(aperçu de) la physique des oxydes de cobalt et de sodium Na_xCoO_2

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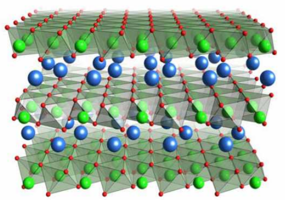
Objectifs de la présentation

1) **Aperçu global du diagramme de phase de Na_xCoO_2 et de ses propriétés électroniques principales (corrélations électroniques)**

2) **Particularité majeure de ces composés :**
mise en ordre des Na^+ et
impact sur les propriétés électroniques



Search for triangular analogs of high T_C's

Cu-based HTc cuprates

Change Cu for Ru → **Sr_2RuO_4**
- metallic, multibands
- *p*-wave superconductor

Change Cu for Ni → **Nickelates La2-xSrxNiO4**
- insulating
- Spin and charge stripes

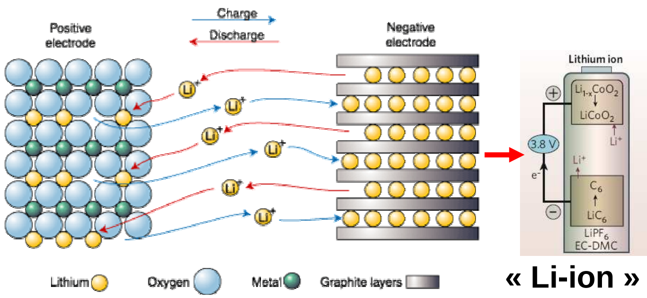
Cut CuO2 planes into slices → **Cu-based spin-ladders**
- spin gap
- *d*-wave superconductor

Change □ for △ → **Cu-based delafossites ($LaCuO_{2.66}$, etc.)**
- No superconductivity
- Insulating
- Magnetic LRO

NaxCoO2

A_xMO_2 genealogy

- **AxCoO2:**
  A = Na, Li, K,
  Sr, Ca, etc.

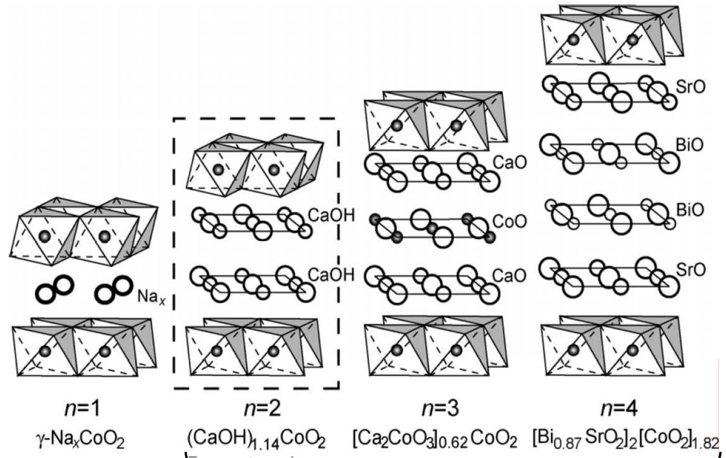


« Li-ion »

Intercalation materials, ionic conductors

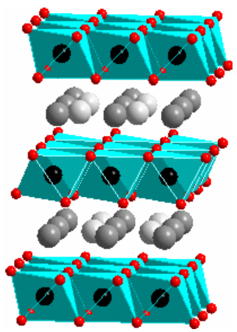
- **LiNiO2, NaNiO2, AgNiO2, *magnetism***
- **LiVO2, LiMn02, *cathode materials***

Cobaltate genealogy

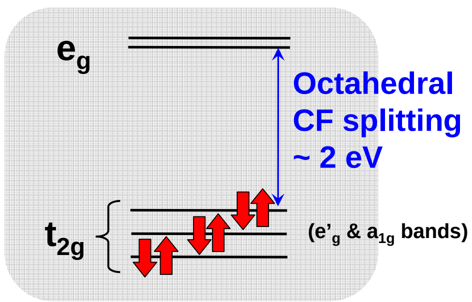


« misfits »

Na_1CoO_2 a band insulator ?

