Thermoelectric Materials by Design, Computational Theory and Structure

David J. Singh
Oak Ridge National Laboratory
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Overview

Timeline:
- Started: FY08
- Completion: FY11
- 35% Complete

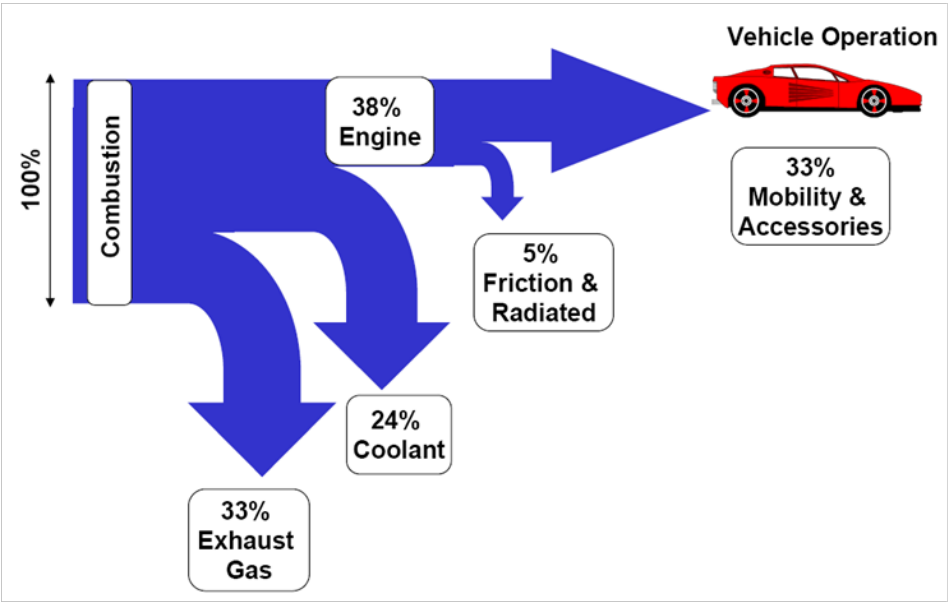
Budget:
- Anticipated Budget: $820K
- 100% DOE
- To date:
  - FY08: $235K
  - FY09: $116K

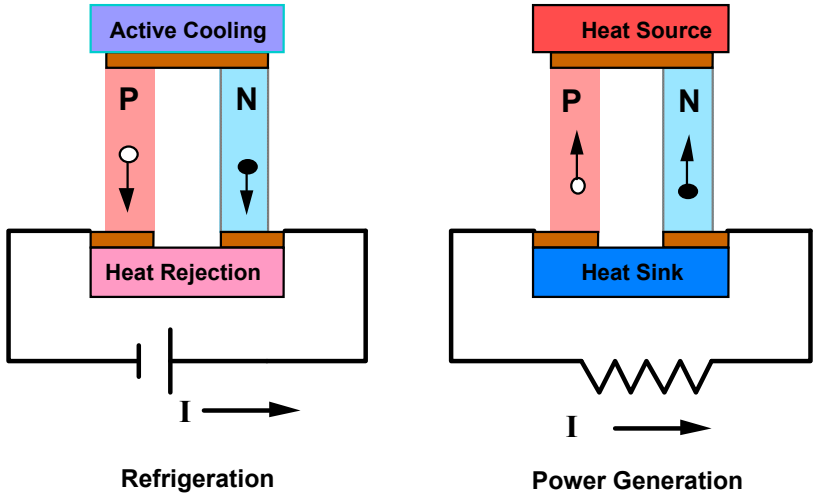
Barriers* Addressed:
- Higher *ZT* thermoelectrics for waste heat recovery (target *ZT*>2 for 10% improvement in fuel consumption).
- Need cost effective (target $1/Watt (desirable $0.2) *p*- and *n*-type manufacturable and durable materials.

Partners/Collaborations:
- General Motors R&D
- Oregon State
- North Carolina State

* DOE FCVT Program Plan, 3.3.4 "Waste Heat Recovery", further details in "Science-Based Approach to Development of Thermoelectric Materials for Transportation Applications: A Research Roadmap", DOE FCVT (2007).

Potential Payoff





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

Discovery of practical materials with $ZT > 2$ for ΔT=400 +/- 50 C can yield fuel savings of 10% in vehicles.

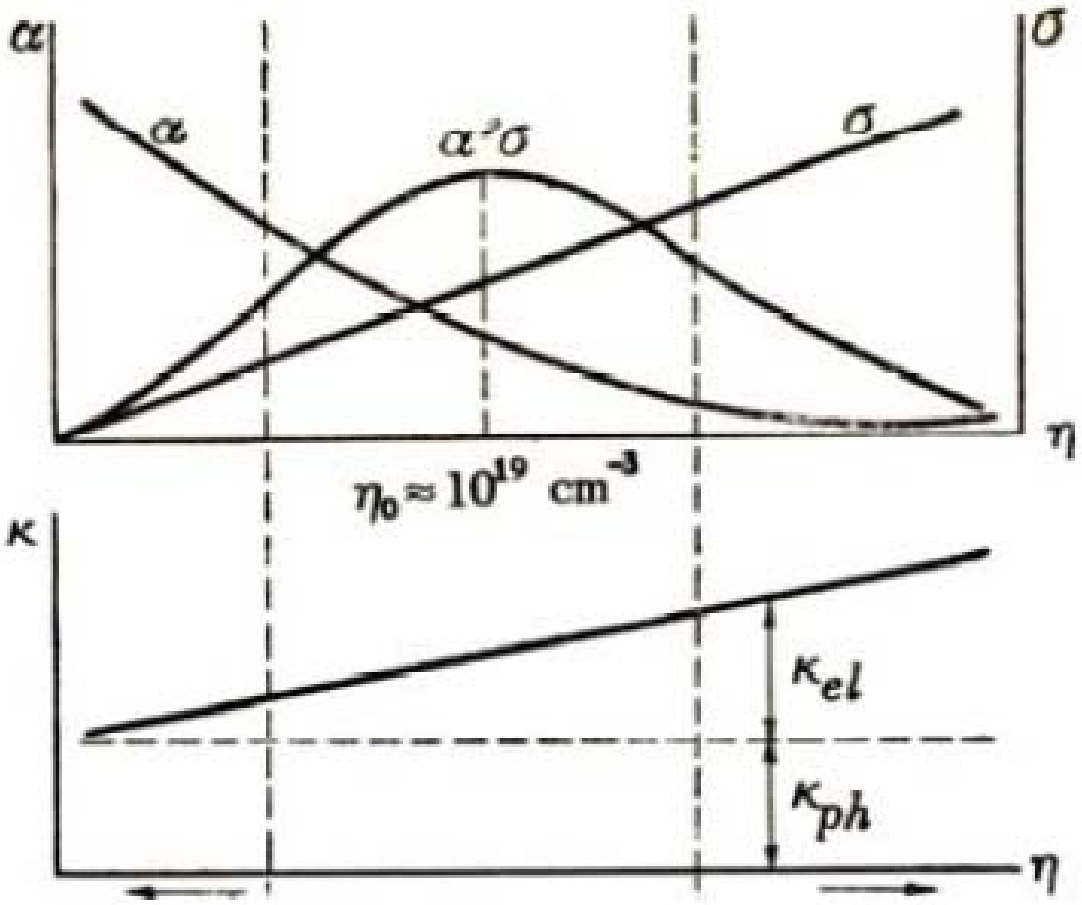
Additional fuel savings are possible using thermoelectrics to enable new climate control concepts, e.g. localized on demand cooling.

