Lecture Notes

Introduction to Strongly Correlated Electron Systems

WS 2014/ 2015

Mohsen Abd-Elmeguid

II. Institute of Physics, University of Cologne, Germany

Introduction to strongly correlated electron systems

I. Introduction

Brief summary of electrons in solids, origin of strong electron correlations

II. Classes of strongly correlated electron systems

(a) Transition metal compounds: 3d-electrons

- Hubbard model, Mott insulator, metal-insulator transition
- Spin, charge, and orbital degrees of freedom and ordering phenomena, selected materials

(b) Heavy fermion systems: 4f (5f) – electrons

- The Kondo effect, heavy fermion systems, non-Fermi liquid behavior,
- Quantum phase transitions, unconventional superconductivity, selected materials

(c) Nanoscale structures:

- Quantum confinement, unusual properties for potential applications

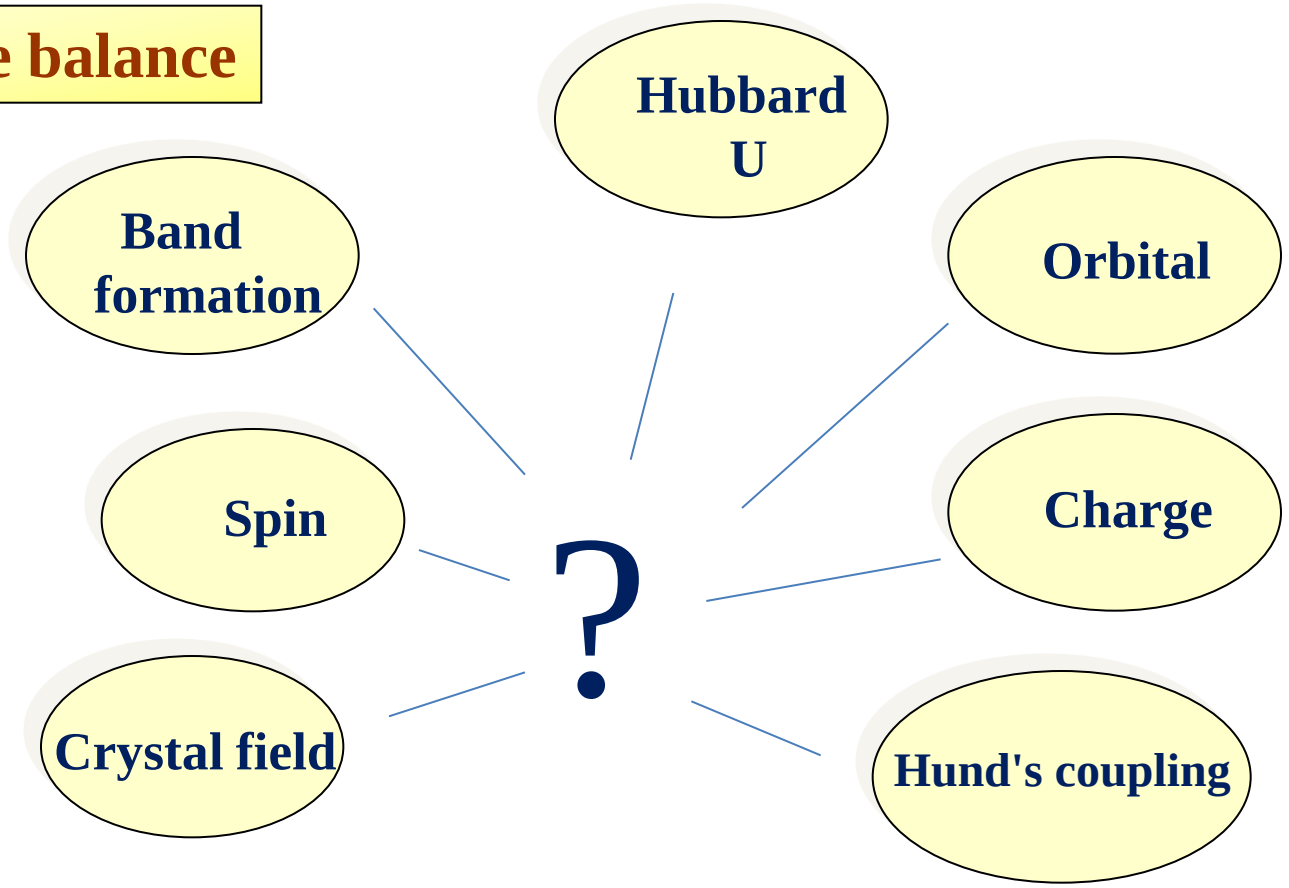
III. Pressure effect on the ground state properties:

- Recent experimental results on heavy fermions and transition metal compounds

IV. Summary and open discussion

Transition metal systems and electron correlations

Delicate balance



systems can be quite close to the borderline U~ W (t)

Thus many interesting transitions to unusual ground states can occur by changing T, P, filling, structure, etc.

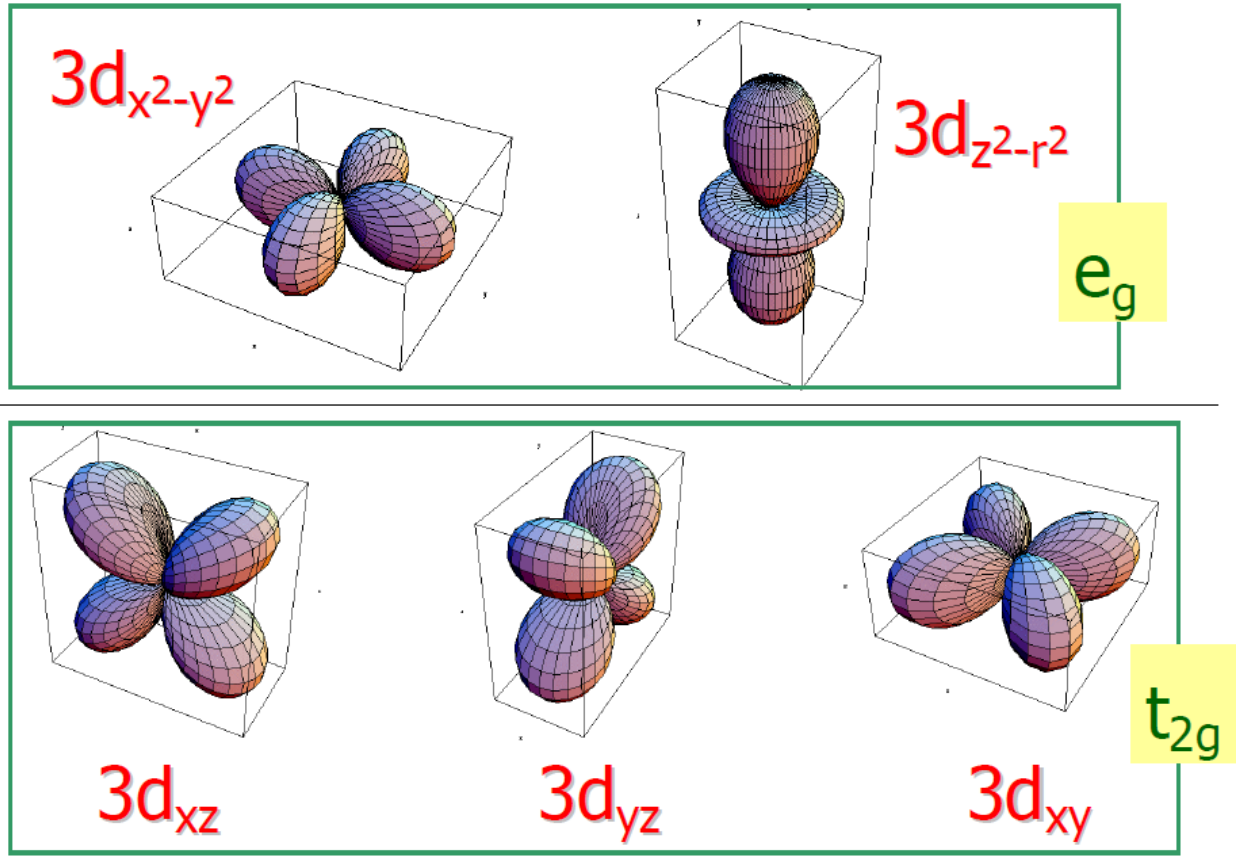
more discussion with examples later!

Orbital degree of freedom

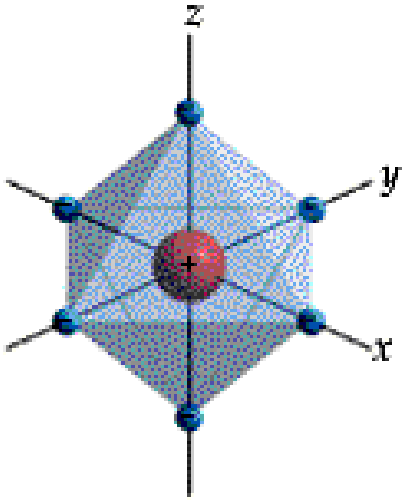
3d orbitals in central potential of a free atom/ ion

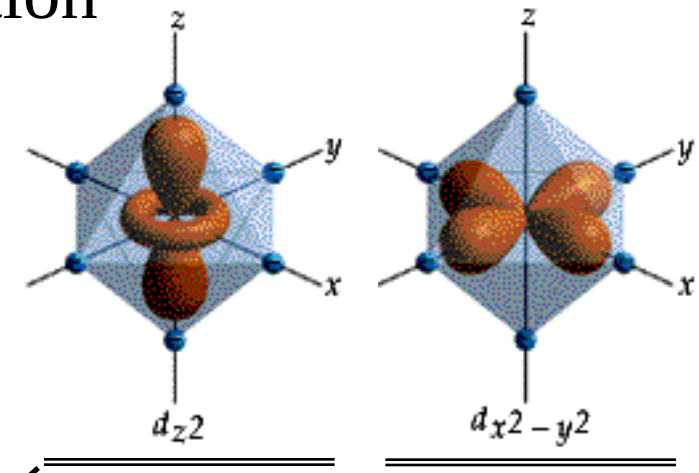
5-fold degenerate 3d orbitals

3d: n=3, ℓ=2, m_ℓ= -2,-1,0,1,2 ⟶ 5 orbitals

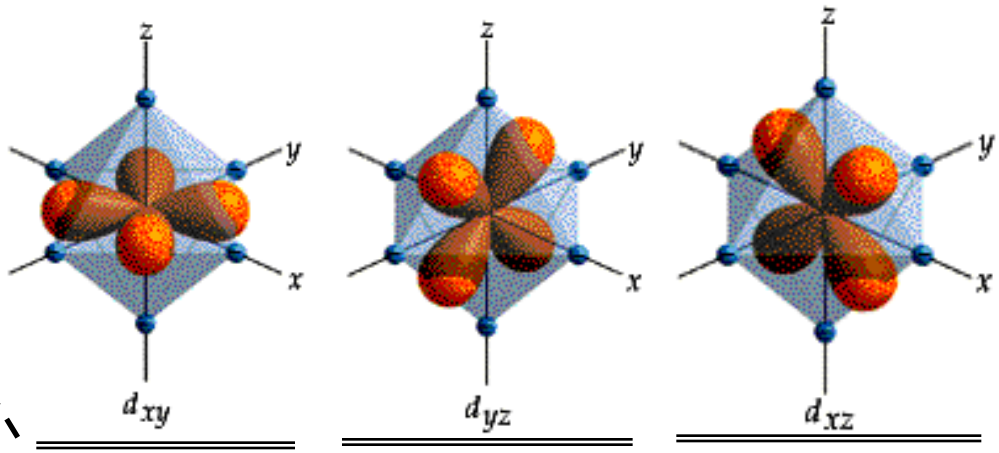


d-Orbitals and Ligand Interaction (Octahedral Field)





d-orbitals pointing directly at axis are affected most by electrostatic interaction

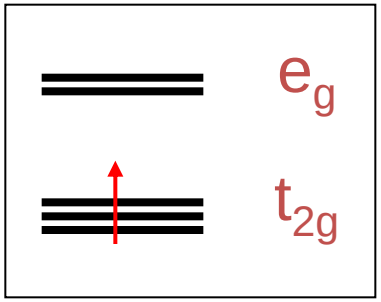


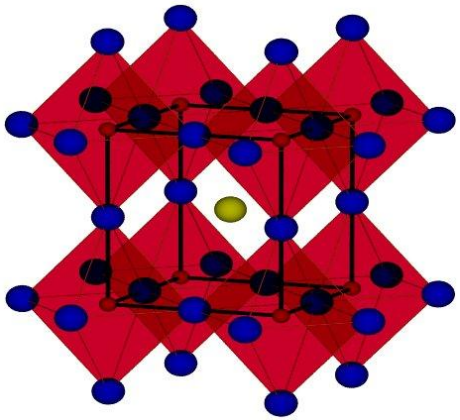
d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

Orbitals degeneracy

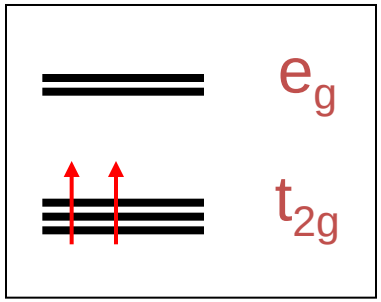
„pseudo-Cubic“ Perovskites

$YTiO_3$
$3d^1$

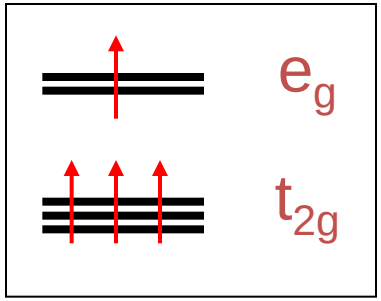


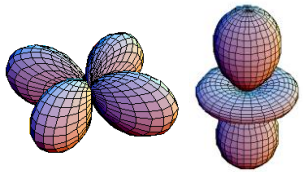


YVO_3
$3d^2$



$LaMnO_3$
$3d^4$





Orbitals degeneracy is lifed by:

1. **Lattice distortion (Jahn-Teller)**
2. ***2.*** **orbital and spin dependent superexchange**

more details later!

orbitals degeneracy

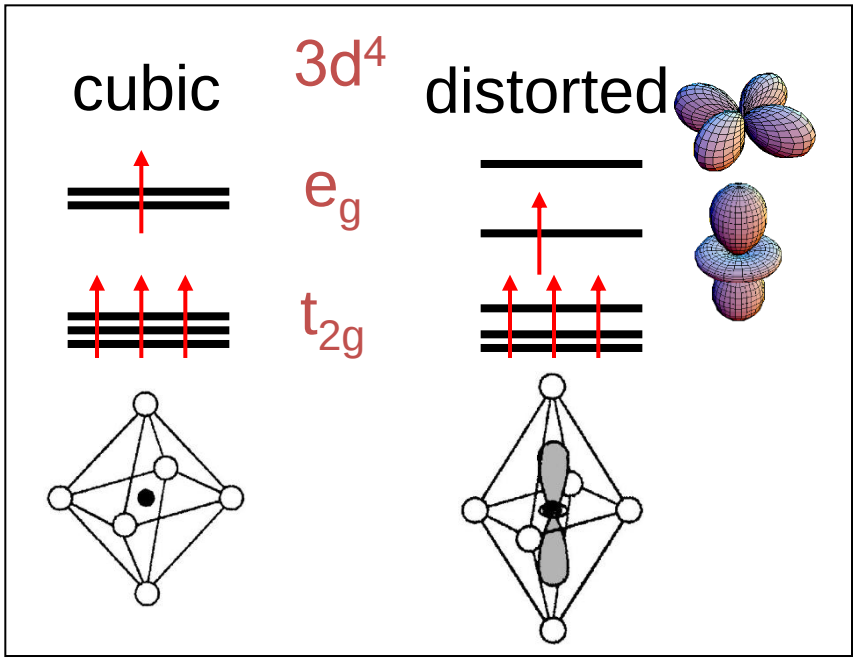
⟹ **orbital degree of freedom**

Differences between Orbitals and Spins

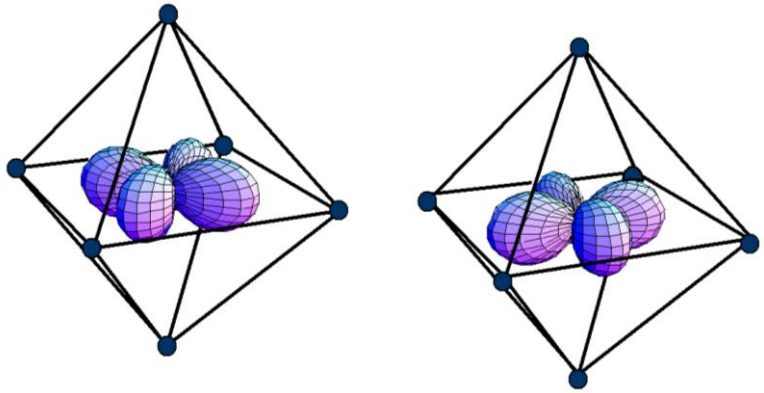
The orbitals are usually strong coupled to the lattice

Distortion

Lifts the orbital degeneracy



Anisotropy

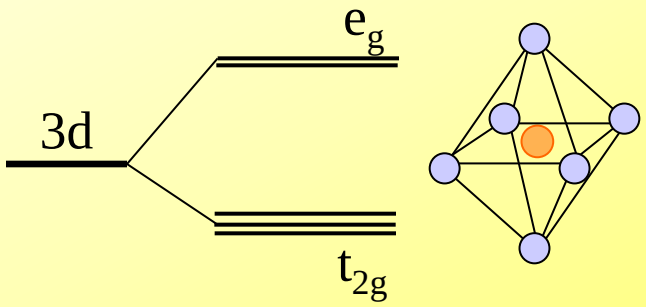


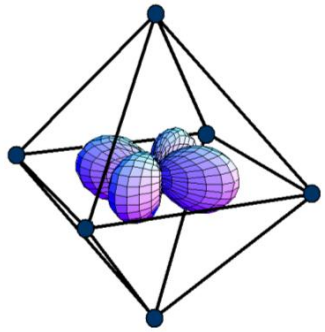
rotated orbitals are not equivalent
Spins in 1. approximation invariant;
e.g. In Ferromagnets alle spins are aligned in the same direction, but this direction is arbitary

If, however, exchange interaction is domenating, orbitals will be strongly coupled to the spins

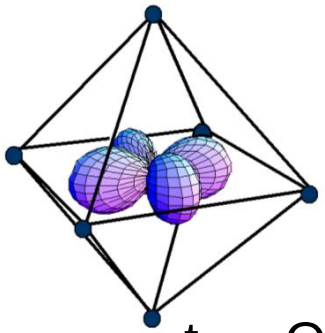
Lower Symmetry

cubic



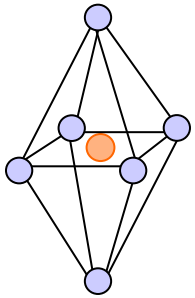


e_g – Orbitals
(x^2-y^2 and $3z^2$-r^2)



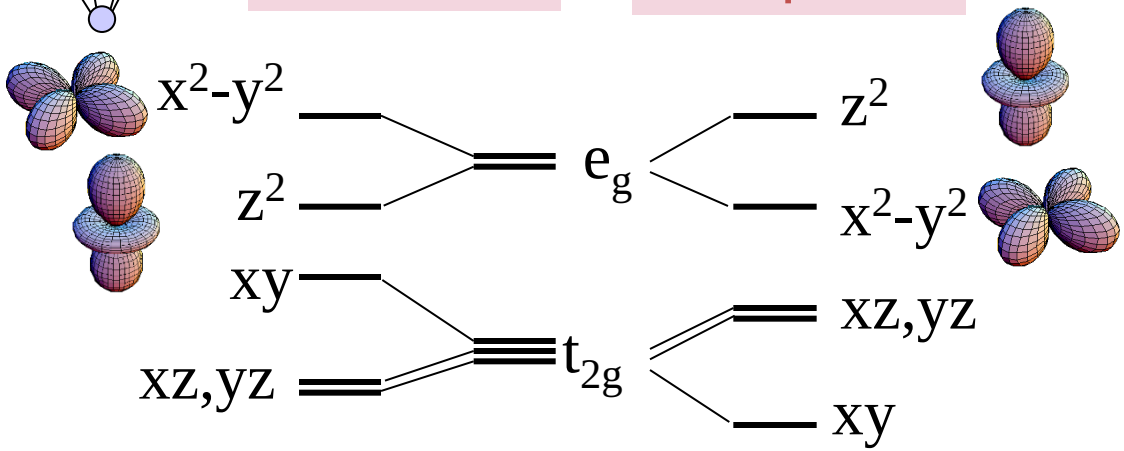
t_{2g} - Orbitals
(xy, xz und yz)

tetragonal

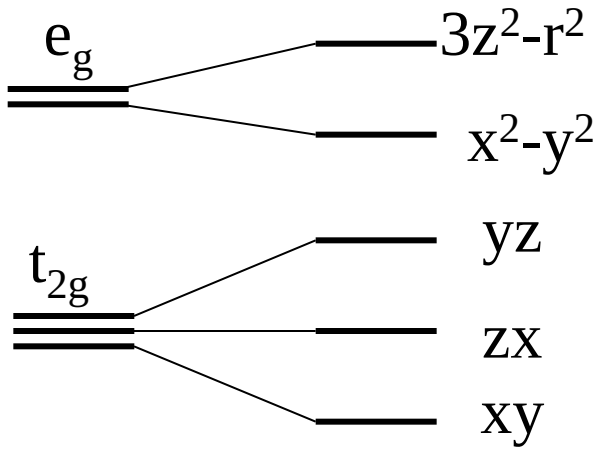


stretch

compress



orthorhombic



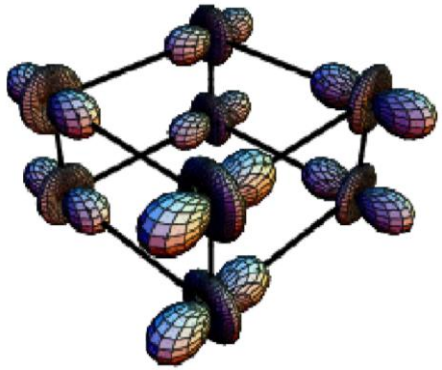
Orbital Order

Orbital degeneracy is lifted by:

1. Lattice distortion (Jahn-Teller) and/ or

***2.* orbital and spin dependent superexchange**

Both mechanisms lead to orbital order

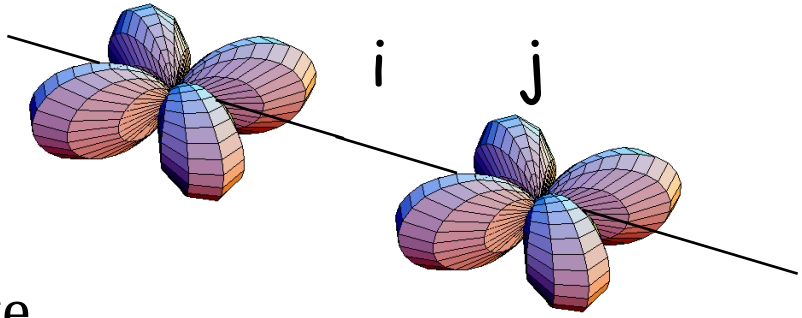


$LaMnO_3$

orbital order:

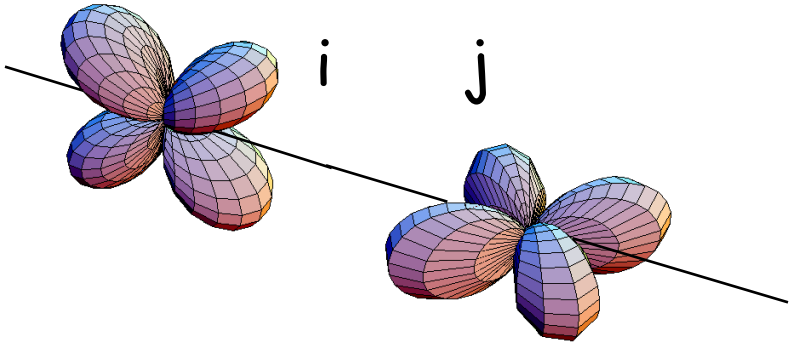
periodic arrangement of specific orbitals which leads to a long-range ordered pattern

Types of orbital ordering



Ferro-orbital ordering:

the same orbital is occupied at each site



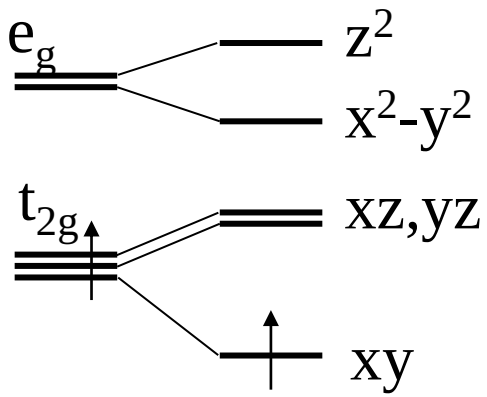
Antiferro-orbital ordering:

different orbitals are occupied at neighboring sites

Jahn-Teller-Effect

Orbitals degeneracy is lifted by spontaneous distortion

e.g.: $3d^1$ in cubic crystal field

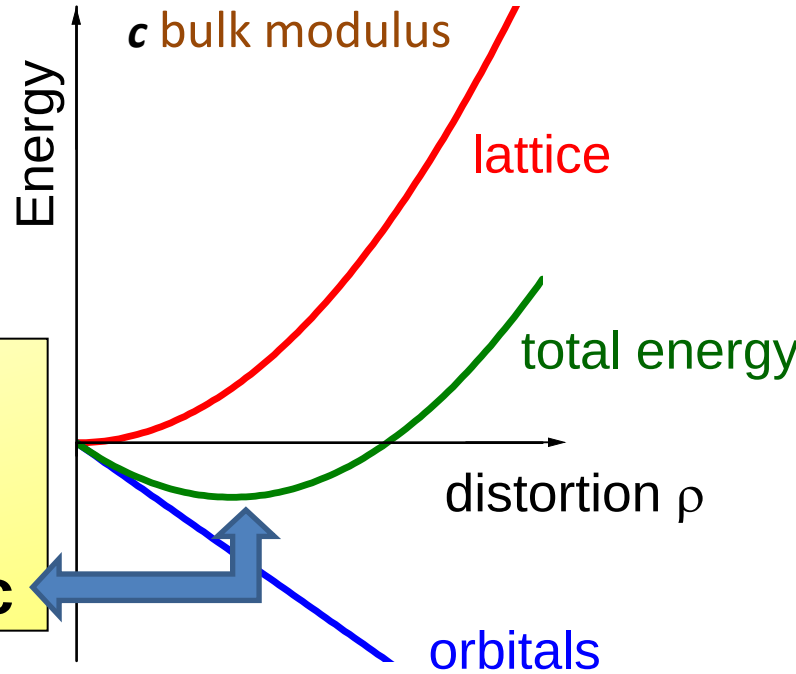


Jahn-Teller active Ions (orbital degeneracy):
1, 2, 4, or 5 elektrons in t_{2g}-Orbitals; or
1 or 3 elektrons in e_g-Orbitals

$$E(\rho) = \frac{c}{2}\rho^2 - g\rho$$

g electron phonon coupling

c bulk modulus



Distortion of the octahedron leads to:
-Linear reduction of the electron energy
-Quadratic increase of the lattice energy

⟹ E(ρ) at minimum when distortion **ρ = g/c**

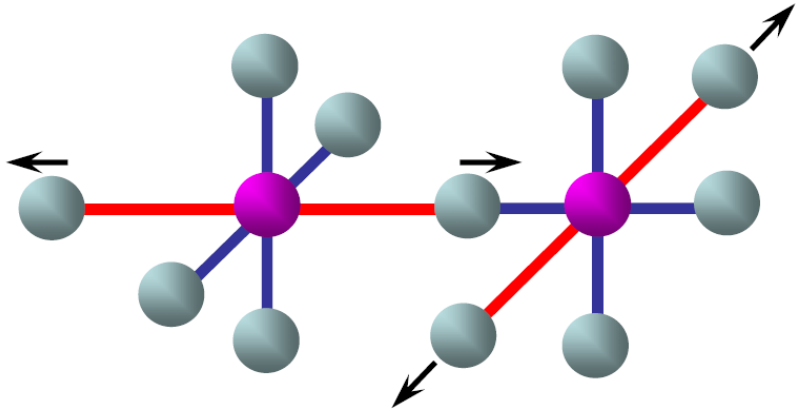
By the distortion, the orbital degree of freedom is „quenched“; but spin degree of freedom remains preserved .