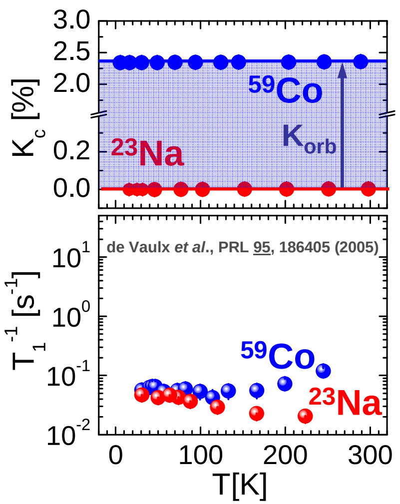


Na^+
(O^{2-}) x 2
⇨ Co^{3+}



Na_1CoO_2 is a band insulator (Co^{3+}, S=0)

NMR
de Vaulx *et al.*, PRL 2005
Lang *et al.,* PRB 2005



- **No spin shift (susceptibility)**
- **Extremely slow nuclear Relaxation (> 10 s)**

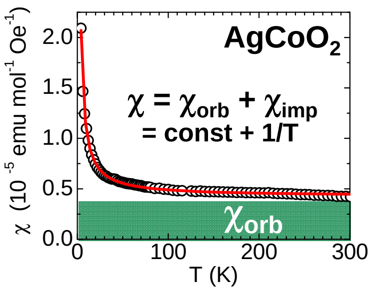
⇨ S = 0
⇨ $N(E_F) = 0$

A_1CoO_2 are all band insulators

(A=Li, Na, K, Ag, etc.)

Although obtaining pure x=1 compounds can be challenging

- **LiCoO2 :** Ménétrier *et al*., Electrochem. Solid-State Lett., 11, A179 (2008)
- **AgCoO2 :** Muguerra *et al*., J. Solid State Chem. 181, 2883 (2008)

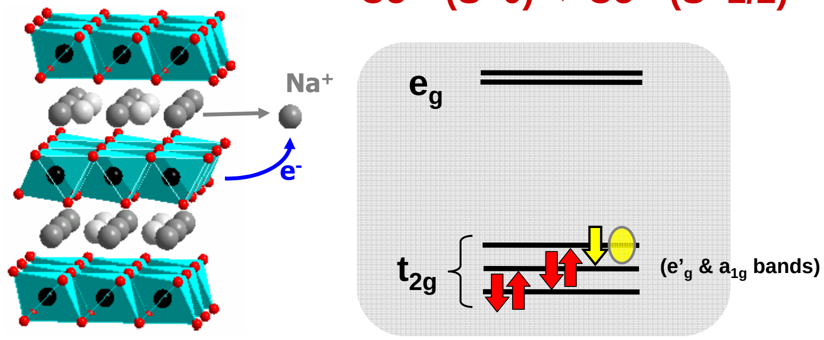


H. Muguerra *et al*.

Hole-doping the x=1 band insulator

By removing x(Na^+) from the layers

Co^{3+} (S=0) ⇨ Co^{4+} (S=1/2)



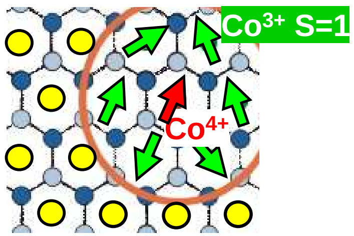
Orbital and band structure issues

Not discussed here…

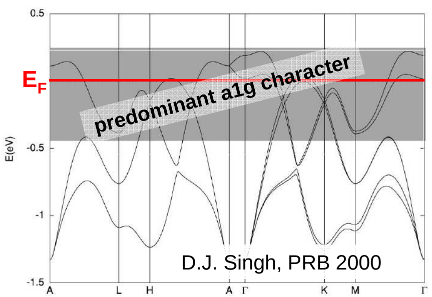
- **Co^{3+} intermediate spin state ?**

(local symmetry breaking)