Objectives

- 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).

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.

Milestones

1. 4QFY09: New composition with improved thermoelectric performance in the temperature range relevant to vehicular waste heat recovery will be predicted and strategies for optimizing materials will be devised. These predictions and their basis in first principles calculations will be described in a technical report prepared in a form suitable for publication.
2. 4QFY09: 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.

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 lattice vibrations → thermal transport functions and 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.

Electrical Transport (Kinetic Theory)

- Valid for mean free path longer than lattice spacing.
- Allows calculation from band structure and scattering mechanisms – BoltzTraP code (Madsen and Singh)
- Conductivity:

$$\sigma_x(T) = e^2 \int d\varepsilon\, N(\varepsilon)\, v_x^2(\varepsilon)\, \tau(\varepsilon, T)(-f'(\varepsilon))$$

- Thermopower:

$$S(T) = (e/T\sigma(T)) \int d\varepsilon\, N(\varepsilon)\, v_x^2(\varepsilon)\, \tau(\varepsilon, T)\, \varepsilon\, (-f'(\varepsilon))$$

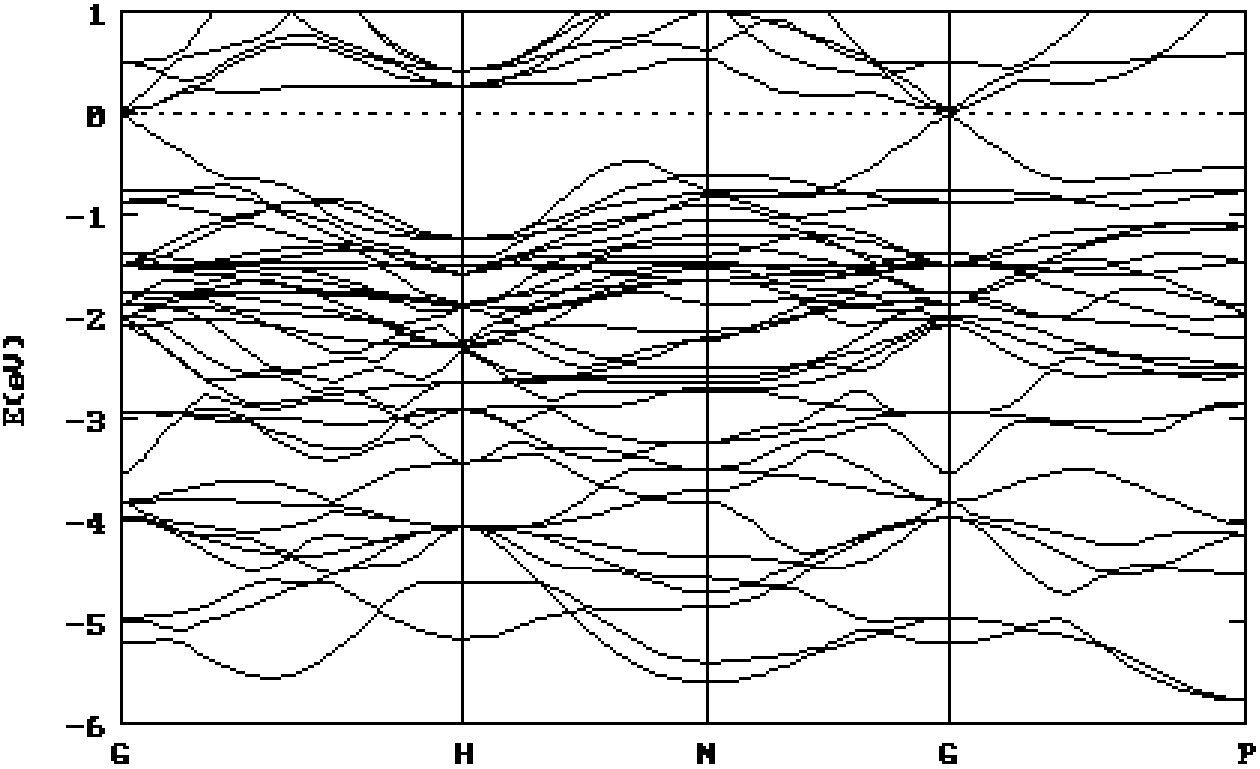
- At low T this is:

$$S(T) = (\pi^2 k^2 T/3e\sigma)\, (d\sigma/d\varepsilon)\ |\ E_F$$

So high S implies high log derivative of σ, *i.e. strong energy dependence of electrical transport*: Band structure and scattering.

Predictive Capabilities

- 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.



