Chaire de Physique de la Matière Condensée

Matériaux et dispositifs à fortes corrélations électroniques

II.1 *Oxydes de métaux de transition Structure et structure électronique*

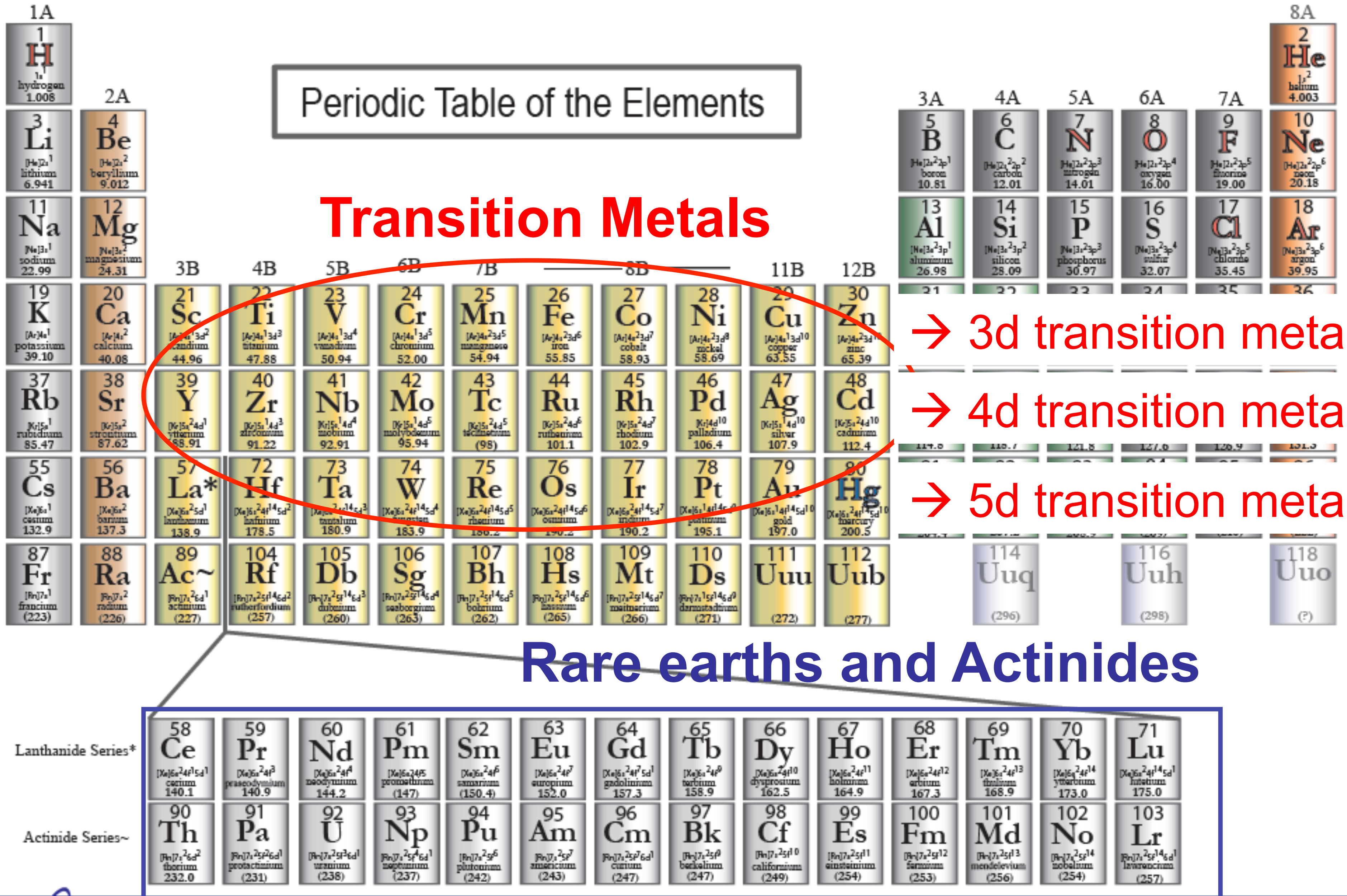
- Introduction-

Cycle 2014-2015
18 mai 2015 – II.1

Antoine Georges

OUTLINE

- Crystal structures
- Crystal/Ligand field
- Band-structure
- Mott *vs.* charge-transfer insulators
- Interactions: not only U



Transition Metals

→ 3d transition metals

→ 4d transition metals

→ 5d transition metals

Rare earths and Actinides

Electronic configuration of neutral isolated atom:


8

O

$[He]2s^2 2p^4$

oxygen

16.00

21	Sc	$[Ar]4s^1 3d^2$	scandium	44.96
22	Ti	$[Ar]4s^1 3d^3$	titanium	47.88
23	V	$[Ar]4s^1 3d^4$	vanadium	50.94
24	Cr	$[Ar]4s^1 3d^5$	chromium	52.00
25	Mn	$[Ar]4s^2 3d^5$	manganese	54.94
26	Fe	$[Ar]4s^2 3d^6$	iron	55.85
27	Co	$[Ar]4s^2 3d^7$	cobalt	58.93
28	Ni	$[Ar]4s^2 3d^8$	nickel	58.69
29	Cu	$[Ar]4s^1 3d^{10}$	copper	63.55
30	Zn	$[Ar]4s^2 3d^{10}$	zinc	65.39

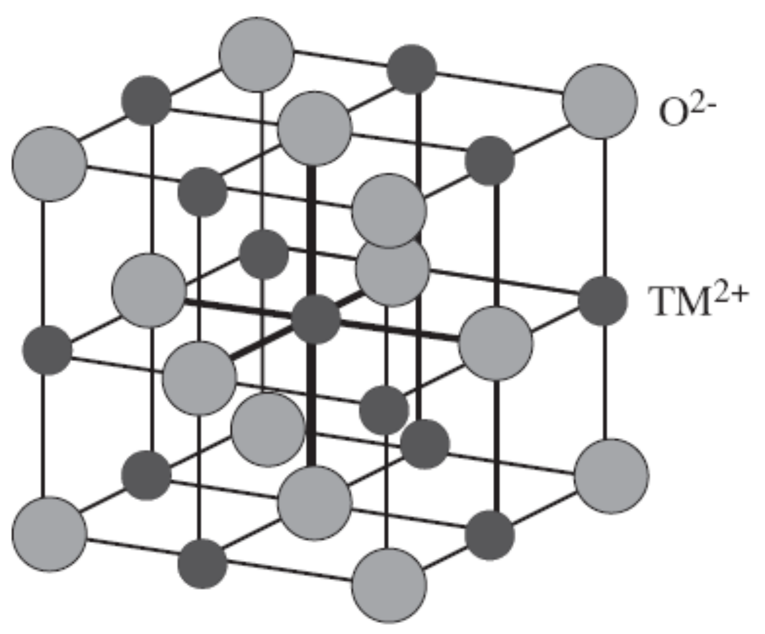
1. Some crystal structures

Structures

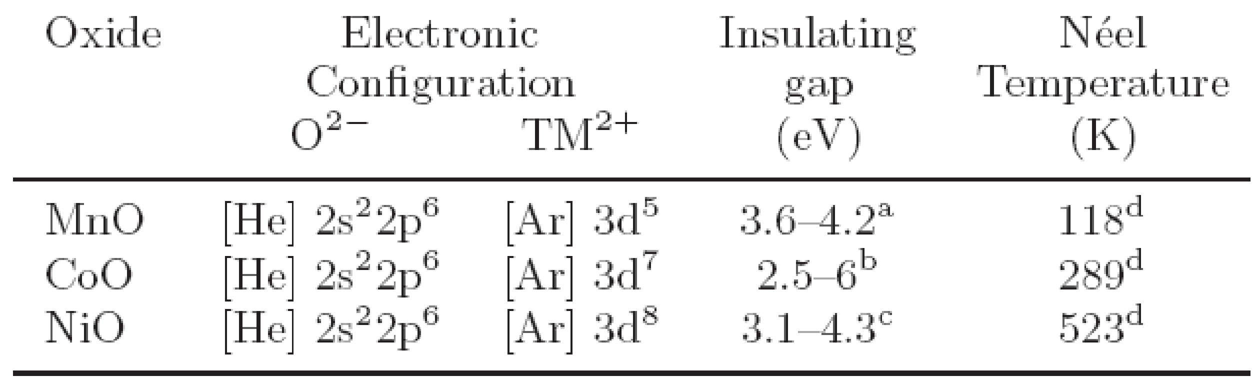
2.1 Monoxides **MO**: not much controllability…

Nominal valences:
(quite ionic)
- Oxygen takes 2 electrons
→ Ligand shell $2s^2 2p^6$ full
- M gives out two electrons:
→ M^{2+}

NaCl structure



TiO, VO: ~ metals
(O-deficient)
MnO, CoO, NiO: Mott
(or charge-transfer)
magnetic insulators
(historic example: NiO)

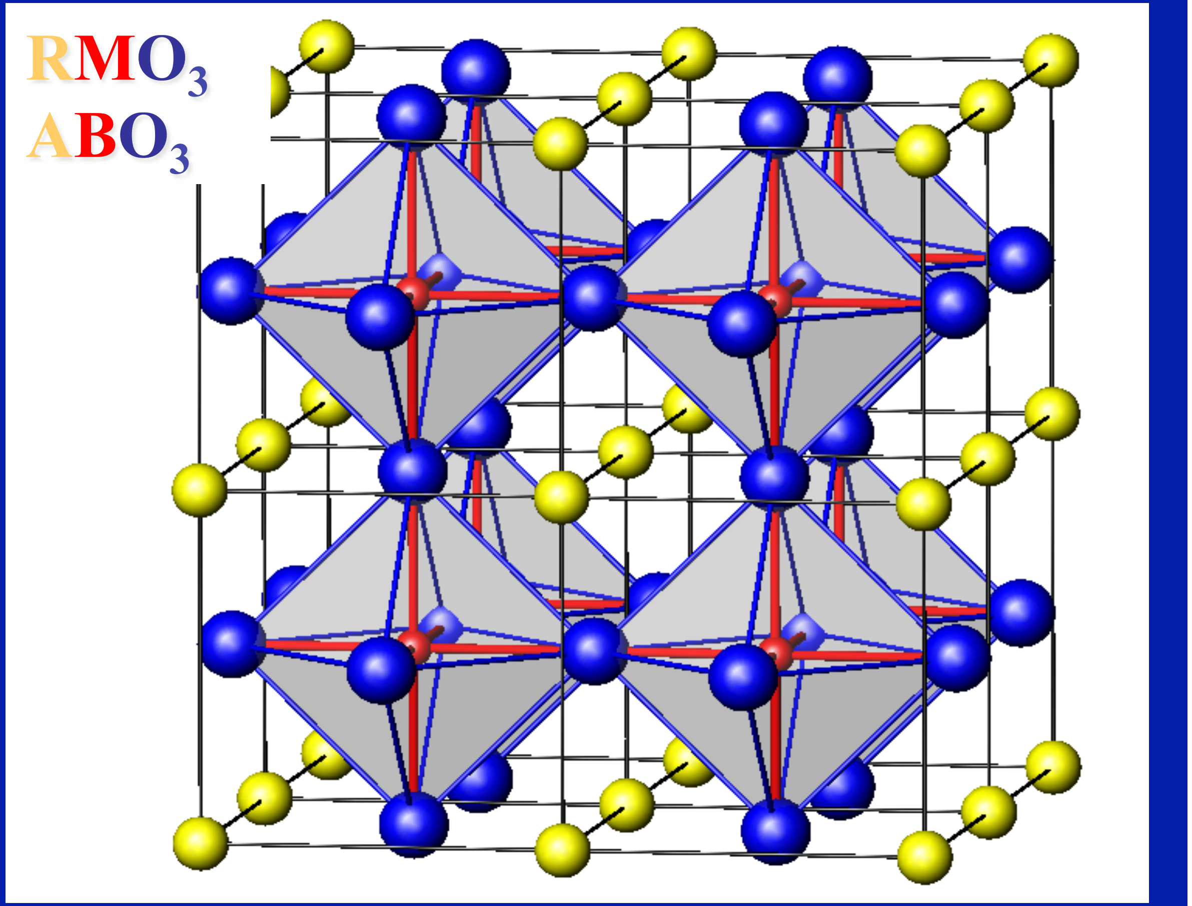


Oxide	Electronic Configuration O^{2-}	TM^{2+}	Insulating gap (eV)	Néel Temperature (K)
MnO	[He] $2s^2 2p^6$	[Ar] $3d^5$	3.6–4.2^a	118^d
CoO	[He] $2s^2 2p^6$	[Ar] $3d^7$	2.5–6^b	289^d
NiO	[He] $2s^2 2p^6$	[Ar] $3d^8$	3.1–4.3^c	523^d

Ternary compounds (and more): the simple (and beautiful) perovskite structure and its descendants…

Perfectly cubic
perovskite RMO_3 :

For example: $SrVO_3$



- transition-metal
Ion M at center of
oxygen octahedra
→MO_6 structural units
- R+O form fcc lattice
- Rare-earth ions R
form simple cubic lattice

[L.A Perovski 1792-1856
Oural mountains samples
discovery of CaTiO3 G.Rose, 1839]

Perovskite: discovery and origin of the name

Count
Lev Alexeievich
Perovski
(1792-1856)
Minister of Interior
under Nicolas 1st
and Mineralogist

Gustav Rose
(1798-1873)
German mineralogist

Roselite
Armand Levy
1824

Perovskite $CaTiO_3$
described in 1839
by Gustav Rose
who named it
after Count Perovski

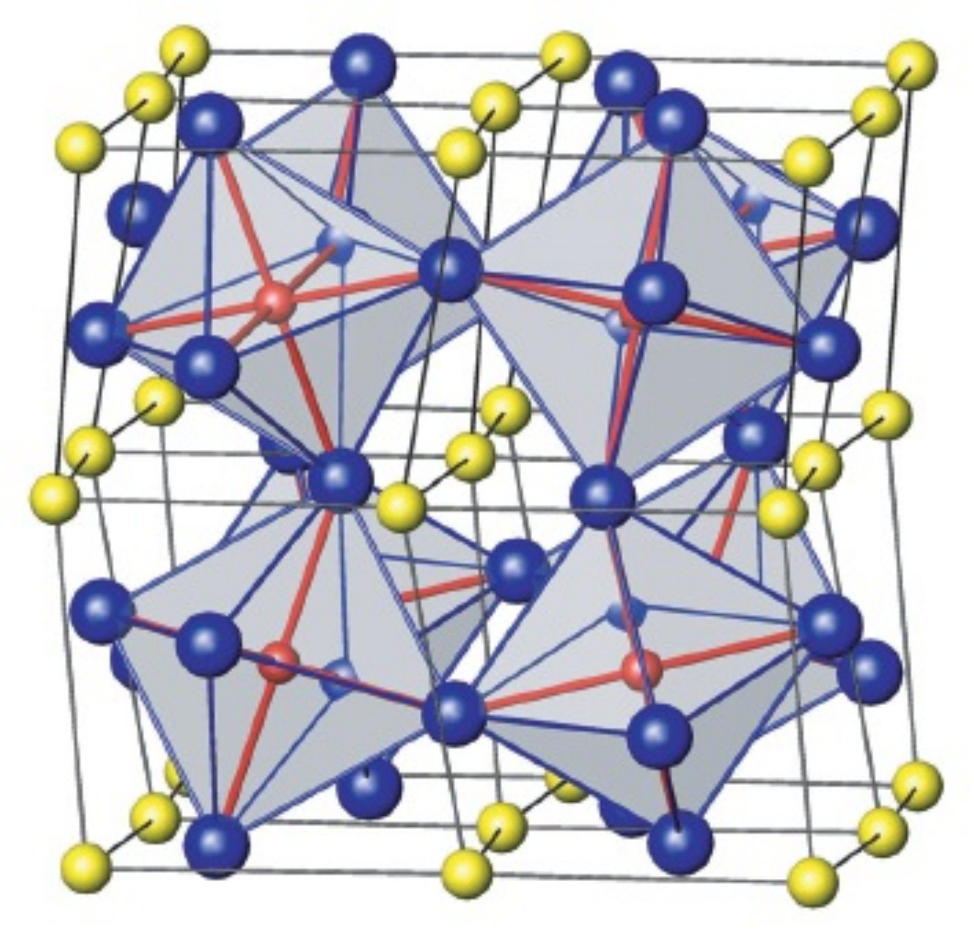
Perovskite: identification of crystal structure

Victor Moritz Goldschmidt
(1888 Zurich-1947 Oslo)
Pioneer of geochemistry
First described perovskite structure. Introduced `tolerance factor’ and coined `lanthanide contraction’ (among many achievements)
Mountain ridge Goldschmidttfjella (Spitzberg)

Helen Dick Megaw
(1907-2002)
Irish crystallographer
X-ray crystallography pioneer
Established perovskite structure
CaSnO3: Megawite
Megaw island-Antarctica (work on ice crystals)

Distorted perovskites

Depending on the ionic radii of the 3 ions, the material often adopts a structure which breaks perfect cubic symmetry (→ e.g. orthorombic)

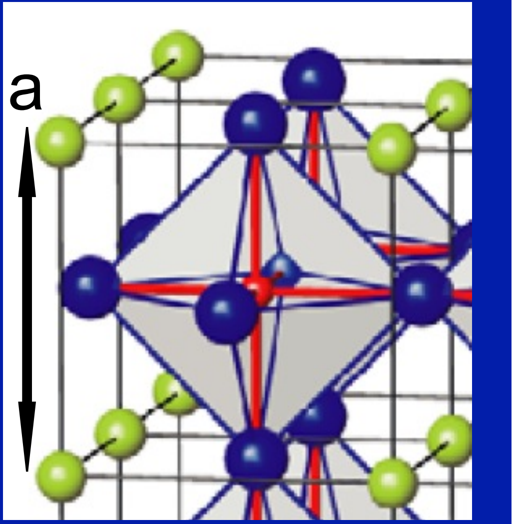


Example:
`$GdFeO_3$' distortion
- Octahedra remain perfect (no or very small Jahn-Teller)
- Rotation of octahedra along [010] and [001]
- Orthorombic symmetry
- 4 M-atoms per unit cell, all equivalent by symmetry
- M-O-M angle becomes π-θ

Other possible distortions e.g rhomboedric, rotation [111]

RMO$_3$: ``tolerance factor’’ (Goldschmidt)

- Consider close packing by hard spheres of radii r_R, r_M, r_O (ionic radii)
- Call a length of cubic cell



$$d(O-R)=\frac{a}{\sqrt{2}}\ ,\ d(O-M)=\frac{a}{2}$$

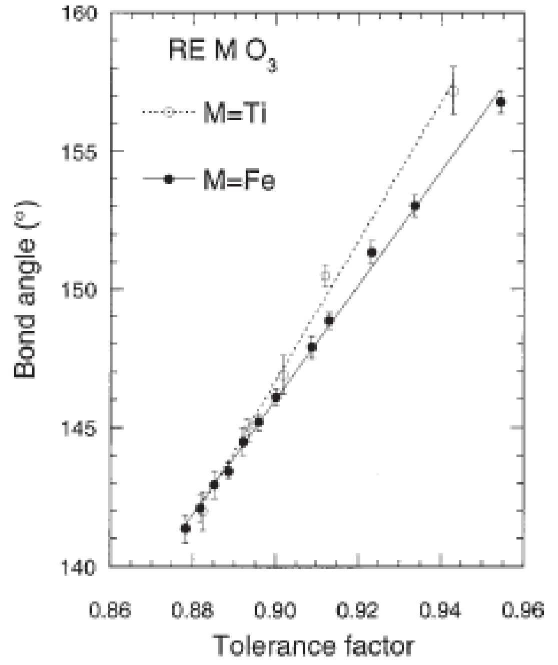
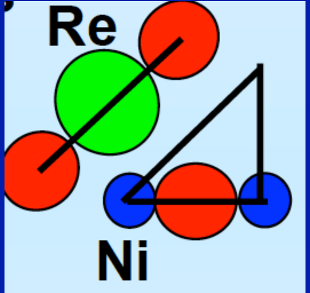


FIG. 62. The metal-oxygen-metal bond angles in an orthorhombically distorted perovskite (GdFeO$_3$-type) as a function of tolerance factor.

