Recent Theoretical Results for Advanced Thermoelectric Materials

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Today's Menu:

- PbTe / PbSe
- Skutterudites
- Mo_3Sb_7

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- Hsin Wang (ORNL)
- D. Ray Johnson

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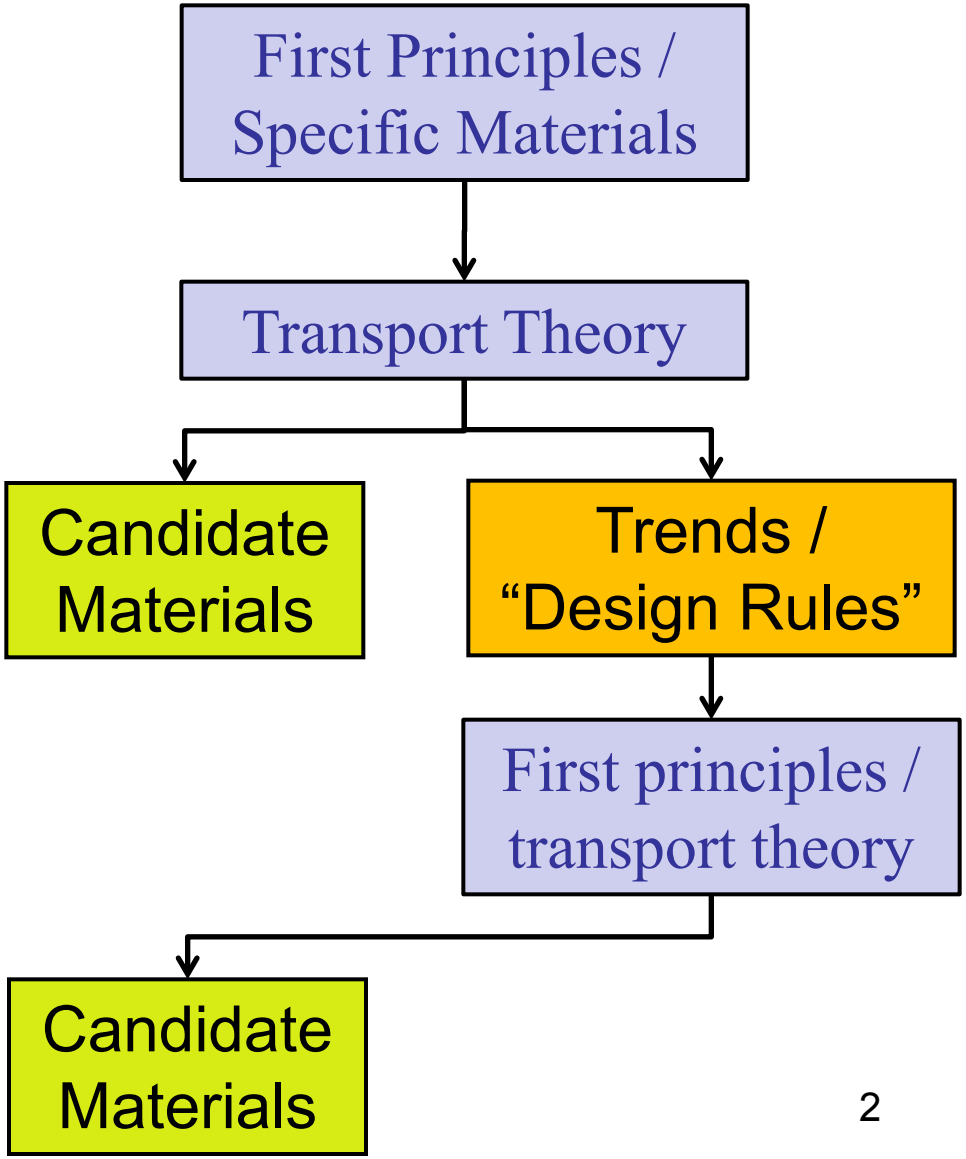
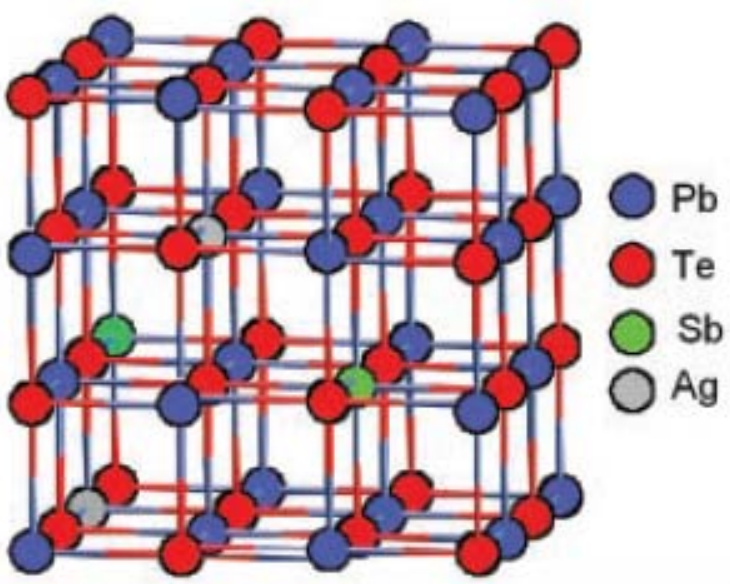
Approach

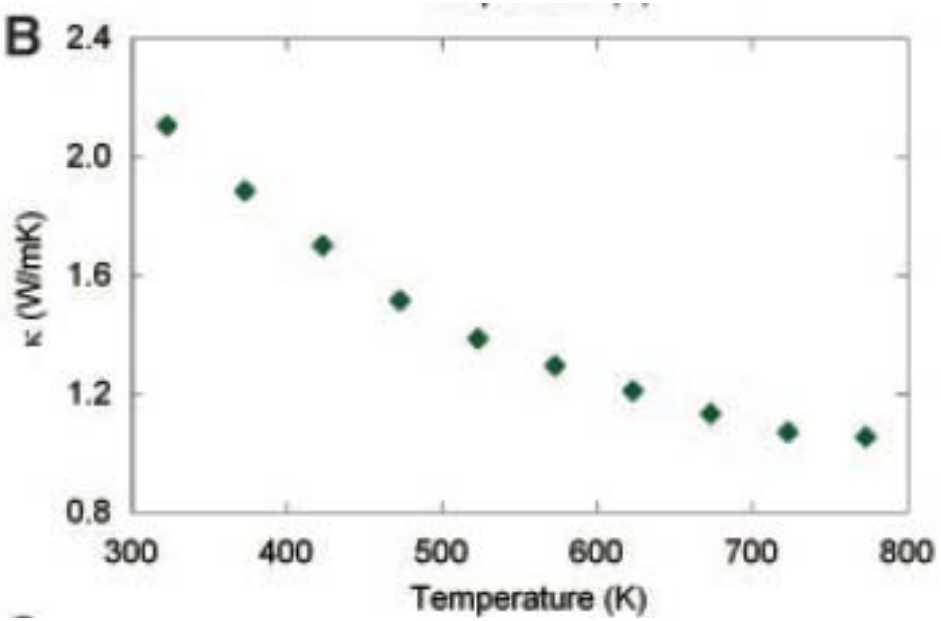
- First principles calculations for electronic and vibrational properties.
- Boltzmann transport theory ➔ electrical transport quantities, especially thermopower, $S(T)$.
  - Done using ORNL developed transport code: BoltzTraP.
- Focus on materials that promise potential low cost.
- Focus on 3D materials.



PbTe

- 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).

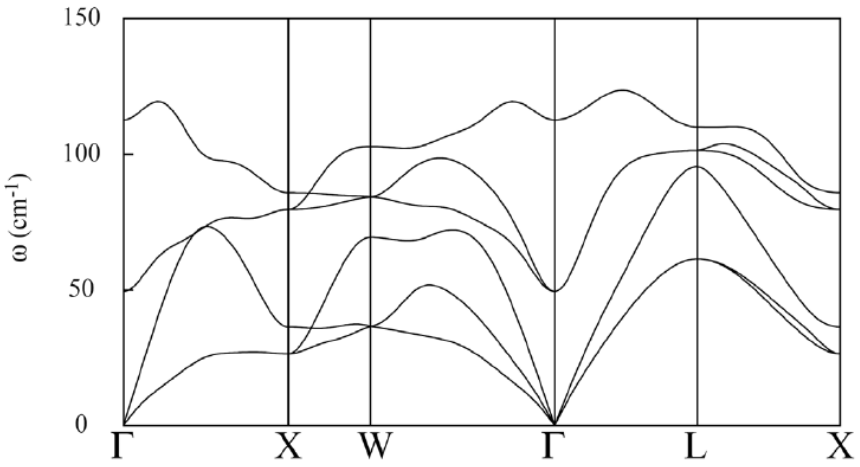




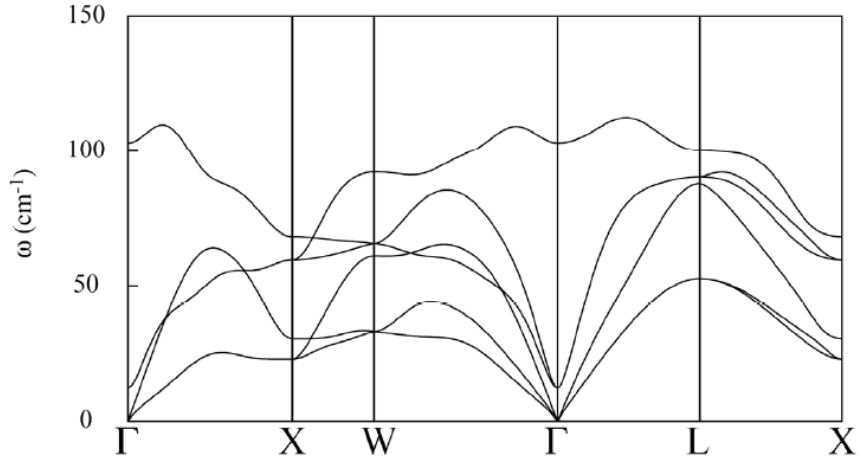
$Ag_{1-x}Pb_{18}SbTe_{20}$, Kanatzidis Group, Science, 2004.

Phonons in PbTe

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).

