When Mott and Peierls meet: interplay of correlation effects with structural and orbital degrees of freedom

Antoine GEORGES

KITP, June 2004

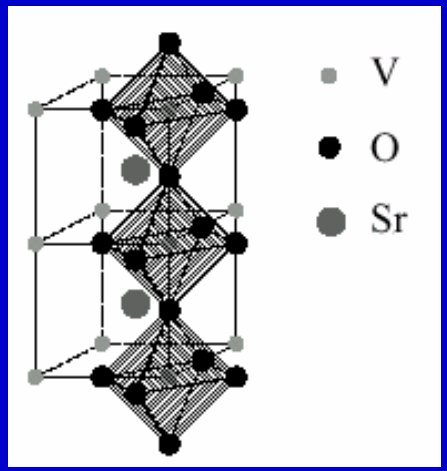
OUTLINE

- Suppression of orbital fluctuations in some d^1 oxides (PRL **92**,176403-2004)
- VO_2 explained: correlations helping the Peierls insulating transition
- The intriguing properties of $BaVS_3$

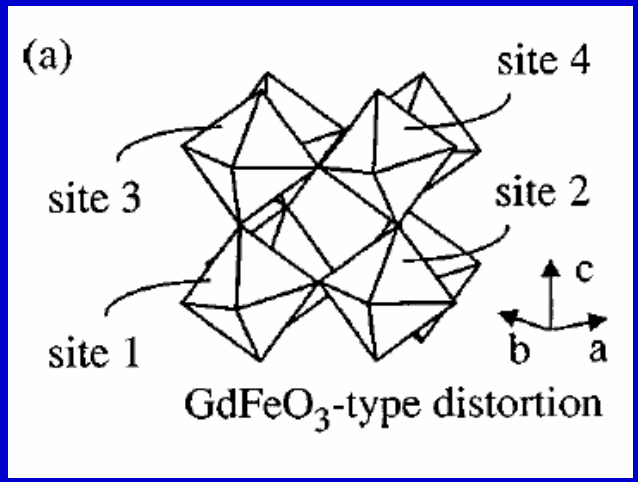
Collaborators:

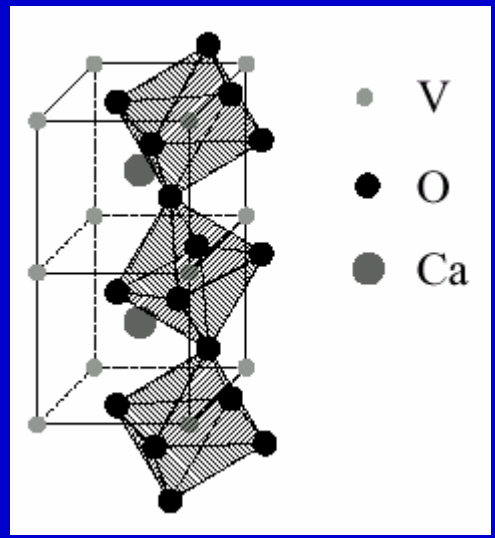
- Silke Biermann, Frank Lechermann (Ecole Polytechnique)
- Alexander Poteryaev (Nijmegen, and E.P)
- Eva Pavarini (Pavia)
- Alexander Lichtenstein (Hamburg)
- Olle K. Andersen (MPI Stuttgart)

d^1 perovskites
$SrVO_3$, $CaVO_3$, $LaTiO_3$, $YTiO_3$

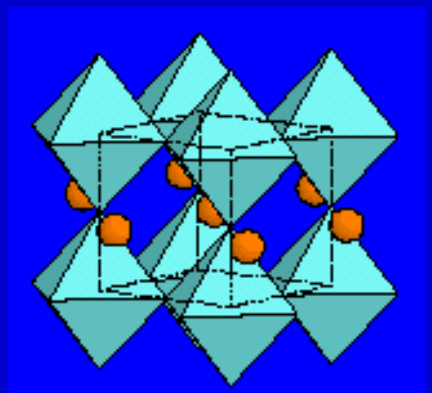


Cubic structure



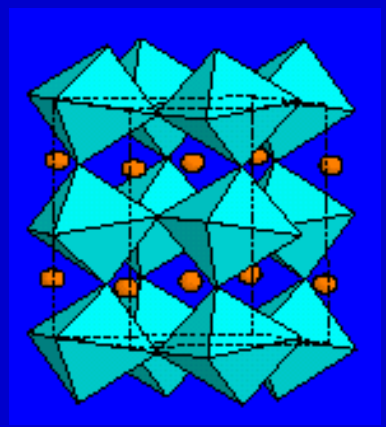


Distorted structure

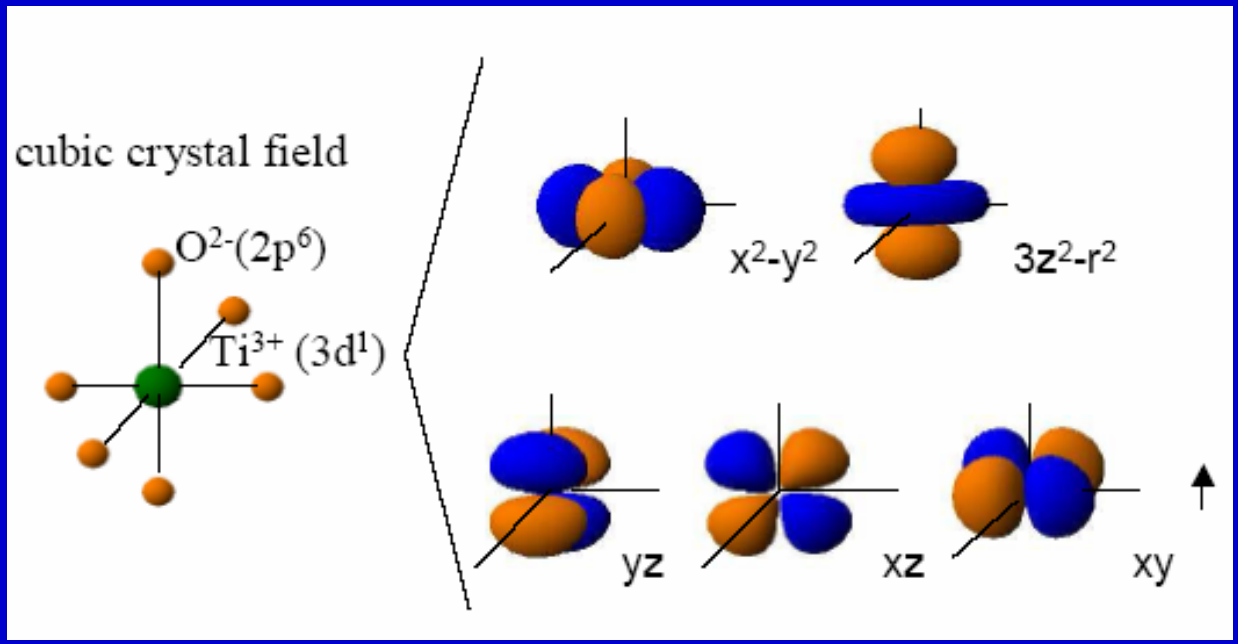


SrVO3 perfectly cubic;
Distortion increases:
CaVO3<LaTiO3<YTiO3

JT distortion is small
(a few %)



CRYSTAL FIELD SPLITTING



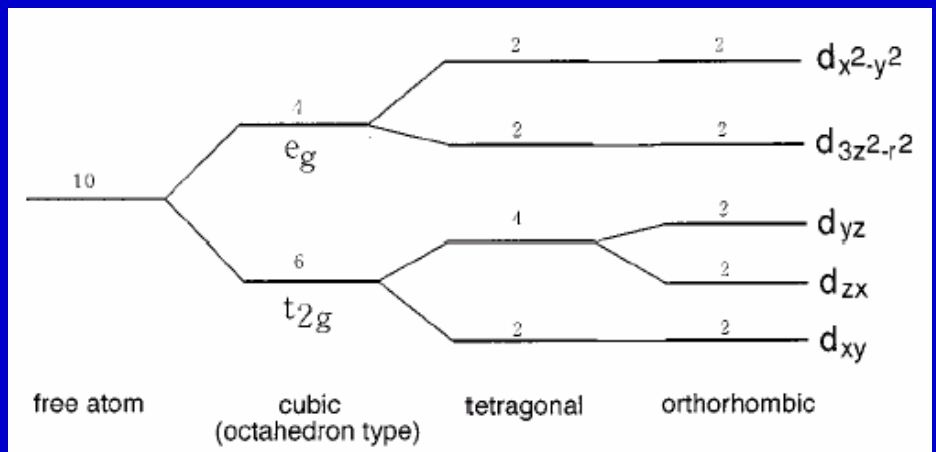
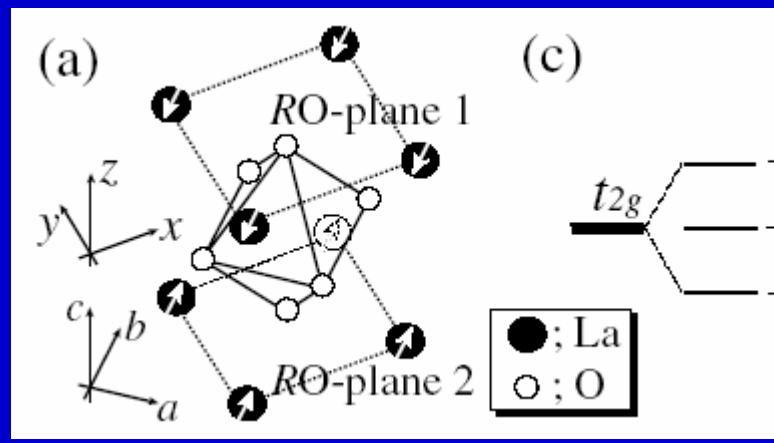


FIG. 2. Crystal-field splitting of 3*d* orbitals under cubic, tetragonal, and orthorhombic symmetries. The numbers cited near the levels are the degeneracy including spins.

