Thermoelectrics Theory and Structure

David J. Singh
Oak Ridge National Laboratory

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PM013

Overview

Timeline

- Started FY08
- Completion FY12
- 50% Complete

Budget

- Total project funding
- 100% DOE.
- FY09: $400K
- FY10: $400K; 300K to date.

* Barriers based on 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).

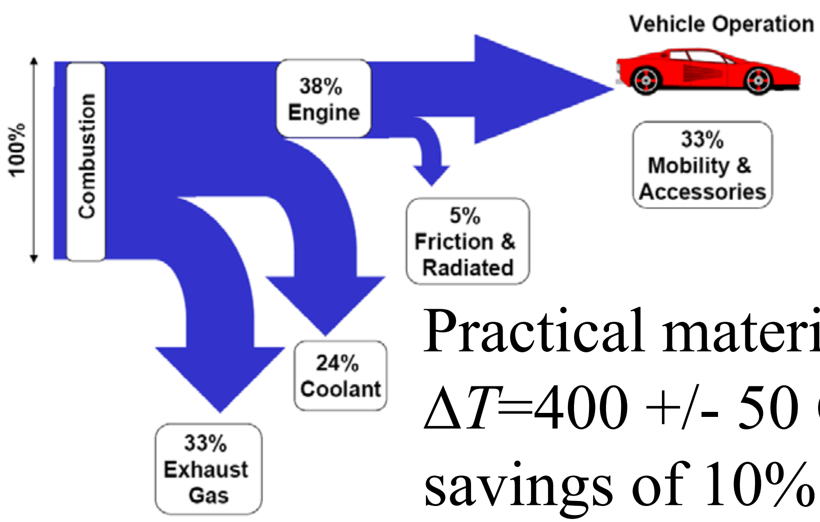
Barriers*

- Need for high *ZT* for waste heat recovery (*ZT*>2) for 10% fuel savings.
- Need cost effective materials (target $1/Watt, desirable $0.2).
- Need durable *p*- & *n*-type materials.

Partners

- Interactions/ collaborations:
  - California Institute of Technology
  - General Motors
  - Naval Research Laboratory
  - Massachusetts Institute of Technology (S^3TEC Center)
  - Oregon State
  - Corning
- Project lead: ORNL

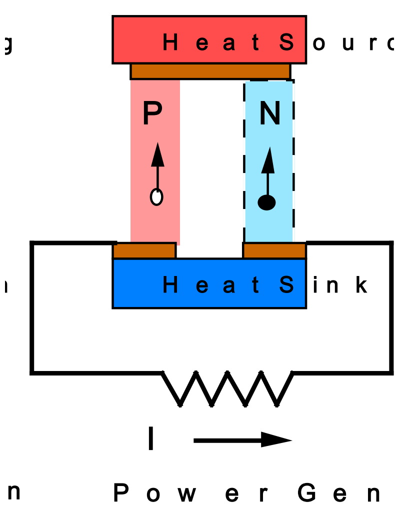
Relevance



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

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, Toyota/Denso, BMW, Volkswagen, Bosch, Visteon. Amerigon/BSST, Siemens, Cummins …

[1] DOE FCVT Program Plan, 3.3.4, "Waste Heat Recovery"
[2] "Science Based Approach to Development of Thermoelectric Materials for Transportation Applications: A Research Roadmap", DOE FCVT (2007).

Relevance

Barriers:

- Need high ZT (ideally ZT=2 or higher).
- Need low cost ($1/watt or better).
- Need p-type and n-type.
- Need high availability, manufacturable materials.
- Desirable to avoid materials with toxic components or potential regulatory issues (e.g. potential classification as hazardous waste).

Te: low abundance, solar cell use.
➔Price has increased by ten fold in a decade to >$100/lb.

Rare earths (La, Ce, …, Yb, Lu): Major concerns about availability.

While China's Rare Earth R&D Becomes Ever More Rarified Others Tremble – Science **325**, 1336 (2009).

As Hybrid Cars Gobble Rare Metals Shortage Looms – Reuters, August 31 (2009).

