Charge ordering as alternative to Jahn-Teller distortion

In collaboration with ***Michelle Johannes[1], Daniel Khomskii[2] (theory) and Mohsen Abd-Elmeguid et al[2], Radu Coldea et al[3] (experiment)***

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[3]University of Bristol

N

vacu

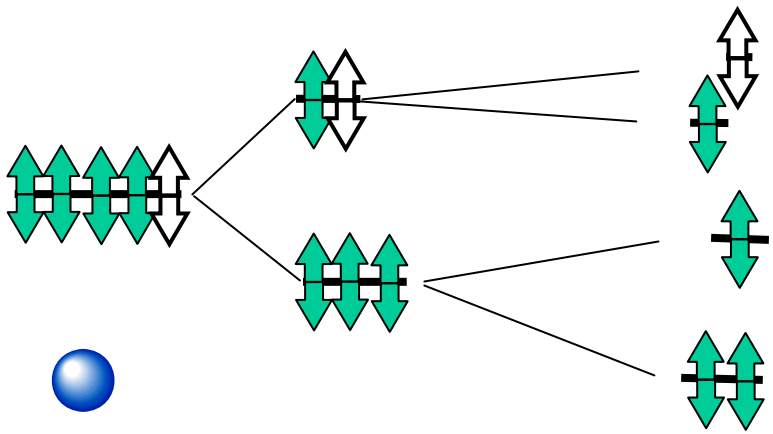
Nature also abhors a vacuum salesman.

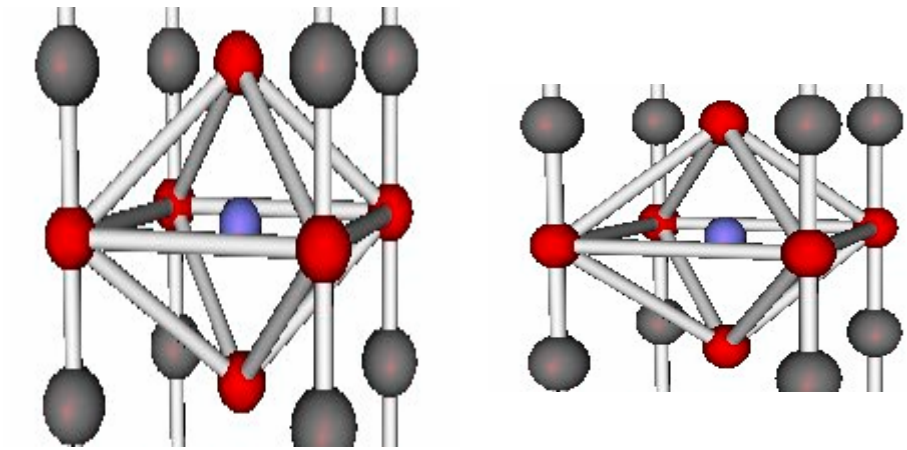
In quantum chemistry, one can equally well say that Nature abhors an orbital degeneracy.
In band theory, it translates in Nature hating high DOS at the Fermi level and loving large gaps.

Jahn-Teller effect:

a manifestation of "natural abhorrence"

Example 1: nonmagnetic Ni^{2+} ion in an octahedral environment

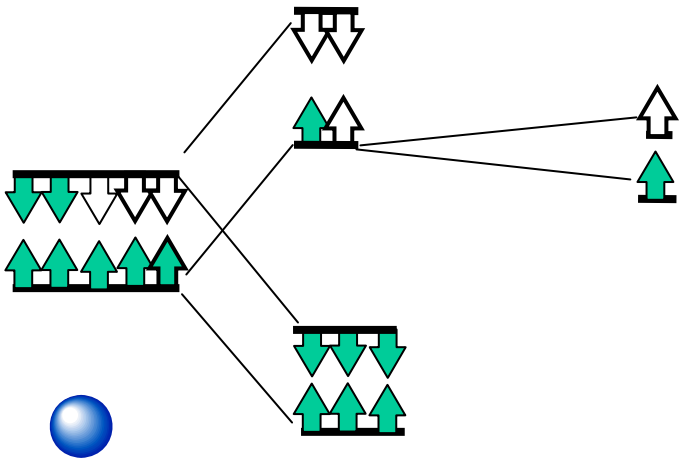


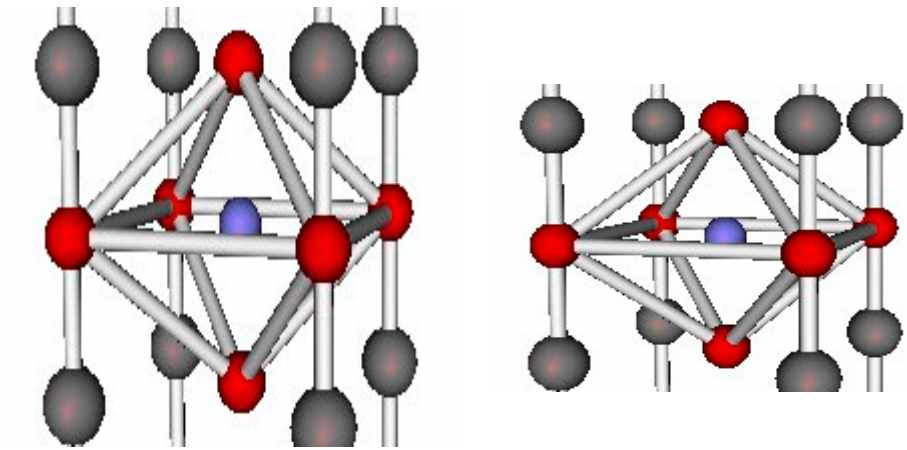


Distortion of the octahedral environment provides crystal-field splitting such as the occupied e_g level goes down and the unoccupied one goes up

Jahn-Teller effect: magnetism

Example 2 (more realistic): magnetic Ni^{3+} ion (*e.g.*, $NaNiO_2$)

