The Road to Room Temperature Superconductivity

Loen, Norway, 17-23 june 2007

The crucial role of crystal chemistry in strongly correlated oxides : from high Tc's to CMR's & thermoelectrics

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High Tc Superconductors

Bi-Sr-Ca-Cu-O

$Bi_2Sr_2CuO_{6+\delta}$

$Bi_2Sr_2CaCu_2O_{6+\delta}$

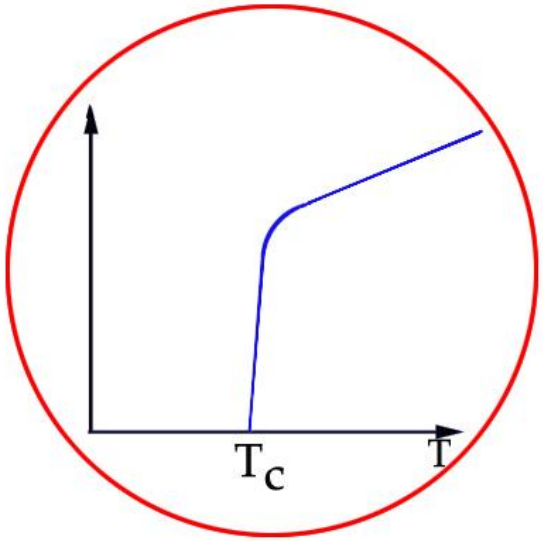
$Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10+\delta}$

