Effects of an heterogeneous distribution of the oxidation states on the magnetic properties of transition metal oxide.

◊ $SrFe_{0.5}Co_{0.5}O_{2.5+y}$ *(Chem. Mater., (2012), 24, 1128–1135)*

◊ Phase 1212 $(Mo_xCu_{1-x})Sr_2LnCu_2O_{7+y}$ *(J. Solid State Chem. (2012) 191, 40-45)*

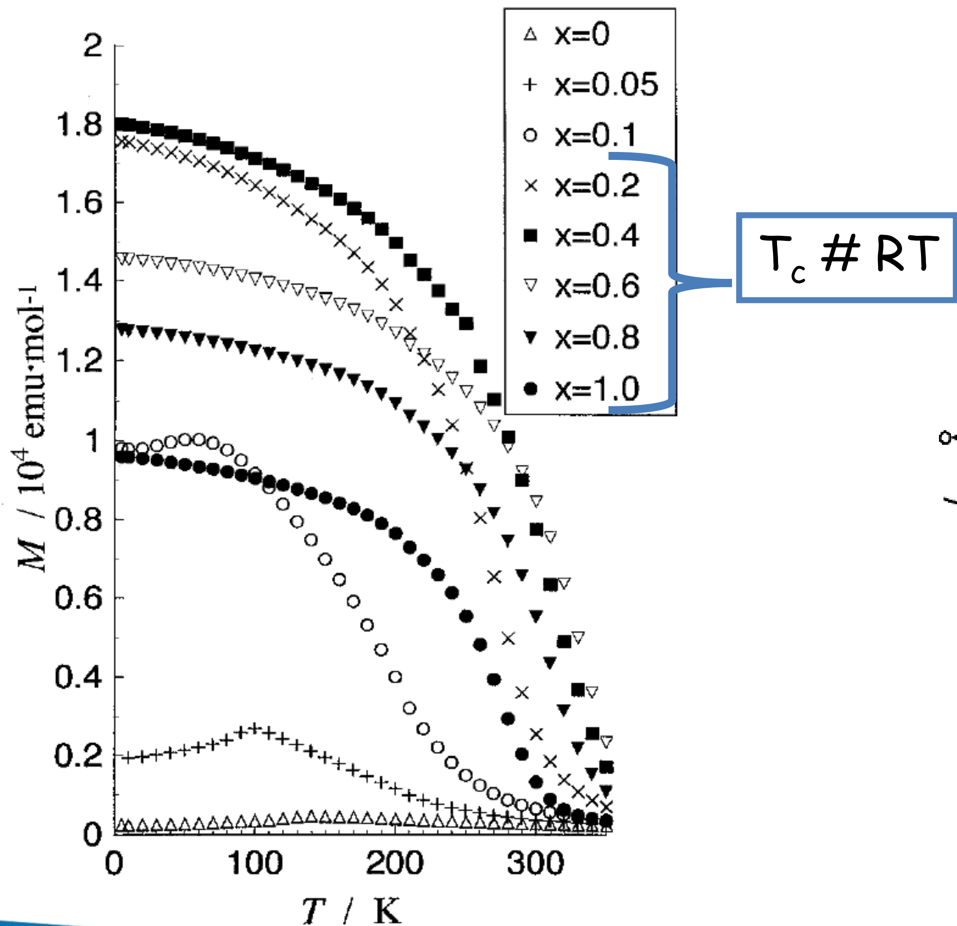
O. Toulemonde

Institut de Chimie et de la Matière Condensée de Bordeaux - CNRS
Université de Bordeaux I

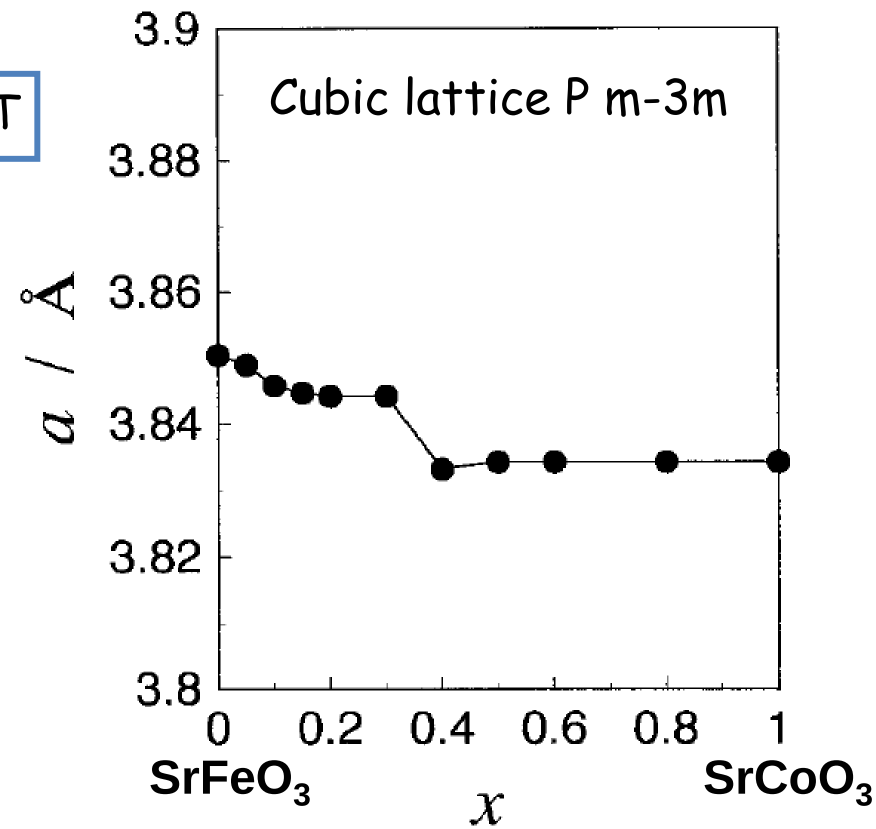
JOURNAL OF SOLID STATE CHEMISTRY **121**, 174–180 (1996)

Ferromagnetic Properties of $SrFe_{1-x}Co_xO_3$ Synthesized under High Pressure

S. Kawasaki,* M. Takano,* and Y. Takeda†



10 wt% of $KClO_4$ /
6 GPa at 600°C for 30 min

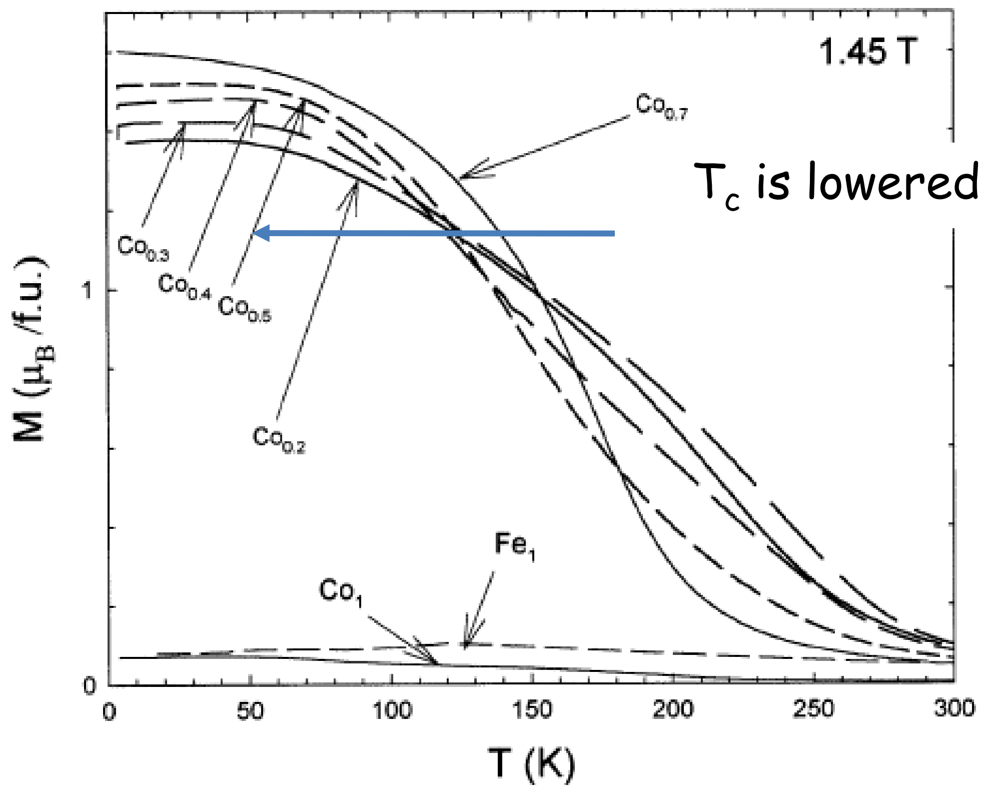


Solid State Sciences 3 (2001) 57–63

Magnetoresistance in the ferromagnetic metallic perovskite $SrFe_{1-x}Co_xO_3$

Antoine Maignan *, Christine Martin, Ninh Nguyen, Bernard Raveau

Post-annealled in oxygen pressure of "**only 15 Mpa**"



