Density Functional and Dynamical Mean-Field Theory (DFT+DMFT) method and its application to real materials

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Method formulation:

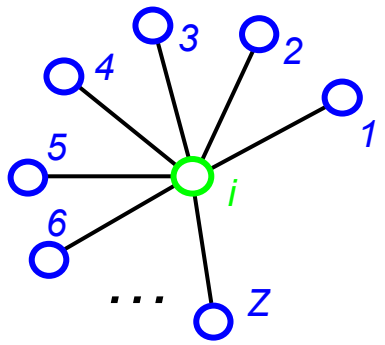
- Dynamical Mean-Field Theory (DMFT)
- Wannier functions as localized orbitals basis
- Determination of Hamiltonian parameters
- “Constrained DFT” calculations for Coulomb interaction parameters
- DFT+DMFT calculation scheme

Results of DFT+DMFT calculations:

Strongly correlated metal $SrVO_3$
Metal-insulator transition in V_2O_3
Heavy fermions in d-system Li_2VO_4
Charge transfer insulator NiO
Metal-insulator transition with pressure in MnO
Correlated covalent insulators FeSi and FeSb2
Novel superconductors LaOFeAs, $BaFe_2As_2$
Jahn-Teller distortions in $KCuF_3$
f-electrons localization in Ce

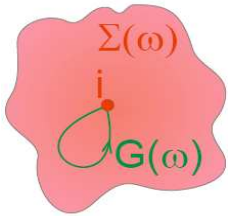
Dynamical Mean-Field Theory

Mapping impurity Anderson model on lattice Hubbard model



Metzner,Vollhardt (1989)

$d \to \infty$
$Z \to \infty$



"single-impurity Anderson model" + self-consistency

Georges and Kotliar (1992)

Hubbard model:

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

- proper time resolved treatment of local electronic interactions
- includes all many-body correlations !

dynamic mean-field (hybridization function):

$$\Delta(\omega) = \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{\omega - \epsilon_{\mathbf{k}}}$$

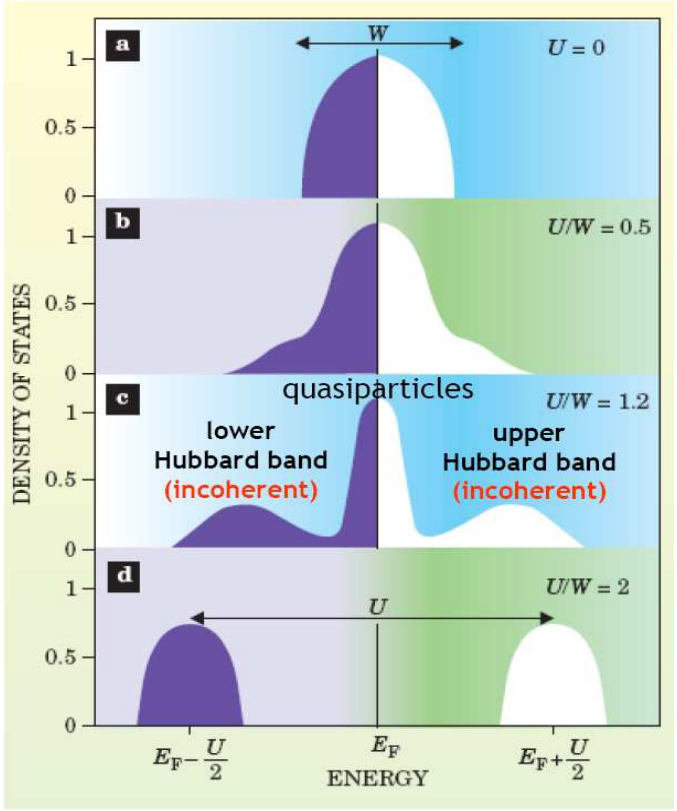
self-consistency condition:

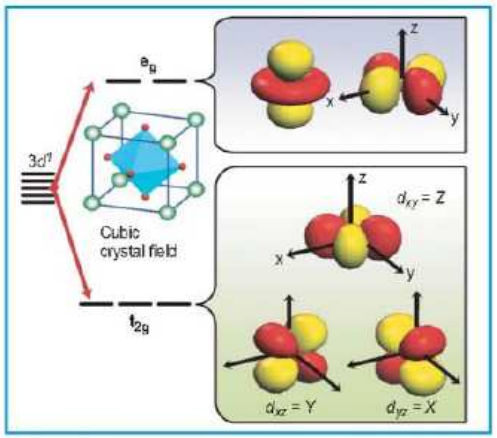
$$G[\Delta(\omega)] = \sum_{\mathbf{k}} \{\omega - \Sigma[\Delta(\omega)] - t_{\mathbf{k}}\}^{-1}$$

$$\Sigma[\Delta(\omega)] \equiv \Delta(\omega) - G^{-1}(\Delta(\omega)) + \omega$$

Effective impurity model defined by hybridization function is solved with an "impurity" solver, e.g., QMC, NRG, ED,…

Including material specific details





Model Hamiltonians:
- input parameters (*t, U, …*) unknown
- systematic many-body approach

Density Functional Theory:
- material specific: *"ab initio"*
- fails for strong correlations

Anisimov *et al.* (1997)
Lichtenstein, Katsnelson (1998)
Kotliar, Vollhardt (2004)

DFT+DMFT

- DFT band structure:

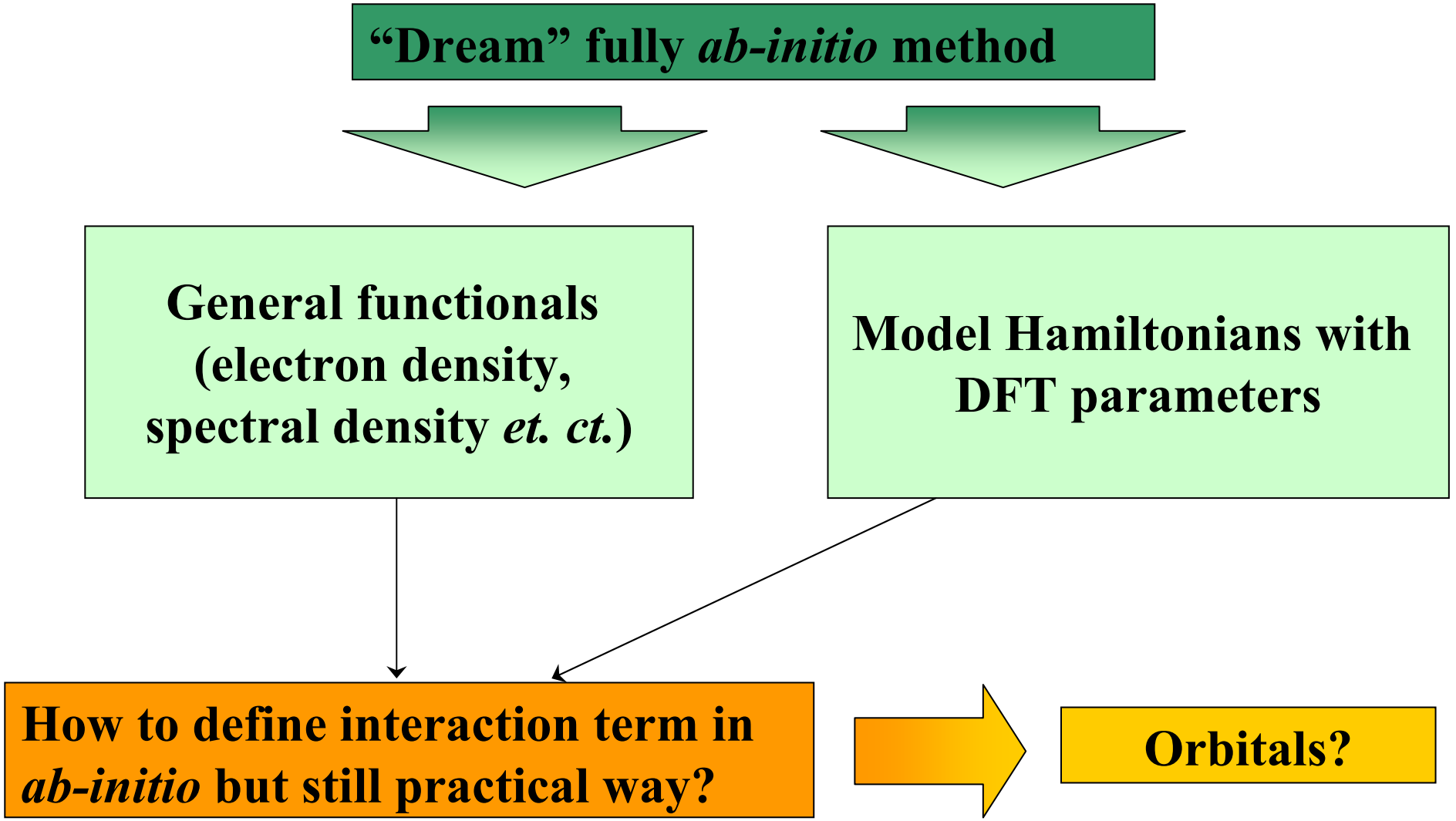
$$\varepsilon_{lml'm'}(k) \rightarrow \hat{H}_{LDA}$$

- + Coulomb *U*

$$\rightarrow \hat{H}_{LDA+corr}$$

- solve $\hat{H}_{LDA+corr}$ by DMFT

Problem


"Dream" fully *ab-initio* method
General functionals (electron density, spectral density *et. ct.*)
Model Hamiltonians with DFT parameters
How to define interaction term in *ab-initio* but still practical way?
Orbitals?

Wannier functions in real space [1]:

$$W_i(\mathbf{r}-\mathbf{T}) = \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{T}} \langle \mathbf{r}|\psi_{i\mathbf{k}}\rangle$$

← Bloch functions

Advantages of Wannier function basis set:

< Explicit form of the orbitals forming complete basis set

< Localized orbitals

< Orbitals are centered on atoms

} like in Hubbard model

Uncertainty of WF definition for a many-band case:

$$|\psi_{i\mathbf{k}}\rangle = \sum_j U_{ji}^{(\mathbf{k})} |\psi_{j\mathbf{k}}\rangle$$

Unitary matrix

[1] G.H. Wannier, Phys. Rev. **52**, 192 (1937)

Wannier functions and projection

WF in k-space – projection of the set of trial functions [2] (atomic orbitals) into Bloch functions subspace :

$$|\widetilde{W}_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2} |\psi_{i\mathbf{k}}\rangle\langle\psi_{i\mathbf{k}}|\phi_n\rangle$$

Bloch functions in DFT basis (LMTO or plane waves):

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_j c_{ji}(\mathbf{k})\phi_j^{\mathbf{k}}(\mathbf{r})$$

Eigenvector element

Bloch sums of LMTO orbitals

$$|\widetilde{W}_{n\mathbf{k}}\rangle = \sum_{i=N_1}^{N_2}\sum_j c_{ji}(\mathbf{k})c_{ni}^{\star}(\mathbf{k})|\phi_j^{\mathbf{k}}\rangle = \sum_j \tilde{b}_{jn}^{\mathbf{k}}|\phi_j^{\mathbf{k}}\rangle$$

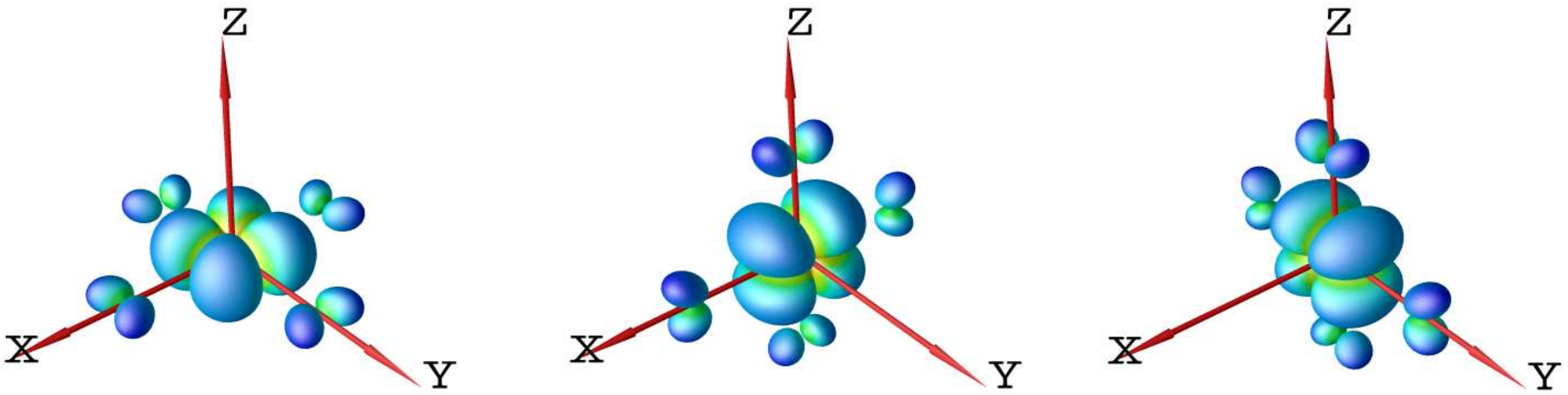
coefficients of WF expansion in LMTO-orbitals:

$$\tilde{b}_{jn}^{\mathbf{k}} = \sum_{i=N_1}^{N_2} c_{ji}(\mathbf{k})c_{ni}^{\star}(\mathbf{k})$$

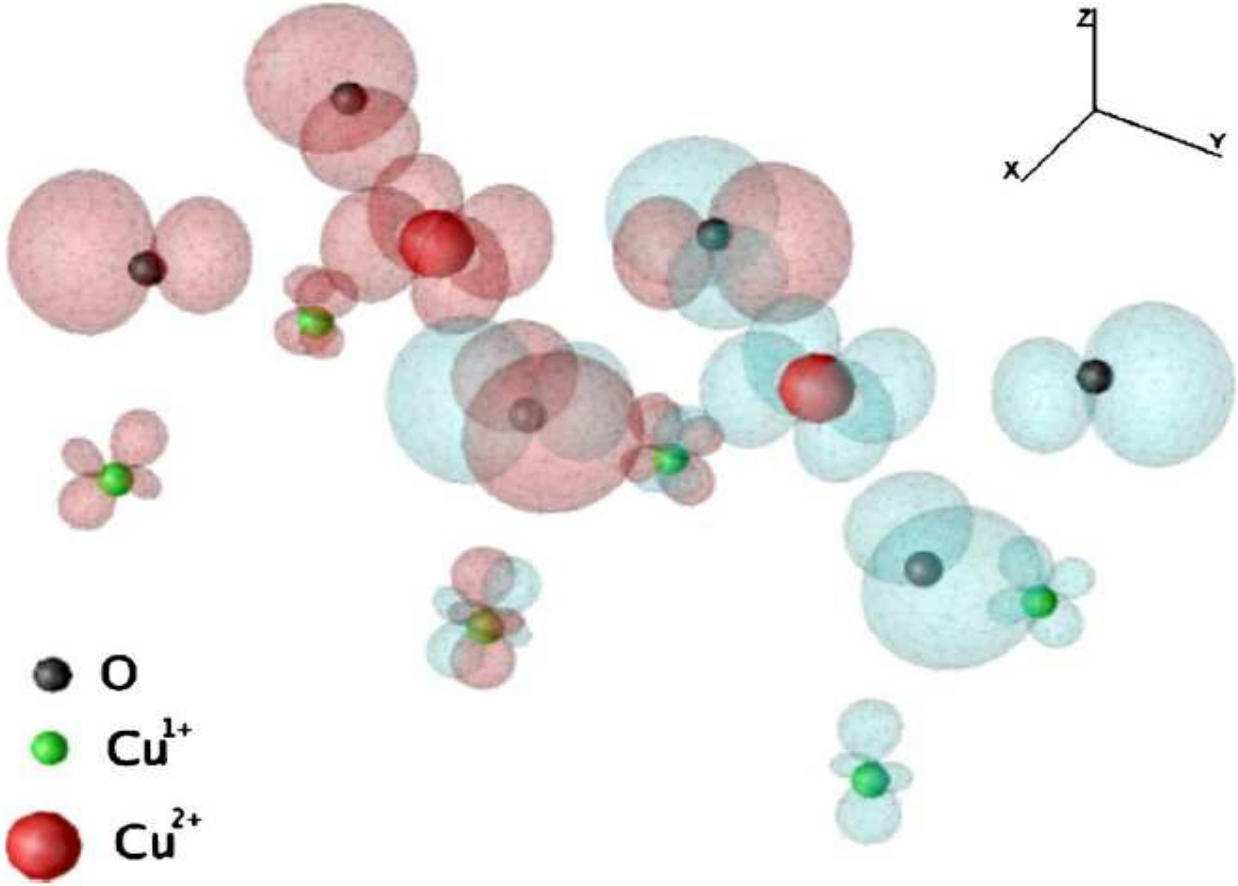
[2] D.Vanderbildt et al, Phys. Rev.B **56**, 12847 (1997)

Example of WF in real space

WF basis set for V-3d (t_{2g}) subband of $SrVO_3$: *XY, XZ, YZ* - orbitals



WF in cuprates



Wannier orbitals centered on neighboring copper atoms along the *y* axis.

