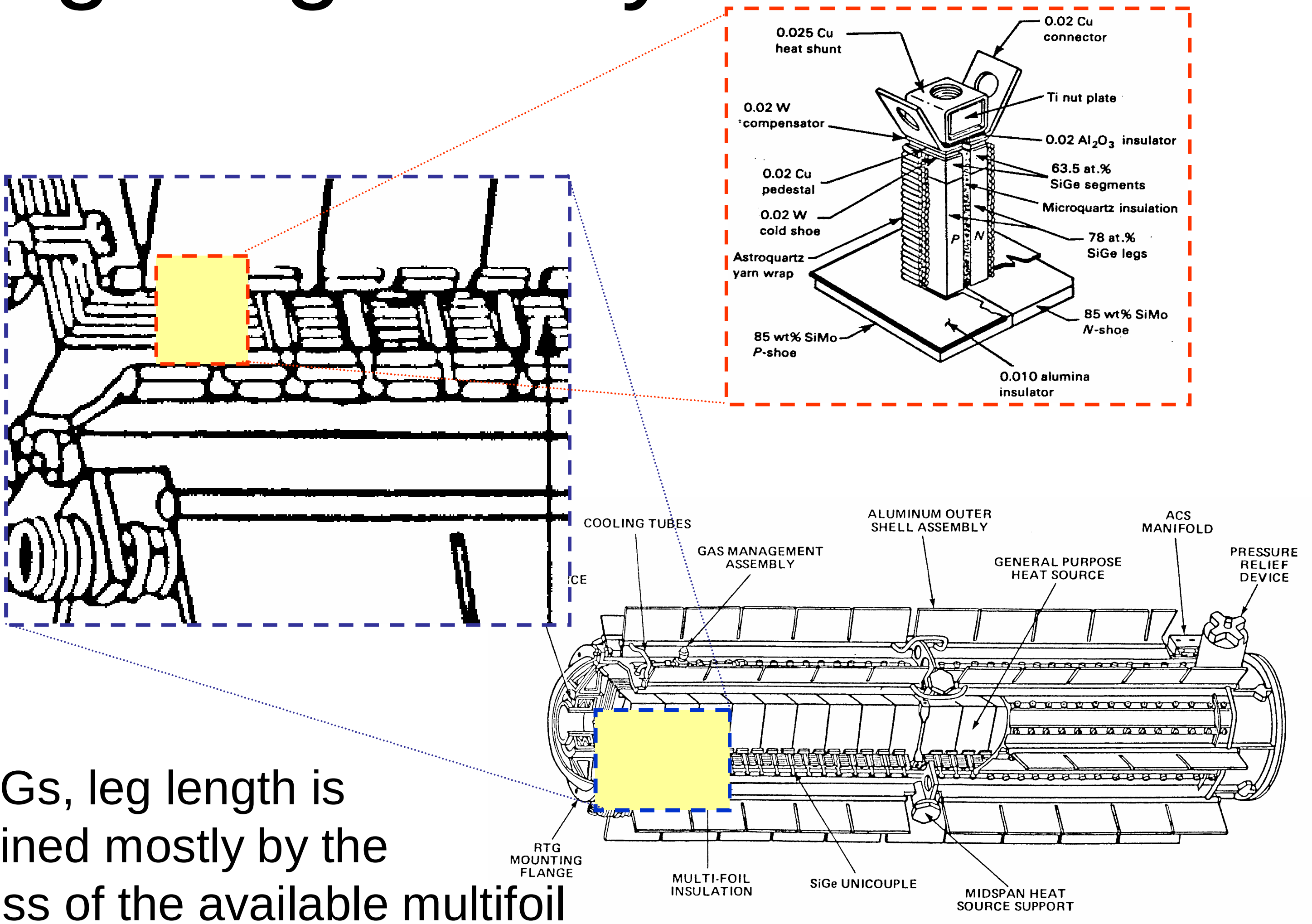
The A/L Issue

Some consequences

- So long as A/L is the same, these thermocouples perform the same (ideally!)
  - Both electrically and thermally
- Contact resistances & Electrode Losses
  - Increase R and/or
  - reduce K
  - Proportionately more important in shorter couples
- Heat flux is proportionately higher with a shorter leg
  - If you *want* a high heat flux, use a shorter leg
  - Prefer the heat to flow through your device, rather than around it.



Leg length is system-driven



- For RTGs, leg length is determined mostly by the thickness of the available multifoil thermal insulation package

Leg Length: Unicouple vs. Bicouple vs. Multicouple

- Leg length gets shorter due to development of better (thinner) multi-foil insulation

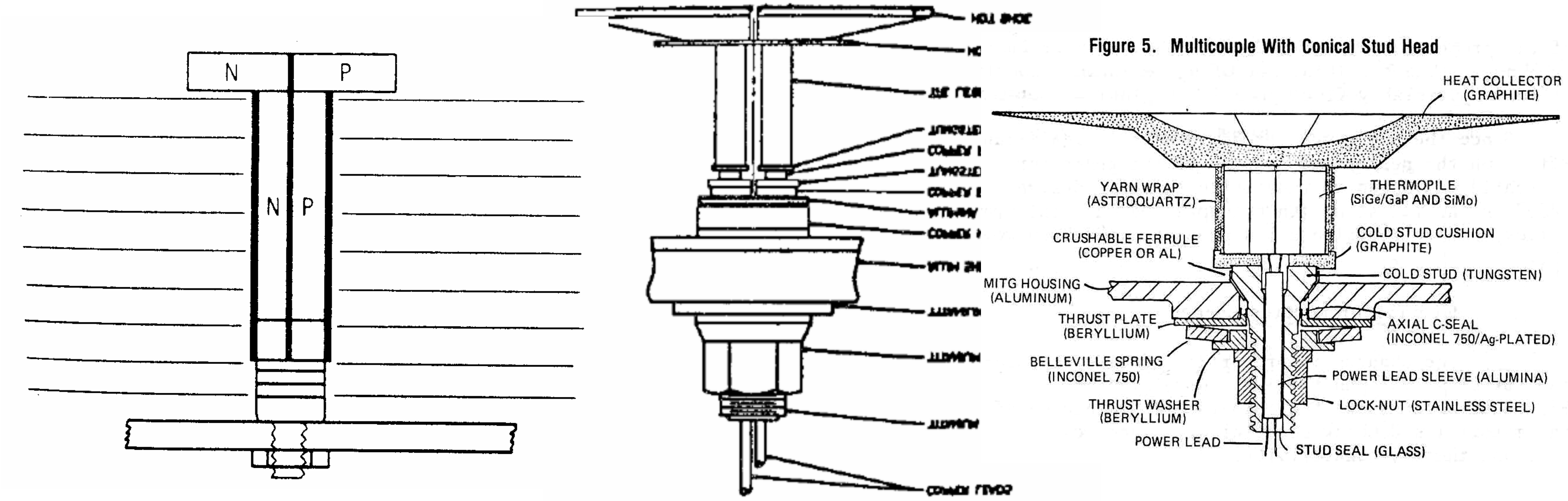


Figure 5. Multicouple With Conical Stud Head

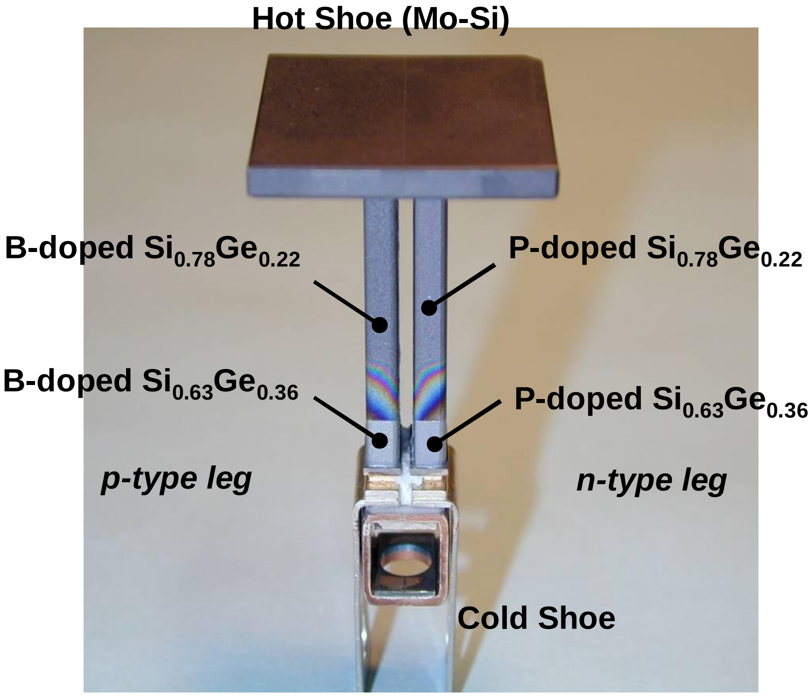
	Unicouple 1969	Bicouple 1984	Multicouple 1983
L (cm)	1.71	0.78	0.76

Other Selected Design Considerations

- Chemical compatibility w.r.t chemical reaction
  - Si is particularly reactive, attacking ***all*** metals
- Thermal stability
  - Melting, vaporization, phase change
- Mechanical
  - Strong in compression, weak in tension (like ceramics)
  - Hot pressed materials much stronger than large-grain size zone-leveled materials
  - Thermal stress from coefficient of thermal expansion mismatch
    - Radiatively coupled devices
      - Greatest thermal stress is typically right after cool down from manufacture
    - Conductively coupled devices
      - Stresses originate both within a single ‘cell’ & from thermal expansion of structural members
  - Launch vibration environment
    - Particular design concern for free-swinging radiatively-coupled designs
- Electromigration
  - Steep electric fields in insulators can drive migration of ions, ultimately causing electrical breakdown & shorts
  - Even modest electric fields within individual cells can drive electrolysis of glass insulators
  - In rare cases, steep temperature gradients & large electrical currents can cause electromigration within thermoelectric semiconductors

Voyager/Galileo-class Unicouple

- 55 kg, 300 W_e, ‘only’ 7 % conversion efficiency
- But > 1,000,000,000,000 device hours without a single failure
- Segmented device: $Si_{0.78}Ge_{0.22}$ at hot end, $Si_{0.63}Ge_{0.36}$ at cold
  - Segmenting is there to better match the thermal expansion coefficient of the $Si_{0.78}Ge_{0.22}$ with the tungsten cold end
  - In this case, segmenting is not driven by efficiency
- The hot shoe is 85% Si – 15 % Mo, essentially a composite designed to match coefficient of thermal expansion
- The bands of rainbow colors visible near the cold end of the $Si_{0.78}Ge_{0.22}$ is from a very thin coating of silicon nitride (Si_3N_4) to slow the loss of volatile Ge
  - further vaporization suppression is achieved by wrapping the entire device in a quartz ‘yarn’



SiGe unicouple

Figure from Fleurial, JPL

Multifoil Insulation

- "Multi-Foil" is a trademark of Thermo Electron
  - Thin metal foils (Ex: Ti)
  - Separated by oxide particles (Ex: ZrO_2)
  - Low effective emissivity ~ 0.03
  - N = 40 ~ 60 layers
  - Vacuum, radiation
  - This is a technology all by itself!

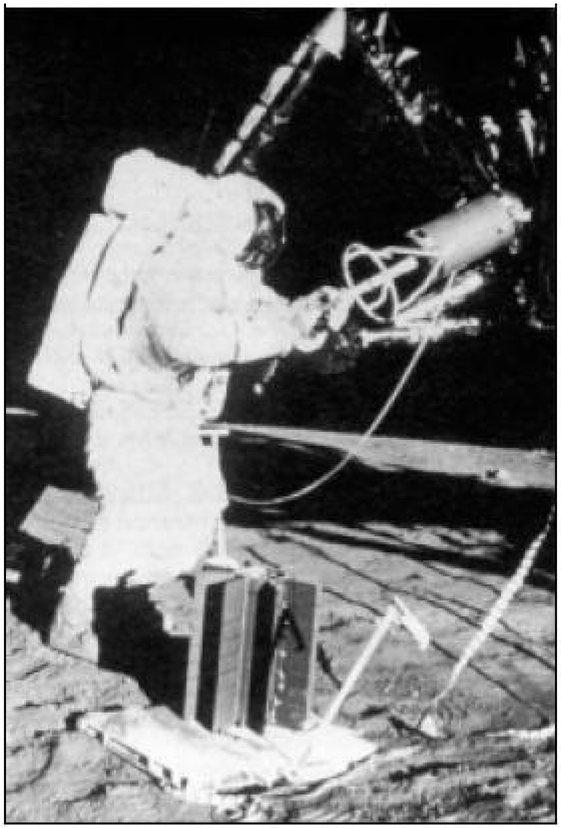
$$f = \frac{1.06x10^{-12}\left(T_h^4 - T_c^4\right)}{0.788N + \left(1.11x10^{-2}\right)N^2} \frac{W}{cm^2} \quad \text{(Determan,1989)}$$

Determan, W. R., J. Emmons, et al. (1989). Multi-Foil Thermal Insulation for teh Dynamic Isotope Power System. Proceedings of the 24th Intersociety Energy Conversion Engineering Conference, Washington, D.C., IEEE p.1115-1120.

Device Gallery

RTGs in Space

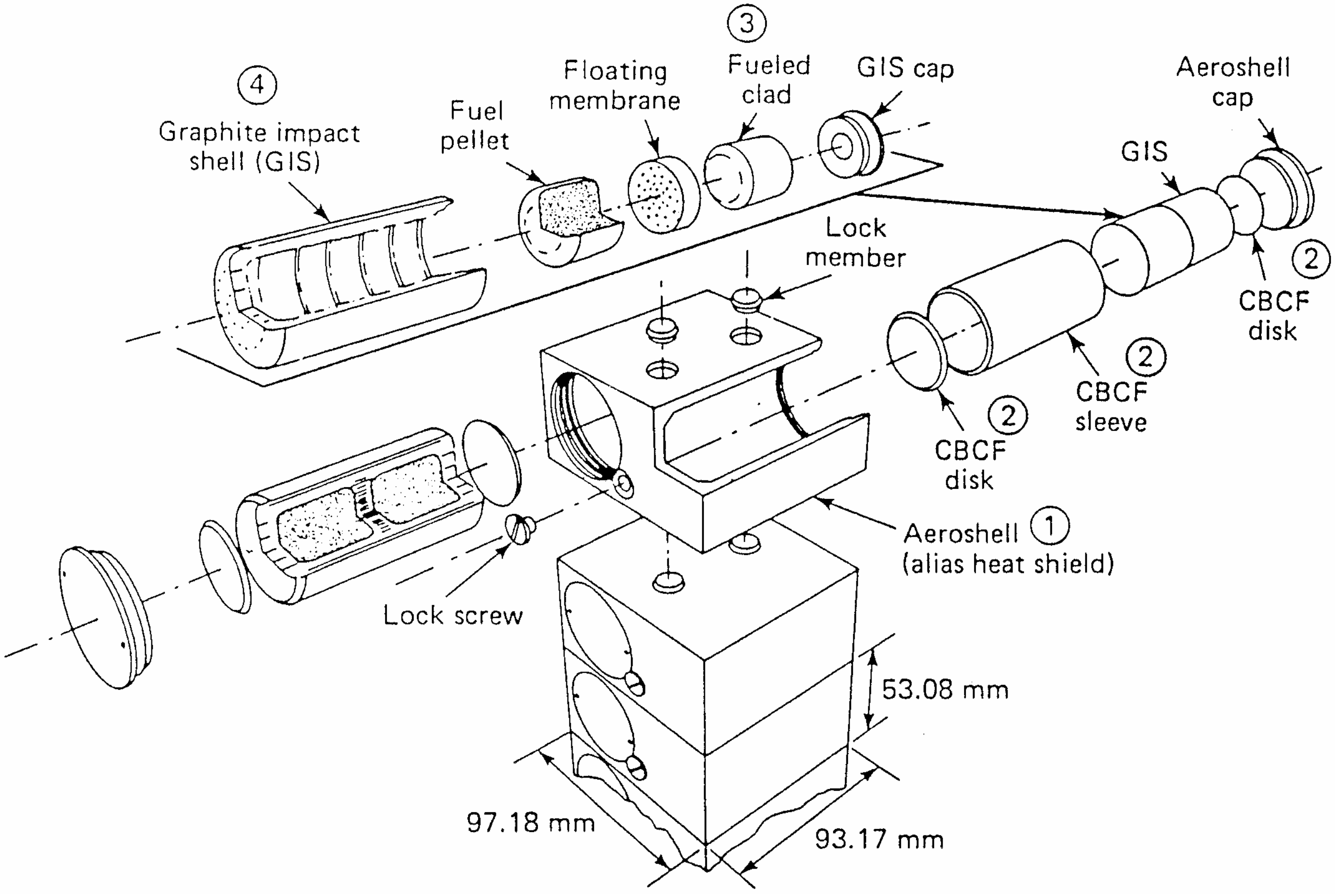
- 25 US spacecraft used 44 RTGs since 1961
  - 2 missions aborted, RTGs performed to design
    - Plutonium was recovered from one mission and reused



Deployment of the SNAP-27 RTG during the *Apollo 12* moon mission, on November 19, 1969 (Source: NASA)

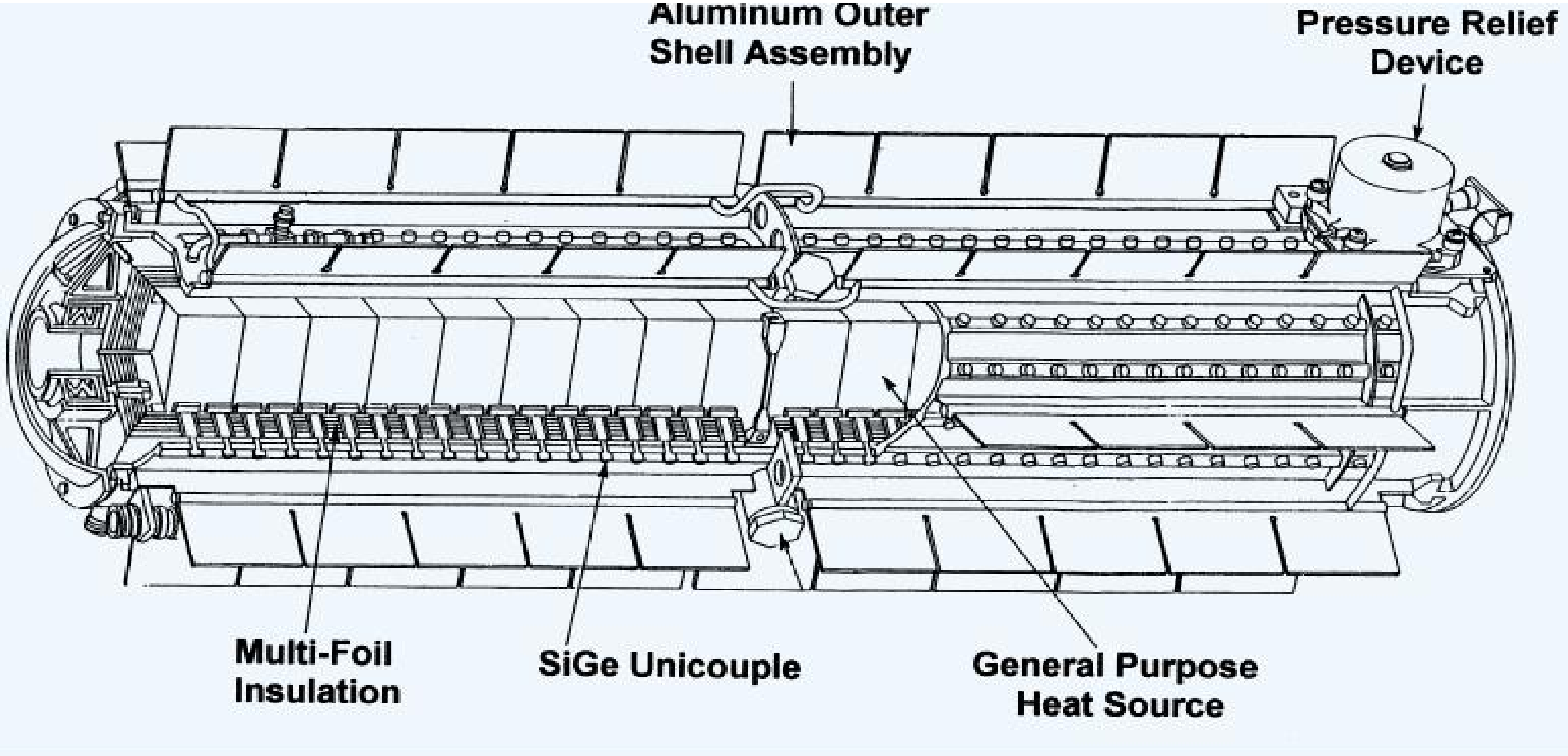
Furlong, R. R. and E. J. Wahlquist (1999). "U.S. space missions using radioisotope power systems." Nuclear News **April**: 26-34.

GENERAL PURPOSE HEAT SOURCE (GPHS) MODULE COMPONENTS AND ASSEMBLIES



The GPHS RTG

Galileo (2), Ulysses (1), Cassini (3)

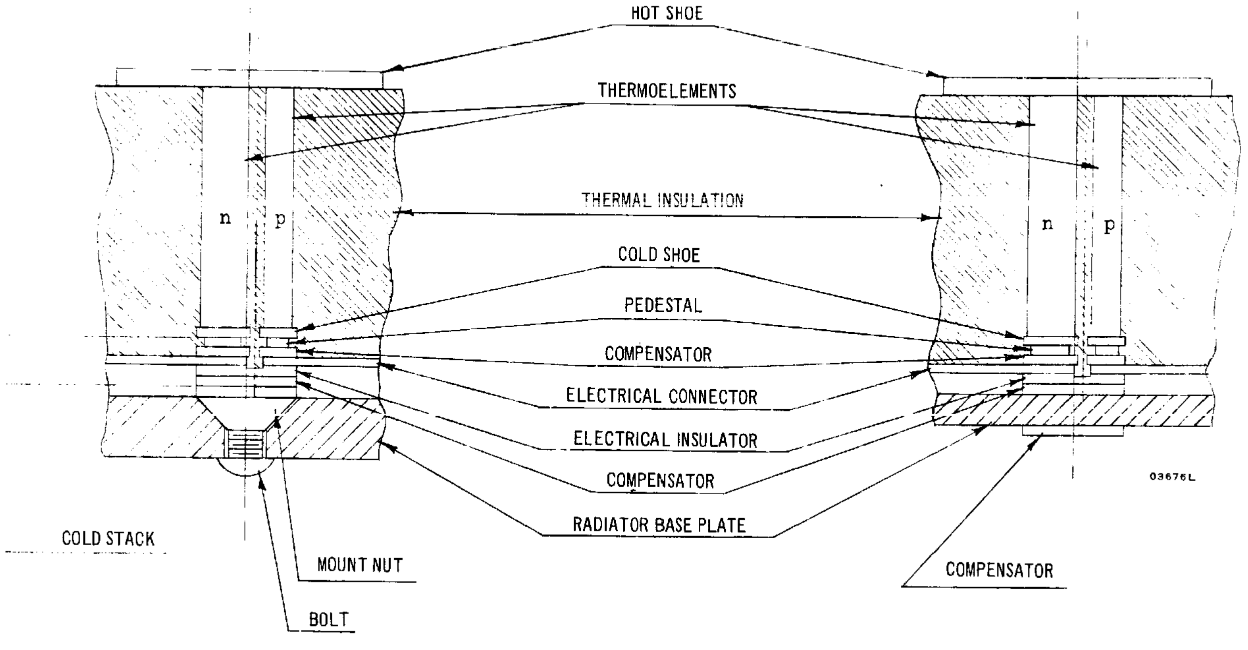


Radioisotope thermoelectric generator (RTG). The length is 44.5 in (113 cm), the diameter is 16.8 in (42.7 cm), and the weight is 124 lb (56.2 kg). (Source: DOE)

Furlong, R. R. and E. J. Wahlquist (1999). "U.S. space missions using radioisotope power systems." Nuclear News April: 26-34.

The SiGe unicouple dates to 1960s

RCA’s ‘AirVac’ technology
intended for air or vacuum operation



A. FLEXIMOD CONSTRUCTION

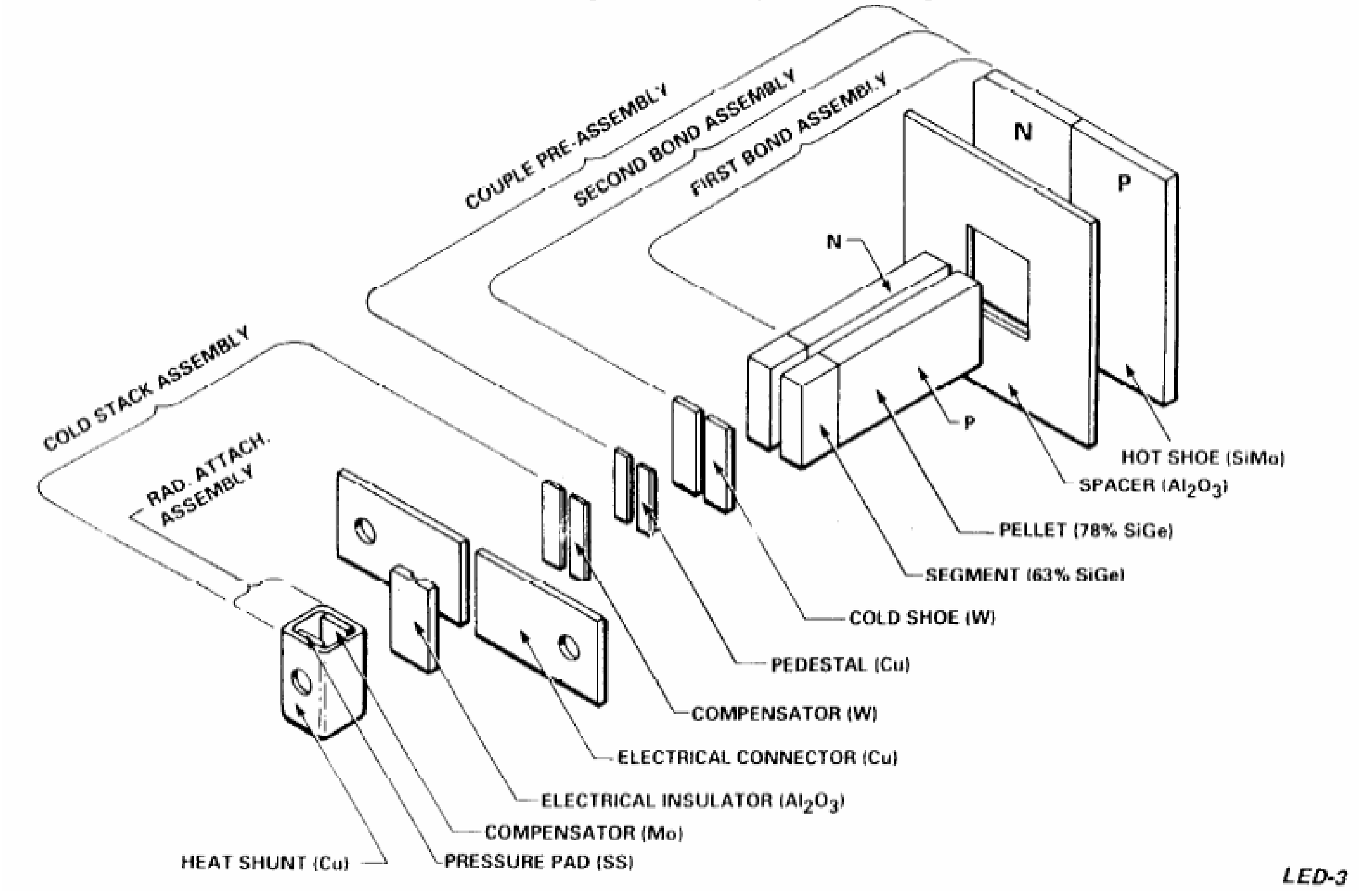
B. BRAZED CONSTRUCTION

Figure 1. Air-Vac Thermocouple, Construction Details

RCA (1969). Topical Report - Silicon Germanium Thermoelectric Materials and Module Development Program. Harrison, NJ USA, RCA**:** 83.

SiGe ‘Unicouple’

deceptively simple



The type used on the Voyager, Galileo and Cassini spacecraft RTGs. (Bennett 2002).

SiGe RTGs
Over 1 Billion device-hrs Served

Through 4/30/2004

Mission	Launched	RTG	# RTGs	couples/RTG	Couple-Hrs
LES 8	3/14/76	MHW-RTG	2	312	153,863,424
LES 9	3/14/76	MHW-RTG	2	312	153,863,424
Voyager 2	8/20/77	MHW-RTG	3	312	219,024,000
Voyager 1	9/5/77	MHW-RTG	3	312	218,664,576
Galileo	10/18/89	GPHS-RTG	2	572	145,736,448
Ulysses	10/6/90	GPHS-RTG	1	572	68,022,240
Cassini	10/15/97	GPHS-RTG	3	572	98,388,576
				Total:	**1,057,562,688**

- @ 0.5 W/couple = 500 Megawatt-hrs
  - About the same as 7+ months of an SP-100

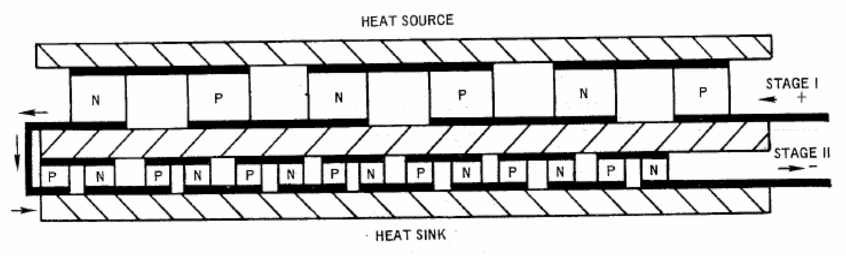
More Advanced TE Device Concepts

Cascading & Segmenting

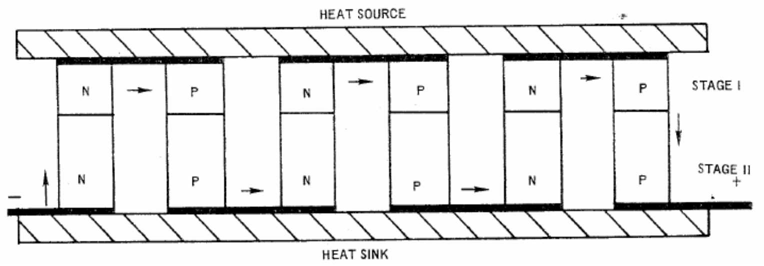
- Alternate device configurations, typically motivated by desire to use the highest available ZT value for each temperature range
  - In SiGe unicouple, segmenting is used to accommodate thermal expansion differences, not to enhance efficiency
- Atomics International (Rocklin, IECEC, 1967) developed a SiGe/PbTe cascaded & segmented device
- Significant efficiency gains
- Significant added complexity

- No free lunch!

Cascade: Stacked thermocouples

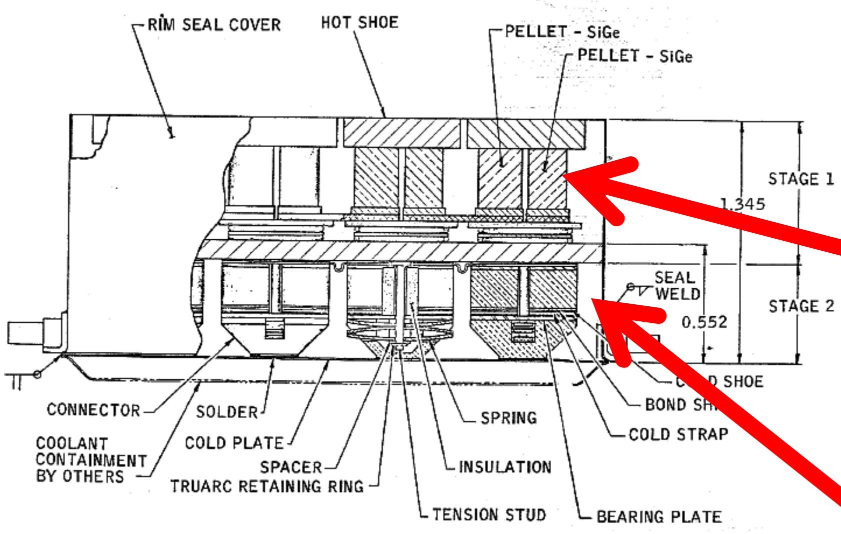


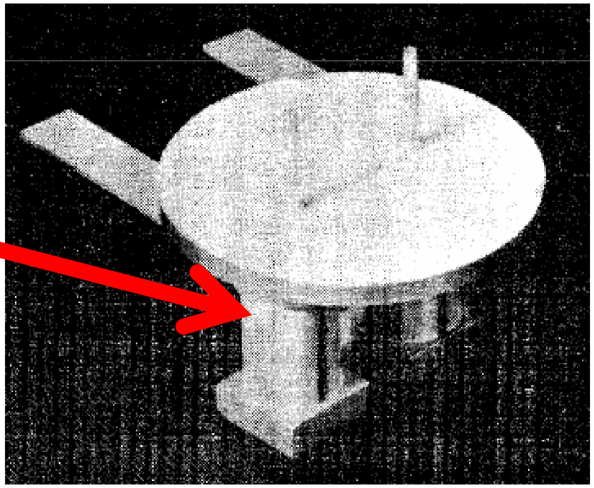
Segmented: Multiple materials per leg

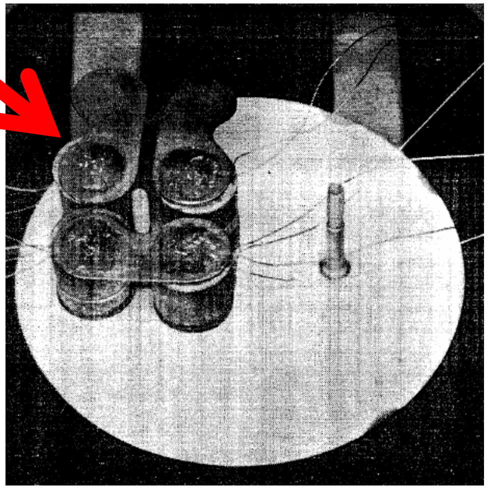


Atomics Int. 1967

SiGe cascaded with segmented PbTe

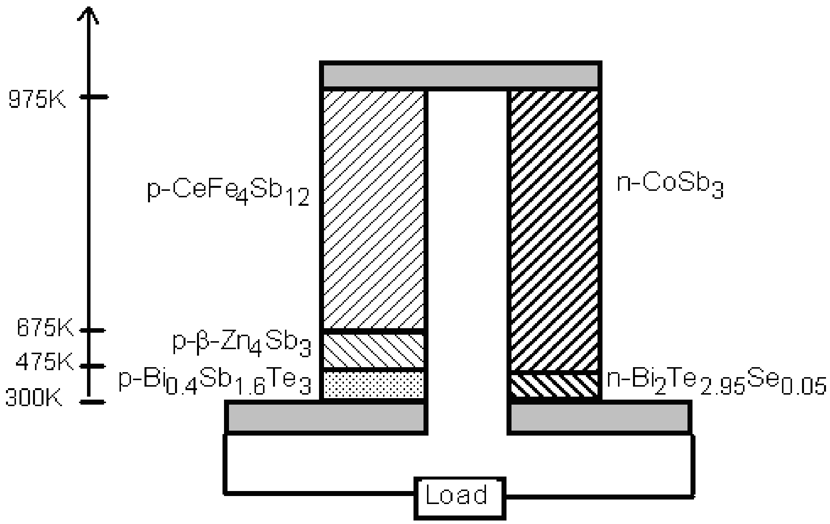


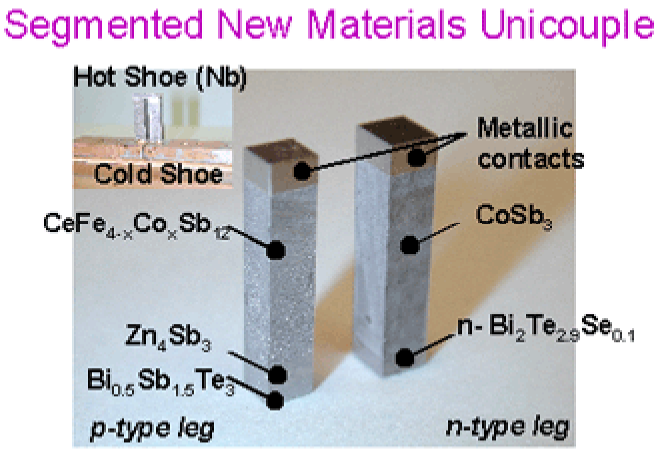


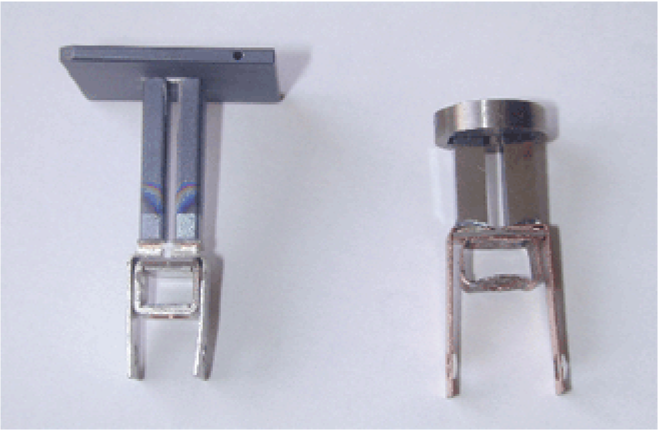


Rocklin, ICECE, 1967

Development effort only





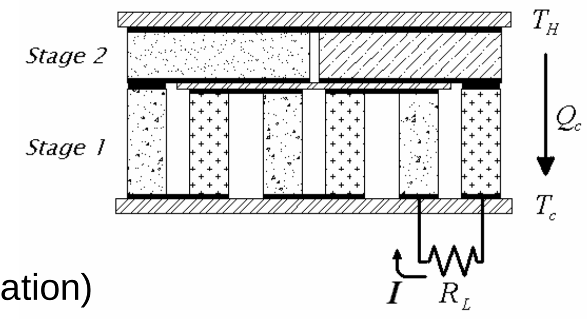


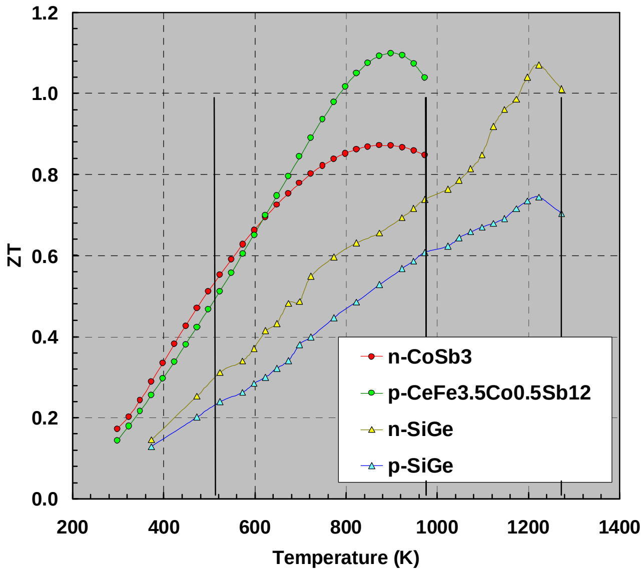
Caillat, T., J.-P. Fleurial, et al. (2001). Development of high efficiency segmented thermoelectric unicouples. Proceedings ICT2001. 20 International Conference on Thermoelectrics, Piscataway, NJ, USA, IEEE p.282-5.

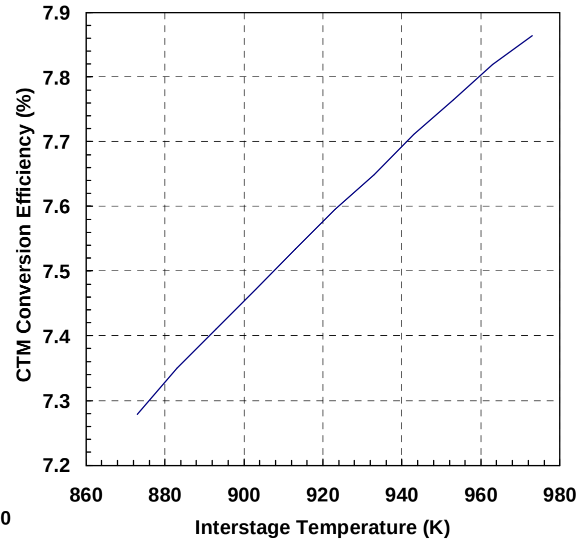
Cascaded Thermoelectric Multicouple

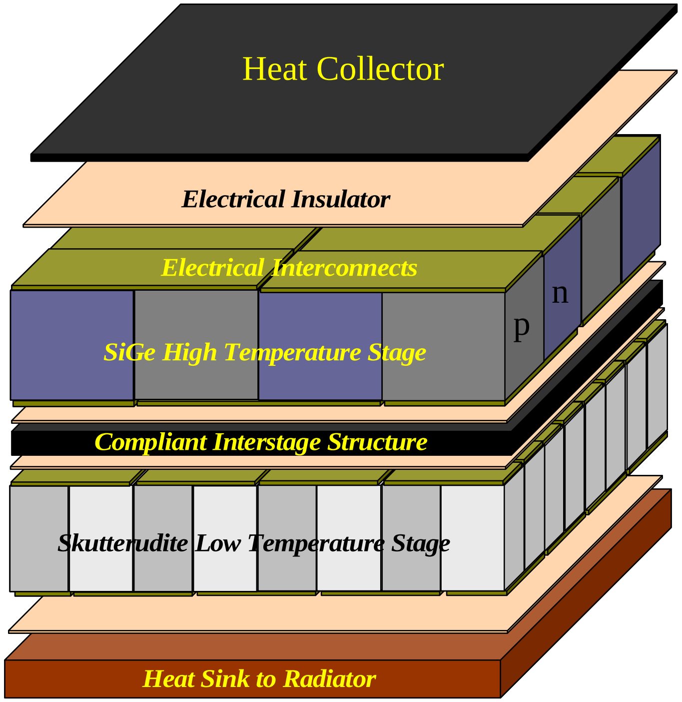
From JPL Presentation

- CTM combines best materials available today in 1275 to 725K
  - SiGe alloys: 1275-975K, Skutterudites: 975K-725K
  - 7.9% to 7.3% cascaded device efficiency with 1275K-725K
    - With interstage temperature varying from 975K to 875K
- Thermally cascaded
  - Can be electrically in series or parallel (in series preferred)
  - Independent optimization of leg geometry (not possible with segmentation)
  - Easier integration of thermomechanical stresses (CTE mismatches)

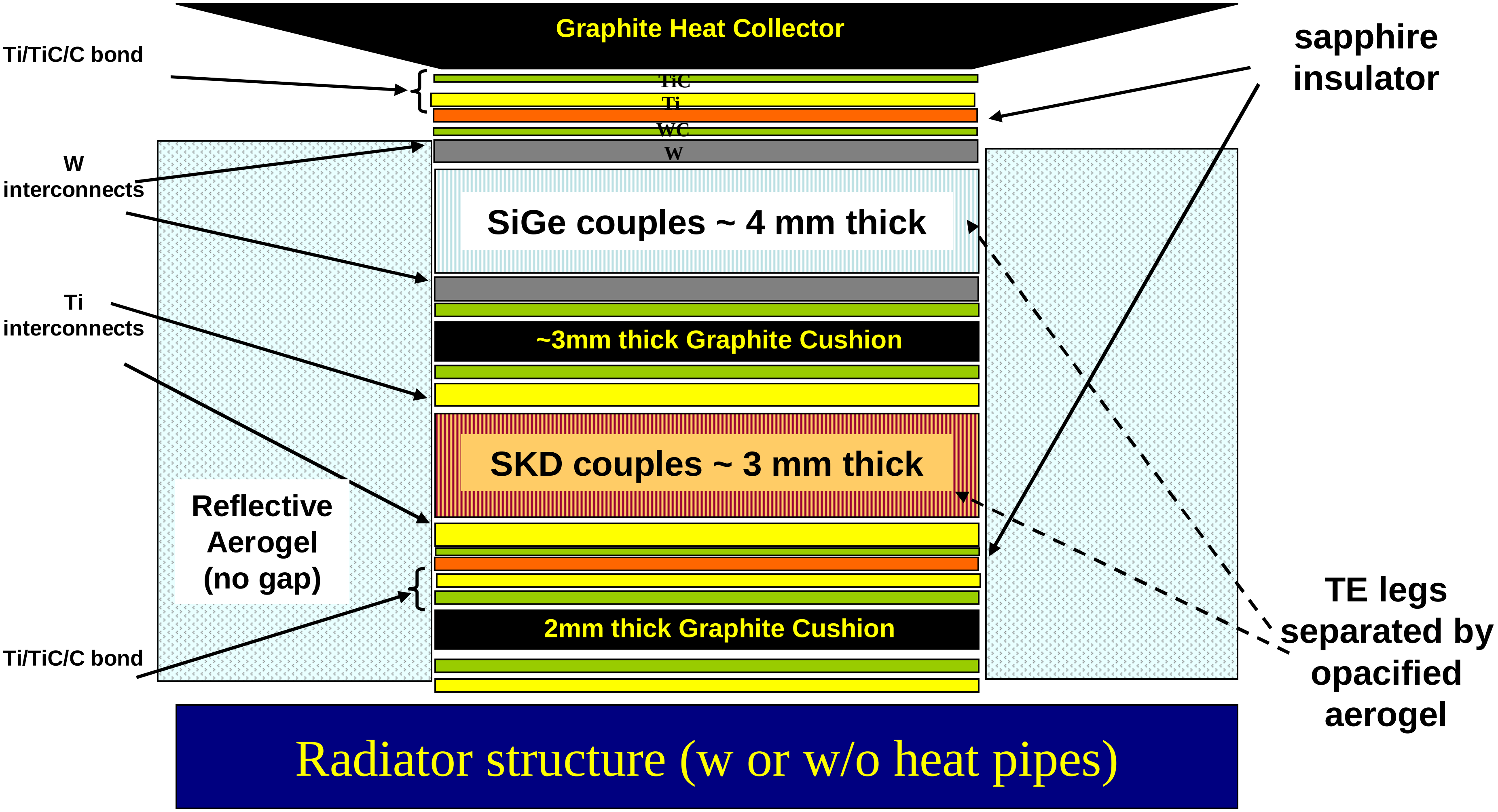








Novel Approach to TE Device Fabrication and Assembly
Figure from JPL Presentation – Count the Novelties



Graphite Heat Collector

Ti/TiC/C bond

TiC
Ti
WC
W

sapphire insulator

W interconnects

SiGe couples ~ 4 mm thick

Ti interconnects

~3mm thick Graphite Cushion

SKD couples ~ 3 mm thick

Reflective Aerogel (no gap)

Ti/TiC/C bond

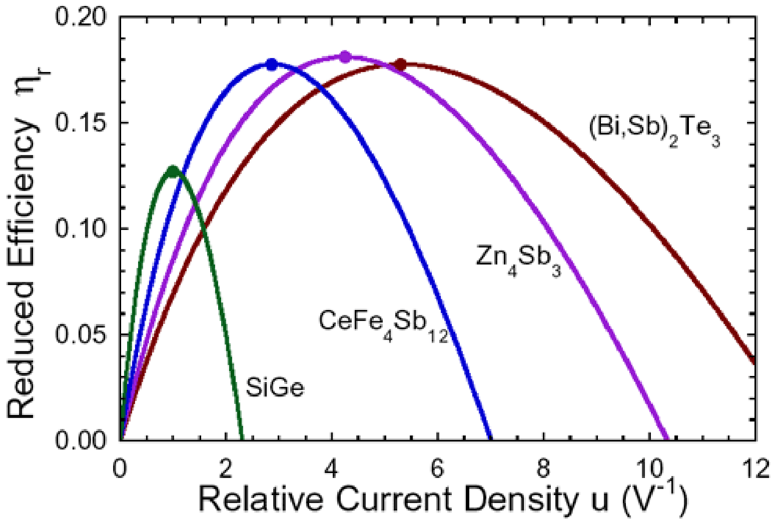
2mm thick Graphite Cushion

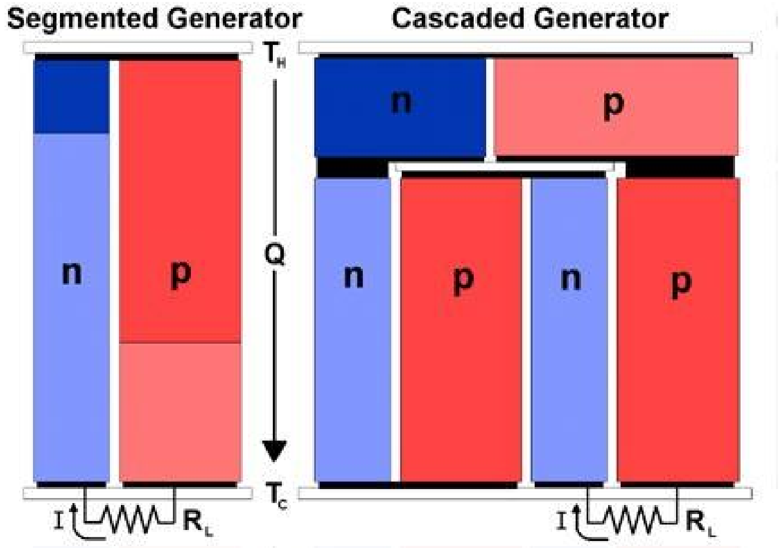
TE legs separated by opacified aerogel

Radiator structure (w or w/o heat pipes)

Snyder's 'Compatibility Factor'

- Some materials don't segment well for mechanical/chemical reasons
  - Thermal expansion
  - Chemical reactions
- Other materials don't segment well for thermoelectric reasons
  - Optimum current density is different for different materials
    - Optimize current density for one, and you can be way off for the other
- Snyder (PRL, 2003) introduced an elegant method to determine if two materials are 'thermoelectrically compatible' for segmenting
  - Based on a parameter 'u' which can be calculated from thermoelectric properties alone, independent of device particulars





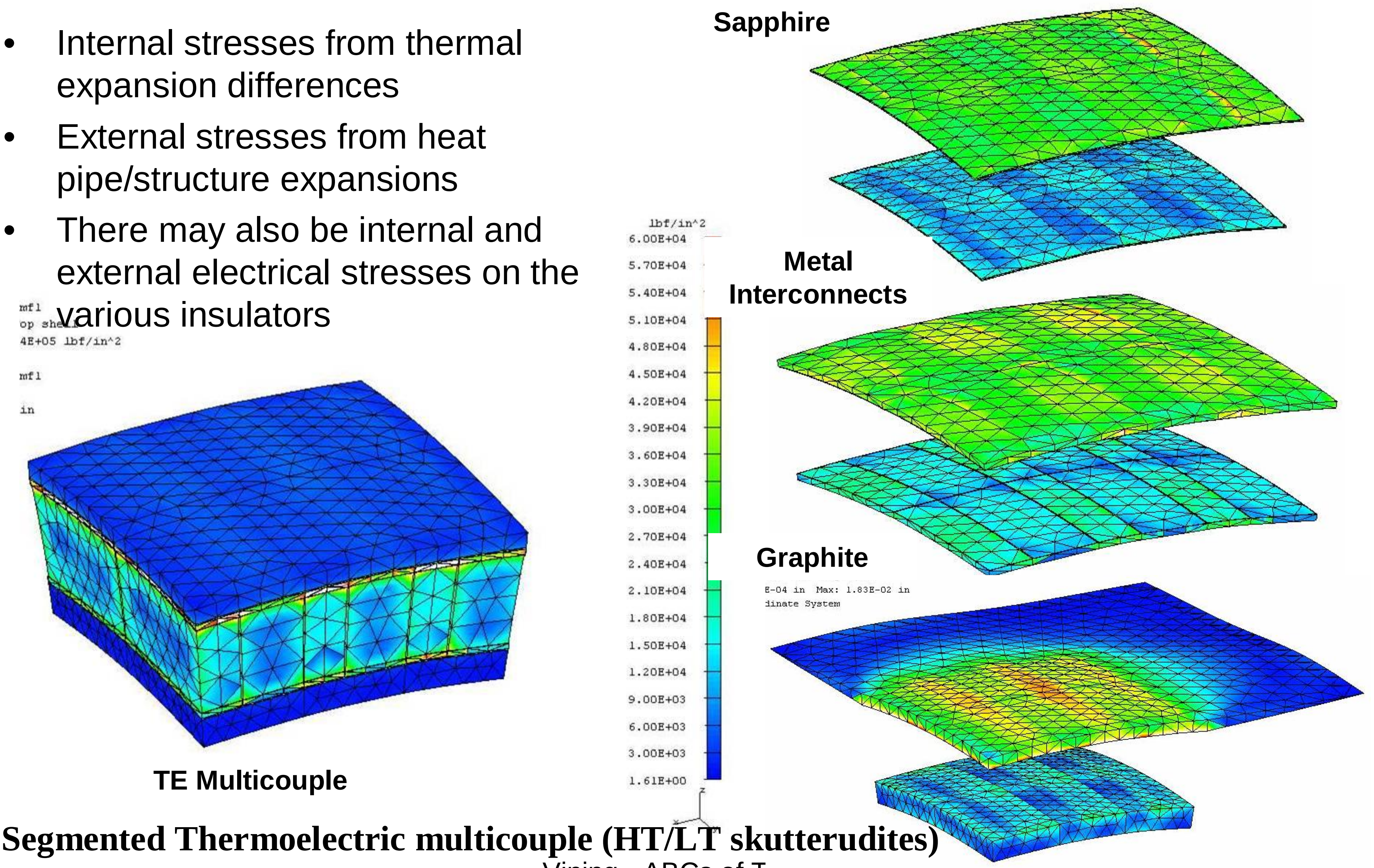
Cascading & Segmenting Seem to be ‘In’

- A serious & legitimate attempt to get more efficiency out of available materials
- May or may not be combined with close-packed ‘multicouple’ construction
- Mechanical & chemical interaction issues are significantly greater
  - Inevitably longer development cycles
- Don’t try to tackle every possible enhancement in one development cycle!
  - It never works

Stresses in Thermoelectric Multicouples

Figures from JPL Presentation

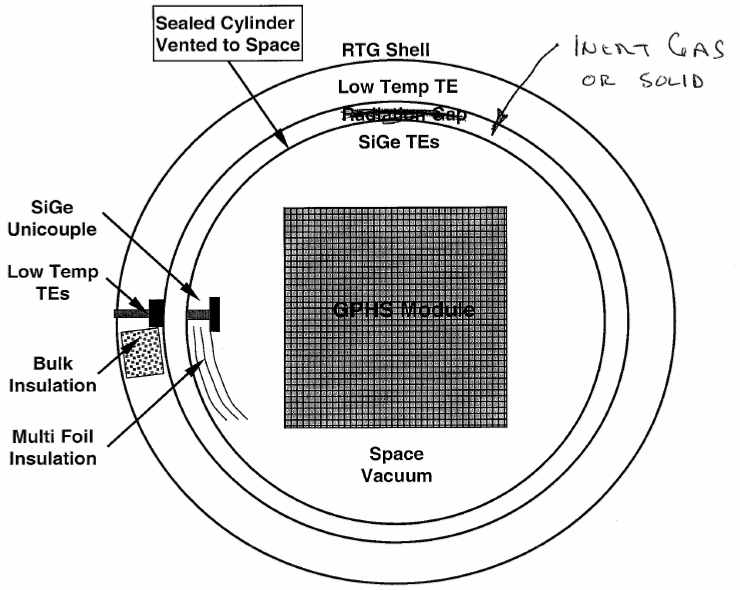
- Internal stresses from thermal expansion differences
- External stresses from heat pipe/structure expansions
- There may also be internal and external electrical stresses on the various insulators



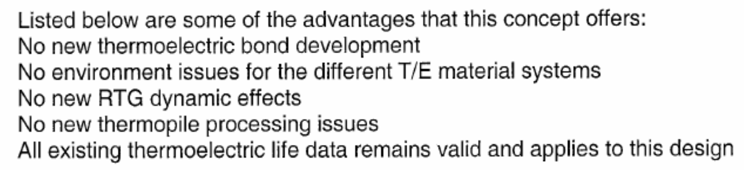
Segmented Thermoelectric multicouple (HT/LT skutterudites)

Mowery et al’s Cascaded RTG

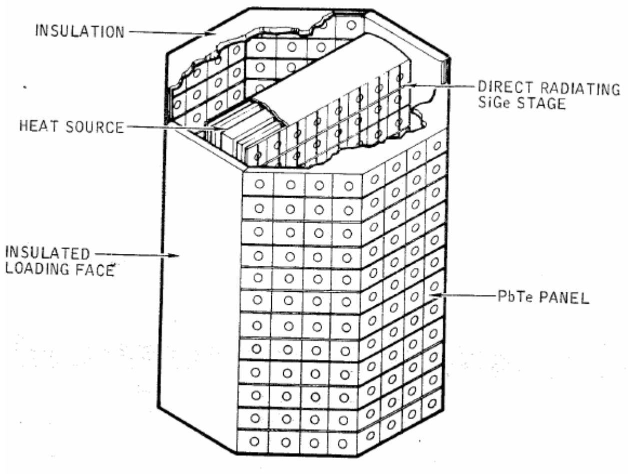
- Mowery et al (unpublished, Jan. 2003) proposed a kind of Cascaded RTG (right)
  - Rather than cascade couples or cells, cascade the entire RTG shell
- Excellent concept
- Brunings (IECEC, 1967) proposed a related concept (below)



Consulting Fee: Cup of Hot Chocolate for Al Mowery and John Dassoulas


Listed below are some of the advantages that this concept offers:
No new thermoelectric bond development
No environment issues for the different T/E material systems
No new RTG dynamic effects
No new thermopile processing issues
All existing thermoelectric life data remains valid and applies to this design

Pu FUELED CASCADED SiGe-PbTe GENERATOR



Thermoelectric Materials

All else being equal

You want higher ZT

But how?