Solid State Sciences 3 (2001) 57–63

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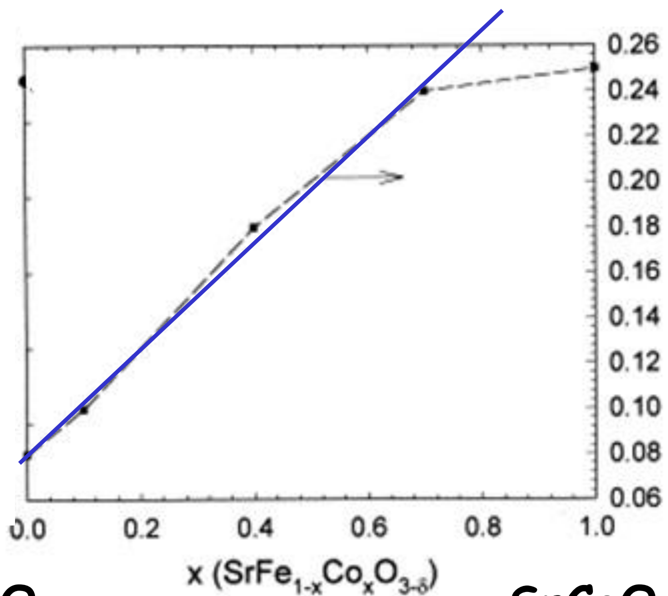
Post-annealled in oxygen pressure of "**only 15 Mpa**" → oxygen vacancies y



0.25

y

0.42

$SrFeO_{2.5+0.42}$ $SrCoO_{2.5+0.25}$

- The oxygen deficiency y increases continuously with the cobalt content until x=0.7

Solid State Sciences 3 (2001) 57–63

Magnetoresistance in the ferromagnetic metallic perovskite $SrFe_{1-x}Co_xO_3$

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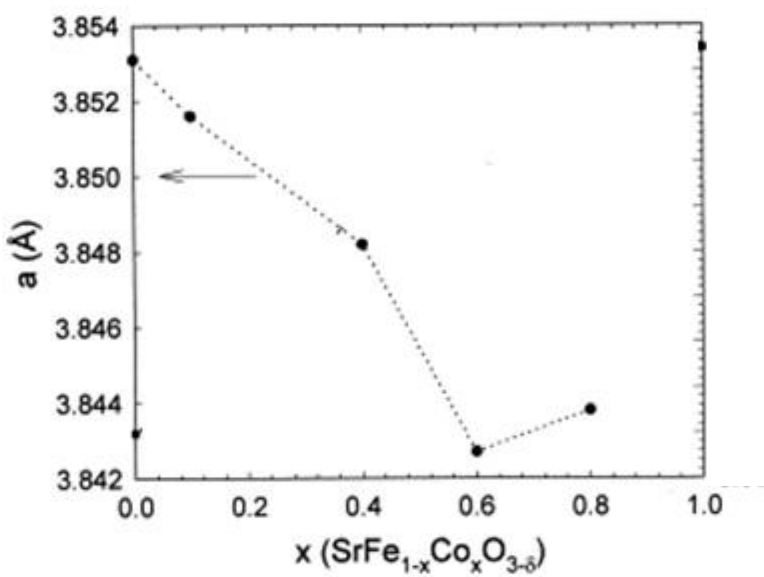
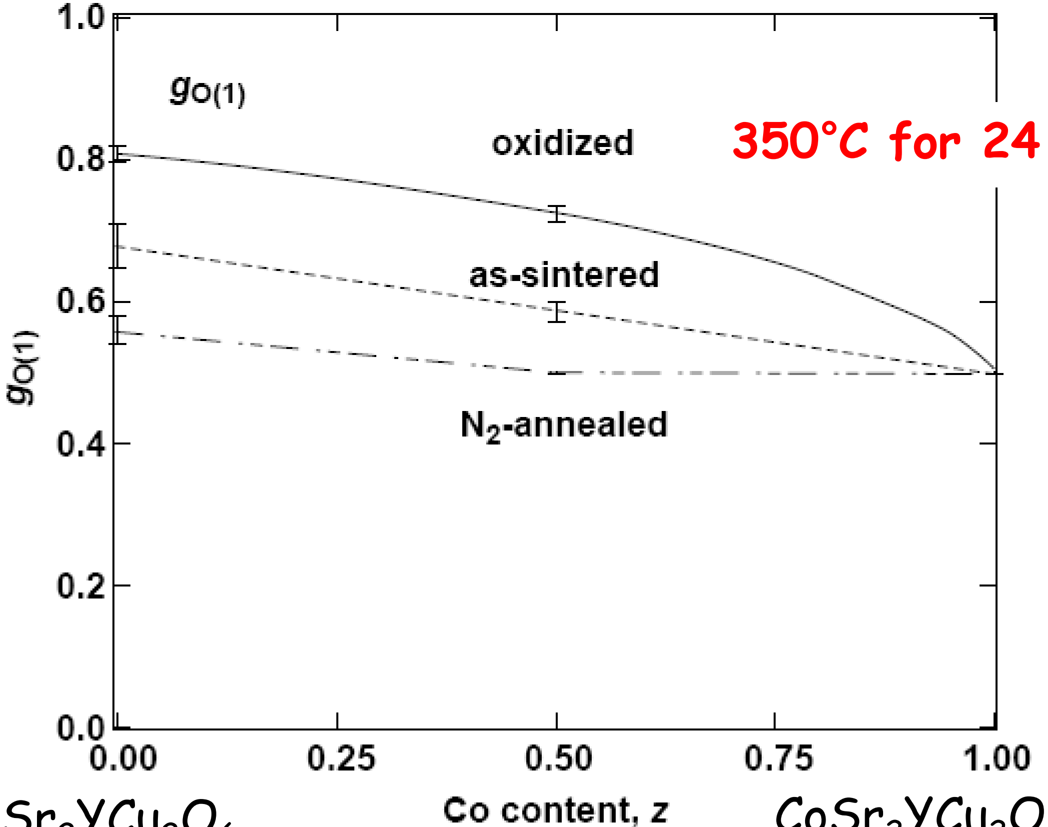


- Cubic lattice is kept ↔ oxygen vacancies disordering

Cu 1212 phase : $(Fe_{1-z}Co_z)Sr_2YCu_2O_{6+y}$

The occupation factor of oxygen at the O(1) site in the CuO chain



350°C for 24 h O_2 / 190 atm ~19 Mpa

✓Oxidation of cobalt cations requires higher oxygen pressure than for iron oxidation

$FeSr_2YCu_2O_{6+y}$ $CoSr_2YCu_2O_{6+y'}$

Journal of Physics: Conference Series **150 (2009) 052166**

✓The oxidation of cobalt cations requires higher oxygen pressure than for iron

✓Does any random distribution of the oxidation states occur (with Fe^{4+} >> Co^{4+}) on mixed Fe/Co materials $SrFe_{0.5}Co_{0.5}O_{2.5+y}$?

OR

✓Does the ratio Fe^{4+}/Co^{4+} is equal to 1 suggesting a charge transfer phenomenon

$$Co^{3+} + Fe^{4+} \leftrightarrow Co^{4+} + Fe^{3+}$$

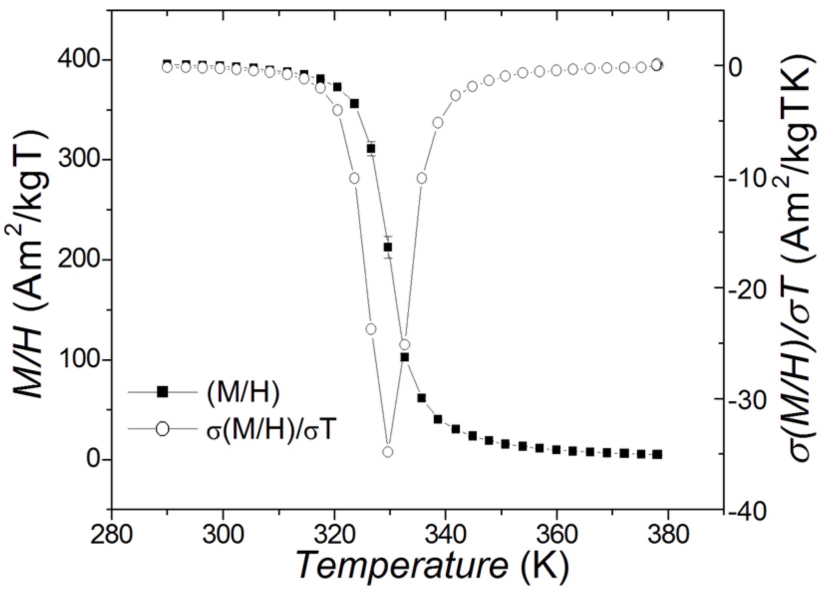
✓ What would be the consequence on the magnetic properties, electronic conductivities ?

