The Explicit Role of Anion States in High-Valence Metal Oxides

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- Introduction
- Importance of the anion states
- Hole doped states in divalent Cu and Ni Oxides
- Undoped negative charge transfer gap systems
- General Classification of transition metal and rare earth compounds Mott Hubbard, Charge transfer, Mixed valent and negative charge transfer
- Negative charge transfer gap systems Nickelates, Bismuthtates
- Mixed valent rare earths SmB6

If we cannot solve a problem exactly
The starting point really matters

Start the thinking with the most likely oxidation state or valence of the cations before switching on the cation - anion hybridization in models

Standard rules for formal cation valence :

1. **Anions are closed shell O(2-), Cl(1-) etc**
2. **Fixed valence cations La(3+), Ca(2+)etc**
3. **valence of omivalent cation – composition**
4. **This puts low energy charge degrees of freedom on the cations**

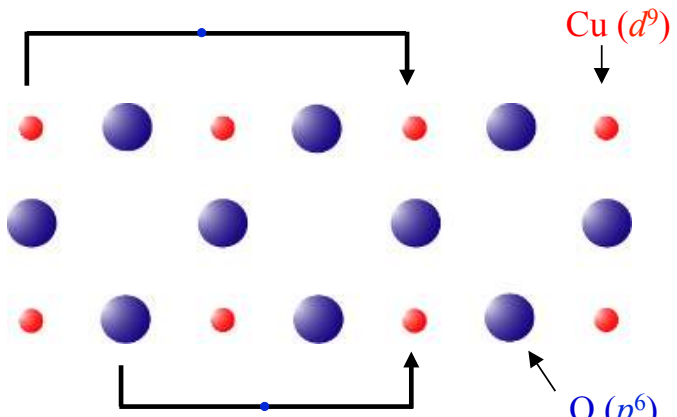
There are many examples where this formal definition is not what happens in reality

Compound(	Formal Valence	Actual valence	Resolution
CrO2	Cr4+	Mixed close to 3+	Holes in O 2p band Half met. ferromag
FeS2	Fe4+	Fe2+ S=0	S2 pairs forming S2(2-)
BaO2	Ba4+	Ba2+	(O2)2- Pairs
KO2	K4+	K1+	(O2)1-pairs S=1/2 Ferron=magnet
La(1-x)SrxCuO4	Cu mixed valent 2/3+	Cu2+	Holes in O2p metal/ high Tc
(Li/Na)NiO2	Ni3+	Ni2+	Holes in O2p
ReNiO3	Ni3+	Ni2+	Holes in O2p

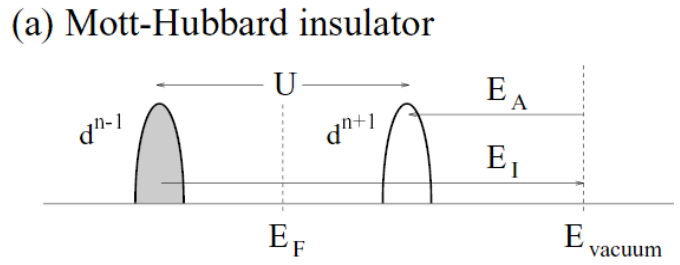
In the doped cuprates should Cu or O be at the center of attention for low energy scale charge degrees of freedom? (not withstanding the importance of Cu)

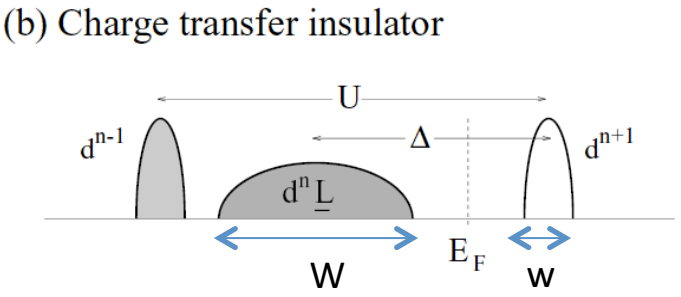
Correlated Electrons in a Solid

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



Δ : $p^6\, d^n \rightarrow p^5\, d^n$ ($\underline{L}$ = p^6)





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

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

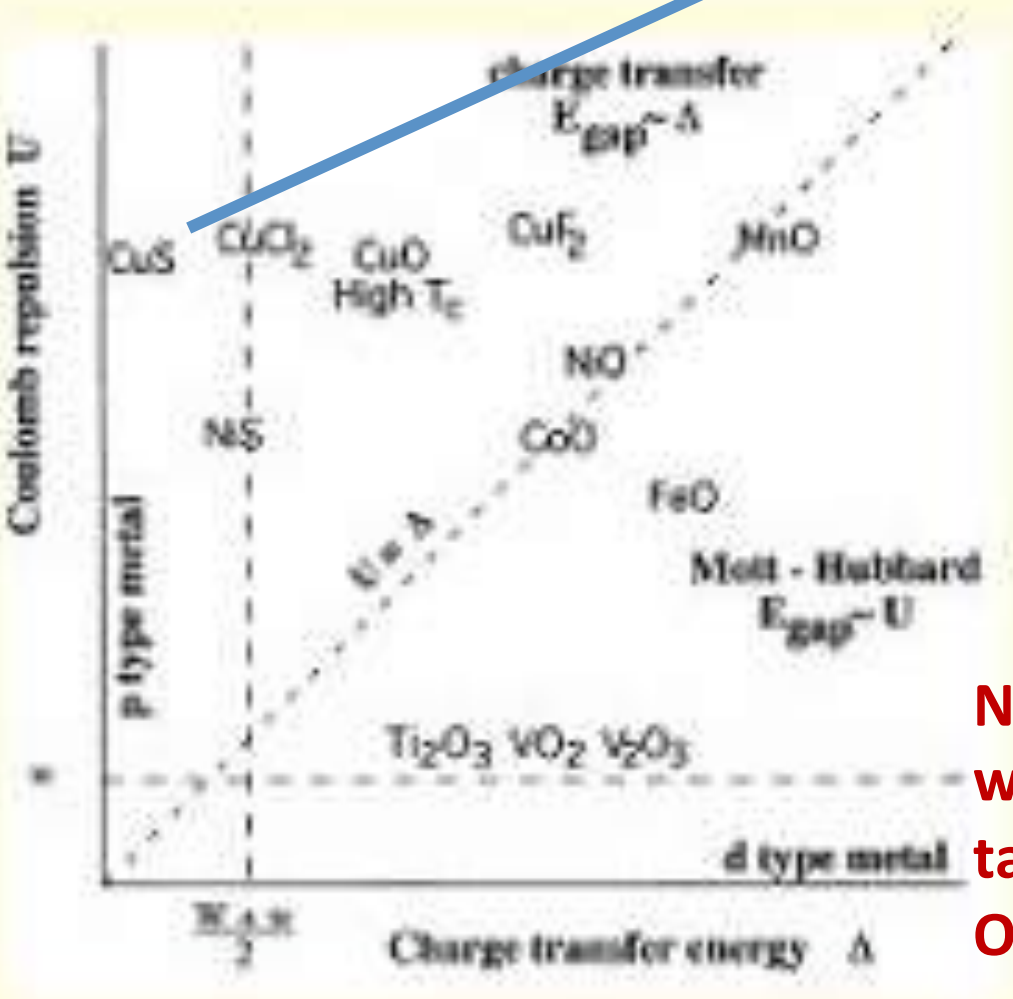
E_I ionization energy
E_A electron affinity energy
E_M Madelung energy

If Δ < (W+w)/2 → Self doped metal (mixed valent!!)

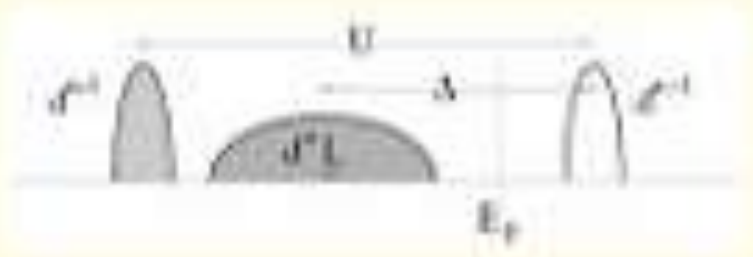
- J.Hubbard, Proc. Roy. Soc. London A 276, 238 (1963)
- ZSA, PRL 55, 418 (1985)

Zaanen et al

Note that in CuS the Cu is 1+ with holes in O 2p
Also in CuCr2S4 and Se4



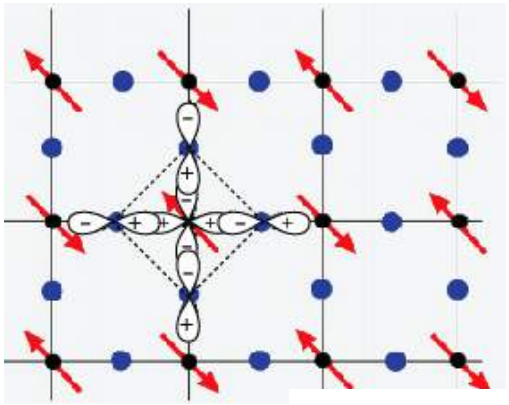
For divalent cations



Note that CT energy decreases as we Move down in the periodic table for The Anion i.e. F-Cl-Br-I Or O –S-Se-Te

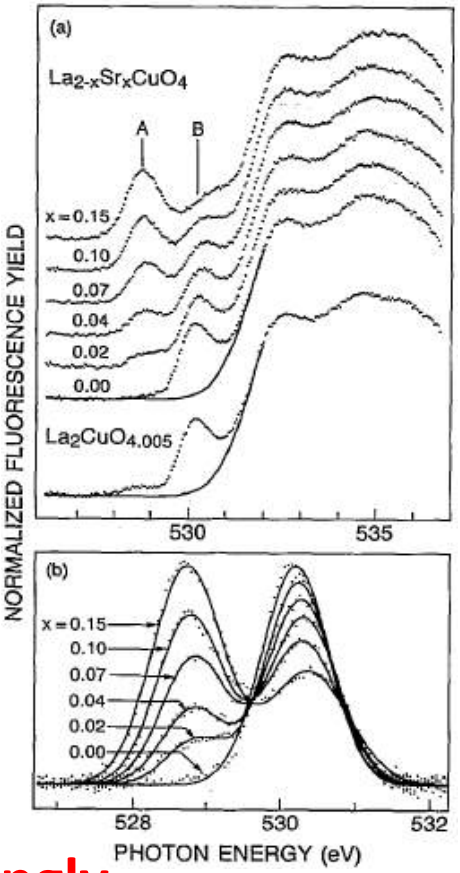
Phys. Rev. Lett. 55, 418 (1985)

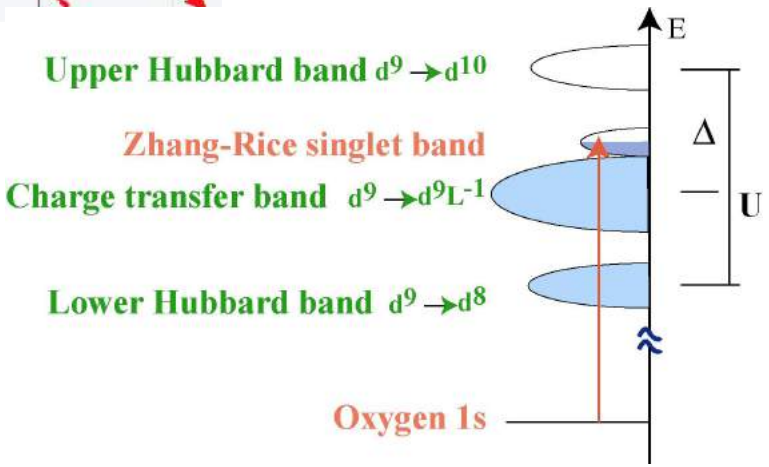
Doped holes in cuprate



C.T.Chen XAS

PRL **68**, 2543 (1992)





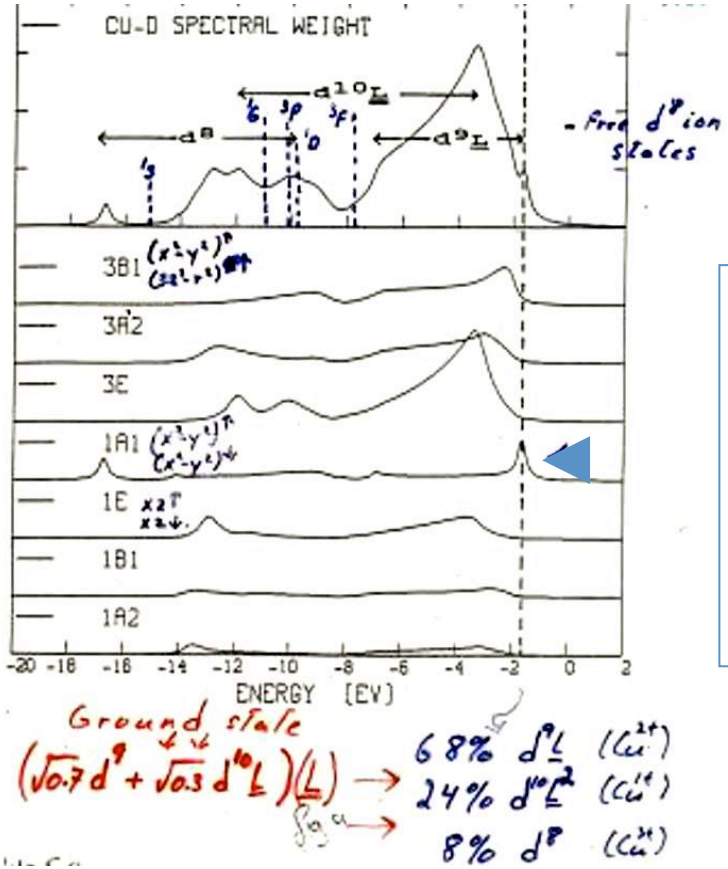
On hole doping the O1s to 2p first peak rises strongly indicating the doped holes are mainly on O 2p.

