The determination of magnetic structures by simulated annealing using the FullProf Suite

Juan Rodríguez-Carvajal
Institut Laue-Langevin
Diffraction Group
Grenoble, FRANCE

Structure Determination by Global Optimisation Methods Simulated Annealing and Genetic Algorithms

Classically, crystal structure determination is considered as a process to determine the "phases" of the structure factors

$$\rho(\mathbf{r}) = \sum_{\{\mathbf{h}\}} F_{\mathbf{h}} \; exp\{-2\pi i \mathbf{hr}\}$$

$$\rho(\mathbf{r}) = \sum_{\{\mathbf{h}\}} |F_{\mathbf{h}}| exp\{-2\pi i(\mathbf{hr} + \Phi_{\mathbf{h}})\}$$

For a centrosymmetric structure $\Phi_{\mathbf{h}}$ is 0 or 1/2

The knowledge of all phases for the measured structure factors provides a density map from which the structure is derived (chemically recognised).

The resolution of the "phase problem" is the goal of the crystal structure determination methods

Direct Methods tackle the problem looking for phase relations (tangent formula) between structure factors of different reflections

Direct methods need a high number of reflections and good resolution (powders)

Direct methods are generally very efficient

But …

sometimes direct methods fail in solving particular structures

or

cannot be applied because poor data quality (low resolution)

Structure factor calculations

$$F(\mathbf{h}) = \sum_{j=1}^{n} O_j \, f_j(\mathbf{h}) T_j \sum_s exp\left\{2\pi i\left[\mathbf{h}\{S|\mathbf{t}\}_s \mathbf{r}_j\right]\right\}$$

If the chemical composition and the space group are known we have to determine just the 3n variables

$$F_{obs}(\mathbf{h})_r \approx \left| \sum_{j=1}^{n} O_j \, f_j \, T_j \sum_s exp\left\{2\pi i\left[\mathbf{h}\{S|\mathbf{t}\}_s \mathbf{r}_j\right]\right\} \right|_r$$

$$\mathbf{h}_r = (h,k,l)_r \quad (r = 1,2,\ldots N)$$

$$\mathbf{r}_j = (x_j, y_j, z_j) \quad (j = 1,2,\ldots n)$$

Direct space methods:

- **Look directly for atom positions explaining the experimental data**
- **Minimise a reliability factor with respect to the**

  "configuration vector" or "chromosome"

$$\varpi = \left| x_1, y_1, z_1, x_2, y_2, z_2, \ldots x_n, y_n, z_n \right\rangle$$

$$R(\varpi) = c \sum_{r=1}^{N} \left| F^2_{obs}(\mathbf{h}_r) - F^2_{calc}(\mathbf{h}_r, \varpi) \right|$$

Solving Crystal structures by Powder diffraction and direct space methods

(1) *Indexing the powder diffraction pattern:* ***DICVOL, TREOR, ITO,...*** **(WinPLOTR)**

(2) *Extracting integrated intensities* ***(FullProf)*** Space Group determination

(3) Use ***ExPo*** to solve the structure

(4) If ***ExPo*** fails then Use Simulated Annealing ***(FullProf, GLOpSAnn)***

What is Simulated Annealing?

Simulated Annealing:

The SA method is a general purpose optimisation technique for large combinatorial problems introduced by:

Kirpatrick, Gelatt and Vecchi, *Science* **220**, 671-680 (1983).

Minimize a cost function, energy E(ω), with respect to the configuration vector ω.

Origin: Monte Carlo methods for simulating properties of liquids (Metropolis algorithm)

Algorithm trying to mimic the process of annealing a sample to obtain a good crystalline state (ground state):

A temperature schedule (starting high temperature + cooling rate) is needed.

Procedure to generate new configurations (Markov chains) and a Boltzmann probability to explore the phase space (importance sampling)

What is Simulated Annealing?

Simulated Annealing (SA):

The SA method applied to structural problems:

- J. Pannetier, J. Bassas-Alsina, J. Rodríguez-Carvajal and V. Caignaert, *Nature* **346**, 343-345 (1990)

- J.M. Newsam, M.W. Deem and C.M. Freeman, Accuracy in Powder Diffraction II. NIST Special Publ. No. **846**, 80-91 (1992)

- J. Rodríguez-Carvajal, Physica B **192**, 55-69 (1993)

The Simulated Annealing Algorithm

begin

Initialize (set to zero useful quantities, do preliminary calculations)

$\tau = 1$

do

do

Perturb the system:

$\omega_{old} \rightarrow \omega_{new}$, $\Delta = E(\omega_{new}) - E(\omega_{old})$

if $\Delta \leq 0$ **then accept, else**

if $\exp(-\Delta/T_\tau) >$ **random[0,1] then accept**

if accept then **Update (replace** ω_{old} **by** ω_{new}**)**

until equilibrium is approached closely enough (Ncyc)

$T_{\tau+1} = f(T_\tau)$ **(decrease temperature, usually** $T_{\tau+1} = q\ T_\tau$**,** $q \approx 0.9$**)**

$\tau = \tau + 1$

until stop criterion is true (maximum τ, convergence, low % accepted...)

