Electronic structure of correlated electron systems

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UBC lecture 10 2011

Go through H2 on a metal singlet triplet

- Linear vs non linear polarizability
- U 2 electrons or holes versus Ei-Ea

Orbital degeneracy

- If there is orbital degeneracy the Jahn Teller theorem tells us that it will be lifted in on way or another at low temperatures. This is because the system can always lower its energy by lifting this degeneracy
- We distinguish to types those involving eg or t2g orbitals. We consider cubic and OH symmetry to start with
- Strong Jahn teller ions $d^4(t_{2g}^3 e_g^1) or - d^9(t_{2g}^6 e_g^3)$
- Weak Jahn Teller ions $d^6(t_{2g}^4 e_g^2) or - d^1, d^2, d^7$
- Strong for strong eg hybridization with ligand and weak for weak t2g hybridization with ligands

How can we lift the degeneracy

- Spin orbit coupling if we have t2g degeneracy. Recall the eg's do not split with SO.
- Jahn Teller distortion i.e. from Cubic to tetragonal would split the eg orbitals into d(3z2-r2) and d(x2-y2) (Examples are cuprates
- Orbital ordering which may be driven by other than electron phonon coupling
- Charge disproportionation i.e. $d^4 + d^4 \rightarrow d^3 + d^5$

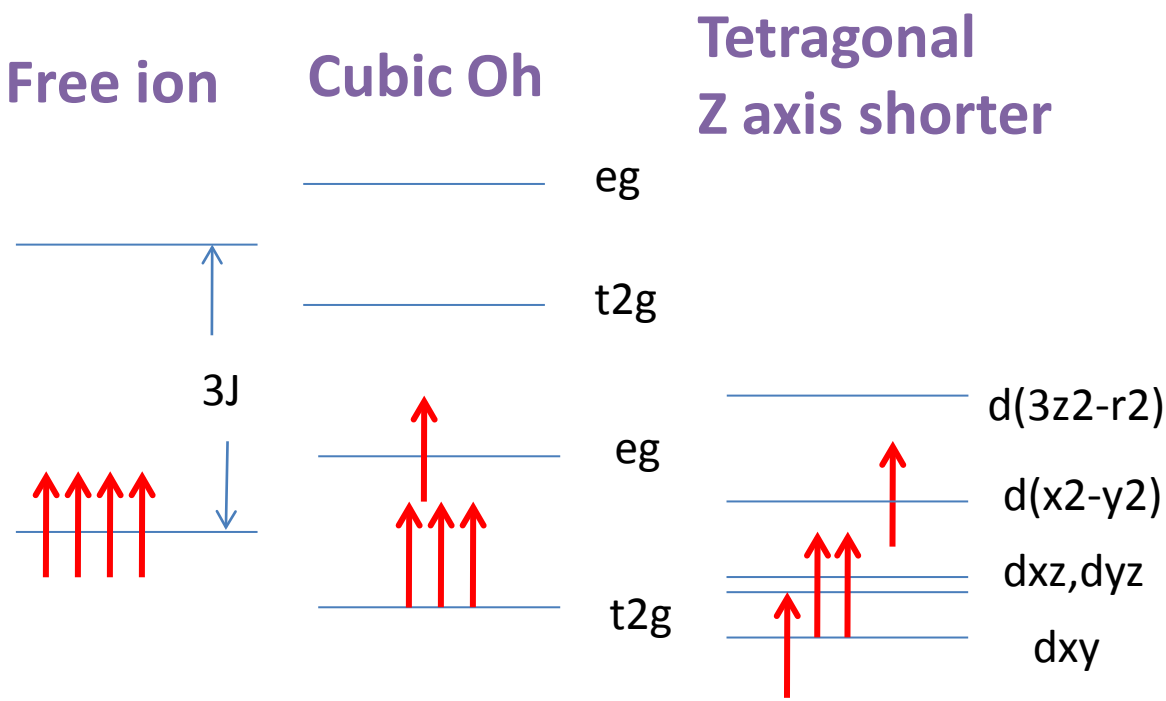
Where both final configurations are not orbitally degenerate. We will see later why this could happen inspite of a large U

Spin Orbit Coupling

- As mentioned before this can split the t2g orbitals into a doublet and a singlet
- We could treat a single electron in a t2g orbital as an l=1 state and s=1/2 which would split into a j=3/2 and ½ state which could lift the degeneracy
- As mentioned before eg states do not mix with spin orbit coupling although they do mix with the t2g's if the SO coupling is not neglegible compared to the crystal and ligand field splittings
- The basics and examples are well descibed in a simple way in Ballhausen's book on ligand field theory or in the more formal treatment in Griffiths book to mention a few of many

Lattice distortions i.e. the Jahn Teller effect

- Operates via electron phonon coupling with asymmetric phonon modes which locally distort the lattice.



- For z axis long the doublet would be lowest This lifts the orbital degeneracy for this case

Orbital ordering

- Consider again the case of Mn3+ with the doubly orbital degenerate eg level in cubic symmetry occupied by only one electron as above.
- It would be logical in a perovskite structure that long bond axis would alternate say along x and y for two Mn ions sandwiching an O anion as in the next slide

For LaMnO3 resonant x ray diffractions yields the orbital occupation structure below with Alternating occupied eg orbitals rotated by 90 degrees as see in the basal plain. The small red arrows indicate the Oxygen displacement resulting from this leading to a so called cooperative Jahn Teller distortion

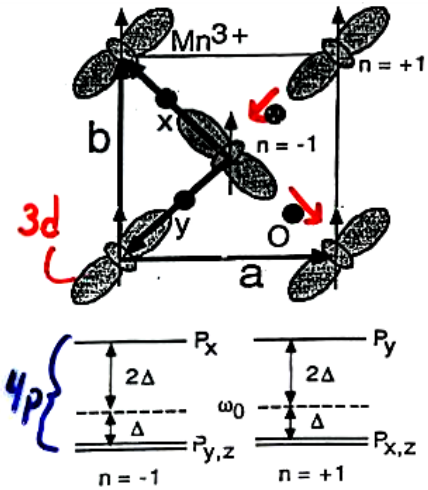


Fig 1

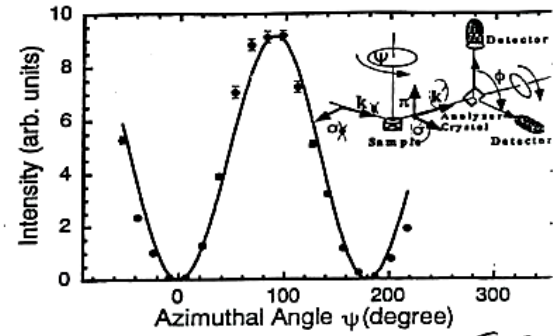


Fig3

For all 17n identical (3,0,0) reflection for bidden

The 300 reflection
Is generally forbidden
but visible at resonance
Because of the orbital
ordering

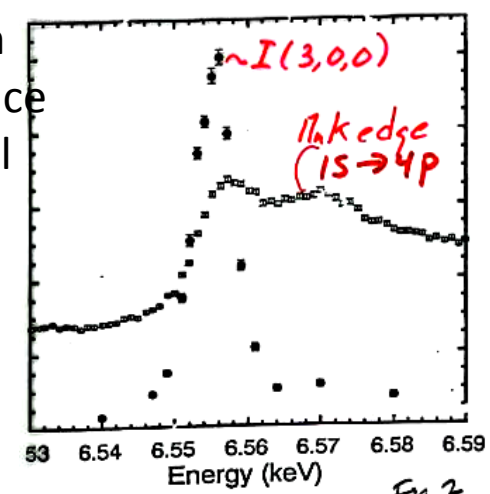


Fig 2

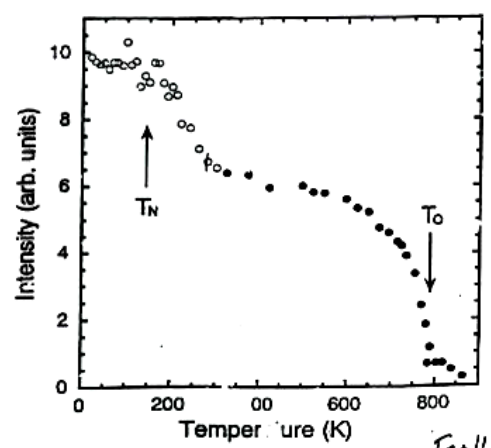


Fig4

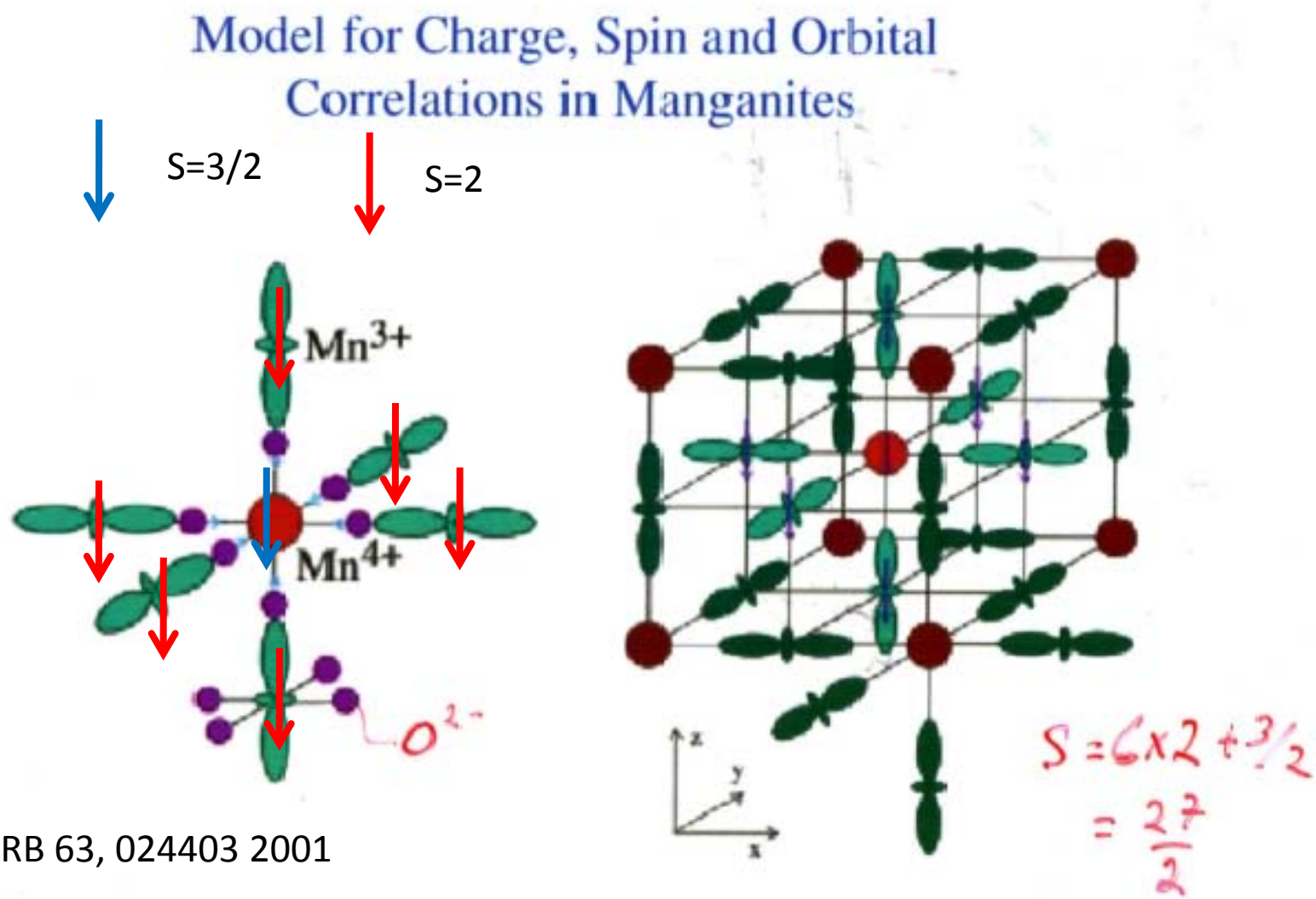
See two transitions.
One at high Temp for
the orbital ordering
and one at low T for
antiferromagnetic
order. The spin
ordering in plain is
ferromagentic as we
would have
predicted

Hamiltonian for orbital and spin order (Kugel Khomskii 1982)

$$H = \sum_{i,j} J_{i,j}^{S} S_i \bullet S_j + \sum_{i,j} J_{i,j}^{O} O_i \bullet O_j + \sum_{i,j} J_{i,j}^{S,O} (O_i \bullet O_j)(S_i \bullet S_j)$$

The first term describes spin structure and magnon excitations
Second term the Orbital order and Orbiton or d-d exciton excitation
Third term is the strong interaction between Orbitons and spin waves
this interaction can lead to new bound or spin polaronic like states.
In addition we really should have included the electron phonon interactio
which would result in lattice distortions depending on the orbital order
and in lattice polaronic like effects coupling with orbitons and magnons.
Since all these interactions are of the same order of magnitude the
situation is very complicated but also very rich in new physical
properties and phenomena

If we now also “dope” the system as in La.75Ca.25MnO3 resulting in some Mn4+



Mizokawa et al PRB 63, 024403 2001

It is the interaction between the charge , Spin , Orbital and Lattice degrees of Freedom that yield this rich phase diagram

