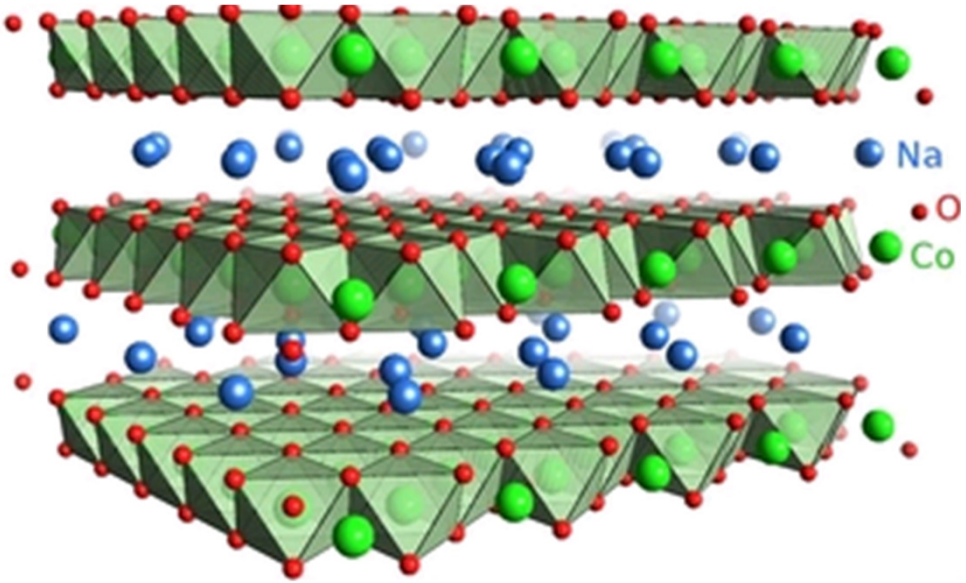
D'où viennent les corrélations dans les cobaltates ?

Véronique Brouet
Laboratoire de Physique des Solides d'Orsay



Outline

- Structure and electronic properties of CoO_2 slabs filled with *x* electrons
  - Superconductivity, magnetism and high thermoelectric power
  - Na and misfit cobaltates

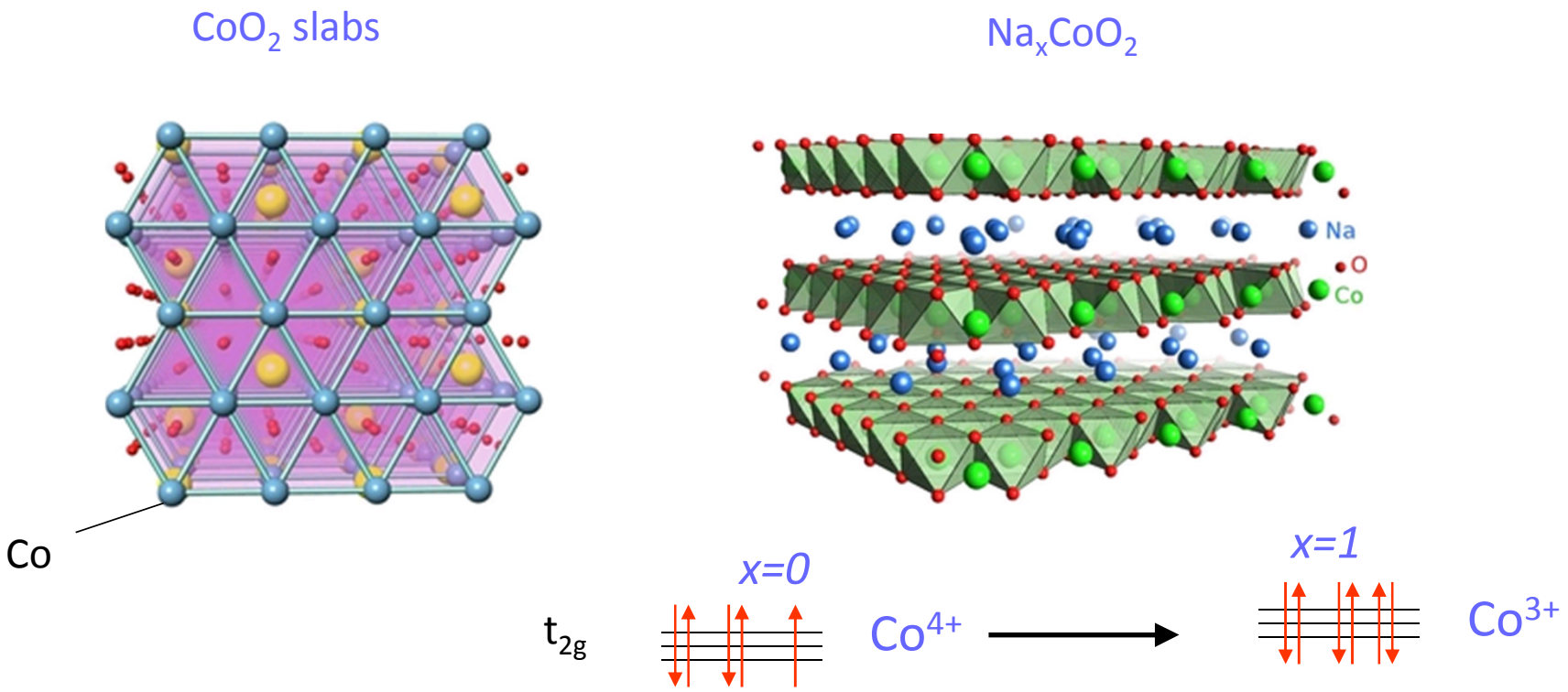
- What is the strength of electronic correlations in these materials ?
  - Would CoO_2 be a Mott insulator ?
  - Unusual signs of strong correlations near the band insulator

    CW susceptibilities, high effective masses, ARPES lineshapes

- Where do electronic correlations come from ?
  - Are they associated to peculiar electronic orders

    and/or coupling between different degrees of freedom

Cobaltates : triangular planes of Co filled by a variable number of electrons

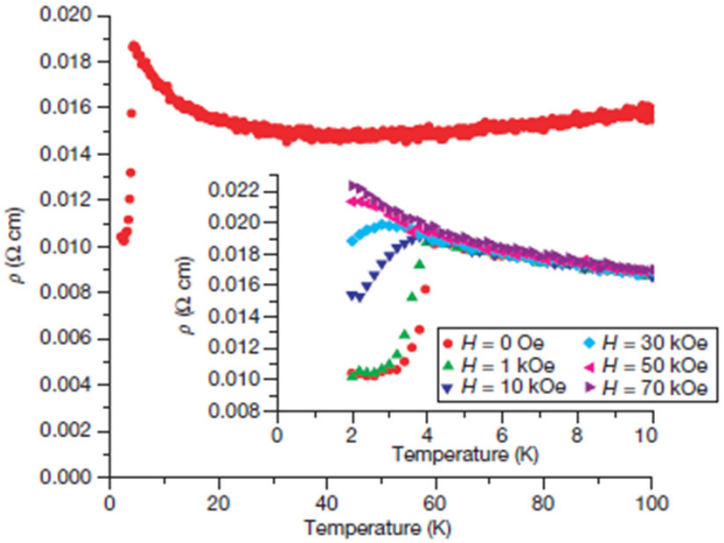


- Metallic phases with charge, spin, orbital degrees of freedom…
  How do they interact ? Does Na plays a role ?
- Used in batteries for a long time (Li_xCoO_2)

2003 : discovery of some unusual properties

Superconductivity in two-dimensional CoO_2 layers

Kazunori Takada*‡, Hiroya Sakurai†, Eiji Takayama-Muromachi†, Fujio Izumi*, Ruben A. Dilanian* & Takayoshi Sasaki*‡

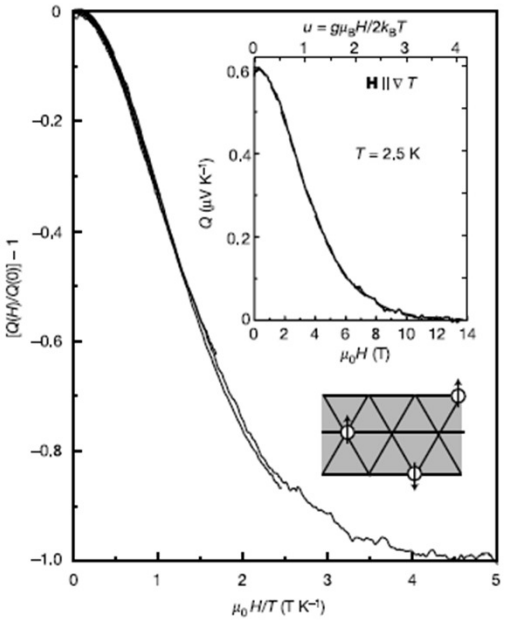


Superconductivity at 4K in $Na_{0,35}CoO_2 \cdot yH_2O$

Takada et al., Nature march 2003

Spin entropy as the likely source of enhanced thermopower in $Na_xCo_2O_4$

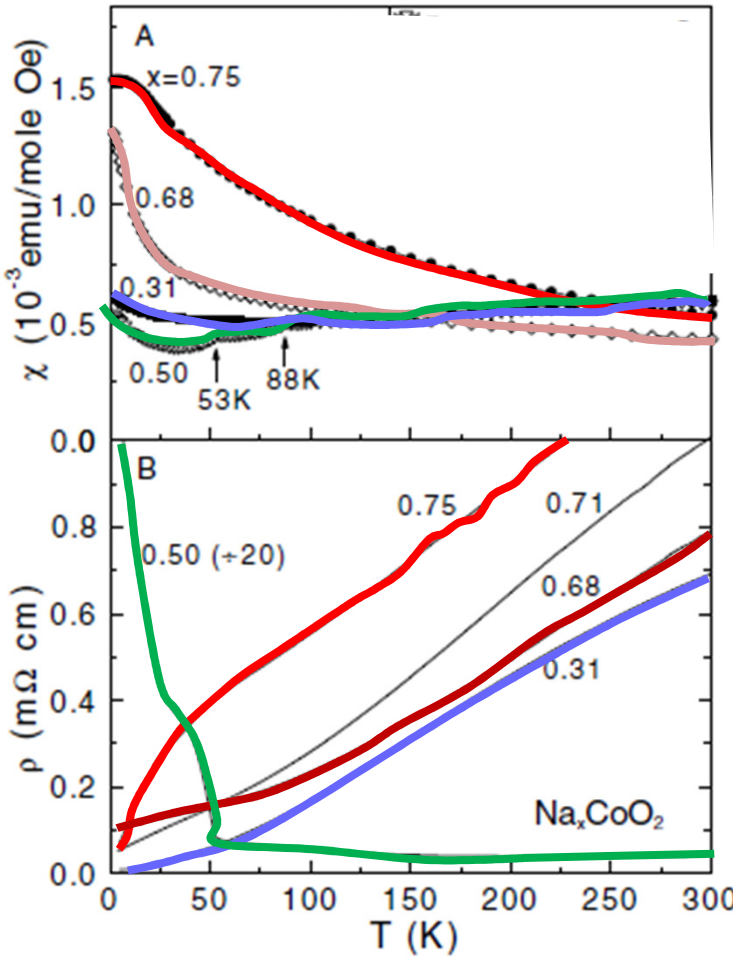
Yayu Wang*, Nyrissa S. Rogado†, R. J. Cava†‡ & N. P. Ong*‡

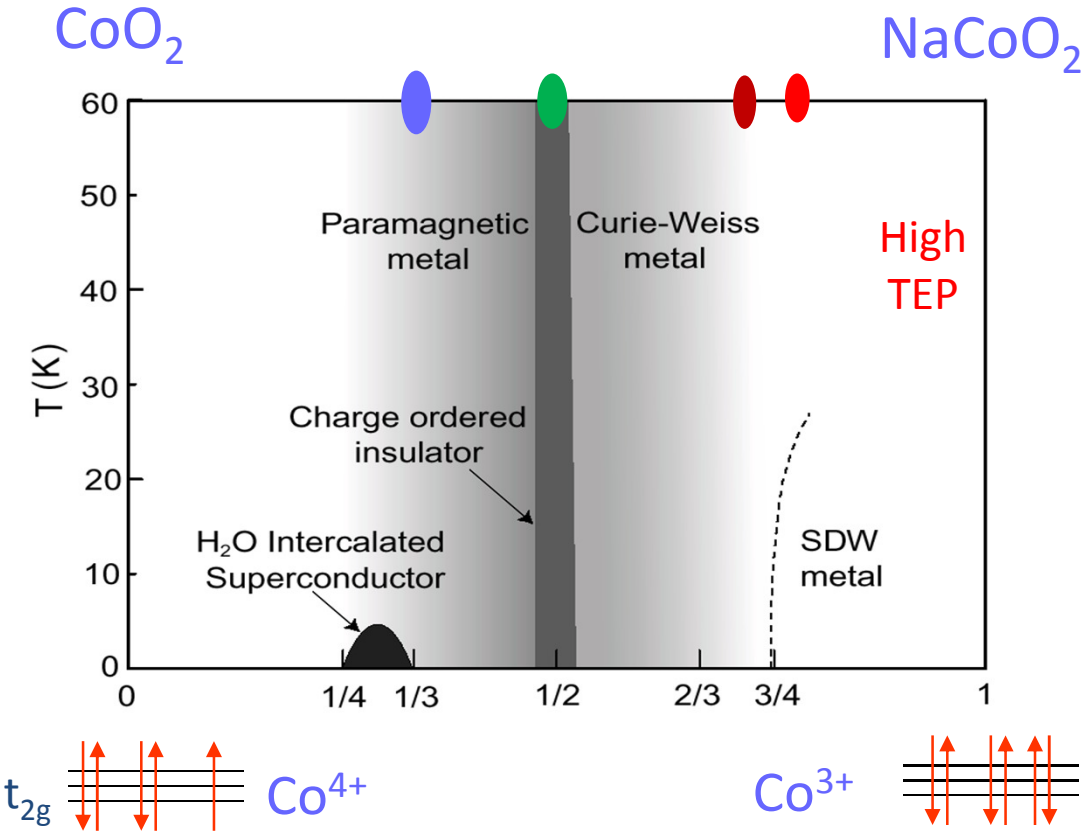


High thermoelectric power of magnetic origin ?

