Thermoelectrics for Vehicle Applications

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Acknowledgement

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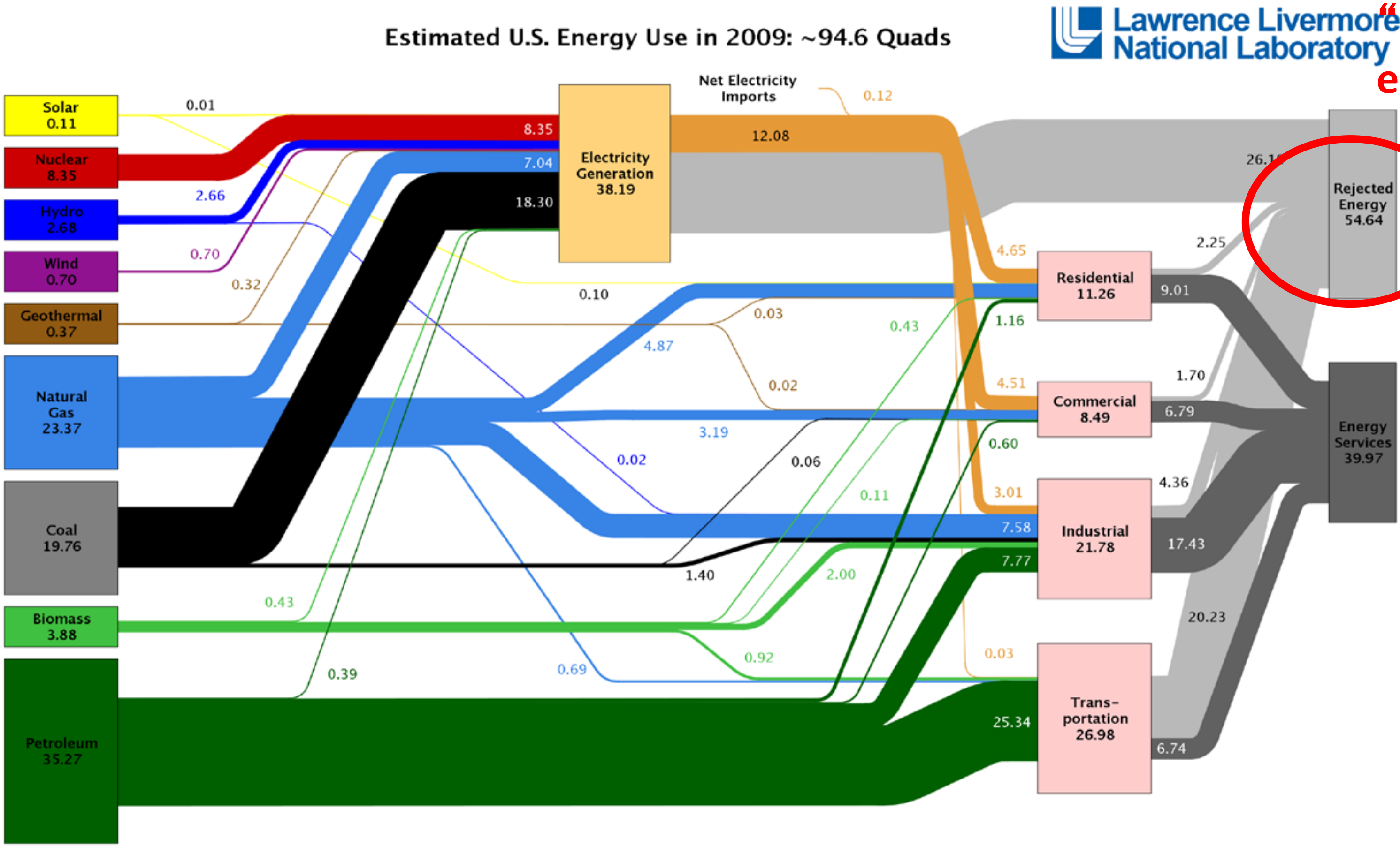
Outline

- Magnitude of Waste Heat
- Automotive TE Commercial Success and Opportunities
- Industrial Technology Development Approach
  - Coupled Materials-Systems Solutions
- TE Materials Research
  - Mechanical Property – Battling the Flaws
  - Semiconductor Carriers Engineering and Thermal Transport
- Conclusions

The Magnitude of Our Waste Energy

massive quantity of "waste" energy

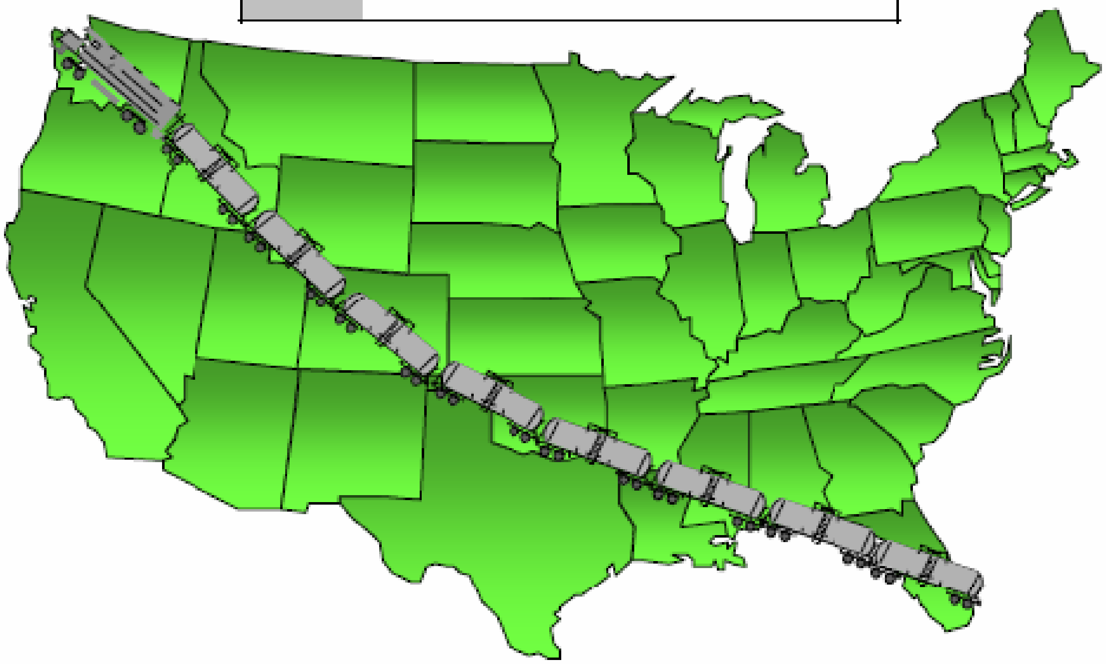


Source: LLNL 2010. Data is based on DOE/EIA-0384(2009), August 2010. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports flows for non-thermal resources (i.e., hydro, wind and solar) in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

- ❑ Waste heat is one of our most abundant sources of alternative energy

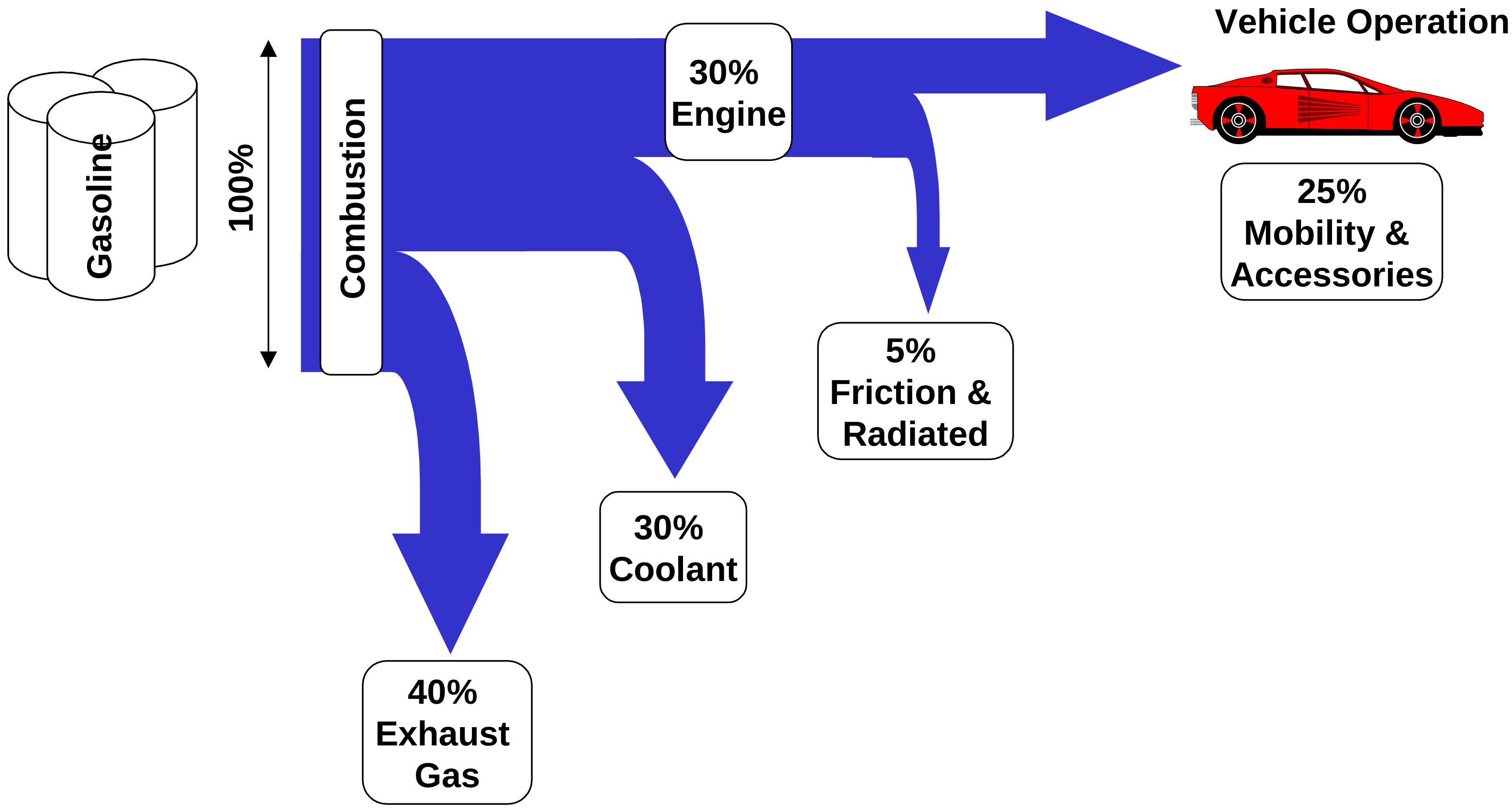
How Much is One Quad?

