workshop **on Energy Dispersive X-ray Absorption Spectroscopy: Scientific Opportunities and Technical Challenges,** Grenoble February 2-5 2009.

An Energy Dispersive X-ray Absorption and Diffraction Investigation of Photomagnetic CoFe Prussian Blue Analogues.

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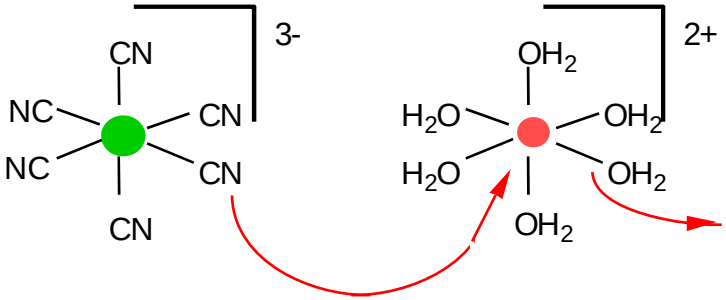
[1]Laboratoire de Chimie inorganique-ICMMO-Orsay

[2]Synchrotron SOLEIL-Gif sur Yvette

CoFe Prussian Blue Analogs



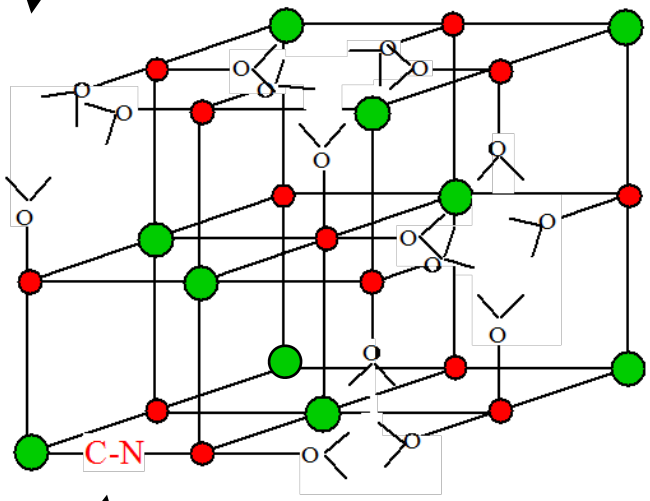
hexacyanometallate hexaaquacomplex

C^+

Alkali metal ion (Na^+, K^+, Rb^+...)

$X/3\ [Fe(CN)_6]^{3-}$

a



$X\ C^+$

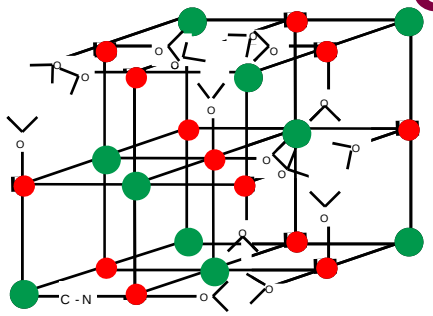
$Co_4[Fe(CN)_6]_{8/3}\square_{4/3}\cdot 18H_2O$

$C_xCo_4[Fe(CN)_6]_{8/3+x/3}\square_{4/3-x/3}\cdot nH_2O$

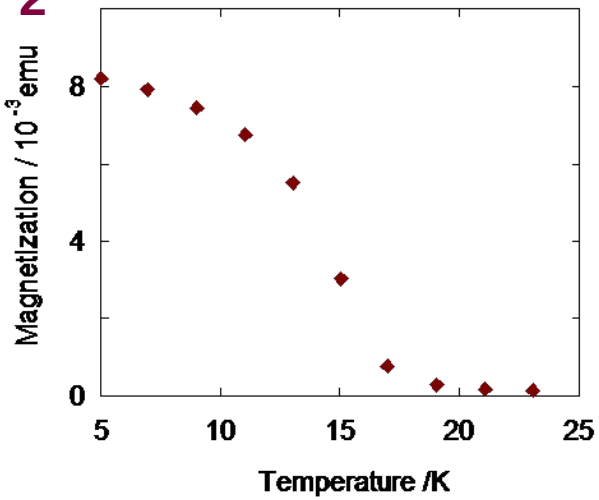
A. Lüdi and H. Güdel, *Structure and Bonding,* **1973**.

Alkali cation free CoFe analog

$Co_4[Fe(CN)_6]_{8/3}\cdot 18H_2O$ (C_0)



