Electronic structure of strongly correlated materials
Part III

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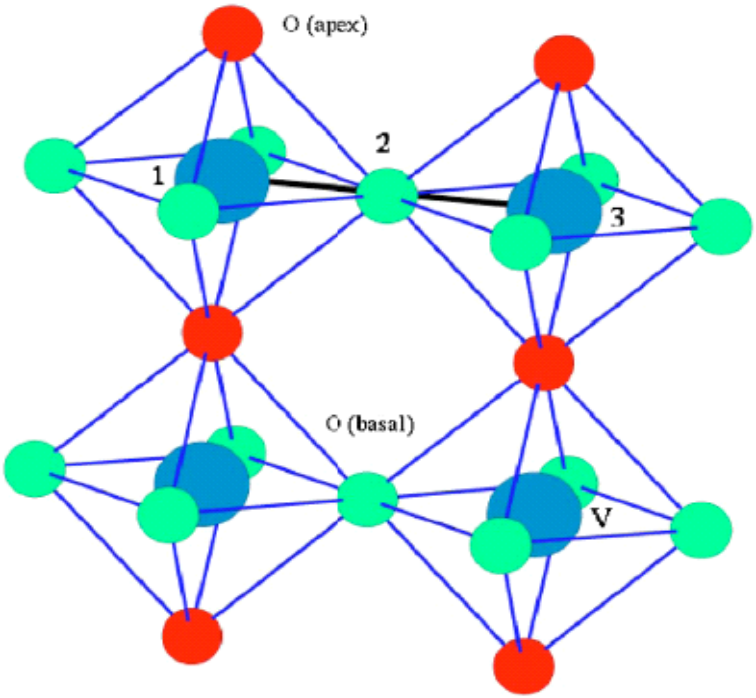
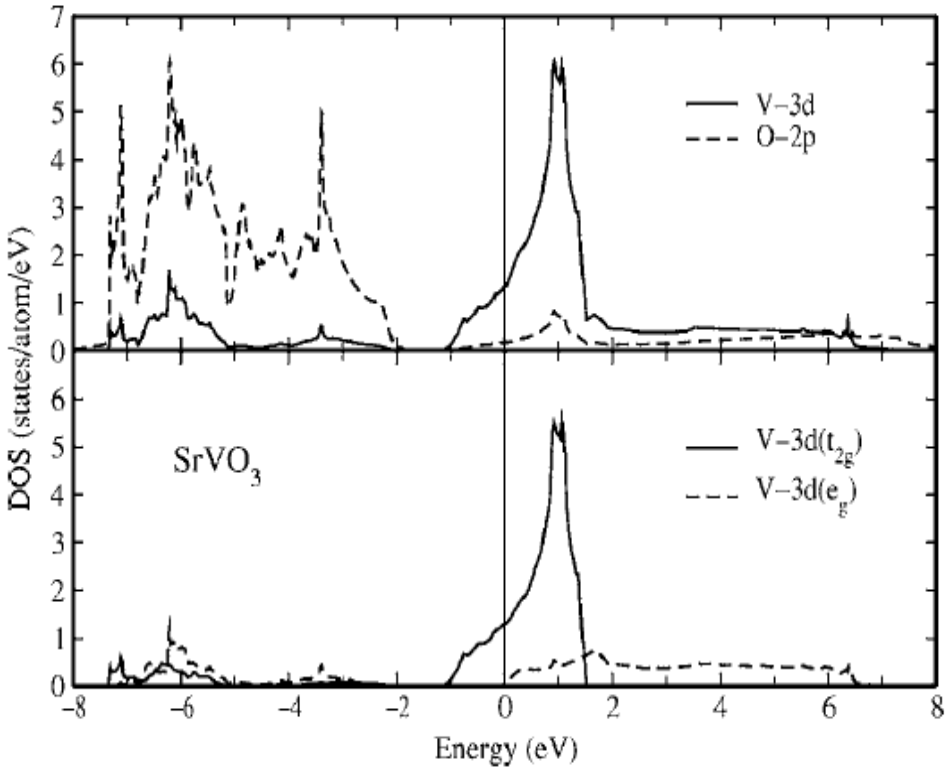
Results of DFT+DMFT calculations:

Strongly correlated metal Sr(Ca)VO_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 superconductor LaOFeAs
Jahn-Teller distortions in $KCuF_3$
f-electrons localization in Ce

Strongly correlated metal $SrVO_3$



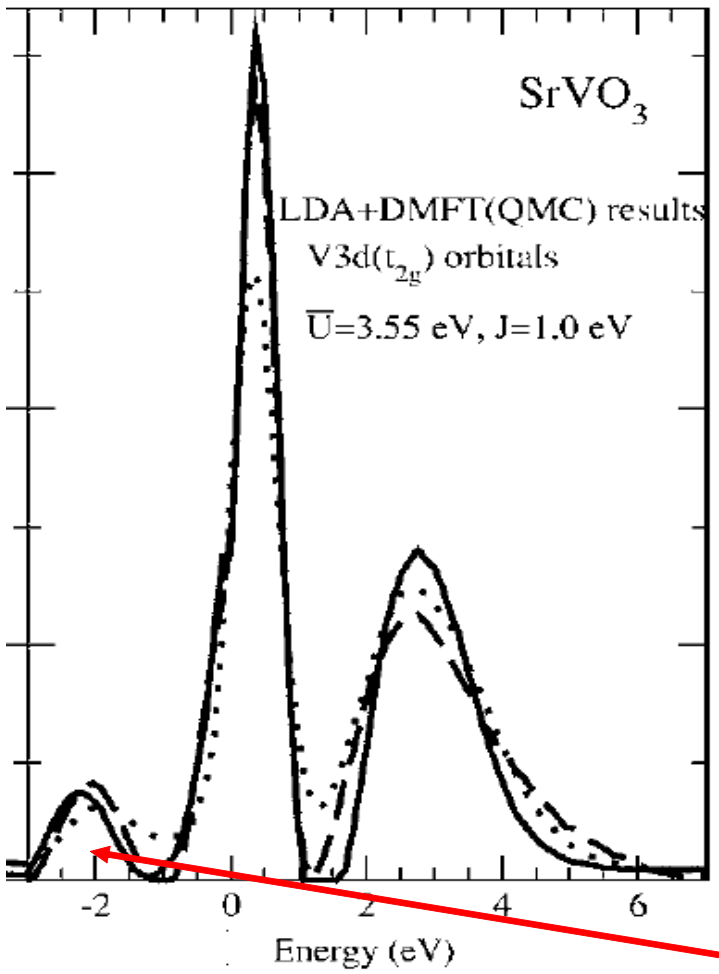


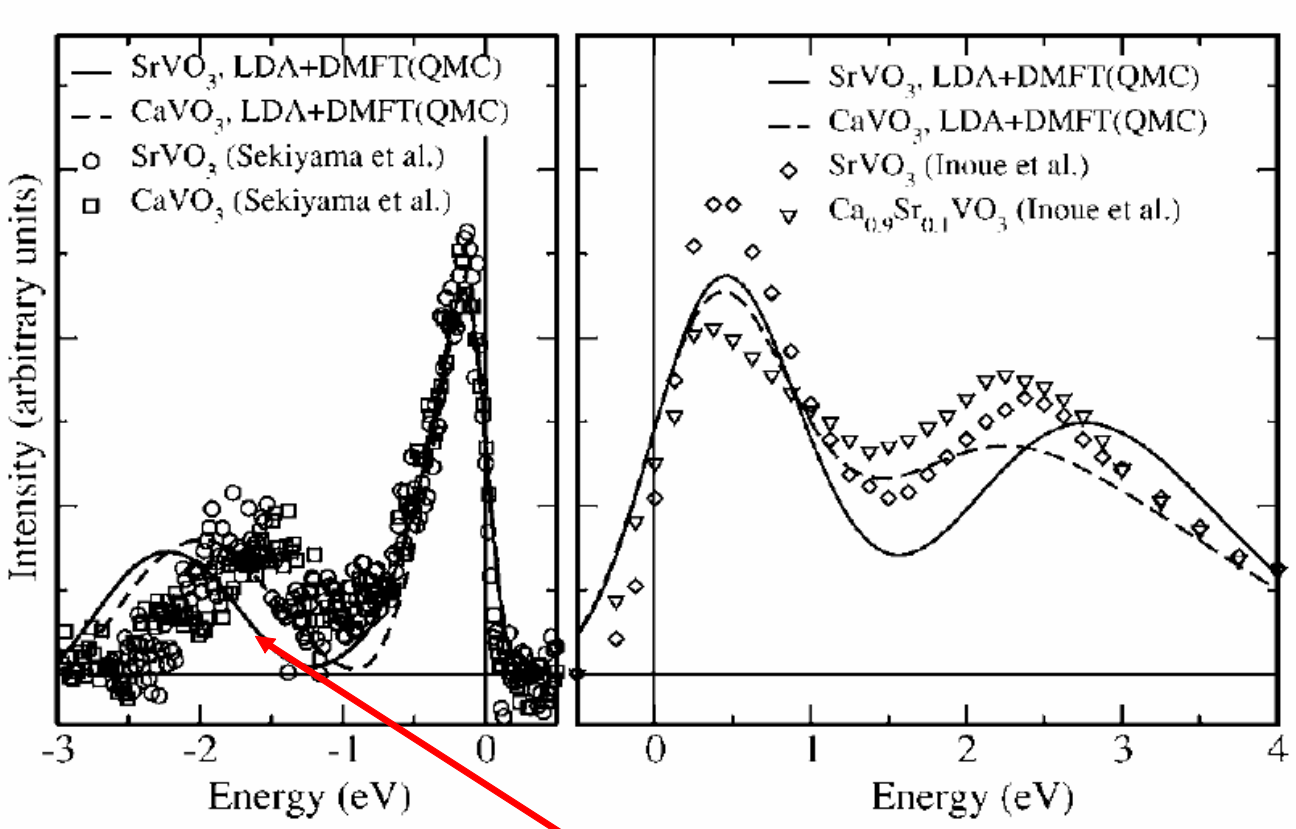
V^{+4} (d^1) ion in cubic perovskite crystal structure

One electron in partially filled t_{2g} band

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

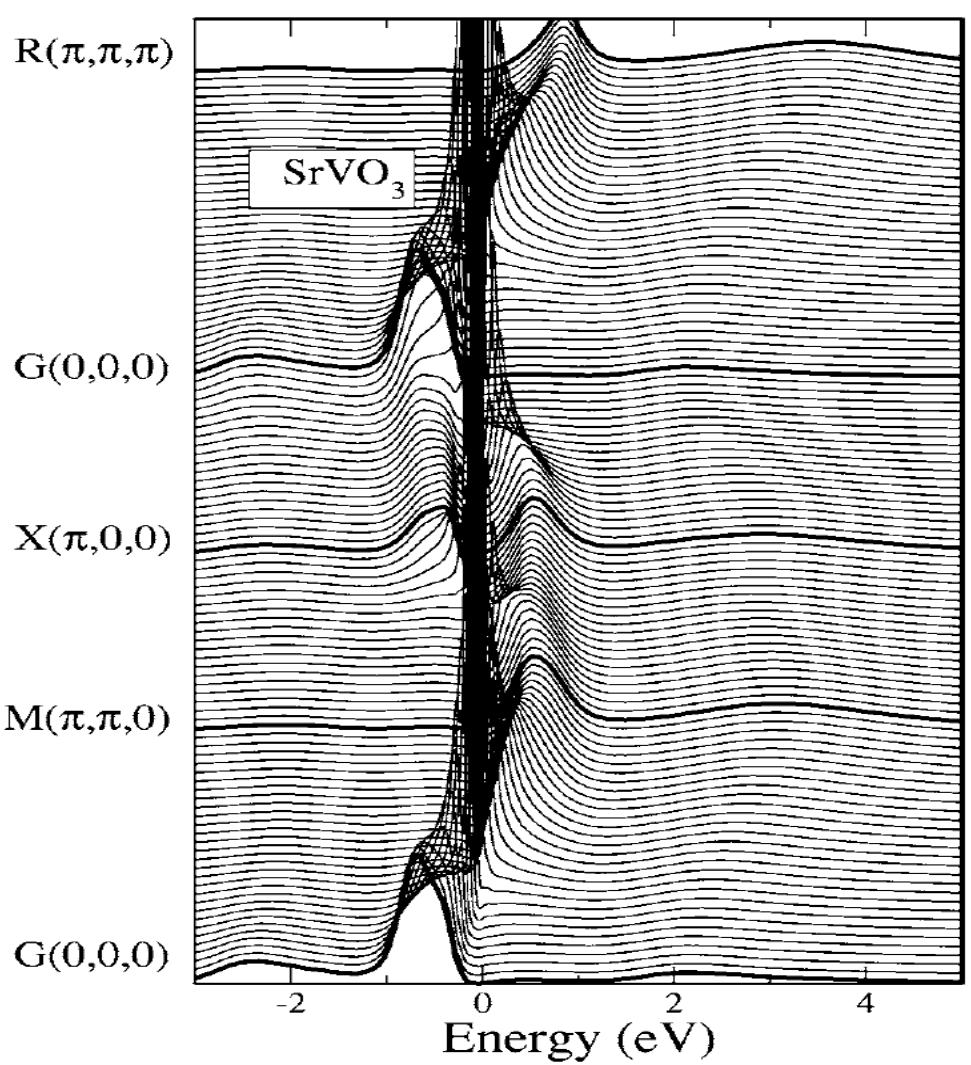
Strongly correlated metal $SrVO_3$

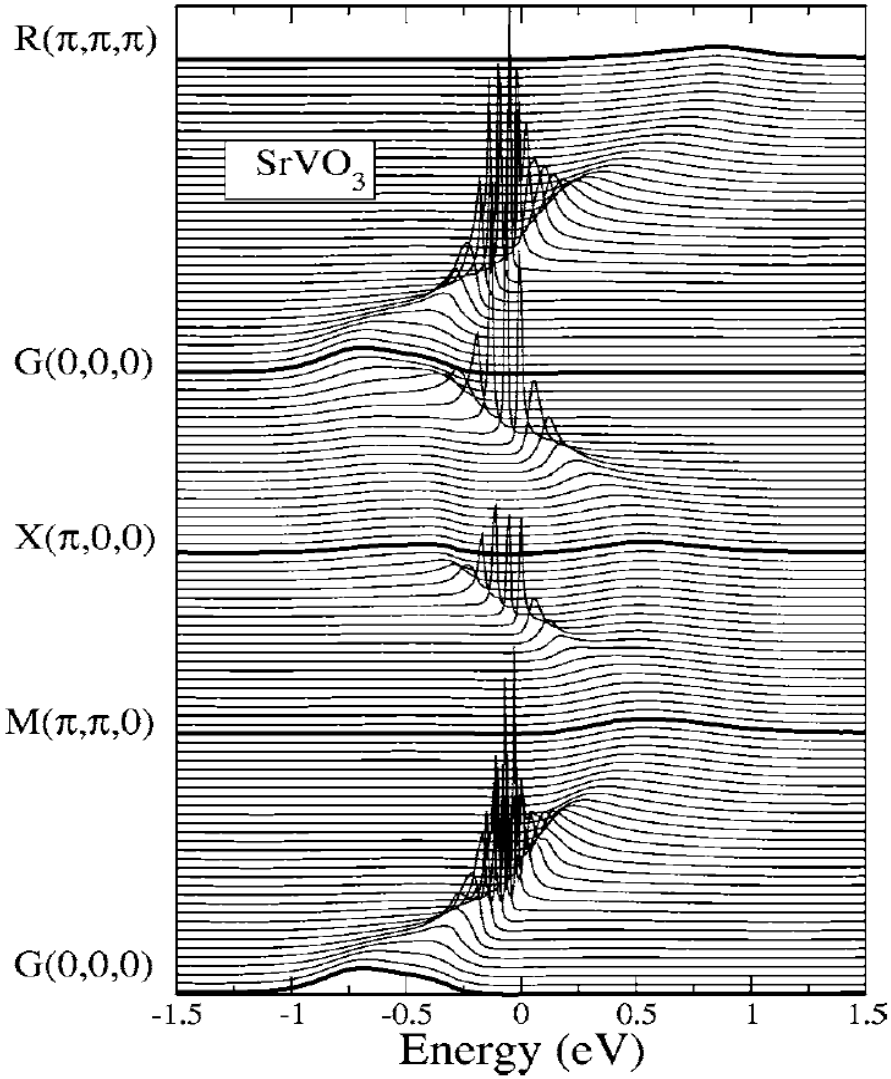




Strongly correlated metal with pronounced Lower Hubbard band (LHB)

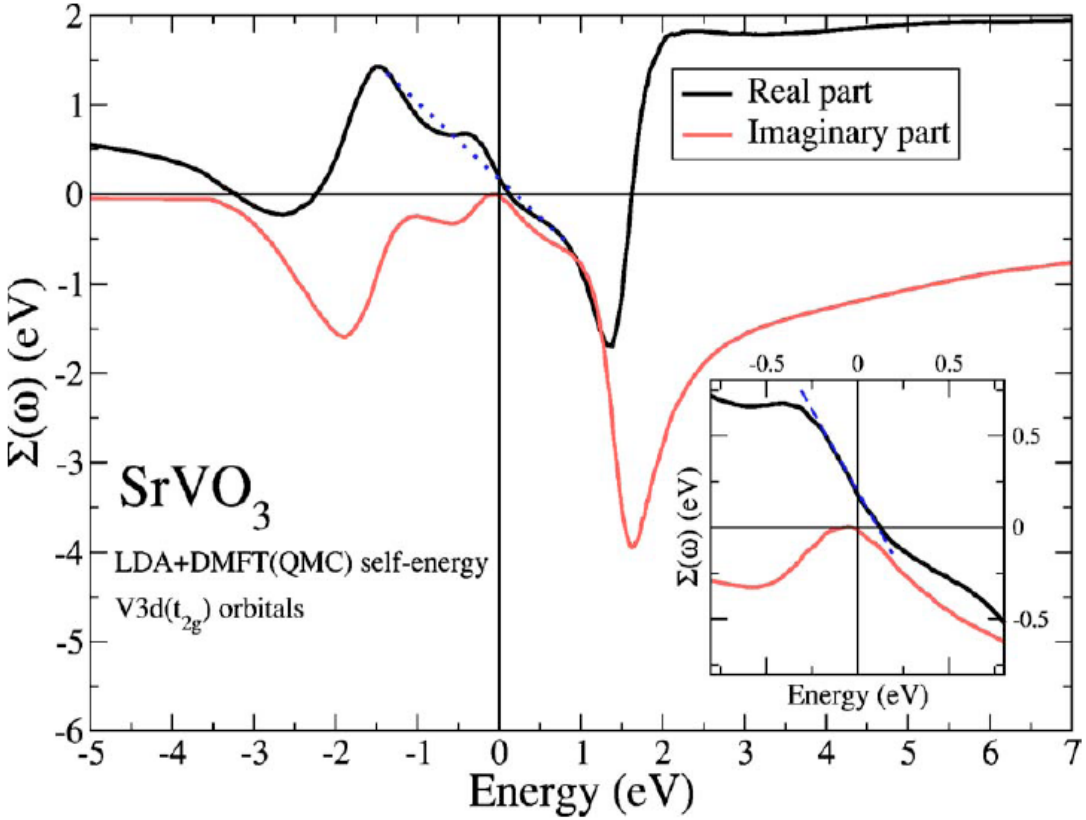
Strongly correlated metal $SrVO_3$

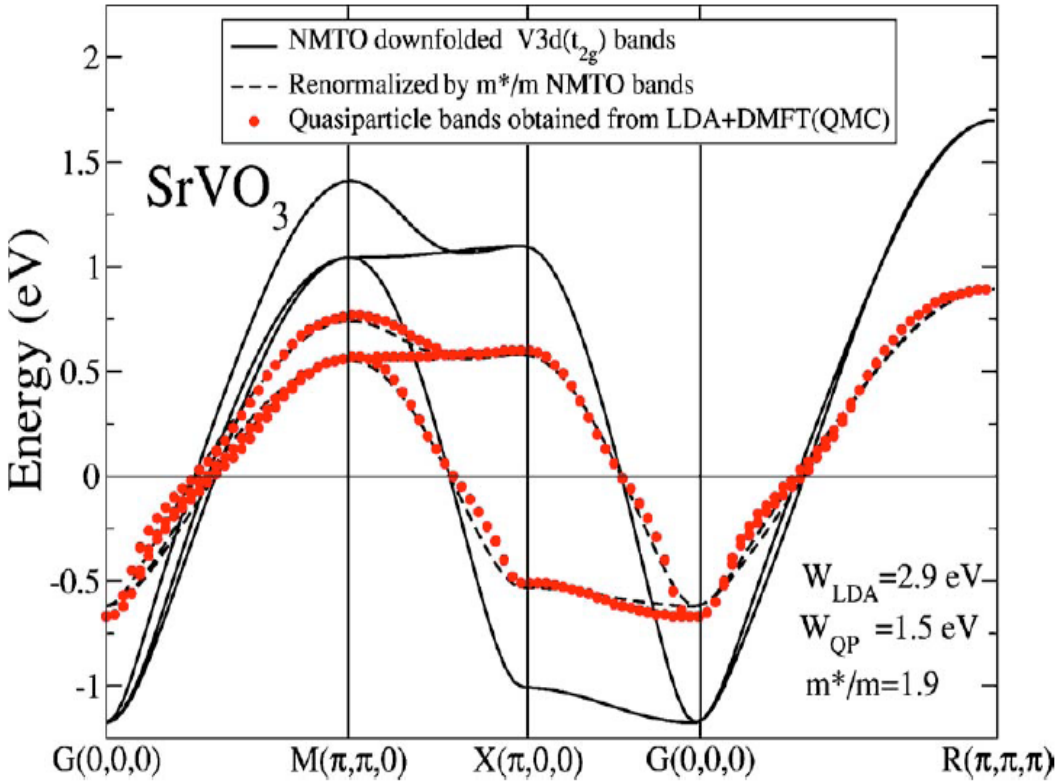




$$\text{Spectral function } A(k,\omega) = -\frac{1}{\pi}\,\mathrm{Im\ Tr}\left[\omega - \Sigma(\omega) - H_0(k)\right]^{-1}$$

