The explicit role of O 2p states in high oxidation state transition metal oxides

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The main people involved

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- **Sara Catalano Geneva**
- **Marta Gibert Geneva**
- **Raoul Scherwitzl Geneva**
- **Jean-Marc Triscone Geneva**
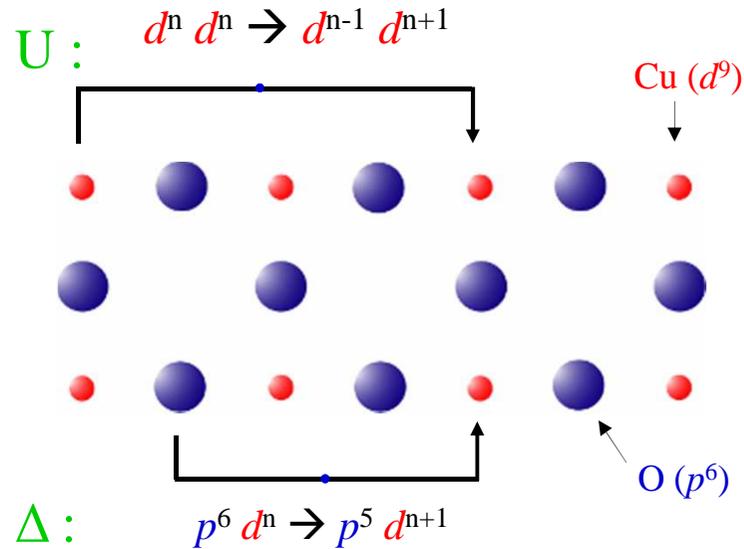- **Pavlo Zubko Geneva**

Summary

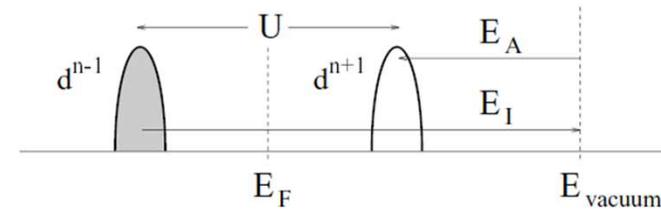# Some examples where anion p states dominate the physics

- Superoxides like KO2 Where K(1+)(S=0) and

(O2 pairs)(1-) (S=1/2) These are ferromagnets

- The Pyrites like FeS2 where Fe(2+ low spin S=0)

(S2 pairs) (2-) (S=0) form valence and conduction bands

- Solid Oxygen O2(S=1) antiferro T<40K (Hunds rule J=1.3eV)

- Cuprate superconductors, Zhang Rice singlets, doped holes on O
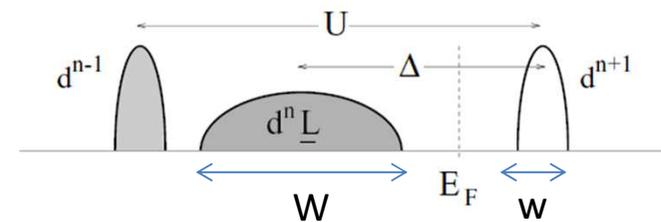
- CrO2 self doped ferromagnet

- And now many more

Correlated Electrons in a Solid

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

Cu (d^9)

O (p^6)

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

(a) Mott-Hubbard insulator

d^{n-1} U d^{n+1} E_A

E_I

E_F E_{vacuum}

(b) Charge transfer insulator

d^{n-1} U d^{n+1}

Δ

$d^n \underline{L}$

E_F

W w

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

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

E_I ionization energy
E_A electron affinity energy
E_M Madelung energy

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

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

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,

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

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-
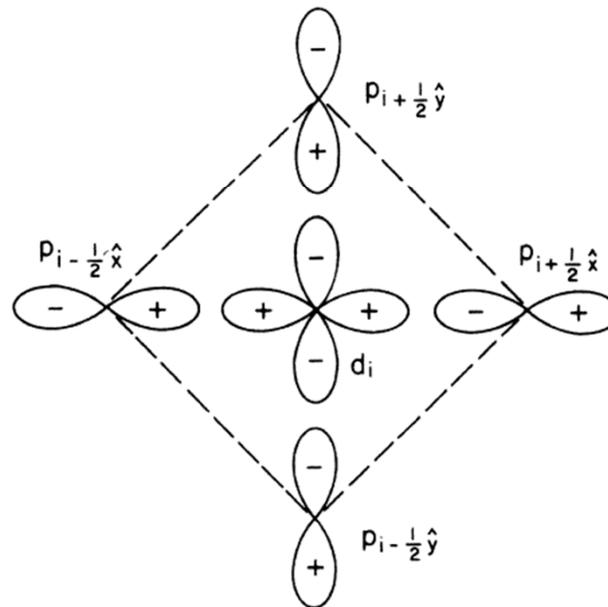

FIG. 1. Schematic diagram of the hybridization of the O hole ($2p^5$) and Cu hole ($3d^9$). The signs $+$ and $-$ represent the phase of the wave functions.
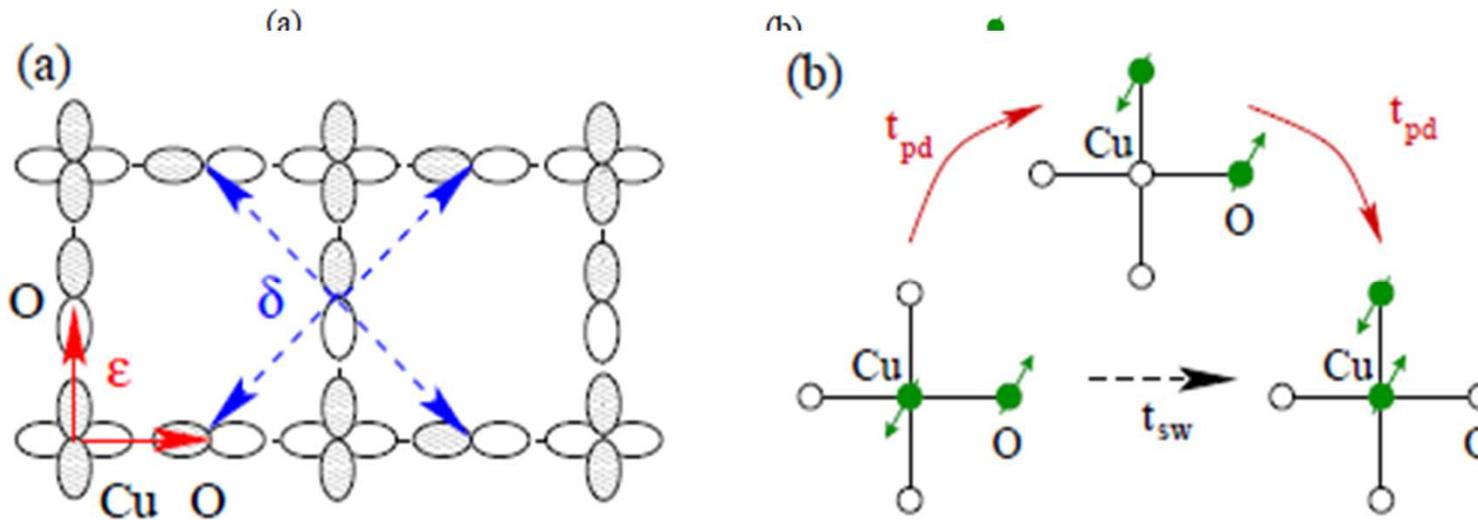
THE MODEL BASICALLY 3 BAND

$$H_{3B} = T_{pd} + T_{pp} + \Delta_{pd} \sum n_{l+\epsilon,\sigma}$$

$$+U_{pp} \sum n_{l+\epsilon,\uparrow} n_{l+\epsilon,\downarrow} + U_{dd} \sum n_{l,\uparrow} n_{l,\downarrow} \quad (1)$$
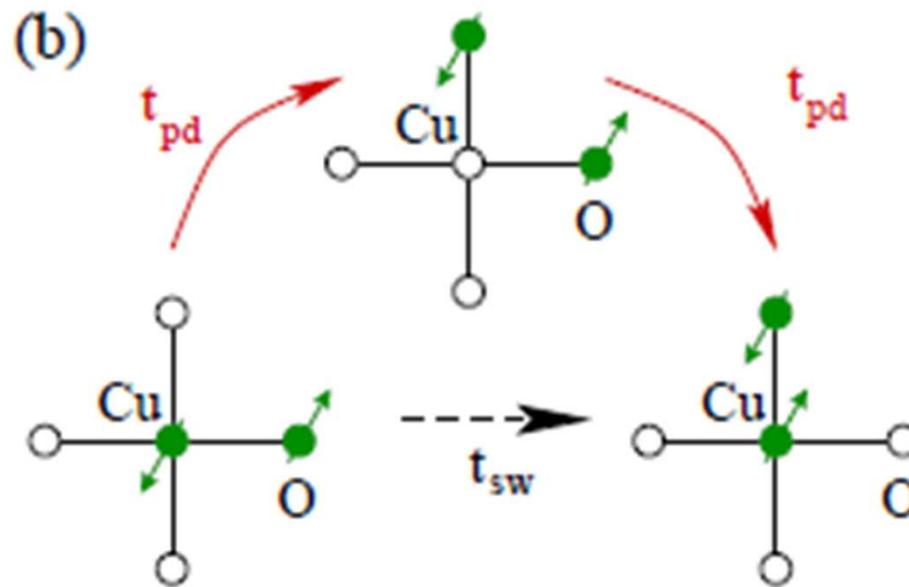
$$H_{\text{eff}} = T_{pp} + T_{\text{swap}} + H_{J_{pd}} + H_{J_{dd}} \quad (2)$$

$$H_{J_{dd}} = J_{dd} \sum \overline{S}_{l\pm2\epsilon} \cdot \overline{S}_l \Pi_\sigma (1 - n_{l\pm\epsilon,\sigma})$$

(a)

(b)

The Tswap term is very important s and it results in an
 effective O 2p-O2p hoping with a spin flip and a
corresponding spin flip on the common Cu neighbor
In a single CuO4 molecule this would be exactly the ZR singlet

However in this work the O 2p hole is free to choose rather
Forcing it into a ZR singlet state.

(b)

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

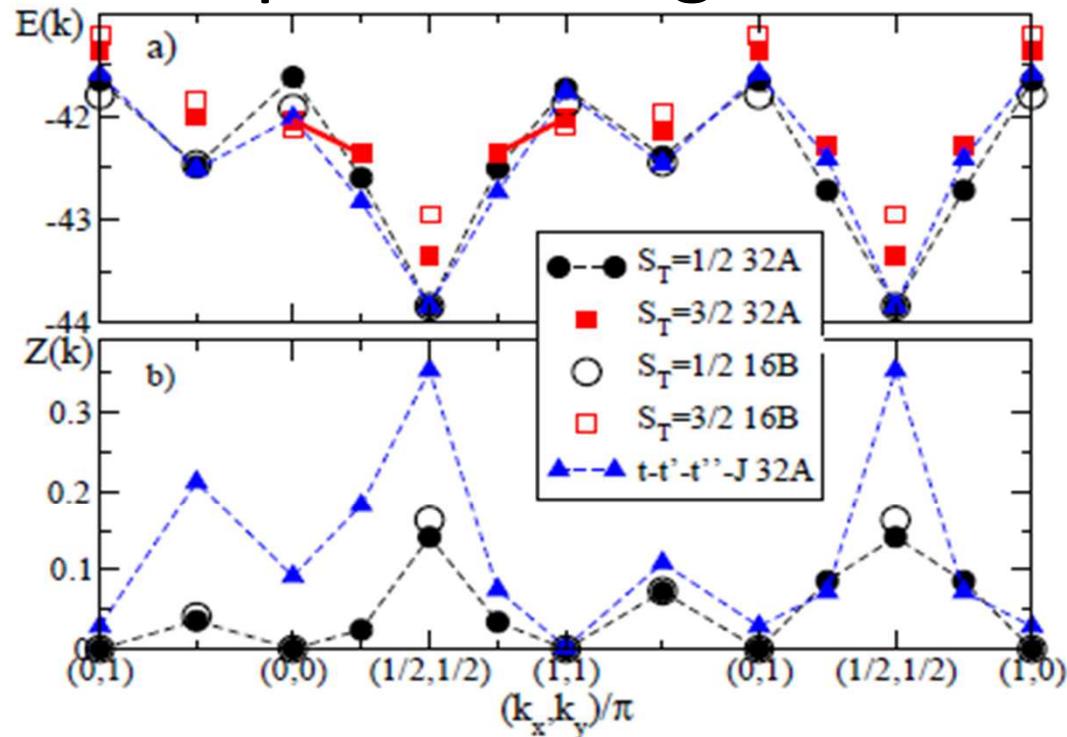# The dispersion and the quasi particle spectral weight

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.