end

Examples of Crystal Structure Determination by Simulating Annealing (SAnn)

```
COMM Ab initio structure solution of PbSO4 (Simulated Annealing, data D1A-ILL)
! Files => DAT-file: pb_san,  PCR-file: pb_san
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   0   1   0   0   0   0   0   0   0   0   0   0  12   3   0   0   0   0
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 Syo Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   0   0   0   1   0   0   0   0   0   0   0
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step        Thmax    PSD    Sent0
  1  0.10  1.00  1.00  1.00  1.00     15.0000     0.0200   120.0400   0.000   0.000
!
   12    !Number of refined parameters
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     7.86
!-------------------------------------------------------------------------------
 PbSO4
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth     ATZ   Nvk Npr More
   5   0   0 0.0 0.0 1.0   0   4   0   0   0       0.00   0   7   0
!
P n m a                  <--Space group symbol
!Atom Typ       X         Y         Z      Biso       Occ      In Fin N_t Poi /Codes
Pb   PB      0.81174   0.23348   0.83479  1.42124  0.50000    0   0   0     0
               11.00     21.00     31.00     0.00     0.00
S    S       0.93358   0.23348   0.32454  0.41603  0.50000    0   0   0     0
               41.00     21.00     51.00     0.00     0.00
O1   O       0.80418   0.23348   0.45910  1.99182  0.50000    0   0   0     0
               61.00     21.00     71.00     0.00     0.00
O2   O       0.59257   0.23348   0.09417  1.47906  0.50000    0   0   0     0
```

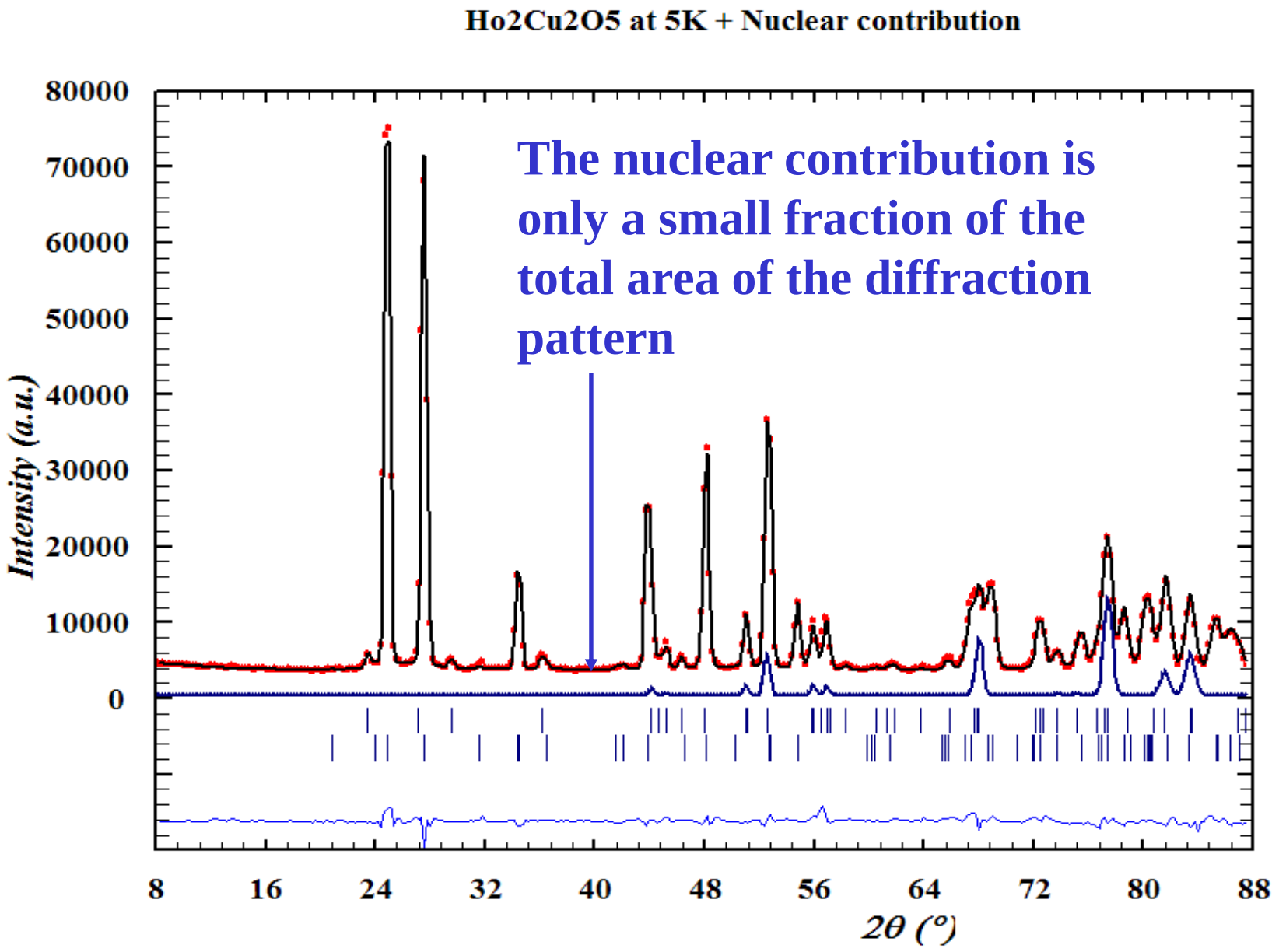
```
!   Sc1          Sc2          Sc3          Sc4          Sc5          Sc6
    1.531        0.000        0.000        0.000        0.000        0.000
         0.00         0.00         0.00         0.00         0.00         0.00
!      a            b            c         alpha        beta         gamma
     8.485130     5.402066     6.964059    90.000000    90.000000    90.000000
     0.00000      0.00000      0.00000      0.00000      0.00000      0.00000

! Limits for selected parameters (+ steps & BoundCond for SA):
    1       0.0000       1.0000       0.0500    1       x_Pb
    2       0.0000       1.0000       0.0500    1   y_Pb_SO1
    3       0.0000       1.0000       0.0500    1       z_Pb
    4       0.0000       1.0000       0.0500    1        x_S
    5       0.0000       1.0000       0.0500    1        z_S
    6       0.0000       1.0000       0.0500    1       x_O1
    7       0.0000       1.0000       0.0500    1       z_O1
    8       0.0000       1.0000       0.0500    1       x_O2
    9       0.0000       1.0000       0.0500    1       z_O2
   10       0.0000       1.0000       0.0500    1       x_O3
   11       0.0000       1.0000       0.0500    1       y_O3
   12       0.0000       1.0000       0.0500    1       z_O3
! T_ini    Anneal    Accept  NumTemps  NumThCyc  InitConf
    8.000    0.900    0.008        60         0         0
! NCyclM    Nsolu  Num_Ref  Nscalef    Algor
     150        1       71        1        2
```

