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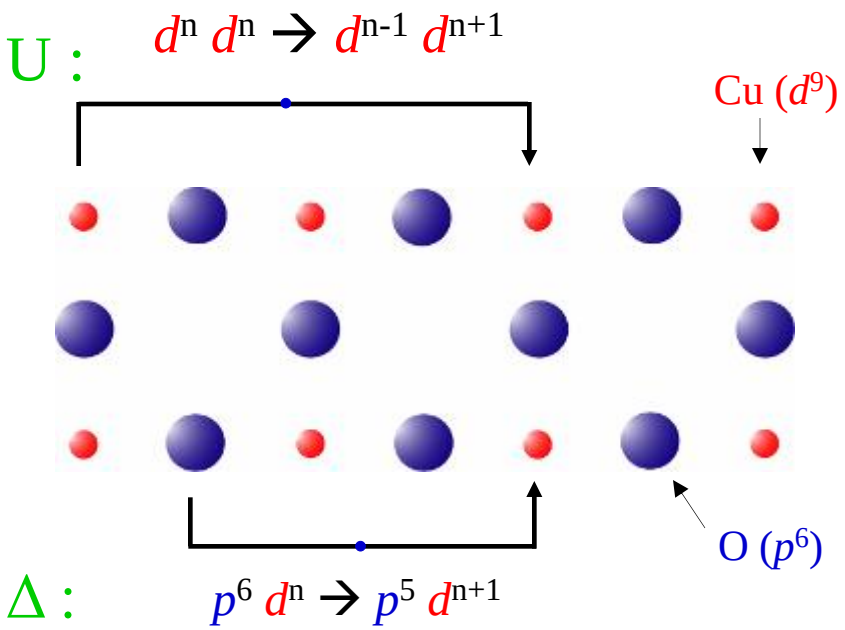
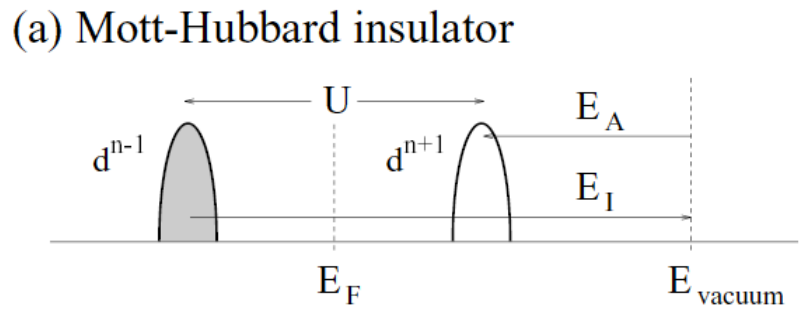
- **Marta Gibert Geneva**
- **Raoul Scherwitzl Geneva**
- **Jean-Marc Triscone Geneva**
- **Pavlo Zubko Geneva**

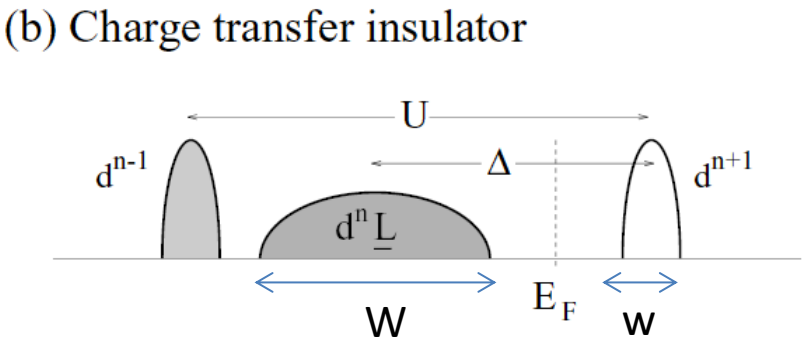
Summary

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 RENiO3**

Correlated Electrons in a Solid







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

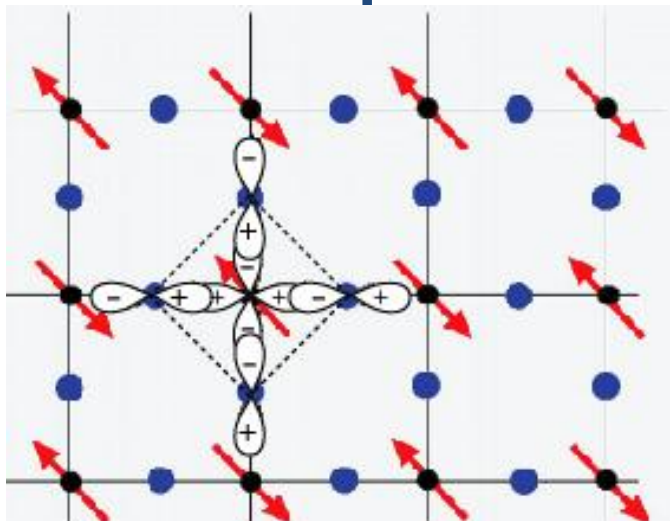
$$\Delta = E_I^{O} - E_A^{TM} - Epol + \delta E_M$$

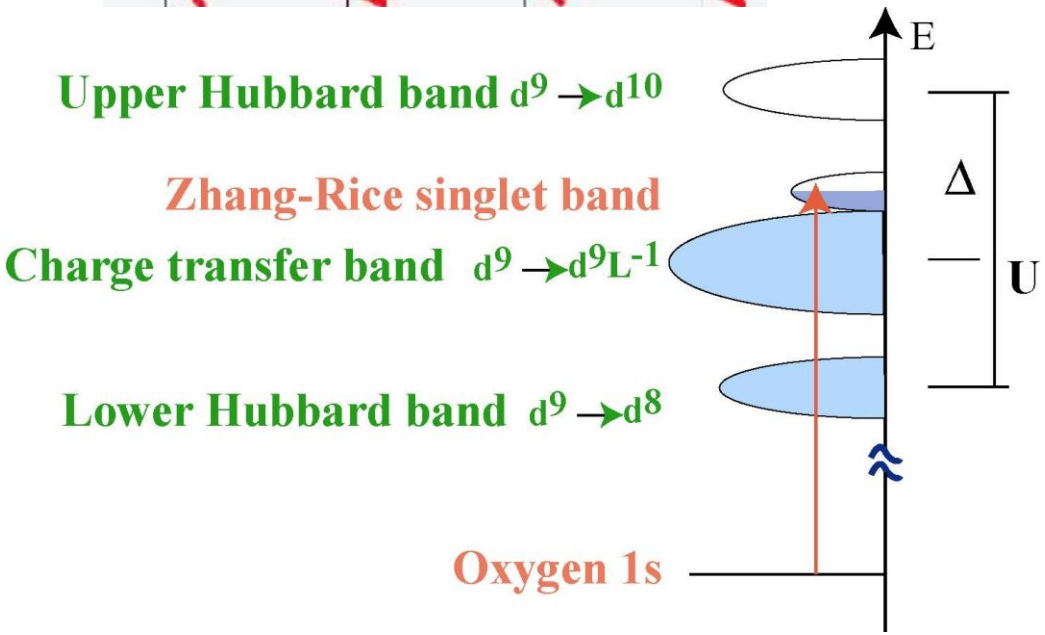
E_I ionization energy
E_A electron affinity energy
E_M Madelung energy

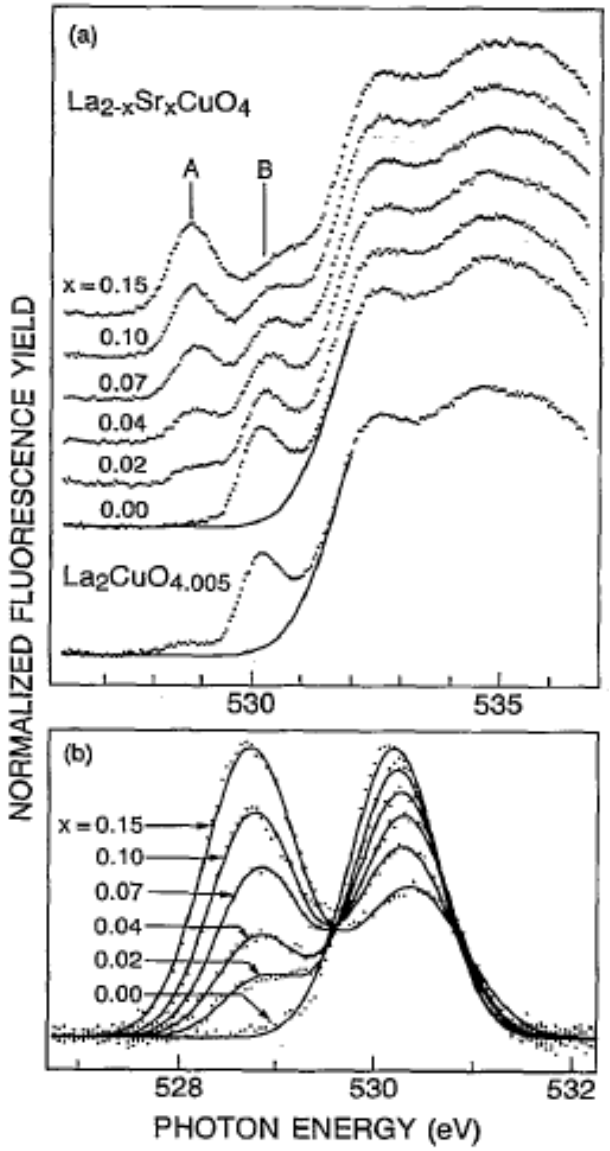
If $\Delta < (W+w)/2$ → Self doped metal

