Thermoelectric Technology of the Future

Cronin B. Vining
Consultant

Defense Science Research Council Workshop
La Jolla, California
July 21, 1994

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 Which means that every icebox in the world is obsolete, as of last week."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

INTRODUCTION

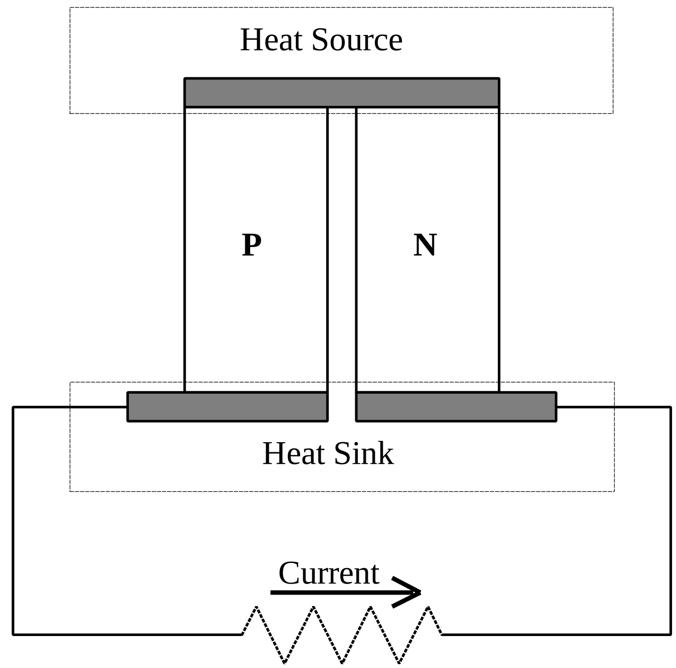
- Energy costs and demand can only increase
- Environmental concerns can only increase
- We need efficient, clean energy conversion for
  - high value-added applications such as space, defense
  - consumer products such as picnic baskets
- Existing thermoelectrics with $ZT \sim 1$ fill niche needs
- But with $ZT \gg 1$, mechanical engines might become as rare as vacuum tubes

Where do we start to look for
Thermoelectric Materials of the Future?

Typical Thermoelectric Device

- Conceptually identical to ordinary thermocouples
- The key to efficiency is selection of materials. Desired Properties:
  - Big EMF=high Seebeck coefficient
  - Small internal losses=low resistivity (ρ)
  - Small heat loss=low thermal conductivity (λ)
- Summarised in the Dimensionless Figure of Merit

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

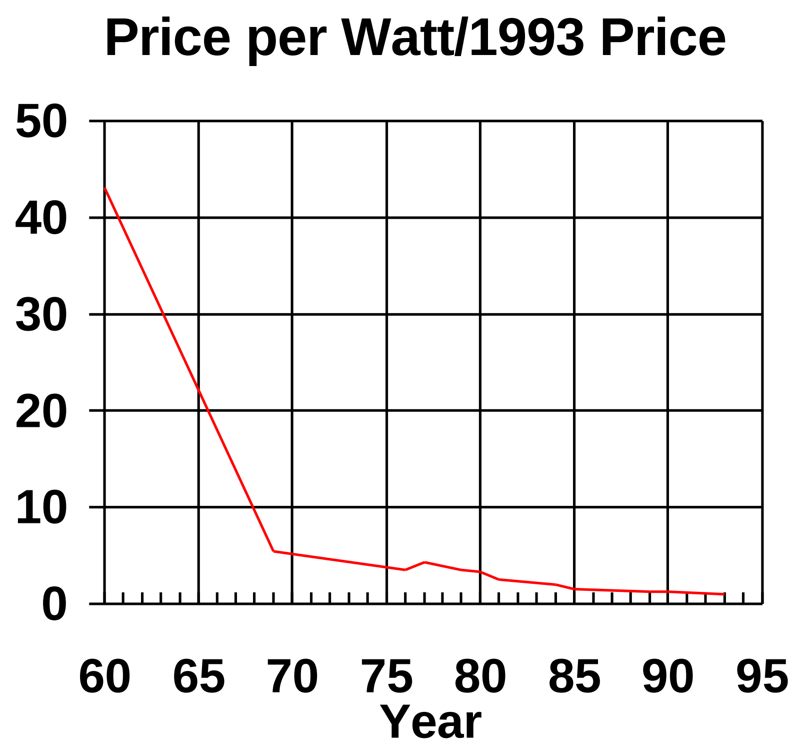


Thermoelectric Applications Today

- Highly reliable, but low efficiency (5%-10%)
- Thermometry
- Space power
  - Radioisotope power sources for deep space probes
  - 250,000,000 device-hours without a single failure
- Remote power
  - Oil pipelines, sea buoys
- Refrigeration
  - 1 rail car, 1 US nuclear submarine
  - Thousands of picnic baskets
  - Thousands of IR detector coolers