V. V. Mazurenko, et al, Phys. Rev. B 75, 224408 (2007)

DFT+DMFT calculations scheme

Local Green function:

$$G^{loc}_{n,n'}(\varepsilon) = \frac{1}{V_{IBZ}} \int_{IBZ} d\mathbf{k} \left(\left[(\varepsilon + E_f^{(N)}) 1 - H_0^{WF}(\mathbf{k}) - \Sigma(\varepsilon) \right]^{-1} \right)_{n,n'}$$

Dyson equation defines bath Green function:

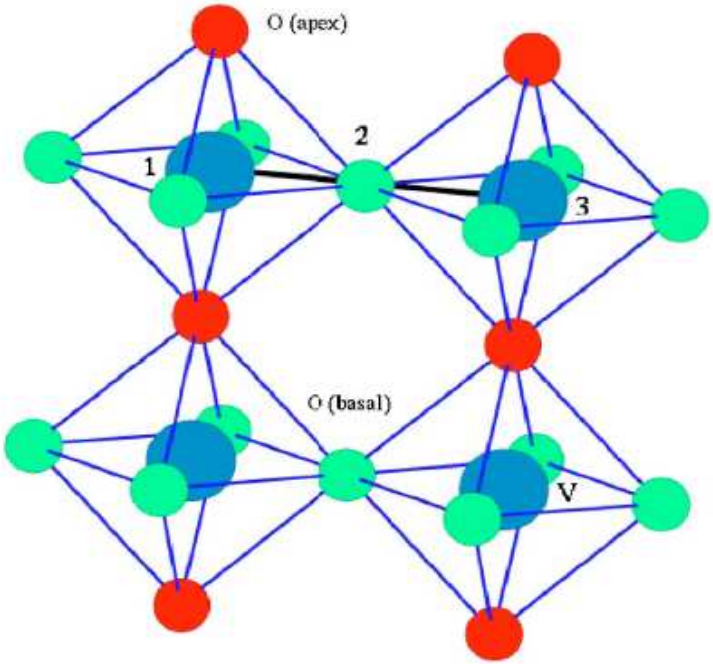
$$\mathcal{G}^{-1} = (G^{loc})^{-1} + \Sigma$$

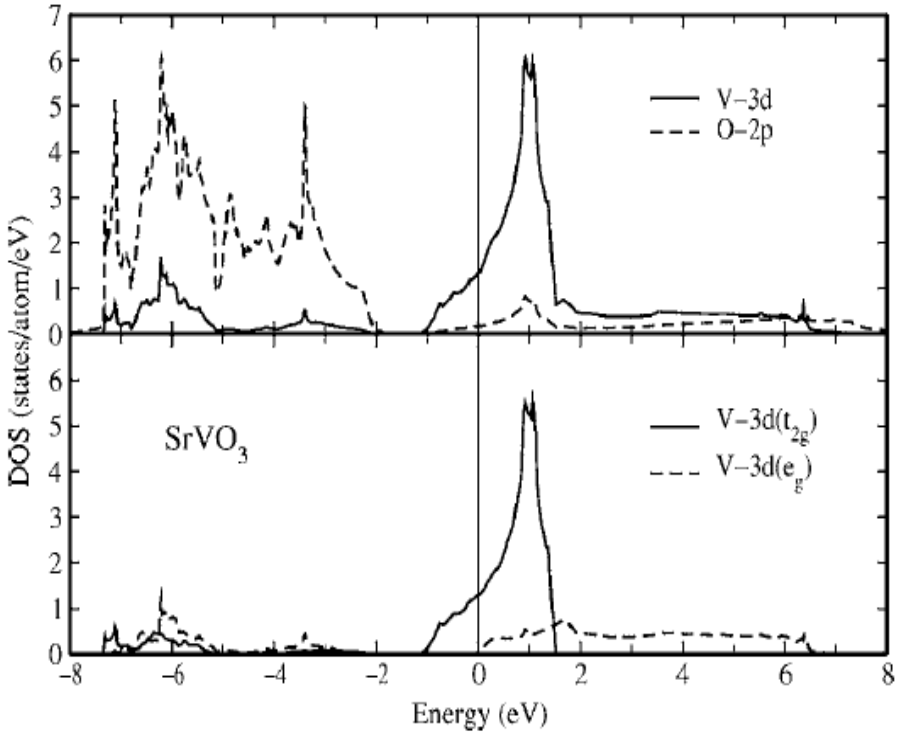
Self-consistent condition:

$$G^{loc} = G^{imp} \Rightarrow \Sigma_{new}$$

Impurity problem defined bath Green function is solved by QMC

Strongly correlated metal $SrVO_3$



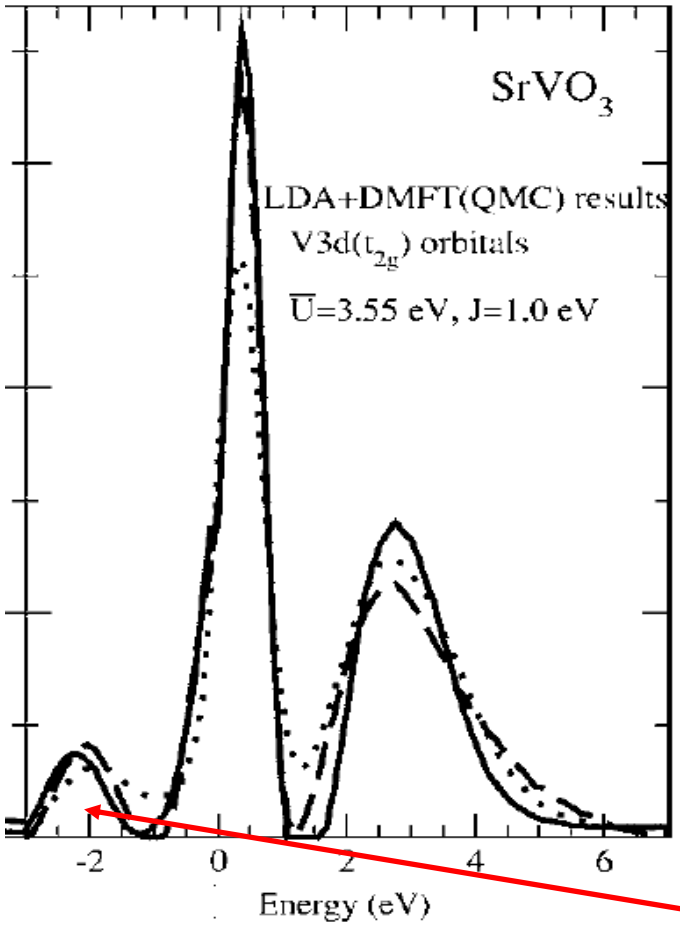


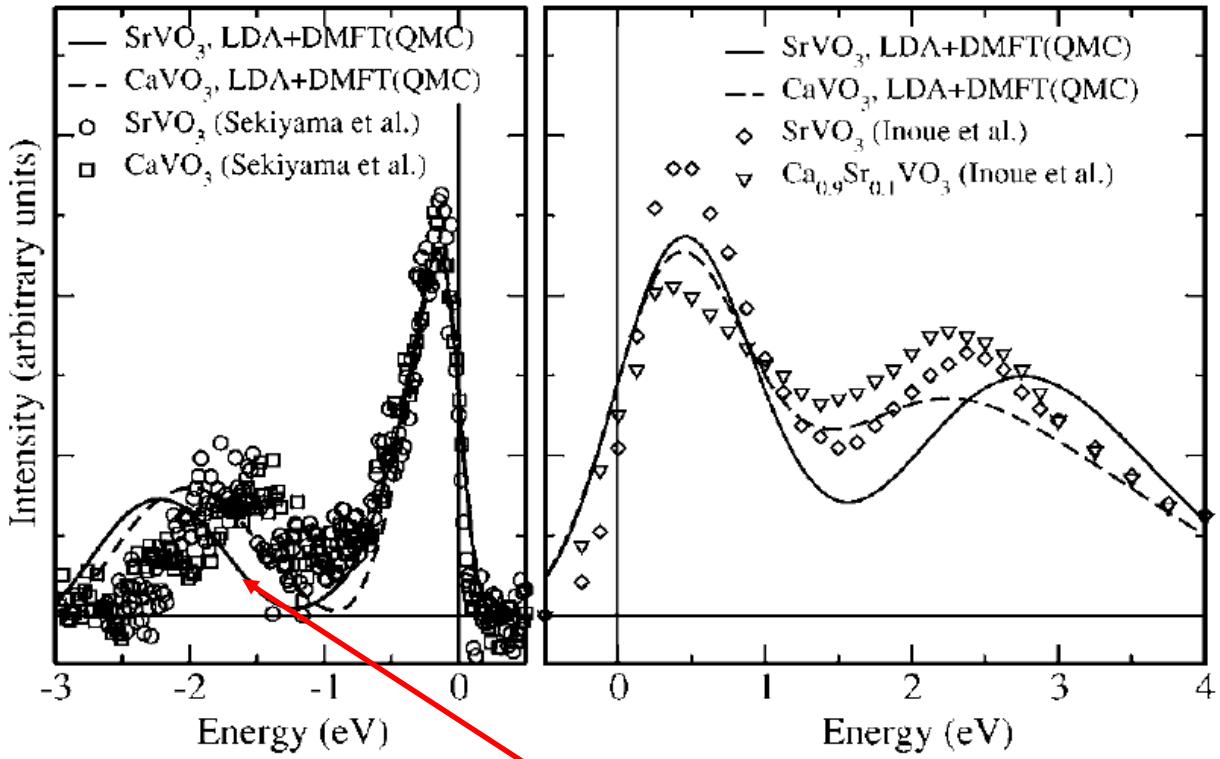
V^{+4} (d^1) ion in cubic perovskite crystal structure

One electron in partially filled t_{2g} band

I.Nekrasov et al, Phys. Rev. B **72**, 155106 (2005), Phys. Rev. B **73**, 155112 (2006)

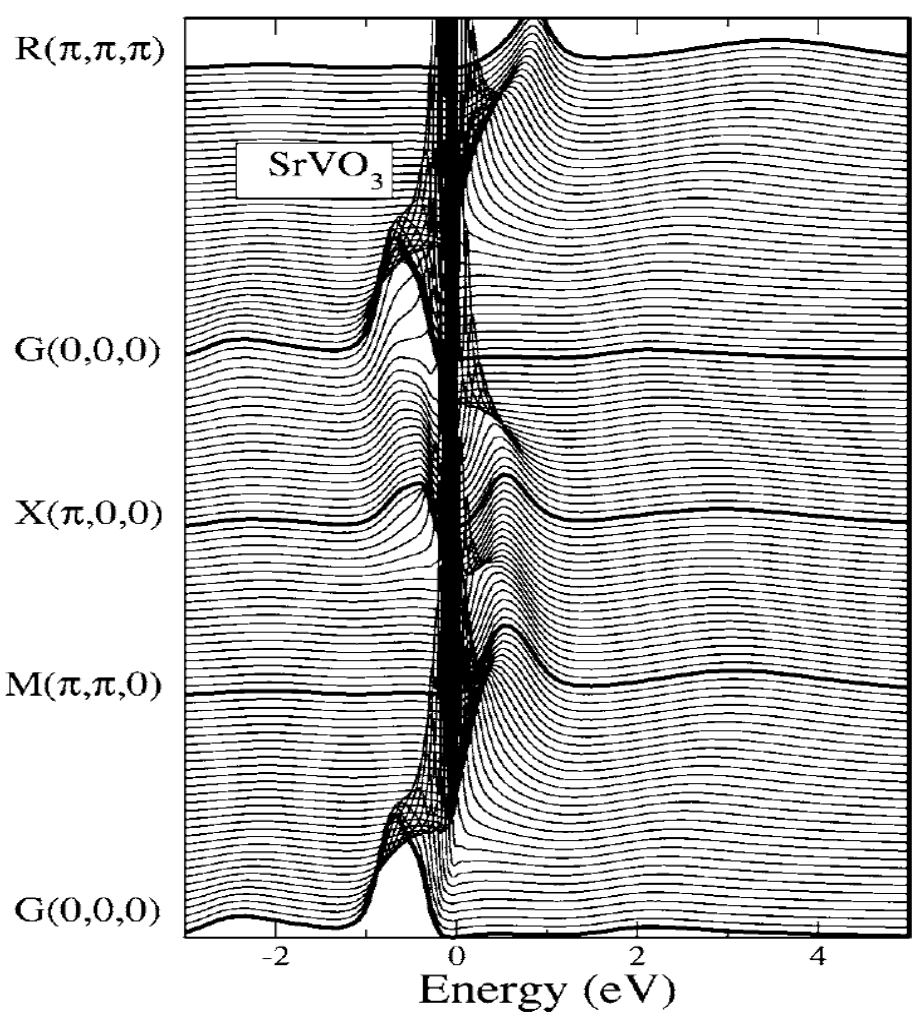
Strongly correlated metal $SrVO_3$

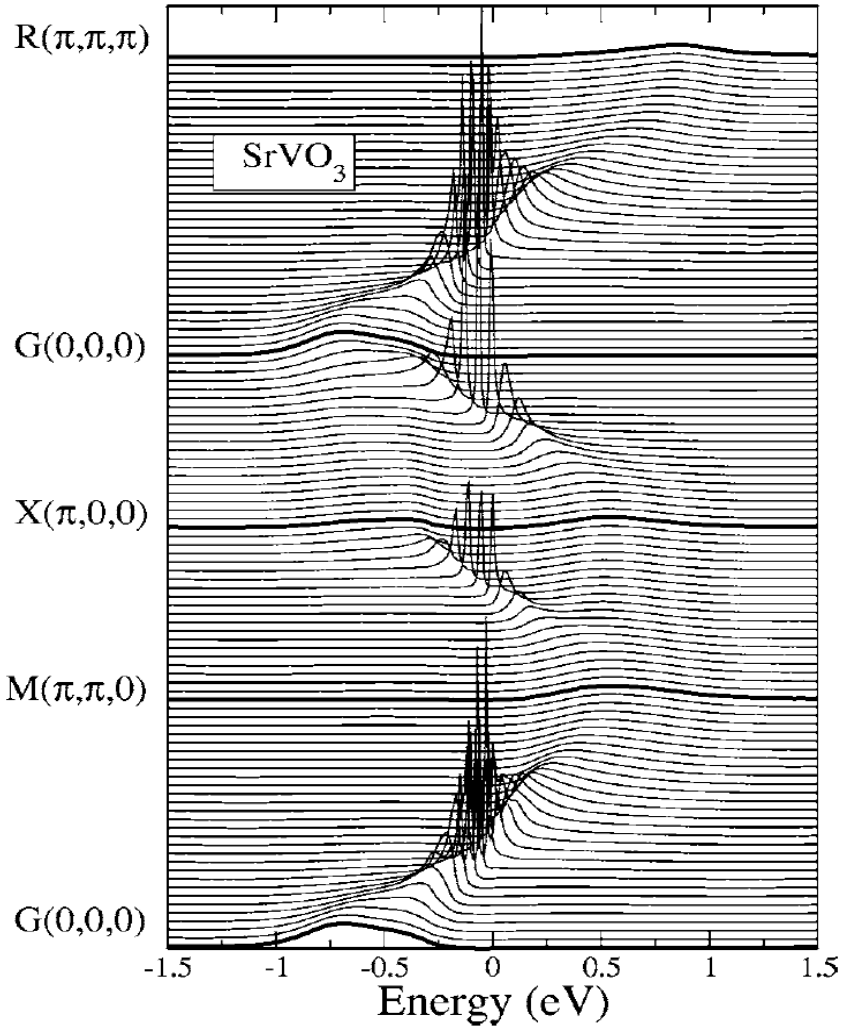




Strongly correlated metal with pronounced Lower Hubbard band (LHB)