Wang et al., Nature may 2003

Phase diagram of Na_xCoO_2

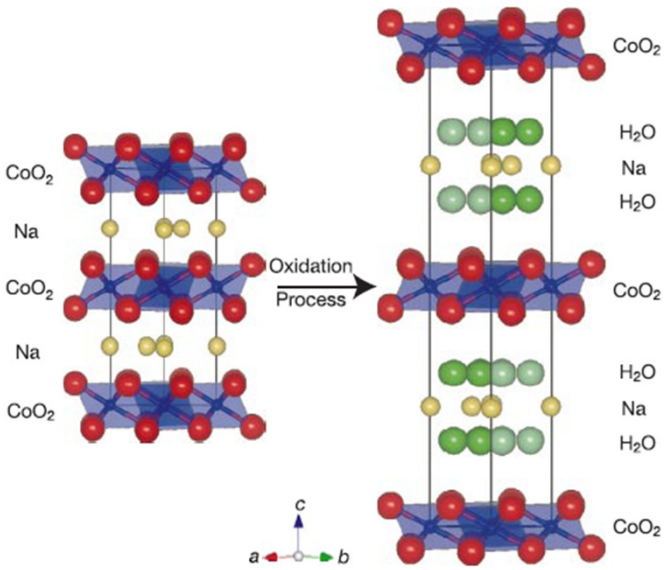




Foo *et al.*, PRL **92**, 247001 (04)

⇒ *Superconductivity, magnetism, metal-insulator transition, high TEP*

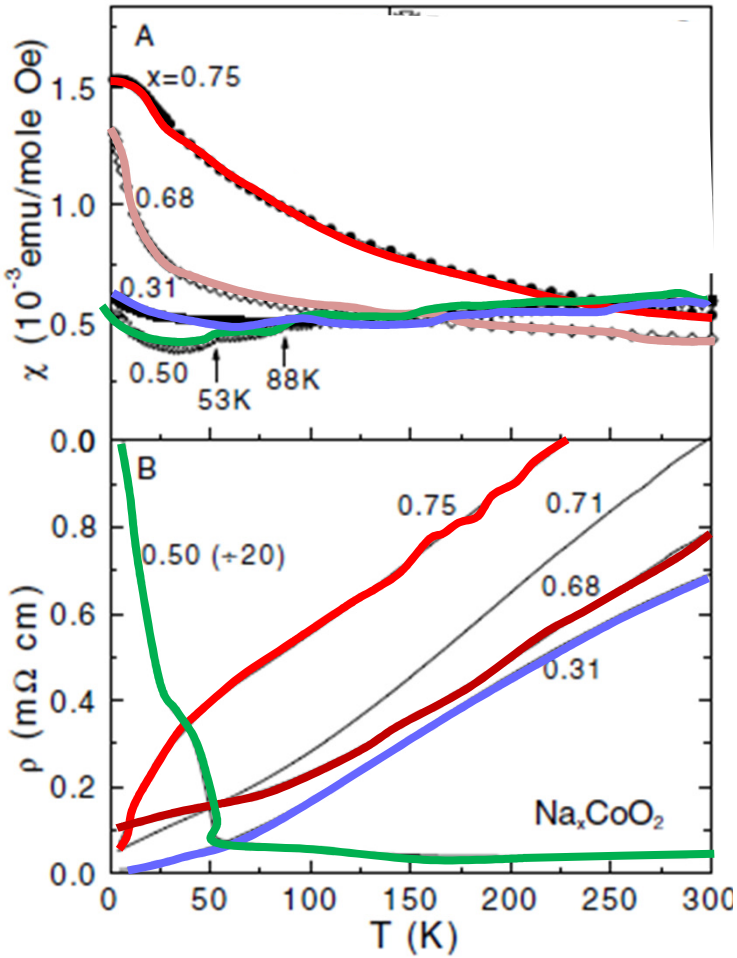
Superconductivity remains confined to $Na_{0,35}CoO_2 \cdot yH_2O$

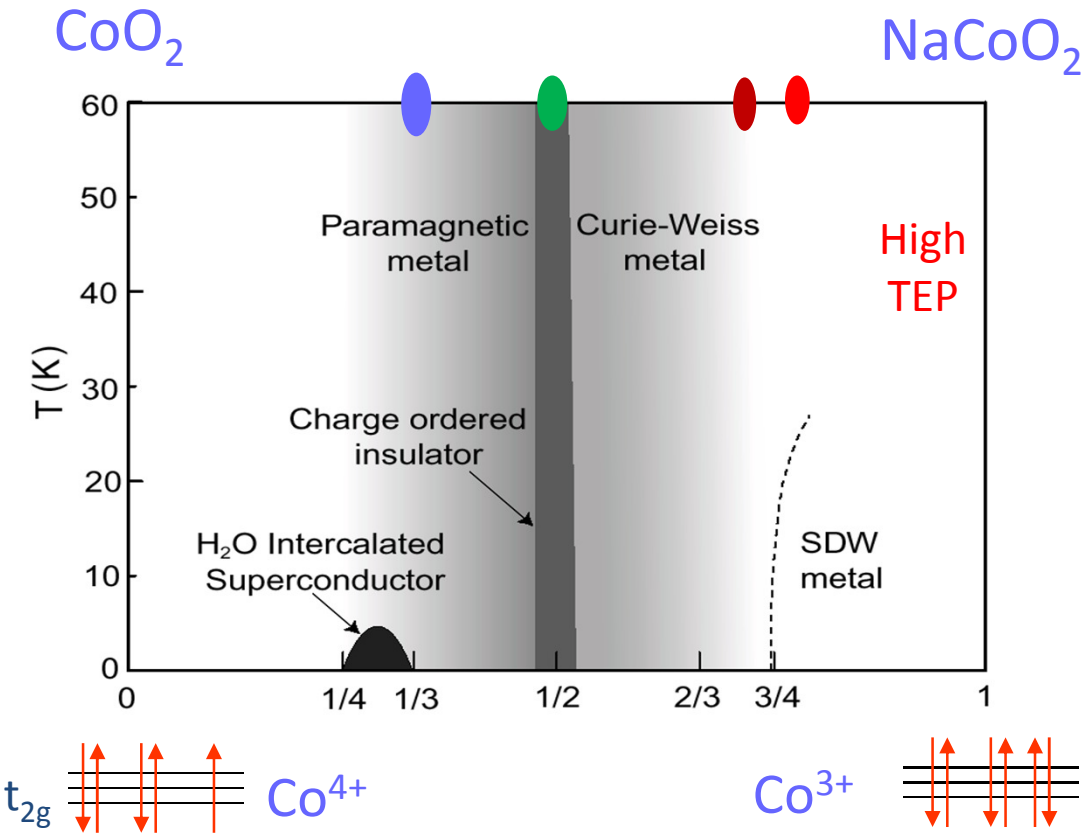


Why does one have to add water to get superconductivity ??

- Is it a strongly correlated superconductor, like cuprates ?
- Frustration on the triangular lattice could allow exotic symmetries (e.g. triplet pairing).
- Experimentally, the situation is not clarified between singlet or triplet pairing. The symmetry of the SC gap is also undefined.
- Co is not expected to have a very strong electron-phonon coupling (J.P. Rueff et al., PRB 2006), but 4K is also not so high...

Phase diagram of Na_xCoO_2



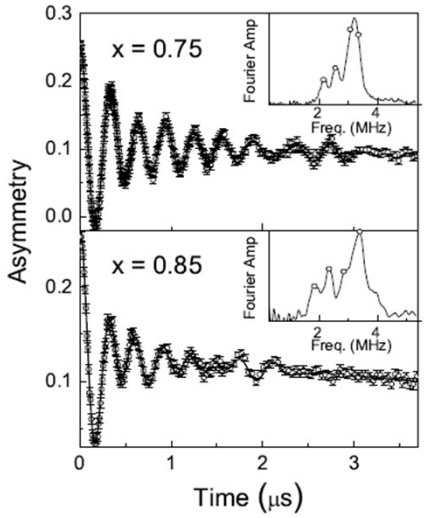


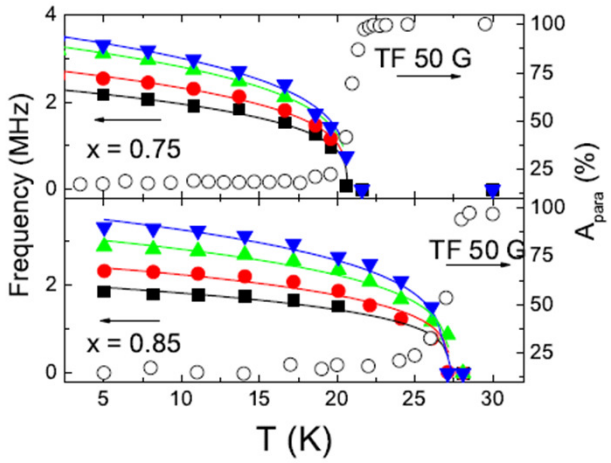
Foo *et al.*, PRL **92**, 247001 (04)

⇒ *Superconductivity, magnetism, metal-insulator transition, high TEP*

Spin Density Waves (x>0,7)

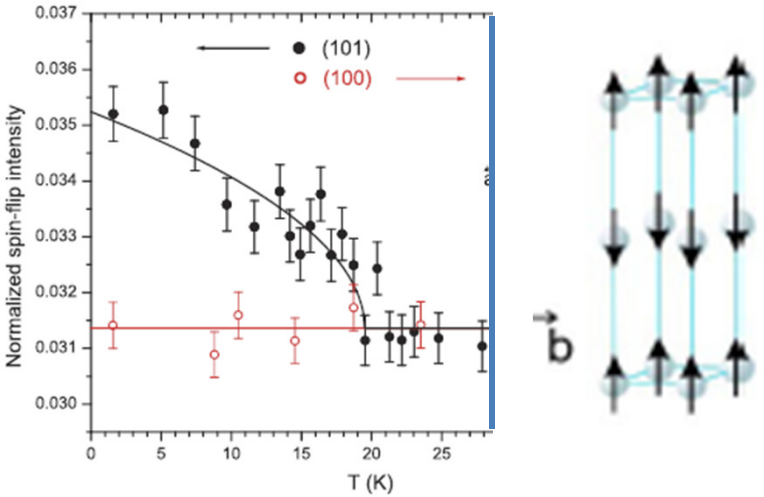
Magnetic phases can be identified by μSR





Mendels et al., PRL 94, 136403 (2005)

Neutrons reveal a ferromagnetic in-plane alignment



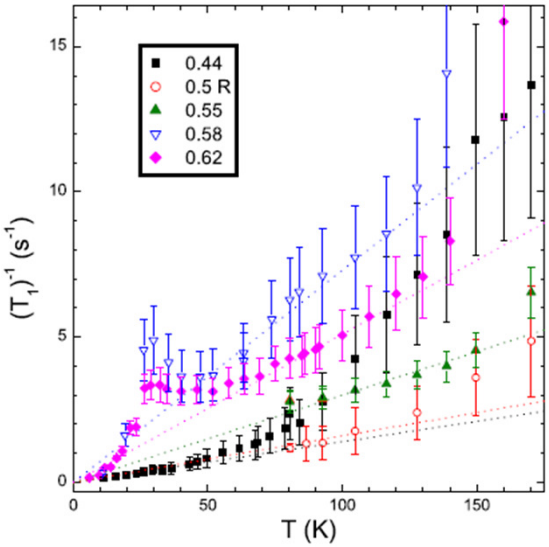
Bairackci et al., PRL **94,** 157205 (2005)

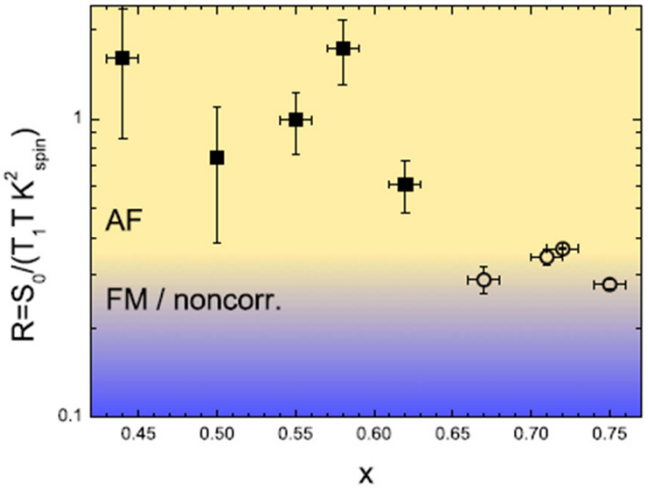
The tendency to itinerant magnetic instabilities can be understood by the high $n(E_F)$.