Magnetic structure determination in complex systems
Simulating Annealing (SAnn)

Steps for magnetic structure determination using powder diffraction

Step	Input
Propagation vector(s) *SuperCell <> K_search*	*Peak positions of* ⇐ *magnetic reflections* *Cell parameters*
Symmetry Analysis *BasIreps, MODY, SARAh*	*Propagation vector* ⇐ *Space Group* *Atom positions*
Extraction of integrated intensities *Le Bail fit with FullProf*	*Experiment profile* ⇐ *Fixed nuclear structure* *propagation vector(s)*
Magnetic structure solution (Sim. Ann.) *FullProf*	*Integrated intensities* ⇐ *Atomic components* *of basis functions*

Magnetic Structure of $Ho_2Cu_2O_5$



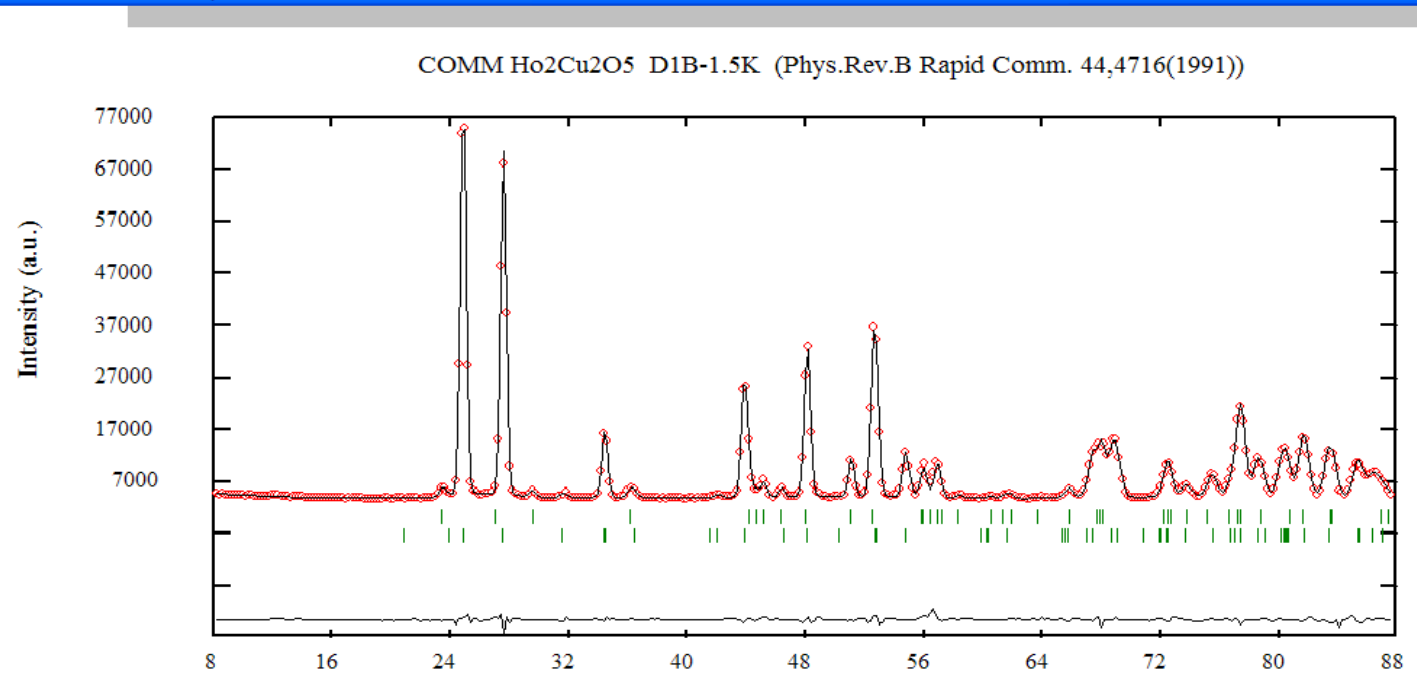
Magnetic Structure of $Ho_2Cu_2O_5$

- **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.