No spin-state transition *ever* observed in Na_xCoO_2



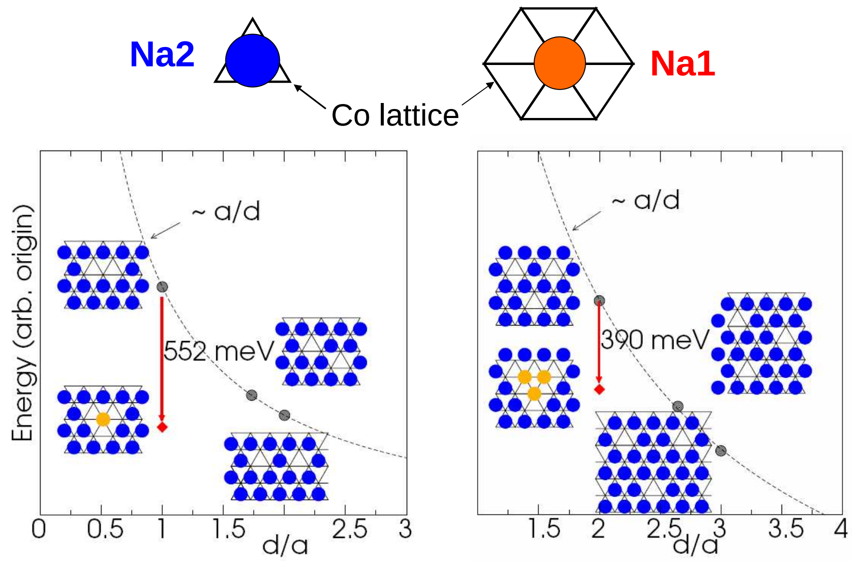
Khaliullin and coworkers



D.J. Singh, PRB 2000

- **a_{1g} & e'_g bands, fermiology…**
- **Hybridization with O_{2p} orbitals**
- **Orbital ordering, spin-orbit coupling ?**

Two kinds of Na sites



M. Roger *et al*., LT25 proceedings & Nature 445, 631 (2007)

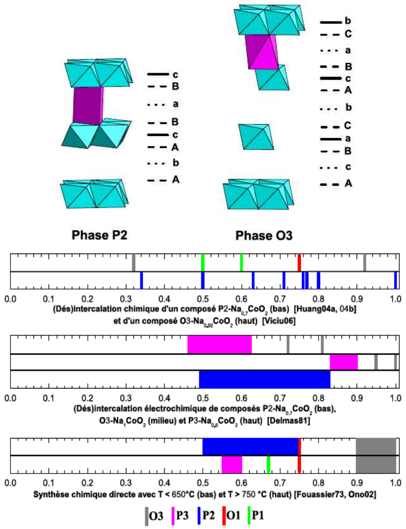
Lots of material issues

- **Observed phases depend on synthesis method & conditions**
  electrochemical, chemical, direct,
  ion-exchange, pulsed laser deposition, etc.

- **Accurate measure of *x*(Na) is challenging (while physical properties can change with variation of *x* ~ 1%)**

- **Surface ordering different from bulk**

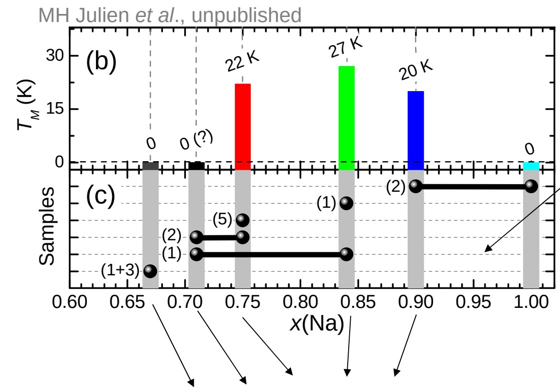
- **Sample aging (Na losses)**



- **Good samples are clean!**
(sharp NMR lines, *Shubnikov–de Haas* oscillations)

