Thermoelectric Materials for Automotive Applications

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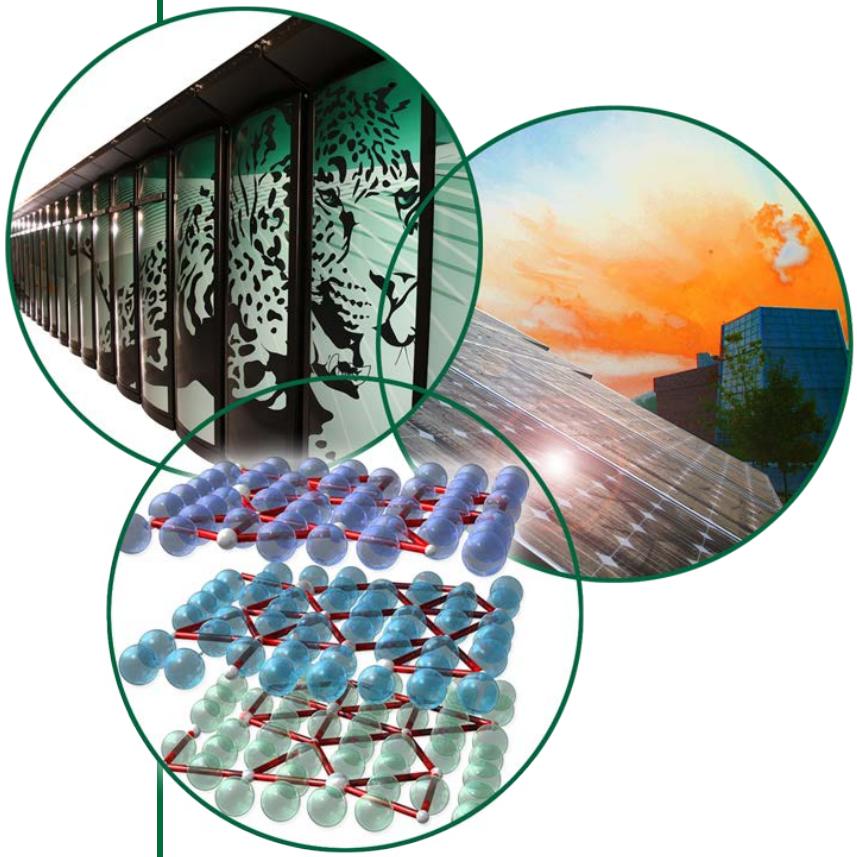

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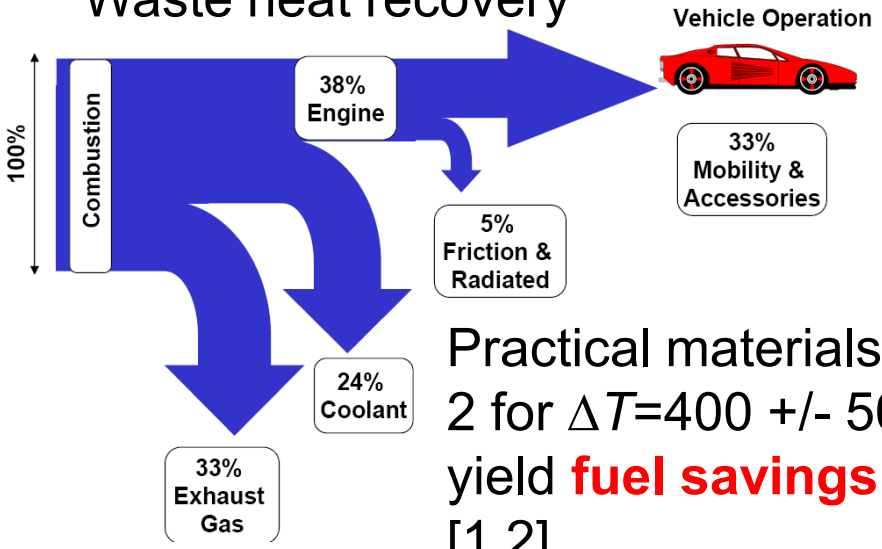
Thermoelectrics for Automotive Applications

