

## Magnetic structures: Formalism of propagation vector

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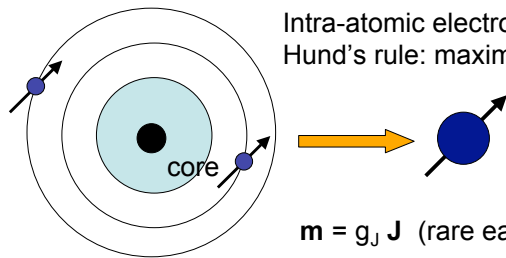
1. What's a magnetic structure?
2. How to describe magnetic structures with the formalism of propagation vector(s).
3. Plotting complex magnetic structure with FStudio.
4. Symmetry, symmetry, symmetry...
5. Strategy for solving magnetic structures, indexation, simulated annealing....

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Atoms/ions with unpaired electrons

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



**Ni<sup>2+</sup>**

$\mathbf{m} = g_J \mathbf{J}$  (rare earths)

$\mathbf{m} = g_S \mathbf{S}$  (transition metals)

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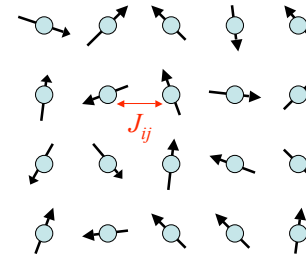


Paramagnetic state:

Snapshot of magnetic moment configuration

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

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



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CCLRC **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**

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CCLRC **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
- .....

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CCLRC **Types of magnetic structures**

**Amplitude-modulated or Spin-Density Waves**

"Longitudinal"

"Transverse"

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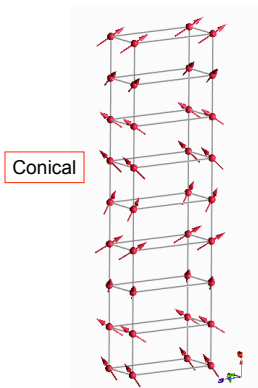
CCLRC **Types of magnetic structures**

**Spiral**

**Cycloid**

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CCLRC **Types of magnetic structures**



Conical

Shubnikov magnetic groups, are limited to:

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

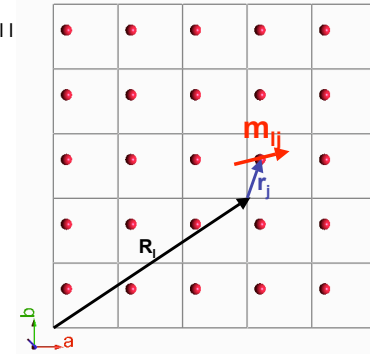
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CCLRC **Formalism of prop. Vector : Basics**

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

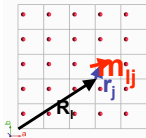
$\mathbf{R}_j = \mathbf{R}_l + \mathbf{r}_j$  where  $\mathbf{R}_l$  is a pure lattice translation



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CCLRC **Formalism of prop. Vector : Basics**



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

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

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

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

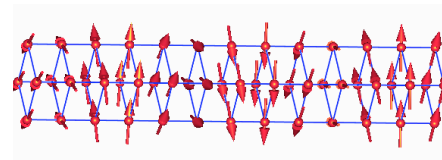
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CCLRC **Formalism of prop. Vector : Basics**

A magnetic structure is fully described by:

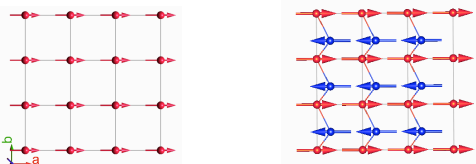
- Wave-vector(s)  $\{\mathbf{k}\}$ .
- Fourier components  $\mathbf{S}_{\mathbf{k}j}$  for each magnetic atom  $j$  and wave-vector  $\mathbf{k}$ .  $\mathbf{S}_{\mathbf{k}j}$  is a complex vector (6 components) !!!
- Phase for each magnetic atom  $j$ ,  $\Phi_{\mathbf{k}j}$



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CCLRC **Single propagation vector**  
 $\mathbf{k} = (0,0,0)$

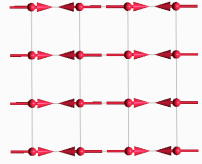


$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \exp\{-2\pi i \mathbf{k} \mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j}$$

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


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CCLRC **Single propagation vector**  
 $\mathbf{k} = 1/2 \text{ H}$



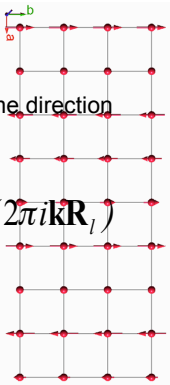
$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \exp\{-2\pi i \mathbf{k} \mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j} (-1)^{n(l)}$$

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

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CCLRC **Fourier coef. of sinusoidal structures**


