Matériaux thermoélectriques: de la structure de bandes aux corrélations électroniques

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Durée du module : 2h

Objectifs

The aim of the course is to develop the basic understanding of the influence of the electronic correlations. The consequences of electronic correlations for single-particle spectroscopies and for the thermoelectric properties of the system will be discussed.

Contenu - programme

1) Electronic correlations, theory and material examples
    - electronic structure of solids: successes and limitations of the band-picture
    - Mott insulators, Hubbard model
    - correlated metals:renormalized quasiparticle band and atomic excitations
    - temperature evolution of the spectra
    - brief introduction to dynamical mean-field theory
2) Seebeck coefficient in a correlated metal
    - calculation of transport, key differences with transport in semiconductors
    - low T Boltzmann transport, influence of velocities and of scattering time
    - high T atomic limit, Heikes formula
    - case of a doped Mott insulator in a dynamical mean-field theory
    - role of entropy, benefits of going to multi-orbital

Electronic correlations and thermoelectricity

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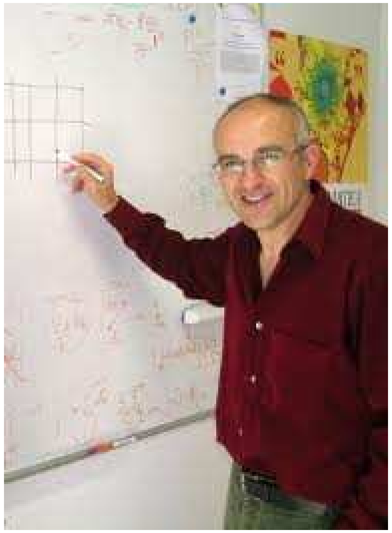
Annecy, 6.6.2014

Benefited from numerous discussions with prof. A. Georges



Lectures on thermoelectricity:
http://www.college-de-france.fr/site/antoine-georges/course-2012-2013.htm

Outline

- Part I: Introduction to electronic correlations
  - What are correlated electrons? Why are they such? How is this observed? What they do?
  - Band-like and atomic-like spectra
  - Doped Mott insulator within DMFT
- Part II: Thermoelectricity of correlated metal
  - Effects of renormalization
  - Effects of atomic physics
  - Doped Mott insulator within DMFT
- Part III: (time permitting) Thermopower in Sr_2RuO_4.

Correlated electrons: THE problem of solid state physics

- Interactions → Electrons not a single Slater determinant of one-el states
- Correlated electrons interesting theoretically:
  - Competing ground states, quantum critical points
  - Heavy fermions, ...
- Have interesting properties for applications:
  - High-temperature superconductivity
  - Giant magnetoresistance
  - **Large Seebeck coefficient (cobaltates, skuterudites with Ce)**

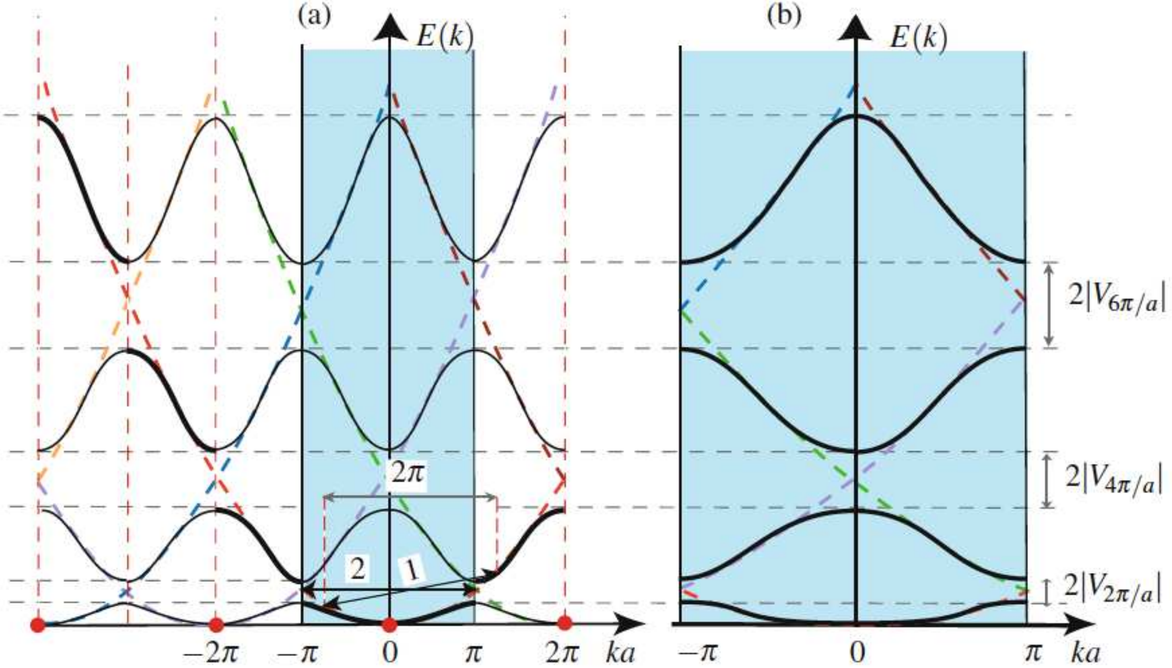
What are correlated electrons?

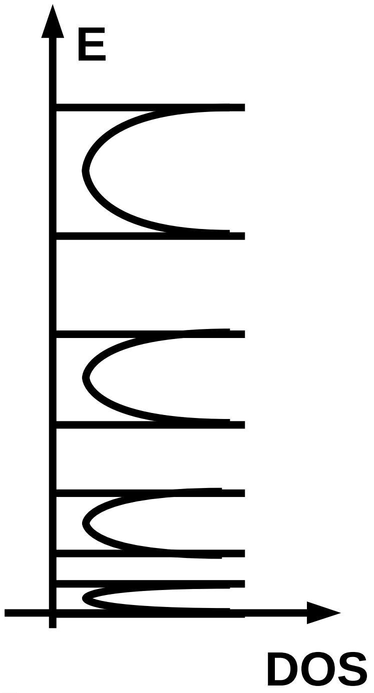
Noncorrelated electrons

- Solids are els. around periodically arr. cores

$$H = -\frac{\hbar}{2m_e}\sum_i \nabla_i^2 - \sum_{iJ}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_i - \vec{R}_J|} + \sum_{ij}\cancel{\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_i - \vec{r}_j|}}$$

No interactions → bands





(from book H. Alloul)

- k-resolved spectrum A(k,E)=δ[E-E(k)]; DOS=Σ_kδ[E-E(k)]
- Eigenstates are just (Slater) product of single-particle states (lowest energy ones for the ground state)

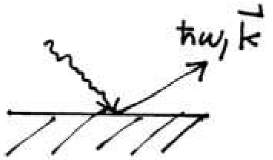
Band theory

- Good methods exist to calculate band structure in solids (that include interactions in mean-field)
- Most-often used is density-functional theory in the local-density approximation (LDA).

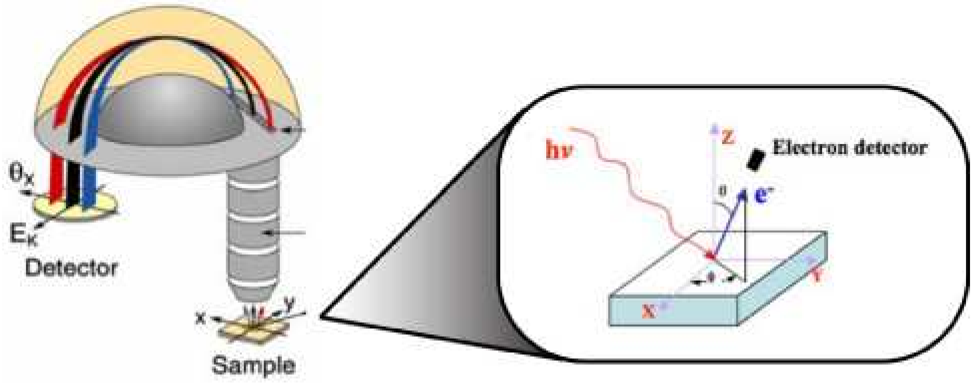
`Hohenberg, Kohn, 1964; Kohn, Sham, 1965`
`W.Kohn, Nobel prize in chemistry, 1998`

- Physical variables in DFT: energy and electron density
- Density expressed in terms of a Slater determinant of auxiliary single el. Kohn-Sham states),where effective potential includes exchange-correlation contribution evaluated for uniform el. gas
- Kohn-Sham energies (bands) in principle auxiliary non-physical quantities, but...

Experimental tests: measuring spectra PES,ARPES

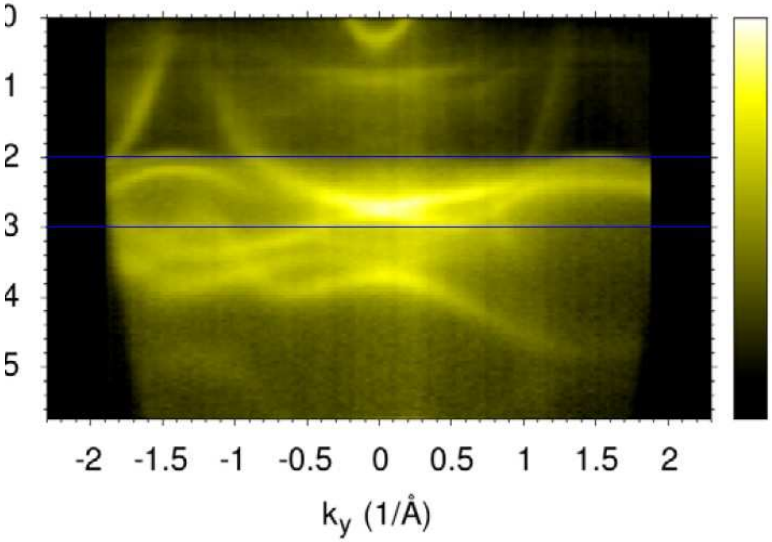


- “Hit” electrons with light and hear how they “sound”
- Probes occupied one-electron states
  I(k,E)=f(E) A(k,E)
- PES : k-integrated, probes DOS=Σ_k A(k,E)
- ARPES : k-resolved, probes A(k,E)



http://www.stanford.edu/group/photontheory/ARPES.html

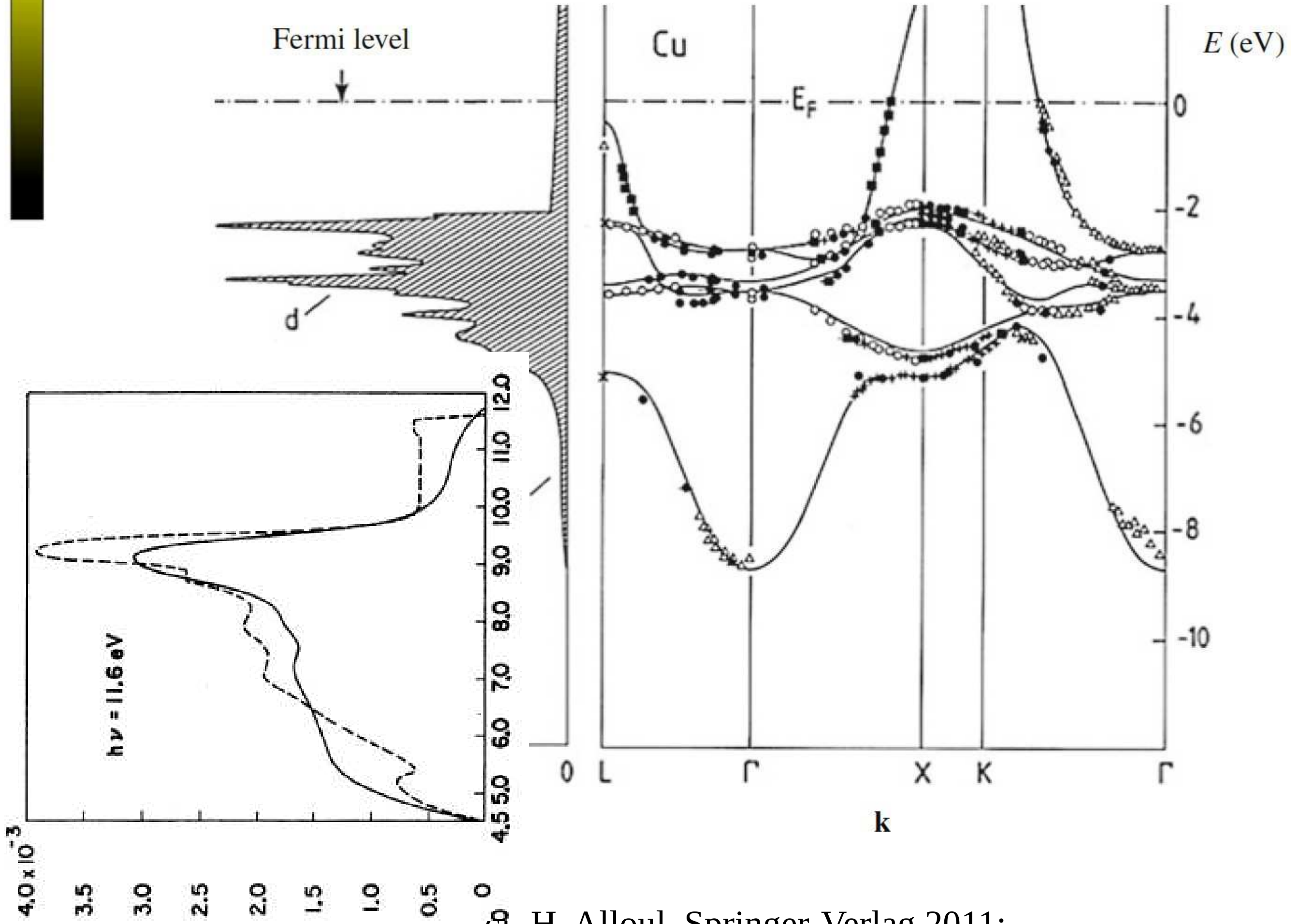
ARPES on Cu



New Journal of Physics **14** (2012) 043009

- Sharp excitations over wide energy range $A(k,E)=\delta(E-E_k)$
- Measured dispersions agree with LDA ones
- Validates band picture!

Symbols: peak of I(k,E)

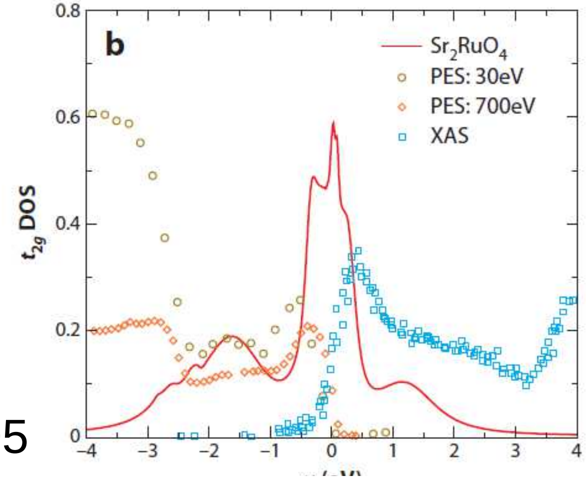


cf. H. Alloul, Springer-Verlag 2011:

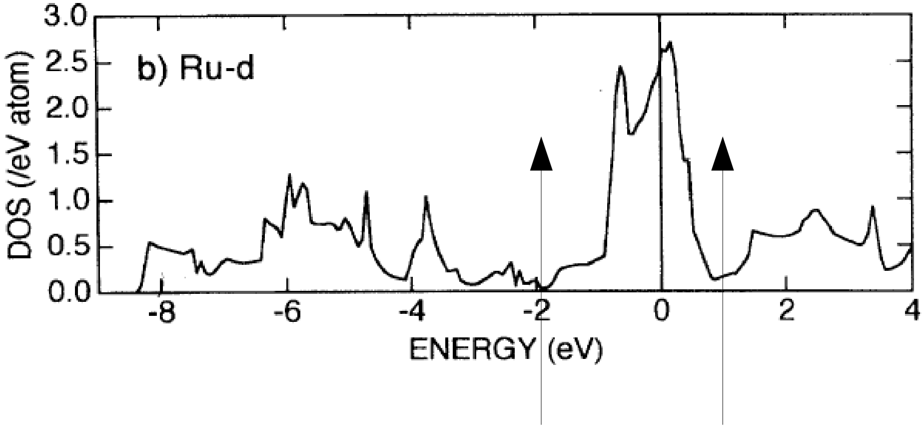
Courths, R., Hüfner, S.: Phys. Rep. **112**, 55 (1984)
Eckardt, H., Fritsche, L., Noffke, J.: J. Phys. F **14**, 97 (1984)

PES/ARPES on Sr_2RuO_4 : DFT fails

- Worse agreement with LDA
- Low energy peak narrowed

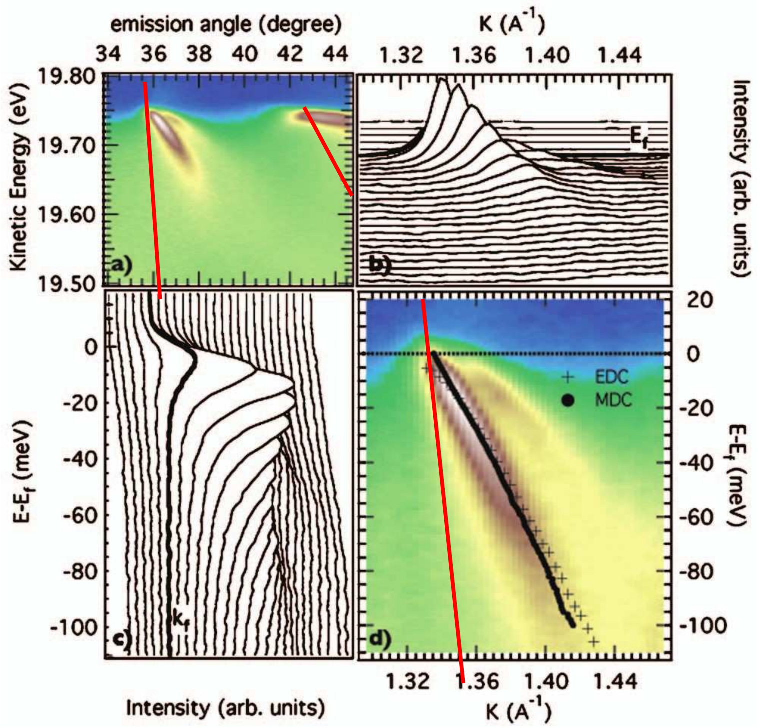


DFT:Oguchi PRB'95



“Satelllites” not there in DFT

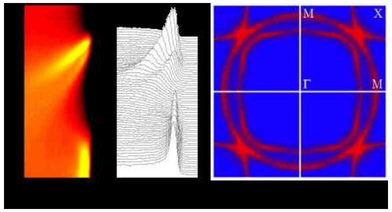
ARPES:No coherence >0.1eV



Ingle et al, PRB`05

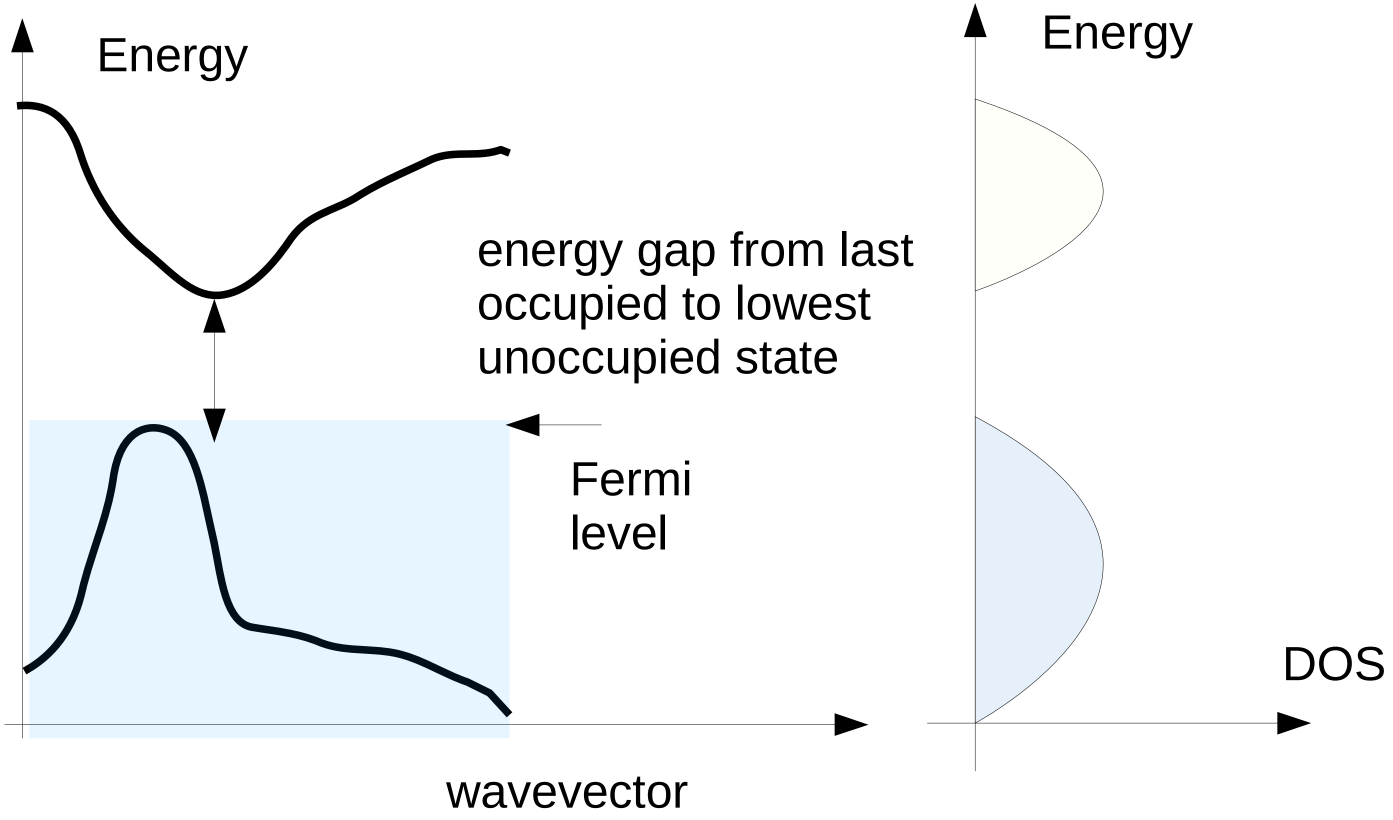
Red: band-theory

Fermi surface formed by Heavy qps. (weak dispersion, ($E=k^2/2m$, $dE/dk = k/m$))



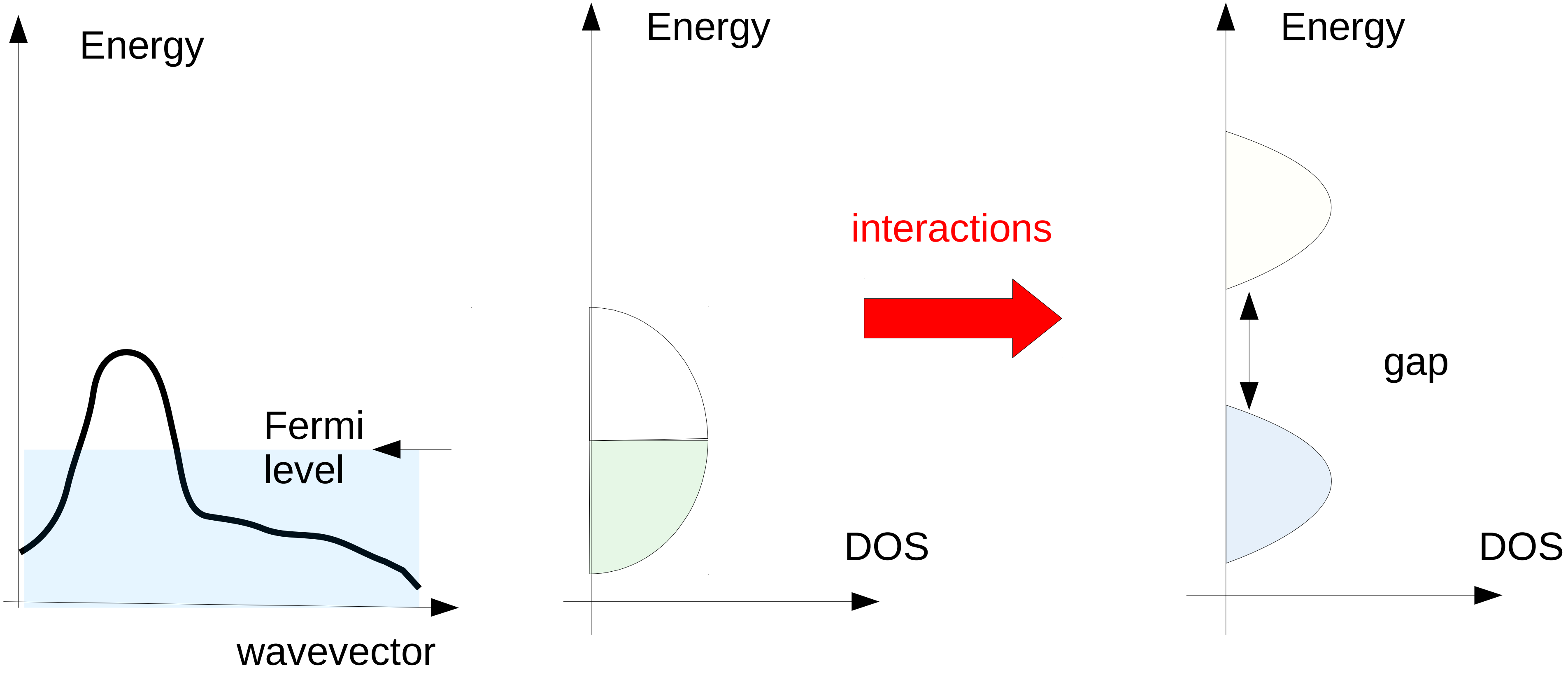
Band vs. Mott insulators

- Mott insulator: insulating state at non-complete filling of bands!
- Band insulator : 2 els per site (per orbital, for degenerate)
- Not possible to have insulating state for 1 el /band, insulating behavior comes from the complete filling.



