Magnetic structures:

Formalism of propagation vector

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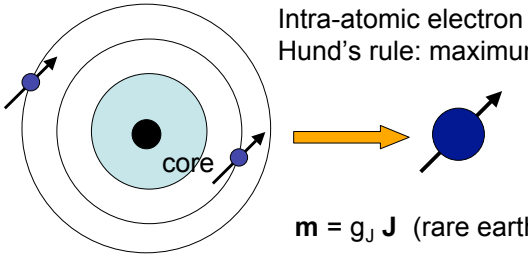
Outline

1. What's a magnetic structure?
2. How to describe magnetic structures with the formalism of propagation vector(s).
3. Plotting complex magnetic structure with FStudio.
4. Symmetry, symmetry, symmetry…
5. Strategy for solving magnetic structures, indexation, simulated annealing….

Ions with intrinsic magnetic moments

Atoms/ions with unpaired electrons

Intra-atomic electron correlation
Hund's rule: maximum S/J



Ni^{2+}

m = g_J **J** (rare earths)

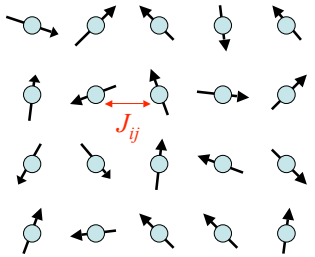
m = g_S **S** (transition metals)

What is a magnetic structure?

Paramagnetic state:
Snapshot of magnetic moment configuration

$$E_{ij} = -J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j$$

$$\langle \mathbf{S}_i \rangle = 0$$

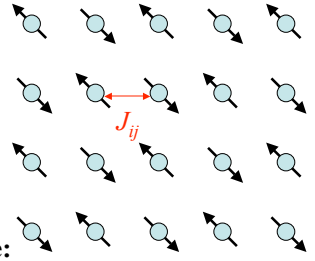


What is a magnetic structure?

Ordered state: Anti-ferromagnetic
Small fluctuations (spin waves) of the static configuration

$$E_{ij} = -J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j$$

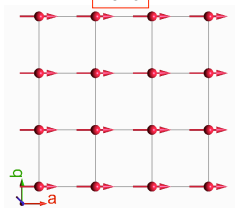
$$\langle \mathbf{S}_i \rangle \neq 0$$



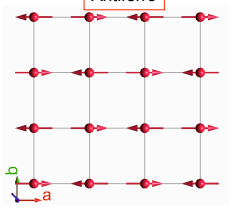
Magnetic structure:
Quasi-static configuration of magnetic moments

Types of magnetic structures

Ferro



Antiferro

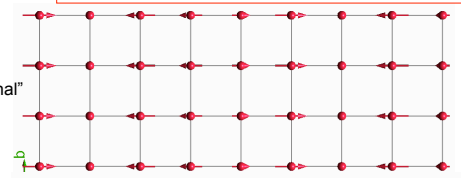


Very often magnetic structures are complex due to :
- competing exchange interactions (i.e. RKKY)
- geometrical frustration
- competition between exchange and single ion anisotropies
-……..

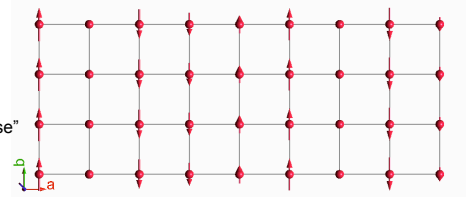
Types of magnetic structures

Amplitude-modulated or Spin-Density Waves

"Longitudinal"

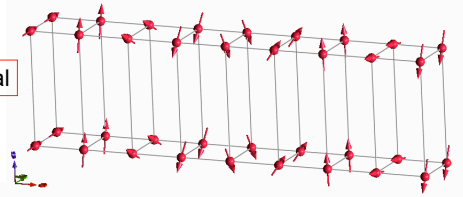


"Transverse"

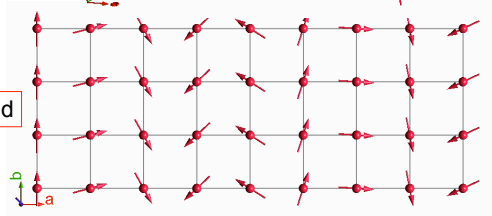


Types of magnetic structures

Spiral

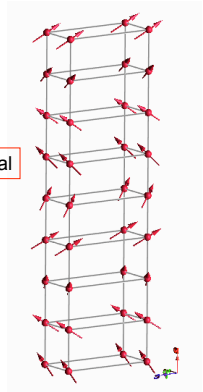


Cycloid



Types of magnetic structures

Conical



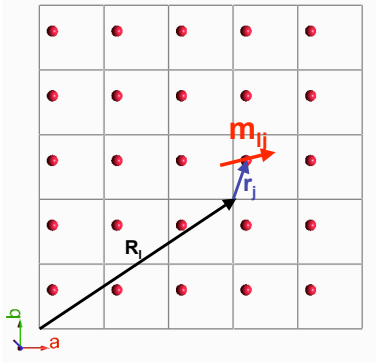
Shubnikov magnetic groups, are limited to:

- Commensurate magnetic structure.
- Real representation of dimension 1.