Fundamentals and Physical Phenomena of TE Materials

Aka: Electrons and Phonons

ZT is fundamental to improving efficiency

- Many aspects of design, construction & operation affect performance of thermoelectric energy conversion
- But other than the operating temperatures, ZT is the most important
  - Efficiency scales directly with ZT
- To make progress on ZT we turn to materials science, chemistry and physics
- In this section we'll outline the main physical principles for understanding ZT
  - The goal is a theory of 'ZT' to guide experimental work

The Intellectual Question

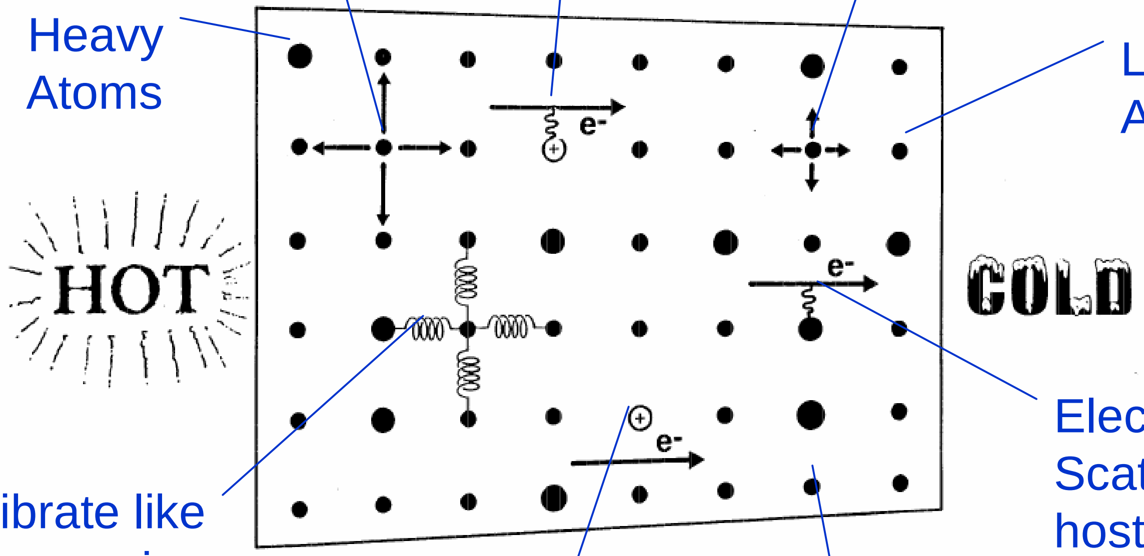
- Transport properties (ρ particularly) can vary by 20 orders of magnitude
- ZT is a transport property
  - Rather, a combination of transport properties
- WHY are there no materials with ZT=10? or 50?
- There is no rigorous answer
- But there are some excellent guidelines

Inside A Solid

Lattice (aka phonons) + Charge Carriers + Interactions

We need 1) A Theory of Electrons, 2) A Theory of Phonons

Challenge: from this picture extract S, ρ, λ & ZT



Hot Atoms Vibrate More

Electrons Scatter off dopants

Cold Atoms Vibrate Less

Heavy Atoms

Light Atoms

Electrons Scatter off host atoms

Atoms vibrate like mass + spring - That is a phonon

‘Dopants’ ionize to produce free electrons

A ‘crystal’ is a regular, periodic array of atoms

Definitions of Transport Coefficients of Interest in TE:

Thermoelectric Property	***Definition***	***Under Condition***	***Type***
Electrical Conductivity	$i = \sigma E$	$\nabla T = 0$	Direct
Thermal Conductivity	$q = -l \nabla T$	$i = 0$	Direct
Seebeck Coefficient	$E = S \nabla T$	$i = 0$	Cross
Peltier Coefficient	$q = \Pi i$	$\nabla T = 0$	Cross

Generalized Ohm's Law, Currents proportional to 'Forces':

$$i = s\,(E - S \nabla T)$$

$$q = \Pi i - l \nabla T$$

Symmetrical Version, Currents are created by Forces

$$i = s E + s S (-\nabla T)$$

$$q = s \Pi E + \left(l + s S^2 T \right) (-\nabla T)$$

Historical Basis

Thermoelectric Property	***Definition***	***Discoverer***	***Year***
Electrical Conductivity	$V = IR$	Ohm's Law	1826-7
Thermal Conductivity	$Q = K\Delta T$	Fourier's Law	1804-7
Seebeck Coefficient	$V = S\Delta T$	Seebeck	1822-5
Peltier Coefficient	$Q = \Pi I$	Peltier	1834

- These are NOT thermodynamic properties
  - Thermodynamics deals with isothermal systems with no (or infinitesimal) flow of charge or heat
  - Theory of irreversible processes is more complex
- By 1909-11 Altenkirch described main TE generator and refrigerator design concepts

Introduction

Correspondence Between Thermal and Electrical Quantities.

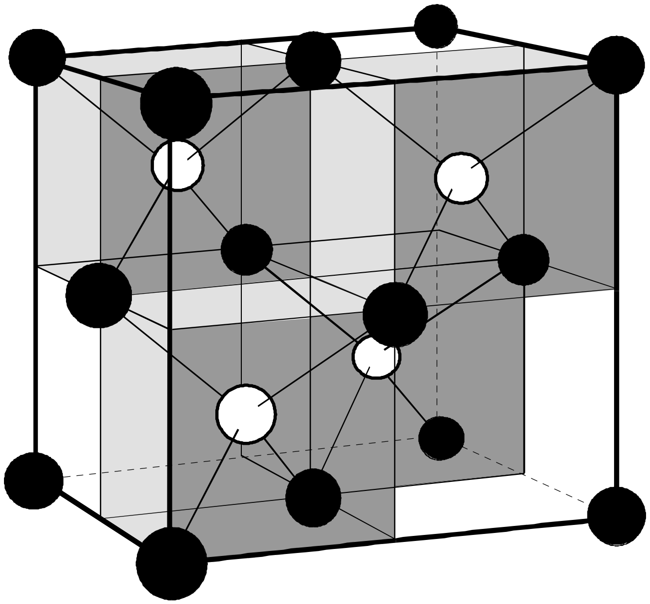
	Thermal	***Electrical***	***Type***
Quantity	Heat	Charge	Reversible
Potential	Temperature	Potential	Reversible
Current Type	Heat Current	Electrical Current	Irreversible
Driving Force	Temperature Difference	Potential Difference	Irreversible

There is only ***One*** Thermoelectric Effect:

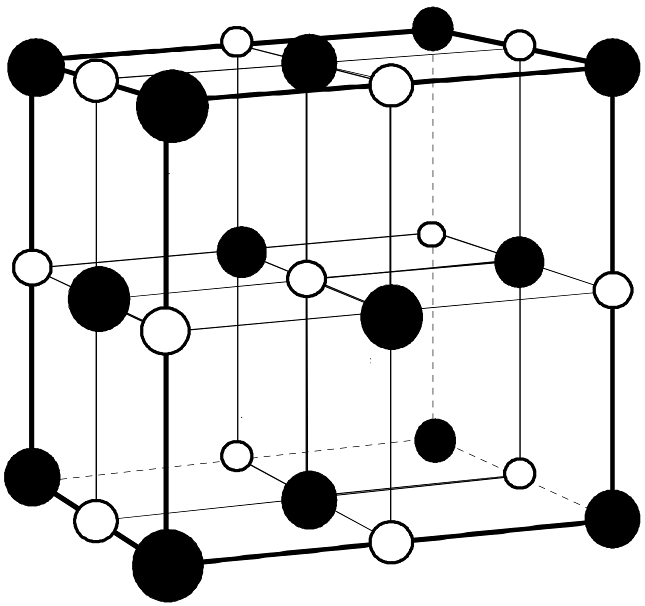
- The Seebeck Effect is an Electrical Reaction from a Thermal Driving Force
    - S
- The Peltier Effect is a Thermal Reaction from an Electrical Driving Force
    - $\Pi = ST$
- The Thomson Effect is Heat Generated due to *Both* Electrical Current and Temperature Gradient
    - This is Just a Consequence of the Temperature Dependence of S
    - $\dot{Q}_{Thompson} = \tau i(-\nabla T)$
    - $\tau = T(dS/dT)$

Unification of the Three Thermoelectric Phenomena was an Intellectual Achievement Comparable to The Unification of Electricity and Magnetism

Crystals:



Diamond Crystal Structure
(if all the atoms are identical)
- Si, Ge, SiGe alloys



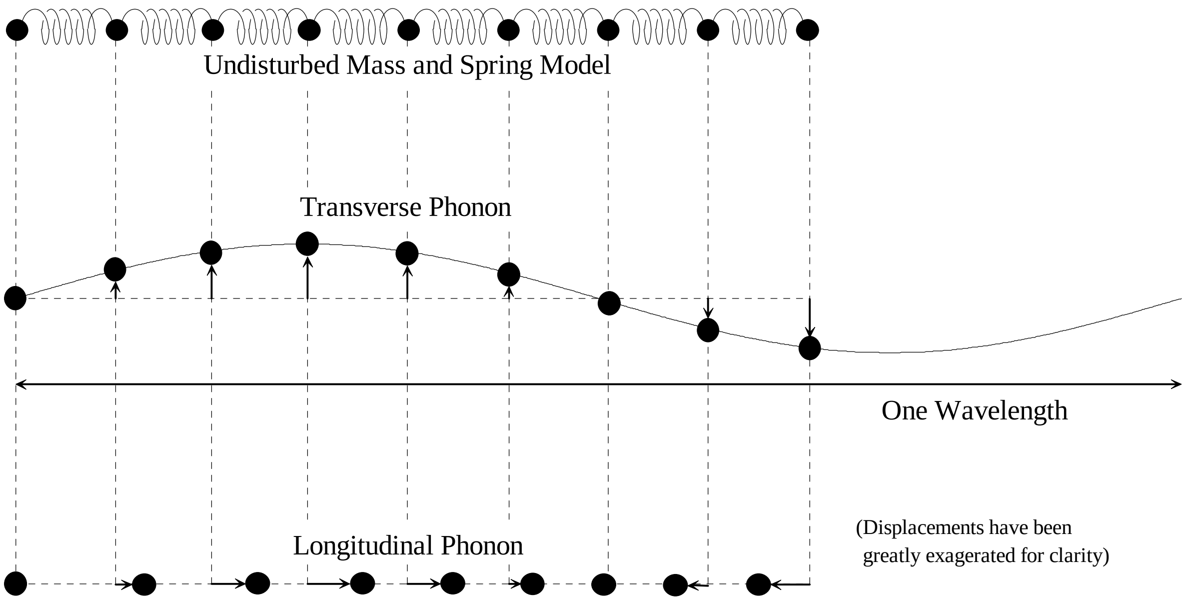
Sodium Chloride Crystal Structure
- PbTe, PbSe and alloys

The Particular Geometrical Arrangement and the Particular Atoms Involved Determine Everything

Towards a Theory of Thermal Conductivity

- This section outlines the main ideas to estimate the thermal conductivity of a solid

Phonons *are* Atomic Vibrations:



Basically Just Masses Connected by Springs

- Motion of one mass affects the others
- Disturbances tend to move in waves called ***phonons***
- Several types of disturbance with the same wavelength
  - Ex: Transverse (aka: sheer) vs. Longitudinal (aka: compression)
  - True of all sound waves, including earthquakes
- Speed and energy of the wave depend on wavelength and type of phonon.
  - Longitudinal waves are faster than transverse

Quantum Mechanics & Phonons

Quantum Mechanics and Waves

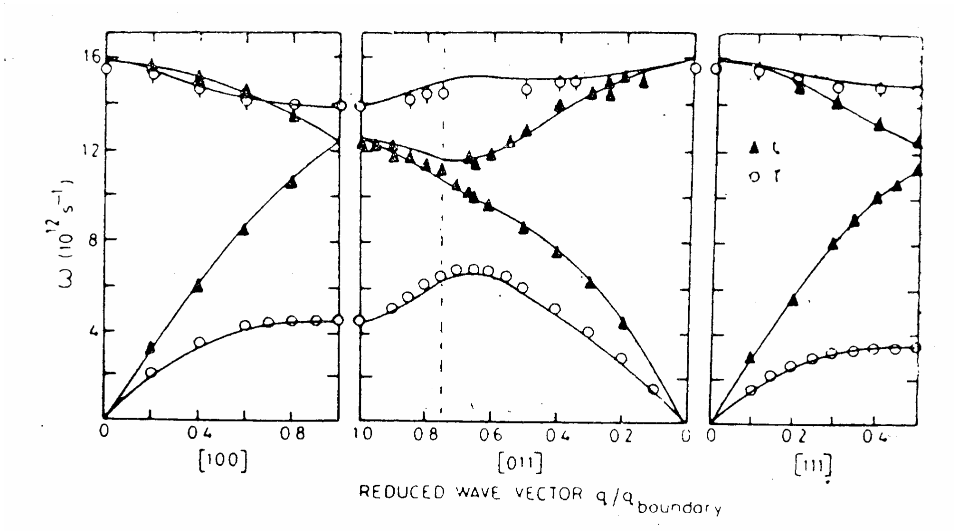
- Every wave has
  - Speed: how fast a *wavecrest* moves
  - Energy: Springs are stretched and atoms are moving
  - Momentum:
    - de Broglie tells us waves and particles are related
    - momentum is h/λ (Plank's constant)/(wavelength)
- Using a series of phonons (like a Fourier Series) *any* disturbance can be described by phonons
- Heat is a broad, thermal distribution of phonons
- Heat conduction is a more phonons flowing in one direction than the other

Need to Know Two Things:

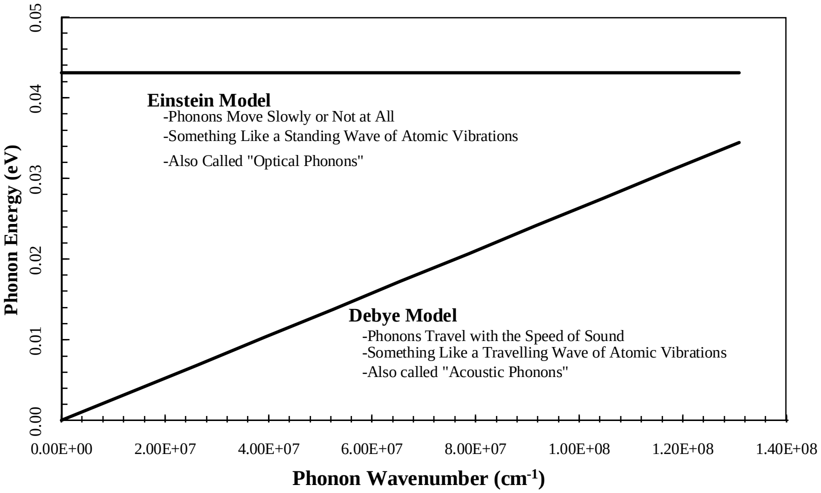
- What phonons are allowed?
  - This is called the phonon dispersion relation
- What phonons are actually present
  - This is called the phonon distribution function

Phonon Dispersion Relation = What Phonons are Allowed?

- Full calculation is a quantum mechanical, 3D ball & spring model of the crystals allowed vibration modes!
- This can (and is sometimes) done, but usually is not necessary for our purposes

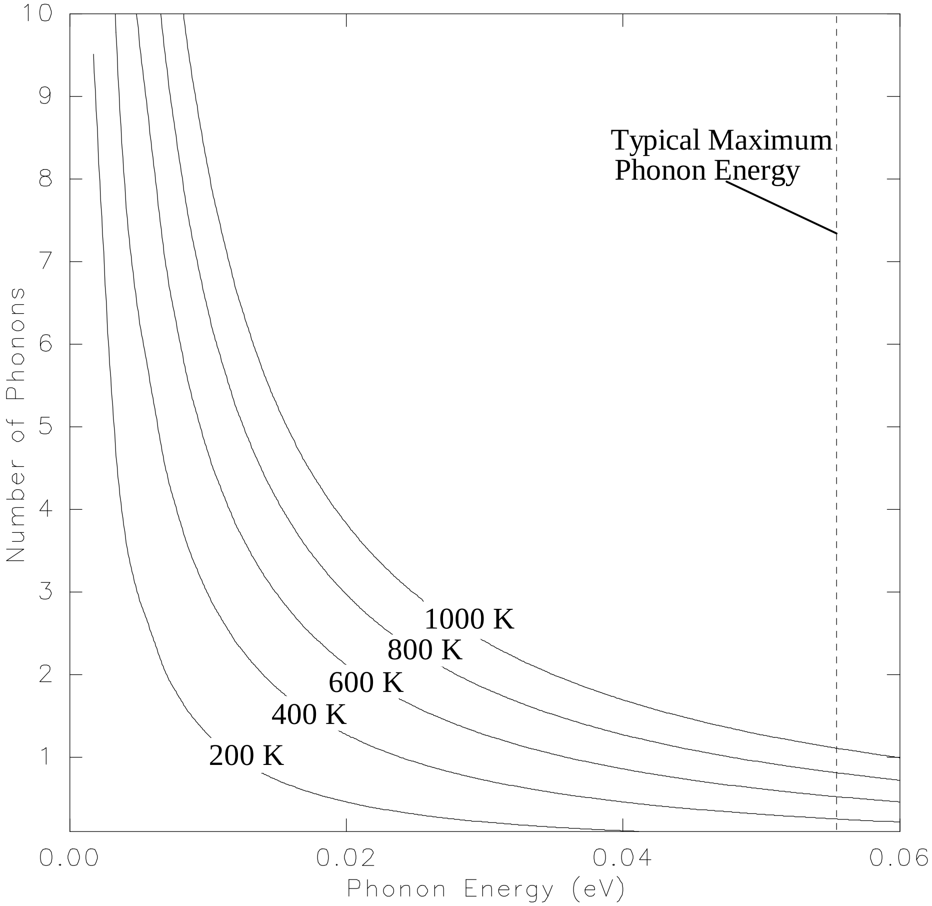


Full Phonon Structure for Si



Approximate Models Commonly Used

Phonon Distribution Function (in Equilibrium):



How can you have a fraction of a phonon?

- Phonons don’t live forever, even in equilibrium
- Distribution function tells you how many of that type, with that energy are present ***on average!***

Procedure for Calculating Thermal Properties:

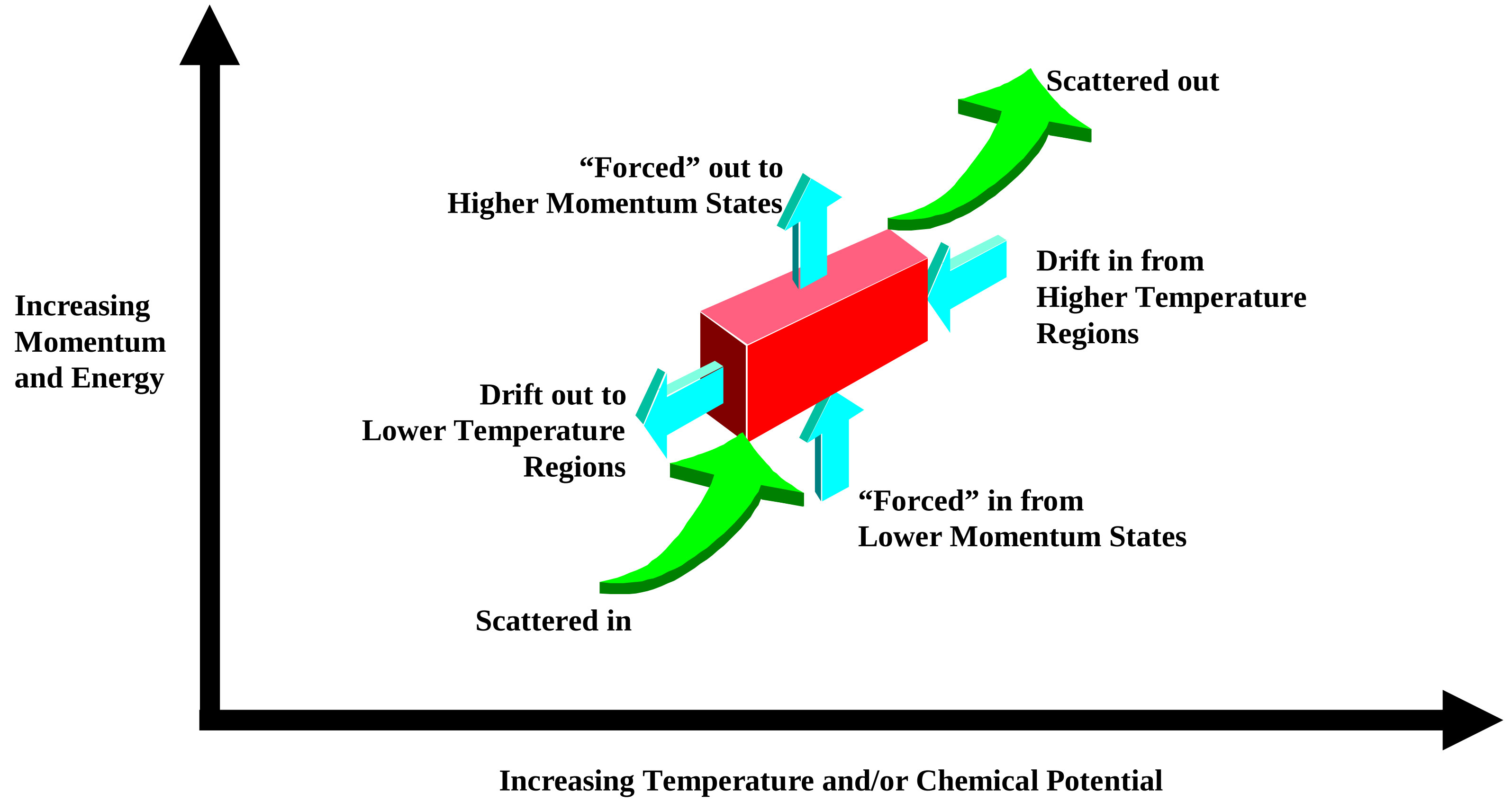
- Total Energy Associated with Phonons

Total Property		Sum over allowed types of phonons, i	Sum over allowed wavenumber, k	Contribution of each phonon	*x*	Distribution Function
		i=1, Longitudinal Acoustic				
		i=2, Transverse Acoustic #1	$k \geq 0$	ε(i,k)	*x*	N(i,k)
Energy	=	i=3, Transverse Acoustic #2	$k \leq 2\pi/a$			
		i=4, Optical #1				
		i=5, Optical #2				
		i=6, Etc.				

The Entire Procedure is Summarized Compactly:

$$E = \sum_{phonon\ ,\ i} \left\{ \int_{allowed\ \ k} e\,(i,\vec{k})\; d^{3}k \right\}$$

Find a New Distribution Function Which Satisfies the Balancing Act



Boltzmann's Equation Determines the Non-Equilibrium Occupation of an Energy State by Balancing the Effects of Scattering, Forces and Drift on a Small Group of Energy States, in a Small Region of the Material

Lattice Thermal Conductivity

Procedure for Calculating Non-Equilibrium Thermal Properties:

- Essentially the same as before

Total Property	Sum over allowed types of phonons, i	Sum over allowed wavenumber, k	Contribution of each phonon	*x*	Distribution Function
Heat Current =	i=1, Longitudinal Acoustic i=2, Transverse Acoustic #1 i=3, Transverse Acoustic #2 i=4, Optical #1 i=5, Optical #2 i=6, Etc.	$k \geq 0$ $k \leq 2\pi/a$	ε(i,k) *x* *v*(i,k)	*x*	N(i,k)

Simple, If you know the non-equilibrium distribution function

- Effects of forces and drift are mechanics problems
- From the scattering rate, Boltzmann's equation can be solved:

$$N(i,k) = N_0(i,k) + \left(-\frac{\tau(i,k) v(i,k) \cdot \nabla T}{T} \right) \varepsilon(i,k) \frac{\partial N_0(i,k)}{\partial \varepsilon(i,k)}$$

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

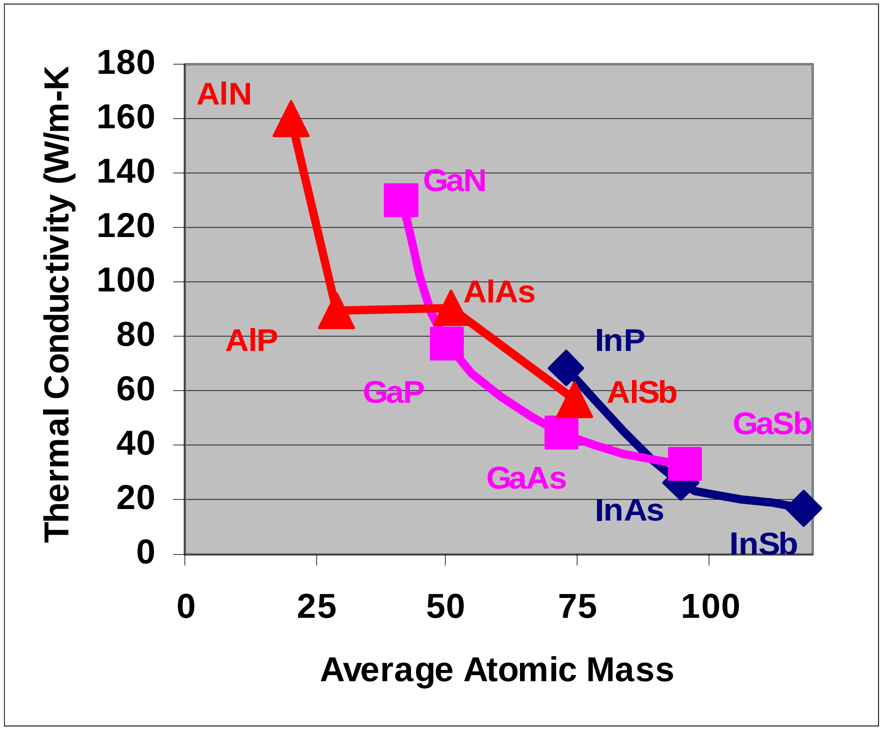
Phonon relaxation time (1/scattering rate)

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

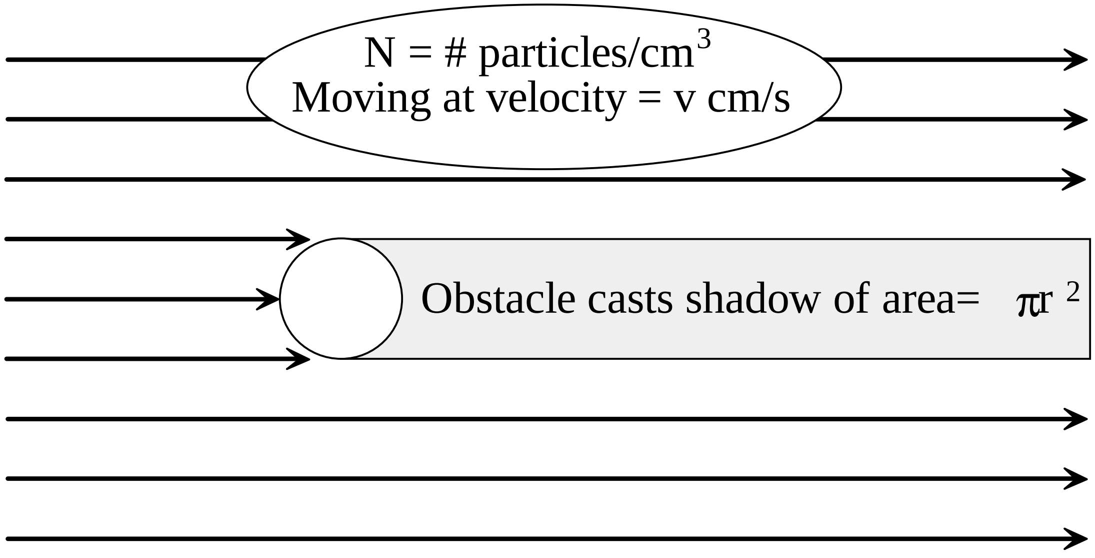
- This is the ‘distilled down’ version of the full-fledged treatment just described
- To reduce thermal conductivity
  - Pick heavy atoms, complex crystal structure
    - Lower speed of sound
  - Introduce as much phonon scattering as possible
    - Without screwing up electrical properties (that’s the 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
  - Comes directly from the ‘mass & spring’ picture of phonons
- 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
  - This is a plus for skutterudites, Clathrates, Chevrel Phase & others



Scattering Rates: The Key To Thermoelectrics



Scattering rate = # particles which hit obstacle/sec

$= 1/\tau$

$= N v \pi r^2$

Essentially a geometry problem:

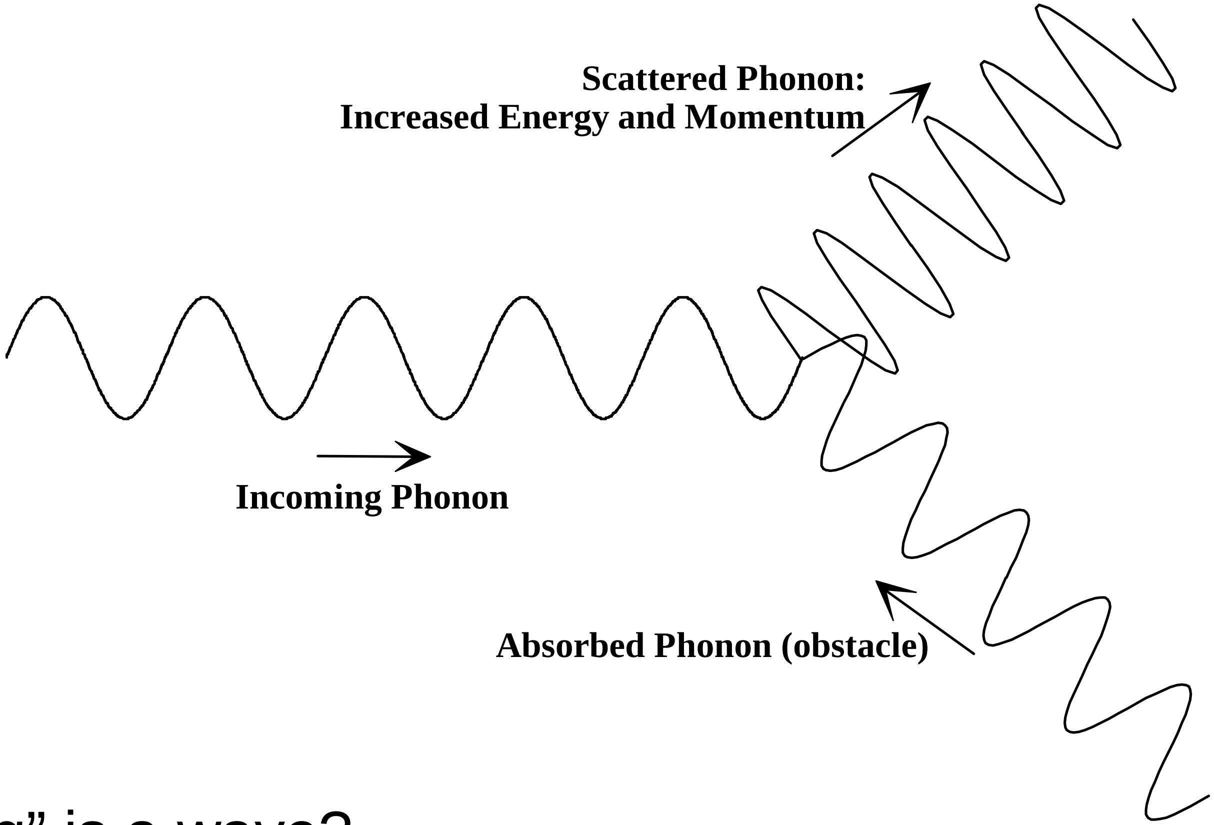
- Collision rate depends on aspects of both the obstacle and the incoming objects
- Mean free time = scattering time =relaxation time
- Scattering rate = collision rate = 1/(relaxtation time)

Phonon Scattering:

- No scattering = *nothing* restores equilibrium
  - So-called ‘ballistic’
  - Currents flow forever, even without temperature gradient
  - Thermal conductivity *not defined!*

- Phonon-phonon scattering
  - If the “springs” were ideal, phonons would just add up without affecting or interacting with each other
  - Many insulators (diamond, sapphire, BeO) are very close to ideal and have very large thermal conductivity
  - Non-ideal springs = phonons *do* interact with each other

Phonon-Phonon Scattering:

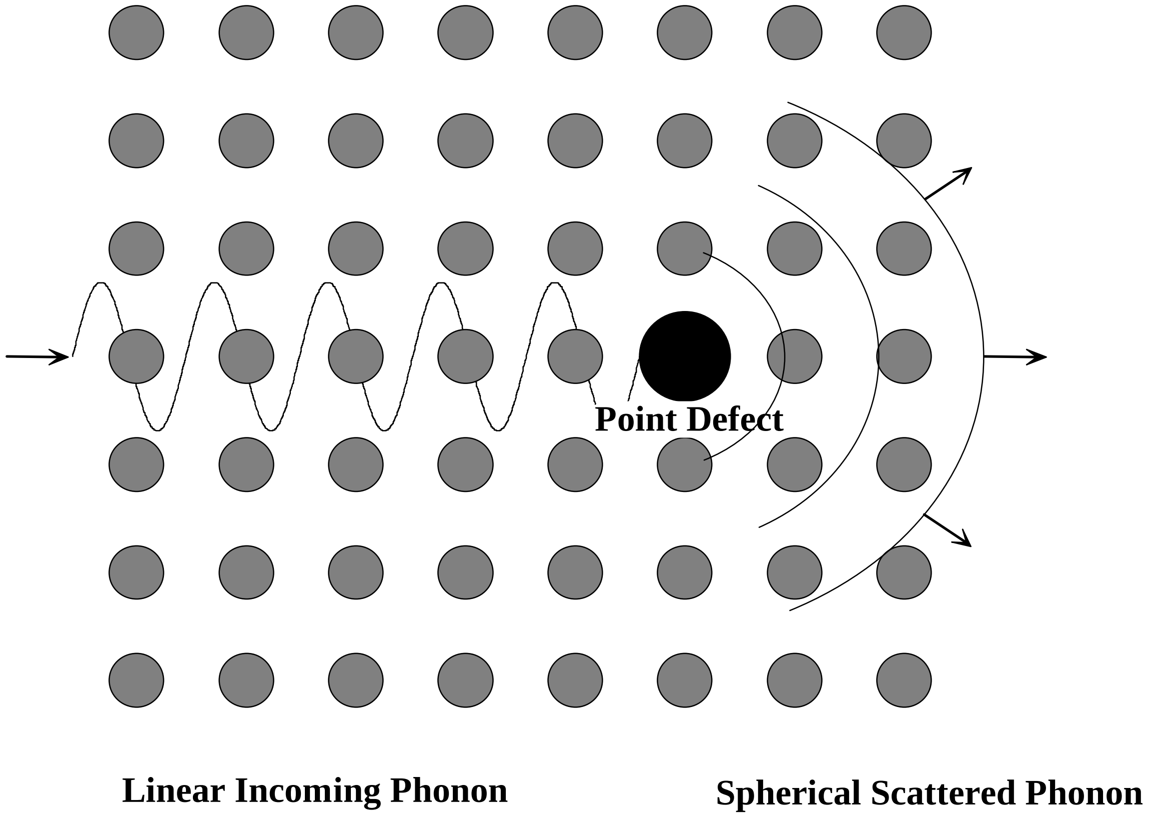


How “big” is a wave?

- Quantum mechanics is required, but you still are just calculating how often they collide.
- There are more phonons at high temperature, so scattering rate goes up with temperature.

Phonon Scattering by Point Defects

- aka Mass Fluctuation or Alloy Scattering



- Very effective at lowering the lattice thermal conductivity.
- High energy/short wavelength phonons most affected

Phonon Scattering by Charge Carriers

- Even a single phonon distorts the lattice
- This distortion shifts *the entire electronic band structure!*
- Therefore, phonons and charge carriers can exchange energy

- First, figure out how often a particular phonon interacts with a particular electron

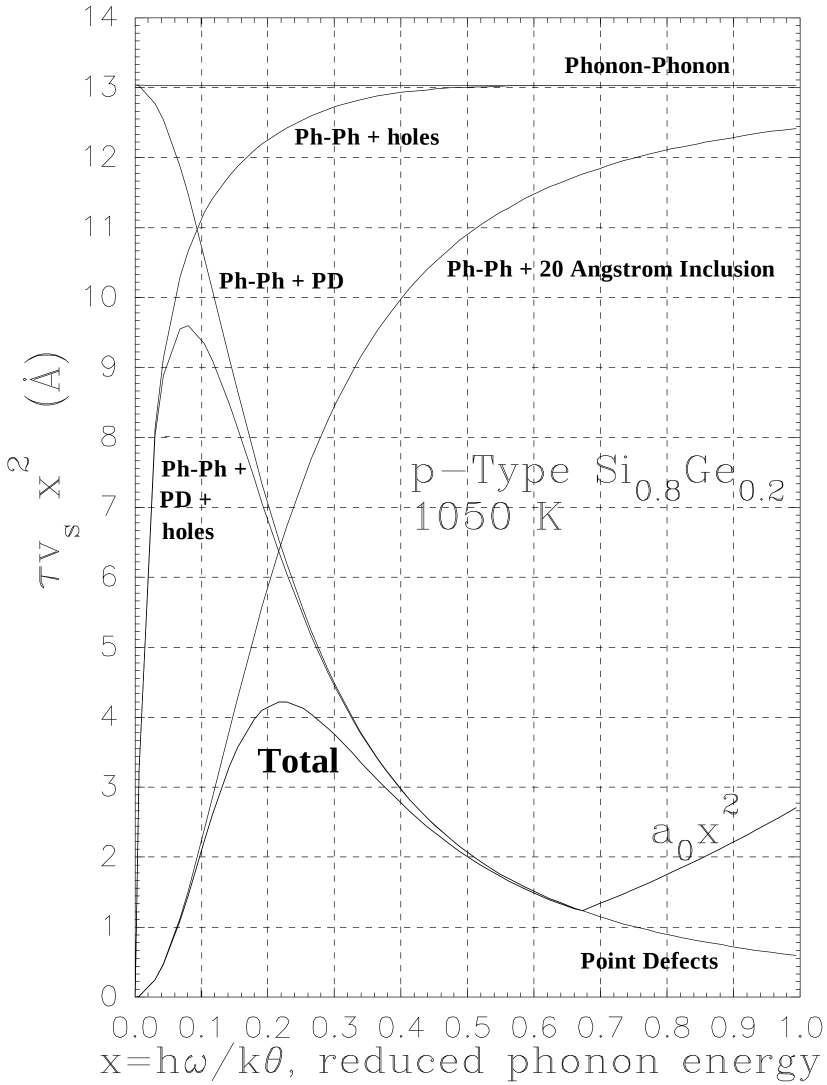
- Then, add up the effect of all electrons and you have the total scattering rate for that phonon.

Phonons Can Scatter Other Ways as Well

- Grain boundaries, inclusions, voids etc.

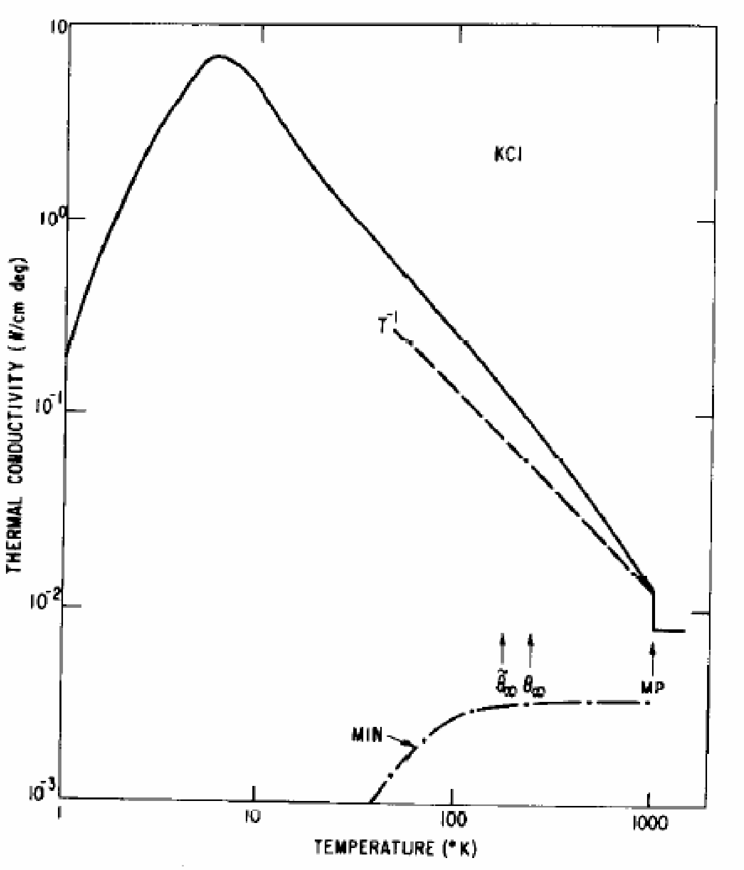
Typical Total Phonon Scattering Rate:

- “Mean Free Path” is the average distance traveled before colliding with something
- Phonon Mean Free Path is:
  - $l = \tau v$
- This figure shows MFP for Various Scattering Mechanisms
- Weighted for Heat Conduction calculation.
- Lattice Thermal Conductivity Given by the Area Under the Curve(s)



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 the 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.

Phonon Scattering Mechanisms

For TE, more phonon scattering is better

- Phonon-Phonon
  - All solids
- Mass & Strain Fluctuation
  - Aka: point defect scattering
  - Typical of solid-solution alloys, including all known thermoelectric materials
- Doping
  - Carriers scatter phonons (& vice versa)
  - Significant in some materials, not so important in others
- Void fillers
  - Aka “rattlers”
  - Especially in skutterudites, clathrates & chevrel phase
- Mixed-valence cations
- Grain boundaries, precipitates
  - Including size effects
  - Tempting, but has not yet been successful in enhancing ZT in bulk materials
  - May be important in superlattices & quantum wells

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
    - Lower speed of sound
  - Introduce as much phonon scattering as possible
    - Without screwing up electrical properties

Charge Carrier Transport

- The problem is treated in a similar manner
- We’ll only summarize key results here

Charge Carriers

We Need to Answer the Same Questions

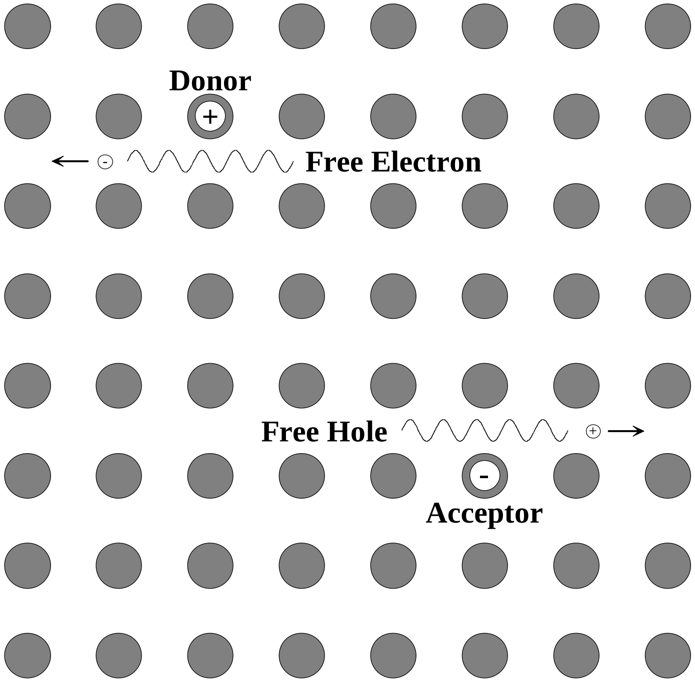
1) What charge carriers are allowed?
   This is the electron (or hole) dispersion relation

and

2) What charge carriers are actually present?
   This is the electron (or hole) distribution function.

Once we know these things, electronic properties are calculated pretty much the same way as phonon properties

Origin of Charge Carriers: ‘Doping’



Charge carriers are also considered to be waves

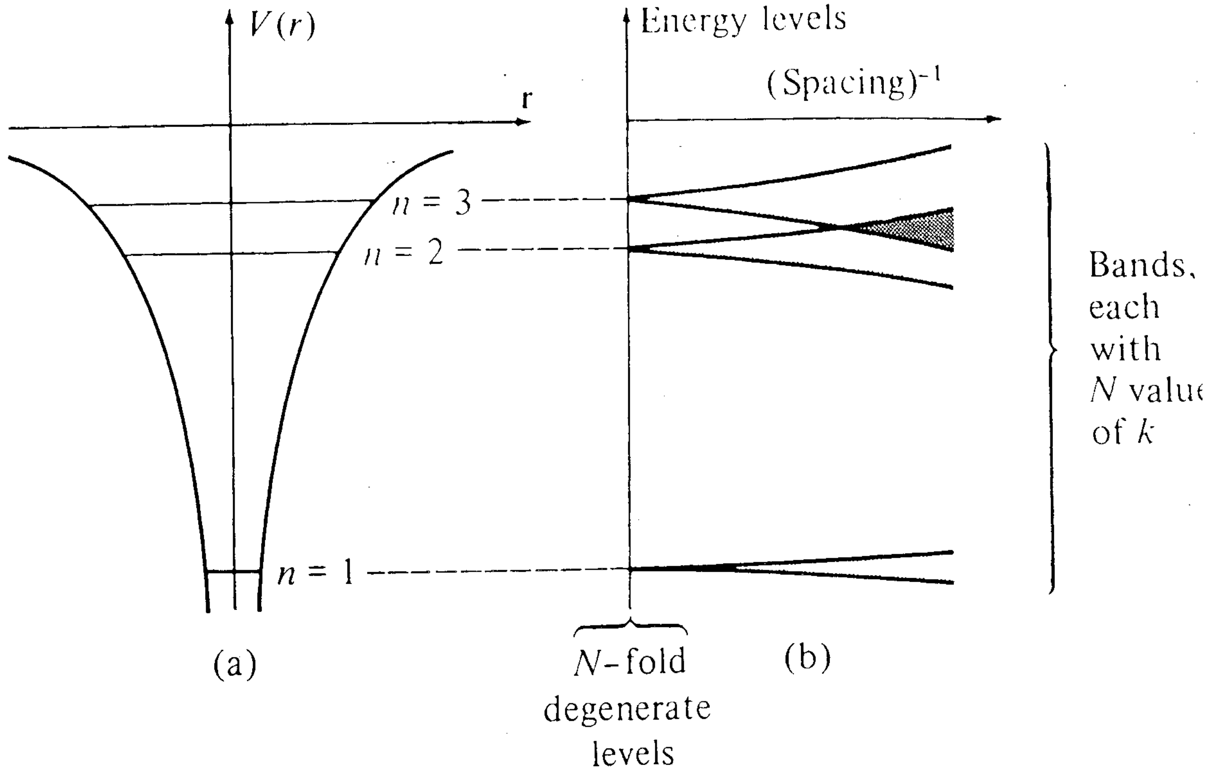
- *Here, too, any spatial distribution of charge can be represented by the waves.*

Usually from defects like substitutional atoms with more (or fewer) valence electrons than the host

Other kinds of defects can also create carriers

Energy Bands

Electronic structure, Band Structure, Electron (or hole) dispersion relation
- All these terms mean the same thing.

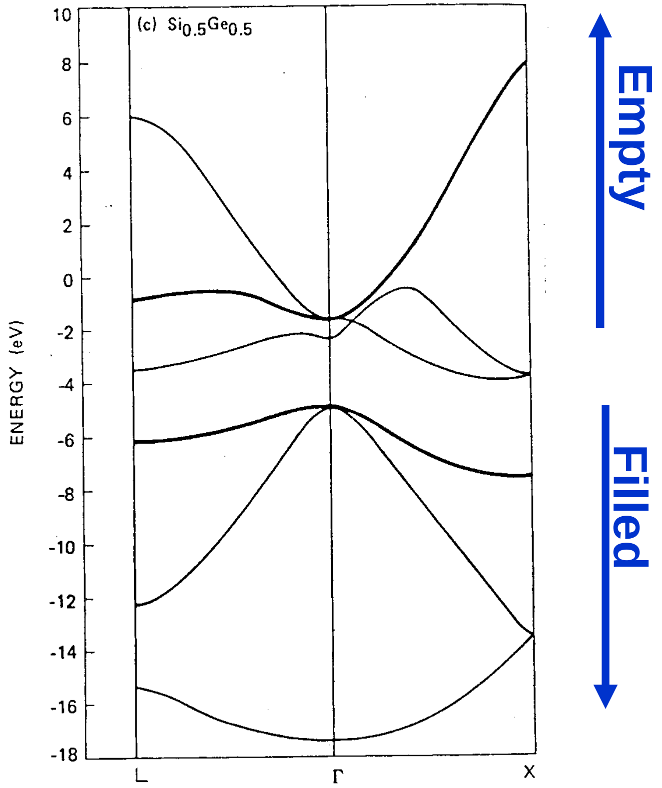


Isolated Atom

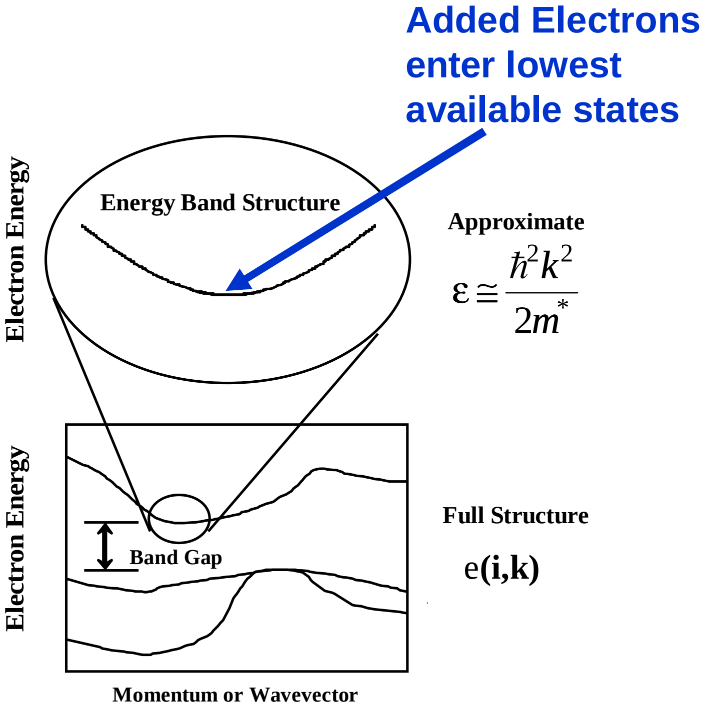
Energy levels form bands when many isolated atoms are brought together.

Electronic Band Structure = What Electrons are Allowed?

- Full calculation is a quantum mechanical, 3D plus & minus charge model of the full crystal lattice!



Full Electronic Band Structure for SiGe



Added Electrons enter lowest available states

Approximate

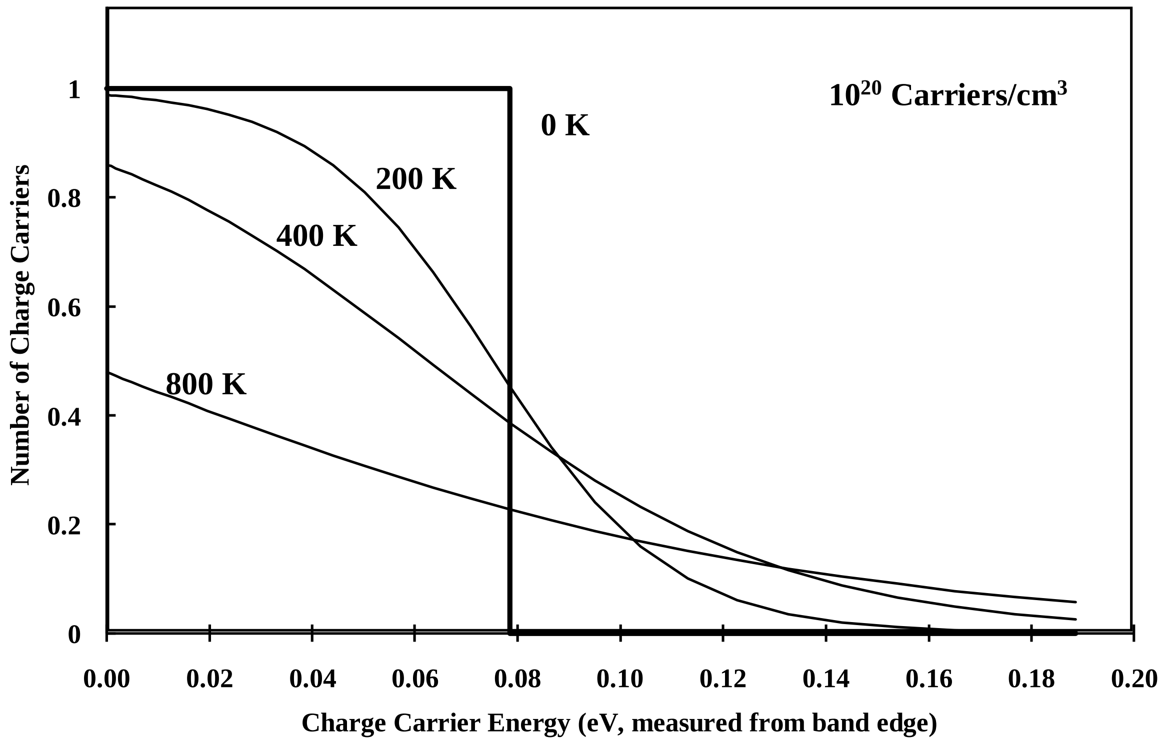
$$\varepsilon \cong \frac{\hbar^2 k^2}{2m^*}$$

Full Structure

$e(\mathbf{i},\mathbf{k})$

Approximate Models Commonly Used

Electron Distribution Function (in Equilibrium):



Pauli Exclusion Principle means no single energy level can be occupied by more than one electron

Calculating the Total Energy Associated with Charge Carriers

Total Property		Sum over allowed types of charge carrier, i	Sum over allowed wavenumber, k	Contribution of each carrier	*x*	Distribution Function
Energy	=	i=1, First Conduction Band i=2, Second Conduction Band i=3, First Valence Band i=4, Second Valence Band i=5, Etc.	$k \geq 0$ $k \leq 2\pi/a$	$\varepsilon(i,k)$	*x*	$f(i,k)$

Completely analogous to the previous phonon calculation

This Completes the Discussion of Equilibrium Properties

- Now, go on to non-equilibrium properties

- The dispersion relations remain unchanged
  - The same phonons/electrons are allowed/unallowed whether in equilibrium or not

- The distribution functions are different
  - Non-equilibrium forces and currents (drifting particles) tend to drive the distribution away from the equilibrium distribution
  - Scattering tends to restore equilibrium

Charge Carrier Scattering:

- No scattering = *nothing* restores equilibrium
  - Currents flow forever
  - Actually happens! --- Superconductors

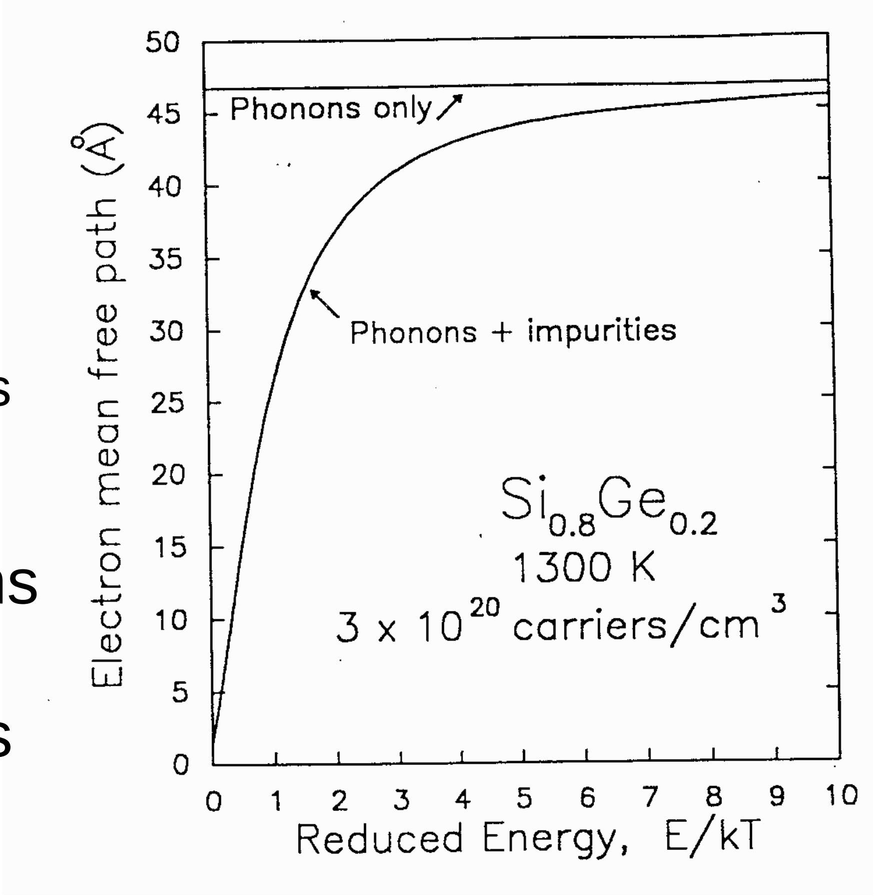
- Electron-phonon scattering
  - Every time a phonon scatters an electron, the electron got scattered too!
  - Often, this is the only really important scattering
  - Scattering increases with temperature

- Charged Impurity Scattering
  - Donors and acceptors contribute to scattering

- Alloy scattering
  - Alloys lower the electrical conductivity, too.