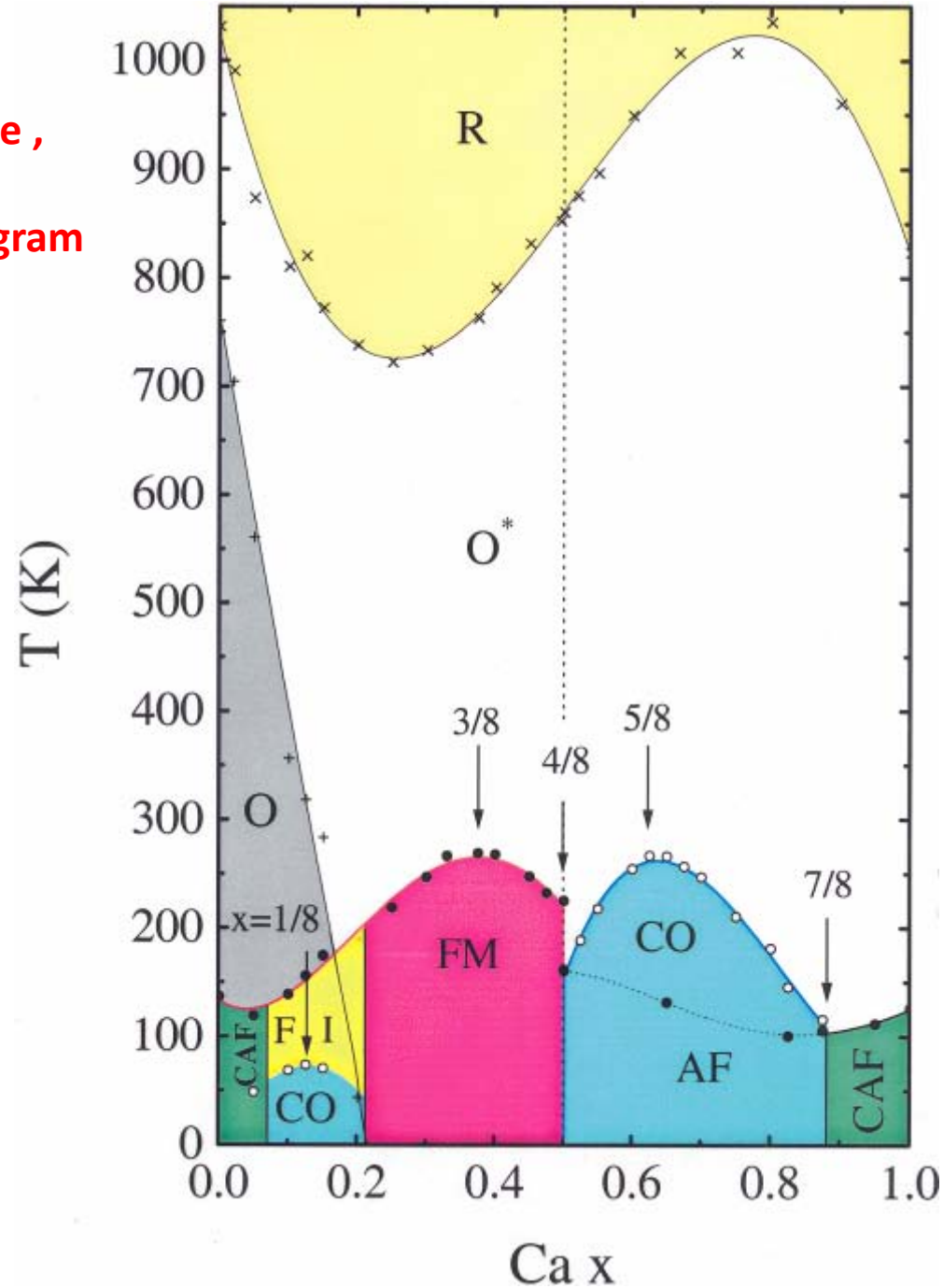
Phase Diagram of $La_{1-x}Ca_xMnO_3$

Uehara, Kim and Cheong

R: Rombohedral

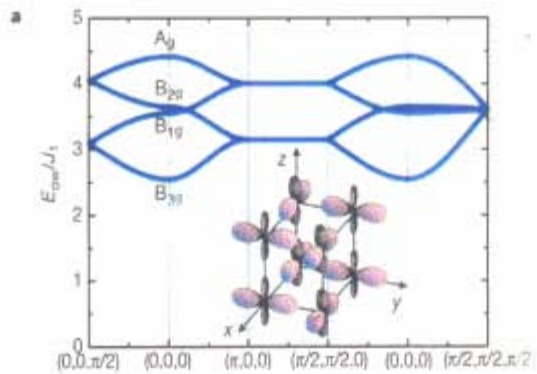
O: Orthorhombic
(Jahn-Teller distorted)

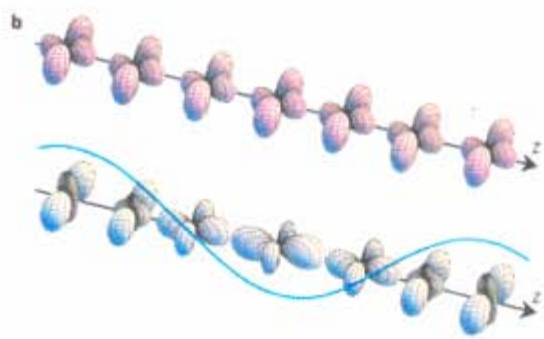
O*: Orthorhombic
(Octahedron rotated)



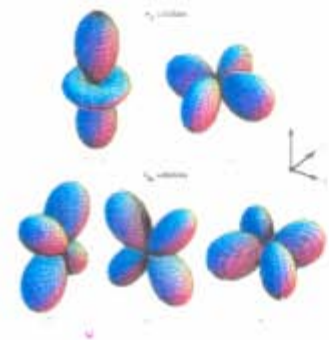
Orbital Degrees of Freedom

Ferromagnetic and AFM Mott Insulators





Maekawa et.al. (2001)



3d-Orbitals

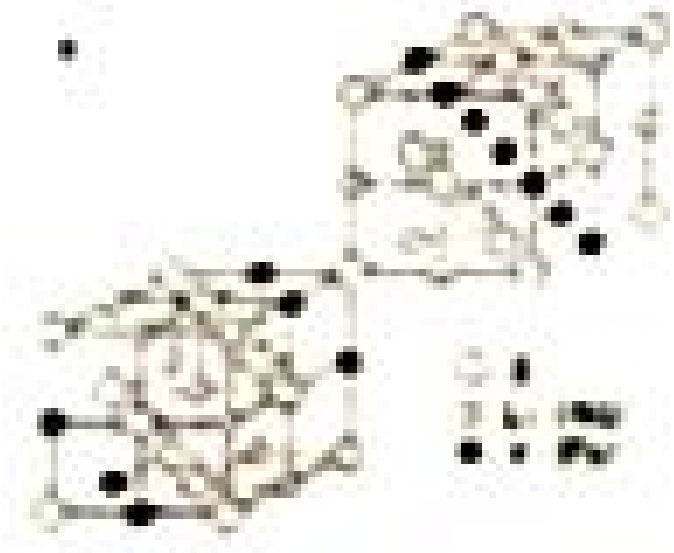
Orbital Excitations fundamentally orgininate from *dd* excitations

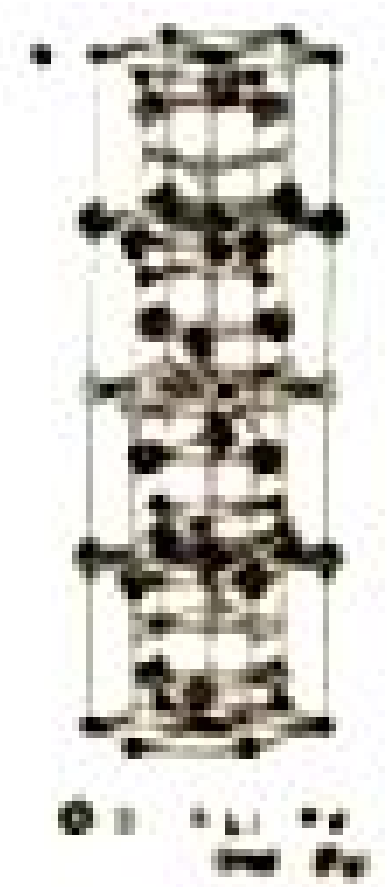
Orbital Order

Orbital Excitations/"Orbitons"

M.Z.Hasan (2002)

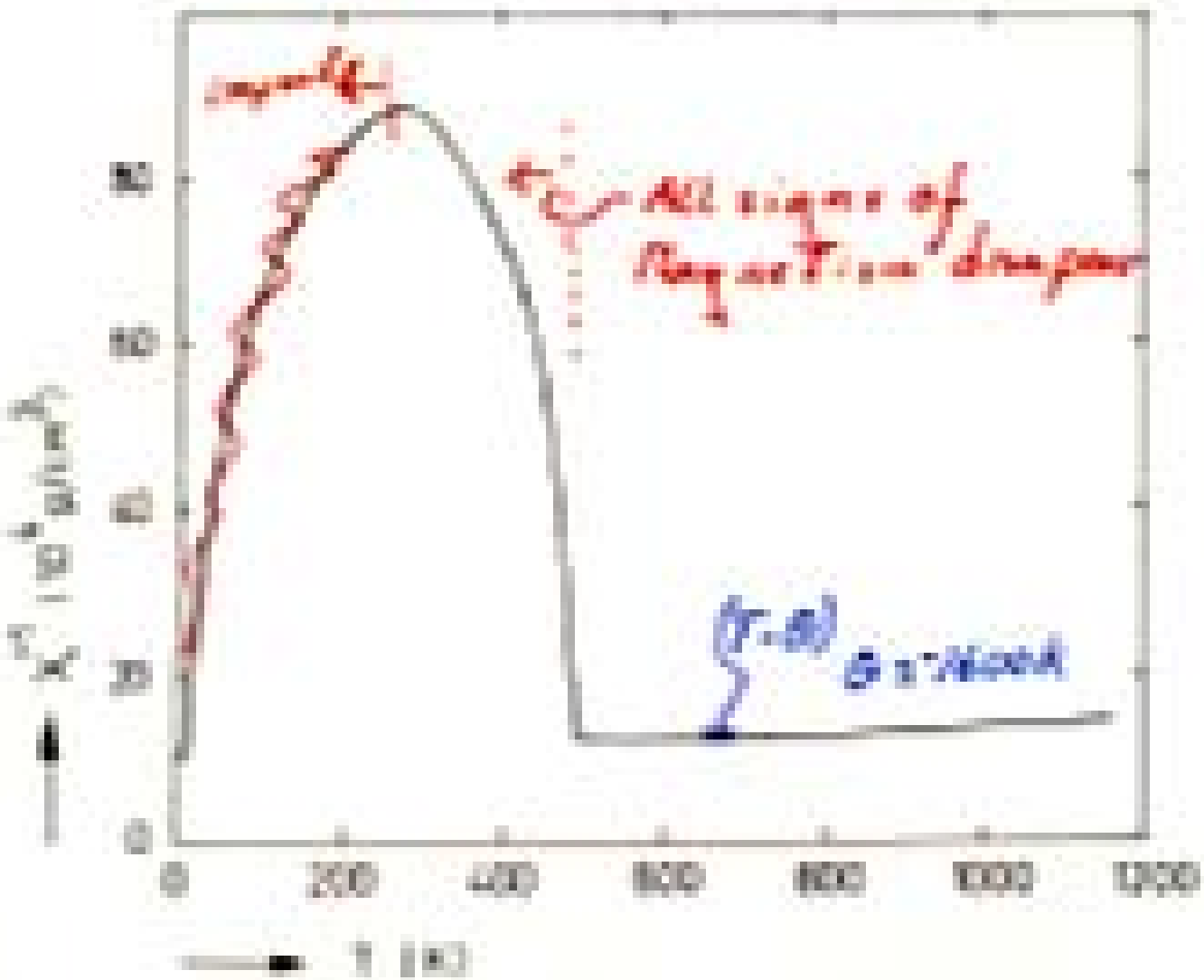
LiVO2 V(d2—S=1), Two electrons in a t2g Orbital Rock salt structure Alternateing V Li O layers in the 111 direction
Each form a triangular
2 dimensional lattice



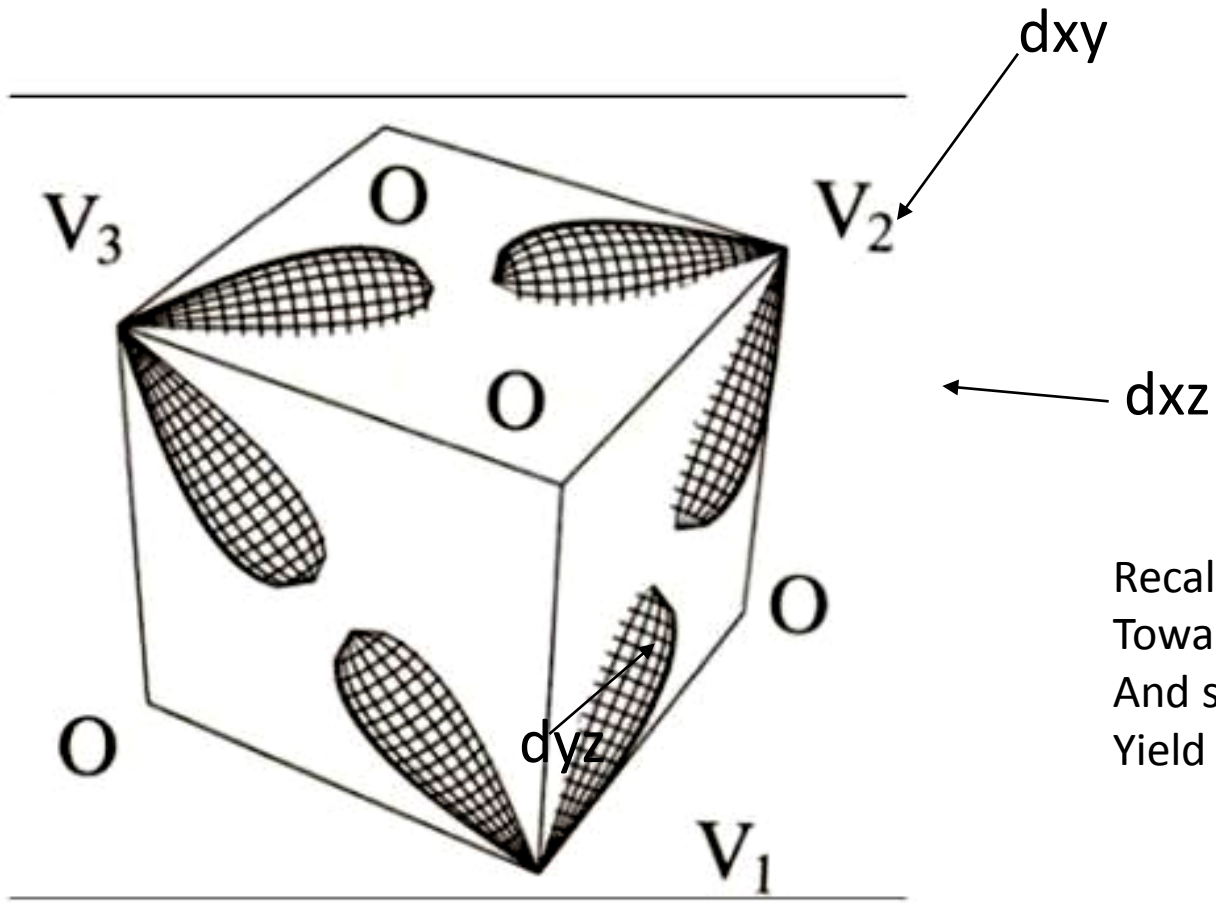


Pen et al PRL 78,1323

LiVO2 V3+ d2 system S=1 in cubic symmetry 3 fold orbital degeneracy
Magnetic susceptibility is Curie Weiss like T>500K and then signs of magnetism disappear



This orbital ordering yields a large internal to the triangle
Antiferromagnetic exchange and a weak
External to the triangle ferromagnetic exchange .