Waste heat recovery



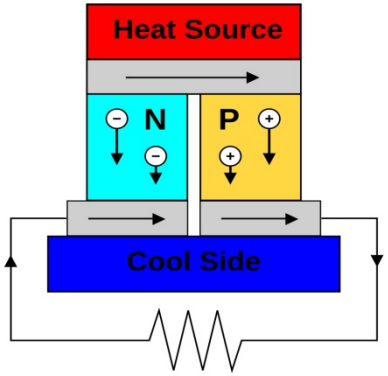


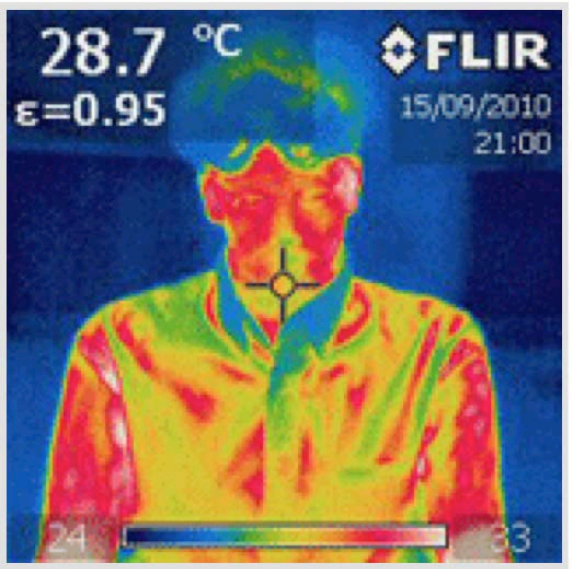
Image courtesy of Ken Brazier

Practical materials with ZT > 2 for ΔT=400 +/- 50 C can yield **fuel savings of 10%**. [1,2]

Synergy with truck electrification.

Efforts at General Motors, Ford, Toyota/Denso, BMW, Volkswagen, Bosch, Amerigon/BSST, Siemens, Cummins …

Zonal cooling/heating



HEV engine not always running, need electricity powered heating/cooling➔ **thermoelectrics –** also zonal saves energy

Bi_2Te_3 material of choice, but Te is trace element, expensive

Image courtesy of Charlie Huizenga, Center for the Built Environment, UC Berkeley

[1] DOE Vehicle Technologies Program Plan 2011-2015
[2] "Science Based Approach to Development of Thermoelectric Materials for Transportation Applications: A Research Roadmap", DOE FCVT (2007).

Outline of Talk

- **Background**: What makes a good thermoelectric?
- "**Field Report**": Three recent ORNL theoretical studies: PbSe, Bi_2Se_3, $CrSi_2$
- **Conclusion**

What makes a good thermoelectric?

- Key point: The expression for ZT –

$$ZT = S^2 \sigma T / \kappa$$

Can be rewritten in this form:

$$ZT = S^2 r / L_0$$

Here r is the ratio of electronic and total (i.e. **electronic + lattice**) thermal conductivity and L_0 is the Lorenz number, i.e., $\kappa_{electronic} = L_0 \sigma T$.

Typically $L_0 = 2.45 \times 10^{-8} (V/K)^2$ (+/-20%)

What makes a good thermoelectric?

$$ZT = S^2 r / L_0$$

This expression means we want r and S as high as possible.

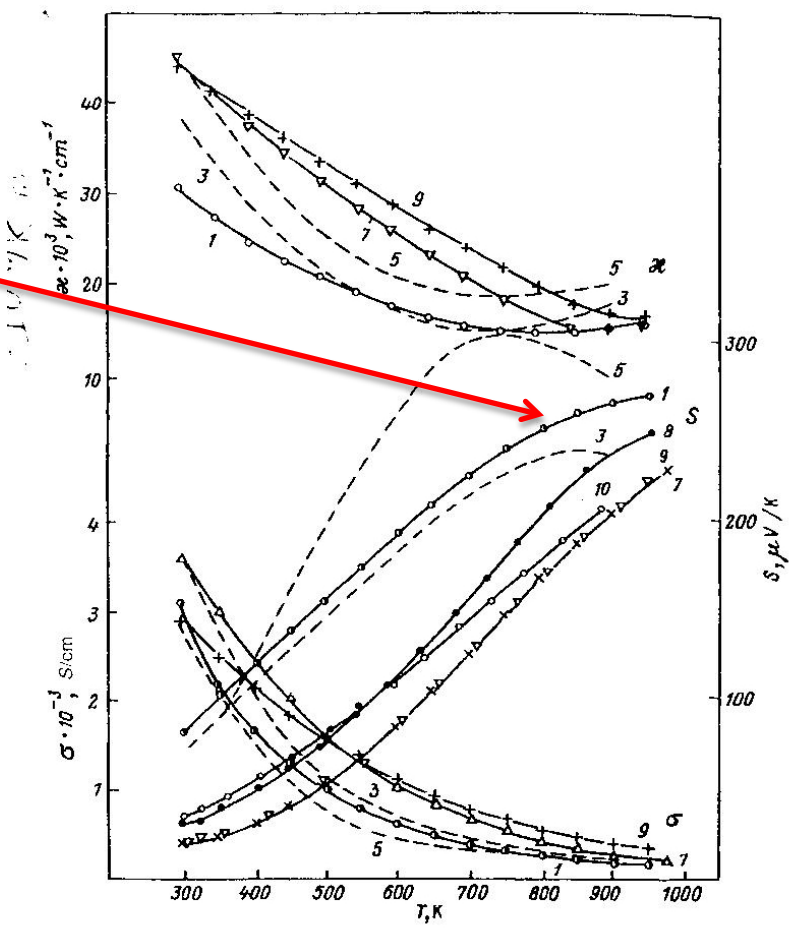
Since $r = \kappa_{electronic} / (\kappa_{electronic} + \kappa_{lattice})$, **$\kappa_{lattice}$ represents wasted heat transfer** – want $\kappa_{lattice}$ as low as possible. This means that the two most important properties of a good thermoelectric are:

high thermopower S and low lattice thermal conductivity $\kappa_{lattice}$.

We'll focus on the **thermopower** – calculated via WIEN2K and Boltztrap.

Overview: PbSe as thermoelectric – A previously overlooked material

- Data of Alekseeva* had suggested doped PbSe may be good TE material - better at high T (~1000 K) than PbTe
- Showed S as high as 280 μV/K, ZT as high as 0.9 depending on doping
- Doping not fully quantified in Alekseeva study, also polycrystalline sample
- PbSe was believed inferior to PbTe
- Could "optimal" sample show enhanced ZT? Did model calculation (experiments followed) to get idea.



G.T. Alekseeva et al data

*Semiconductors **30**, 1125 (1996).

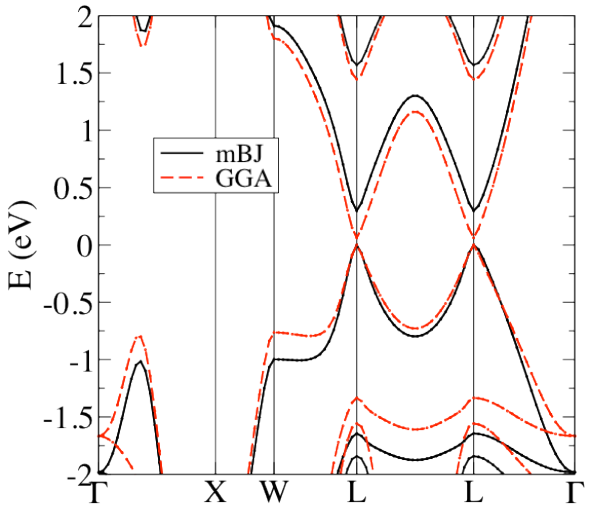
Thermoelectricity in PbSe - Model

All results based on first principles calculation of bandstructure and associated quantities, from the GGA approximation in WIEN2K, spin-orbit coupling included

Transport (thermopower) calculated using Boltztrap code – **co-developed by ORNL and Univ. Aarhus.**

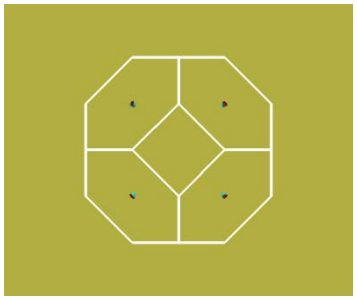
Rigid band approximation used to study effect of chemical doping with holes (originally expected to be more effective than electrons)

Two cases – earlier calculation – red dashed, revised using improved band gap approximation - black

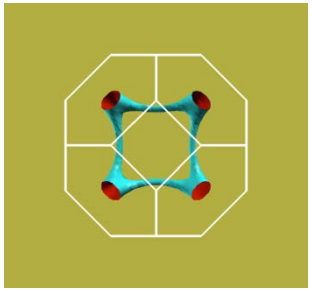


Calculated bandstructure, cubic fcc PbSe (rocksalt structure)

