The Abdus Salam
International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

International Atomic Energy Agency

SMR.1824 - 22

13th International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods

11 - 13 January 2007

Charge ordering as alternative to Jahn-Teller distortion

Igor MAZIN
Naval Research Laboratory
Code 6391
4555 Overlook Ave. S/W
Washington, DC 20375-5345
U.S.A.

Charge ordering as alternative to Jahn-Teller distortion

Theory: ***Igor Mazin[1] and Daniel Khomskii[2]***

Computations: ***Igor Mazin[1]***

Experiment: ***R. Lengsdorf[2] and Mohsen Abd-Elmeguid[2], with assistance from J. A. Alonso, W. G. Marshall, R. M. Ibberson, A. Podlesnyak, M. J. Martnez-Lope***

[1]Naval Research Laboratory

[2]II. Physikalisches Institut, Universität zu Köln

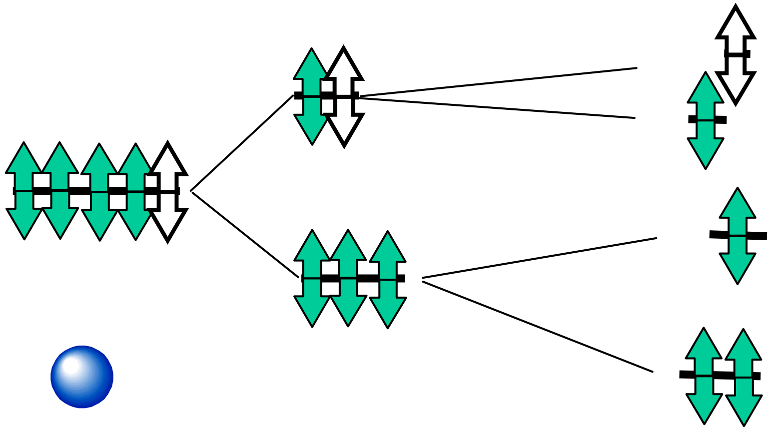
Nature abhors a vacuum
(*Aristotle, 384-322 b.c.e.*)

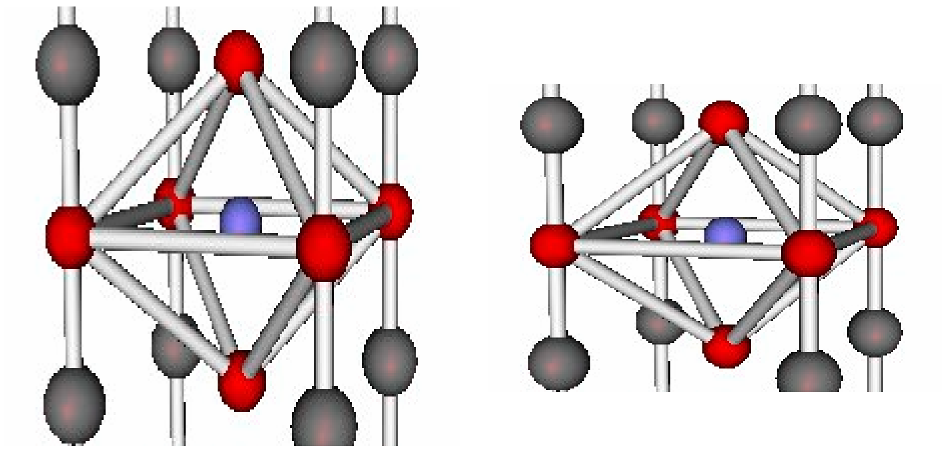
In quantum chemistry, one can equally well say that Nature abhors an orbital degeneracy.
In band theory, it translates in Nature hating high DOS at the Fermi level and loving large gaps.

Jahn-Teller effect:

a manifestation of “natural abhorrence”