Y-Ba-Cu-O

$YBa_2Cu_3O_7$

La-Ba-Ca-Cu-O

$La_{2-x}Ba_xCuO_4$



Tl-Ba-Ca-Cu-O

$Tl_2Ba_2CuO_6$, $TlBa_2CuO_5$

$Tl_2Ba_2CaCu_2O_8$, $TlBa_2CaCu_2O$

$Tl_2Ba_2Ca_2Cu_3O_{10}$, $TlBa_2Ca_2Cu_3O_9$

Hg-Ba-Ca-Cu-O

$HgBa_2CuO_{4+d}$, $HgBa_2CaCu_2O_{6+\delta}$

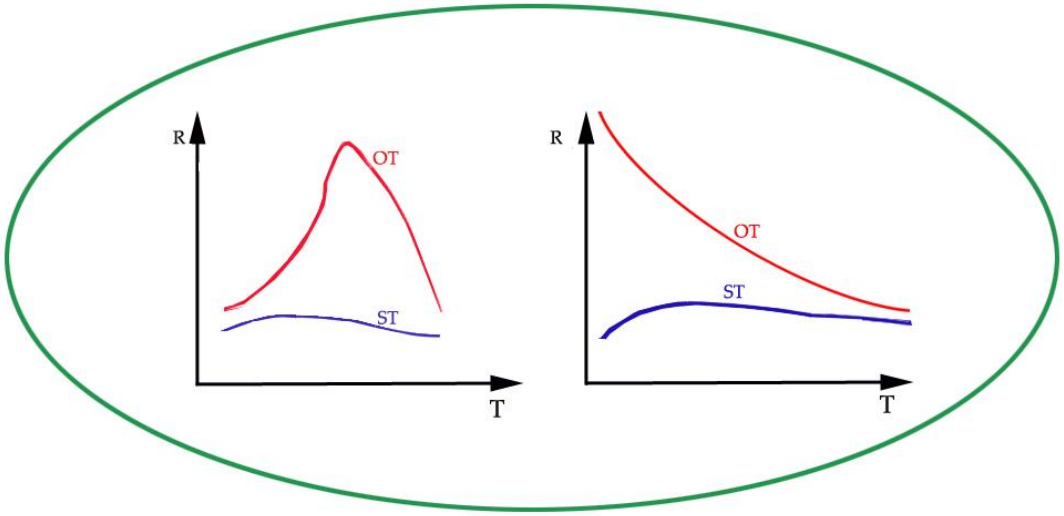
$HgBa_2Ca_2Cu_3O_{8+\delta}$

MIXED VALENCE Cu^{3+}/Cu^{2+}

Colossal Magnetoresistance CMR

$Ln_{1-x}A_xMnO_3$ & $Ln_{2-x}A_{1+x}Mn_2O_7$

Ln=La to Ho **A=Ca, Sr, Ba, Pb**



MIXED VALENCE Mn^{3+} / Mn^{4+}

Thermoelectrics :$Z = S^2 / \rho K$

Na-Co-O

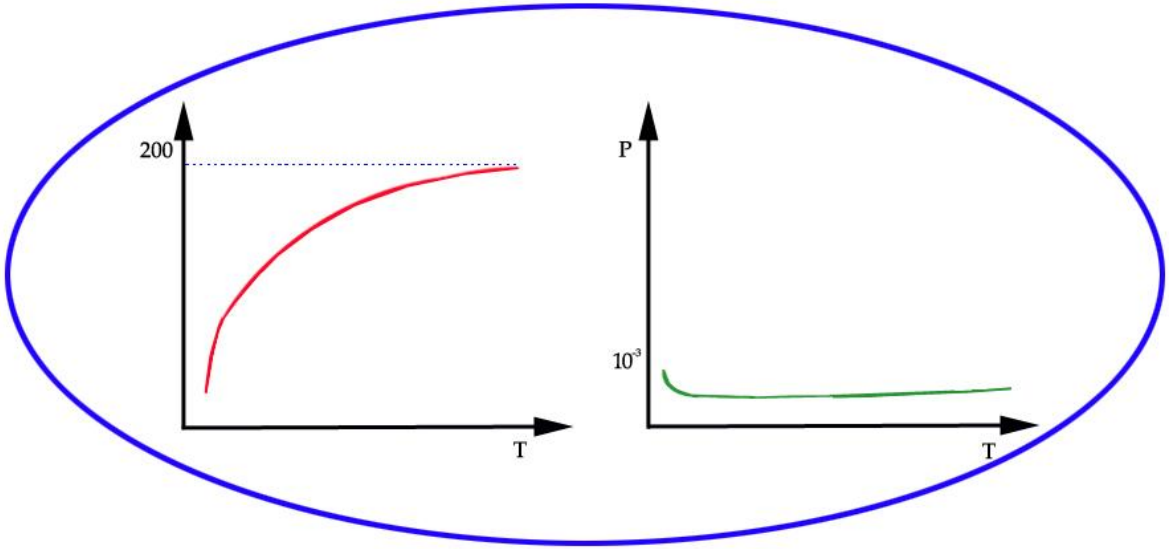
$NaCo_2O_4$

Ca-Co-O

$Ca_3Co_4O_9$

TL-Sr-Co-O

$[Tl_{0.8}Sr_2Co_{0.2}O_3][Co_2]_{1.79}$



Bi-Sr-Co-O

$[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$

Pb-Sr-Co-O

$[Pb0.3Co_{0.7}Sr_2O_3]_2[CoO_2]_{1.8}$

MIXED VALENCE Co^{3+}/ Co^{4+}

Role of the various factors

Geometry : dimensionality of the structure

Oxygen vacancies :content & ordering

Nature of counter cations : size, ordering, electronic structure

Structural distortions - Jahn Teller effect

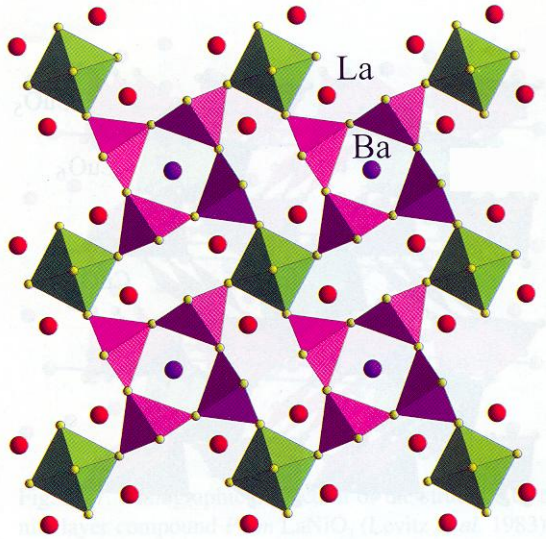
Charge & orbital ordering

Phase separation

Doping at A & B sites

Dimensionality :High Tc Cuprates

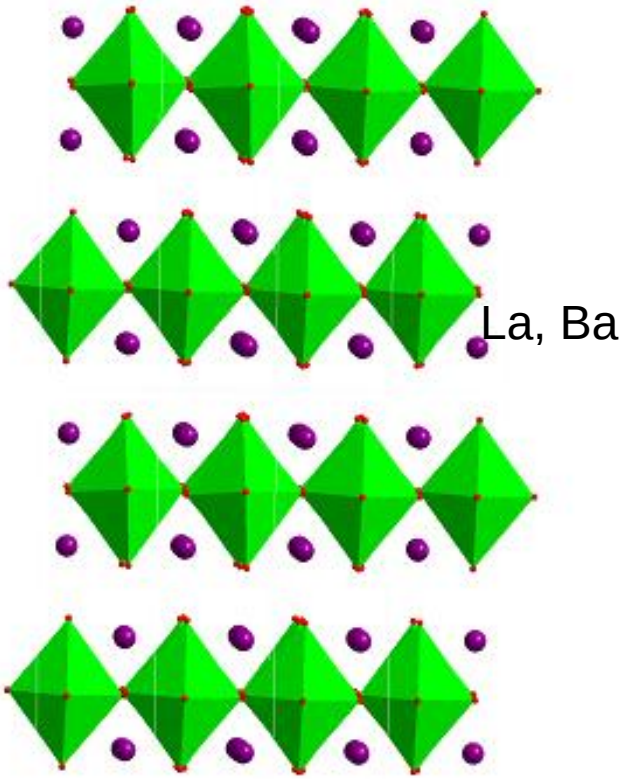
$La_4BaCuO_5O_{13}$



Metallic non superconductive

$S=10^3\text{-}10^4$ O^{-1} cm^{-1}

$La_{2-x}Ba_xCuO_4$

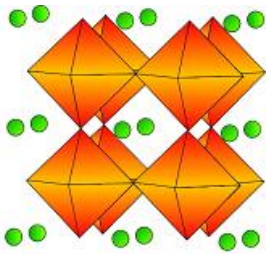


Superconductor Tc=38K

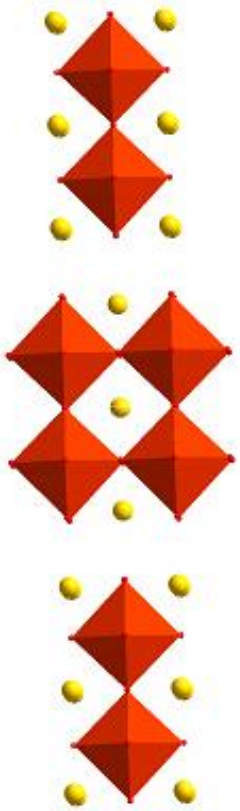
Superconductivity requires 2D

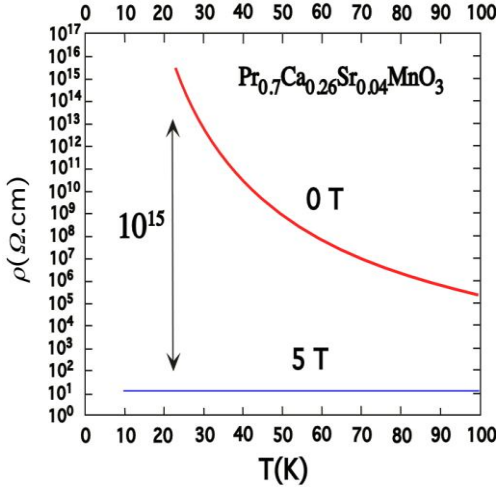
Dimensionality :CMR & thermoelectric manganites

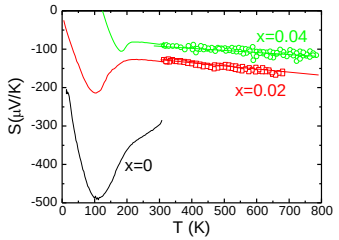
$La_{1-x}A_xMnO_3$



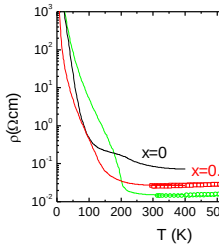
$La_{2-2x}Sr_{1+2x}Mn_2O7$

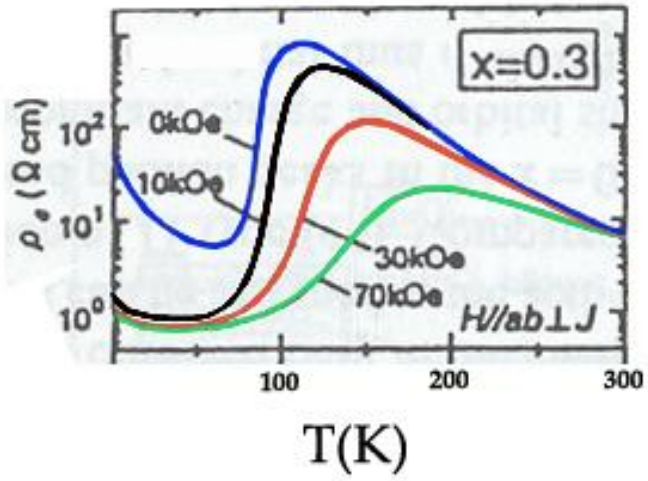






$SrMn_{1-x}Mo_xO_3$

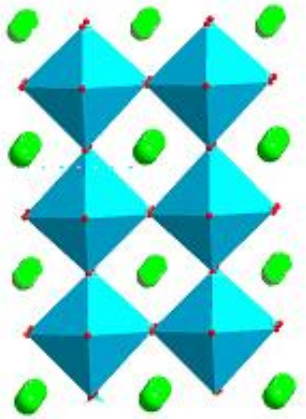


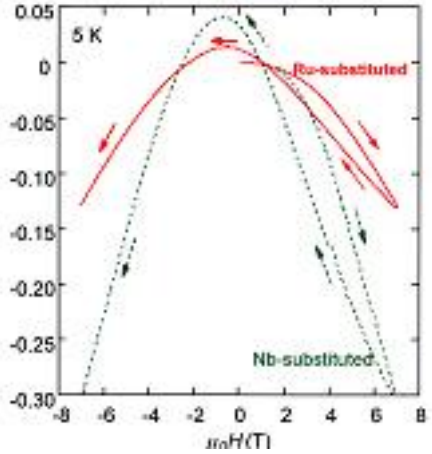


3D is better for CMR & negative thermoelectrics

Dimensionality in cobaltites : MR, super cond., thermoelectricity

$SrCo_{1-x}Nb_xO_{3-\delta}$

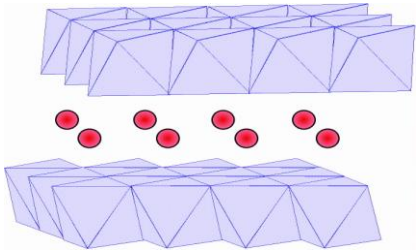




MR up to60 %

Requires 3D

Na_xCoO_2 & y H_2O

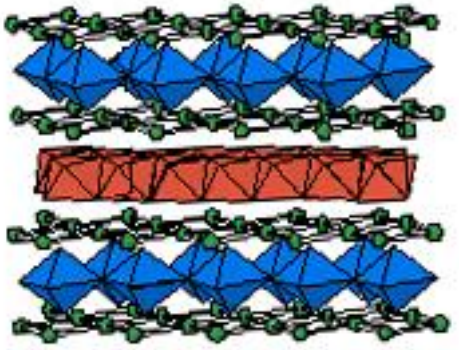


Superconductivity:
Tc = 5 K

Thermoelectricity :
S =100 µV/ K
$\rho = 10^{-4}$ Ω cm

Require 2D

Ca3Co4O9



Thermoelectric misfit
S= +125 µV / K
$\rho = 5\ 10^{-3}$ Ω cm

Requires 2D

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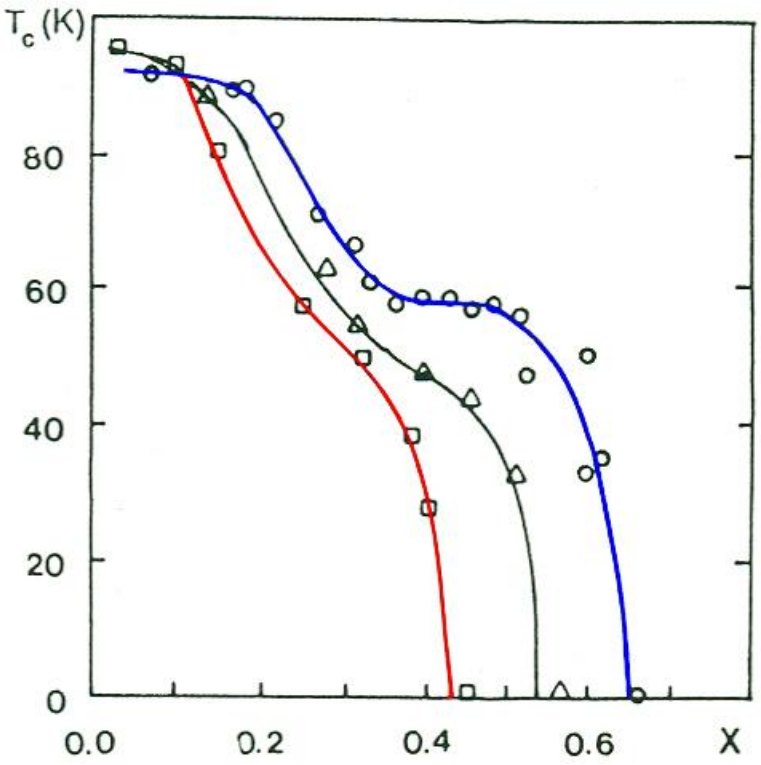
Oxygen vacancies : order- disorder phenomena