✓ $SrFe_{0.5}Co_{0.5}O_{2.5+y}$ (Standard Solid State synthesis)

- Y = 0.18 as prepared (air / 1050°C)
- Y = 0.25 post annealed O_2 / 600°C
- Y = 0.33 Room Temperature Electrochemical oxidation process
- $y \rightarrow 0.5$ RT Electrochemical oxidation process

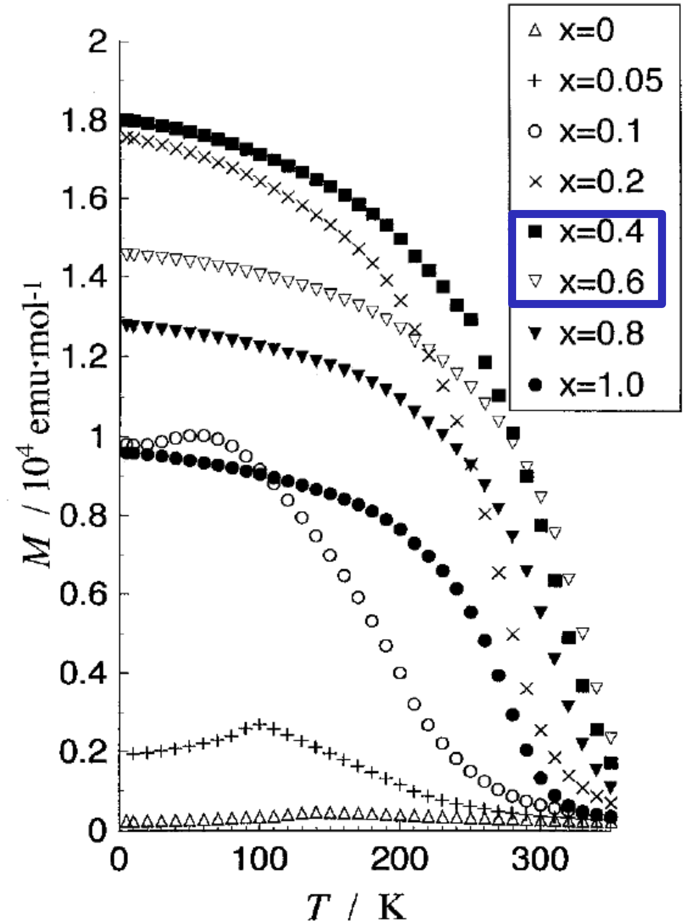
Oxygen deficiency controlled by Mohr Salt Tm^{4+} titration

$SrFe_{0.5}Co_{0.5}O_3$ / T_C = 330K
Oxidized with electrochemical set up



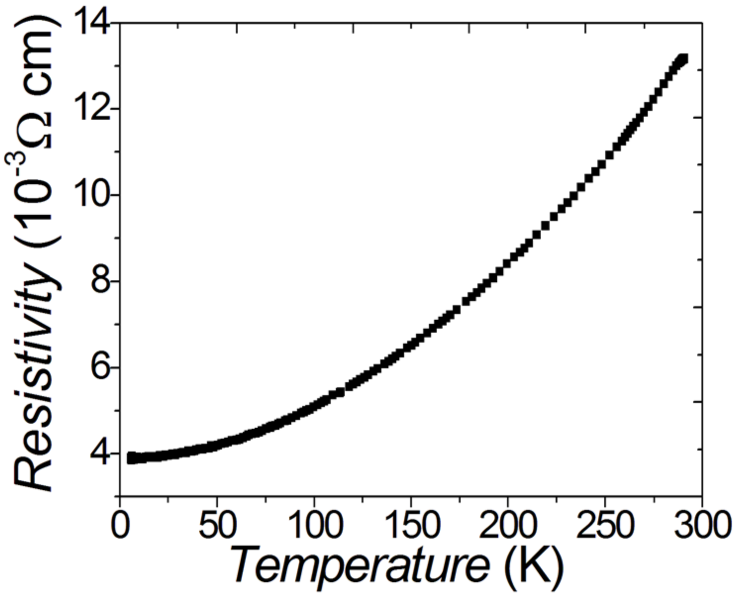
JSSC 184, 3228 (2011)

$SrFe_{1-x}Co_xO_3$
Oxidized with oxygen HP set up



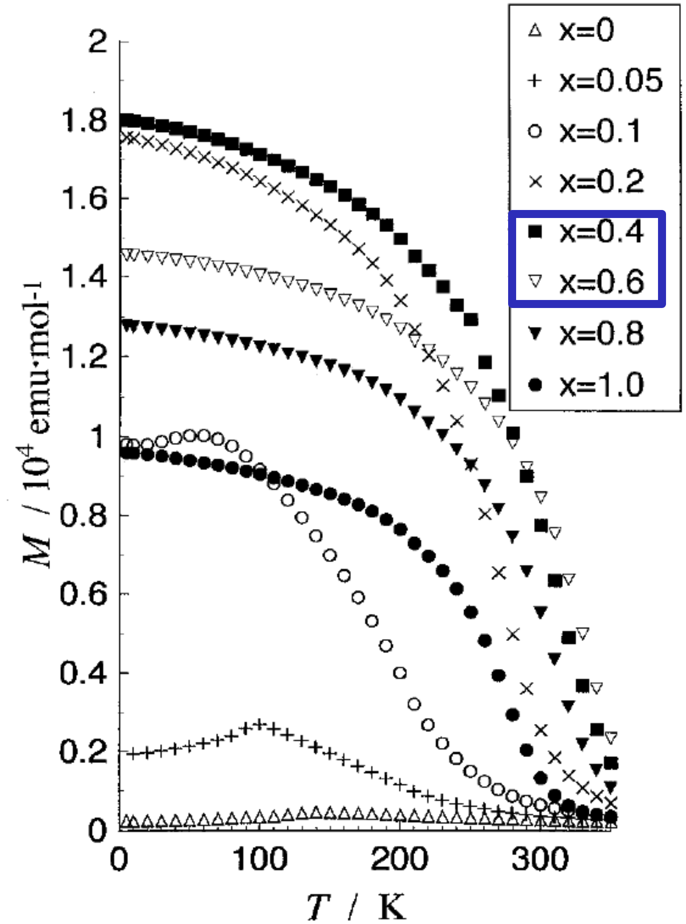
JSSC 121, 174 (1996)

$SrFe_{0.5}Co_{0.5}O_3$ / T_C = 330K
Oxidized with electrochemical set up



JSSC 184, 3228 (2011)

$SrFe_{1-x}Co_xO_3$
Oxidized with oxygen HP set up



JSSC 121, 174 (1996)

✓OUTLINE

$SrFe_{0.5}Co_{0.5}O_{2.5+y}$ (0.18<y<0.33)

Structure-Property Relationships In Solid State Materials

→ Structure crystalline and electronic (oxidation state)

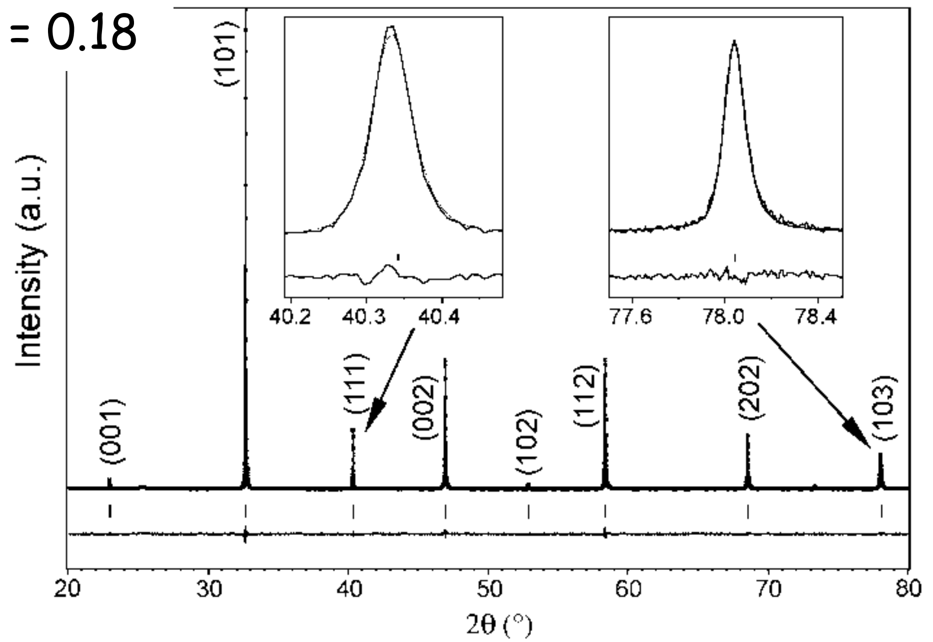
- X-Ray & Electron diffractions studies versus oxygen deficiency
- Mossbauer Spectroscopy + Mohr Salt titration → Chemical formulas
- Magnetization versus oxygen deficiency
- Conclusions & remarks

XRD paterns / Cubic symetry
P m-3m

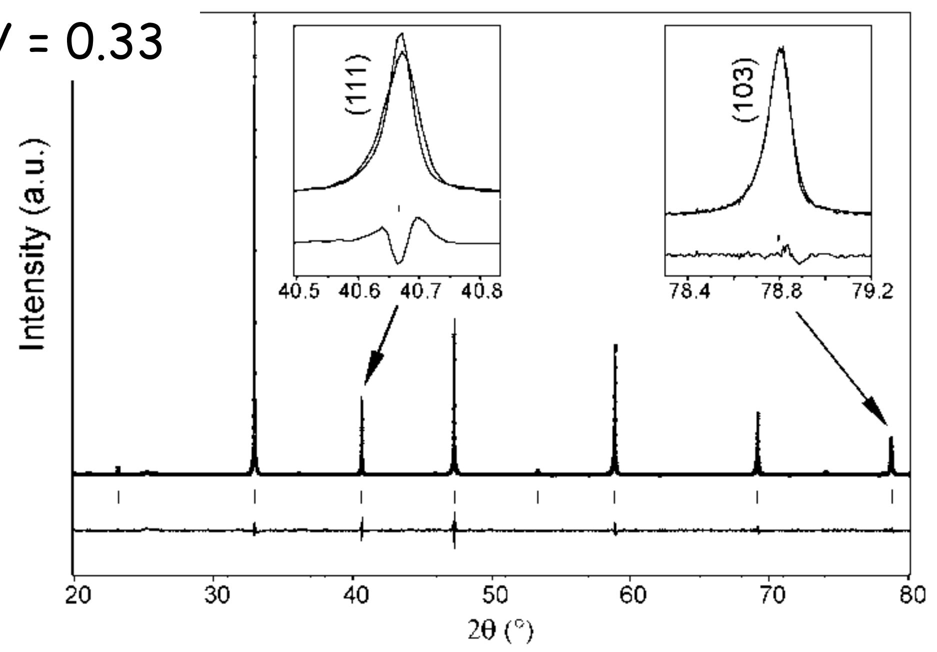
y	Lattice parameter (Å)
0.18	3.86833(4)
0.25	3.85794 (5)
0.33	3.83611 (11)
0	3.8335(1)

✓The broadening of the peaks does not concern the same crystallographic directions and cannot be attributed to an usual cell distortion.