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

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, [illegible] (1991)

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

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+

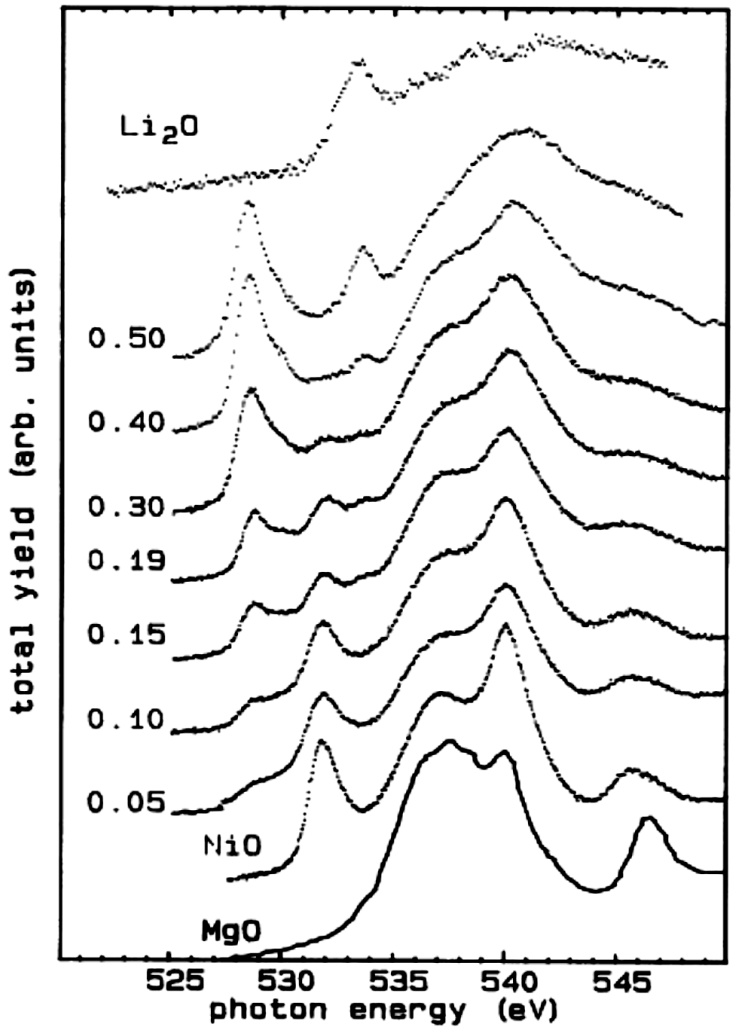
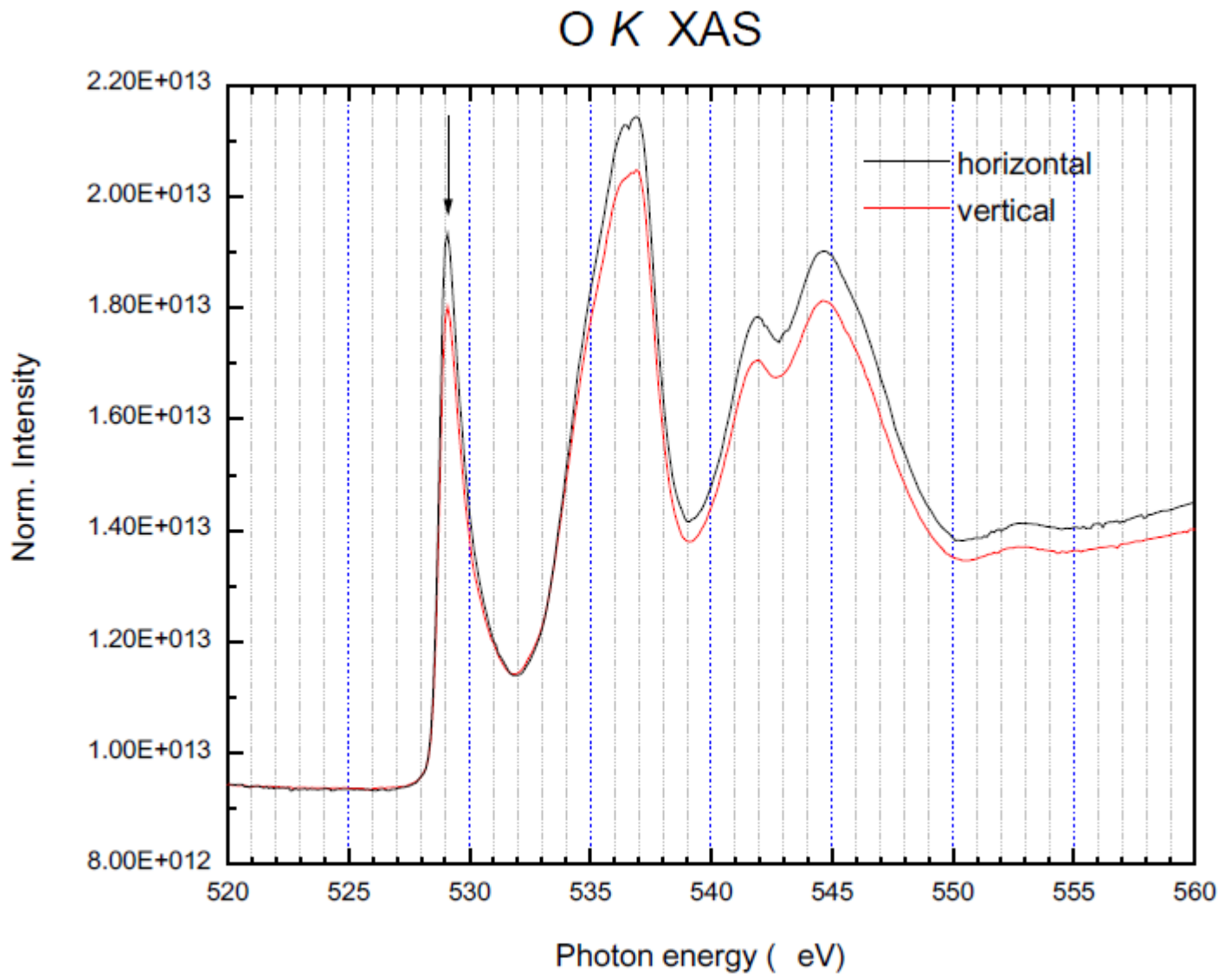


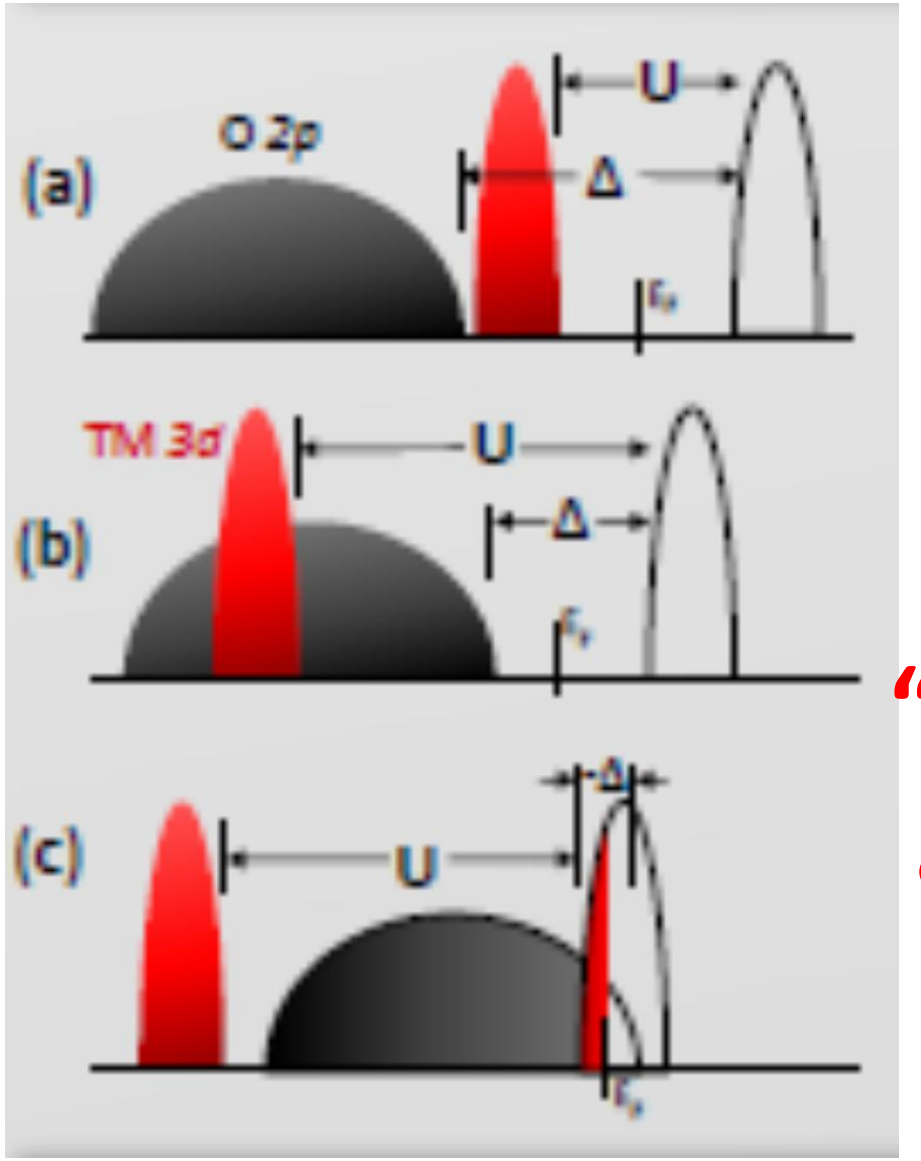
FIG. 1. Oxygen *K*-edge absorption spectra of MgO (Ref. 26), NiO, $Li_xNi_{1-x}O$ for indicated values of x, and Li_2O.

