Solving and refining crystal structures using symmetry modes: FullProf + AMPLIMODES.

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Outline

- ➔ Overview of the *Symmetry Analysis* in phase transitions

- ➔ How is implemented the use of symmetry modes in *FullProf*

- ➔ Detailed examples:
  Janh-Teller transition in $LaMnO_3$

Symmetry and Phase Transitions

In a displacive phase transition the symmetry-breaking distortion (with respect to the high symmetry phase) is mainly **caused by the freezing of the *primary mode, associated* with the order parameter**.

In general, ***secondary modes are* also triggered at the transition** and can have non-zero amplitudes in the distorted structure.

The symmetry-mode analysis of a structural phase transition consists on **the calculation of the amplitudes** of the **symmetry modes frozen** in the distortion characterized by the **eigenvectors** of both primary and secondary modes present in the distortion.

Symmetry and Phase Transitions

Modes are **collective correlated atomic displacements** fulfilling certain symmetry properties. Structural distortions can be decomposed into contributions from different modes with symmetries given by **irreducible representations** of the parent space group.

In general, the **use of symmetry-adapted modes** in the description of distorted structures introduces a **natural physical hierarchy among the structural parameters**. This can be useful not only for investigating the **physical mechanisms** that stabilize these phases, but also for **pure crystallographic purposes**.

Mode Crystallography

The team of the Bilbao Crystallographic Server has developed the computer program: **AMPLIMODES**, that allows an easy calculation of the decomposition in modes of a distorted crystal structure with respect to a (virtual) high symmetry structure.

The originality of this approach with respect to more classical ones (e.g. BasIreps, MODY, Sarah, …) is that **the polarization vectors are referred to the basis of the low symmetry phase**, allowing to use conventional crystallographic approaches (asymmetric unit and space group operators) to the crystal structure analysis.

AMPLIMODES: Symmetry mode analysis on the Bilbao Crystallographic Server,
D. Orobengoa, C.Capillas, M.I. Aroyo and J.M. Perez-Mato, **JApplCryst.** (in press)

Distorted structures in terms of modes

Let $\mathbf{r}(\mu)$ be the positions of the atoms μ ($\mu = 1,\ldots s$) within an asymmetric unit of the parent structure with space group **H**. The asymmetric unit of the observed distorted structure with lower space group **L**, subgroup of **H**, will in general have a larger number of atoms due to the splitting of the Wyckoff orbits in **H**.

$$\boxed{\mathbf{r}(\mu,i) = \mathbf{r}_0(\mu,i) + \mathbf{u}(\mu,i)} \qquad \mu = 1,2,\ldots s, \quad i = 1,2,\ldots n_\mu$$

$$\boxed{\mathbf{u}(\mu,i) = \sum_{\tau,m} A_{\tau,m}\, \boldsymbol{\varepsilon}(\tau,m\,|\,\mu,i)}$$

The indices τ and m label all possible distinct allowed symmetry-adapted distortion modes. τ stands for the possible different mode symmetries, while m ($m = 1,\ldots n_\tau$) enumerates the possible different independent modes of a given symmetry.

Distorted structures in terms of modes

$$\boxed{\mathbf{u}(\mu,i)=\sum_{\tau,m} A_{\tau,m}\ \boldsymbol{\varepsilon}(\tau,m\,|\,\mu,i)}\qquad \mu=1,2,\ldots s,\quad i=1,2,\ldots n_{\mu}$$

The mode $(\tau,\ m)$ is defined by the polarisation vectors:

$$\boldsymbol{\varepsilon}(\tau,m\,|\,\mu,i)$$

One can refers to the global polarization vector $\boldsymbol{\varepsilon}\,(\tau,\ m)$, taking all atoms simultaneously, of the mode $(\tau,\ m)$

The displacements of an atom (μ',i') related by the symmetry operator $\{\mathbf{R}|\mathbf{t}\}$ to the atom (μ,i) are given directly by:

$$\mathbf{R}\,\boldsymbol{\varepsilon}(\tau,m\,|\,\mu,i)$$

Distorted structures in terms of modes

The normalization of the polarisation vectors is chosen to verify:

$$\boxed{\sum_{\mu,i} mult_{\mu,i} \left|\boldsymbol{\varepsilon}(\tau, m \mid \mu, i)\right|^2 = 1}$$

“$mult_{\mu,i}$” represents the multiplicity in a primitive cell of the space group **L** for the Wyckoff position (μ, i).

The following orthogonality relation is verified by the polarization vectors:

$$\boxed{\sum_{\mu,i} mult_{\mu,i} \boldsymbol{\varepsilon}(\tau, m \mid \mu, i)\, \boldsymbol{\varepsilon}(\tau', m' \mid \mu, i) = \delta_{\tau\tau'}\, \delta_{mm'}}$$

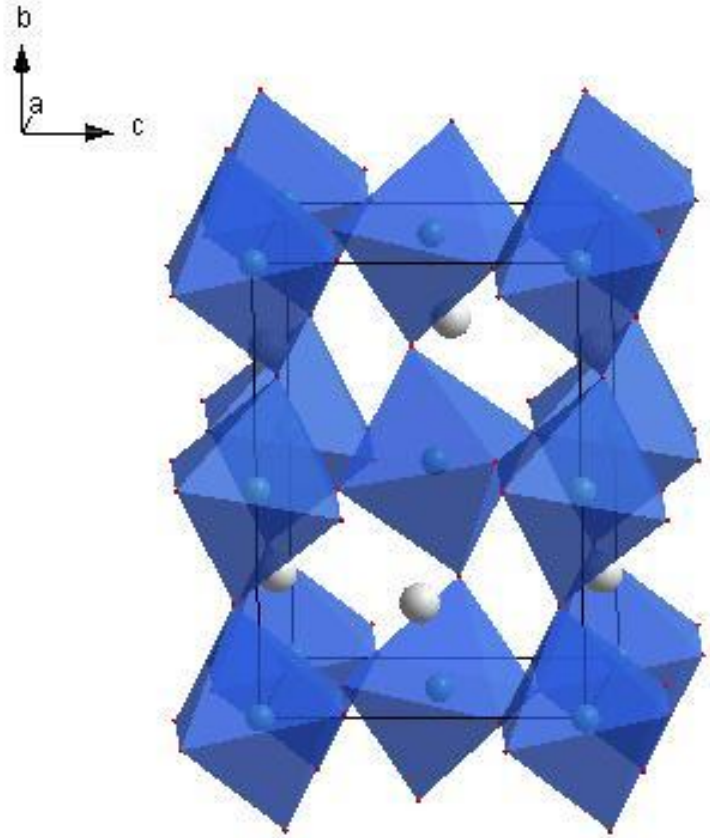
Distorted structures in terms of modes

The distortion modes of the phase with group **H** having **isotropy group** equal to **L** can be called **primary**, while those with **isotropy groups** given by **subgroups** of **H** which are distinct **supergroups** of **L**, are usually termed **secondary**.

