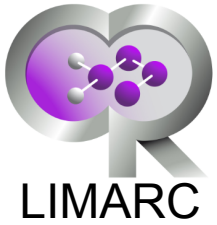


Ab initio methods in thermoelectrics

working more to relax more accurately

Matthieu Verstraete

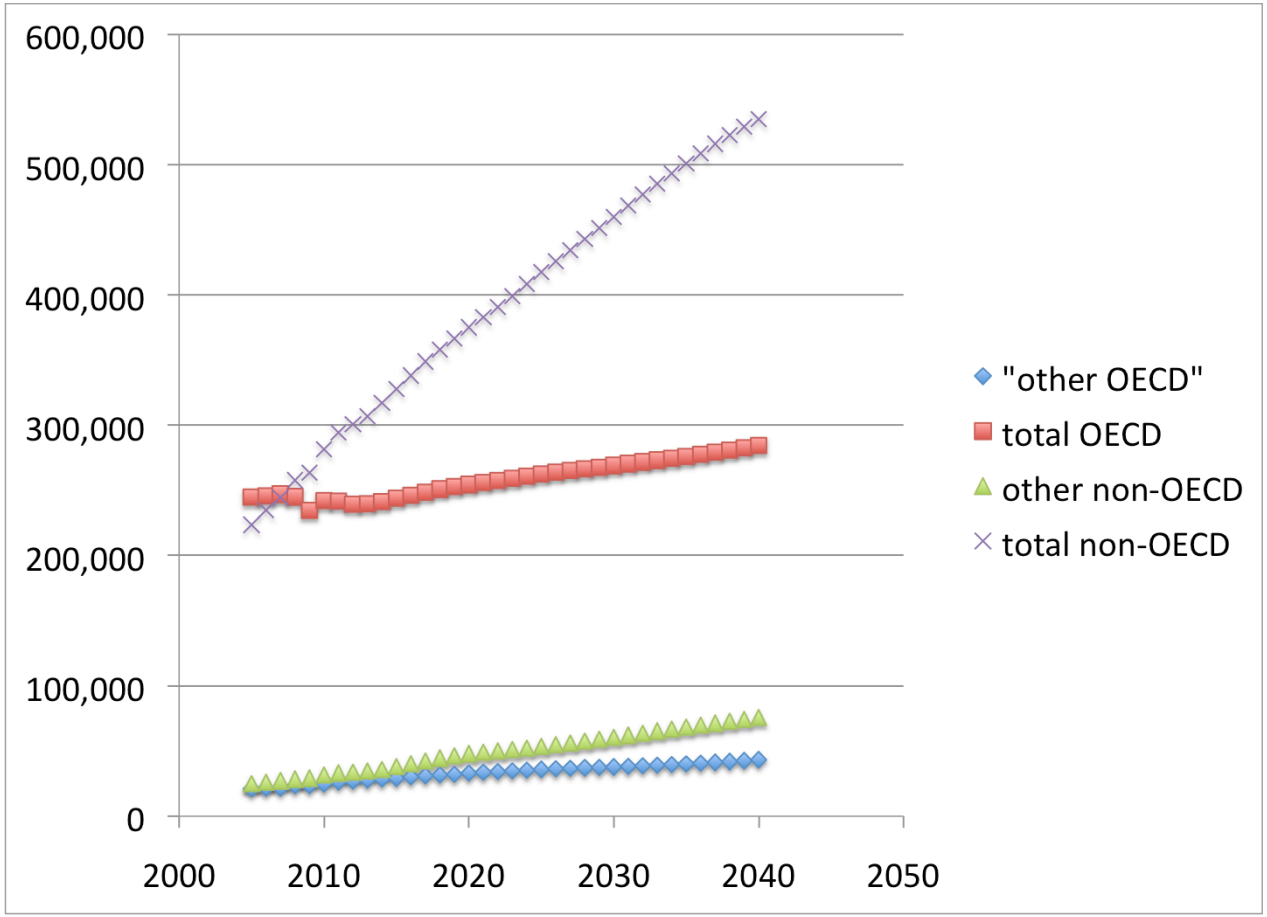
University of Liège, Belgium

IPAM workshop IV - Nov 2013

You're from where?

More numbers on energy!

- www.iea.gov in 10^{15} BTU

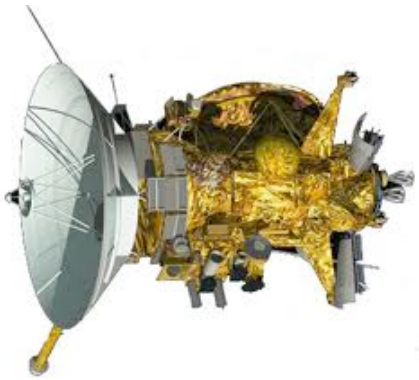


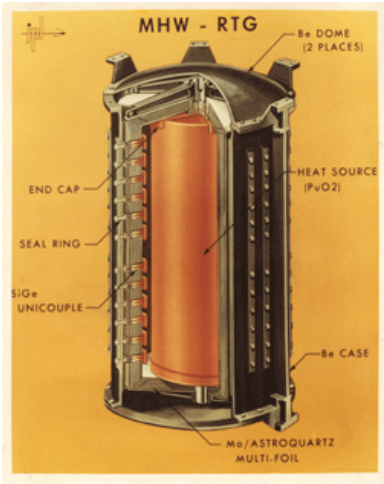
Energy issues

- Post-petroleum scramble for new energies
- Nuclear?
- Solar, Wind
- Biomass (still carbon)
- Efficiency and recovery

Thermoelectrics

- integrated device Q → V or vice versa
- waste heat harvesting
- power generation (satellites)
- solid state cooling/heating
- cpu spot cooling





Quality factor of TE materials

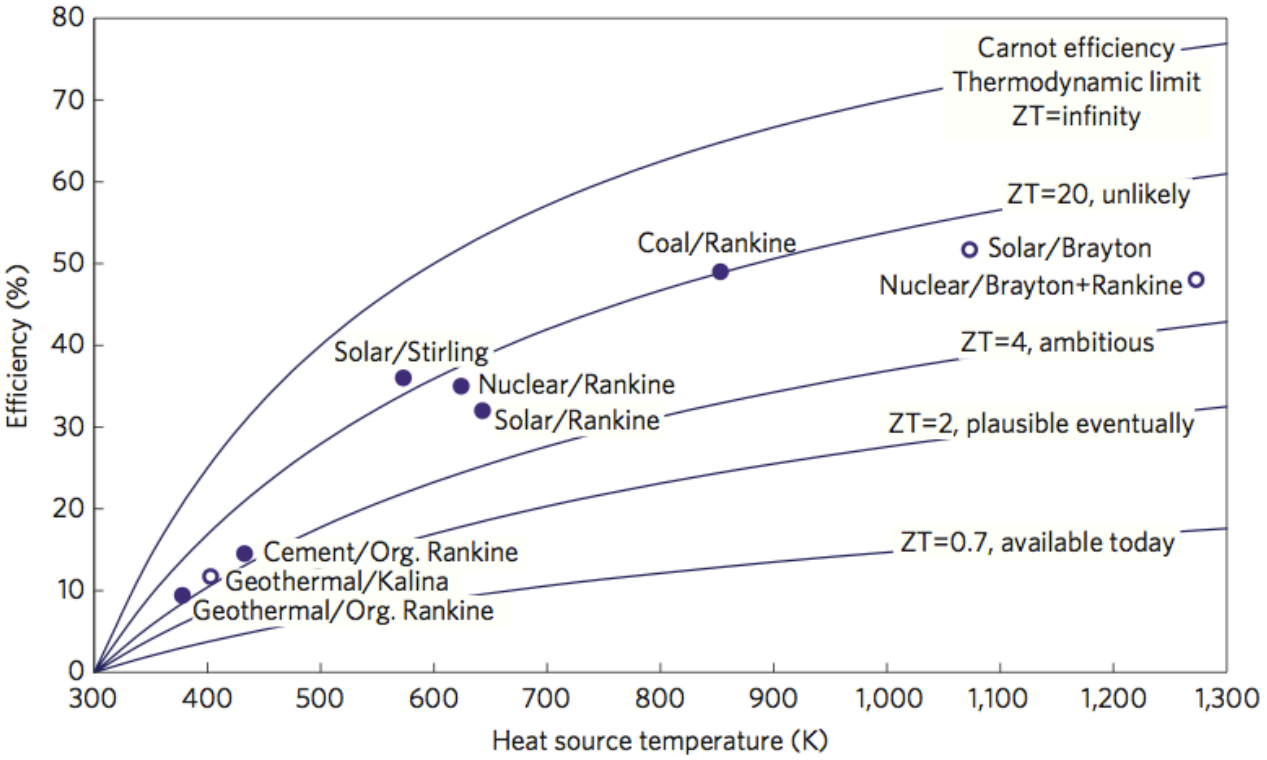
- Figure of merit: material vs device

$$Z = \frac{S^2\sigma}{\kappa} \qquad Z = \frac{(S_p - S_n)^2}{\left(\sqrt{\kappa_p/\sigma_p} + \sqrt{\kappa_n/\sigma_n}\right)^2}$$

- real criteria depends on usage
- electron crystal: large σ
- phonon glass: low κ

Thermodynamic caveat

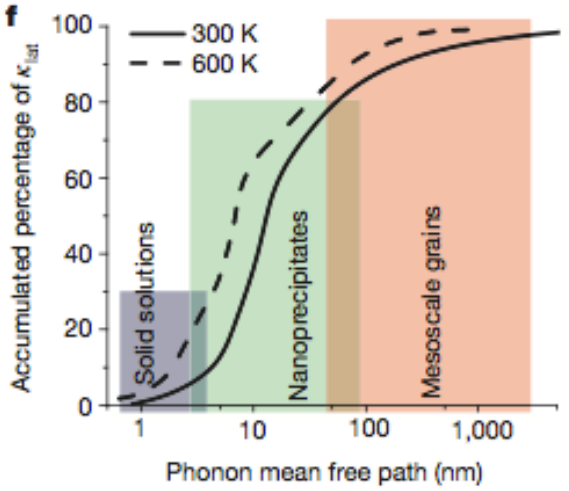
- hot/cold source separation
- e^- fluid loses too much heat