Production Cost Reduction

- Production costs have decreased steadily
- Significant consumer markets have opened
  - Picnic Baskets use >500,000 modules / year (Igloo, Coleman, etc...)
- Reliability is very high
- Efficiency remains near 1960 levels



After R.J. Buist, 1993

Current Status

- Niche applications will continue to grow
  - Reduced manufacturing costs opening new markets
- Japanese have initiated major waste-heat recovery program
  - High energy costs more important than capital costs
  - Where there is abundant waste heat, TE makes sense
- CFC-ban should increase markets for all sorts of alternate refrigeration technologies

Need New Materials

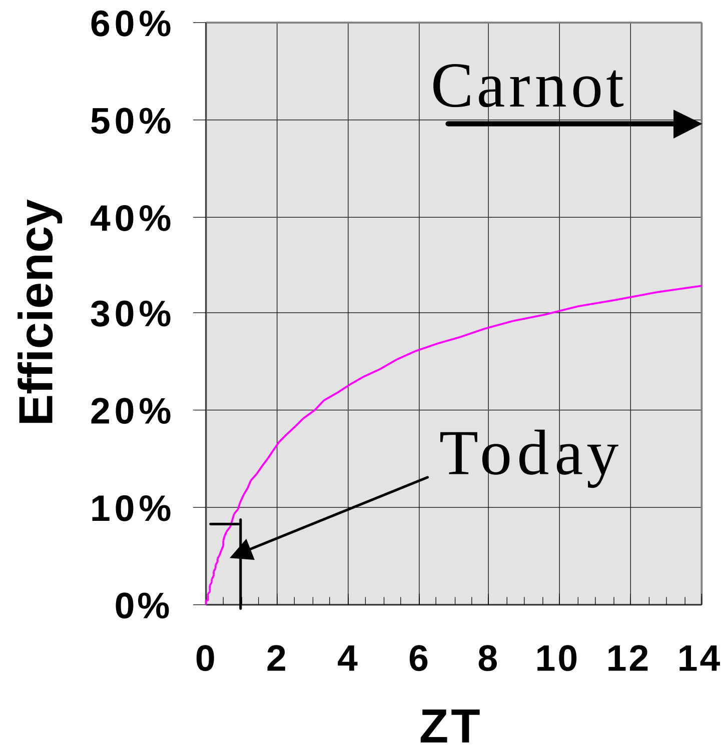
- The key to major expansion is a major improvement in materials efficiency
- Current TE markets are too small by themselves to sustain the required R&D
- Are there new, untried ideas?

