Multiferroic properties of layered triangular compounds

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E. Elkaïm *Soleil Synchrotron*
J. Rouquette *Institut Charles Gerhardt*

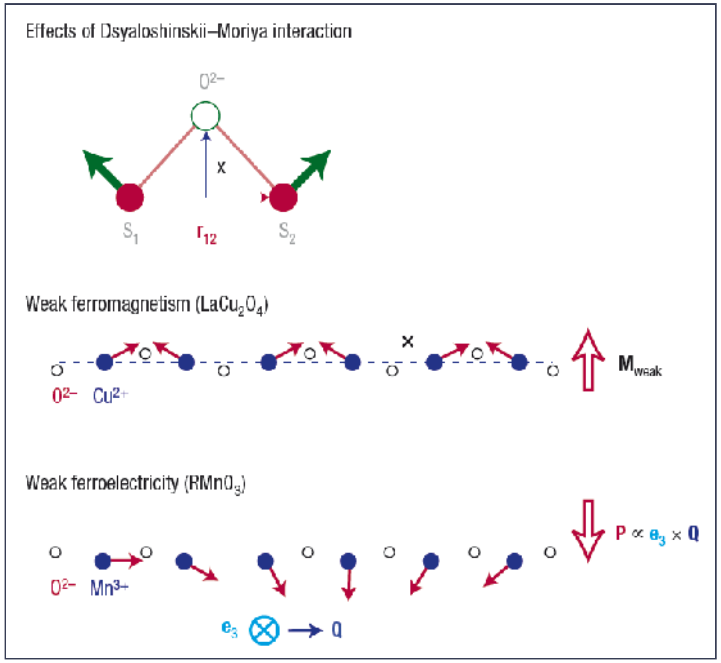
Ferroicity

Ferroicity describes the coupling between two order parameters (like P and M)

A multiferroic (M-P) compound cannot have either time or space reversal symmetry

Magnetic ordering implies breaking the time reversal symmetry
If cycloidal or helicoidal : breaking of space reversal symmetry too!

Complex magnetic structures



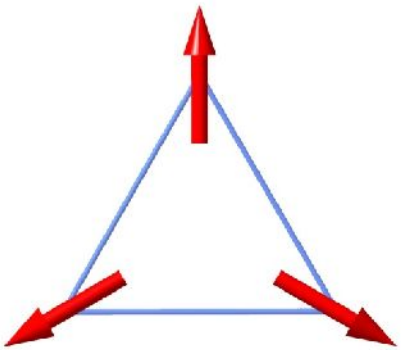
Spin current mechanism involving a Dzyaloshinskii-Moriya (DM) interaction to explain multiferroicity for a cycloidal magnetic structure.

S.W. Cheong & M. Mostovoy, Nature Mat. 6, 13 (2007)

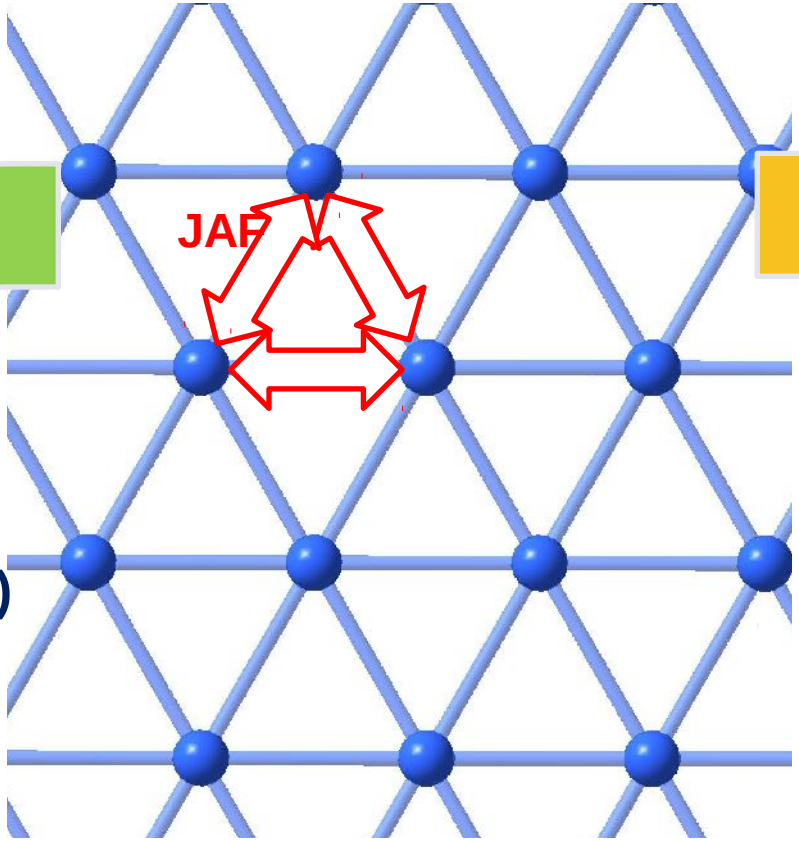
The triangular lattice

Heisenberg spins

120° ordering (0 K)



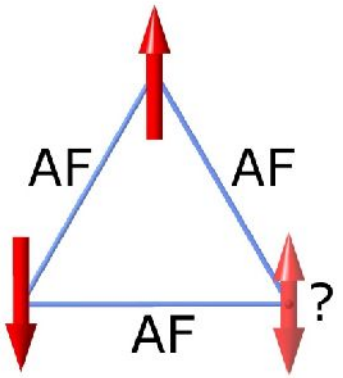
Non colinear magnetic structure



1st neighbour JAF magnetic exchange is antiferromagnetic

Axial magnetic anisotropy Ising spin

Degenerate ground state



The AMO2 metal oxides family

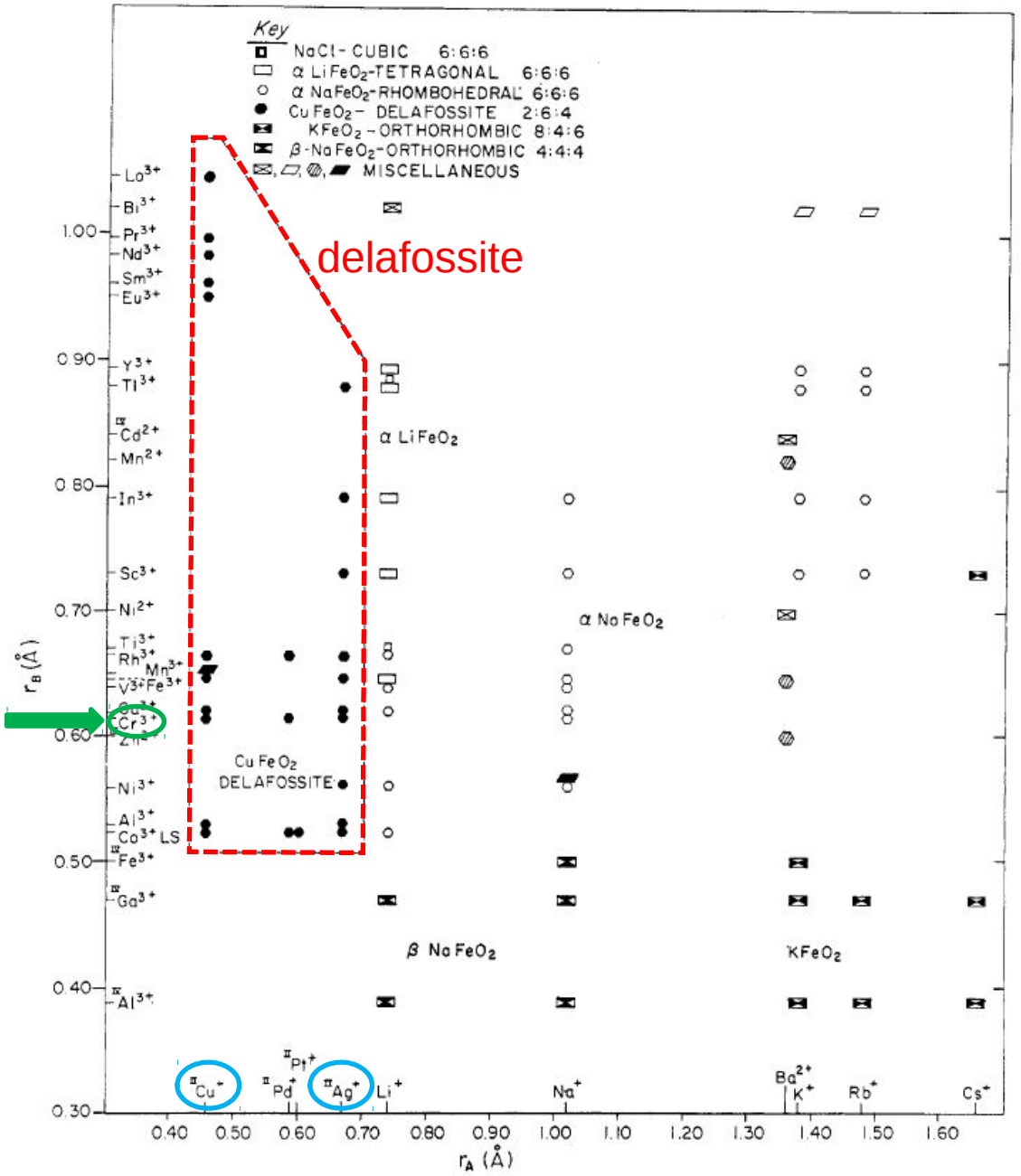
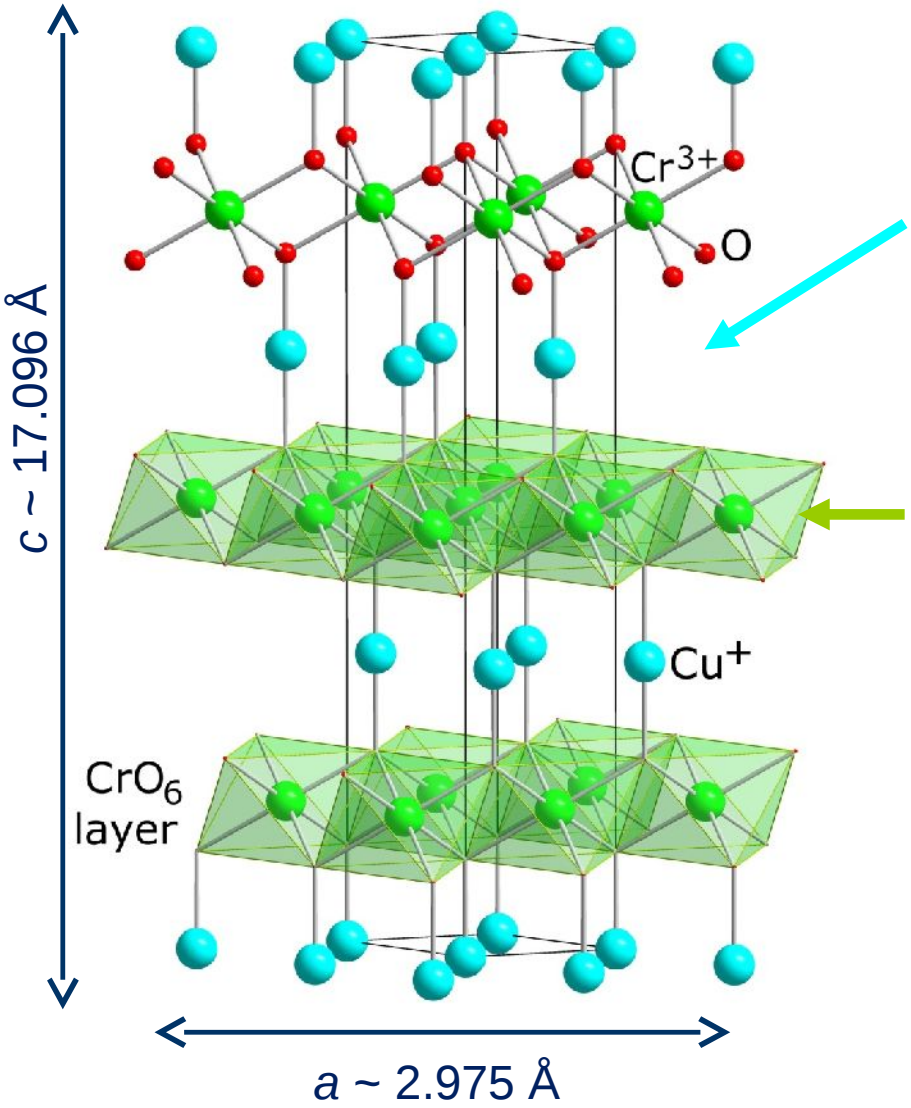


Figure 2.—Plot of r_A *vs.* r_B for various ABO_2 phases.

Delafossite : a highly anisotropic structure

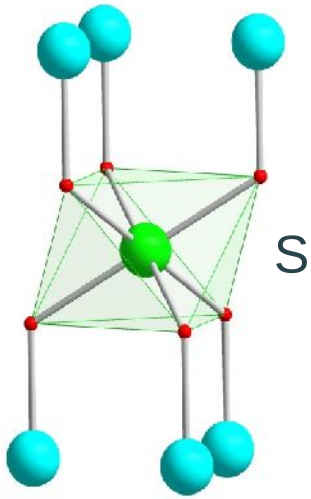
Rhombohedral *R*-3*m*



CuCrO2

Cu+ linearly coordinated :
O-Cu-O dumbbells

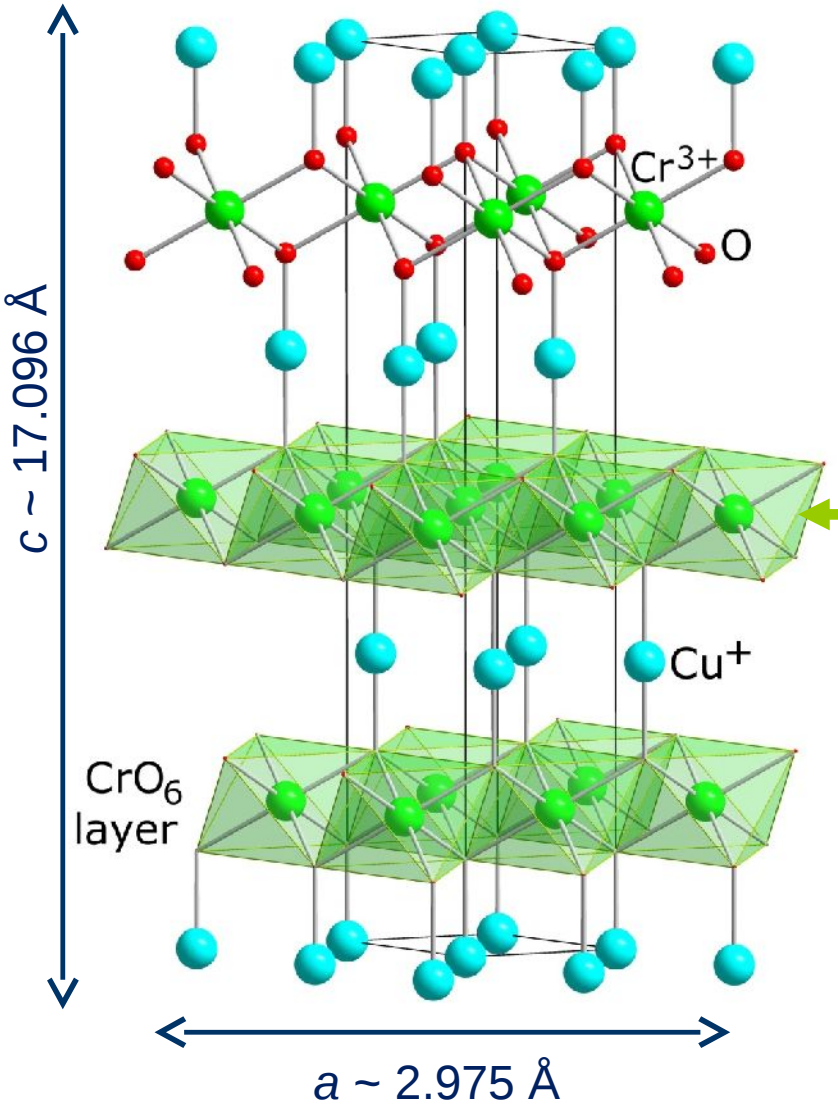
compact layers
of CrO6 octahedra



6 equal Cr-O distances
Slight compression along *c*
D3d symmetry

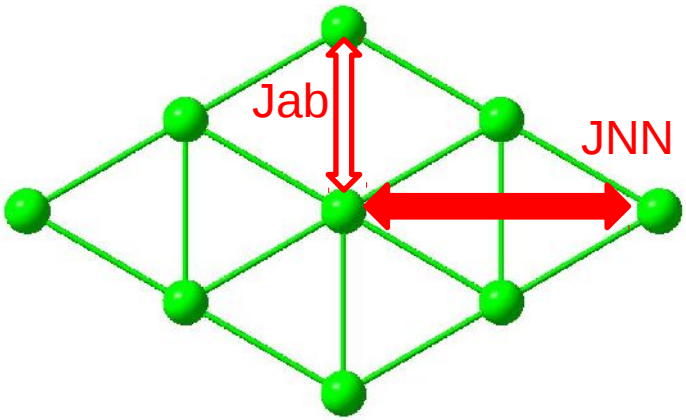
Delafossite : a highly anisotropic structure

Rhombohedral *R*-3*m*



Cr3+ ions form
a triangular array

Cr3+ - Cr3+ interactions AFM
geometric frustration?



