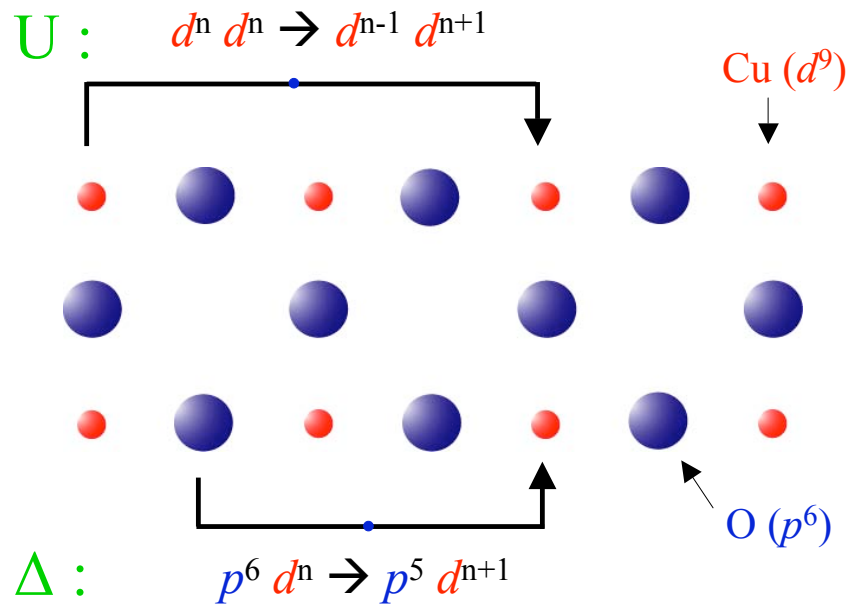


Discussion on the Role of O in TM Oxide modelling

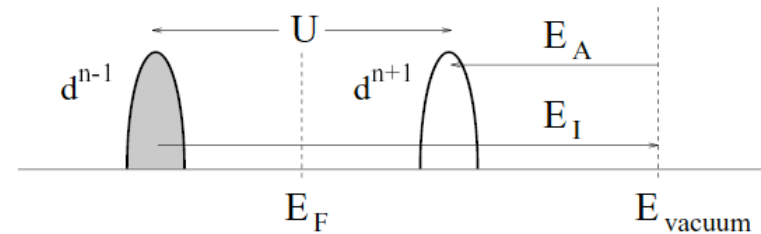
When can we if ever use a single
band like model?

George Sawatzky UBC

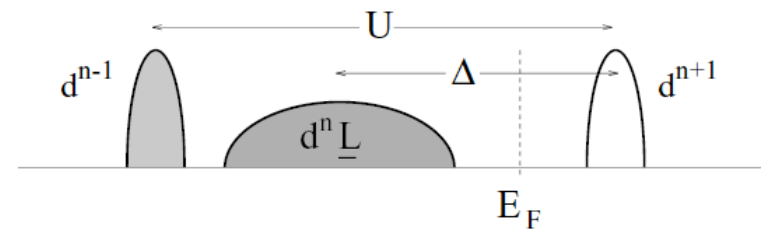
Correlated Electrons in a Solid



(a) Mott-Hubbard insulator



(b) Charge transfer insulator



$$U = E_I^{\text{TM}} - E_A^{\text{TM}} - E_{\text{pol}}$$

$$\Delta = E_I^{\text{O}} - E_A^{\text{TM}} - E_{\text{pol}} + \delta E_{\text{M}}$$