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

Three early papers all in 1988 with O playing a central role

Anderson Impurity calculation for ARPES starting from Cu(d10) full O 2p band, full d-d multiplet interaction using respectively the one (d9 ground state and optical spectrum) and two particle Greens function for ARPES

H. Eskes et al PRL 61, 1415 (1988). Thesis Groningen 2000



Dashed lines are the Multiplets Of FREE Cu d8

Note the large Energy scale Covered by each Irreducible representations Of two d holes in the D4h point group

Local spin compensated State LIKE Zhang Rice singlet

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

Example Cu2+ as in LaCuO4 (d9 s=1/2)

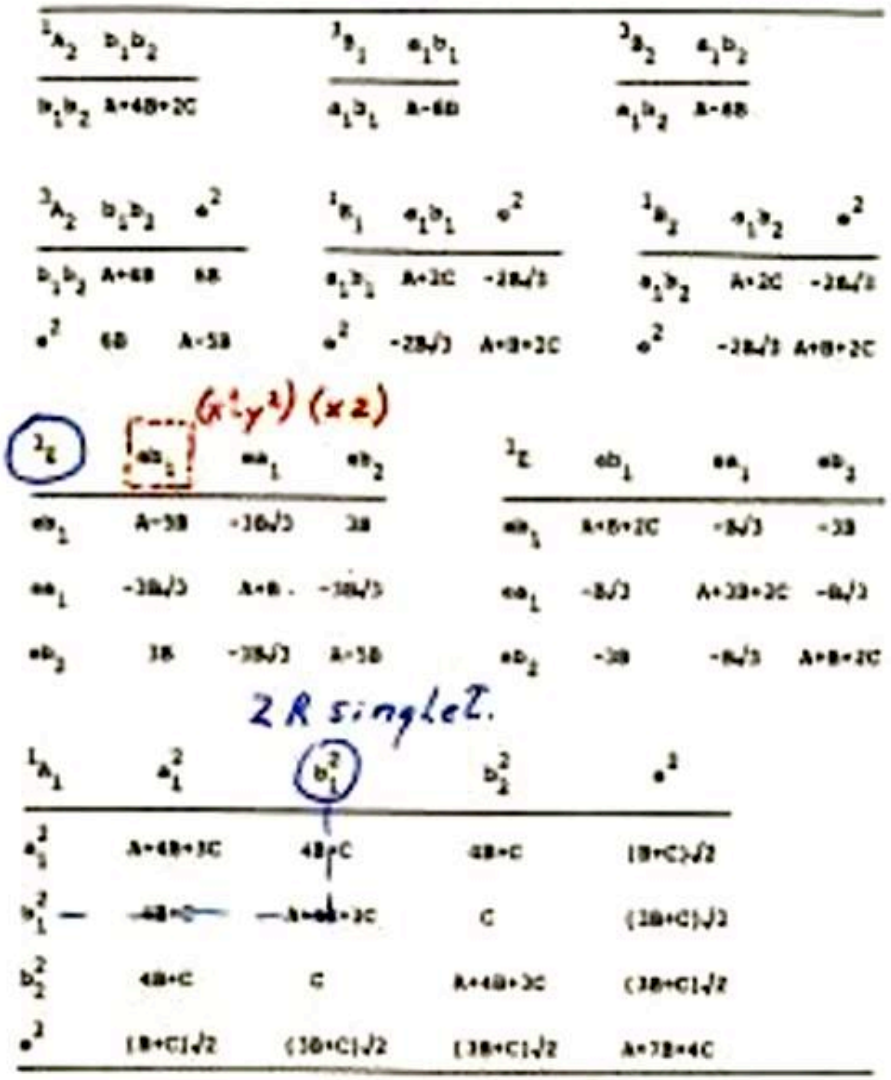
For the N-1 electron states we need d8, d9L, d10L2 where L denotes a hole in O 2p band. The d8 states exhibit multiplets

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

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

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

D8 with 2 holes in x2-y2
As in most Hubbard theories
Is part of a 4X4 Matrix in D4h



Emery Reiter Phys. Rev. B 38, 4547 (1988)

Doped Holes mainly on O but O has TWO Cu nn so equally shared between them leading to a 3 SPIN POLARON

Zhang Rice Phys.Rev. B 37, 3759 (1988)

Doped holes mainly on O but form a molecular orbital about a selected Cu with x2-y2 symmetry

Is single band Hubbard justified for Cuprates?

Zhang Rice PRB 1988
37,3759

Strong argument for tJ or single band Hubbard

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-

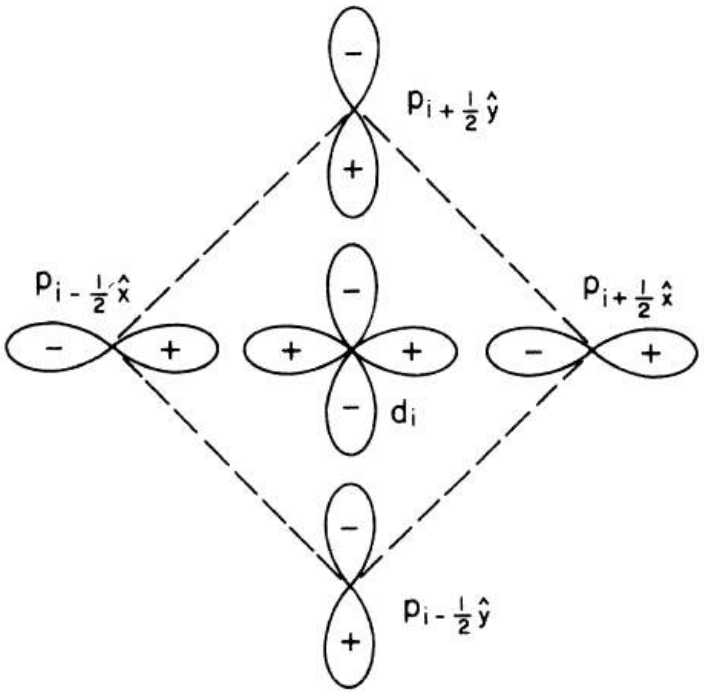


FIG. 1. Schematic diagram of the hybridization of the O hole ($2p^5$) and Cu hole ($3d^9$). The signs + and − represent the phase of the wave functions.

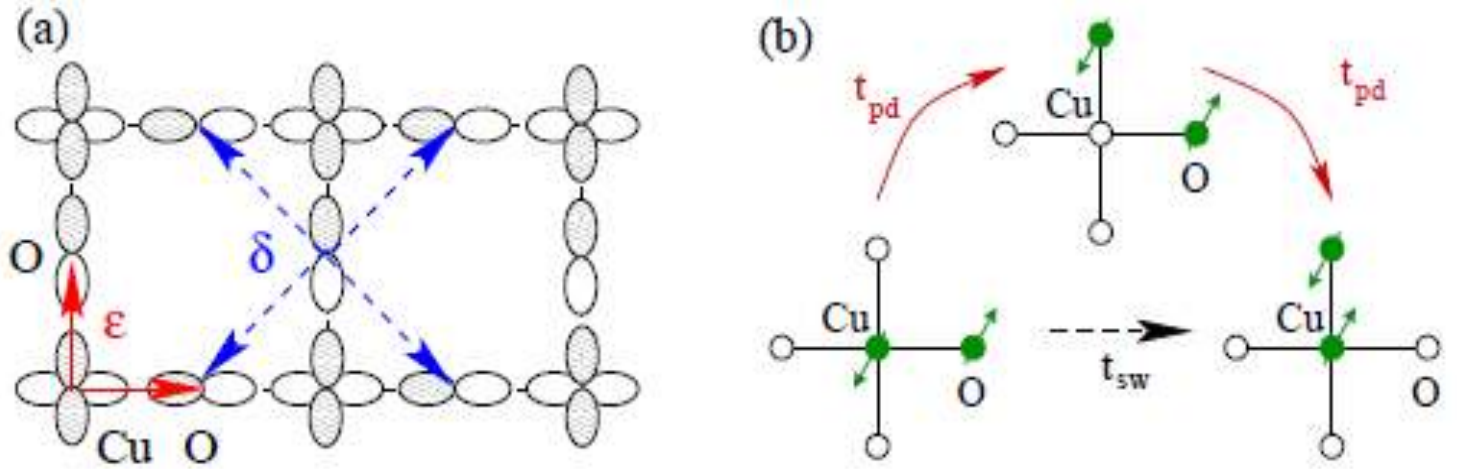
More recent Large scale exact diagonalization of 3 band like model Bayo Lau Thesis UBC 2011

Bayo Lau et al :PRB 81, 172401 (2010)
PhysRevLett.106.036401, (2011)
PhysRevB.84.165102 (2011)

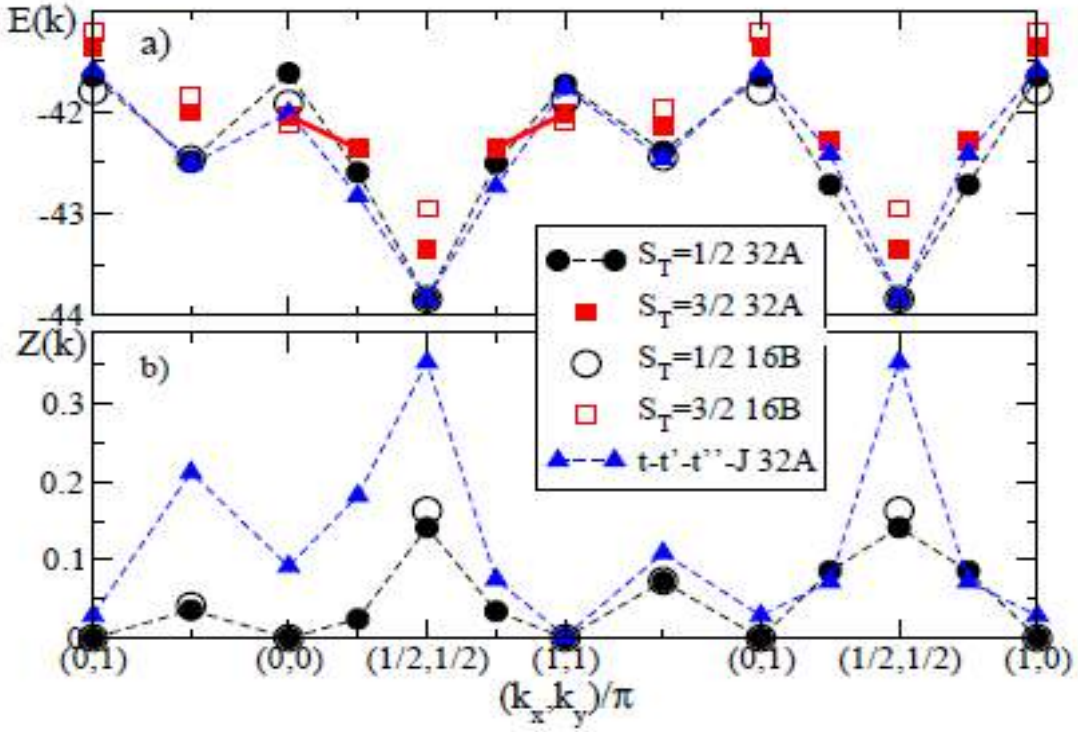
$$H_{3B} = T_{pd} + T_{pp} + \Delta_{pd} \sum n_{l+\epsilon,\sigma} + U_{pp} \sum n_{l+\epsilon,\uparrow} n_{l+\epsilon,\downarrow} + U_{dd} \sum n_{l,\uparrow} n_{l,\downarrow} \quad (1)$$

$$H_{\text{eff}} = T_{pp} + T_{\text{swap}} + H_{J_{pd}} + H_{J_{dd}} \quad (2)$$

$$T_{swap} = -t_{sw} \sum s_\eta \, p^\dagger_{l+\varepsilon+\eta,\sigma} p_{l+\varepsilon,\sigma'} \left| \sigma'_{l_{\varepsilon,\eta}} \right\rangle \left\langle \sigma_{l_{\varepsilon,\eta}} \right|$$



The dispersion and the quasi particle spectral weight periodic cluster 32Cu 64 O



Bayo Lau et al PRB 81, 172401
PhysRevLett.106.036401, (2011)
PhysRevB.84.165102 (2011)
Bayo Lau Thesis UBC 2012

FIG. 2. a) Energy and b) quasiparticle weight (bottom) for the lowest eigenstates with $S_T = \frac{1}{2}$ and $\frac{3}{2}$ vs. momentum. Different sets are shifted so as to have the same GS energy.

Exact diagonalization studies of 32Cu 64O

Note a quantum spin ½ antiferromagnet has a nn spin correlation of -.33 , singlet -.75, A Neel antiferromagnet =- .25, and a ferromagnet =+.25

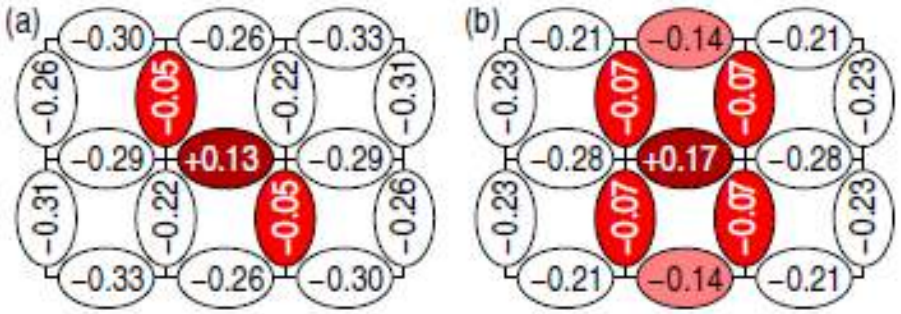
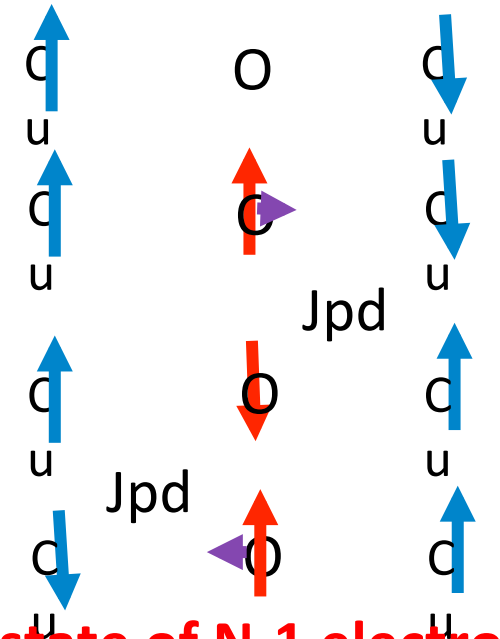


FIG. 3. $\langle C_x(\delta, a)\rangle$ for the lowest energy state at (a) $(\frac{\pi}{2}, \frac{\pi}{2})$ with $S_T = \frac{1}{2}$, and (b) at (π,π) with $S_T = \frac{3}{2}$. The darkly-shaded bullet denotes the oxygen position at $l + e_x$. Each

Shows strong ferro correlations close to the doped hole.
This does not look like a ZR singlet but actually
The spatial O hole has x2-y2 symmetry at pi/2pi/2

Antiferro CuO2 lattice

hole notation



O displacement (phonon)

Remove an up spin electron from O i.e.ARPES or DOPING

Act with Jpd >>Jdd

Act with Jpd >>Jdd

Eigenstate of N-1 electron system is a linear combination of these three states and has a strong phonon component

HOLE ON O2P STRONGLY DRESSED BY A PHONON PLUS TWO MAGNONS

What would this isolated 3 spin SPIN ½ polaron look like

Sz=1 triplet state

Wavefunction	Total Spin	$\frac{\langle H_{J_{pd}} \rangle}{J_{pd}}$
$\vert\Uparrow\rangle = \sqrt{\frac{1}{3}} p_{\uparrow}^{\dagger} \frac{\vert\uparrow\downarrow\rangle + \vert\downarrow\uparrow\rangle}{\sqrt{2}} - p_{\downarrow}^{\dagger} \sqrt{\frac{2}{3}} \vert\uparrow\uparrow\rangle$	$\frac{1}{2}$	-1
$\vert\Downarrow\rangle = \sqrt{\frac{1}{3}} p_{\downarrow}^{\dagger} \frac{\vert\uparrow\downarrow\rangle + \vert\downarrow\uparrow\rangle}{\sqrt{2}} - p_{\uparrow}^{\dagger} \sqrt{\frac{2}{3}} \vert\downarrow\downarrow\rangle$	$\frac{1}{2}$	-1
$\vert 0+\rangle = \sqrt{\frac{1}{3}} p_{\uparrow}^{\dagger} \frac{\vert\uparrow\downarrow\rangle - \vert\downarrow\uparrow\rangle}{\sqrt{2}}$	$\frac{1}{2}$	0
$\vert 0-\rangle = \sqrt{\frac{1}{3}} p_{\downarrow}^{\dagger} \frac{\vert\uparrow\downarrow\rangle - \vert\downarrow\uparrow\rangle}{\sqrt{2}}$	$\frac{1}{2}$	0
$\vert\frac{3}{2}, \frac{3}{2}\rangle = p_{\uparrow}^{\dagger} \vert\uparrow\uparrow\rangle$	$\frac{3}{2}$	$\frac{1}{2}$
$\vert\frac{3}{2}, \frac{1}{2}\rangle = \sqrt{\frac{2}{3}} p_{\uparrow}^{\dagger} \frac{\vert\uparrow\downarrow\rangle + p_{\downarrow}^{\dagger} \vert\downarrow\uparrow\rangle}{\sqrt{2}} + \sqrt{\frac{1}{3}} p_{\downarrow}^{\dagger} \vert\uparrow\uparrow\rangle$	$\frac{3}{2}$	$\frac{1}{2}$
$\vert\frac{3}{2}, -\frac{1}{2}\rangle = \sqrt{\frac{2}{3}} p_{\downarrow}^{\dagger} \frac{\vert\uparrow\downarrow\rangle + \vert\downarrow\uparrow\rangle}{\sqrt{2}} + \sqrt{\frac{1}{3}} p_{\uparrow}^{\dagger} \vert\downarrow\downarrow\rangle$	$\frac{3}{2}$	$\frac{1}{2}$
$\vert\frac{3}{2}, -\frac{3}{2}\rangle = p_{\downarrow}^{\dagger} \vert\downarrow\downarrow\rangle$	$\frac{3}{2}$	$\frac{1}{2}$