	1973	1997
U.S.	74 Quads	91 Quads
World	225 Quads	365 Quads



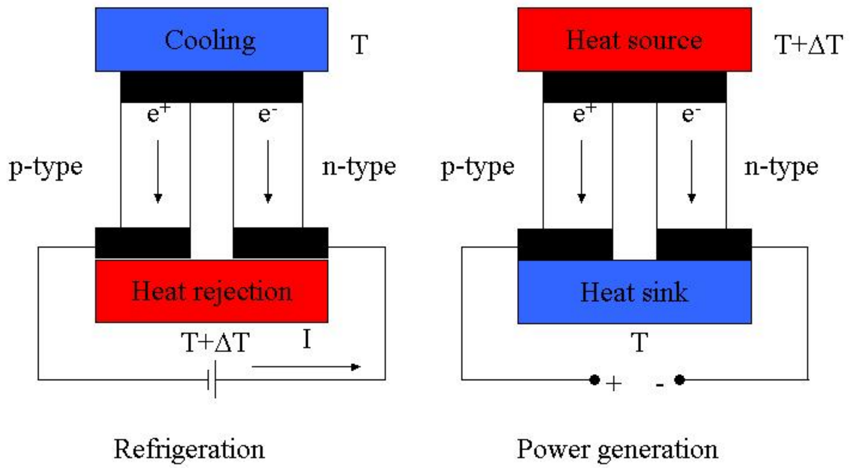
- 1 Quad (quadrillion btu) of energy is equivalent to 340,000 tank cars of crude oil stretched from Miami to Seattle (3,300 miles)
- In the area of energy, scale matters!

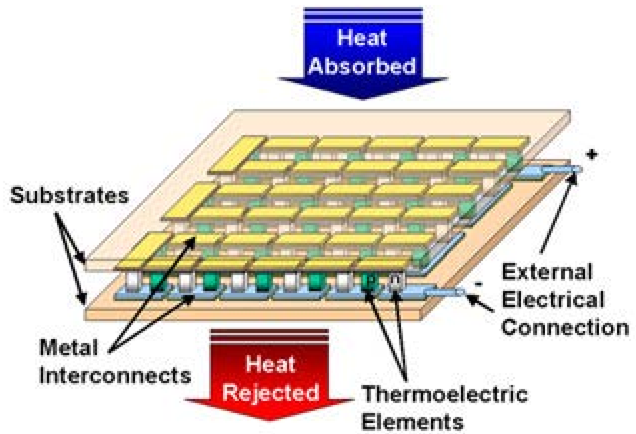
Typical Energy Path in Gasoline Fueled Internal Combustion Engine Vehicles



- ❑ Today's ICE-based vehicles: < 20% of fuel energy is used for propulsion
- ❑ > 60% of gasoline energy (waste heat) is not utilized

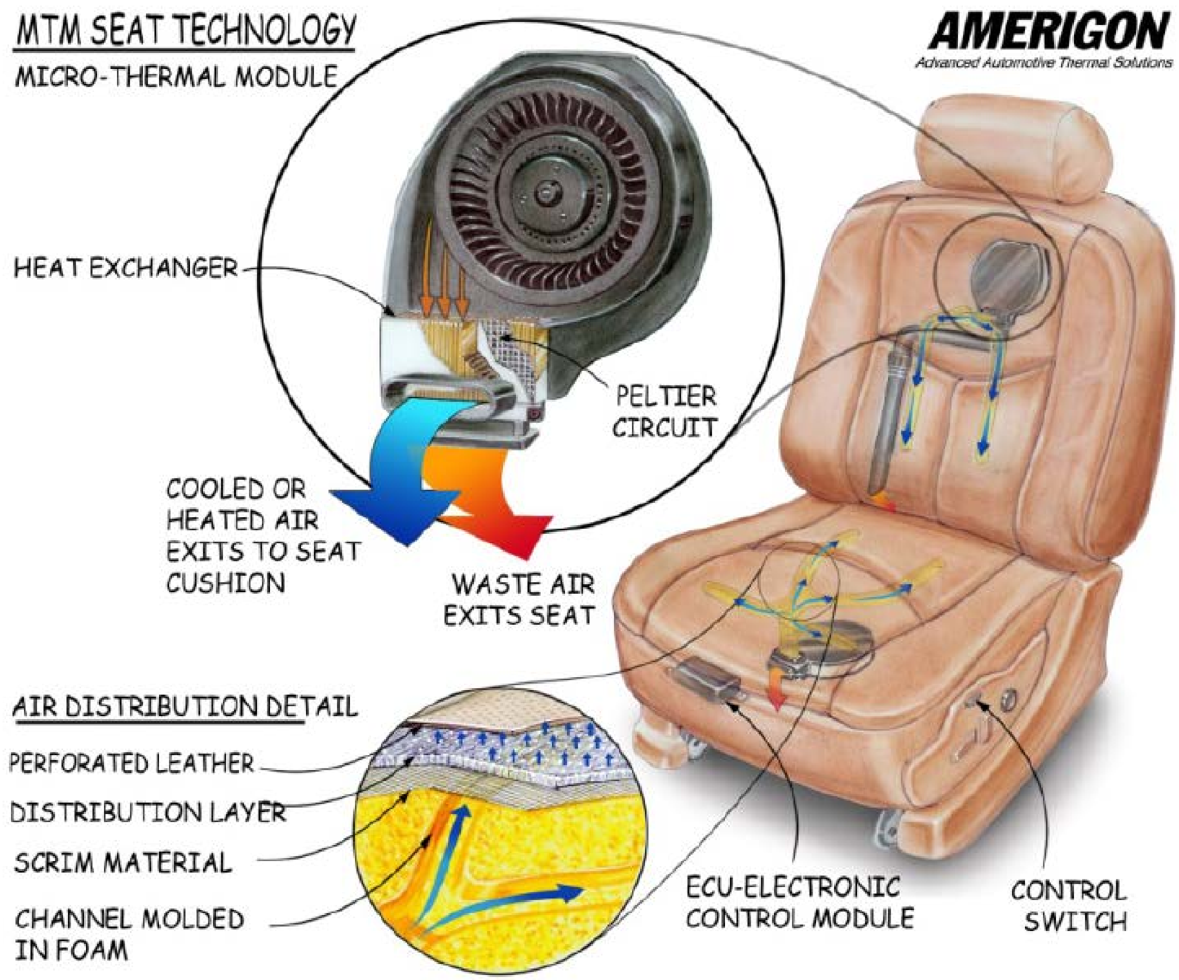
TE Cooling and Power Generation





- ❑ Solid state heat engines with electrons and holes as working fluids

Commercial Success of TE



- > 10 million thermoelectric-based seat systems sold (Feb. 2013, Gentherm PR)

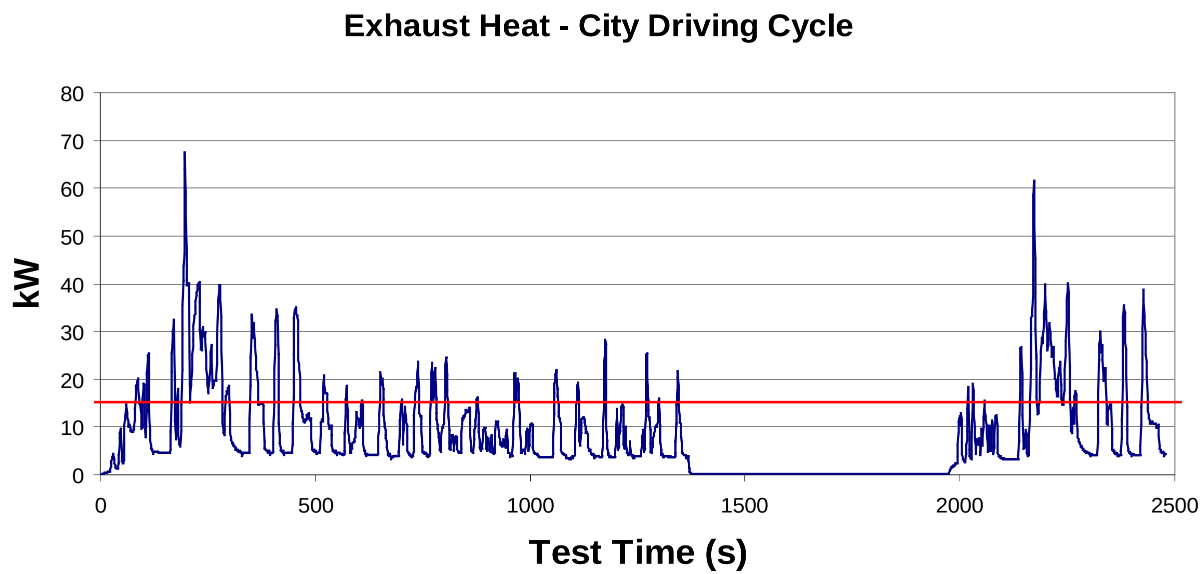
Vehicular TE Waste Heat Recovery Development