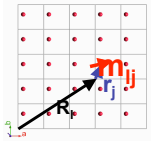
Formalism of prop. Vector : Basics

Position of atom j in unit-cell l is given by:

$R_{lj}=R_l+r_j$ where R_l is a pure lattice translation



Formalism of prop. Vector : Basics



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

$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j = l_1\mathbf{a} + l_2\mathbf{b} + l_3\mathbf{c} + x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$$

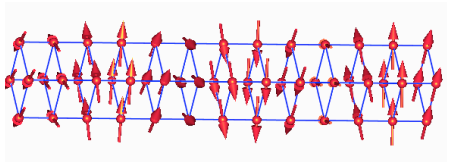
Necessary condition for real $\mathbf{m}_{lj}$

$$\mathbf{S}_{-\mathbf{k}j} = \mathbf{S}_{\mathbf{k}j}^{*}$$

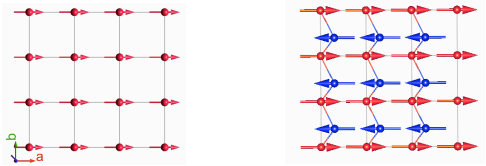
Formalism of prop. Vector : Basics

A magnetic structure is fully described by:

- Wave-vector(s) {k}.
- Fourier components $\mathbf{S}_{\mathbf{k}j}$ for each magnetic atom j and wave-vector k.
  $\mathbf{S}_{\mathbf{k}j}$ is a complex vector (6 components) !!!
- Phase for each magnetic atom j, $\mathbf{\Phi}_{\mathbf{k}j}$



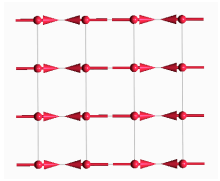
Single propagation vector
k = (0,0,0)



$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \; exp\{-2\pi i \mathbf{k}\mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j}$$

- The magnetic structure may be described within the crystallographic unit cell
- Magnetic symmetry: conventional crystallography plus time reversal operator: crystallographic magnetic groups

Single propagation vector
k=1/2 H



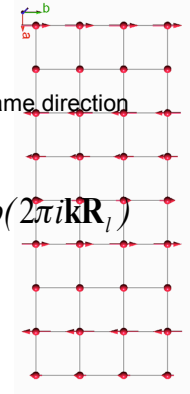
$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \; exp\{-2\pi i \mathbf{k}\mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j}(-1)^{n(l)}$$

REAL Fourier coefficients ≡ magnetic moments
The magnetic symmetry may also be described using crystallographic magnetic space groups

Fourier coef. of sinusoidal structures

- k interior of the Brillouin zone (pair k, -k)

- Real S_k, or imaginary component in the same direction as the real one

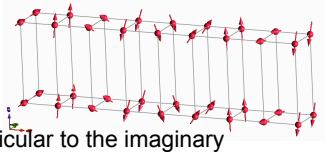


$$\mathbf{m}_{lj} = \mathbf{S}_{\mathbf{k}j} \; exp(-2\pi i \mathbf{k}\mathbf{R}_l) + \mathbf{S}_{-\mathbf{k}j} \; exp(2\pi i \mathbf{k}\mathbf{R}_l)$$

$$\mathbf{S}_{\mathbf{k}j} = \frac{1}{2} m_j \mathbf{u}_j exp(-2\pi i \phi_{\mathbf{k}j})$$

$$\mathbf{m}_{lj} = m_j \mathbf{u}_j \cos 2\pi(\mathbf{k}\mathbf{R}_l + \phi_{\mathbf{k}j})$$

Fourier coefficients of helical structures

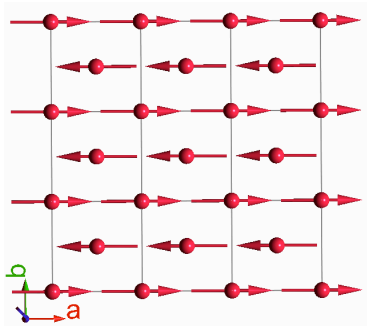


- k interior of the Brillouin zone
- Real component of S_k perpendicular to the imaginary component

$$\mathbf{S}_{\mathbf{k}j} = \frac{1}{2}\left[m_{uj}\mathbf{u}_j + i m_{vj}\mathbf{v}_j\right] \; exp(-2\pi i \phi_{\mathbf{k}j})$$