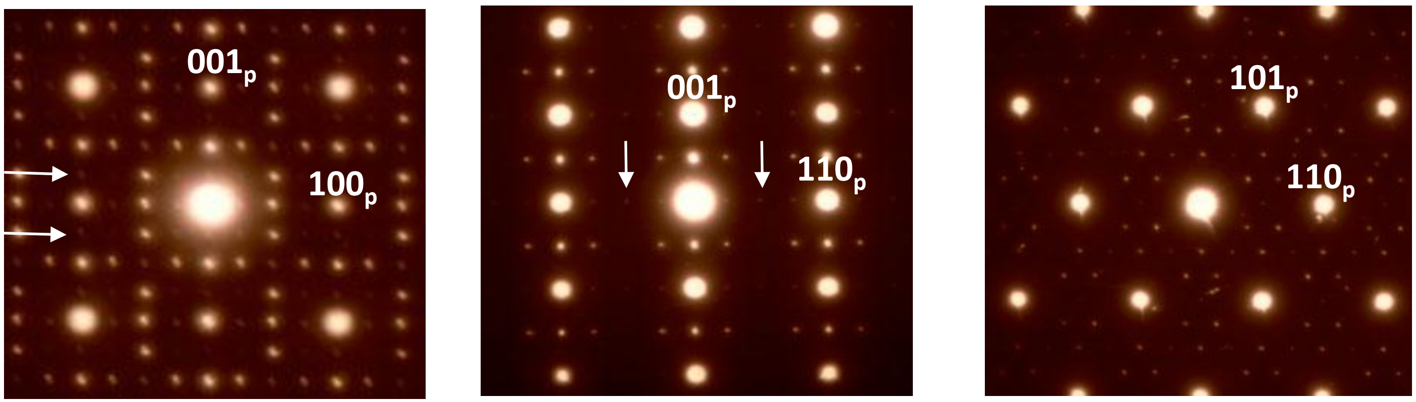
Y = 0.18



Y = 0.33



$SrFe_{0.5}Co_{0.5}O_{2.68}$ Oxygen vacancies Ordering Phenomenon

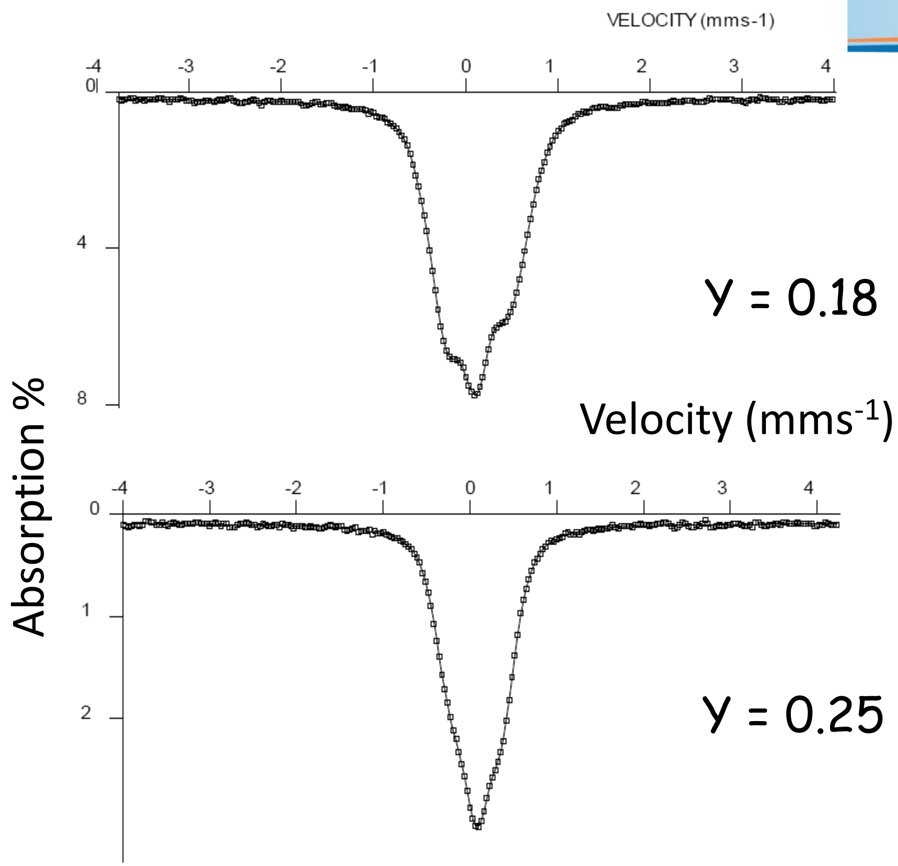


$\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$: Anion vacancies ordering

As expected, the oxygen vacancies ordering related to

- $Sr_3LnCo_4O_{10.5}$ (the so-called "314" phase) stacking sequence of O_h-T_d
- $Sr_4Fe_4O_{11}$ phase / stacking sequence of O_h-SbPy

Susana Garcia-Martin « Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, Madrid 28040, Spain »



Mossbauer Spectroscopy Study:

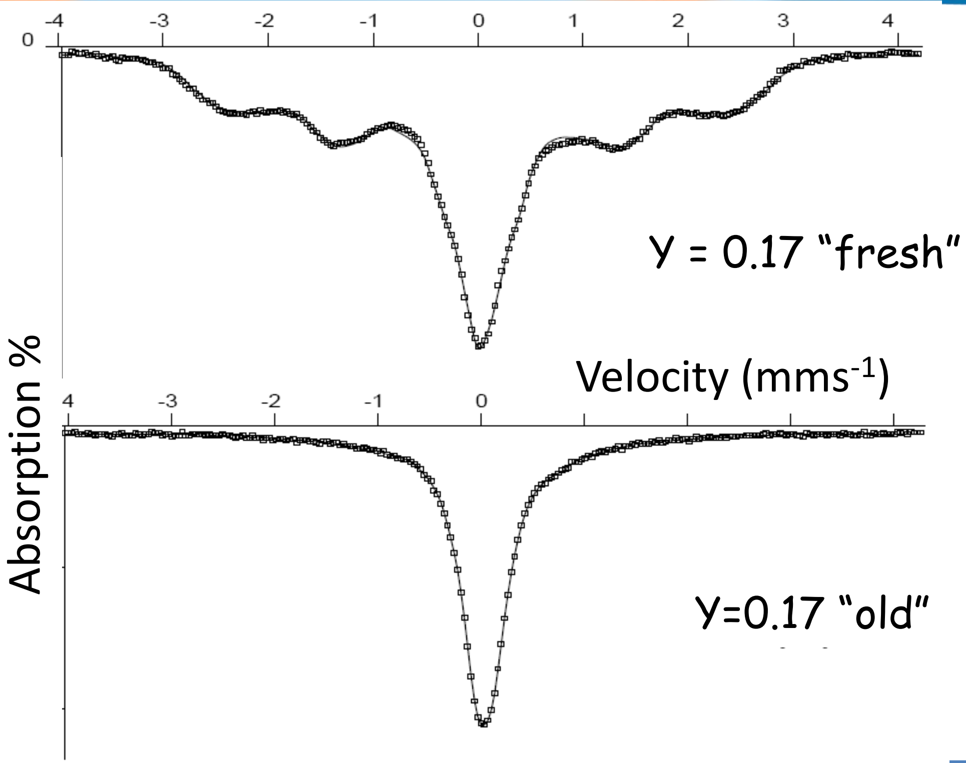
a large content of Fe^{4+} is highlighted

Mohr Salt titration Tm^{4+}
RT Mossbauer Spectroscopy

Studied Samples	DIS	δ (mm.s^{-1})	Relative Abundance (%)
Y = 0.18	A	0.11	44
	B	0.15	56
Y = 0.25	A	0.09	33
	B	0.11	67