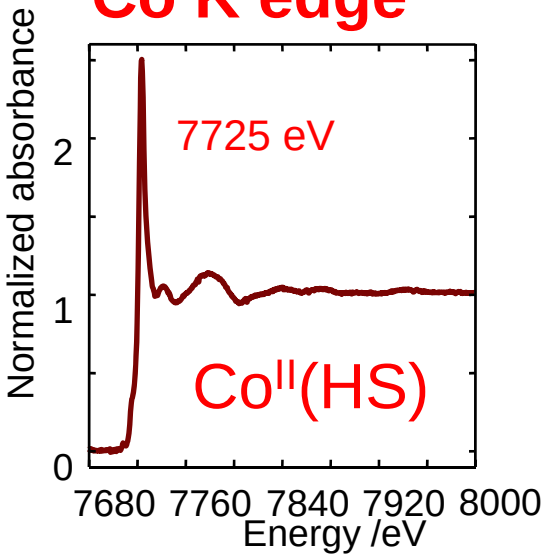
Lacunary structure



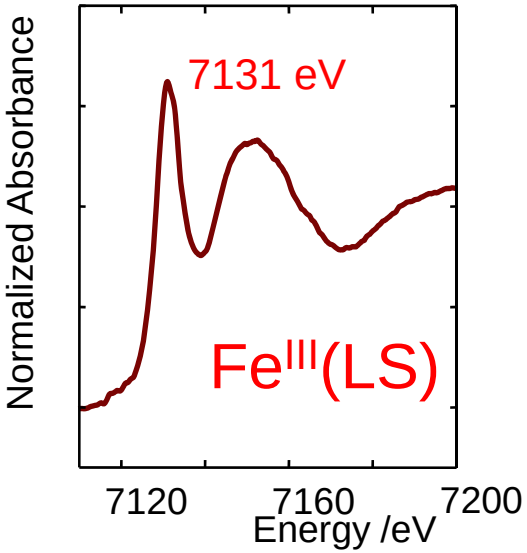
EDXAS

Room temperature

Co K edge



Fe K edge



Magnet below Tc = 16 K
No effect of light

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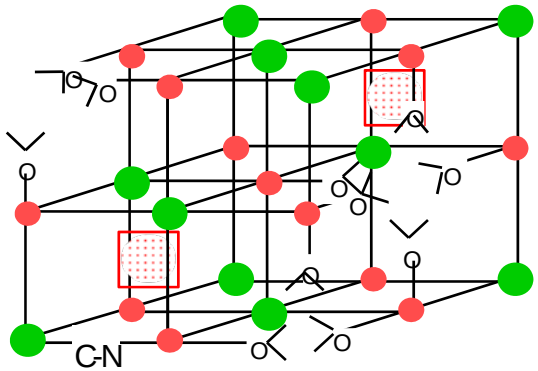
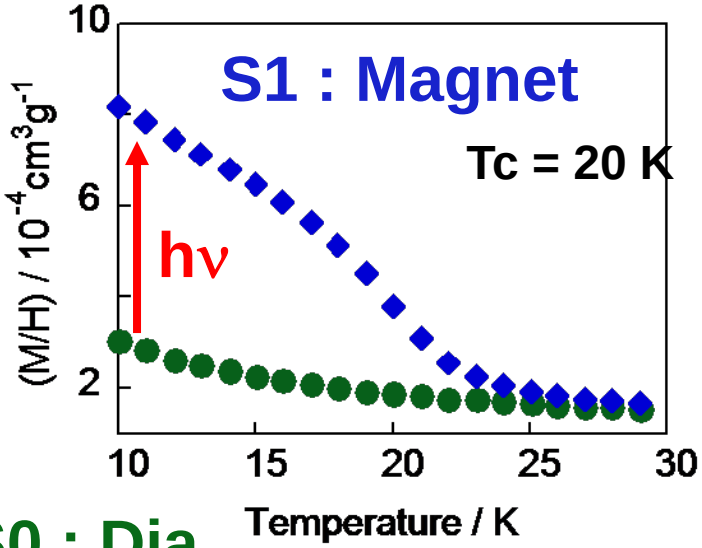
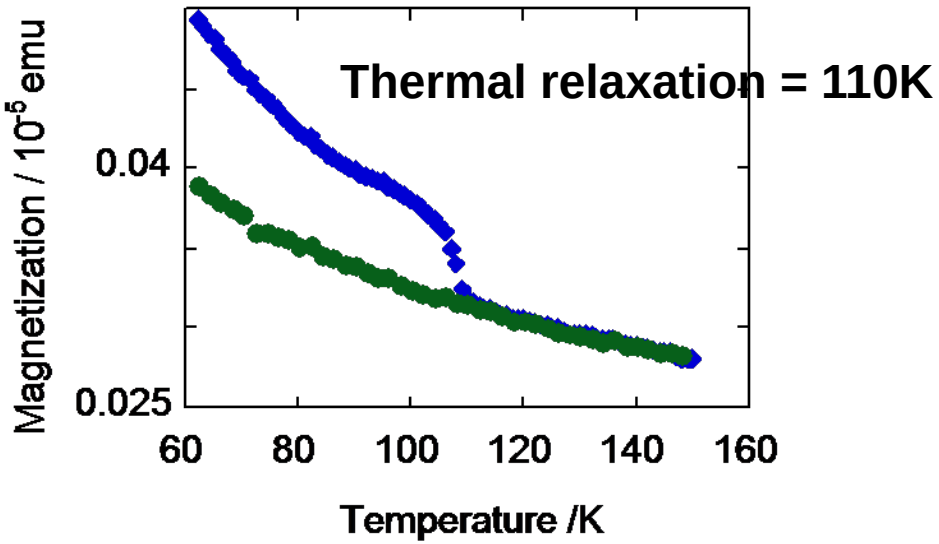
$Rb_2Co_4[Fe(CN)_6]_{3.3}\bullet 11H_2O$







Photomagnetic effect

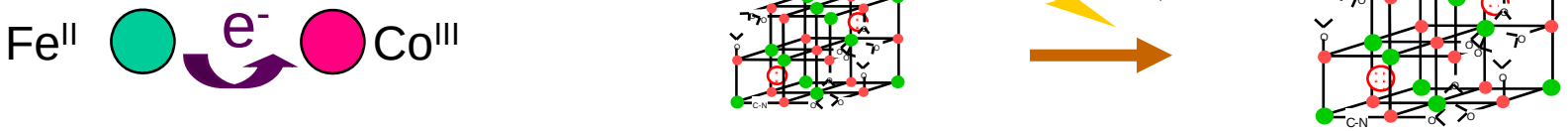
Promising candidates for future molecular memories

J. Am. Chem. Soc., 6648-6652, *122*, **2000**., Eur. Phys. Chem., 115-124, *14*, **2000**.

OUTLINE

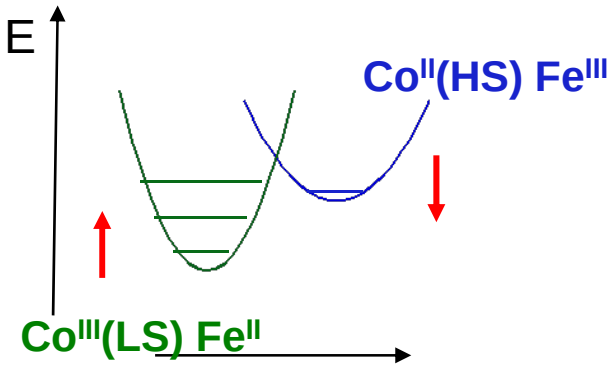
1- Study of the States implied in the Photomagnetic Effect :

An EDXAS and XMCD investigation at low temperature before and after irradiation.

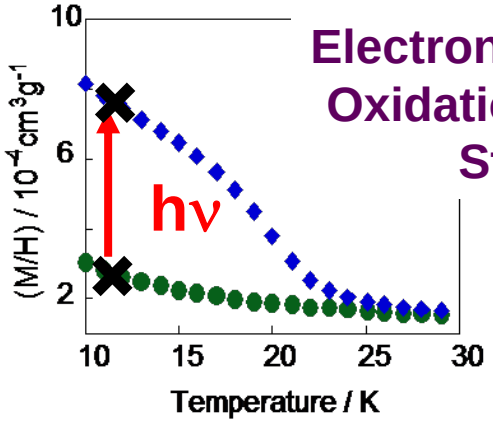


2 - Control of the Photomagnetic Effect :

Variable Pressure X-ray Absorption and Diffraction study.



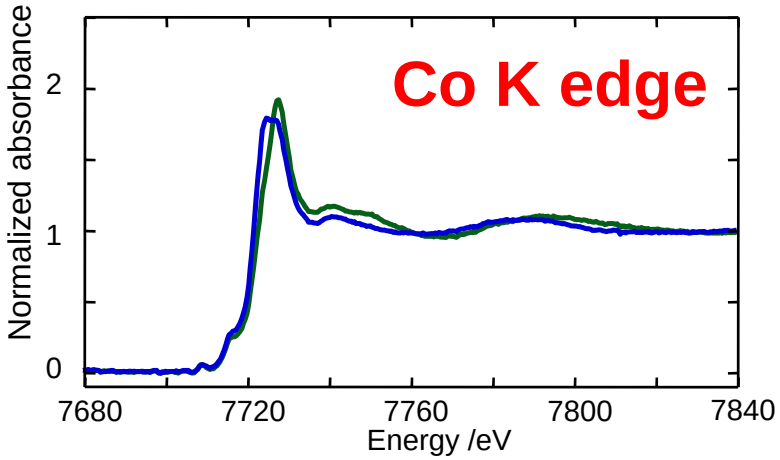
workshop **on Energy Dispersive X-ray Absorption Spectroscopy: Scientific Opportunities and Technical Challenges,** Grenoble February 2-5 2009.

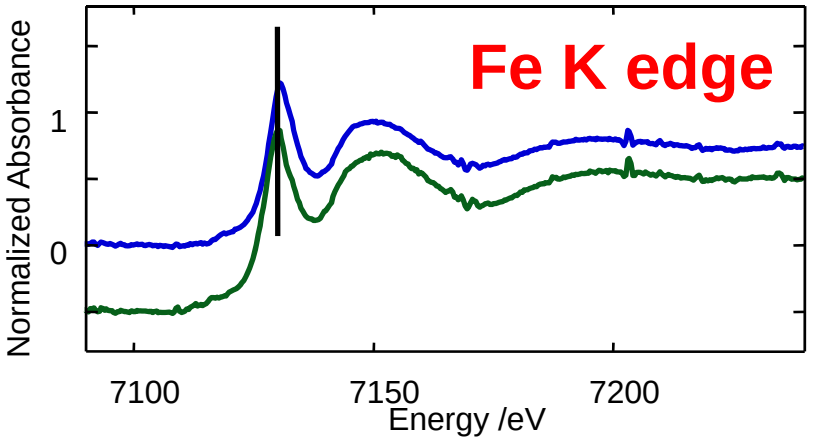


Electronic structure : Oxidation and Spin States ?