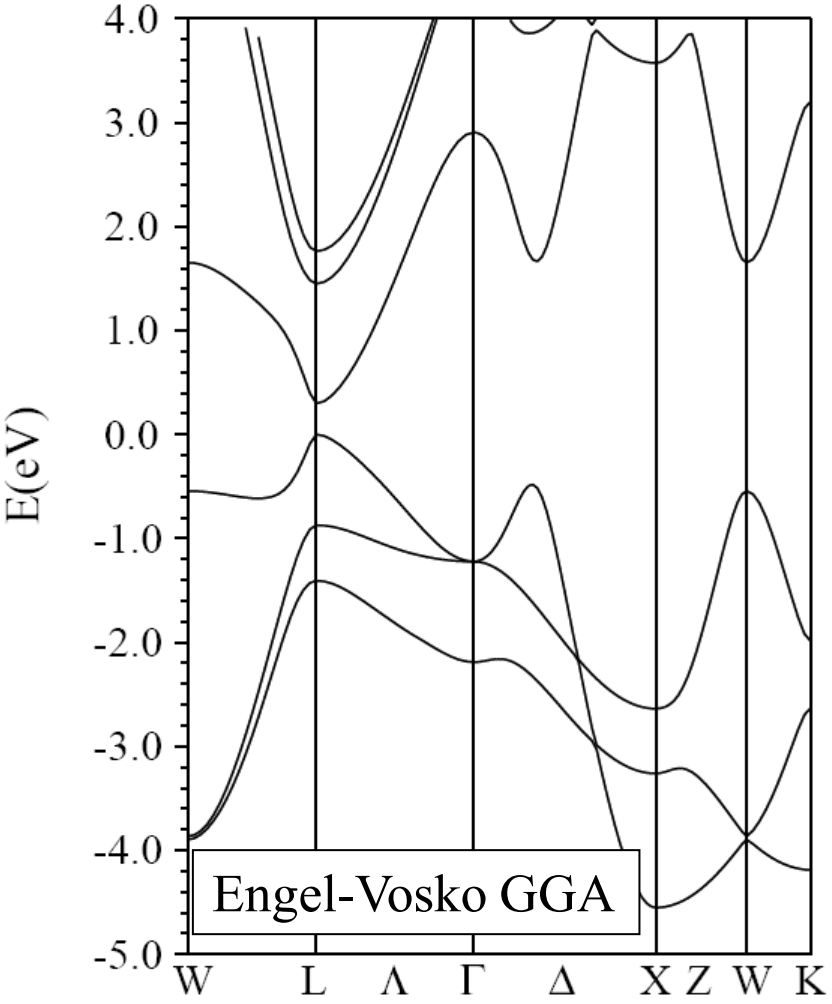
Key Points:

PbTe is near ferroelectricity.

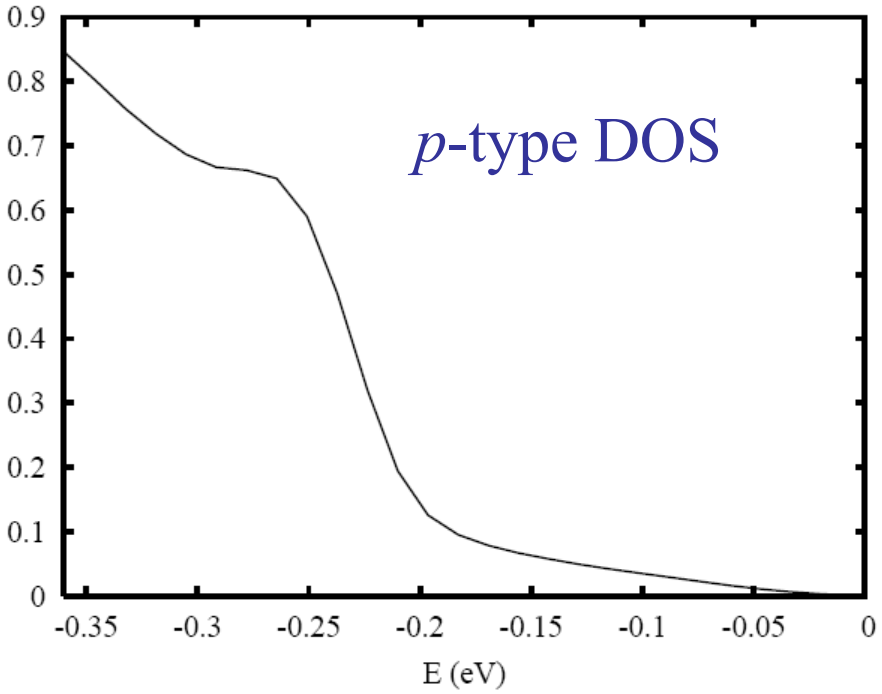
c.f. GeTe which is ferroelectric when undoped – basis of TAGS (GeTe – AgSbTe).

PbTe Band Structure

- First principles calculations

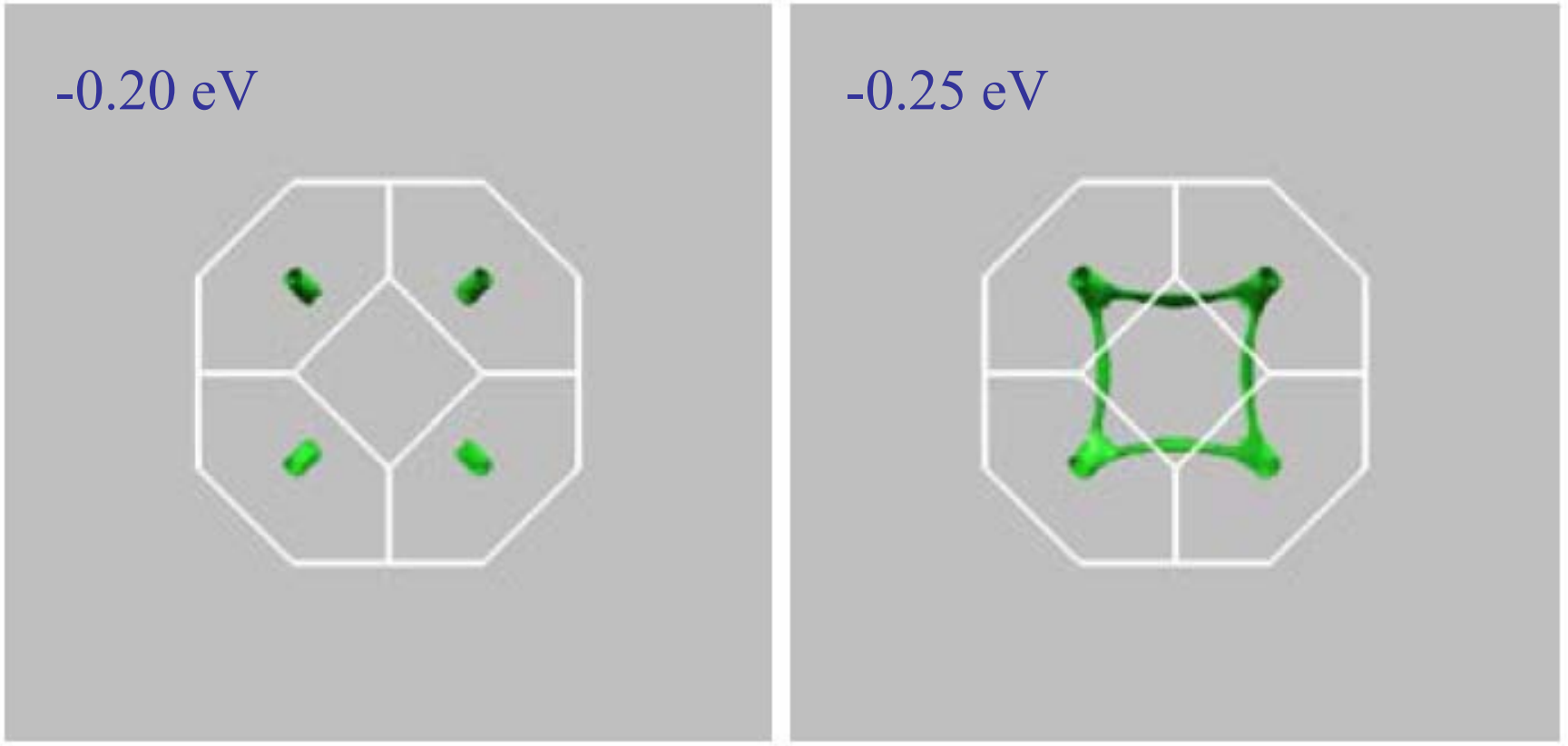


- Light mass non-parabolic band structure near the band edges.
- Becomes much heavier away from the band edge.