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

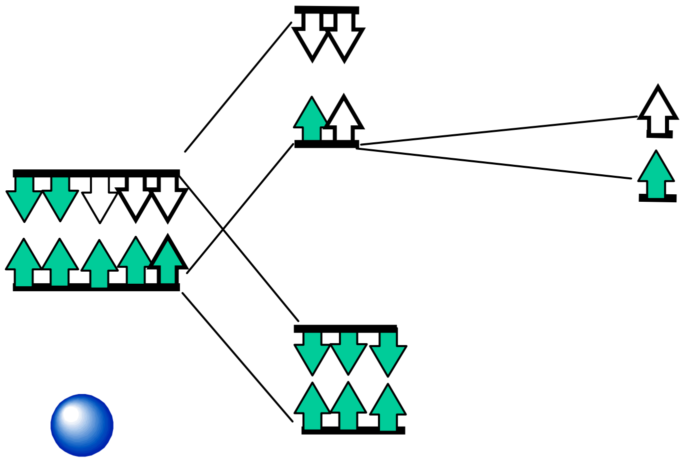


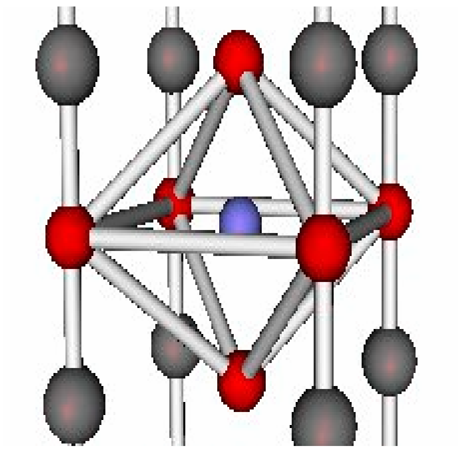


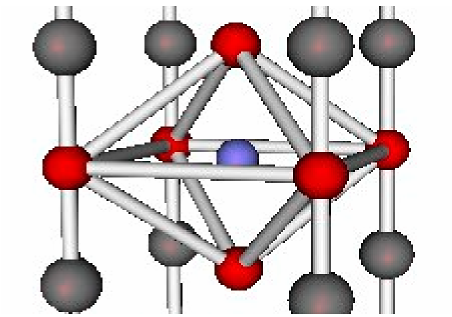
Distortion of the octahedral environment provides crystal-field splitting such as the occupied e_g level goes down and the unoccupied one goes up

Jahn-Teller effect: magnetism

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



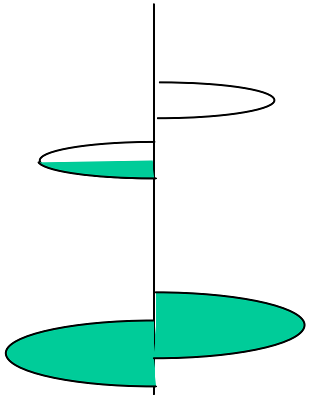


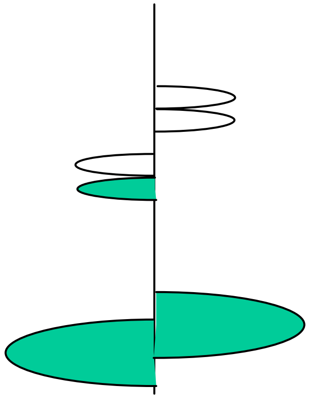


Distortion of the octahedral environment provides crystal-field splitting such as the occupied e_g level goes down and the unoccupied one goes up *in one spin channel*

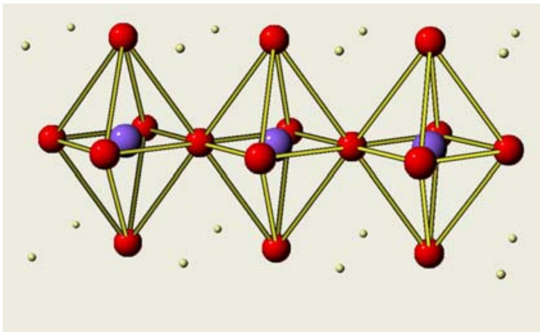
Band (cooperative) Jahn-Teller effect

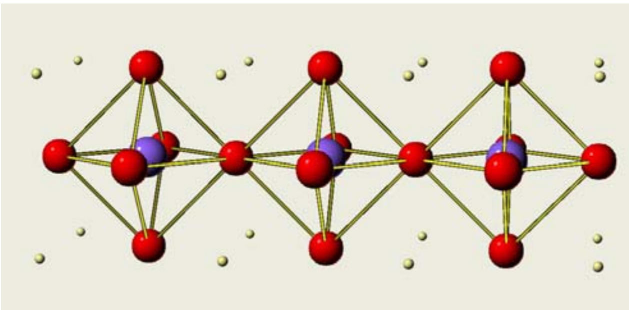
Example 3: Ni^{3+} bands





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





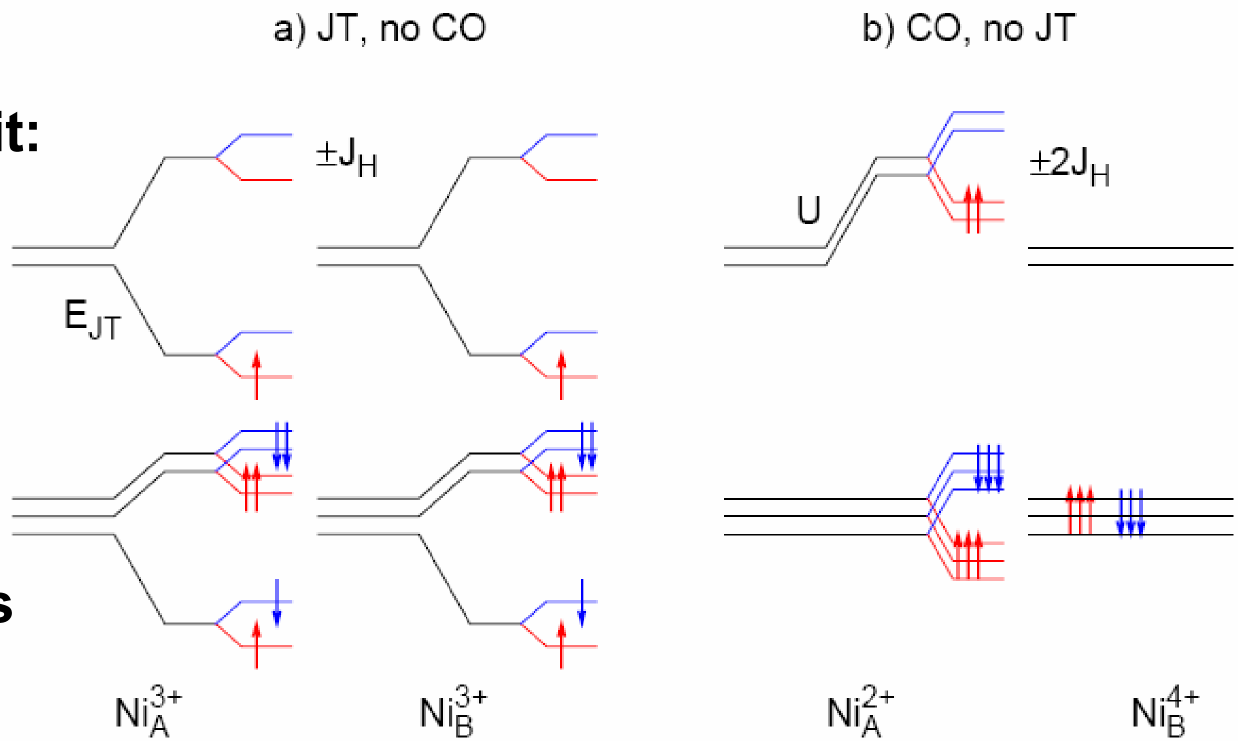
Itinerant or localized?

