Université de Liège

ETSF
European Theoretical Spectroscopy Facility

Electronic Transport

with a bias towards diffusion from phonons

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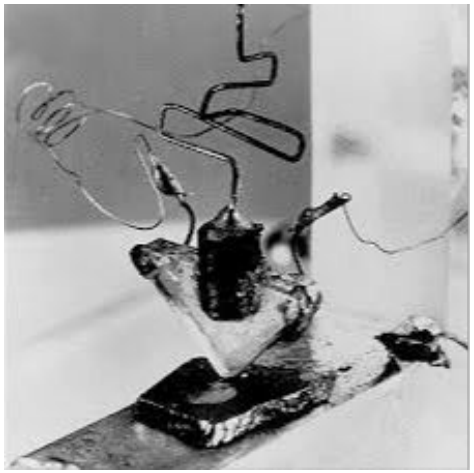
University of Liège Belgium

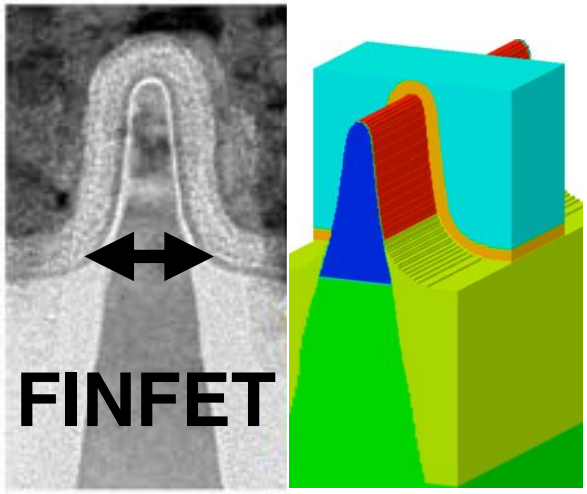
MP-EPFL Summer School
Ringberg Castle 28 July 2015

Not your grandfather's electronics…

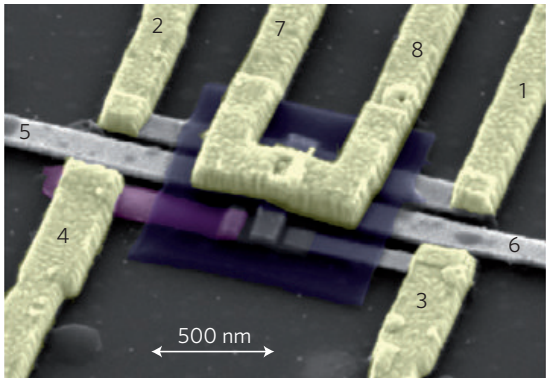
- Nanoelectronics
- Spintronics
- Organics/Molecular
- MEMS NEMS …



14 nm

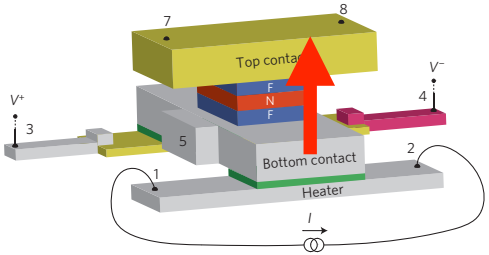


electronicsweekly.com

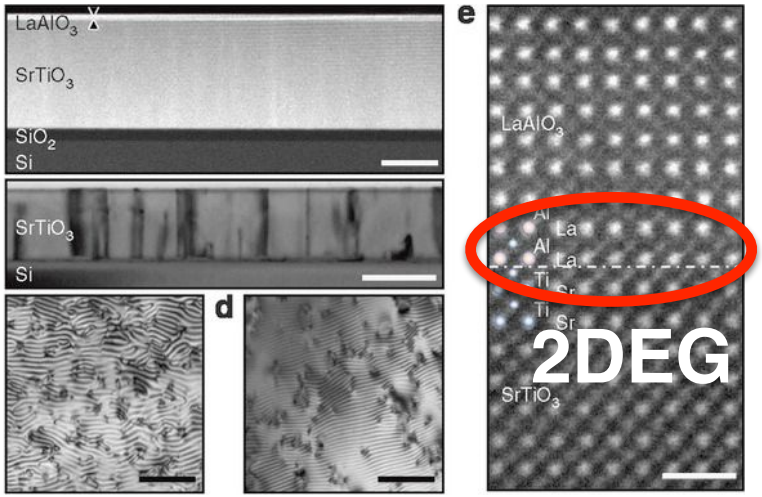


Nature Physics 9 636 (2013)

Thermal spin current

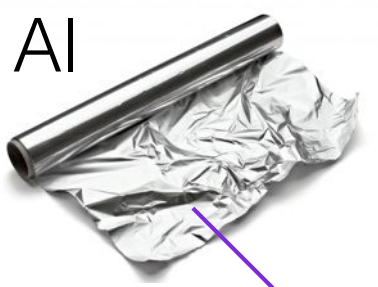


Nature Comm 1 94 (2010)

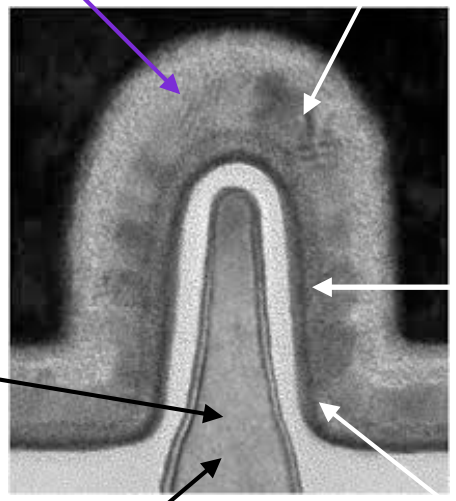


Materials and their issues

- Metals, SC, insulators
- New materials:
  - graphene, CNT, TMD
  - conducting polymers
  - nanowires
  - topological matter
- Interfaces, heterostructures
- Anisotropy, texturing

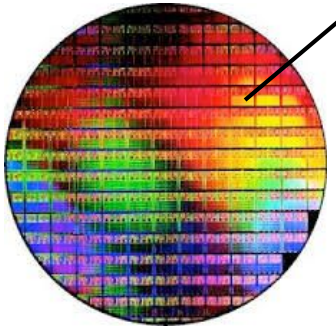


Si_3N_4



Ge

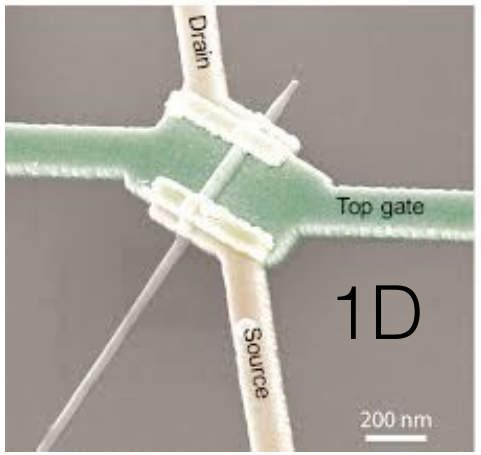
HfO_2



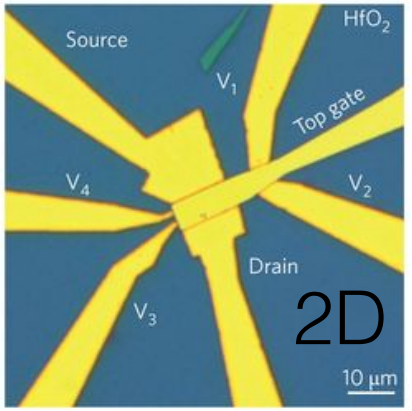
Si

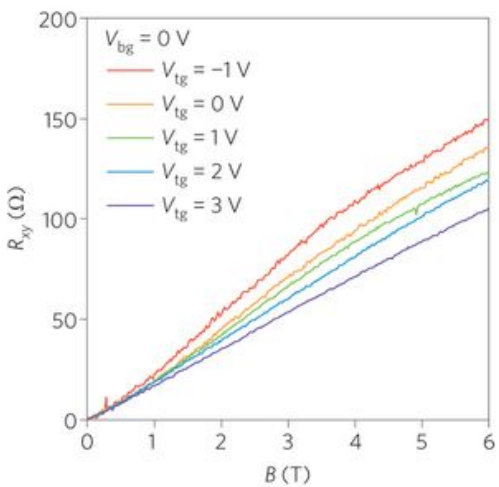
Universal utility

- Standard characterisation tool
- Sample quality, purity
- Signatures of physical effects
  - Phase transitions
  - Luttinger, Kondo
  - Anderson…



http://www.nano.lu.se





MoS2 FET Nature Nanotechnology 8, 147–148 (2013)

Ambition for this lesson

- Overview of electronic transport
- Classical theory and qualitative regimes
- What can we calculate from first principles?
- Details for diffusive transport
- Some thermal effects

Bibliography

- Mark Lundstrom *Fundamentals of carrier transport,* Cambridge University Press (2009)

- Supriyo Datta *Quantum Transport Atom to Transistor* (2005); *Electronic transport in mesoscopic systems* (1997), Cambridge University Press

- H. Bruus and K. Flensberg, *Many-body Quantum Theory in Condensed Matter Physics*, Oxford University Press (2004)

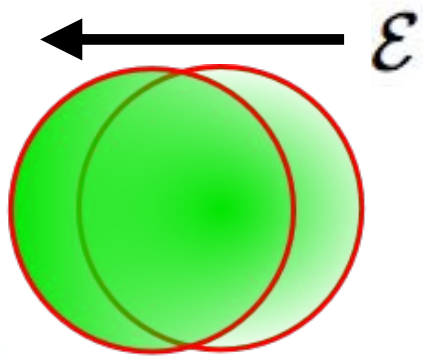
- M. Di Ventra, *Electrical Transport in Nanoscale Systems,* Cambridge University Press (2008).

- E. Economou, *Green's Functions in Quantum Physics,* Springer (1995)

Electron transport

(Semi) Classical theory

- Apply E field to free electron gas



- Displace Fermi sphere:

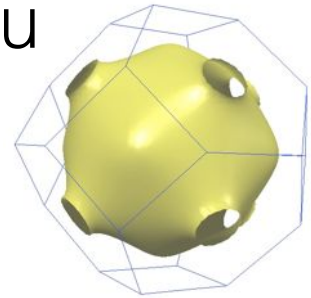
$$\delta E = \nabla_{\mathbf{k}} E(\mathbf{k}) \delta \mathbf{k} = \hbar \mathbf{v}.\delta \mathbf{k} = -e\mathcal{E}.\mathbf{v}\delta t$$

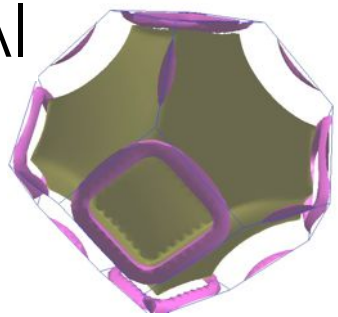
$$\hbar \dot{\mathbf{k}} = -e\mathcal{E} \longrightarrow m\dot{v} + \frac{m}{\tau} v_D = -e\mathcal{E}$$

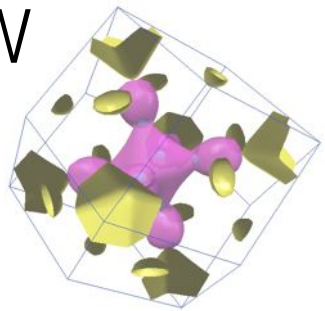
- Viscous force of (so far) unknown source
- Scattering / relaxation time / mean free path

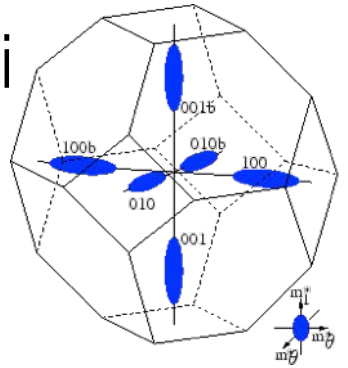
How good is Drude?