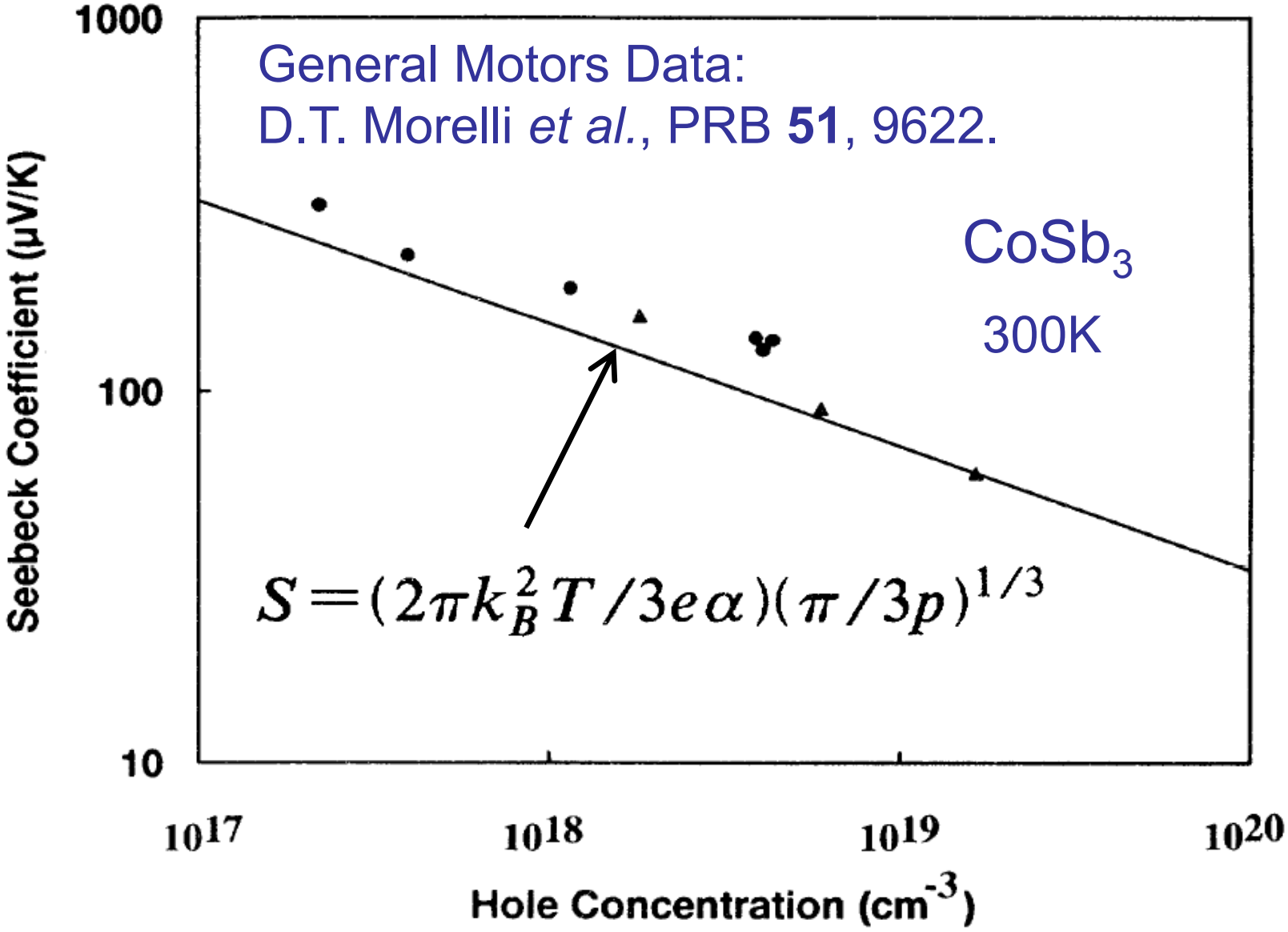
$CoSb_3$

← Light non-parabolic (linear) valence band.

Kinetic Transport:

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

Predictive Capabilities

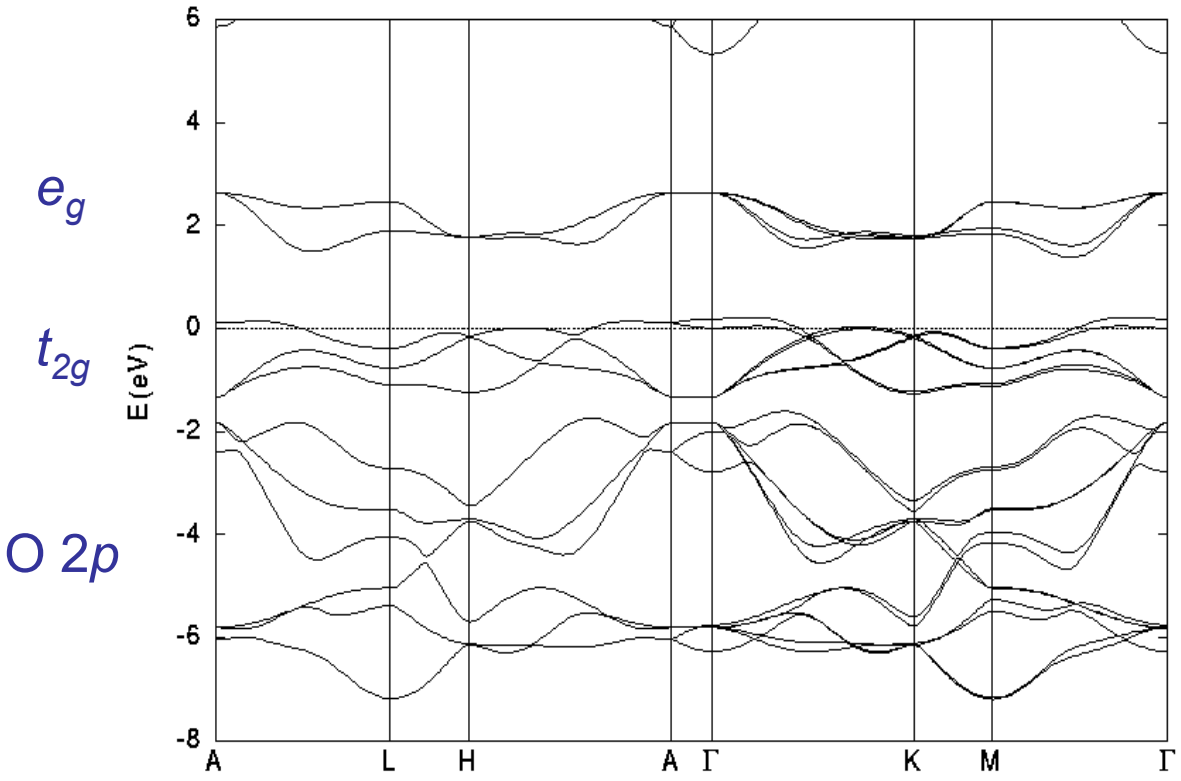


Oxide Thermoelectrics

Terasaki's discovery of high *ZT* in single crystals of Na_xCoO_2

- Paradigm change: High *ZT* in high carrier density metal (not semiconductor).

Electronic Structure (Singh):

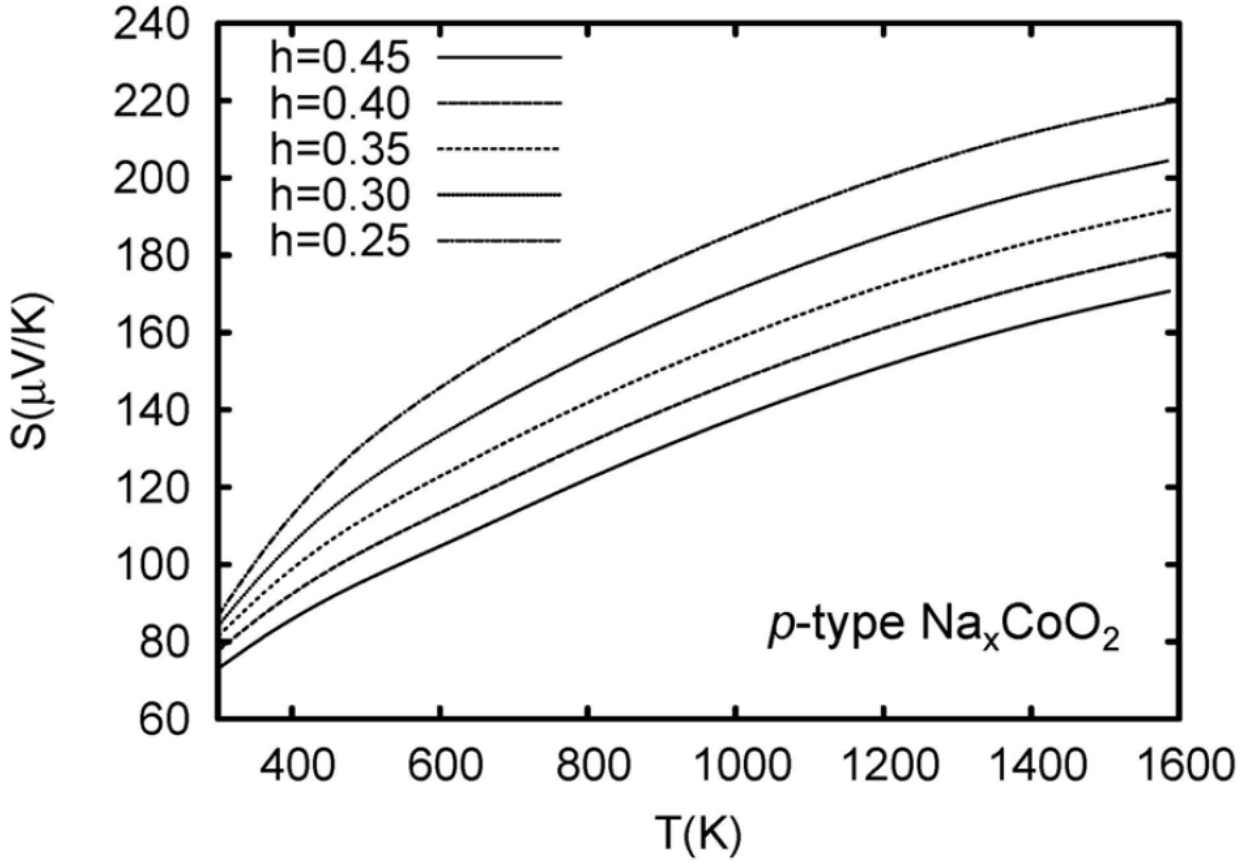


Fermi energy is at the top of a very narrow manifold of t_{2g} bands associated with cobalt.

