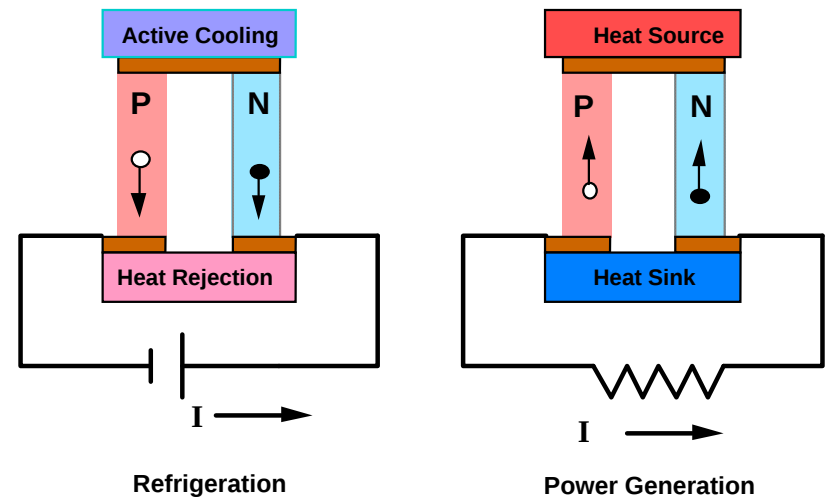
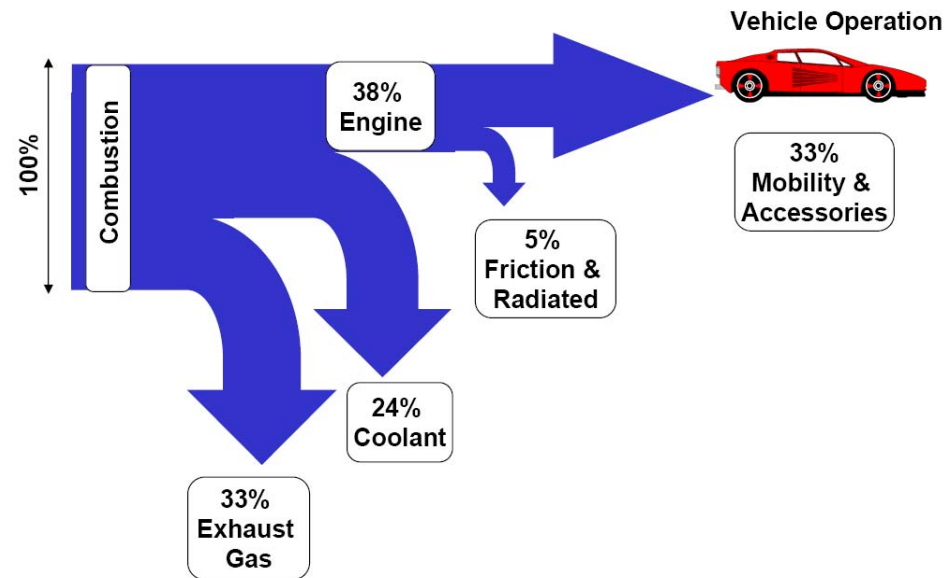


Thermoelectric Materials by Design: Computational Theory and Structure*

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

**This presentation does not contain any proprietary or confidential information*

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PURPOSE OF WORK

- Find promising new thermoelectric compositions for waste heat recovery in vehicles (waste heat → electric power).
- Focus on potentially inexpensive materials.
- Use science based approach especially materials design strategies employing first principles calculations.
- Primary emphasis is materials with high figure of merit at temperatures relevant for waste heat recovery.
 - $ZT = \sigma S^2 T / \kappa$
- Other potential benefit: Improved materials for automotive climate control (All electric distributed A/C).

