



Influence of temperature and high pressure on the structural and physical properties in **Fe**-based **C**harge **O**rders systems

Note: The results from this document can be cited only after the publication

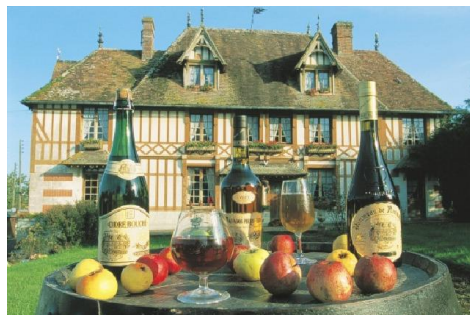
-2014-



Partners



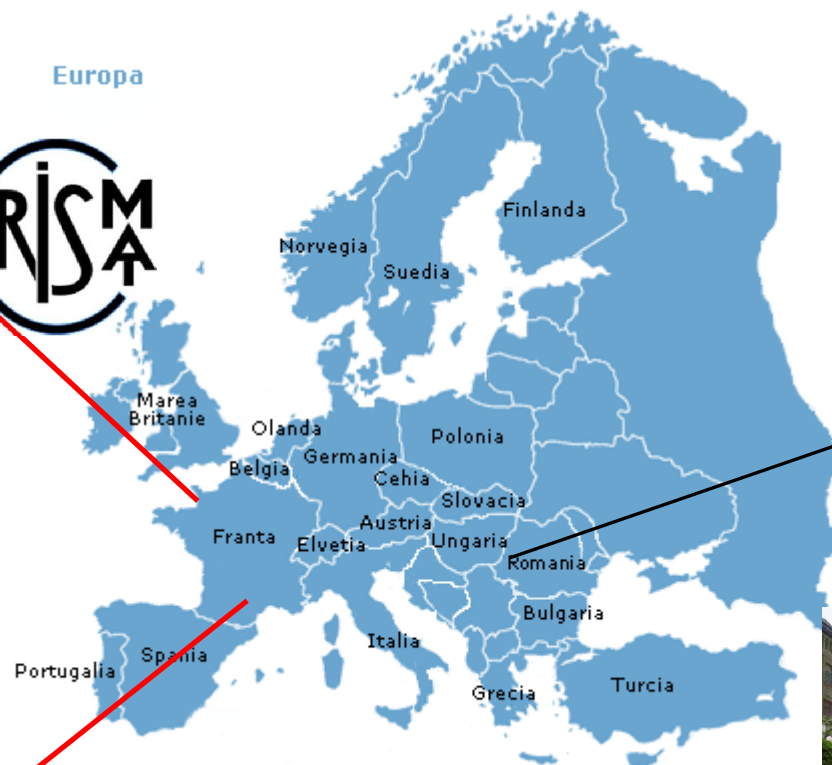
**Laboratoire Crismat
Caen**



**ICG
Montpellier**

**Institut Charles Gerhardt
Montpellier**

Europa



Timisoara



Results

➤ Phosphates

- $\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$ (Barboselite and lipscombite)
- $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ (giniite)

➤ Borates

- Cu_2FeBO_5

➤ Phosphite

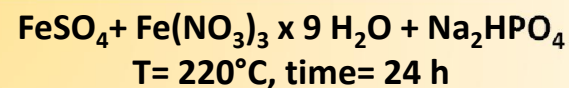
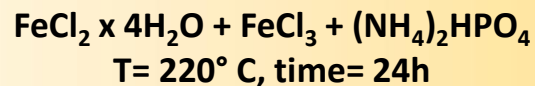
- $\text{Ni}_{11}\square(\text{HPO}_3)_8(\text{OH})_6$

Fe₃(PO₄)₂(OH)₂

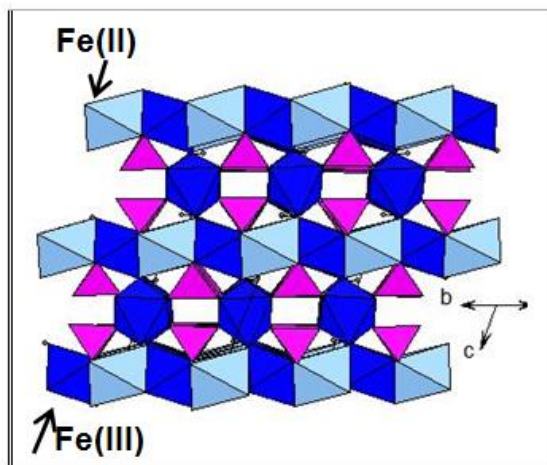
Barbosalite

Hydrothermal synthesis

Lipscombite

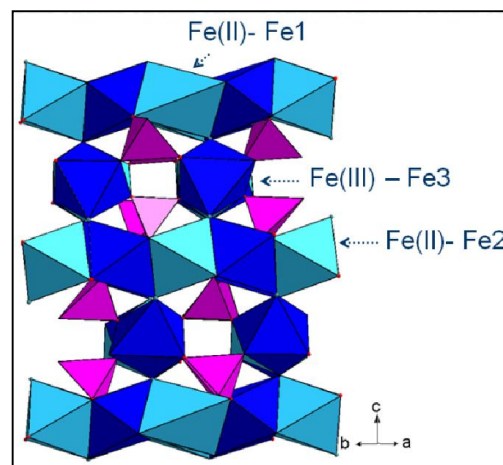


• $P 2_1/n$
 $a = 7,3294 \text{ \AA}$
 $b = 7,4921 \text{ \AA}$
 $c = 7,4148 \text{ \AA}$
 $\beta = 118,433^\circ$

