Theory of correlated fermionic condensed matter

2. Electronic correlations - from models to materials

b. Merging DMFT with density functional theory (LDA+DMFT) and application to transition-metal oxides

XIV. Training Course in the Physics of Strongly Correlated Systems
Salerno, October 6+7, 2009

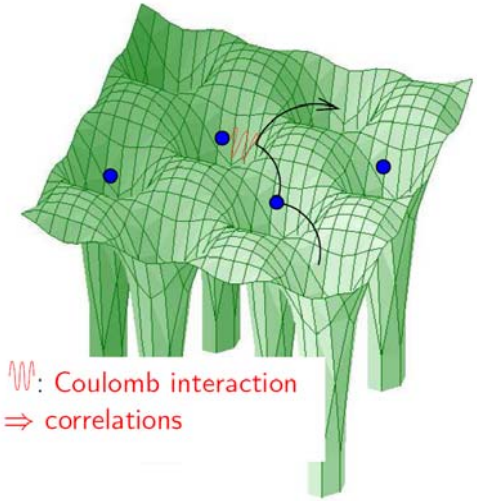
Dieter Vollhardt

Supported by Deutsche Forschungsgemeinschaft through SFB 484

Outline:

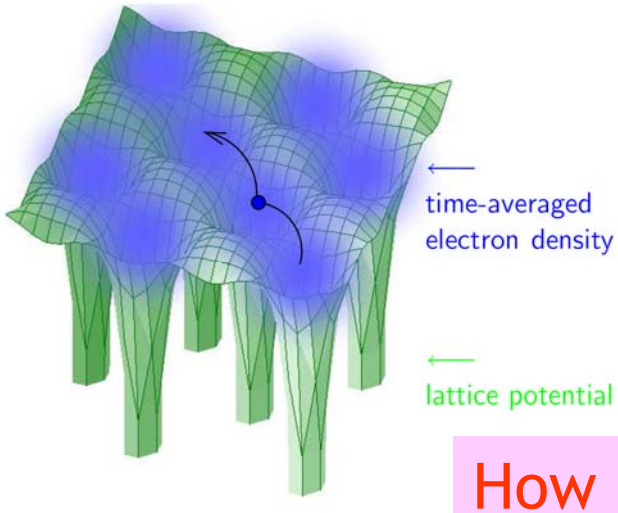
- Merging of density functional theory with DMFT ("LDA+DMFT")
- Application to transition-metal oxides

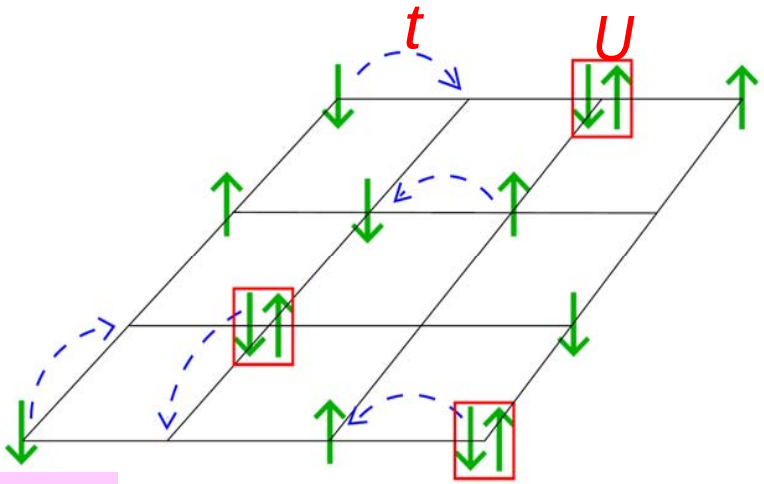
Correlated Electron Materials: LDA+DMFT



Held©2004

DFT/LDA		Model Hamiltonians	
+	material specific: "ab initio"	−	input parameters unknown
−	fails for strong correlations	+	systematic many-body approach
+	fast code packages	−	computationally expensive





How to combine?

Computational scheme for correlated electron materials:

Material specific electronic structure
(Density functional theory: **LDA,GW,...**)

+

Local electronic correlations
(Many-body theory: **DMFT**)

→ **LDA+DMFT**

Anisimov, Poteryaev, Korotin, Anokhin, Kotliar (1997)
Lichtenstein, Katsnelson (1998)
Nekrasov, Held, Blümer, Poteryaev, Anisimov, DV (2000)

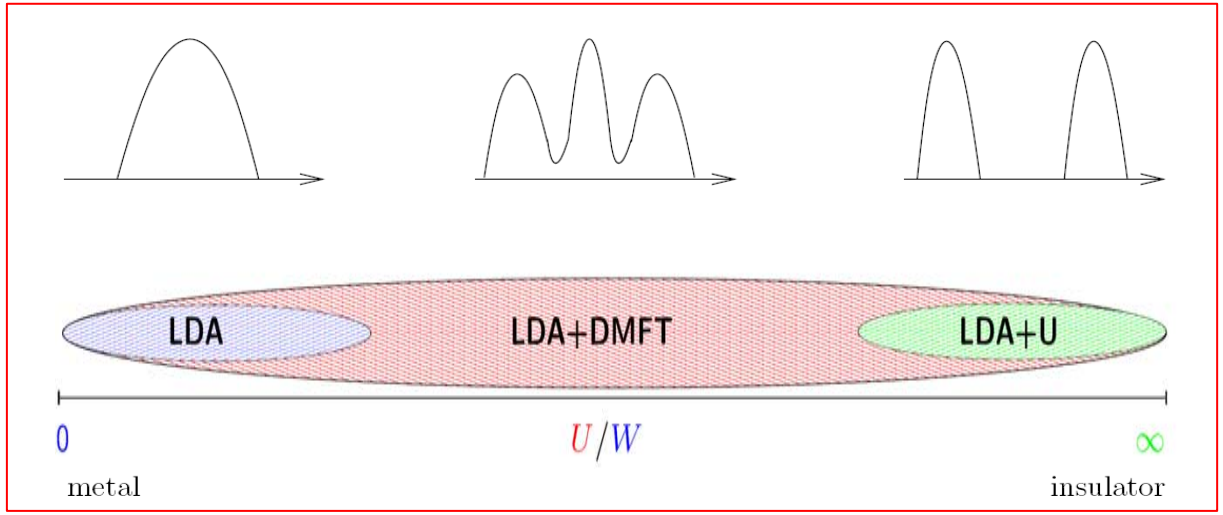
Physics Today, March 2004; Kotliar, DV

Computational scheme for correlated electron materials:

Material specific electronic structure
(Density functional theory: **LDA,GW,...**)

+

Local electronic correlations
(Many-body theory: **DMFT**)



LDA+DMFT (simplest version)

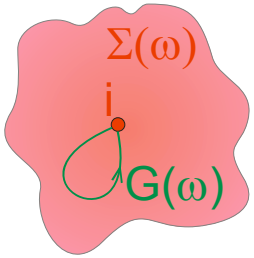
1) Calculate LDA band structure: $\varepsilon_{lml'm'}(k) \rightarrow \hat{H}_{LDA}$

2) Supplement LDA by local Coulomb interaction (only for correlated bands)

$$\hat{\mathcal{H}} = \underbrace{\sum_{\mathbf{k}\, lm\, l'm'\sigma} \epsilon_{lm\, l'm'}(\mathbf{k})\, \hat{c}^{\dagger}_{\mathbf{k}lm\sigma}\, \hat{c}_{\mathbf{k}l'm'\sigma}}_{\text{LDA}} \underbrace{- \sum_{\substack{i=i_d,\\ \ell=\ell_d}} \sum_{m\sigma} \Delta\varepsilon_d \hat{n}_{i\ell m\sigma}}_{\text{double counting correction}}$$

$$+ \underbrace{\sum_{\substack{i=i_d,\\ l=l_d}} {\sum_{m\sigma,m'\sigma'}}' \frac{U^{\sigma\sigma'}_{mm'}}{2} \hat{n}_{ilm\sigma}\hat{n}_{ilm'\sigma'}}_{\text{local Coulomb interaction}} \underbrace{- \sum_{\substack{i=i_d,\\ l=l_d}} {\sum_{m\sigma,m'\sigma'}}' J_{mm'} \hat{c}^{\dagger}_{ilm\sigma}\hat{c}^{\dagger}_{ilm'\sigma'}\hat{c}_{ilm'\sigma}\hat{c}_{ilm\sigma'}}_{\text{Hund's rule coupling}}$$

3) Solve self-consistently with an impurity solver,
e.g., QMC: LDA+DMFT(QMC)



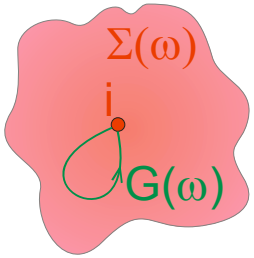
(i) Effective single impurity problem

$$G = -\frac{1}{Z}\int \mathcal{D}[\psi\psi^*]\psi\psi^* e^{\psi^*[G^{-1}+\Sigma]\psi - U\psi^*\psi\psi^*\psi + J\psi^*\psi\psi^*\psi}$$

(ii) *k*-integrated Dyson equ. (orbital degeneracy)

$$G(\omega) = \int d\varepsilon \frac{N^{LDA}(\varepsilon)}{\omega - \Sigma(\omega) - \varepsilon}$$

3) Solve self-consistently with an impurity solver,
e.g., QMC: LDA+DMFT(QMC)



(i) Effective single impurity problem

$$G = -\frac{1}{Z}\int \mathcal{D}[\psi\psi^*]\psi\psi^* e^{\psi^*[G^{-1}+\Sigma]\psi - U\psi^*\psi\psi^*\psi + J\psi^*\psi\psi^*\psi}$$

(ii) *k*-integrated Dyson equ. (general)

$$G^{\sigma}_{mm'}(\omega) = \frac{1}{V_B}\int d^3k \left[(\omega - \Sigma^{\sigma}(\omega))\delta_{m,m'} - \left(H^{0\ eff}_{LDA}(\mathbf{k})\right)_{m,m'}\right]^{-1}$$

LDA+DMFT(X): Search for the "best" impurity solver X

Hubbard I
IPT
NCA

ED
QMC (Hirsch-Fye)
NRG

Recent:

PQMC
DDMRG
CT-QMC

Application of LDA+DMFT

Spectral function ("interacting DOS") in DMFT

k-integrated spectral function
→ PES

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

k-resolved spectral function
→ ARPES

$$\mathbf{G}(\mathrm{k},\omega) = [\omega - \boldsymbol{\Sigma}(\omega) - \mathbf{H}^{0}_{LDA}(\mathrm{k})]^{-1}$$

Matrices in orbital space

$$A(\mathrm{k},\omega) = -\frac{1}{\pi}\,\mathrm{Im}\;Tr\,\mathbf{G}(\mathrm{k},\omega)$$