Typical Total Electron Scattering Rate:

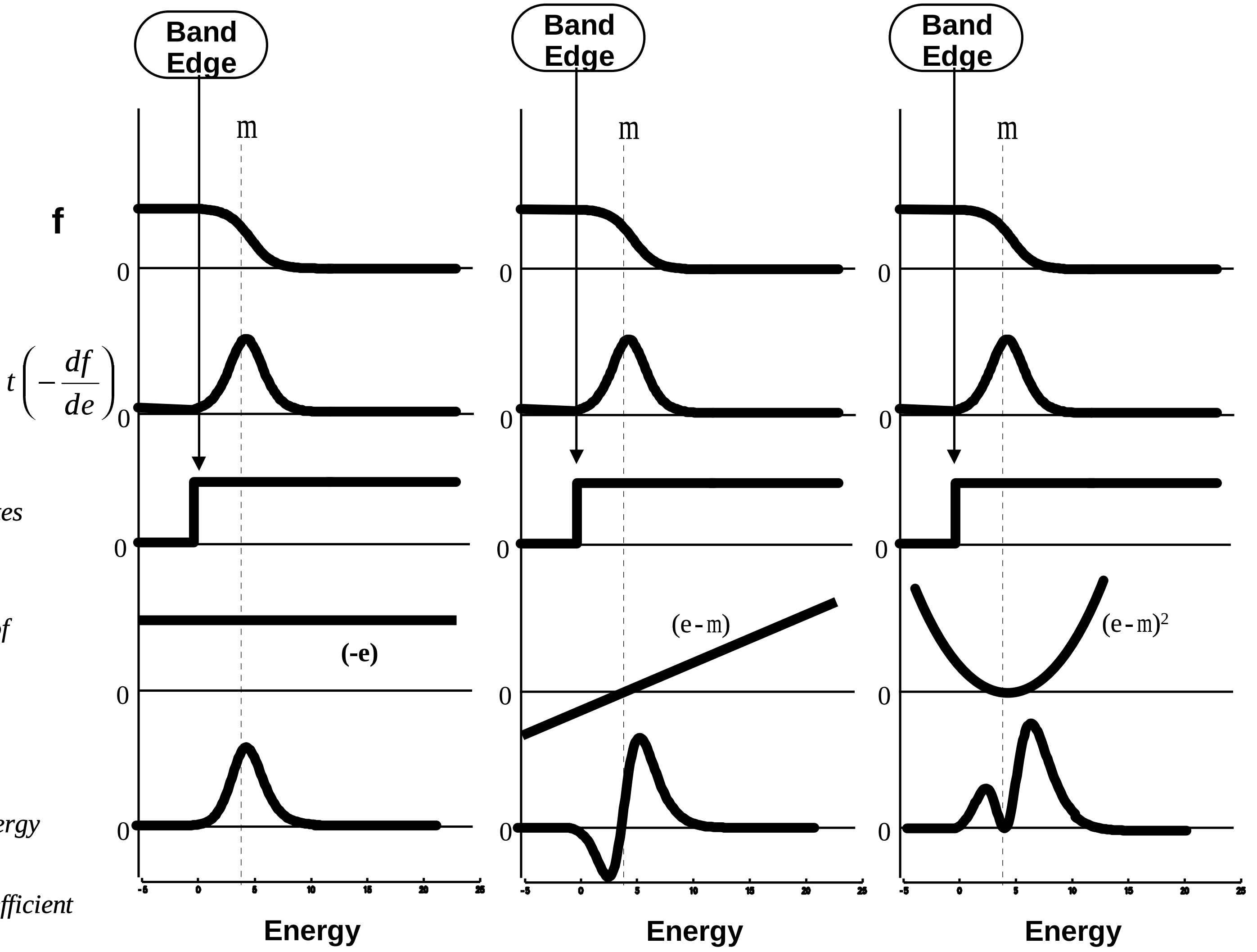
- Electron Mean Free Path
  - $l_e = \tau_e v_e$
  - Phonon and Impurity Scattering
  - Typically, these are the main carrier scattering mechanisms
    - Poor sample quality, cracks, grain boundaries etc.
- Phonons scatter all electrons
- Charged impurities mostly scatter low energy electrons
- It is much easier to reduce the mobility than to improve it!



Electronic Properties

- From the scattering rate (τ^{-1}) & electron distribution function, can calculate each of the important electronic properties:
  - σ, electrical conductivity
  - S, Seebeck coefficient
  - λ_e, electrical contribution to thermal conductivity
- They are each intimately related
  - Each is calculated by a weighted average of τ
    - Just a different weighting factor
  - If one changes, they all change in highly predictable ways

Putting It All Together for Charge Carriers



Equilibrium Distribution Function

Deviation from Equilibrium

Density of States

Contribution of Each Carrier

Weighted Contribution from Each Energy

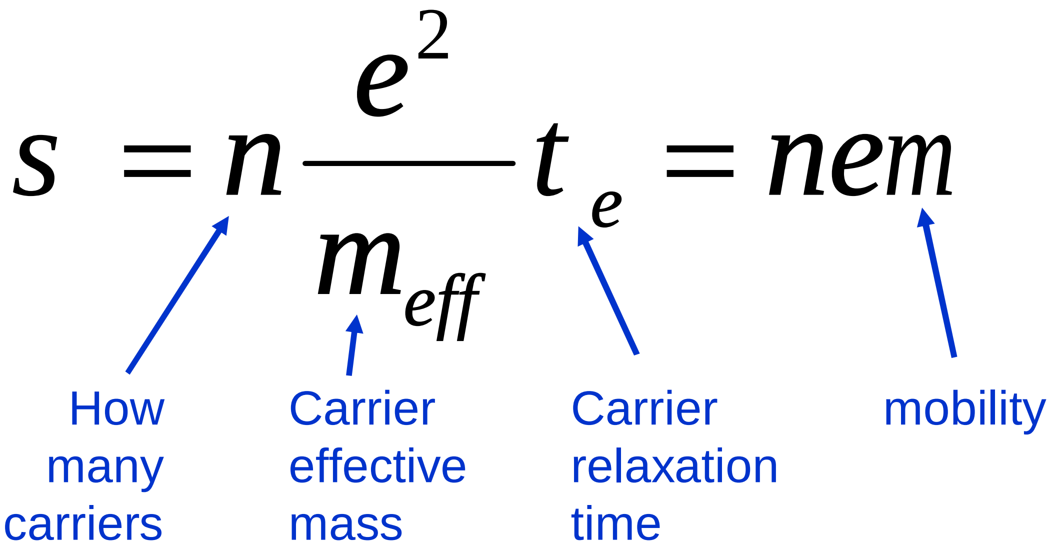
Transport Coefficient Given by Area Under Curves:

$I_0 = \sigma$

$I_1 = \sigma |S|$

$I_2 = \lambda + \sigma S^2 T$

Carrier Relaxation Time & Mobility



$$s = n\frac{e^2}{m_{eff}}t_e = nem$$

How many carriers

Carrier effective mass

Carrier relaxation time

mobility

- The carriers behave a lot like ordinary electrons
  - EXCEPT they have a different “effective” mass
- The mobility can be directly measured
  - Ex: by Hall effect
- μ represents ‘how well’ each carrier conducts electricity
  - As opposed to n which represents ‘how many’ carriers there are
- We always want a bigger μ
  - Make better quality samples!
  - Choose compounds with small electronegativity differences
- But carrier concentration generally needs to be optimized

Seebeck Coefficient

The simplest formula

$$\left|S\right| = \frac{k_B}{e}\left(2 - \ln\left(\frac{n}{n_o}\right)\right) = \frac{k_B}{e}\left(2 + \frac{3}{2}\ln\left(\frac{T}{300}\right) + \frac{3}{2}\ln\left(m_{eff}\right) - \ln\left(\frac{n}{2.5x10^{19}\ \mathrm{cm}^{-3}}\right)\right)$$

A Normalized Carrier concentration

86 μV/K

Increases with carrier mass

Decreases slowly with carrier concentration

- Looks a bit complex, but it is essentially the same as the entropy of an ideal gas
- Seebeck is the most robust property, with respect to sample quality
- We generally want a higher effective mass
- Carrier concentration is to be optimized

Electronic Contribution to λ

$$\lambda = \lambda_p + \lambda_e = \lambda_p + L_o\left(\frac{k_B}{e}\right)^2 \sigma T$$

Phonon contribution

Electronic contribution

Lorentz number between 2 & $\pi^2/3$

- The Lorentz number depends weakly on carrier concentration
  - Pick the larger number to be conservative, or
  - Use a more complete model to calculate L_o
- The lattice (aka phonon) thermal conductivity can be measured directly only in rotten electrical conductors
  - For doped semiconductors & metals, λ is measured & λ_p estimated by subtraction

Simplest theory of ZT

- Take the simplest theory of semiconductors
- Connect each property to the carrier concentration
- ZT depends on
  1. The carrier concentration through ‘x’
  2. A materials parameter ‘β’, which acts as a kind of ‘Figure of merit’ for ZT
- Finding a large ZT is now a problem of finding a large ‘β’ and optimizing the doping

$$\frac{1}{r} \equiv s \equiv enm$$

$$S = \frac{k_B}{e}\left(2 - \ln\left(\frac{n}{n_0}\right)\right)$$

$$l = l_e + l_p = 2\left(\frac{k_B}{e}\right)^2 sT + l_p$$

$$ZT = \frac{S^2 sT}{l} = \frac{x(2 - \ln(x))^2}{2x + \frac{1}{b}}$$

where

$$x = \frac{n}{n_0}\text{, a normalized carrier concentrat ion}$$

$$b = \left(\frac{k_B}{e}\right)^2 \frac{en_0 mT}{l_p}$$

$$= 9x10^{-6}\frac{mm_{eff}^{1.5}}{l_p}T^{2.5}$$

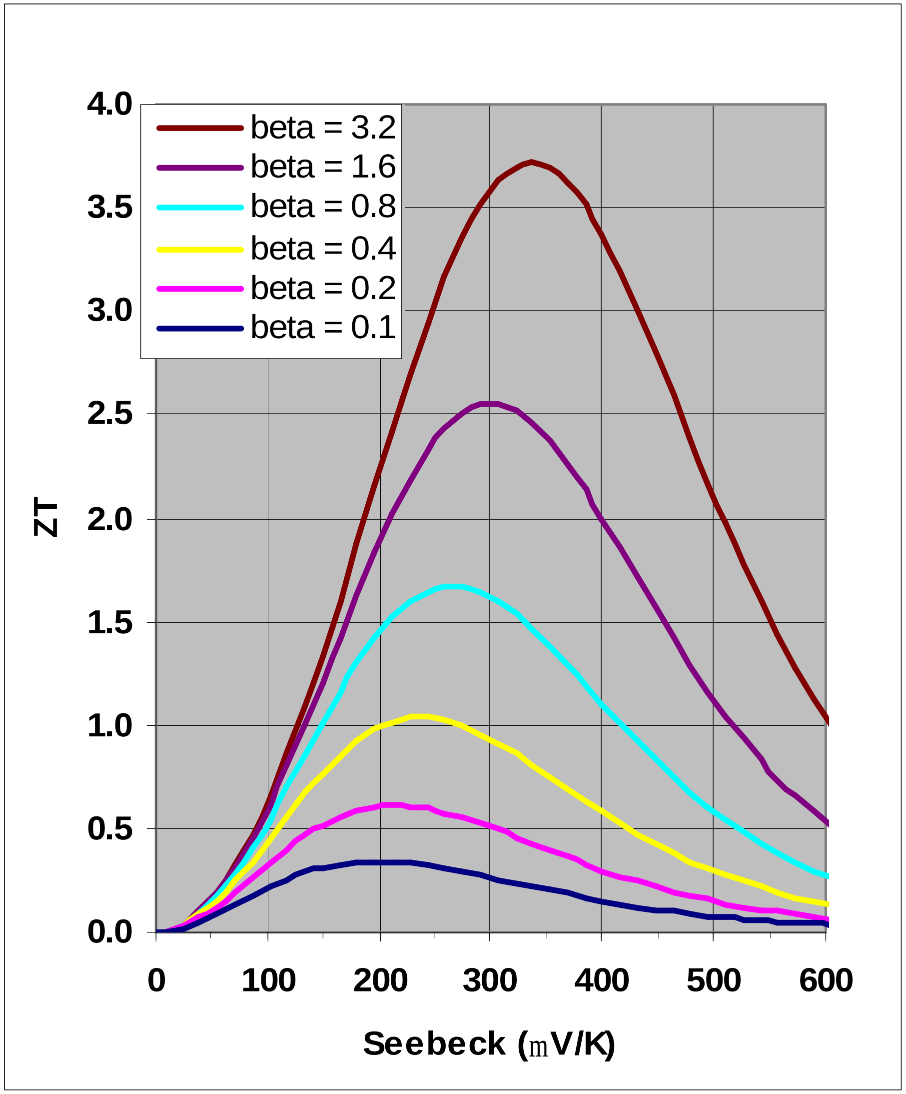
Optimize the Carrier Concentration

- 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

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

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

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



Slack's "Weighted Mobility" Vs. Electronegativity

- Slack introduced the term 'weighted mobility' in 1995
  - $U = m^{3/2}\mu$
  - The electrical part of β, predicts high ZT
- U seems larger for small electronegativity differences
  - Empirical & theoretically 'reasonable'
  - But not rigorous
- Most all good thermoelectrics have small electronegativity differences
- Extremely useful for selecting candidate compounds for closer scrutiny

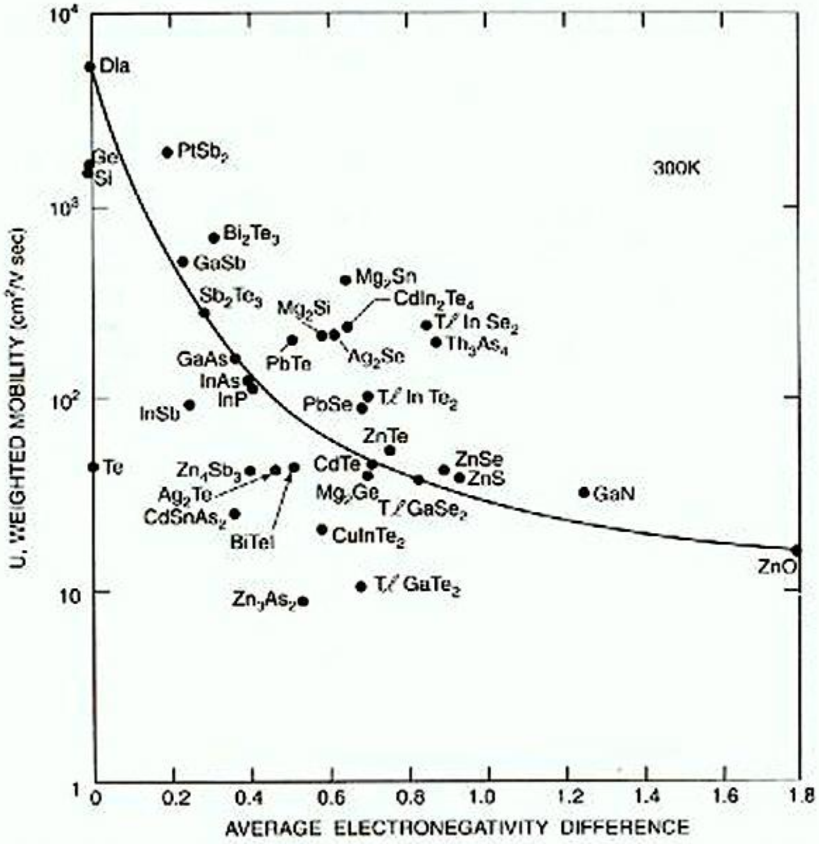
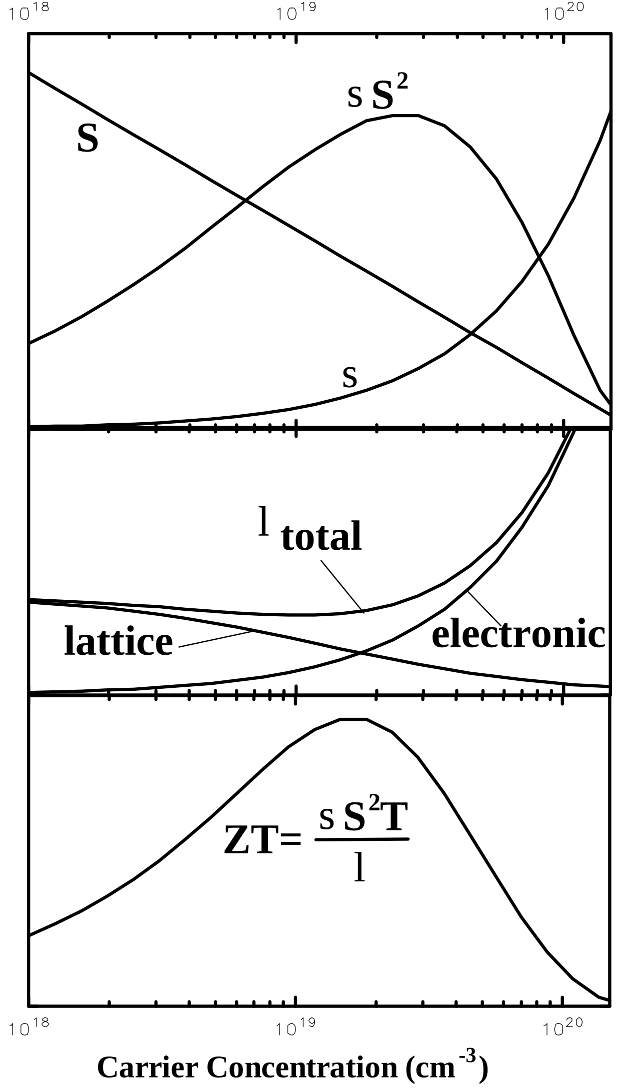
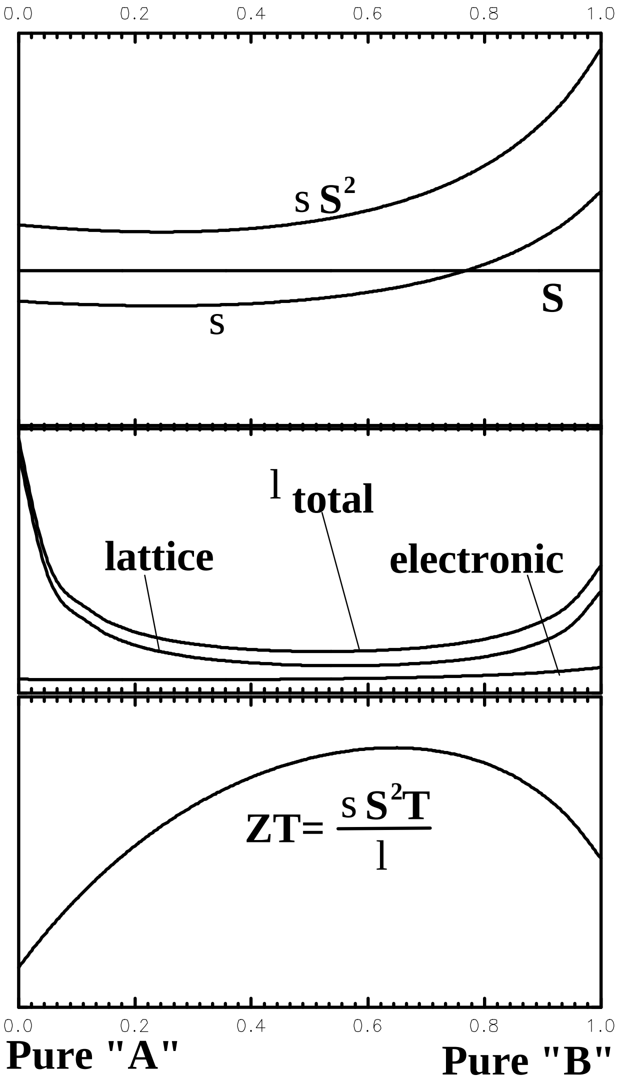


FIGURE 11 The weighted mobility, U, at room temperature for lightly doped or intrinsic samples as a function of the average electronegativity difference, $|\overline{\Delta X}|$.

Slack, G. A. (1995). New materials and performance limits for thermoelectric cooling. <u>CRC Handbook of Thermoelectrics</u>. D. M. Rowe. Boca Raton, FL USA, CRC Press, Inc.: 407.

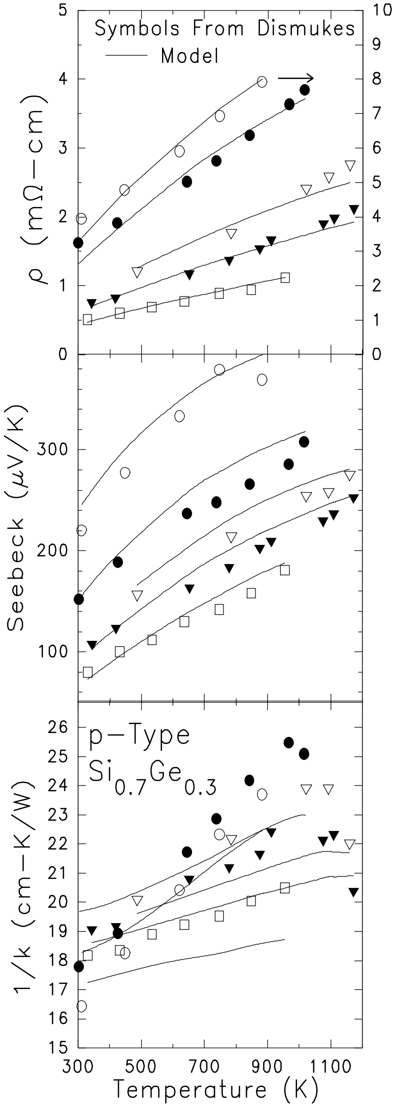
Conclusion: Doping and Alloying are the Major Classical Effects
$A_{1-x}B_x$: optimize doping & ‘x’

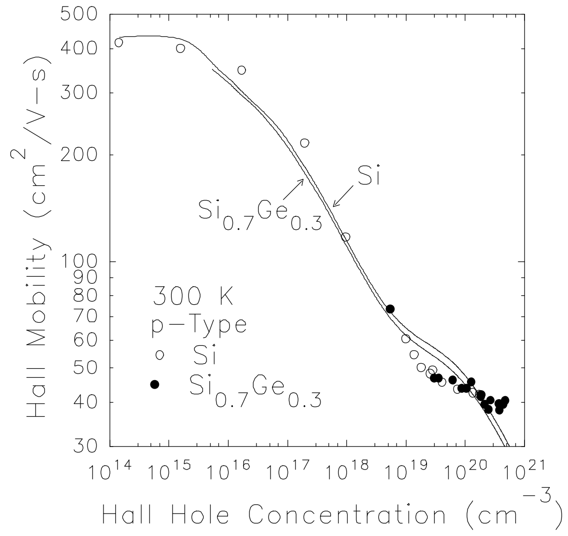




More Detailed Model

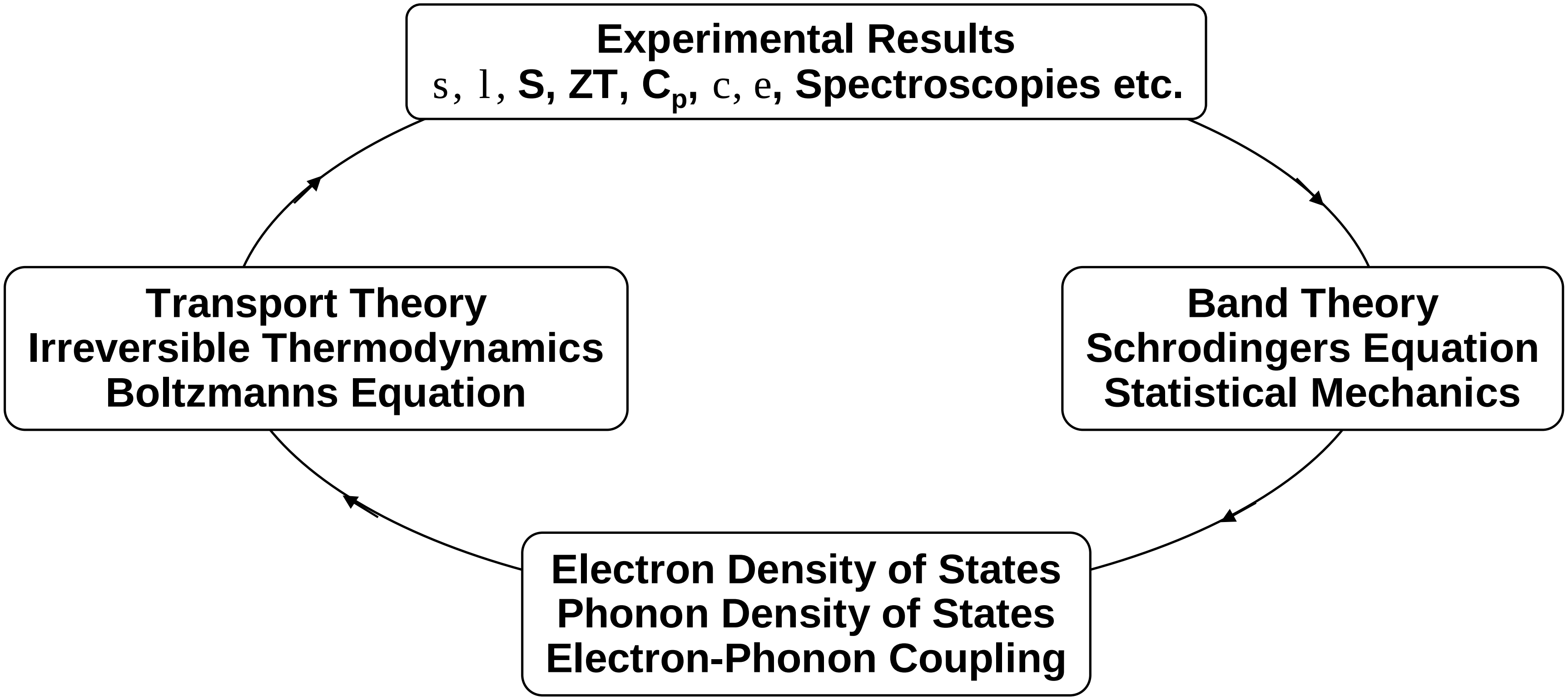
- **Today, increasingly detailed and quantitative models are possible**
- **Any transport or thermodynamic property of interest can be calculated self-consistently**
- **Quantitative agreement with mature materials is excellent**





There is no rigorous, theoretical upper limit on ZT

- **Theory has been iterated to *force* agreement with experiment**
- **The success of theory for known materials is powerful and gratifying**
- **BUT, this says NOTHING AT ALL about fundamental limits**



Experimental Results
s, l, **S, ZT, C_p,** c, e**, Spectroscopies etc.**

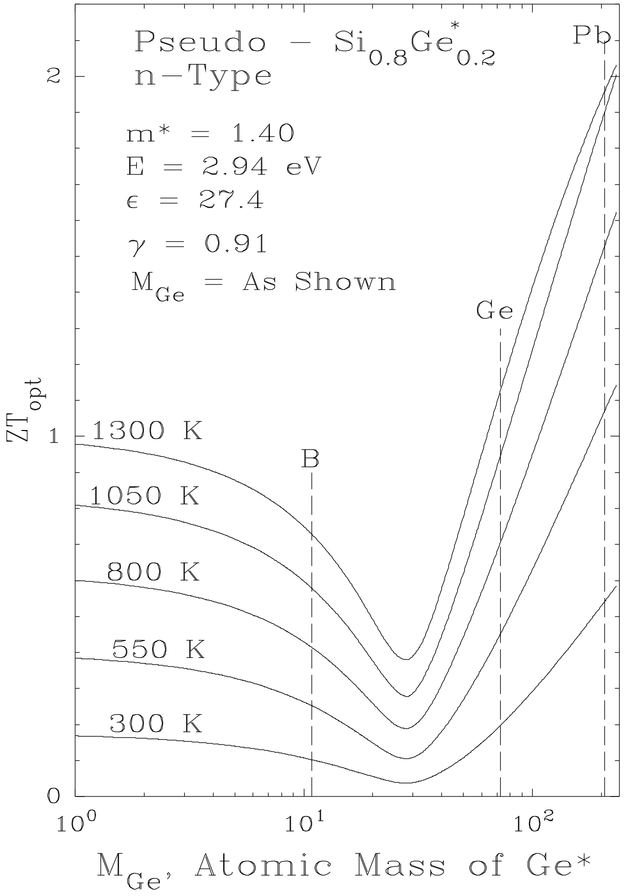
Band Theory
Schrodingers Equation
Statistical Mechanics

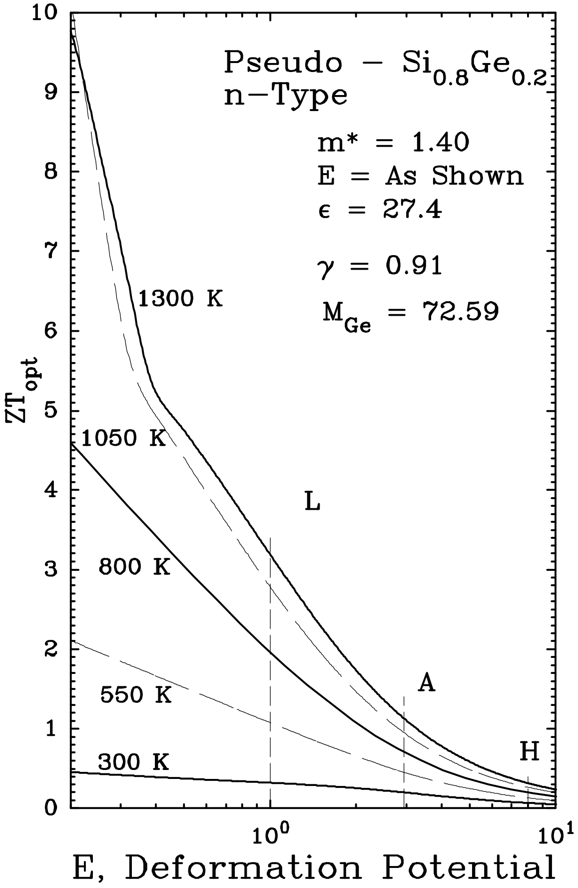
Electron Density of States
Phonon Density of States
Electron-Phonon Coupling

Transport Theory
Irreversible Thermodynamics
Boltzmanns Equation

Model Extrapolations

- **Even detailed models, constrained to accurately describe real materials, allow larger ZT values**
- **Physically plausible variations of microscopic parameters can yield several fold improvements in ZT**





How To Increase ZT

- **All approaches fall into one of three categories:**

1. Decrease the lattice thermal conductivity
  - **Focus on phonons**
  - **Larger unit cell and higher mass to decrease sound velocity**
  - **Increase disorder to decrease phonon mean free path**
  - **‘rattlers’**
  - **Superlattices**

2. Increase the carrier mobility
  - **New, covalently bonded materials**
    - **Small electronegativity difference (Slack)**
  - **Heterostructures to physically separate carriers from scattering centers**
    - **Proposed, but little progress to date**

3. Increase the thermopower
  - **Larger effective mass materials**
    - **Quantum wells essentially adjust the effective mass**
  - **Barriers to inhibit transport of low energy carriers**
  - **Novel band structures and/or scattering mechanisms**

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 U)

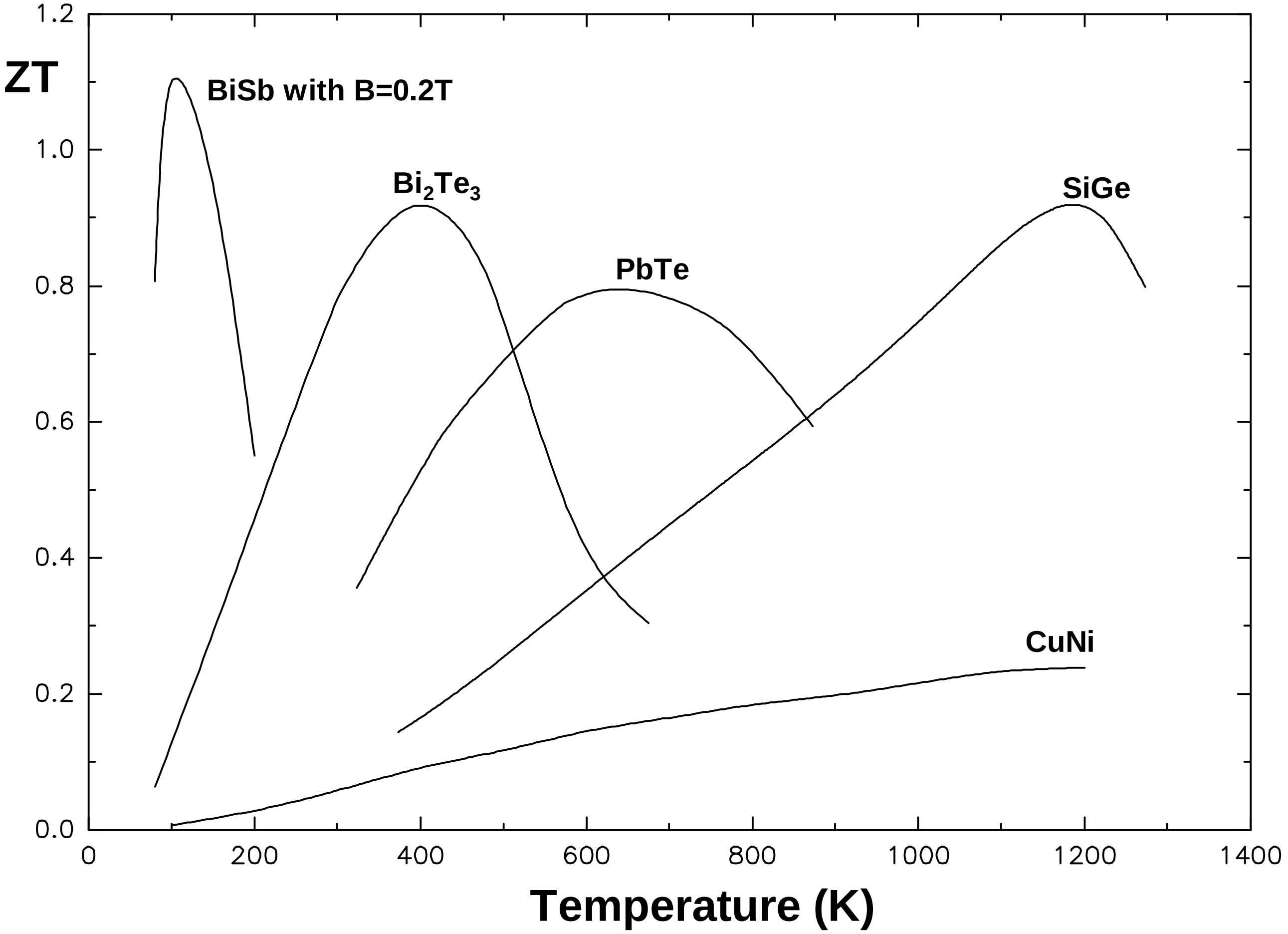
- Slack introduced the PGEC concept for the 'ideal' thermoelectric
  - Conducts heat like a glass
  - Conducts electricity like a perfect crystal
    - Introduced the small electronegativity guideline for high mobility
- The PGEC concept has proved a powerful motivation for experimentalists and theorists 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
- Higher values (if possible) likely require 'Quantum' effects

Materials Science & Developing New TE Materials

The art of Materials Selection

- We’ve actually learned a lot:
  - We need materials that can be doped to get S~200 μV/K
    - Nearly rules out all metals
  - We need decent carrier mobility values
    - Nearly rules out amorphous & glassy materials
  - We need materials that conduct heat poorly
    - Nearly *REQUIRES* amorphous or glassy materials!!
  - Requirements are somewhat contradictory
- What exactly is
  - The effective mass
  - Lattice thermal conductivity
  - Electrical mobility
- How do I estimate & control them?
- Where do I look for favorable materials?

Pre 1992 Experimental ZT Results



Constantan:

- An alloy of 50% Cu – 50% Ni
- Cheap, easy to make
- Has ZT~0.25 @ 1200 K
- Don't be impressed unless you can do better than that!

Measurement Techniques

INTRODUCTION

- ZT requires determination of at least three properties
  - σ, λ, S
  - usually also interested in R_H, μ_H, C_p, thermal diffusivity, and sometimes others
  - optimum geometry differs for different properties
  - But you need to know all the properties for the same sample, in the same ‘state’
- Transport properties are notoriously difficult to measure
  - Often, not all properties are measured on the same sample
    - Unavoidable in the early stages of development
    - Risky!
  - Standards, Standards, Standards
- Novel materials may initially be available only in inconvenient forms
- Thin-films may require totally new measurement techniques

Measurement Theory

Linear Response

$$\bar{i} = s\left(\bar{E} - S\bar{\nabla}T\right)$$

$$\bar{q} = \bar{i}ST - l\,\bar{\nabla}T$$

$$\text{Charge conservation} \quad \dot{\mathrm{n}} + \bar{\nabla}\cdot\bar{i} = 0$$

$$\text{Heat balance} \quad C_p\dot{T} - \bar{\nabla}\cdot l\,\bar{\nabla}T = \bar{i}\cdot\left(\bar{i}\,r - T\,\frac{\P S}{\P T}\,\bar{\nabla}T\right)$$

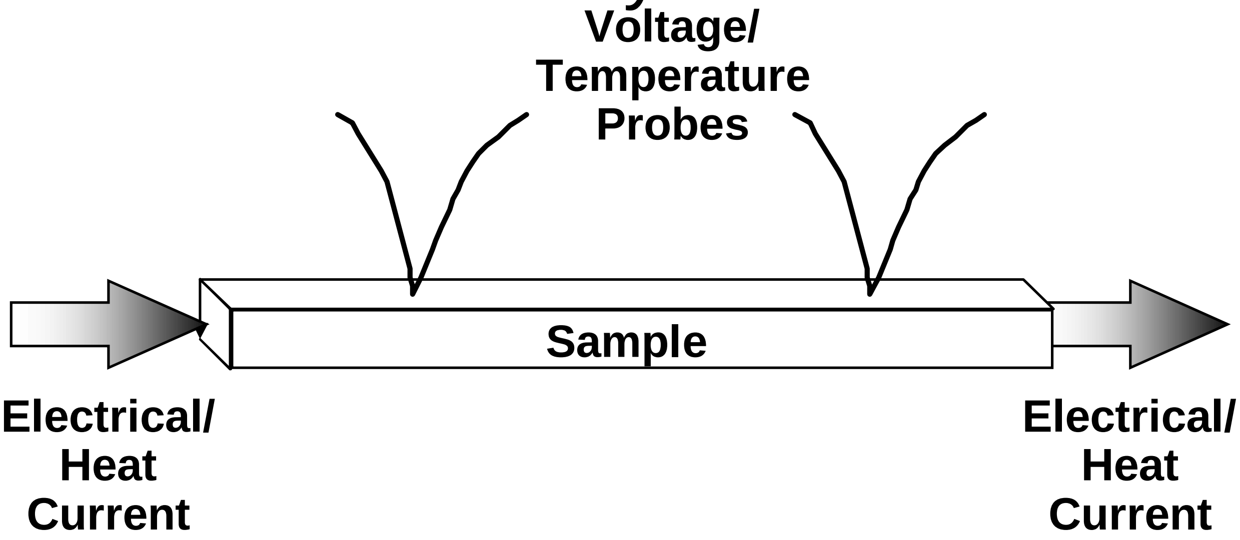
Boundary conditions: $\bar{i}, \bar{q}$, T and/or V defined along boundary surfaces

Usually reliable simplifying assumptions: $\dot{n} = 0, \frac{\P\, l}{\P T} = 0, \frac{\P S}{\P T} = 0$

Essentially the same issues as arise when designing a device

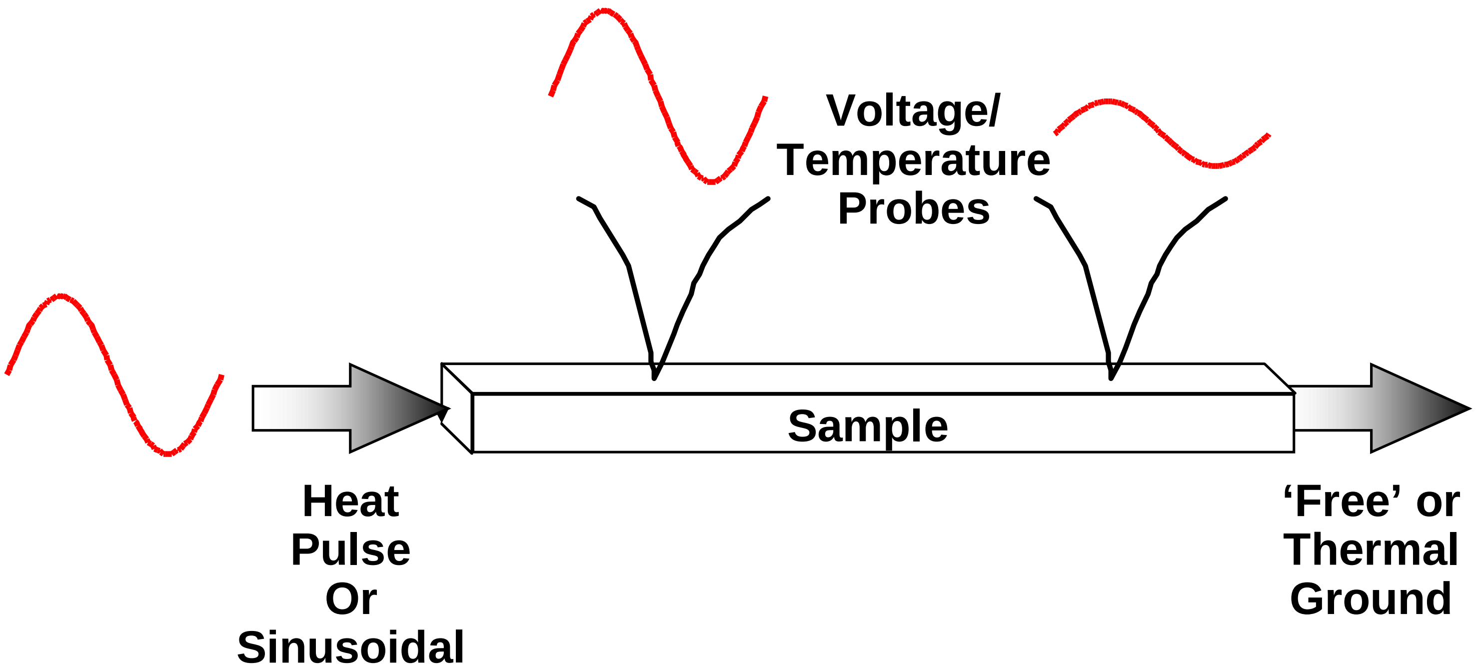
Measurement is a device optimized for accuracy & precision, at the expense of efficiency & power

Classic Steady State Methods



- **Advantages:**
  - **Simple analysis of data, eg.** $s = \frac{L}{A}\frac{I}{\Delta V},\ l = \frac{L}{A}\frac{Q}{\Delta T},\ \mathrm{S} = \frac{\Delta V}{\Delta T}$
- **Disadvantages**
  - **Requires special sample geometry**
    - **long samples not always available**
  - **May be difficult maintaining boundary conditions**
    - **Especially heat losses**
  - **Sensitive to noise**

Dynamic Thermal Methods



- **Thermal Diffusivity determined from the (smaller) response along the sample**
- **Advantages:**
  - **Much less sensitive to loses like radiation**
  - **Less sensitive to noise due to 'characteristic' thermal response**
- **Disadvantages**
  - More complex data analysis
  - Require separately measured heat capacity to get $\lambda=C_p\alpha$

Dynamic Methods

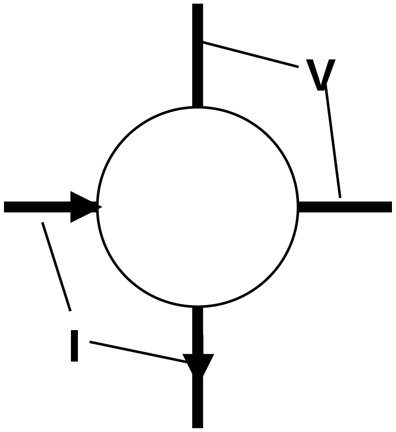
- **Many variations are possible**
- **Typically fast, so measurement can be repeated**

- **Measurement information has characteristic form, distinct from noise**
  - **AC response is only at the excitation frequency**

- **Thermal relaxation typically much slower than electrical**
  - **Current reversal or AC resistance measurement eliminates thermal EMF**

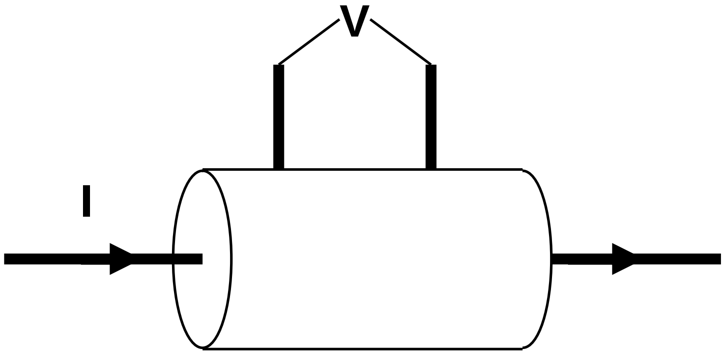
- **Reduced heat losses in dynamic thermal conductivity techniques**
  - **Ångstrom method**
  - **Flash method**
  - **3-w method**

Alternate Geometries



- Van der Pauw’s method
- Resistivity, Hall effect

$$r = [geometry\ factor]\frac{V}{I}$$



- Point contact current probes
- Developed at JPL for cylinders

Geometry correction factors may be reliably calculated from the boundary value problem even for relatively complex geometries

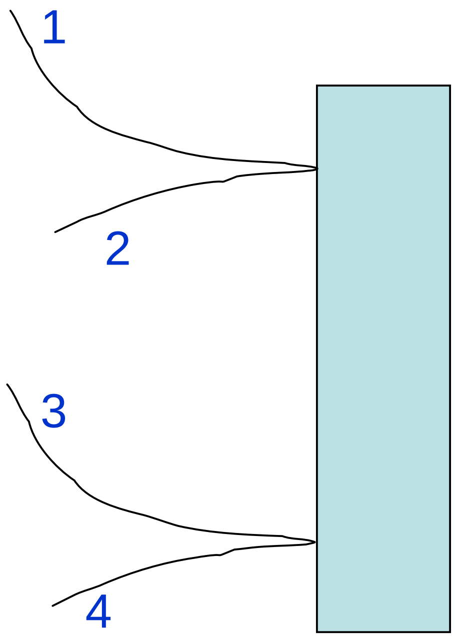
Place burden on analysis more than sample

Seebeck Measurement

- Geometry Independent

$$S_{sample} = S_1 + \frac{\Delta V}{\Delta T} = S_1 + S_{1-2}\frac{V_{1-3}}{V_{1-2} - V_{3-4}}$$

- Only as good as your ability to measure small temperature differences
- Correct for the Seebeck coefficient of the lead wire
- Be sure there is no heat flowing down wire
  - i.e. thermocouple joint should be same temperature as sample surface
- Seems simple, but high precision isn't always easy
- Standards with high Seebeck coefficient are not available



RCA's modified Ångstrom

- Allowed simultaneous measurement of
  - Thermal diffusivity
    - Need heat capacity & density to get λ
  - Electrical conductivity
  - Seebeck coefficient
- Developed in 1960 & used by RCA through 1960's
- Sadly, appears to not have been replicated despite excellent results

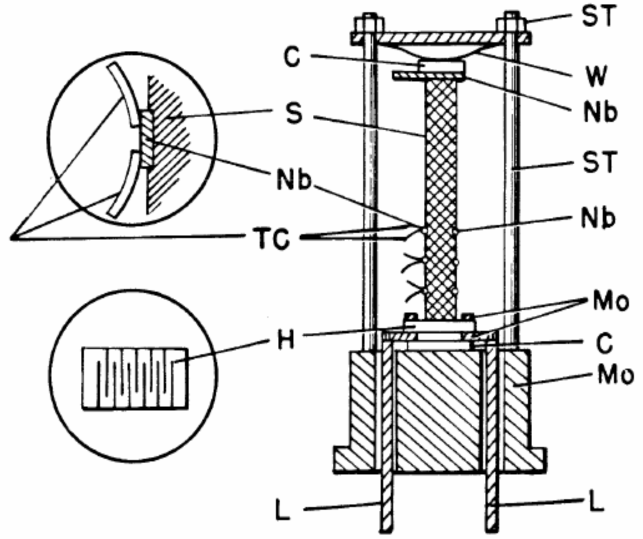


Fig. 27. Sample holder: C, ceramic spacer; H, metallized ceramic heater; L, molybdenum heater current leads; Mo, molybdenum; Nb, niobium; S, sample; ST, stainless steel; TC, chrome-alumel thermocouples; W, tungsten

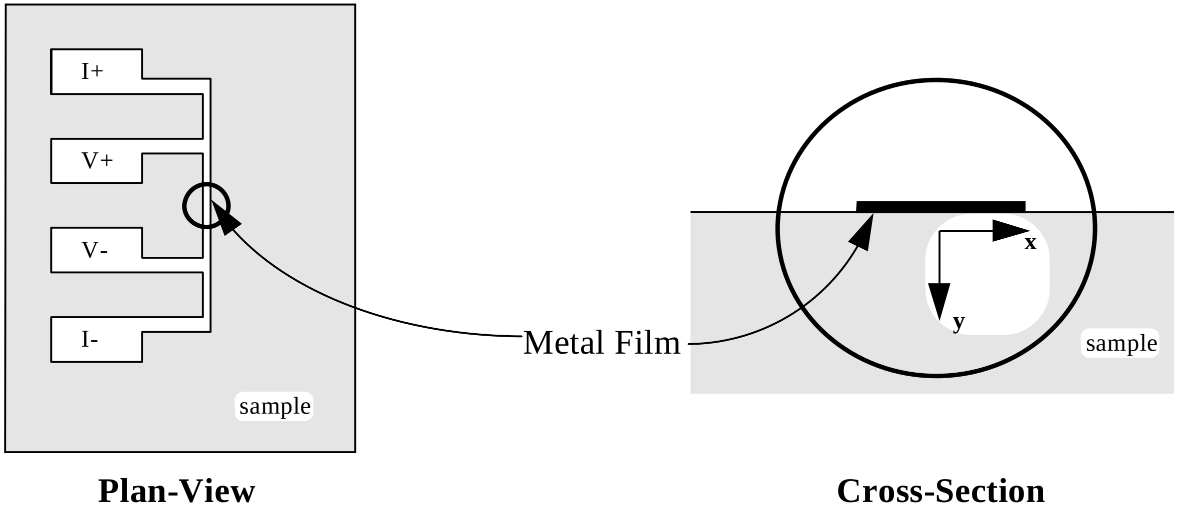
Harman-Like Methods

- **In an isothermal sample**
  - **V=IR**
  - **with some geometry factor relating R to resistivity**

- **The same sample, if thermally isolated instead, yields**
  - **V=IR(1+ZT)**

- **Harman's method and Parker's small area contact method use this idea**
  - **In principle, determines ZT directly**
  - **Contact resistances and heat loss can reduce reliability**

3-ω Method



- Measure film resistance and temperature dependence of film resistance
- Apply a current to the metal film at frequency w
- Primary signal at voltage probes is at frequency w
- But, I^2R heating in film results in temperature variations at frequency 2w
- Because film resistance varies with temperature, secondary signal at voltage probes varies at frequency 3w
- Analysis of secondary signal yields thermal conductivity
- Using additional thermometers, thin films less than 100 Ångstroms have been measured

SUMMARY

- A wide variety of measurement methods are available
  - No single method is likely to serve in all situations of interest
- Each method has characteristic strengths and weaknesses
  - Significant results require duplication by alternate methods
- Standards, Standards, Standards
- Expect and demand to see error bars
  - And understand method of estimating errors
  - Accuracy: How close to the real, absolute value
  - Precision: Ability to reproduce the same answer
  - Systematic errors can be highly precise, but very inaccurate
  - Random errors can be accurate if averaged over large numbers of observations
- 1% error each in S, ρ, C_p, thermal diffusivity, density yields ± 6% error in ZT
- Measurements are too often given short shrift

Case Study I: SiGe

Early History of SiGe

- In 1960 RCA began a broad-based general study of high temperature materials
  - Particularly needed better understanding of phonon thermal transport @ high temperatures
  - Began an extensive program to simply catalog and understand the properties of Ge, Si, Ge-Si alloys and related III-V compounds
  - New theoretical understanding & new data led to a thorough study of SiGe alloys
  - SiGe was not so much “discovered” as it was the natural outgrowth of a general, systematic study of the basic science of poorly understood materials
- The basic science & feasibility studies were done at RCA’s R&D Laboratory in Princeton, NJ beginning about 1957
- Within about 4 years from the decision to focus research on SiGe in RCA’s Princeton Laboratories, the technology was transferred to an RCA operating division (Harrison, NJ) where modules were fabricated.
  - An amazing pace from basic R&D, to feasibility, to use in space

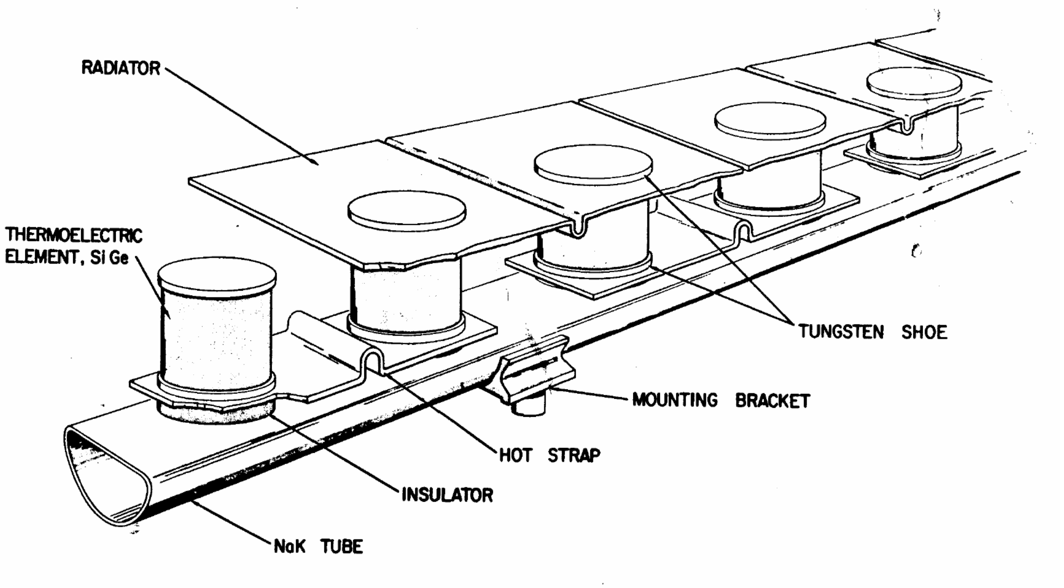
- Note that all the early basic science work was funded by the US Navy, Bureau of Ships for potential use in the nuclear Navy
  - Experimental efficiencies as high as 10% achieved ΔT=925 oC – 25 oC = 900 oC
  - Attracted DoE & NASA attention in the early 1960’s

Concept to Space Flight

- In 1960 there were no TE materials that could operate above 500-600 ^{o}C
- By 1962 had measured & published 7.3% efficiency in SiGe couple between 300-1140 K
  - Abeles, B., D. S. Beers, et al. (1962). "Thermal Conductivity of Ge-Si Alloys at High Temperatures." Phys. Rev. **125**(1): 44-46.
- By 1965 SiGe modules were launched in space
- In the words of the inventors:
  - "..testimony to the serendipitous outcome of long-range and basic research"
  - Cody, G. D., B. Abeles, et al. (1990). Research and development of the silicon-germanium thermoelectric power generator: the long term payoff of basic research. Proceedings of the IX International Conference on Thermoelectrics (ICT90), Pasadena, CA, Jet Propulsion Laboratory p.182-205.