D.J. Singh, PRB 61, 13397 (2000)

Transition from ferromagnetic to antiferromagnetic correlations as a function of x

From NMR « Korringa ratio »





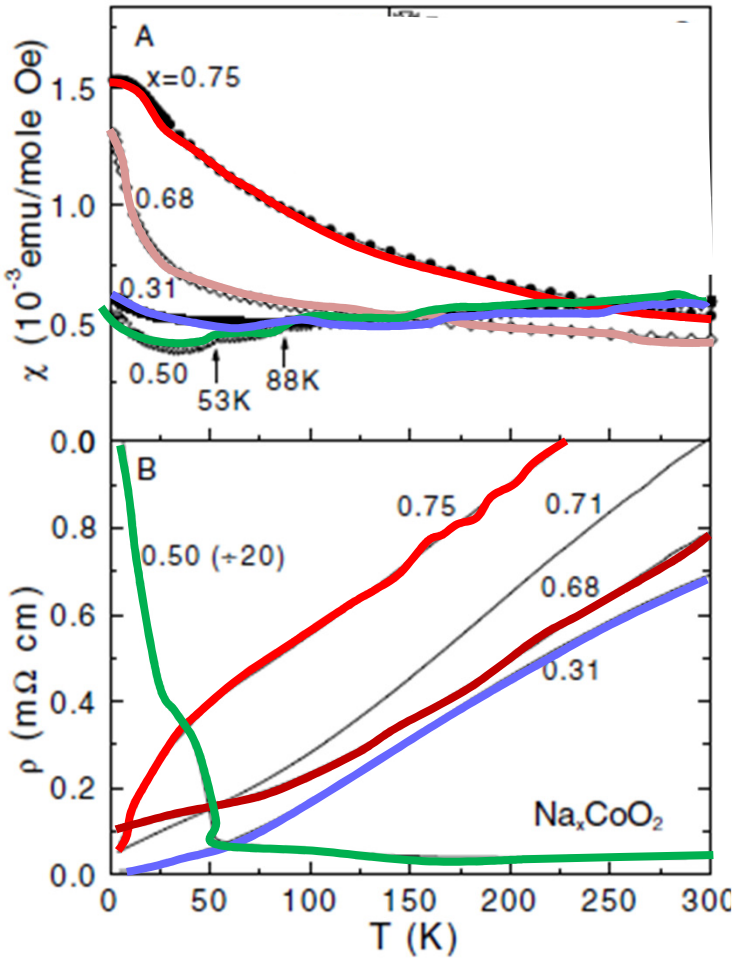
G. Lang et al., PRB 78, 155116 (2008)

This could be why the susceptibility evolves from « Pauli » to « Curie-Weiss »

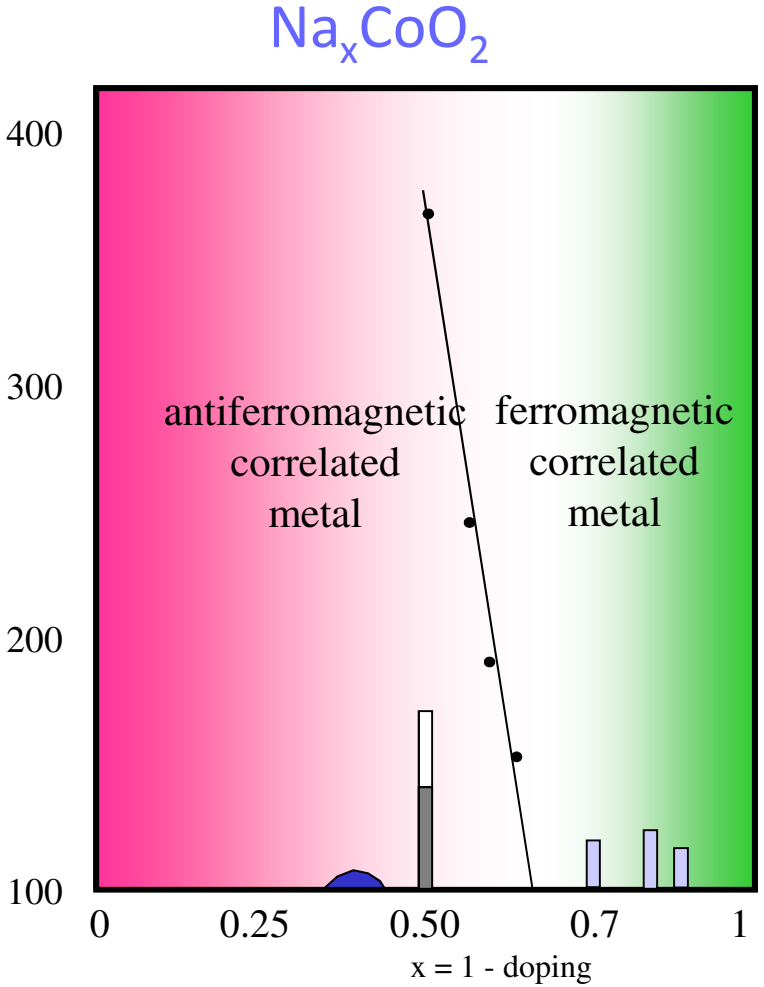
Why is there such an evolution ?

- Magnetic coupling between nearest neighbors results from a delicate balance between different terms (Landron and Lepetit, PRB 2006).
- Fermi Surface property with new hole band appearing around Γ at high *x* ? Okamoto, PRB 2010

Phase diagram of Na_xCoO_2



Foo *et al.*, PRL **92**, 247001 (04)

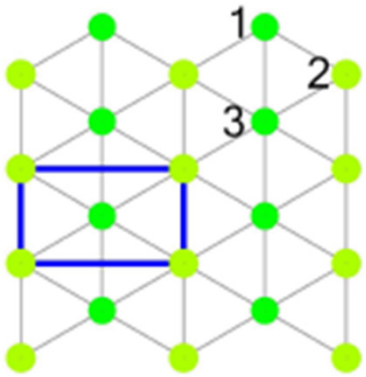


G. Lang et al., PRB 78, 155116 (2008)

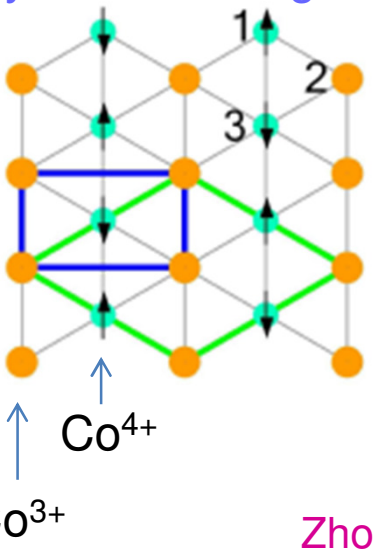
⇒ *Superconductivity, magnetism, metal-insulator transition, high TEP*

The case of $Na_{0,5}CoO_2$

There is a well defined Na order…



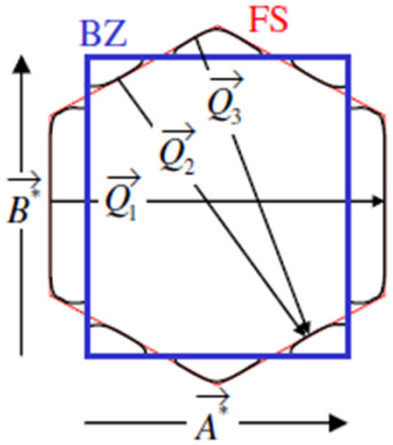
which may induce charge segregation ?



$T_N = 86K$
$T_{MI} = 51K$

Zhou et al., PRL 07

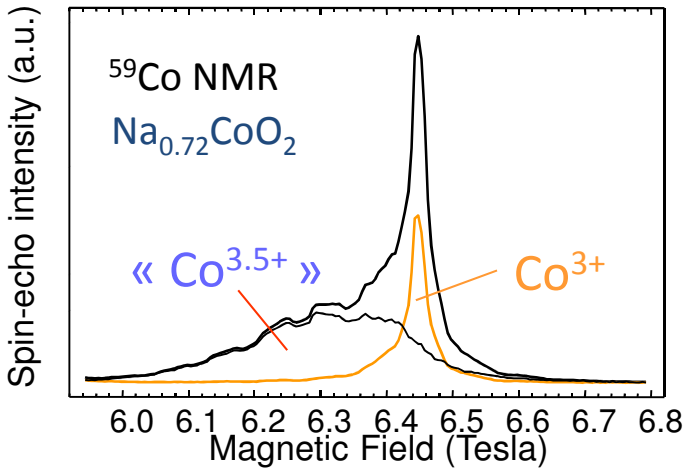
Probably not a true charge segregation, but Na order probably reconstructs the Fermi Surface.



Bobroff et al., PRL 05

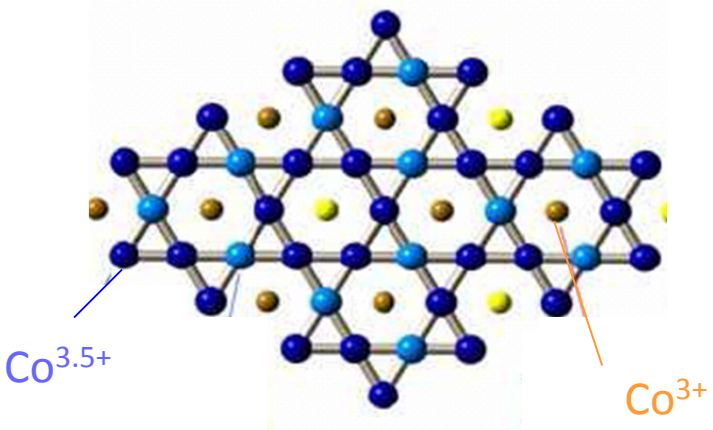
Charge ordering related to Na structures

NMR detects inequivalent Co sites at high *x*



I.R. Mukhamedshin *et al.*, PRL 2005

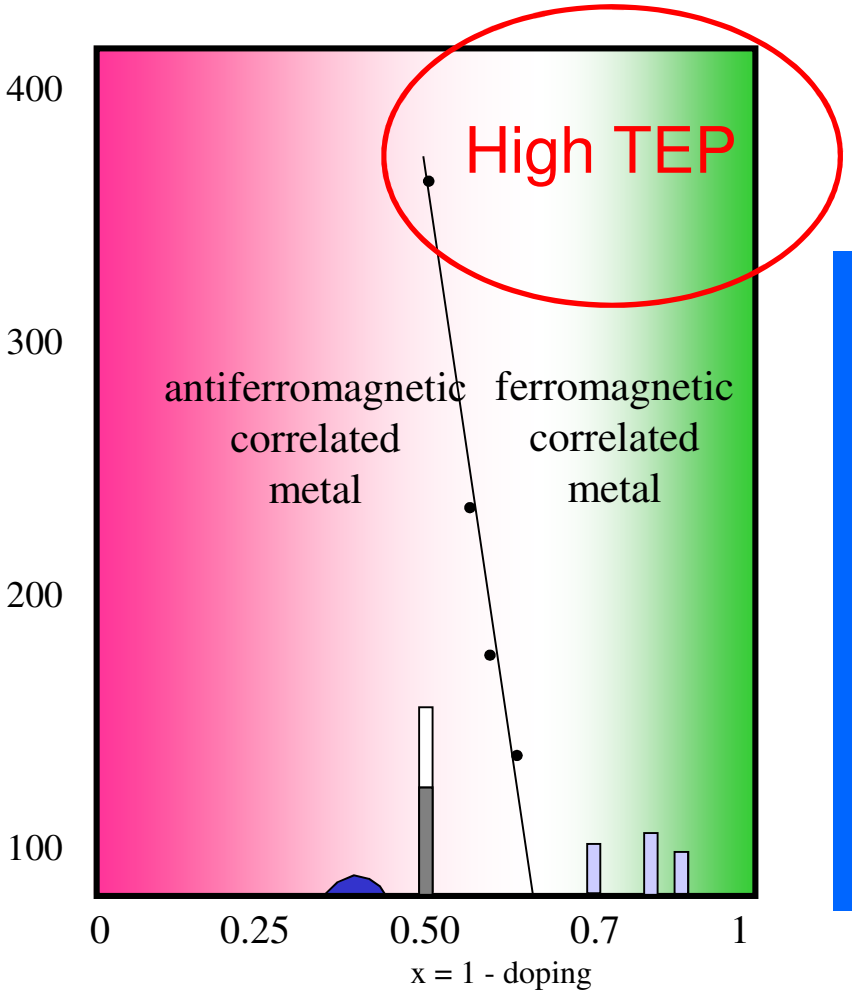
The charge order is induced by Na order

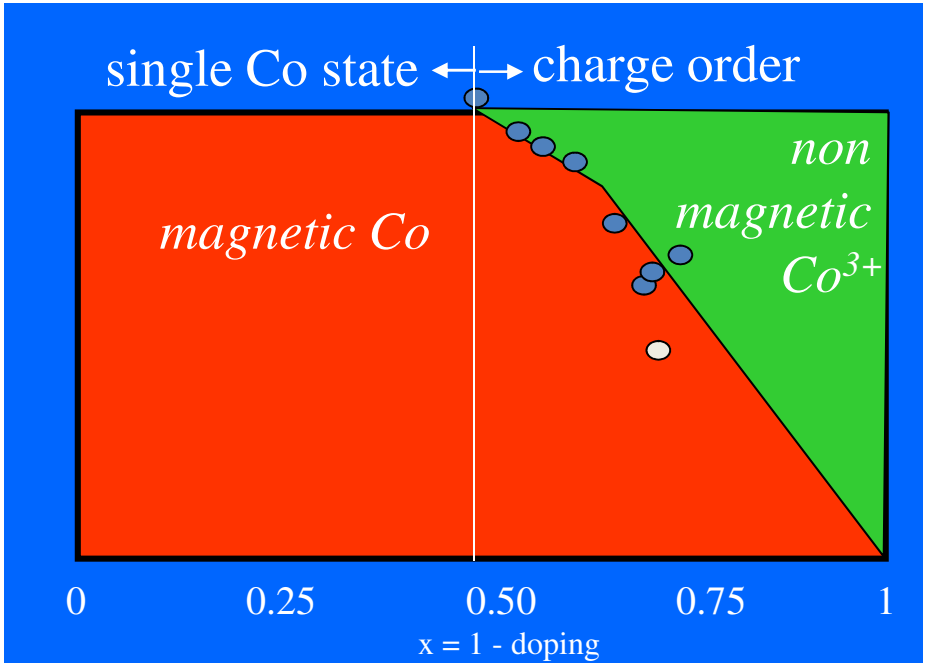


H. Alloul *et al.*, EPL 2009

Consequence for the metallic state of this inhomogeneous charge distribution ?