Thermoelectric Efficiency

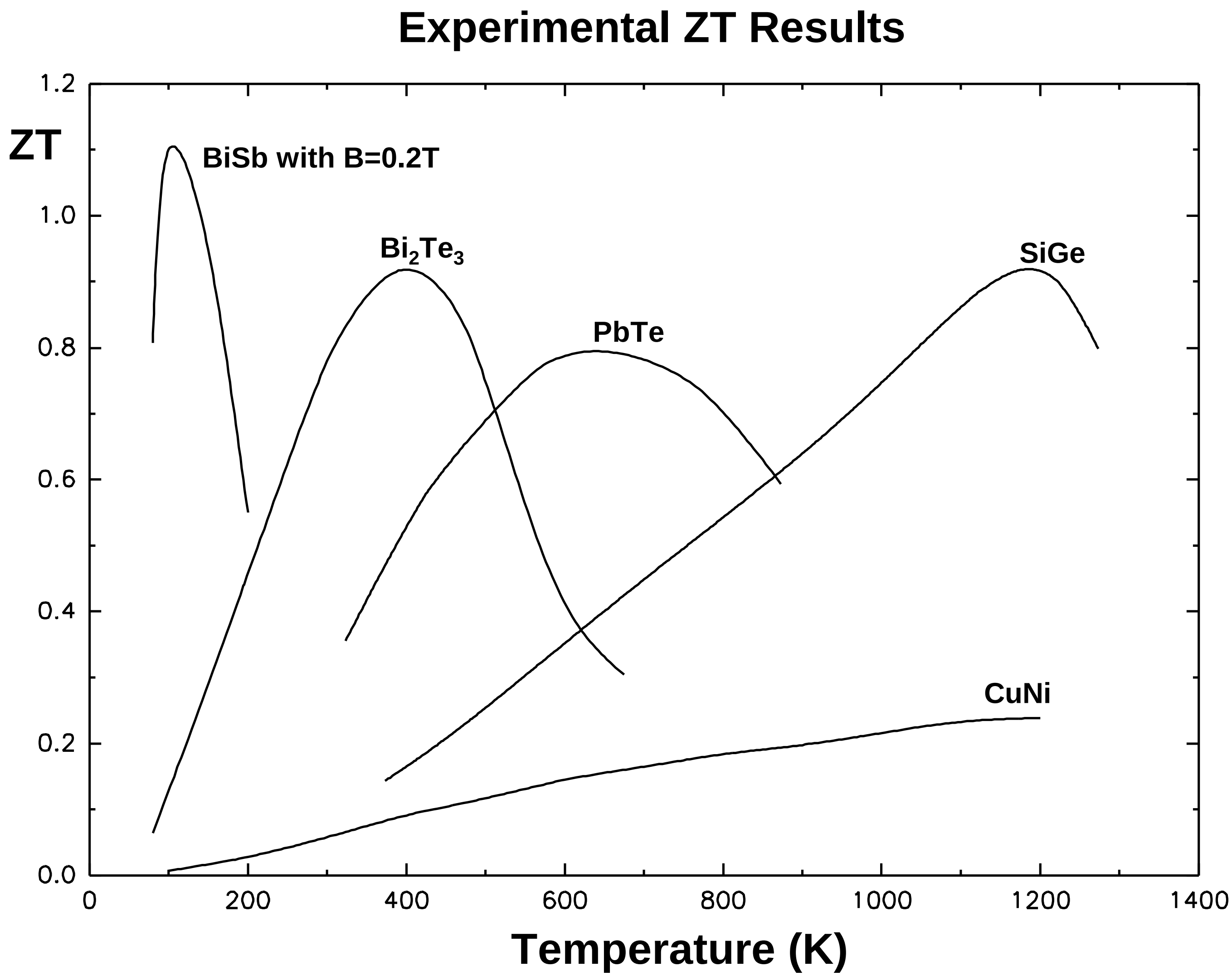
- For a single stage TE power generator:

$$h = \left[\frac{\Delta T}{T_h}\right] \bullet \left[\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+{T_c}/{T_h}}\right]$$

- For current materials, $ZT_{max} \sim 1$
- But ***<u>There is no known theoretical limit</u>***