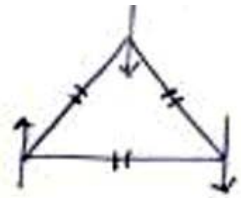


Recal lobes pointing
Towards each other
And single occupied
Yield antiferro coupling

Pen et al PRL 78,1323

Orbital ordering removes frustration
of interactions between these triangles

3 spins in a triangle with an exchange interactions was a home work problem
The ground state for spins of 1 is S=0 i.e. singlet and these result in zero susceptibiltiy
With vanishing temperature . Above the orbital ordering transition the magnetic susceptibility shows a strong antiferromagnetic coupling according to the Weiss constant



$$\mathcal{H} = +\frac{J}{2}\sum_{ij} S_i \cdot S_j \qquad (\text{ALL bonds eq})$$

$$S^2 = (\vec{S}_1 + \vec{S}_2 + \vec{S}_3)^2 = 3S^2 + \sum_{ij} S_i \cdot S_j$$

$$\sum_{ij} S_i \cdot S_j = S^2 - 3S^2$$

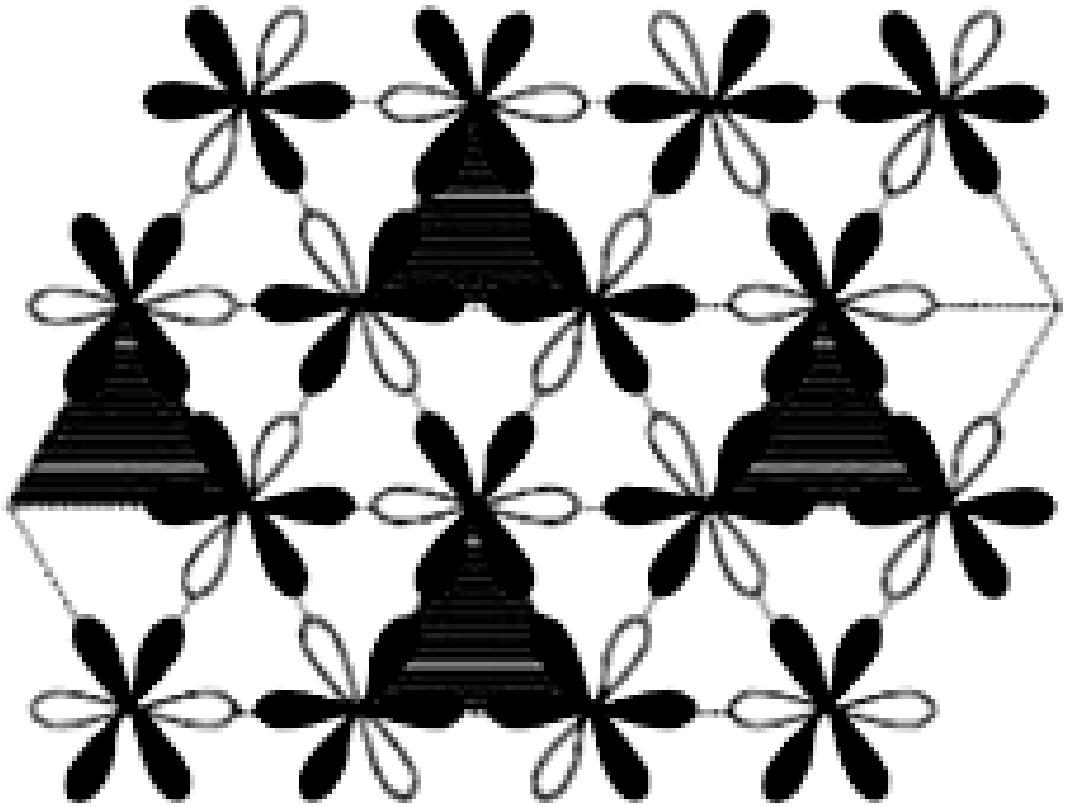
$$= S(S+1) - 3(S)(S+1)$$

$$S = 0, 1, 2, 3$$

$$\sum_{ij} S_i \cdot S_j = \begin{array}{ll} -6 & (S=0) \\ -4 & (S=1) \\ 0 & (S=2) \end{array}$$

H.F.Pen et al PRL 78, 1323 (1997)
Orbital ordering in a 2d triangular lattice

Result of orbital ordering is a lattice of spin zero triangles
The coupling between triangles is weakly ferromagnetic



YVO3 Pervoskite structure
V(3+) 2 electrons in T2g
Orbitals S=1.
Note the tilted and
Rotated octahedra. Results in a
Staggered magnetic anisotropy
And this breaks the inversion
Symmetry at O sites and allows
For DM coupling and canted
antiferromagnets

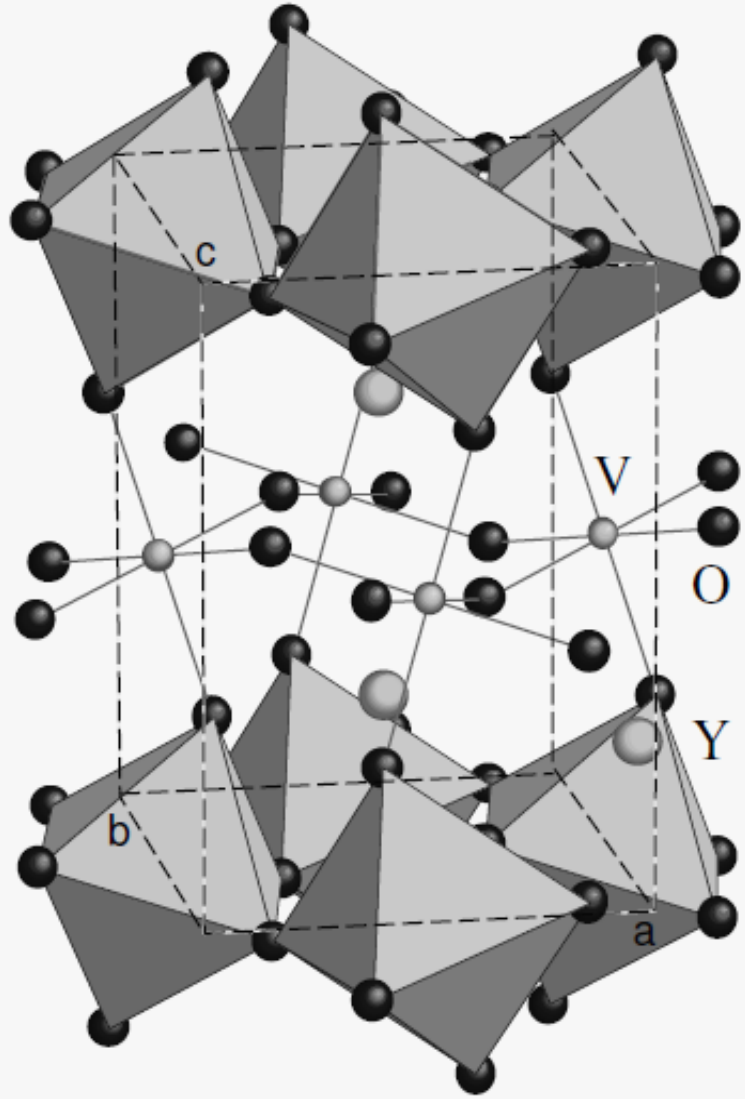
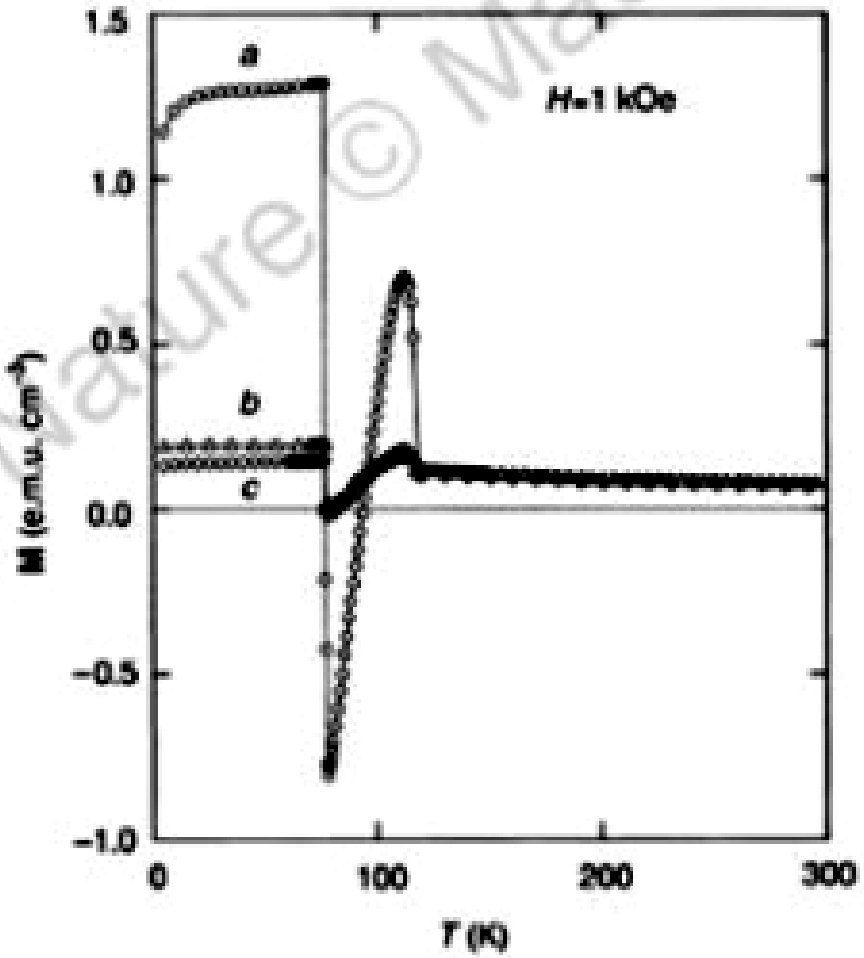


FIG. 1: *Pbnm* orthorhombic crystal structure of YVO_3.

Tsvetkov et al
PRB 69, 075110 (2004)

Temperature induced magnetization reversal
Ren et al Nature 396, 441 (1998)

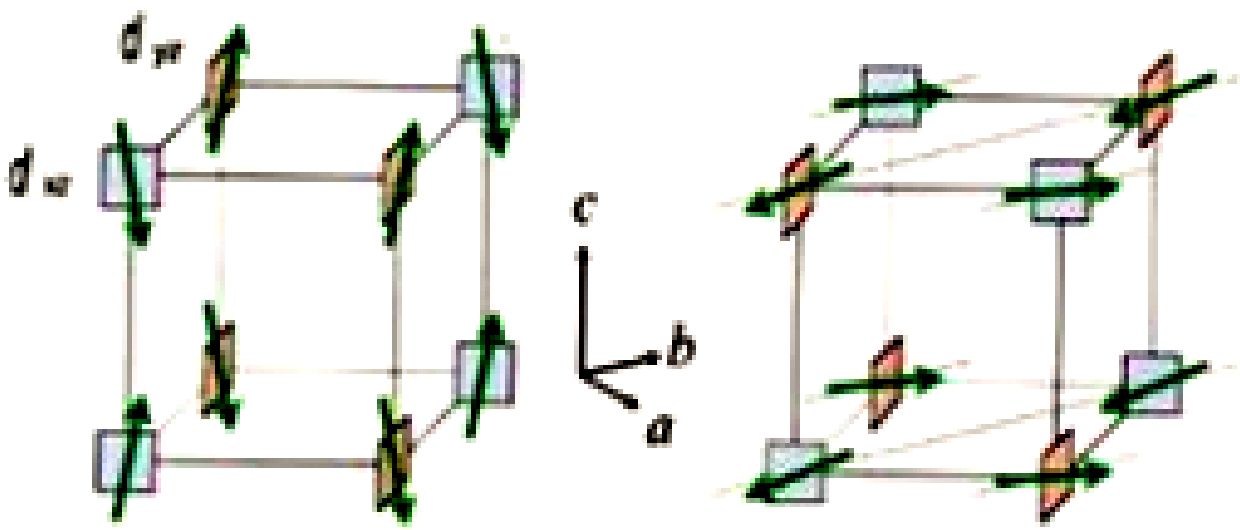


YVO3 Perovskite
V(d2 S=1) O not
In inversion symmetry
DM canting competing
With staggered magnetic
Anisotropy . See Aharoni's
lectures

All V have one electron in a dxy orbital which is not shown and causes
An antiferromagnetic coupling in the between V in the basal plane

O between the V ions are not in inversion center
Tilted Octahedra D.SxS interactions compete
With local staggered anisotropy

Spin & orbital orderings



T < 77 K

C-type orbital-ordering
G-type spin-ordering

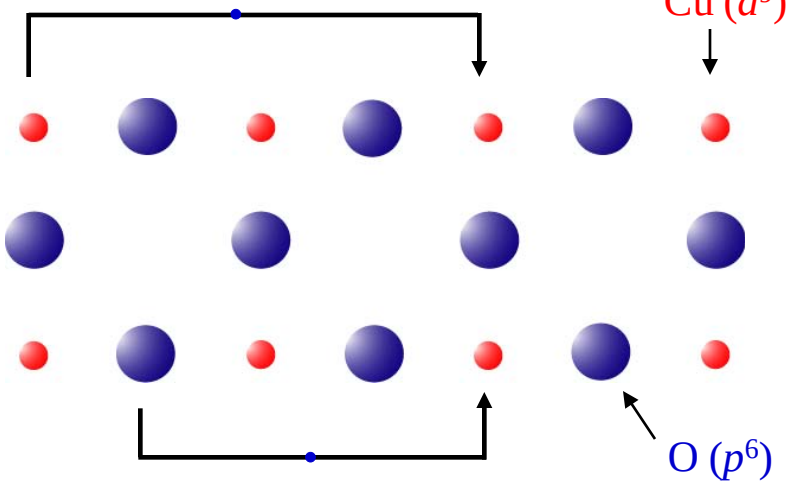
T > 77 K

G-type orbital-ordering
C-type spin-ordering

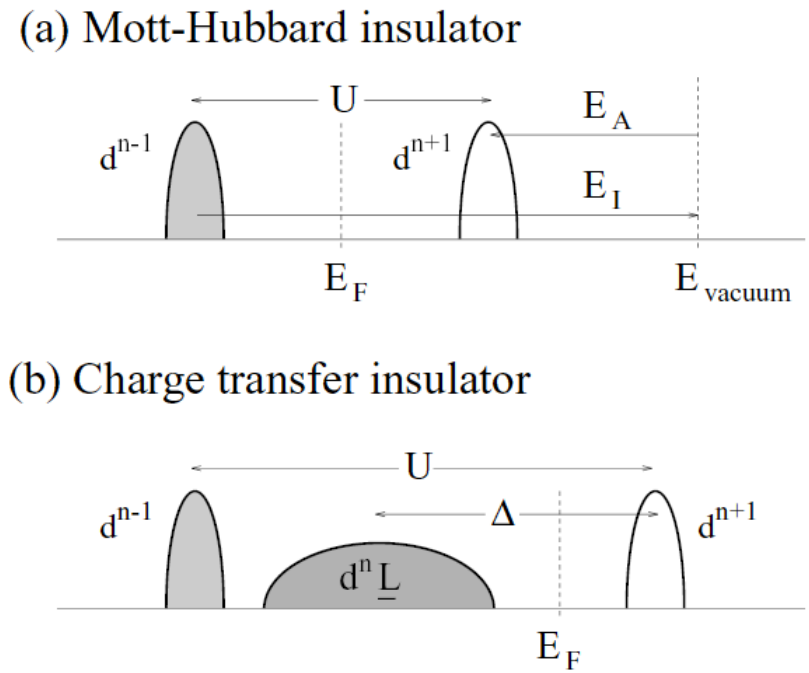
Systemtics in the electronic structure of TM compounds across the 3d series for the chalcogenides and Halides Mott Hubbard vs charge transfer gap behaviour