- $\mathbf{k}$  interior of the Brillouin zone (pair  $\mathbf{k}$ ,  $-\mathbf{k}$ )
- Real  $\mathbf{S}_{\mathbf{k}}$ , or imaginary component in the same direction as the real one



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


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

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

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CCLRC **Fourier coefficients of helical structures**

- $\mathbf{k}$  interior of the Brillouin zone
- Real component of  $\mathbf{S}_{\mathbf{k}}$  perpendicular to the imaginary component

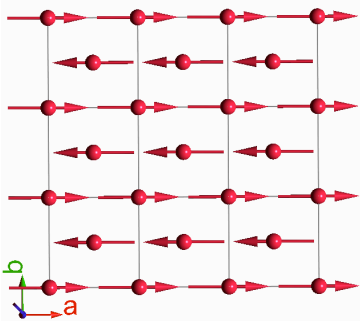


$$\mathbf{S}_{\mathbf{k}j} = \frac{1}{2} [m_{uj} \mathbf{u}_j + im_{vj} \mathbf{v}_j] \exp(-2\pi i \phi_{\mathbf{k}j})$$


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

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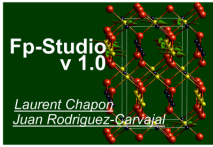
CCLRC **Centred cells!**



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

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CCLRC **Examples. Fstudio**




[www-llb.cea.fr/fullweb](http://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
}


```

Type of lattice P, C, I, F.....  
Propagation vector(s)  
List of symmetry operators with associated magnetic operator  
Magnetic atom  
Fourier coefficients and phase

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CCLRC **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

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CCLRC **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.

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**CCLRC Representation theory**

**Spectroscopy**

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

**MO-LCAO**

N   3H

-15.5 eV   -13.5 eV

(2p<sub>x</sub>, 2p<sub>y</sub>)   s<sub>1</sub>   s<sub>2</sub> + s<sub>3</sub>

(2p<sub>z</sub>)   s<sub>1</sub>   s<sub>2</sub> - s<sub>3</sub>

(2s)   s<sub>1</sub>   s<sub>2</sub> + s<sub>3</sub>

-25.6 eV   -17.0 eV   -31.0 eV

SALCs of H atoms

**Free ion**

Ground state multiplet

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

$\Delta J = 0; +1; -1$

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**CCLRC Phase transitions in solids**

Phase transitions often take place between phases of different symmetry.

High symmetry phase, Group  $G_0$

(I.P.)

Low symmetry phase, Group  $G_1$

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

A simple example: Paramagnetic → Ferromagnetic transition

"Time-reversal" is lost

- Symmetry under reversal of the electric current

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**CCLRC Landau theory**

- Ordering is characterized by a function  $\rho(x)$  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

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**CCLRC Landau theory (2)**

$\Phi$  is invariant under operations of  $G$ , each order of the expansion can be written is given by some polynomial invariants of  $c_i^n$ .

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

$T > T_c$

- 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.

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

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

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### Symmetry Analysis

Fourier coefficients as linear combinations of the basis functions of the irreducible representation of the propagation vector group  $G_k$

$$S_{kjs} = \sum_{n\lambda} C_{n\lambda}^v S_{n\lambda}^{kv} (js)$$



$$M(\mathbf{h}) = p \sum_{j=1}^n O_j f_j(\mathbf{h}) T_j \sum_{n\lambda} C_{n\lambda}^v \sum_s S_{n\lambda}^{kv} (js) \exp \{ 2\pi i [\mathbf{h}_s \mathbf{r}_j - \Phi_{kj}] \}$$

### Symmetry Analysis

$$S_{kjs} = \sum_{n\lambda} C_{n\lambda}^v S_{n\lambda}^{kv} (js)$$

The coefficients  $C_{n\lambda}^v$  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

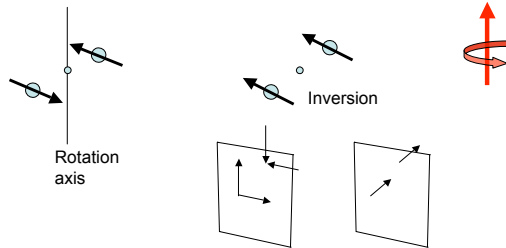
$v$  : reference to the irreducible representation  $\Gamma_v$

$n$  : index running from 1 up to  $n_v \Rightarrow \Gamma_{Mag} = \sum_{\oplus v} n_v \Gamma_v$

$\lambda$  : index running from 1 up to  $\dim(\Gamma_v)$

### Symmetry Analysis

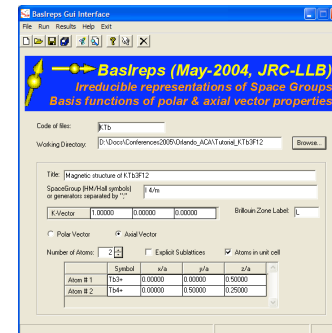
Magnetic moment is an axial (pseudo) vector.  
Transformation under symmetry operation different to polar vector:



### Representation analysis

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

Software:  
-MODY  
-SarAh  
-BasReps





## The different ways of treating magnetic structures in FullProf

Standard Fourier coefficients refinement:

A magnetic phase has  $\mathbf{Jbt} = +/- 1$

$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^n O_j f_j(\mathbf{h}) T_j \sum_s S_{kjs} \exp \left\{ \pi i [(\mathbf{H} + \mathbf{k}) \cdot \mathbf{S} \cdot \mathbf{r}_j - \Phi_{kj}] \right\}$$

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

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## 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 0.000000
0.00 0.00 0.00
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```



## The different ways of treating magnetic structures in FullProf

Coefficients of basis functions refinement:

A magnetic phase has  $\mathbf{Jbt} = +/- 1$  and  $\text{Isy} = -2$

$$\mathbf{M}(\mathbf{h}) = p \sum_{j=1}^n O_j f_j(\mathbf{h}) T_j \sum_{n\lambda} C_{n\lambda}^v \sum_s S_{n\lambda}^{kv}(js) \exp \left\{ \pi i [\mathbf{h} \cdot \mathbf{r}_j - \Phi_{kj}] \right\}$$

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  $C1, C2, C3$ .

$$S_{kjs} = \sum_{n\lambda} C_{n\lambda}^v S_{n\lambda}^{kv}(js)$$

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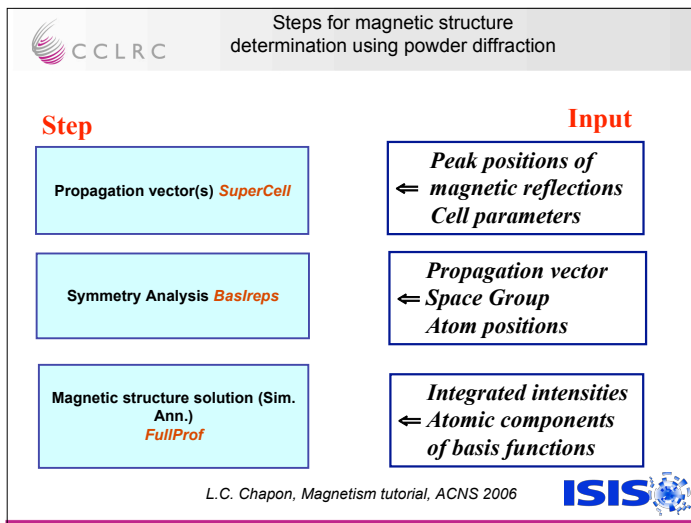


## Basis functions coefficients refinement

