Lecture Notes

Introduction to Strongly Correlated Electron Systems

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High pressure studies on Mott insulators

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Examples for high pressure studies

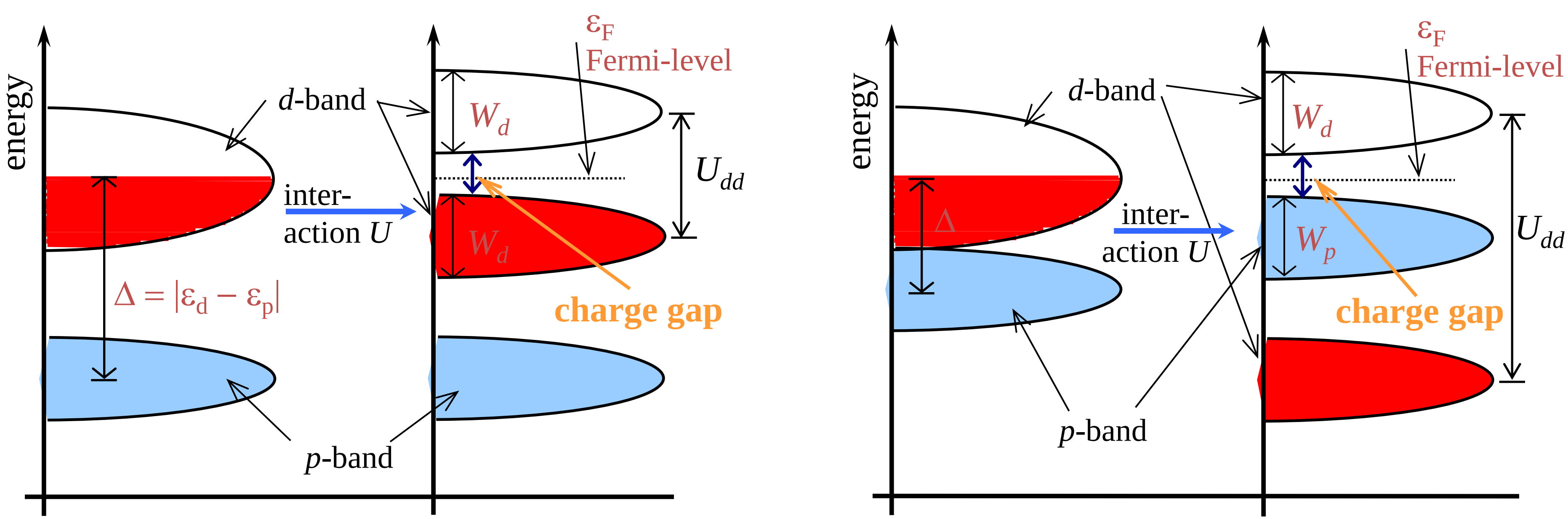
$RNiO_3$:

Mott insulator with charge degree of freedom

$(La,Sr)CoO_3$:

Mott insulator with spin-state degree of freedom

Mott-Insulators



(a) Mott-Hubbard insulator:

(b) Charge-transfer insulator:

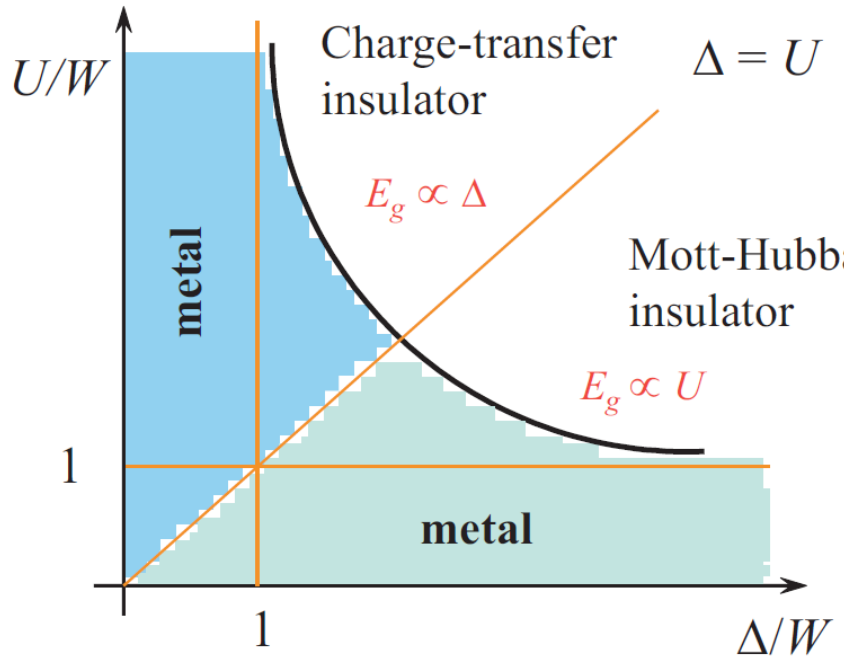
U, on-site Coulomb interaction

Δ, charge transfer energy

W, bandwidth; (hopping t)

→ Pressure acts on the bond length and bond angle

General Zaanen-Sawatzky-Allen phase diagram



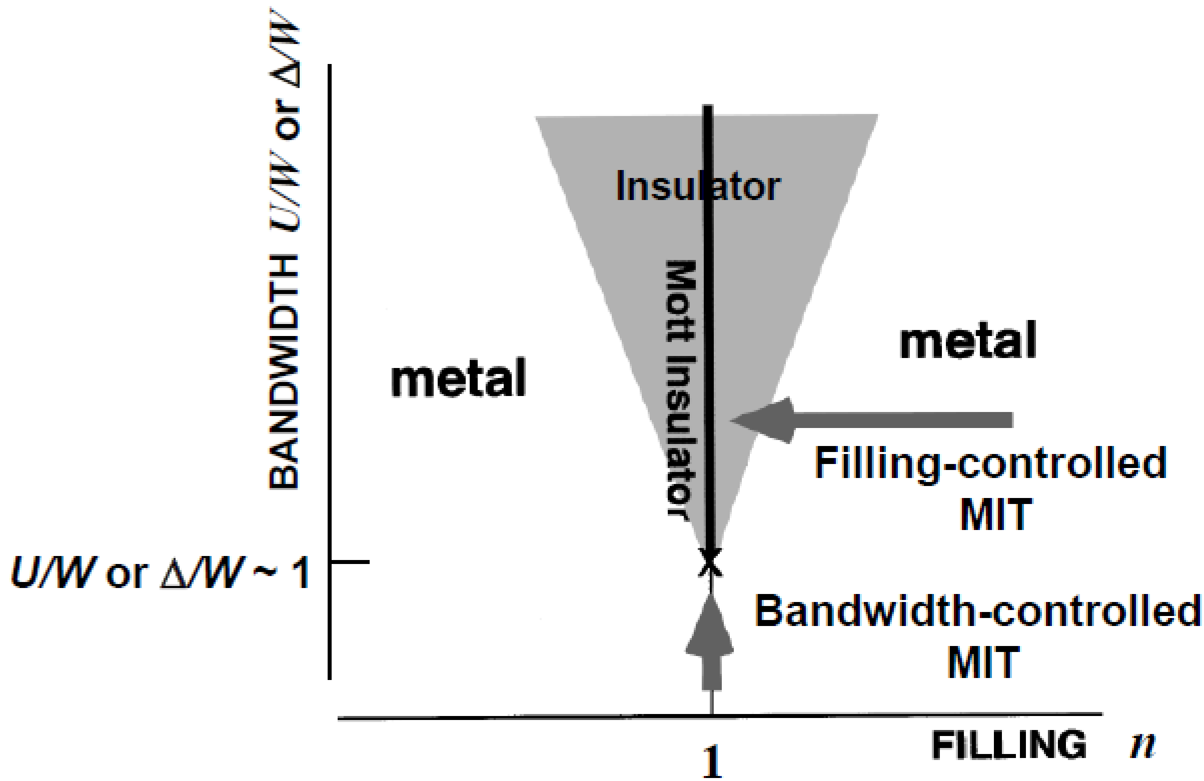
Phy. Rev. Lett. 55, 418(1985)

For U/W > Δ /W the band gap is of p−d type and the anion or ligand p-band is located between the lower and upper Hubbard bands. This gap is a charge-transfer gap and the corresponding compounds (NiO, FeO, LaMnO3, etc.) **are charge-transfer insulators**.

If U/W < Δ /W, the band gap is of d−d type and thus a Mott-Hubbard insulator. They have a band gap of the magnitude U. The straight line U = separates the Mott-Hubbard and the charge-transfer regimes. The diagram also contains a metallic region near the D /W-axis (d-metals as TiO, YTiO3) or near the U/W- axis (p-metal as V2O3). This classification scheme is very useful for oxide materials science. More examples can be found in an excellent review article by:

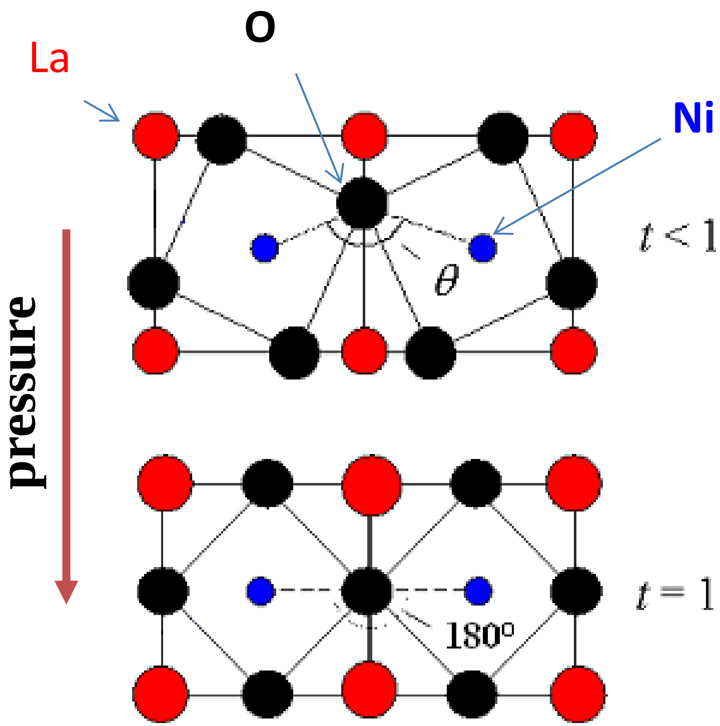
M. Imada et al; Rev. Mod. Phys. 70. 1039 (1998).

Metal Insulators transition filling and bandwidth controlled

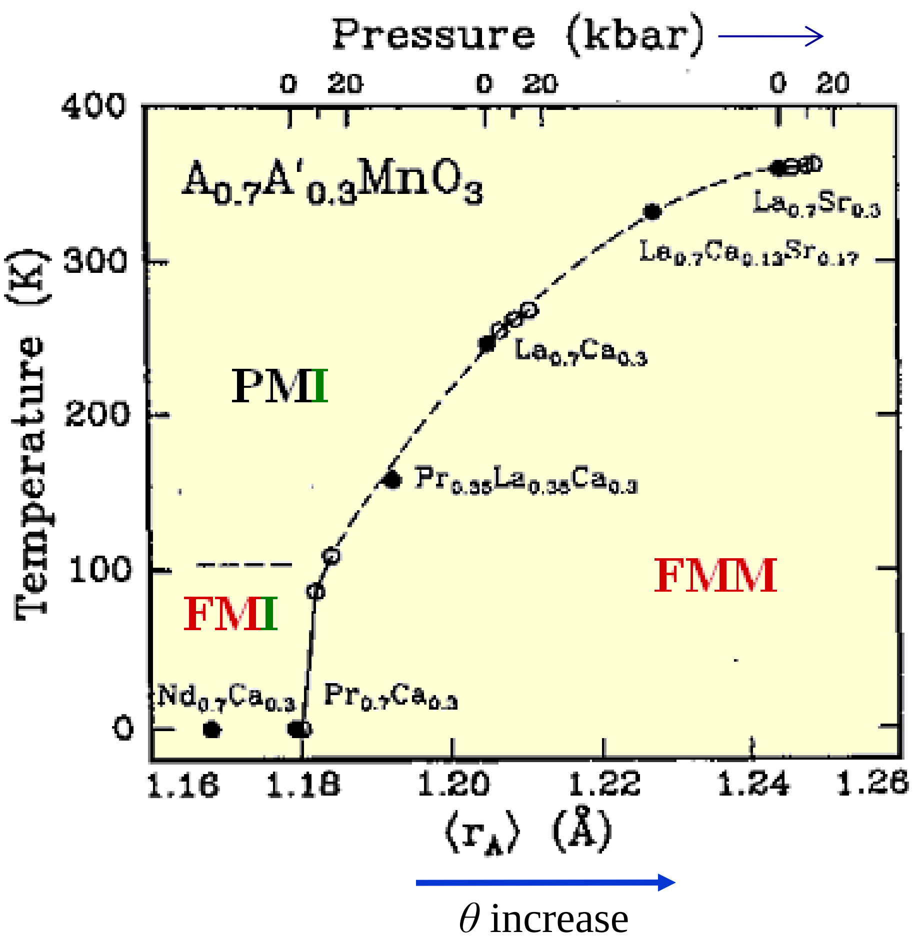


M. Imada, A. Fujimori and Y. Tokura, Rev. Mod. Phys. 1998

Example: doped $LaMnO_3$



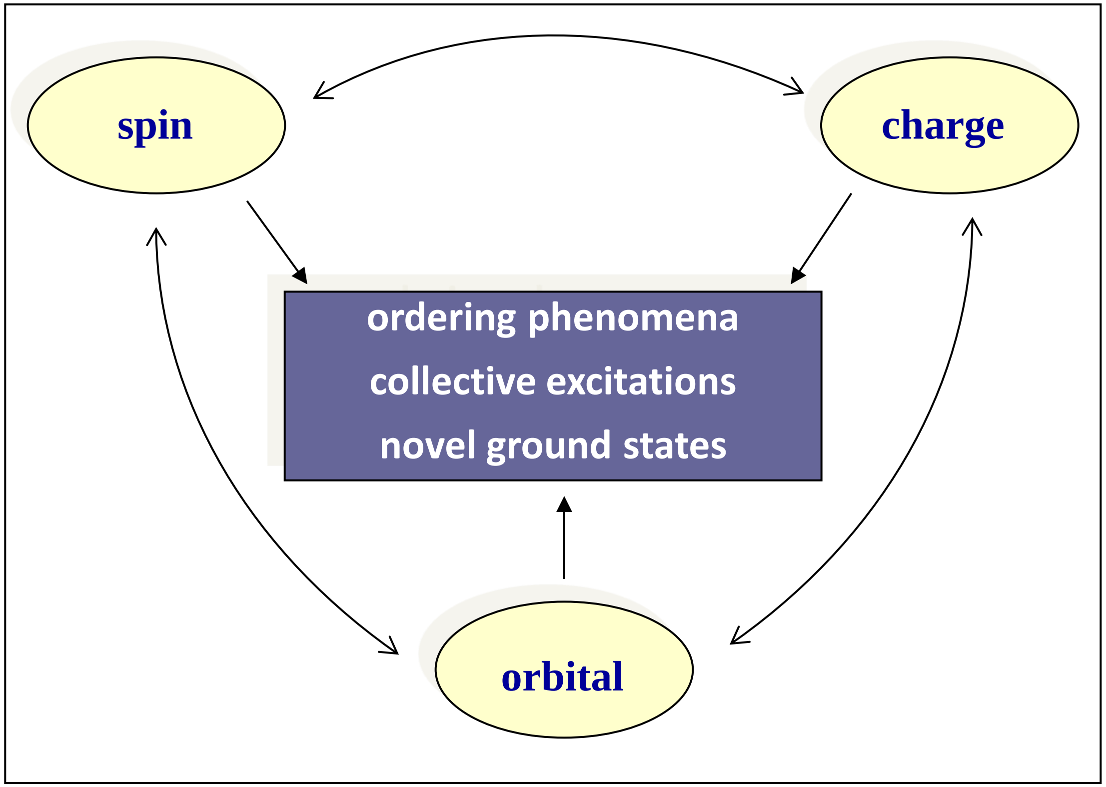
H. Y. Hwang et al. *PRB* **52**, 15046 (1995)

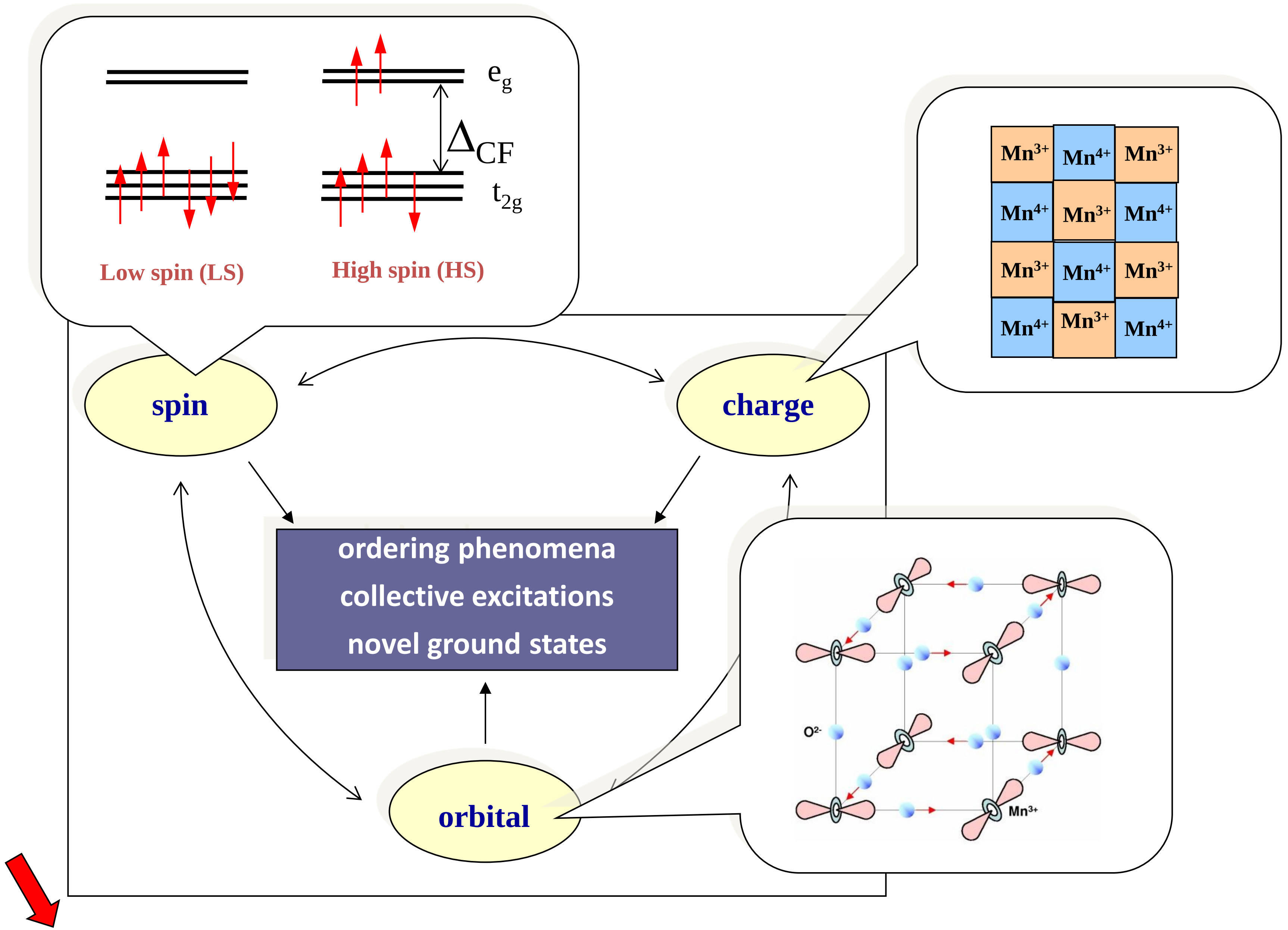


t = tolerance factor:

$$t = \frac{1}{\sqrt{2}} \frac{d_{La-O}}{d_{Co-O}}$$

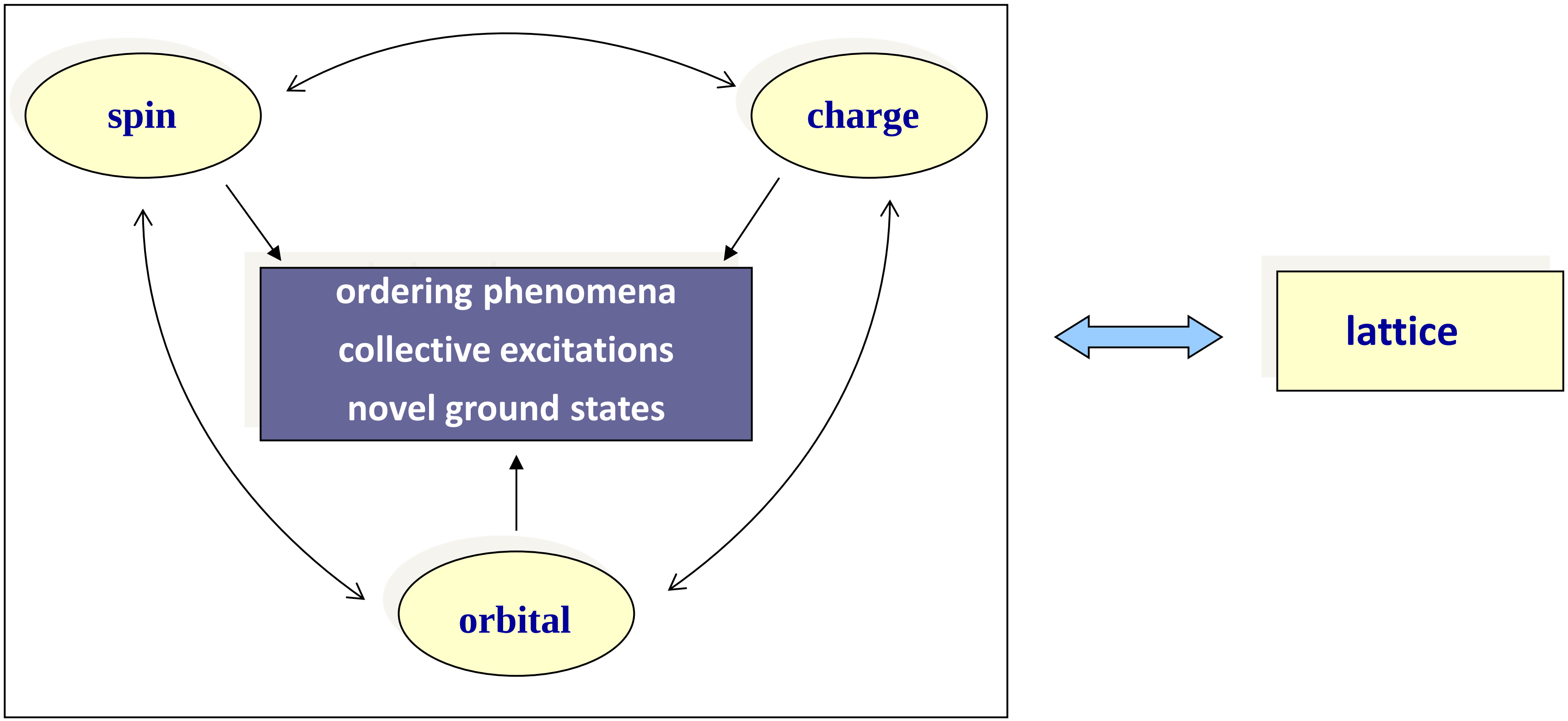
Correlated oxides → spin, charge and orbital degrees of freedom



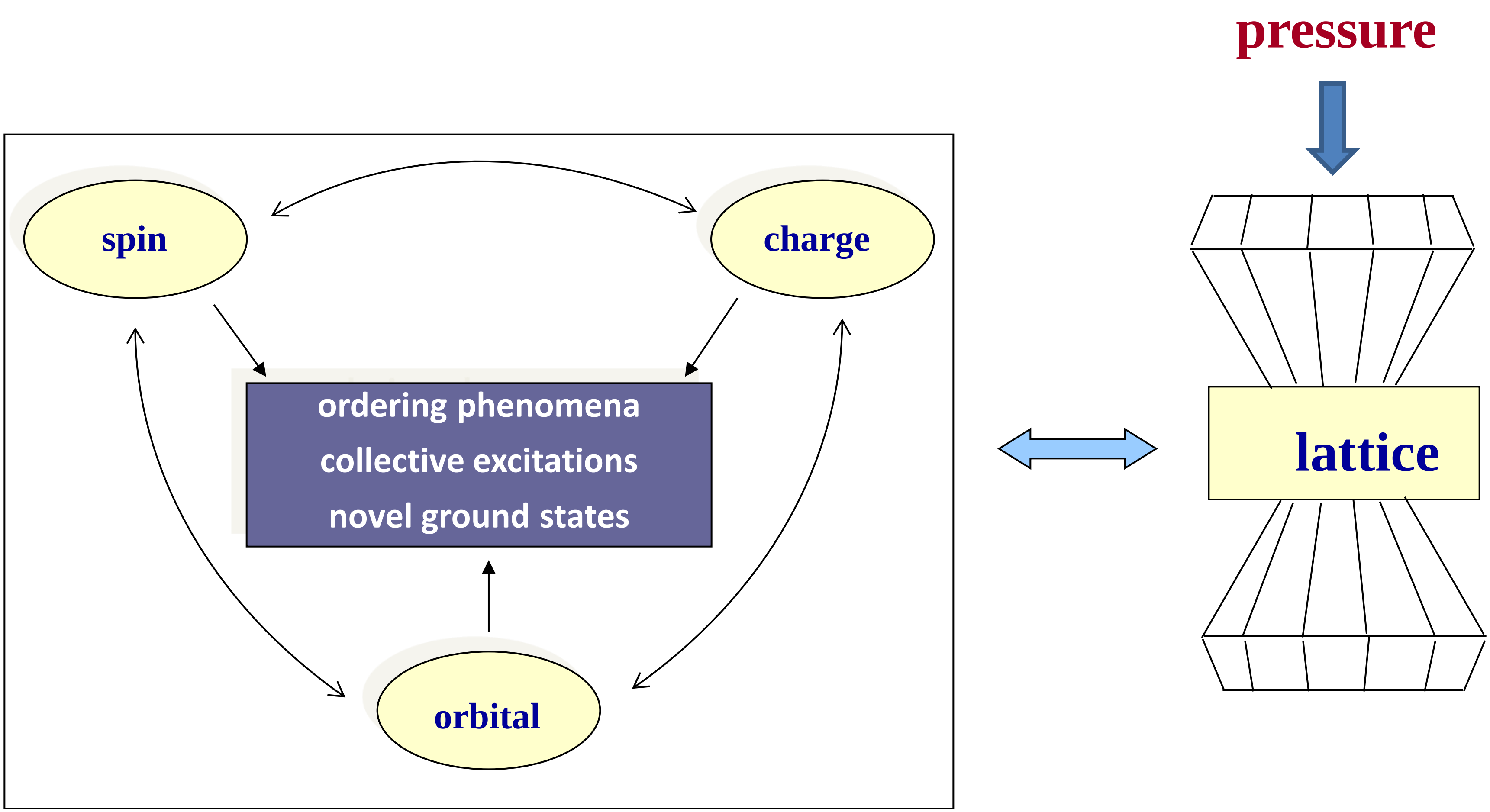


Metal insulator transition is driven by an interplay between these degrees of freedom!