Orbital Order- Cooperative JT effect

Coupling between local distortions on different sites

Jahn-Teller effect mediates interaction between orbitals of next neighbors sites, thereby leading to orbital order

Cooperative Jahn-Teller effect



stretching of next neighbors Octahedra in direction perpendicular to each other.

2. Orbital and spin dependent superexchange

exchange mechanism which couples Orbital and magnetic order

⟹ **Kugel-Khomskii model**

description and comments, see board!

For more details, see:

K. I. Kugel and D. I. Khomskii, Sov. Phys. JETP 37, 725 (1973);
K. I. Kugel and D. I. Khomskii, Sov. Phys. Ups. 25, 231 (1982)

Orbital order : Kugel – Khomskii model

* Consider orbital ordering for the case of double degeneracy ($U \gg t$) and with 1 electron per site, $n = 1$ ⇒ ; only e_g electrons, no Jahn-Teller distortion

* localized electrons are characterized by

1. Spin σ ($\sigma^z = \pm \frac{1}{2}$) ⇒ double deg = 2

2. Index of occupied orbital ($\alpha = 1$ or 2)
   ⇒ extra double degeneracy :
   effective pseudospin operator $\tau^z = \pm \frac{1}{2}$
   $\tau^z = +\frac{1}{2}$ for orbital 1
   $\tau^z = -\frac{1}{2}$ " " 2
   ⇒ orbital degeneracy = $2\tau^+ + 1 = 2$

Description of the spin-orbital interaction by the degenerate Hubbard model, which includes the intra-atomic exchange responsible for Hund's rule coupling

$$\mathcal{H} = \sum_{\langle i,j\rangle,\,\alpha\beta} t_{ij}^{\alpha\beta}\, c^{+}_{i\alpha\sigma}\, c_{j\beta\sigma} + U \sum_{i,\,\alpha\beta,\,\sigma\sigma'} n_{i\alpha\sigma}\, n_{i\beta\sigma'} - J_H \sum_{\substack{i \\ \alpha\neq\beta}} \left(\tfrac{1}{2} + 2\vec{S}_{i\alpha}\vec{S}_{i\beta}\right)$$

sites i,j — spin σ — orbital $\alpha,\beta = 1,2$

hopping, same spin direction

different spins

same state (i); different orbitals!

$$-J_H \sum_{\alpha\neq\beta} \left(\tfrac{1}{2} + 2\vec{S}_{i_1}\cdot\vec{S}_{i_2}\right)$$

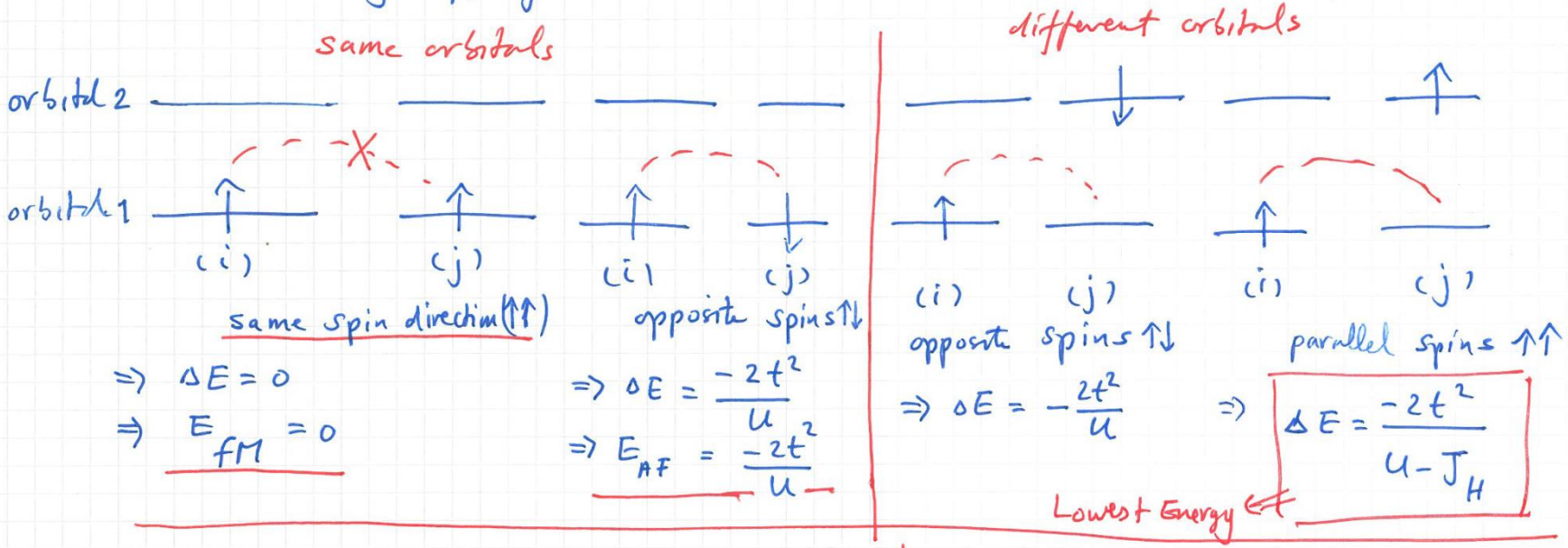
for $\uparrow\uparrow$: $\vec{S}_{i_1}\vec{S}_{i_2} \Rightarrow \frac{1}{4} \Rightarrow -J_H$

for $\uparrow\downarrow$: $\vec{S}_{i_1}\cdot\vec{S}_{i_2} \Rightarrow -\frac{1}{4} \Rightarrow 0$

$\Rightarrow$ Difference $= -J_H$

How do orbital correlations drive magnetism (Kugel-Khomskii model)

assume: only hopping between the same orbitals $\Rightarrow t^{11} = t^{22} = t$, $t^{12} = 0$



$\Rightarrow$ Results:

ferro orbital ordering $\Rightarrow$ antiferromagnetic order

Results:

antiferro-orbital ordering $\Rightarrow$ ferromagnetic ordering

$\Rightarrow$ Virtual hoppings lead ~~to both~~ simultaneously to both orbital and spin ordering

effective exchange Hamiltonian (Kugel-Khomskii); 2 eg electrons, 2 orbitals, 2 spin directions ↑↓

$$\mathcal{H} = \sum \left\{ J_s \vec{S}_i \cdot \vec{S}_j + J_\tau \vec{\tau}_i \cdot \vec{\tau}_j + J_{s\tau} (\vec{S}_i \cdot \vec{S}_j)(\vec{\tau}_i \cdot \vec{\tau}_j) \right\}$$

spins — orbitals — coupling between spin and orbital degrees of freedom.

$\Rightarrow$ total 4 degeneracy:

$$\vec{S} = \frac{1}{2} \begin{cases} S_z = +\frac{1}{2} \uparrow \\ S_z = -\frac{1}{2} \cdot \downarrow \end{cases} ; \quad \vec{\tau}_z = \frac{1}{2} \begin{cases} +\frac{1}{2} \text{ for orbital 1} \\ -\frac{1}{2} \text{ for orbital 2} \end{cases}$$

$\Rightarrow$ 4 states for 2 eg electrons

$|1, \uparrow\rangle \Rightarrow |\tau^z = +\frac{1}{2}, S^z = +\frac{1}{2}\rangle$ (1: orbit, ↑: spin)

$|2, \uparrow\rangle \Rightarrow |\tau^z = -\frac{1}{2}, S^z = +\frac{1}{2}\rangle$

$|1, \downarrow\rangle \Rightarrow$

$|2, \uparrow\rangle \Rightarrow$

Directional nature of orbitals and exchange interactions

⇒ orbital occupancy determine the sign and magnitude of the exchange interactions

⇒ magnetic ground state !

Examples :

Examples:

orbital occupancy determine the sign and magnitude of exchange interaction, see board!

$KCuF_3$: JT distortion ⇒ elongation along the ab plan

Cubic perovskite

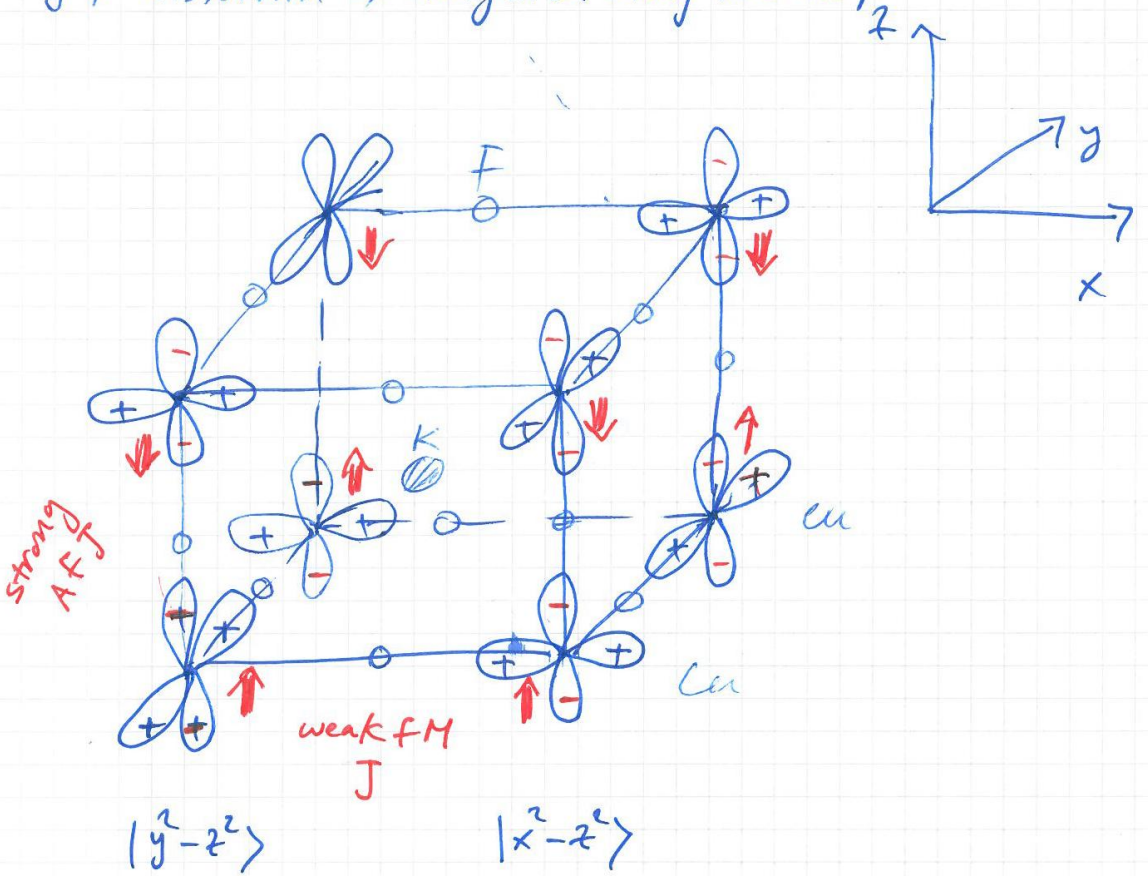
Cu^{2+} $(3d^9)$: t_{2g} system

y^2-z^2/x^2-z^2

e_g 1 d hole (e_g)

$3x^2-r^2/3y^2-r^2$

t_{2g}

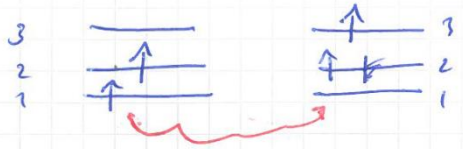


$J_c/J_a \simeq 100$!

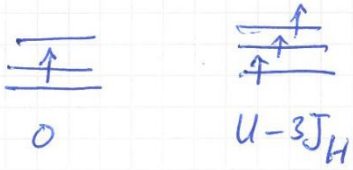
⇒ 1 dimensional AF chain ∥ to z !, despite cubic structure!