Combination of narrow bands and conduction is responsible for high thermopower at high carrier density.

Validation for Oxides

- Oxides offer advantages for vehicles (cost and manufacturability).
- Discovery of high *ZT* in metallic oxide Na_xCoO_2 was surprising and not understood. In particular, high *S*(*T*) was not anticipated and therefore might imply physics beyond standard theories.



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

Key Points

Metallic Conduction:

- **Mixed valence transition element ion (Co).**
- **Very strong metal – oxygen hybridization.**

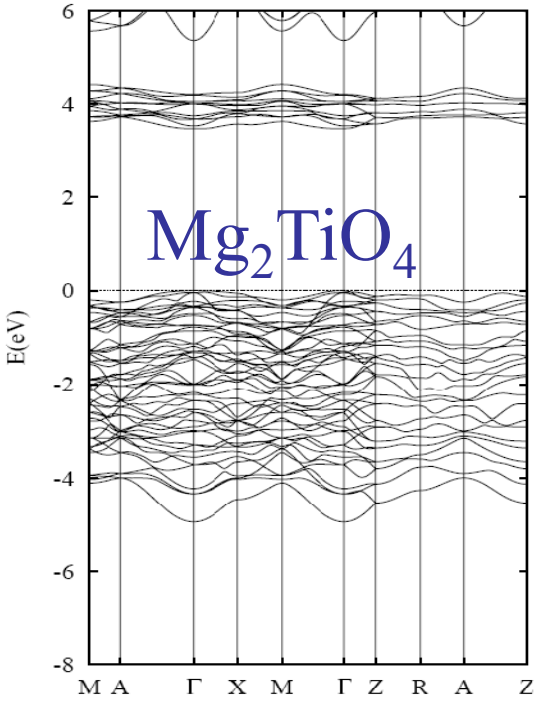
High Thermopower at High Carrier Density:

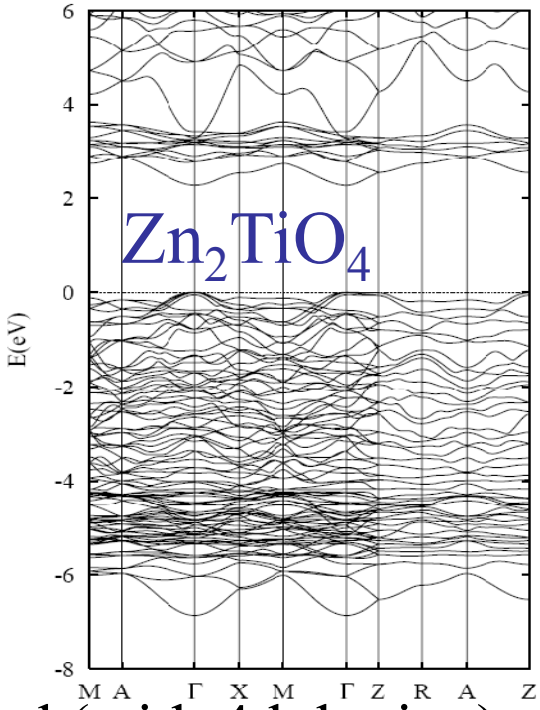
- **Very narrow bands: A consequence of bonding topology (near right angle M-O-M bonds in edge sharing octahedra).**
- **Electron count near crystal field gap.**

Use this to find more practical materials.

Spinel Type Titanates

- Oxides with valence intermediate between Ti^{+4} and Ti^{+3} are often highly conductive: e.g. O deficient $SrTiO_{3-x}$.
- Spinel Structure has edge sharing octahedra ➔ are there any with narrow bands, Fermi energy near band edge, and strong Ti-O hybridization?





First principles electronic structure.

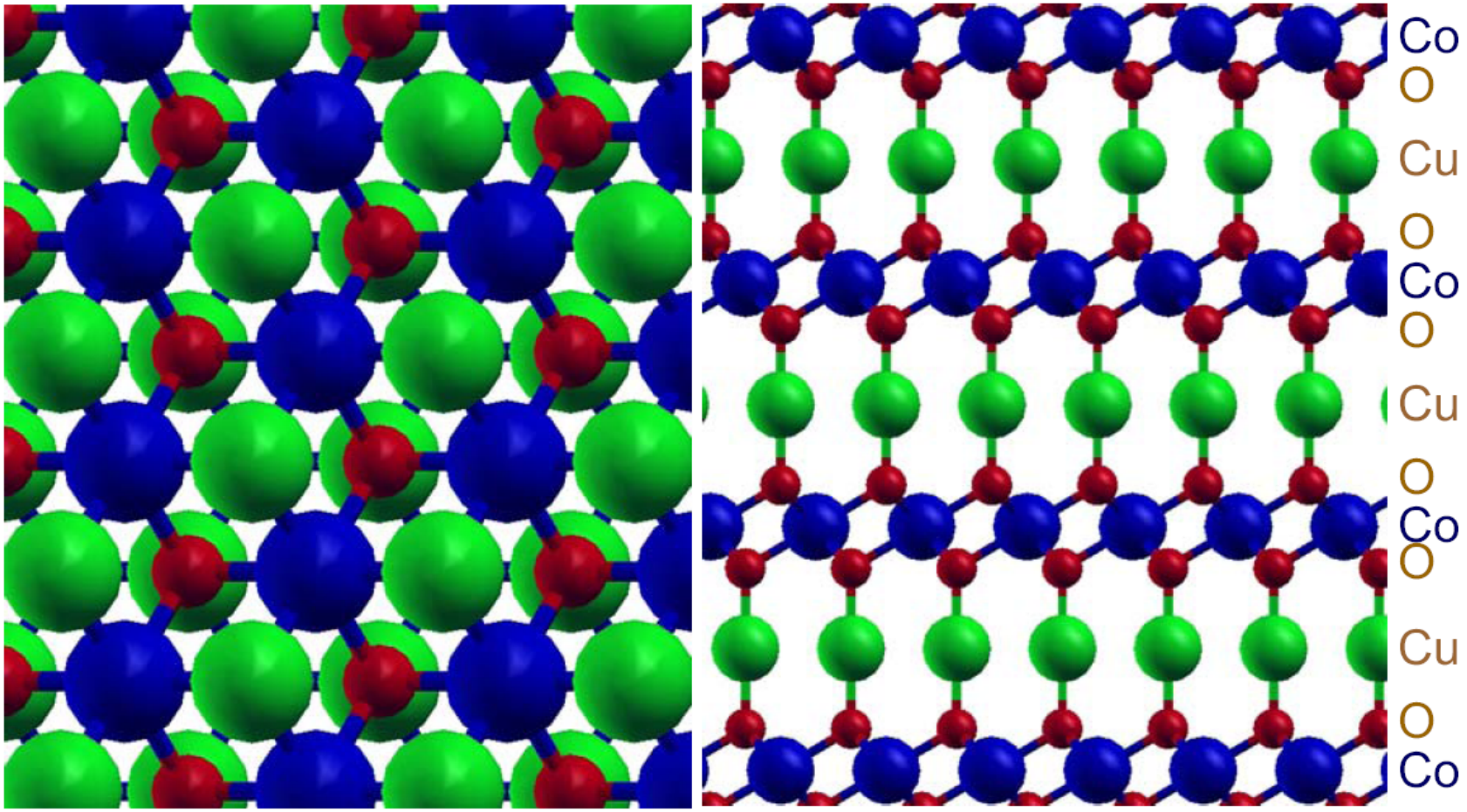
Relaxed crystal structure – ordered tetragonal spinel type.