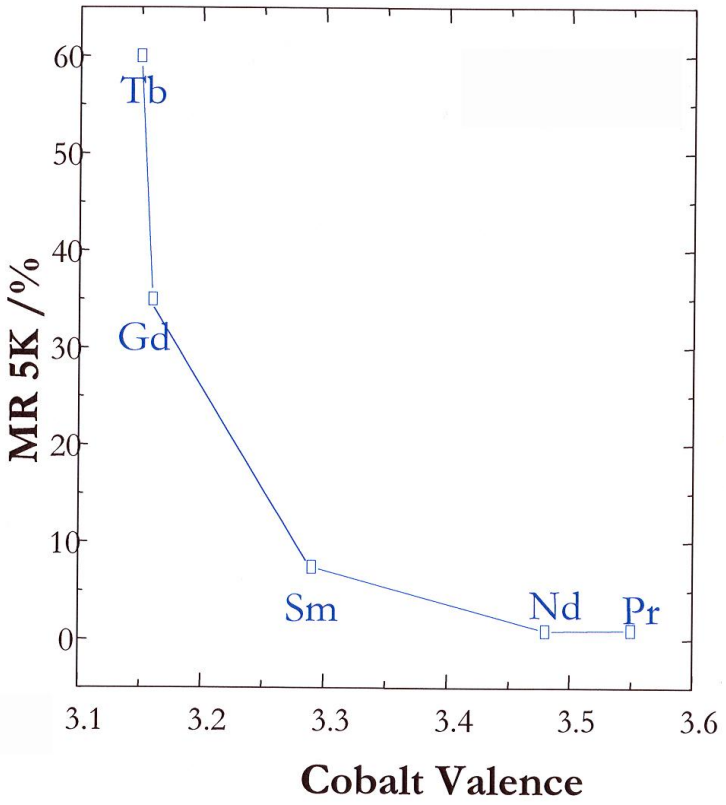
$YBa_2Cu_3O_{7-\delta}$



Tc decreases as δ increases

semi-ordered

$Sr_{0.8}Ln_{0.2}Co_{3-\delta}$



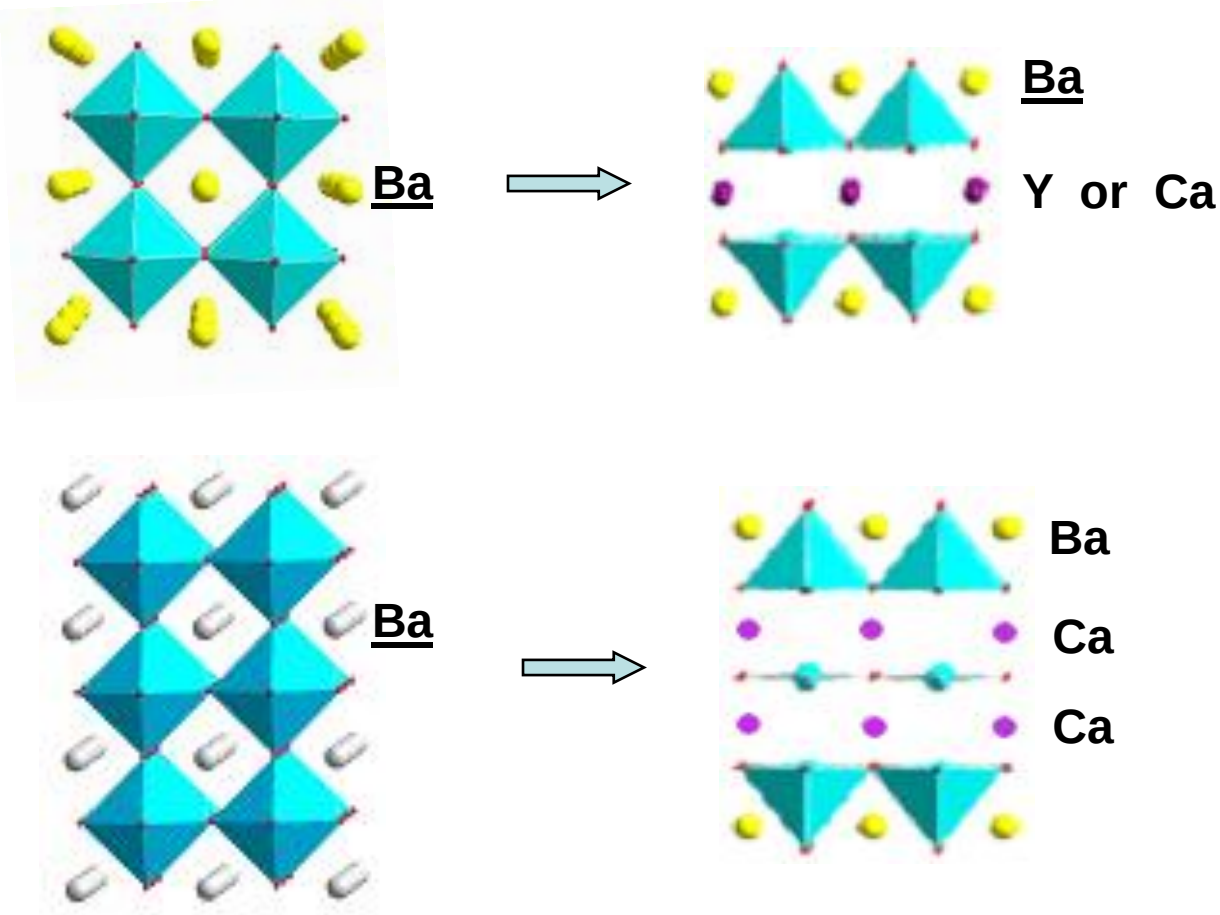
MR increases as δ increases

disordered or modulated

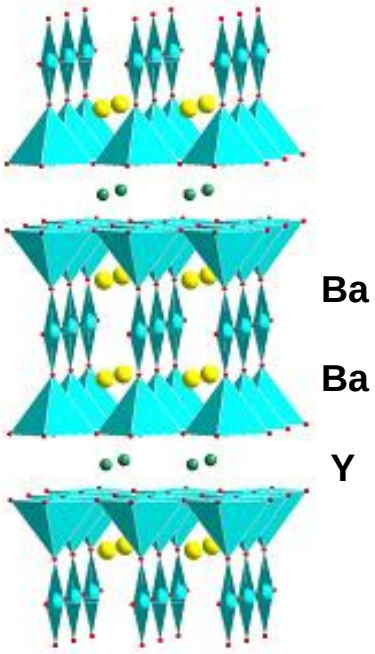
Ordering of oxygen vacancies & counter cations :closely related

Size & charge difference of A cations ⟹ ordering of A cations ⟺ ordering of O vacancies ⟸ Jahn Teller effect of M cations

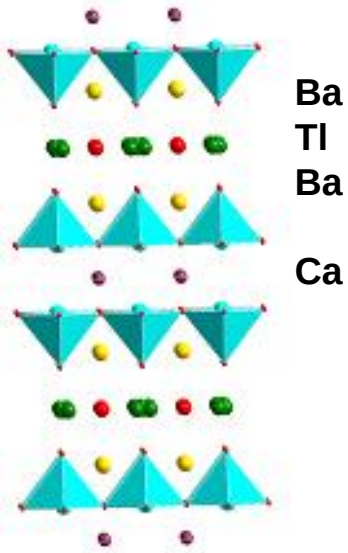
LAYERS



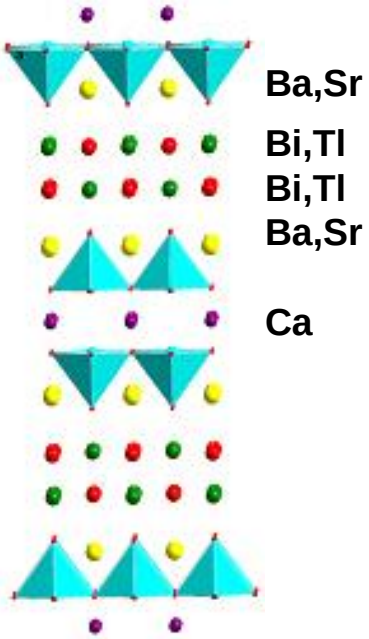
Ordering of O vacancies & A Cations in cuprates