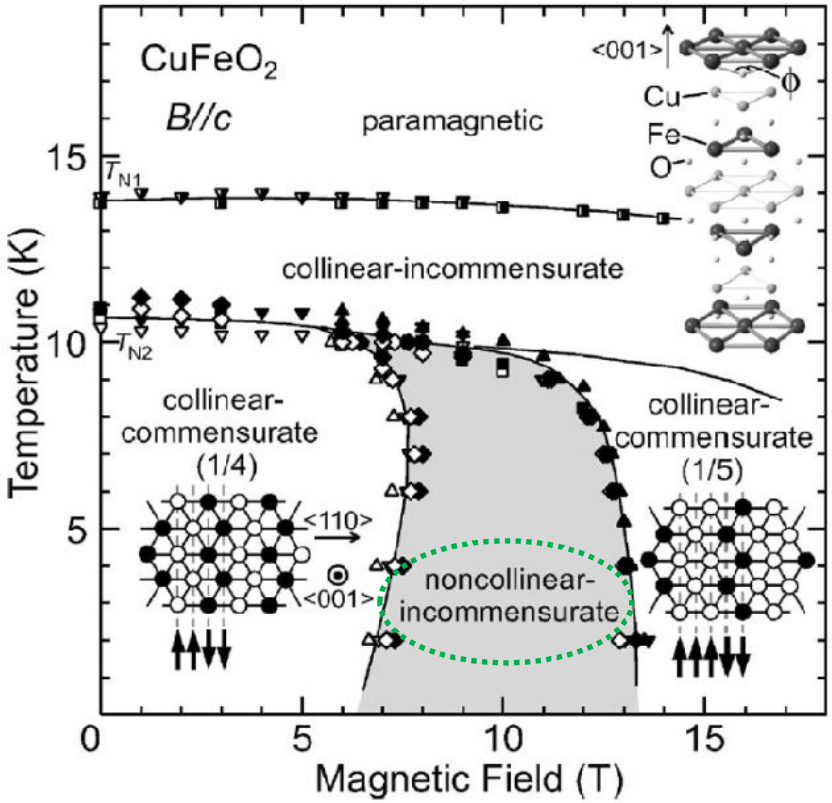
Jintra (3Å) >> Jinter (5.8Å) ≠ 0

TN ~ 24K

Other transition metals…

CuFeO2 : magnetic field or substitution

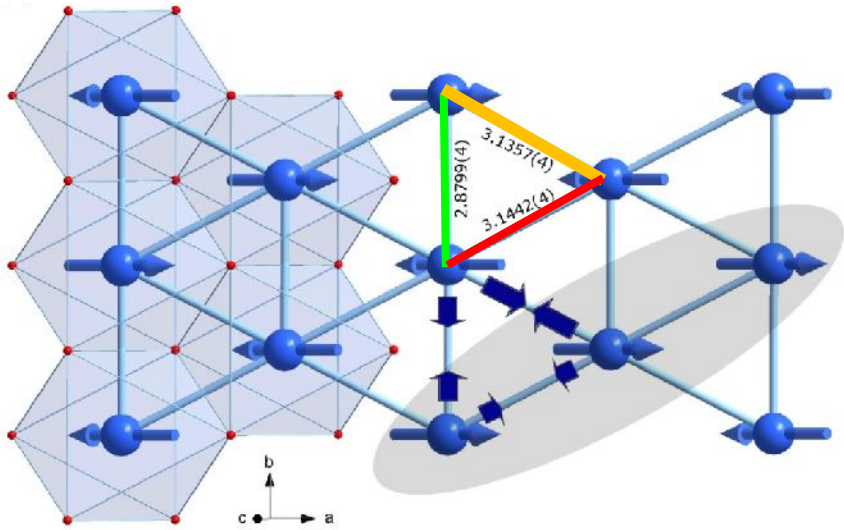
T. Kimura et al., **PRB** 73, 220401(R) (2006)



AgFeO2 : ferroelectric below 9K

N. Terada et al., **PRL** 109, 097203 (2012)

CuMnO2 : no ferroelectricity



Release of the magnetic frustration by symmetry lowering
Colinear magnetic structure (JT)

F. Damay et al., **PRB** 80, 094410 (2009)

CuCrO2

PRL **101,** 067204 (2008) PHYSICAL REVIEW LETTERS week ending 8 AUGUST 2008

Spin-Driven Ferroelectricity in Triangular Lattice Antiferromagnets $ACrO_2$ (A = Cu, Ag, Li, or Na)

S. Seki,[1] Y. Onose,[1,2] and Y. Tokura[1,2,3]

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[2]*Multiferroics Project, ERATO, Japan Science and Technology Agency (JST), Tokyo 113-8656, Japan*
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(Received 24 January 2008; published 7 August 2008)

The correlation between the dielectric and magnetic properties is investigated on the triangular-lattice antiferromagnets $ACrO_2$ (A = Cu, Ag, Li, or Na) with a 120-degree spiral structure. For the A = Cu and Ag compounds with a delafossite structure, the ferroelectric polarization emerges with a spiral-spin order, implying strong coupling between ferroelectricity and the spiral-spin structure. For the A = Li and Na compounds with an ordered rock salt structure, on the other hand, no spontaneous polarization is discerned, while the clear anomaly in the dielectric constant can be observed upon the transition to the spiral-spin ordered state. This feature can be ascribed to the possible antiferroelectric state induced by the alternate stacking of the Cr-spin sheet with opposite vector spin chirality.

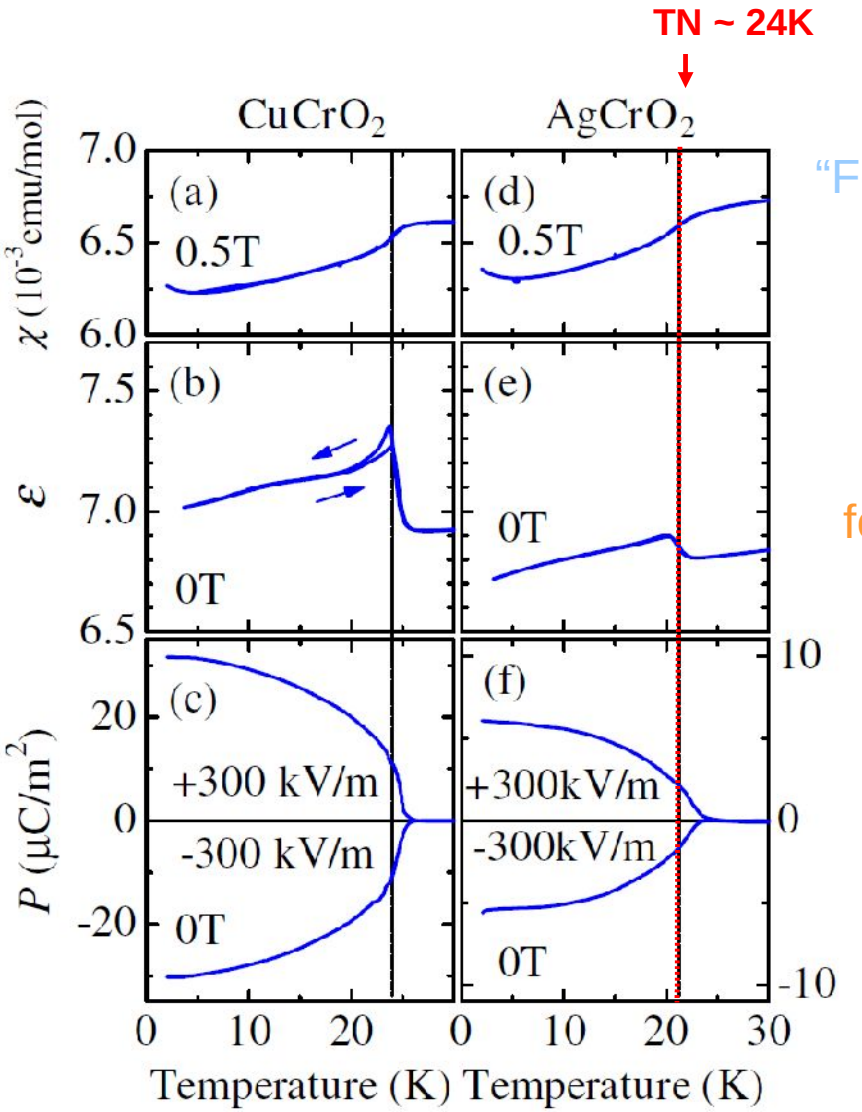
Spin-Driven Ferroelectricity in Triangular Lattice Antiferromagnets $ACrO_2$ (A = Cu, Ag, Li, or Na)

S. Seki,[1] Y. Onose,[1,2] and Y. Tokura[1,2,3]

Magnetic susceptibility

Dielectric constant

Electric polarisation

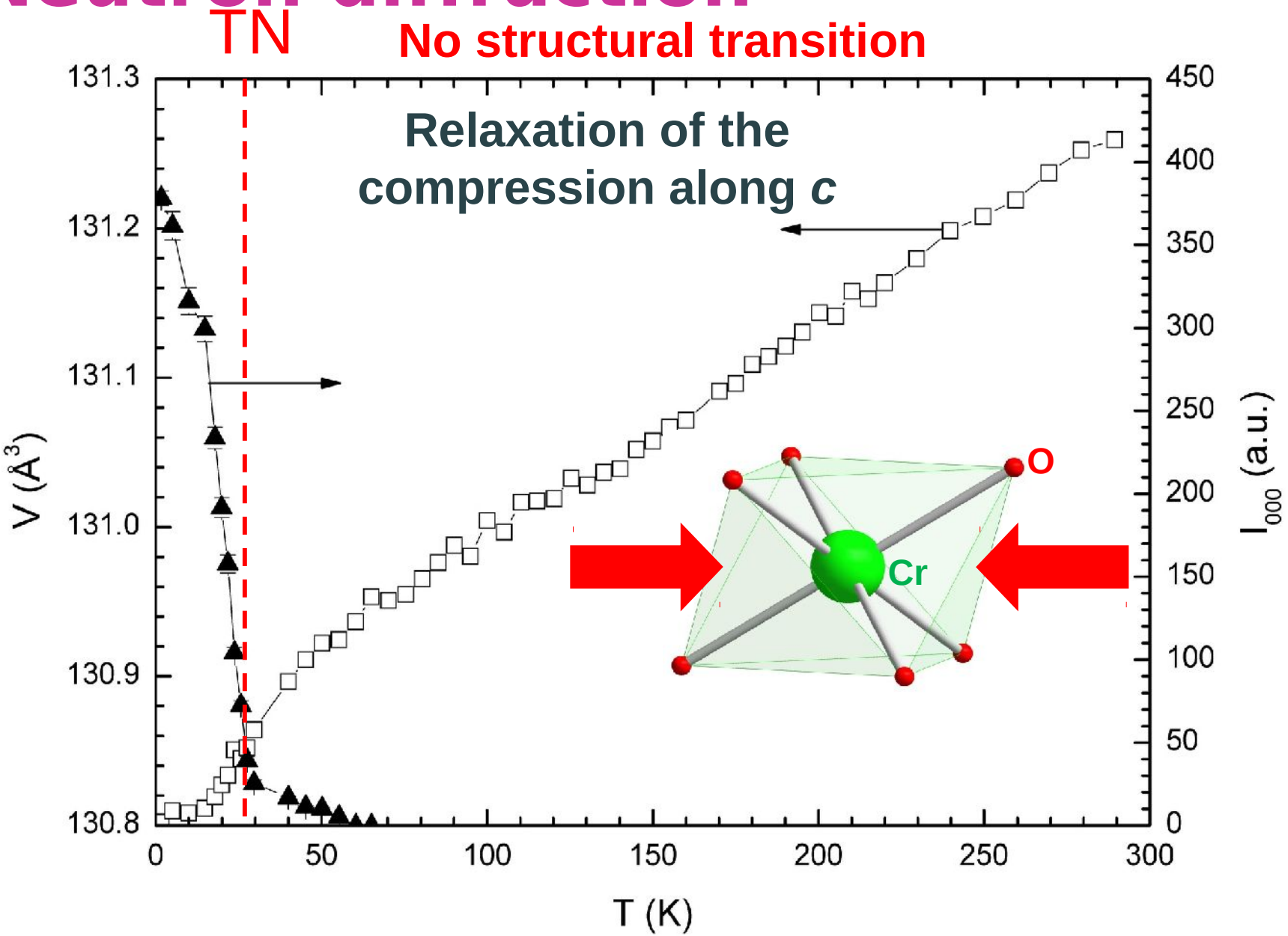


"Ferroelectric polarisation emerges upon the spiral spin order"

"Strong coupling between the ferroelectricity and the spiral spin structure"

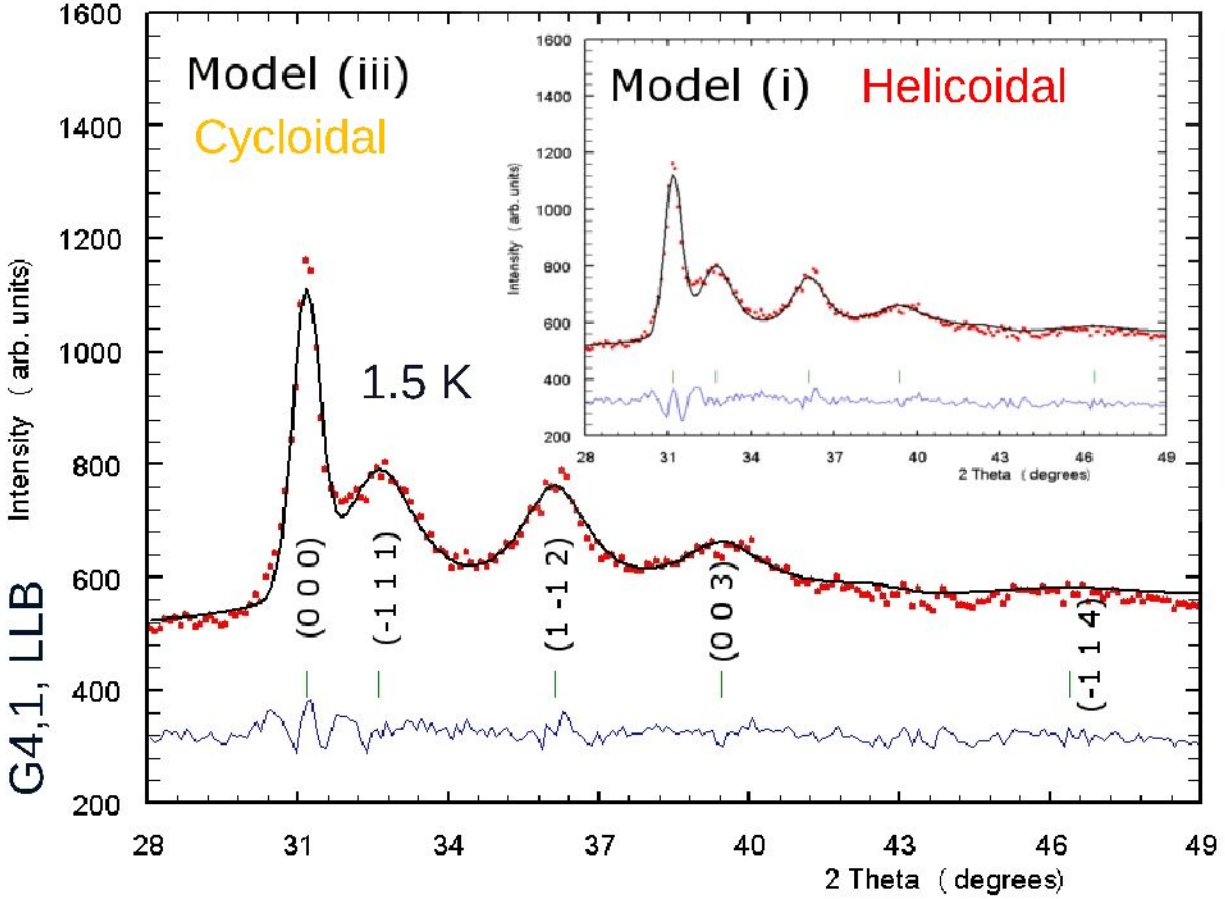
"Microscopic origin unclear"

Neutron diffraction



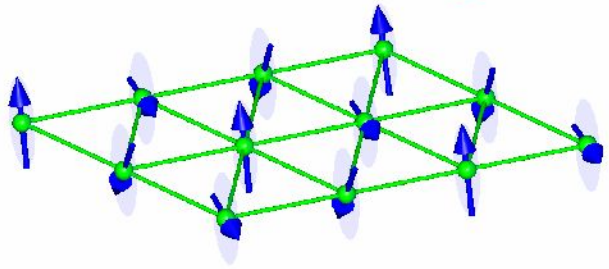
Neutron diffraction

Broad and overlapped magnetic peaks
Incommensurate propagation vector (q q 0) (q ~ 0.329)

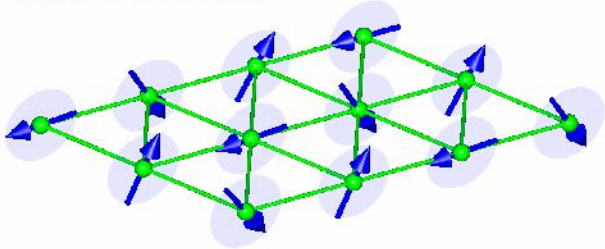


Two models with polar magnetic point groups can be proposed for the magnetic structure

Modulated helicoidal (i)



Cycloidal (iii)