If $\Delta < (W+w)/2 \rightarrow$ Self doped metal

E_{pol} depends on surroundings!!! $E_{\text{p}} = \frac{ze^2 a}{R^4}$

- E_I ionization energy
- E_A electron affinity energy
- E_{M} Madelung energy

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

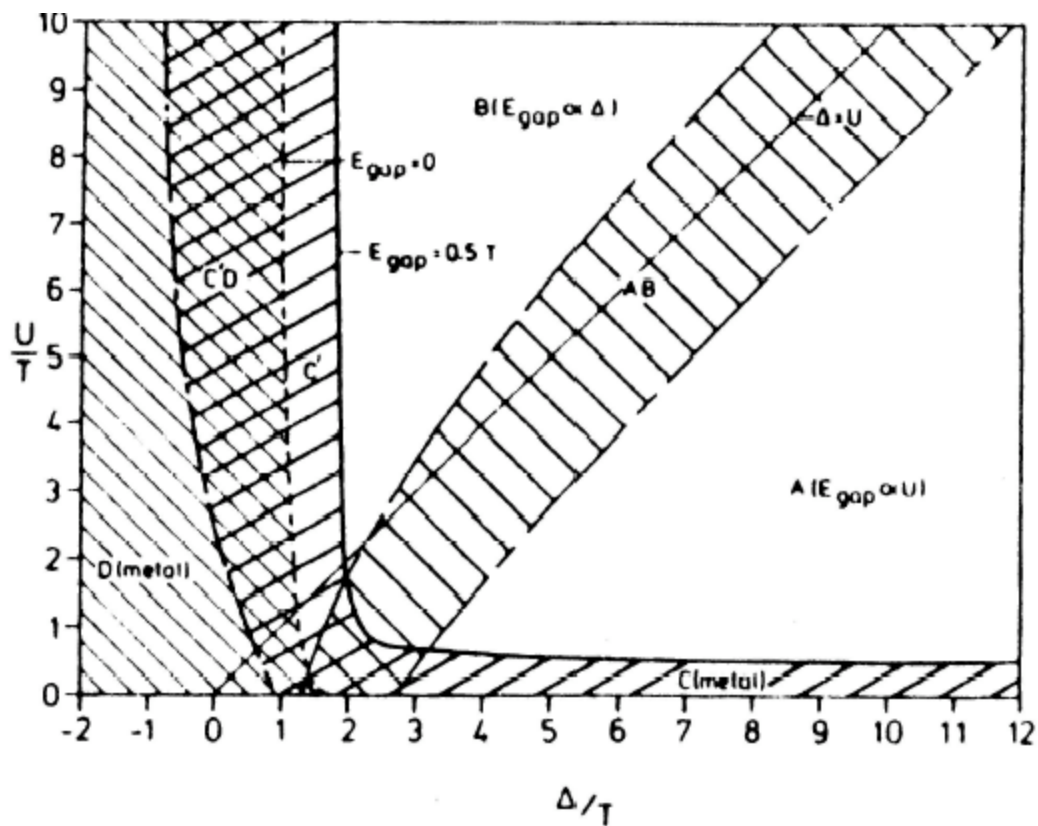


FIG. 3. A phase diagram exhibiting the various regions discussed in the text. The heavy solid line is the semiconductor-metal separation line.

Well known effects

- Important in determining superexchange the Goodenough Kanamori Anderson rules
- Ligand field contributions to the crystal field splittings
- The band gaps in charge transfer gap insulators
- Low energy charge degrees of freedom in doped charge transfer gap systems or in negative charge transfer gap systems (D.D.Sharma)

Less well known role of O

- High polarizability contributes to reduction of the TM U
- Strong non local effects at interfaces and low Dimensional systems
- Magnetic if 2p band is not full –strong Hund's rule coupling as well as strong U
- Charge disproportionation without moving charge
- Very strong covalency for high oxidation state systems like Ti or Co 4+ or even 3+

Is single band Hubbard justified for Cuprates?

The localized states of (5) are, however, not orthogonal because the neighboring squares share a common O site. Thus,

$$\langle P_{i\sigma}^{(S)} | P_{j\sigma'}^{(S)\dagger} \rangle = \delta_{\sigma\sigma'} (\delta_{i,j} - \frac{1}{4} \delta_{(ij),0}) , \quad (6)$$

Zhang Rice PRB 1988
37,3759

where $\delta_{(ij),0} = 1$ if i, j are nearest neighbors. In analogy to the treatment of Anderson for the isolated spin quasiparticle,⁶ we construct a set of Wannier functions ($N_S = \text{num-}$

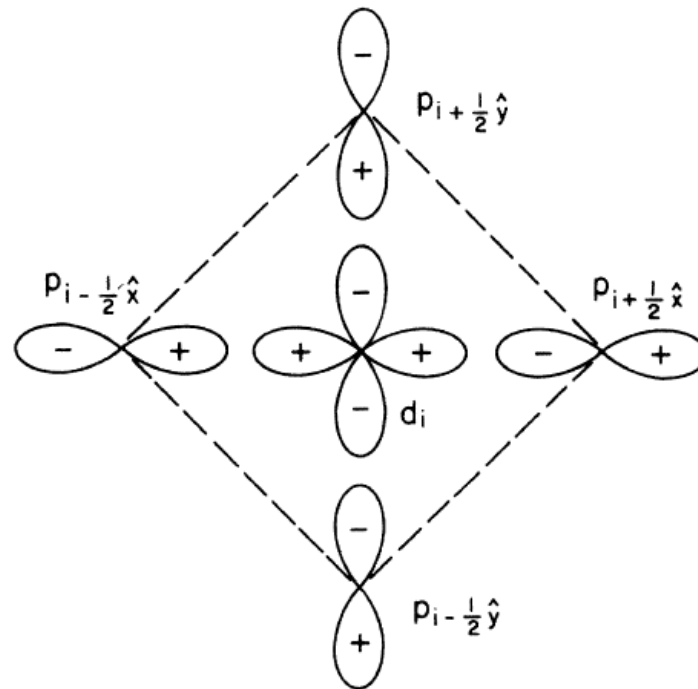


FIG. 1. Schematic diagram of the hybridization of the O hole ($2p^5$) and Cu hole ($3d^9$). The signs + and - represent the phase of the wave functions.

Actually Local 2 R only
 Clearly exists around $\vec{0}$ at Γ

$$\phi_{i\sigma} = N_S^{-1/2} \sum_{\mathbf{k}} P_{\mathbf{k}\sigma} \exp(i\mathbf{k} \cdot \mathbf{R}_i), \quad (7)$$

$$P_{\mathbf{k}\sigma} = N_S^{-1/2} \beta_{\mathbf{k}} \left(\sum_i P_{i\sigma}^{(S)} \exp(-i\mathbf{k} \cdot \mathbf{R}_i) \right), \quad (8)$$

where $\beta_{\mathbf{k}}$ is a normalization factor

$$\beta_{\mathbf{k}} = [1 - \frac{1}{2} (\cos k_x + \cos k_y)]^{-1/2}. \quad (9)$$

$\infty (0,0)$, $0.5 (\pi/2, \pi/2)$, (π, π)

The functions $\phi_{i\sigma}$ are orthogonal, and are complete in the symmetric O-hole space. $\phi_{i\sigma}$ combines with the Cu hole at site i to form a spin singlet (-) or triplet (+):

$$\psi_i^{\pm} = (1/\sqrt{2}) (\phi_{i\uparrow} d_{i\downarrow} \pm \phi_{i\downarrow} d_{i\uparrow}), \quad (10)$$

with energies in second-order perturbation theory, of

$$E_{\pm} = \sum_{\{w\}} |\langle \psi_i^{\pm} | H' | w \rangle|^2 / \Delta E_w, \quad (11)$$

Be careful with ARPES

Problem with ZR singlets

- The combination of O 2p states is not compatible with a band structure state
- The wave functions are non orthogonal

$$\phi_{i\sigma} = N_S^{-1/2} \sum_{\mathbf{k}} P_{\mathbf{k}\sigma} \exp(i\mathbf{k} \cdot \mathbf{R}_i) , \quad (7)$$

$$P_{\mathbf{k}\sigma} = N_S^{-1/2} \beta_{\mathbf{k}} \sum_i P_{i\sigma}^{(S)} \exp(-i\mathbf{k} \cdot \mathbf{R}_i) , \quad (8)$$