- Ideal packing will have:

$$t\equiv\frac{r_R+r_O}{\sqrt{2}(r_M+r_O)}=1$$

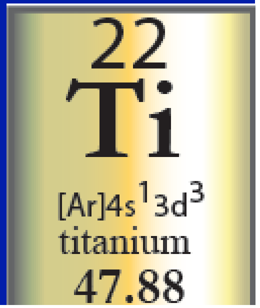


* t=1: ideal cubic perovskite
* t<1: deforms to rhomboedral, then orthorombic
* t too small (<0.86): unstable

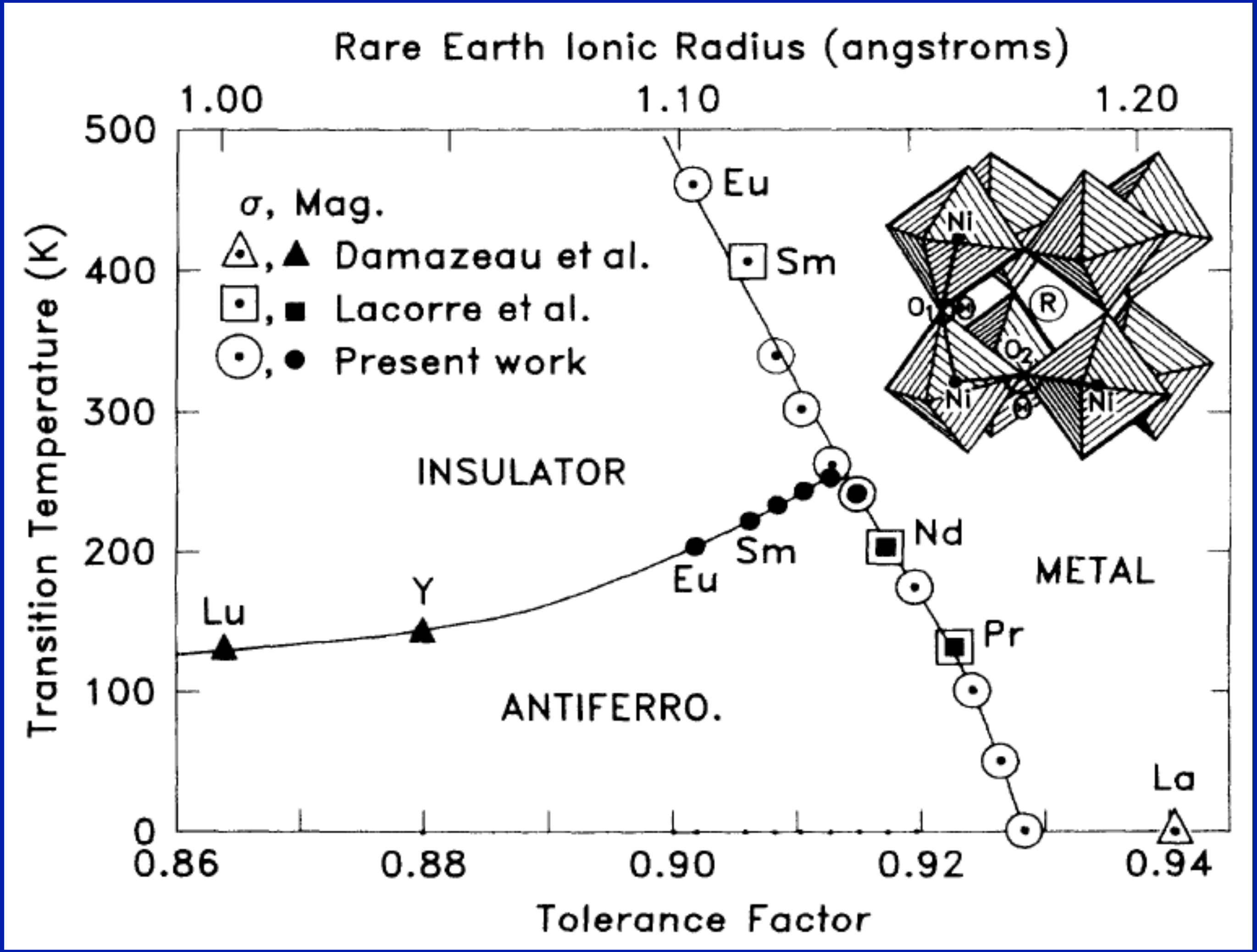
All this offers control on the material:

- Substitutions on R-site allow for a control of the (nominal) valence of M-ion (`doping')
- e.g: $LaTiO_3 \rightarrow La^{3+}$ [Xe], Ti^{3+} : [Ar]$3d^1$ config.
- $SrTiO_3 \rightarrow Sr^{2+}$ [Xe], Ti^{4+} : [Ar]$3d^0$ config.
- Iso-valent substitutions on R-site allow for a control of the distortion, hence of:

- Bandwidth (see below)
- And importantly of the splitting between d-levels



Sensitivity to distortion: $RNiO_3$ compounds (cf also lecture 1)

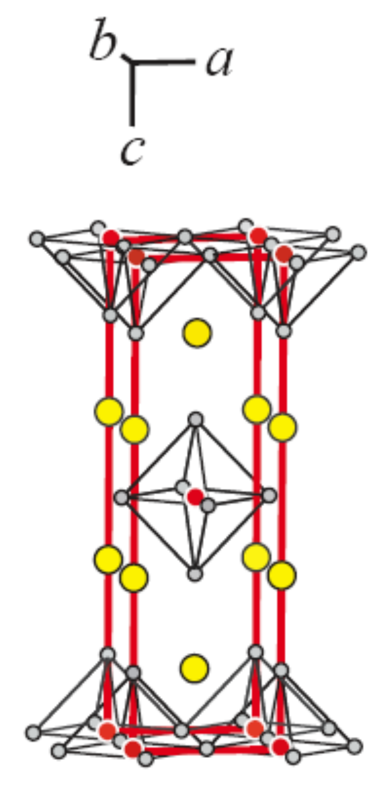


Torrance at al. Phys Rev B 45 (1992) 8209

Controlling dimensionality: the Ruddlesden-Popper series $R_{n+1}M_nO_{3n+1}$ (`layered perovskite')

Unit-cell

MO$_2$ layer →

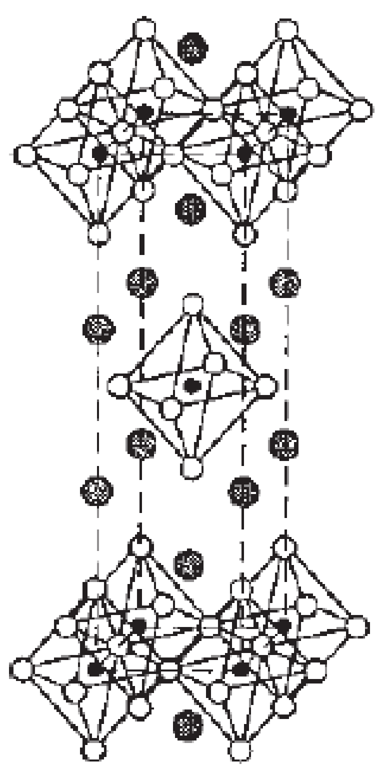


MO$_2$ layer →

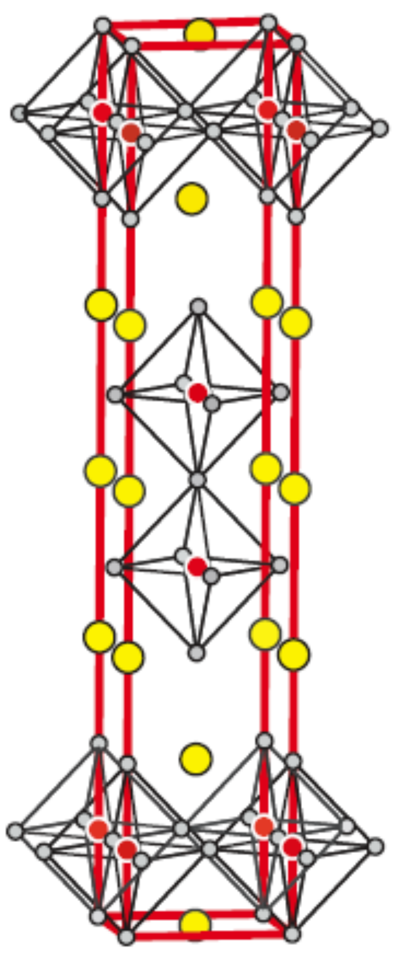
I4/mmm

Sr_2RuO_4

n=2



n=3



$Sr_3Ru_2O_7$

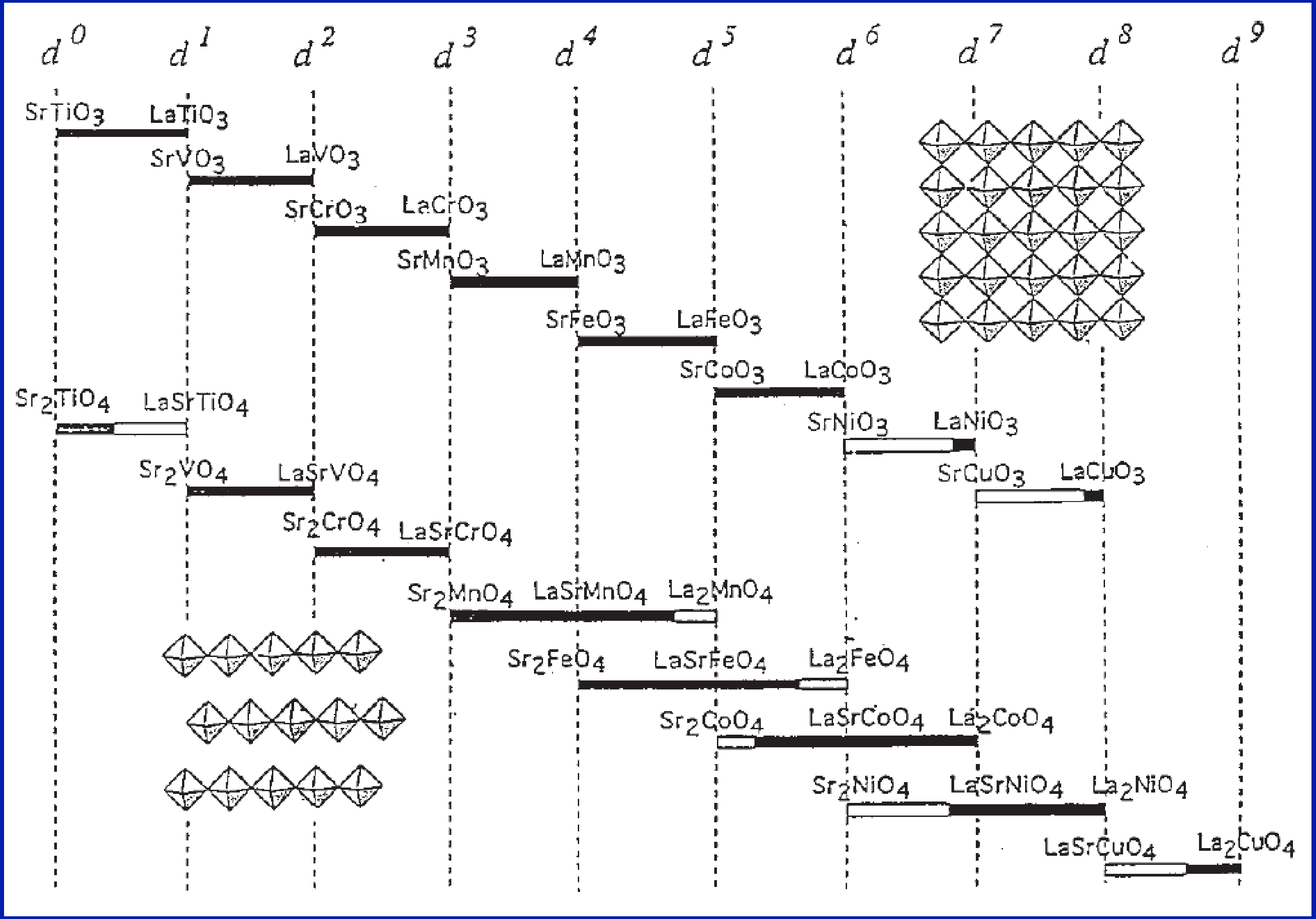
I4/mmm

Increasing n : ``from d=2 to d=3”

Usual perovskite RMO_3 corresponds to n→infinity

Some examples:

alloying on R-site changes nominal valence of M



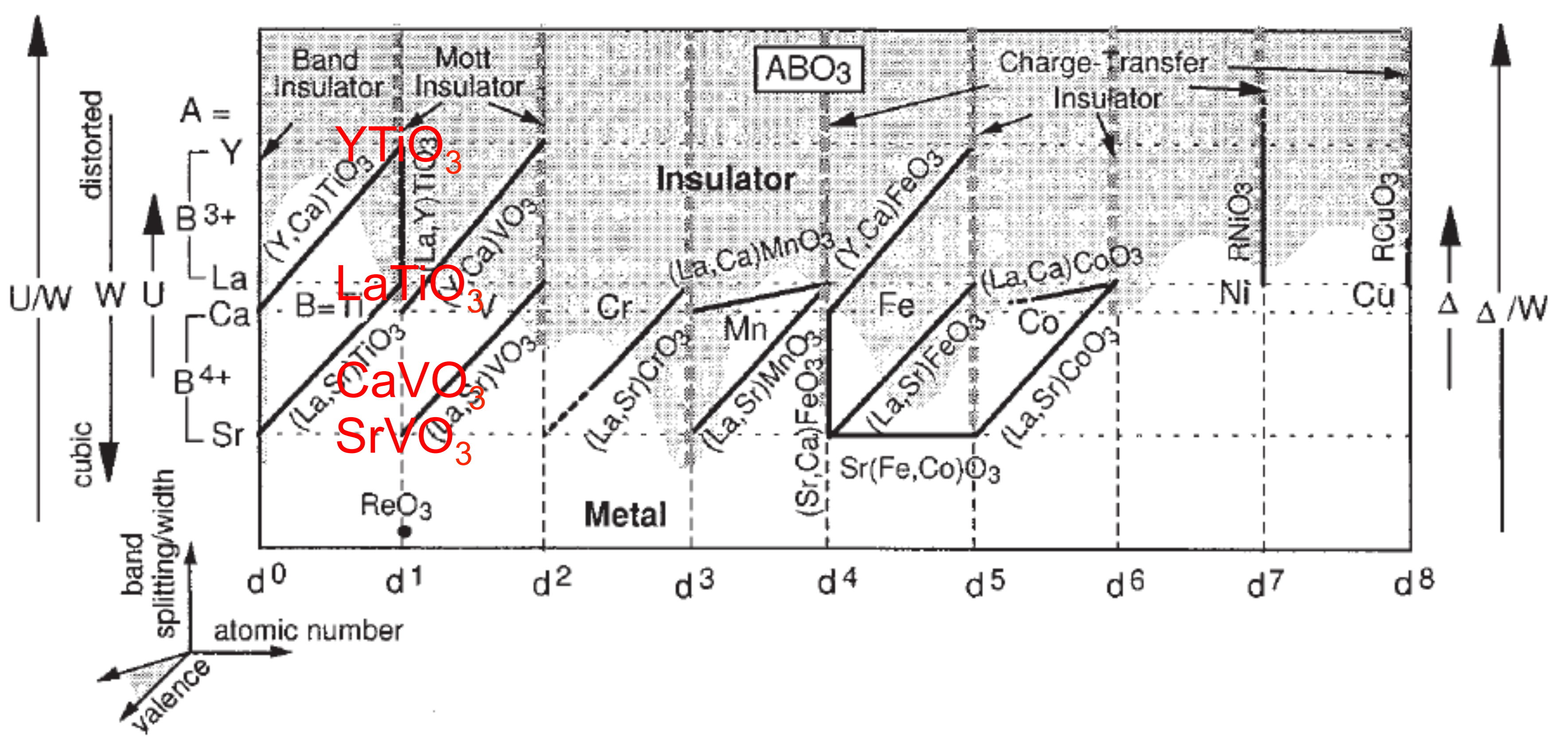
$Sr_{n+1}M_nO_{3n+1}$: 2(n+1)+4n-2(3n+1)=0 →M remains 4+ for all n

e.g. M=Ti 3d^1 shell (titanates); M=Ru 4d^4 shell (ruthenates)

$La_{n+1}M_nO_{3n+1}$: La^{3+} →nominal valence of M is (3n-1)/n +

e.g. $(La,Ba)_2CuO_4$ first discovered hi-Tc SC

The Mott phenomenon plays a key role



``Atsushi Fujimori's map of RMO$_3$ perovskites''

J.Phys Chem Sol. 53 (1992) 1595

Partially filled d-shells… and yet often insulators

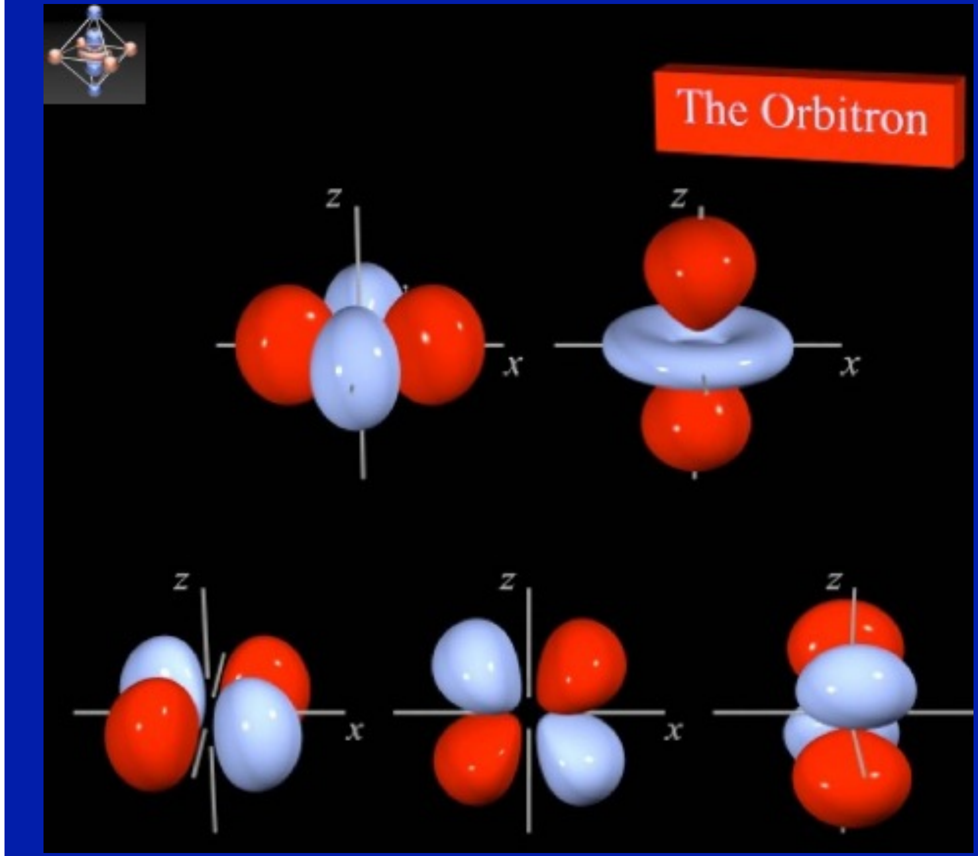
2. Crystal-Field Theory

Simple notions

(Bethe, van Vleck ~ 1930s)

Orbitals: from the isolated atom to the solid
Crystal-field splitting (Bethe, van Vleck)

Cubic-symmetry adapted 3d-orbitals:



3d orbitals are quite localized:
- No nodes in radial part
- Large centrifugal barrier $l(l+1)/r^2$

$$d_{x^2-y^2}\ ,\ d_{3z^2-r^2}$$

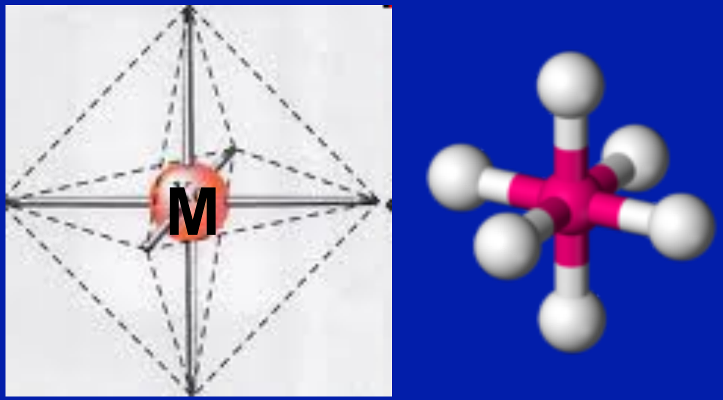
→ The e_g doublet

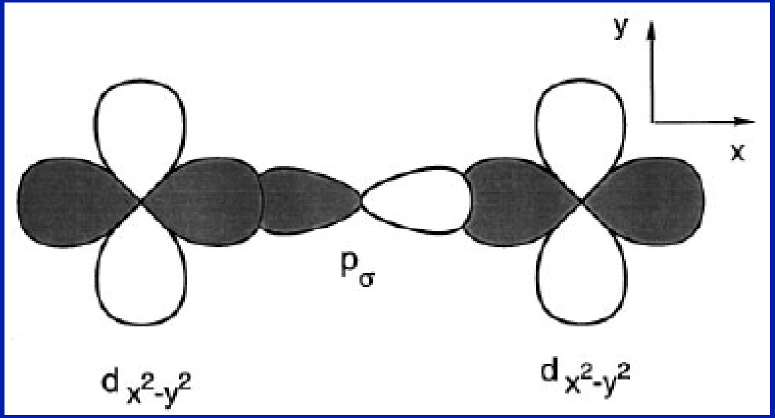
$$d_{xy}\ ,\ d_{xz}\ ,\ d_{yz}$$

→ The t_{2g} triplet

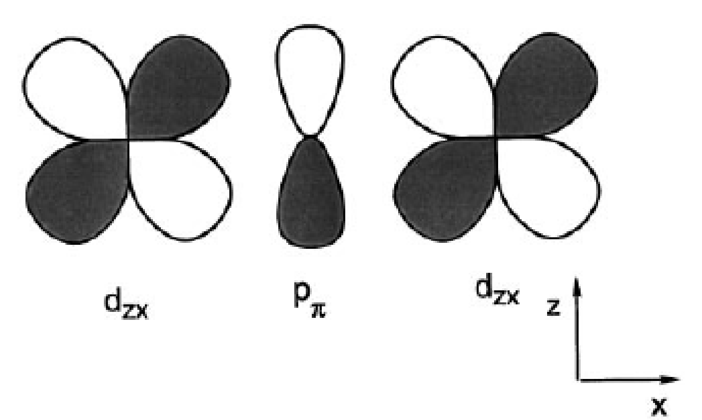
http://winter.group.shef.ac.uk/orbitron

Crystal-field splitting in octahedral environment :





e_g orbitals point towards oxygen atoms(sigma-bonding)
→feel larger Coulomb potential
→ pushed to higher energy



t_{2g} orbitals point away from oxygen atoms(pi-bonding)
→feel smaller Coulomb potential
→ lower energy than e_g

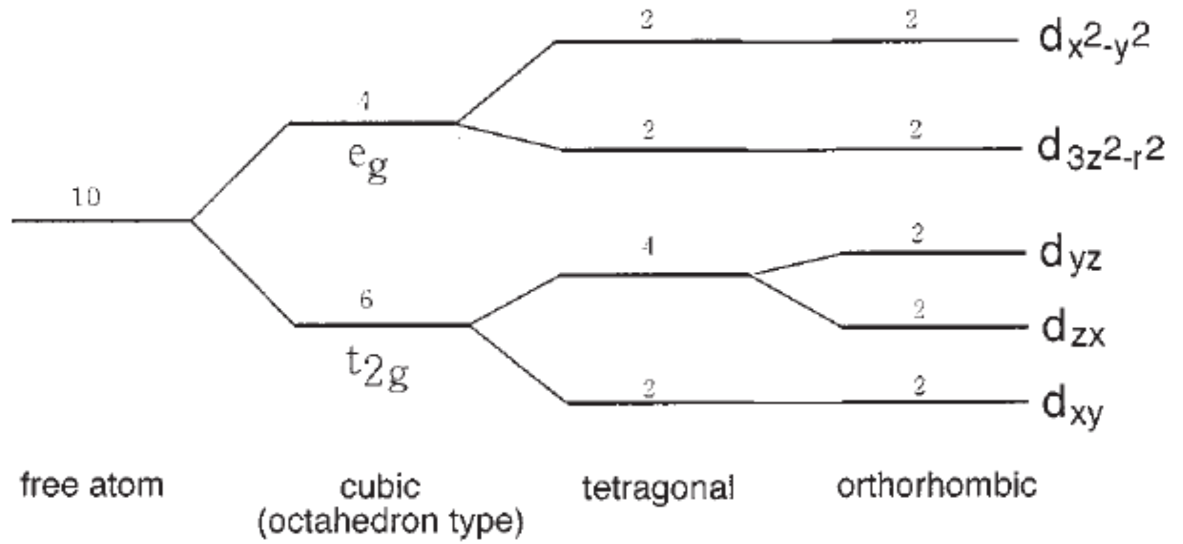


FIG. 2. Crystal-field splitting of $3d$ orbitals under cubic, tetragonal, and orthorhombic symmetries. The numbers cited near the levels are the degeneracy including spins.

Intra e_g splitting

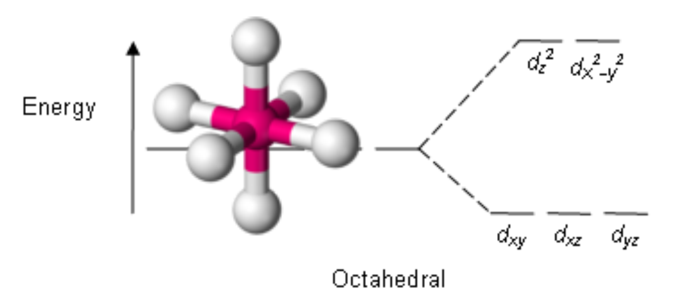
Intra-t_{2g} splitting

Lowering further the crystal symmetry (distort from cubic)
Induces additional lifting of degeneracy

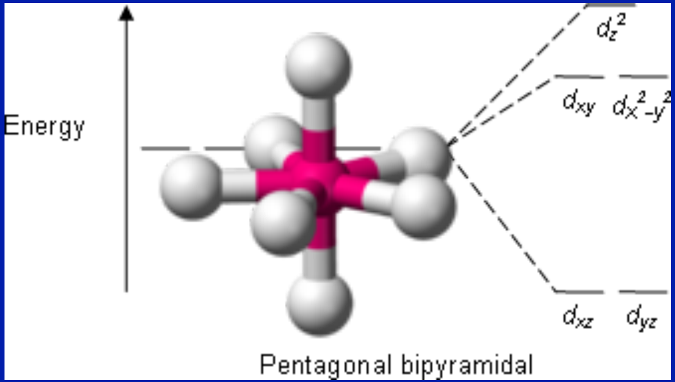
Orthorombic perovskite → Fully lifted

Tetrahedral environment (MO_4):
e_g has lower energy, t_{2g} higher

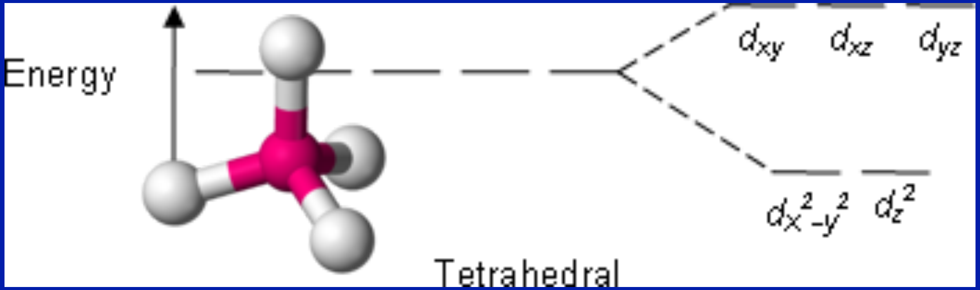
Other environments



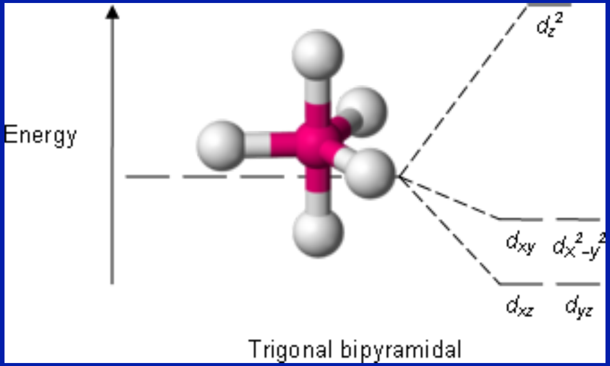
Octahedral



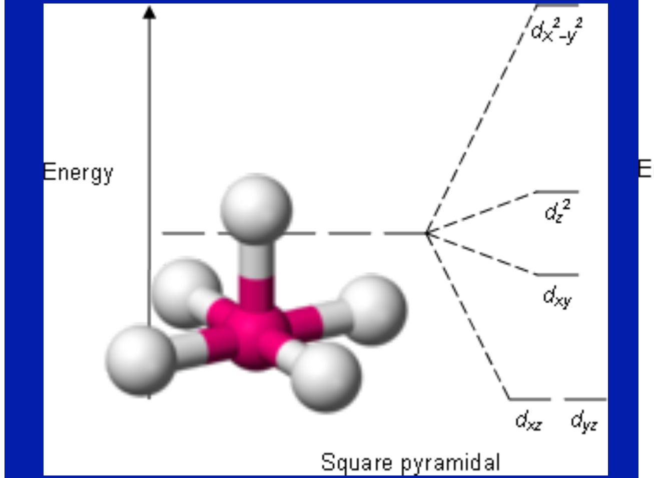
Pentagonal bipyramidal



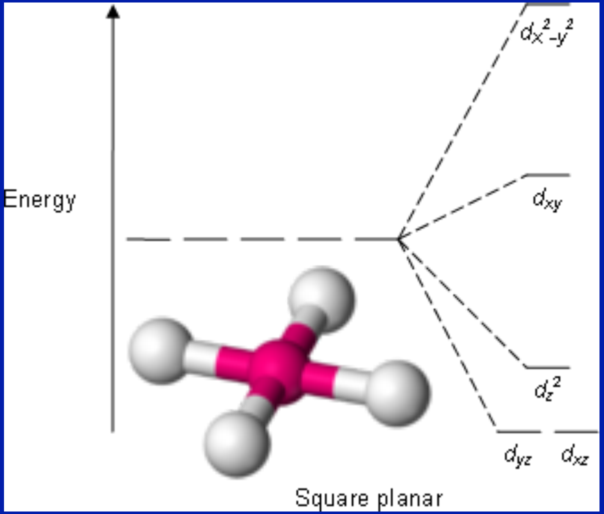
Tetrahedral



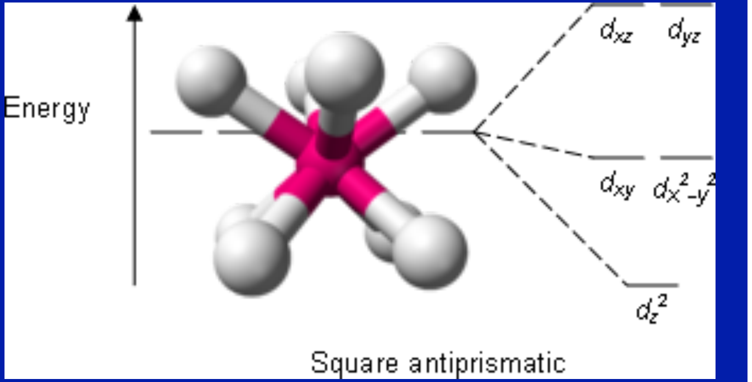
Trigonal bipyramidal



Square pyramidal

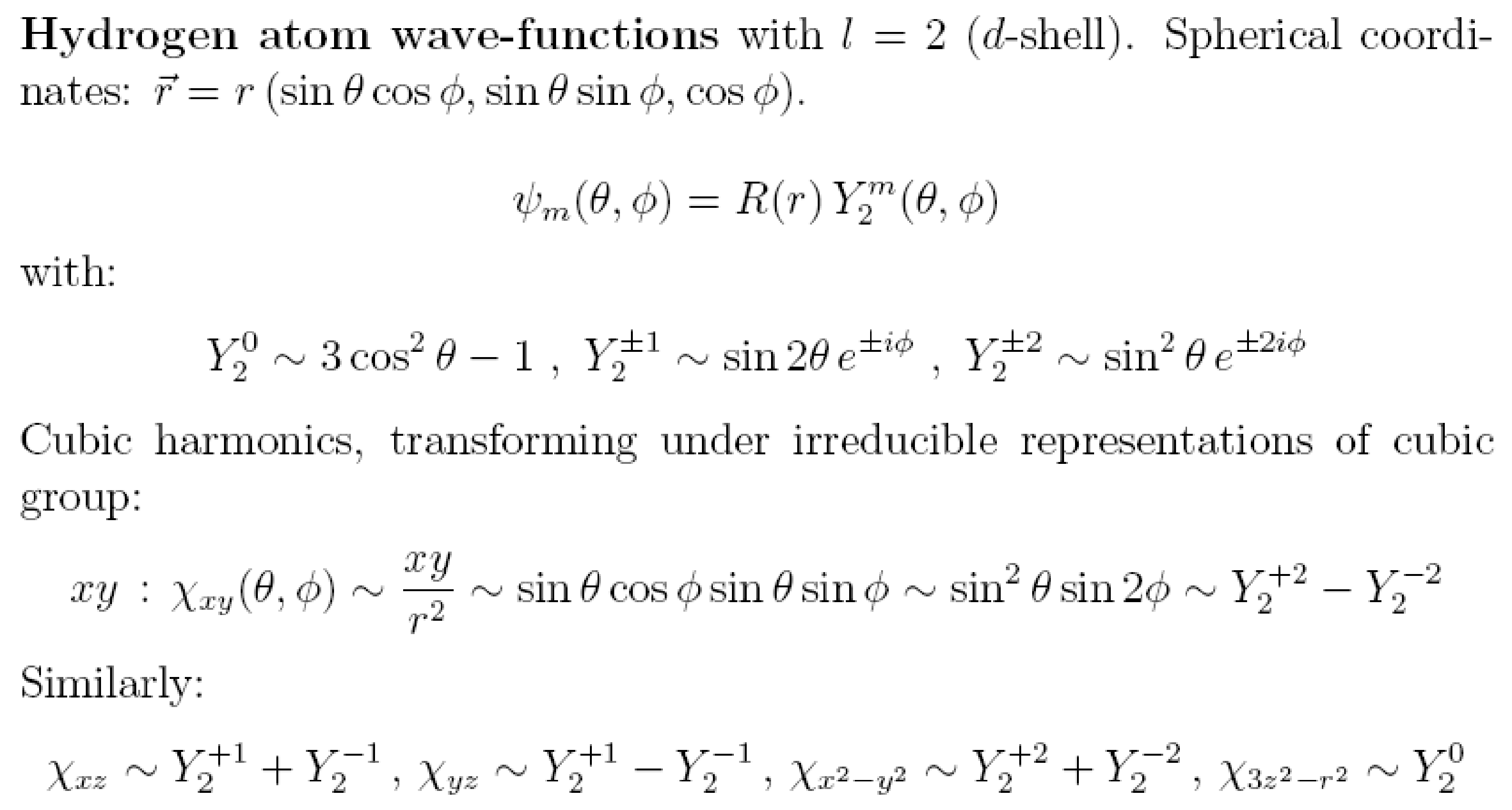


Square planar



Square antiprismatic

A crystal-field theory primer…



Hydrogen atom wave-functions with $l = 2$ (d-shell). Spherical coordinates: $\vec{r} = r\,(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\phi)$.

$$\psi_m(\theta,\phi) = R(r)\,Y_2^m(\theta,\phi)$$

with:

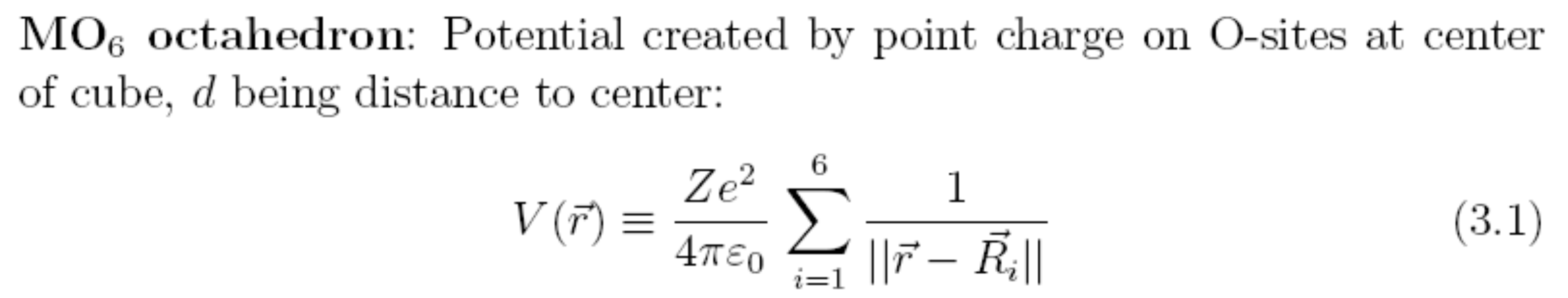
$$Y_2^0 \sim 3\cos^2\theta - 1\ ,\ Y_2^{\pm1} \sim \sin 2\theta\, e^{\pm i\phi}\ ,\ Y_2^{\pm2} \sim \sin^2\theta\, e^{\pm 2i\phi}$$

Cubic harmonics, transforming under irreducible representations of cubic group:

$$xy\ :\ \chi_{xy}(\theta,\phi) \sim \frac{xy}{r^2} \sim \sin\theta\cos\phi\sin\theta\sin\phi \sim \sin^2\theta\sin 2\phi \sim Y_2^{+2} - Y_2^{-2}$$

Similarly:

$$\chi_{xz} \sim Y_2^{+1} + Y_2^{-1}\ ,\ \chi_{yz} \sim Y_2^{+1} - Y_2^{-1}\ ,\ \chi_{x^2-y^2} \sim Y_2^{+2} + Y_2^{-2}\ ,\ \chi_{3z^2-r^2} \sim Y_2^0$$



MO$_6$ octahedron: Potential created by point charge on O-sites at center of cube, d being distance to center:

$$V(\vec{r}) \equiv \frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{6}\frac{1}{||\vec{r} - \vec{R}_i||} \tag{3.1}$$

Expand:

$$\frac{4\pi\varepsilon_0}{Ze^2}V(r) = \frac{6}{d} + \frac{7\sqrt{\pi}}{3}\frac{r^4}{d^5}\left[Y_4^0(\theta,\phi) + \sqrt{\frac{5}{14}}\left(Y_4^4(\theta,\phi) + Y_4^{-4}(\theta,\phi)\right)\right] + \cdots \tag{3.2}$$

Treat second term as perturbation $\delta V(r,\theta,\phi)$: breaks spherical symmetry. Because of proper choice of cubic orbital above:

$$\begin{aligned} \langle \chi_m | \delta V | \chi_{m'} \rangle &= \Delta_t\, \delta_{mm'} \text{ for } m = xy, xz, yz \\ &= \Delta_e\, \delta_{mm'} \text{ for } m = x^2-y^2, 3z^2-r^2 \end{aligned}$$

with:

$$\boxed{\Delta_e - \Delta_t = 1.67\,\frac{Ze^2}{4\pi\varepsilon_0\, d^5}\int_0^\infty r^4 R(r)^2\, r^2 dr \equiv \text{“}10Dq\text{''}}$$

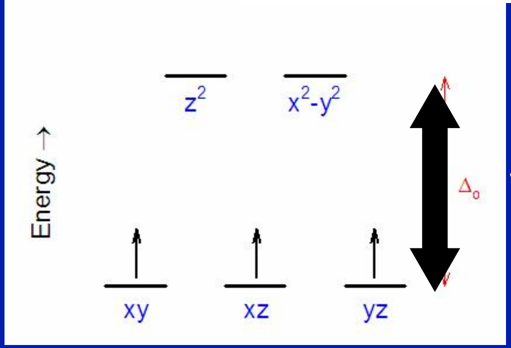
Why is ruby red ?