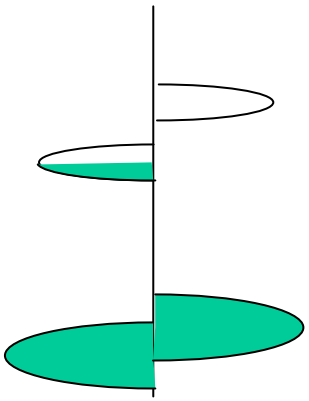


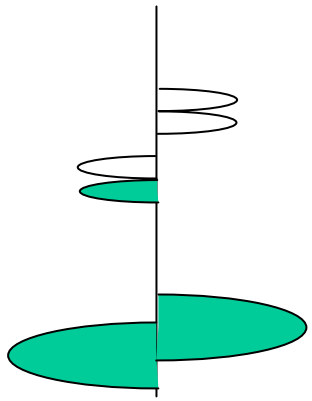


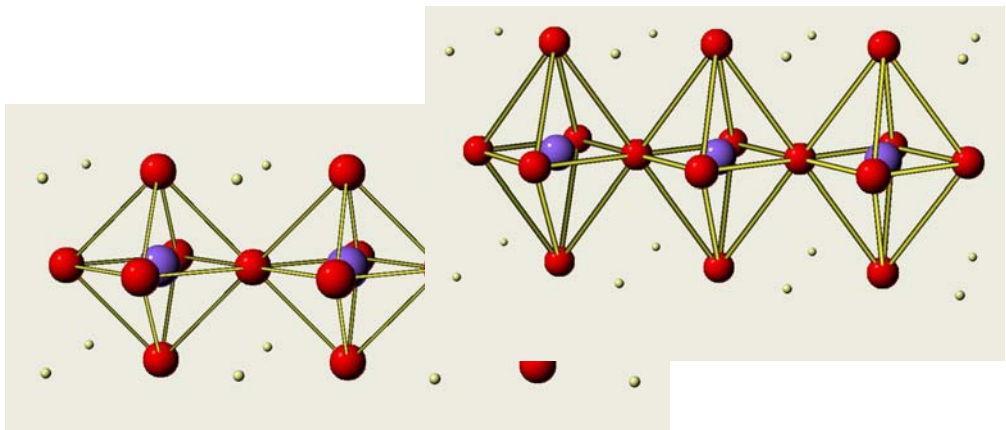
Distortion of the octahedral environment provides crystal-field splitting such as the occupied e_g level goes down and the unoccupied one goes up *in one spin channel*

Band (cooperative) Jahn-Teller effect

Example 3: Ni^{3+} bands







As long as the additional crystal field is larger than (or at least comparable with) the band width, the distortion is energetically favorable.

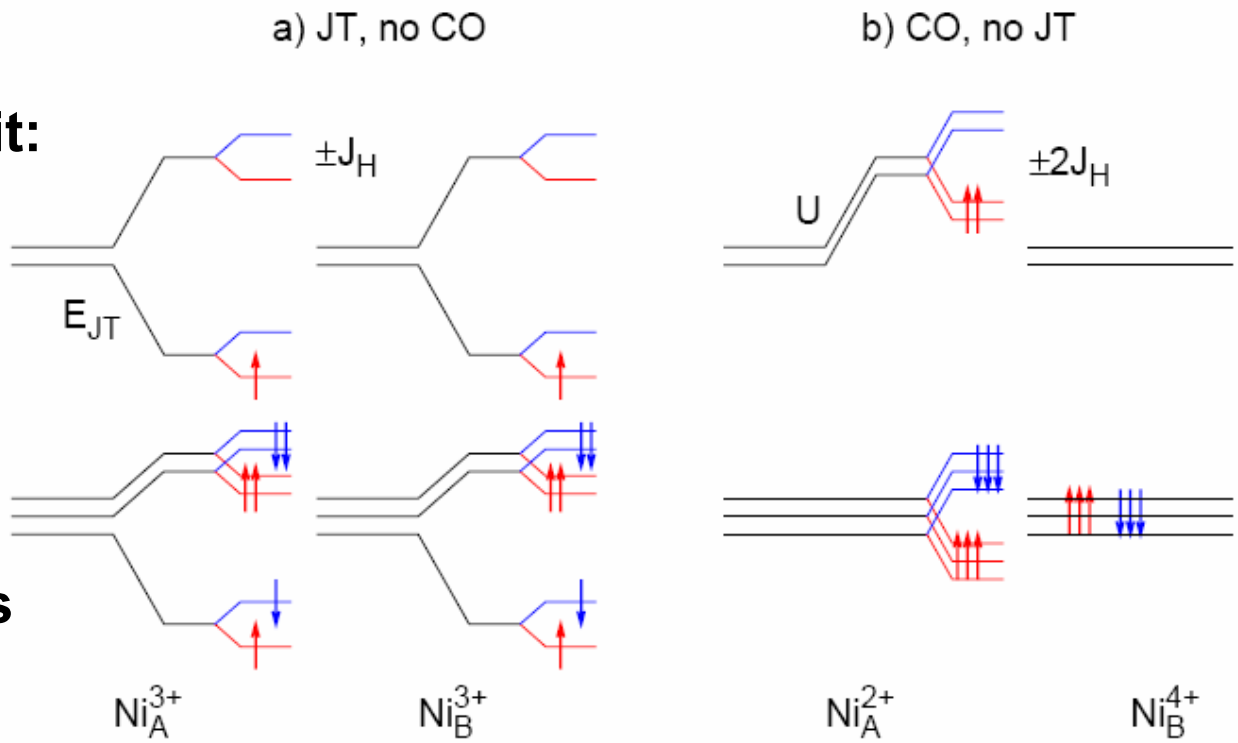
Itinerant or localized?

Localized limit: JT

Fully itinerant limit: No distortion

What about a crossover?

In the crossover charge ordering is an option!



Energy balance

$$H = \sum_{i \neq j, \alpha\beta} t_{i\alpha j\beta} c^{\dagger}_{i\alpha\sigma} c_{j\beta\sigma} + U \sum_{i, \alpha\sigma \neq \beta\sigma'} n_{i\alpha\sigma} n_{i\alpha\sigma'} \qquad (1)$$

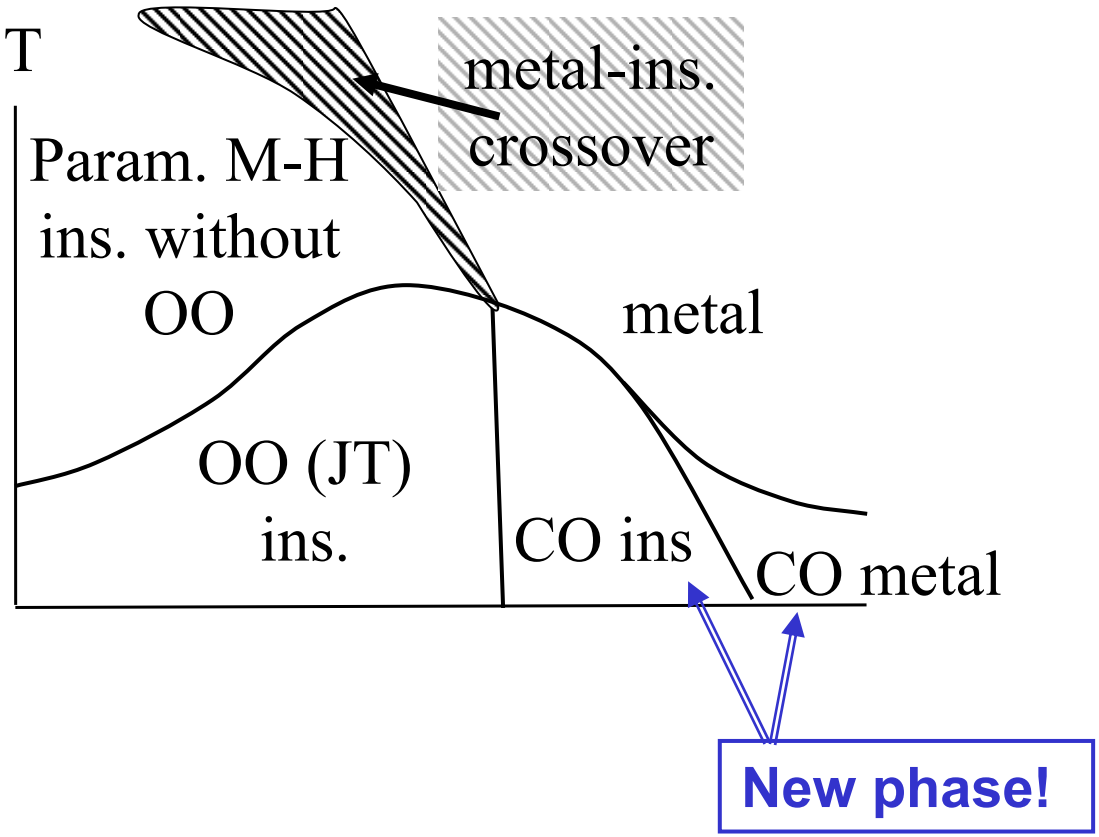
$$- J_H \sum_{i, \alpha \neq \beta} \vec{S}_{i\alpha} \vec{S}_{i\beta} - \sum \{E_{JT} - E_{strain} + E_{breath}\}.$$