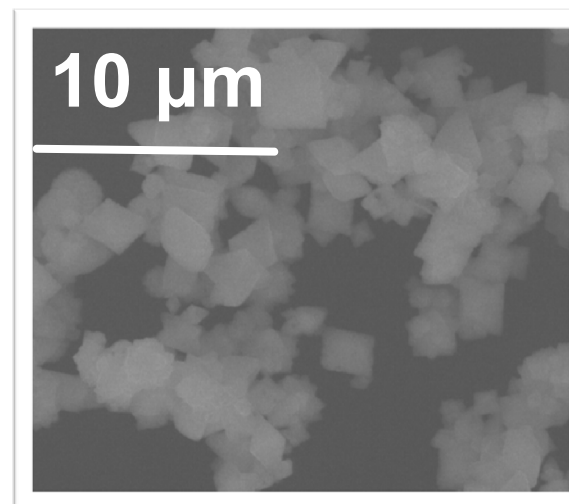
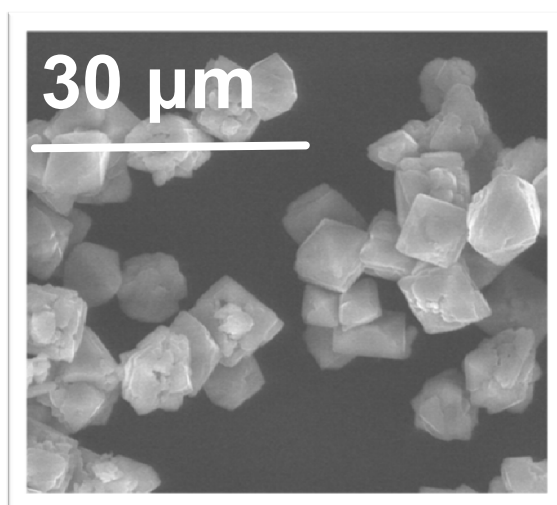


