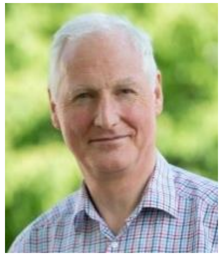
A-Arevalo-Lopez
C. minaud
H. Nimoh

C .Colin

M. Lü

R. Glaum



SOME EXOTIC LOW-D MAGNETIC INORGANIC SYSTEMS, FRUSTRATION *VS.* MAGNETIC ORDERING

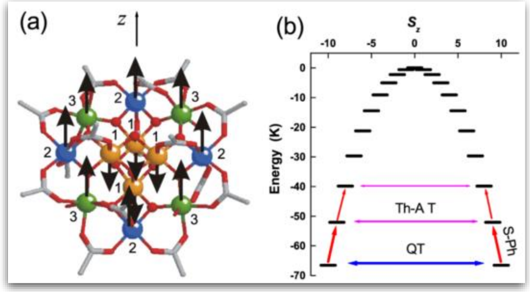
Olivier Mentré UCCS, Univ. Lille-Artois/Ecole Centrale/CNRS, France

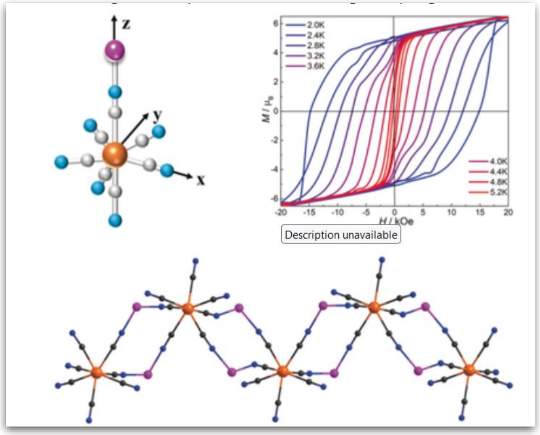
JAM2, Mittelwihr, Novembre 2023

Molecular magnetism

Inorganic magnetic materials

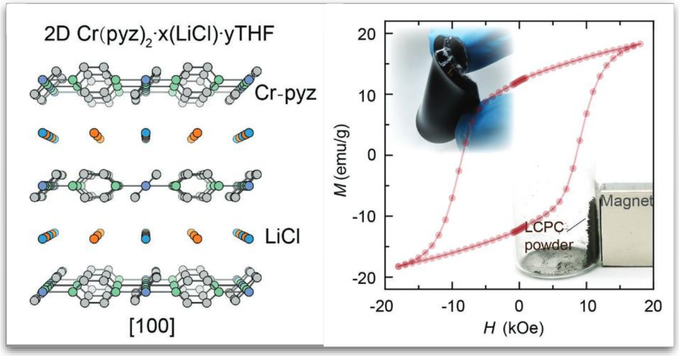
Single Molecule Magnet
quantum tunneling



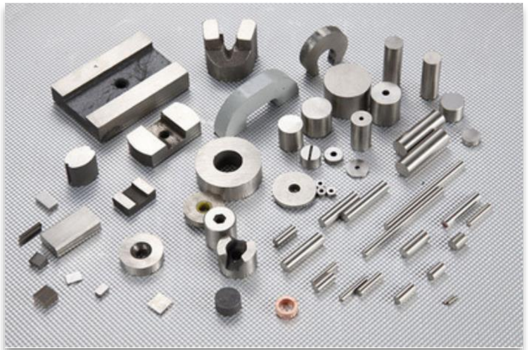


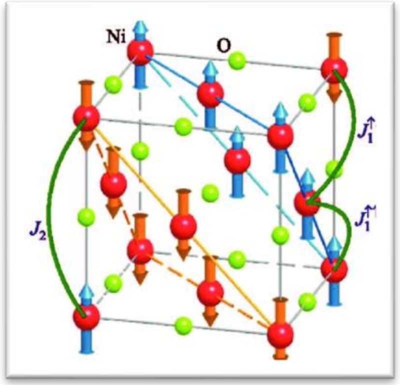
Single Chain Magnet
slow-spin relaxation → FM

2D-Molecular magnets
anisotropy



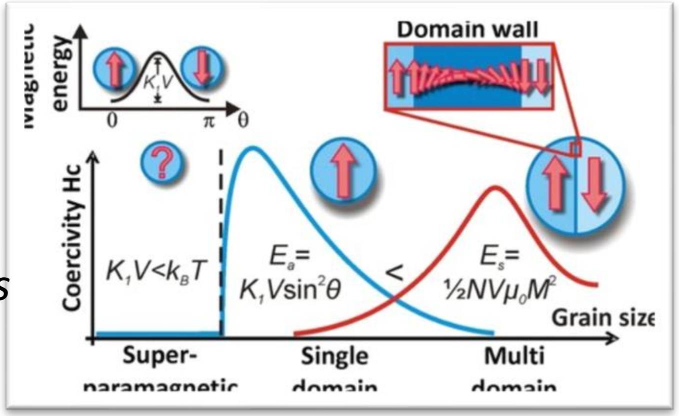
Intermetallics
permanent magnets





Magnetic Oxides, Sulfides, etc
3D magnetic ordering

Nano-Magnetism
thin Films, particles, Spintronics



Exploration of Low-D Inorganic chemical systems

UCCS
UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

Towards low-D units

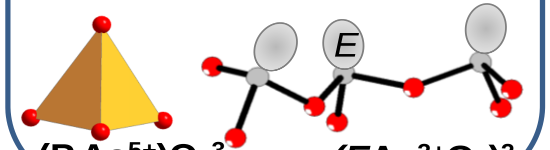
Co^{2+}, Fe^{2+} → SOC

Mn^{2+}, Fe^{3+} (L=0)

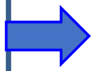
Ca^{2+} — r =1.00 Å

Sr^{2+} — 1.18 Å

Ba^{2+} — 1.35 Å



$(P,As^{5+})O_4^{3-}$ $(EAs^{3+}O_3)^{2-}$



Alkali K, Rb, Cs

Inorganic Chemistry

pubs

Slow Spin Dynamics between Ferromagnetic Chains in a Pure-Inorganic Framework

Rénald David,[†] Houria Kabbour,[†] Silviu Colis,[‡] and Olivier Mentré[†,*]

[†]UMR 8181 CNRS, Unité de Catalyse et de Chimie du Solide (UCCS USTL), Université d'Ascq, France

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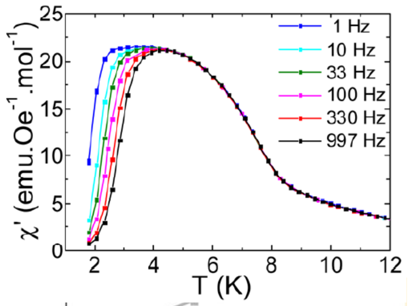

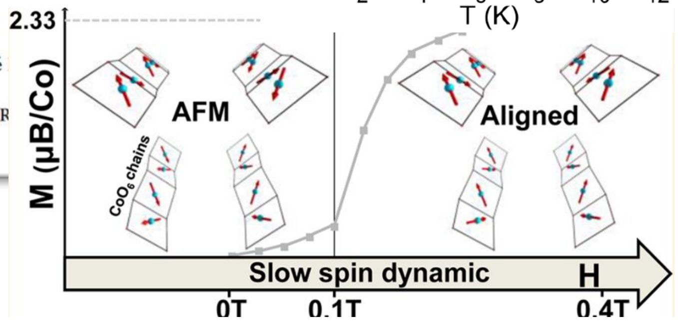

Inorganic Chemistry

Article

Cite This: Inorg. Chem. 2019, 58, 12609−12617

pubs.acs.org/IC

Metamagnetic Transitions versus Magnetocrystalline Anisotropy in Two Cobalt Arsenates with 1D Co^{2+} Chains

Bastien Leclercq,[†] Houria Kabbour,[†] Françoise Damay,[‡] Claire V. Colin, Angel M. Arevalo-Lopez,[†] and Olivier Mentré[*,†]

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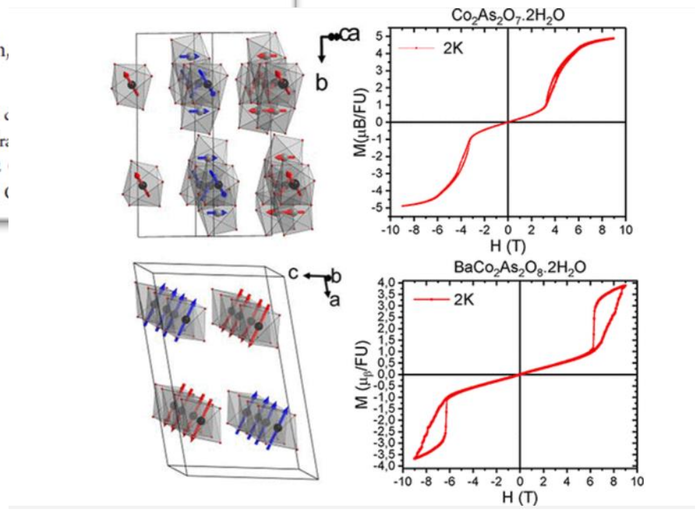


- Teflon-lined bomb : autogeneous pressure
- Hydrazine red. agent: stabilization low-redox

aim of this « *tutorial* » *… as requested by G. Chastanet* …

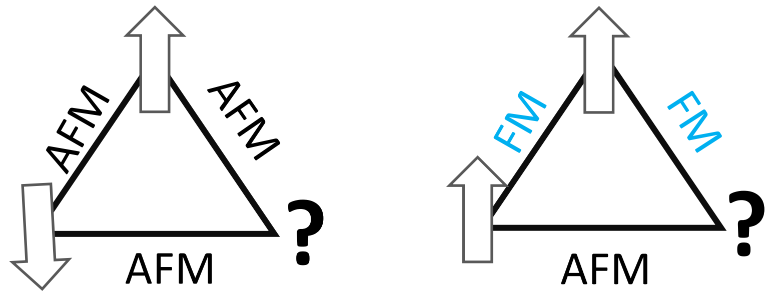
Initiation to the refinement of a magnetic Structures

I will use two examples of Strongly frustrated Low-D inorganic Materials

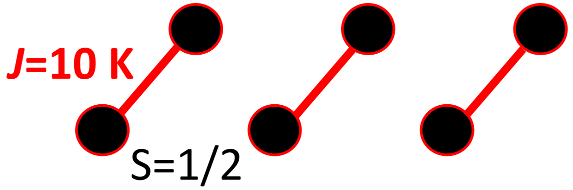
1) Frustration → original spin structures
2) Frustration → kills the magnetic ordering … QSL state

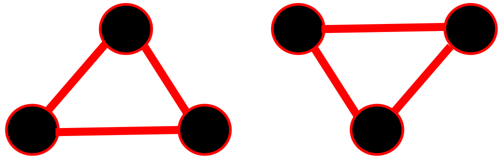
Frustration :
the "standard model"

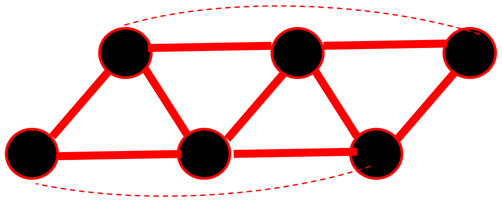
In most "real" materials it depends on the relative J1,J2,J3

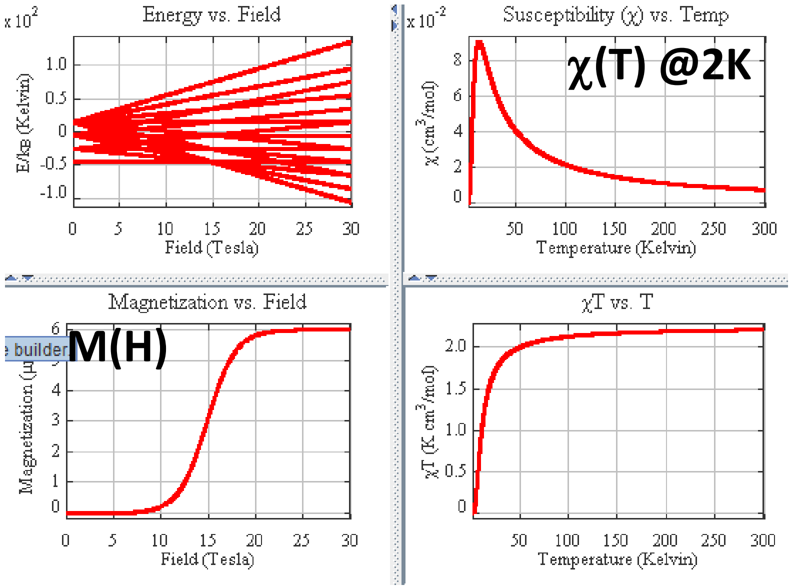


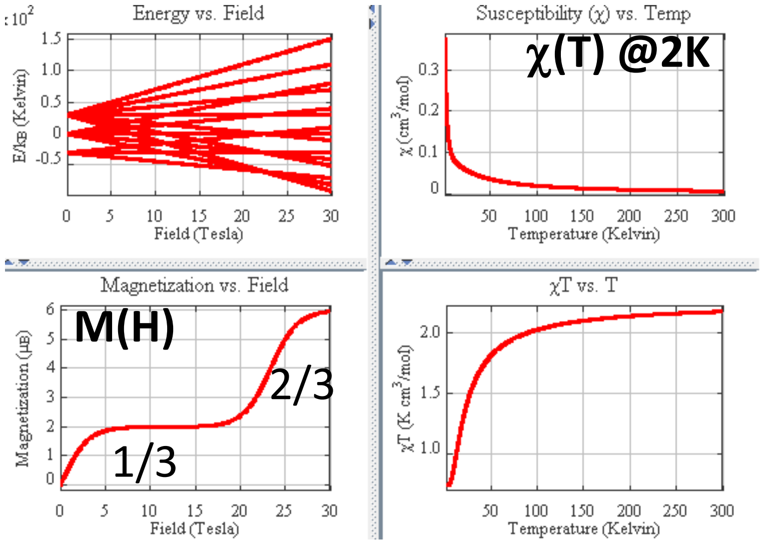
Exact diagonalization, S=1/2, Heisenberg

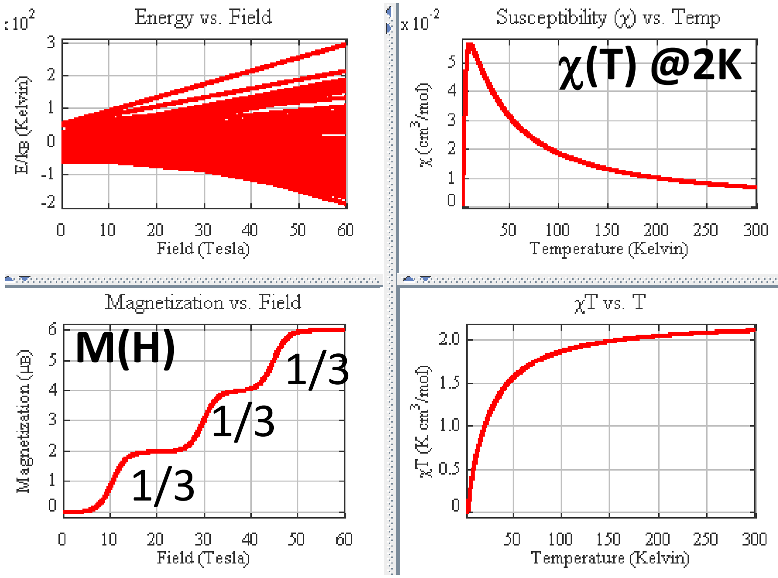












Frustration effects : **1.** "Fragilize" the AFM ground state **2.** "Fragmentation" of M(H)

Neutron-atom elastic interaction

same order of magnitude

$$A = b + 2BI \cdot S + (\gamma r_0/2) f(K) \mathbf{M}_\perp \cdot \mathbf{S}$$

nuclear origin /diffraction

Neutron spin and nuclear spin → incoherent

neutron spin and magn. moment/ diffraction

$$\text{Int}_{\text{diffr.}} = \{F_N(\mathbf{K})\}^2 + \{|\mathbf{F}_{\perp M}(\mathbf{K})|\}^2.$$

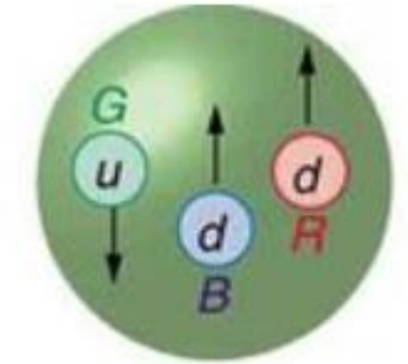
cryst. Struct. Magn. Struct.

. Phys. IV France **11** (2001)
) EDP Sciences, Les Ulis

:tructures magnétiques et symétries cristallines

. Schweizer

:EA-Grenoble, DRFMC/SPSMS/MDN, 38054 Grenoble cedex, France



Neutron *3 quarks*

$$-\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{1}{2}$$

Collection SFN **9** (2008) 65–85
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DOI: 10.1051/sfn:2008006

Structures magnétiques, diffraction de neutrons et symétrie

F. Bourée[1] et J. Rodrí

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[2] Institut Laue-Langevin, E

Crystallography on magnetic moments: Magn structure Factor :

$$\mathbf{F}_{\perp M}(\mathbf{K}) = 0.27 \cdot 10^{-12} \sum_i f_j(\mathbf{K}) \{ \mathbf{m}_j(\mathbf{k}) - (\mathbf{e} \cdot \mathbf{m}_j(\mathbf{k})) \cdot \mathbf{e} \} \exp\{2\pi i \, \mathbf{K} \, \mathbf{r}_j\}$$

Neutron-atom elastic interaction

same order of magnitude

$$A = b + 2B\mathbf{I}\cdot\mathbf{S} + (\gamma r_0/2)f(K)\mathbf{M}_\perp\cdot\mathbf{S}$$

nuclear origin /diffraction

Neutron spin and nuclear spin → incoherent

neutron spin and magn. moment/ diffraction

$$\text{Int}_{\text{diffr.}} = \{F_N(\mathbf{K})\}^2 + \{|\mathbf{F}_{\perp M}(\mathbf{K})|\}^2.$$

cryst. Struct. Magn. Struct.