Note narrow Ti d conduction bands

Synthesis is being attempted (with 4d doping) to assess feasibility of producing conducting samples.

Delafossite Structure

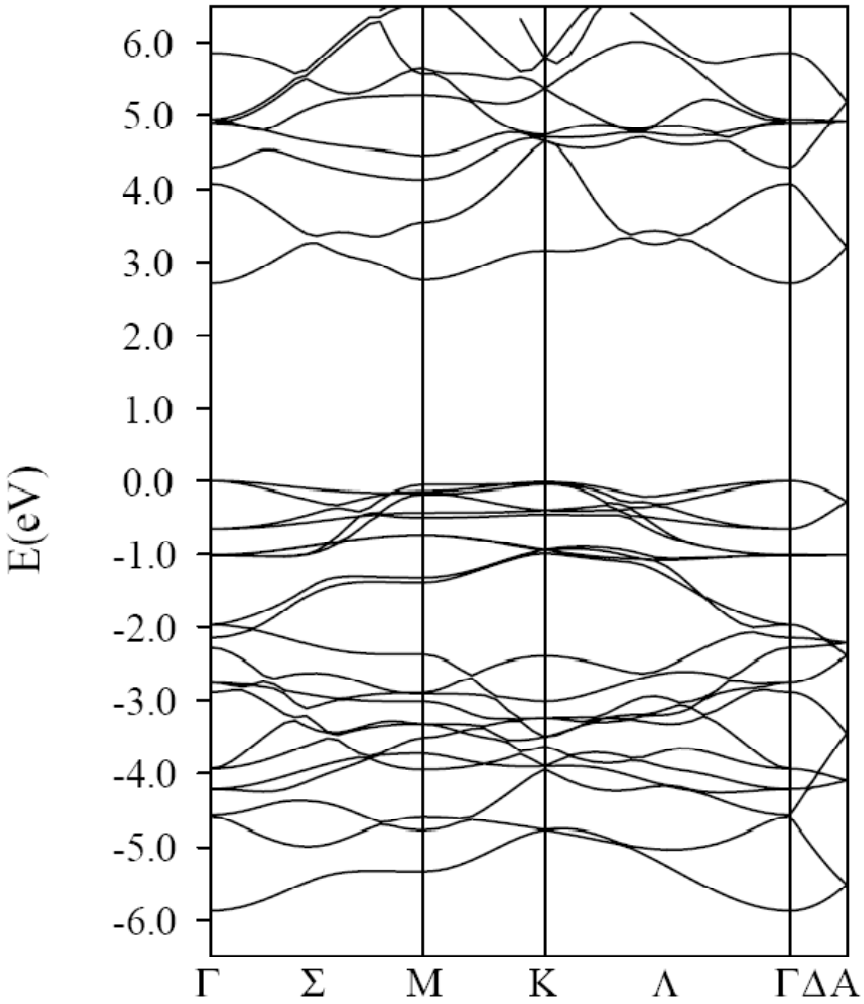
- $CuCoO_2$ and $AgCoO_2$ are known insulators, $PdCoO_2$ is metal
- Recent work by Shibasaki et al. on Rh delafossite shows high *S*.

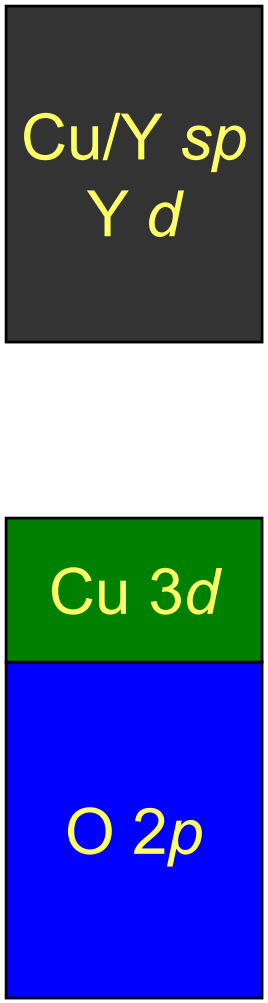


$CuCoO_2$ and many other compounds.

$YCuO_{2+x}$ Delafossite

Known conducting compound (transparent conductor).
Potentially low cost.
Variable O stoichiometry.