G. J. Redhammer et al.
 Phys Chem Minerals (2000)
 27: 419-429

• $P 4_3 2_1 1$
 $a = 7,31 \text{ \AA}$
 $c = 13,312 \text{ \AA}$

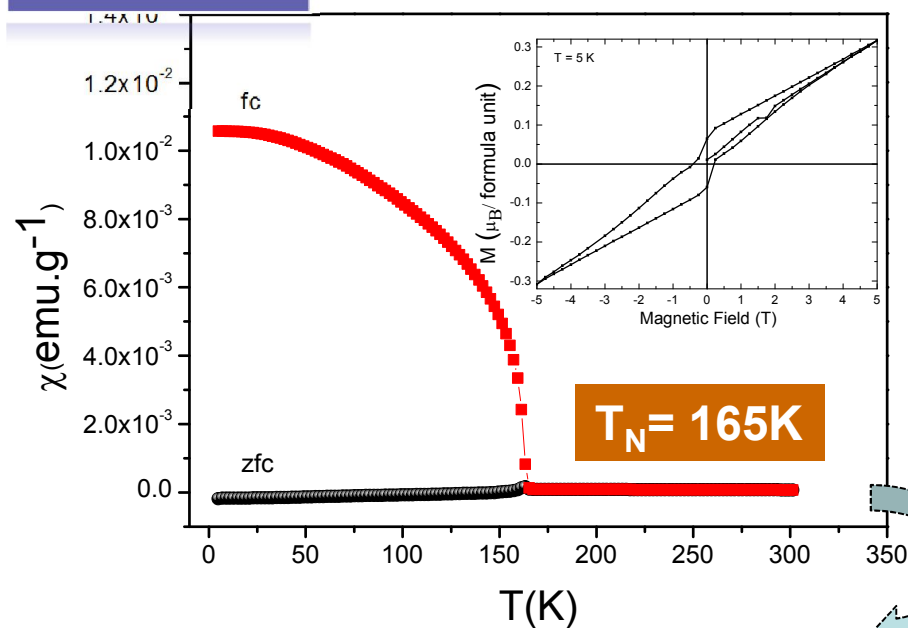


I. Vencato et al,
 American Mineralogist (1989),
 74: 456

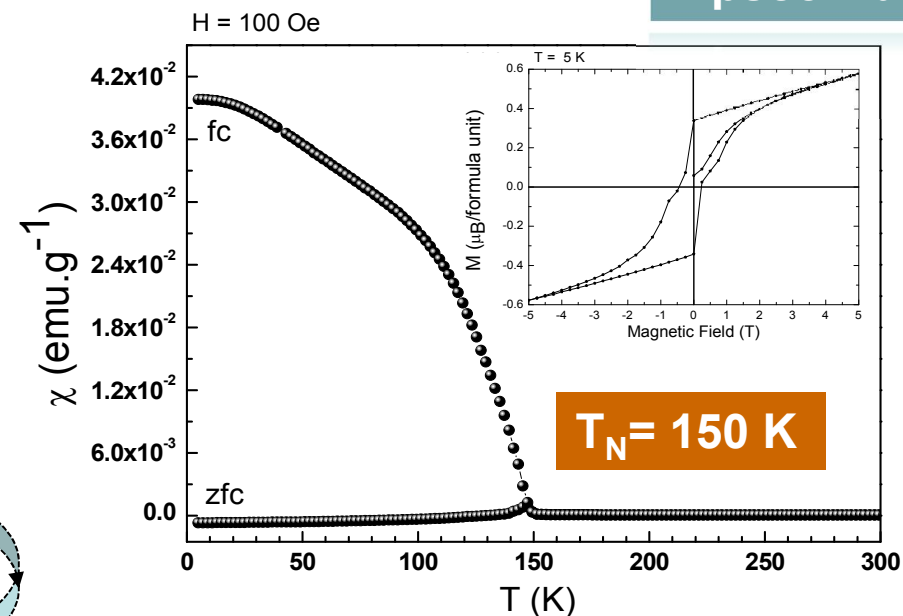


Fe₃(PO₄)₂(OH)₂

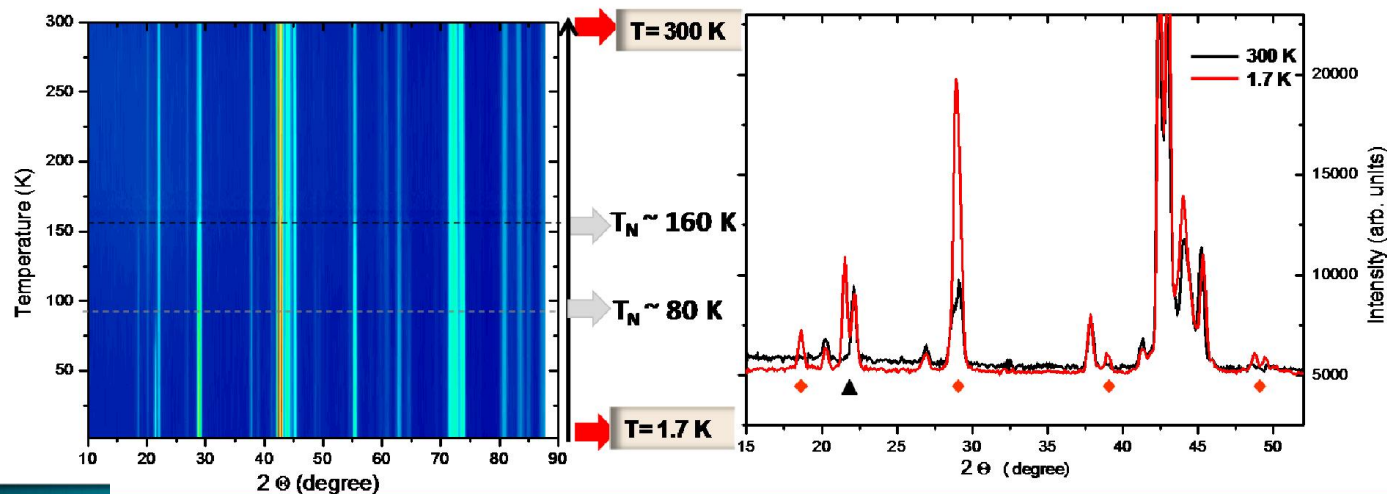
Barbosalite



Lipscombite



Neutron Powder diffraction- barbosalite : LLB Saclay