Spin, charge and orbital degrees of freedom coupled to the lattice

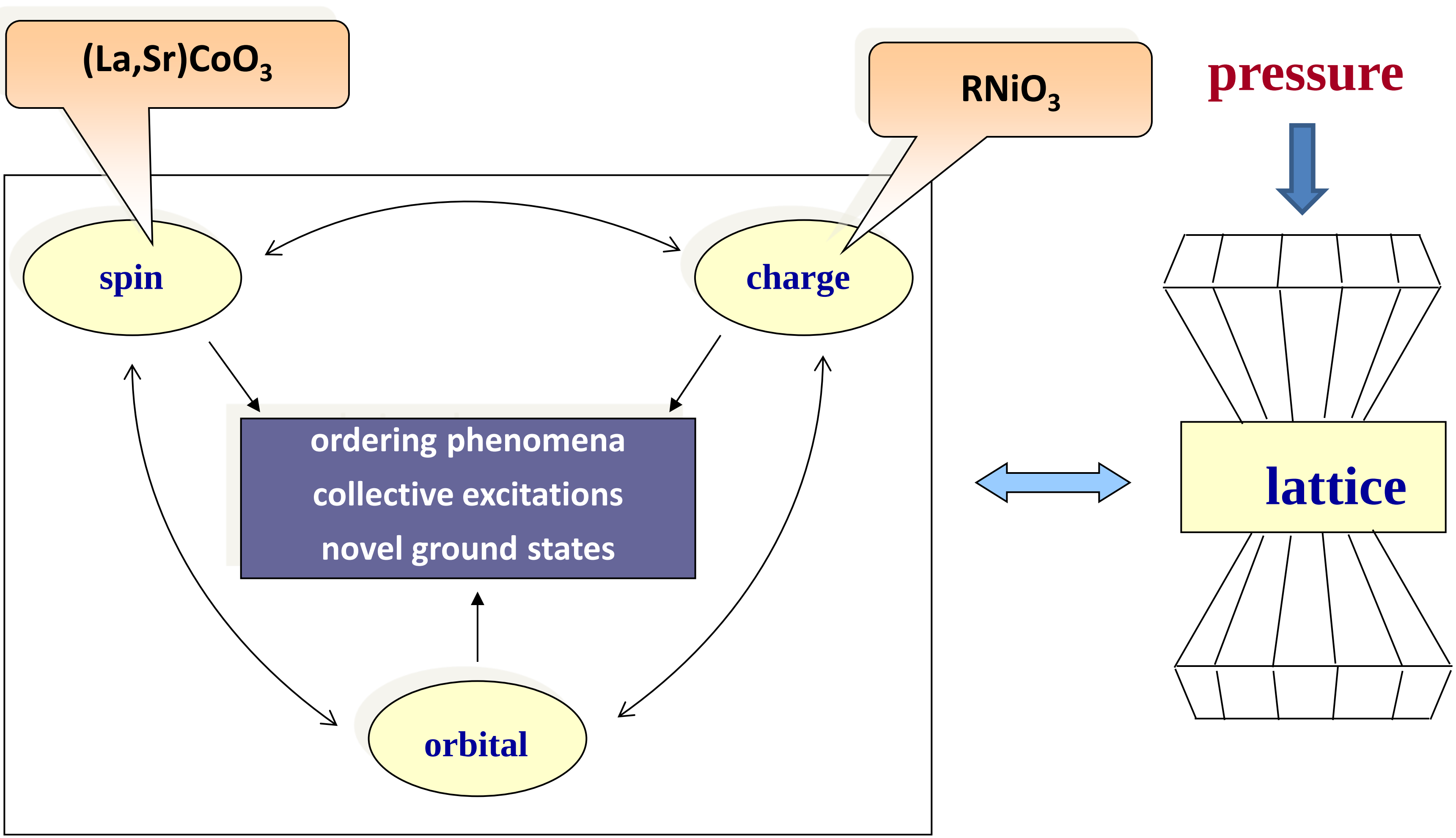


Tuning the interplay between degrees of freedom by external pressure



Investigation of the mechanism of the metal insulator transition!

Selected correlated oxides



Investigation of the mechanism of the metal insulator transition!

$RNiO_3$

Mott insulator with charge degree of freedom

$RNiO_3$ perovskites (R = rare earth 3+ ion, La → Lu)

Interesting aspects:

- **Ni^{3+}:** t_{2g}^6 e_g^1, low spin (S = ½) state → JT-active, but NO JT distortion → **orbitally degenerate system!**

- all members (*R* ≠ La) are insulators with **very small energy gap (Δ ~ 100 meV).**

⇒ **metal-insulator transition can be driven by changing the size of the *R*$^{3+}$-ion (chemical pressure) or temperature.**

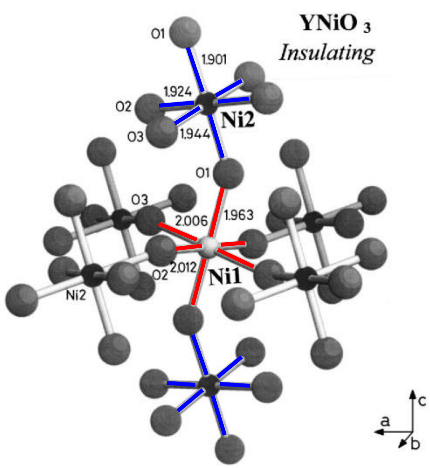
- insulating state is **charge ordered**.

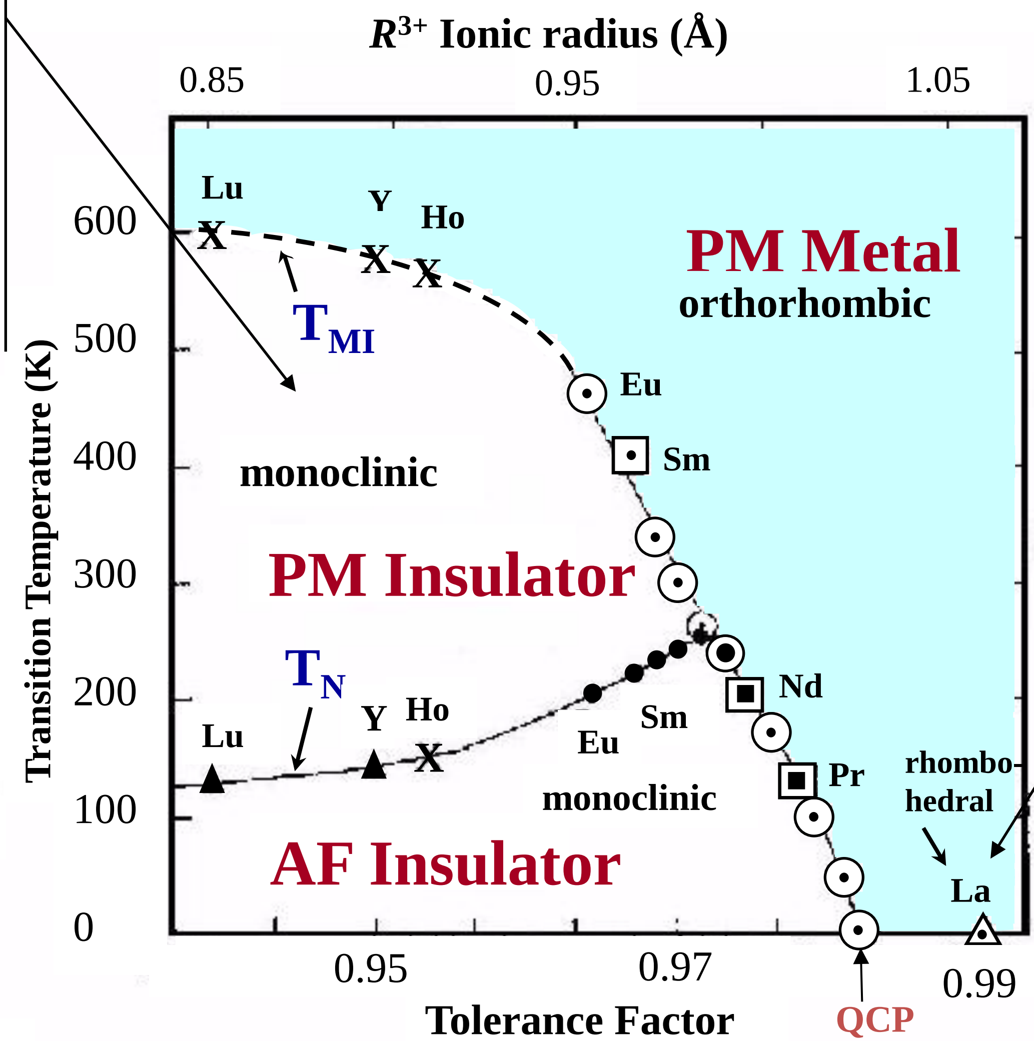
- ground state (*R* ≠ La): **antiferromagnetic insulator**

$RNiO_3$ phase diagram

Curie-Weiss paramagnetic insulator

charge ordering:
$2Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$
($\delta \approx 0.35$)

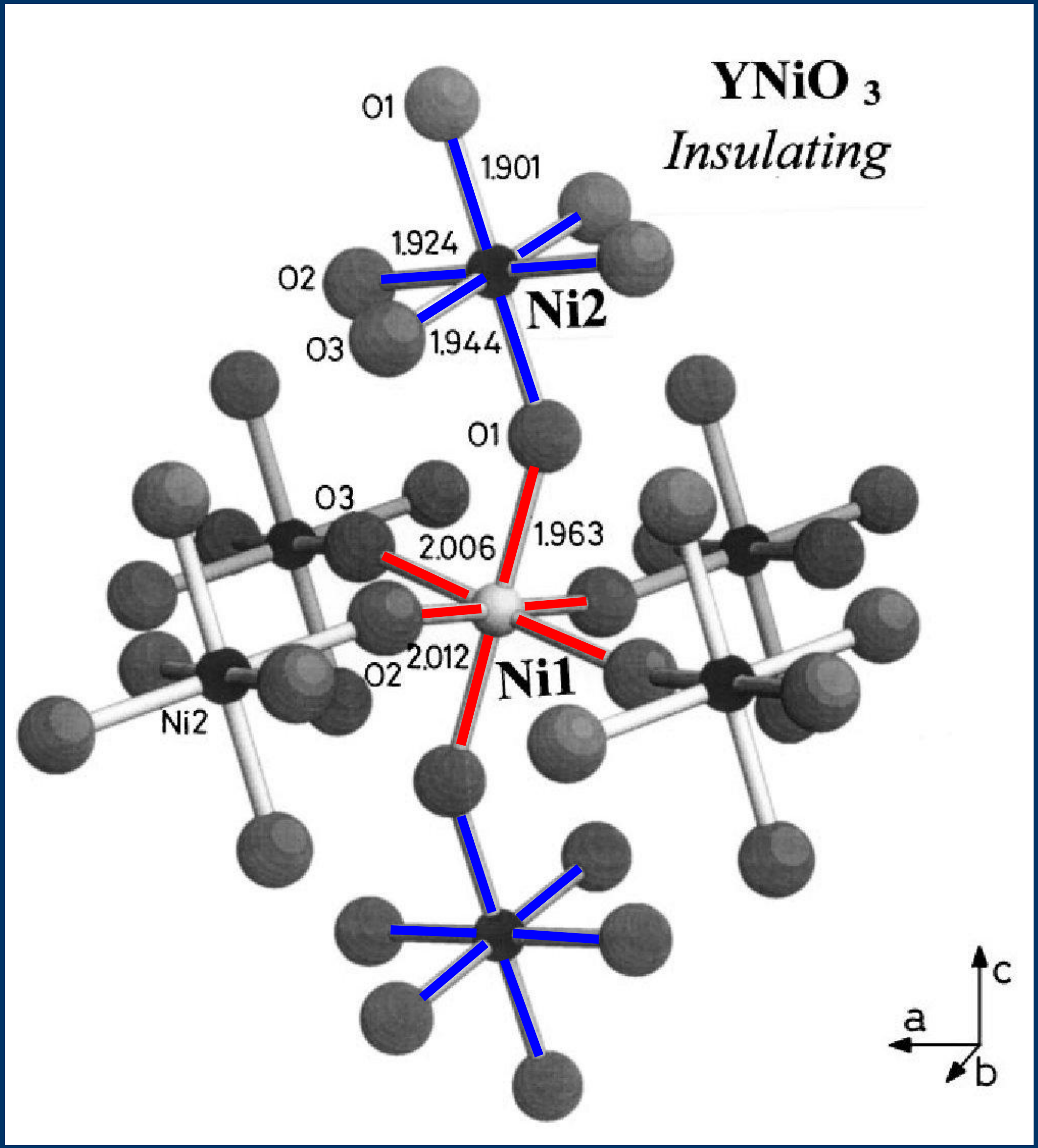




enhanced Pauli paramagnetic metal

Temperature-induced MI transition connected with:

- **Structural phase transition / charge ordering**
- **Crossover from insulating magnetic to metallic nonmagnetic state!**



YNiO 3
Insulating
O1
1.901
1.924
O2
Ni2
O3
1.944
O1
O3
2.006
1.963
O2
2.012
Ni1
Ni2
c
a
b

Selected systems for high pressure experiments

- $SmNiO_3$, $EuNiO_3$, $YNiO_3$ and $LuNiO_3$:

High pressure techniques:

-electric resistivity

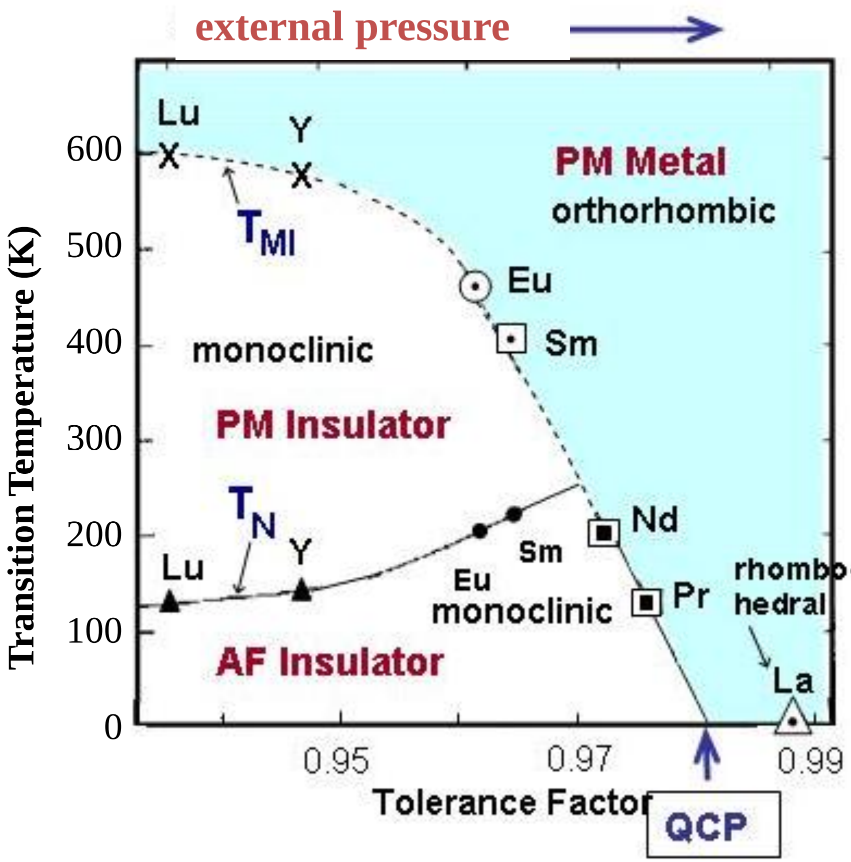
-energy dispersive x-ray diffraction (Hasylab)

-angle resolved x-ray diffraction (ESRF)

-nuclear resonant scattering

-magnetization measurements

-high resolution neutron diffraction

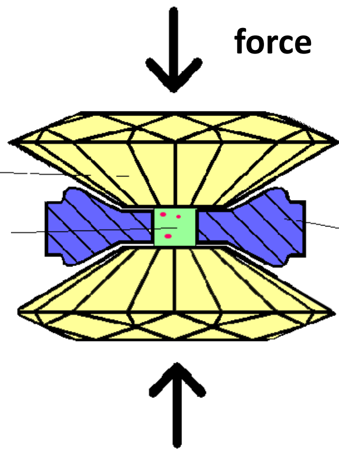


High pressure is expected to close the small charge transfer gap!

- pressure-induced insulator-metal transition – structural changes?
- crossover magnetic insulator → nonmagnetic metal?
- nature of the metallic state - nonmagnetic or magnetic?

Experimental setup: Diamond Anvil Cell

x-ray diffraction



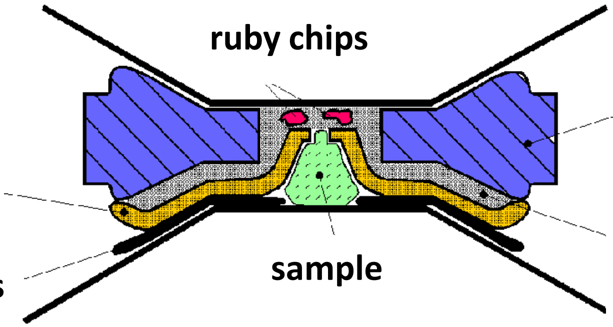
sample chamber Ø = 100 - 300µm;

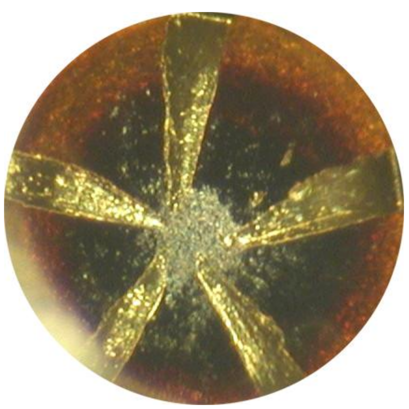
height: 25-50 µm

$p_{max} \approx$ 100 GPa (= 1 Mbar)

Pressure media: e.g. **Methanol:Ethanol 4:1**, liquid Nitrogen, liquid Argon, liq. Helium, Oil, Epoxy, etc.

resistivity measurements



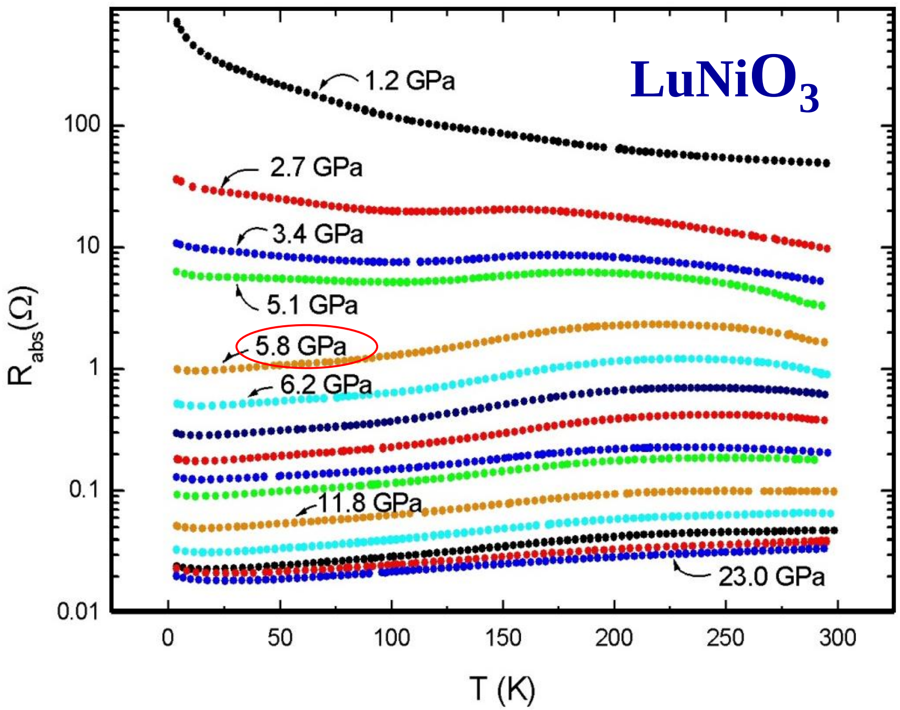


sample chamber Ø ≈ 100 µm

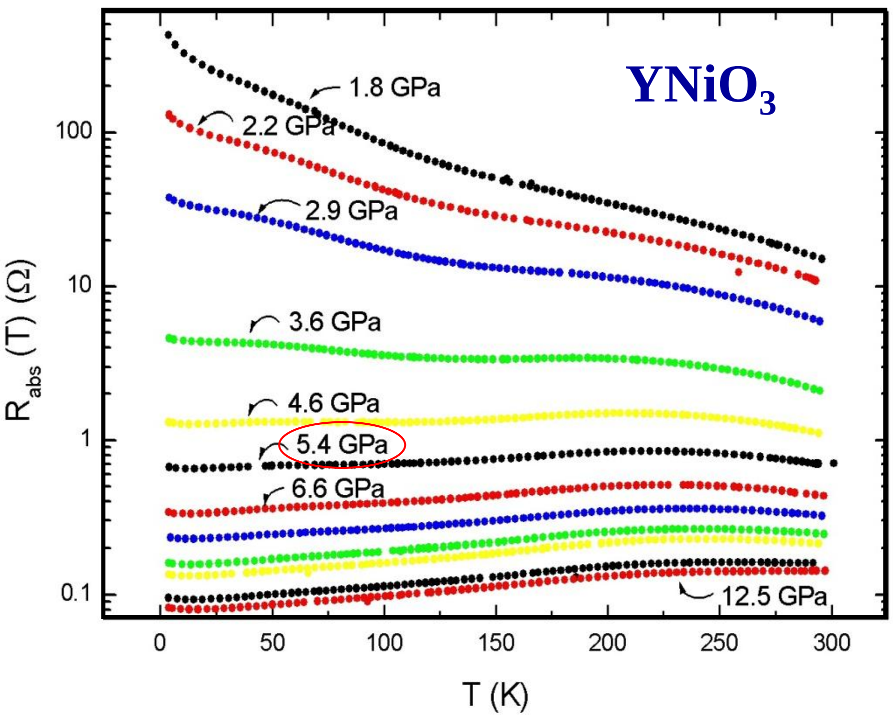
Results: Pressure-induced insulator-metal transition

Electrical resistance: (measured in a Diamond Anvil Cell (DAC))