Recent exact diagonalization studies of 32Cu 64O clusters

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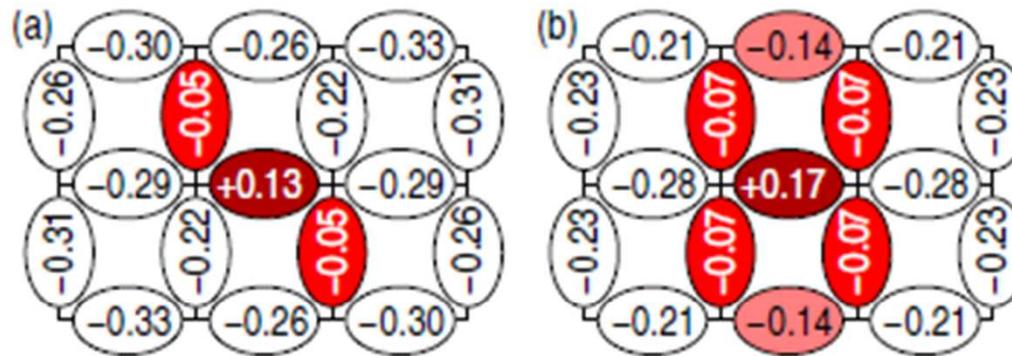A Neel antiferromagnet =- .25, and a ferromagnet =+.25

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

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

Consider antiferro CuO2 lattice
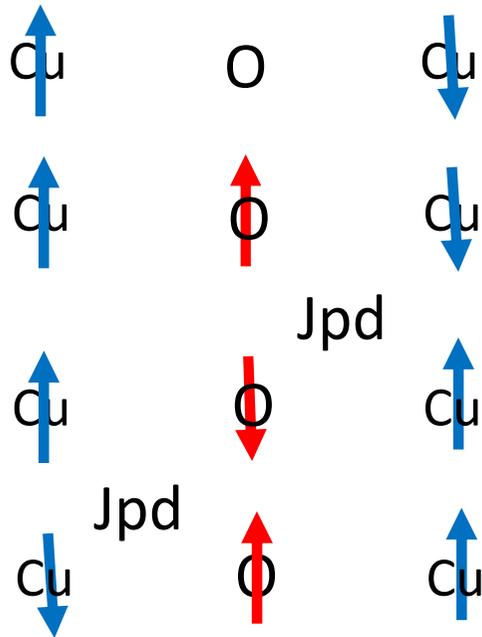
Ground state undoped spins are for d holes

Remove and 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

What would this isolated 3 spin polaron look like

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

You can also write the 3 spin ½ polaron as

This is a variational calculation starting from Neel ordered spin state.
The dynamics of a doped hole in cuprates is not controlled by spin fluctuations

Hadi Ebrahimnejad, GAS and Mona Berciu

Magnon-Mediated Interactions Depend Strongly on the Lattice Structure and if the introduced holes electrons are on the same site as the local spin
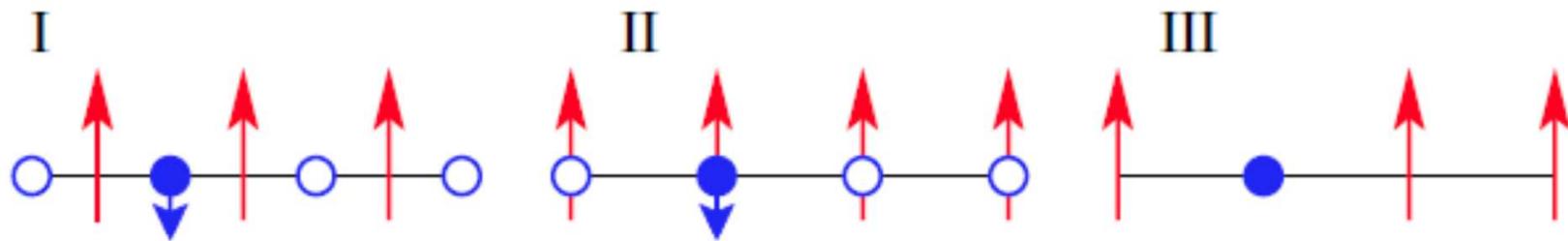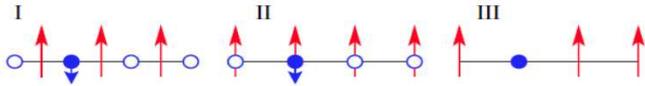
FIG. 1 (color online). Models I and II have two bands: one occupied by spins (arrows), and one (empty circles) hosting carriers introduced by doping (filled circles, with arrow showing the spin). In the "parent" model I, these are on different sublattices. In model II, they are on the same lattice. Model III has one band which hosts both spins (arrows) and ZRS-like polaron cores (filled circle).

FIG. 1 (color online). Models I and II have two bands: one occupied by spins (arrows), and one (empty circles) hosting carriers introduced by doping (filled circles, with arrow showing the spin). In the "parent" model I, these are on different sublattices. In model II, they are on the same lattice. Model III has one band which hosts both spins (arrows) and ZRS-like polaron cores (filled circle).
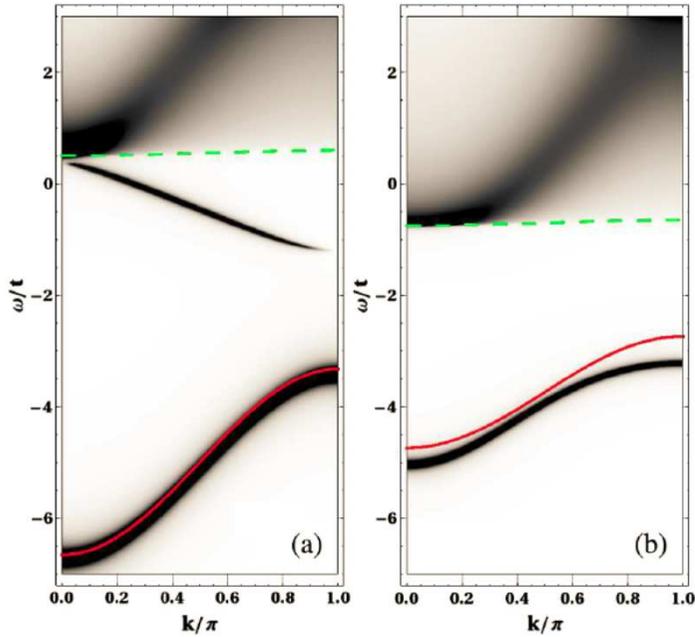
Single particle dispersion

FIG. 2 (color online). (a) Model I, and (b) model II density of states $\rho_\downarrow(k, \omega) = -\frac{1}{\pi} \mathrm{Im} G_\downarrow(k, \omega)$. Contour plots show exact results. Full lines are Eqs. (1) and (2), while dashed lines mark the expected onset of the continuum, at $\min_q(E_{k-q,\uparrow} + \Omega_q)$. Here $J/t = 0.05$, $J_0/t = 5$, $\eta/t = 0.02$.
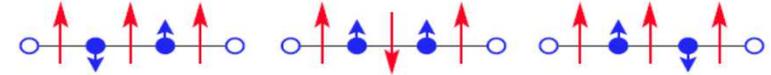
Two particle spectral weight at total K=0

FIG. 4 (color online). The three highest weight configurations contributing to the low-energy bipolaron of model I.
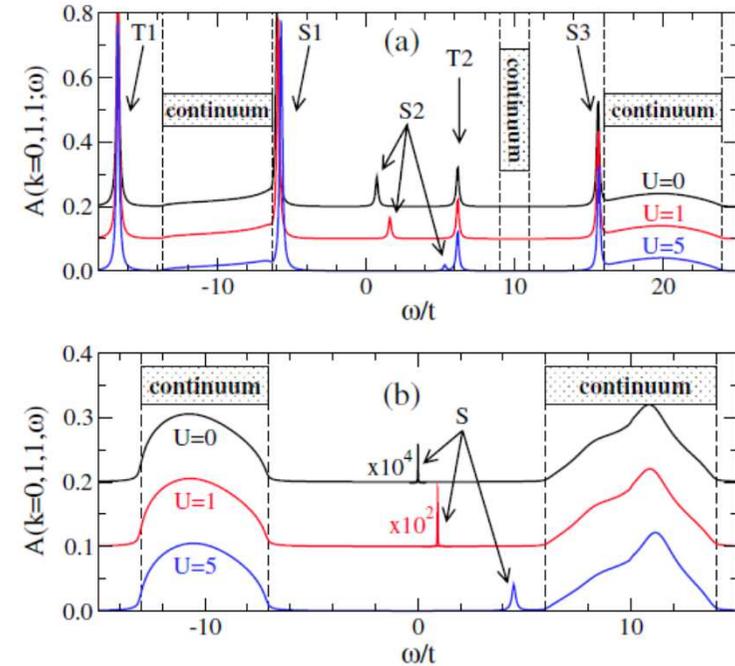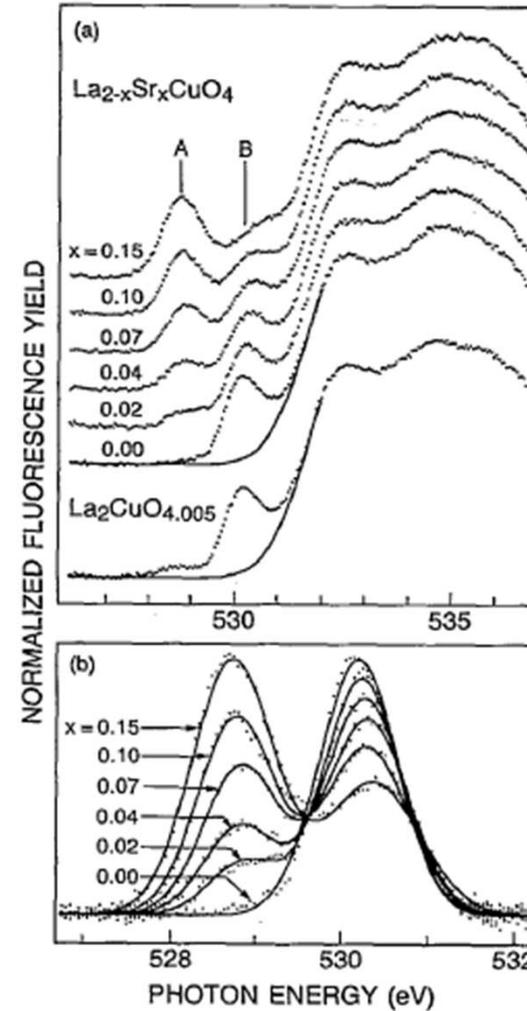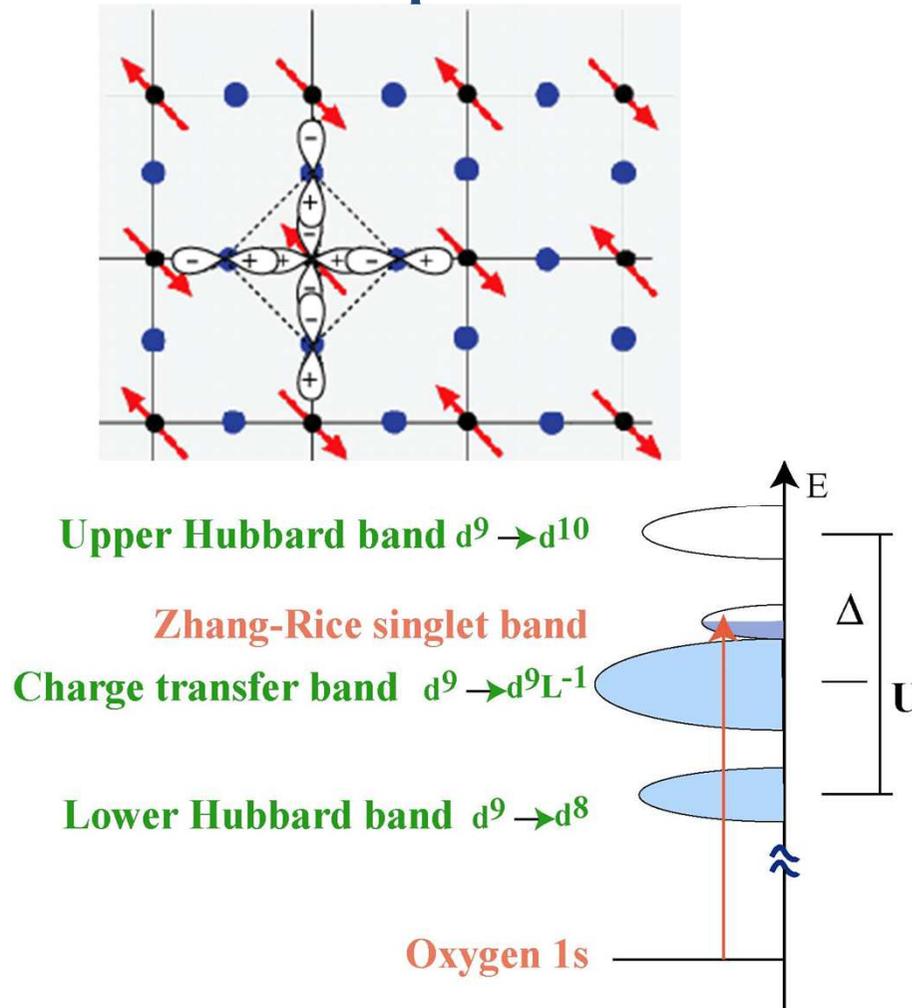

FIG. 3 (color online). Spectral weight $A(k = 0, n = n' = 1, \omega)$ for model I (a) and II (b). Expected continua locations are marked, as are triplet (T) and singlet (S) bipolarons (arrows). Here $J_0/t = 20$, $J/t = 0.05$, $\eta/t = 0.1$ and $U/t = 0, 1, 5$.