BMW

GM

Ford

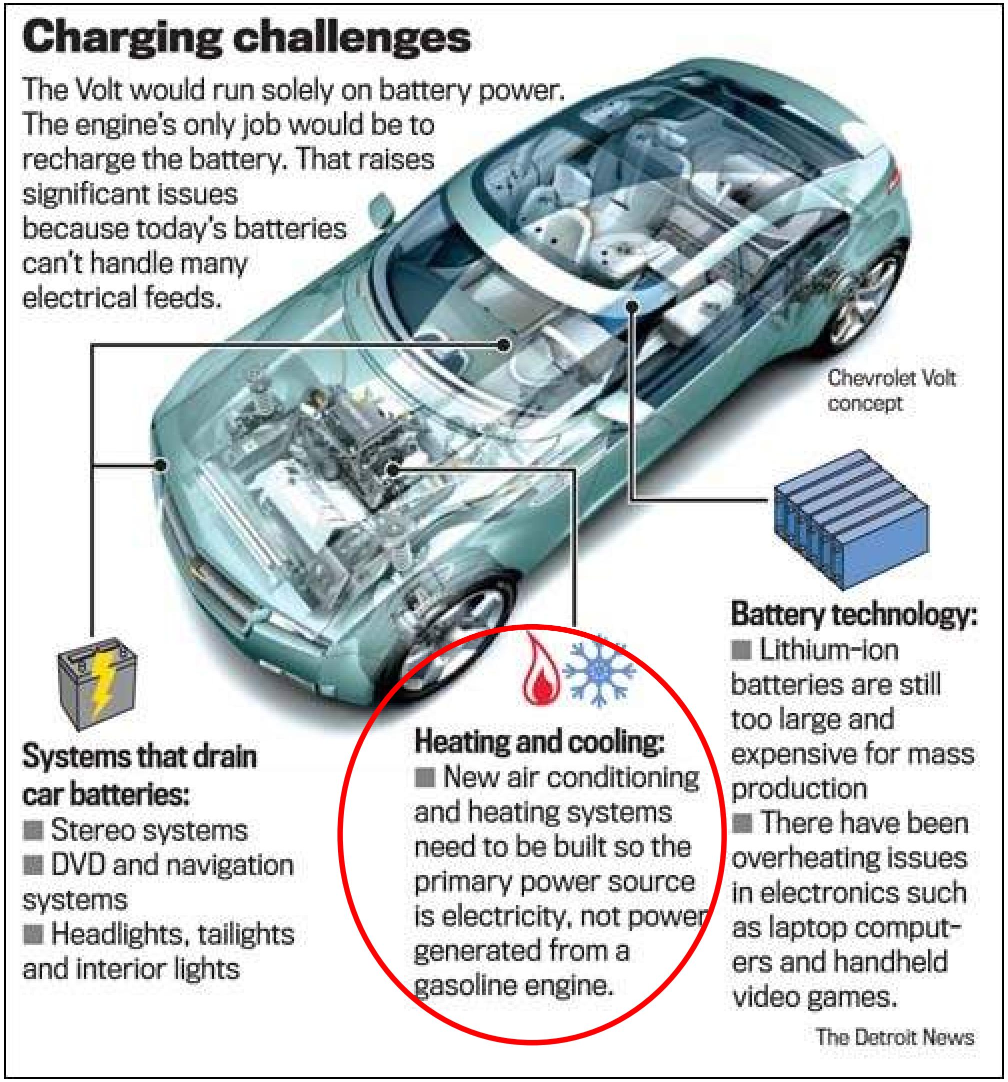
Exhaust Data - Chevy Suburban



- The Suburban was selected as a test vehicle because it simplified the modifications and installation of the prototype.

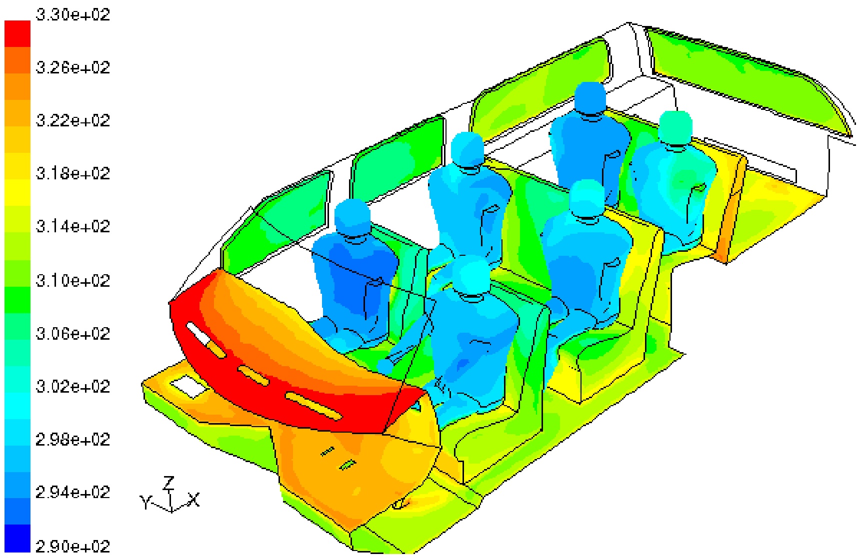
- Fuel efficiency improvement will be better in small, fuel efficient vehicles than in large vehicles because the electrical load in small vehicles is a larger portion of the engine output.

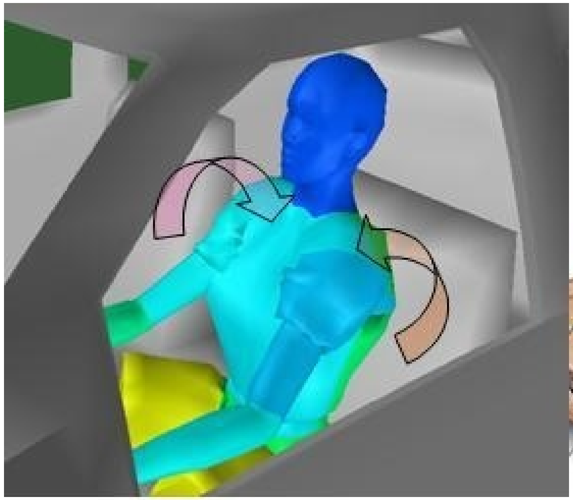
Opportunity for TE Cooling



Distributed Cooling for High Efficiency HVAC System

- ❑ Reduce onboard AC without sacrifice passenger comfort level
- ❑ Improve fuel economy and CO_2 emission
- ❑ Work funded by DOE

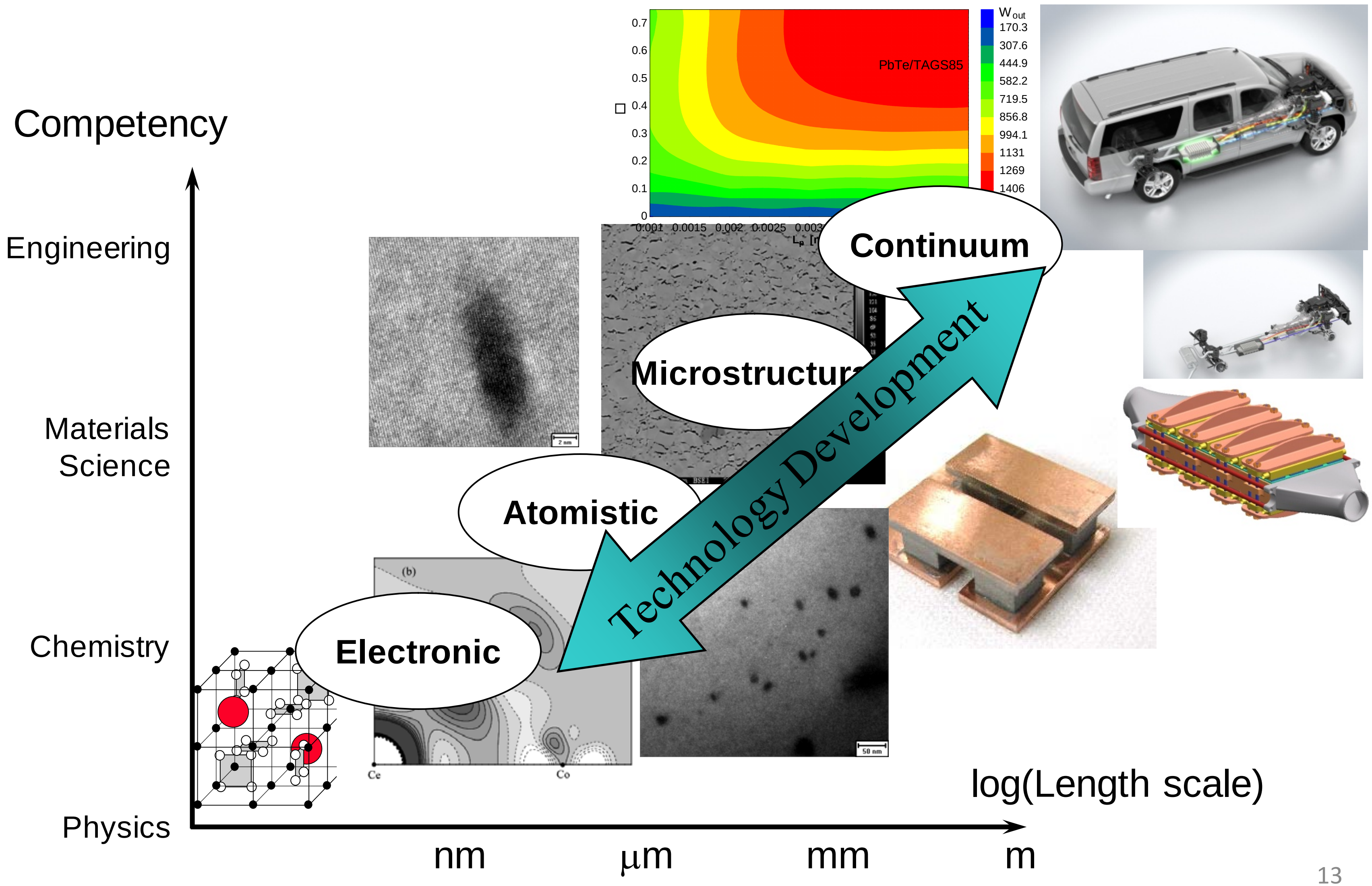




"If all passenger vehicles had ventilated seats, we estimate that there could be a 7.5 % reduction in national air-conditioning fuel use. That translates to a savings of 522 million gallons of fuel a year,"

John Rugh, project leader for NREL's Vehicle Ancillary Loads Reduction Project.