From (La,Y)-CATION:
Cf Mochizuki and Imada
PRL 2003



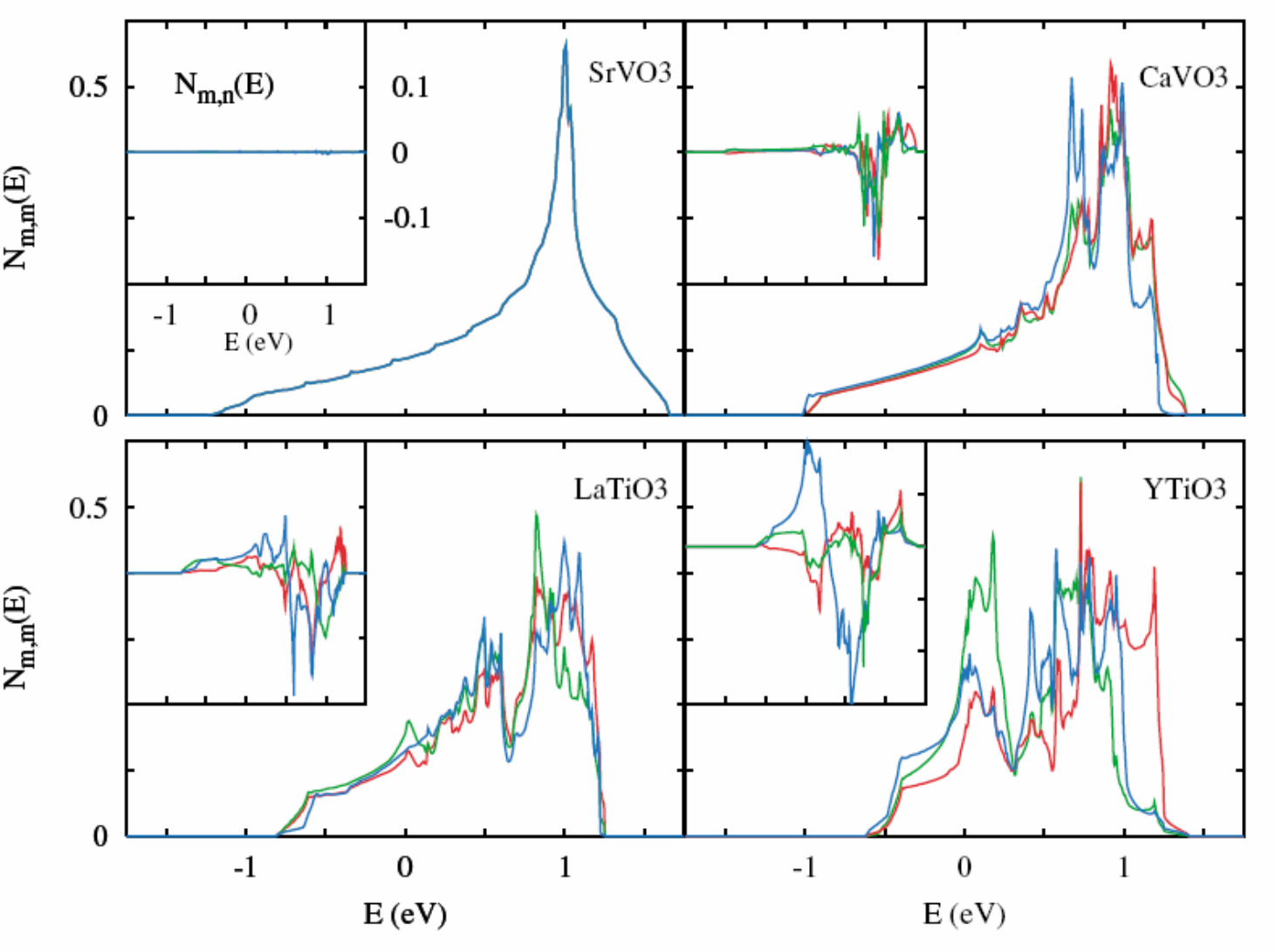
Metals *vs.* Insulators

$Sr/CaVO_3$ are METALS while $La/YTiO_3$ are INSULATORS with quite different gaps (0.2 eV vs. 1 eV)

WHY ?

- Bandwidth smaller due to tilting ?
- >> Tilting lifts orbital degeneracy and correlations suppress further orbital fluctuations, inducing the Mott insulating state w/ orbital polarisation

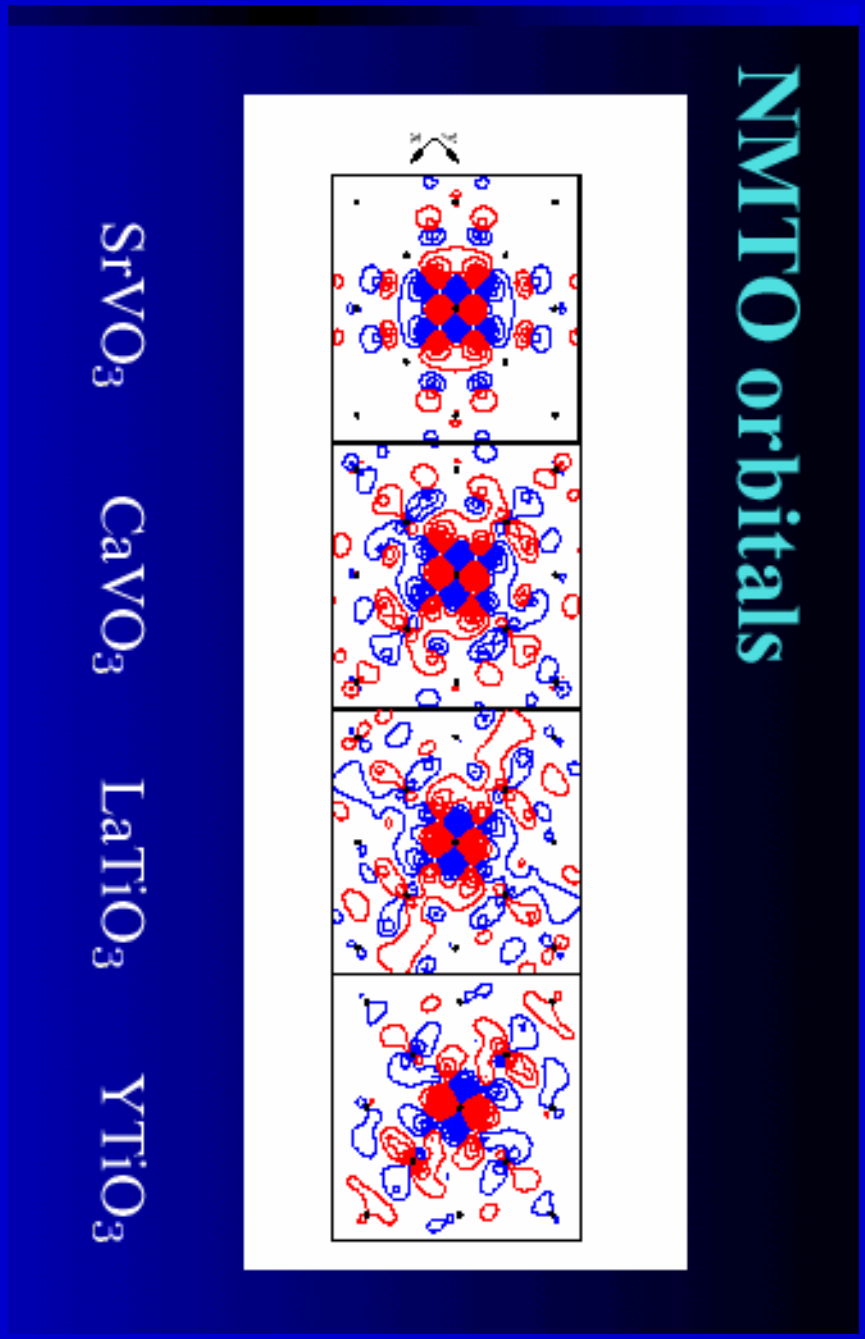
(NO orbital liquid)



LDA-NMTO results (all metallic as expected)

Note: bandwidths 2.8, 2.4, 2.1, 2.0 eV

Xtal-field splitting up to 330 meV for YTiO3



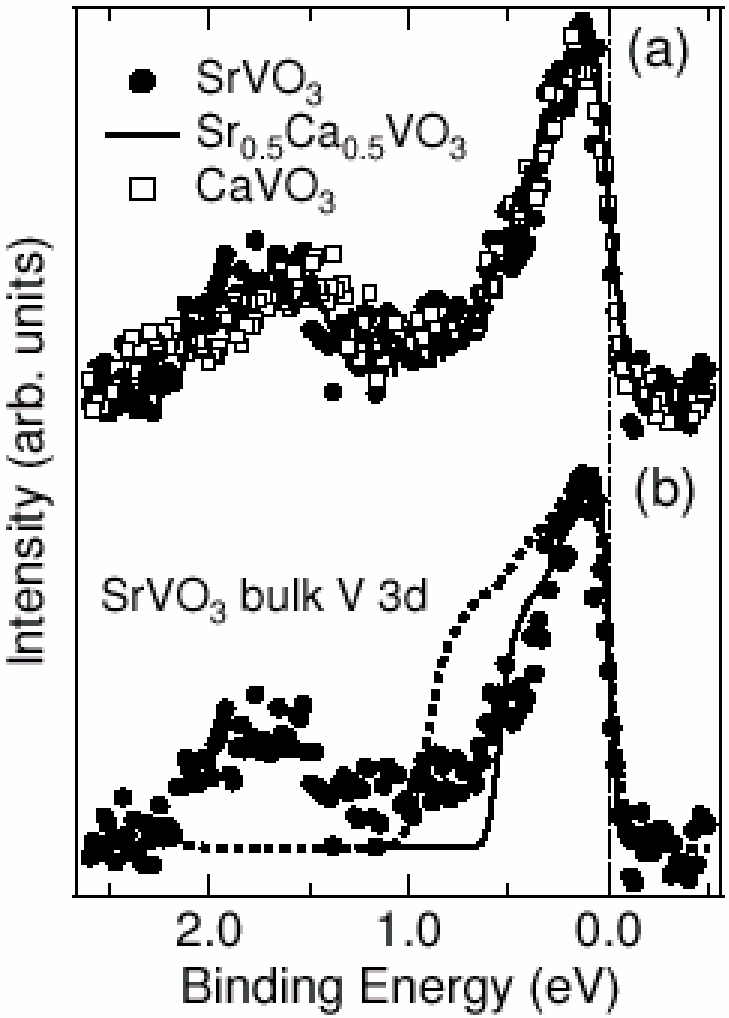
The NMTO method:

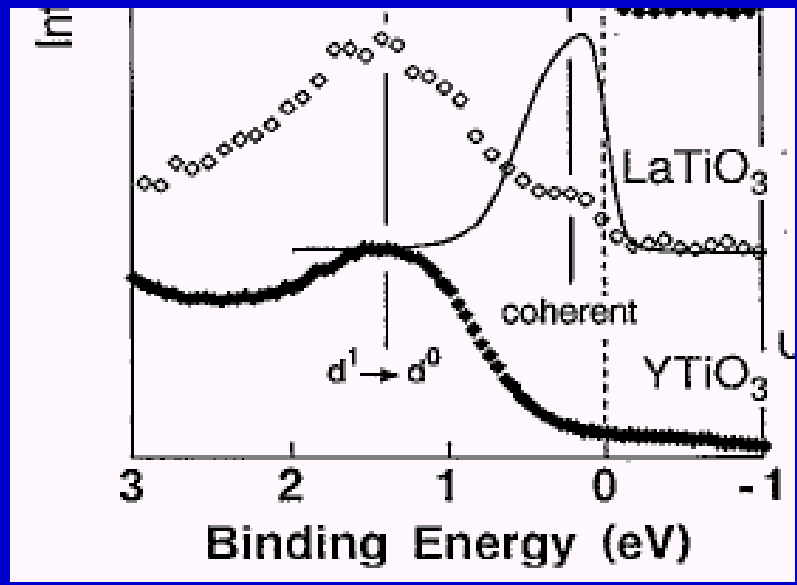
ab-initio construction of low-energy hamiltonian in a minimal basis set of Wannier-like localised orbitals

(projection method)

Andersen et al.