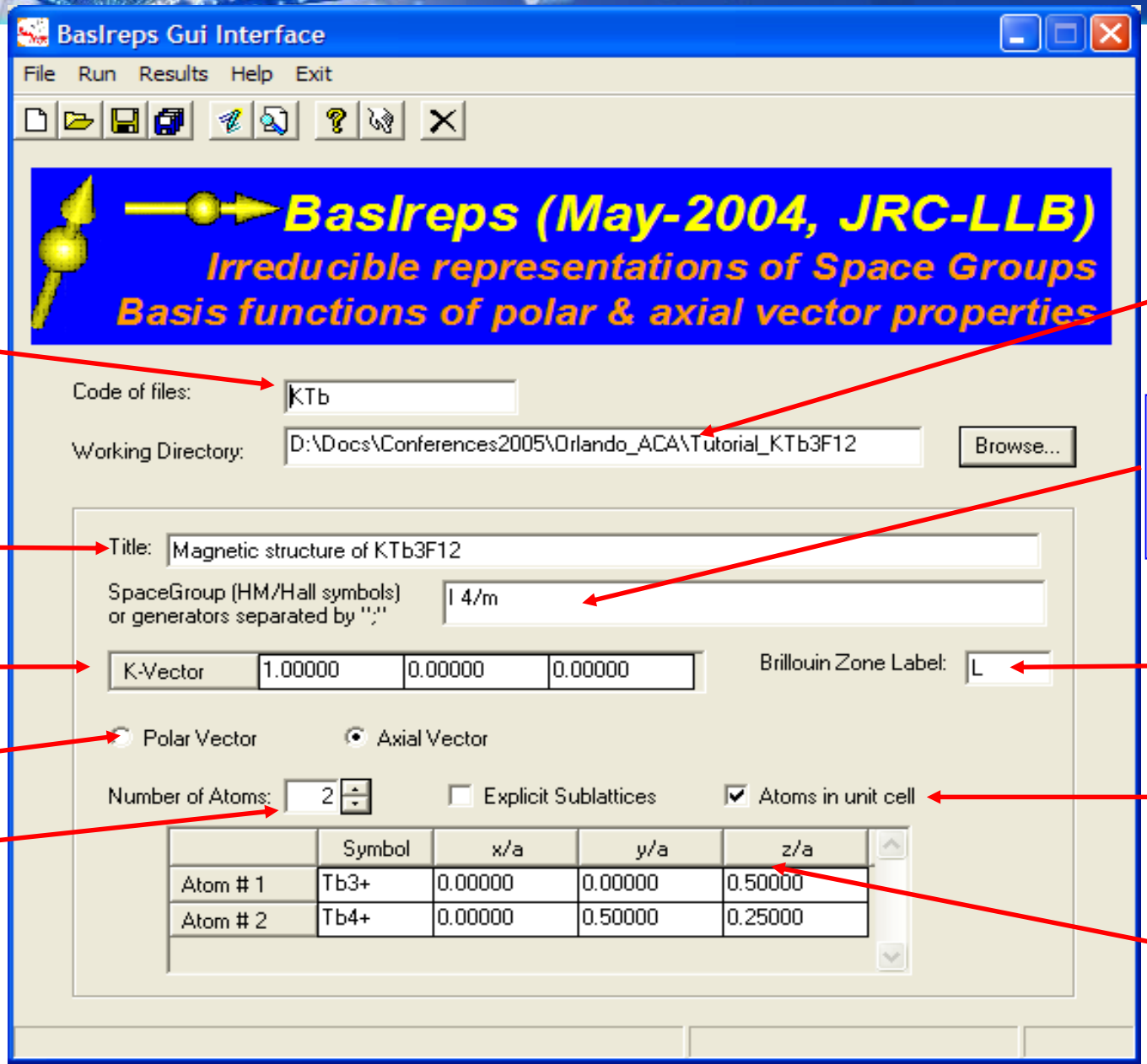
FullProf.2k_Multi_Pattern

```
=> 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



GUI for BasIreps



Code of files

Working directory

Title

Space group symbol or generators

k-vector

Brillouin Zone label

Axial/polar

Atoms in Unit Cell

Number of atoms

Atoms positions

Output of BasIreps

BasIreps **provides the basis functions (normal modes) of the irreducible representations of the wave-vector group $\mathbf{G_k}$**

$$\mathbf{m}_{ljs} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}js} exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}$$

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$$

Output of *BasIreps* ⇒ Basis Functions (constant vectors)

$$\mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$$

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

Simulated Annealing for magnetic structures

The Simulated Annealing method applied to magnetic structural problems from experimental data was treated for the first time in 1993

J. Rodríguez-Carvajal, Physica B **192**, 55-69 (1993)

(program MAGSAN)