LDA+DMFT: Collaborators

Augsburg

K. Byczuk
V. Eyert
K. Held
G. Keller
M. Kollar
J. Kuneš
I. Leonov
T. Pruschke
X. Ren

Ekaterinburg

V. I. Anisimov
D. E. Kondakov
A. V. Kozhevnikov
A. V. Lukoyanov
I. A. Nekrasov
Z. Pchelkina
S. L. Skornyakov

UC Davis

R. T. Scalettar

Lawrence Livermore

A. K. McMahan

MPI Stuttgart

O. K. Andersen

Osaka

S. Suga
A. Sekiyama

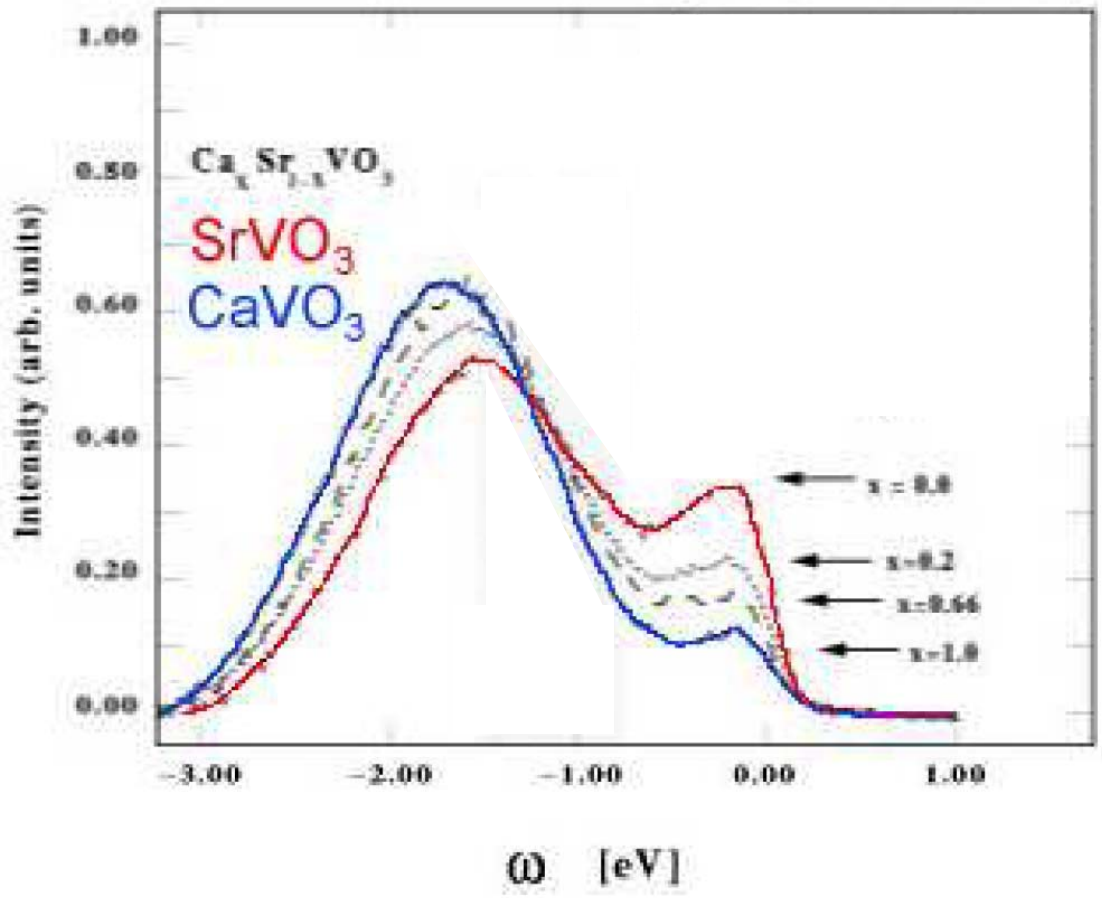
Ann Arbor

J. W. Allen
S.-K. Mo

1. Application:
$3d^1$ system $(Sr,Ca)VO_3$

$3d^1$ system: (Sr,Ca)VO_3

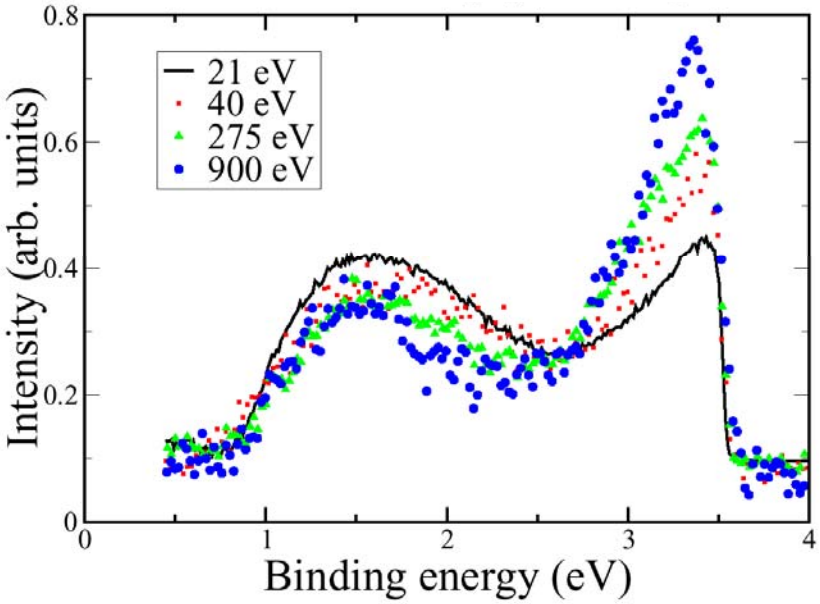
Photoemission spectroscopy (PES)



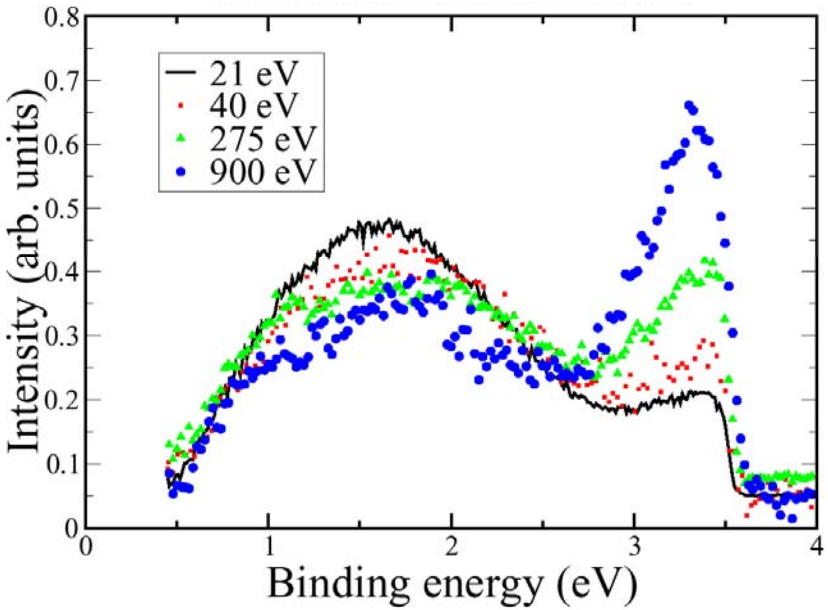
Inoue *et al.*, PRL (1995)

Experiment

Photoemission spectra at high photon energies



$SrVO_3$

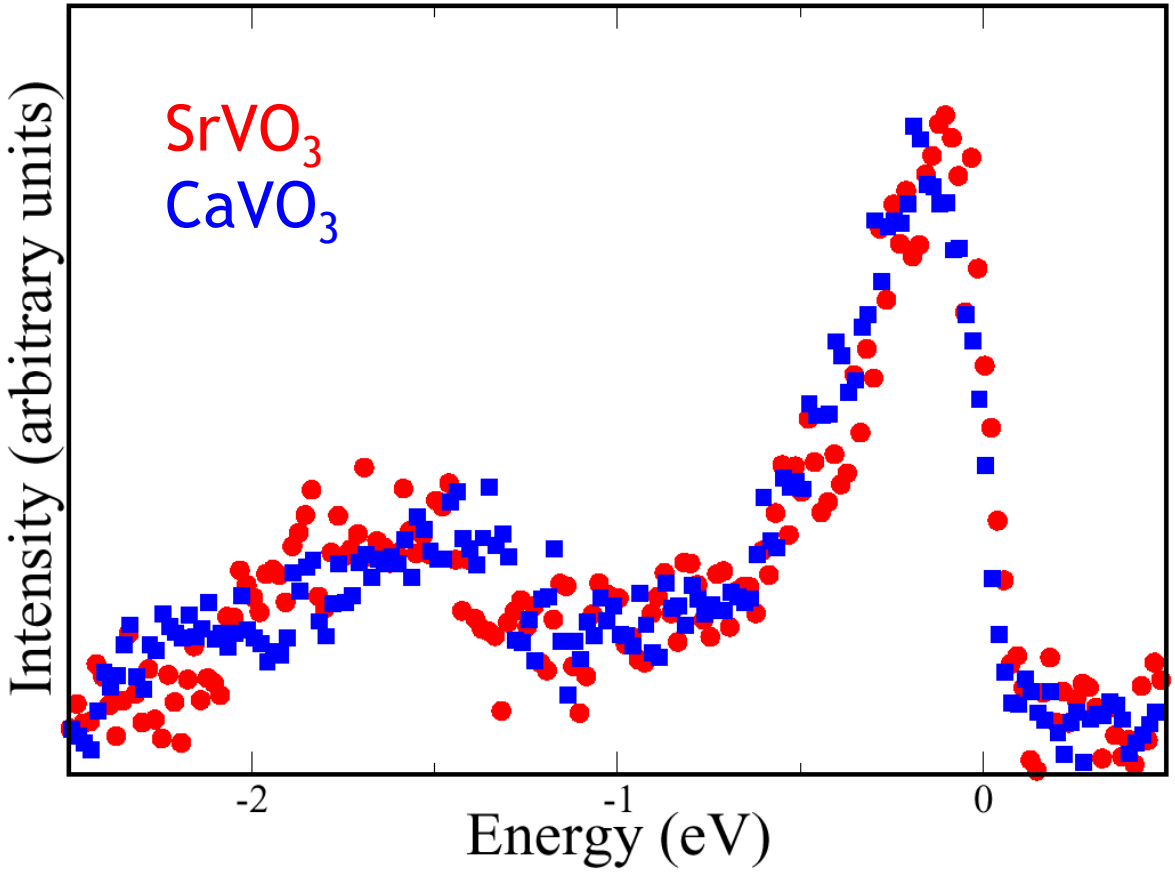


$CaVO_3$

Osaka – Augsburg – Ekaterinburg collaboration: Sekiyama *et al.*; PRL (2004)

Experiment

Photoemission spectra at high photon energies



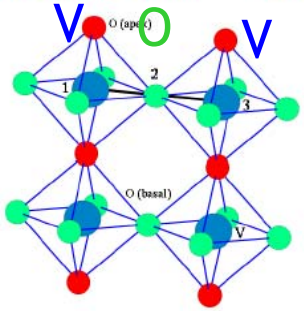
Osaka – Augsburg – Ekaterinburg collaboration: Sekiyama *et al.*; PRL (2004)