Finite number of stable phases

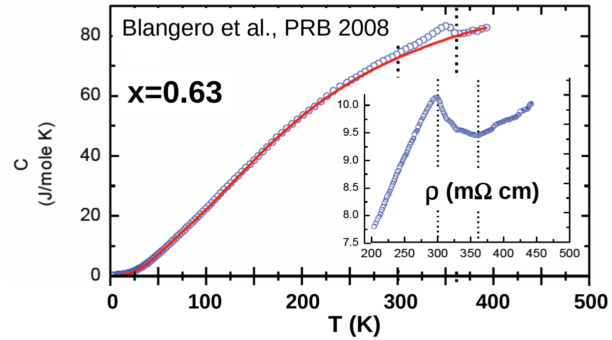
Ubiquitous phase separation for 0.67 < x < 0.9



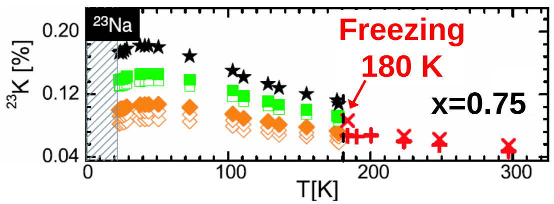
Na_xCoO_2
Delmas, *Solid State Ionics (1981)*
de Vaulx, *PRL (2005)*
Lee, *Nature Materials (2006)*
Li_xCoO_2
Van der Ven, *PRB (1998)*
Ménétrier, *J. Mater. Chem. (1999)*
Marianetti, *Nature Materials (2004)*

(some of the) stable phases

T and *x* dependent Na^+ mobility



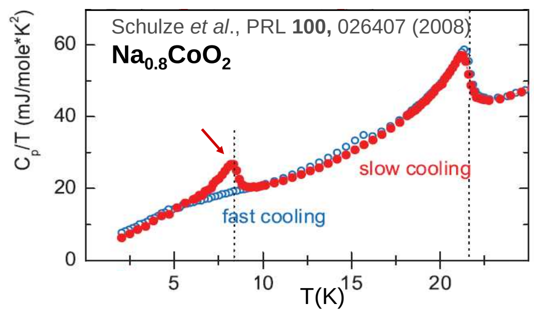
High T anomalies in transport measurements



Slow dynamics detected in NMR down to ~180 K
Julien *et al.*, PRL 2008
Lang *et al.*, PRB 2008

Impact of Na^+ ordering on magnetism

Apparition of a magnetic transition at 8 K, depending on cooling protocol above ~200 K

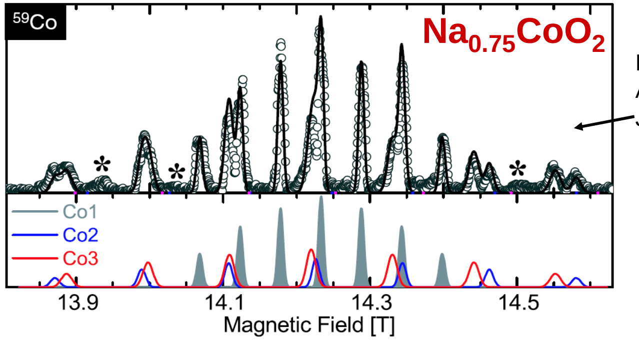


Neither 1 nor 2 ^{59}Co NMR sites

3 different sites *(at long time scale, ~ 10^{-6} s)*

30% (not 75%) of <u>localized</u> Co^{3+}

no Co4+



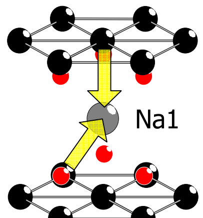
Mukhameshin, PRL (2005)
Alloul *et al*., EPL (2008)
Julien *et al*., PRL (2008)

« charge disproportionation », « charge ordering », « electronic texture », electron localization

But itinerant character remains!