Many anomalous properties concentrate on thehigh doping side



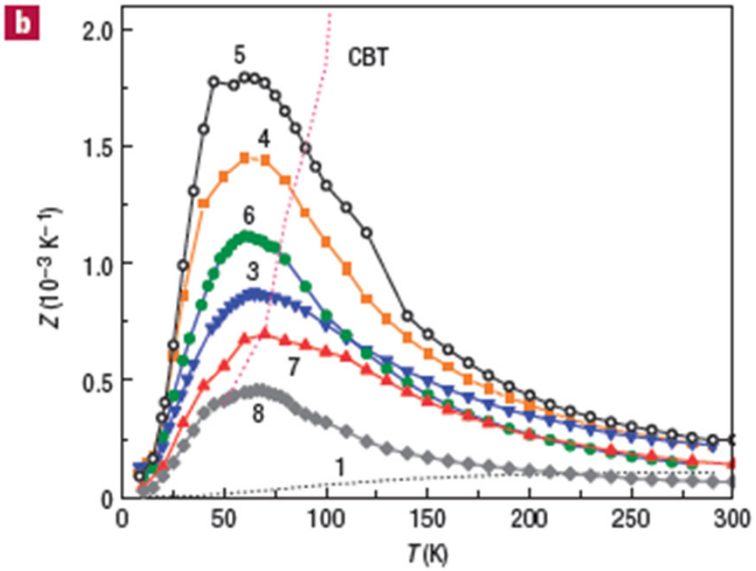


G. Lang et al., PRB 78, 155116 (2008)

Strong thermoelectric power in the « anomalous » doping region

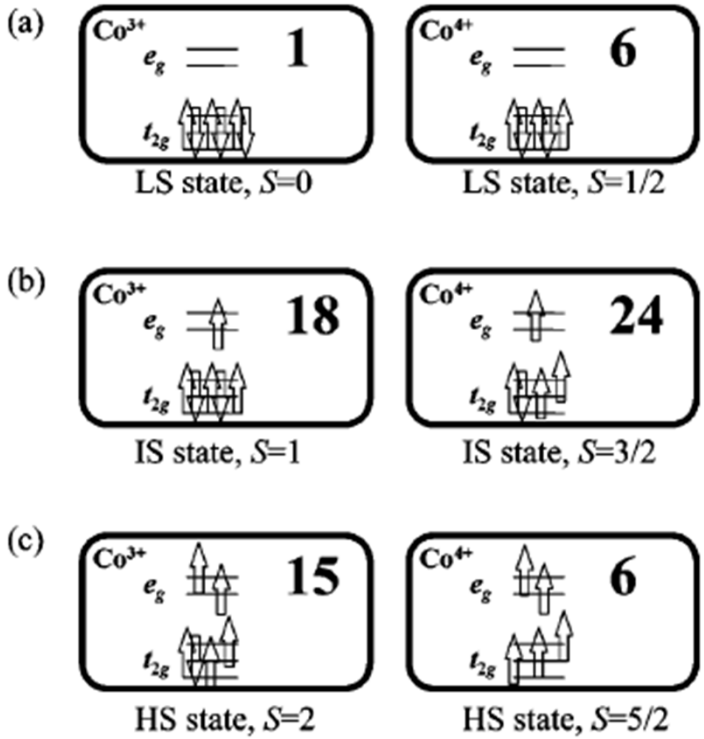
- What is unusual is the coexistence of good metallicity and high thermoelectric power. Entropy is usually quenched in a metal.
- Interesting for applications !

Figure of merit $Z=S/\kappa\rho$ for x=0,71 to 0,96
=> peak at x=0,88



Lee *et al.*, Nature Materials 2006

Different accessible states in « atomic » picture



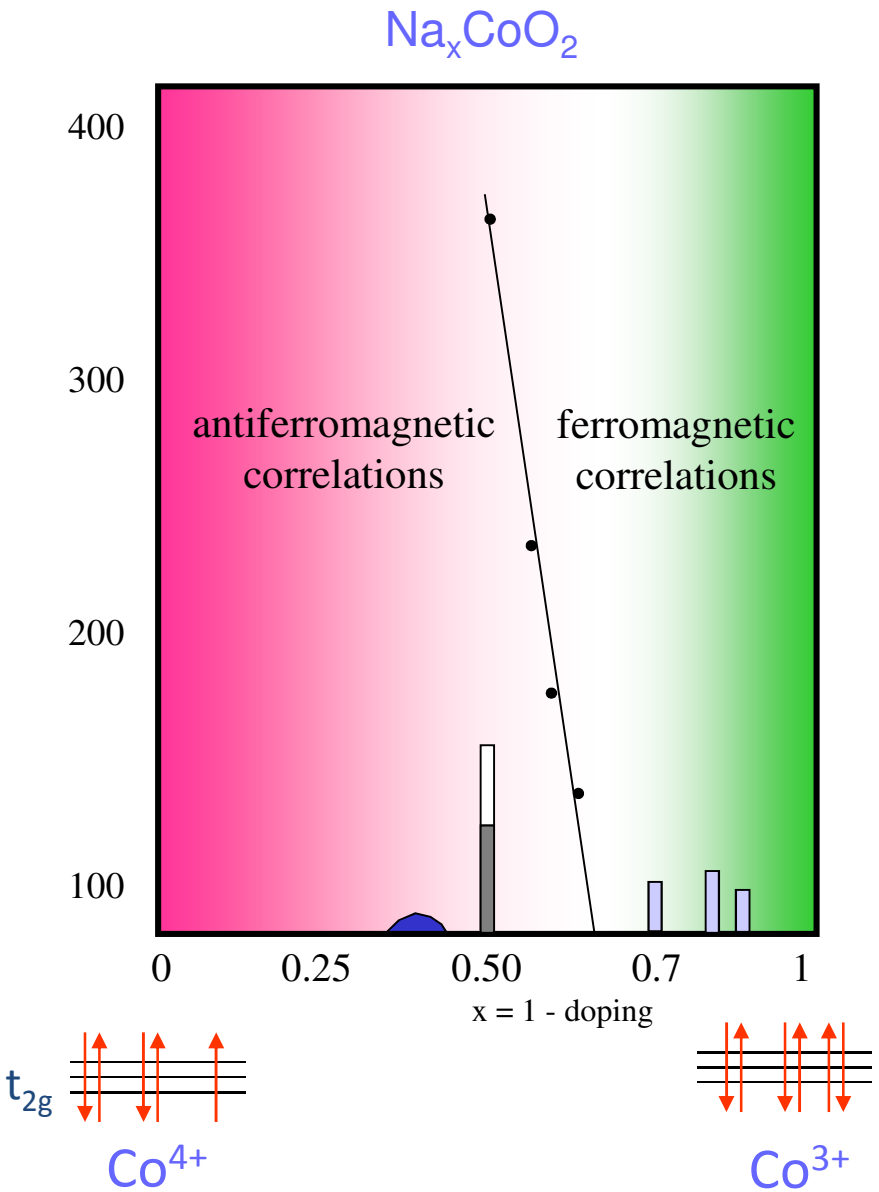
Koshibae *et al.*, PRB 2000

Finally…

- Two quite different doping regions
  - x < 0,6 : Pauli susceptibility, antiferromagnetic correlations
  - x > 0,6 : Curie-Weiss susceptibility, ferromagnetic correlations, magnetic ground states, high thermoelectric power, charge orderings…

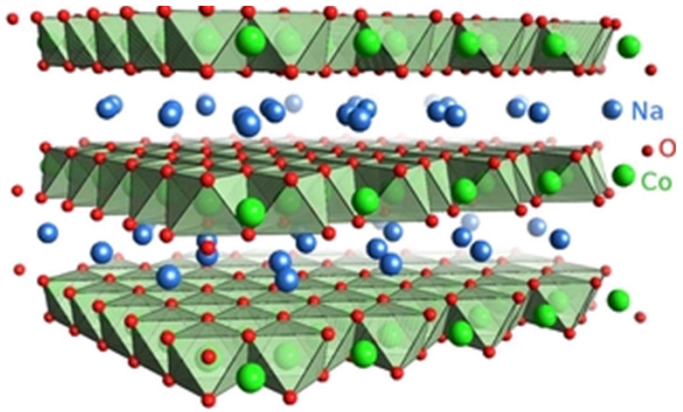
The high doping side « looks » like a correlated metal, while it is not obvious for the low doping side.
This is counter-intuitive ! One would rather expect strong correlations near x=0 (one hole in t_{2g}) !

- *Role of orbital degeneracy ?*
- *Influence of Na orderings (at x=0.5 and at higher x) ?*

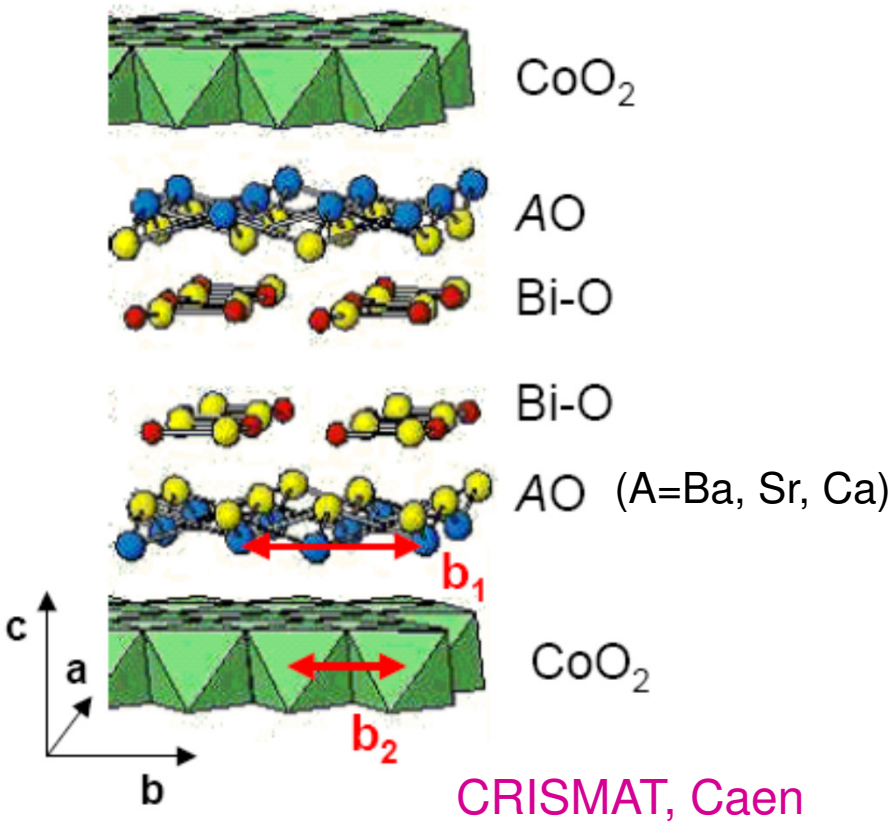


Two families of cobaltates : Na and misfits

Na_xCoO_2



$[Bi_2A_2O_4]\,[CoO_2]_{b1/b2}$

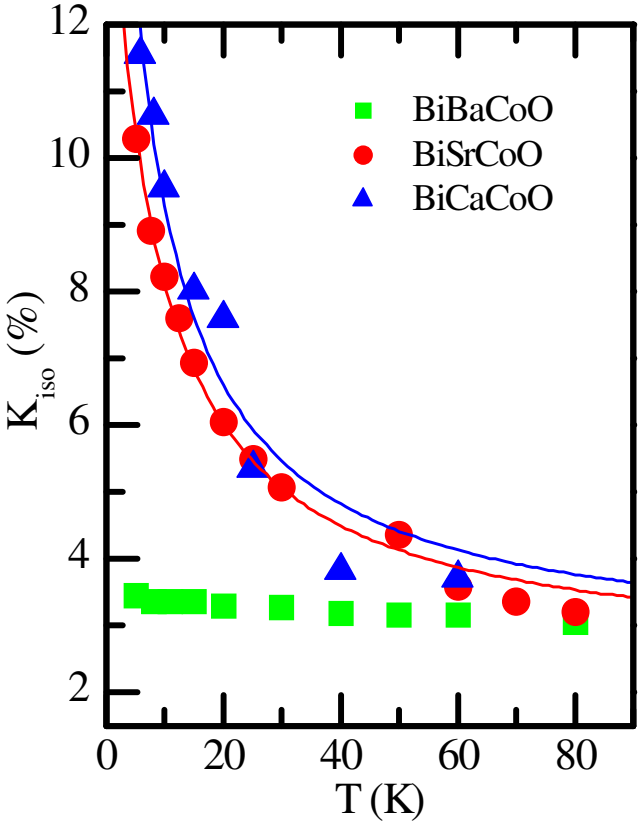


CRISMAT, Caen

- Charge transfer from Rock-Salt planes to CoO_2 planes
- Doping equivalent to x=0.7-0.9
- Different 3D environment

Electronic properties of misfit cobaltates

Pauli to Curie-Weiss susceptibilities

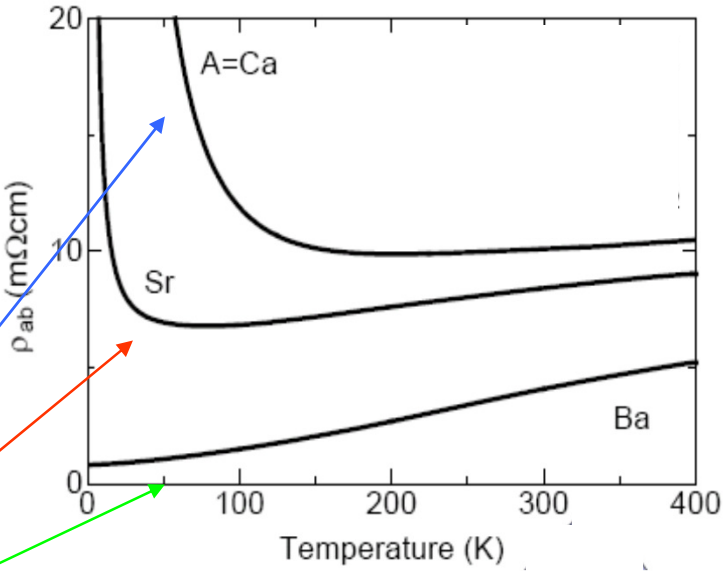


J. Bobroff *et al.* PRB 2007

High TEP values

x=0.85
x=0.75
x=0.7

Resistivity vs Temperature



W. Kobayashi *et al.*

Same magnetic interactions
& different charge order / disorder ?