cf e.g: http://www.chm.davidson.edu/vce/CoordChem/CFT.html

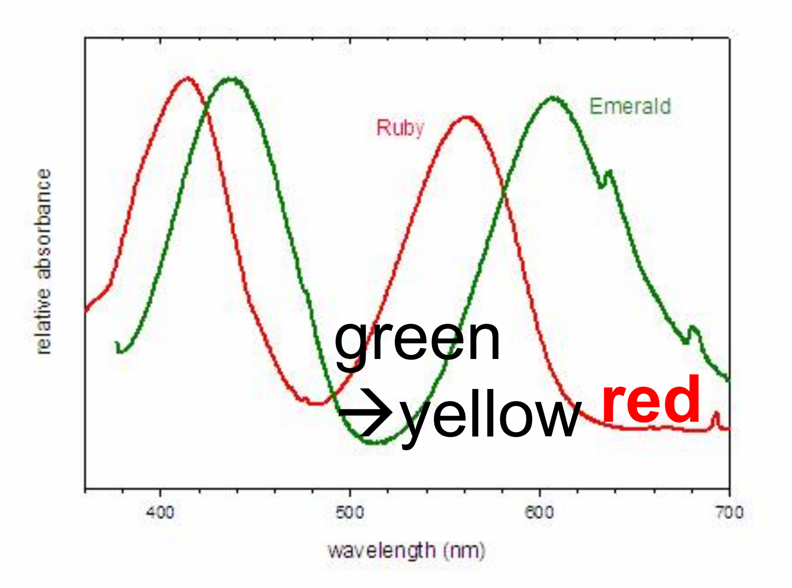
Ruby: small amount
Of Cr $^{3+}$ impurities
Substituting Al^{3+} in
Al_2O_3 (corundum),
a large-gap
transparent insulator

Cr3+ ($3d^3$) 3 electrons in t_{2g} shell

$$\Delta_0 = 2.21\,\mathrm{eV} \rightarrow \lambda \simeq 561\,\mathrm{nm}$$



absorption of most visible
wavelength beyond red

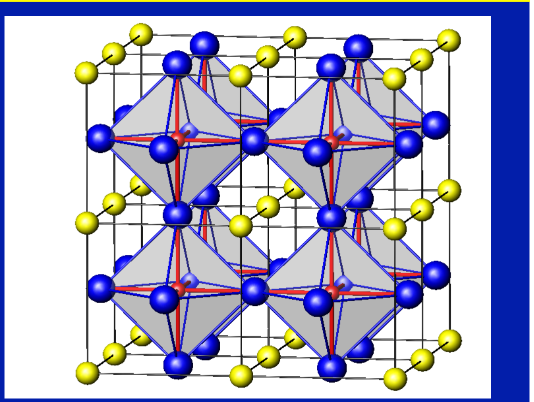


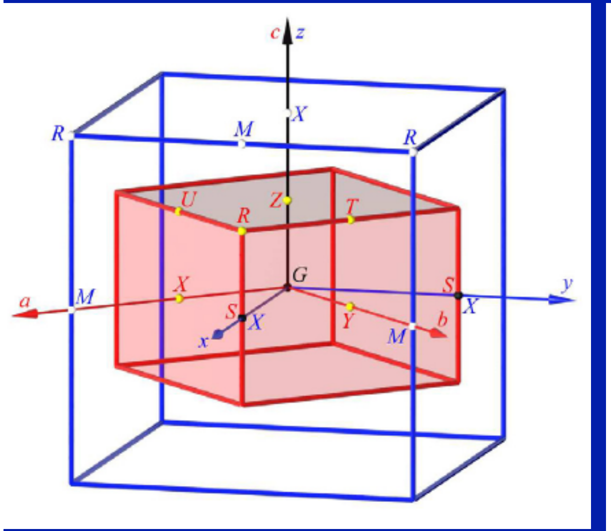
3.From Crystal Field Theory to Band Structure

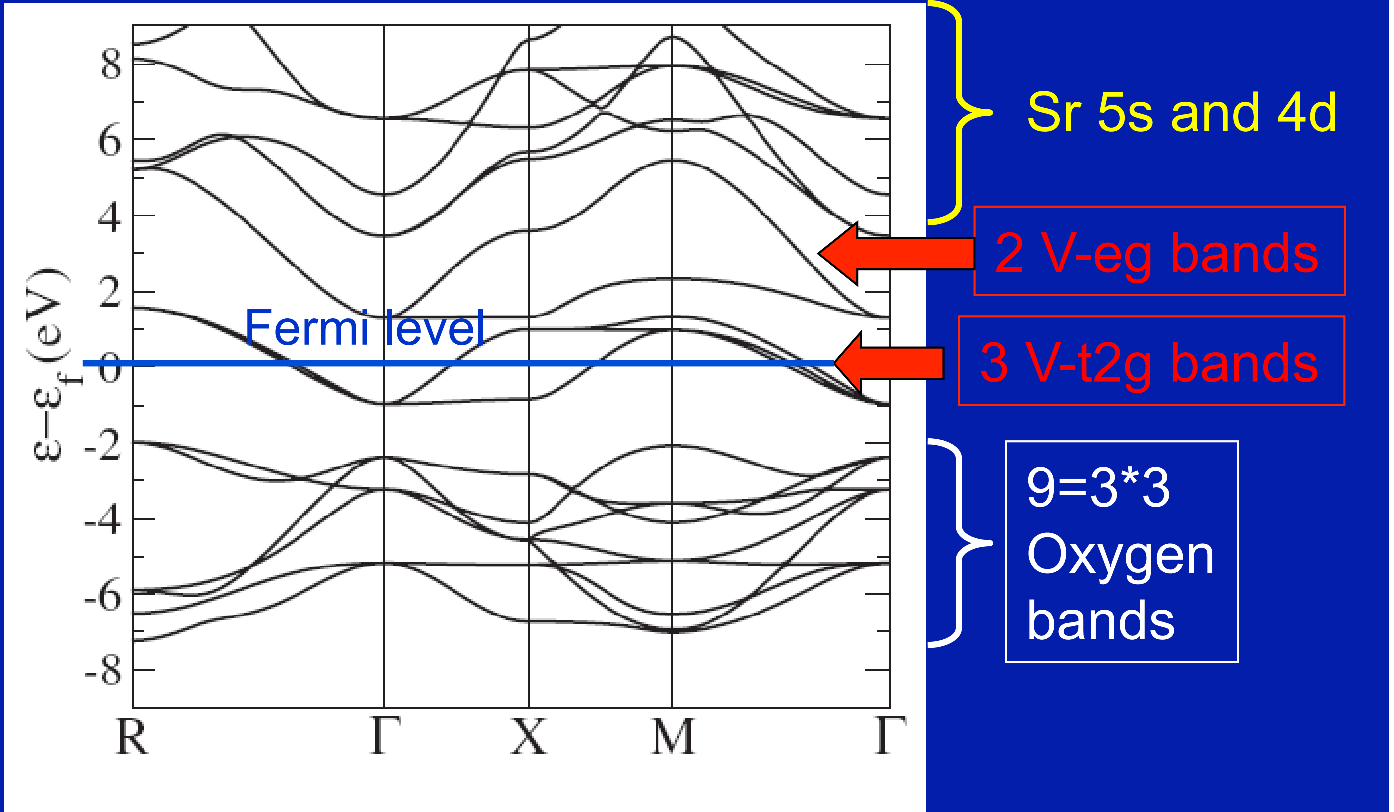
From the atom to the full solid: energy bands of oxides

(or: how to make sense of a plate of spaghettis…)

A simple case: cubic $SrVO_3$







Sr 5s and 4d

2 V-eg bands

3 V-t2g bands

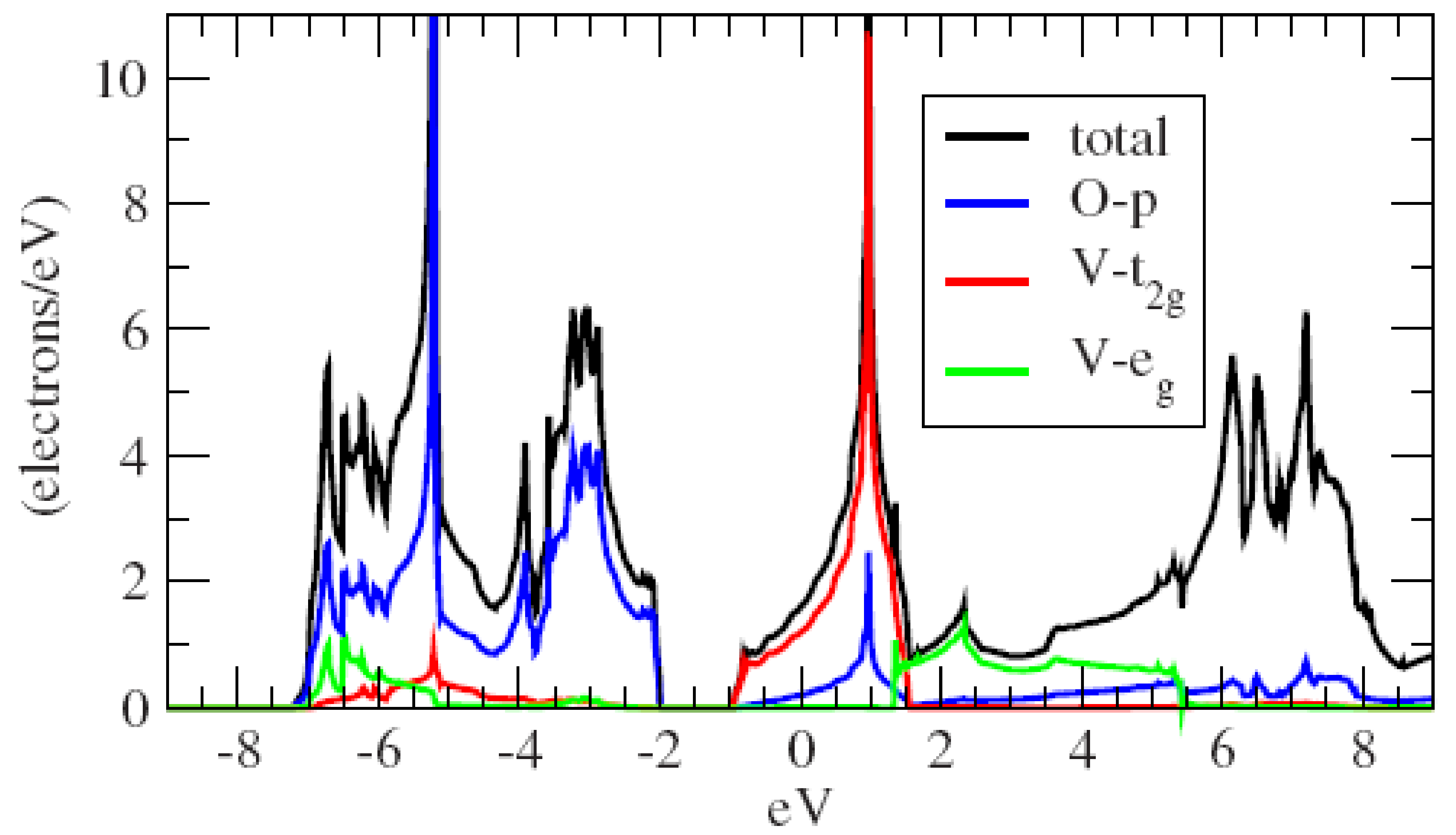
9=3*3
Oxygen
bands

FIG. 1. LDA band structure for $SrVO_3$.

Pavarini et al.
PRL 92 (2004) 176403
New J.Phys 7 (2005) 188
Amadon et al.
PRB 77 (2008) 205112

Density of states:

(orbitally-resolved, i.e projected on ~ atomic orbitals)



Strong mixing of V-eg states with oxygen

t2g bandwidth ~ 2.6 eV

To understand orbital character better, plot `fat bands':

Project Bloch functions onto atomic-like orbitals and plot matrix element at each k-point: $\left|\langle\psi_{\mathbf{k}\nu}|\phi_{lm}\rangle\right|^2$

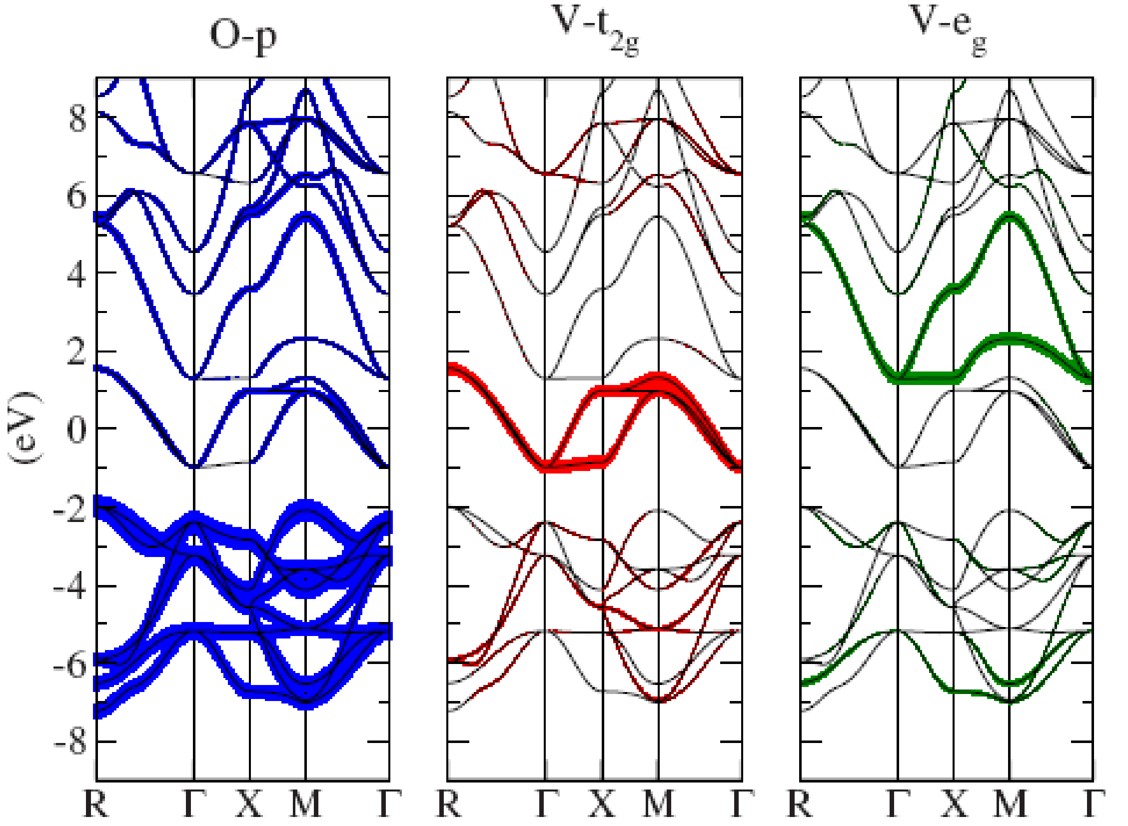


FIG. 3. (Color online) LDA band structure for $SrVO_3$ computed in PAW, with "fatbands" to show the amplitude of the projection of each band on a given atomic orbital (O p, V t_{2g}, and V e_g).

Mixing of oxygen with d-states obvious, especially for eg

Summarize key infos from band-structure, in this (quite) simple case:

- t_{2g} manifold of 3 bands well-separated from oxygen (below) and e_g bands (above)
- t_{2g} bands occupied by 1 electron in total (as requested)
- t_{2g} bandwidth around 2.6 eV
- Distance between center of t_{2g} and center of oxygen band: about 6.5 eV (only 1eV from top of O to bottom of t2g though) → `charge-transfer energy' is large
- Bandstructure (LDA) is that of a METAL
- Effective mass (from specific heat) is found to be roughly a factor of 2 larger than the one from LDA

More on the bandwidth: hopping is *via oxygen*

- Each Vanadium is in a cage of 6 oxygens

→Direct d-d hopping is difficult, hence direct t_{dd} is small *(this is one of the two main differences between a pure Transition metal and its oxide, the other one being that the 4s orbital is empty in the oxyde → oxydes have narrow bands)*

- Hopping of electrons on V-sites occurs through hybridization between O p-orbitals and V d-orbitals, with amplitude t_{pd}

-Roughly, when the charge-transfer energy Δ (see below) is large, the amplitude of the effective d-d hopping is of order:

$$t_{\text{eff}}^{dd} \sim t_{pd}^2/\Delta$$

Distortion: covalency between O and cation (Sr,La)

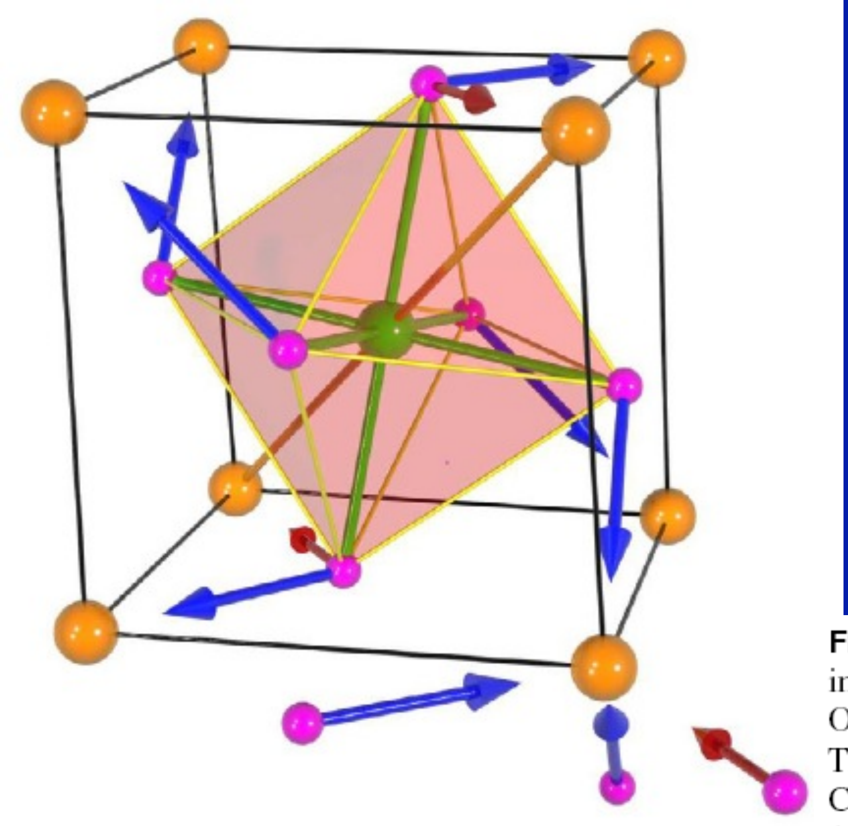
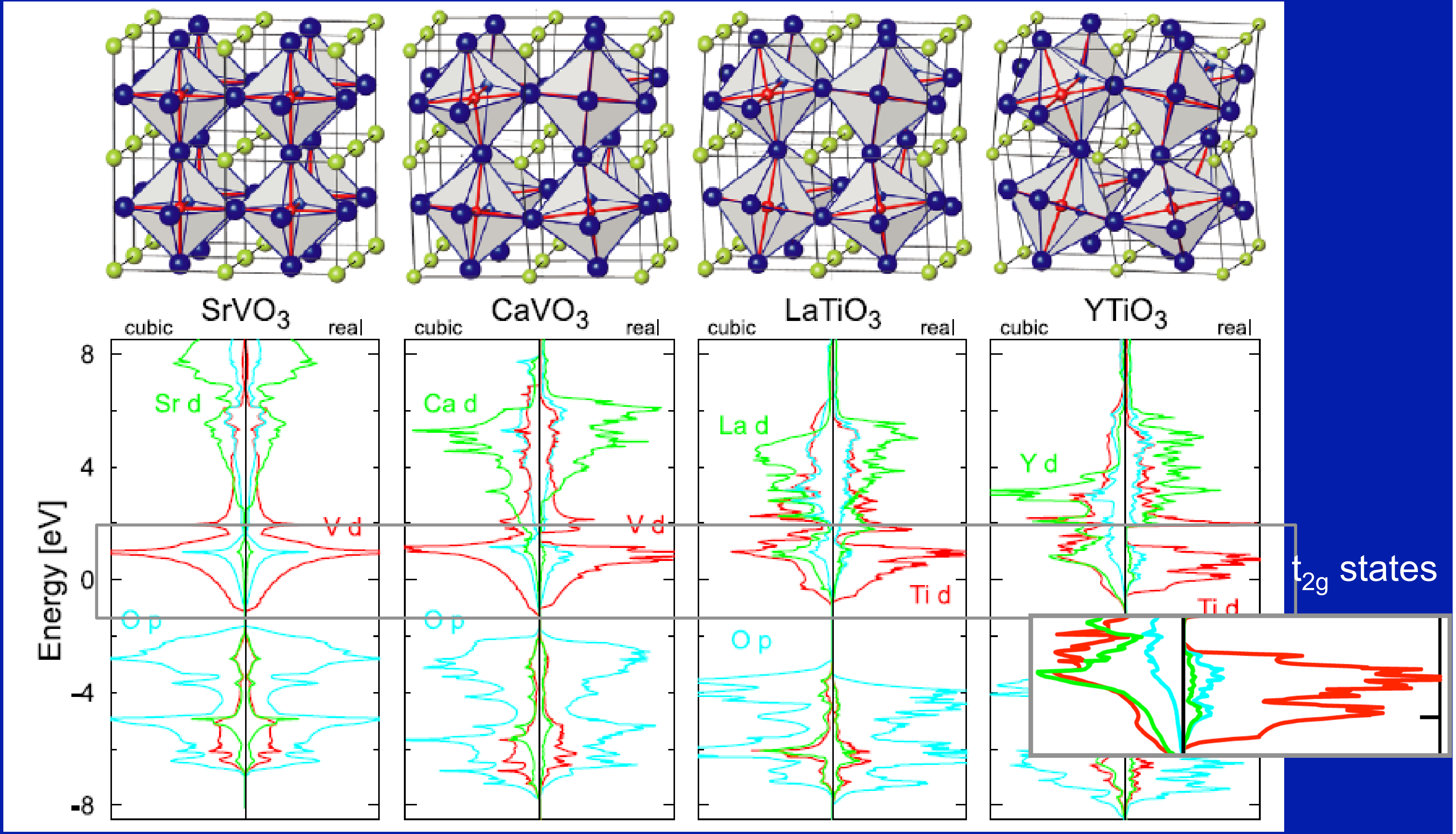