Strongly correlated metal $SrVO_3$





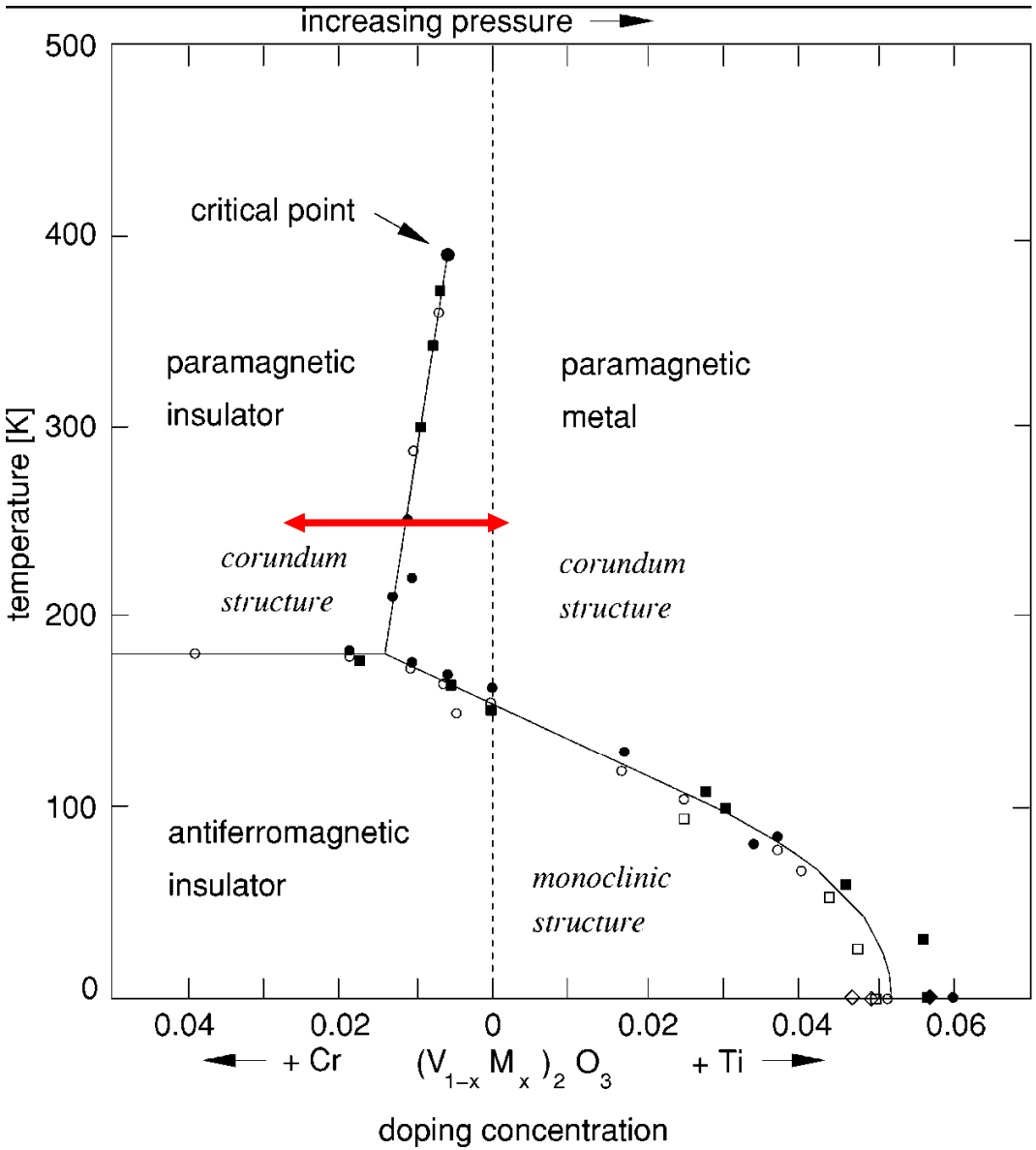
Effective electron mass

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

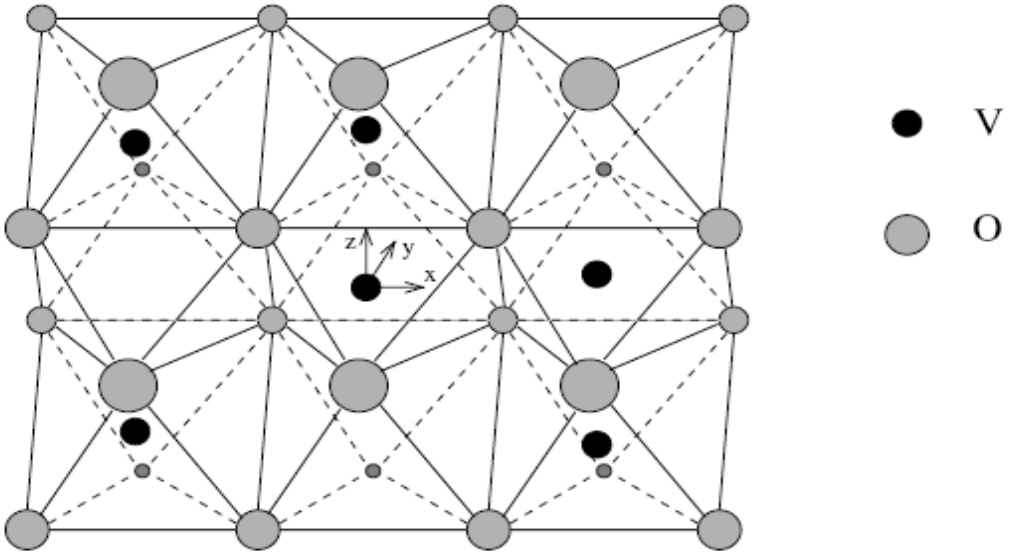
Bands narrowing

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

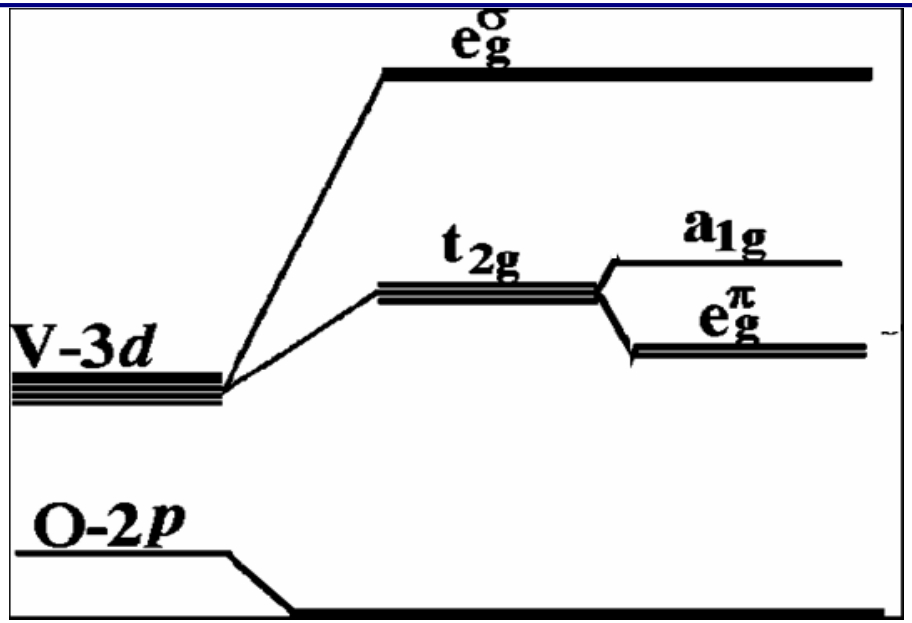
Mott insulator V_2O_3

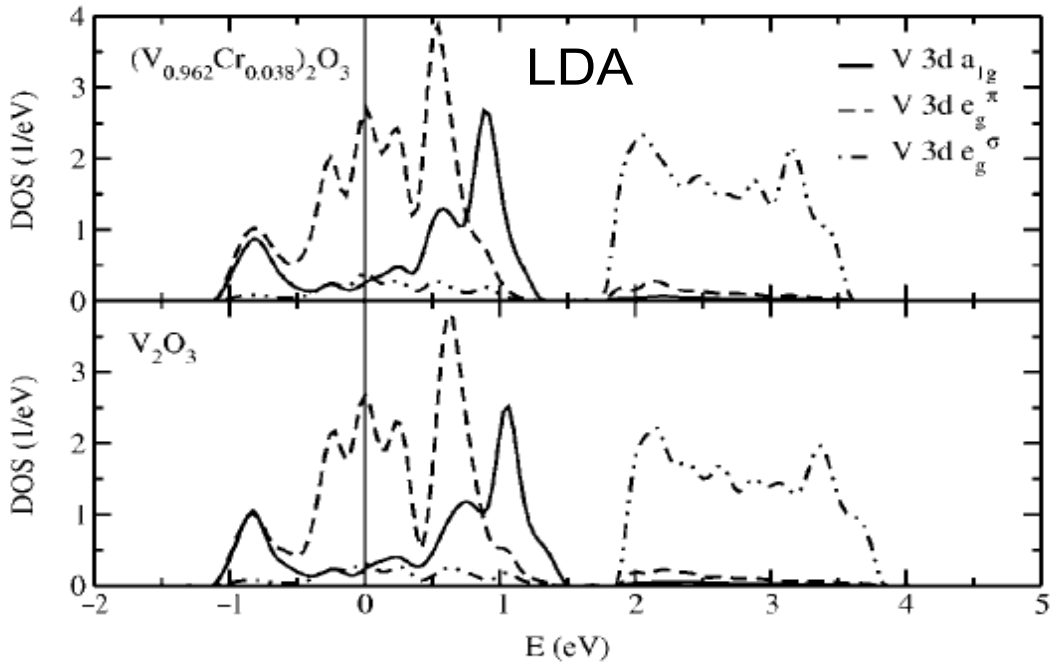


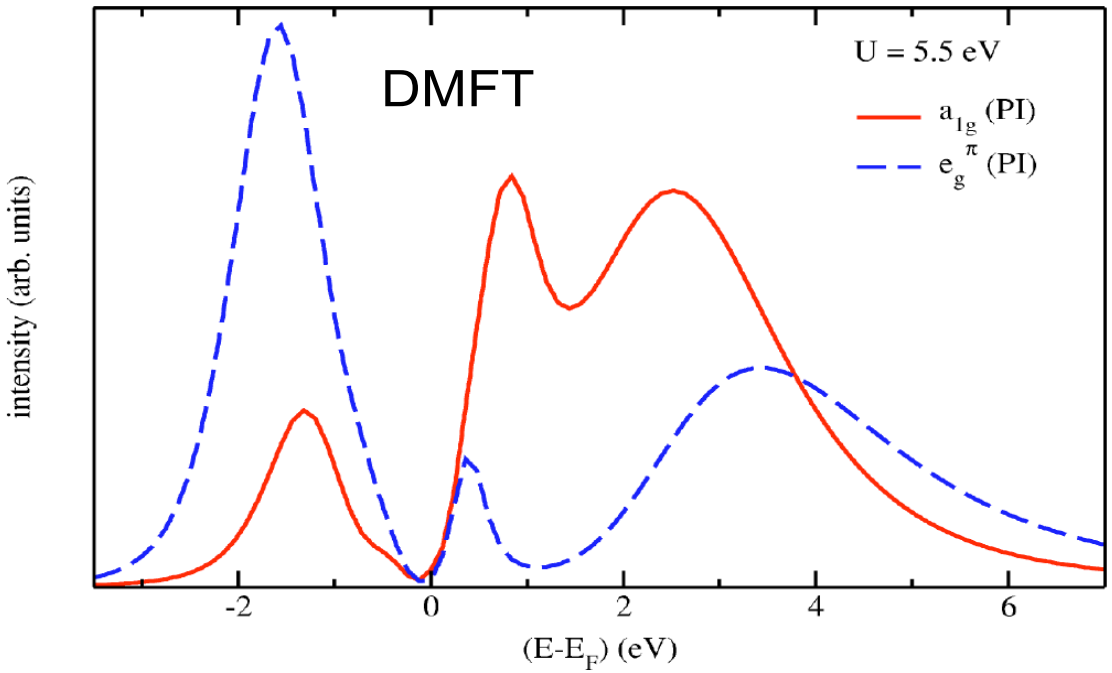
Prototypical Mott insulator.
Iso-structural paramagnetic metal to paramagnetic insulator transition with small volume change due to chemical negative pressure.



Mott insulator V_2O_3

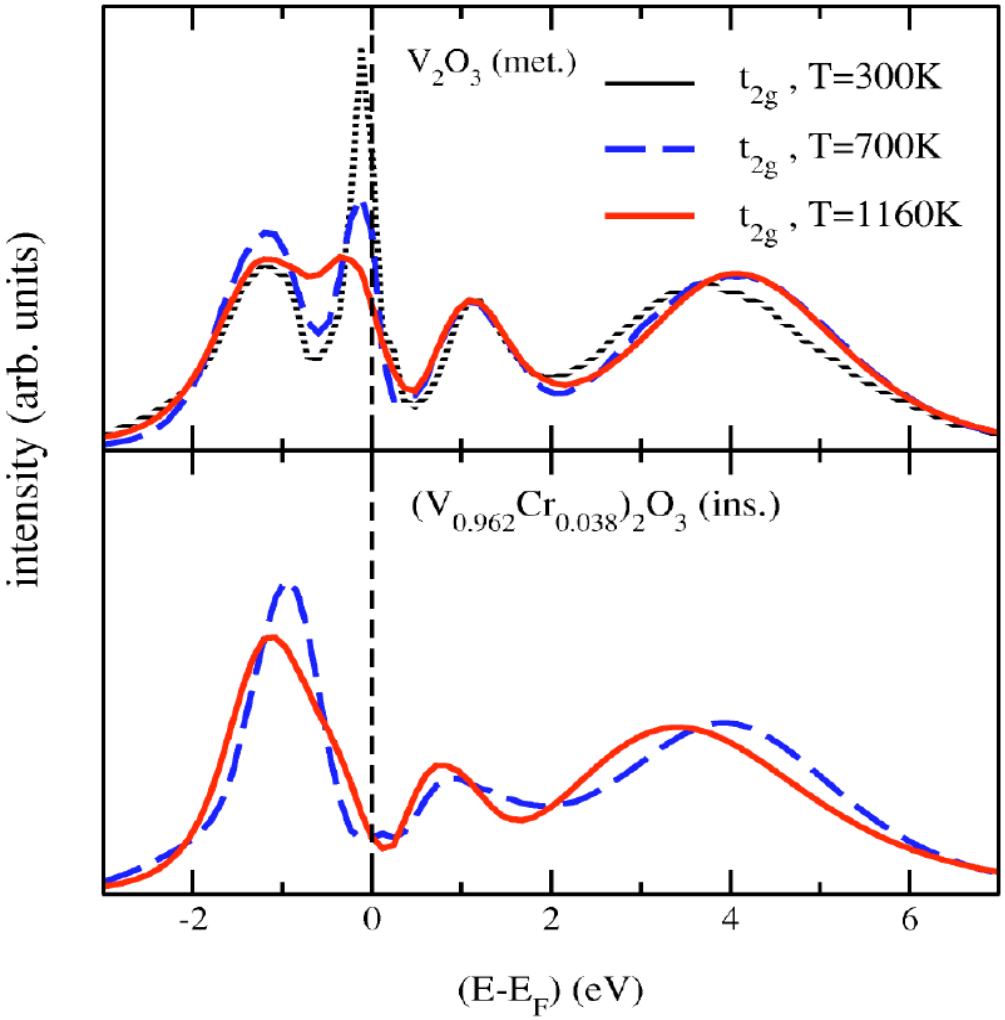


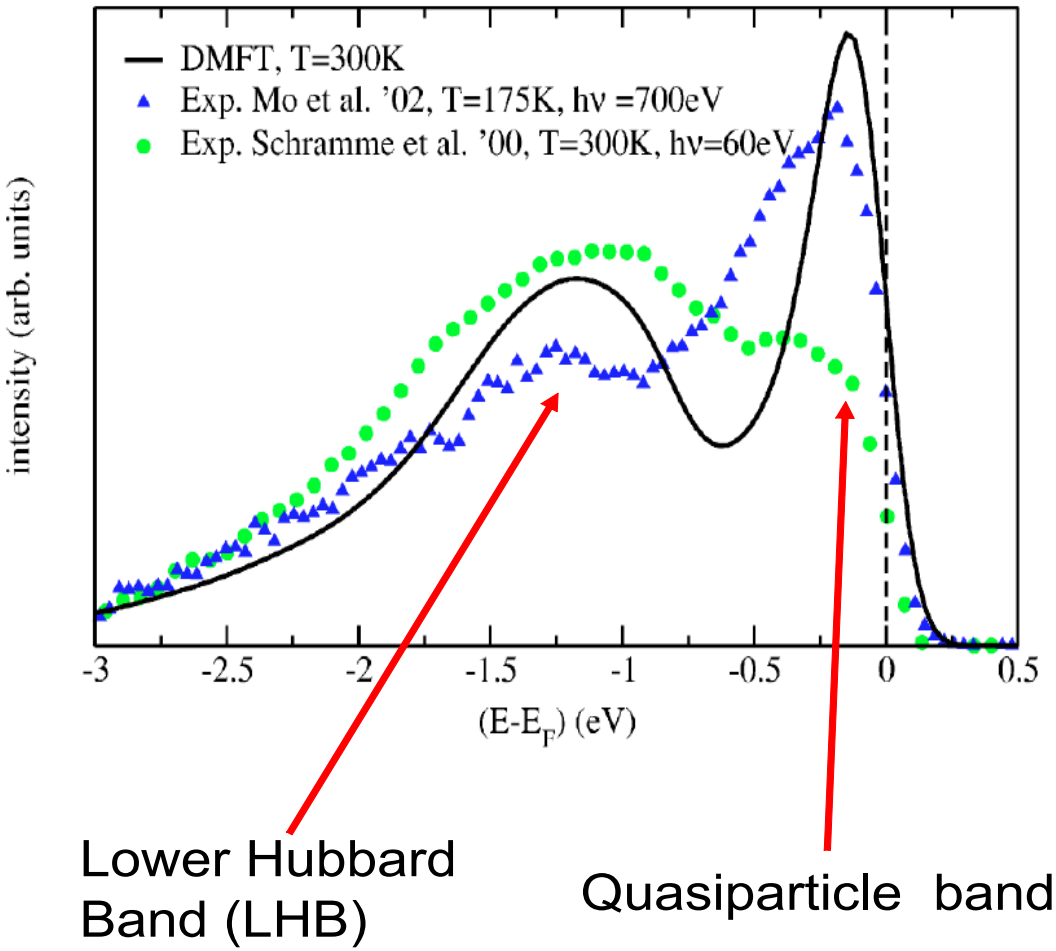




V^{+3} (d^2) ion in trigonal symmetry corundum crystal structure.
Two electrons in t_{2g} band (W~2.5 eV).
Trigonal crystal field splitting ~0.3 eV leads to orbital polarization in DMFT