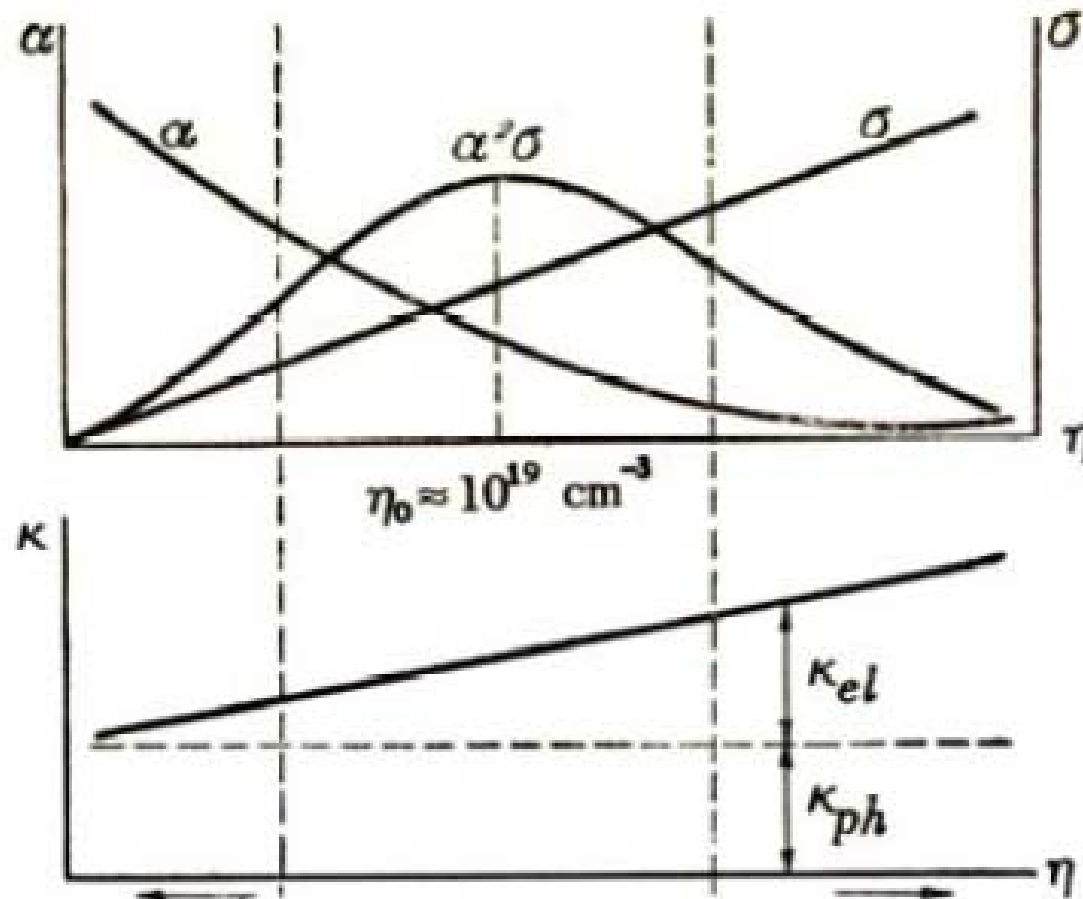
BARRIERS*

- Need higher ZT materials at operating temperature
 - Target is temperature averaged $ZT=2$, with $\Delta T \sim 400 \pm 50$ C, which could yield 5% fuel efficiency improvement.
 - Both n -type and p -type materials.
- Must be cost effective. Target is \$1/W but lower is desired (\$0.20/W).
- Must be manufacturable and durable (mechanical properties / stability).

* “Science-Based Approach to Development of Thermoelectric Materials for Transportation Applications: A Research Roadmap”, Office of FreedomCar and Vehicle Technologies, DOE (2007).

DOPING DEPENDENCE OF THERMOELECTRIC PROPERTIES

Ioffe (1957)



Note strong doping dependence.