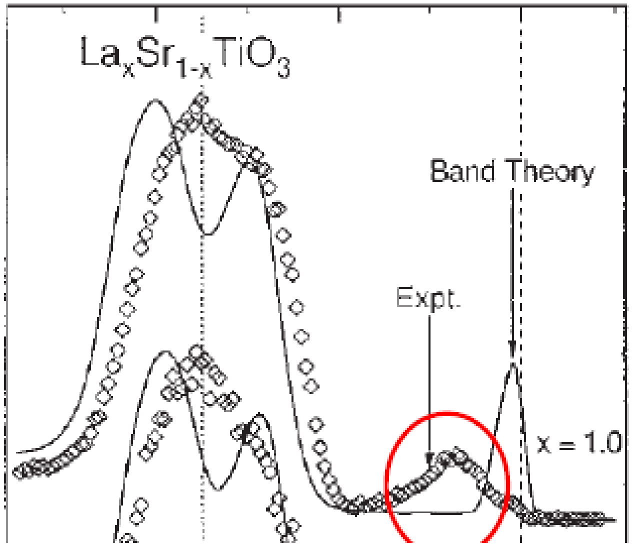
When repulsion kills a metal: Mott insulator

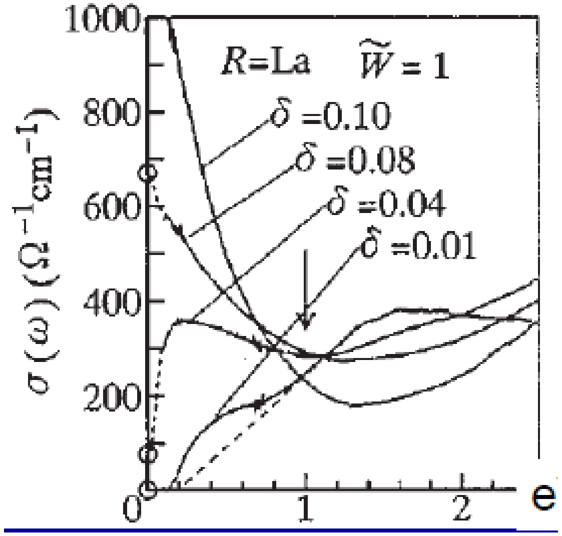
- Opening of a gap in half-filled bands.
- Interactions lead to appearance of atomic features: Hubbard bands



Mott insulators

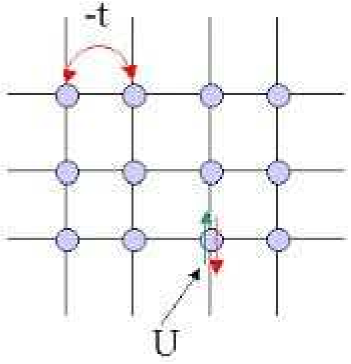
- Gap in photoemission
- Gap in resistivity
- In optical spectrum
- Often (but not always!) magnetically ordered
- Insulating also above ordering temperature!
- (In contrast to Slater insulators, e.g. $NaOsO_3$)





MIT; Hubbard model and challenges to solve it

- Hubbard model



$$H = -t\sum_{\langle ij\rangle}(c^{\dagger}_{i\sigma}c_{j\sigma} + c^{\dagger}_{j\sigma}c_{i\sigma}) + U\sum_{i} n_{i\uparrow}n_{i\downarrow} - \mu\sum_{i} n_{i}$$

Kinetic (band) part repulsion chemical pot.

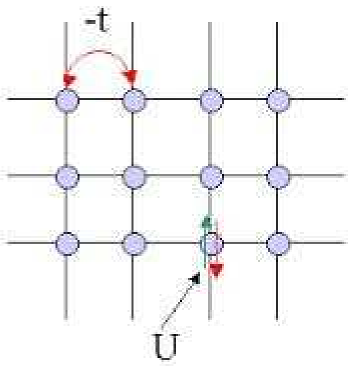
- Not solvable (for d>1). Exact diagonalization limited to N=4x5 sites. (Hilbert space grows as 4^N)
- Approximate solutions

MIT from localized side (Mott picture)

- Hubbard model

$$H = -t\sum_{\langle ij\rangle}(c^\dagger_{i\sigma}c_{j\sigma} + c^\dagger_{j\sigma}c_{i\sigma}) + U\sum_i n_{i\uparrow}n_{i\downarrow} - \mu\sum_i n_i$$

Kinetic (band) part   repulsion   chemical pot.



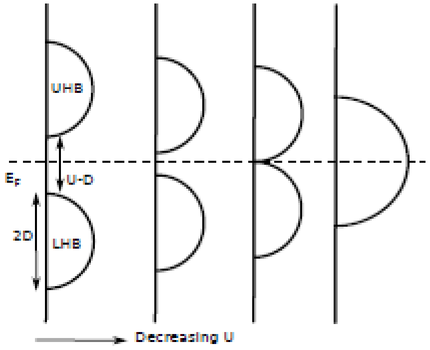
- Atomic limit (single site) at half filling

$$E(0) = 0$$

$$E(1) = -\mu$$

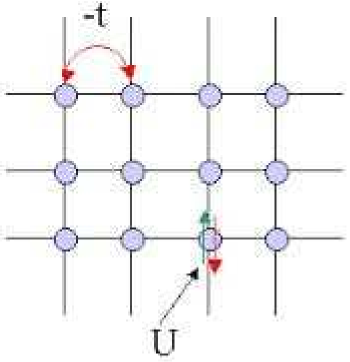
$$E(2) = U - 2\mu$$

- Hopping broadens atomic excitations into bands



Mott: when bands overlap: metal

MIT from itinerant side (Brinkman-Rice)



- Hubbard model

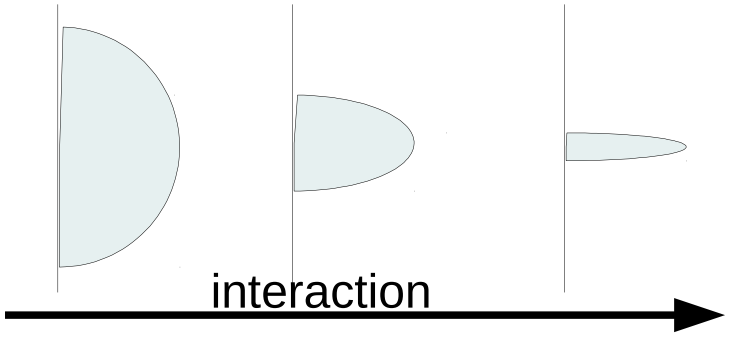
$$H = -t\sum_{\langle ij\rangle}(c^\dagger_{i\sigma}c_{j\sigma} + c^\dagger_{j\sigma}c_{i\sigma}) + U\sum_i n_{i\uparrow}n_{i\downarrow} - \mu\sum_i n_i$$

Kinetic (band) part repulsion chemical pot.

- Gutzwiller projecting double occupancies out of Slater det.

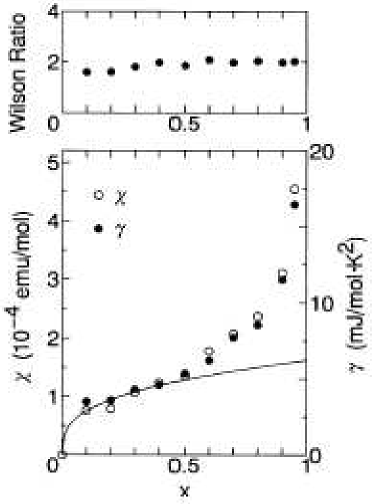
$$\Psi_{GWF} = \prod_i[1-(1-\eta)^\nu n_{i\uparrow}n_{i\downarrow}]\Phi_0 = g^{\hat{D}}\Phi_0$$

- Narrowing of bands W → Z W (Z<1)



Specific heat coefficient and susceptibility enhanced by 1/Z.

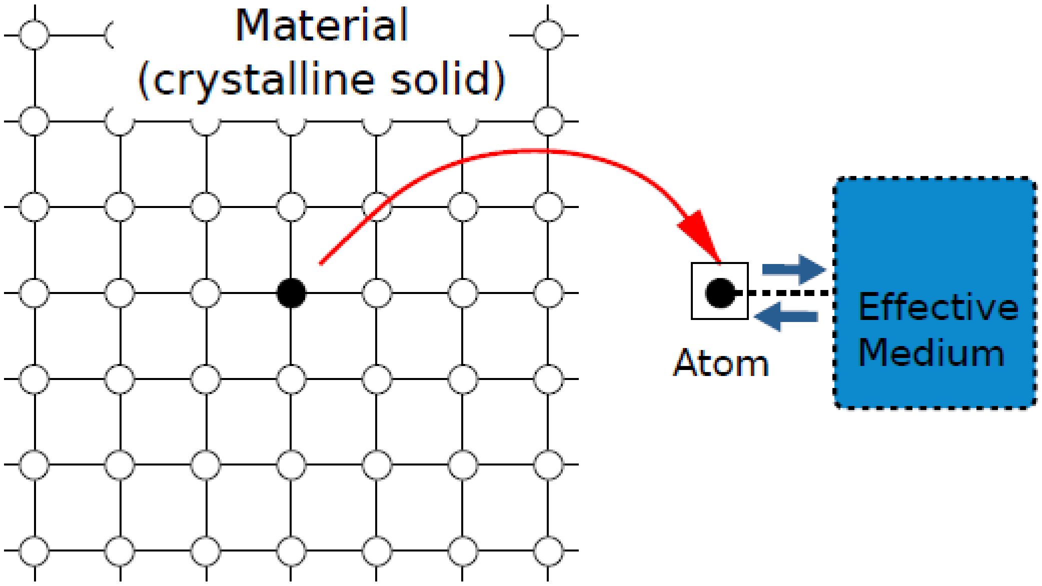
“Effective mass” m*/m=1/Z



- For doped Mott insulator, Z~δ , vanishes at δ->0
-

Dynamical mean-field theory

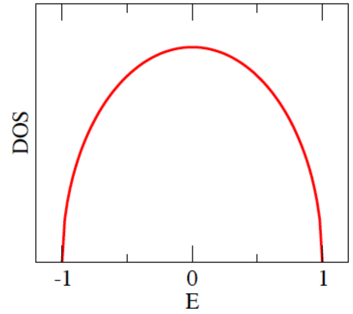
- In large d limit, simplification of perturbation theory
- Can be phrased as a mean-field theory with energy dependent order parameter (hence dynamical)
- Maps bulk to an atom in effective medium solvable by reliable numerical techniques

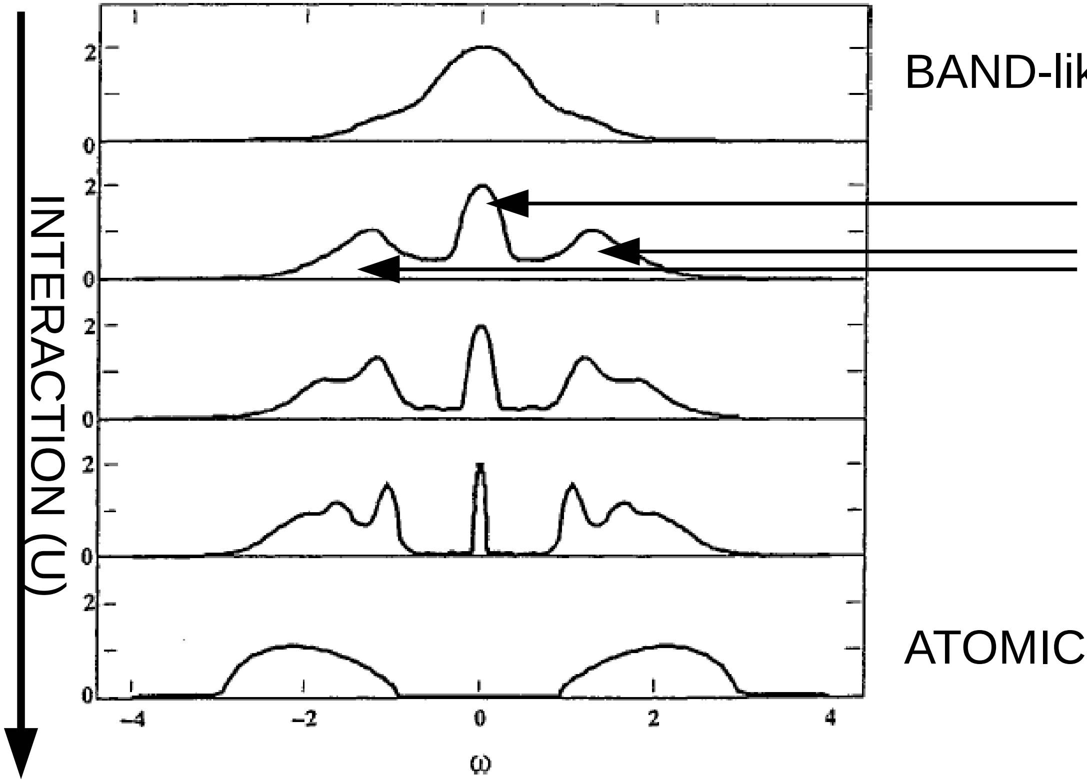


Georges et al. RMP'96

DMFT results

- Correct description of QP and Hubbard bands
- Metal-insulator transition



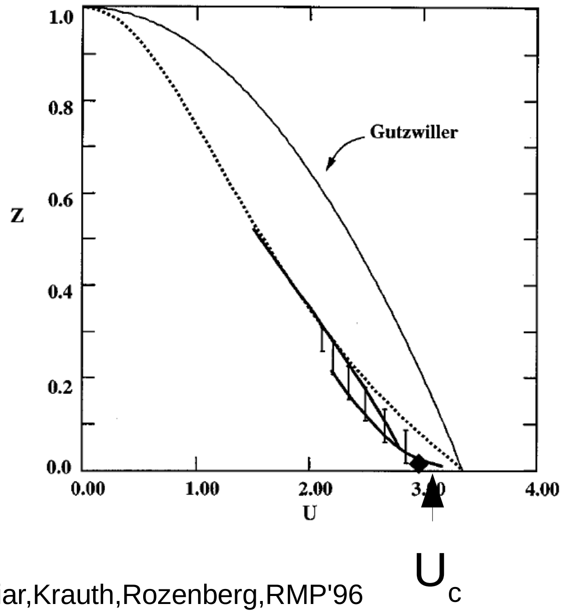


BAND-like

Quasiparticle band (weight Z)

Atomic satellites (weight 1-Z)

ATOMIC-like

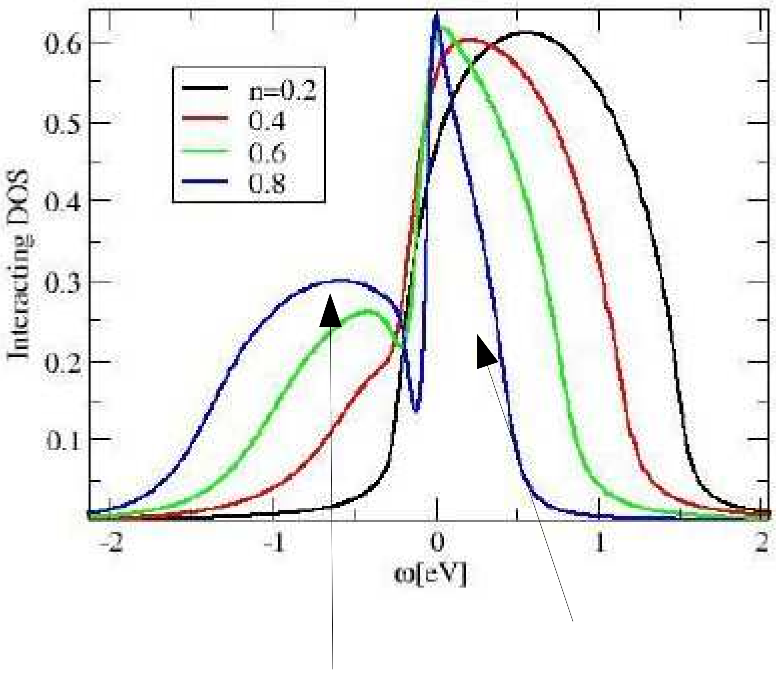


- Describes well vanadates, titanites,... Georges, Kotliar,Krauth,Rozenberg,RMP'96

Doping driven Mott transition

- Interactions mean DOS that depends on filling
- Evolution of DOS in Hubbard model with doping
- QP peak shrinks as doping (w.r.t half filling) → 0
- $Z \sim \delta$

R.Zitko, …,JM, A.Georges, and S. Shastry, PRB'13

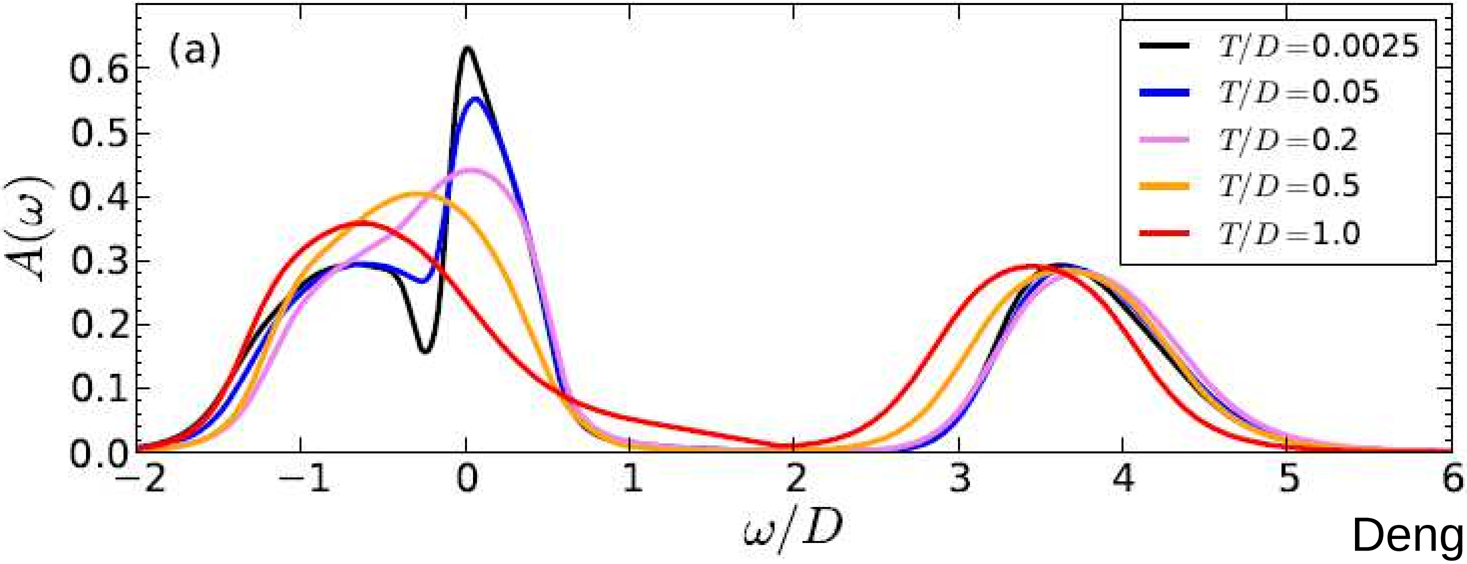


Upper Hubbard band not visible
(U very large)

Lower Hubbard band nicely separated from QP band, as δ → 0

Temperature dependence of DOS

- Strong T-dependence of DOS



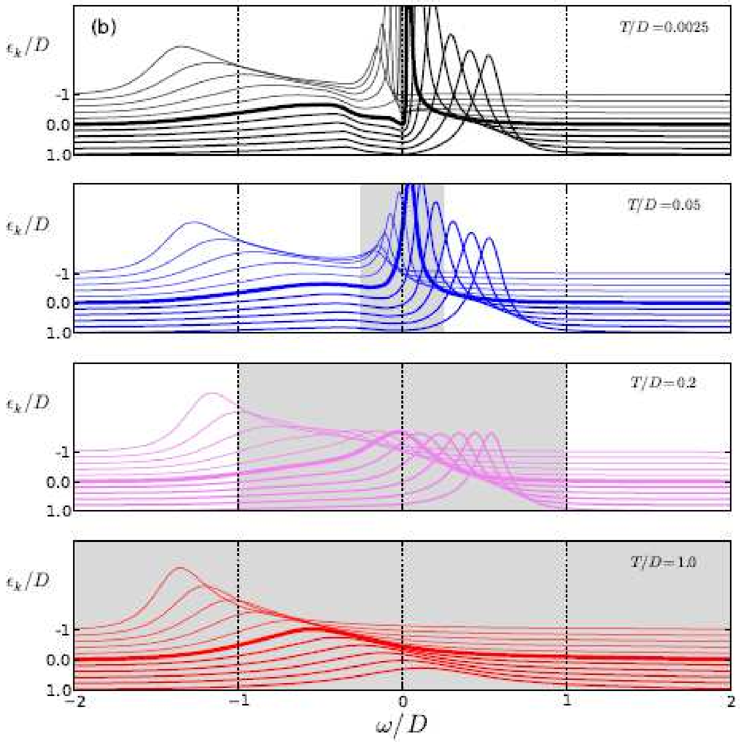
Deng, JM et al, PRL'13

Quasiparticle band vanishes at high T.