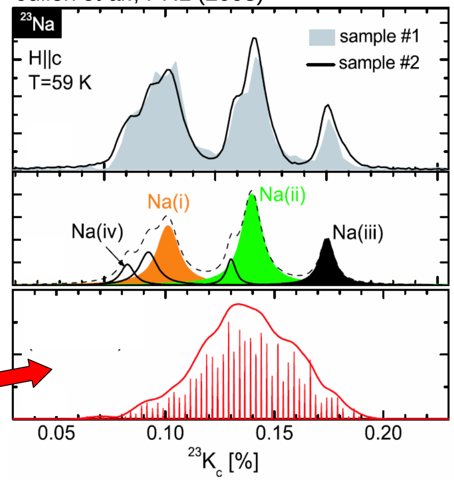
Finite number of ^{23}Na NMR lines

Demonstrates spatial ordering of the different Co states



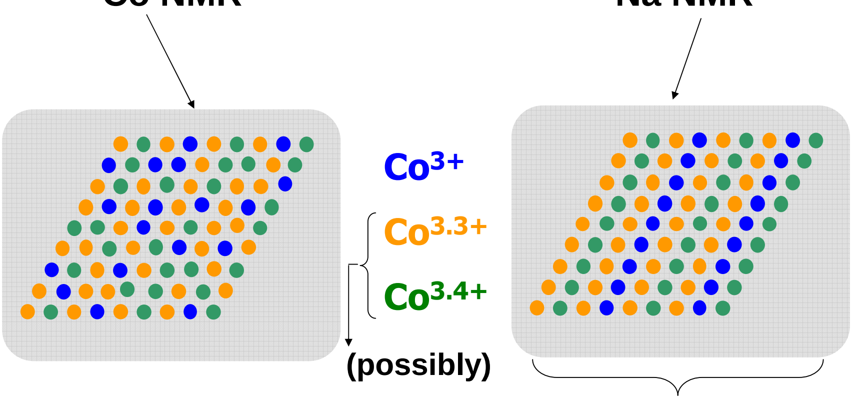
Hyperfine field transferred from Co to Na

Julien *et al*., PRL (2008) **x=0.75**



^{23}Na spectrum if Co states were at random positions (simulation)

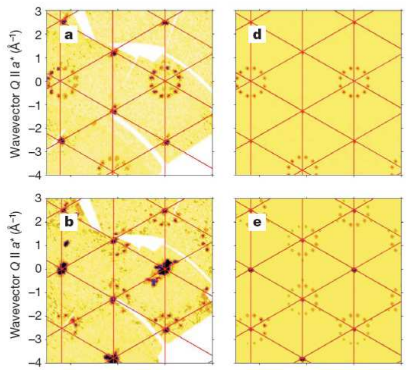
NMR summary



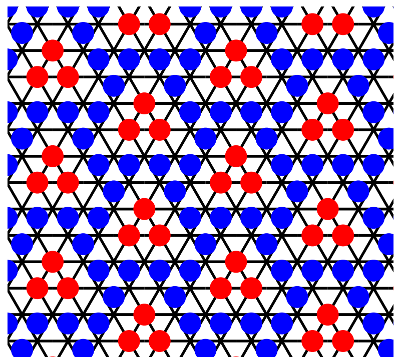
***One* example of possible ordered pattern**

Na^+ ordering is observed

***e.g.* vacancy clustering for x ~ 0.8**



M. Roger *et al*., Nature <u>445</u>, 631 (2007)

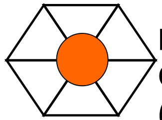


Na1-Na2 stripe correlations for x < 0.7 (G. Collin)

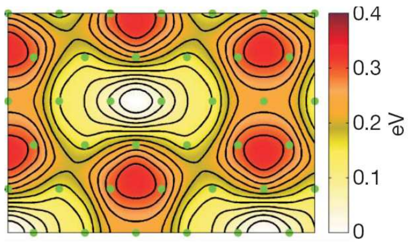
Details are controversial (accuracy of x values ?)

Electrostatic potential from Na+ ions

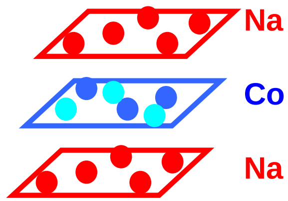
Modulates charge density in cobalt planes



Na1 should dislike Co^{4+} more than Co^{3+} (Coulomb repulsion)



M. Roger *et al*., Nature 2007



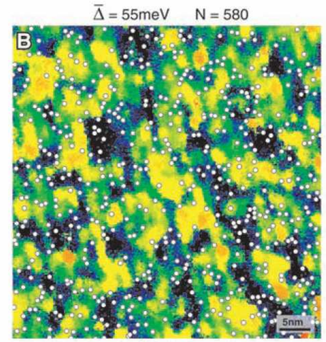
« Texture » in cobalt planes depends on 3D stacking of Na^+ ordering pattern