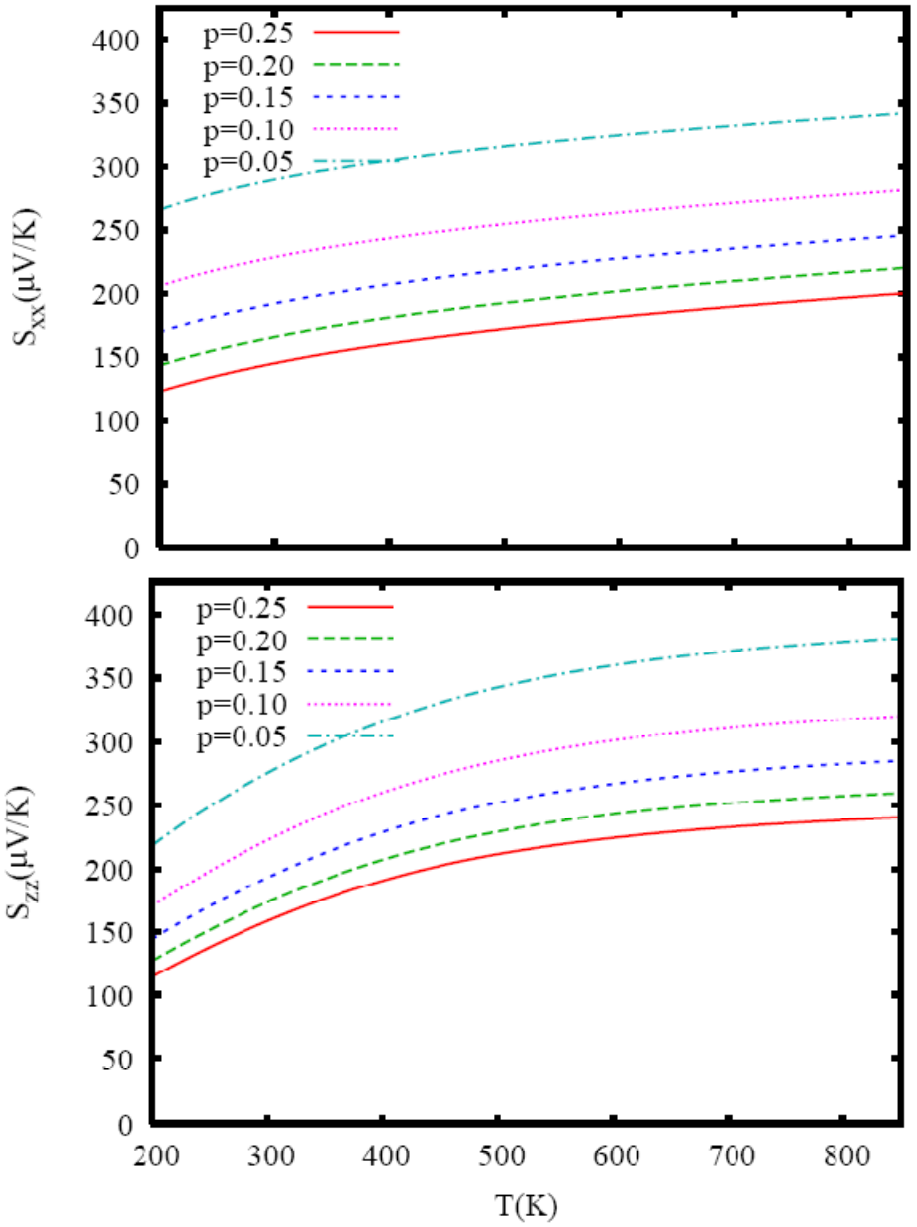




p-type carriers are in narrow Cu *d* bands

c.f. Mattheiss

$YCuO_2$ Thermopower

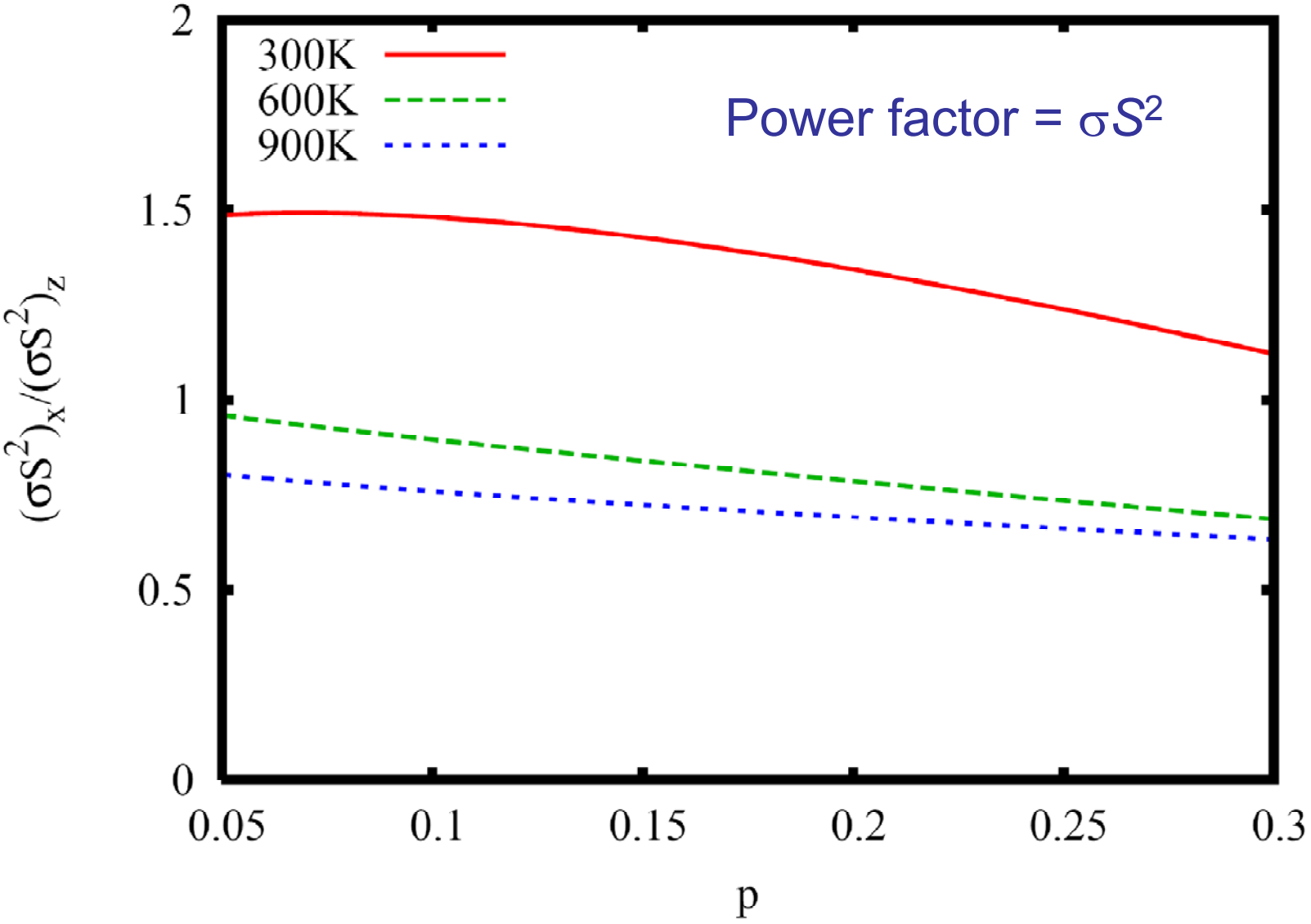


Very high thermopowers, exceeding that of Na_xCoO_2 for comparable doping levels.

Anisotropy of thermopower is modest, unlike Na_xCoO_2.

Reason is 3D bands vs.2D bands.