Localized limit: JT

Fully itinerant limit: No distortion

What about a crossover?

In the crossover charge ordering is an option!



Energy balance

$$H = \sum_{i\neq j,\alpha\beta} t_{i\alpha j\beta} c^{\dagger}_{i\alpha\sigma} c_{j\beta\sigma} + U \sum_{i,\alpha\sigma\neq\beta\sigma'} n_{i\alpha\sigma} n_{i\alpha\sigma'} - J_H \sum_{i,\alpha\neq\beta} \vec{S}_{i\alpha}\vec{S}_{i\beta} - \sum \{E_{JT} - E_{strain} + E_{breath}\}\,. \quad (1)$$

JT : energy gain of $2E_{JT}$ per 2 nickels

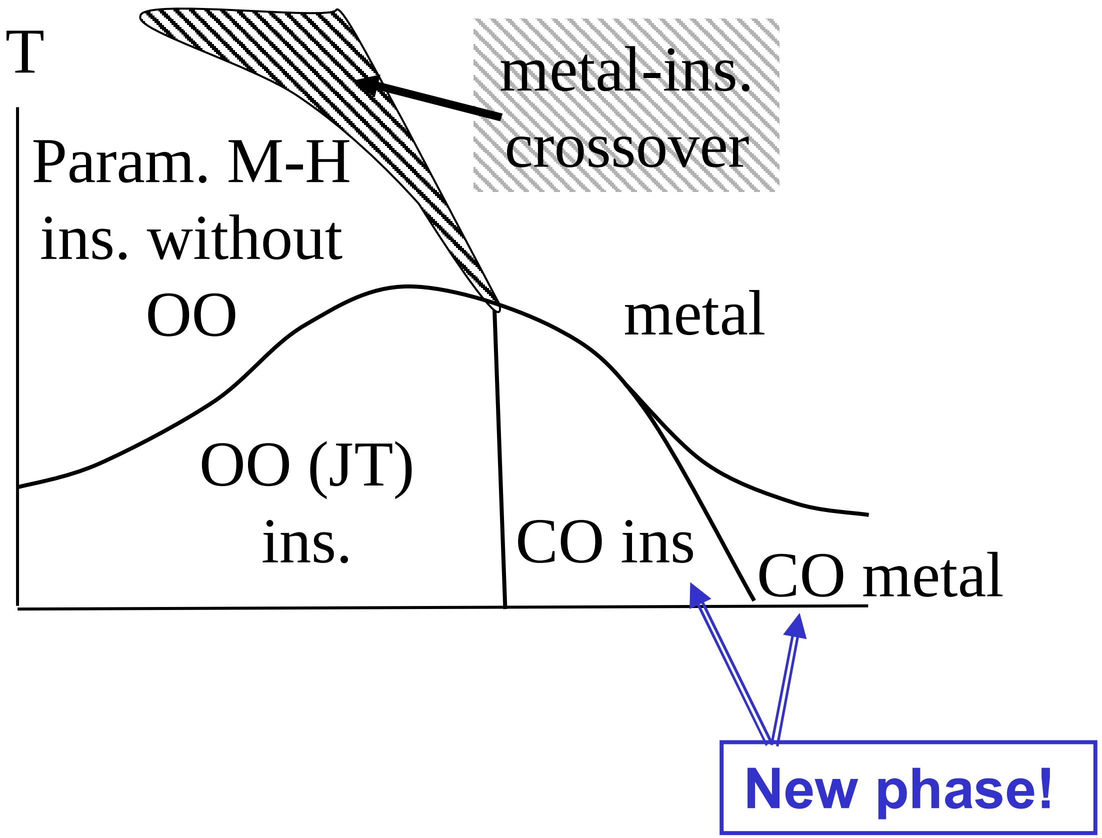
CO : energy *loss* of U and an energy *gain* of J_H