Strongly correlated system (Mott insulator):

Fully itinerant metal

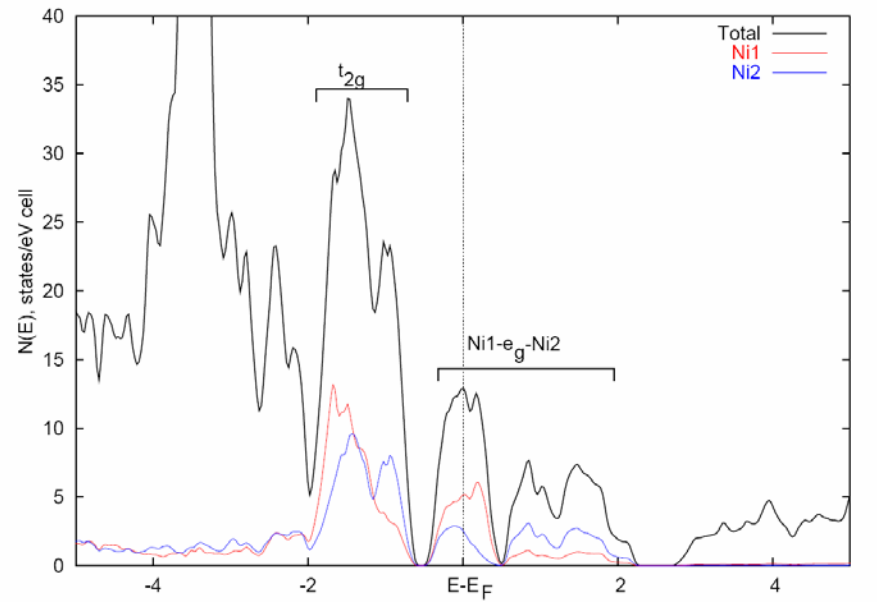
Intermediate case (vicinity of Mott transition)

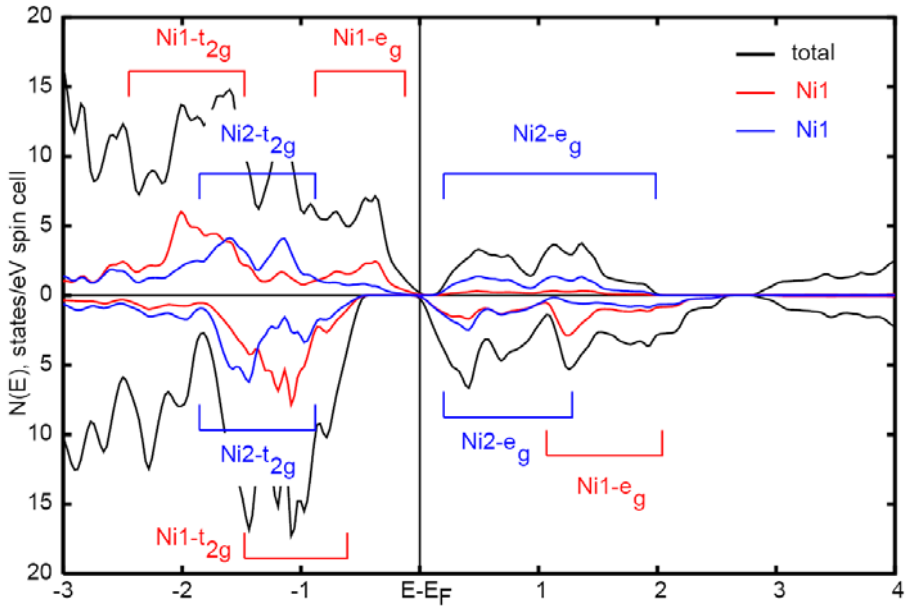
Phase diagram



T-dependent part of this diagram is highly speculative (no calculations)!

Band structure calculations





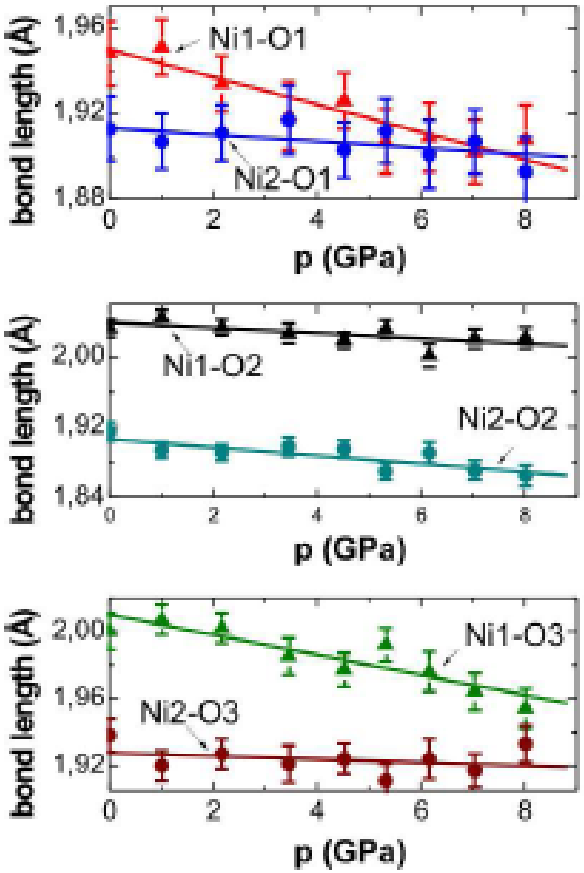
DOS of *nonmagnetic* $LuNiO_3$. Note that Ni1 e_g is half-filled, and Ni2 is empty

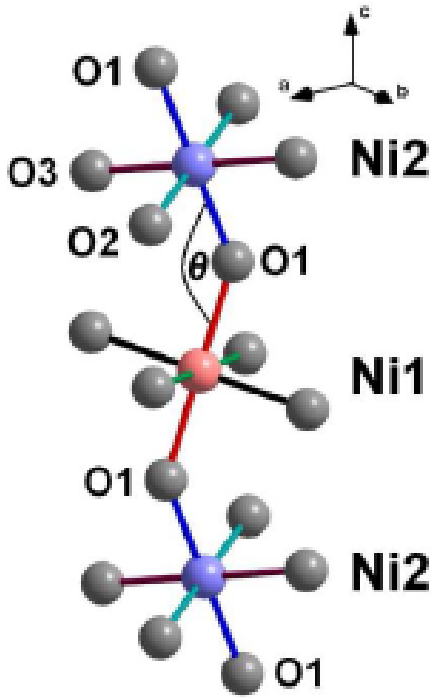
Structure optimization eliminates OO!