SNAP-10A – Launched 1965

- 100 modules made from zone leveled SiGe
- T_c=327 ^oC, T_h=483 ^oC, 1.9% efficiency (!)
- 500 Watts @ 30 V



SNAP 10A Module Section

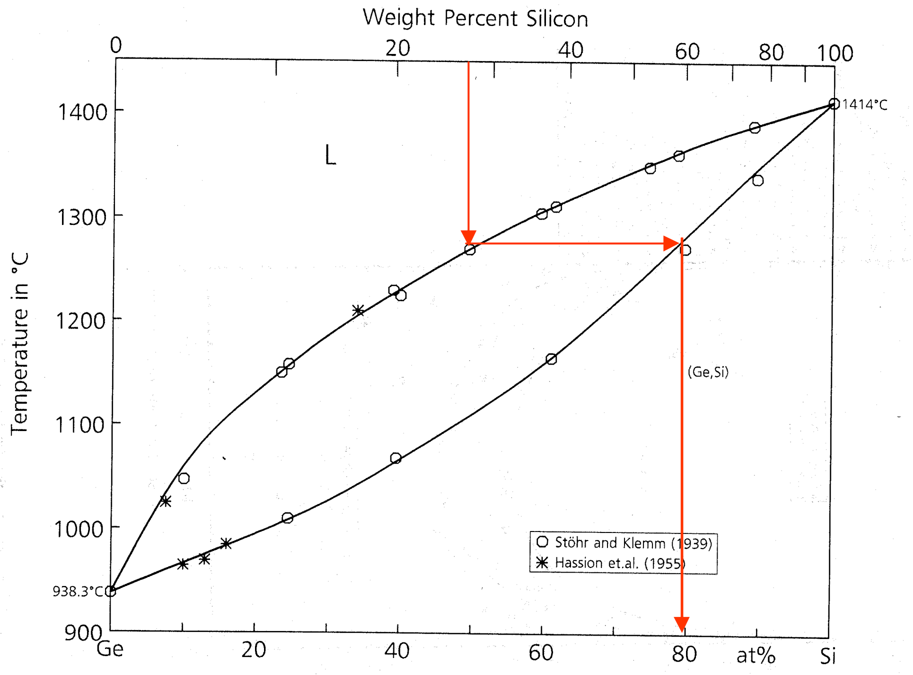
Preparation & Properties of SiGe

Why SiGe

- Si & Ge are good, classical semiconductors with high melting point
- Expected to have reasonably attractive electrical properties
  - Mobility, Seebeck, resistivity
- As pure, undoped elements they have quite high thermal conductivity values
- Can doping & alloying reduce the thermal conductivity enough to give reasonable ZT?
  - Initial estimates at RCA in ~1959 were not promising
  - But experimental work initiated anyway, to gain a better understanding

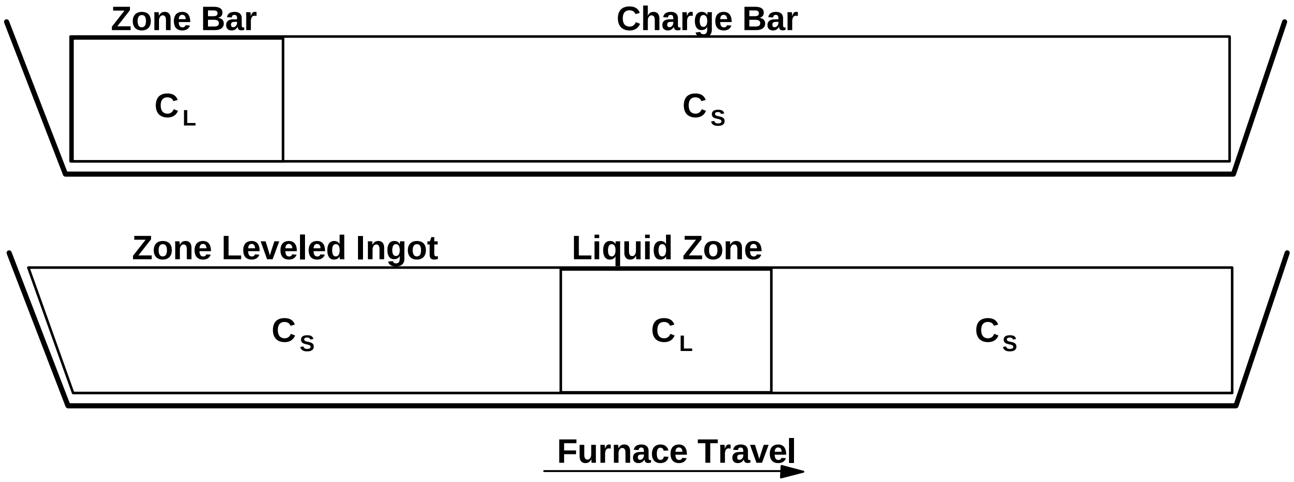
SiGe Phase Diagram

- Homogeneous SiGe can not be prepared by simply cooling from the melt
  - Ex: $Si_{0.8}Ge_{0.2}$ solidifies only from a liquid of composition $Si_{0.5}Ge_{0.5}$
- If you simply mix Si & Ge, melt it and cool you get grains with a wide range of compositions
- Two general strategies:
  1. Maintain a fixed composition of the melt
     - Ex: Zone Leveling used at RCA through the 1960's
  2. Employ time and temperature to homogenize the material through interdiffusion
     - Ex: Hot Pressing
- There are many, many variations that have been and can be tried



Si-Ge phase diagram indicating solidification of $Si_{0.8}Ge_{0.2}$ from a melt of composition $Si_{0.5}Ge_{0.5}$

Zone Leveling



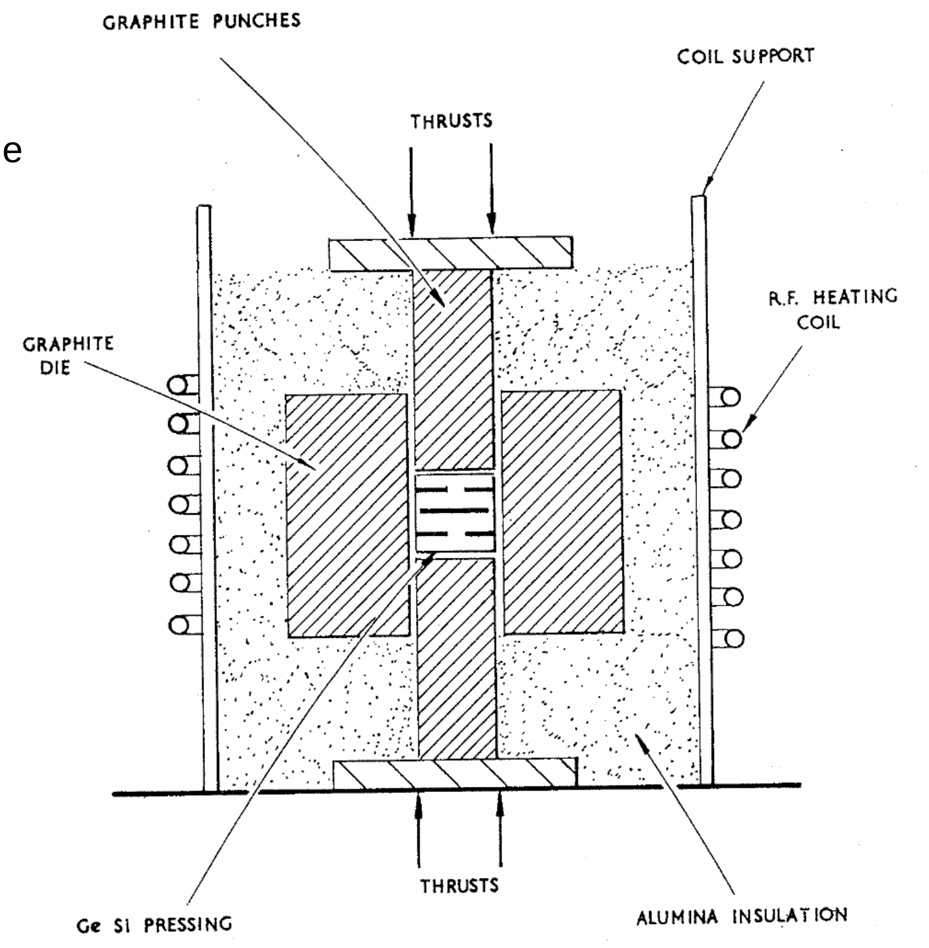
- Schematic of the zone leveling procedure showing the initial arrangement of the materials (above) and the situation during zoning (below).
- Produces excellent quality, homogeneous material
- Results are reproducible from run-to-run and from laboratory-to-laboratory
- Used by RCA in the 1960’s to successfully determine the potential of SiGe
- Used in the SNAP-10A nuclear reactor in 1965
- Slow & expensive

Hot Pressing

aka: Pressure Sintering

- Simpler, faster, less expensive
  - Powder metallurgy is heavily studied for ceramics
- Can realize ZT values indistinguishable from Zone Leveled materials
  - With optimized pressing conditions
  - Typically slightly higher ρ compensated by slightly lower λ
- Many preparation parameters can (and do) influence TE properties
  - Particle size & distribution
  - Comminution method
  - Pressing time, temperature & pressure
  - Post-pressing heat treatments & thermal history
- Used in all US space SiGe RTGs

- Piper, M. J. (1966). Germanium-Silicon Thermoelectric Material Development. Industrial Applications for Isotopic Power Generators. A.E.R.E. Harwell, European Nuclear Energy Agency, Organisation for Economic Co-operation and Development: 349-361.



Alloying & Doping Effect on λ

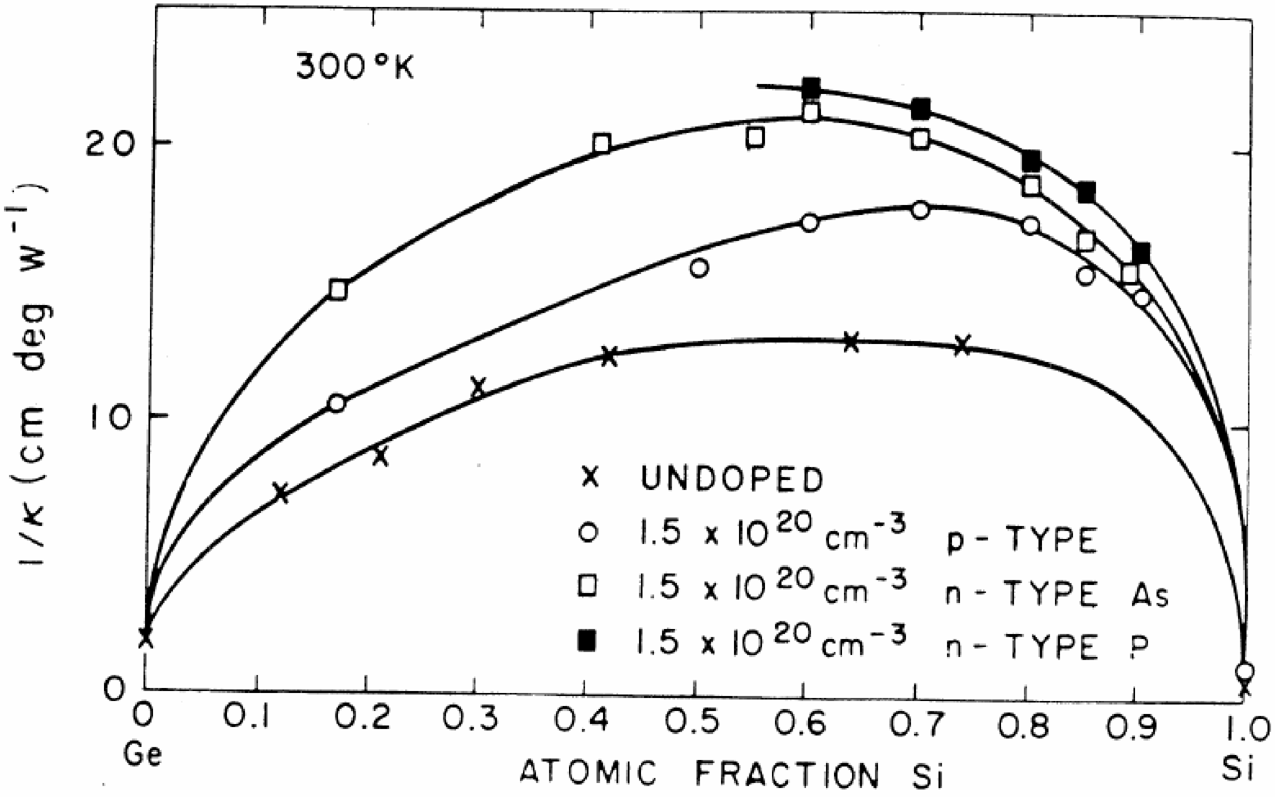


Fig. 44. The thermal resistivity of undoped and doped, p–and n–type Ge–Si alloys as a function of alloy composition at 300 °K.

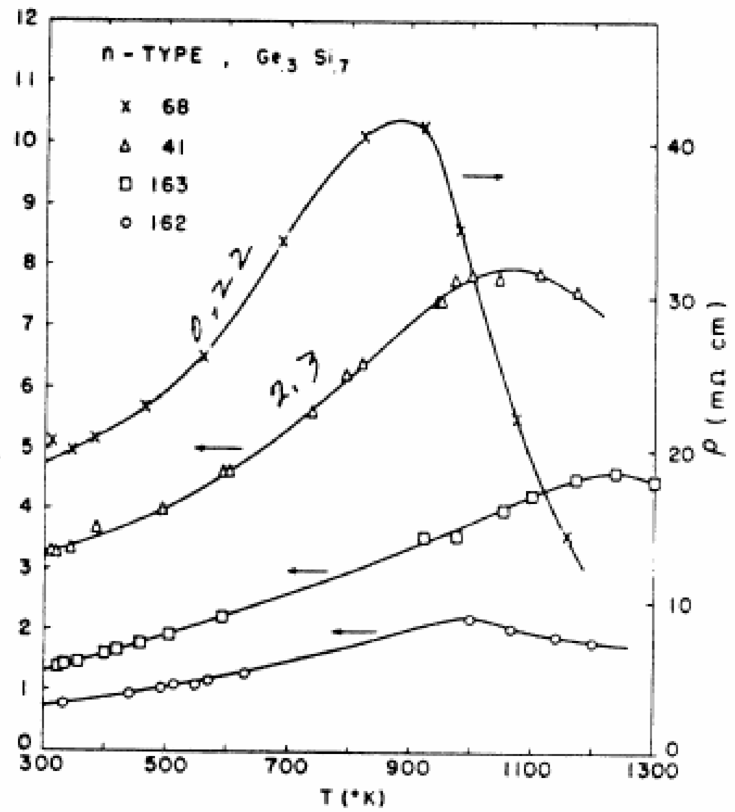
- Doping & alloying combine to reduce λ by about 30x compared to pure Si

N-Type, ZL SiGe Resistivity

- Doping reduces the resistivity

$$r = \frac{1}{enm} \approx \frac{T^{1.5}}{n}$$

- At the highest temperatures, resistivity drops
    - Two different mechanisms, both connected to carrier concentration changes
    - Low doping + high temperature = excitation of electron-hole pairs
    - High doping + high temperatures = dopant (phosphorus) becomes more soluble

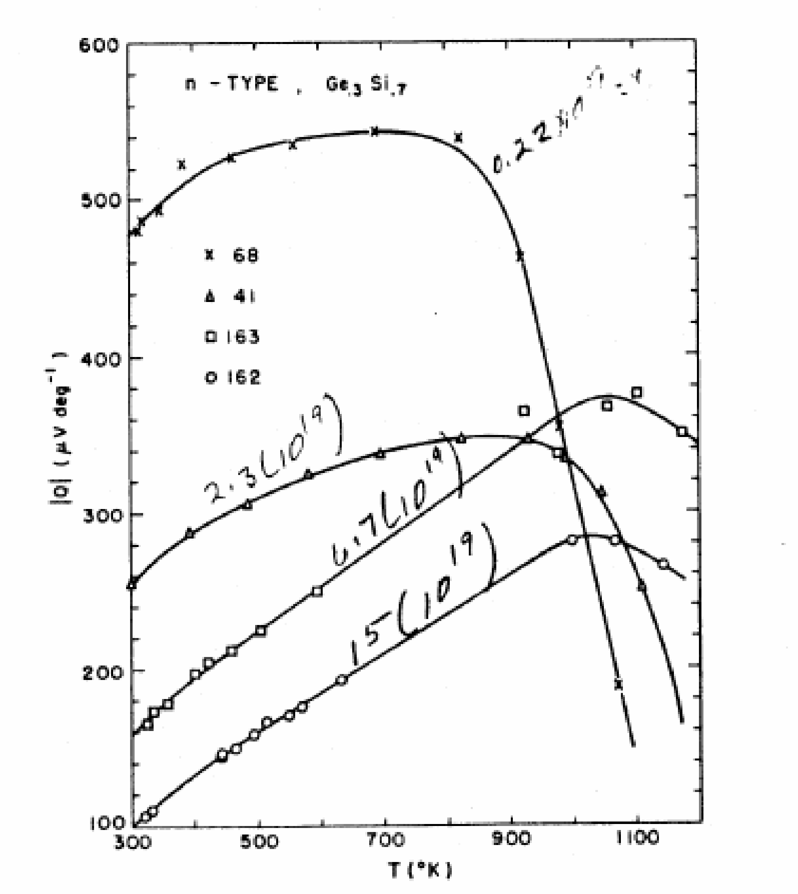


N-Type, ZL SiGe Seebeck Coefficient

- Doping also reduces the Seebeck

$$|S| \approx 86\,m\mathrm{V/K}\left(2+\frac{3}{2}\ln(T)-\ln\left(\frac{n}{n_0}\right)\right)$$

- S & ρ both depend on carrier concentration: when one changes, so must the other
  - And the amount of change is predictable
- As with ρ, at the highest temperatures, Seebeck drops
  - Two different mechanisms
  - Low doping + high temperature = excitation of electron-hole pairs
  - High doping + high temperatures = dopant (phosphorus) becomes more soluble



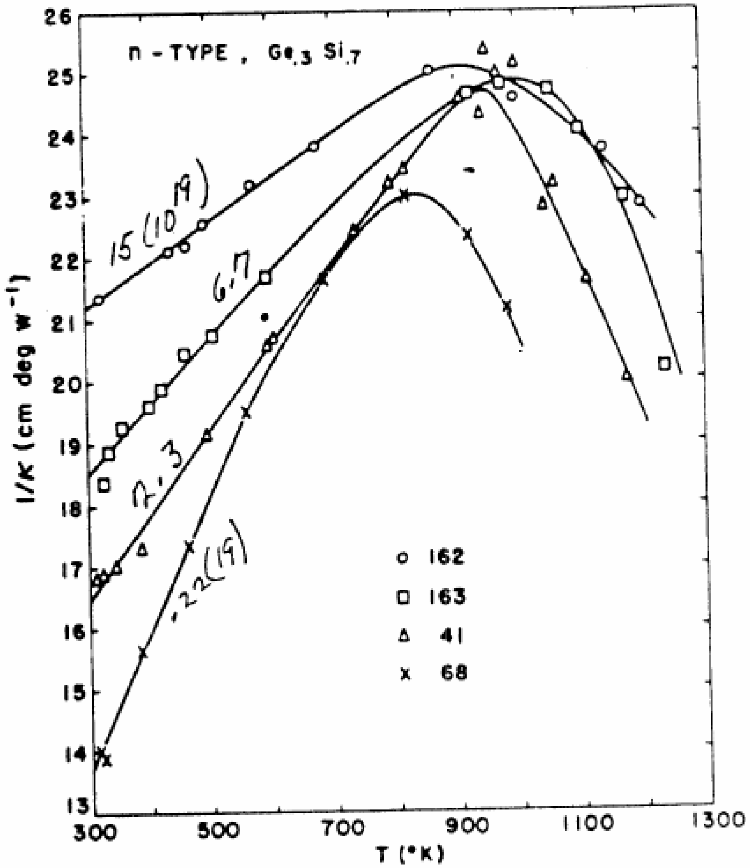
N-Type, ZL SiGe Thermal Conductivity

or equivalently, thermal resistivity

- Doping also reduces λ

$$l = l_e + l_{phonon} = LsT + l_{phonon}$$

- λ has an electronic contribution + a “phonon” contribution
- Both depend on carrier concentration, but the dependence is much weaker than for either S or ρ
- λ_e can be calculated from ρ
- For many materials λ_{phonon} is considered independent of doping, but for SiGe λ_{phonon} decreases with doping

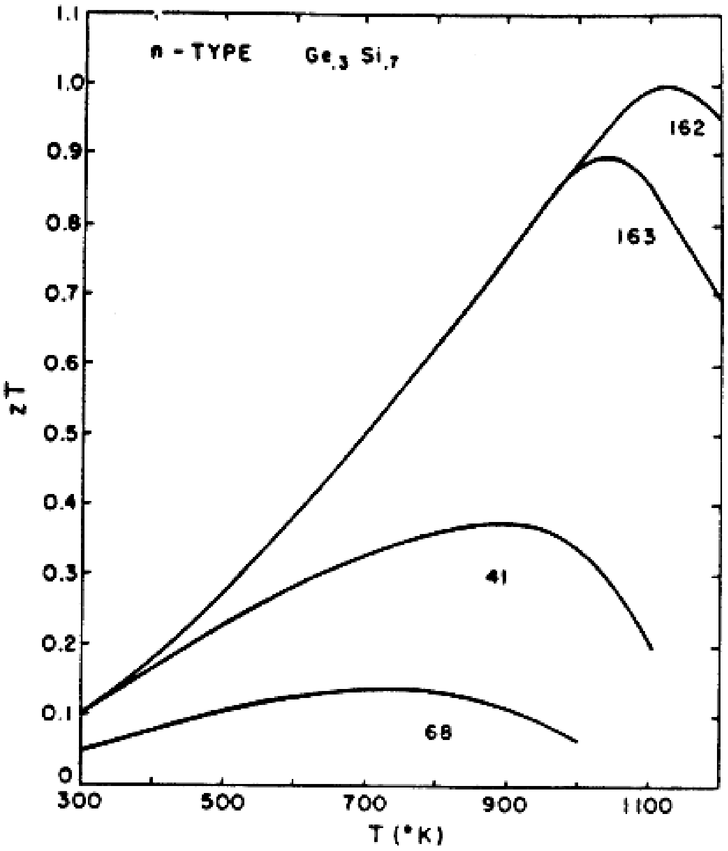


N-Type, ZL SiGe ZT

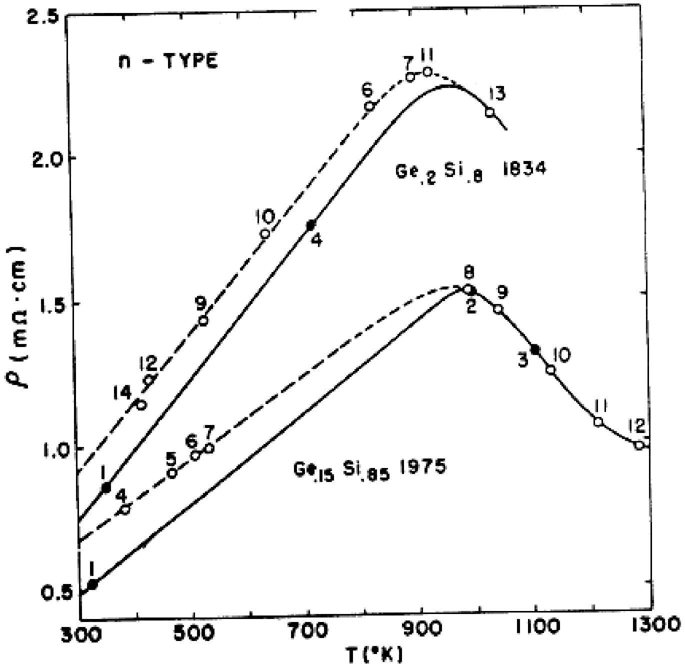
- In SiGe, doping reduces S, ρ & λ

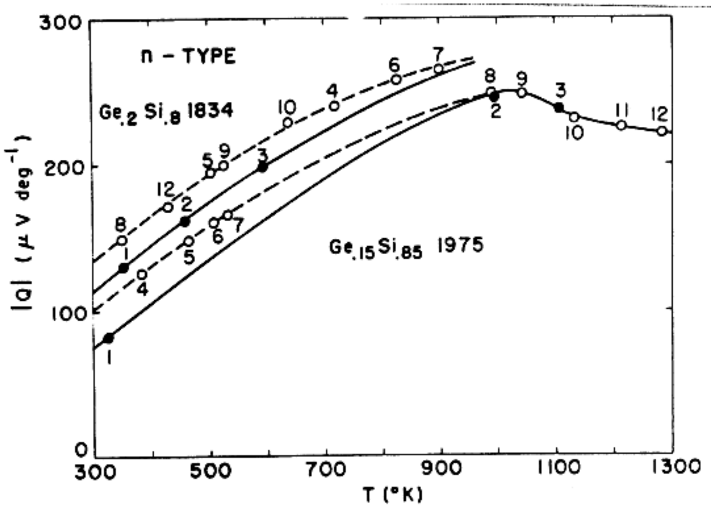
$$ZT = \frac{S^2 T}{r\,l}$$

- Optimum ZT is a balance between compensating effects
- ZT continues to increase up to nearly the highest doping levels studied
  - Limited by the solubility of phosphorus
  - ZT would eventually reach a peak and decrease with further doping
  - We will need theory to estimate how much more ZT could be achieved with more doping



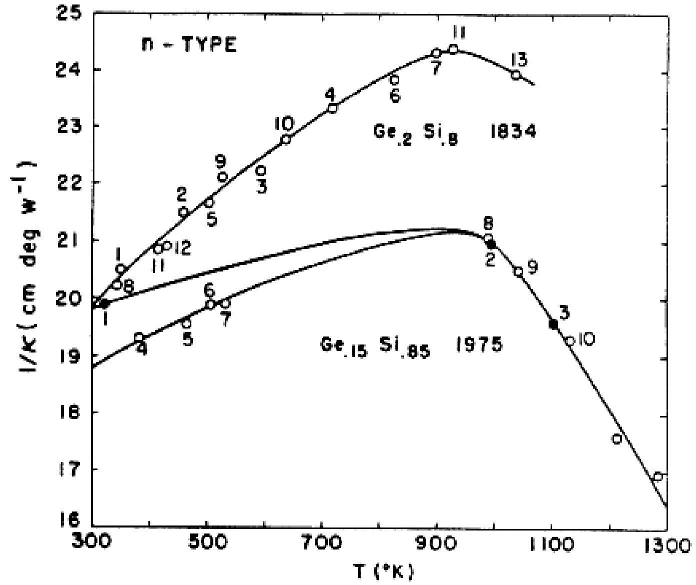
Dopant precipitation





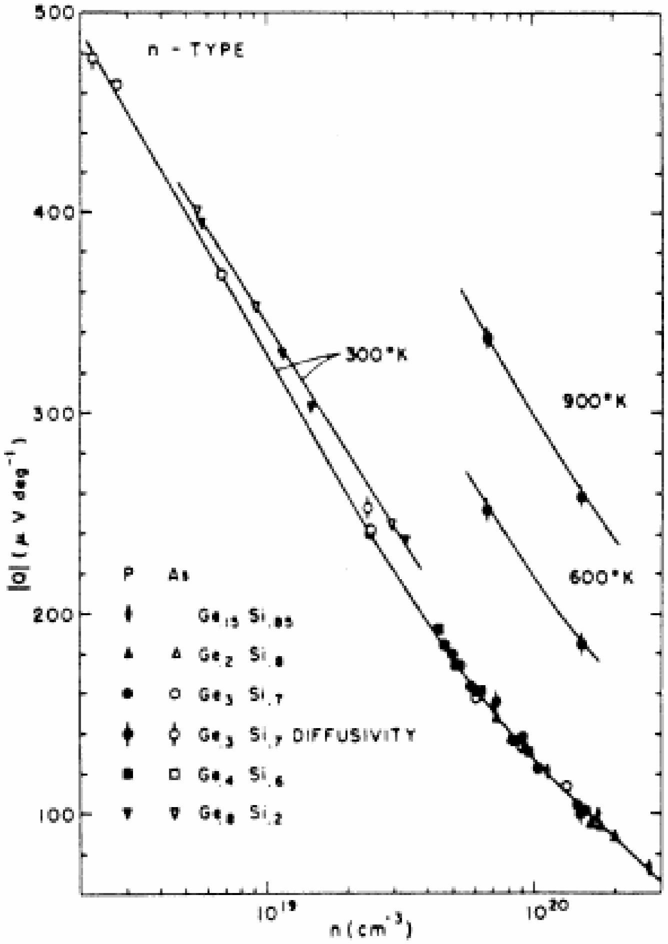
From the earliest studies in the 1960’s, properties were observed to change during measurements.

Identified as ‘dopant precipitation’, this important effect has been heavily studied.



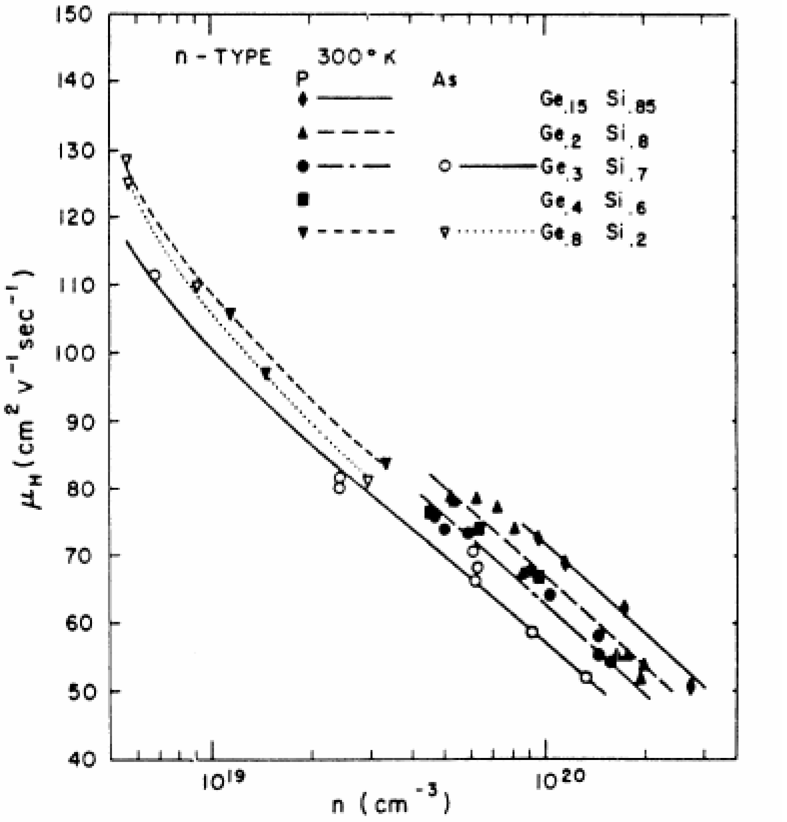
Seebeck depends on doping

- Seebeck is a direct indication of doping level
  - Depends on temperature and composition
  - Quite insensitive to other preparation details
  - Entirely independent of sample geometry
  - If the Seebeck changes with time it means either
    1. Measurement issues or
    2. Dopants are moving (such as precipitation or dissolving)



Mobility in SiGe

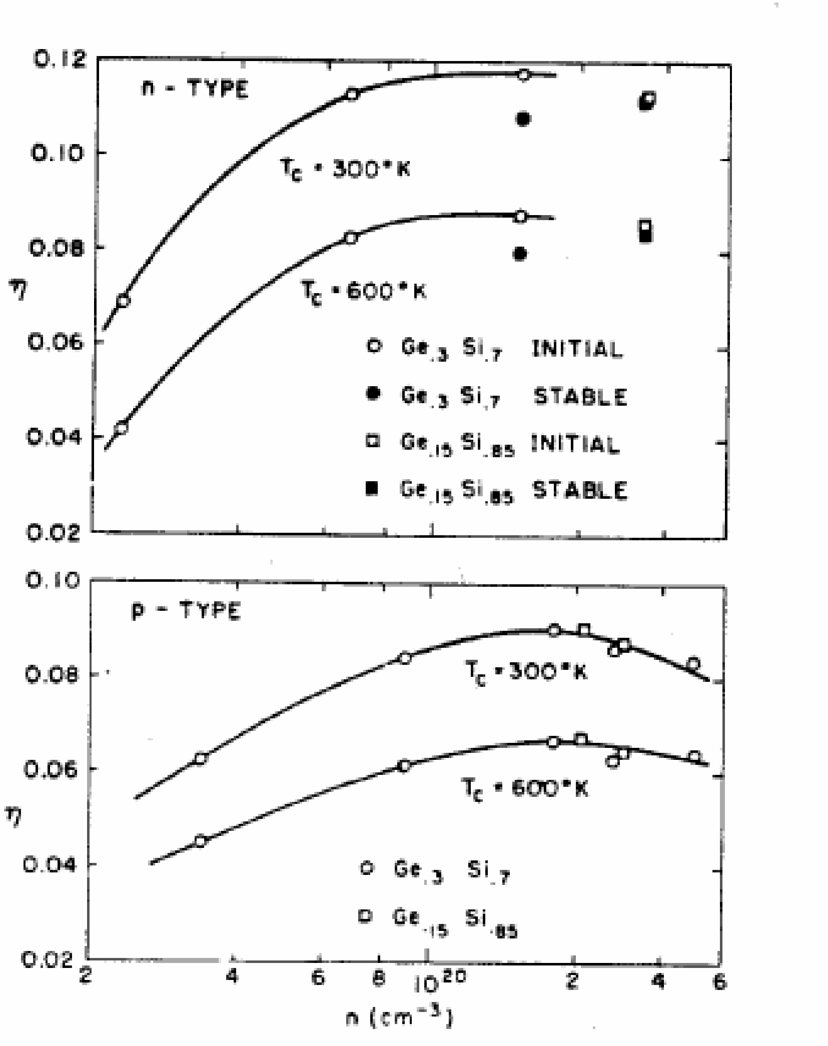
- Electrical mobility is one of the most important properties to study for thermoelectricity
- ZT depends directly on mobility
  - Bigger is better
- If the mobility is good enough, it may be worth learning to control doping to optimize ZT
- If you've made a high quality, low defect sample and the mobility is still low, most likely it will never be a good thermoelectric



SiGe efficiency vs. doping

T_h = 1200 K

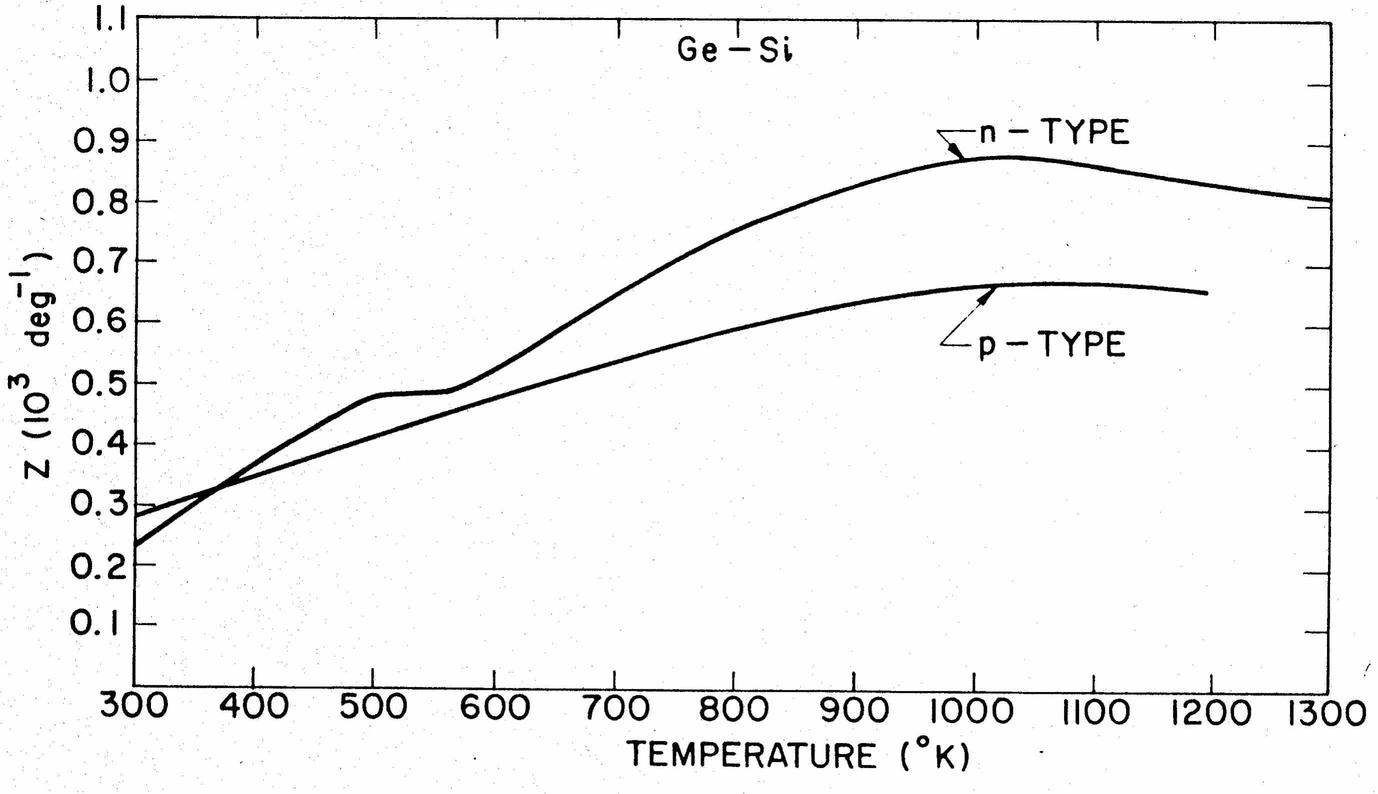
- For p-type SiGe, optimum doping levels can be achieved
- For n-type SiGe, the question of optimum doping is a bit more subtle.
  - We will revisit that shortly
- Fortunately, ZT & efficiency have fairly broad, flat maxima vs. doping
  - Variations in the individual properties are, to a considerable extent, compensated by each other.



RCA 'Z' values for zone-leveled SiGe

First measured ~ 1961

Very close to data used today



Rosi, F.D., 1968, Solid-State Electronics, 11, 833-868.

Typical physical properties of hot pressed silicon-germanium.

	T (K)	Units	p-type $Si_{0.8}Ge_{0.2}$	n-type $Si_{0.8}Ge_{0.2}$
Density	300	gm/cm^3	2.99	2.99
Thermal Expansion	300	10-6/K	3.98	4.20
	600	10-6/K	4.26	4.43
	900	10-6/K	4.55	4.66
	1200	10-6/K	4.84	4.89
	1400	10-6/K	5.03	5.05
Porosity			1%	1%
Dopant			Boron	Phosphorus
Nominal Composition		atomic %	0.23	0.59
Compressive Strength^a				
Maximum Stress	300	MPa (20%)	653	473
Maximum Strain	300	% (25%)	0.42	0.37
Modulus	300	GPa (7%)	154	129
Tensile Strength^b				
Maximum Stress	300	MPa (20%)	201	129
	875	MPa (20%)	292	143
	1375	MPa (20%)	310	182*
Maximum Strain	300	% (25%)	0.15	0.11
	875	% (25%)	0.20	0.10
	1375	% (25%)	0.49	>0.69*
Modulus	300	GPa (7%)	137	145
	875	GPa (7%)	151	165
	1375	GPa (7%)	103	114*

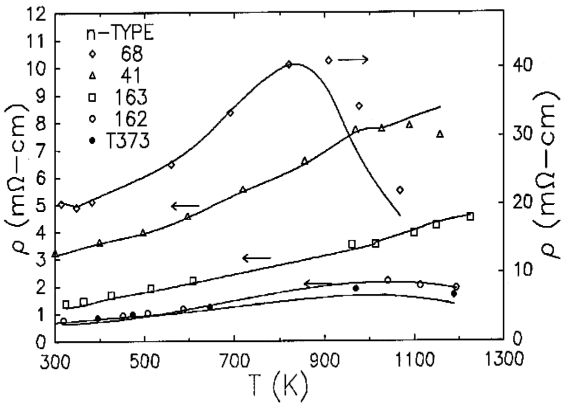
Test Methods:
a – cylinders
b - 4 point flexure,
*Two of three samples tested did not fail due to high ductility at 1375 K.

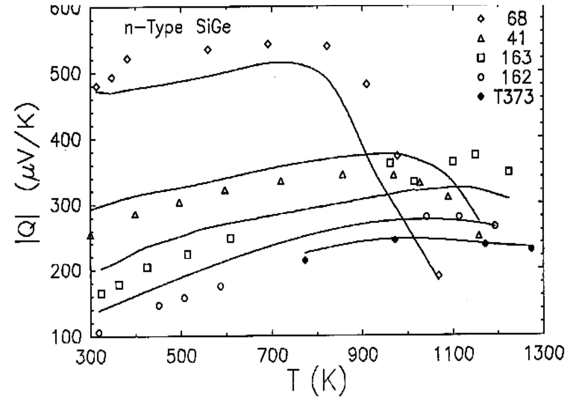
ZT Theory – n-type SiGe

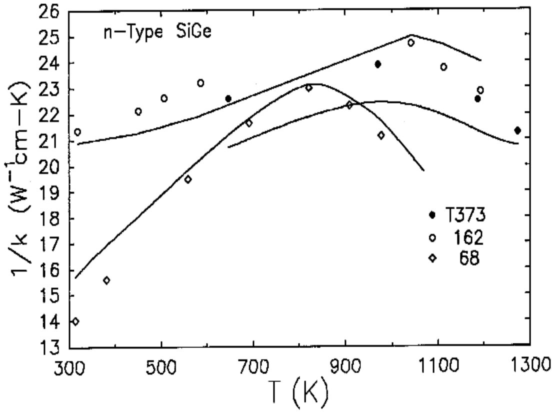
Theory & SiGe

Comparison to data

- N-Type SiGe
  - Open symbols 1964 RCA-data on zone leveled $Si_{0.7}Ge_{0.3}$
  - Filled symbols 1989 ‘high ZT’ JPL data on hot pressed & annealed SiGe/GaP
- SiGe/GaP is well within the population of data
  - Somewhat higher carrier concentration







SiGe TE Properties Model

- Reproduces all qualitative trends well
  - Temperature, doping & Si/Ge composition
- Thermal conductivity is well described
  - 2 parameters from the literature needed to describe undoped silicon
  - No further adjustable parameters are required, beyond those needed for fitting the electrical properties alone
- Greatest errors are:
  - Over-estimation of Seebeck at the lower temperatures
  - Under estimation of carrier concentration at the highest temperatures
    - Equivalent to saying model overestimates mobility at highest temperatures

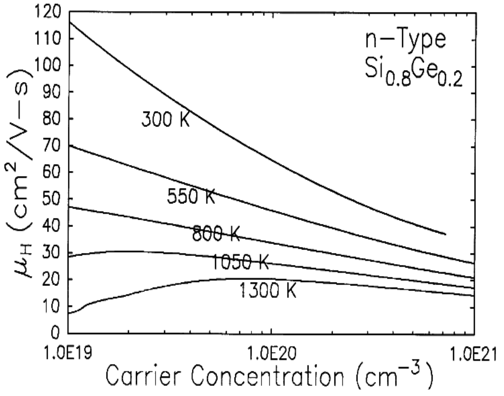
Carrier Concentration Dependencies

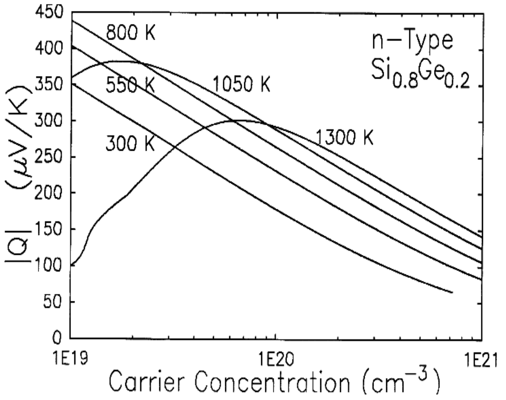
Electrical Properties

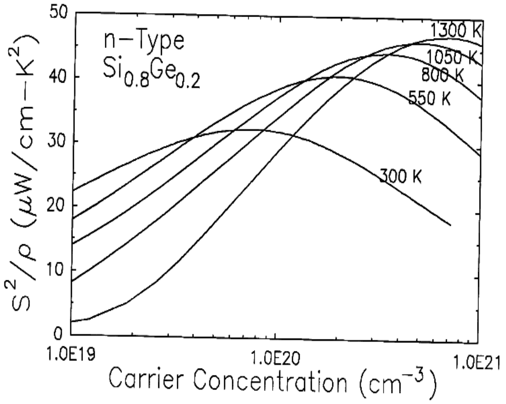
- Mobility (μ) is, in a sense, more fundamental than ρ
  - μ tells you how easily each carrier moves
  - Larger is better!

$$r \equiv \frac{1}{s} \equiv \frac{1}{enm}$$

- Maximum power factor (S^2/ρ) occurs in the range of 2-7 x 10^{20} cm^{-3}
  - Can you dope enough to achieve the maximum S^2/ρ?
    - Not always
  - Do you want the maximum S^2/ρ?
    - Not quite: you want maximum ZT!



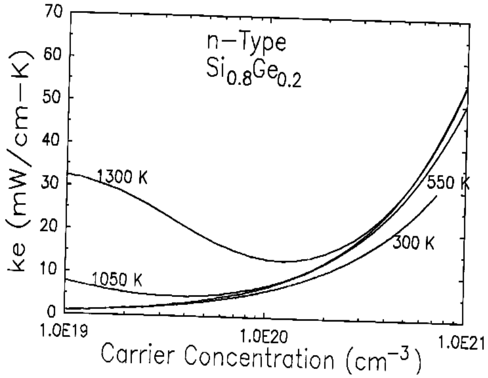


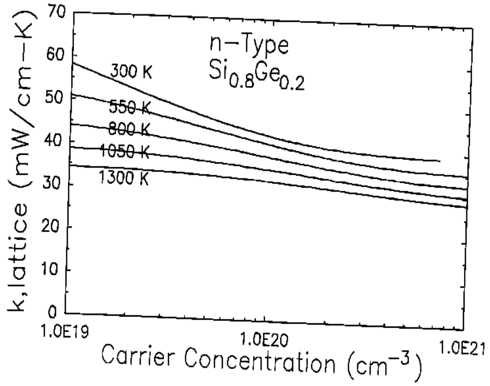


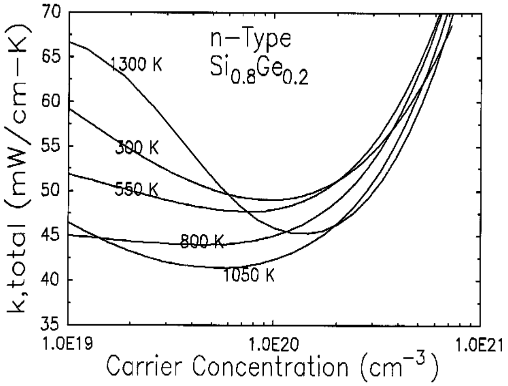
Carrier Concentration Dependencies

Thermal Conductivity

- Thermal conductivity has two contributions:
  - $l = l_e + l_p = LsT + l_p$
  - You can only measure the total, and estimate the two contributions
  - Electronic contribution (λ_e) heat carried by the electrons (or holes)
    - Related to the electrical conductivity
    - More carriers = bigger λ_e
  - Thermal contribution (λ_p), heat carried by the lattice
    - ‘phonon’ is another name for a vibration of the atoms forming the crystal lattice
    - Electrical carriers actually interact with lattice vibrations
    - More carriers = smaller λ_p
- Total λ has a minimum vs. carrier concentration

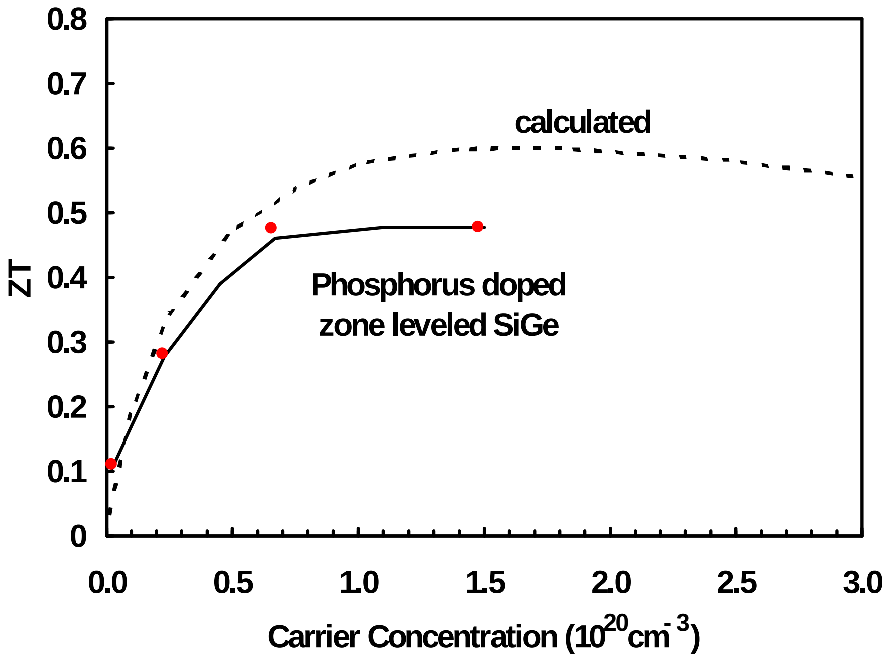






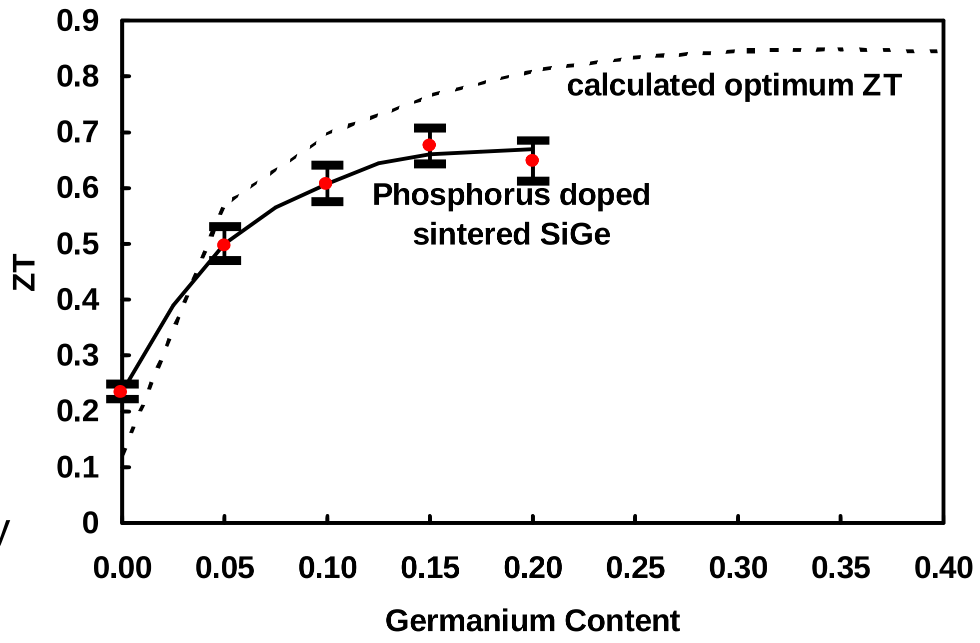
Optimum Doping for ZT in SiGe

- Dimensionless figure of merit (averaged from 300 to 1000 K) for zone leveled n-type $Si_{0.7}Ge_{0.3}$ and the dashed line is calculated using the model described in previously.
- Similar results obtained on hot pressed $Si_{0.8}Ge_{0.2}$



Variation of SiGe Content

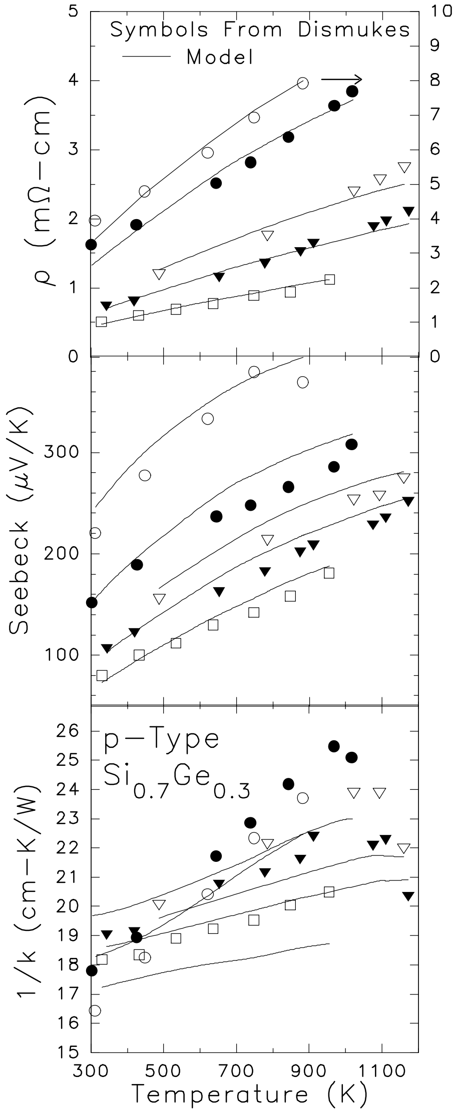
- Dimensionless figure of merit averaged from 575 to 1275 K. The points are experimental results on sintered n-type Si-Ge with 2 atomic percent phosphorus[i] and the dashed line is the theoretical maximum ZT calculated using the model described in reference .[ii]
- $Si_{0.85}Ge_{0.15}$ may be ever so slightly better than $Si_{0.8}Ge_{0.2}$
  - Slightly higher ZT, higher melting point, dopant more soluble (so slightly more stable)
- RCA reported similar results in 1969 on zone leveled material



[i]. Gorsuch, P. D., Nakahara, J., Slack, G. A., Feingold, E., and Vining, C. B., Development of Improved Thermoelectric Materials for Space Nuclear Power Systems, Final report for contract no. DE-AC01-84NE-32123, U. S. Department of Energy, Washington, D.C., 1989.

[ii]. Vining, C.B., A model for the high-temperature transport properties of heavily doped n-type silicon-germanium alloys, *Journal of Applied Physics*, 69, 331, 1991.

A Model for p-Type SiGe



- Resistivity, Seebeck and thermal conductivity for p-type $Si_{0.7}Ge_{0.3}$. The points are experimental results[i] and the lines are calculated.[ii]

- [i]. Dismukes, J. P., Ekstrom, L., Steigmeier, E. F., Kudman, I., and Beers, D. S., Thermal and electrical properties of heavily doped Ge-Si alloys up to 1300 K, *Journal of Applied Physics*, 35, 2899, 1964.
- [ii]. Vining, C.B., A model for the high-temperature transport properties of heavily doped p-type silicon-germanium alloys, *Modern Perspectives on Thermoelectrics and Related Materials*, Materials Research Society Symp. Proc. Vol. 234, Allred, D. D., Vining, C. B., and Slack, G. A., Materials Research Society, Pittsburgh, Pennsylvania, 1991, 95.

Typical thermoelectric properties for p-type silicon-germanium

as prepared

T (K)	Electrical Resistivity (10^{-5} W-m)	Seebeck Coefficient (mV/K)	Thermal Conductivity (W/m-K)	Heat Capacity (J/gm-K)	ZT unitless
300	**1.14**	**121**			
400	**1.32**	**144**	**4.80**	**0.647**	**0.131**
500	**1.51**	**161**	**4.70**	**0.649**	**0.184**
600	**1.71**	**176**	**4.57**	**0.658**	**0.237**
700	**1.93**	**189**	**4.41**	**0.672**	**0.295**
800	**2.16**	**203**	**4.25**	**0.687**	**0.359**
900	**2.41**	**216**	**4.12**	**0.703**	**0.423**
1000	**2.68**	**228**	**4.07**	**0.719**	**0.478**
1100	**2.96**	**237**	**4.14**	**0.736**	**0.505**
1200	**3.19**	**240**	**4.38**	**0.754**	**0.501**
1300	**3.26**	**233**	**4.84**	**0.772**	**0.446**

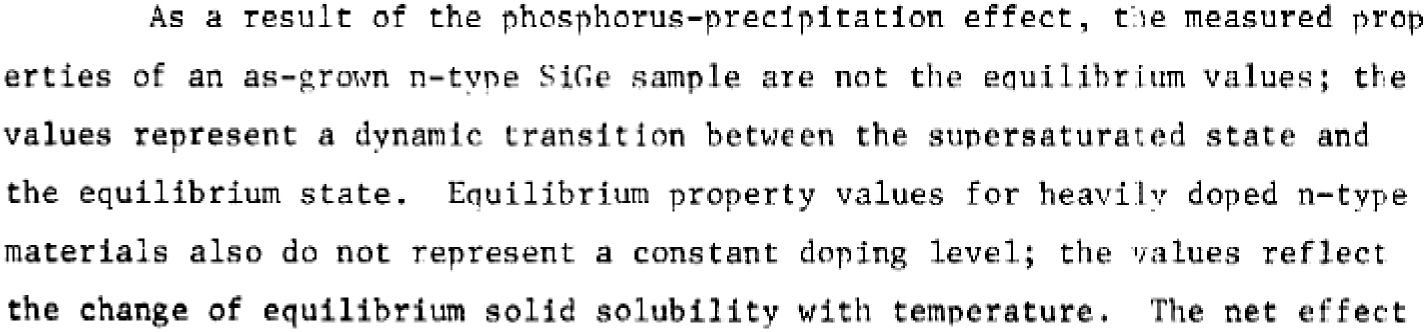
Typical thermoelectric properties for n-type silicon-germanium

as prepared

T (K)	Electrical Resistivity (10^{-5} W-m)	Seebeck Coefficient (mV/K)	Thermal Conductivity (W/m-K)	Heat Capacity (J/gm-K)	ZT unitless
300	0.85	-108			
400	1.01	-136	4.45	0.647	0.165
500	1.17	-165	4.31	0.649	0.269
600	1.36	-190	4.19	0.658	0.380
700	1.61	-213	4.08	0.672	0.486
800	1.86	-233	3.99	0.687	0.583
900	2.06	-247	3.93	0.703	0.679
1000	2.11	-253	3.93	0.719	0.775
1100	1.97	-250	4.01	0.736	0.870
1200	1.78	-242	4.20	0.754	0.938
1300	1.91	-243	4.53	0.772	0.890

Dopant Precipitation in SiGe

Dopant precipitation has long been recognized and (usually) accounted for



As a result of the phosphorus-precipitation effect, the measured properties of an as-grown n-type SiGe sample are not the equilibrium values; the values represent a dynamic transition between the supersaturated state and the equilibrium state. Equilibrium property values for heavily doped n-type materials also do not represent a constant doping level; the values reflect the change of equilibrium solid solubility with temperature. The net effect

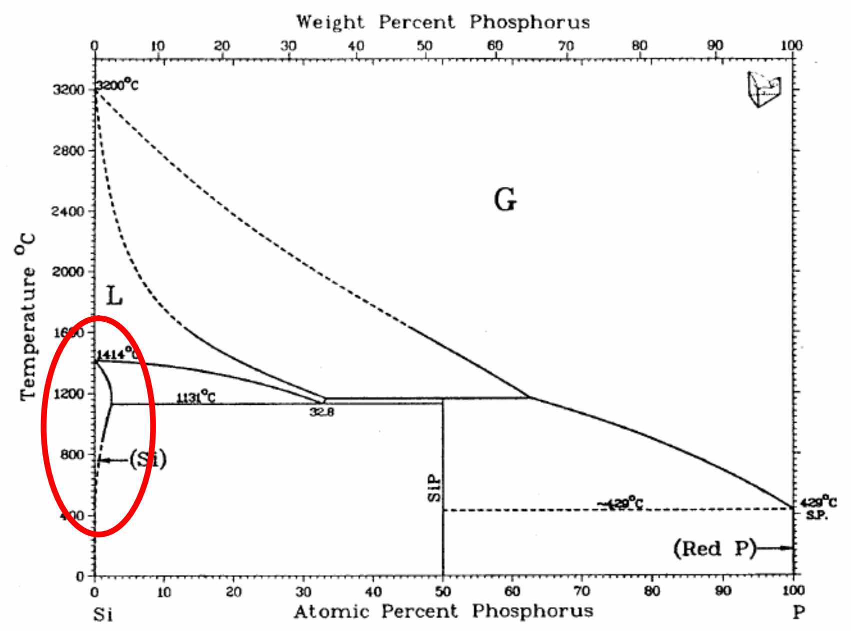
RCA (1969). Topical Report - Silicon Germanium Thermoelectric Materials and Module Development Program. Harrison, NJ USA, RCA: 83.