Mott insulator V_2O_3





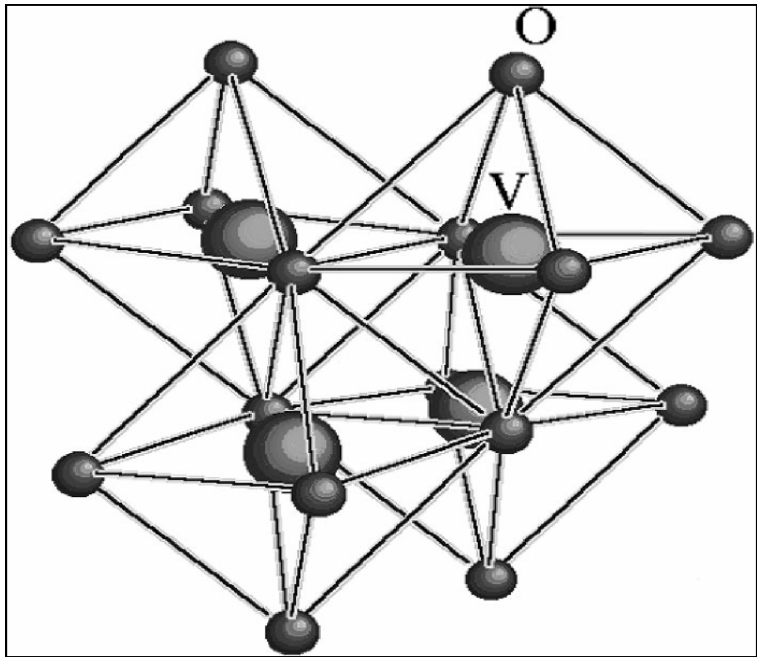
Lower Hubbard Band (LHB)

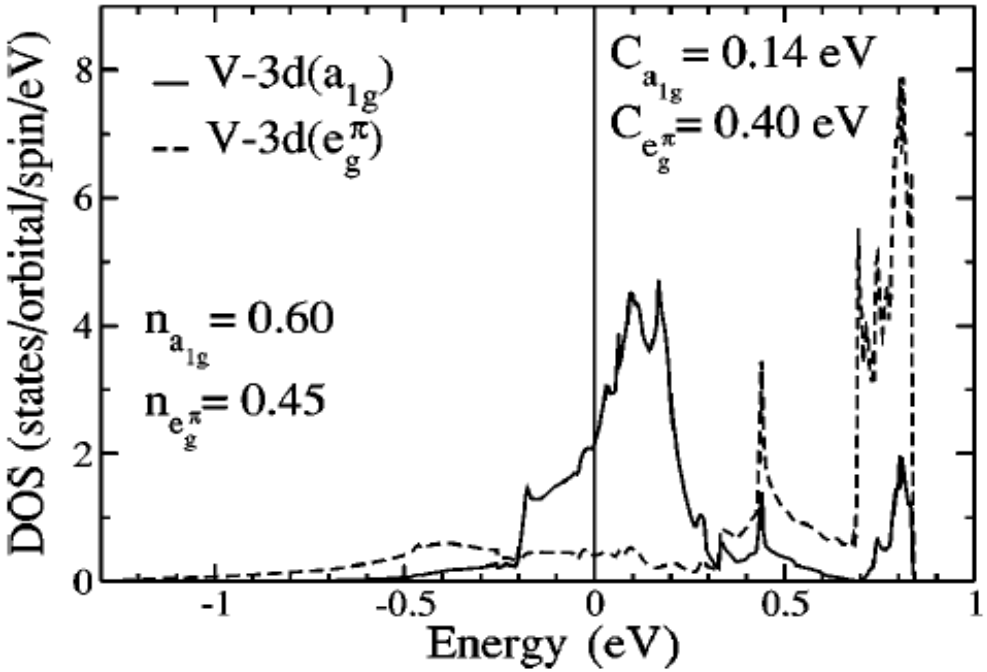
Quasiparticle band

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

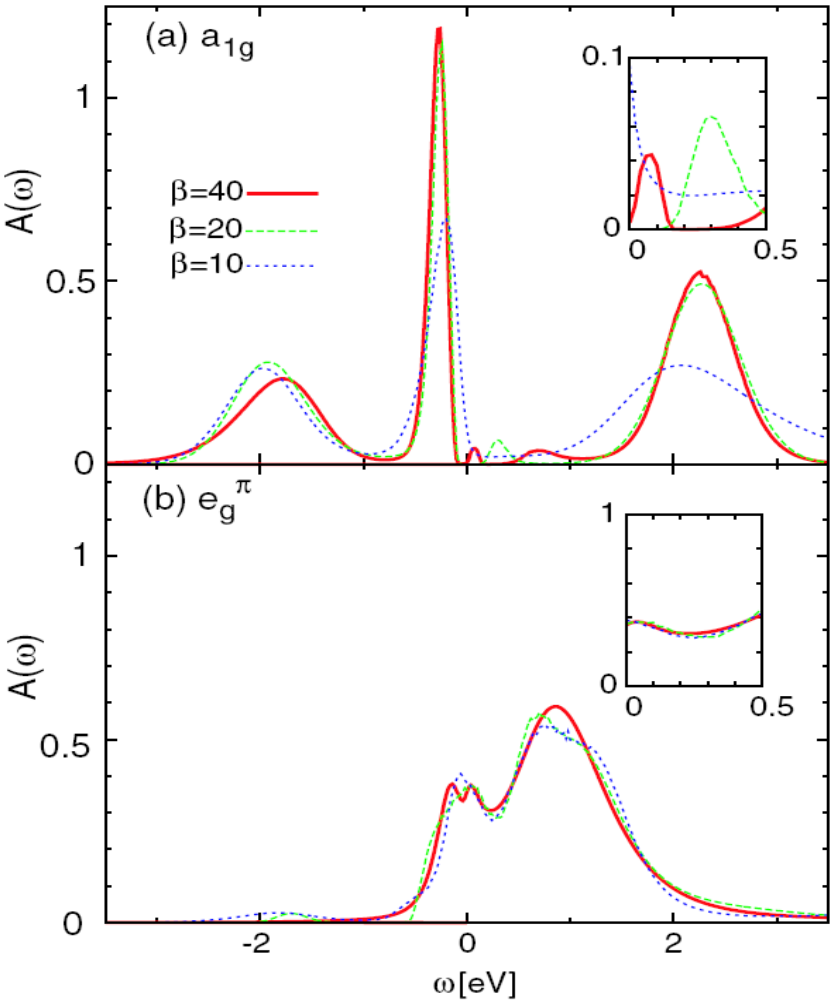


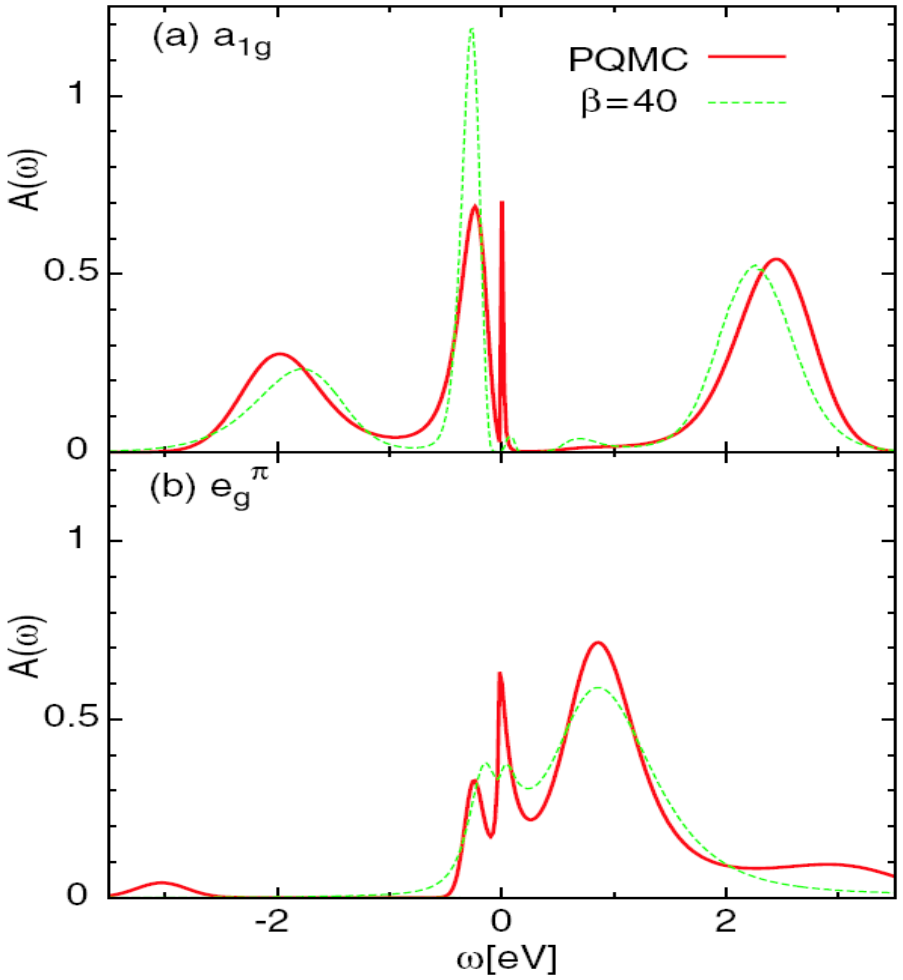


Heavy-fermions without f-electrons:
linear specific heat coefficient
γ=420 mJ/molK^2,
effective electron mass m^*/m =25
below T_K ~28 K

Cubic spinel crystal structure
with local trigonal symmetry

Heavy fermions material LiV_2O_4

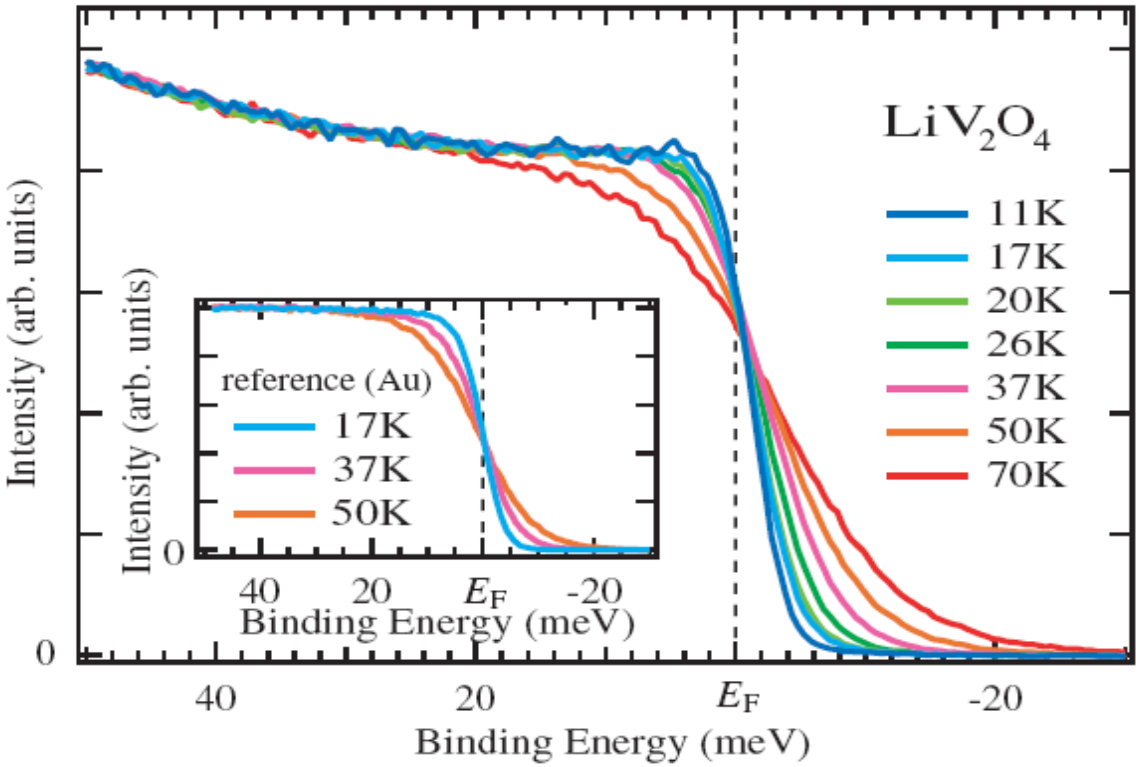


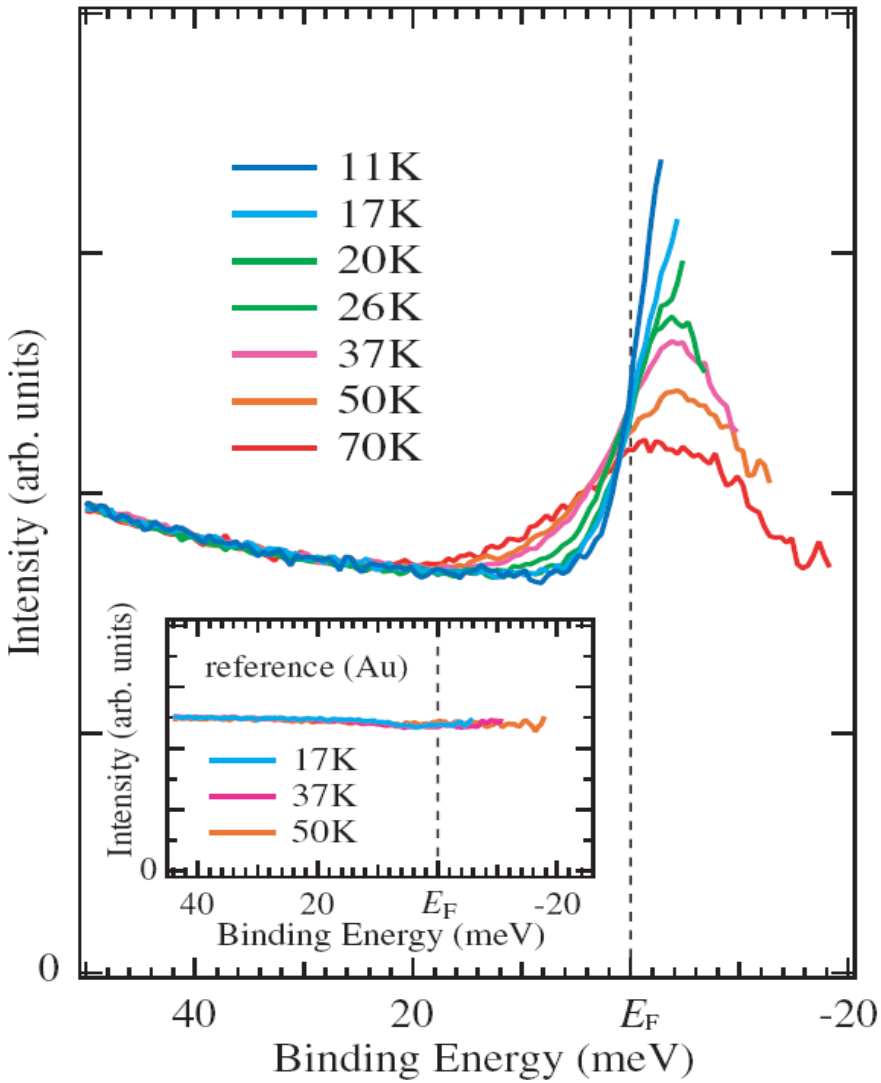


Sharp quasiparticle peak above the Fermi for T=0 limit (PQMC)