DOS of *ferromagnetic* $LuNiO_3$. Note that Ni1 e_g is now fully spin-split.

Structure optimization sustains OO!

Effect of pressure (M. Abd-Elmeguid et al)





P=0: gap ~ 70 meV

LDA: 0-20 meV

LDA+U: ~1 eV

P=8 GPA: gap ~0

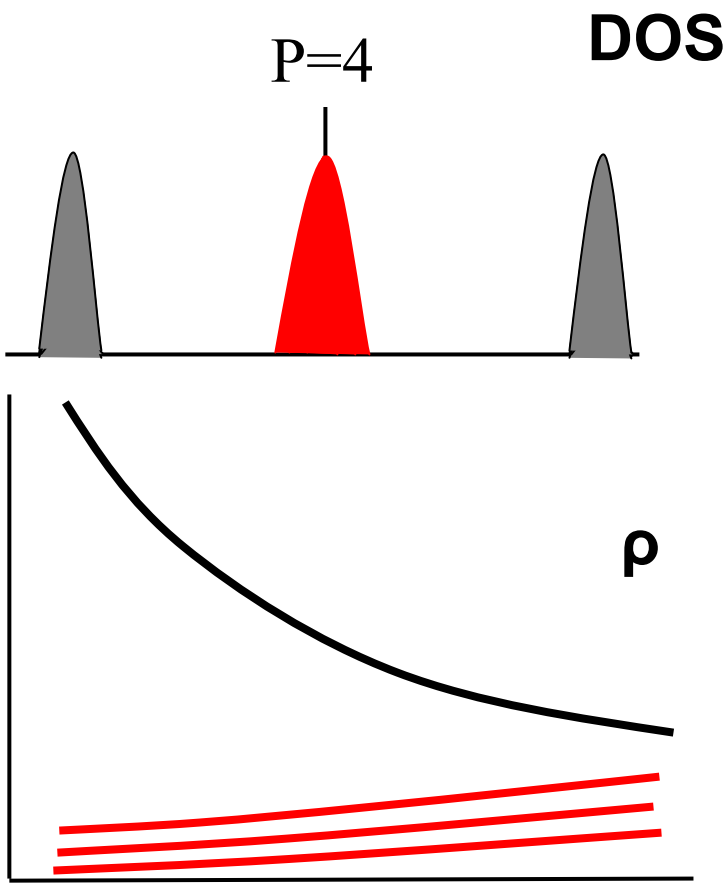
LDA: –100 meV

LDA+U: ~ 1 eV

LDA+U does *not* agree with the experiment, in accord with the weak-correlation scenario!

Mott Insulator or Band Insulator?

Litmus test: character of the gap closure - ρ(T). (*cf. DOS evolution)*



Mott insulator:

1. The gap is large → the current is carried by the metal component.
2. The spectral weight is gradually transferred from the insulating component to the metal component
3. The activation energy changes little with pressure; the character of the conductivity changes at the transition

Mott Insulator or Band Insulator?

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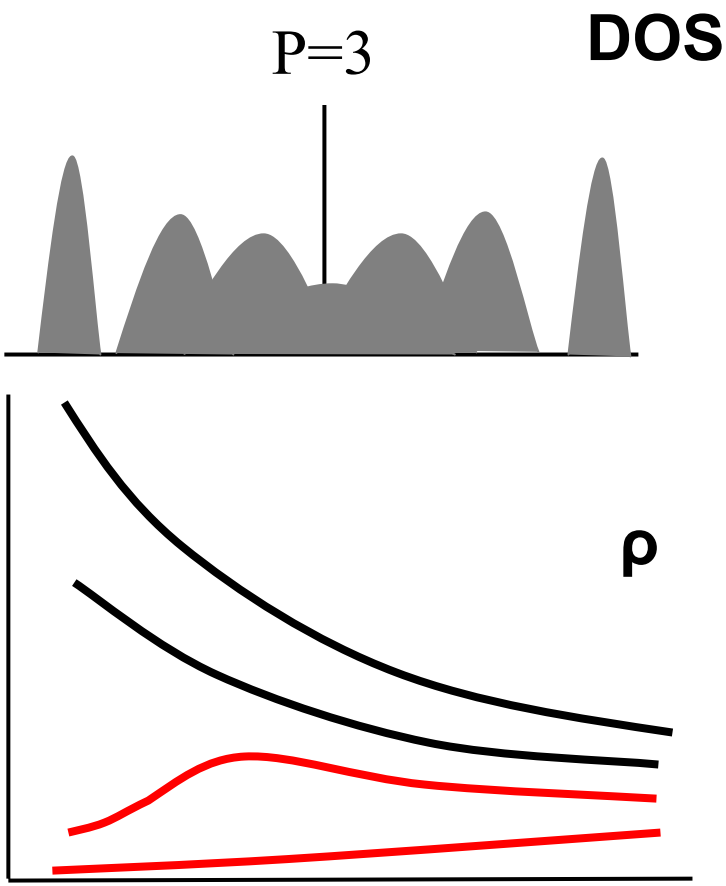
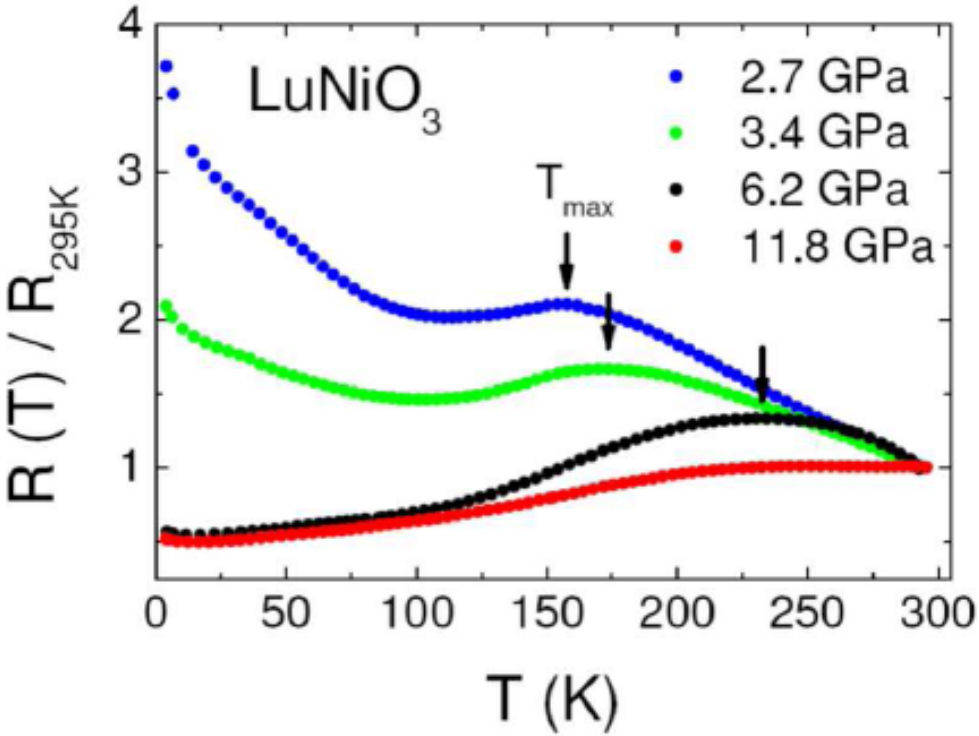