Fermi surfaces



E_F at VBM



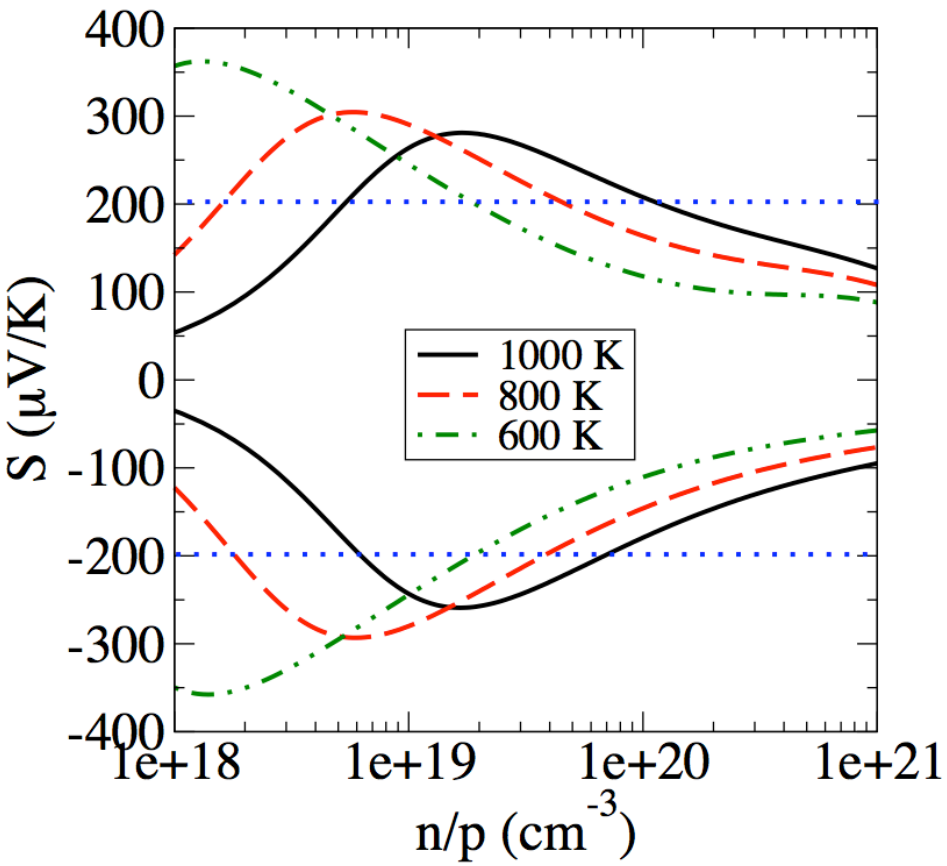
E_F 0.4 eV in VB

Calculated Thermopower in PbSe

- Substantial doping ranges (10^{19} cm^{-3}< n,p < 2 x10^{20} cm^{-3}) where **|S| > 200 μV/K**

•Use of revised DFT approximation corrects GGA band gap underestimation, n-type good as well

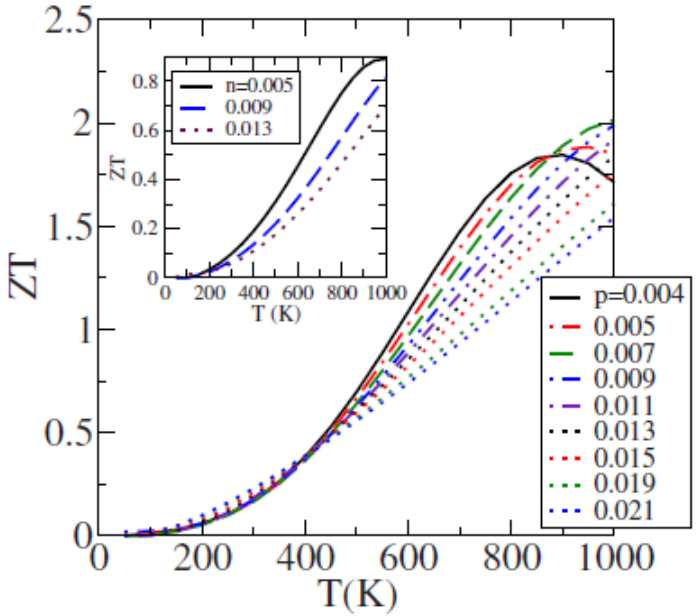
- Significant waste heat recovery temperature range (600-1000 K) where good performance expected, will be best at highest temps (lower $\kappa_{lattice}$)