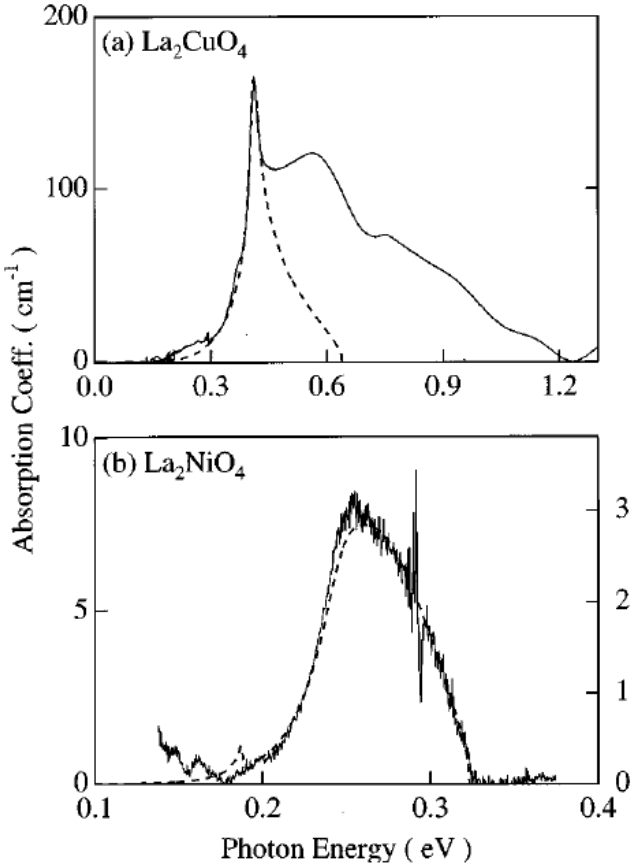
THE main hole dressing is
"A PHONON PLUS TWO MAGNONS"

This is an important contributor to the MIR optical spectrum
Jose Lorenzana, Thilo Kopp, Markus Grueninger, Dirk van der Marel, (1995-2002)

J.D.Perkins et al. ,Phys. Rev. Lett. '7l, 1621 (1993)
Experiment Optical absorption

J. Lorenzana and GAS PRL, 74, 1867 (1995)
Ibid PRB 52 9576 (1995) THEORY

Phonon plus two magnon virtual bound State in Cuprates / Nickelates



J.D.Perkins et al. , Phys. Rev. Lett. '7l, 1621 (1993)
Experiment Optical absorption

J. Lorenzana and GAS PRL, 74, 1867 (1995)
Ibid PRB 52 9576 (1995) THEORY

Taken from Grueninger
Thesis Groningen 1999

Note that the valence of Cu in say $LaSrCuO_4$ (formally 3+) would likely be 2+ with 0ne hole per 2 O in the CuO_2 plane

i.e. Negative charge transfer

Kuiper et al PRL 62 221 (1989) LixNi1-x O

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

Just as in the cuprates
doped holes mainly on O
NOT Ni3+

Ni(1-x)Li(x)O

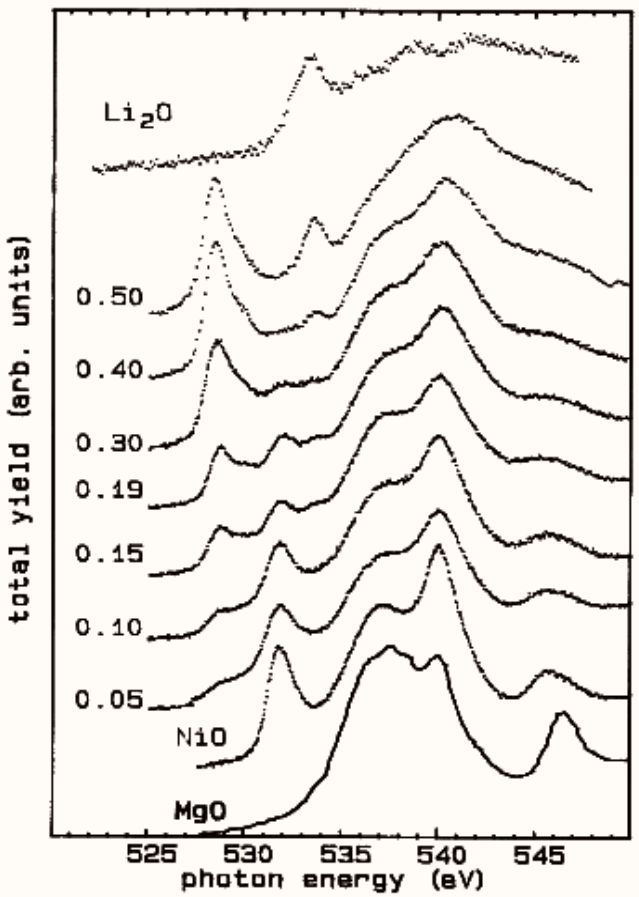
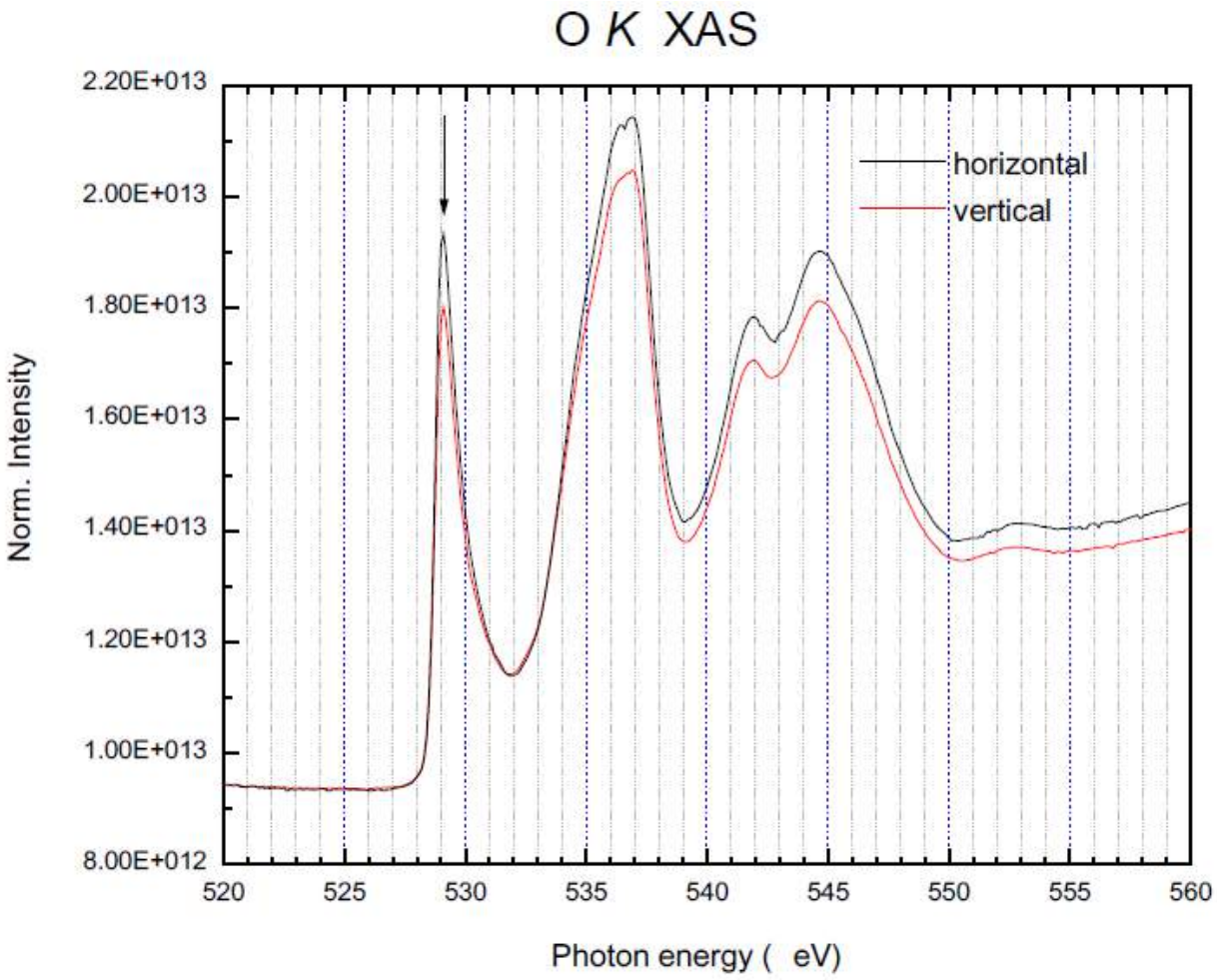


FIG. 1. Oxygen *K*-edge absorption spectra of MgO (Ref. 26), NiO, $Li_xNi_{1-x}O$ for indicated values of x, and Li_2O.

LaNiO3 thin film on LSAT Sutarto, Wadati, Stemmer UCSB



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

Before going on an example of how crystal field splitting and Hunds rule coupling determine the ground state ionic configuration

Ni3+ (d7) in Oh symmetry

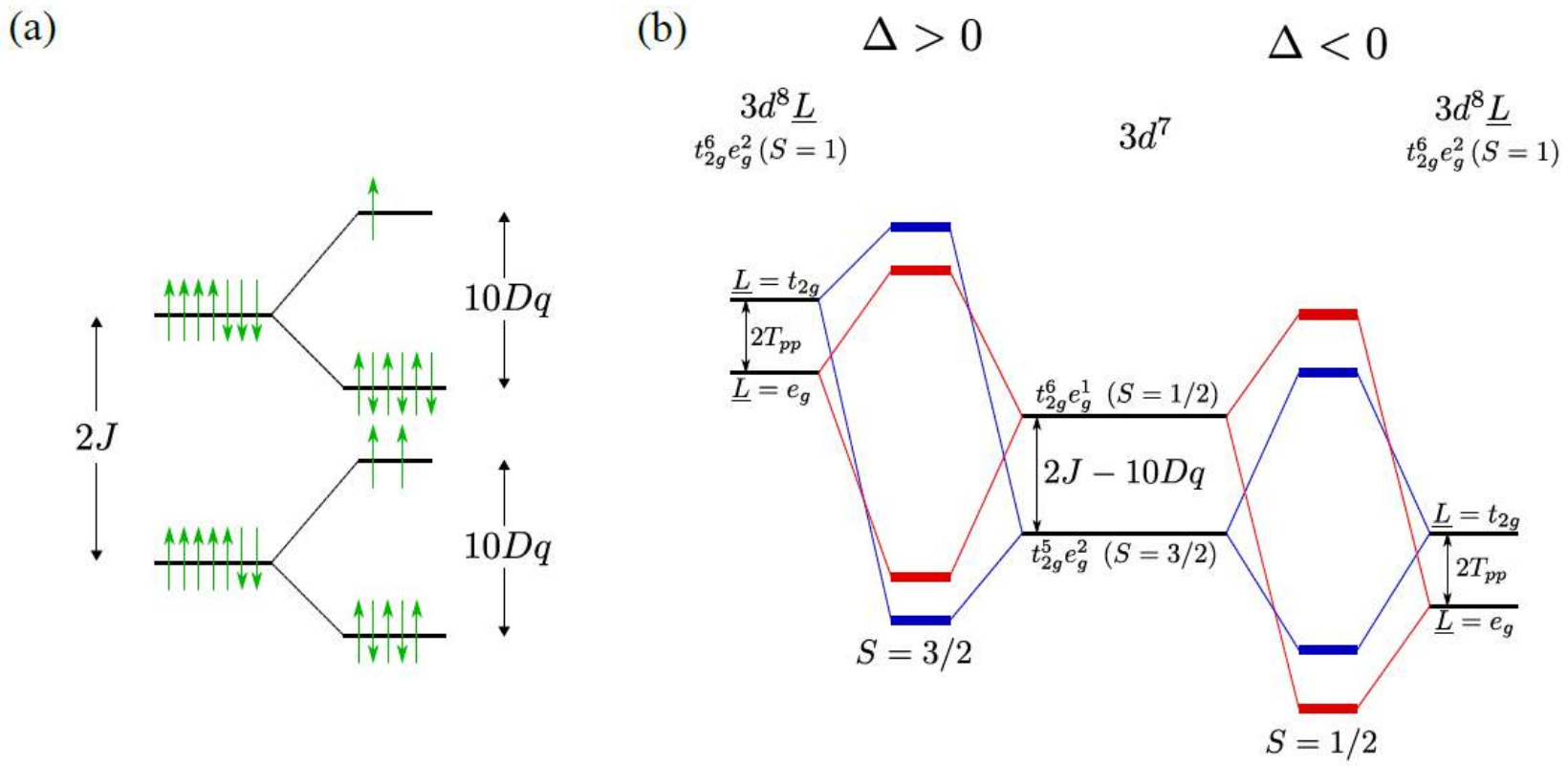


Fig. 1: *(a) The Hund's rule and crystal field energetics are introduced for a Ni^{3+} (d^7) system.*