δ=0.2

k-resolved spectral function

- Low T very sharp peaks close to Fermi surface, broader away



Effects of interactions encoded
In self energy

$$A(k,\omega) = -\frac{1}{\pi}\mathrm{Im}G(k,\omega) = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega - \epsilon_k - \Sigma(\omega)}$$

$$A(\omega) = \sum_k A(k,\omega)$$

- High T disappearance of qp band

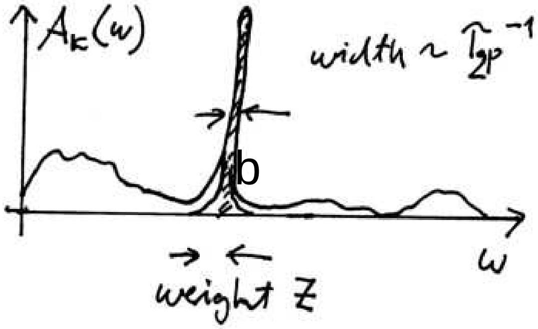
$$A(k,\omega) = -\frac{1}{\pi}\mathrm{Im}G(k,\omega) = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega - \epsilon_k - \Sigma(\omega)}$$

$$A(\omega) = \sum_k A(k,\omega)$$

- Impurity scattering (single peak)

$$\Sigma(\omega) = -i\Gamma \qquad G(k) = \frac{1}{\omega - \epsilon_k + i\Gamma}$$

- Interactions: peaks + incoherent background



- Peaks become sharp close to Fermi surface (Fermi liquid...)

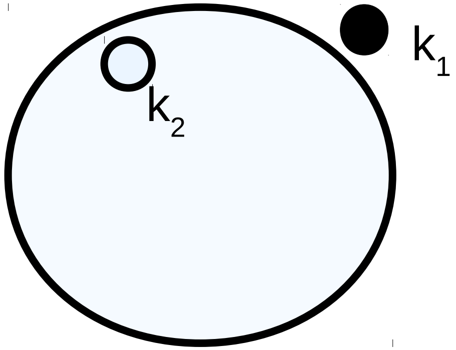
$$\Sigma(\omega) = -iA\omega^2 + (1 - 1/Z)\omega$$

Quasiparticles have suppressed:
Weight, dispersion, scattering rate

$$G(k) = \frac{1}{\omega - \epsilon_k - (1-1/Z)\omega + iA\omega^2} = \frac{1}{\omega/Z - \epsilon_k + iA\omega^2} = \frac{Z}{\omega - Z\epsilon_k + iZA\omega^2}$$

Fermi liquid at low T and E

- In metals, formation of Fermi surface, long-lived quasiparticle excitations
- Constraint on the scattering: adding an el to Fermi sea

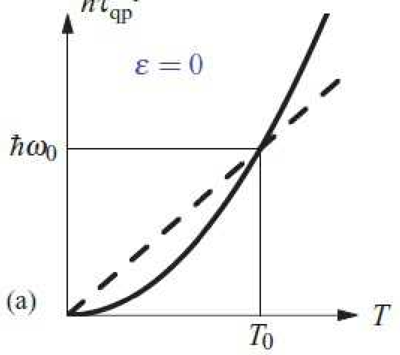


$$\Gamma \propto \sum_{k_2 k_1' k_2'} |\langle k_1' k_2' | U | k_1 k_2 \rangle|^2 n(k_2)(1-n(k_1'))(1-n(k_2')\delta(\epsilon_{k_1}+\epsilon_{k_2}-\epsilon_{k_1'}-\epsilon_{k_2'})\delta(k_1+k_2-k_1'-k_2')$$

$$\Gamma < |\tilde{U}|^2 \rho^3(0) \int_0^{\epsilon_{k_1}} d\omega_1' \int_0^{\epsilon_{k_1}-\omega_1'} d\omega_2' = |\tilde{U}|^2 \rho^3(0) \epsilon_k^2/2$$

As one approaches Fermi surface, life-time diverges. Well defined Fermi surface. Many oscillations before scattering.

$$\boxed{\Gamma_{\mathrm{FL}} \propto (\omega^2 + \pi^2 T^2)}$$



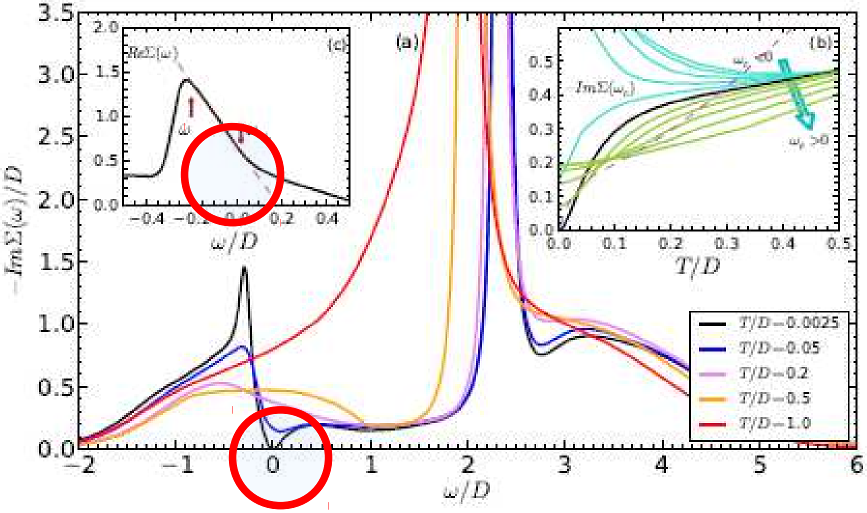
Quadratic dependence also in T.

In DMFT

Fermi liquid
at low T:

$$\Sigma(\omega) = -iA\omega^2 + (1 - 1/Z)\omega$$

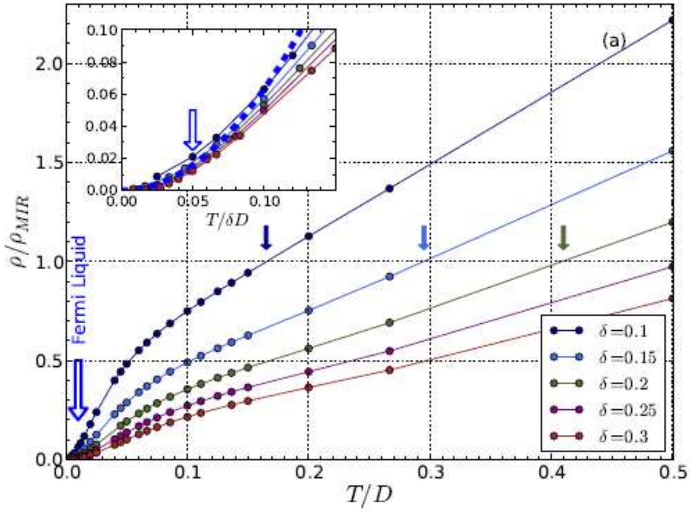
Behavior of real part
follows from KK.



Limited to low-T and ω.

Bad metal
at high T:

High T behavior: crossing of Mott-Ioffe-Regel criterion. Complete vanishing of quasiparticles there. Saturated scattering.



Summary

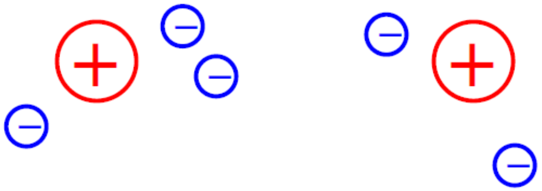
- Correlations are effects beyond band picture
- Electrons retain atomic spectroscopic signatures at a high energy (solids are made of atoms, after all!)
- At low energies they form dispersing quasiparticle bands
- Filling and temperature dependent DOS
- (doped) Mott insulators in DMFT
- Consequences of all this for Seebeck ? (… part II)

End of part I:

what follows is support material that I may discuss if time permits (depending also a bit on the background of students and the taste)

When is mean-field treatment acceptable?

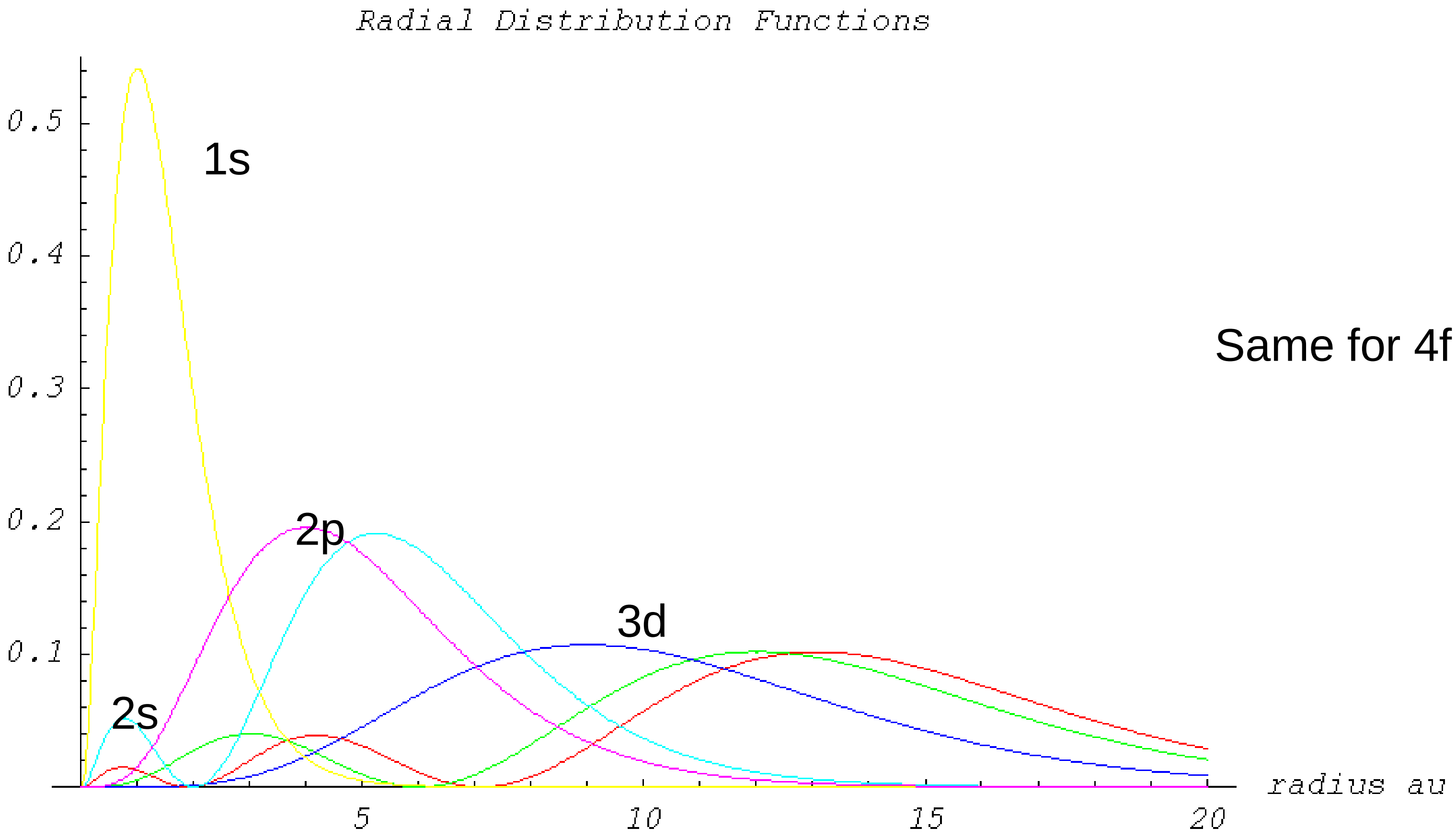
- bandwidth, W~few eV,
- Interaction cost, taking r~0.1nm 20eV: $+\sum_{ij}\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_i-\vec{r}_j|}$
- Screening of repulsion by other electrons diminishes U to few eV!



- U ~ W, depending on U/W band picture is acceptable or not

Why partially filled 3d are correlated?

- 3d orbitals don't have nodes, reach further into core, therefore charge is screened less

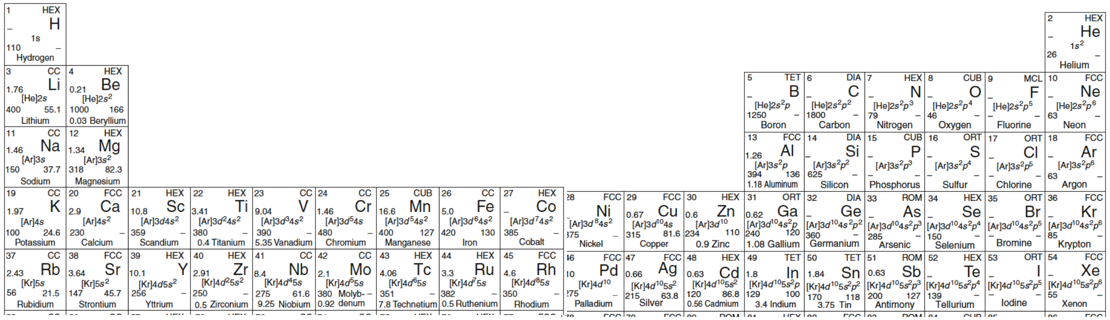


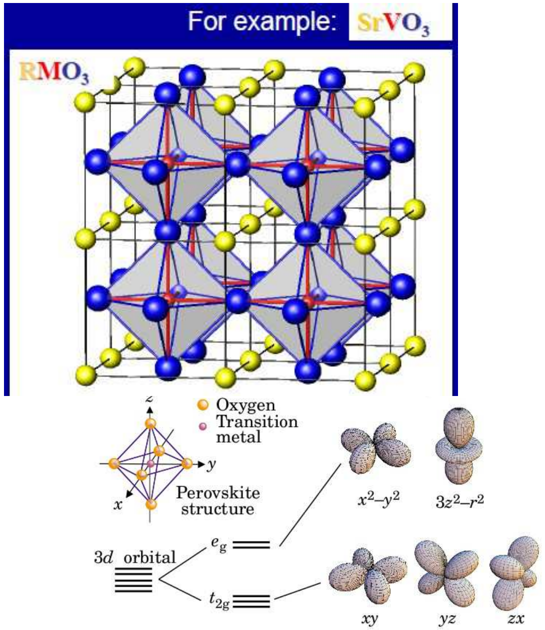
Same for 4f -heavy fermions

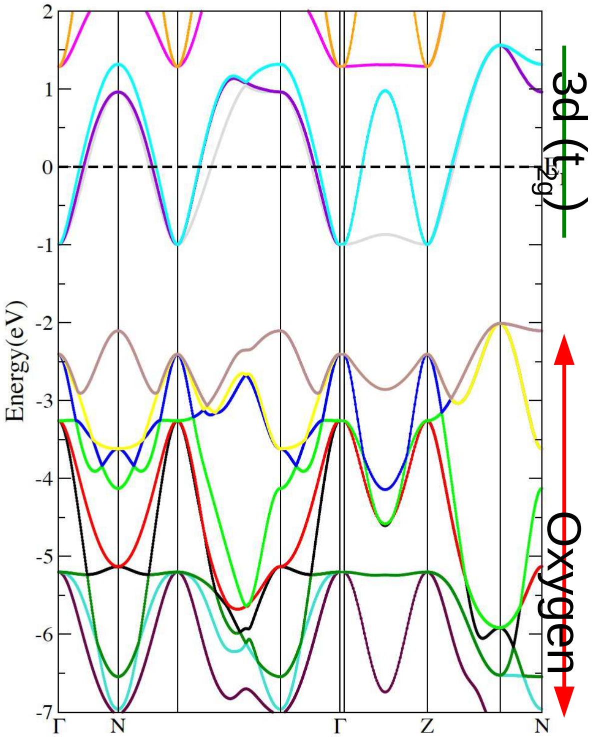
4d metals, pnictides different: cf. Hund's metals

Georges • de' Medici • Mravlje Annu. Rev. Condens. Matter Phys. 2013. 4:137–78

Transition metal oxides; structure and band-structure







Electronic correlations and thermoelectricity
Part II : Seebeck coefficient in correlated metal

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Annecy, 6.6.2014

Boltzmann transport (reminder)

- Theory of a gas of particles, with x **and** p
- Quantum aspects of theory are Fermi-Dirac distribution and taking group velocity

$$dN = d^3x d^3p f(x,p)$$

$$p = \hbar k$$

$$f(x,p,t) = f_0(x,p) + \delta f(x,p,t)$$

$$v = \dot{x} = \frac{1}{\hbar}\frac{\partial \epsilon_k}{\partial k}$$

$$f_0(k) = \frac{1}{\exp\left[\beta(\epsilon_k + \mu) + 1\right]}$$

$$\frac{df}{dt} = \frac{\partial f}{\partial x}\dot{x} + \frac{\partial f}{\partial p}\dot{p} + \frac{\partial f}{\partial t} = \mathcal{L}f$$

$$\beta = \frac{1}{k_B T}$$

- Relaxation time approximation

$$\frac{df}{dt} = \mathcal{L}f = -\frac{f - f_0}{\tau}$$

$$j = \sum_k e v_k \delta f_k$$

Conductivity and Seebeck in a Boltzmann theory

- Conductivity

$$\sigma = 2\pi \frac{e^2}{V_0} \sum_k \left(-\frac{\partial f_0}{\partial \epsilon}\right)\Big|_{\epsilon=\epsilon_k-\epsilon_F} v_k v_k \tau_k$$

band transport function

$$\Phi(\epsilon) = \frac{e^2 2\pi}{V_0} \sum_k v_k^2 \delta(\epsilon - \epsilon_k)$$

$$\sigma = \int (-f_0')\Phi(\epsilon)\tau(\epsilon)d\epsilon$$

- Seebeck coeff.

$$S = -\frac{k_B}{e} \frac{\int (-f_0')\Phi(\epsilon)\tau(\epsilon)\frac{\epsilon-\epsilon_F}{k_B T} d\epsilon}{\int (-f_0')\Phi(\epsilon)\tau(\epsilon)d\epsilon}$$

- Transport integrals

$$L_n = \int d\epsilon (-f_0')\Phi(\epsilon)(\epsilon-\epsilon_F)^n \tau(\epsilon)d\epsilon$$

$$S = -\frac{1}{eT}\frac{L_1}{L_0}$$

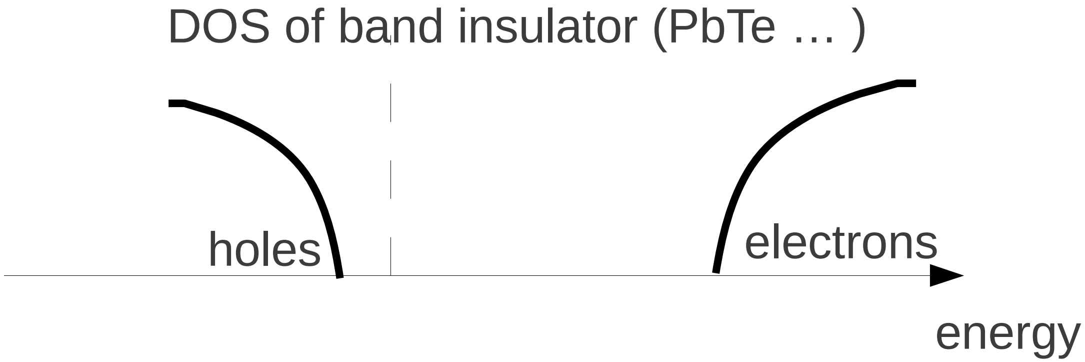
- Seebeck due to particle hole asymmetry in Φ and/or τ

Boltzmann theory of standard thermoelectric materials

- Text book treatment of doped band insulator then evaluates

$$S = -\frac{k_B}{e}\frac{\int(-f_0')\Phi(\epsilon)\tau(\epsilon)\frac{\epsilon-\epsilon_F}{k_BT}d\epsilon}{\int(-f_0')\Phi(\epsilon)\tau(\epsilon)d\epsilon}$$

separating hole and electron contributions, taking



- Most ph asymmetry due to Fermi level close to band edge
- energy dependence of $\tau(\epsilon)$ come from being close to edge,too.
- Temperature dependence encoded in Fermi function

What about systems with strong interactions?

- We have seen in Part I that correlations profoundly modify spectra
- Wave-vector k is not associated to a single frequency component ε_k, so (semi-classical) Boltzmann formulation seems not to be applicable
- What about different T regimes?

Transport in an interacting system

- Kubo formula: expresses response of systems to small perturbations in terms of correlations functions

$$J = -\frac{1}{T}L^{j,j}\nabla\tilde{\mu} + L^{j,j_Q}\nabla(\frac{1}{T})$$

$$J_Q = -\frac{1}{T}L^{j_Q,j}\nabla\tilde{\mu} + L^{j,j}\nabla(\frac{1}{T})$$

$$\tilde{\mu} = \mu + eV$$

$$j_Q = j_E - \mu j$$

$j_E = \sum_k v_k \epsilon_k n_k$ For free el., more complicated in general.

Skipping several parts of derivation. Consult Mahan.

Similarity with Boltzmann expressions

- In large-d (no vertex corrections), one has

$$\sigma = \int \sum_k (-\partial f/\partial\omega)\, v_k A_k(\omega) v_k A_k(\omega) d\omega$$

$$S = -\frac{1}{eT}\frac{L_1}{L_0}$$

- Again one can define transport integrals

$$L_n = \int \sum_k (-\partial f/\partial\omega)\, v_k A_k(\omega) v_k A_k(\omega)\omega^n d\omega$$

Not being careful about constants here.
Will cancel in S.

- Rewriting with transport function

$$L_n = \int d\omega d\epsilon \Phi(\epsilon) A_\epsilon(\omega) A_\epsilon(\omega)(-\partial f/\partial\omega)\omega^n$$

$$\Phi(\epsilon) = \sum_k v_k v_k \delta(\epsilon - \epsilon_k)$$

$$A_\epsilon(\omega) = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega + \mu - \epsilon - \Sigma(\omega)}$$

$$\Gamma_{\mathrm{qp}}(\omega) = -Z\mathrm{Im}\Sigma(\omega)$$

Oudovenko et al. PRB'06

One more integral than in Boltzmann formulation! (states are not poles as a function of energy)

Low T : qp approximation

$$L_n = \int d\omega d\epsilon \Phi(\epsilon) A_\epsilon(\omega) A_\epsilon(\omega) (-\partial f/\partial\omega)\omega^n$$

At low T, however, QP approximation can be made

$$A_\epsilon(\omega) = -\frac{1}{\pi}\mathrm{Im}\frac{Z}{\omega - Z\epsilon + i\Gamma_{\mathrm{qp}}(\omega)} \approx Z\delta(\omega - Z\epsilon)$$

Leading to:

$$L_n = \int d\omega \Phi(\omega/Z)(-\partial f_0/\partial\omega)\omega^n \tau(\omega)$$

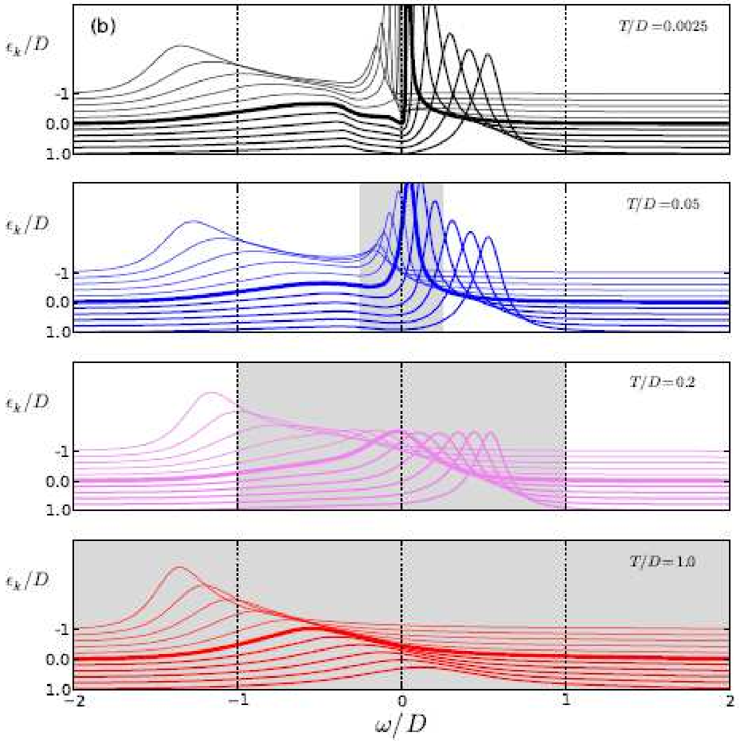
In low T limit, similar form as Boltzmann, but taking transport function at ω/Z, leading to enhancement !