China's Control of Rare Earth Metals Threatens Jobs, Tech – Business Week, March 17 (2010).

To save energy a technology must not only work – it must be used.

Thermoelectrics Theory and Structure

- Find promising thermoelectric compositions for waste heat recovery in vehicles (waste heat → electrical power).
- Focus on inexpensive materials that can be used.
- Use science based approach especially materials design strategies based on first principles.
- Emphasis is on materials with high *ZT* at relevant temperature.
- Potential benefit: Improved materials for climate control systems.

Identify trends / strategies /design rules

Thermoelectric Compositions

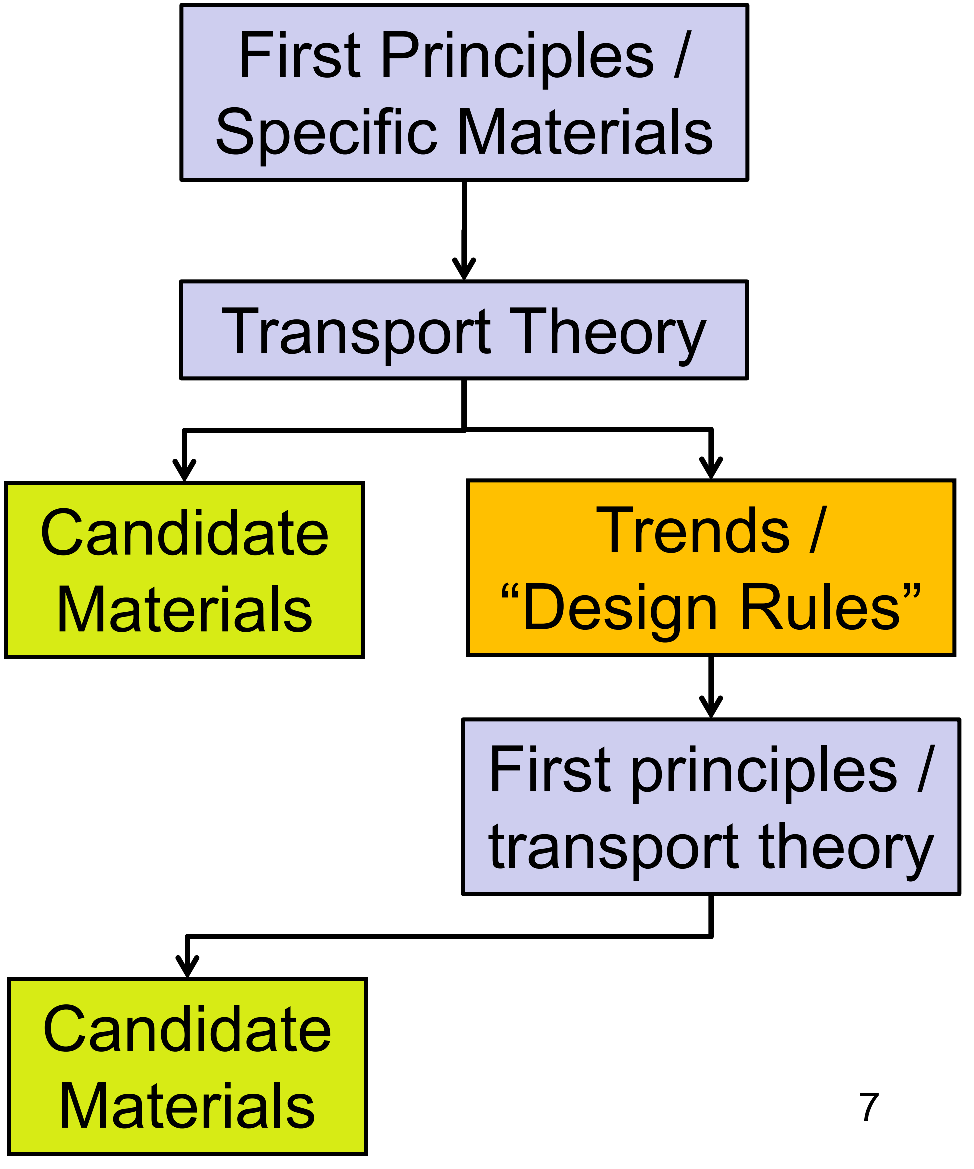
FY08 FY09 FY10

Milestones

Month/Year	Milestone or Go/No-Go Decision
Sept-09	Prediction of new composition with improved performance and strategies for optimizing materials. Predictions and their basis to be described in a technical report. Predictions for delafossite $YCuO_2$ were made, heavily doped PbSe, and PbSe – WSe_2 intergrowths. Optimization strategies for oxides and chalcogenides in terms of doping were formulated. Technical reports are Physical Review B **79**, 153101 (2009), Physical Review B **80**, 075117 (2009).