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

Heavy fermions material LiV_2O_4

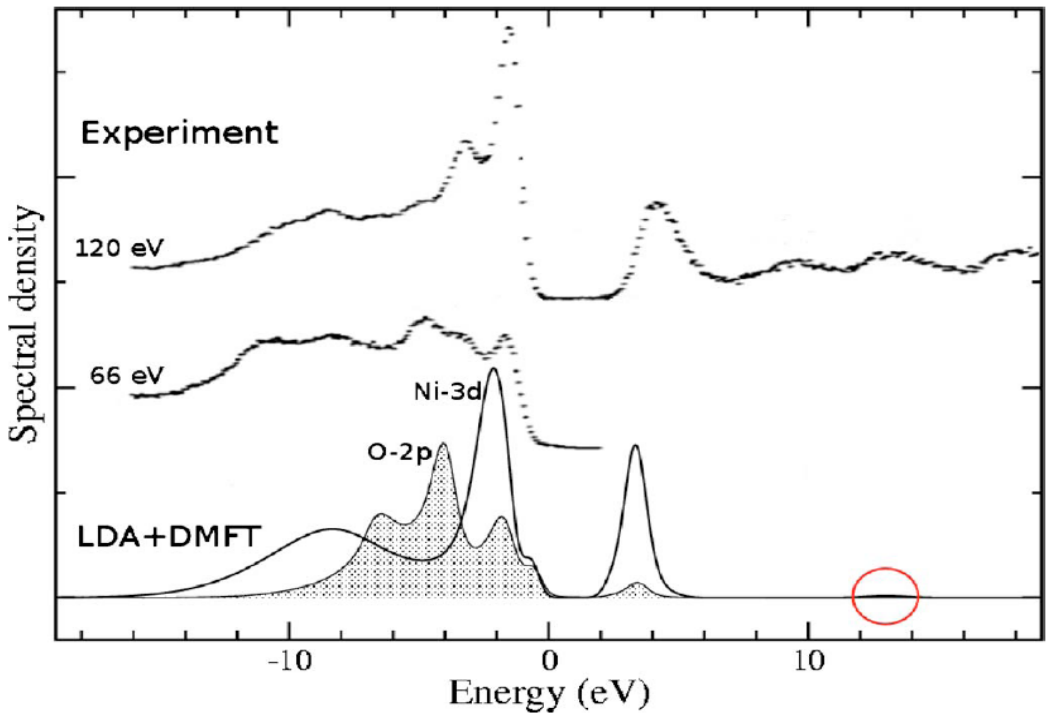


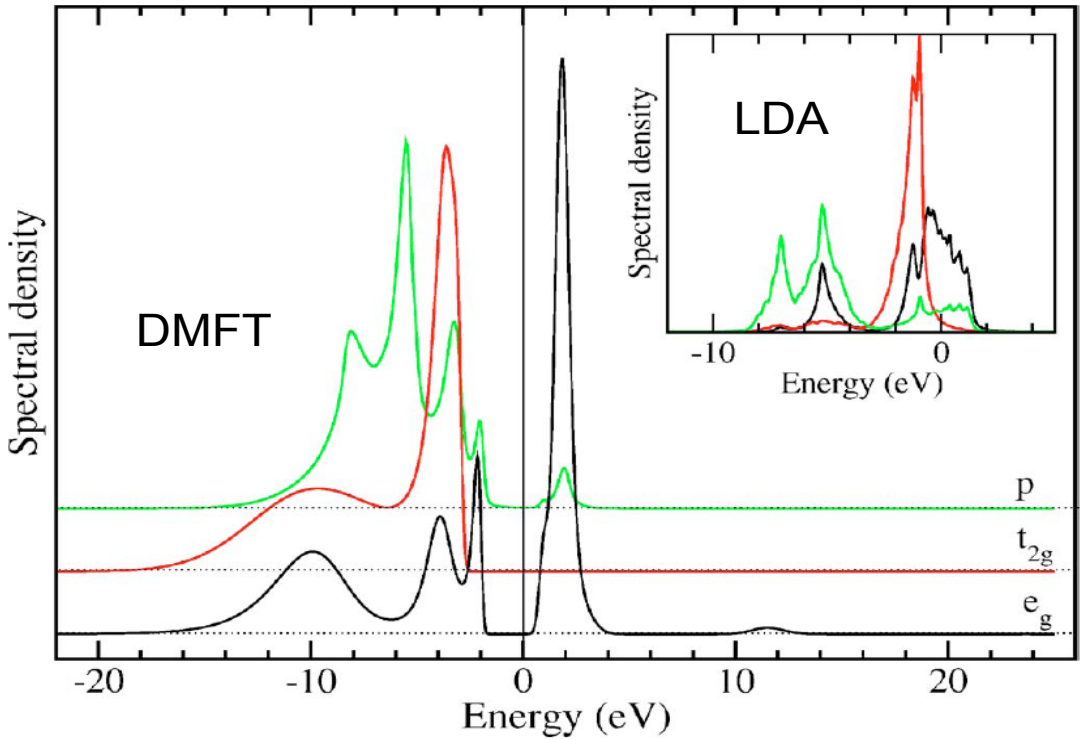


XPS => Quasiparticle peak 10 meV width
4 meV above the Fermi

A. Shimoyamada, et al, Phys. Rev. Lett. 96, 026403 (2006)

Charge transfer insulator NiO

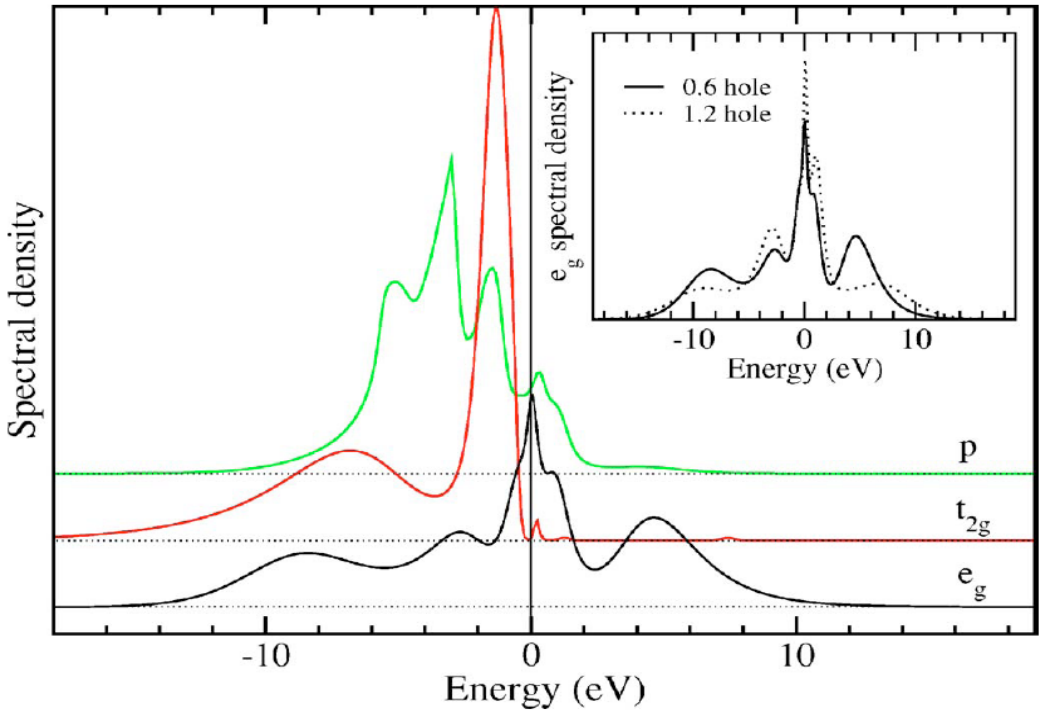


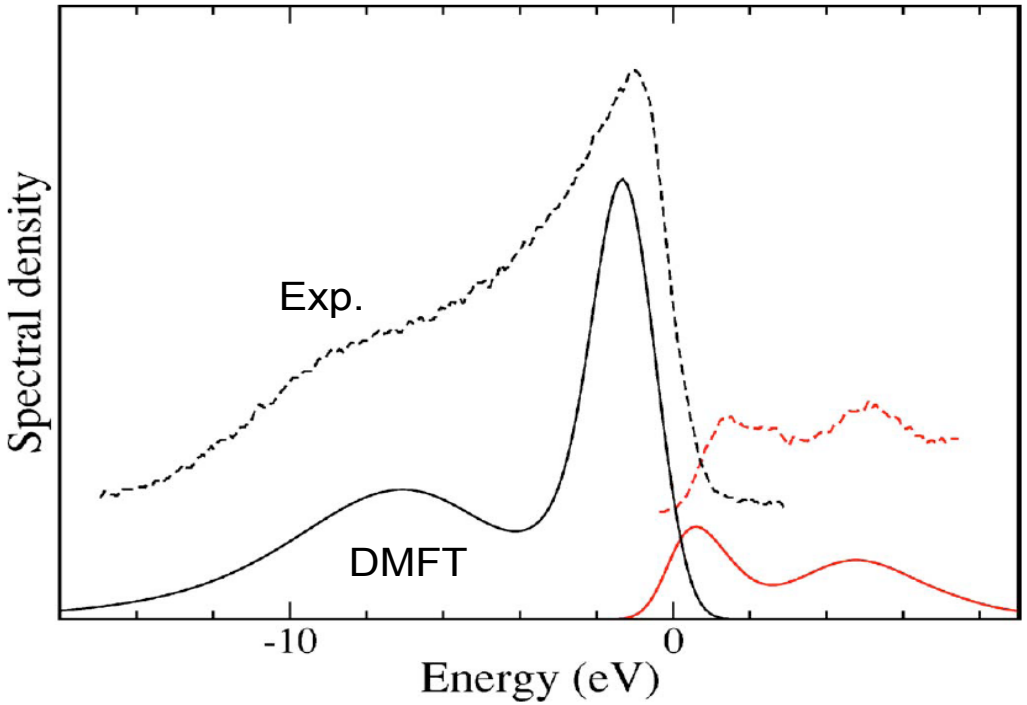


Charge transfer insulator in paramagnetic phase.
Ni^{+2} (d^8) ion in cubic rock salt crystal structure

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

Charge transfer insulator NiO



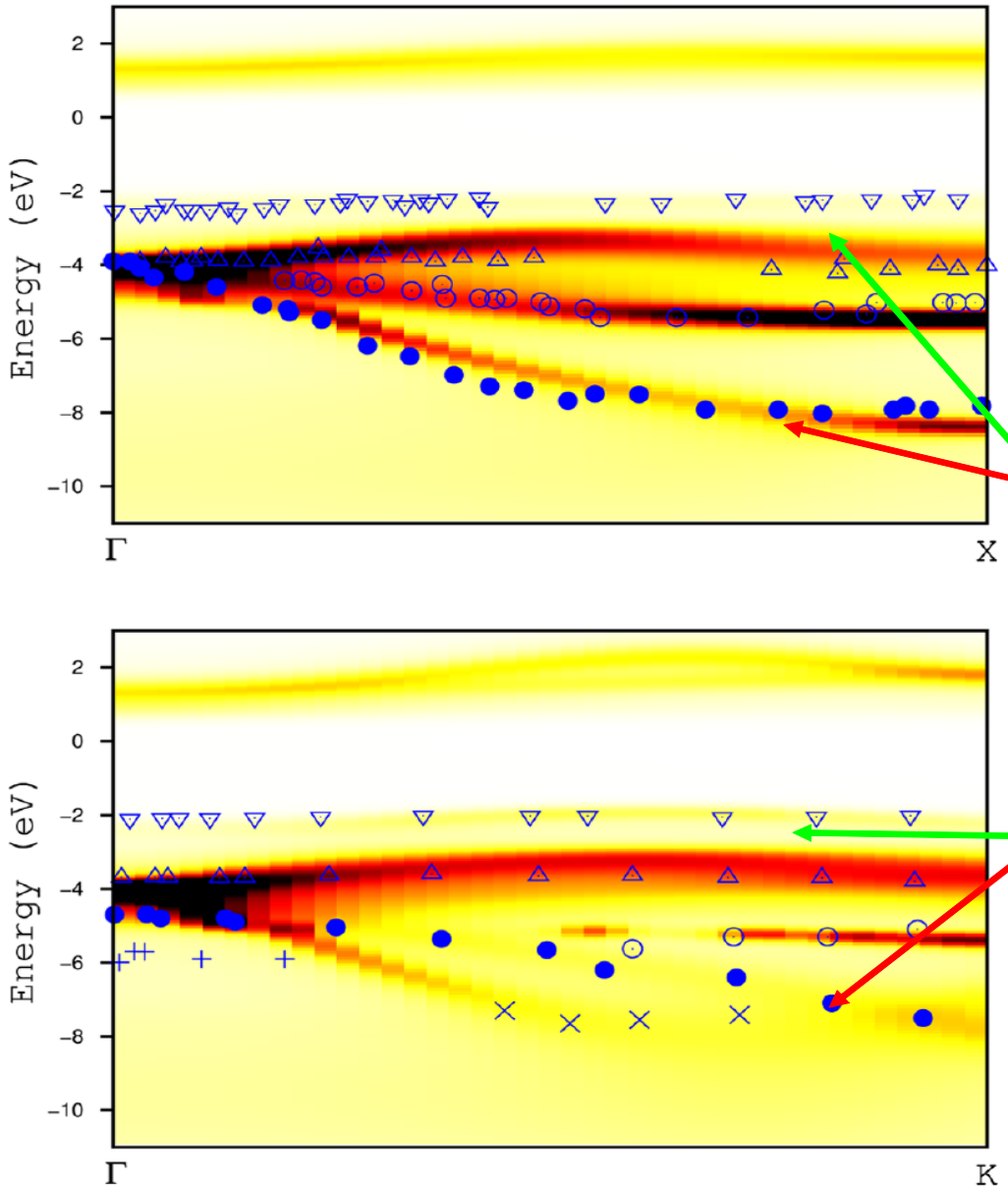


$Li_xNi_{1-x}O$ spectra

n_h	n_{e_g}	$n_{t_{2g}}$	n_p	m_d
0	0.547	1.000	0.969	1.85
0.6	0.531	0.994	0.885	1.61
1.2	0.530	0.980	0.800	1.45

Holes in charge transfer insulator have predominantly oxygen 2p character.

Charge transfer insulator NiO



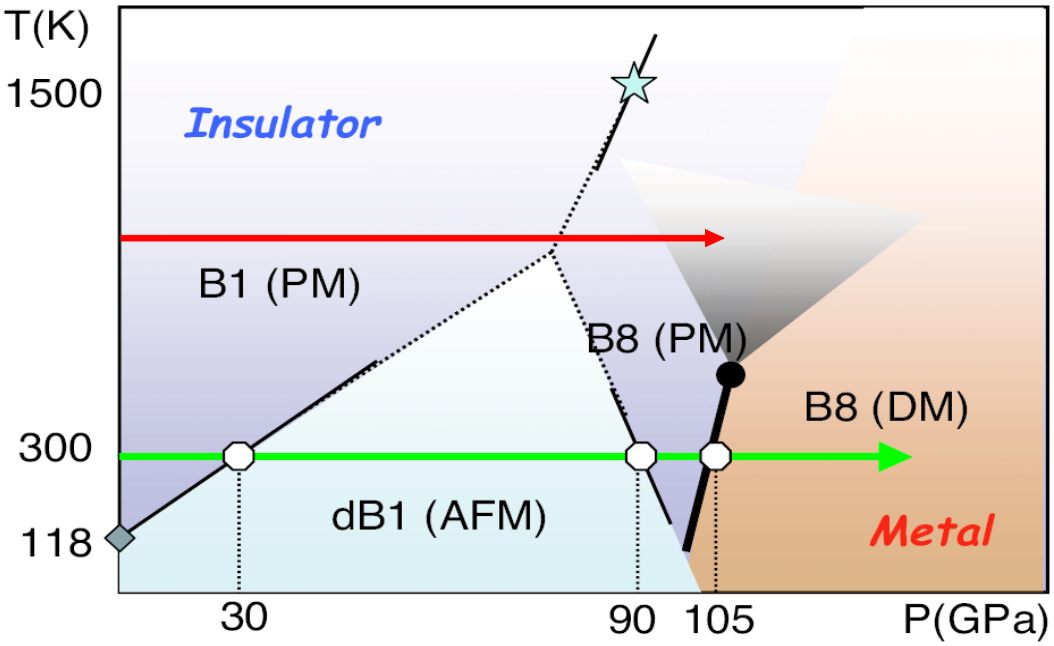
Band structure of charge transfer insulator combines dispersive (itinerant states) and flat bands (localized states).