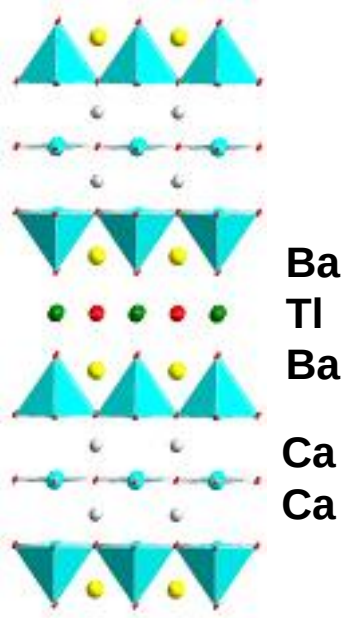
$YBa_2Cu_3O_7$



TlBa2CaCu2O7



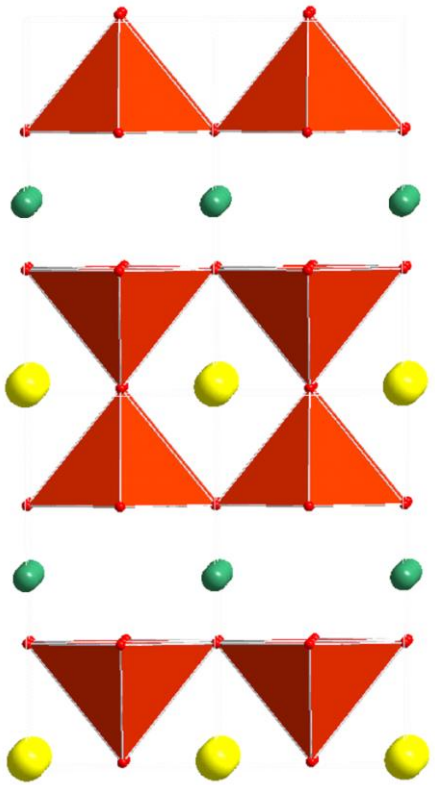
$Tl_2Ba_2CaCu_2O_8$
$Bi_2Sr_2CaCu_2O_8$



TlBa2Ca2Cu3O9

Strong relations between A cation size & J.T. effect

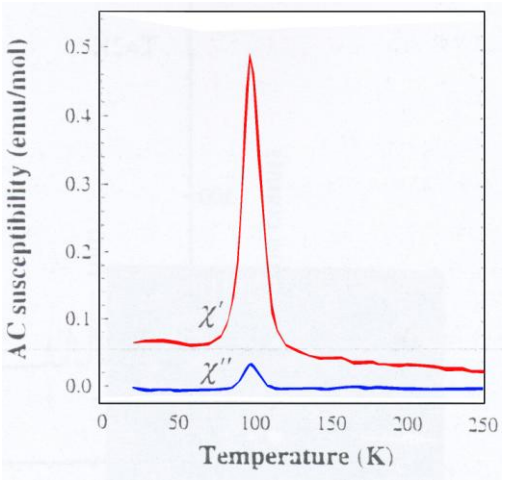
Manganites & cobaltites : Layered Ordering of oxygen vacancies & counter cations