Theory

Electronic structure

Crystal structure

$SrVO_3$: $\angle V - O - V = 180°$

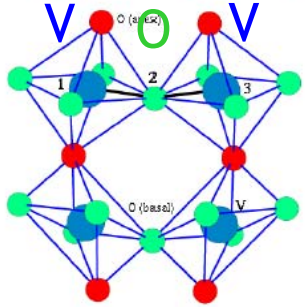


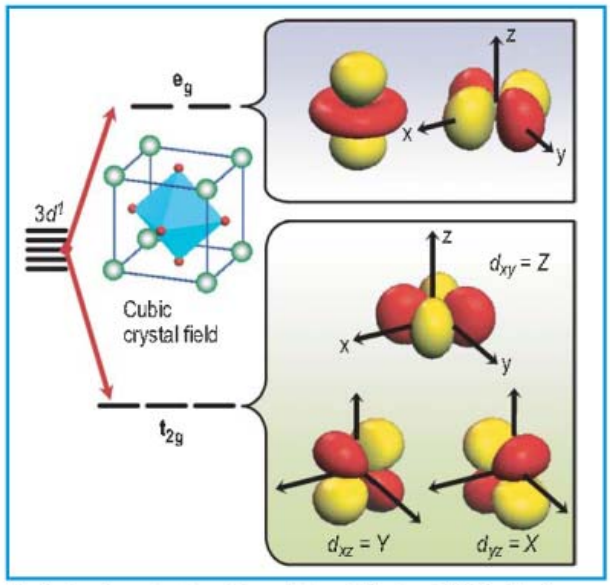
$\Downarrow$

orthorhombic distortion

$\Downarrow$

$CaVO_3$: $\angle V - O - V \approx 162°$



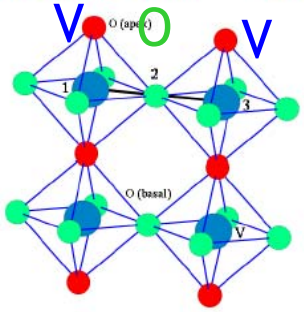


Theory

Electronic structure

Crystal structure

$SrVO_3$: $\angle V - O - V = 180°$

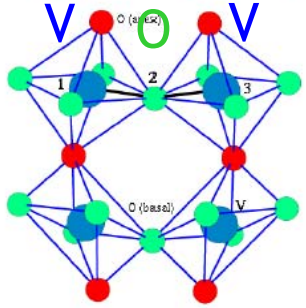


⇓

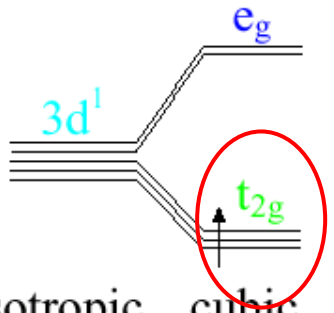
orthorhombic distortion

⇓

$CaVO_3$: $\angle V - O - V \approx 162°$

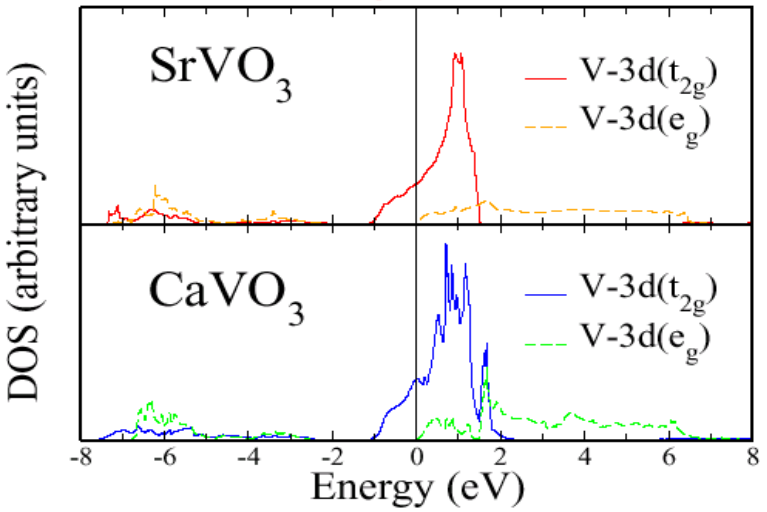


Band scheme



isotropic cubic

LDA density of states



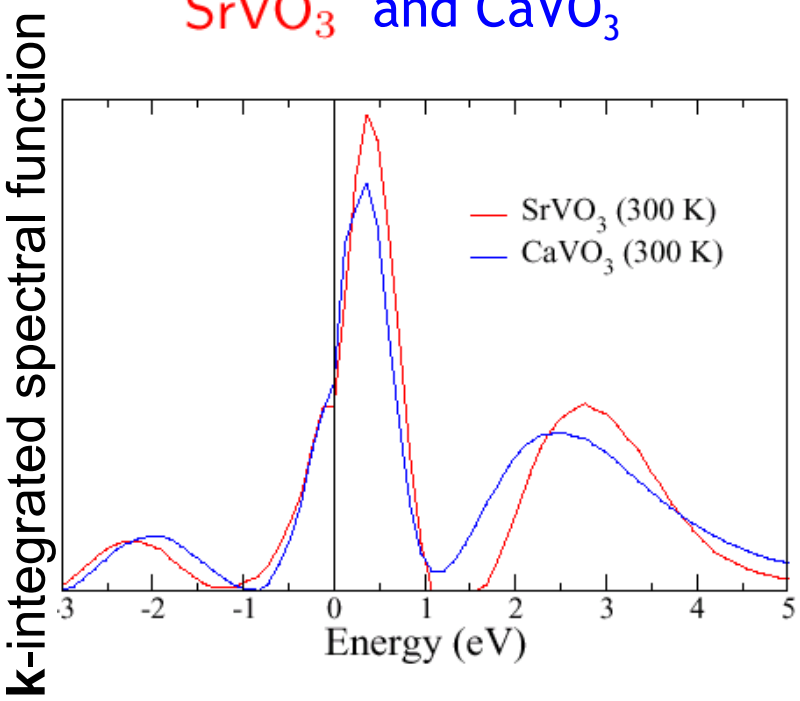
No correlation effects/spectral transfer

LDA+DMFT results

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

constrained LDA:
U=5.55 eV, J=1.0 eV

$SrVO_3$ and $CaVO_3$



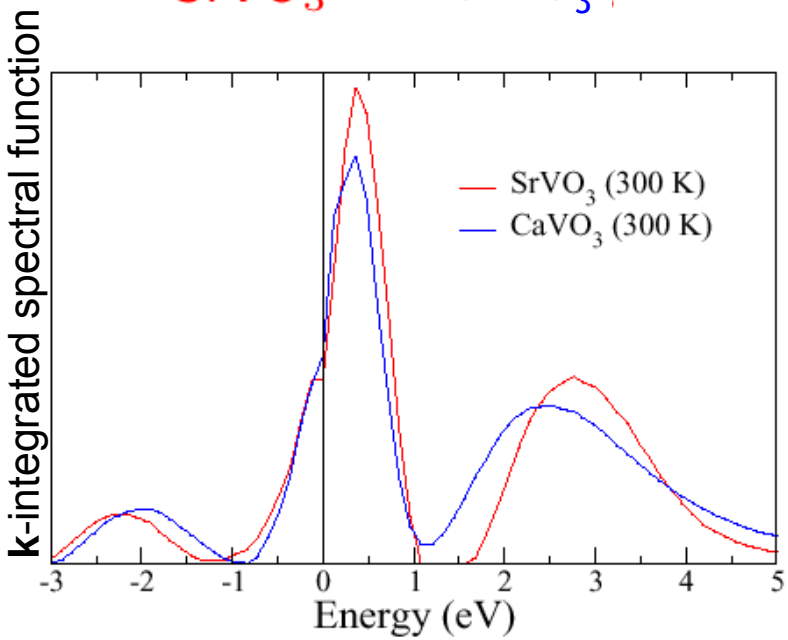
Correlation induced spectral transfer
→3-peak structure

Strongly correlated paramagnetic metal
(Mott-Hubbard system)

Osaka – Augsburg – Ekaterinburg collaboration: Sekiyama *et al.*; PRL (2004)

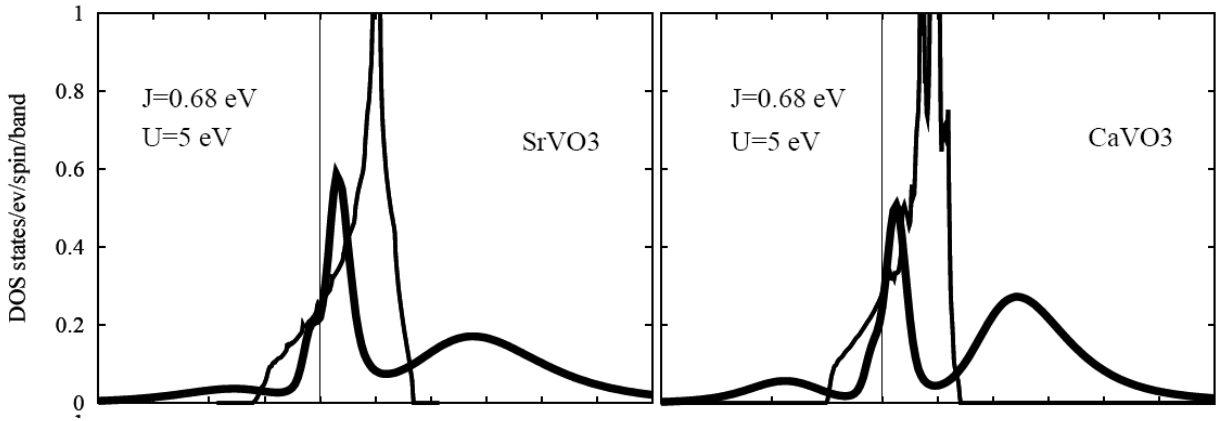
LDA+DMFT results

$SrVO_3$ and $CaVO_3$



Constrained LDA:
U=5.55 eV, J=1.0 eV

Osaka – Augsburg – Ekaterinburg collaboration: Sekiyama *et al.*, PRL **93**, 156402 (2004)



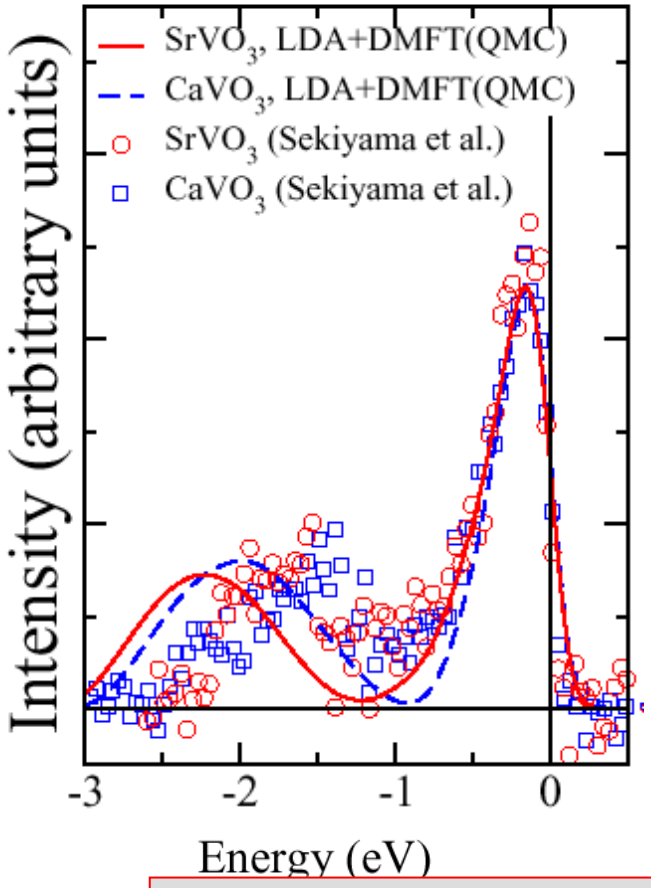
Pavarini, Biermann, Poteryaev, Lichtenstein, Georges, Andersen (2004)

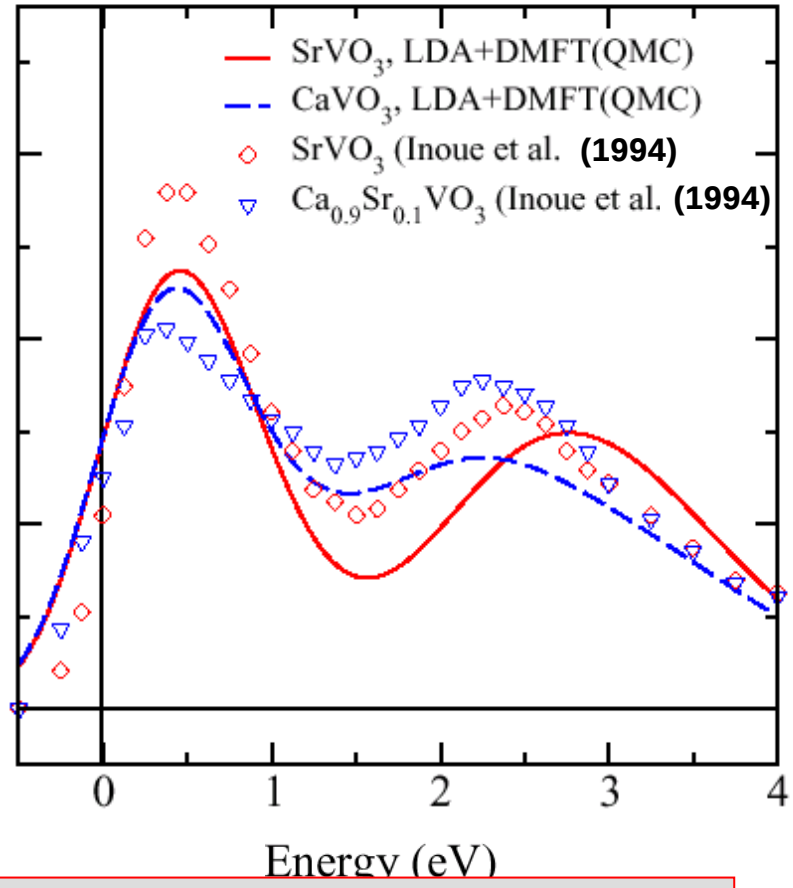
Comparison with experiment

Osaka – Augsburg –Ekaterinburg collaboration,
Sekiyama *et al.*, PRL (2004)
Nekrasov *et al.*, PRB (2005)

- (i) bulk-sensitive high-resolution photoemission spectra (PES)
- (ii) $1s$ x-ray absorption spectra (XAS)