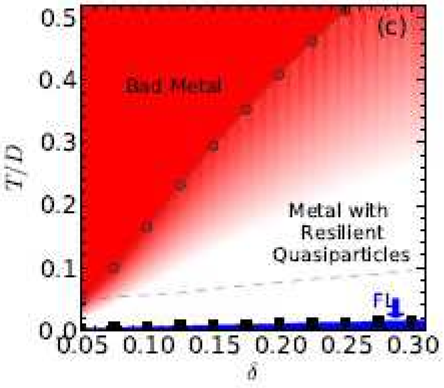
$$S = -\frac{k_B}{eT}\frac{L_1}{L_0} = (1/Z) \times S(\text{for } Z = 1)$$

Resillient quasiparticles

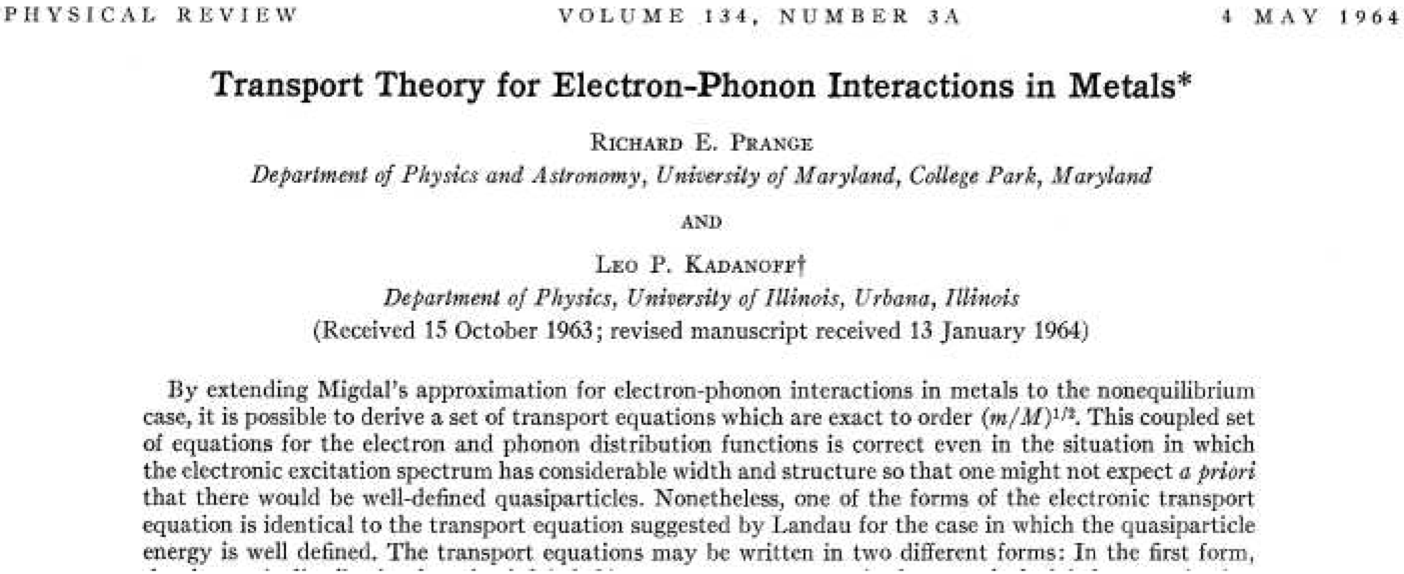
- Recent work within DMFT finds dispersing resillient quasiparticle states which validates applicability of Boltzmann-like description even in interacting systems well above Fermi liquid scale

Deng, JM et al. Phys. Rev. Lett. 110, 086401 (2013)
Xu, Haule, Kotliar, Phys.Rev.Lett. 111, 036401 (2013)
Deng et al, arXiv:1404.6480





- Established much earlier for e-p coupling



PHYSICAL REVIEW VOLUME 134, NUMBER 3A 4 MAY 1964

Transport Theory for Electron-Phonon Interactions in Metals*

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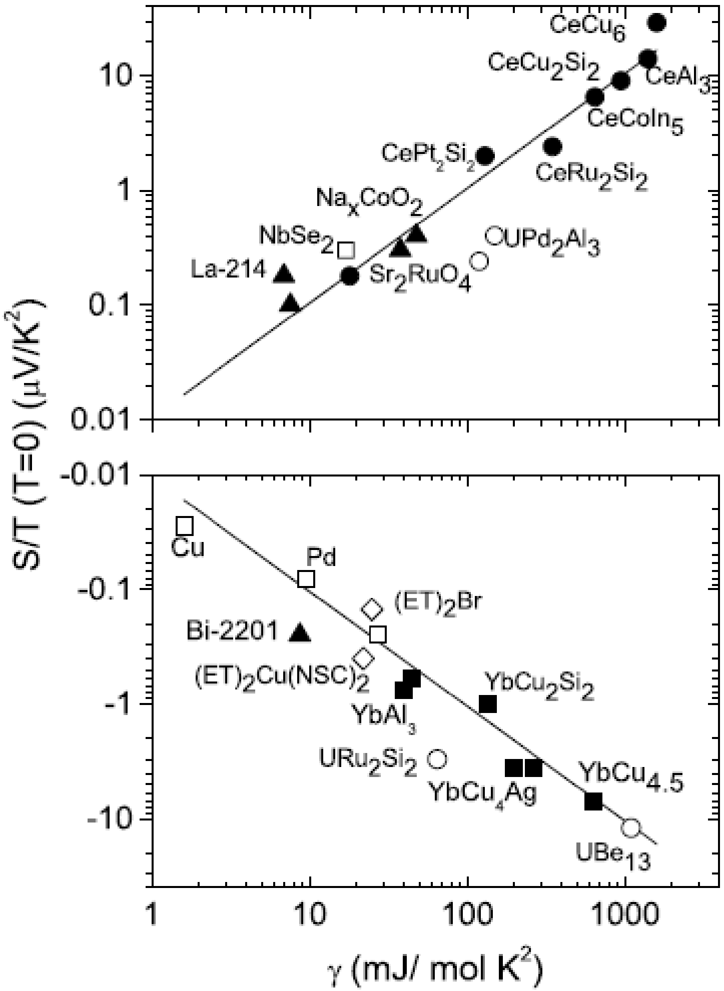
(Received 15 October 1963; revised manuscript received 13 January 1964)

By extending Migdal's approximation for electron-phonon interactions in metals to the nonequilibrium case, it is possible to derive a set of transport equations which are exact to order $(m/M)^{1/2}$. This coupled set of equations for the electron and phonon distribution functions is correct even in the situation in which the electronic excitation spectrum has considerable width and structure so that one might not expect *a priori* that there would be well-defined quasiparticles. Nonetheless, one of the forms of the electronic transport equation is identical to the transport equation suggested by Landau for the case in which the quasiparticle energy is well defined. The transport equations may be written in two different forms: In the first form,

Low T slope of Seebeck



Scales with 1/Z, like linear coefficient in specific heat.

Behnia, Jaccard, Flouquet
J.Phys CM 2004

Correlations enhance Seebeck!

High-T limit

- As chem. pot ~ T at large T, it is convenient to rewrite

$$j_Q = j_E - \mu j$$

$$\alpha = \Delta V/\Delta T = -\frac{1}{eT}\frac{L^{j,j_Q}}{L^{j,j}} = -\frac{1}{eT}\frac{L^{j,j_E}}{L^{j,j}} + \frac{\mu}{eT}$$

- Assuming energy is bound, the first term vanishes in the high T limit, and Seebeck coefficient is expressed in terms of the thermodynamic values

$$\alpha_{\text{Heikes1}} = \mu/eT,$$

- In metal, Seebeck → 0, at low T is somewhat better behaved

$$\alpha_{\text{Heikes}} = \frac{\mu - \mu(T=0)}{eT}.$$

Evaluating Heikes in atomic limit

From thermodynamic relation (**S** entropy)

$$dE = Td\mathbf{S} - pdV + \mu dN$$

reexpress

$$S_{\text{Heikes}} = \mu/(eT) = -1/e(\partial\mathbf{S}/\partial N)_{E,V}$$

Example 1: single band Hubbard model U →0
spin up and down independent, entropy twice the spin up result

$$\mathbf{S}/k_B = -2\left[(n/2)\log(n/2) + (1-n/2)\log(1-n/2)\right]$$

$$S = -1/e\partial\mathbf{S}/\partial n = -(k_B/e)\log\left[\frac{2-n}{n}\right]$$

Chaikin, Beni, PRB'76

Diverges as n → 0 and n → 2.
Vanishes for particle-hole sym n → 1

Evaluating Heikes in atomic limit

From thermodynamic relation (**S** entropy)

$$dE = Td\mathbf{S} - pdV + \mu dN$$

reexpress

$$S_{\text{Heikes}} = \mu/(eT) = -1/e(\partial\mathbf{S}/\partial N)_{E,V}$$

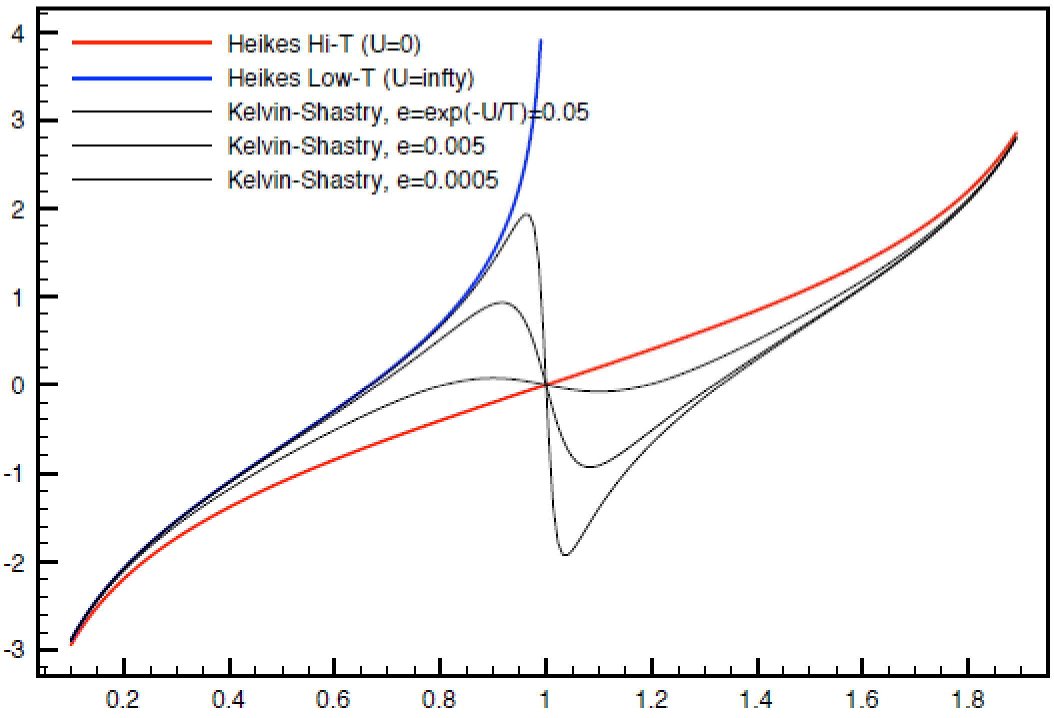
Example 2: single band Hubbard model U → infinity
for el density n means one has (in atomic limit)

$$\mathbf{S}/k_B = -n\log(n/2) - (1-n)\log(1-n)$$

$$S = -k_B/e\partial\mathbf{S}/\partial n = -k_B/e\log\left[\frac{2(1-n)}{n}\right]$$

Diverges as n → 0 **and** n → 1. Large Seebeck in Mott insulators.

Seebeck in atomic limit for finite interactions



Influence of orbital degeneracies

Doped case with orbital degeneracies d

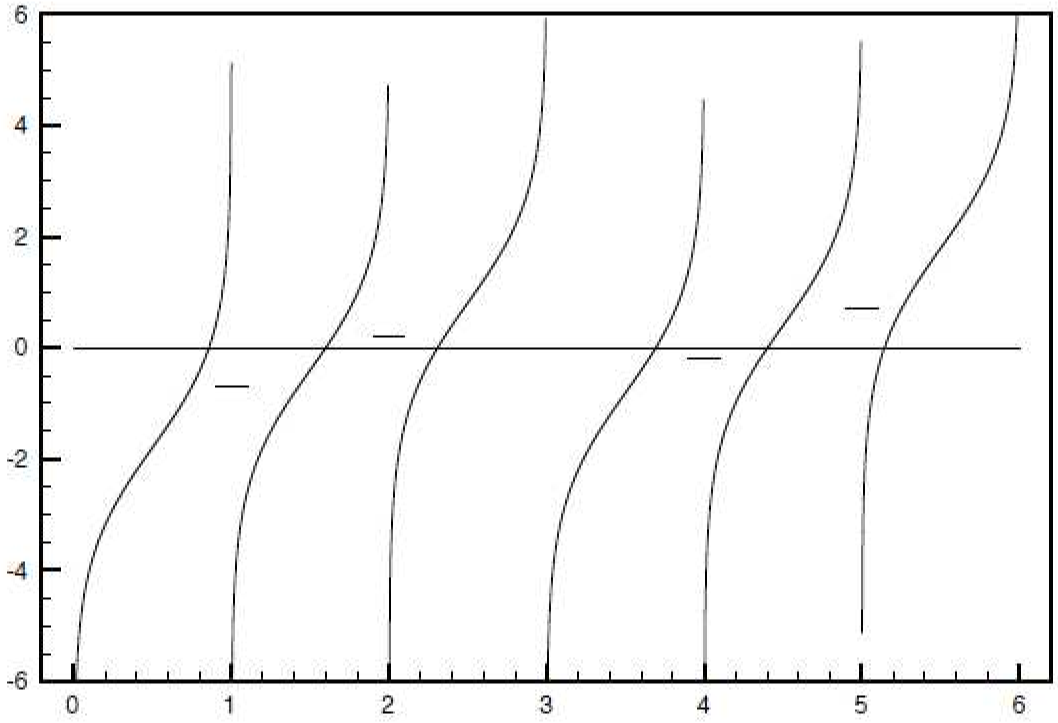
$$S = -(1/e)\partial \mathbf{S}/\partial n = -k_B/e \log\left[\frac{d_{N+1}(N+1-n)}{d_N(n-N)}\right]$$

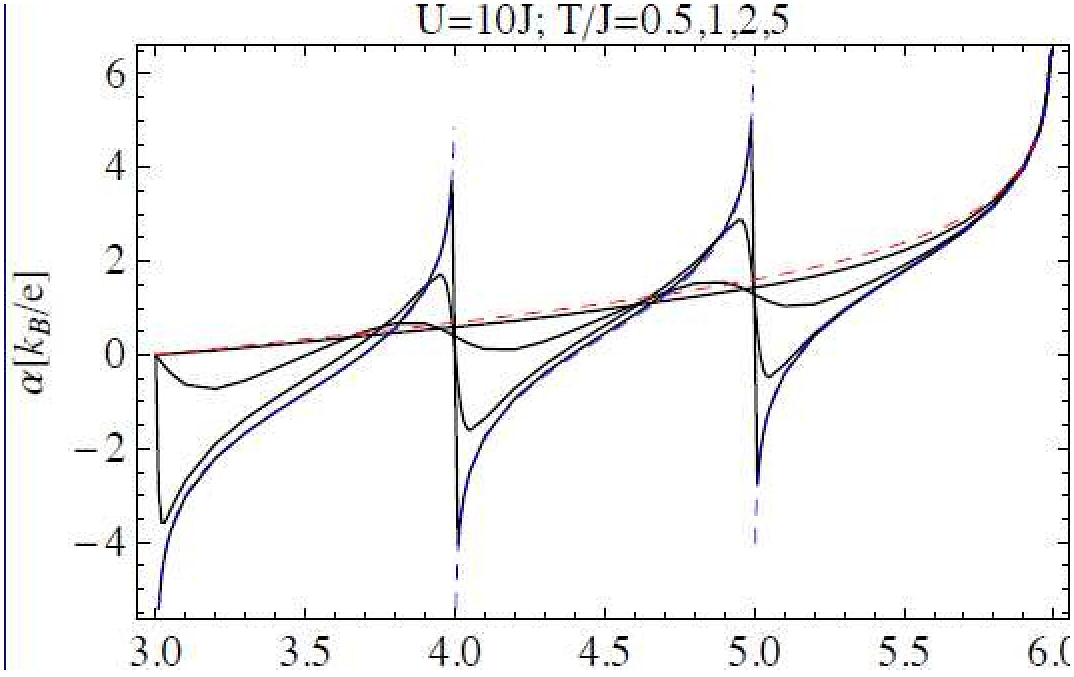
Integer filling

$$S = -(1/e)\partial \mathbf{S}/\partial n = \frac{k_B}{2e}\log\left[\frac{d_{N-1}}{d_{N+1}}\right]$$

JM and A. Georges, unpublished

Large ratio between degeneracies increases Seebeck.
Cobaltates $d_6=1$, $d_5=6$. Log 6 additive contribution!


6
4
2
0
-2
-4
-6
0
1
2
3
4
5
6


U=10J; T/J=0.5,1,2,5
$\alpha[k_B/e]$
6
4
2
0
−2
−4
3.0
3.5
4.0
4.5
5.0
5.5
6.0

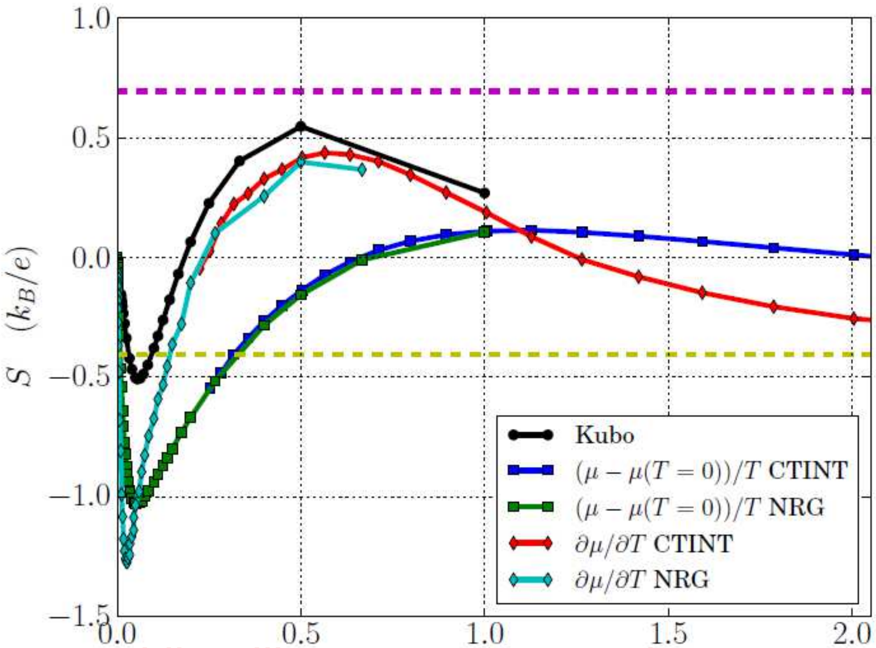
Seebeck coefficient of a doped Mott insulator in DMFT

Same simulation as discussed in part I.
Hole-doped Mott insulator in DMFT.
As the DOS temperature is increased, DOS undergoes rich evolution:

- renormalized metal at low T
- atomic like behavior at high T

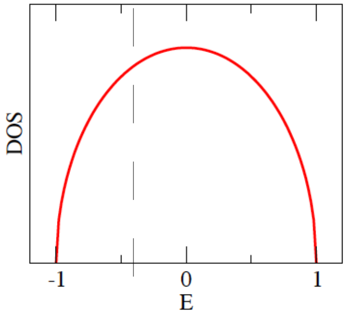
How is this reflected in Seebeck?

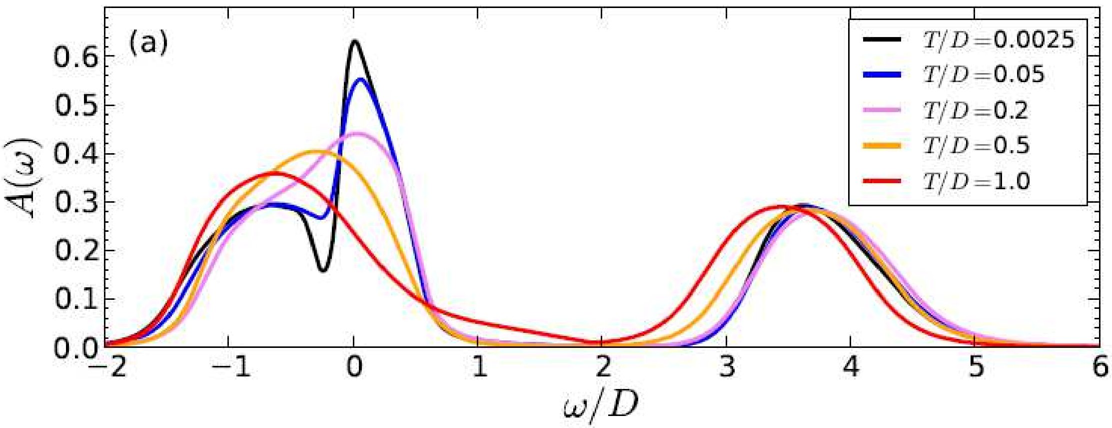
Seebeck coefficient in doped Hubbard model: low T