Correlated Electrons in a Solid

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



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



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

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

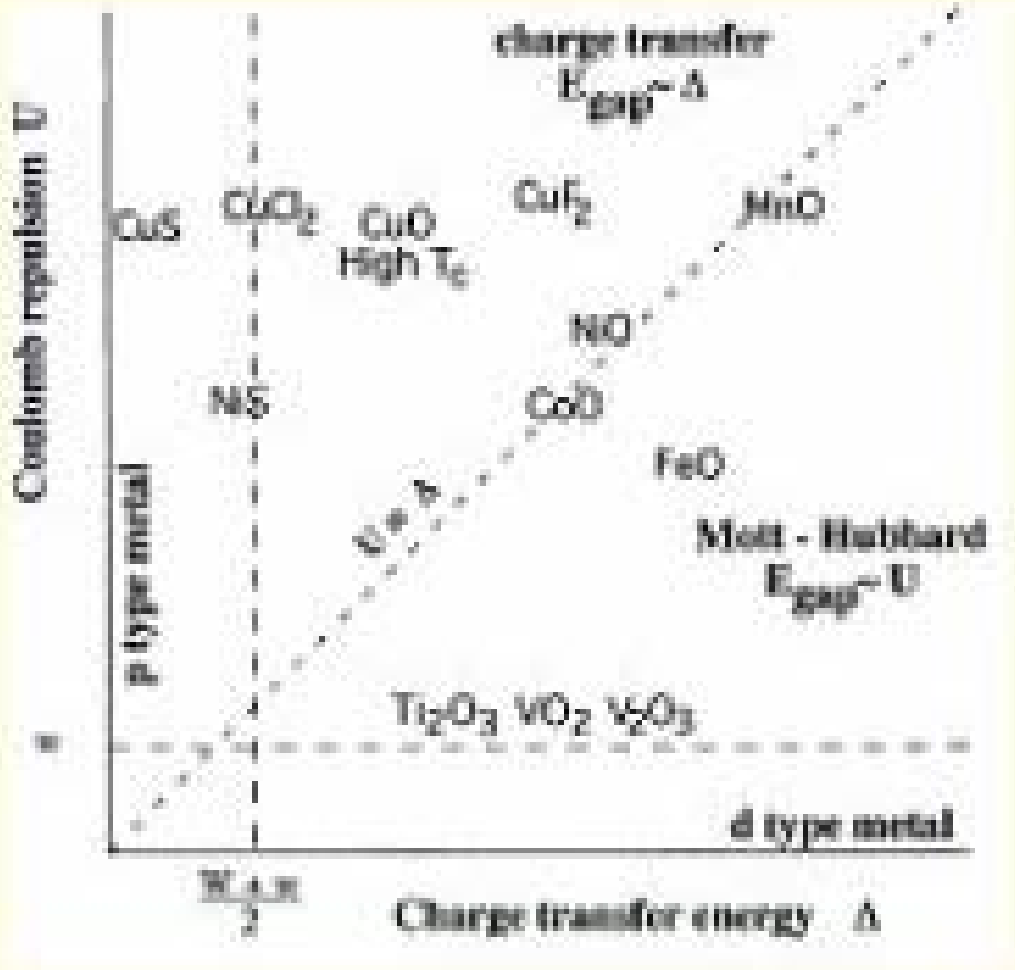
If $\Delta < (W+w)/2$ → Self doped metal

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)**

Zaanen et al.



For divalent cations

Phys. Rev. Lett. 55, 418 (1985)

3 most frequently used methods

- Anderson like impurity in a semiconducting host consisting of full O 2p bands and empty TM 4s bands including all multiplets

Developed for oxides in early 1980's, Zaanen, Kotani, Gunnarson,-----

- Cluster exact diagonalization methods. O cluster of the correct symmetry with TM in the center. Again include all multiplets crystal fields etc

Developed for oxides in early 1980's Fujimori, Thole, Eskes, ------

General soft ware by de Groot , Tanaka

- Dynamic Mean Field methods, CDMFT, DCA which to date do not include multiplets

Developed in the late 1990's: Kotliar, George, Vollhart---

To calculate the gap we calculate the ground state of the system with n,n-1, and n+1 electrons
Then the gap is

$$E(Gap)= E(n-1)+E(n+1)-2E(n)$$

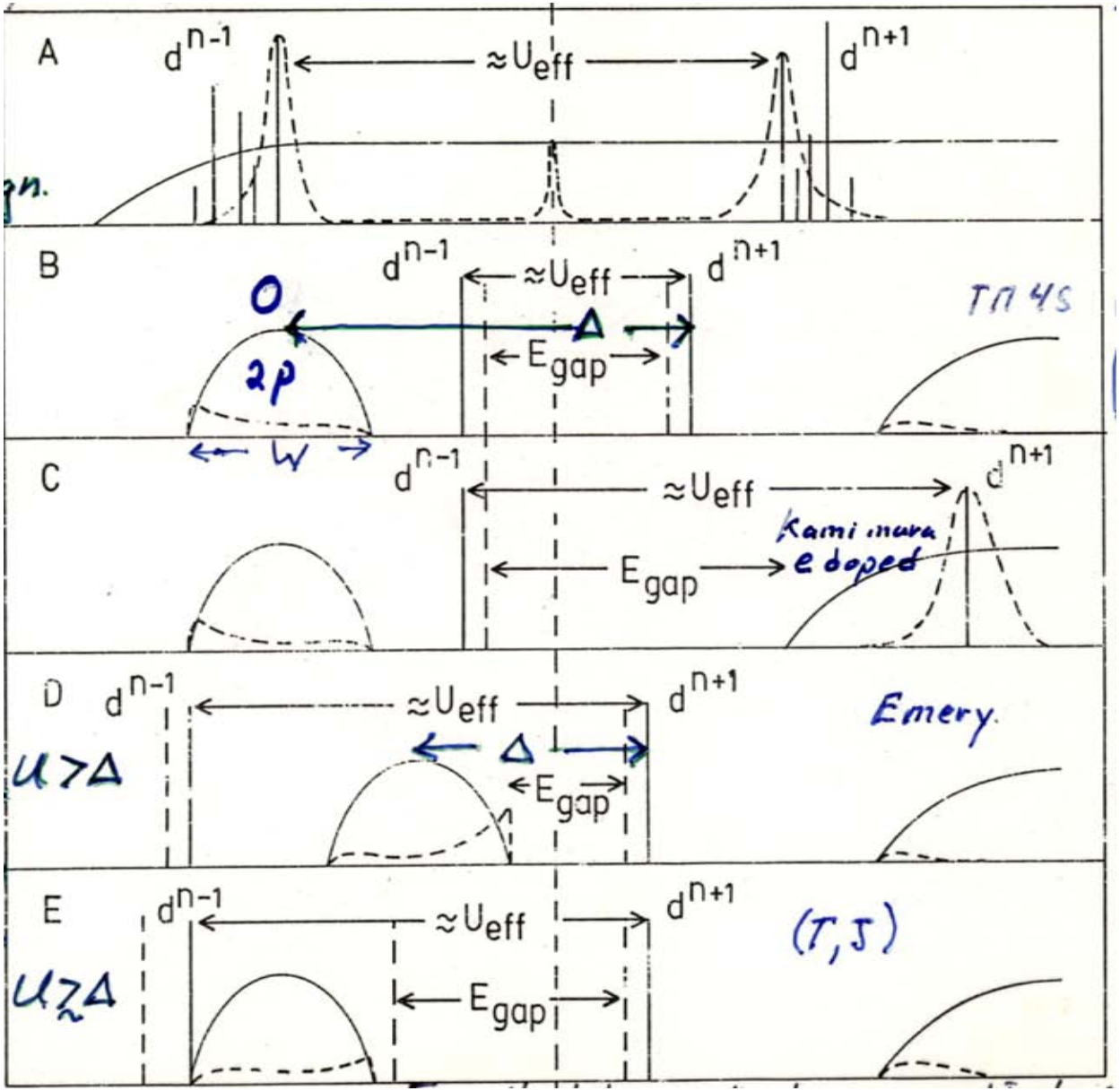
An artists concept of an impurity like calculation for various hosts i.e. metallic, Mott Hubbard, d-s gap, and charge transfer gap,

TM magnetic impurity in or on a sp band metal. Note the n-1 and n+1 "Virtual " bound states and Kondo or Abrikosov –Shul resonance at Ef

Mott Hubbard insulator for an oxide

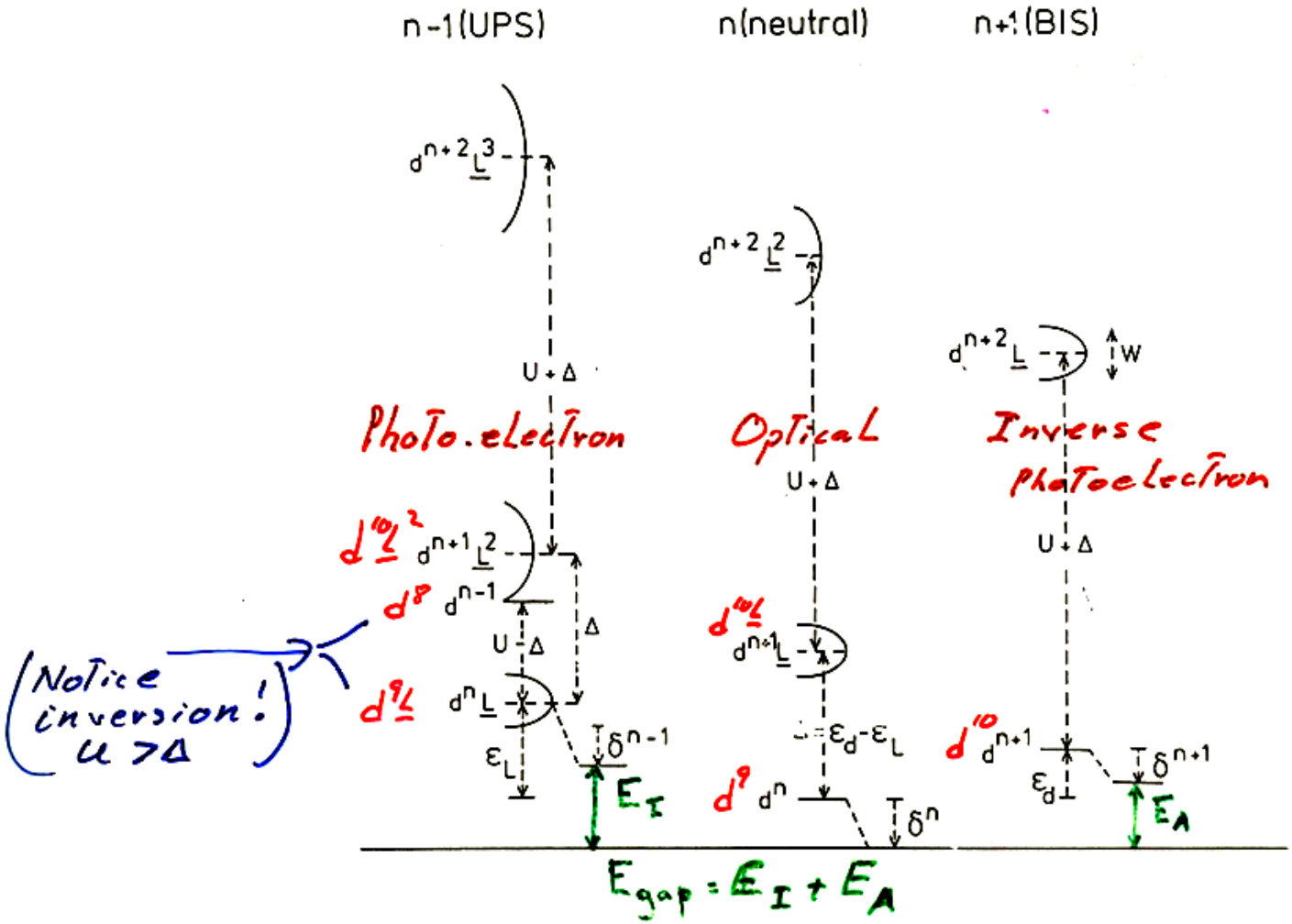
The dashed lines are the d Partial density of states after Hybridization with O 2p

Charge transfer gap insulator for an oxide



Zaanen et al Jmag and Mag Mat. 54, 607 1986

Schematic for the calculation of the conductivity gap in the impurity Model. The broad bands represent the O 2p bands



See ZSA PRL 55,418 (1985)

$$E_{gap} = \Delta + 2\delta^n - \delta^{n-1} - \delta^{n+1}$$

Δ = charge transfer energy

$= E(d^n) \rightarrow E(d^{n+1}\underline{L})$

$\underline{L}$ denotes a hole in anion(np)

$\Delta = \varepsilon_d - \varepsilon_L$ [with ε_d the electron addition energy $d^n \rightarrow d^{n+1}$]

Using impurity theory

Gunnarson - Schönhammer PRL 50, 604
PRB 28, 4315 (83); 31, 4815 (85)

we can get δ^n

$$\delta^n = 2\int_{-W/2}^{W/2} \frac{T^2 \rho(\varepsilon)\, d\varepsilon}{\delta^n - \Delta - \varepsilon - 2\Gamma(\delta^n - 2\Delta - U - \varepsilon)} \qquad T = T_{pd\sigma}$$

$$\Gamma(z) = \int_{-W/2}^{W/2} \frac{T^2 \rho(\varepsilon)\, d\varepsilon}{z - \varepsilon}$$

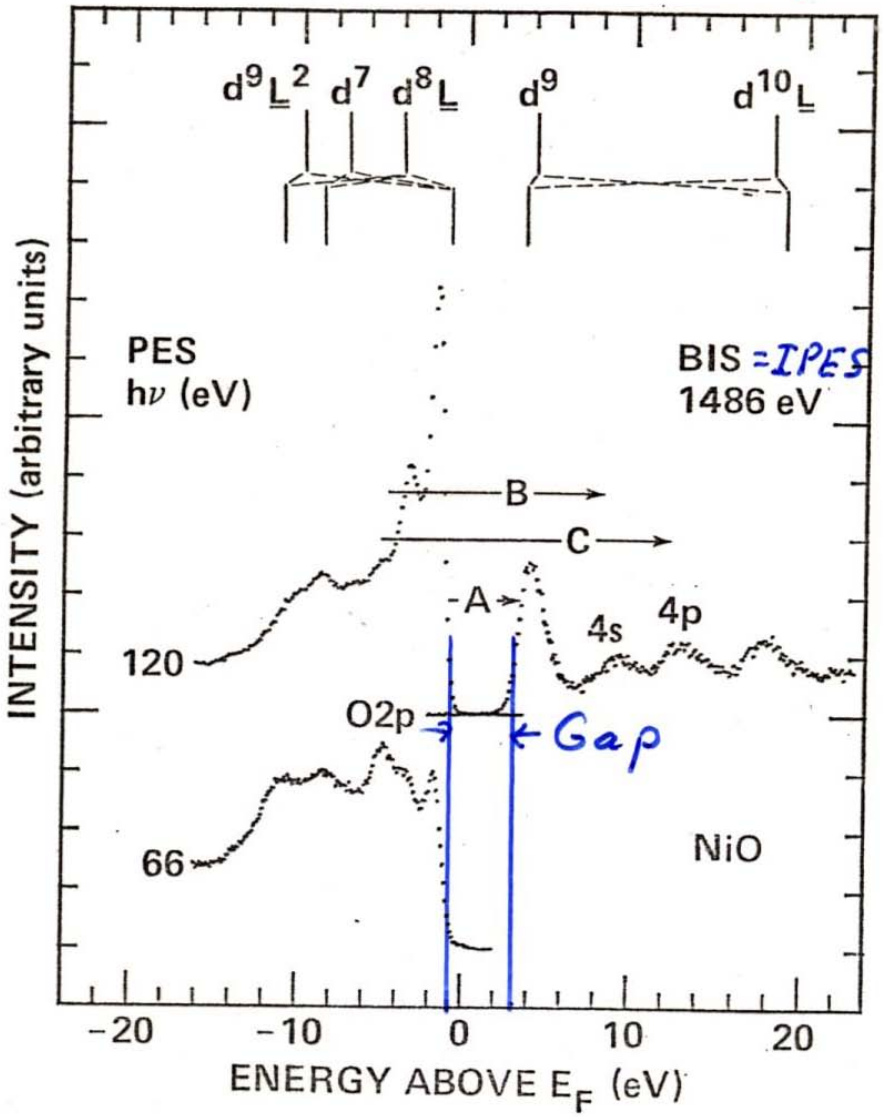
[Take a hemispheric band for (np)