PHOTOEMISSION…





Fujimori et al.
PRL 69(1992)1796

<< Brinkman-Rice
+Hubbard bands

(Sekiyama et al. cond mat/0206471)

High photon energy >>> bulk.

…vs LDA

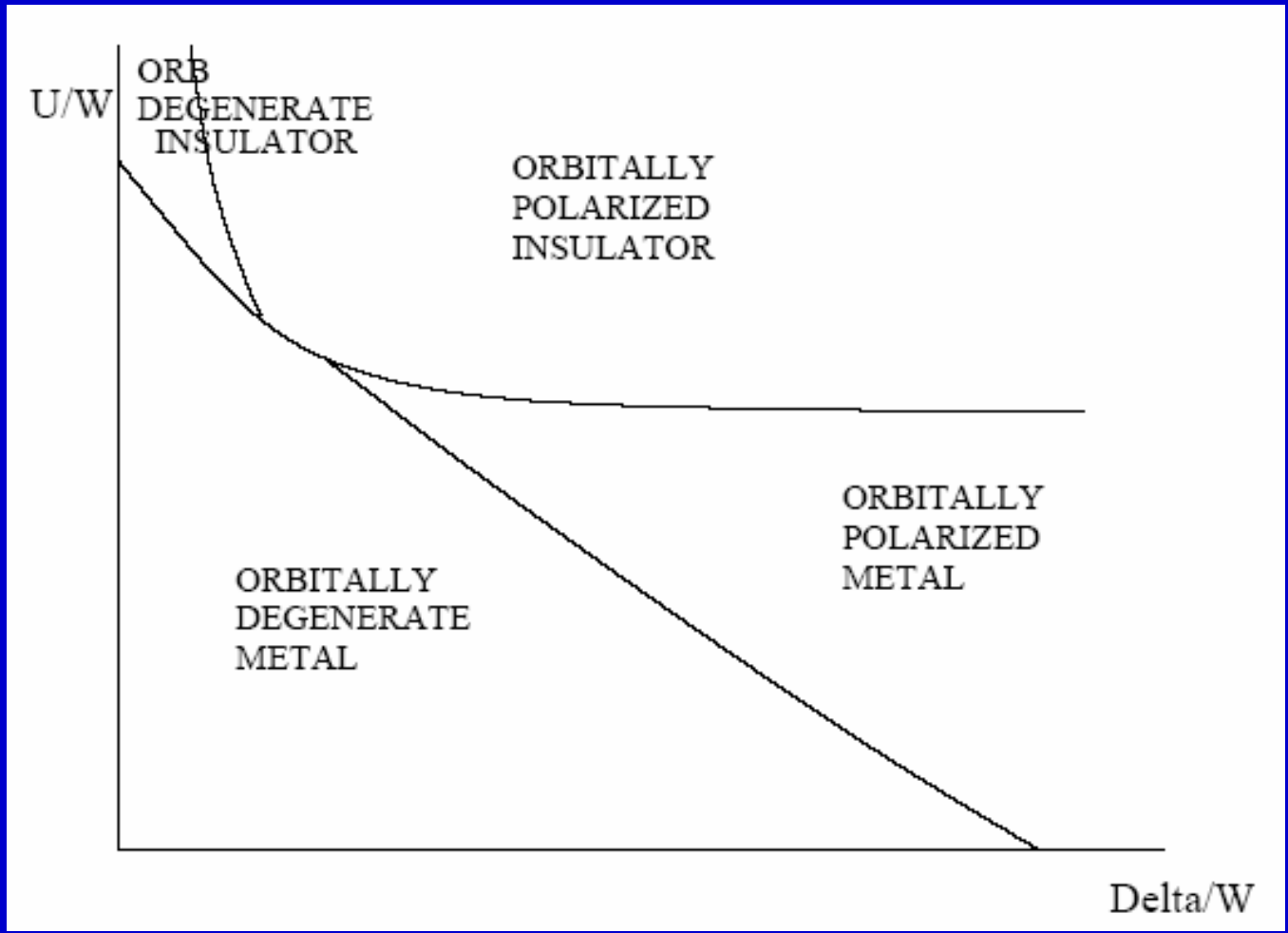
Some qualitative ideas

- Critical U_c for Mott insulating state **increases with orbital degeneracy**
- Crystal-field splitting induces **orbital polarisation** (acts as external field)
- **Polarisation is increased as U/W is increased** (think of atomic limit: just put single electron in lowest level !)
- Can orbital fluctuations restore an orbital liquid ? (Khaliullin)

Compare typical scale for crystal-field splitting, to:

- **Quasiparticle coherence scale = ZW**
  (Brinkman-Rice reduced)
  in the correlated metal

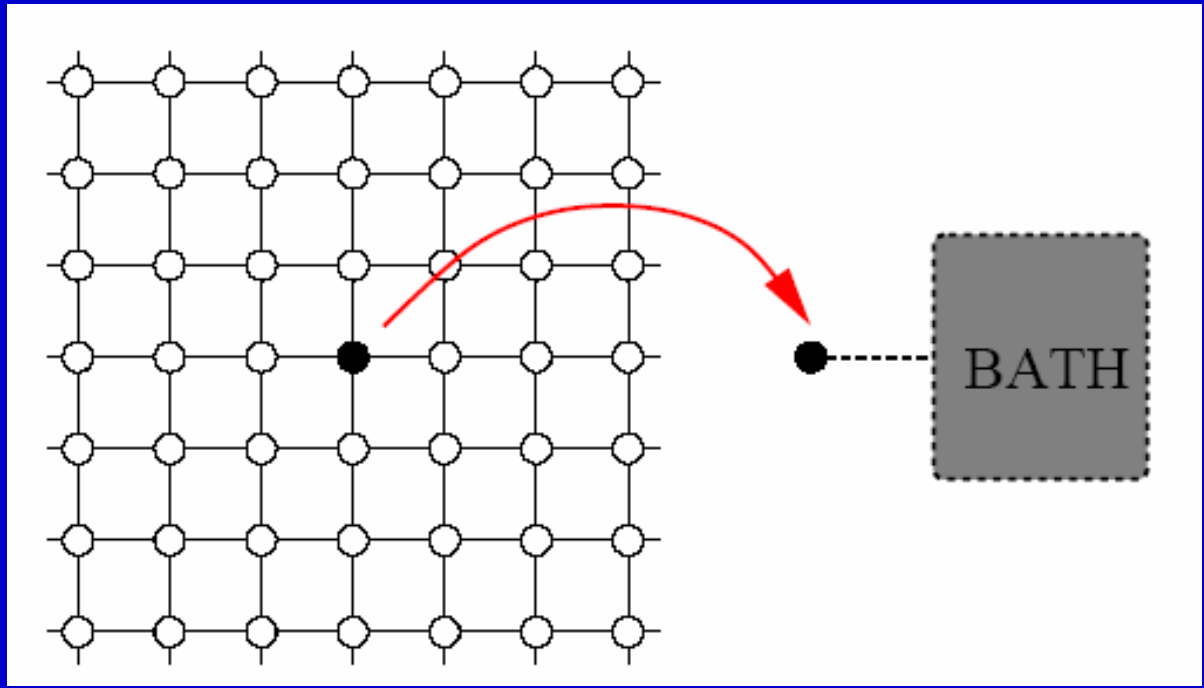
  - t^2/U in the correlated insulator



The various regimes (schematic)

Cf. Manini et al. PRB 66, 115107 (2002)

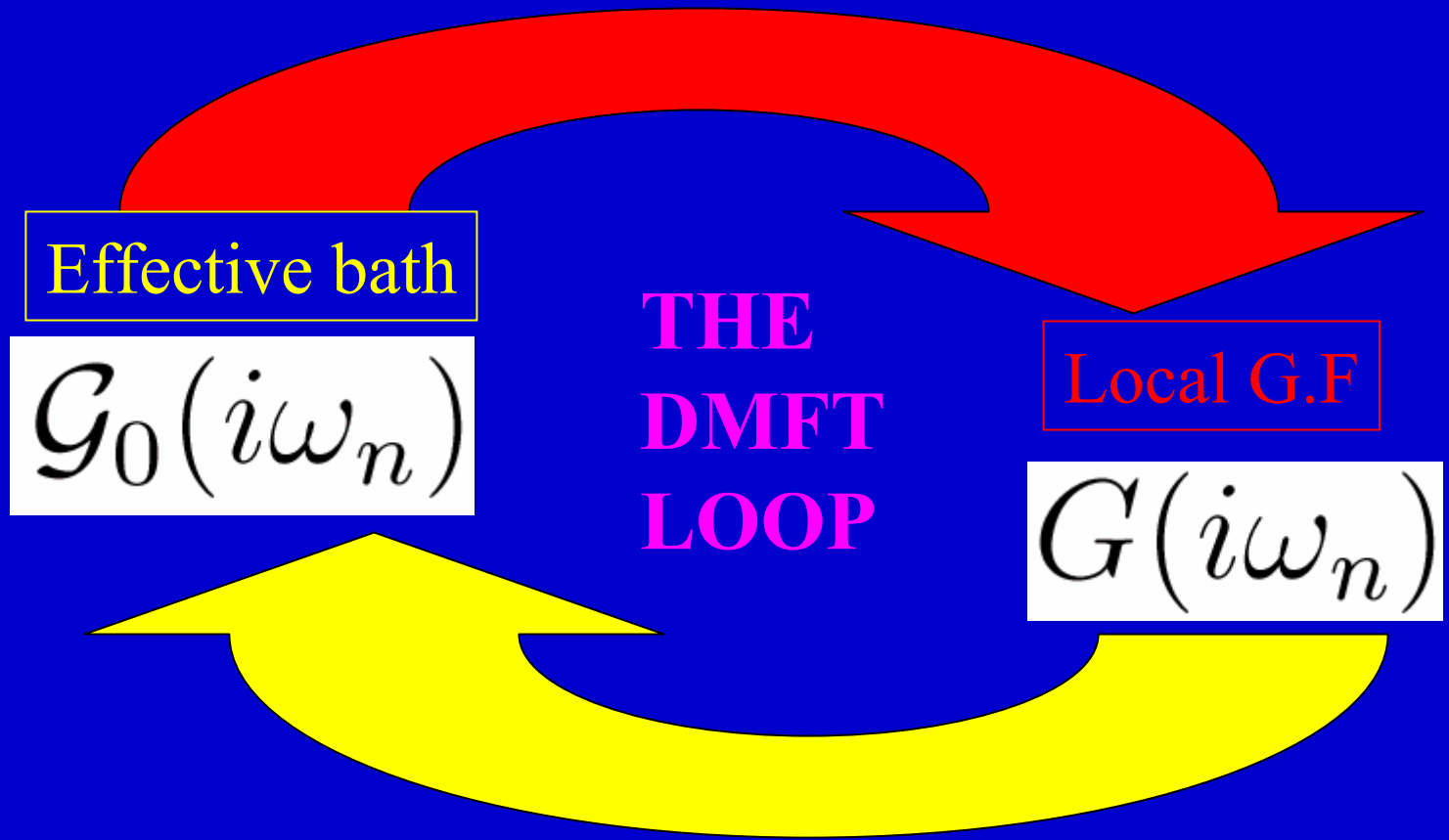
Quantitative study using DMFT combined with LDA