Recent advances in magnetic structure determination by neutron powder diffraction

Juan Rodríguez-Carvajal

Laboratoire Léon Brillouin (CEA-CNRS), Centre d'Etudes de Saclay, Gif sur Yvette, France and Institut Laue–Langevin, Grenoble, France

Simulated Annealing for magnetic structures

Look directly for coefficients of the expansion:

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu}(js)$$

or components of $\mathbf{S}_\mathbf{k}$ and phases, explaining the experimental data

Minimize a reliability factor with respect to the "configuration vector"

$$\boldsymbol{\omega} = \left| C_1, C_2, C_3, C_4, C_5, \ldots C_m \right\rangle$$

$$R_m(\boldsymbol{\omega}) = c \sum_{r=1}^{N} \left| G^2_{obs}(\mathbf{h}_r) - G^2_{calc}(\mathbf{h}_r, \boldsymbol{\omega}) \right|$$

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.

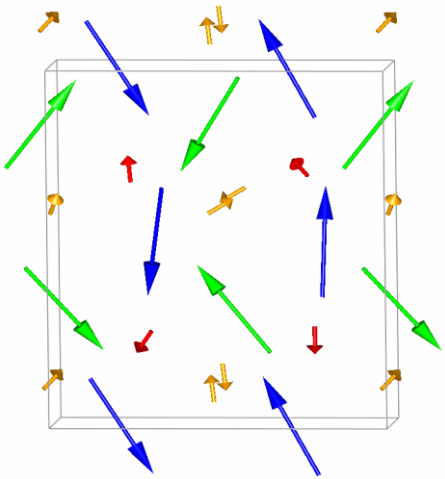
One can try to solve the magnetic structure running a long Simulated Annealing job constraining the magnetic moments of the like ionic species to have the same magnitude

m (Ho1) = m(Ho2) , 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

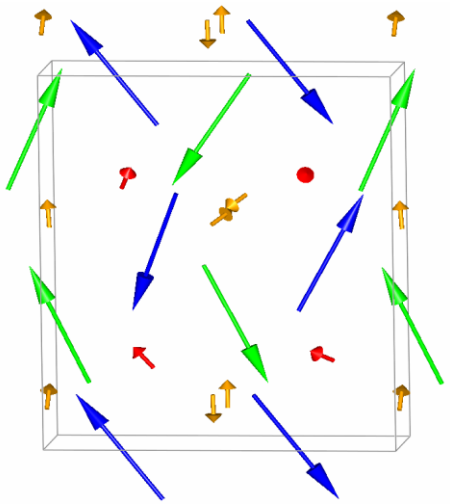