LNO thin film on LSAT Sutarto, Wadati, Stemmer UCSB

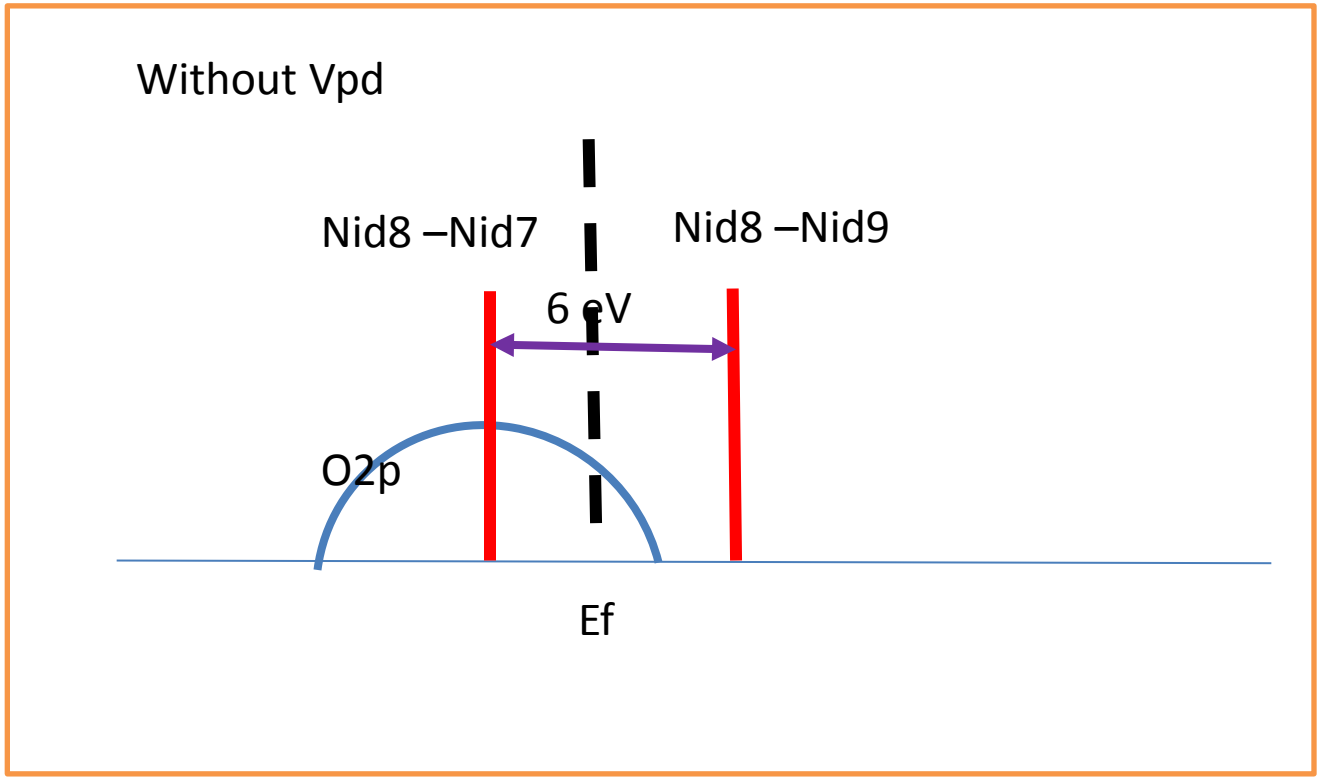
Note the huge O 1s -2p prepeak just as in the cuprates HOLES ON O



Concept of negative charge transfer gap



"Self doped system" as in CrO2


Without Vpd
Nid8 –Nid7
Nid8 –Nid9
6 eV
O2p
Ef

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– Kondo Lattice ansatz**
- Cu2+ with 1 hole per CuO2 planer unit cell
- Could be a Kondo lattice insulator? Use the O 2p holes to screen the Cu spin i.e. a non magnetic insulator

Nickelates RENiO3

Torrance et al PRB 42, 8209

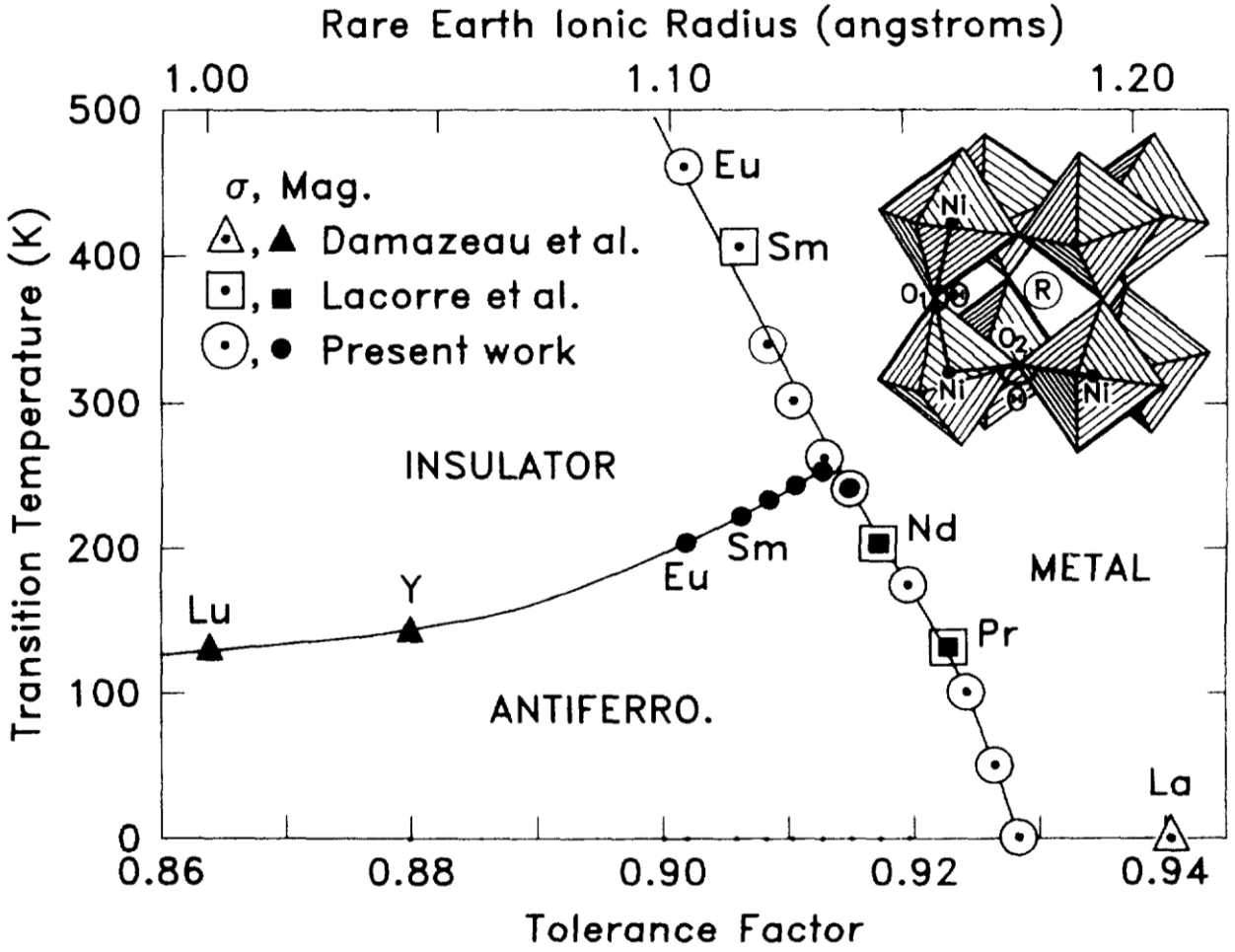


FIG. 2. Insulator-metal-antiferromagnetic phase diagram for $RNiO_3$ as a function of the tolerance factor and (equivalently) the ionic radius of the rare earth (R).