♦ Magnetic peaks of barbosalite

$T_N \sim 160\text{ K}$

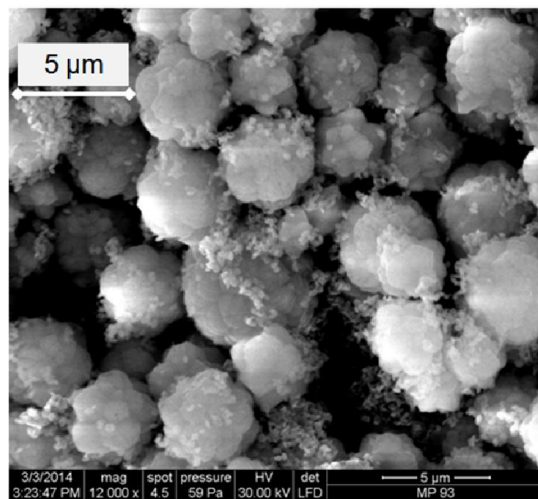
▲ Magnetic peaks

Fe₄(PO₄)₃(OH)₃

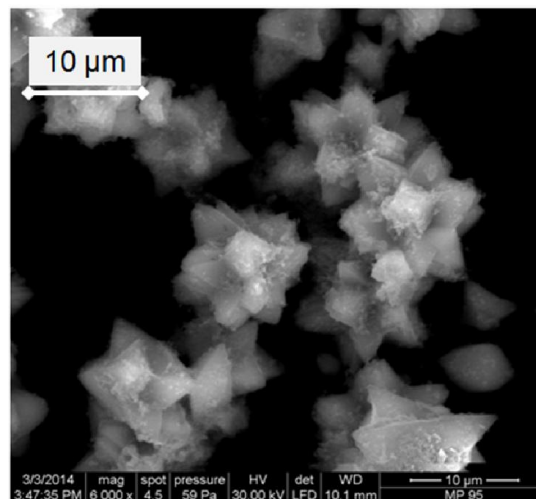
$T_N \sim 80\text{ K}$

$\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$

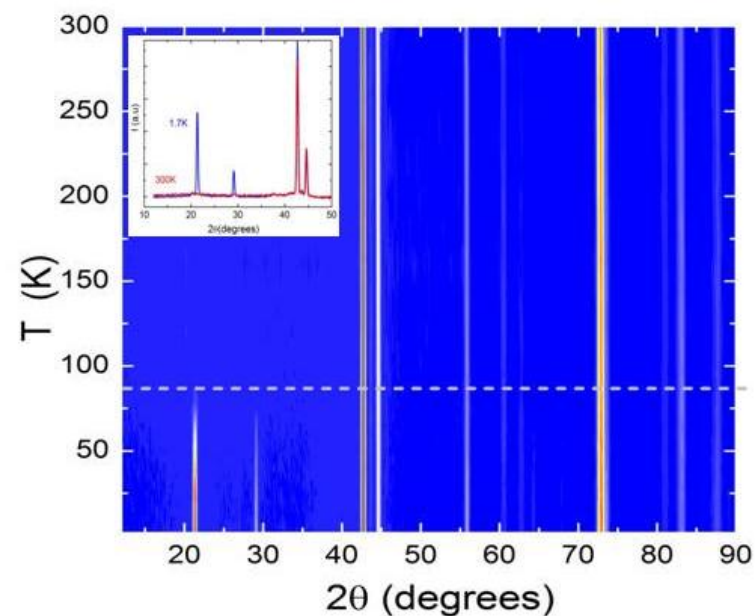
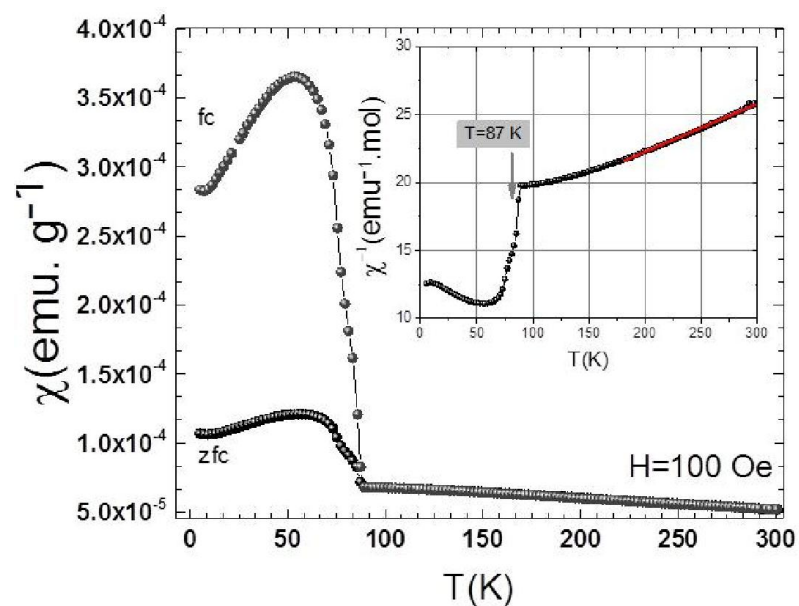
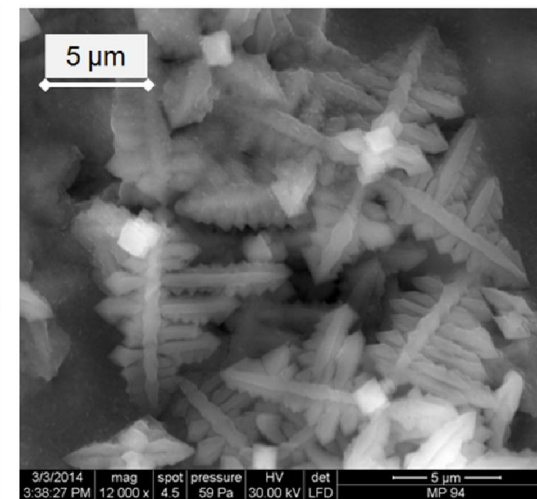
pH=1.5



