FullProf
for magnetic structure determination and refinement
example: $Ho_2Cu_2O_5$

Juan Rodríguez-Carvajal

Laboratoire Léon Brillouin (CEA-CNRS)
DRECAM-CEA/Saclay, France

Steps for magnetic structure determination using powder diffraction

Step	Input
Propagation vector(s) ***SuperCell***	***Peak positions of magnetic reflections*** ⇐ ***Cell parameters***
Symmetry Analysis ***BasIreps***	***Propagation vector*** ⇐ ***Space Group*** ***Atom positions***
Magnetic structure solution (Sim. Ann.) ***FullProf***	***Integrated intensities*** ⇐ ***Atomic components of basis functions***

Problems of magnetic structure refinement using powder diffraction

Input

Magnetic structure Refinement
FullProf

⇐ ***Complete structural model should be provided***

Different runs of SAnn jobs may give you an idea of the degeneracy of solutions for your particular problem.

In many cases the number of free parameters is too much high to be refined by LSQ: try to reduce the number of parameters or make soft constraints.

Use spherical components of Fourier coefficients in order to have better control of the amplitude of the magnetic moment

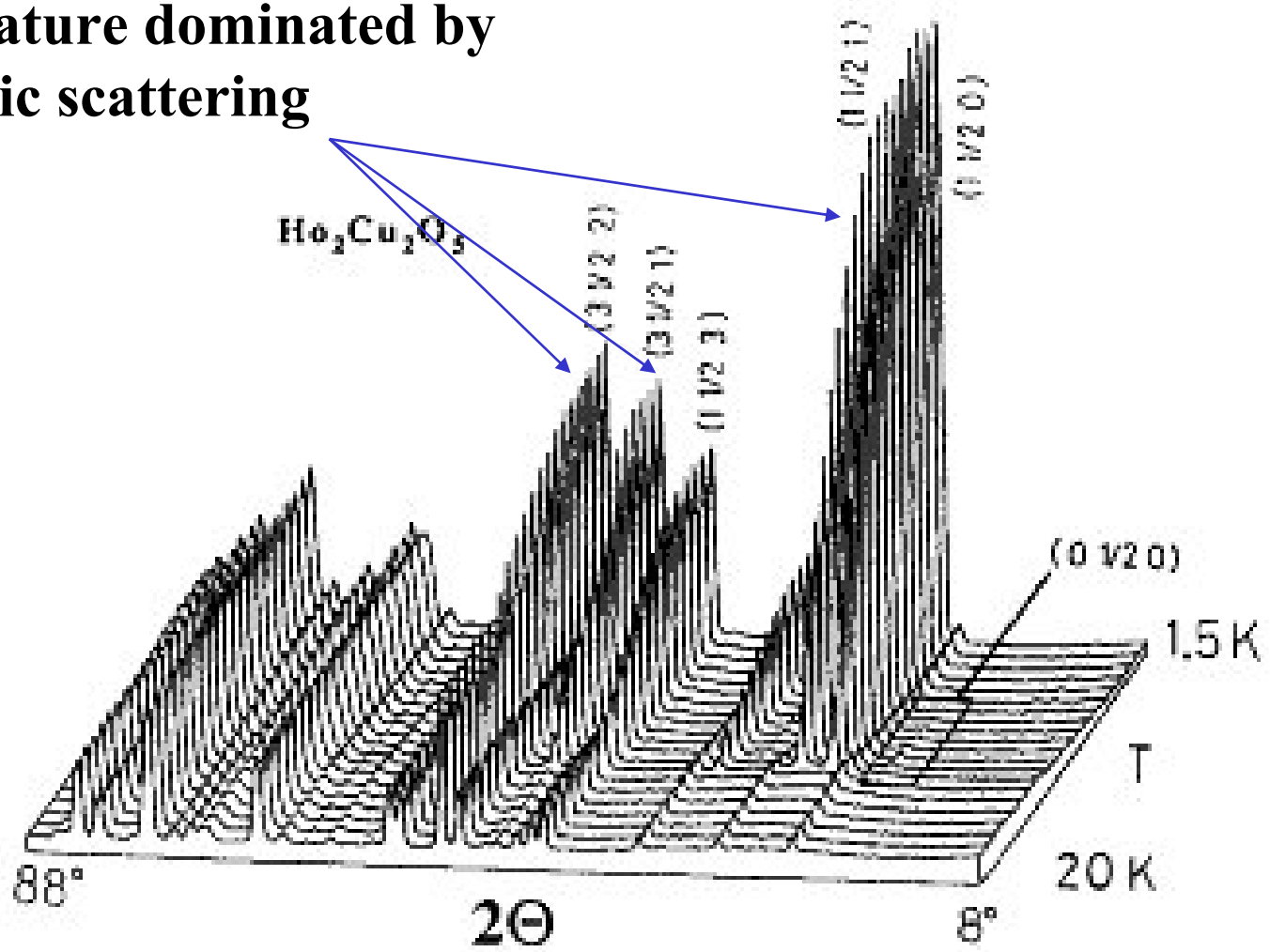
Tutorial
Magnetic Structure of $Ho_2Cu_2O_5$