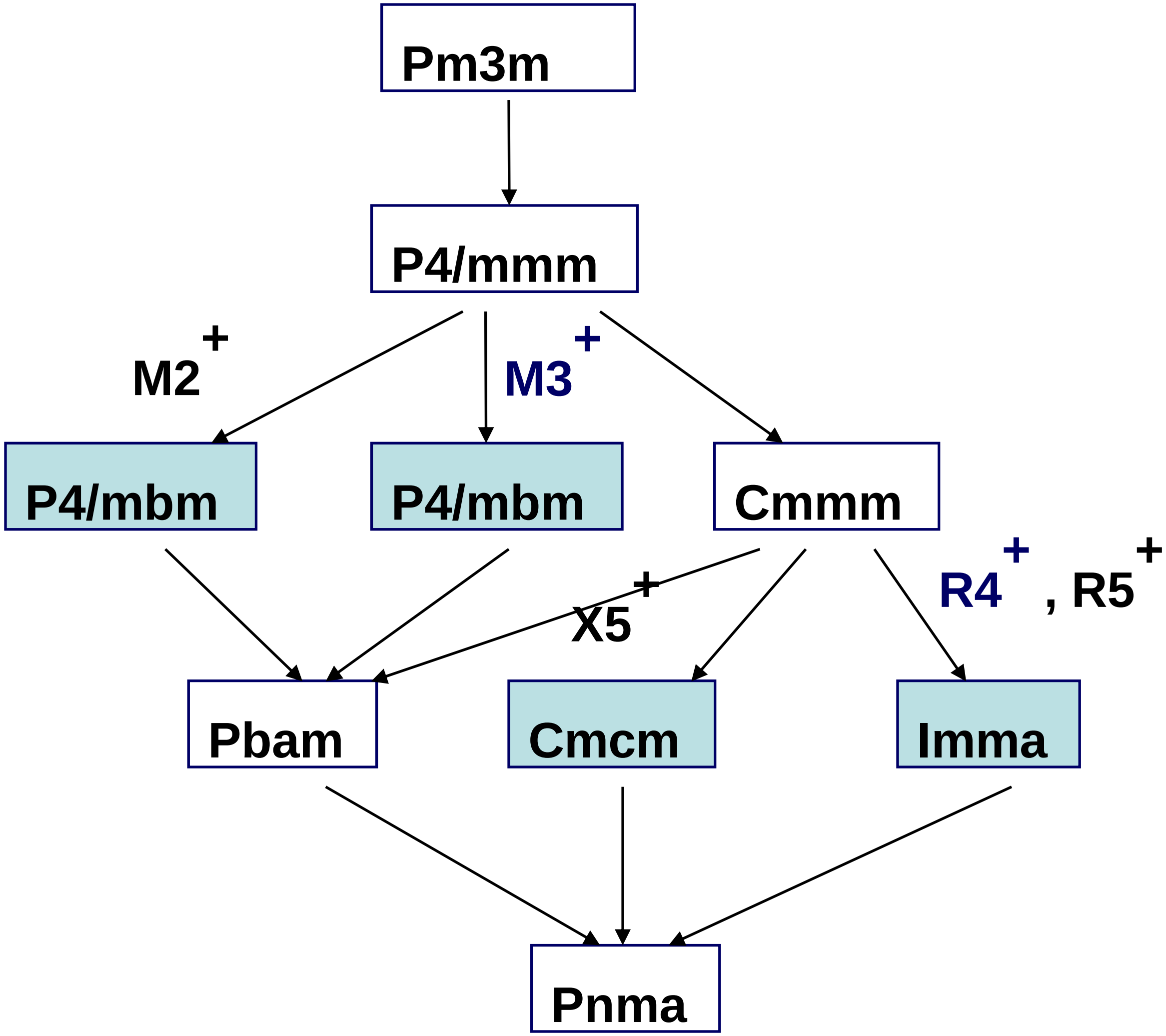
A **primary distortion mode** is sufficient to produce the observed symmetry breaking between **the parent** and **the observed** structure, while **secondary distortion modes** alone would yield **a higher symmetry**.

Distorted perovskite: structure type $GdFeO_3$

Space group: *Pnma*, parent structure *Pm3m*



Group-subgroup chains relating *Pm3m* and *Pnma*



Pm3m

P4/mmm

$M2^+$

$M3^+$

P4/mbm

P4/mbm

Cmmm

$X5^+$

$R4^+$, $R5^+$

Pbam

Cmcm

Imma

Pnma

Distorted structures in terms of modes

It is also in general very convenient to express the global distortion in terms of the different symmetry components (this is done in AMPLIMODES):

$$\mathbf{u}(\mu,i) = \sum_{\tau,m} A_{\tau,m}\,\boldsymbol{\varepsilon}(\tau,m\,|\,\mu,i) = \sum_{\tau} A_{\tau}\,\mathbf{e}(\tau\,|\,\mu,i)$$

$$A_{\tau} = \left(\sum_{m} A_{\tau,m}^{2}\right)^{1/2}$$

$$\mathbf{e}(\tau\,|\,\mu,i) = \sum_{m} a_{\tau,m}\,\boldsymbol{\varepsilon}(\tau,m\,|\,\mu,i); \quad a_{\tau,m} = \frac{A_{\tau,m}}{\left(\sum_{m} A_{\tau,m}^{2}\right)^{1/2}}$$

Outline

➔ Overview of the *Symmetry Analysis* in phase transitions

➔ How is implemented the use of symmetry modes in *FullProf*

➔ Detailed examples:
Janh-Teller transition in $LaMnO_3$

Refinement of crystal structures using amplitudes of symmetry modes instead of atom positions in *FullProf*

In **FullProf** the refinement of a crystal structure can be done in terms of symmetry adapted modes.