Results of a Configuration interaction calculation

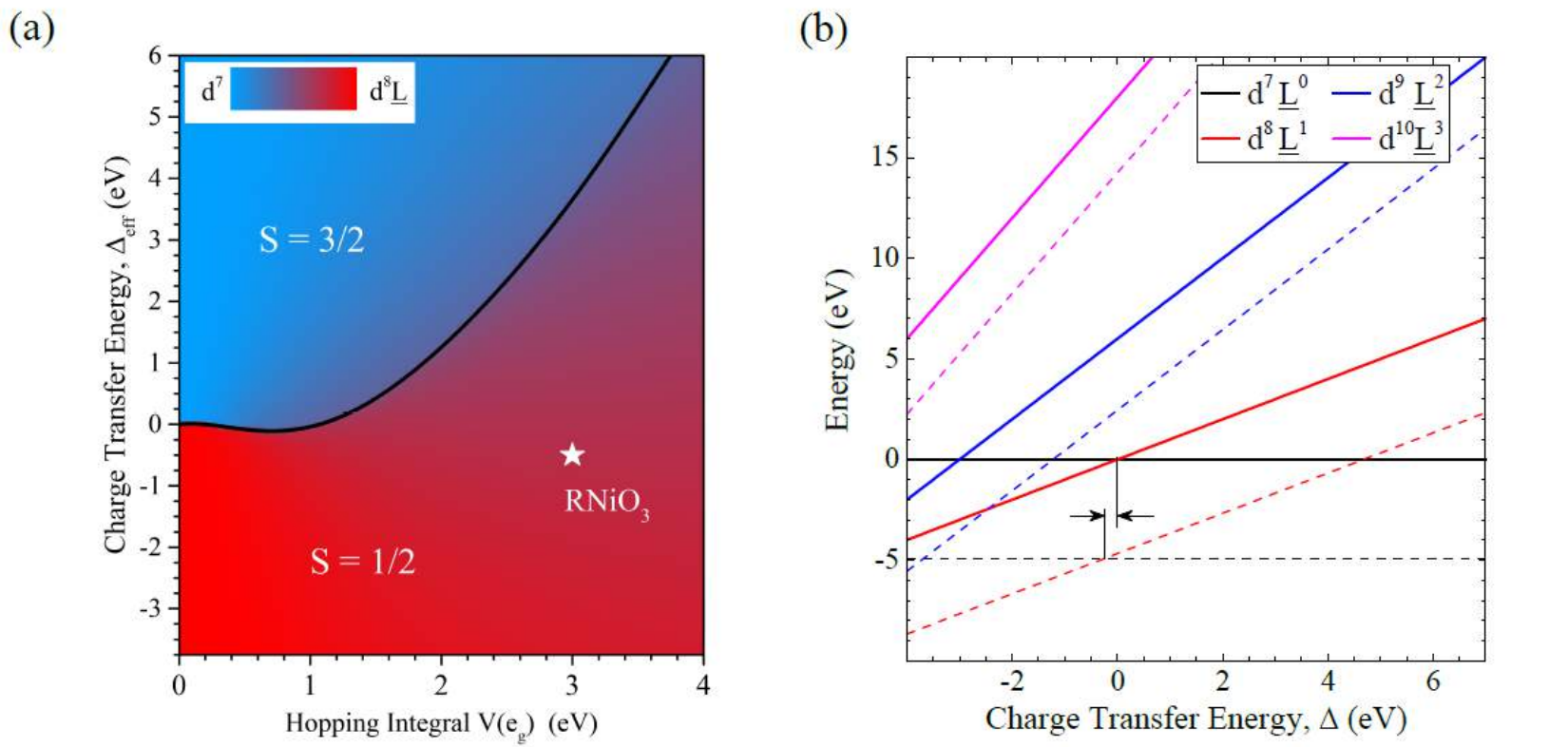
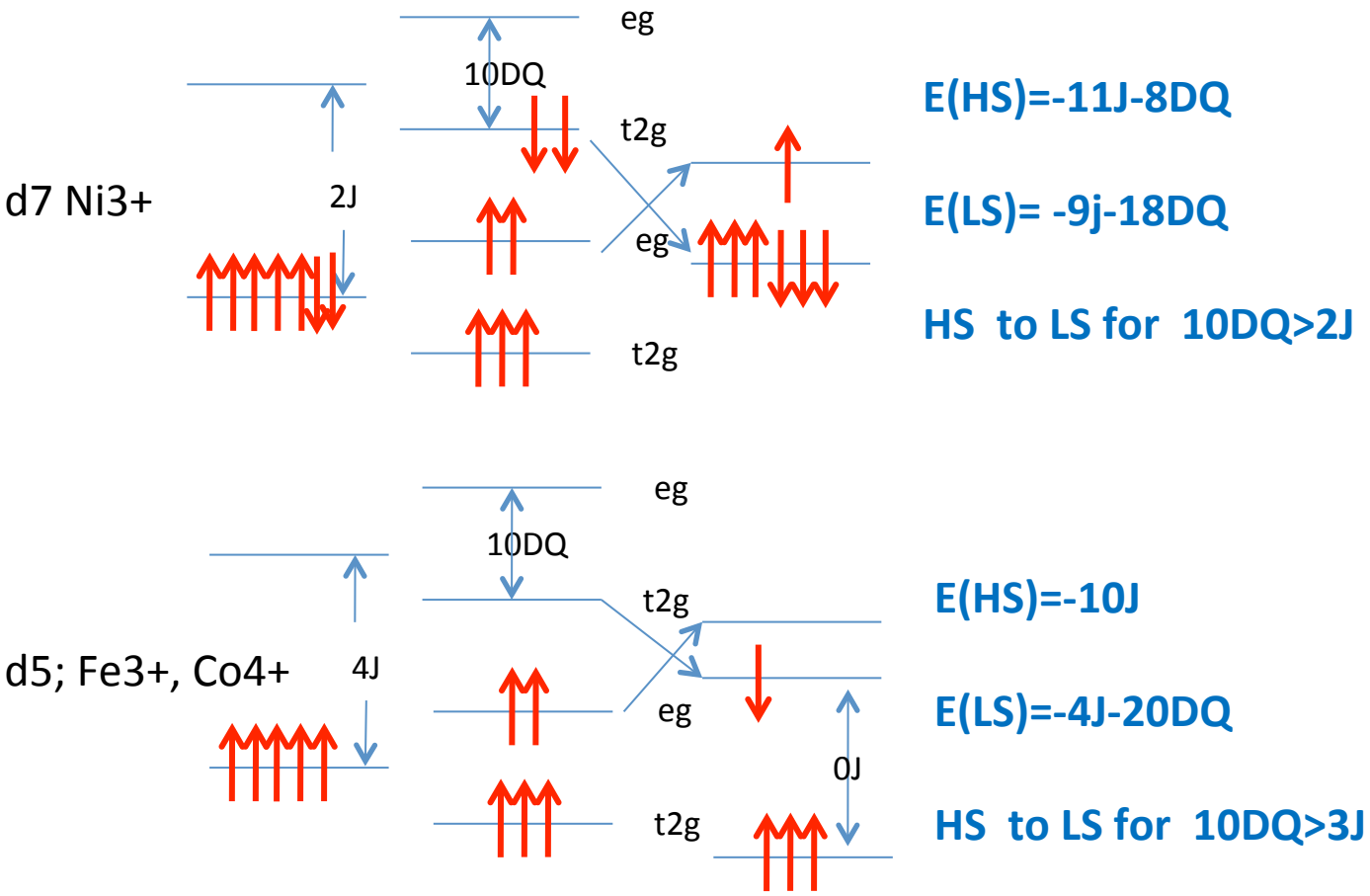


Fig. 2: *Results of a full configuration interaction calculation. (a) The low spin phase space is*

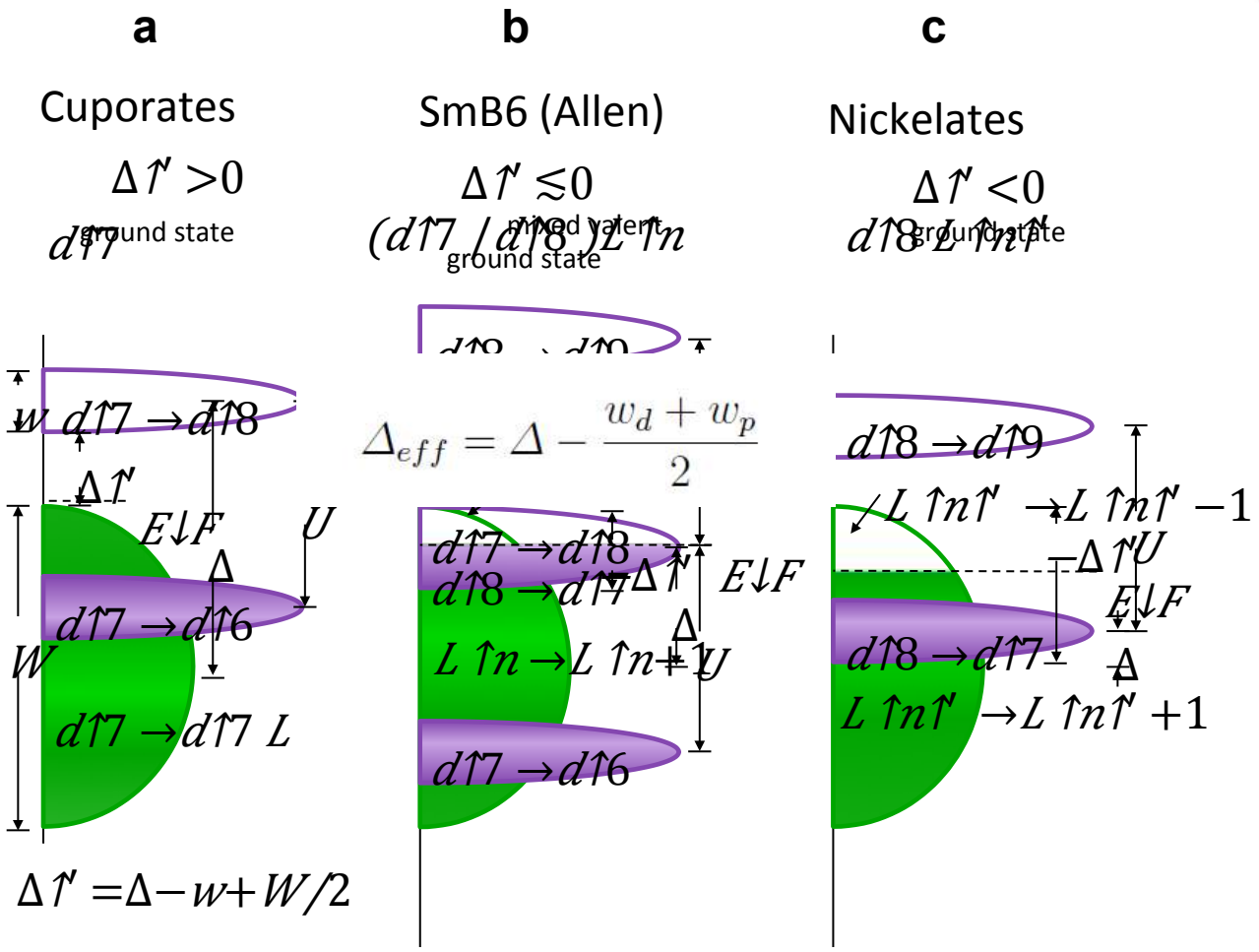
You can understand that for large hybridization low spin can also occur for positive charge transfer energy

Physical picture for high spin to low spin transition



Three cases: Charge transfer, Mixed valent, and Negative charge transfer

$$\Delta_{eff} = \Delta - \frac{w_d + w_p}{2}$$



Recall the O band (18 electrons / unit cell) in 3d perovskite (RENiO3)
For negative CT there would be 1 hole per 3 oxygens and NI (2+) 3d8

Moving from MH to CT to Mixed valent to Negative CT (holes on anions)

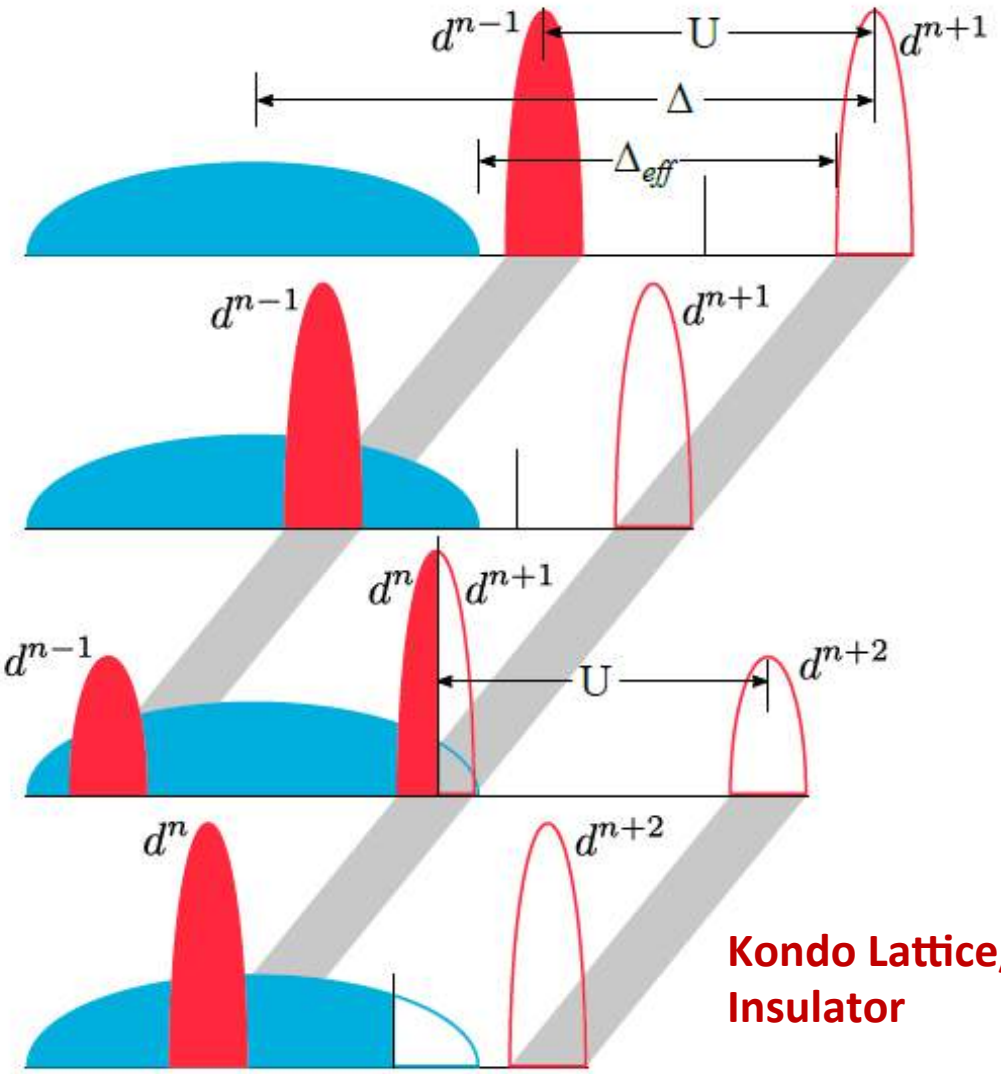
Increasing formal Cation valence

Mott-Hubbard
$|\psi_0\rangle = |d^n\rangle$

Positive Charge Transfer
$|\psi_0\rangle = |d^n\rangle$

Mixed Valence
$|\psi_0\rangle = ?$

Negative Charge Transfer
$|\psi_0\rangle = |d^{n+1}\underline{L}\rangle$



Kondo Lattice/ Kondo Insulator

The mixed valent state wave function or ground state has been a mistery for as long as I can remember

- Could be charge ordered Verwey transition in Fe3O4
- Could be a charge density wave.
- We will describe later that it could also form a coherent state where the mixed valence is in momentum SmB6
- Excitonic insulator?
- Could be a simple metal if U and the multiplet splittings are much less than the d-d intercite hopping
- Perhaps you have other ideas

Nickelates RENiO3: formally Ni would be 3+ d7 (low spin)
However Ni3+ is a strong Jahn Teller Ion but there is no Evidence for distortions resulting from this