From ZR PRL 37,3759

where $\beta_{\mathbf{k}}$ is a normalization factor

$$\beta_{\mathbf{k}} = [1 - \frac{1}{2} (\cos k_x + \cos k_y)]^{-1/2} . \quad (9)$$

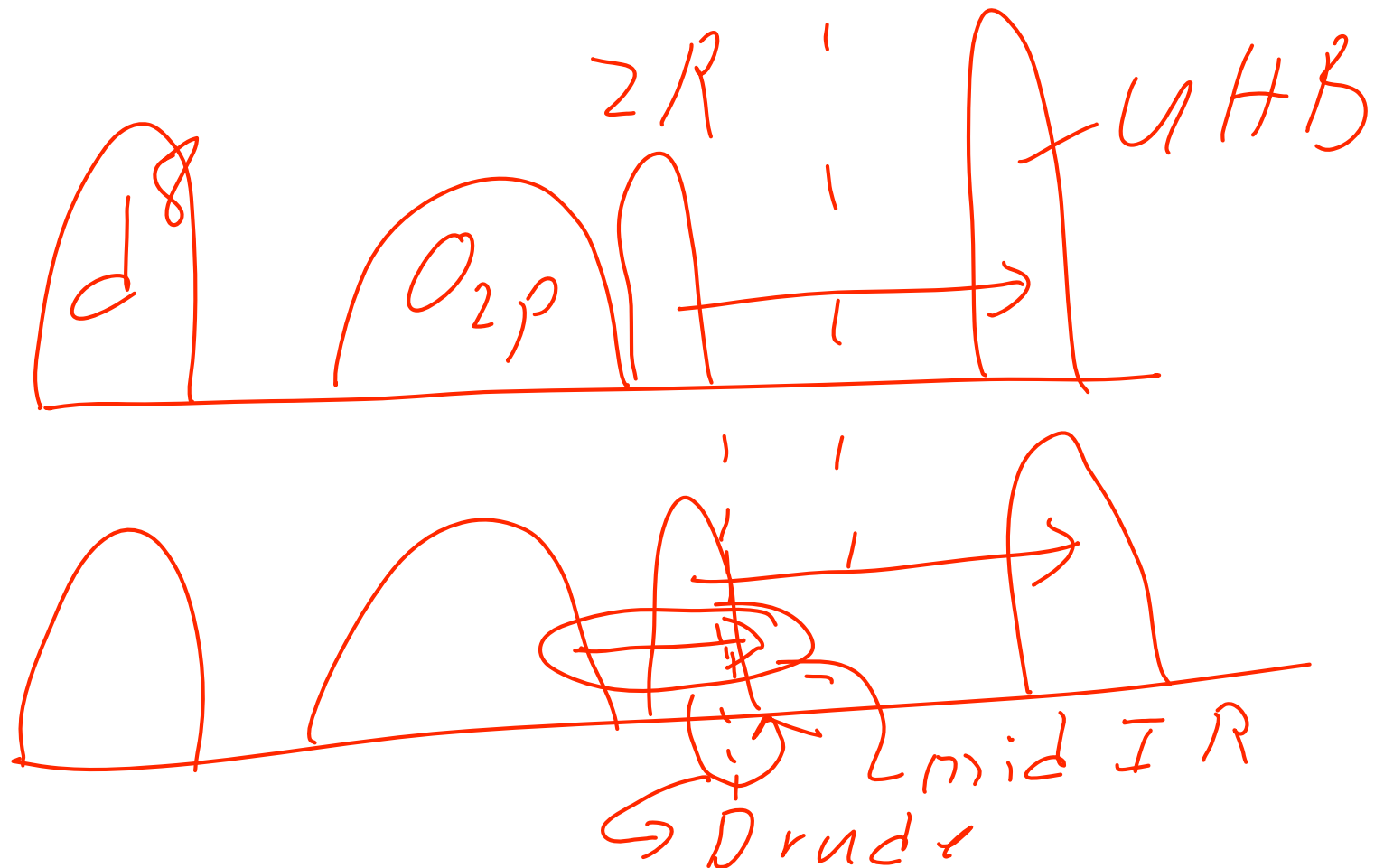
Note it goes to infinity at $k=0$, should we see it at Gamma in ARF
 Luckily it goes to 1 for $K= \text{Pi}/2, \text{Pi}/2$ where the doped holes go

In band theory O 2p does not mix with Cu $dx^{**2}-y^{**2}$ at Gamma!!!! SO HOW TO I
 THIS PROPERLY ?