http://www.ill.eu/sites/fullprof/

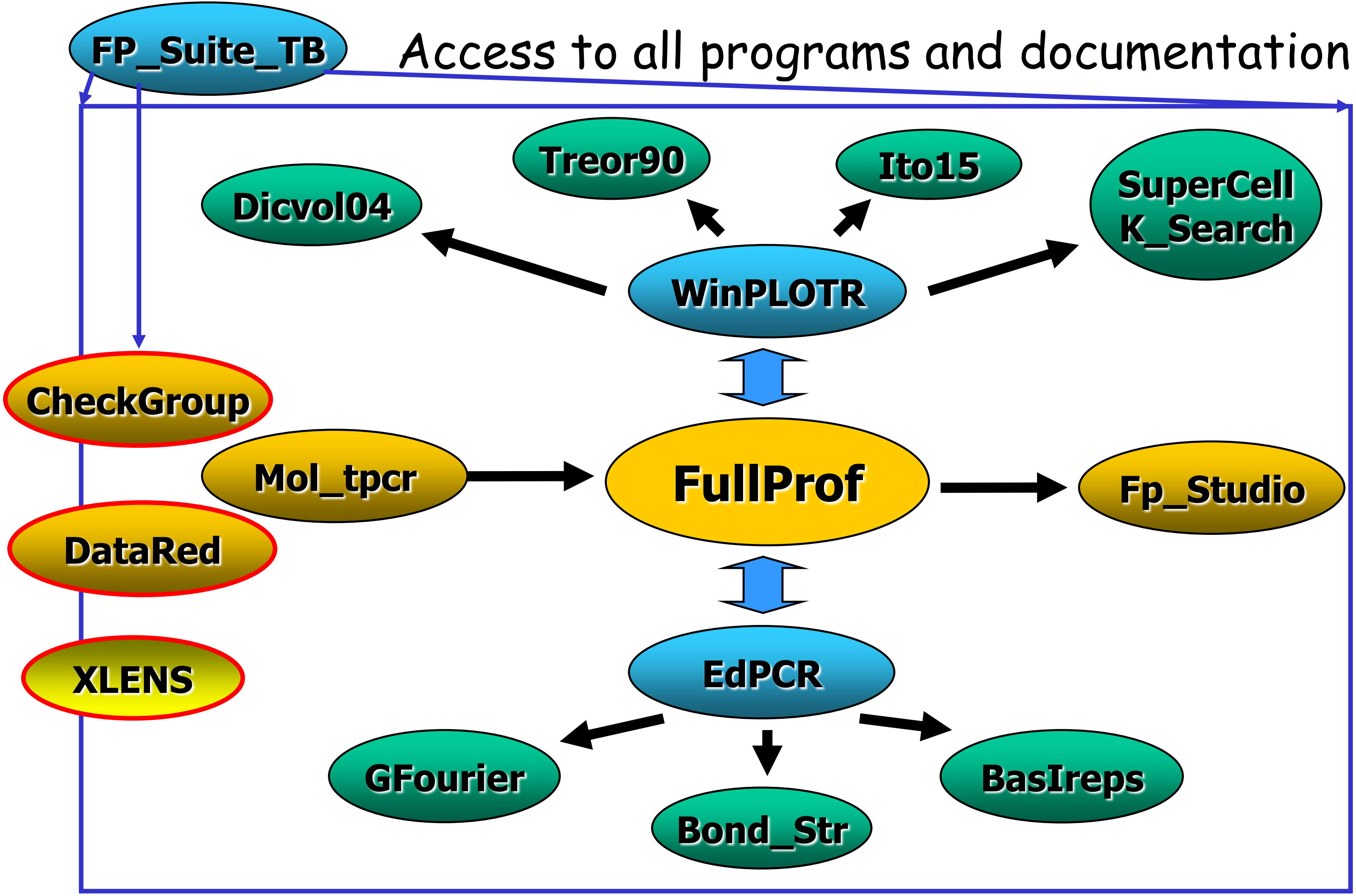
FullProf uses the polarisation vectors obtained from the output of the program **AMPLIMODES** from the Bilbao Crystallographic Server

http://www.cryst.ehu.es/cryst/amplimodes.html

A low symmetry (LS) crystal structure (Space Group L) is supposed to derive (from a phase transition) from a high symmetry (HS) structure (Space Group H) with $L \subset H$.

The free parameters, instead of atom positions, are the amplitudes of a combination of allowed symmetry modes.

FullProf Suite



Magnetic structures
Magnetic moment of each atom: Fourier series

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

The program **Fp_Studio** performs the above sum and represents graphically the magnetic structure.
This program can help to learn about this formalism because the user can write manually the Fourier coefficients and see what is the corresponding magnetic structure immediately.

Web site: http://www.ill.eu/sites/fullprof/

Group Theory: Symmetry Analysis

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

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

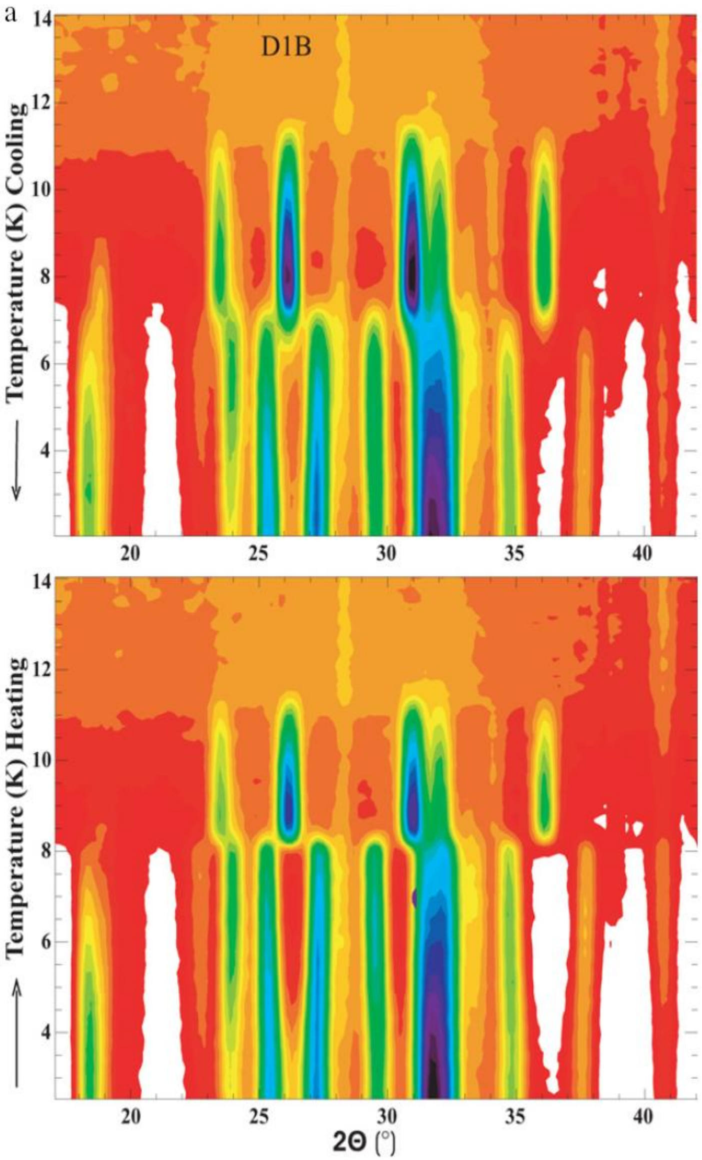
$$\downarrow$$

$$\boxed{\mathbf{M} \;\; \mathbf{h} \;\; = p \sum_{j=1}^{n} O_j f_j \;\; \mathbf{h} \;\; T_j \sum_{n\lambda} C_{n\lambda}^{\nu} \sum_{s} \mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu} \;\; js \;\; exp \;\; 2\pi i \, \mathbf{h}_s \mathbf{r}_j}$$