Relevance to high Tc cuprates

Dopant–induced electronic inhomogeneity

Atomic-Scale Sources and Mechanism of Nanoscale Electronic Disorder in $Bi_2Sr_2CaCu_2O_{8+\delta}$

K. McElroy,[1,2] Jinho Lee,[1] J. A. Slezak,[1] D.-H. Lee,[2] H. Eisaki,[3] S. Uchida,[4] J. C. Davis[1*]

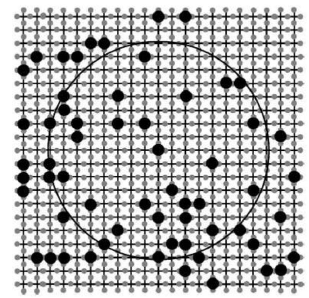


12 AUGUST 2005 VOL 309 SCIENCE

PHYSICAL REVIEW LETTERS 28 JANUARY 2002

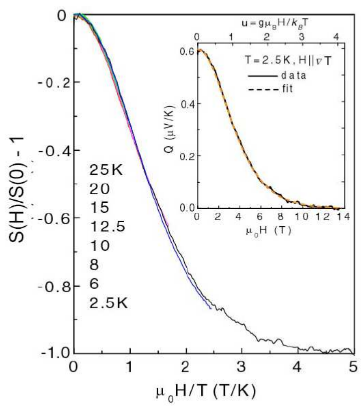
^{63}Cu NQR Evidence for Spatial Variation of Hole Concentration in $La_{2-x}Sr_xCuO_4$

P. M. Singer, A. W. Hunt, and T. Imai



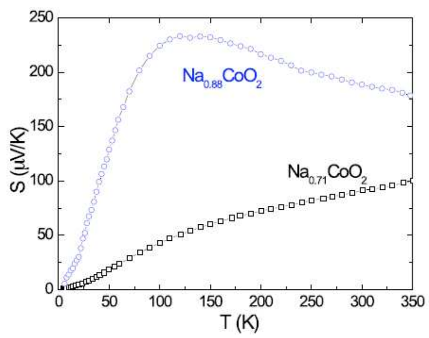
High values of the thermoeletric power

Magnetic field dependent



Wang et al., Nature (2003)

Strongest at the highest *x*(Na)



Lee et al, Nature Materials (2006)

Magnetic properties / electron correlations are involved

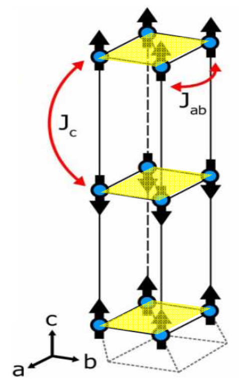
Magnetic properties

- **Curie-Weiss bulk magnetization**
- **Magnetic transitions**

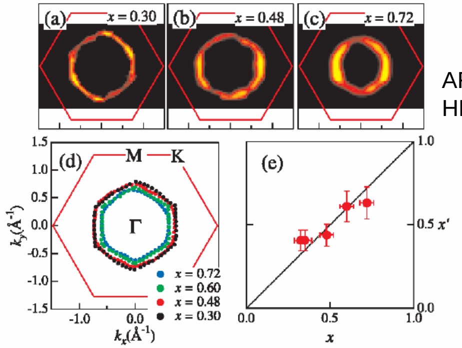
Ex: T_M = 22 K for x = 0.75
***None* for x = 0.67 and x = 0.71**

- **A-type antiferromagnet**

Bayrakci PRL (2005), Helme PRL (2005)
FM planes ⇨ no frustration ⇨ too bad…



Signature of electron correlations



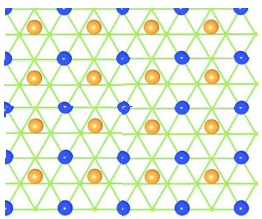
ARPES
HB Yang, PRL (2005)

t < 0 and |t| ~ 10 meV (bandwidth < 100 meV)