- A complex case where symmetry analysis gives too much degrees of freedom.
- Space Group: *Pna2*$_1$, prop. vector **k**=(0,1/2,0) (a=10.78Å, b=3.49Å,c=12.42Å), 4 magnetic atoms {Ho_1,Ho_2, Cu_1,Cu_2} in general positions (16 magnetic atoms per primitive unit cell)

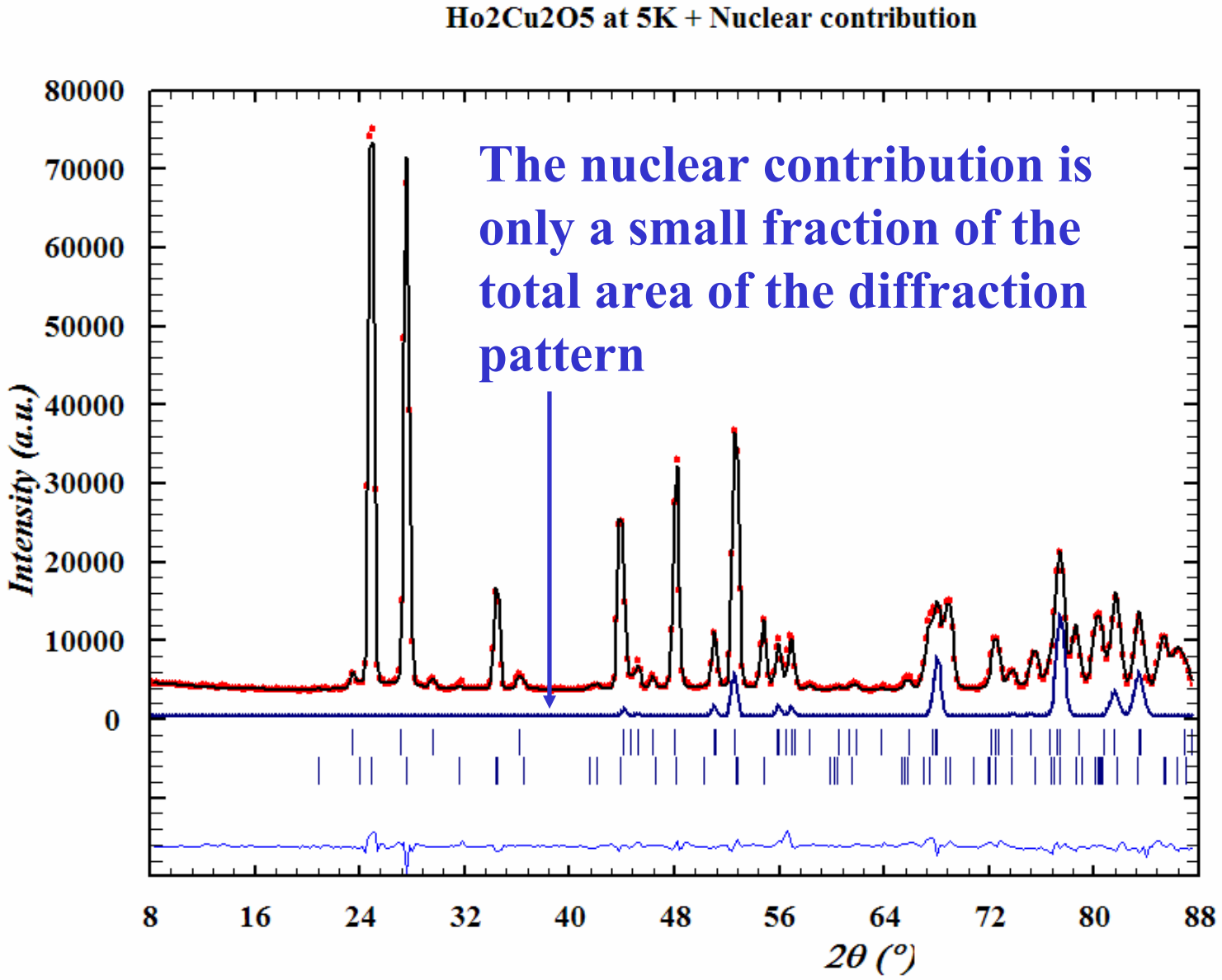
  A single 2D-Irrep, giving rise to 12 degrees of freedom per site (12×4=48).
- The final magnetic structure can be reduced to a problem of only four parameters