What is the strength of correlations in this system ?

- Strong Coulomb repulsion on Co (U~4,5eV)
- Narrow electronic bands (W~1eV)

  => Insulators for integer filling ?

Na_xCoO_2 = (1-x) holes in t_{2g}

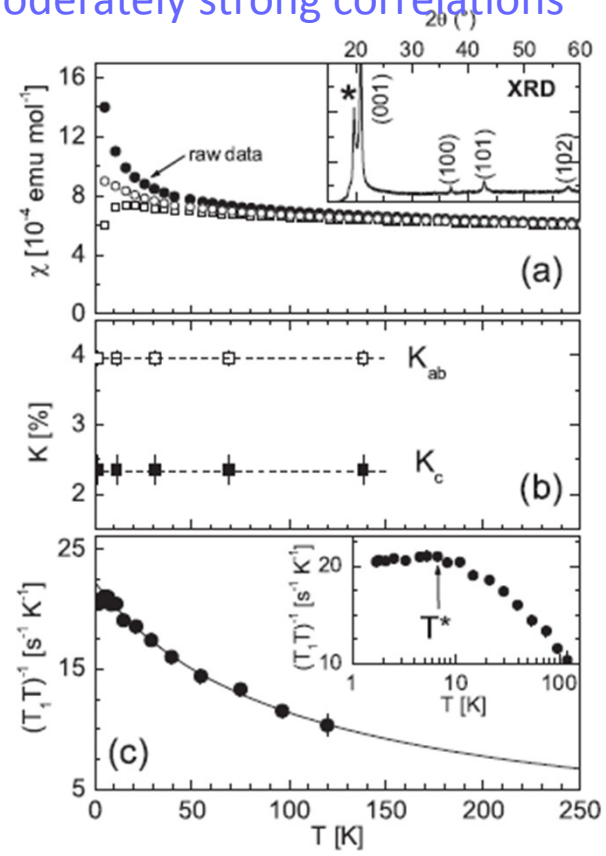
Mott insulator ?

Band insulator

Would CoO_2 be a Mott insulator ?

CoO_2 is difficult to stabilize…

A NMR study finds it metallic, with moderately strong correlations

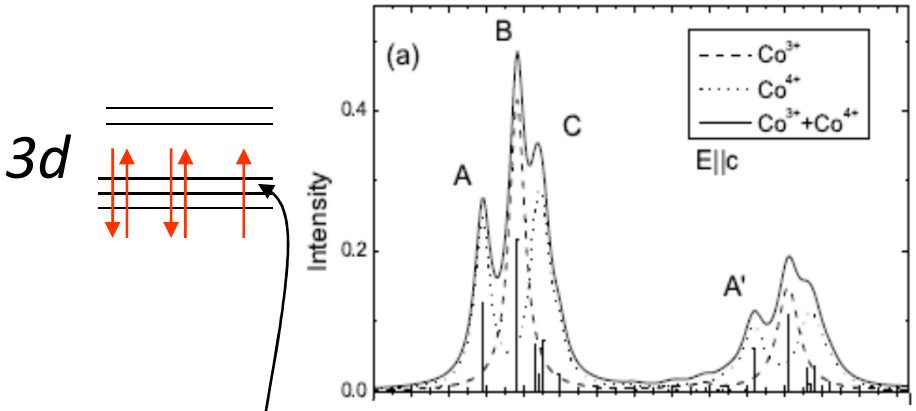


De Vaulx et al., PRL 2007

The U/W ratio at which a MIT is expected will depend on :

- Orbital degeneracy
- Geometry (triangular lattice)
- Strong covalency with oxygen

X-ray absorption measurements evidence a strong covalency with oxygen

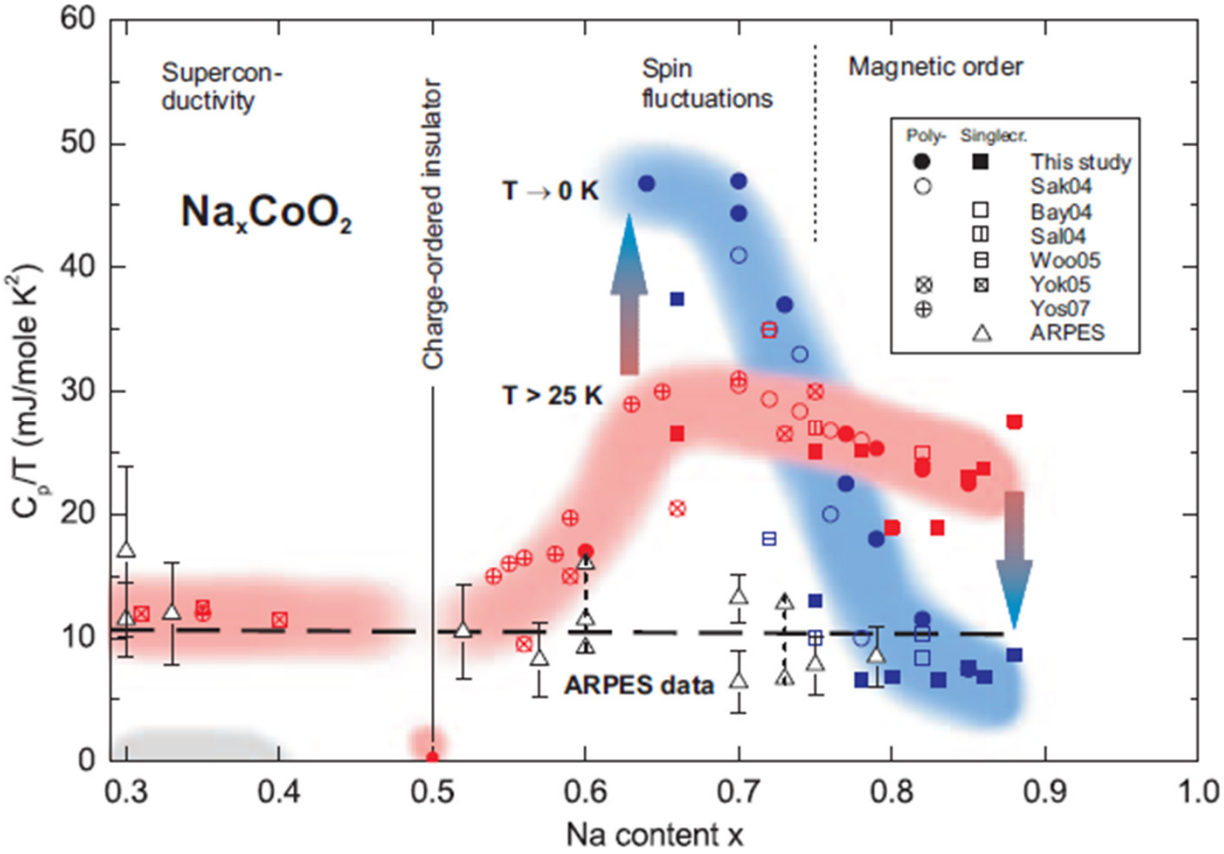


Co^{3+} Groundstate		Co^{4+} Groundstate	
d^6	0.30	d^5	0.14
d^7L^1	0.47	d^6L^1	0.40
d^8L^2	0.20	d^7L^2	0.35
d^9L^3	0.03	d^8L^3	0.10
$d^{10}L^4$	0.00	d^9L^4	0.01
		$d^{10}L^5$	0.00

Kroll et al., PRB 2007

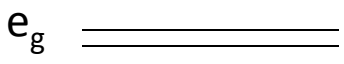
Evolution of the correlation strength

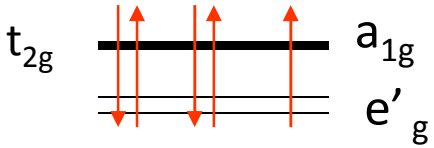
Effective mass obtained from specific heat measurements



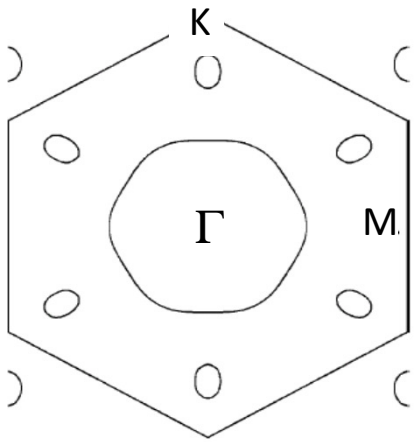
Schulze *et al.*, PRB **78**, 205101 (2008)

Band structure of a CoO_2 plane (from LDA)



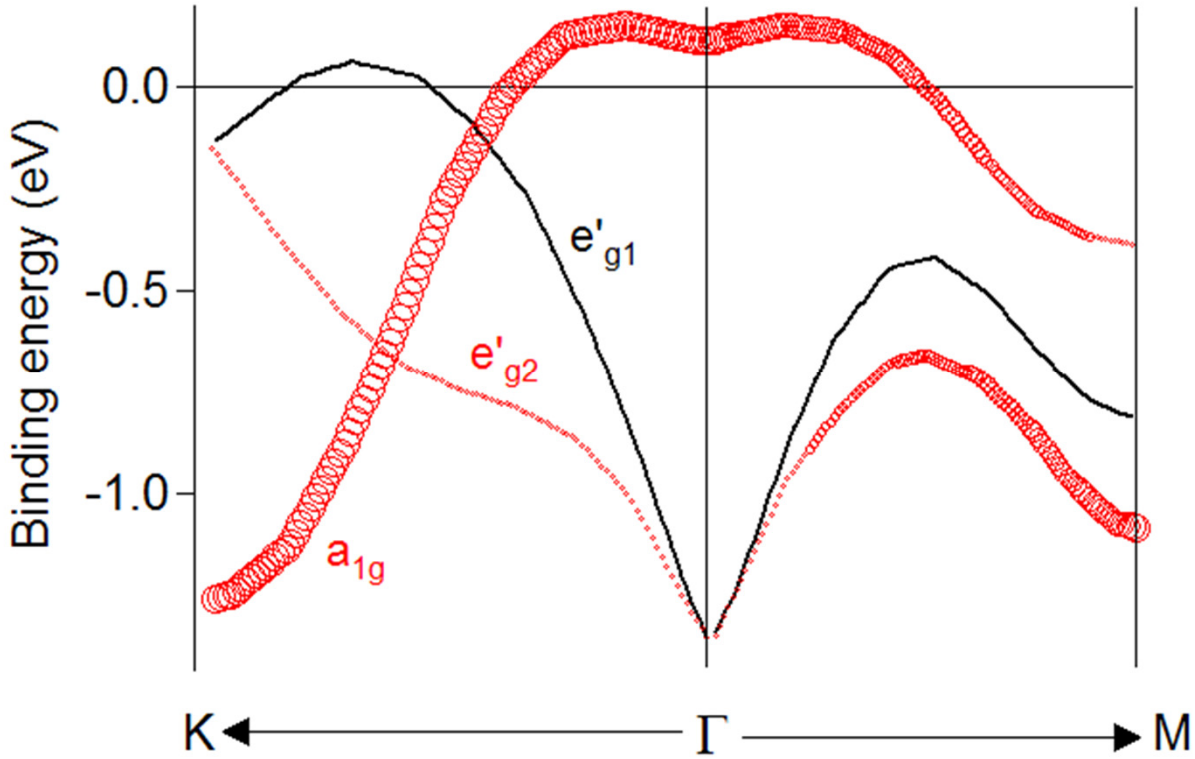


Co^{4+} + *x* electrons
on a triangular lattice



Surface de Fermi

$Na_{0.5}CoO_2$

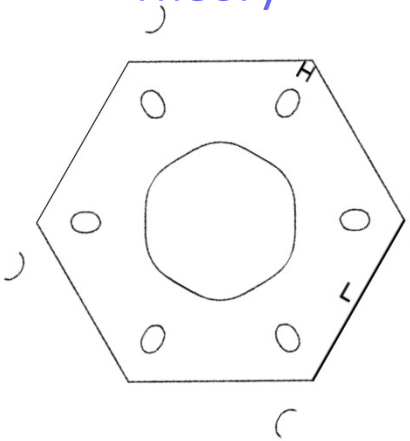


Singh *et al.*, PRB 2000; Lee *et al.*, PRB 2004

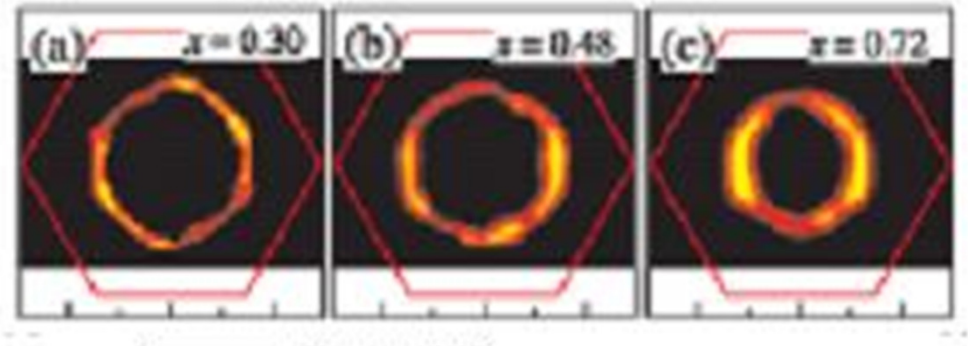
Comparison with ARPES

- A Fermi Surface without « e'_g pockets »

