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

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Summary

1. Basic concepts: electronic structure of transition metal compounds
3. Charge transfer vs Mott Hubbard gap
4. Negative charge transfer gap materials and self doping
5. Experimental evidence in high oxidation state TM oxides
6. Basic theoretical concepts
7. The phase diagram of the nickelates RENiO$_3$
8. Ba and SrBiO$_3$ electronic structure
Some examples where anion p states dominate the physics

- Superoxides like KO$_2$ Where K(1+)(S=0) and (O$_2$ pairs)(1-) (S=1/2) These are ferromagnets
- The Pyrites like FeS$_2$ where Fe(2+ low spin S=0) (S$_2$ pairs) (2-) (S=0) form valence and conduction bands
- Solid Oxygen O$_2$(S=1) antiferro T<40K (Hunds rule J=1.3eV)
- Cuprate superconductors, Zhang Rice singlets, doped holes on O
- CrO$_2$ self doped ferromagnet
- And now many more
Correlated Electrons in a Solid

If $\Delta < (W+w)/2 \Rightarrow \text{Self doped metal}$

- ZSA, PRL 55, 418 (1985)
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,

\[ \langle P_{i\sigma}^{(5)} | P_{j\sigma'}^{(5)} \rangle = \delta_{\sigma\sigma'} \delta_{i,j} - \frac{1}{4} \delta_{(ij),0}, \]

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 \( \{ \Psi_S \} = \ldots \)

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**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

\[ H_{3B} = T_{pd} + T_{pp} + \Delta_{pd} \sum n_{l+\epsilon,\sigma} + U_{pp} \sum n_{l+\epsilon,\uparrow} n_{l+\epsilon,\downarrow} + U_{dd} \sum n_{l,\uparrow} n_{l,\downarrow} \]  

(1)

\[ H_{\text{eff}} = T_{pp} + T_{\text{swap}} + H_{J_{pd}} + H_{J_{dd}} \]  

(2)

\[ H_{J_{dd}} = J_{dd} \sum \overline{S}_{l \pm \epsilon} \cdot \overline{S}_{l} \Pi_{\sigma} (1 - n_{l \pm \epsilon,\sigma}) \]
The Tswap term is very important 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 than being forced into a ZR singlet state.

The dispersion and the quasi particle spectral weight

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

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 $32\text{Cu} \ 64\text{O}$ clusters

Note a quantum spin $\frac{1}{2}$ antiferromagnet has a nn spin correlation of $-0.33$
A Neel antiferromagnet $= -0.25$, and a ferromagnet $= +0.25$

![Diagram showing spin correlations](image)

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 $(\pi, \pi)$ 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 CuO$_2$ lattice

Ground state undoped spins are for d holes

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

Act with Jpd $\gg$ Jdd

Act with Jpd $\gg$ Jdd

Eigenstate of N-1 electron system is a linear combination of these three states
What would this isolated 3 spin polaron look like

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 Ebrahimpnejad, GAS and Mona Berciu
Nature Physics in press
Magnon-Mediated Interactions Depend Strongly on the Lattice Structure and if the introduced holes electrons are on the same site as the local spin

Mirco Moller, GAS, Mona Berciu PRL 108, 216403 (2012)

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

Two particle spectral weight at total $K=0$
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.
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) Li\(_x\)Ni\(_{1-x}\)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 Ni\(^{3+}\)
LNO thin film on LSAT  Sutarto, Wadati, Stemmer UCSB

Note the huge O 1s -2p prepeak just as in the cuprates **HOLES ON O**
Concept of negative charge transfer gap

“Self doped system” as in CrO2
FOR NEGATIVE CHARGE TRANSFER GAP IN Ni $3+ (d^7)$ WE START WITH Ni $(d^8 \; s=1)$ AND ONE HOLE PER Ni IN O $2p$ BAND

THIS IS AN ANDERSON LATTICE PROBLEM WHICH MAY EVOLVE INTO A KONDO LATTICE PROBLEM
Conceptual example based on Cuprates

- La$_2$CuO$_4$ is a charge transfer gap insulator
- The doped holes in La$_{2-x}$Sr$_x$CuO$_4$ go mainly into O 2p states
- Yields a large pre-peak in the XAS at the O 1s edge
- LaSrCuO$_4$ if it existed in the same structure would be a negative charge transfer gap i.e. Cu$^{3+}$ → Cu$^{2+}$ L Anderson or Kondo Lattice ansatz
- Cu$^{2+}$ with 1 hole per CuO$_2$ planer unit cell
If we cannot solve a problem exactly
The starting point really matters

• So for Nickelates like NdNiO3
• Could start with Ni$^{3+}$ d$^7$ low spin i.e. 3 d holes in eg FULL O2p
• Or Ni$^{2+}$ d$^8$ 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 RENiO$_3$

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
e_g's have lobes pointing to anion forming
sigma bonds and the t_2g'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 t$_{2g}$ orbitals and 1 in an e$_{g}$ orbital

STRONG Jahn Teller ion

WHICH IS NOT OBSERVED!
How to get rid of JT?

Charge disproportionation $d_7 + d_7$ into $d_6$ and $d_8$ 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
RIXS spectra of NdNiO$_3$ – 15 K

This clearly involves a broad band of states \( \perp \rightarrow O \, 2p \) HOLE BAND

This involves bound local Multiplet states

Result of strong core Hole d electron interaction
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 fluorescence.

So peak A in XAS involves the excited d electron and 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 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.
  - $\text{Cu}^{3+} \rightarrow \text{Cu}^{2+}$ $\text{Ni}^{3+} \rightarrow \text{Ni}^{3+}$ $\text{Co}^{4+} \rightarrow \text{Co}^{3+}$
  - $\text{Fe}^{4+} \rightarrow \text{Fe}^{3+}$ $\text{Mn}^{4+}???$

  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


Consider ReNiO$_3$ as Ni$^{2+}$L (1 O 2p hole per 3 O)
Then each Ni is surrounded by on average 2 L holes in an octahedron of O.

Each second Ni$^{2+}$ has a STRONGLY COMPRESSED octahedron of O with two holes of Eg symmetry in bonding orbital's I.e. d$^8$ L$^2$ (S=0)

No Jahn Teller problem anymore
Charge disproportionation without charge transfer


Hartree Fock and exact diagonalization

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

Note the gap forming for displacements of > .09Å.
Indicates Ni in Compressed Octahedra resulting in a $1/2,1/2,1/2$ superstructure

The other Ni are Ni d8 S=1

Kondo–Mott insulator
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

THIS IS AN ANDERSON LATTICE PROBLEM WHICH MAY EVOLVE INTO A KONDO LATTICE PROBLEM
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 stabilizes the charge Disproportionation?

Cluster model

Definition of hopping parameters

\[ t_{pp} = \frac{1}{2}(t_{pp\sigma} - t_{pp\pi}) \]

\[ t'_{pp} = \frac{1}{2}(t_{pp\sigma} + t_{pp\pi}) \]

Elfimov et al  PRL89, 216403 (2002)
Exact diagonalization results

Single-particle picture

Three lowest states for two particles

(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 SrBiO₃. Projections are made onto combinations of the O-\(p_\sigma\) orbitals of a collapsed O₆ 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-$p_x$ 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 SrBiO₃ projected onto the Bi-6s orbital and combinations of the O-pσ orbitals of a collapsed (top) and expanded (bottom) BiO₆ 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-pσ 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 $\chi(q, \omega = 0)$, 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.