Magnetic Structure

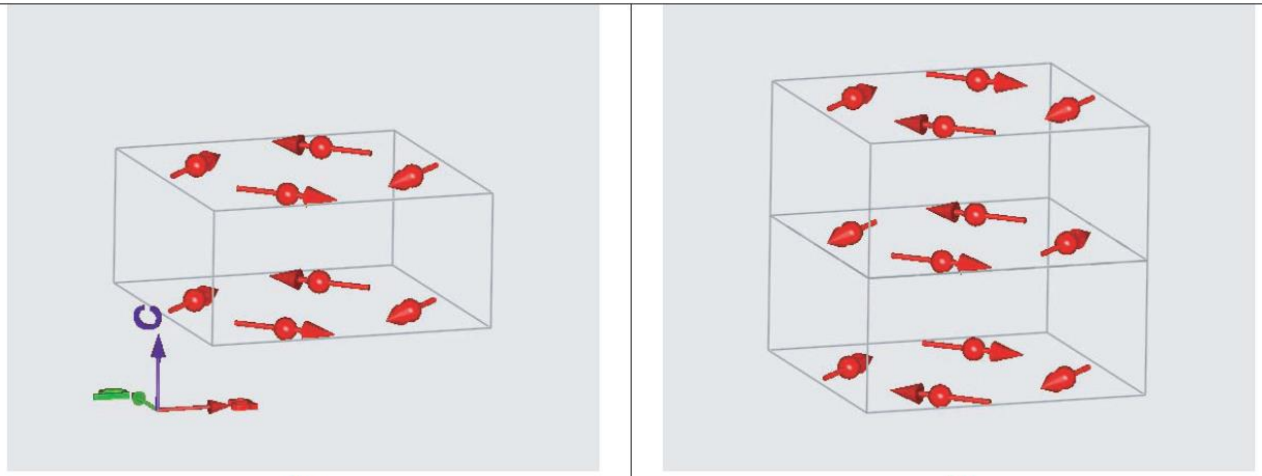
Below T_{order} the periodic magnetic struct. established will minimized the free energy of the system (m, J, k)

K= propagation vector / periodicity of the magn. structure

$$U = -N\sum_{j,j'}\sum_{\alpha,\beta} J_{jj'\alpha\beta}(\vec{k})\; m^{\vec{k}}_{j\alpha}\; m^{-\vec{k}}_{j'\beta}$$

$\vec{K}$ propagation vector

Supercell R* vector, rationnal or incommensurate

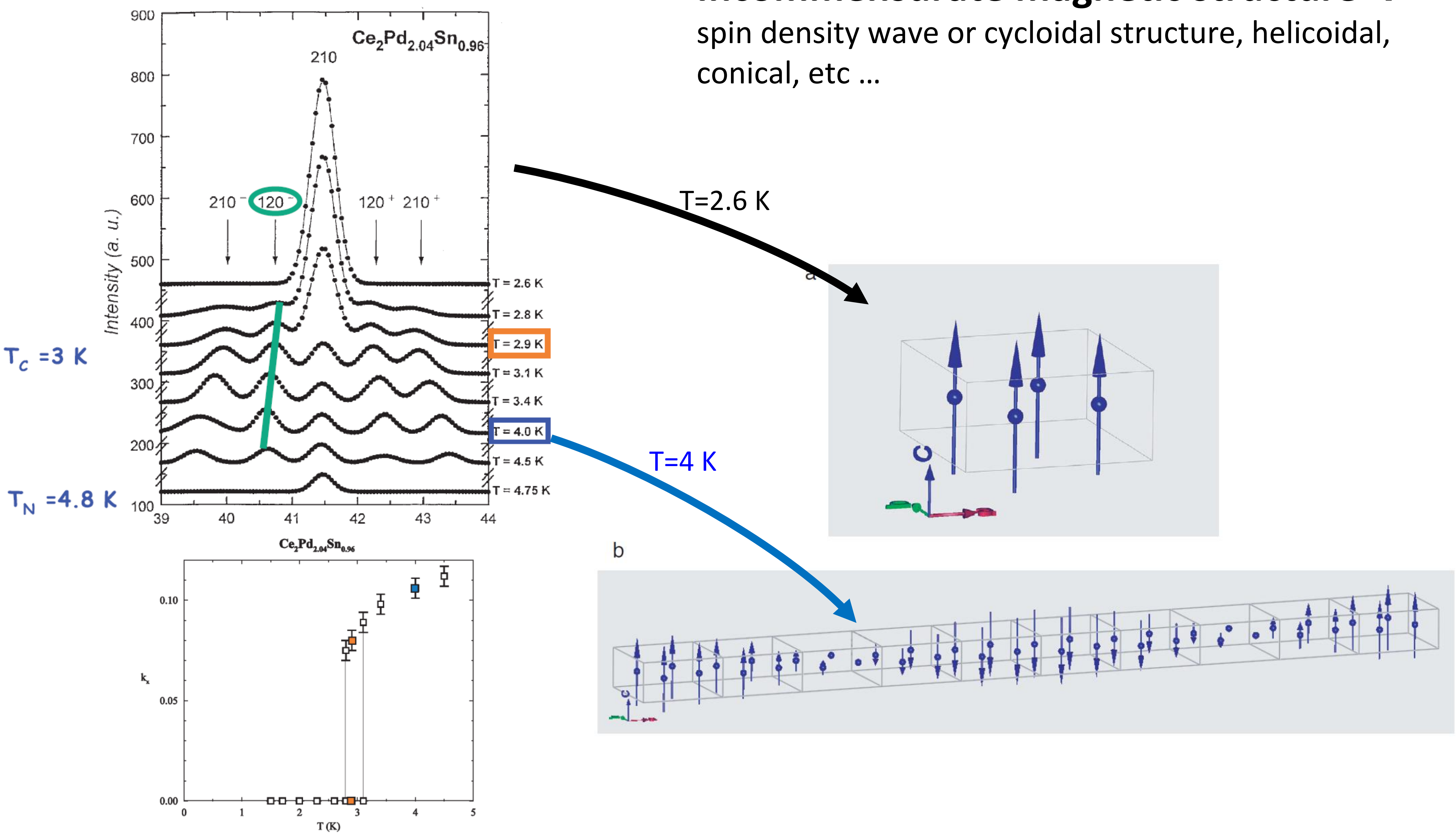


1a — U_2Pd_2In – U_2Pd_2Sn – k = (0 0 0)

1b — $U_2Pd_{2.4}Sn_{0.6}$ - k = (0 0 ½)

Incommensurate magnetic structure →

spin density wave or cycloidal structure, helicoidal, conical, etc …



Solving a magnetic Structure → group Theory analyzis (*softwares : Sarah , Basireps* ISOTROPY Software Suite, Bilbao Cryst….)

1• $\vec{k}$ vector + Space group (G) → subgroup of k : G_k

2 • G_k + magn. atoms → magn. Matrix dim. 12

Ex : U_2Pd_2In, k=(0,0,0) , G: P4/mbm = G_k

Notation	Loi de transformation (vecteur polaire)	Symbole (symétrie ponctuelle)	Translation	Situation	Notation Kovalev [13]
SYM(1)	x, y, z	1			h_1
SYM(2)	-x, -y, z	2_z			h_4
SYM(3)	½-x, ½+y, -z	2_y	[0 ½ 0]	[¼ 0 0]	h_3
SYM(4)	½+x, ½-y, -z	2_x	[½ 0 0]	[0 ¼ 0]	h_2
SYM(5)	½+y, ½+x, -z	$2_{[110]}$	[½ ½ 0]		h_{16}
SYM(6)	½-y, ½-x, -z	$2_{[1\bar{1}0]}$		[0 ½ 0]	h_{13}
SYM(7)	y, -x, z	4_z^3			h_{15}
SYM(8)	-y, x, z	4_z			h_{14}
SYM(9)	-x, -y, -z	$\bar{1}$			h_{25}
SYM(10)	x, y, -z	m_z			h_{28}
SYM (11)	½+x, ½-y, z	m_y	[½ 0 0]	[0 ¼ 0]	h_{27}
SYM(12)	½-x, ½+y, z	m_x	[0 ½ 0] b	[¼ 0 0]	h_{26}
SYM(13)	½-y, ½-x, z	$m_{[110]}$		[0 ½ 0]	h_{40}
SYM(14)	½+y, ½+x, z	$m_{[1\bar{1}0]}$	[½ ½ 0]		h_{37}
SYM(15)	-y, x, -z	$\bar{4}_z^3$			h_{39}
SYM(16)	y, -x, -z	$\bar{4}_z$			h_{38}

4 atoms x **3** (Mx, My, Mz)

U_1	x_U	½ + x_U	½
U_2	1 - x_U	½ - x_U	½
U_3	½ - x_U	x_U	½
U_4	½ + x_U	1 - x_U	½

	U1 Mx	U1 My	U1 Mz	U2			U3			U4		
U1 Mx	-1											
U1 My		-1										
U1 Mz			1									
U2				-1								
					-1							
						1						
U3							-1					
								-1				
									1			
U4										-1		
											-1	
												1

3 • 16 symmetries → 16 magn. Matrix of dim. 12

• All together → representation Γ of the G_k group of dim. 12

• The magn repr. Γ can be reduced in irreducible representation Γ_{IR} of various dimensions

Symmetry

P4/mbm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	1	1	1	-1	-1						
Γ_3	1	1	1	1	-1	-1	-1	-1	1	1						
Γ_4	1	1	1	1	-1	-1	-1	-1	-1	-1						
Γ_5	1	1	-1	-1	1	1	-1	-1	1	1						
Γ_6	1	1	-1	-1	1	1	-1	-1	-1	-1						
Γ_7	1	1	-1	-1	-1	-1	1	1	1	1						
Γ_8	1	1	-1	-1	-1	-1	1	1	-1	-1						
Γ_9	1 0 0 1	–1 0 0 –1	1 0 0 –1	–1 0 0 1	0 1 1 0	0 -1 -1 0	0 -1 1 0	0 1 -1 0	–1 0 0 –1	1 0 0 1						
Γ_{10}	1 0 0 1	–1 0 0 –1	1 0 0 –1	–1 0 0 1	0 1 1 0	0 -1 -1 0	0 -1 1 0	0 1 -1 0	1 0 0 1	–1 0 0 –1	1 0 0 –1	–1 0 0 1	0 1 1 0	0 -1 -1 0	0 -1 1 0	0 1 -1 0

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

• by orthogonality it can be decomposed

in n Γ_{IR}, each associated with an order m ⟶ $\Gamma = \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 \oplus \Gamma_9 \oplus 2\Gamma_{10}$

$$\Gamma = \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 \oplus \Gamma_9 \oplus 2\Gamma_{10}$$

Each of the Γ_{IR} gives a magnetic structure and needs to be tested against the diffr. data

For instance Γ_2

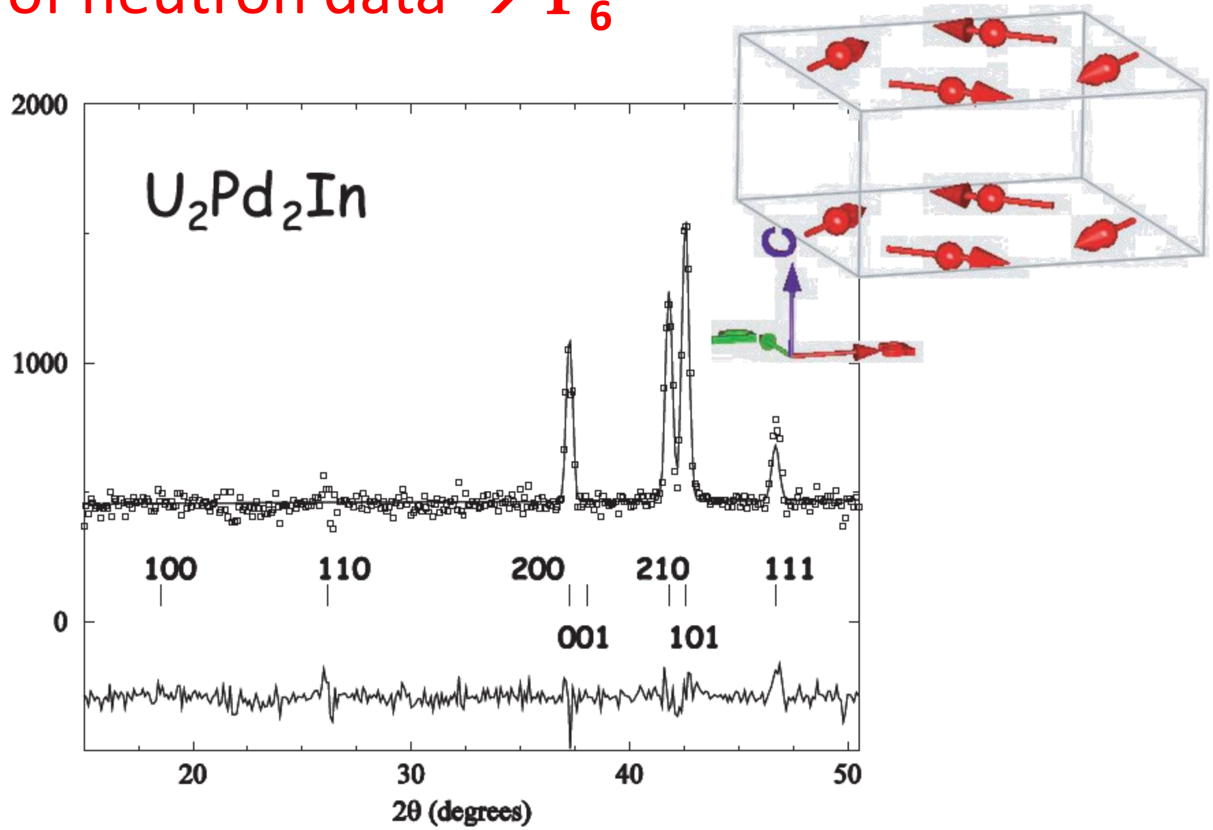
```
      U1 SYMM x,y,z
0.2700  0.7700  0.5000
         sk(1): (u,u,0)

      U2 SYMM -x,-y,z
0.2700 -0.7700  0.5000
         sk(2): (-u,-u,0)

         U3 SYMM -x+1/2,y+1/2,-z
0.2300  1.2700 -0.5000
         sk(3): (-u,u,0)

         U4 SYMM x+1/2,-y+1/2,-z
0.7700 -0.2700 -0.5000
         sk(4): (u,-u,0)
```

Rietveld refinement of neutron data → Γ_6



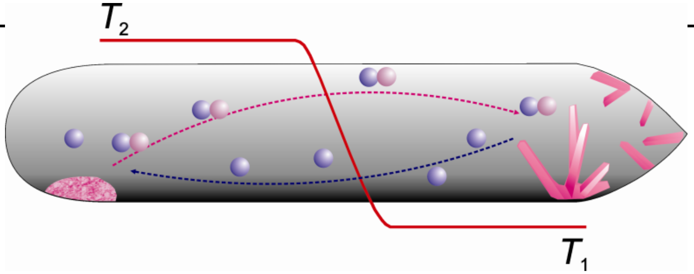
Frustration drives idle spin in $Sr_2Cr(PO_4)_2$

Cr dissolved in HCl/HNO_3 acid, + $(NH_4)_2HPO_4$

$$2\ Sr_3(PO_4)_2(s) + 2\ CrPO_4(s) + Cr(s) \rightarrow 3\ Sr_2Cr(PO_4)_2(s)$$

1273 K, air

Single crystals, CVT I2 as transport agent



Cr^{2+} , d4, S=2, L=2, strong JT effect

Unstable in oxide, easily oxidized

CrO does not exist → Cr_2O_3 too stable

Cr^{2+} is stabilized by oxo-anions (SiO_4^{4-}, BO_4^{5-}, PO_4^{3-} ··· F^-) by inductive effect, e.g CrF_2