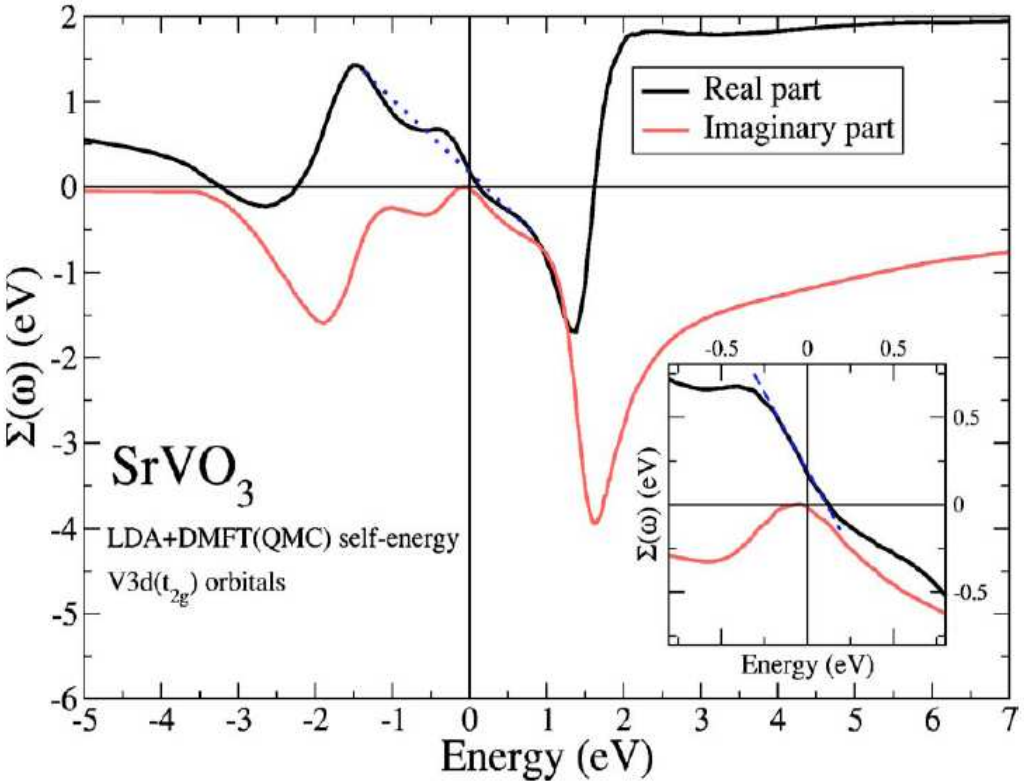
Strongly correlated metal $SrVO_3$

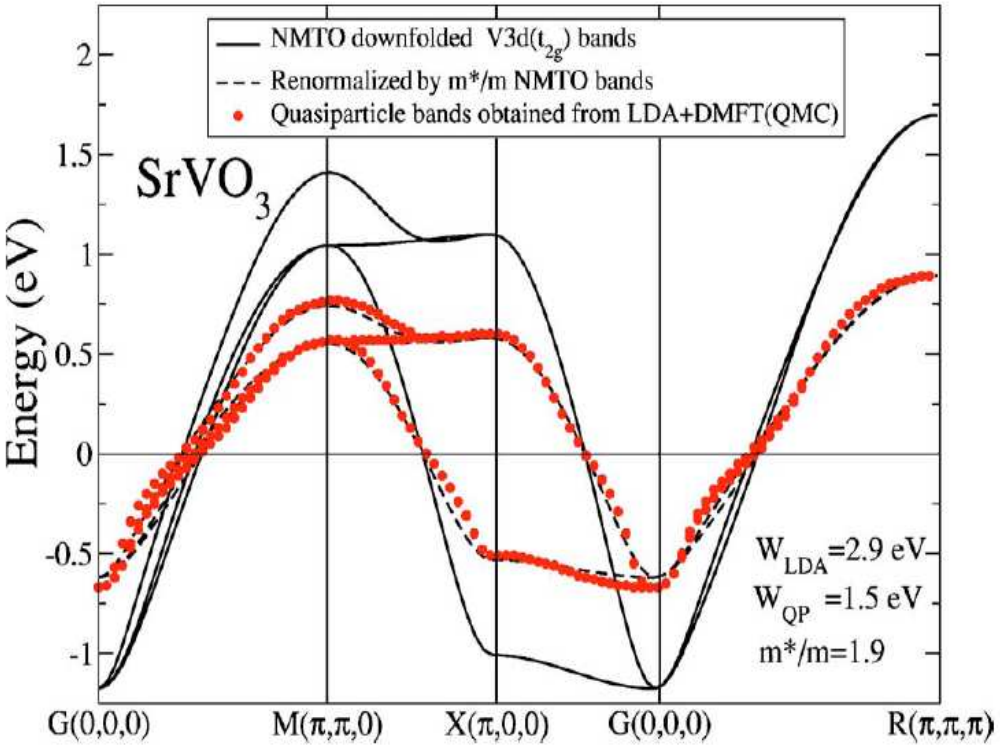




$$\text{Spectral function } A(k,\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\left[\omega - \Sigma(\omega) - H_0(k)\right]^{-1}$$

Strongly correlated metal $SrVO_3$





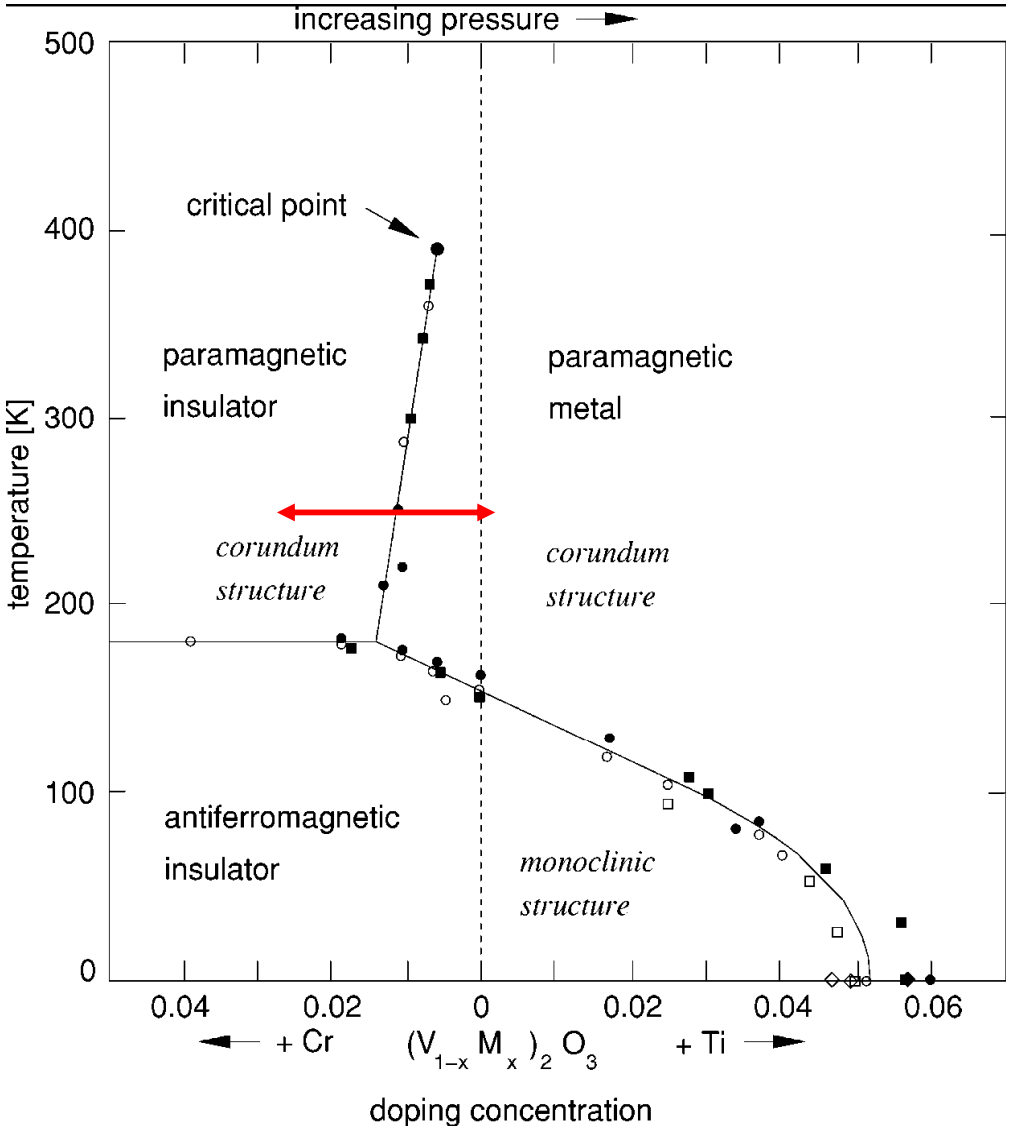
Effective electron mass

$$\frac{m^*}{m} = 1 - \frac{\partial\, \mathrm{Re}\,\Sigma(\omega)}{\partial\omega}\Big|_{\omega=0} \approx 2$$

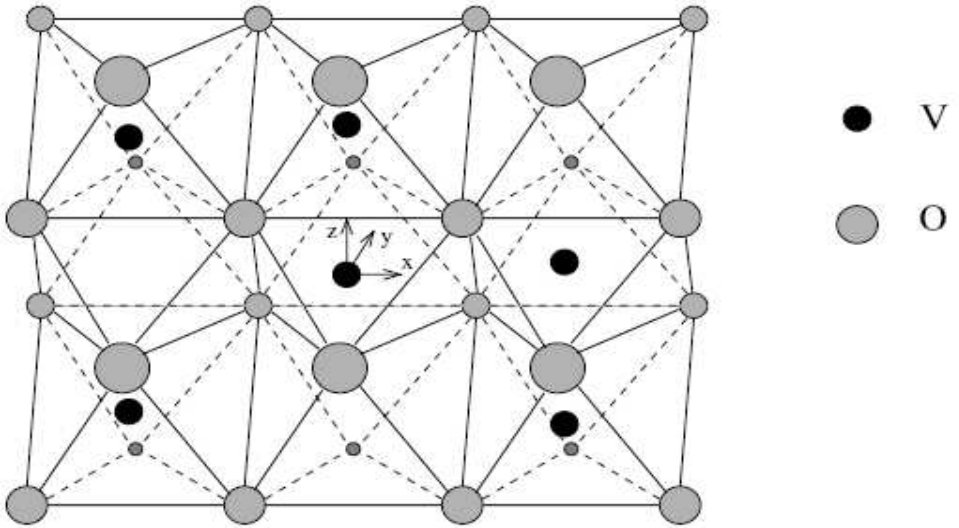
Bands narrowing

$$\tilde{\varepsilon}\,(\mathrm{k}) = \left(\frac{m^*}{m}\right)^{-1} \varepsilon_0(k)$$