Strongly correlated system (Mott insulator):

Fully itinerant metal

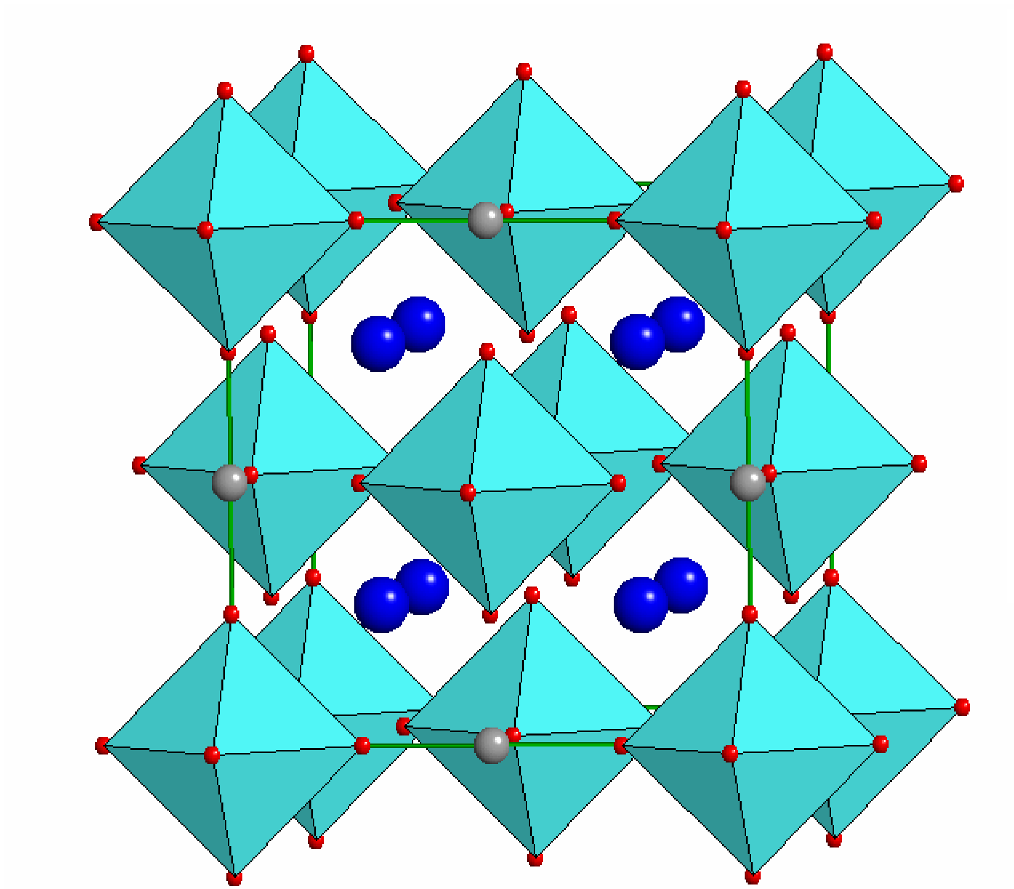
Intermediate case (vicinity of Mott transition)