```
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
BASR 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
BASR 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
BASR 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
BASR 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 0.00 131.00 0.00
0.000 0.000 0.000 0.000 0.000 0.000000
0.00 0.00 0.00
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```








CCLRC 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.

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CCLRC 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,  $E(\omega)$  to be optimised with respect to the configuration described by the vector state  $\omega$  is called the "cost" function.

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CCLRC 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)

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CCLRC Simulated Annealing run of FullProf

```

FullProf.Zk_Multi_Pattern
=> NT: 69 Teap: 0.01 (%Acc): 42.40 <Step>: 0.2036 <R-factor>: 13.3120
=> NT: 70 Teap: 0.01 (%Acc): 40.60 <Step>: 0.1972 <R-factor>: 13.3079
=> NT: 71 Teap: 0.01 (%Acc): 41.60 <Step>: 0.1710 <R-factor>: 13.3025
=> NT: 72 Teap: 0.01 (%Acc): 46.60 <Step>: 0.1551 <R-factor>: 13.2982
=> NT: 73 Teap: 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 :
=> Rmon_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

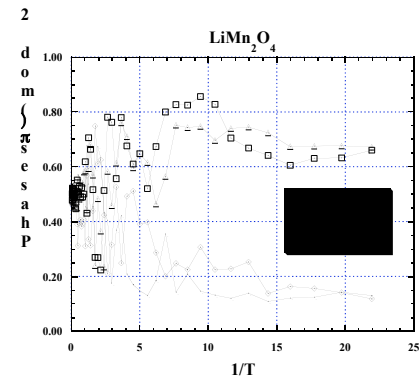
=> END Date:10/07/2003 Time => 07:25:40.413

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

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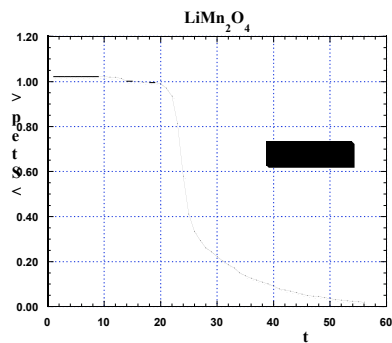
CCLRC Behavior of parameters in Simulated Annealing runs



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CCLRC Average step ... Corana algorithm



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