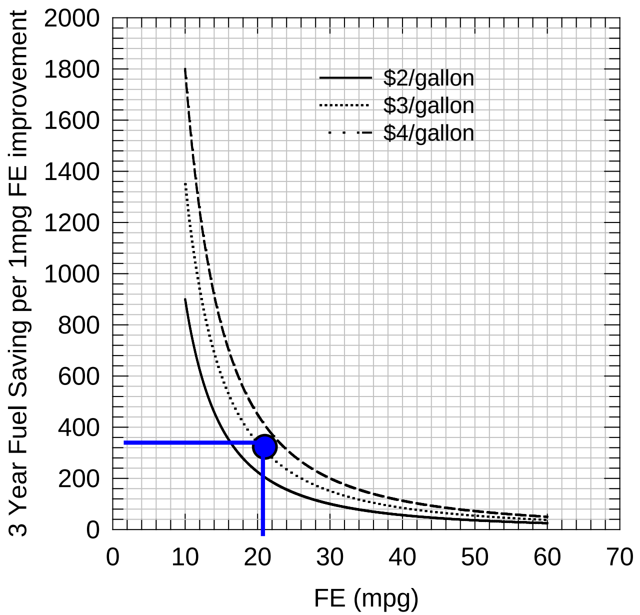
Typical Industrial Development - Multi-Scale, Interdisciplinary …



$/W – a Program Metric

- $/W (not only ZT) is used for balancing various material, module, and subsystem options

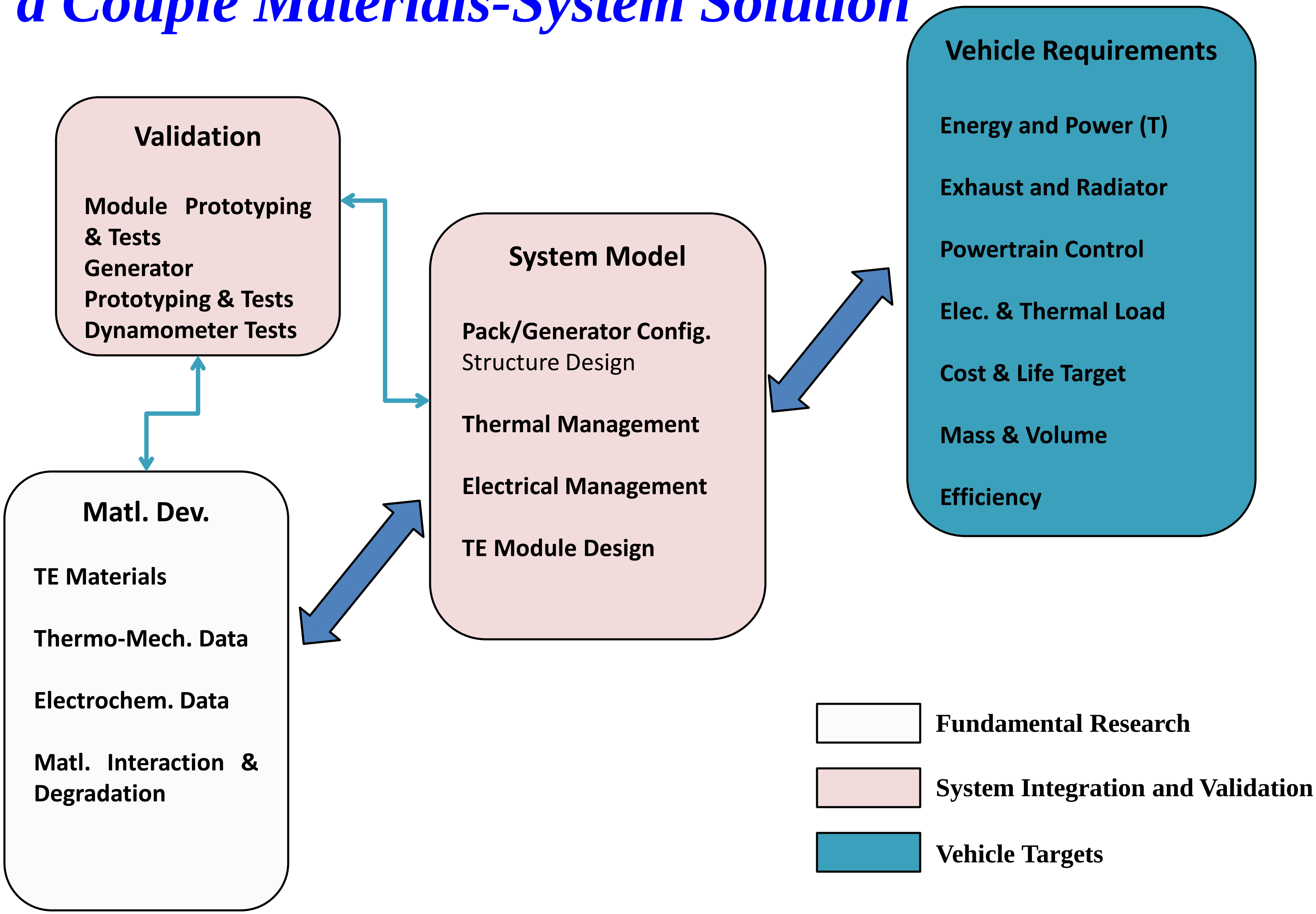
- $/W can be readily converted to $/Δmpg, and $/Δmpg < Savings/Δmpg is necessary to provide consumer value



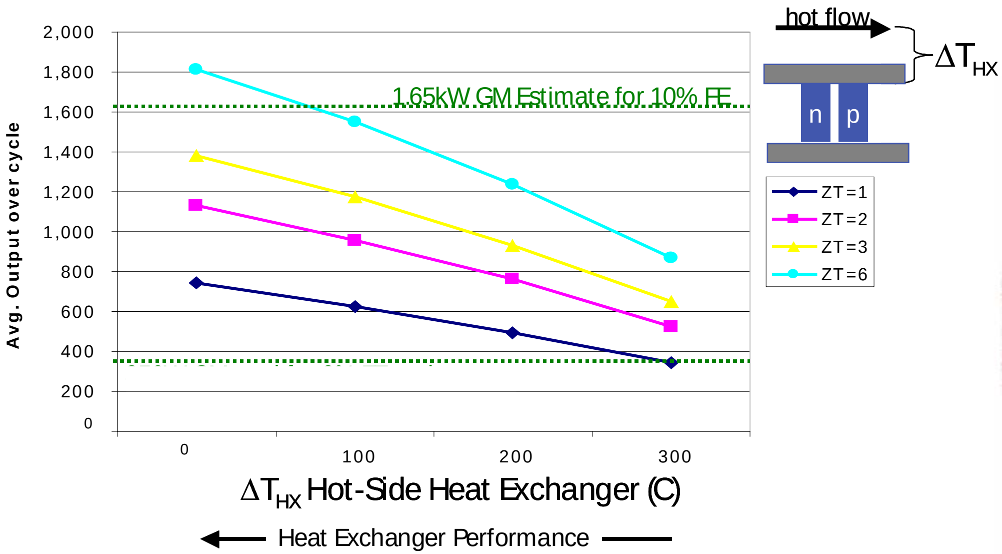
Consumer Fuel Savings/Δmpg ≈ $300-400/Δmpg (15000 mile/yr., 3yrs., 18-20 mpg)

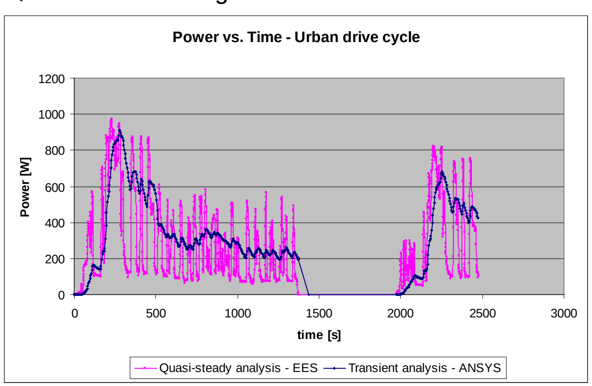
Approach

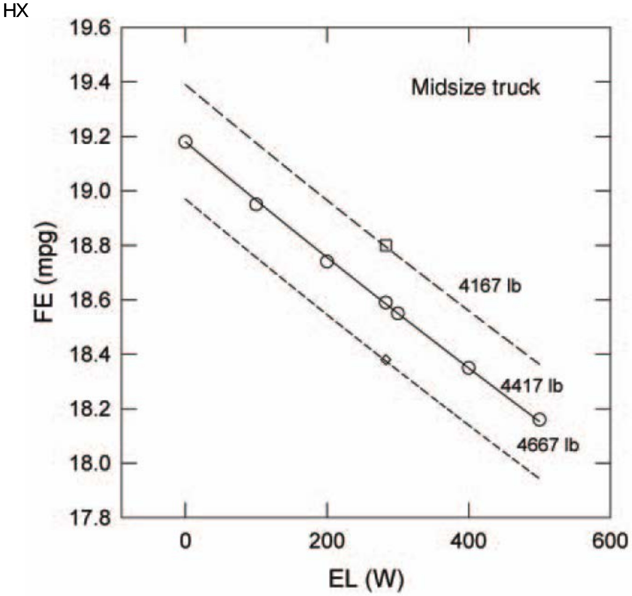
– a Couple Materials-System Solution



Great Power in Solving Problems Using Coupled Materials-Systems Solutions







J. Yang and T. Caillat, *MRS Bulletin* **31**, 3, 224 (2006)

- ❑ System requirements can be quickly translated to revised materials requirements
- ❑ Material advances can be quickly translated into system impact

Challenges for TE Technology Development

- Materials
  - High ZT: p-type skutterudites, composites…
  - Manufacturing and processing for enhanced thermo-mechanical properties
- Modules
  - Joining, diffusion barrier, …
  - Design to mitigate thermal and vibrational stress
- Systems
  - Heat exchanger, thermal management, packaging, electrical interface, mechanical interface, by-pass
  - Design to mitigate thermal and vibrational stress
- Integration and Control
  - Cycle-averaged output design and control

Mechanical Properties of TE Materials - Battling Flaws

- Of concern is the long term survival of the TE elements under vehicle operating conditions – vibration, thermal cycle, thermal shock…

- TE materials are typical brittle ceramics, Tensile Strength << Compressive Strength - manage tensile stress for conservative design

$$R_{Therm} = \frac{\sigma_{Tens}(1-\nu)\kappa}{CTE \bullet E}$$

Kingery, J. Am. Cer. Soc., 38:3-15 (1955).