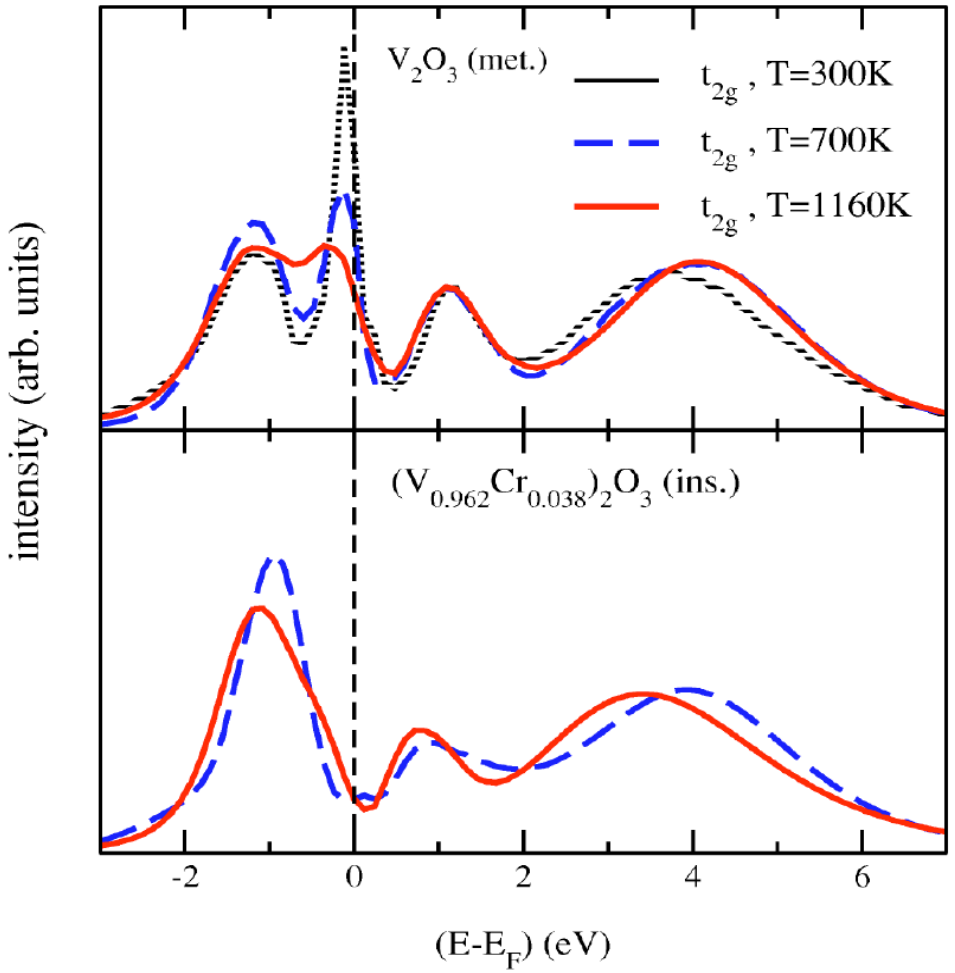
Mott insulator V_2O_3

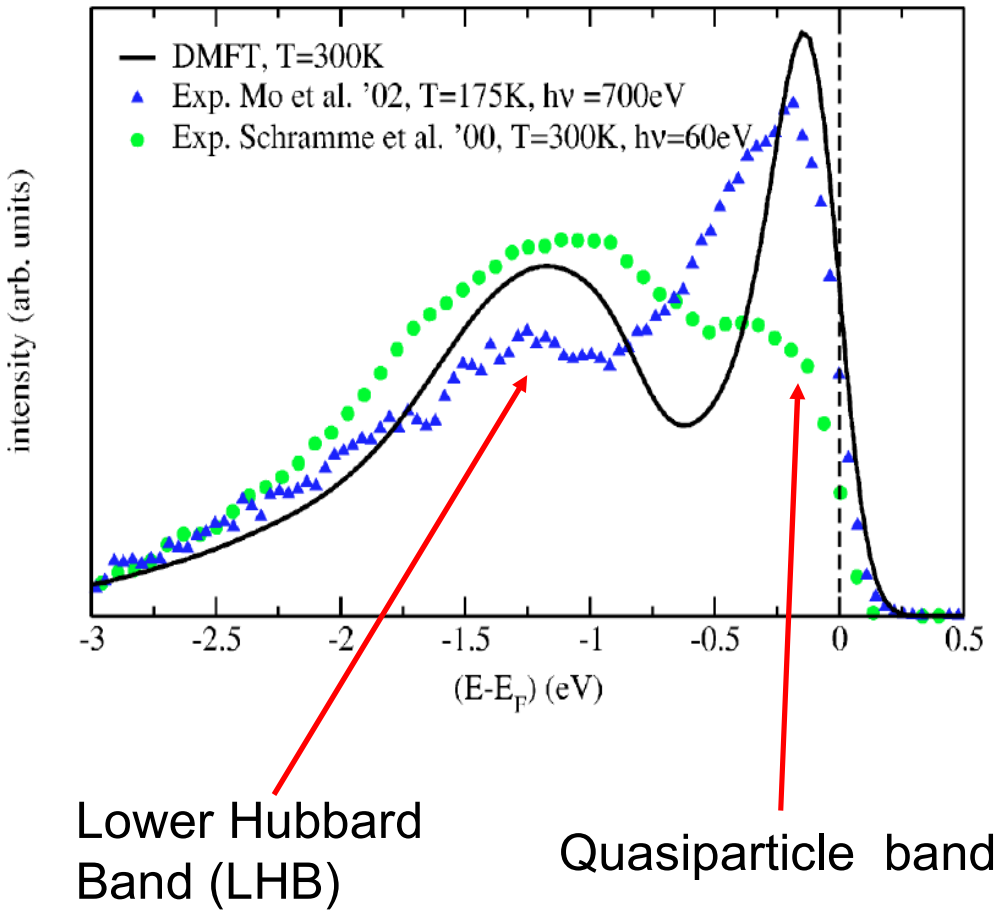


Prototypical Mott insulator.
Iso-structural paramagnetic metal to paramagnetic insulator transition with small volume change due to chemical negative pressure.



Mott insulator V_2O_3





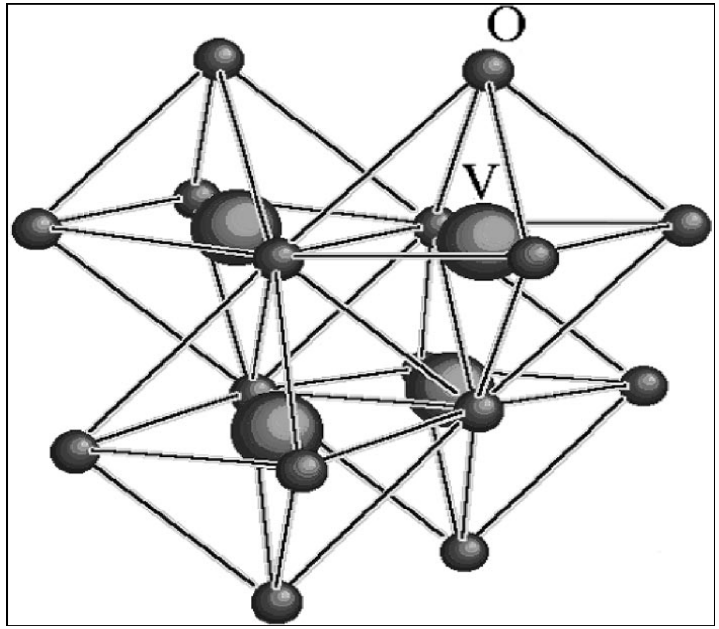
Lower Hubbard Band (LHB)

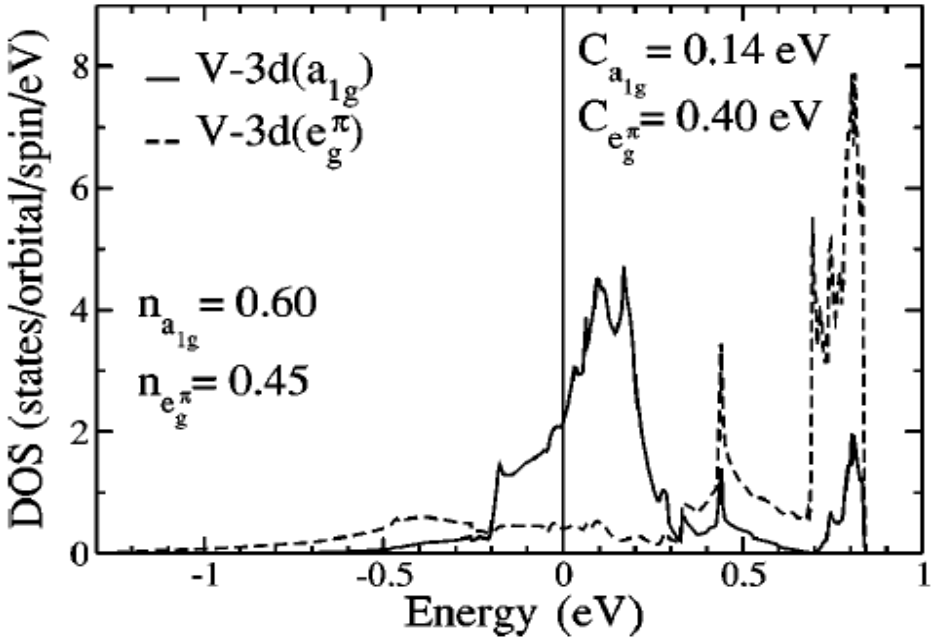
Quasiparticle band

Paramagnetic metal to paramagnetic insulator transition with small change in corundum crystal structure parameters

K.Held et al, Phys. Rev. Lett. 86, 5345 (2001), G.Keller et al, Phys. Rev. B 70, 205116 (2004)

Heavy fermions material LiV_2O_4

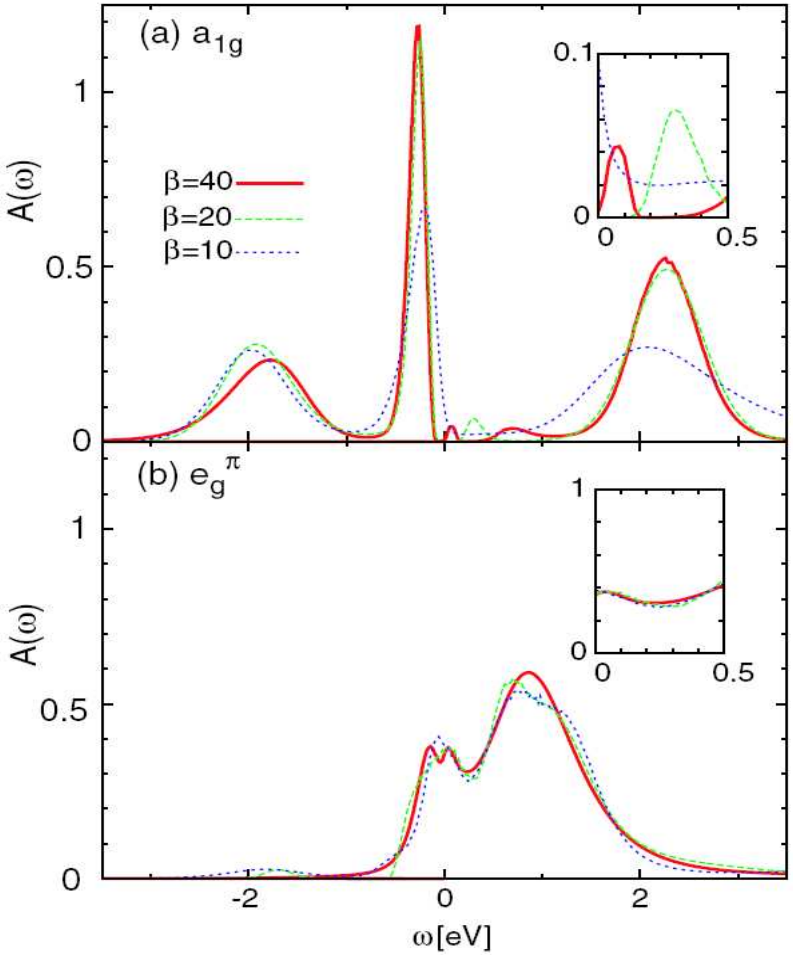


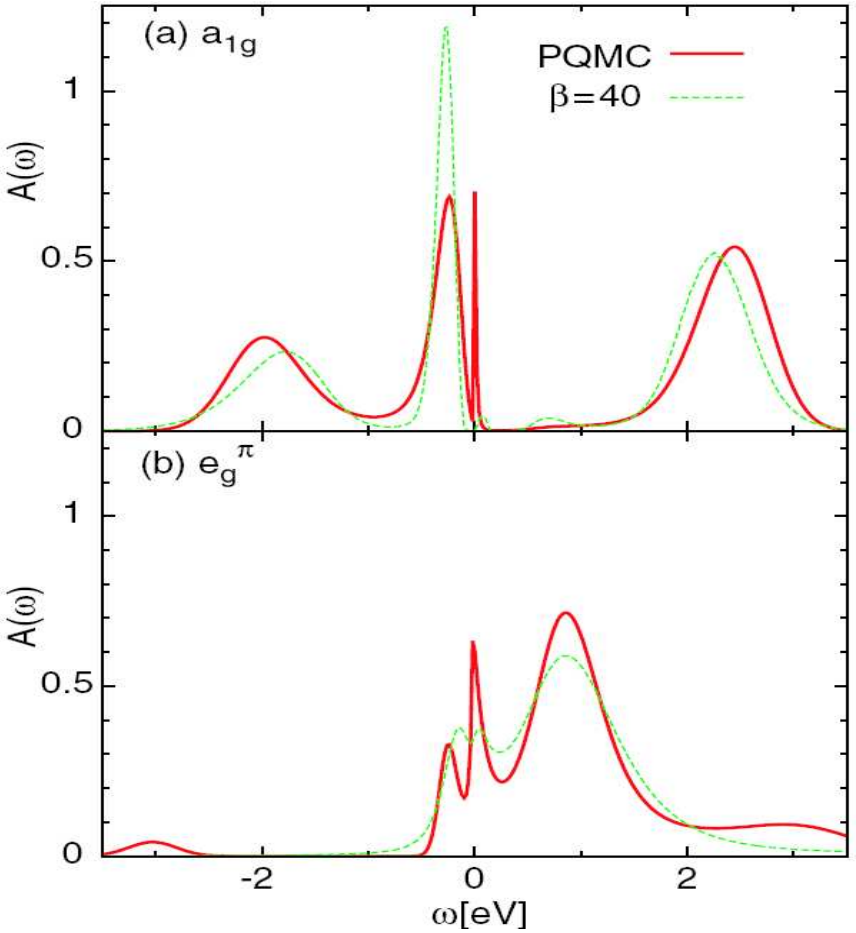


Heavy-fermions without f-electrons:
linear specific heat coefficient
γ=420 mJ/molK^2,
effective electron mass m^*/m =25
below T_K ~28 K

Cubic spinel crystal structure
with local trigonal symmetry

Heavy fermions material LiV_2O_4





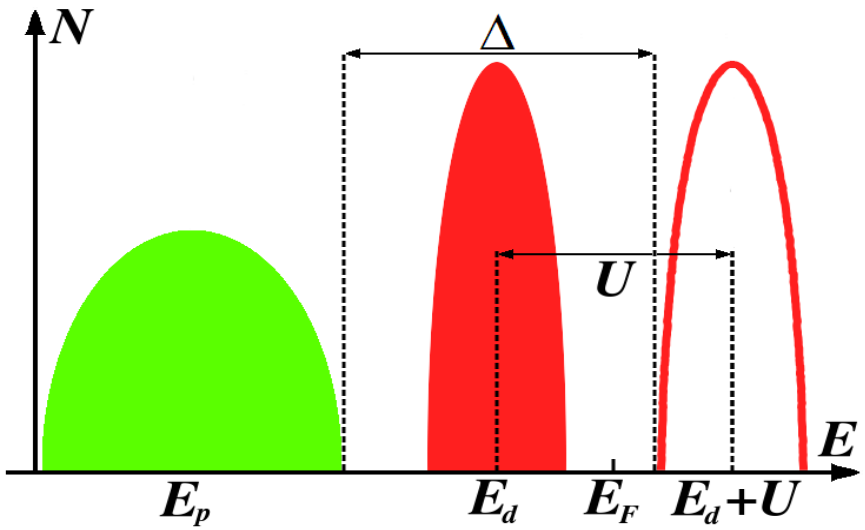
Sharp quasiparticle peak above the Fermi for T=0 limit (PQMC)

R.Arita et al, Phys. Rev. Lett. 98, 166402 (2007)