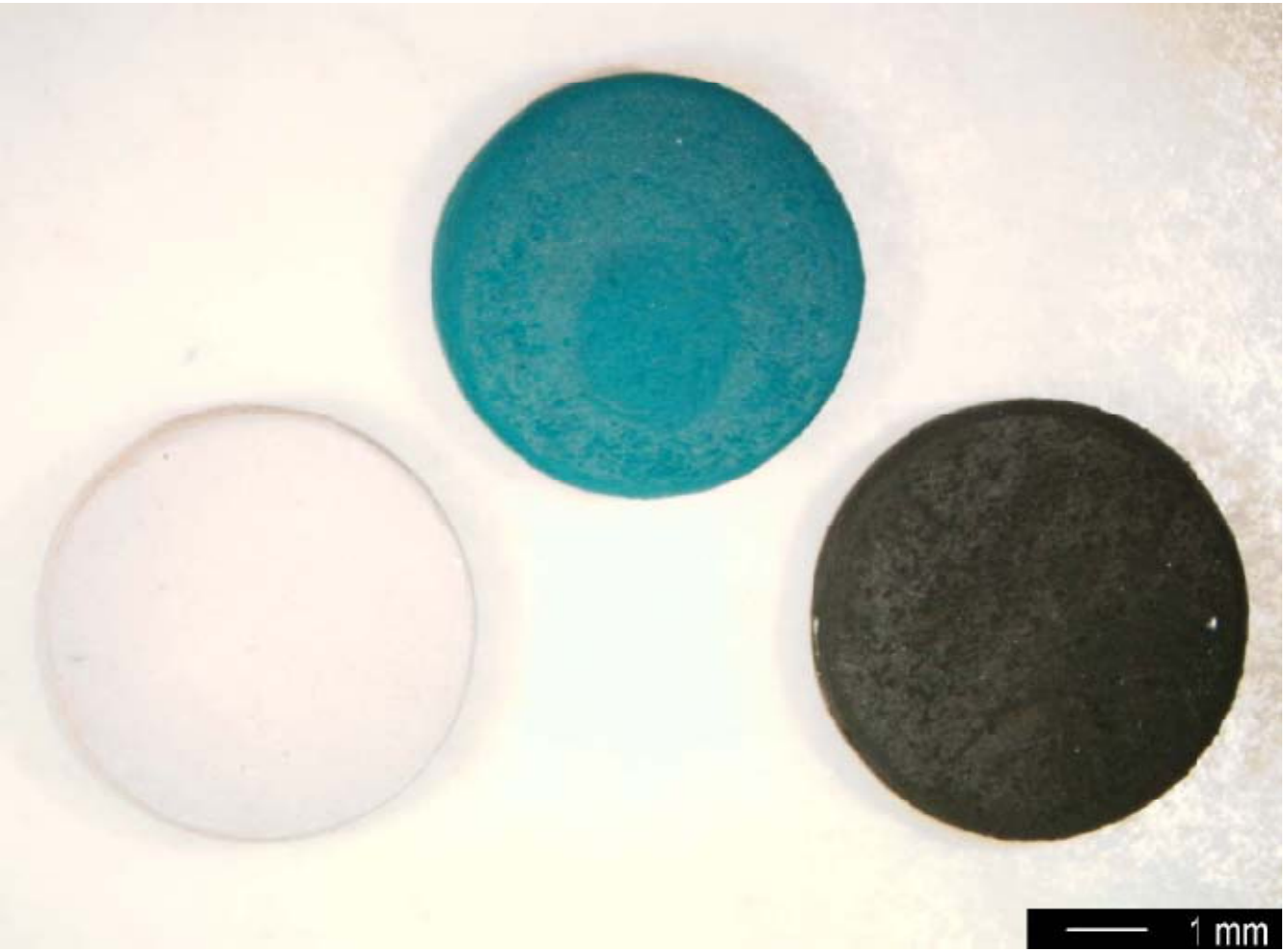
Power Factor Anisotropy of $YCuO_2$



Dominated by anisotropy of *S*. Anisotropy is ~1.5 or smaller.

Experiment (C. Narula, ORNL)

C. Narula* (ORNL) and co-workers prepared samples for suitable for testing and showed that doping can be controlled by treatments.

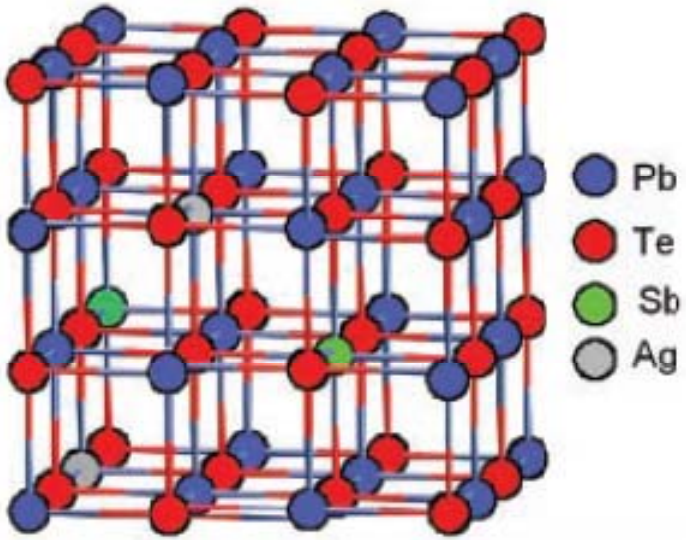


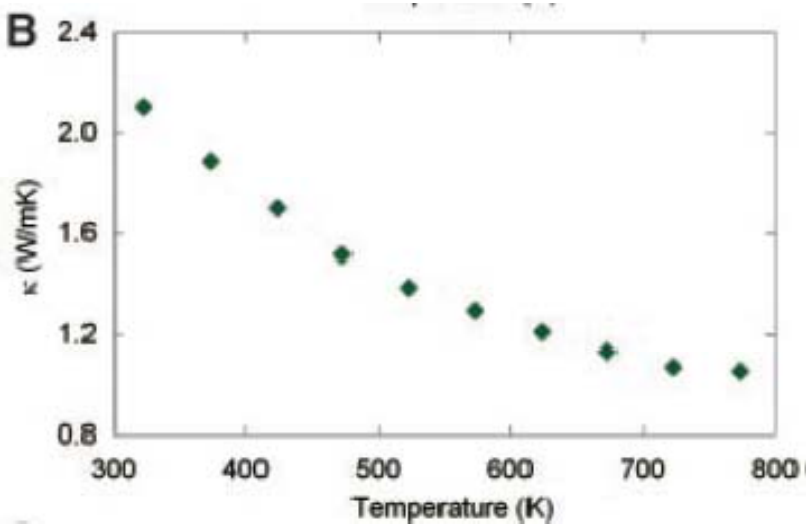
*Other funding.

What About PbTe?

Investigation motivated by General Motors (Yang) request.

- PbTe has simple cubic rock-salt structure with two atoms per unit cell. Well packed, well coordinated structure.
- Many excellent thermoelectrics are based on PbTe:
  - •Artificial nanostructures (Harman et. al.).
  - •LAST (Kanatzidis group).
  - •PbTe with Tl resonant enhancement (Heremans).

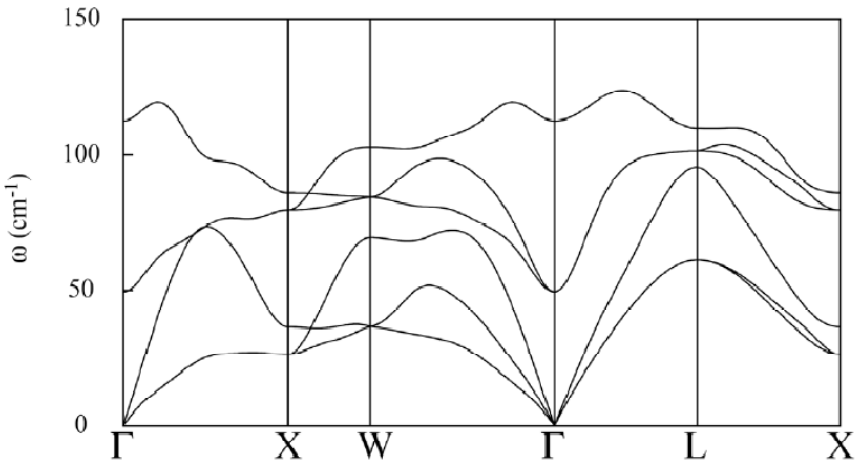




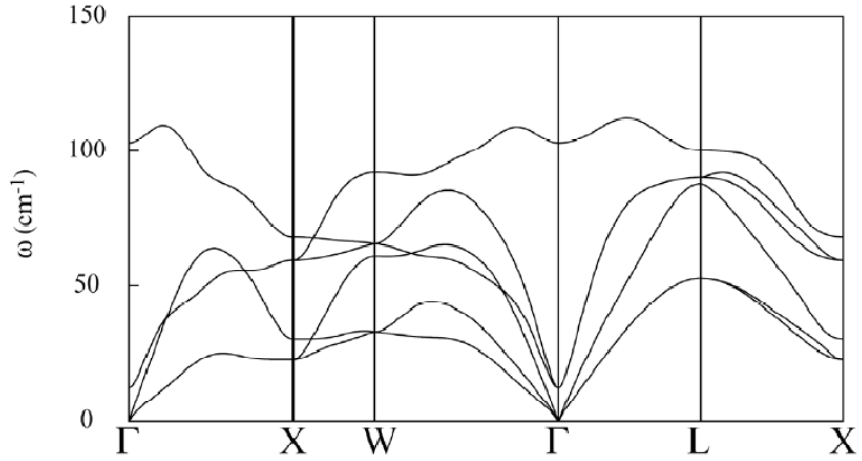
$Ag_{1-x}Pb_{18}SbTe_{20}$, Kanatzidis Group, Science, 2004.