Band insulator:

1. The gap is genrally smaller and closes gradually
2. The activated component gradually develops metallic behavior
3. Nonmonotonic T-dependence possible when the average gap is ~ Debye temperature

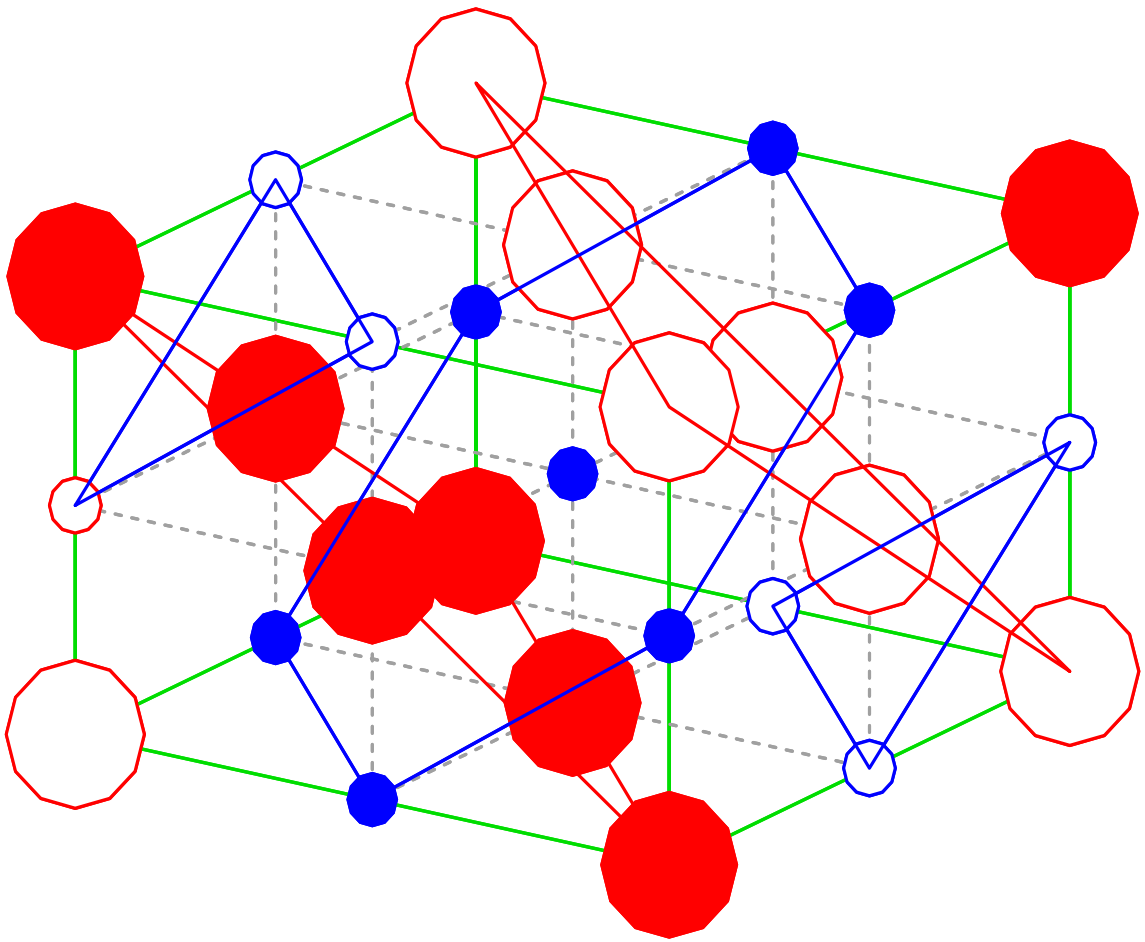
Experimental resistivity



M. Abd-Elmeguid, R. Lenzdorf *et al*, Cologne

Not a “typical Mott-Hubbard transition”!

Magnetism



Highly unusual magnetic structure!

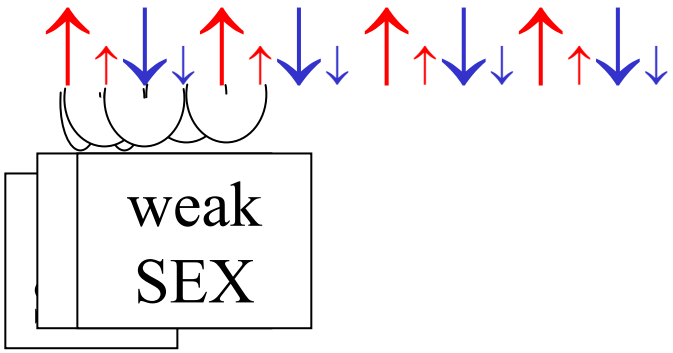
1. Alternating large and small moments
2. Ordering along the Ni-O-Ni direction is ↑↑↓↓
3. Ordering direction for Ni^{4+} is 111, for Ni^{2+} is $\bar{1}11$

Large symbols: M=1.4 μ_B Filled symbols: up

Small symbols: M=0.7 μ_B Open symbols: dn

Magnetism

Highly unusual antiferromagnetism:



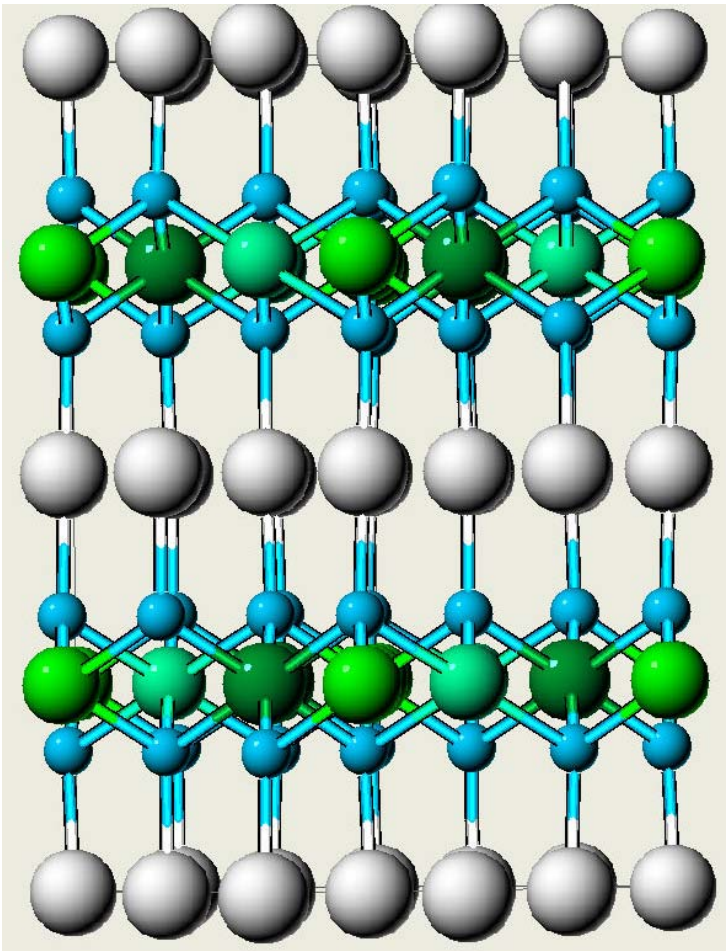
Superexchange path is

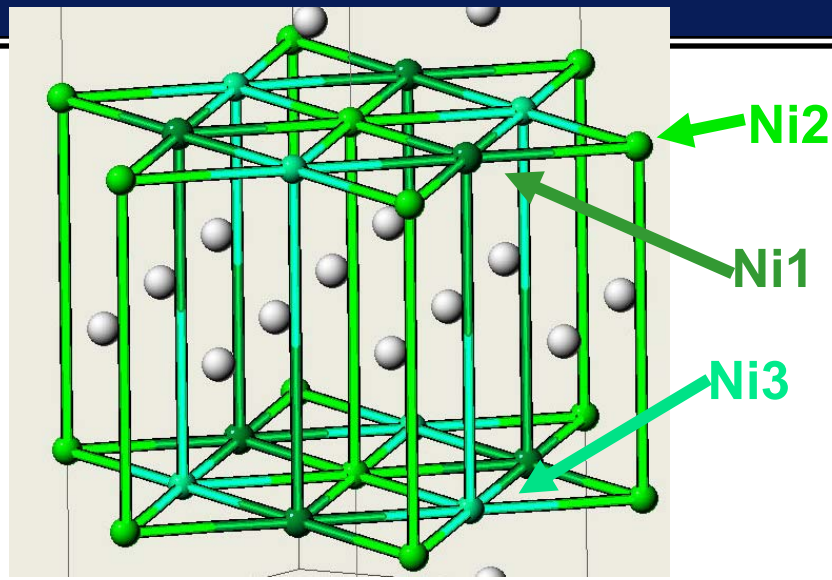
Ni1-O-Ni2-O-Ni1

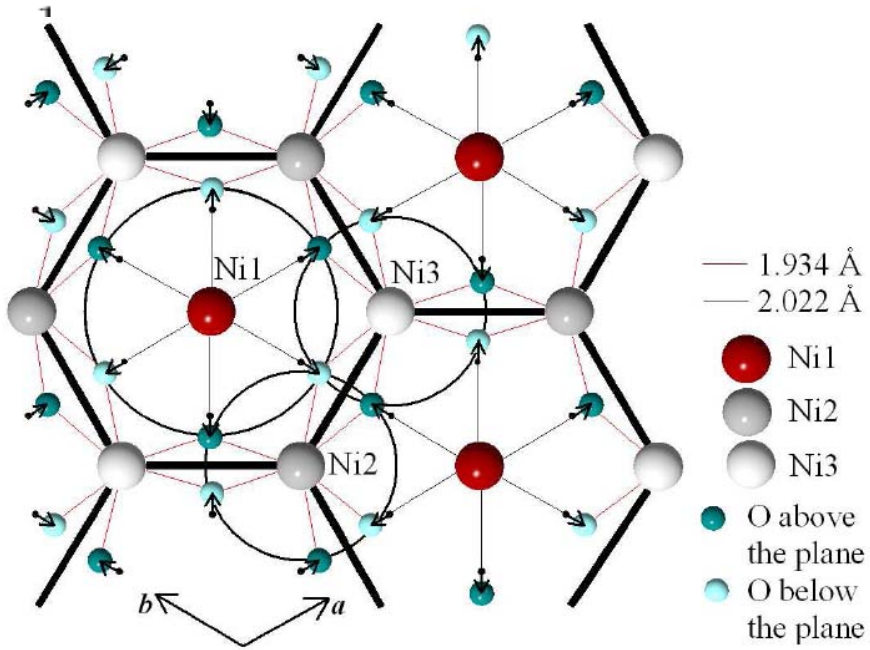
"Double" antiferromagnetic ordering follows naturally.

To read more: I.I. Mazin, D.I. Khomskii, M.M. Abd-Elmeguid, et al, Phys. Rev. Lett. ***98****, 176406 (2007)*

Example 2: Ag_2NiO_3





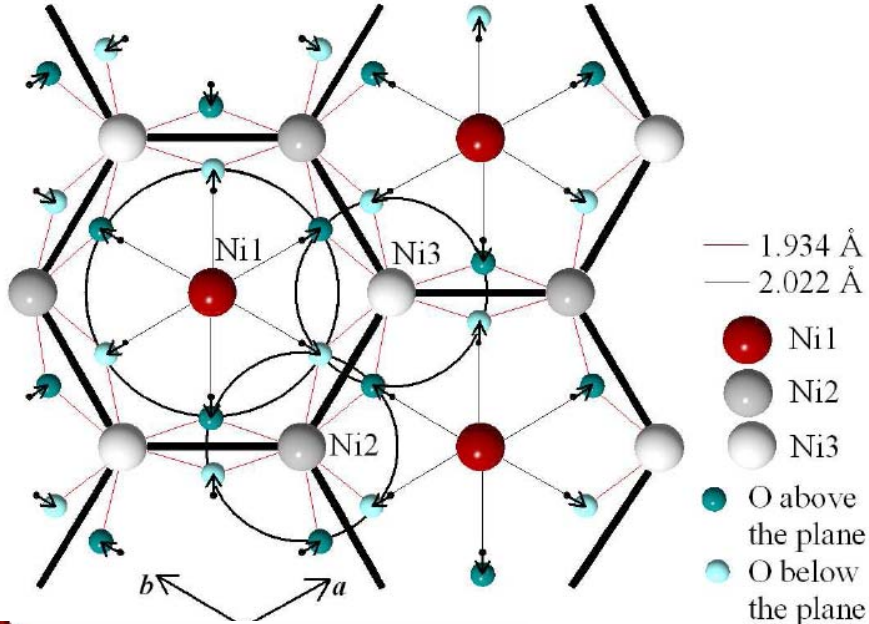


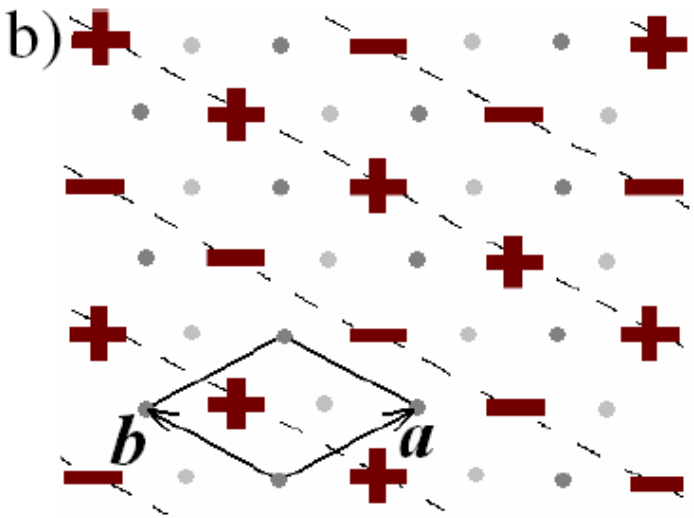
After neutron experiments from Coldea et al, Bristol