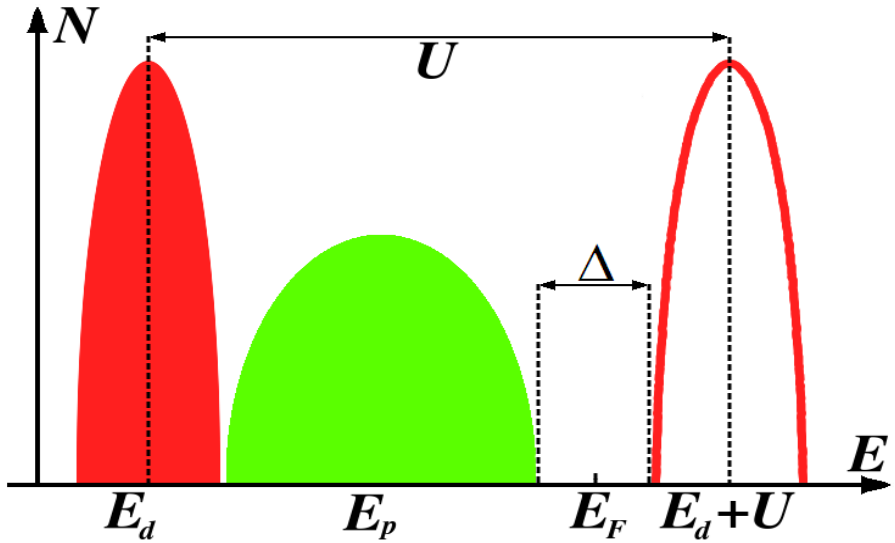
Charge transfer insulator NiO

Zaanen-Sawatzky-Allen classification scheme
for transition metal compounds

Mott-Hubbard insulators

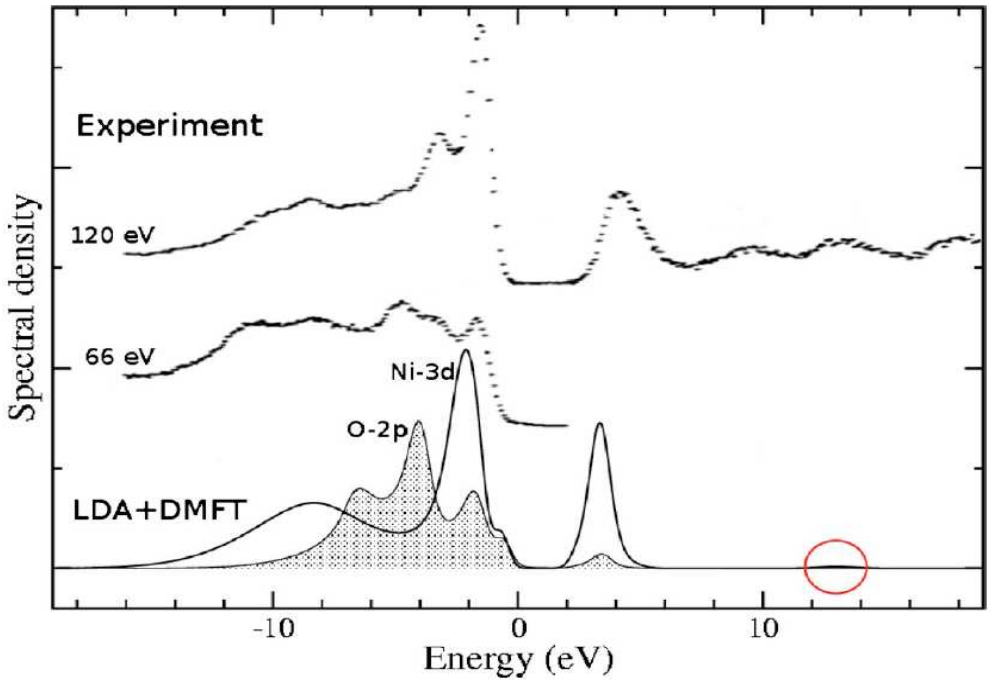


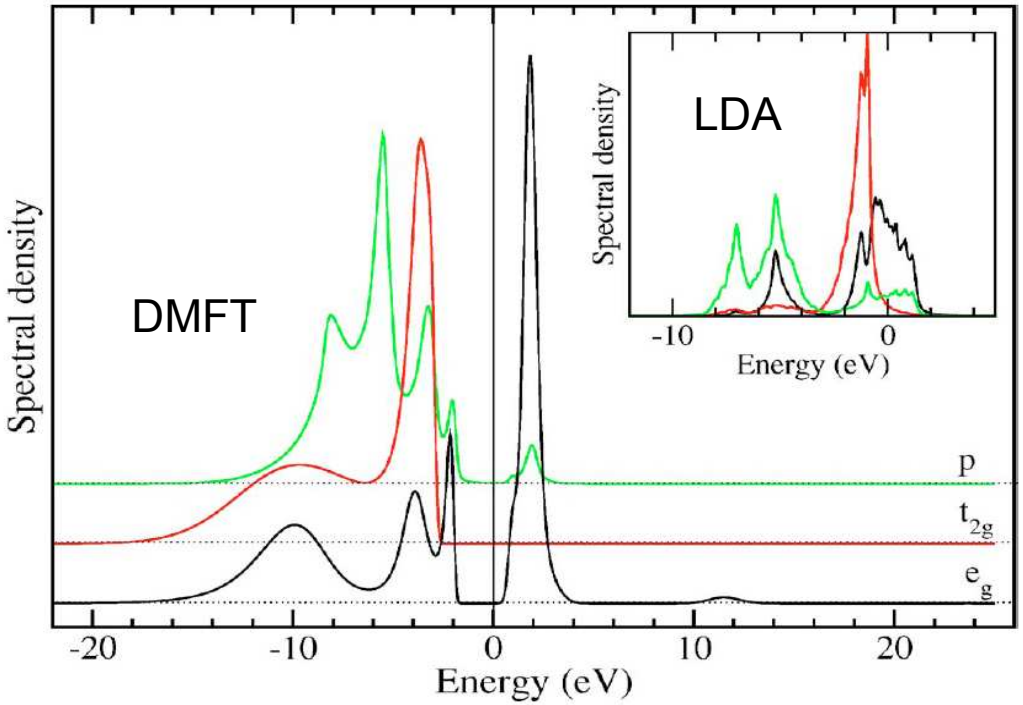
Charge transfer insulators



Zaanen et al, PRL **55**, 418 (1985)

Charge transfer insulator NiO

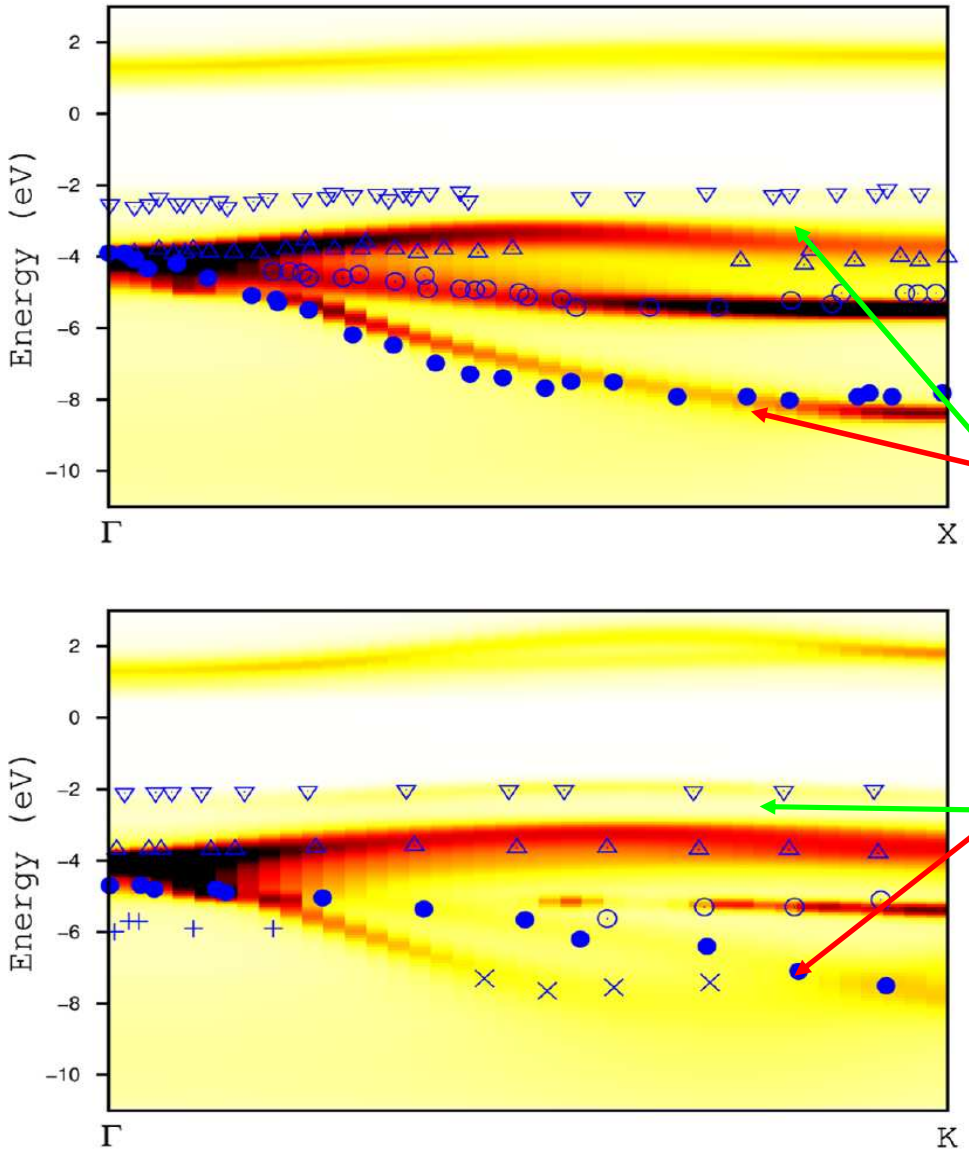




Charge transfer insulator in paramagnetic phase.
Ni^{+2} (d^8) ion in cubic rock salt crystal structure

J. Kuneš, et al, Phys. Rev. B 75, 165115 (2007)

Charge transfer insulator NiO



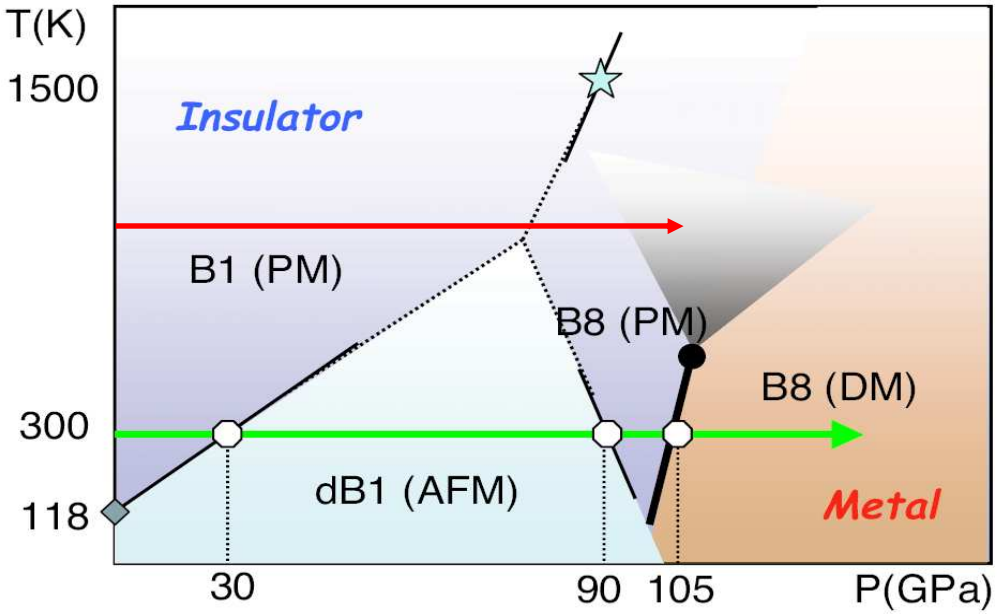
Band structure of charge transfer insulator combines dispersive (itinerant states) and flat bands (localized states).

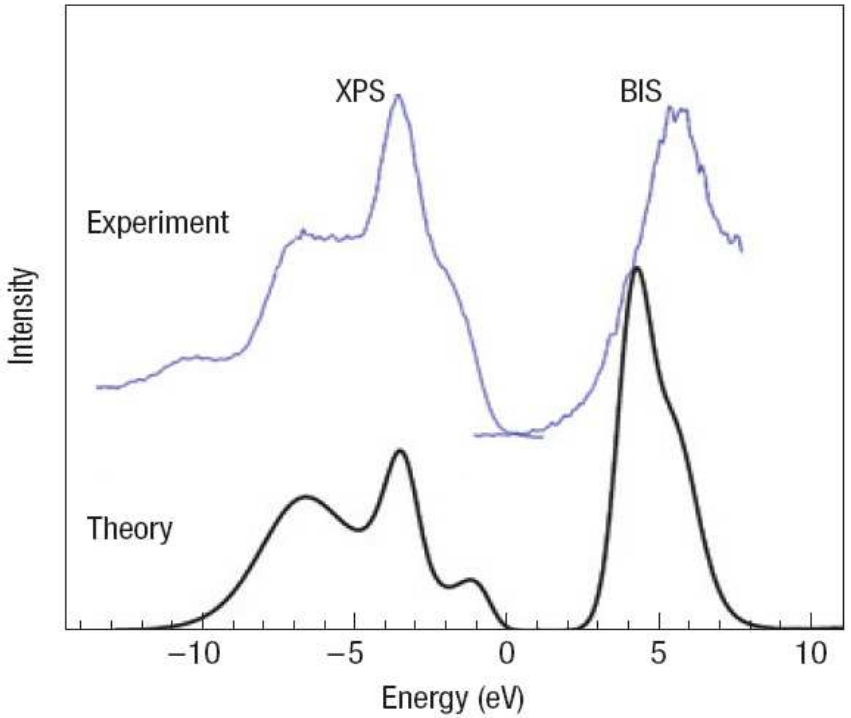
O2p bands

Ni3d bands

J. Kunes et al, Phys. Rev. Lett. 99, 156404 (2007)

Metal-insulator transition in MnO

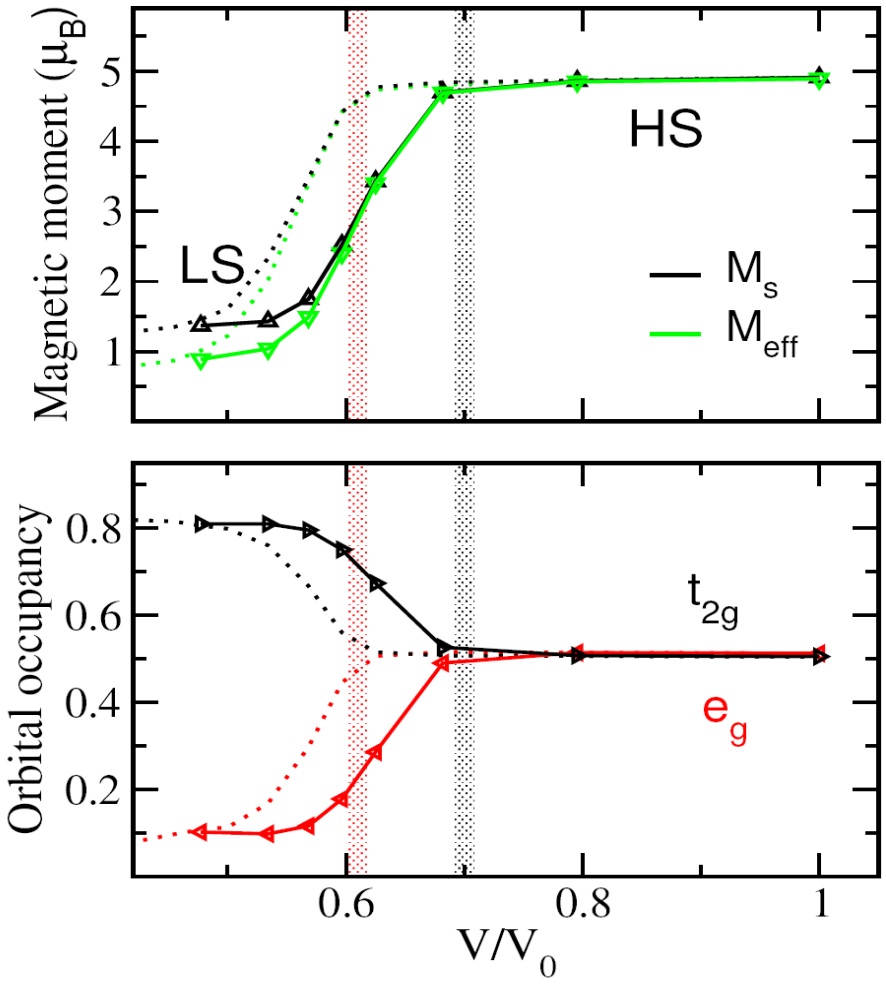


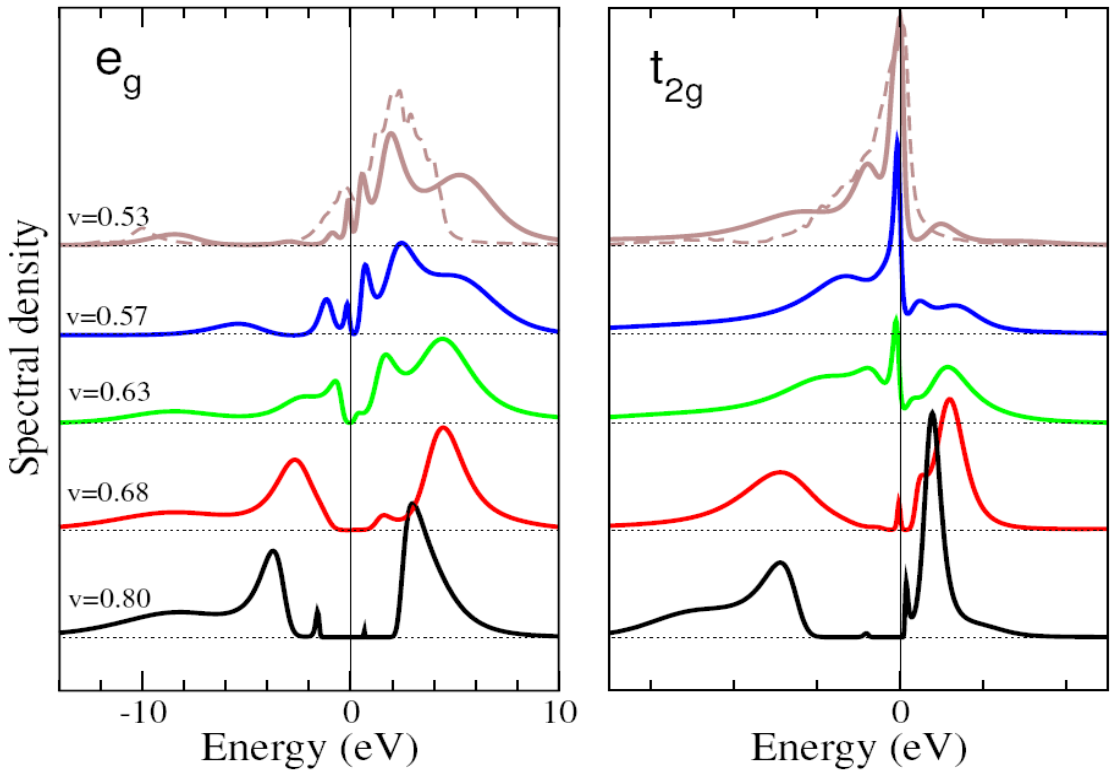


Metal-insulator transition (paramagnetic insulator to paramagnetic metal) with pressure in MnO accompanied with high-spin to low-spin state transition.