Efficiency for $T_c / T_h = 0.5$



Thermoelectric Materials of Today

For technology, this will probably not change soon

The Intellectual Question

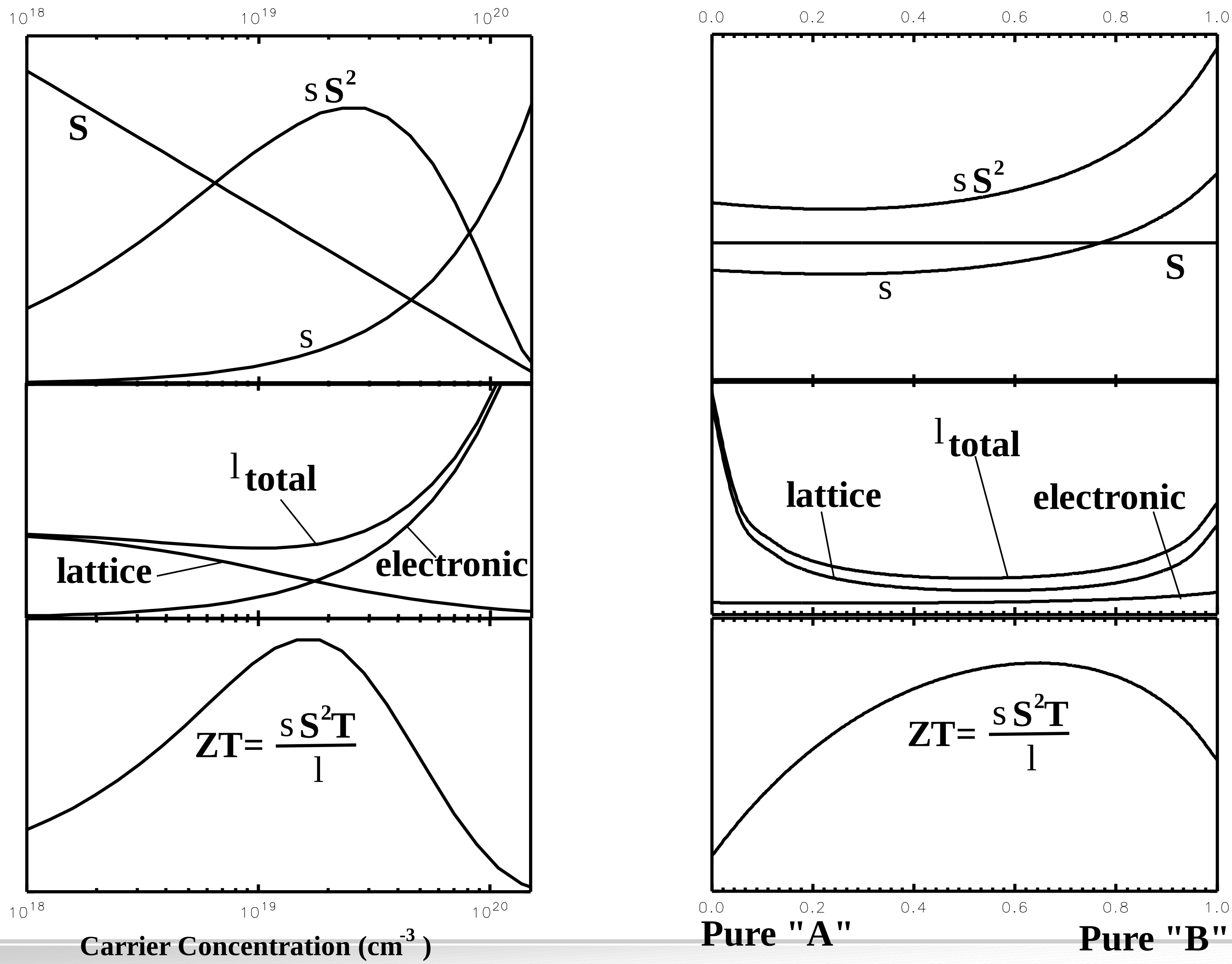
- Transport properties can vary by 20 orders of magnitude
- ZT is a transport property
  - or a combination of transport properties
- WHY are there no materials with ZT=10? or 50?

Where do we start to look?

Start with materials of today:

- Today's materials are based on: Bi_2Te_3, PbTe, SiGe
  - might also include BiSb, TAGS and $FeSi_2$
- These will not be replaced in the near future
  - Mature device technologies available
  - Current markets are too small to develop new technologies quickly
- By establishing a deeper understanding of today's materials we lay the foundation for new materials
  - Use well understood materials to test novel ideas