EDXAS
10 K before and after irradiation

1) Small amount of matter
2) irradiation of the sample at low temperature





$$Co^{III}(LS)\text{-}Fe^{II}(LS) \xrightarrow{h\nu} (Co^{II}(HS)\text{-}Fe^{III}(LS))^*$$

S = 0, Dia

J. Am. Chem. Soc. **2000**, *122*, 6653-6658.

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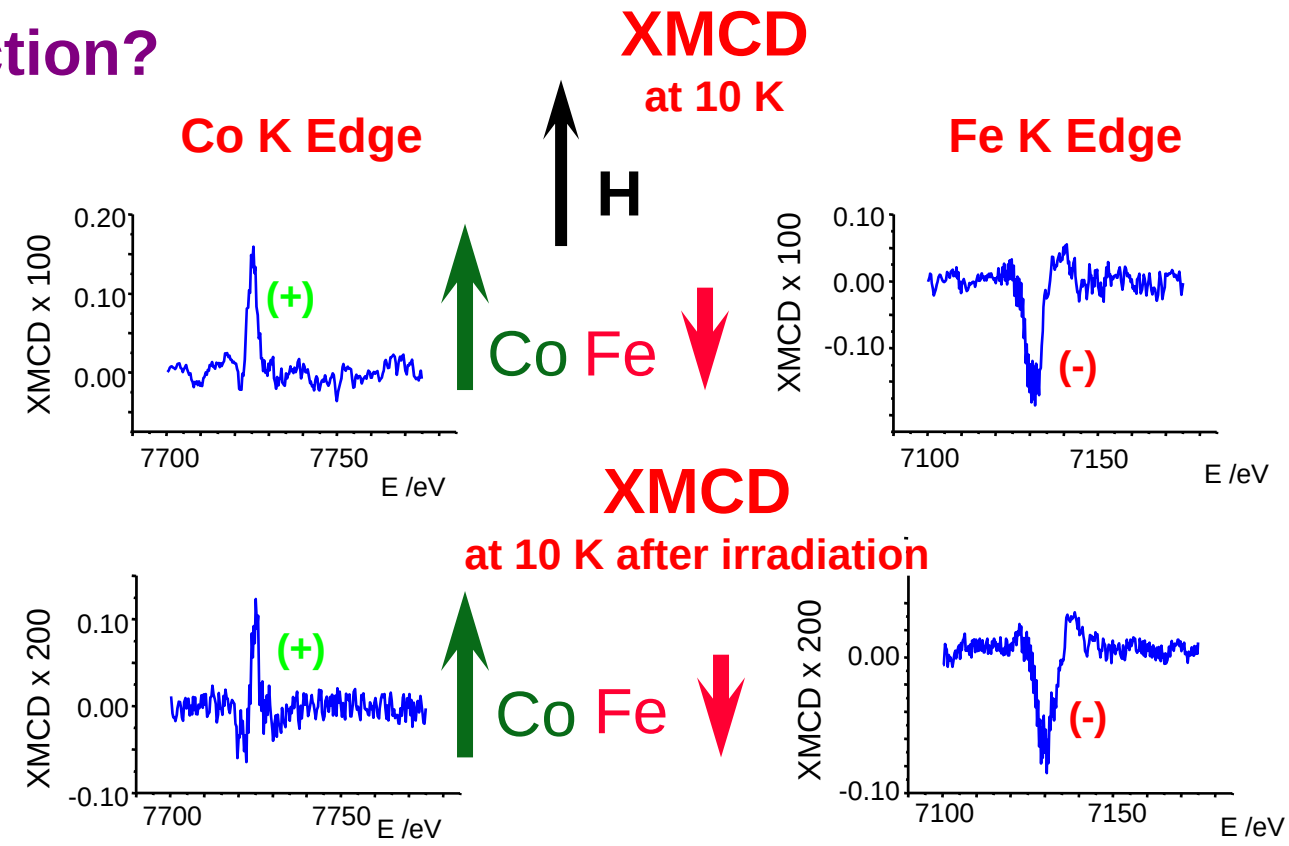
Exchange Interaction?

CoFe

Ferrimagnetic Model Compound

RbCoFe

Photomagnetic compound after irradiation

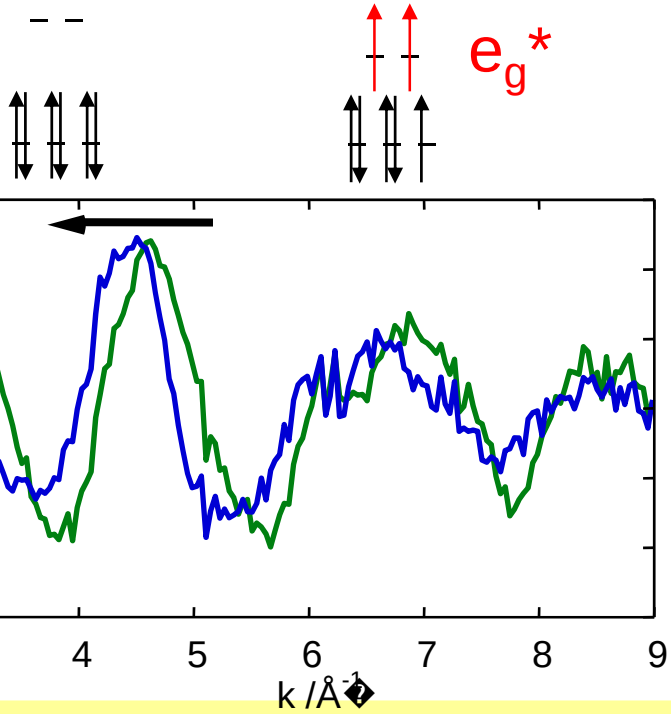


J. Am. Chem. Soc., **2001**, *123*, 12544.

$$Co^{III}(LS)\text{-}Fe^{II}(LS) \xrightarrow{h\nu} (Co^{II}(HS)\text{-}Fe^{III}(LS))^*$$

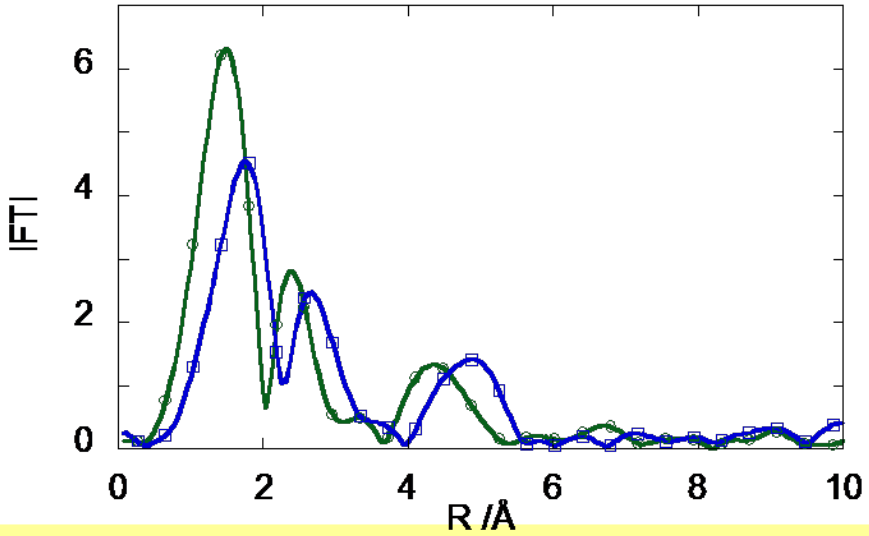
S = 0, Dia **S = 1, Ferrimagnetic**

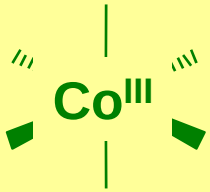
$Co^{III}(LS) \xrightarrow{h\nu} Co^{II}(HS)^*$



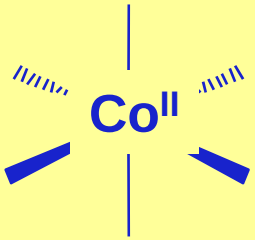
Structure :
Co Coordination Polyhedron ?

ED EXAFS at the Co K-edge
at 10 K before and after irradiation





$Co^{III}(LS) \xrightarrow{h\nu} Co^{II}(HS)^*$



$d(Co^{III}\text{-}L) = 1.91$ Å

$d(Co^{II}\text{-}L) = 2.08$ Å

$\Delta r = 0.17$ Å

J. Am. Chem. Soc. **2000**, *122*, 6653-6658.

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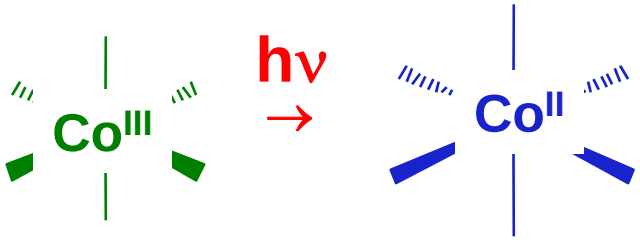
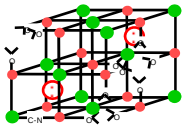


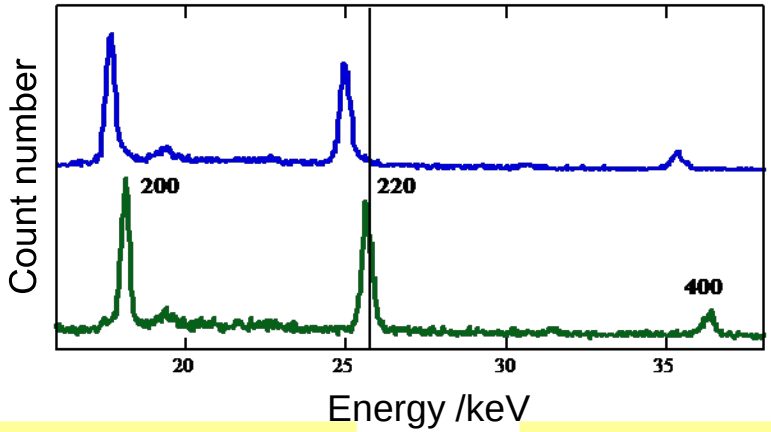
Structure : Long Range Order ?