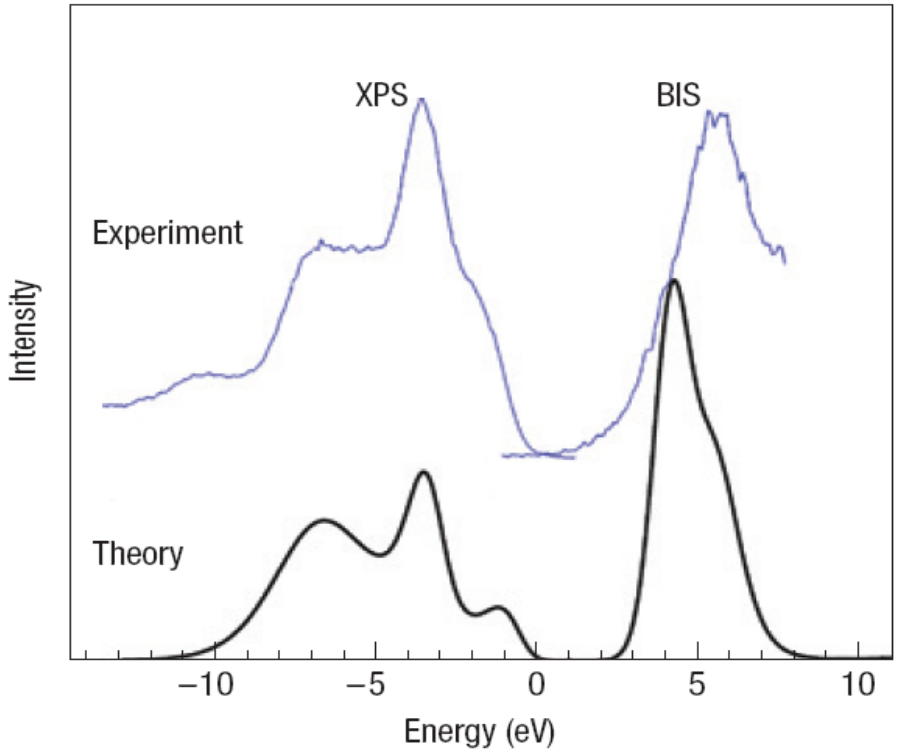
O2p bands

Ni3d bands

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

Metal-insulator transition in MnO

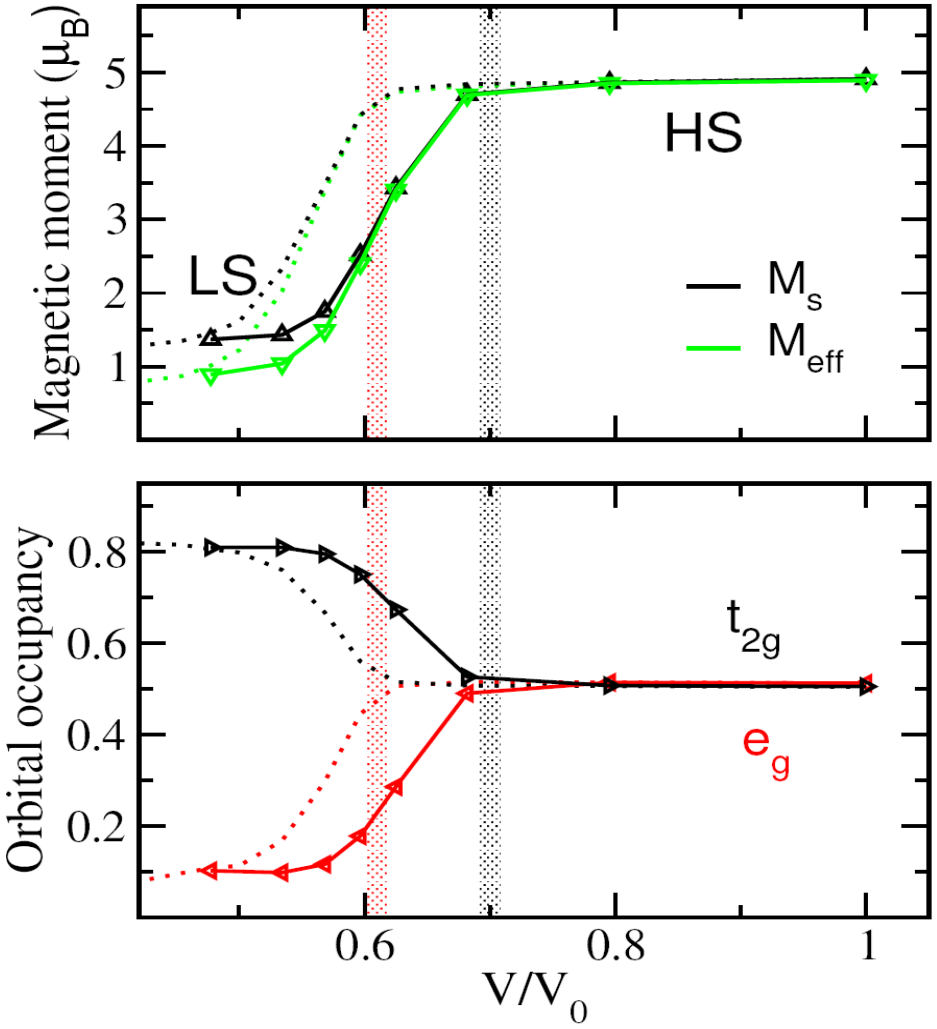


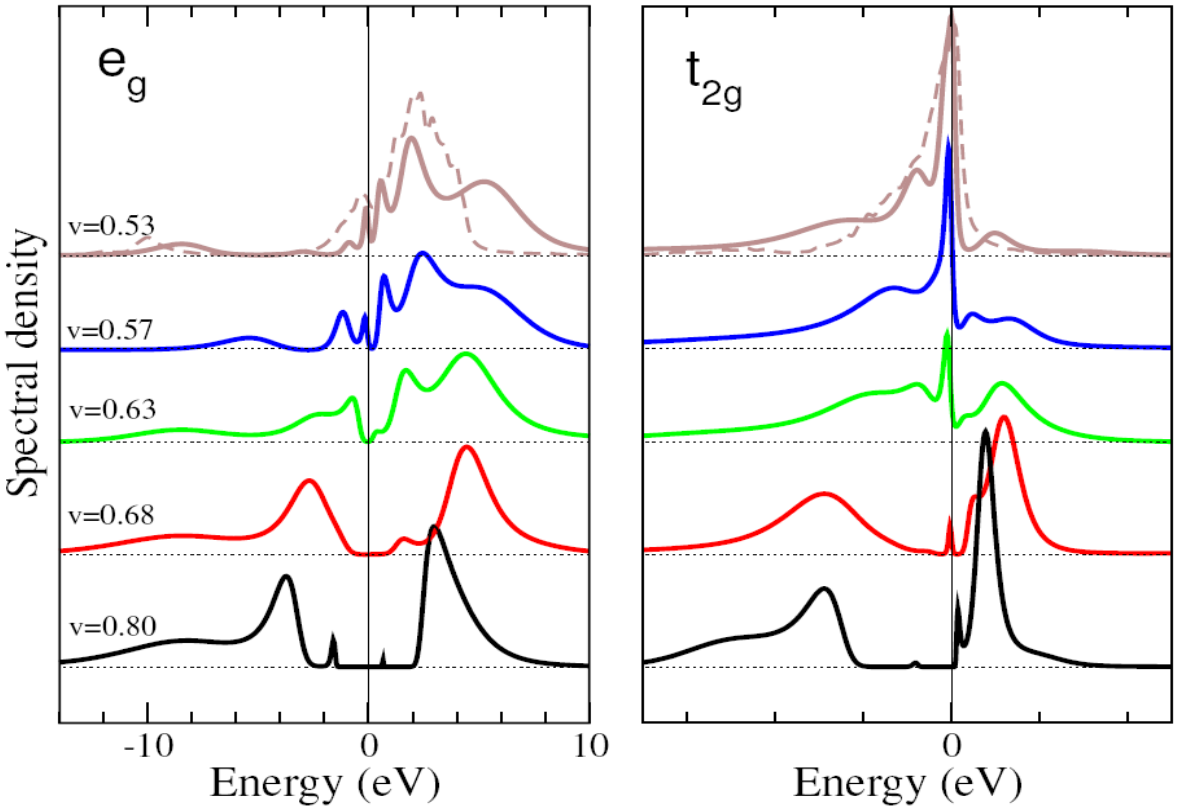


Metal-insulator transition (paramagnetic insulator to paramagnetic metal) with pressure in MnO accompanied with high-spin to low-spin state transition.

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

Metal-insulator transition in MnO

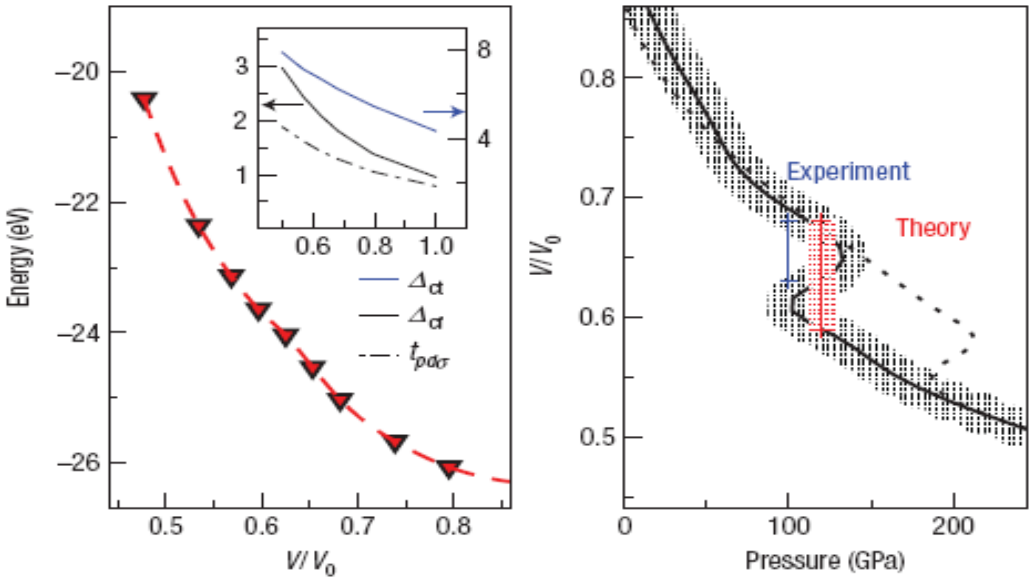


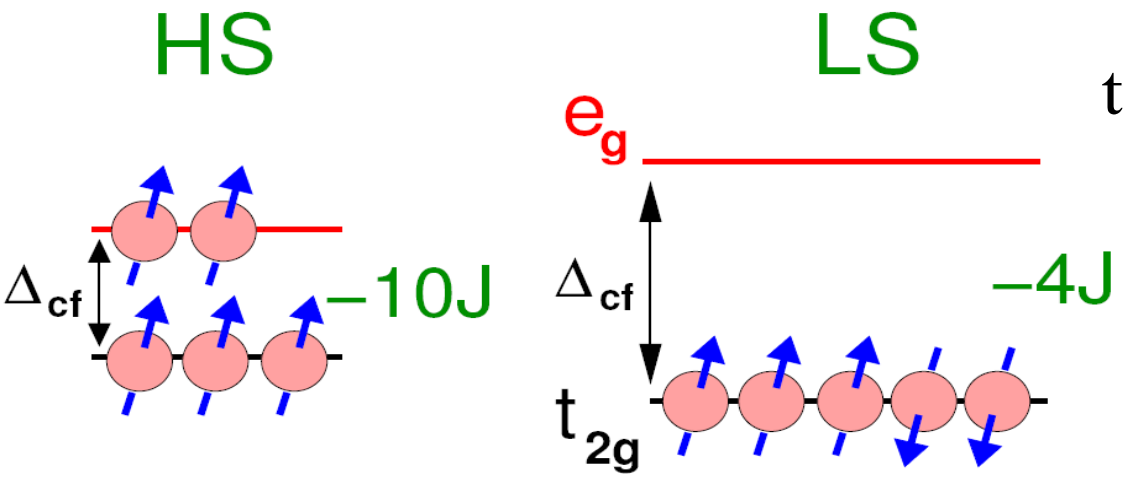


High-spin state (HS) - $t^3_{2g}\ e^2_g$ configuration

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

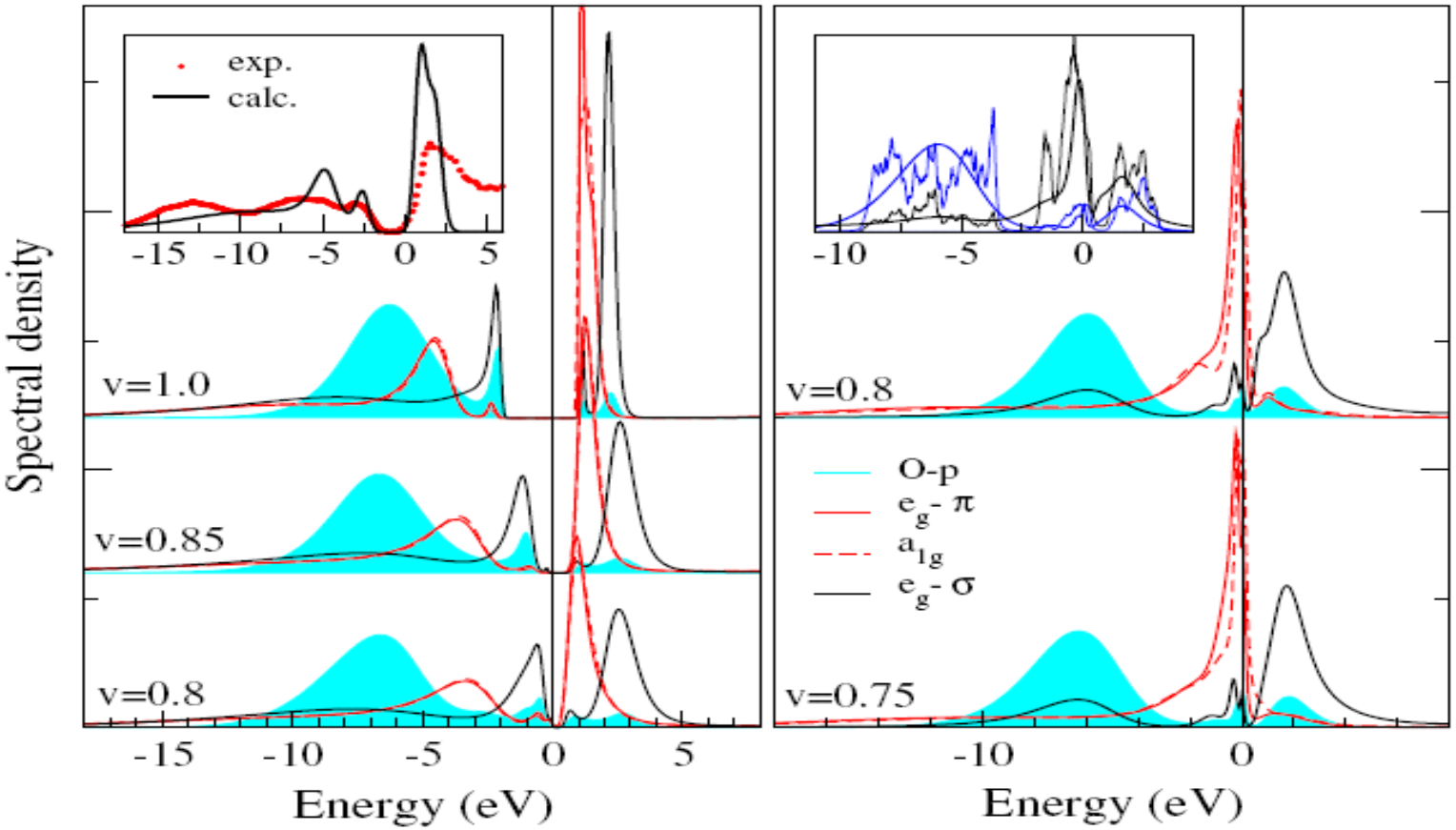
Metal-insulator transition in MnO





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.

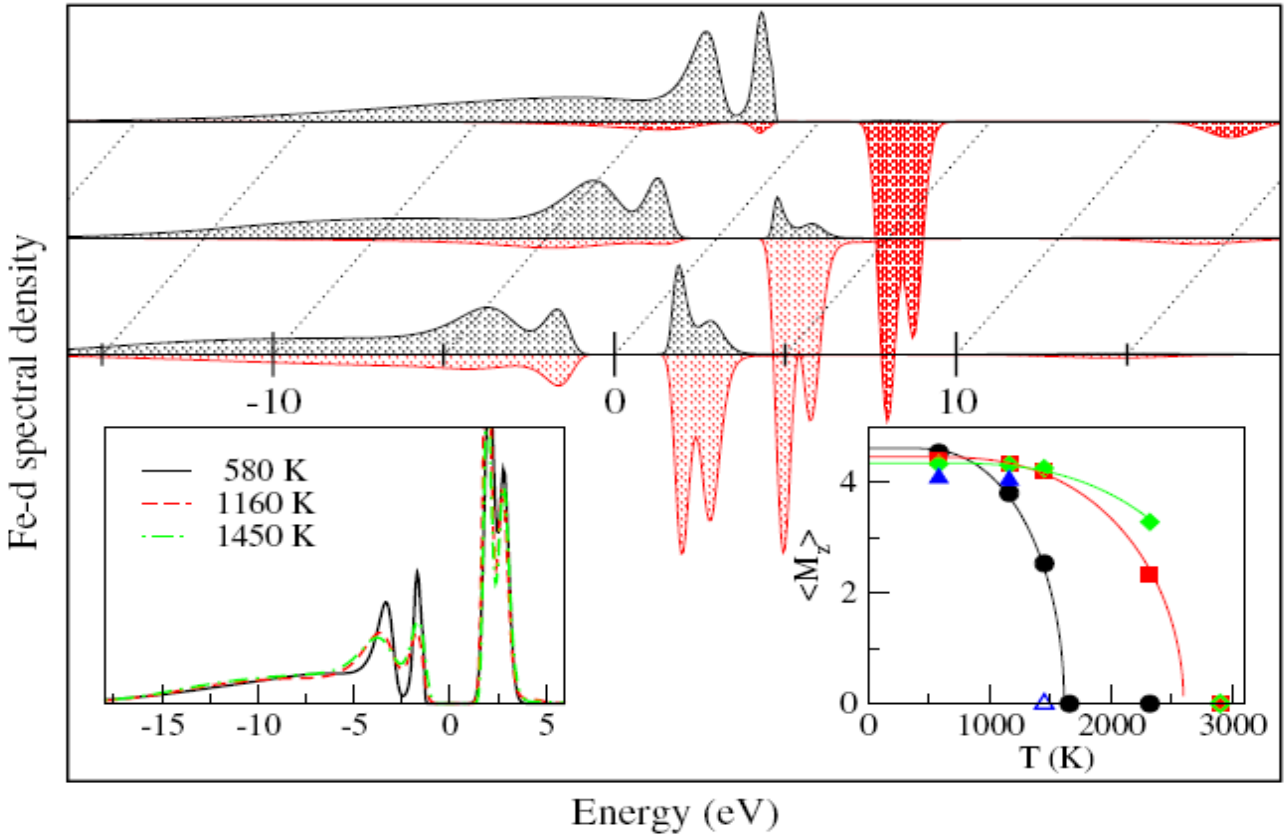
Metal-insulator transition in Fe_2O_3



Evolution of the paramagnetic state single-particle spectra with pressure (T = 580 K).

J. Kunes et al, PRL 102, 146402 (2009)

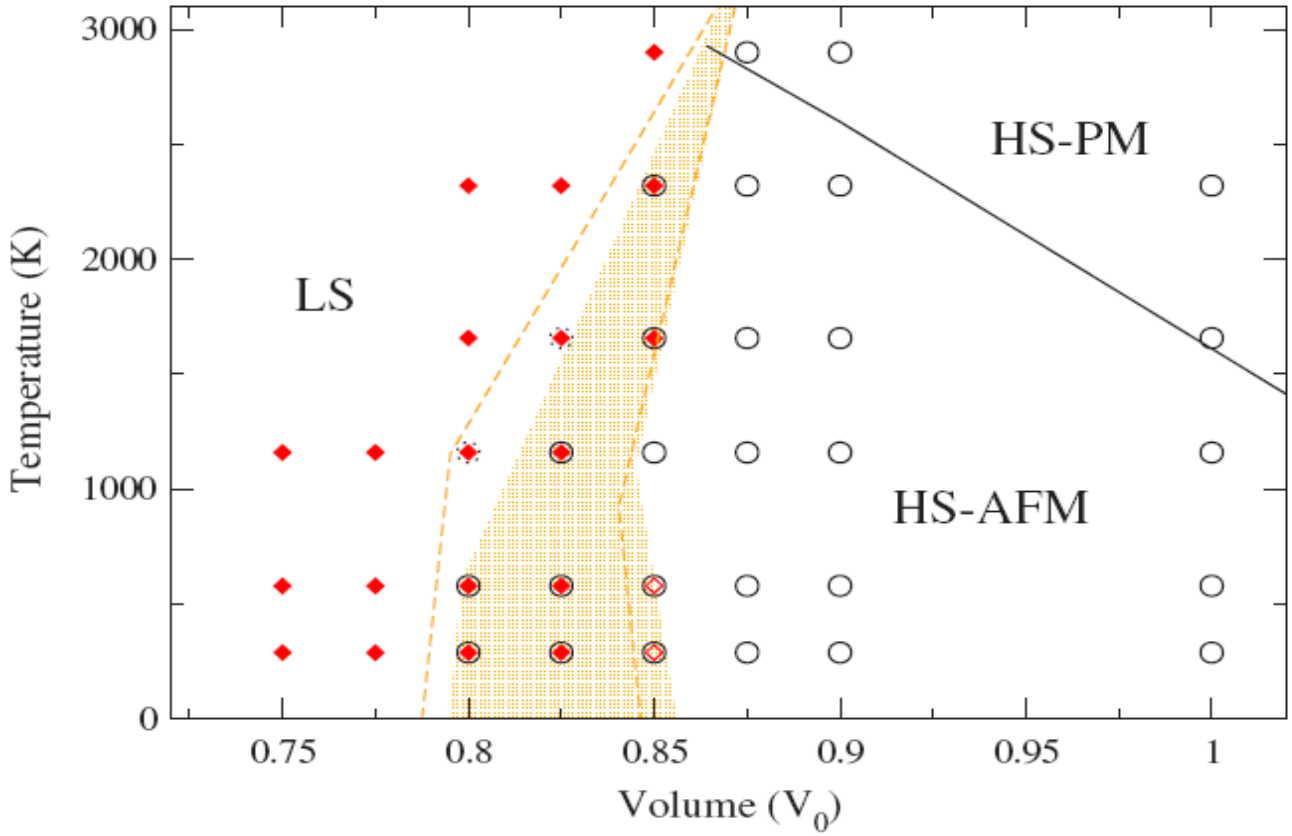
Metal-insulator transition in Fe_2O_3



Spin-polarized Fe-d spectra at the ambient pressure for 580, 1160, and 1450 K (top to bottom). Left-hand inset: The same spectra averaged over spin. Right-hand inset: The staggered magnetization versus temperature curves for various volumes.