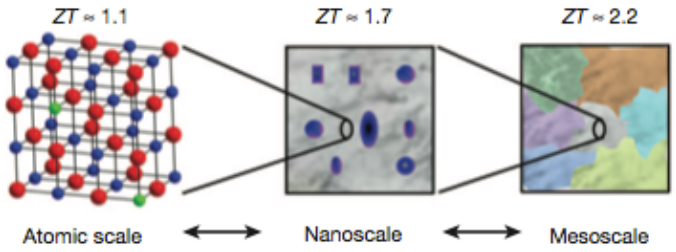


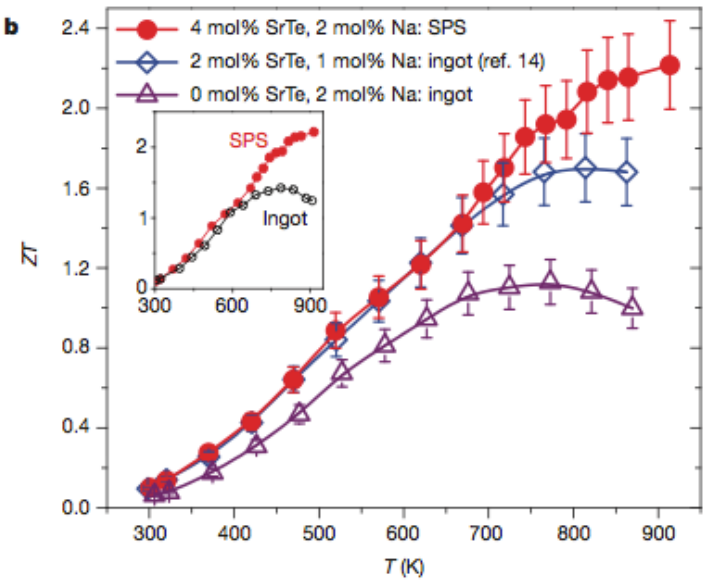
CB Vining Nature Materials **8** 83 (2009)

Improving ZT at all length scales

- optimization of:
  - dopants
  - nanoscale
  - mesoscale
- systematic phonon killing







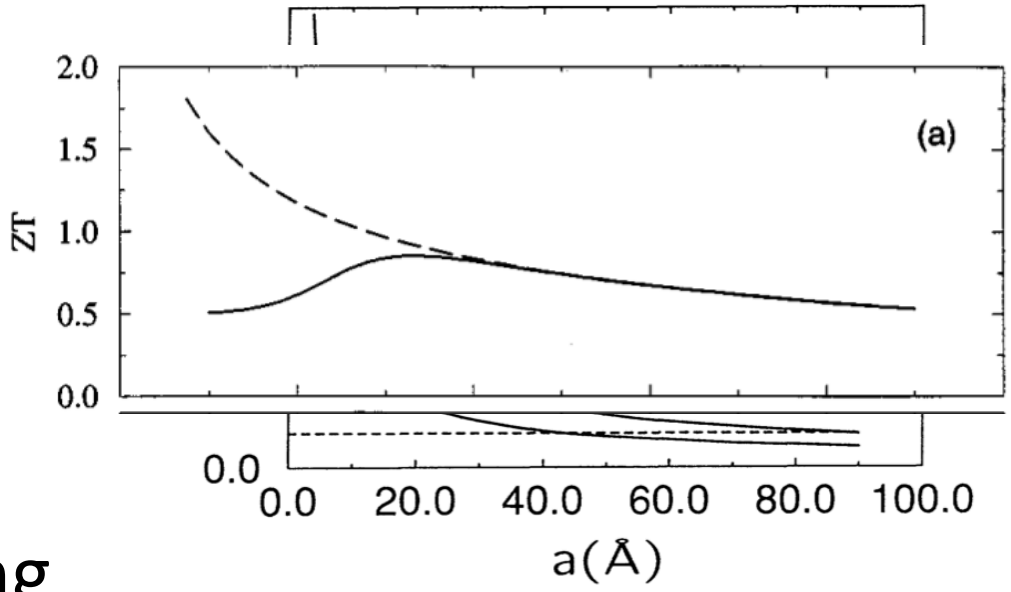
Biswas Nature **489** 414 (2012)

Electronic structure + BTE

Where it all began: Hicks and Dresselhaus

The calculations assume a one-band material. This is because one-band materials (such as heavily doped semiconductors) give the best Z

- BTE + RTA + m^*
- analytical solution
- param on Bi_2Te_3
- no κ_{latt} limitation
- 2D and 1D structuring

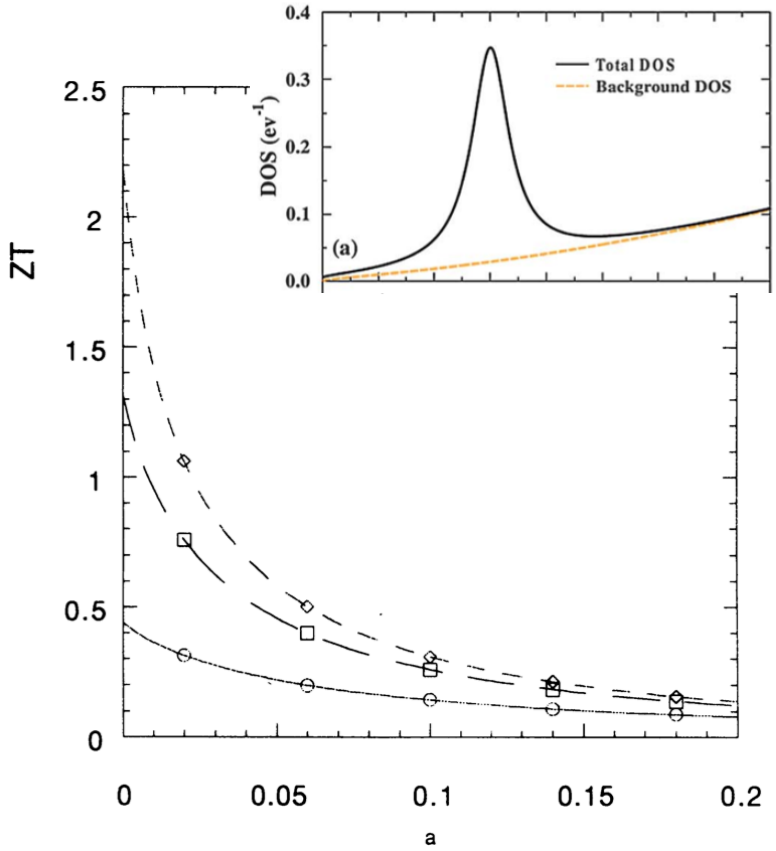


Hicks & Dresselhaus PRB **47** 12727 + 16631 (1993)
but! Sofo & Mahan APL **65** 2690 (1994)

Where it all began: Mahan+Sofo

- Dope with f- or d-metals
- resonant levels
- huge dN/dε
- binding is critical:
- Goldilocks hybridization

$$N(\varepsilon) = \frac{n_i}{k_B T}\,[\delta(x-b)+a]$$



Mahan Sofo PNAS **93** 7436 (1996)
Heremans En Env Sci **5** 5510 (2011)

Boltzmann transport equations

- Boltzmann equations

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f + \vec{E} \cdot \frac{\partial f}{\partial k} = \left(\frac{\partial f}{\partial t} \right)_{coll}$$

$$\vec{j}_q = \sum_k \epsilon_k \vec{v}_q \left(-\frac{\partial f}{\partial \epsilon_k} \right)$$

- single mode lifetime approx $\left(\frac{\partial f}{\partial t} \right)_{coll} = \frac{\delta f}{\tau_k}$

- variational approx $\left(\frac{\partial f}{\partial t} \right)_{coll} = \sum_i Q_{ji} \phi_i$

  basis set $\delta f = \sum_i c_i \phi_i$

Industry standard scheme

- Boltzmann equations + constant RTA

$$\sigma_{\alpha\beta}(i,\mathbf{k}) = e^2 \tau_{i,\mathbf{k}} v_\alpha(i,\mathbf{k}) v_\beta(i,\mathbf{k})$$

$$\sigma_{\alpha\beta}(T;\mu) = \frac{1}{\Omega}\int \sigma_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\right]\mathrm{d}\varepsilon,$$

$$\nu_{\alpha\beta}(T;\mu) = \frac{1}{eT\Omega}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)\left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\right]\mathrm{d}\varepsilon,$$

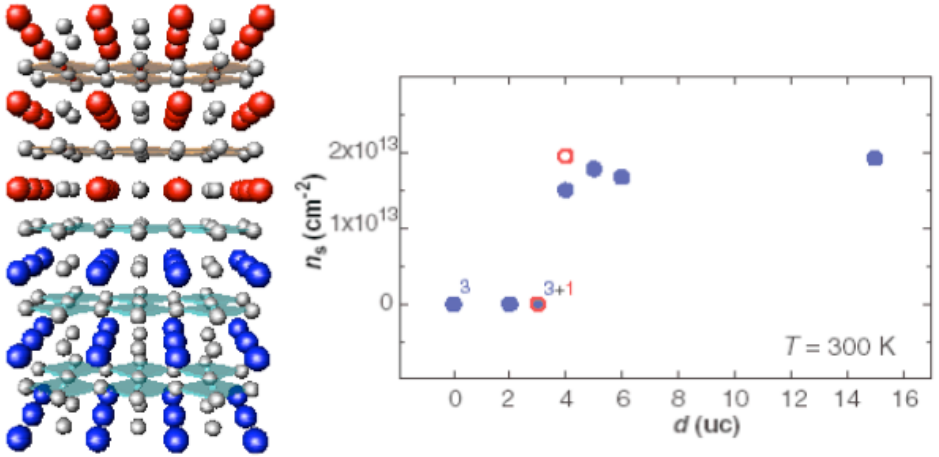
$$S_{ij} = E_i(\nabla_j T)^{-1} = (\sigma^{-1})_{\alpha i}\nu_{\alpha j}$$

- BoltzTrap - Madsen&Singh CPC **175** 67 (2007)

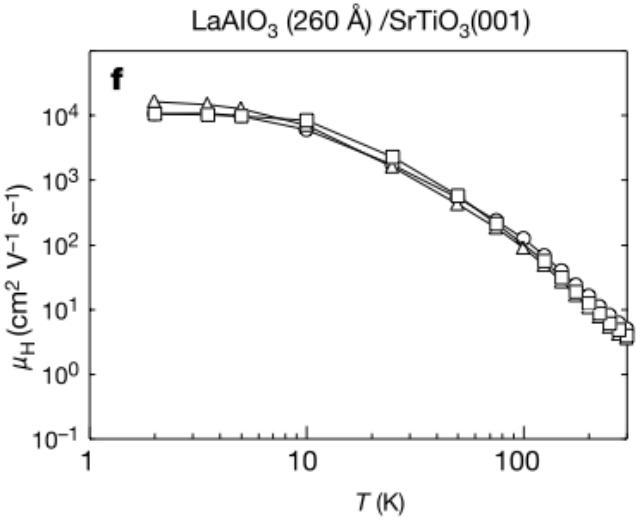
Multiband interference with nanostructuring

The 2DEG@ STO/LAO system

- Oxide-oxide interface
- Zener polar breakdown creates 2DEG
- Good mobilities – what about TE?