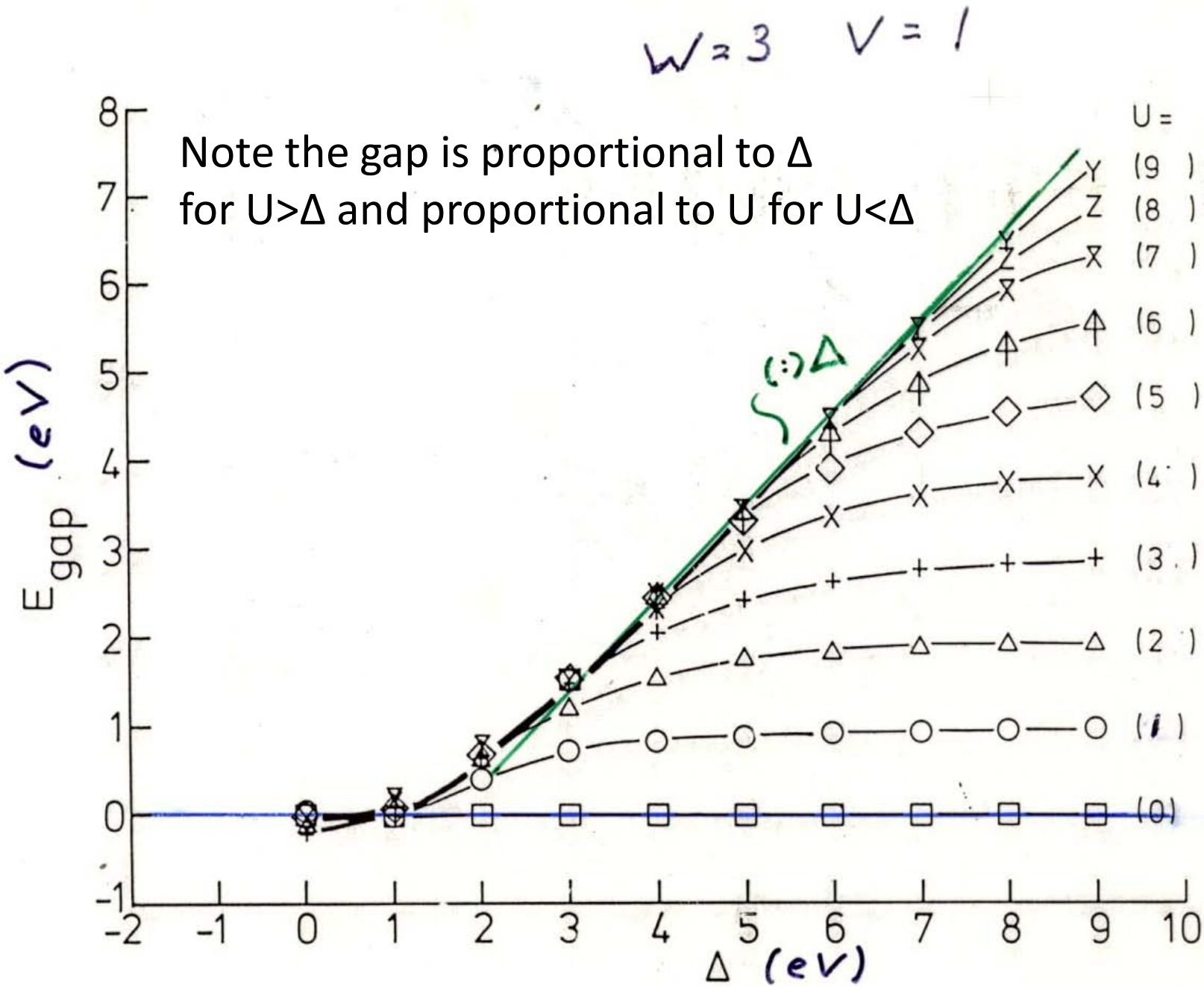
See ZSA PRL 55,418 (1985)

Get U & Δ by fitting PES/IPES

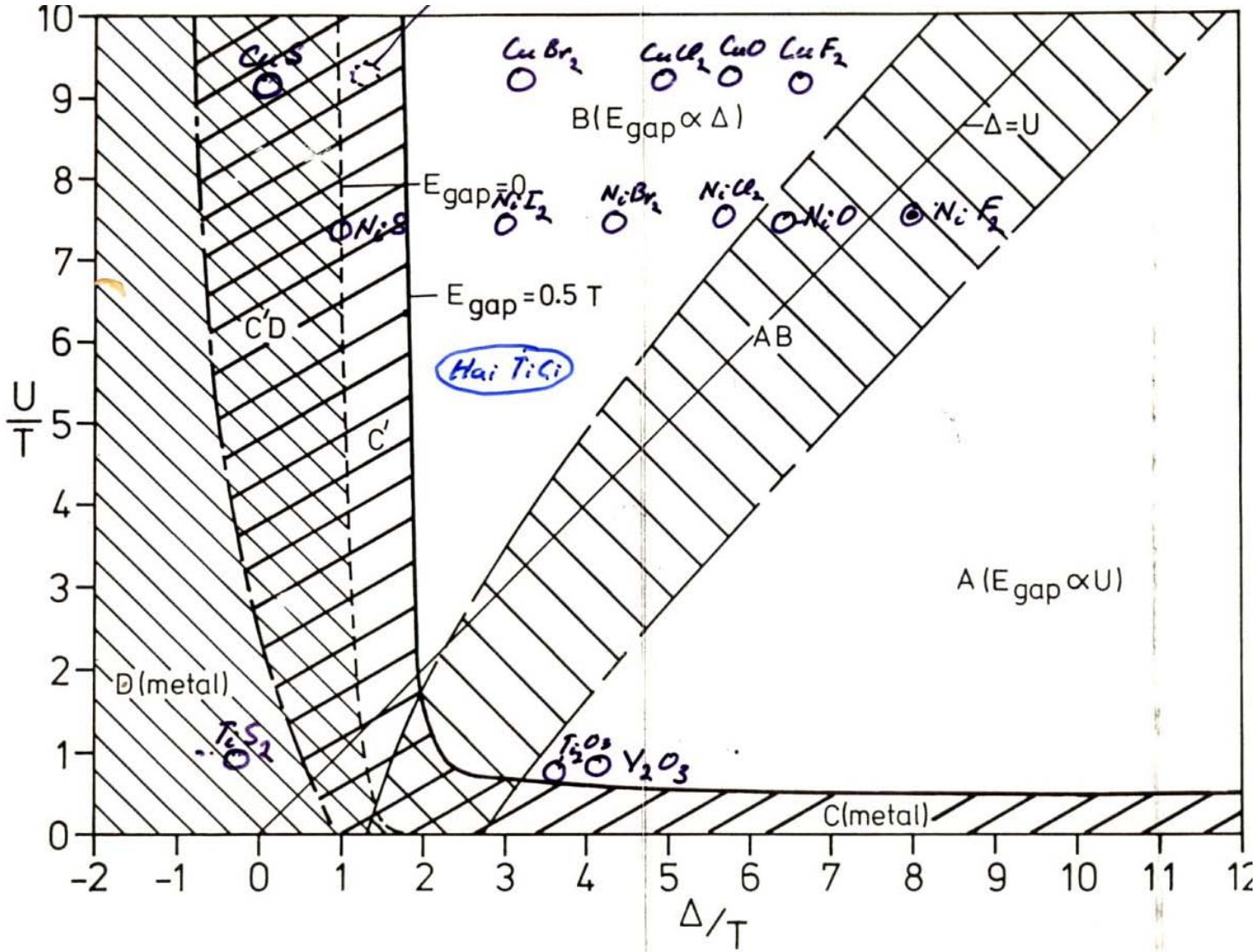
$\lesssim 1$ eV

NiO (Ni^{2+} $3d^8$, O^{2-} $2p^6$)

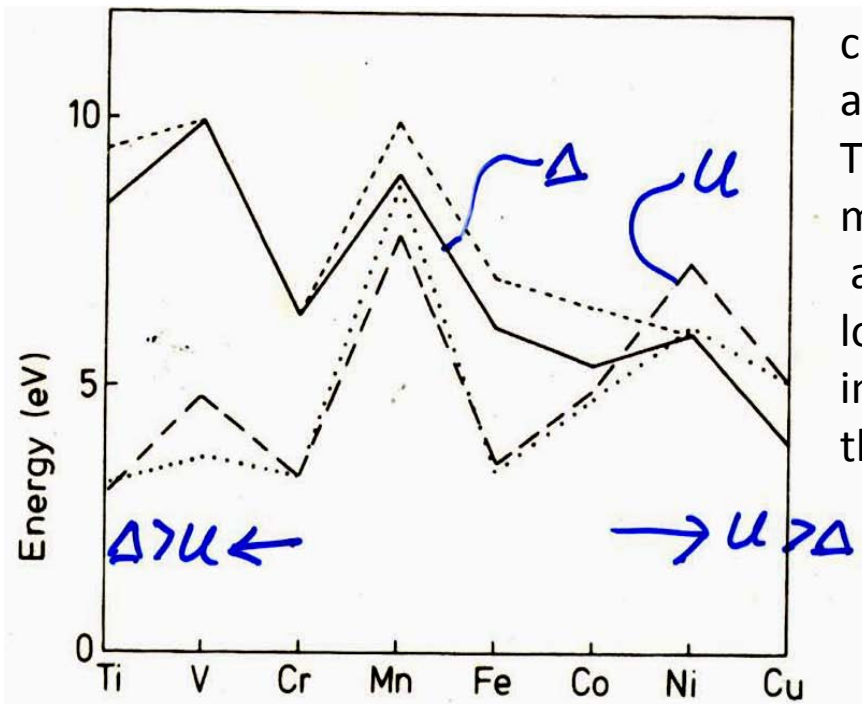



W = 3 V = 1
Note the gap is proportional to Δ
for U>Δ and proportional to U for U<Δ
U =
(9)
(8)
(7)
(6)
(5)
(4)
(3)
(2)
(1)
(0)
(:) Δ
E gap (eV)
Δ (eV)

Classification scheme according to ZSA



Δ ,Ueffective for the the divalent TM oxides in the rock salt structure like NO,CoO--. The large fluctuations are because of The multiplet structure and Hunds' rule ground states



4. The charge-transfer energy (Δ_{Cr}, solid line) and U_{eff} (U_{Cr}, dashed line) including the electrostatic crystal field contributions compared to the quasi-atomic $\bar{\Delta}$ and $\bar{U}$ (dashed line, resp. dotted line).

From this the late TM oxides are charge transfer gap like NiO and CuO and the early ones are Mott Hubbard like. This is rather important since for a CT gap material we have to include the O bands and the d states explicitly to describe the low energy scale charge fluctuations while in the MH systems we can get away with only the d states in a single band like Hubbard model

B, C Not Screened → Multiplet's (d^n)

Summary of some Racah parameters hoping integrals, charge transfer energies and U effective taking the Hunds rule ground states as well as the conductivity Gaps for transition metl oxides. These are determined from Experimental electron Spoectroscopy data

Parameter	MnO	FeO	CoO	NiO	CuO
Racah A	3.9	5.5	5.2	6.6	6.5
B	0.12	0.13	0.14	0.13	0.15
C	0.41	0.48	0.54	0.60	0.58
pdσ	1.3	1.3	1.3	1.3	1.5
pdπ	−0.6	−0.6	−0.6	−0.6	--
(ppσ−ppπ)	−0.7	−0.7	−0.7	−0.7	−1.0
Δ	8.8	7.0	5.5	6.2	2.8
U	A+14B+7C	A−8B	A+B	A+B	A+4B+2C
U	8.5	4.5	5.3	6.7	8.3
$E_{gap,theo}$	5.3	3.5	3.1	5.0	1.8
$E_{gap,exp}$	3.9	--	2.5	4.3	1.4
ZSA	Int	MH	Int	CT	CT
f.i.s.s.	^5E_g	$^6A_{1g}$	$^3T_{1g}$	^2E_g	$^1A_{1g}$

able 2. Parameters for the different late transition metal monoxides, for MnO, oO and NiO see the following chapters. CuO is taken from Eskes et al. [7], ho used a similar cluster calculation. All the values are in eV. In the bottom SA stands for Zaanen, Sawatzky, and Allen phase diagram [6], Int is inter-ediate region, MH is Mott-Hubbard region and CT is charge transfer region. he last line shows the first ionization state symmetry (f.i.s.s.) in O_h and D_{4h} CuO) symmetry.

These are the U values based on The multiplet average energies Rather than the hunds rule Ground state energies

CuO	d^9	U= A−8B	5.3 eV
		U_a= A+4B+2C	8.3 eV
NiO	d^8	U= A+B	6.7 eV
		U_a= A+21B+5C−$\sqrt{(193B^2+8BC+4C^2)}$	10.0 eV
CoO	d^7	U= A+B	5.3 eV
		U_a= A+5B+4C	8.1 eV
FeO	d^6	U= A−8B	4.5 eV
MnO	d^5	U= A+14B+7C	8.5 eV

Van Elp et al PRB

Example Cu2+ as in LaCuO4 (d9 s=1/2)
For the N-1 electron states we need d8, d9L, d10L2 where L denotes a hole in O 2p band. The d8 states exhibit multiplets

$$3d(x^2-y^2, 3z^2-r^2, xy, xz, yz)$$

$$b_{1g}, a_{1g}, b_{2g}, e_g$$

Given here are the various representations spanned by 2 d holes in D4h symmetry and the Coulomb matrix elements in terms Of the A,B,C Racah parameters

$^1A_2$	b_1b_2
b_1b_2	A+4B+2C

$^3B_1$	a_1b_1
a_1b_1	A-6B

$^3B_2$	a_1b_2
a_1b_2	A-6B

$^3A_2$	b_1b_2	e^2
b_1b_2	A+6B	6B
e^2	6B	A-5B

$^1B_1$	a_1b_1	e^2
a_1b_1	A+2C	$-2\sqrt{3}B$
e^2	$-2\sqrt{3}B$	A+B+2C

$^1B_2$	a_1b_2	e^2
a_1b_2	A+2C	$-2\sqrt{3}B$
e^2	$-2\sqrt{3}B$	A+B+2C

(x^2-y^2) (xz)

^1E	eb_1	ea_1	eb_2
eb_1	A-5B	$-3\sqrt{3}B$	3B
ea_1	$-3\sqrt{3}B$	A+B	$-3\sqrt{3}B$
eb_2	3B	$-3\sqrt{3}B$	A-5B

^1E	eb_1	ea_1	eb_2
eb_1	A+B+2C	$-B\sqrt{3}$	-3B
ea_1	$-B\sqrt{3}$	A+3B+2C	$-B\sqrt{3}$
eb_2	-3B	$-B\sqrt{3}$	A+B+2C

2R singlet.