J. Kunes et al, Nature Materials 7, 198 (2008)

Metal-insulator transition in MnO

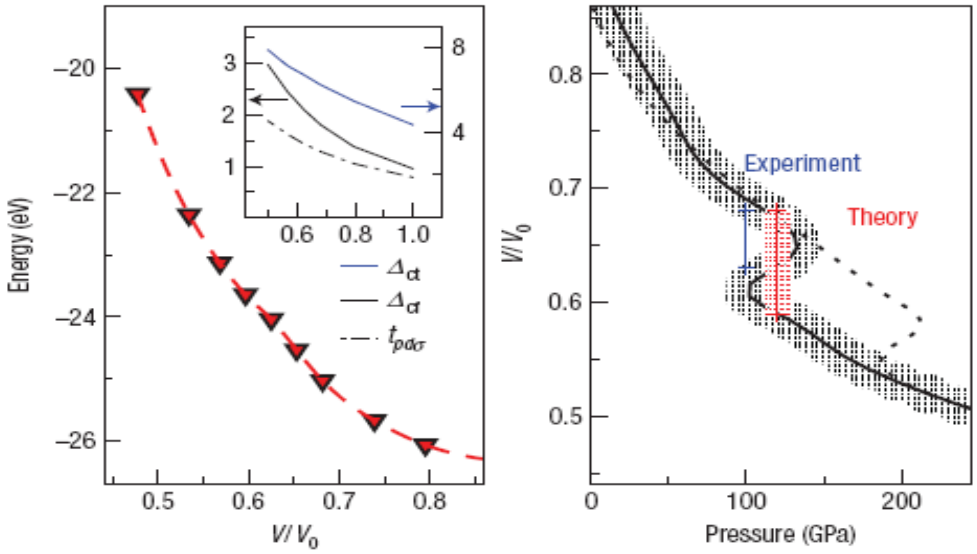


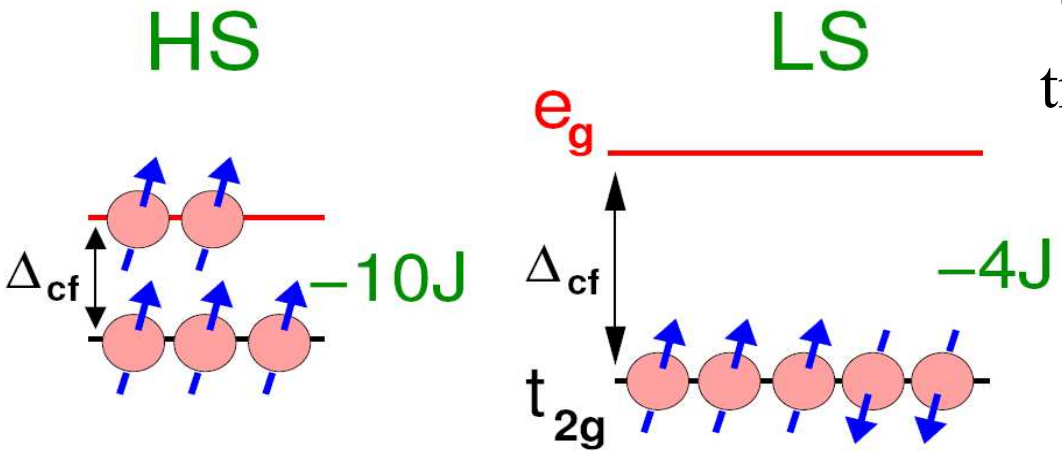


High-spin state (HS) - $t^3_{2g}\, e^2_g$ configuration

Low-spin state (LS) - $t^5_{2g}\, e^0_g$ configuration

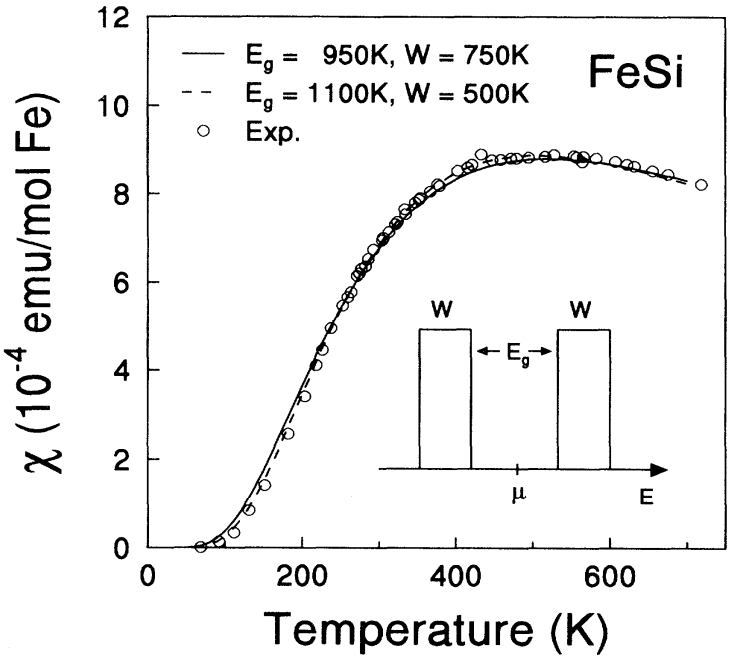
Metal-insulator transition in MnO

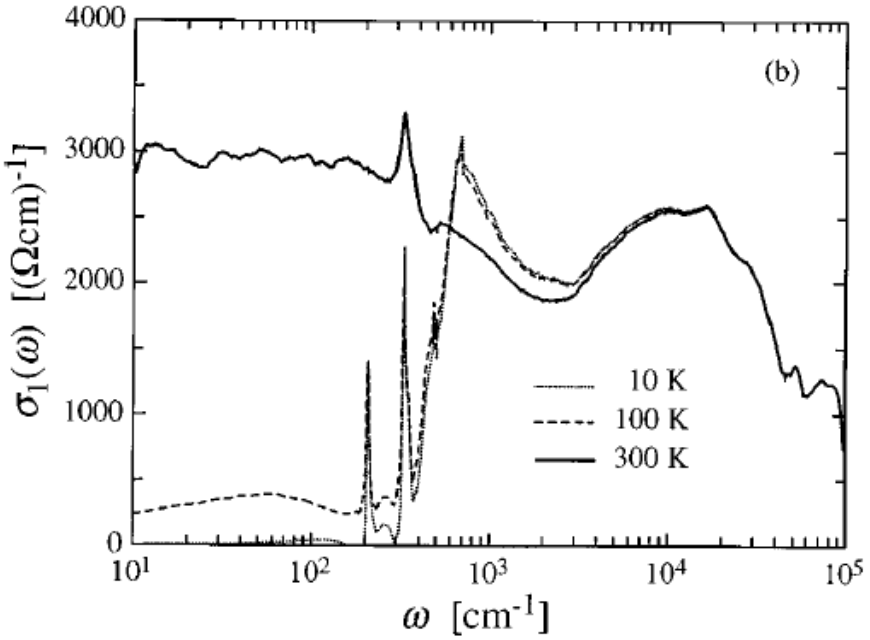




Decreasing volume with pressure increases crystal field spliting Δ_{cf} competing with exchange energy J that results in HS $\rightarrow$ LS transition with volume collapse.

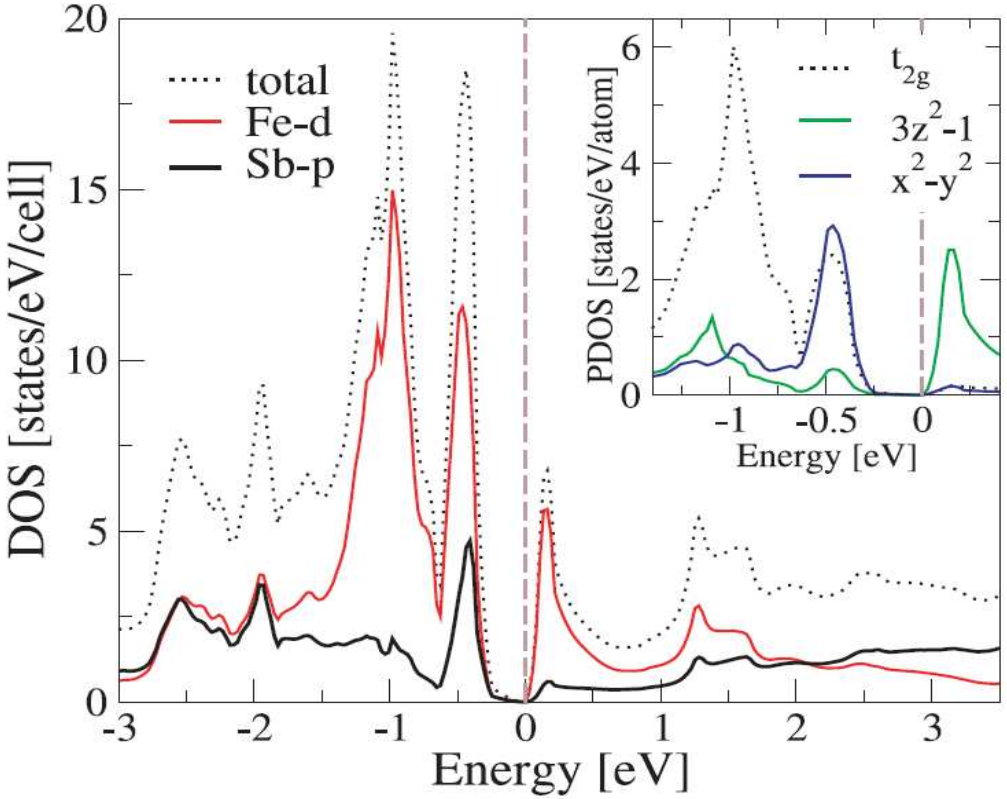
Correlated covalent insulators FeSi and $FeSb_2$

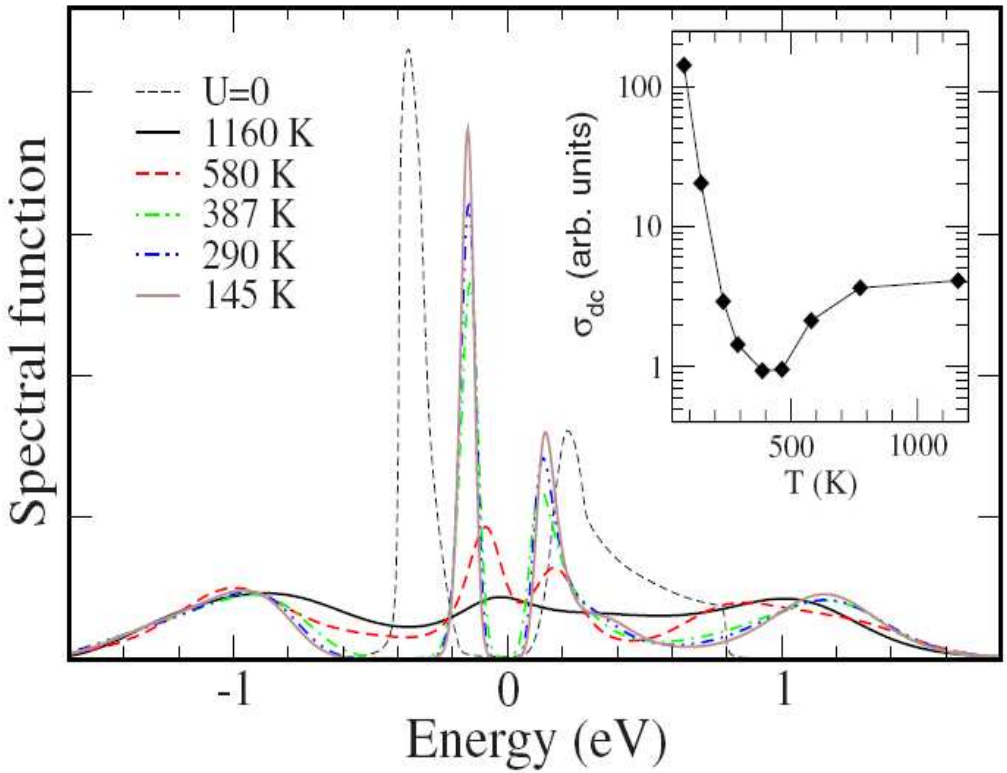




Transition from non-magnetic semiconductor to paramagnetic metal with temperature increase in FeSi and $FeSb_2$. Electron doping in $Fe_{1-x}Co_xSi$ results in ferromagnetic metallic state.