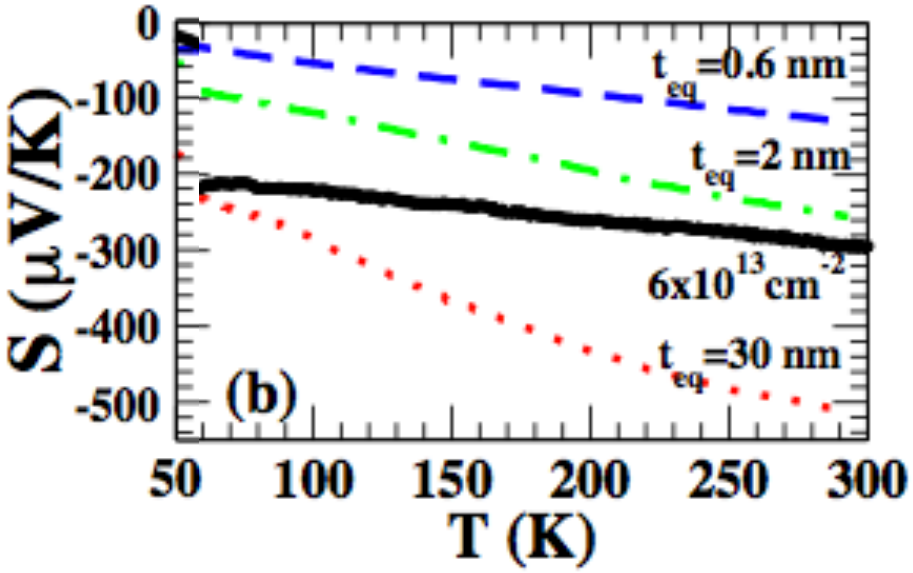
Thiel Science 2006



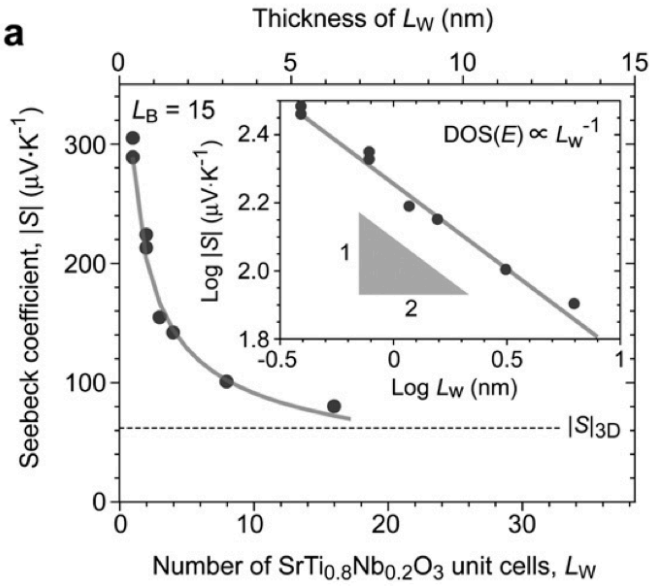
Ohtomo Nature 2004

Contradictory experiments

- Oxide 2DEG enhances S... sometimes
- no in LAO/STO yes in $(STO/Nb\text{-}STO)_n$



experiment D Marre'



Ohta TSF **516** 5916 (2008)

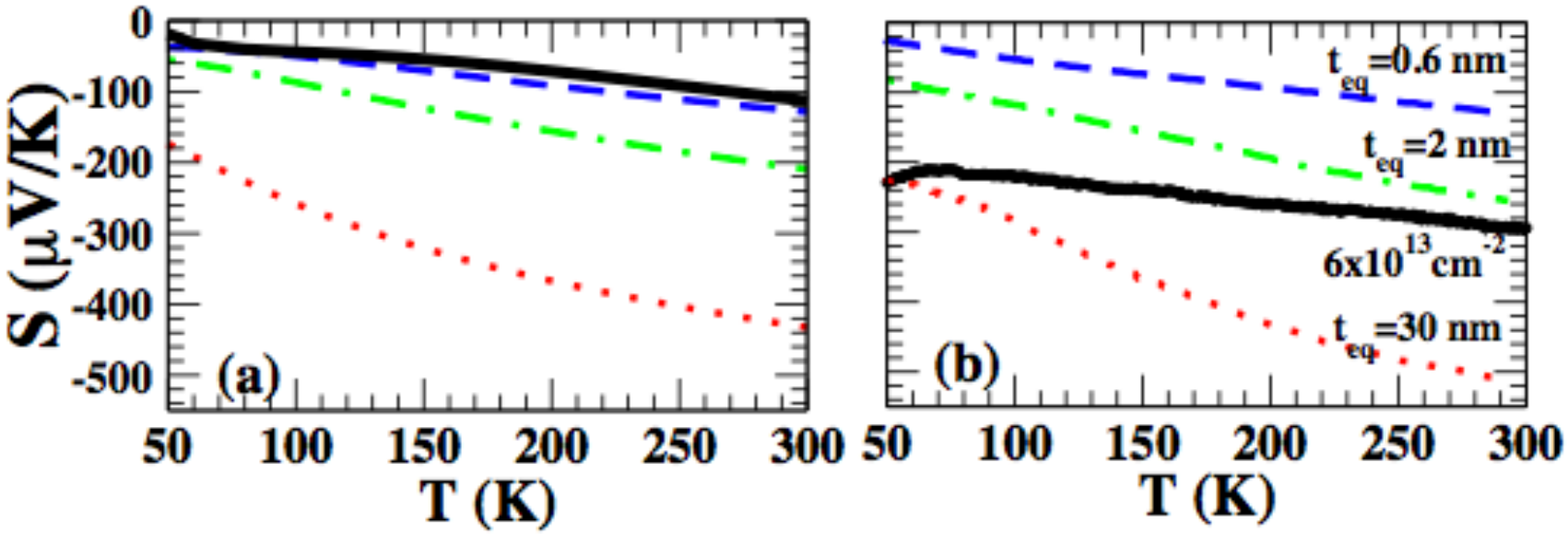
STO/LAO transport

- nano-S is not better? DFT+Boltztrap agrees!
- Need model lifetime

$$\tau(\epsilon) = \tau_{\mathrm{ref}} \left(\frac{T_{\mathrm{ref}}}{T}\right)^{\lambda} \left(\frac{\epsilon - \epsilon_0}{K_B T}\right)^{\lambda}$$

Durczewski Ausloos PRB **61** 5303 (2000)

- Compare with Nb doped 3D STO

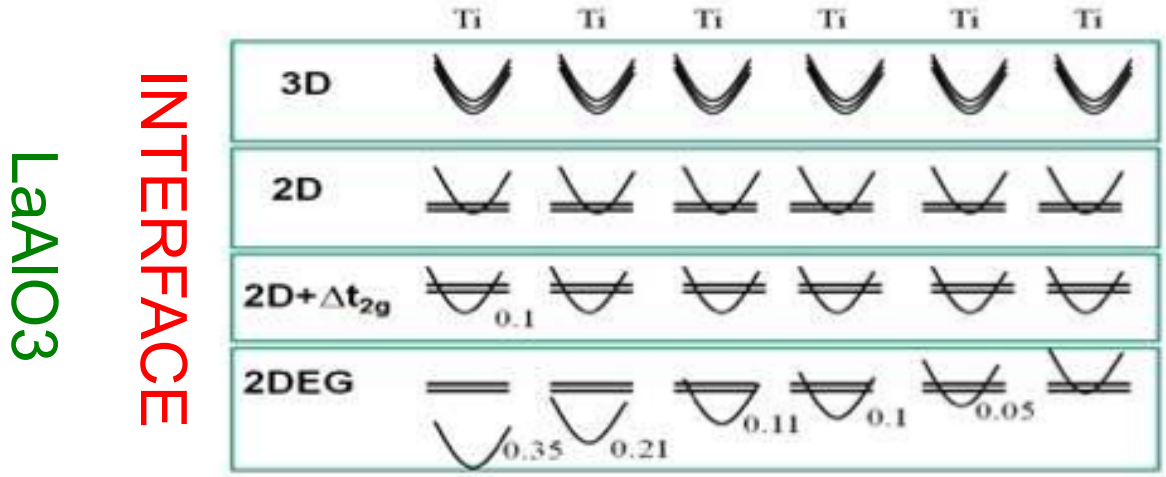


pseudo SIC Q-espresso

experiment D Marre'