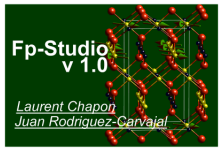
$$\mathbf{m}_{lj} = m_{uj}\mathbf{u}_j \cos 2\pi(\mathbf{k}\mathbf{R}_l + \phi_{\mathbf{k}j}) + m_{vj}\mathbf{v}_j \sin 2\pi(\mathbf{k}\mathbf{R}_l + \phi_{\mathbf{k}j})$$

Centred cells!



k=(1,0,0) or (0,1,0) !!!!!

Examples. Fstudio



www-llb.cea.fr/fullweb

```
{
LATTICE P
K 0.5 0.0 0.0
SYMM x,y,z
MSYM u,v,w,0.0
MATOM Ce1 CE 0.0 0.0 0.0
SKP 1 1 2.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
}
```

Type of lattice P, C, I, F…..

Propagation vector(s)

List of symmetry operators with associated magnetic operator

Magnetic atom

Fourier coefficients and phase

Symmetry analysis

- Problem is underdetermined:

-large number of parameters

(6 Fourier coefs.+phase per magnetic atom and per k)

-usually few observations, especially in powder patterns.

- Magnetic form factor

Representation theory

- Method for simplifying analysis of a problem in systems possessing some degree of symmetry.

- What is allowed vs. what is not allowed

Keyword : Invariance of the physical properties under application of symmetry operators.

Representation theory

Spectroscopy

$T = \int \phi^0 \mu \phi^1$ $T = \int \phi^0 \alpha \phi^1$

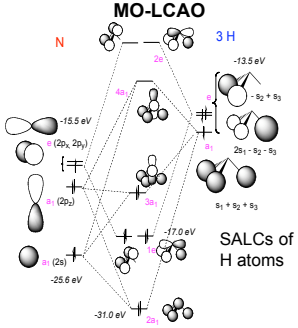
Free ion

Ground state multiplet

$T = \int \phi^0 J_z \phi^1$

ΔJ=0;+1;-1

MO-LCAO



Phase transitions in solids

Phase transitions often take place between phases of different symmetry.

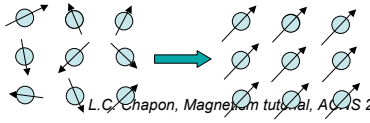
High symmetry phase, Group G_0

(T,P)

Low symmetry phase, Group G_1

- This is a "spontaneous" symmetry-breaking process.
- Transition are classified as either 1st order (latent heat) or 2d order (or continuous)

A simple example: Paramagnetic -> Ferromagnetic transition



"Time-reversal" is lost
- Symmetry under reversal of the electric current

Landau theory

- Ordering is characterized by a function ρ(x) that changes at the transition.
- Above T_c, $\rho_0(x)$ is invariant under all operations of G_0
- Below T_c, $\rho_1(x)$ is invariant under all operations of G_1

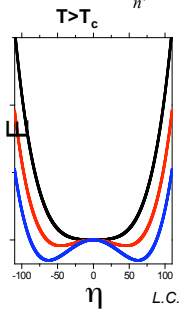
$$\delta\rho = \rho_1 - \rho_0 = \sum_n \sum_i c_i^n \Phi_i^n(x)$$ → Basis functions of irreducible Representation of G_0.

- At $T=T_c$, all the coefficients c_i^n vanish

Landau theory (2)

Φ is invariant under operations of G, each order of the expansion can be written is given by some polynomal invariants of c_i^n.

$$\Phi = \Phi_0 + \sum_n A^n(P,T) \sum_i (c_i^n)^2 + ...$$



- Thermodynamic equilibrium requires that all A are >0 above T_c.
- In order to have broken symmetry, one A has to change sign at the transition.

$$\Phi = \Phi_0 + \frac{1}{2} a(T)(T - T_c)\eta^2 + C\eta^4 + ...$$

In a second order phase transition, a single symmetry mode is involved.