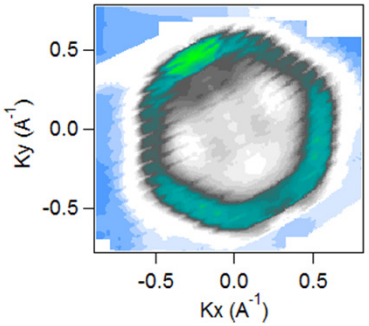
Theory



Na_xCoO_2 (Yang et al, PRL 2005)

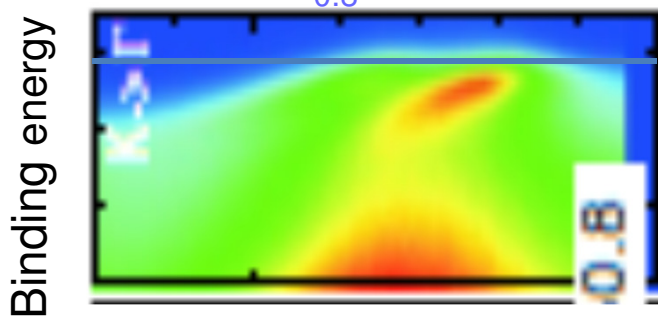


$[Bi_2Ba_2O_4]$ $[CoO_2]_2$
(Brouet et al, PRB 2007)



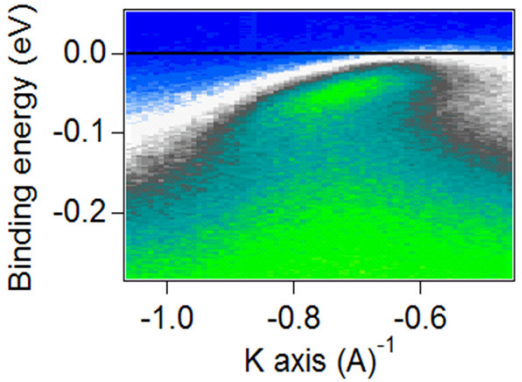
- A very narrow a_{1g} band : 0,1eV instead of 1eV

$Na_{0.8}CoO2$



Qian et al, PRL 2006

$[Bi_2Ba_2O_4]$ $[CoO_2]_2$

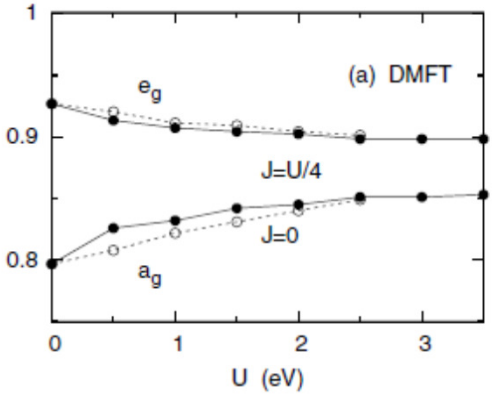


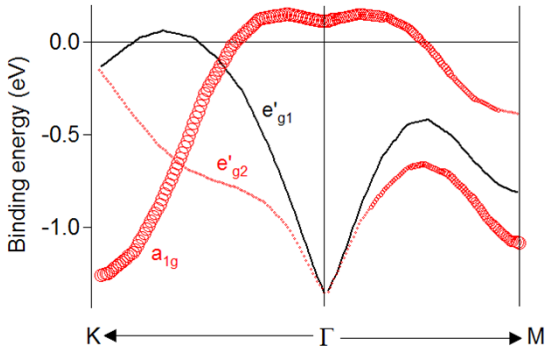
Brouet et al, PRB 2007

The problem of e'$_g$ pockets

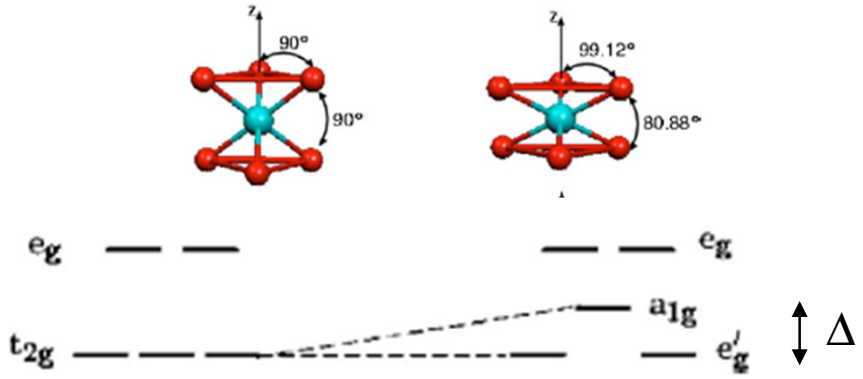
- Controversy on the impact of correlations on e'g pockets

Enlarge : Ishida et al. PRL 05
Suppress : Zhou et al., PRL 05





- a_{1g}/e'_g crystal-field splitting Δ sensitively depends on the octahedra distortion



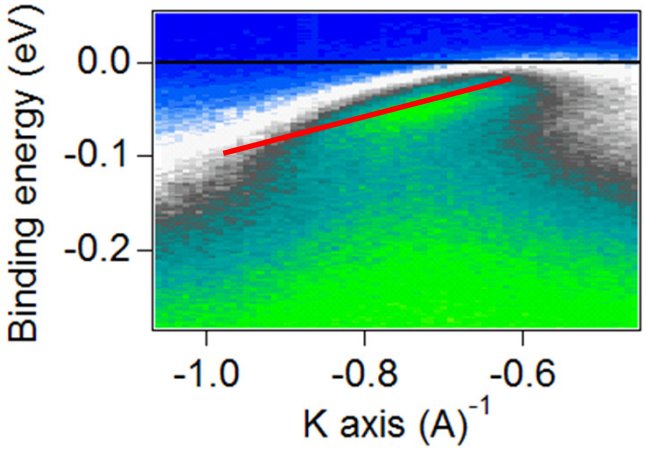
Landron and LePetit, PRB 07

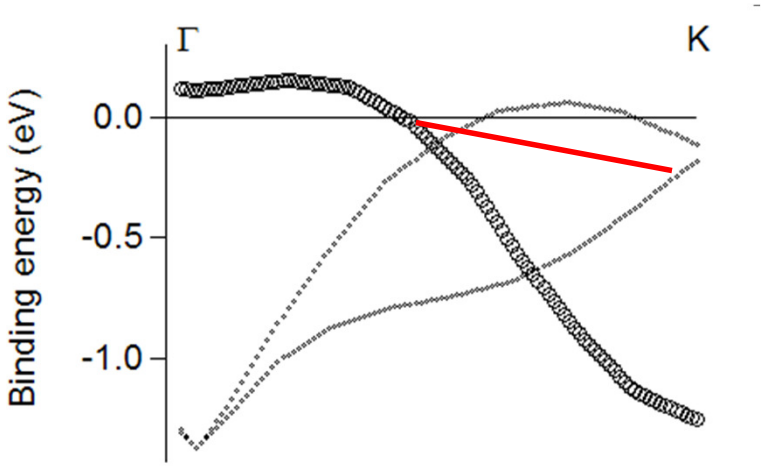
Δ = 300meV in cluster calculation,
Δ = -10meV in LDA

Marianetti et al., PRL 07

=> e'$_g$ pockets are likely not present in the bare band structure

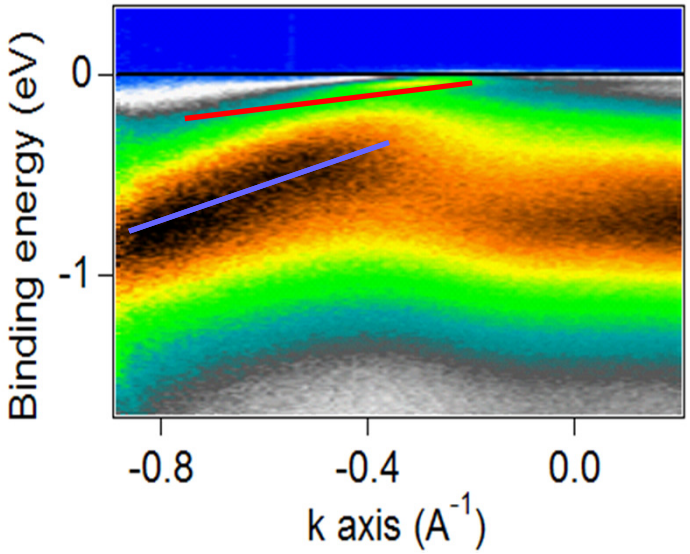
Why is the a_{1g} band so narrow ?

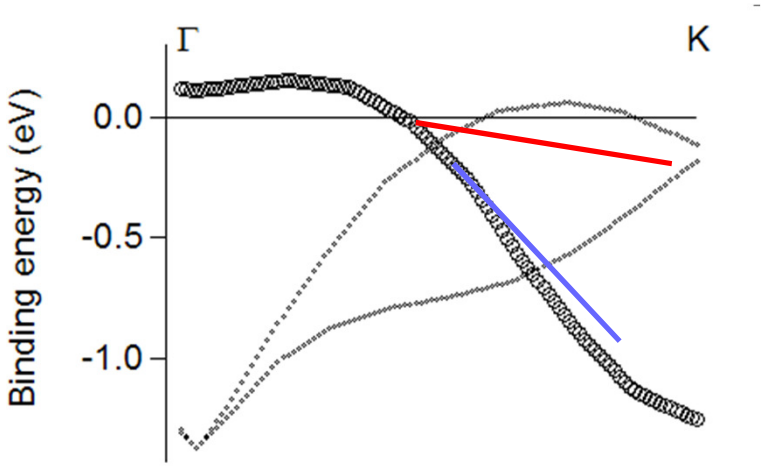




- Strongly renormalized a_{1g} band !

Why is the a_{1g} band so narrow ?

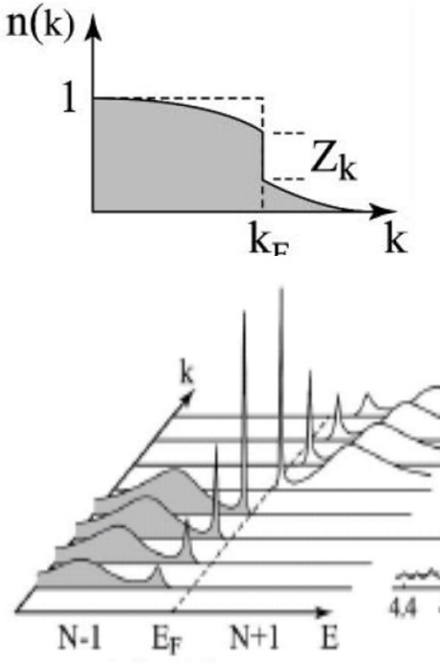




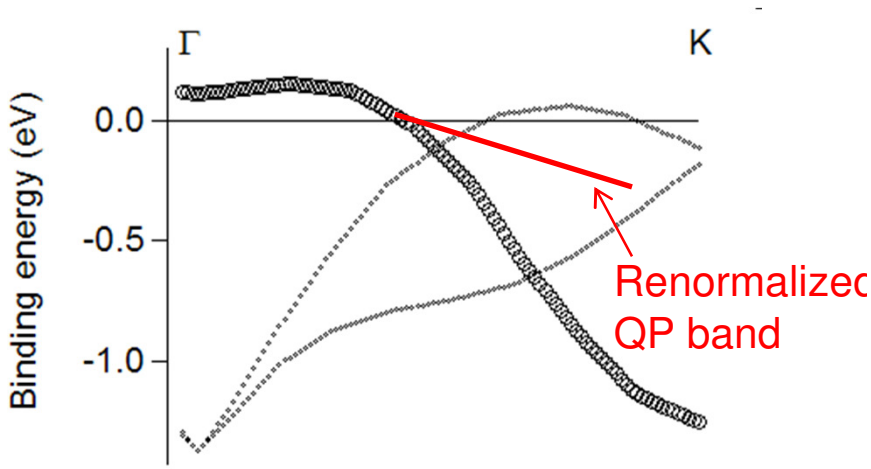
- Strongly renormalized a_{1g} band !
- or complicated structure ?