R. Lengsdorf et al. (2005)



R. Lengsdorf et al. (2005)



Insulator to metal transition for

$p \geq 5.8$ GPa

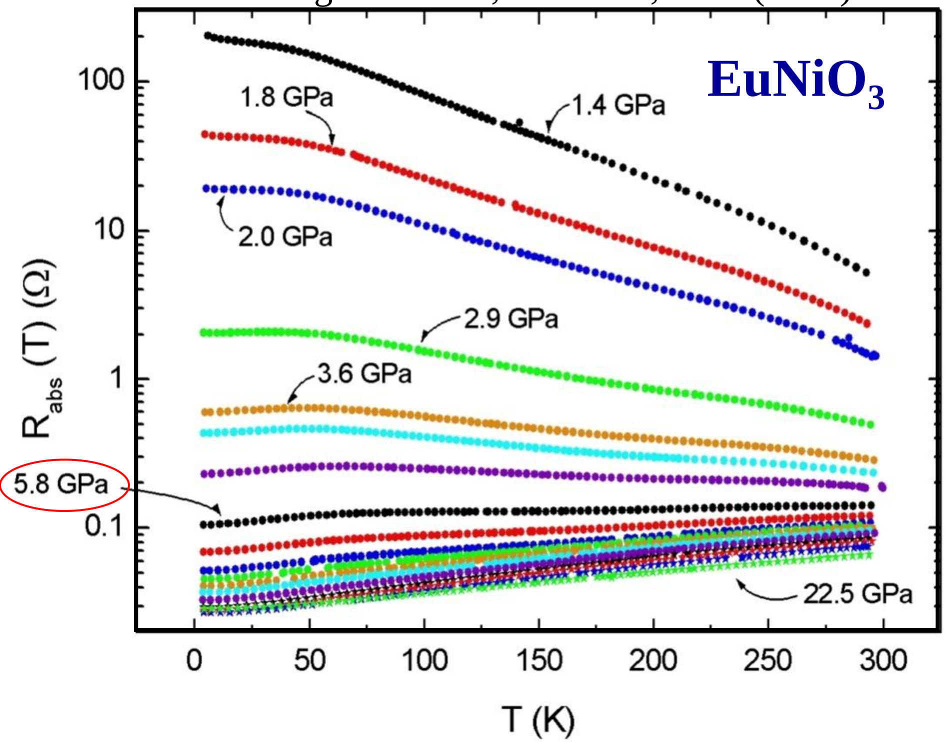
Insulator to metal transition for

$p \geq 5.4$ GPa

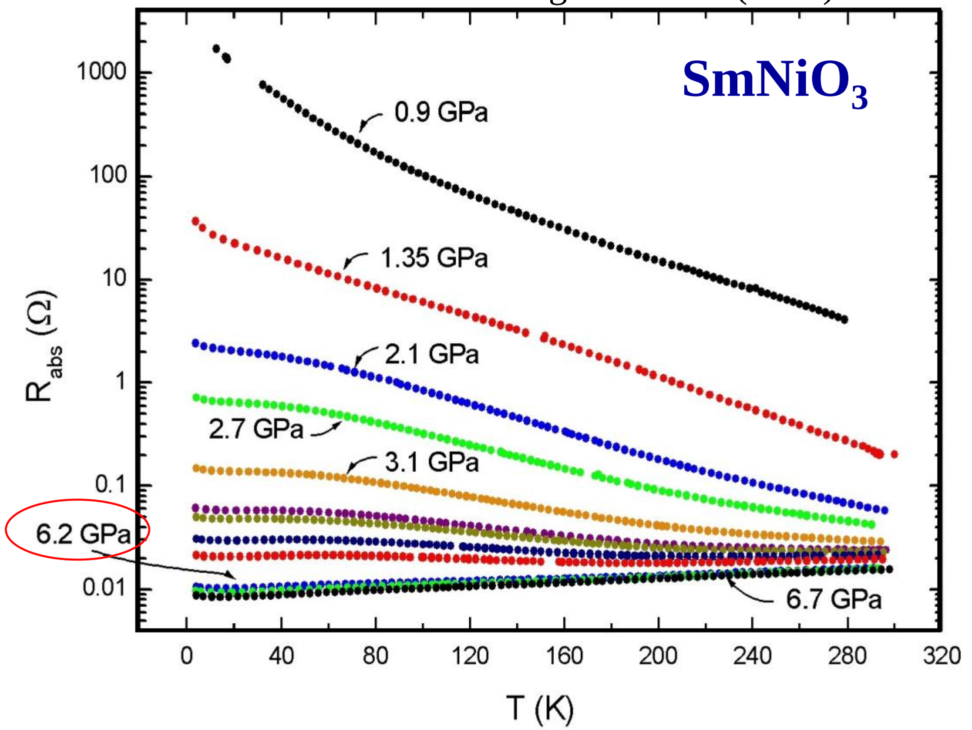
Results: Pressure-induced insulator-metal transition

Electrical resistance: (measured in a Diamond Anvil Cell (DAC))

R. Lengsdorf et al., JPCM 16, 3355 (2004)



R. Lengsdorf et al. (2005)



Insulator to metal transition for

p ≥ 5.8 GPa

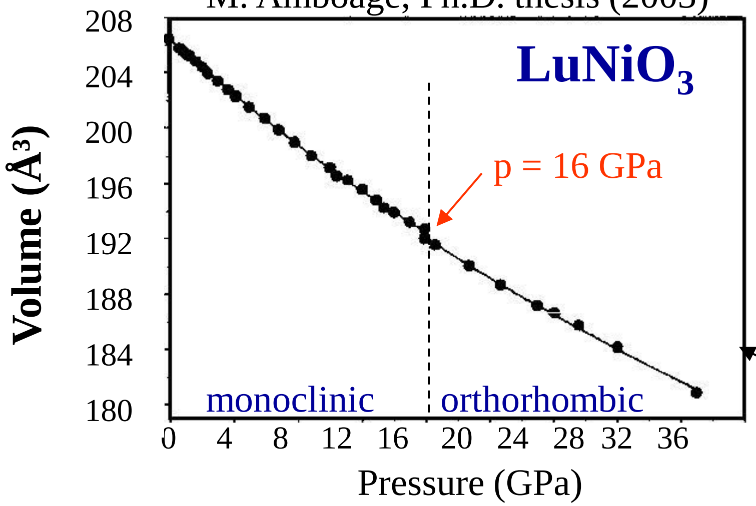
Insulator to metal transition for

p ≥ 6.2 GPa

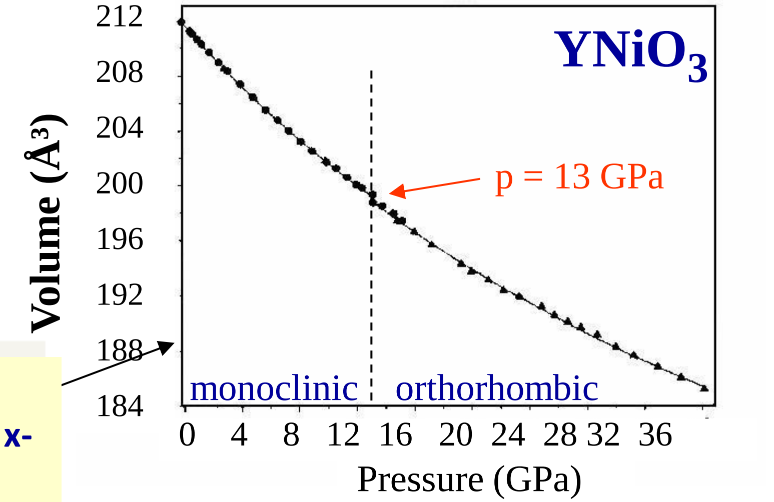
Structural stability:

- structure stable at the insulator-metal transition, no structural anomalies!
- structural phase transition from monoclinic → orthorhombic occurs

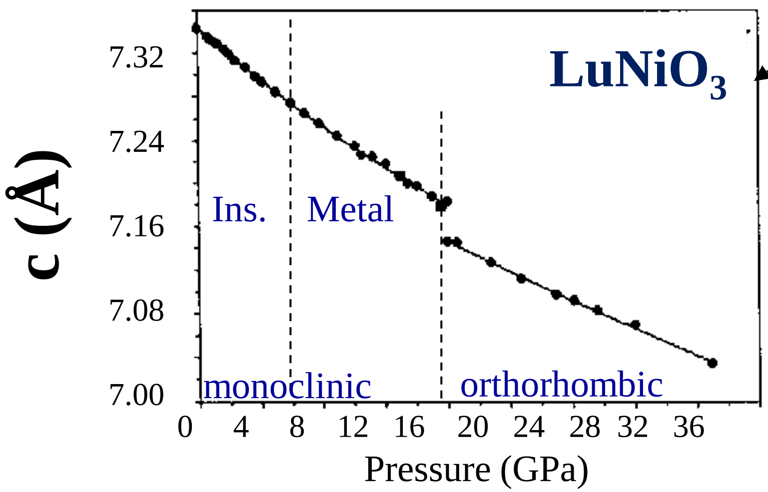
M. Amboage, Ph.D. thesis (2003)

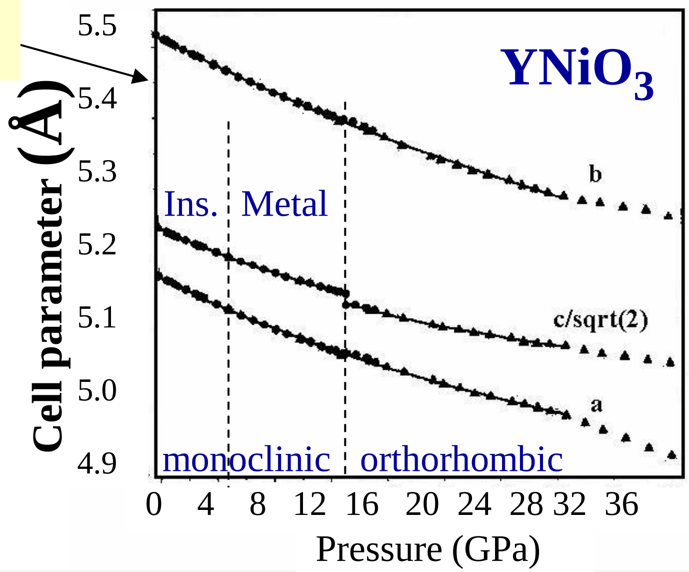


J.L. García-Munoz et al., PRB 69, 094106 (2004)



angle resolved x-ray diffraction (ESRF)





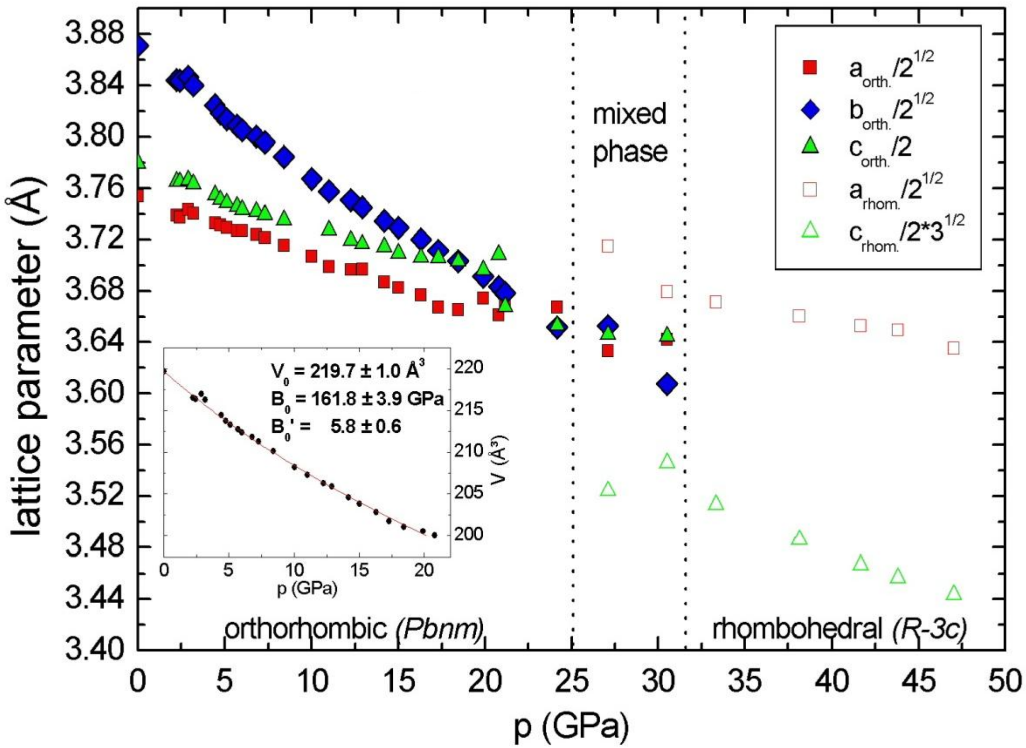
Pressure-induced insulator-metal transition is not connected to structural phase transition!

Structural stability:

$EuNiO_3$

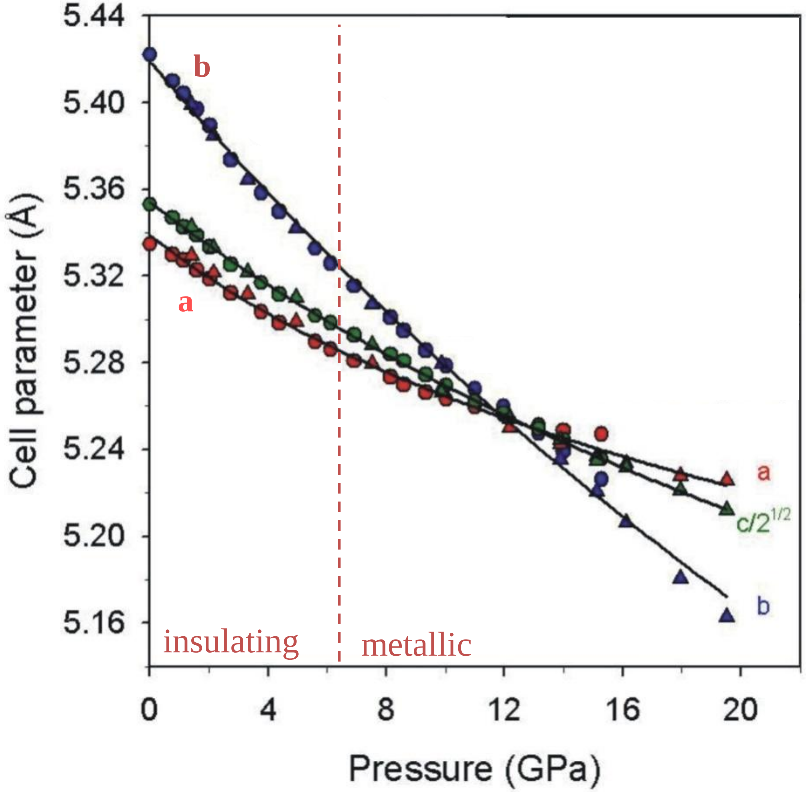
(measured in the DAC @Hasylab and T = 300 K)

R. Lengsdorf, et al. (2005)



$SmNiO_3$

M. Amboage et al. JPCM **17**, 783 (2005)



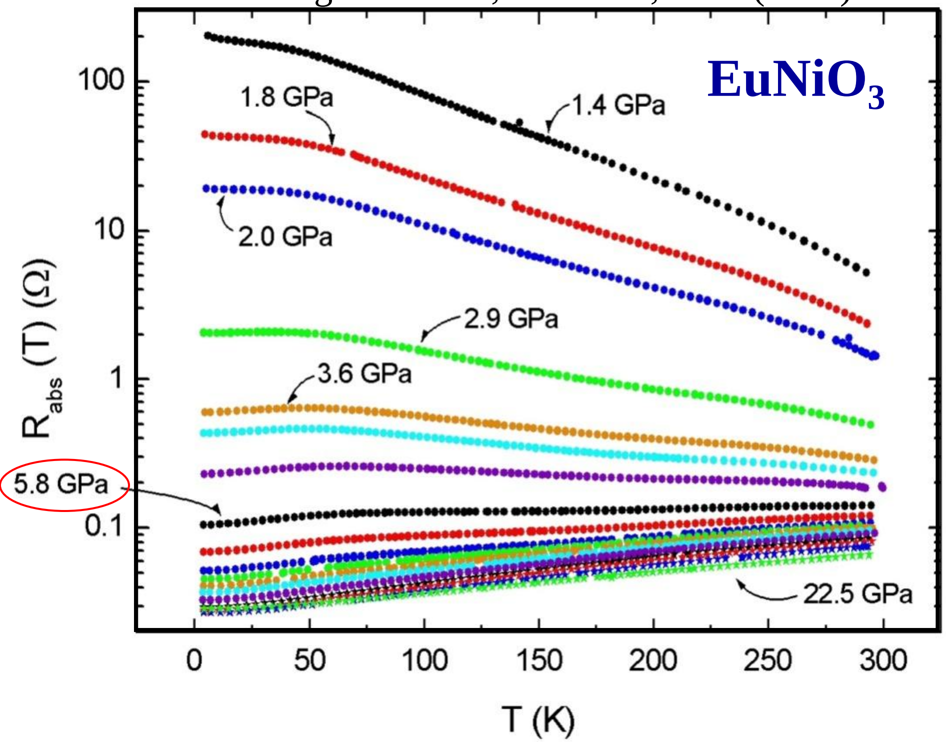
→ **structure stable up to ~ 30 GPa**

→ **above 30 GPa orthorhombic → rhombohedral phase transition**

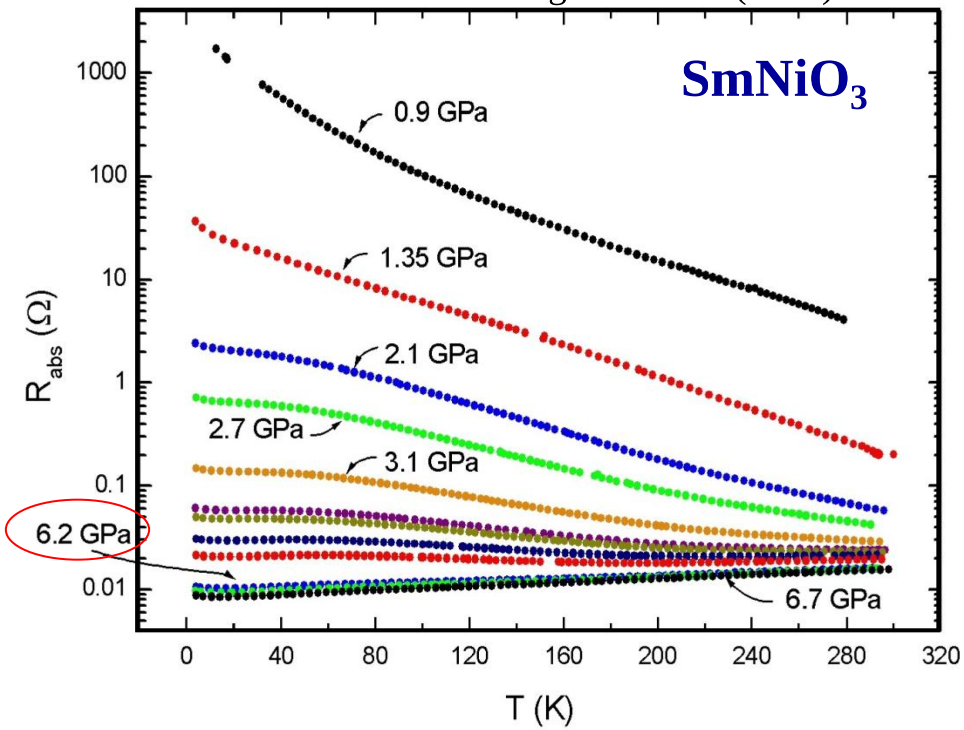
Results: Pressure-induced insulator-metal transition

Electrical resistance: (measured in a Diamond Anvil Cell (DAC))