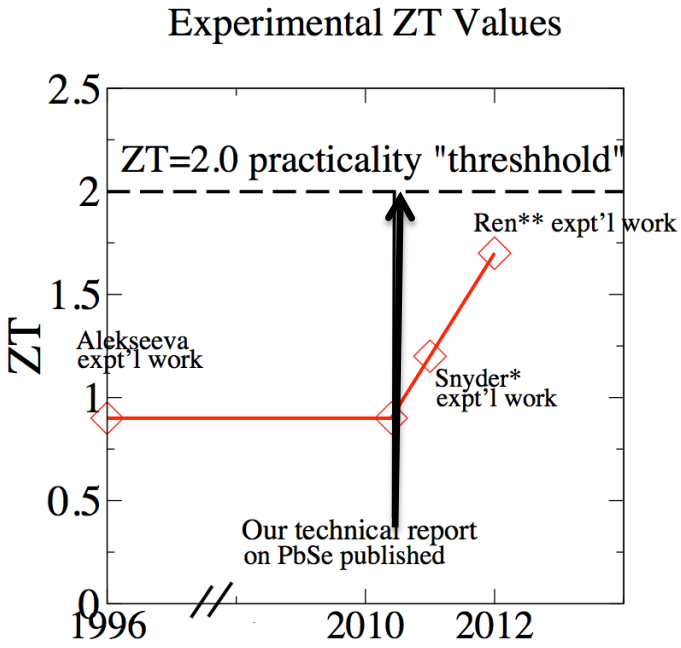


Calculated thermopower (no adjustable parameters) for p and n-type PbSe

PbSe: ZT Predictions vs. Experiment

We made **prediction* of p-type ZT as high as 2** at 1000 K, 1.7 at 800 K





1.7 ZT confirmed, 2.0 nearly confirmed

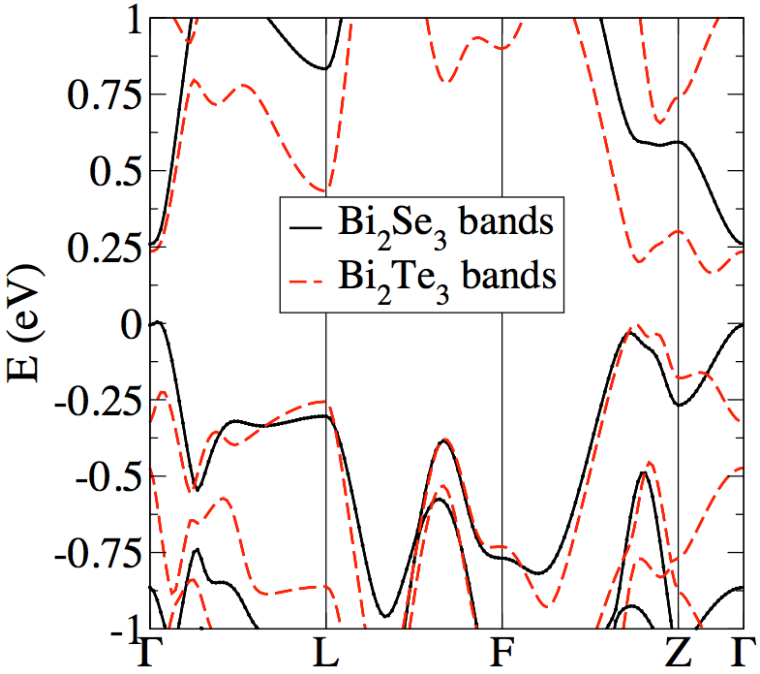
n-type ZT of 1.3 found by Ren+ (our calculations now find this also)

*D. Parker and D.J. Singh, Phys. Rev B **82**, 035204 (2010)

Y. Pei et al, Adv. Mat. **23, 1367 (2011); ***Q. Zhang et al, unpublished (2012); +Q. Zhang et al, Energy and Env. Sci **5**, 5246 (2012)

Introduction: Potential thermoelectric performance from optimization of hole-doped Bi_2Se_3 (Phys. Rev. X 1, 021005(2011))

- Bi_2Te_3 well-known "classic" thermoelectric material, shows ZT ~ 1 for optimized bulk material, about 1.5 for nanostructured bulk[1,2]
- However, Bi_2Te_3 performance limited to temperature < 400 K, also Te is trace element – problem for vehicle applications
- Can we find a substitute with **comparable or better 400-600 K performance** (lower end of waste heat recovery temperatures) without Te?