$Sr^{2+}Fe^{3+}_{0.14}Fe^{4+}_{0.36}Co^{3+}_{0.50}O_{2.68\pm0.02}$

$Sr^{2+}Fe^{3+}_{0.10}Fe^{4+}_{0.40}Co^{3+}_{0.40}Co^{4+}_{0.10}O_{2.75\pm0.02}$



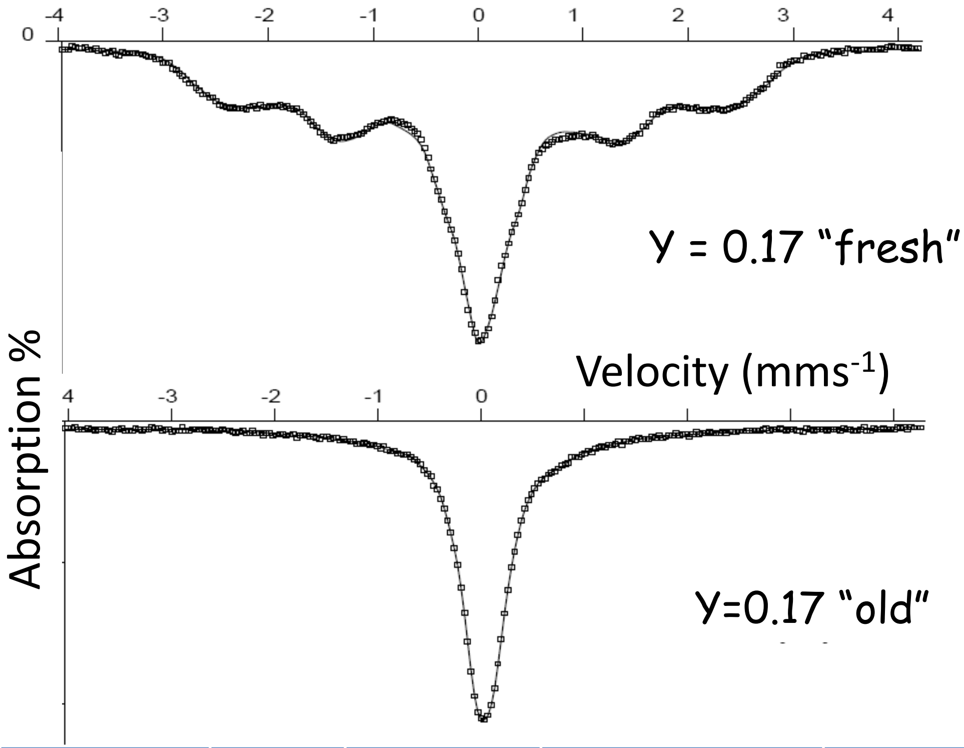
RT Mossbauer Spectroscopy Study:

✓ only Fe^{4+} is present on fresh sample

✓ RT : On the edge the ordered Temperature

✓ Fe^{3+} appears with ageing but remains paramagnetic contrary to Fe^{4+} at RT

Studied Samples y = 0.17	DIS	δ (mm.s^{-1})	Relative Abundance (%)	H_{hf} (T)
fresh	A	0.03	40	/
	B	0.03	60	10.8
old	A	0.04	39	/
	B	0.05	46	0.7
	C	0.39	15	/



Mohr Salt titration Tm^{4+}
RT Mossbauer Spectroscopy

Fresh : $Sr^{2+}Fe^{4+}_{0.50}Co^{3+}_{0.34}Co^{4+}_{0.16}O_{2.83}$

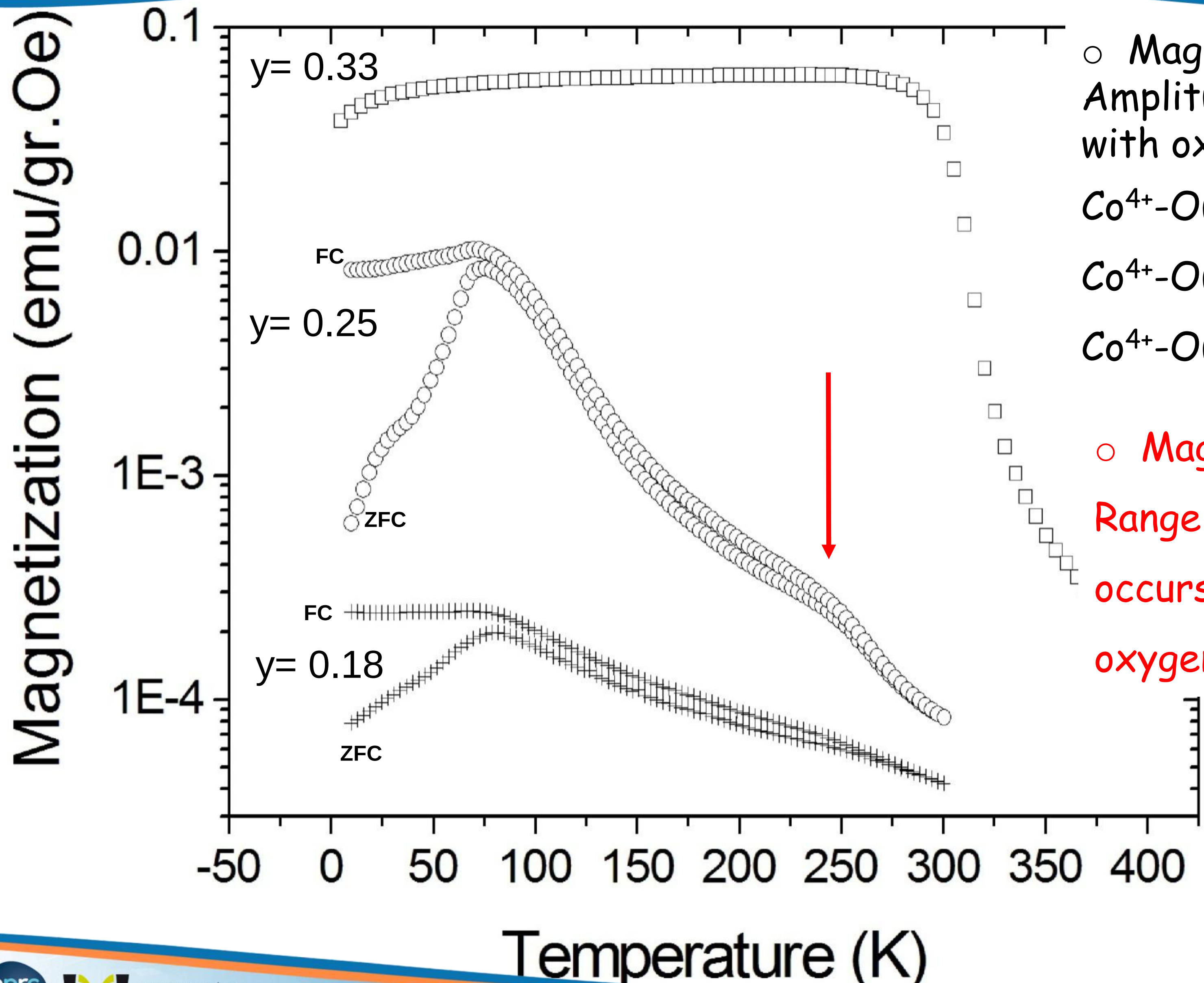
Old :

hypothesis 1
$Sr^{2+}Fe^{4+}_{0.40}Fe^{3+}_{0.10}Co^{3+}_{0.44}Co^{4+}_{0.06}O_{2.73}$

hypothesis 2
$Sr^{2+}Fe^{4+}_{0.40}Fe^{3+}_{0.10}Co^{3+}_{0.34}Co^{4+}_{0.16}O_{2.78}$

Oxygen Content deduced from the proposed cation oxidation state distribution

Studied Samples y = 0.17	DIS	δ ($mm.s^{-1}$)	Relative Abundance (%)	H_{hf} (T)
fresh	A	0.03	40	/
	B	0.03	60	10.8
old	A	0.04	39	/
	B	0.05	46	0.7
	C	0.39	15	/



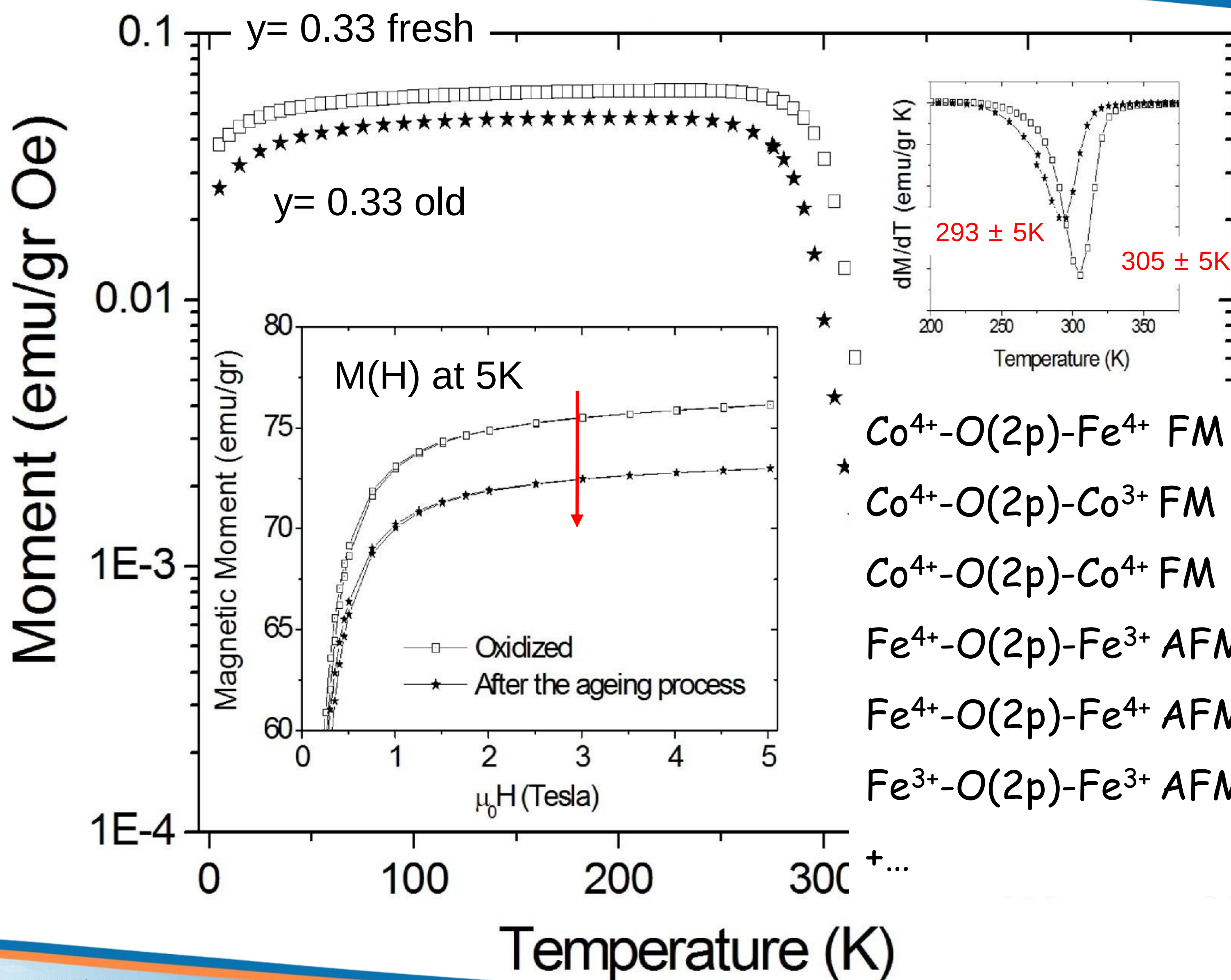
- Magnetization Amplitude increases with oxidation

Co^{4+}-O(2p)-Fe^{4+} FM

Co^{4+}-O(2p)-Co^{3+} FM

Co^{4+}-O(2p)-Co^{4+} FM

- Magnetic Short Range Ordering occurs for high oxygen deficiency.