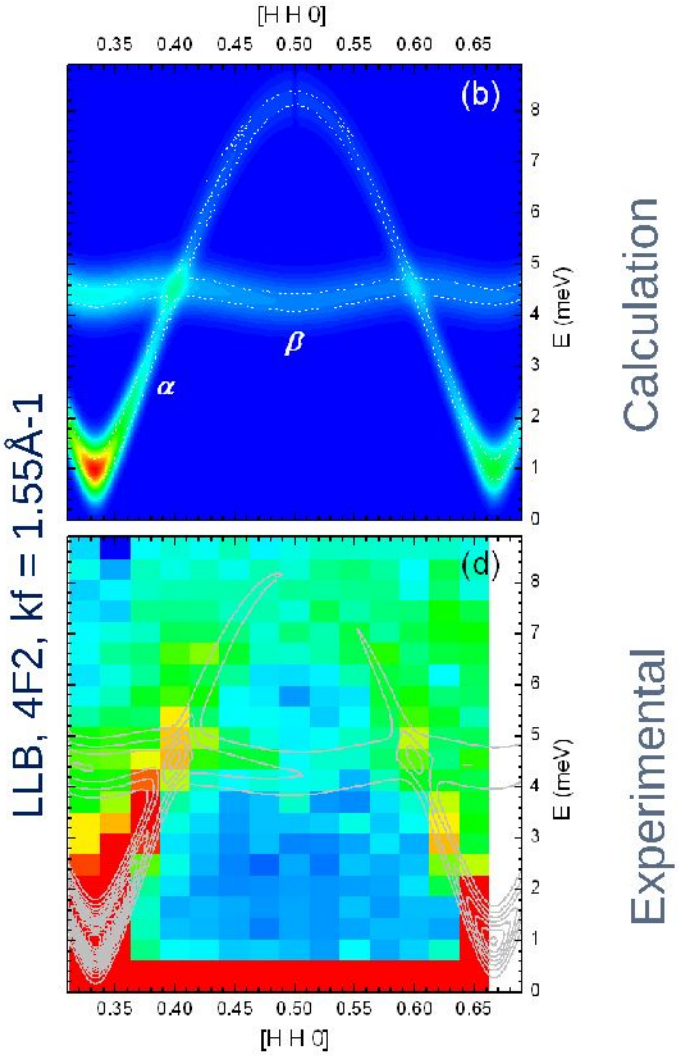


Elliptical enveloppe in the (110) plane

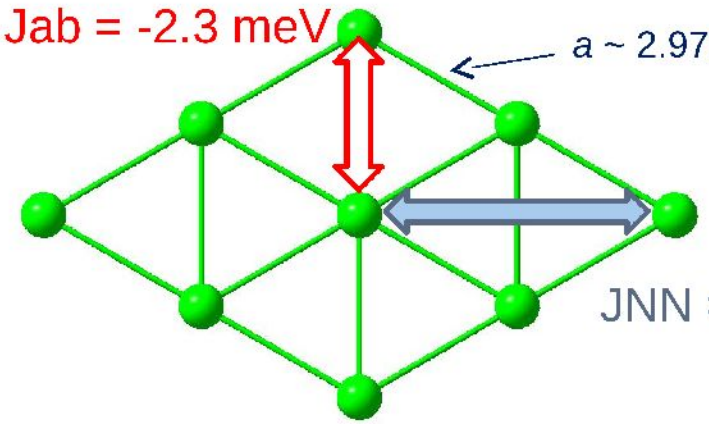
Refinement considering platelet-like shaped crystallites with disordered stacking along *c* (size-model = 1 in Fullprof)

Modelling the spin dynamics

$$H = J_{ab} \sum_{i,j}^{\substack{in\\plane}} S_i S_j + J_{NN} \sum_{i,j}^{\substack{in\\plane}} S_i S_j + J_c \sum_{k,l}^{\substack{inter\\plane}} S_k S_l + D \sum_i (S_i \cdot n_i)^2 \qquad (5)$$



All in-plane magnetic interactions are antiferromagnetic



Jc is vanishingly small (either ferro or antiferromagnetic)

Confirm the 2D character, and the importance of 2nd neighbour exchange

Multiferroic properties…

…still to be understood!

Helicoidal magnetic model
Polarization in the *ab* plane

Precludes the spin current model

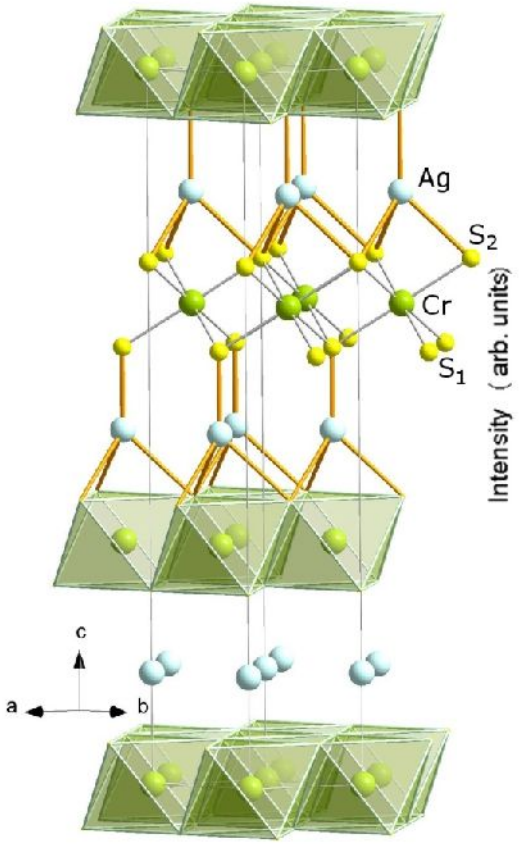
Arima's model* based on the variation of the hybridisation metal-ligand

Study of parent compound with different ligand ions (S, Se, Te…)

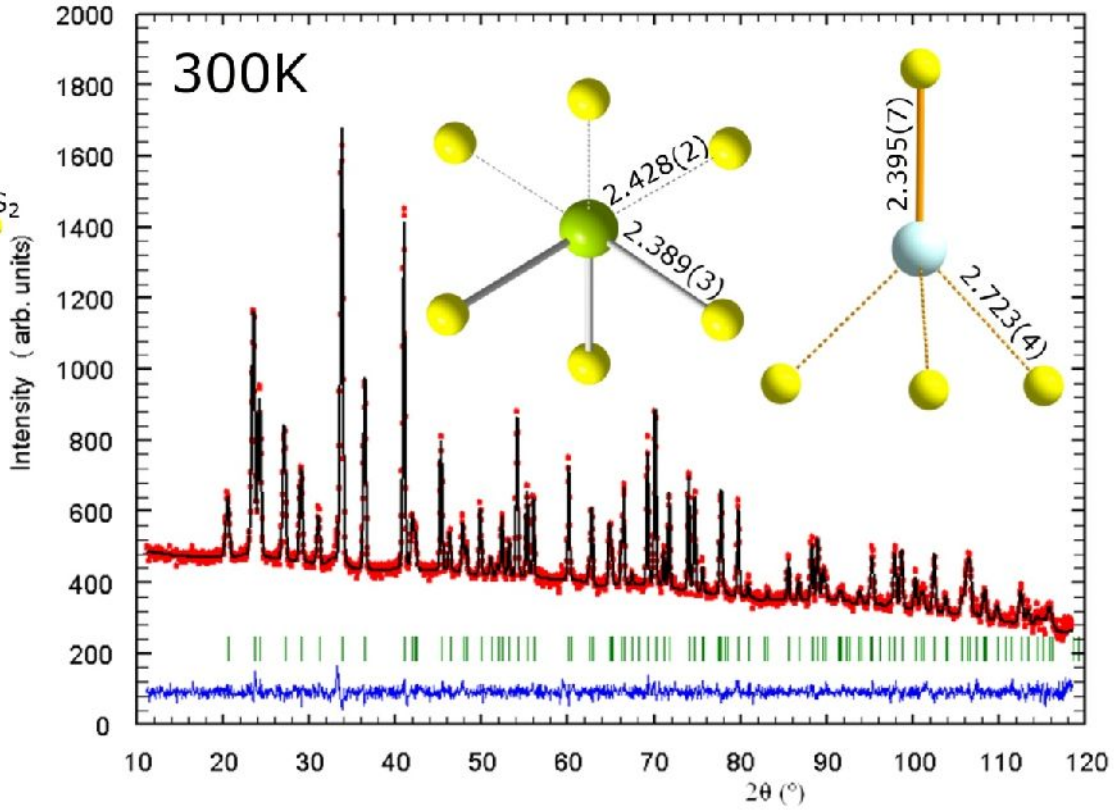
**T. H. Arima J. Phys. Soc. Japan 76, 073702 (2007)*
Polarisation related to the variation of the hybridisation metal-ligand because of spin-orbit coupling (P parallel to **k**)

How to understand the role of the ligand ion in the framework of Arima's model?

AgCrS2 : same magnetic lattice topology as CuCrO2



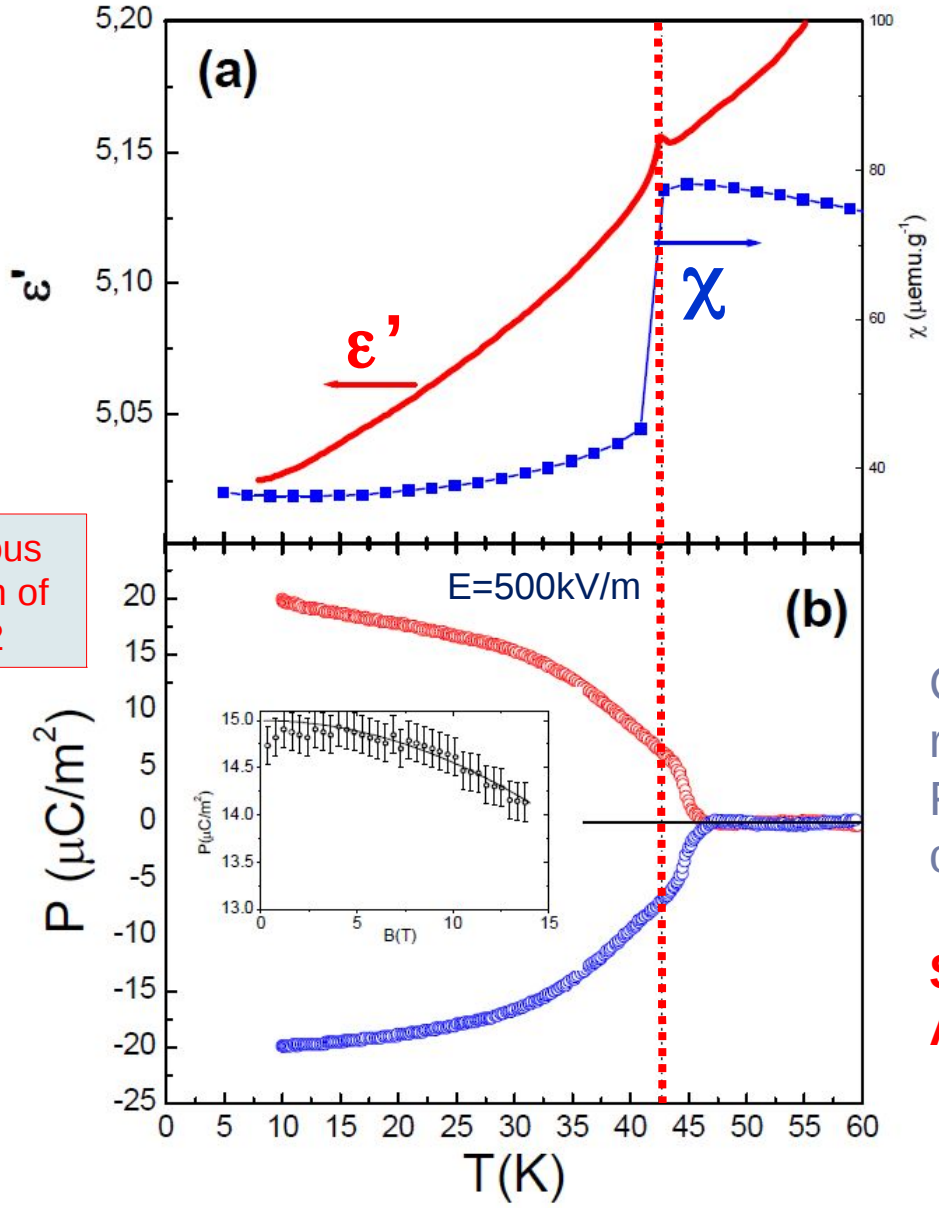
a = 3.49 Å, *c* = 20.54 Å



Polar R3m layered structure at 300K

Large anisotropic displacement factor of Ag+

AgCrS2 : dielectric permittivity, polarisation



Spontaneous polarisation of 20μC.m-2

Charge/spin coupling ?

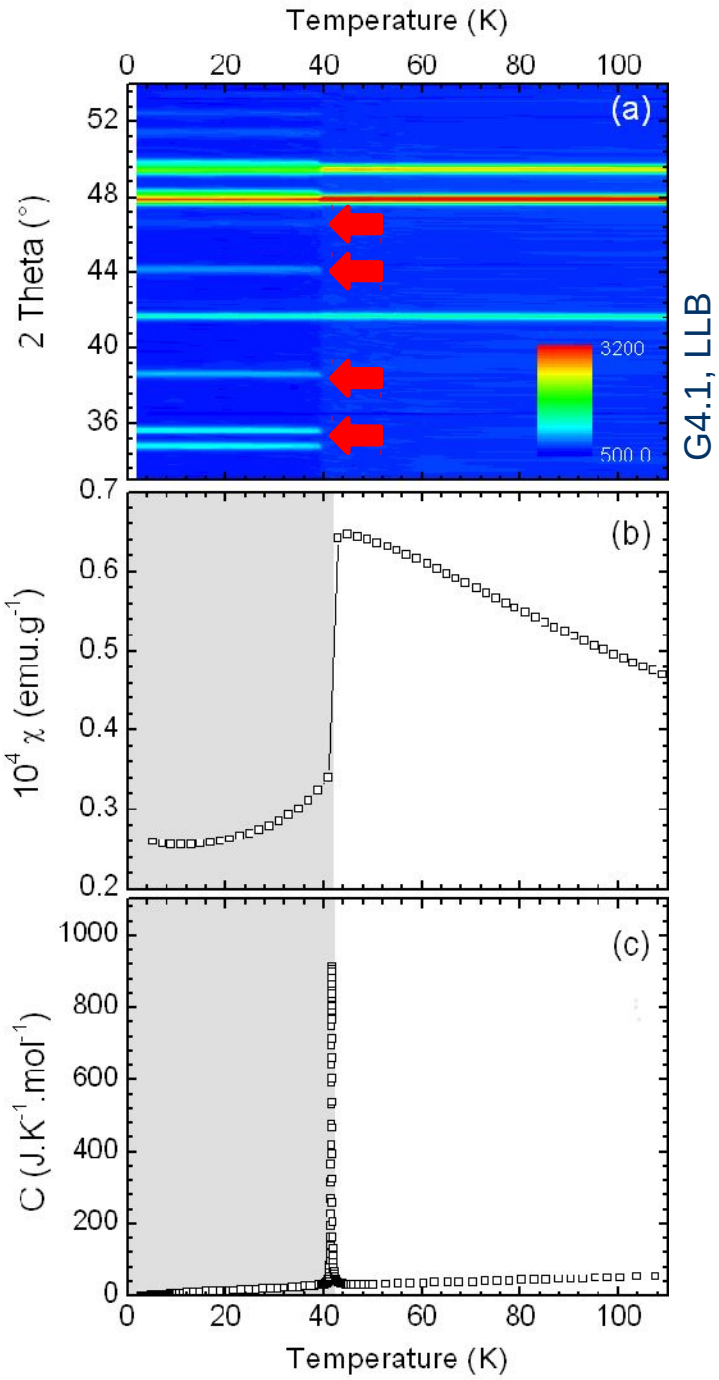
Clear transition in the TN region
Reversing E induces a sign change of ΔP.

Spin driven ferroelectricity of AgCrS2?