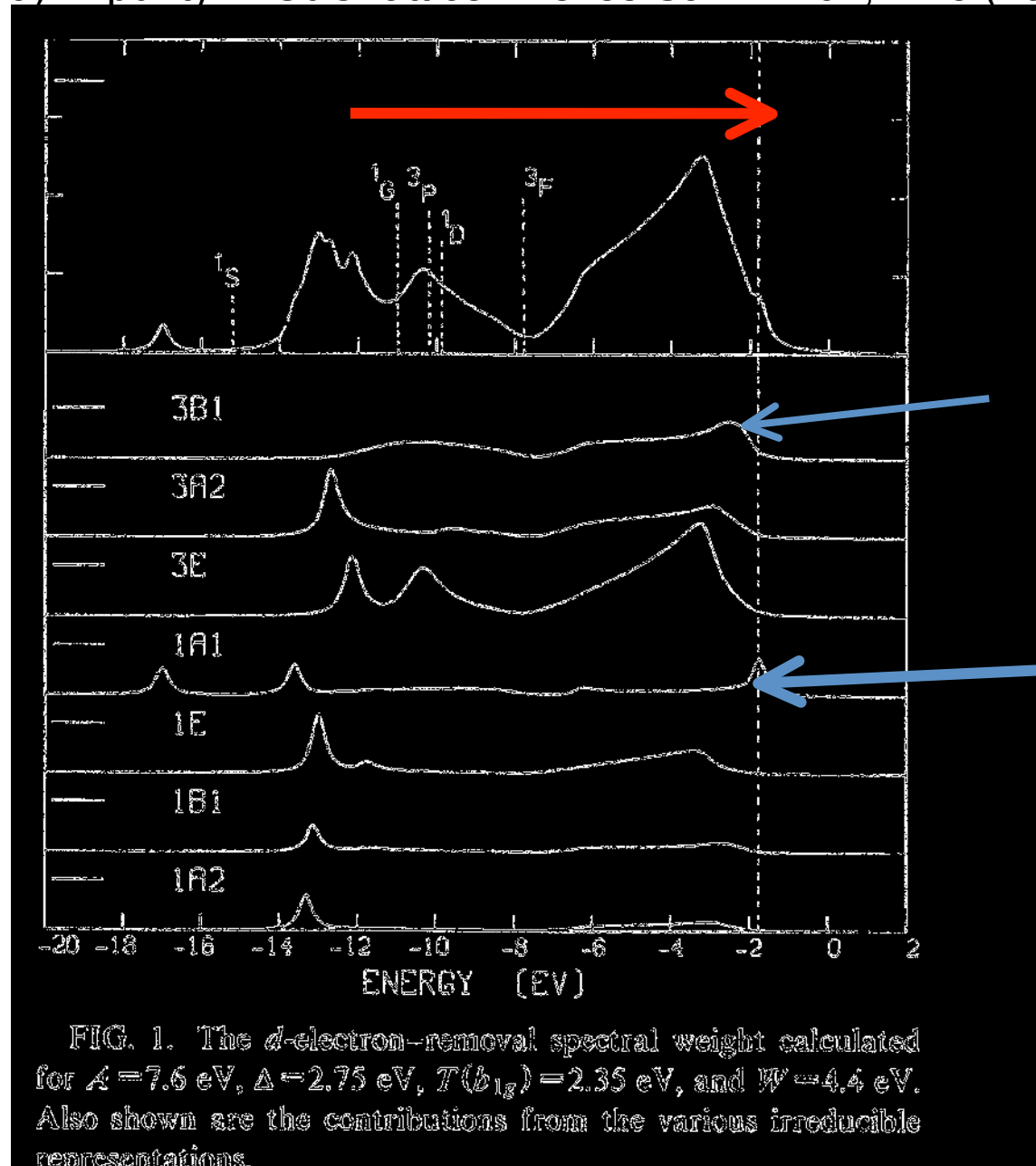
Optical spectroscopy doping dependent

- Single band models like Hubbard in high T_c 's can be very misleading
- Importance of high energy scale states and multiband models in optical spectroscopy

Single band model is only valid at low energy scales i.e. less than .5 eV!!! In doped systems



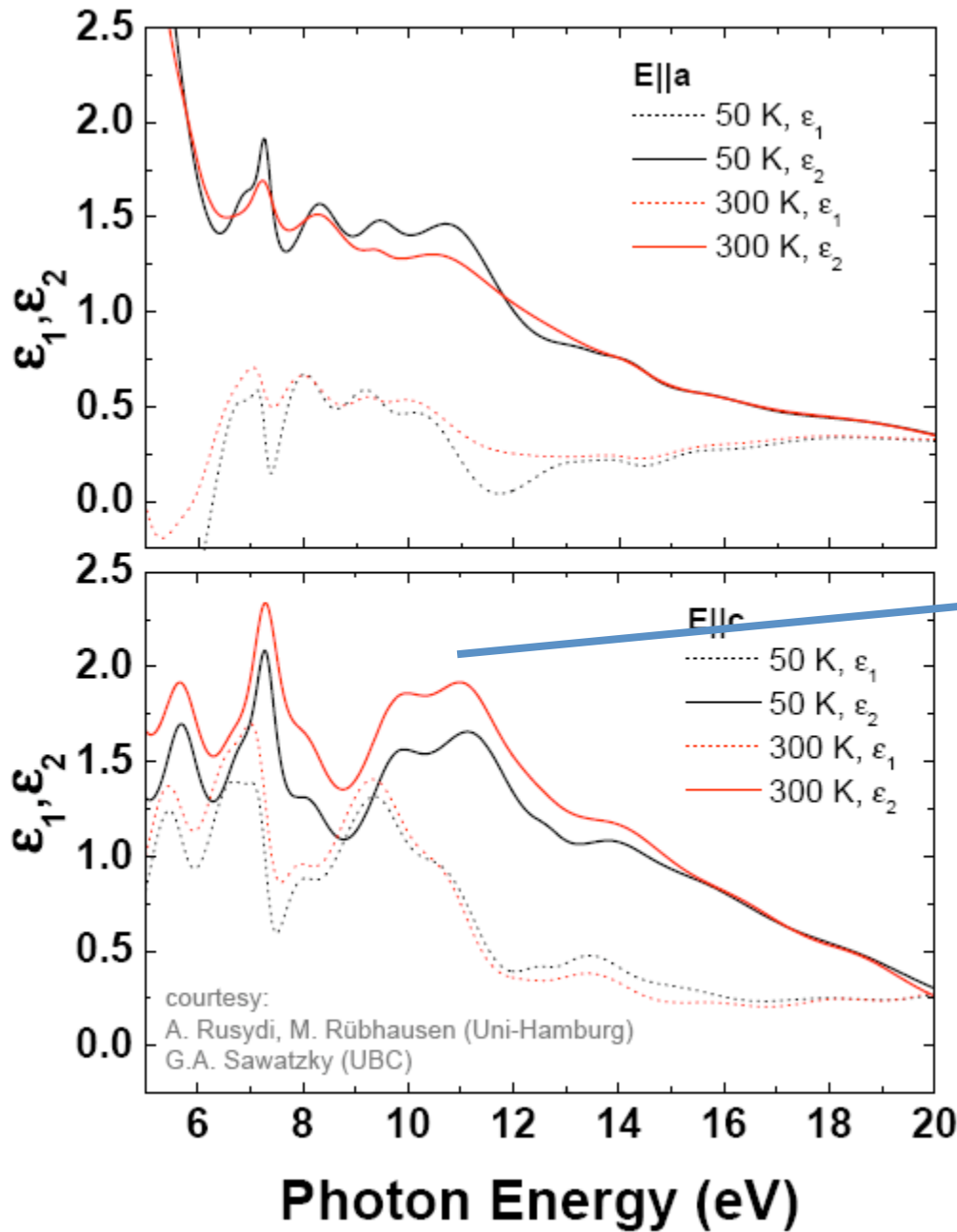
Cu²⁺ (d⁹) Impurity in CuO lattice Eskes Sa PRL 61,1475 (1988)