R_{Therm} = Thermal shock resistance parameter (the larger the better)
σ_{Tens} = Tensile stress or strength
ν = Poisson's ratio
κ = Thermal conductivity
CTE = Coefficient of thermal expansion
E = Elastic modulus

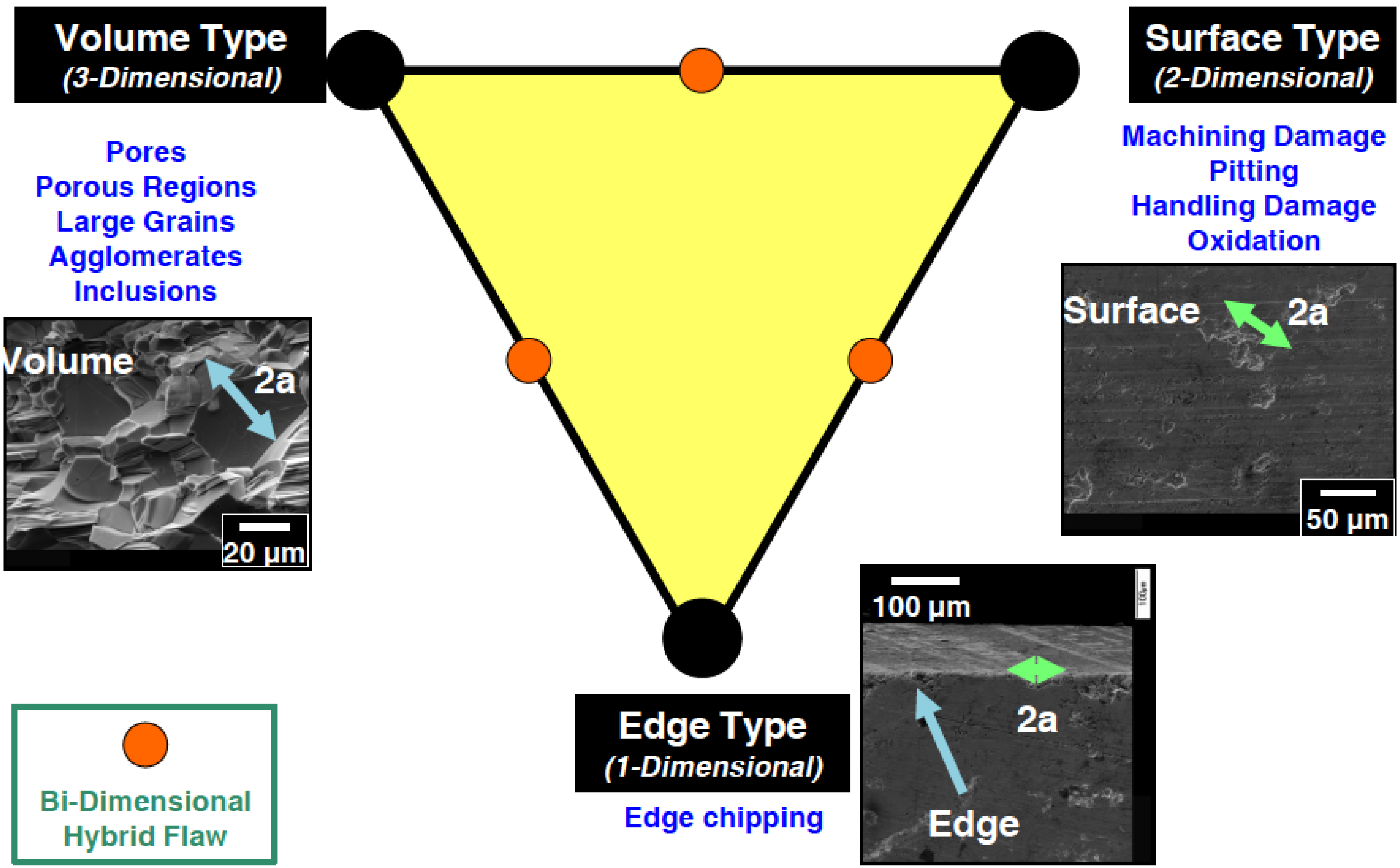
Griffith Criterion

$$\sigma_{Tens} = \frac{K_{Ic}}{Y\sqrt{a}}$$

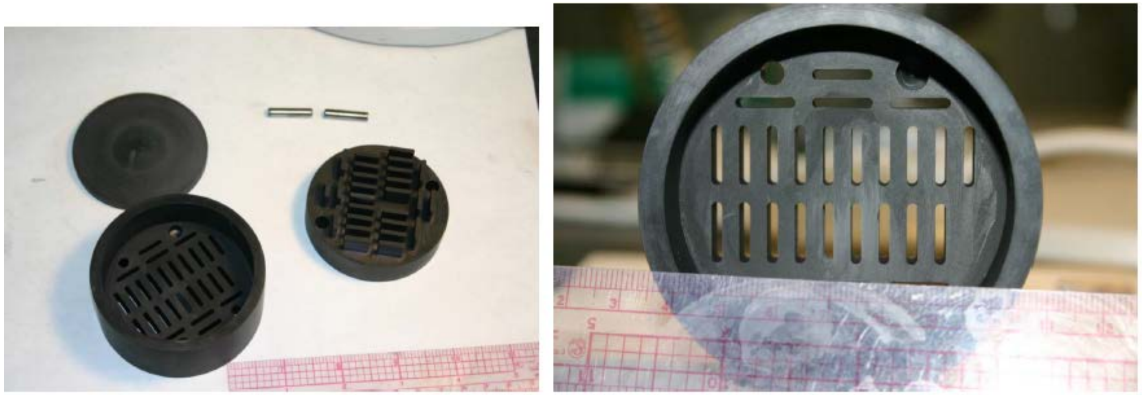
K_{Ic} = Fracture toughness
Y = Crack shape factor
a= Griffith flaw size

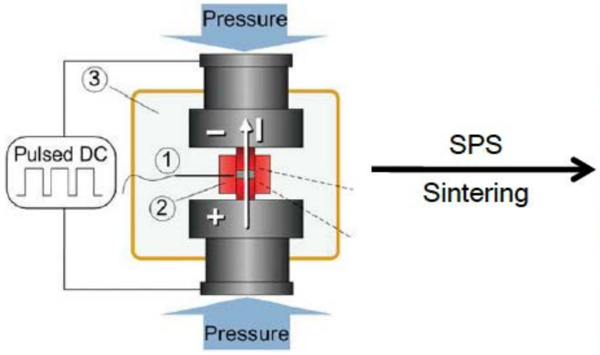
- Must minimize flaw sizes

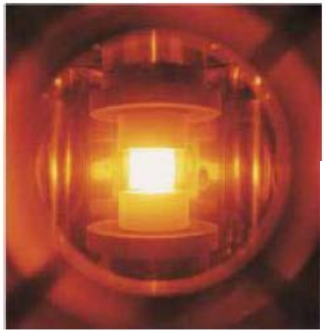
Strength-Limiting Flaw Classification For Brittle Materials

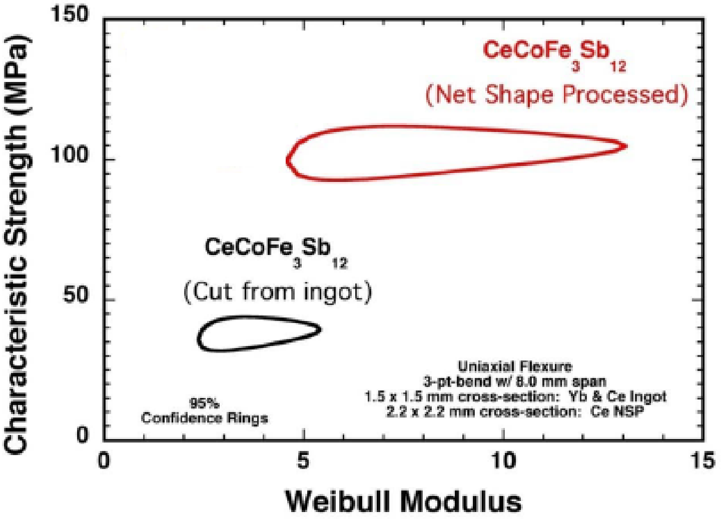


Net-Shape Processing









Salvador, et al., Science of Advanced Materials Vol. 3, 577–586, 2011

TE Figure of Merit ZT

Power Generation Equation:

$$\varepsilon = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_C}{T_H}}$$

Cooling Equation:

$$COP = \frac{T_c}{T_H - T_C} \frac{\sqrt{1+ZT} - \frac{T_H}{T_C}}{\sqrt{1+ZT} + 1}$$