Dopant Precipitation in SiGe

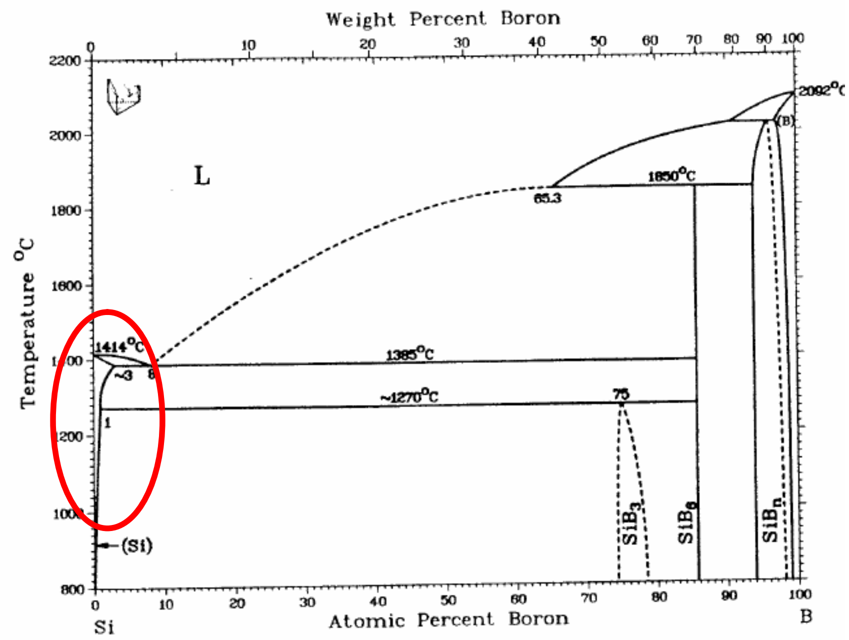
- The most soluble dopants for SiGe are
  - Phosphorus (P) for n-type and
  - Boron (B) for p-type
- The solubility of P & B in SiGe is of the so-called ‘retrograde’ type
  - Solubility is fairly low at melting point (MP_{Si}=1414 ^oC)
  - Solubility peaks at
    - ~ 1200 ^oC for P in Si
    - 1385 ^oC for B in Si
  - Then drops ~ exponentially at lower temperatures
- Over most of the temperature range of interest, SiGe alloys are doped to well beyond the solubility limit (to get the best ZT)
  - When heated up to ~ 1200 ^oC dopants dissolve into solution, creating charge carriers
  - When cooled to lower temperatures, excess dopants will precipitate out of solution, reducing the number of charge carriers

- Think of sugar in your tea: hot tea dissolves more sugar than cold

Silicon-dopant Phase Diagrams



- Silicon-Phosphorus phase diagram
- SiGe generally has 2% or less P
- Second phase precipitates of SiP are generally present
- Si-Ge-P is more complex, but the salient features persist:
- retrograde solubility + precipitates



- Silicon-Boron phase diagram
- SiGe generally has less than 1% B
- Second phase is a boron-rich phase
- Boron-doped SiGe is harder (ex: harder to machine) than Phosphorus doped due to the precipitates

Phosphorus Precipitation

- Precipitation is a complex process
  - Fortunately, it is a technologically important process and heavily studied
    - think: steel
    - Major interest to semiconductor industry too
  - Nucleation followed by diffusion-limited growth
    - Diffusion is typically an activated process
    - Exponentially faster at higher temperatures
  - Precipitation takes time!
    - “Quench” a sample quickly from high temperature and the phosphorus is “frozen” in solution
    - Doped SiGe is only meta-stable, existing in a highly supersaturated state over most of the temperature range of interest
  - Results in a distribution of precipitate particle sizes
- The reverse process: dissolving precipitates
  - Also takes time
  - Small dissolve much faster than large precipitates
- Leads to rich, but largely understandable behavior
  - Excellent models worked out in the 1960s
  - Probably worth revisiting in the light of 40 years of R&D!

P Precipitation Kinetics

- Carrier concentrations, initially above the solubility limit at that temperature, gradually approach the equilibrium solubility limit at that temperature
- Rate of precipitation slows with time
- Initial rates can be rather large, easily observable over a few minutes
- All the thermoelectric properties vary with carrier concentration
  - So they all vary with time also
- Solid lines are calculated from a fairly simple theory

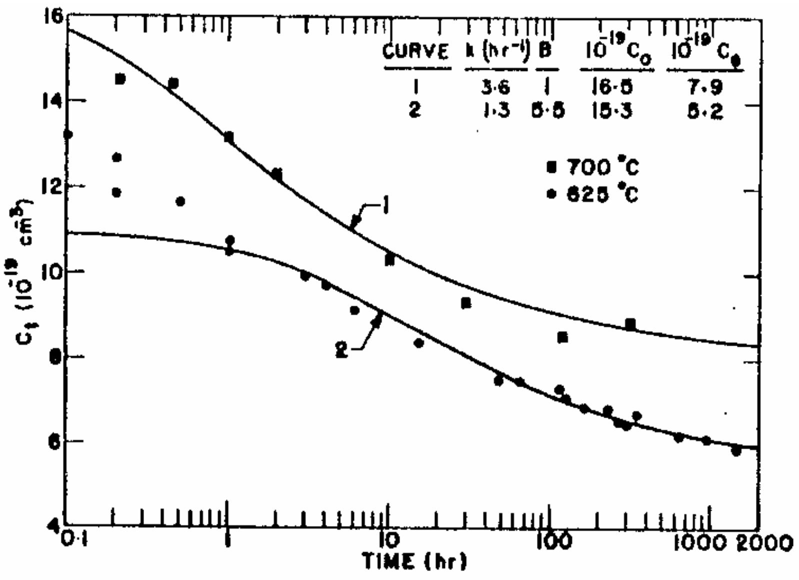


FIG. 1. Change in carrier concentration, C_t, with annealing time for phosphorus-doped $Ge_{0.3}Si_{0.7}$ alloy at the indicated temperatures. The solid curves are calculated from equation (3) using the values tabulated.

Ekstrom, I. and J. P. Dismukes (1966). "Precipitation of Phosphorus from Solid Solution in Ge-Si Alloy." J. Phys. Chem. Solids **27**: 857-863.

Reversion

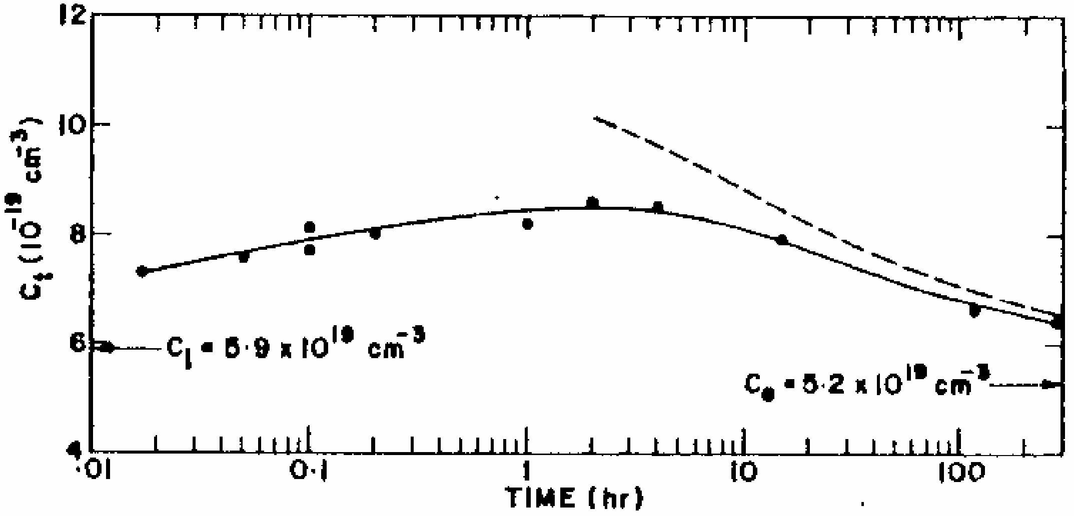


FIG. 4. Change in C_t with annealing time at 625°C for a sample previously annealed for 50 hr at 500°C. The solid line is drawn to fit the data. The dashed line is the curve for isothermal annealing at 625°C.

- Hold a sample at one temperature for a period of time, then quickly heat to a higher temperature
- Small precipitates will rapidly dissolve, momentarily ***increasing*** the carrier concentration before eventually decreasing toward the solubility limit
- This “reversion”, occurs even though the sample is supersaturated the entire time.
- “Reversion” occurs all the time, including during every high temperature measurement ever made of n-type SiGe!
- Also occurs in RTGs whenever temperatures go up.

Ekstrom, I. and J. P. Dismukes (1966). "Precipitation of Phosphorus from Solid Solution in Ge-Si Alloy." J. Phys. Chem. Solids **27**: 857-863.

Reversion: Example

- Here, an n-type SiGe sample is successively heated
- After each heat, the carrier concentration initially increases before decreasing toward the solubility limit
- I'm not aware of a quantitative model for the time dependence of reversion
  - Reversion is an *expected* feature of the theory of dopant precipitation
  - Probably a model could be developed today, if there were interest

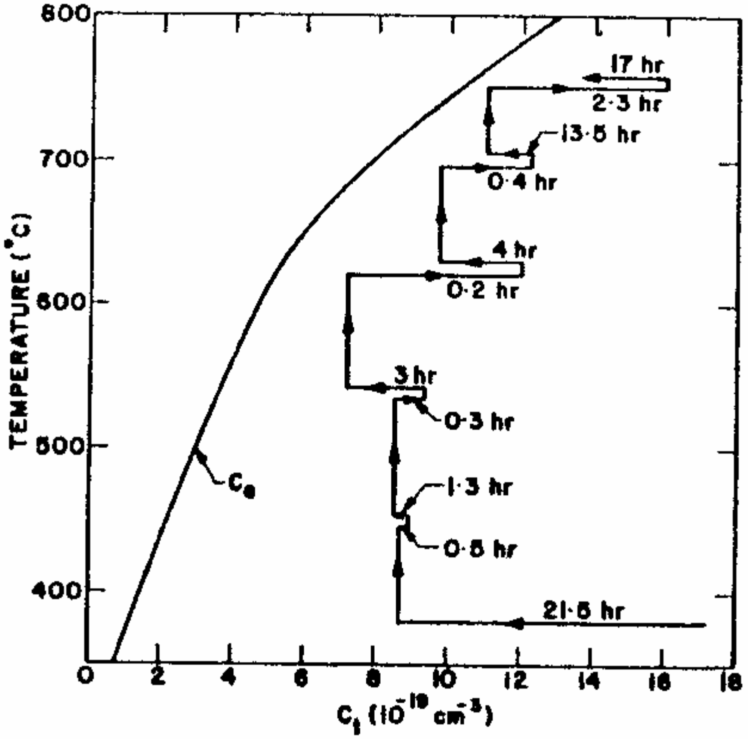
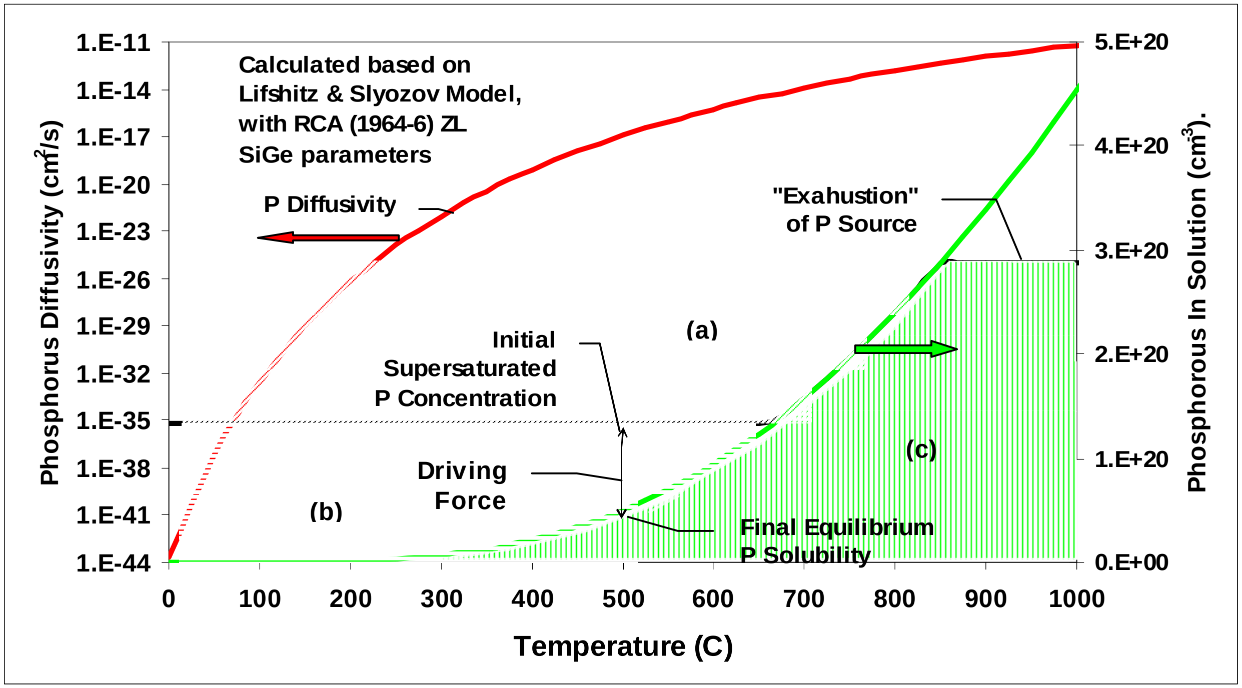


FIG. 5. Annealing at a series of increasing temperatures. The effect shown in Fig. 5 is observed at each temperature. The pairs of horizontal lines represent the change in C_t from its initial to its maximum value and from its maximum value until annealing at that temperature was terminated. They are drawn separated on the temperature scale only for clarity. The total times for these two stages are indicated.

Principles of Dopant Precipitation

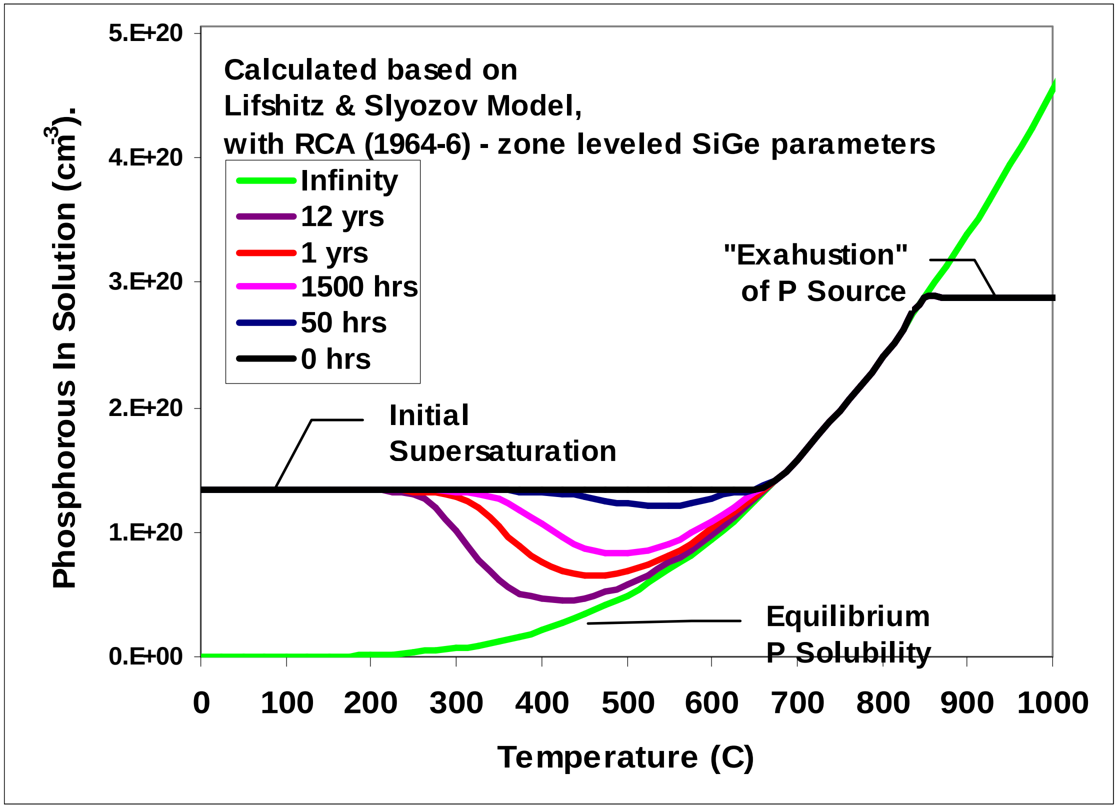
- Neglect reversion & the very short term initial period
- Rate of precipitation determined by:
  1. The degree of supersaturation (i.e, “driving force”)
  2. Diffusion-limited growth of phosphorus precipitates
- “Standard” SiGe is doped with 0.6 a/o P ~ 3 x 10^{20} cm^{-3}
  - Less than the solubility limit above ~ 800 ^{o}C
  - Carrier concentration for more heavily doped samples would continue to increase along the green equilibrium solubility curve



- (a) Pink region: electrically inactive P precipitates
- (b) Yellow region: metastable P in solution
- (c) Green region: stable P in solution

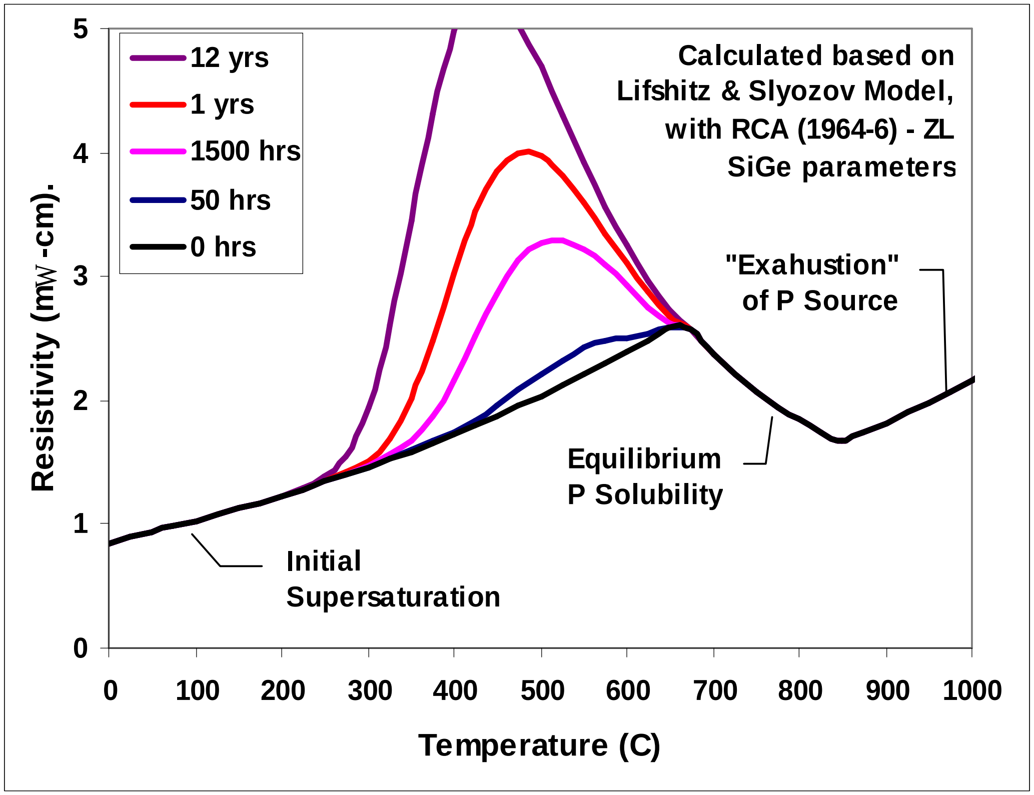
Carrier Concentration vs. Time

- “Exhaustion” occurs in samples doped below the solubility @ 1000 °C
- Carrier concentration does not change with time when equilibrium solubility limit is greater than the initial amount of P in solution
- At lower temperatures the sample is supersaturated and the carrier concentration decreases with time toward the solubility limit
- Below ~ 300 °C the P diffusion is so slow that precipitation practically stops

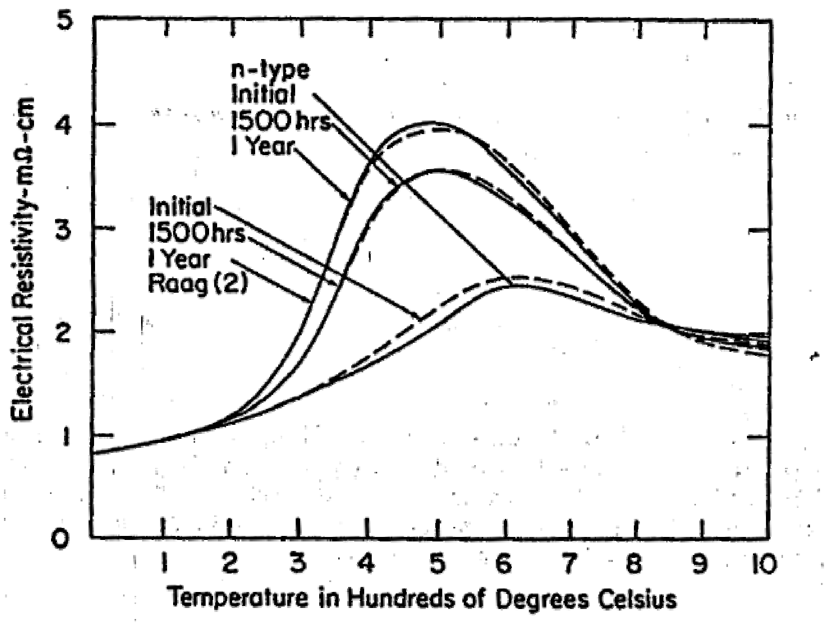


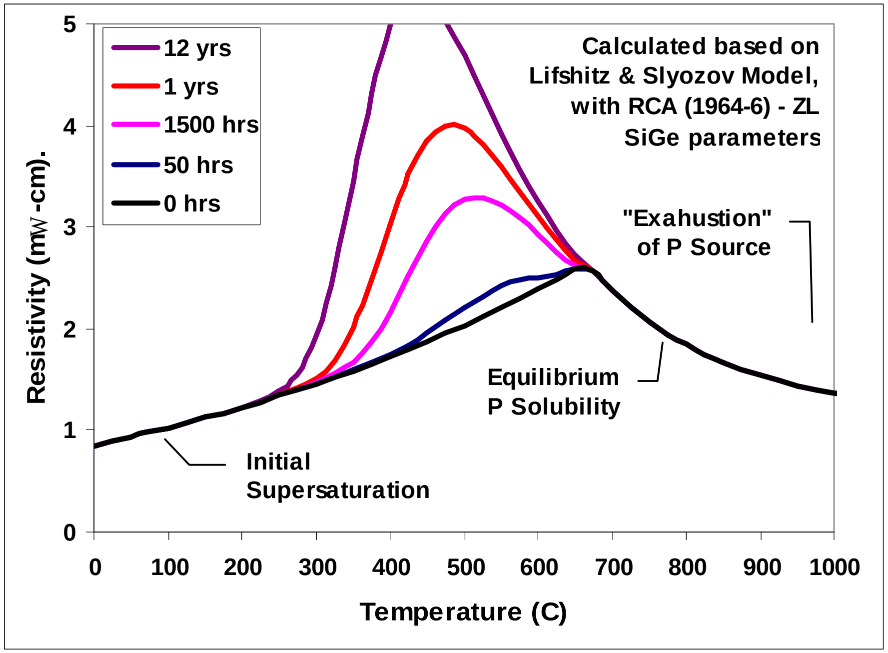
Resistivity vs. Time - Model

- All of the thermoelectric properties can then be calculated from the carrier concentrations
  - Requires either a theoretical model or tables
  - This calculation is based on 40 year old data
- The upturn above 800 ^{o}C may or may not be observed, depending on how much total P is in the sample



Resistivity vs. Time - Data





Data on Hot Pressed SiGe:

- Dashed Lines = Raag, 1978
- Solid Lines = Tschetter, 1990

Model based on solubility & diffusion studies of Zone Leveled SiGe (Ekstrom, 1966)

Tschetter, M. J. and B. J. Beaudry (1990). Effect of GaP on the resistivity versus time at elevated temperatures of n-type Si80Ge20 alloys. Proceedings of the Intersociety Energy Conversion Engineering Conference, Reno, NV, USA, Publ by IEEE, Piscataway NJ p.382-386.

Dopant Precipitation in SiGe

Basis for the “JPL Database”

- Most comprehensive estimate of ρ, S, & λ vs. time is (Raag, 1978)
- First tabulated S vs. ρ at each temperature
  - Using data on samples with different doping levels
- Then measured ρ vs. time
- Extrapolated everything else
- This so-called “JPL Database” forms the basis still used today for all dopant precipitation estimates
- Not actually a model, but a table look-up scheme
- Can not properly handle situations where the temperature changes with time
- Nevertheless, a powerful tool

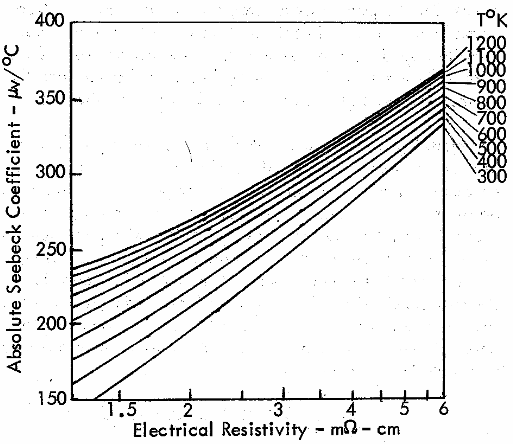


Figure 1 - Seebeck Coefficient Dependence on Electrical Resistivity for Silicon-Germanium Alloys (n-type)

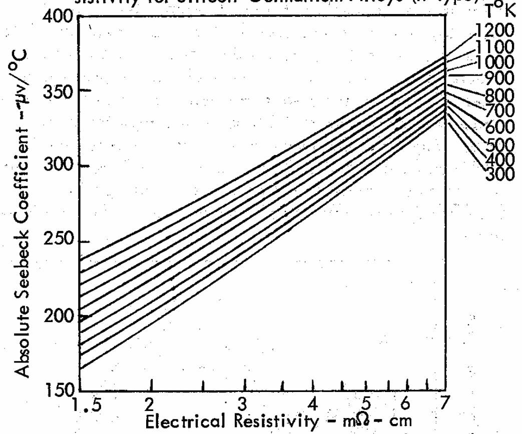


Figure 2 - Seebeck Coefficient Dependence on Electrical Resistivity for Silicon-Germanium Alloys (p-type)

Raag, V. (1978). Comprehensive Thermoelectric Properties of N- and P-Type 78a/o Si - 22a/o Ge Alloy. 2nd International Conference on Thermoelectric Energy Conversion, Arlington, Texas, IEEE Catalog number 78CH1313-6 REG.5 p.54-59.

ρ, S & λ vs. Temperature & Time

Hot Pressed $Si_{0.78}Ge_{0.22}$

The only SiGe used in space RTGs to date

p-Type

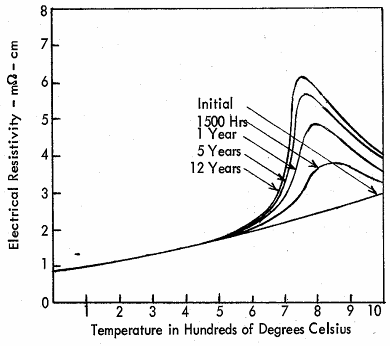


Figure 5 – Resistivity of p-type 78 a/o Si – 22 a/o Ge Alloy

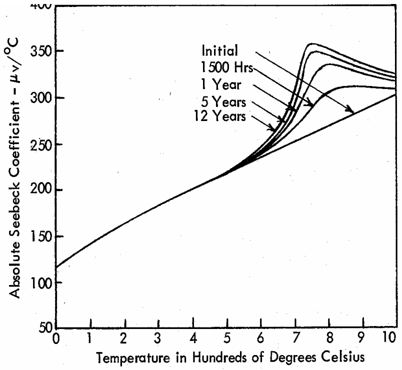


Figure 6 – Seebeck Coefficient of p-type 78a/oSi-22a/oGe Alloy

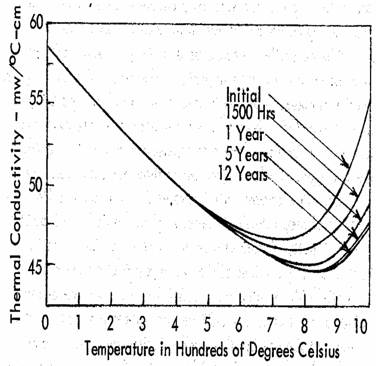


Figure 8 – Thermal Conductivity of p-type 78a/oSi-22a/oGe Alloy

n-Type

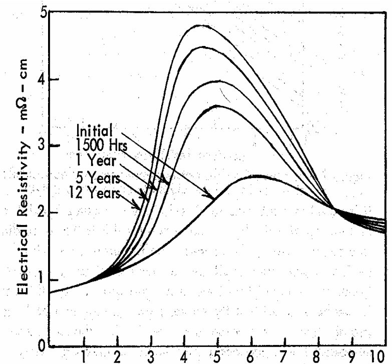


Figure 3 – Resistivity of n-type 78 a/o Si – 22 a/o Ge Alloy

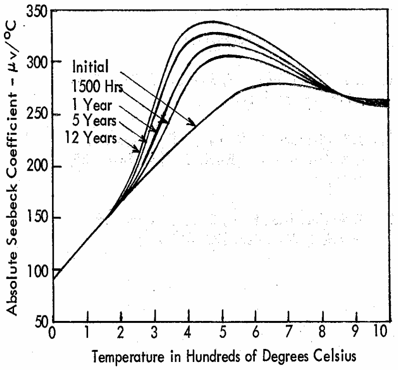
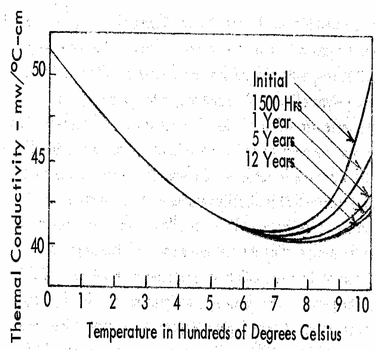


Figure 4 – Seebeck Coefficient of n-type 78a/oSi-22a/oGe Alloy



igure 7 – Thermal Conductivity of n-type 78a/oSi-22a/oGe Alloy

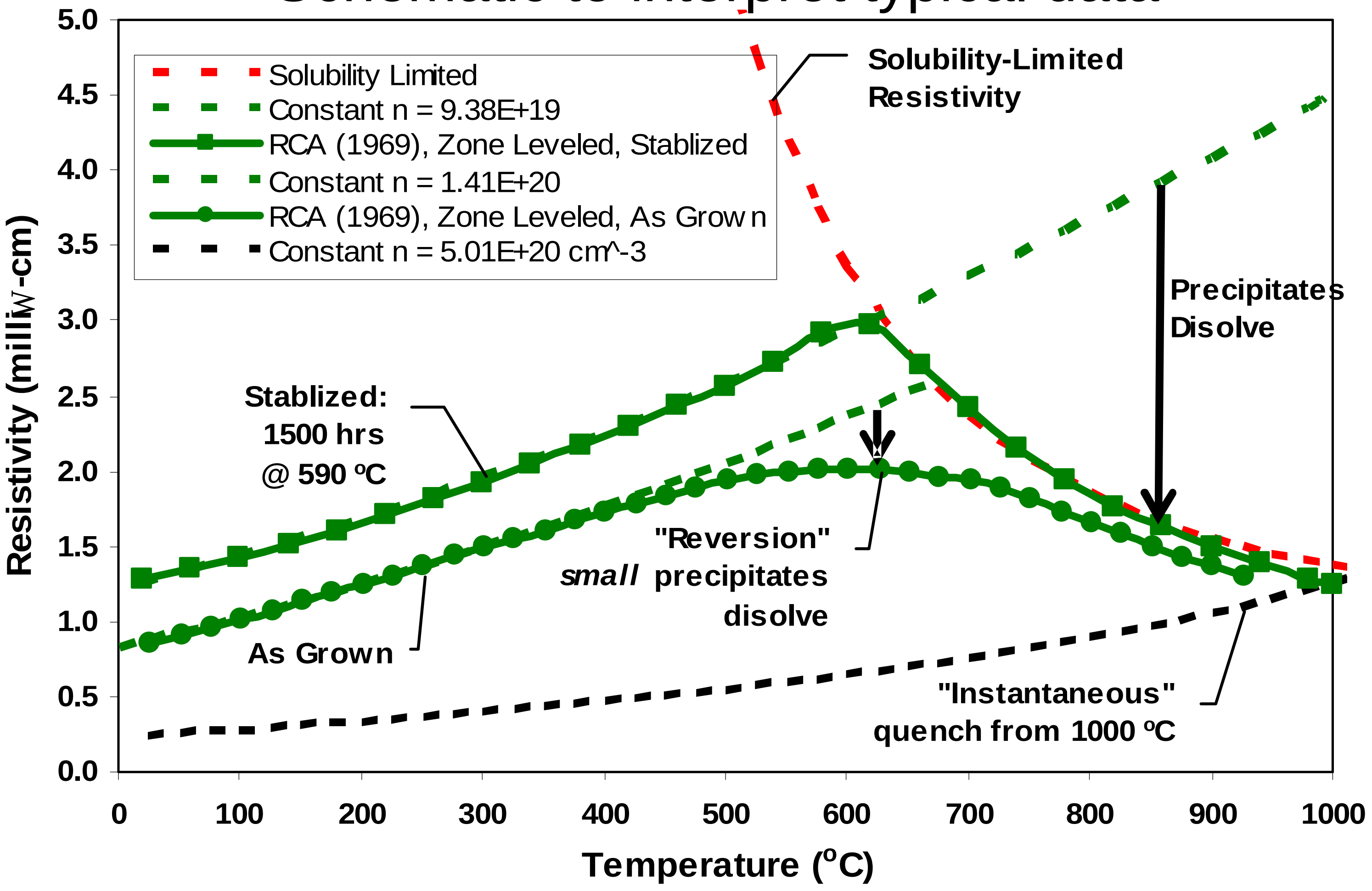
Resistivity Seebeck Thermal Conductivity

Comments on dopant precipitation

- Dopant precipitation (and re-solution, the reverse process) affect every aspect of SiGe technology
  - Preparation, to get enough dopant in solution
    - Elaborate ‘annealing’ procedures favored by some to get the most amount of dopant in solution
  - Measurements
    - Properties change during & between measurements
    - Through creative use of thermal history, you can get a wide range of properties out of a single sample.
    - Essential to measure S & ρ simultaneously because both strongly depend on doping
  - Design: do you want to design to initial properties, or properties expected 5 years from now?
- Models of dopant precipitation are in excellent shape
  - EXCEPT for the first few hours, where quantitative models for effects like “reversion” are not available

SiGe changes *during* measurements

Schematic to interpret typical data



RCA (1969). Topical Report - Silicon Germanium Thermoelectric Materials and Module Development Program. Harrison, NJ USA, RCA: 83.

Other SiGe Degradation Mechanisms

Unicouple Degradation Modes

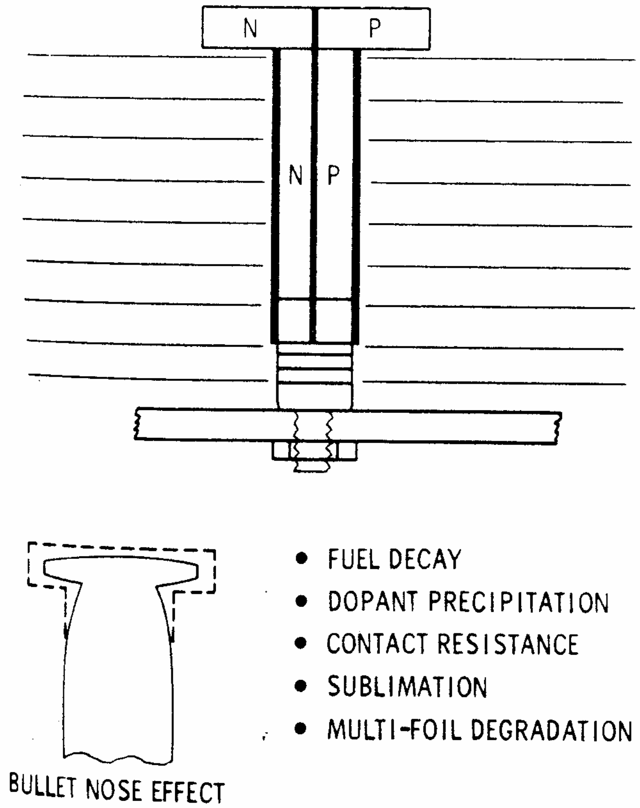


Fig. 1. - Single couple configuration

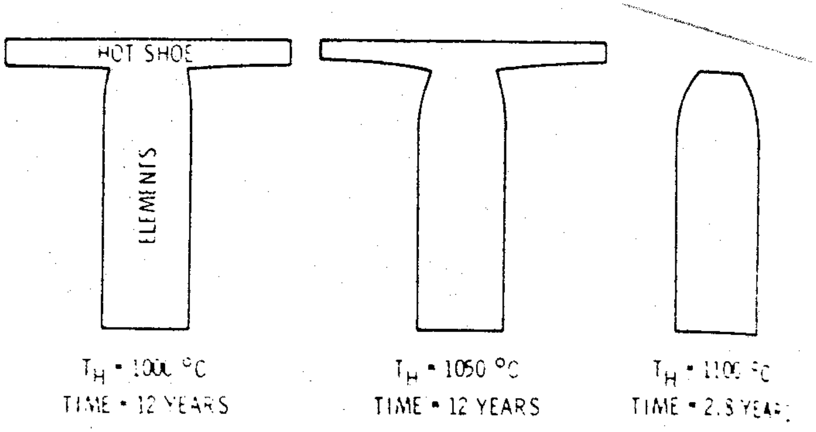
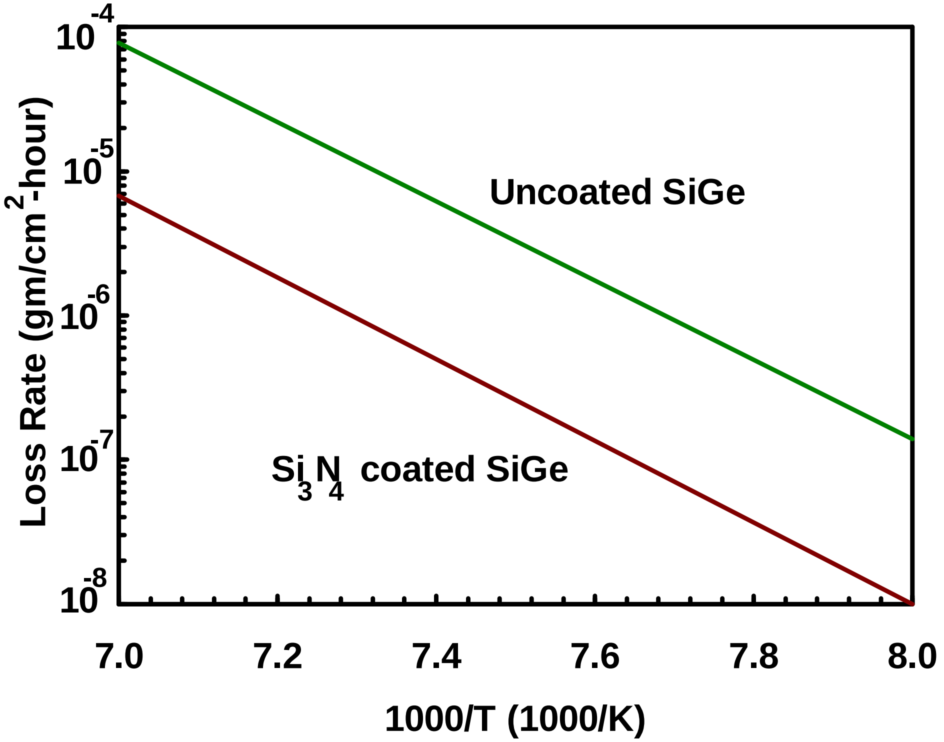


Fig. 4. - Sublimation effect on geometry

- Unchecked sublimation predicted to yield catastrophic failure
  - Si_3N_4 & quartz yarn suppress sublimation
- Life testing & predictive models developed for each degradation mode
- Stapfer, G. and V. Truscello (1974). Model to predict the degradation of a SiGe thermopile. Proceedings of the IECEC p.174-179.

Silicon Nitride Coating



- Material loss rates for $Si_{0.78}Ge_{0.22}$ with and without a 1200 nm coating of Si_3N_4.[i]
- Failure modes estimated from measured loss rates

[i]. Shields, V., and Noon, L., Sublimation measurements and analysis of high temperature thermoelectric materials and devices, in *Proc. of the 18th Intersociety Energy Conversion Engineering Conference*, Vol. 1, American Institute of Chemical Engineers, New York, 1983, 235.

DEGRA

- JPL & Lockheed-Martin have developed fairly detailed computer codes to predict the degradation of SiGe RTGs with time
  - The JPL code is called ‘DEGRA’
- These codes do an excellent job, accounting for
  - Isotope decay
  - Dopant precipitation
  - Contact resistance growth (due to material loss)
  - Sublimation
  - Multifoil insulation degradation
- Isotope decay is by far the main effect
  - Even approximate models are adequate because the total effects are not so large
- The dopant precipitation model is a table-look-up scheme, and therefore inadequate to cope with complex or short-term temperature excursions

- Stapfer, G. and V. Truscello (1974). Model to predict the degradation of a SiGe thermopile. Proceedings of the IECEC p.174-179.

Case Study II: SiGe/GaP

Case Study II:
History of GaP additions to SiGe

- Misconceived attempt at thermal conductivity reduction
- Device tests
- JPL solubility enhancement concept
- Present Status

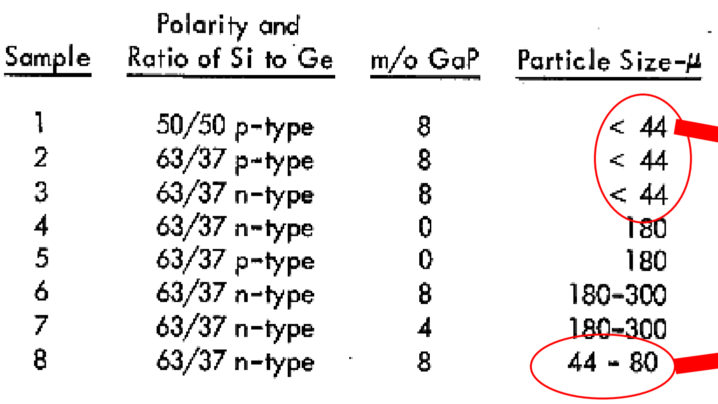
Case Study II: History of GaP additions to SiGe

- GaP is a semiconductor with the same crystal structure and similar lattice parameter to $Si_{0.8}Ge_{0.2}$
- JPL-funded program at Syncal Corp. (bought by ThermoElectron ~1982) hypothesized as early as 1977:
  - 1) GaP formed a solid-solution with SiGe
  - 2) would lower thermal conductivity
- Both hypotheses proved false, but through 1987 it was generally accepted that
  - 1) GaP did lower thermal conductivity
  - 2) also degraded electrical properties
  - 3) Z was improved by about 23%
- Attempts to reproduce thermal conductivity reduction failed, or more precisely indicated the effect was due to smaller grain size rather than GaP content
- In 1987 JPL presented data suggesting GaP actually improved the electrical properties
  - Eventually the idea emerged that GaP enhanced the carrier concentration, thereby improving ZT

- SiGe/GaP is an important case-study illustrating many features of pathological science
  - 27 years later, long-lasting improvement in ZT remains an open question

SiGe/GaP: The early idea

- JPL funded experimental work at Syncal 1977-1985
- First paper:
  - Pisharody, R. K. and L. P. Garvey (1978). Modified Silicon-Germanium Alloys with Improved Performance. 13th Intersociety Energy Conversion Engineering Conference, San Diego, CA, Society of Automotive Engineers, Warrendale, PA.
- Hypothesis & Conclusion: GaP lowers thermal conductivity & increased ZT
  - But even this first paper suggested particle size plays a role



Sample	Polarity and Ratio of Si to Ge	m/o GaP	Particle Size-μ
1	50/50 p-type	8	< 44
2	63/37 p-type	8	< 44
3	63/37 n-type	8	< 44
4	63/37 n-type	0	180
5	63/37 p-type	0	180
6	63/37 n-type	8	180-300
7	63/37 n-type	4	180-300
8	63/37 n-type	8	44 - 80

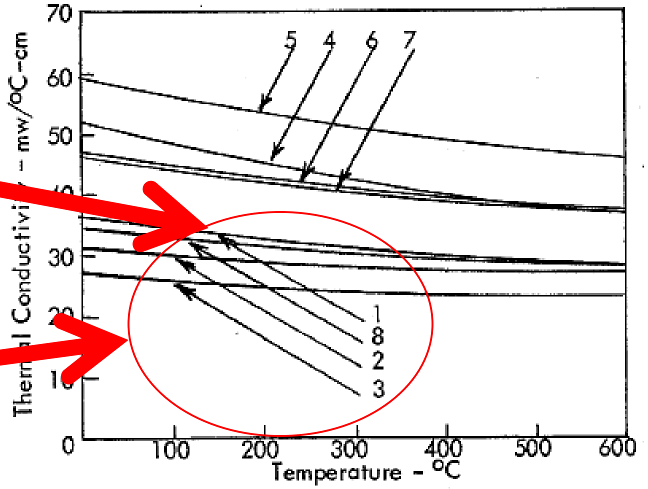


Figure 2 - Thermal Conductivity as a Function of Temperature of the Test Samples Identified in Table 2.

SiGe/GaP: The early idea

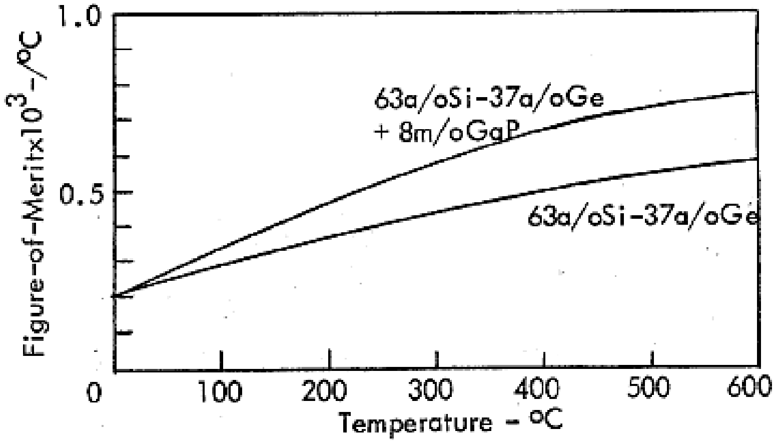
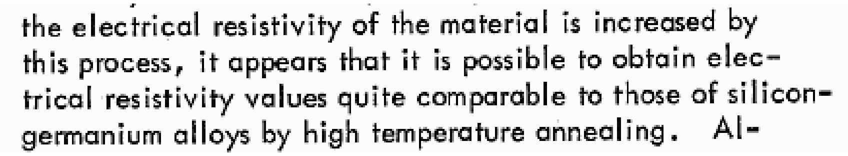


Figure 5 - Figure-of-Merit as a Function of Temperature of Test Samples 2 and 5 Identified in Table 2.


the electrical resistivity of the material is increased by this process, it appears that it is possible to obtain electrical resistivity values quite comparable to those of silicon-germanium alloys by high temperature annealing. Al-

- Pishorody, 1978

- Conclusions:
  - λ reported reduced 40-50%
  - ZT improved, but didn't say by how much
  - ρ degraded
- The process used to incorporate GaP involved grinding to fine powders
  - more GaP, finer powders & lower λ
- Inadequate controls were done to study effect of grain/particle size alone
- 92-97% theoretical density
  - Compared to 99+% for prior SiGe

Mass Alloy Scattering in SiGe/GaP

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

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

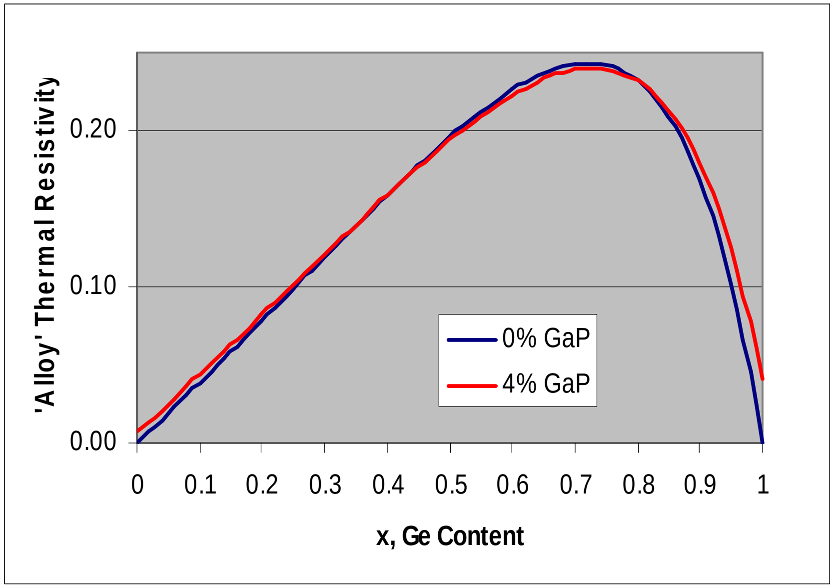
$$\overline{M} = \sum_i y_i M_i = \text{Average Atomic Mass}$$

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

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



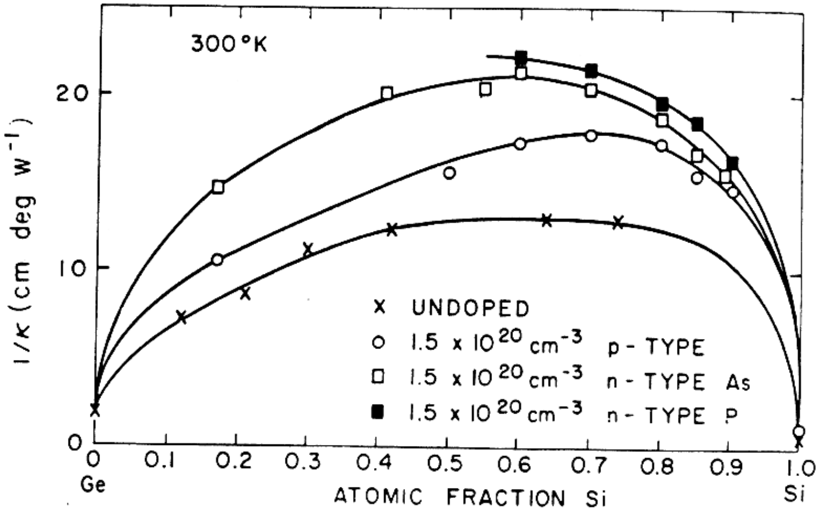


Fig. 44. The thermal resistivity of undoped and doped, p–and n–type Ge–Si alloys as a function of alloy composition at 300 °K.

Dismukes, 1964

The “Ames-Purdue” data on SiGe/GaP

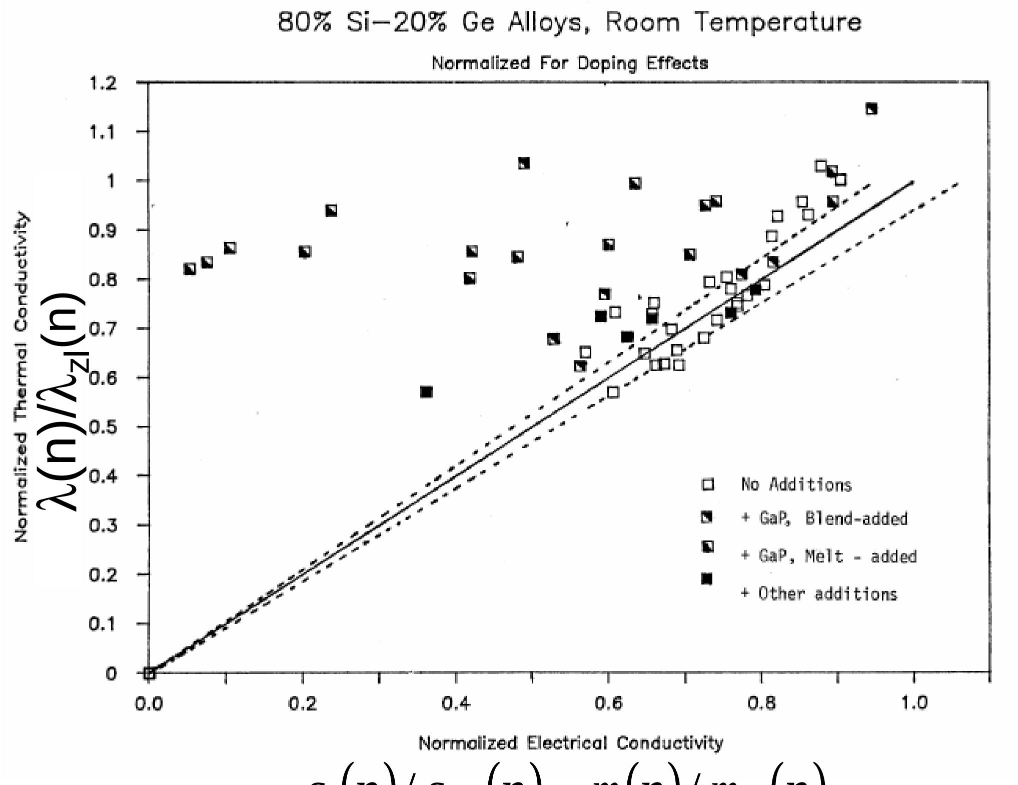
- Independent verification of the early Syncal claims was sought
  - Apparently No facility in the US could measure all three (S, ρ, λ)
  - Syncal sent samples to US-DoE’s Ames Laboratory (Ames, Iowa) for S and ρ measurement
  - Sent samples to Purdue Universities Thermophysical Properties Research Lab for λ measurements
- This dataset became known as the “Ames-Purdue” data & was for years accepted as the appropriate basis for device design work
- But different samples were sent to Ames & to Purdue
  - Purdue got some low density, low thermal conductivity samples
  - Ames got high density samples with decent electrical properties

Unicouple & Bicouple Tests

- 1982 Syncal is bought out by ThermoElectron & begins making SiGe/GaP (both n-type & p-type) for device fabrication at ThermoElectron & GE
- The p-Type SiGe/GaP is quickly abandoned, because the material becomes n-type in a short time
- GE fabricates a number of SiGe/GaP unicouple modules
  - All perform miserably
  - results are never reported & have since been lost (AFAIK)
- 1983-4 GE fabricates 8 ‘bicouples’: 4 with SiGe/GaP and 4 ‘fine grain’ SiGe
  - The bicouple consisted essentially of 2 unicouples in a single unit
  - Bicouples were never built with ‘standard’ SiGe – poor controls
  - The first set of 8 bicouples were accidentally melted during testing at Fairchild
  - A second set of 8 bicouples were built by GE
    - Using SiGe/GaP from ThermoElectron & ‘fine grain’ SiGe made at GE
    - Tested at Fairchild
    - All 8 bicouples performed less than expected, and less than predicted for standard SiGe
    - But the lousy SiGe/GaP bicouples were better than the lousy ‘fine grain’ SiGe
- The Myth is now complete: devices have proved SiGe/GaP is improved
  - The analysis is much more ambiguous, proving only that SiGe/GaP had a lower thermal conductivity than the ‘fine grain’ SiGe used in the test
  - But the meme that SiGe/GaP works is by now firmly implanted

Effect of GaP additions on λ

- Samples vary in doping level, particle size, and other processing variables
- Normalize the electrical and thermal conductivity to account for doping variations
- λ can indeed be reduced as much as 50% by processing, as claimed
  - But the correlation is with particle size, not GaP content
  - And electrical conductivity is reduced as much, or more
- Samples below the solid line have improved β & ZT
  - There aren't any!