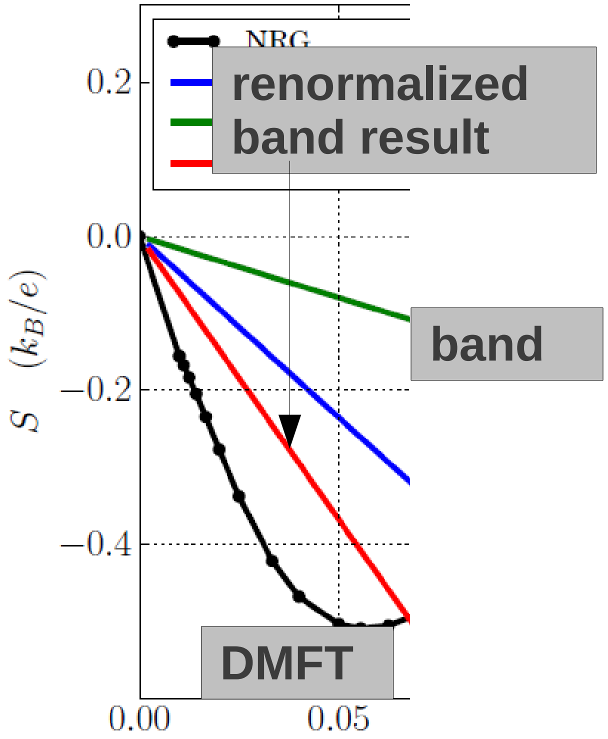
i,ii, iii, iv

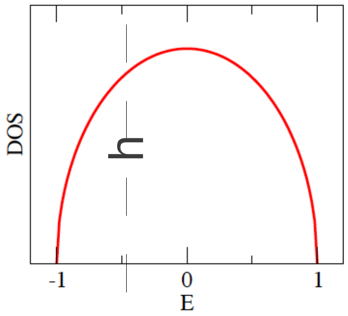
2 changes of signs.
2 extrema.
4 regimes.
i) FL
ii) Resillient qp
iii)lower Hubbard band
iv) upper Hubbard band





i) Low-T: renormalized FL with NFL additional corrections





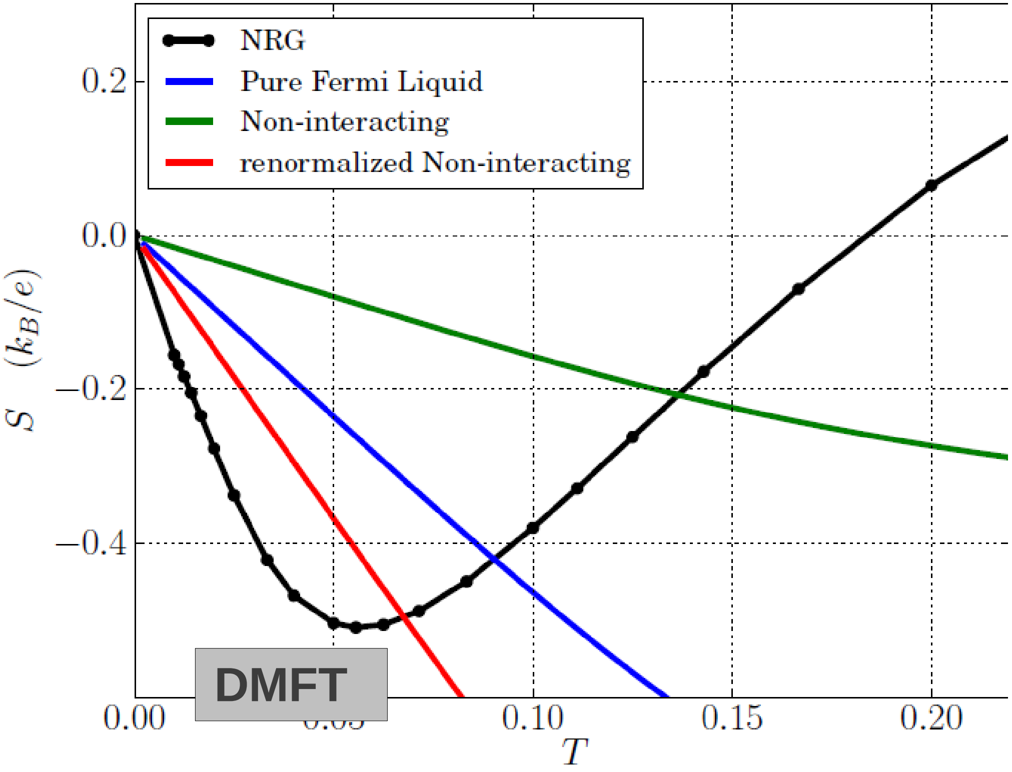
- Linear in T metallic dependence [el-like]
- Low T slope enhanced compared to band result
- Enhancement larger than 1/Z=m*/m (influence of particle-hole asymmetric non-Fermi liquid corrections in scattering rate)

$$\Sigma''(\omega) = \Sigma^{(2)}(\omega) + \Sigma^{(3)}(\omega) + \cdots$$

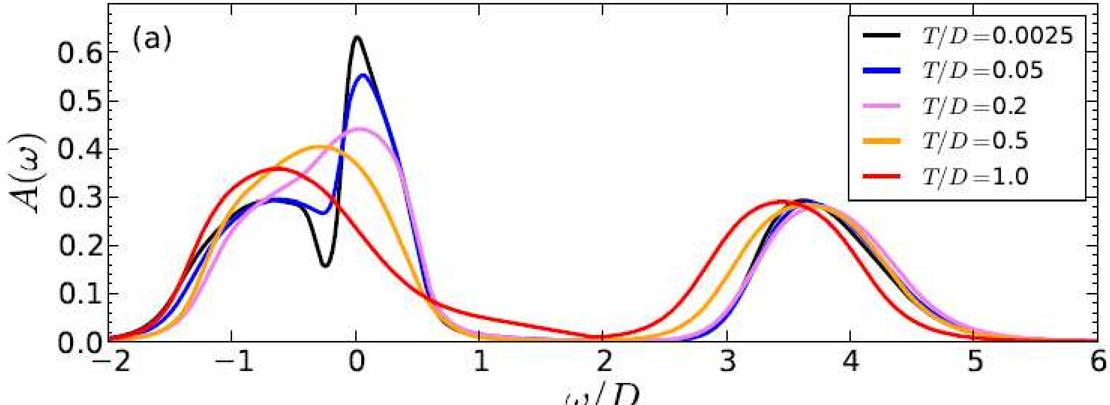
$$\Sigma^{3}(\omega) = \frac{(a_1 \omega^3 + a_2\, \omega T^2)}{Z^3}$$

Haule and Kotliar arXiv:0907.0192
Deng, JM et al, PRL'13

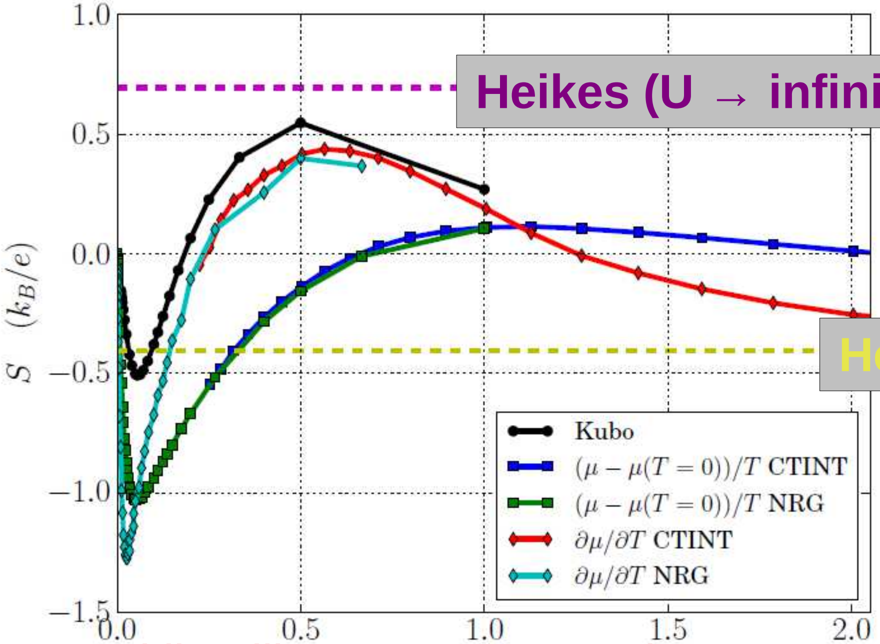
ii)Intermediate T: resillient quasiparticle regime



- Maximum of S
- Progressive but slow decay of resillient quasiparticle excitations



iii) and iv) High T 1st and 2nd Heikes regime



Heikes (U → infinity)

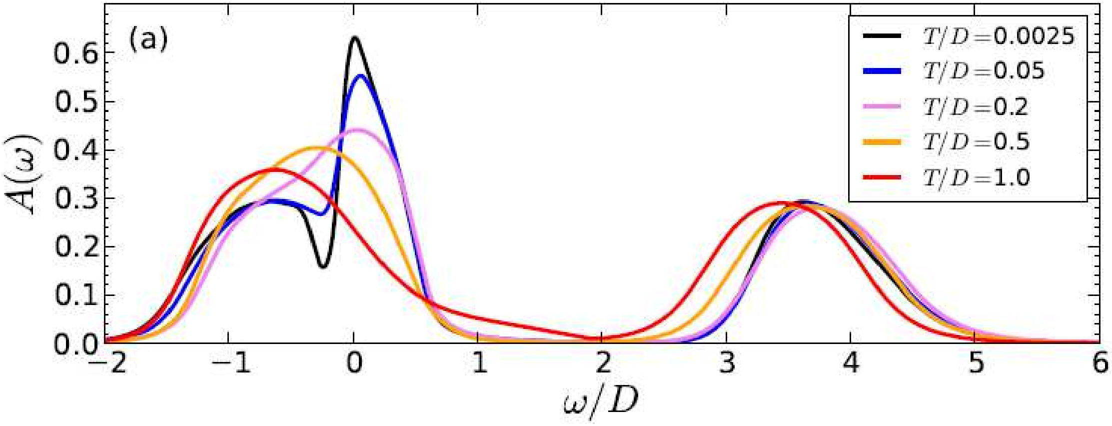
Heikes (U → 0)

i,ii, iii, iv

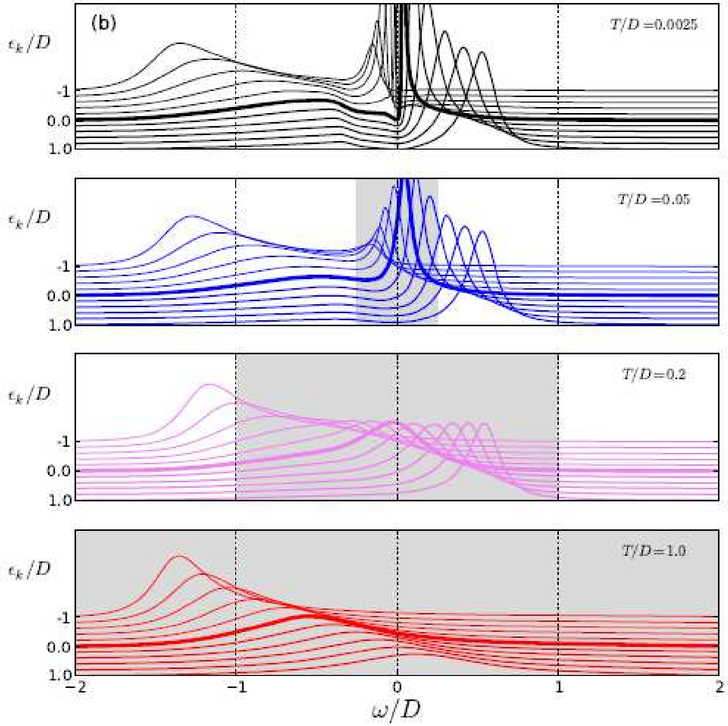
Physics of isolated atom (Hubbard bands).

1st Heikes regime W_K<T<U

2nd Heikes regime T>U

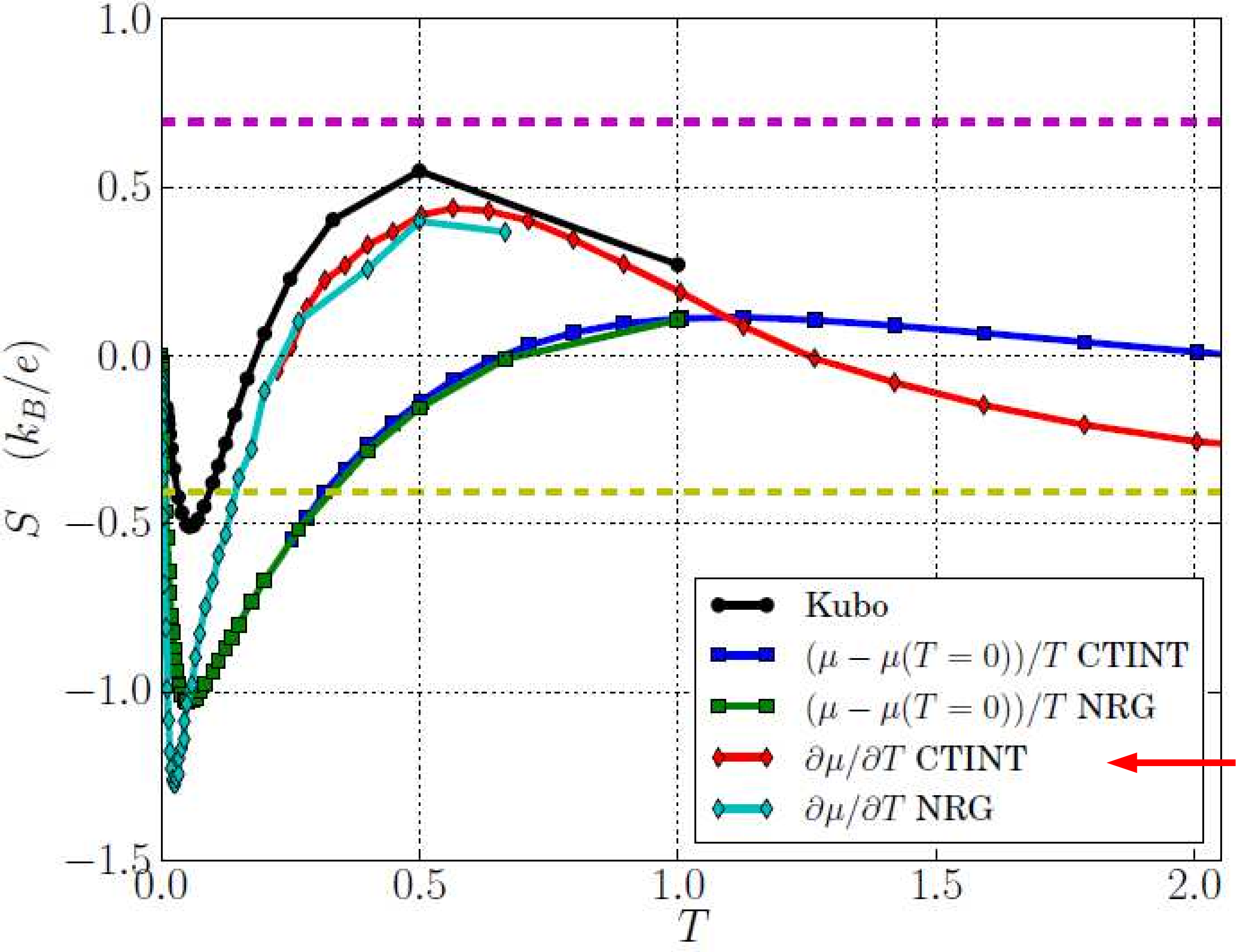


Progressive broadening of T window



High T regime

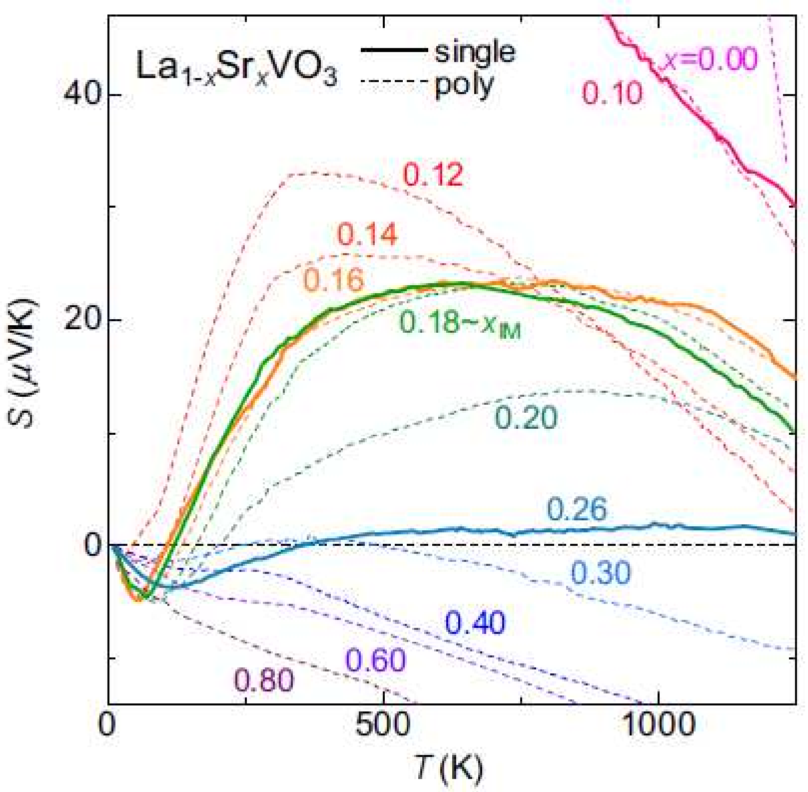
Approaches atomic limits at high T.

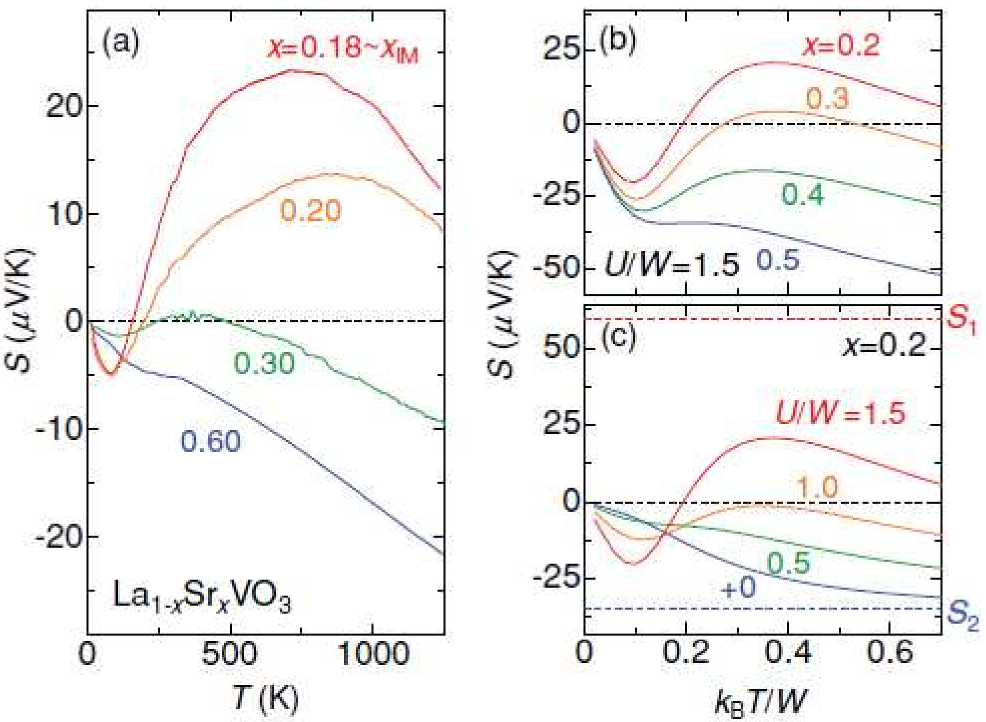


Kelvin formula works
Well.Peterson, Shastry
PRB'2010.

Experiment on doped Mott insulator

- Similar tendencies as theory, several changes of sign, but experimental temperature scale 10 X smaller





DMFT

Uchida et al. PRB'11

- More experiments and applicability of Heikes formla: cf. Sylvie Hebert

Summary

- T-dependent spectral properties manifest also in rich T dependence of Seebeck coeff (changes of sign with T)
- In the low T limit, Kubo formula in quasiparticle approximation equivalent to Boltzmann
- At high T, atomic estimates apply. Entropic content.
- Enhanced Seebeck coefficient at low-T and perhaps also at high-T (potentially, as there is more entropy)

- Not discussed: - successful calculations of thermopower in correlated materials within LDA+DMFT. -figure of merit and challenges associated with optimization
- Perhaps potentially useful even for apliccations, but even if not, understanding of thermopwer important as a probe.

More on entropic content of thermopower

- On board (time permitting)

$$\mathbf{j}_E=\frac{i}{2}\sum_{\substack{\mathbf{k}\\ \mu\nu\\ \sigma}}\nabla_{\mathbf{k}}\epsilon_{\mathbf{k}}^{\mu\nu}\left(c_{\mathbf{k},\sigma}^{\dagger\mu}\dot{c}_{\mathbf{k},\sigma}^{\nu}-\dot{c}_{\mathbf{k},\sigma}^{\dagger\mu}c_{\mathbf{k},\sigma}^{\nu}\right)$$

$$+\frac{i}{2}\sum_{\substack{\mathbf{k}\mathbf{k}'\\ \mu\nu\\ \sigma\sigma'}}\nabla_{\mathbf{k}}V_{\mathbf{k},\sigma\sigma'}^{\mu\nu}\left(c_{\mathbf{k}',\sigma}^{\dagger\mu}\dot{n}_{\mathbf{k},\sigma'}^{\nu}c_{\mathbf{k}'-\mathbf{k},\sigma}^{\mu}\right.$$

$$\left.-\dot{c}_{\mathbf{k}',\sigma}^{\dagger\mu}n_{\mathbf{k},\sigma'}^{\nu}c_{\mathbf{k}'-\mathbf{k},\sigma}^{\mu}-c_{\mathbf{k}',\sigma}^{\dagger\mu}n_{\mathbf{k},\sigma'}^{\nu}\dot{c}_{\mathbf{k}'-\mathbf{k},\sigma}^{\mu}\right),$$

I.Paul & G.Kotliar Phys Rev B 67, 115131 (2003)
M.Jonson and G.D.Mahan Phys Rev B 21, 4223 (1980)
G.Beni Physical Review B 10, 2186 (1974)
J.S. Langer, Phys Rev 128, 1101 (1962)

Electronic correlations and thermoelectricity
Part III : Seebeck coefficient in Sr_2RuO_4

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Jozef Stefan Institute, Ljubljana

CPHT Polytechnique, Palaiseau

Annecy, 6.6.2014

On entropic content of thermopower

- Seebeck coefficient is not (always) entropy per carrier
- Will not discuss maths here but rather show concrete example when entropic content is clear
- And then will kill my own theory by looking at the c-axis response

Before I start

- I need to convince you that theory works

Thermopower in strongly correlated Sr_2RuO_4 from first principles

Hvar, `11

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& Josef Stefan Institute, Ljubljana, Slovenija

Antoine Georges

Kristjan Haule, Gabriel Kotliar

[M. Aichhorn, T. Miyake, L. Pourovski, V. Vildosola, O. Parcollet, S. Biermann and M. Ferrero]

Outline

- Thermopower in simple metals
- Thermopower in correlated metals
- Sr_2RuO_4 from LDA+DMFT; coherence-incoherence crossover

⇕

- Thermopower in Sr_2RuO_4

Thermopower in simple metals

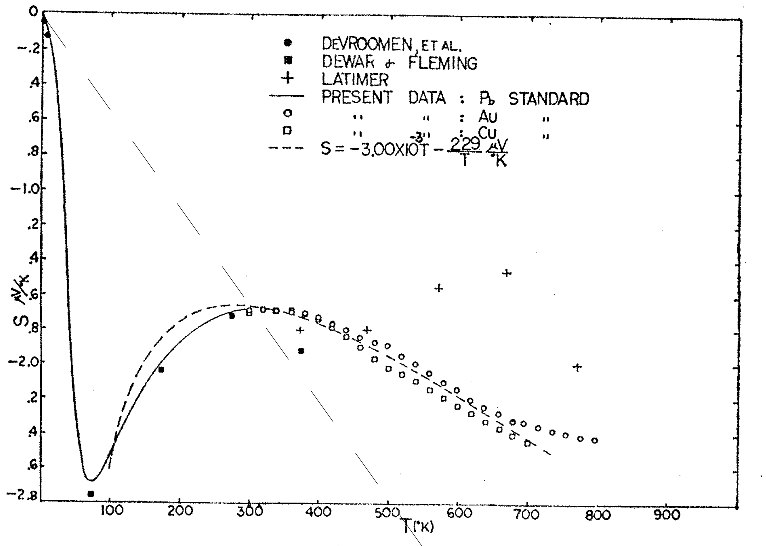


FIG. 2. The thermopower of pure aluminum.