Magnetic Structure of $Ho_2Cu_2O_5$

Diffraction pattern at low temperature dominated by magnetic scattering



Magnetic Structure of $Ho_2Cu_2O_5$



Laboratoire Léon Brillouin

Magnetic Structure of $Ho_2Cu_2O_5$

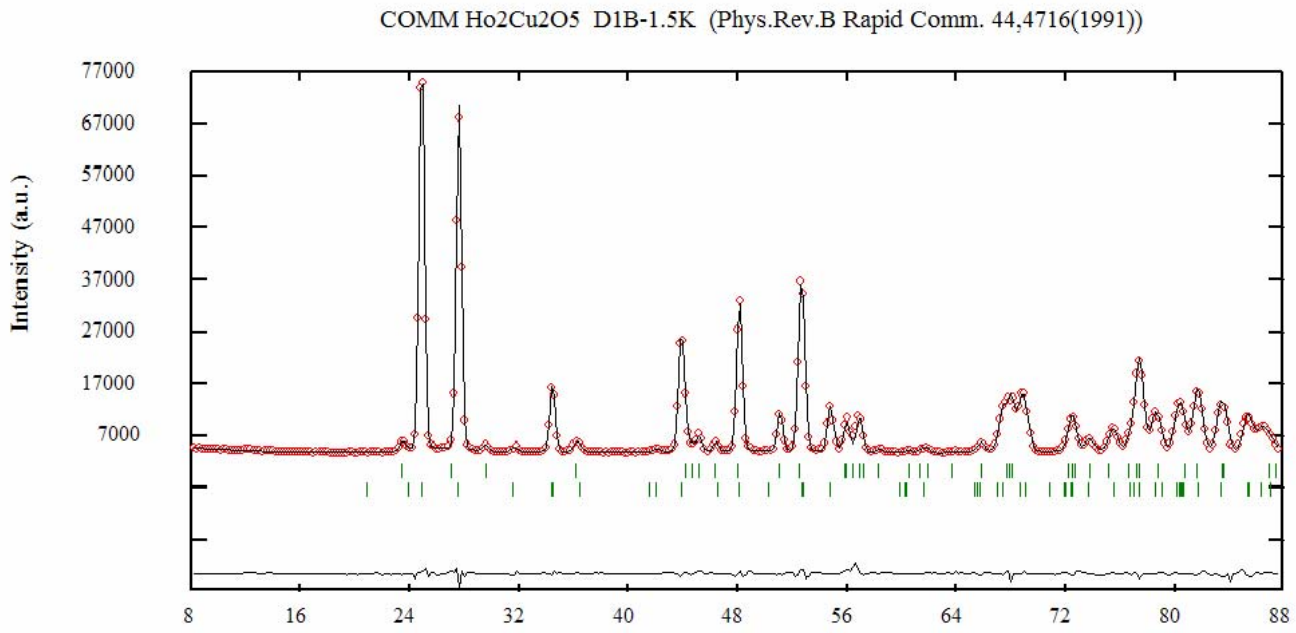
- **First step: Indexing** is this case is trivial: All magnetic reflections can be indexed using the propagation vector **k**=(0,1/2,0)
- **Second step: Extraction** of integrated intensities using a Le Bail fit with **FullProf**. It is supposed that the crystal structure has been refined with a high resolution powder diffraction pattern.