Ferromagnetic insulator $LaVO_3$; V^{3+} $(3d^2)$: t_{2g} system (assuming hopping to same orbital)

parallel spins at i and j (FM pair)



initial $-J_H$ $-J_H$ $\Rightarrow -2J_H$



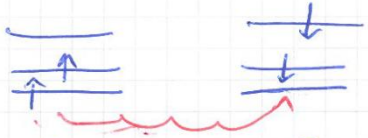
find $\Rightarrow U-3J_H$

0 $\quad U-3J_H$

$\Delta E_{\uparrow\uparrow} = (U-3J_H)-(-2J_H)$

$\boxed{\Delta E_{\uparrow\uparrow} = U-J_H}$

antiparallel spins (AF pair)



initial $-J_H$ $-J_H$ $\Rightarrow -2J_H$

find $\Rightarrow U-J_H$

0 $\quad U-J_H$

$\Delta E_{\uparrow\downarrow} = U-J_H-(-2J_H)$

$\boxed{\Delta E_{\uparrow\downarrow} = U+J_H}$

$\Rightarrow$ ~~Ground FM state is favorable~~ $\Rightarrow$ FM along the z direction

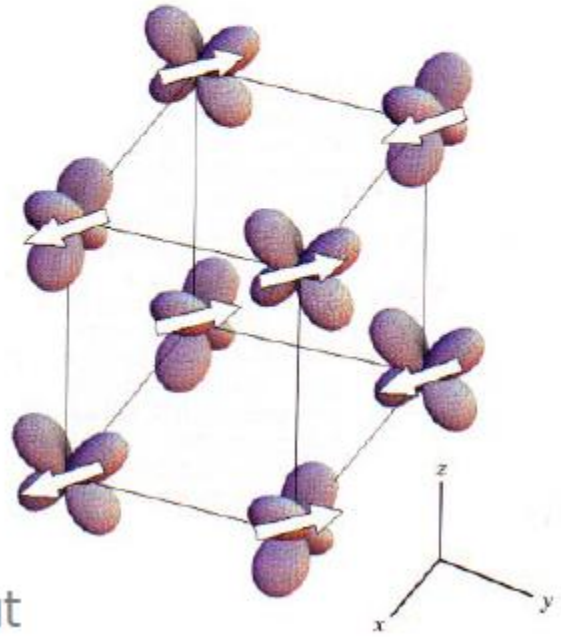
FM chains despite cubic structure !

order patterns: LaVO3

- La = 3+, O_3 = 6-, thus V = 3+

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn

- V^{3+} means $3d^2$: a system with partial t_{2g} occupation



d_{xy} left out

orbital-spin pattern:

spin z: FM chains

spin xy: AFM

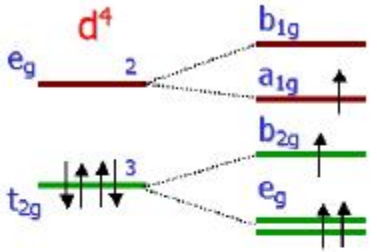
orbital: d_{yz} and d_{xz} alternate in x, y and z

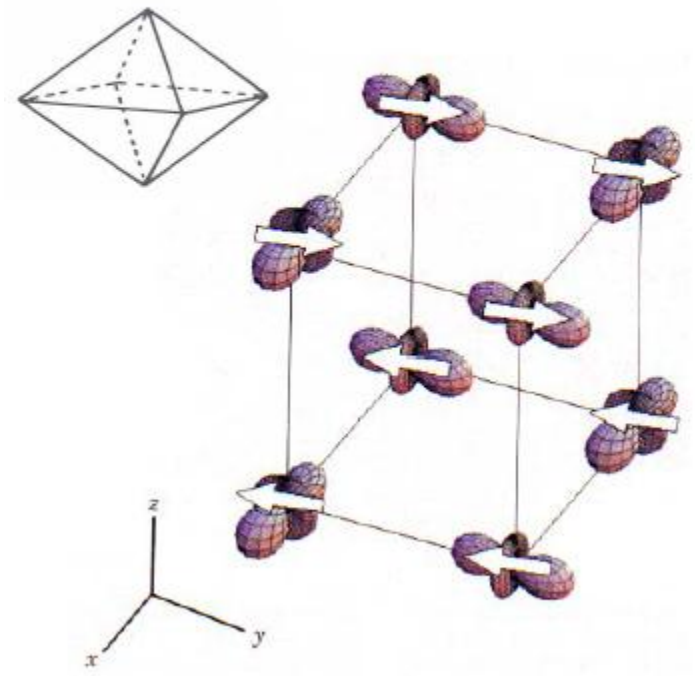
anisotropic despite cubic structure !

order patterns: LaMnO3

- La = 3+, O_3 = 6-, thus Mn = 3+
- Mn^{3+} means $3d^4$: a Jahn-Teller system.

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn





orbital degeneracy lifted by JT:

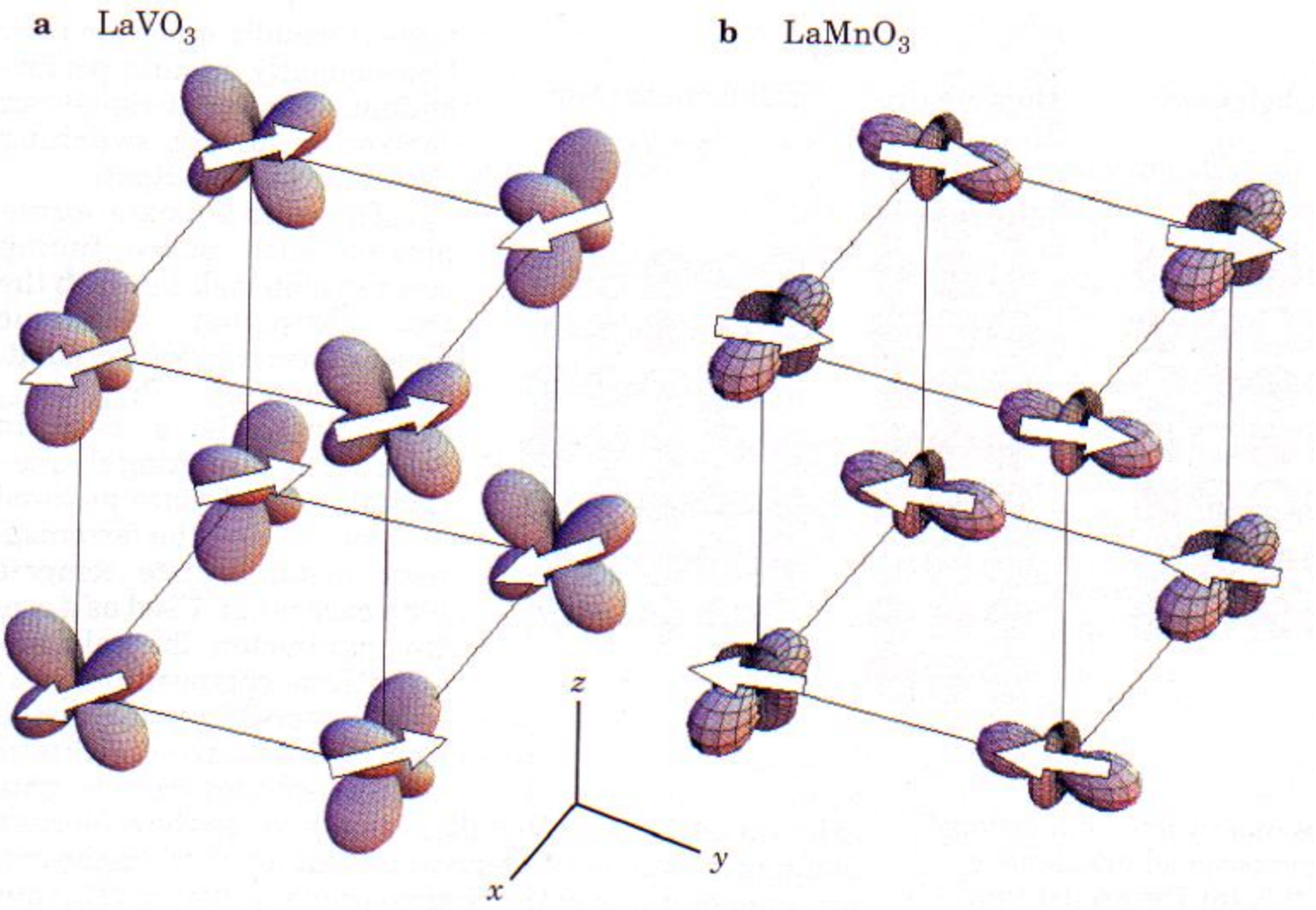
favours occupation of either

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

linear combination alternating:

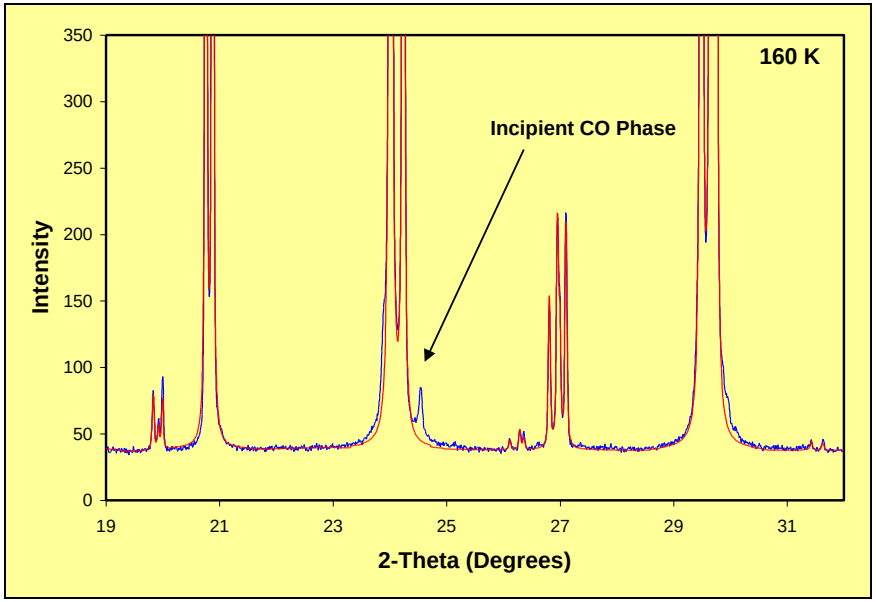
$3d_{x^2-r^2}$ and $3d_{y^2-r^2}$

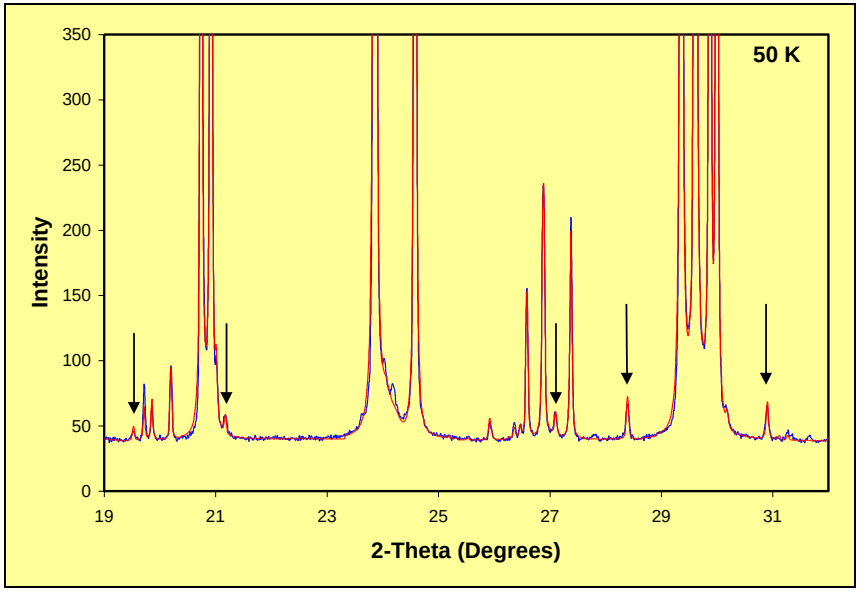
e_g – Orbitals
(x^2-y^2 and $3z^2$-r^2)


a LaVO3
b LaMnO3
z
y
x

Experimental methods for investigation of Orbital Ordering

Charge Ordering in $Nd_{0.5}Sr_{0.5}MnO_3$



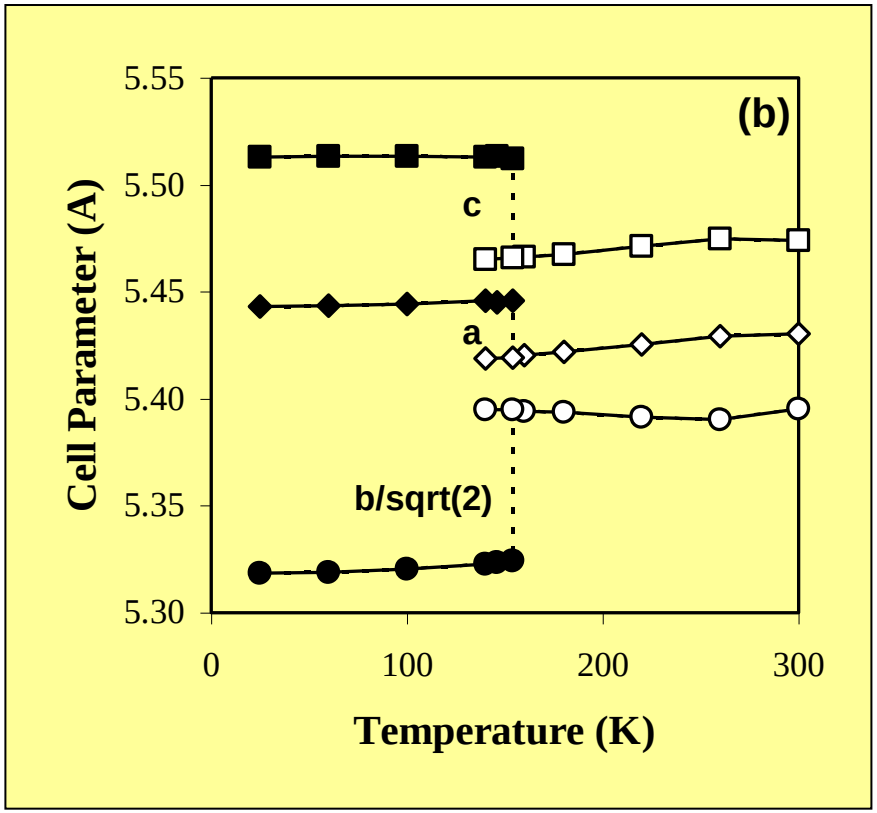


Synchrotron X-ray Powder Diffraction Data (NSLS-X7A)

A series of weak superstructure reflections arise (1% intensity at the strongest) that indicate doubling of the *a* -axis.