Measurement at O K-edge:
no symmetry breaking of V 2p
shell in final state (XAS ≈IPES)

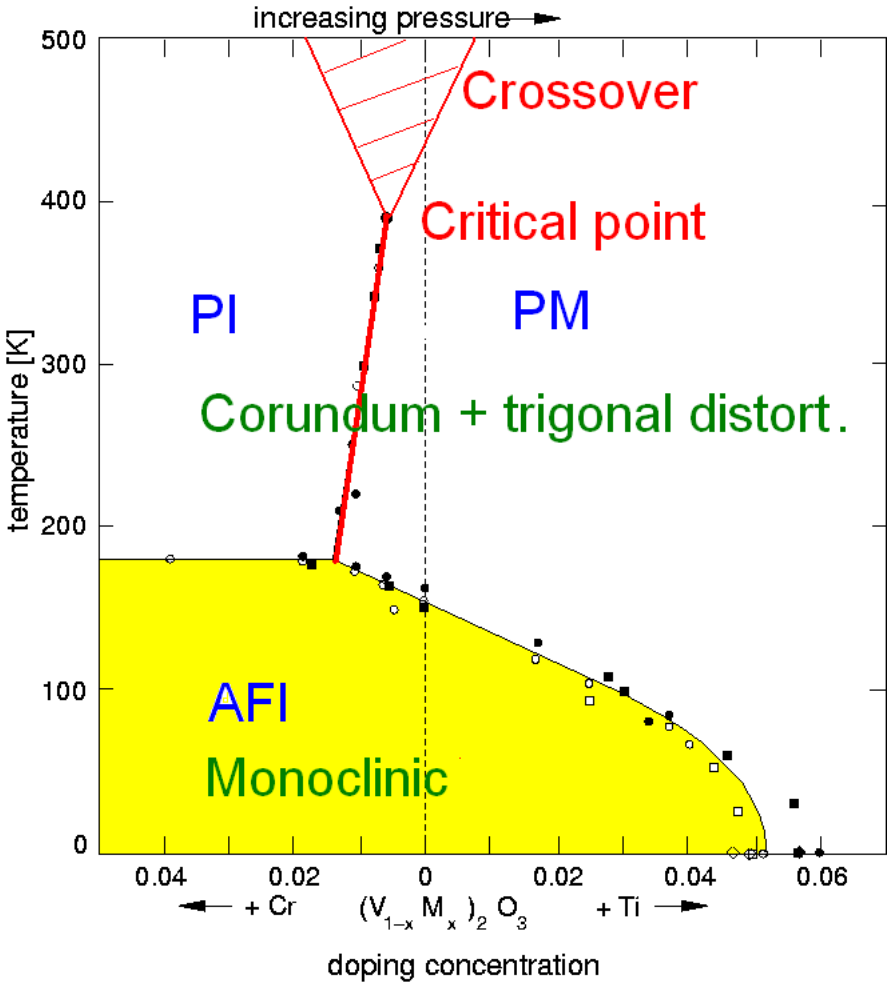


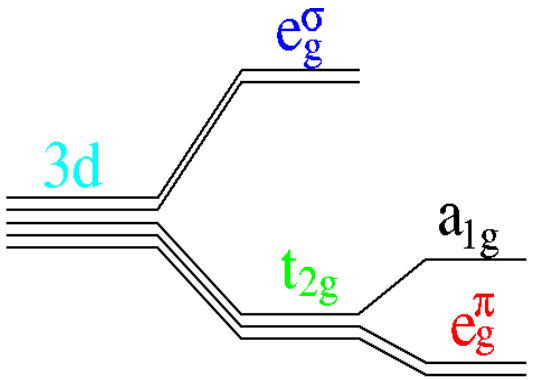


Confirmation of three-peak structure in correlated bulk systems

2. Application:
$3d^2$ system: V_2O_3

$3d^2$ system: V_2O_3

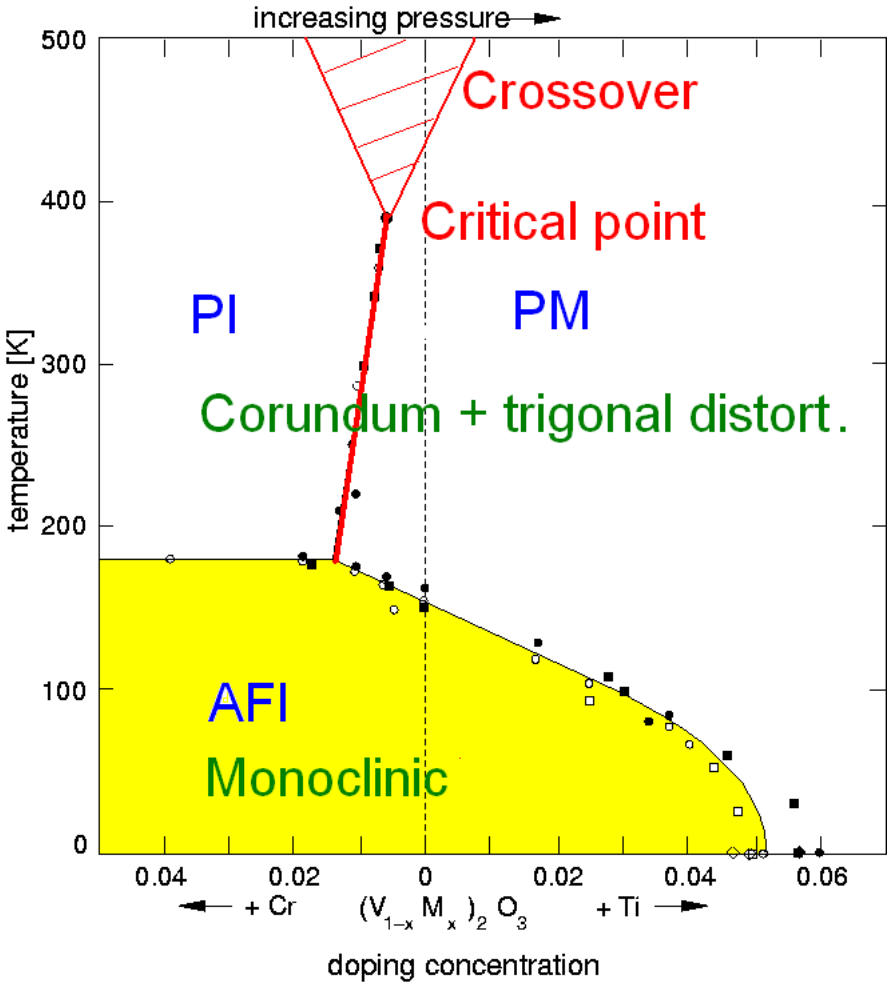




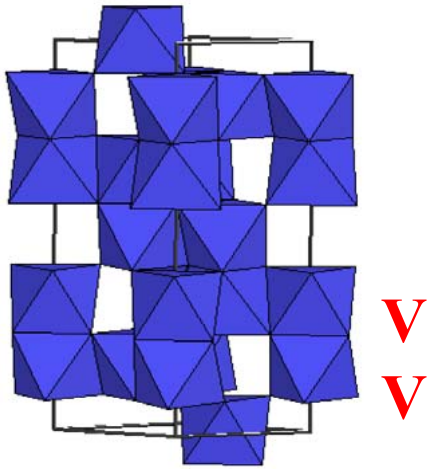
isotropic cubic trigonal

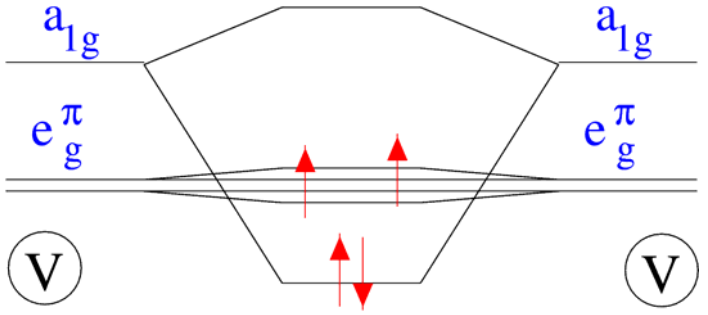
← increasing interaction U

$3d^2$ system: V_2O_3



← increasing interaction U

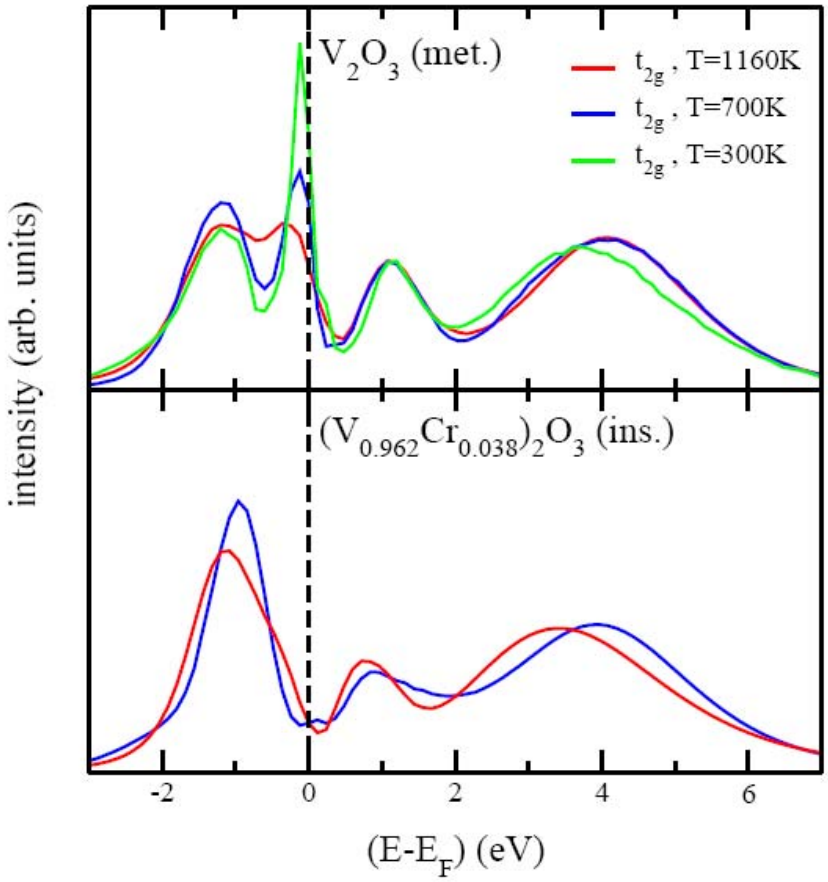




Castellani, Natoli, Ranninger (1978)