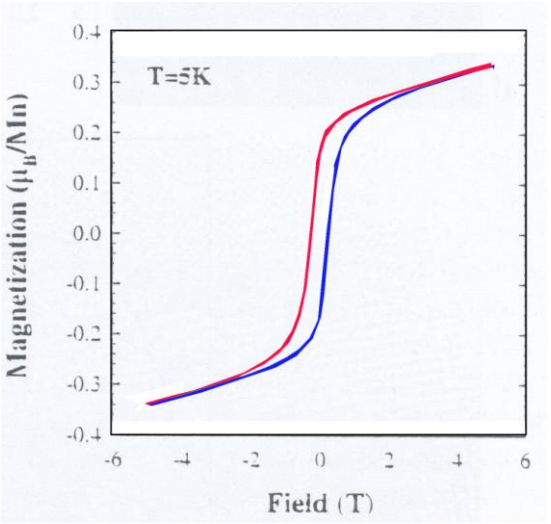


Mn or Co

La or Ho

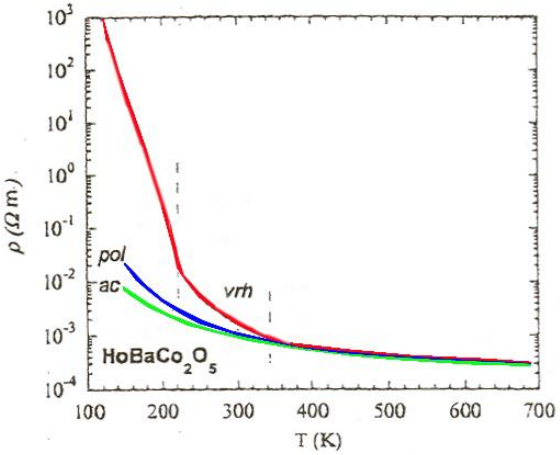
Ba



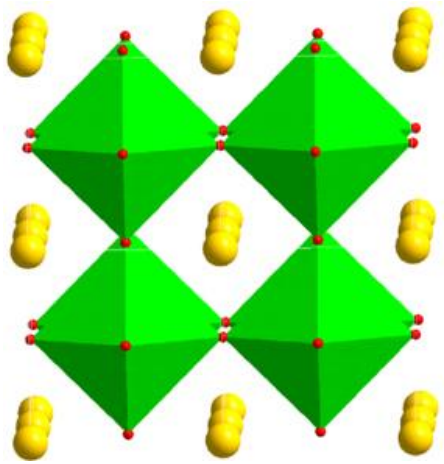


$LaBaMn_2O_5$

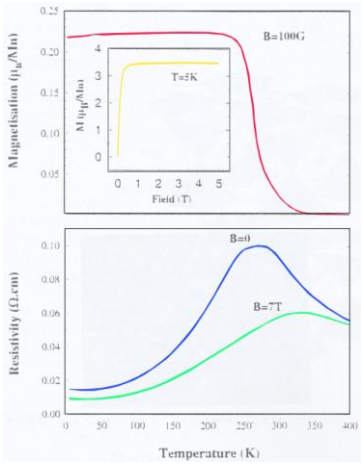
$HoBaCo_2O_5$



Manganites : Layered ordering of counter cations

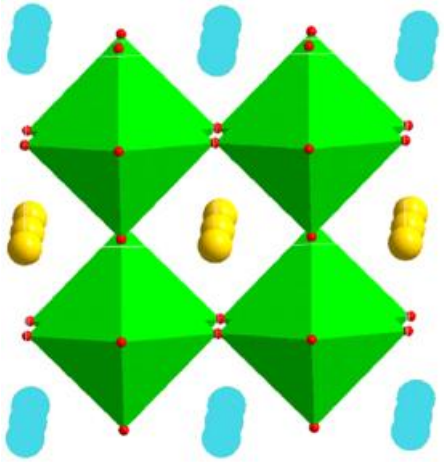


La0.5Ba0.5MnO3

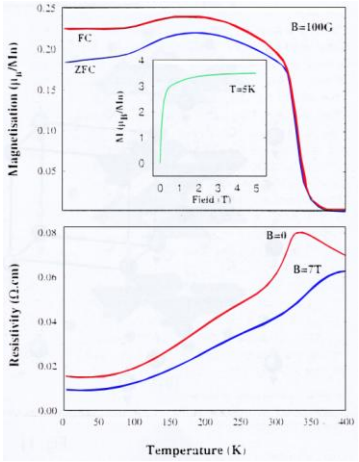


T_C =270 K

metallic Ferromagnet



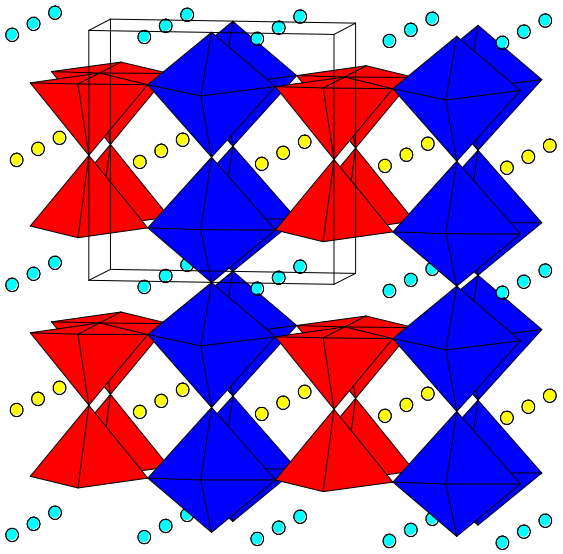
$LaBaMn_2O_6$

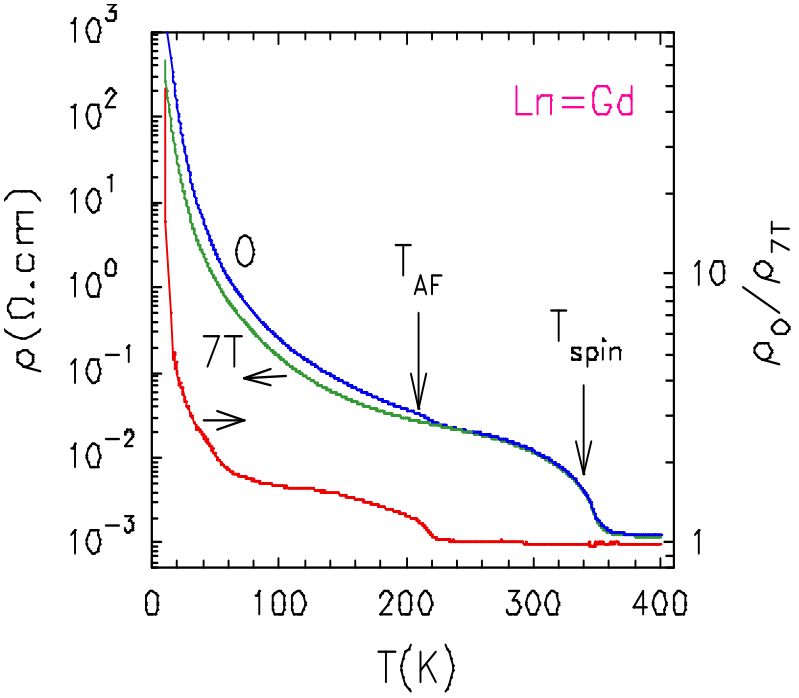


TC =320 K

metallic ferromagnet

Cobaltites : Layered ordering of oxygen vacancies & A cations



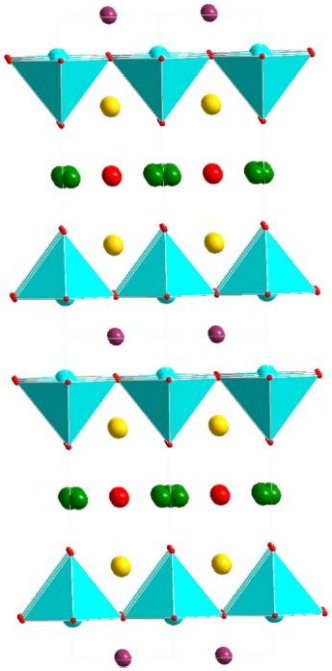


$GdBaCo_2O_{5.5}$ **metal-insulator transition, « ferrimagnetic »**

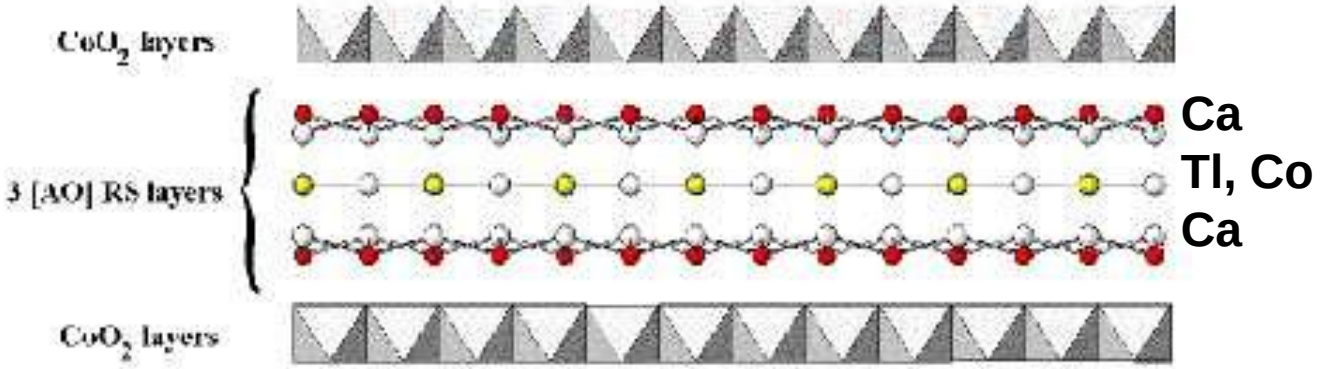
$HoBaMn_2O_{5.5}$ **FM spin ladders antiferromagnetically coupled**

A.Maignan,V.Caignaert, B.Raveau, D.Khomskii, G. Sawatzky Phys.Rev. Letter, 93,026401(2004)

Electronic structure of the A cation : « Tl^{3+} d^{10} »



Sr
Tl
Sr



$TlSr_2CaCu_2O_7$

Tc (110 K) increases with respect to $La_{2-x}Sr_xCaCu_2O_6$ (60 K)

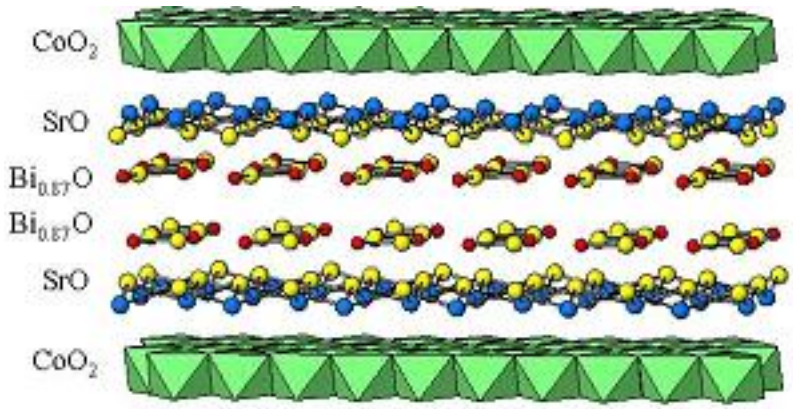
$[Tl_{0.8}Ca_{1.9}Co_{0.3}][CoO_2]_{1.65}$

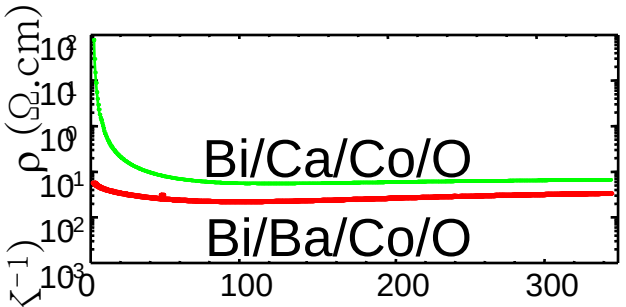
S =100 µV / K & $\rho = 10^{-2}$ Ω cm at 300K

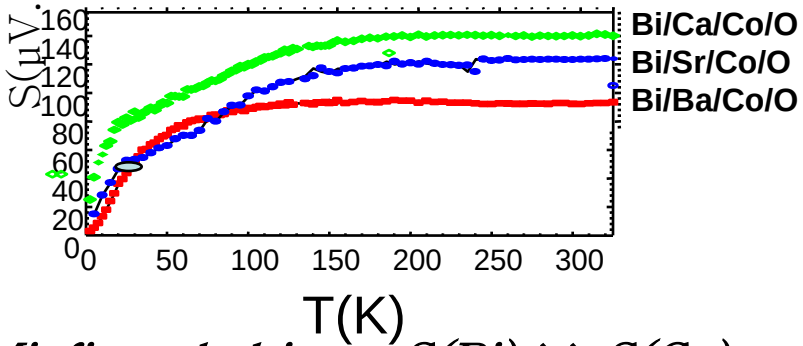
S increases with respect to

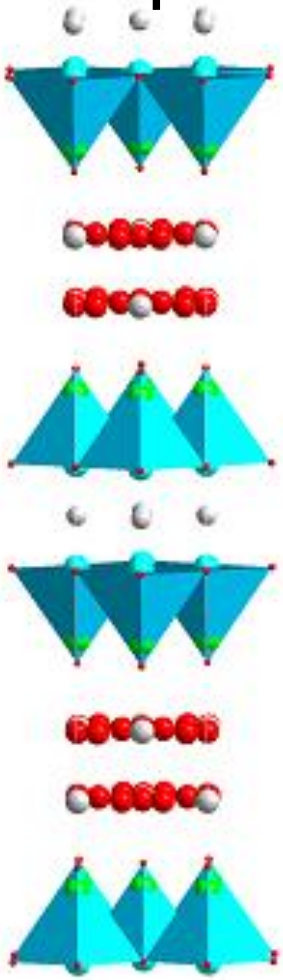
$[Ca_2CoO_3][CoO_2]_{1.62}$

Electronic structure of the counter cation : lone pair of Bi^{3+}









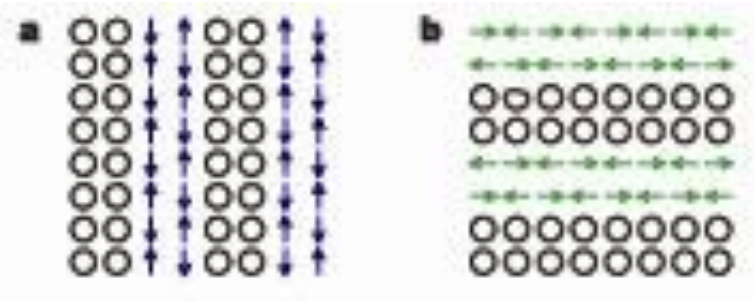
Tc Bi 2212 >> Tc 0212

Misfit cobaltites : S(Bi) >> S(Ca)