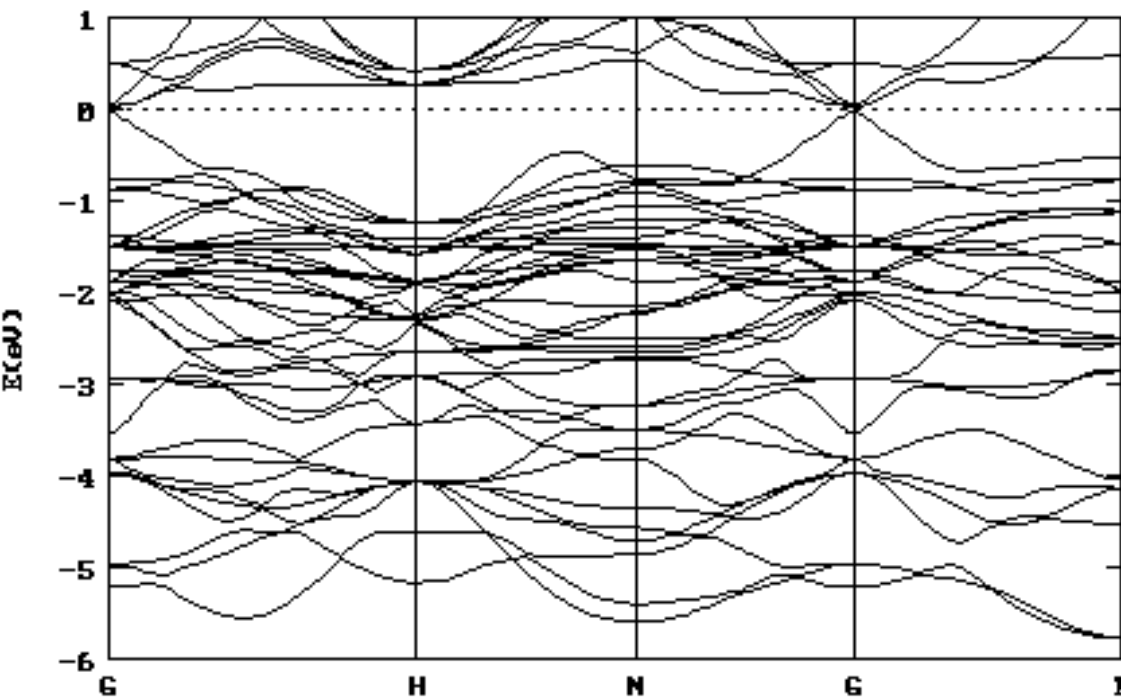
Can explore entire doping range with theory reducing the need for extensive synthesis & characterization to find optimal composition.

APPROACH

- First principles calculations to obtain electronic structure and vibrational properties.
- Boltzmann transport theory applied to first principles band structures to obtain electrical transport quantities, especially thermopower, $S(T)$.
 - Done using ORNL developed transport code: BoltzTraP.
- Apply linear response and direct methods for phonon frequencies → thermal transport functions.
- Apply Green-Kubo method to molecular dynamics calculations for thermal conductivity.
- Focus on materials such as oxides and chalcogenides that promise potential low cost.
- Focus on 3D materials: otherwise requirement for highly textured or single crystal material increases cost. Anisotropies are often accompanied by poor mechanical properties.

BASIS FOR APPROACH: PREDICTIVE POWER

- Skutterudites and Filled Skutterudites are important materials for power generation.
- Calculated band structure of IrSb_3 and CoSb_3 disagreed with literature. Zero and small band gaps and non-parabolic bands predicted, vs. reported conventional semiconducting behavior.