Figure 7. Schematic representation of the O-A covalent bonds shown for $LaTiO_3$ in figures 5 and 6: O1 binds to *two* while O2 binds to *one* of the four A-neighbours. One of the two O1-A bonds is relatively weak and is indicated by a short, red arrow. The resulting $GdFeO_3$-type distortion shortens the O-A bonds correspondingly. In $CaVO_3$, $LaTiO_3$, and $YTiO_3$, the shortest O1-A bond is shortened by respectively 10, 17, and 28% with respect to the average, the 2nd-shortest O1-A bond by respectively 4, 11, and 23%, and the shortest O2-A bond by respectively 12, 16, and 22%. The oxygen coordination of the A-ion is reduced from 12 to 4, with two of the near oxygens being in the horizontal, flat face of the distorted A-cube, and the two others in *one* of the vertical, buckled faces. The A-B-A diagonal (orange bar) lying in the plane of the short, red arrows is shortened by respectively 3, 7, and 9% of the average. The unit shown is the front bottom left one (subcell 1) seen in e.g. figure 2.

Effect**s** of the orthorombic distortion: SrVO$_3$, CaVO$_3$,LaTiO$_3$,YTiO$_3$ (all d^{1,} ***ALL METALS in LDA !)***



t_{2g} states

Left panels: hypothetical cubic; Right panel: real structure

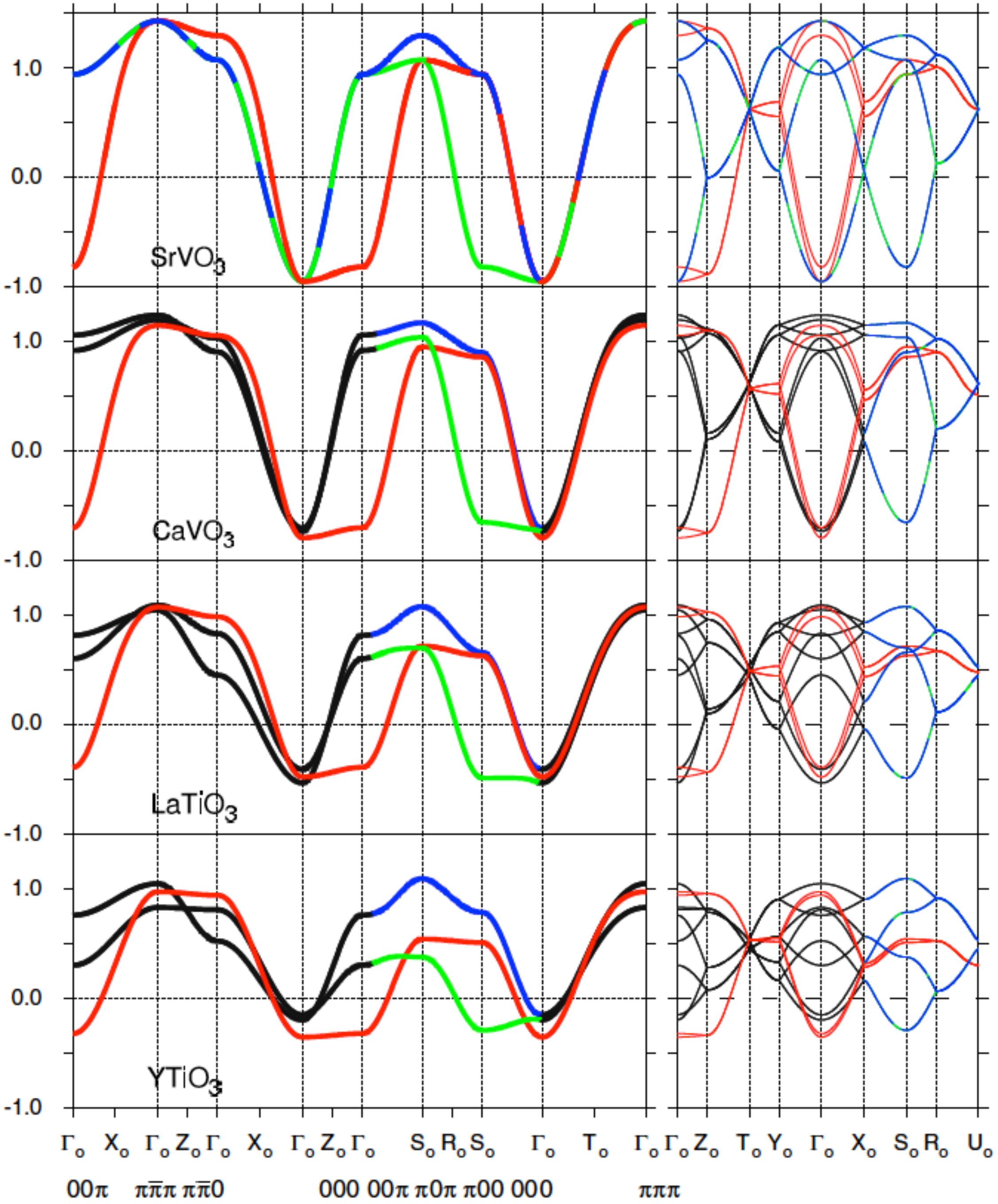


Figure 11. Cubically averaged ($\mathbf{Q}=\mathbf{0}$) t_{2g} LDA bandstructures in eV, in the primitive monoclinic BZ (left), and folded into the orthorhombic BZ (right).

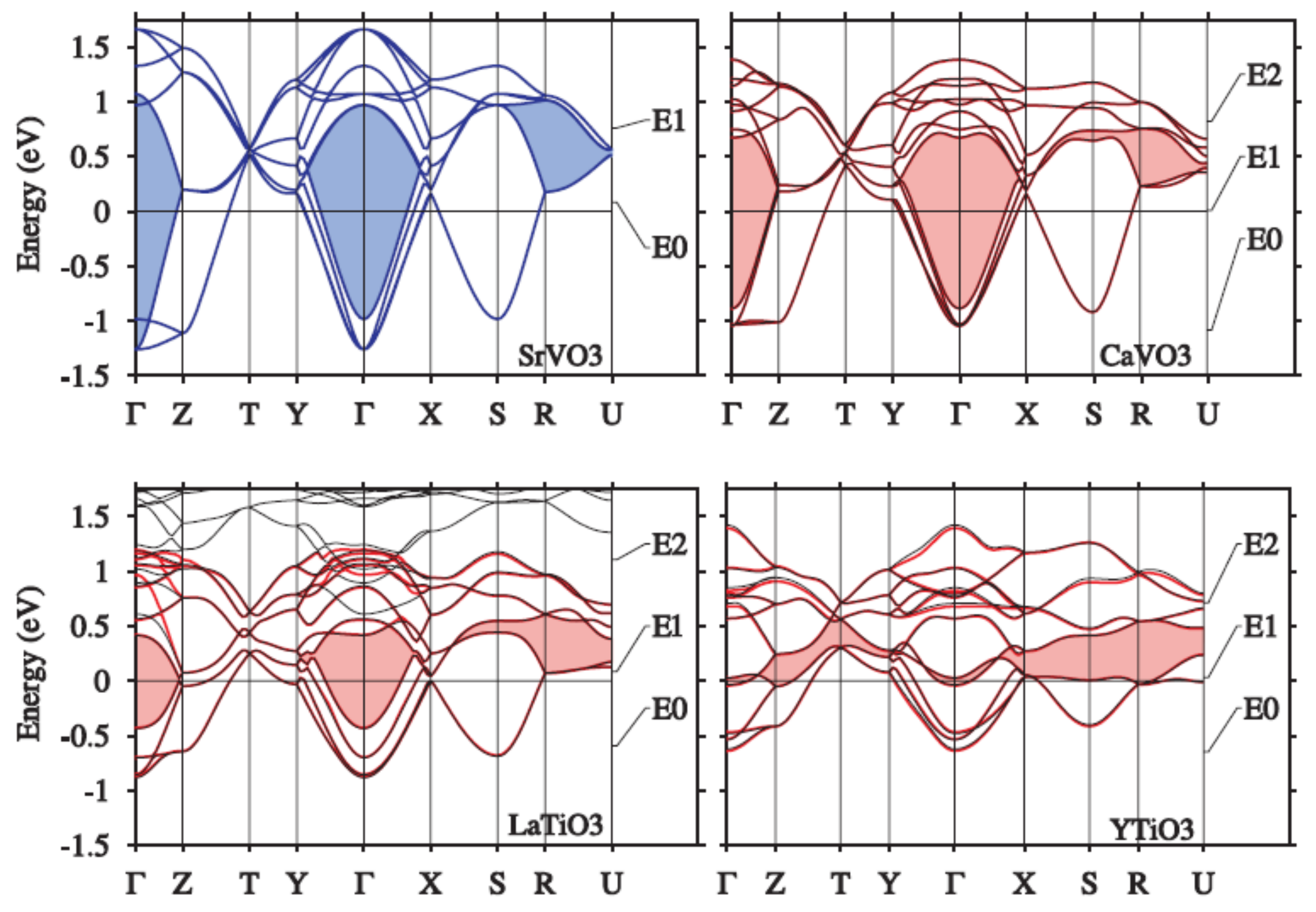


Figure 10. Low-energy LDA bandstructures of $SrVO_3$, $CaVO_3$, $LaTiO_3$, and $YTiO_3$. The cubic bands for $SrVO_3$ (figure 3) have been folded into the orthorhombic BZ (figure 9). The black bands were obtained with a large NMTO basis, while the coloured ones were obtained with the truly-minimal B $d(t_{2g})$ basis. The two are indistinguishable, except for $LaTiO_3$ where the bottom of the La 5*d*-band overlaps the top of the Ti t_{2g}-band because the older structural data [44] was used here. With the recent, slightly more distorted structure [12], O-A covalency removes this overlap as discussed in section 2 and figure 1, and as shown in figures 4, 12, and 17. In order to emphasize the development of the bandstructure along the series, the gap between the lower 1/3 and the upper 2/3 of the bands has been shaded.

The two effects of distortion:

- 1) Reduction of total t_{2g} bandwidth:

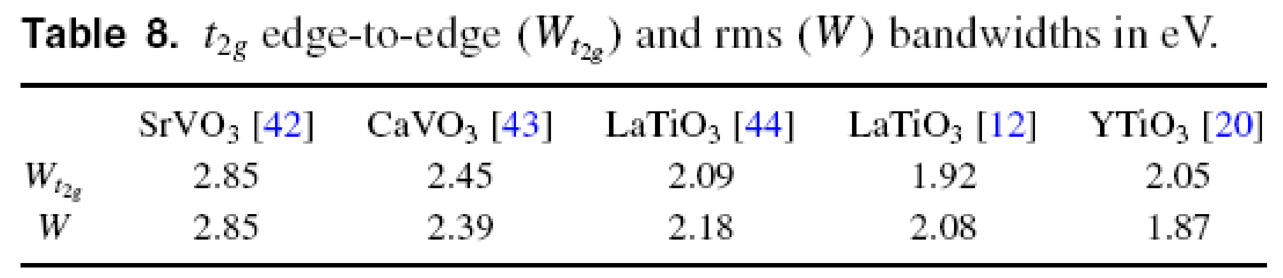


Table 8. t_{2g} edge-to-edge ($W_{t_{2g}}$) and rms (W) bandwidths in eV.

	$SrVO_3$ [42]	$CaVO_3$ [43]	$LaTiO_3$ [44]	$LaTiO_3$ [12]	$YTiO_3$ [20]
$W_{t_{2g}}$	2.85	2.45	2.09	1.92	2.05
W	2.85	2.39	2.18	2.08	1.87

This is because the O-M-O bond is no longer straight
→ pi-bonding less efficient

2) Splitting between t_{2g} orbitals (<u>lifting of orbital degeneracy</u>)

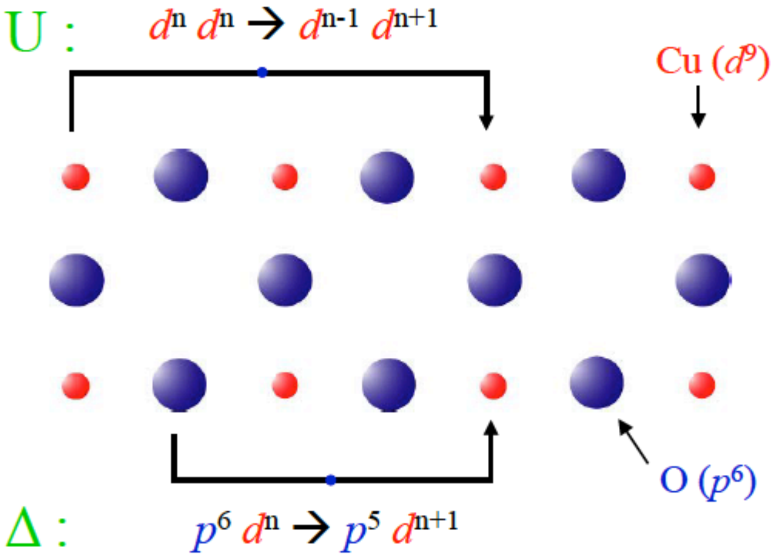
(140,200) meV for LaTiO3 ;
(200,330) meV for YTiO3

→***Both effects*** are responsible for the Mott insulating nature of $LaTiO_3$ and $YTiO_3$ (see below)

4.The role of the Ligand (oxygen) states

- Hopping is through oxygens: M-O-M bond
- What costs less: removing an electron from Metal or from Oxygen (i.e. forming a ligand hole) ?

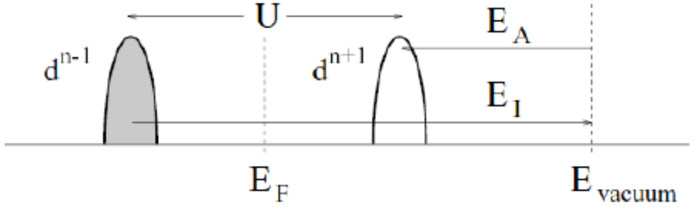
Charge-Transfer Energy



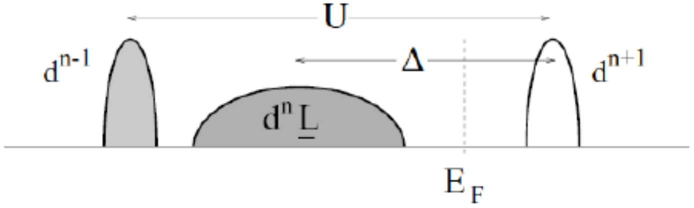
U : $d^n\ d^n \rightarrow d^{n-1}\ d^{n+1}$

Δ : $p^6\ d^n \rightarrow p^5\ d^{n+1}$

(a) Mott-Hubbard insulator $\boxed{\Delta > U}$



(b) Charge transfer insulator $\boxed{\Delta < U}$



$$U = E_I^{TM} - E_A^{TM} - Epol$$

$$\Delta = E_I^{O} - E_A^{TM} - Epol + \delta E_M$$

If Δ < (W+w)/2 → Self doped metal

E_I	ionization energy
E_A	electron affinity energy
E_M	Madelung energy

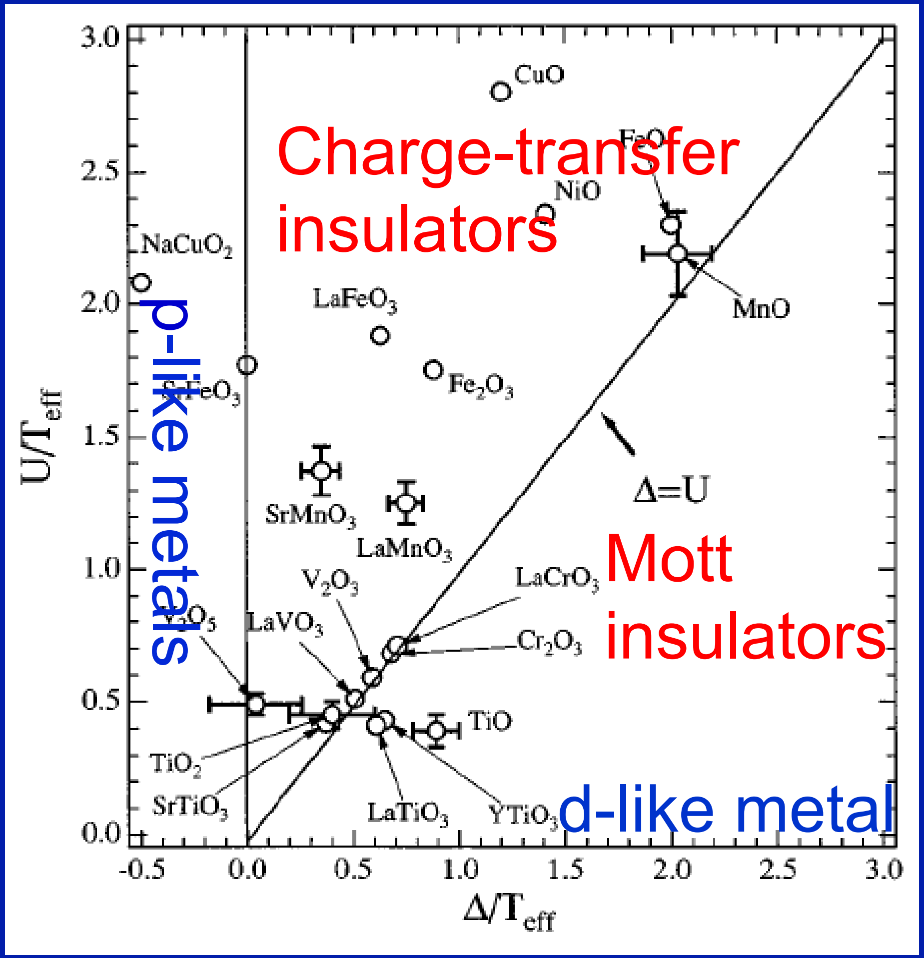
Epol depends on surroundings!!!