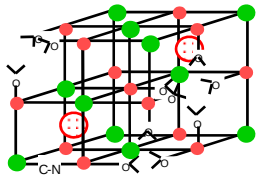
Energy Dispersive X-Ray Diffraction

at 10 K before and after irradiation



FCC
a = 9.96 Å

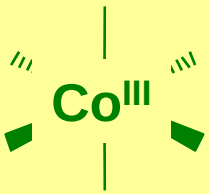


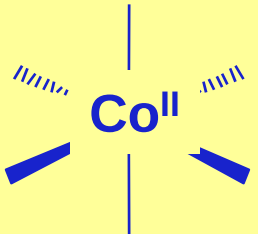


FCC
a = 10.28 Å

J. Phys. Chem. B, 4763-4767, *107*, **2003**.

$$Co^{III}(LS)\text{-}Fe^{II}(LS) \xrightarrow{h\nu} (Co^{II}(HS)\text{-}Fe^{III}(LS))^*$$





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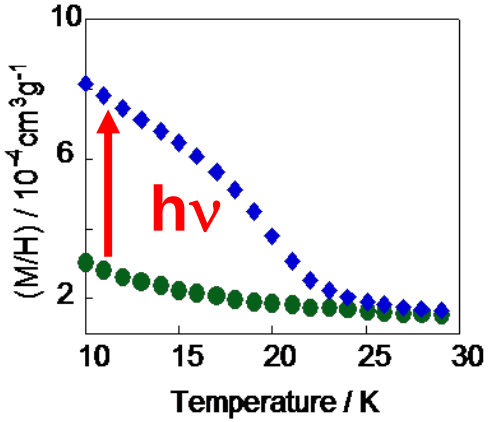
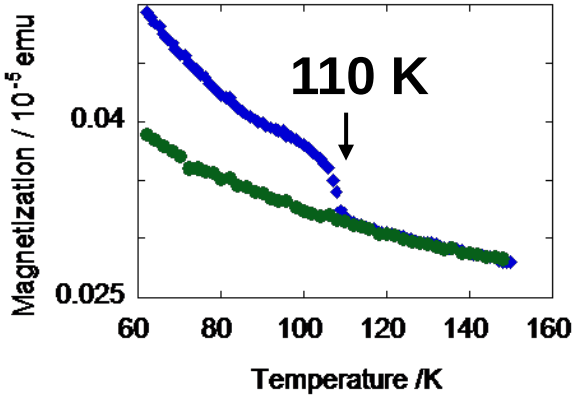
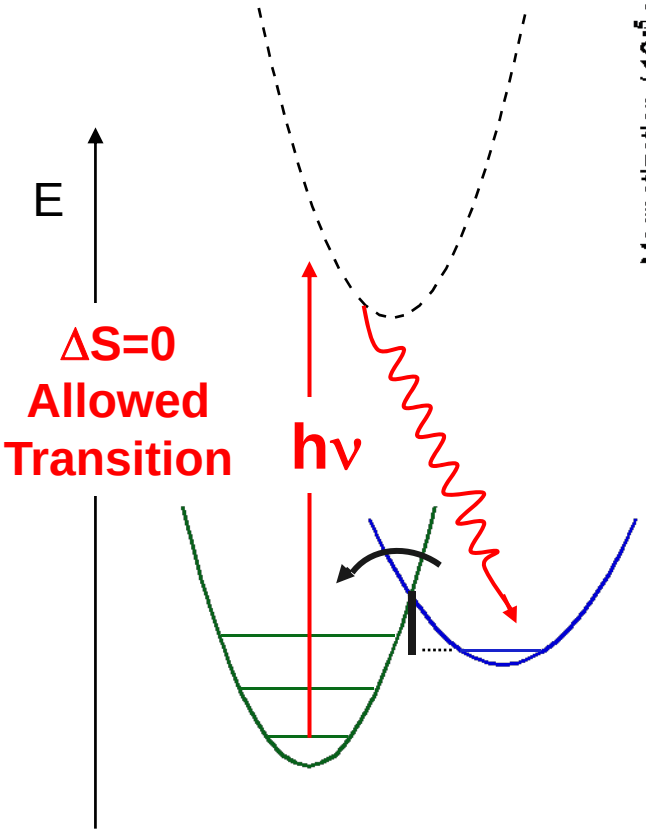
Structure and electronic structure of the States implied in the Photomagnetic Effect