Competing multi-q magnetic structures in HoGe$_3$ (I & II)

P Schöbinger-Papamantellos, J Rodríguez-Carvajal, LD Tung, C Ritter and KHJ Buschow

J. Physics: Condensed Matter **20** (2008) 195201 (12pp)
195202(13pp)



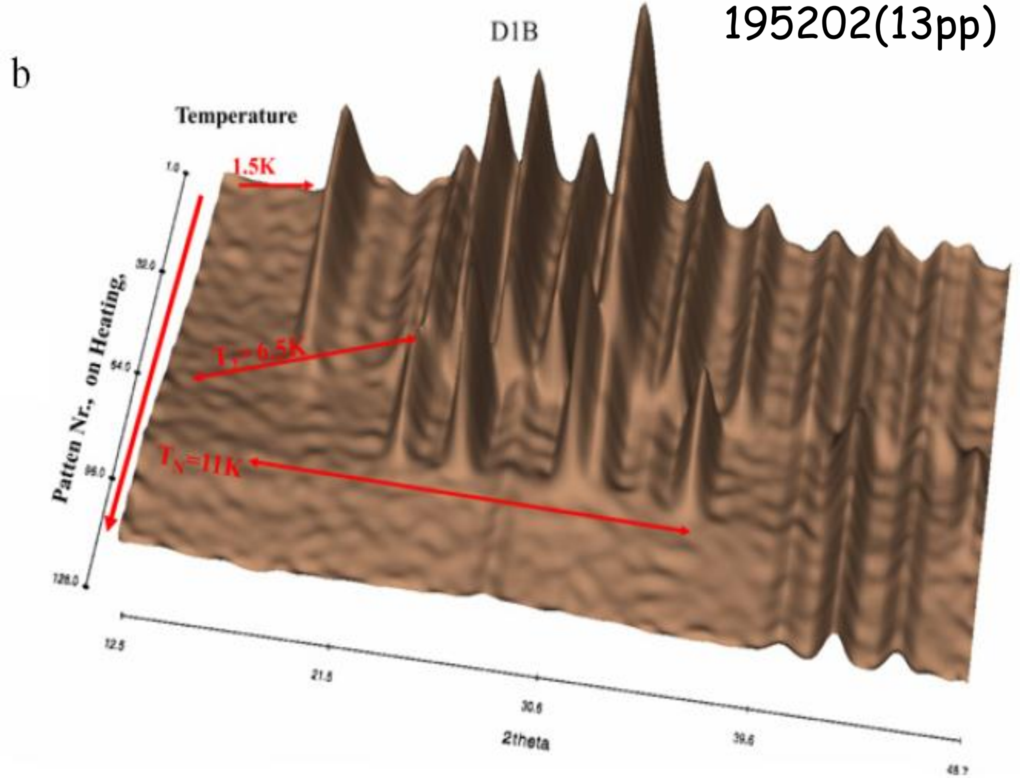


Figure 6. Thermodiffractogram of HoGe$_3$: (a) in a 2D projection on heating and cooling showing the succession of magnetic phase transitions below $T_N = 11$ K at $T_2^H = 8.1$ K and $T_3^H = 4.8$ K (temperatures given on heating) and (b) in a 3D view on cooling.

Refinement of crystal structures using amplitudes of symmetry modes instead of atom positions in *FullProf*

The atoms position are calculated from the following formula:

$$\boxed{\mathbf{r}_j^{LS} = \mathbf{r}_j^{HS} + \sum_m c_m Q_m \, \boldsymbol{\varepsilon}(m \mid j)}$$

Where *j* runs over the atoms in the asymmetric unit of the LS phase
The index *m* runs over all contributing modes. It may content modes corresponding to different representations and wave vectors of the H space group (Isotropy subgroups) that are compatible with the L space group.

The polarisation vectors $\boldsymbol{\varepsilon}(m \mid j)$ have normalized components referred to the conventional cell of the LS phase and are provided by **AMPLIMODES**. The refined parameters are the amplitudes Q_m. c_m are normalisation coefficients.

A representation of the modes using arrows and the HS phase can be visualised using **FullProf Studio**

Example of PCR file for **FullProf** corresponding to the compound $LaMnO_3$

Symmetry modes option

```
LaMnO3
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth    ATZ      Nvk Npr More
   4   0   0 0.0 0.0 1.0   6   0   0   0   7    967.370    0   7   1
P b n m                     <--Space group symbol
!Atom    Typ        X        Y        Z       Biso      Occ
La       LA       0.00000  0.50000  0.25000  0.35050  0.50000
                     0.00     0.00     0.00   251.00     0.00
Mn       MN       0.00000  0.00000  0.00000  0.21228  0.50000
                     0.00     0.00     0.00   261.00     0.00
O1       O        0.75000  0.25000  0.00000  0.43965  1.00000
                     0.00     0.00     0.00   271.00     0.00
O2       O        0.50000  0.50000  0.75000  0.50234  0.50000
                     0.0                                  .00
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES    12
! Nm  Atm      Irrep          Vx         Vy        Vz          Coeff
   1  O1       R4+       0.000000   0.000000   0.031721     1.000000
   1  O2       R4+       0.063442   0.000000   0.000000     1.000000
   2  La       R5+      -0.089721   0.000000   0.000000     1.000000
   3  O1       R5+       0.000000   0.000000  -0.031721     1.000000
. . . . . . . . . . . . .
   7  O2       M3+       0.000000   0.000000   0.000000     1.000000
! Amplitudes of Symmetry Modes
```

keyword

Number of polarisation vector modes

Indices of the modes

Normalisation coefficients

Example of PCR file for *FullProf* corresponding to the compound $LaMnO_3$

Indices of the modes

Symbols of the Irreducible representations

Polarisation vectors components

```
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES    12
! Nm Atm       Irrep           Vx         Vy         Vz          Coeff
   1  O1         R4+        0.000000   0.000000   0.031721    1.000000
   1  O2         R4+        0.063442   0.000000   0.000000    1.000000
   2  La         R5+       -0.089721   0.000000   0.000000    1.000000
   3  O1         R5+        0.000000   0.000000  -0.031721    1.000000
  . . . . . . . . . . . .
   7  O2         M3+        0.000000   0.000000   0.000000    1.000000
! Amplitudes of Symmetry Modes
A_MODES     7       1 1 1 1 1 1 1
Q1_R4+         -1.189680  181.0000
Q2_R5+         -0.086467  191.0000
Q3_R5+          0.018171  201.0000
Q4_X5+         -0.546082  211.0000
Q5_X5+         -0.139910  221.0000
Q6_M2+          0.355652  231.0000
Q7_M3+          0.901264  241.0000
!-------> Profile Parameters for Pattern #  1
!  Scale          Shape1       Bov      Str1     Str2     Str3   Strain-Model
 0.86919E-01    0.00000    0.00000   0.0000   0.0000   0.0000        0
. . . . . . . .
```