Comparison; added particles in the same sublattice or in a different sublattice (single band vs 3 band)

- The single particle addition states form polarons in both cases
- They have bound polaron states in both cases with similar dispersion
- For the two particle case however the two cases show very different properties
- There is a strong magnon exchange based attraction between the two particles in the 3 band case leading to two particle low energy bound states but not in the single band case.

Doped holes in cuprate

C.T.Chen XAS

PRL **68**, 2543 (1992)

Upper Hubbard band $d^9 \rightarrow d^{10}$

Zhang-Rice singlet band

Charge transfer band $d^9 \rightarrow d^9L^{-1}$

Lower Hubbard band $d^9 \rightarrow d^8$

Oxygen 1s

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.

Is the O pre edge peak an issue only 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

Ni(1-x)Li(x)O

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

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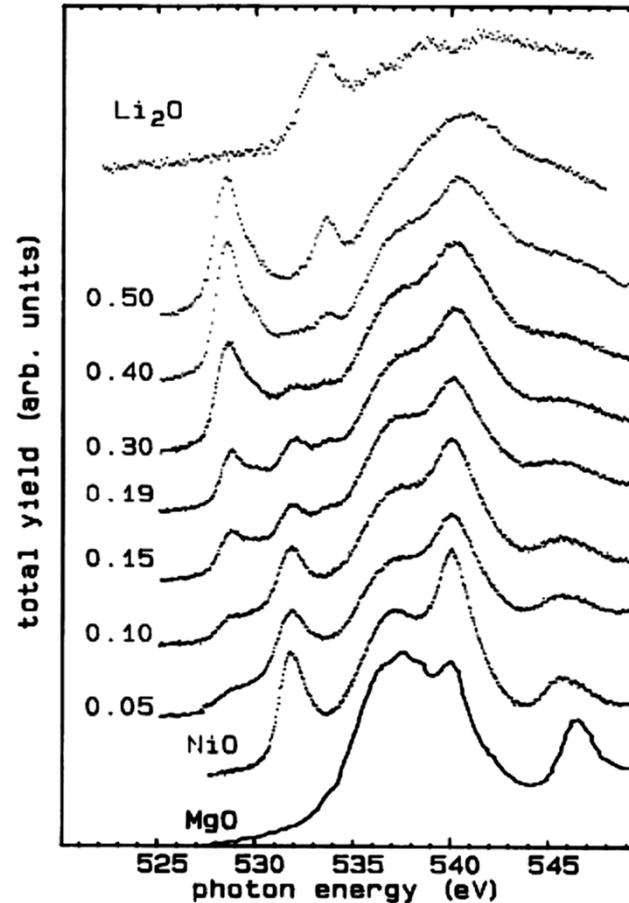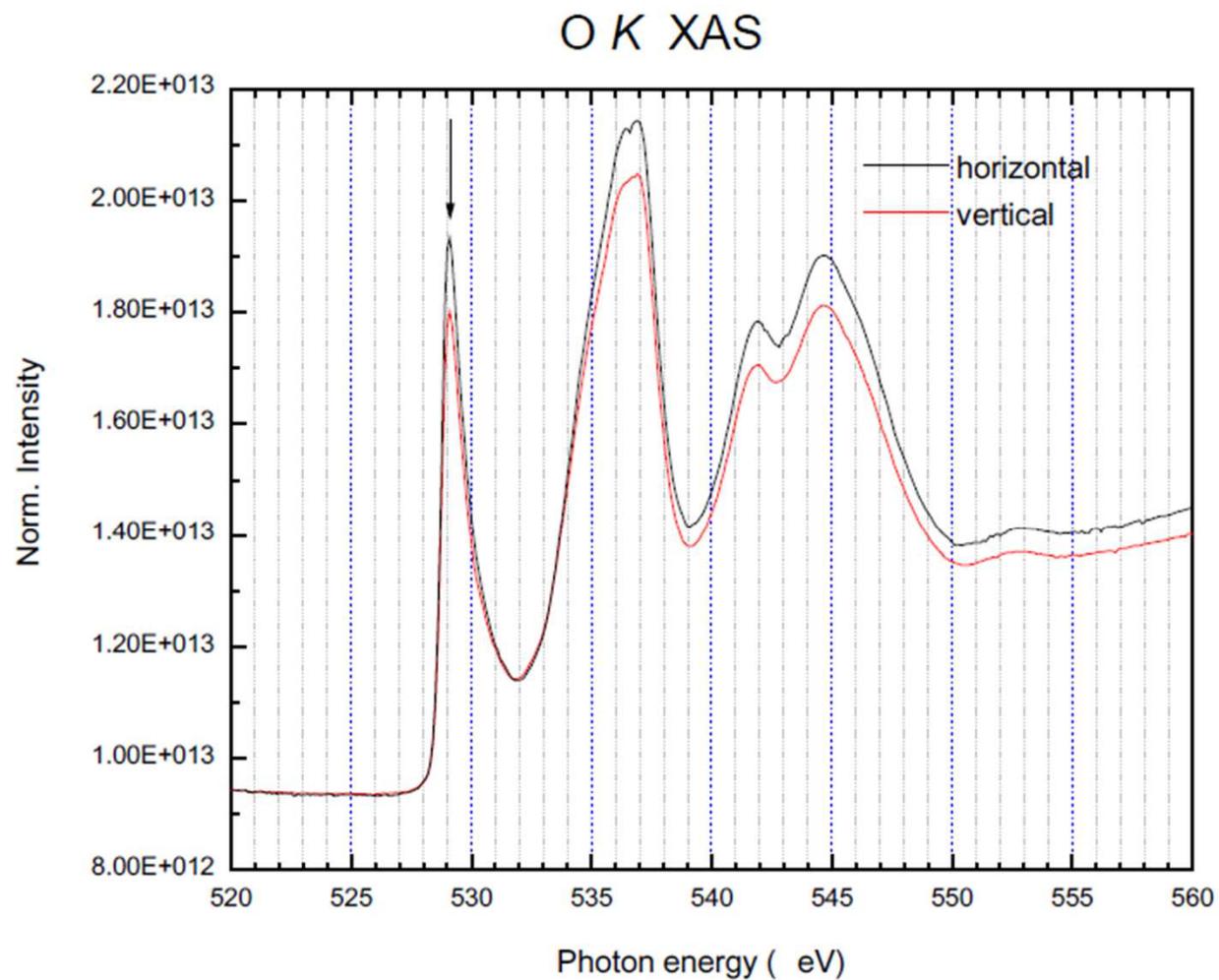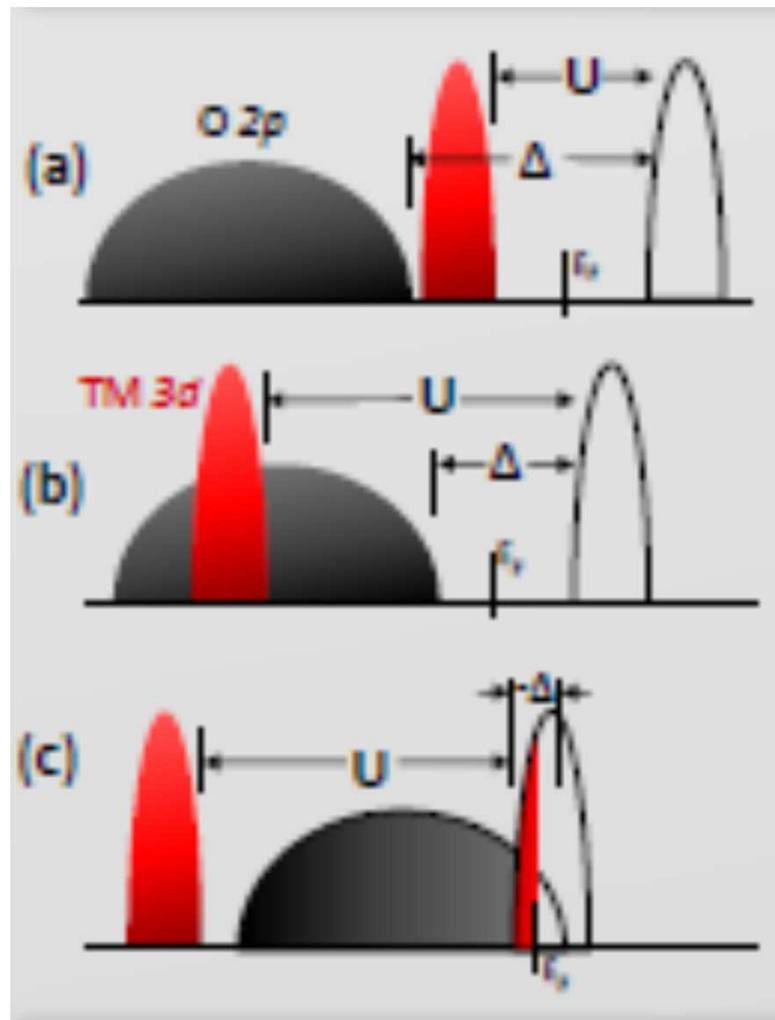# doped holes mainly on O
NOT Ni3+

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

LNO thin film on LSAT   Sutarto, Wadati, Stemmer UCSB

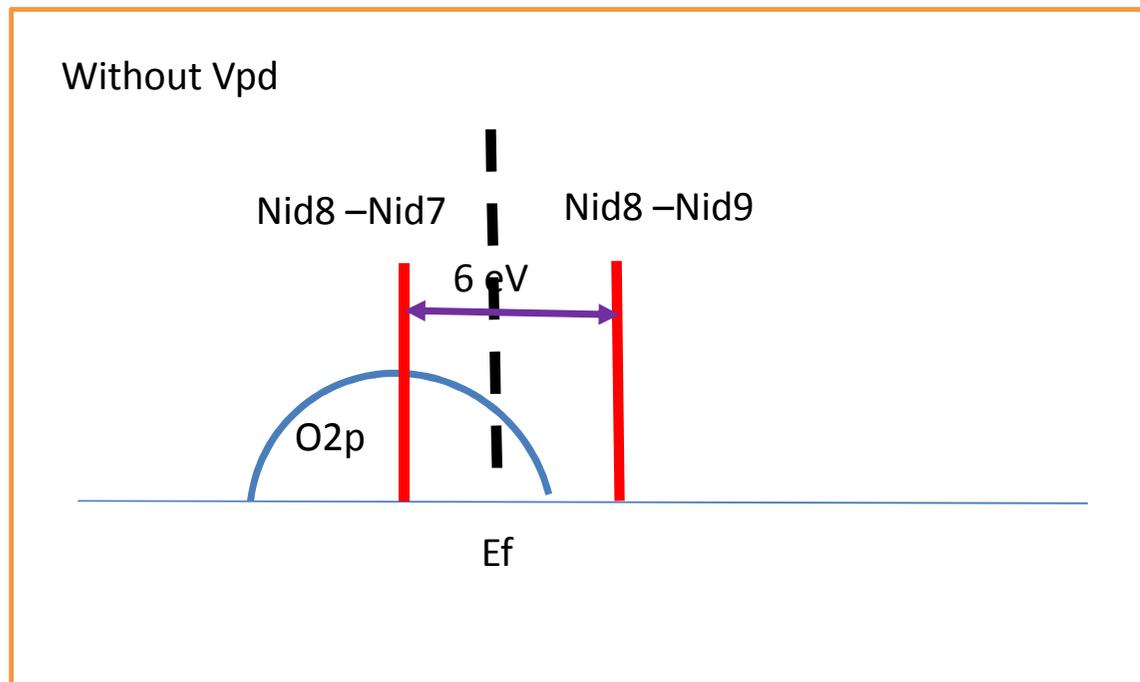Note the huge O 1s -2p prepeak just as in the cuprates HOLES ON O