pH=3.5



pH=4.5

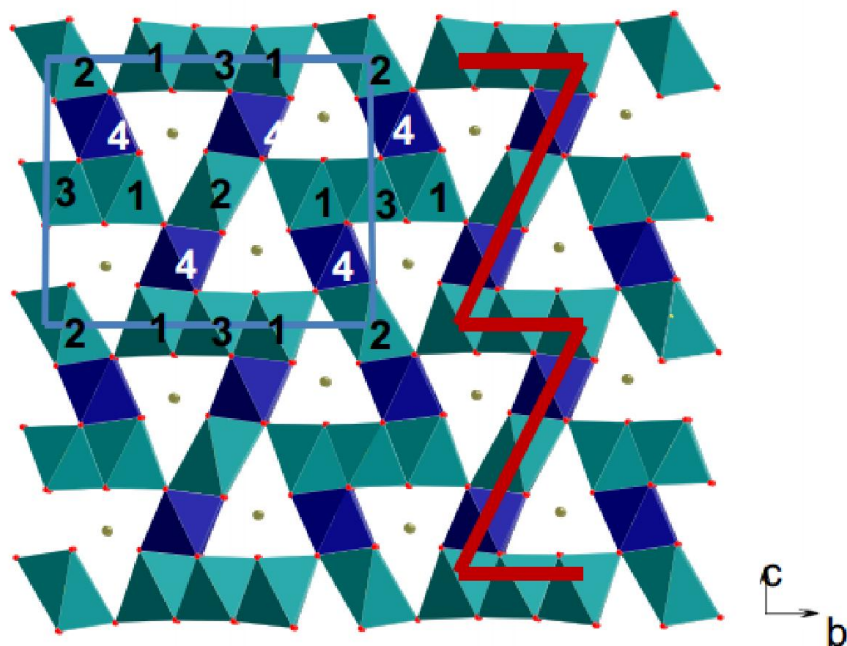
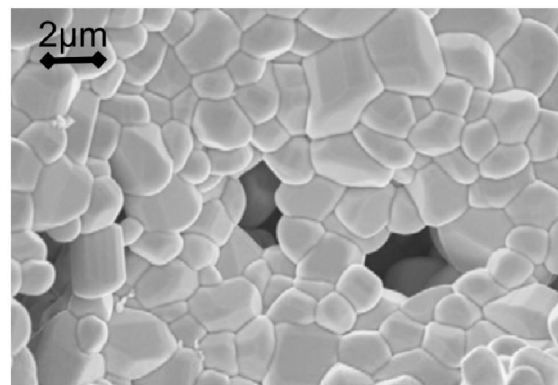