Keyword, # of modes, output for FST

Names of amplitudes, values and refinement codes (allowing constraints)

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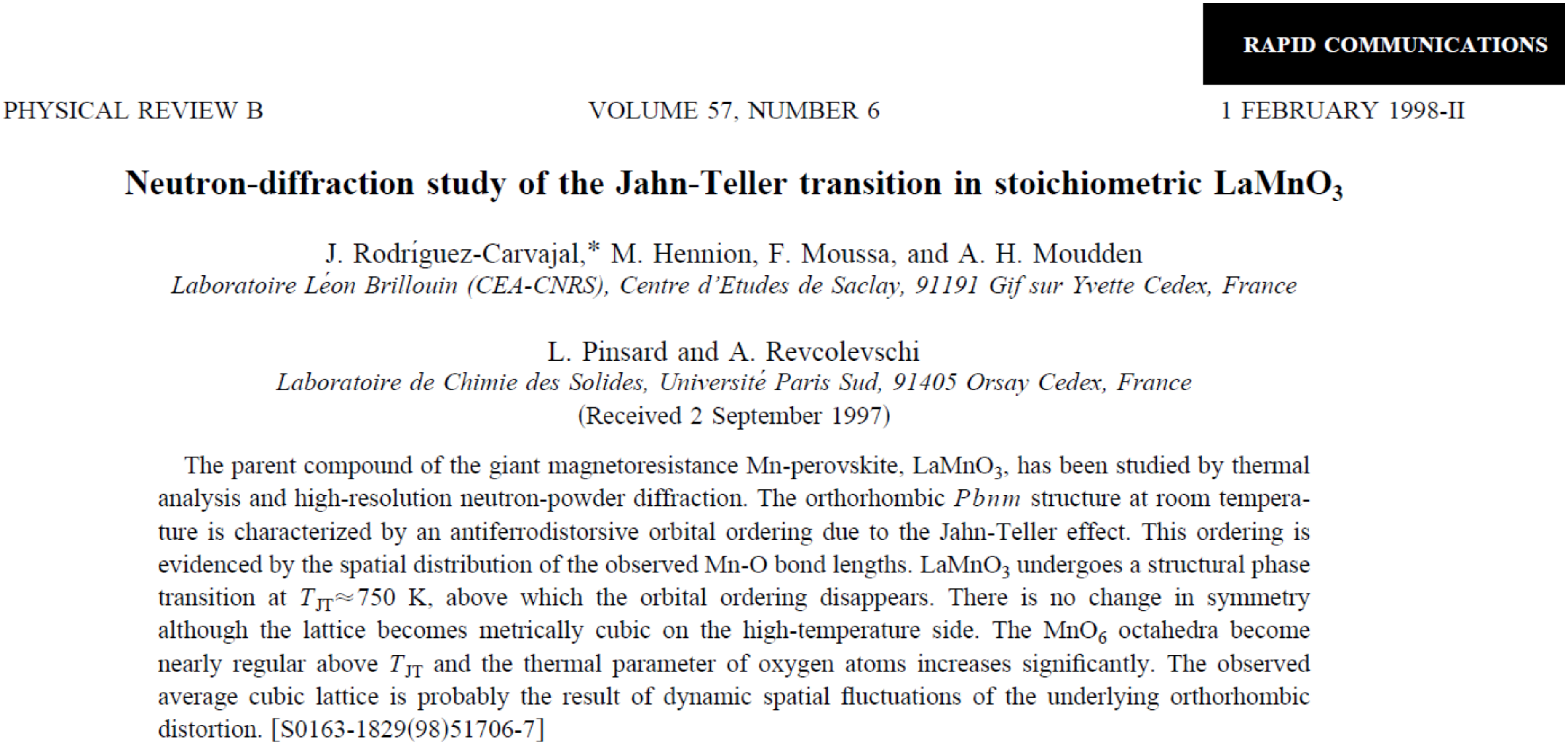
- ➔ Overview of the *Symmetry Analysis* in phase transitions
- ➔ How is implemented the use of symmetry modes in *FullProf*
- ➔ Detailed example:
  Janh-Teller transition in $LaMnO_3$

Example: The Janh-Teller transition in $LaMnO_3$



RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 57, NUMBER 6 1 FEBRUARY 1998-II

Neutron-diffraction study of the Jahn-Teller transition in stoichiometric $LaMnO_3$

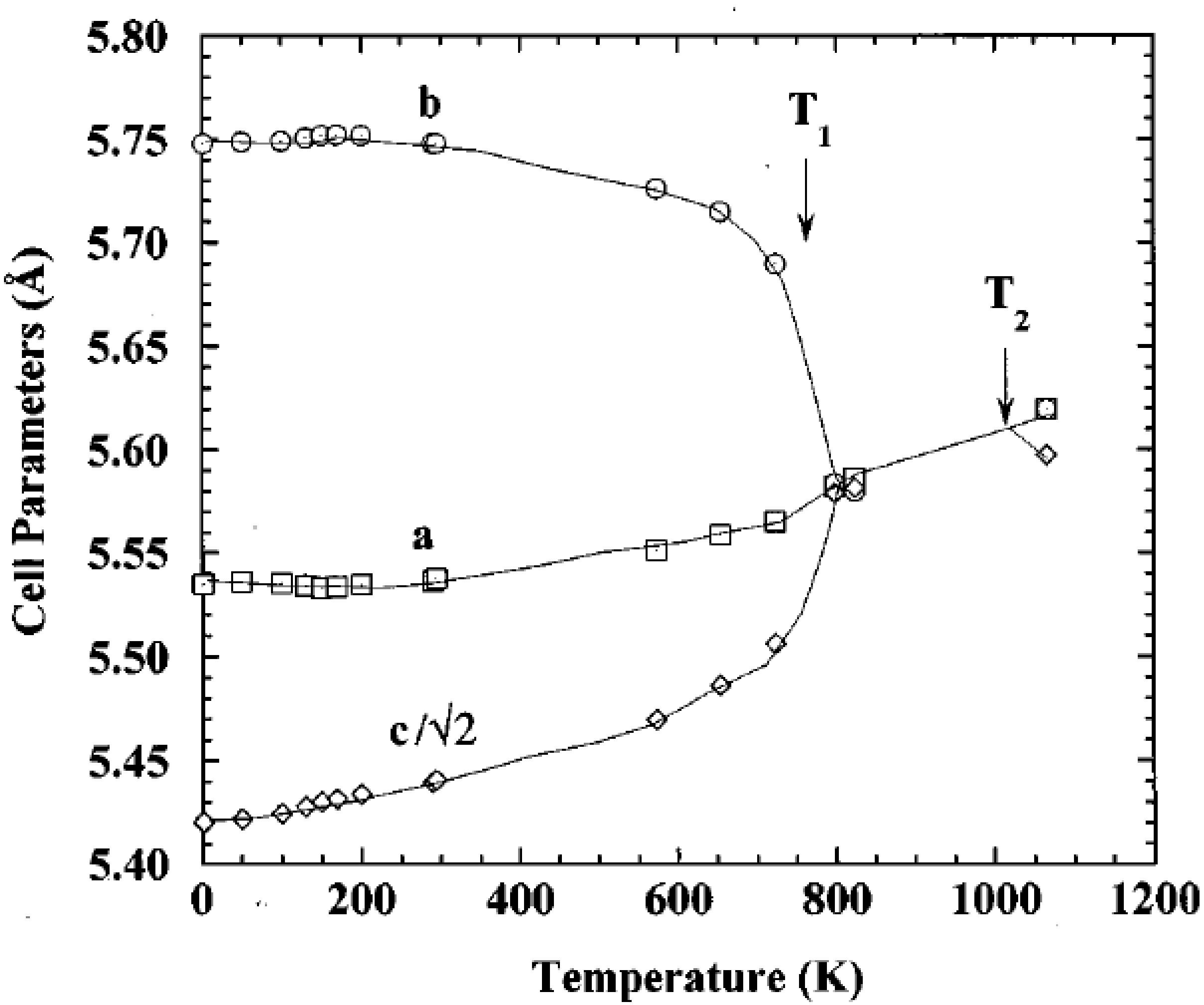
J. Rodríguez-Carvajal,* M. Hennion, F. Moussa, and A. H. Moudden
Laboratoire Léon Brillouin (CEA-CNRS), Centre d'Etudes de Saclay, 91191 Gif sur Yvette Cedex, France