O K XAS

Concept of negative charge transfer gap

"Self doped system" as in CrO2

FOR NEGATIVE CHARGE TRANSFER GAP IN Ni 3+(d7) WE START WITH Ni (d8 s=1) AND ONE HOLE PER Ni IN O 2p BAND

Without Vpd

Nid8 –Nid7   Nid8 –Nid9

6 eV

O2p

Ef

THIS IS AN ANDERSON LATTICE PROBLEM WHICH MAY EVOLVE INTO A KONDO LATTICE PROBLEM

Conceptual example based on Cuprates

- La2CuO4 is a charge transfer gap insulator
- The doped holes in La2-xSrxCuO4 go mainly into O 2p states
- Yields a large pre-peak in the XAS at the O 1s edge
- LaSrCuO4 if it existed in the same structure would be a **negative charge transfer gap i.e. Cu3+ → Cu2+L Anderson or Kondo Lattice ansatz**
- Cu2+ with 1 hole per CuO2 planer unit cell

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

- So for Nickelates like NdNiO3

- Could start with Ni3+ d7 low spin i.e. 3 d holes in eg FULL O2p

- Or Ni2+ d8 S=1 and one hole per Ni on O

- If we now do an impurity like calculations these two systems will yield very different results
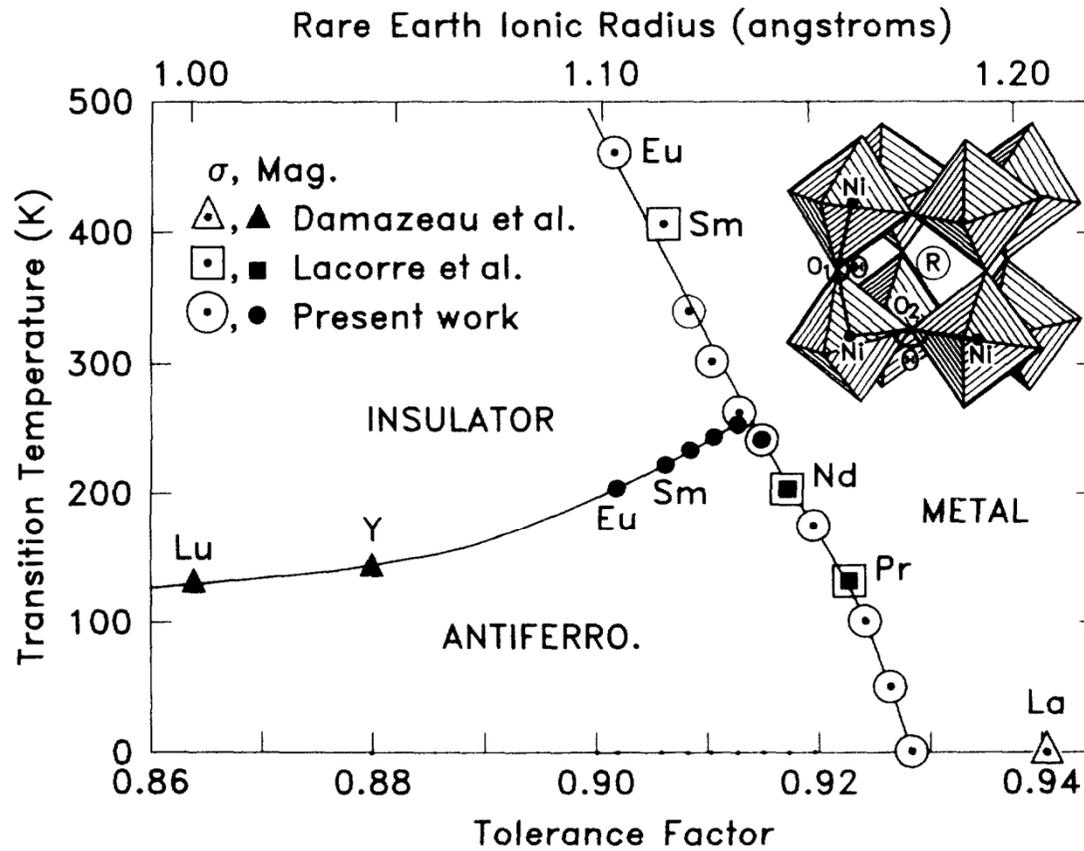
Nickelates RENiO3

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).

Real d orbitals in Octahedral coordination eg's have lobes pointing to anion forming sigma bonds and the t2g's have lobes pointing between the anions with pi bonds
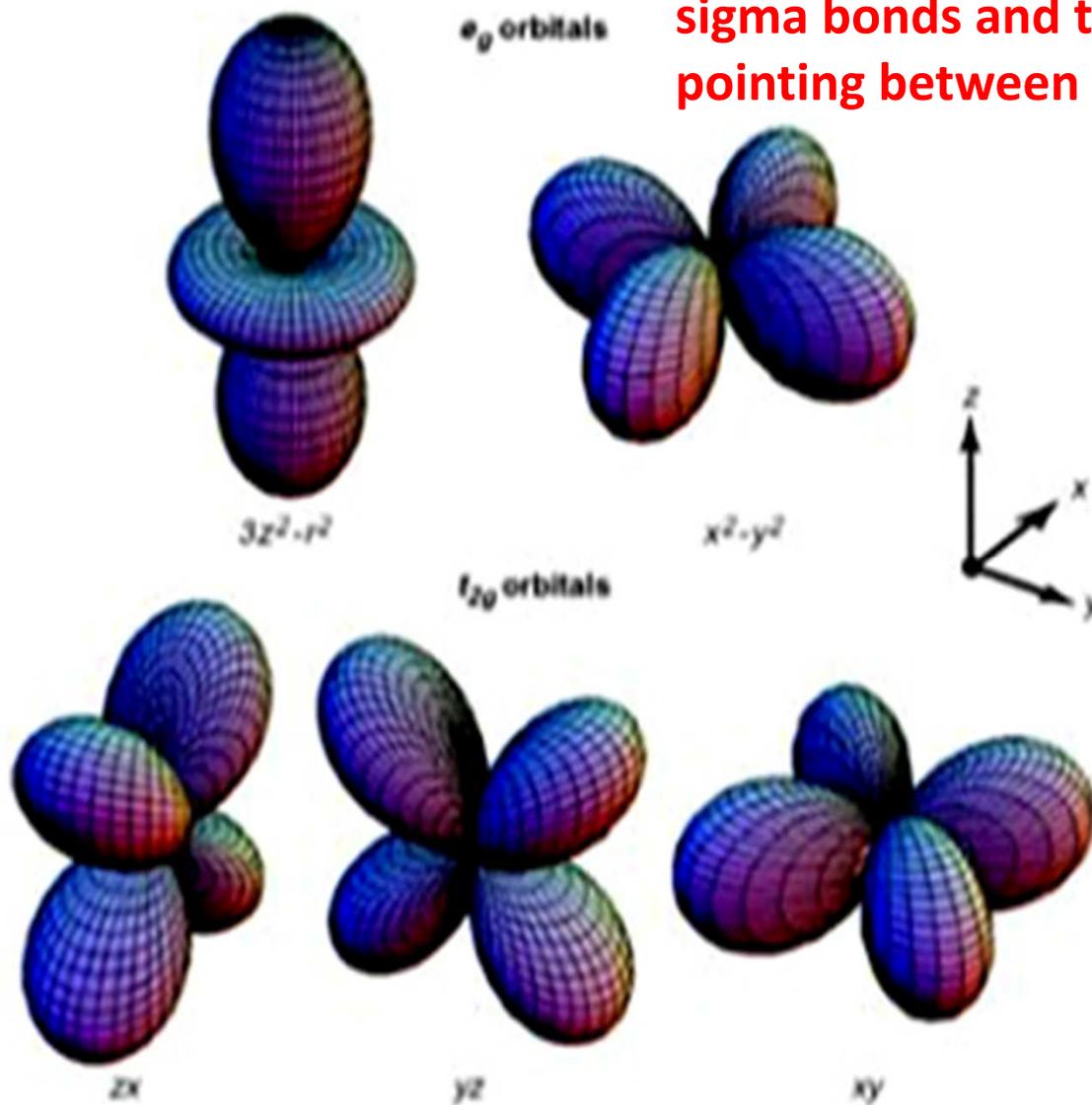
Conventionally RENiO3 would involve Ni3+ which is expected to be low spin i.e. S=1/2 with 6 electrons in t2g orbitals and 1 in an eg orbital

STRONG Jahn Teller ion
WHICH IS NOT OBSERVED!

How to get rid of JT ?

Charge disproportionation d7 + d7 into d6 and d8 would solve this problem.
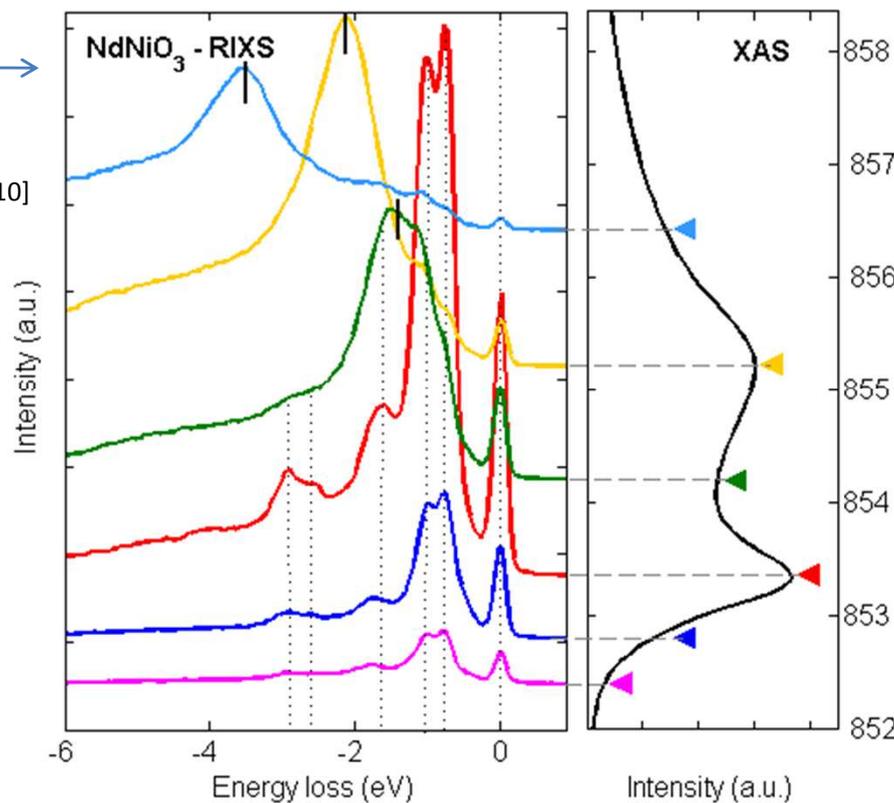
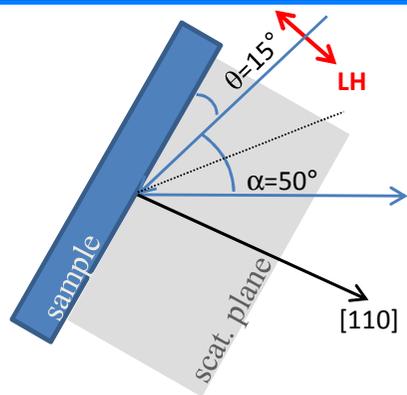But this costs U which is about 6-8 eV