Co^{4+}-O(2p)-Fe^{4+} FM

Co^{4+}-O(2p)-Co^{3+} FM

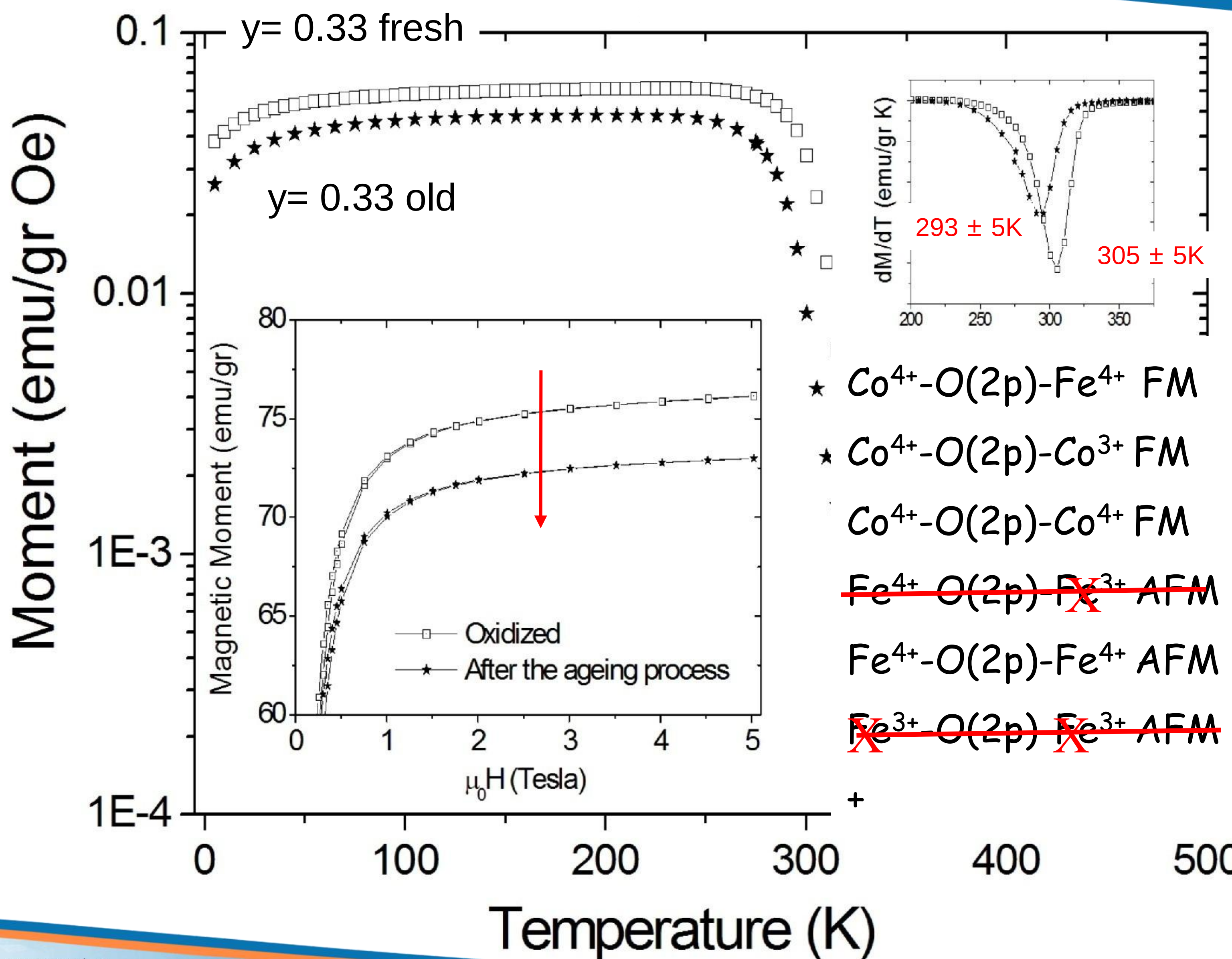
Co^{4+}-O(2p)-Co^{4+} FM

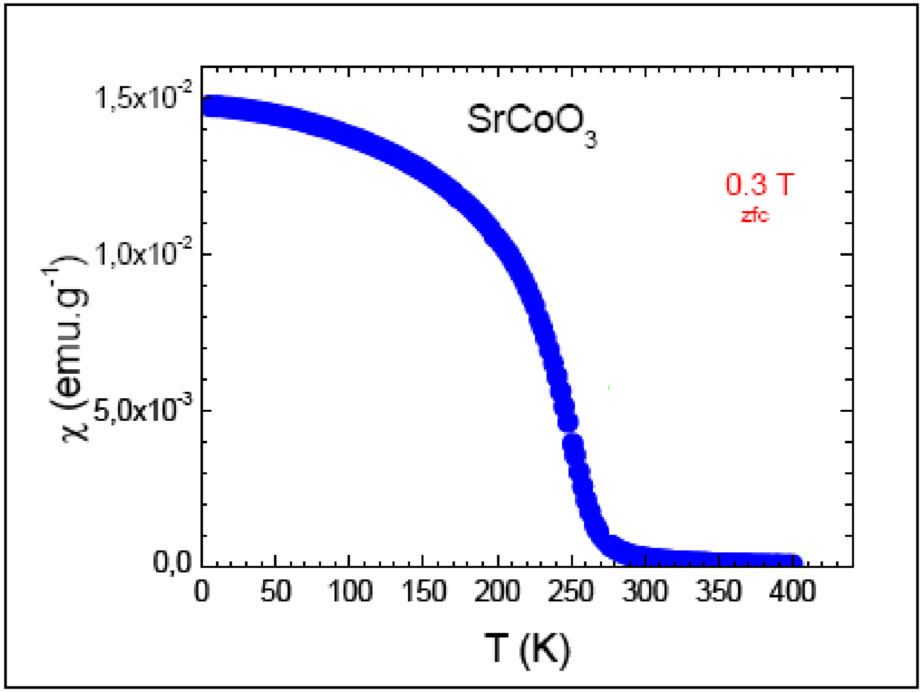
Fe^{4+}-O(2p)-Fe^{3+} AFM

Fe^{4+}-O(2p)-Fe^{4+} AFM

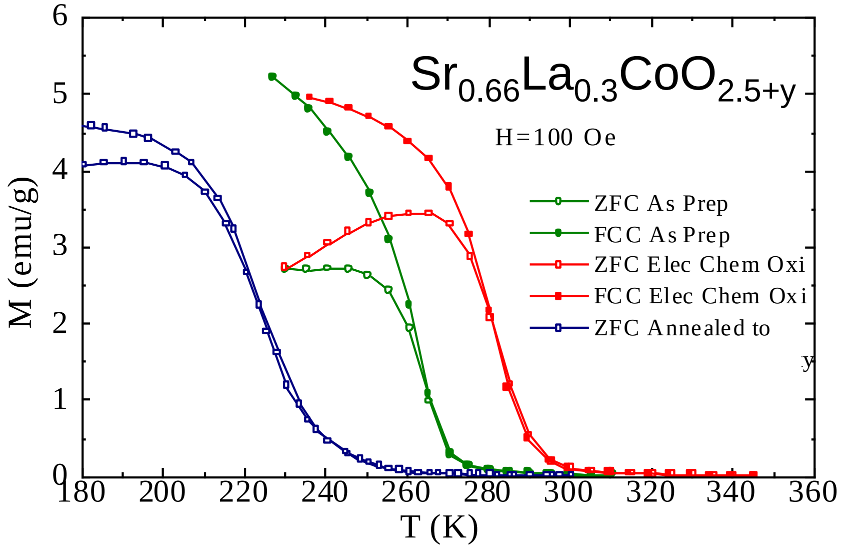
Fe^{3+}-O(2p)-Fe^{3+} AFM

+…


y= 0.33 fresh
y= 0.33 old
Moment (emu/gr Oe)
0.1
0.01
1E-3
1E-4
0
100
200
300
400
500
Temperature (K)
Magnetic Moment (emu/gr)
80
75
70
65
60
μ0H (Tesla)
Oxidized
After the ageing process
dM/dT (emu/gr K)
293 ± 5K
305 ± 5K
200
250
300
350
Co4+-O(2p)-Fe4+ FM
Co4+-O(2p)-Co3+ FM
Co4+-O(2p)-Co4+ FM
Fe4+-O(2p)-Fe3+ AFM
Fe4+-O(2p)-Fe4+ AFM
Fe3+-O(2p)-Fe3+ AFM
+