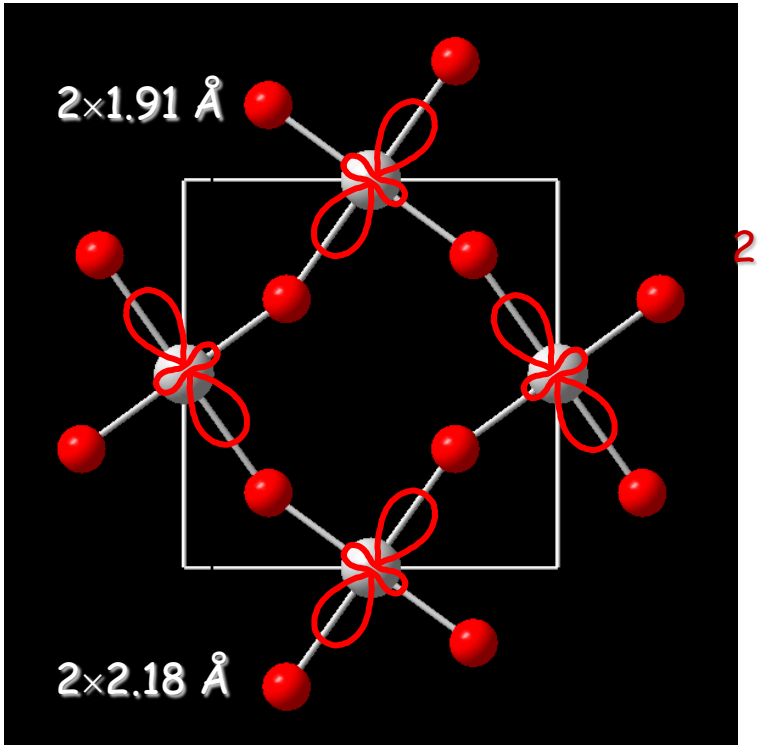
Woodward, Cox, Vogt, Rao, Cheetham, *Chem. Mater.* **11**, 3528-38 (1999).

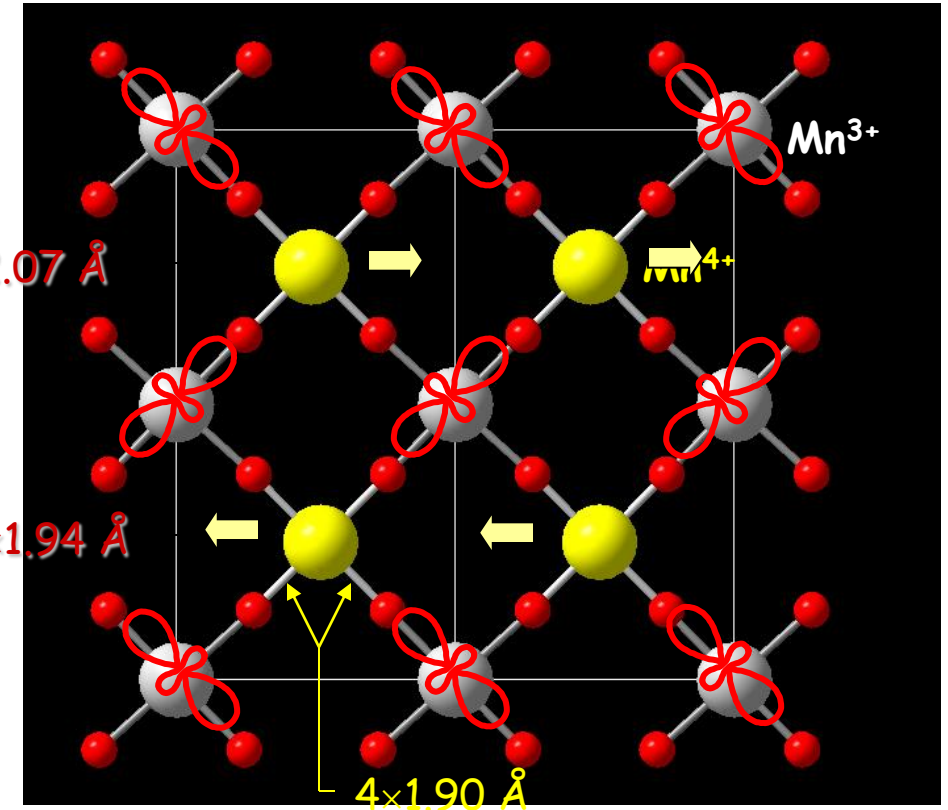
Orbital Ordering in $Nd_{0.5}Sr_{0.5}MnO_3$



Upon cooling below 150 K, the *a* & *c*-axes expand and the *b*-axis contracts. This is the signature of orbital ordering

Examples of Orbital Ordering





$LaMnO_3$ (298 K)

Rodriguez-Carvajal, et al. Phys. Rev. B **57**, R3189 (1998).

$NdSrMn_2O_6$ (50 K)

Woodward, et al. Chem. Mater. **11**, 3528-38 (1999).

Experimental methods for investigation of Orbital Ordering

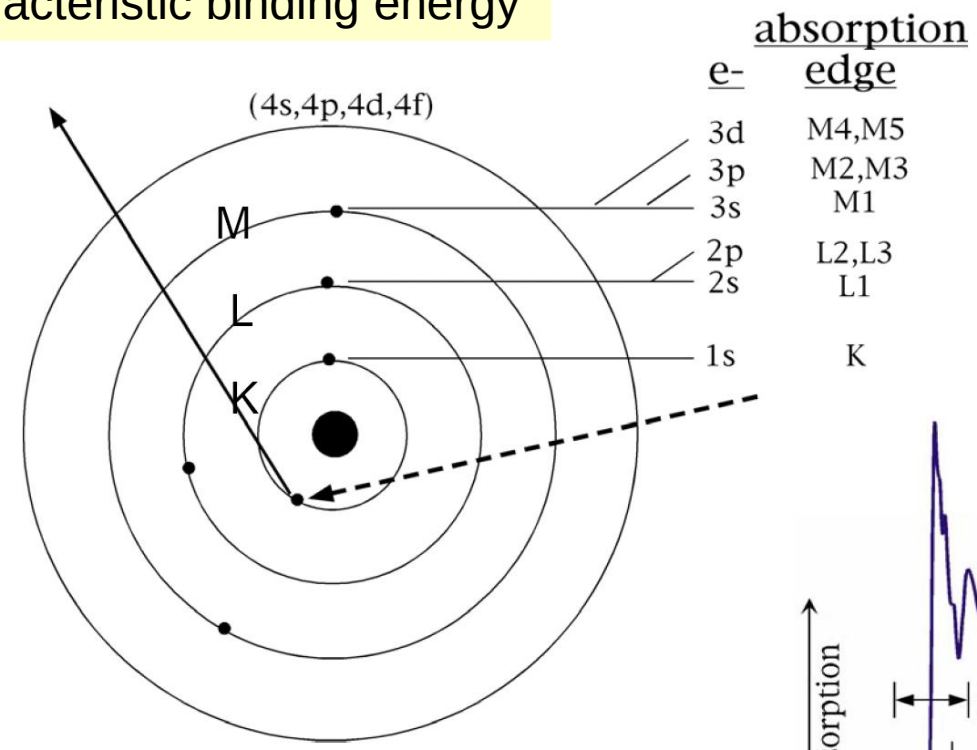
Resonant **I**nelastic **X**-ray **S**cattering (**RIXS**)

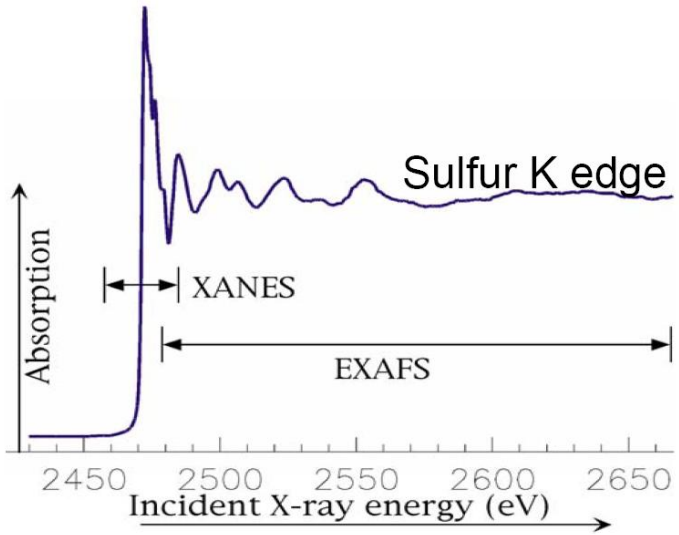
For an excellent review see:
Amen et. al; Rev. Mod. Phys. 83 705 (2011)

First in short: X-ray absorption spectroscopy

X-ray absorption spectroscopy

Each edge of each element has a characteristic binding energy

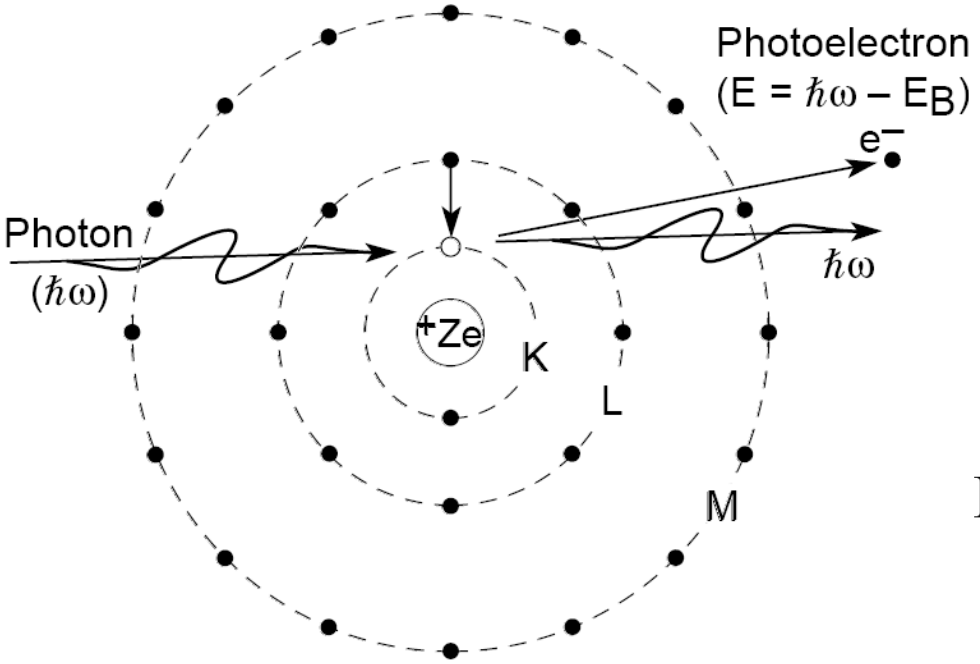




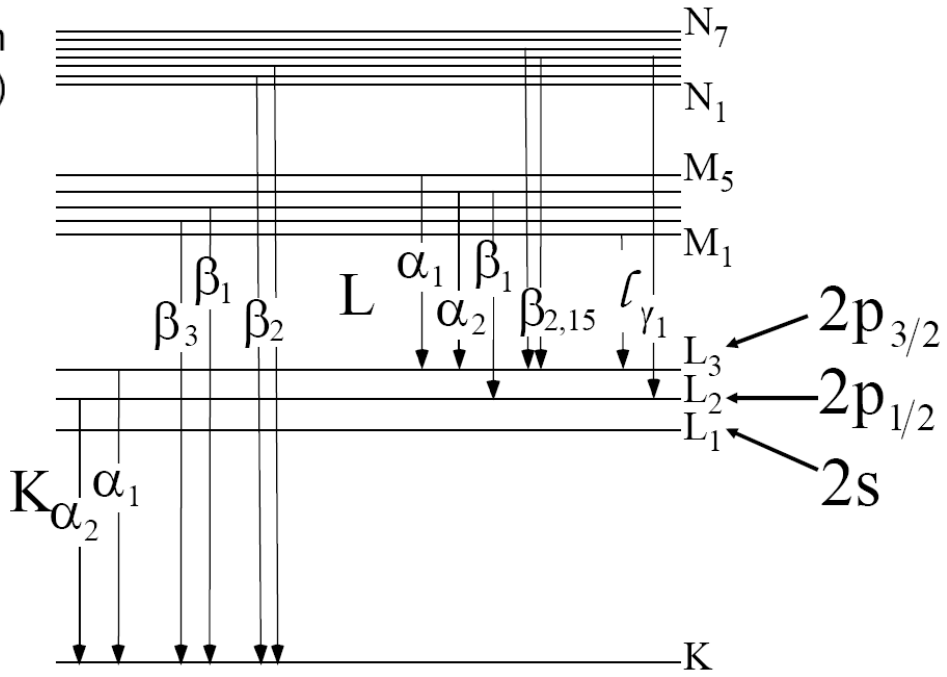
Absorption occurs when the energy of the incident photon is sufficient to eject the electron.