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 ?

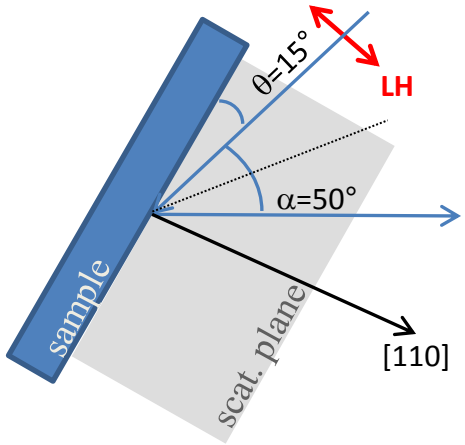
Charge disproportionation into d6 and d8 would solve this problem. But experiments show only very low CDW amplitude in the insulating phase

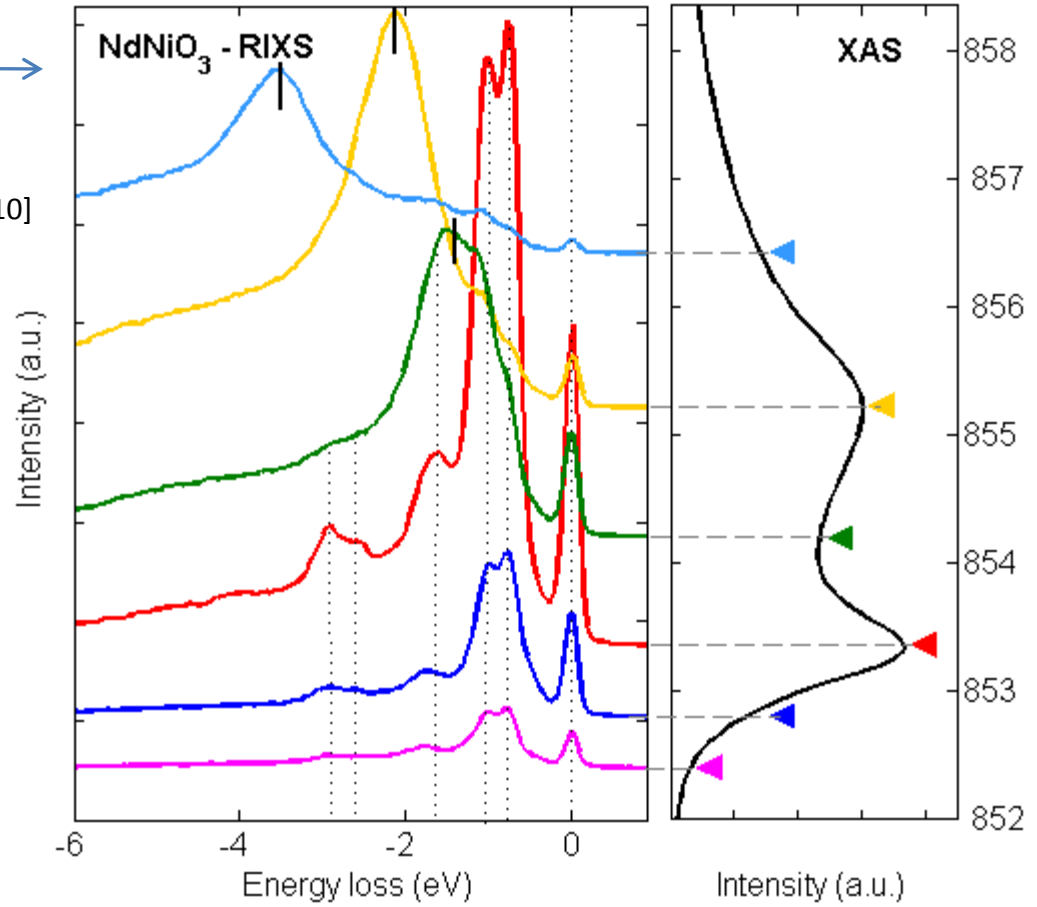
Recent RIXS point to a strongly negative charge transfer gap system results obtained by