Gripshover et al., Phys Rev **163**, 598 (1967)

LDA-Boltzmann
Relaxation-time approx.

$$S = -\frac{k_B}{e_0}\frac{\mathcal{A}_1}{\mathcal{A}_0}$$

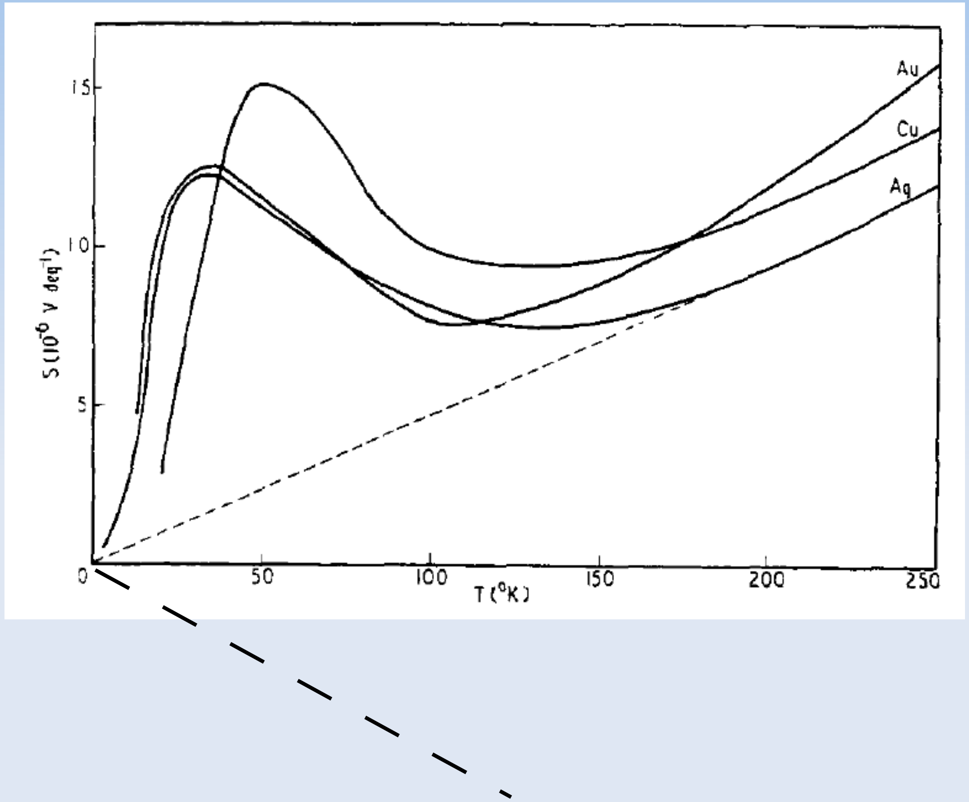
$$\mathcal{A}_n = \frac{2\pi}{\beta\hbar}\int_{-\infty}^{\infty} d\omega \Phi(\omega)(-\partial f/\partial\omega)(\beta\omega)^n$$

$$\Phi(\omega) = \frac{1}{V}\sum_k \mathrm{Tr}\left[A_k v_k A_k v_k\right]$$

$$A(k)_{\nu\nu'} = -\frac{1}{\pi}\mathrm{Im}\left[\omega - \epsilon_k\delta_{\nu\nu'} - \Sigma(w,k)_{\nu\nu'}\right]^{-1}$$

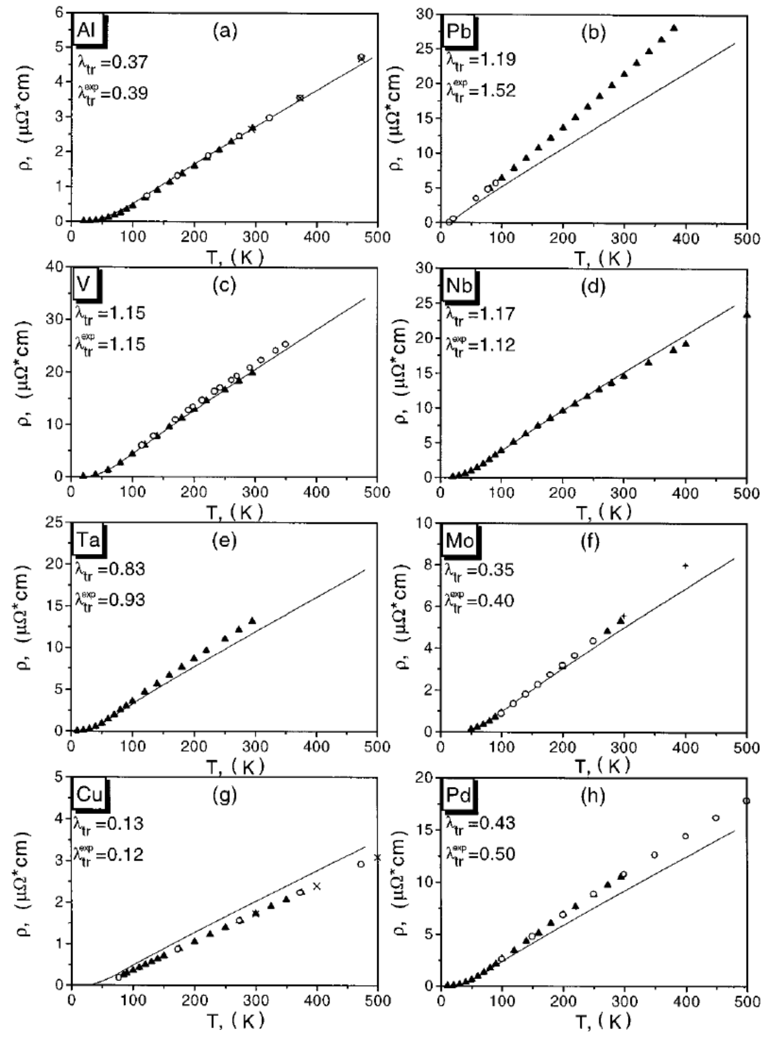
-Not just a Mott formula!
-Phonon-drag at low T.
-Effects of the el.-ph. coupling
-Nontrivial el. scattering also at high T.

Thermopower in simple metals



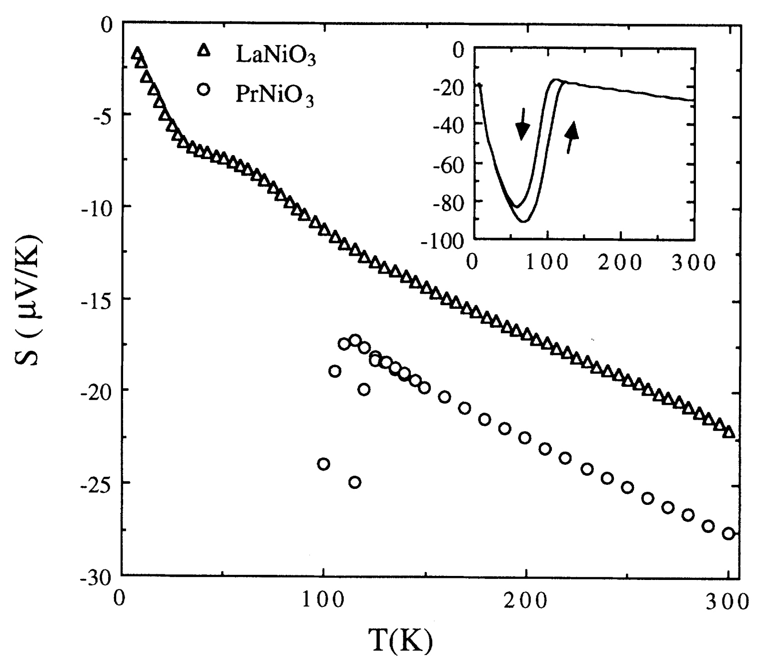
Macdonald and Pearson, Proc. Phys. Soc. **78** 306 (1961)

LDA+Boltzmann fails! Any hope to calculate thermopower in correlated systems from first principles?



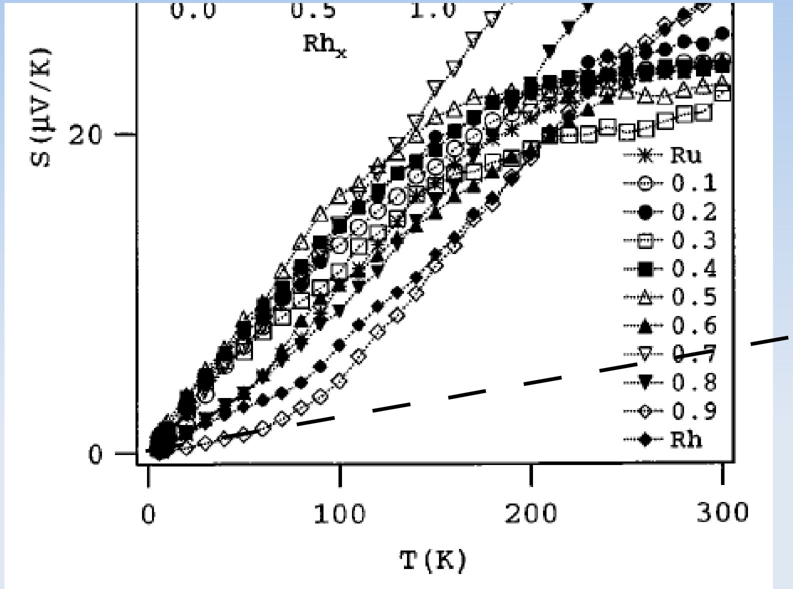
Savrasov & Savrasov, PRB 1996

Thermopower in correlated metals



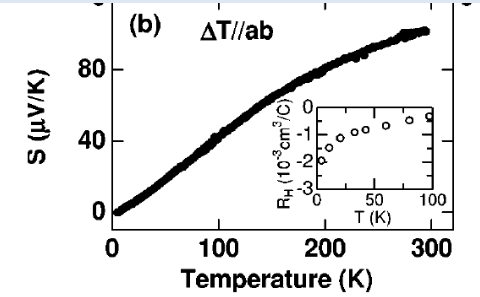
LaNiO$_3$

Xu et al, PRB. **48** 1112 (1993)



SrRuO$_3$

Yamaura et al, PRB. **69** 024410 (2004)



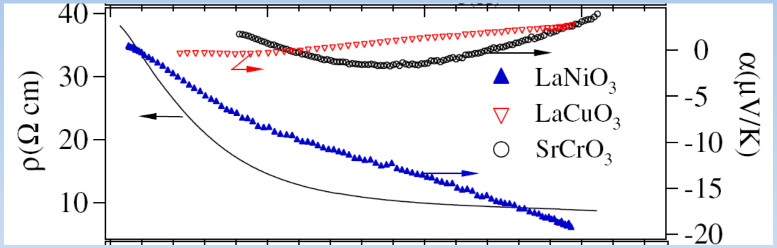
Na$_{0.5}$CoO$_2$

I. Terasaki et al,PRB. **56** 12685 (1997)

In correlated systems, different Seebeck is seen:

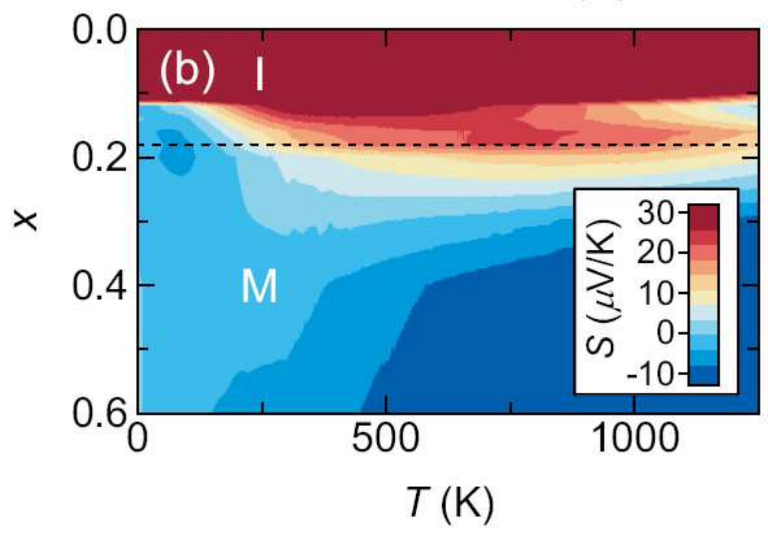
- larger values, slope at low T; enhancement over LDA
- saturation at higher T
- pronounced phonon-drag peak not seen

Thermopower in correlated metals



SrCrO$_3$

J.-S.. Zhou et al,PRL.
96 046408 (2004)



La$_{1-x}$Sr$_x$VO$_3$

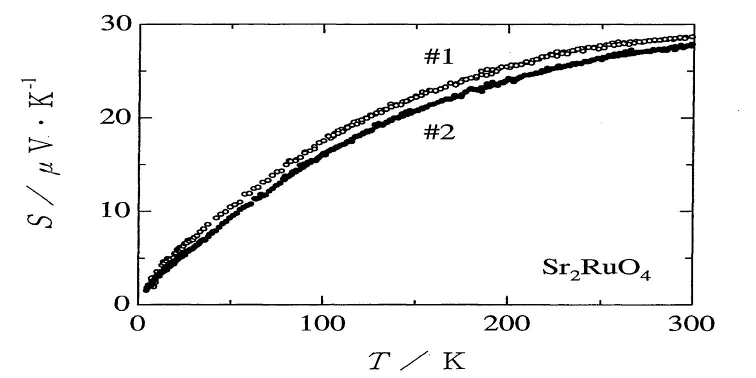
M. Uchida et al,PRB.
83 165127 (2011)

S can also be nonmonotonic.
Can one reproduce this pronounced T dep.?
What happens for Sr$_2$RuO$_4$ at high T?

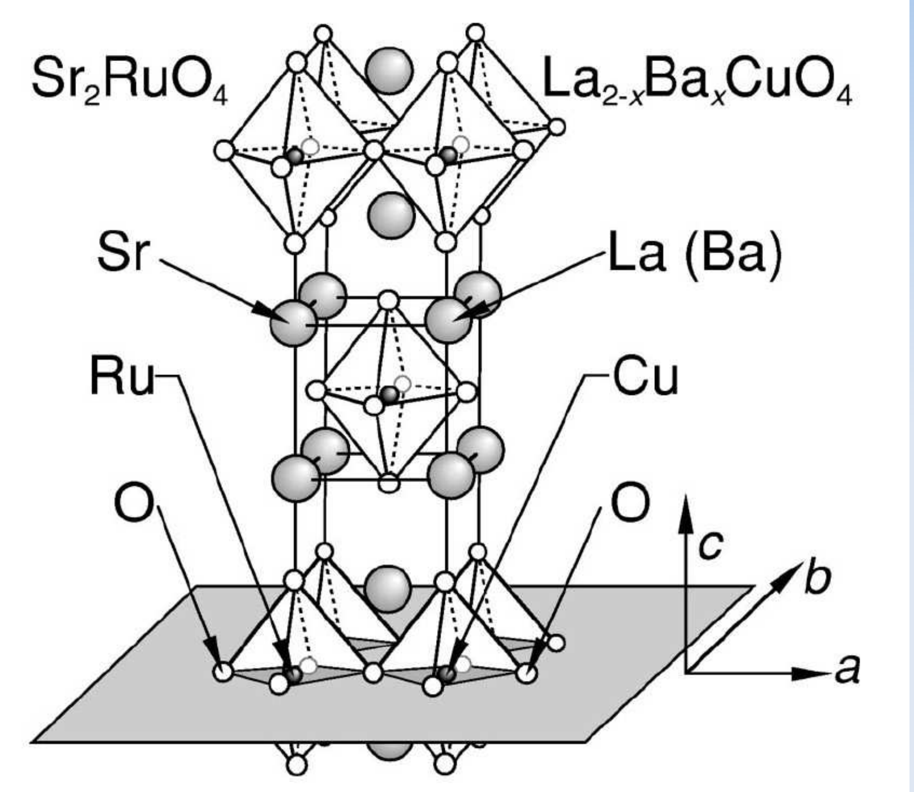
Let's look closer

Sr$_2$RuO$_4$

Yoshino et al, J. Phys. Soc. Jpn. **65** 1548 (1996)



Sr_2RuO_4:Basic properties



Perovskite

Unconven. supercond.

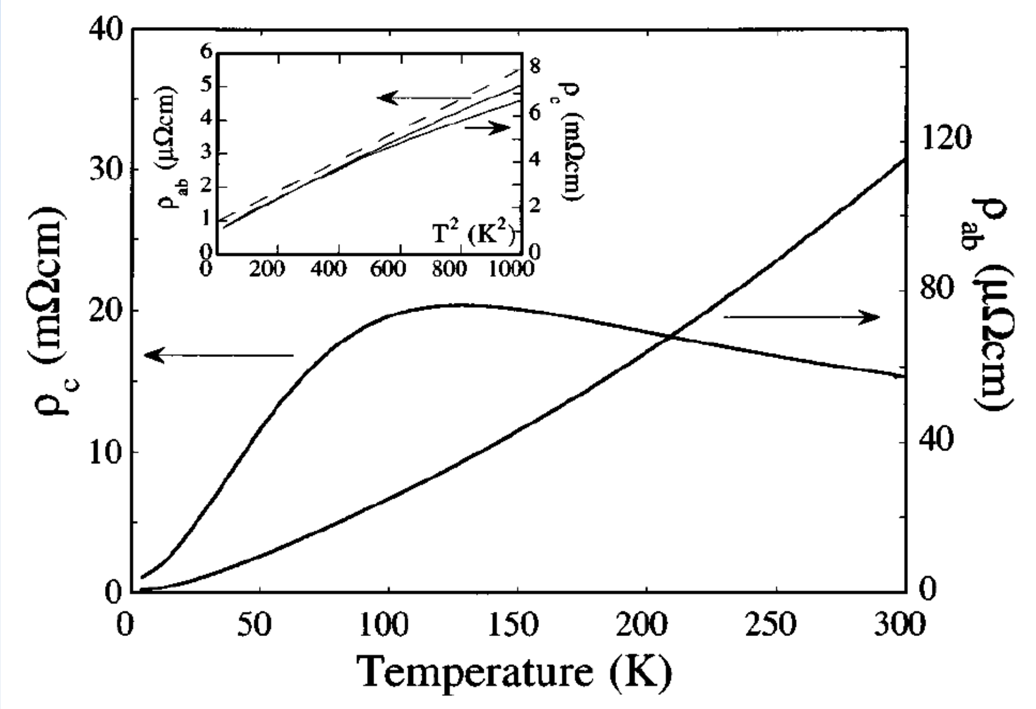
T_c ~2K

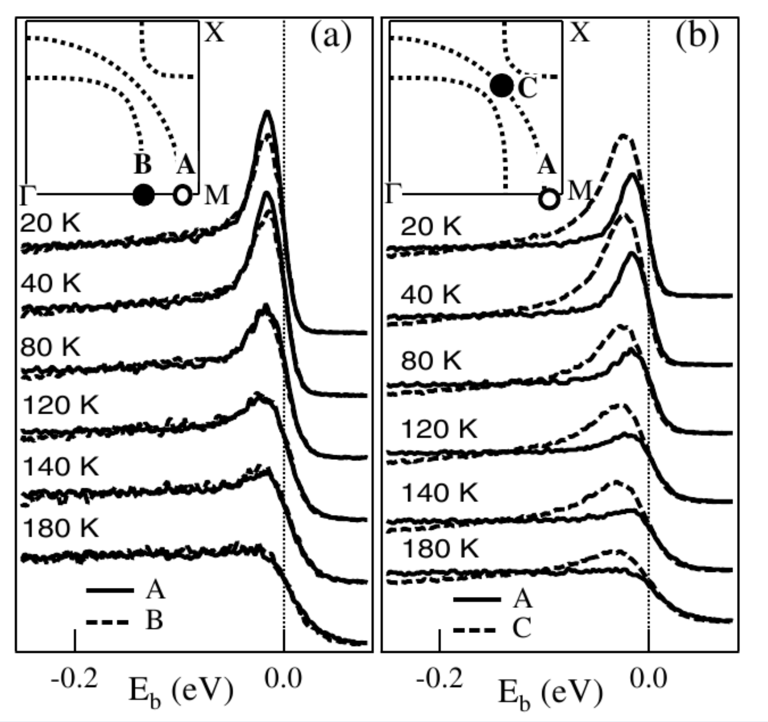
Maeno et al., Nature'94

Rice and Sigrist ,
J.Phys.CM'95

Correlated metal: Fermi liquid, (m*/m~4)

Coherence-incoherence crossover



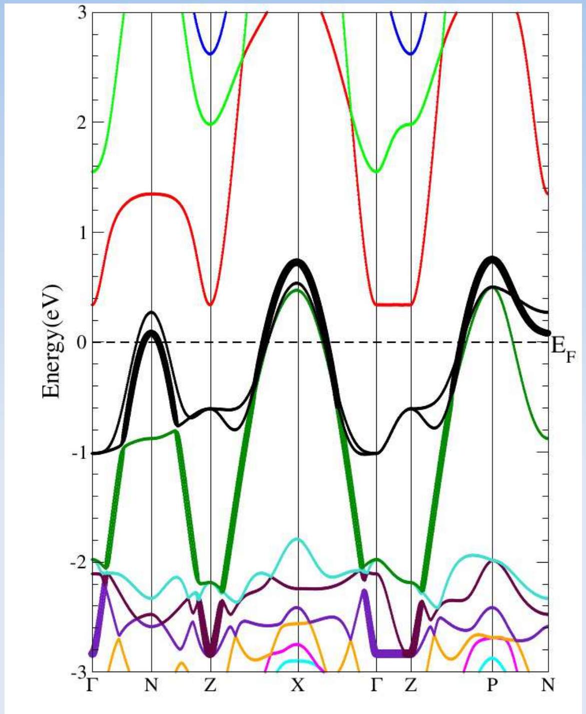


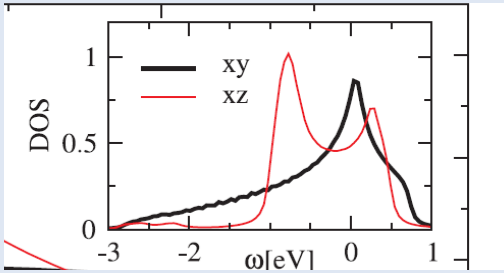
Hussey, Mackenzie, et al. PRB'98

Wang, ...,Valla, Johnson et al. PRL'04

Qps dissapear at ~100K

Sr$_2$RuO$_4$: el. structure



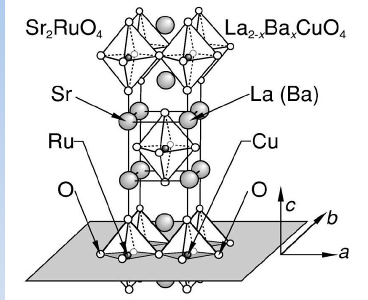


In ionic picture, 4 electrons on Ru; crystal field splitting → t_{2g} orbitals: xy and degenerate xz, yz

Wide xy band (2d like ϒ sheet); narrower xz, yz quasi 1d.

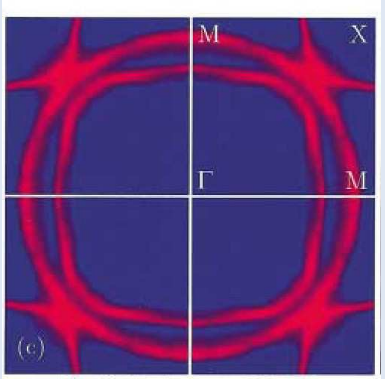
Fermi surfaces of DFT, quantum oscillations, ARPES agree quite well

Mackenzie et al, PRL'96



Oguchi, PRB'95
Singh, PRB'95

Damascelli, Shen et al., PRL'00



Quantum oscillation

Carriers in the widest band renormalized most

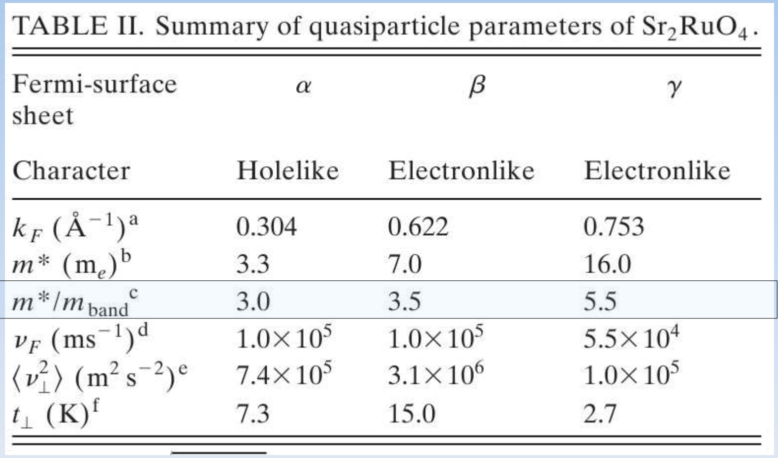


TABLE II. Summary of quasiparticle parameters of Sr_2RuO_4.