experiments show only very low CDW amplitude in the insulating phase

Recent RIXS point to a negative charge transfer gap system results obtained by

Valentina Bisogni and Thorsten Schmitt from PSI

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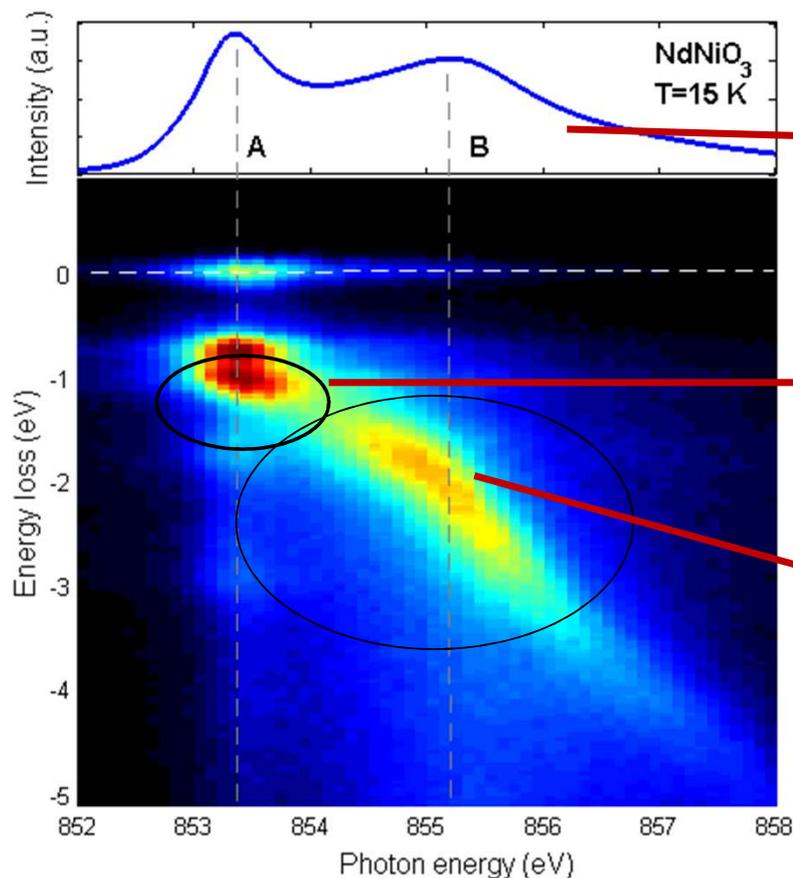Jean-Marc Triscone, and Pavlo Zubko From
Geneva

This clearly involves a broad band of states
L -- O 2p HOLE BAND

This involves bound local Multiplet states
Result of strong core Hole d electron interaction

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.
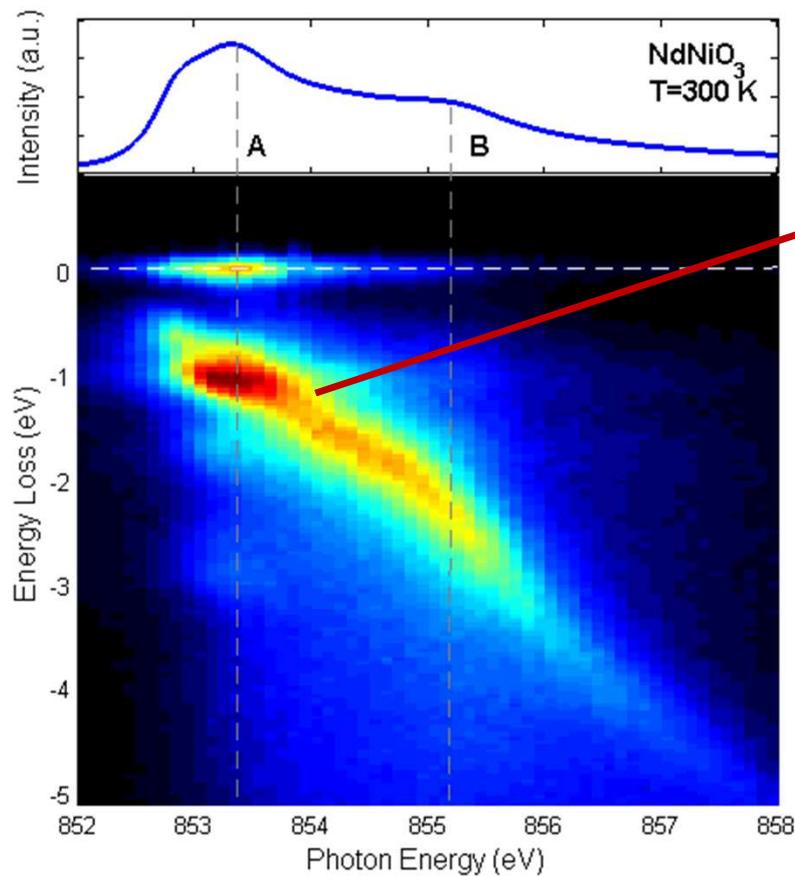
Strong T dependence of the XAS

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

High oxidation state TM compounds

- In general we expect the charge transfer energy to strongly decrease for higher oxidation states
- This could mean a different starting point i.e.
- $Cu^{3+} \longrightarrow Cu^{2+}\underline{L}$ $Ni^{3+} \longrightarrow Ni^{3+}\underline{L}$ $Co^{4+} \longrightarrow Co^{3+}\underline{L}$
- $Fe^{4+} \longrightarrow Fe^{3+}L$ $Mn^{4+}???$

The charge degrees of freedom are in Oxygen 2p bands

# 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

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.

$d8\underline{L} + d8\underline{L}$ ---- $d8 + d8\underline{L2}$

● Ni2+ no JT
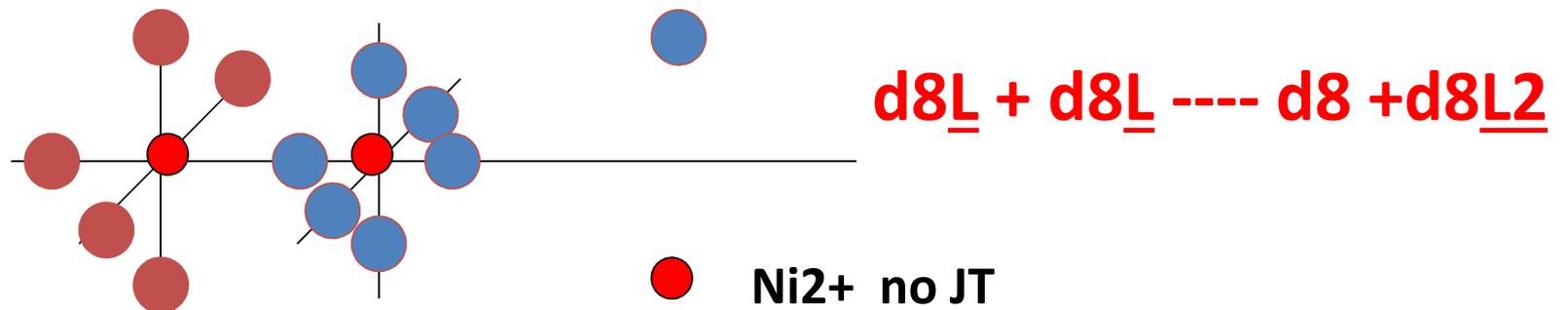
Each second Ni2+ has a STRONGLY COMPRESSED octahedron of O with two holes
of Eg symmetry in bonding orbital's I.e. d8 L2 (S=0)

No Jahn Teller problem anymore

Charge disproportionation without charge transfer
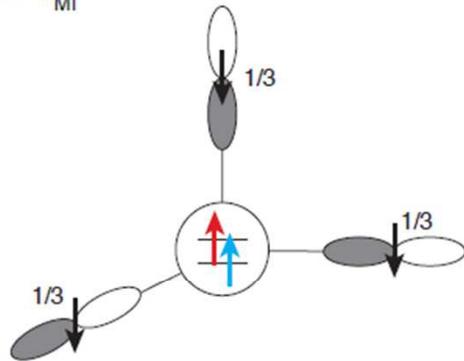
Steve Johnston, Mona Berciu, GAS arXiv:1310.2674 , Phys. Rev. Lett. 112, 106404 (2014)