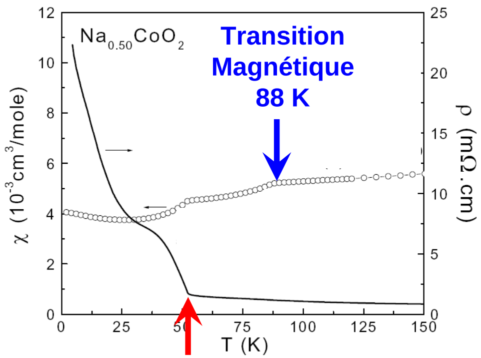
U ~ 2 – 4 eV

As well as in transport measurements
(T-linear resistivity, m*/m ~ 3 - 10)

$Na_{0.5}CoO_2$



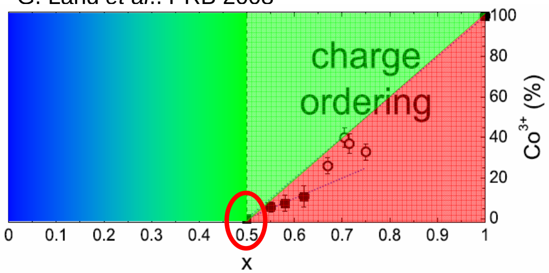
Huang, PRB 2004

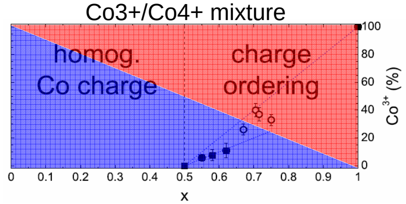


Fermi surface instability at x=0.5

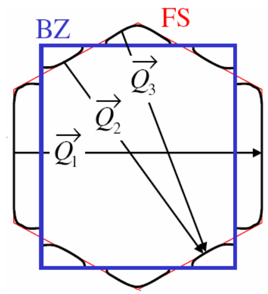
Very small charge differentiation

G. Lang *et al*., PRB 2008



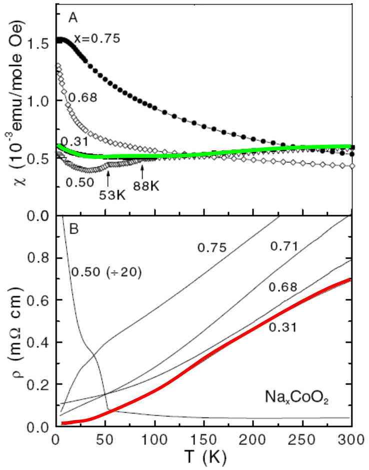


J. Bobroff *et al*., PRL 2006



Na order
⇨ FS reconstruction
⇨ Nesting
⇨ Transition

Weak electron correlation at x = 0.3



Foo et al., PRL (2004)

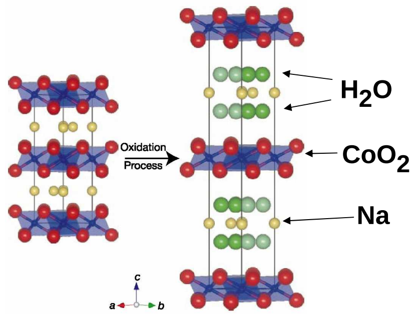
Pauli-like χ_{spin}

$\rho \propto T^2$ below ~ 30 K

Fermi liquid ?

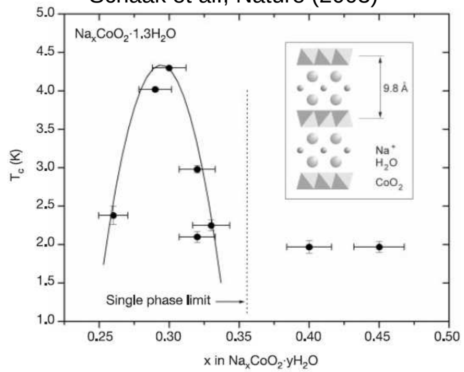
Water-induced superconductivity

in $Na_{0.3}CoO_2 \cdot yH_2O$



Takada et al., *Nature* (2003)