X-ray fluorescence spectroscopy (XFS)

Principle:

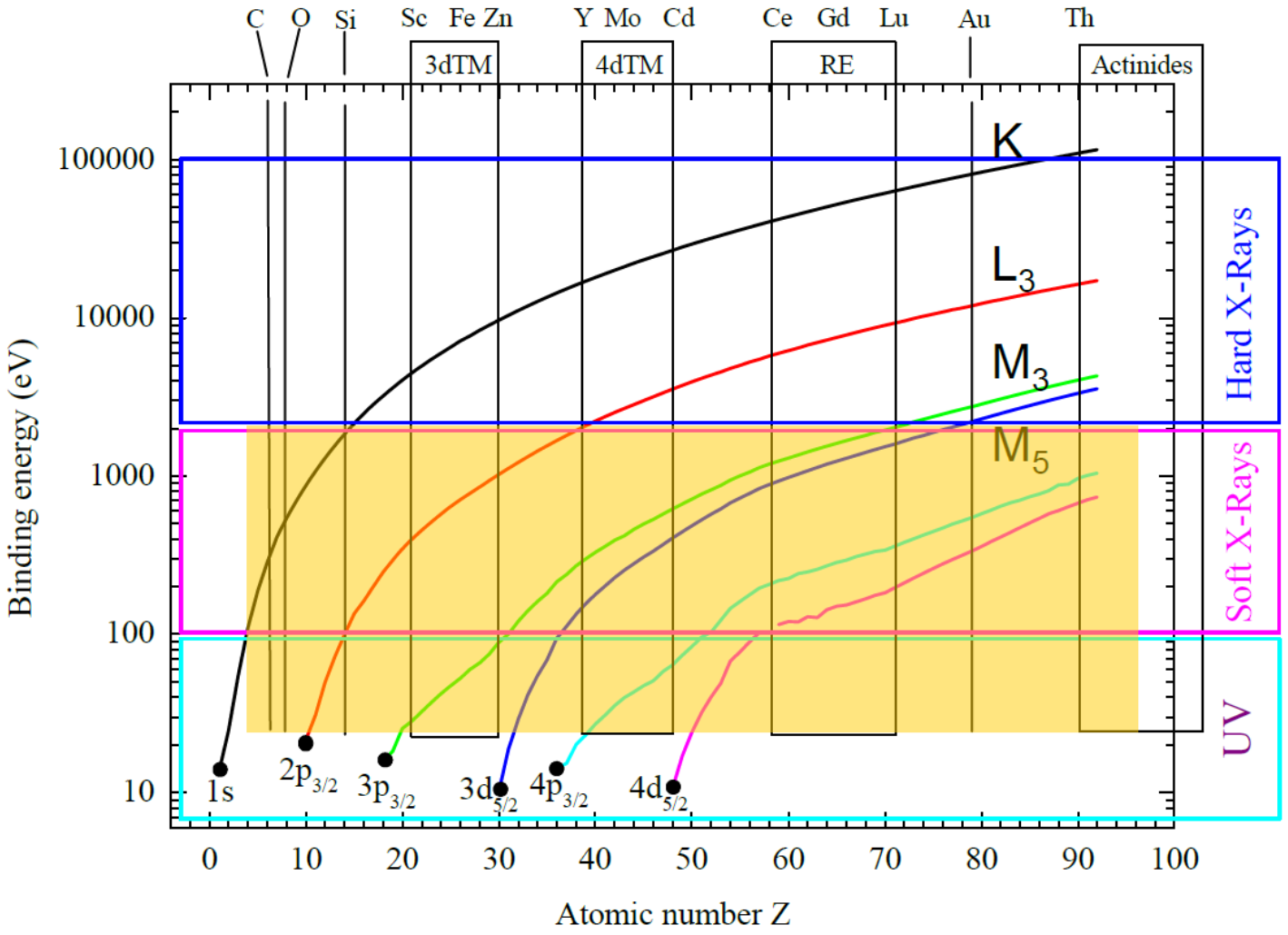


X-ray fluorescence lines:



an element specific technique!

core level energies



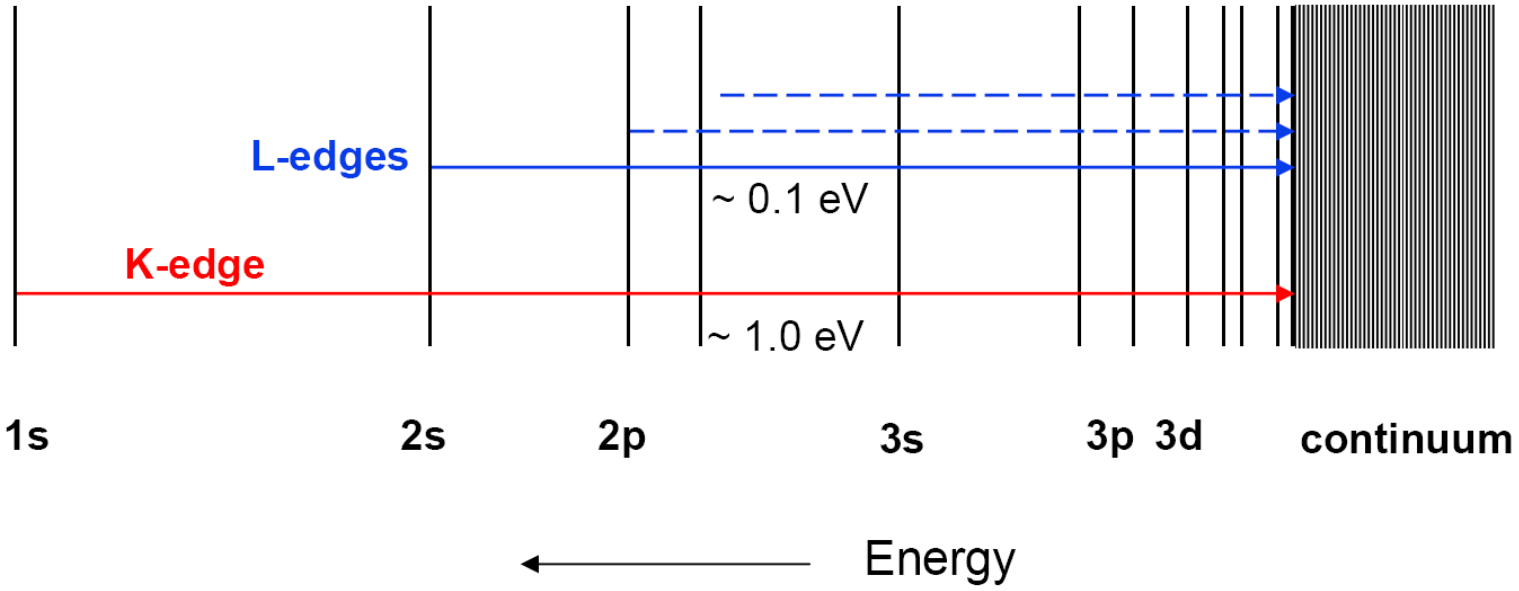
Examples for different edges

Examples:

Cu K-edge ~9000 eV
Cu L-edges ~930 eV
Cu M-edges ~70-120 eV

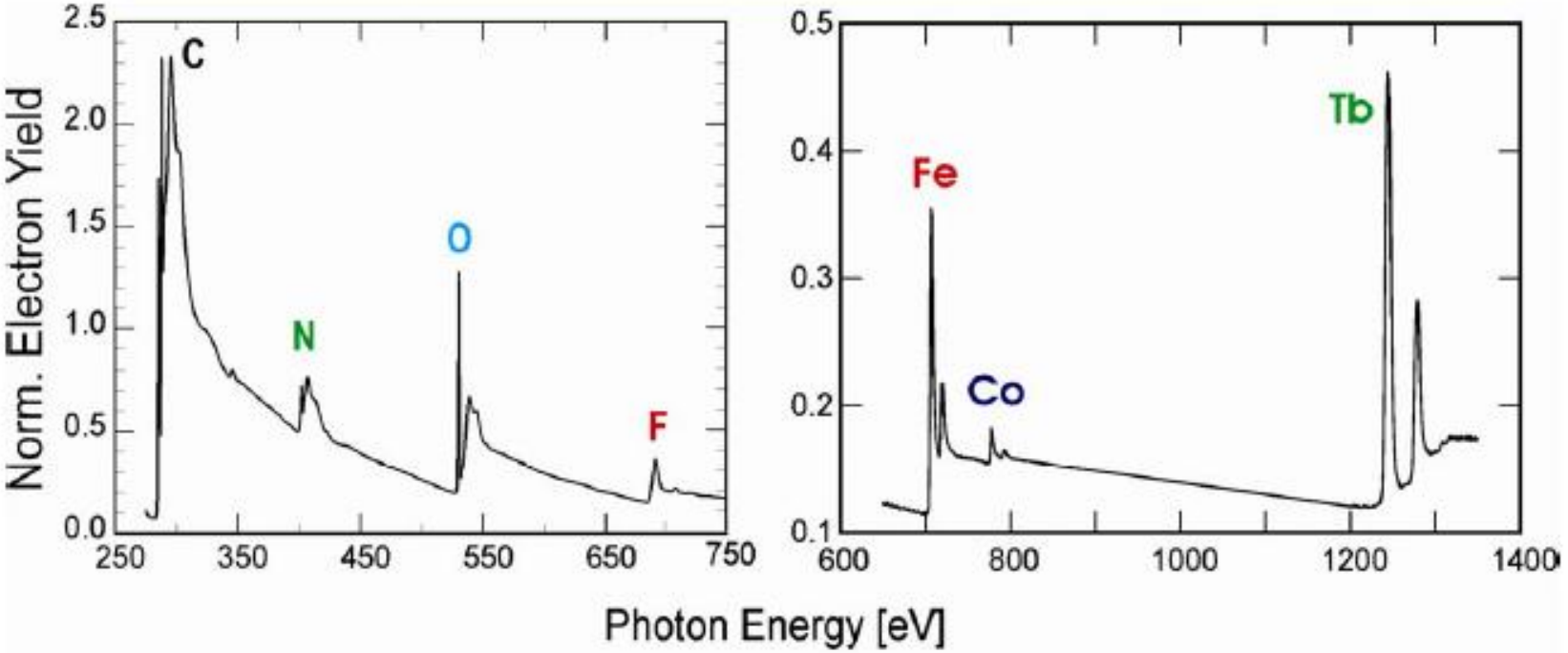
Fe K-edge ~7000 eV
Fe L-edges ~720 eV
Fe M-edges ~50-100 eV

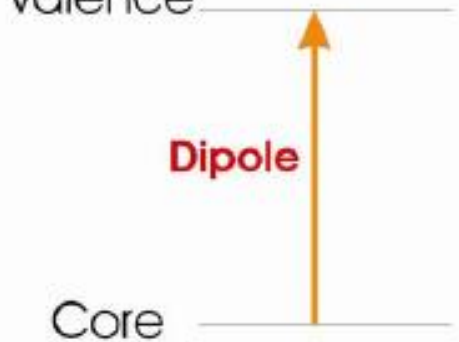
S K-edge ~2472 eV
S L-edges ~200 eV



- An edge results when a core electron absorbs energy equal to or greater than its binding energy
- Results in transitions to unoccupied atomic or molecular orbitals
- Edges are labeled according to the shell the core electron originates from

Tunable x-rays offer elemental specificity

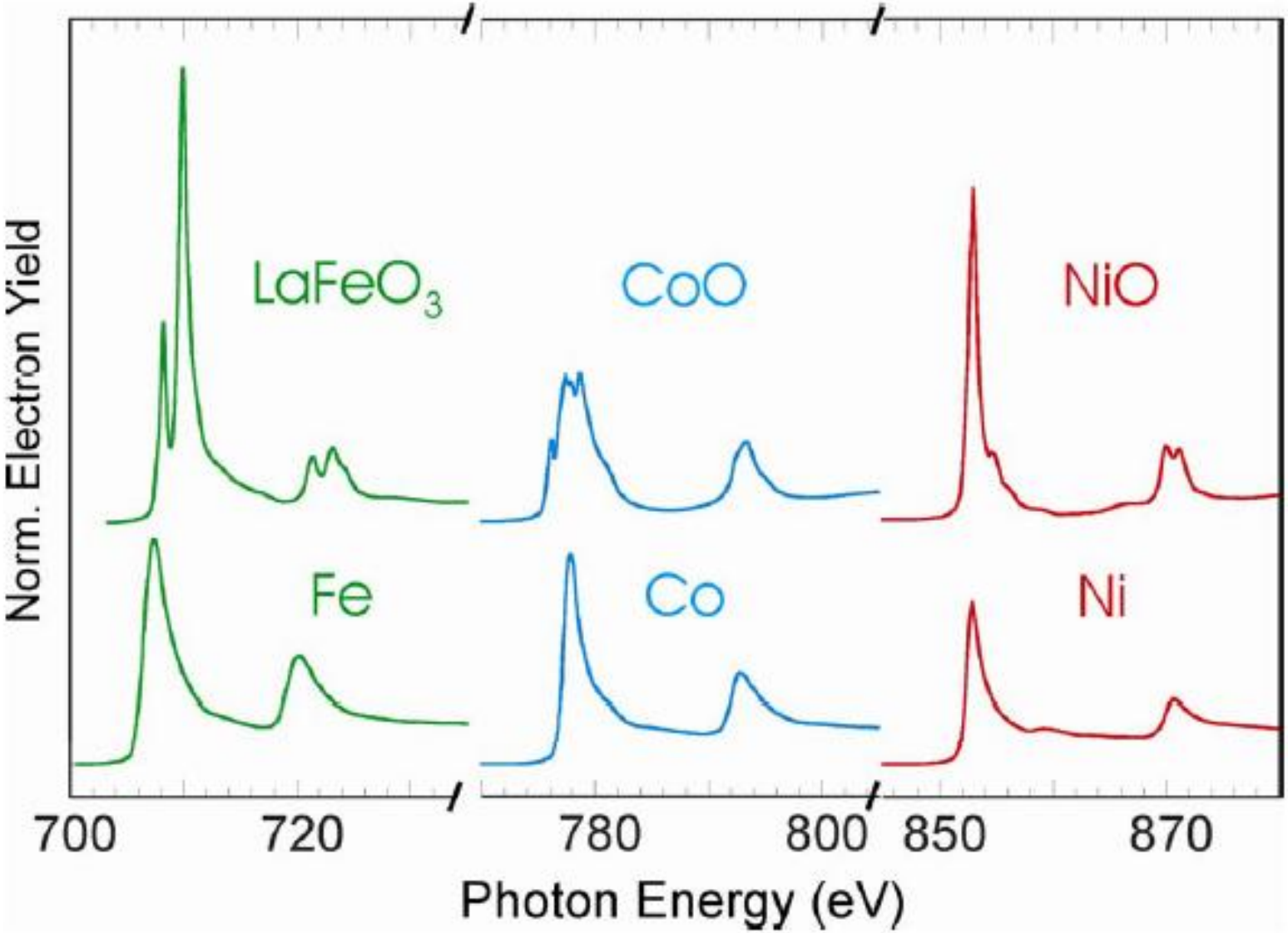




Polymers: p-orbitals
Trans. Met.: d-orbitals
Rare Earths: f-orbitals

1s	K-edge
2p	L edge
3d	M edge

Rich “multiplet structure” reveals local bonding



Orbital Order

Jahn-Teller distortion and/ or Superexchange lead to orbital order

Excitations are different!