Other symmetry states start at about 0.8 eV below ZR

Lang rice singlet

FIG. 1. The *d*-electron-removal spectral weight calculated for $A=7.6$ eV, $\Delta=2.75$ eV, $T(b_{1g})=2.35$ eV, and $W=4.4$ eV. Also shown are the contributions from the various irreducible representations.



Sr14Cu24O41 Going through the CDW transition

Transition to a final state d(8) land
A filled ZR singlet on another site. i.e.
Only possible for doped system
Strongly magnetic order dependent.

Effective p-d hybridization for empty E_g states

- i.e. Ti 2,3,4+ , Co 3+ low spin-----
- We have 4 degenerate excited states $d(n+1)L$ and each mixes with at least 4 ligands (e.g. $d(x^2-y^2)$)
- Effective hopping integrals are square root of the degeneracy times t_{pd}
- Or $4 \times t_{pd}$. t_{pd} is 1.5-2 eV so the effective hybridization matrix element is 6-8 eV THAT'S REALLY VERY LARGE
- STRONGLY COVALENT.

Wu et al PRL 94, 146402 (2005)
O Kedge XAS Na_{0.5}CoO₂

Note the large prepeak
in O XAS

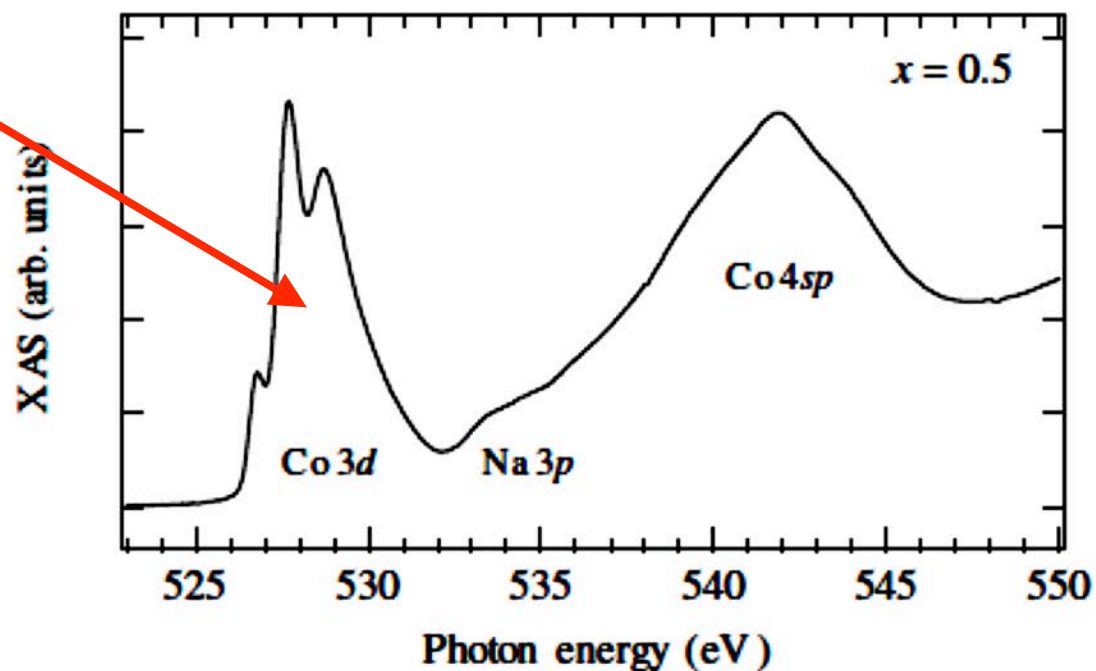


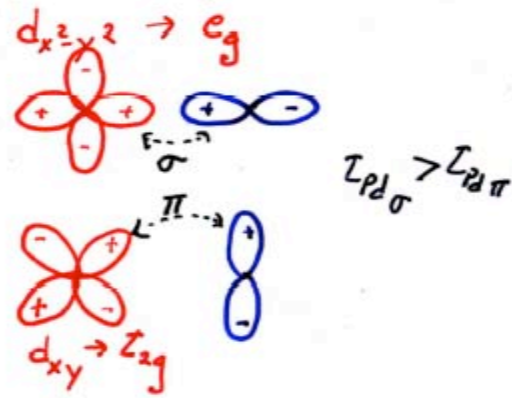
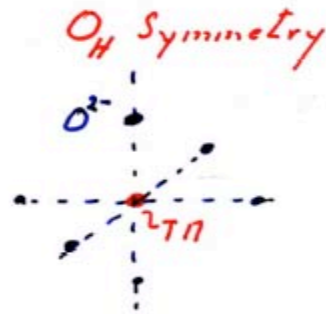
FIG. 2. O 1s XAS spectrum of Na_{0.5}CoO₂ measured in the total electron yield mode. The unoccupied bands with which O 2p states hybridize are denoted in the plot.