J. Kunes et al, PRL 102, 146402 (2009)

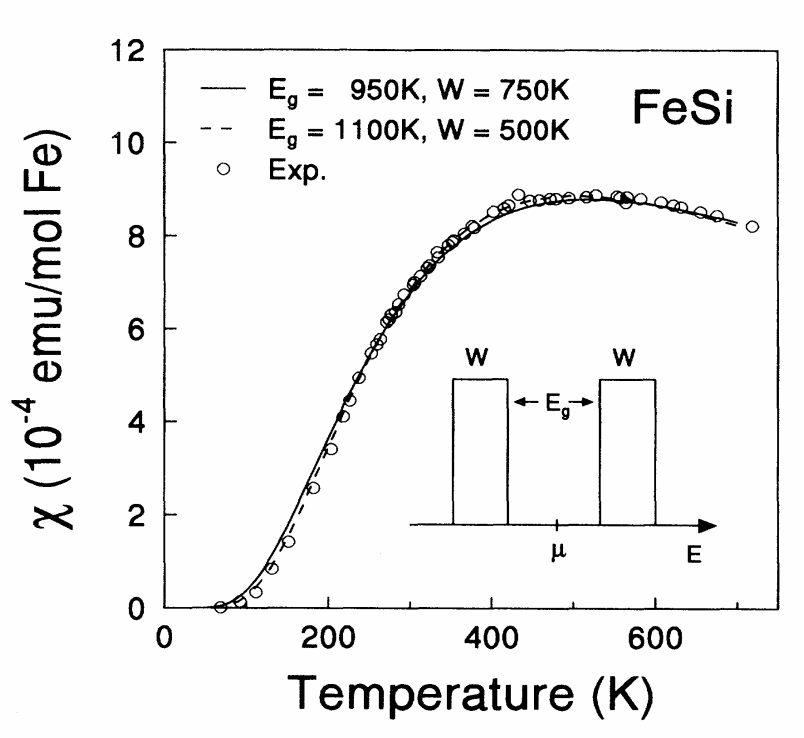
Metal-insulator transition in Fe_2O_3

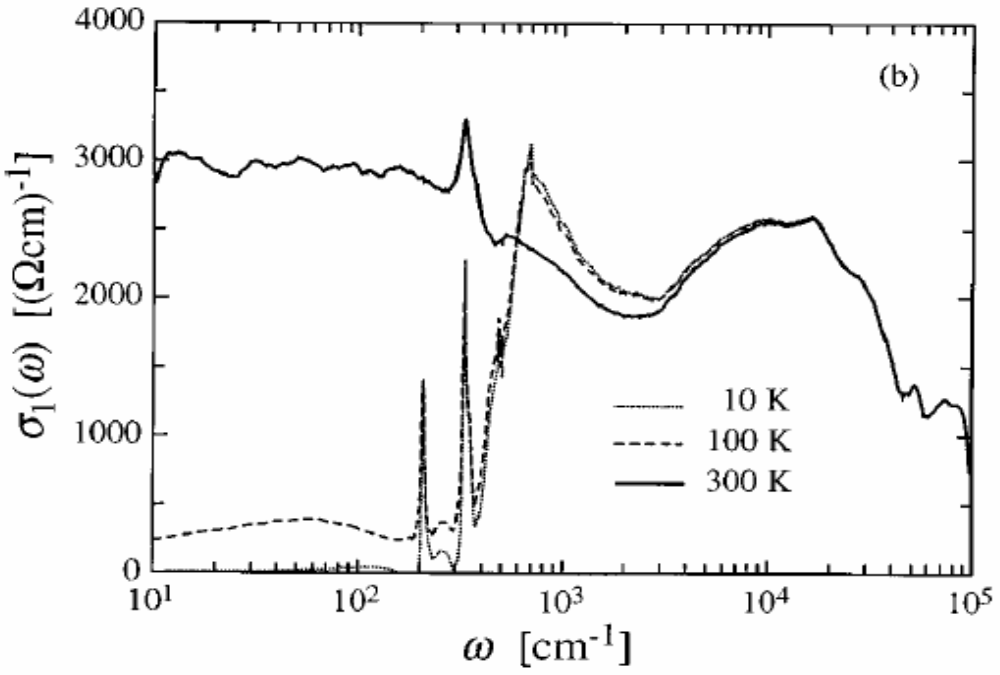


Calculated *V-T* phase diagram of hematite.

J. Kunes et al, PRL 102, 146402 (2009)

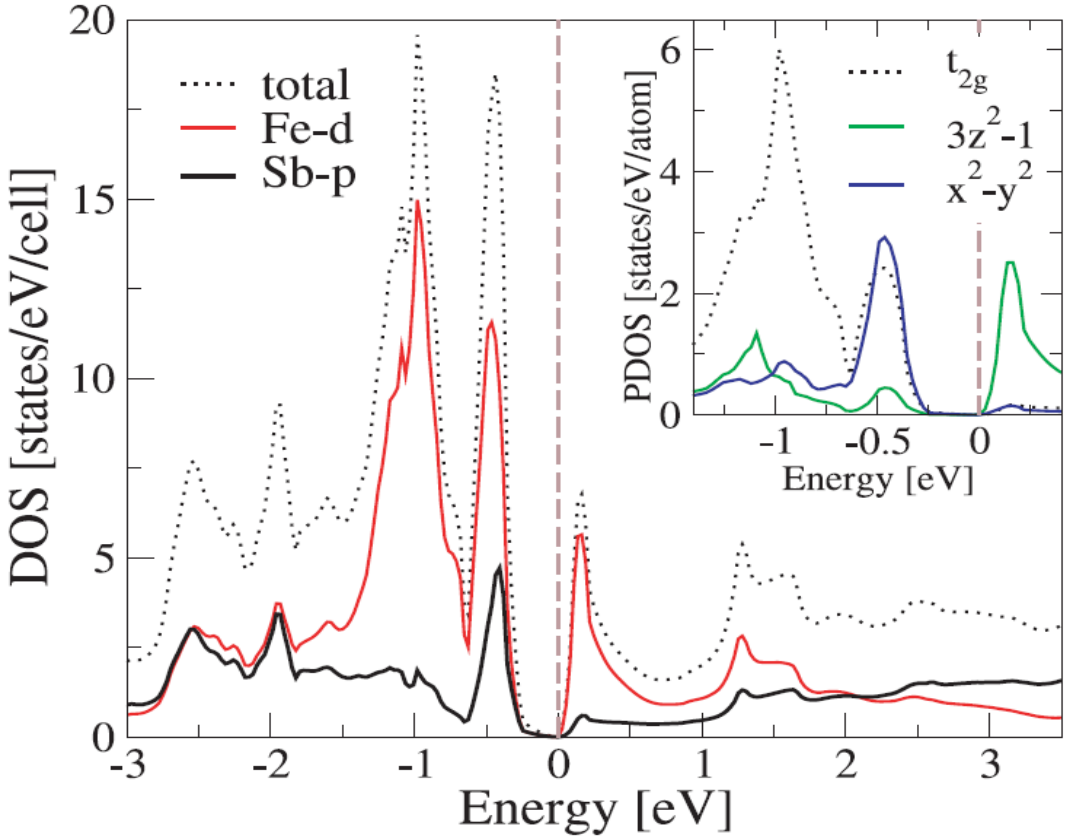
Correlated covalent insulators FeSi and $FeSb_2$

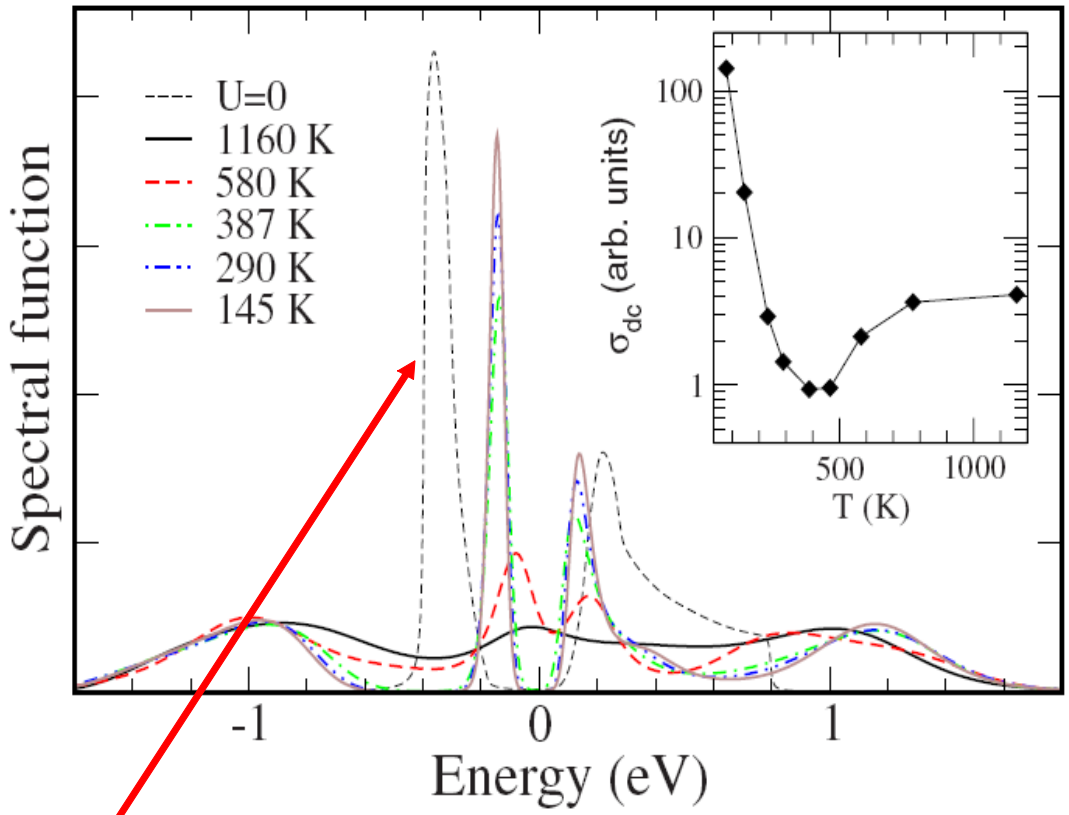




Transition from non-magnetic semiconductor to paramagnetic metal with temperature increase in FeSi and $FeSb_2$. Electron doping in $Fe_{1-x}Co_xSi$ results in ferromagnetic metallic state.

Correlated covalent insulators FeSi and $FeSb_2$

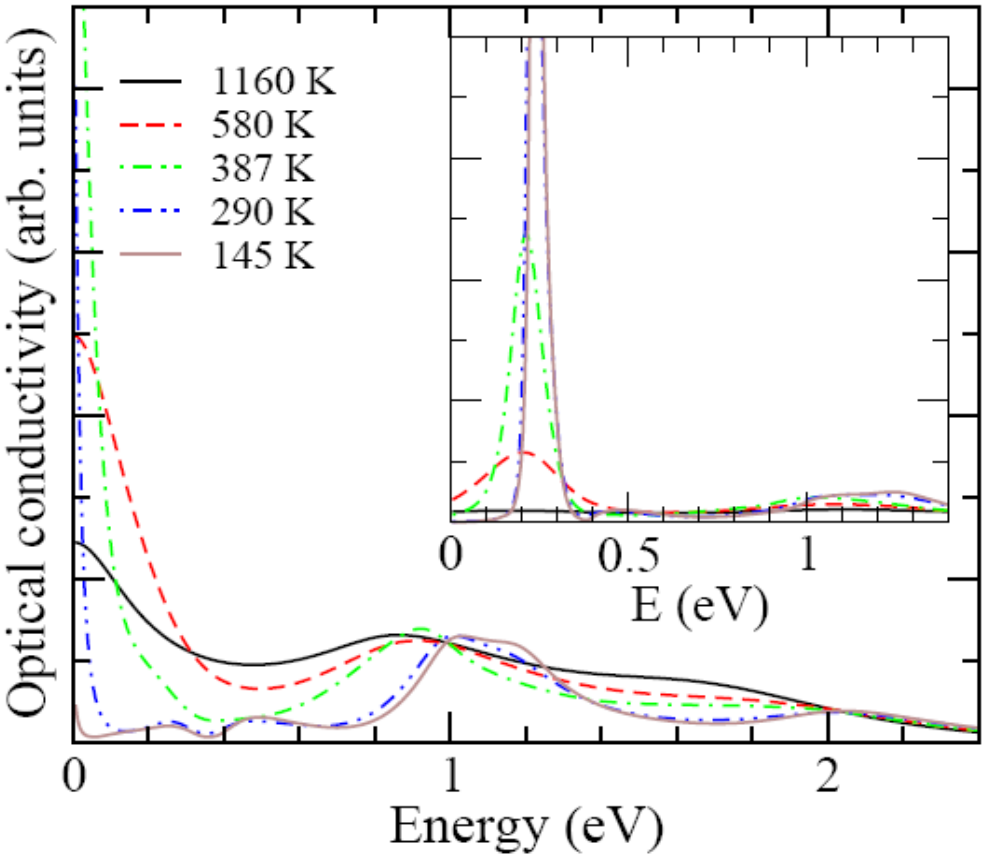


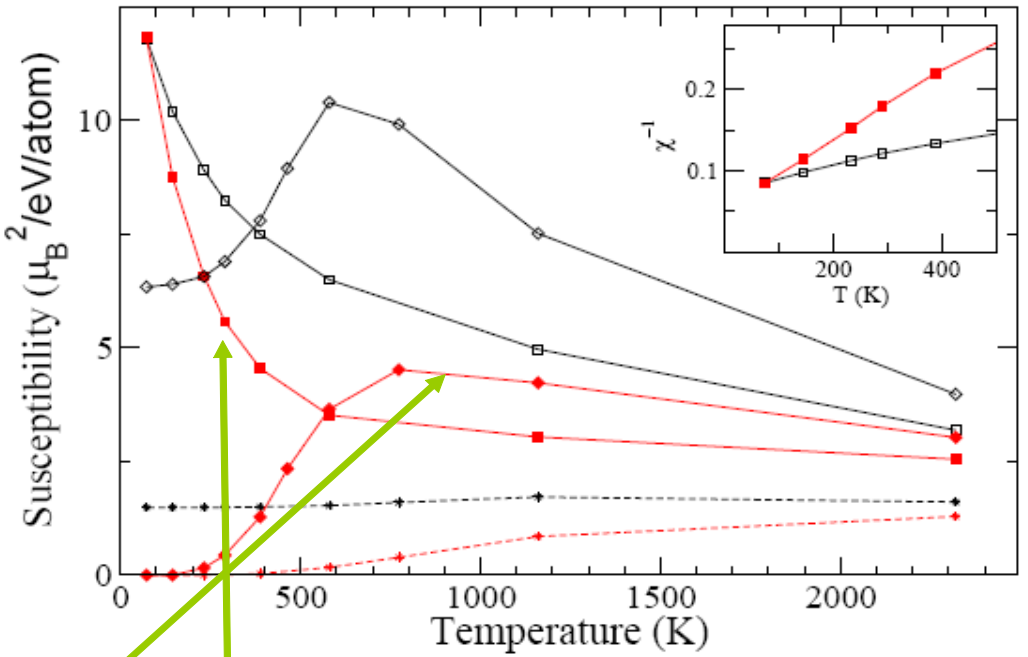


Effective one-orbital per Fe ion model corresponding to covalent insulator

J. Kunes et al, Phys.Rev. B 78, 033109 (2008)

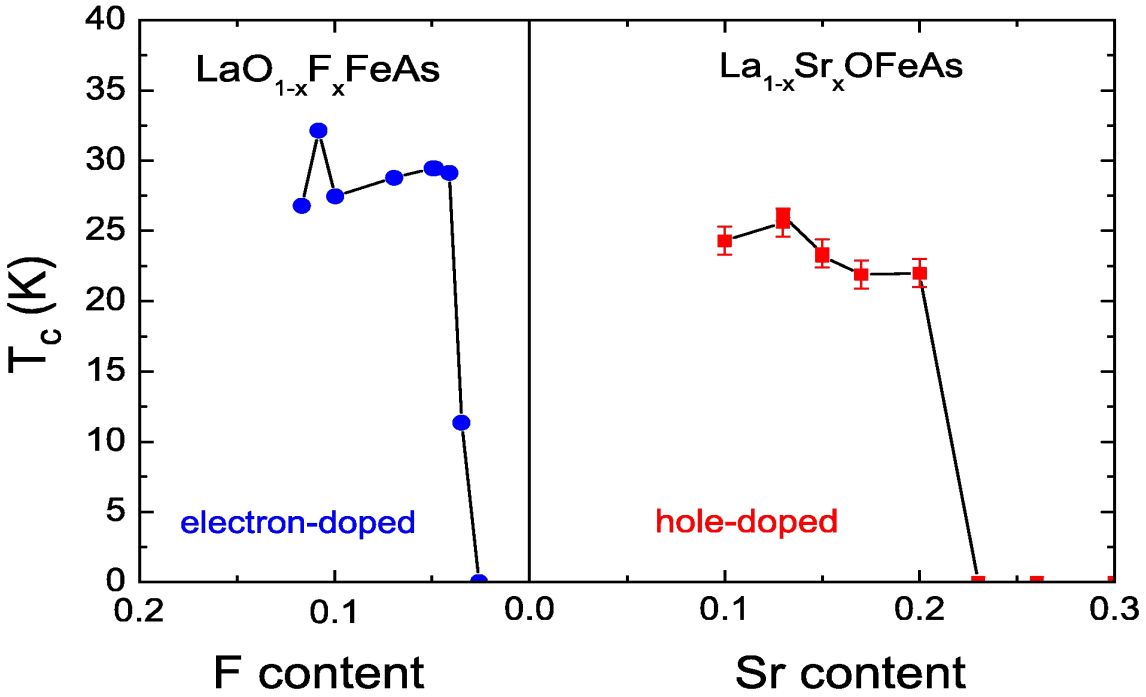
Correlated covalent insulators FeSi and $FeSb_2$

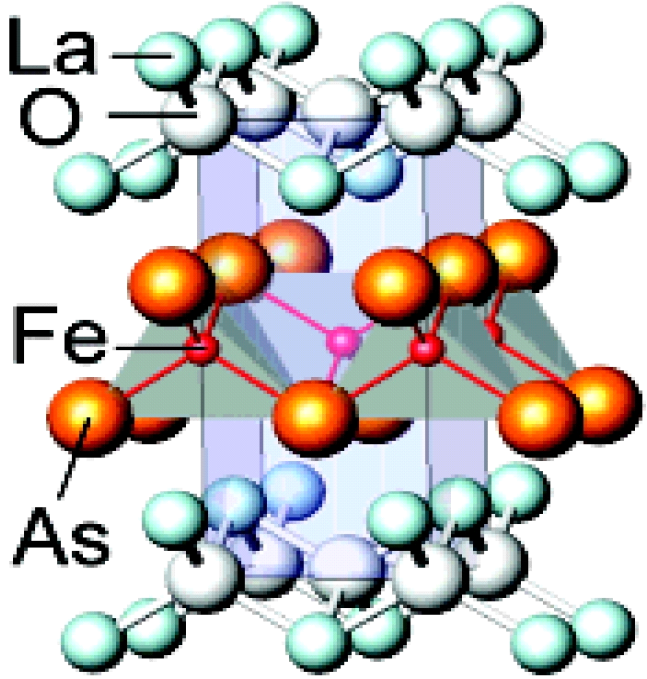




Temperature increase results in transition from nonmagnetic covalent insulator to bad metal with local moments. Electron doping leads to divergence of susceptibility for low T indicating ferromagnetic instability