Local crystal field excitations vs. dispersing orbitons

Superexchange: spins and orbitals entangle.

Jahn-Teller: spins and orbitals decouple, orbitals frozen out at low temperatures.

Elementary excitations in condensed matter

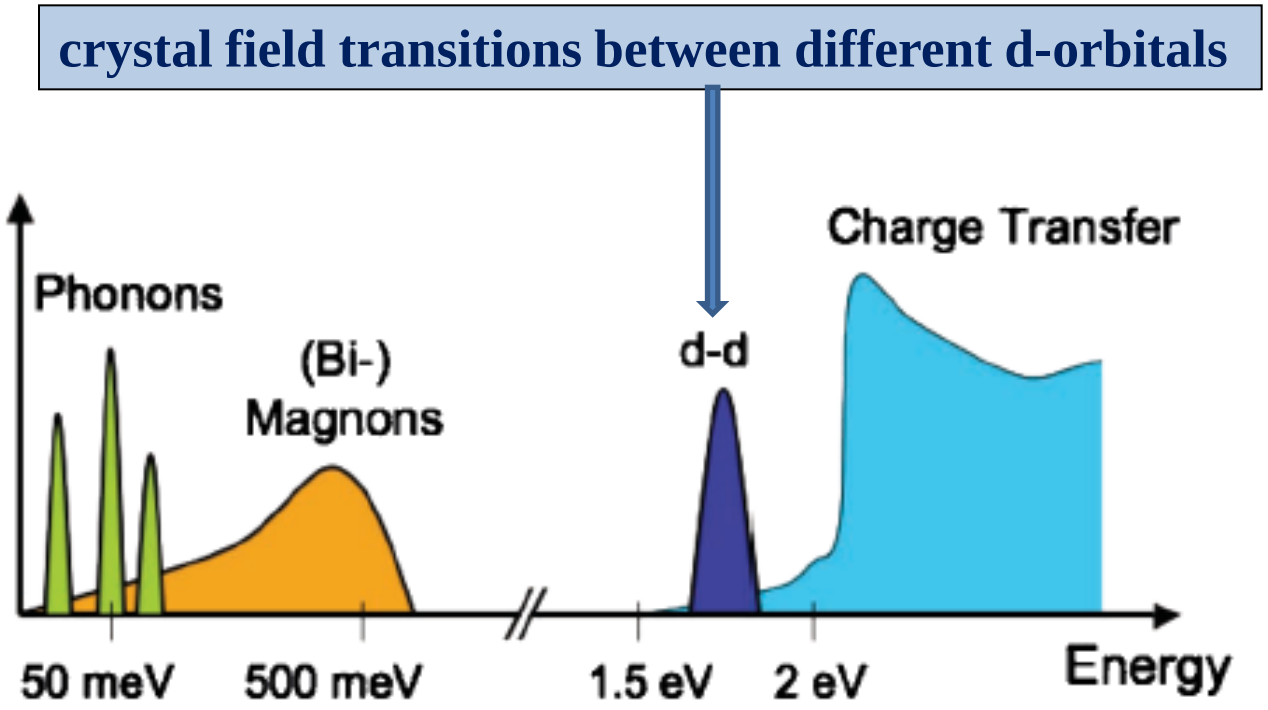


FIG. 6 (color). Different elementary excitations in condensed matter systems and their approximate energy scales in strongly correlated electron materials such as transition-metal oxides.

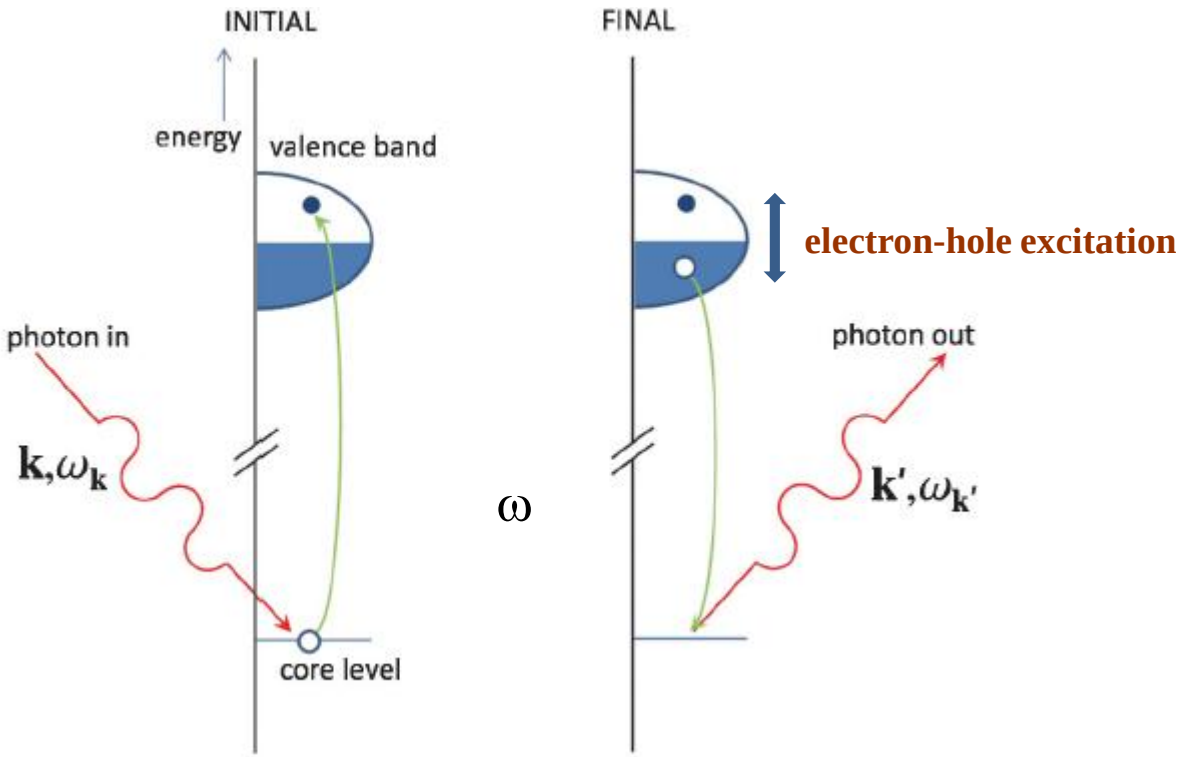
Ament et. al; Rev. Mod. Phys. 83 705 (2011)

Resonant **I**nelastic **X**-ray **S**cattering (**RIXS**)

For an excellent review see:
Amen et. al; Rev. Mod. Phys. 83 705 (2011)

Amen et. al; Rev. Mod. Phys. 83 705 (2011)

Direct RIXS



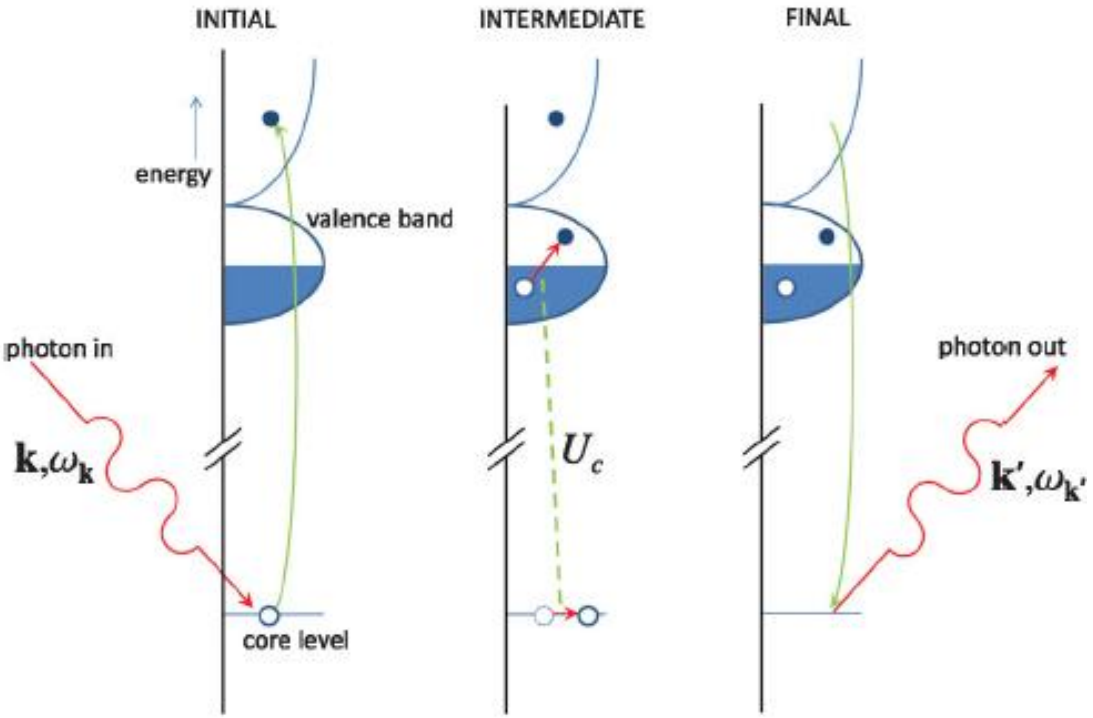
Photon promotes a core electron to empty band

electron from a different state in valence band decays and annihilates the core level hole

RIXS creates excitation in the valence band with momentum $\hbar\mathbf{k}'$- $\hbar\mathbf{k}$ and energy $\hbar\omega_{k'}$ - $\hbar\omega_{k}$

Amen et. al; Rev. Mod. Phys. 83 705 (2011)