$^1A_1$	a_1^2	b_1^2	b_2^2	e^2
a_1^2	A+4B+2C	4B+C	4B+C	$(3B+C)\sqrt{2}$
b_1^2	~~4B+C~~	~~A+4B+2C~~	C	$(3B+C)\sqrt{2}$
b_2^2	4B+C	C	A+4B+2C	$(3B+C)\sqrt{2}$
e^2	$(3B+C)\sqrt{2}$	$(3B+C)\sqrt{2}$	$(3B+C)\sqrt{2}$	A+7B+4C

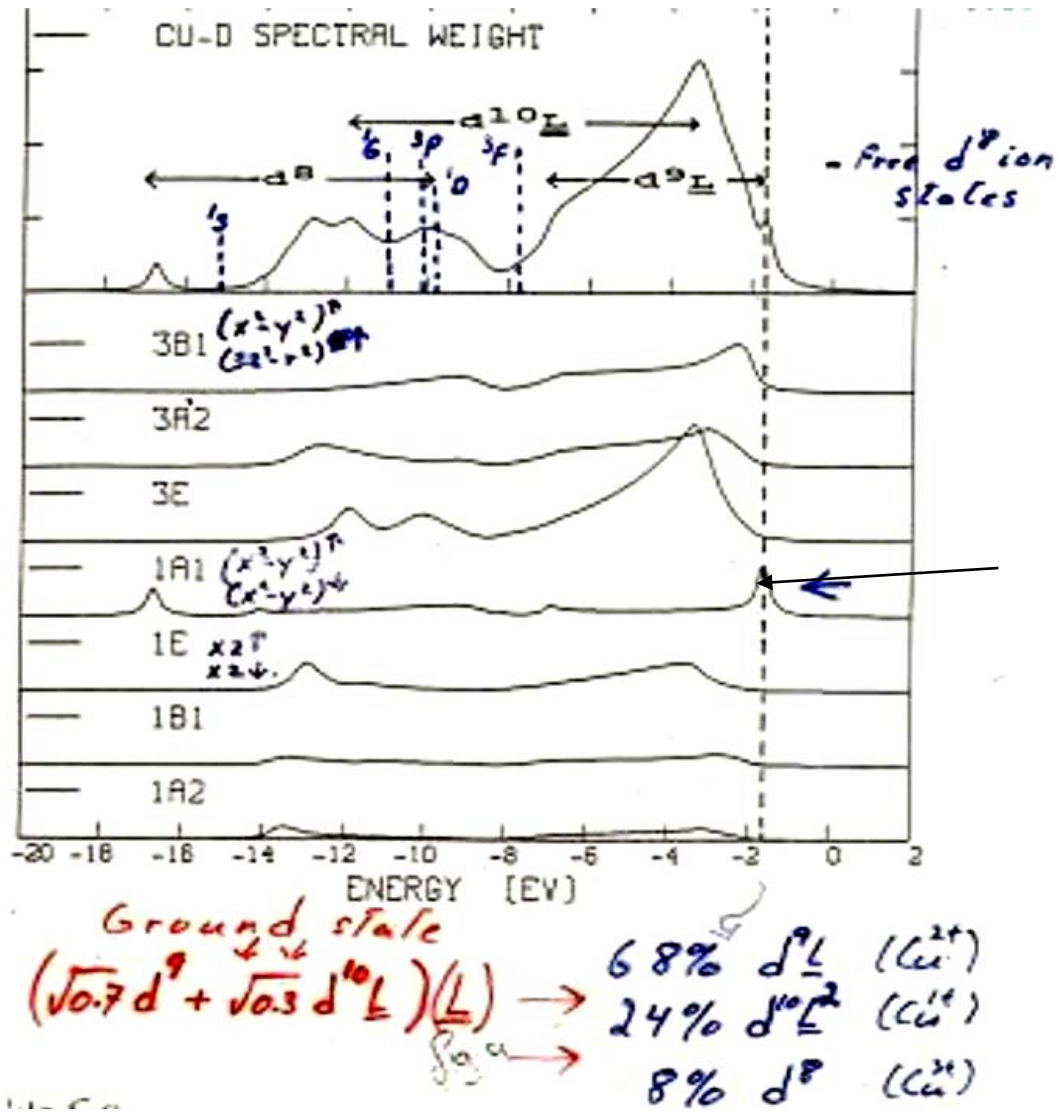
To calculate the PES spectrum

- Consider a Cu 2+ impurity in a O Lattice
- The ground state and optical spectrum will be given by the one hole Greens function taking the vacuum state to be Cud10 (i.e. Cu1+) and a filled O 2p band as we did before .
- The PES spectrum will be given by the two hole Greens function which also includes the lowest energy electron removal state of the various possible symmetries and spins.

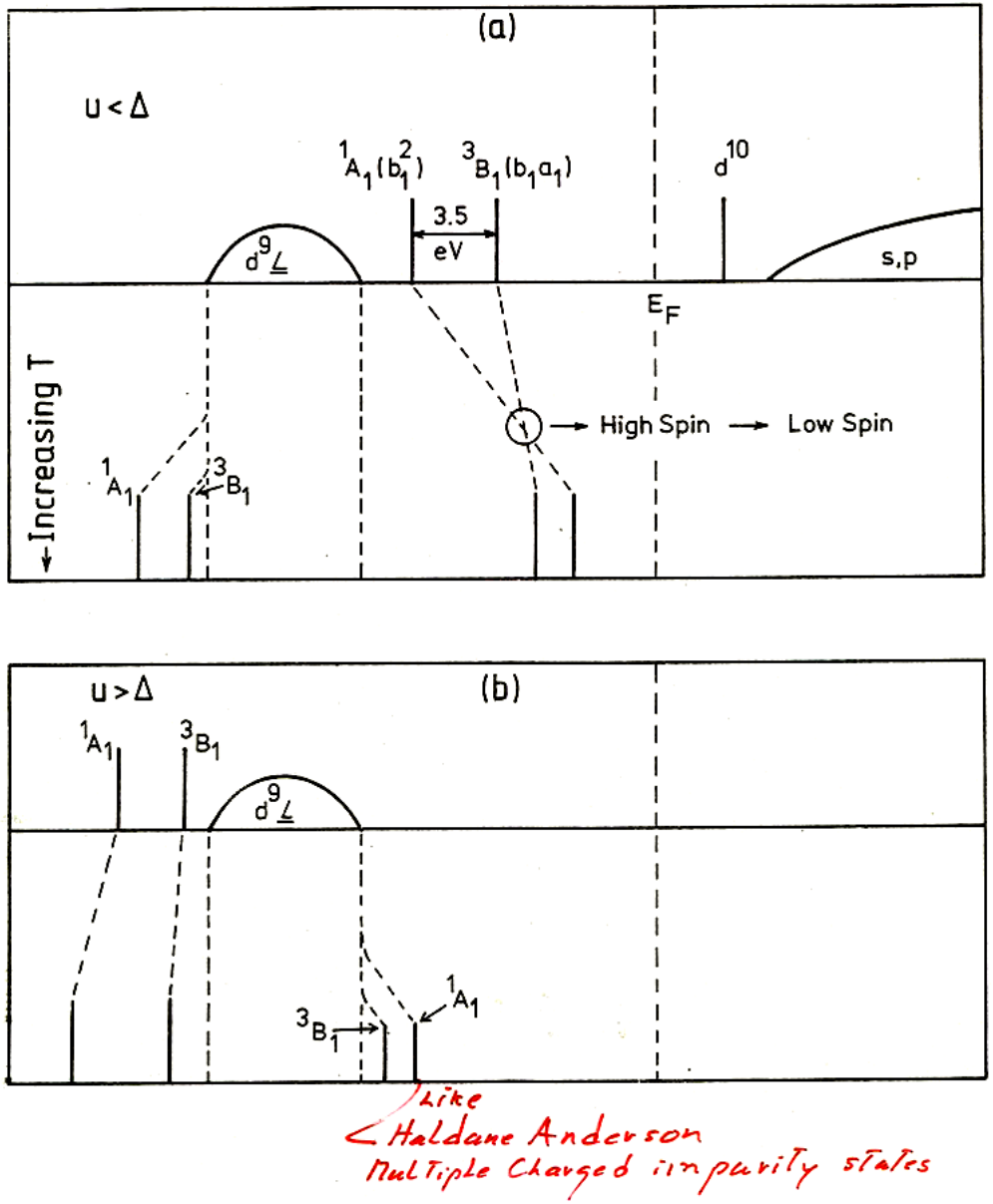
H. Eskes et al PRL 61, 1415 (1988).

Anderson Impurity calculation

Note the large Energy scale Covered by each State!!



Zhang Rice singlet



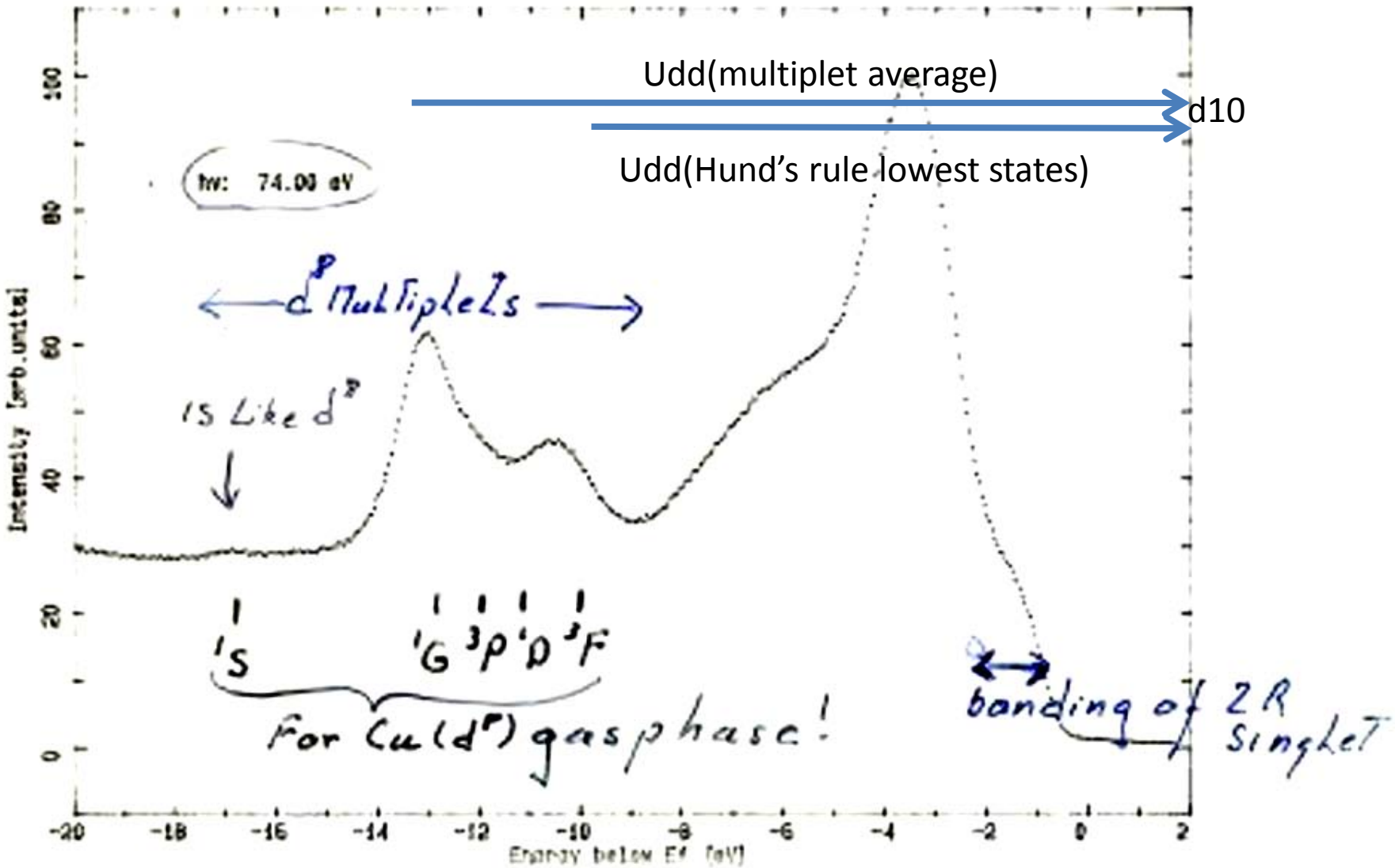
This shows how the usually Expected high spin d8 state for U<Δ and would reguire a huge crystal field to invert this is naturally inverted even for low crystal fields for the ZR like states if U>Δ. The low energy states are bound states pushed out of the O 2p bands. This is a result of the hybridization involving the 3z2-r2 orbital is a lot smaller than that involving the x2-y2 orbital.

The upper plots in each case are for no hybridization and the dashed lines show what happens if we switch on the hybridization

J. Ghijsen et al

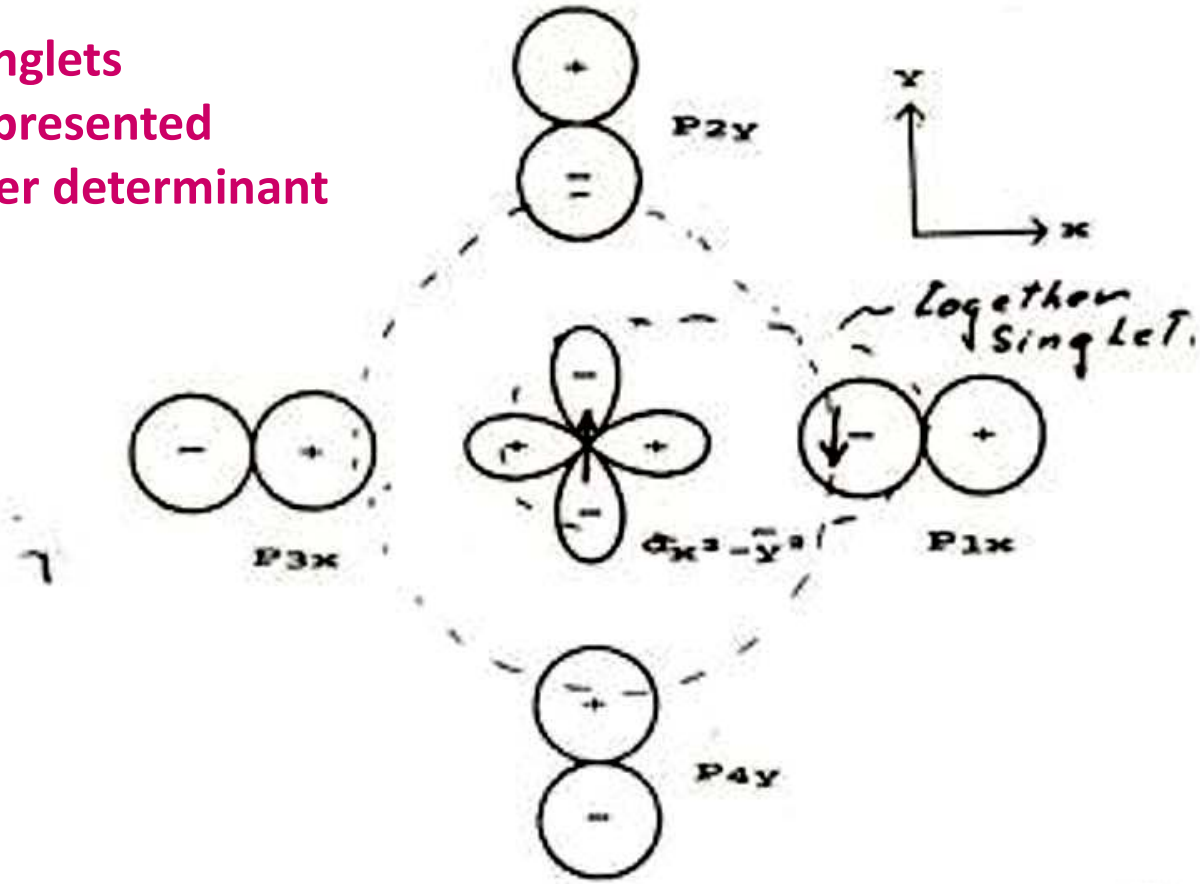
Phys. Rev. B. 42, (1990) 2268.