K. Singh et al., *Chem. Mater.* **21**, 5007 (2009)

AgCrS2

At TN = 41.5K



Structural transition +
Antiferromagnetic Bragg peaks

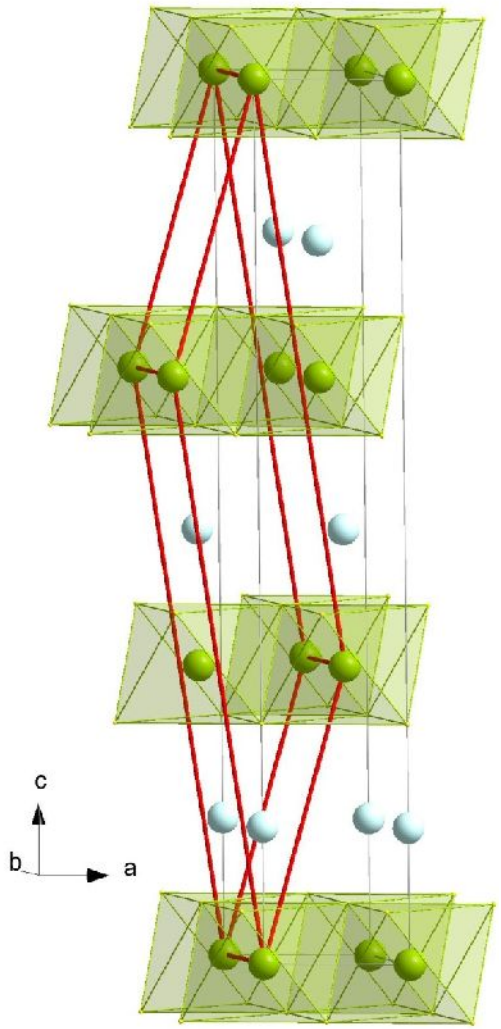
In agreement with susceptibility data

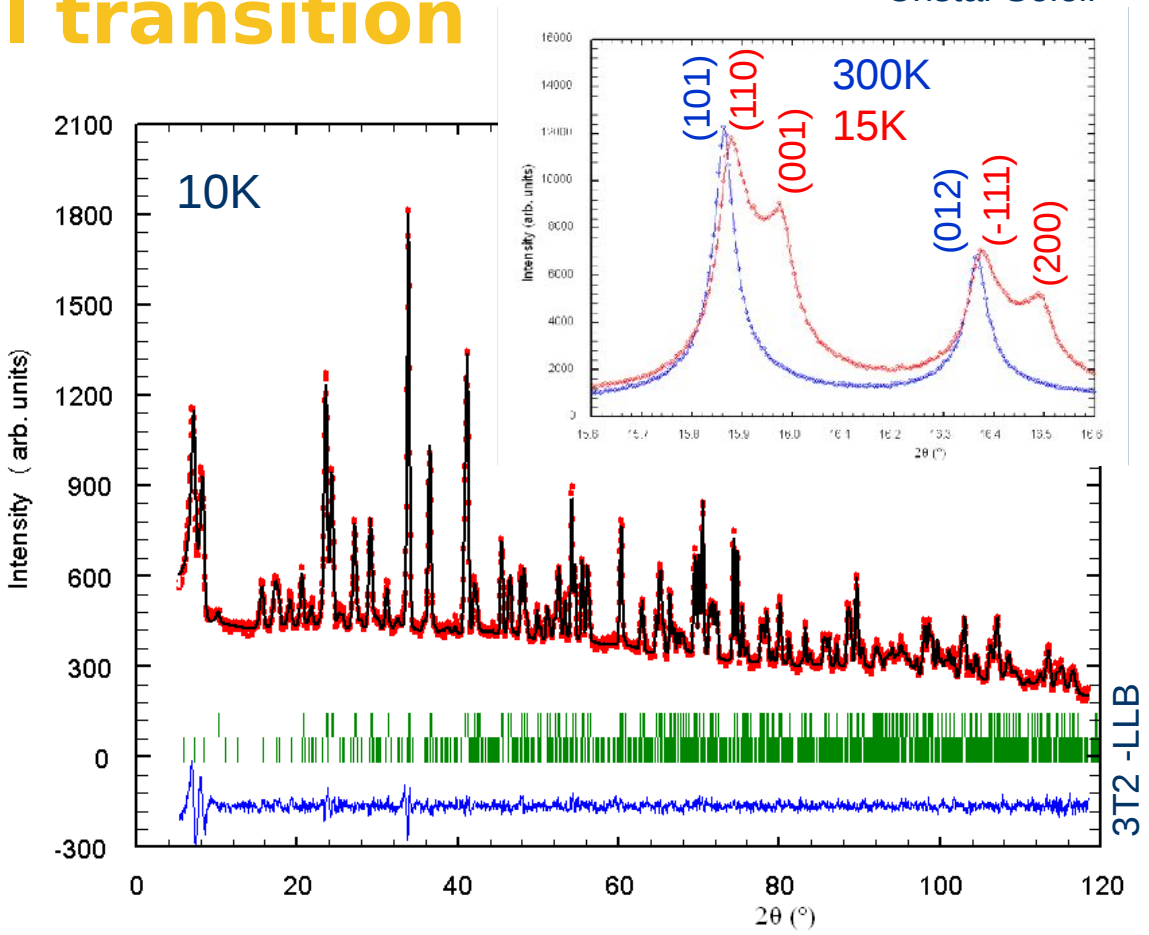
Transition is first-order

AgCrS2 structural transition

Cristal-Soleil

R3m➡Cm

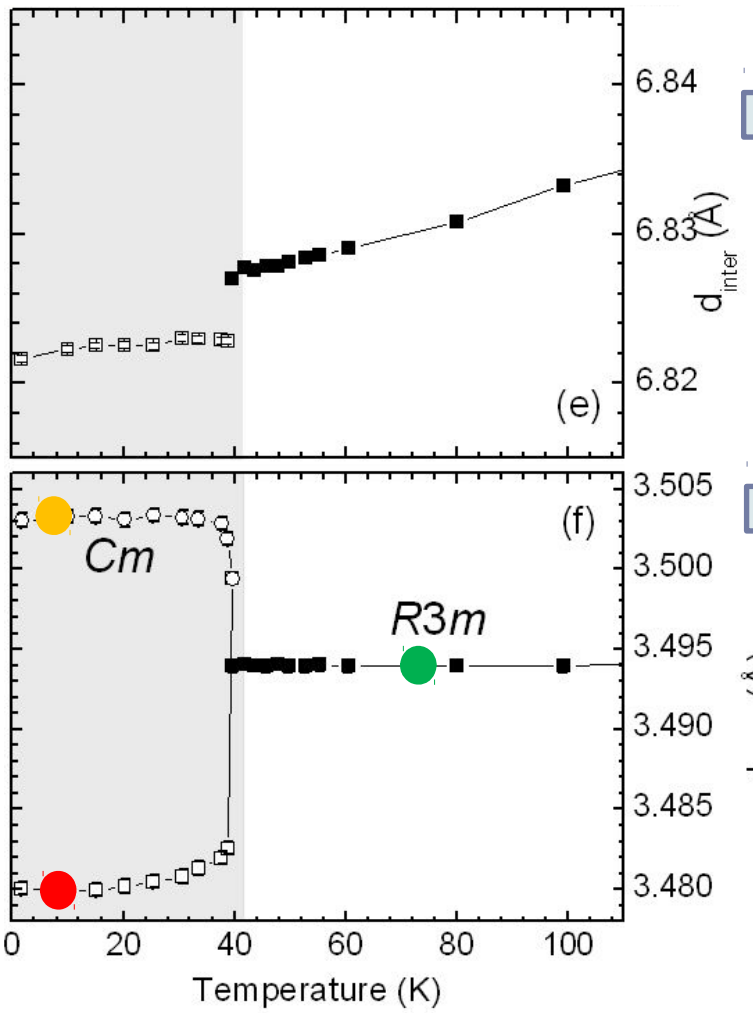




Polar monoclinic cell below TN :

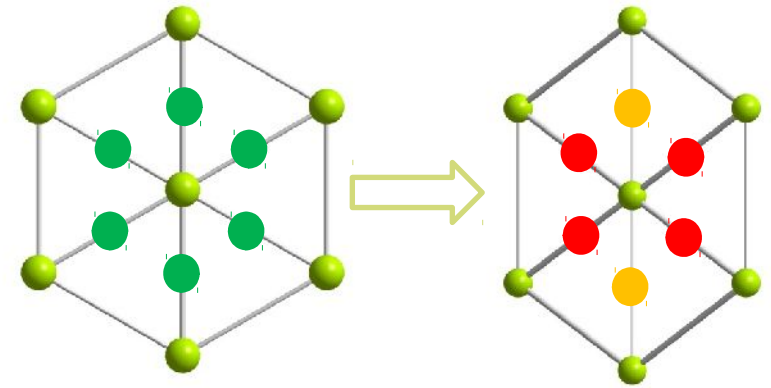
a = 13.7861(2) Å
b = 3.5042(1) Å
c = 7.1132(1) Å
β = 155.28(5) °

AgCrS2 TN



Large striction of the distance between magnetic planes

Distortion of the regular triangular lattice : partial lift of the frustration!



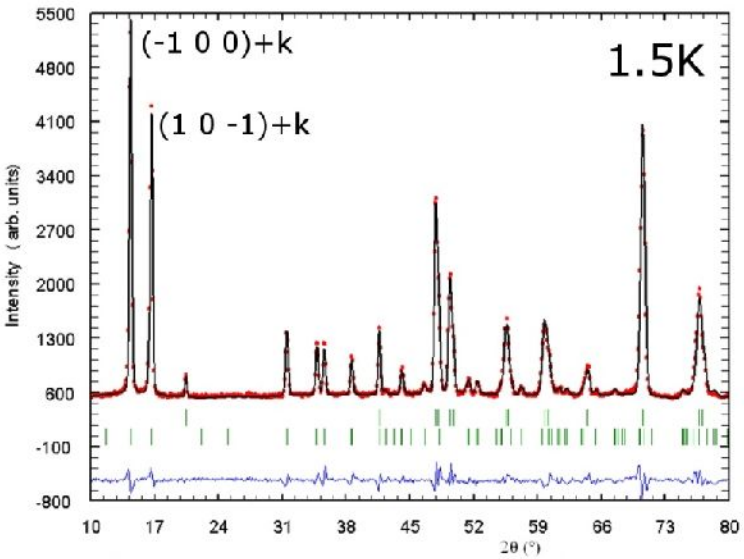
3.4979(4)Å

3.5042(10)Å

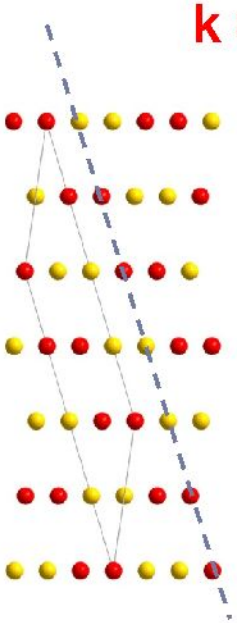
3.4796(10)Å

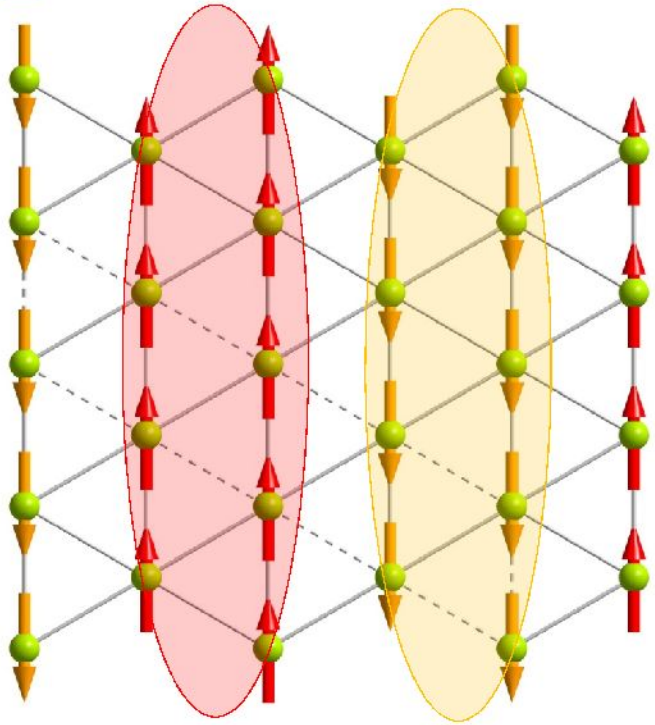
Magnetic order in AgCrS2

G4,1, LLB



k = (0 0 0.25)

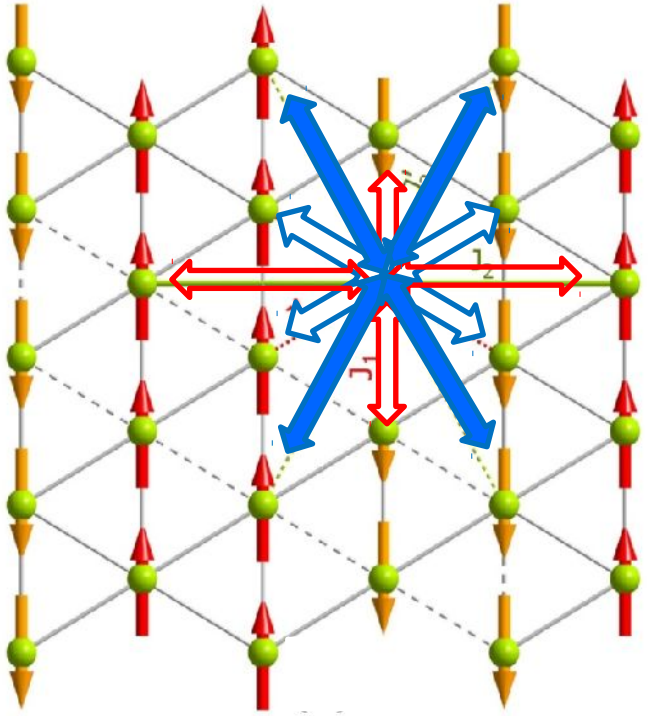




Within the triangular plane : double ferromagnetic « stripes » coupled antiferromagnetically
Colinear magnetic structure with moment *// b*

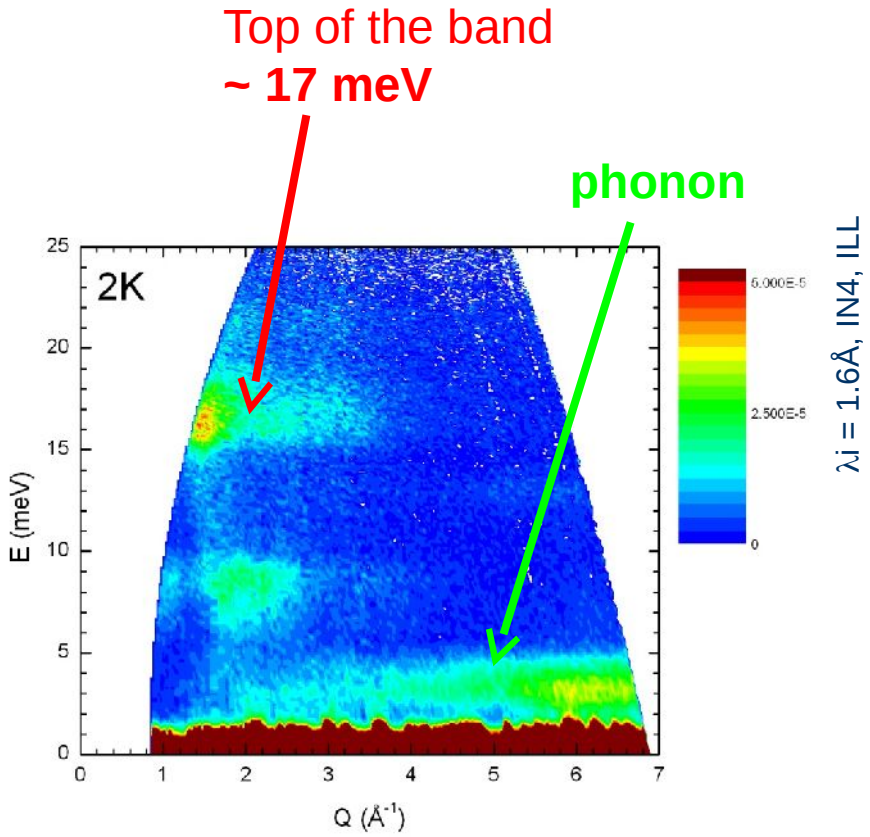
Stacking along *c* has double stripe configuration too

Understanding AgCrS2 magnetic structure

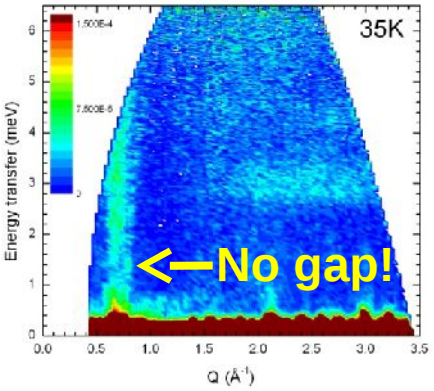


In- plane interactions…
Jab, J'ab, JNN, J'NN
…and additionnal out-of-plane exchanges!

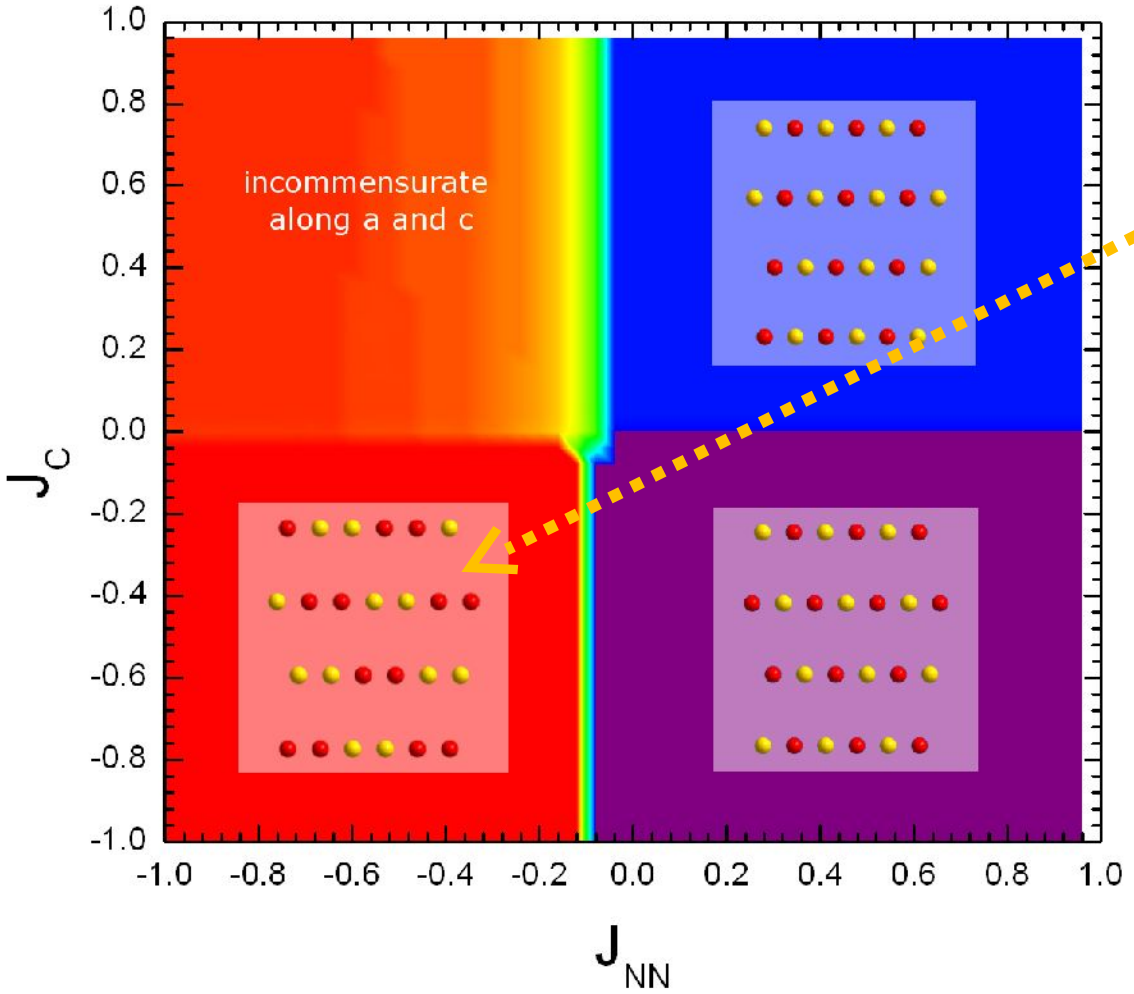
TOF inelastic scattering spectra



Magnetic phase diagram



Mean-field calculations results (no anisotropy term)