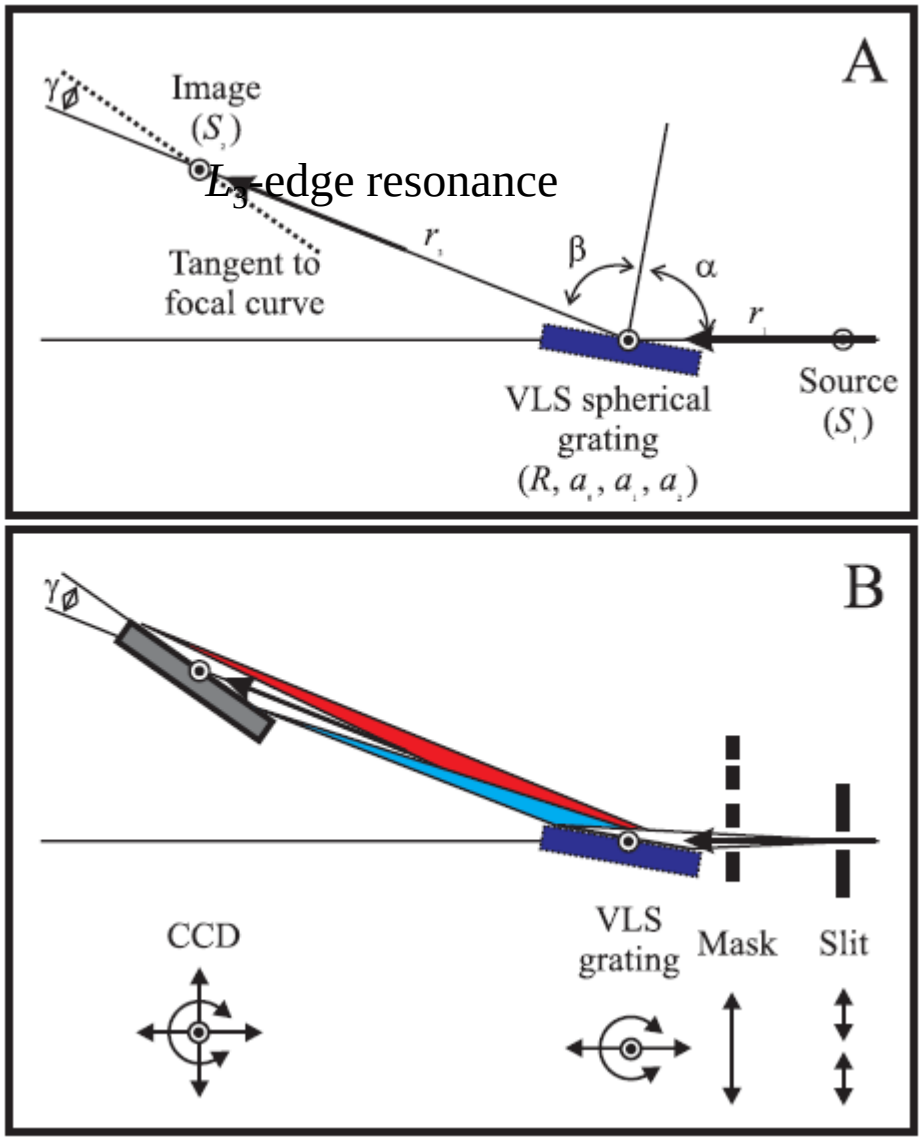
Indirect RIXS

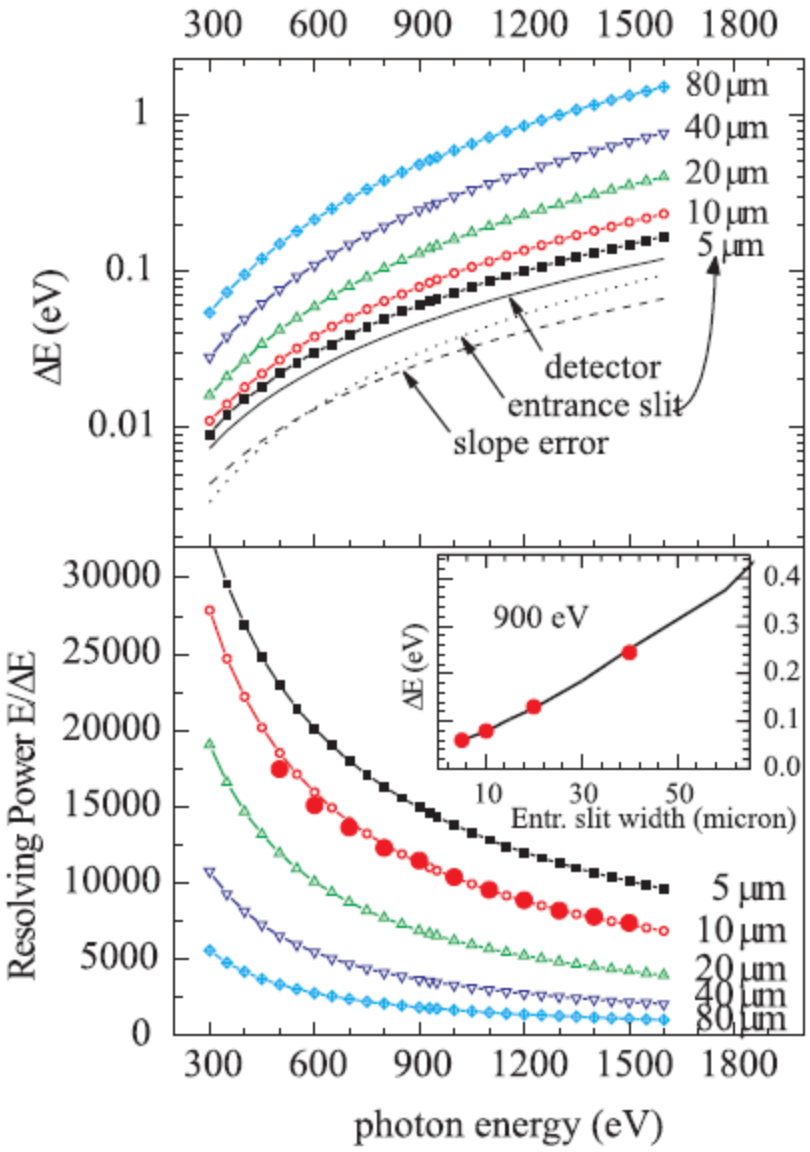


electron is excited from a deep-lying core level into the valence shell. Excitations are created through the Coulomb interaction $\boldsymbol{U_c}$ between the core hole (and in some cases the excited electron) and the valence electrons. The photoelectron subsequently decays leaving behind an excitation in the valence band with momentum $\hbar\mathbf{k}' - \hbar\mathbf{k}$ and energy $\hbar\omega_{\mathbf{k}'} - \hbar\omega_{\mathbf{k}}$

The measured photon energy transfer and momentum transfer in a RIXS experiment is directly related to the energy and momentum of the created excitations (spinons, orbitons)

RIXS Instrument f0r soft x-rays: SAXS at the Swiss Light Source




300
600
900
1200
1500
1800
1
0.1
0.01
ΔE (eV)
80 μm
40 μm
20 μm
10 μm
5 μm
detector
entrance slit
slope error
30000
25000
20000
15000
10000
5000
0
Resolving Power E/ΔE
900 eV
ΔE (eV)
0.4
0.3
0.2
0.1
0.0
10
30
50
Entr. slit width (micron)
5 μm
10 μm
20 μm
40 μm
80 μm
photon energy (eV)

RIXS Instrument for hard x-rays: IDB 30 beamline at APS, USA

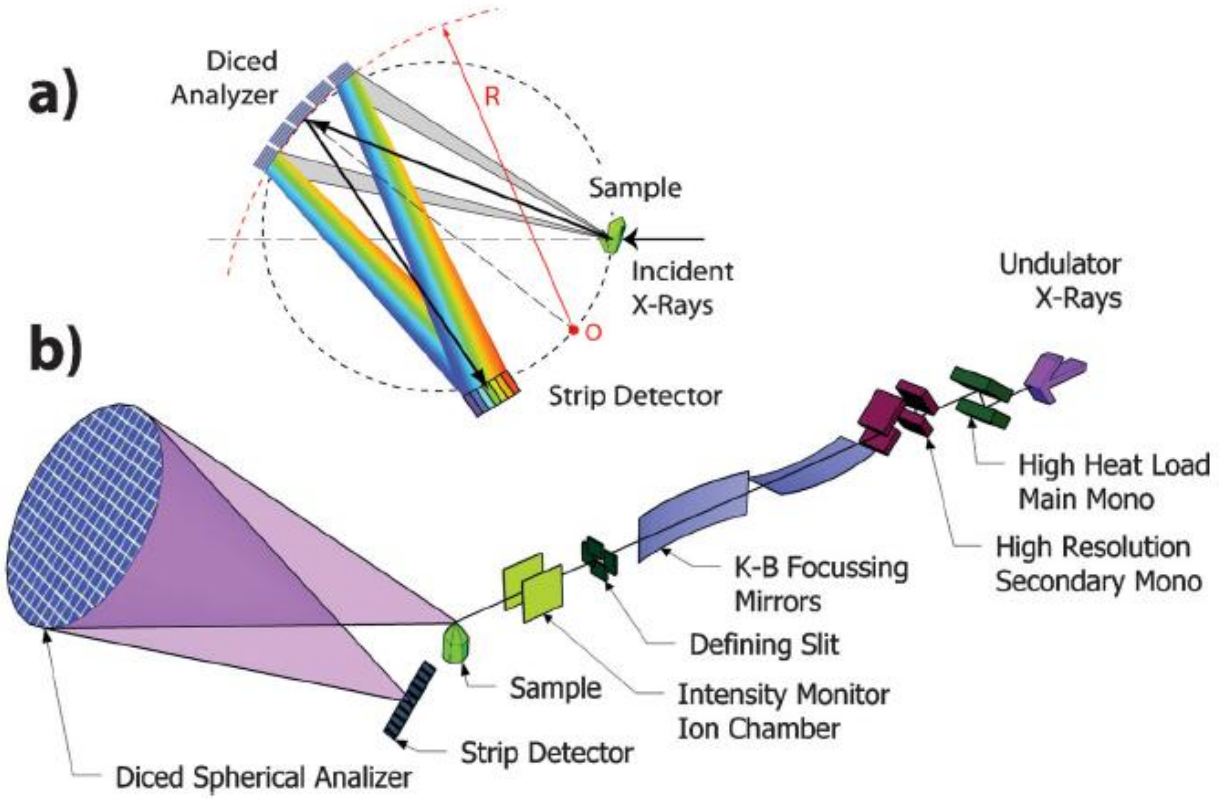
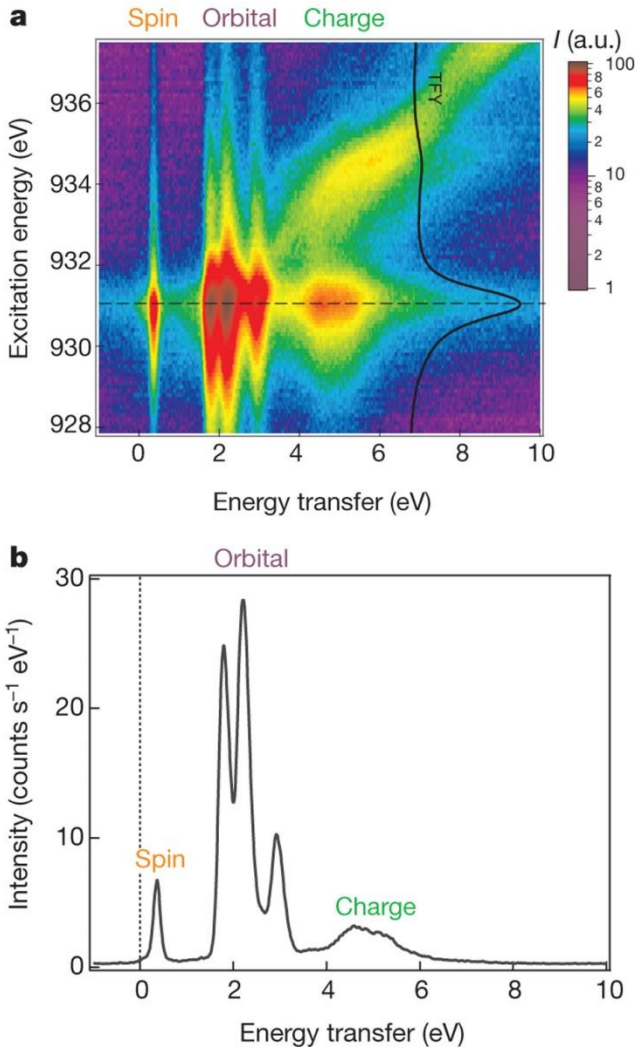


FIG. 15 (color). Schematic of optical components in the 30 IDB inelastic x-ray scattering beam line at the Advanced Photon Source, USA. Figure courtesy of D. Casa (APS).

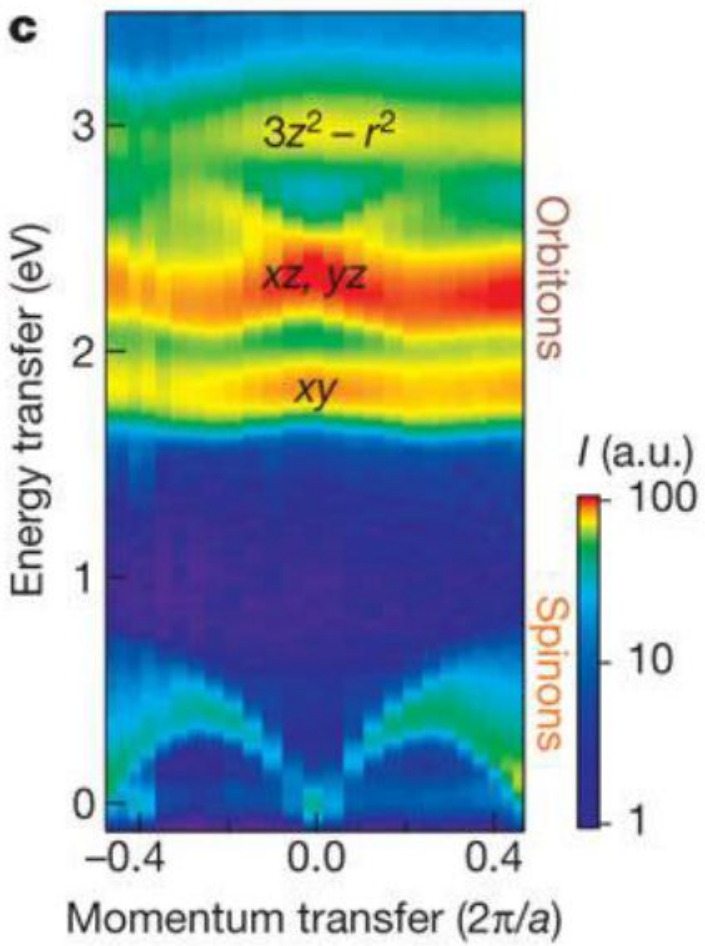
Energy dependence of elementary excitations in Sr_2CuO_3 observed with RIXS at the copper L_3-edge resonance.

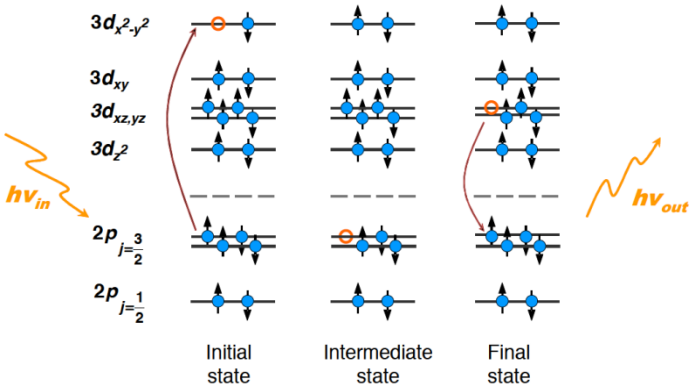


J Schlappa *et al*. *Nature* **485, 82** (2012)

dispersion of orbital and spin excitations across the first Brillouin zone

J Schlappa *et al*. *Nature* **485, 82** (2012)





orbital excitation from the ground-state copper $3d\ x^2 - y^2$ orbital to an excited copper $3d$ *xy* or *xz* orbital