Symmetry Analysis

Fourier coefficients as linear combinations of the basis functions of the irreducible representation of the propagation vector group $G_{\mathbf{k}}$

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

$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j \sum_{n\lambda} C^{\nu}_{n\lambda} \sum_{s} \mathbf{S}^{\mathbf{k}\nu}_{n\lambda}(js) exp\left\{2\pi i\left[\mathbf{h}_s \mathbf{r}_j - \Phi_{\mathbf{k}j}\right]\right\}$$

Symmetry Analysis

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

The coefficients $C^{\nu}_{n\lambda}$ are the free parameters of the magnetic structure (order parameters of the phase transition in the Landau theory)

Indices:

k : reference to the propagation vector

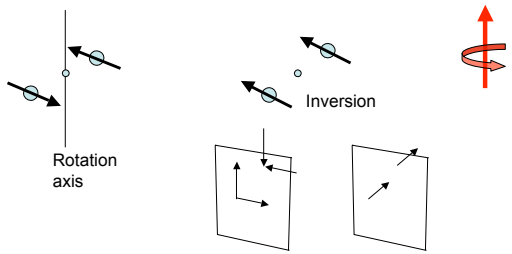
ν : reference to the irreducible representation Γ_{ν}

n : index running from 1 up to $n_{\nu} \Rightarrow \Gamma_{Mag} = \sum_{\oplus \nu} n_{\nu} \Gamma_{\nu}$

λ : index running from 1 up to $\dim(\Gamma_{\nu})$

Symmetry Analysis

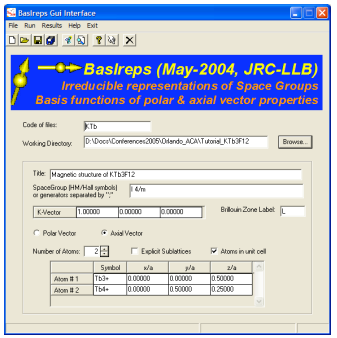
Magnetic moment is an axial (pseudo) vector.
Transformation under symmetry operation different to polar vector:



Representation analysis

Kovalev's book:
"Irreducible representations of space group"

Software:
-MODY
-SarAh
-Baslreps



The different ways of treating magnetic structures in FullProf

Standard Fourier coefficients refinement:
A magnetic phase has **`Jbt = +/- 1`**

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j \sum_{s} \mathbf{S}_{kjs}\, exp\left\{2\pi i\left[(\mathbf{H}+\mathbf{k})\{S|\mathbf{t}\}_s \mathbf{r}_j - \Phi_{kj}\right]\right\}$$

The magnetic symmetry is introduced together with explicit symmetry operators of the crystal structure. The refined variables are directly the components of the $\mathbf{S}_{kjs}$ vectors

Standard Fourier components refinement

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:     4.09
!-------------------------------------------------------------------------------
LaMnO3
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   0  -1   0   0          0.000   0   7   0
!
P m m m                      <--Space group symbol
!Nsym Cen Laue MagMat
   4   1   3   1
!
SYMM   x,y,z
MSYM   u,v,w,0.0
SYMM   -x,-y,z+1/2
MSYM   -u,-v,w,0.0
SYMM   -x+1/2,y+1/2,-z+1/2
MSYM    u,-v,w,0.0
SYMM   x+1/2,-y+1/2,-z
MSYM   -u, v,w,0.0
!
!Atom Typ  Mag Vek     X       Y       Z       Biso    Occ       Rx       Ry       Rz
!     Ix      Iy      Iz     beta11  beta22  beta33   MagPh
Mn1  MMN3  1  0  0.50000 0.00000 0.00000 0.04338 1.00000    0.000    3.847    0.000
                    0.00    0.00    0.00    0.00    0.00     0.00   131.00     0.00
   0.000   0.000   0.000   0.000   0.000   0.000   0.000 0.00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
```


The different ways of treating magnetic structures in FullProf

Coefficients of basis functions refinement:
A magnetic phase has **`Jbt = +/- 1 and Isy=-2`**

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j \sum_{n\lambda} C^{\nu}_{n\lambda} \sum_{s} \mathbf{S}^{\mathbf{k}\nu}_{n\lambda}(js)\, exp\left\{2\pi i\left[\mathbf{h}_s \mathbf{r}_j - \Phi_{kj}\right]\right\}$$

The basis functions of the Irreps (in numerical form) are introduced together with explicit symmetry operators of the crystal structure. The refined variables are directly the coefficients C1, C2, C3, ….

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

$$C^{\nu}_{n\lambda}$$

Basis functions coefficients refinement