DMFT replaces the solid by an effective atom coupled a self-consistent bath

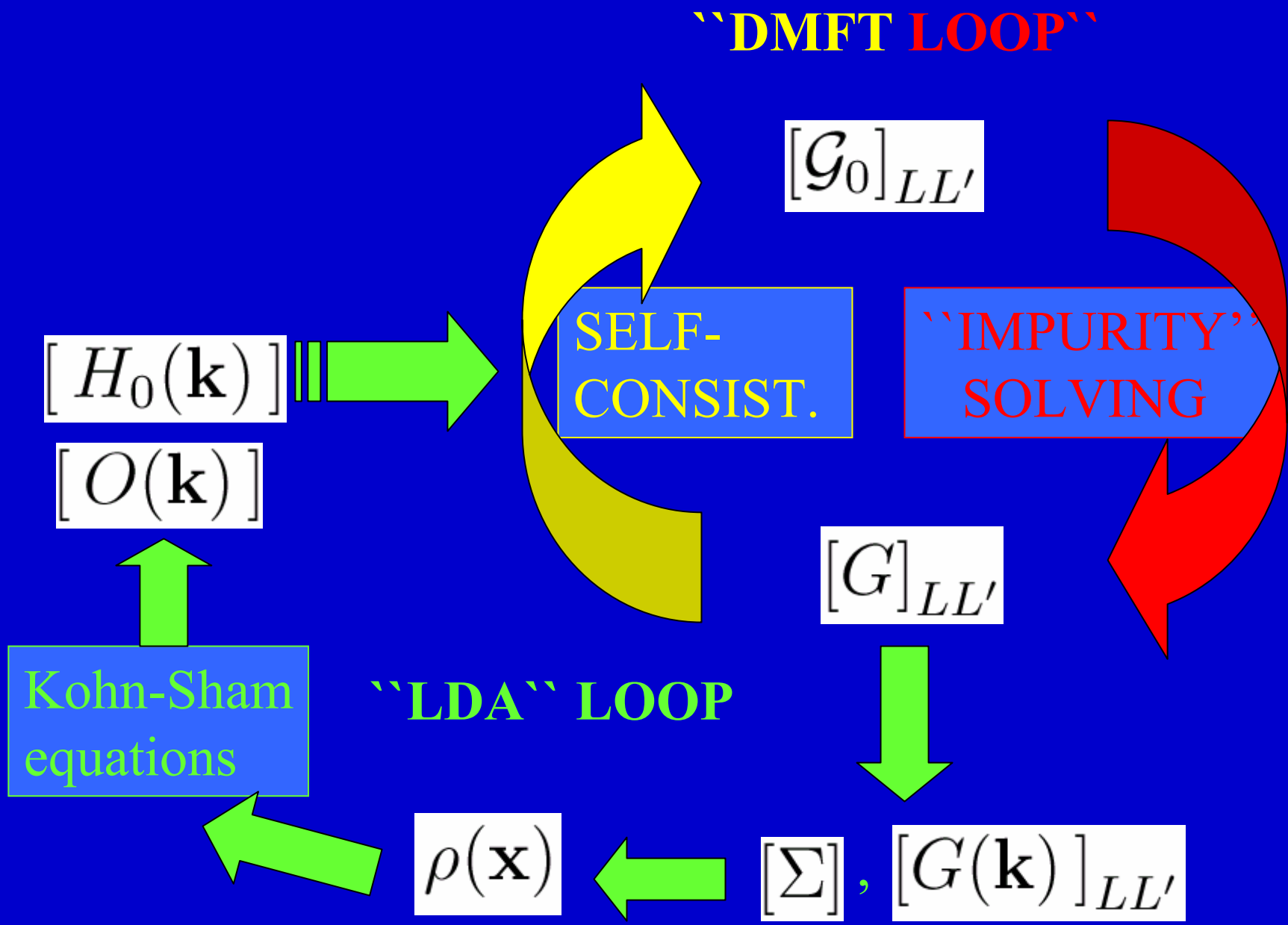
$$S_{eff} = -\int_0^\beta d\tau \int_0^\beta d\tau' \sum_\sigma c_\sigma^+(\tau)\mathcal{G}_0^{-1}(\tau-\tau')c_\sigma(\tau') + U\int_0^\beta d\tau\, n_\uparrow(\tau)n_\downarrow(\tau)$$

EFFECTIVE LOCAL IMPURITY PROBLEM



SELF-CONSISTENCY CONDITION

$$G(i\omega_n) = \sum_{\boldsymbol{k}} \frac{1}{i\omega_n + \mu - \epsilon_{\boldsymbol{k}} - \left[\mathcal{G}_0^{-1}(i\omega_n) - G^{-1}(i\omega_n)\right]}$$



Full self-consistency important in **total energy calculations**

LDA(NMTO) combined w/DMFT: results for d1 oxides

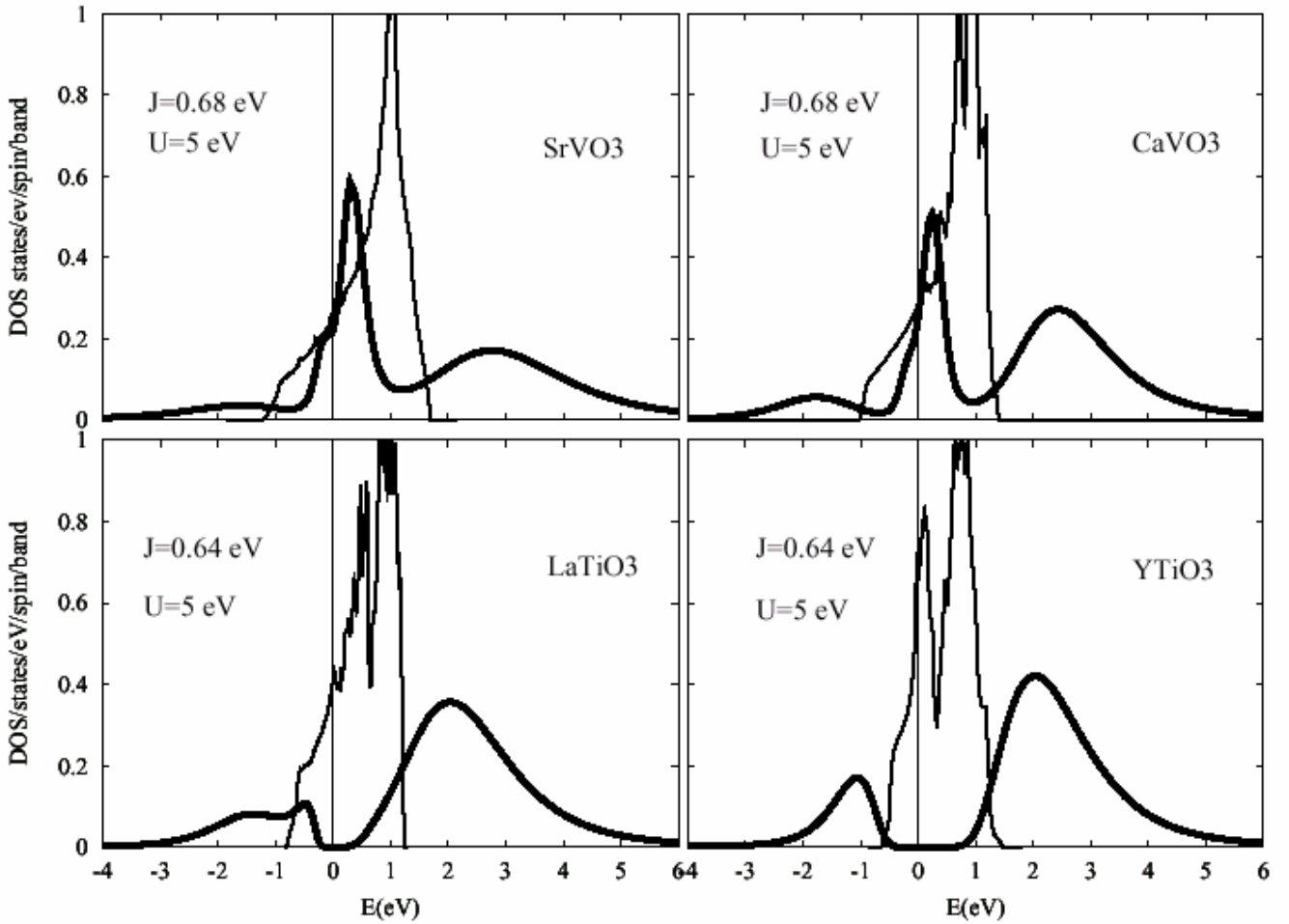


FIG. 3: DMFT spectral function at $T = 770K$ (thick line) and LDA DOS (thin line). $\mu \equiv 0$.