L. Pinsard and A. Revcolevschi
Laboratoire de Chimie des Solides, Université Paris Sud, 91405 Orsay Cedex, France

(Received 2 September 1997)

The parent compound of the giant magnetoresistance Mn-perovskite, $LaMnO_3$, has been studied by thermal analysis and high-resolution neutron-powder diffraction. The orthorhombic *Pbnm* structure at room temperature is characterized by an antiferrodistorsive orbital ordering due to the Jahn-Teller effect. This ordering is evidenced by the spatial distribution of the observed Mn-O bond lengths. $LaMnO_3$ undergoes a structural phase transition at $T_{JT} \approx 750$ K, above which the orbital ordering disappears. There is no change in symmetry although the lattice becomes metrically cubic on the high-temperature side. The MnO_6 octahedra become nearly regular above T_{JT} and the thermal parameter of oxygen atoms increases significantly. The observed average cubic lattice is probably the result of dynamic spatial fluctuations of the underlying orthorhombic distortion. [S0163-1829(98)51706-7]

Example: The Janh-Teller transition in $LaMnO_3$



AMPLIMODES: Bilbao Crystallographic Server

bilbao crystallographic server

[The crystallographic site at the Condensed Matter Physics Dept. of the University of the Basque Country]

[Space Groups] [Layer Groups] [Rod Groups] [Frieze Groups] [Wyckoff Sets]

CrystallographyOnline: International School on the Use and Applications of the Bilbao Crystallographic Server

REGISTRATION OPEN

PhD Studentship

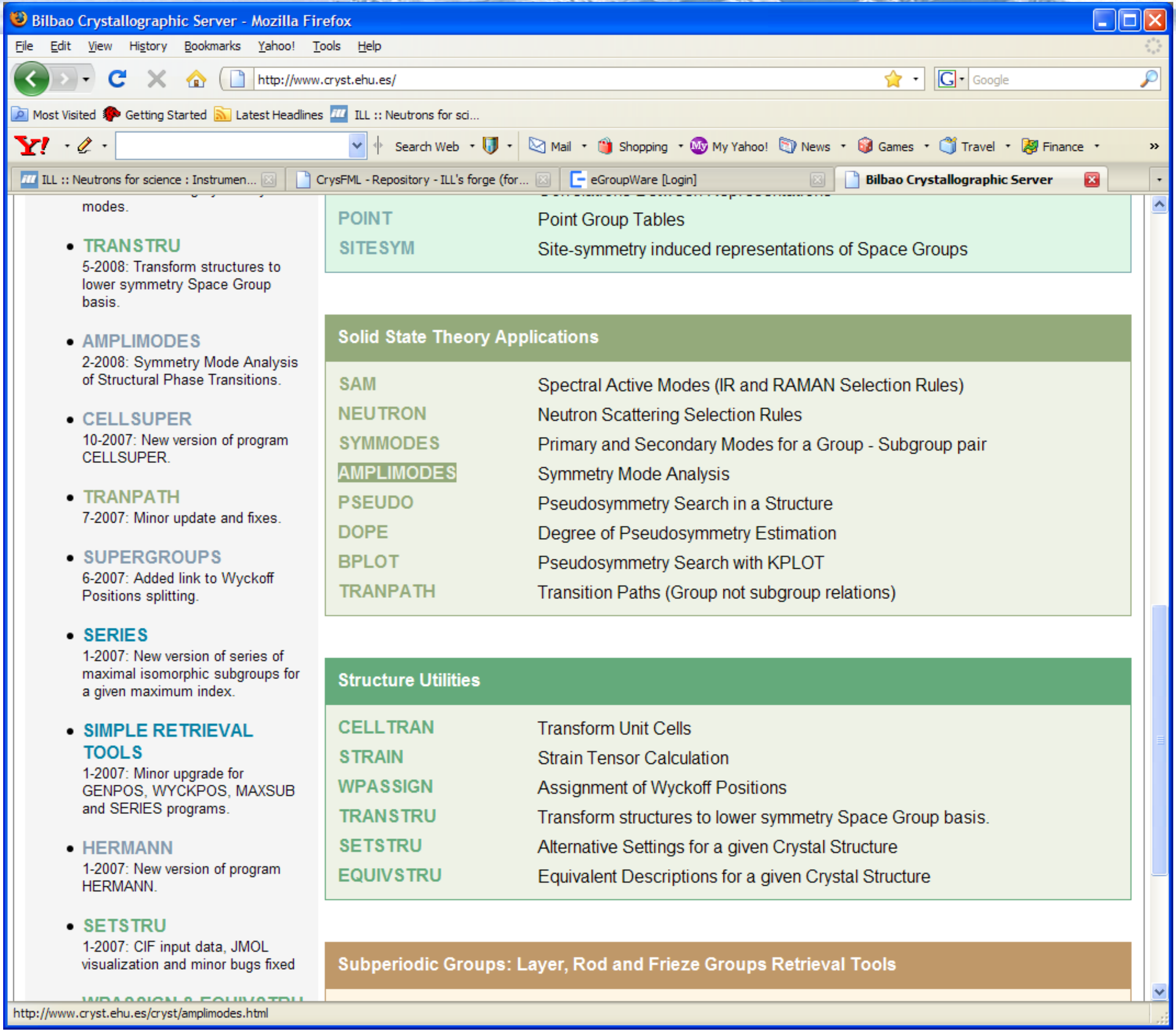
Sections

- Retrieval Tools
- Group-Subgroup
- Representations
- Solid State
- Structure Utilities
- Subperiodic