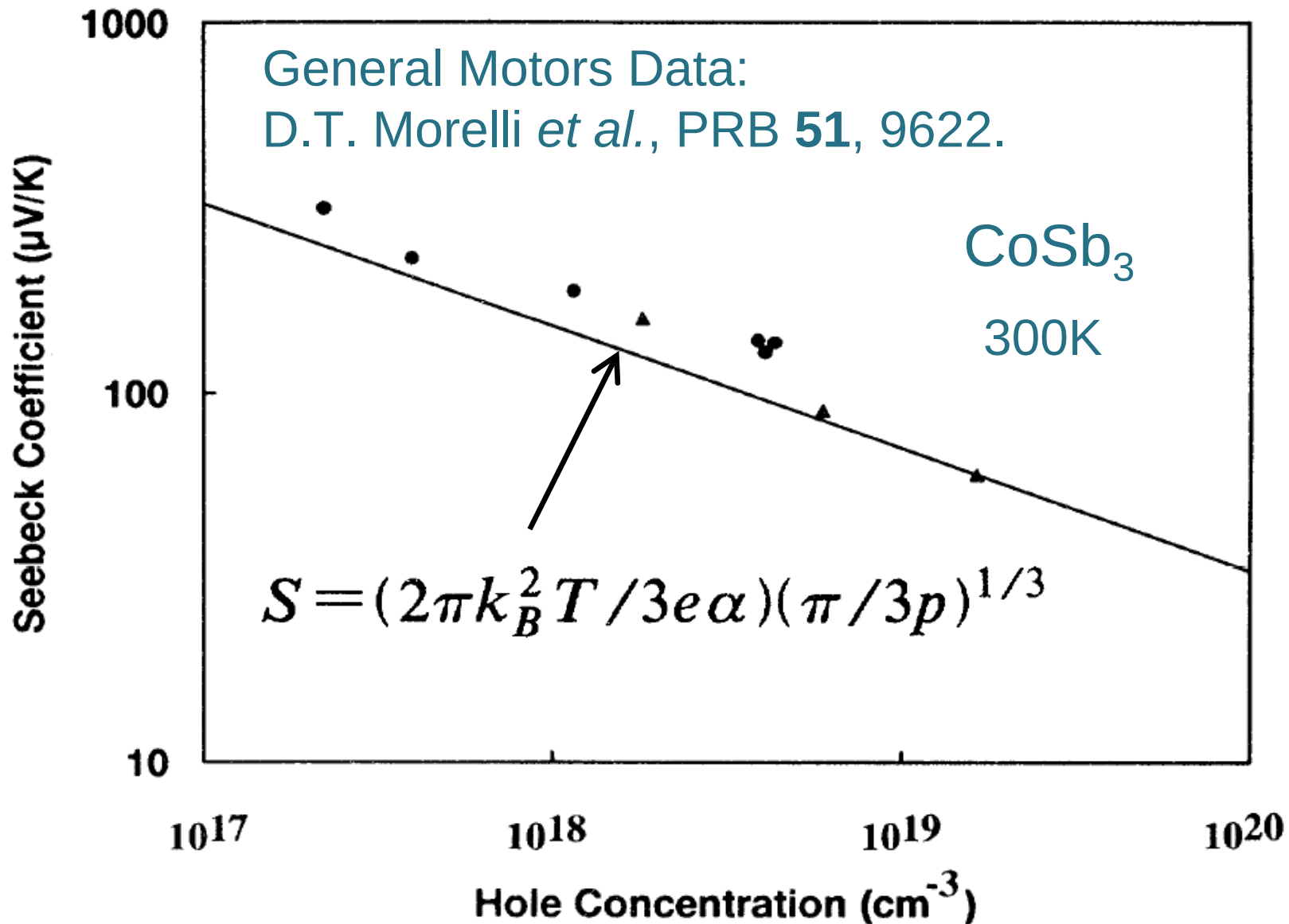
CoSb_3

← Light non-parabolic
(linear) valence band.