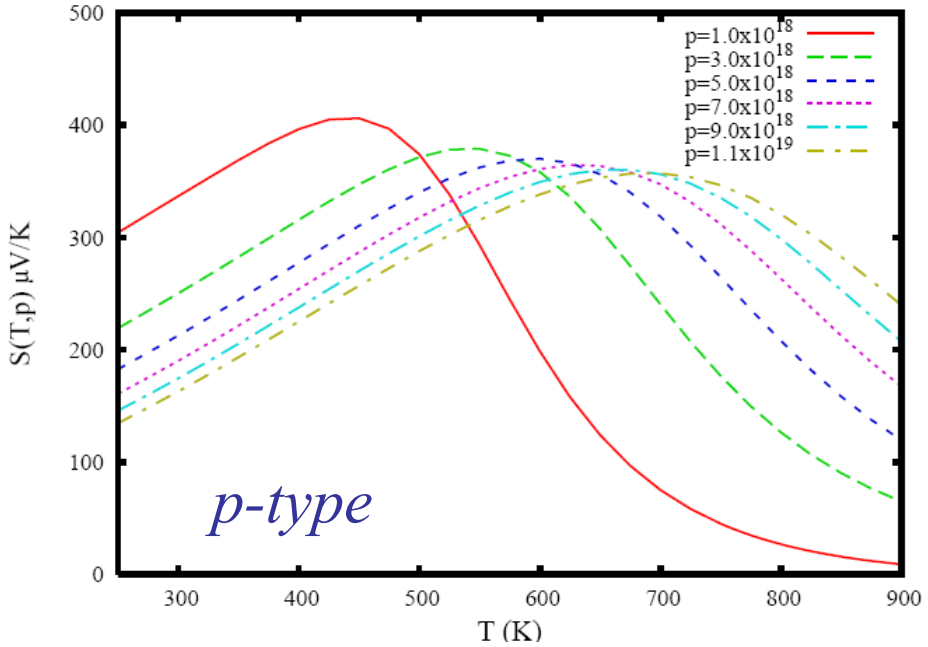


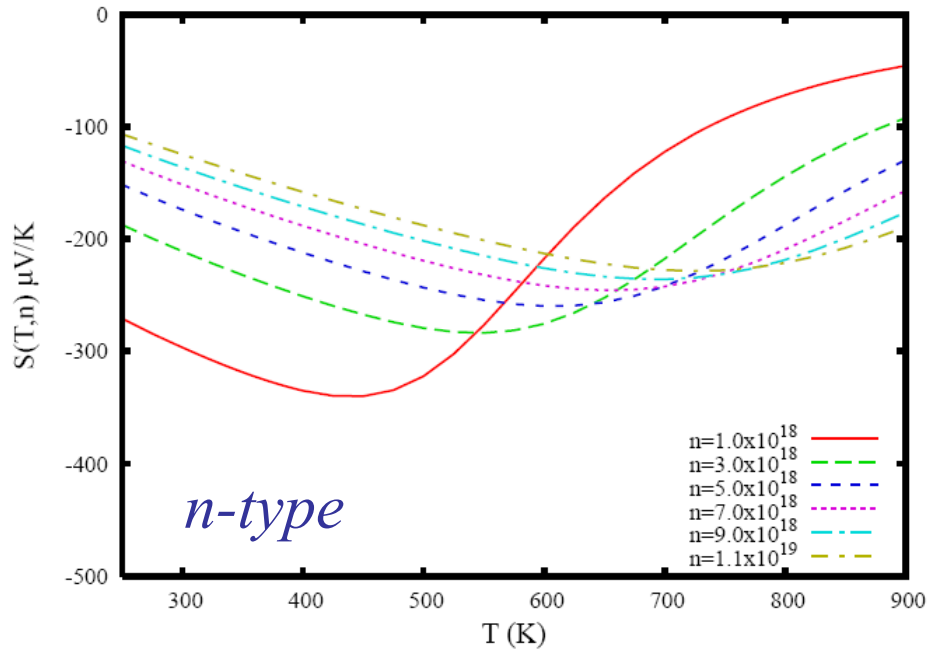
Origin of High DOS below 0.2 eV

- Hole pockets at the L-points become connected along ~001 (not symmetry lines).



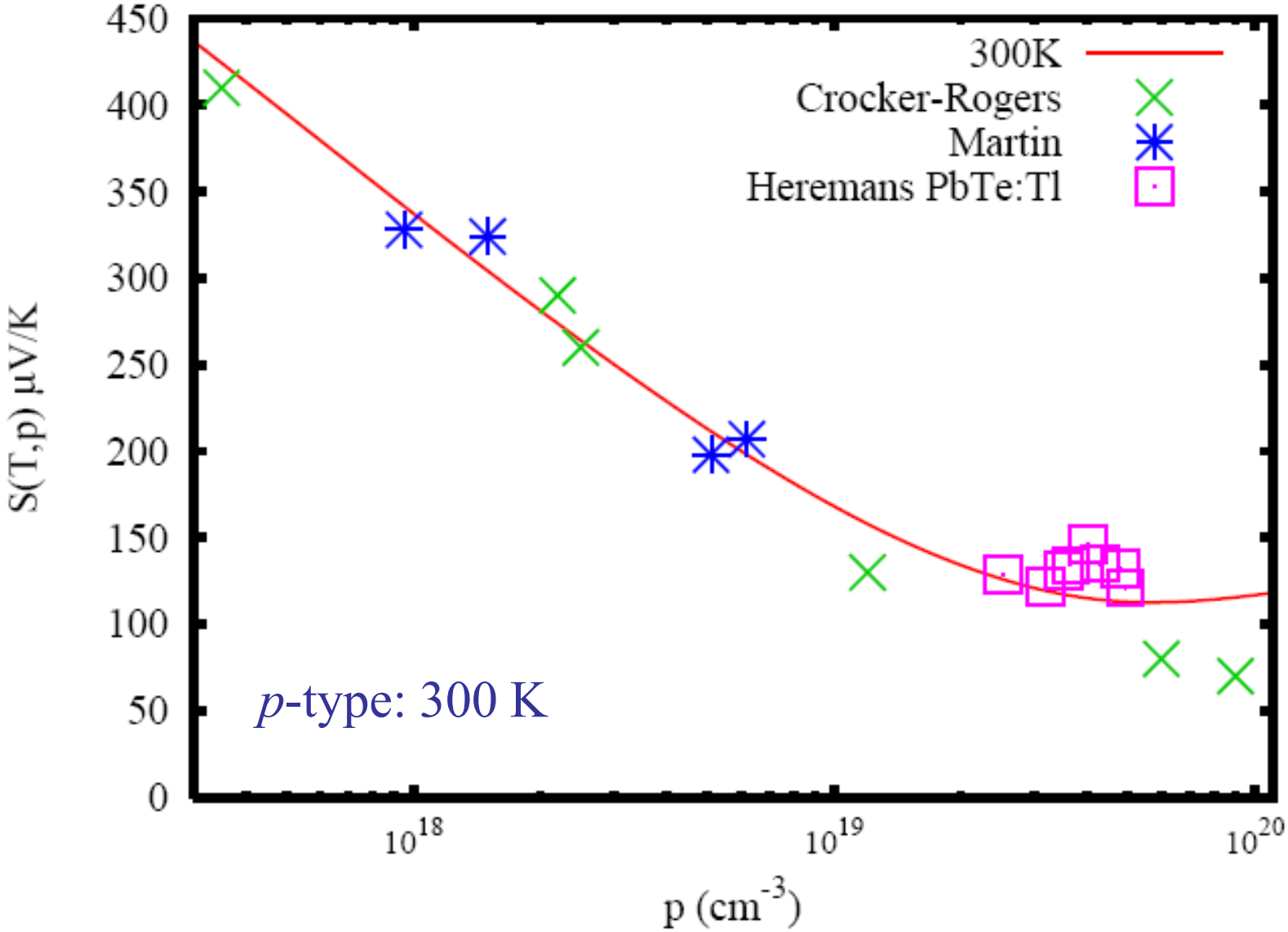
PbTe Thermopower





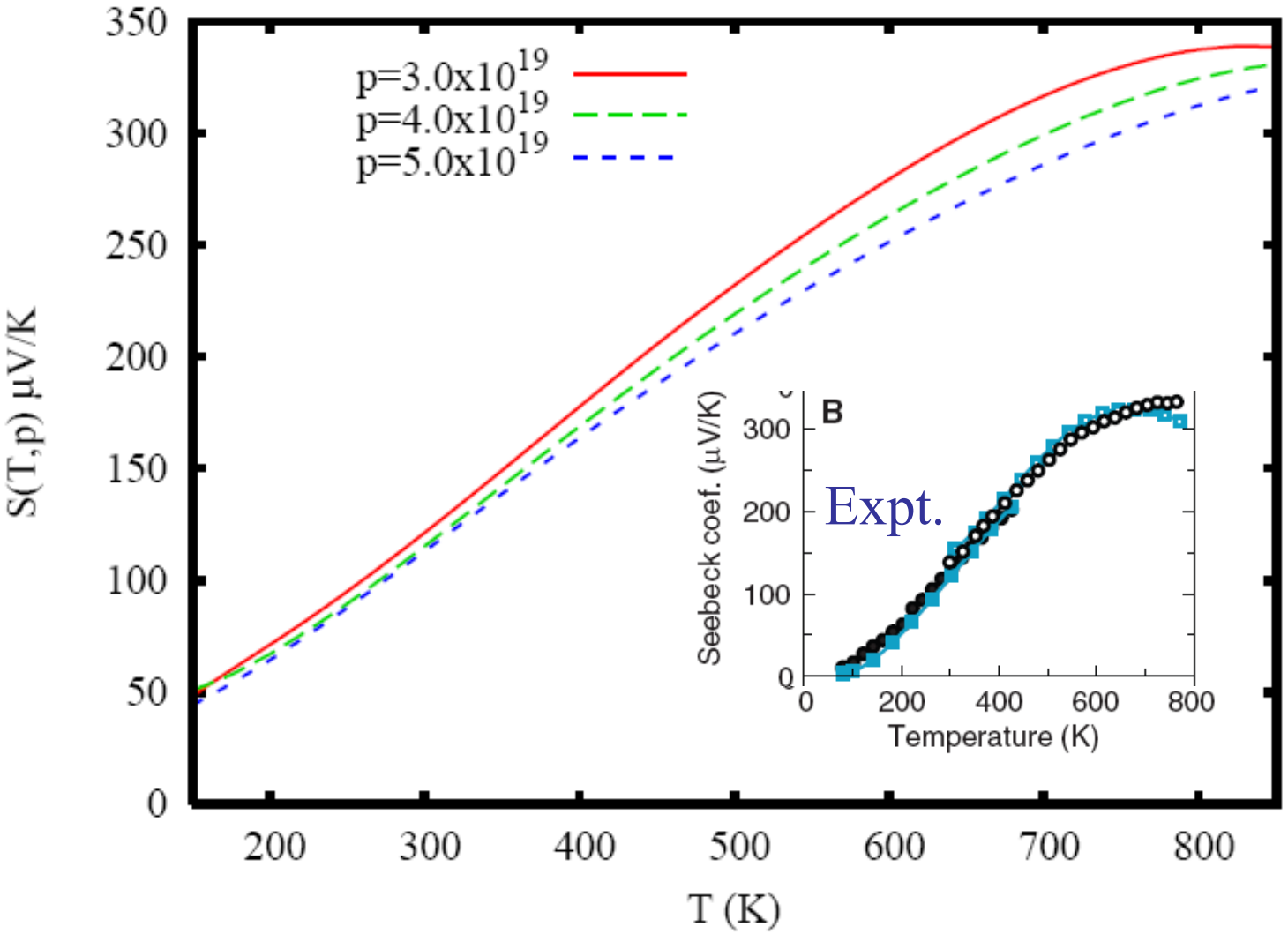
- Boltzmann Transport Calculations (constant scattering time approx.).
- Enhanced thermopower at high doping levels and high temperatures, especially for *p*-type.
- Reflects non-parabolic bands, which become heavier away from the band edge → sampled more in thermopower at high *T* and *p*.
- Very high *p*-type doping should be favorable for *ZT* – solubility limit of standard dopants is a problem.