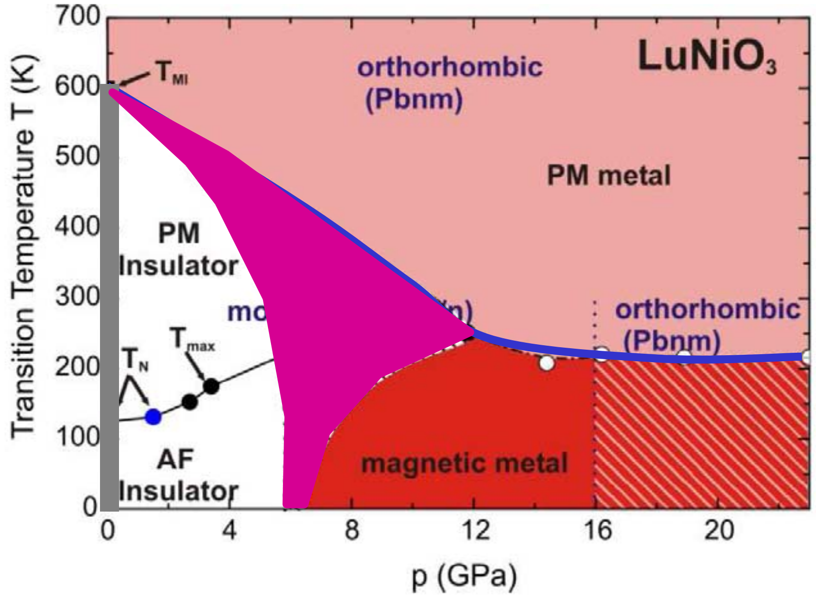
Phase diagram



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

Example: $\mathit{RE}\mathrm{NiO}_3$





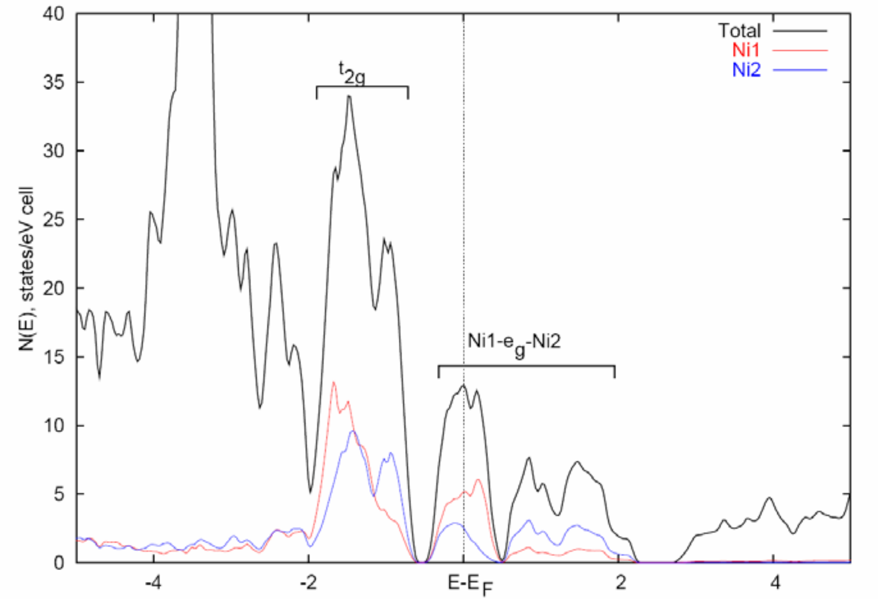
Charge disproportionation takes place at ambient P and low temperature.

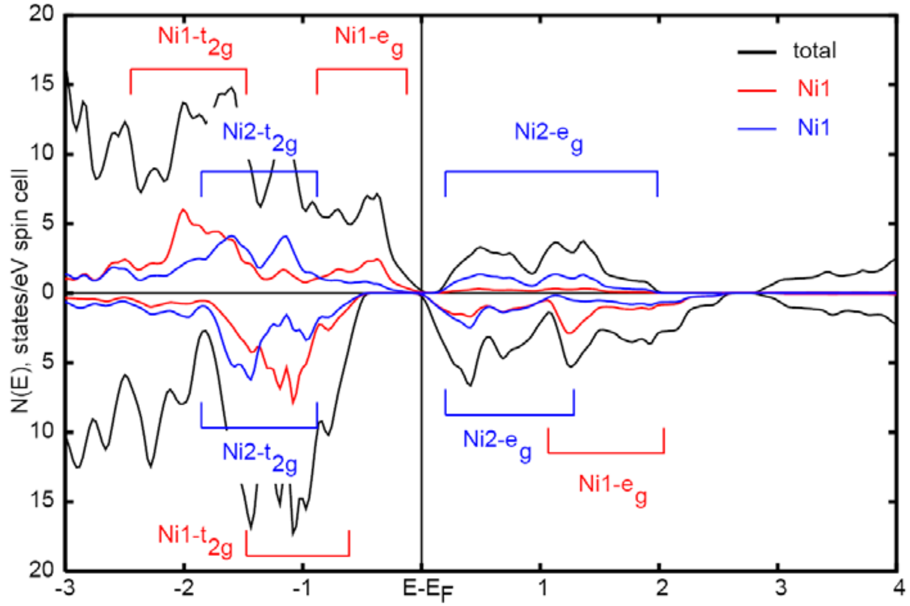