Ground state

$Co^{III}LS$ Fe^{II}

S=0

Diamagnetic

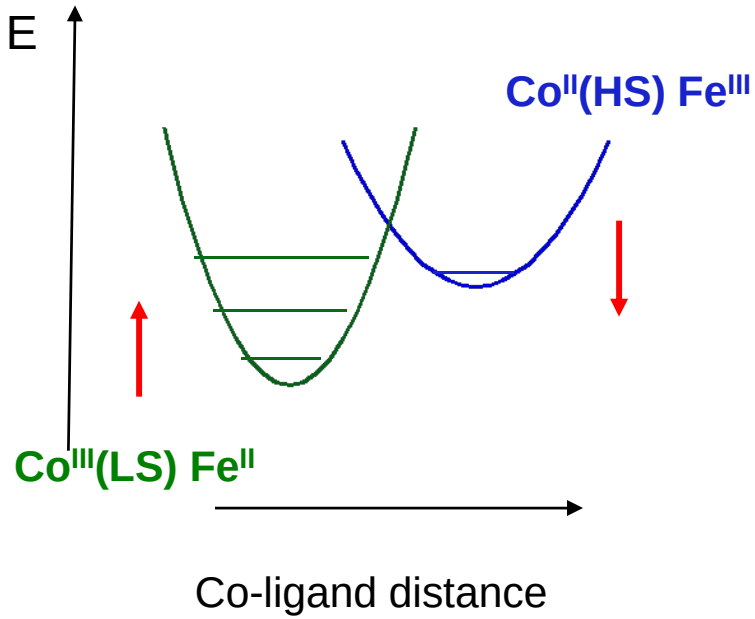
Metastable excited state

$Co^{II}HS$ Fe^{III}

S=1

Ferrimagnetic

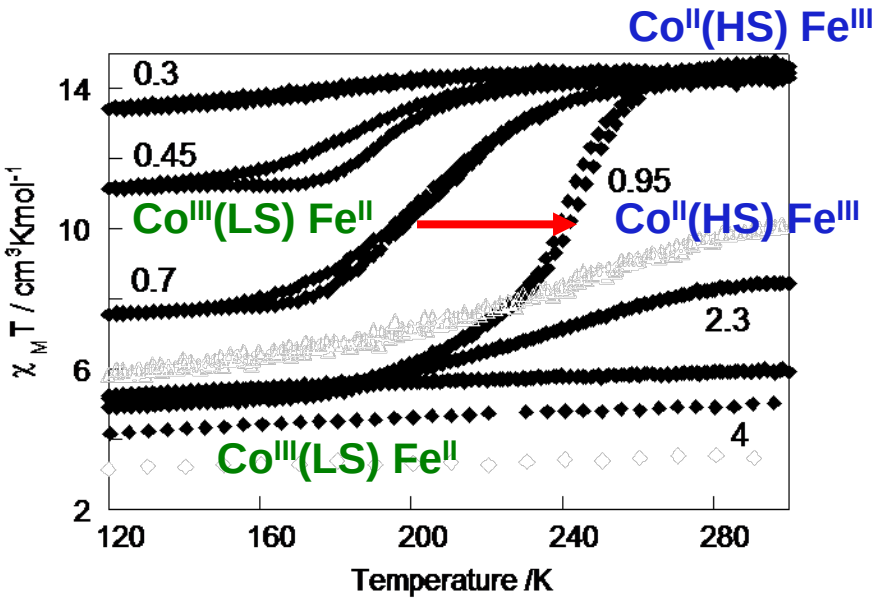
Control of the switching properties

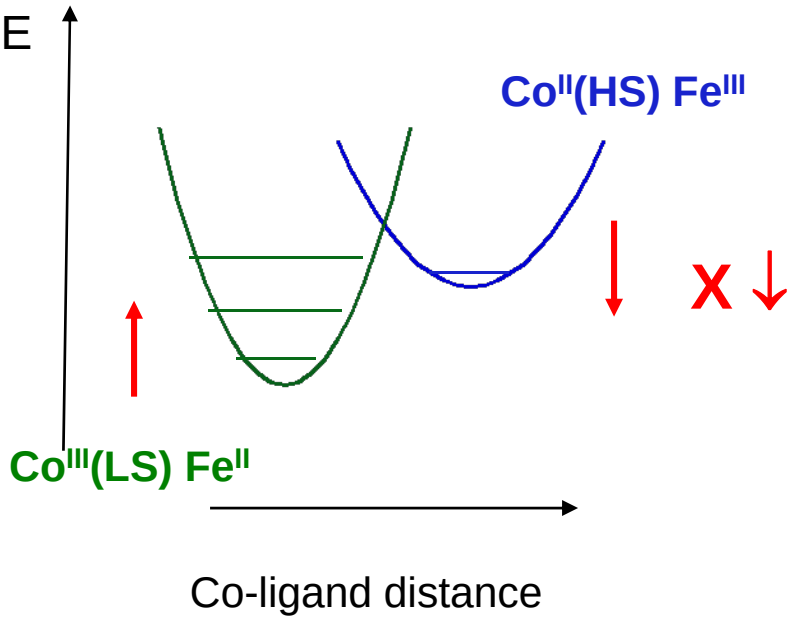


Control of the potential wells energy position :
High temperature bistability ⇔ close energy position

Chemical Control : $C^+ = Cs^+$, x varies

$Cs_xCo_4[Fe(CN)_6]_{8/3+x/3}$ $_{4/3-x/3}$





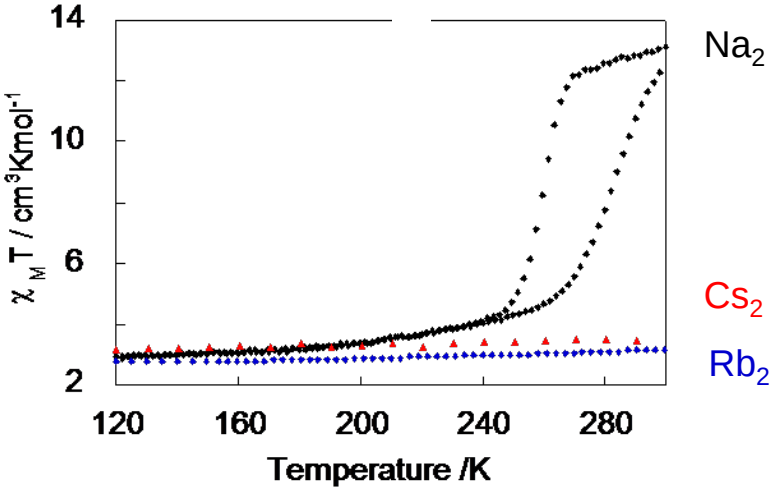
X ↑ **Closer energy of the Co^{III}-Fe^{II} and $Co^{II}Fe^{III}$ states, TR increases**
But decrease of the magnitude of the switching properties

$Co(NC)_y(OH_2)_{6-y}$

J. Am. Chem. Soc., 12536-12543, *123*, **2001**.

Chemical Control : x = 1.8, C^+ varies

$C_{1.8}Co_4[Fe(CN)_6]_{3.3}$ $_{0.7}$



Co-NC-Fe

⋮

C^+

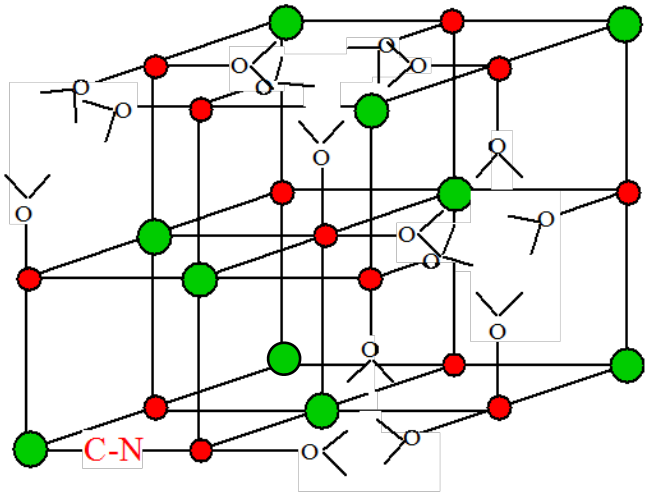
Competitive interactions
Variable Pressure
X-ray Absorption and Diffraction study