Torrance et al PRB 42, 8209

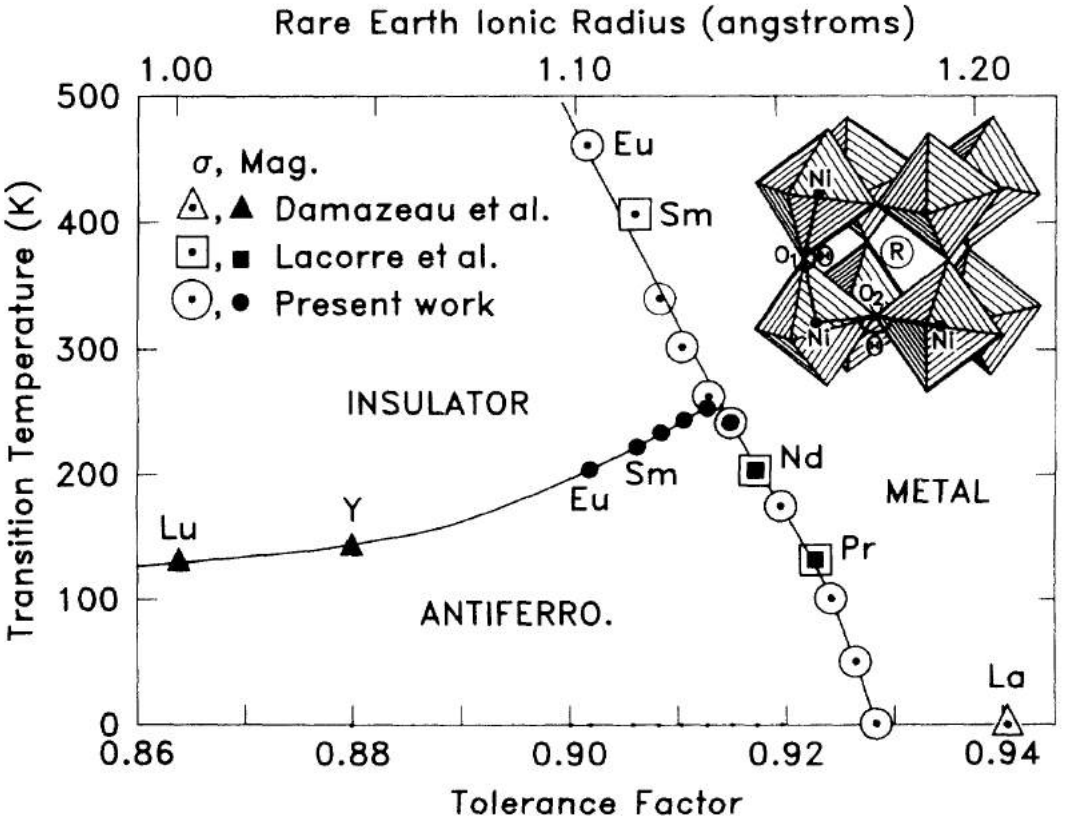


FIG. 2. Insulator-metal-antiferromagnetic phase diagram for $RNiO_3$ as a function of the tolerance factor and (equivalently) the ionic radius of the rare earth (R).

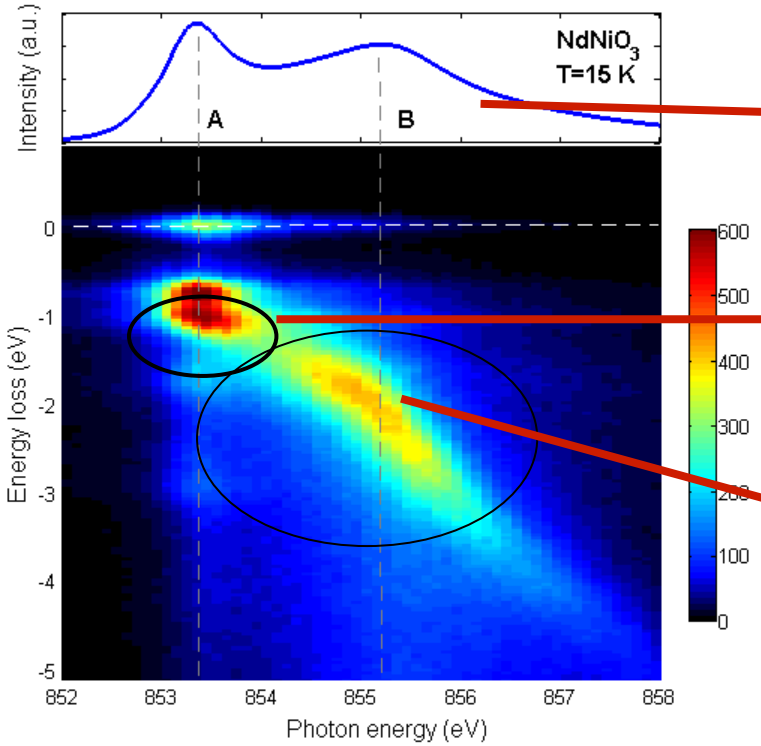
Aside from the XAS of O Recent RIXS point to negative charge transfer gap system (results obtained by)

Valentina Bisogni and
Thorsten Schmitt from PSI

Sara Catalano, Marta
Gibert , Raoul Scherwitzl
Jean-Marc Triscone, and
Pavlo Zubko From Geneva

Valentina Bisogni et all Nature communications in press

RIXS map of $NdNiO_3$ – 15 K insulating phase



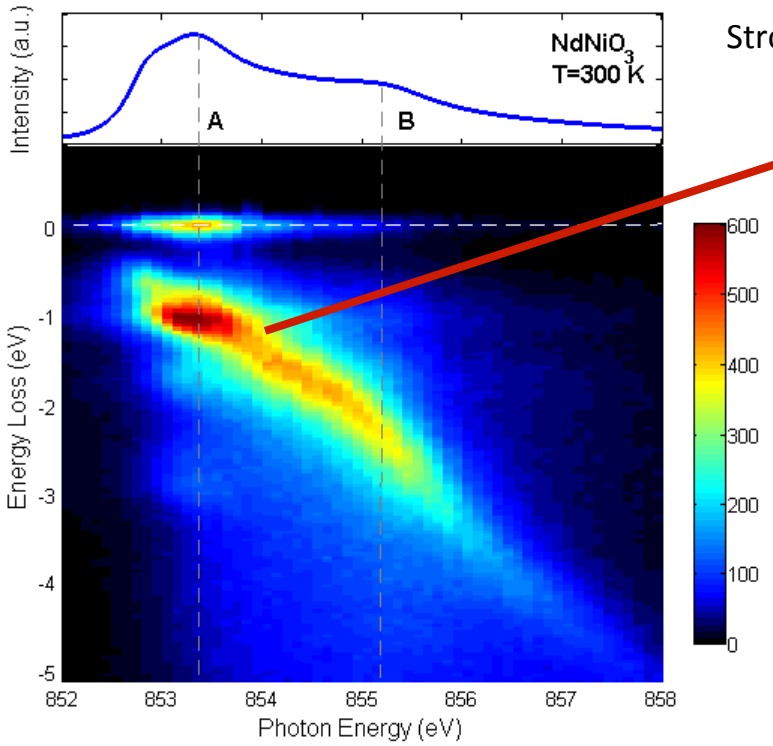
Ni 2p XAS energy region : Up to now the peaks A and B were considered to be ,multiplet structure in the final 2p5 3d8 local states

RIXS demonstrates that a local d-d like description is OK for peak A with photon energy independent peak positions in RIXS

Near linear dependence of the "Loss" energy With photon energy show that this is not RIXS but more like x ray flourescence.

So peak A in XAS involves the excited d Electronand Ni 2p core hole intimately bound while peak B must involve an excitation into a delocalized continuum band state. The continuum starts at most 1 eV above the bound state. This has implications for the ground state and low energy excitations and the properties.

RIXS map of $NdNiO_3$ – 300 K Metallic Phase



Strong T dependence of the XAS

Here the continuum states merge
With the "bound states or resonances"
Extending to zero loss energy i.e.
A METALLIC STATE

High oxidation states

- In general we expect the charge transfer energy to strongly decrease for higher oxidation states
- This would mean a different starting point i.e.
- $Cu3+ \rightarrow Cu2+\underline{L}$ $Ni3+ \rightarrow Ni2+\underline{L}$
- $Co4+ \rightarrow Co3+\underline{L}$ $Fe4+ \rightarrow Fe3+L$ $Mn4+???$

  The charge degrees of freedom are mainly on Oxygen

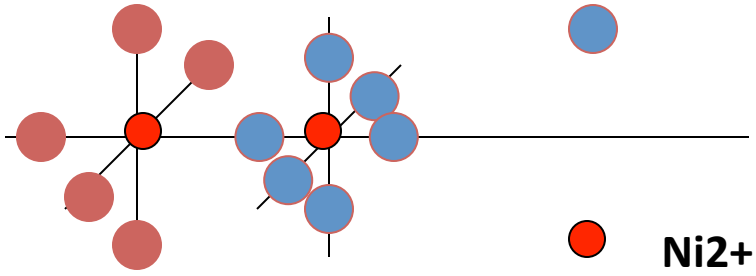
BASIC STARTING POINT FOR NEGATIVE CHARGE TRANSFER GAP

- high density of large U Ni2+(d8) states with strong hybridization and exchange with the holes on O.
- THIS IS An ANDERSON LATTICE PROBLEM BUT WITH Vkd TOO LARGE FOR A Schrieffer Wolff transformation to KONDO.
- Also for KONDO we have a Nozieres exhaustion principle at work i.e. only enough holes to screen the spins of ½ of the Ni's
- Would likely remain metallic as in LaNiO3 (BAD METAL) UNLESS
- We include strong electron phonon interaction in Tpd

Negative charge transfer yields Charge disproportionation without moving charge

FIRST suggested by T. Mizokawa, D. I. Khomskii, and GAS Phys.Rev. B 61, 11263 (2000).

Consider ReNiO3 as Ni2+L (1 O 2p hole per 3 O)
Then each Ni is surrounded by on average 2 L holes in an octahedron of O.



d8L + d8L ---- d8 +d8L2

Ni2+ no JT

Each second Ni2+ has a STRONGLY COMPRESSED octahedron of O with two holes of Eg symmetry in bonding orbital's I.e. d8 L2 (S=0)

=

No Jahn Teller problem anymore
BOND DISPROPORTIONATION

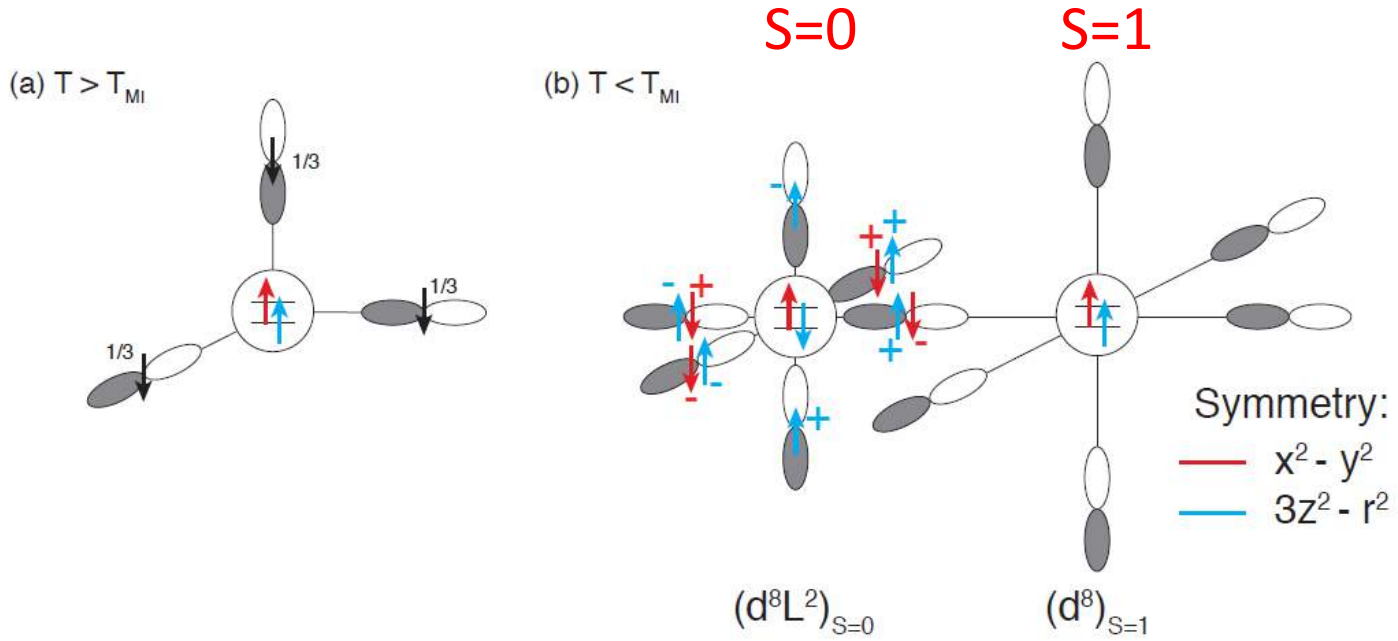
Charge disproportionation without charge transfer

Steve Johnston, Mona Berciu, GAS arXiv:1310.2674 , Phys. Rev. Lett. 112, 106404 (2014)

Hartree Fock and exact diagonalization

FIRST suggested by T. Mizokawa, D. I. Khomskii, and GAS Phys.Rev. B 61, 11263 (2000).

See also H. Park, A. J. Millis, and C. A. Marianetti, PRL 109, 156402 (2012). B. Lau , A. J. Millis, Phys. Rev. Lett. 110, 26404(2013) and D. Puggioni, A. Filippetti, and V. Fiorentini, Phys. Rev.B 86, 195132 (2012).

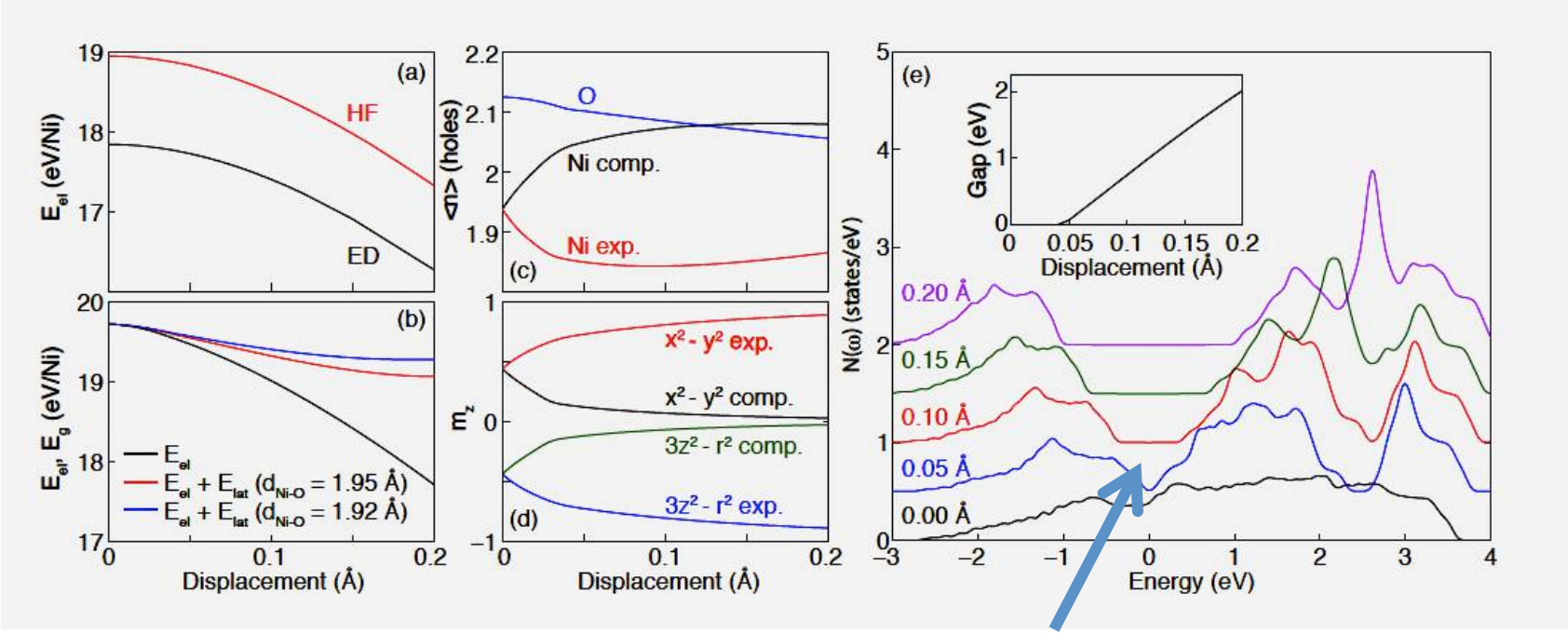


Crystalized Bipolarons (electron phonon) in 1/2,1/2,1/2, superstructure

In the insulating phase NOTE THAT THE SYMMETRY OF THE SHORT BOND LENGTH STATE IS EXACTLY THE SAME AS NI4+ LOW SPIN.