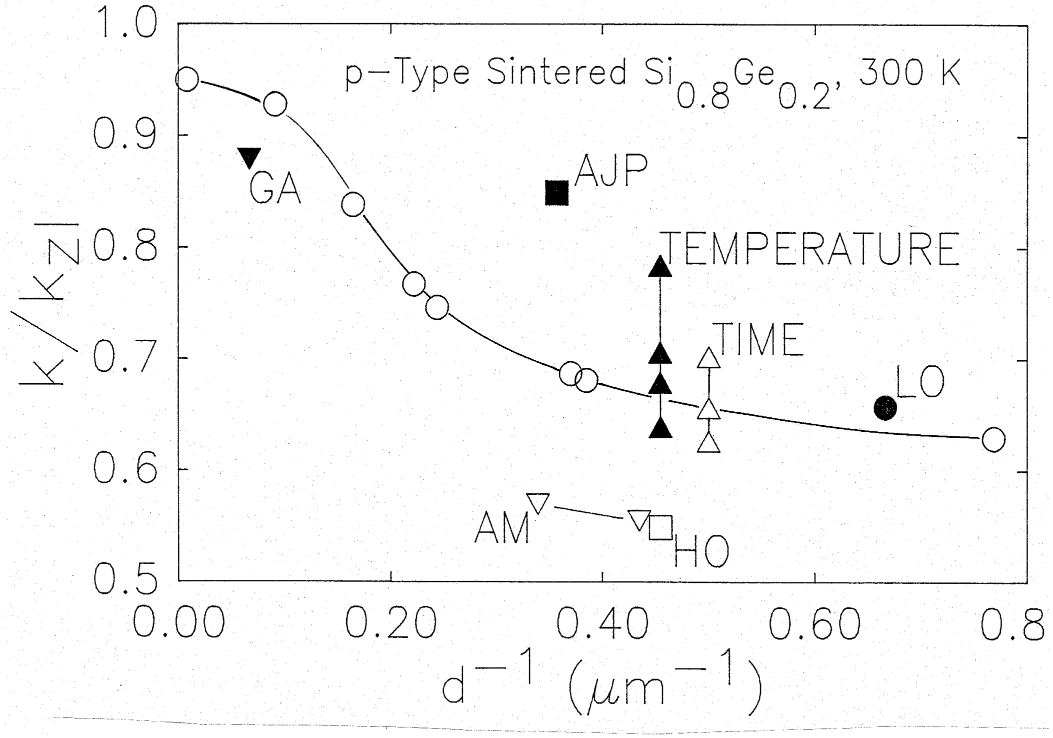


$$s(n)/s_{zl}(n)=m(n)/m_{zl}(n)$$

- Vining, C. B. (1985, unpublished memo). Thermoelectric Performance of Sintered Silicon-Germanium Alloys Compared to Zone Leveled Alloys. King of Prussia, PA, General Electric (GE): 9.

The real reason for λ reductions

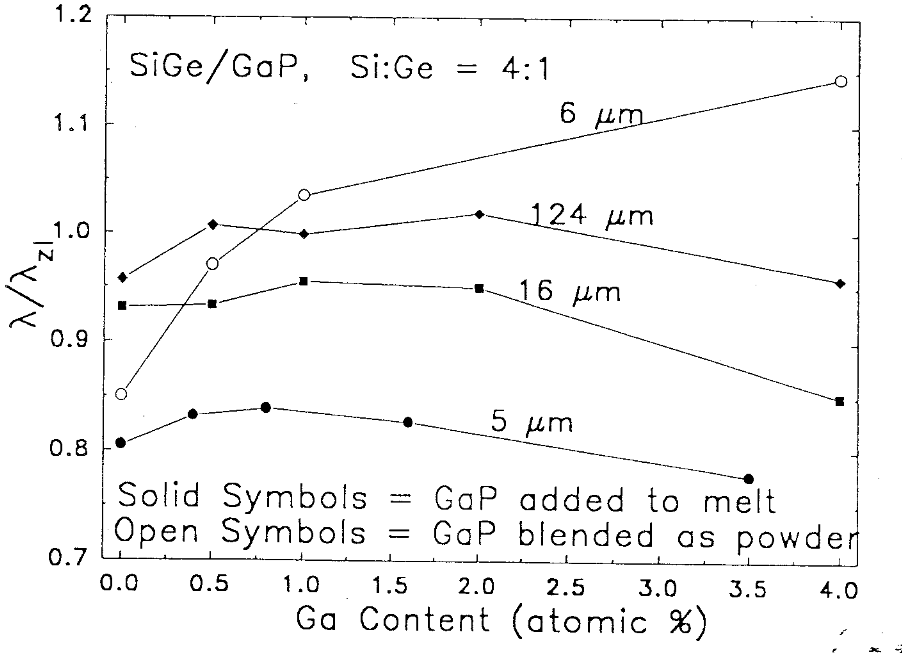
- Particle size & other processing conditions can reduce λ
- Sadly μ (& therefore σ) is also reduced
- Concluded ZT improved 11 ± 4% by reduced particle size
- Received little fanfare, but since about 1986 Lockheed-Martin (then GE) has used somewhat smaller grain size SiGe than had been used in GPHS-RTGs
- Small grain-size material is also stronger



Vining, C. B., W. Laskow, et al. (1991). "Thermoelectric Properties of Pressure-Sintered Si0.8ge0.2 Thermoelectric Alloys." Journal of Applied Physics **69**(8): 4333-4340.

End of an era: GaP doesn't reduce λ

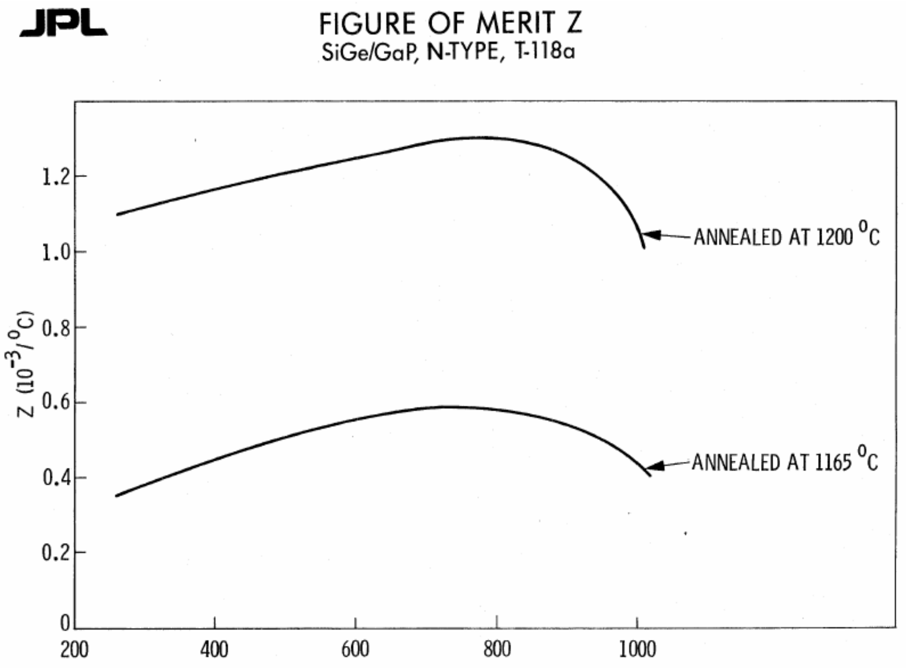
- Particle size & processing much more important than GaP content
  - Studies done at GE 1984-7
- Once accounting for carrier concentration effects, in no case was ZT improved



Vining, C. B. and J.-P. Fleurial (1994). Silicon-Germanium: An Overview of Recent Developments. A Critical Review of Space Nuclear Power and Propulsion 1984-1993. M. S. El-Genk. New York, American Institute of Physics: 87-120.

The new GaP: same ZT, different reason

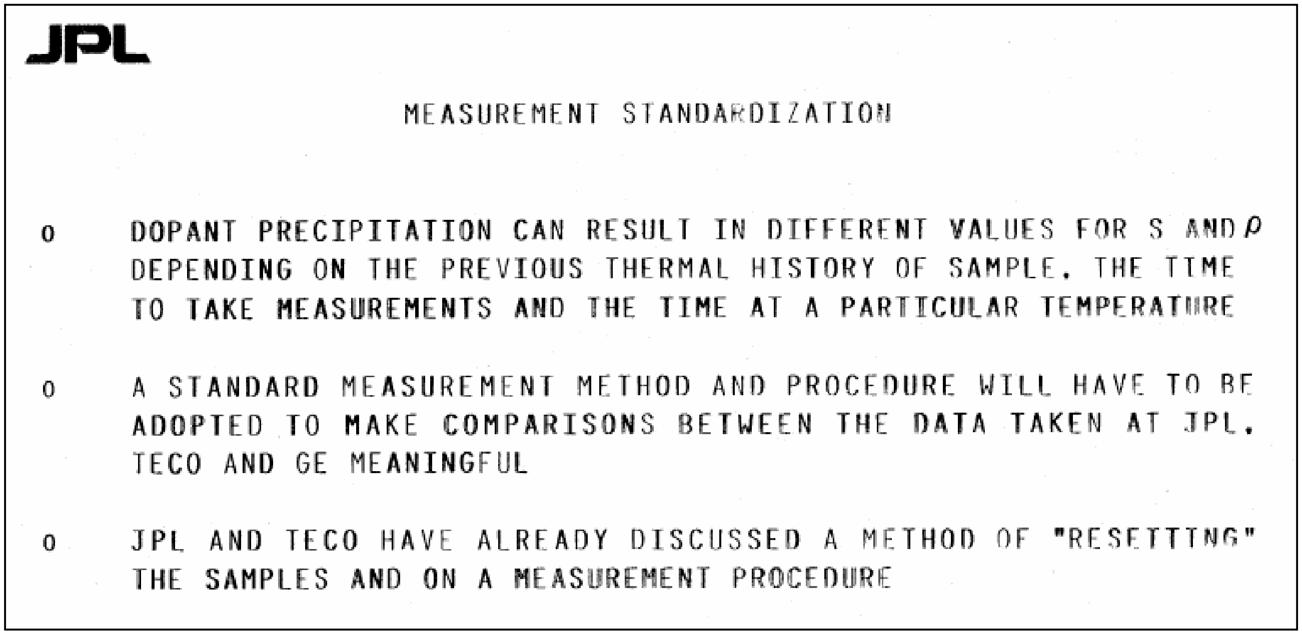
- In 1987 JPL (Vandersande) presented results of ‘annealing’ studies on SiGe/GaP
  - Z (& ZT) roughly doubled!
  - Primarily due to improved electrical properties, not lower λ
- For some time sample T-118a was the best sample reported
  - Never reproduced



Vandersande, J. W. (1987). Quarterly Review, Space Subsystems Technology, JPL In-House Effort. Presented at Germantown, MD, USDoE**:** 43.

Dopant Precipitation & SiGe/GaP

- Even in the first 1987 report, dopant precipitation was recognized to complicate data interpretation



JPL

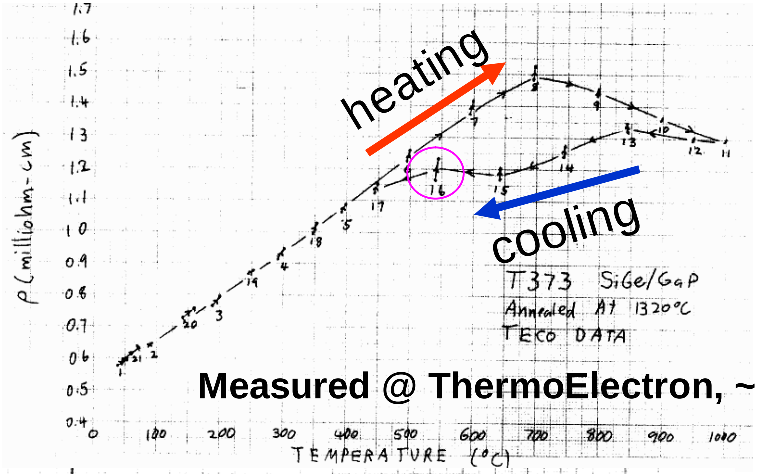
MEASUREMENT STANDARDIZATION

- o DOPANT PRECIPITATION CAN RESULT IN DIFFERENT VALUES FOR S AND ρ DEPENDING ON THE PREVIOUS THERMAL HISTORY OF SAMPLE. THE TIME TO TAKE MEASUREMENTS AND THE TIME AT A PARTICULAR TEMPERATURE
- o A STANDARD MEASUREMENT METHOD AND PROCEDURE WILL HAVE TO BE ADOPTED TO MAKE COMPARISONS BETWEEN THE DATA TAKEN AT JPL, TECO AND GE MEANINGFUL
- o JPL AND TECO HAVE ALREADY DISCUSSED A METHOD OF "RESETTING" THE SAMPLES AND ON A MEASUREMENT PROCEDURE

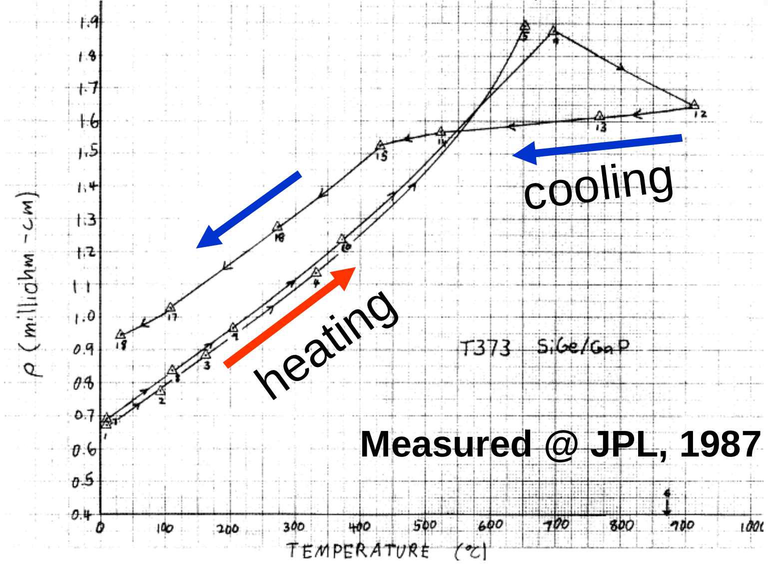
Vandersande, J. W. (1987). Quarterly Review, Space Subsystems Technology, JPL In-House Effort. Presented at Germantown, MD, USDoE: 43.

TE properties change *During* measurements

- T373 was for years one of the best n-type SiGe/GaP samples reported.
  - S & ρ measured simultaneously at ThermoElectron
  - At that time, JPL measured S & ρ in entirely different apparatus
    - Essentially different samples!
- Characteristic thermal hysteresis
  - Different results on cooling, depending on time for dopant precipitation
- ThermoElectron was in the habit of measuring resistivity twice:
  - Once before measuring S
  - Again after measuring S
  - Note ρ can be clearly seen to change *during the time it takes to measure the Seebeck*
- In the wrong hands, amounts to an elaborate "Etch-a-Sketch"



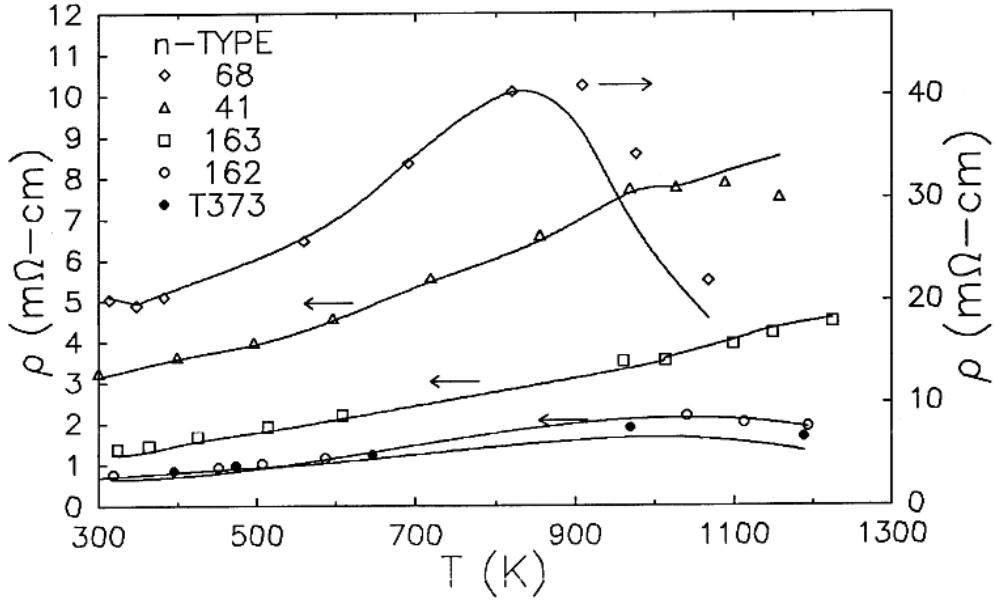
Measured @ ThermoElectron, ~1987



Measured @ JPL, 1987

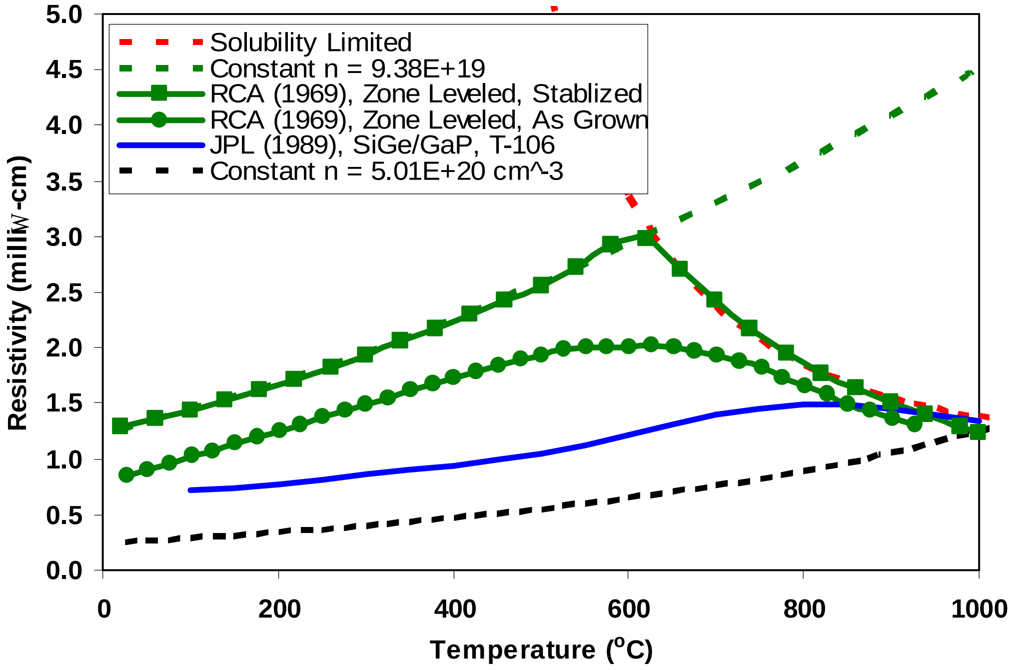
Comparison of SiGe/GaP with ZT theory

- Solid lines are theoretical calculations
- The best n-type SiGe/GaP available at that time (T-373) is indistinguishable from ‘standard’ SiGe
  - Except for an initially higher carrier concentration



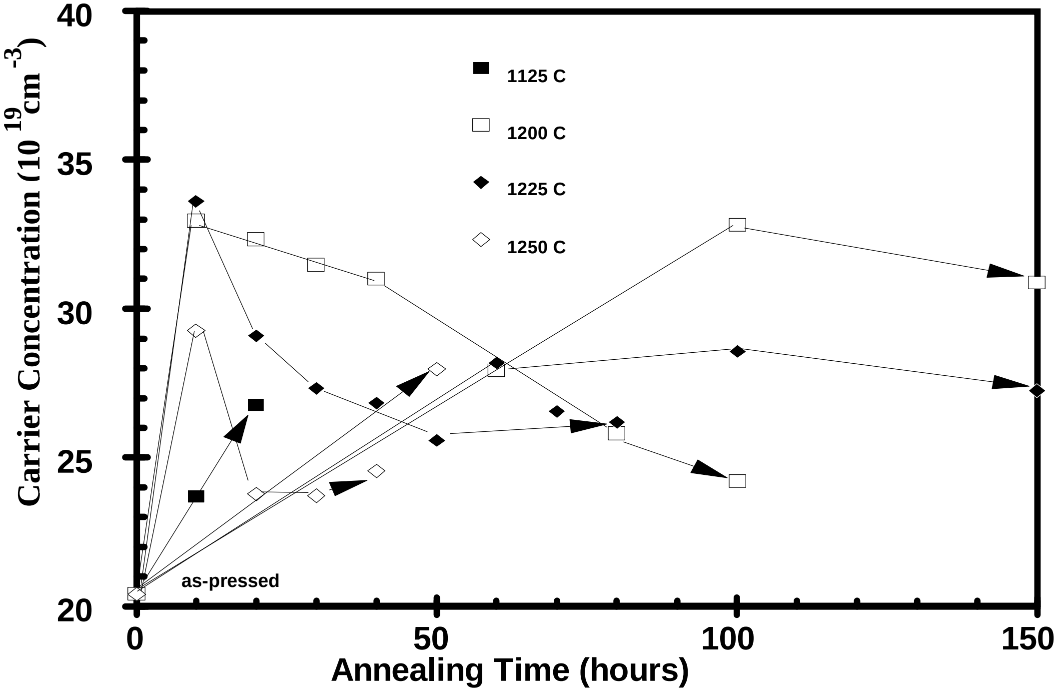
SiGe/GaP seems similar to zone-leveled SiGe

- At 1000 oC ρ is limited by solid solubility of phosphorus
  - – GaP appears to have no effect at 1000 oC, so solubility appears to be unchanged
- At lower temperatures, ρ is increasingly determined by the thermal history and degree of supersaturation
  - – Time-at-temperature studies needed to determine kinetics of dopant precipitation



SiGe/GaP Sensitivity to history

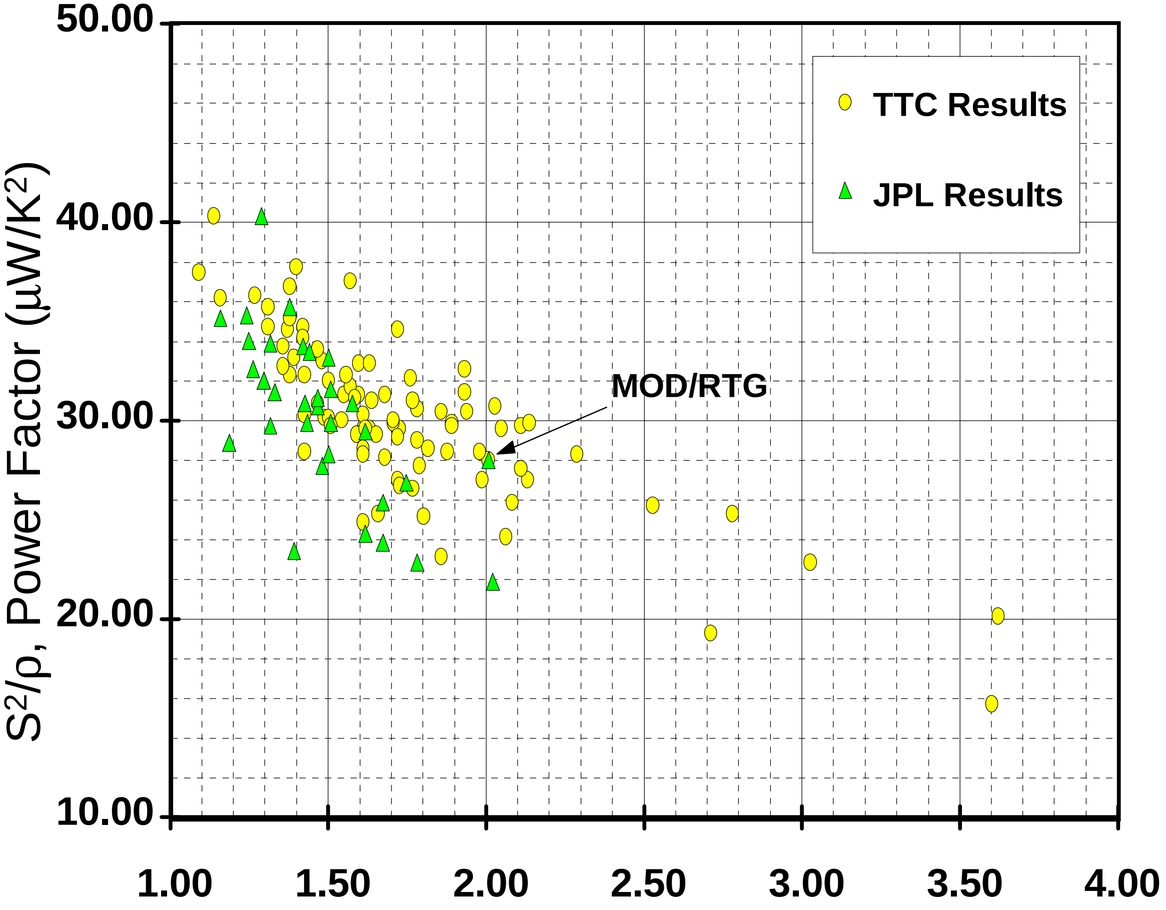
- Thermal history affects the initial room temperature carrier concentration
    - Initial room temperature carrier concentrations can be increased from about 2x10^{20} cm^{-3} to about 3.5x10^{20} cm^{-3}
    - Nice study, but hardly surprising
    - Fairly sensitive to thermal history
- Note that this may *not* evidence of increased solubility of phosphorus
    - Consistent with being simply a greater degree of initial supersaturation
    - Similar affects observed as early as the 1960s with phosphorus-only doped material
    - Proper controls were not done to determine how much of this effect can be explicitly attributed to GaP



Changes in Room Temperature Carrier Concentrations of SiGe/GaP Samples With Annealing Time and Temperature, Redrawn From (Fleurial 1991b).

Effect of GaP on Power Factor

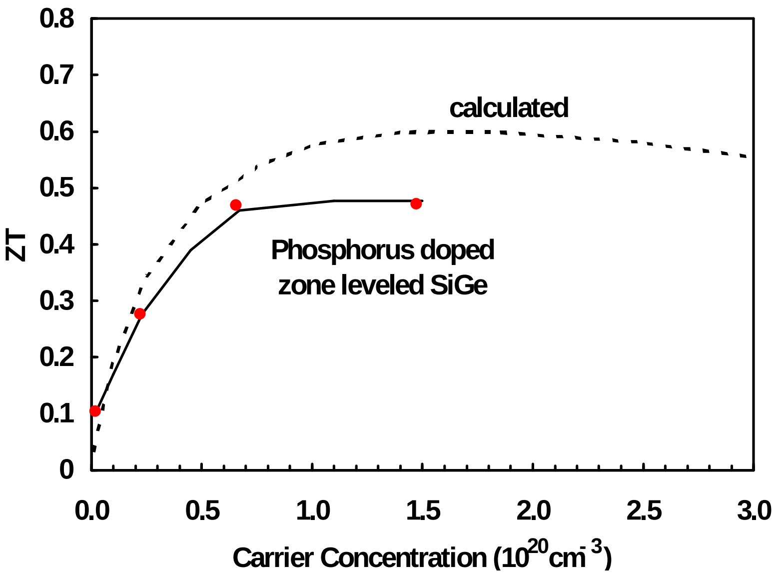
- GaP additions to SiGe, and the subsequent thermal annealing(s), are entirely consistent with affecting the carrier concentration only
    - Other processing effects, such as reduced μ & λ due to small grain size must also be accounted for
- Questions:
    - How much can the *initial* ZT be improved by this method?
    - How long can the initial improvements be expected to last?

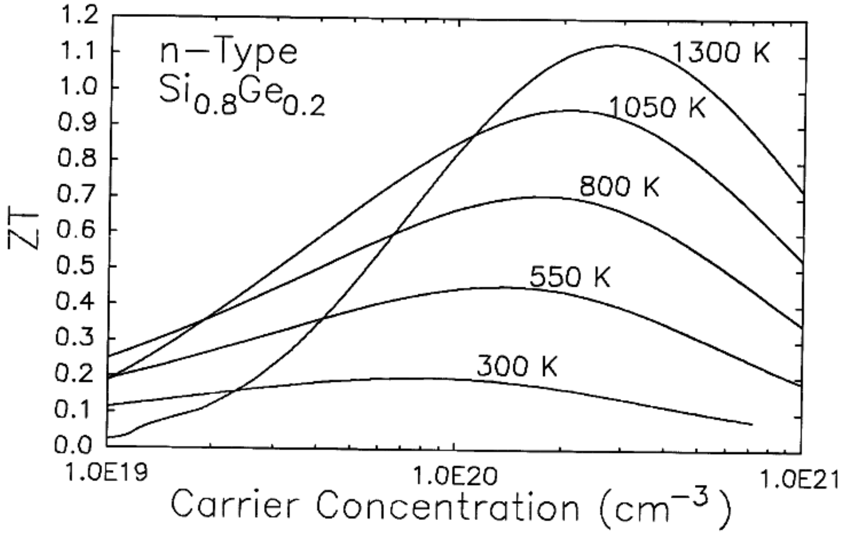


600-1000 C Integrated Average Power Factor of recent n-Type SiGe/GaP Samples Versus Integrated Average Electrical Resistivity, Redrawn From (Fleurial 1993a).

ZT is a graceful function of carrier concentration

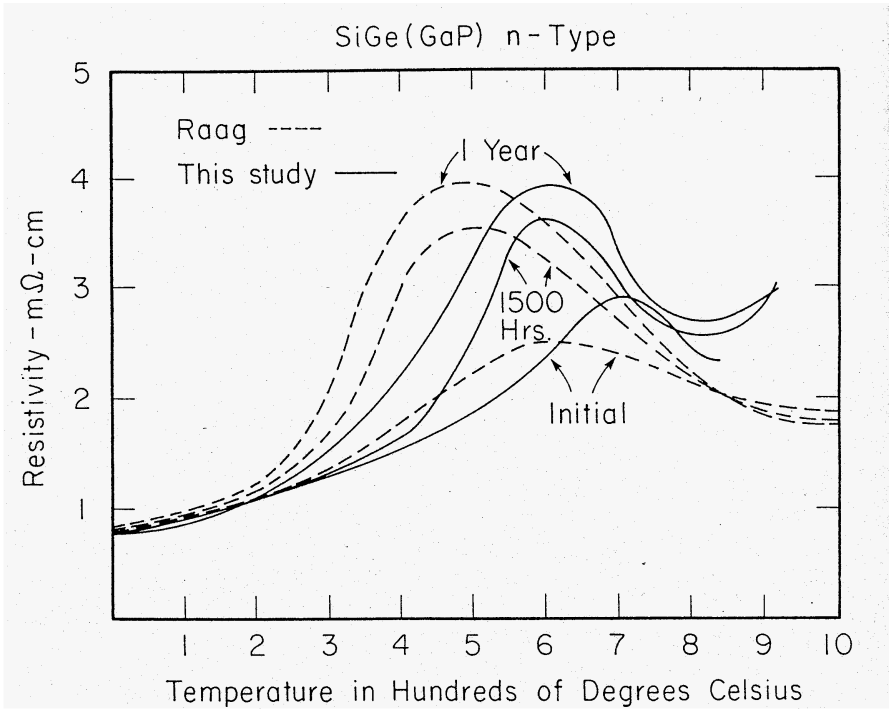
- Dimensionless figure of merit (averaged from 300 to 1000 K) for zone leveled n-type $Si_{0.7}Ge_{0.3}$
  - dashed line is calculated using the model described in previously.
- Similar results obtained on hot pressed $Si_{0.8}Ge_{0.2}$
- Above ~ 1100 K, phosphorus quickly reaches the solubility limit
- An estimated 20% improvement in ZT ***if*** carrier concentration can be maintained near optimum levels over time





Dopant Precipitation in SiGe/GaP

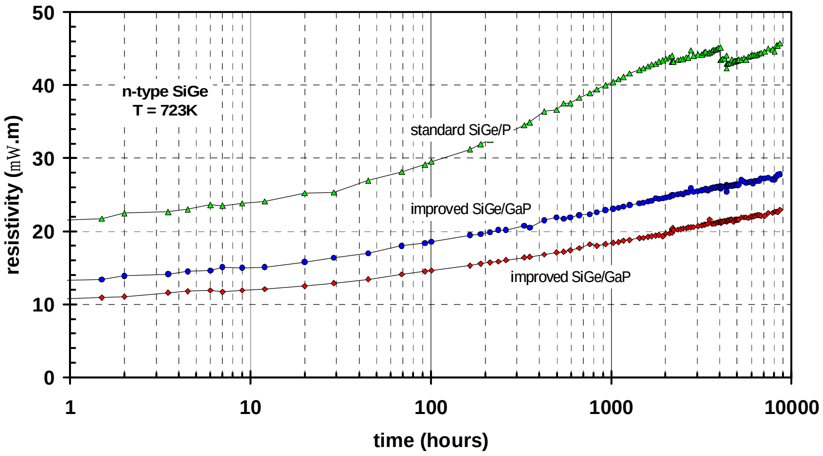
- A dopant precipitation study of SiGe/GaP was done at Ames Laboratory (1990)
  - Using n-type SiGe/GaP made at GE
    - Known to not have improved ZT (!), but it was available
- ‘Standard’ SiGe tested as a control agreed well with previous results
- Distinct differences in the rates of precipitation below 700 ^{o}C
- No evidence for increased solubility!
  - High temperature resistivity is actually higher
  - Several possible explanations, but none can be certain

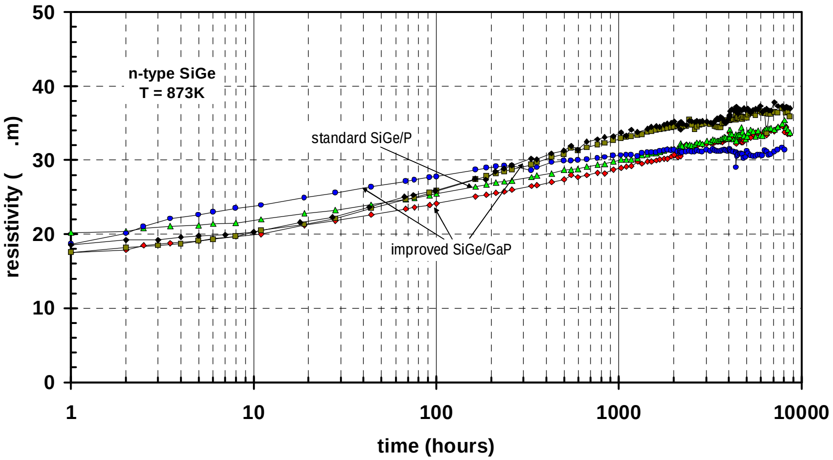


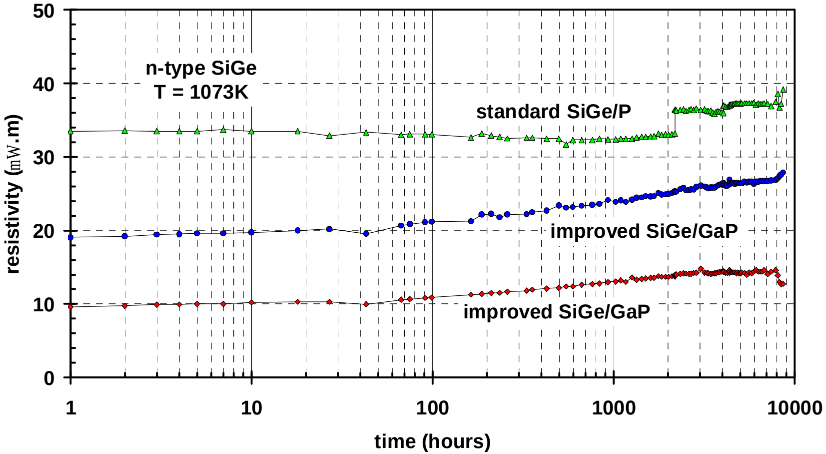
- Tschetter, M. J. and B. J. Beaudry (1990). Effect of GaP on the resistivity versus time at elevated temperatures of n-type Si80Ge20 alloys. Proceedings of the Intersociety Energy Conversion Engineering Conference, Reno, NV, USA, Publ by IEEE, Piscataway NJ p.382-386.

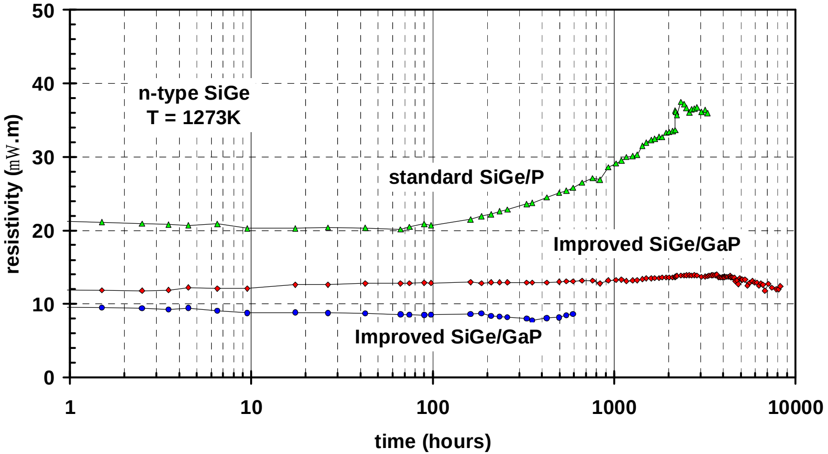
Long term dopant precipitation study @ JPL

- Longer duration dopant precipitation study underway at JPL (Fleurial, 2003)
  - Has yet to be analyzed with standard dopant precipitation model
- Hard to understand the T=1273 K data
  - Unexpected rise in ρ for ‘standard’ SiGe
  - Unexpectedly low ρ for ‘Improved SiGe/GaP’









SiGe/GaP ZT vs. Time

Averaged between 300 °C – 1000 °C

			S^2/ρ µW/cm-K²	λ W/cm-K	ZT
1982	Made by Syncal/Raag Measured @ Ames/Purdue	SiGe/GaP	31.1	0.0315	0.91
1987	Vandersande/JPL (T-106)	SiGe/GaP	41.8	0.0430	0.90
1981/ 1986	Syncal/Raag made Sample Measured @ GE	SiGe/GaP	29.9	0.0447	0.62 ± 0.03
1986	GE's Best SiGe/GaP	SiGe/GaP	24.0	0.0323	0.69 ± 0.03
1986	GE - "Precursor", used to make SiGe/GaP	$Si_{0.8}Ge_{0.2}$	29.9	0.0406	0.68 ± 0.04
1984	GE - GPHS Spec	$Si_{0.78}Ge_{0.22}$	28.6	0.0409	0.65 ± 0.03
1987	GE	Si	36.2	0.1506	0.22 ± 0.01
1995	Ames - Only SiGe/GaP ZT data in a refereed Journal!	SiGe/GaP	34.4	0.0375	0.85

Status of SiGe/GaP

- Initially thought to lower λ
  - Sloppy interpretation of bad theory = WRONG
- Suddenly the mechanism of how GaP works shifted to: increasing the carrier concentration
  - Oddly, ZT remained unchanged following this shift in mechanism
  - Substantial increases in carrier concentration can be achieved by a combination of GaP additions, hot pressing conditions & elaborate ‘heat treatments’
  - How much of this effect is due to GaP an how much is due to the other processing variables has never been carefully studied
- It has been suggested that a permanent increase in solid solubility has occurred
  - Available data strongly suggest SiGe/GaP has no more electrically active P in solution @ 1000 °C than regular SiGe
  - Higher *equilibrium* carrier concentrations have yet to be demonstrated
    - only higher initial carrier concentration have been demonstrated
- If initially enhanced carrier concentrations can survive the device manufacturing cycle, much less survive time at temperature, isn’t clear
- Even if achieved, higher carrier concentrations have only modest effect on ZT
- In his paper on the maximum efficiency of SiGe Slack (1991) remarked
  - “The utility/futility of GaP additions and grain-boundary scattering as methods to increase the efficiency is discussed.”

The Bizarre Logic of making SiGe/GaP devices

- Since the early 1980s SiGe technology programs have adopted SiGe/GaP for device work
  - This despite the fact that SiGe/GaP with reproducible ZT values better than standard material ***has never been available outside the lab*** (if anywhere).
  - The recipe used for SiGe/GaP under the MOD-RTG & SP-100 programs is (and was) known to have lower ZT values than the 'standard' SiGe from which it was made
- The logic of this practice always escaped me
  - One has to presume that the materials development people would eventually figure out a reliable recipe for high ZT SiGe/GaP and would teach it to the people making devices
  - In the mean time, the manufacturing techniques would have already been developed
    - Assuming the final recipe is 'close enough' to the flavor used in device development
  - But this has not happened yet in the 26 years since SiGe/GaP was first reported
  - Lockheed-Martin simply made the best SiGe/GaP they know how, and used that to make devices.
- Many early bicouple and MOD-RTG multicouple difficulties were directly traced to the GaP
  - First, the bonding techniques need to be modified (temperatures & times) to account for the different chemistry of SiGe/GaP, small as it is
  - Free Ga is an electrically conducting liquid
  - Put in too much GaP and the Ga "cries" out of sample, leading to:
    - Electrical shorts
    - Reaction with glasses
    - Debonding
  - Extensive glassing efforts have focused on containing the Ga
- Device development is difficult and should never be squandered on an unqualified TE material
  - Although there are even worse examples than SiGe/GaP
  - Such as the all n-leg lanthanum sulfide modules SP-100 built in 1985-6 because there was no p-leg available!

Selected SiGe/GaP Device Tests

	Report Organizations	Remarks
Unicouple	Circa 1982-3 Nothing published GE, Thermo-Electron	More than one 18-couple module built with SiGe/GaP unicouples. All the reports I saw indicated significantly reduced performance. I haven't seen any of these reports in 17 years
Bicouple	1984 GE ThermoElectron Fairchild	4 SiGe/GaP & 4 'fine grain' SiGe tested SiGe/GaP electrical properties worse than expected & degraded faster than expected Tests did suggest a lower λ
MITG Multicouple	Eck, 1983 ThermoElectron Fairchild	2 tests of eight SiGe/GaP multicouples Shorts Rapid Increase in internal resistance Cold end cracking – in SiGe Ge diffusion on hot side
MOD-RTG Multicouple	1984-1993+? GE Fairchild	Many devices tested. Early on, similar to MITG failures: shorts, debonding, glass degradation By ~1993, most failure modes seemed reasonably controlled
SP-100 Cell	1997 Lockheed-Martin (was GE) JPL	GE: "100 % successful" BUT a number of "engineering development" issues. Based on 4 cells & 14,000 to 23,000 hrs of testing. Debonding within cell & probably compliant pad. 83-100% of expected power after 'normalizing'. Counting internal losses, 57-77% of expected power.

Other Notable Warts

The ‘Selenides’ Saga

Intended RTG for Galileo

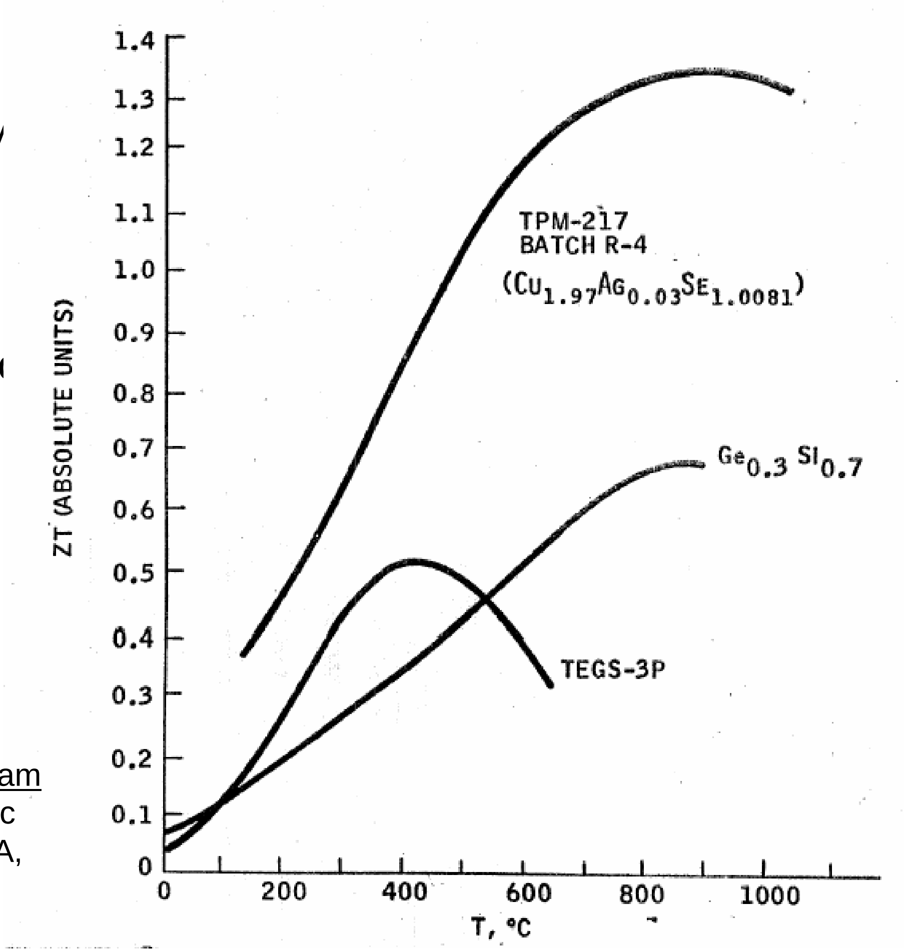
Origins of ‘The Selenides’

- 3M Developed two novel selenium-based TE materials
  - P-type: Cu_2Se ($Cu_{1.97}Au_{0.03}Se_{1.0045}$)
  - N-type: $GdSe_{1.5-x}$ ($x < 0.01$)
  - Very high ZT values
  - 3M called them ‘TPM-217’
  - Most everyone else called them: ‘The Selenides’
- USDoE funded from 1968 through ~1980
- Intended for use on Galileo with target launch date 1981
  - Galileo launched with SiGe RTG in 1989

Hinderman, J. D., E. F. Hampl, Jr., et al. (1978). Selenide thermoelectric converter technology. Proceedings of the 13th Intersociety Energy Conversion Engineering Conference (IECEC), p.1938-45.

P-Type Cu_2Se

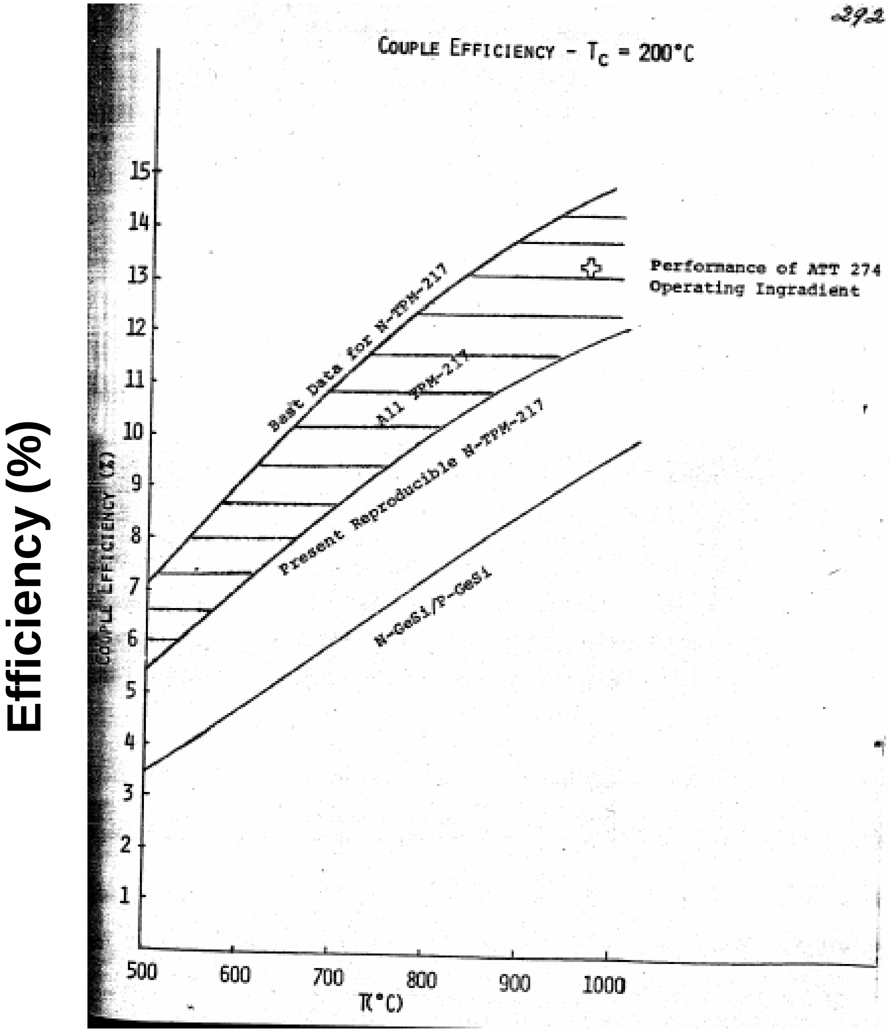
- Irresistible ZT!
- Not clear if this is measured or 'Future Potential', but reported by 3M
- Concerns about long term stability
  - Cu ions flow with applied electric current
  - Se vapor pressure
- 3M reported extensive life tests, up t 56,000 hrs
- Independent technology studies @ JPL & General Atomics
- By 1978 JPL believed 'a reliable selenide RTG can be developed'



Hampl, E. F., Jr. (1975). TPM-217 Technology Program Review. Sixth Annual Short Course on Thermoelectric Devices and Their Applications, Arlington, Texas USA, University of Texas at Arlington p.233-310.

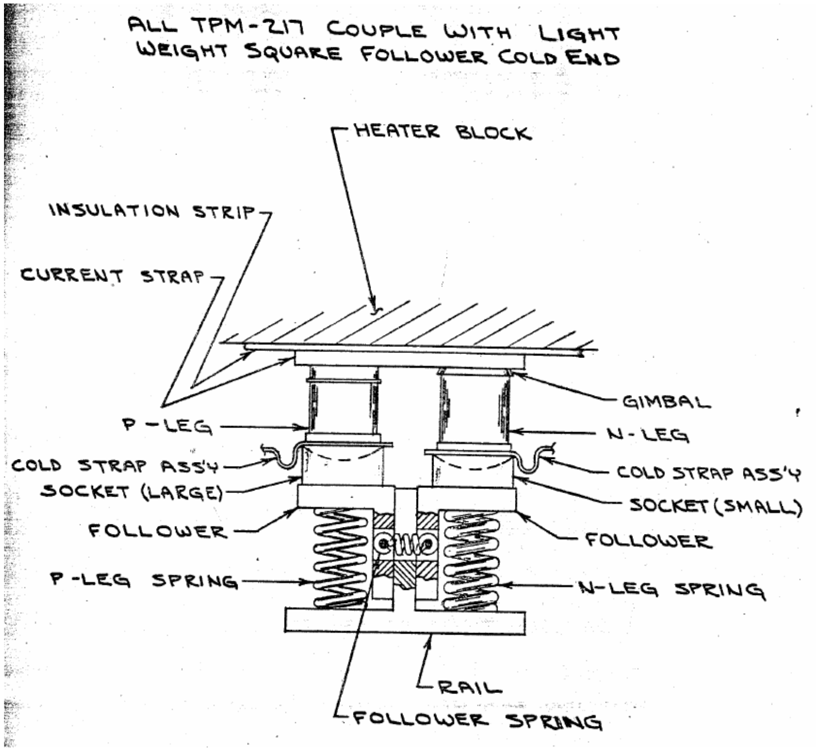
N-type $GdSe_{1.5-x}$

- Extensive life testing
  - Up to 13,500 hours
- Apparently stable



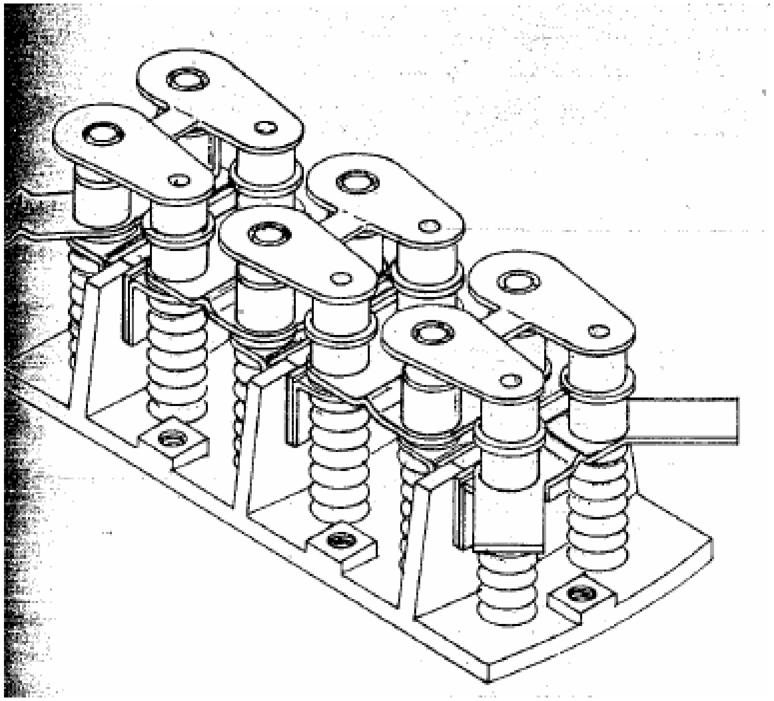
Selenide Couple

- Lots of hardware tested
- Couples built into various sized modules
- Tested 'in-gradient'
- Everything looked good to go for Ground Demonstration System (GDS)
    - Next step: Galileo flight system



Selenide Ground Demonstration System

- 3M built a 156 couple ground demonstration system
  - A flight system would consist of 2 such units
  - Placed on test end of 1977
  - No public report of test results AFAIK
- Catastrophic failure
  - According to observers present when GDS placed on test, power output dropped precipitously, & in discrete steps, within the first 12-24 hours
  - Afterwards it was determined the n-legs ($GdSe_{1,.5-x}$) were cracking, resulting in loss of power
- Apparently an inherent property of $GdSe_{1,.5-x}$
  - $GdSe_{1,.5-x}$ comes in two crystal structures
    - A cubic phase with good ZT, stable at high temperatures
    - An orthorhombic phase with much lower ZT, stable ***at operating temperatures!***
  - Under operation $GdSe_{1,.5-x}$ changes crystal structure
    - The associated change in volume results in cracks & failure



Some Consequences of Selenide GDS Failure

- By early 1980s, DoE abandons selenide technology & moves to re-establish SiGe RTG capability for Galileo
- 3M gets out of thermoelectrics & space power
  - Stops taking federal study contracts of any kind
  - TE personnel leave 3M and form Global Thermoelectrics, still operating out of Calgary
- GE (now Lockheed-Martin) establishes Valley Forge, PA SiGe facility
  - Using RCA developed technology (including some fabrication equipment) & as many RCA personnel as could be found
  - RCA SiGe facility had been shut down & they were not interested in re-establishing capability
  - Cost of re-establishing SiGe technology (not counting actual cost of building new converters): ROM
    - \$10M in early 1980s \$
  - Value of salvaging Galileo mission: priceless
- A legacy within DoE & NASA to eschew new thermoelectric technology
  - Witness the irrational effort put into SiGe/GaP, in part because it appeared familiar and a ‘plug & play’ replacement for SiGe

- The Selenide failure is probably a major contributor to retarding thermoelectric development

How did Selenide GDS Failure Happen?

- I don't know
- Everything seemed OK
  - Lots of test data, including long term life tests
  - Various hardware configurations built
  - The eventual problem ($GdSe_{1.5-x}$ phase change) was not even discussed in the published reports AFAIK
  - Independent technology support at Teledyne (the prime contractor), JPL & General Atomics all failed to identify problem beforehand
- Possible contributing factors (?)
  - Inadequate peer review on basic science
    - Nothing ever appeared in refereed literature
    - Contrast with Navy run programs which produced lots of excellent open literature publications
  - Complacency
    - Previous RTG projects had worked so well
    - But prior to the selenides NASA & DoE had largely inherited extensive experience from Navy programs
  - Lack of transparency from 3M?
  - Inadequate oversight?

Can Such Failures Be Avoided?

- Yes: Freeze Technology Development
- No, if you want to move forward
  - – With development comes risk
  - – But consequences can be minimized

- Expensive Lesson:
  - – Don't toss out the previous technology until the next one really works

Boron-Carbide Faux-Breakthrough

- In early stages of SP-100 (1985-87) p-type Boron-Carbide (B_xC) & n-type Lanthanum Sulfide (LaS_x) or Lanthanum Telluride ($LaTe_x$) were baselined
  - In spite of the fact that sufficiently high ZT values had not yet been achieved, bonding, couple & cell development was initiated (!)
- At a routine technology meeting circa 1986-7, JPL announced a single mobility measurement on B_xC indicating about 10x increase
  - Theoretically, ZT should be comparably improved
- For several months the SP-100 community was abuzz
- Eventually, JPL found the measurement was in error
  - A graphite deposit on the sample gave a false Hall effect reading

- Lesson: everyone makes mistakes
  - Openness & due diligence go a long ways toward self-correction

Next Generation TE Materials

Bulk Materials

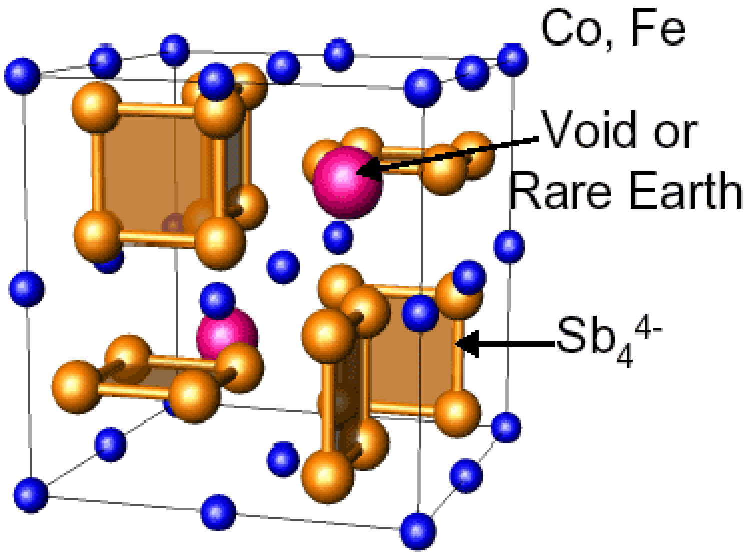
Skutterudites

Skutterudites

- First mentioned in the literature as a possible thermoelectric by Dudkin, 1956
- ‘Rediscovered’ independently & simultaneously by
  - Caillat (JPL) August, 1992 and
  - Slack (GE) September, 1992
- Both groups identified $IrSb_3$ as attractive because of:
  - High mobility semiconductor
  - Heavy atomic masses, suggesting low λ may be possible
- Caillat, T., A. Borshchevsky, et al. (1992). Search for New High Temperature Thermoelectric Materials. Proceedings of the 27th Intersociety Energy Conversion Engineering Conference, SAE, Warrendale, PA, USA p.3.499-3.503.