```
LaMnO3
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   0  -2   0   0          0.000   0   7   0
!
P m m m                      <--Space group symbol
! Nsym   Cen   Laue Ireps N_Bas
    4     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,-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+1/2,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
!
!Atom Typ  Mag Vek     X       Y       Z       Biso    Occ       C1       C2       C3
!     C4      C5      C6      C7      C8      C9     MagPh
Mn1  MMN3  1  0  0.50000 0.00000 0.00000 0.04338 1.00000    0.000    3.847    0.000
                    0.00    0.00    0.00    0.00    0.00     0.00   131.00     0.00
   0.000   0.000   0.000   0.000   0.000   0.000   0.000 0.00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
```

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*

The Program *SuperCell*

Program: ***SuperCell*** (J.Rodríguez-Carvajal, LLB-December-1998)

- This program can be used to index superstructure reflections from a powder diffraction pattern.
- The first approach consist in searching the best "magnetic unit cell" compatible with a set of observed SUPERSTRUCTURE lines in the powder diffraction pattern.
- If the first approach fails to give a suitable solution, the superstructure may be incommensurate and a direct search for the propagation vector and one of its harmonics have to be used.

Simulated Annealing (SA):

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

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

The function, E(ω) to be optimised with respect to the configuration described by the vector state ω is called the "cost" function.

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) (program MAGSAN)

Simulated Annealing (SA):

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 chain) and a Boltzmann probability to explore the phase space (importance sampling)

The Simulated Annealing Algorithm

begin
  Initialise (set to zero useful quantities, do preliminary calculations)
  t = 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 $\exp(-\Delta/T_t) >$ random[0,1] **then accept**
          if accept then **Update** (replace ω_{old} **by** ω_{new})
    until equilibrium is approached closely enough (Ncyc)
    $T_{t+1} = f(T_t)$ **(decrease temperature, usually** $T_{t+1} = q\ T_t$, **q≈0.9)**
    t = t + 1
  until stop criterion is true (maximum **t, convergence, low % accepted...)**
end

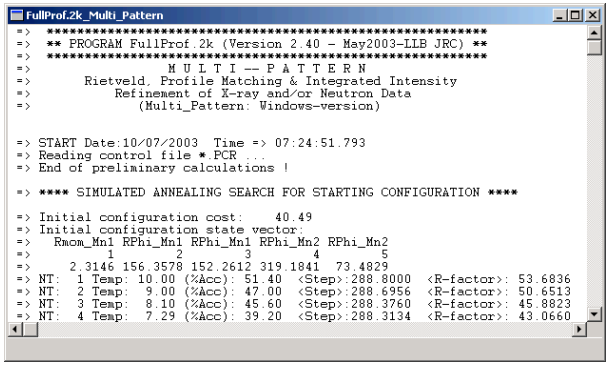
Simulated Annealing for magnetic structures:

- Look directly for the components of S_k and phases, explaining the experimental data
- Minimize a reliability factor with respect to the "configuration vector"

$$\hat{\mathbf{u}} = \left| C_1, C_2, C_3, C_4, C_5, \ldots C_m \right\rangle$$

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

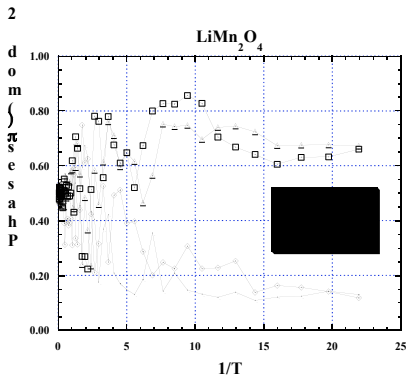
Simulated Annealing run of *FullProf*



Simulated Annealing run of *FullProf*

```
FullProf.2k_Multi_Pattern
=> NT: 69 Temp:   0.01 (%Acc): 42.40  <Step>:   0.2036  <R-factor>: 13.3120
=> NT: 70 Temp:   0.01 (%Acc): 40.60  <Step>:   0.1972  <R-factor>: 13.3079
=> NT: 71 Temp:   0.01 (%Acc): 41.60  <Step>:   0.1710  <R-factor>: 13.3025
=> NT: 72 Temp:   0.01 (%Acc): 46.60  <Step>:   0.1551  <R-factor>: 13.2982
=> NT: 73 Temp:   0.01 (%Acc): 35.80  <Step>:   0.1404  <R-factor>: 13.2960

=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   150 reflections):

=> Sol#: 1 RF2=  13.282 ::
=>   Rmom_Mn1 RPhi_Mn1 RPhi_Mn1 RPhi_Mn2 RPhi_Mn2
=>        1         2         3         4         5
=>     2.9250  53.2323 324.9417 217.1961 144.8587


=>              CPU Time:    48.610 seconds
=>                           0.810 minutes

=> END   Date:10/07/2003  Time => 07:25:40.413

=> Data Files :
=>          - simann
=> PCR  File  : simann-t
```


Behavior of parameters in Simulated Annealing runs



Average step … Corana algorithm