Novel superconductor LaOFeAs

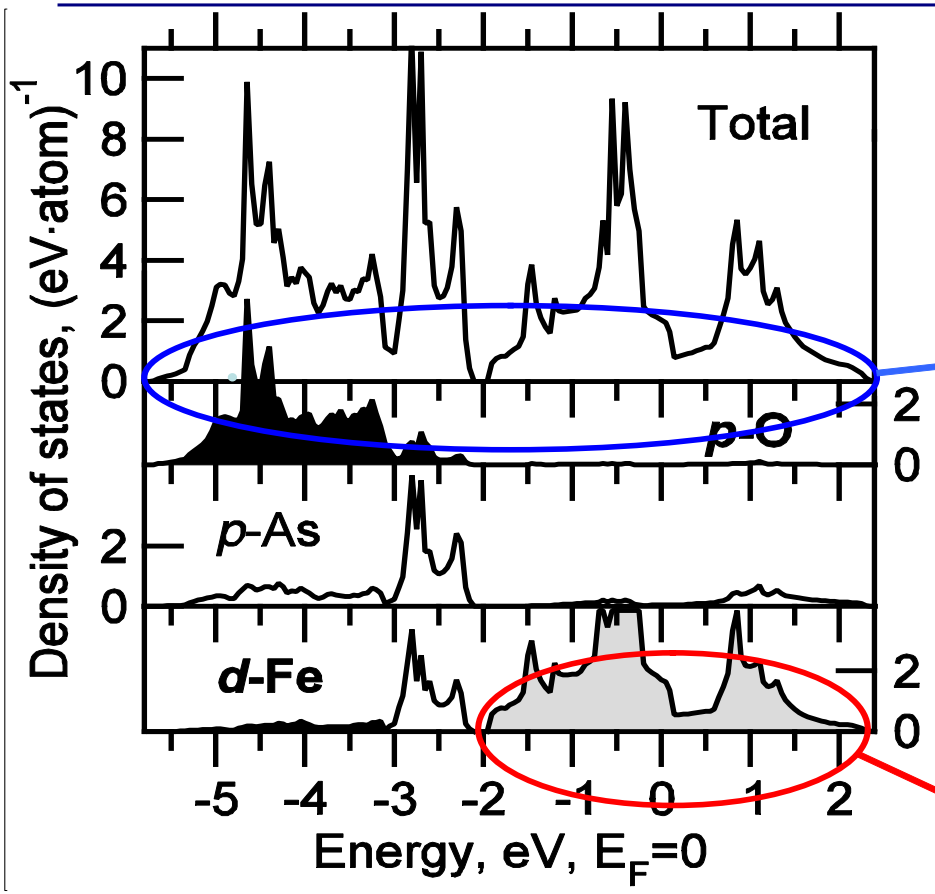


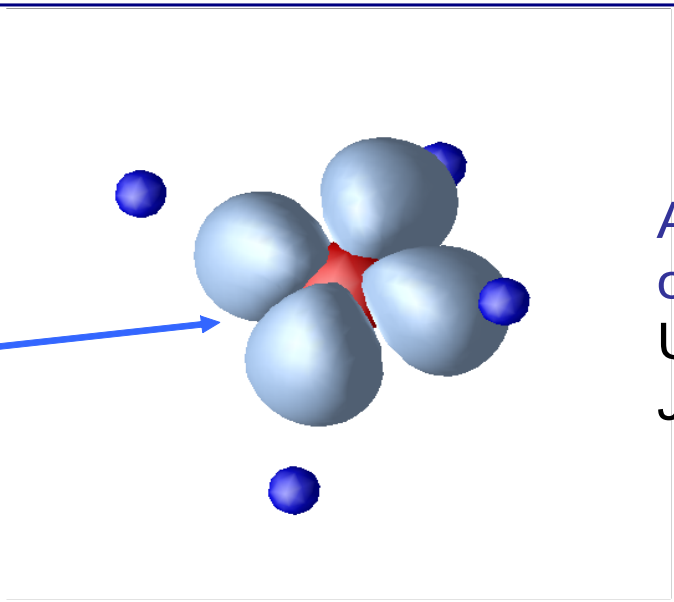


Tc=26K for F content ~11%

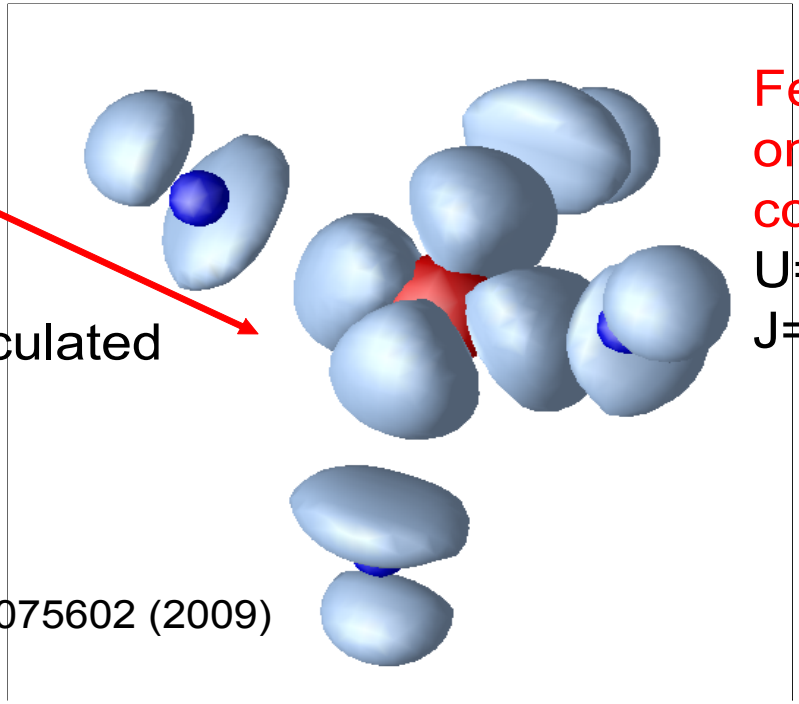
Y. Kanamura *et al.* J. Am. Chem. Soc. 130, 3296 (2008)

Novel superconductor LaOFeAs





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

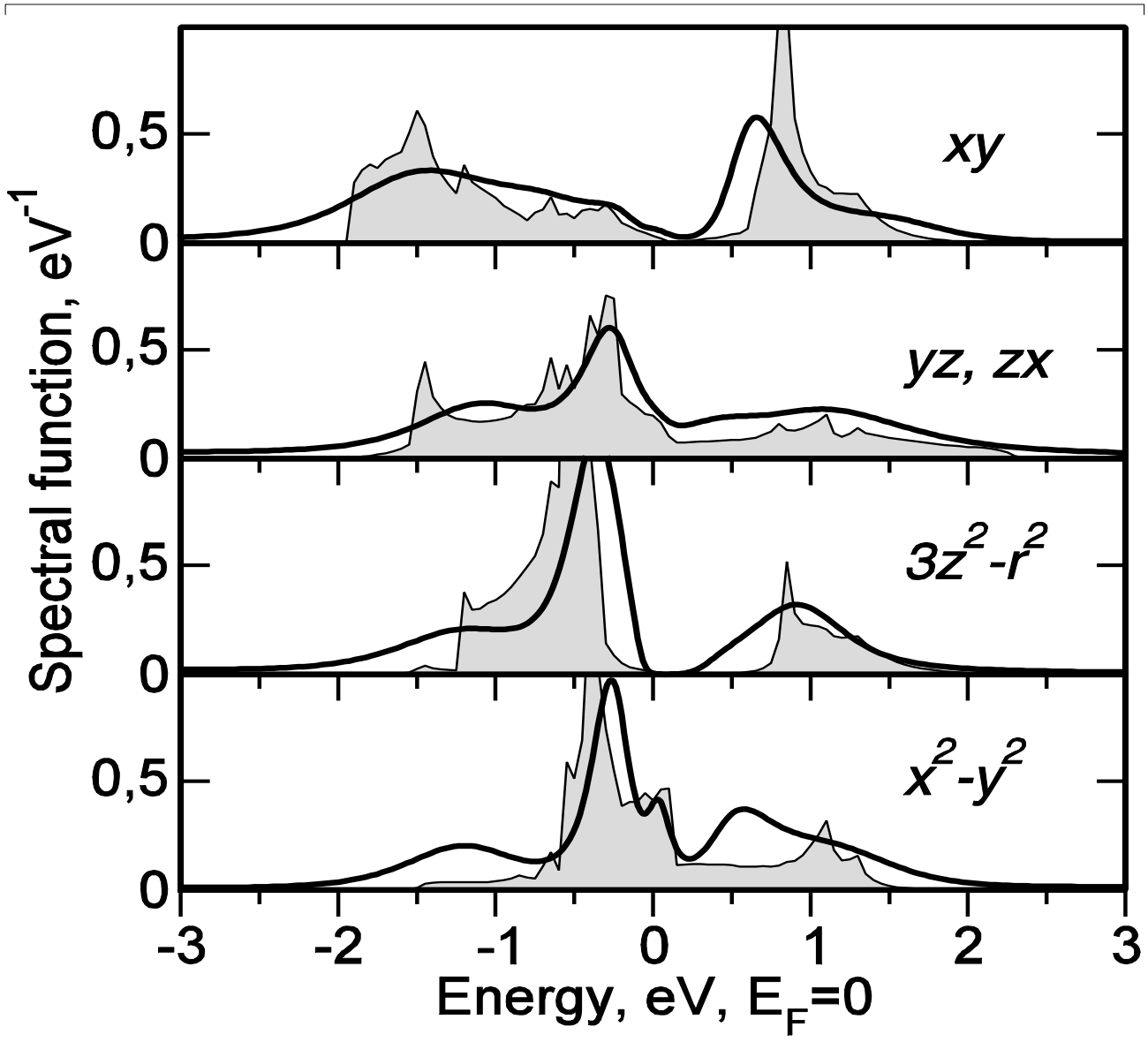


Fe3d band
only WF
constrain DFT
U=0.8 eV
J=0.5 eV

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)

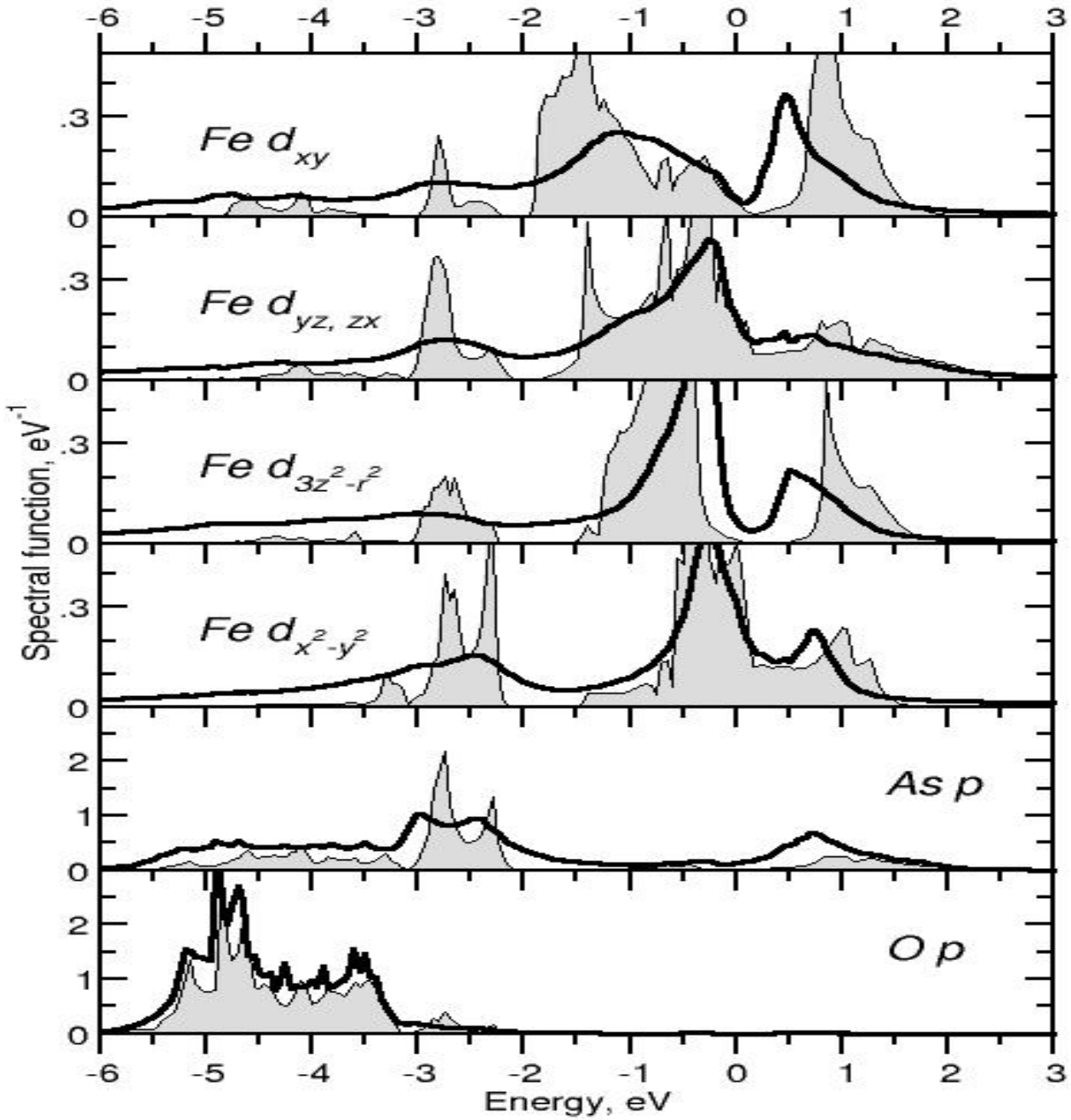
Novel superconductor LaOFeAs



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

Weakly correlated regime!

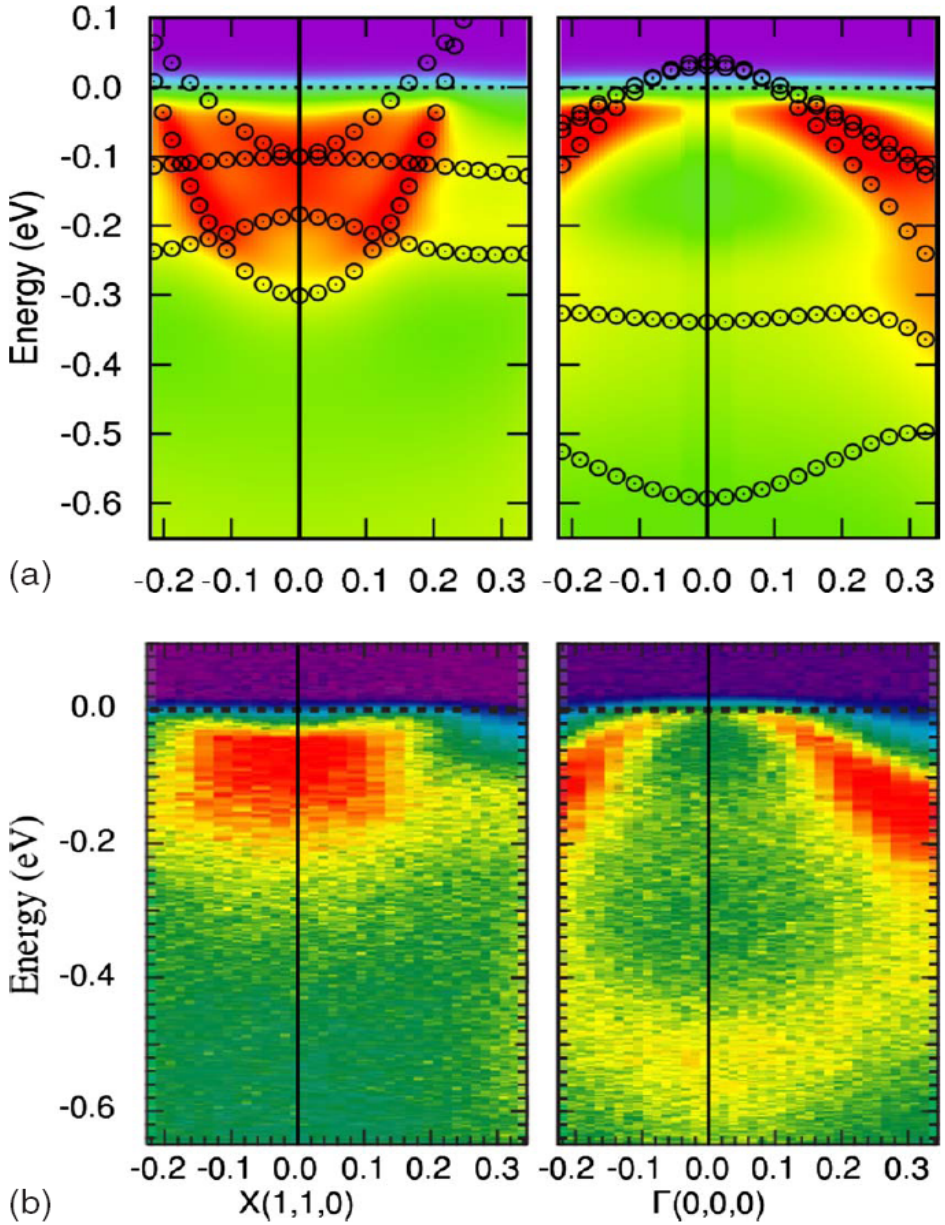
Novel superconductor LaOFeAs



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

Weakly correlated regime!

ARPES for novel superconductor $BaFe_2As_2$



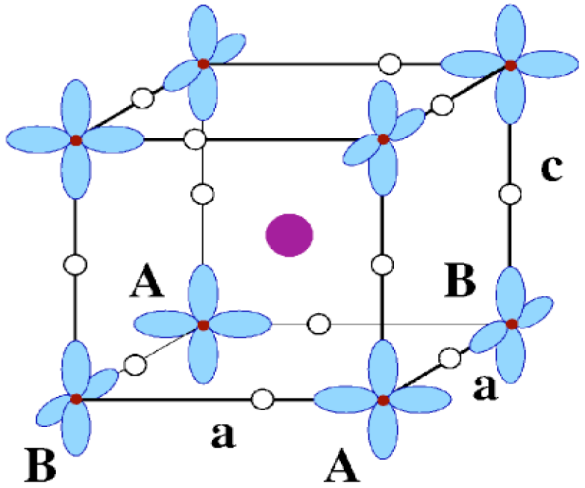
The **k**-resolved total spectral function $A(\mathbf{k},\omega)$ of $BaFe_2As_2$ near the Γ and X points in the Brillouin zone.
Upper panel: LDA+DMFT spectral function including the renormalized band structure circles obtained by plotting the peak positions of the spectral function $A(\mathbf{k},\omega)$.
Lower panel: The corresponding experimental ARPES intensity map.