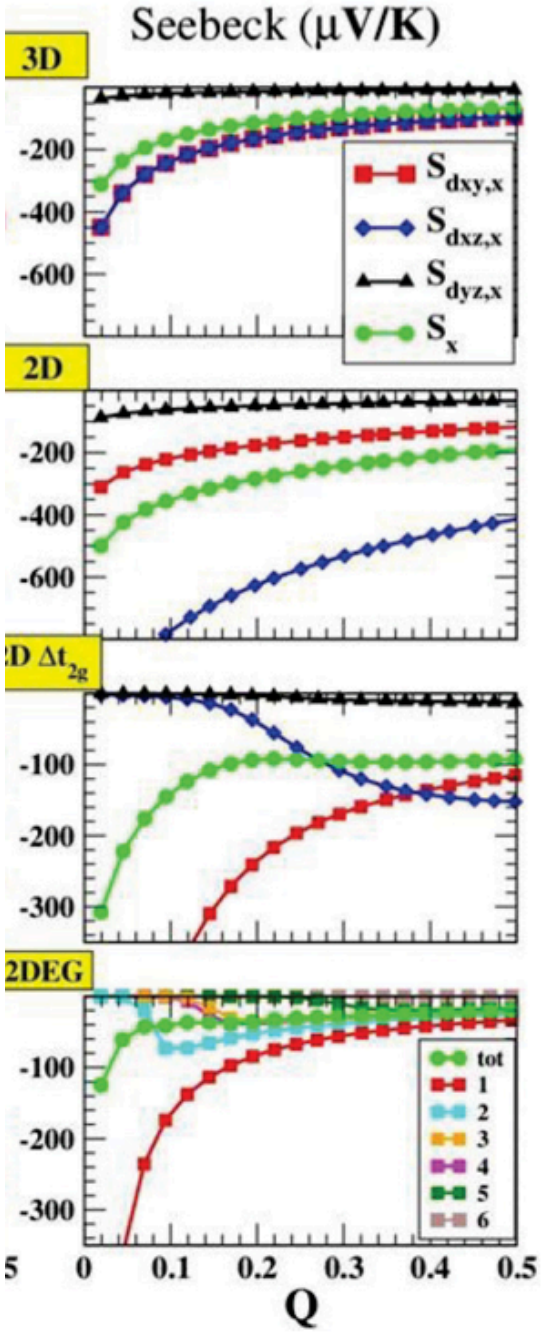
Parabolic bands model

- fit eff mass BS to ab initio
- position of E_F gives boost



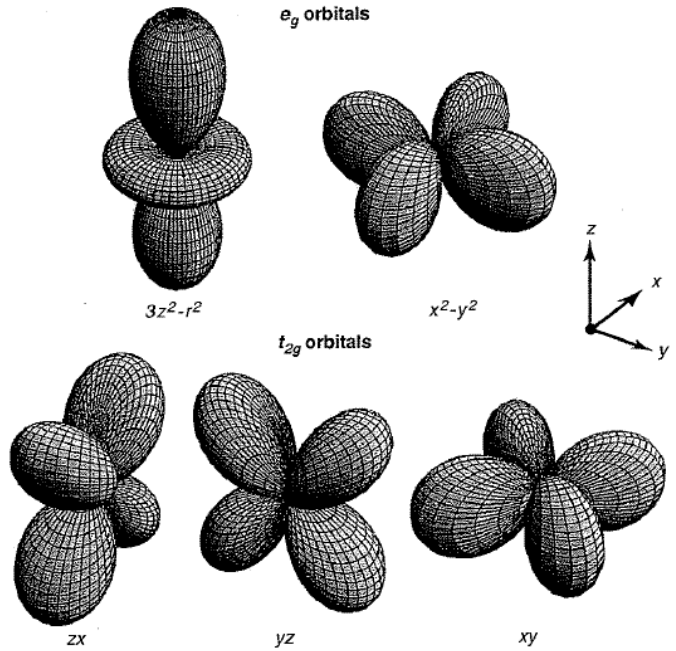
- t_{2g} shifts reduces S
- relative shift of layers kills S

PRB **86** 159301 Filippetti (2012)



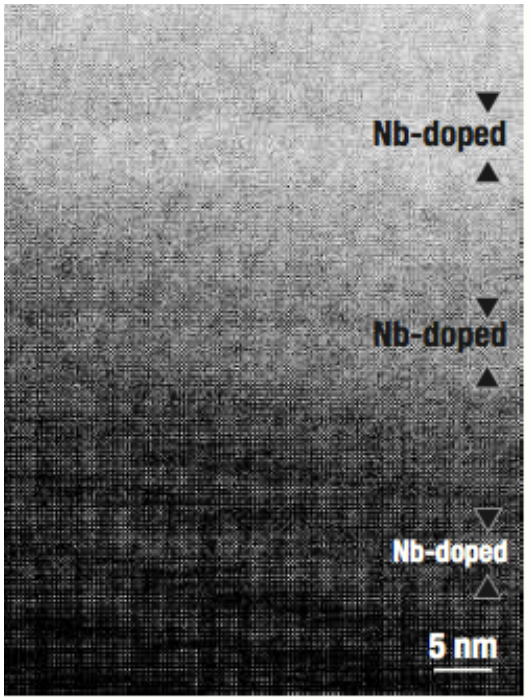
Parabolic bands model

- H&D are correct about 1 band... but...
- also suppose 1 subband in whole Qwell
- not « single » 2DEG
- shift linked to t2g shape
- change d orbital ordering?



$STO/SrTi_xNb_{1-x}O_3$ superlattices

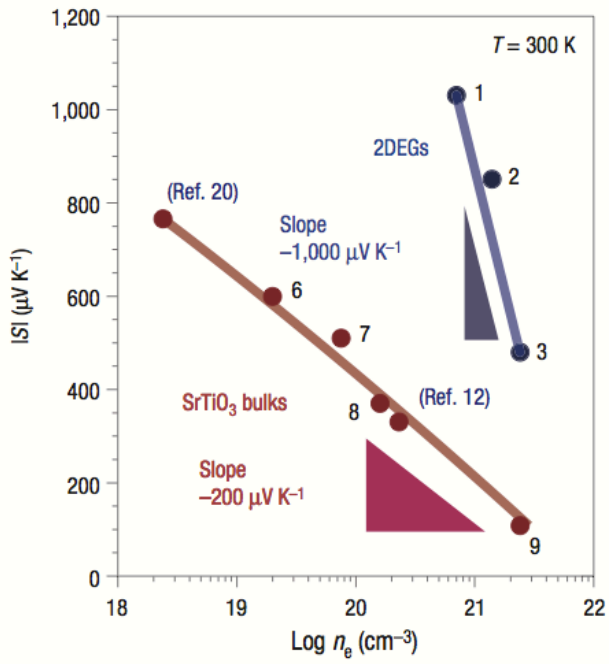
- Deposit doped STO layers
- modulate heterostructure
- and Nb doping level
  - confinement changes
  - enhanced S for low doping
- 2 new degrees of freedom

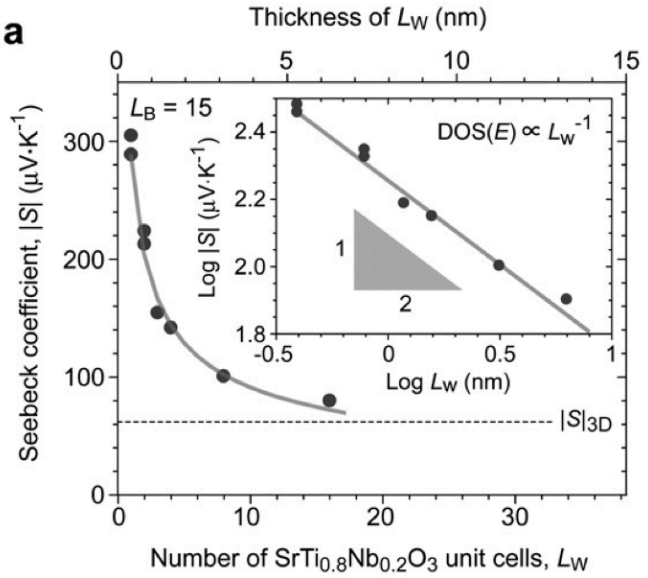


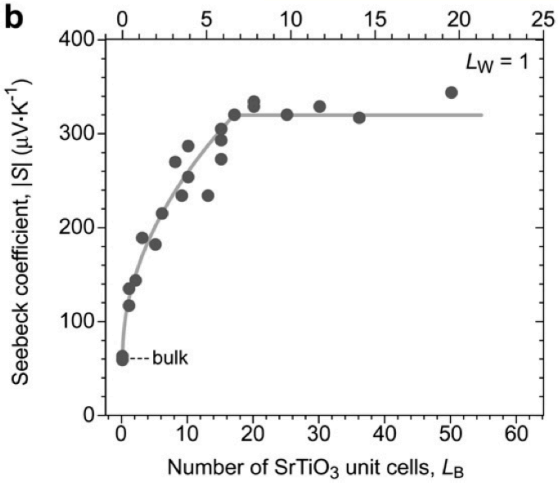
Ohta Nature Nat **6** 129 (2007)

STO/$SrTi_xNb_{1-x}O_3$ superlattices

- Thin Nb-STO layers
- Sufficient spacing
- Which elec structure?