Correct phase is stabilised for :

Jab > 0

JC and JNN < 0

Jab' + JNN' small

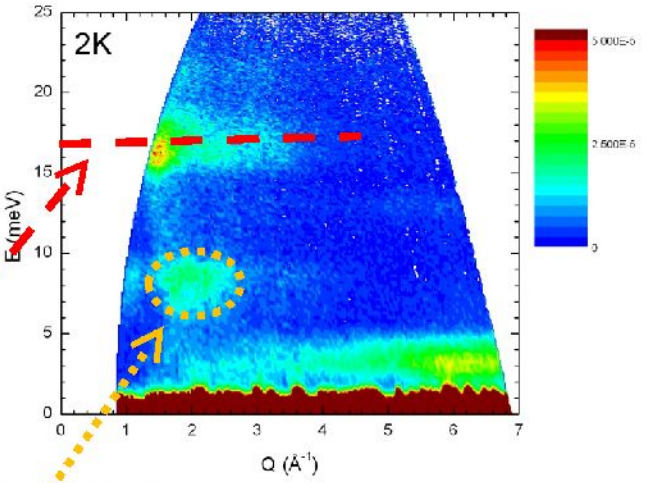
JC' = 0

Magneto-elastic coupling is the key to the 4-sublattice magnetic structure in AgCrS2

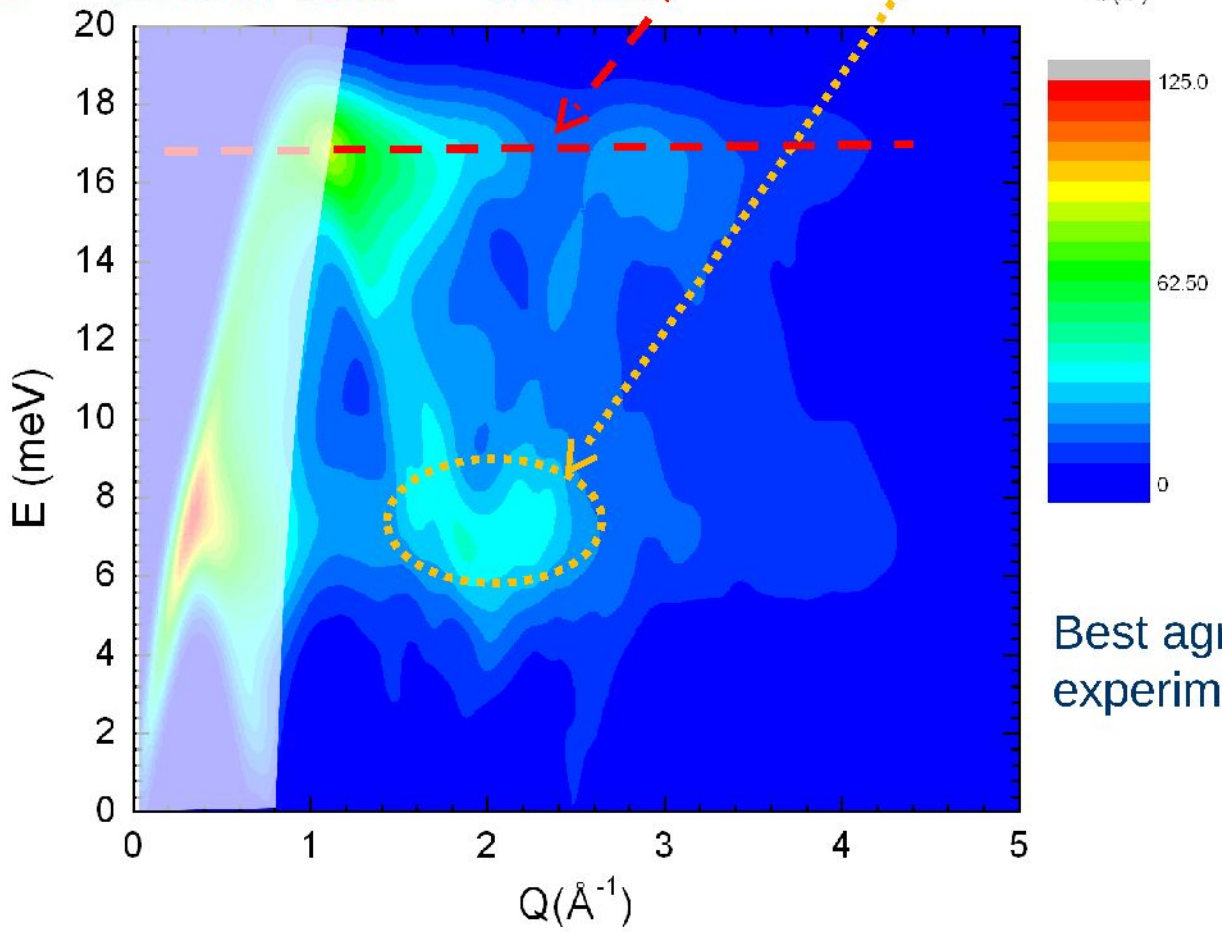
Powder averaged spin-wave calculation

Calculations performed for different points of the phase diagram

Jab = 1.8 meV ; JNN = -1.0 meV
JC = -0.6 meV ; Jab' = -0.05 meV



IN4, ILL



Best agreement with experimental data

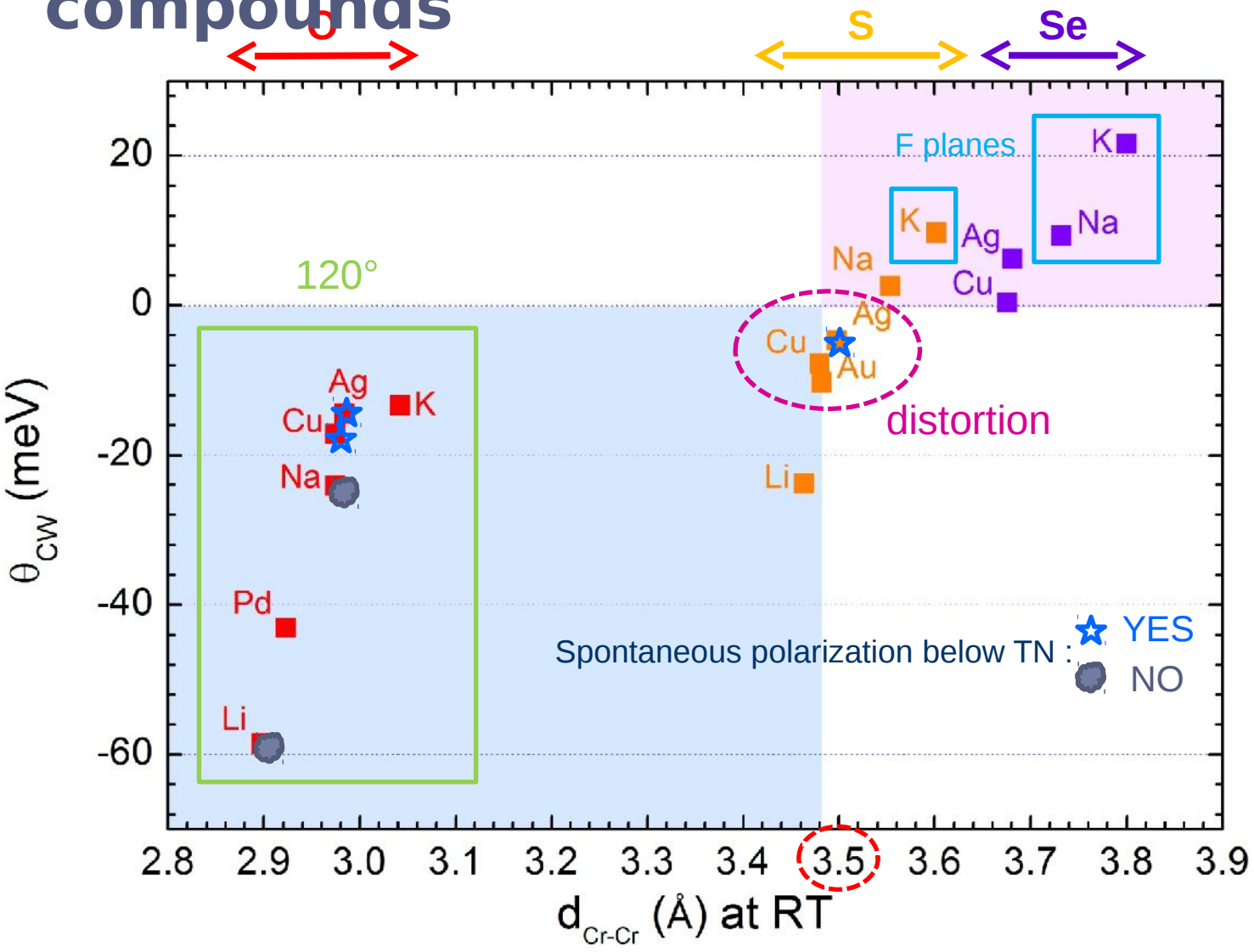
Multiferroic properties…

In AgCrS2 as well, ferroelectricity remains to be understood : new mechanisms can be invoked, in particular large atomic displacements at the magnetoelastic transition (polar crystal structure)

Note that in AgCrS2, Jab > 0 (unlike CuCrO2) : threshold* value of dCr-Cr

*F.M.R Engelsman et al., J. Solid State Chem. 6, 574 (1973)

Properties of layered ACr(O,S,Se)2 compounds



Another way to play with the topology of the triangular lattice : $LuFe_2O_4$

nature Vol 436|25 August 2005|doi:10.1038/nature04039

LETTERS

Ferroelectricity from iron valence ordering in the charge-frustrated system $LuFe_2O_4$

Naoshi Ikeda[1], Hiroyuki Ohsumi[1], Kenji Ohwada[2], Kenji Ishii[2], Toshiya Inami[2], Kazuhisa Kakurai[3], Youichi Murakami[4], Kenji Yoshii[2], Shigeo Mori[5], Yoichi Horibe[5] & Hijiri Kitô[6]

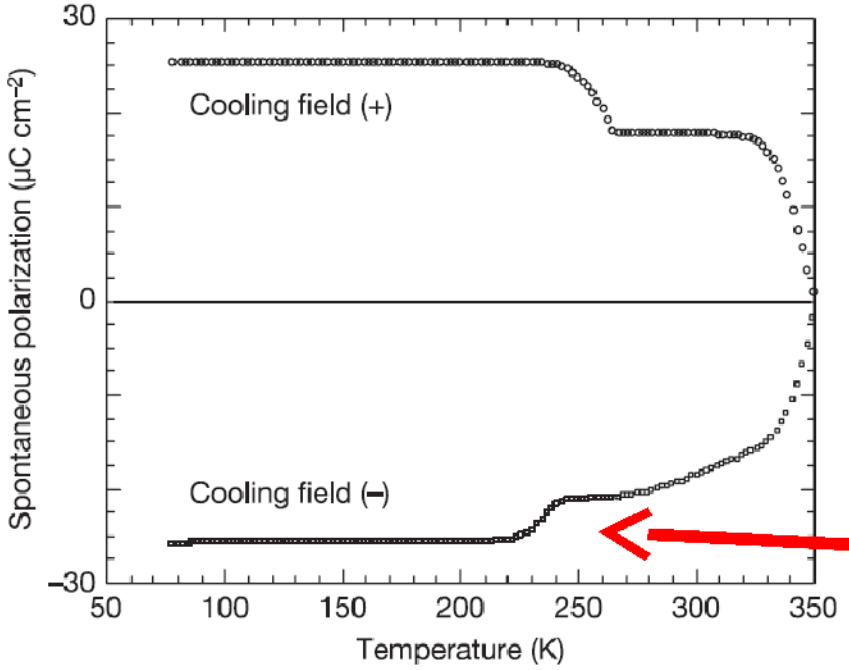


Figure 3 | Temperature variation of the electric polarization of $LuFe_2O_4$. The plot is the integration of a pyro-electric current measurement. The current flow from the sample was recorded on heating after electric field cooling along the *c* axis. The direction of the electric polarization depends on the direction of electric field, which indicates that $LuFe_2O_4$ possesses macroscopic electric polarization.

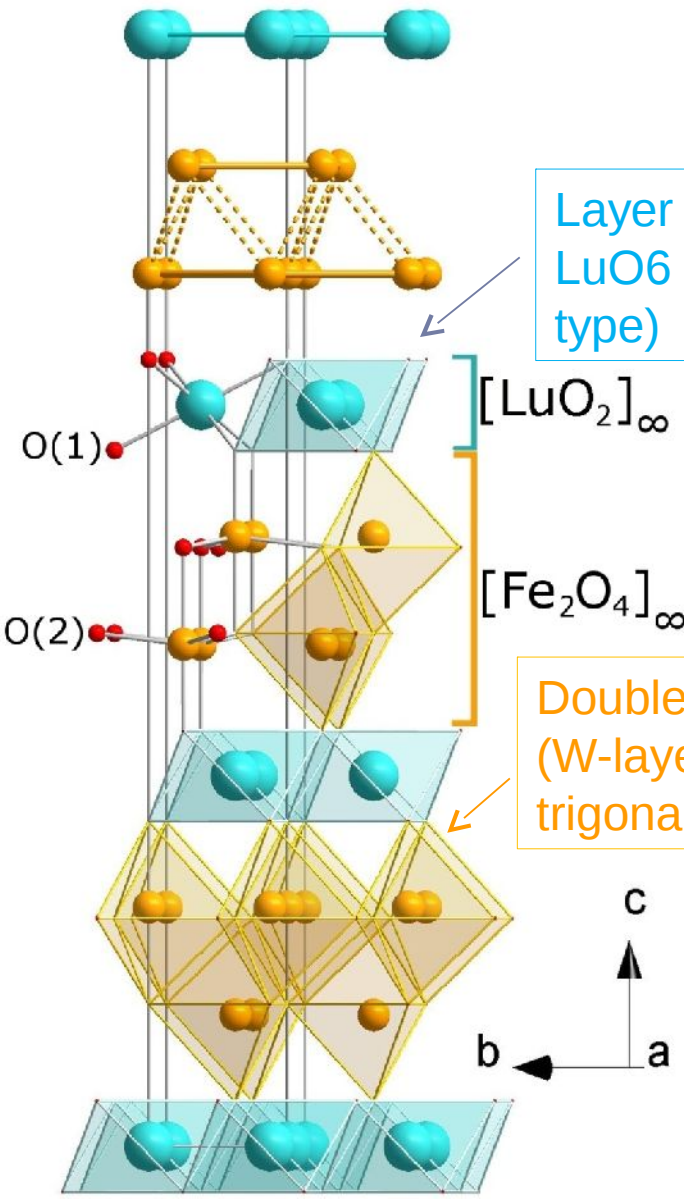
Possible magneto-electric coupling

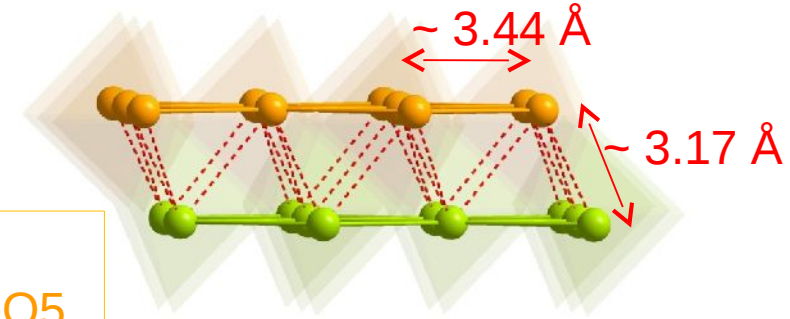
LuFe2O4 at a glance : crystal structure

Rhombohedral *R*-3*m*
a = 3.44 Å
c = 25.25 Å

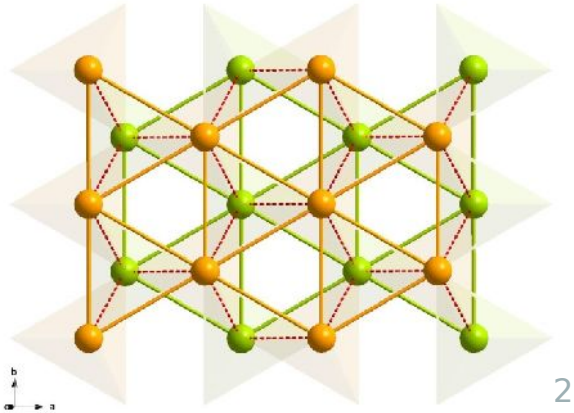
Layer of edge-sharing LuO6 octahedra (CdI2 type)