Comparison with Experiment



Enhancement at high *p*: agrees quantitatively with Hereman's data for PbTe:Tl, but not older Crocker-Rogers data (doping?)

T-Dependence at High *p*-Type Doping Levels

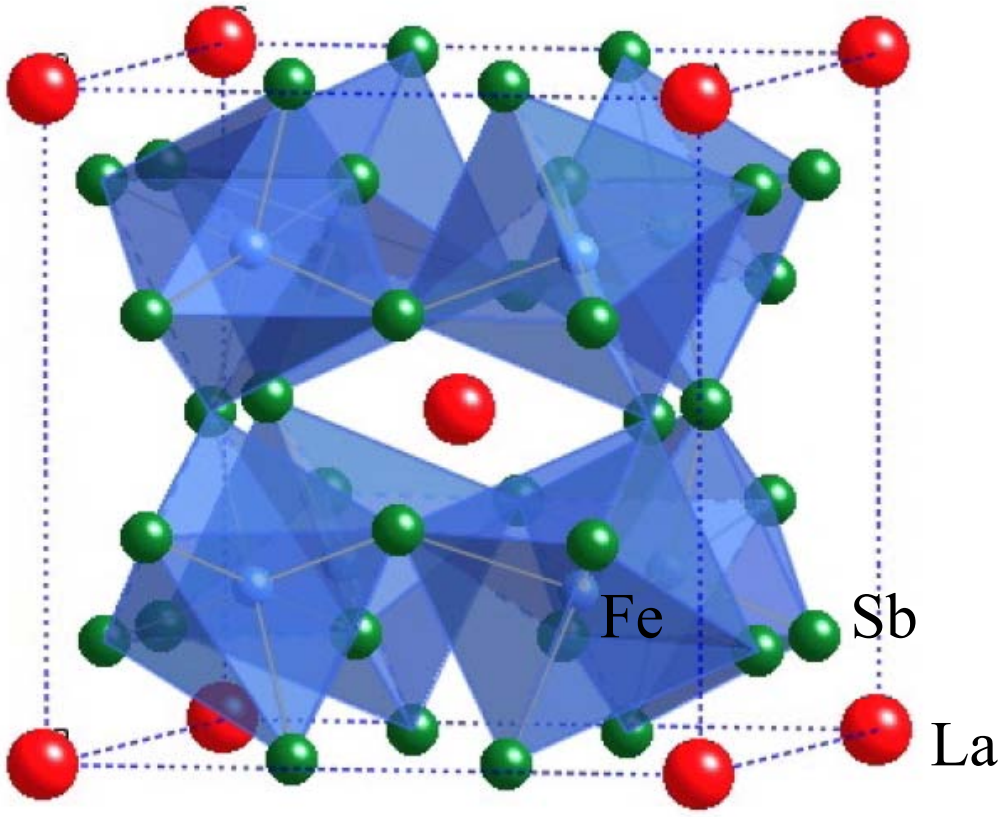


Phys. Rev. B **81**, 195217 (2010)

Similar to PbTe:Tl experimental data – may be possible to get high *ZT* without Tl. --- We also find behavior indicative of high *ZT* in p-type PbSe especially at elevated *T*.

High ZT Zintl Phases

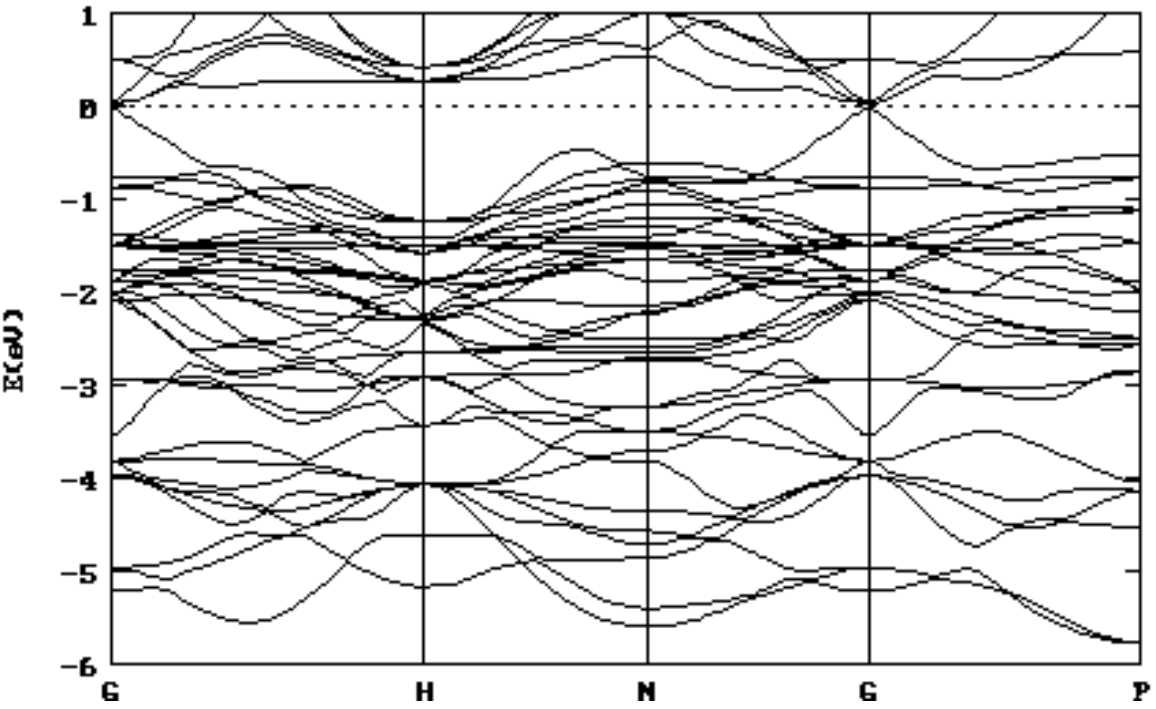
- These are generally thermoelectric materials with an anionic metallic/covalent network stabilized by cations.
  - $La_y(Fe,Co)_4Sb_{12}$
  - $Ba_8Ga_{16}Ge_{30}$
  - $CsBi_4Te_6$
  - Zn_4Sb_3
  - $Yb_{14}MnSb_{11}$
  - …



Filled skutterudite (Sales)

SKUTTERUDITE BAND STRUCTURE

$CoSb_3$ ($IrSb_3$ is similar):



← Light non-parabolic (linear) valence band.

- Heavy degenerate c.b. highly favorable

Kinetic Transport:

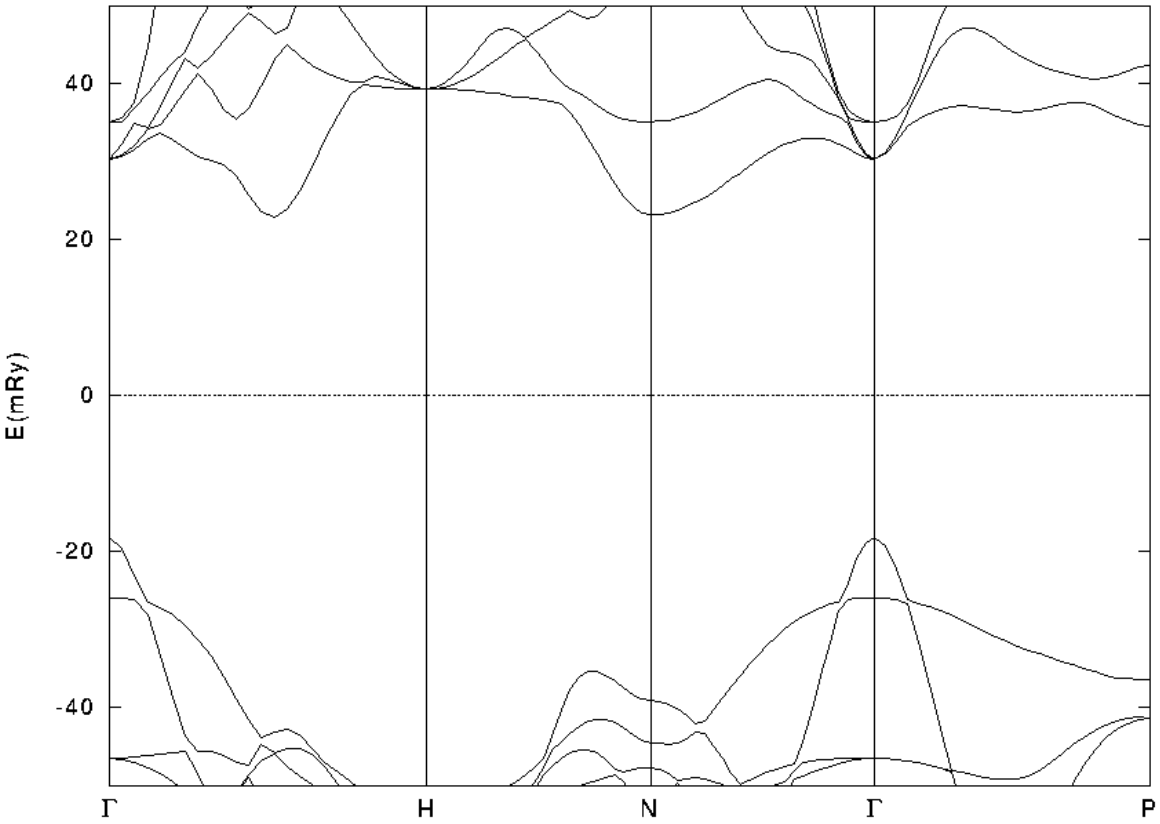
- parabolic: $S/T \propto n^{-2/3}$
- linear: $S/T \propto n^{-1/3}$

Band structure not favorable for p-type TE.
Very good for n-type.

RARE EARTH FILLED SKUTTERUDITES

- Antimonides:
  - Strongly reduced κ_l (~15 mW/cmK)
  - High S and high ZT in $La(Fe,Co)Sb_{12}$, $CeFe_4Sb_{12}$ and others.

$La(Fe,Co)_4Sb_{12}$



Light band is pushed down near to heavy band onset.