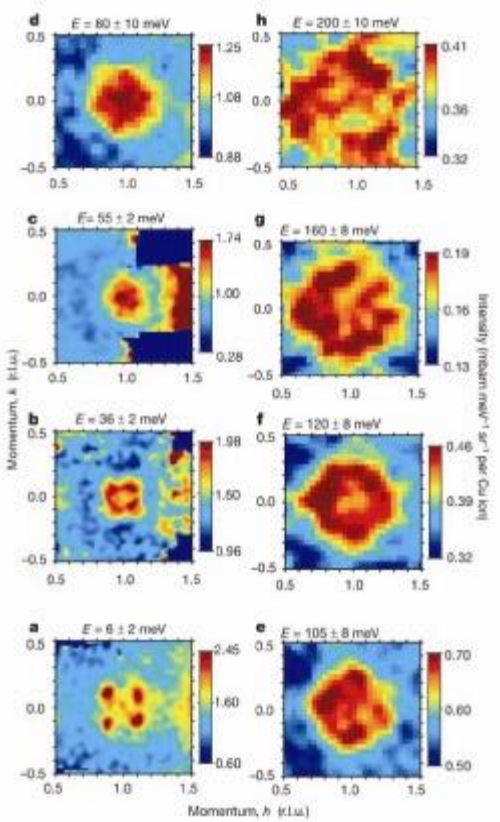
A. Maignan et al., J. Phys. Cond. Mat. 15. 2711. (2003)
M. Hervieu et al., Phys. Rev. B 67, 045112, (2003)

High Tc cuprates : stripes in $La_{2-x}Ba_xCuO_4$

Neutron scattering : *hole doped Cu stripes alternate with undoped AFM Cu rows (spin ladders)*

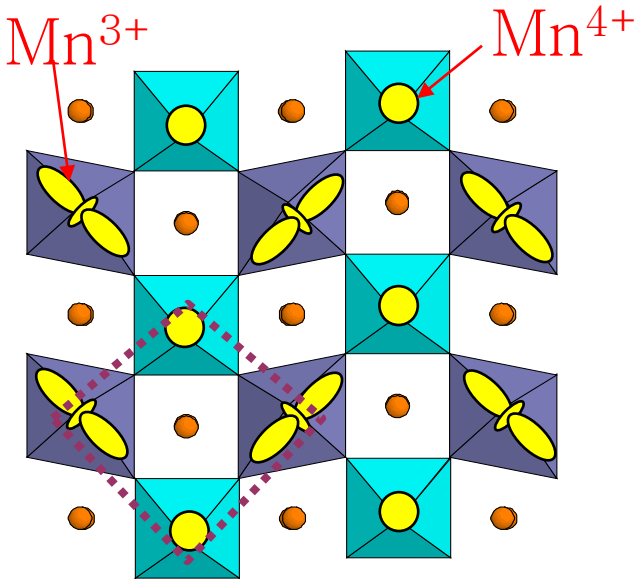


Constant energy slices through the measured Scattering at 12K for different neutron energies Showing coexistence of stripes with AFM Regions & evolution from incommensurate to Commensurate ordering of the stripes



J.M.Tranquada et al Nature, 429, 534 (2004)

CMR Manganites : Stripes in $Pr_{0.5}Ca_{0.5}MnO_3$

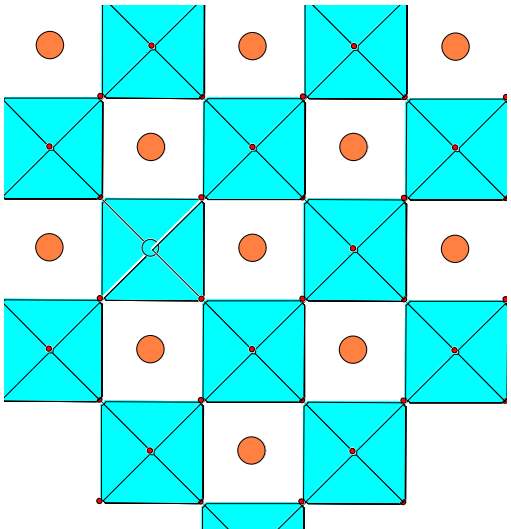


Charge and Orbital Ordering

Jahn Teller effect

Insulating antiferromagnet

H >25 T



metallic ferromagnet

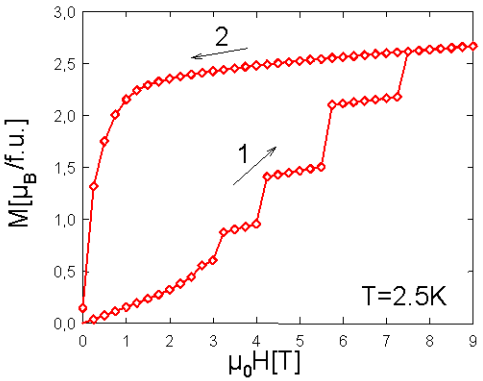
Double Exchange

Mn^{3+} O Mn^{4+}

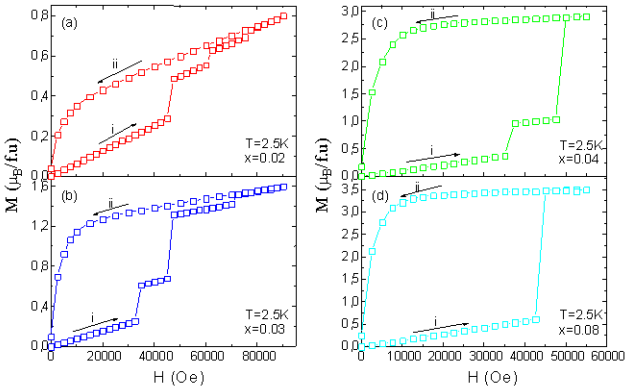
Phase Separation in Manganites

$Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$ at 2.5K

Magnetization M

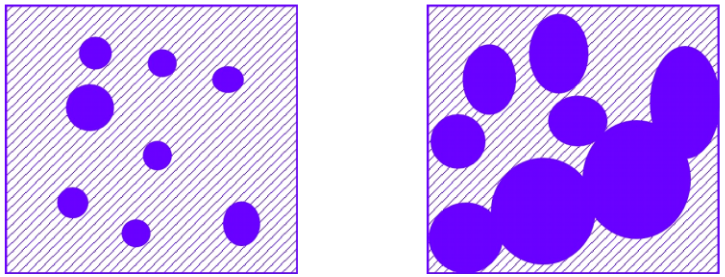


$Pr_{0.5}Ca_{0.5-x}Ba_xMnO_3$



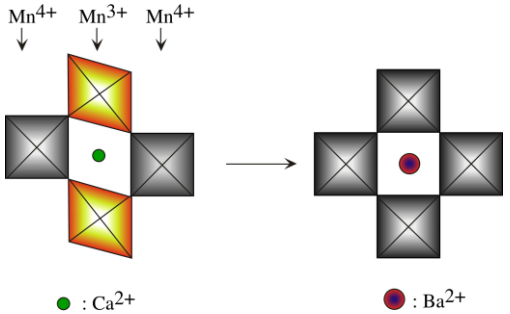
Phase separation scenario

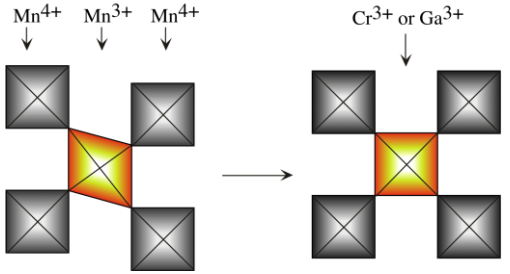
Darkened regions correspond to ferromagnetism which develops around Ga ions in the AFM matrix



a) x = 0.02 FM "clusters"

b) x = 0.05, the FM regions expand and tend to percolate





FM more symm than AFM

Stress at the boundary : Martensitic phenomenon

Phase Separation in High Tc cuprates : electronic « cluster glass »

STM observations in underdoped $Bi_2Sr_2Dy_{0.2}Ca_{0.8}Cu_2O_{8+\delta}$ (atomic-resolution tunneling-asymetry imaging)