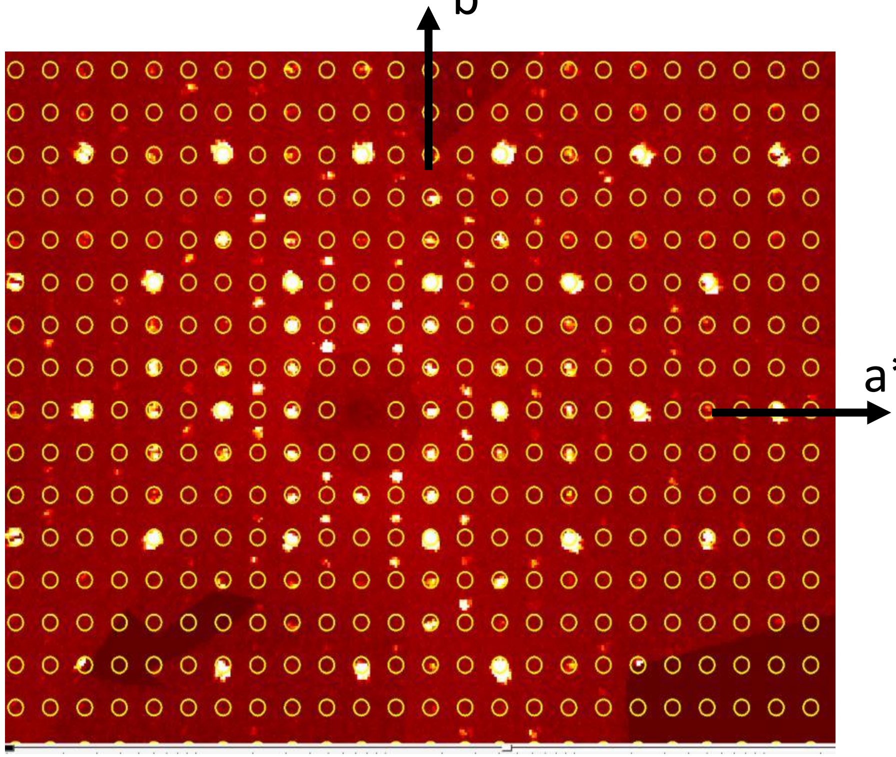
Cr^{2+} >> O >> P

$Sr_2Cr(PO_4)_2$: Crystal structure

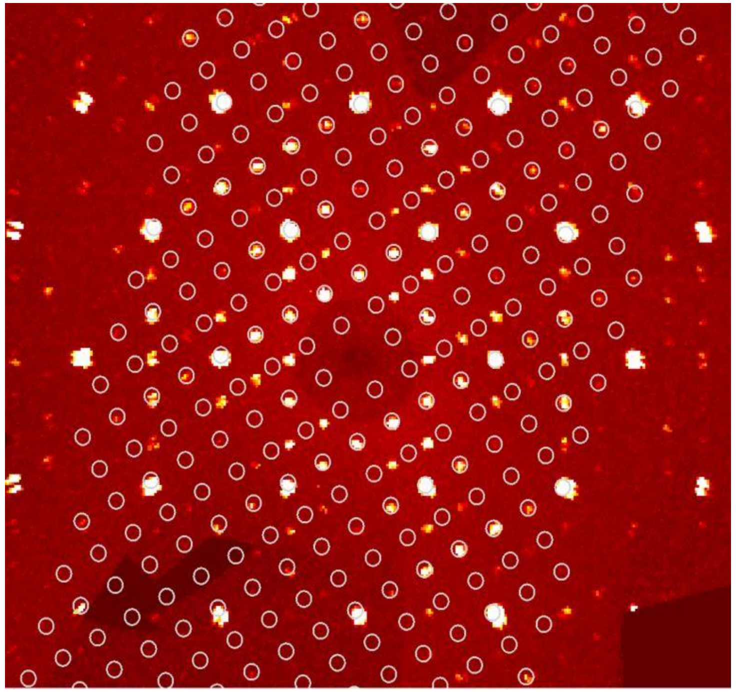
- Orthorhombic Pbca
- Two indiviadual layers
- Pseudo trigonal

P b c a (61)
a=10.7064(6) Å
b=9.2730(5) Å
c=21.2720(7)

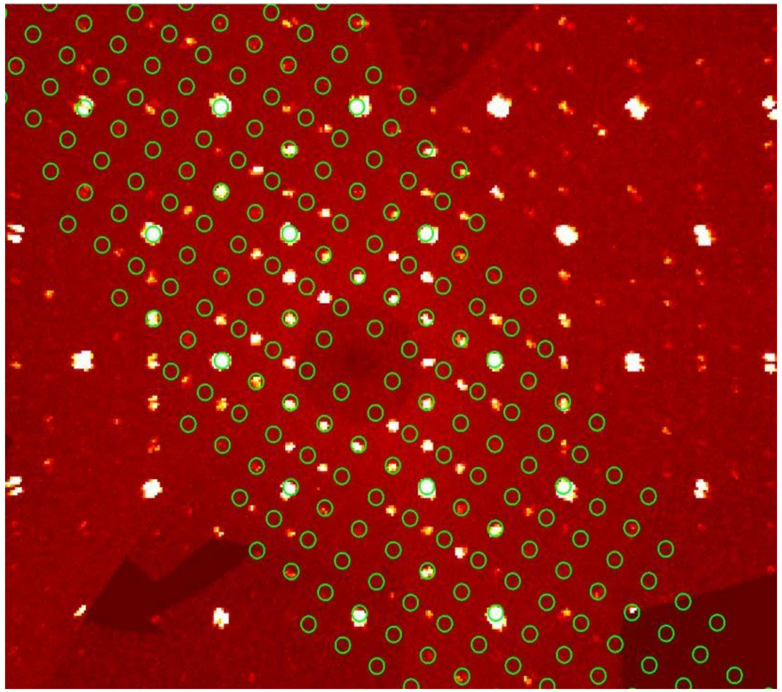
*hk*0 – domain 1



hk0 – domain 2

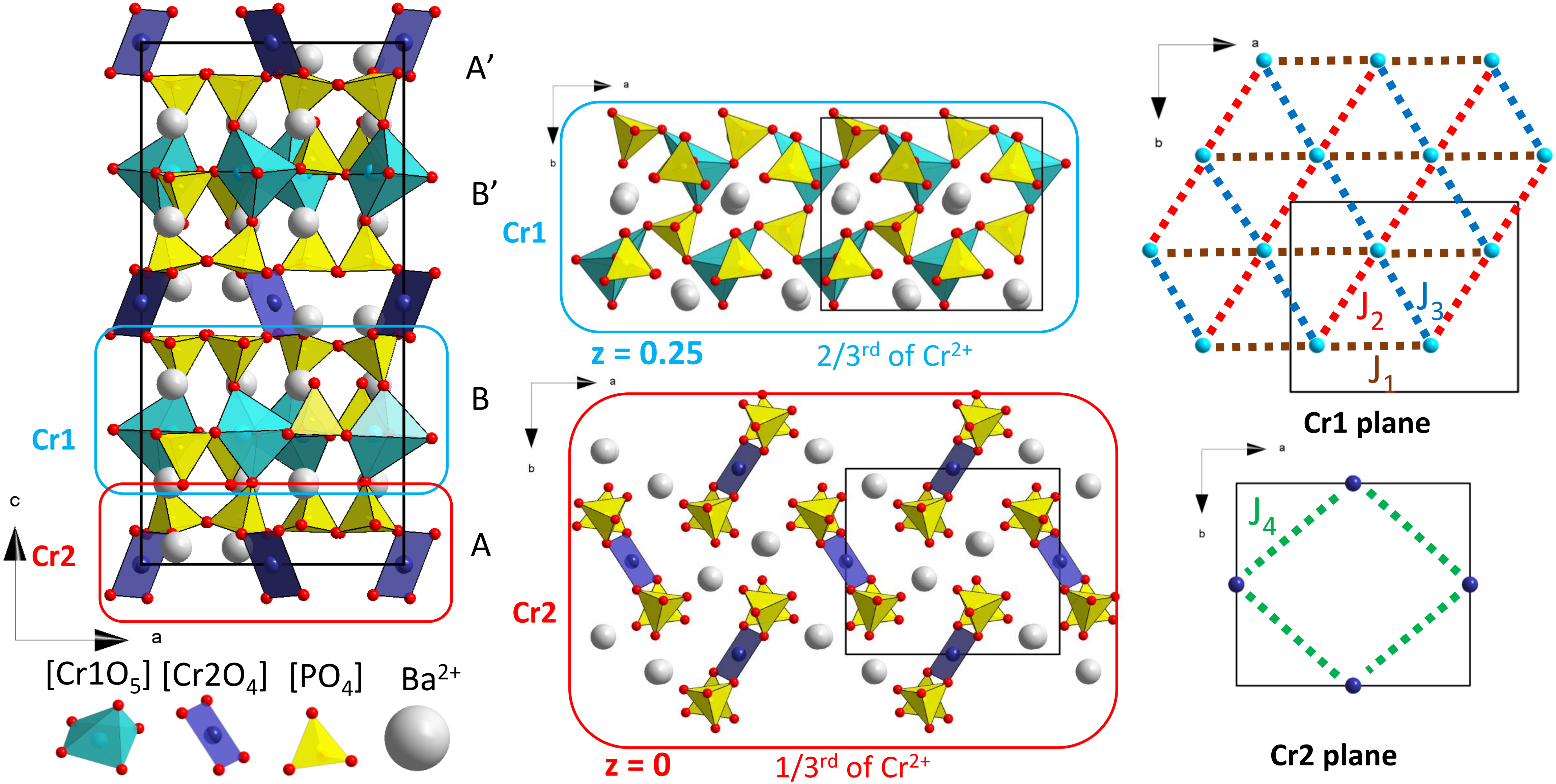


hk0 – domain 3



$Sr_2Cr(PO_4)_2$: Crystal structure

- Orthorhombic Pbca
- Two indiviadual layers
- Pseudo trigonal



$Sr_2Cr(PO_4)_2$: Crystal structure

- Orthorhombic Pbca
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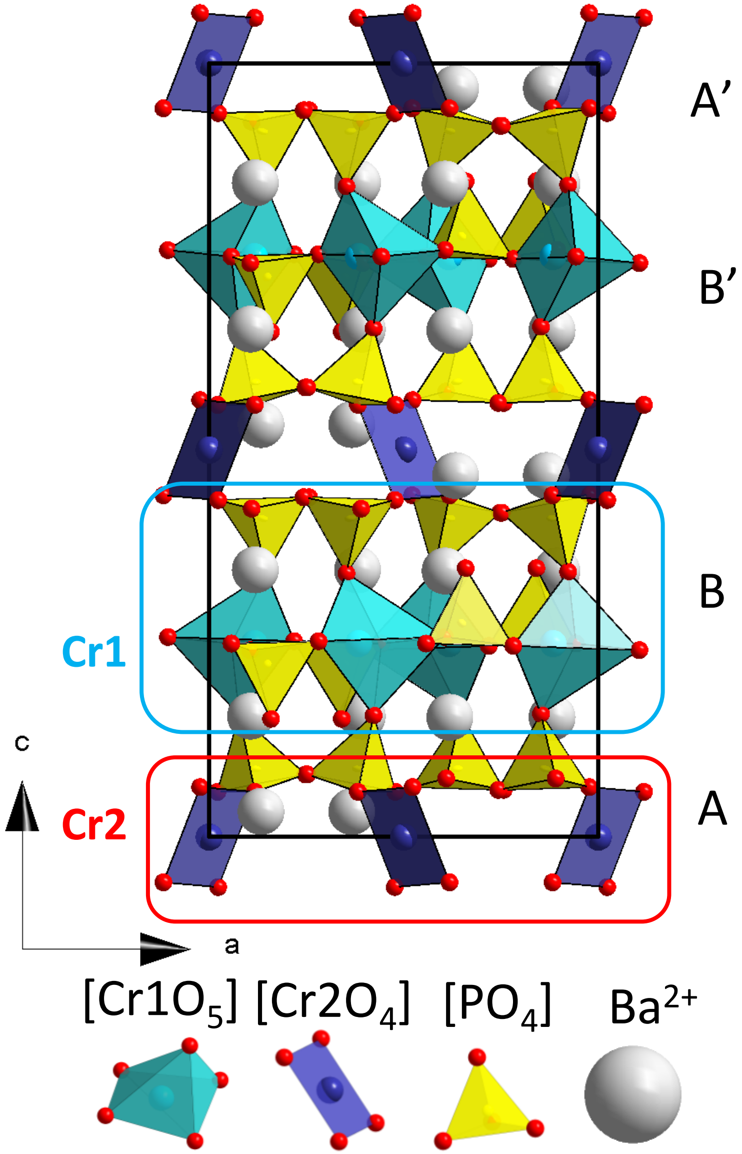
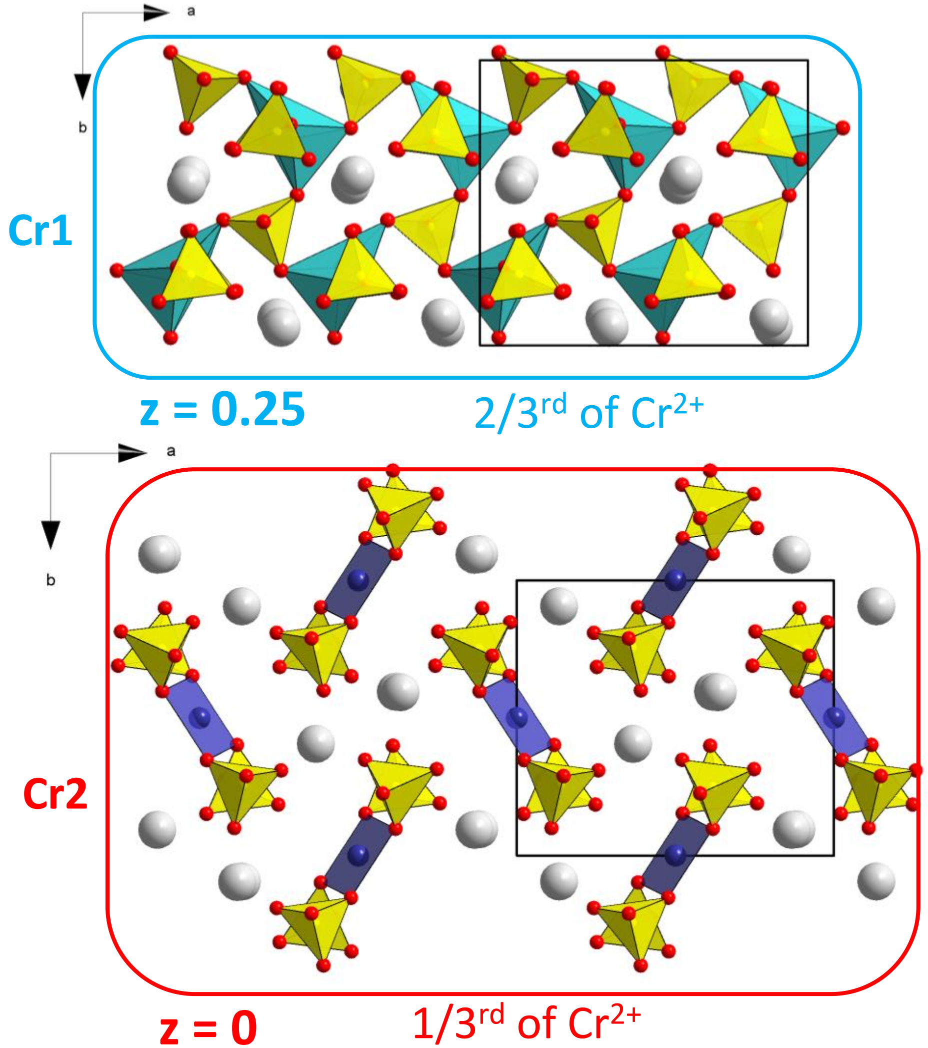
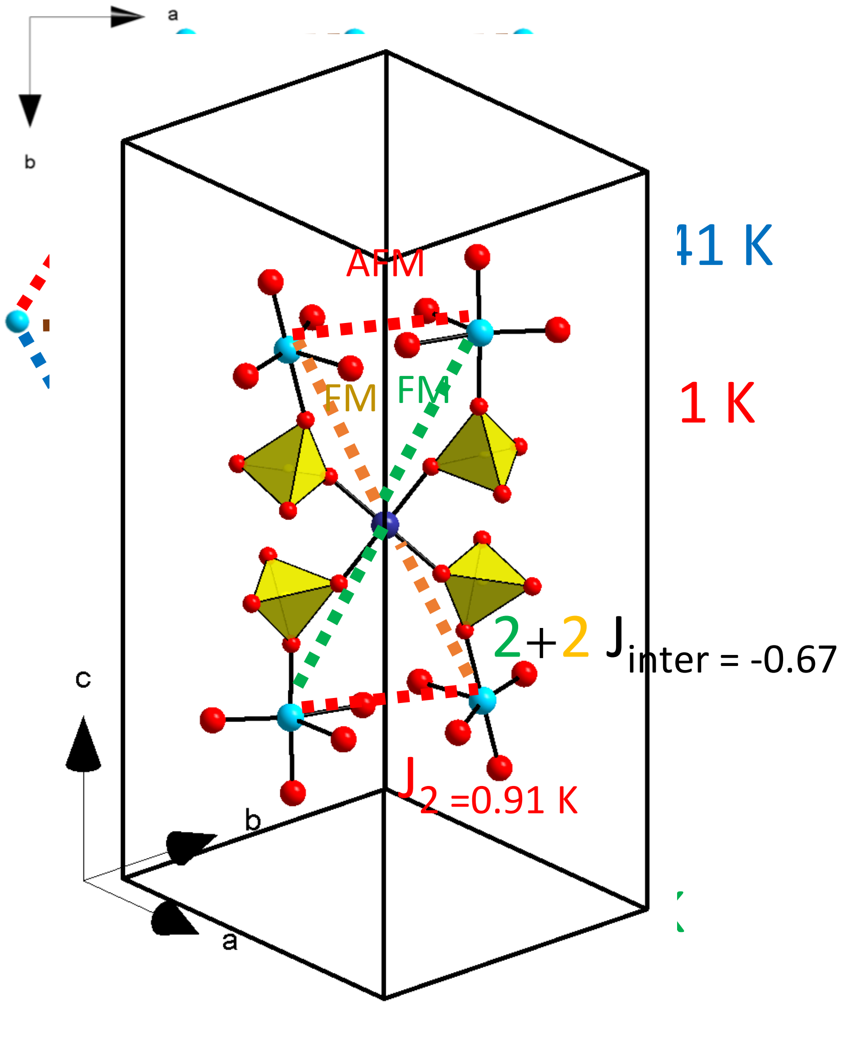
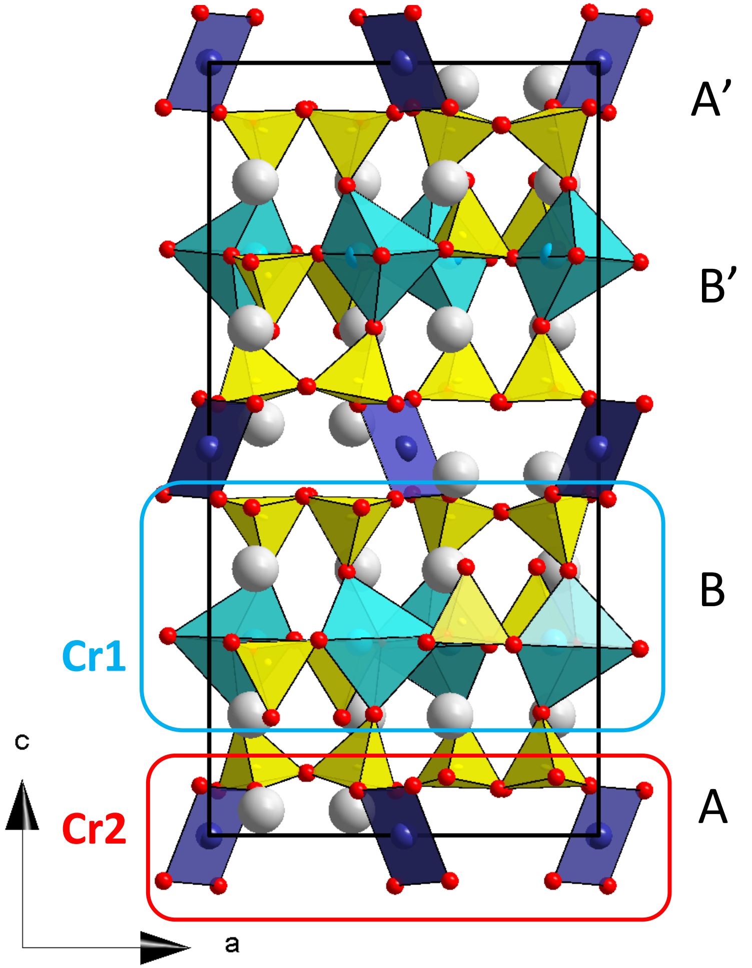
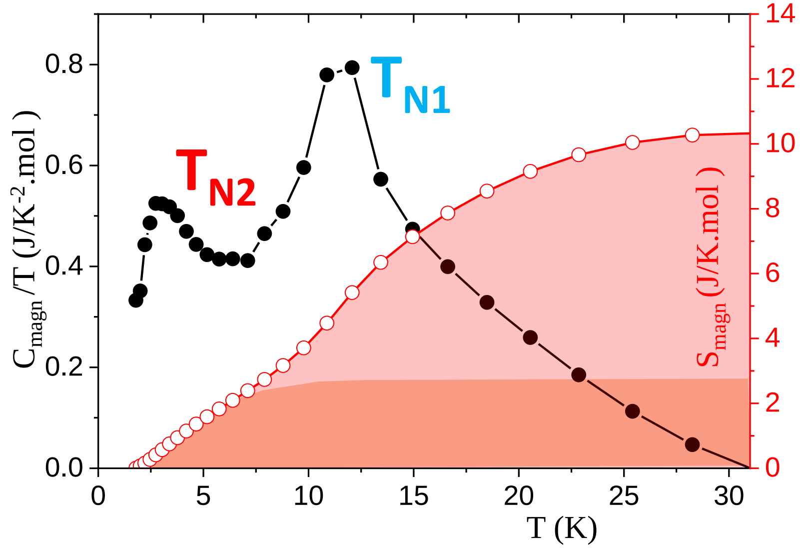