a_{1g} singlet

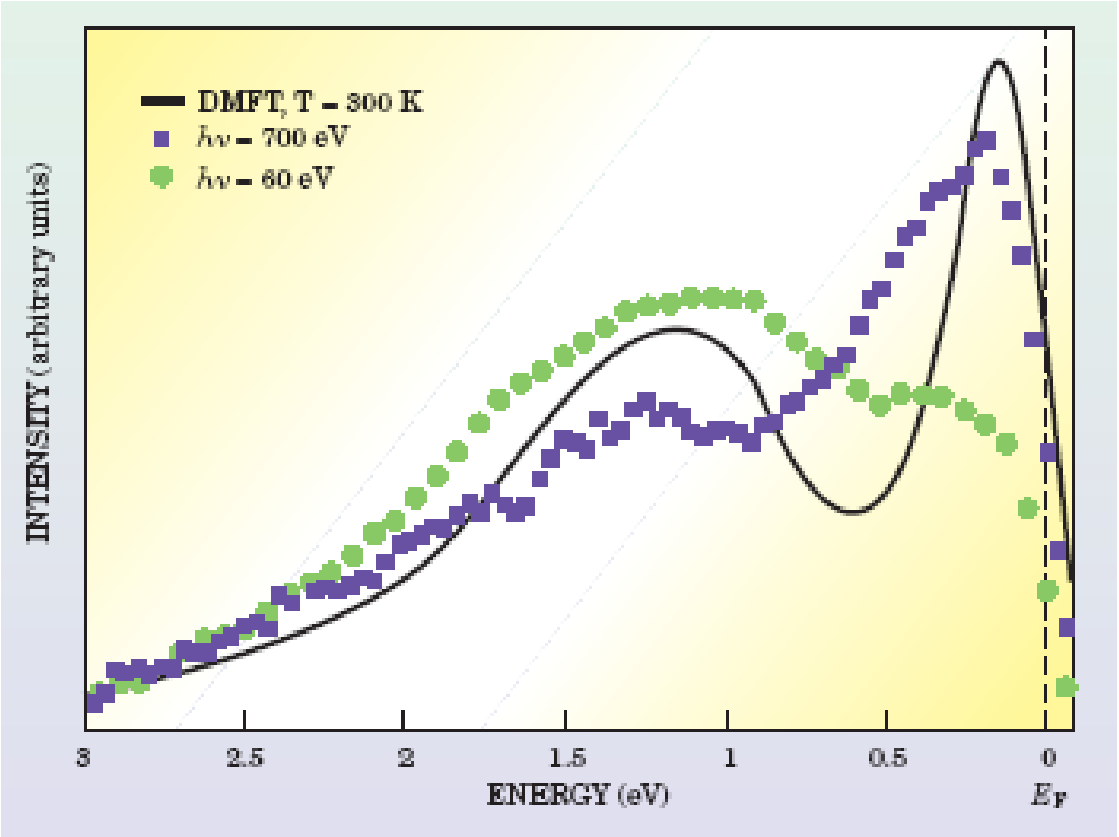
V_2O_3: LDA+DMFT Spectra



U=5.0 eV, J=0.93 eV

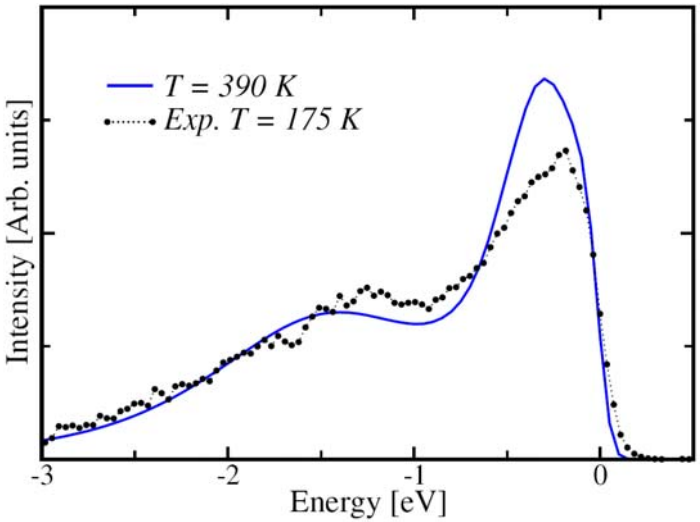
Held, Keller, Eyert, DV, and Anisimov, PRL (2001),
Keller, Held, Eyert, DV, and Anisimov; PRB (2004)

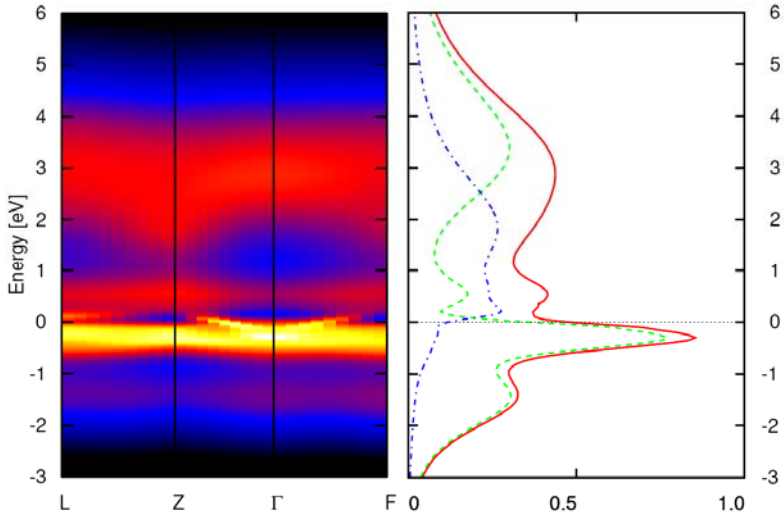
Metallic V_2O_3: Photoemission Spectra



Ann Arbor – Osaka – Augsburg – Ekaterinburg collaboration; Mo *et al.*, PRL (2003)

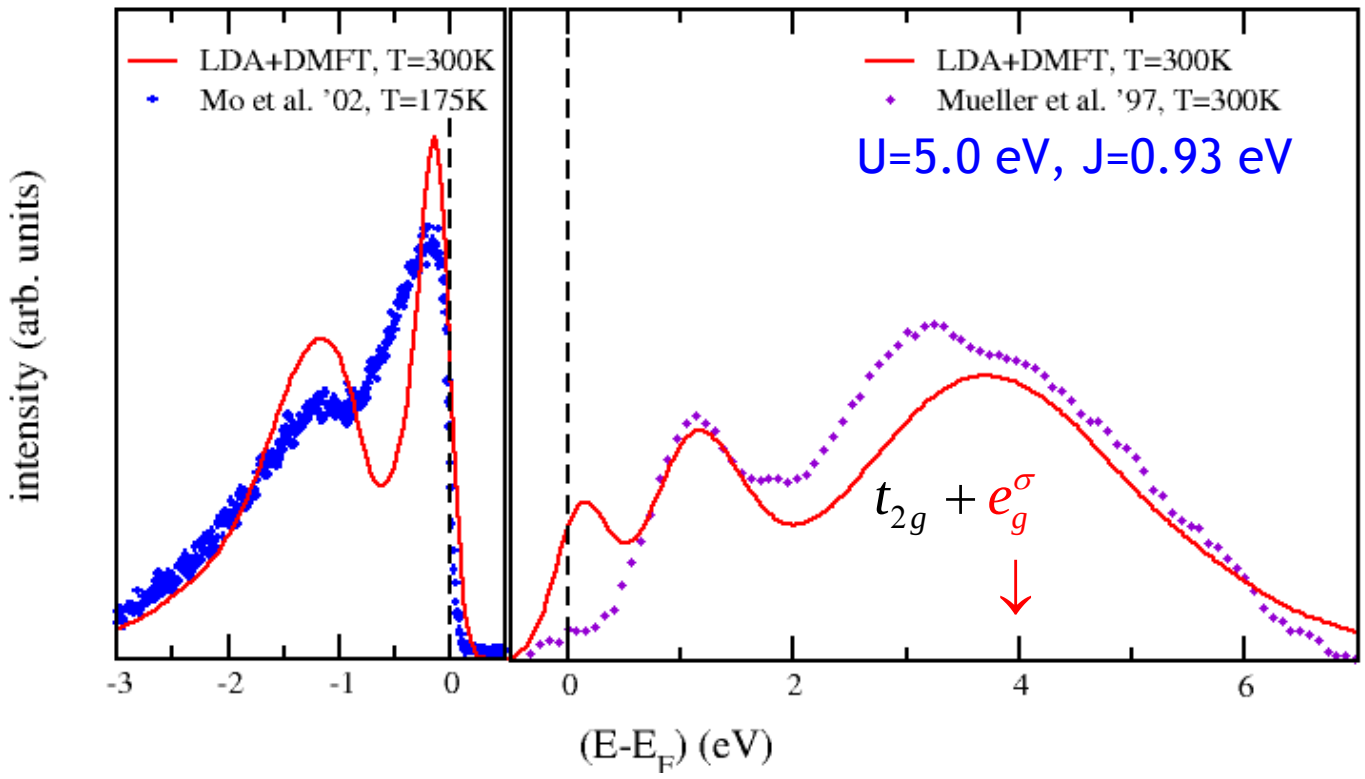
Metallic V_2O_3: Photoemission Spectra in LDA+DMFT and Experiment





Poteryaev, Tomczak, Biermann, Georges, Lichtenstein, Rubtsov, Saha-Dasgupta, Andersen (2007)

Metallic V_2O_3: Photoemission and XAS Spectra in Theory and Experiment

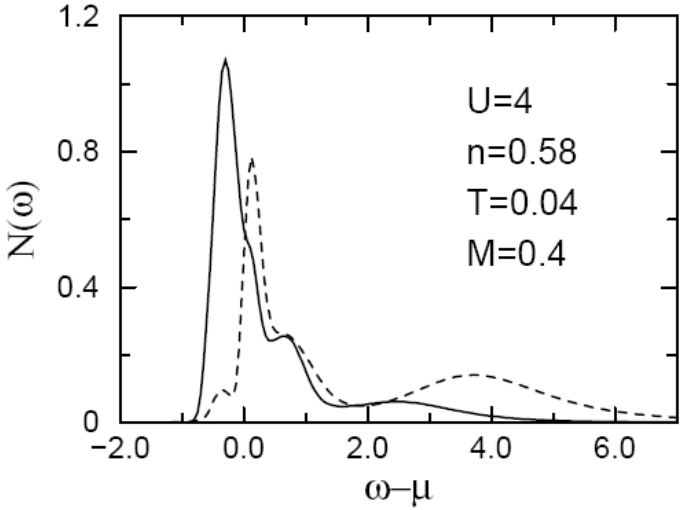


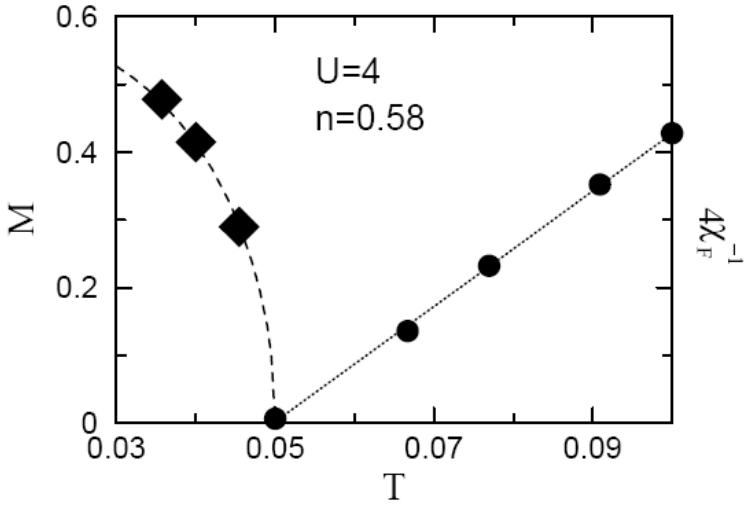
Ann Arbor – Osaka – Augsburg – Ekaterinburg collaboration; Mo *et al.*, PRL (2003)

3. Application:
Ferromagnetic Materials

DMFT: Ferromagnetism in the one-band Hubbard model

Ulmke (1998)

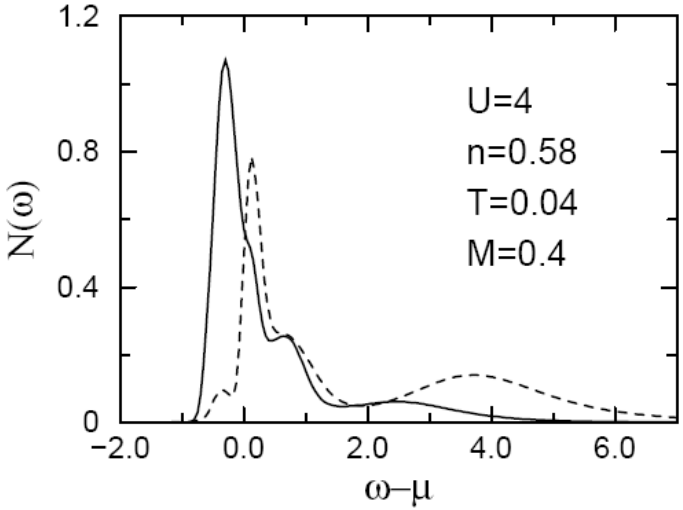


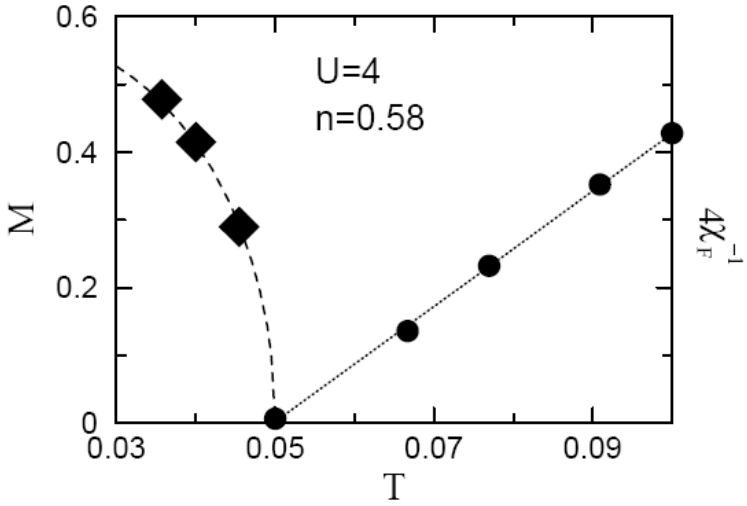


Generalized fcc lattice ($Z \to \infty$)