R. Lengsdorf et al., JPCM 16, 3355 (2004)



R. Lengsdorf et al. (2005)



Insulator to metal transition for

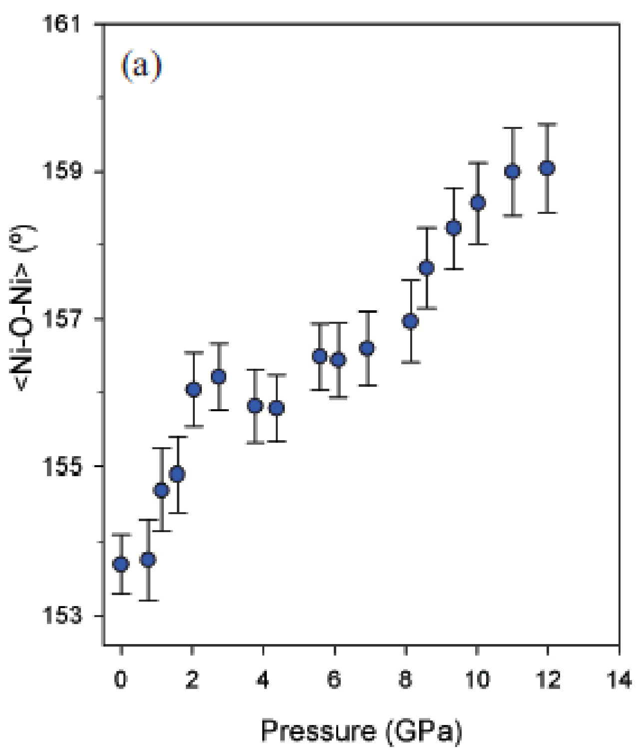
p ≥ 5.8 GPa

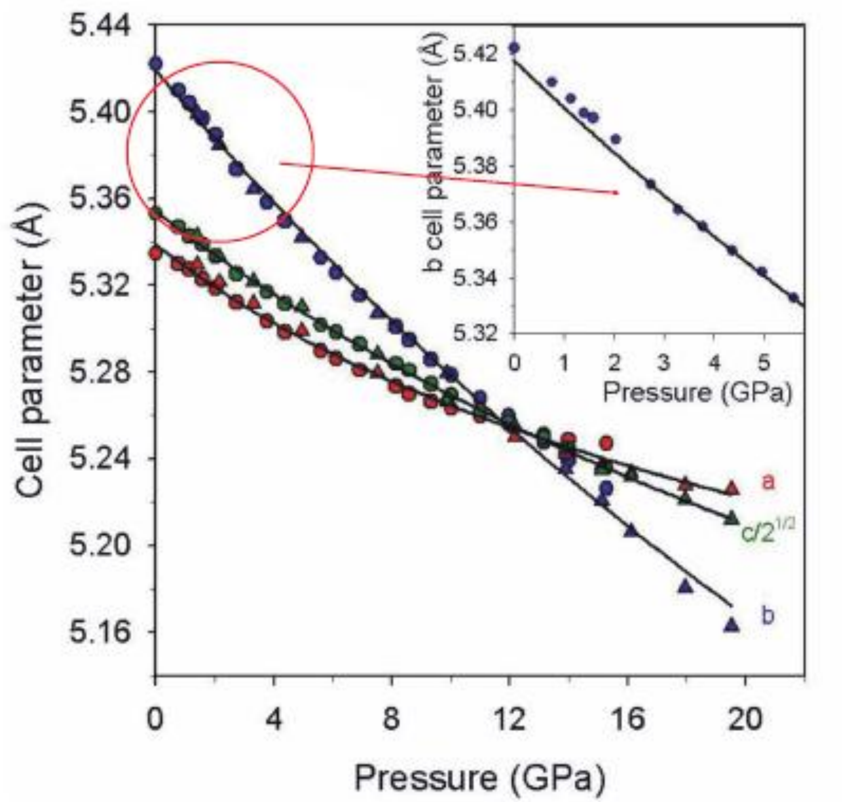
Insulator to metal transition for

p ≥ 6.2 GPa

Close look at the structural parameters

M. Amboage et al. JPCM **17**, 783 (2005)

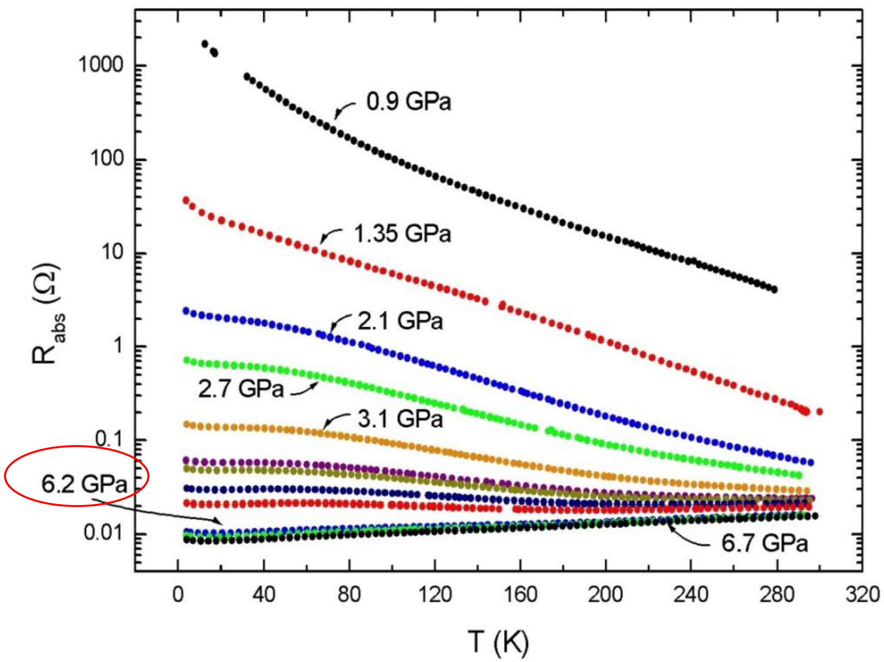


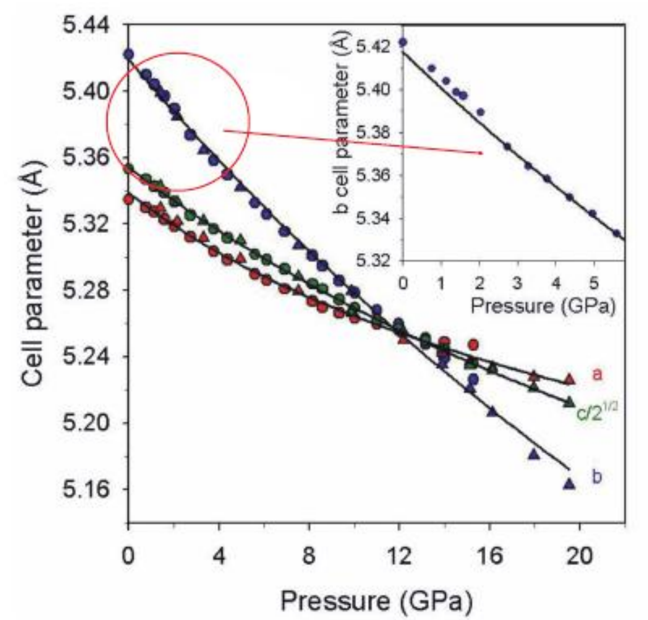


Pressure-induced insulator-metal transition

SmNiO$_3$

R. Lengsdorf et al. (2005)

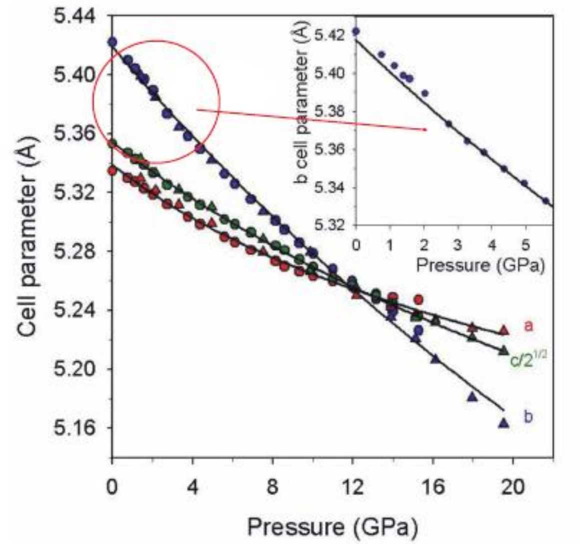


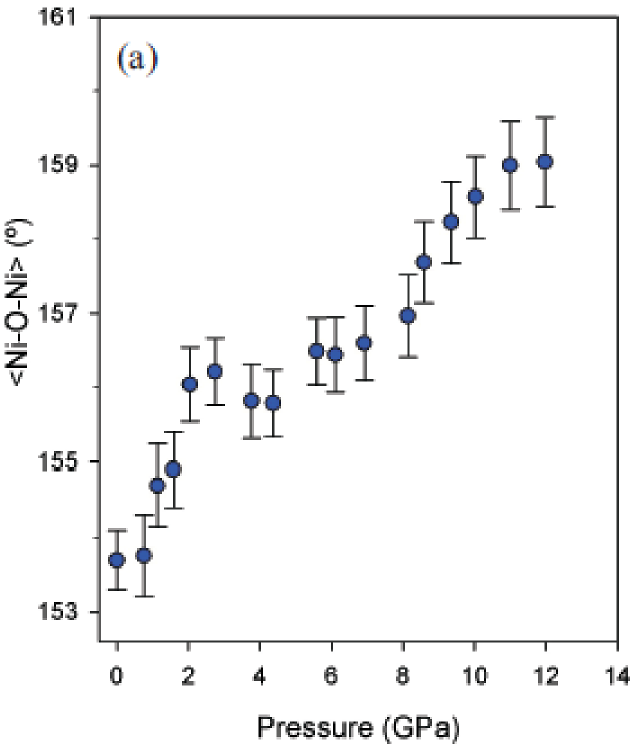


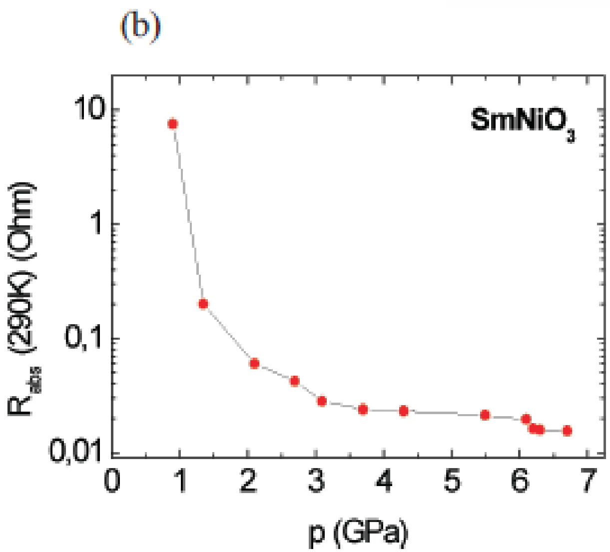
Insulator to metal transition for

p ≥ 6.2 GPa

M. Amboage et al. JPCM **17**, 783 (2005)







R. Lengsdorf, PhD (2005)

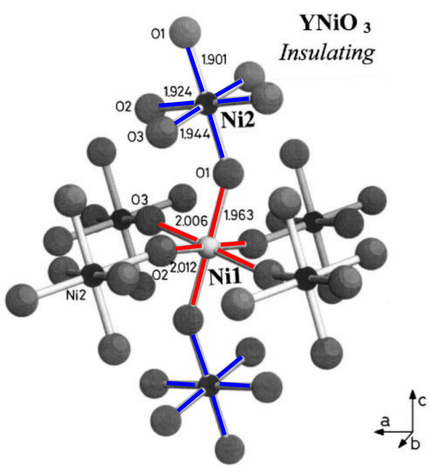
$SmNiO_3$

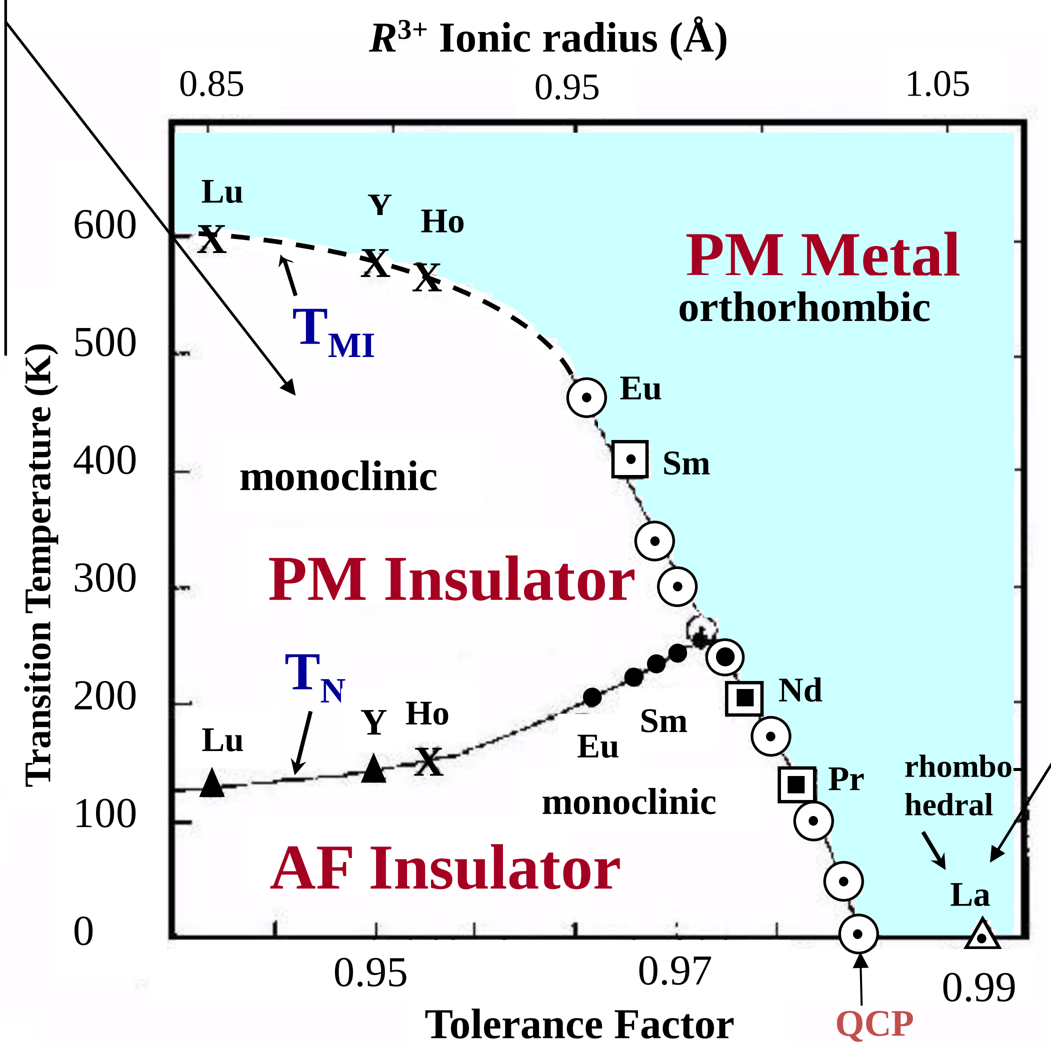
Pressure dependence of the insulator metal temperature

RNiO_3 phase diagram

Curie-Weiss paramagnetic insulator

charge ordering:
$2Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$
($\delta \approx 0.35$)





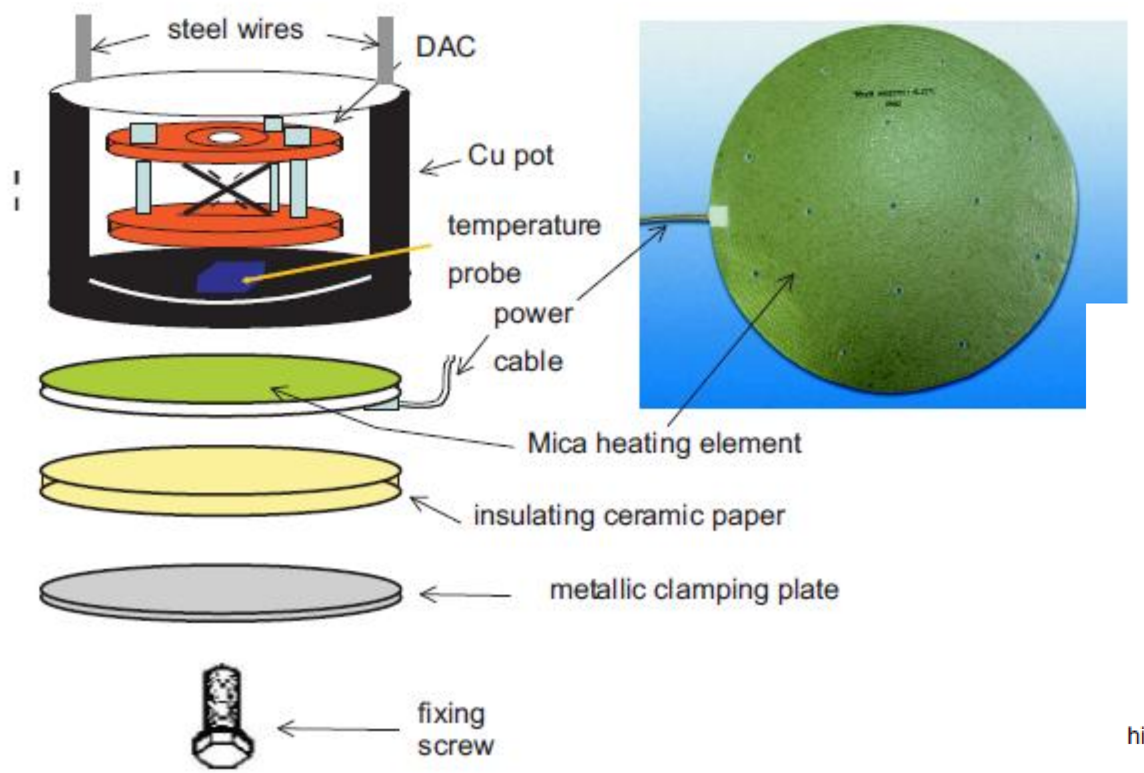
enhanced Pauli paramagnetic metal

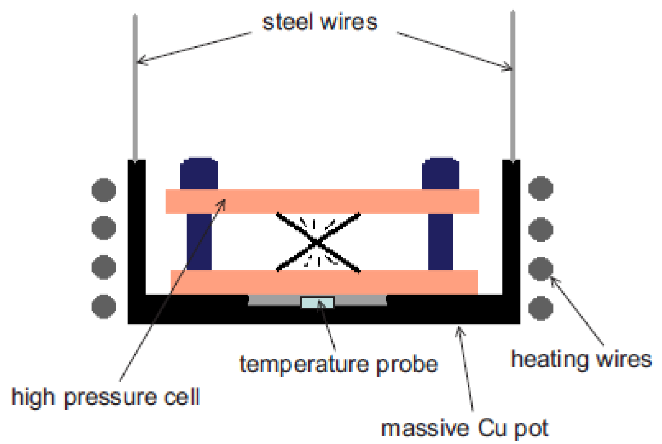
Temperature-induced MI transition connected with:

- **Structural phase transition / charge ordering**
- **Crossover from insulating magnetic to metallic nonmagnetic state!**

Using the DAC for high pressure up to 600 K!

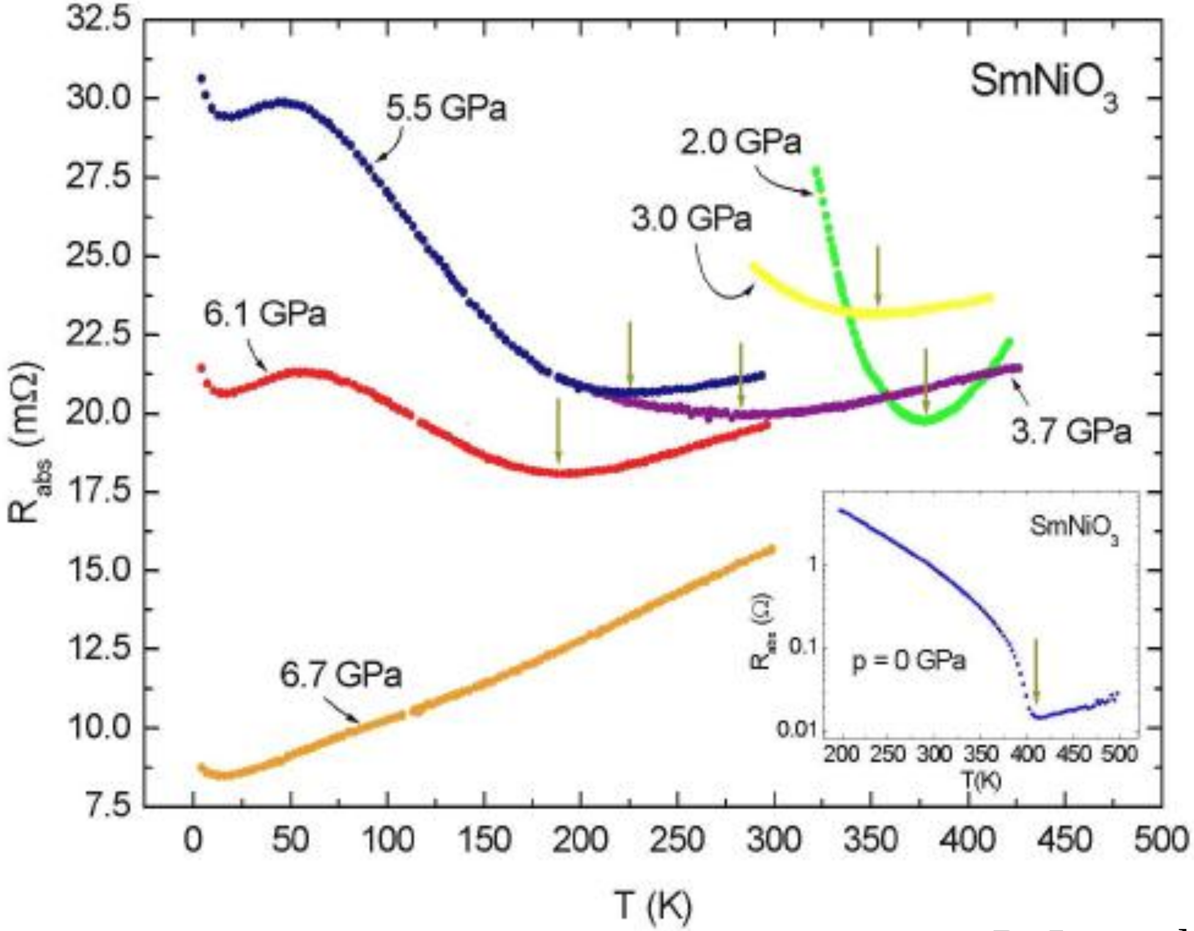
R. Lengsdorf, PhD (2005)



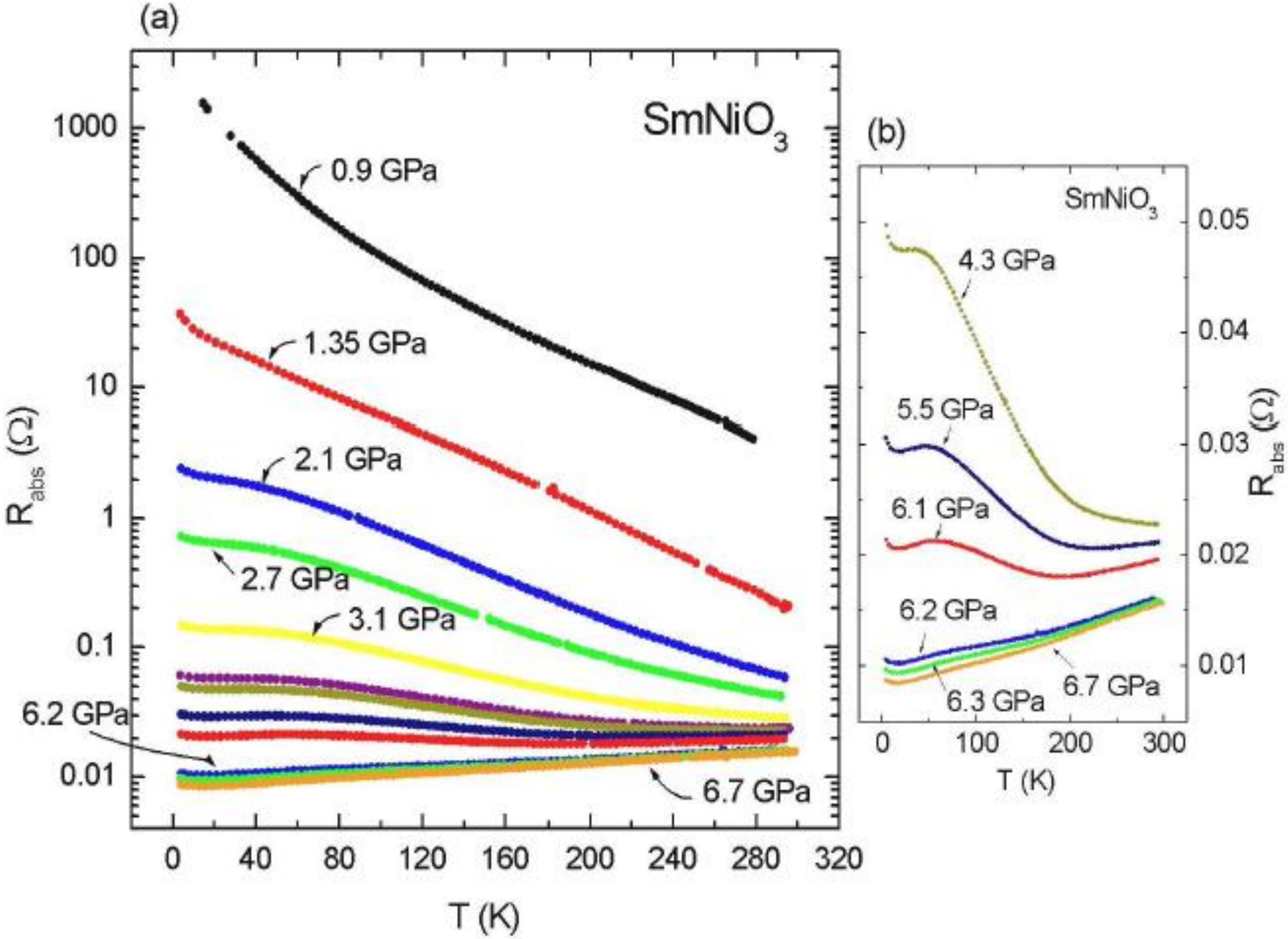


Schematic view of the high temperature insert with the Mica heating element mounted below the Cu pot.

Pressure dependence of the resistivity across the metal insulator transtion temperature (TMI)

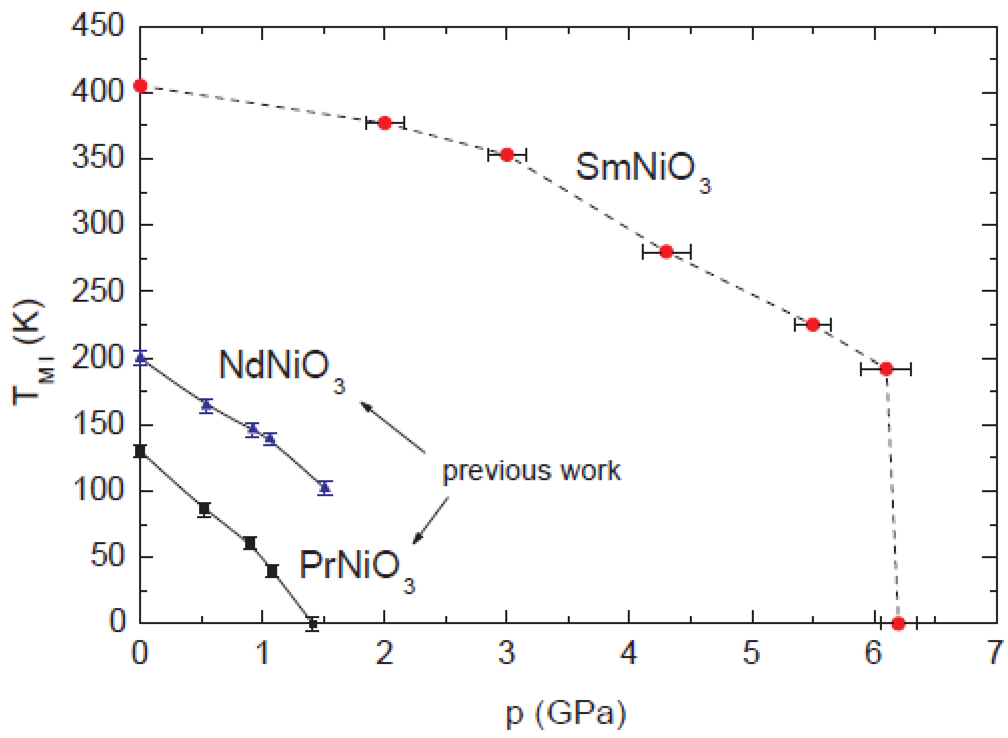


R. Lengsdorf, PhD (2005)

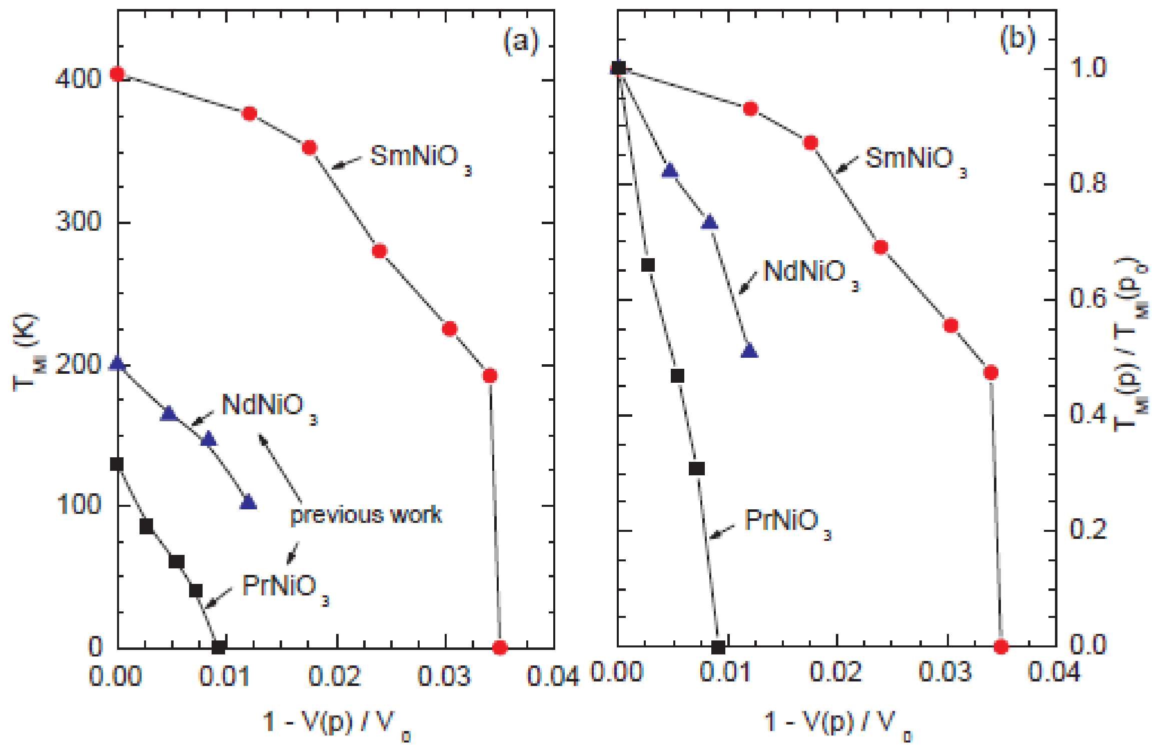


(a)
SmNiO$_3$
0.9 GPa
1.35 GPa
2.1 GPa
2.7 GPa
3.1 GPa
6.2 GPa
6.7 GPa
R$_{abs}$ (Ω)
1000
100
10
1
0.1
0.01
0
40
80
120
160
200
240
280
320
T (K)
(b)
SmNiO$_3$
4.3 GPa
5.5 GPa
6.1 GPa
6.2 GPa
6.3 GPa
6.7 GPa
0.05
0.04
0.03
0.02
0.01
R$_{abs}$ (Ω)
0
100
200
300
T (K)

Pressure dependence of the resistivity across the metal insulator transtion temperature (TMI)



Pressure dependence of the resistivity across the metal insulator transtion temperature (TMI)



Comparison with NdNiO3 and PrNiO3

Nature of the pressure-induced metallic state in RNiO3

In all investigated $RNiO_3$:

→ **pressure-induced metal-insulator transition is not connected with structural phase transition**

In $YNiO_3$ and $LuNiO_3$:

Metallic conductivity in the monoclinic structure with charge ordering???; What is the nature of the metallic state?