Double layer (W-layer/bilayer) of FeO5 trigonal bipyramids

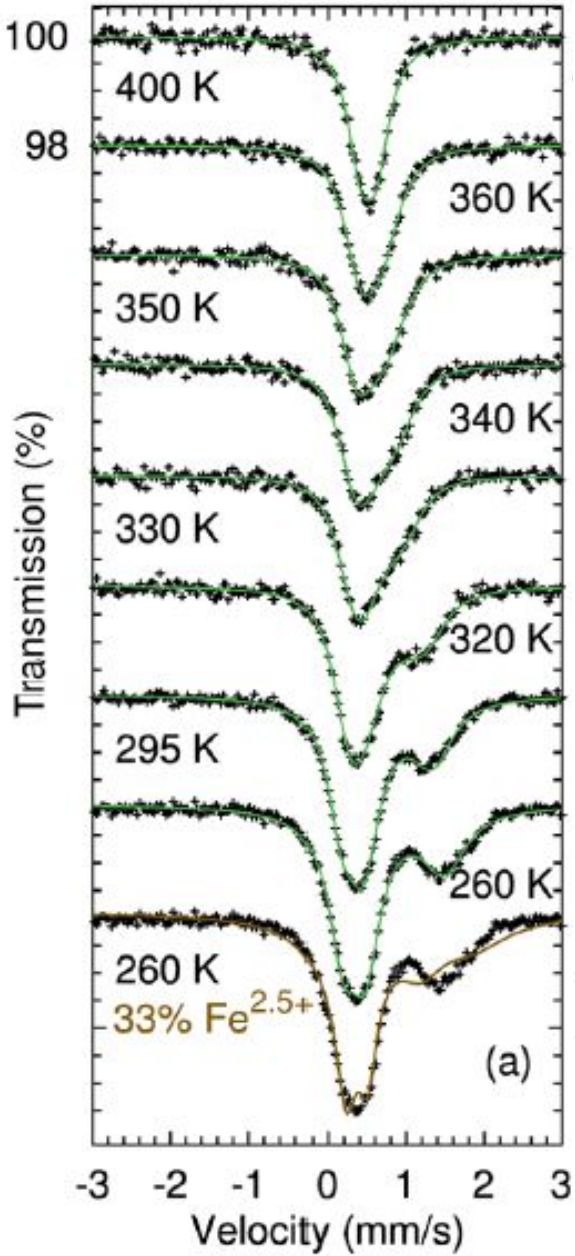




Stacked triangular planes

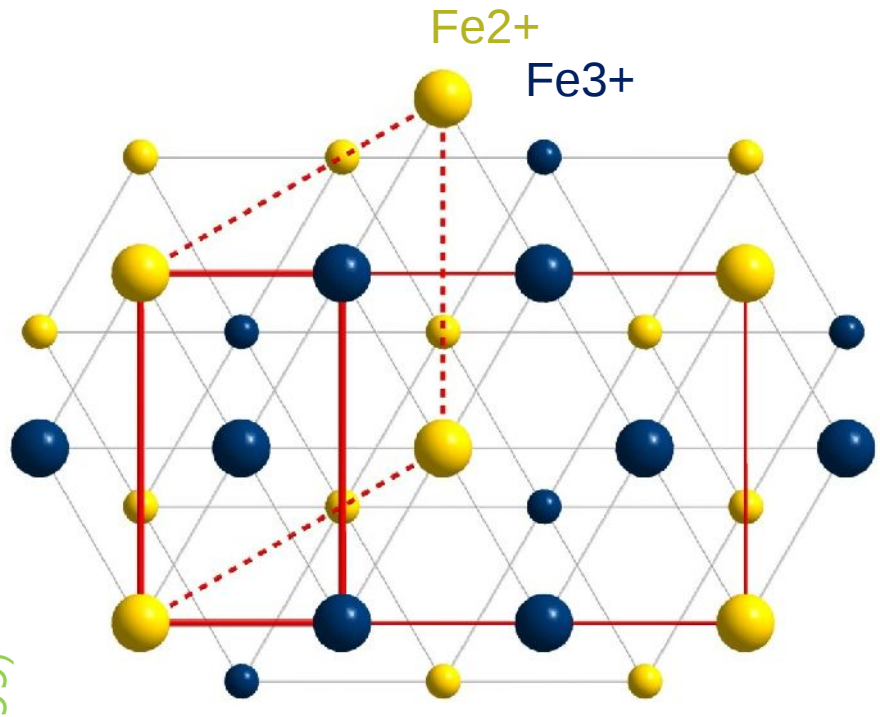


LuFe2O4 at a glance : charge ordering



Mossbaüer spectra, X. S. Xu et al. Phys. Rev. Lett. **101** , 227602 (2008)

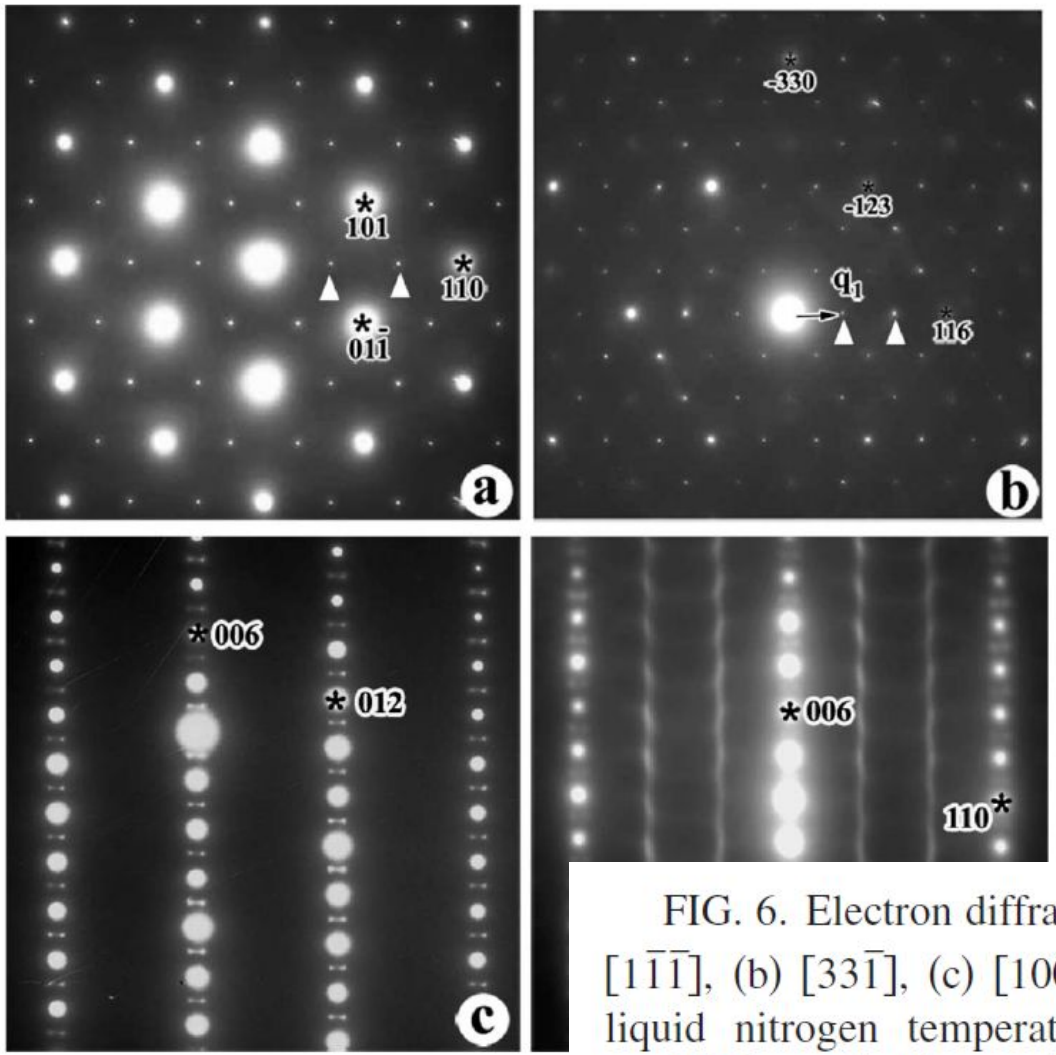
Charge ordering of the Fe2+ and Fe3+ species in a bilayer



Ikeda et al., *Ferroelectrics* **222**, 227 (1999)

Polar √3 x √ 3 superstructure

LuFe2O4 at a glance



CO superstructures are confirmed by electron diffraction studies

Modulation vectors of the type
kCO = 1/3 1/3 *l*
l =0, 3/2, 2,… reports differ!

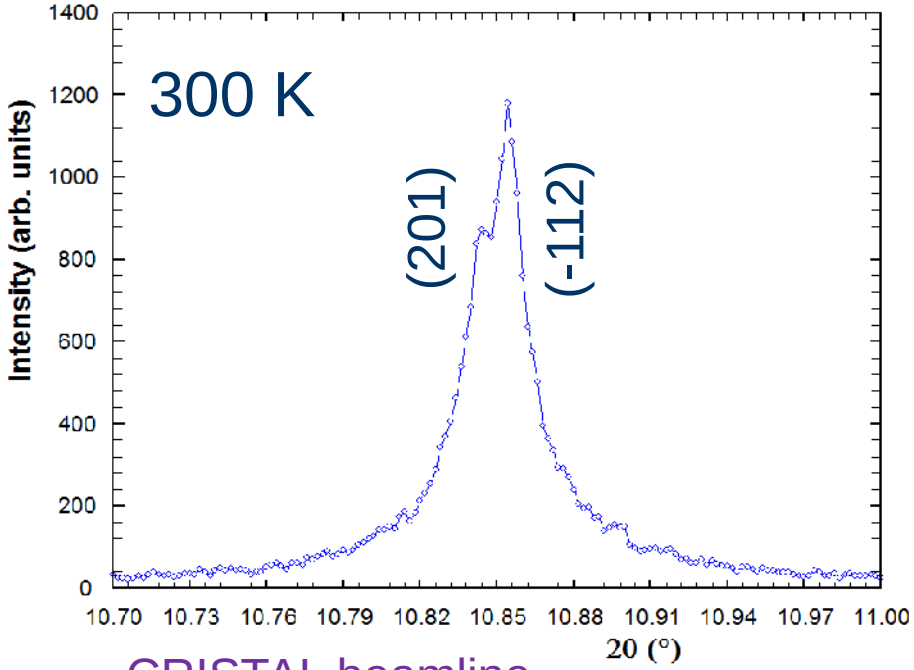
FIG. 6. Electron diffraction patterns of $LuFe_2O_4$ taken along (a) $[1\bar{1}\bar{1}]$, (b) $[33\bar{1}]$, (c) [100], and (d) $[1\bar{1}0]$ zone-axis directions at liquid nitrogen temperature, respectively. The intensity of the modulation reflections at (1/3 1/3 *L*) becomes visibly stronger, and new pairs of satellites show up at (0 0 3*L*/2) at low temperature.

Zhang et al. PRB 76 184105 (2007)

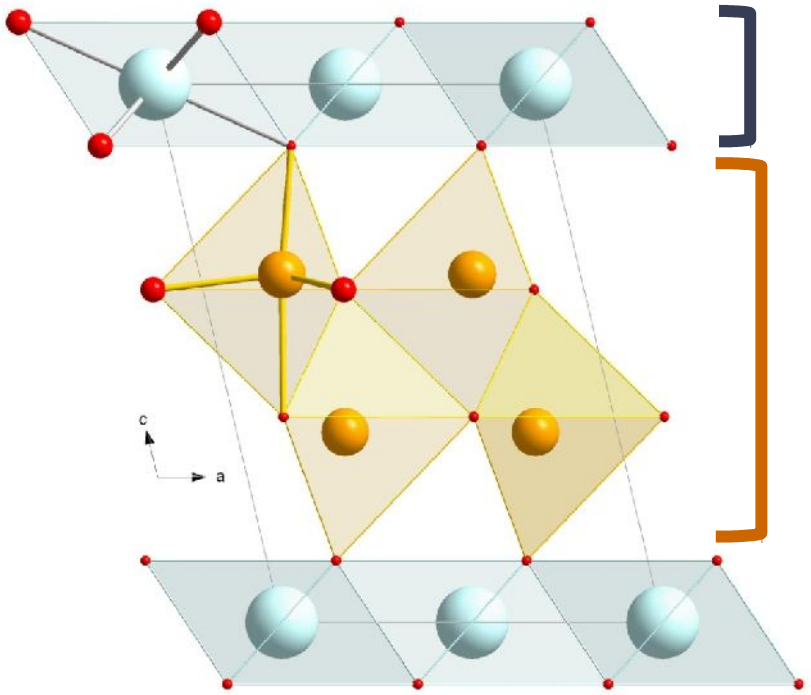
Crystal structure

At RT, LuFe2O4 is monoclinic

Splitting of the rhombohedral (015)R



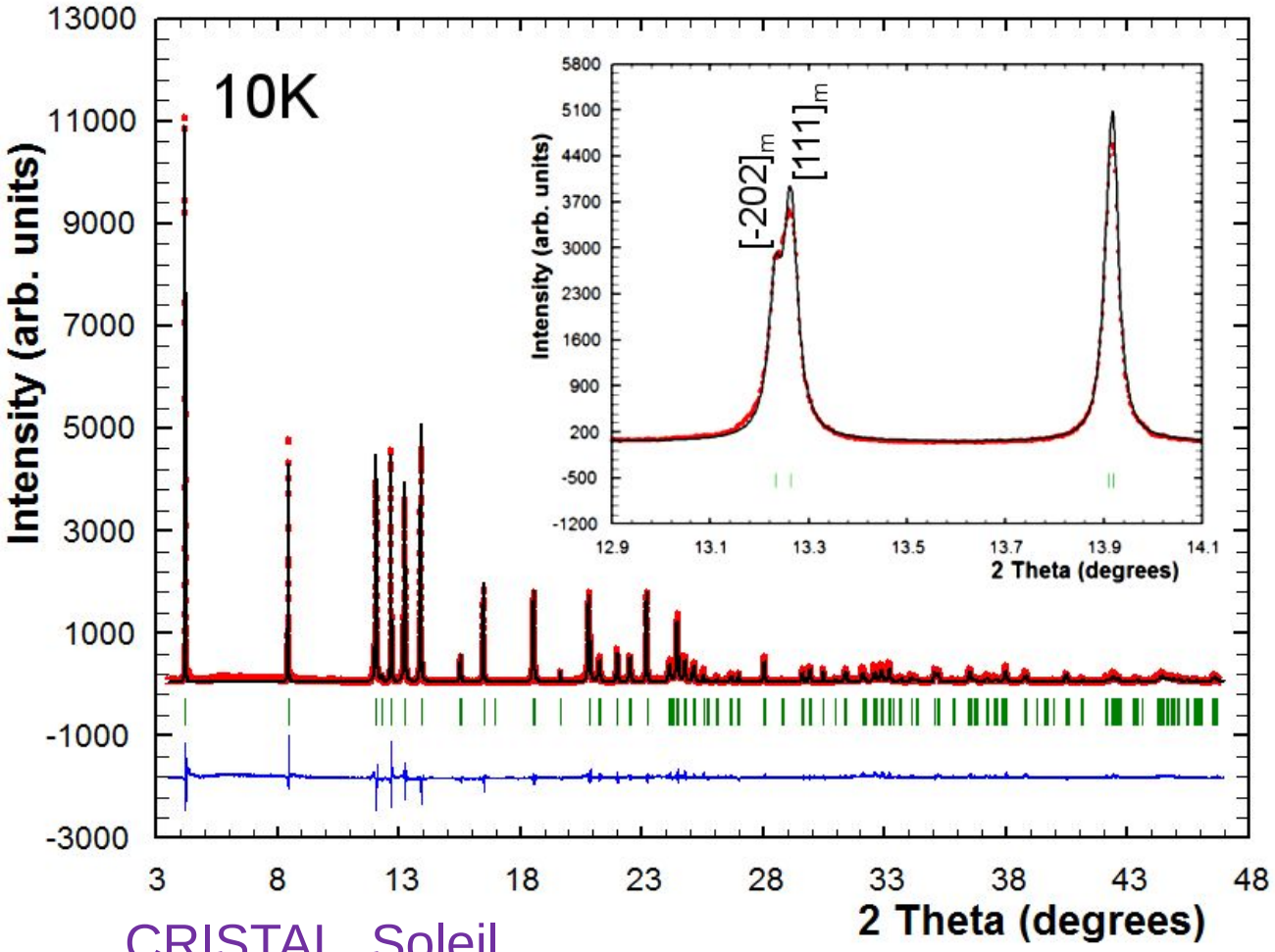
CRISTAL beamline



Slight distortion of the triangular lattice

Crystal structure at 10 K (< TCO)

Clear increase of the monoclinic distortion - impact on the anisotropy of the triangular lattice stays slight. No symmetry lowering at TN