FullProf.2k_Multi_Pattern

```
=> Pattern:   1  hocu
=> Ordering reflections contributing to each point for pattern:       1
=> Calculation of Yi for all points + Normal Matrix & Vector...
=> Calculation for pattern:       1
=> Writing results for cycle      50
=> R-Factors:  2.47     3.79     Chi2:  10.2     DW-Stat.:  1.2567   Patt#:  1
=> Expected :          1.19                                1.6864
=> Conventional Rietveld R-factors for Pattern:       1
=> Rp: 5.51     Rwp: 6.73     Rexp:    2.10                    Chi2:  10.2
   => Global user-weigthed Chi2 (Bragg contrib.):   11.63
   => ---------> Pattern#       1
   => Phase:       1
   =>    Bragg R-factor:   4.933
   =>    RF-factor     :   3.225
   => Phase:       2
   =>    Bragg R-factor:  0.7364E-01
   =>    RF-factor     :  0.9981E-01
=> Normal end, final calculations and writing...


=>              CPU Time:     6.437 seconds
=>                            0.107 minutes

=> END   Date:22/05/2005  Time => 14:03:32.184

=> Data Files :
=>           - hocu
=> PCR  File  : hocu-pm
```

FullProf Refinement for pattern # 1

50/50



Magnetic Structure of $Ho_2Cu_2O_5$

- **Third step: Symmetry analysis** is not of much help. There is only a single Irrep of dimension 2 and the magnetic representation contains 6 times the Irrep, so 6×2=12 basis functions exist for each site. A total of 48 degrees of freedom defines the magnetic structure: all moments are independent!
- One can reduce a little bit this number by considering only constant moment magnetic structures, but it is tedious to try all combinations.

Magnetic Structure of $Ho_2Cu_2O_5$

Irreducible representation of $Pna2_1$ for **k**=(0,1/2,0)

$Pna2_1$	1	2_{1z}	a	n
	(x,y,z)	$(-x,-y,z+1/2)$	$(x+1/2,-y+1/2,z)$	$(-x+1/2,y+1/2,z+1/2)$
Γ	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}0&1\\1&0\end{pmatrix}$	$\begin{pmatrix}0&-1\\1&0\end{pmatrix}$

Basis Functions for the general position:

$\mathbf{S_k}(1)$: (u+d,v+e,w+f) $\mathbf{S_k}(2)$: (-u+d,-v+e,w-f)

$\mathbf{S_k}(3)$: (-p-a,q+b,-r-c) $\mathbf{S_k}(4)$: (-p+a,q-b,r-c)