Sept-09	Develop “Materials Design Rules” for high *ZT* oxides. Rules were formulated based on results of first principles calculations: They include (1) strong metal oxygen hybridization (localization avoidance); (2) specific bonding topologies and structure types to obtain narrow bands at high doping levels by suppression of d-p sigma hopping; (3) d-band oxide metals are better; (4) magnetism is not needed but may appear as a consequence of narrow bands; (5) combination of heavy and light bands is particularly favorable.
Sept-10	Identify a phase with predicted high temperature thermoelectric performance that can exceed that of PbTe, but without tellurium or rare earth elements. Describe this material and the scientific basis for the predictions in a technical report.

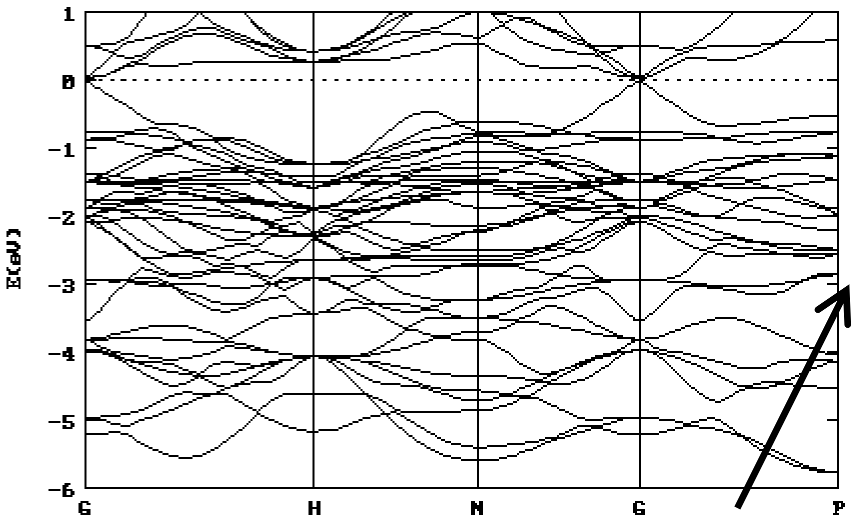
Approach/Strategy

- First principles calculations for electronic and vibrational properties.
- Boltzmann transport theory ➔ electrical transport quantities, especially thermopower, $S(T)$.
  - Done using ORNL developed transport code: BoltzTraP.
- Focus on materials that promise potential low cost.
- Focus on 3D materials: otherwise need for highly textured or single crystal material increases cost.