- Works in many cases:
  - Metals w/ large DOS and Fermi Surface
  - Doped semiconductors w/ small pockets
- But it is not predictive!
- We will come back to an improved version

Cu 

Al 

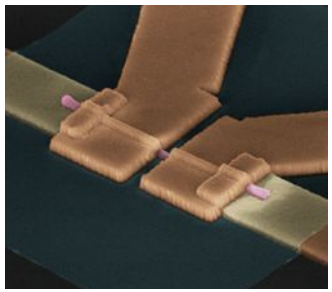
W 

Si 

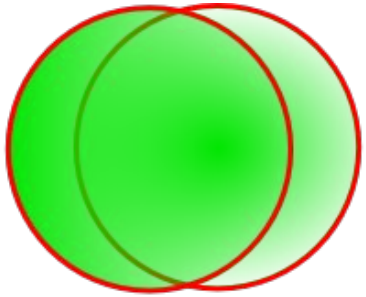
Transport coefficients

- Steady state current $j = -envv_D = \frac{e^2 \tau n}{m} \mathcal{E}$
- Conductivity $\sigma = e^2 \tau n / m$
- mobility $\mu = \sigma / e n = e \tau / m$
- Thermal conductivity κ_{el}
- **Idea**: distribution of electrons

$f_k = f_0(\varepsilon_k) + \delta f_k$

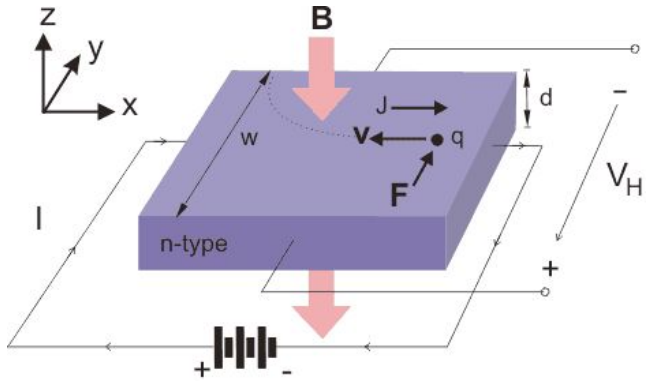


http://www.nano.lu.se
InAs nanowire conductivity

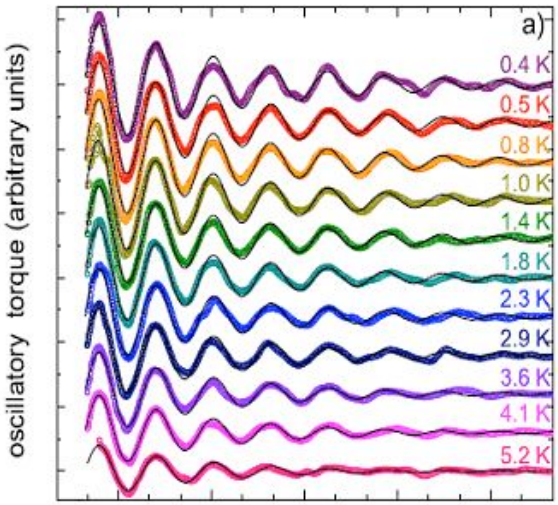


Magnetic effects

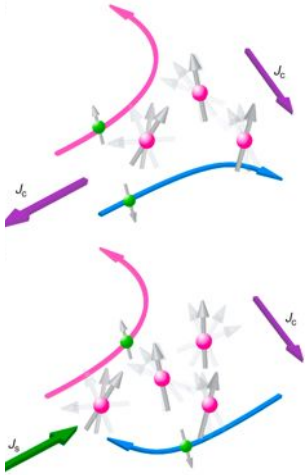
- "Normal" Hall effect
- AHE, SHE, ISHE, QHE
- Rashba, Topological Insulators
- de Haas van Alphen



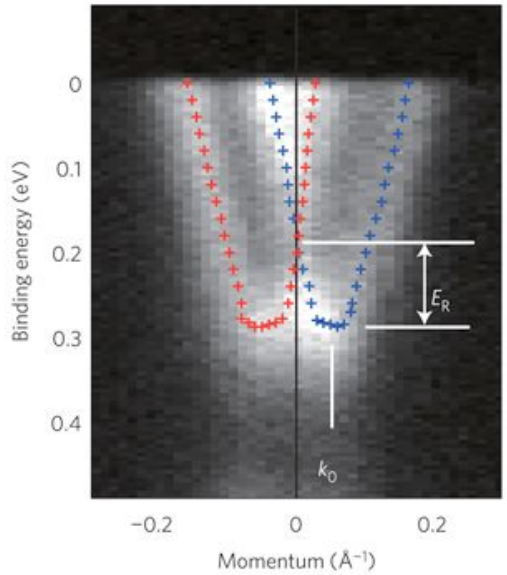
www.britneyspears.ac



Phys. Rev. Lett. 100, 187005 (2008)
YBCO cuprate Fermi Surface



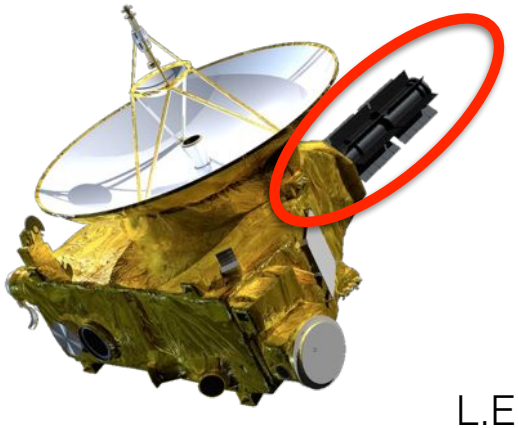
Nature Comms 3,1058 (2012)
SHE ISHE

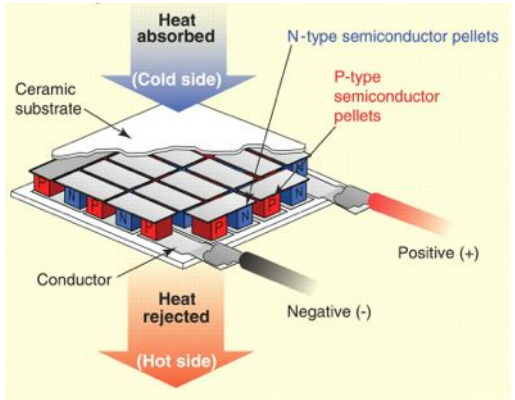


Nature Materials 10, 521 (2011)
BiTeI giant Rashba splitting

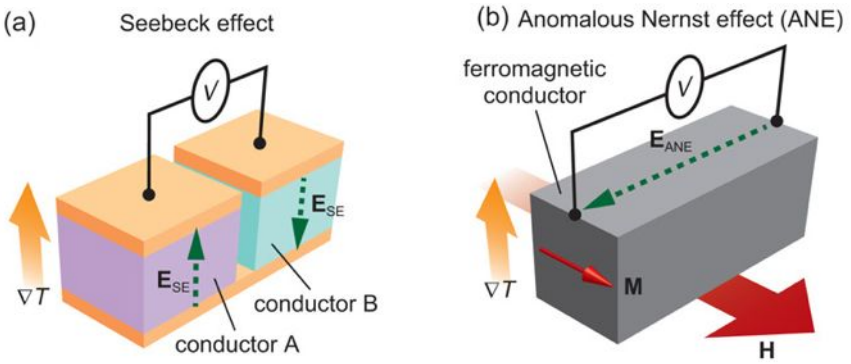
Thermal effects

- Seebeck / Peltier
- Spin dependent Seebeck
- Nernst (B+T → $I_{\perp}$)
- ANE + Spin Seebeck

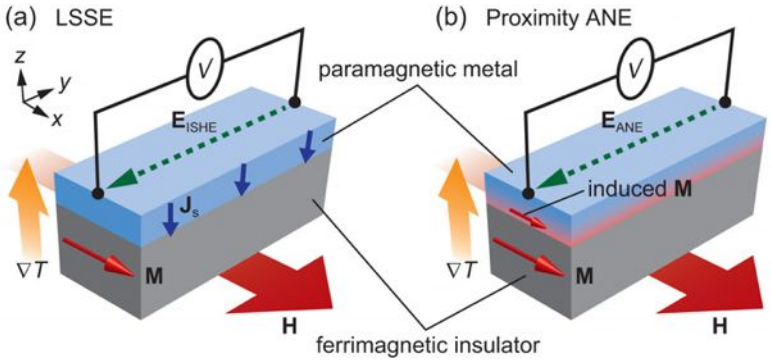




L.E. Bell, Science 321, 1457 (2008)

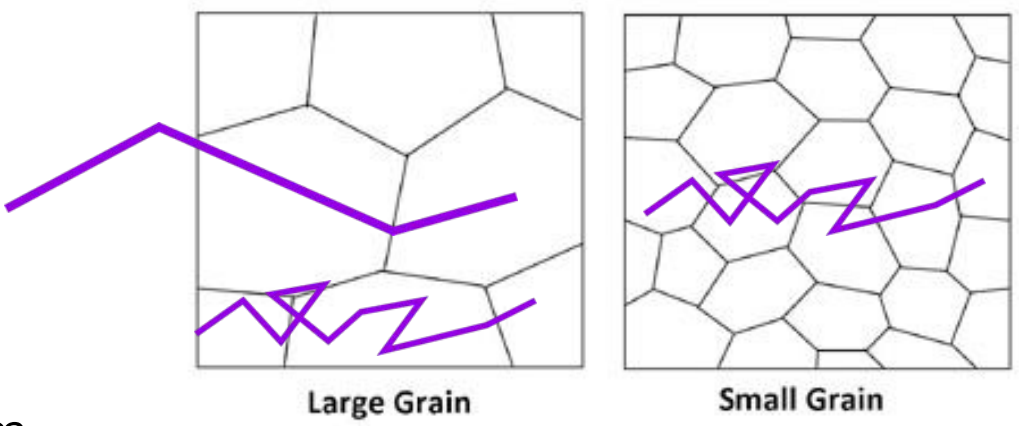


J. Phys.: Condens. Matter **26** (2014) 343202



Regimes for transport

- All transport eventually stops: interactions, boundaries…
- (De)localization of electrons: mfp = λ
- Which mean free path?
- Which system size?
- Localized: λ < few nm
- Diffusive: 10 nm < λ < 1 μm
- Coherent: system size < λ (0.1 - 100 μm)
- Beyond steady state: see Hardy (Mon) and Ivano (Wed)