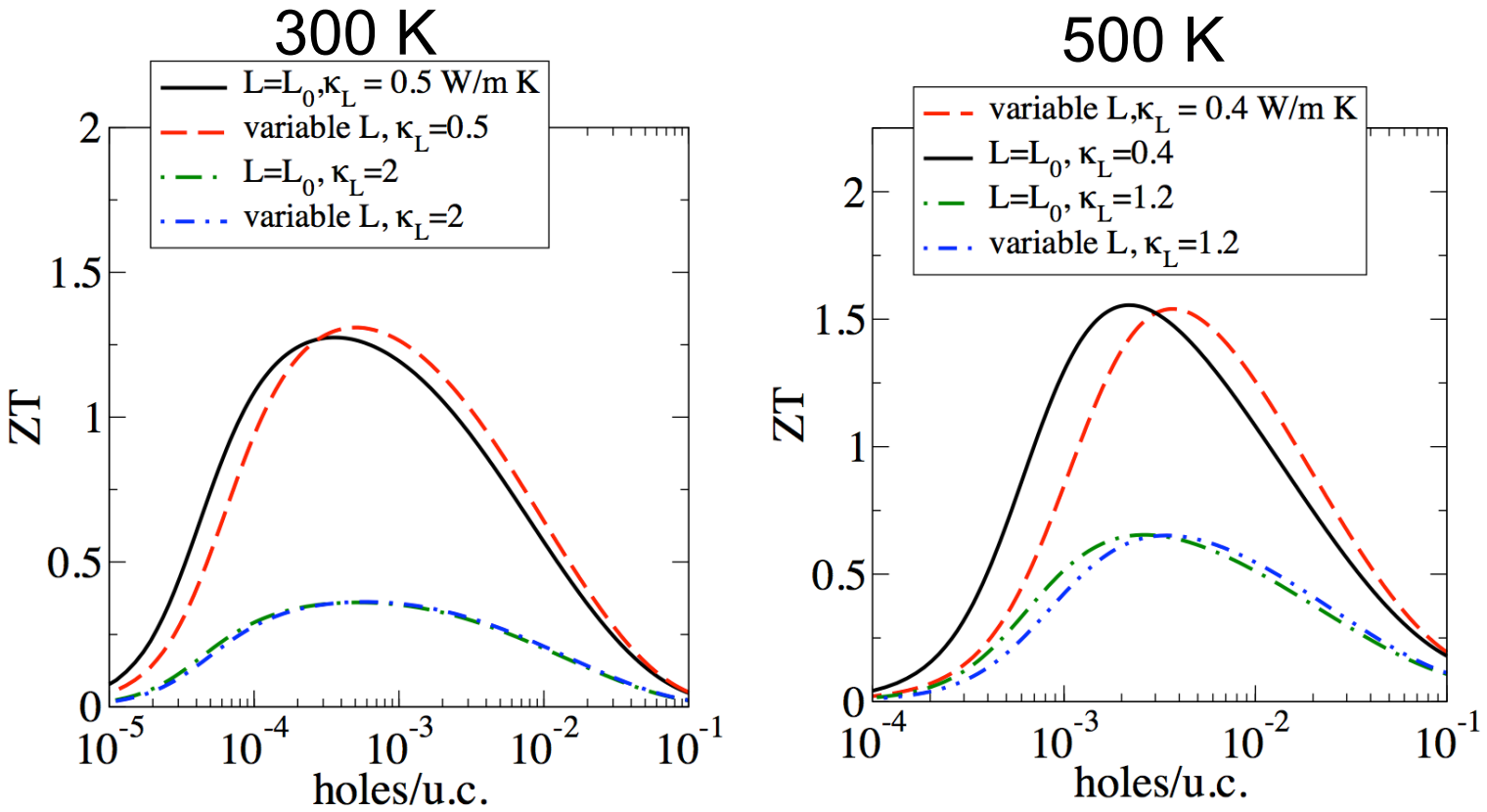


Bi_2Se_3/Bi_2Te_3 band structure

p-type Bi_2Se_3 has two advantages relative to Bi_2Te_3 – **larger band gap** (0.3 eV vs 0.16) and **energy-degenerate VBM – better thermopower, less bipolar conduction**

1. B. Poudel, Q. Hao et al, Science **320**, 634 (2008).
2. W. Xie et al, Appl. Phys. Lett. **94**, 102111 (2009).

Results: ZT Predictions for Bi_2Se_3



- ZT values **over unity at 300 K**, and **as high as 1.5 at 500 K**, may be achieved if substantial (67-75%) $\kappa_{lattice}$ reduction achieved by alloying/**bulk** nanostructuring (hot press, melt spin)

- Optimal doping about 0.001/u.c. at 300 K (7×10^{18} cm^{-3}) and about 0.004/u.c. (3×10^{19} cm^{-3}) at 500 K

Discussion

- Actual ZT's found will depend on how much $\kappa_{lattice}$ can be reduced (alloying, "bulk" nanostructuring) without significantly impacting hole mobility.