No JT distortion!

Why ??

Also: T_{OO} decreases with P.
Metallization is very gradual and occurs *inside* the OO phase

Band structure calculations





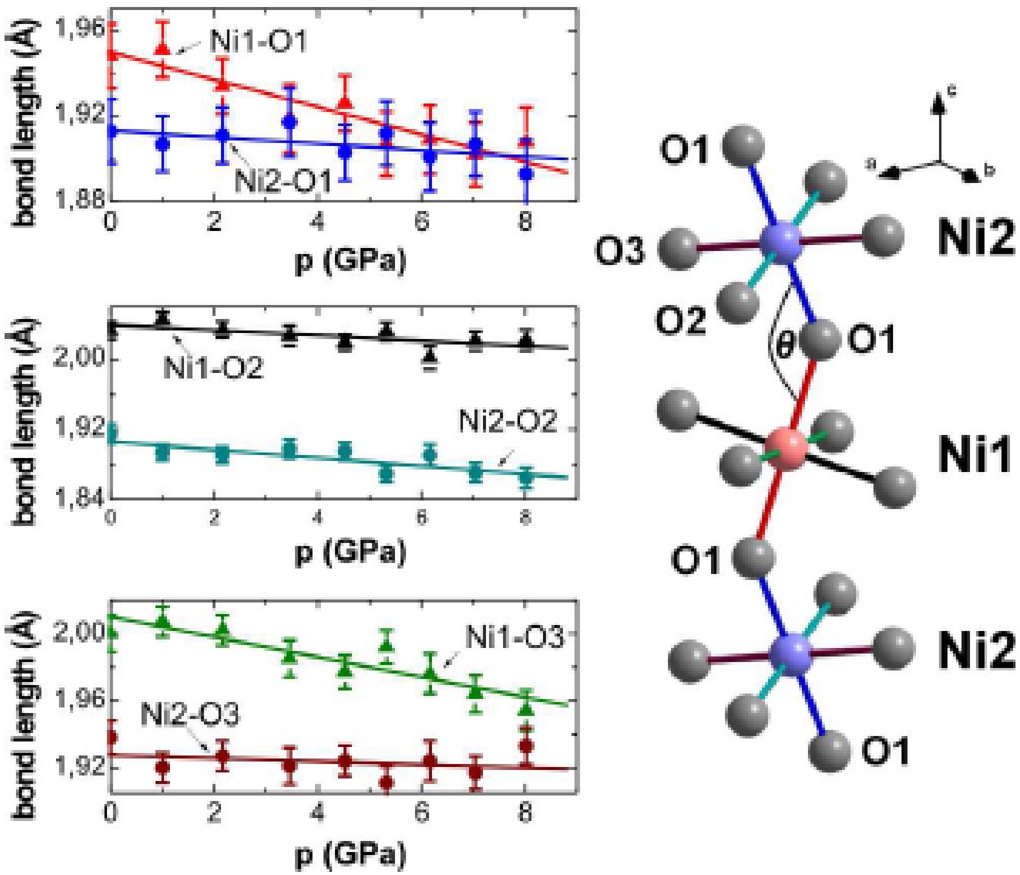
DOS of *nonmagnetic* $LuNiO_3$. Note that Ni1 e_g is half-filled, and Ni2 is empty