Kinetic Transport:

- parabolic: $S/T \propto n^{-2/3}$
- linear: $S/T \propto n^{-1/3}$

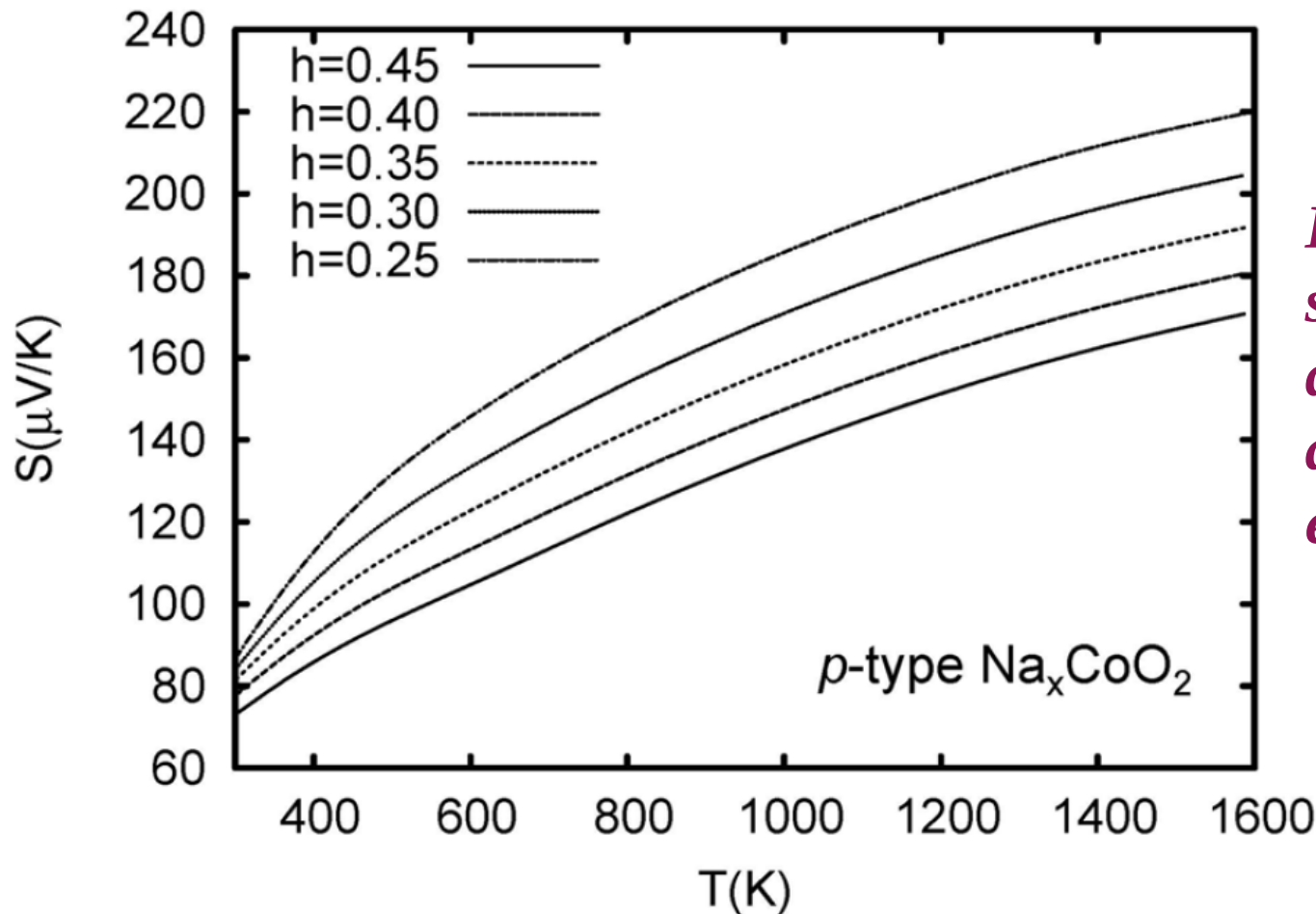
BASIS FOR APPROACH: PREDICTIVE POWER



BASIS FOR APPROACH - VALIDITY

- Discovery of high ZT in metallic oxide Na_xCoO_2 was surprising and not understood. In particular, high $S(T)$ was not anticipated and was thought to suggest unconventional physics.