- **J.Hubbard, Proc. Roy. Soc. London A 276, 238 (1963)**
- **ZSA, PRL 55, 418 (1985)**

slide courtesy G.Sawatzy, MaNEP school 2015

The ZSA `phase diagram’

Zaanen, Sawatzky, Allen
PRL 55, 418 (1985)

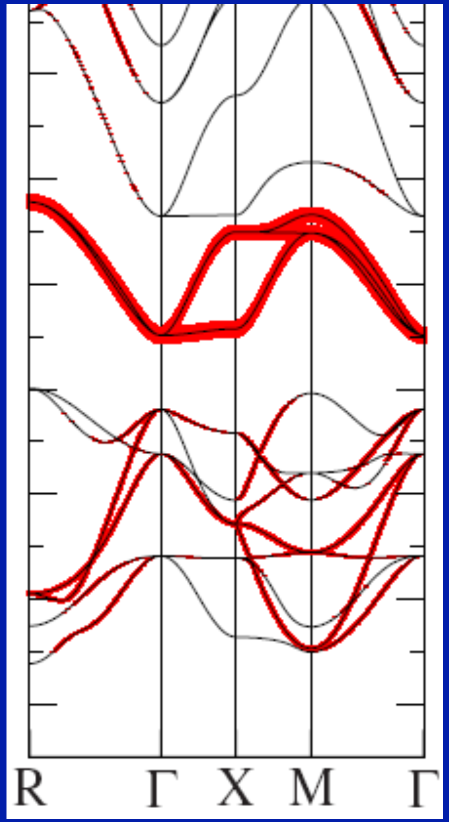


Bocquet et al.
PRB 1996

Late TMOs are charge-transfer insulators $(U > \Delta)$: attractive potential of nucleus is larger, Hence large electron removal energy $d^n \rightarrow d^{n-1}$ and less screening

Effective model depends on choice of selected energy range

Decide for which bands (or rather: for which energy window) an effective model will be constructed



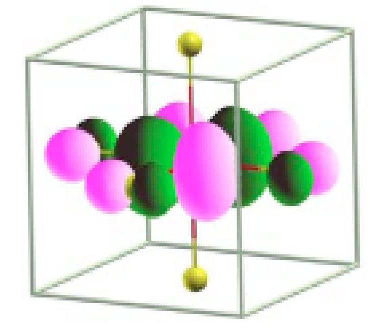
V-t_{2g} states only
(3 bands)

<u>Small energy window</u>
→Wannier functions will leak on oxygen sites to capture V-O hybridization

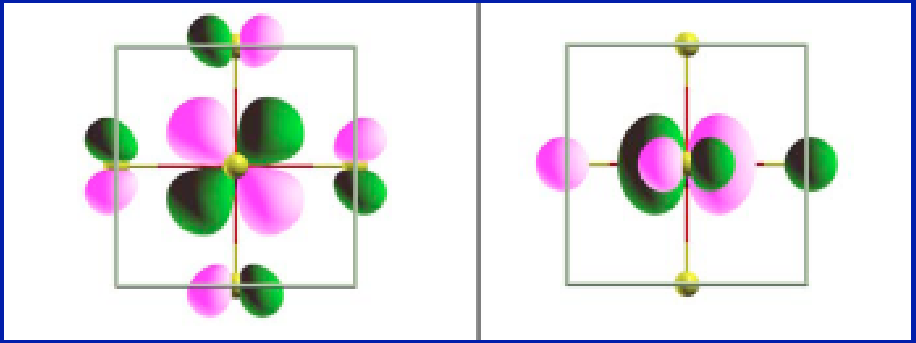
V-t2g and eg states
And O –states
(14 bands)

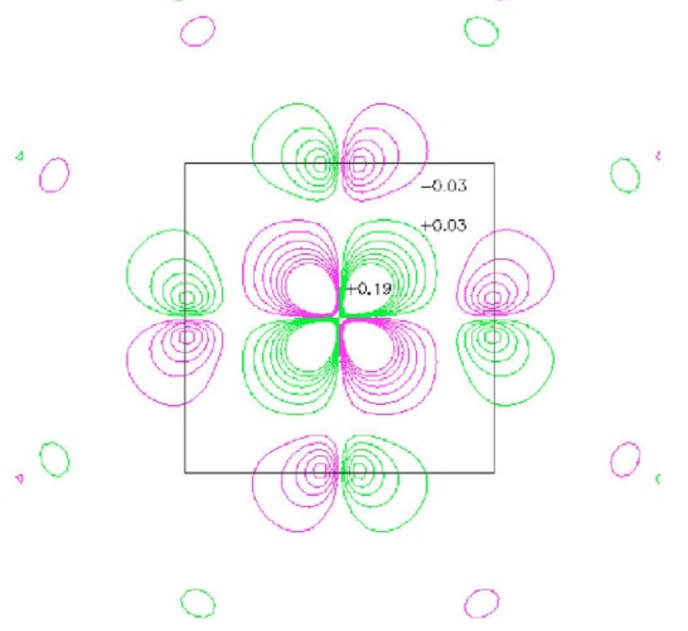
<u>Large energy window</u>
→Wannier functions are quite localized and atomic-like

t_{2g} only: extended Wanniers

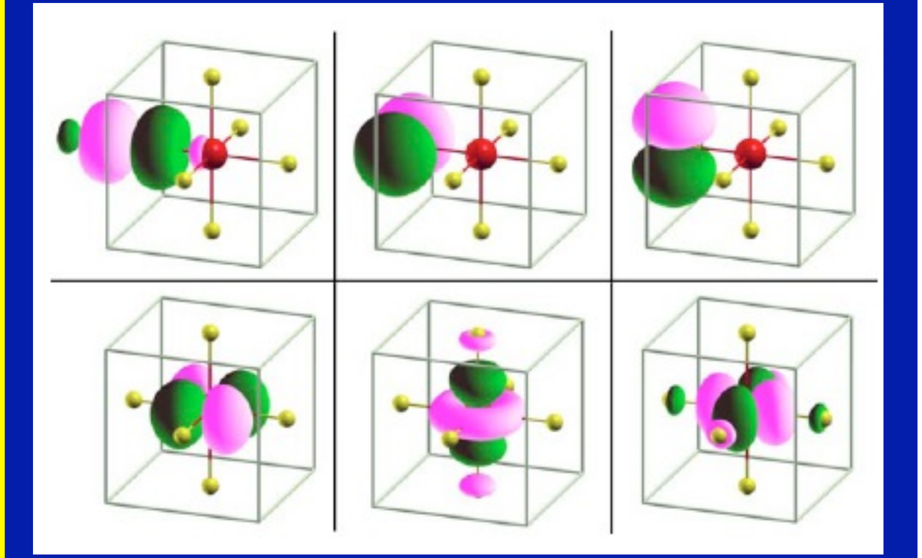


``Low energy"





V t_{2g}+e_g and O: very localized Wanniers



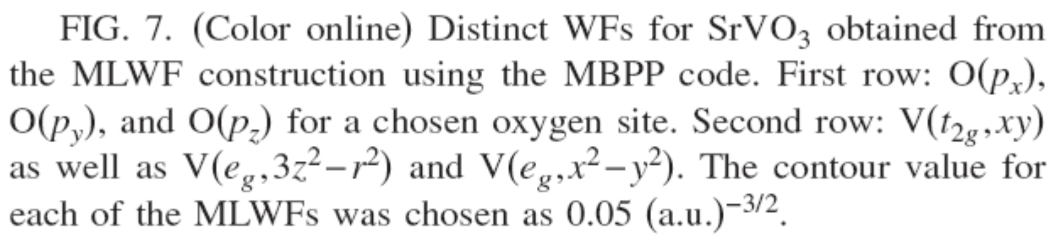


FIG. 7. (Color online) Distinct WFs for SrVO$_3$ obtained from the MLWF construction using the MBPP code. First row: O(p_x), O(p_y), and O(p_z) for a chosen oxygen site. Second row: V(t_{2g},xy) as well as V(e_g,$3z^2-r^2$) and V(e_g,x^2-y^2). The contour value for each of the MLWFs was chosen as 0.05 (a.u.)$^{-3/2}$.

F.Lechermann et al.
Phys Rev B 74 (2006) 125120

Models (very schematic – ignoring important 'details')

Full d-p:

$$-\,t_{pd}\sum_{i\in M\, j\in O} d_i^\dagger p_j + \varepsilon_d \sum_i d_i^\dagger d_i + \varepsilon_p \sum_j p_j^\dagger p_j +$$

$$+\,\frac{1}{2}U_{dd}\sum_i \hat{n}_{di}(\hat{n}_{di}-1) \qquad \Delta = \varepsilon_d - \varepsilon_p + n_d U_{dd}$$

Low-energy (extended Wanniers on M-sites):

$$-t_{\mathrm{eff}}\sum_{ii'\in M} c_i^\dagger c_{i'} + \frac{1}{2}U_{\mathrm{eff}}\sum_i \hat{n}_i(\hat{n}_i-1)$$

$t_{\mathrm{eff}} \sim \frac{t_{pd}^2}{\Delta}$, $U_{\mathrm{eff}} \sim \Delta$ (in $\Delta > U_{dd}$ charge-transfer regime)

5. Interactions

For simplicity, I will not describe the full structure of interactions for a 5-orbital d-shell (i.e. Slater-Racah parametrization of $U_{m1m2m3m4}$)
→ see my 2009-2010 College de France lectures

I will instead focus on a t_{2g} (3-fold) or e_g (2-fold) shell in cubic symmetry (Kanamori)

The Platters said:

« Only U can do
make all this world
seem right… »

… Take-home message here:

« Not only U…

…. also Hund's rule coupling J_H *» !*

Friedrich Hund
1896-1997

For a t_{2g} triplet, only 3 independent Coulomb integrals:

$$\begin{aligned} U &= \int d\mathbf{r}d\mathbf{r}'\, |\phi_m(\mathbf{r})|^2\, V_c(\mathbf{r},\mathbf{r}')\, |\phi_m(\mathbf{r}')|^2 \\ U' &= \int d\mathbf{r}d\mathbf{r}'\, |\phi_m(\mathbf{r})|^2\, V_c(\mathbf{r},\mathbf{r}')\, |\phi_{m'}(\mathbf{r}')|^2 \qquad m \neq m' \\ J &= \int d\mathbf{r}d\mathbf{r}'\, \phi_m(\mathbf{r})\phi_{m'}(\mathbf{r})\, V_c(\mathbf{r},\mathbf{r}')\, \phi_m(\mathbf{r}')\phi_{m'}(\mathbf{r}') \end{aligned}$$

Indeed:
J=J' (real wave-functions)
$U_{m'mmm}$=0 by symmetry

V_c: SCREENED Coulomb interaction in the solid

Hence, Kanamori hamiltonian:

[J.Kanamori, Prog. Theor. Phys. 30 (1963) 275]

$$
\begin{aligned}
H_{\mathrm{K}} = U \sum_{m} \hat{n}_{m\uparrow}\hat{n}_{m\downarrow} + U' \sum_{m\neq m'} \hat{n}_{m\uparrow}\hat{n}_{m'\downarrow} + (U'-J) \sum_{m<m',\sigma} \hat{n}_{m\sigma}\hat{n}_{m'\sigma} + \\
-J \sum_{m\neq m'} d^{+}_{m\uparrow} d_{m\downarrow}\, d^{+}_{m'\downarrow} d_{m'\uparrow} + J \sum_{m\neq m'} d^{+}_{m\uparrow} d^{+}_{m\downarrow}\, d_{m'\downarrow} d_{m'\uparrow}
\end{aligned}
$$

EXACT for a t_{2g} shell

Useful reference: Sugano, Tanabe & Kamimura,
Multiplets of transition-metal ions in crystals
Academic Press, 1970

Assuming furthermore ~ spherical symmetry of the screened interaction V_c , one can show that: U’ = U-2J

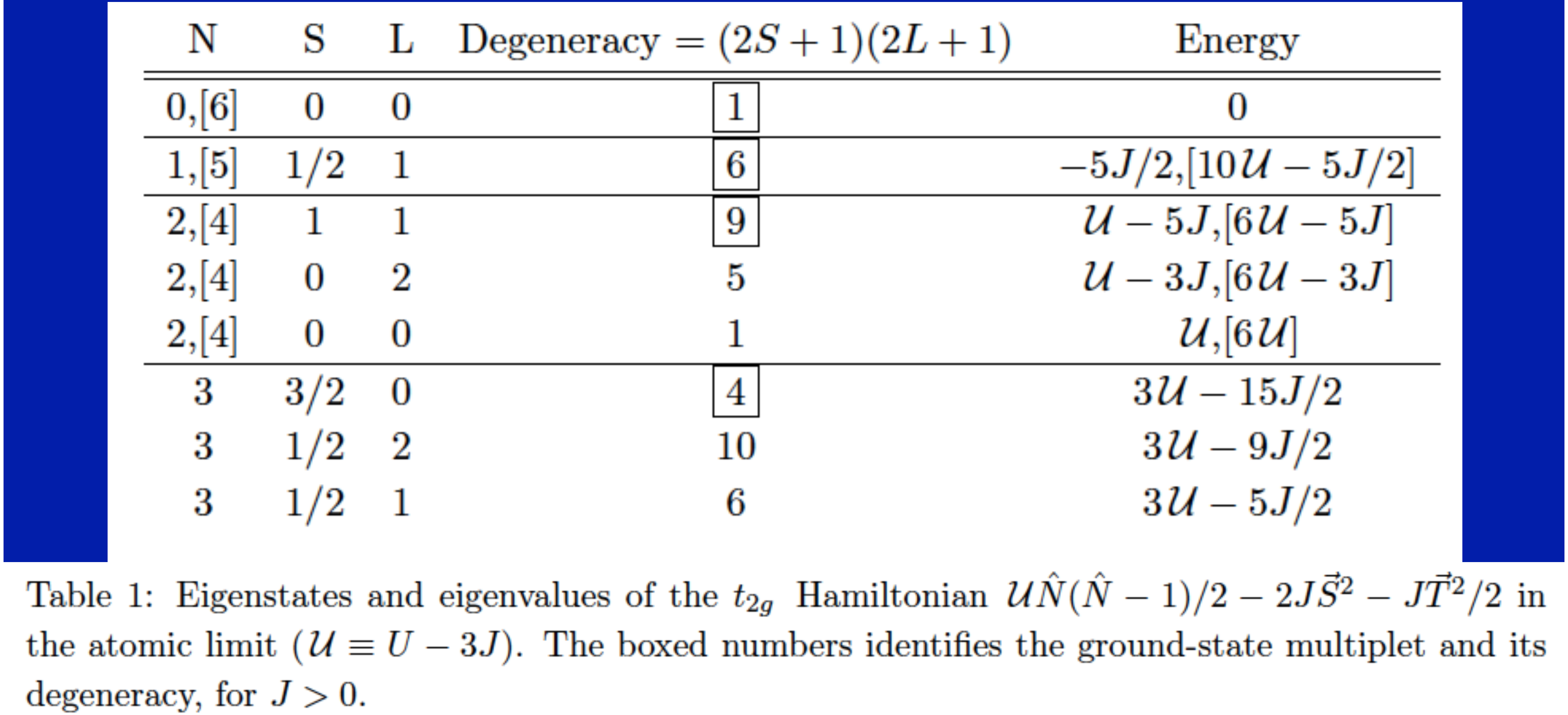
In this case, the hamiltonian can be written:

$$H_{t_{2g}} = (U-3J)\,\frac{\hat{N}(\hat{N}-1)}{2} - 2J\,\vec{S}^2 - \frac{J}{2}\vec{L}^2 + \frac{5}{2}J\,\hat{N}$$

$$\hat{N} = \sum_{m\sigma} \hat{n}_{m\sigma} \ , \ \vec{S} = \frac{1}{2}\sum_{m}\sum_{\sigma\sigma'} d^{\dagger}_{m\sigma}\vec{\tau}_{\sigma\sigma'}d_{m\sigma'} \ , \ L_m = i\sum_{m'm''}\sum_{\sigma}\epsilon_{mm'm''}d^{\dagger}_{m'\sigma}d_{m''\sigma},$$

Total charge, spin and orbital iso-spin operators

Spectrum of atomic t_{2g} hamiltonian with U'=U-2J



N	S	L	Degeneracy $= (2S+1)(2L+1)$	Energy
0,[6]	0	0	$\boxed{1}$	0
1,[5]	1/2	1	$\boxed{6}$	$-5J/2$,[$10\mathcal{U}-5J/2$]
2,[4]	1	1	$\boxed{9}$	$\mathcal{U}-5J$,[$6\mathcal{U}-5J$]
2,[4]	0	2	5	$\mathcal{U}-3J$,[$6\mathcal{U}-3J$]
2,[4]	0	0	1	$\mathcal{U}$,[$6\mathcal{U}$]
3	3/2	0	$\boxed{4}$	$3\mathcal{U}-15J/2$
3	1/2	2	10	$3\mathcal{U}-9J/2$
3	1/2	1	6	$3\mathcal{U}-5J/2$

Table 1: Eigenstates and eigenvalues of the t_{2g} Hamiltonian $\mathcal{U}\hat{N}(\hat{N}-1)/2 - 2J\vec{S}^2 - J\vec{T}^2/2$ in the atomic limit ($\mathcal{U} \equiv U - 3J$). The boxed numbers identifies the ground-state multiplet and its degeneracy, for $J > 0$.

- Hund's rule ground-state in each particle-number sector
- Symmetry broken by J from SU(6) to U(1)c×SU(2)s×SO(3)o
- → Degeneracies lifted by J

Hund’s rules

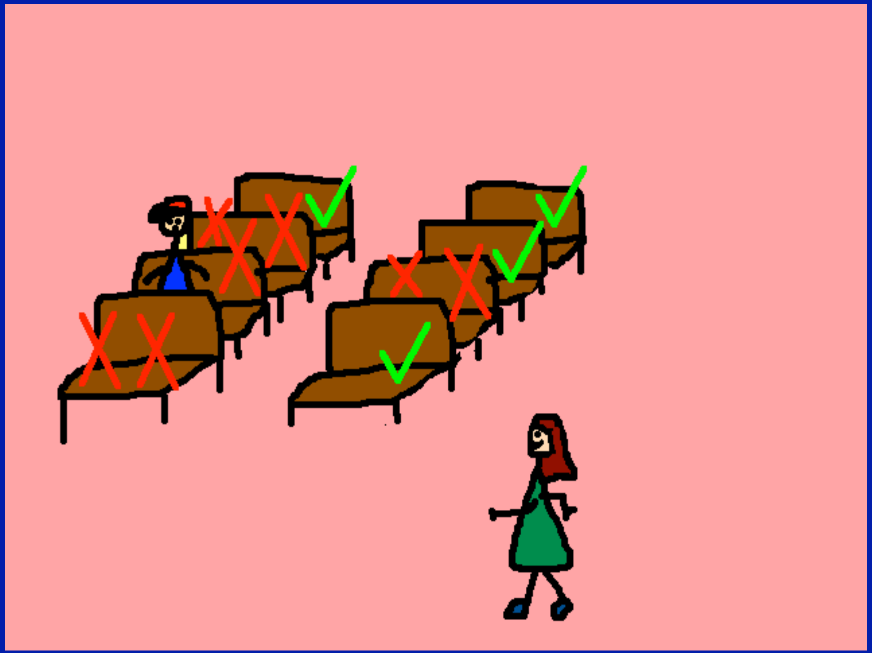
(1925 – Z.Physik
On atomic spectra of transition metals)

N electrons in a M=2l+1-fold degenerate shell

- Maximize S [= N/2 N<M ; = M-N/2 N>M]
- Given S, maximize L
- Given (S,L) lowest J=|L-S| if N<M (less than ½ filling) , highest J=L+S if N>M

``The bus-seat rule''

For example a d-shell with 3 electrons (less than half-filling corresponding to 5 electrons) will have $\uparrow, \uparrow, \uparrow, 0, 0$ and with 7 electrons $\uparrow\downarrow, \uparrow\downarrow, \uparrow, \uparrow, \uparrow$. These rules are sometimes referred to as the 'bus-seat' rule: singly-occupied spots are filled first, then double occupancies are created when singly-occupied spots are no longer available.