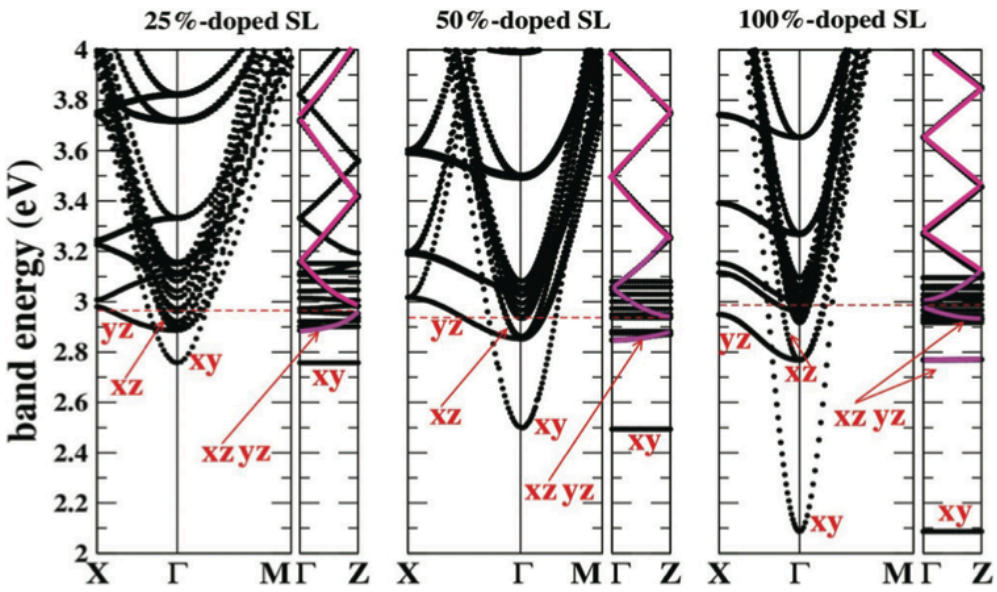






$STO/SrTi_xNb_{1-x}O_3$ superlattices

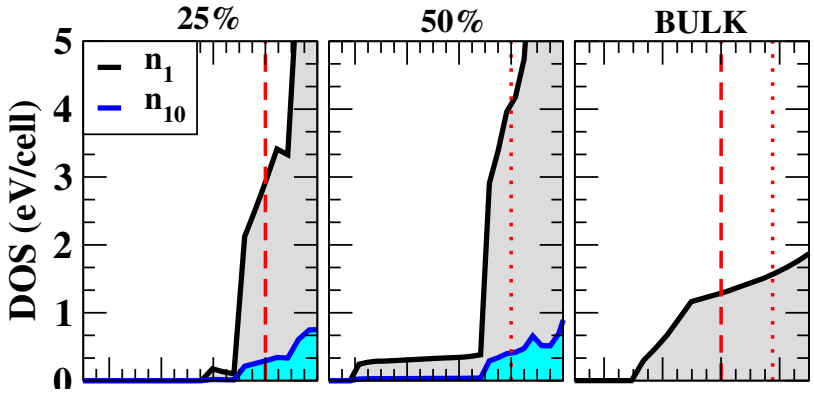
- 10 layers, 1 doped with Nb (extra e^- shared)
- Doping fraction will:
  - increase confinement
  - decrease dilution n_e
  - reduce $m^*_{xz,yz}$
- xz yz bands in violet
- (PSIC, Qespresso...)

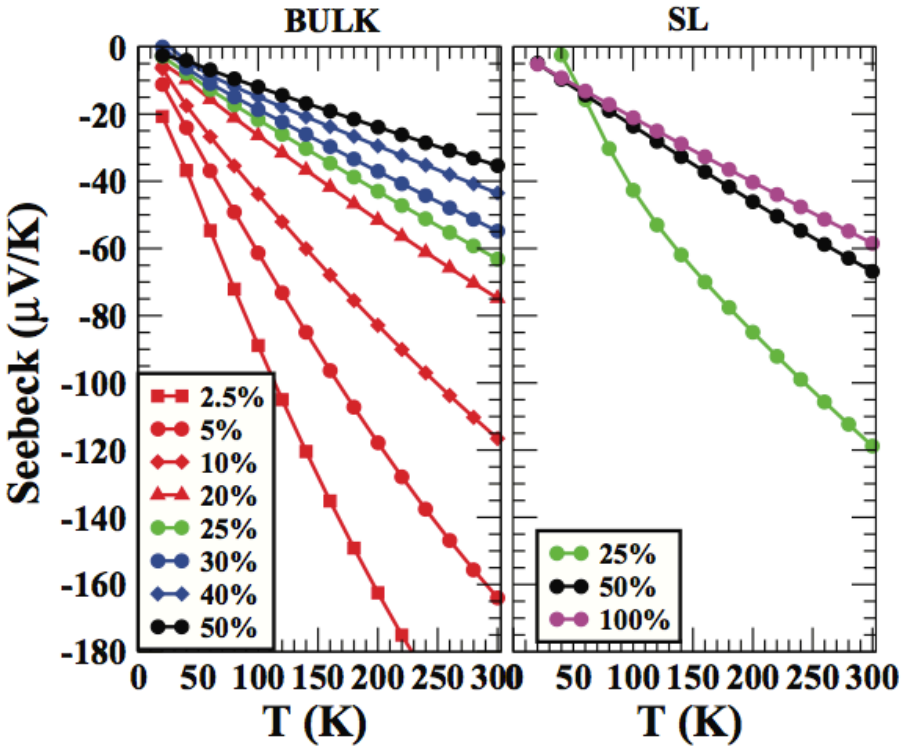


$STO/SrTi_xNb_{1-x}O_3$ superlattices

- Dilution enhances S!
- Smaller effective DOS
- Cutler Mott

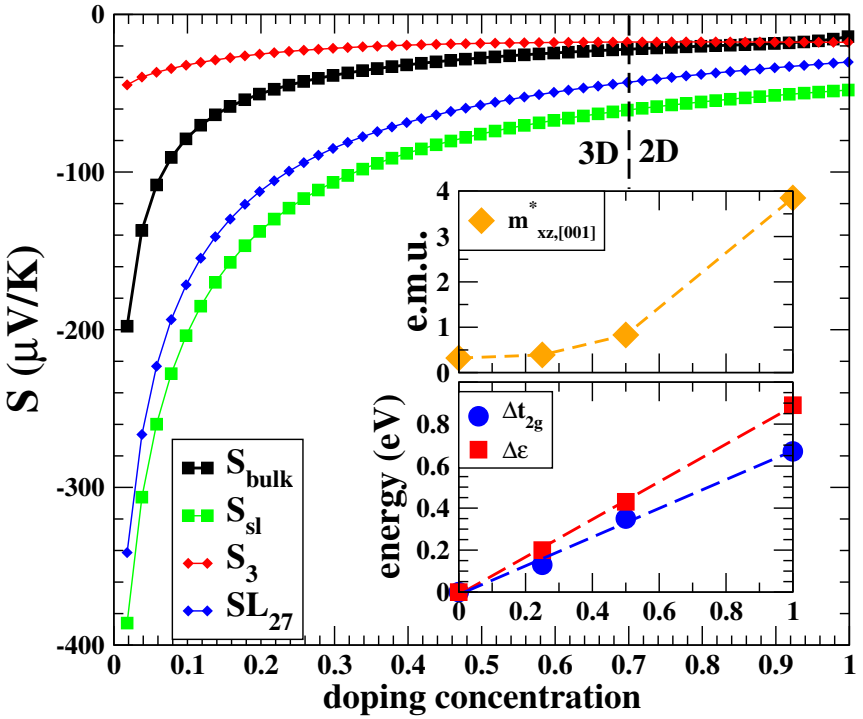
$$S = \frac{\pi^2 k_B^2 T}{3e}\left|\frac{\partial(\ln n)}{\partial\epsilon} + \frac{\partial(\ln \mu)}{\partial\epsilon}\right|$$





$STO/SrTi_xNb_{1-x}O_3$ superlattices

- Weak confinement works better
- dilution ≠ n_e reduction
- dilution → E_F rises wrt bulk states
- multiband effect

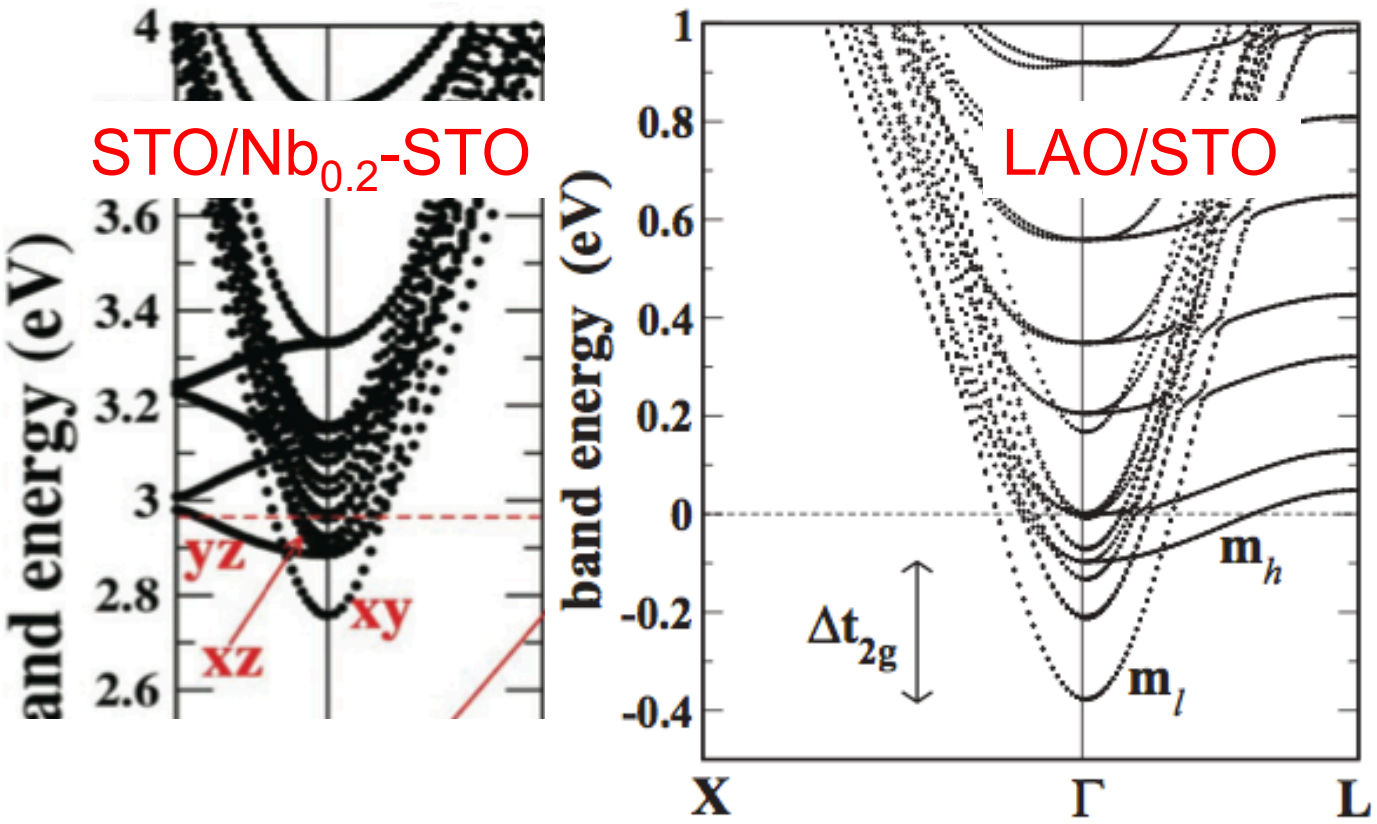


- m* model for any doping
- S effect in upper manifold

Delugas PRB **88** 045310 (2013)