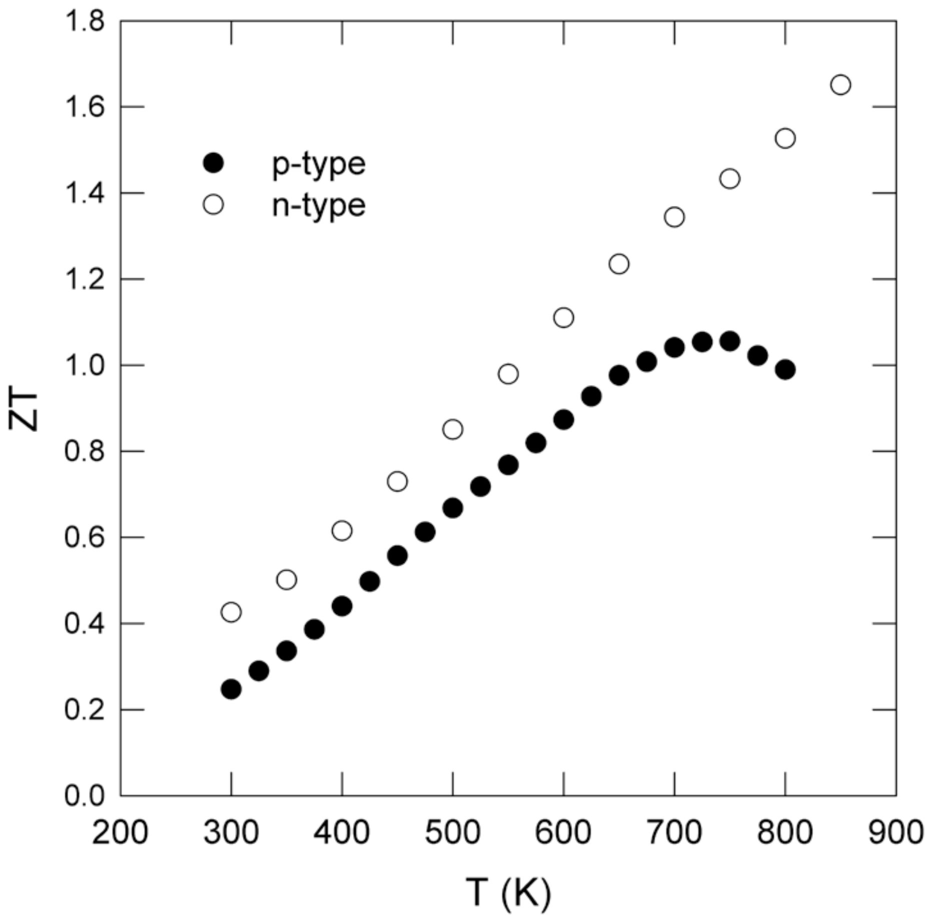
$$Z = \frac{S^2}{\kappa_T \rho} = \frac{S^2}{(\kappa_L + \kappa_e)\rho}$$

S - Thermopower
κ_T - Total thermal conductivity
κ_L - Lattice thermal conductivity
κ_e - Electronic thermal conductivity
ρ - Electrical resistivity

Z has the dimension of T^{-1}. ZT is usually called dimensionless Figure of Merit

- The performance of a TE module is determined by the intrinsic materials *ZT*

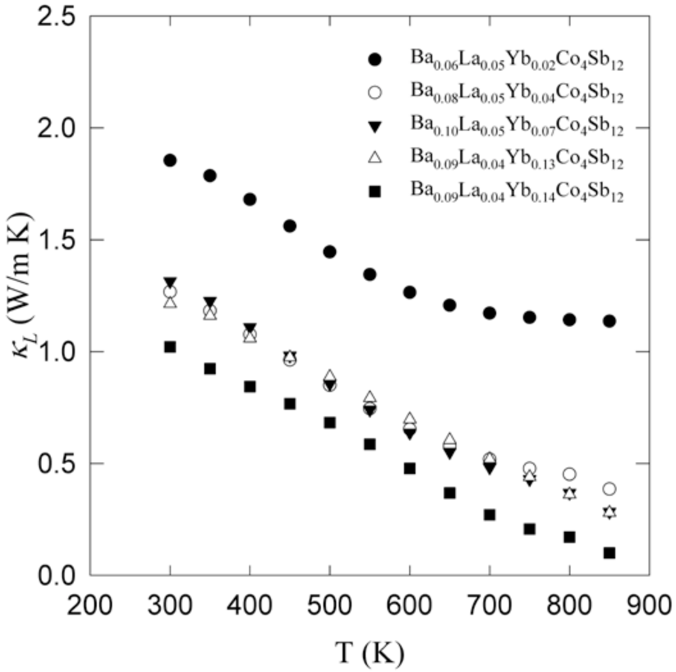
ZT Mismatch – Device Challenge



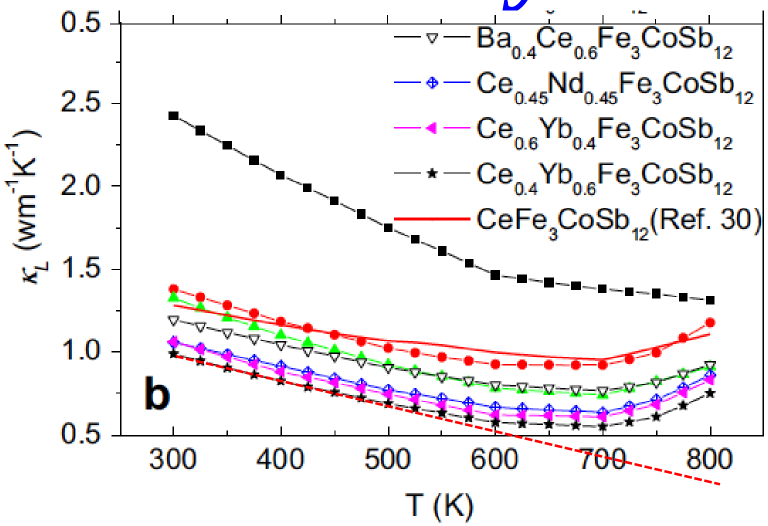
1. X. Shi, et al, J. Am. Chem. Soc. **133**, 7837 (2011)
2. R. Liu, et al., Intermetallics **19**, 1747 (2011)
3. Y. Wang, et al., Phys. Rev. Lett. **102**, 175508 (2009)
4. L. Xi, et al.,J. Am. Chem. Soc. **131**, 5560, (2009).
5. X. Shi, et al., Phys. Rev. Lett. **95**, 185503 (2005).

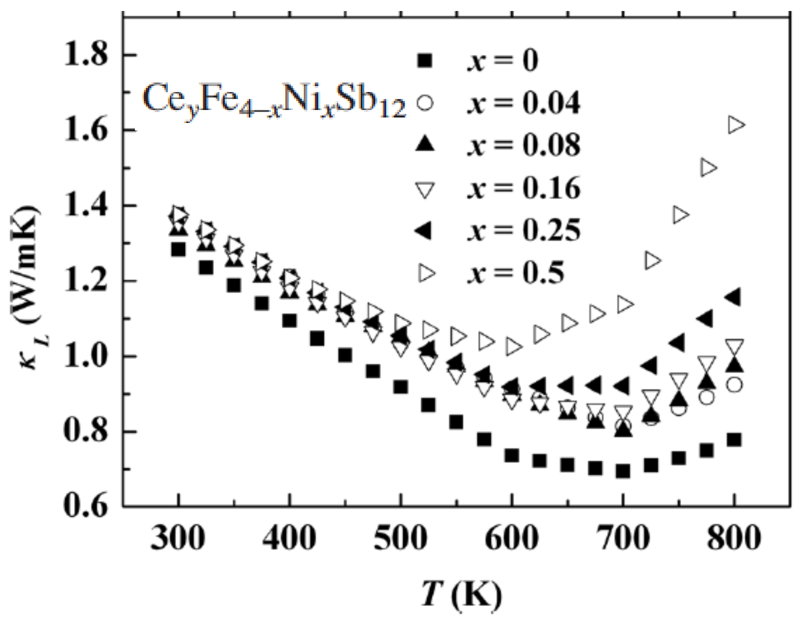
Lattice Thermal Conductivity

n-type



p-type



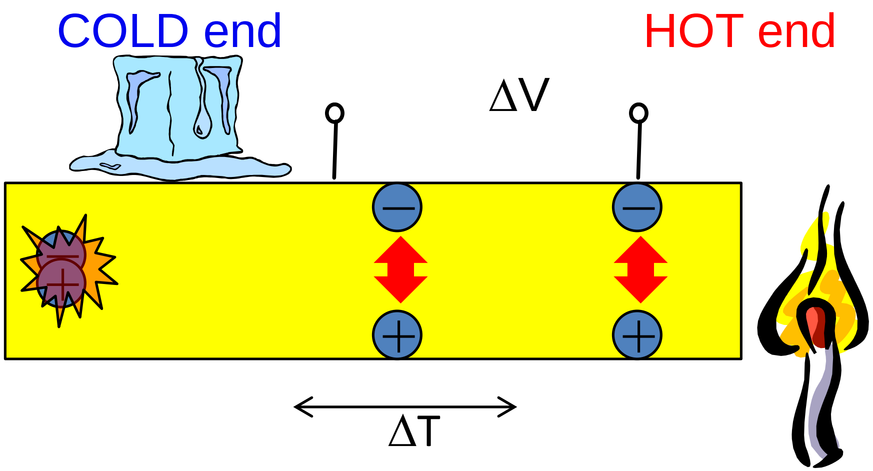


1. X. Shi, et al, JACS **133**, 7837 (2011)
2. R. Liu, et al., Intermetallics **19**, 1747 (2011)
3. Qiu et al., JAP **111**, 023705 (2012)
4. Cho et al., Acta Mater. 60, 2104 (2012)

❑ p-type has higher κ_L, especially at high temperatures

Bipolar Thermal Conductivity

- A Hallmark of Electron-Hole Coupling in Semiconductors



- Electrons and holes (excitons) are **coupled** at hot end, **diffuse collectively** through the material, **annihilate** at the cold end – give up energy ~ E_g
- This transport of energy is in addition to that carried by electrons and holes
- This has been reported in many semiconductors – Bi_2Te_3, Si, Ge, PbTe..