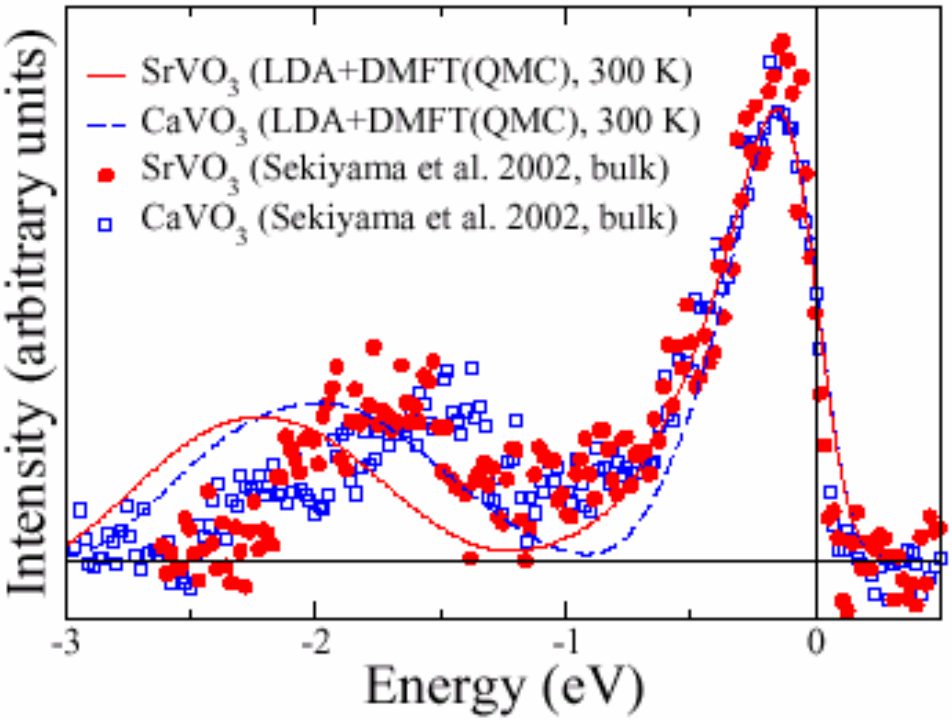


FIG. 4: Comparison of the calculated, parameter-free LDA+DMFT(QMC) spectra of $SrVO_3$ (solid line) and $CaVO_3$ (dashed line) with bulk-sensitive high-resolution PES ($SrVO_3$: circles; $CaVO_3$: rectangles) [4]. Horizontal line: experimental subtraction of the background intensity.

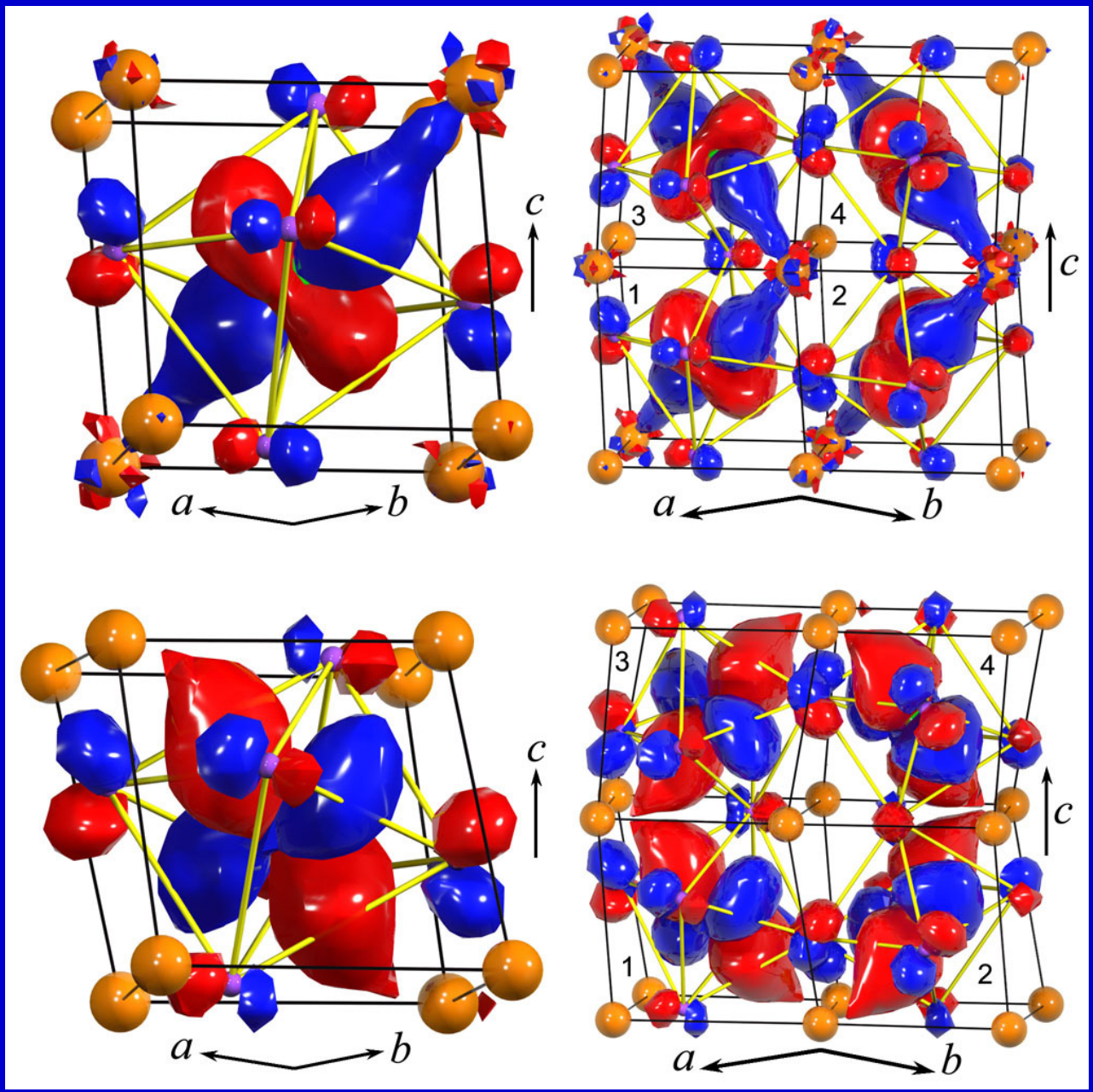
Nekrasov et al.

Comparison to photoemission

Strong orbital polarisation found for the two insulating compounds

Eigenvector of local density matrix with highest occupancy has :

$LaTiO_3$	0.45 electrons in LDA
	0.88 electrons in DMFT
$YTiO_3$	0.50 in LDA
	0.96 in DMFT



LaTiO3

Violet: Oxygen

Orange: cations

YTiO3

Conclusion (I) and puzzles…

-Driving mechanism is lifting of orbital degeneracy: crystal-field induces orbital polarisation, which is considerably enhanced by Hubbard repulsion.

- Orbital liquid unlikely for these compounds

-Challenge: explain observed isotropy of magnon dispersion (Keimer) as well as
antiferro vs. ferro for La/Y
Cf. Mochizuki and Imada PRL 2003

VO_2: ``correlation-assisted'' Peierls insulating state

VO_2 undergoes a first-order transition at T=340K between:

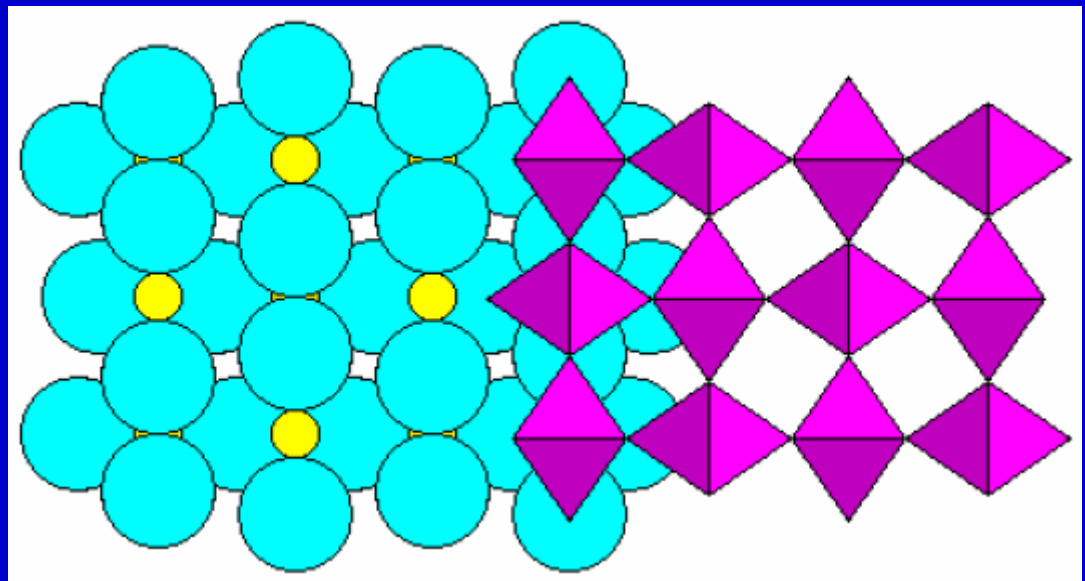
- A high-temperature metallic phase with rutile (TiO_2) structure
- A low-T insulating phase with monoclinic structure

  The insulating phase is **NON-MAGNETIC**, with dimerisation into V-V pairs

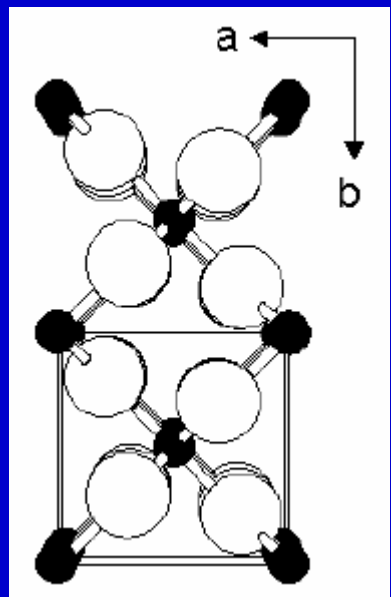
However, despite this Peierls-like distortion, electronic structure calculations based on LDA are **unable to account** for the insulating character of the low-T phase