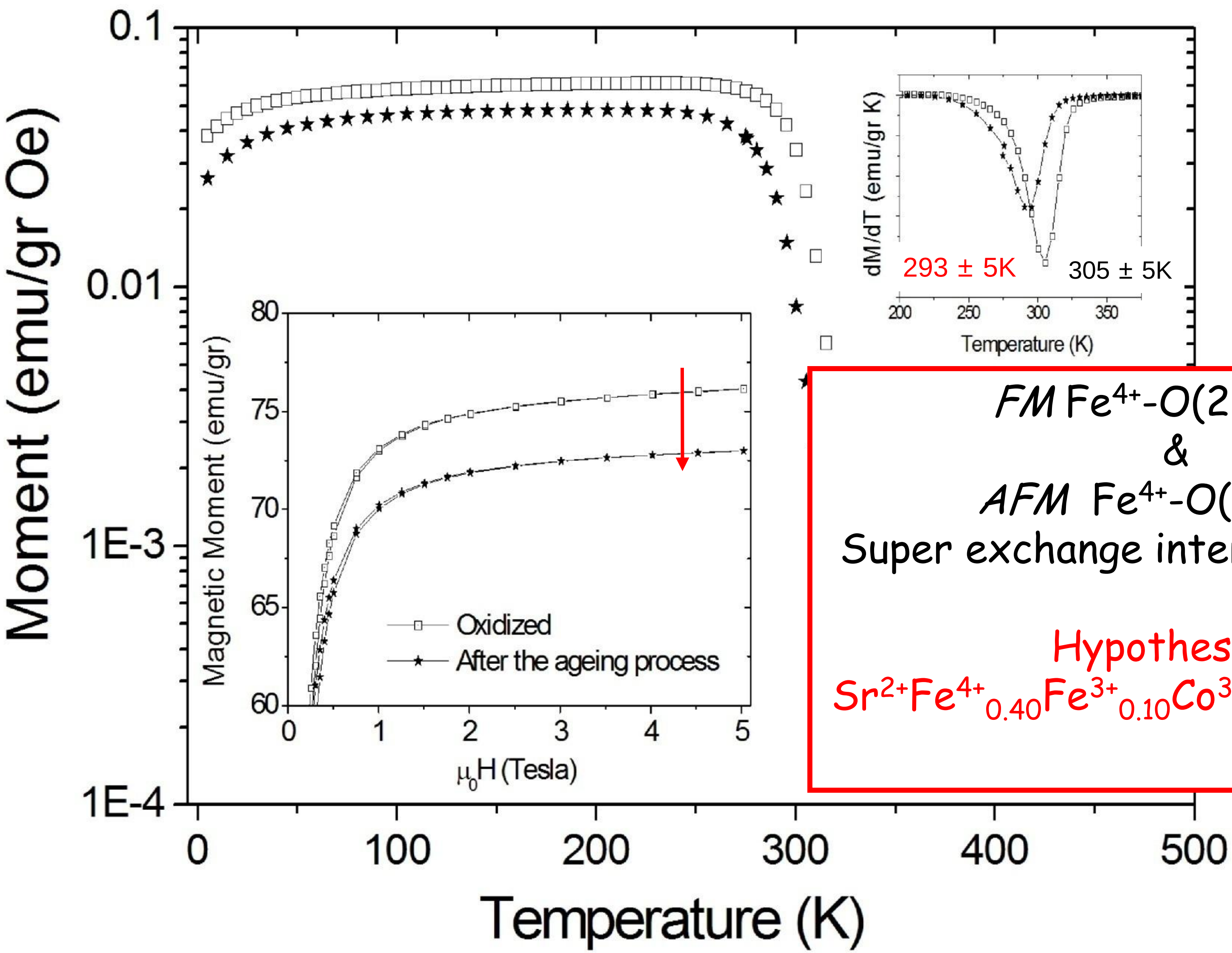


P. Bezdicka, A. - J.C. Grenier - A. Wattiaux
Z. Anorg. Allg. Chem (1993) & Chem. Mater (1999)



M. Chennabasappa & E. Petit (ICMCB)

Co^{3+}-O(2p)-Co^{4+} and Co^{4+}-O(2p)-Co^{4} super exchange give T_c around 275±5K



FM Fe^{4+}-O(2p)-Co^{4+}

&

AFM Fe^{4+}-O(2p)-Fe^{4+}

Super exchange interaction support

Hypothesis 2

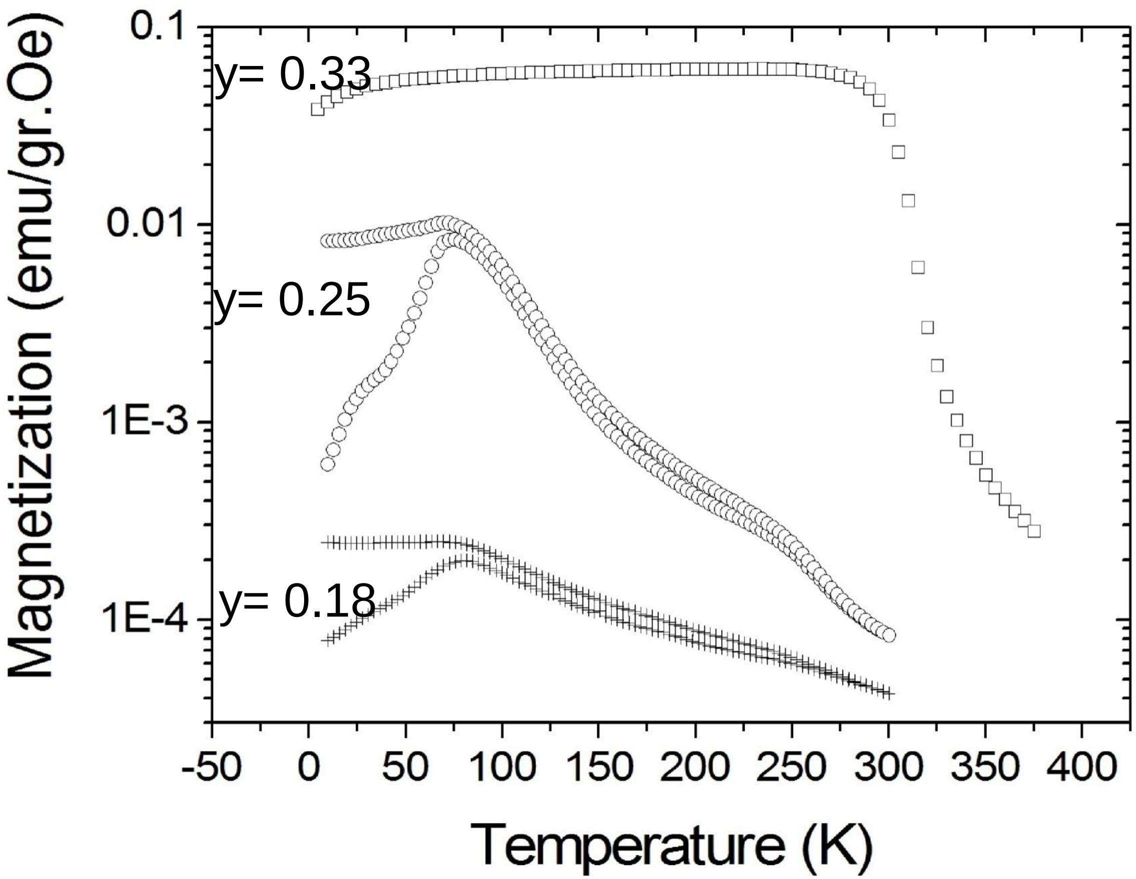
$Sr^{2+}Fe^{4+}_{0.40}Fe^{3+}_{0.10}Co^{3+}_{0.34}Co^{4+}_{0.16}O_{2.78}$

Hypothesis 1 (both Fe^{4+} and Co^{4+} are reduced on the same way)

$Sr^{2+}Fe^{4+}_{0.40}Fe^{3+}_{0.10}Co^{3+}_{0.44}Co^{4+}_{0.06}O_{2.73}$

Hypothesis 2 (Only Fe^{4+} is reduced / the Co^{4+} content is kept)