Physical origin: exchange (QM)

- Minimize cost of inter-electron Coulomb repulsion
- Ex: For 2 electrons, S=1 forces an antisymmetric orbital wave-function (`electrons further apart'), in contrast to S=0
- Actually, screening of nucleus-electron interaction (smaller in singly occupied orbitals) actually plays a key role (cf. Levine, Quantum Chemistry) in lowering the energy of singly-occupied states
- 3rd rule due to spin-orbit

The critical coupling for the Mott MIT depends crucially on Hund’s rule coupling and on the filling of the shell

cf. van der Marel & Sawatzky PRB 37 (1988) 10674
van der Marel PhD’s thesis
L. de’ Medici PRB 83 (2011) 205112

Energetic of the Mott gap – a) the atom

cf. van der Marel&Sawatzky PRB 37 (1988) 10674 ;
L. de' Medici PRB 83 (2011) 205112

$$\Delta_g = E_0(N+1) + E_0(N-1) - 2E_0(N)$$

Hund's rule ground-state E_0 not affected by spin-flip and pair-hopping terms.

N<M (N>M) : Max spin state only U'-J = U-3J matters

$$\Delta_g^{at} \equiv U_{eff} = U - 3J$$

→ Atomic gap and U_{eff} REDUCED by J for N<M, N>M

N = M (half-filled shell) :

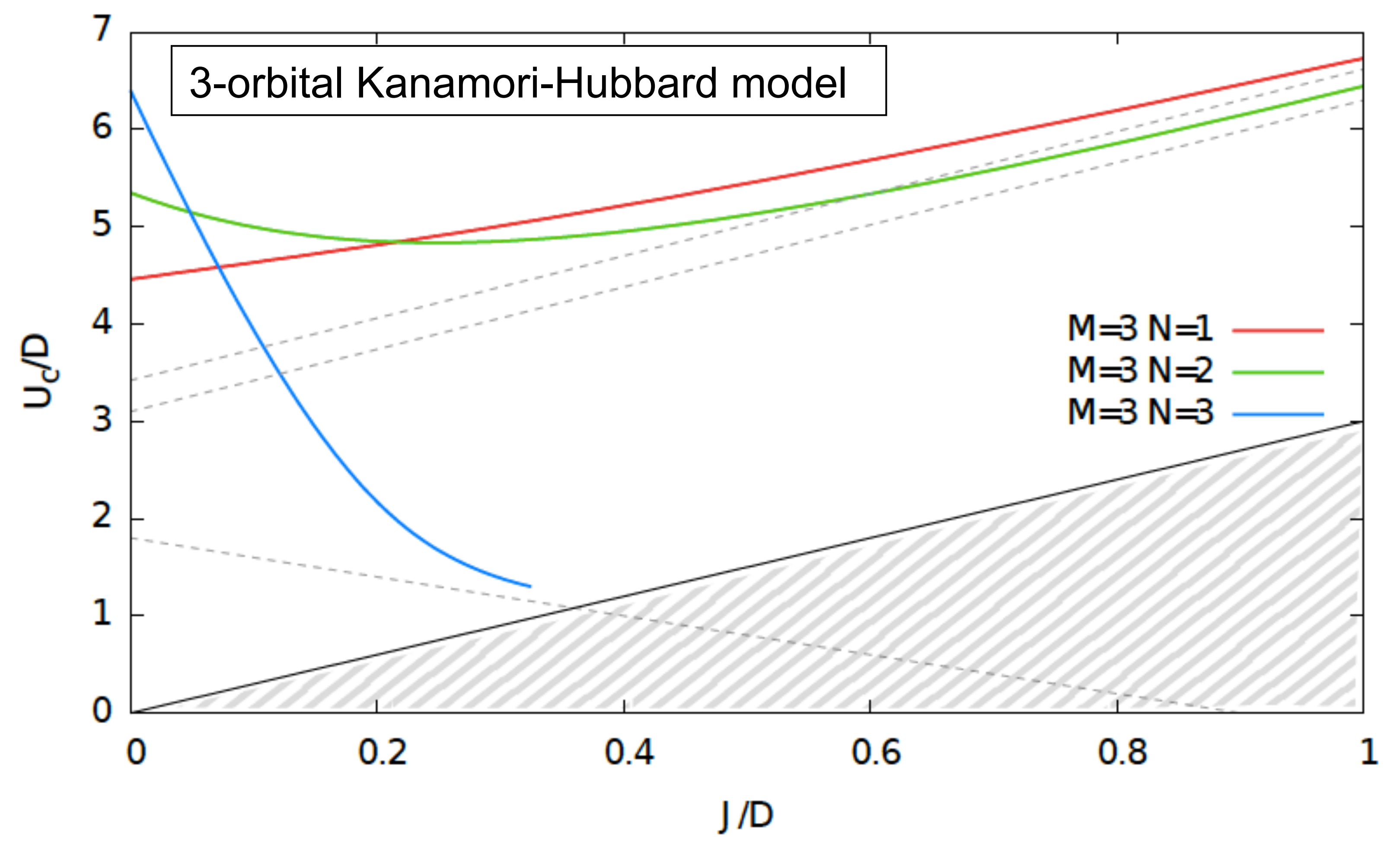
Excited state with M+1 electrons has higher energy: $|\uparrow\downarrow, \uparrow, \uparrow\rangle$

$$E_0(M+1) = (U'-J)\times M(M-1)/2 + U\times 1 + U'\times(M-1) = (U'-J)M(M+1)/2 + (U-U'+MJ)$$

$$\Delta_g^{at} \equiv U_{eff} = (U'-J) + (U-U'+MJ) = U + (M-1)J$$

→ Atomic gap gap and U_{eff} INCREASED by J for N<M, N>M

Crucial effect on Mott gap in the solid:

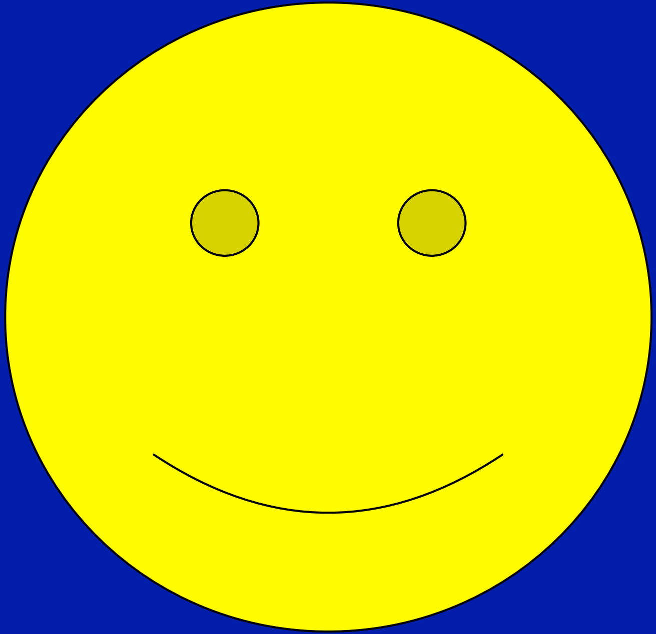


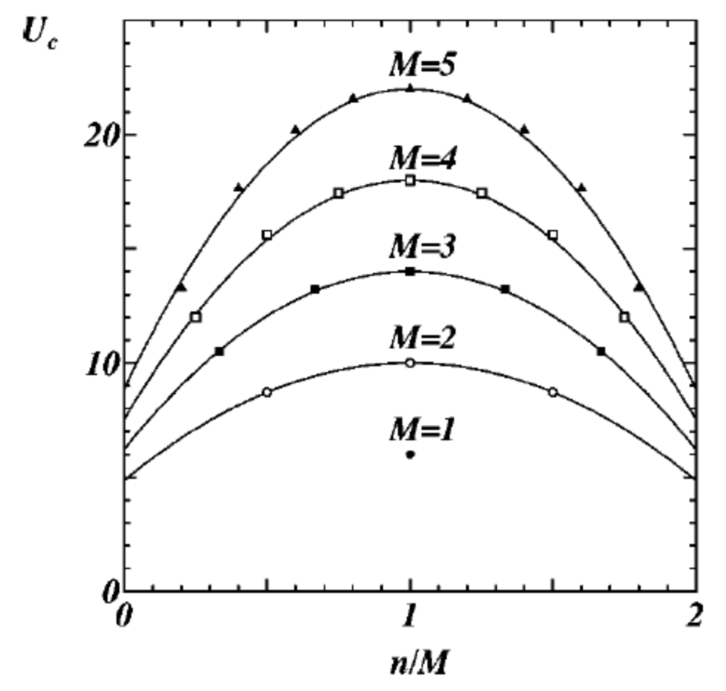
L. de' Medici, PRB 83, 205112 (2011)

cf. early work on V_5S_8
Fujimori et al. PRB (1991)

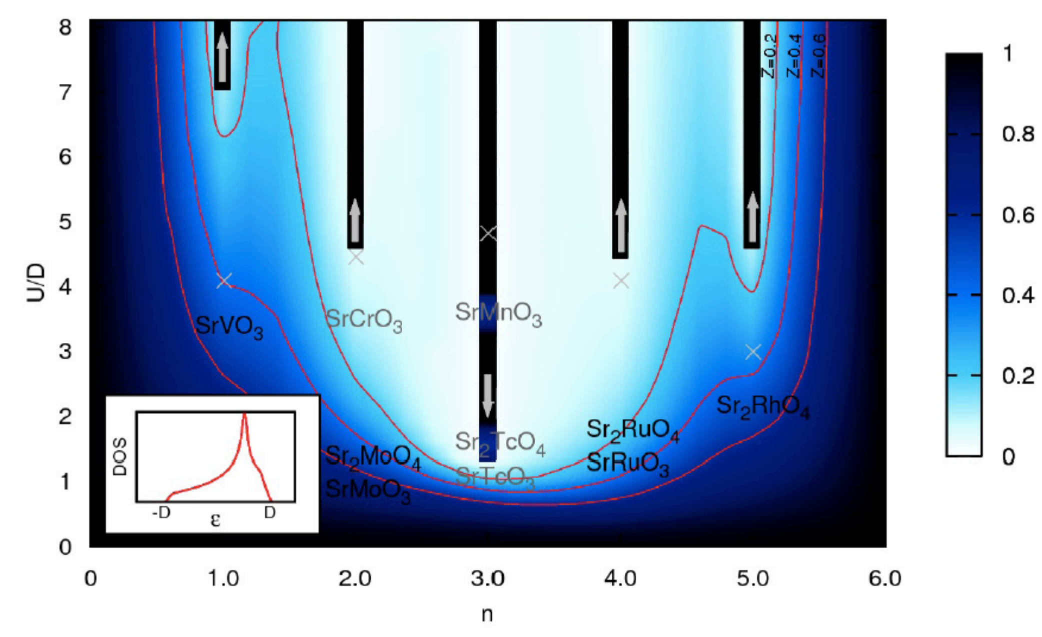
J=0

J≠0





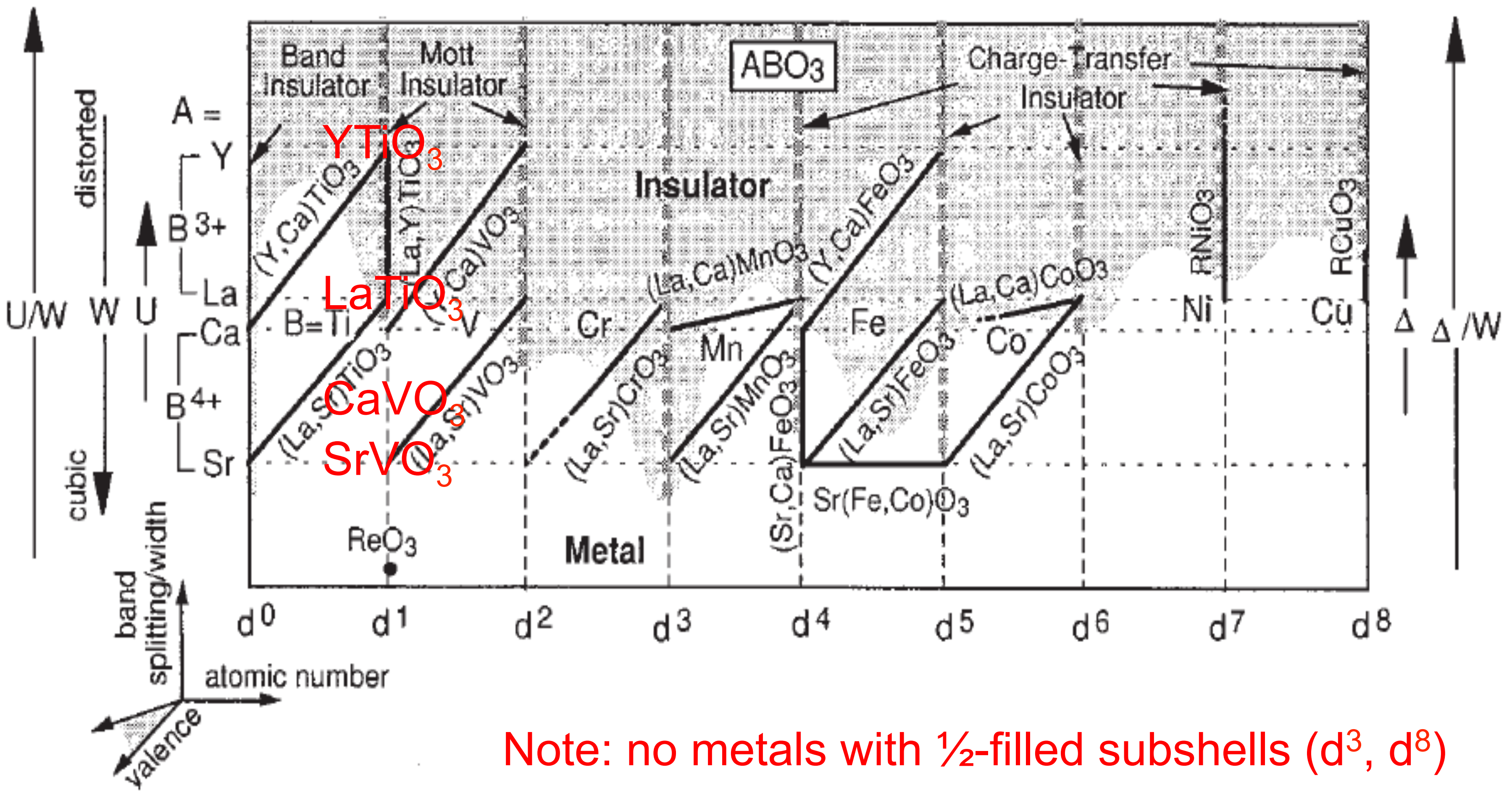
Crucial dependence of U_c on filling



``Atsushi Fujimori's map of RMO_3 perovskites"

J.Phys Chem Sol. 53 (1992) 1595

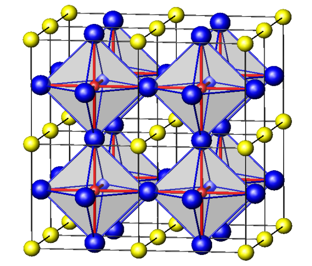
Imada, fujimori, Tokura, Rev.Mod.Phys (1998)

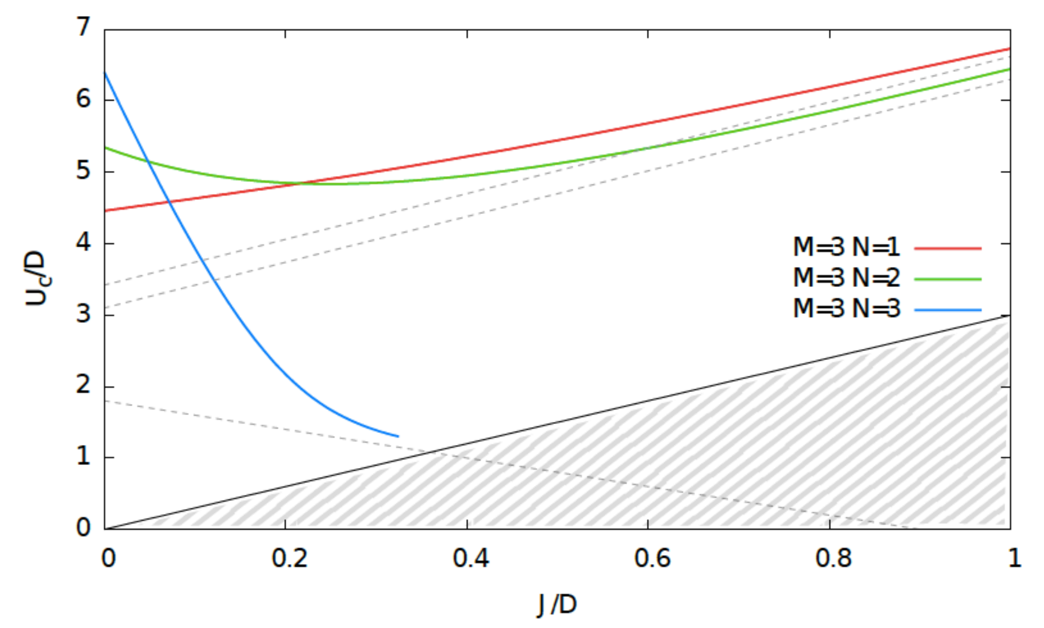


Note: no metals with ½-filled subshells (d^3, d^8)

Hund's J is crucial to make contact with real-life !

Metallic vanadates vs. Insulating Titanates: solving the puzzle





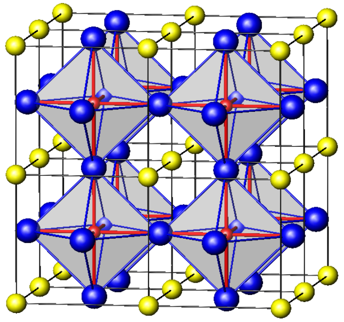
Cubic deg M=3 : $D \simeq 1.5eV\, J/D \simeq 0.45 \Rightarrow U_c \simeq 8eV!$

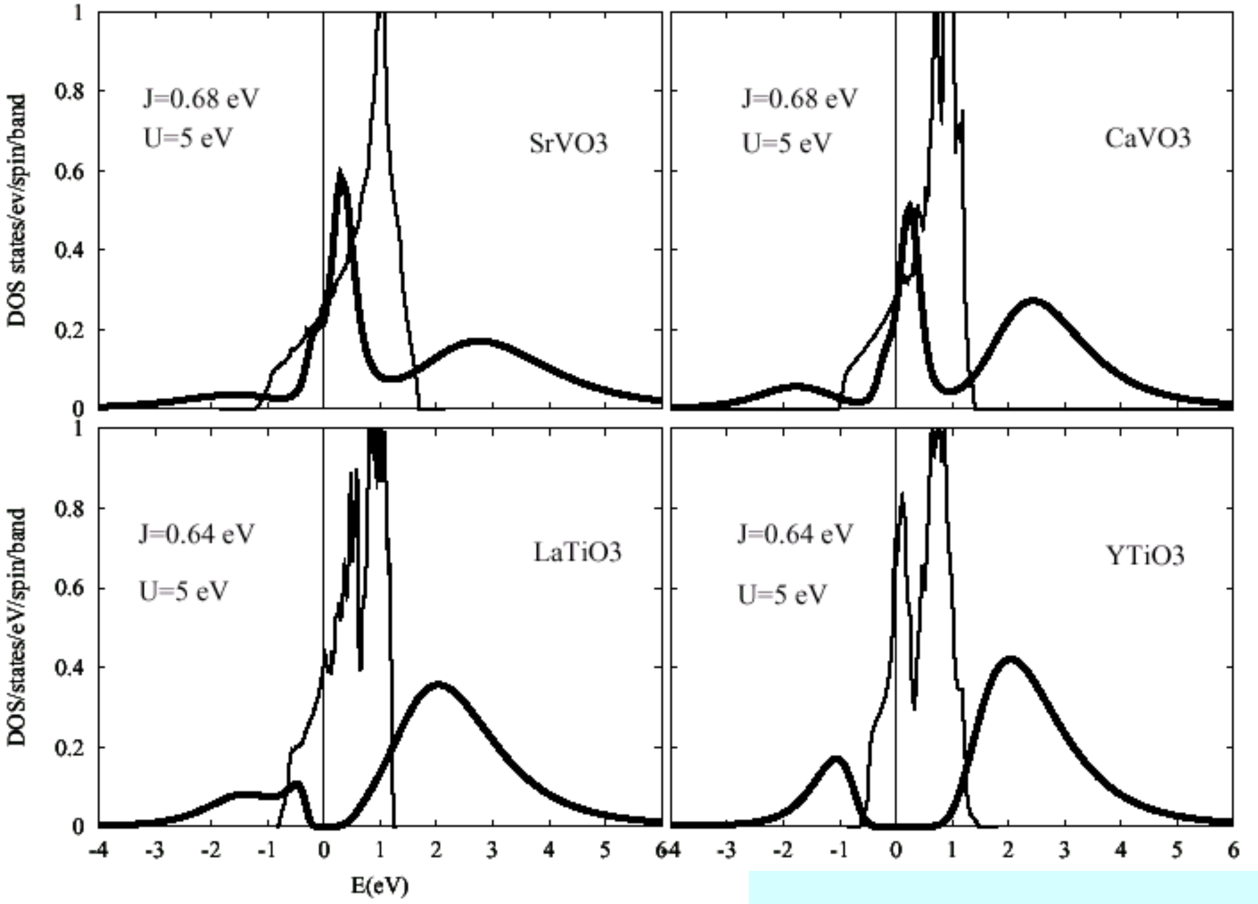
Full t_{2g} splitting M=1: $D \simeq 1eV \Rightarrow U_c \simeq 3D = 3eV!$

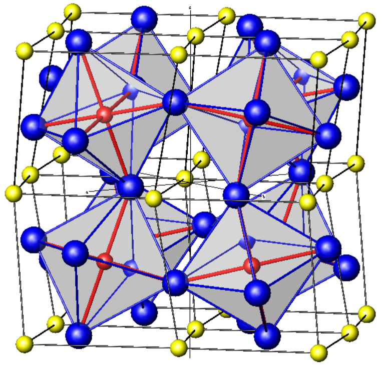
Reduction of orbital deg. and Hund's play a key role, not only/primarily reduction of bandwidth by distortion !