Resonant Photoemission spectrum of CuO



Energy below Ef in eV

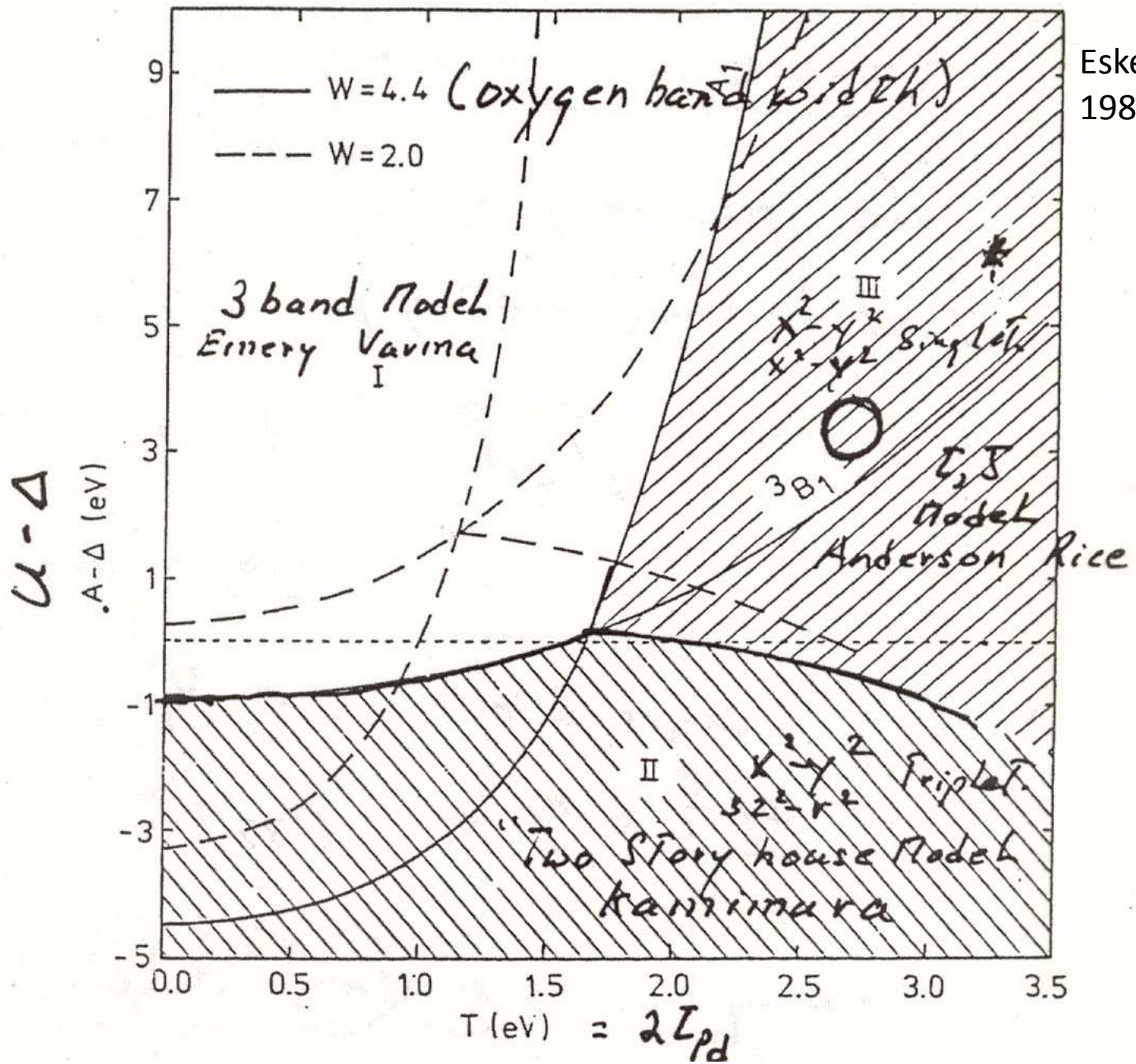
Zhang Rice singlets
Cannot be represented
By single Slater determinant



$$\psi_{x^2-y^2} = \frac{1}{\sqrt{4}}\left[-p_{1x} + p_{2y} + p_{3x} - p_{4y}\right]$$

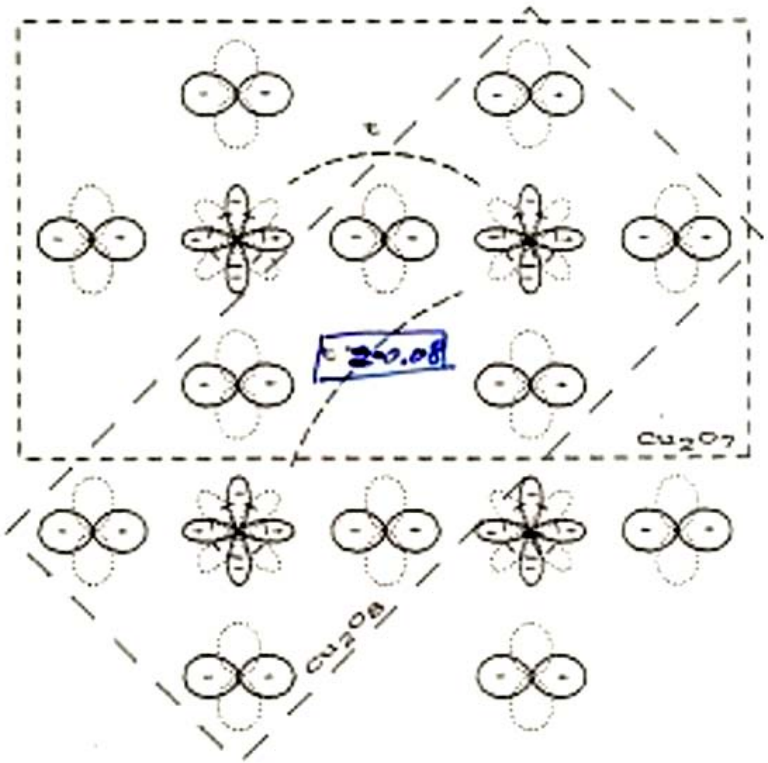
$T_{pd}(b_1) = 2\,T_{pd}(\text{single bond})$

Singlet stabalized by $J \sim \dfrac{4[2T_{pd}]^2}{\Delta_{CT}}$



Eskes et al PRL 61, 1415 1988

Example of two cluster calculations to obtain the parameters
For a low energy theory (single band Hubbard or tJ)

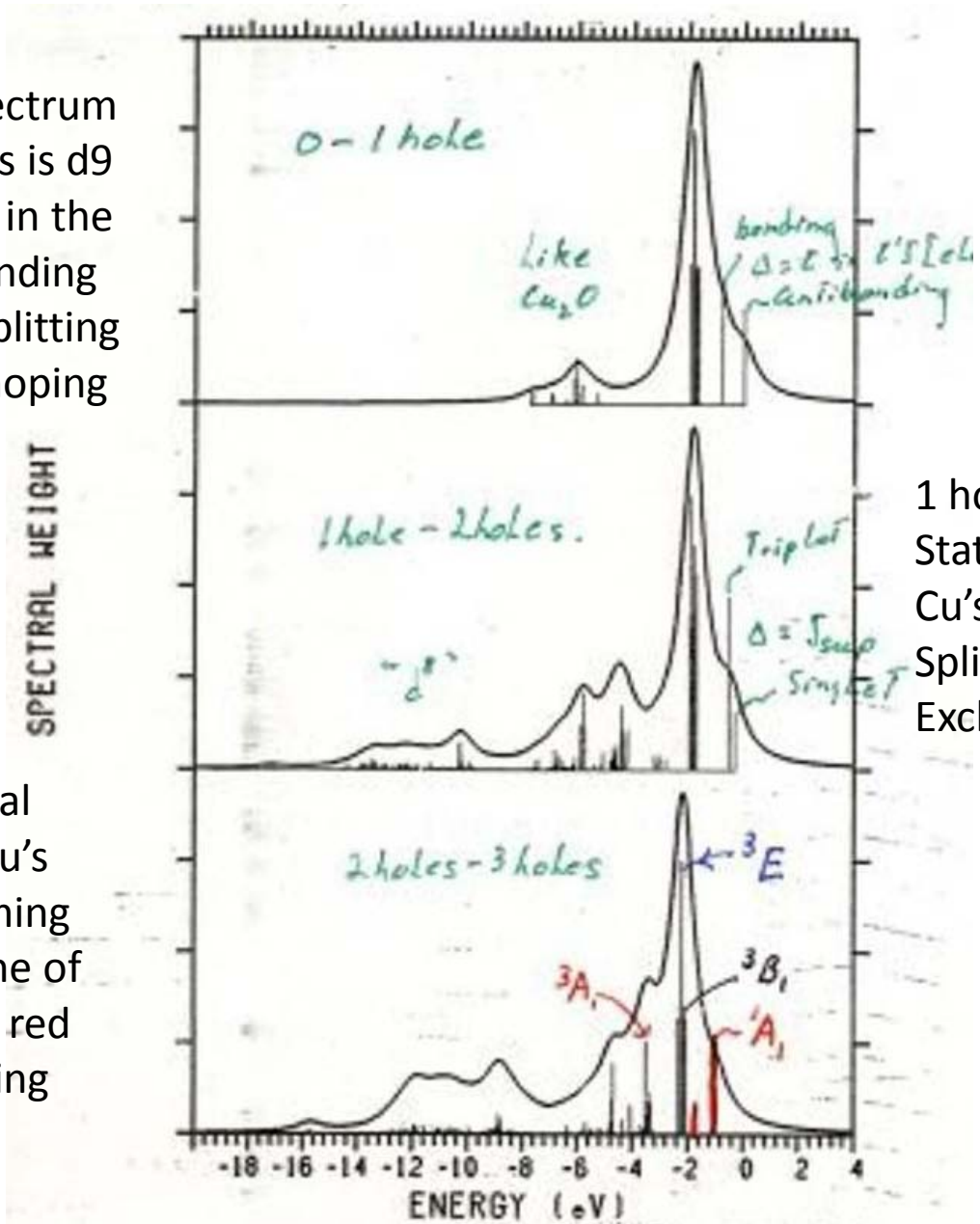


$$\left.\begin{array}{l} t \sim 0.4 \\ J \sim 0.17 \end{array}\right\} \text{ t, J model}$$

Band width for $t = 0.4$ = 3.2eV

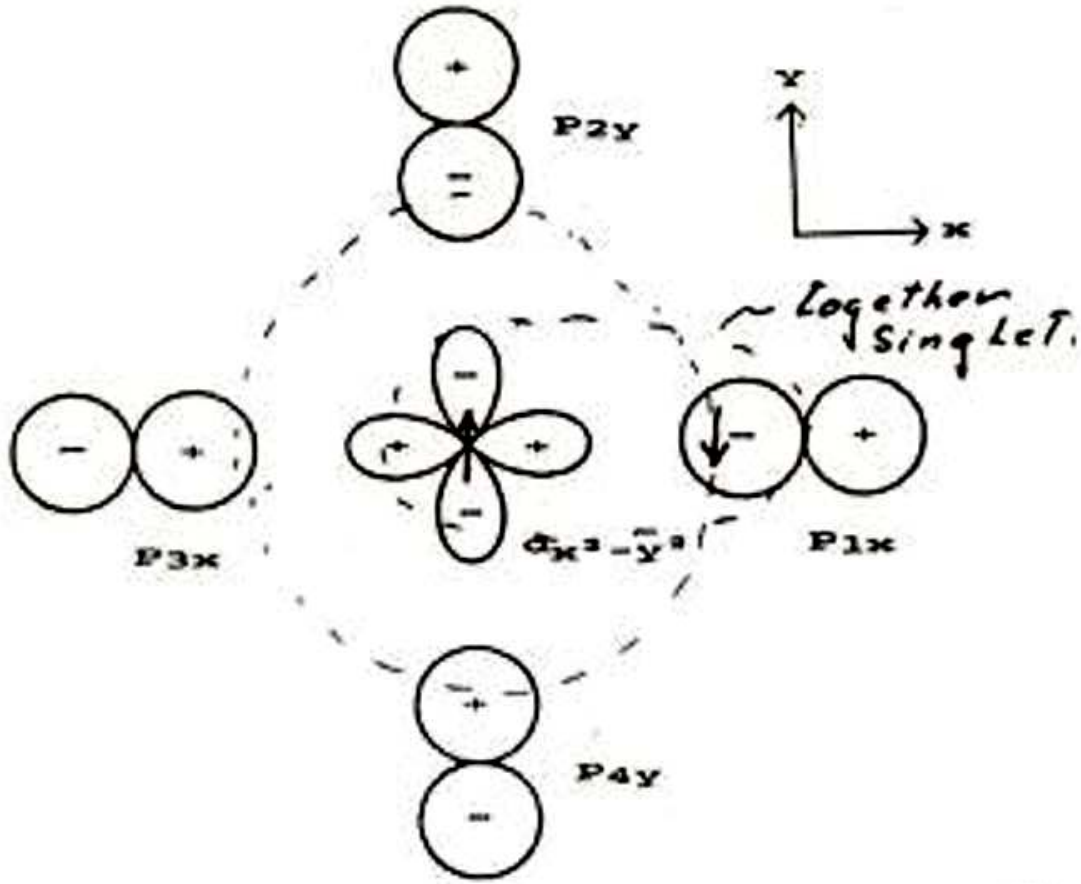
Eskes etal PRB
44,9656, (1991)

0 to 1 hole spectrum
One of the Cu's is d9
The other d10 in the
Final state. Bonding
Antibonding splitting
Measure d-d hoping



1 hole to 2 holes final
State is od9 on both
Cu's Triplet singlet
Splitting yields super
Exchange J

2 holes to 3 holes final
state is d9 for both Cu's
Plus a hole on O forming
A singlet (ZR) with one of
The Cu's . Splitting in red
Yields the ZR-ZR hoping
integral as in tJ