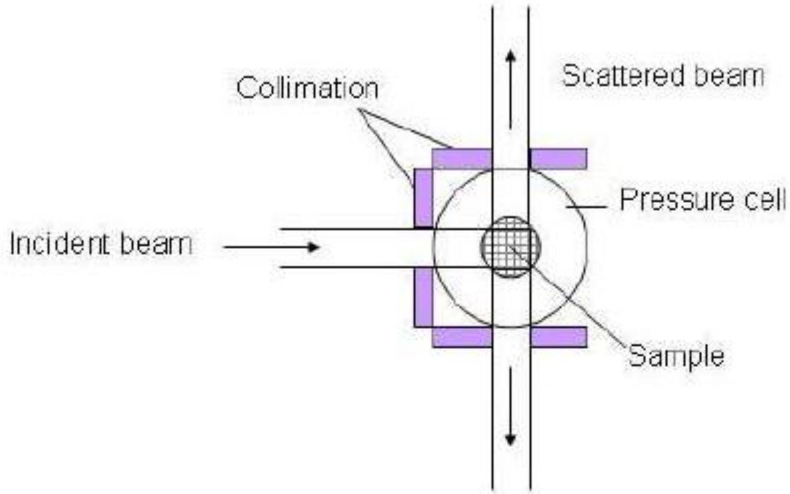
↓

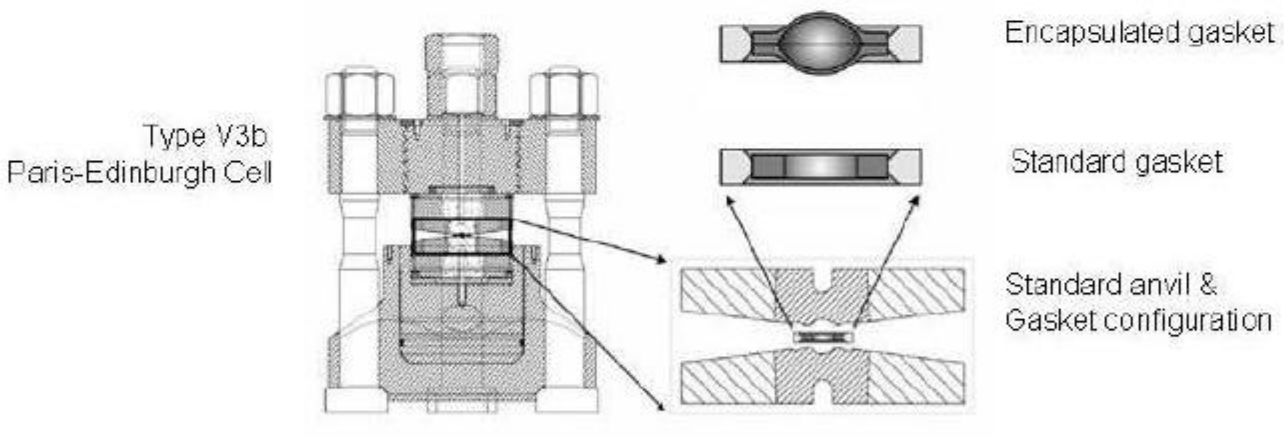
Determination of structural parameters under pressure

→ e.g. bond angles and bond lengths

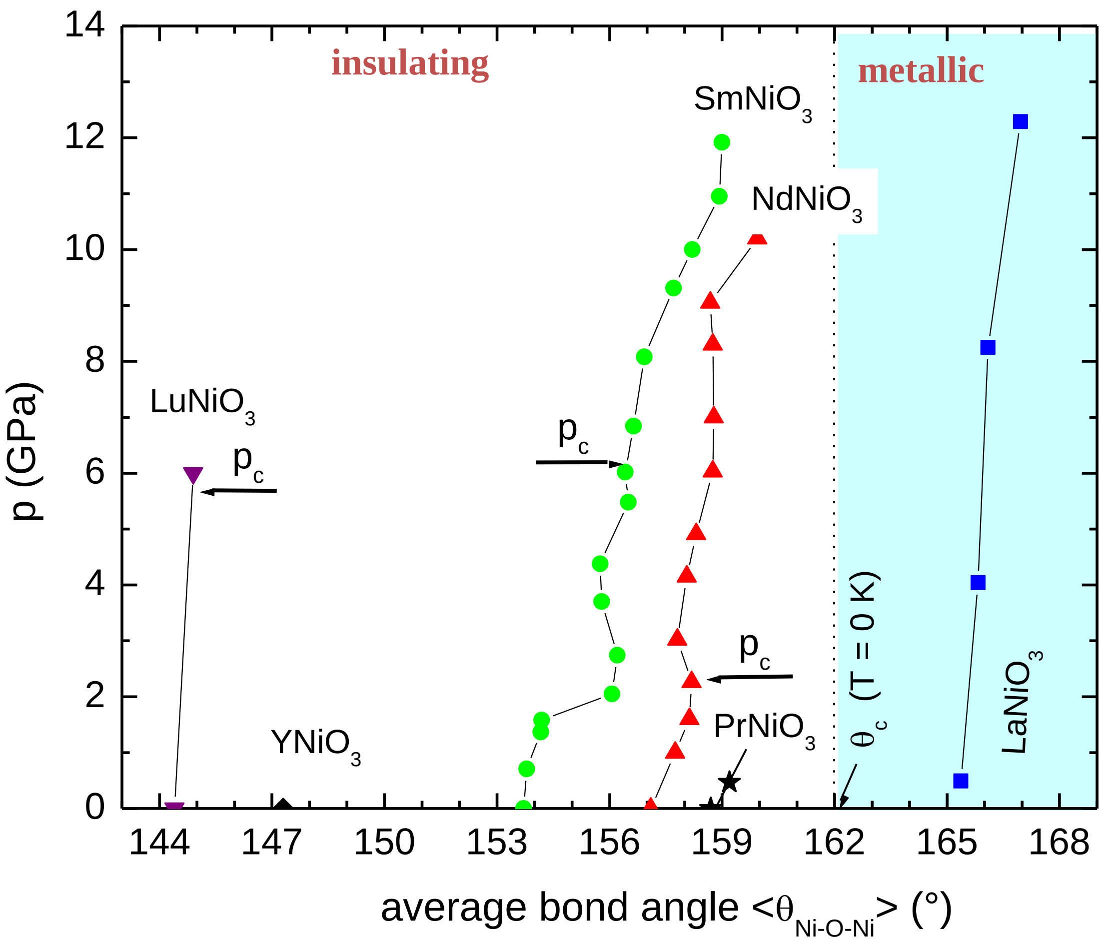
Determination of structural parameters under pressure

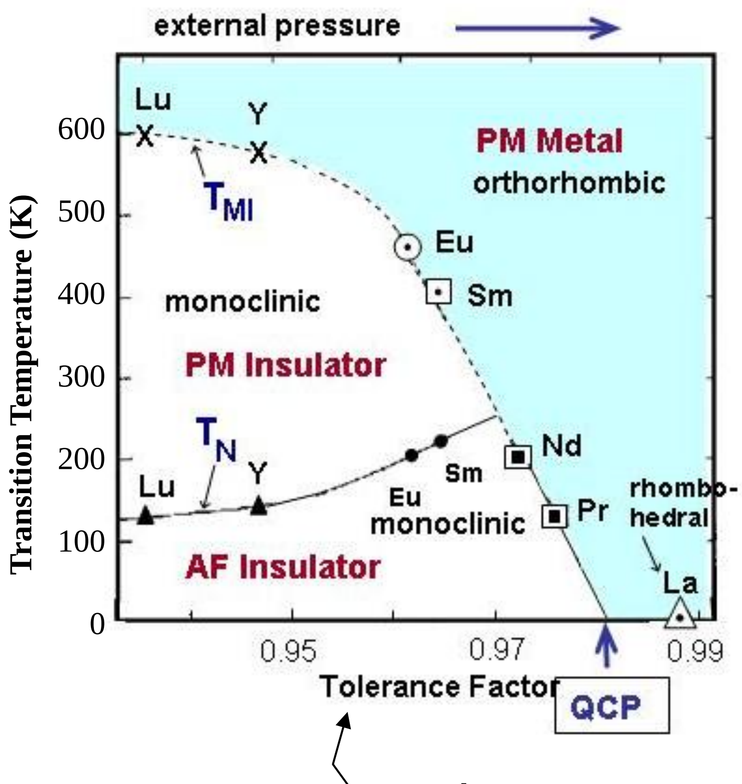
→**high resolution neutron powder diffraction measurements on $LuNiO_3$ at ISIS (Oxford)**





a.) pressure dependence of $RNiO_3$ bond angles



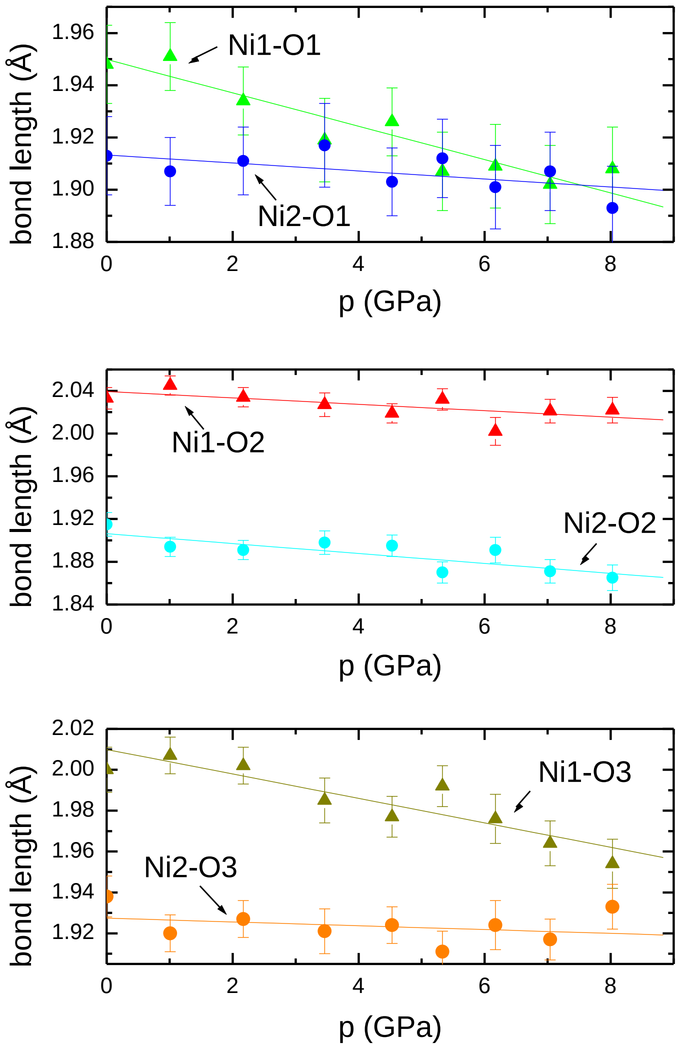


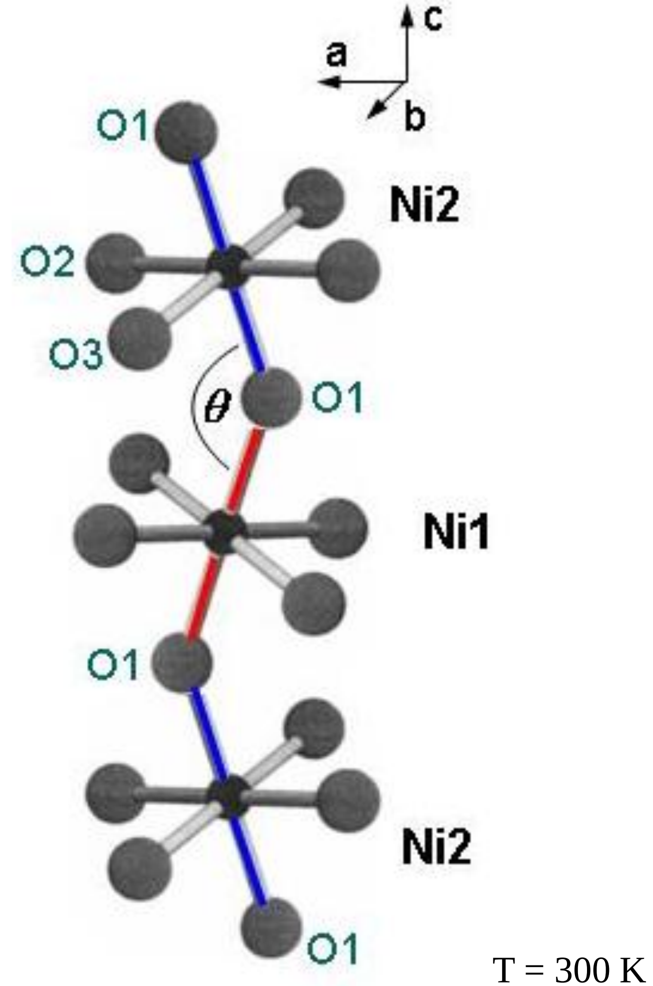
$$t = \frac{1}{\sqrt{2}} \frac{d_{R-O}}{d_{Ni-O}}$$

→ q for small $RNiO_3$ far from $q_{critical}$ → Bond angle not responsible for the pressure-induced MI transition!

b.) bond lengths

→ high resolution neutron powder diffraction measurements on $LuNiO_3$ at ISIS (Oxford)





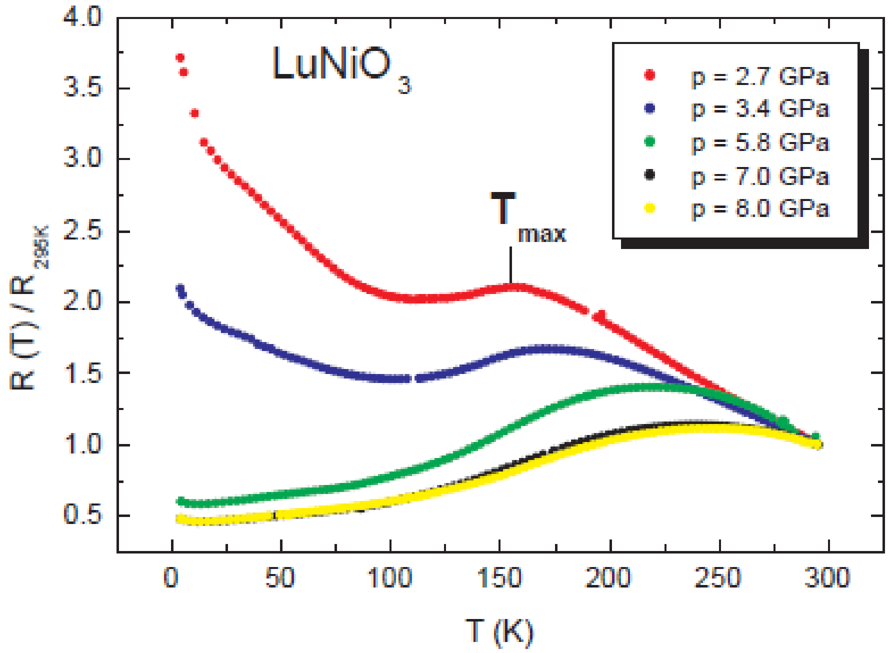
T = 300 K

I.I. Mazin, et al., PRL (2007)

Anisotropic response of the bond lengthes of the (Ni1O6)- and (Ni2O6) octahedra to pressure → modification of their periodicity → gradual melting of charge ordering

Pressure dependence of the magnetic ordering temperature

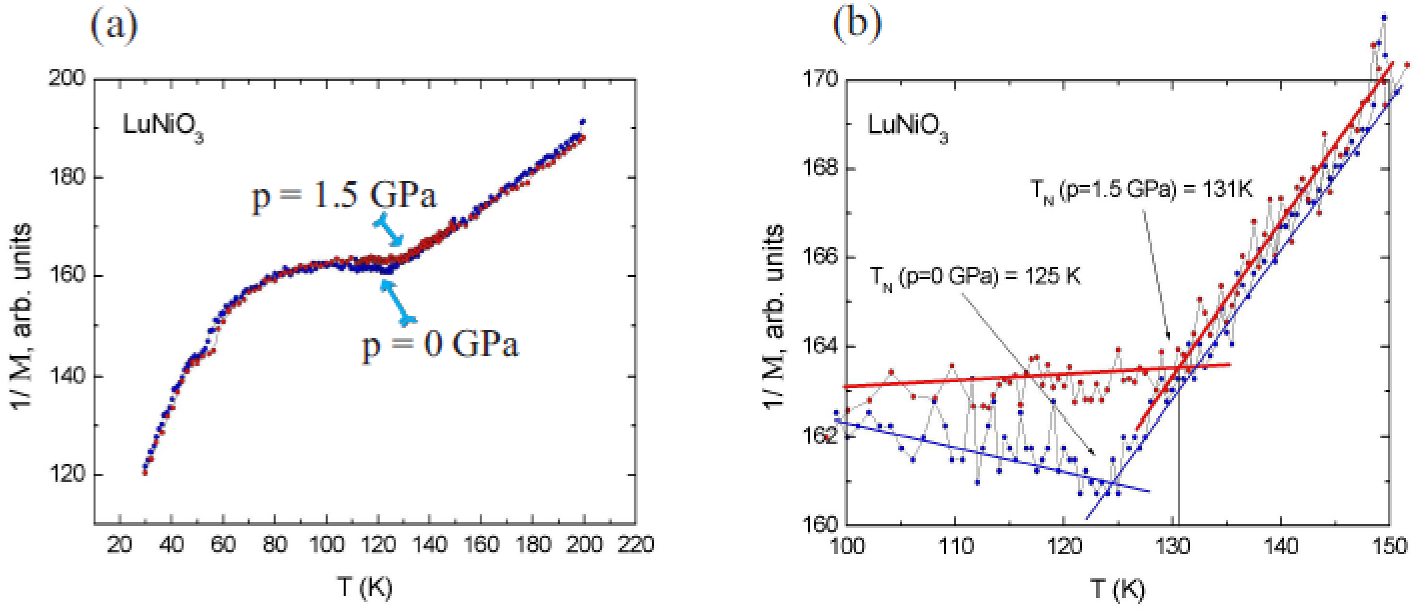
(a) Electrical resistivity:



assumption: Tmax is related to TN
observation: Tmax (TN) increases with pressure

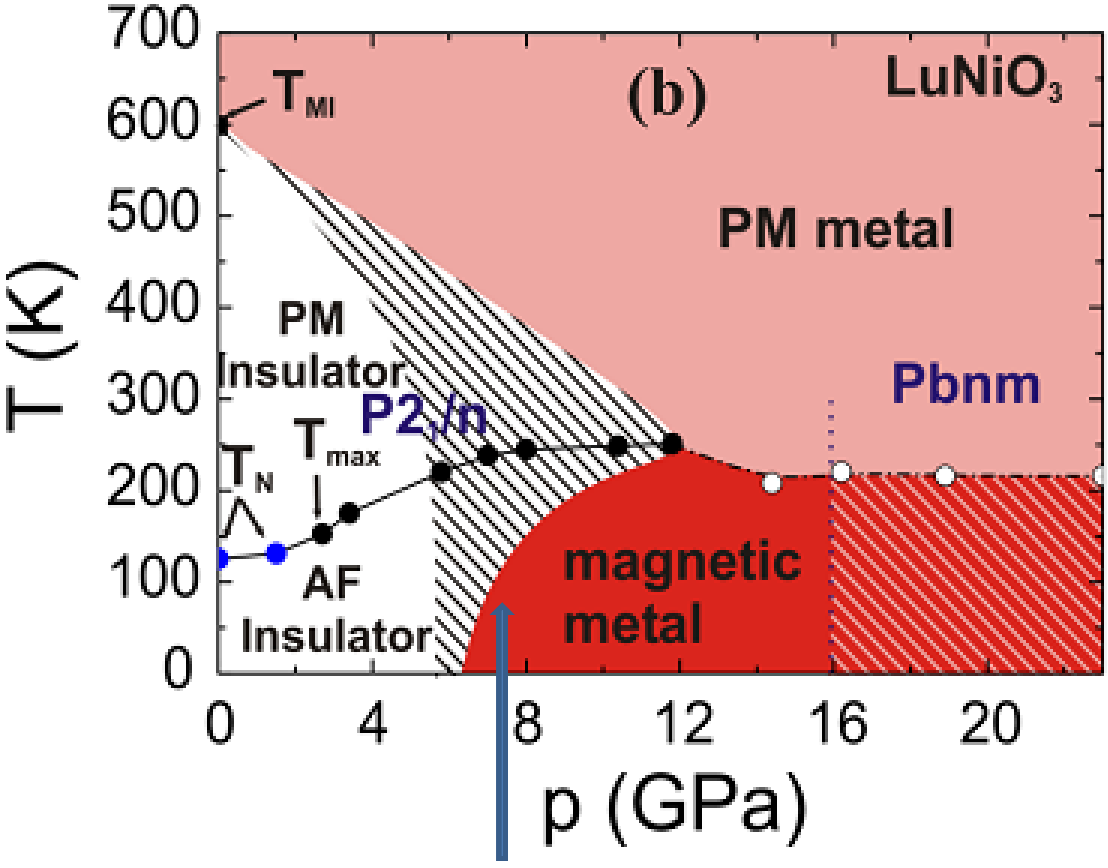
Pressure dependence of the magnetic ordering temperature

(b) Magnetization measurements up to 1.5 GPa:



TN increases from 125 to 131 K

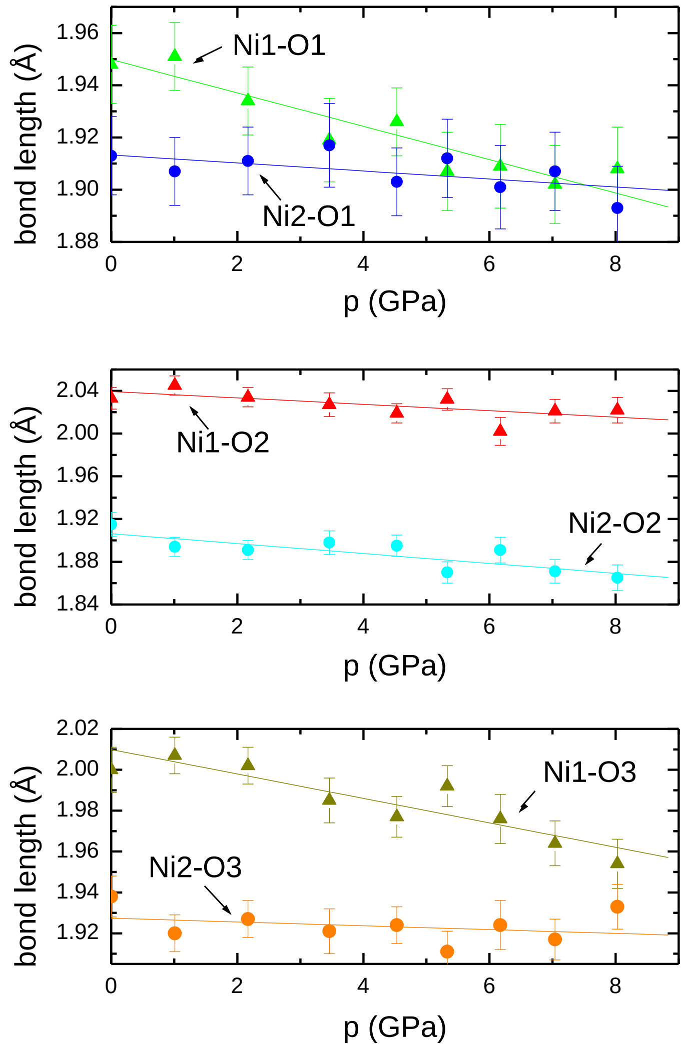
proposed magnetic phase diagram

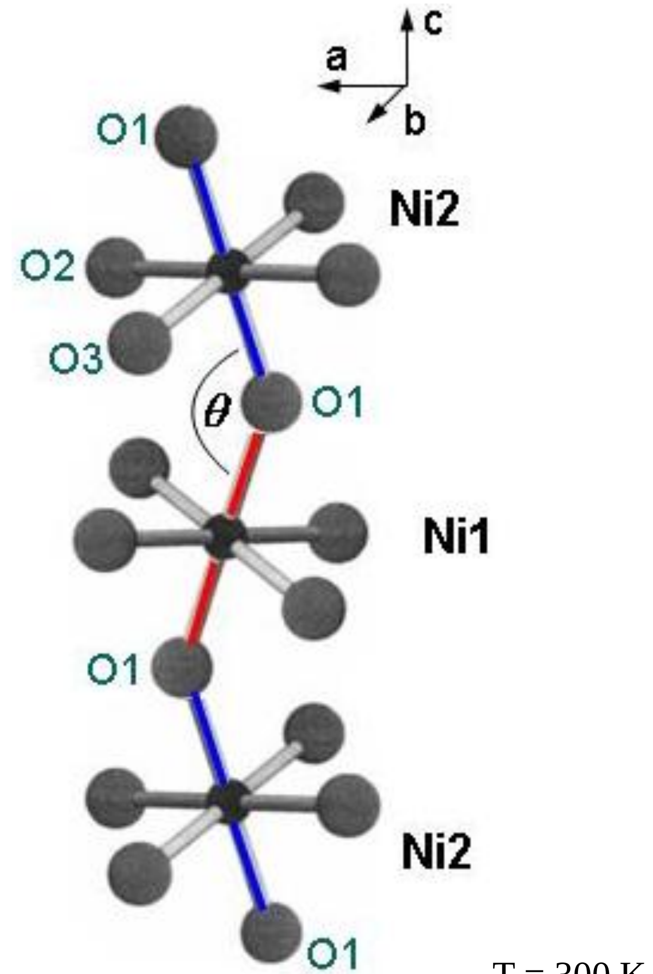


Intermediate magnetic state is metallic and charge ordered!

b.) bond lengths

→ **high resolution neutron powder diffraction measurements on $LuNiO_3$ at ISIS (Oxford)**





T = 300 K

I.I. Mazin, et al., PRL (2007)

Anisotropic response of the bond lengthes of the (Ni1O6)- and (Ni2O6) octahedra to pressure → modification of their periodicity → gradual melting of charge ordering

Theoretical description of the unusual intermediate magnetic state

$RNiO_3$ perovskites (R = rare earth 3+ ion, La → Lu)

Interesting aspects:

- **Ni^{3+}:** t_{2g}^{6} e_{g}^{1}, low spin (S = ½) state → JT-active, but NO JT distortion → **orbitally degenerate system!**

- all members (*R* ≠ La) are insulators with **very small energy gap (Δ ~ 100 meV).**

⇒ **metal-insulator transition can be driven by changing the size of the *R*$^{3+}$-ion (chemical pressure) or temperature.**

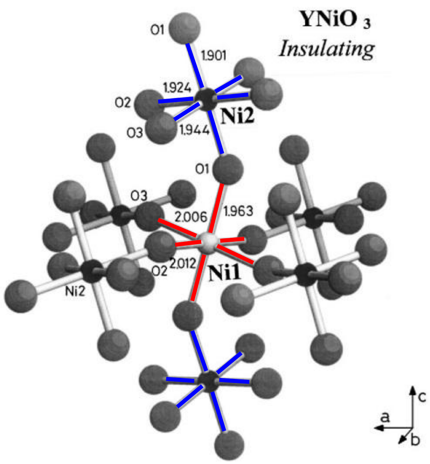
- insulating state is **charge ordered**.