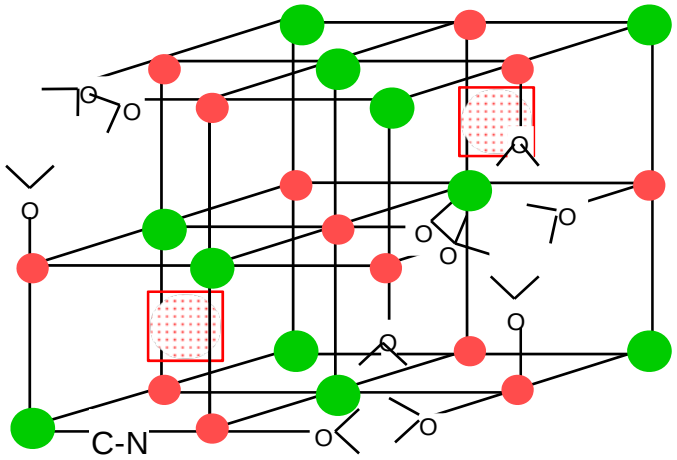
Variable Pressure Study

Co ↔ NC ↔ Fe

↕

C





$Co_4[Fe(CN)_6]_{8/3}•18H_2O$
(C_0)
No alkali metal ion

$Co^{II}Fe^{III}$

$Cs_2Co_4[Fe(CN)_6]_{3.3}•11H_2O$
(Cs_2)
2 big Cs^+ ions

$Co^{III}Fe^{II}$

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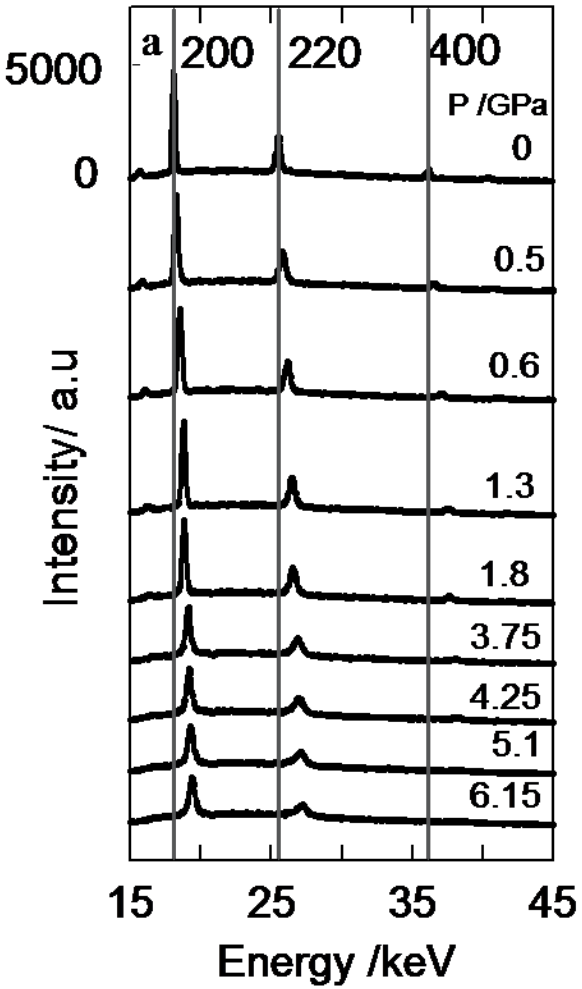
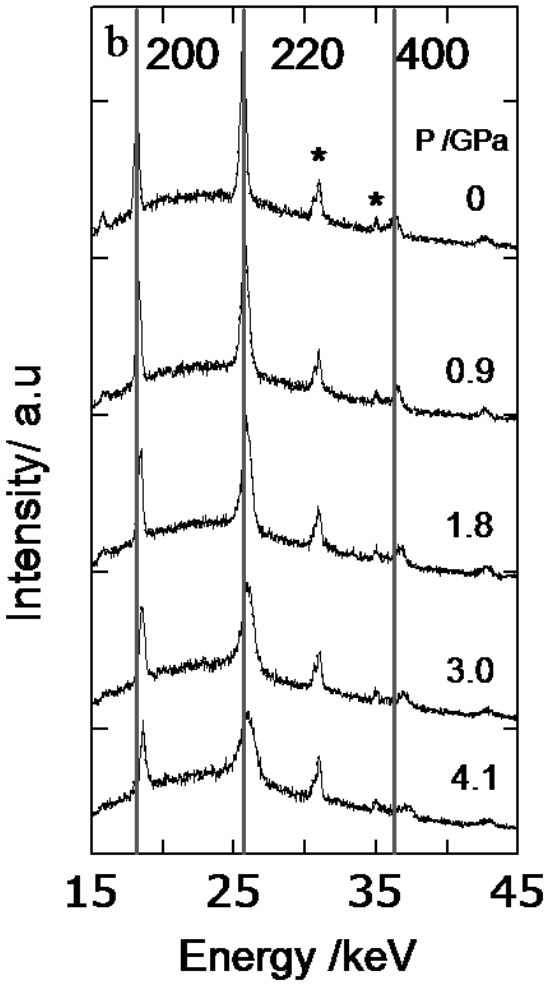
Variable Pressure EDXD

C_0

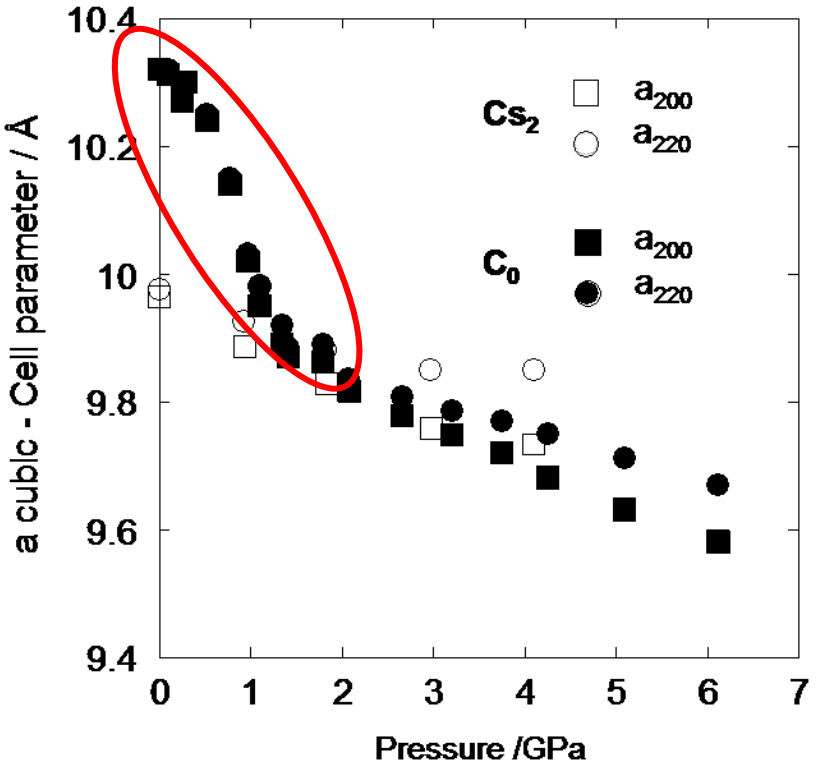


Cs_2



J. Phys. Chem. C, *112*, 17709-17715, **2008**.

Cell Parameter Pressure Dependence



C_0 : 0-1 GPa

C_0 cell parameter reaches the Cs_2 one !!!

Pressure-induced electron transfer ?

Cs_2 and C_0 > 1 GPa Distortion from the cubic structure.

Rhombohedral F
Pseudo cubic space

$$d_{hkl} = \frac{1}{a * \sqrt{h^2 + l^2 + h^2 + \cos\alpha * (hk + kl + hl)}}$$

J. Phys. Chem. C, *112*, 17709-17715, **2008**.

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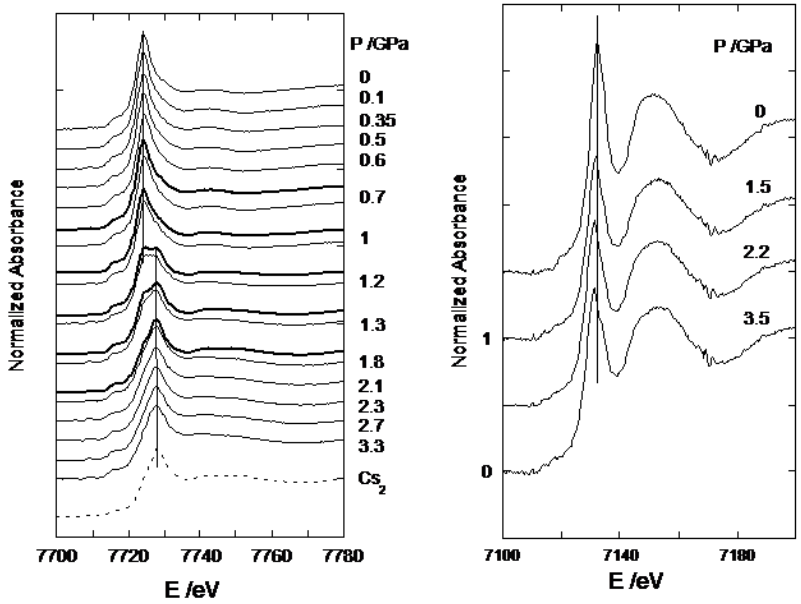
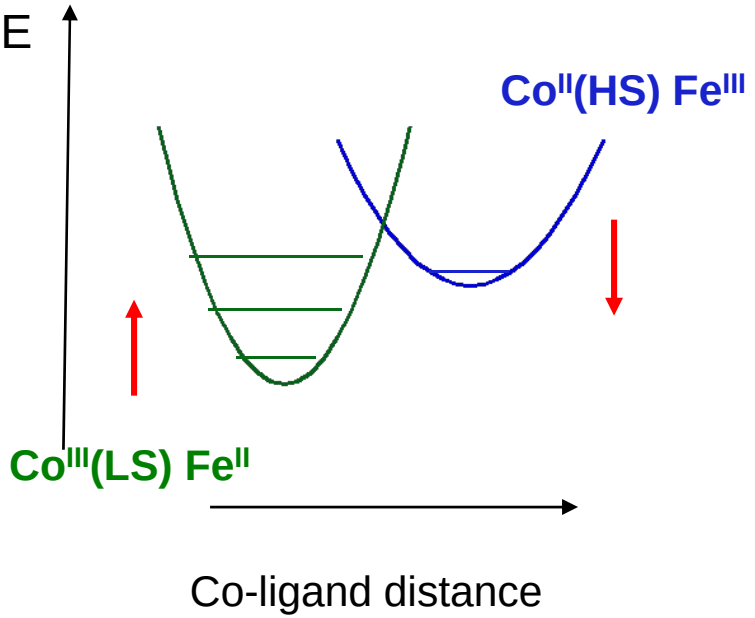
Pressure-induced Electron Transfer