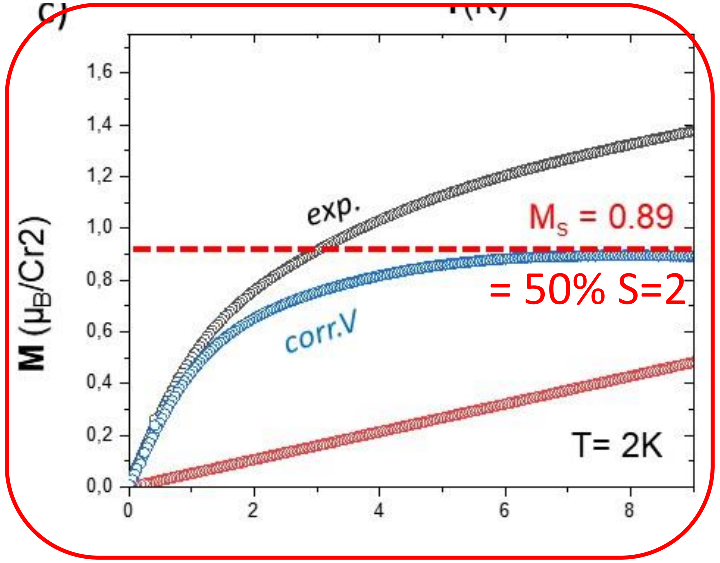




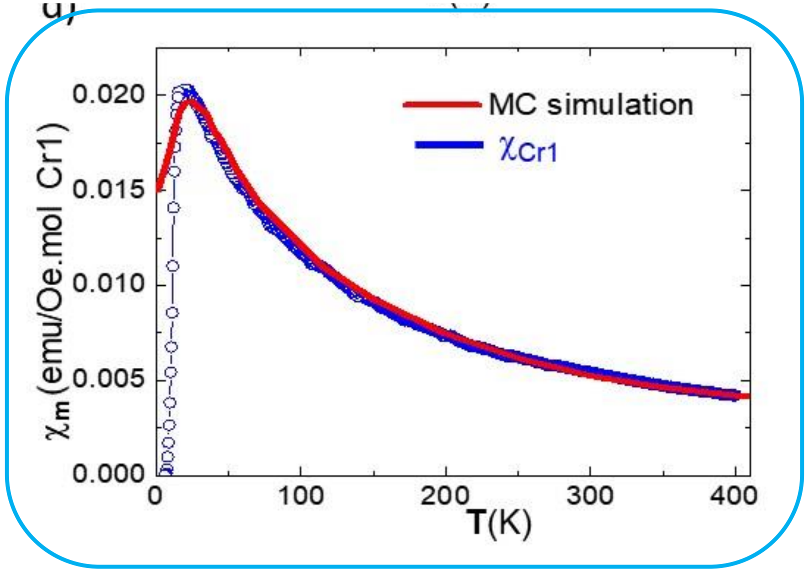
$Sr_2Cr(PO_4)_2$: The contibution of the two sublattices





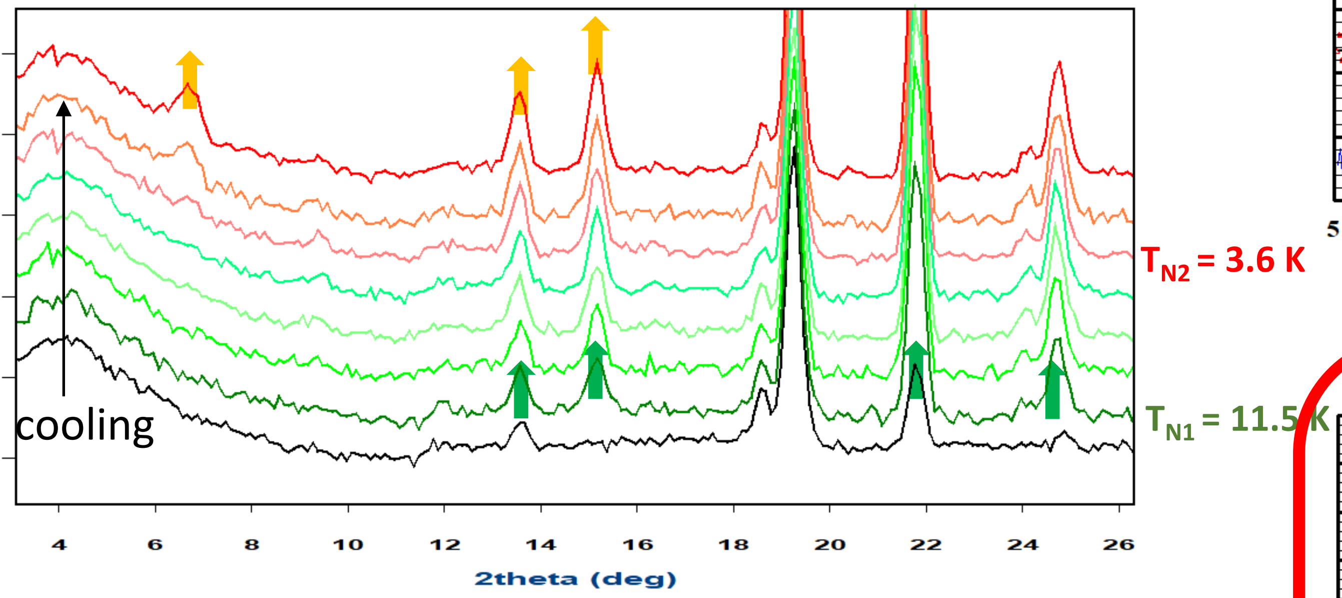


Low T: 50% only of the Cr2 seems fluctuating , 50% ordered

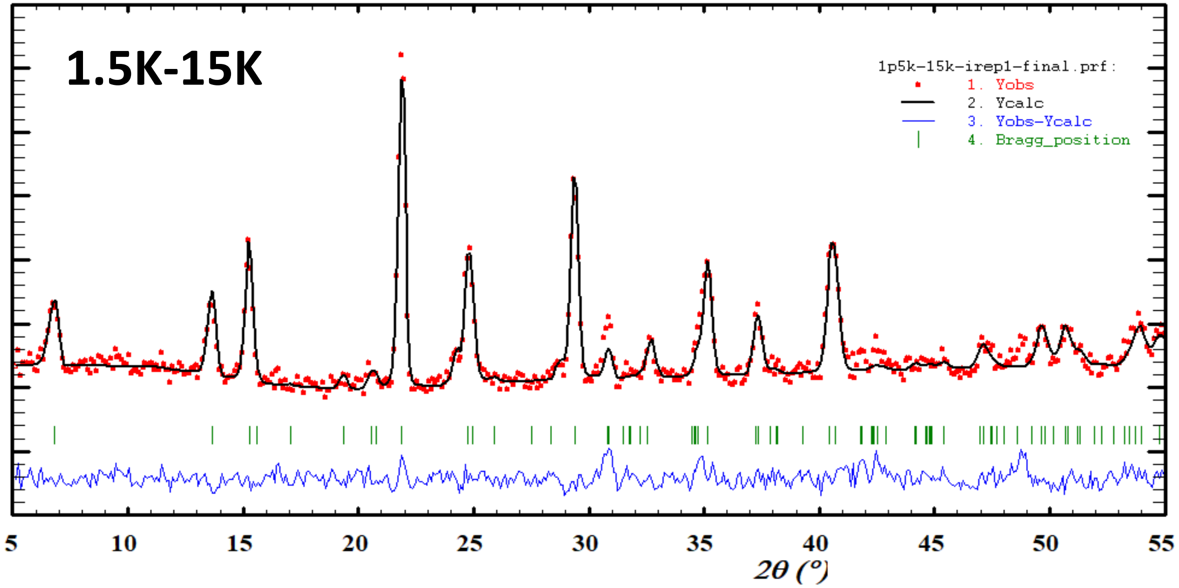


Cr1 AFM-2D lattice ordering at 13.6 K + Cr2 idle = "quasi-paramagn."

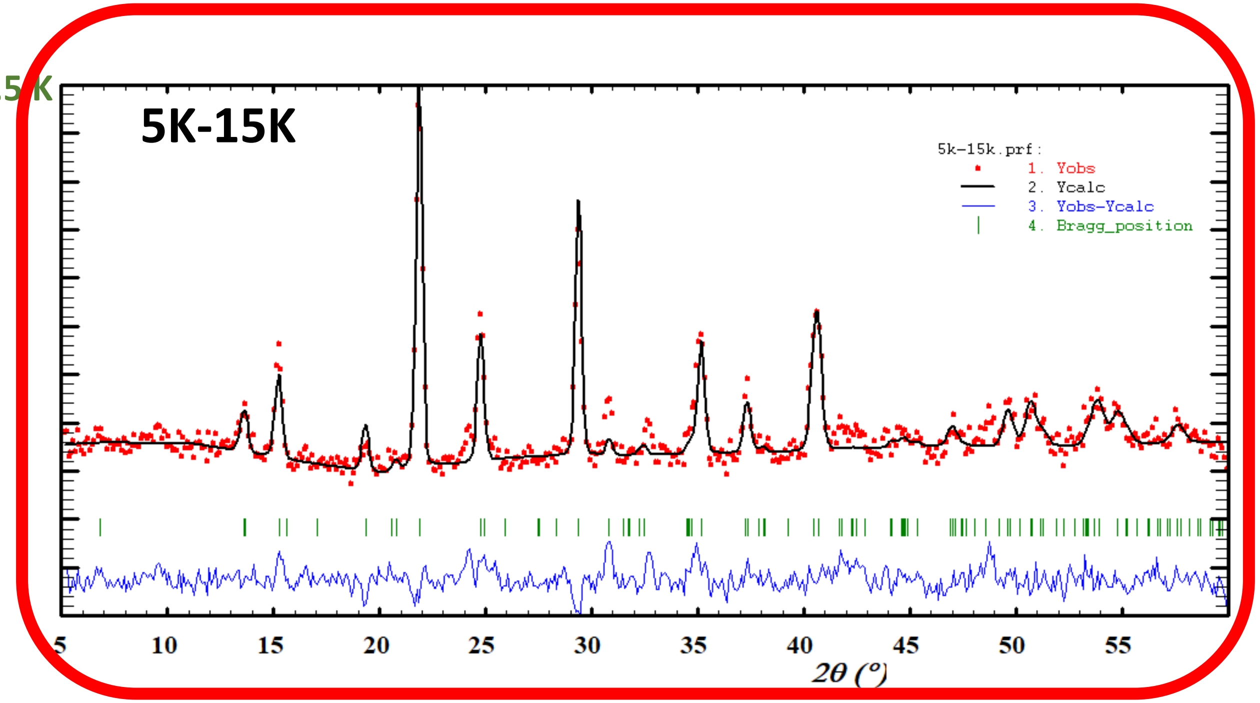
NPD, D1B ILL



cooling
T_{N2} = 3.6 K
T_{N1} = 11.5 K
4 6 8 10 12 14 16 18 20 22 24 26
2theta (deg)



1.5K-15K
1p5k-15k-irep1-final.prf:
1. Yobs
2. Ycalc
3. Yobs-Ycalc
4. Bragg_position
5 10 15 20 25 30 35 40 45 50 55
2θ (°)



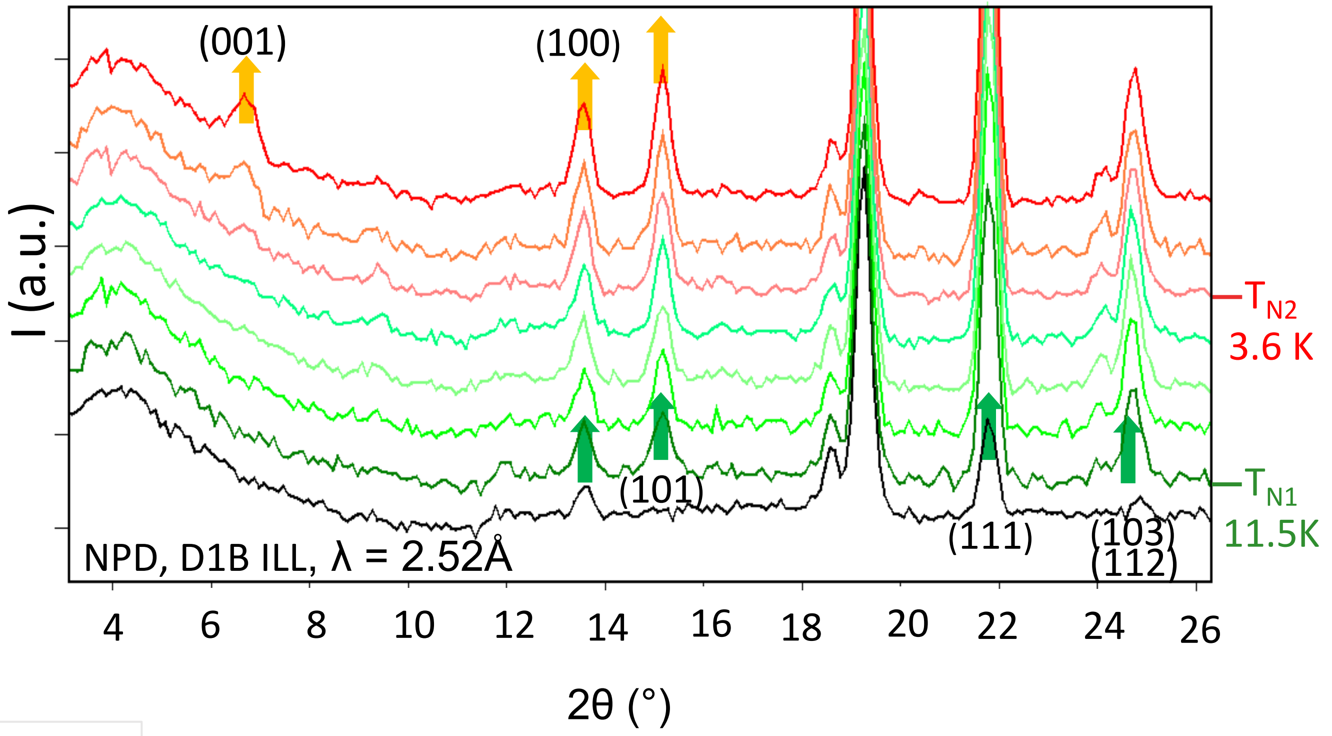
5K-15K
5k-15k.prf:
1. Yobs
2. Ycalc
3. Yobs-Ycalc
4. Bragg_position
5 10 15 20 25 30 35 40 45 50 55
2θ (°)

Solving the Magnetic Structure at 5K

1st step : find the propagation k vector

All magn. peaks are indexable in the crystal cell

→ **K = (0,0,0)**



2nd step : Group theory analyzis

```
==============================
    CALCULATIONS FOR SITE : Cr(1)
    ==============================

 => Decomposition of the Magnetic/Mechanic
representation:

 -> GAMMA(Magnetic):   3 Irep_k( 1) + 3
Irep_k( 2) + 3 Irep_k( 3) + 3 Irep_k( 4) +
3 Irep_k( 5) + 3 Irep_k( 6) + 3 Irep_k( 7)
+ 3 Irep_k( 8)
```

```
==============================
    CALCULATIONS FOR SITE : Cr(2)
    ==============================

 => Decomposition of the Magnetic/Mechanic
representation:

 -> GAMMA(Magnetic):   3 Irep_k( 1) + 3
Irep_k( 3) + 3 Irep_k( 5) + 3 Irep_k( 7)
```

demo

What represent these IRreps ?