There is no phase transition between the bond disproportionated and Charge disproportionated states but rather a crossover.

Total energy, charge density, magnetic moment, and density of states vs. checker board O octahedron compression/ expansion



Note the gap forming
for displacements of > .09A

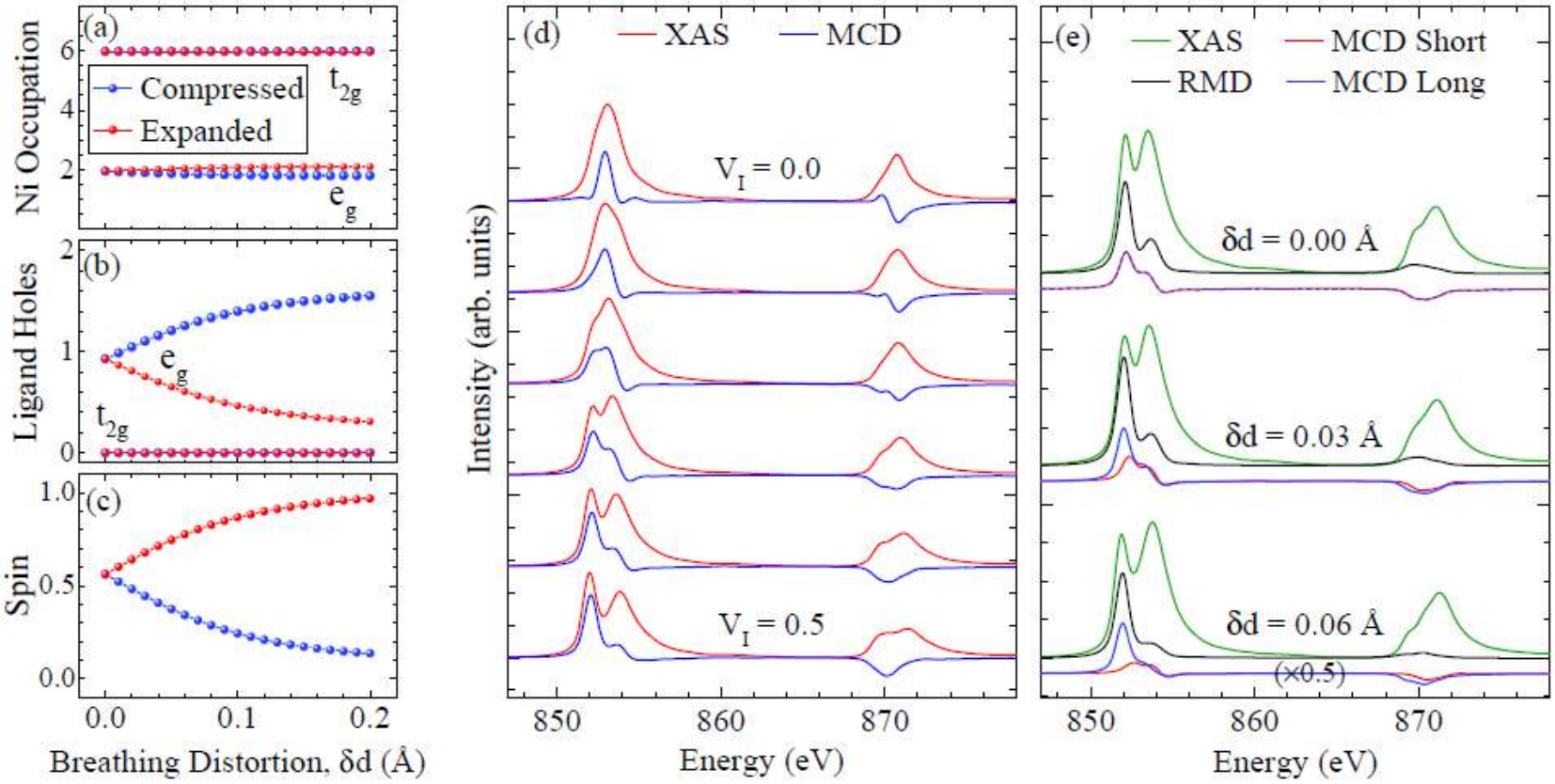
Nickelates in the magnetic phase have a 1/4,1/4,1/4 magnetic superstructure due to anti ferromagnetic ordering which has been assumed to be up up:down down in all three directions

The Johnson calculation predicts Up zero; down zero

Lets look at resonant magnetic x ray diffraction

Bond disproportionation and dynamical charge fluctuations in the perovskite rare earth nickelates

R. J. Green,[1,2,3,*] M. W. Haverkort,[3] and G. A. Sawatzky[1,2]



Note the short bond length has virtually no Magnetic diffraction intensity i.e. S~0 Long bond S~1

Recent experiments by Mathias Hepting MPI Stuttgart and coworkers on $NdNiO_3$ thin epitaxial films show magnetic diffraction energy dependence in almost too perfect agreement with the theory

To Be Published

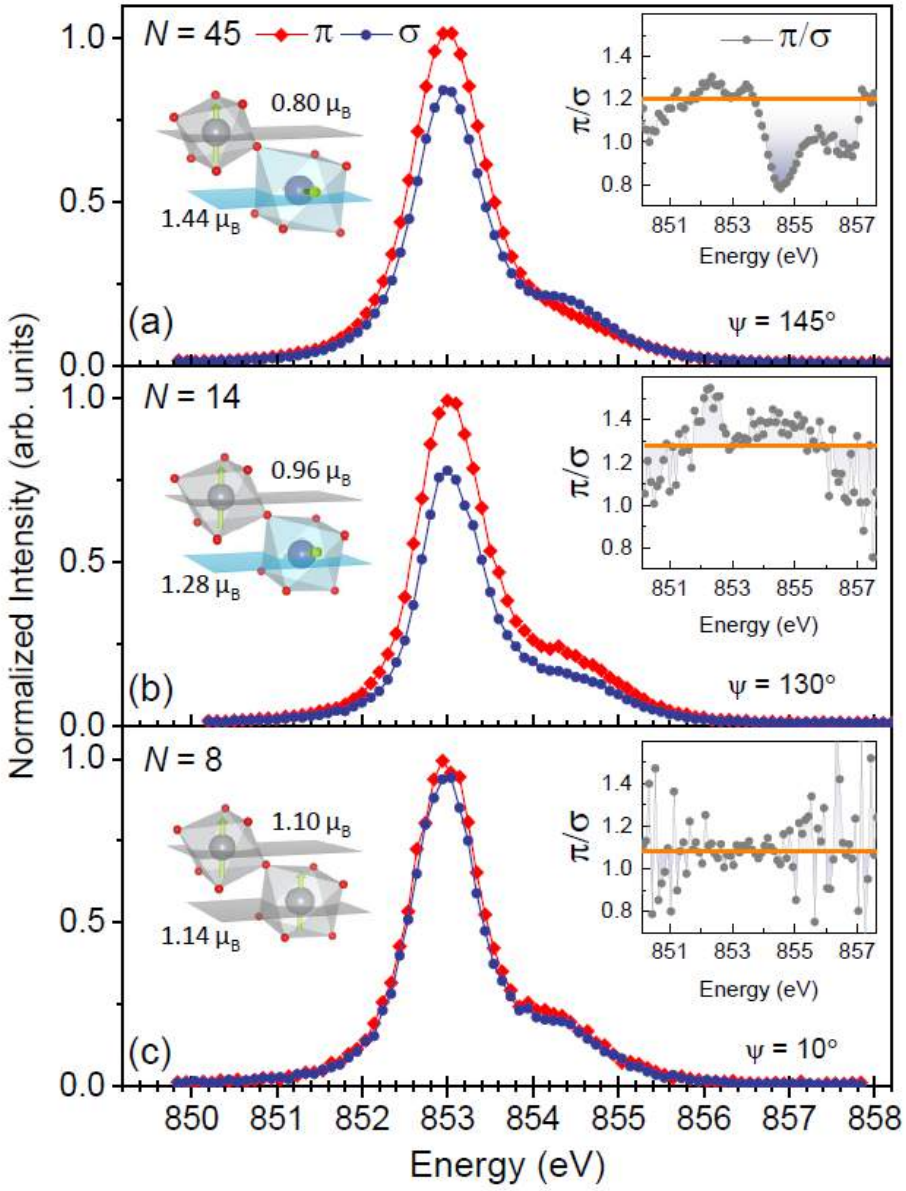


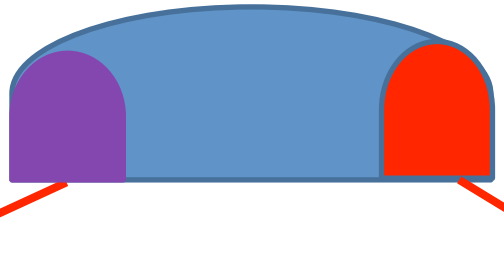
Fig. 5: **Energy dependence of magnetic scattering and tuning of mag-**

How are systems like Ba or SrBiO3 different?

- Weak correlation if any
- Band theory should work
- Is there charge disproportionation? 2Bi4+-- Bi3+ + Bi5+ or Bi3+ and one hole per Bi in the O 2p band
- How about electron phonon coupling?
- Is this in the end similar to Nickelates? Also (1/2,1/2,1/2) superstructure

Kateryna Foyevstova et al
Phys. Rev. B 91, 121114(R) (2015

Projection of O 2p molecular orbitals onto the O 2p band structure in a perovskite structure



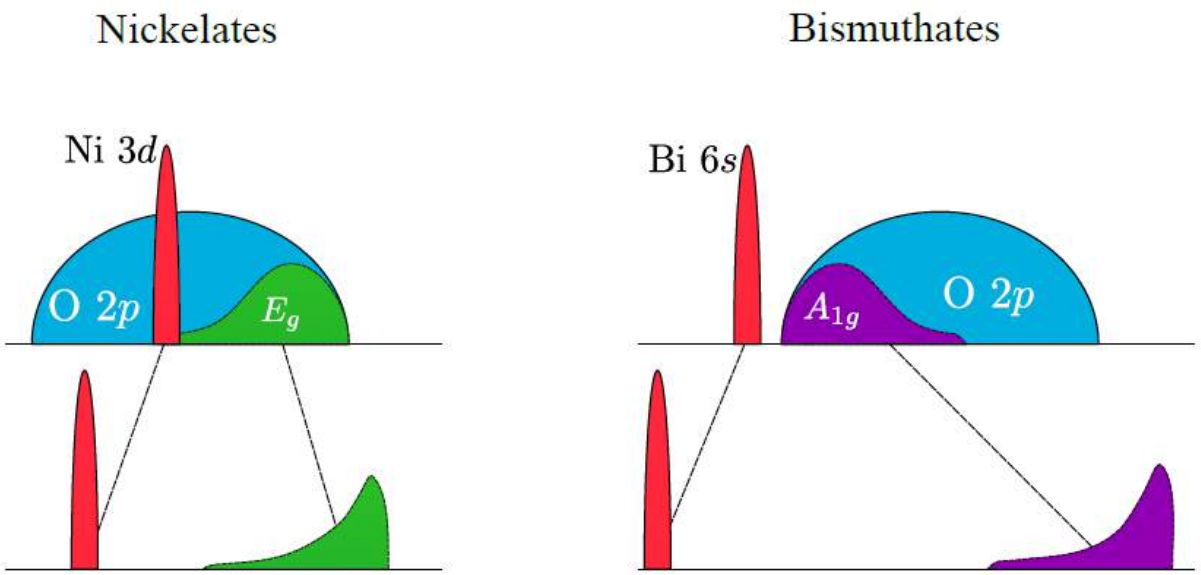
A1g symmetry combination of O2p states in an octahedron Mix with s states i.e Bi 6s states

Eg symmetry combination of O2p states In an octahedron Mix with eg d states i.e. Ni3d eg

GAS and Robert Green Julich Lectures sept 2016

Before hybridization
Nid7 Bi6s1 below O

After hybridization
Note the “bound “state
Of Eg or A1g symmetry

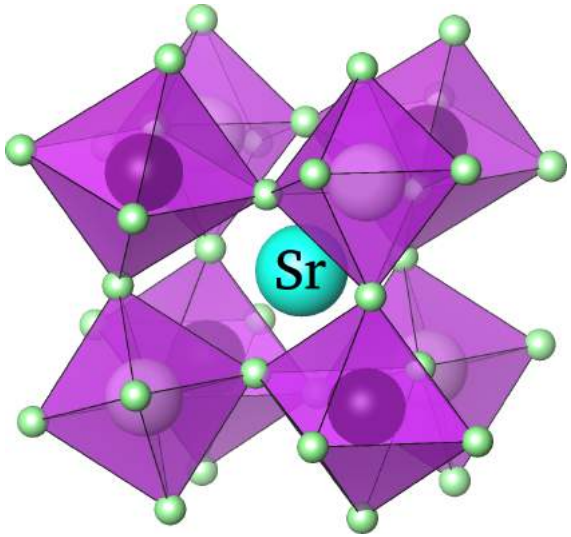


The Bi6s-O 2p hybridization
\is extremely large from DFT

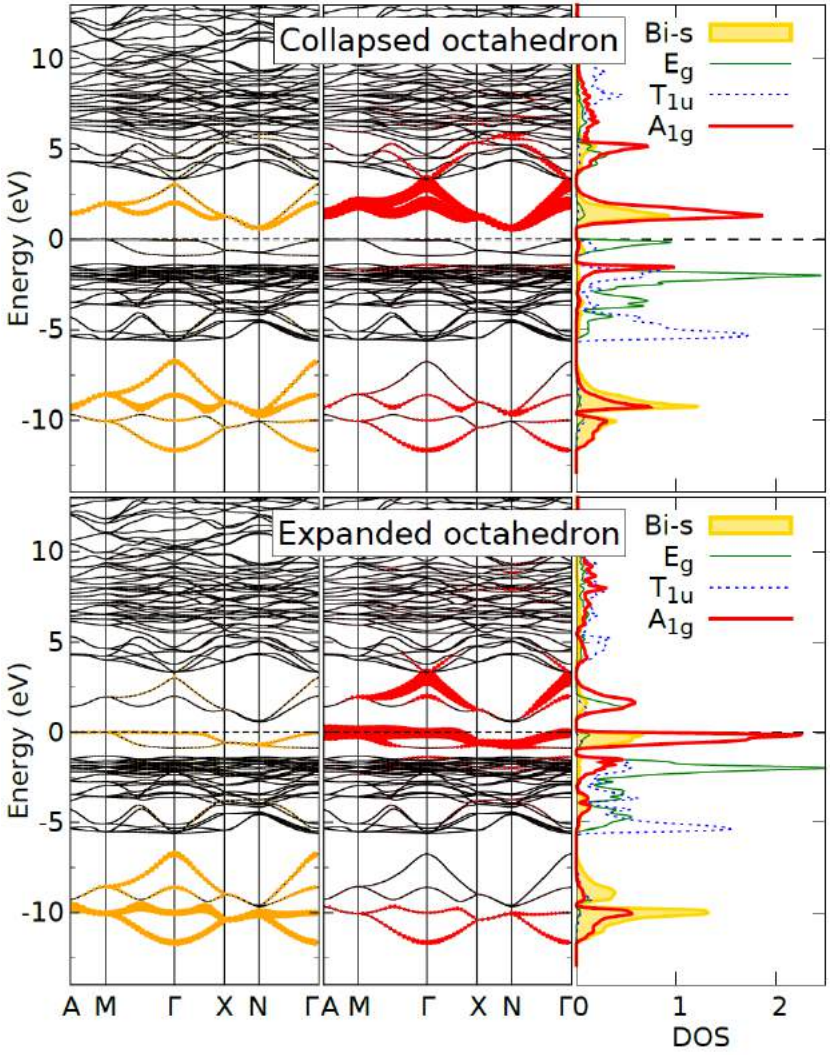
Hybridization –bond disproportionation effects in bismuth perovskites