Electronic structure + Many-Body (DMFT) calculations:

accouting for metallic/insulating nature of vanadates/titanates







E.Pavarini et al., PRL 2004

cf. also Sekiyama et al. (Ca/SrVO3) PRL 2004

- **Narrowing of quasiparticle bands** due to correlations (the Brinkman-Rice phenomenon)
- **Hubbard satellites** (i.e extension to the solid of atomic-like transitions)

Quantitative comparison with experiments

quasiparticles + lower Hubbard band clearly resolved
in bulk-sensitive photoemission experiments

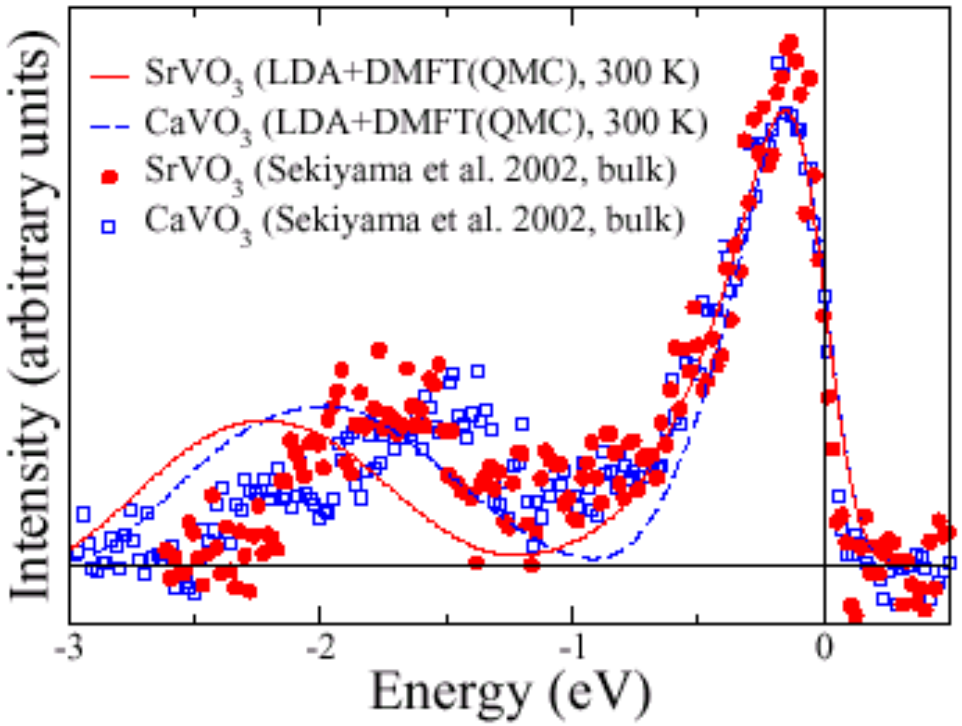
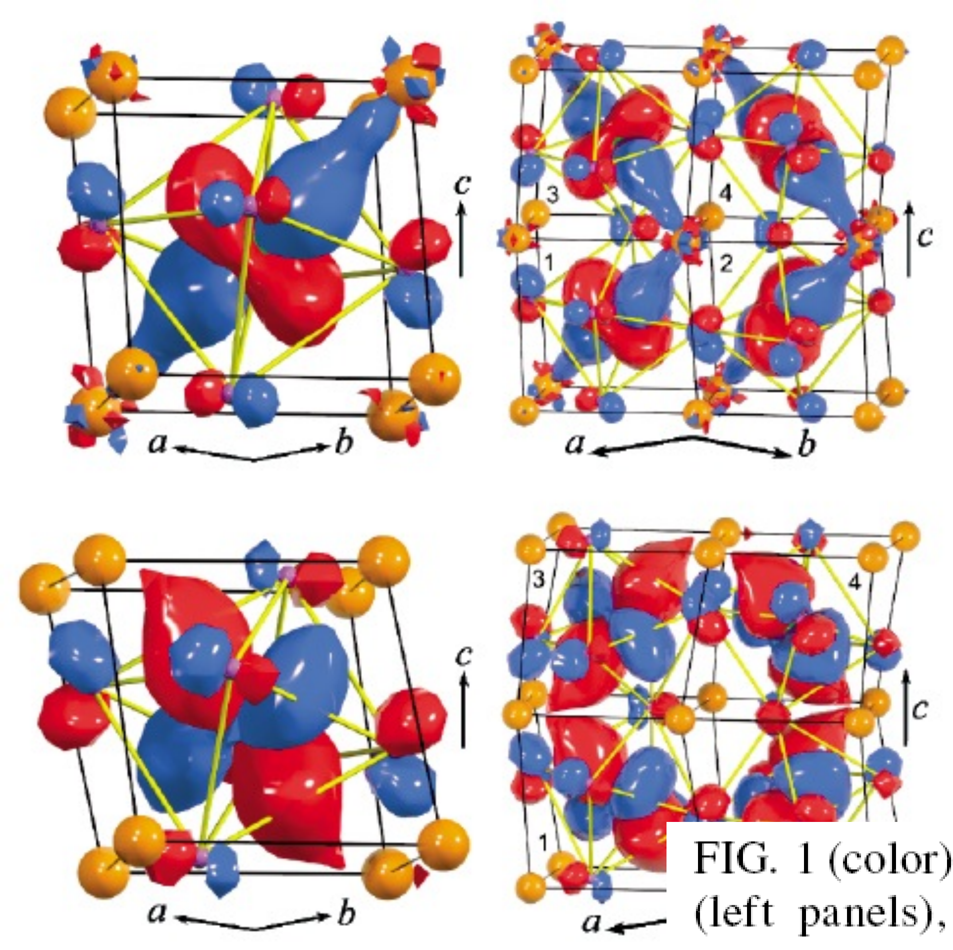


FIG. 4: Comparison of the calculated, parameter-free LDA+DMFT(QMC) spectra of $SrVO_3$ (solid line) and $CaVO_3$ (dashed line) with bulk-sensitive high-resolution PES ($SrVO_3$: circles; $CaVO_3$: rectangles) [4]. Horizontal line: experimental subtraction of the background intensity.

Sekiyama et al,
Ca/SrVO3

Strong orbital polarization predicted in the insulating materials :



$0.586|xy\rangle + 0.275|xz\rangle + 0.762|yz\rangle$ for $LaTiO_3$

(88% of d1 electron population)

$0.622|xy\rangle - 0.029|xz\rangle + 0.782|yz\rangle$ for $YTiO_3$

(96% of d1 electron population)

LDA+DMFT calculations

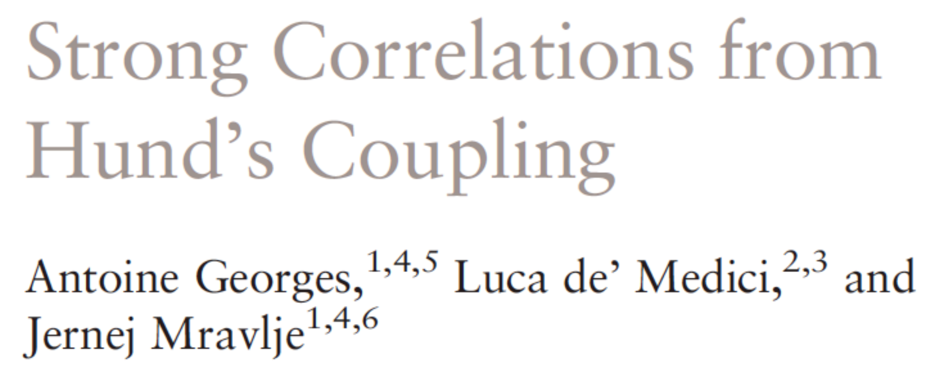
FIG. 1 (color). *Pbnm* primitive cells (right panels), subcells 1 (left panels), and the occupied t_{2g} orbitals for $LaTiO_3$ (top panels) and $YTiO_3$ (bottom panels) according to the LDA + DMFT calculation. The oxygens are violet, the octahedra yellow, and the cations orange. In the global, cubic *xyz* system

Advertisement for Hund's physics afficionados:

``Hund's metals''

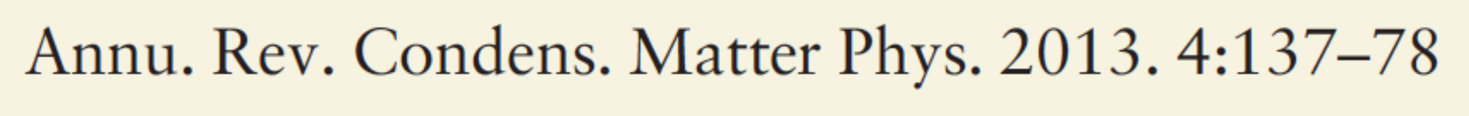
(e.g. Ruthenates, Fe-based SC)

→ See 2012 lectures @ College



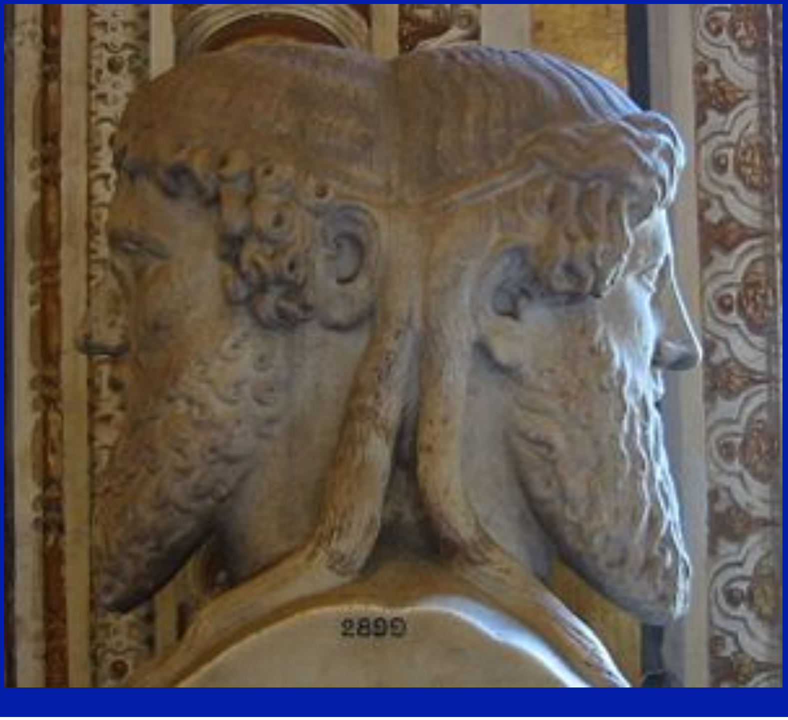
Strong Correlations from Hund's Coupling

Antoine Georges,[1,4,5] Luca de' Medici,[2,3] and Jernej Mravlje[1,4,6]



Annu. Rev. Condens. Matter Phys. 2013. 4:137–78

J is « Janus-faced » : it has two ANTAGONISTIC effects



Janus is the latin god of beginnings/ transitions and is often associated with doors and entrances and has two faces.
He was first promoted to being a physicist by Pierre-Gilles de Gennes (“Janus grains”)

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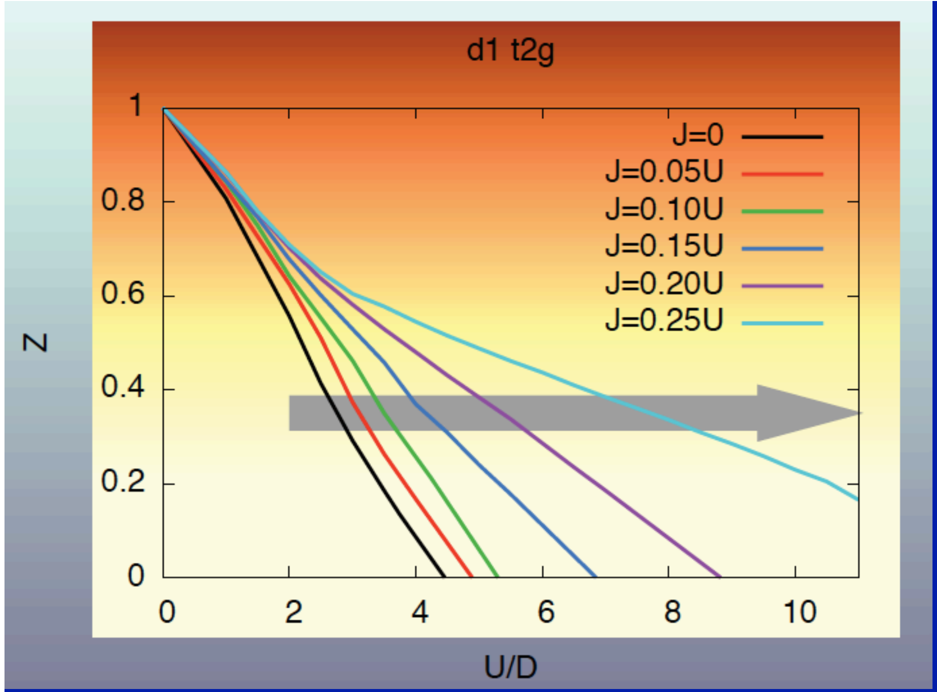
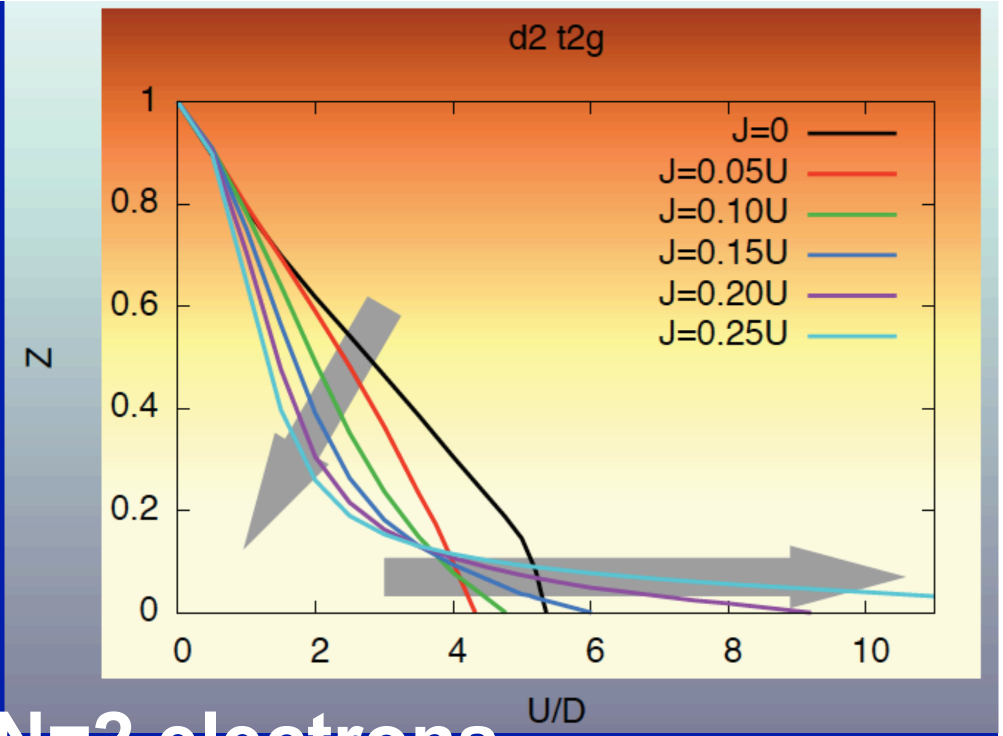
Janus-Faced Influence of Hund’s Rule Coupling in Strongly Correlated Materials

Luca de’ Medici,[1] Jernej Mravlje,[2,3,4] and Antoine Georges[2,4,5,6]

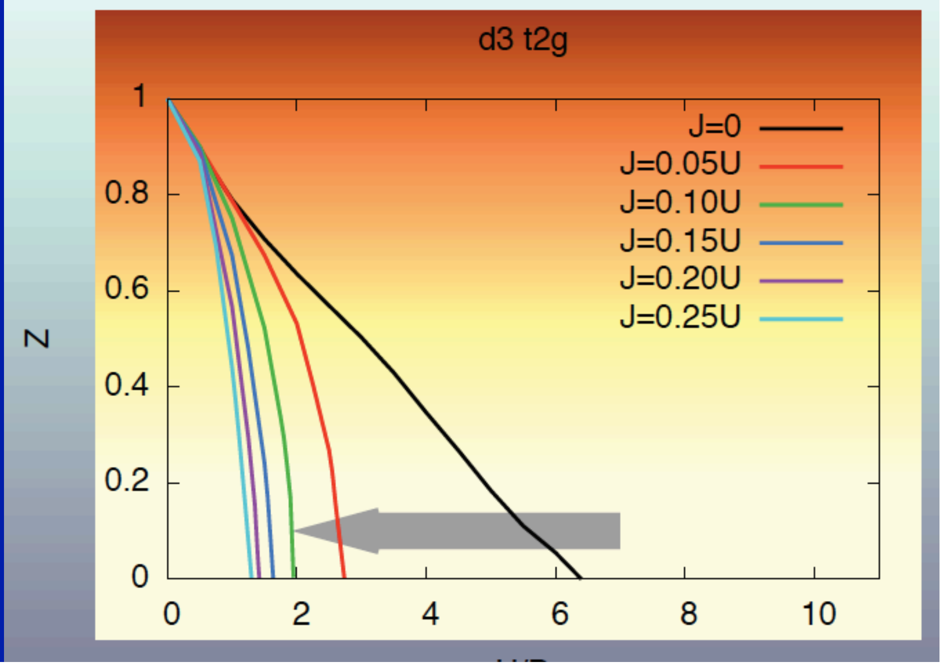


N=1 electron



N=2 electrons

Quasiparticle weight Z vs. U/D



N=3 electrons

WRAP-UP:
Key energy scales & parameters

- Bandwidth
- Crystal-fields, Distortions
- Filling of shell , Doping
- Interactions (U,J,…)
- Charge-transfer energy

→ What are the CONTROL knobs ?

CONTROL: Traditional and Novel routes

Bandwidth	Pressure Size of rare-earth Distortion Tolerance factor 3d,4d,5d metal	Strained thin films and heterostructures Light/non-linear phononics
Crystal field, Orbital degeneracy	Size of rare-earth Distortion Tolerance factor	- Same -
Filling of shell	Chemistry	Ionic liquids Gating
Doping	$Sr,Ca^{2+} \rightarrow La, R^{3+}$	
Interaction strength	3d,4d,5d metal	Tunable dielectric gating ? Light ?
Charge-Transfer	Change apical oxygen distance Change ligand: $O \rightarrow S, Se\ldots$	Light ?

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