Comparison with LAO/STO

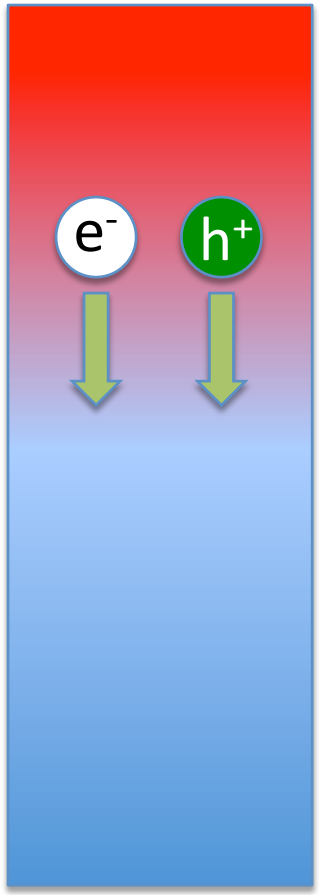
- T2g shift + #degenerate bands
- Never homogeneous in z for LAO/STO



Ab initio Seebeck coefficients

Seebeck coefficient in simple metals

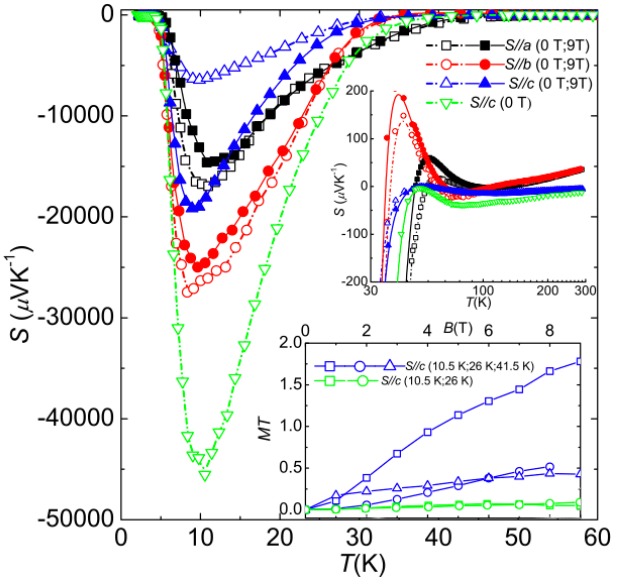
- Normal picture: carriers = e^-
- More and faster e^- so $S < 0$
- Li Au Ag Cu have $S > 0$
- Jones: not free electron dispersion
- Robinson: mfp(ε) and exotic EPC



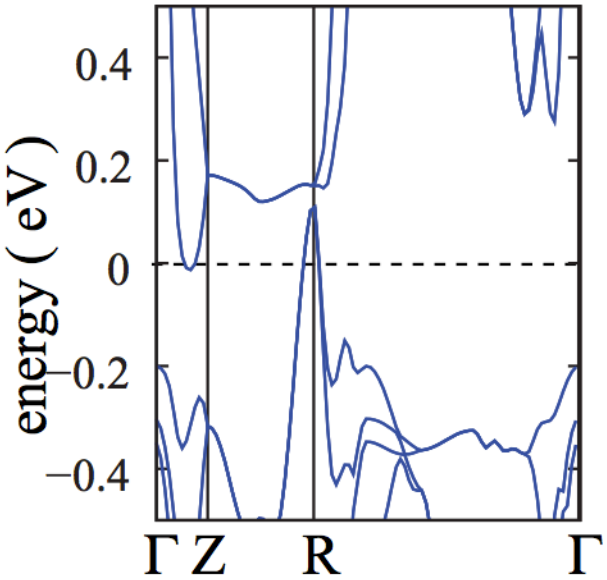
Robinson PR **161** 533 (1967) PR **171** 815 (1968)
Jones Proc. Phys. Soc. A **68** 1191 (1955)

Normal anomalous cases

- Signature: n_H vs S
- Possible for multi-band BS Ex: $FeSb_2$
- Not the case in simple Li: beyond RTA



Bentien EPL **80** 17008 (2007)



Diakhate PRB **84** 125210 (2011)

Allen theory

- Metals or heavily doped SC
- Variational approximation to BTE
- FSH basis $F_\alpha(\mathbf{k}) = v_\alpha(\mathbf{k})/v_\alpha(\epsilon_\mathrm{F})$

$$v_\alpha^2(\epsilon) = \left[\sum_\mathbf{k} v_\alpha^2(\mathbf{k})\delta(\epsilon_\mathbf{k} - \epsilon)\right]/N(\epsilon)$$

- Closed solution of BTE with scattering matrix between basis states $Q_{\alpha n,\beta n'}$
- Lowest Order VA (n = 0, 1) No RTA at all!

Allen theory – Seebeck coefficient

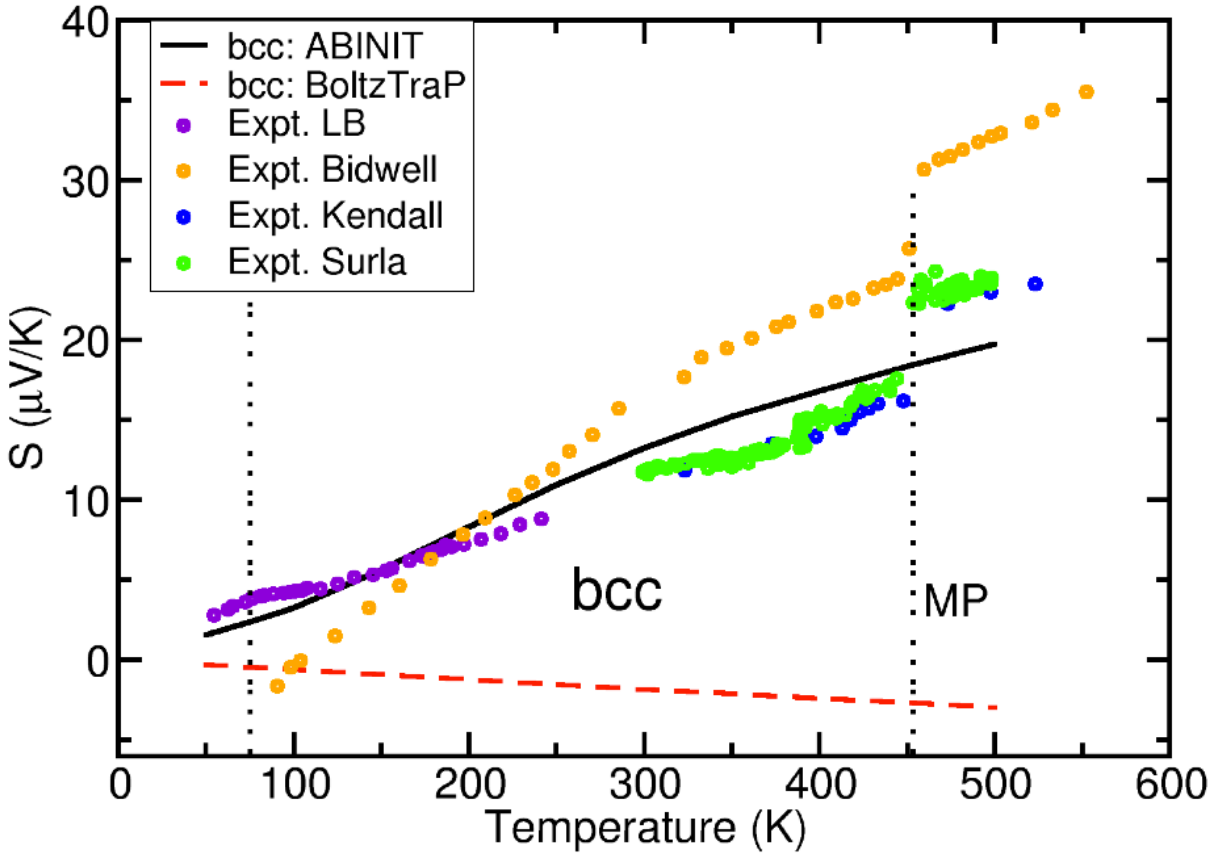
- Simplest: elastic LOVA, but S=0
- Inelastic LOVA $S_{\alpha\beta} = \frac{\pi k_B}{\sqrt{3}e} \frac{Q_{\alpha 0,\beta 1}}{Q_{\alpha 1,\beta 1}}$
- Get Q from DFPT:

$$Q_{\alpha n,\beta n'} = \frac{2\pi V_{cell} N(\epsilon_F)}{\hbar k_B T} \int d\epsilon \int d\epsilon' \int d\omega \sum_{s,s'=\pm 1}$$

$$\alpha^2_{\mathrm{tr}} F(s,s',\alpha,\beta,\epsilon,\epsilon',\omega) J(s,s',n,n',\epsilon,\epsilon') f(\epsilon)\left[1-f(\epsilon')\right]$$
$$\times \left\{\left[N(\omega)+1\right]\delta(\epsilon-\epsilon'-\hbar\omega) + N(\omega)\delta(\epsilon-\epsilon'+\hbar\omega)\right\}$$