Conclusion: Doping and Alloying are the Major Effects



Conventional, 1-Band Semiconductor

$$(1) \quad s = nem$$

$$(2) \quad S = \frac{k}{e}(r - h)$$

$$(3) \quad h = \ln\left(\frac{\mathrm{n}}{n_o}\right)$$

$$(4) \quad n_o = 2\left(\frac{2pmkT}{h^2}\right)^{3/2}$$

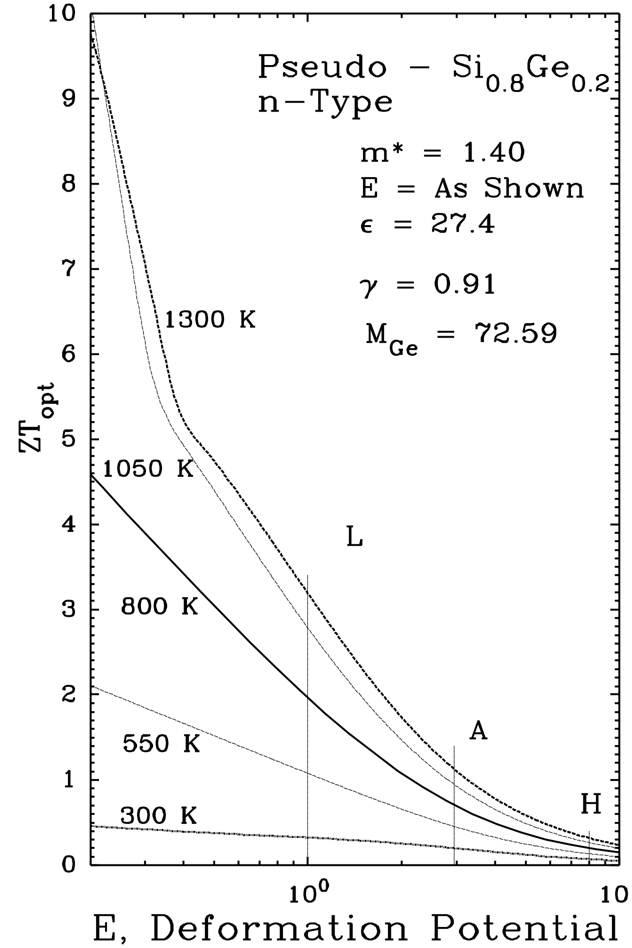
$$(5) \quad l = l_{phonon} + l_{electronic}$$

$$= l_{phonon} + r\left(\frac{k}{e}\right)^2 sT$$

$$(6) \quad ZT = \frac{S^2 sT}{l}$$

$$= \frac{(r - h)^2}{e^h b^{-1} + r}$$

$$(7) \quad b = \left(\frac{k}{e}\right)^2 \frac{e n_o m}{l_p} T$$



Smaller deformation potential yields larger mobility and larger ZT

Conventional Semiconductors

- Are there semiconductors which “work” according to conventional rules, but have more favorable parameters?
  - – Large m_{eff}, & m
  - – Small l_{ph} (approach the minimum possible)
  - – E_g > 4kT
- Binary Compounds
  - – Most (but not all) binary compounds have already been studied
  - – Novel binary compounds studied at JPL in recent years:
    - – B_4C, $La_{3-x}S_4$, $La_{3-x}Te_4$
    - – Ru_2Si_3, Ir_3Si_5, $IrSi_3$, Ru_2Ge_3, Re_3Ge_7, $Mo_{13}Ge_{23}$, $Cr_{11}Ge_{19}$, $CoGe_2$
    - – $RuSb_2$, $IrSb_2$, $IrSb_3$, and $CoSb_3$

Conventional Semiconductors

- Ru_2Si_3 - related materials
  - p-type appears promising on paper, but doping to date has been disappointing
  - Os_2Si_3 is isostructural and worth a closer look
- $IrSb_3$
  - very high mobility values reported by Caillat, Borshchevsky, and Fleurial

Conventional Semiconductors

- TiB_2, ZrB_2, and HfB_2
  - Do *not* have high ZT values
  - Do not even have a full bandgap
  - But r < 10 mW-cm, n~1-3 x 10^{21} cm^{-3} and m > 200 cm^2/V-s
  - If a bandgap could be opened up, ZT might be fairly high
    - alloys? superlattices? strain?
- Slack has surveyed *all* the binary compounds!
  - To be published in CRC handbook
  - Key: small electronegativity difference for high mobility values
  - 28 candidate binary compounds tabulated!
  - Particularly promising:
    - $IrSb_3$, Re_6Te_{15}, and Mo_6Te_8

Ternary and More Complex Compounds

- **Vast number of ternary compounds known**
  - ***Thousands*** **have been studied for superconductivity**
  - **Sufficient thermoelectric data available for only a very few**
- **$Mn_4Al_3Si_5$ - studied by Marchuk et al**
  - **R_H small, like a metal, but |S| up to 100 mV/K**
  - **R_H and S are of opposite signs**
  - **Such anomalous results are always worth careful study**
- **HfNiSn - studied by Dashevsky et al**
  - **Several isostructural compounds, promising power factor and thermal conductivity**
  - **67% metal and still a semiconductor!**
- **Copper Oxides - evaluated by Mason**
  - **only low ZT expected, due to poor mobilities**