Approach – Predictive

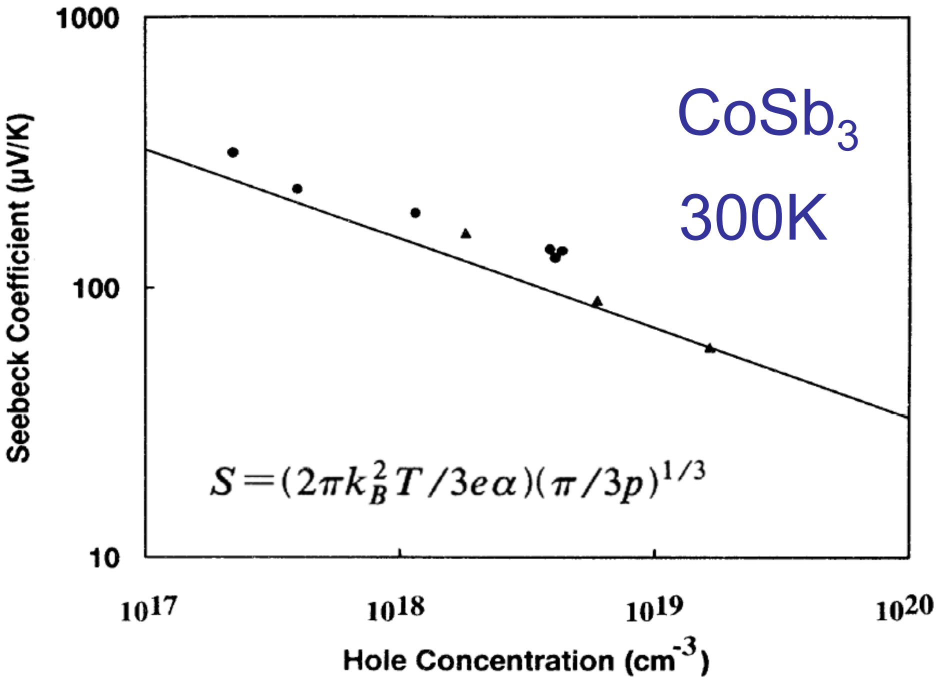
$CoSb_3$ – basis of skutterudite thermoelectrics:



We found very small gap and linear dispersion - not expected. Boltzmann prediction:

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

General Motors Data: D.T. Morelli *et al.*



Prediction confirmed

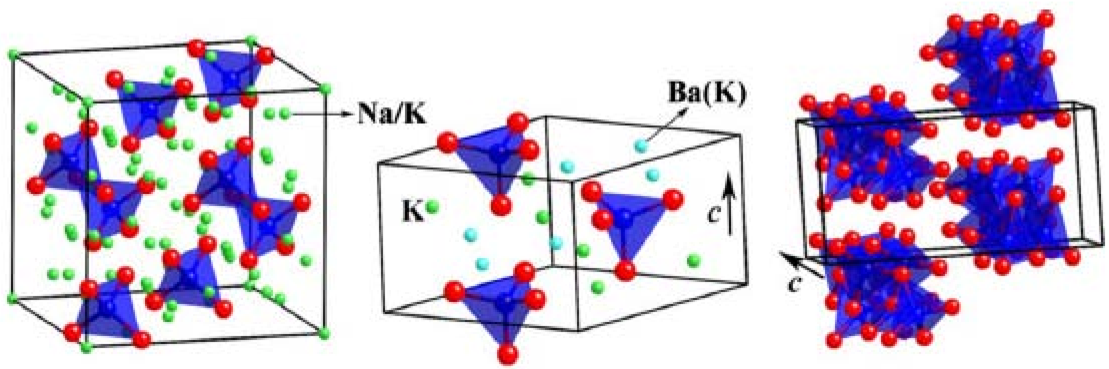
Current Year Accomplishments (1)

(since last year's merit review)

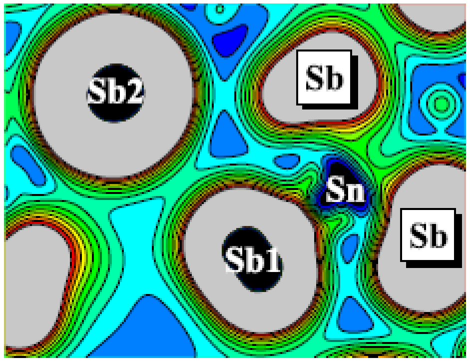
Heavy band / light band mixture for high *ZT* completed:

- Collaboration with California Institute of Technology for part.
- Showed that high thermopower and conductivity can be obtained together from mixture of heavy and light bands at band edge.
- Robust against disorder – studied La-Te and various Zintl type Sn-Sb phases.