In-plane (out of plane is opposite sign).



LDA band structure → quantitative (10%) agreement with experiment.

PERFORMANCE MEASURES

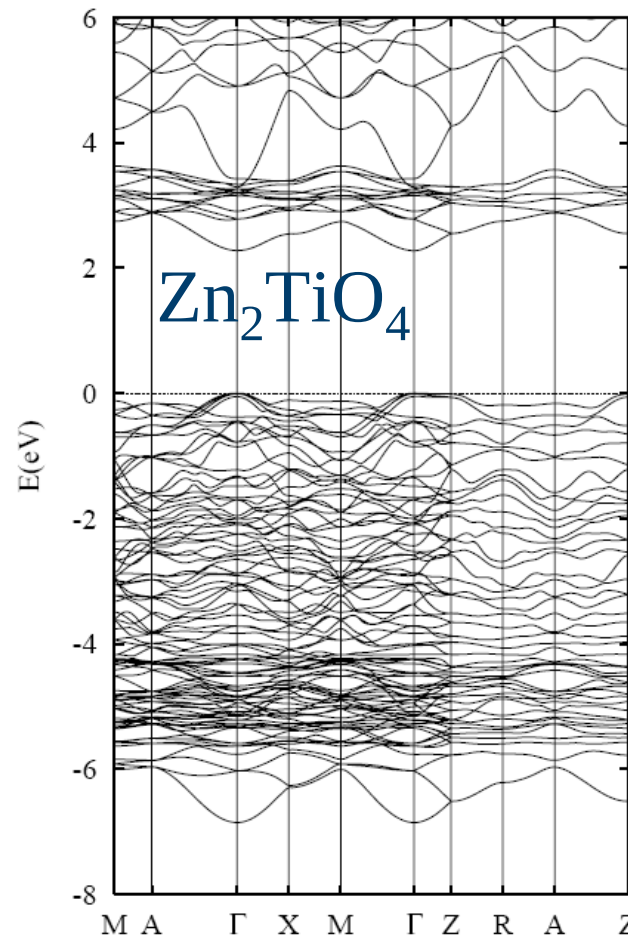
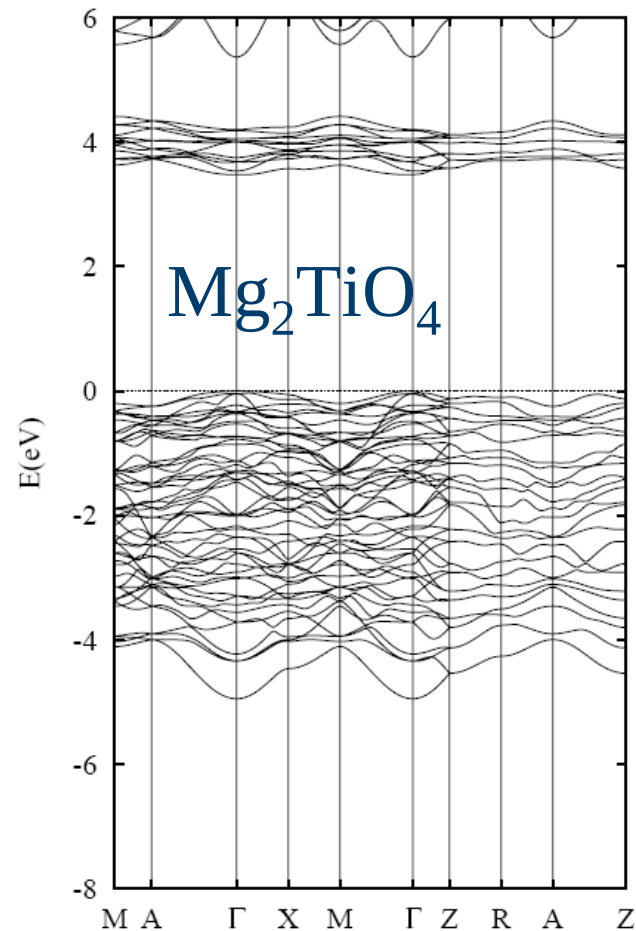
- Prediction of new thermoelectric compositions with high ZT based on potentially inexpensive material suitable for automotive application.
- Dissemination of results via reports to DOE and open literature and patents / invention disclosures as appropriate.