Un-conventional Semiconductors

- **Not all semiconductors work the same way**
  - **In hopping conductors, carriers interact so strongly with "phonons" that the lattice distorts around the carrier**
  - **In other materials, charge carriers interact with each other so strongly that electrons cannot be considered as "independent"**
  - **Conventional selection criteria fails for such materials**

Pursue the anomalies

Strong Carrier-Lattice Interaction

- n-type $FeSi_2$ is a hopping conductor
  - b for n-type $FeSi_2$ is about 50 times smaller than b for SiGe
  - but ZT_{max}~0.4 for $FeSi_2$, less than 3 times small than for SiGe
  - low cost and “anomalous” behavior are good reasons for further studies
- B_xC has ZT~0.4-0.5
  - too small mobility (m ~ 1 cm^2/V-s), too high carrier concentration (~10^{21} cm^{-3})
  - Very high melting point and composed of very light elements
  - All conventional rules suggest this material has no promise
  - Still, it is within 2-3 of the very best

Strong Carrier-Carrier Interaction

- **$U_3Pt_3Bi_4$ - suggested by Slack**
  - **many isostructural compounds, such as $Ce_3Pt_3Bi_4$**
  - **so-called "heavy fermion semiconductor"**
  - **carriers behave as if they have large effective mass**
    - **Should have high Seebeck values**
- **Other heavy fermion materials suggested by Louie and Radebaugh**
  - **$(Ce_{1-x}La_x)Ni_2$, $(Ce_{1-x}La_x)In_3$, $CePd_3$, and $CeInCu_2$**

Organic Conductors

- **Many organic polymers with high electrical conductivity are now known**
  - **Doped polyacetylene can have electrical conductivity comparable to good metals**
  - **At low doping levels, high Seebeck values (>1000 mV/K) have been observed**
  - **Sometimes, electrical mobility values can be quite good**
  - **Give the low cost and the great ability to modify organic materials, some closer attention seems justified**

Heterostructures

- Apply modern fabrication techniques to thermoelectric materials
  - allows materials and properties not previously possible
  - extensively applied to control electronic properties
  - extension to thermal and thermoelectric properties is only starting
- Quantum point contacts at very low temperatures
  - "Quantized" Seebeck coefficient values have been observed under conditions where Hall coefficient and electrical conductivity are also quantized.
  - Theory and experiment agree even under quite extreme conditions
  - Provides confidence that theory is reliable