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



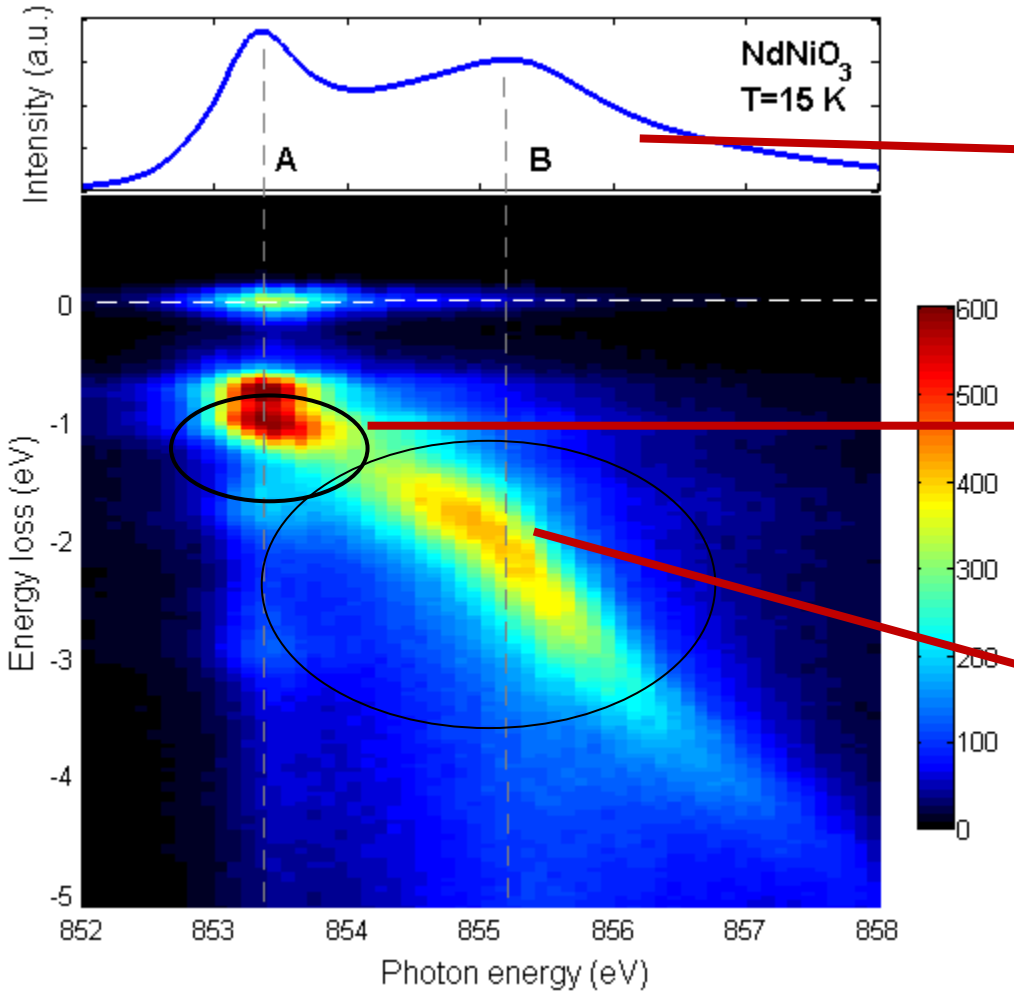


This clearly involves a broad band of states

L -- O 2p HOLE BAND

This involves bound local Multiplet states

RIXS map of $NdNiO_3$ – 15 K insulating phase



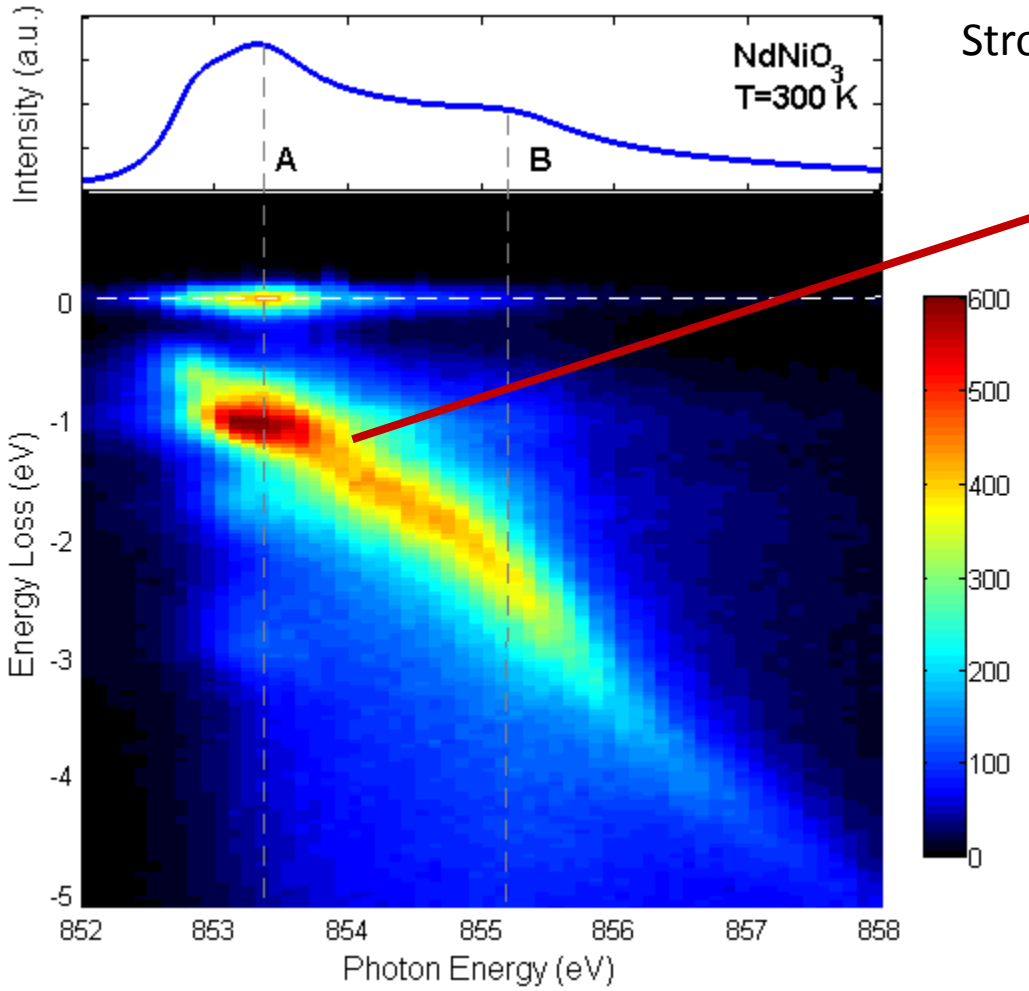
Ni 2p XAS energy region : Up to now the peaks A and B were considered to be ,multiplet structure in the final 2p5 3d8 local states

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 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.
- $Cu^{3+} \rightarrow Cu^{2+}\underline{L}$ $Ni^{3+} \rightarrow Ni^{3+}\underline{L}$ $Co^{4+} \rightarrow Co^{3+}\underline{L}$
- $Fe^{4+} \rightarrow Fe^{3+}L$ Mn^{4+}???

The charge degrees of freedom are in Oxygen 2p bands

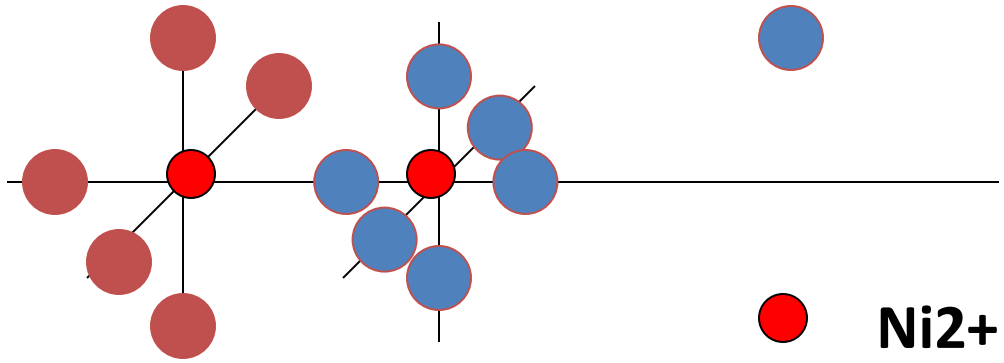
BASIC STARTING POINT FOR NEGATIVE CHARGE TRANSFER GAP

- 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.



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

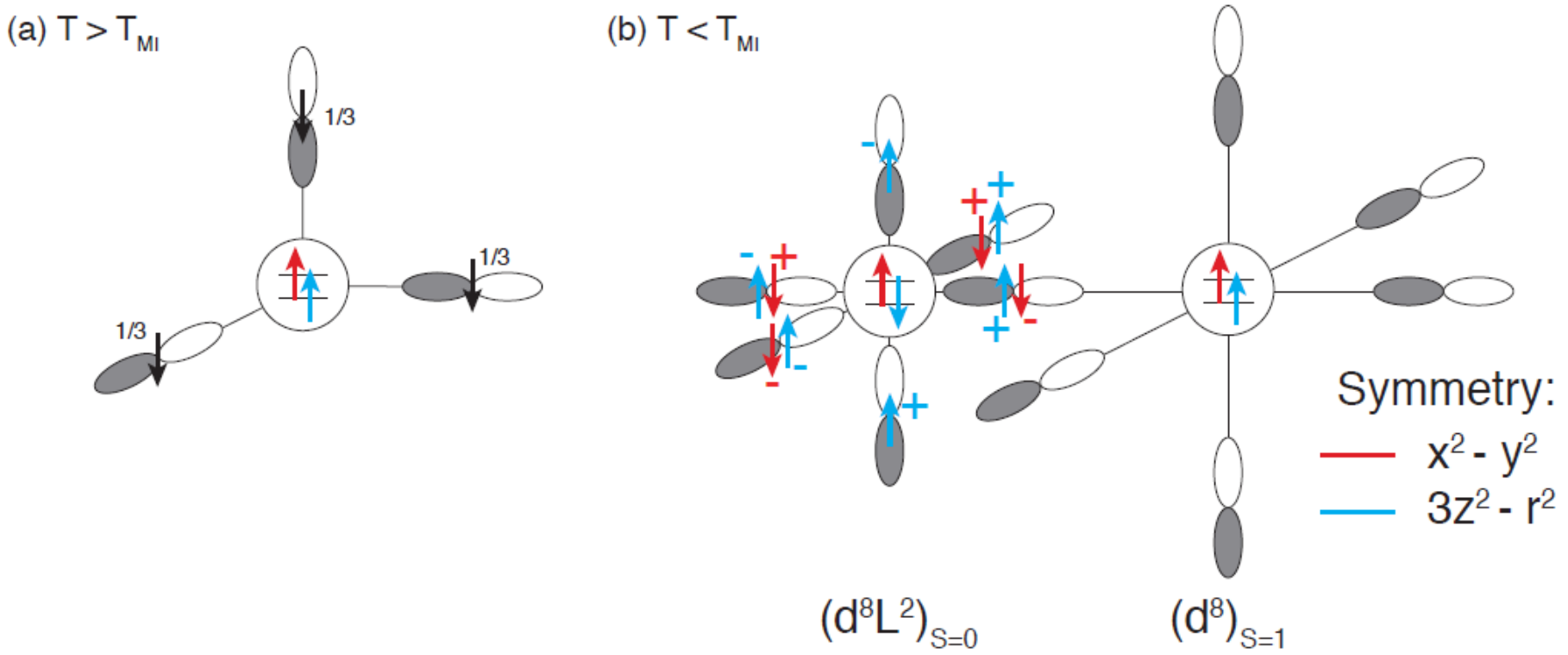
Charge disproportionation without charge transfer