➔Mechanism for high S

➔La vacancies scatter

Multiple heavy bands for *n*-type

Light – Heavy mixture for *p*-type

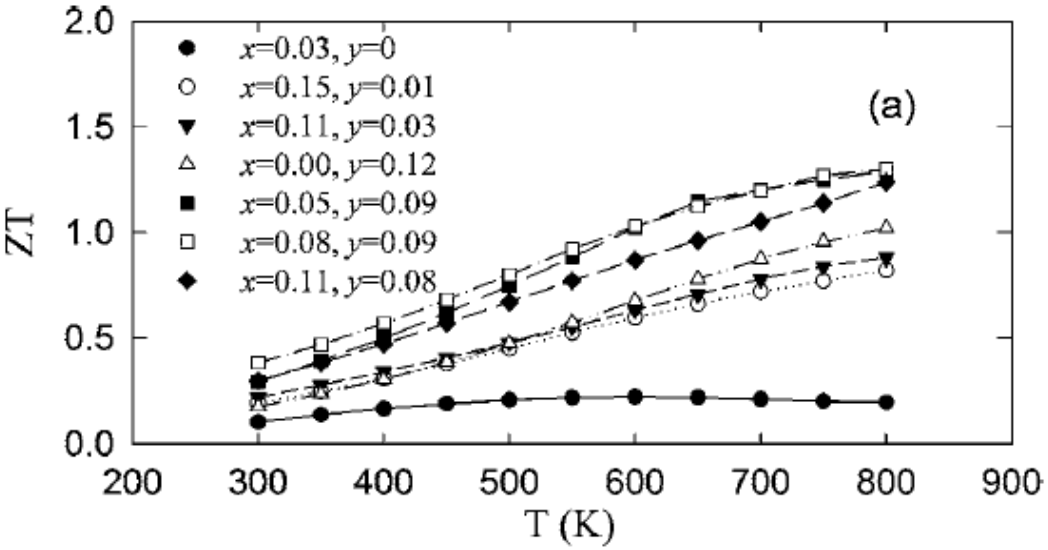
Recent Experimental Results on Skutterudites

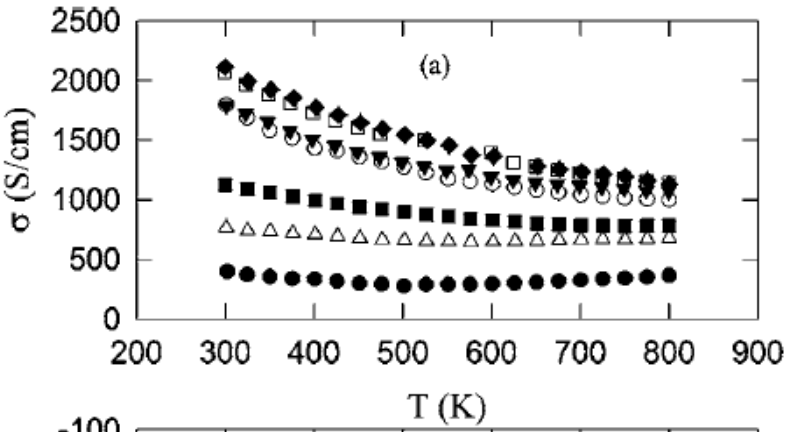
e.g. X. Shi et al., APL (2008): $(Ba_xYb_y)Co_4Sb_{12}$:

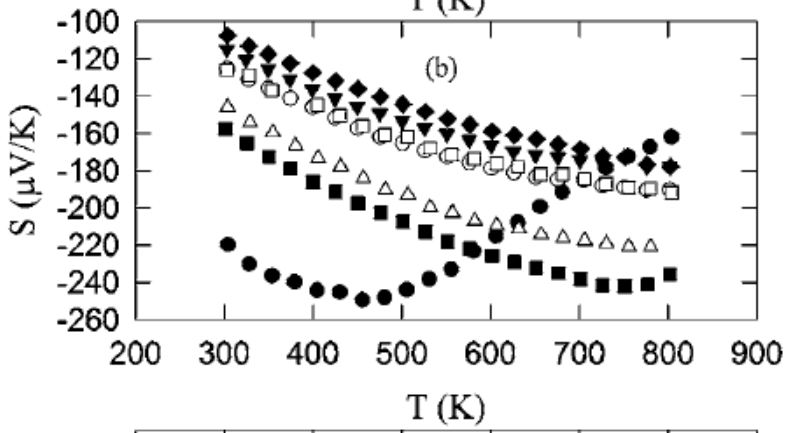
- Multiple filling with different atoms strongly reduces lattice thermal conductivity.
- Evidence for bi-polar conduction with low filling. Filling and doping level are connected.

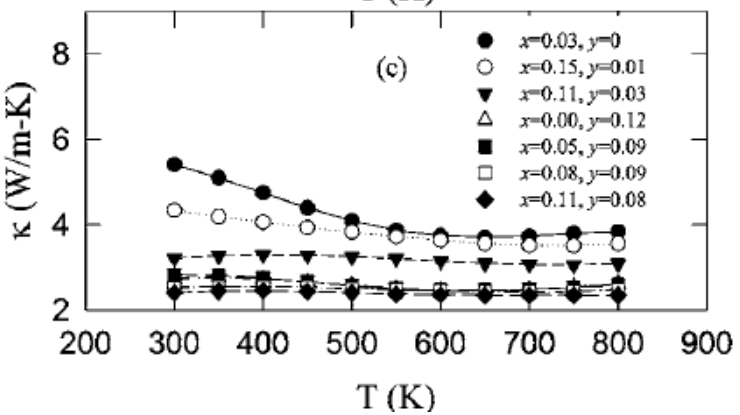
Is there a way to have high, possibly multiple filling, and at the same time high S(T)?

Can p-type ZT be improved?

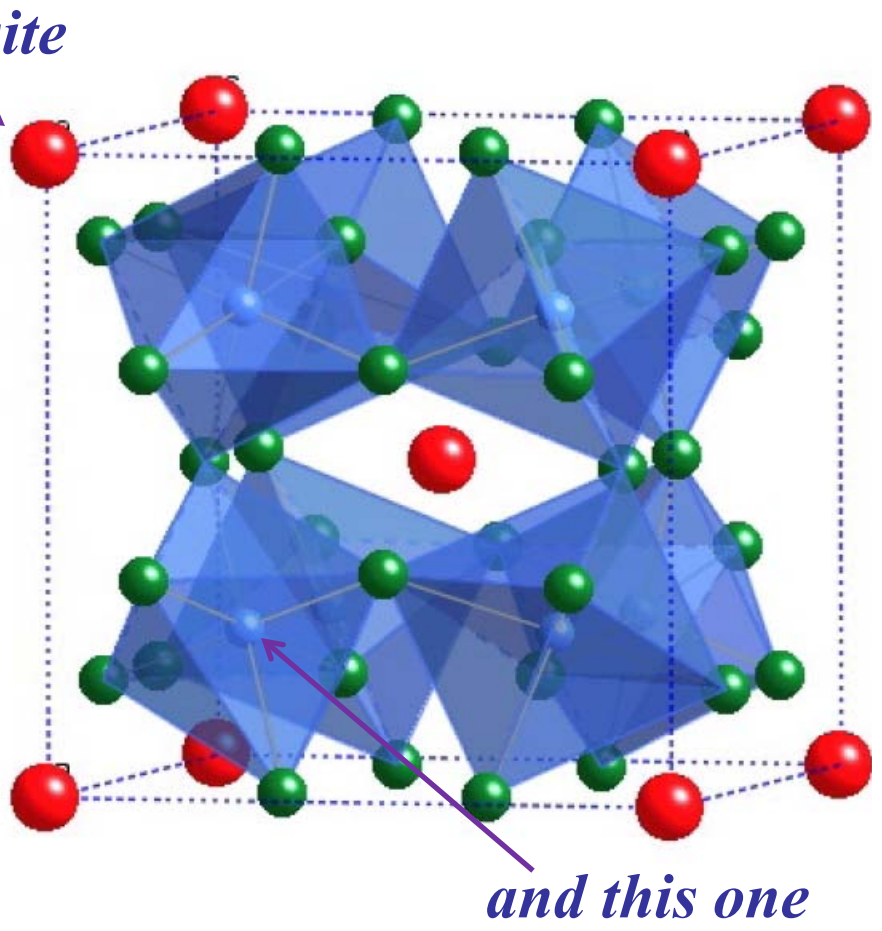








Can we use the transition element?



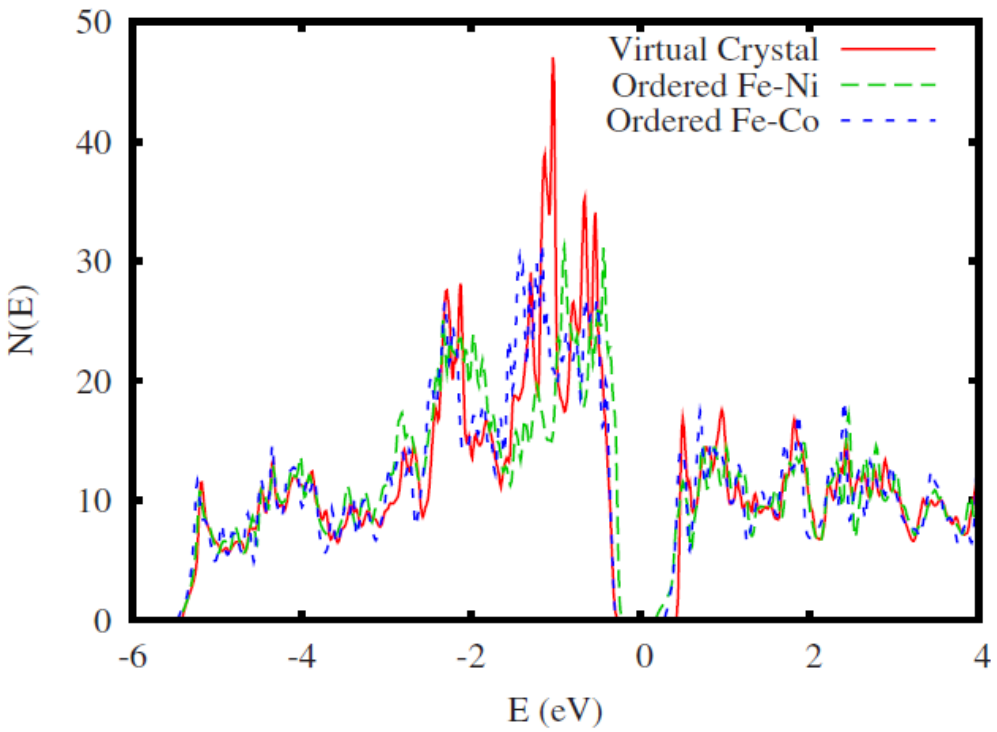
We want to control gap opening, lattice thermal conductivity, and carrier concentration.