Co^{3+}		Co^{4+}	
Groundstate		Groundstate	
d^8	0.30	d^5	0.14
d^7L^1	0.47	d^6L^1	0.40
d^8L^2	0.20	d^7L^2	0.35
d^9L^3	0.03	d^8L^3	0.10
$d^{10}L^4$	0.00	d^9L^4	0.01
		$d^{10}L^5$	0.00

TABLE I: Overview of the hole distribution for the ground states. The numbers give the hole distribution in percent.

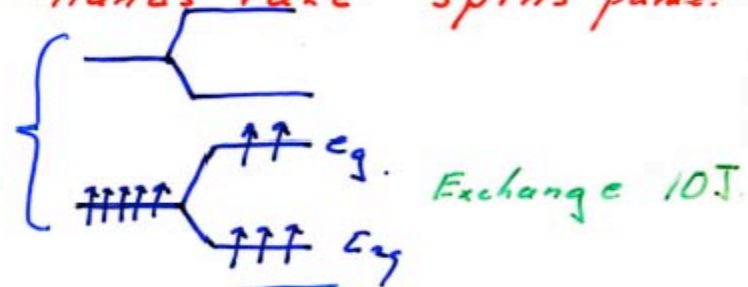
IF THE PARENT CONFIGURATION OCCUPATION IS LESS THAN 50% THERE MUST BE OTHER STATES LOWER IN ENERGY I.E. “NEGATIVE CHARGE TRANSFER ENERGY”

Crystal fields / Multiplets / Hund's Rule

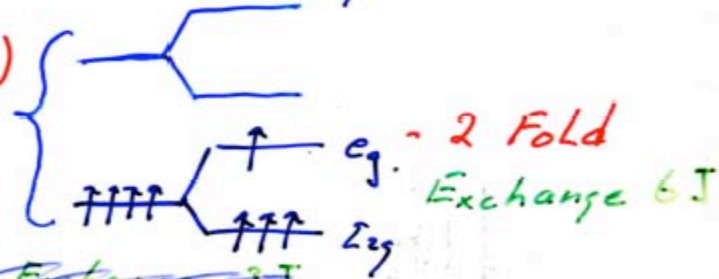


$e_g (d_{x^2-y^2}, d_{z^2-r^2})$ $t_{2g} (d_{xy}, d_{xz}, d_{yz})$
 $\Delta e_g - \Delta t_{2g} = 10Dq$ For $10Dq > \Delta_{s.o}$ $\langle L_z \rangle = 0$
 $10Dq \sim 1-2eV$ $\Delta_{s.o} \sim 30meV$
 For $\langle L_z \rangle = 0$ Hund's rule spins parallel!

$d^5 (17n^{2+}, Fe^{3+})$



$d^4 (17n^{3+}, Fe^{4+}, Cr^{2+})$

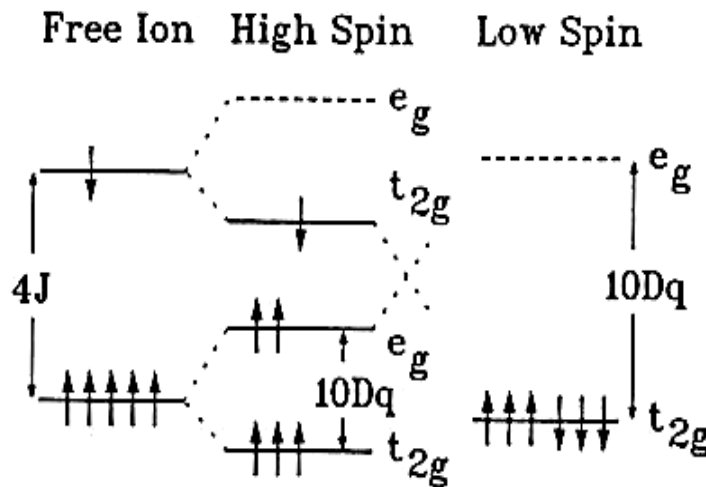


~~$d^3 (17n^{4+}, Cr^{3+})$~~

~~Exchange 3J~~

d^6

J = Hunds rule
Coupling / parallel
spin pair



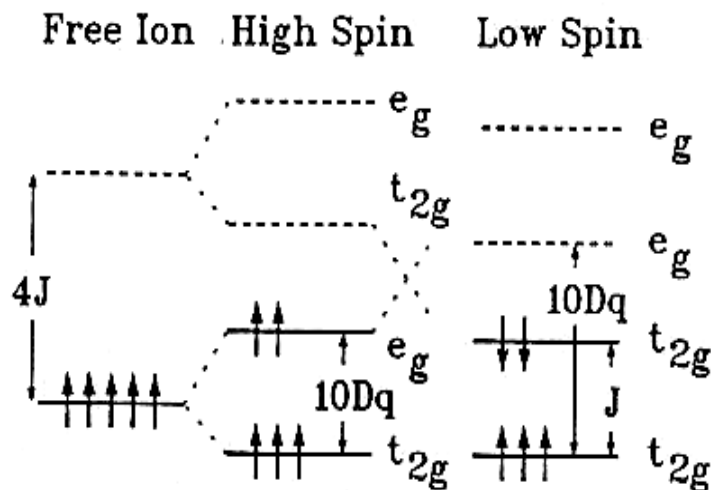
$$E(HS) = -10J - 4Dq$$

$$E(LS) = -6J - 24Dq$$

$$LS \text{ for } 10Dq > 2J$$

Removing 1 electr.
From d^6 Could change
S by $5/2!!!$

d^5



Very heavy QP??