u, v, w, p, q, r, a, b, c, d, e, f are real numbers

Constant moment Magnetic Structures

1	d=e=f=0	a=b=c=0	u = p	v = q	w = r	(+ - - - ; + - + + ; + + - +)	
2	d=e=f=0	a=b=c=0	u =-p	v =-q	w =-r	(+ - + + ; + - - - ; + + + -)	
3	d=e=f=0	a=b=c=0	u =-p	v = q	w = r	(+ - + + ; + - + + ; + + - +)	
4	d=e=f=0	a=b=c=0	u = p	v =-q	w = r	(+ - - - ; + - - - ; + + - +)	
5	d=e=f=0	a=b=c=0	u = p	v = q	w =-r	(+ - - - ; + - + + ; + + + -)	
6	d=e=f=0	a=b=c=0	u =-p	v =-q	w = r	(+ - + + ; + - - - ; + + - +)	
7	d=e=f=0	a=b=c=0	u = p	v =-q	w =-r	(+ - - - ; + - - - ; + + + -)	
8	d=e=f=0	a=b=c=0	u =-p	v = q	w =-r	(+ - + + ; + - + + ; + + + -)	
9	u=v=w=0	p=q=r=0	d = a	e = b	f = c	(+ + - + ; + + + - ; + - - -)	<=
10	u=v=w=0	p=q=r=0	d =-a	e =-b	f =-c	(+ + + - ; + + - + ; + - + +)	
11	u=v=w=0	p=q=r=0	d =-a	e = b	f = c	(+ + + - ; + + + - ; + - - -)	
12	u=v=w=0	p=q=r=0	d = a	e =-b	f = c	(+ + - + ; + + - + ; + - - -)	
13	u=v=w=0	p=q=r=0	d = a	e = b	f =-c	(+ + - + ; + + + - ; + - + +)	
14	u=v=w=0	p=q=r=0	d =-a	e =-b	f = c	(+ + + - ; + + - + ; + - - -)	
15	u=v=w=0	p=q=r=0	d = a	e =-b	f =-c	(+ + - + ; + + - + ; + - + +)	
16	u=v=w=0	p=q=r=0	d =-a	e = b	f =-c	(+ + + - ; + + + - ; + - + +)	
17	d=e=f=0	p=q=r=0	u = a	v = b	w = c	(+ - - + ; + - + - ; + + - -)	
18	d=e=f=0	p=q=r=0	u =-a	v =-b	w =-c	(+ - + - ; + - - + ; + + + +)	
19	d=e=f=0	p=q=r=0	u =-a	v = b	w = c	(+ - + - ; + - + - ; + + - -)	
20	d=e=f=0	p=q=r=0	u = a	v =-b	w = c	(+ - - + ; + - - + ; + + - -)	
21	d=e=f=0	p=q=r=0	u = a	v = b	w =-c	(+ - - + ; + - + - ; + + + +)	
22	d=e=f=0	p=q=r=0	u =-a	v =-b	w = c	(+ - + - ; + - - + ; + + - -)	
23	d=e=f=0	p=q=r=0	u = a	v =-b	w =-c	(+ - - + ; + - - + ; + + + +)	
24	d=e=f=0	p=q=r=0	u =-a	v = b	w =-c	(+ - + - ; + - + - ; + + + +)	
25	u=v=w=0	a=b=c=0	d = p	e = q	f = r	(+ + - - ; + + + + ; + - - +)	
26	u=v=w=0	a=b=c=0	d =-p	e =-q	f =-r	(+ + + + ; + + - - ; + - + -)	
27	u=v=w=0	a=b=c=0	d =-p	e = q	f = r	(+ + + + ; + + + + ; + - - +)	
28	u=v=w=0	a=b=c=0	d = p	e =-q	f = r	(+ + - - ; + + - - ; + - - +)	
29	u=v=w=0	a=b=c=0	d = p	e = q	f =-r	(+ + - - ; + + + + ; + - + -)	
30	u=v=w=0	a=b=c=0	d =-p	e =-q	f = r	(+ + + + ; + + - - ; + - - +)	
31	u=v=w=0	a=b=c=0	d = p	e =-q	f =-r	(+ + - - ; + + - - ; + - + -)	
32	u=v=w=0	a=b=c=0	d =-p	e = q	f =-r	(+ + + + ; + + + + ; + - + -)	

Magnetic Structure of $Ho_2Cu_2O_5$

☞ **Fourth step: Simulated annealing** in this case is a useful tool to explore the possible constant magnetic moment structures. Hidden symmetries can be found empirically.

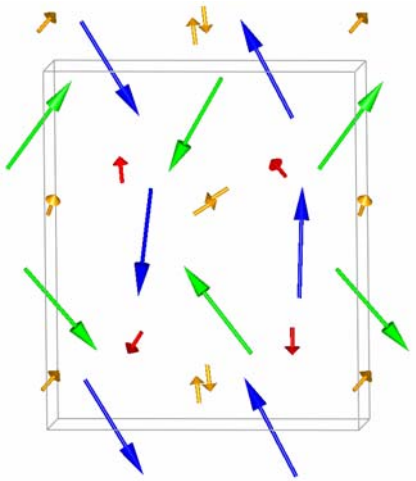
One can try to solve the magnetic structure running a long Simulated Annealing job constraining the magnetic moments of the like ionic species to have the same magnitude

$$m(Ho1) = m(Ho2), \quad m(Cu1) = m(Cu2)$$

This gives 2 magnetic moment parameters and $4 \times 4 \times 2 = 32$ angular parameters, so a maximum of 34 parameters

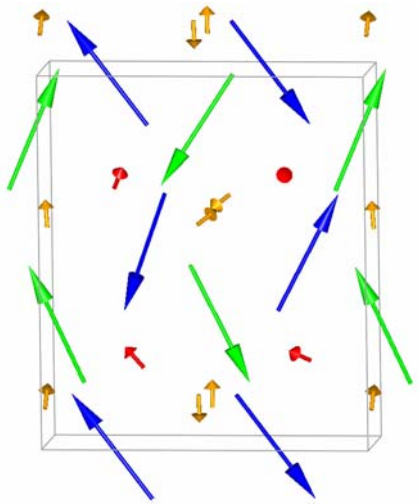
Some simulated annealing results

All runs have been performed using 2 moment parameters and 32 angular parameters (34 parameters)