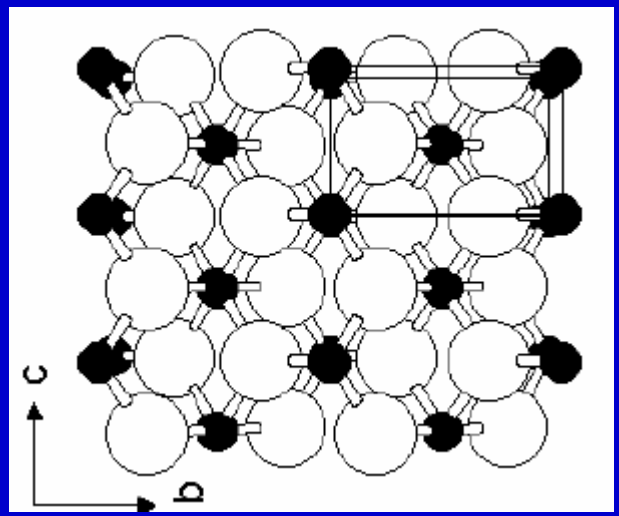
THE RUTILE STRUCTURE

From P.Dutch's homepage:
http://www.uwgb.edu/dutchs

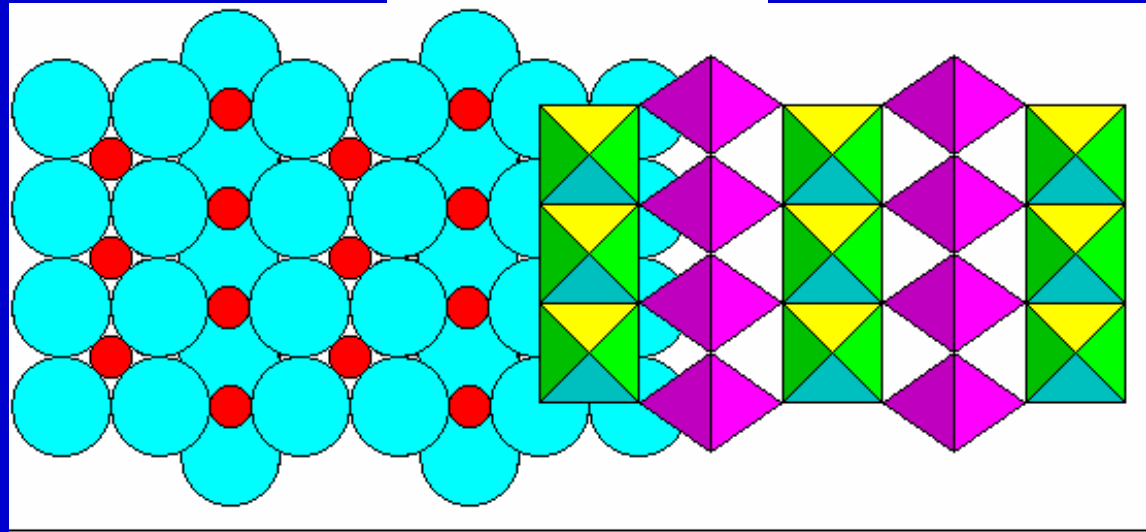


Viewed down the fourfold symmetry axis, the rutile structure looks like this. Octahedra with Ti at their centers enclose square tunnels.



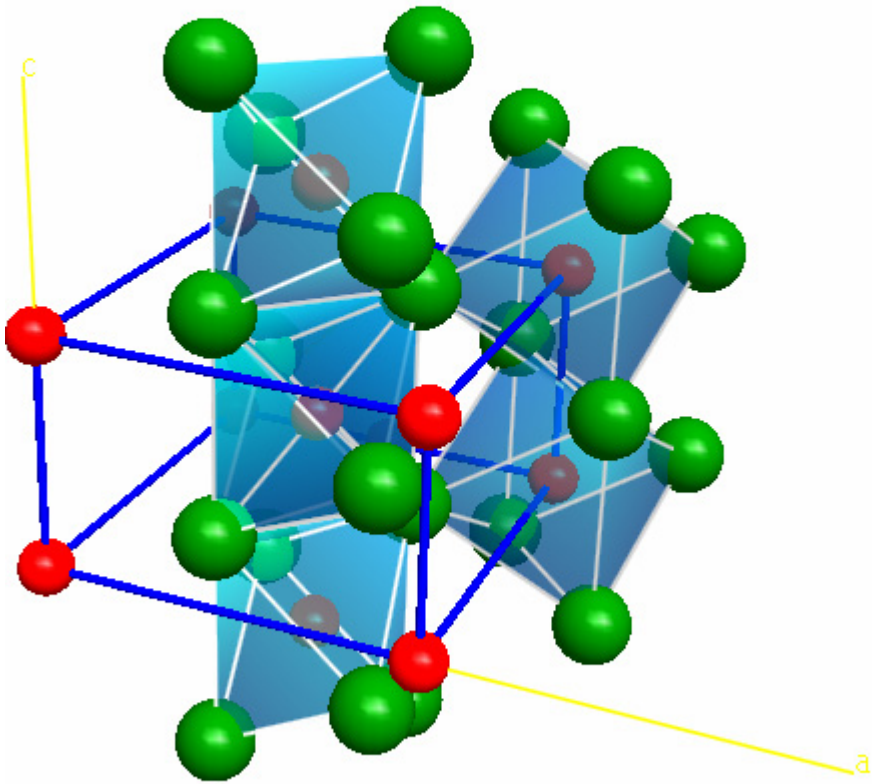


Chains of V along c-axis

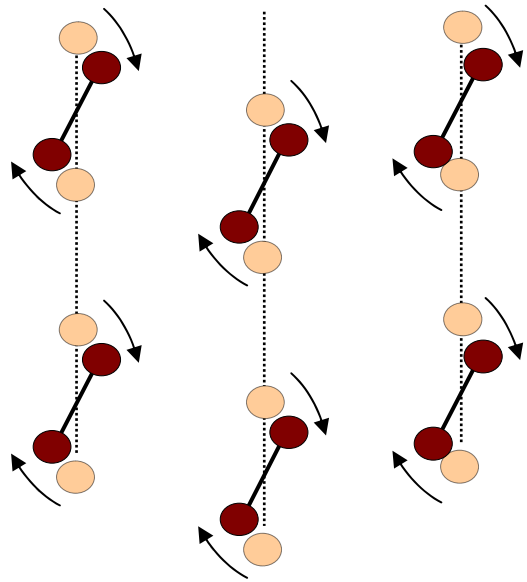


Seen from the side, the rutile structure looks like this. Alternating chains of octahedra run parallel to the fourfold symmetry axis.

Dimerisation and tilting in the monoclinic phase.



Rutile structure

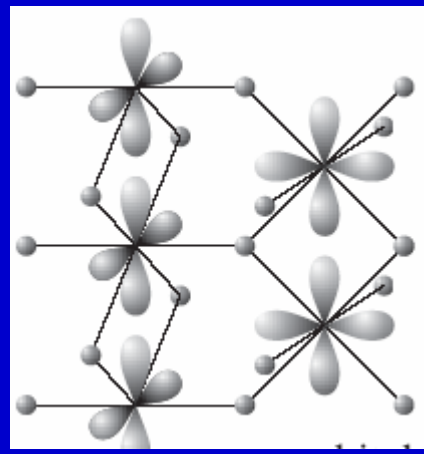


Monoclinic distortion in the insulating phase

Basic electronic structure and Goodenough's qualitative picture (1971)

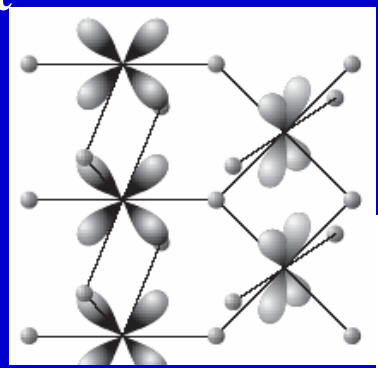
V^{4+}, octahedral environment:

1 d-electron in t_{2g} multiplet, e_g empty.

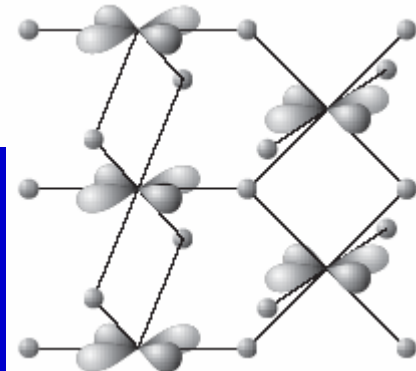


Non-cubic: t2g further splitted into:

- $\mathbf{a_{1g}}$ orbital (or $\mathbf{d}_{//}$) with efficient sigma-bonding along c-axis

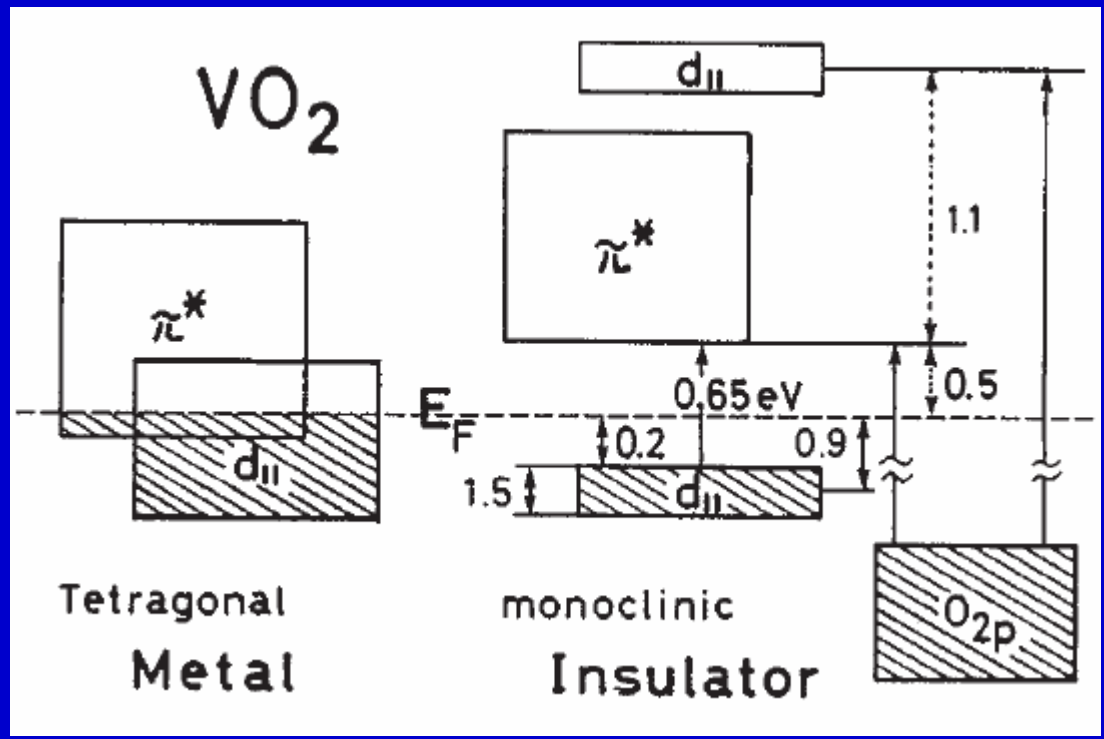


- e_g^{π} $(or \pi^*)$ doublet providing efficient pi-like bonding in (a,b) plane