Cu_2FeBO_5

Synthesis: under vacuum in a silica tube

$\text{CuO}, \text{Fe}_2\text{O}_3, \text{B}_2\text{O}_3$

850°C, 48h



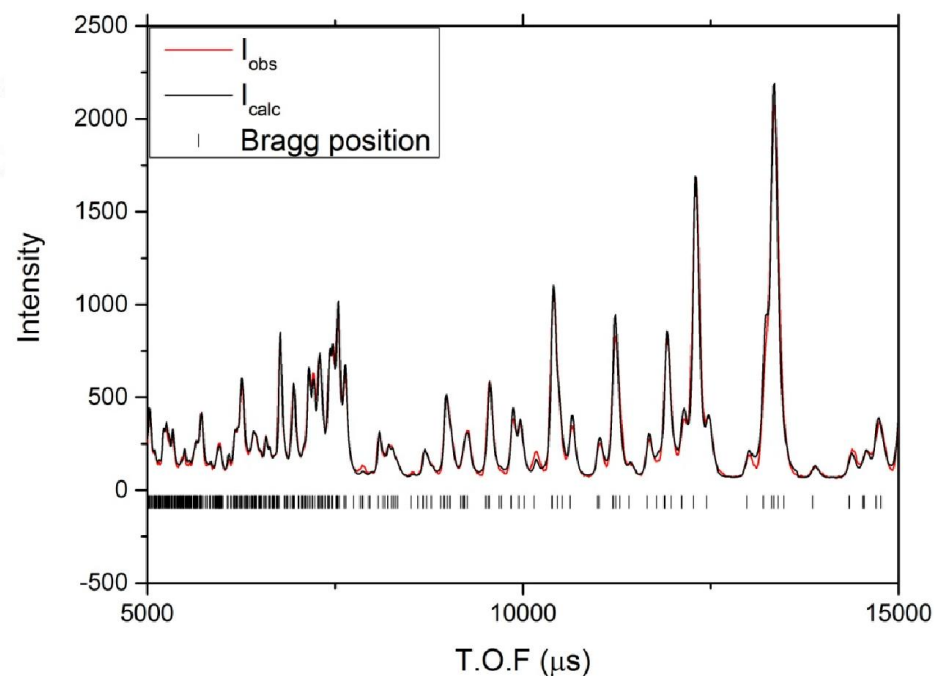
$P2_1/c$

$a = 3.1137(3) \text{ \AA}$, $b = 11.986(1) \text{ \AA}$,

$c = 9.4621 \text{ \AA}$, $\beta = 97.046(5)^\circ$

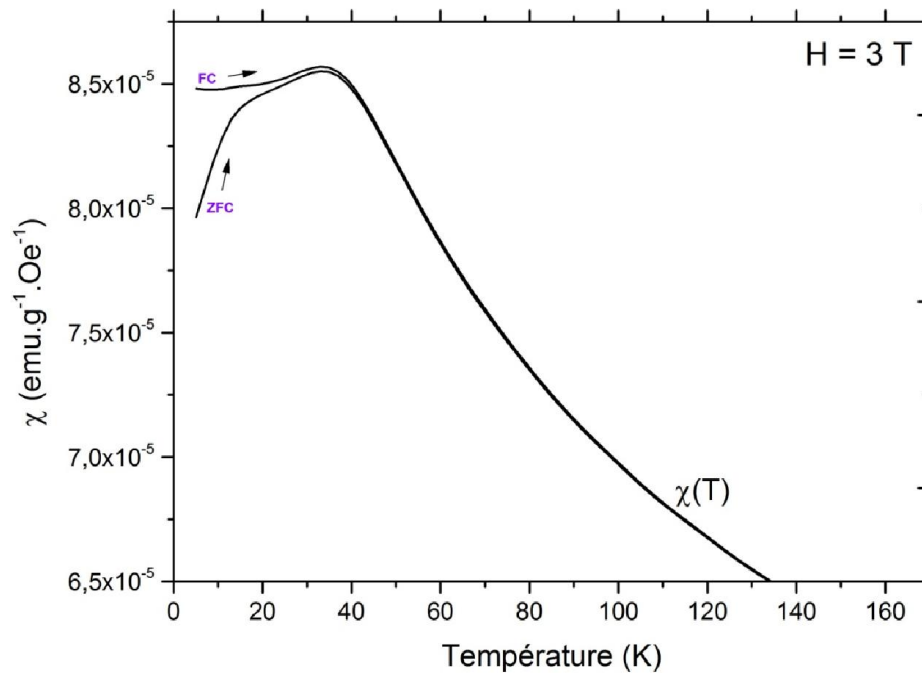
J.Schaefer et al; Z. Anorg. Allg. Chem. 621, 571(1995)

Neutron powder diffraction at RT- GEM(ISIS)

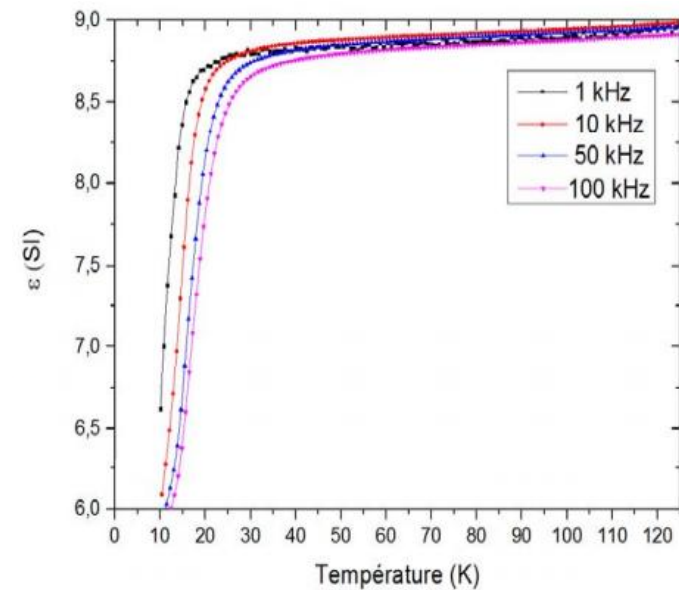
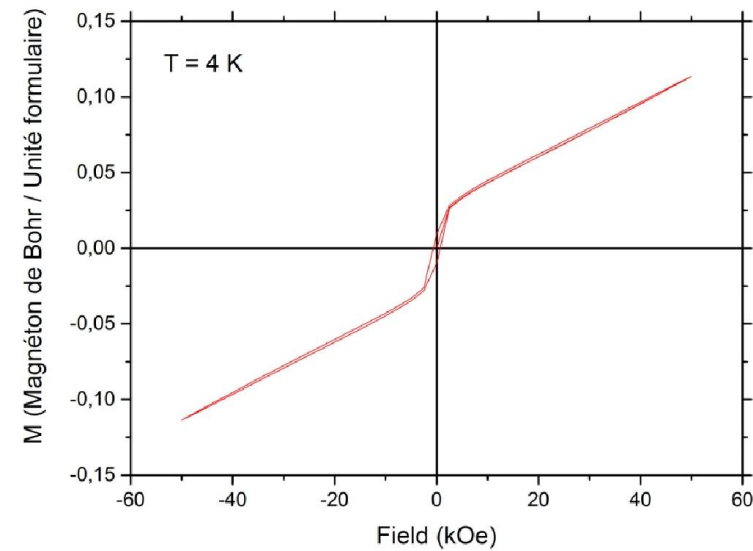


Cu_2FeBO_5

Physical properties



- two magnetic transitions at $T \approx 20 \text{ K}$ and $T \approx 40 \text{ K}$;
- magnetic behavior different from Fe_3BO_5 ;
- coupling between magnetic and electric transition at $T \approx 20 \text{ K}$.