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

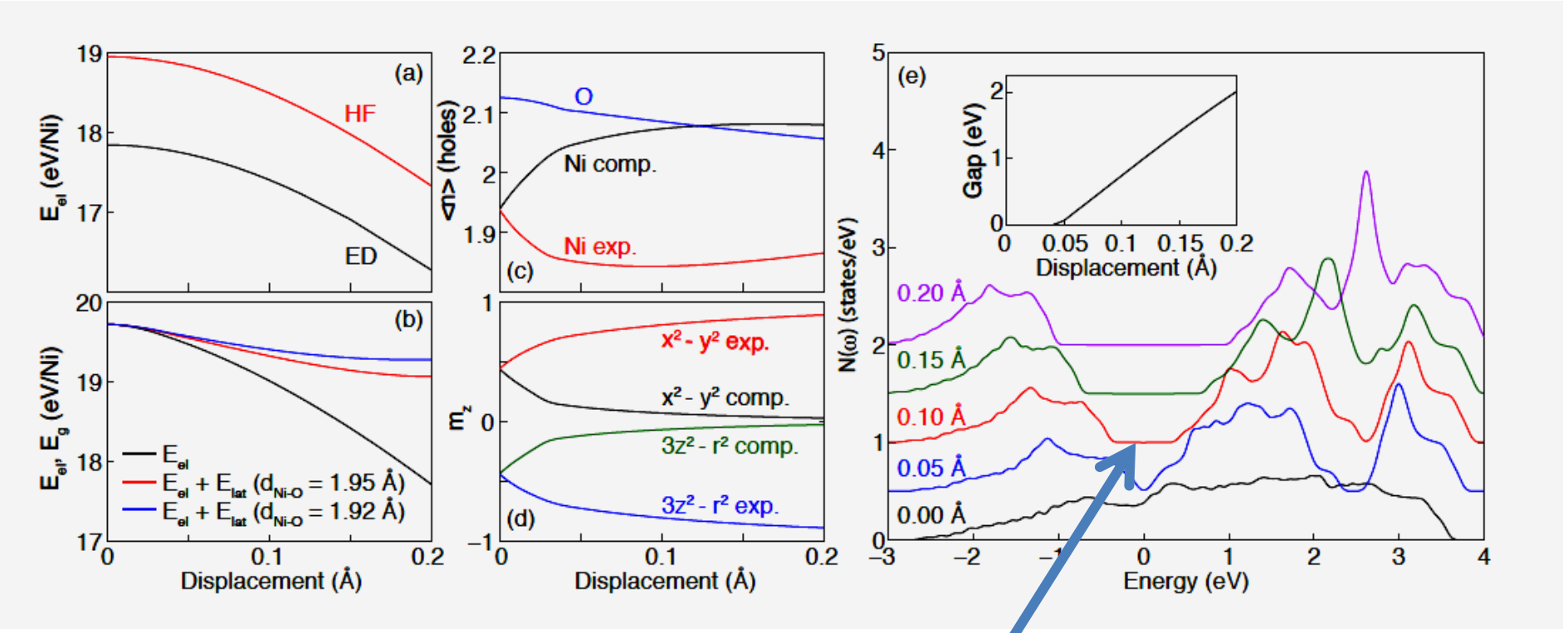
Hartree Fock and exact diagonalization

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).

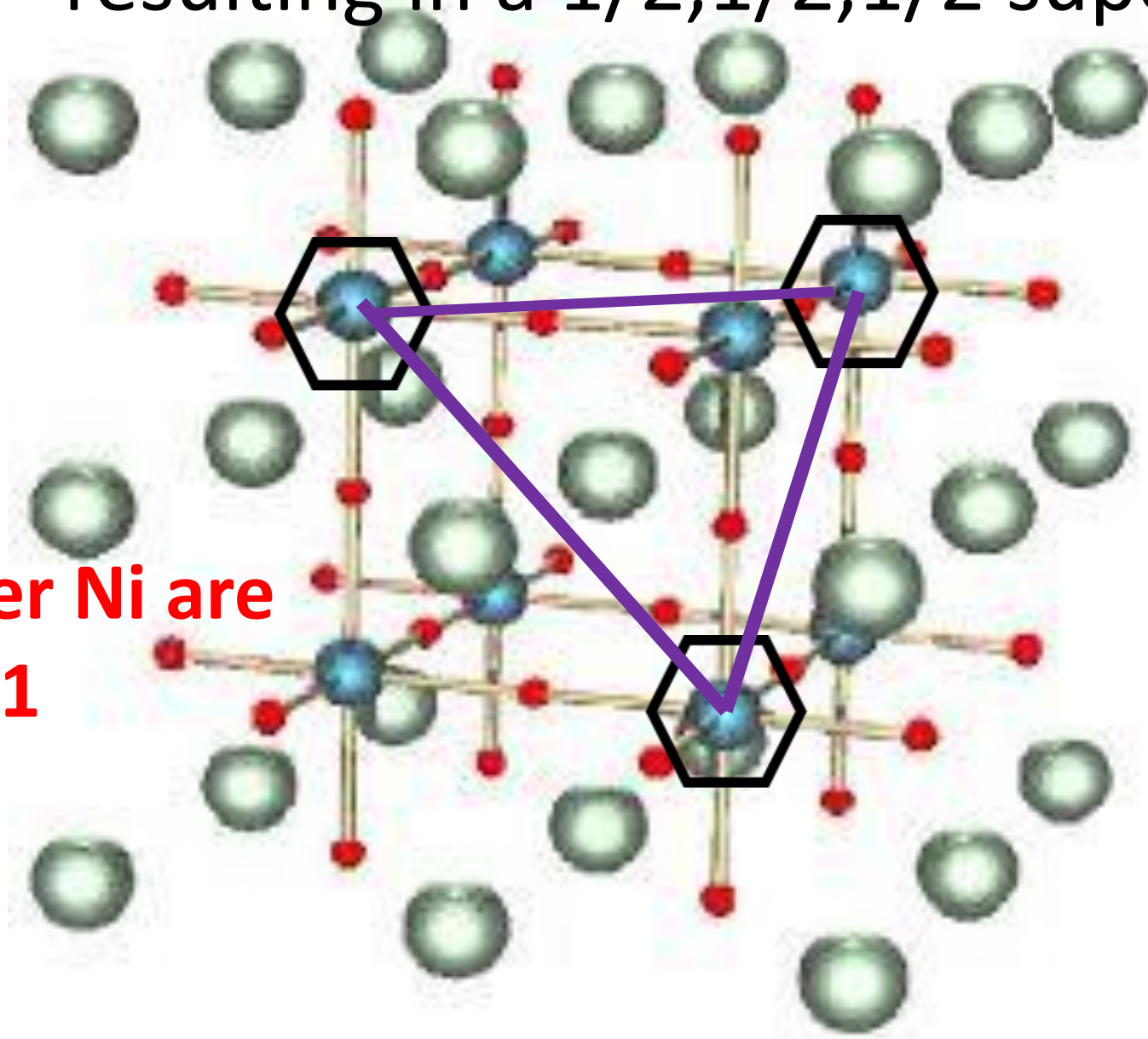


Total energy, charge density, magnetic moment, and density of states vs. checker board O octahedron compression/ expansion