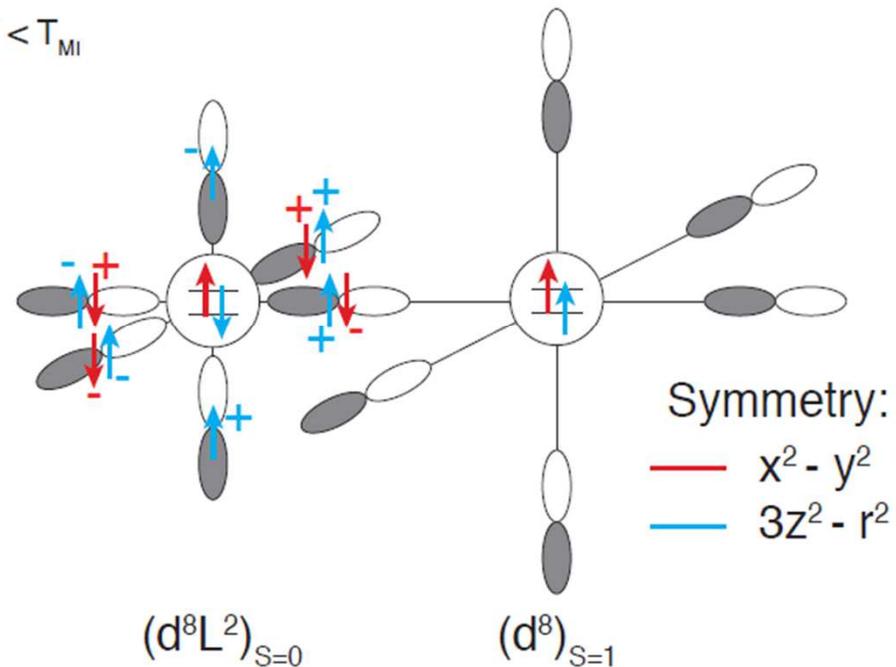# Hartree Fock and exact diagonalization

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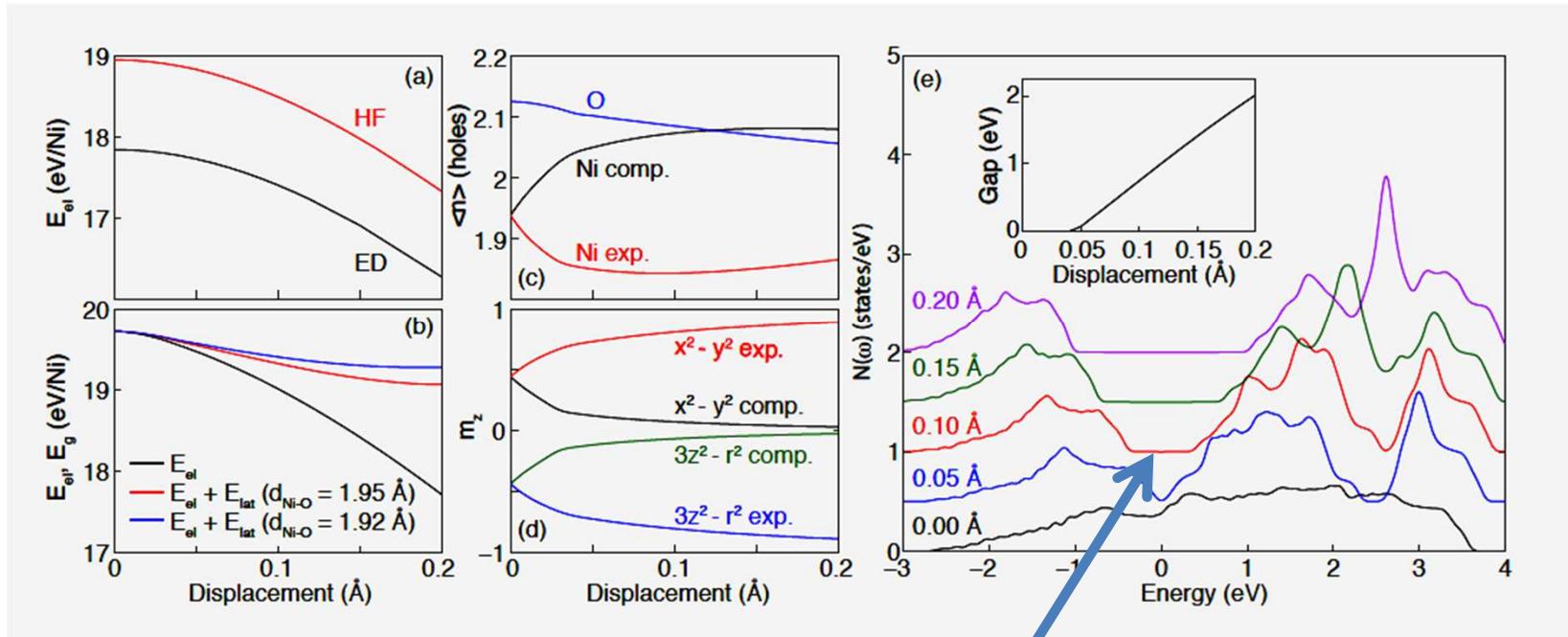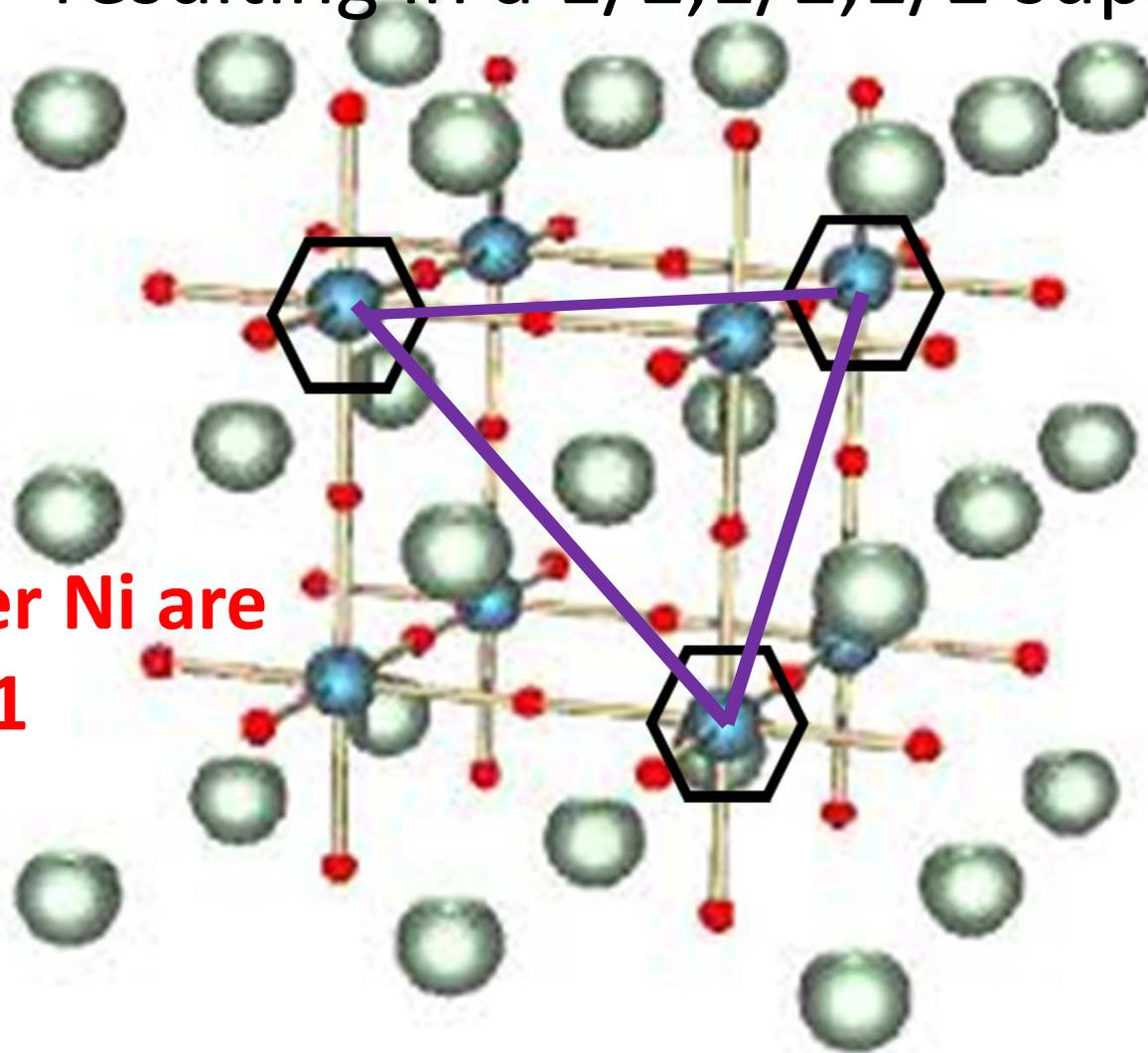
Total energy, charge density, magnetic moment, and density of states vs. checker board O octahedron compression/ expansion
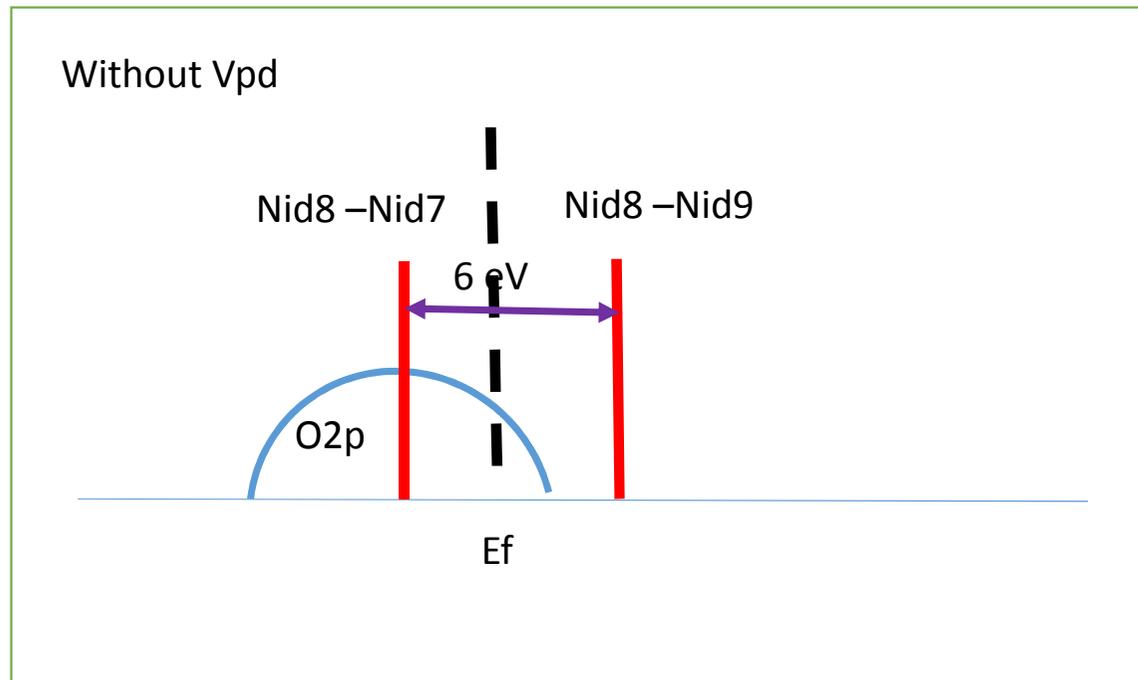

Note the gap forming
for displacements of > .09A

Indicates Ni in Compressed Octahedra resulting in a 1/2,1/2,1/2 superstructure

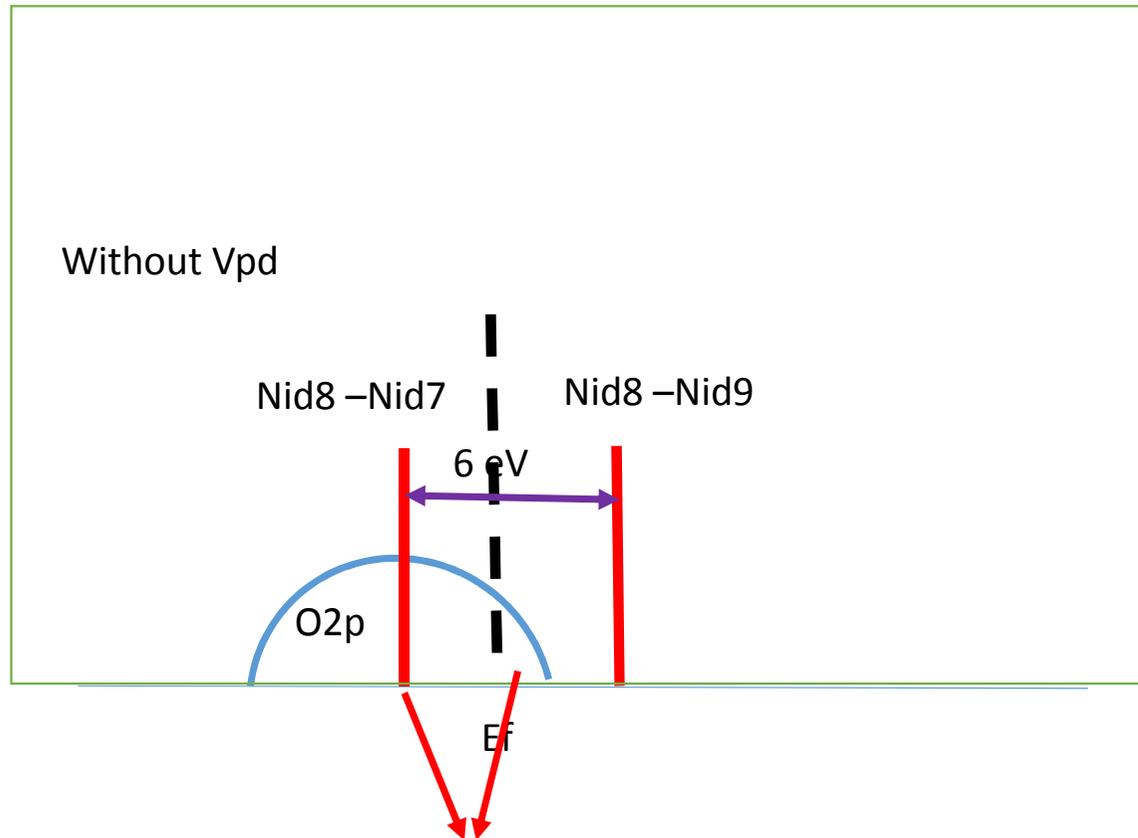Kondo—Mott insulator

The other Ni are Ni d8 S=1

FOR NEGATIVE CHARGE TRANSFER GAP IN Ni 3+(d7) WE START WITH Ni (d8 s=1) AND ONE HOLE PER Ni IN O 2p BAND

Without Vpd

Nid8 –Nid7   Nid8 –Nid9

6 eV

O2p

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Without Vpd

Nid8 –Nid7   Nid8 –Nid9

6 eV

O2p

Ef

The eg holes in d7 hybridize strongly
with the O2p holes of eg symmetry
Resulting in a bound state and a gap at low T

How are systems like Ba or SrBiO3 different?

- Weak correlation if any
- Band theory should work
- Is there charge disproportionation? Bi4+ is 6s1 system
- How about electron phonon coupling?
- Is this in the end similar to Nickelates?

Two holes in O Octahedron

What stabalizes the charge Disproportionation?