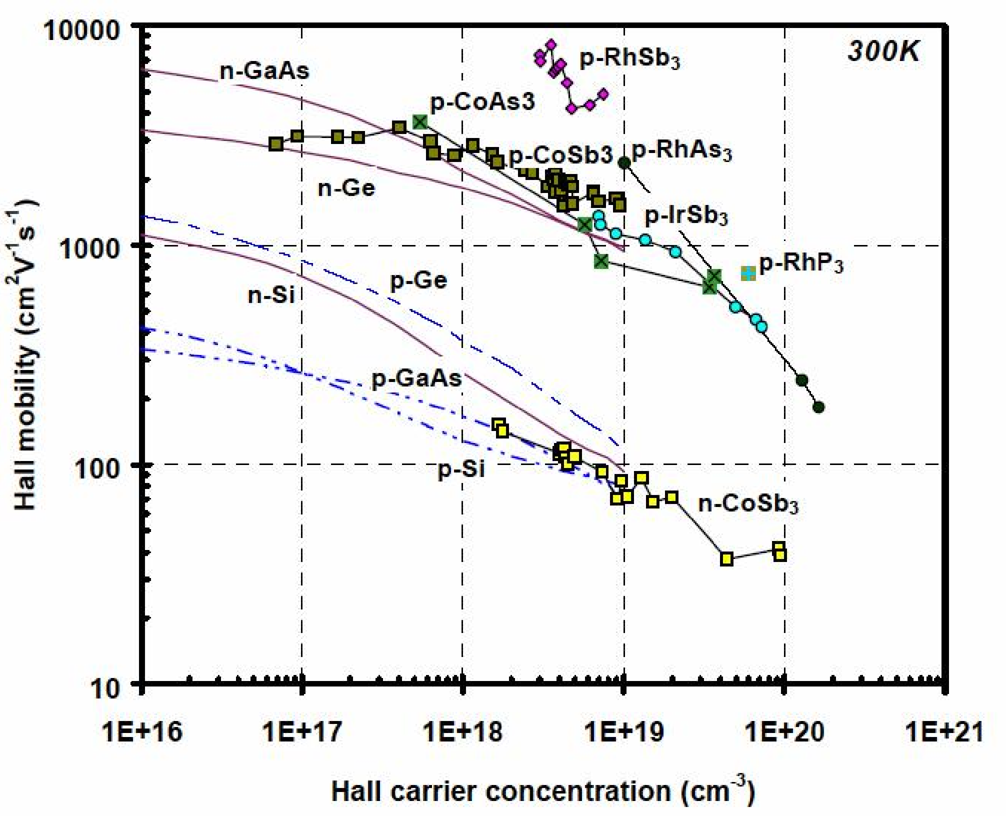
Skutterudite Crystal Structure

- >10 Binary compounds
  - $CoSb_3$
  - Large list of substitutions possible for Co & Sb
  - large unit cell, heavy elements
    - Low λ_p
  - Dopable semiconductor
    - Good possibility to optimize carrier concentration
  - Small electronegativity difference
    - High μ
    - P-type mobility is among the highest known
- Ternary ‘Filled Skutterudites”
  - In binary TPn_3 2 of the 8 octants are empty, but big enough to hold large atoms
  - $CeFe_4Sb_{12}$
  - Ce enters the 2 empty octants
  - Further reduces λ_p
- A huge number of chemical substitutions possible
  - Big job to systematically study the possibilities
  - But a good chance of engineering a good ZT



P-type Skutterudites: High μ

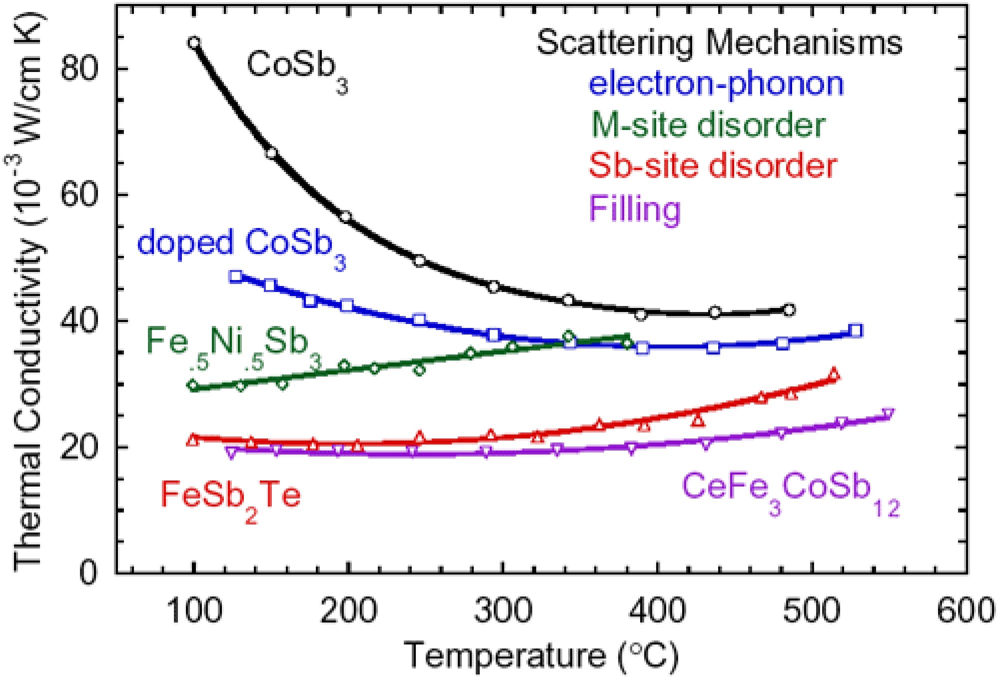
- Some p-type skutterudites have remarkably high mobility
  - Comparable to the best known materials
- N-type mobilities are OK, but not extraordinary
- Sadly, most λ_p reduction substitutions also tend to reduce μ
  - Otherwise it would be too easy!



Fleurial, J.-P., T. Caillat, et al. (1997). Skutterudites: An Update. International Conference on Thermoelectrics, ICT, Proceedings, Dresden, Germany p.1-11.

Identified mechanisms to control λ_p

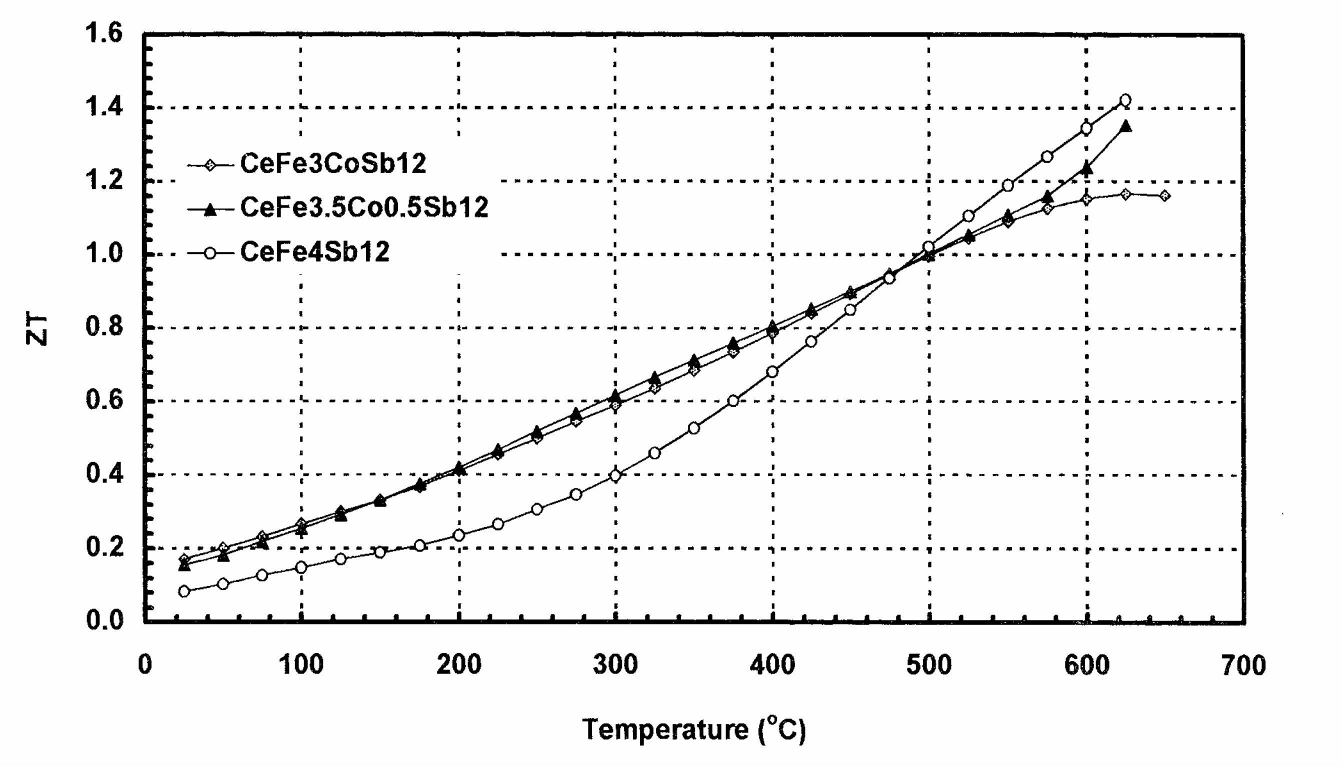
- Several distinct phonon scattering mechanisms have been identified
  - Phonon-phonon
  - Electron-phonon
  - Disorder (aka mass-fluctuation)
  - ‘Rattling’ (aka filling)
  - Possibly valence fluctuation
- Except for valence fluctuation scattering, all these mechanisms were fully expected
  - More theory is needed, but the general understanding appears in reasonably good shape
- ‘Rattling’ is a newly identified mechanism
  - Very effective & promising
- Good example of applying modern understanding of physics of to materials design



http://www.its.caltech.edu/~jsnyder/thermoelectrics/index.htm

P-type Filled Skutterudites

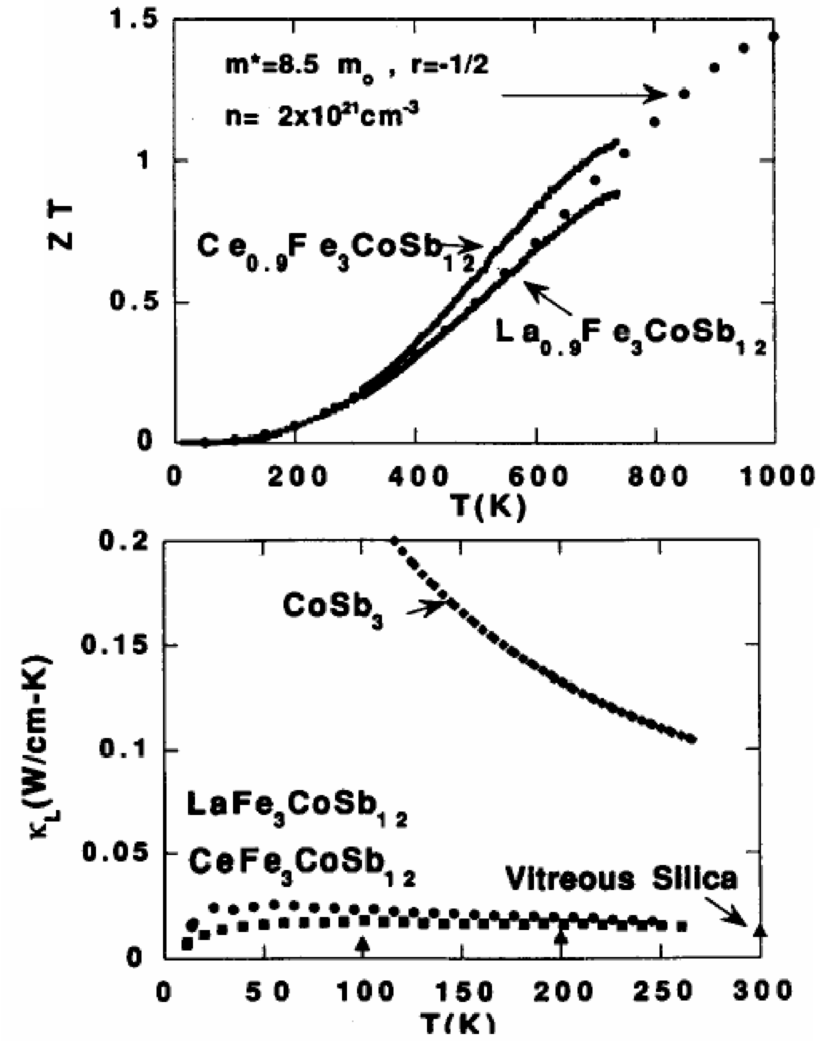
JPL Results



Fleurial, J.-P., A. Borshchevsky, et al. (1996). High figure of merit in Ce-filled skutterudites. International Conference on Thermoelectrics, ICT, Proceedings, Pasadena, CA USA p.91-95.

P-Type Filled Skutterudites

- Add Ce or La to lower λ_p
- Adjust the doping
- ZT=1.4 here is an *extrapolated* number
- AFAIK, only JPL has actually reported measuring ZT=1.4
  - Part of the problem is the small number of high temperature measuring facilities



Sales, B. C. (1997). "Novel thermoelectric materials." Current Opinion in Solid State and Materials Science **2**(3): 284-289.

N-Type Skutterudites

Huge family of semiconductors

Closed circles: $Ba_{0.3}Co_4Sb_{12}$

Open circles: $Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$

Open squares: $Yb_{0.19}Co_4Sb_{12}$

Close squares: $Yb_{0.25}Co_4Sb_{12}$

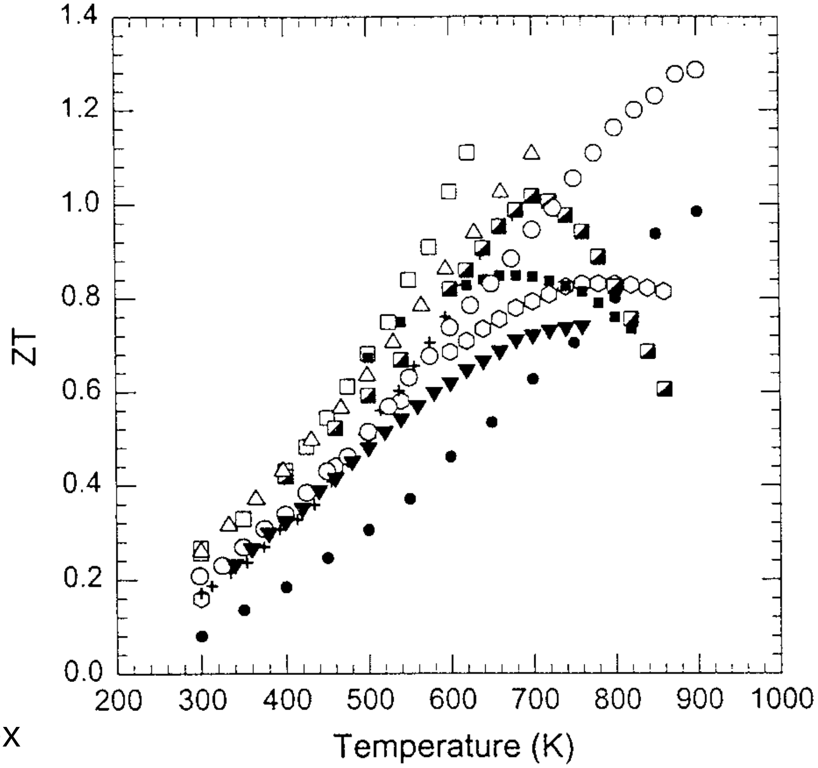
½ filled squares: $Yb_{0.24}Co_{3.88}Pt_{0.12}Sb_{12}$

Open triangles: $Eu_{0.42}Co_4Ge_{0.4}Sb_{11.37}$

Hexagons: $Co_{3.6}(Pd,Pt)_{0.4}Sb_{12}$

Crosses: $Ce_{0.2}Co_{3.88}Pd_{0.12}Sb_{12}$

Filled triangles: $Tl_{0.2}Co_4Sb_{12}$

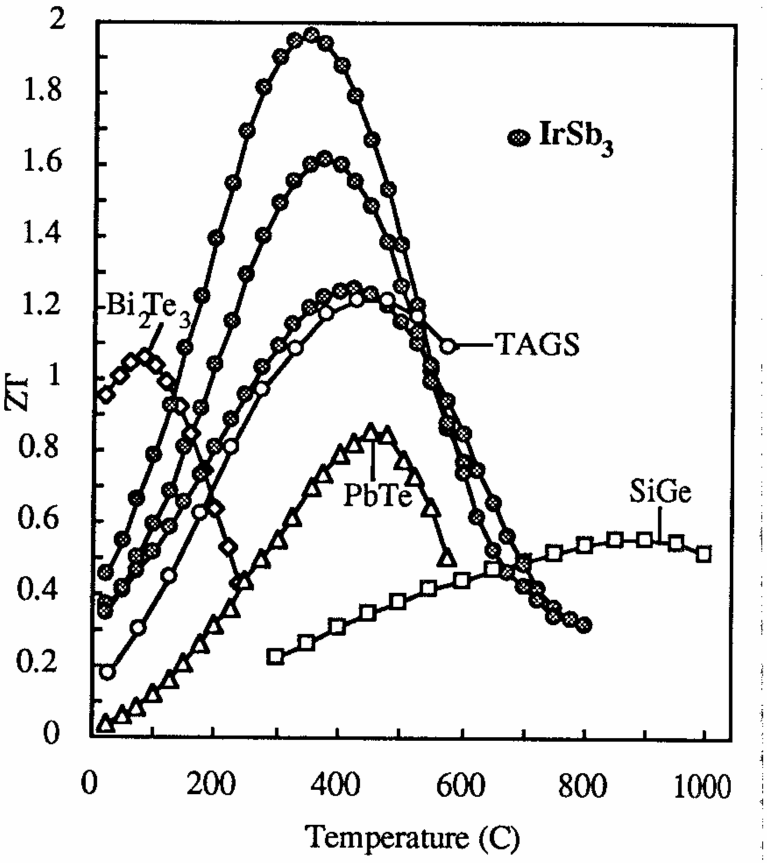


- Filling the voids lowers λ ~ x10
  - ‘rattling’
  - Also affects electrical properties in complex ways
  - The game is to find a combination of ‘rattlers’ & substitutions that lower λ but don’t overly damage electrical properties
- Antimonides have a typical peritectic decomposition ~ 1146 K
  - Probably not useful above ~ 1000 K
  - Lifetime issues are TBD

Uher, C. (2001). "Skutterudites: Prospective novel thermoelectrics." Recent Trends In Thermoelectric Materials Research I **69**: 139-253.

P-type $IrSb_3$ ZT=2: 1993 False Alarm

- In 1993 JPL reported ZT~2
- Was never repeated
- Believed to be related to loss of Sb during measurements
  - Full story never published AFAIK
  - S & ρ measured separately
  - Apparently, Sb lost during Seebeck measurement gave an irreproducible Seebeck enhancement
- Sadly, these things happen sometimes
- Measurements are hard & unglamorous
  - Measurement technique development is rarely given enough emphasis
  - Be skeptical. Be very skeptical
  - Especially of your own data
  - Especially if it is exactly what you expected (or hoped for)



Caillat, T., A. Borshchevsky, et al. (1993). Novel Transition Metal Compounds with Promising Thermoelectric Properties. The Twelfth International Conference on Thermoelectrics, ICT, Proceedings, Yokohama, Japan, Institute of Electrical Engineers of Japan, Tokyo p.132-136.

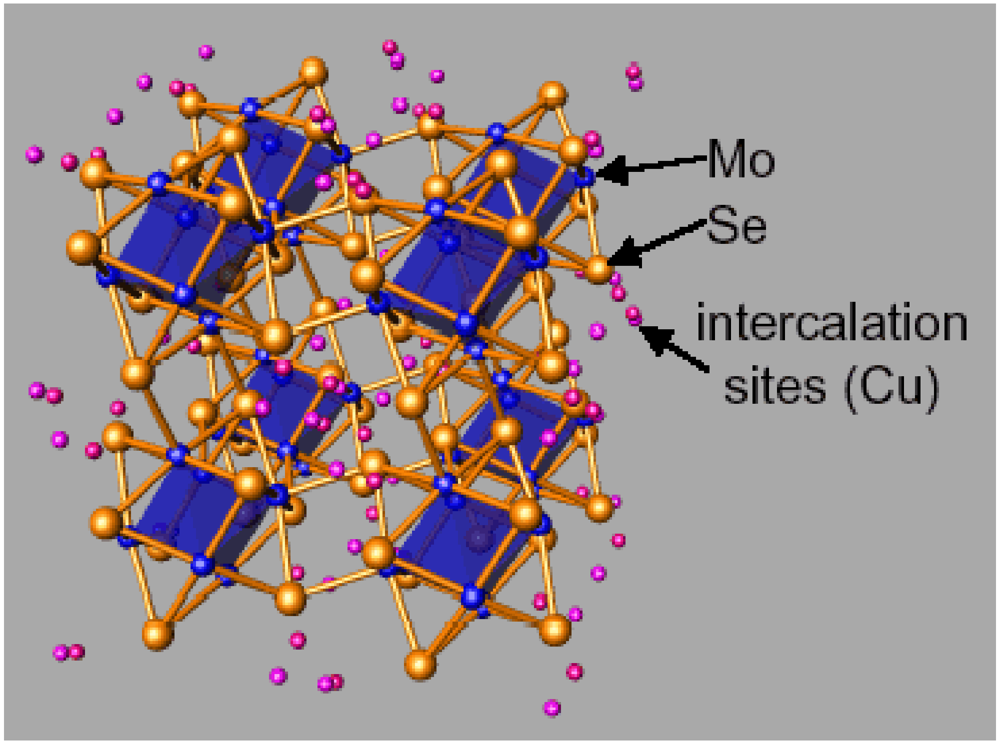
Chevrel Phase Materials

Chevrel Phase Materials

- Many hundreds of compounds known
  - Most are metals & many are superconductors
  - Chemistry & basic physics heavily studied in 1970s-80s due to interest in superconductivity
  - Some can be semiconductors
  - Relatively high melting point, up to 1700 ^{o}C
  - Relatively little data on key thermoelectric properties

Chevrel Phase Crystal Structure

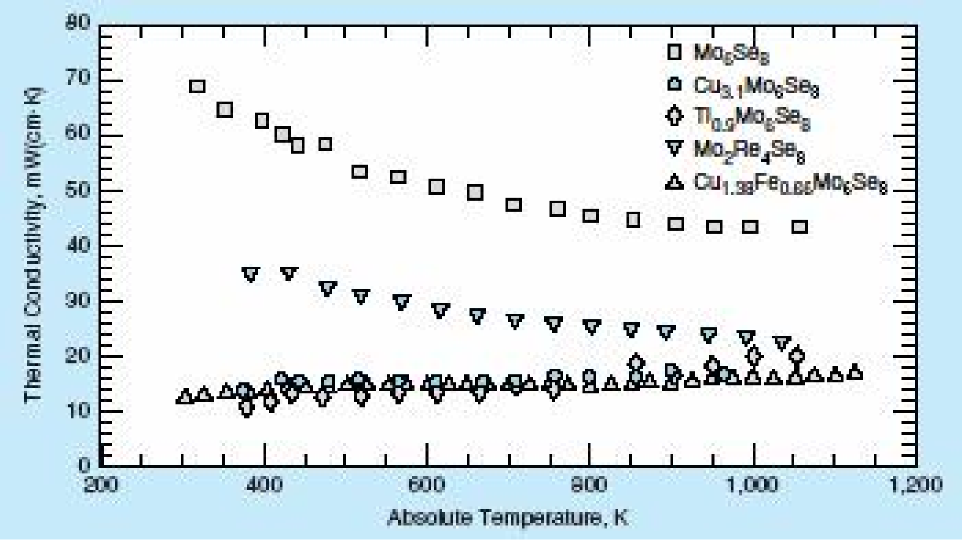
- Ex: $Cu_{1.38}Fe_{0.66}Mo_6Se_8$
  - Cu & Fe go into the intercalation sites
- So-called “molecular crystals”
  - Mo_6Se_8 “molecules” form the basic building block
- Low λ
  - “molecules” relatively weakly bonded to each other
  - Large, complex unit cell
  - Possible ‘rattle-like’ behavior in intercalation sites



Snyder, http://www.its.caltech.edu/~jsnyder/thermoelectrics/science_page.htm

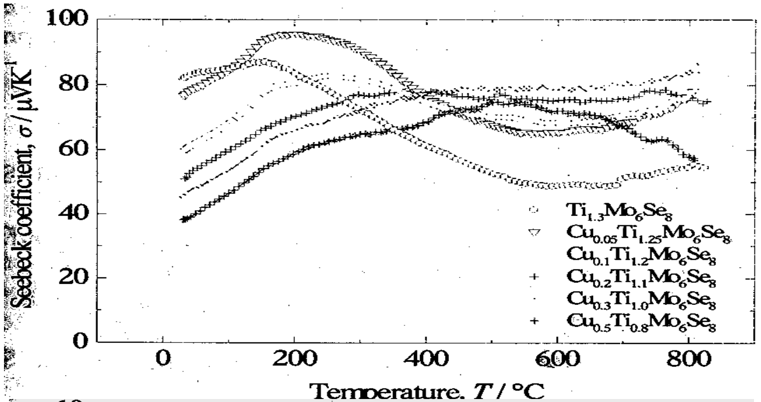
Chevrel Phase Materials

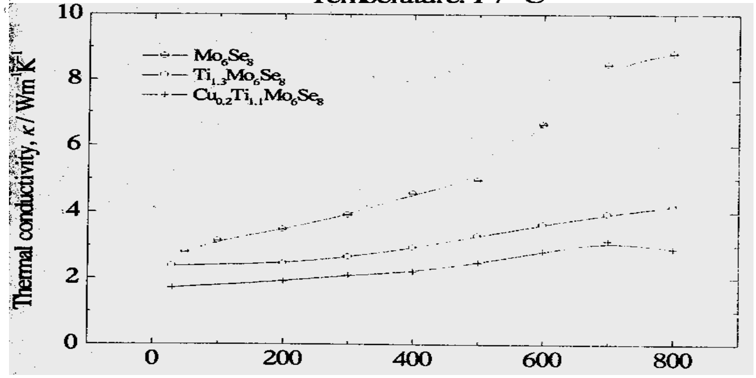
- Relatively low λ_{ph}
  - Probable ‘rattler’
- Relatively low μ also
  - Need higher μ, which may or may not be possible
- $Cu_{1.38}Fe_{0.66}Mo_6Se_8$, p-type, ZT~0.6 @ 1150 K
  - Full details TBD
  - Caillat, T., J.-P. Fleurial, et al. (2002). "Chevrel Phases as Potential Thermoelectric Materials." Nasa Tech Briefs **26**(5): 36-37.
- Mo_6Te_8 ZT~0.015 @ 1000 K
  - Kurosaki, K., A. Kosuga, et al. (2003). "Thermoelectric properties of Chevrel phase $Mo_6Te_{8-x}S_x$." Journal of Alloys and Compounds 351: 208-11.

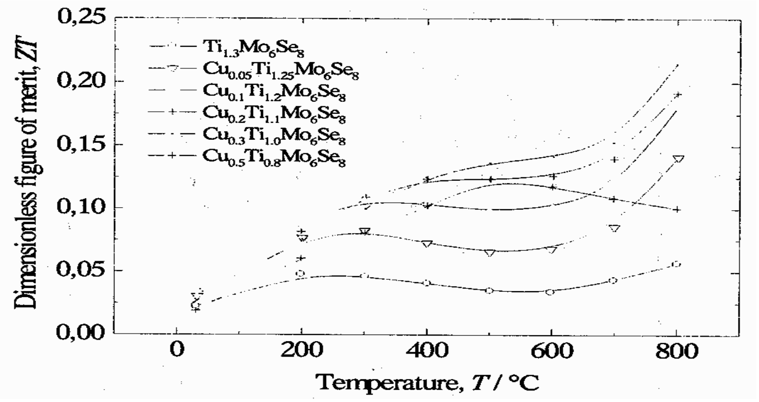


$Cu_{0.3}TiMo_6Se_8$

- ZT~0.22 @ 1073 K
  - – λ as low as 2-3 W/m-K
  - – S ~ 80-100 μV/K
  - – Need lower carrier concentration to optimize ZT
  - – Ohta, ICT, 2003







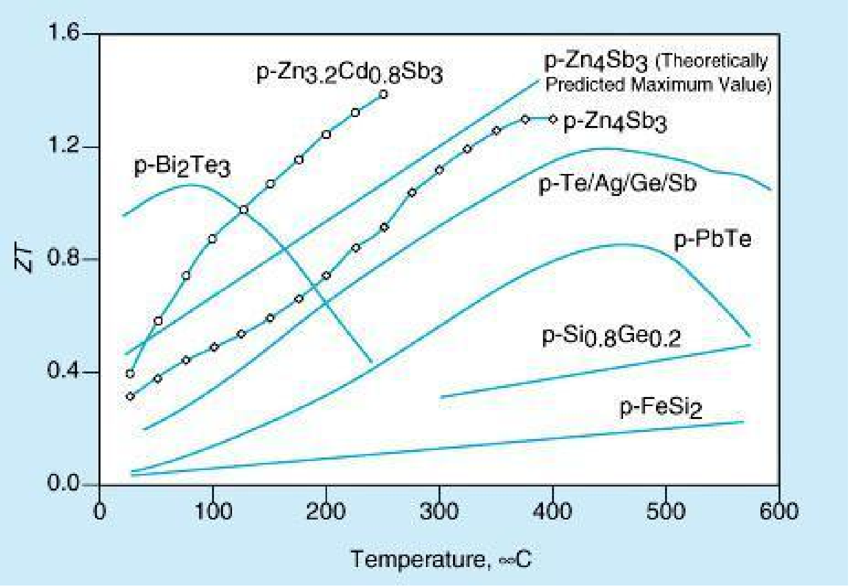
Chevrel Phase Summary

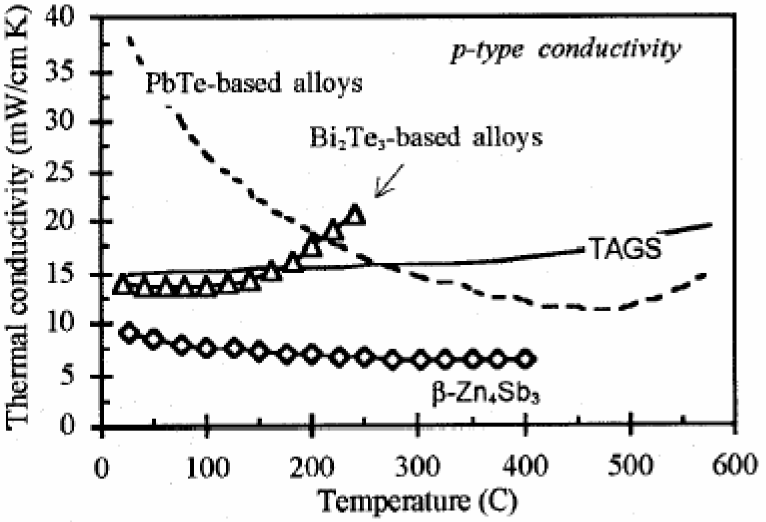
- Large family of materials
  - Only a fraction of them are semiconctors
  - Expect low λ_p
  - Also expect low μ
    - Might be acceptable
- Still in the ‘hunch’ stage of development

Zinc Antimony: Zn_4Sb_3

β-Zn_4Sb_3

Caillat, ICT (1996), NASA Tech Briefs (1999)



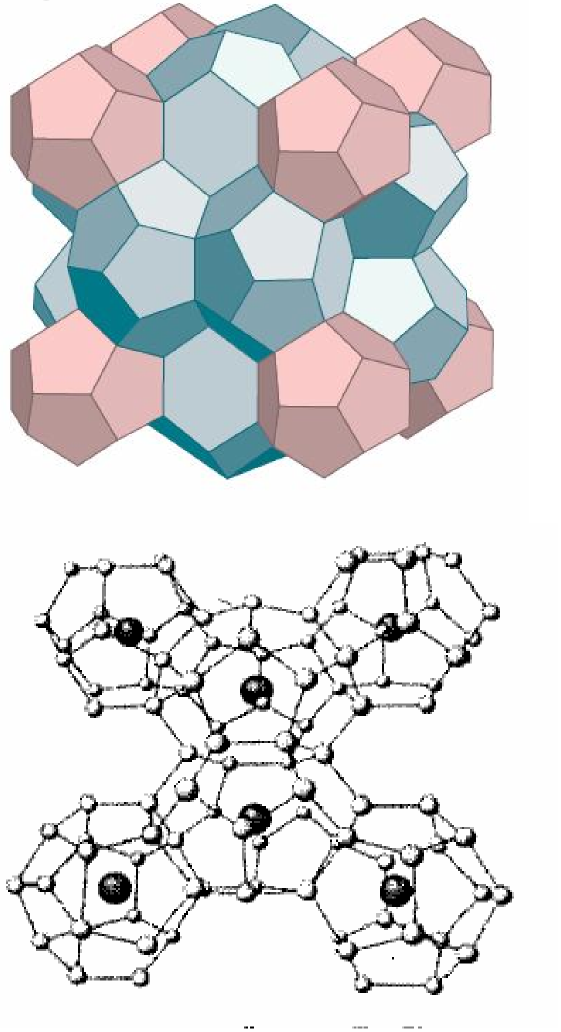


- Stable between -10 °C & 492 °C
- Unique crystal structure
  - Very few chemical substitutions possible (Cd, for one)
- Heavy atoms, complex structure yield low λ_p
- Accidentally useful: not much room to engineer this material!

Clathrates

Clathrates

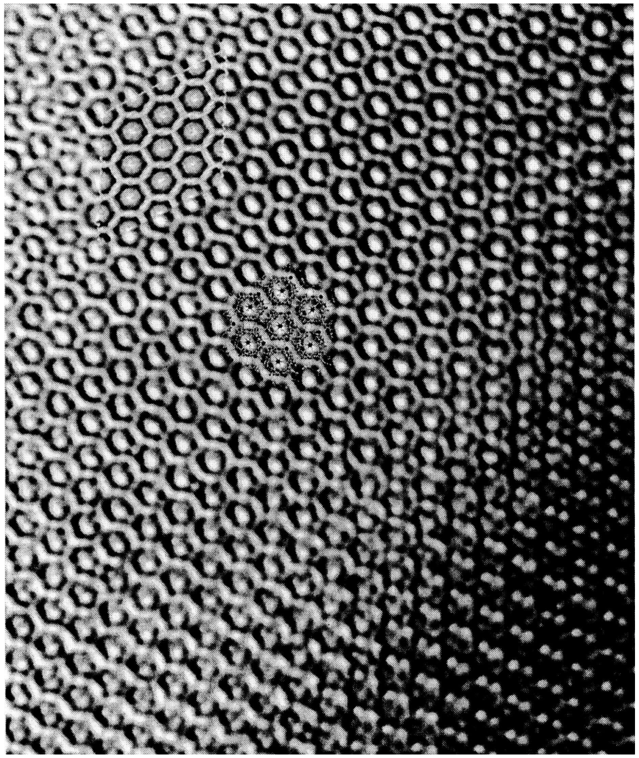
- Another huge family of materials inspired by Slack's "Phonon Glass-Electron-Crystal" concept
- Characterized by a cage-like crystal structure
  - With room in the polyhedra for a "guest" atom to sit loosely bound & 'rattle' phonons
- Examples:
  - $X_8Ga_{16}Ge_{30}$ (where X = Eu, Sr, Ba)
  - Na_8Si4_6
  - Na_xSi_{136}
  - & very recently, a new form of silicon: Si_{136} (Nolas, 2003)



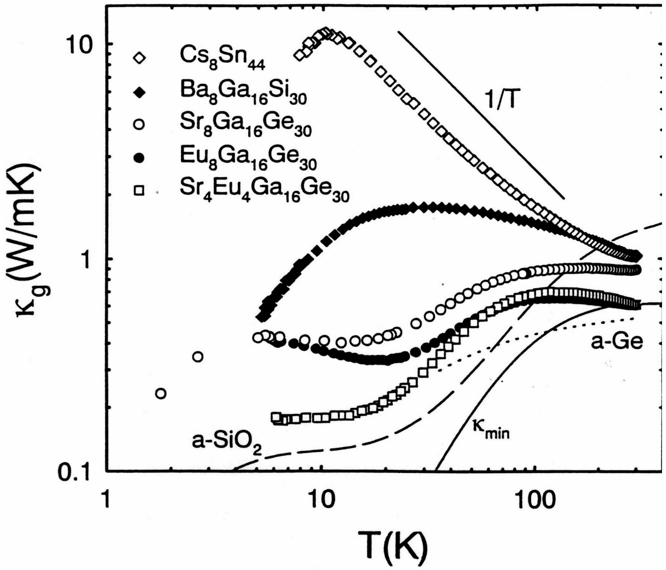
Polyhedral views of clathrate X_8E_{46}-structure type, [Nolas, 1999].

Clathrates

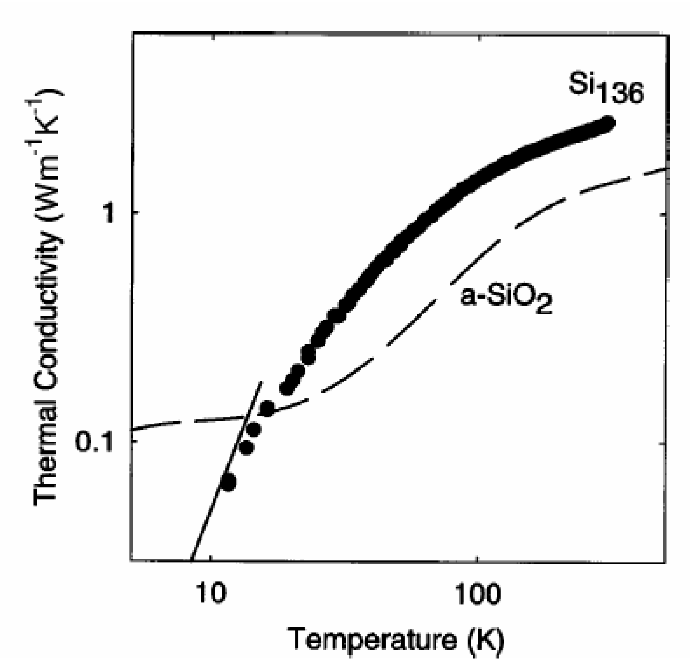
- TEM image of a highly regular clathrate surface. The diamond-shaped region in upper left and the seven hexagons near center are computer simulations of the ideal crystal structure [Nolas].
- The big unit cell & rattling strongly favor low λ, on general principles



Conduct heat like a glass



Thermal conductivity of various clathrates, some of which exhibit nearly glass-like behavior [Nolas].



Phonon Mean-Free-Path ~ 6 Å !

Nolas, G. S., M. Beekman, et al. (2003). "Thermal conductivity of elemental crystalline silicon clathrate Si136." Applied Physics Letters **82**(6): 910-12.

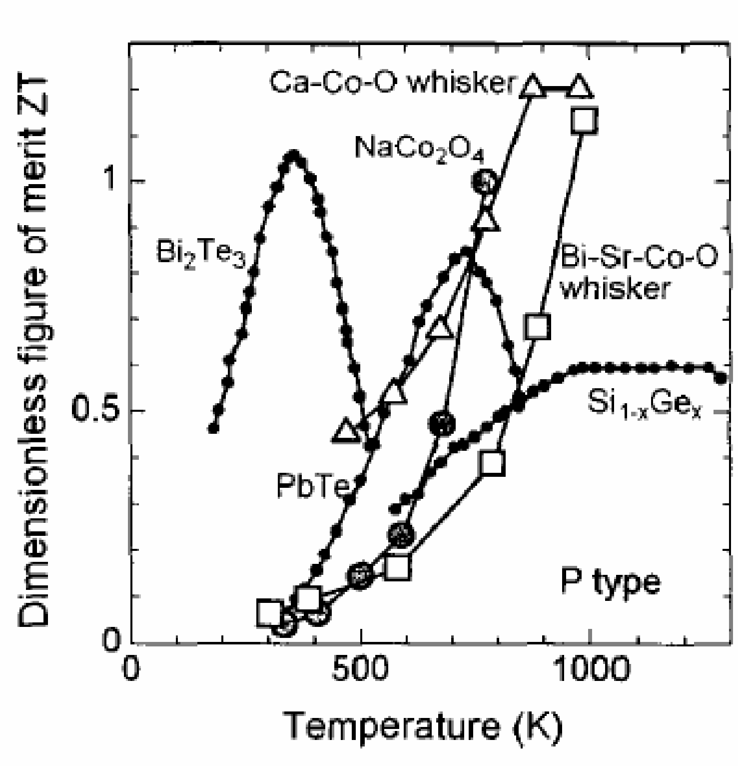
Clathrates

- Doping & thermal conductivity reduction can be achieved by putting atoms in the ‘cages’
  - Main lattice is largely undisturbed
  - Possibility of crystal-like mobility values
- ZT~0.25 has been reported @ 300 K
  - Extrapolate ZT>1 above 700 K
- Very early stages of development

Other High Temperature Materials

Sodium Cobalt Oxides

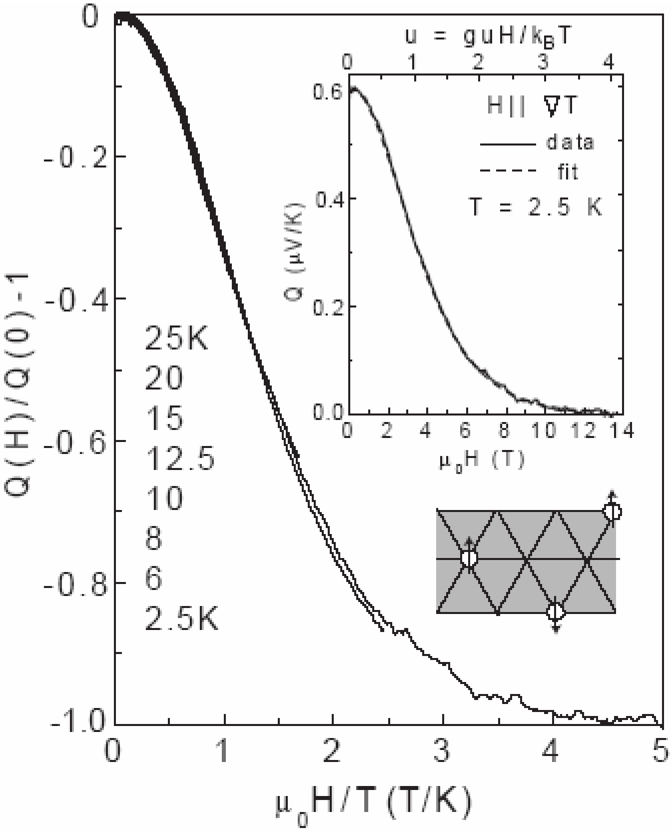
- ZT~1.2 has been reported for $NaCo_2O_4$
- Essentially doped CoO_2
- Oxides fail the classical selection criteria
  - Ionic bonding = low μ
  - But they are expected to have low λ_p
- These materials have surprisingly large Seebeck coefficients
  - New physics!
  - Previous models need not apply!
    - Or at least require major modification
- Na conductivity small, but not negligible
  - Could be a concern over time



Terasaki, ICT (2003)

‘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
- This is presumably the origin of high ZT
- This opens an entirely new class of materials, which work on different basic principles than all that have gone before
  - Previous estimates of limits on ZT must be re-examined entirely
  - Very exciting science!
- Most of the work on these oxides is in Japan



Wang, Y., N. S. Rogado, et al. (2003). "Evidence that spin entropy is the source of enhanced thermopower in NaxCo2O4." Nature **423**(6938): 425-428..

Selected High Temperature Materials Examined at JPL

- Since the 1980s JPL has maintained an active new thermoelectric materials effort
- A large number of compounds have been identified using generalized screening criteria
- Promising ones 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

Quantum Wells
Quantum Wires (aka: Nanowires)
Quantum Dot Superlattices

Thin film grown approaches

- Two main ideas
  1. ‘Confinement’ of charger carriers increases the effective mass, Seebeck & ZT
  2. Repeated layers scatter phonons, reducing lattice thermal conductivity & increasing ZT
- There are other ideas as well
- Both ideas are ~ 10 years old
- Both have achieved ZT = 2+ in the lab
- Most likely of interest for cooling, at least initially
  - At elevated temperatures there has to be concern about diffusion & stability
- It is a whole new ballgame!

Hicks & Dresselhaus: ZT>7?

- Hicks PhD Thesis ~1992
  - Curious about the effect of low dimension materials on ZT
- A ‘Quantum Well’ is semiconductor so thin that the charge carriers can only move in 2 dimensions, in the plane of the film
- Need to be ‘quantum’ thin to see effect
- All properties can be effected
- Initial expectation:
  - Seebeck enhancement

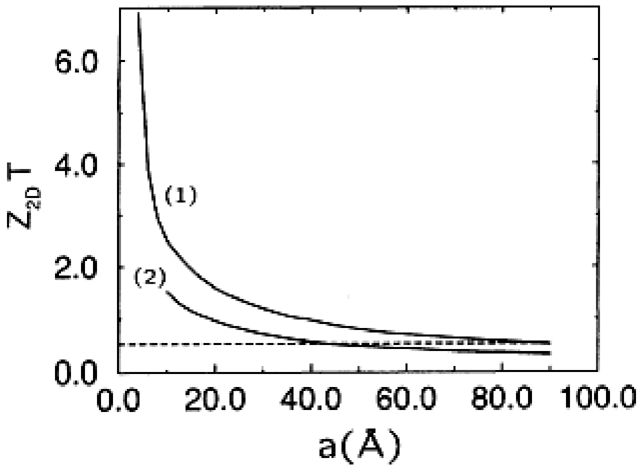


FIG. 5. Plot of $Z_{2D}T(\zeta^*_{\text{opt}})$ vs layer thickness a for (1) a_0-b_0 plane layers and (2) a_0-c_0 plane layers. The dashed line indicates the best ZT for 3D bulk Bi_2Te_3.

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.

QW Theory

- Repeat the same ZT calculation we did before
  - ZT depends on doping and a factor ‘B’ involving effective mass, mobility & λ_p
- Very similar result in 2-D
  - Main difference is in ‘B-prime’
    - Effective mass is different
    - Now involves a geometry factor, which you can adjust
- QWs offer a new method to modify material properties

3-D

$$Z_{3D}T = \frac{\frac{3}{2}\left(\frac{5F_{3/2}}{3F_{1/2}} - \zeta^*\right)^2 F_{1/2}}{\frac{1}{B} + \frac{7}{2}F_{5/2} - \frac{25F_{3/2}^2}{6F_{1/2}}},$$

where

$$B = \frac{1}{3\pi^2}\left(\frac{2k_BT}{\hbar^2}\right)^{3/2}(m_xm_ym_z)^{1/2}\frac{k_B^2T\mu_x}{e\kappa_{\text{ph}}}.$$

Compare masses

2-D

$$Z_{2D}T = \frac{\left(\frac{2F_1}{F_0} - \zeta^*\right)^2 F_0}{\frac{1}{B'} + 3F_2 - \frac{4F_1^2}{F_0}},$$

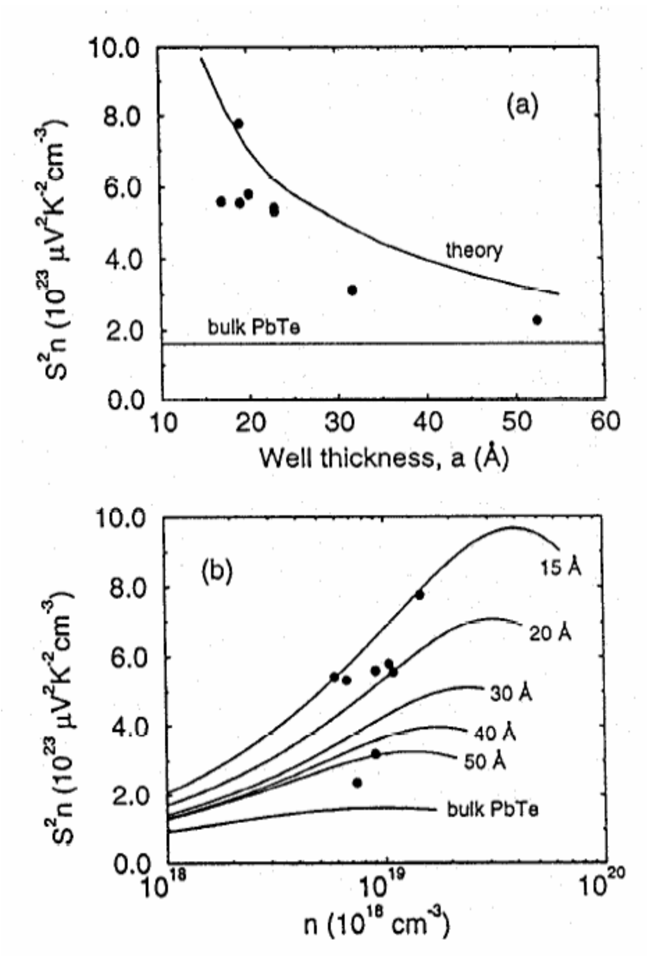
where

$$B' = \frac{1}{2\pi a}\left(\frac{2k_BT}{\hbar^2}\right)(m_xm_y)^{1/2}\frac{k_B^2T\mu_x}{e\kappa_{\text{ph}}}.$$

Depends on thickness!

Not a Duck?

- Experimental proof of principle
- Multiple Quantum Wells
  - PbTe QW layers
  - PbEuTe barrier layers (to force confinement
  - PbTe is relatively well understood
- Measured Seebeck & carrier concentration
  - For the same ‘n’, Seebeck is bigger
  - Gets bigger as well thickness gets smaller
  - Both results predicted by theory
  - Essentially, the ‘effective mass’ of the carriers has been increased
- Q for Harman: “Does this prove the theory?”
  - Harman: “It looks like a duck. It walks like a duck. And it sounds like a duck. But it just might not be a duck!”



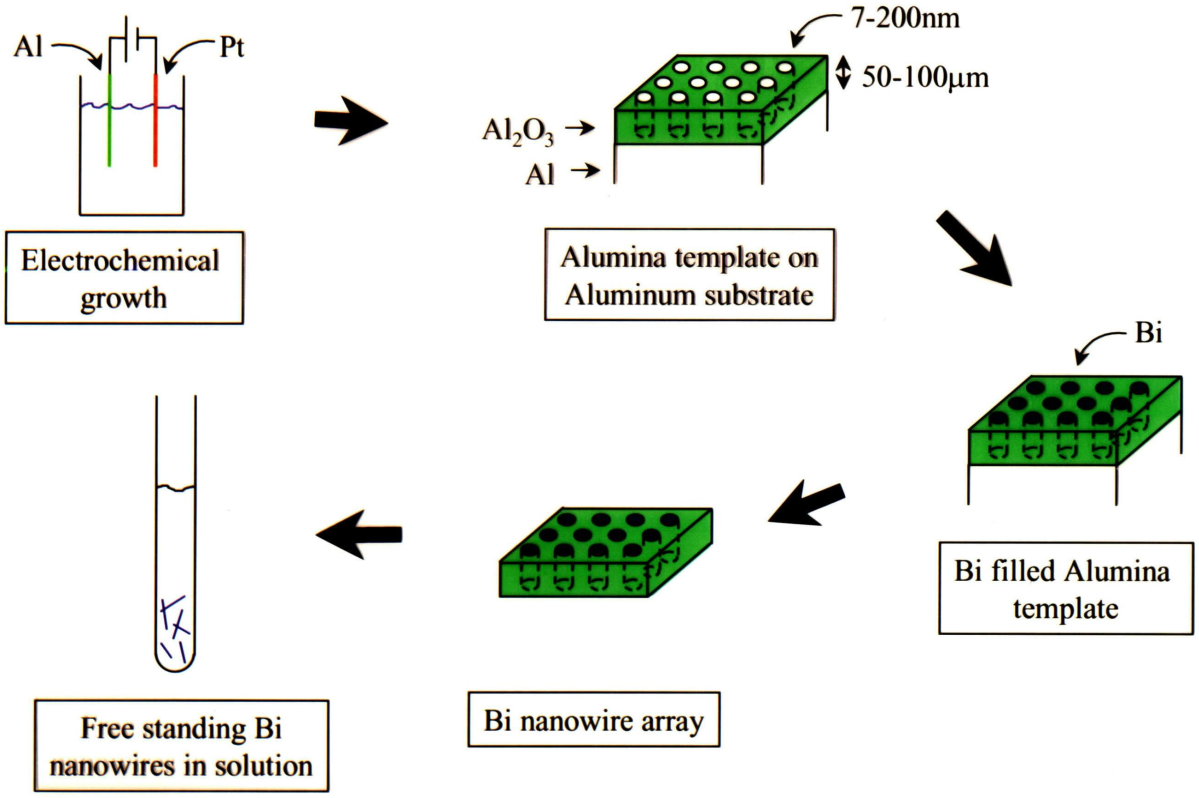
Hicks, L. D., T. C. Harman, et al. (1996). Experimental study of the effect of quantum-well structures on the thermoelectric figure of merit. International Conference on Thermoelectrics, ICT, Proceedings, Pasadena, CA, USA p.450-453.

QW Theory II

- If 2-D is good, then 1-D is better!
  - So people are also studying ‘quantum wires’
- What’s lower dimensions than a wire?
  - A quantum dot!
  - Enter the Quantum Dot Superlattice: QDSL
- Since the initial papers on QW thermoelectrics, most theory has predicted much more modest gains in ZT
  - Sometimes none
- Still, the experiments definitely show Seebeck enhancement
  - The early ‘primitive’ theory works better than it should
  - Wouldn’t be the first time a naïve theory worked

Nanowire Fabrication

One method from MIT

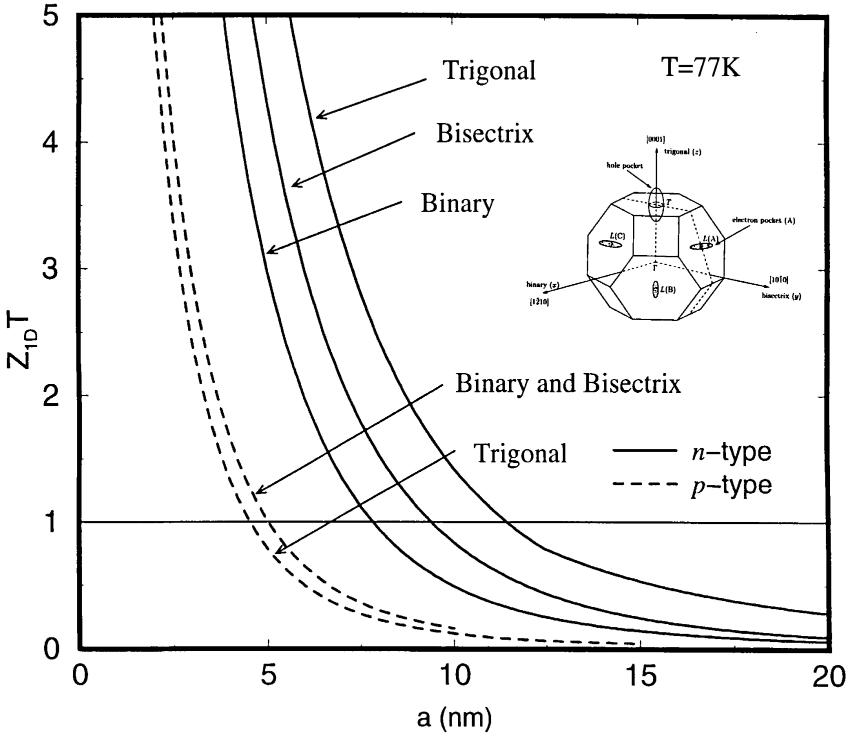


Q: How do you make a device from a bundle of wires?

Bi nanowire fabrication technique can yield either bundles of wires, or individual wires [Cronin, 1999].

Nanowires – Seebeck Enhancement

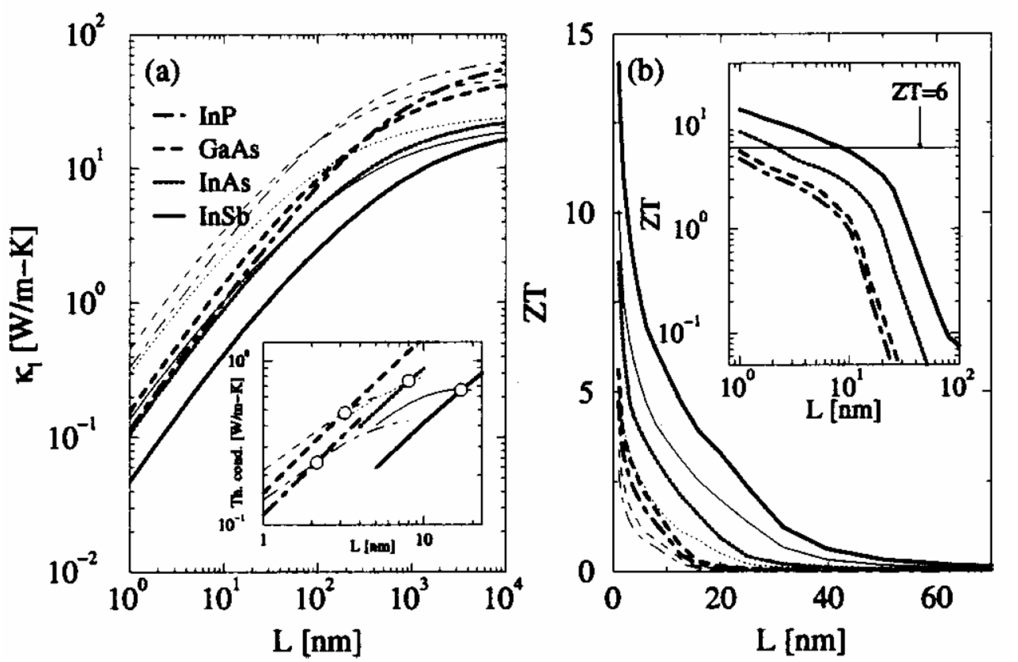
- Enhanced ZT values are expected in Bi nanowires of achievable dimensions [Cronin].
- Extension of the Hicks Quantum Well idea to 1-D
  - Seebeck enhancement



Nanowires - λ reduction

- Nanowires are variously claimed to
  - Enhance mobility
  - Enhance seebeck
  - And/or reduce λ
- Impressive theoretical predictions have been made for ~ 10 years
- Experimental work is very difficult
- How do you make, handle and measure a 'wire' 20 nm in diameter?
- How do you make a device?
- Can it survive at elevated temperatures?