- Experience with Bi_2Te_3 suggests much can be done, i.e. :

  ZT with only **carrier concentration** optimization: **0.6**

  ZT with **alloying (Sb/Se)** optimization: **1.0**

  ZT with **nanostructuring**: **1.5**

Optimizing all three strategies for p-type Bi_2Se_3 should yield **performance** in 400 – 600 K range **far exceeding current expectations -** potentially suitable for waste heat recovery applications.

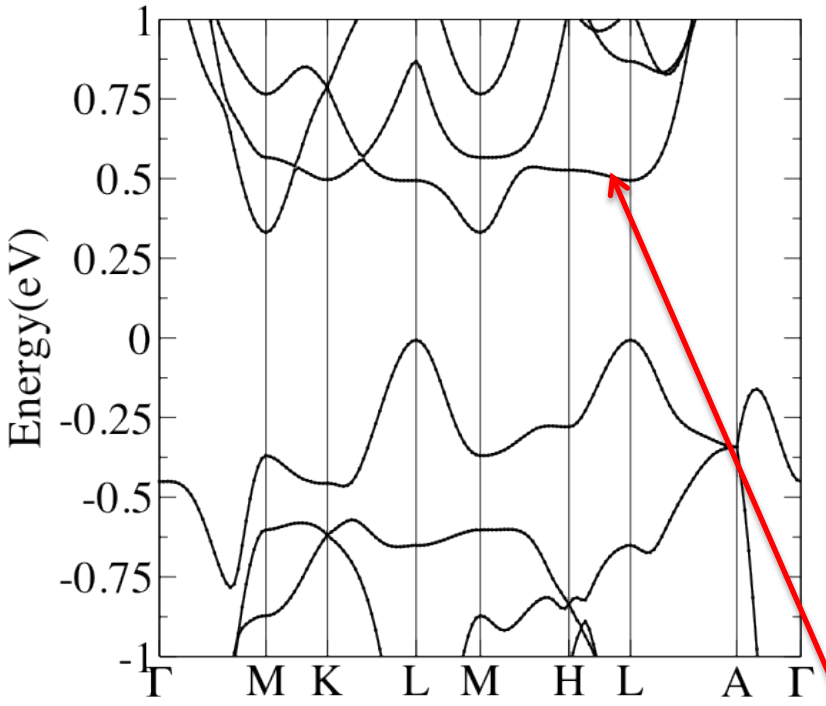
Introduction: Very heavily electron doped $CrSi_2$ as a high performance thermoelectric material (to appear in New Journal of Physics)

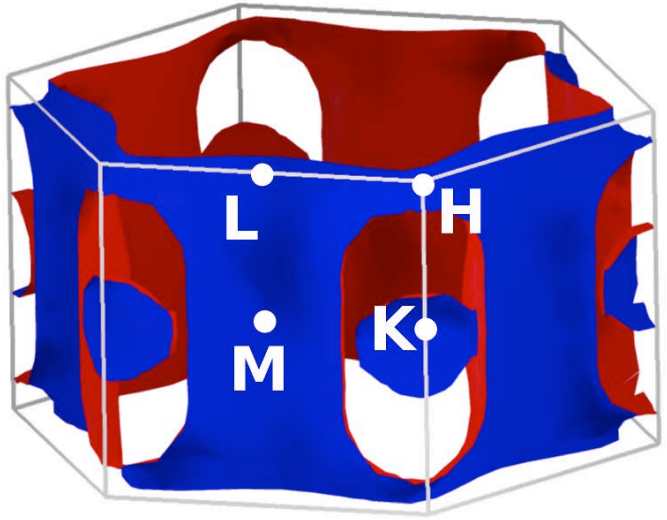
- $CrSi_2$ well known refractory (T_{melt}= 1711 K) material, narrow band gap (~ 0.35 eV) semiconductor

- Commonly believed that due to narrow band gap, not a useful high-temperature thermoelectric

- Will see that **very heavily (~10^{21} cm^{-3}) electron-doped $CrSi_2$ may show good performance** in 850 – 1000 K range – upper end of exhaust heat waste recovery temperatures

Very heavily electron doped $CrSi_2$ as a high performance thermoelectric material