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, unpublished)



P=0: gap ~ 70 meV

LDA: 0-20 meV

LDA+U: ~1 eV

P=8 GPA: gap ~0

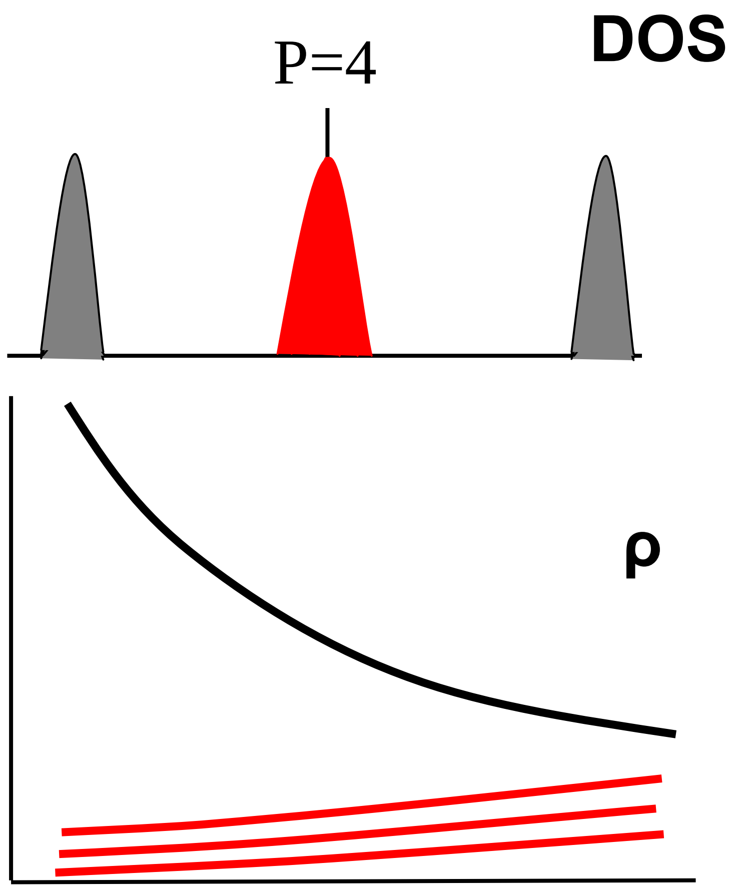
LDA: –100 meV

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)*

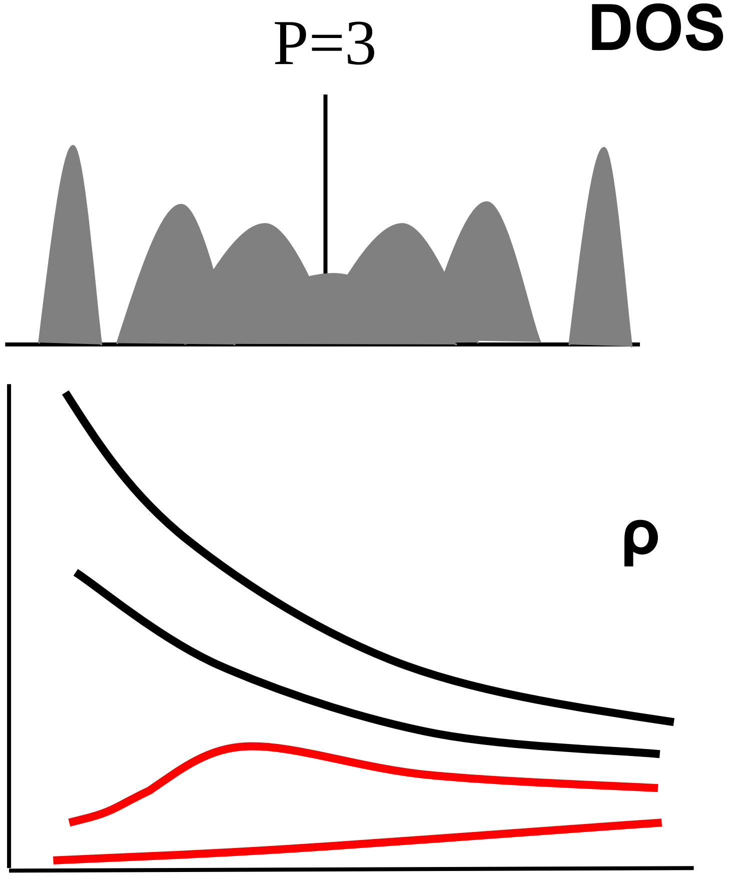


Mott insulator:

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?

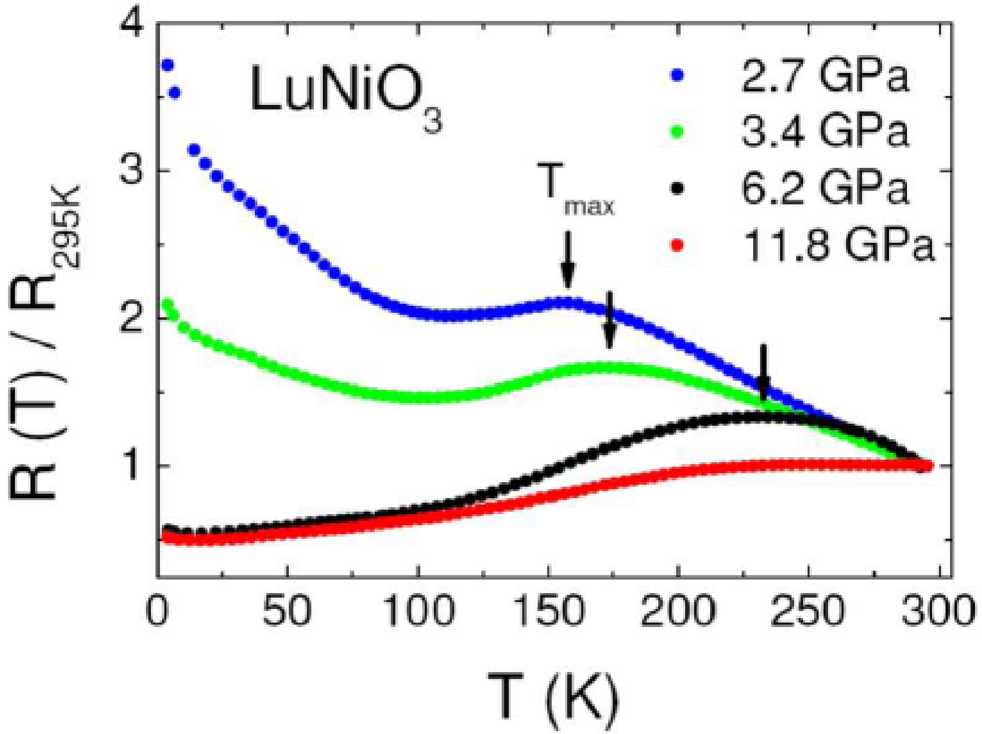
Litmus test: character of the gap closure - ρ(T). (*cf. DOS evolution)*