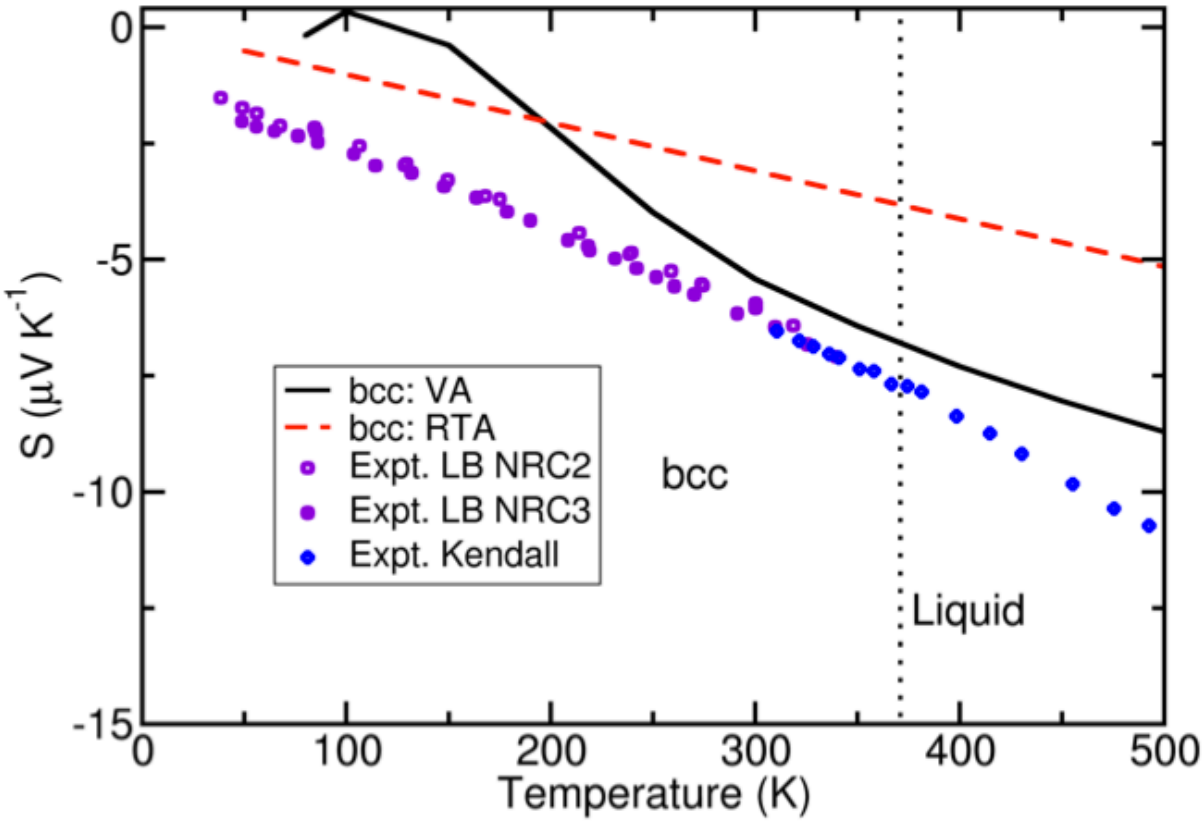
$$\alpha^2_{\mathrm{tr}} F(s,s',\alpha,\beta,\epsilon,\epsilon',\omega) = \frac{1}{2N(\epsilon_F)} \sum_{\mathbf{k}\mathbf{k}'} |g_{\mathbf{k}\mathbf{k}'}|^2$$
$$\times \left[F_\alpha(\mathbf{k}) - sF_\alpha(\mathbf{k}')\right] \times \left[F_\beta(\mathbf{k}) - s'F_\beta(\mathbf{k}')\right]$$
$$\times \delta(\epsilon_{\mathbf{k}} - \epsilon)\delta(\epsilon_{\mathbf{k}'} - \epsilon')\delta(\omega_{\mathbf{q}} - \omega)$$

Lithium



- VA is great, RTA fails miserably

Sodium



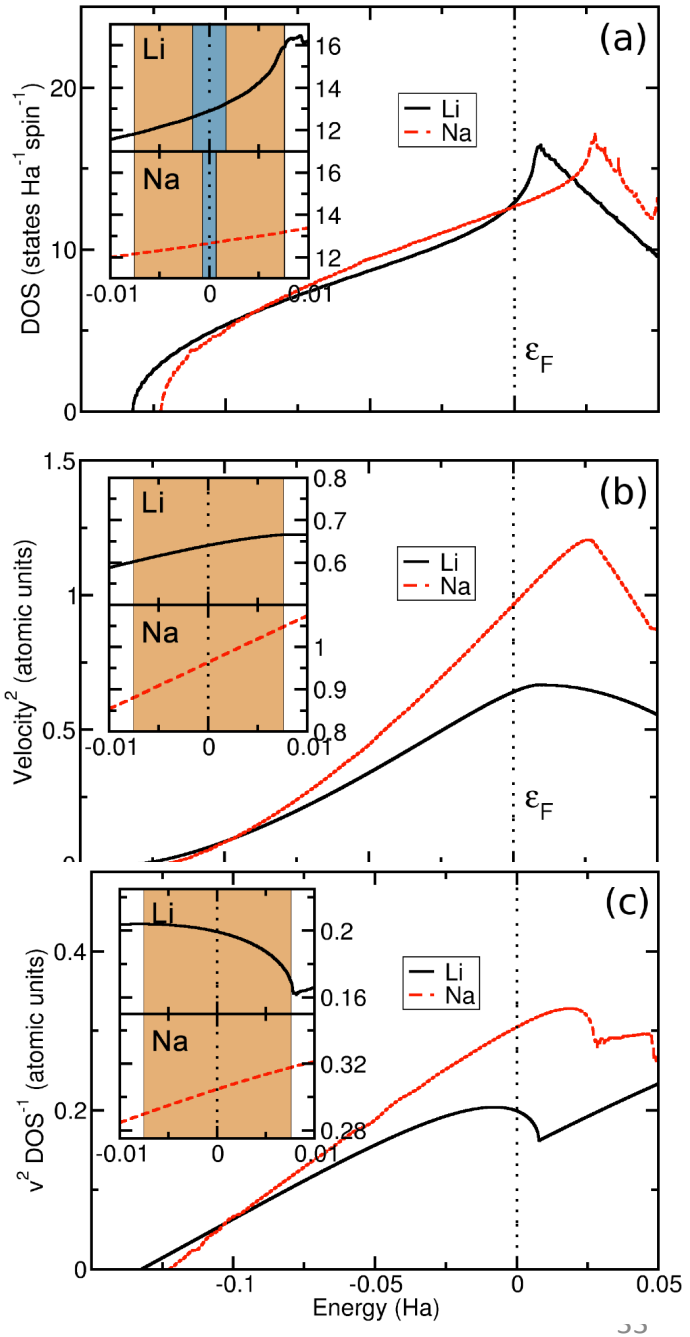
- « normal » S behavior. Still better than RTA

A « simple » explanation

- Drude $\sigma = ne^2\tau/m^*$

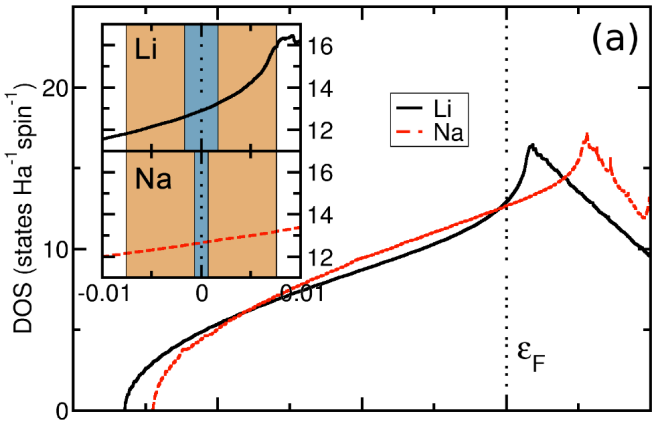
$$S = -\frac{\pi^2 k_B^2 T}{3e}\left[\frac{1}{\sigma}\frac{d\sigma(\epsilon)}{d\epsilon}\right]_{\epsilon=\epsilon_F}$$

- Model $\tau(\varepsilon) \sim 1/N(\varepsilon)$
- $\sigma(\varepsilon) \sim v^2/N(\varepsilon)$
- $\sigma(E_F)$ slope → - sign of S
- $|g| = 1$ still $S > 0$

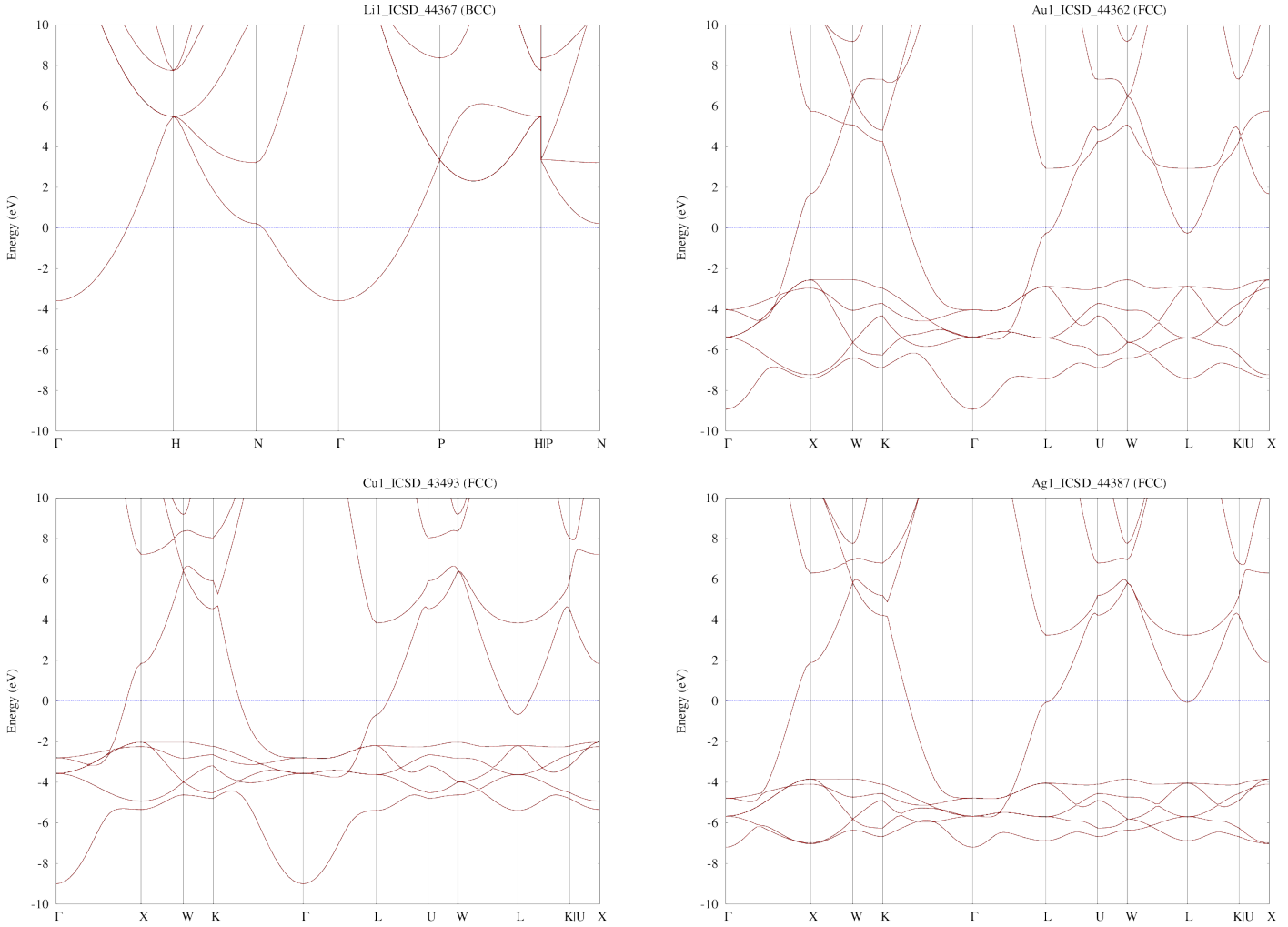


A « simple » explanation

- More electrons than holes
- They are marginally faster
- BUT Li E_F close to BZ edge
- Shorter τ for e^-
- Net effect is $S > 0$