DMFT: Ferromagnetism in the one-band Hubbard model

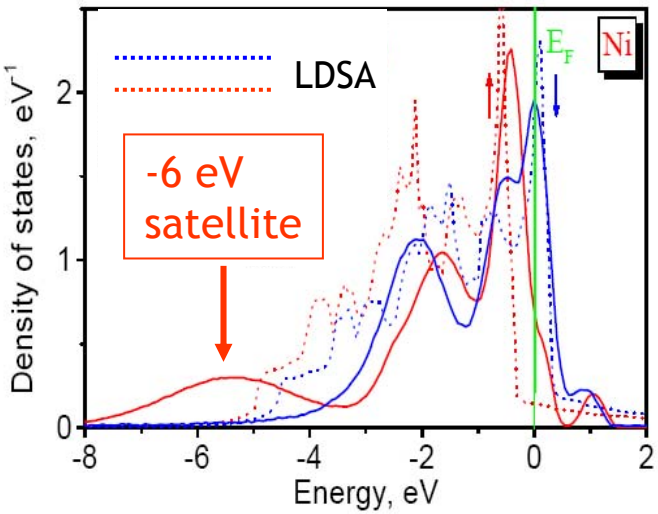
Ulmke (1998)

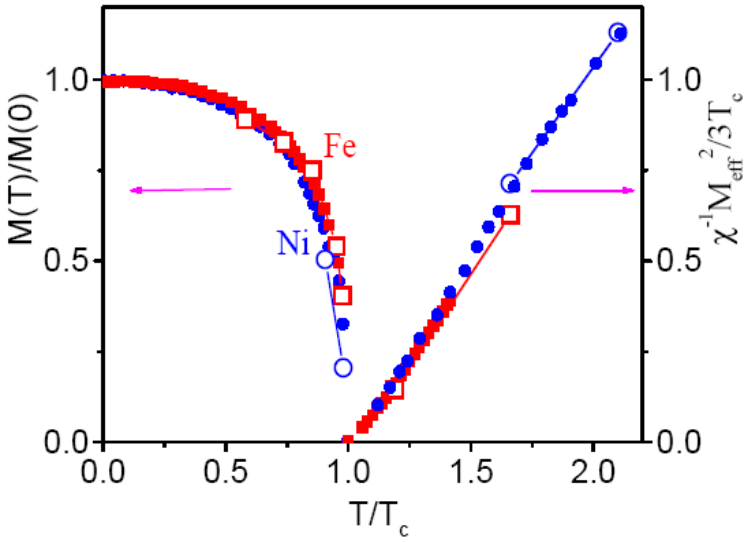




LDA+DMFT for ferromagnetic Ni

Lichtenstein, Katsnelson, Kotliar (2004)



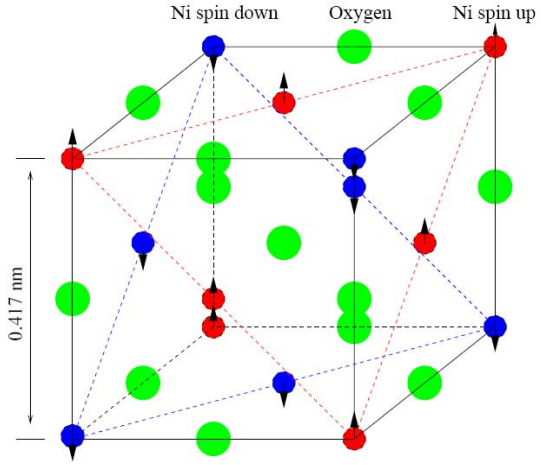


4. Application:
Mott-Hubbard vs. charge-transfer insulator

NiO

NiO: Mott-Hubbard vs. Charge-Transfer Insulator

NiO (Bunsenite)



- Rock-salt structure
- Type II antiferromagnet (AF), T_N= 523 K
- Moment $\sim$ 1.8 μ_B
- Insulator with large energy gap $\sim$ 4 eV; persists up to > 1000 K

LDA: metallic ground state

LSDA: AF, but
- gap + moment too small
- gap due to AF

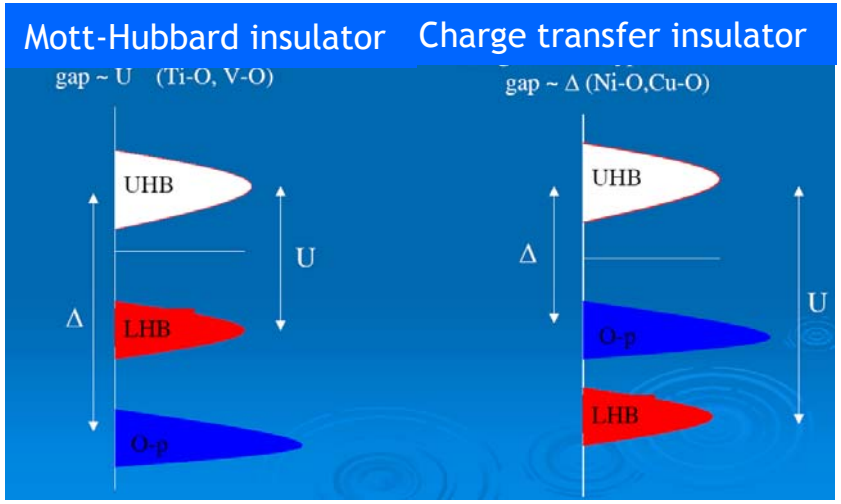
NiO

"Surprising properties of materials with incompletely filled 3*d* bands"

Boer, Verwey (1937)
Peierls, Mott (1937)

- Antiferromagnet, T_N= 523 K
- Insulator with gap ~ 4 eV; persists up to > 1000 K

NiO: Really a prototypical Mott-Hubbard insulator?



Mott (1949)
Hubbard (1963, 1965)

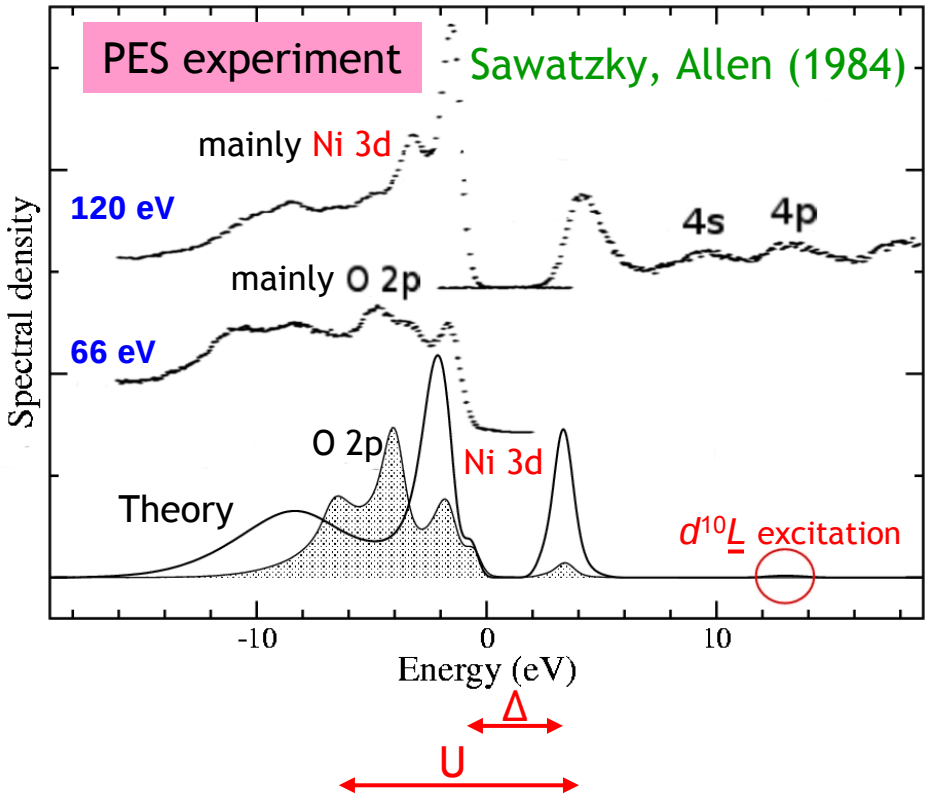
Zaanen, Sawatzky, Allen (1985)

→ Need to include correlated Ni-3d + O-2p states (p-d hybridization)

NiO: LDA+DMFT in Wannier function basis

p-d hybridization in LDA+DMFT → 8-band Hamiltonian

Kuneš, Anisimov, Lukoyanov, DV; PRB (2007)



- charge-transfer gap clearly seen
- correct position of p-band
- valence band: p-d character
- conduction band: d-character
- lower Hubbard at -9 eV

p-d hybridization is essential

NiO: LDA+DMFT in Wannier function basis

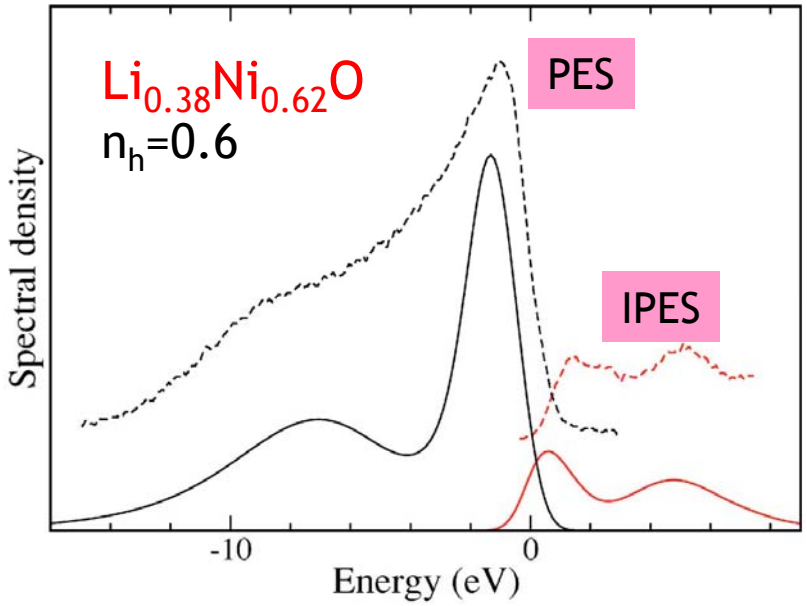
p-d hybridization in LDA+DMFT → 8-band Hamiltonian

Kuneš, Anisimov, Lukoyanov, DV; PRB (2007)

Hole doping of NiO

$Li_xNi_{1-x}O$ van Elp, Eskes, Kuiper, Sawatzky (1992)

$xNi^{2+} \rightarrow Li^{1+} \Rightarrow n_h \approx \frac{x}{1-x}$ per Ni site



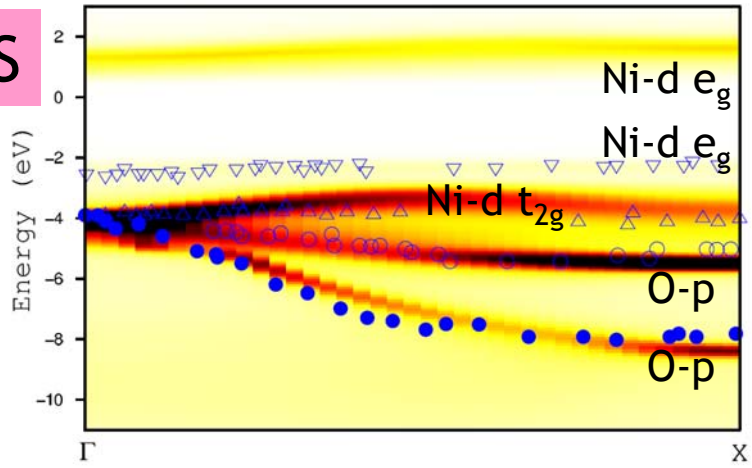
Spectral transfer → Mott gap filled

NiO: LDA+DMFT in Wannier function basis

p-d hybridization in LDA+DMFT → 8-band Hamiltonian

Kuneš, Anisimov, Lukoyanov, DV; PRB (2007)