Space Groups Retrieval Tools	
GENPOS	Generators and General Positions of Space Groups
WYCKPOS	Wyckoff Positions of Space Groups
HKLCOND	Reflection conditions of Space Groups
MAXSUB	Maximal Subgroups of Space Groups
SERIES	Series of Maximal Isomorphic Subgroups of Space Groups
WYCKSETS	Equivalent Sets of Wyckoff Positions
NORMALIZER	Normalizers of Space Groups
KVEC	The k-vector types and Brillouin zones of Space Groups

Group - Subgroup Relations of Space Groups	
SUBGROUPGRAPH	Lattice of Maximal Subgroups
HERMANN	Distribution of subgroups in conjugated classes
COSETS	Coset decomposition for a group-subgroup pair
WYCKSPLIT	The splitting of the Wyckoff Positions
MINSUP	Minimal Supergroups of Space Groups
SUPERGROUPS	Supergroups of Space Groups

AMPLIMODES: Bilbao Crystallographic Server



modes.

- **TRANSTRU**
  5-2008: Transform structures to lower symmetry Space Group basis.
- **AMPLIMODES**
  2-2008: Symmetry Mode Analysis of Structural Phase Transitions.
- **CELLSUPER**
  10-2007: New version of program CELLSUPER.
- **TRANPATH**
  7-2007: Minor update and fixes.
- **SUPERGROUPS**
  6-2007: Added link to Wyckoff Positions splitting.
- **SERIES**
  1-2007: New version of series of maximal isomorphic subgroups for a given maximum index.
- **SIMPLE RETRIEVAL TOOLS**
  1-2007: Minor upgrade for GENPOS, WYCKPOS, MAXSUB and SERIES programs.
- **HERMANN**
  1-2007: New version of program HERMANN.
- **SETSTRU**
  1-2007: CIF input data, JMOL visualization and minor bugs fixed

POINT	Point Group Tables
SITESYM	Site-symmetry induced representations of Space Groups

Solid State Theory Applications

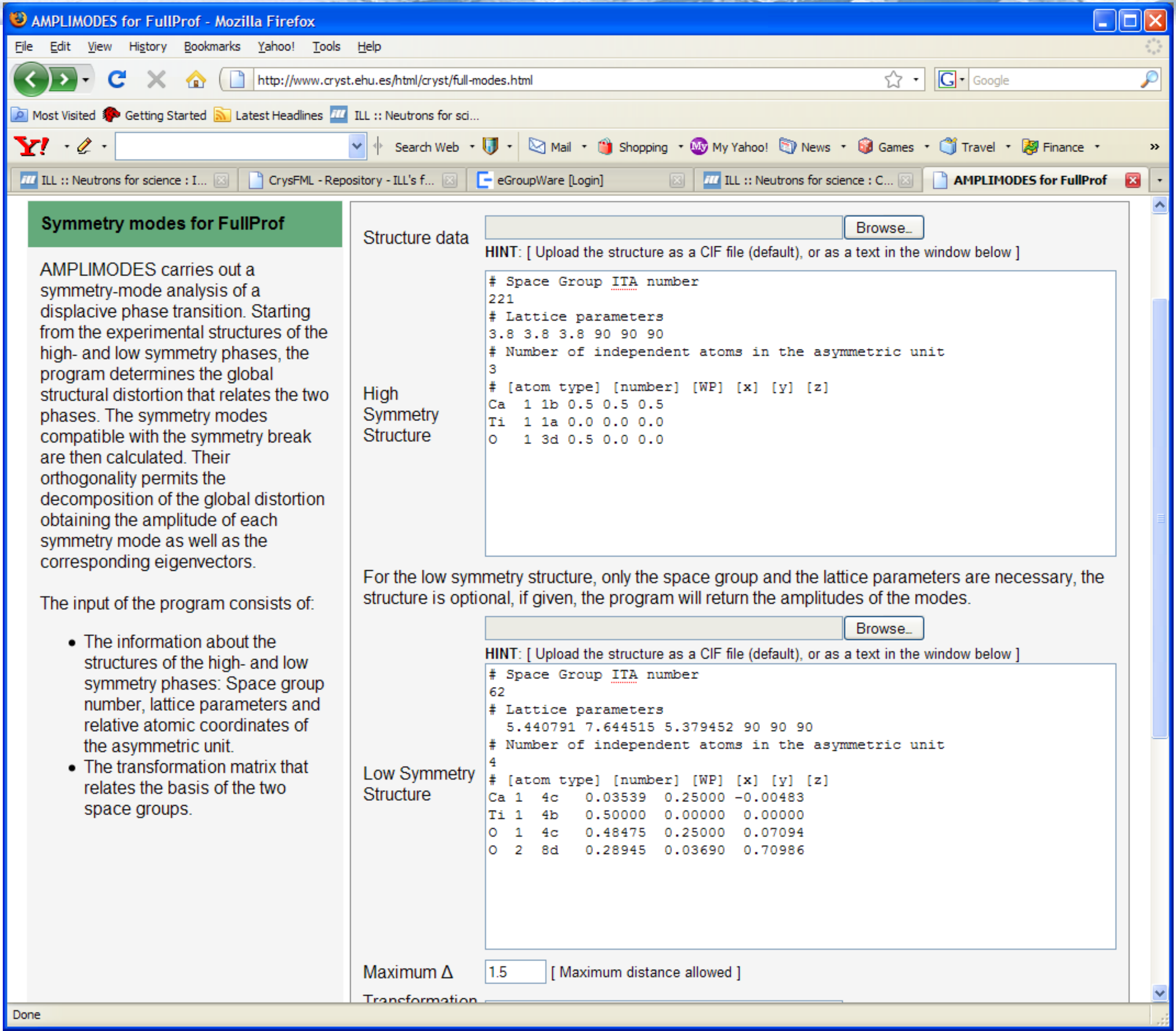
SAM	Spectral Active Modes (IR and RAMAN Selection Rules)
NEUTRON	Neutron Scattering Selection Rules
SYMMODES	Primary and Secondary Modes for a Group - Subgroup pair
AMPLIMODES	Symmetry Mode Analysis
PSEUDO	Pseudosymmetry Search in a Structure
DOPE	Degree of Pseudosymmetry Estimation
BPLOT	Pseudosymmetry Search with KPLOT
TRANPATH	Transition Paths (Group not subgroup relations)

Structure Utilities

CELLTRAN	Transform Unit Cells
STRAIN	Strain Tensor Calculation
WPASSIGN	Assignment of Wyckoff Positions
TRANSTRU	Transform structures to lower symmetry Space Group basis.
SETSTRU	Alternative Settings for a given Crystal Structure
EQUIVSTRU	Equivalent Descriptions for a given Crystal Structure

Subperiodic Groups: Layer, Rod and Frieze Groups Retrieval Tools

AMPLIMODES: Bilbao Crystallographic Server



Symmetry modes for FullProf

AMPLIMODES carries out a symmetry-mode analysis of a displacive phase transition. Starting from the experimental structures of the high- and low symmetry phases, the program determines the global structural distortion that relates the two phases. The symmetry modes compatible with the symmetry break are then calculated. Their orthogonality permits the decomposition of the global distortion obtaining the amplitude of each symmetry mode as well as the corresponding eigenvectors.