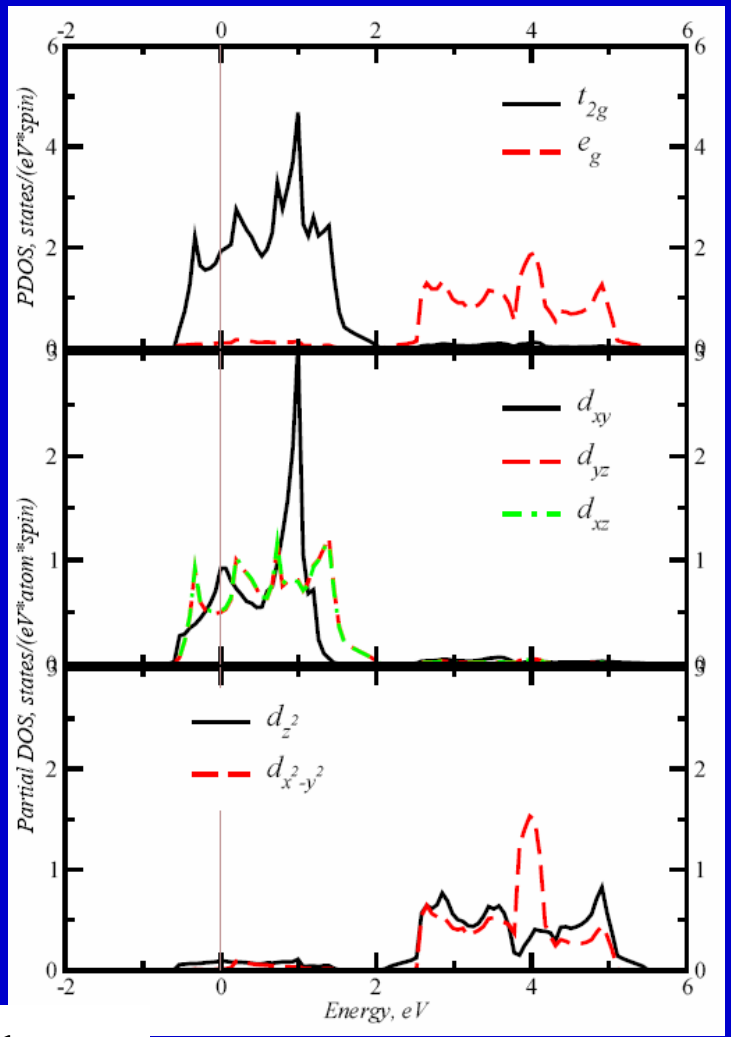


Goodenough's picture:
- Dimerisation opens a Peierls (bonding-antibonding) gap into d// orbital. The bonding combination is fully occupied.
- Increased covalency with oxygen pushes the Pi* orbitals upwards: they are now empty

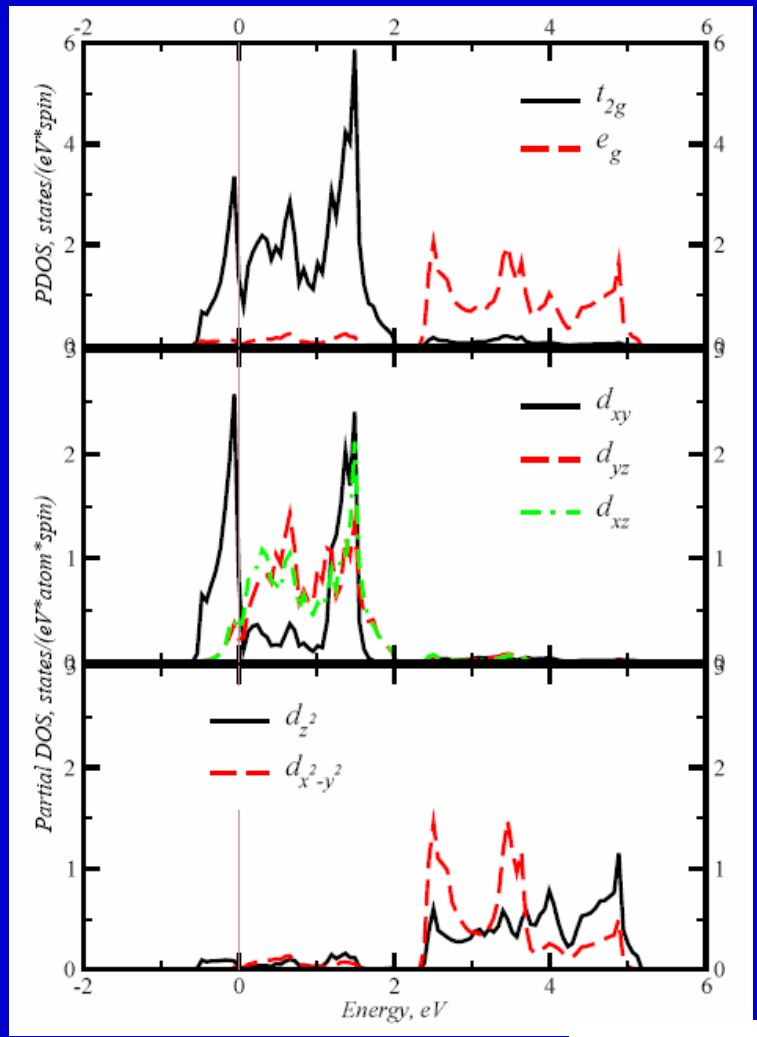
>> INSULATOR (basically Peierls)



LDA calculations consistent with these qualitative aspects, but the insulator does not quite make it…



R phase



M1 phase

Poteryaev et al.

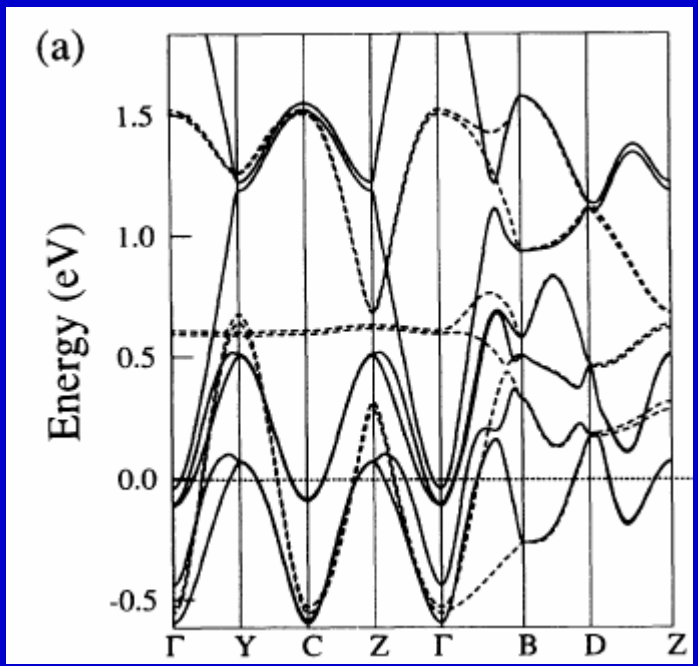
Wentzcovich et al PRL (1994):

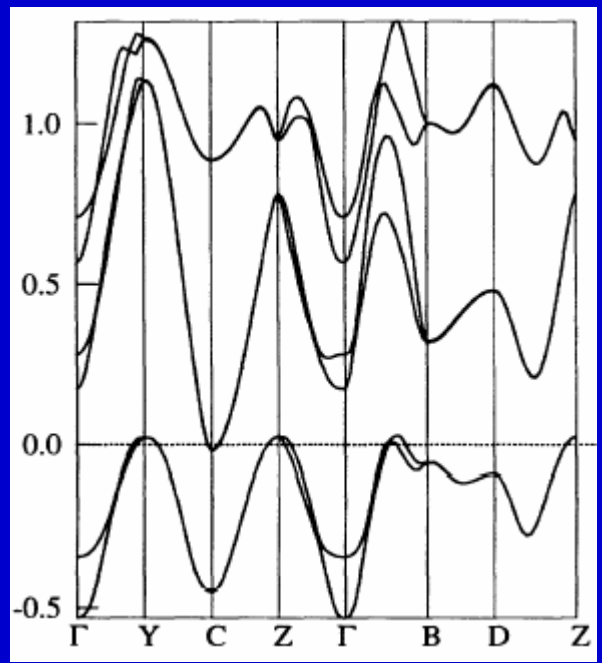
VO_2: Peierls or Mott-Hubbard? A View from Band Theory

Renata M. Wentzcovitch*
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

Werner W. Schulz† and Philip B. Allen
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794-3800
(Received 24 November 1993)

The electronic and structural properties of VO_2 across its metal-insulator transition are studied using the local-density approximation. Band theory finds a monoclinic distorted ground state in good agreement with experiment, and an almost open gap to charge excitations. Although rigid criteria for distinguishing correlated from band insulators are not available, these findings suggest that VO_2 may be more bandlike than correlated.





Experimental evidence for importance of correlations:

substitutions on V-site

(Marezio et al, 1972;Pouget et al., 1974)

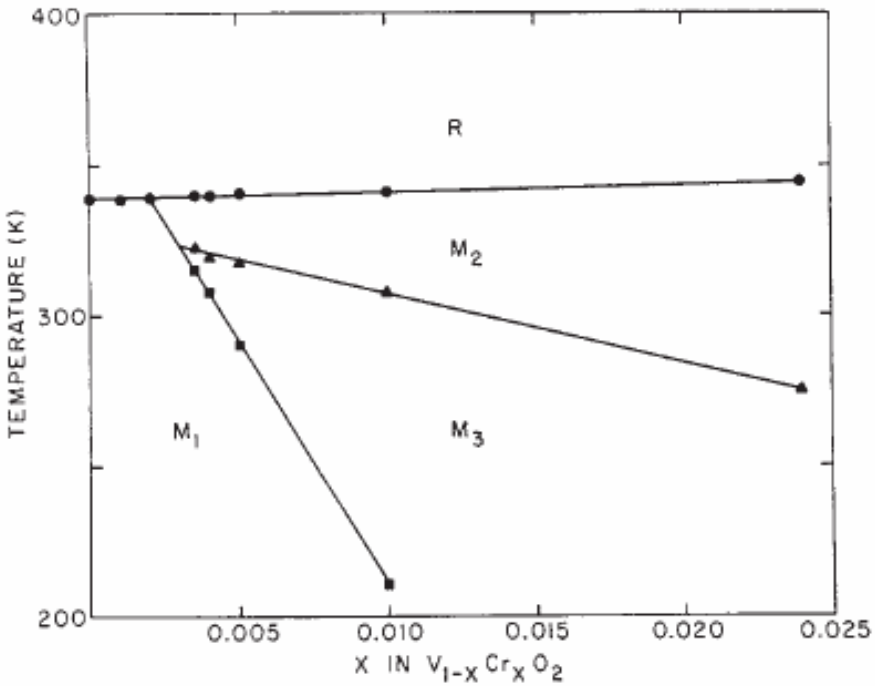


FIG. 217. The $T-x$ phase diagram for $V_{1-x}Cr_xO_2$ (Marezio *et al.*, 1972; Villeneuve, Drillon, and Hagenmuller, 1973).