ARPES



Exp.:
Shen *et al.* (1990,1991)

Theory:
Kuneš, Anisimov, Skornyakov, Lukoyanov, DV; PRL (2007)

- Ni-d bands only weakly dispersive
- O-p bands dispersive
- Result of d-correlations + p-d hybridization

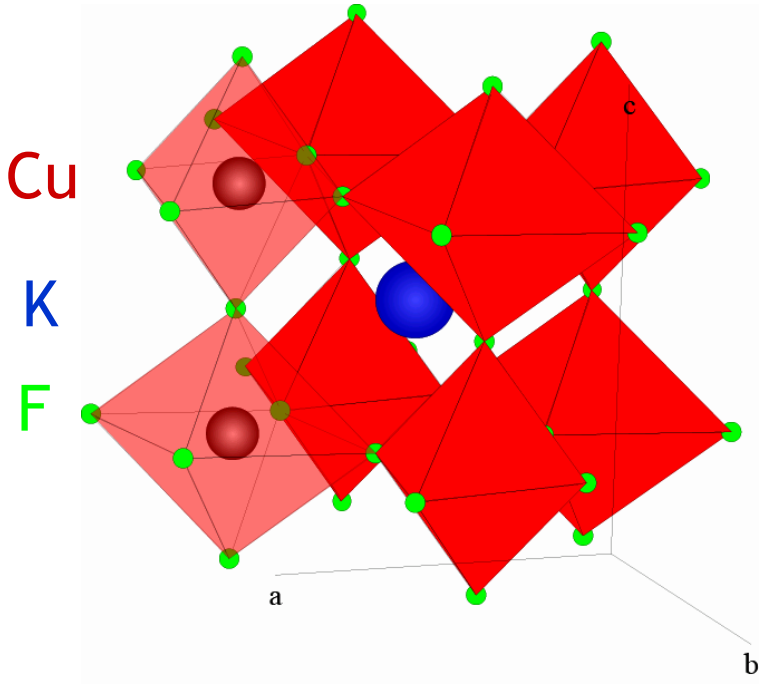
5. Application:
Correlation-induced structural transformation

$KCuF_3$

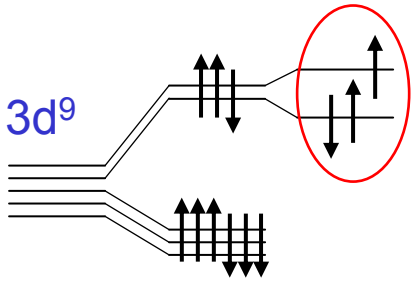
$KCuF_3$: Prototypical Jahn-Teller system

Room temperature crystal structure:

Kugel, Khomskii (1982)
Liechtenstein, Anisimov, Zaanen (1995)



Band scheme:



← single hole

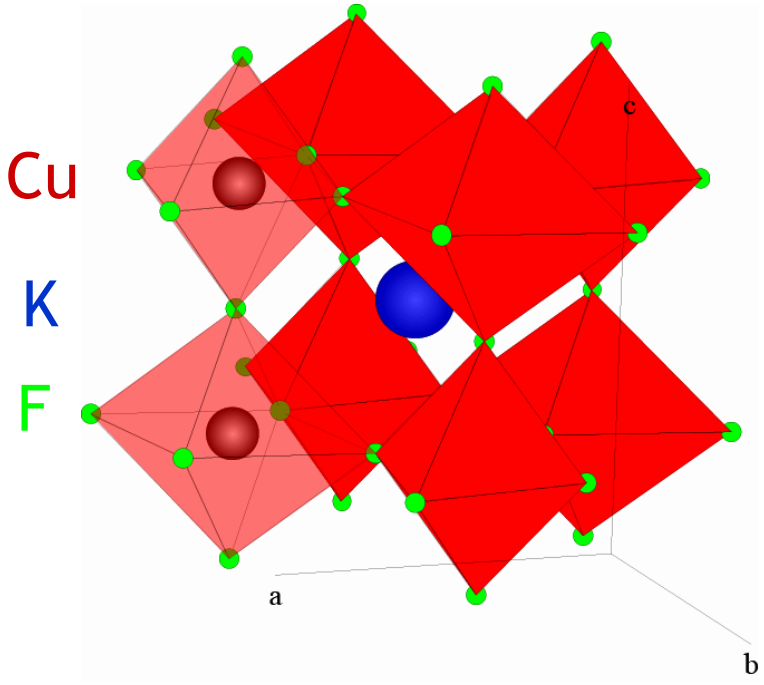
isotropic O_h tetragonal [I4/mcm] (c/a < 1)

- insulating, pseudo-cubic perovskite
- T_{Neel} ~38 K

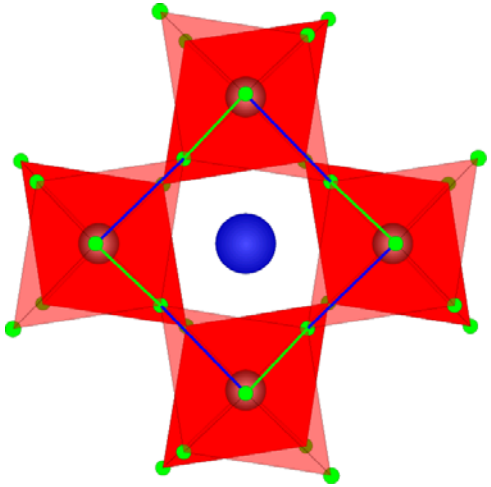
Cooperative JT distortion = spontaneous lifting of orbital degeneracy
→ orbital order → structural relaxation with symmetry reduction

$KCuF_3$: Prototypical Jahn-Teller system

Room temperature crystal structure:



Kugel, Khomskii (1982)
Liechtenstein, Anisimov, Zaanen (1995)

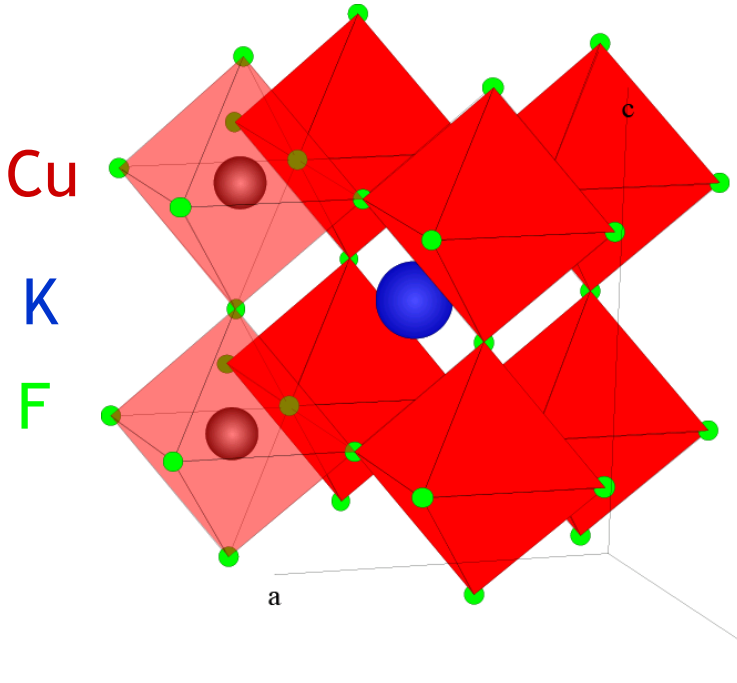


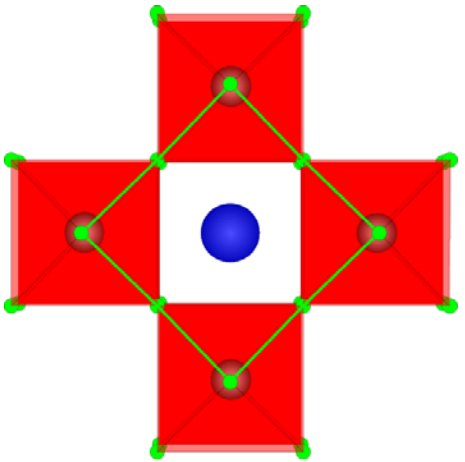
Cooperative JT distortion

$KCuF_3$: Prototypical Jahn-Teller system

Room temperature crystal structure:

Kugel, Khomskii (1982)
Liechtenstein, Anisimov, Zaanen (1995)

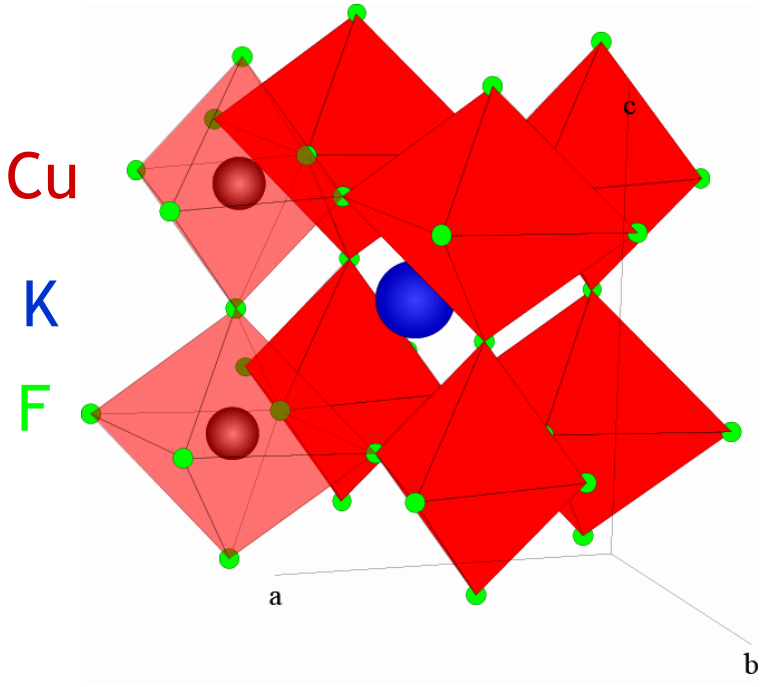




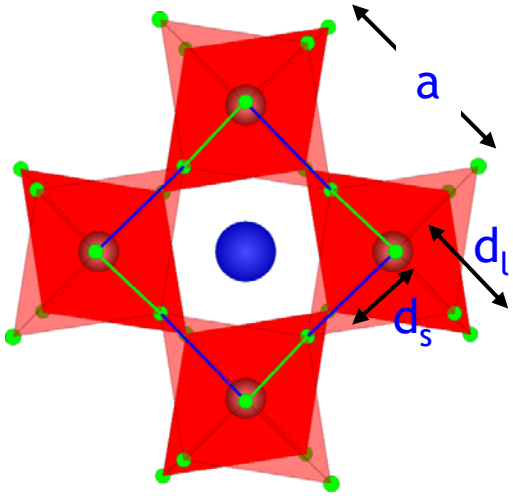
Undistorted structure

$KCuF_3$: Prototypical Jahn-Teller system

Room temperature crystal structure:



Kugel, Khomskii (1982)
Liechtenstein, Anisimov, Zaanen (1995)



JT-distortion $\delta_{JT} = (d_l - d_s)/a$

$T > T_N \sim 38$ K : Correlated paramagnetic insulator with strong JT distortion

LDA/GGA+U predicts magnetic LRO

How to determine - cooperative JT-distortion ?
- correct orbital order ?