$$E(HS) = -10J$$

$$E(LS) = -4J - 20Dq$$

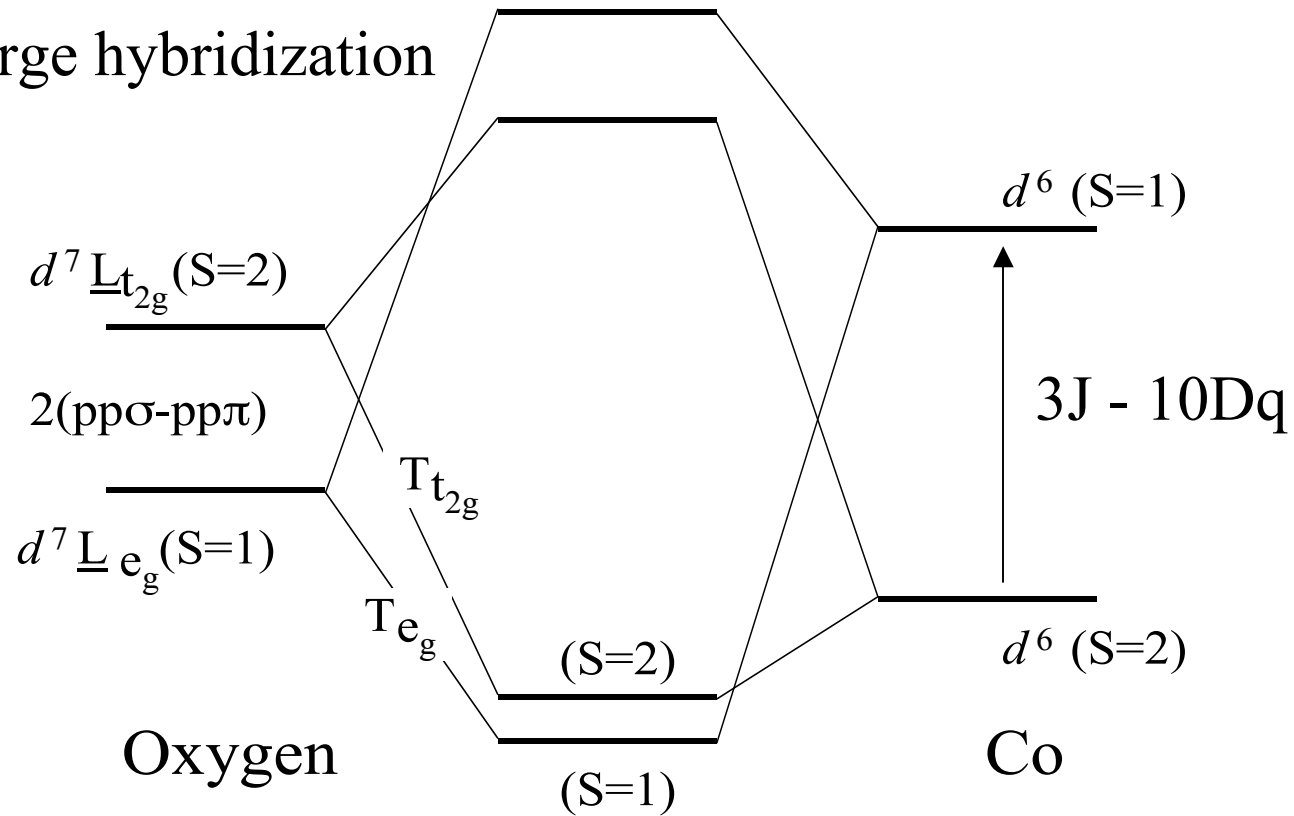
$$LS \text{ for } 10Dq > 3J$$

Is Intermediate spin possible?

- Note in a simple crystal or ligand field picture
- Possible if charge transfer is small or negative

Possible intermediate spin ground state for Co^{3+}

Small Delta large hybridization



An artist's impression of the Li doped strongly covalent ground state of " Co^{3+} " in $\text{Li}_x\text{Co}_{1-x}\text{O}$.