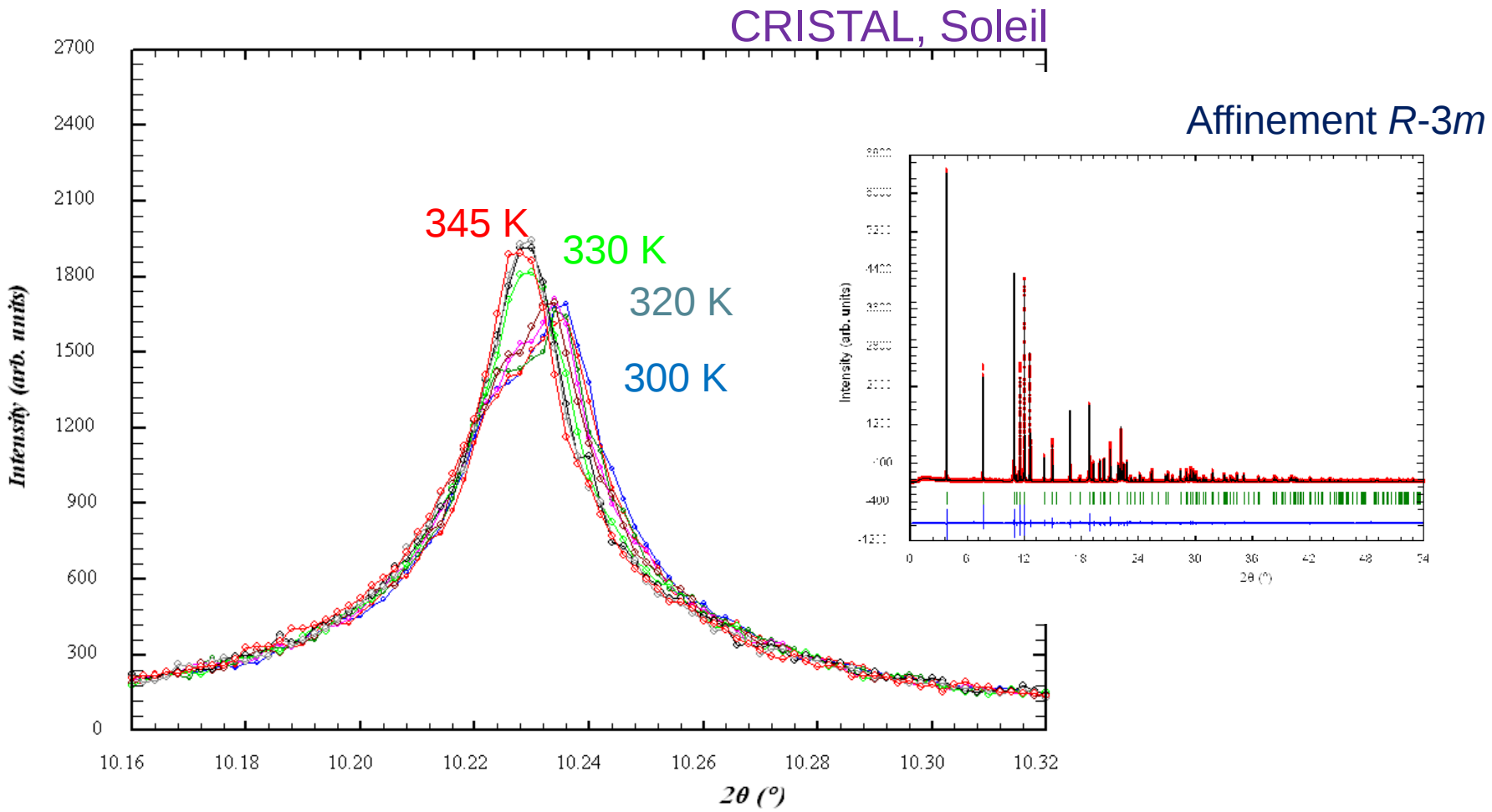


CRISTAL, Soleil

Contraction in the *ab* plane
Expansion along *c* with respect to RT

Crystal structure

This monoclinic distortion disappears above TCO

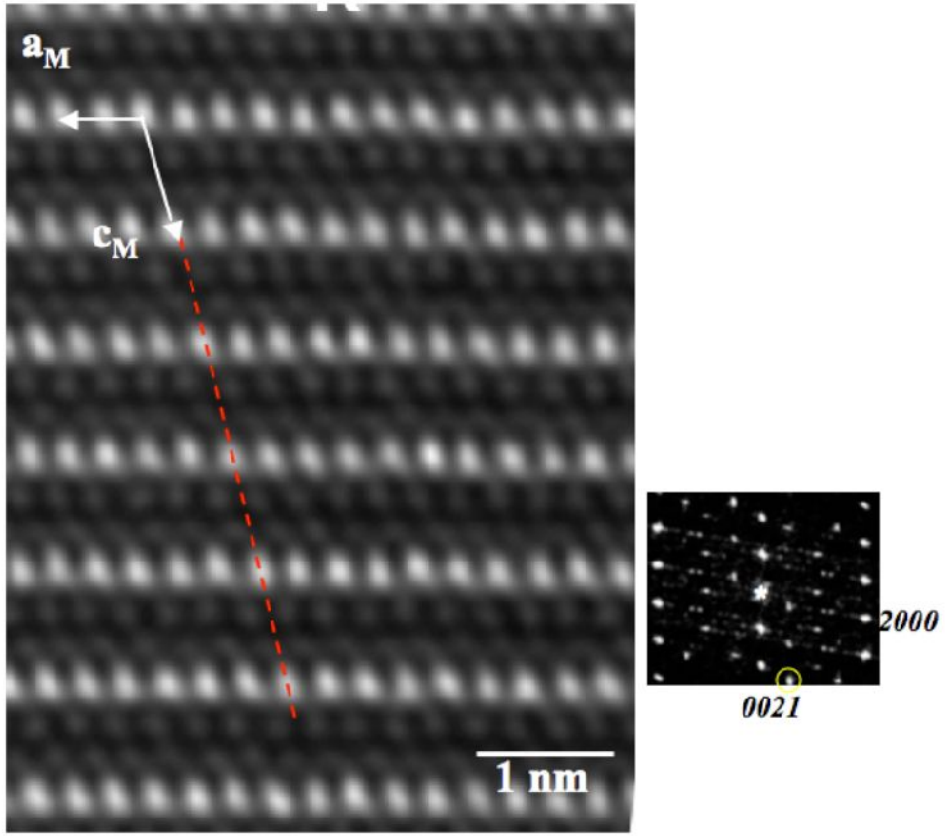


Crystal structure : modulations

Several modulations are observed in the sample at RT

kCO1 = (0 2/3 1/2)*m*
kCO2 = (0 2/3 1/6)*m*

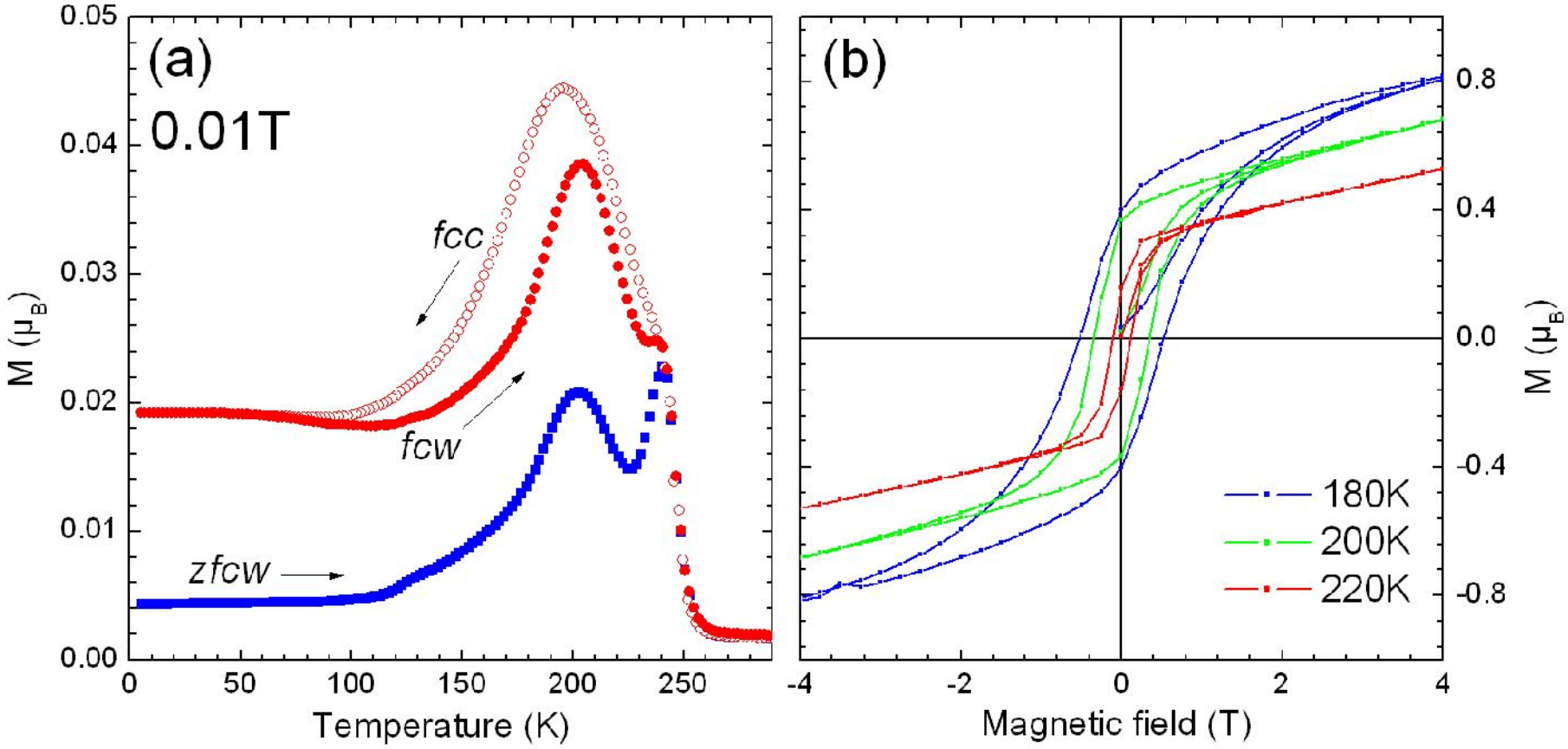
+ q1 linked with oxygen excess modulation of the atomic positions in a Lu layer
q1 = $\alpha a^* + \gamma c^*$ ($\alpha \sim 0.55$, $\gamma \sim 0.13$)
Easy oxygen intake, explain in part the discrepancies in the literature, as properties depend on δ (in $LuFe_2O_{4+\delta}$)



q1 modulated domain

Structural defects are rather scarce, mainly linked with stacking faults

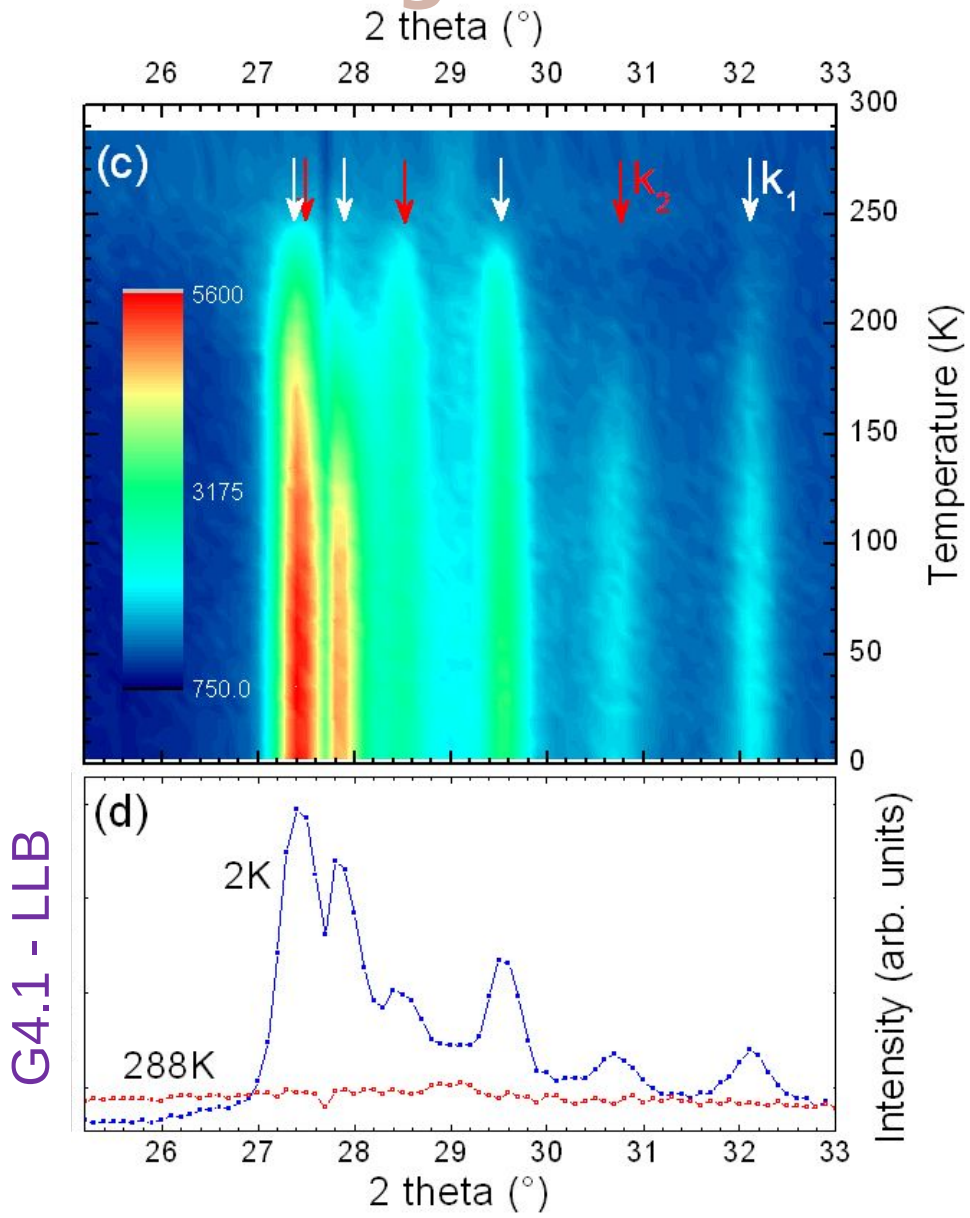
Magnetisation M(T) and M(H) measurements



Two transition temperatures
Thermal hysteresis
Influence of field cooling process

Hysteretic M(H) loops
Ferrimagnetism?