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

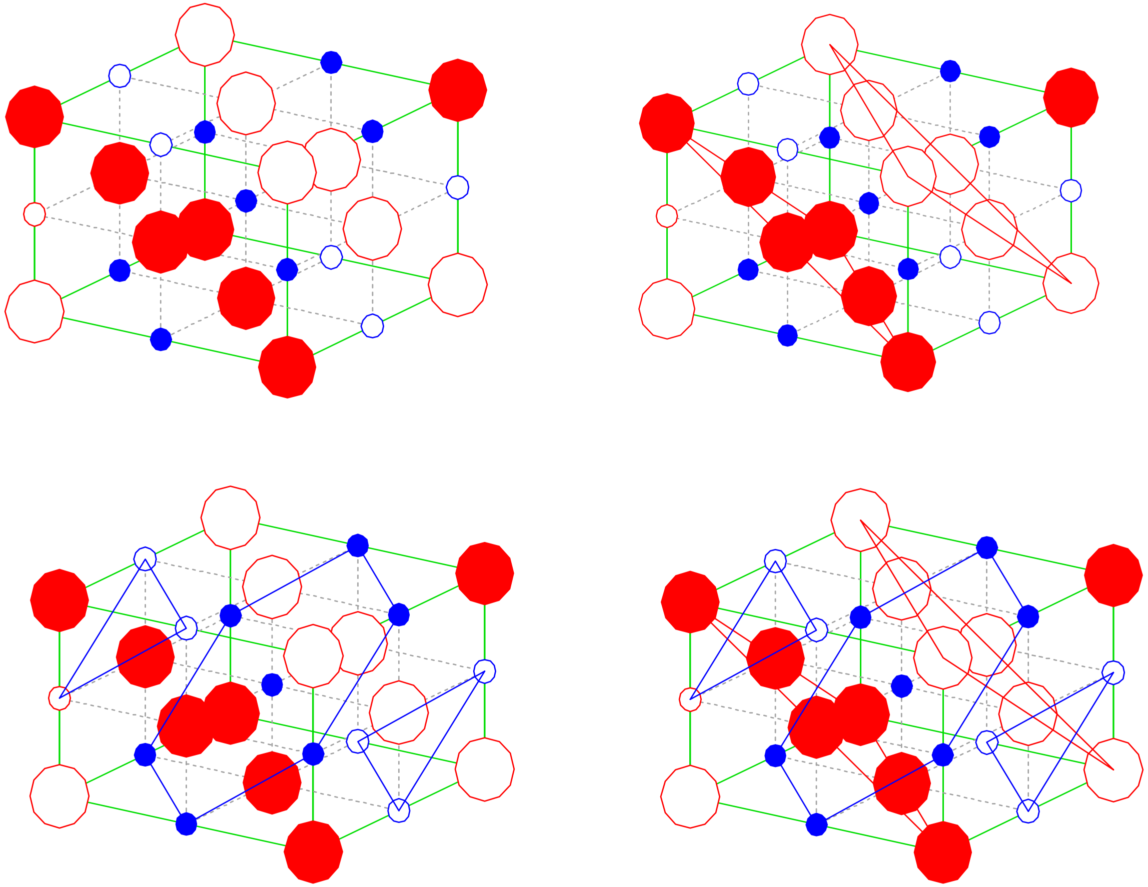
Experimental resistivity



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

Not a "typical Mott-Hubbard transition"!

Magnetism

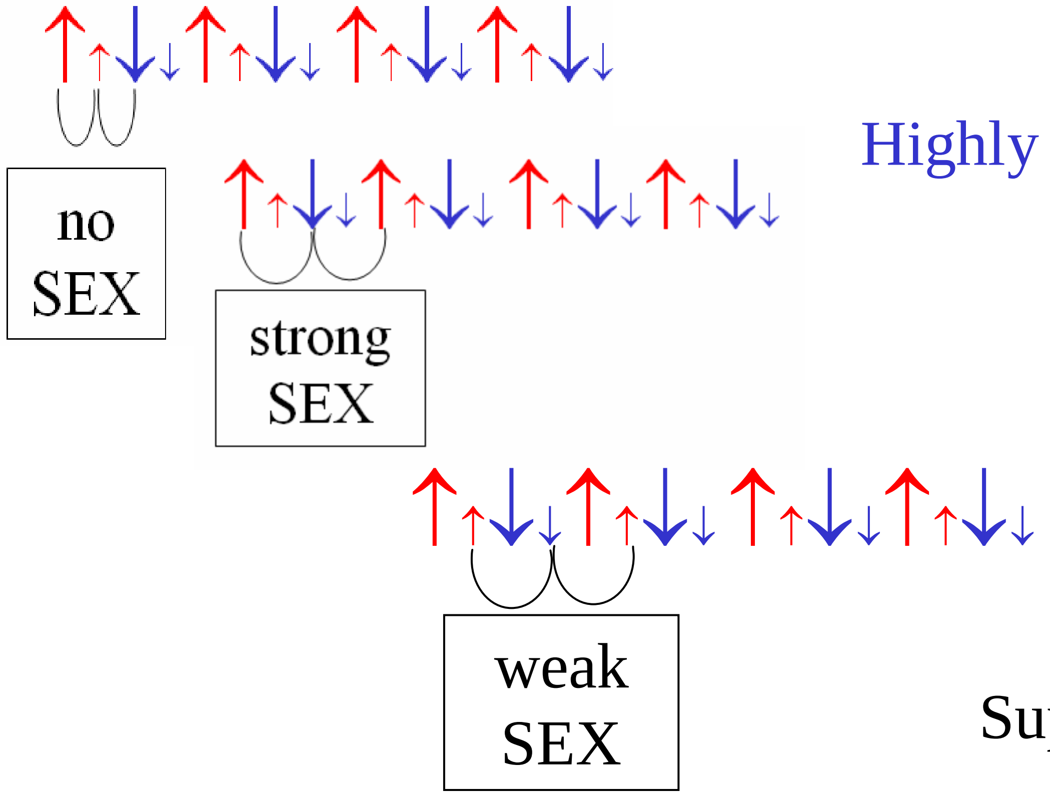


Highly unusual magnetic structure!

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.

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+}
- $AgNiO_3$ – Ni^{3+} on a triangular lattice charge orders into $2Ni^{(3+x)+}$ and $Ni^{(3-2x)+}$
- Ag_2NiO_3 – a structural transition of unknown nature: a disordered JTCO?
- Dynamic JTCO – bipolaron?
- transport, optical, superconducting ramifications?

Summary

1) Perovskite nickelates present a clear example of a novel phenomenon: Jahn-Teller-driven charge ordering in orbital-degenerate (Jahn-Teller) systems.

2) JTCO occurs in the 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 by the magnetic (Hund-rule energy)

5) Reduction of the Hubbard *U* is a key prerequisite.

6) Unusual magnetic ordering emerges 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.