« Intense spatial variations in tunneling asymmetry

Occuring at the planar oygen sites ;their spatial

Arrangement appears to be a Cu-O-Cu bond centered

Electronic glass with $4a_0$-wide electronic domains

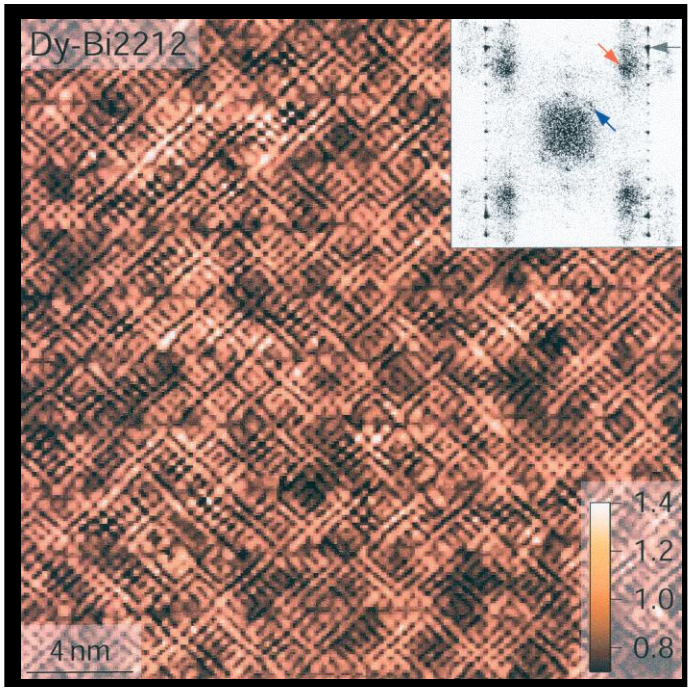
Dispersed throughout. »

Competition between locaisation of holes in an intrisic

Electronic glass and delocalisation in a simple band

Which supports the highest Tc

Y.Kohsaka et al

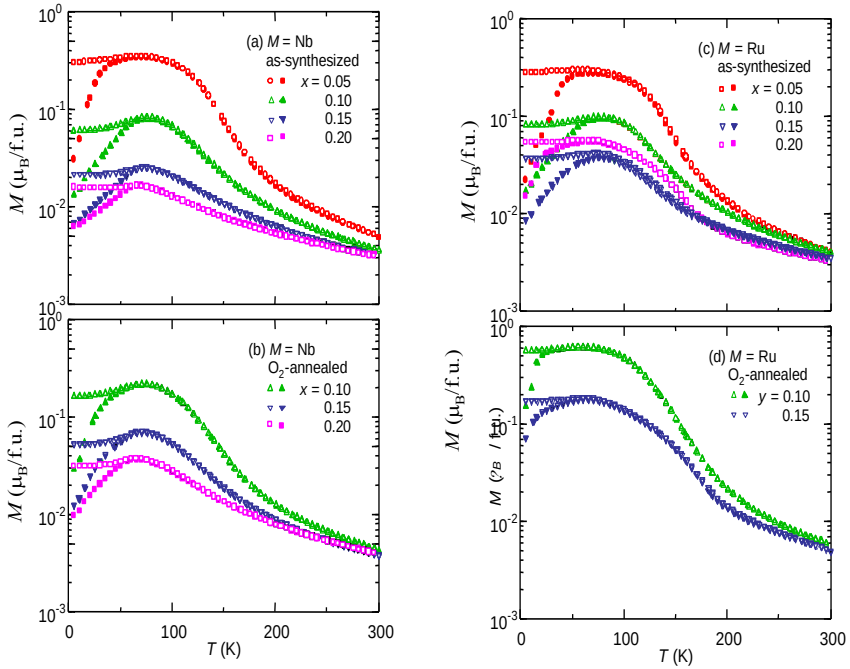


50 nm square R map taken at 50 V

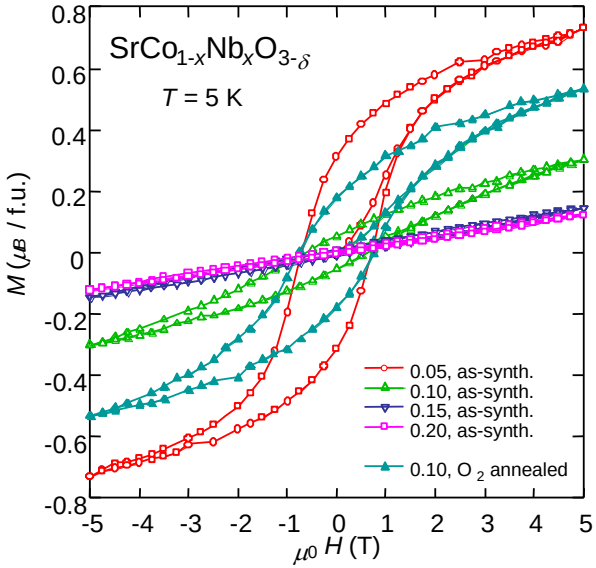
Phase Separation in Cobaltites

Competition between ferromagnetism and spin glass in oxygen deficient perovskites $SrCo_{1-x}M_xO_{3-\delta}$ $M = Nb,\ Ru$