Note the gap forming
for displacements of > .09A

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



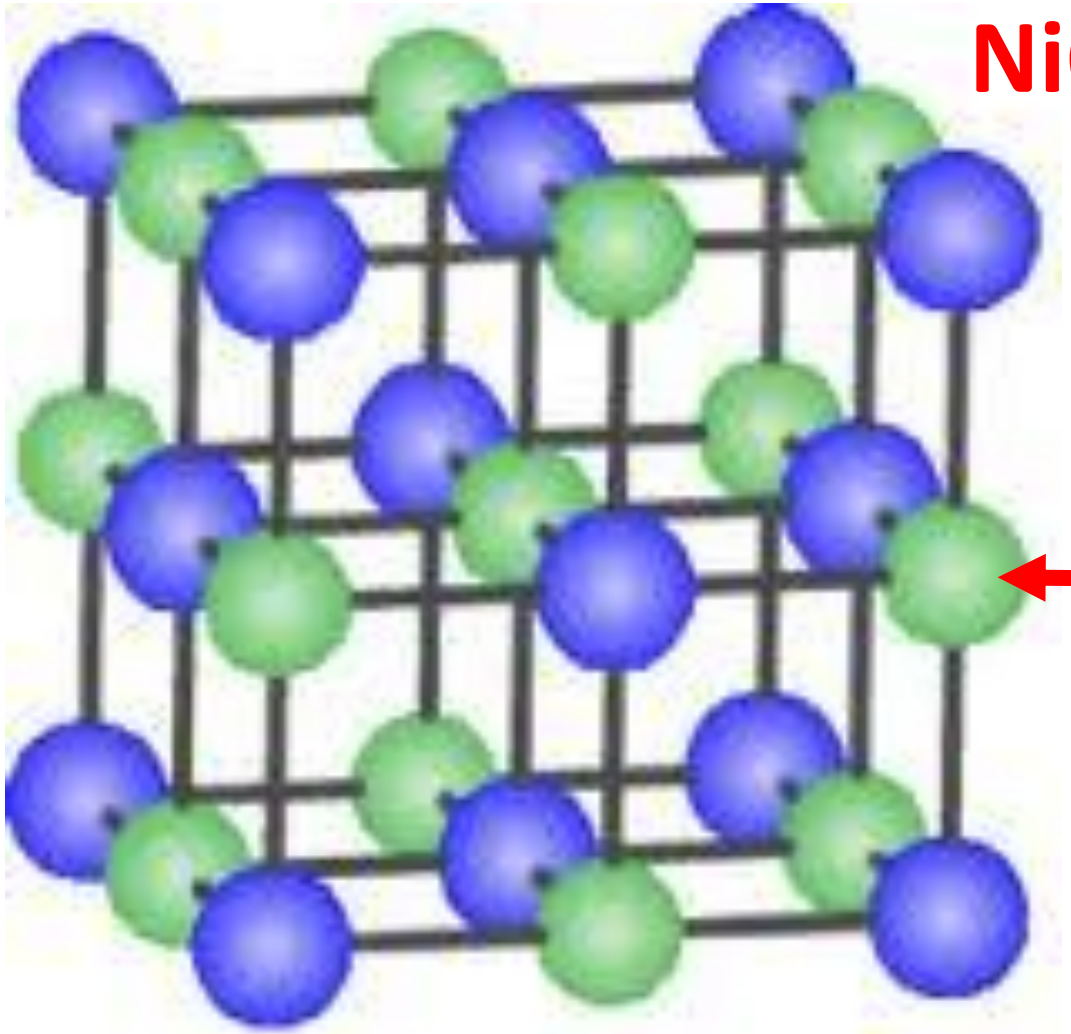
Kondo—Mott insulator

The other Ni are Ni d8 S=1

Relation to the Magnetic structure to NiO

- Replace O in NiO with the collapsed NiO_6 Octahedron S=0 and leave the Ni^{2+} S=1. as in NiO
- This results in a rock salt structure just like NiO
- The collapsed octahedron now replaces the O in NiO to provide the superexcahnge path for the antiferromagnetic coupling between the Ni^{2+} with S+1 each
- This yields 4 antiferromagnetic 3d sublattices with a frustrated interaction between them as in NiO
- This frustration is lifted by dipole- dipole interactions or weak trigonal distortions as in NiO

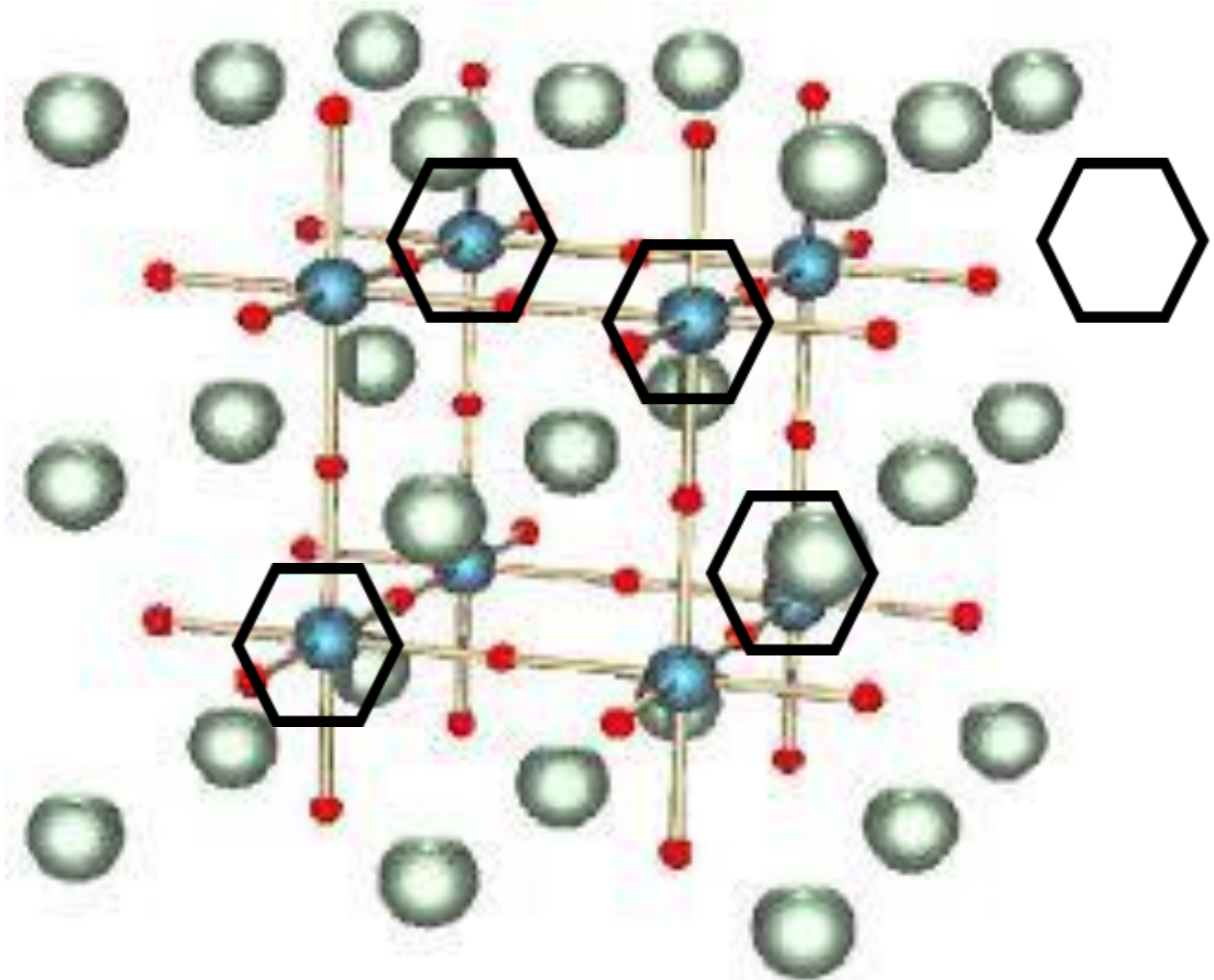
NiO Rock Salt Structure



Replace all O with the Ni
in compressed Octahedra

The compressed Octahedra with total spin zero now act as the Superexchange path antiferromagnetically coupling the other Ni's with S=1 into An antiferromagnetic structure

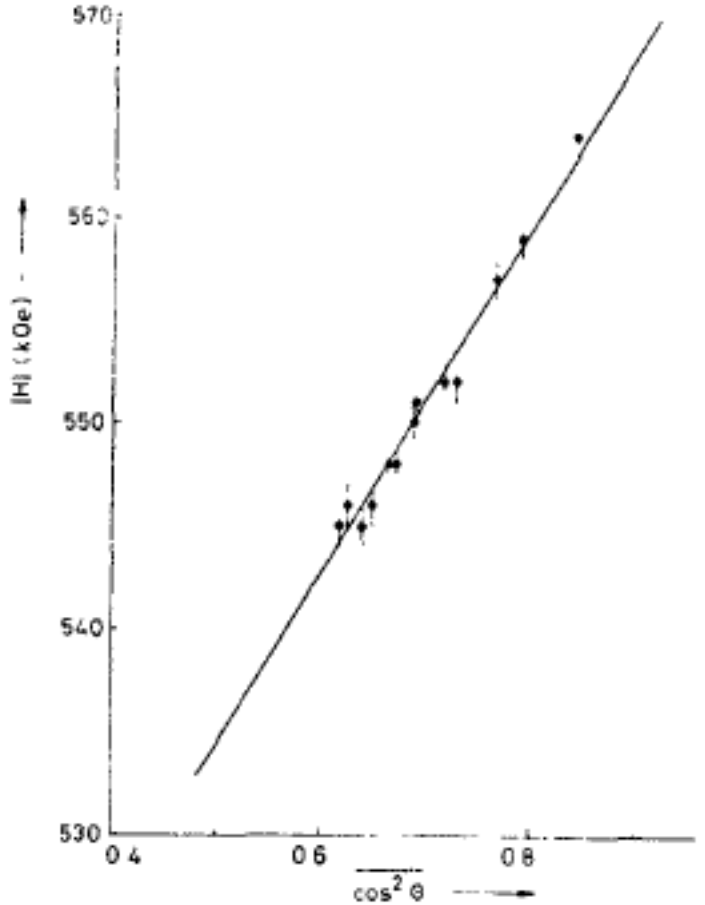
Each of the 4 Ni S=1 form their own AF structure with a frustrated interaction between them as in NiO



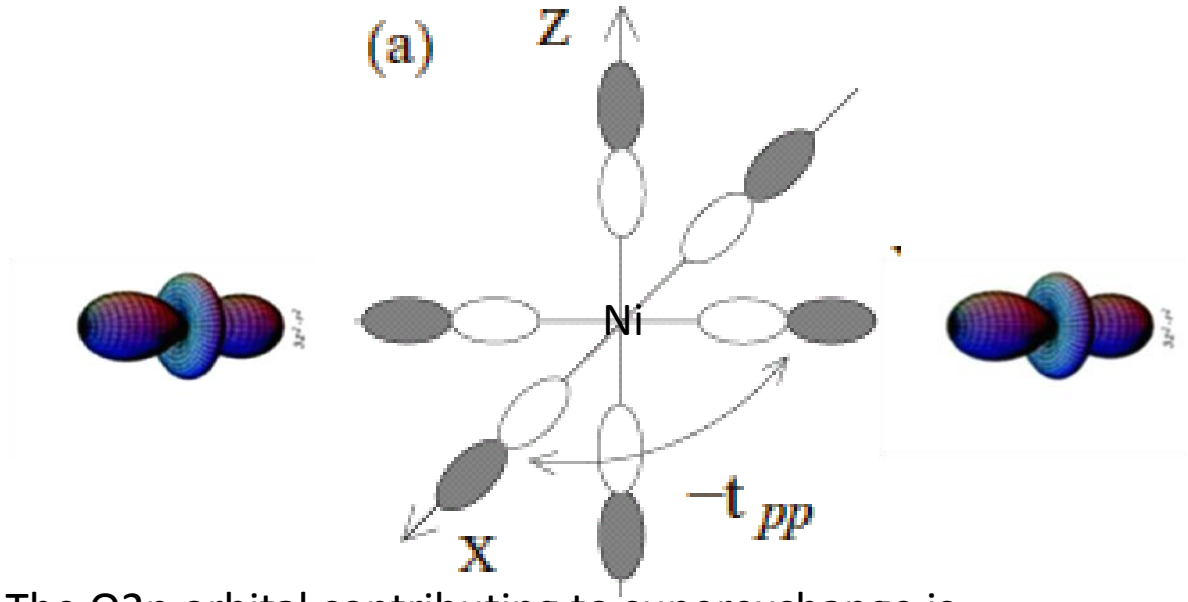
Are Ni with S=1

[4] Boekema, C. van der Woude, F. and Sawatzky, G.A.,
Int. J. Magnetism 3 (1972) 341.