Bipolar Thermal Conductivity

- Theory

$$\kappa_{total} = \kappa_L + \kappa_e = \kappa_L + L_{eff}\sigma T$$

$$\kappa_e = \kappa_n + \kappa_p + (\sigma_n + \sigma_p)T(\frac{k_B}{e})^2 \frac{\sigma_n \cdot \sigma_p}{(\sigma_n + \sigma_p)^2}(\frac{E_g}{k_B T} + 4)^2$$

1. B. Davydov and I. Shmushkevitch, Usp. Fiz. Nauk SSSR 24, 21 (1940)
2. P. J. Price, Phil. Mag. 46, 1252 (1955)

- For intrinsic Semiconductors $n = p$, Significant bipolar thermal conductivity when the mobilities of electrons and holes are similar

$$\kappa_e = \kappa_n + \kappa_p + \frac{b}{(1+b)^2}(\frac{E_g}{k_B T} + 4)^2(\frac{k_B}{e})^2\sigma T \qquad b = \mu_n / \mu_p$$

$$\left.\frac{b}{(1+b)^2}\right|_{b=1} = \left[\frac{b}{(1+b)^2}\right]_{\max} = 1/4$$

Bipolar Effect for Heavily Doped Semiconductors a Longstanding Puzzle

- Surprisingly in the case of heavily doped semiconductors, the mechanisms for this seemingly simple process remains a puzzle after decades of research

- For example, in an n-type materials n >> p, the mobilities of the n- and p-type are usually differ by order(s) of magnitude

$$\boldsymbol{b} = \mu_n / \mu_p << 1$$

- Noticeable BP effect has been observed in many TE materials

κ_b Numerical Model

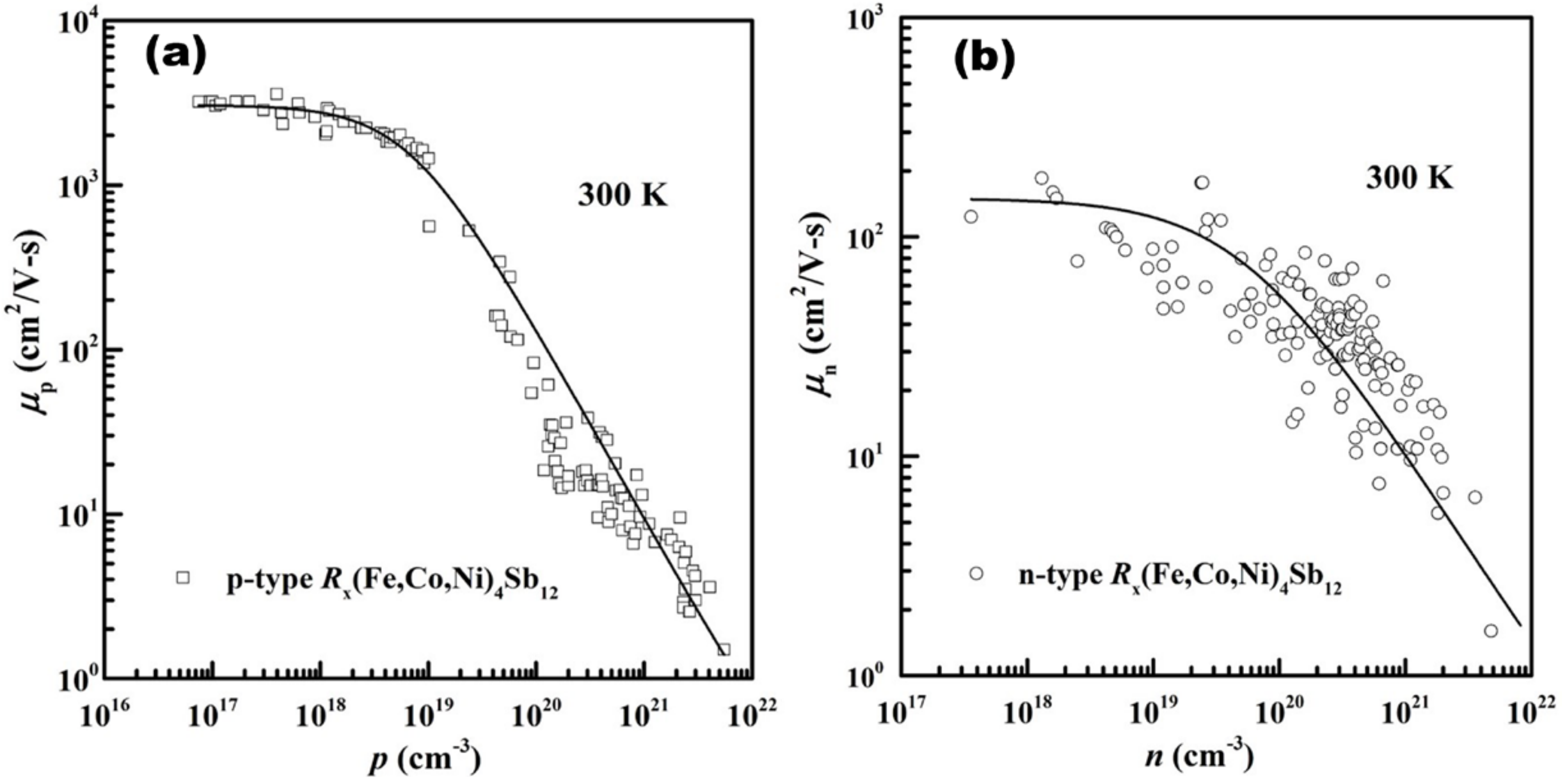
$$\kappa_b = \kappa_{total} - \kappa_L - \kappa_p = (\sigma_n + \sigma_p)T(\frac{k_B}{e})^2 \frac{\sigma_n \cdot \sigma_p}{(\sigma_n + \sigma_p)^2}(\frac{E_g}{k_B T} + 4)^2$$

- $\sigma_n(T) = en(T)\mu_n(T) \qquad \sigma_p(T) = en(T)\mu_p(T)$
- We can calculate *n(T)* and *p(T)* using semiconductor statistics, provided we have electronic band structure, E_F, m^*, etc.

$$n(T) = N_C \int_{E_C}^{\infty} \frac{x^{1/2}dx}{(1+e^{x-\eta_F^C})} = \frac{2(2\pi m_C^* k_B T)^{3/2}}{h^3} \int_{E_C}^{\infty} \frac{x^{1/2}dx}{(1+e^{x-\eta_F^C})} \qquad \eta_F^C = {(E_F - E_c)}/{k_B T}$$

$$p(T) = N_V \int_{E_V}^{\infty} \frac{x^{1/2}dx}{(1+e^{x-\eta_F^V})} = \frac{2(2\pi m_V^* k_B T)^{3/2}}{h^3} \int_{E_V}^{\infty} \frac{x^{1/2}dx}{(1+e^{x-\eta_F^v})} \quad \eta_F^C = {(E_V - E_F)}/{k_B T}$$

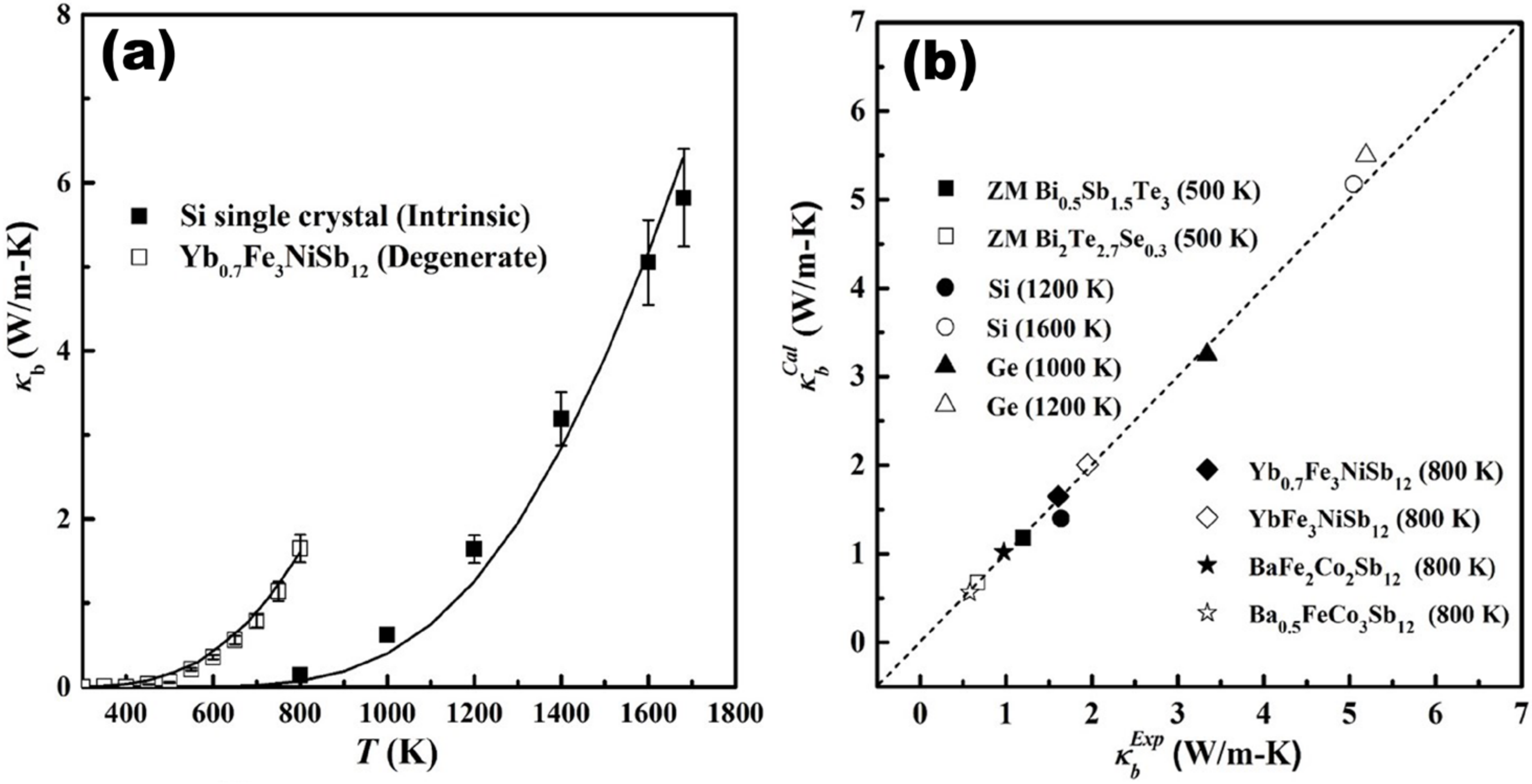
Mobility vs. n and p - Key Enabling Step