Some simulated annealing results

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

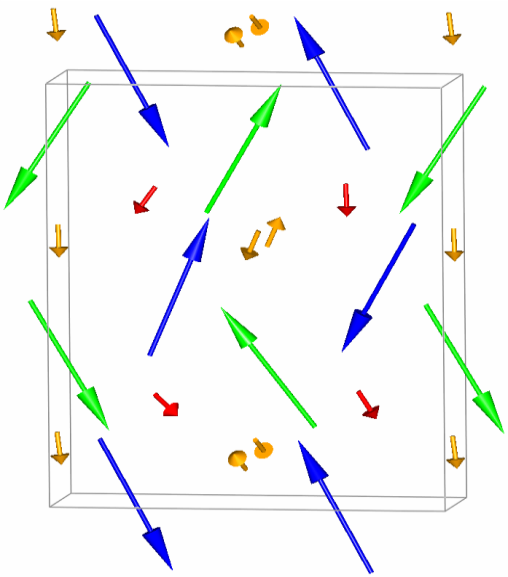


$R(F^2)= 4.20\%$

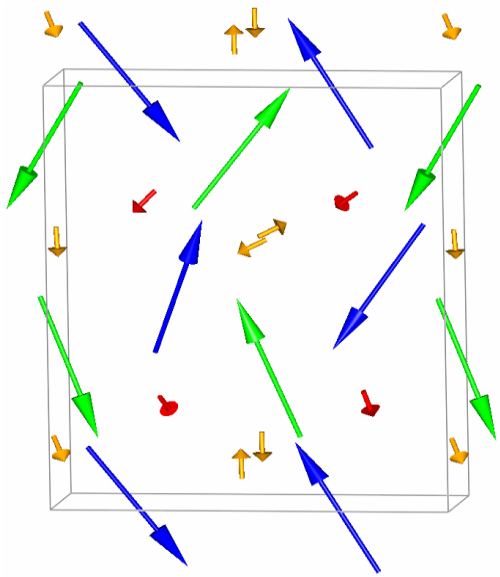
$R(F^2)= 3.28\%$



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



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



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

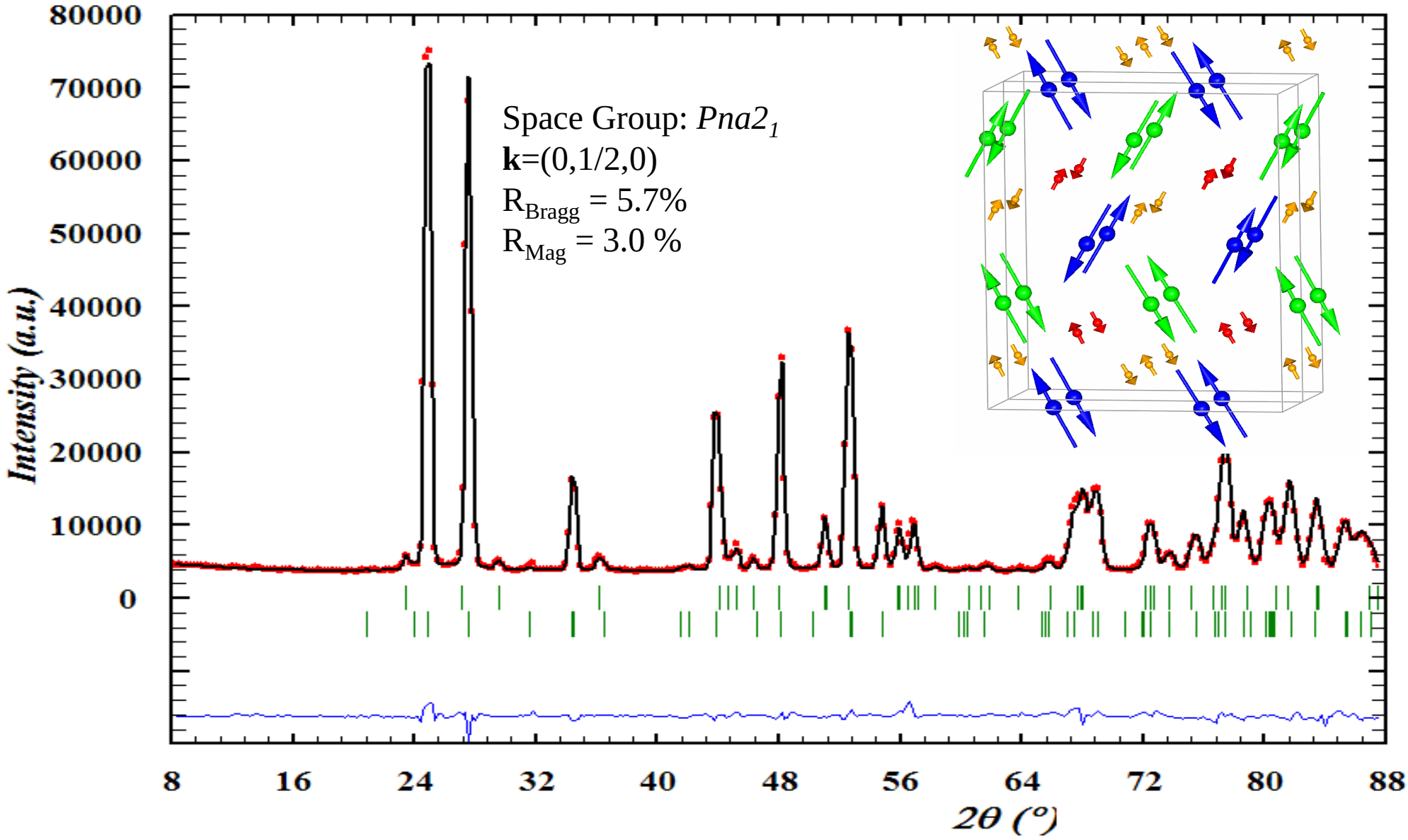
Refinement of the Magnetic Structure of $Ho_2Cu_2O_5$

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

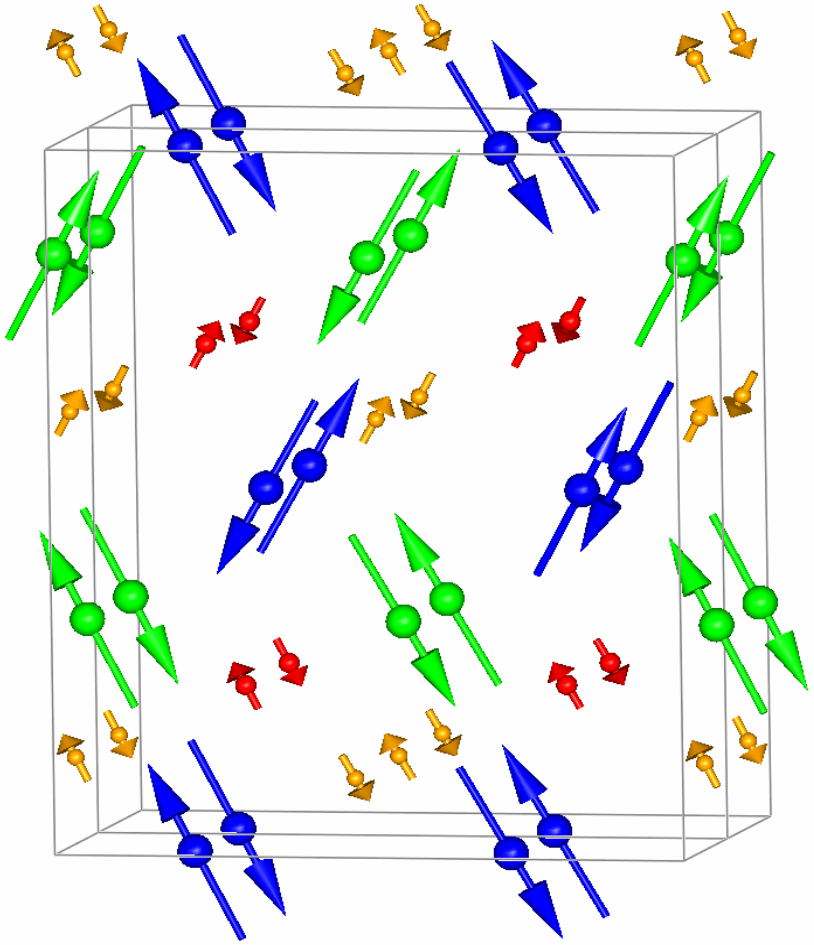
A part the fact that the coupling mode can be considered the same for all sites, we can see from SAnn that the Ho1 and Ho2 sites have also nearly the same components, so **only 3 free parameters can be selected for all Ho^{3+} ions.**

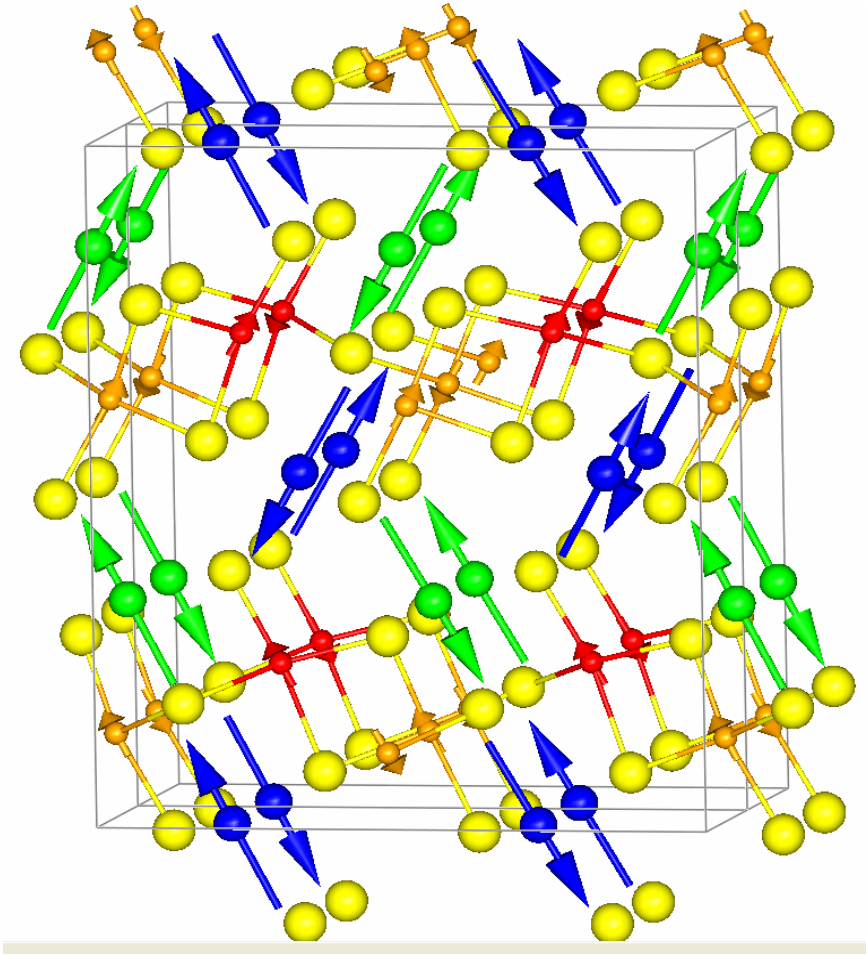
The Cu^{+2} ions contribution is much lower but we can consider (as seen in some SAnn results) that the moments are aligned to those of the Ho ions, so **only the amplitude of the Cu^{+2} magnetic moment** is the additional parameter to fix the magnetic structure