Schaak et al., Nature (2003)

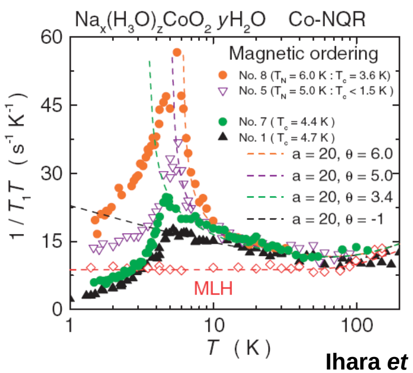


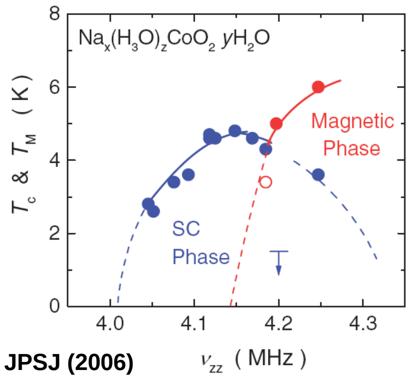
T_c max = 4.8 K

Unconventional superconductivity ?

- **Type II**
- **Short coherence length (~100 Angstrom)**
- **Singlet pairing**
- **Pairing symmetry ?**

AFM spin fluctuations and proximity to magnetic ordering

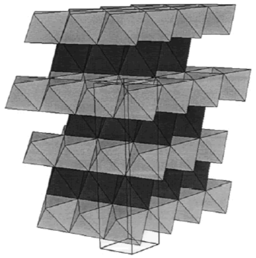




Ihara *et al.*, JPSJ (2006)

The x = 0 limit

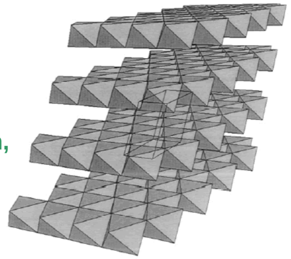
$LiCoO_2$



Full electrochemical extraction of Li^+

Amatucci, Klein & Tarascon, J. Electrochem. (1996)

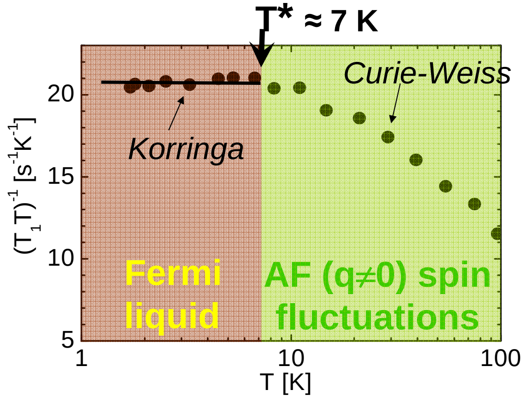
CoO_2



CoO_2 is *not* a Mott insulator

But a correlated metal

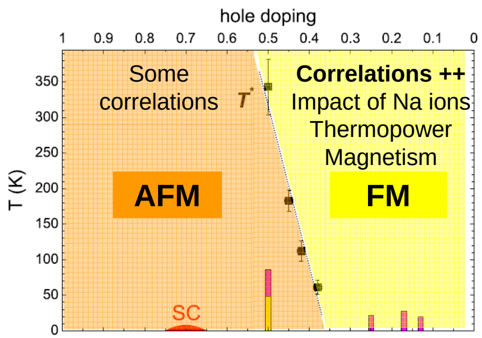
^{59}Co NMR :
de Vaulx *et al.*, PRL 2007



(Metal-insulator) Mott transition occurs for U/t ≈ 10-12 on the triangular lattice

Na_xCoO_2 summary

- **Carrier concentration can be varied over a wide range (1 elect./cell)**
- **Electron correlations throughout the phase diagram**
- **Unexpectedly, correlations are strongest at high Na concentrations**
- **Correlations can be enhanced by Na^+ potential**
- **Limited analogy with high Tc's**



G. Lang et al. PRB (2008)