Heterostructures

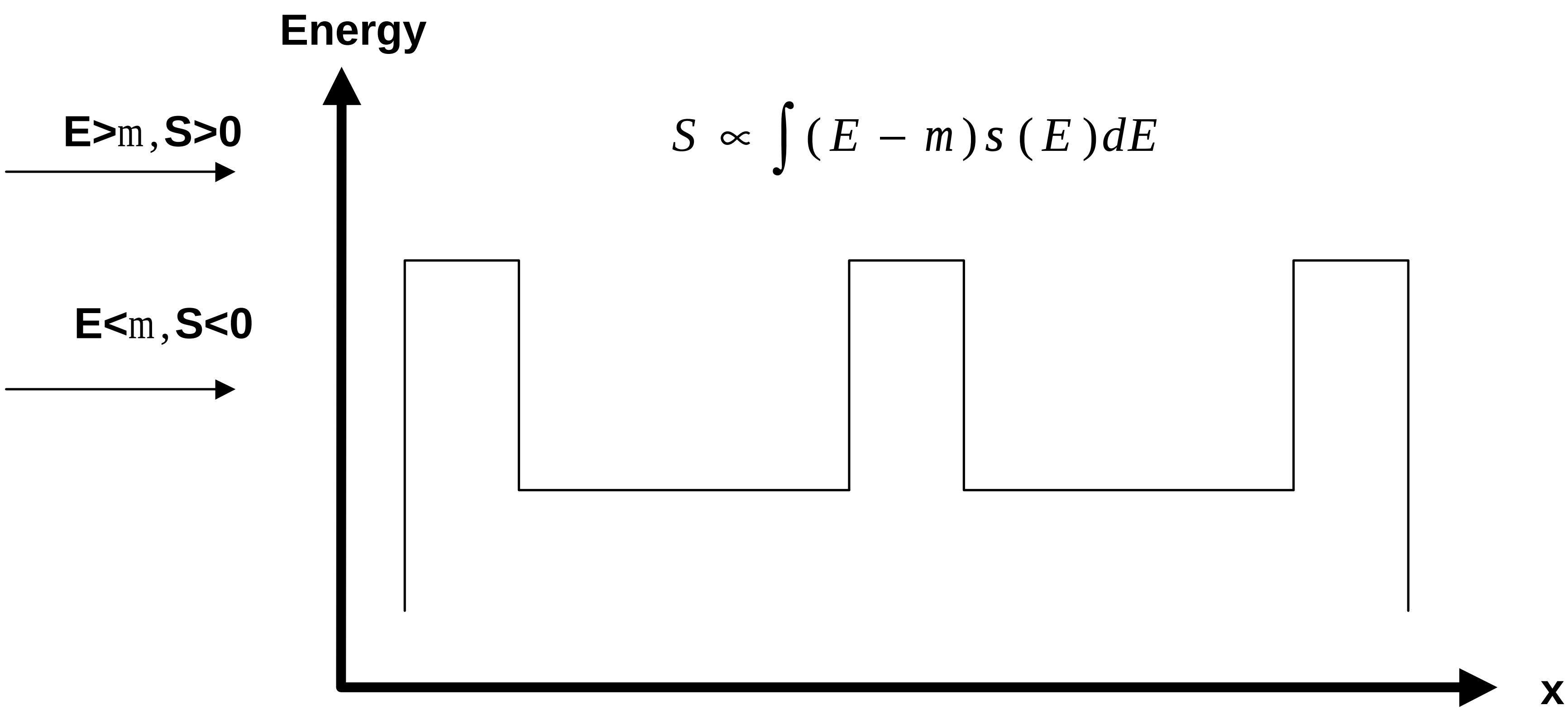
- Pioneering studies in this direction
  - Anatychuk et al discuss very small thermoelements
    - charge carrier temperature $\neq$ phonon temperature
  - Balmush et al and Dashevsky et al discuss p-n junction in a temperature gradient
    - usually p-n junction itself is isothermal
    - non-linear effects can be significant
- Thermoelectric effects in small structures are bound to exhibit a variety of new effects

Great Theoretical and Experimental Opportunities

Heterostructures

- **Moizhes and Nemchinsky: Barriers enhance the Seebeck**
  - **Carriers below the chemical potential degrade the Seebeck**
  - **Energy barriers allow “good carriers” to pass, inhibit bad carriers**

$$S \propto \int (E - m)\, s(E)\, dE$$



Heterostructures

- Hicks and Dresselhaus: Quantum wells
  - ZT increases with decreasing size of quantum well
  - Factor of 14 increase in ZT predicted for Bi_2Te_3!
- Other effects could also enhance ZT
  - Mobility enhancement due to physical separation between carriers and ionized impurities
  - Phonon scattering and/or Bragg reflection at heterostructure boundaries
- Harman at MIT Lincoln Labs is pursuing this type of approach by Molecular Beam Epitaxy

Metals

- **Metals are poor thermoelectrics because S is small (<20 mV/K).**
- **Even under the most favorable circumstances:**
  - l_{ph} **=0, acoustic scattering and nondegeneracy:**

$$ZT \leq \frac{S^2}{2\left(\frac{k}{e}\right)^2}$$

  - **so, S must be at least 122 mV/K to reach ZT=1**
- **But there is no proof that metals *must* have low Seebeck values**
  - **$Cu_{0.5}Ni_{0.5}$ has S=73 mV/K at 1200 K**
  - **Clearly this is still *very* degenerate**
  - **Can S be even larger? What about in a multilayer?**

Very Low Temperatures

- **Kapitulniks suggestion**
  - **at low temperatures,** $l_{ph} \sim T^3$
  - **So, b becomes very large**
  - **With careful doping, ZT should also be very large**
  - **Might make a good refrigerator below 4 K**
  - **More importantly, could demonstrate the principle that large ZT is possible**

SUMMARY

- There is no easy path to large ZT
- But there are *many* plausible approaches that have yet to be tried
- Persistent efforts are bound to yield exciting results

The challenge is not the generation of plausible ideas, but the rapid and accurate evaluation of those ideas