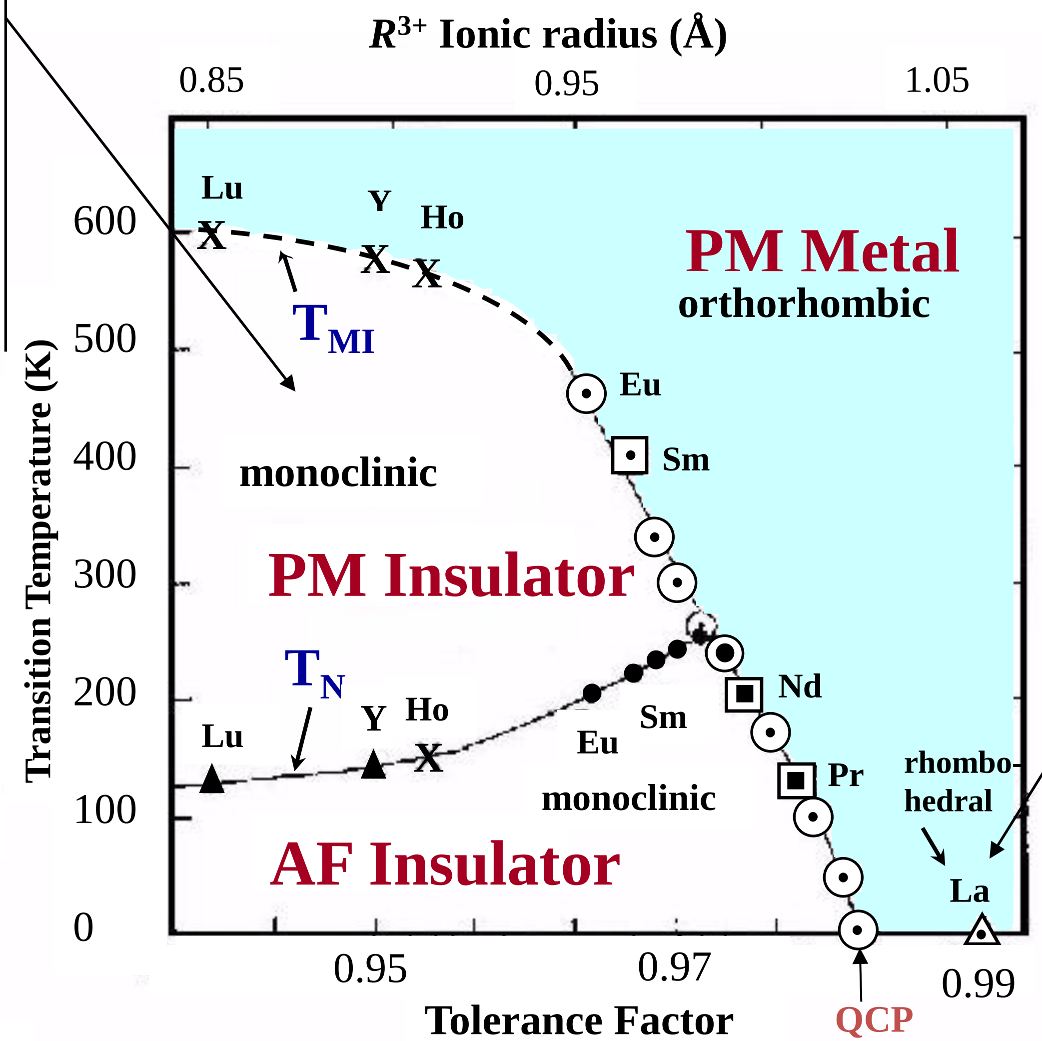
- ground state (*R* ≠ La): **antiferromagnetic insulator**

RNiO$_3$ phase diagram

Curie-Weiss paramagnetic insulator

charge ordering:
$2Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$
($\delta \approx 0.35$)





enhanced Pauli paramagnetic metal

Temperature-induced MI transition connected with:

- **Structural phase transition / charge ordering**
- **Crossover from insulating magnetic to metallic nonmagnetic state!**

PRL 98, 176406 (2007) PHYSICAL REVIEW LETTERS week ending 27 APRIL 2007

Charge Ordering as Alternative to Jahn-Teller Distortion

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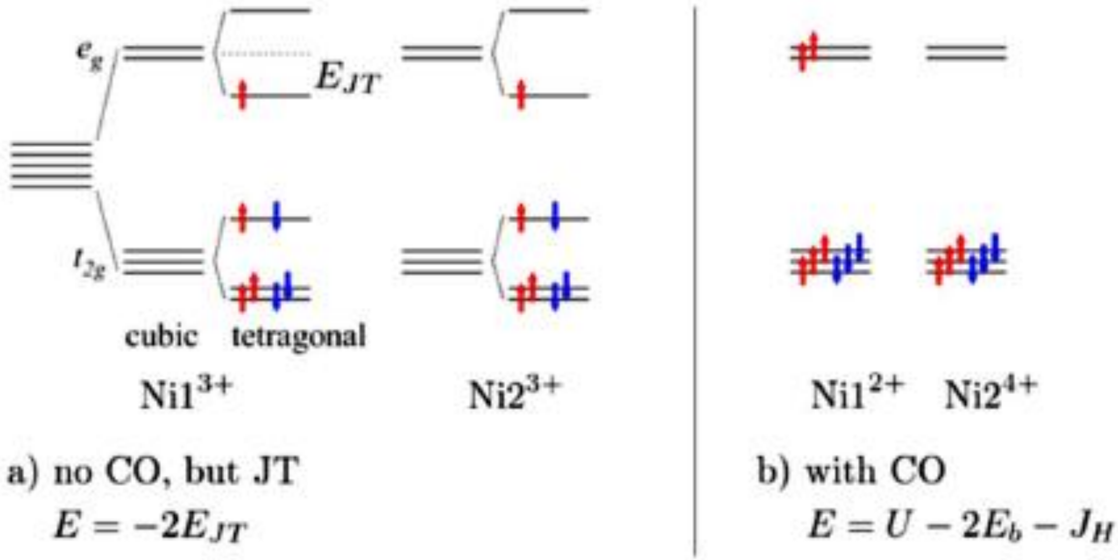
(Received 12 February 2007; published 26 April 2007)

We show that the Mott transition in orbitally degenerate systems can, and often does, proceed not in the standard "Mott insulator—weakly correlated metal" sequence, but via a novel intermediate phase with a charge (rather than orbital) ordering. Lifting an orbital degeneracy this way can be viewed as an alternative to a Jahn-Teller distortion. This may occur in a crossover between localized and itinerant regimes, if Hund's rule coupling overcomes the on site Coulomb repulsion. We show both by calculations and by experiment that this scenario is realized in rare-earth nickelates, and argue that the same phenomenon takes place in many other systems.

lifting of orbital degeneracy by CO rather than by JT distortion



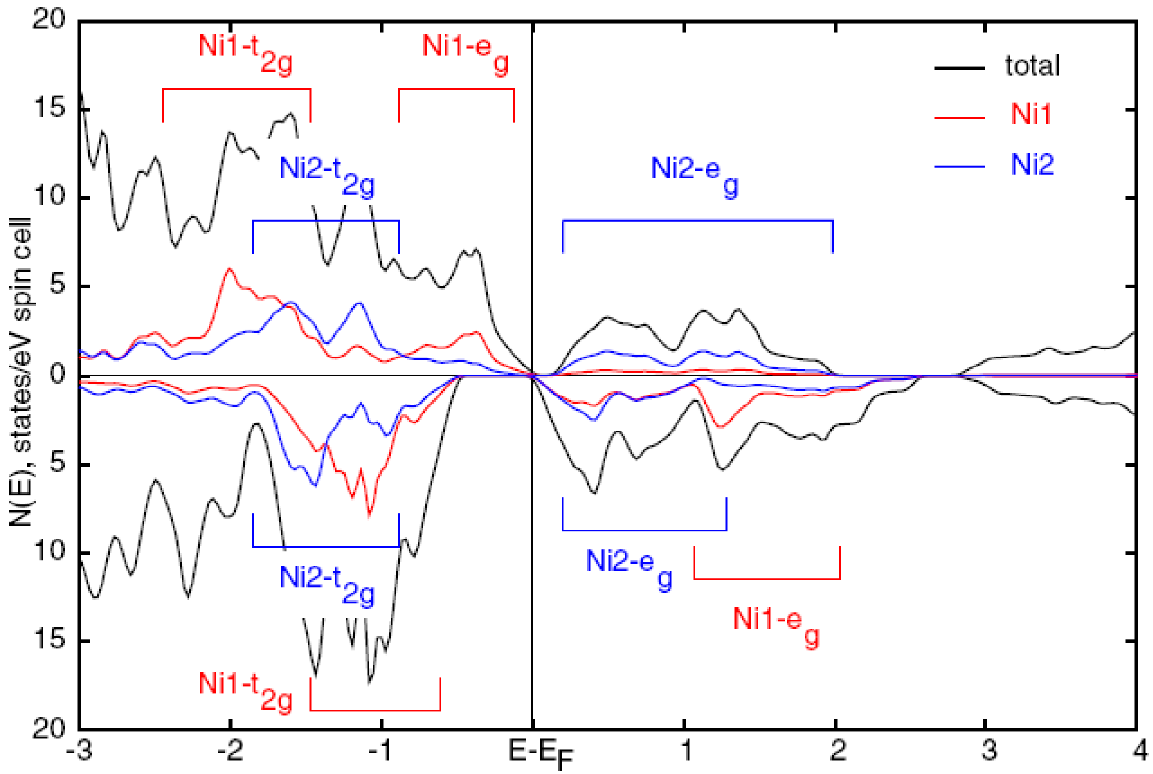
$$H = \sum_{i \neq j, \alpha\beta} t_{i\alpha j\beta} c^{\dagger}_{i\alpha\sigma} c_{j\beta\sigma} + U \sum_{i, \alpha\sigma \neq \beta\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'} - J_H \sum_{i, \alpha \neq \beta} \vec{S}_{i\alpha} \vec{S}_{i\beta} - \sum \{E_{\mathrm{JT}} + E_{\mathrm{breath}}\}.$$

Here J_H is the Hund's rule interaction, E_{JT} is the energy gain due to a JT distortion for $Ni3^+$, E_{breath} is the energy regained by allowing oxygen to breath around $Ni4^+$ and $Ni2^+$ in case of CO.

I.I. Mazin, et al., PRL (2007)

Band structure calculations

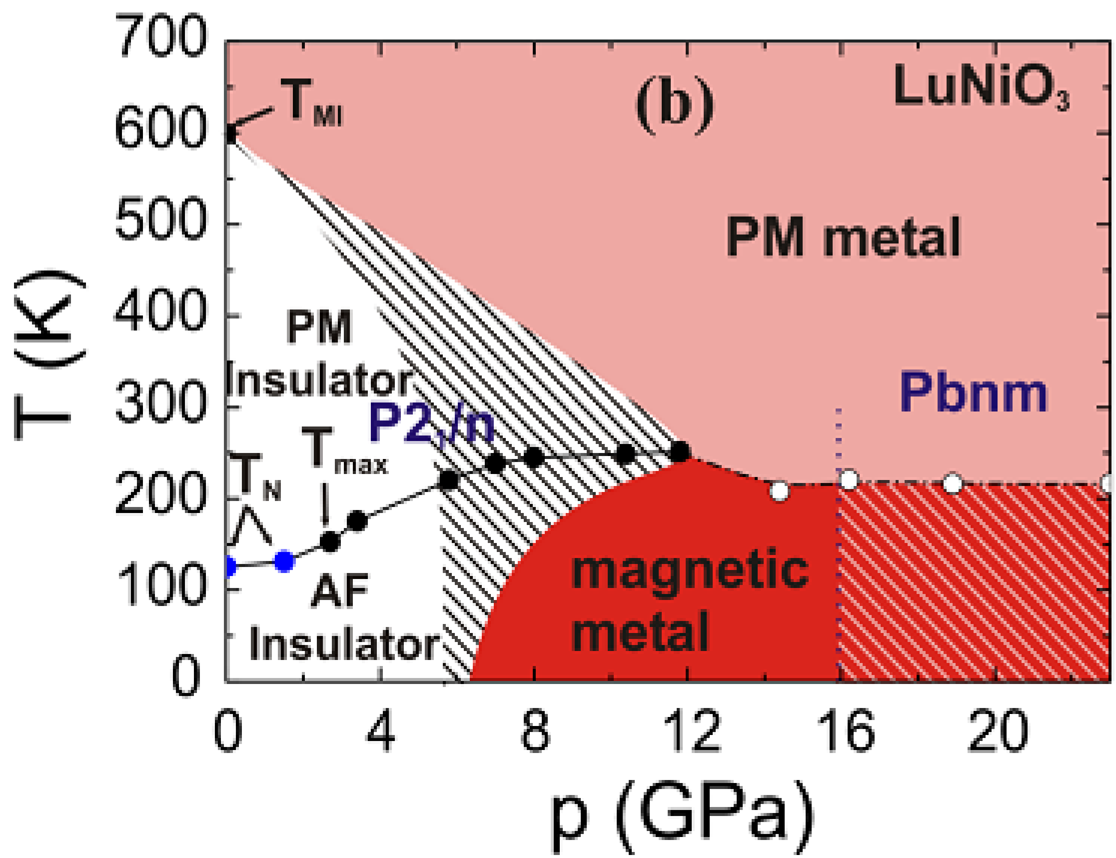
I.I. Mazin, et al., PRL (2007)



description with LDA rather than with LDA+U
→ weak correlation scenario!

gap formation and its pressure collaps consistent with experiment

Proposed phase diagram for $LuNiO_3$



the system remains charge ordered in the metallic magnetic state
→ novel intermediate phase !

I.I. Mazin, et al., PRL (2007)

Theory ⟺ Experiment: Physical picture

***R*NiO$_3$ are not „real“ Mott insulators, but rather in a crossover regime closer to the itinerant site → band insulators (large bandwidth)!**

<u>Consequences:</u>

- **lifting of orbital degeneracy by CO rather than by JT distortion**
- **under pressure, this gap closes and CO does not change much and the system remains CO in the metallic magnetic state**

  ⇒ novel intermediate phase

- **CO would melt at larger values of t/U when the system becomes a normal metal**

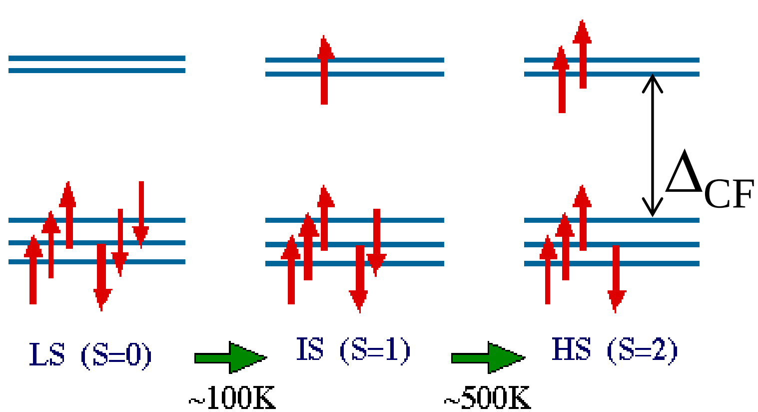
$La_{1-x}Sr_xCoO_3$

$\Rightarrow$ A perovskite transition metal oxide with a spin-state degree of freedom

$La_{1-x}Sr_xCoO_3$ rhombohedral distorted perovskite structure

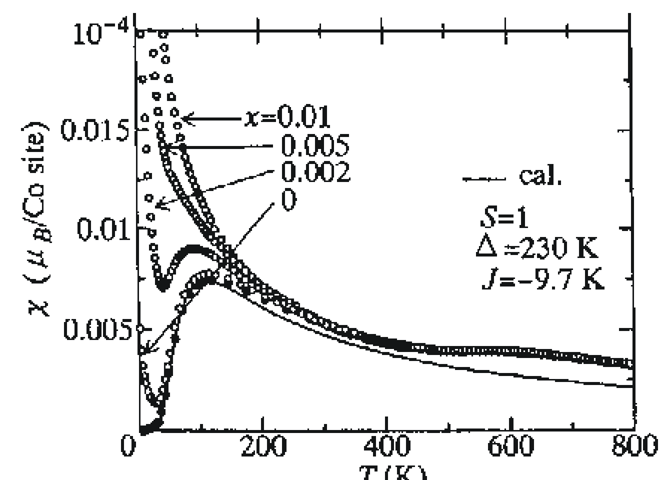
$LaCoO_3$: (undoped)

- Co^{3+}, $3d^6$, Low-Spin (LS) state (S = 0)
- ground state: nonmagnetic, insulator
- temperature-induced spin transition (T ~ 100K)
- temperature-induced insulator-metal transition (T ~ 500K)



$La_{1-x}Sr_xCoO_3$: (doped)

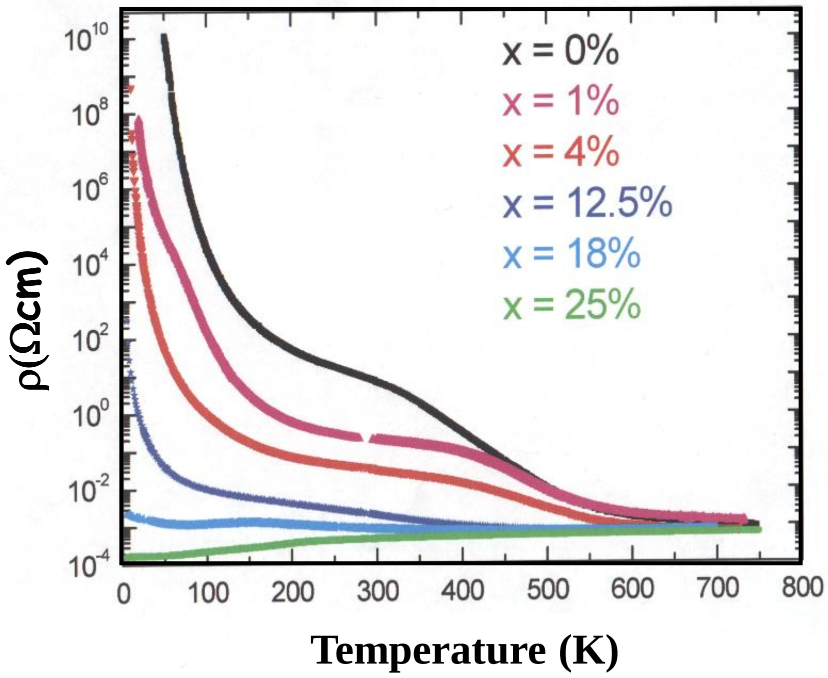
- $Co^{3+} \rightarrow Co^{4+}$ ($3d^5$) increasing valence due to Sr^{2+} (hole-) doping
- ground state: LS-state is suppressed: nonmagnetic $\rightarrow$ spin glass $\rightarrow$ $x \geq 0.18$ ferromagnetic
- $x \geq 0.18$ insulator-metal transition
- rhombohedral distortion decreases with x and $\rightarrow$ cubic for x ~ 0.50



Electrical and magnetic properties of $La_{1-x}Sr_xCoO_3$

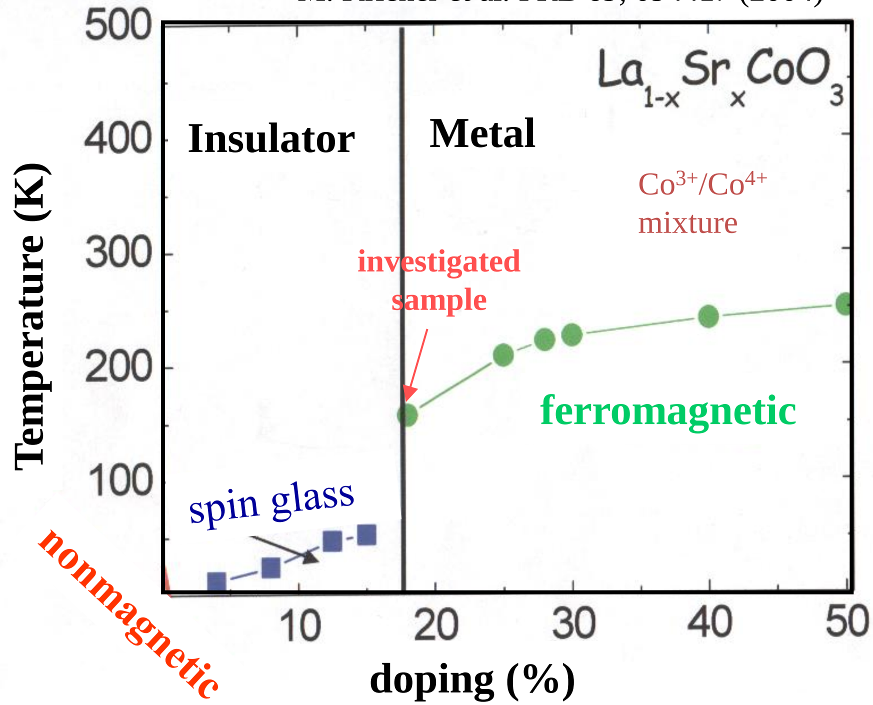
electrical resistivity

Ch. Zobel et al. PRB **66,** 020402 (2002)



magnetic phase diagram

M. Kriener et al. PRB **69**, 094417 (2004)



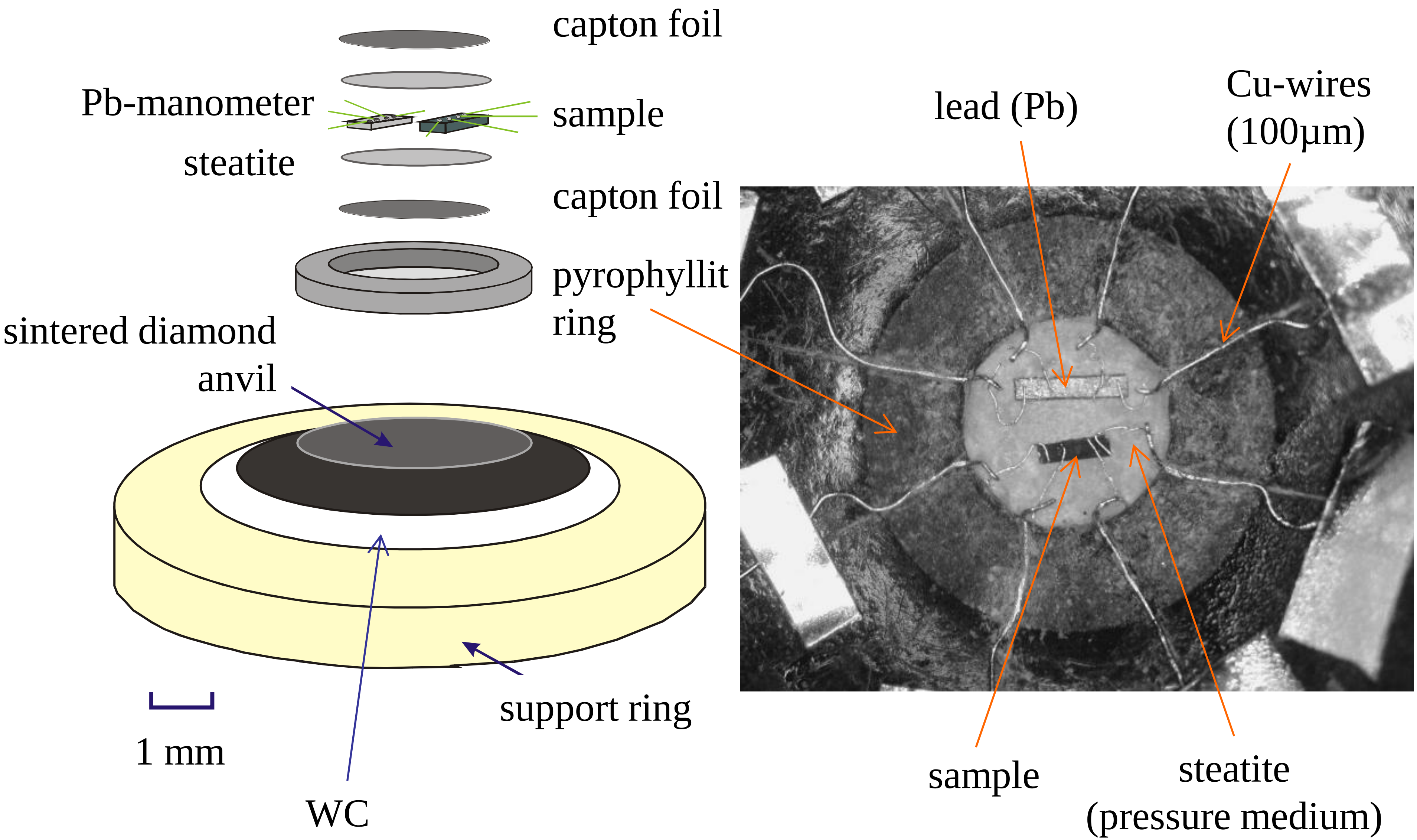
⇒ **insulator-metal transition at $x \geq 0.18$**