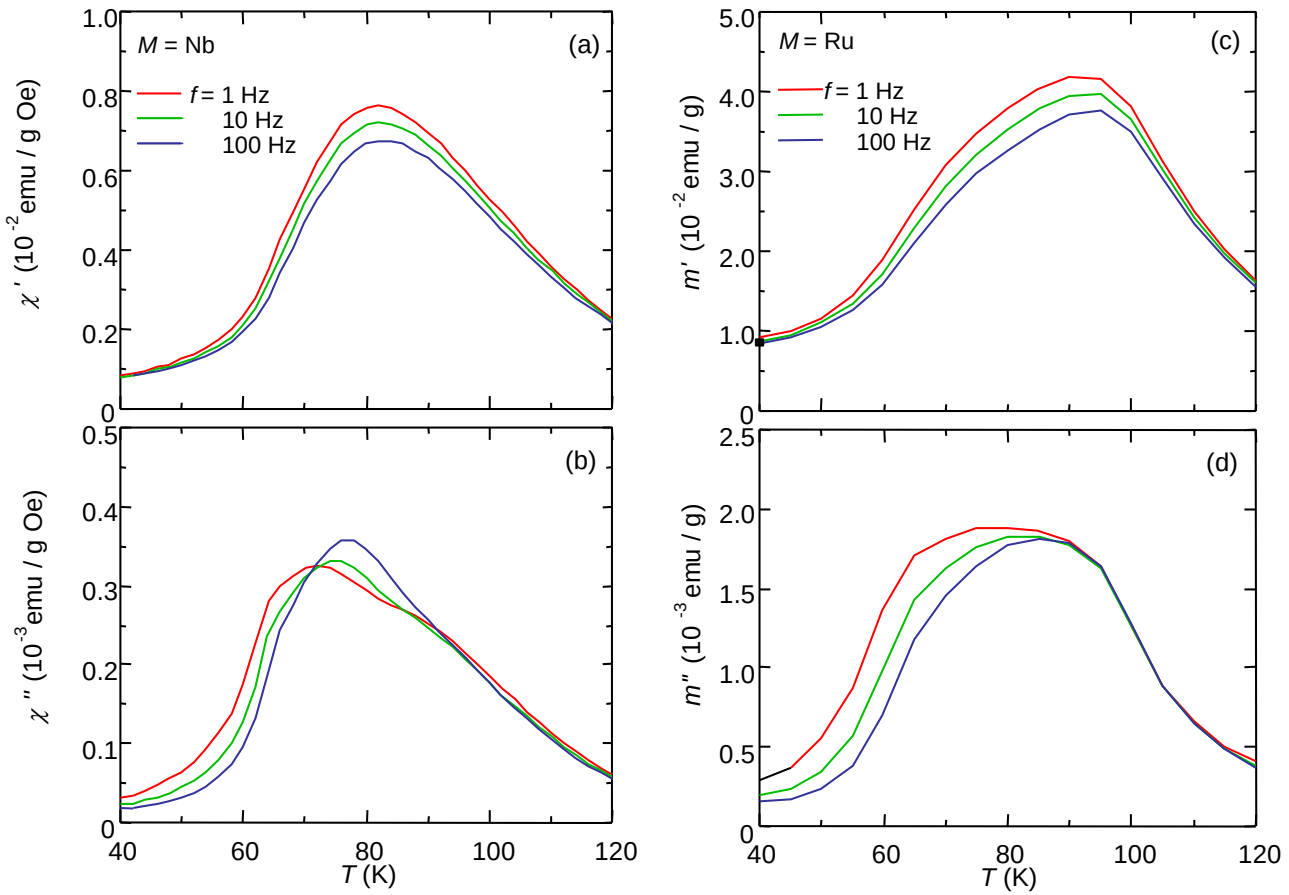
Magnetoresistance at low temperature



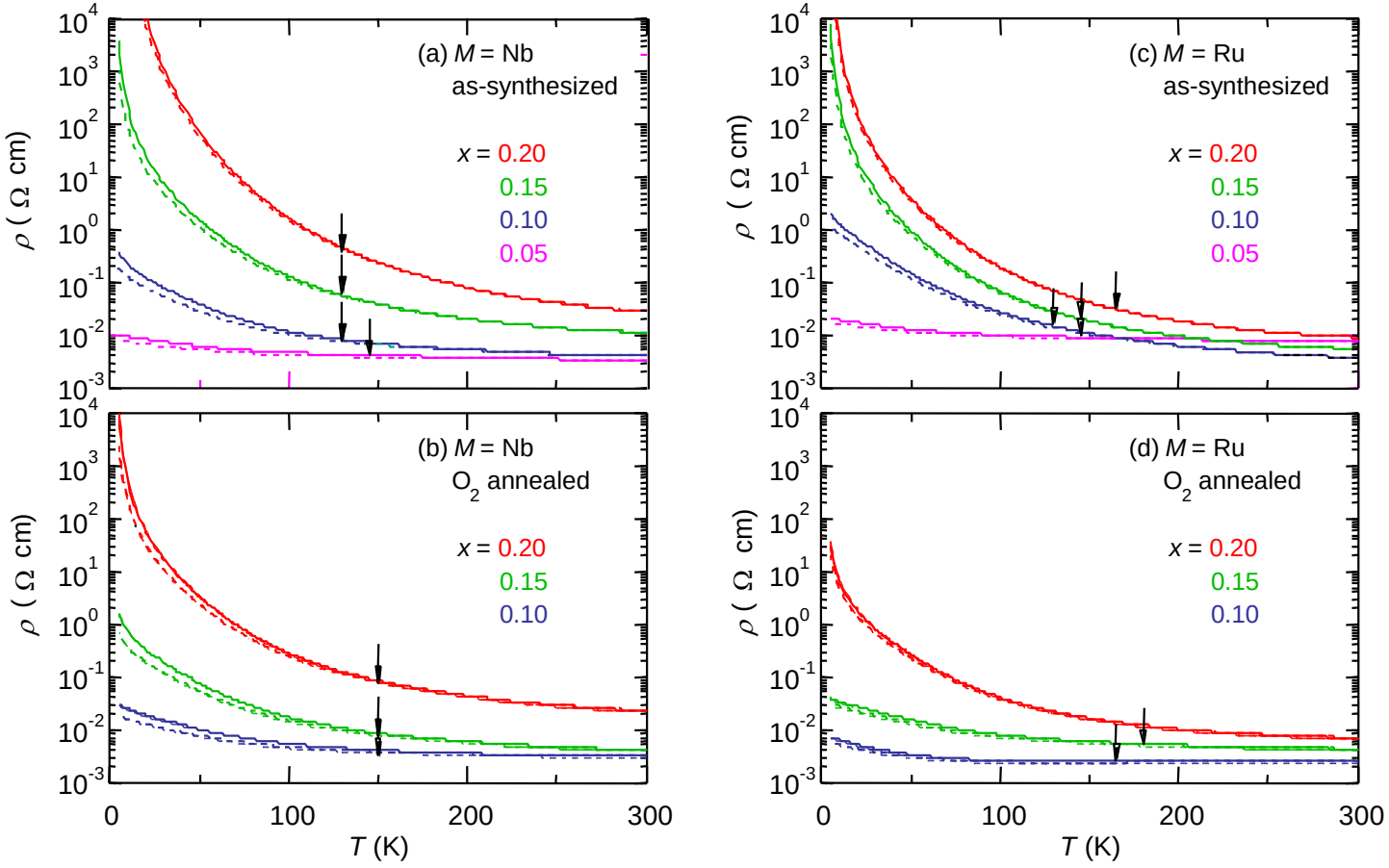
M(T) vs x for $SrCo_{1-x}Nb_xO_{3-\delta}$ and $SrCo_{1-x}Ru_xO_{3-\delta}$ recorded in 0.3 T



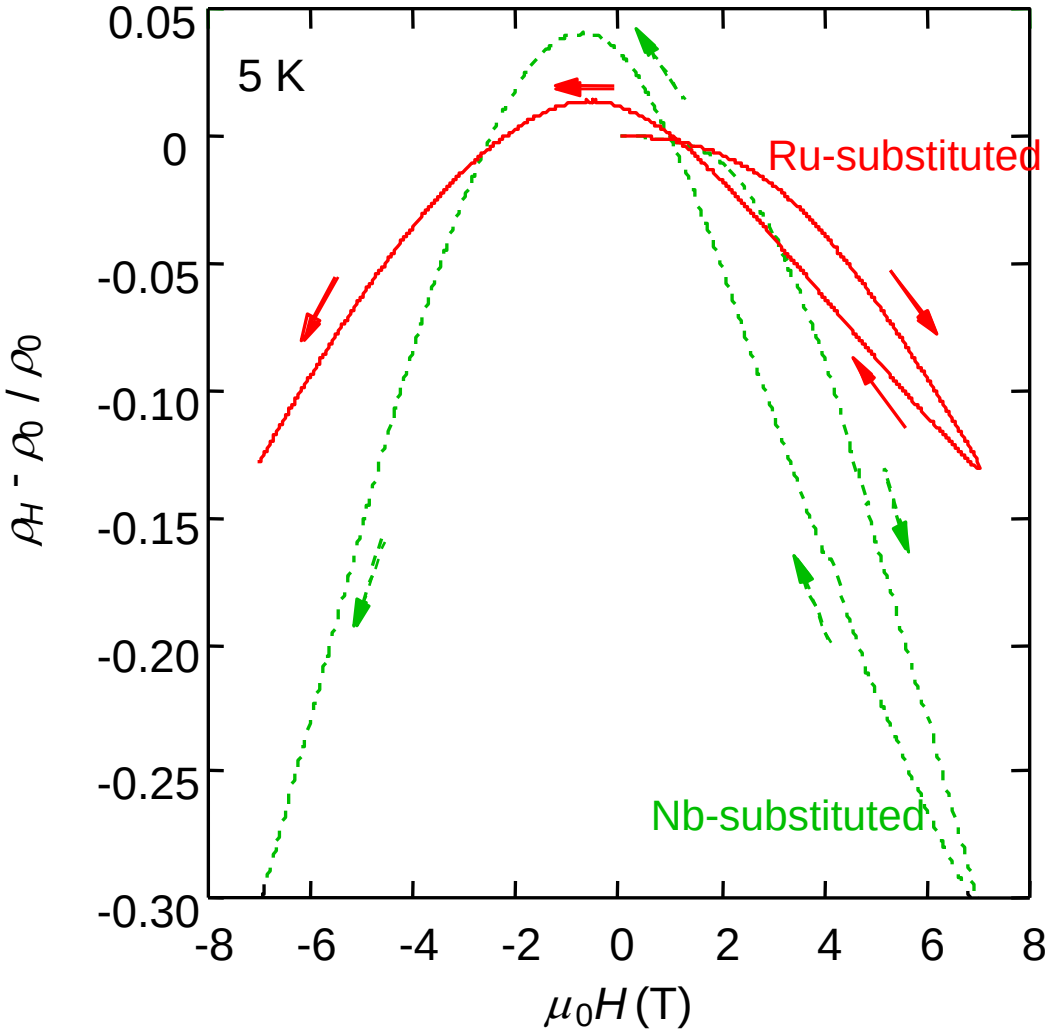
M(H) loops for $SrCo_{1-x}Nb_xO_{3-\delta}$ at 5 K



ac- susceptibility vs T for O_2 - annealed $SrCo_{0.9}Nb_{0.10}O_{2.76}$ and $SrCo_{0.90}Ru_{0.10}O_2$, recorded under 3 Oe



ρ (T) curves for $SrCo_{1-x}Nb_xO_{3-\delta}$ and $SrCo_{1-x}Ru_xO_{3-\delta}$ recorded in 0 T (continuous line) and 7 T (dashed line)



Magnetoresistance of O_2 – annealed $SrCo_{0.85}Nb_{0.15}O_{2.78}$ and $SrCo_{0.85}Ru_{0.15}O_2$

Some conclusions

- Ferromagnetism $\Longleftrightarrow$ Co^{4+} (oxygen content)
- Spin Glass $\Longleftrightarrow$ Nb(Ru) for Co substitution
- MR$\Longleftrightarrow$ competition between FM and SG
- $Nb^{5+}(d^0)$ does not participate to conduction
- $Ru5+(d^3)$ impurity band(Ru 4d hybridisation)

$\square$ ρ(Ru) < ρ (Nb)

$\blacktriangleright$ Ru-band deteriorates spin scattering

- MR-Ru <MR-Nb

PERSPECTIVES

Cobaltite misfits : ***oxygen nonstoichiometry***
A cation vacancies
intergrowths
new A cations

Cuprate misfits : ***with Bi, Tl, Hg***

Other triangular lattices : ***pyrochlores***
delafossites etc..

Soft chemistry, nanochemistry
electrochemistry, thin films

Go back to ladder cuprates using electrochemistry
To change Cu valency & ladder distances


my-Sweet-nuages