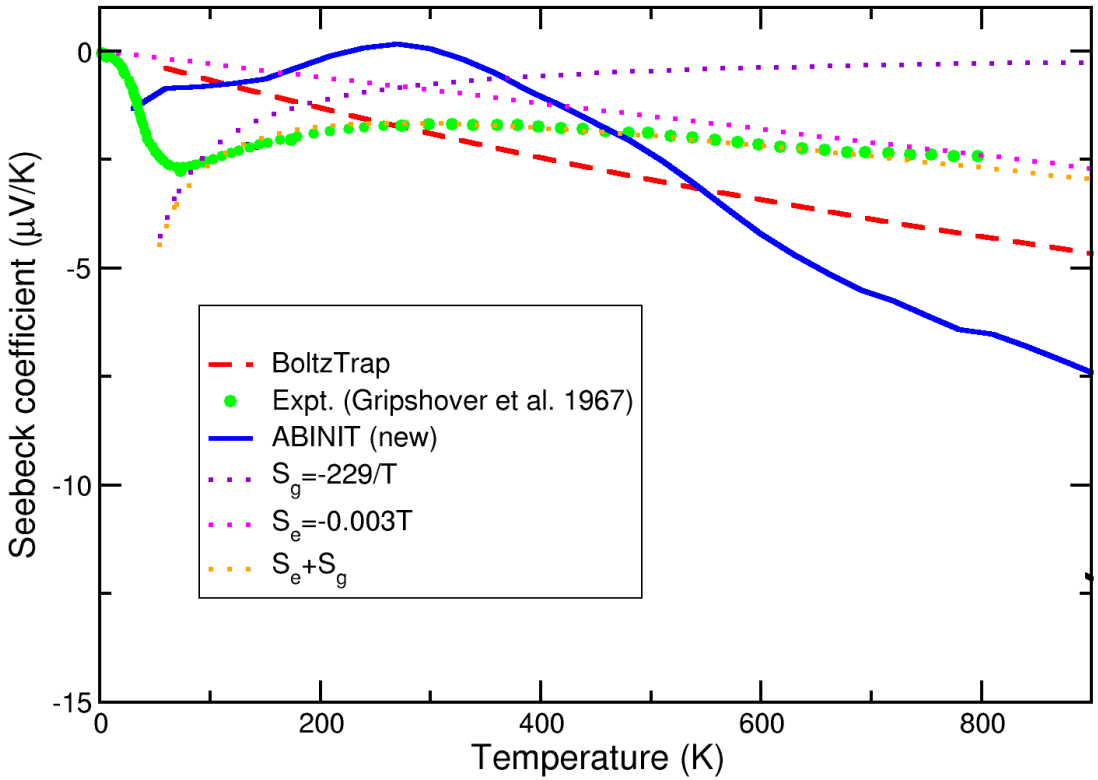
Other anomalous cases



AFLOW.org

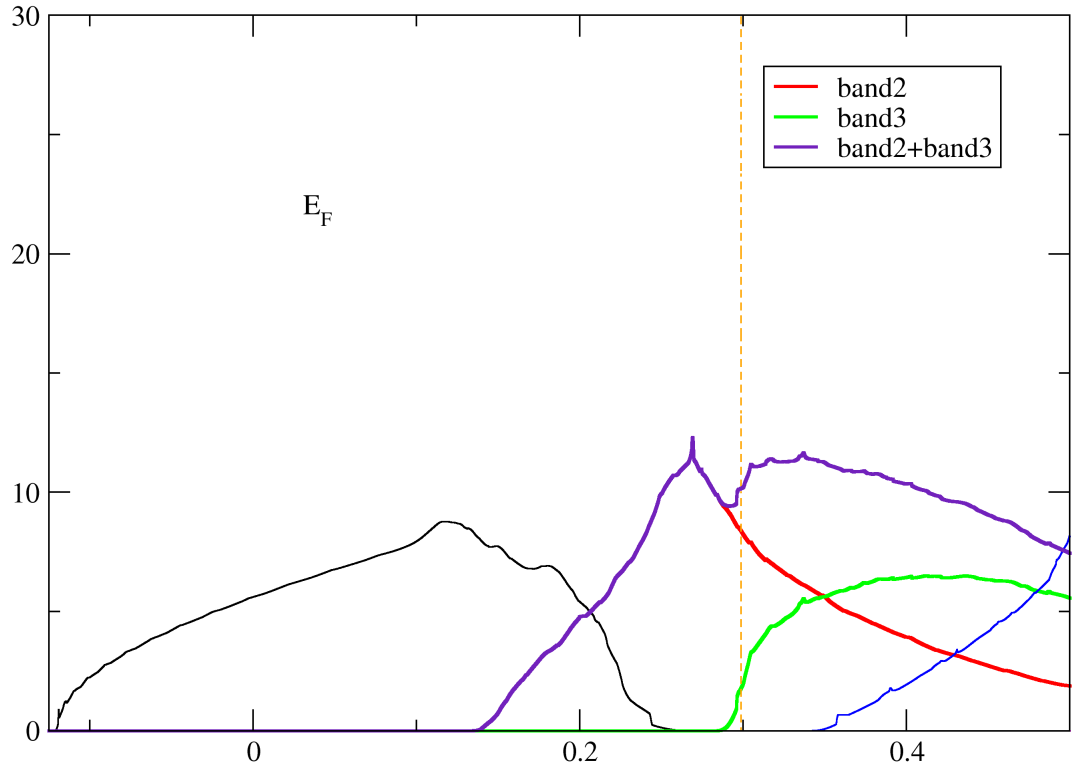
- Smaller DOS effect: |g| and FS count
- Simple RTA(ε) ~ 1/N(ε) fails

Multiband case: FCC Al



- FS more complex
- more painful convergence in k...

Why is S so small in Al?

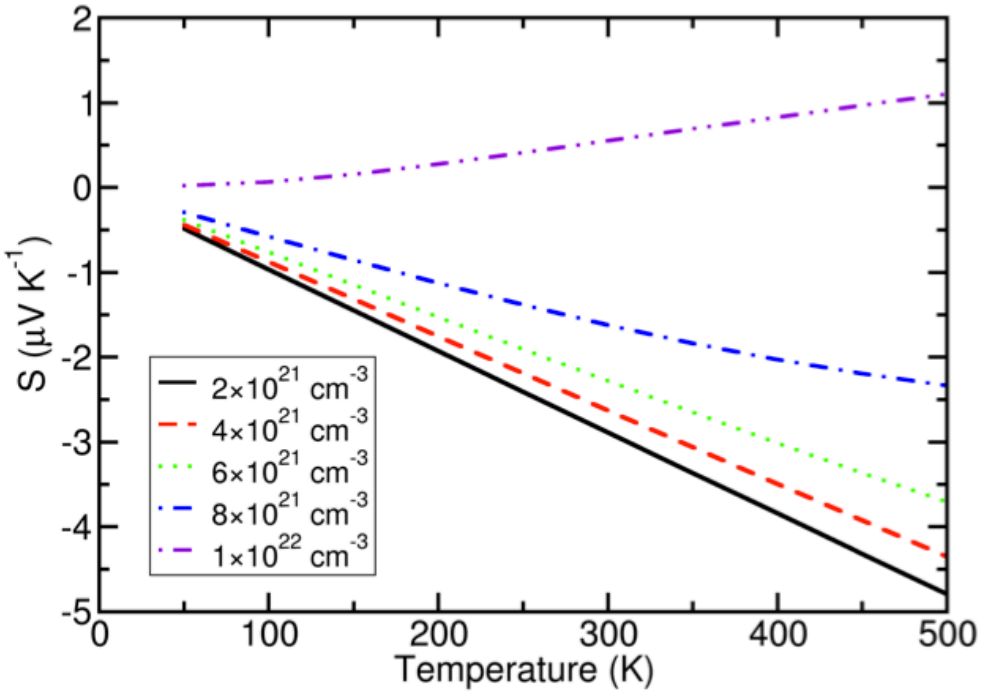


- Not so simple metal
- 2 opposing contributions

Can we exploit the anomaly?

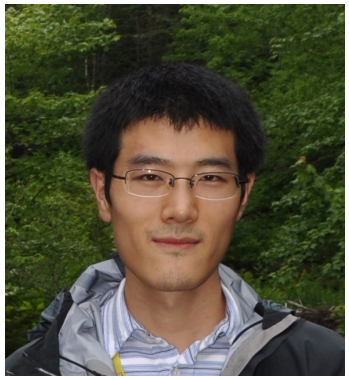
- Li_xMg_{1-x} doping exists
- What about Na?
- Sign change works!

  so it's not impossible...
- Apply to TE materials?
- DOS distortion & lifetime effect is key



Conclusions?

- Don’t worry, I’m looking for trouble
- RTA usually works
- RTA(ε) general and flexible (phonons too)
- Dresselhaus paradigm usually wrong,
  but so inspirational...
- Variational method for phonons?
  Need a good basis







- Bin Xu, G Madsen (Boltztrap)
- A Filippetti, P Delugas, V Fiorentini, D Marre'
- Aldo Romero, Olle Hellman
- Belgian ARC grant
- UCagliari visiting prof
- SEGI/CECI/PRACE

Thank you for your attention!