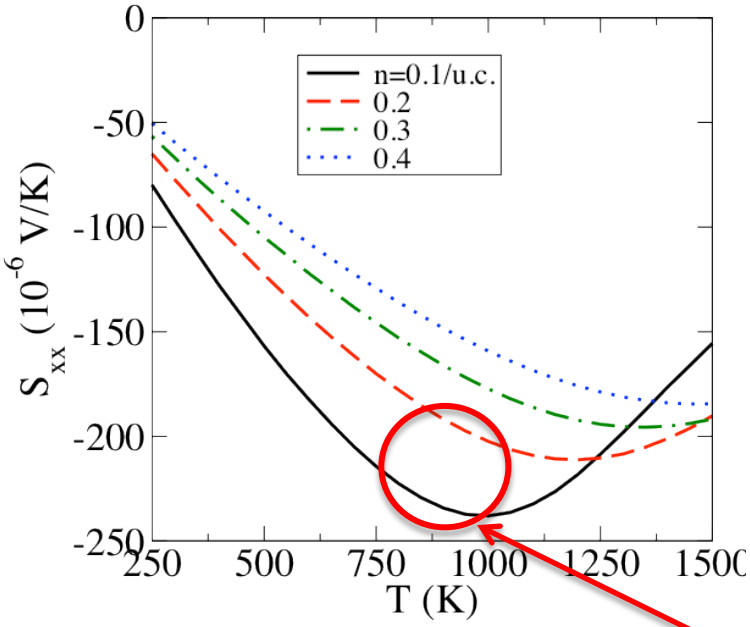


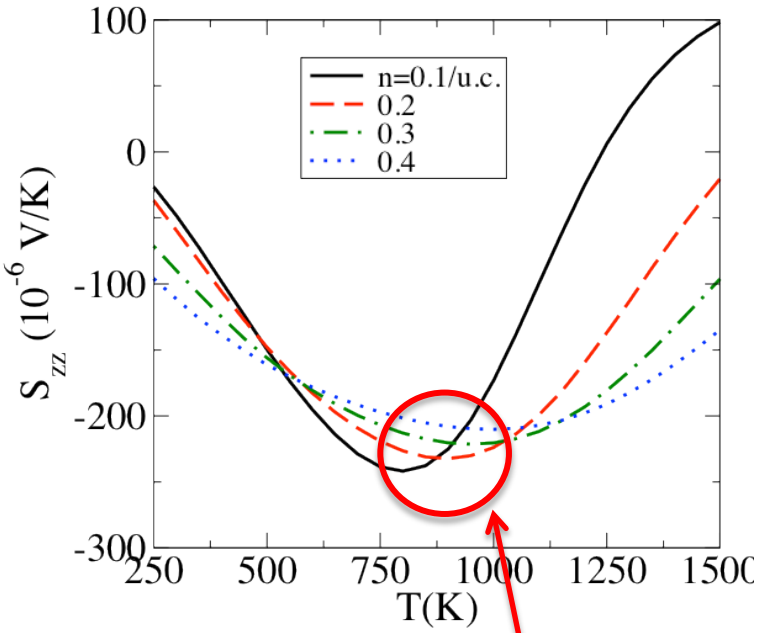


Calculated band structure - note very heavy conduction, valence bands – favorable for large thermopower

Fermi surface for E_F set 0.19 eV into conduction band – catches this flat band

Calculated thermopower of n-type $CrSi_2$





Calculated thermopower for in-plane (left) and c-axis (right). Note that 0.1/unit cell = 9.25 x 10^{20} cm^{-3}. Note thermopowers larger in absolute value than 200 μV/K at dopings between 1 and 2 x $10^{21}cm^{-3}$ between 750 and 1000 K – upper end of exhaust temperature range

Discussion and Conclusion – $CrSi_2$

- High lattice thermal conductivity ($\kappa_{lattice}$= 8 W/m K @ 300 K) means highest temperatures most favorable. However, evidence* that heavy doping, as considered here, may reduce lattice term significantly.

- Material composed of cheap, abundant elements – substantial practical advantage

- Hole doping (not shown) may show fair performance at similar doping ranges; thermopower slightly lower

- Take-away point; **very heavily electron-doped $CrSi_2$** is a **potentially high performance thermoelectric** at elevated exhaust waste heat recovery temperatures **that should be investigated experimentally**

*Pan et al, Scripta Mat. **56**, 257 (2007).

Conclusion – General

- Thermoelectric materials are approaching efficiencies at which automotive applications such as waste heat recovery and zonal heating/cooling begin to be plausible.

- First principles density functional theory can yield important information regarding thermoelectric performance, in particular:

- **where optimal doping is** for a given material.
- **what optimal performance is** for a given material.