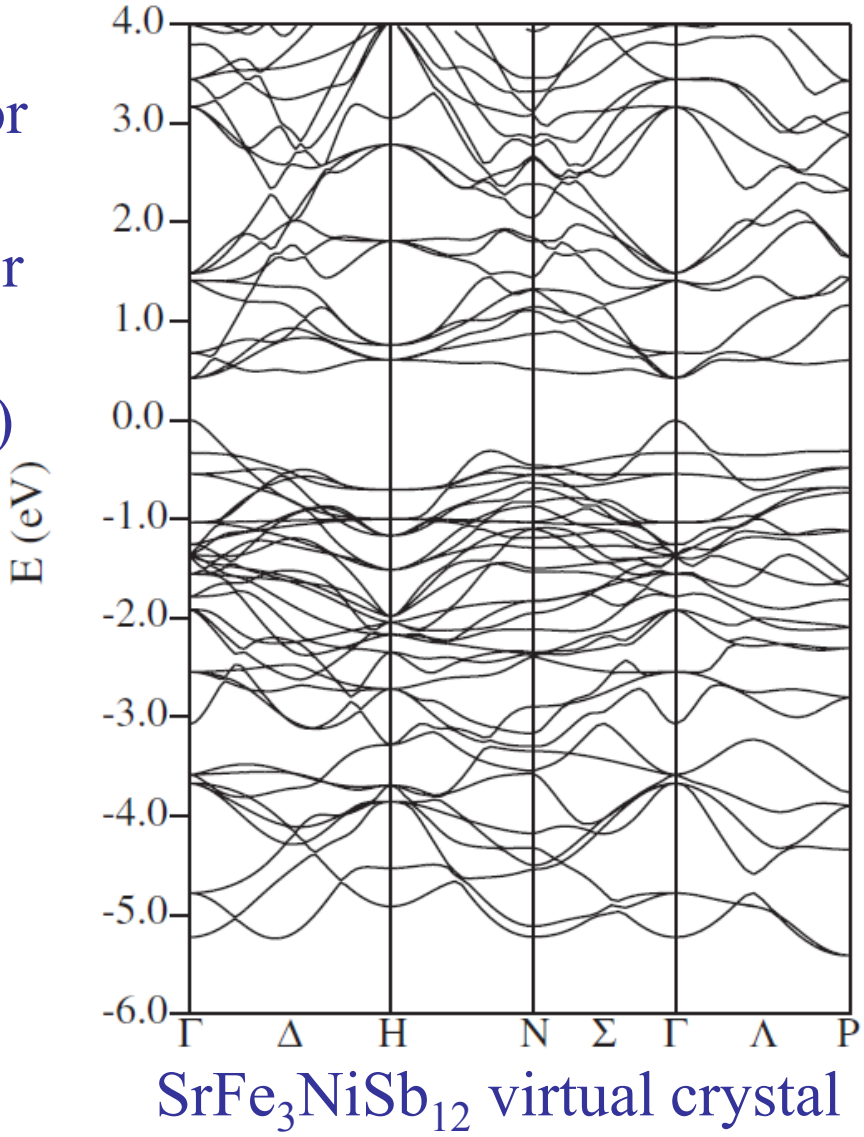
- Replace Co by $Fe_{1-y}Ni_y$ or perhaps $Fe_{1-y}Co_y$ with y selected for a lower electron count
- Use a high filling fraction of electro-positive elements.
  - *e.g.* $Ae_xFe_{4-y}Ni_ySb_{12}$
  - Low cost is desirable.

High filling ➔ large gap opening and low thermal conductivity
Control of carrier concentration on metal site ➔ high thermopower

Band Structure

- *Ae* filling with Fe and Ni opens a sizable gap and yields heavy/light valence band structure ➔ favorable for ***both*** *p*- and *n*-type.
- Mitigates bi-polar reduction of $S(T)$ for *n*-type.
- Ni works like Co (Ni is much cheaper)

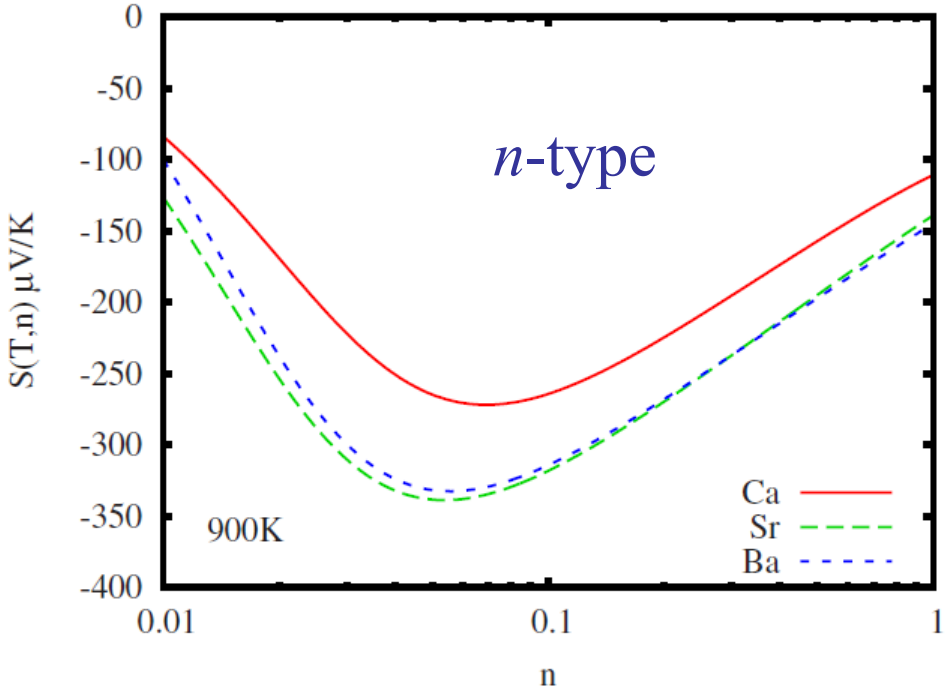


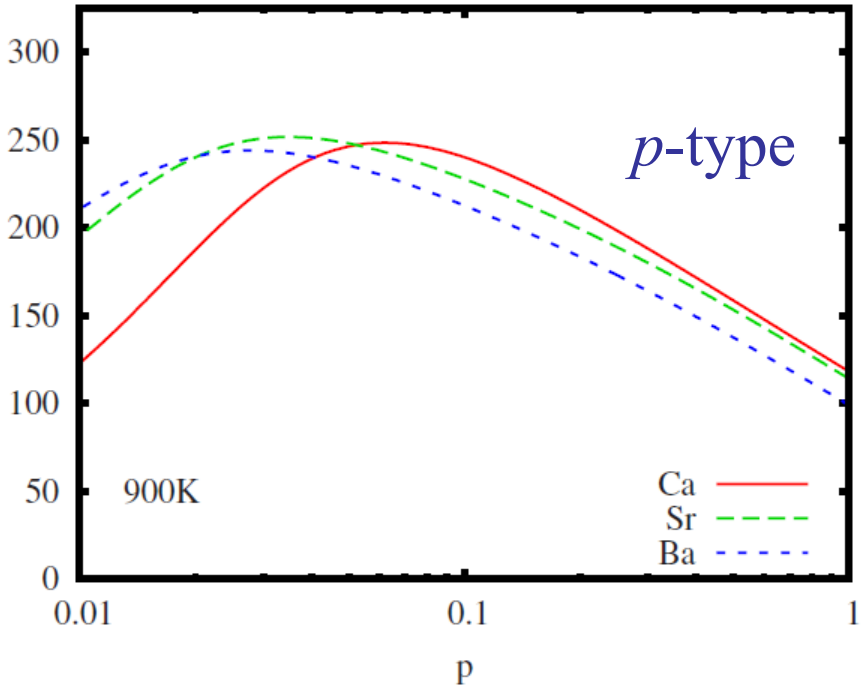


$SrFe_3NiSb_{12}$ virtual crystal

Transport

- Best currently known skutterudites are better for n-type than p-type.
- We find that they can be good thermoelectrics, including p-type.
- The thermopower is enhanced in filled skutterudites using Fe-Ni instead of Co. This is connected also with the filling.