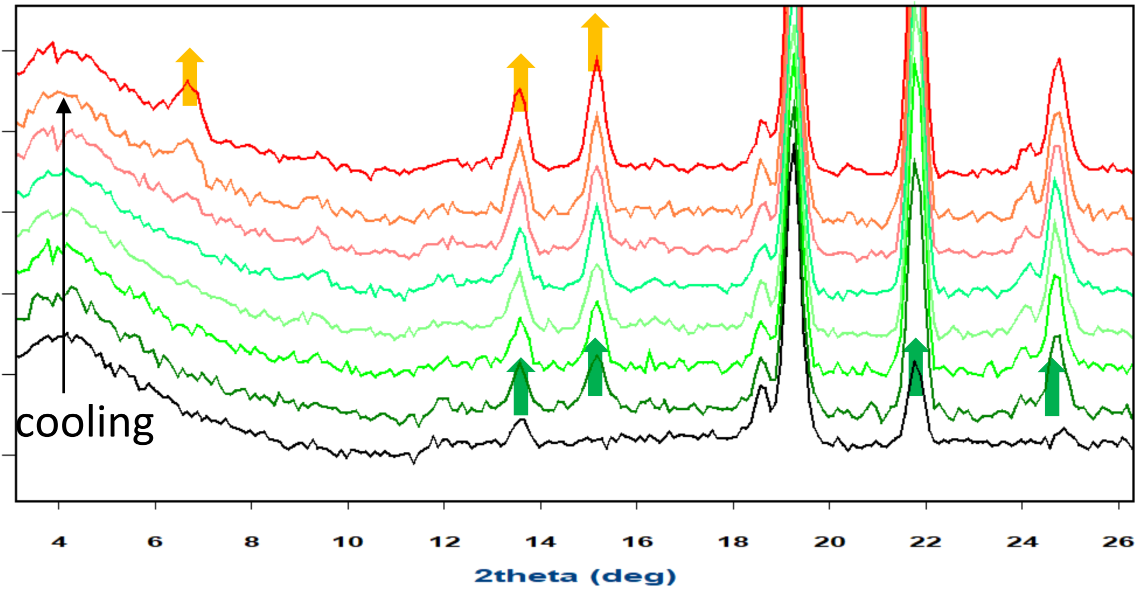
```
=> Basis functions of Representation IRrep(  8) of dimension   1 contained  3 times in GAMMA
     Representation number     :  8 for Site:  1
     Number of basis functions:  3

 ----- Block-of-lines for PCR start just below this line
P -1                        <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
    8     1     1    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
SYMM x,y,z
BASR   1  0  0    0  1  0    0  0  1
BASI   0  0  0    0  0  0    0  0  0
SYMM -x+1/2,-y,z+1/2
BASR   1  0  0    0  1  0    0  0 -1
BASI   0  0  0    0  0  0    0  0  0
SYMM -x,y+1/2,-z+1/2
BASR   1  0  0    0 -1  0    0  0  1
BASI   0  0  0    0  0  0    0  0  0
SYMM x+1/2,-y+1/2,-z
BASR   1  0  0    0 -1  0    0  0 -1
BASI   0  0  0    0  0  0    0  0  0
SYMM -x,-y,-z
BASR  -1  0  0    0 -1  0    0  0 -1
BASI   0  0  0    0  0  0    0  0  0
SYMM x+1/2,y,-z+1/2
BASR  -1  0  0    0 -1  0    0  0  1
BASI   0  0  0    0  0  0    0  0  0
SYMM x,-y+1/2,z+1/2
BASR  -1  0  0    0  1  0    0  0 -1
BASI   0  0  0    0  0  0    0  0  0
SYMM -x+1/2,y+1/2,z
BASR  -1  0  0    0  1  0    0  0  1
BASI   0  0  0    0  0  0    0  0  0
 ----- End-of-block of lines for PCR
```

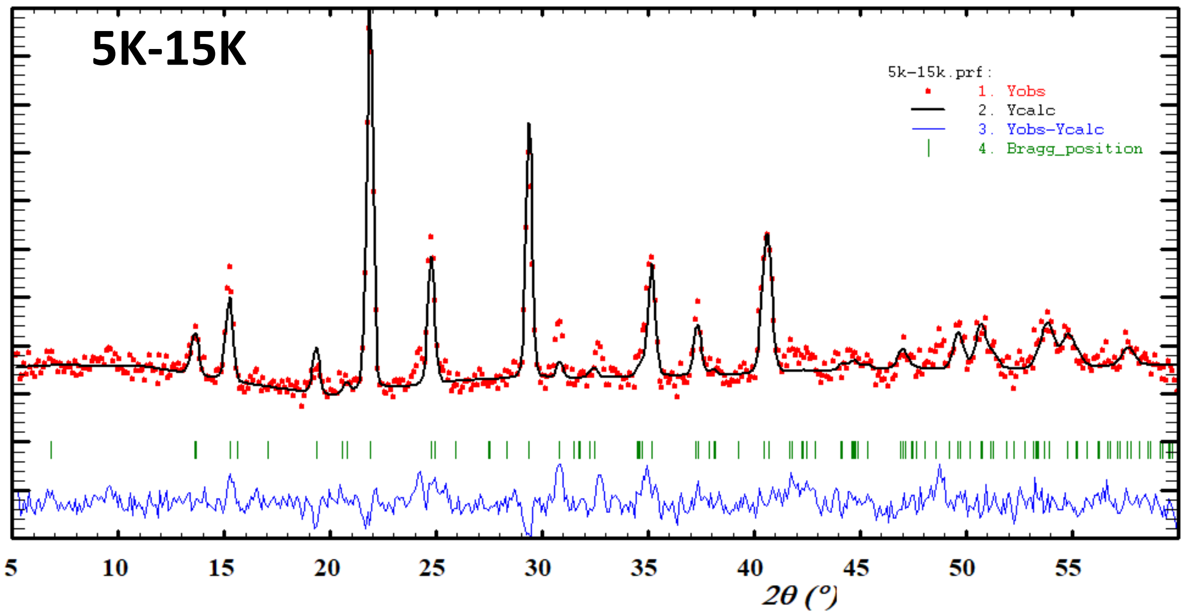
Mx *My* *Mz*

3rd step : test all IRreps → refinement of magnetic structure

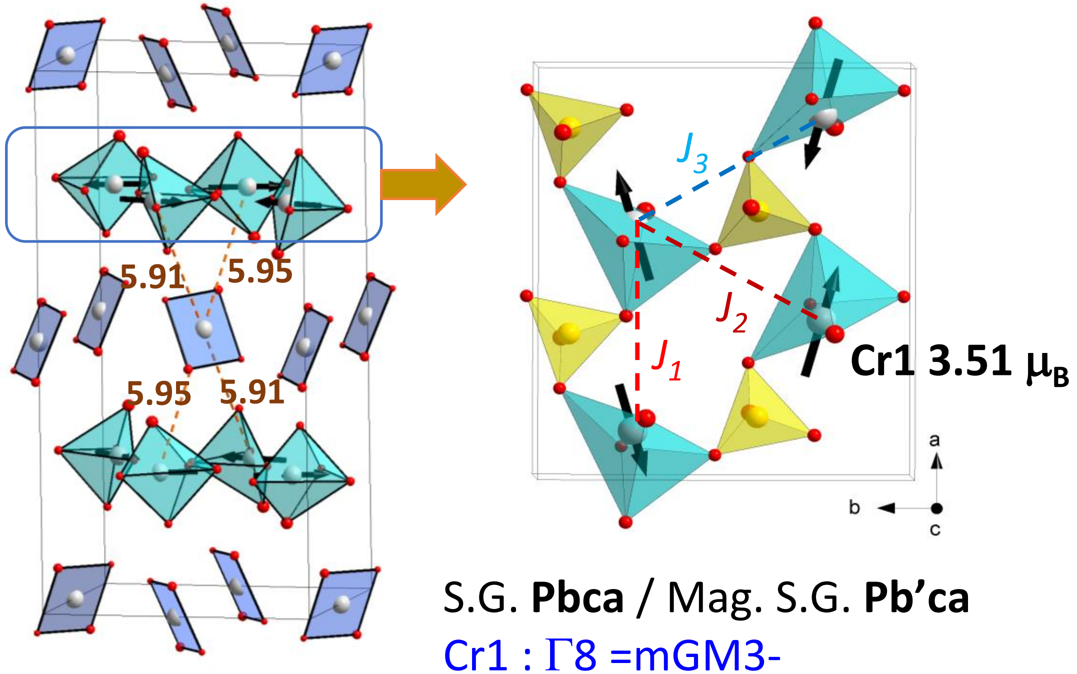
demo

NPD, D1B ILL



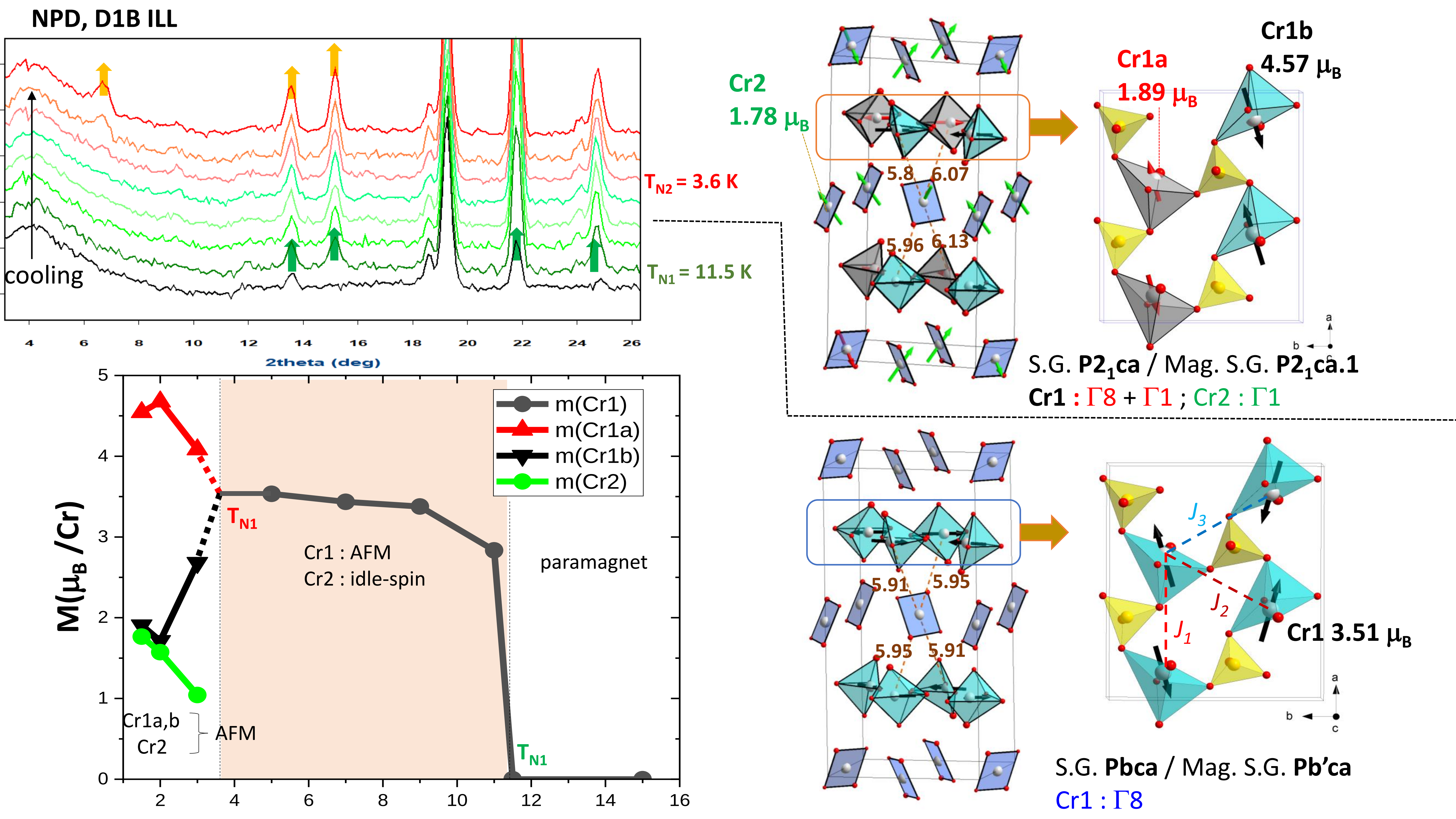


Cr(1) AFM-2D lattice ordering between 13.6 K - 3.6 K + Cr2 idle = "quasi-paramagn."