Orders of magnitude

- Definitions of lifetime:

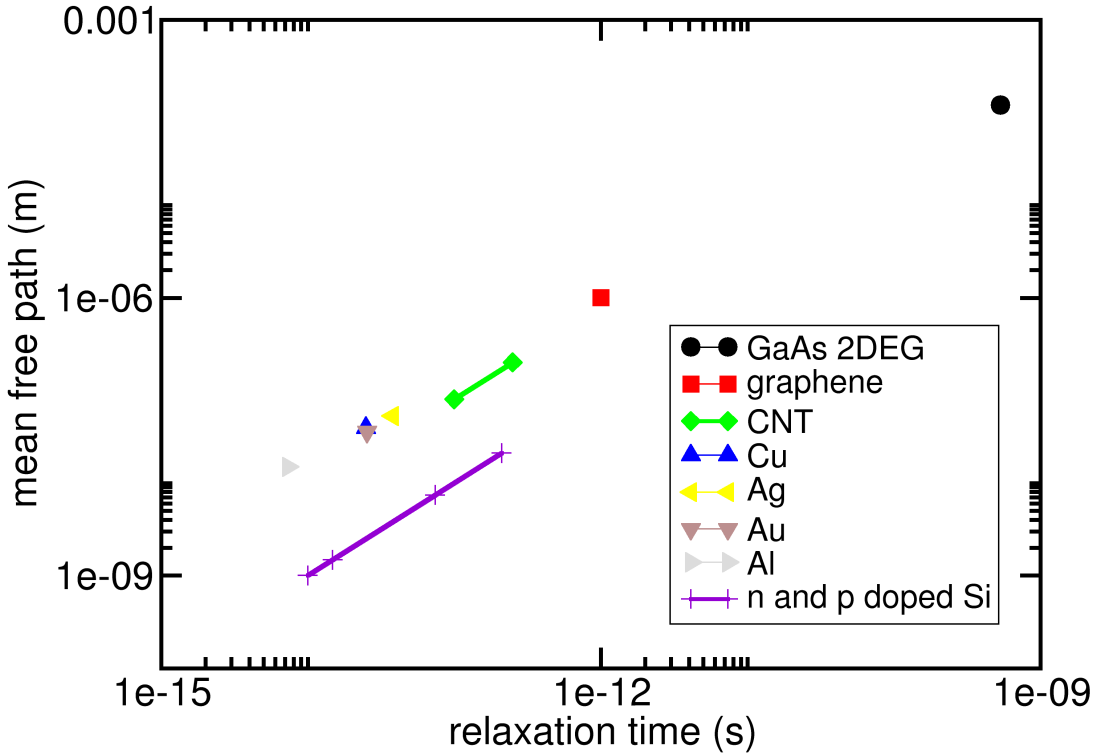
  momentum: k → k’

  energy: E → E’

  spin: s → s’

  others…

- Effective speed (v_F, v_{th})
- We observe averaged quantities…



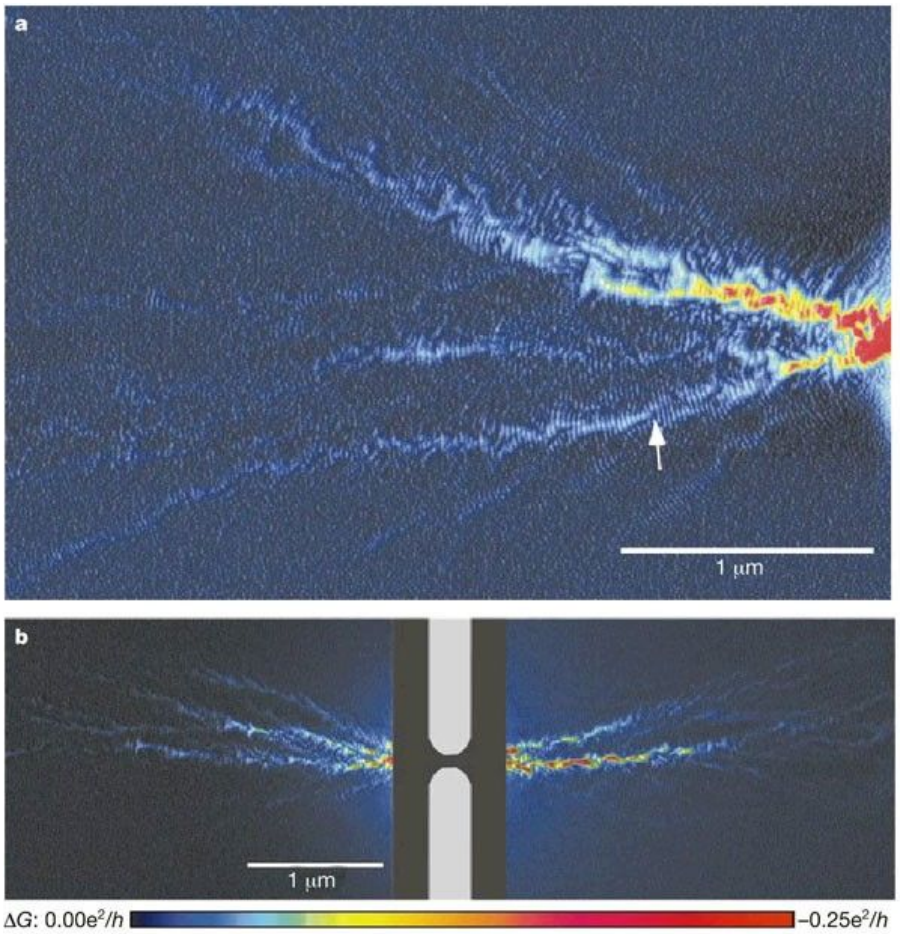
Non-diffusive transport

Coherent transport

- Coherence → interference
- Ballistic, boundary effects
- Aharonov-Bohm, Anderson, weak localization…
- Classical waves/billiards work
- Usually through 1D channel:

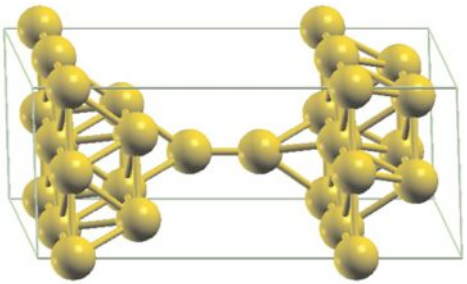
  Conductance is central object

  Kapitza + contact resistance



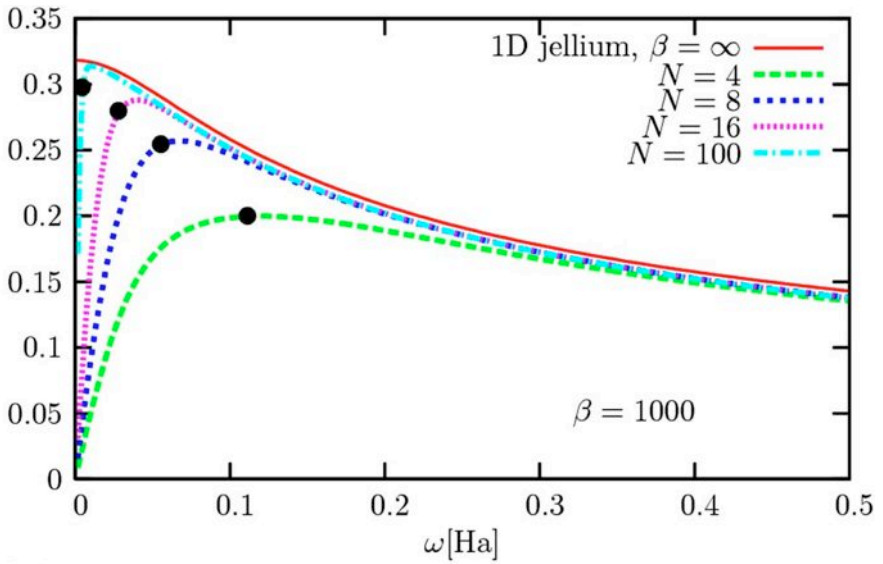
Nature 410, 183 (2001)
STM ~ current density in GaAs 2DEG

Linear response



- Dielectric response χ or polarisability P
- Conductance $= \omega \int_{-\infty}^{0} \int_{0}^{\infty} P(x,x';i\omega)dxdx'$
- Infinite size and 0 frequency limit
- Easy in principle
- Any electronic structure:
- (TD)DFT, GW, + more

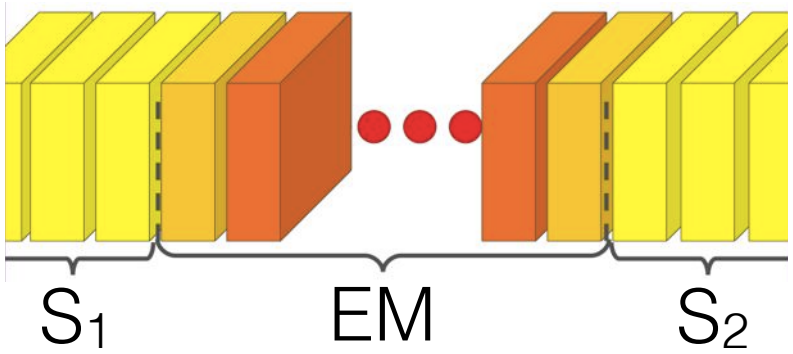
  (Hardy&Claudia on Monday)



J. Chem. Phys. **130**, 124715 (2009)

Green's functions

- Green's function: $HG = \delta(x-x')\delta(t-t')$ $G \sim H^{-1}$
- **NB**: also for other types of transport
- Equilibrium or non equilibrium ($\Delta V \neq 0$)
- 1D conductance $= \frac{e^2}{h} \int_{-\infty}^{\infty} T^{12}(E) \left(-\frac{\partial f}{\partial E} \right) dE$
- Usually in real space description



New J. Phys. 16 093029 (2014)

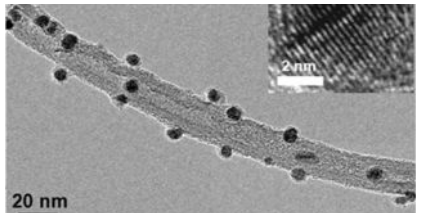
Phys. Rev. B 73 085414 (2006)

Nature Materials 4, 335 (2005)

Green's functions

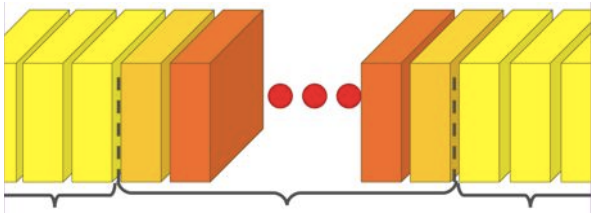
- Embedding "potential" for central region
- Atomic orbitals + DFT Hamiltonians:

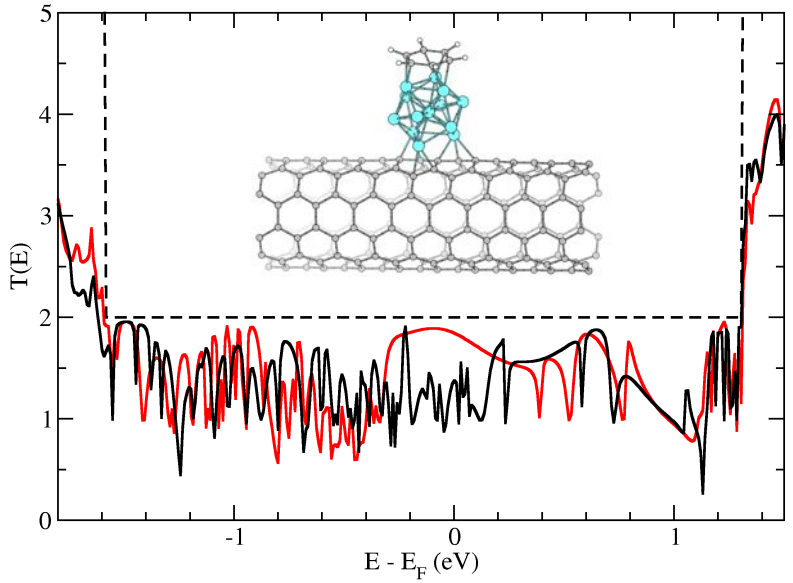
  GOLLUM, SMEAGOL, TRANSIESTA…



$$\begin{pmatrix} G_{S,0}^{-1} & -K^{\mathrm{coup}} \\ -\left(K^{\mathrm{coup}}\right)^{\dagger} & -\mathcal{K}^{\mathrm{EM}} \end{pmatrix} \begin{pmatrix} G_S & G^{\mathrm{SM}} \\ G^{\mathrm{MS}} & \mathcal{G}^{\mathrm{EM}} \end{pmatrix} = I$$

$$\mathcal{G}^{\mathrm{EM}} = -\left(\mathcal{K}^{\mathrm{EM}} + \left(K^{\mathrm{coup}}\right)^{\dagger} G_{S,0}^{-1} K^{\mathrm{coup}} \right)^{-1}$$

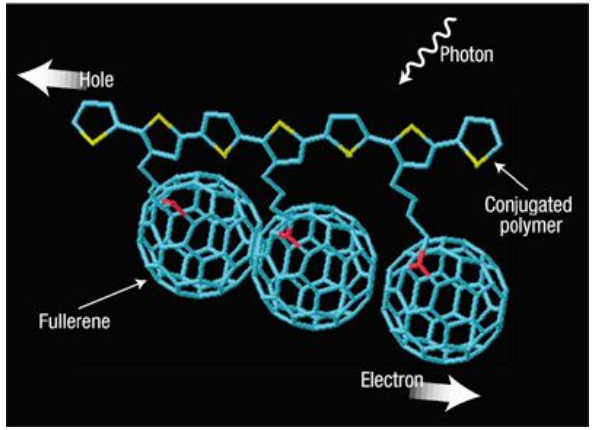




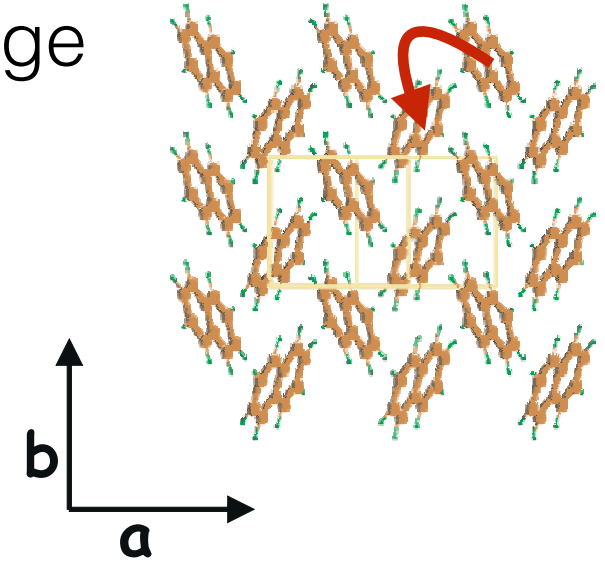
ACS Nano 5, 4592 (2011)
CNT + Ni clusters

Hopping

- Localized electronic states
- Fit model systems / Hamiltonians
- Thermal or quantum transfer of charge
- Organic molecular conductors
- Charge transfer complexes
- Small-medium sized polarons



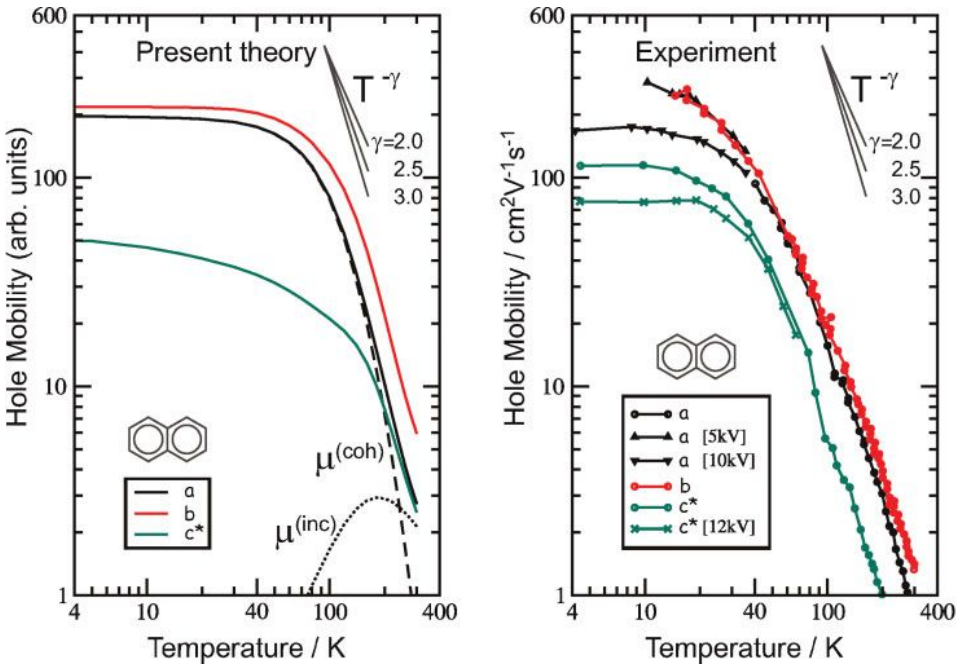
Nat Mat 2 360 (2003)
double wire polymer + C_{60}



Phys. Status Solidi B 248 511 (2011)
naphthalene herringbone

Ab initio polaron mobility

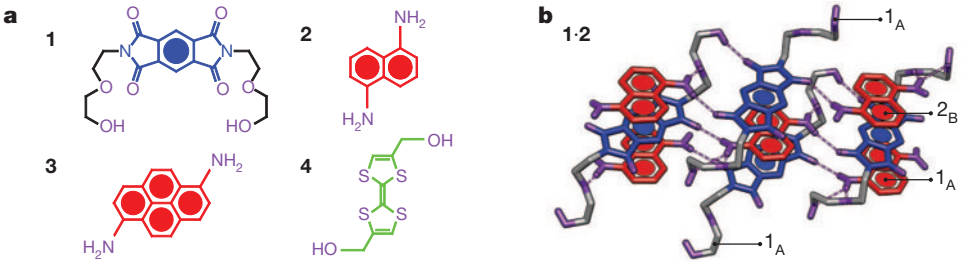
- Tight binding limit parametrized with DFT
- No phonon dispersion
- EPC ~ shift in bands
- All polaron strengths
- Missing full bands…
- + some quantum effects

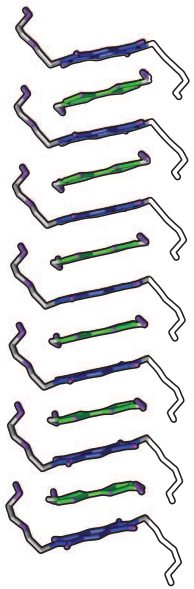


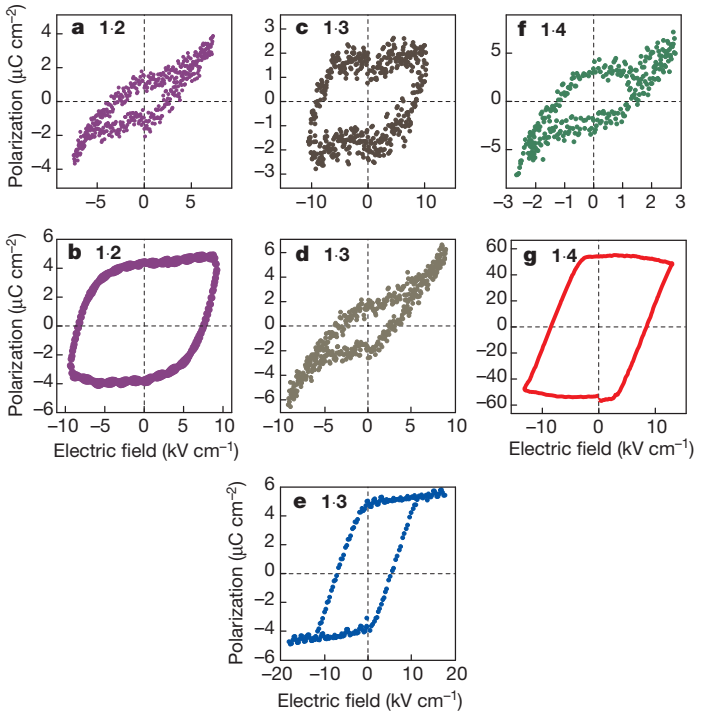
Phys. Status Solidi B 248 511 (2011)
naphthalene hole transport

Charge transfer dynamics

- Donor acceptor stacks
- Neutral to ionic transition
- Polarization vs E field
- DFT fit of simple model H
- + electrostatics