Magnetic Structure of $Ho_2Cu_2O_5$



Magnetic Structure of $Ho_2Cu_2O_5$





Conclusions about the determination of the magnetic structure of $Ho_2Cu_2O_5$

Symmetry Analysis:

The single irreducible representation involved in the magnetic phase transition, does not put enough constraints for the magnetic structure. This is quite usual when 2D representations and general positions are involved.

Simulated Annealing:

The magnetic structure can be obtained without symmetry constraints. Only putting constant moment constraints an analysis of the results of different runs helps to find a hidden symmetry that is consequence of the symmetry of the exchange Hamiltonian.

Refinement

A final structure with only 4 parameters can be refined to convergence. LSQ does not converge by freeing more parameters.

Refinement of magnetic structures using neutron 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

Genetic Algorithms

The method was developed by **John Holland** over the course of 1960s and 1970s

Adaptation in Natural and Artificial Systems
Ann Arbor: The University of Michigan Press, 1975

Popularised by one of his students: **David Goldberg**
Genetic Algorithms in Search, Optimization, and Machine Learning, New York: Addison-Wesley, 1989

Genetic Algorithms

- Optimises with continuous or discrete large number of parameters. Parallel computers.
- Doesn't require derivative information.
- Simultaneous searches from wide sampling of the cost hypersurface.
- Provides a list of optimum configurations, not just a single solution

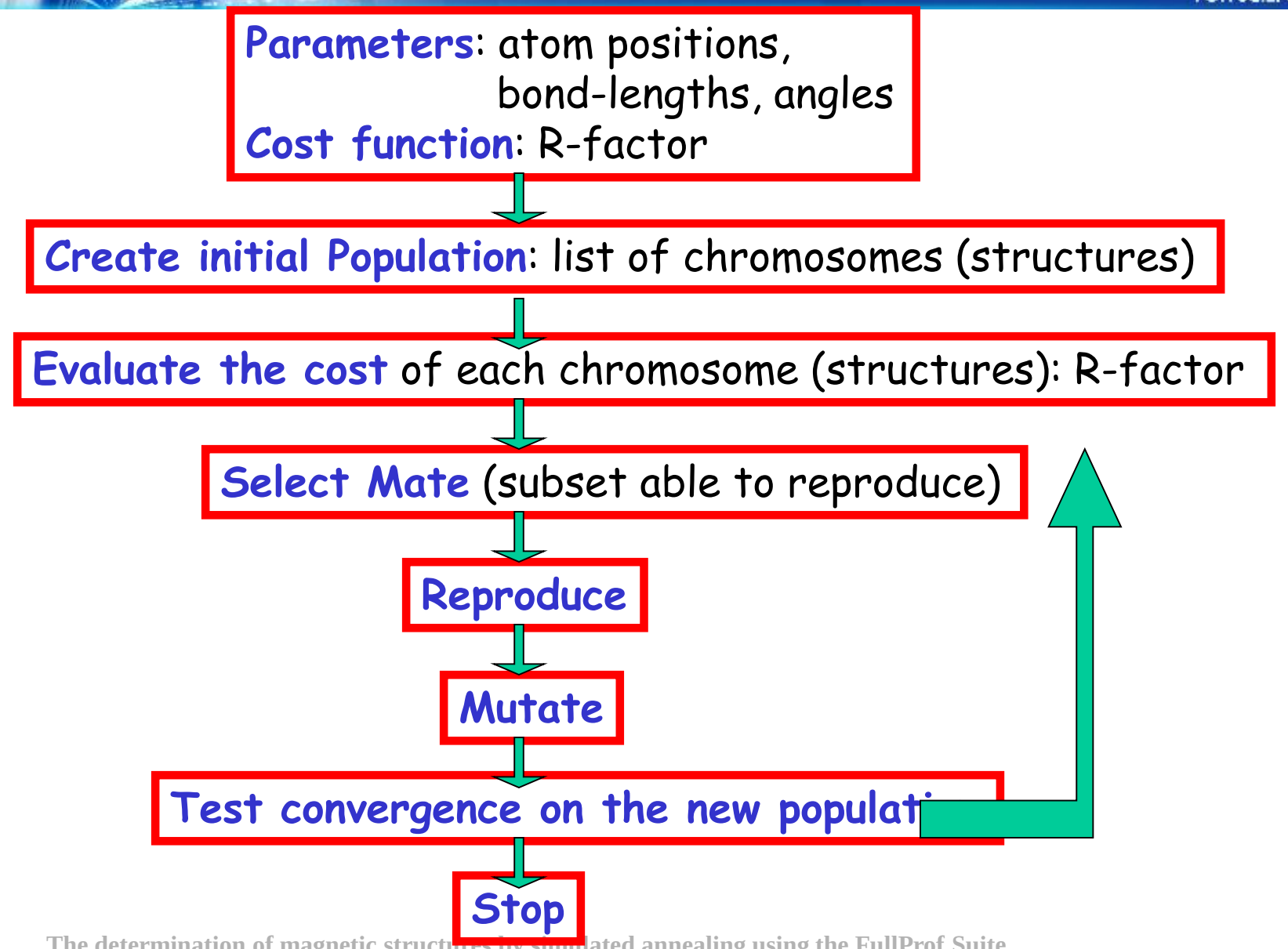
Genetic Algorithms

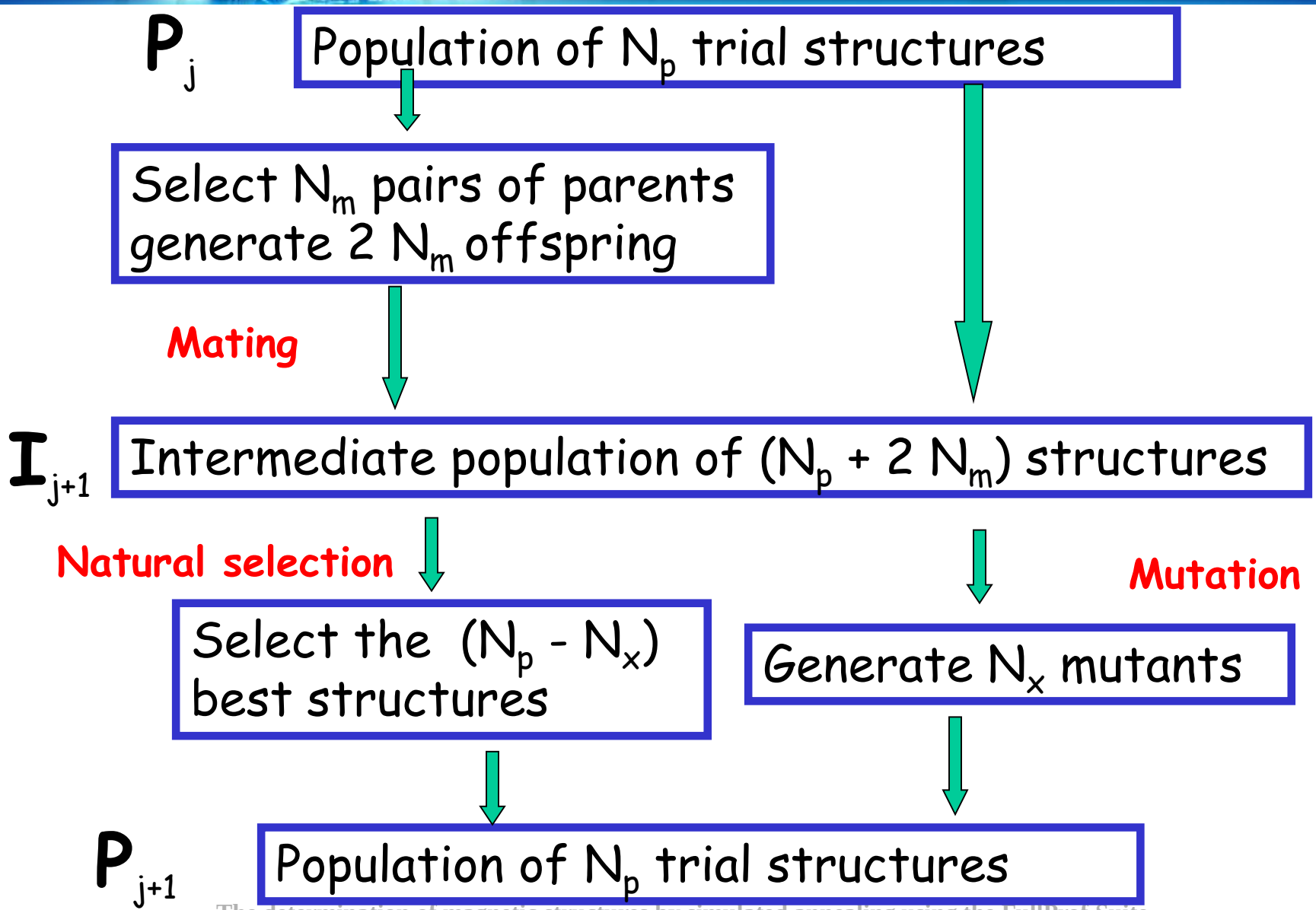
The application of GA to crystal structure determination has been started by two groups:

- K. Shankland, W.I.F. David and T. Csoka, *Z. Kristallogr* **212**, 550-552 (1997)

- B.M. Kariuki, H. Serrano-González, R.L. Johnston and K.D.M. Harris, *Chem. Phys. Lett.* **280**, 189-195 (1997)

Continuous parameter GA




P_j
Population of N_p trial structures
Select N_m pairs of parents
generate 2 N_m offspring
Mating
I_{j+1}
Intermediate population of (N_p + 2 N_m) structures
Natural selection
Mutation
Select the (N_p - N_x)
best structures
Generate N_x mutants
P_{j+1}
Population of N_p trial structures