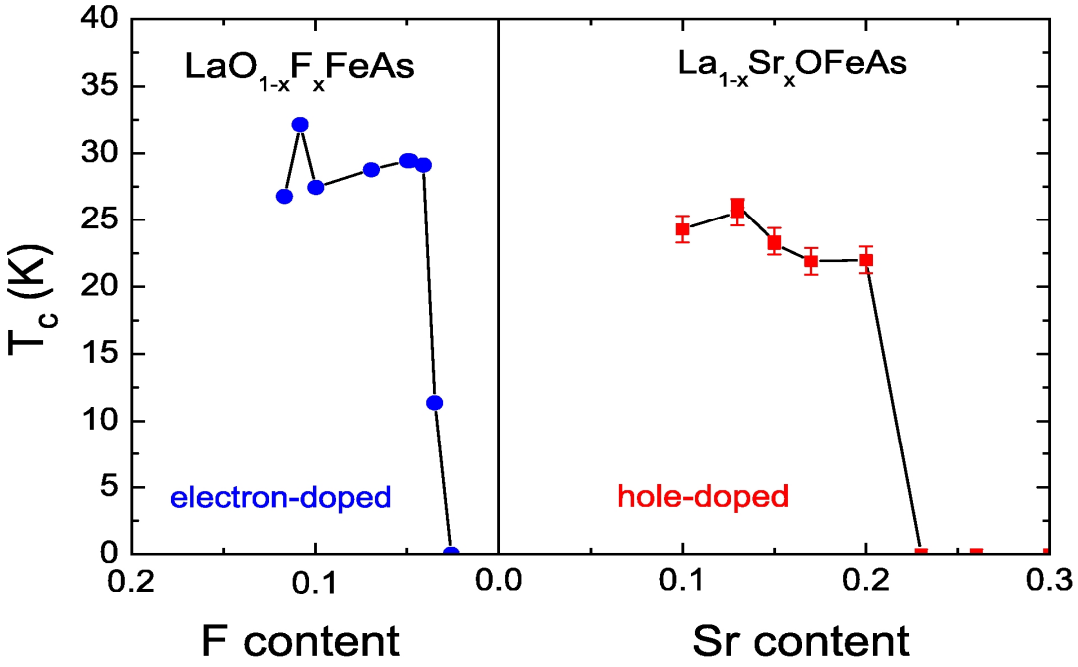
Correlated covalent insulators FeSi and $FeSb_2$

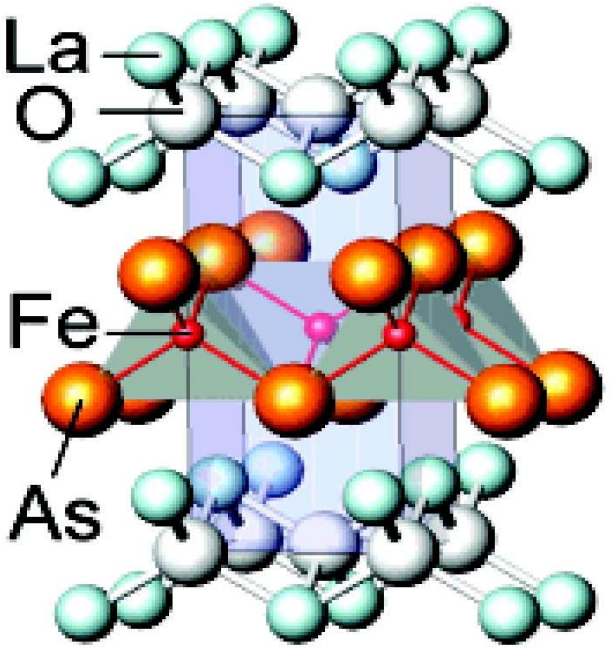




J. Kunes et al, Phys.Rev. B 78, 033109 (2008), V. Mazurenko et al, Phys. Rev. B 81, 125131 (2010)

Novel superconductor LaOFeAs

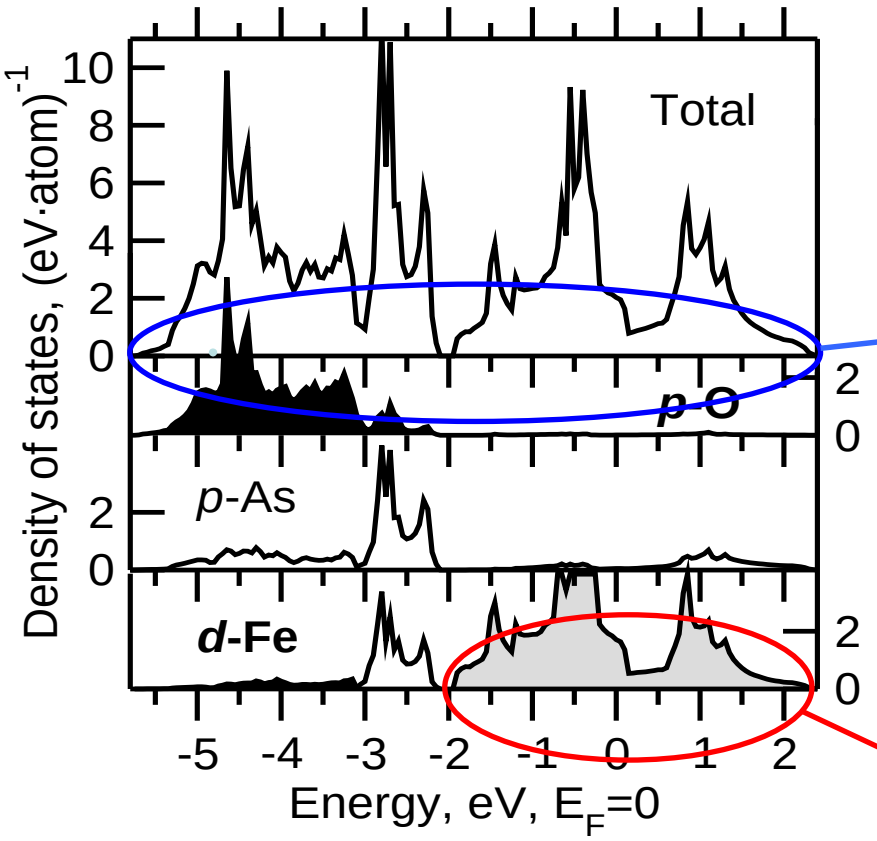


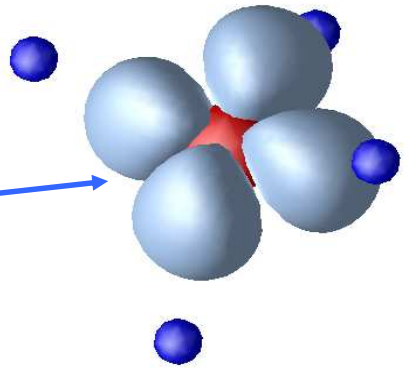


Tc=26K for F content ~11%

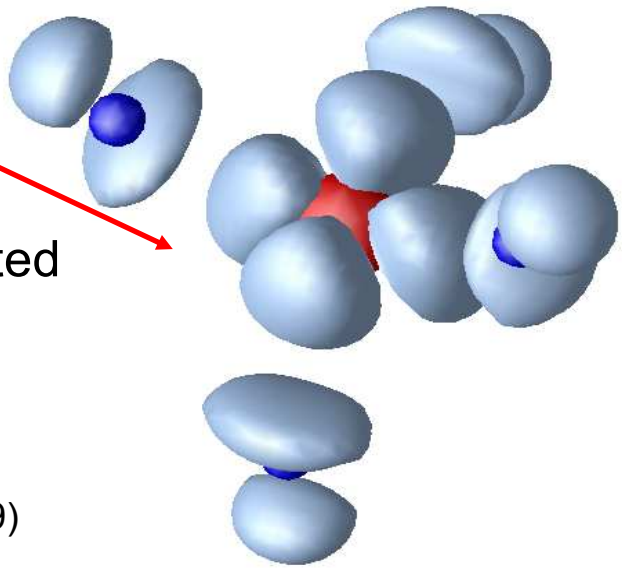
Y. Kanamura *et al.* J. Am. Chem. Soc. 130, 3296 (2008)]

Novel superconductor LaOFeAs





All bands WF
constrain DFT
U=3.5 eV
J=0.8 eV

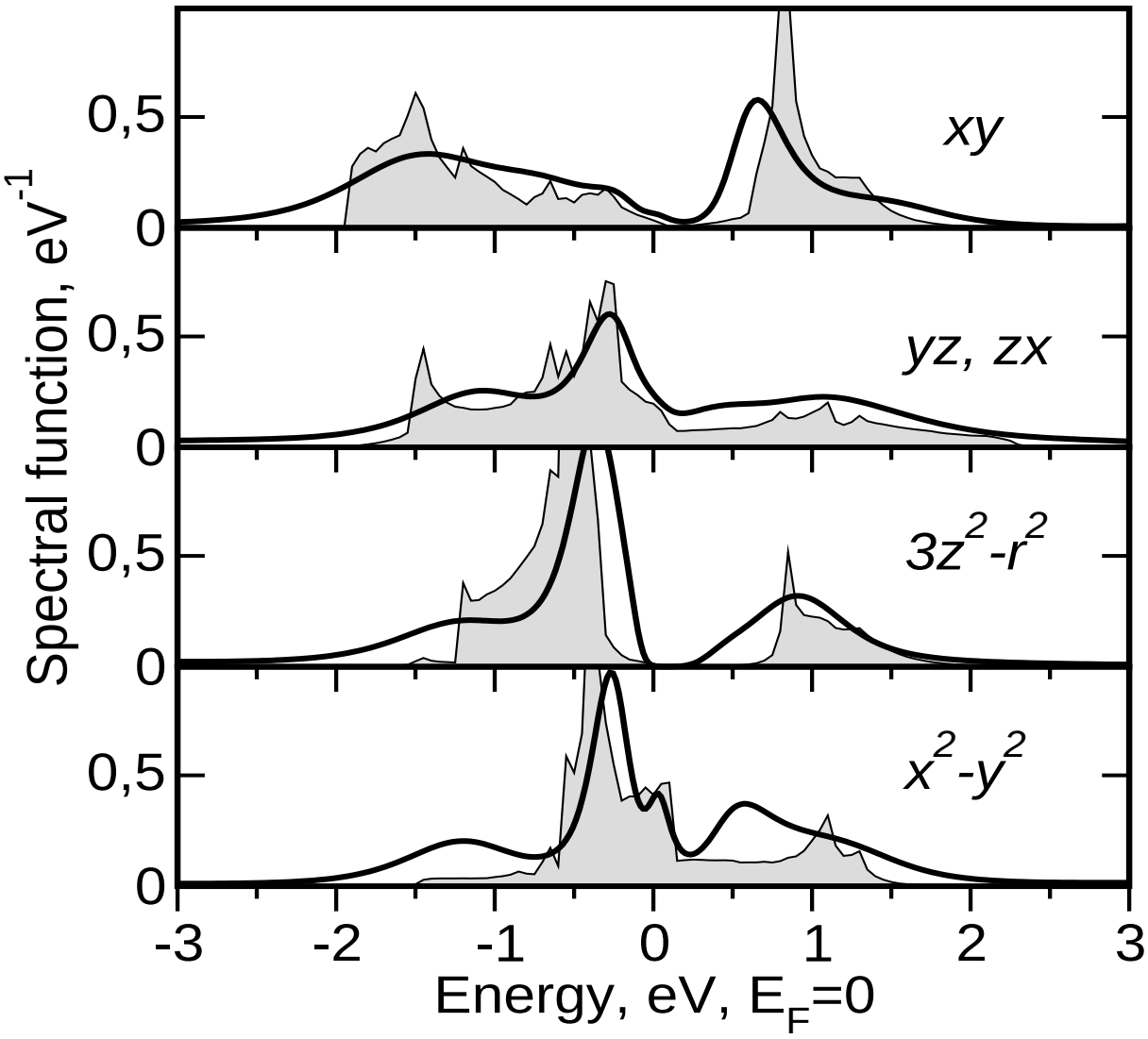


Fe3d band
only WF
constrain DFT
U=0.8 eV
J=0.5 eV

d (x^2-y^2) Wannier functions (WF) calculated
for all bands (O2p,As4p,Fe3d) and
for Fe3d bands only

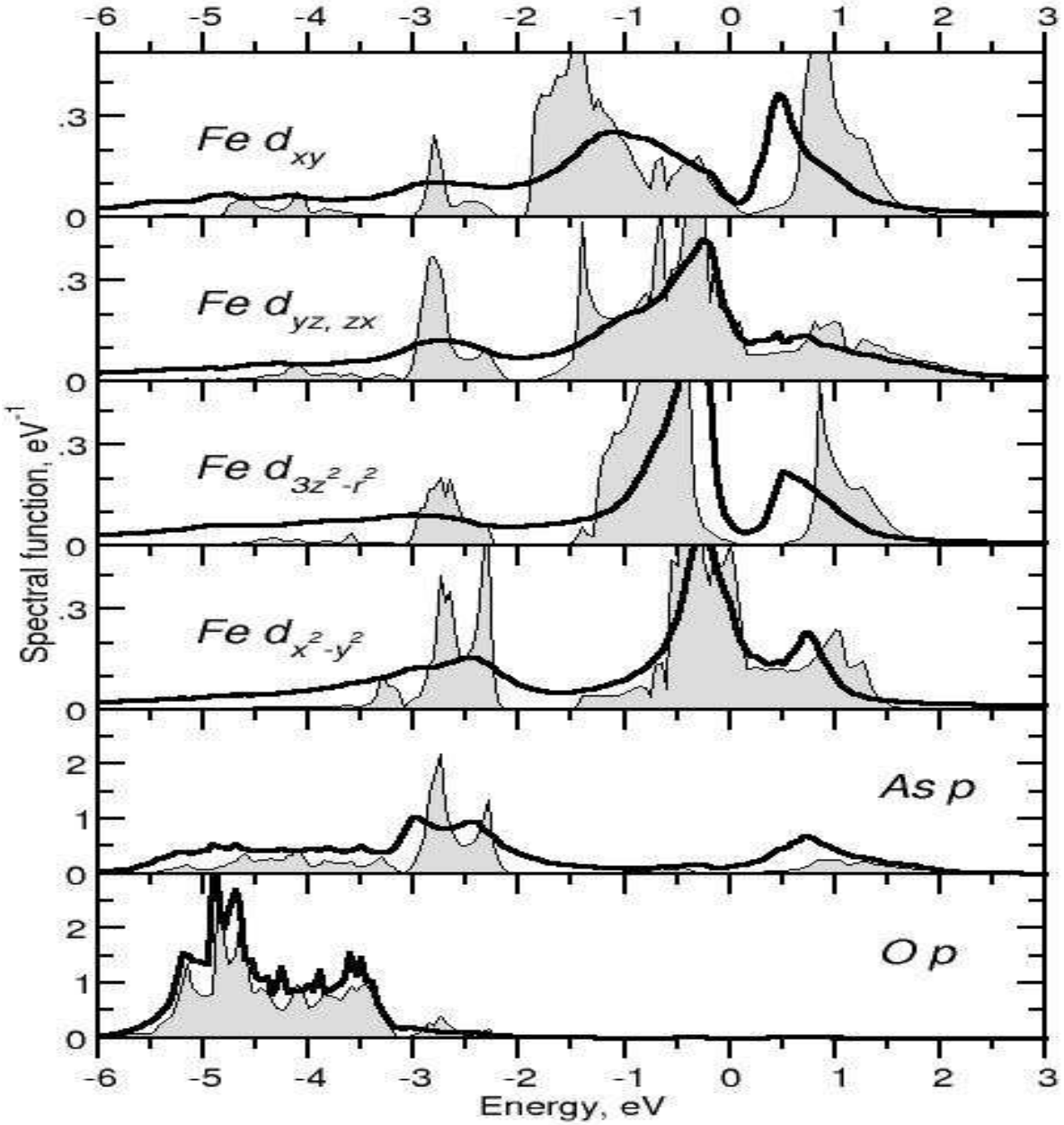
V.Anisimov et al, J. Phys.: Condens. Matter 21, 075602 (2009)

Novel superconductor LaOFeAs



DMFT results for Hamiltonian and Coulomb interaction parameters calculated with Wannier functions
for Fe3d bands only
U=0.8 eV
J=0.5 eV

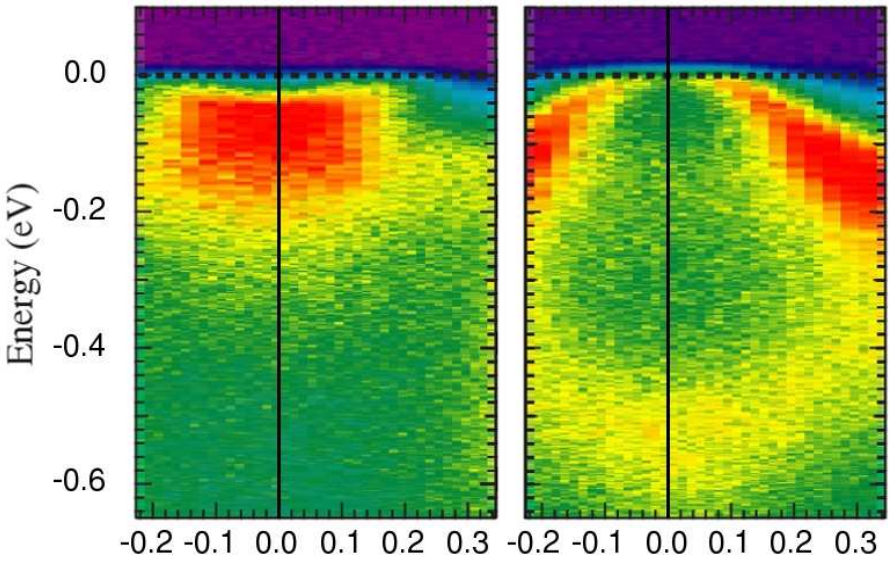
Novel superconductor LaOFeAs



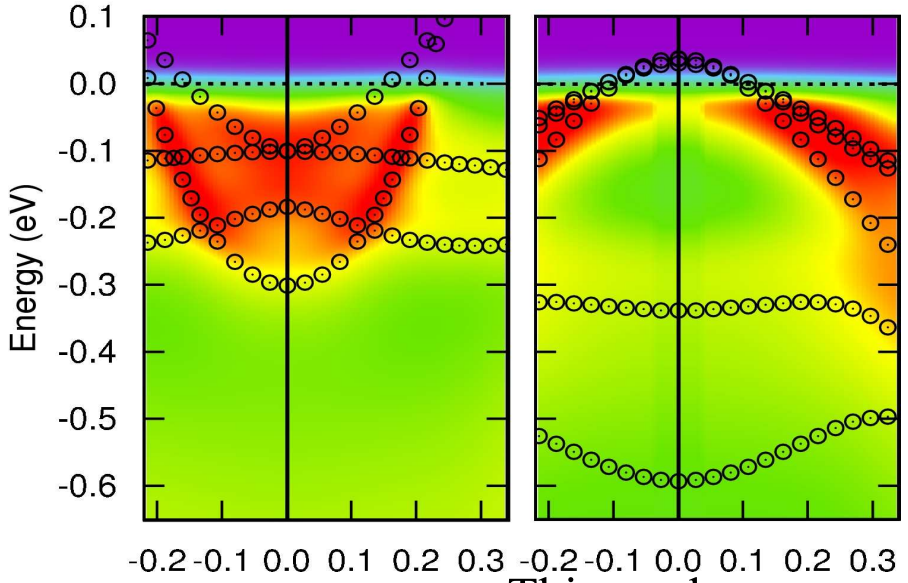
DMFT results for Hamiltonian and Coulomb interaction parameters calculated with Wannier functions
for all bands (O2p,As4p,Fe3d)
U=3.5 eV
J=0.8 eV

Moderately correlated regime with significant renormalization for electronic states on the Fermi level (effective mass m^*~2) but no Hubbard band.