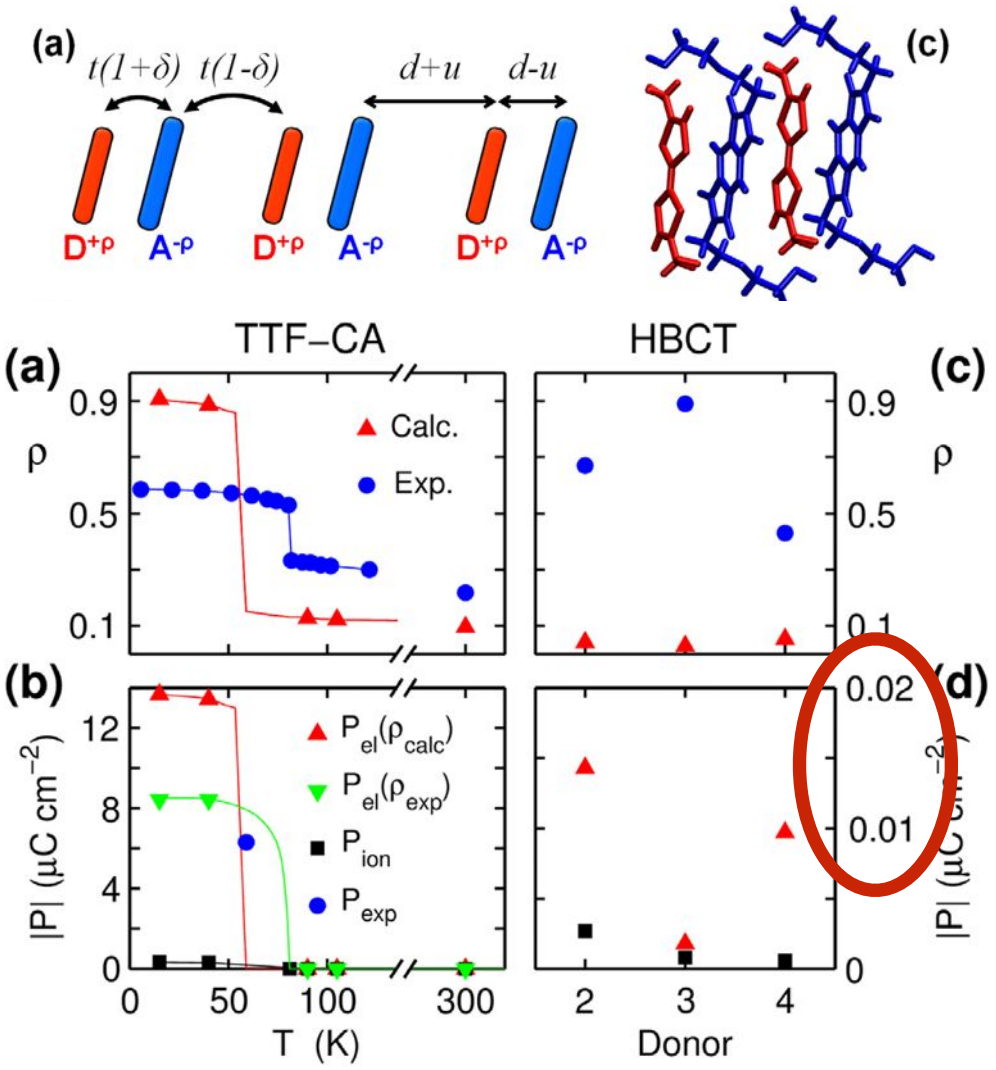




Nature **488** 485 (2012)

Charge transfer dynamics

- Hubbard chain+dimerization
- DFT for molecule pairs
- Polarizable model screening
- P and ρ are tiny in HBCT!
- Infirm experiments on new hydrogen bonded molecules!



Phys Rev Lett 113, 237602 (2014)

Diffusive transport

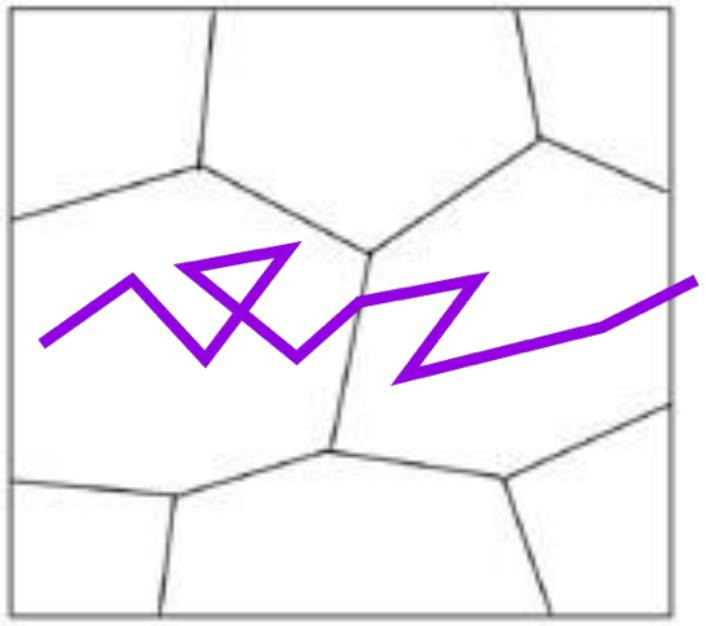
Diffusive transport

- Goldilocks regime (most common):

  Frequent scattering, but not too strong

- Ohmic conductance I ~ V
- Semi-classical BTE
- or Green-Kubo

  (cf Christian Wed)

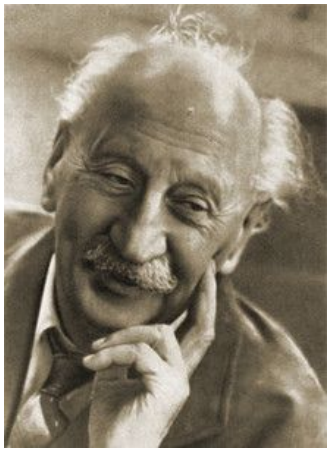


Scattering mechanisms

- Phonons
- Impurities / defects
- Magnons, electrons
- Dislocations / grains / surfaces…
- Easy to add scattering terms (Matthiessen)

$$\frac{1}{\tau} = \frac{1}{\tau_{imp}} + \frac{1}{\tau_{ph}} + \frac{1}{\tau_{bdy}} + \frac{1}{\tau_{el}}$$

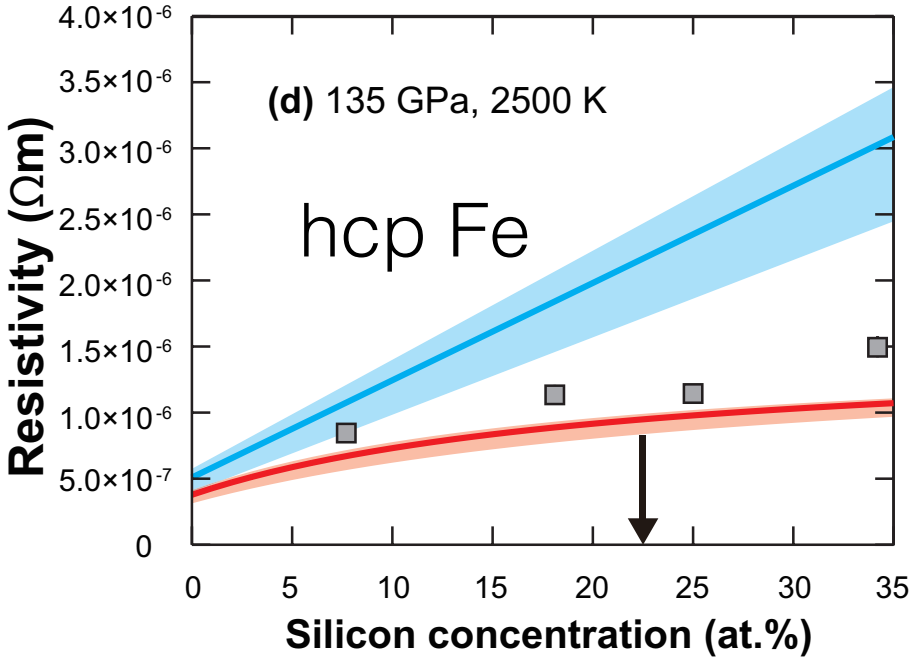
Ioffe Regel



- Large T or strong impurity limits
- How often can you scatter?
- Fundamentally: $\lambda > a$

Ioffe Regel Prog. Semicond. 4, 237 (1960)
DFT: Gunnarsson RMP 75 1085 (2003)

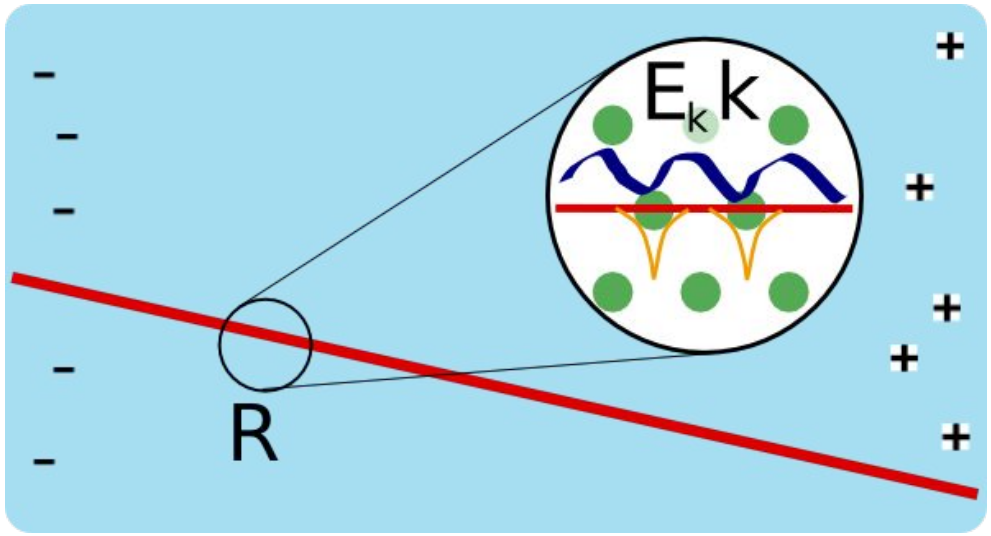
- Ex: Earth's core σ larger than expected



Gomi et al. PEPI 224 88 (2013)

Boltzmann equations

- Stat mech equations
- Mixed k and R space
- Add quantum statistics
- Diffusive scattering
- Extract current
- Transport coefficients

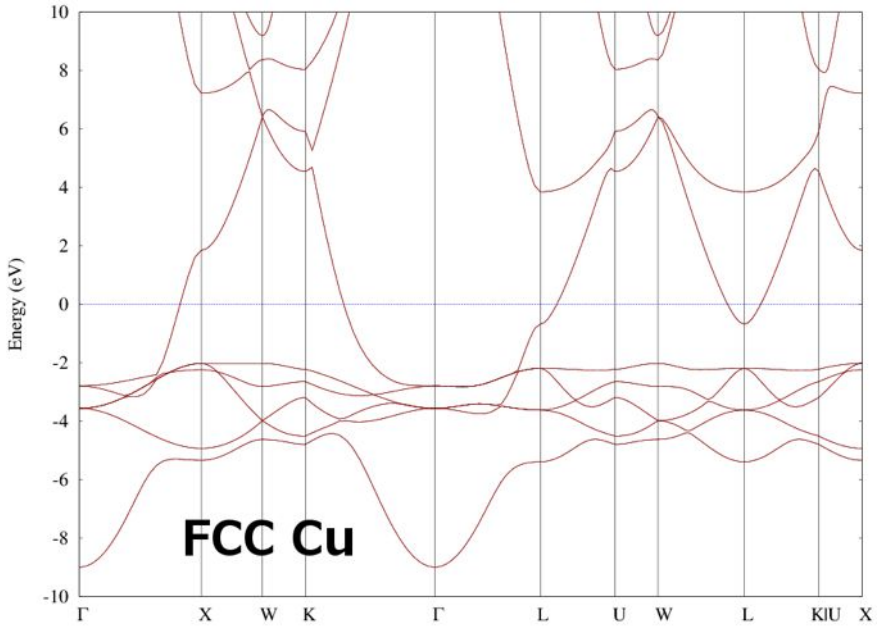


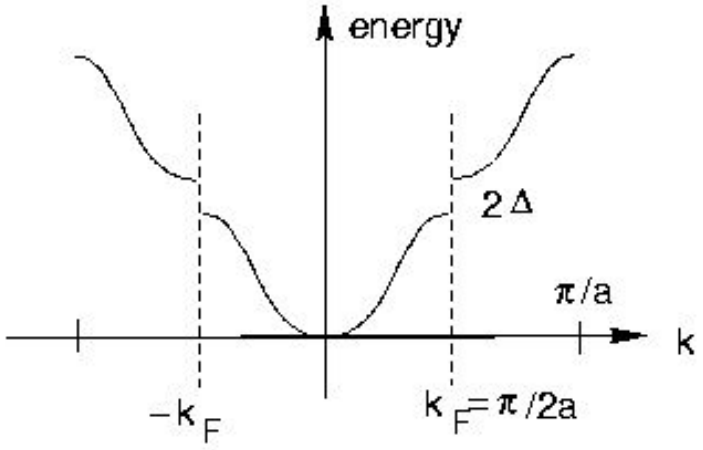
$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f + \vec{E} \cdot \frac{\partial f}{\partial k} = \left(\frac{\partial f}{\partial t} \right)_{coll}$$