What about negative charge transfer energy

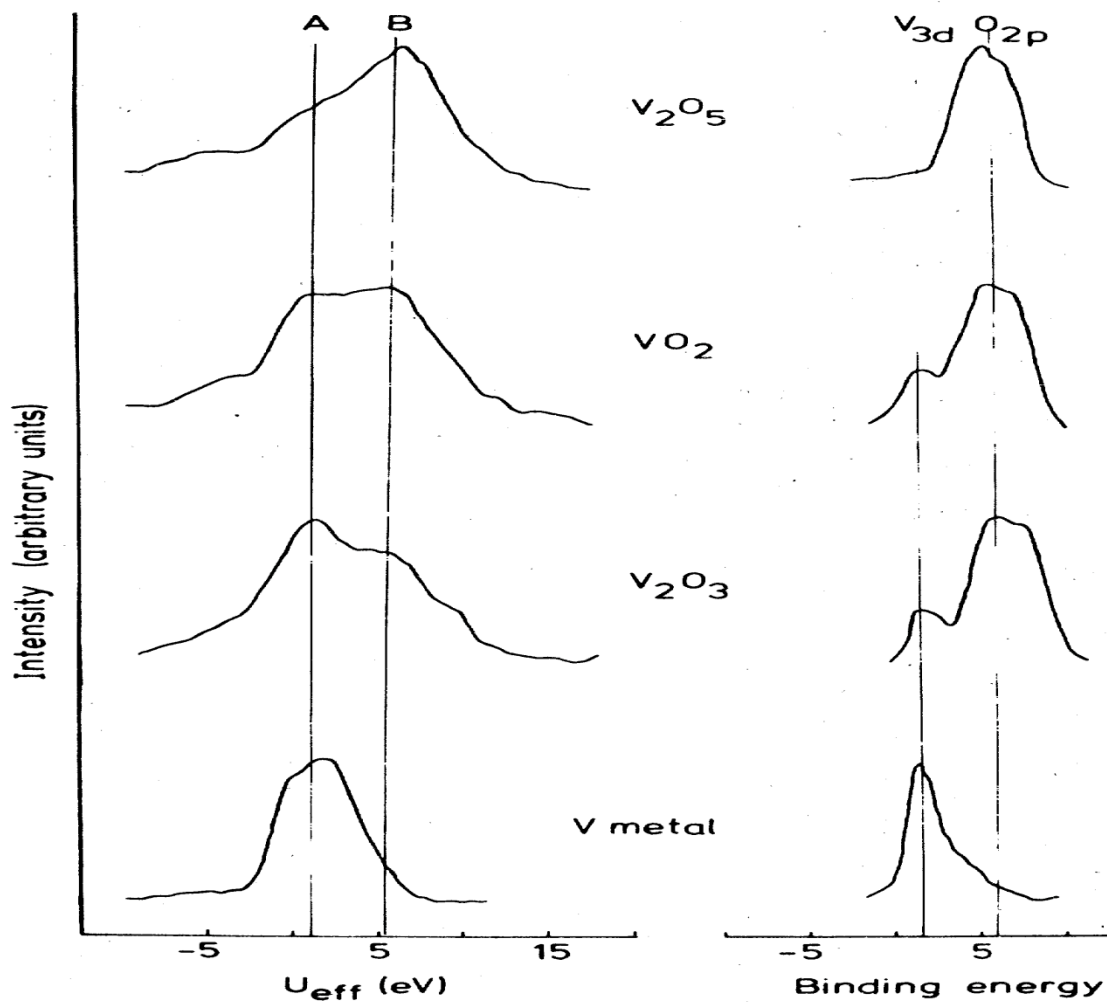
- We Know this happens in CuS (superconductor with holes in the S p band) i.e. Cu d⁹----Cu d¹⁰ L (Ligand hole)
- This also happens in CuCr₂S₄ (Cu¹⁺)
- Delta decreases as we go from O –S-Se-Te and F-Cl-Br-I Because of electron negativity
- Delta decreases as we go from Co²⁺ to 3+ to 4+

²⁴F. Jellinek, *Inorganic Sulphur Chemistry* (Elsevier, Amsterdam, 1968), p. 669; *MTP International Review of Science, Inorganic Chemistry Series I* (Butterworths, London, 1972), Vol. 5, p. 339.

L3 M23M45 (2p-3p,3d auger)

valence band

Saw. and Post PRB 20,
1546 (1979)



with oxidation state. It is interesting to note that the total *d* occupancy is nearly constant for these compounds; 2.5, 2.6, and 3.1 for V₂O₅, VO₂, and V₂O₃, respectively, and is close to the V-metal value of 3.

What do we mean by oxidation state?

- We mean that bare ion state that one should use to start with in a configuration interaction like approach to the problem.
- So for V^{5+} we start with $S=0$, and zero d electrons. Switching on the hybridization with O will not change the spin or the local symmetry even if the covalent mixing is very strong leading to effectively 3 d electrons

On ionizing Co^{3+} are the holes mostly on O??
i.e Delta negative in ZSA diagram?

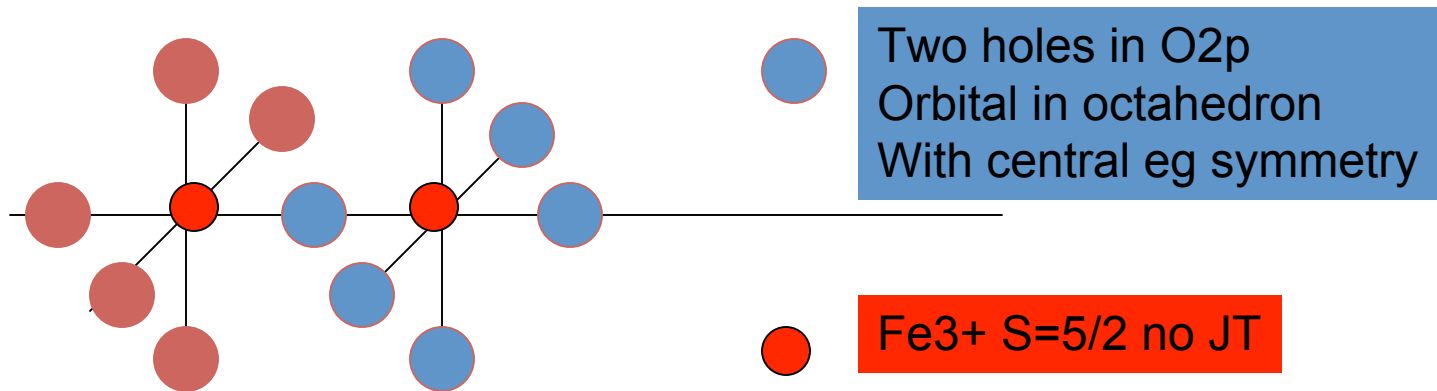
In SrCoO_3 we would have Co^{3+} and $1/3$ hole per O
Or 2 holes per octahedron!!!! These could be associated
With alternating Co^{3+} removing the orbital degeneracy
And resulting in what would look like charge disproportionation
Without actually moving the charge around. I.e It would look
Like Co^{5+} and Co^{3+}

This is what happens in SrFeO_3 !!!

It is unlikely to happen in Co oxides because here open t_{2g} orbitals
Are involved but it is something to keep in mind

Charge disproportionation without moving charge

Consider SrFeO_3 Fe^{4+} on average but label it as Fe^{3+L}
 Then each Fe is surrounded by 2 L holes in SrFeO_3 (1 hole per 3 O)
 $2\text{Fe}^{4+} \longrightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$



Each second Fe^{3+} has an octahedron of O with two holes
 Of E_g symmetry in bonding orbital's I.e. $d^5 L$

≡

No Jahn Teller problem anymore