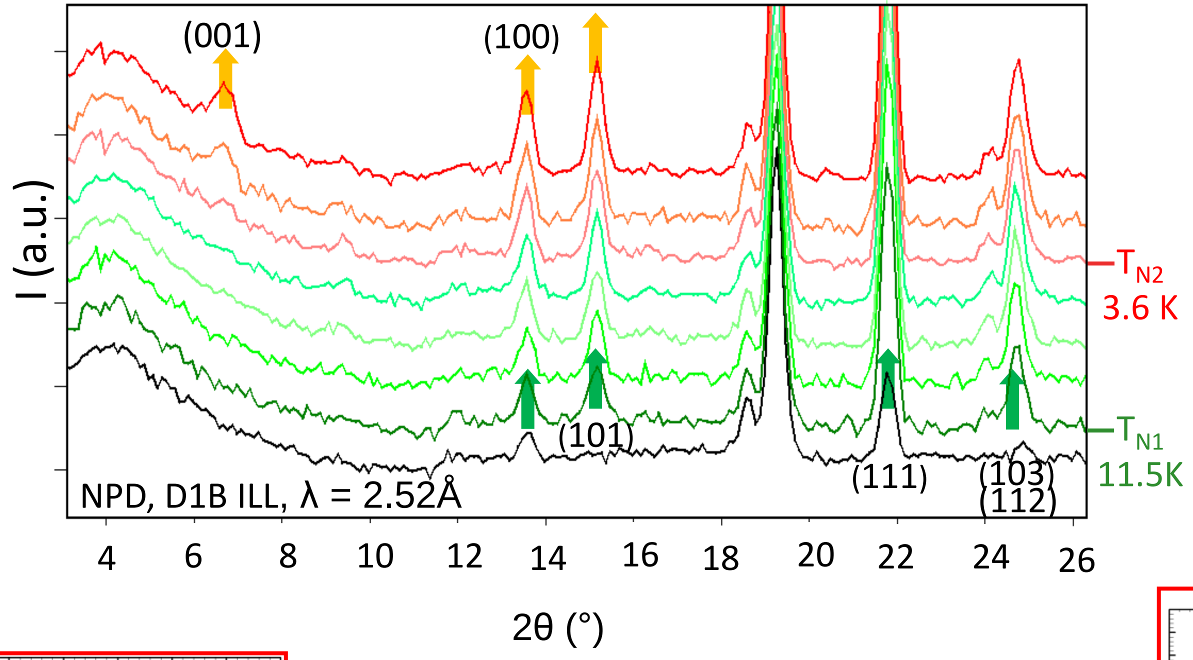
S.G. **Pbca** / Mag. S.G. **Pb'ca**

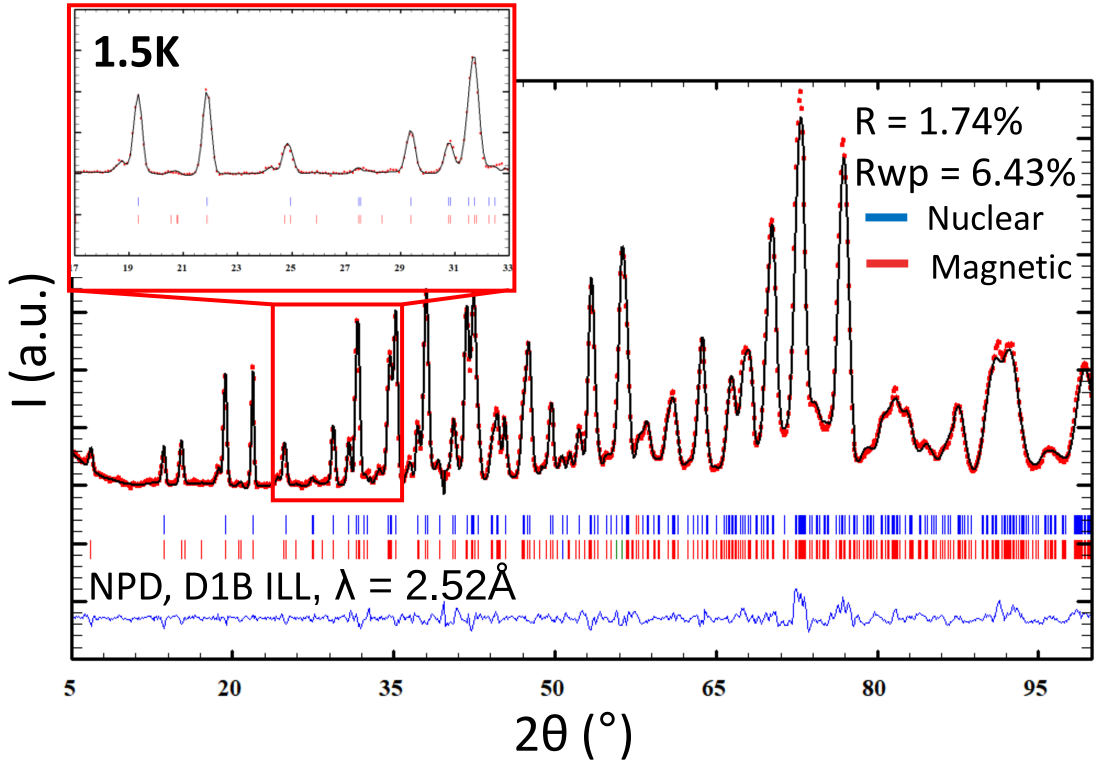
Cr1 : Γ8 =mGM3-

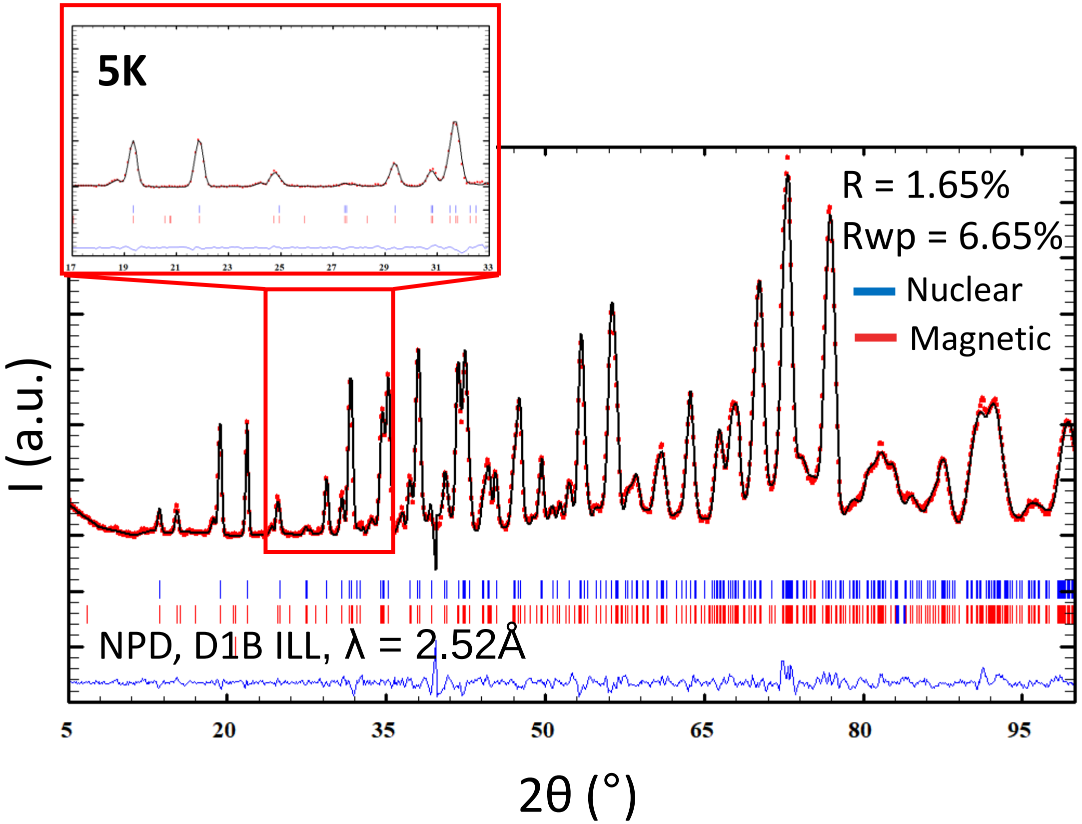


NPD, D1B ILL
cooling
T_{N2} = 3.6 K
T_{N1} = 11.5 K
2theta (deg)
Cr2
1.78 μ_B
Cr1a
1.89 μ_B
Cr1b
4.57 μ_B
5.8
6.07
5.96
6.13
S.G. $P2_1ca$ / Mag. S.G. $P2_1ca.1$
Cr1 : Γ8 + Γ1 ; Cr2 : Γ1
m(Cr1)
m(Cr1a)
m(Cr1b)
m(Cr2)
$M(\mu_B /Cr)$
T_{N1}
Cr1 : AFM
Cr2 : idle-spin
paramagnet
Cr1a,b
Cr2
AFM
5.91
5.95
5.95
5.91
J_3
J_2
J_1
Cr1 3.51 μ_B
S.G. Pbca / Mag. S.G. Pb'ca
Cr1 : Γ8

We can also refine the full NPD pattern : nuclear + magnetic







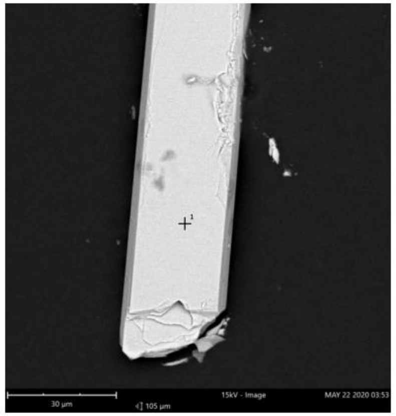
Frustration … Towards « true » Quantum Spin Liquid

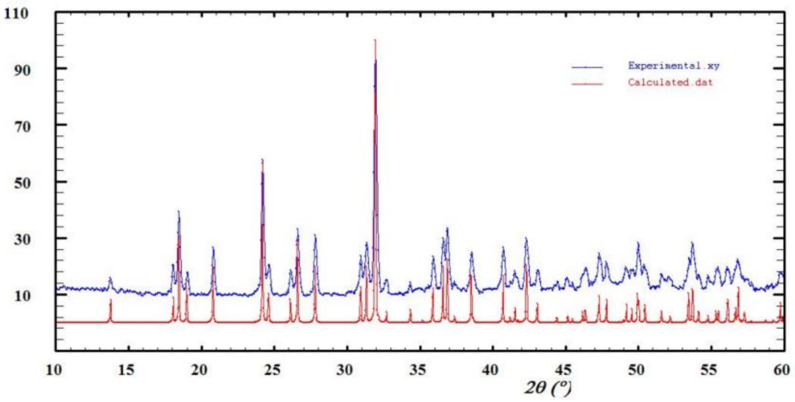
Synthesis

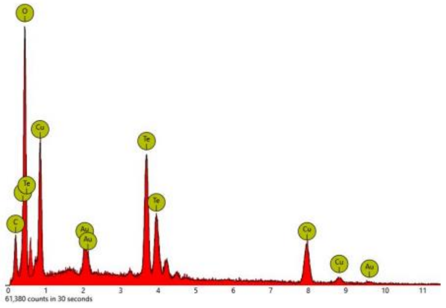
- ***The $Cu_3Te_2O_5(OH)_4$ compound***

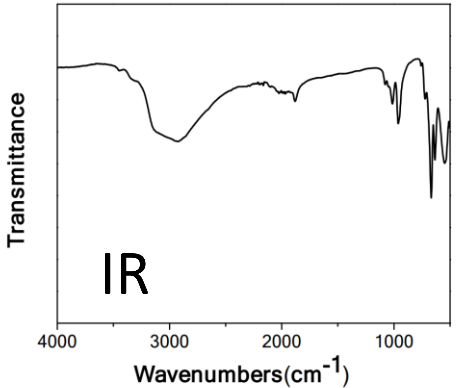
- **Teflon-lined bomb : autogeneous pressure**
- **Hydrazine red. agent: stabilization low-redox**
- **Fluoride-rich media (HF)**

$Cu_2(OH)_2CO^3$ (Alfa Aesar, >55%), TeO_2 (Alfa Aesar, 99%), HF (Energy Chemical, 48% wt in H_2O), Hydrazine monohydrate, (Sinopharm, >85%)





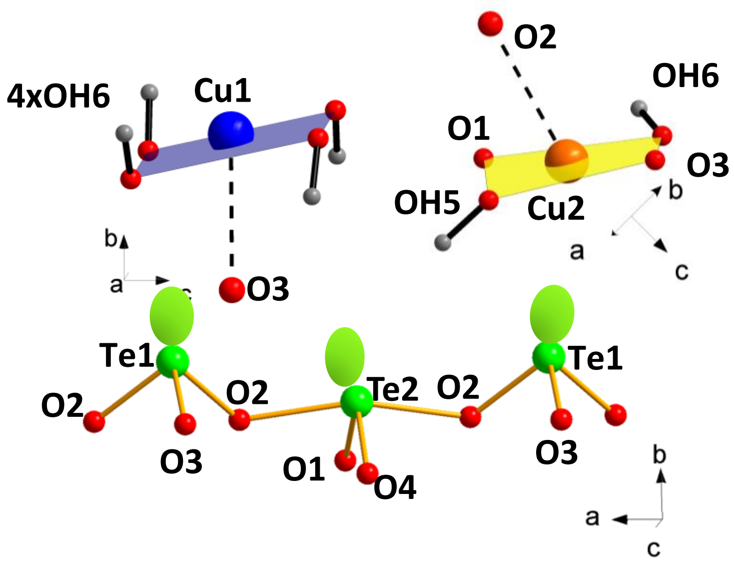


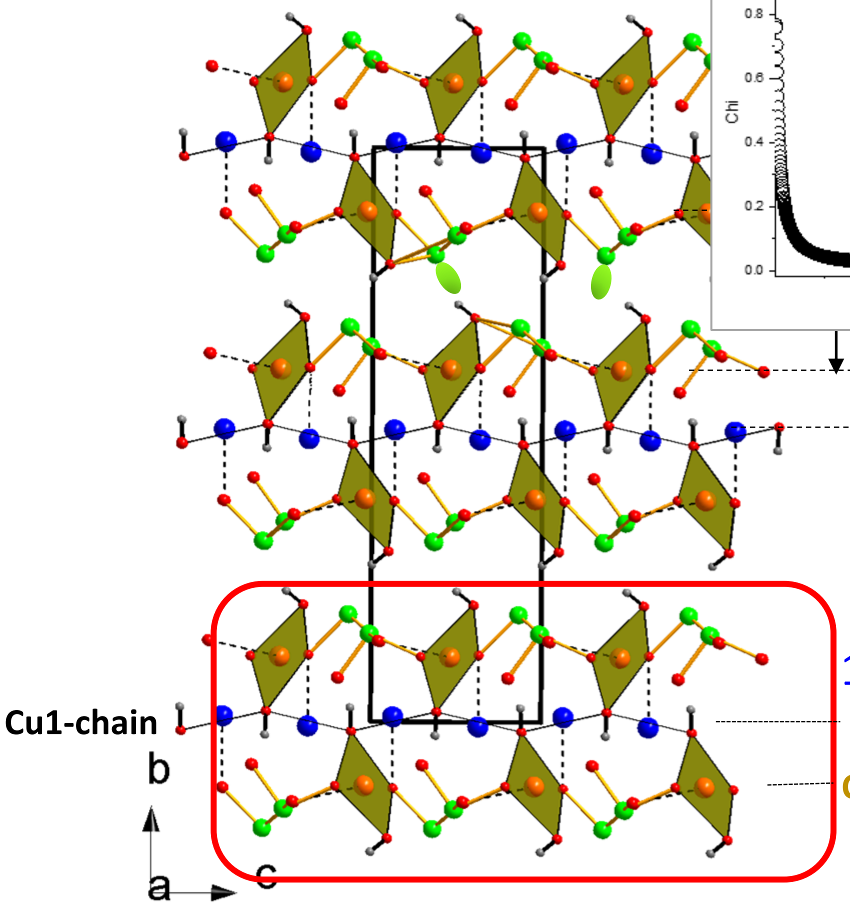


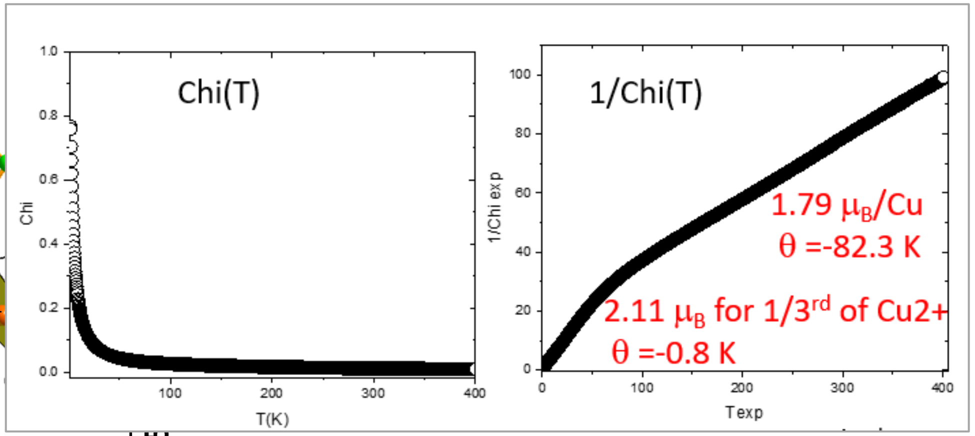
Frustration … Towards « true » Quantum Spin Liquid

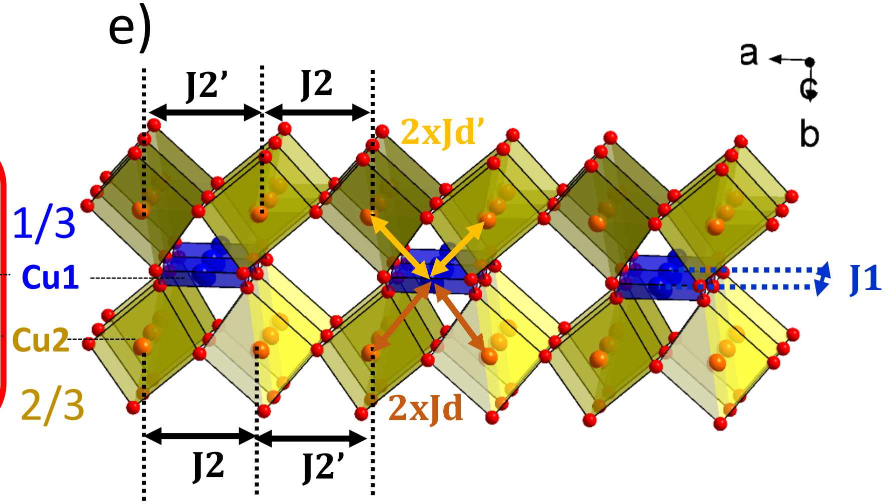
… requires « perfect » frustrated Spins …