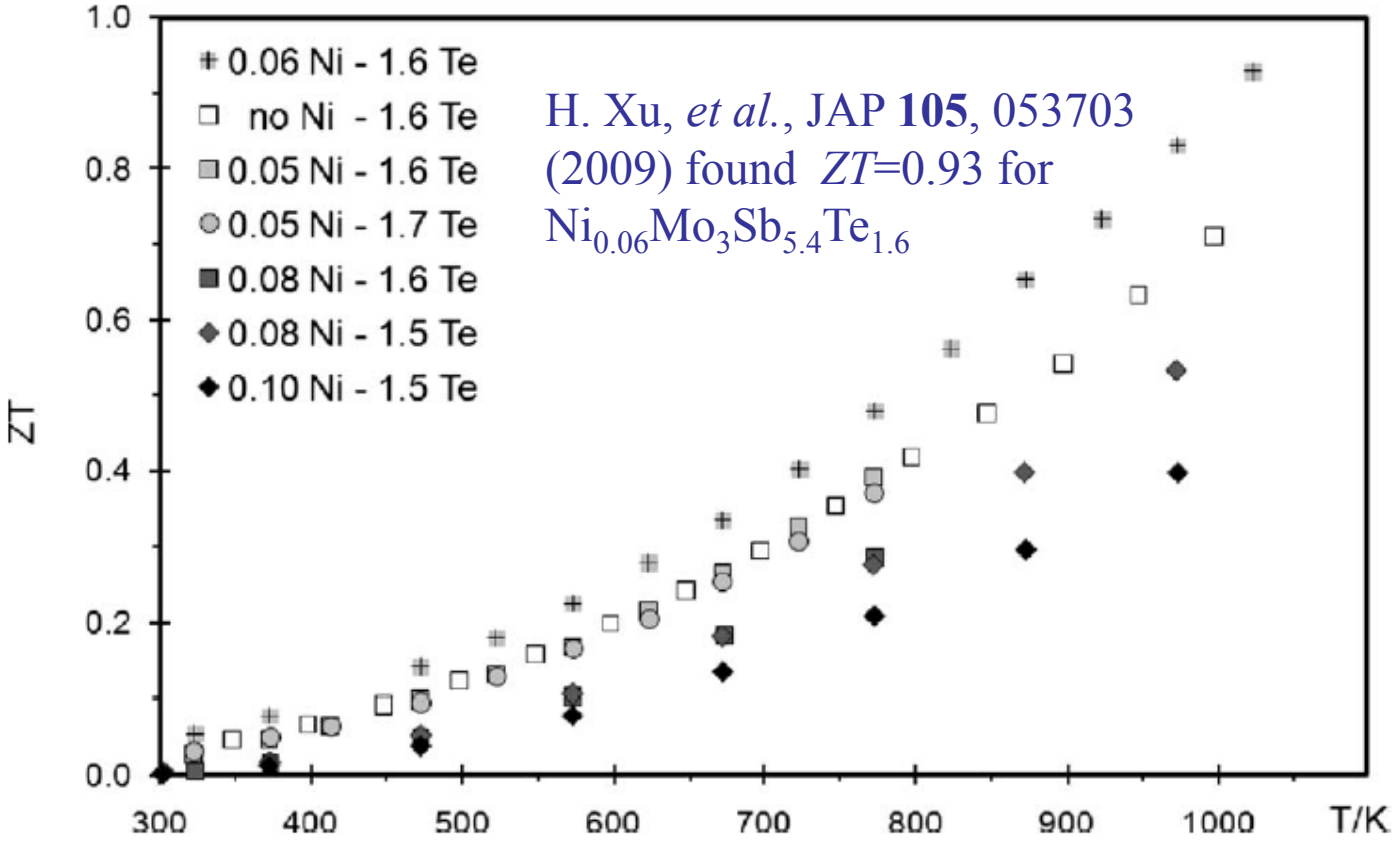




- Phonon calculations (not shown) ➔May be possible to mix alkaline earths to lower thermal conductivity.

Mo_3Sb_7

- Cubic p-type thermoelectric material based on relatively inexpensive elements.



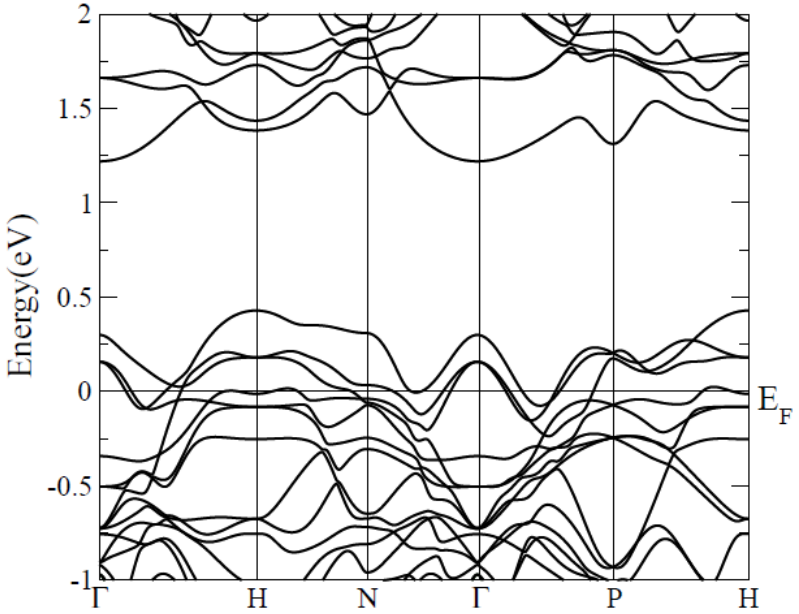
H. Xu, *et al.*, JAP **105**, 053703 (2009) found ZT=0.93 for $Ni_{0.06}Mo_3Sb_{5.4}Te_{1.6}$

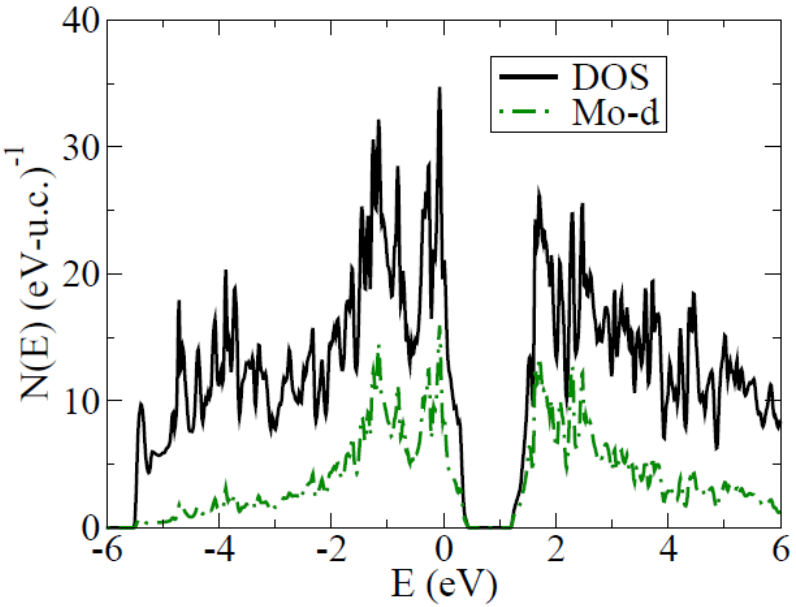
Is this optimized?

Can high ZT be obtained without Te?

FIG. 9. Thermoelectric figure of merit ZT of $Ni_yMo_3Sb_{7-x}Te_x$.

Electronic Structure





Stoichiometric Mo_3Sb_7 is a metal due to electron deficiency. Band edge is three electrons per formula unit higher.

Two strategies have been followed:

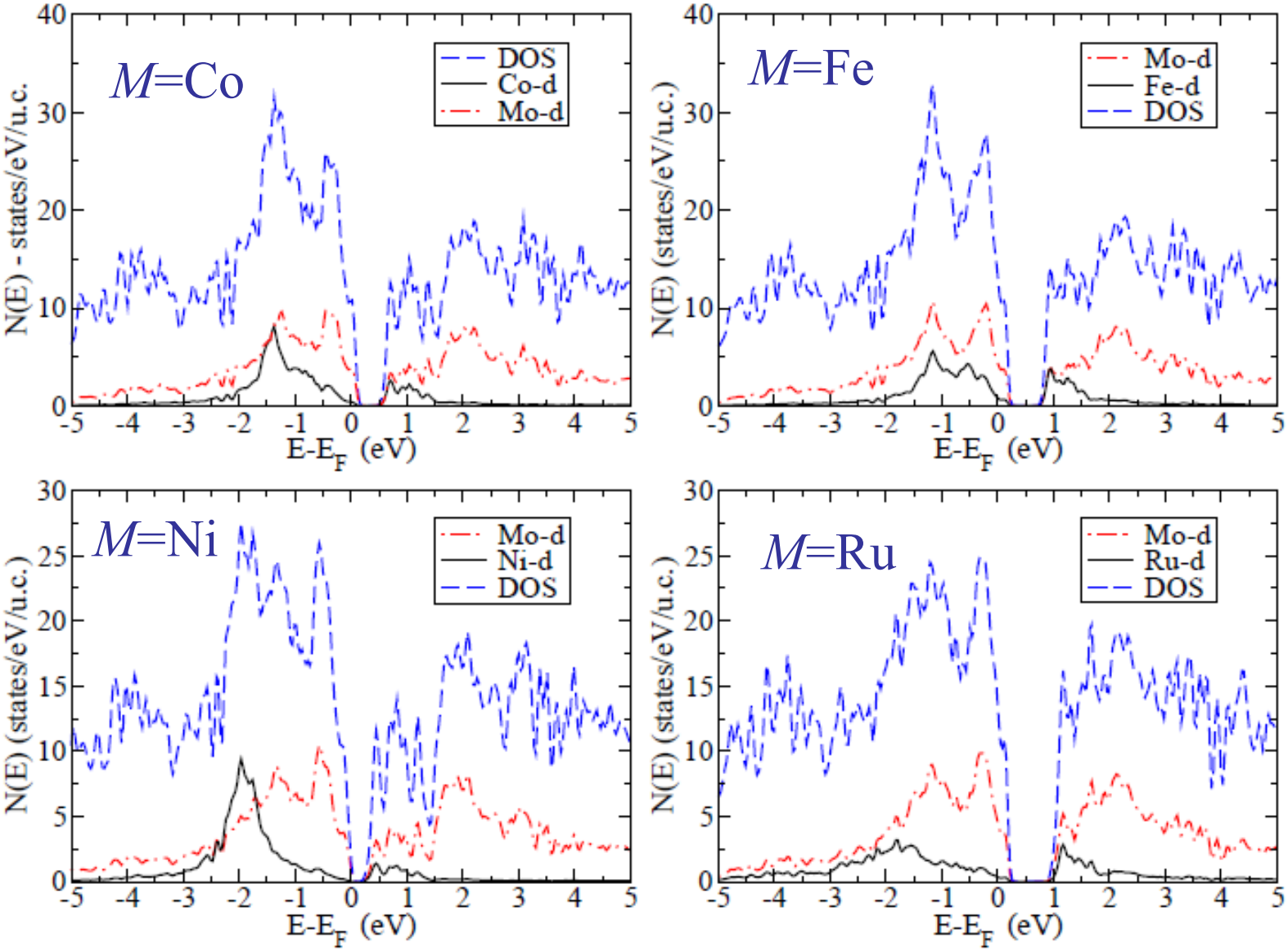
(1) Alloying Sb with Te.

(2) Alloying Mo with Ru, Fe, Ni or Mn

Issue in both cases is solubility limit.