⇒ **onset of ferromagnetic ordering at $x \geq 0.18$**

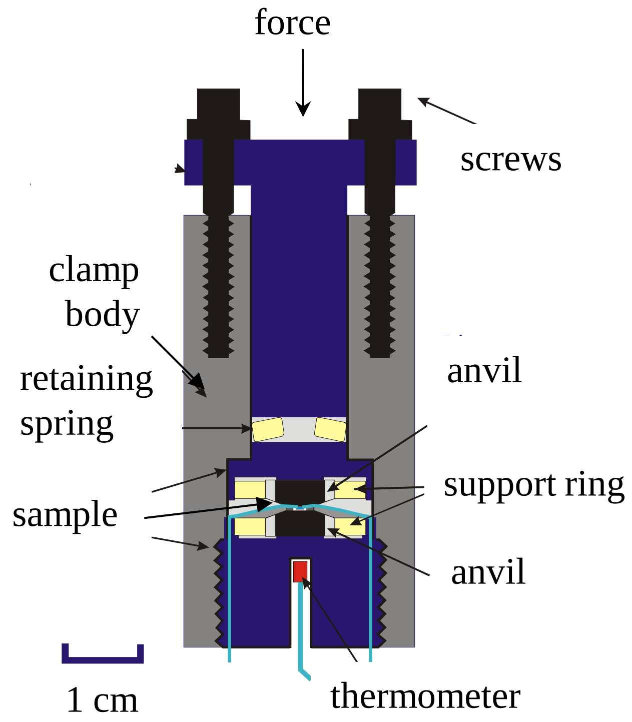
Open questions

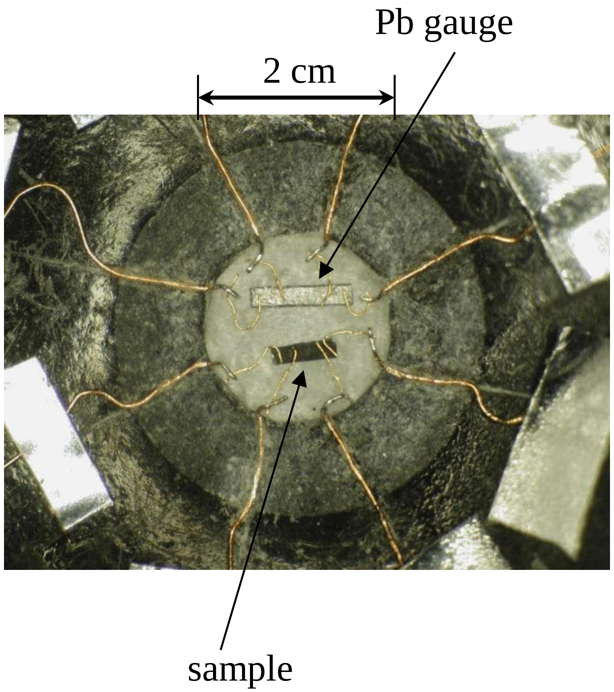
- **whether and to what extent the spin degree of freedom (spin transitions) affects the insulator-metal transition?**

→ **better understanding of the connection between the metal-insulator transition and onset of ferromagnetic ordering.**


capton foil
Pb-manometer
sample
steatite
capton foil
pyrophyllit
ring
sintered diamond
anvil
1 mm
WC
support ring
lead (Pb)
Cu-wires
(100µm)
sample
steatite
(pressure medium)

High pressure technique: large-volume clamp





anvil culet: ~ 2 – 8 mm;
sample chamber: ~ 1 – 4 mm;
p_{max} ~ 40 GPa, quasihydrostatic

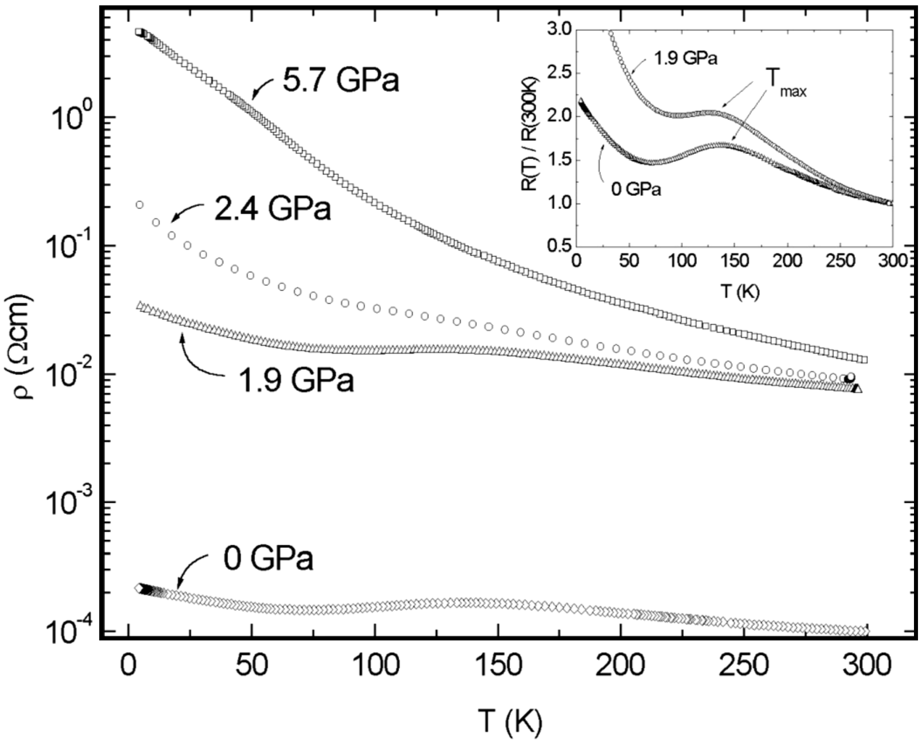
Benefits:

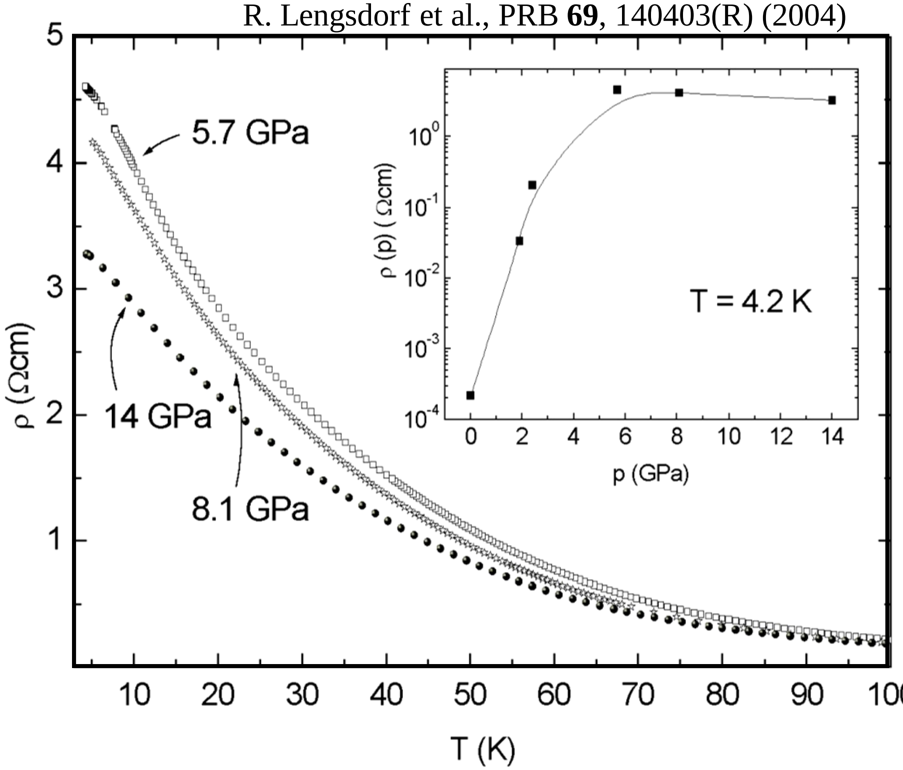
- large volume, large samples
- single crystals
- direction dependent electric transport

Pressure dependence of the electrical resistivity of $La_{0.82}Sr_{0.18}CoO_3$

electrical transport ρ(T,p):

R. Lengsdorf et al., PRB **69**, 140403(R) (2004)





$0 \leq p \leq 5.7$ GPa

$5.7 \leq p \leq 14$ GPa

⇒ dramatic increase of the electrical resistivity of about 4 orders of magnitude!

⇒ strong reduction of electron hopping with increasing pressure

⇒ no further increase of the electrical resistivity; ρ(T,p) even decreases by about 30%

⇒ opposite behavior at higher pressures

How can we understand such an opposite
behavior to all known 3d correlated systems?

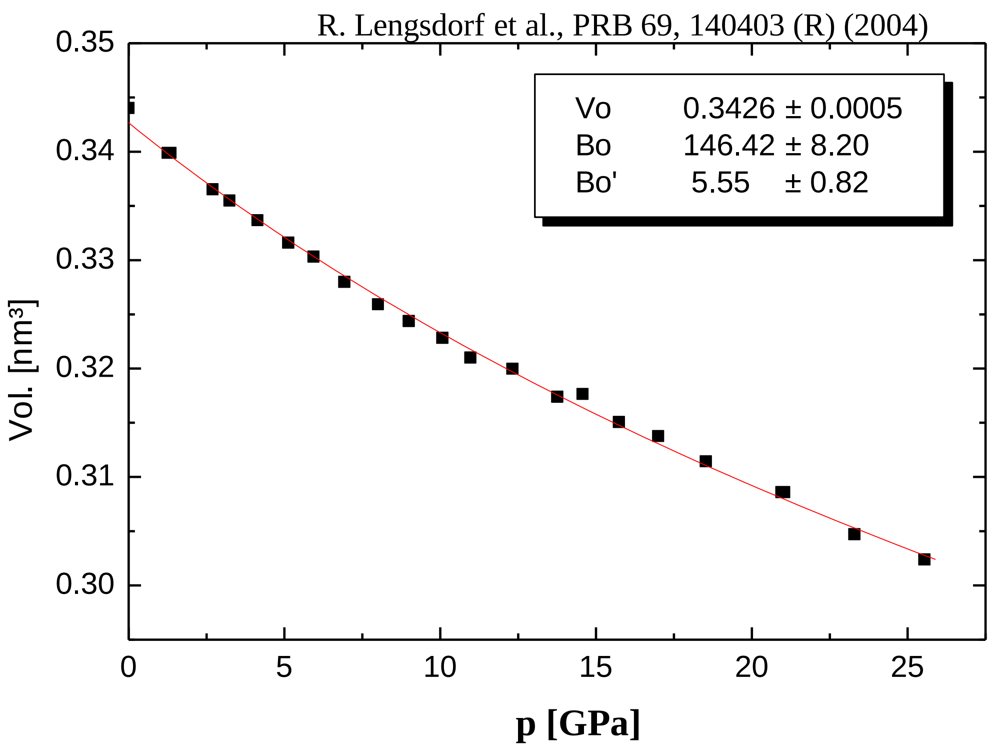
↓

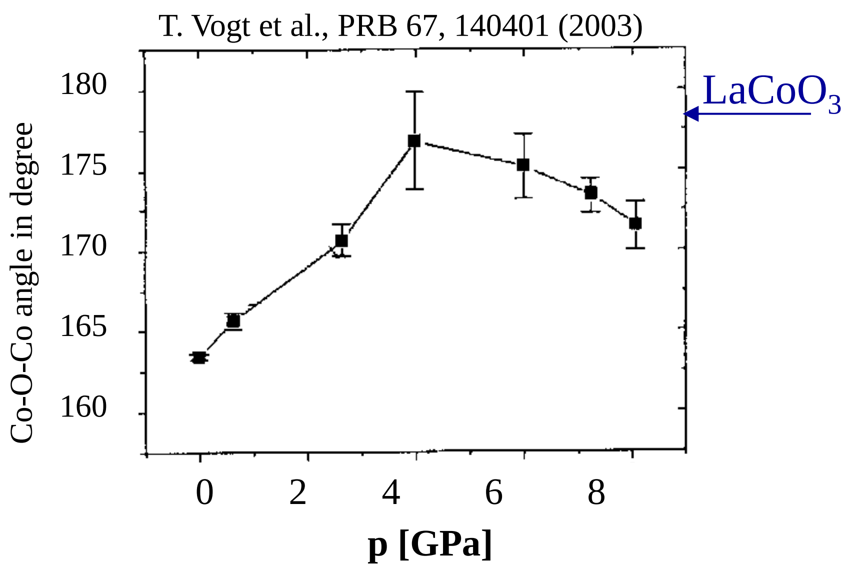
suppression of the electron hopping and reduction of T_C

- unusual change of the structure? (local structure?)
- change of the Co^{3+} spin-state?

(1) Effect of pressure on the structure

volume dependence of $La_{0.82}Sr_{0.18}CoO_3$ as a function of pressure





structure stable up to 25 GPa.

→ no structural phase transition!

strong increase of Co-O-Co bond angle usually leads to strengthen of magnetic interactions and enhancement of electron hopping => metallic like behavior.

→ **we find excatly the opposite!**

(2) Change of the Co^{3+} spin-state

pressure-induced IS → LS transition

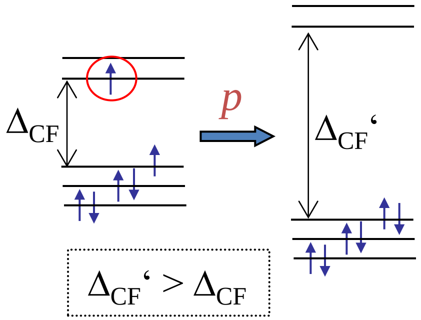
Based on two <u>experimental facts</u>:

(a) ionic radius of LS Co^{3+} (0.545 Å) is smaller than that of HS/IS Co^{3+} (0.61Å)

(b) crystal field splitting (Δ_{CF}) of $LaCoO_3$ increases with pressure

IS - Co^{3+} ($S = 1$, $t_{2g}^{5}\, e_g^{1}$) $\xrightarrow{p}$ LS - Co^{3+} ($S = 0$, $t_{2g}^{6}\, e_g^{0}$)

magnetic **nonmagnetic**

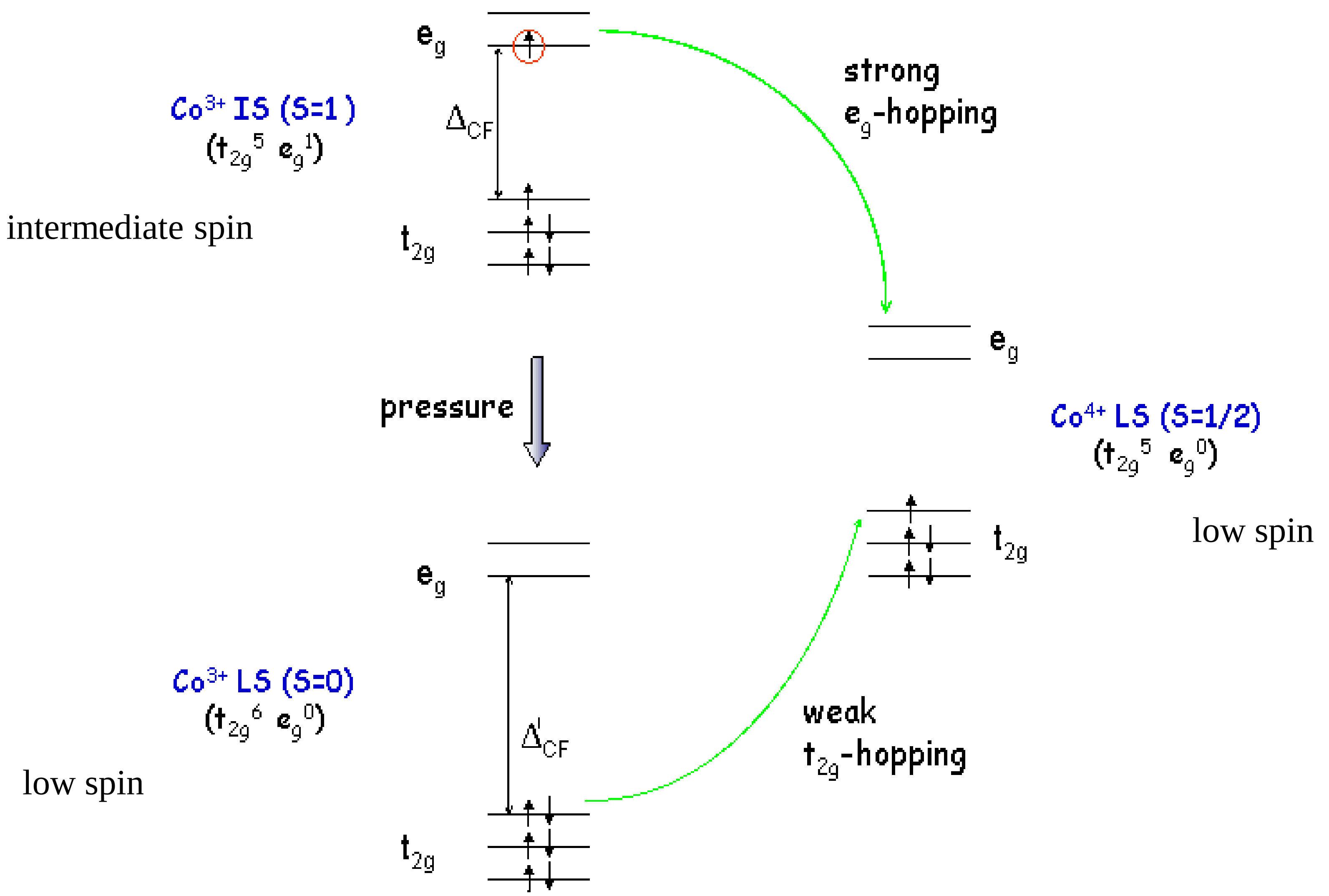


→ continuous depopulation of the IS state with pressure

suppression of electron hopping and reduction of T_C

→ also a reduction of μ_{Co} with pressure is expected!

pressure-induced IS → LS transition ➔ Suppression of electron hopping



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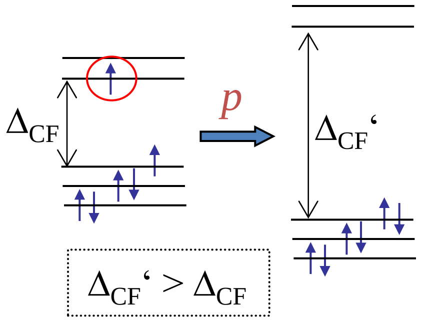
IS - Co^{3+} (S = 1, t_{2g}^{5} e_g^{1}) —*p*→ LS - Co^{3+} (S = 0, t_{2g}^{6} e_g^{0})

magnetic **nonmagnetic**



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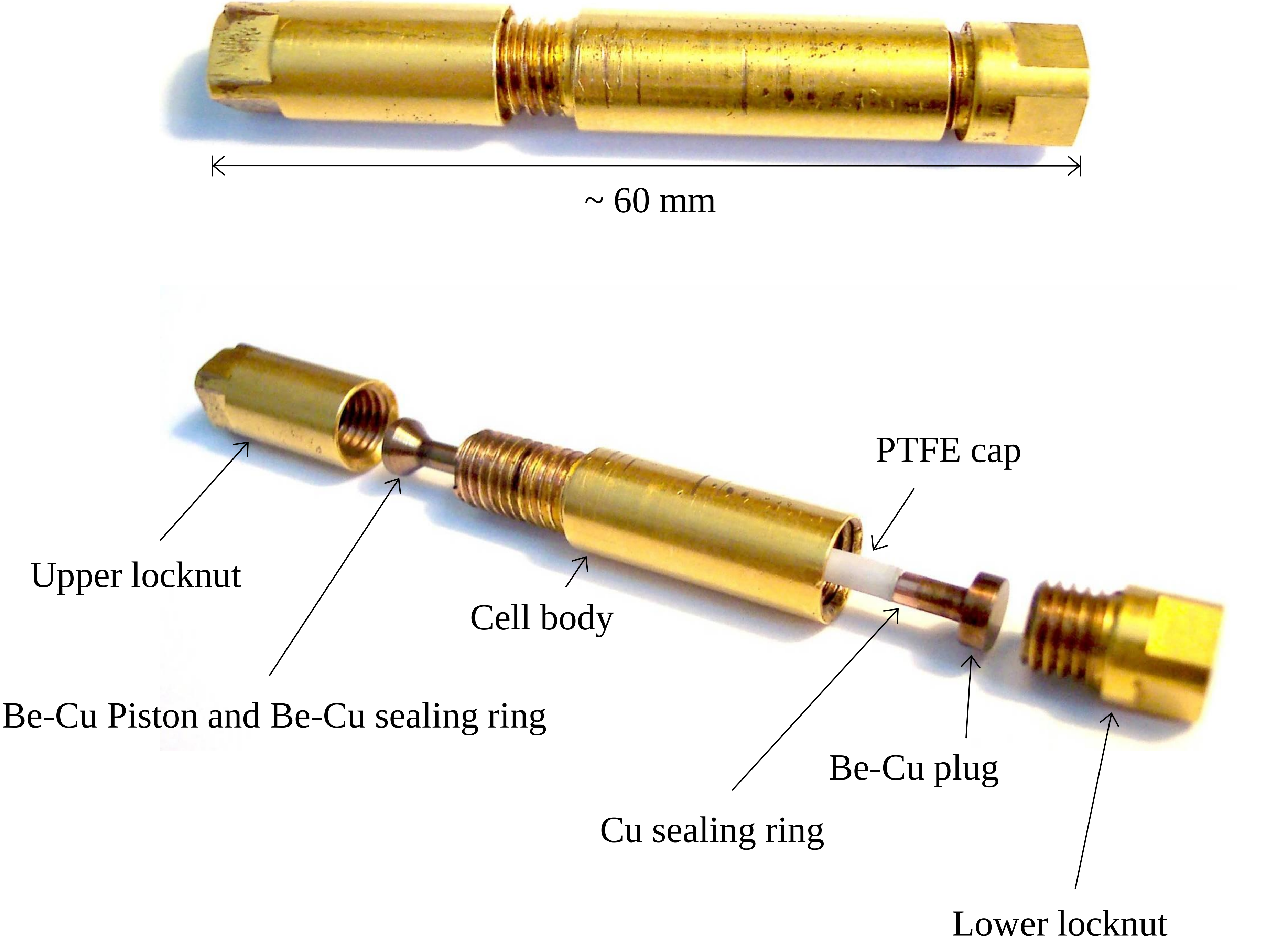
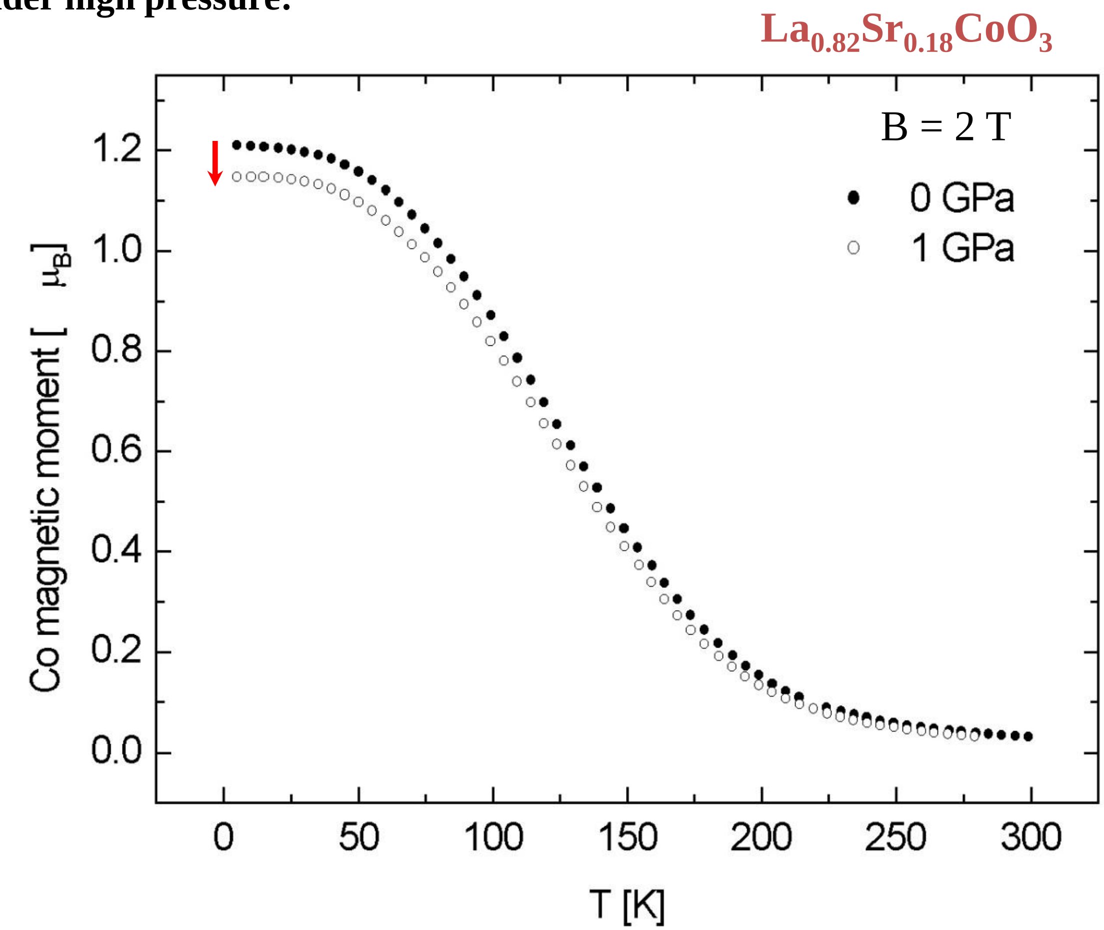

~ 60 mm
PTFE cap
Upper locknut
Cell body
Be-Cu Piston and Be-Cu sealing ring
Be-Cu plug
Cu sealing ring
Lower locknut

Experimental support for pressure-induced HS/IS-LS transition

Magnetization under high pressure:



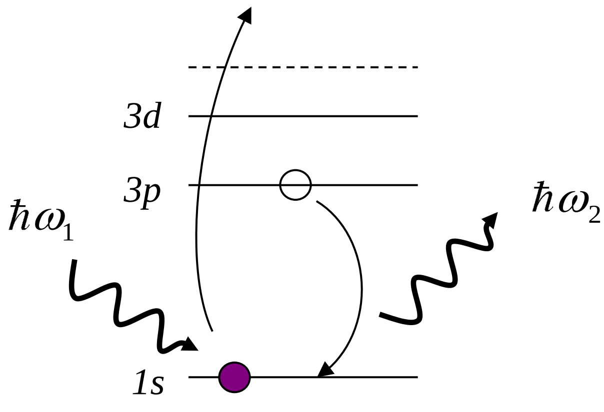
Decrease of μ_{Co} from 1.11(1) μ_B at ambient pressure to 1.05(1) μ_B at 1 GPa, i.e. 5.4 % or at least 30 % at 5.7GPa.