Continentino et al; Eur. Phys. J. B 9, 613-618 (1999)

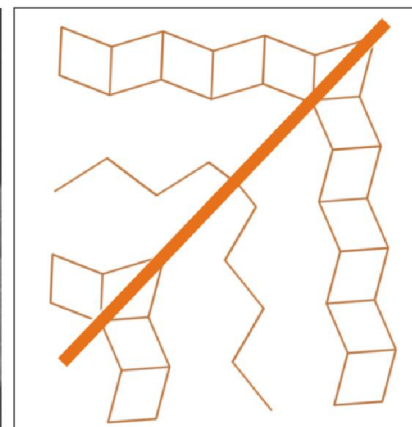
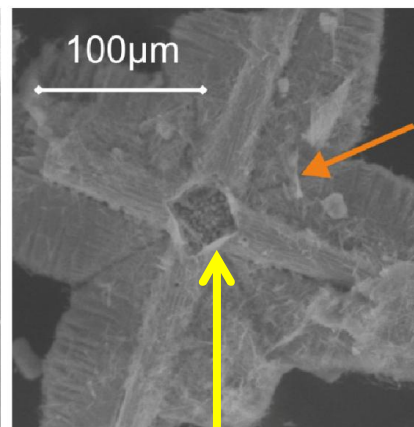
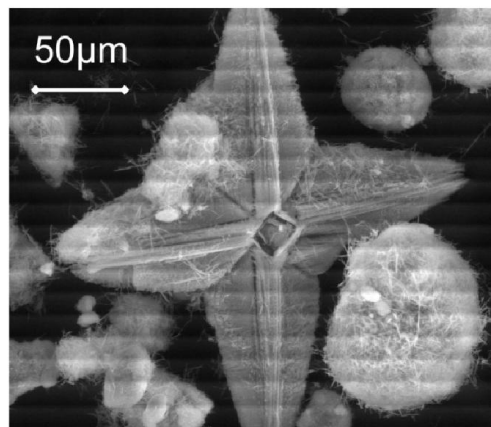


Hydrothermal synthesis

$T=310^\circ\text{C}$

Different hierarchical superstructures in function of pressure

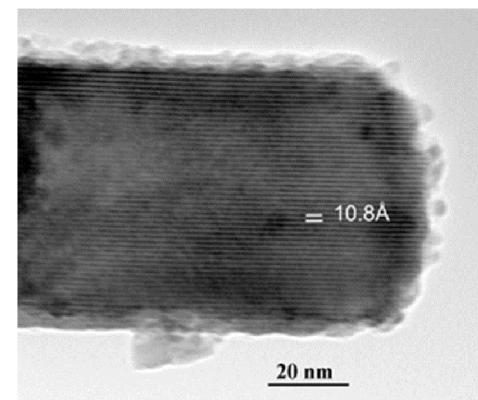
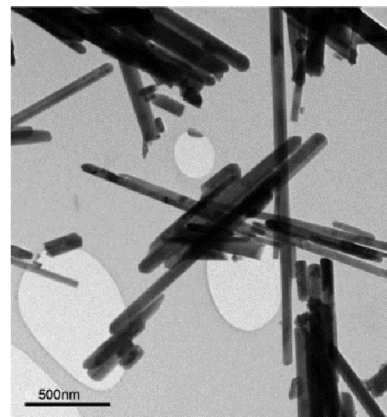
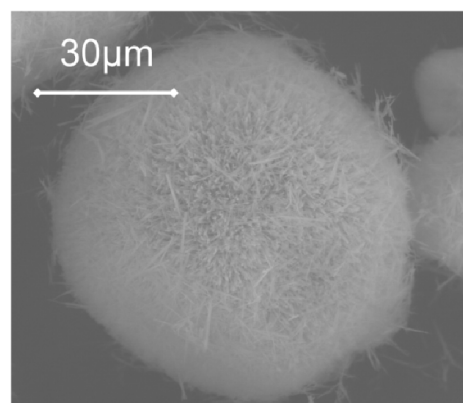
P= 800 bars



New original cross- shaped star!