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

General Arguments

- Depends on:
  - Band picture
  - Group velocity
- Works **far** beyond formal range of applicability
- Too weak disorder: $\sigma \rightarrow \infty$
- Too strong disorder: $v_g \rightarrow 0$





BTE solutions

- Relaxation time approx $\left(\frac{\partial f_k}{\partial t}\right)_{coll} = -\frac{\delta f_k}{\tau_k}$
- Basis set Ansatz $\delta f = \sum_i c_i \phi_i$
- Full discretization of f $\delta f_k \;\; \forall k \in 1\mathrm{BZ}$
- + Monte Carlo sampling of $\left(\frac{\partial f_k}{\partial t}\right)_{coll}$

Relaxation time approximation

- (constant) Relaxation Time Approximation
- Average and isotropic tau $\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f - f_0}{\tau}$
- Similar to superconducting dirty limit
- Bands + velocities → spectral conductivity:

$$\sigma(\epsilon) = e^2 \tau \sum_{i,k} v^{\alpha}_{i,k} v^{\beta}_{i,k} \frac{\delta(\epsilon - \epsilon_{i,k})}{d\epsilon}$$

- Still need estimate for τ !!!

Boltztrap : Madsen Singh CPC 175 67 (2005)

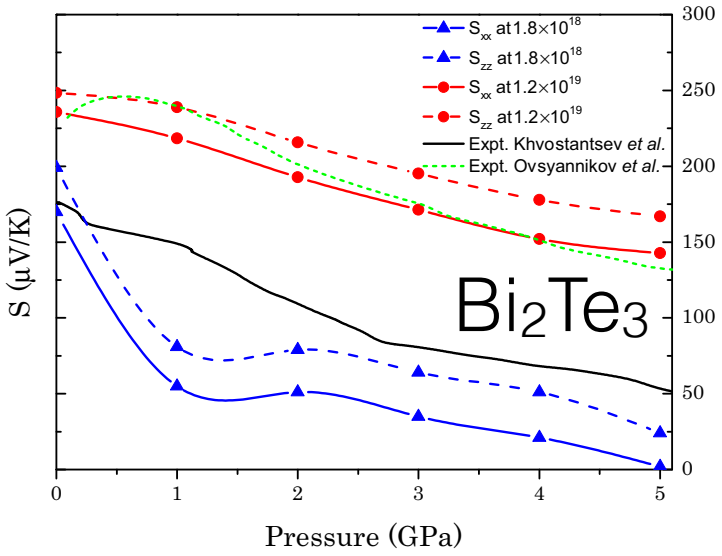
Transport coefficients

- Closed form solution BTE
- DFT+ in bands+transport
- T, μ dependency is ok
- S does not need lifetime

$$\sigma = \int \sigma(\epsilon) \left(-\frac{\partial f_0}{\partial \epsilon} \right)$$

$$S = \frac{1}{\sigma T} \int \epsilon \, \sigma(\epsilon) \left(-\frac{\partial f_0}{\partial \epsilon} \right)$$

$$\kappa = \frac{1}{T} \int \epsilon^2 \, \sigma(\epsilon) \left(-\frac{\partial f_0}{\partial \epsilon} \right)$$



Madsen Singh CPC 175 67 (2005)
Ibarra PRB **90**, 245204 (2014)

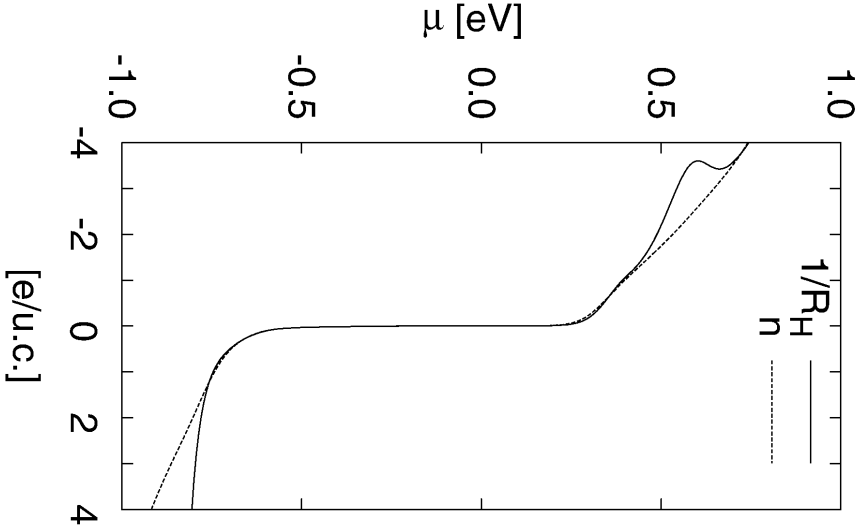
Hall effect

$$\sigma_{\alpha\beta\gamma}(\epsilon) = \tau^2 \epsilon_{\gamma u v} v^{\alpha}_{i,k} v^{v}_{i,k} M^{-1}_{\beta u}$$

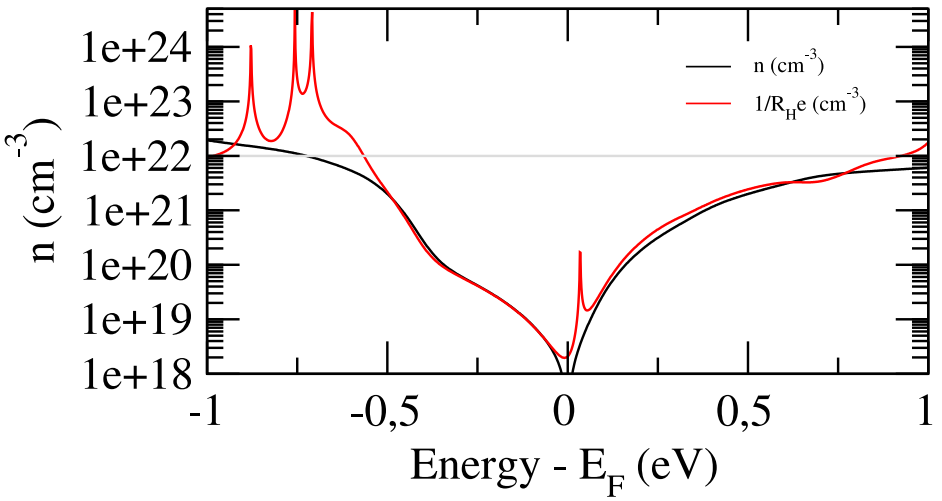
$$\sigma_{\alpha\beta\gamma} = \frac{1}{T} \int \sigma_{\alpha\beta\gamma}(\epsilon) \left(-\frac{\partial f_0}{\partial \epsilon} \right)$$

$$R_H = (\sigma^{-1})_{\alpha j}\, \sigma_{\alpha\beta k} (\sigma^{-1})_{i\beta}$$

- In general n ≠ 1/R_H
- Only for parabolic bands
- Issue in experiment too!!!



CPC 175 67 (2005) - CoSb3



S Lemal submitted - FeSb3 skutterudite

Variational approximation

- Variational basis $\delta f_k = \sum_i c_i \phi_i(k)$
- Matrix equation for scattering

$$-\sum_i c_i Q_{ji} = \vec{E} \cdot e \int \phi_j(k) \vec{v}_k \left(-\frac{\partial f_k}{\partial \epsilon} \right) = \Omega \vec{j} \cdot \vec{E}$$

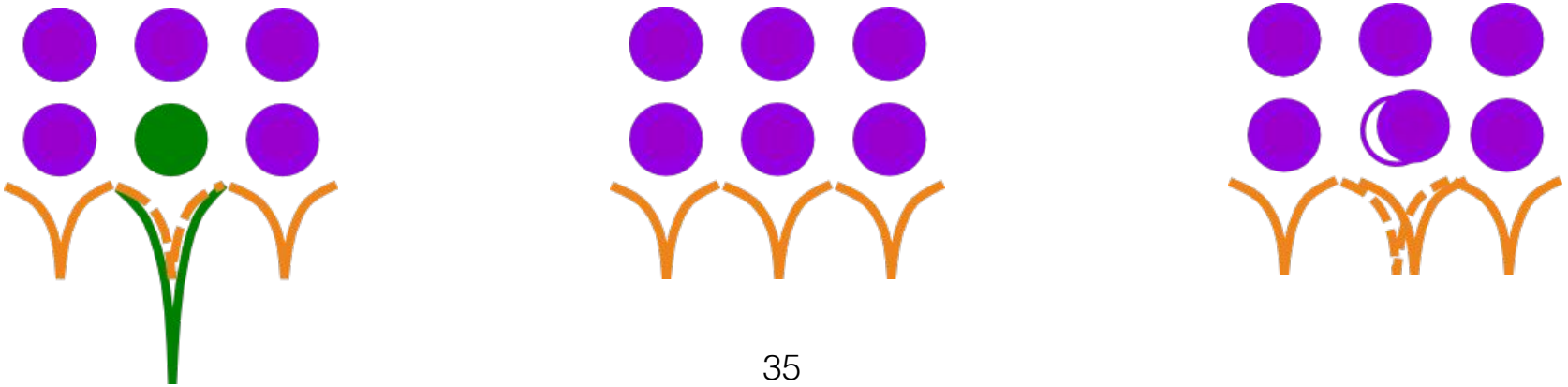
- Thermodynamics → c_i which maximize entropy
- Need first principles Q as well as bands

PB Allen PRB 17 3725 (1978)
Quant Theo Real Mater chap 17 (1996)
… and others

First principles scattering

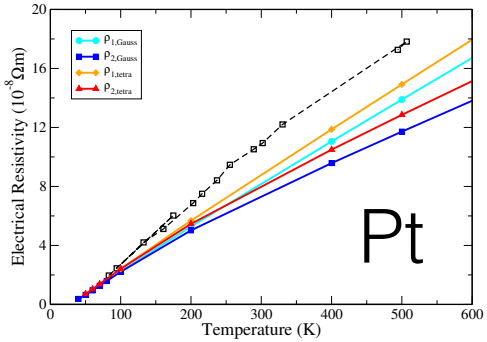
- Deformed potential scatters electrons
- Matrix element + Fermi's Golden Rule:
- Elastic vs Inelastic: neglect ω before E_F
- + Fermi smearing