- Challenging work, but excellent basic science
- This example lowers λ, theoretically

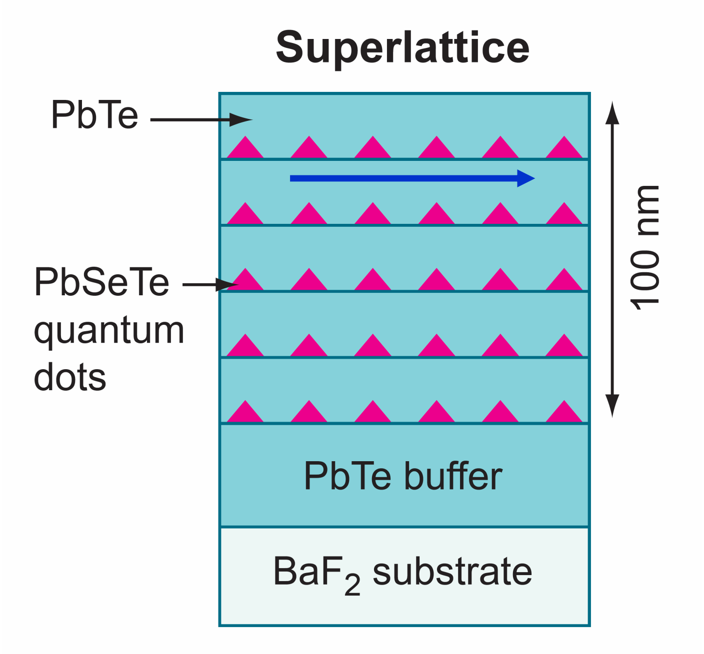


a) Lattice thermal conductivity vs thickness, for InSb, InAs, GaAs, and InP nanowires. b) Calculated *ZT* vs thickness

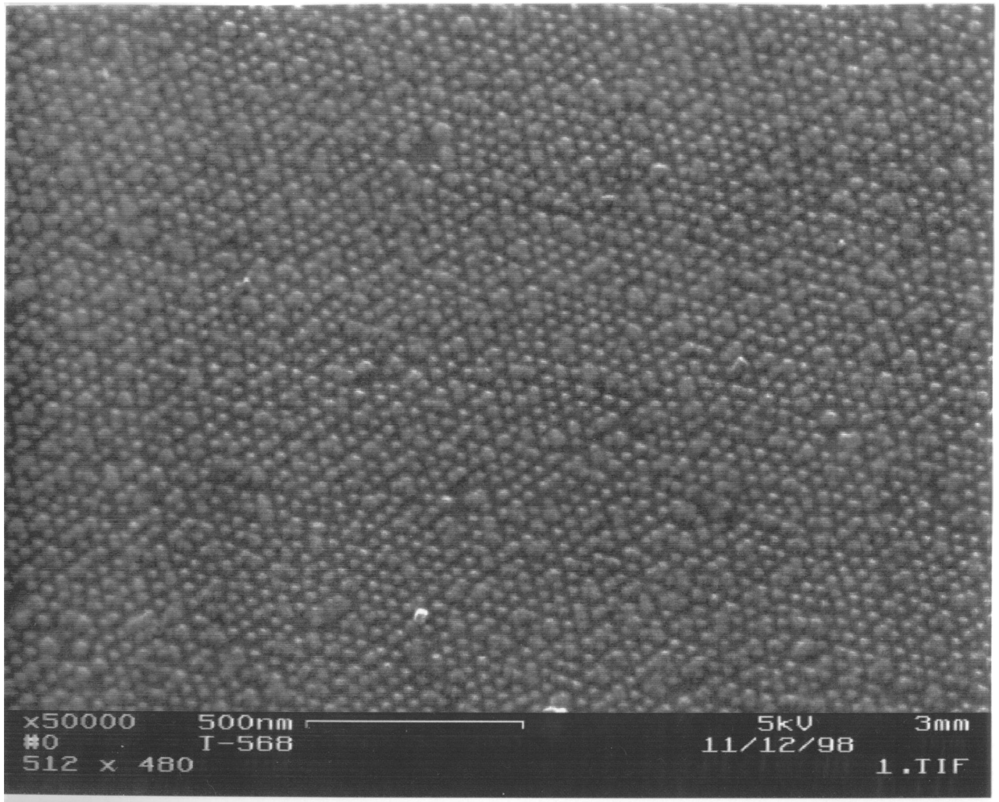
Mingo, N. (2004). "Thermoelectric figure of merit and maximum power factor in III--V semiconductor nanowires." Applied Physics Letters **84**(14): 2652-2654.

NASA-Ames Center for Nanotechnology.

Harman’s Quantum Dot Superlattice



Current Flows in the plane



FE-SEM image at 50,000x of a $PbSe_{0.98}Te_{0.02}$/PbTe quantum dot superlattice structure. ***7200*** such layers were deposited by MBE, forming the first true 3D array of quantum dots. Each dot is in the shape of a pyramid roughly 20-30 nm on a side [Harman, ICT 2002].

ZT~1.6 @ 300 K in a PbTe QDSL Device

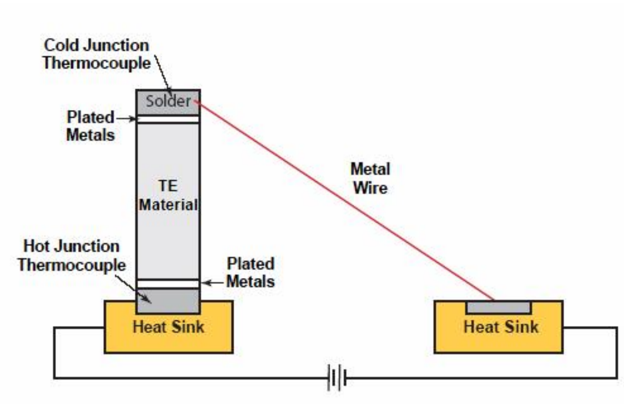


Fig. 1. Schematic of the one-leg thermoelectric cooling device test setup. The setup consists of a thermoelement (TE) with plated metals at both ends of the slab. One end of the TE has a cold junction thermocouple (TC) and a metal wire soldered to the metallized layer. The hot junction end of the TE is soldered to a copper heat sink. A TC is embedded in the solder. The other end of the metal wire is soldered to the second massive copper heat sink. An electrical current source is connected to the two copper

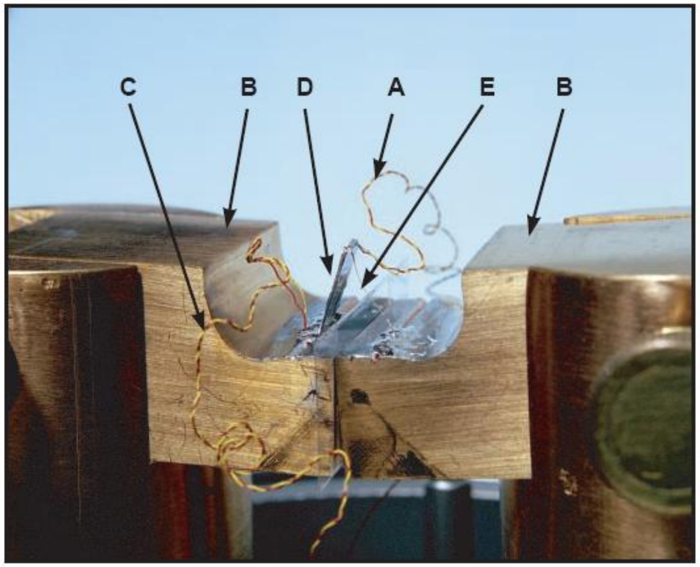


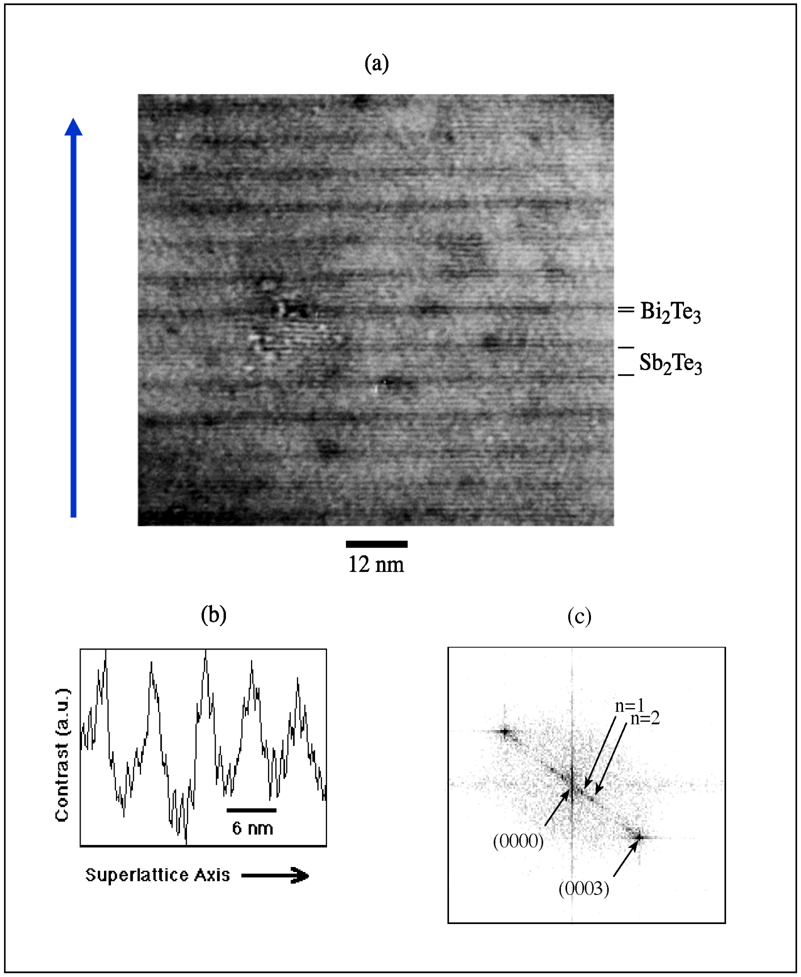
Fig. 2. Photograph of a one-leg thermoelectric refrigerator cooling device test setup made from MBE grown thick film QDSL material. (**A**) Cold junction TC [TC consisted of a twisted pair of chromel (yellow)/alumel (red) wires] soldered to the copper block and metallized end region of the TE. (**B**) Copper heat sinks, which also act as electrical conductors. (**C**) Hot junction thermocouple wires stuck in the soldered end region of the metallized TE. (**D**) MBE grown film QDSL TE. (**E**) Gold ribbon that connects the cold junction region to one of the copper heat sunk blocks. A mylar foil electrically insulates the one copper heat sink block from the other copper heat sink block.

An actual Quantum-Dot device

Harman, T. C., P. J. Taylor, et al. (2002). "Quantum Dot Superlattice Thermoelectric Materials and Devices. (Cover story)." Science 297(5590): 2229.

Superlattices

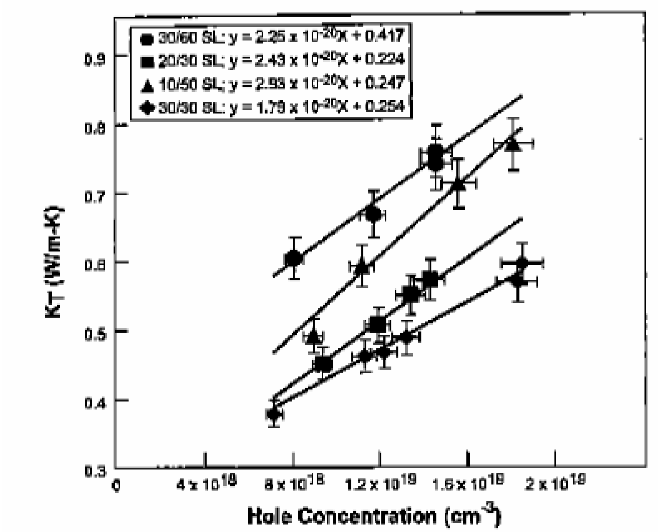
RTI’s Nano-structured Superlattice Material

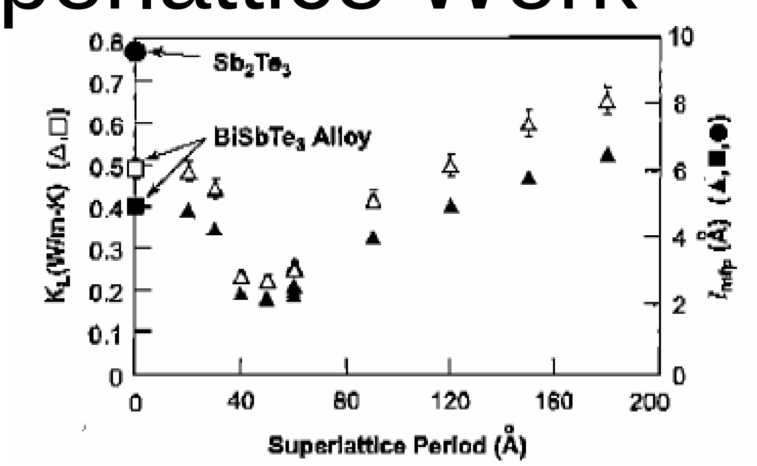


Applied Physics Letters, 75, 1104 (1999)

- Venkatasubramanian at Research Triangle Institute
- Heat & Current flow ***perpendicular*** to the planes
- 10Å/50Å Bi_2Te_3/Sb_2Te_3 Structure
- CVD grown
- Optimized for disrupting heat transport while maintaining or enhancing electron transport perpendicular to the superlattice interfaces

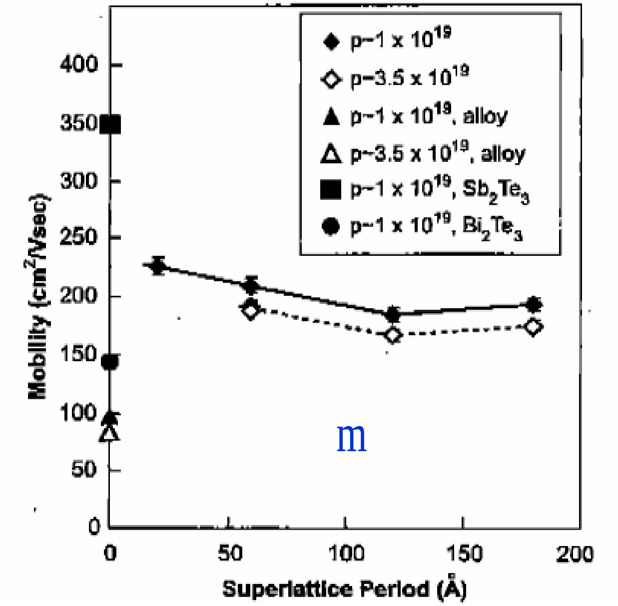
RTI’s Bi_2Te_3 Superlattice Work





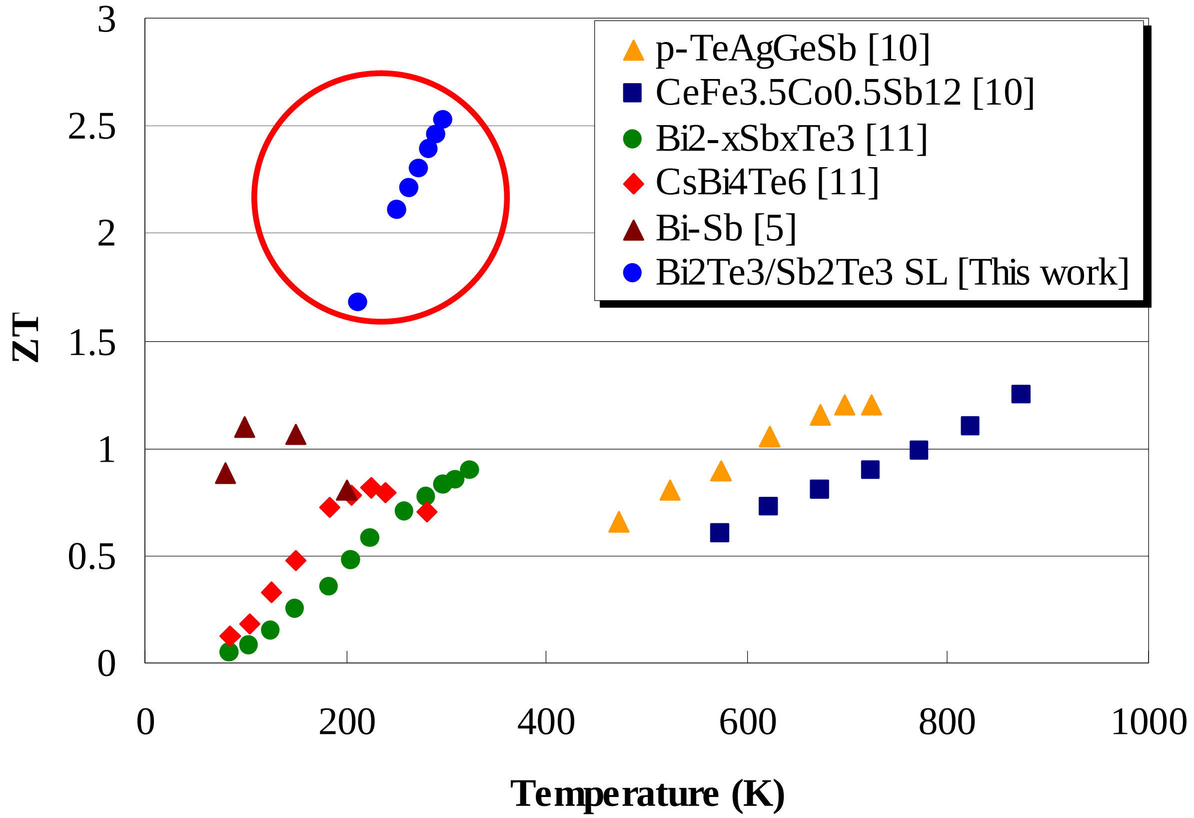
- Astonishingly low λ_p
- Maintained high μ

- Systematic studies, reproducible results
- Expect it! Demand it!



Venkatasubramanian, R. (2001). Phonon blocking electron transmitting superlattice structures as advanced thin film thermoelectric materials. Recent Trends in Thermoelectric Materials Research III. **71:** 175-201.

Temperature dependence of ZT in p -type Bi_2Te_3/Sb_2Te_3 Superlattices (213-300K) – promise for cryogenic applications



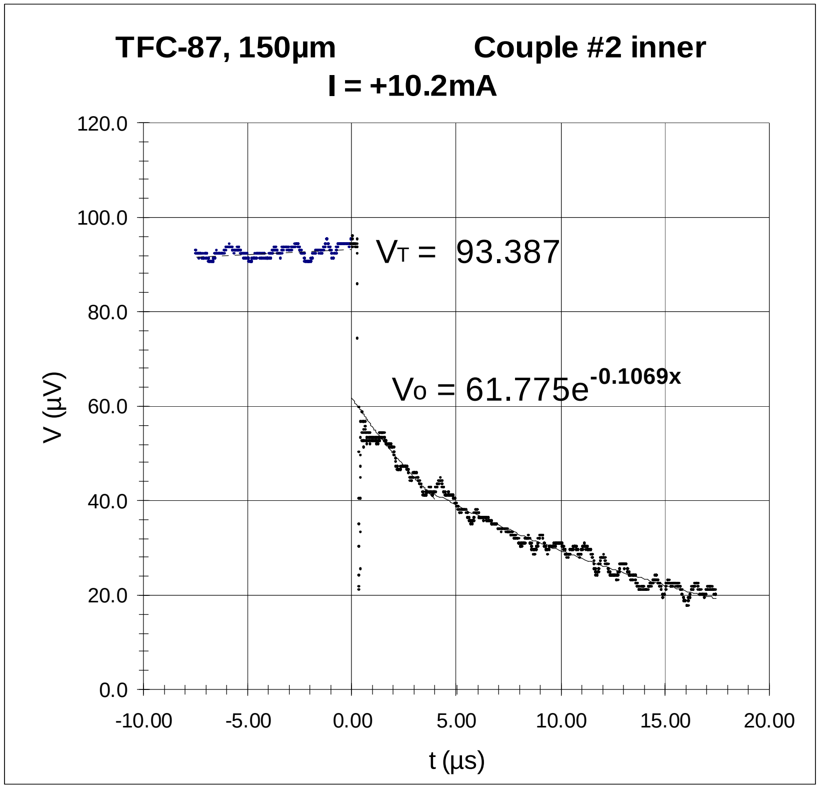
***Nature*, 413, 597 (2001)**

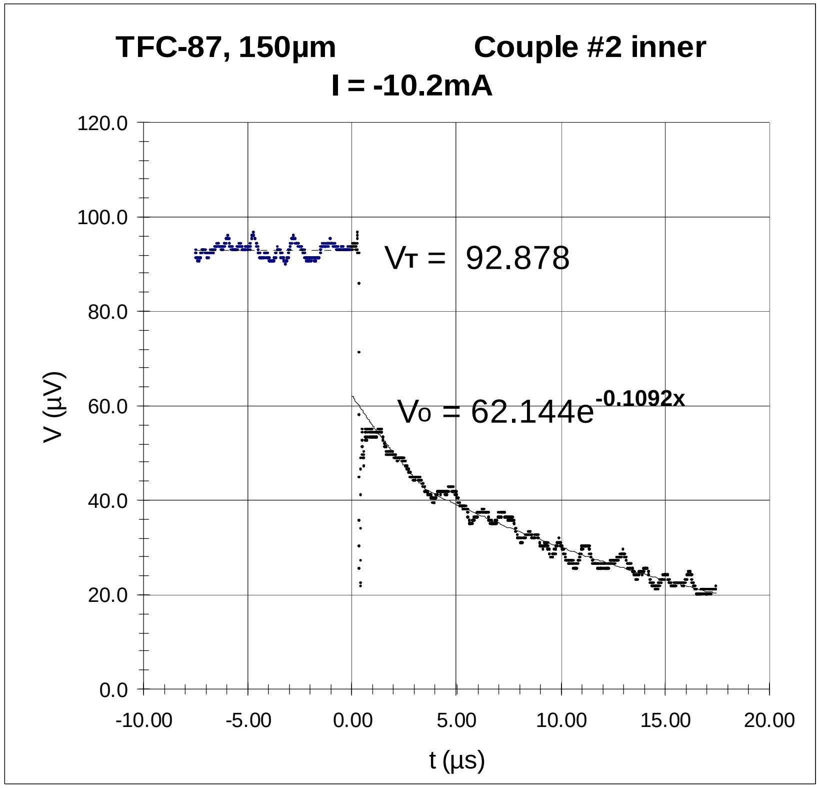
Transient Method ZT On P-n Couple

Overcomes The Interconnect Resistance Issue

ZT ~1.95

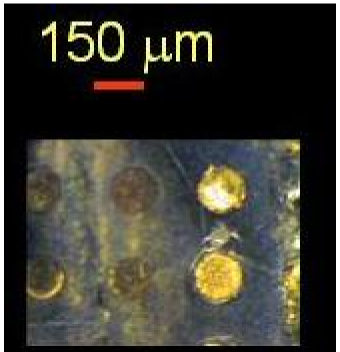
ZT ~2.02



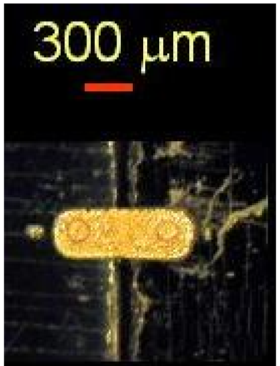


- **RTI had to develop novel cross-plane measurement methods**
- **Measurements on similar bulk p-n couple shows ZT ~ 0.77**

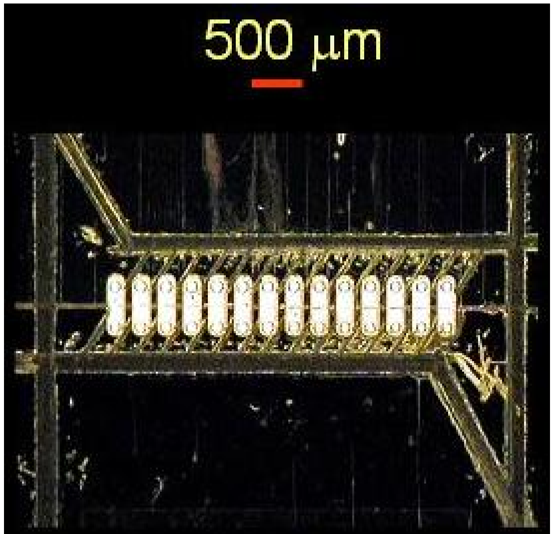
RTI’s Superlattice Thermoelectric Module Technology



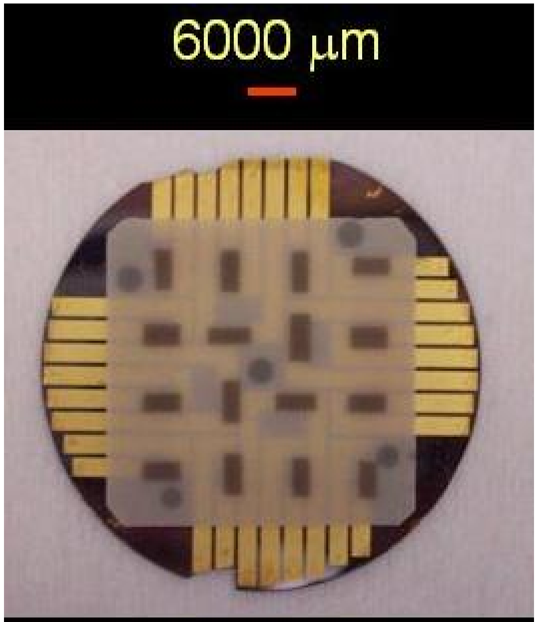
Single p-type-element
32K Cooling
(Ref: *Nature*)



P-N Couple



14 P-N Couples
Series Connected
Mini-module



Wafer-Scale
Integrated Module
Composed of 16
mini-modules

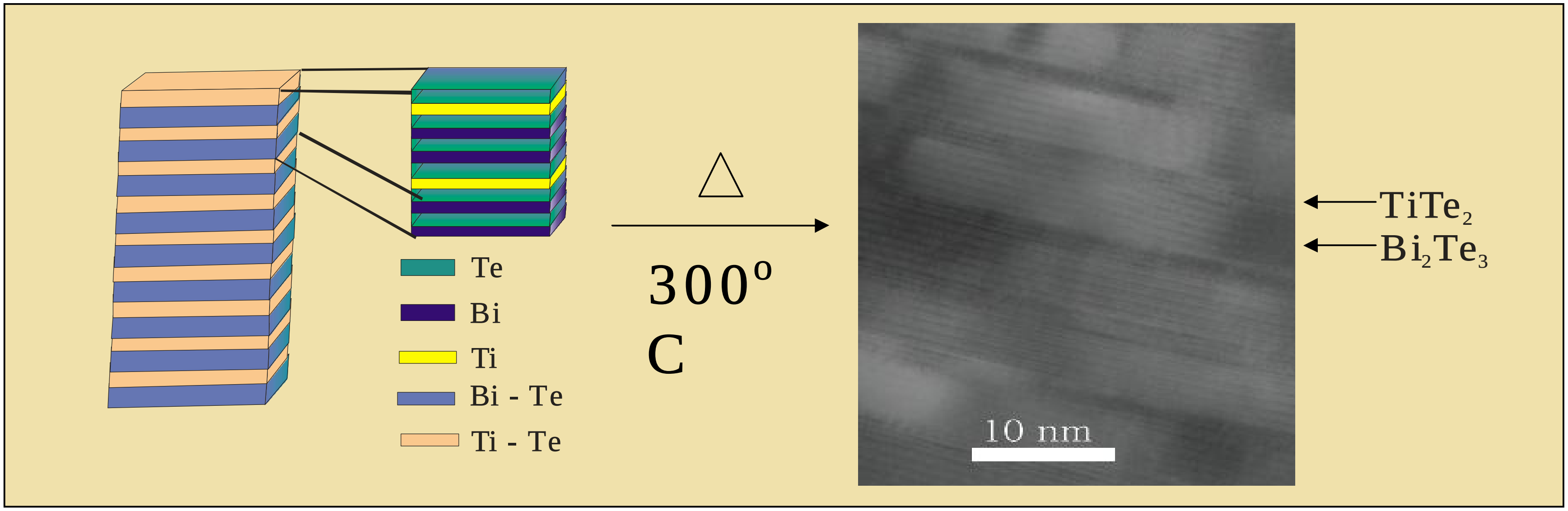
Johnson & Harris (U. Oregon)

- Novel part-bulk, part nano-scale fabrication technique

- Johnson, D. C. 2002 The synthesis of metastable skutterudites and crystalline superlattices. In *XXI International Conference on Thermoelectrics*. Long Beach, CA USA: IEEE.

Nanoscale Tailoring of Materials using Modulated Elemental Reactants

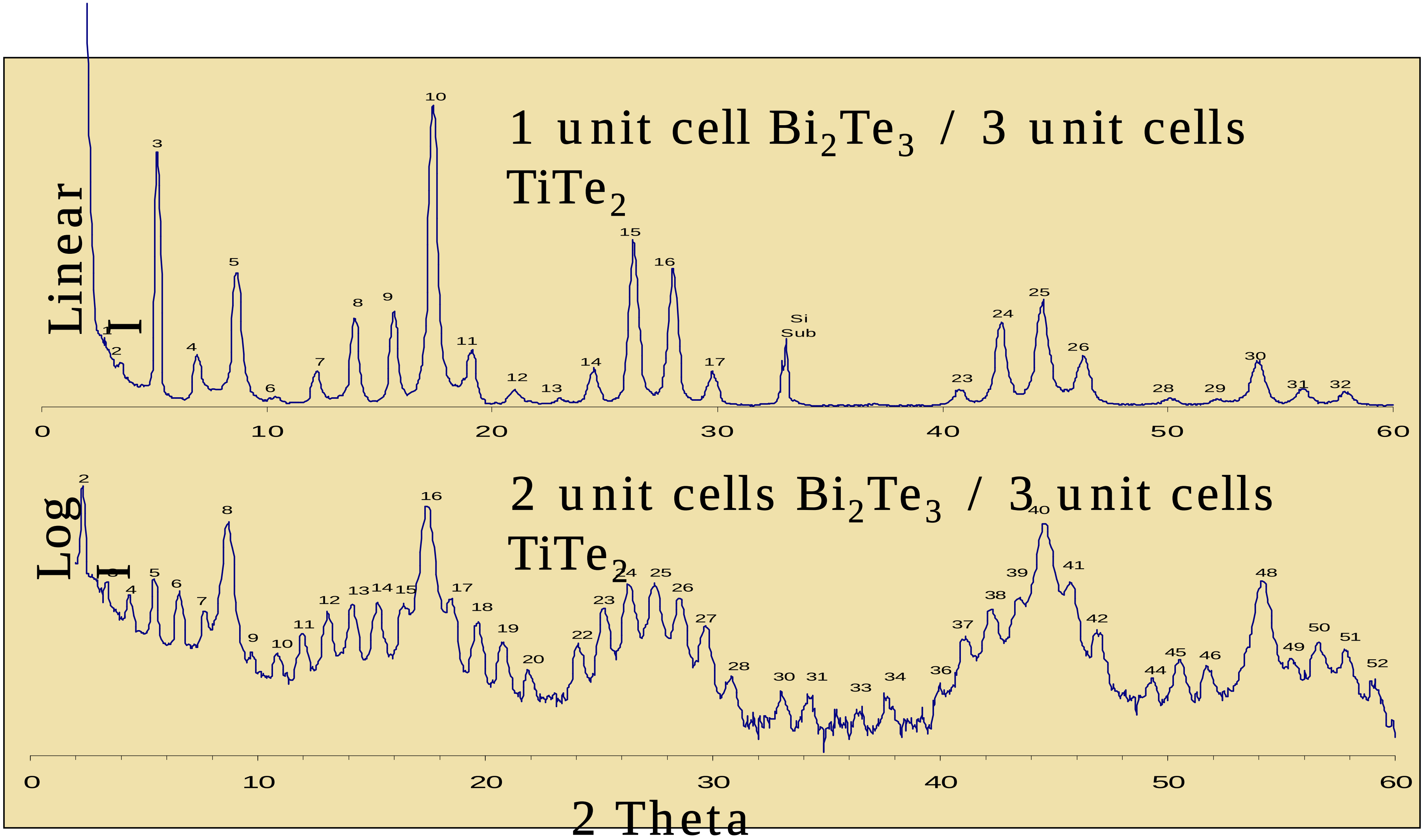
Fred R. Harris and David C. Johnson, Materials Science Institute,
The University of Oregon, Eugene, OR 97403



- Can prepare new compounds not found on phase diagrams
  - (Example: Sb from effusion cell @ 0.5 Å/sec. - CBV)
- Can prepare superstructures by design of initial reactants
- Permits study of interdiffusion and compound formation at reacting interfaces

UNIVERSITY
OF OREGON

XRD patterns of Bi_2Te_3 / $TiTe_2$ Superlattices Showing Unit Cell Control



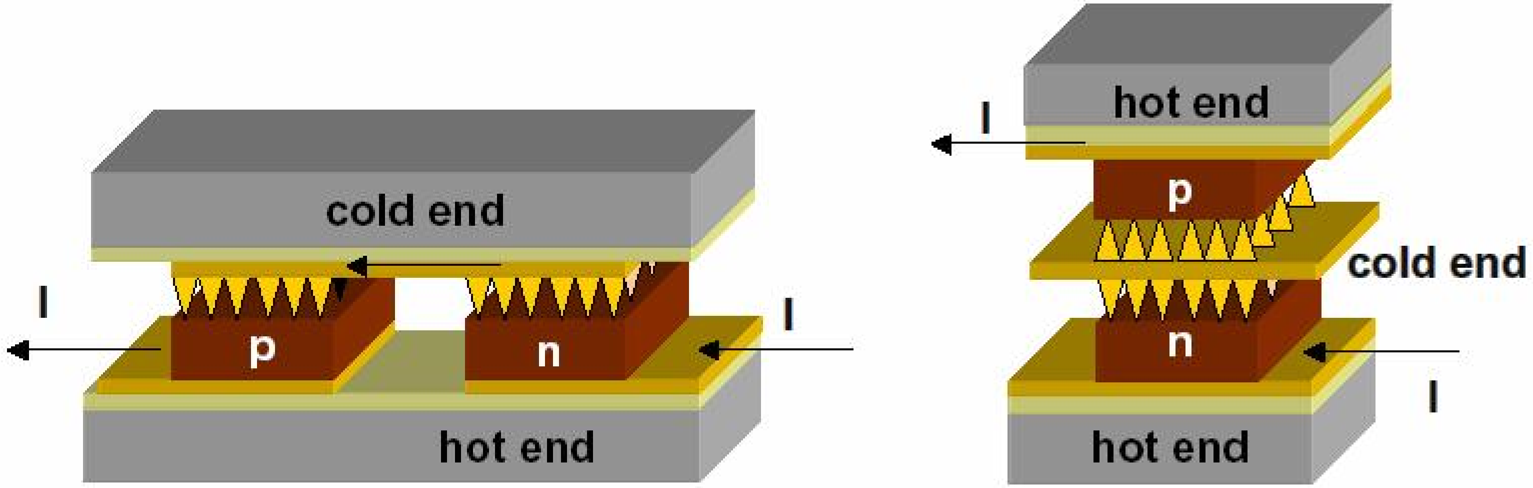
1 unit cell Bi_2Te_3 / 3 unit cells $TiTe_2$

2 unit cells Bi_2Te_3 / 3 unit cells $TiTe_2$

Ghoshal (Nanocoolers/$_{\text{IBM}}$)

- Ghoshal, U. & Shi, L. 2002 Design and characterization of cold point thermoelectric coolers. In *XXI International Conference on Thermoelectrics*. Long Beach, CA USA: IEEE.

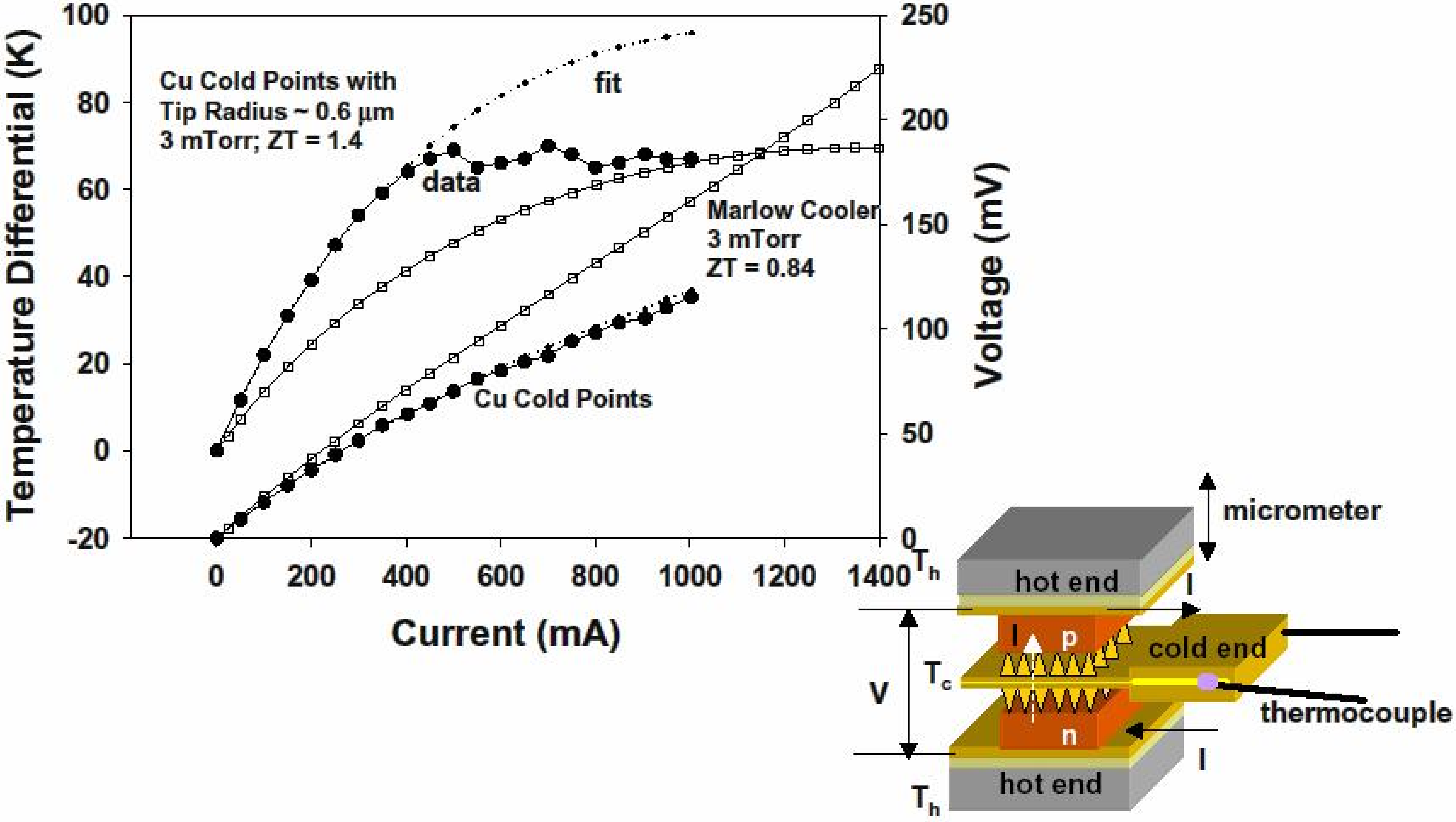
Cold Point Thermoelectric Coolers



p: Bi/Sb/Te n: Bi/Te/Se

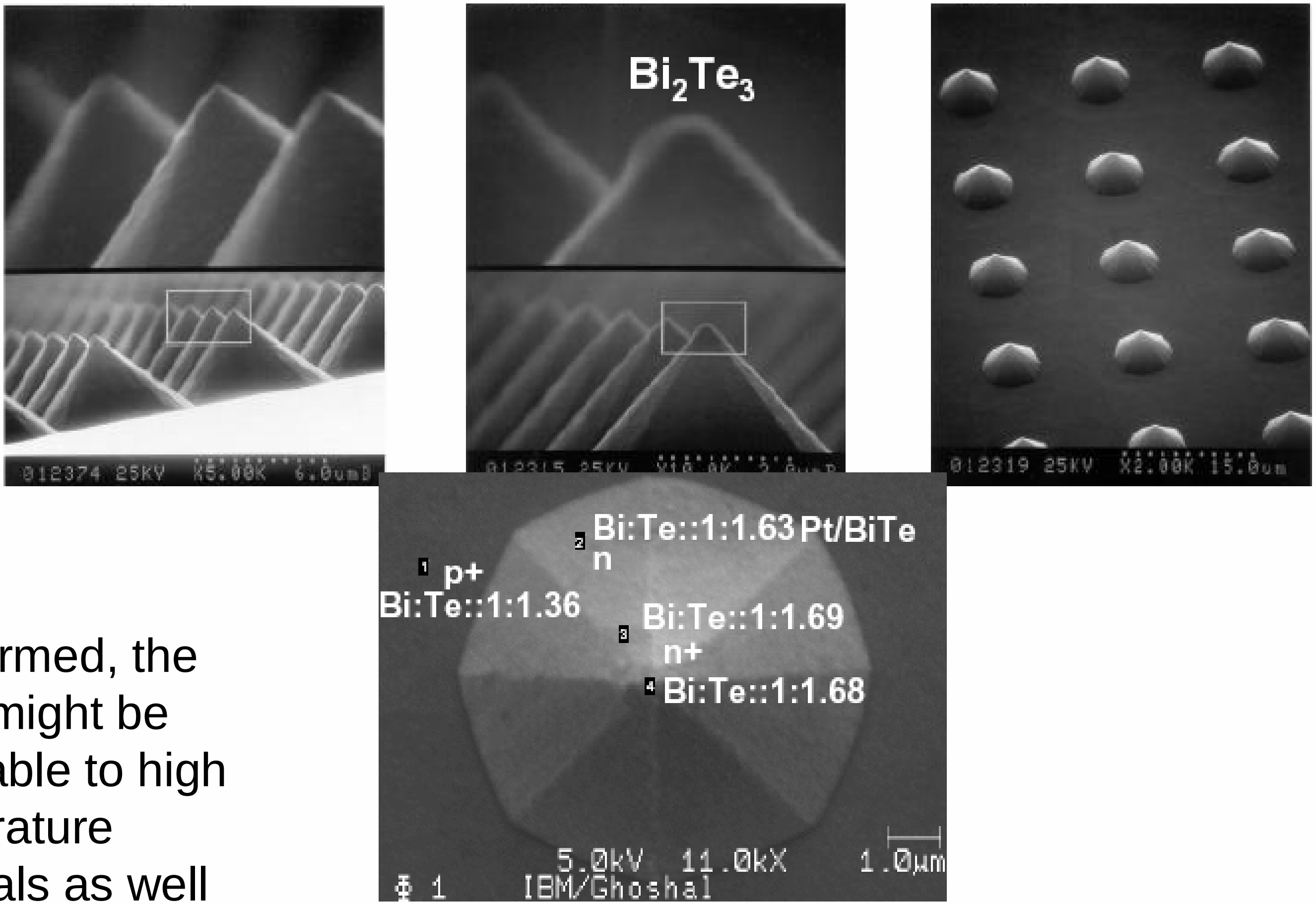
Interface Effects: Ju and Ghoshal, *J. Appl. Phys.* (2000)

The sharp points are thought to restrict the flow of phonons more than the flow of electrons, effectively lowering λ_p & increasing ZT



Ghoshal *et al.*, *Appl. Phys. Lett.* (2002)

TE Cold Points on Metal/Si



If confirmed, the effect might be applicable to high temperature materials as well

Solid State Thermionics

Solid State Thermionics

- Alternating layers of semiconductors alloys ‘design’ of the work function
- Thermionic emission occurs at much lower temperatures
- Some modest (1-10 K) cooling has been demonstrated
- Unclear if this approach can be more efficient than thermoelectrics
  - Some theory says ZT>5 may be possible

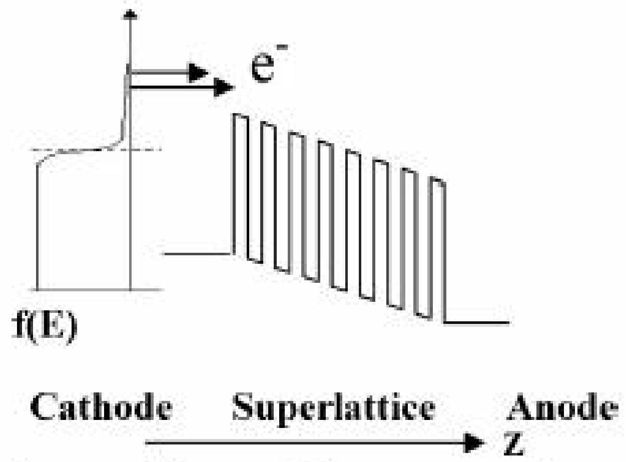


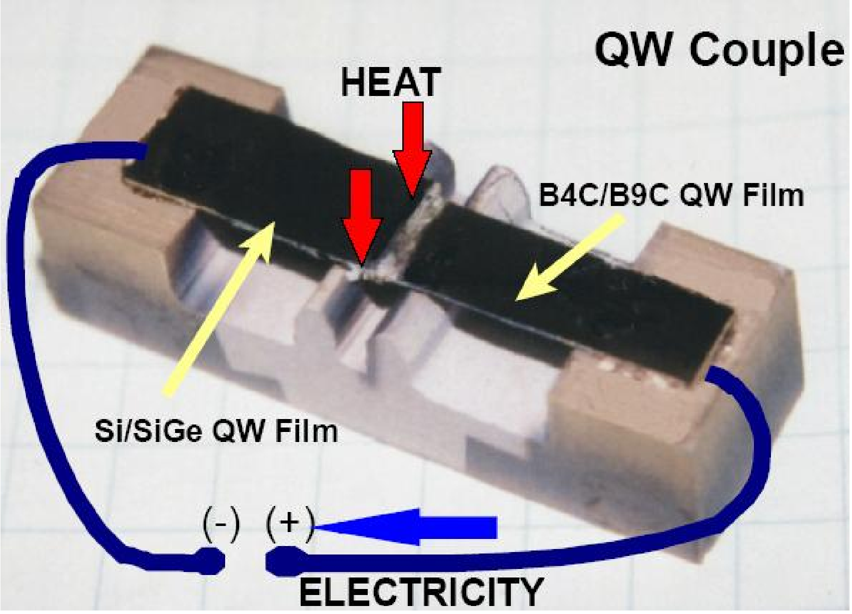
FIG. 1. Schematic energy diagram of a heterostructure integrated thermionic (HIT) microcooler along with electron energy distribution and the Fermi level.

Vashaee, D. Â. and A. Shakouri (2004). "Electronic and thermoelectric transport in semiconductor and metallic superlattices." Journal of Applied Physics **95**(3): 1233-1245.

Wild Claims

- At any given time there are a number of wild claims of huge efficiencies
- I am openly skeptical, as a rule
- Independent verification would help
- 3 selected claims are briefly described

2002 News Release
“Hi-Z Announces High Efficiency Thermoelectric Materials”
Ghamaty, ICT2002



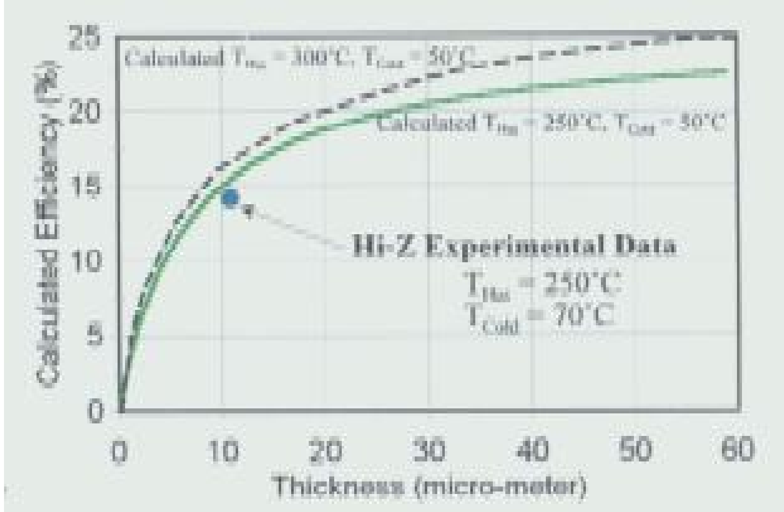
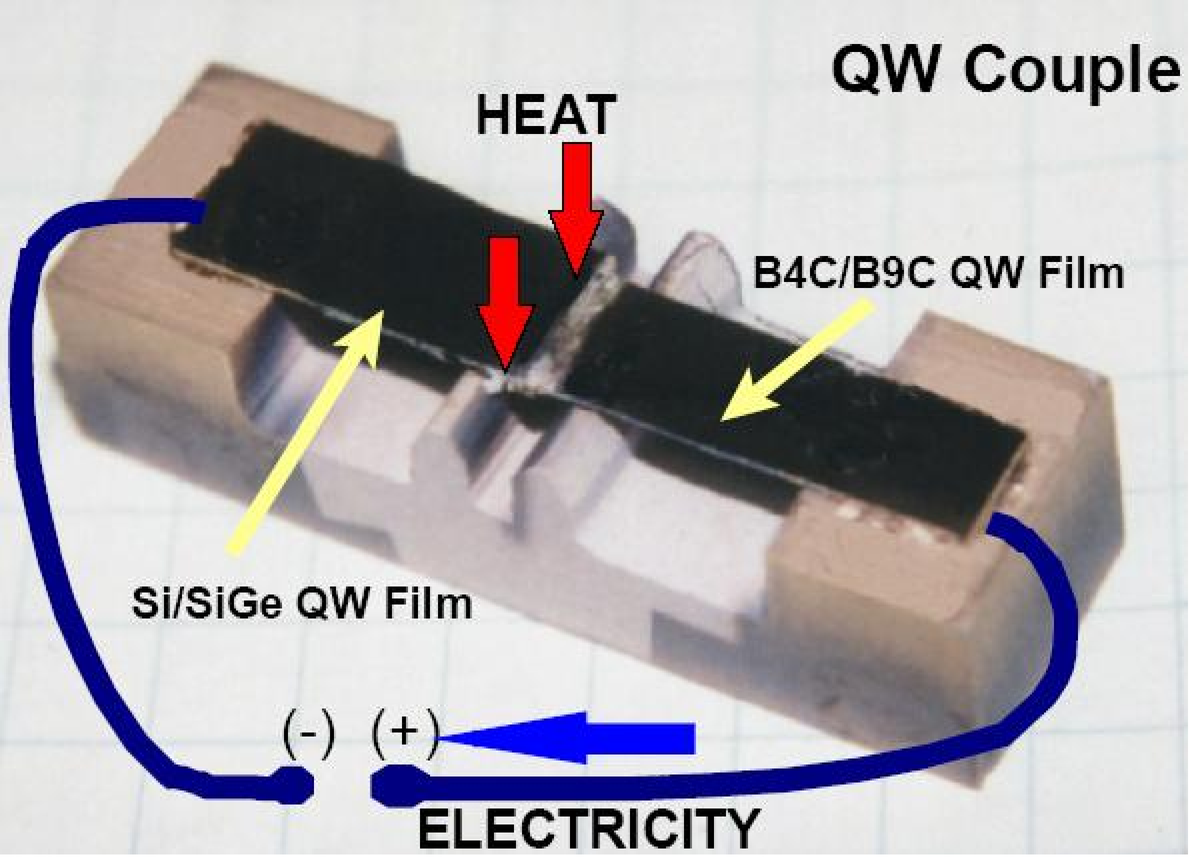


Figure 2. Efficiency of QW couple versus film thickness on a 5μm Si substrate. Hi-Z experimental and predicted values are shown for comparison for N type Si/SiGe and P type B_4C/B_9C.

- Claim to have measured 14% efficiency
  - Power out/heat in
  - Deduce ZT_{dev}=3.56!
- Said to be quantum wells of n-type Si/SiGe & p-type B_4C/B_9C
- If it works, I have no idea how!


QW Couple
HEAT
B4C/B9C QW Film
Si/SiGe QW Film
(-)
(+)
ELECTRICITY

ENECO's 'Thermal Diode'

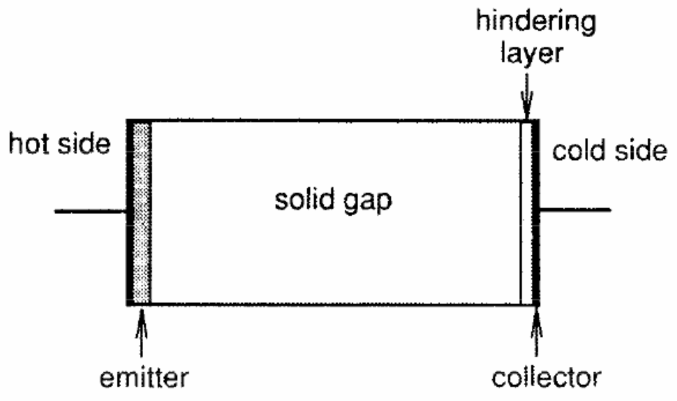


FIG. 1. Schematic of basic thermal diode structure. A highly doped emitter on the hot side injects current into a solid gap region, where carriers diffuse to the collector. A hindering layer near the collector makes it so that a greater thermally induced potential is required to develop an ohmic return current.

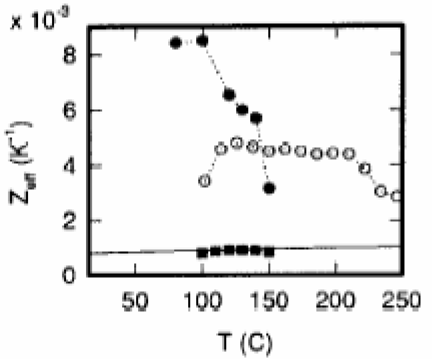


FIG. 4. Effective integral figure of merit as a function of the temperature. Solid line: Model thermoelectric result for an ideal intrinsic $Hg_{0.86}Cd_{0.14}Te$ slab. Closed squares: Experimental result for a $Hg_{0.86}Cd_{0.14}Te$ slab with copper cladding. Closed and open circles: Data for the same devices as those shown in Fig. 2.

- Device efficiency = 35%, $Z_{eff}T=3.2$
- The theory of how it works has always eluded me. Perhaps because it has changed so often.
- If it works, I have no idea how!

Hagelstein, P. L. and Y. Kucherov (2002). "Enhancement figure of merit in thermal to electrical energy conversion using diode structures." Appl. Phys. Lett. **81**(3): 559-561.

Power Chips, Inc.’s ‘Thermotunnel’ Device

- Almost a vacuum thermionic device
  - But make gap so small (4-10 nm) that tunneling occurs
  - Effective work function is reduced
- Have claimed upwards of 55-70% of Carnot efficiency, but no details have been made public
- A Stanford group has reported 0.001 K cooling achieved, with horrible efficiency
- This one does have a story worth checking out, but remains a long shot

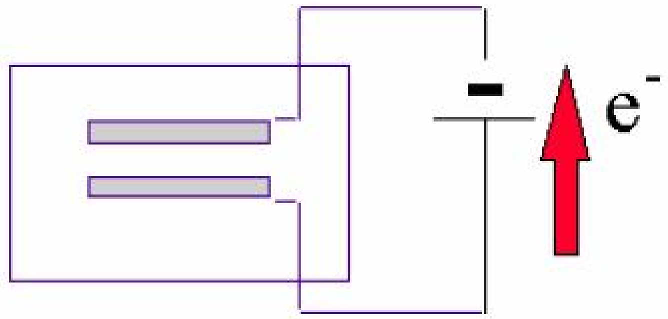


FIGURE 2. Gap-Diode Power Converter.

FIGURE 5. Sandwich in Operating Position. Gap is Created Using Mirrored Diodes.

Cox, I. W. and A. Tavkhelidze (2004). Power Chips for Efficient Energy Conversion. SPACE TECHNOLOGY AND APPLICATIONS INTERNAT.FORUM-STAIF 2004, Albuquerque, New Mexico (USA), AIP p.1238-1246.

Closing Remarks

Closing Remarks

- This course has covered some remarkable advances in thermoelectrics
  - > 1,000,000,000 device-hours for SiGe unicouples
  - ZT=2+ really has been achieved in at least a few cases
- But also some notable failures & false alarms
  - The Selenides & SiGe/GaP
- The successes resulted from 40+ years experience
  - And persevering through the failures
- Today SiGe RTGs set a durability benchmark that is hard to meet
  - And may not be reasonable to expect for any new technology

- Success breeds complacency
- ‘Failure’ is a chance to learn & improve
  - We won’t repeat past mistakes. We’ll make new ones all our own.
- Note that none of the ‘failures’ ever made it into space
  - The system worked to catch problems before they affected a mission

Alternate/Supplementary Slides

Good Enough for Science Fiction

“You’ve heard of the Peltier Effect?”

“Of course ... every domestic icebox has depended on it since 2001, when the environmental treaties banned fluorocarbons.”

“Exactly. ... Our physicists have discovered a new class of semiconductors - a spin-off of the *super*conductor revolution - that ups efficiency several times. Which means that every icebox in the world is obsolete, as of last week.”

From: *The Ghost from the Grand Banks,* 1990
by Arthur C. Clarke, inventor of communications satellite

Good Enough for Zener

The Westinghouse Thermoelectric Generator Program goal for efficiency was "only 35%" because

"Frankly, I wish the goal to be one that we can attain."

From C. Zener, 1959