ACCOMPLISHMENTS

- New project for FY2008.
- Initial focus:
 1. Use understanding from prior work on Na_xCoO_2 to identify promising three dimensional oxide materials based on inexpensive elements.
 - Strong metal O covalency.
 - Bent bonds ($\sim 90^\circ$).
 - Mixed valent transition metal (for dopability).
 2. Explore doping dependence in La_3Te_4 thermoelectrics to determine if the operating temperature can be brought into the range needed for waste heat recovery.

ACCOMPLISHMENTS

Mg_2TiO_4 and Zn_2TiO_4 are reported to form in either cubic (disordered) or tetragonal structures depending on annealing. We focused on the ordered structure due to its expected higher conductivity.



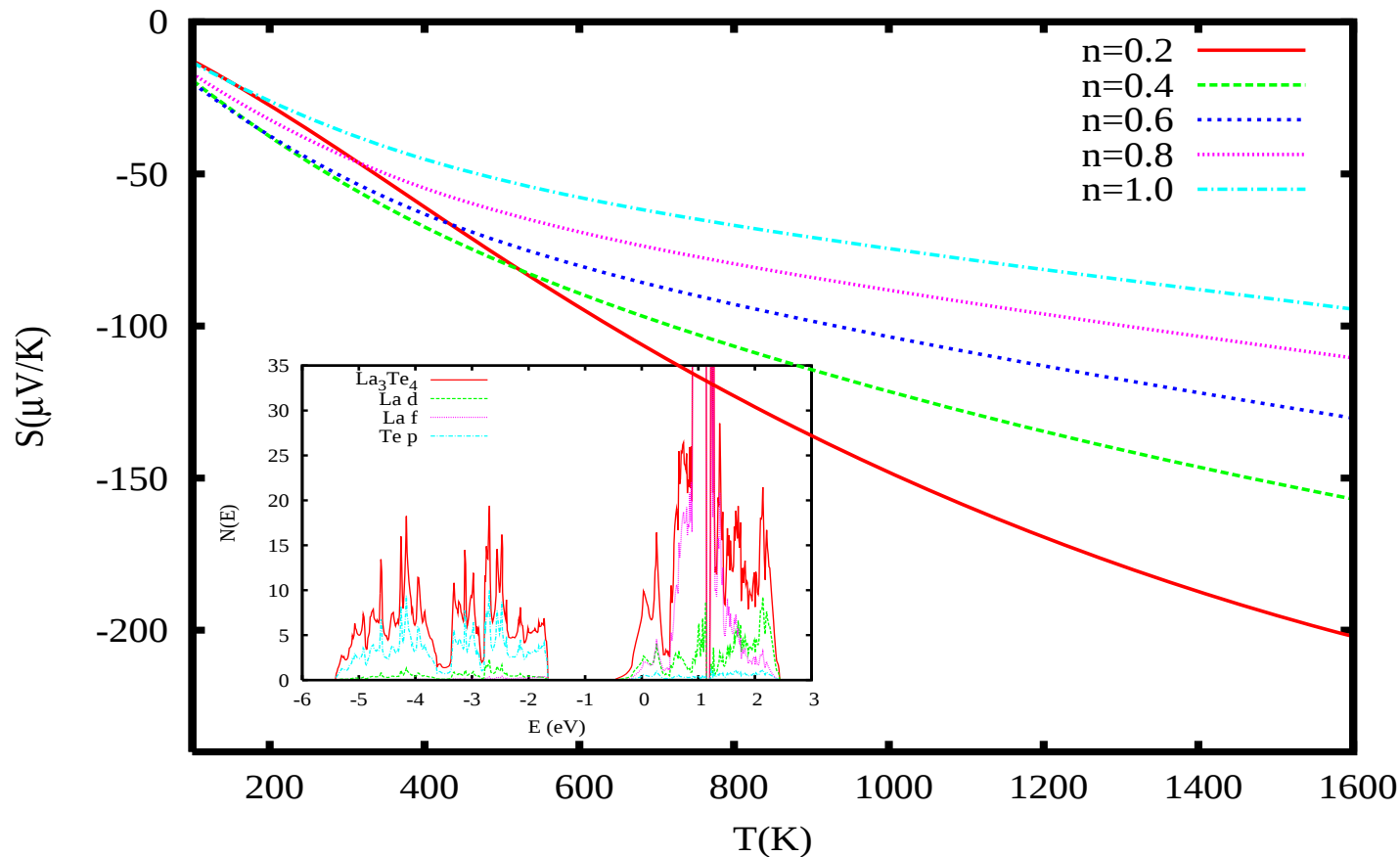
First principles
electronic
structure.