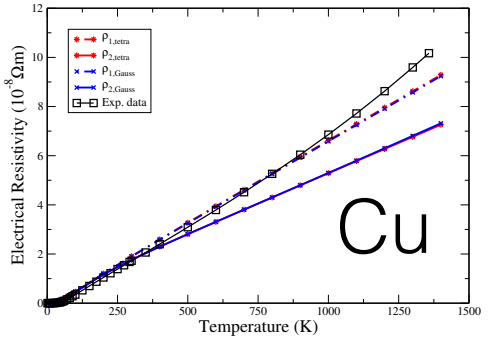
$$Q_{kk'} = \sum |\langle k'|\delta V_q|k\rangle|^2 f_0(1-f_0')N_q\delta(\epsilon_{k'} - \epsilon_k - \omega_q)$$

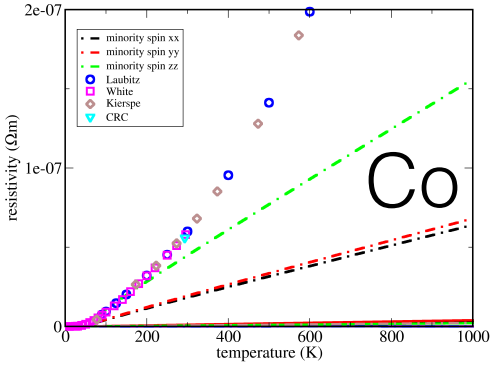


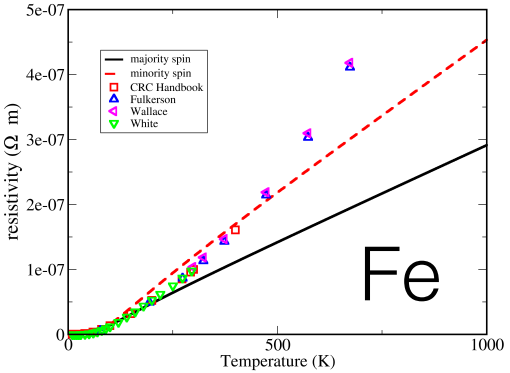
Electrical resistivities

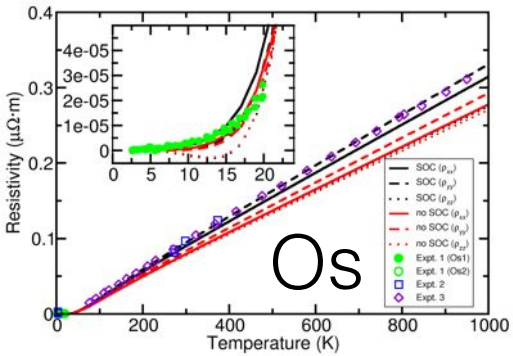
- DFPT matrix elements
- Phonons only…
- Simple metals, d, spin orbit
- Heavily doped SC

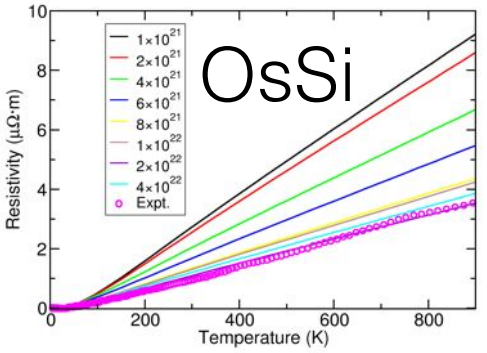








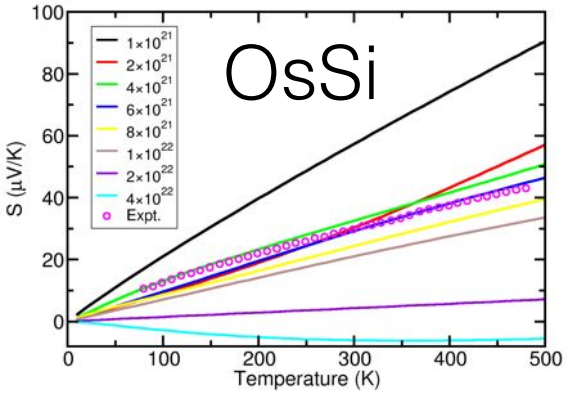


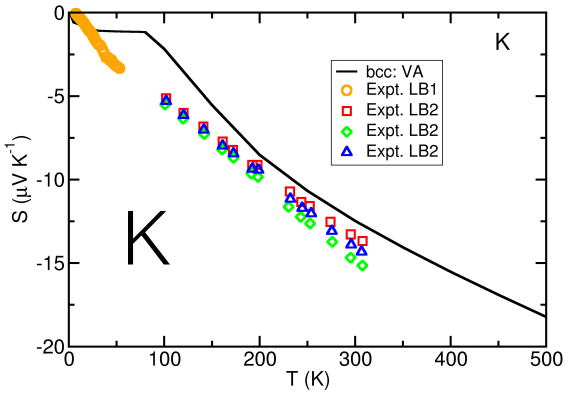


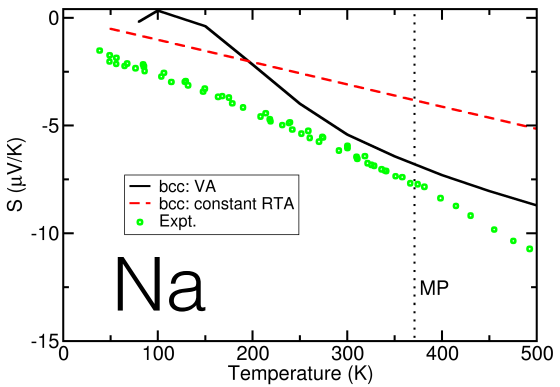
MJV JPCM 2013
B. Xu + MJV PRB 87 134302 (2013)
Di Gennaro unpublished

Seebeck coefficients

- RTA simple / High throughputable
- cRTA is sometimes very wrong…
- NB: S = 0 in elastic approximation
- LOVA excellent for simple metals

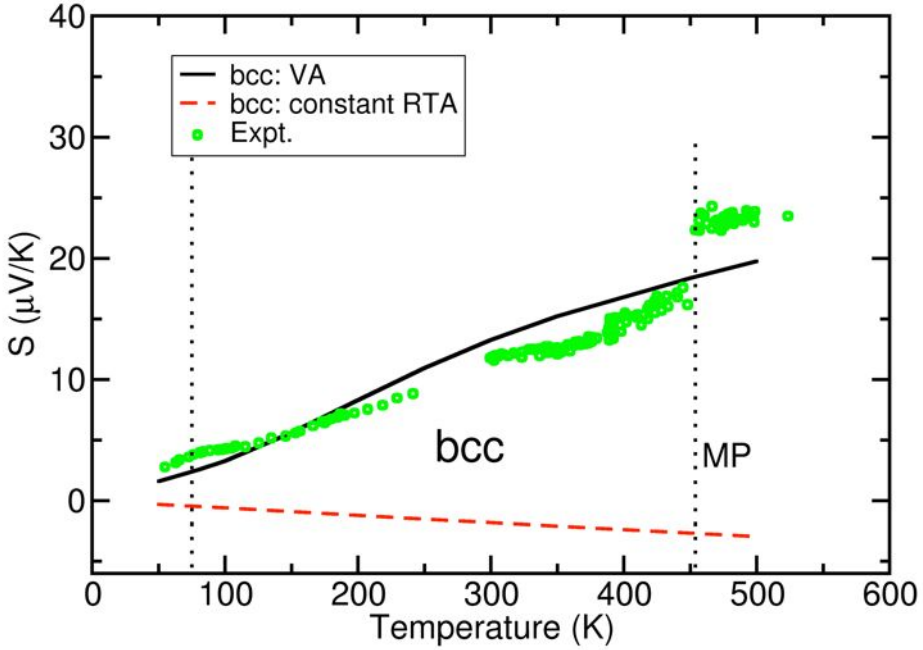






Anomalous Li Seebeck

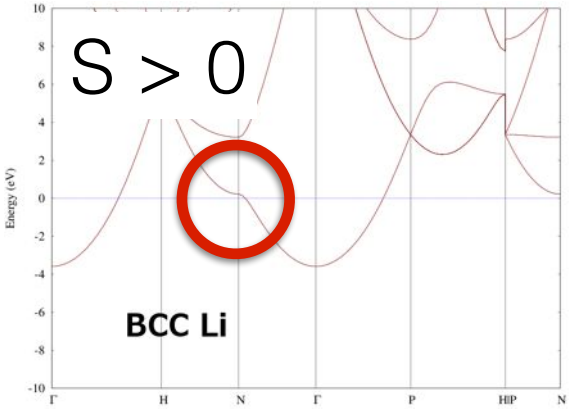
- Electron carriers: S < 0
- Not in Li! (or Au, Cu, Ag…)
- Propositions in the 60s:
  - spectral mfp, exotic EPC
  - "unfree" electron gas

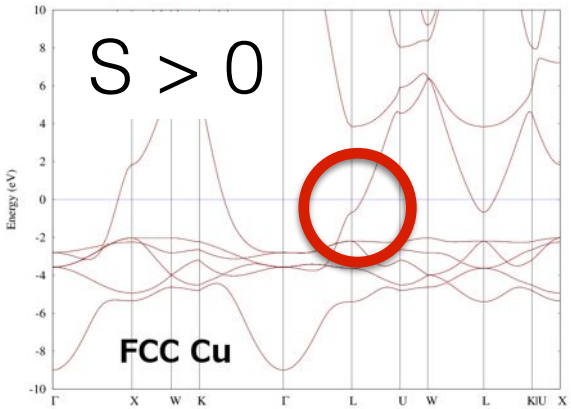


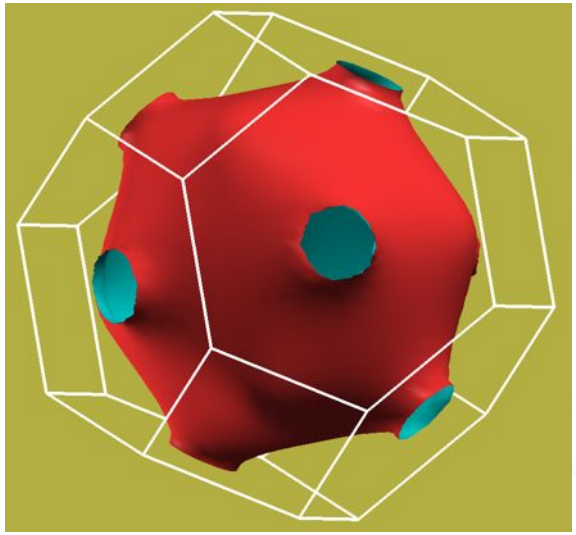
Robinson, Phys. Rev. 161, 533 (1967)
Robinson and Dow, PR 171, 815 (1968)
Jones Proc. Phys. Soc. A 68 1191 (1955)

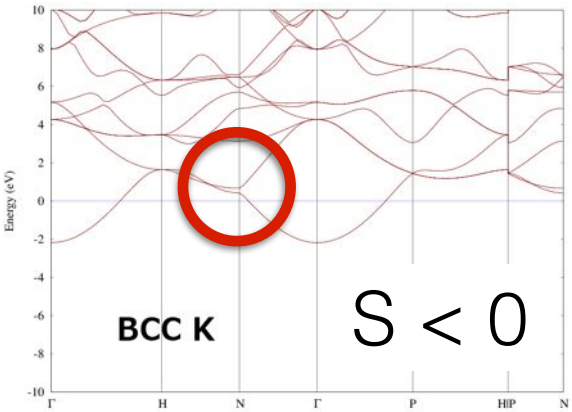
B. Xu + MJV PRL 112 196603 (2014)

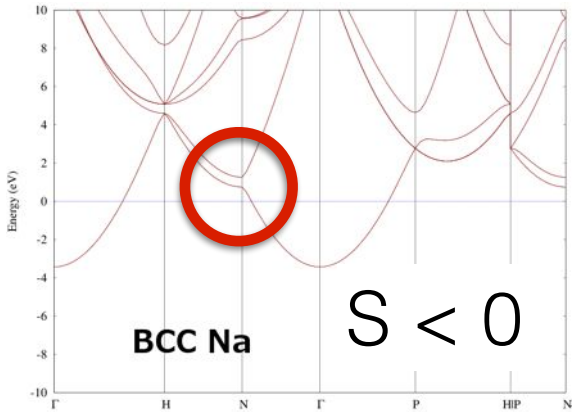
Band Structure effect?