The narrow a_{1g} band is due to strong correlations

Expectation in case of correlations…



Band structure

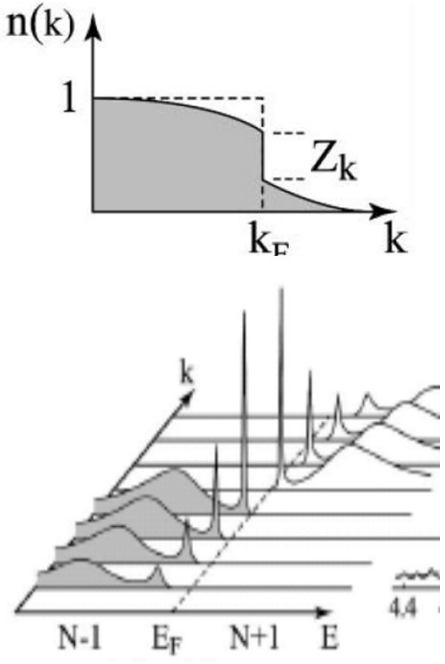


- QP weight Z
- Band renormalized by Z
- Weight « 1-Z » transferred to incoherent structures

Damascelli et al., RMP 2003

The narrow a_{1g} band is due to strong correlations

Expectation in case of correlations…



- QP weight Z
- Band renormalized by Z
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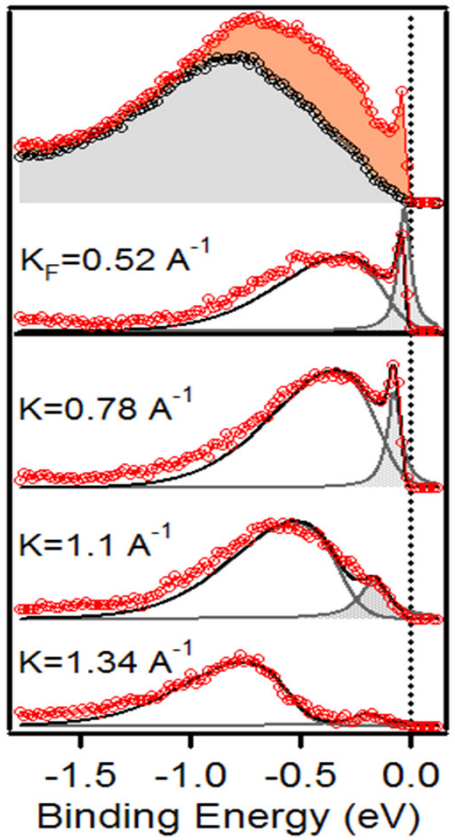
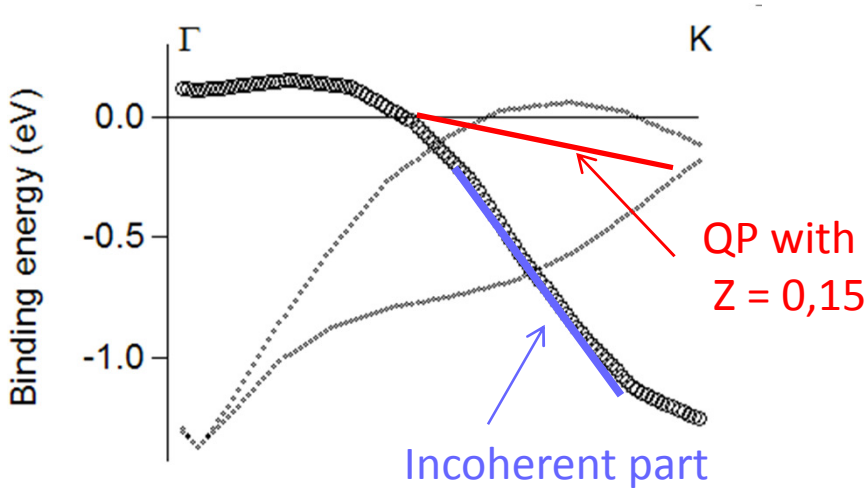
Damascelli et al., RMP 2003

ARPES spectra are consistent with a strong incoherent weight (Nicolaou et al., PRL 10)

ARPES spectra



Band structure

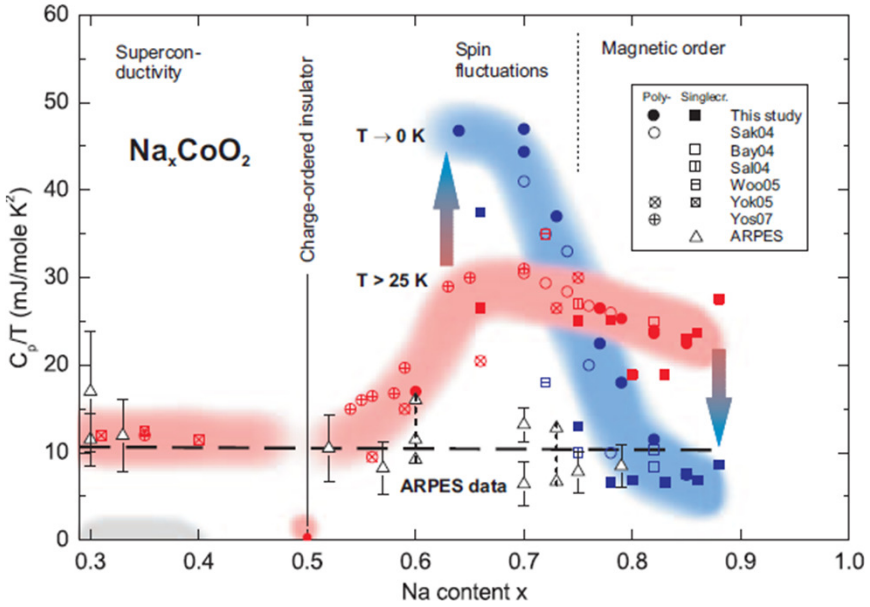


$W_{QP} = Z^*(W=1eV) = 0,15eV$

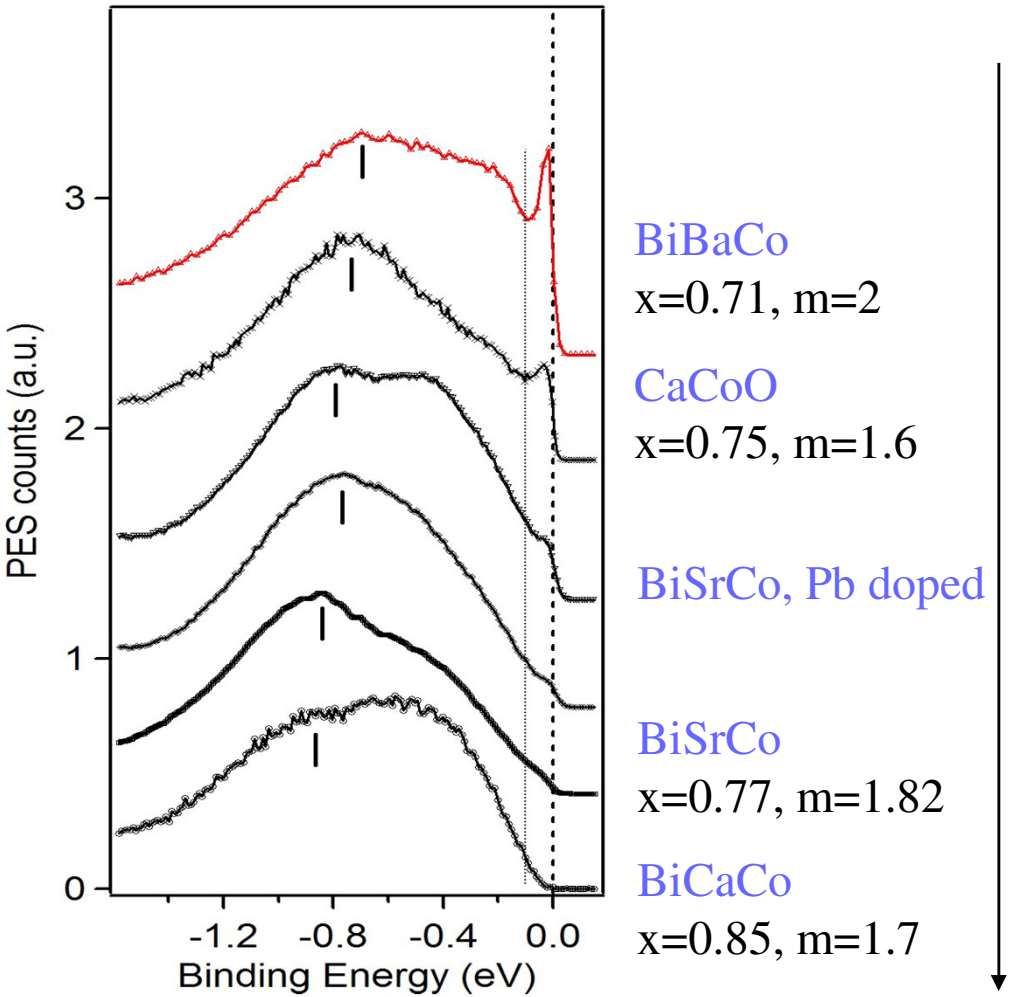
There is indeed a very small QP energy scale

The correlations are strong ar x>0,6

Agreement between specific heat and ARPES : m*/m ~ 3-5



Moreover, in misfits, correlation *increase* near x=1



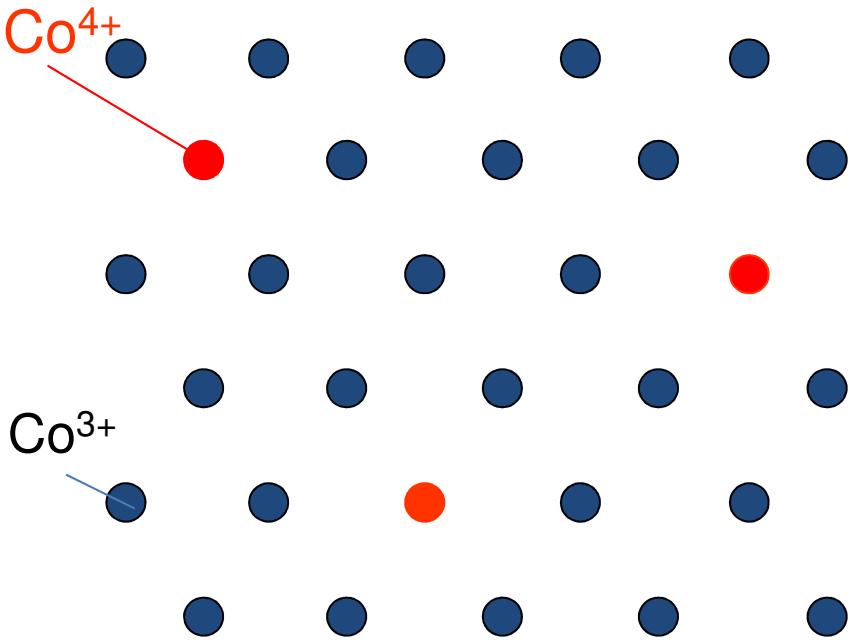
Where do correlations at high *x* come from ?

- Why are they strong near the band insulator limit ?