Frontier charge showing origin of light / heavy bands at valence band edge



Some phases based on $SnSb_4$ clusters that were investigated



Current Year Accomplishments (2)

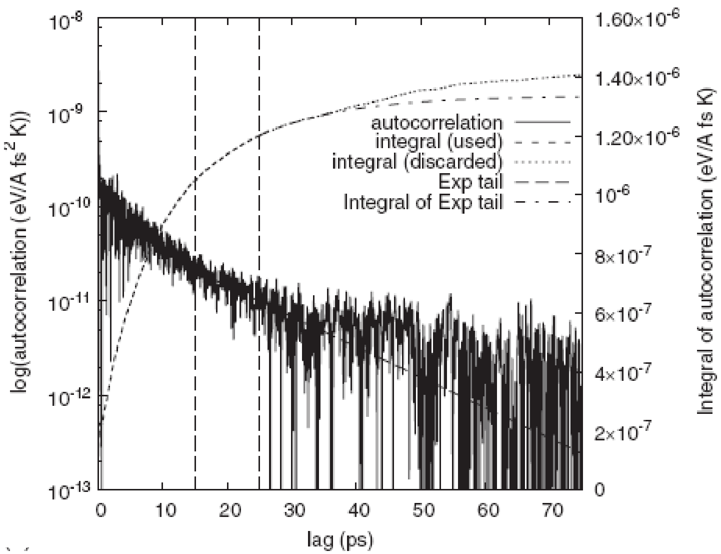
(since last year's merit review)

Thermal conductivity of filled skutterudites:

- Collaboration with Naval Research Laboratory
- First principles calculations, modeling and Green-Kubo theory.

$$\kappa = \frac{V}{3k_B T^2}\int_0^\infty \langle \mathbf{q}(t)\cdot\mathbf{q}(0)\rangle dt,$$

$$\mathbf{q}V = \frac{1}{2}\sum_{i>j}(\mathbf{v}_i + \mathbf{v}_j)\cdot\mathbf{F}_{ij}\mathbf{r}_{ij}^0$$



Autocorrelation (log scale)

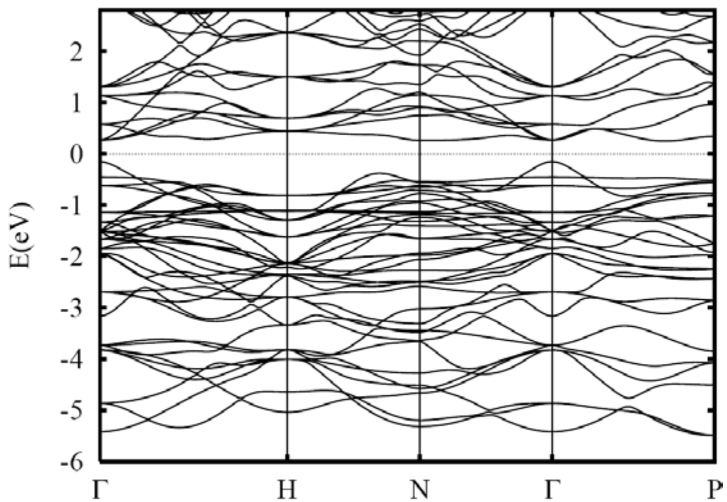
Key Findings:

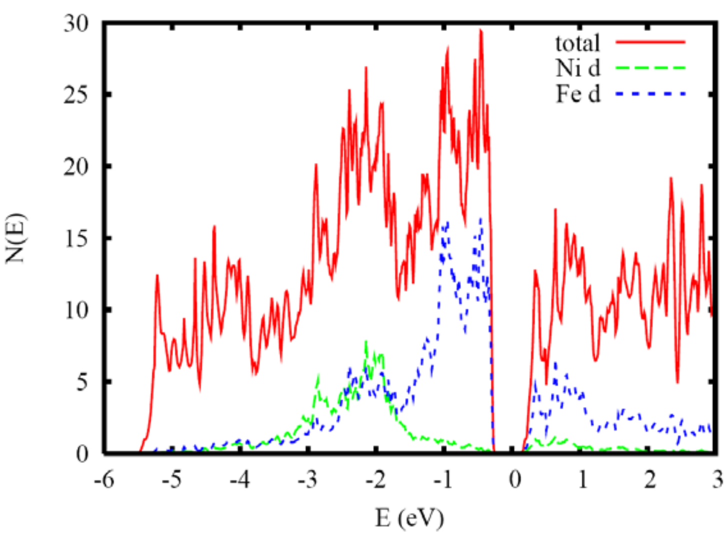
- Quantitative thermal conductivity for filled skutterudite.
- Rare earth vibration is soft but rather harmonic
- Thermal resistance not from special interactions of rare earth chemistry.
- Rare earth is not critical – vibrational frequency is – Ca/Sr can work.

Current Year Accomplishments (3)

(since last year's merit review)

Results suggested investigation of a new material: (Ca,Sr)$Fe_{4-x}Ni_xSb_{12}$





First principles supercell and virtual crystal calculations for $CaFe_3NiSb_{12}$ & $SrFe_3NiSb_{12}$.

- Note opening of band gap and heavy / light band feature at both conduction and valence band edges (both p-type and n-type).
- Mass enhancement related to Ni-Fe differences.
- Very favorable results for thermoelectric material ➔ expected performance when optimized for doping level is equal to or better than best current multiple filled skutterudites at lower cost.

Accomplishment: Material Cost (4)

Bi_2Te_3:

- Bi: very cheap
- **Te: ~$100/lb limited supply, price fluctuations**

PbTe, LAST:

- **Pb: very cheap, environment?**
- **Te: ~$100/lb limited supply, price fluctuations**

Filled skutterudite, RCo_4Sb_{12}:

- ***R*: La, Ce (<$10/lb), others expensive supply?**
- **In: ~$300/lb**
- Co: ~$20/lb
- Sb: ~$3/lb
- Fe: very cheap (<$0.3/lb)

$(Ca,Sr)Fe_{4-x}Ni_xSb_{12}$:

- Ca and Sr in compounds are very cheap and safe.
- Eliminated rare earth elements.
- Replaced Co (~$20/lb) by half the quantity of Ni (~$12/lb).
- Results indicate similar if not superior performance.

Goal is high performance material at acceptable (low) cost.

Collaborations

- California Institute of Technology
  - Elucidation of heavy / band light band approach for high *ZT* involving theory at ORNL and experimental data from CalTech.
- Naval Research Laboratory
  - Thermal conductivity of skutterudites based on first principles calculations at ORNL and molecular dynamics at NRL.
- Massachusetts Institute of Technology
  - S^3TEC center - thermoelectric power generation technology.
  - MIT very synthesis oriented → good avenue for transitioning results.
- General Motors
  - Discussions/communications.
  - Did calculations on PbTe dynamics in response to a request from GM.
- Oregon State
  - Nanostructured thermoelectrics – intergrowth compounds.
- Corning
  - Interaction on oxide thermoelectrics.

Proposed Future Work – FY11

- Complete transport calculations and study dynamics of (Ca,Sr)$Fe_{4-x}Ni_xSb_{12}$ including disorder and in relation to conventional rare earth - Co based filled skutterudites.
- Look for related compounds.
- Continue efforts on Zintl phase thermoelectrics.
- Study lower cost oxide thermoelectrics to find combination of high performance and cheap available components.
- Establish optimization strategies for improving the thermoelectric performance of existing materials.

Summary: Thermoelectrics Theory and Structure

- Project addresses key barriers to the implementation of thermoelectric waste heat recovery: (1) materials performance, (2) need for p-type and n-type material, (3) need for low cost materials → *overcoming these barriers can yield 10% fuel savings*.
- Identified trends, and established design rules for thermoelectric materials – results published in peer reviewed technical journals.
- Found a low cost skutterudite thermoelectric with excellent potential – need to complete transport calculations for this material.