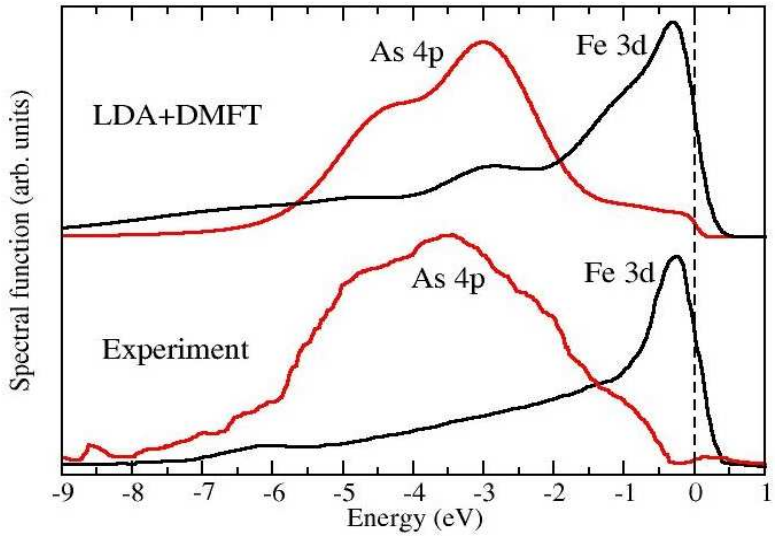
$BaFe_2As_2$: DMFT results vs ARPES experiment



Chang Liu *et al*. (2008)



This work



S. de Jong *et al*. (2009)

- Good agreement with PES and ARPES data

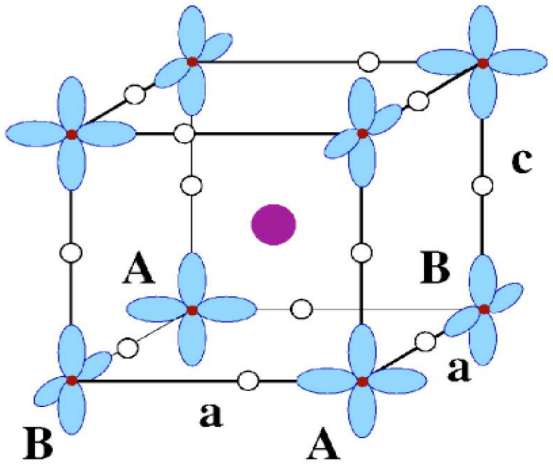
- DMFT bands $\varepsilon_{DMFT}(k)$ are very well represented by scaling

$$\varepsilon_{DMFT}(k)=\varepsilon_{LDA}(k)/(m^*/m)$$

Correlations and lattice distortion: $KCuF_3$

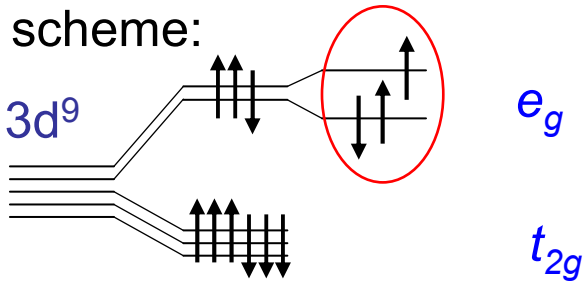
$KCuF_3$: a prototype e_g ($3d^9$) Jahn-Teller system

Crystal structure and Orbital order (OO):



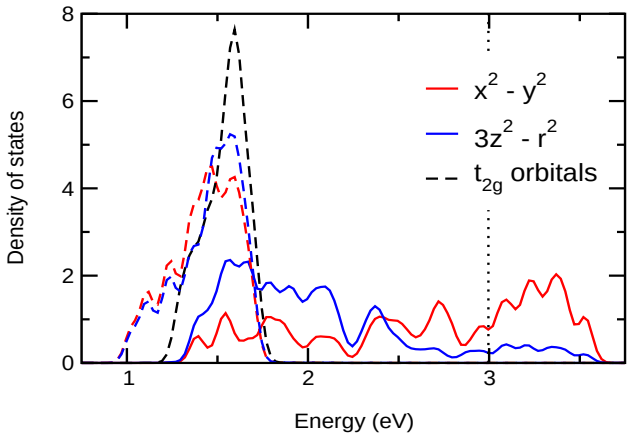
- pseudo cubic perovskite I4/mcm
- cooperative JT distortion below 1000 K
- *Neel* temperature ~38 K
- $d_{x^2-y^2}$ hole antiferroorbital ordering

d-level scheme:



free ion cubic tetragonal (c/a < 1)

GGA (Cu *3d*) density of state:



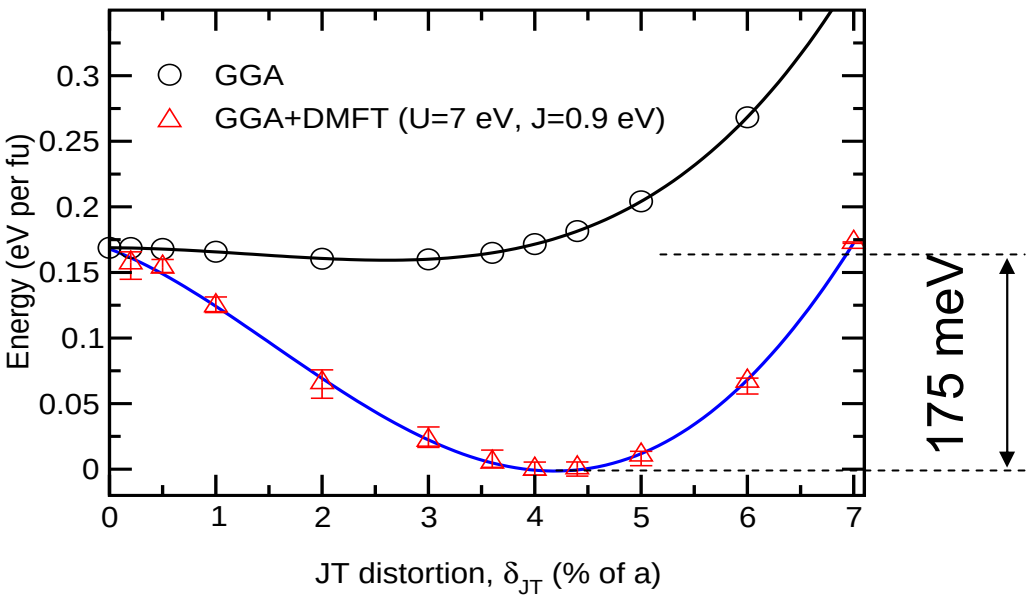
metallic solution -> inconsistent with exp

Correlations and lattice distortion: $KCuF_3$

$KCuF_3$: GGA+DMFT results

U = 7.0 eV, J = 0.9 eV

Total energy:



→ structural relaxation due to electronic correlations !

Leonov *et al.,* Phys. Rev. Lett. 101, 096405 (2008)

GGA:

- *metallic* solution
- total energy almost const for JT distortion < 4 %
- no JT distortion (orbital order) for T > 100 K !

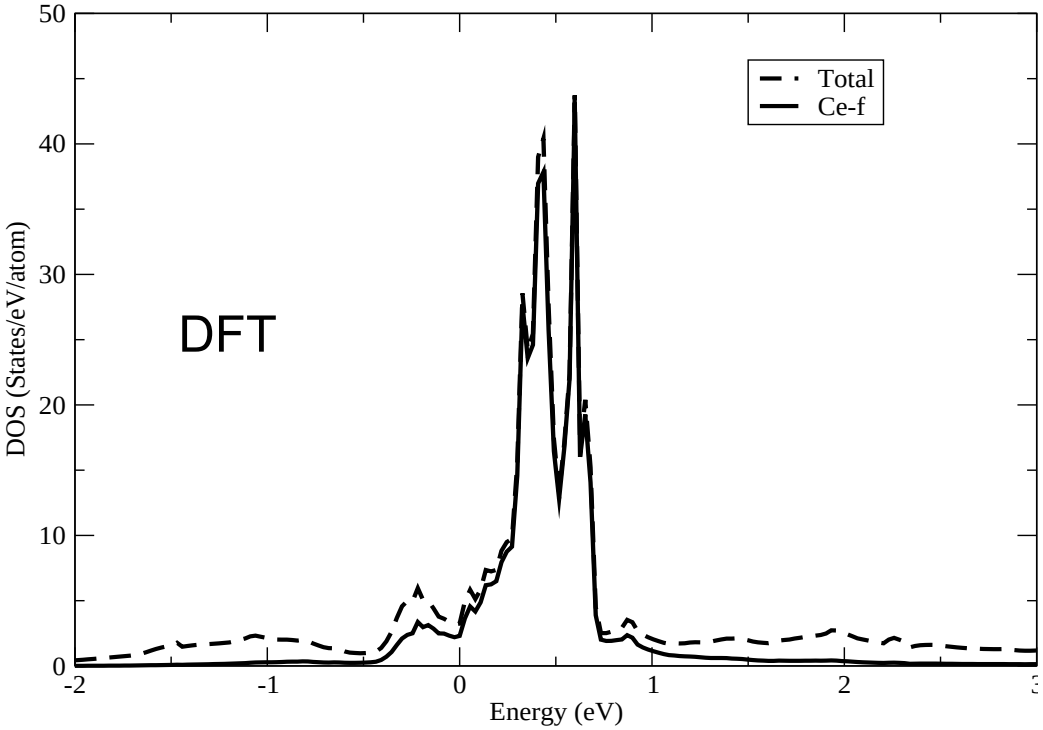
→ inconsistent with experiment

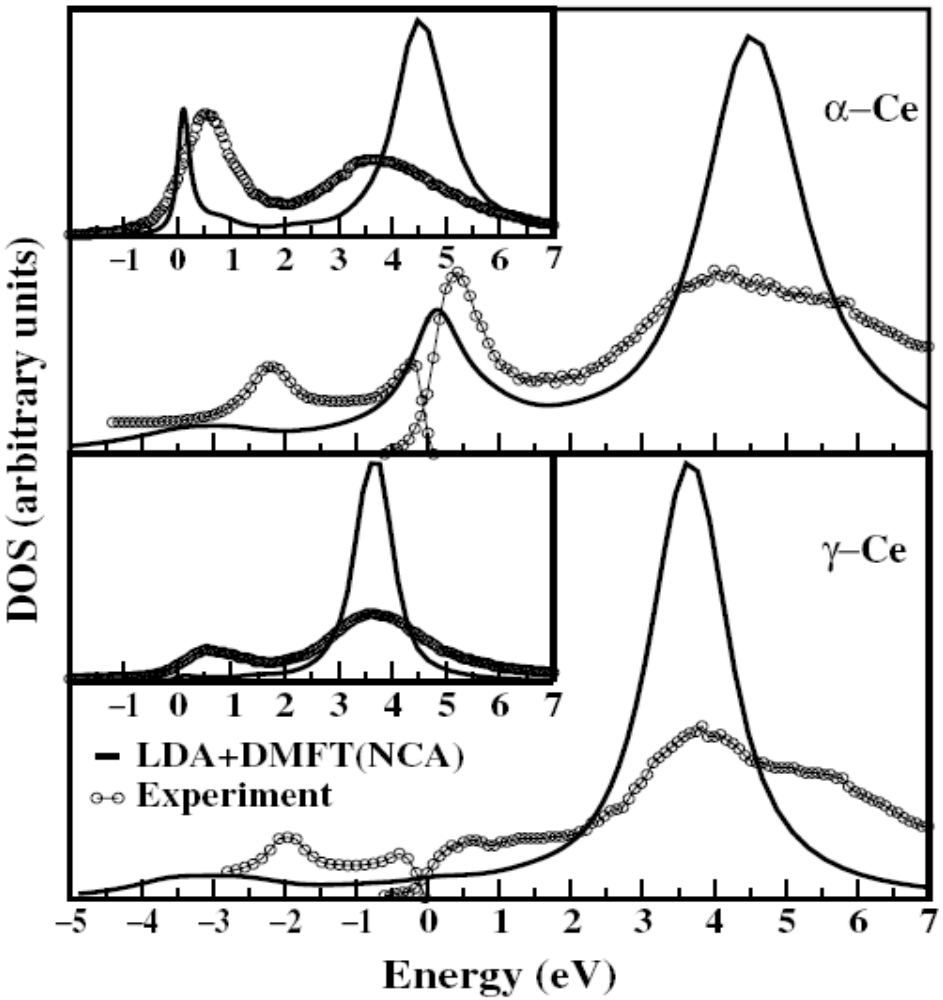
GGA+DMFT:

- *paramagnetic* insulator
- energy gain of ~ 175 meV
- antiferro-orbital order
- optimal JT distortion at 4.2 %
- JT distortion persists up to 1000 K (melting tem-re)

→ in good agreement with exp

f-electrons localization in Ce





Ce $\alpha - \gamma$ transition with 15% volume change.
Kondo temperature T_K 1000K (α) , 30K (γ)

M.B. Zoelfl et al, Phys. Rev. Lett. 87, 276403 (2001)

Conclusions

- **Dynamical mean-field theory (DMFT) is a powerful tool to study correlation effects**
- ***Ab-initio* definition of correlated orbitals and interaction strength (U) between them based on Wannier functions formalism results in "first-principles" DFT+DMFT calculations scheme**
- **DFT+DMFT method was successful in describing paramagnetic Mott insulators, correlated metals, charge transfer insulators, metal-insulator transitions with pressure and temperature, cooperative Jahn-Teller lattice distortions**