REFeO3 showing the Neel Temperature VS Fe-O-Fe Bond angle squared

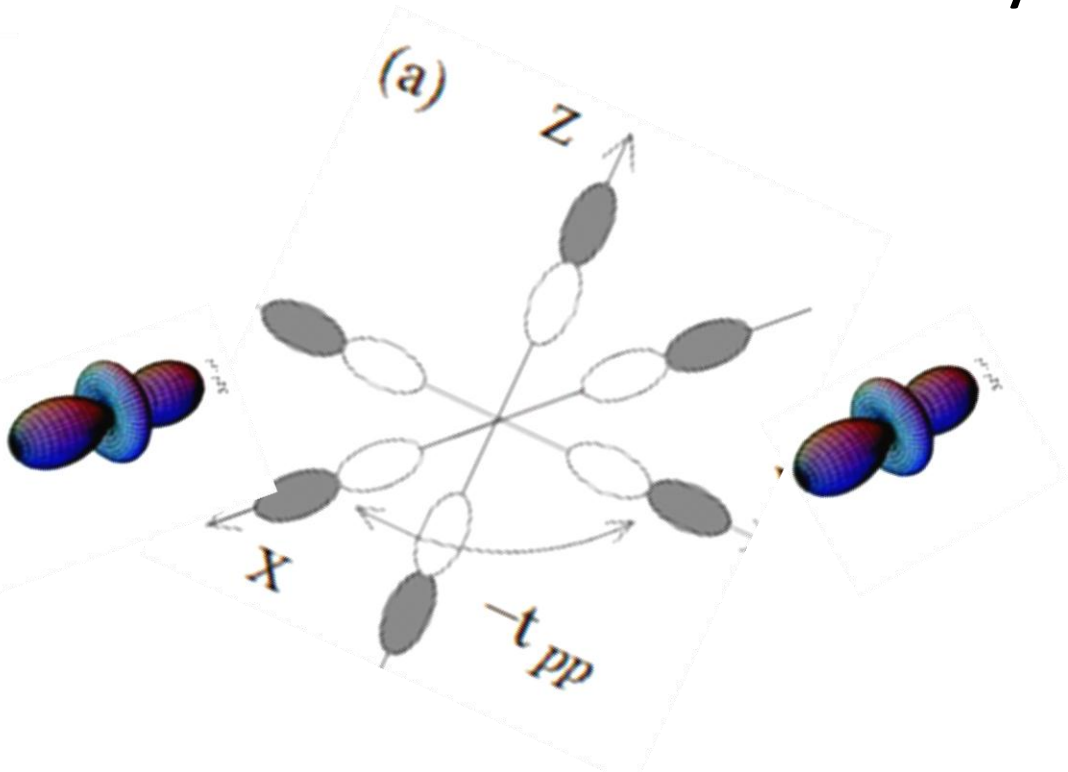


Octahedral rotations and superexchange in the ½ collapsed phase of ReNiO3



The O2p orbital contributing to superexchange is
A linear combination of Eg symmetry about the
Central Ni

Local rotated coordinate system



Again goes as COS**2(ϕ)

Tn decreases with ϕ

Tc for CDW increases withϕ

Nickelates RENiO3

Torrance et al PRB 42, 8209

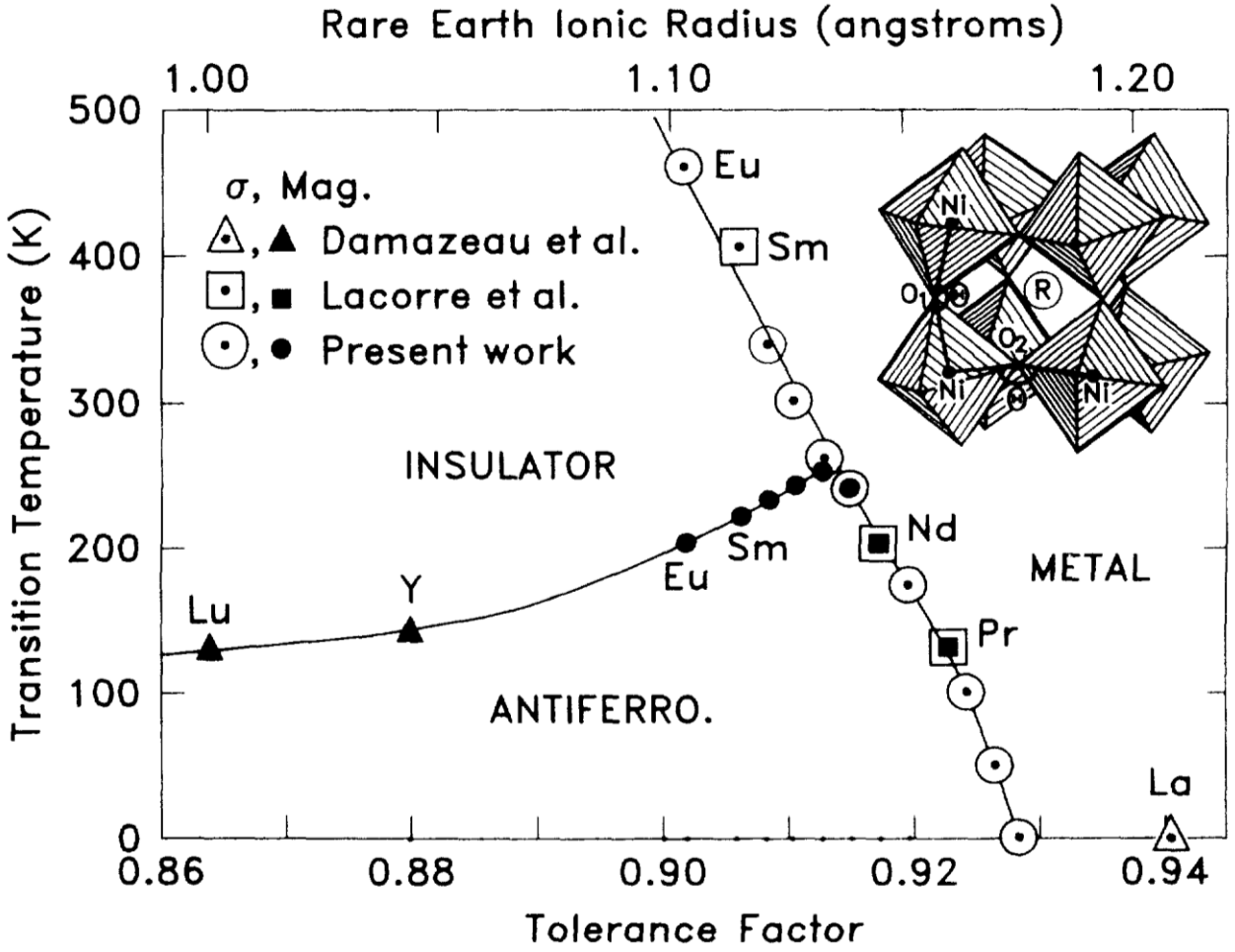


FIG. 2. Insulator-metal-antiferromagnetic phase diagram for $RNiO_3$ as a function of the tolerance factor and (equivalently) the ionic radius of the rare earth (R).

The phase diagram of RENiO3

- Nickelates are negative charge transfer gap materials with Ni2+and 1/3 holes per O
- Including electron phonon get an insulating phase above a critical value of breathing mode O compression in a 1/2,1/2,1/2 superstructure. The Tc will strongly increase with Octahedral tilting
- The compressed Octahedra with S=0 act as the superexchange path for the other Ni each with S=1 forming a 1/4,1/4,1/4 antiferromagnetic superstructure similar to that of NiO
- Tn will strongly decrease with Octahedral tilting as observed.