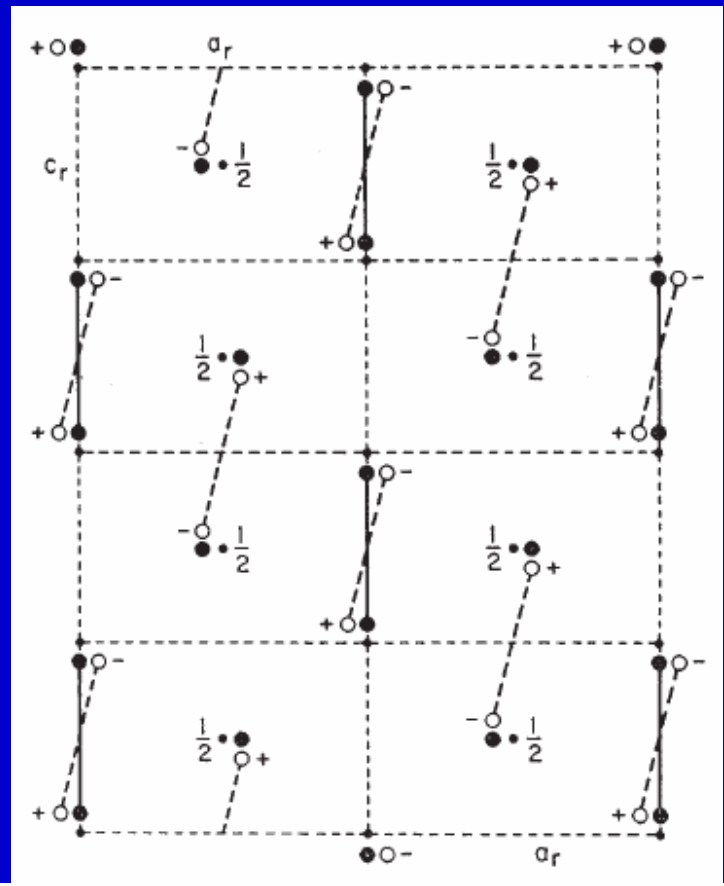


FIG. 215. Comparison of V-V pairing in the three phases, R, M_1, and M_2, in VO_2. In M_1 (open circles) all the vanadium atoms both pair and twist from the rutile positions. In M_2 (filled circles) one-half of the vanadium atoms pair but do not twist and the other half form unpaired zigzag chains. (The distortions are exaggerated by a factor of 2 for clarity.) From Marezio *et al.*, 1972.

cf also Zylbersztejn and Mott

In M2 phase: ½ of V's do NOT pair, yet an insulator

DMFT study of the Rutile (metallic) phase

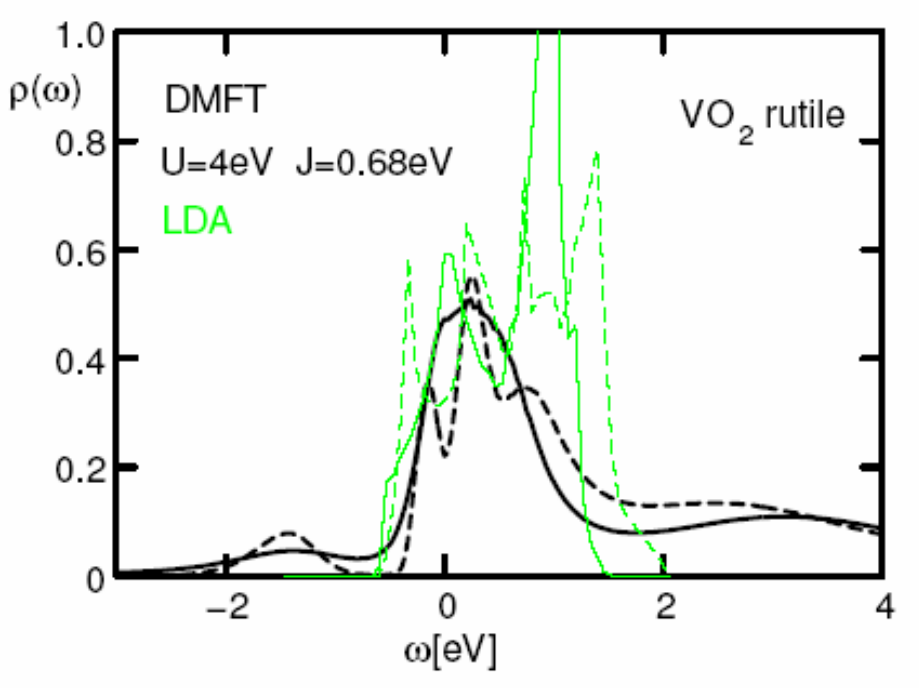
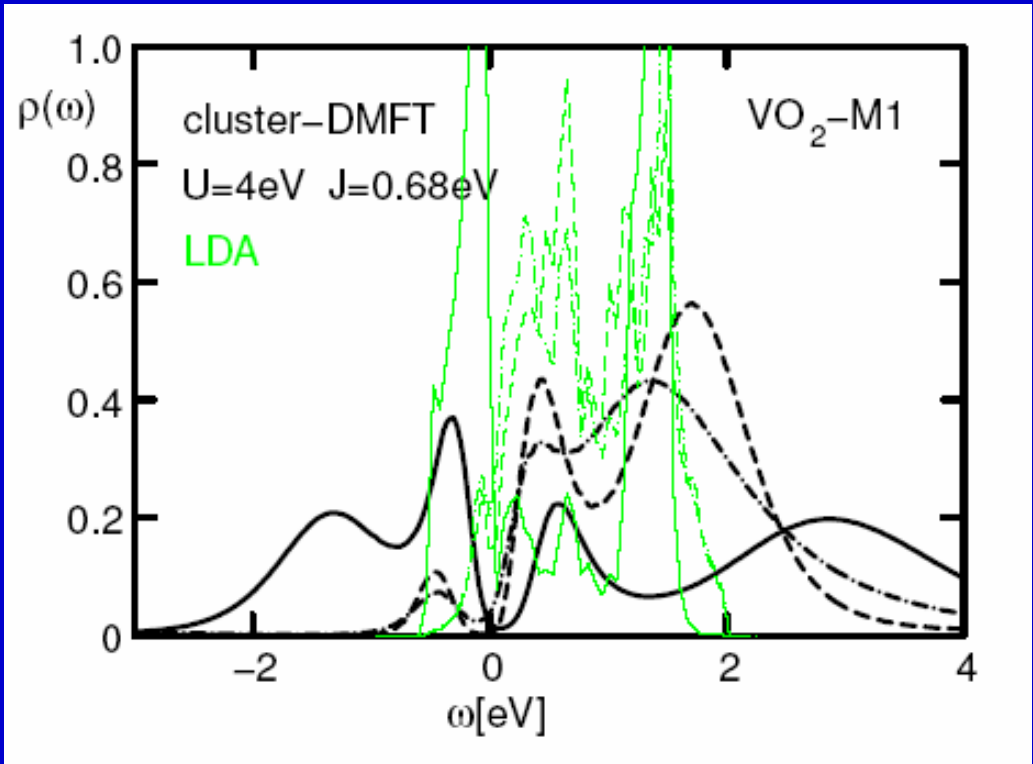
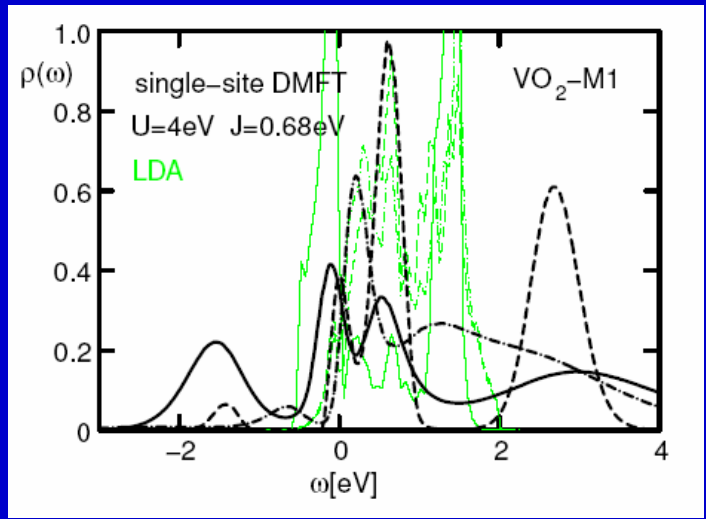


FIG. 1: Spectral function for the rutile phase as calculated within (single-site)-DMFT with $U = 4$eV, $J = 0.68$eV (black lines) in comparison to the LDA-DOS (green lines). The solid (dashed) lines show the partial contributions of the a_{1g} (e_g^{π}) bands.

(2)

Cluster-DMFT in the M1-insulating phase



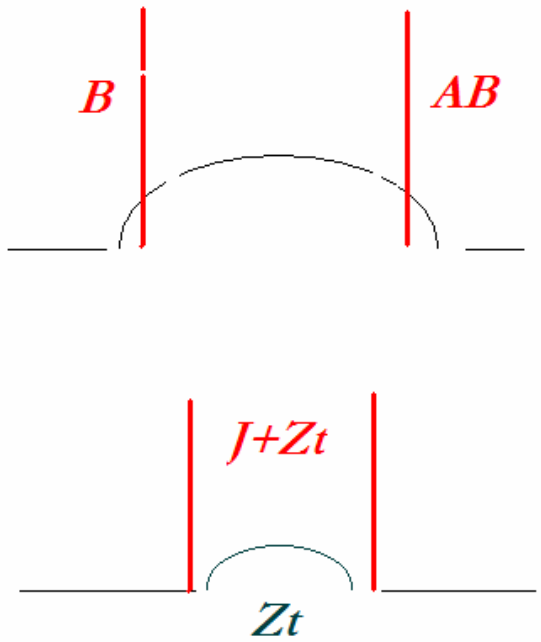


1-site DMFT inadequate

Our results are consistent with the following qualitative picture:

1) The structural distortion splits the d// band and pushes up the pi* orbitals, as anticipated by Goodenough and seen in LDA.

2) Correlations effects reduce the pi* bandwidth AND the B-AB splitting by a Brinkman-Rice effect, BUT the latter is reduced less, due to the strong intra-dimer superexchange J
>> the bonding band splits off, and is fully occupied



Simple slave-boson picture: hoppings get the Brinkman-Rice reduction factor $Z=\langle b^2 \rangle$, while superexchange (link decoupling) is not critically reduced (also the reason why J is effective source of pairing in original RVB ideas) in regime $J/Zt \gg 1$

Conclusion

- Interplay of orbital degeneracy, structural aspects and strong correlations
- DMFT-based techniques combined with electronic structure now able to describe this interplay (predictive ?)