EDXAS

Room temperature

Co K edge **Fe K edge**





P ↑

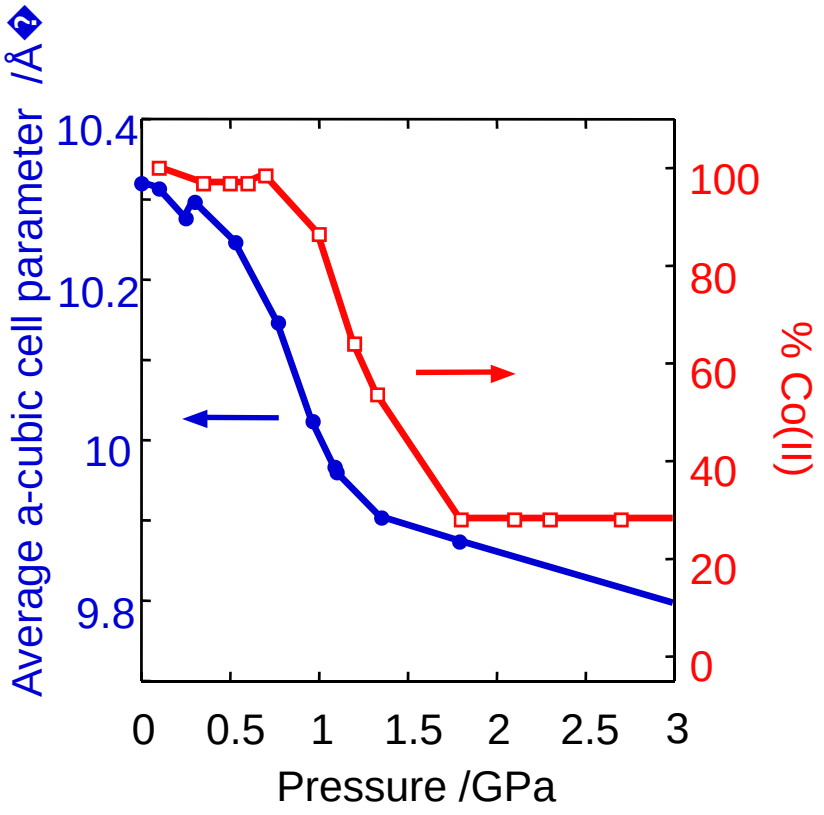
$Co^{II}_4[Fe^{III}(CN)_6]_{2.7}\cdot 18H_2O \rightarrow Co^{III}_{2.7}\,Co^{II}_{1.3}[Fe^{II}(CN)_6]_{2.7}\cdot 18H_2O$ **0.7 - 2 Gpa !!**

The electron transfer is total !!!

Minimum amount of CN bridges : TR should be high !!!

J. Phys. Chem. C, *112*, 17709-17715, **2008**.

Chronology of the Structural and Electronic Events

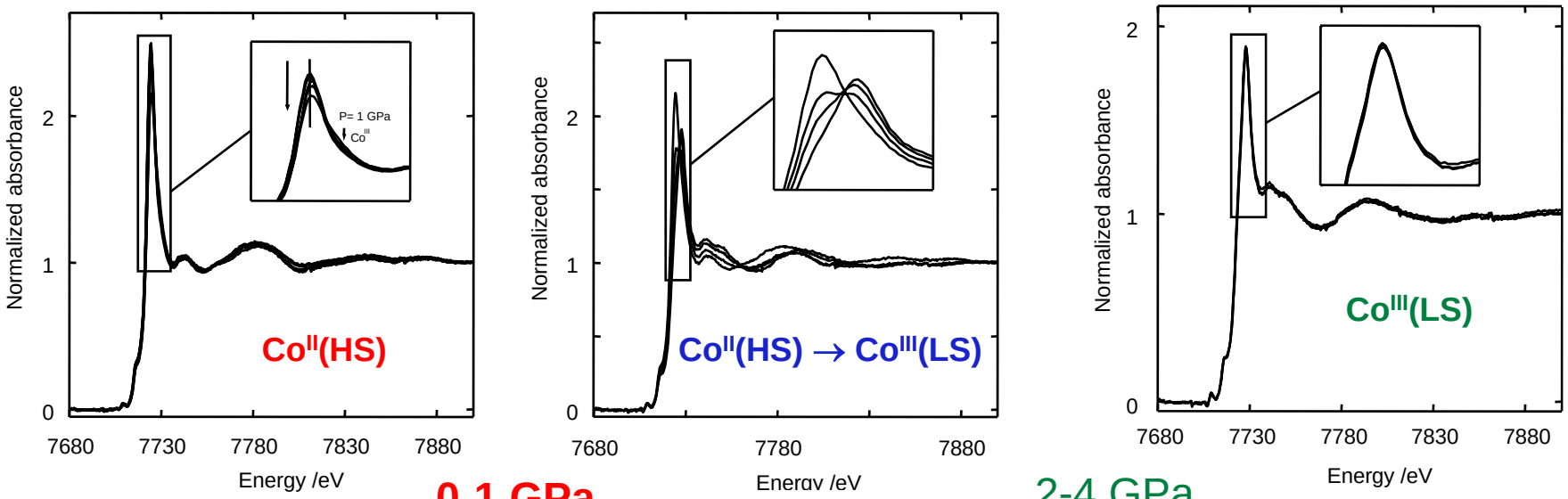


The strong cell parameter decrease precedes the $Co^{II}(HS) \rightarrow Co^{III}(LS)$ transformation