S. L. Skornyakov et al, Phys. Rev. B 80, 092501 (2009)

Correlations and lattice distortion: $KCuF_3$

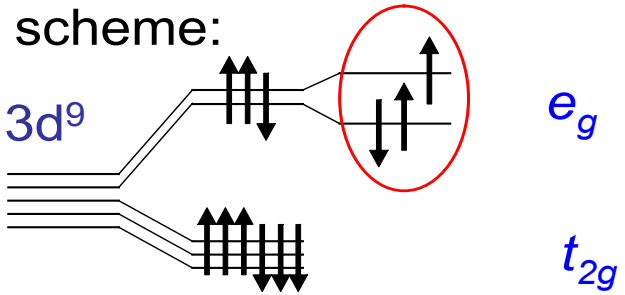
$KCuF_3$: a prototype e_g ($3d^9$) Jahn-Teller system

Crystal structure and Orbital order (OO):



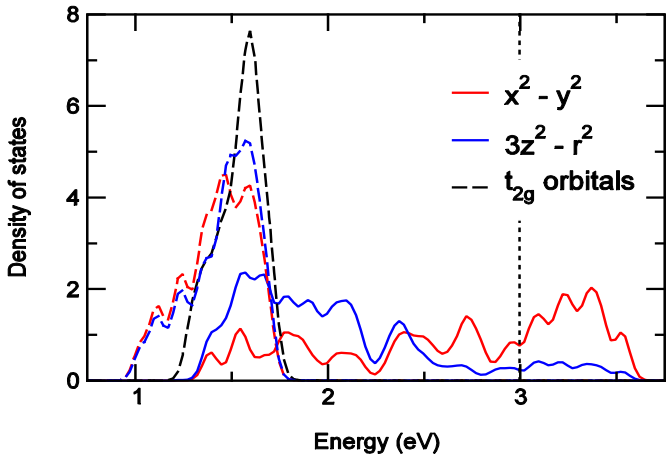
- pseudo cubic perovskite I4/mcm
- cooperative JT distortion below 1000 K
- *Neel* temperature ~38 K
- $d_{x^2-y^2}$ hole antiferroorbital ordering

d-level scheme:



free ion — cubic — tetragonal ($c/a < 1$)

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



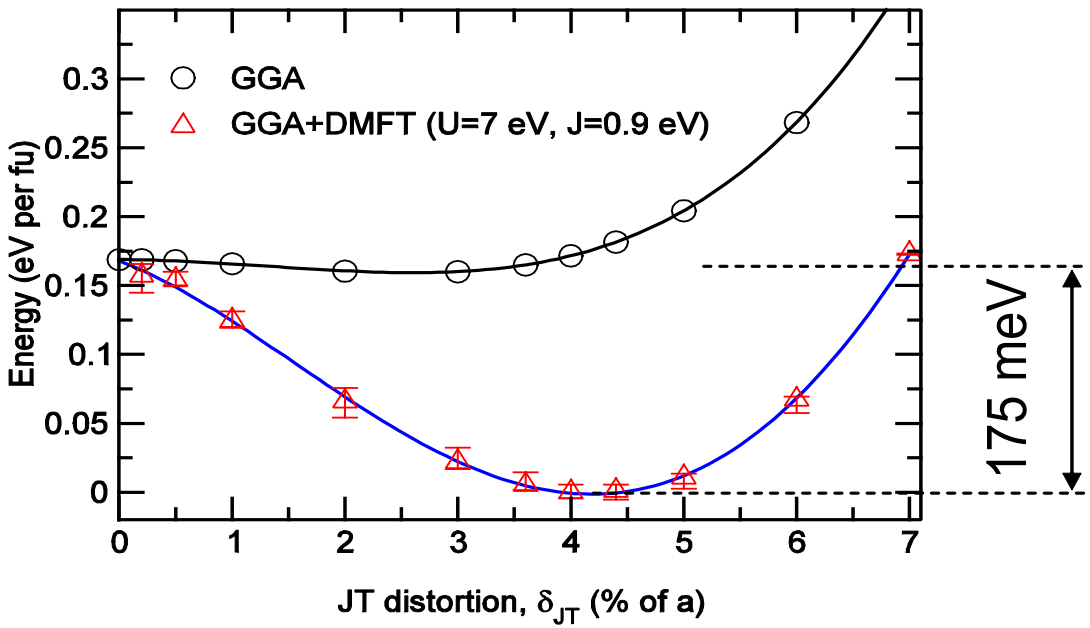
metallic solution -> inconsistent with exp

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)

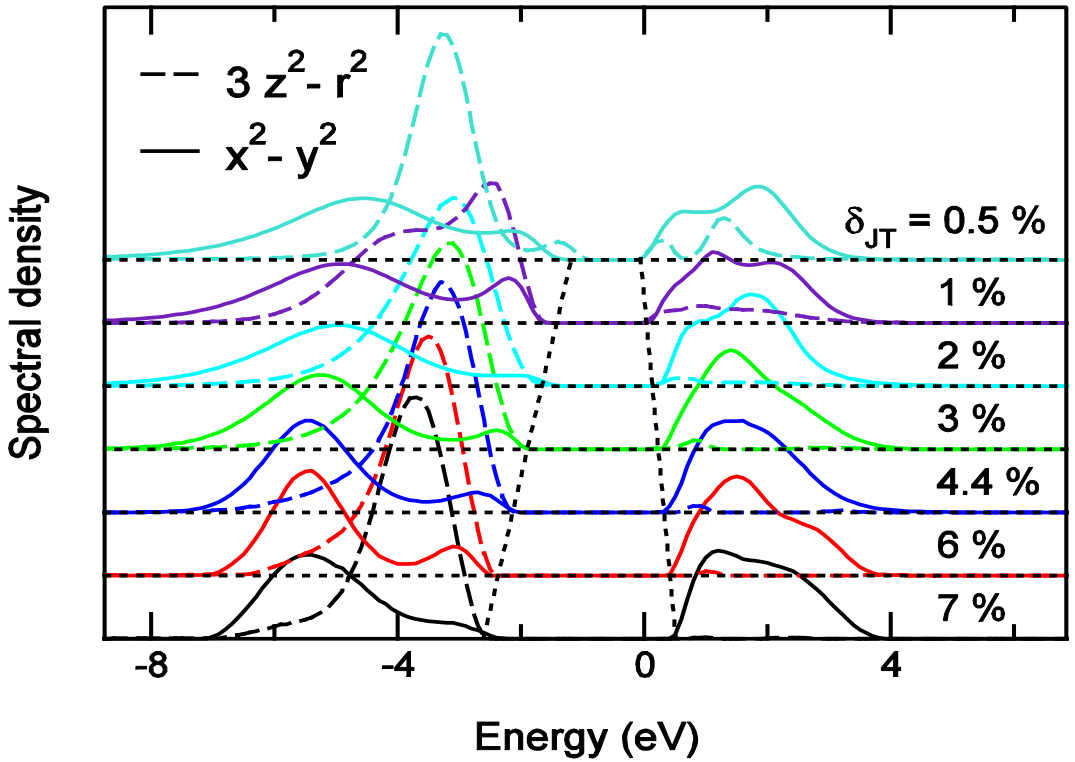
→ in good agreement with exp

Correlations and lattice distortion: $KCuF_3$

$KCuF_3$: GGA+DMFT results

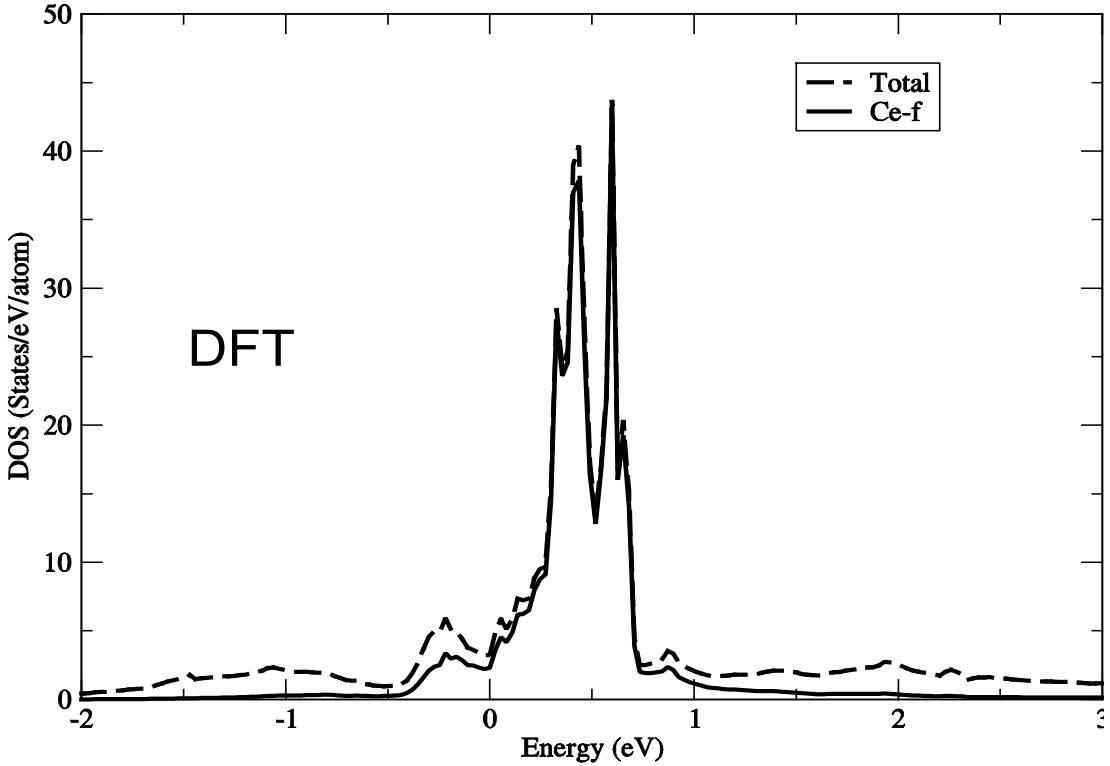
U = 7.0 eV, J = 0.9 eV

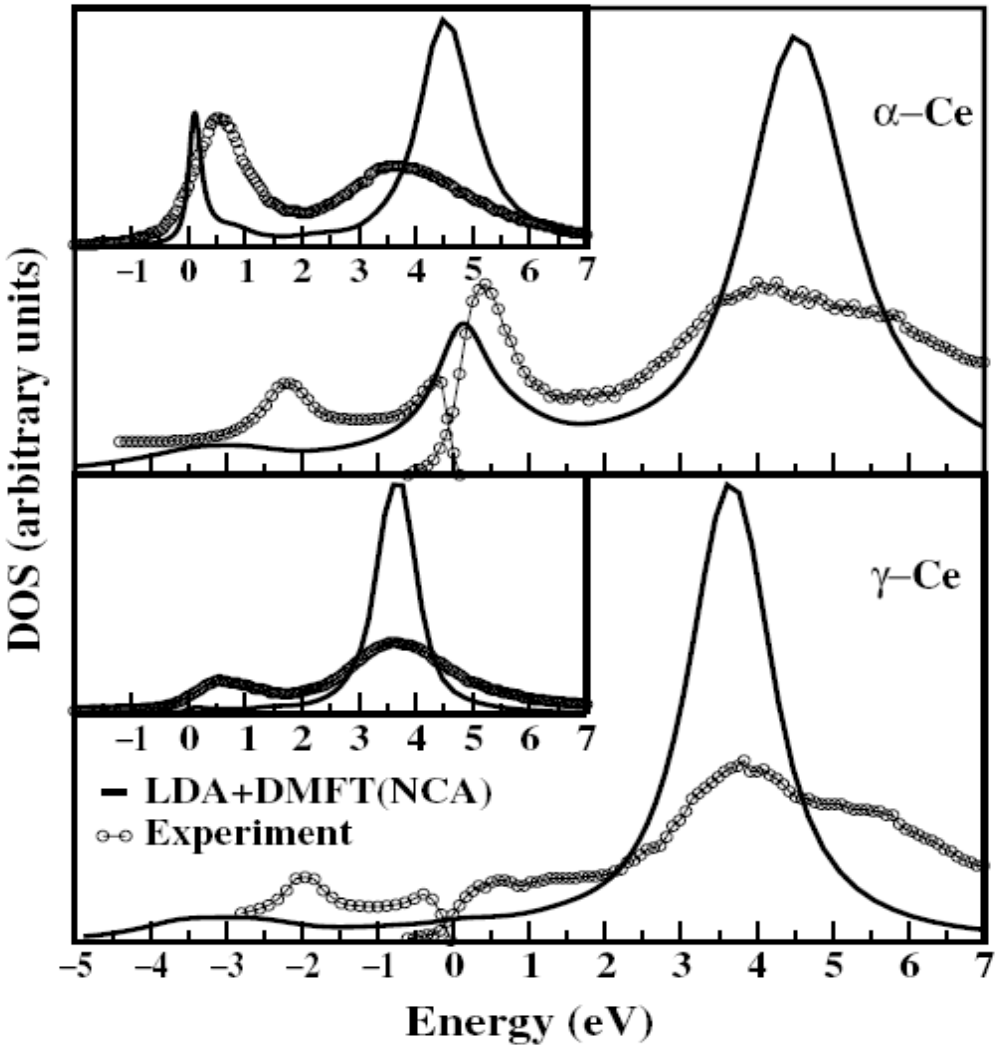
e_g spectral density:



- *paramagnetic* insulator
- gap gradually increase with the JT distortion
- but large even at ~0.5 %
- hole orbital polarization on $x^2 - y^2$ (in LCS with *z-axis* along the longest Cu-F bond)

ons localization in Ce

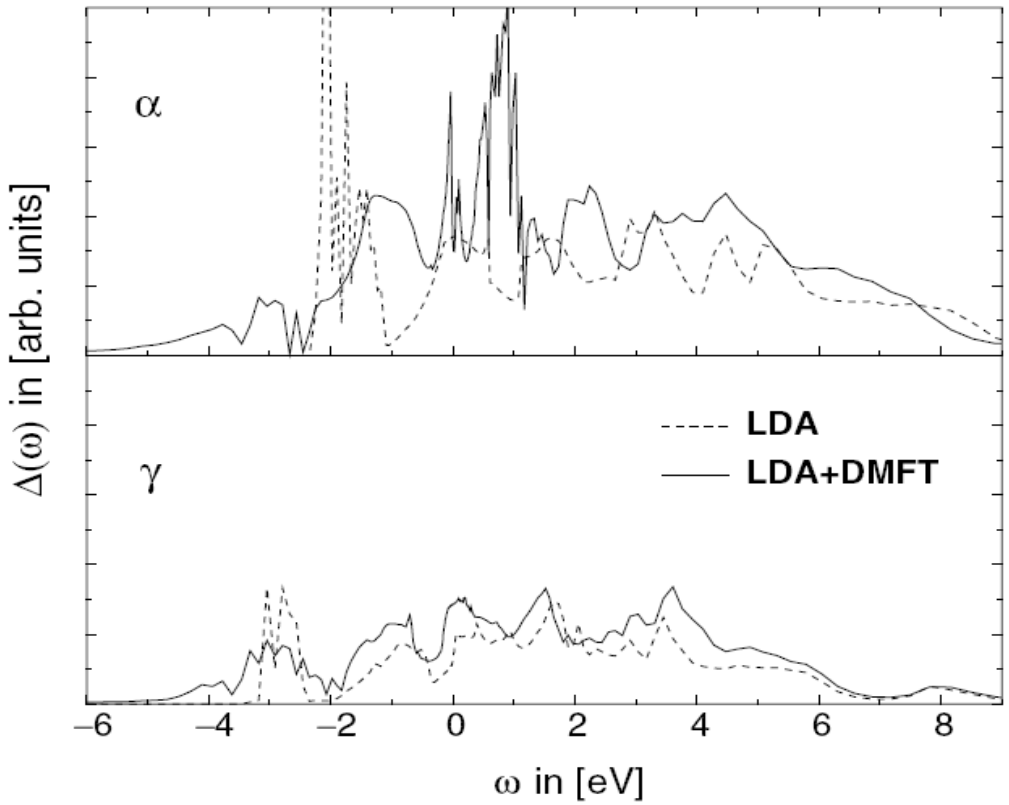




Ce $\alpha - \gamma$ transition with 15% volume change.
Kondo temperature T_K 1000K (α) , 30K (γ)

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

f-electrons localization in Ce



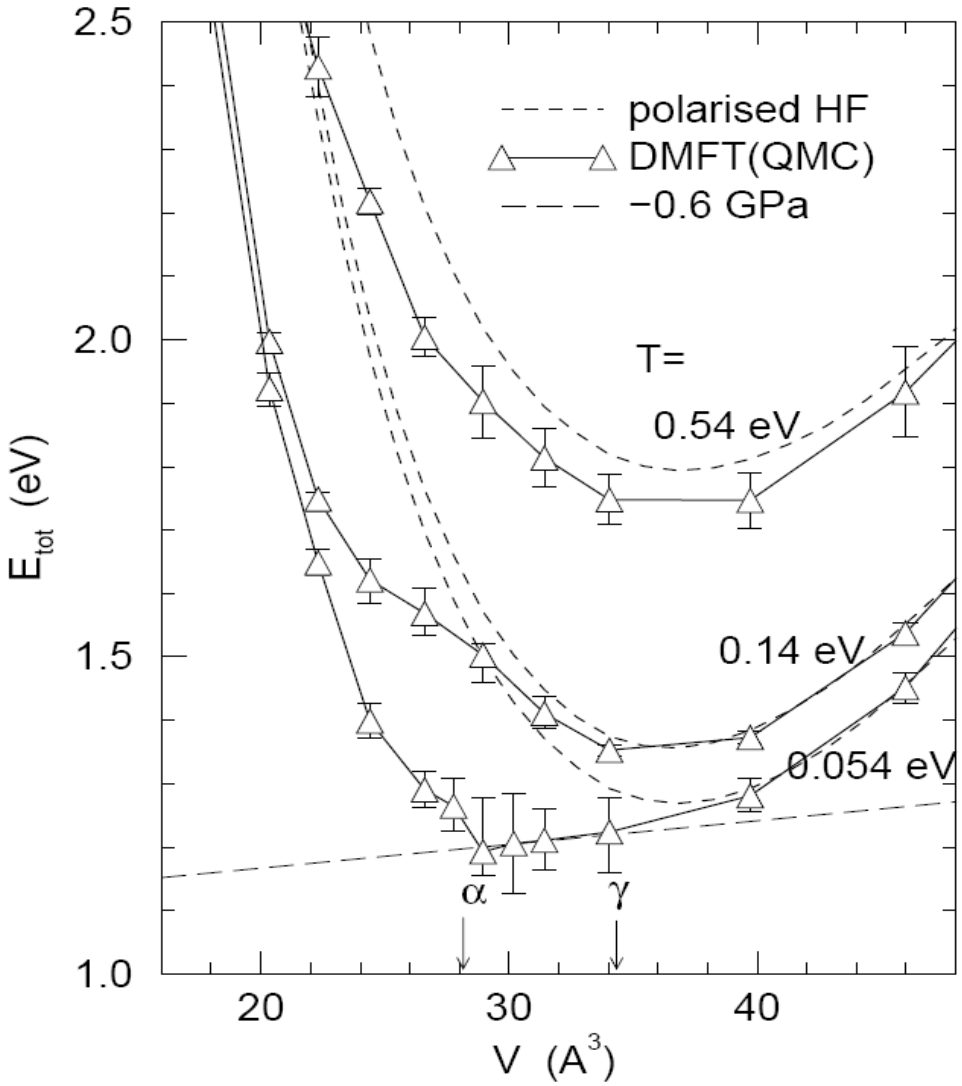
Hybridization of the site orbitals with the rest of the crystal in effective single impurity model is described by effective hybridization function $\Delta\ (i\omega_n)$ or effective non-interacting bath Green function $G_0(i\omega_n)$:

$$\mathcal{G}_0(i\omega_n) = (i\omega_n + \mu - \Delta(i\omega_n))^{-1}$$

$$\mathcal{G}_0^{-1}(i\omega_n) = G^{-1}(i\omega_n) + \Sigma(i\omega_n)$$

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

f-electrons localization in Ce



Total energy for Ce calculated in LDA+DMFT(QMC) (solid line) and in polarized Hartree-Fock approximation (dashed line) for three temperature values. Long dashed line corresponds to pressure for α–γ- transition: $E = -P_{exp}V$.

A.K. McMahan, K. Held, R.T. Scalettar, Phys. Rev. B 67, 075108 (2003)

Conclusions

- ***Ab-initio*** **LDA+correlation Hamiltonian is defined with definition of correlated orbitals and interaction strength (U) between them based on Wannier functions representation .**
- **Static mean-filed approximation lead to LDA+U method and dynamical mean-filed approximation to LDA+DMFT**
- **LDA+U method describes all kinds of spin, orbital and charge order effects in Mott insulators**
- **LDA+DMFT method is adequate for paramagnetic strongly correlated metals**