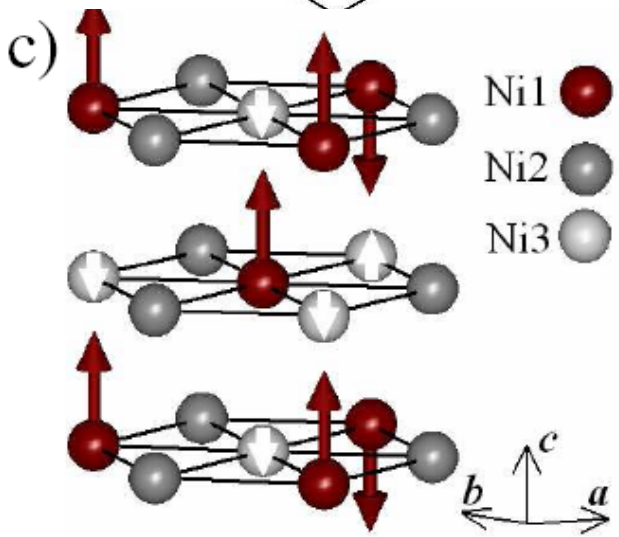
Magnetism

	$Ni1^{2+}$	$Ni2^{3.5+}$	$Ni3^{3.5+}$
exp	1.52	0	0
calc	1.3-1.5	0.05-0.1	0.1-0.15

E. Wawrzynska, R. Coldea, et al, cond-mat:0705.0668







Questions:

- Why charge disproportionation?
- Why $3Ni^{3+} \rightarrow Ni^{2+} + 2Ni^{3.5+}$, and not $2Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+}$, as in $YNiO_3$?
- Why Ni^{2+} has 1.5 μ_B and not 2, and $Ni^{3.5+}$ <0.15 μ_B and not 0.5
- Why collinear (Ni^{2+} has L=0)?
- Why net interplanar Ni1-Ni1 exchange is FM
- Why stripes?

Questions:

- Why charge disproportionation?

Before charge ordering:

$M_1=M_2=M_3=1\ \mu_B \quad N_1=N_2=N_3=\tilde{N}$

$E_{Hund}=\Sigma M^2(I-N^{-1})/4= 3(I-\tilde{N}^{-1})/4$

After charge ordering

$M_1=2\ \mu_B, M_2=M_3=0\ \mu_B \quad N_1>\tilde{N}>N_2=N_3$

$E_{Hund}=4(I-N_1^{-1})/4>3(I-\tilde{N}^{-1})/4$

- There is also a gain in covalence energy (W. Harrison) that I do not discuss here

Questions:

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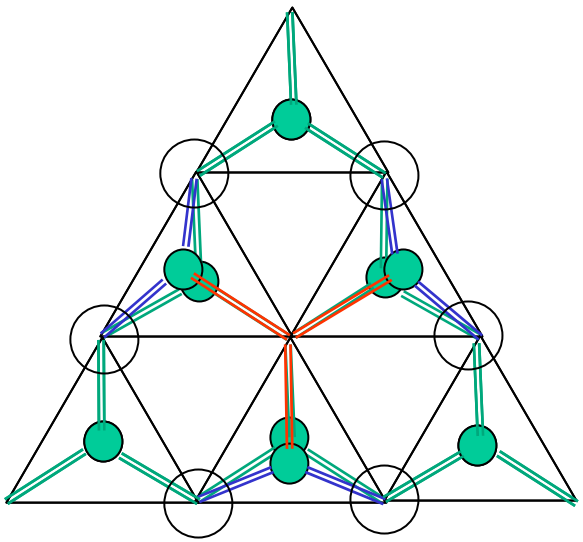
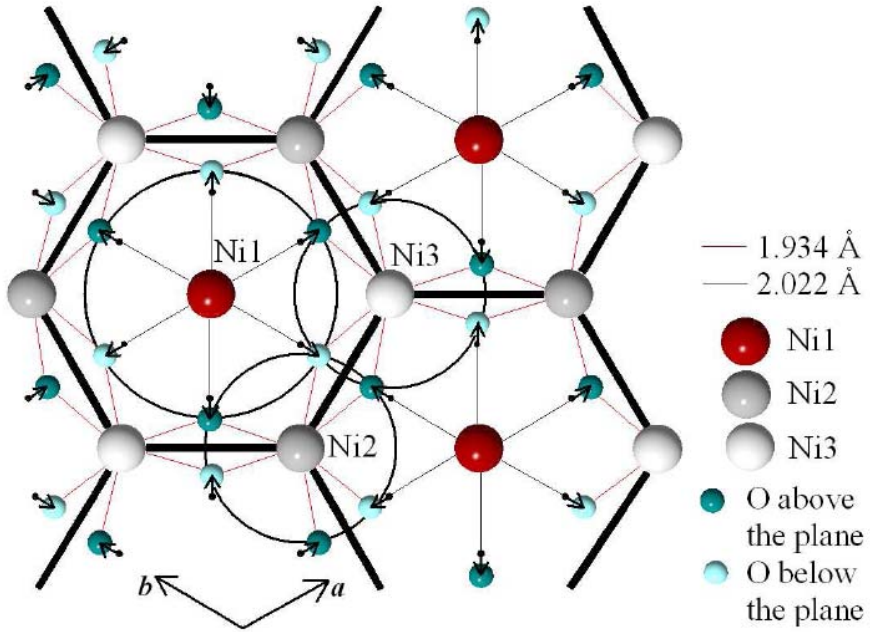
It is impossible to make to make every other O breath in and out on a triangular lattice!