$$\mu(300\text{K}) = \mu_0 + \frac{\mu_{\text{max}} - \mu_0}{1 + \left(\frac{n}{n_{\text{Ref}}}\right)^a}$$

$$\mu(T) = \mu(300\,K)\left(\frac{T}{300}\right)^{-3/2}$$

Bipolar Thermal Conductivity - Predictable



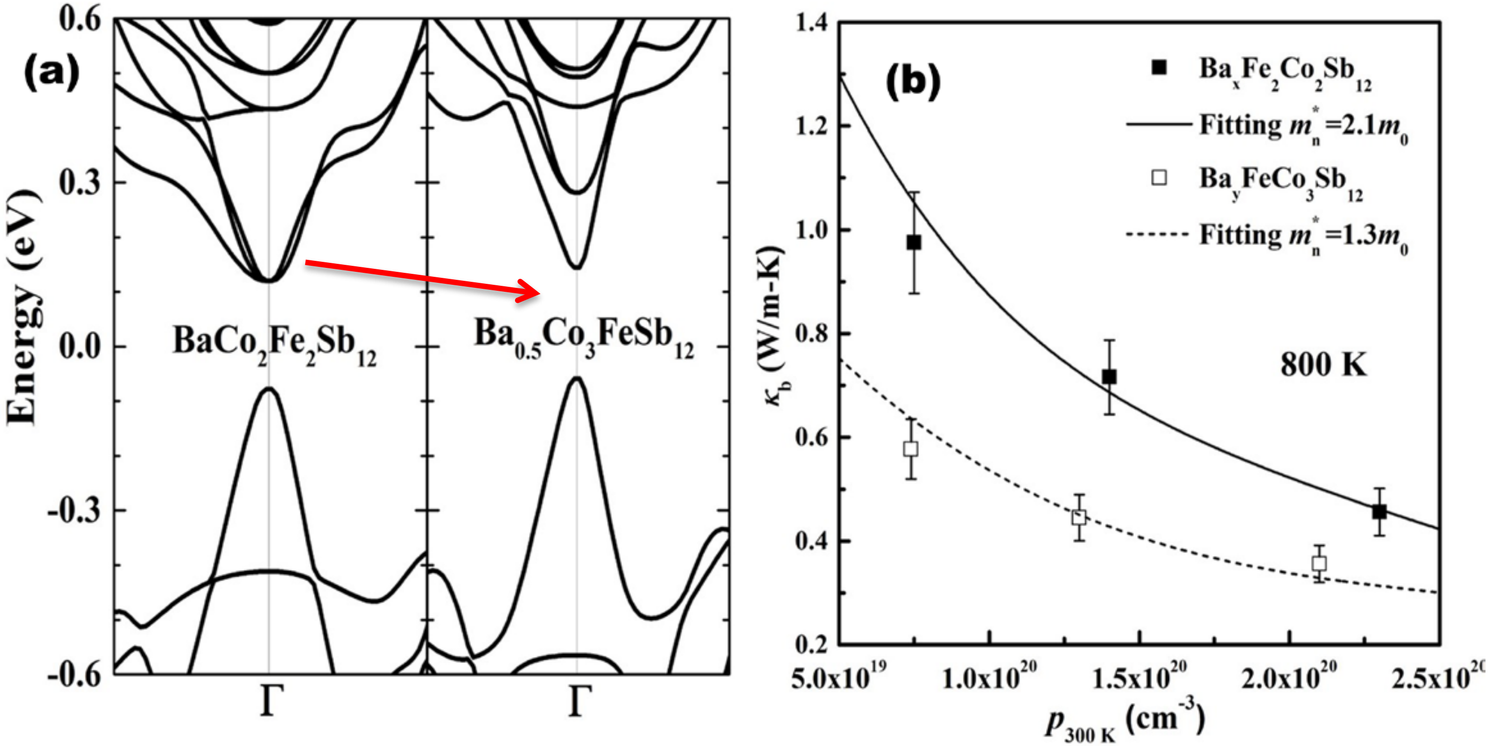
Bipolar Thermal Conduction
- a "Conductivity-Limiting" Phenomenon

For a given material, variation is negligible

$$\frac{\left(\frac{k_B}{e}\right)^2 \left(\frac{E_g}{k_B T} + \frac{2F_1(\xi_p)}{F_0(\xi_p)} + \frac{2F_1(\xi_n)}{F_0(\xi_n)} \right)^2 T}{\kappa_b} = \frac{1}{\sigma_n} + \frac{1}{\sigma_p}$$

- ***Dominated by the minority carriers for heavily doped semiconductors***

Reducing Bipolar Thermal Conductivity
- Band Structure Modulation

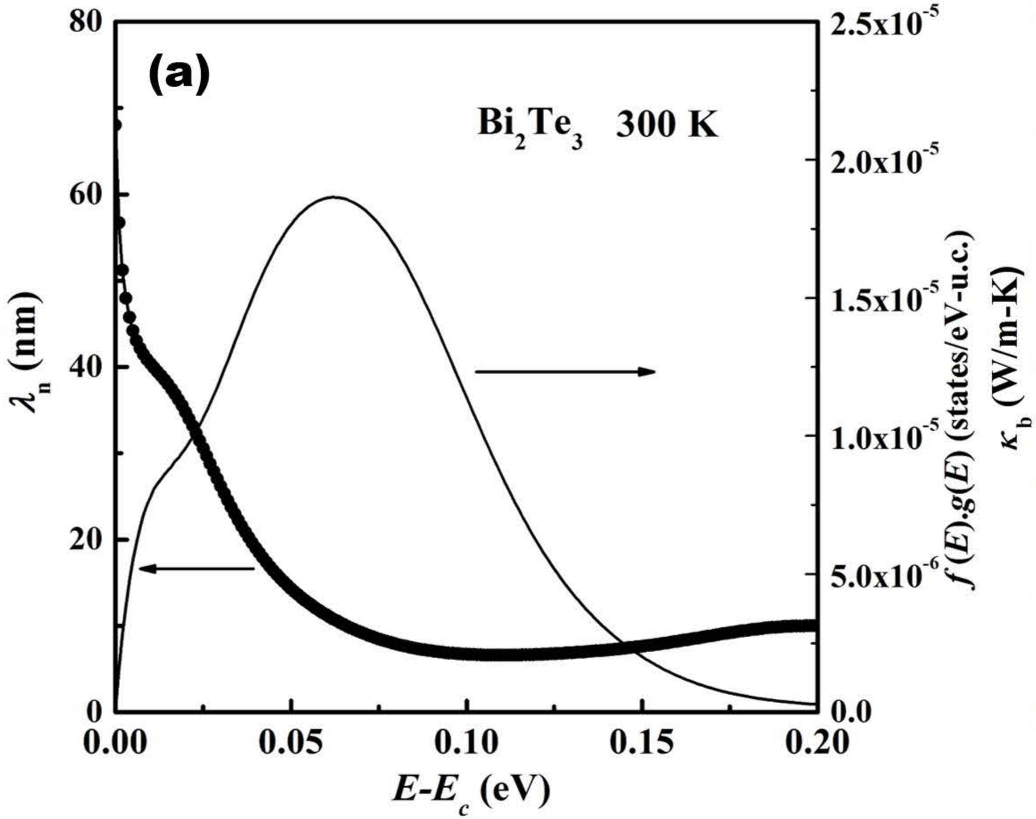


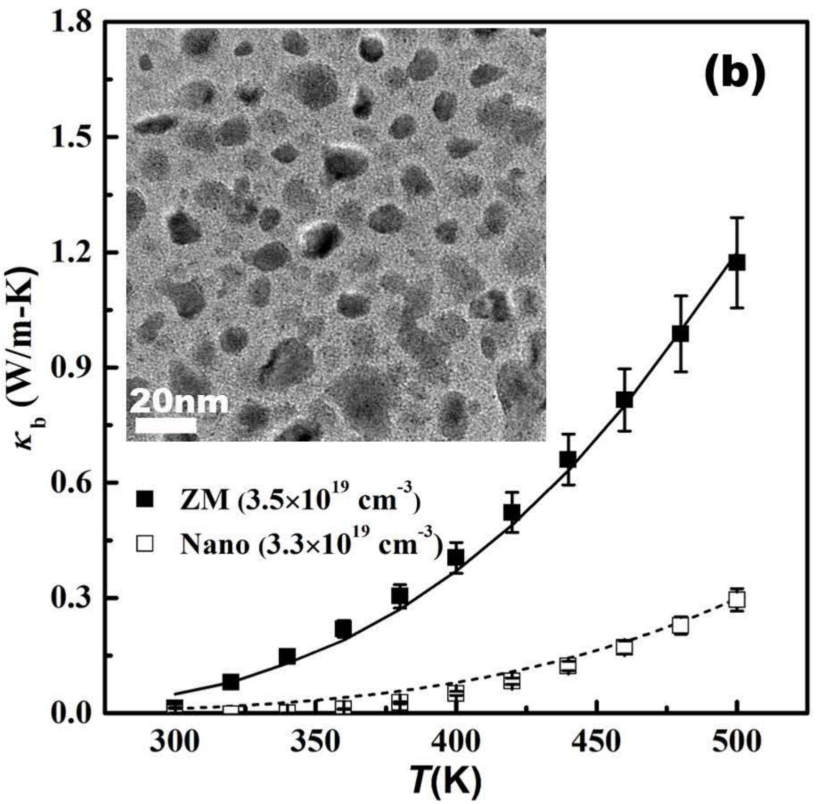
$$\sigma \propto \sqrt{m^*}$$

- ❑ Conduction band minimum splitting – reduced effective mass (minority carriers)

Reducing Bipolar Thermal Conductivity

- Nanostructure Effect





- Bi_2Te_3 made by zone-melting (ZM) and melt-spinning/SPS (contains nanoprecipitates)

Conclusions

- Automotive waste heat recovery and thermal management are ongoing challenges

- TE could offer unique technological solutions

- Industrial research is driven by application and system requirement, and of course cost

- There are still plenty of opportunities for exciting engineering and science.