Kateryna Foyevstova et al

Phys. Rev. B 91, 121114(R) (2015



In bond-disproportionated state, holes condense onto A_{1g} O 2p +Bi6s molecular orbital states of the collapsed octahedra



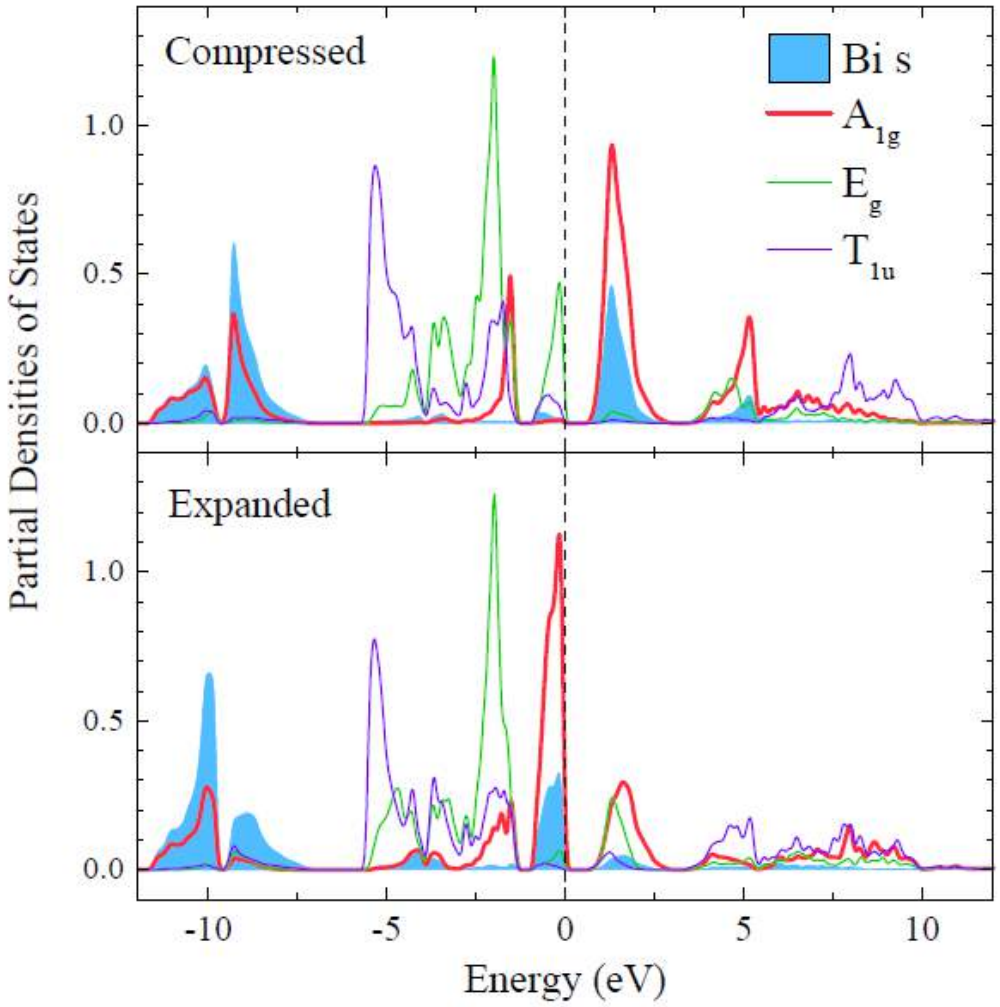
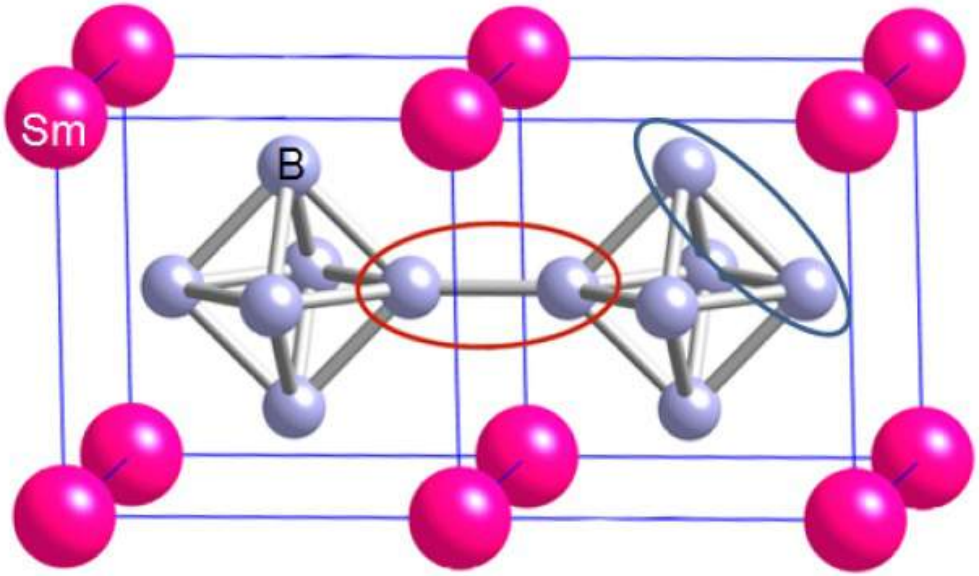


Fig. 8: *Projected densities of states for the compressed (upper) and expanded (lower) octahedra in the low temperature, breathing distorted phase of* $SrBiO_3$.

Bulk SmB6 a mixed valent, “in momentum space,” ground state

Alfred Cheung, Robert Green, Mona Berciu,
Ilya Elfimov and George Sawatzky

Physics department and Max Plank/UBC
center for quantum materials



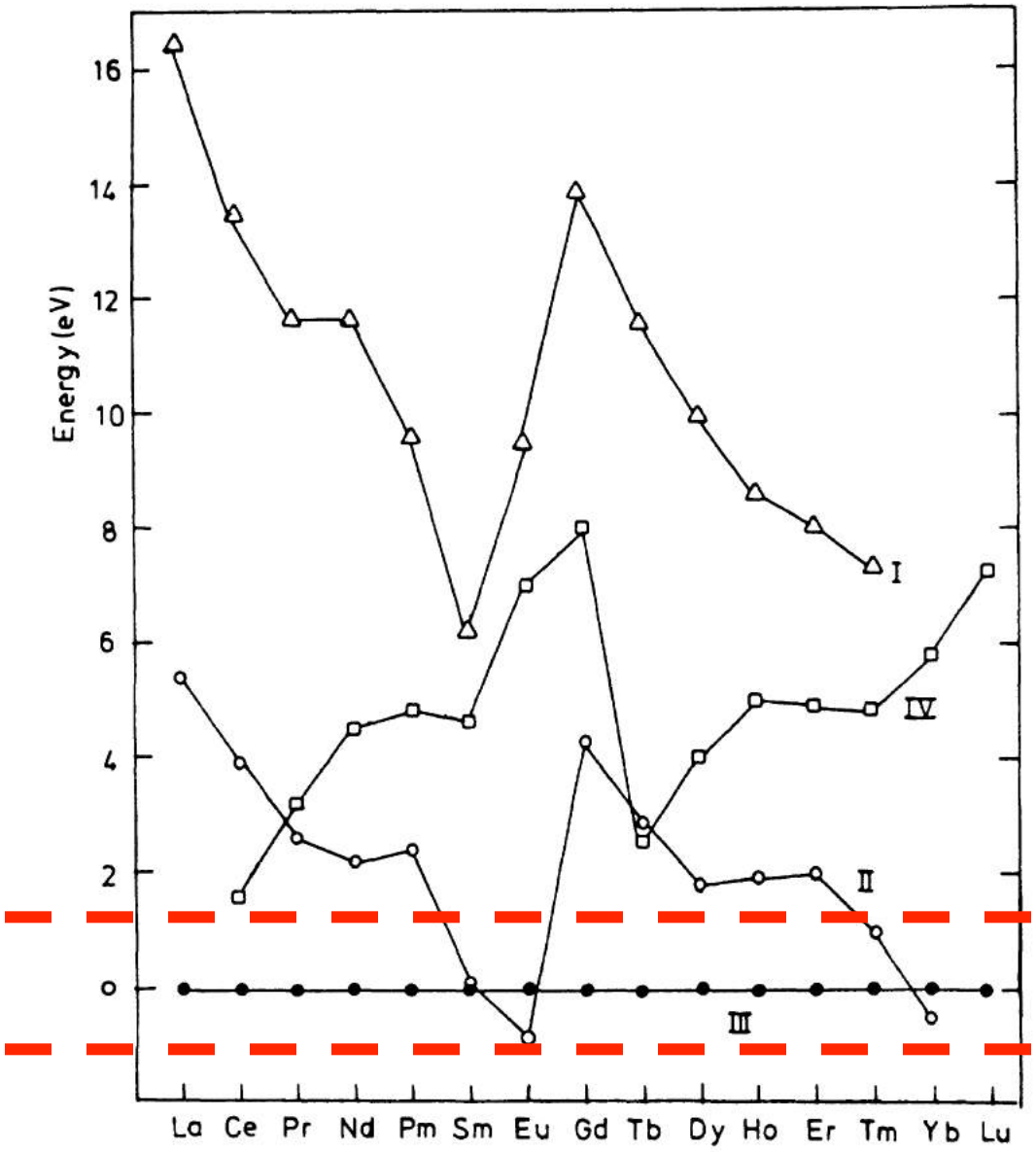
Sm has 24 B NN

From extensive studies in 60's and 90's
Very low work function
Very unstable and complicated surfaces
Great thermionic emitters

VERY recent (Piers) potential topological Insulators.

SmB6 is strongly mixed valent from numerous studies; spectroscopy XPS, XAS, EELS, ME and optics and magnetic susceptibility

close to 50/50 ; 2+(f6)/3+(f5)
charge is compensated with 5d/Bp
band occupation changes



VanderMarel etal PRB 37 , 10674 (1988)