Temperature evolution of neutron diffractograms



G4.1 - LLB

Magnetic scattering observed below 260K

Two magnetic propagation vectors

k1 = (0 2/3 0)*m*

and **k2** = (0 2/3 1/2)*m*

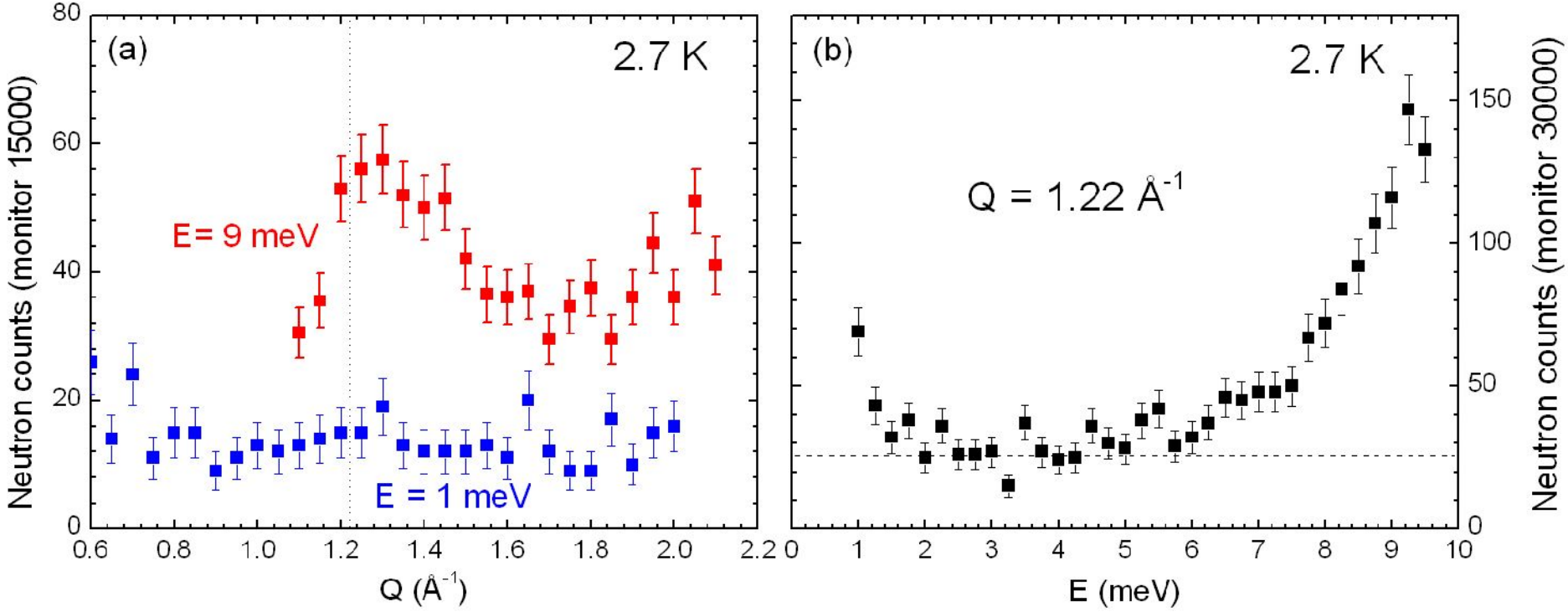
ou (0 2/3 1/6)*m*

hkl **broadening** : disordered stacking of magnetic platelets

Neutron inelastic scattering

4F.1 - LLB

kf = 1.55Å-1



~7- 8 meV gap in the magnetic excitation spectrum

Uniaxial type of magnetic anisotropy

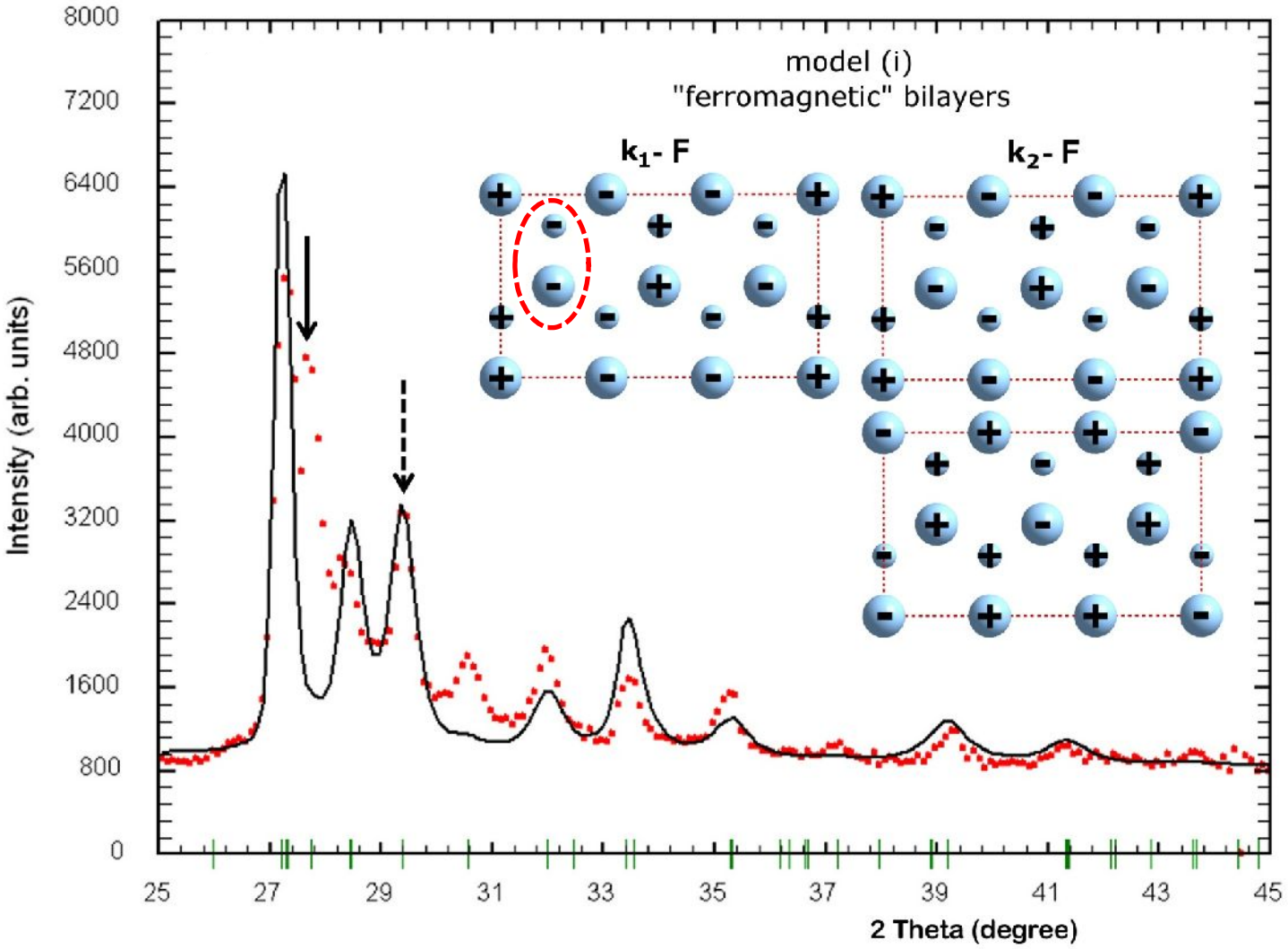
Modelling the magnetic structure

Average moment
on Fe2+ and Fe3+ sites (4.5 μB)

From symmetry analysis, **two types of configurations** for a bilayer, for either k1 and k2 :
F (↑ ↓ ↓ ↑ ↓ ↓)
AF (↑ ↓ ↓ ↓ ↑ ↑)

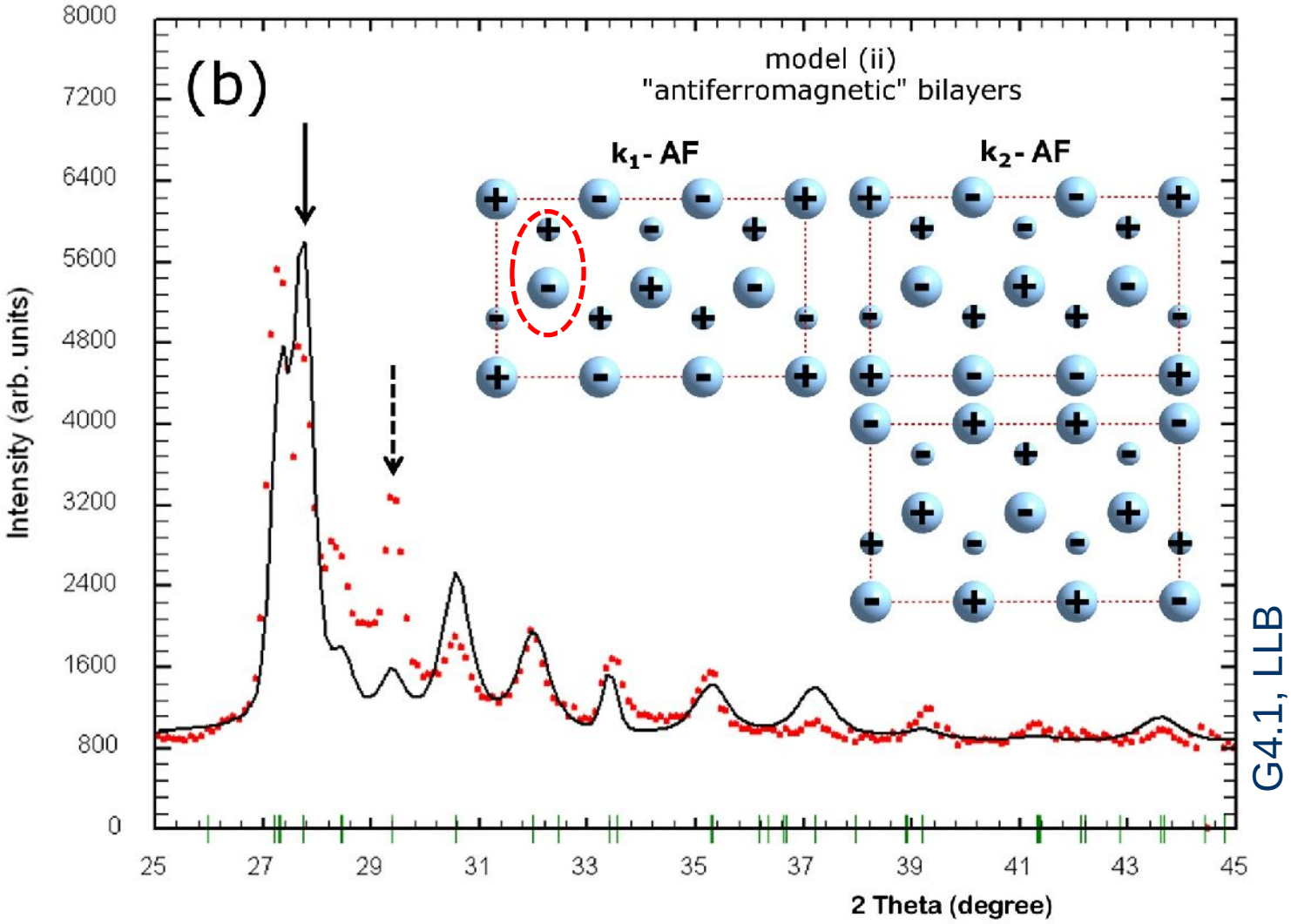
Broadening of *hkl* peaks modeled with a stacking disorder along *c*

Ferromagnetic bilayers



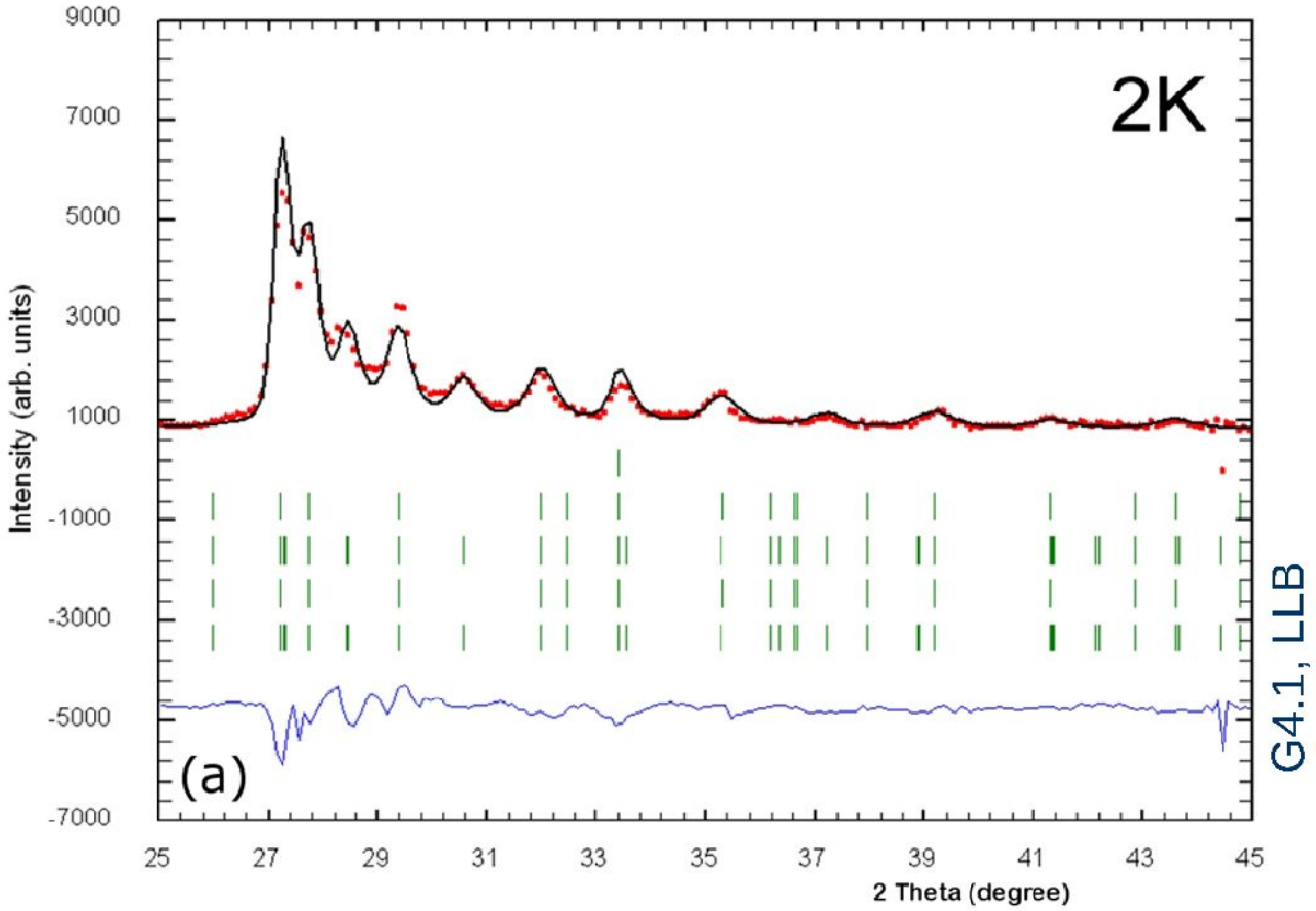
G4.1, LLB

Antiferromagnetic bilayers



G4.1, LLB

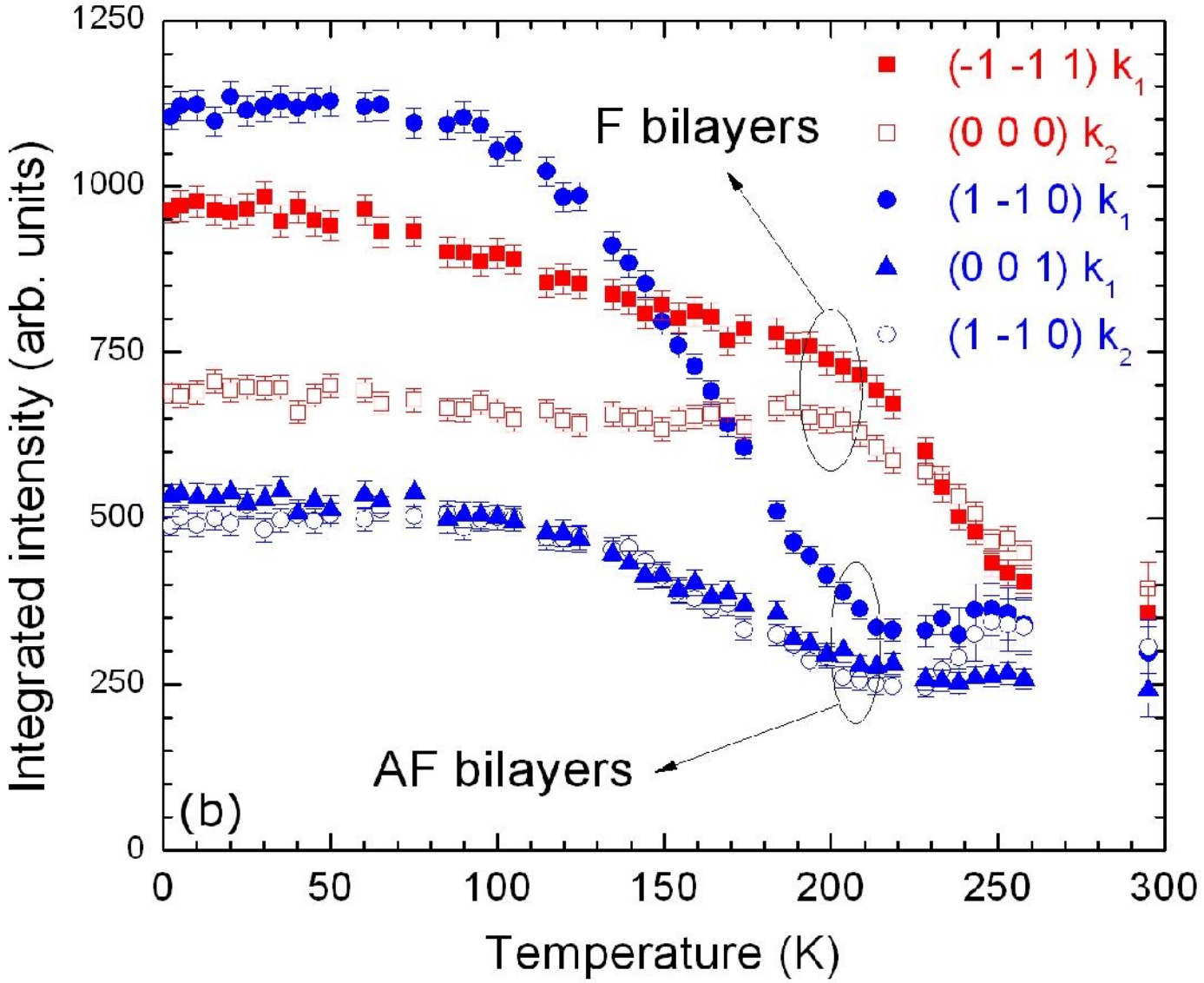
Necessity to use **both** type of configurations to get reasonable agreement with the data



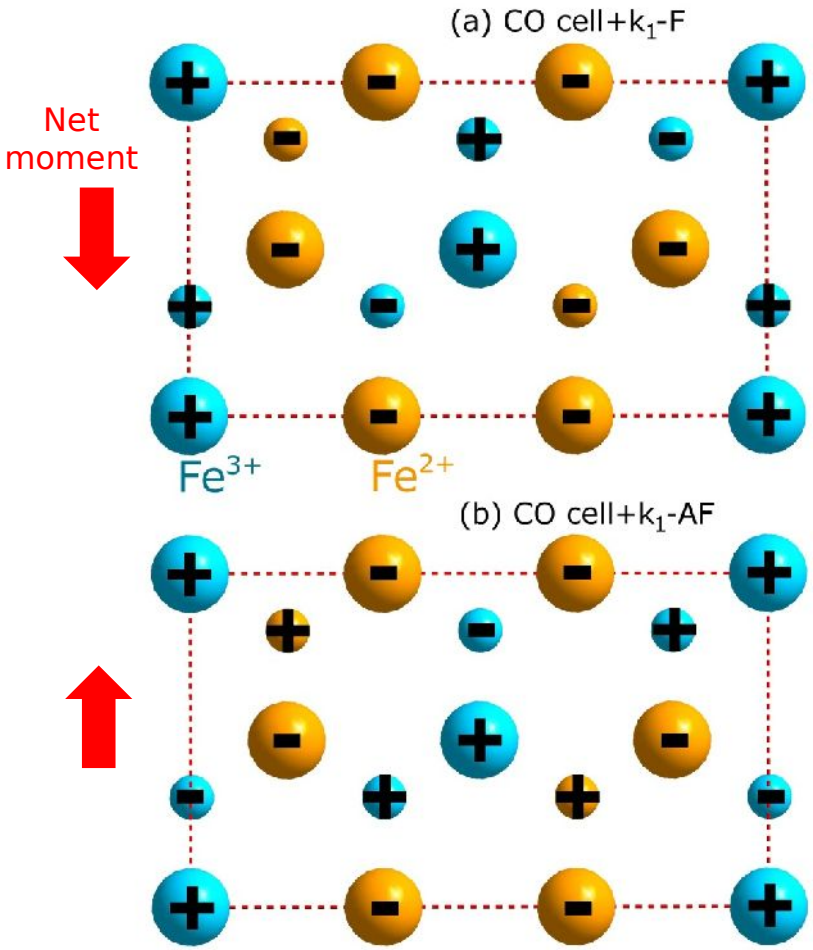
Evolution with temperature of magnetic peak intensities

~250 K : ordering of the F bilayers

~200 K : ordering of the AF bilayers



Spin-charge relationship?



From X-ray absorption spectroscopy

3Fe2+ ↘1Fe3+ //
2Fe3+ //

F bilayer : model OK

AF bilayer…

The complexity of the magnetic ground state derives from the **degeneracy** of the **inter- and intra- bilayer interactions**

Geometrical frustration + strong axial anisotropy? Charge-ordering?

$LuFe_2O_4$

Very complex compound, degenerate charge order, degenerate magnetic order, spin-charge coupling unclear

In addition : intrinsic ferroelectricity is now questioned….

Conclusion

Triangular lattices offer a vast playground for solid state chemists and physicists alike!!
Multiferroicity is just an aspect of it.

Thank you for your attention