Fermi-surface sheet	α	β	γ
Character	Holelike	Electronlike	Electronlike
k_F (Å^{-1})[a]	0.304	0.622	0.753
m^* (m_e)[b]	3.3	7.0	16.0
m^*/m_{band}[c]	3.0	3.5	5.5
v_F (ms^{-1})[d]	1.0×10^5	1.0×10^5	5.5×10^4
$\langle v_\perp^2\rangle$ ($m^2 s^{-2}$)[e]	7.4×10^5	3.1×10^6	1.0×10^5
$t_\perp$ (K)[f]	7.3	15.0	2.7

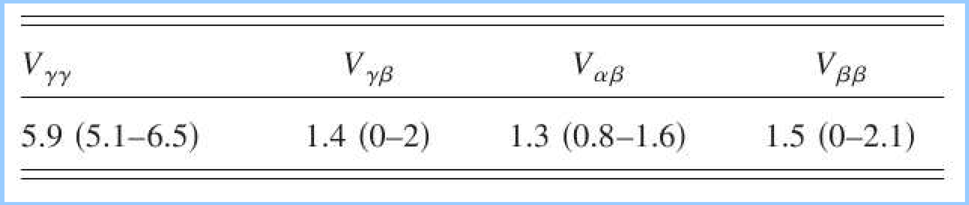
Mackenzie and Maeno RMP'03

$$\frac{C}{T} = \frac{\pi k_B^2 N_A a^2}{3\hbar^2} \times \sum m_i^\star = 1.48\,\mathrm{mJ\,mol^{-1}K^{-2}} \times \sum\left(\frac{m_i^\star}{m}\right)$$

Thermodynamic: 38 mJ/(mol K^2)
From eff. mass: 39

Puzzles

- Low coherence scale (although U<W)
- Puzzling largest renormalization in widest band



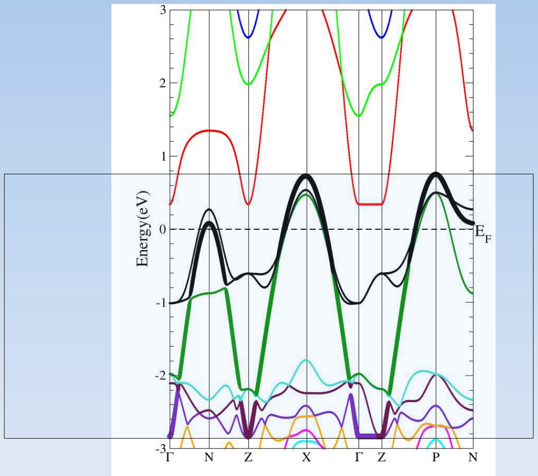
$V_{\gamma\gamma}$	$V_{\gamma\beta}$	$V_{\alpha\beta}$	$V_{\beta\beta}$
5.9 (5.1–6.5)	1.4 (0–2)	1.3 (0.8–1.6)	1.5 (0–2.1)

Konik and Rice, PRB'07

LDA+DMFT

- Wannier function constructed out of t2g only
- Full rotationaly invariant vertex is used
- Constrained RPA to calculate U & J (found isotropic!)
- Hybridization expansion CTQMC

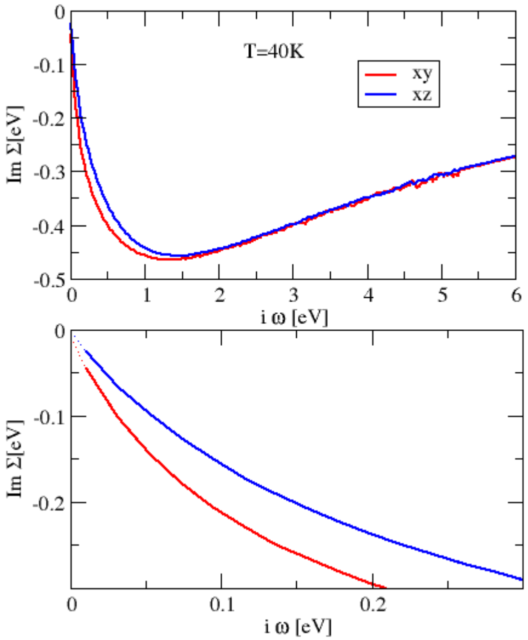
Werner et al, PRL'06



$$
\begin{aligned}
H_I = U \sum_m n_{m\uparrow} n_{m\downarrow} + \sum_{m<n,\sigma} & [U' n_{m\sigma} n_{n\bar{\sigma}} \\
& + (U'-J) n_{m\sigma} n_{n\sigma} - J c^\dagger_{m\sigma} c_{m\bar{\sigma}} c^\dagger_{n\bar{\sigma}} c_{n\sigma}] \\
& - J \sum_{m<n} [c^\dagger_{m\uparrow} c^\dagger_{m\downarrow} c_{n\uparrow} c_{n\downarrow} + h.c.]
\end{aligned}
$$

LDA+DMFT self energies

$$m^*/m_{\mathrm{LDA}} = Z^{-1}\big|_{T\to 0}$$



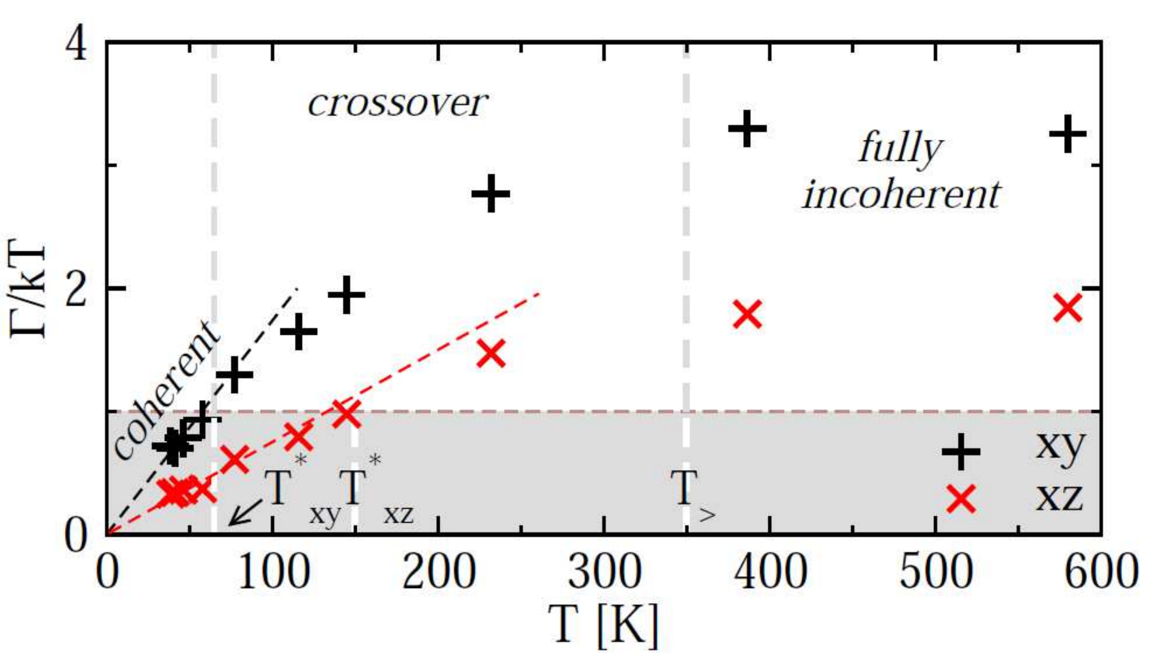
- $Z^{-1} = 1 - \partial \mathrm{Im}\Sigma(i\omega)/\partial\omega\big|_{\omega\to 0^+}$
- larger xy renormalization as in experiment
- So is scattering rate

$$\Gamma = -Z\,\mathrm{Im}\Sigma(\mathrm{i}0^+)$$

Crossover to incoherent regime

- Scattering rate:
  Fermi liquid $\Gamma = -Z\mathrm{Im}\Sigma(i0^+)$ < kT

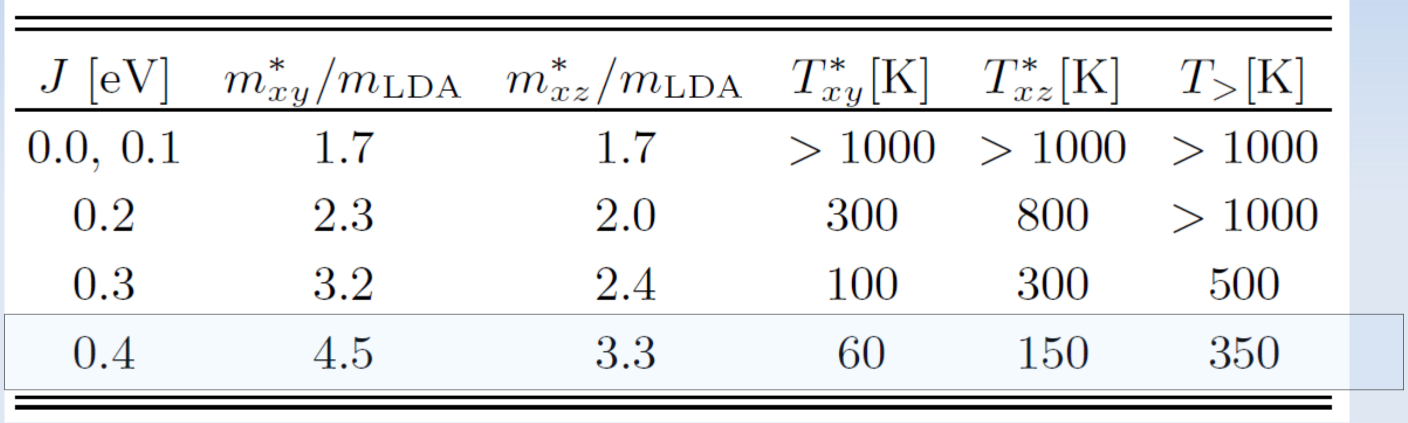
  crosses over above T^* from ~T^2 to ~ T



At T*: Gamma/kT =1

Hund's rule coupling

- LDA + DMFT reproduces exp. masses



J [eV]	$m^*_{xy}/m_{\mathrm{LDA}}$	$m^*_{xz}/m_{\mathrm{LDA}}$	T^*_{xy}[K]	T^*_{xz}[K]	$T_>$[K]
0.0, 0.1	1.7	1.7	> 1000	> 1000	> 1000
0.2	2.3	2.0	300	800	> 1000
0.3	3.2	2.4	100	300	500
0.4	4.5	3.3	60	150	350

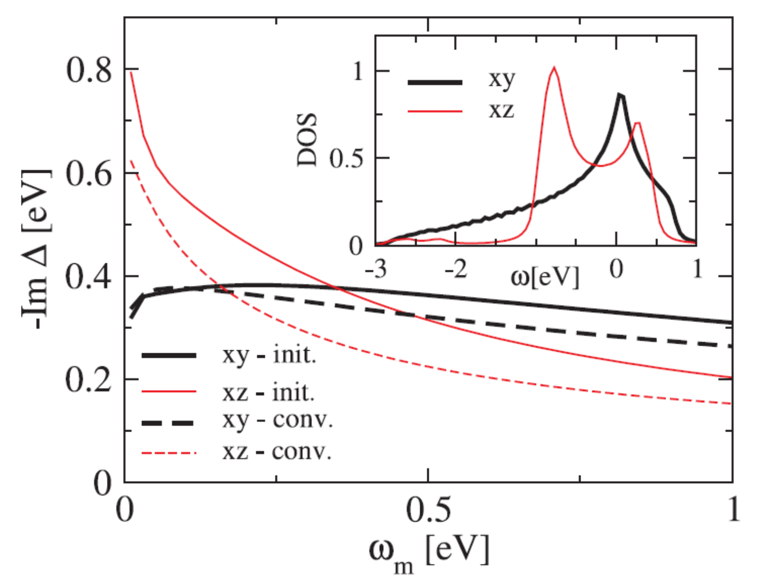
- J is essential to orbital differentiation and low coherence scale
- If J=0, U=5 must be used, even then no orbital diff found: m*/m =4.5 for xy and xz

Hund's metals: A.Georges, L.de-Medici, JM, Annual reviews of CM 2013

Orbital differentiation

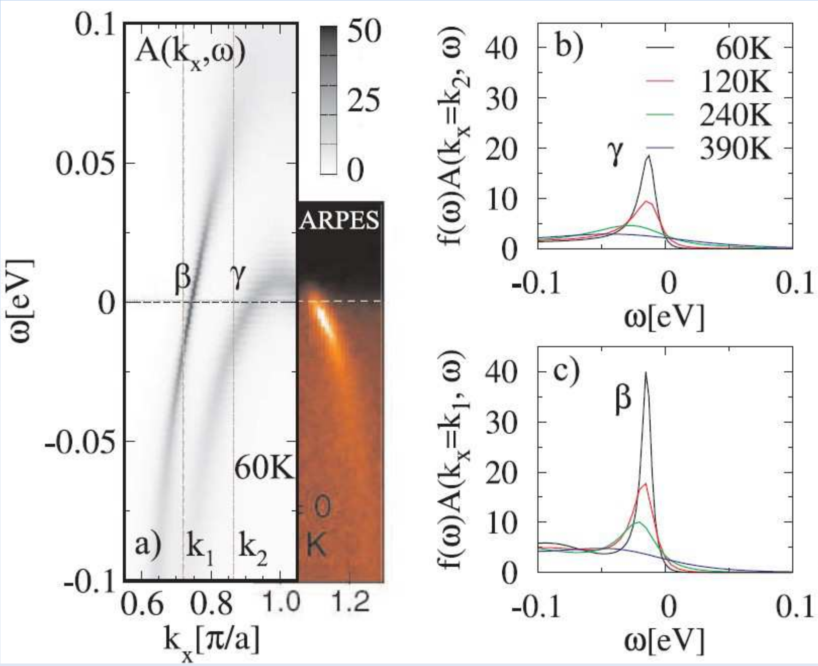
- Low frequency hybridization larger for xy due to van Hove singularity

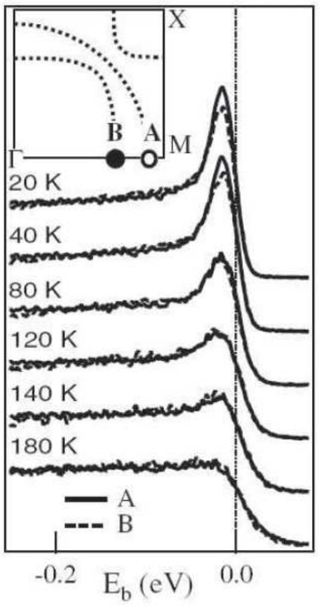
$$\mathrm{Im}\Delta(i\omega \to 0) = G_{\mathrm{loc}}^{-1} = -\frac{\mathrm{Im}G_{\mathrm{loc}}}{(\mathrm{Re}G_{\mathrm{loc}})^2 + (\mathrm{Im}G_{\mathrm{loc}})^2}$$

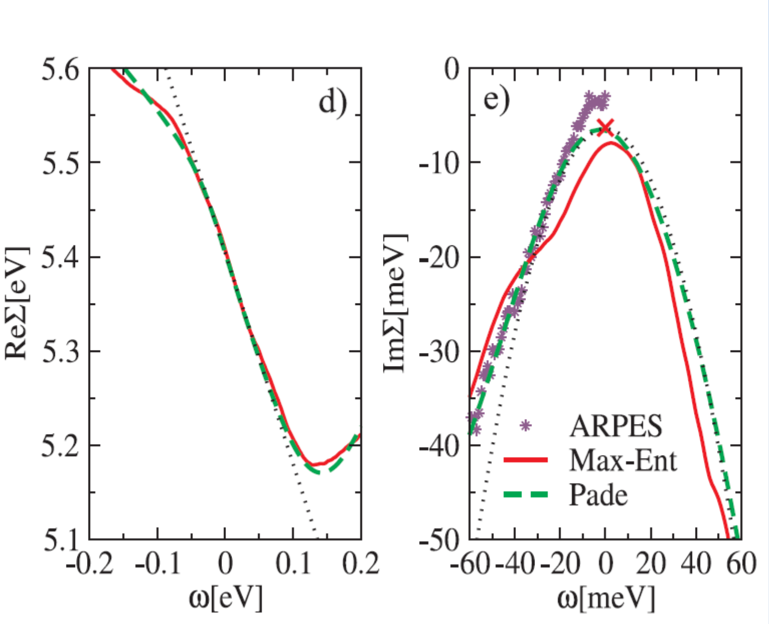


Zitko et al, PRB'09, Schmitt, PRB'10

ARPES







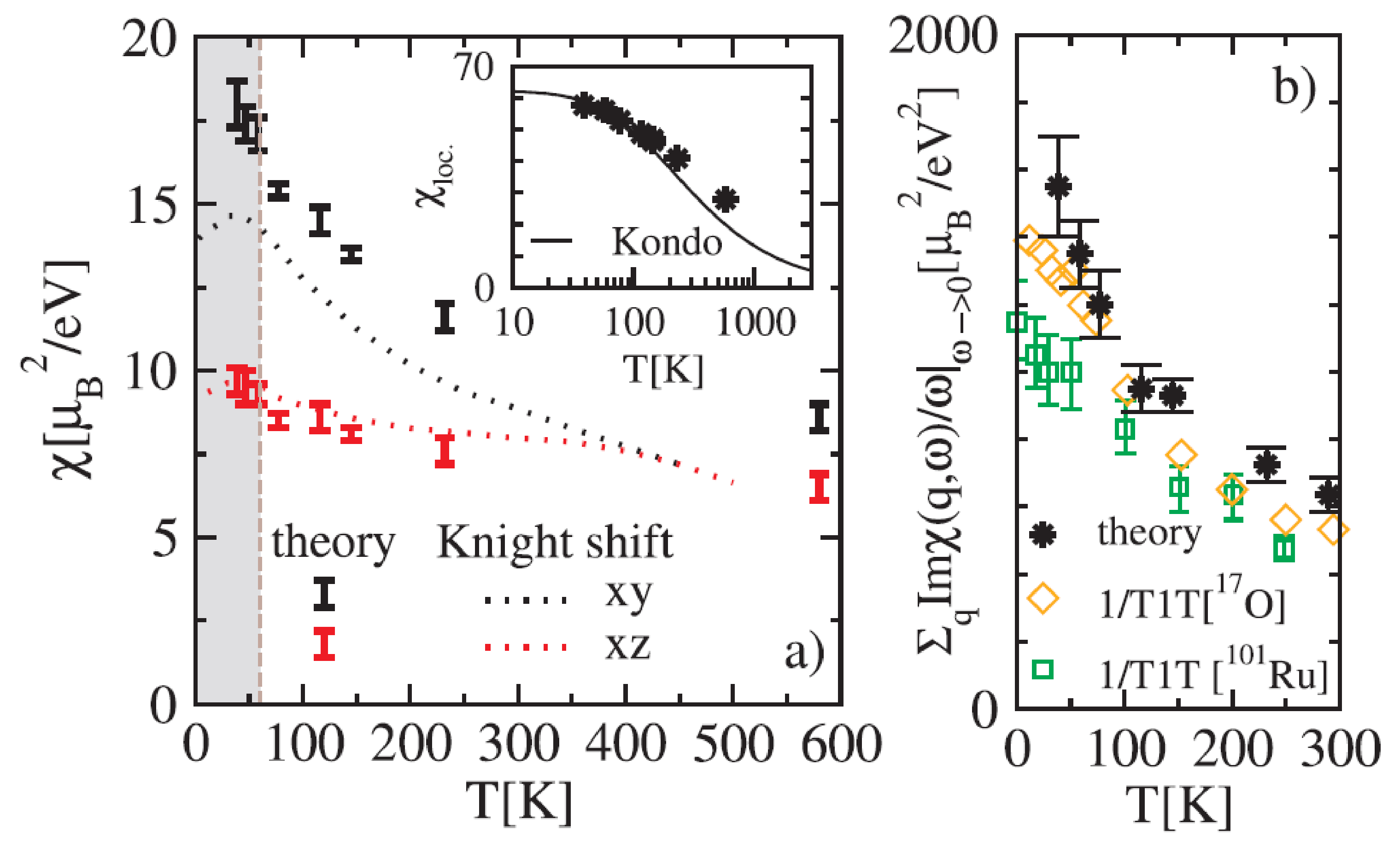
Shen et al.,PRL'07

Wang et al.,PRL'04

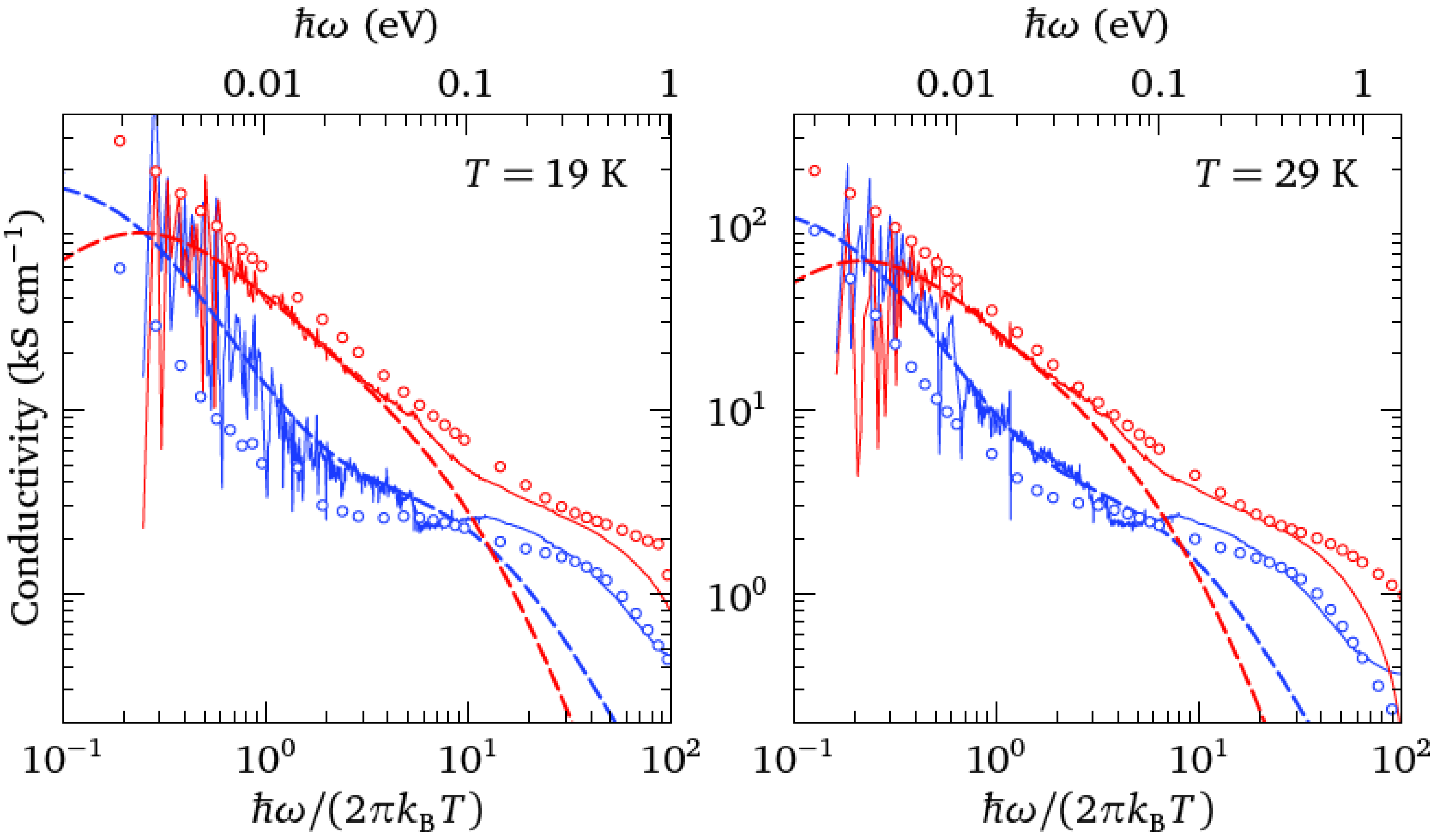
Ingle et al.,PRB'05

Good agreement of theory with experiment.
Disappearence of q.ps. at high T

NMR



J.Mravlje, M.Aichhorn, T.Miyake,K.Haule,G.Kotliar and A.Georges, PRL`11

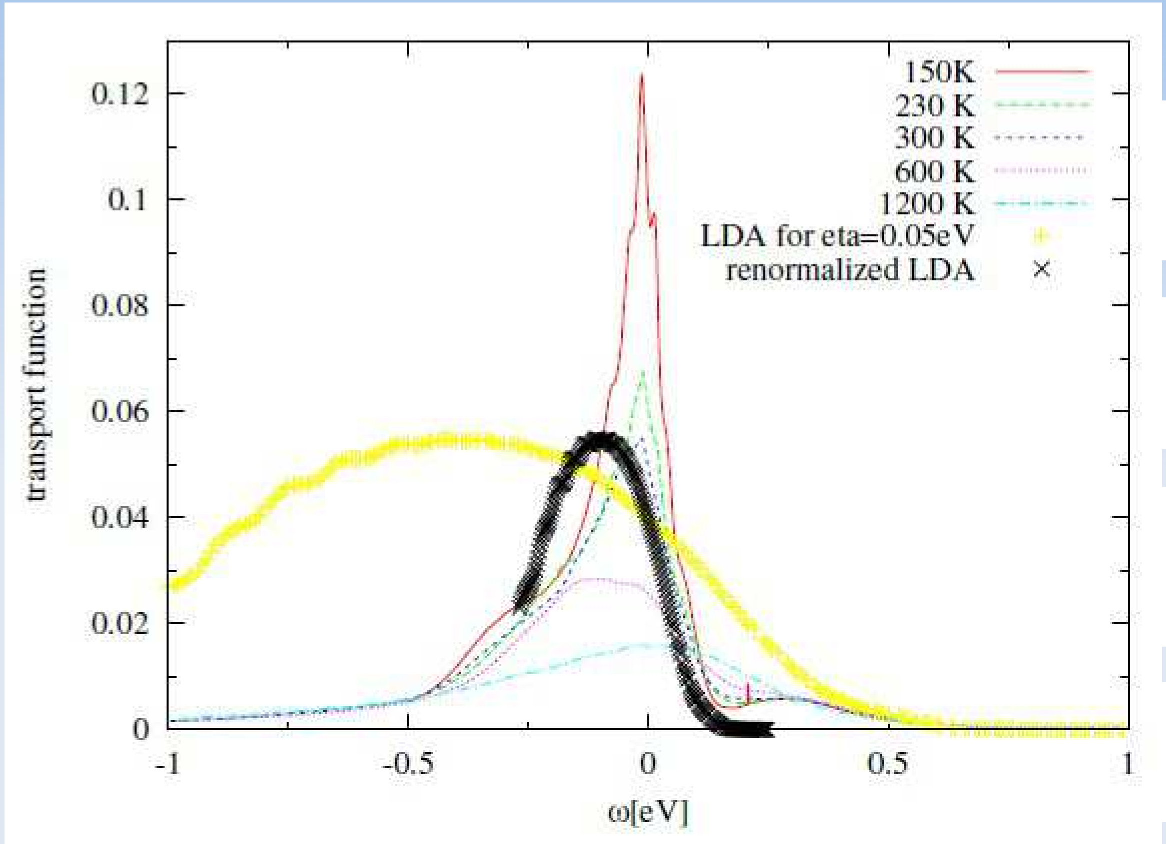


Optics :D. Stricker, JM, …, A.Georges, and D van der Marel

- Coherence-incoherence crossover; Good agreement with exp.