Hunds' Rule

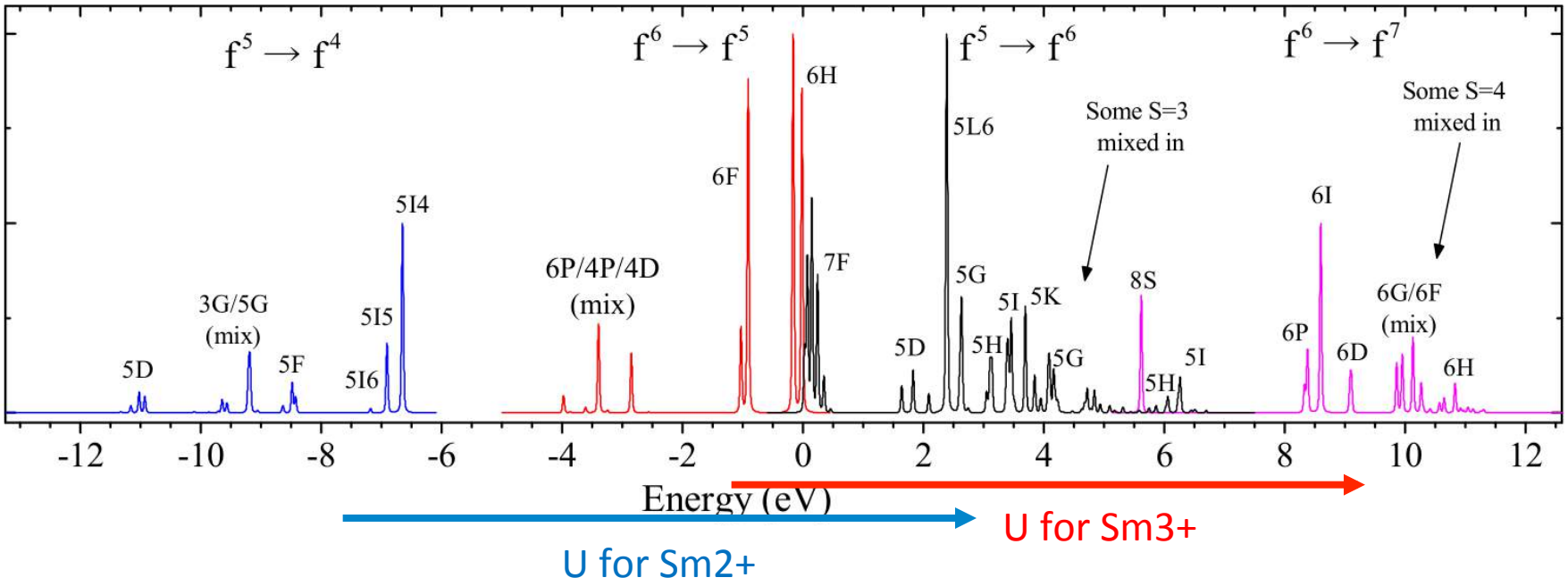
J=L-S

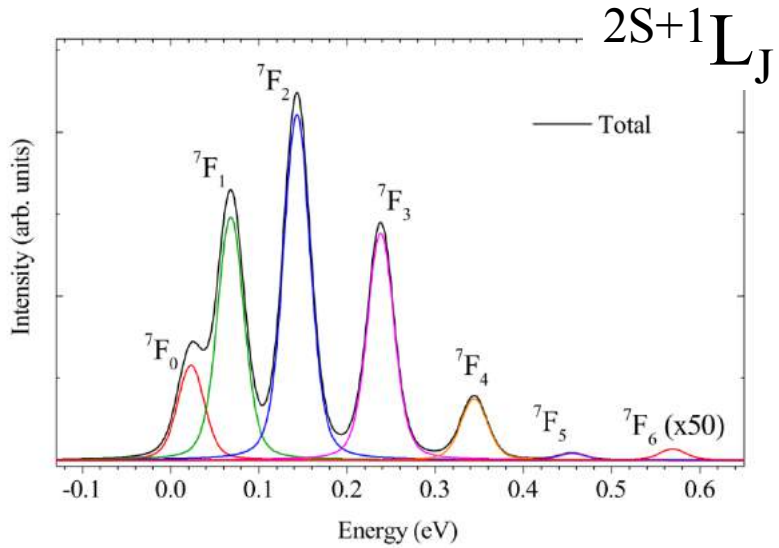
J=L+S

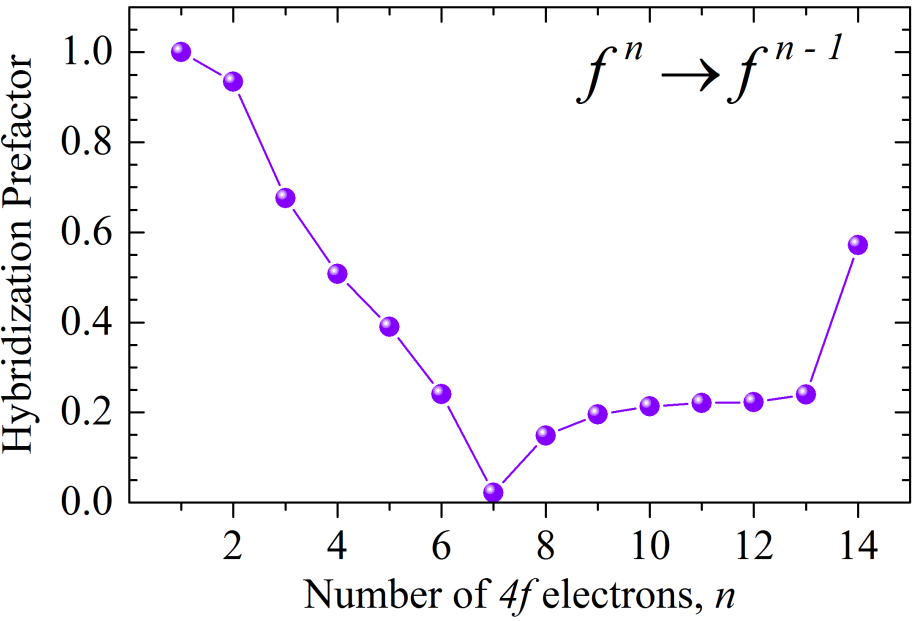
RE element	No F electrons	S	L	J
Ce 3+	1	1/2	3	5/2
Pr 3+	2	1	5	4
Nd 3+	3	3/2	6	9/2
Pm 3+	4	2	6	4
Sm 3+	**5**	**5/2**	**5**	**5/2**
Eu 3+ orSm2+	**6**	**3**	**3**	**0**
Gd 3+	7	7/2	0	7/2
Tb 3+	8	3	3	6
Dy 3+	9	5/2	5	15/2
Ho 3+	10	2	6	8
Er 3+	11	3/2	6	15/2
Tm 3+	12	1	5	6
Yb 3+	13	½	3	7/2
Yb 2+	14	0	0	0

J=5/2 is very different from one electron missing in a full DFT SO split Sm2+ band

SmB_6 – Multiplets and Spin-orbit splitting Robert Green electron removal and addition spectra for the free ions oin a mixed valent wcenario







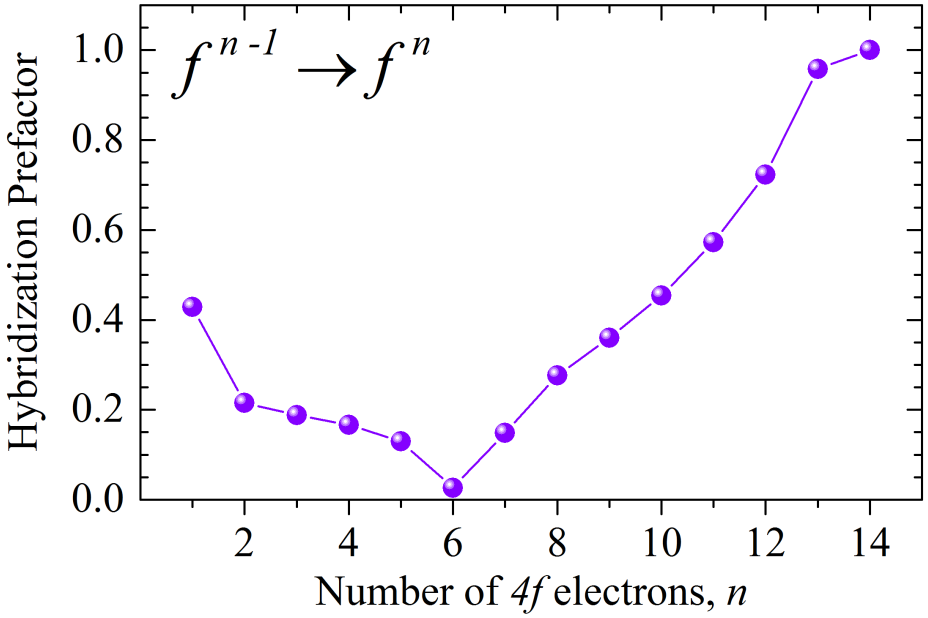
Coefficients of fractional parentage

Sm 2+7F0 to Sm3+ 6H5/2 ~ 0.03

Sm3+ 6H5/2 to Sm2+7Fo ~ 0..03

From Hirst PRB 15,1 (1977)

Gerken J. Phys. F: Met. Phys. **13** (1983) 703-713.

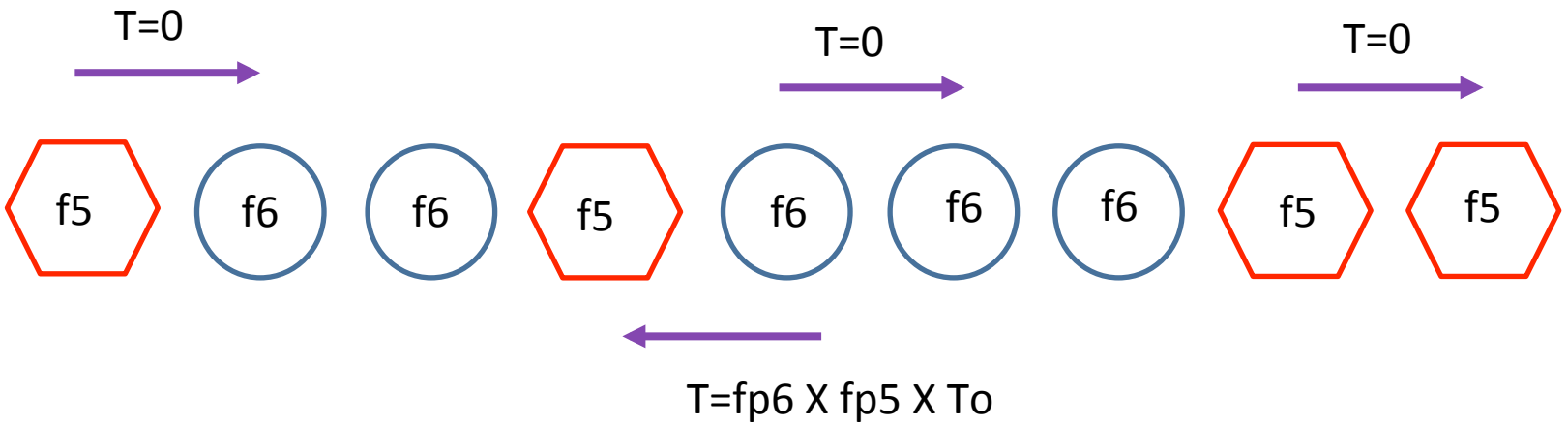


These are the factors reducing the hoping Integrals and increasing the effective mass Because of local atomic correlations

Effective hopping integral pre-factors multiplying the DFT obtained hoping integrals

fp6=coefficient of fractional parentage to remove an electron from the J=0,S=3,L=3 f6 state leaving a f5(J=5/2,S=5/2,L=5) state

fp5= same for the addition of an electron from the J=5/2,S=5/2,L=5 f5 state to J=0, S=3, L=3 f6 state



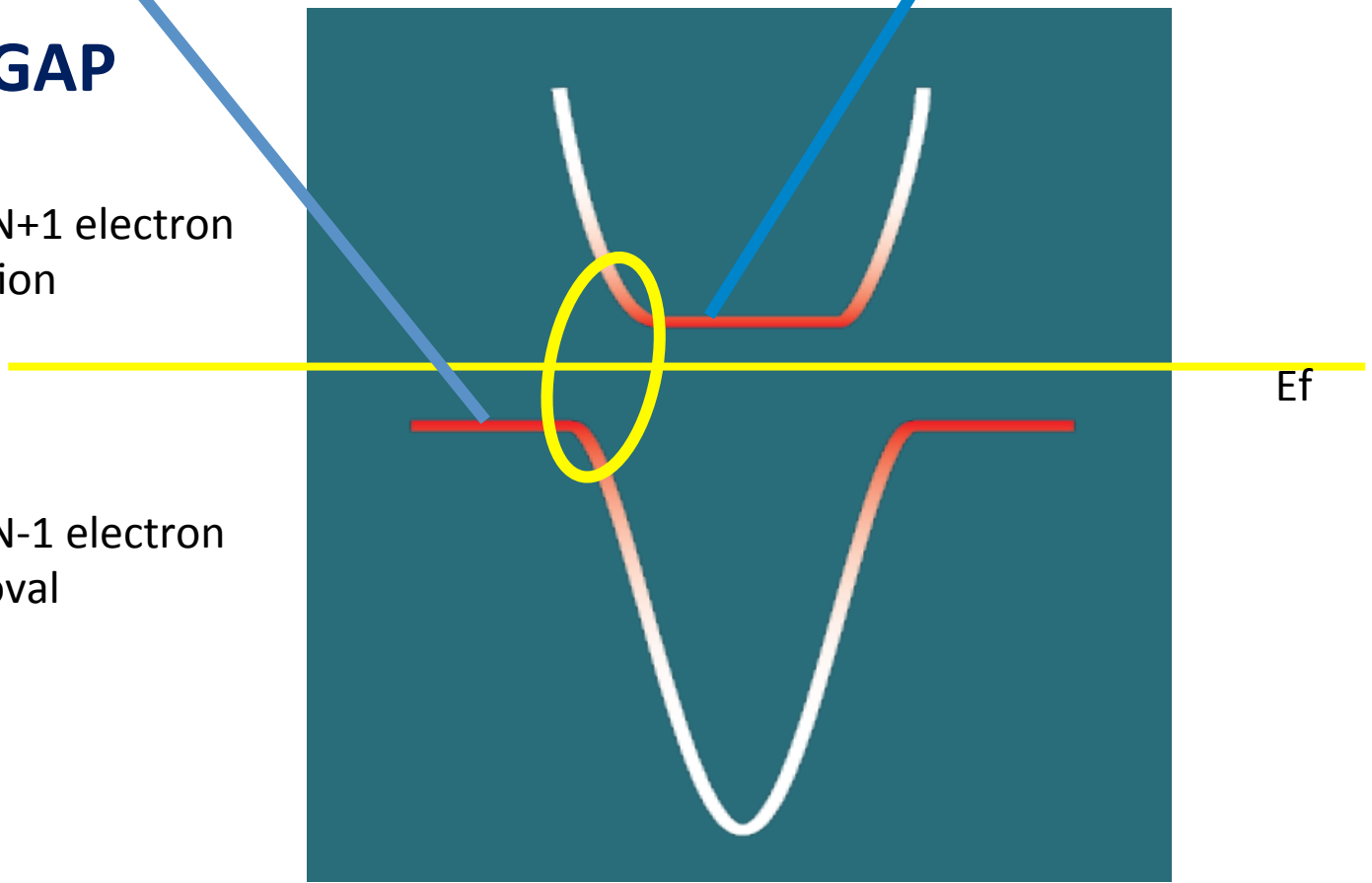
This can be described by a spinless Fermion model

Switch on f-Smd; f-Bp Hybridization

Must be Sm2+J=0 to Sm3+ J=5/2 Exist around K=0

Must be Sm3+ J=5/2 to Sm2+ J=0 Exist around X

INDIRECT GAP



SmB_6 Photoemission: Past and Present

Jonathan D. DENLINGER*, James W. ALLEN[1], Jeong-Soo KANG[2], Kai SUN[1], Byung-Il MIN[3], Dae-Jeong KIM[4] and Zachary FISK[4] arXiv:1312.6637

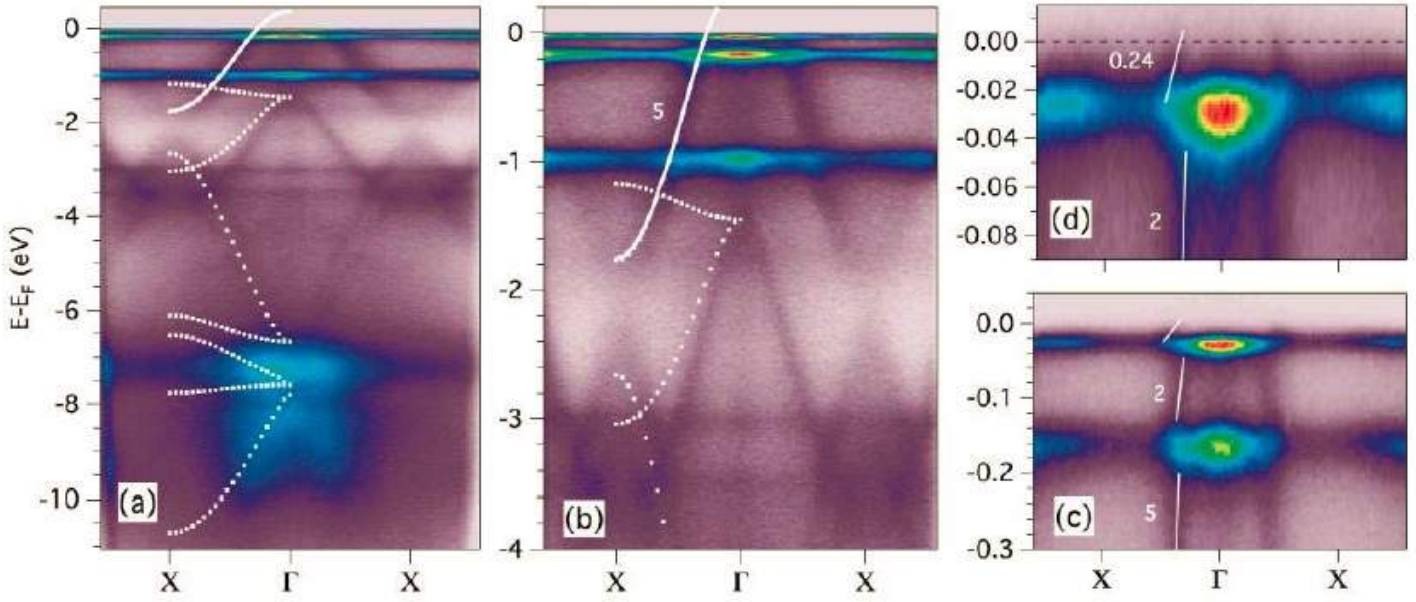


Fig. 4. (Color online) (a-d) Progressive zoom of the X-□-X valence band spectra measured at h□=70 eV using a sum of LH and LV photon polarizations and with comparison to theoretical B 2*p* (dotted) and 5d (solid) bands from LaB_6. X-point *d*-band velocity values in units of eV-Å are also labeled.

Summary

- Oxides with formally high oxidation states - negative CT
- The mobile charge degrees of freedom mainly O 2p bands
- Nickelates - lowest energy O2p hole states- eg symmetry
- Bismuthates- they are of a1g symmetry , in cuprates eg
- Short bond length states- O2p hole (bi) polarons condensing into a bond disproportionated ground state
- SmB6 fascinating “mixed valent state in momentum space”
- Strongly further reduced f-f hoping due to low coeficients of fractional parentage ---- strong atomic increase of effective mass
- The “pseudo” Fermi surface gives a Luttinger count which agrees with the concentration of Sm3+