Relaxed crystal
structure.

***Note narrow Ti
d conduction
bands –
transport
calculation in
progress.***

ACCOMPLISHMENTS

- First principles band structure and thermopower calculations for $\text{La}_{3-x}\text{Te}_4$



- La_3Te_4 based material will require much lower doping than is used in RTGs if it is to be used for waste heat recovery.

TECHNOLOGY TRANSFER

- Technology Transfer Plans:
 - Dissemination of results via scientific literature, meeting presentations and patents.
 - Collaboration with synthesis and characterization activities at ORNL, especially C.K. Narula and D. Mandrus (oxide/chalcogenide synthesis), H. Wang (thermoelectric measurements).
 - Results on Mg_2TiO_4 and Zn_2TiO_4 have been communicated to C. Narula who is evaluating methods for synthesis of these phases.
 - Vehicle Technologies Solid Waste Heat Recovery Program is configured so that new materials can be inserted into the program relatively easily (by design of the hardware).

ACTIVITIES FOR NEXT FISCAL YEAR

1. Explore oxide/chalcogenide materials using first principles electronic structure and transport calculations.
 - Guided by trends identified from previous calculations.
2. Develop “Materials Design Rules” for high ZT oxides: selection criteria for materials that are likely to have high thermopower and high ZT . Goal is to use these rules in the selection of materials for further investigation by first principles.
3. Implement phonon calculations for thermoelectric materials.
Implement Green-Kubo method for calculating thermal conductivity.
Apply to thermoelectric materials.

SUMMARY

- Application of first principles calculations and theory to identify promising thermoelectric materials for waste heat recovery.
- Focus is on potentially inexpensive materials that are suitable for vehicular applications.
- Promising initial results for Mg-Ti-O and Zn-Ti-O ordered spinels → next steps are:
 - completion of transport calculations
 - detailed prediction of doping dependence
 - identification of related promising compositions
 - communication of results as appropriate for experimental validation.

PUBLICATIONS, PRESENTATIONS, PATENTS

- H.J. Xiang and D.J. Singh, *Suppression of the thermopower of Na_xCoO_2 by an external magnetic field: Boltzmann transport combined with spin-polarized density functional theory*”, Physical Review B **76**, 195111 (2007).
- D.J. Singh, *Oxide Thermoelectrics*, Mater. Res. Soc. Symp. Proc. **1044**, U02-05 (2008).
- D.J. Singh, *Oxide Thermoelectrics*, Materials Research Society Meeting, Boston, MA, November 2007 (INVITED TALK).