Interplay between Structural and Electronic Events

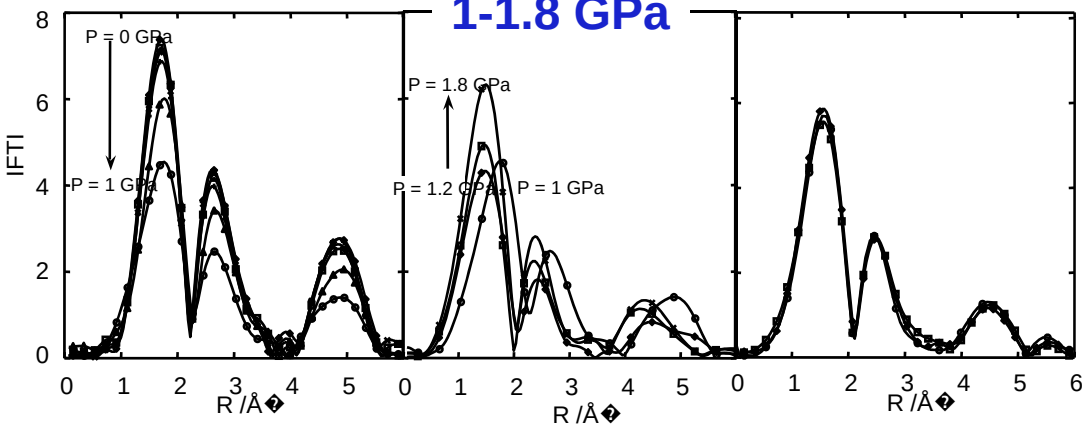
Co K edge

0-1 GPa **1-1.8 GPa** 2-4 GPa



0-1 GPa **1-1.8 GPa** 2-4 GPa

Intensity decrease
Disorder

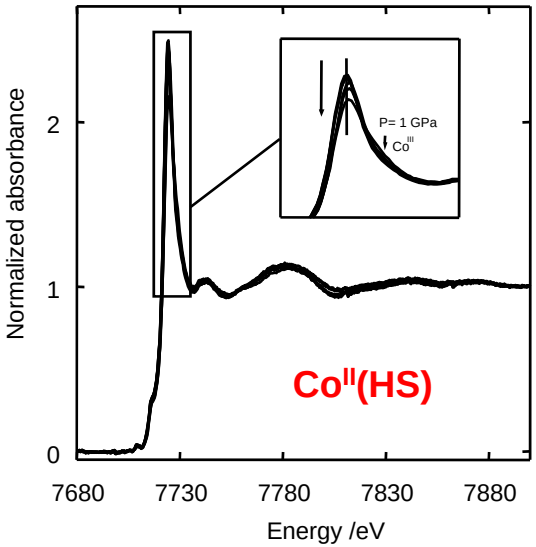


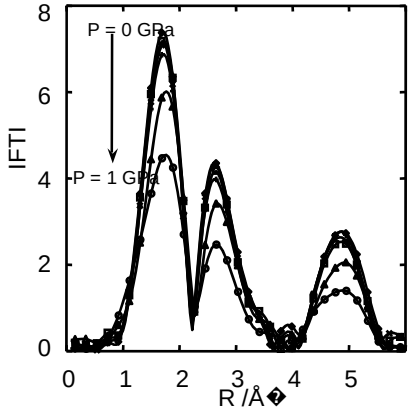
Co to ligand bond shortening

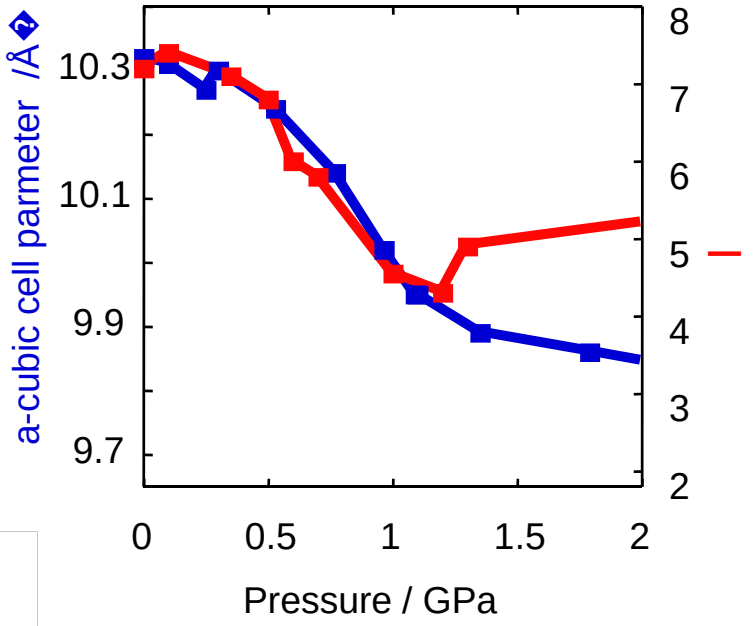
J. Phys. Chem. C, *112*, 17709-17715, **2008**.

Interplay between Structural and Electronic Events

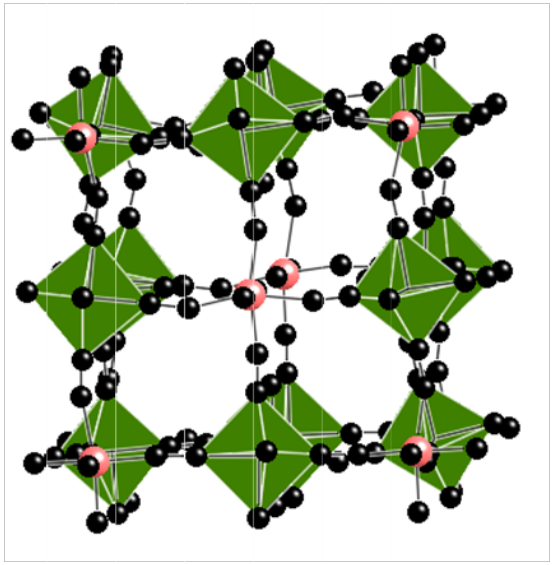
0-1 GPa





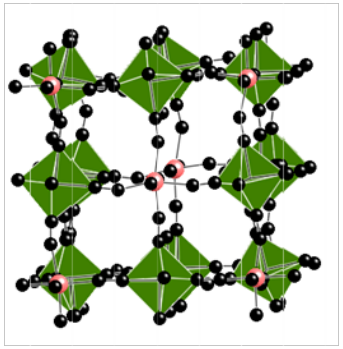


Tilt of the transition metal ion coordination polyhedra

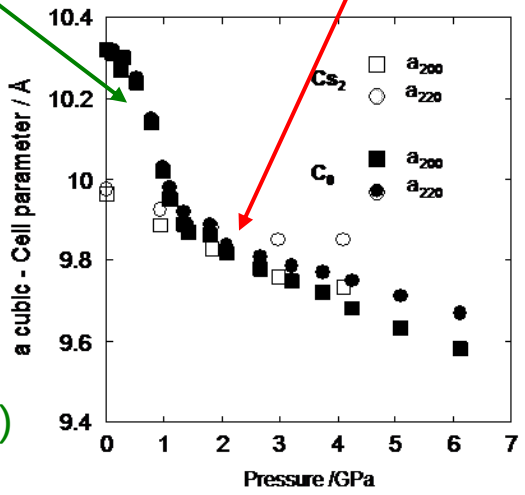


Perspectives

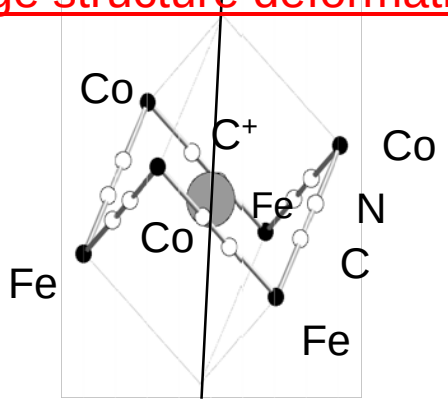
Structural event preceding the electronic event



Local structure
around the transition metal ions
Variable Pressure XAS studies
of non-switching compounds (Ni,Fe)



Long range structure deformation



- Cyanide-alkali ion interaction Variable XAS Pressure (Rb)
- Cubic to rhombohedral change effect on the magnetic properties : XMCD

Study of the photomagnetic effect
Exhibited by the alkali cation free CoFe
PBA under applied Pressure.

Variable Pressure and temperature XAS study of C_0 (Co, Fe)

Acknowledgement

Synchrotron radiation

F. Villain, V. Briois

C. Cartier dit Moulin, G. Champion

M.A. Arrio, Ph. Sainctavit

F. Fortuna, J.-J. Gallet

J.P. Itié, P. Münsch

F. Baudelet

E Dartyge, C. Georgetti

P. Roy

Chemistry

V. Escax

C. Lomenech

P. Higel

S. Bidault

A. Bachschmidt

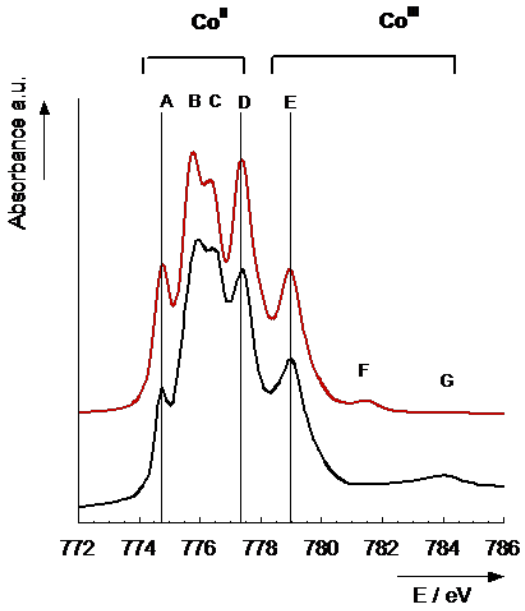
J.-D. Cafun

G. Fornasieri

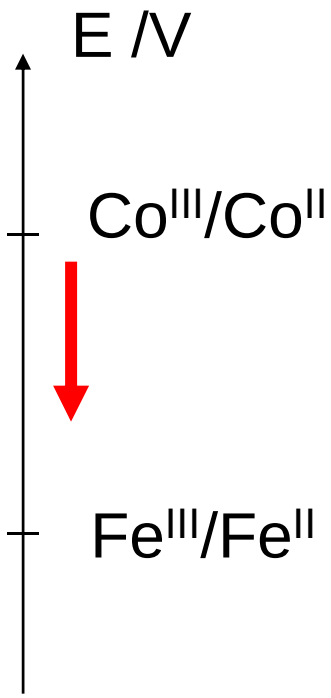
M. Verdaguer

Chemical Control : $C^+ = Cs^+$, x varies

XAS at the Co L_3 edge



Fe^{II}-C≡N-Co^{III}



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Role of the cyanide bridge as an active electron transfer bridge
Redox potential modulation

Angew. Chem. Int. Ed., *44*, 4798-4801, **2005**, Angew. Chem. Int. Ed., *46*, 1-4, **2007**.