- What about thermopower?

Transport function



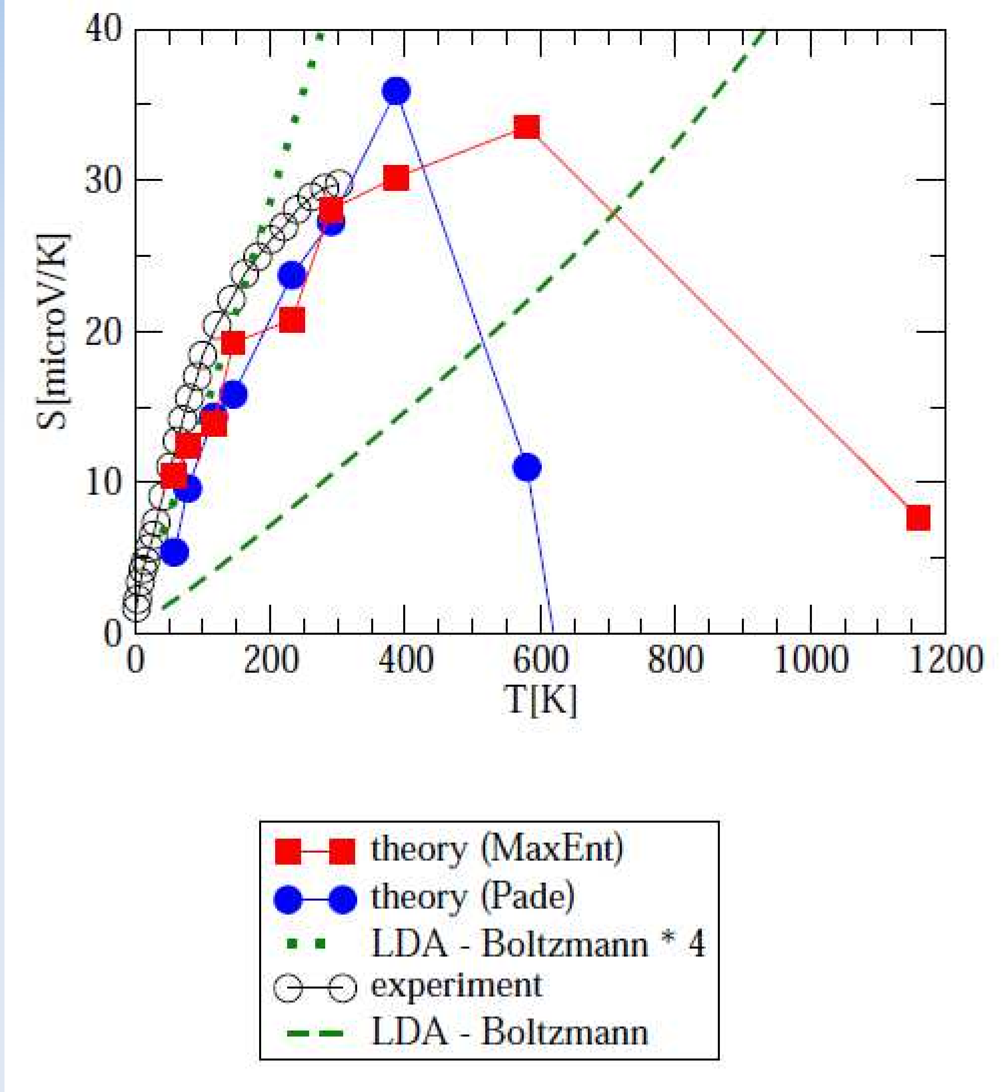
$$S = -\frac{k_B}{e_0}\frac{\mathcal{A}_1}{\mathcal{A}_0}$$

$$\mathcal{A}_n = \frac{2\pi}{\beta\hbar}\int_{-\infty}^{\infty} d\omega\Phi(\omega)(-\partial f/\partial\omega)(\beta\omega)^n$$

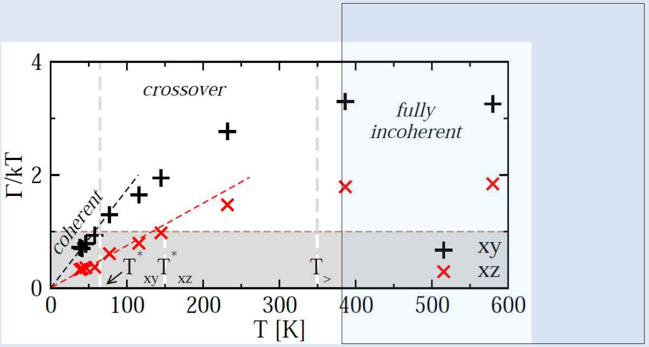
$$\Phi(\omega) = \frac{1}{V}\sum_k \mathrm{Tr}\left[A_k v_k A_k v_k\right]$$

$$A(k)_{\nu\nu'} = -\frac{1}{\pi}\mathrm{Im}\left[\omega - \epsilon_k\delta_{\nu\nu'} - \Sigma(w,k)_{\nu\nu'}\right]^{-1}$$

Seebeck coefficient



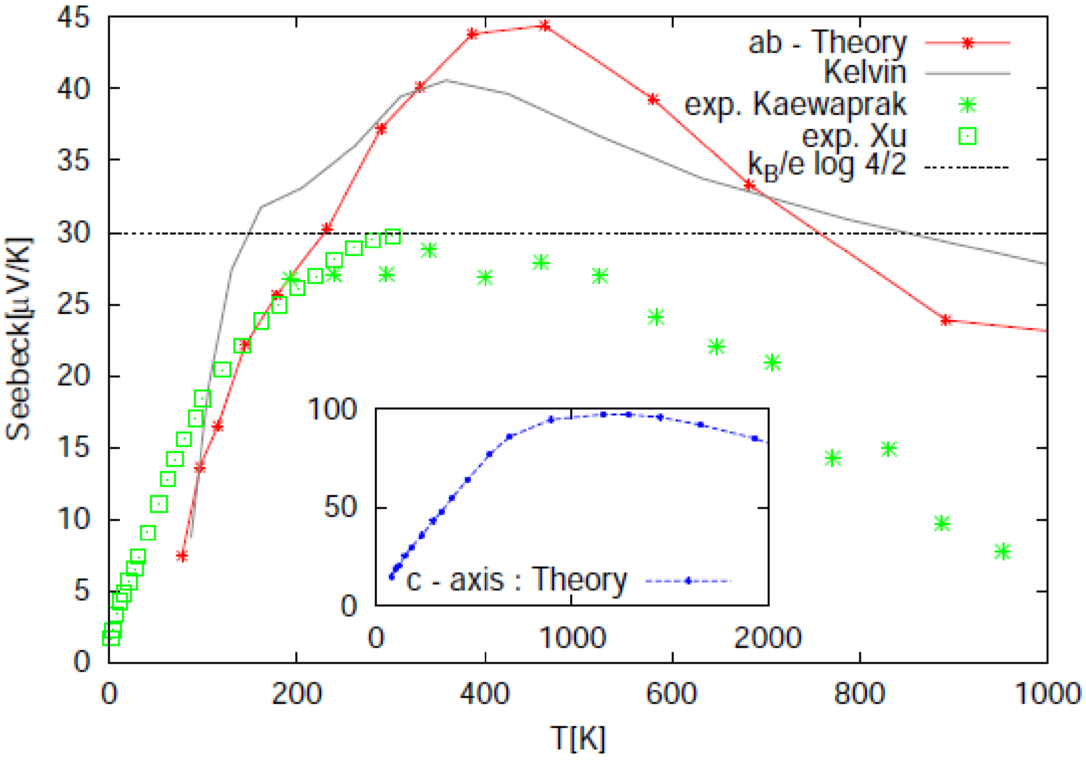
-Similar to exp.
-At low T enhanced S/T as m*
-At higher T difficult analytical continuation.
-change of sign at large T



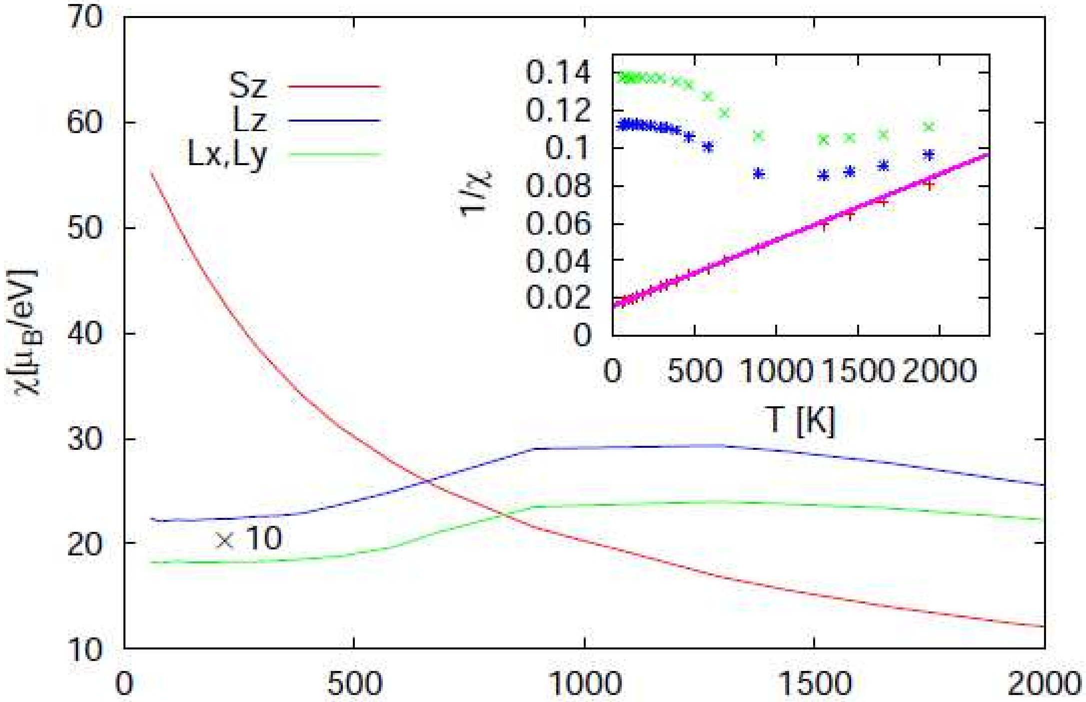
Fully incoherent regime has structure!

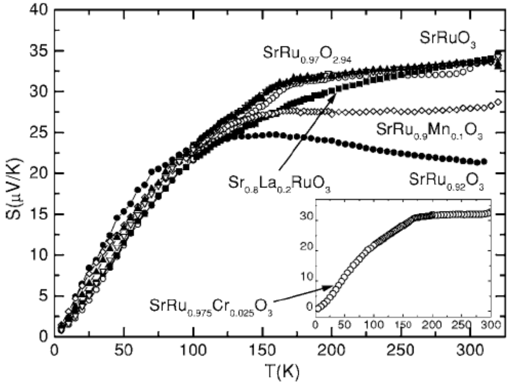
Seebeck : theory vs experiment

- Note: no adjustable parameters



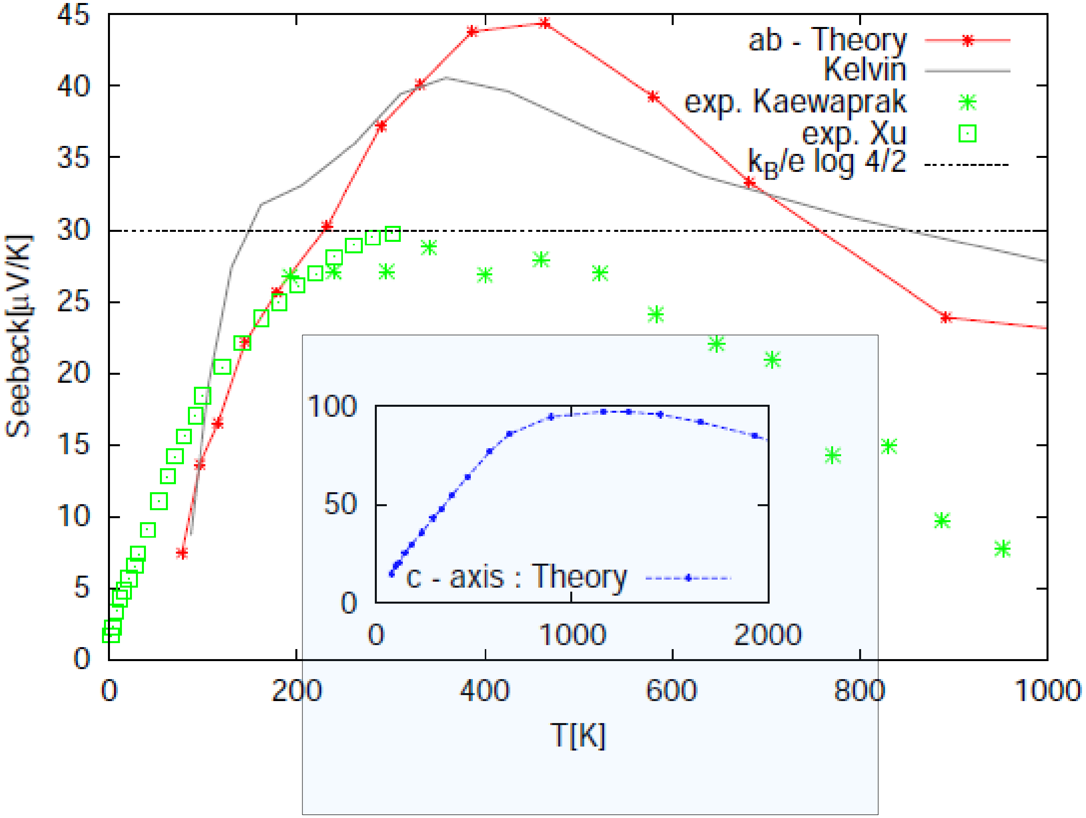
Quenched orbital moments fluctuating spins



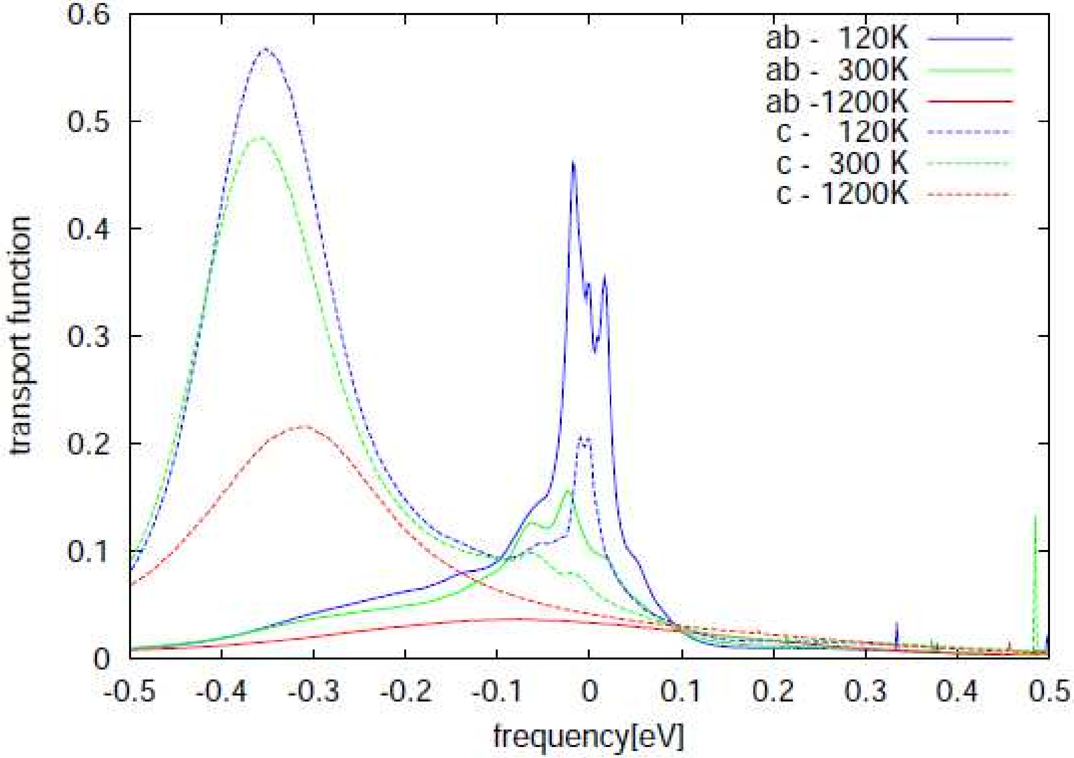


Validates entropic picture keeping just spins
as proposed by Klein, Hebert, Maignan,Kolesnik,
Maxwell, Dabrowski that gives 30microV/K

- C-axis, however behves quite differently!



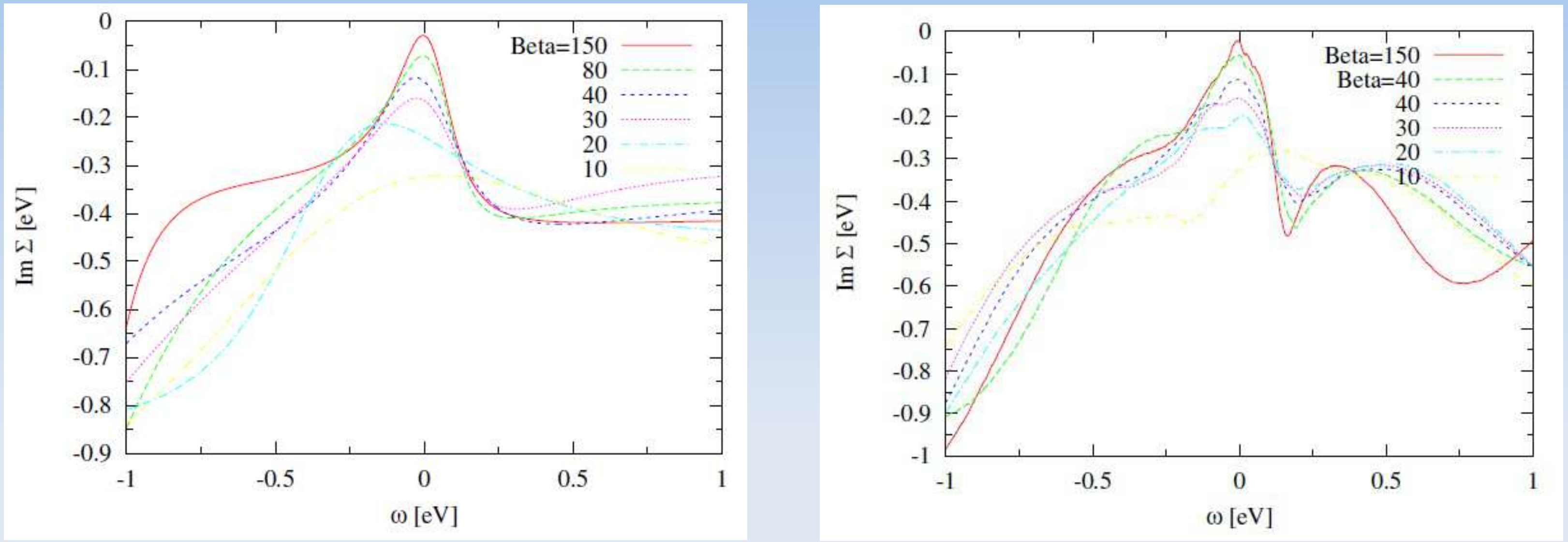
LDA+DMFT transport function



Summary

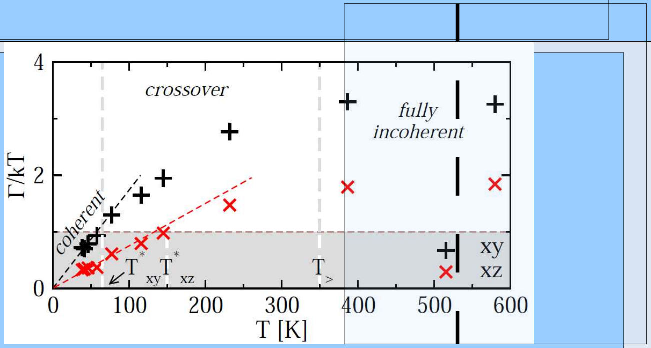
- LDA+DMFT gives good description of Sr2RuO_4
- Inplane Seebeck compatible with entropic considerations
- Out-of-plane Seebeck incompatible
- One can beat the entropy!

Asymmetry in Σ(ω)



Pade

- ω^2 at low T
- Decoherence as T increases
- Opposite asymmetry at high T
- “Fully incoherent” regime has structure!



Summary & outlook

- Coherence-incoherence crossover in Sr_2RuO_4 at low T and renormalization of wide band els. due to J and van Hove
- Good agreement of LDA+DMFT with quantum oscillation, NMR and ARPES
- Seebeck enhanced for m*/m at low T, saturates above T* (as in exp.), changes sign at high T (prediction)
- Influence of doping,magnetic field, pressure?