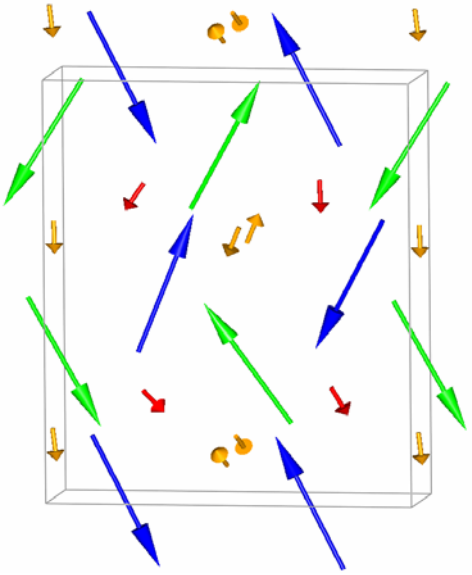


$R(F^2)= 4.20\%$

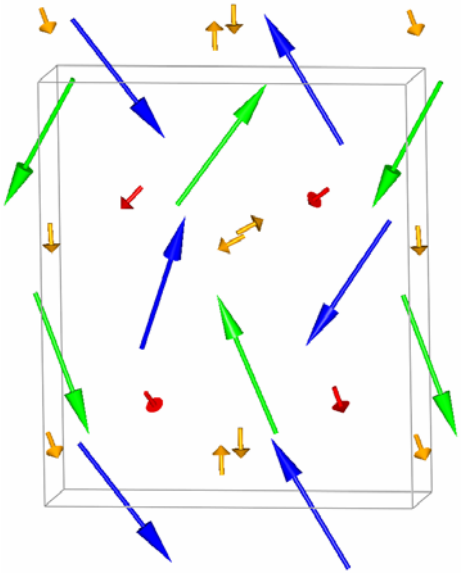
$R(F^2)= 3.28\%$



$R(F^2)= 2.83\%$



$R(F^2)= 2.92\%$



Some simulated annealing results

One of the results obtained without symmetry constraints is the following:

It is clear that the coupling mode of the Ho sublattices along x and z is

Sx (+ + - +)
Sz (+ - - -)

The coupling mode along y is not clear, but looking in the symmetry table it must be **(+ + + -)**

```
Sol#: 1 RF2=   2.926 ::
Atom         Rx          Ry          Rz

Ho11     -4.4034      0.2361      7.5183
Ho12     -3.5360     -1.0080     -7.9026
Ho13      3.4545      1.1668     -7.9168
Ho14     -3.2197      1.6990     -7.9194

Ho21     -3.2673     -0.6635      8.0532
Ho22     -4.7332     -0.3892     -7.3086
Ho23      4.8049     -0.3962     -7.2612
Ho24     -4.9525     -1.4590     -7.0224

Cu11      0.0353      0.4925      0.7774
Cu12     -0.0833     -0.0805     -0.9137
Cu13      0.1932      0.1403     -0.8895
Cu14     -0.0846     -0.8771     -0.2680

Cu21     -0.8461     -0.2405      0.2730
Cu22     -0.0024     -0.0187     -0.9208
Cu23      0.4949      0.6256     -0.4604
Cu24     -0.5870      0.3512     -0.6168
```

Magnetic Structure of $Ho_2Cu_2O_5$

☞ **Fifth step: The analysis of SAnn** results allows to find a hidden symmetry.

The coupling mode of the Ho ions (when using the automatic numbering given by ***BasIreps***) is given by the sequence:

Sx Sy Sz

(+ + - + ; + + + - ; + - - -)

This corresponds to the basis function in which we put the conditions:

u=v=w=0 p=q=r=0 d = a e = b f = c

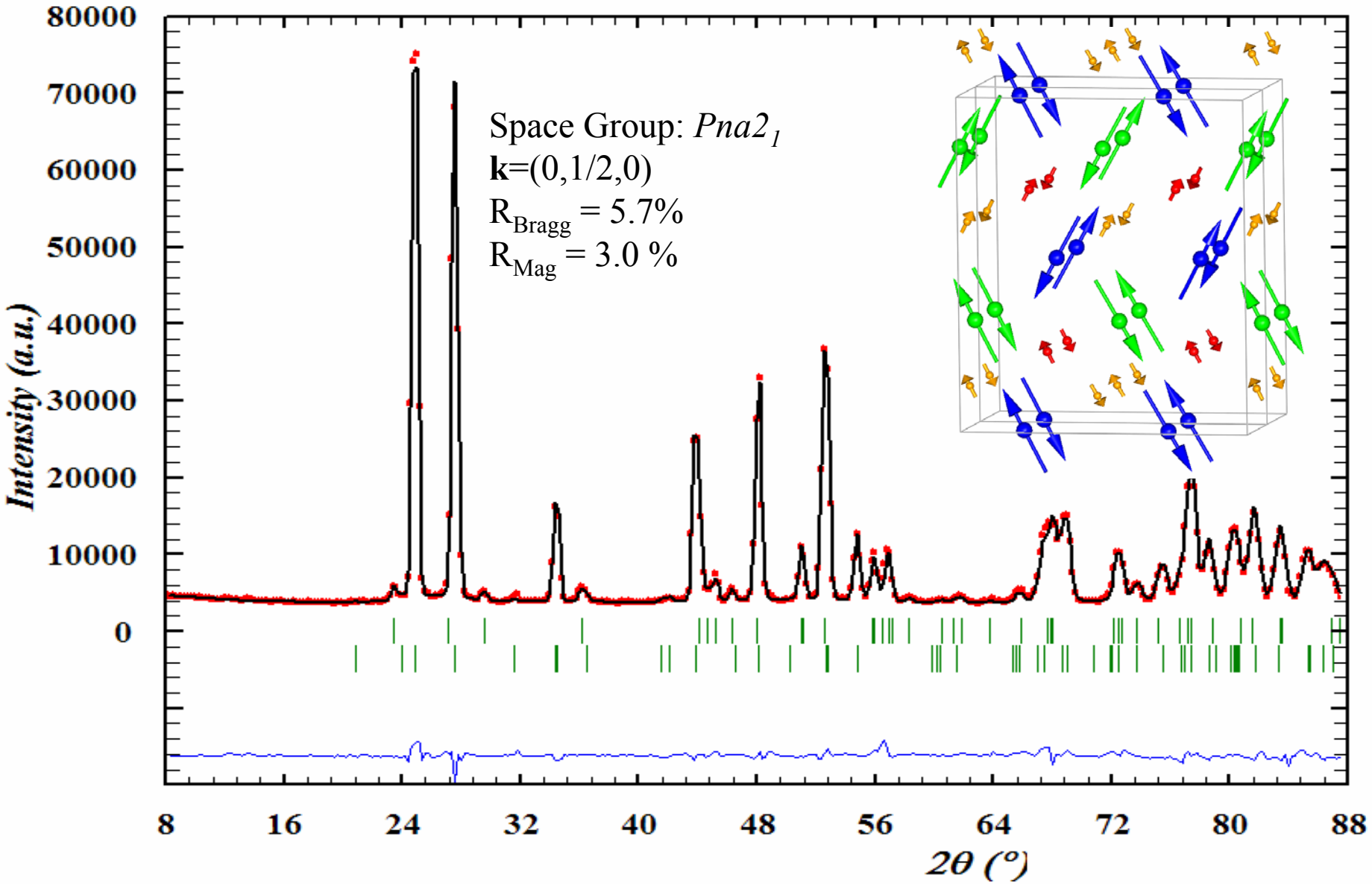
Refinement of the Magnetic Structure of $Ho_2Cu_2O_5$

☞ **Last step: The refinement** of the magnetic structure by the Rietveld method is perfectly stable if we select the proper free parameters