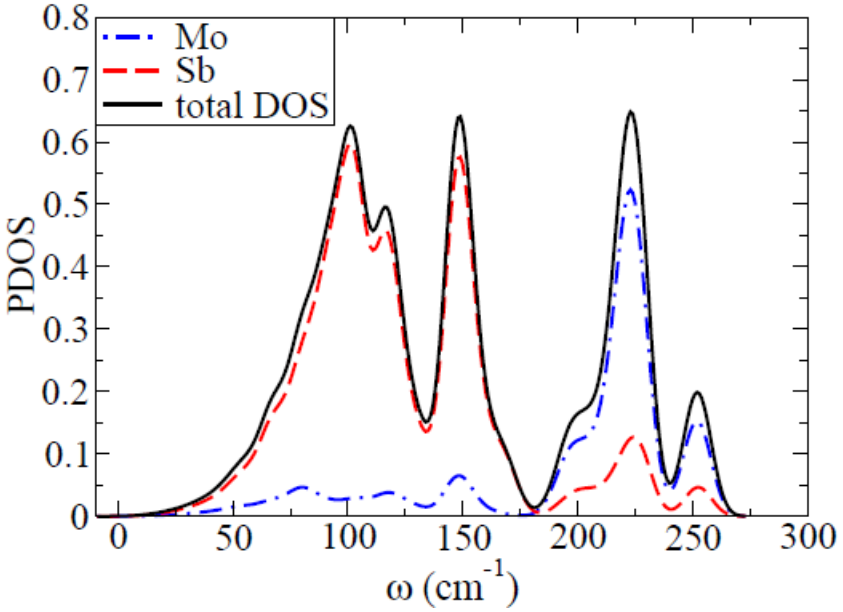
We did virtual crystal and supercell calculations in order to address the doping dependence, as well as phonon calculations.

Supercell Electronic Structures – Mo_5MSb_{14}



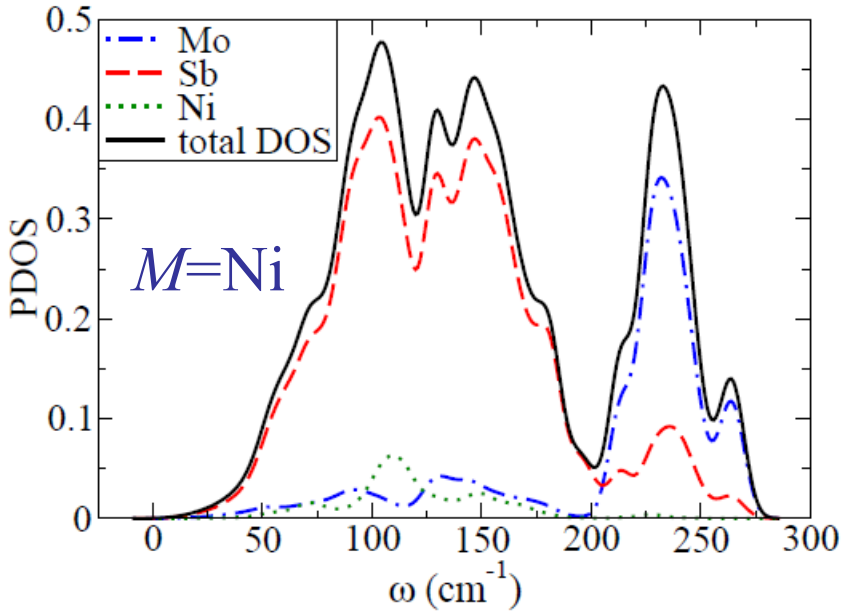
Fe and Ru show a DOS that is more coherent with Mo than do Ni or Co.

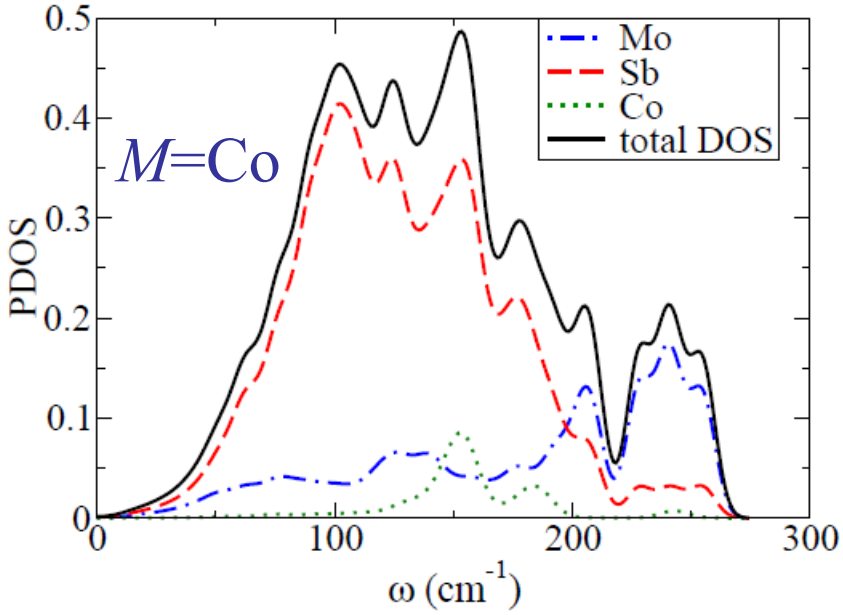
Vibrational Properties



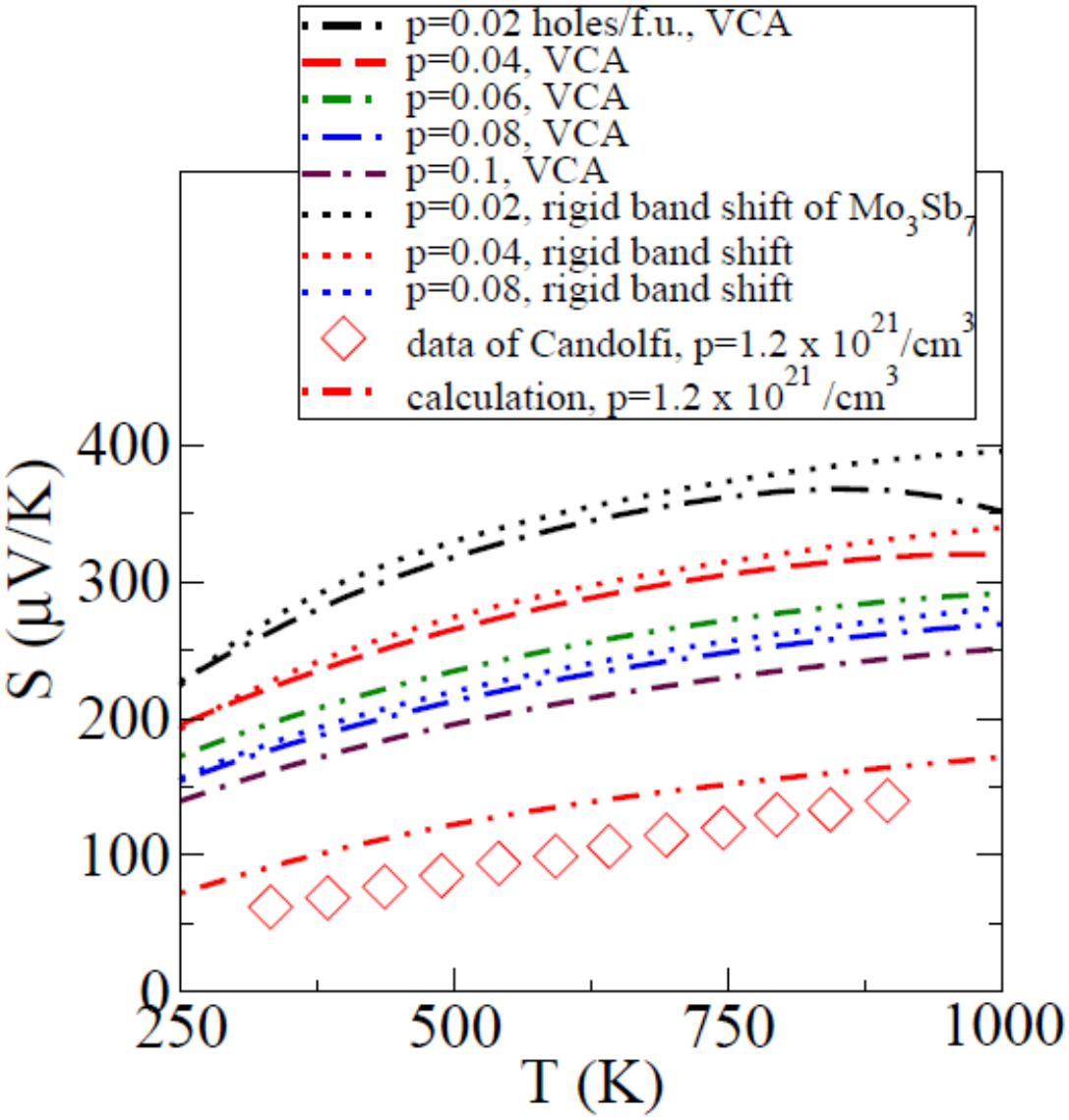
Pure compound – acoustic type modes extend to ~100 cm^{-1} – these are the phonons that we need to scatter to lower lattice thermal conductivity.

Fe, Co and Ni modes are at high frequency, though there is some mixing – probably a minor effect.





Transport: p-type Thermopower



- Calculated $S(T,p)$ in relation to experiment implies that lower carrier concentrations will yield higher ZT – neither Te nor metal doped material are at their optimum carrier concentrations.
- Issue is solubility limit of metal on the Mo site.
- The structure of the densities of states suggest that co-doping with Fe and Co or Ni may be effective.

Summary

(1) PbTe/PbSe: Thermopower for p-type behaves similarly to observed behavior in PbTe:Tl with high doping, but without Tl.

- Can obtain high *ZT* as reported in PbTe:Tl without the use of the toxic element, Tl.
- Heavily doped *p*-type PbSe may be a useful Te free material.

(2) Skutterudites: Can use alloying on the Co site with Fe and Ni to separately control carrier concentration and filling.

- Potential for lower cost compositions using alkaline earth filling and Ni instead of Co.
- Enhanced thermopowers and higher *ZT*.

(3) Mo_3Sb_7: Current material is not at the optimum carrier concentration.

- Use of co-doping or other ways to lower the carrier concentration may lead to higher *ZT*.