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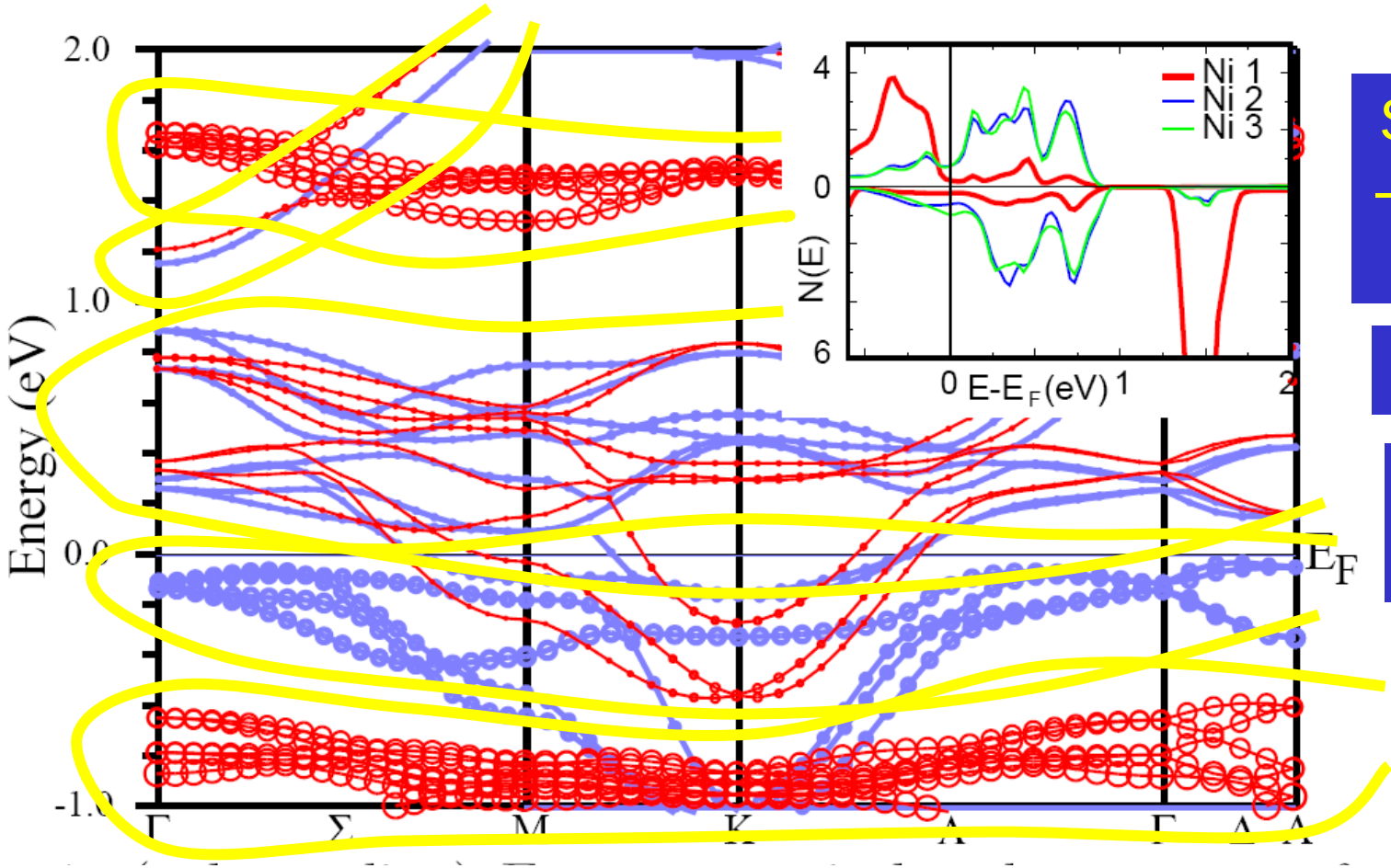

Silver "s" – entirely empty

Ni1 e_g dn

Ni2,3 e_g up *and* dn

Ni1 e_g up

Ni1 t_{1g} dn

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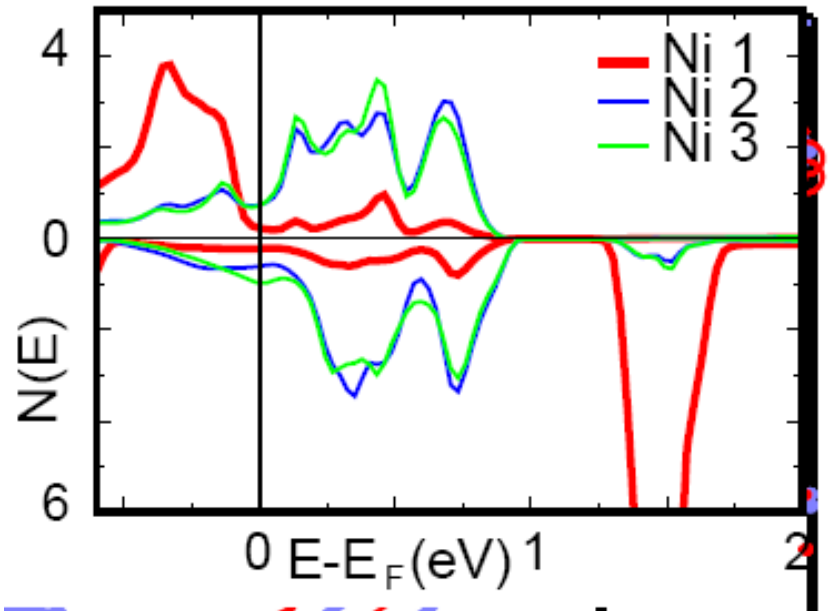

= NiO (bands fully spin polarized, observable moment reduced by hybridization)
+ Ag_2O (nonmagnetic band insulator)
+ compressed NiO_2 metal (large band width, small DOS, stoner criterion not satisfied, NI<1

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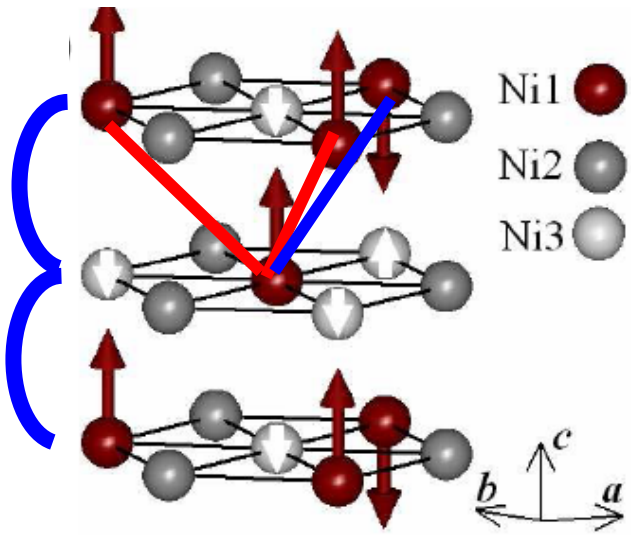
-
- Why net interplanar Ni1-Ni1 exchange is FM
-

Because it is not,

The *shortest path* is AFM, although it involves small moments.



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- Why stripes?

Because stripes have the same in-plane exchange energy but lower interplane energy

I don't know.

Most likely, has something to do with interplanar interactions as well.

Other JTCO materials

- $CaFeO_3$, $Sr_3Fe_2O_7$, $Sr_{2/3}La_{1/3}FeO_3$ – Fe^{4+} charge orders into Fe^{3+} and Fe^{4+}
- $LuFe_2O_4$?
- Ag_2NiO_2 – a structural transition of unknown nature: a disordered JTCO?
- Dynamic JTCO – bipolaron?
- transport, optical, superconducting ramifications?

Summary

1) A novel phenomenon: Jahn-Teller-driven charge ordering in orbital-degenerate (Jahn-Teller) systems.
2) JTCO occurs in a crossover region between the localized and itinerant regime.
3) In JTCO the orbital degeneracy is lifted not by the usual JT lattice distortion, but rather by charge disproportionation.
4) The energy balance in this case is driven mostly by the magnetic (Hund-rule energy)
5) Reduction of the Hubbard *U* is a key prerequisite.
6) Unusual magnetic orderings emerge as a result of charge disproportionation.
7) A possibility of a *dynamic* JTCO (in analogy to the dynamic JT) suggests a whole range of new phenomena.