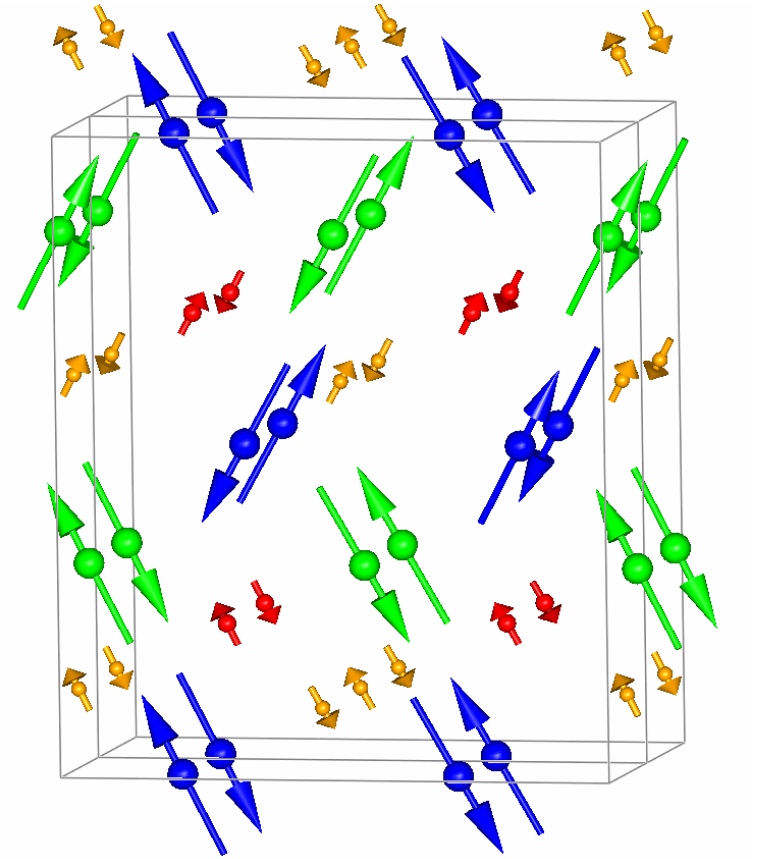
A part the fact that the coupling mode can be considered the same for all sites, we can see from SAnn that the Ho1 and Ho2 sites have also nearly the same components, so **only 3 free parameters can be selected for all Ho^{3+} ions.**

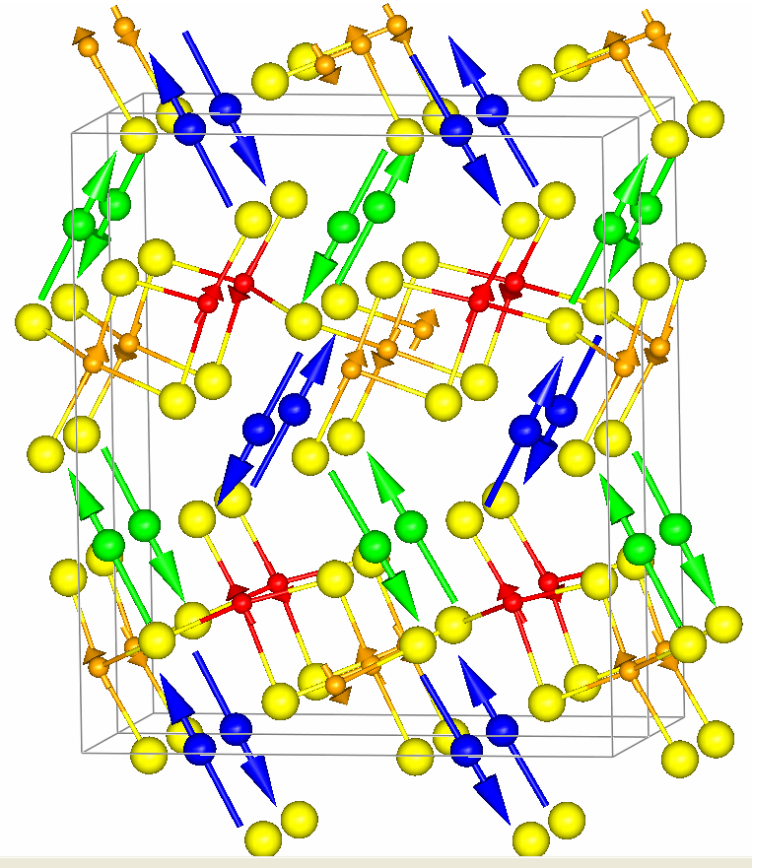
The Cu^{+2} ions contribution is much lower but we can consider (as seen in some SAnn results) that the moments are aligned to those of the Ho ions, so **only the amplitude of the Cu^{+2} magnetic moment** is the additional parameter to fix the magnetic structure

Magnetic Structure of $Ho_2Cu_2O_5$



Magnetic Structure of $Ho_2Cu_2O_5$





The end

Downloading of Software **http://www.ccp14.ac.uk**

Graphical tutorial run-through of most of this software is located via (**"look before you try"**):

http://www.ccp14.ac.uk/tutorial/

FullProf Suite and related programs:

ftp://ftp.cea.fr/pub/llb/divers/

Set of directories with different programs, documents, tutorials and examples of powder diffraction data analysis