Ni/Fe $\approx$ 2

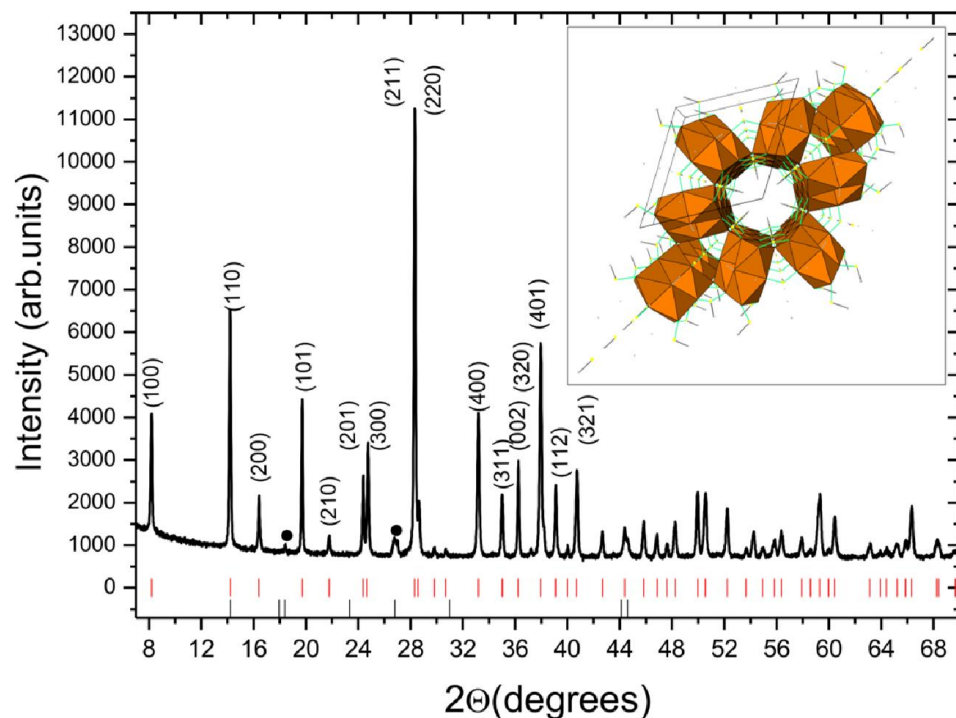
P= 1200 bars



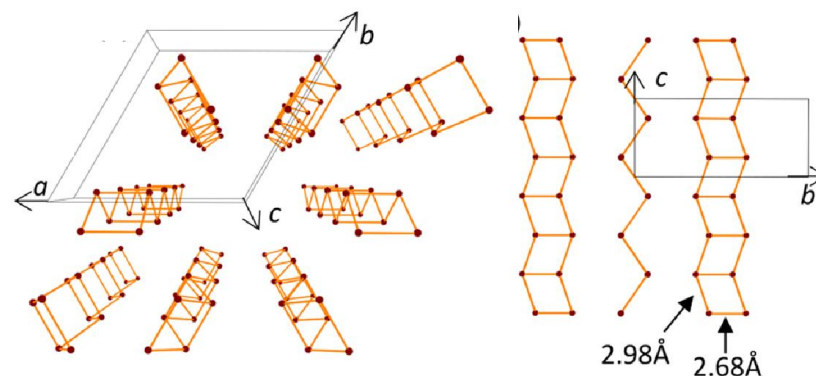
$\text{Ni}_{11}\square(\text{HPO}_3)_8(\text{OH})_6$

$P6_3mc$, $a = 12.4589(1)\text{\AA}$, $c = 4.9543(1)\text{\AA}$

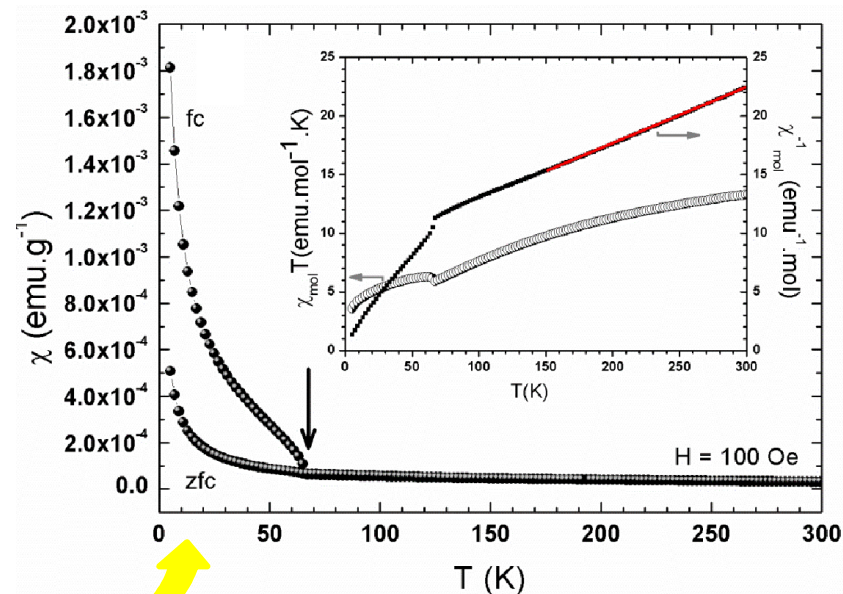
M. D. Marco et al., J. P. Attfield, Chem. Mater. 5 (1993) 121-128



Complex magnetic behaviour is observed at low temperature ($T=67\text{K}$)



Ni_2O_9 dimers share edges to form double chains of such dimers running along the c -axis.



Perspectives - 2015



- ❑ Further studies on the obtained materials :
 - Laboratory and large scale instruments;
 - in function of temperature and pressure;
 - Structure-Properties relationship.

- ❑ Communication : conferences and articles.

- ❑ Funding application : Call for proposal PICS-2014 Romania -France-
pending