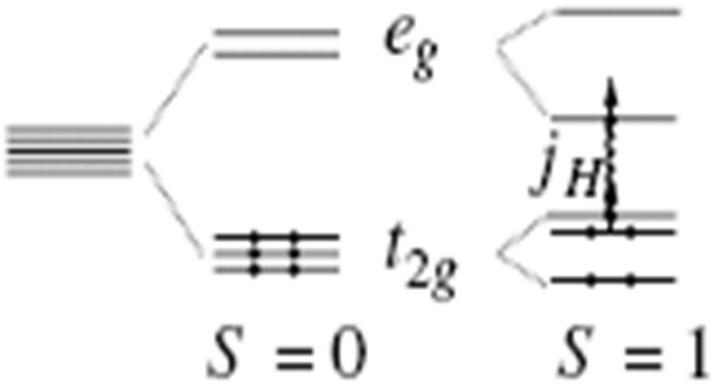
- Coupling between many degrees of freedom ?
  - => spin-orbital polarons *Khaliullin et al.*

- Charge order effects / electronic orderings *Kotliar et al.*

« Spin orbital polarons » for few carriers

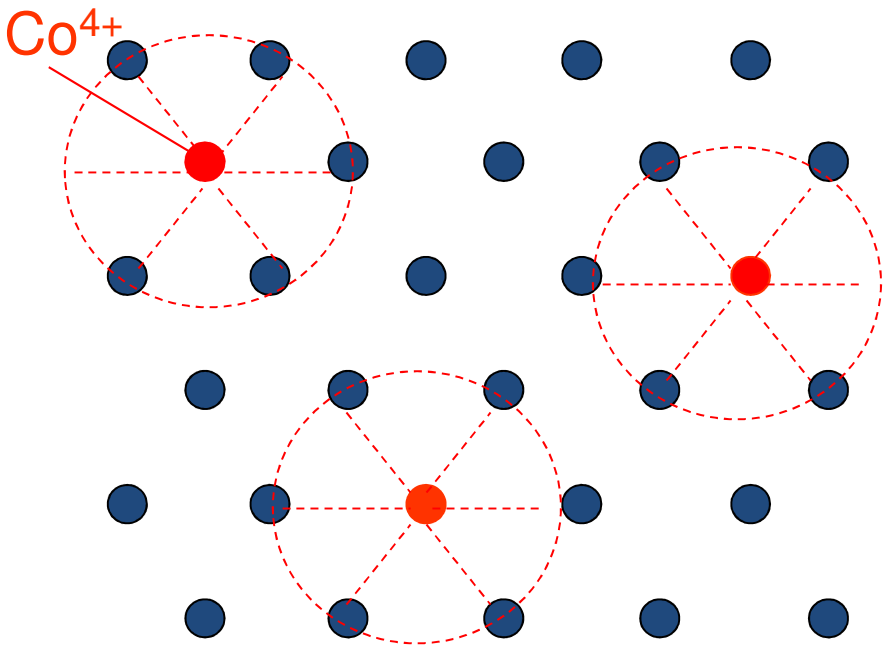


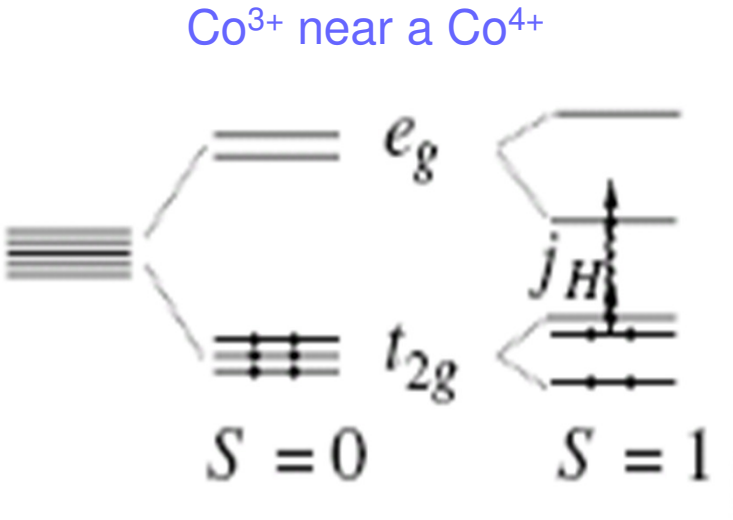
Co3+ near a Co4+



M. Daghofer et al., PRL 96, 216404 (06)
cond-mat/07072364, cond-mat/07080543

Spin orbital polarons for few carriers

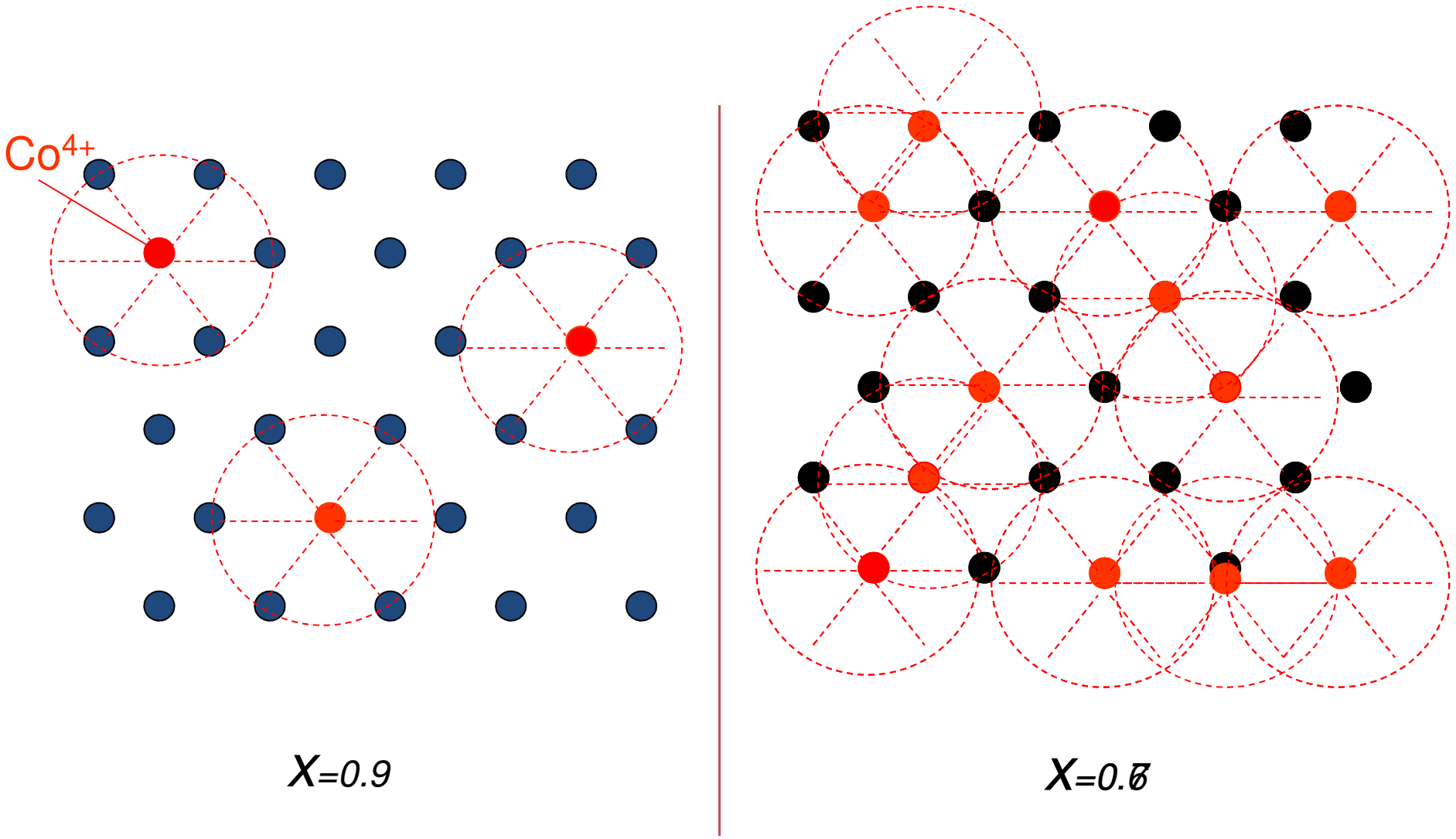




M. Daghofer et al., PRL 96, 216404 (06)
cond-mat/07072364, cond-mat/07080543

Coupling between different degrees of freedom create complex objects, which are the elementary excitations of the system

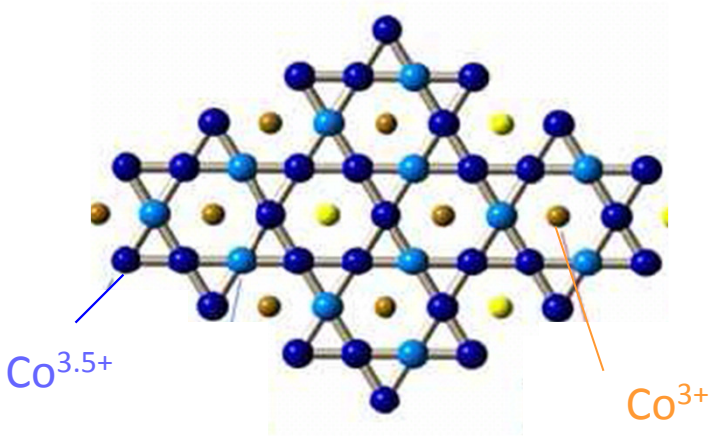
Overlap between multi-site excitations



Consequence of the charge order ?

Charge ordered state

- less neighbors
- different average filling
  - *Stronger correlations*



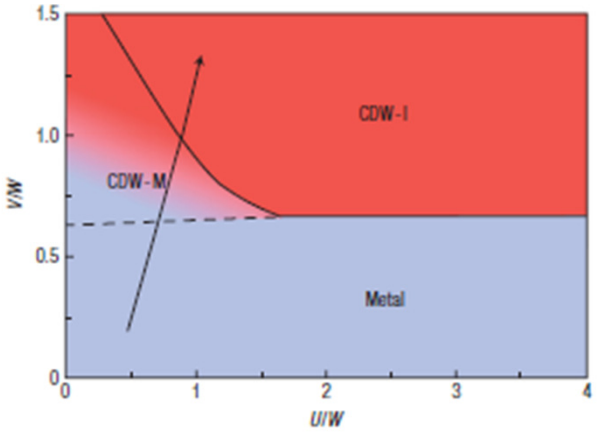
H. Alloul *et al.*, EPL 2009

Na induced correlations ?

Very narrow « impurity-like » band

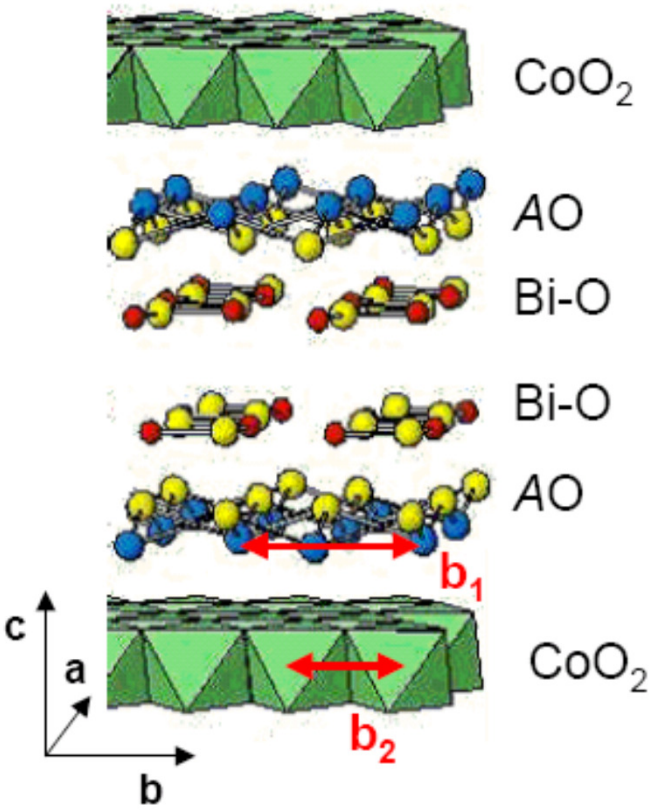
Marianetti and Kotliar, PRL 2007

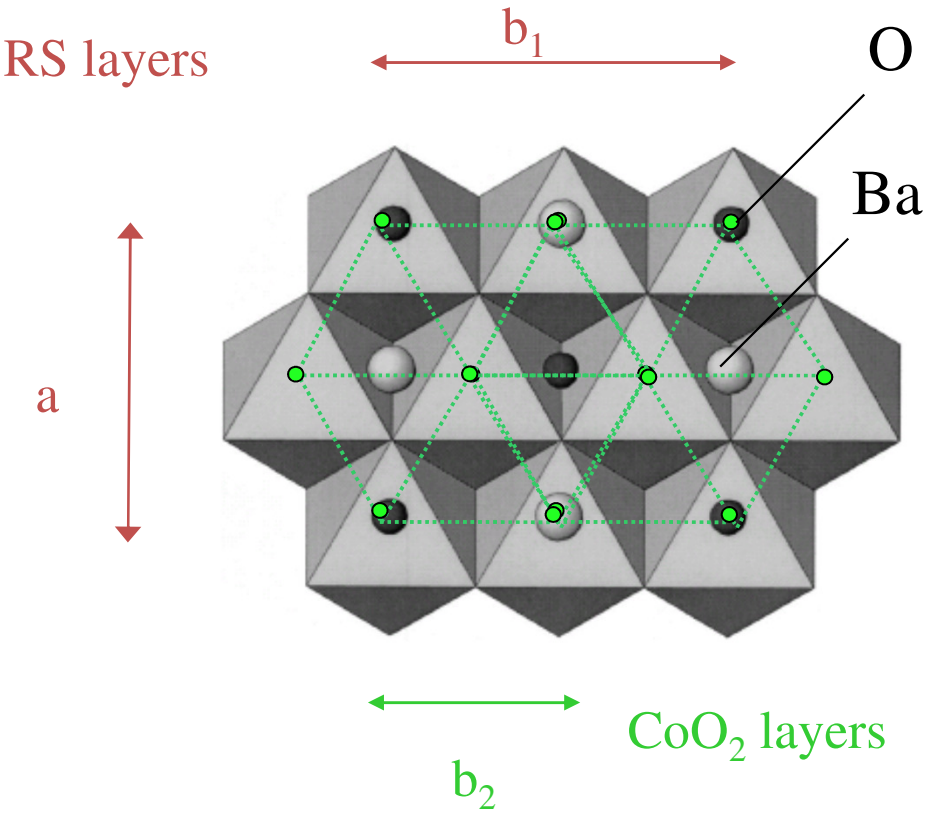
Interplay between on-site and inter-site correlations



Camjayi et al., Nat physics 4, 932 (2008)

The rock-salt layers in misfit cobaltates may play a similar role as Na layers





Inequivalent Co sites with respect to Ba^{2+} positions.

=> Situation may be analogous to Na_xCoO_2

=> Co^{3+} may form directly below a Ba^{2+} *cf* Nicolaou EPL 2010

Conclusions

Tendency to charge localization at high x, intrinsic to CoO_2 slabs

Very small QP energy scale (0.2eV)

High sensitivity to external perturbations, like Na or RS potentials

Is the small QP energy scale the consequence or the origin of the strong correlations ?

What is the role of disorder on the charge localization ?

=> Rich phase diagram with original properties, potentially interesting for applications