Cluster model

Definition of
hopping parameters

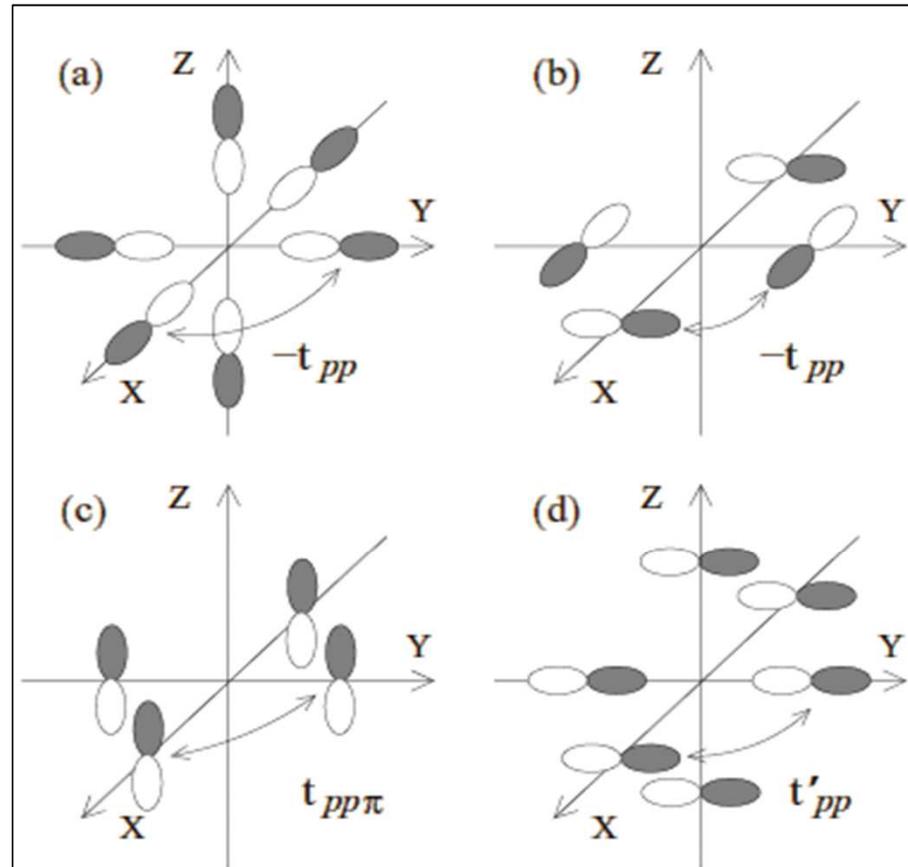$t_{pp}=1/2(t_{pp\sigma}-t_{pp\pi})$

$t'_{pp}=1/2(t_{pp\sigma}+t_{pp\pi})$

FIG. 1: An artists concept of the oxygen σ (a) and π (b,c) bonding orbitals relative to the O-vacancy bond direction surrounding a Ca vacancy. Also shown are the definitions of the hopping integrals (b) t_{pp}, (c) $t_{pp\pi}$, and (d) t'_{pp} given in terms of electrons.
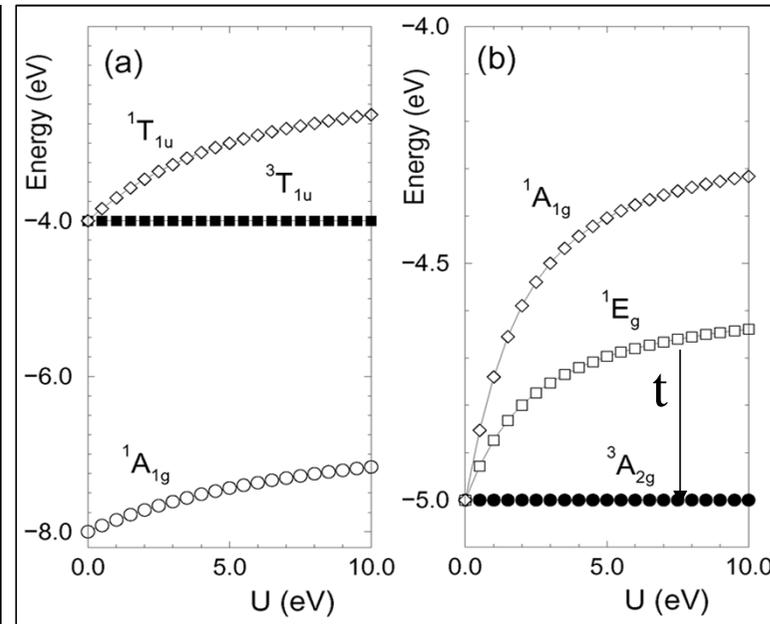
Exact diagonalization results

Single-particle picture

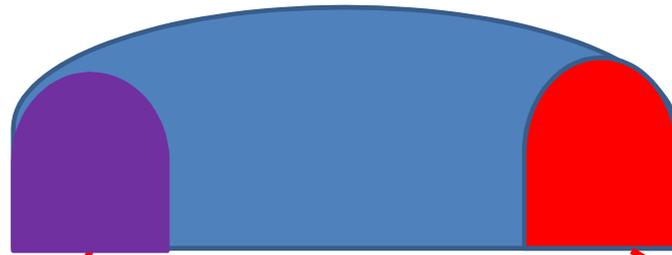## Three lowest states for two particles

Bismuthates
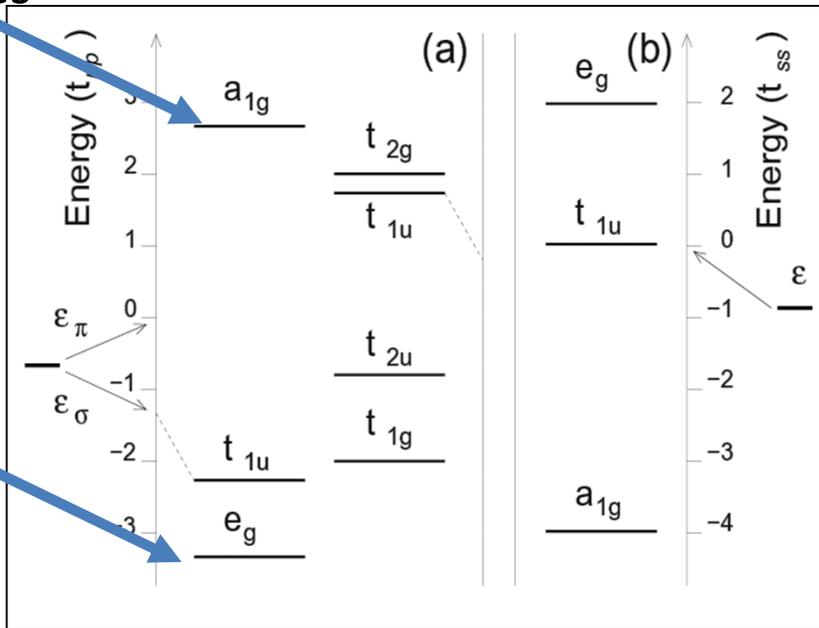
Nickelates

(a) HOLES in anion orbitals and
(b) ELECTRONS in cation orbitals.

U on O is about 6 eV

(a) ELECTRONS in cation orbitals and
(b) HOLES in anion orbitals.
Solid symbols are for triplet state

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

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

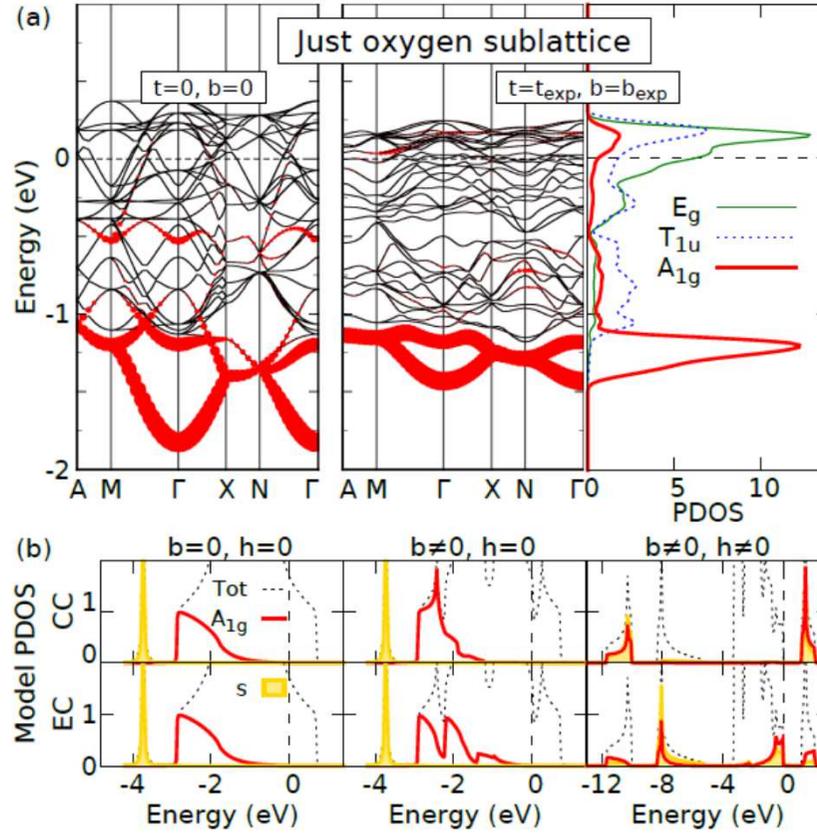**Eg symmetry combination of O2p states In an octahedron Mix with eg d states i.e. Ni3d eg**

FIG. 4: (a) LDA electronic structure of the oxygen sublattice of $SrBiO_3$. Projections are made onto combinations of the O-p_σ orbitals of a collapsed O_6 octahedron. (b) Model density of states as a function of breathing b and hybridization between s- and p-orbitals h. CC (EC) stands for a collapsed (expanded) p-site cage. The model states are 90% filled, $i.\ e.$, there is one hole per s-orbital; Fermi energy is set to zero and marked with black dashed vertical lines.