Phonon Dispersions

a) Compressed: $a = 6.300$Å -2.2%



b) Ambient (120K) $a = 6.4384$Å



J. An, A. Subedi and D.J. Singh, 2008

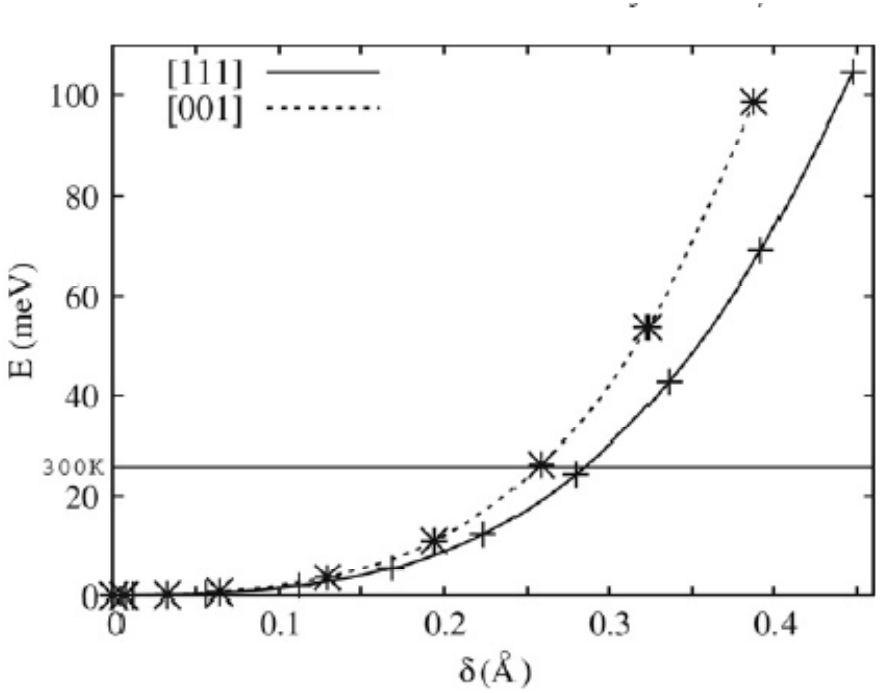
Linear response calculations ➔ zone center soft mode with super-strong strain coupling – (longitudinal acoustic to transverse optic).

Key Points:

PbTe is near ferroelectricity.

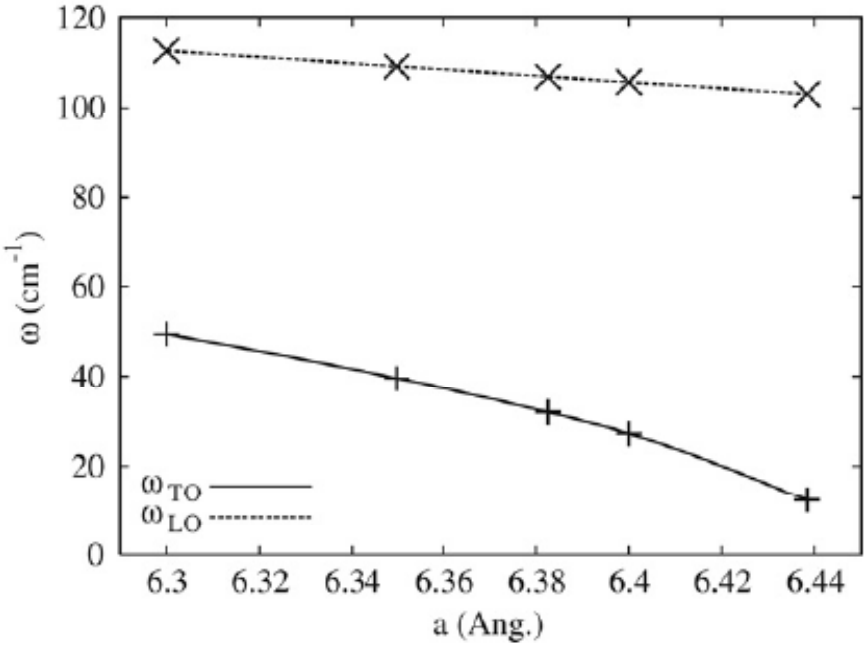
c.f. GeTe which is ferroelectric when undoped – basis of TAGS (GeTe – AgSbTe).

Anharmonicity



Large anharmonicity of TO mode.

Strong anharmonic coupling between TO and LA modes



Can we engineer soft mode materials either as thermoelectrics or as interfaces in thermoelectrics? Is there a Te-free material like PbTe?

Accomplishments

- Finding of narrow conduction bands and strong hybridization for tetragonal spinel type $(Mg,Zn)_2TiO_4$.
- Electronic structure and transport calculations for delafossites: Prediction of high thermopower and thermoelectric performance in low O content $YCuO_{2+x}$.
- Phonons and anharmonicity due to near lattice instability of PbTe – strategy for finding other low thermal conductivity compounds.
- Two band electronic structure of La_3Te_4: doping dependence, and conduction – understanding of favorable conductivity in a material with a large defect concentration. (Collaboration with CalTech).
- Investigation of "inexpensive" potential thermoelectric material $BaMn_2Sb_2$ / $BaMn_2As_2$ (theory and experiment).
- Dissemination of results leading to experimental study of titanates (Narula, ORNL), $YCuO_2$ (Narula, ORNL), $BaMn_2As_2$ (Sefat, ORNL).

Activities for Next Fiscal Year

Oxides:

- Identify additional high performance oxide candidates, focusing on materials with reasonably isotropic properties and potential low cost.
- Specific need is for *n*-type material. Will continue investigation of titanates as candidates as well as other *n*-type oxide materials.

Chalcogenides, Antimonides and Related:

- Use understanding gained from study of PbTe and La_3Te_4 to find tellurium-free materials with similar properties (i.e. PbSe – WSe_2 and related inter-growth materials and materials near zone center lattice instabilities).
- Examine potentially low cost Zintl type phases in skutterudite, $ThCr_2Si_2$ and related structures.

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 results found for delafossite $YCuO_2$ and for Mg_2TiO_4 and Zn_2TiO_4 ordered tetragonal spinels.
- Identified principles for thermoelectric performance in PbTe and La_3Te_4.
- Studied $BaMn_2Sb_2$ and $BaMn_2As_2$: Not promising.
- Next steps:
  - Alternate oxide compositions.
  - Tellurium free analogues of telluride thermoelectrics.
  - Zintl phases.