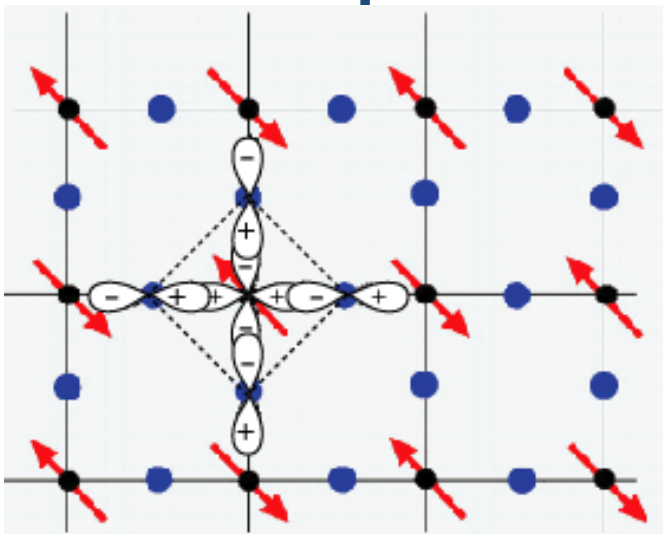


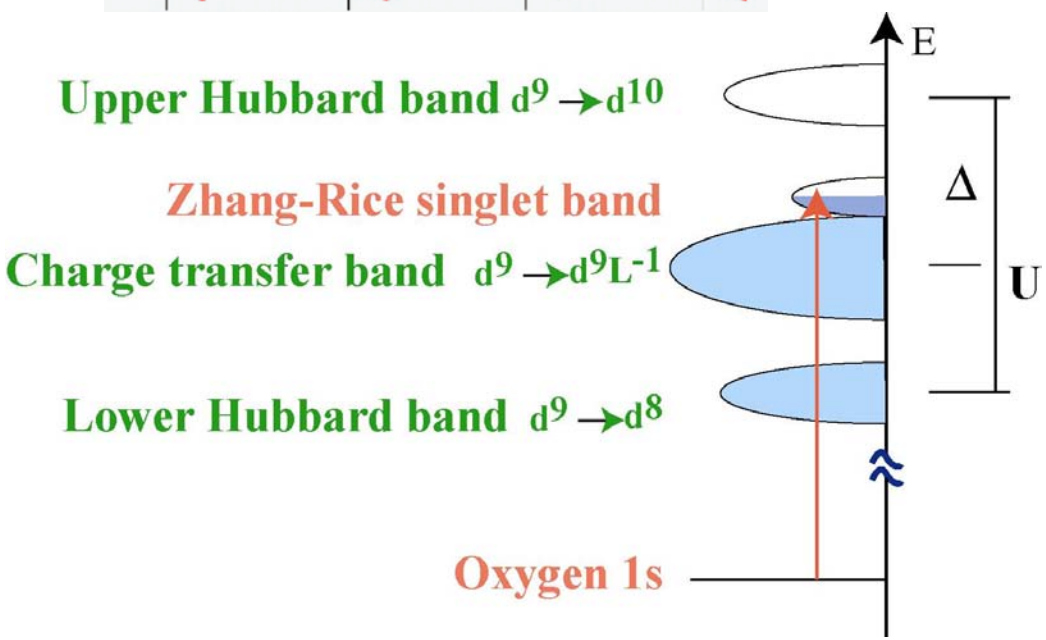
$$\psi_{x^2-y^2} = \frac{1}{\sqrt{4}}\left[-p_{1x} + p_{2y} + p_{3x} - p_{4y}\right]$$

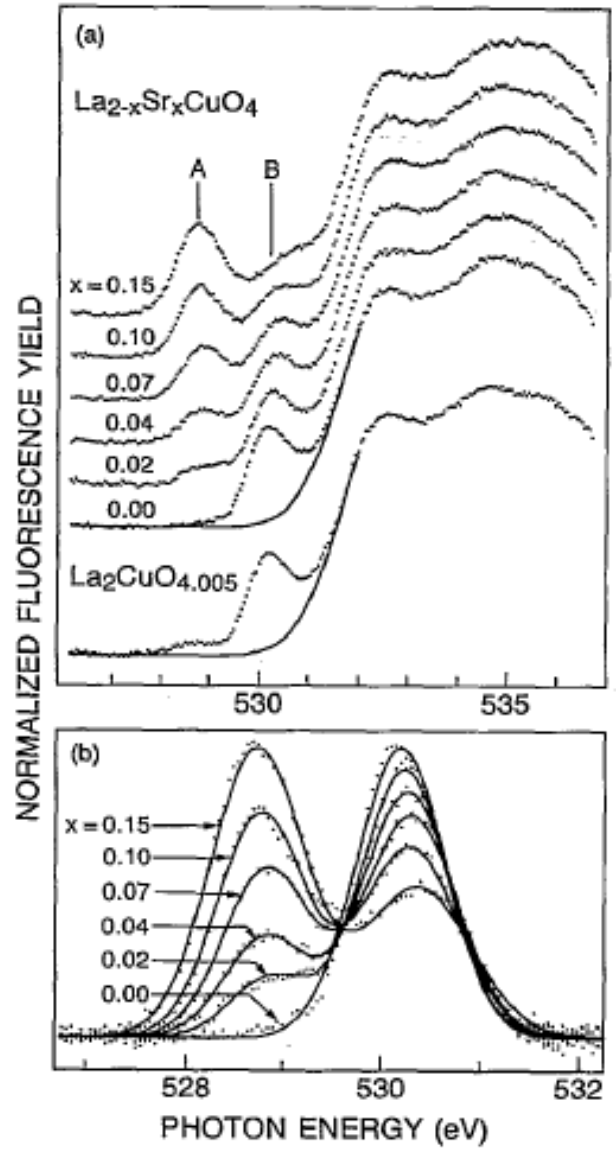
$T_{pd}(b_1) = 2\,T_{pd}(\text{single bond})$

Singlet stabalized by $J \sim \dfrac{4[2T_{pd}]^2}{\Delta_{CT}}$

Doped holes in cuprate







As we hole dope the system the O1s to 2p first peak rises very strongly indicating That the doped holes are mainly on O 2p.

C. T. Chen et al. PRL 66, 104 (1991)

Is single band Hubbard justified for Cuprates?

Zhang Rice PRB 1988
37,3759

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

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

where $\delta_{\langle ij\rangle,0} = 1$ 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 = num-

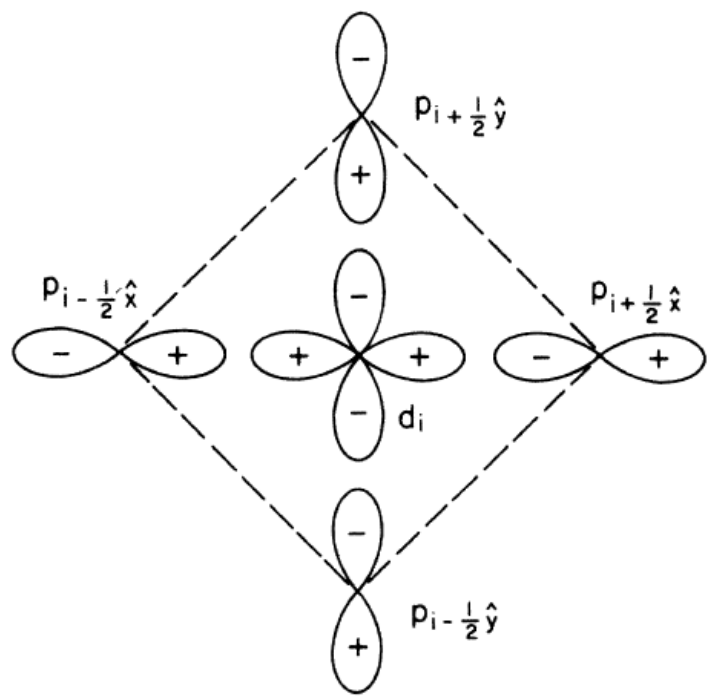


FIG. 1. Schematic diagram of the hybridization of the O hole ($2p^5$) and Cu hole ($3d^9$). The signs + and − represent the phase of the wave functions.

Problem with ZR singlets

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

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

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

From ZR PRL 37,3759

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

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

Note it goes to infinity at k=0, should we see it at Gamma in ARPES? Luckly it goes to 1 for K= Pi/2,Pi/2 and anywhere along the AF zone boundary where the doped holes go

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

Is this only a problem for the Cuprates?

What about the Nickalates, Manganites, Cobaltates etc?

Kuiper et al PRL 62 221 (1989) LixNi1-x O
A CHARGE TRANSFER GAP SYSTEM HOLES IN O

Note the high "pre-Edge feature and the Spectral weight Transfer from high To low energy scales

Just as in the cuprates The holes are mainly on O and not on Ni.!!

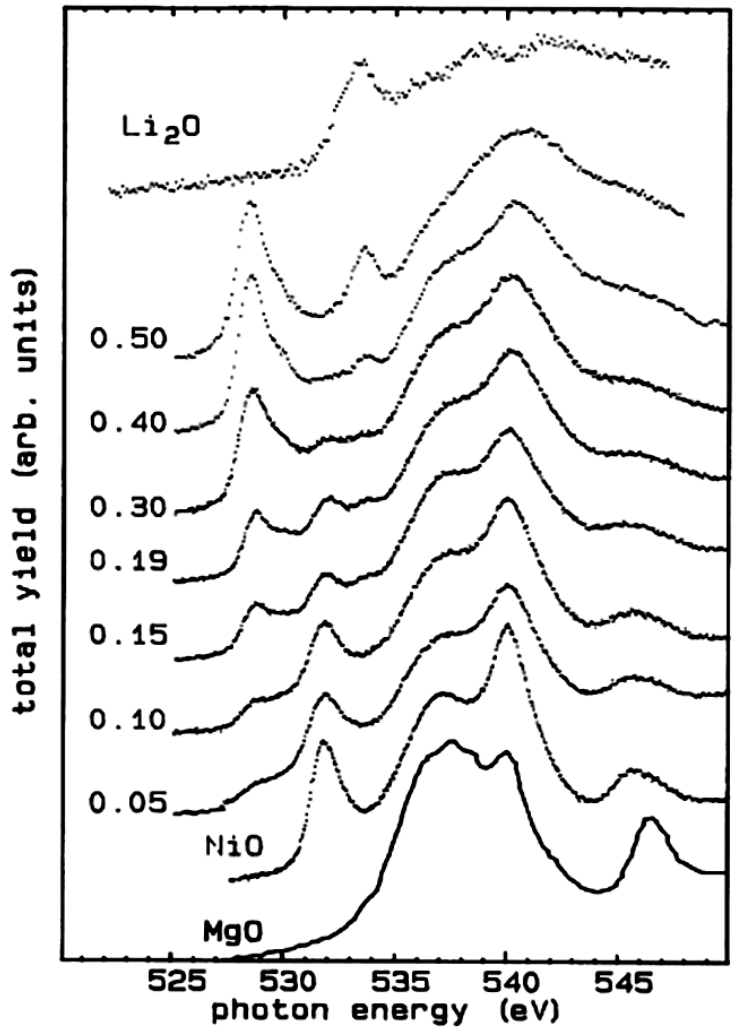
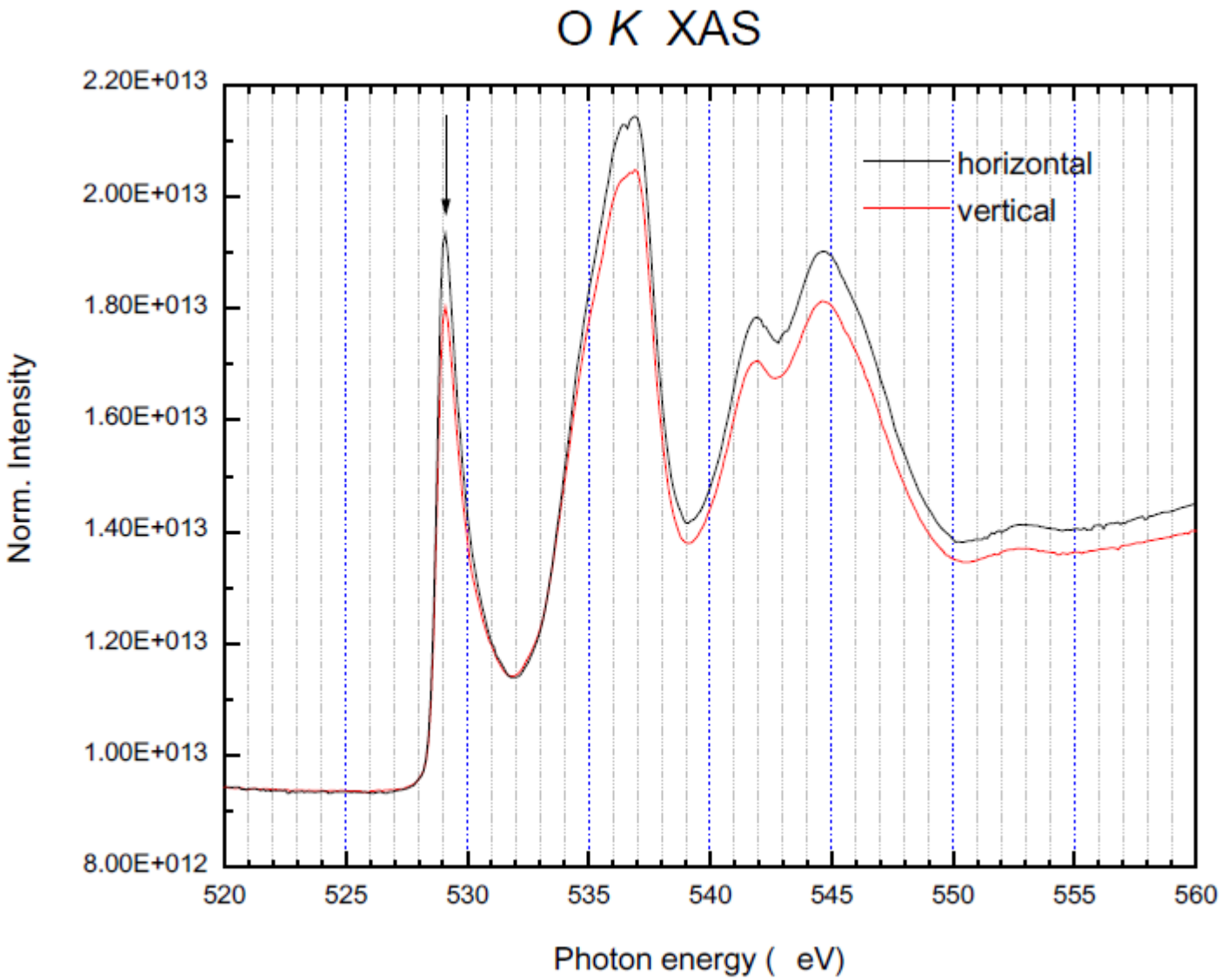


FIG. 1. Oxygen K-edge absorption spectra of MgO (Ref. 26), NiO, $Li_xNi_{1-x}O$ for indicated values of x, and Li_2O.

LNO thin film on LSAT Sutarto, Wadati, Stemmer UCSB

Note the huge O 1s -2p prepeak just as in the cuprates HOLES ON O



Can we renormalize and get rid of the anion states?

Similar to the Zhang Rice singlets in the cuprates?