Hybridization –bond disproportionation effects in bismuth perovskites

Kateryna Foyevtsova
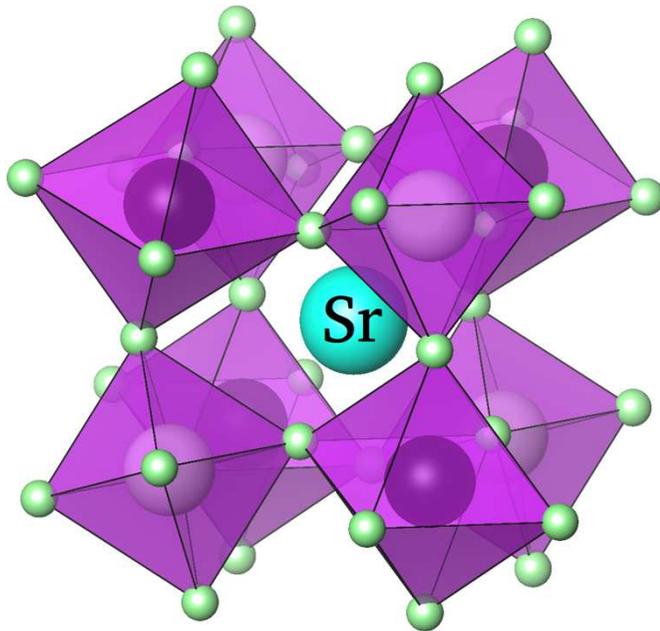
In bond-disproportionated state, holes condense onto A_{1g} states of the collapsed octahedra
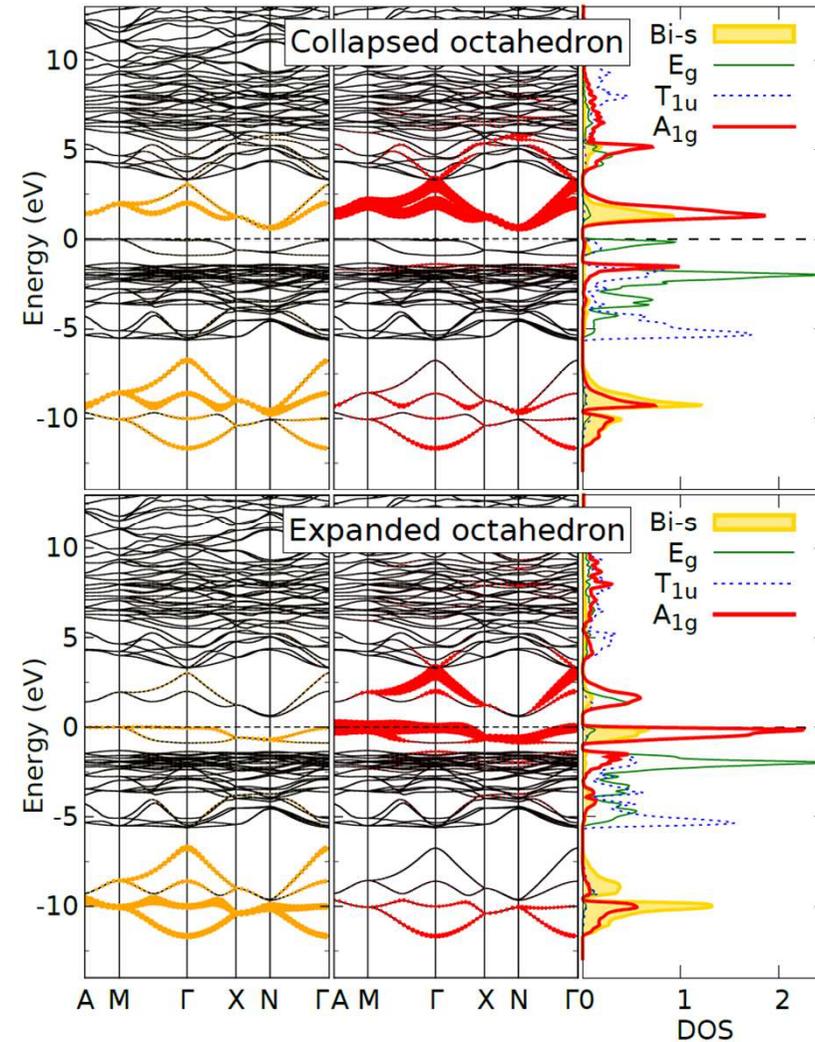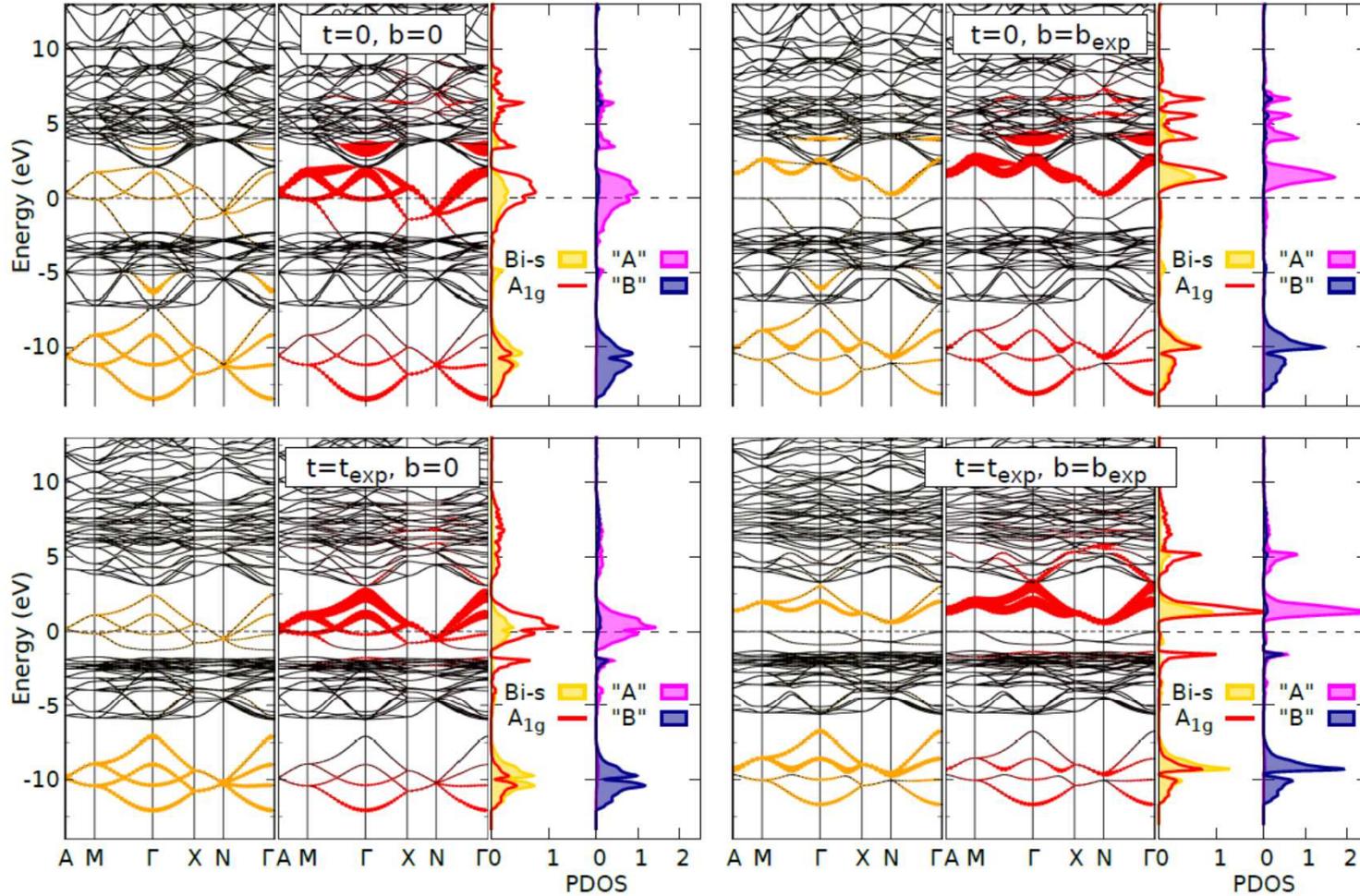
FIG. 3: LDA electronic structure of $SrBiO_3$ as a function of breathing b and tilting t. Projections are made onto the Bi-$6s$ orbital and the A_{1g} combination of the O-p_σ orbitals of a collapsed BiO_6 octahedron, as well as their bonding ("B") and anti-bonding ("A") combinations.
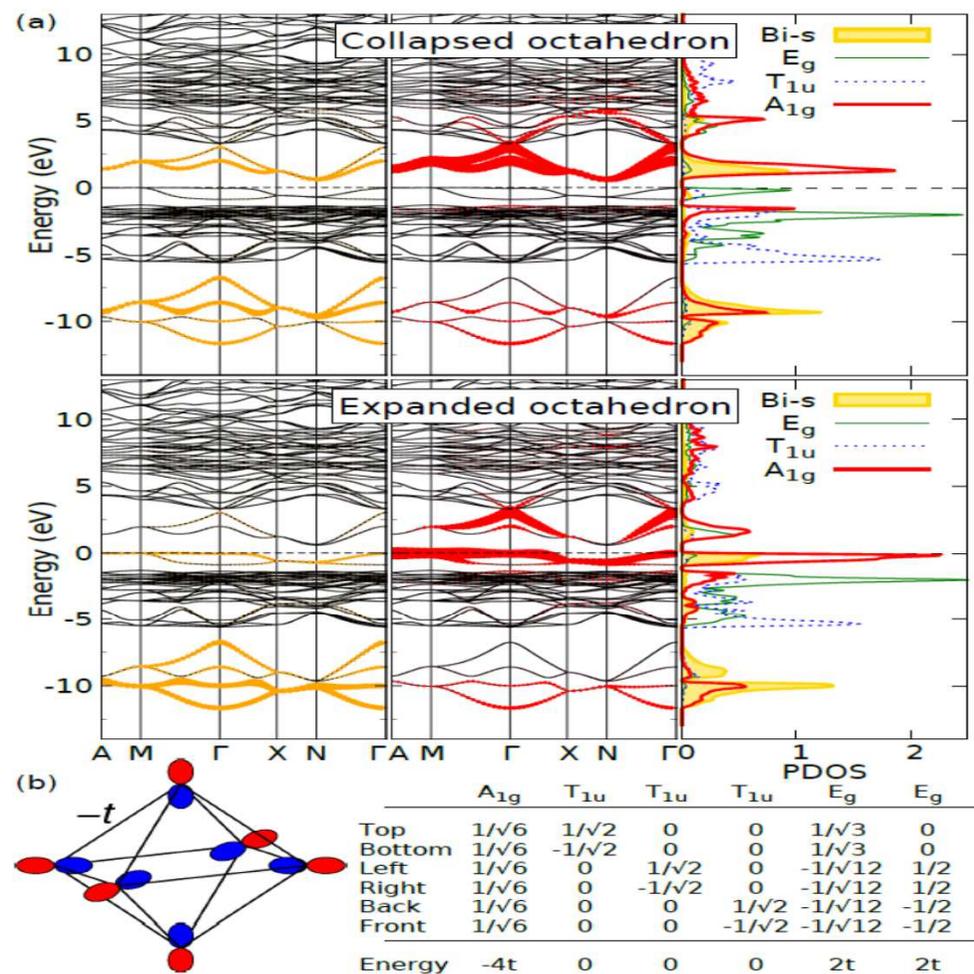
FIG. 1: (a) LDA electronic structure of SrBiO$_3$ projected onto the Bi-6s orbital and combinations of the O-p_σ orbitals of a collapsed (top) and expanded (bottom) BiO$_6$ octahedron. For the doublet E_g and the triplet T_{1u}, only one projection is shown. The Fermi level is set to zero, and PDOS stands for projected density of states and is given in states/eV/cell. (b) An octahedron of O-p_σ orbitals coupled via nearest-neighbor hopping integrals $-t$ and its eigenstates.

Solid and (dashed) lines
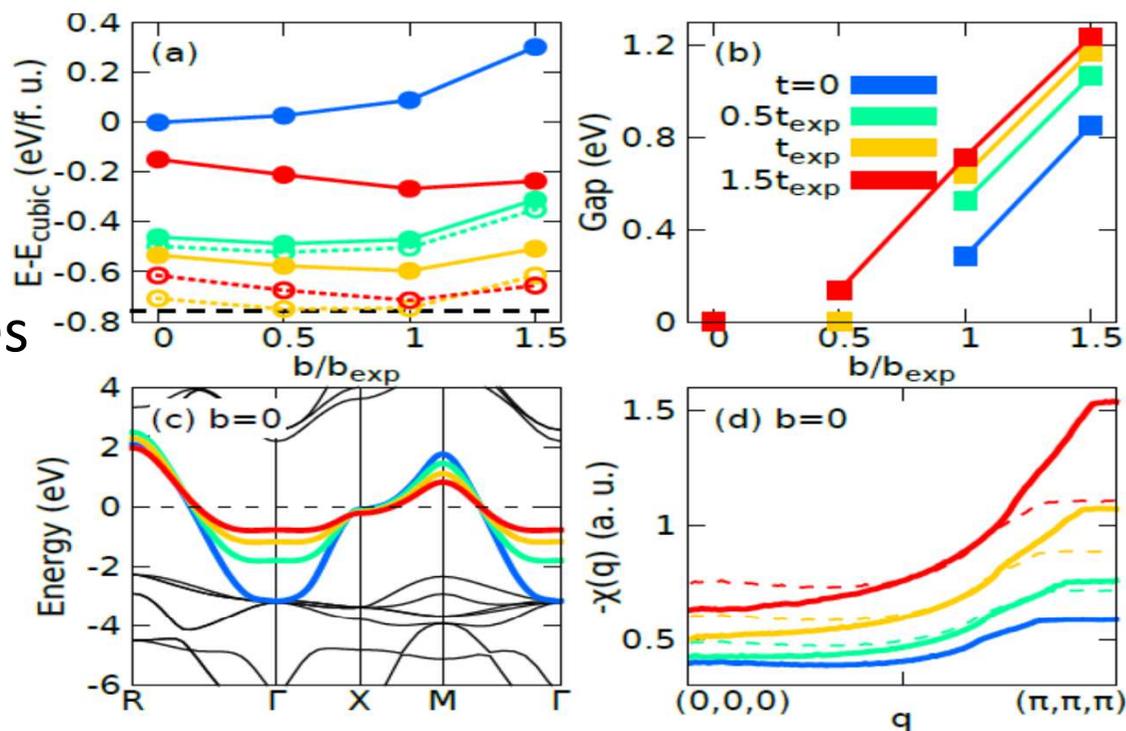Are for Sr atoms in
Unrelaxed (relaxed)
 positions

FIG. 2: (a), (b): LDA characterization of $SrBiO_3$ model structures with varying degrees of the BiO_6 octahedra's tilting, t, and breathing, b: (a) total energy per formula unit (f. u.) and (b) charge gap. In (a), solid lines and filled circles (dashed lines and open circles) represent model structures with fixed (relaxed) Sr atoms. The horizontal dashed line marks the energy of the experimental $SrBiO_3$ structure. (c), (d): The effect of tilting on (c) the half-filled band and on (d) the static susceptibility $\chi(\mathbf{q}, \omega = 0)$, at zero breathing. In (d), solid (dashed) lines represent calculations where non-linear effects due to tilting are (are not) taken into account.

Summary

- Oxides with formally high oxidation state elements can be negative CT systems
- The charge degrees of freedom are then in mainly O 2p bands
- O 2p hole states in the low T phase for molecular (Octahedron) like states
- In the Nicklates the O2p hole states are of eg symmetry
- In the Bismuthates they are of a1g symmetry
- The semiconductor metal transition in Bi and Ni systems are similar resulting in a breathing like polaron mode which condenses into a bond disproportionated ground state
- In the Bi this competes with a potential superconducting state because of the strong attractive interaction between the 2 O 2p holes in a collapsed octahedron
- If we can get rid of the spatial ordering we could expect a high Tc superconductor