- ***The $Cu_3Te_2O_5(OH)_4$ compound***





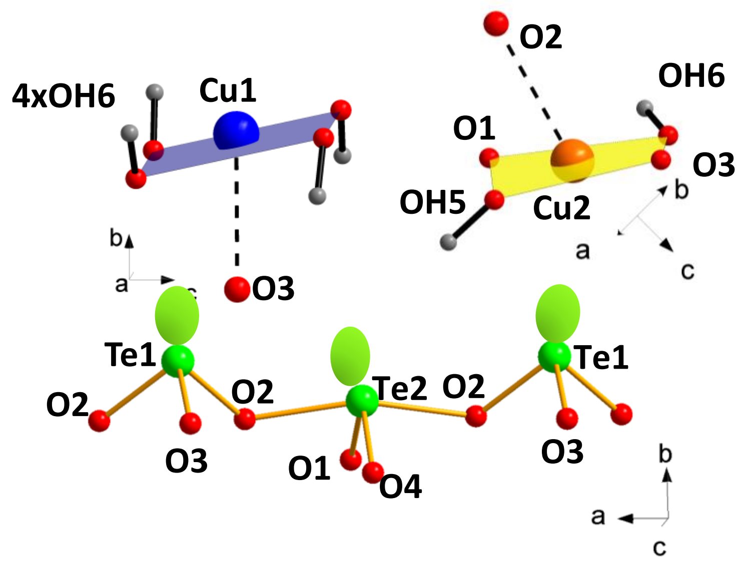


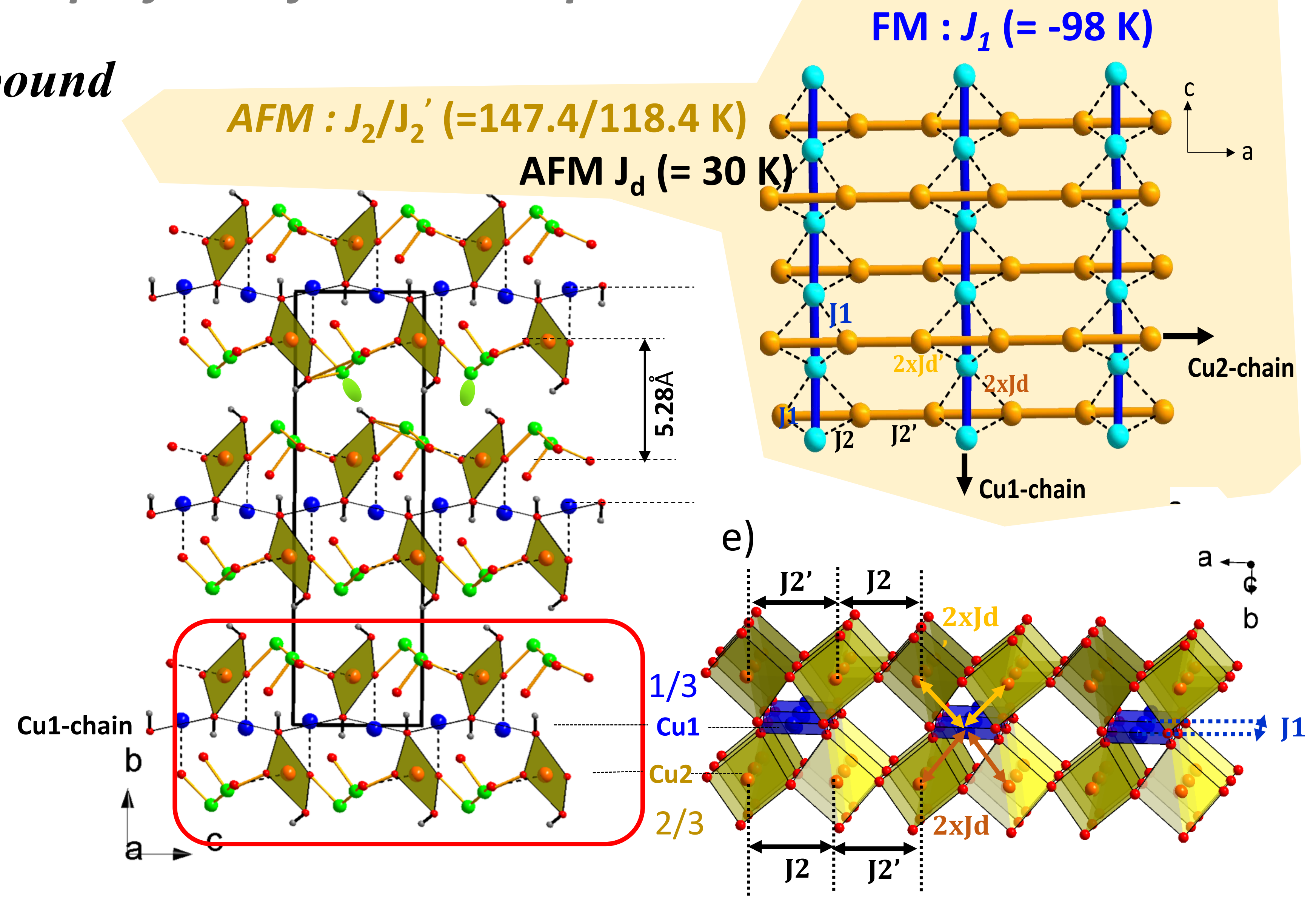


Frustration … Towards « true » Quantum Spin Liquid

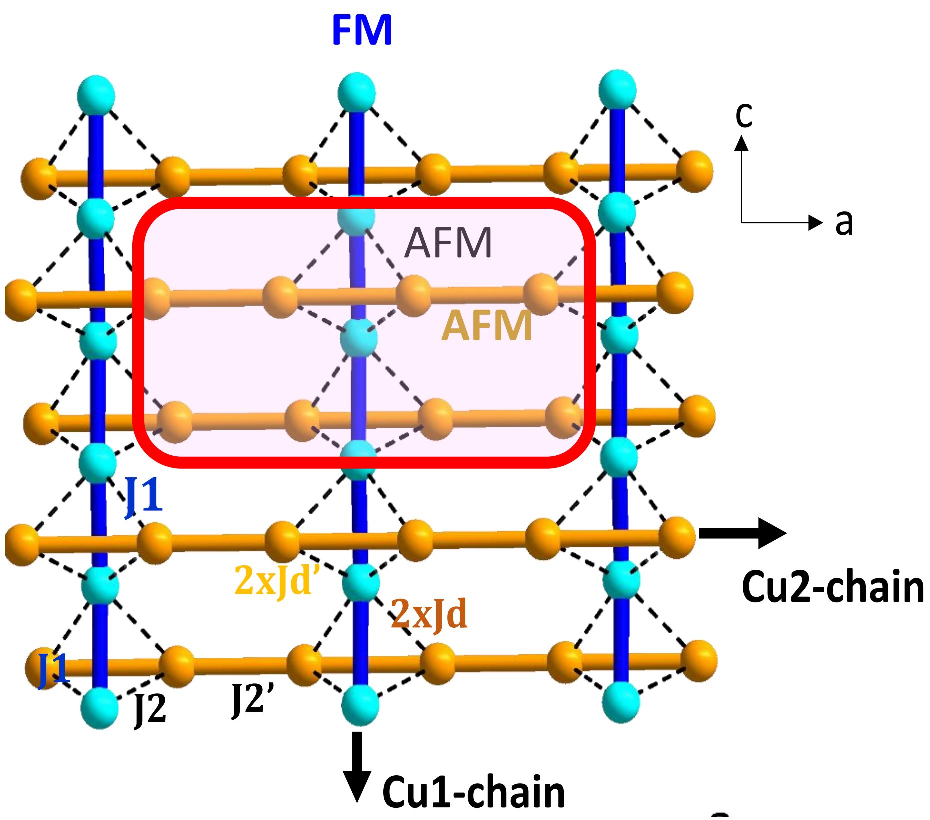
… requires « perfect » frustrated Spins …

- ***The $Cu_3Te_2O_5(OH)_4$ compound***



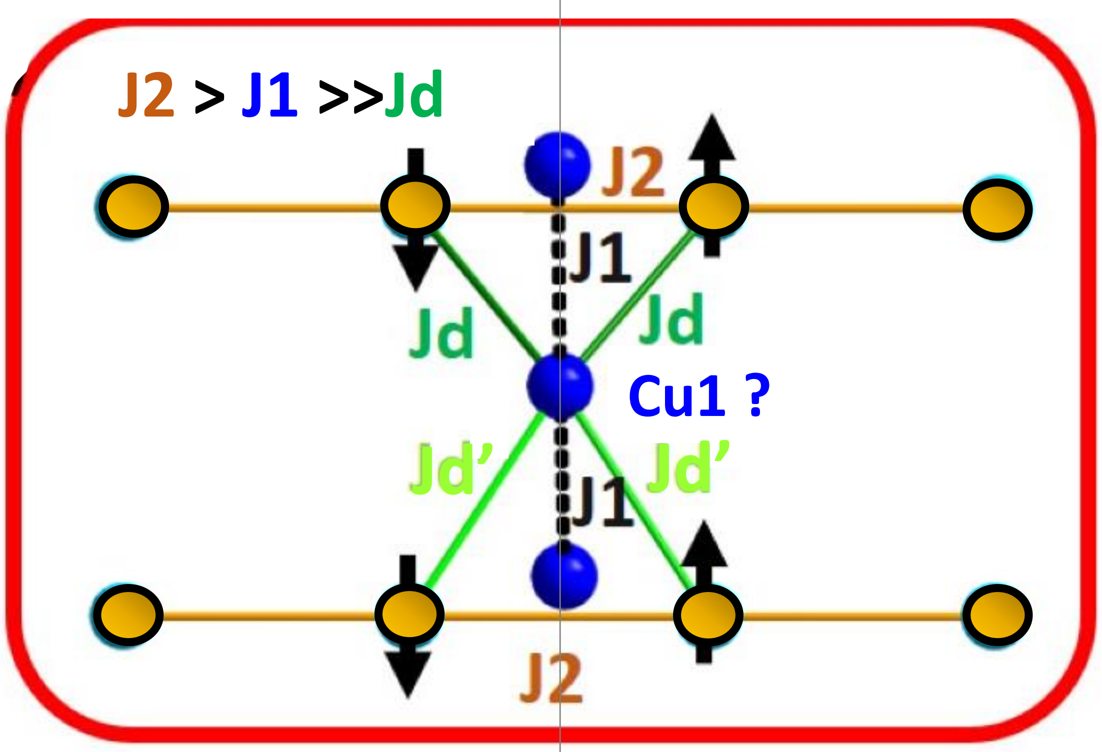


Towards « true » Quantum Spin Liquid



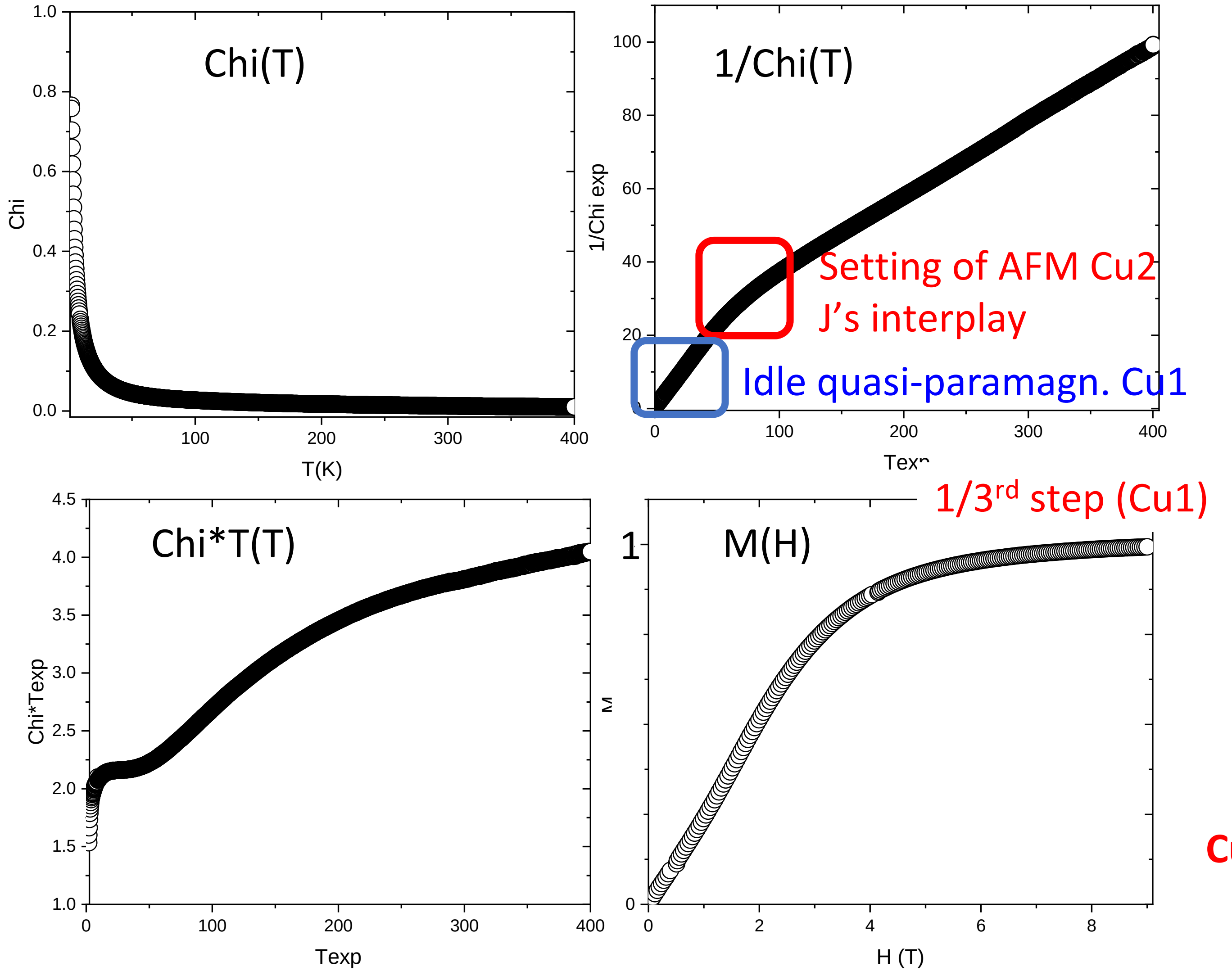
Cu1, strategical role :

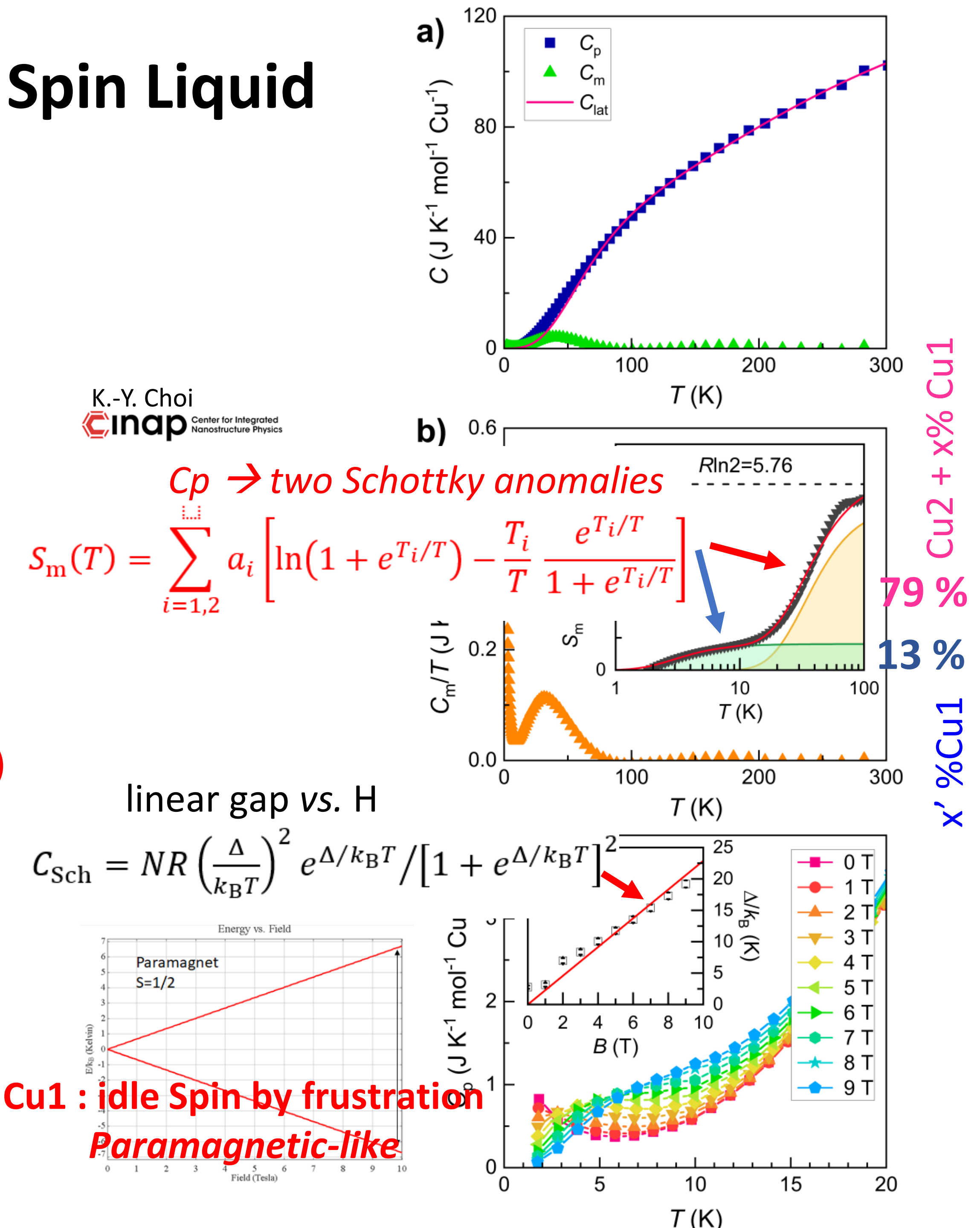
- pivotal for 3D ordering
- but … Ideally frustrated…