Microscopic evidence for pressure-induced IS-LS transition

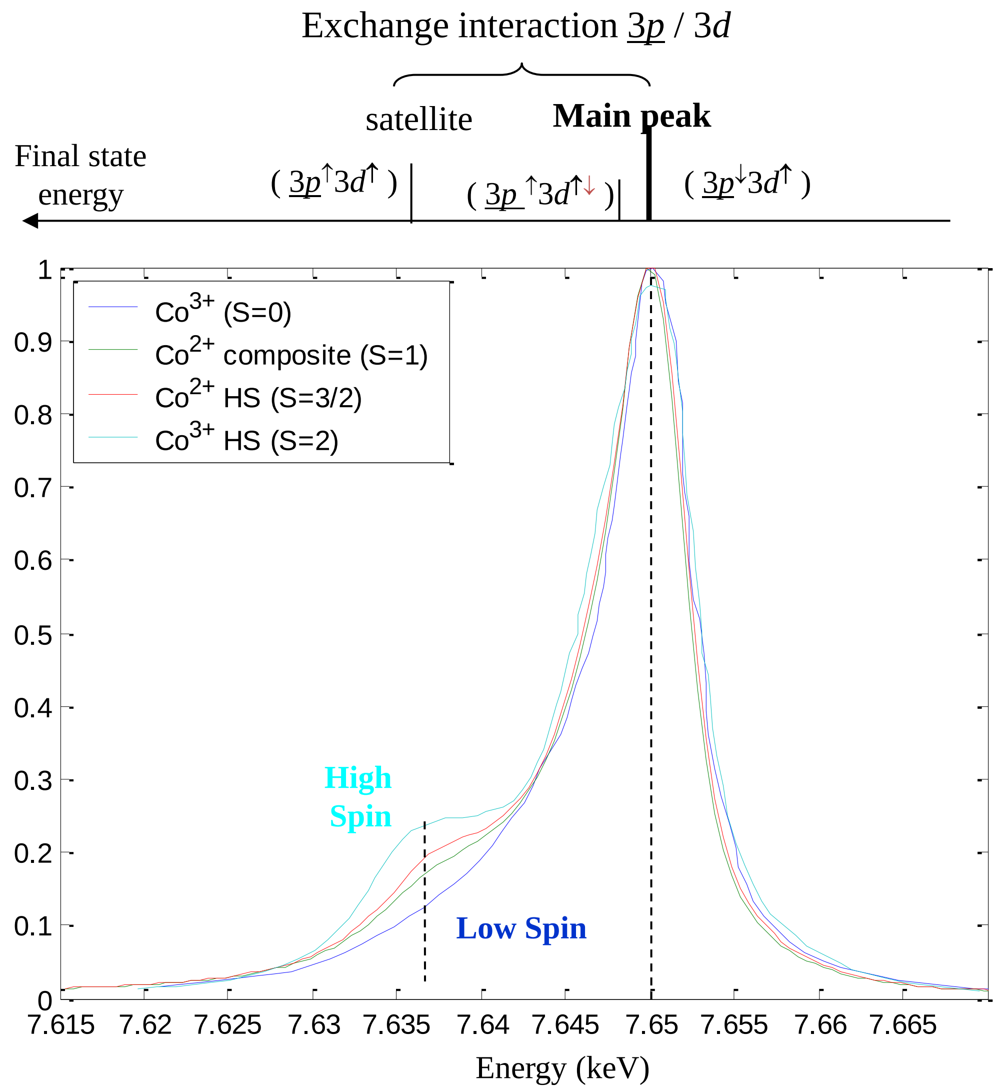
x-ray emission spectroscopy (XES) at the K β line

ESRF, ID16

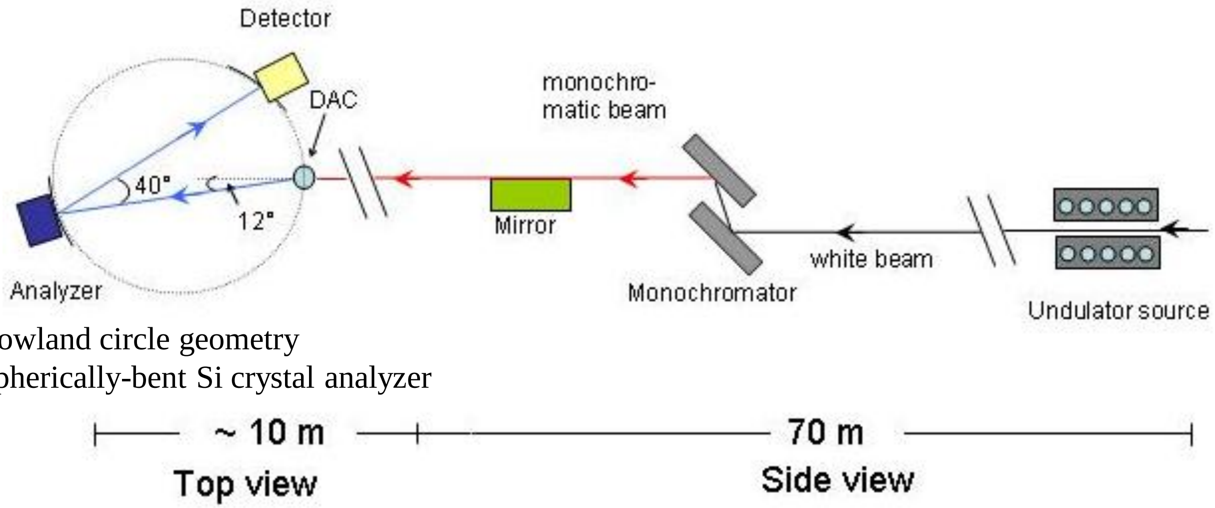
Kβ emission process



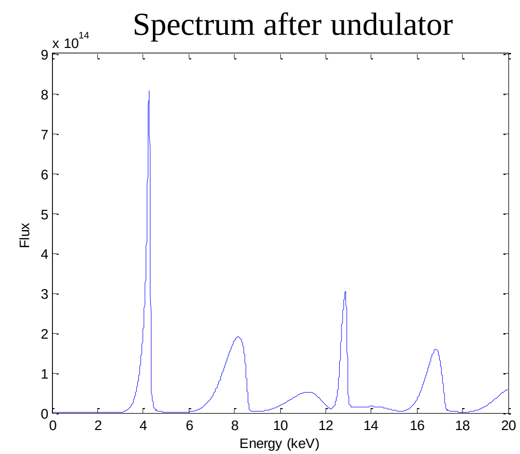
→ extremely sensitive to the spin state of the transition metal atom

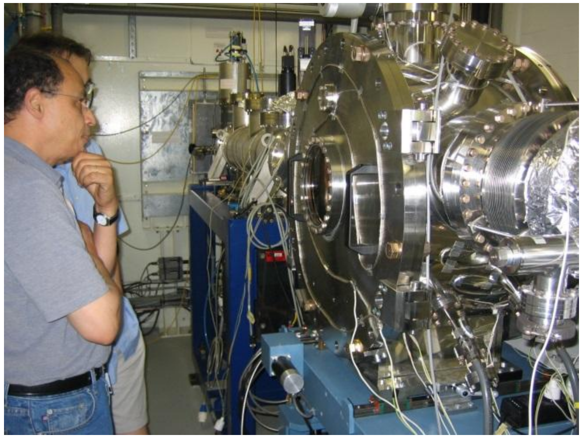


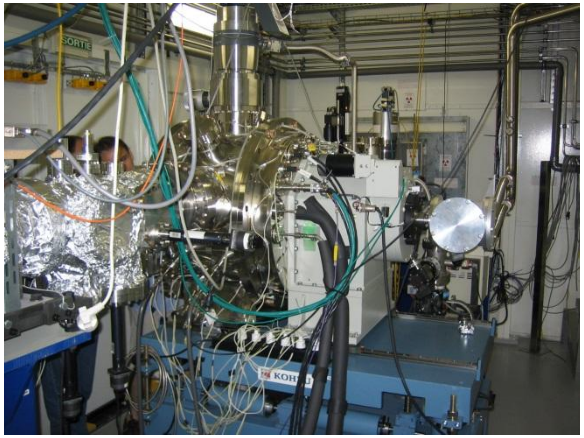
Experimental setup at beamline ID16 at ESRF

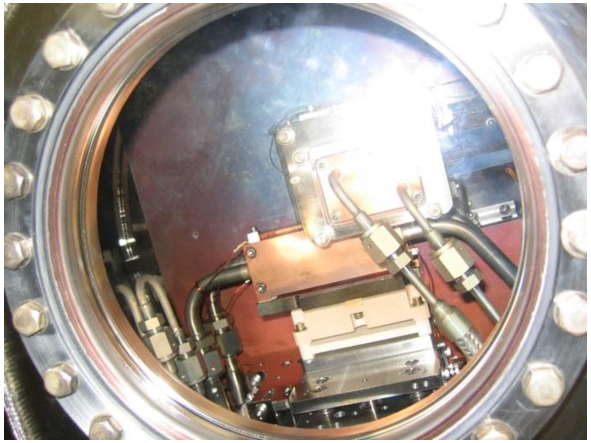


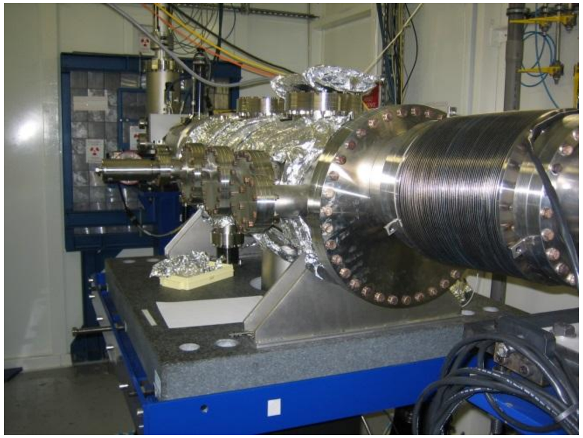
Rowland circle geometry
Spherically-bent Si crystal analyzer

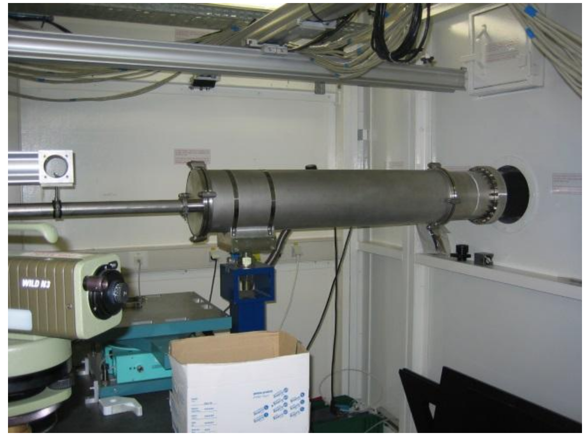


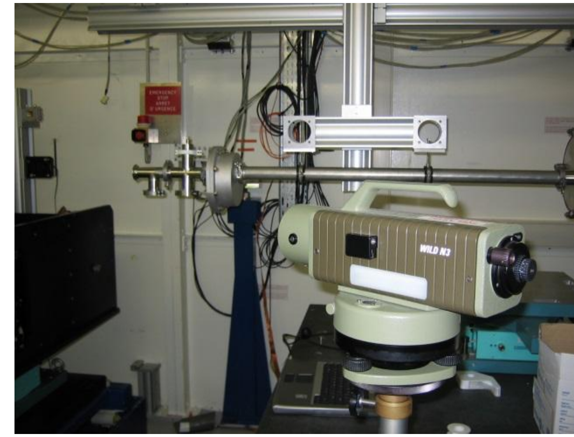




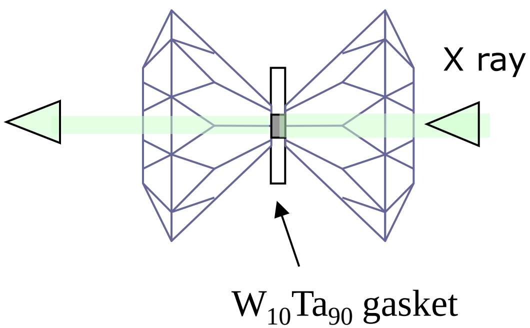


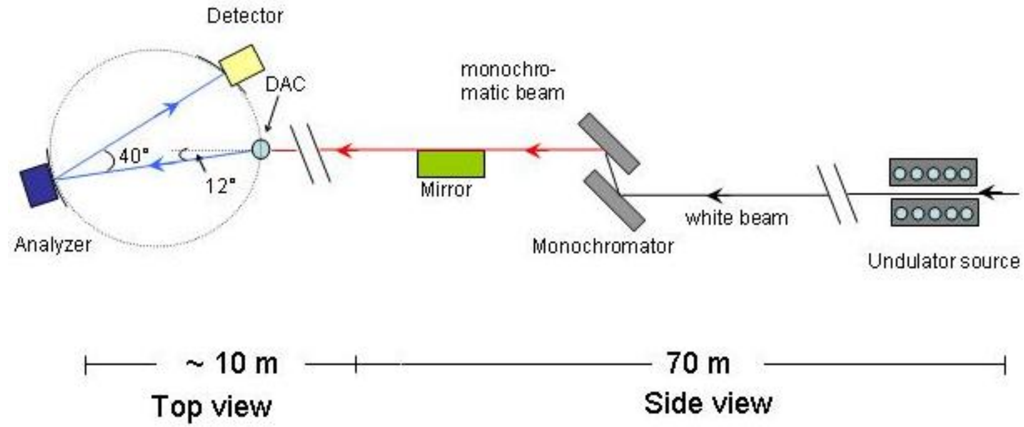


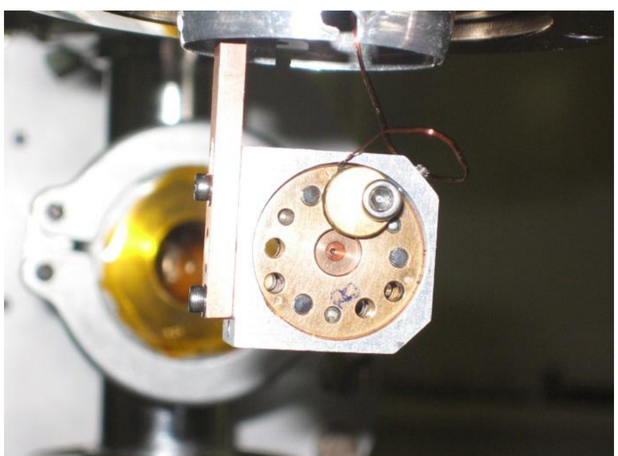


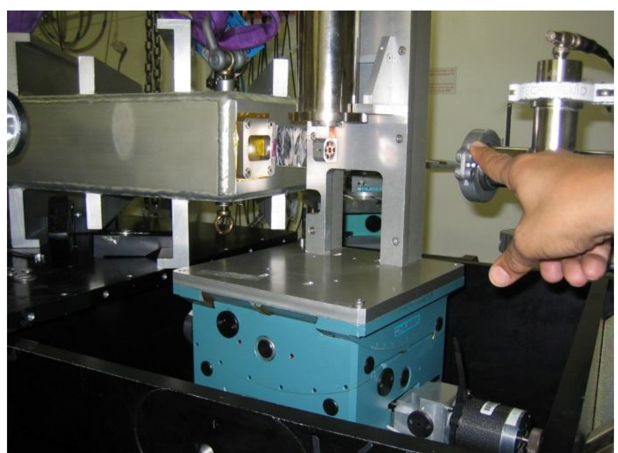


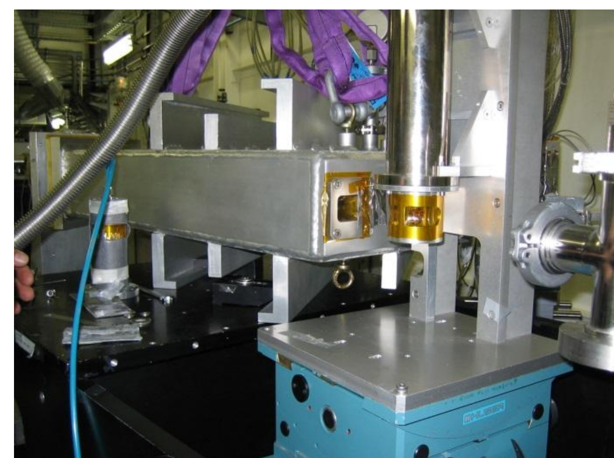
Transmission geometry





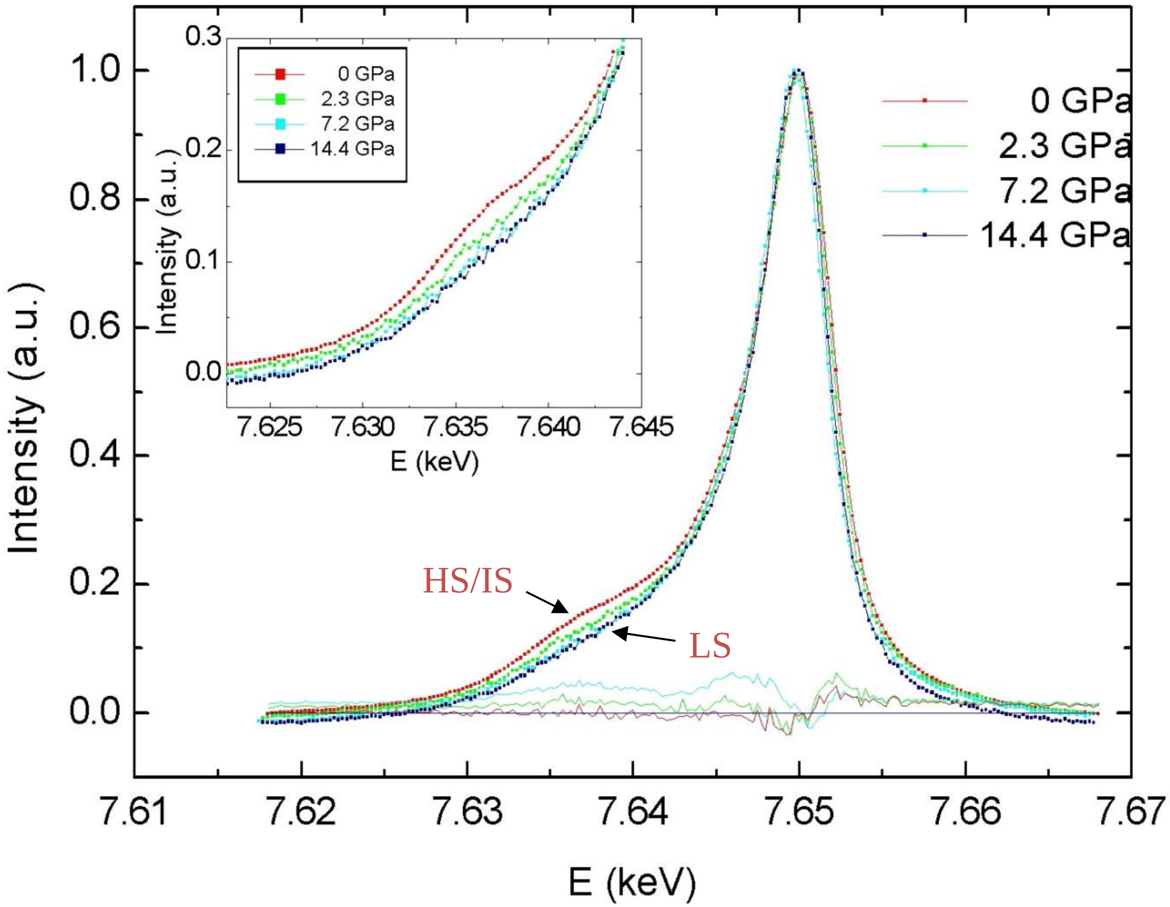


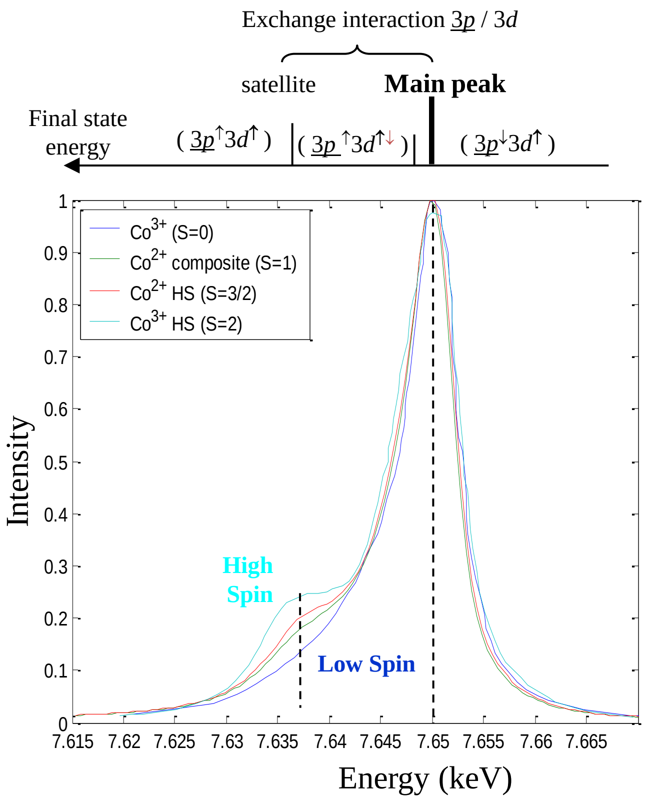




Microscopic evidence for a pressure-induced spin-state transition

Kβ x-ray emission spectroscopy of $La_{1-x}Sr_xCoO_3$, x=18% @T=300K





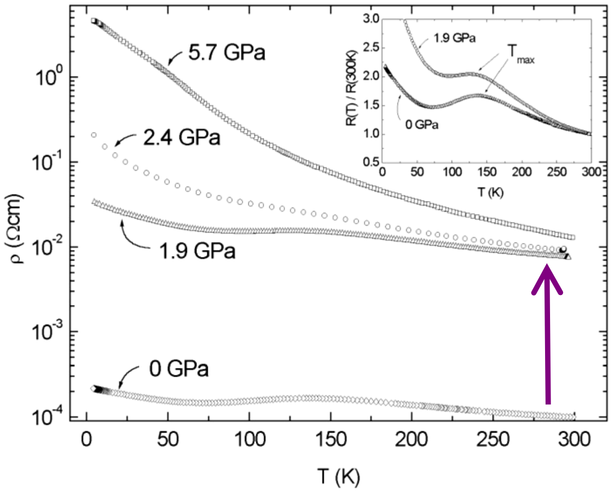
R. Lengsdorf, et al., PRB (2007)

→ Suppression of satellite peak with increasing pressure

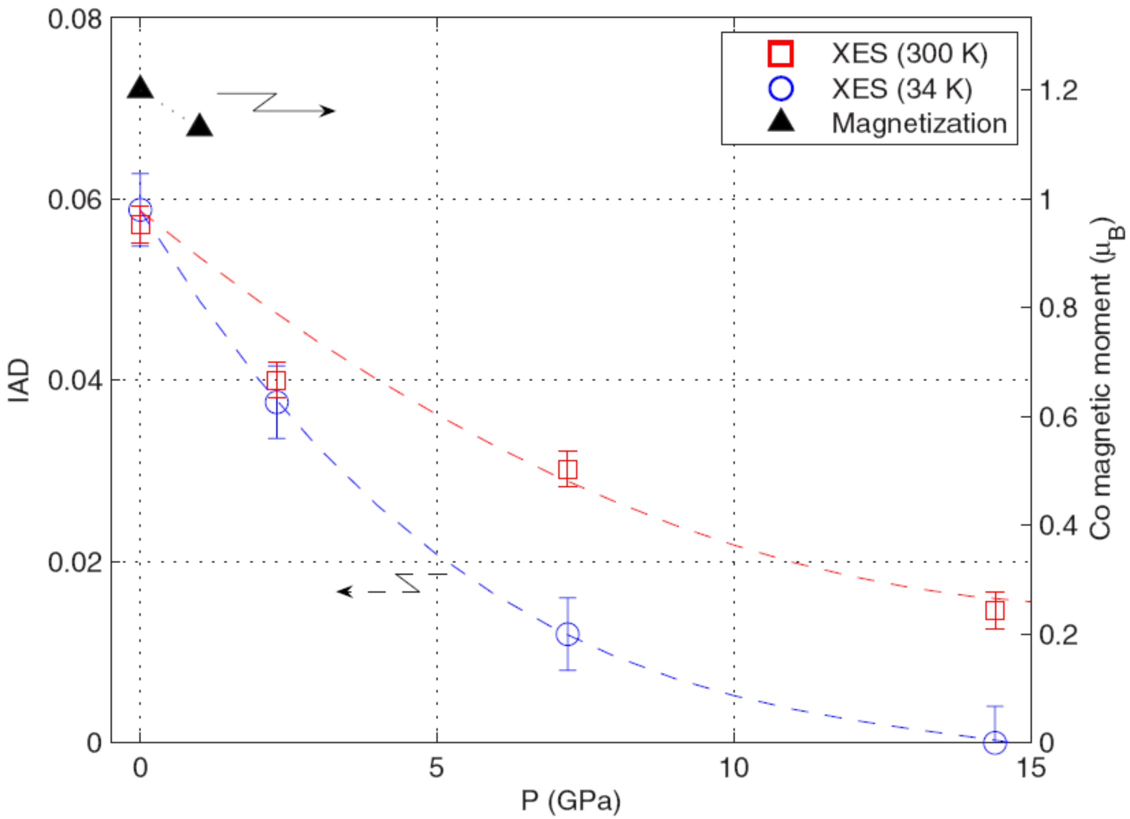
→ gradual HS/IS → LS transition

Microscopic evidence for a pressure-induced spin-state transition

to remind:



integrated absolute difference



R. Lengsdorf, et al., PRB (2007)

→ gradual spin state transition from HS/IS to LS state with pressure