$Sr^{2+}Fe^{4+}_{0.40}Fe^{3+}_{0.10}Co^{3+}_{0.34}Co^{4+}_{0.16}O_{2.78}$



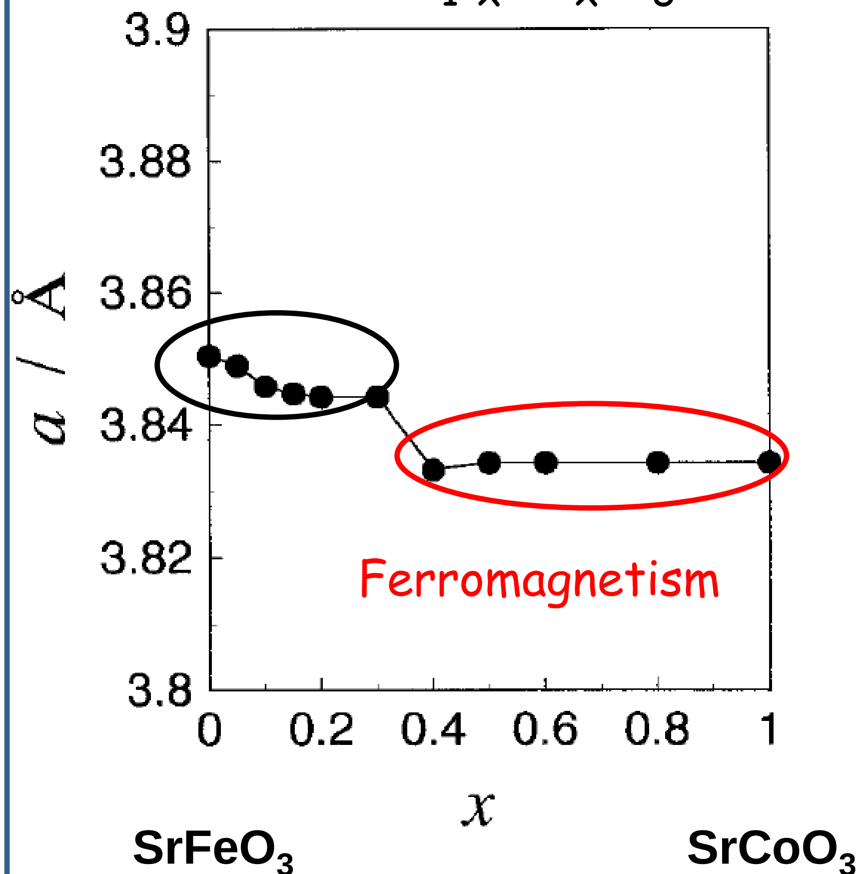
XRD paterns / Cubic symetry P m-3m

$SrFe_{0.5}Co_{0.5}O_{2.5+y}$

y	Lattice parameter (Å)
0.18	3.86833(4)
0.25	3.85794 (5)
0.33 / old	3.8385(2) Å
0.33 / fresh	3.83611 (11)
0	3.8335(1)

Magnetoelastic
effect coinciding with the
magnetic transition ?

$SrFe_{1-x}Co_xO_3$



Kawasaki JSSC 1996

Conclusions on $SrFe_{0.5}Co_{0.5}O_{2.5+y}$

- T_c can be tuned by the oxygen content around RT

- The high T_c of FM transition suggests

  that a significant number of Co^{4+} cations is kept upon reduction (ageing)

- Only Fe^{4+} cations would contribute to the FM interaction at RT.

(temperature dependence of Mossbauer spectroscopy and XMCD are planned).

- The average distribution of Co^{4+} and Fe^{4+} often considered is wrong.

On a synthesis done by an oxidation process : Fe^{4+} content is larger than the Co^{4+} one's.

On a synthesis done by a reduction process ? $SrFe_{0.5}Co_{0.5}O_{2.5} \leftrightarrow SrFe_{0.5}Co_{0.5}O_{2.75} \leftrightarrow SrFe_{0.5}Co_{0.5}O_3$

Effects of an heterogeneous distribution of the oxidation states on the magnetic properties of transition metal oxide.

○ Manganites : $Ln_{0.5}Ca_{0.5}MnO_{3-y}$ Mn↔Co,Ni

From XAS (Ni^{2+} or Co^{2+}) + Mn^{4+} (Toulemonde *Solid State Com. 2001* / Burnus *Phys.Rev B 2008*)

○ HTCS : (Mo_xCu_{1-x})Cu-1212 phase during an annealing process under oxygen

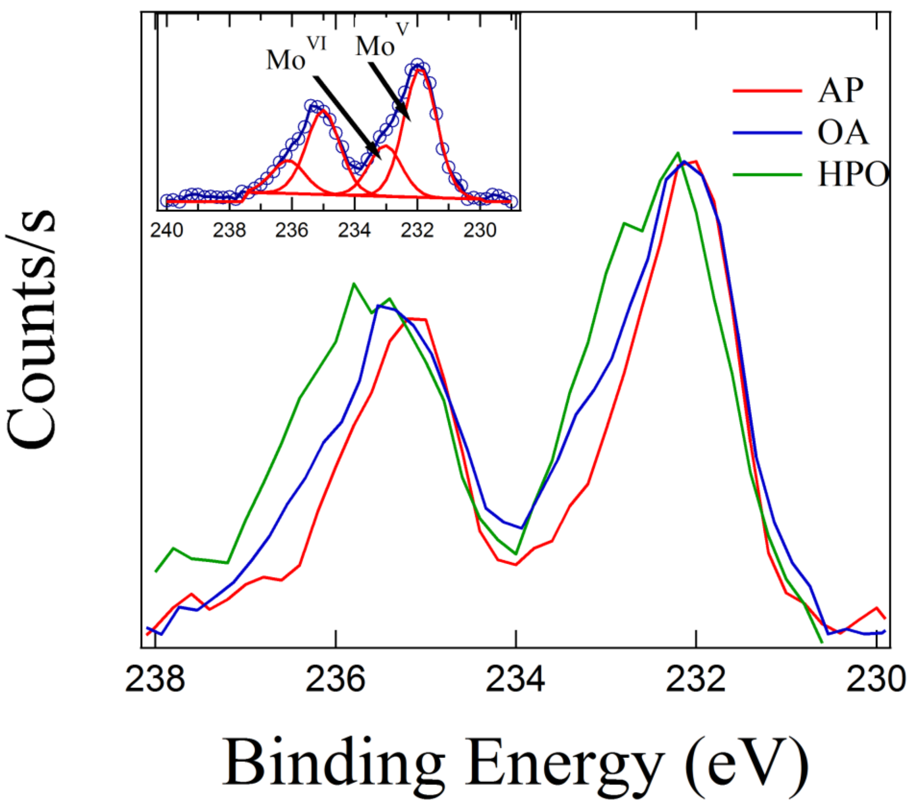
$Mo^{5+}{}_{1-x}Mo^{6+}{}_x + Cu^{2+}Cu^{3+} \leftrightarrow Mo^{5+}{}_{1-x}Mo^{6+}{}_x + Cu^{2+}{}_{1+x}Cu^{3+}{}_{1-x}$ charge transfer equation

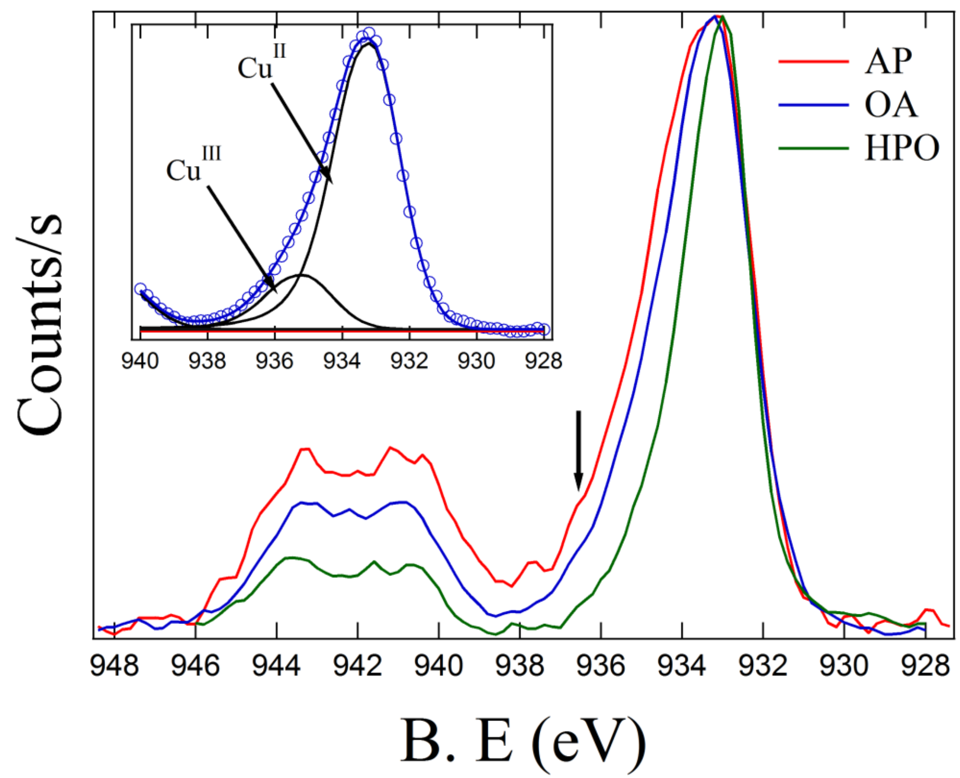
in relation with transition to superconducting state

(Marik JSSC 2012)

$Mo_{0.3}Cu_{0.7}Sr_2ErCu_2O_y$

Sample	AP	OA	HPO
Synthesis	1273 K Air 48 hours	873K O_2 48h Cooling rate 0.5 K/min	Belt HP $KClO_3$ (~33 mol%)
Y (from ND)	7.35	7.45	7.55
T_c	/	33K	84K





Acknowledgments:

➢Dr J. Abel Master's degree /now « Pôle Pluridisciplinaire de la Matière et de l'Environnement » Université de la Nouvelle-Calédonie / **y= 0.18 & y = 0.33**

➢Dr C. Yin « Soprano » Post-Doc / now MPI für Festkörperforschung Stuttgart » / **y= 0.25 and y=0**

➢Dr. A. Wattiaux (Mossbauer Spectroscopy) ; Dr. E. Gaudin (XRD)

➢Dr S. Garcia-Martin from UCM (Electron Diffraction)

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" **S**pin and **O**rbital **P**hysics: **R**esearch of **A**dvanced **N**ew **O**xides"
FP7- PEOPLE – 2007 –ITN-214040 *(2008-2012)*

- " **RM**^{2}" Energy research program from CNRS