$KCuF_3$: GGA+DMFT results

Leonov, Bingelli, Korotin, Anisimov, Stojic, DV; PRL (2008)

Implementation with plane-wave pseudo-potentials

U = 7.0 eV, J = 0.9 eV

GGA:

- metallic solution
- very shallow minimum of energy at δ_{JT} = 2.5 %
  → δ_{JT} = 0 for T > 100 K
  (no orbital order)

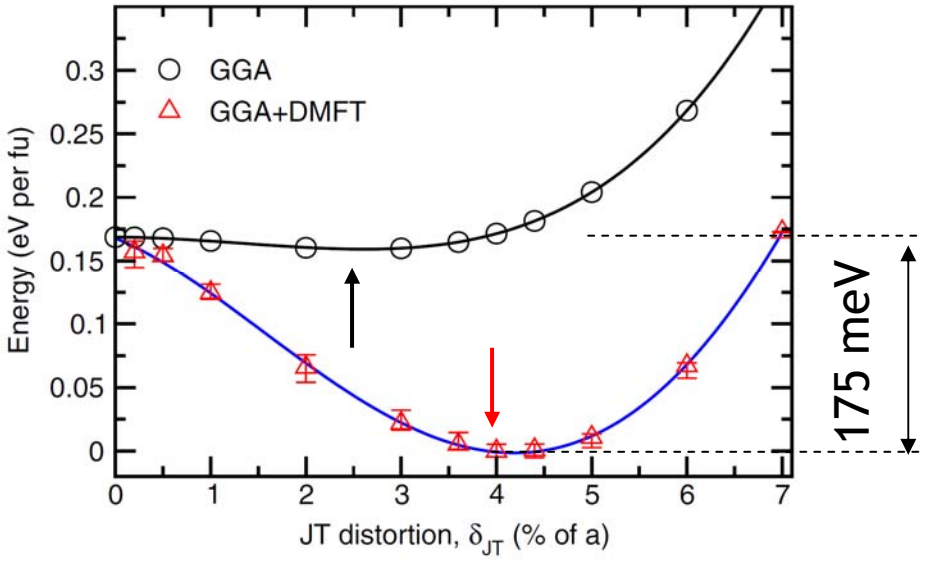
Inconsistent with experiment

GGA+DMFT:

- paramagnetic insulator
- δ_{JT}^{opt}= 4.13% → JT distortion persists up to 1000 K (melting)
- AF orbital order

Good agreement with experiment at 300 K

Total energy

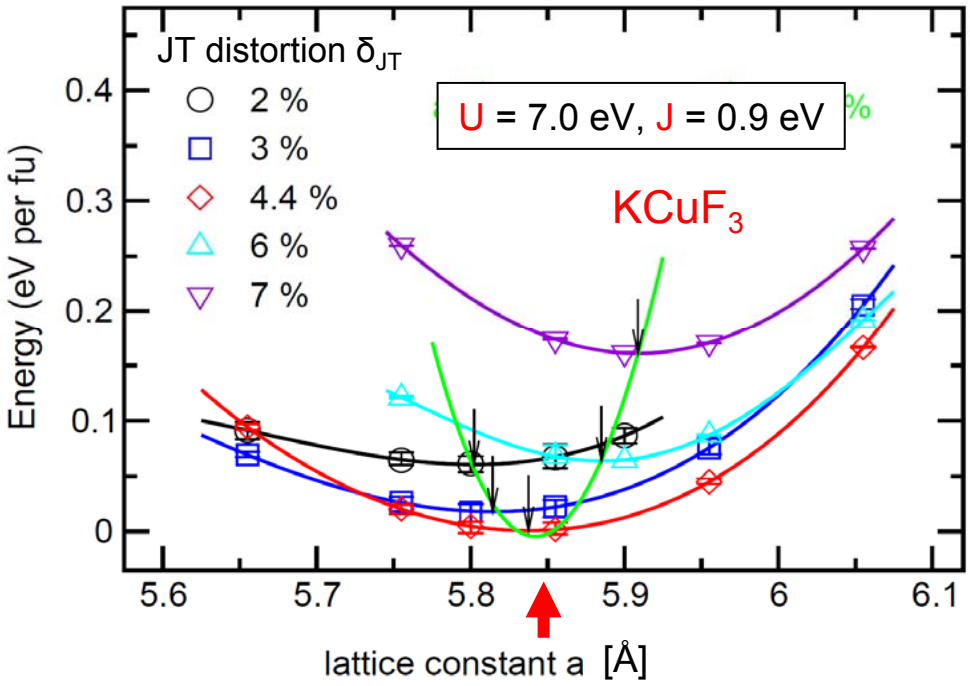


→ Structural transformation caused by electronic correlations

$KCuF_3$: GGA+DMFT results

Leonov, Bingelli, Korotin, Anisimov, Stojic, DV; PRL (2008)

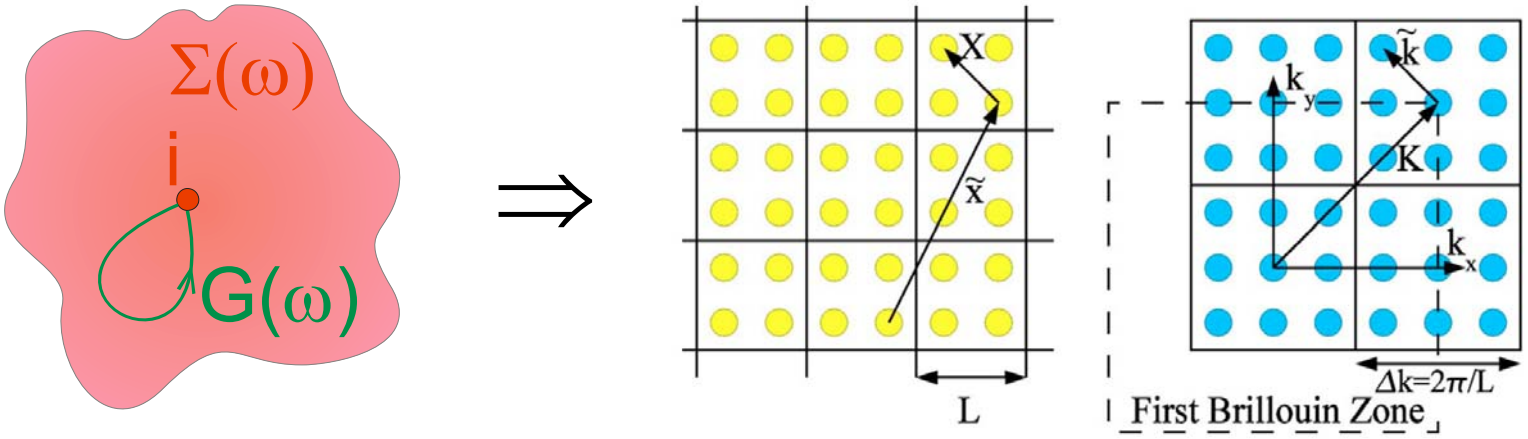
Implementation with plane-wave pseudo-potentials



Beyond DMFT

Cluster Extensions

- Dynamical cluster approx. (DCA) — Hettler *et al.* (1998, 2000)
- Cluster DMFT (CDMFT) — Kotliar *et al.* (2001)
- Self-energy functional theory — Potthoff (2003)

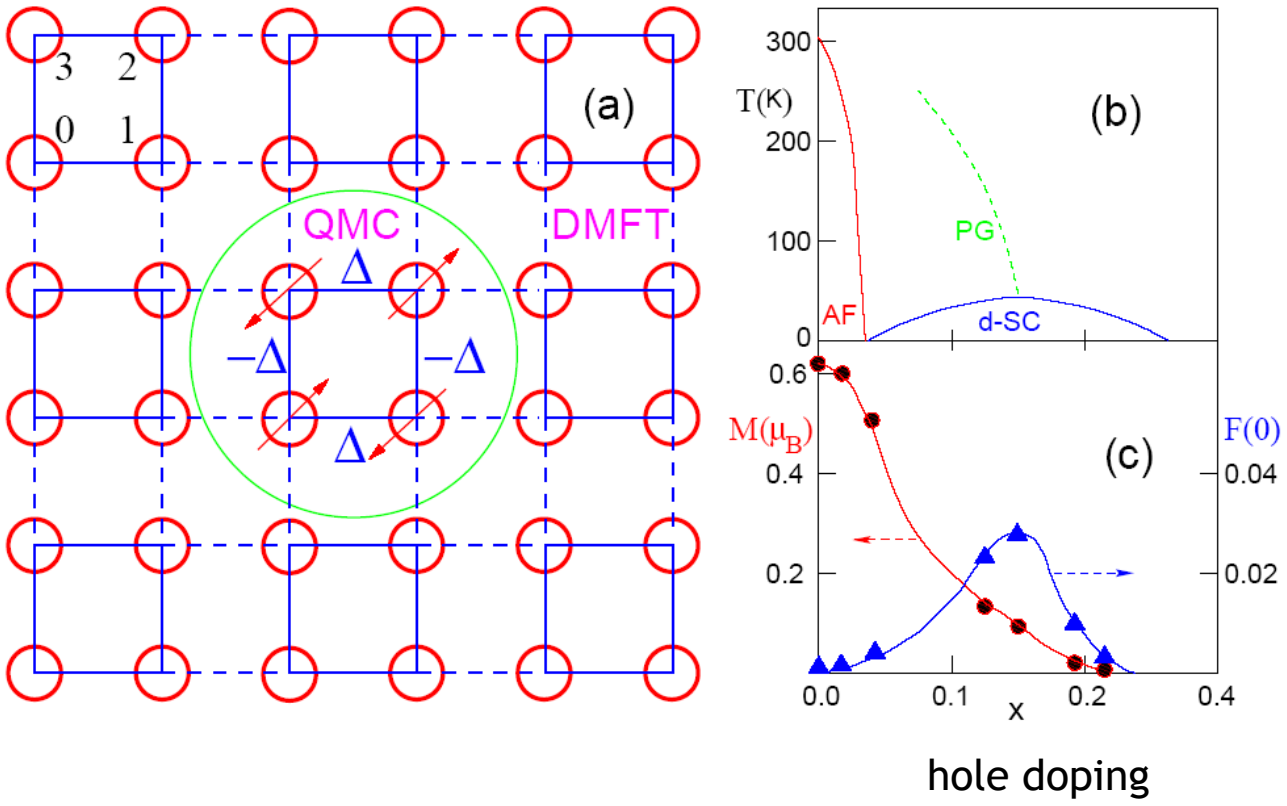


Dynamical vertex approximation (DΓA)

Local + non-local self-energy diagrams from local irred. vertex

Toschi, Katanin, Held (2006)

Antiferromagnetic *d*-wave
2 × 2 periodically repeated cluster

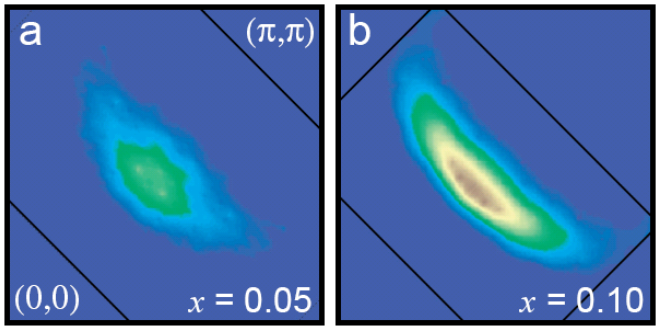


hole doping

Lichtenstein, Katsnelson (2000)

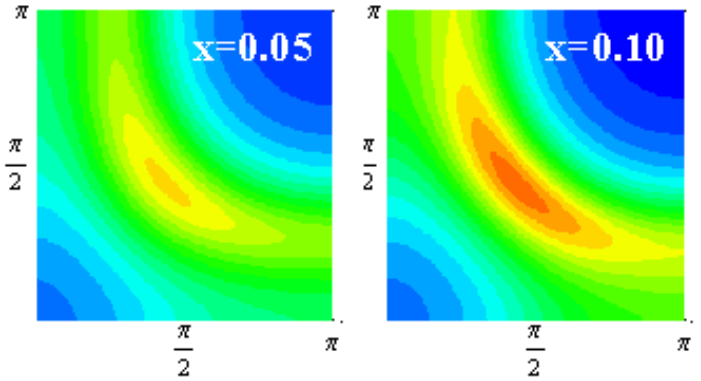
Comparison with Experiments in Cuprates: Spectral Function $A(\mathbf{k}, \omega \to 0)$ vs. $\mathbf{k}$

hole doped



Shen *et al.* (2004)

2x2 CDMFT



Civelli, Capone, Kancharla, Parcollet, Kotliar (2005)

Long-term goal

Explanation + prediction of general properties of complex correlated electron materials, e.g.,