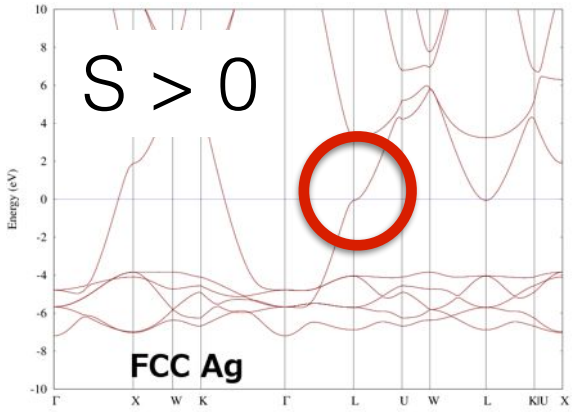












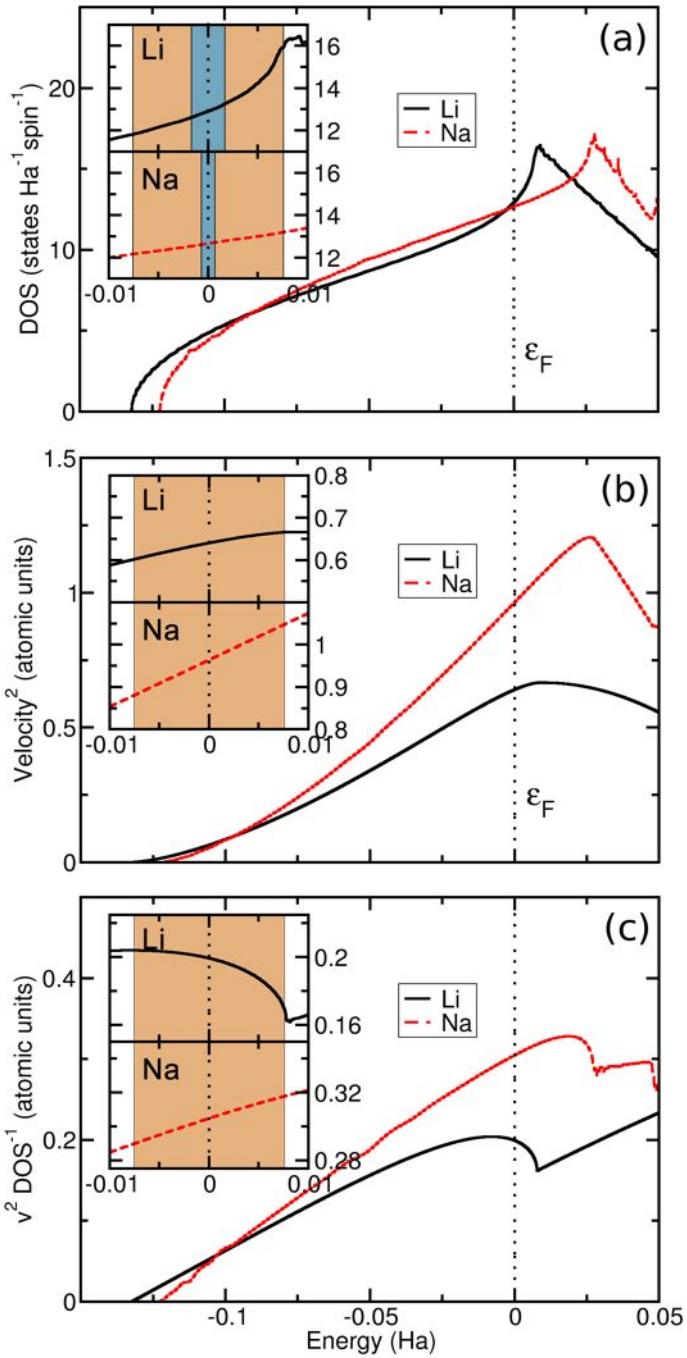
Extracted from AFLOW.lib

In a way…

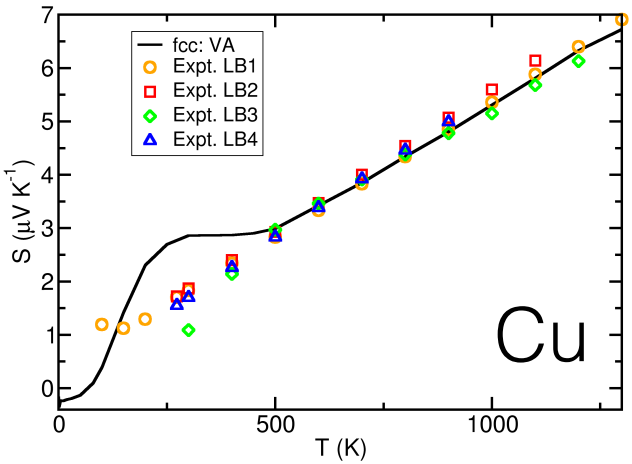
- EPC is not important
- Bare band RTA not enough
- Scattering(E) ~ $v^2(E) / N(E)$
- Both Robinson and Jones are (in)correct

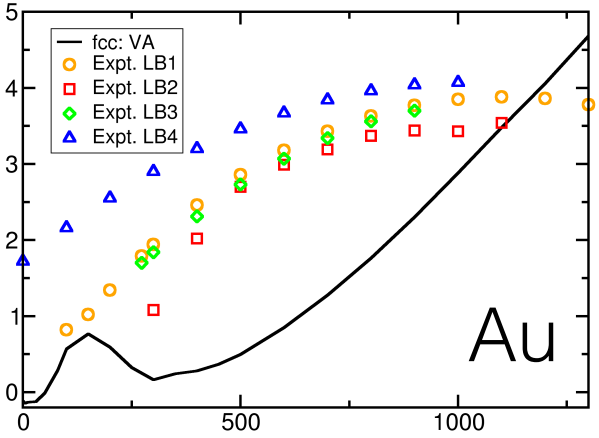
$$S = -\frac{\pi^2 k_B^2 T}{3e}\left[\frac{1}{\sigma}\frac{d\sigma(\epsilon)}{d\epsilon}\right] \qquad \sigma = ne^2\tau/m^*$$

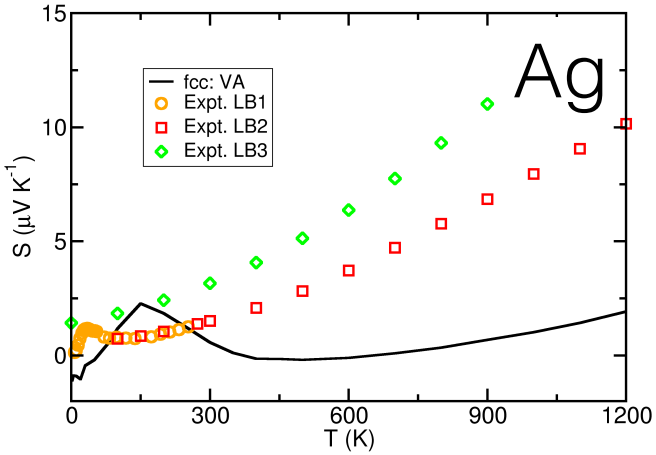
B. Xu + MJV PRL 112 196603 (2014)



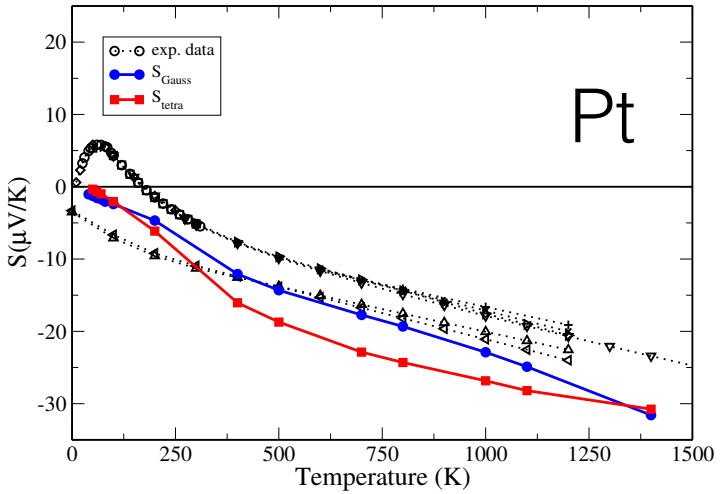
Other positive S





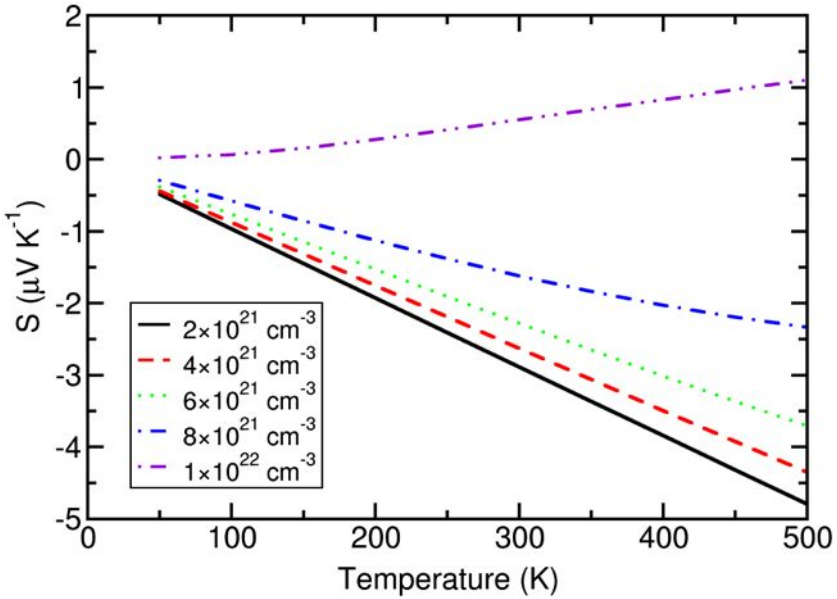


- Sign+magnitude ok
- details more complicated
- d electron Fermi Surfaces delicate



Belhadji, Di Gennaro, Xu, Verstraete unpublished

Useful to engineer S?



- In some cases: Na electron doped (e.g. with Ca)
- Realistic TE materials are case by case
- Tailor dopant for carrier density *and* for lifetimes

Summary

- The need for first principles transport
- Overview of transport regimes: λ and τ
- Ballistic and hopping transport
- Diffusive BTE solutions: RTA and variational
- Ab initio conductivity and Seebeck