Cu1 ideally frustrated by the mirror-symmetry

Towards « true » Quantum Spin Liquid

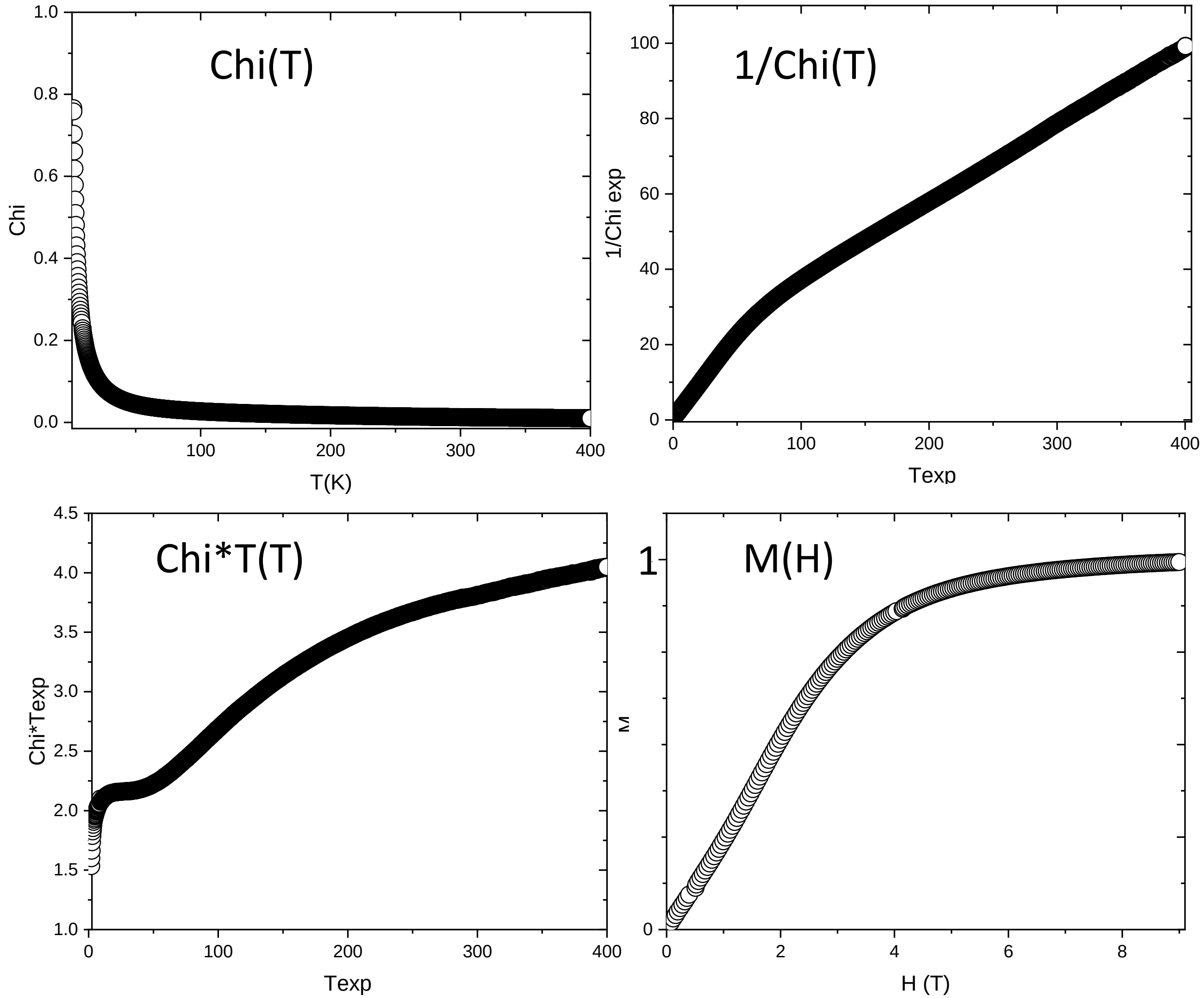




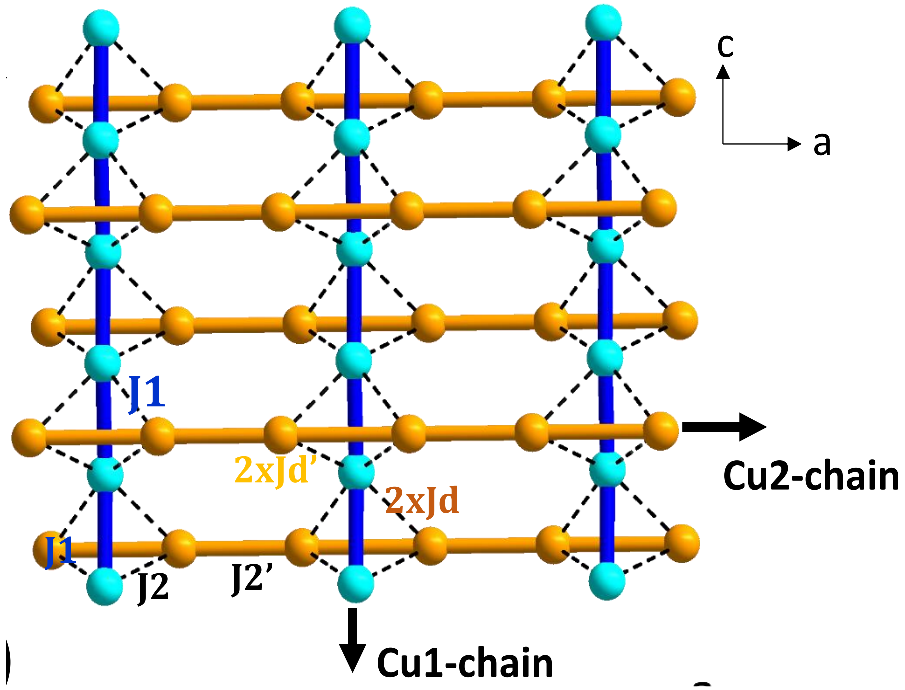
$$S_{\mathrm{m}}(T) = \sum_{i=1,2} a_i \left[\ln\left(1 + e^{T_i/T}\right) - \frac{T_i}{T} \frac{e^{T_i/T}}{1 + e^{T_i/T}} \right]$$

$$C_{\mathrm{Sch}} = NR\left(\frac{\Delta}{k_{\mathrm{B}}T}\right)^2 e^{\Delta/k_{\mathrm{B}}T} / \left[1 + e^{\Delta/k_{\mathrm{B}}T}\right]^2$$

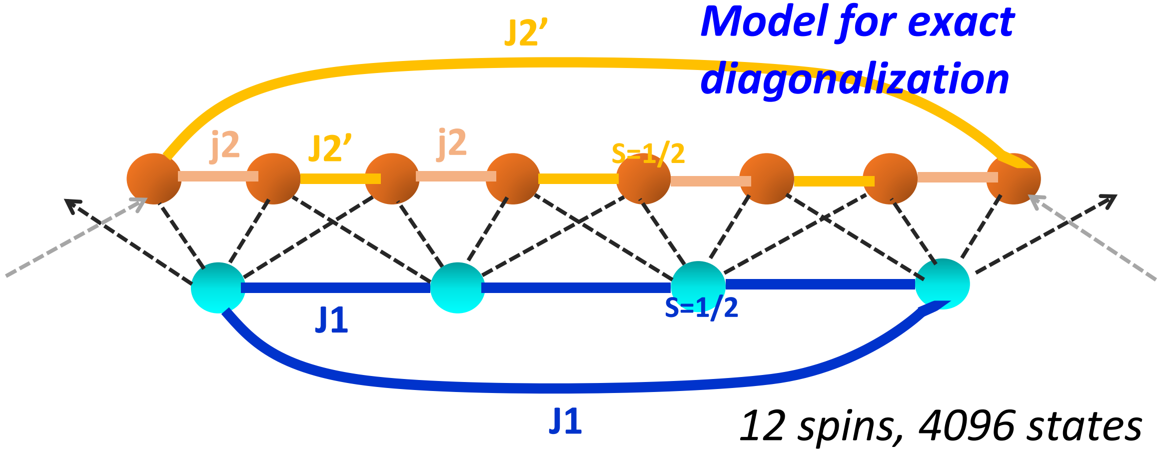
Towards « true » Quantum Spin Liquid



Structural Model



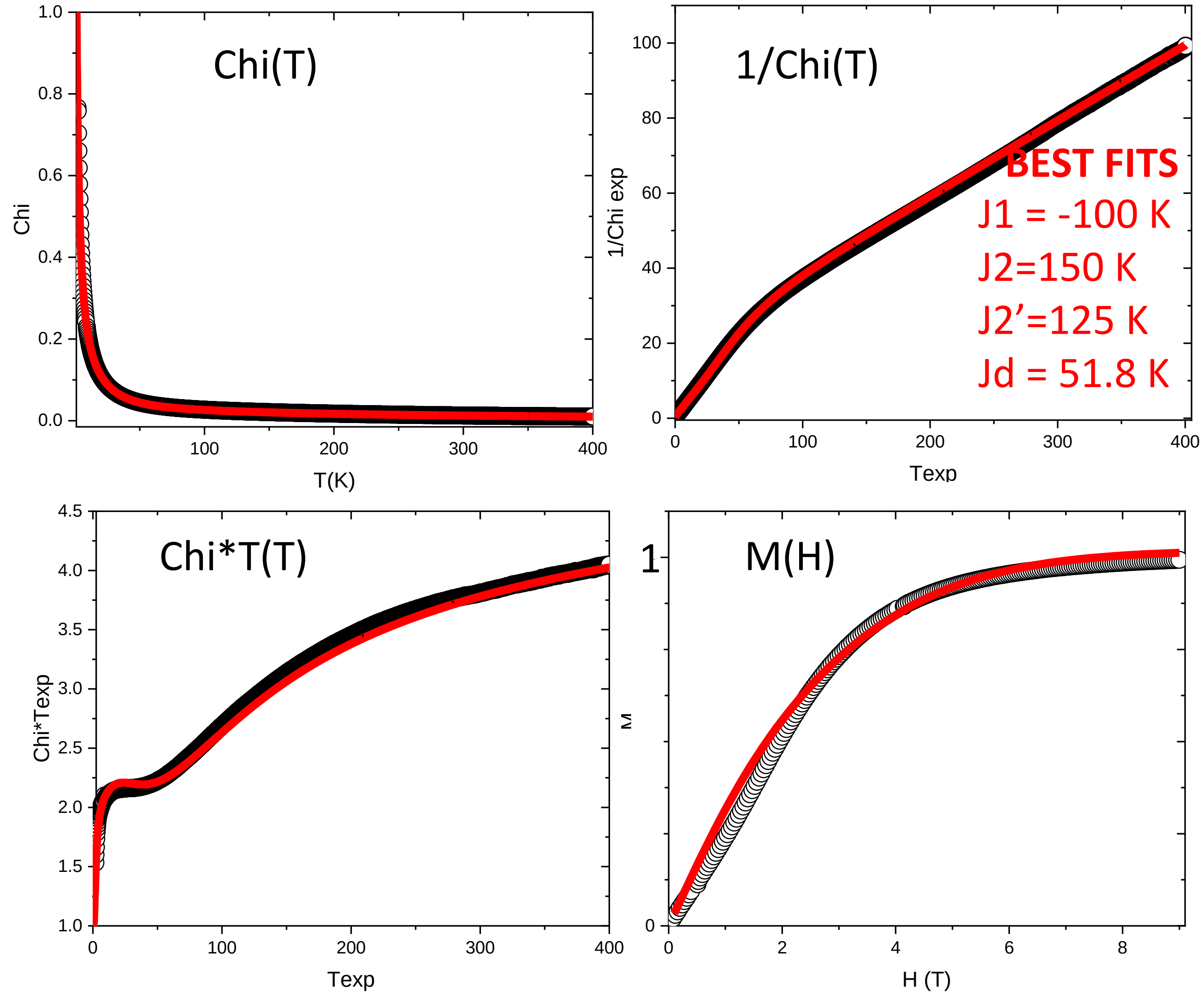
Model for exact diagonalization



12 spins, 4096 states

Towards « true » Quantum Spin Liquid

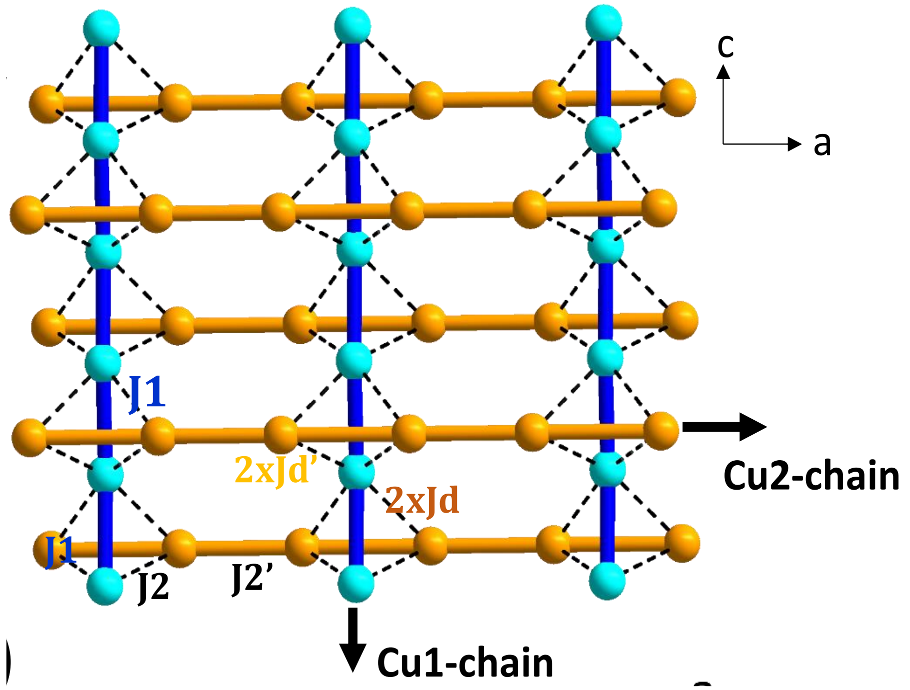
Quantum spin liquid



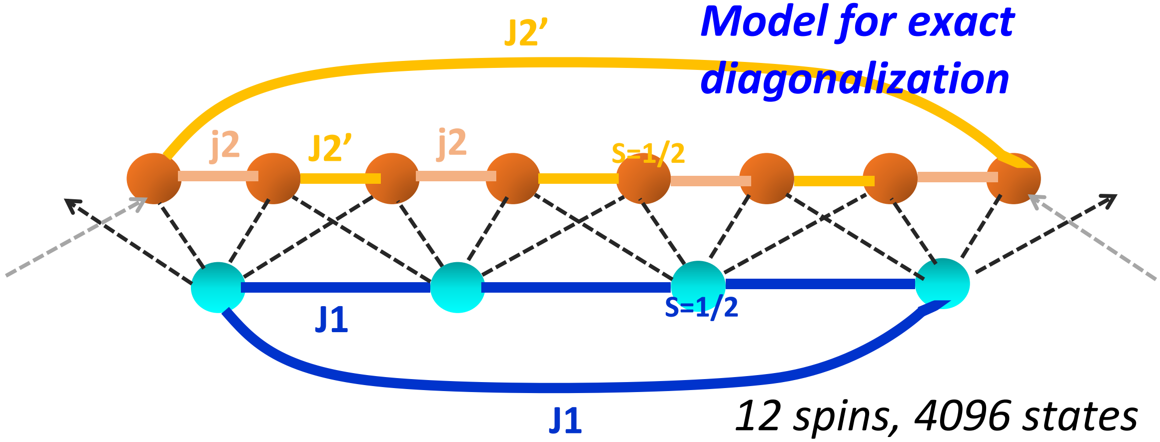
BEST FITS
J1 = -100 K
J2=150 K
J2'=125 K
Jd = 51.8 K

DFT+U
J1 = -98 K
J2=147.4 K
J2'=118.4 K
Jd = 30 K

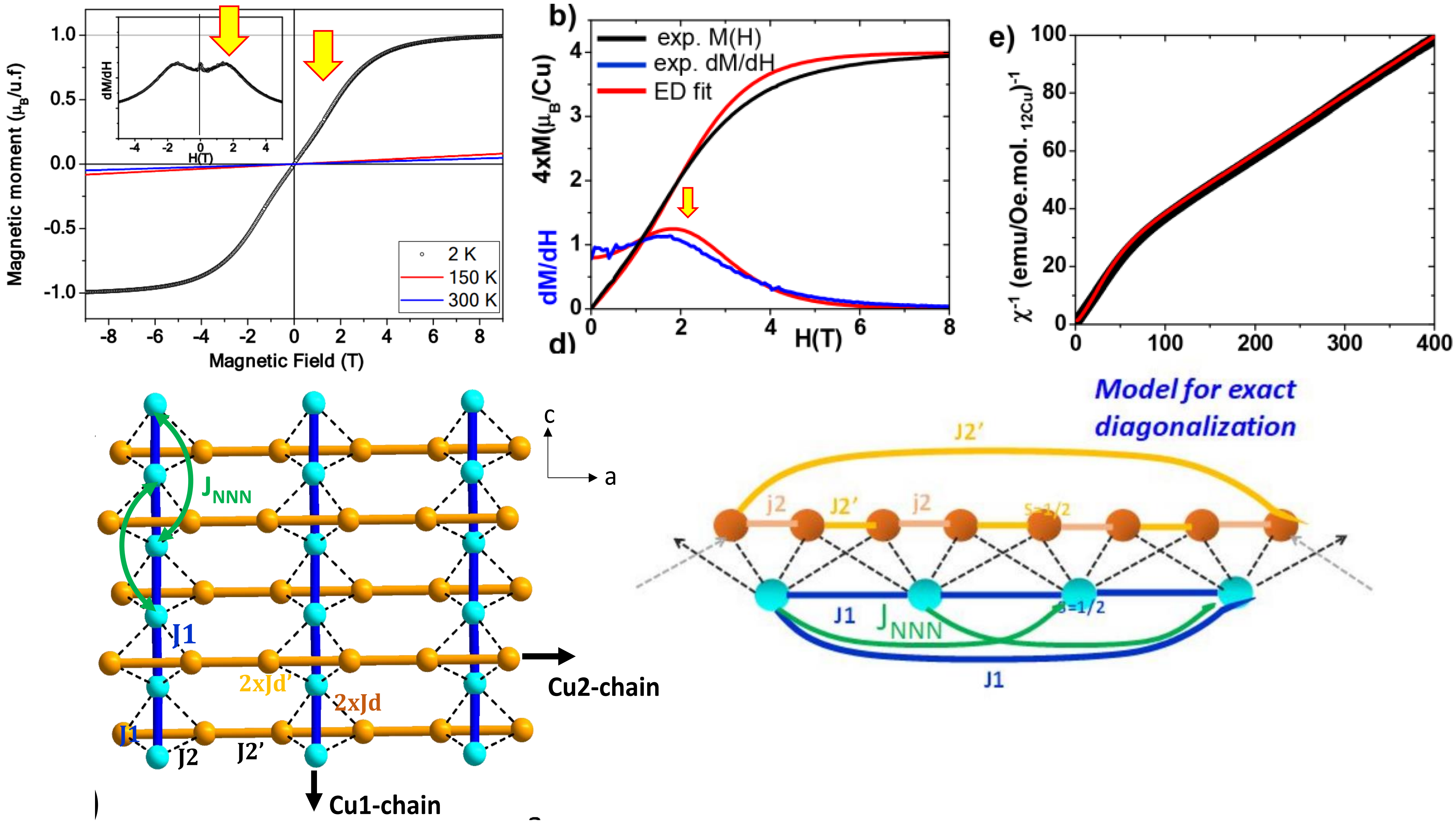
Structural Model



Model for exact diagonalization



12 spins, 4096 states



Magnetic moment (μB/u.f)
Magnetic Field (T)
dM/dH
H(T)
2 K
150 K
300 K
b)
exp. M(H)
exp. dM/dH
ED fit
4xM(μB/Cu)
dM/dH
H(T)
d)
e)
χ-1 (emu/Oe.mol. 12Cu)-1
c
a
JNNN
J1
2xJd'
2xJd
J2
J2'
Cu2-chain
Cu1-chain
Model for exact diagonalization
J2'
j2
S=1/2
J1
JNNN

Towards « true » Quantum Spin Liquid

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CHEMISTRY OF MATERIALS

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$Cu_3Te_2O_5(OH)_4$: A Frustrated Two-Dimensional Quantum "Magnetic Raft" as a Possible Pathway to a Spin Liquid

Tianyu Zhu,[▽] Bei Zhu,[▽] Olivier Mentré,* Suheon Lee, Dan Chen, Yanling Jin, Wenxuan Zhu, Ángel M. Arévalo-López, Claire Minaud, Kwang-Yong Choi, and Minfeng Lü*

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