The input of the program consists of:

- The information about the structures of the high- and low symmetry phases: Space group number, lattice parameters and relative atomic coordinates of the asymmetric unit.
- The transformation matrix that relates the basis of the two space groups.

Structure data

HINT: [Upload the structure as a CIF file (default), or as a text in the window below]

High Symmetry Structure

```
# Space Group ITA number
221
# Lattice parameters
3.8 3.8 3.8 90 90 90
# Number of independent atoms in the asymmetric unit
3
# [atom type] [number] [WP] [x] [y] [z]
Ca  1 1b 0.5 0.5 0.5
Ti  1 1a 0.0 0.0 0.0
O   1 3d 0.5 0.0 0.0
```

For the low symmetry structure, only the space group and the lattice parameters are necessary, the structure is optional, if given, the program will return the amplitudes of the modes.

HINT: [Upload the structure as a CIF file (default), or as a text in the window below]

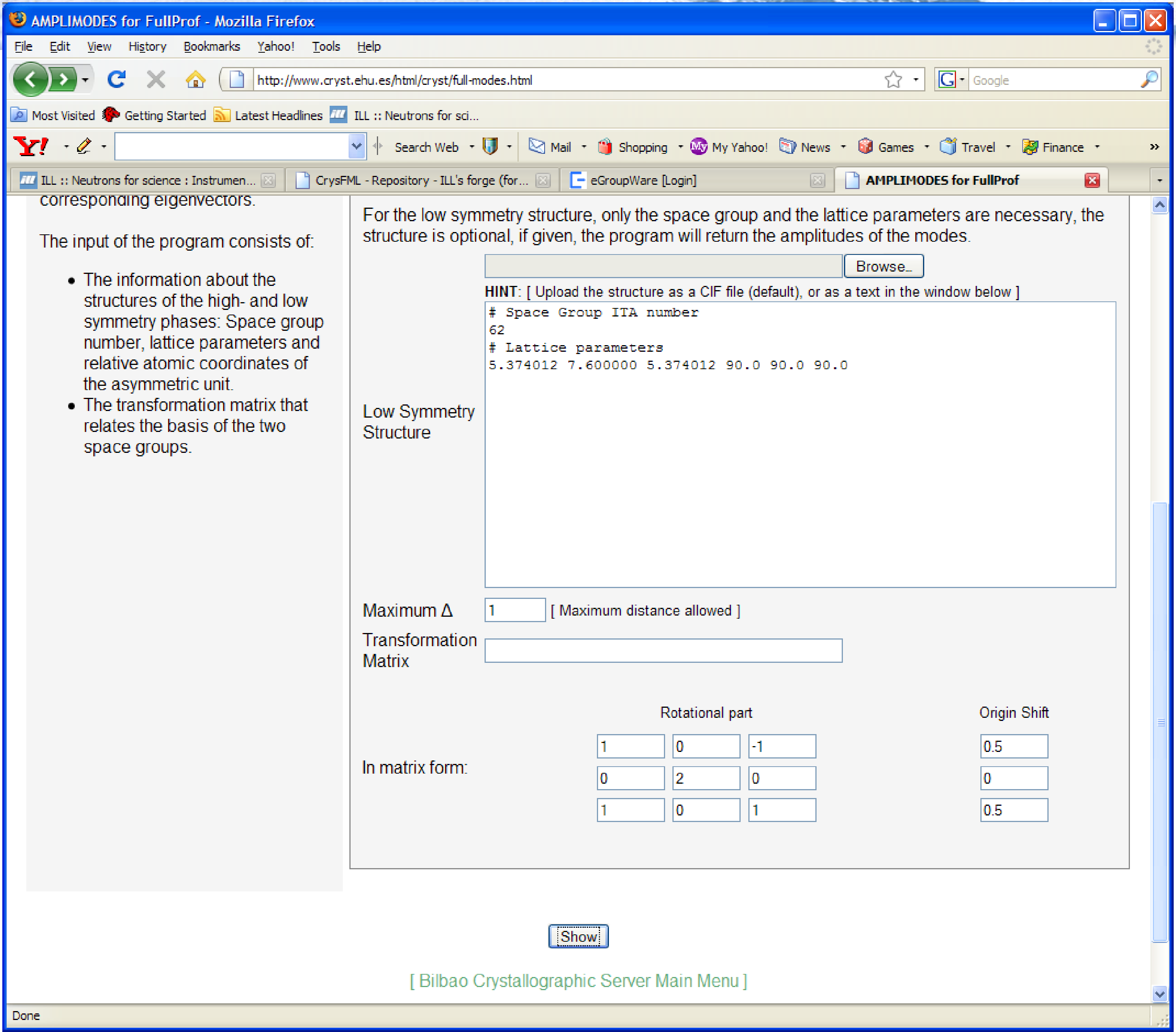
Low Symmetry Structure

```
# Space Group ITA number
62
# Lattice parameters
  5.440791 7.644515 5.379452 90 90 90
# Number of independent atoms in the asymmetric unit
4
# [atom type] [number] [WP] [x] [y] [z]
Ca 1  4c   0.03539  0.25000 -0.00483
Ti 1  4b   0.50000  0.00000  0.00000
O  1  4c   0.48475  0.25000  0.07094
O  2  8d   0.28945  0.03690  0.70986
```

Maximum Δ 1.5 [Maximum distance allowed]

Transformation

AMPLIMODES: Bilbao Crystallographic Server



corresponding eigenvectors.

The input of the program consists of:

- The information about the structures of the high- and low symmetry phases: Space group number, lattice parameters and relative atomic coordinates of the asymmetric unit.
- The transformation matrix that relates the basis of the two space groups.

For the low symmetry structure, only the space group and the lattice parameters are necessary, the structure is optional, if given, the program will return the amplitudes of the modes.

HINT: [Upload the structure as a CIF file (default), or as a text in the window below]

Low Symmetry Structure

```
# Space Group ITA number
62
# Lattice parameters
5.374012 7.600000 5.374012 90.0 90.0 90.0
```

Maximum Δ: 1 [Maximum distance allowed]

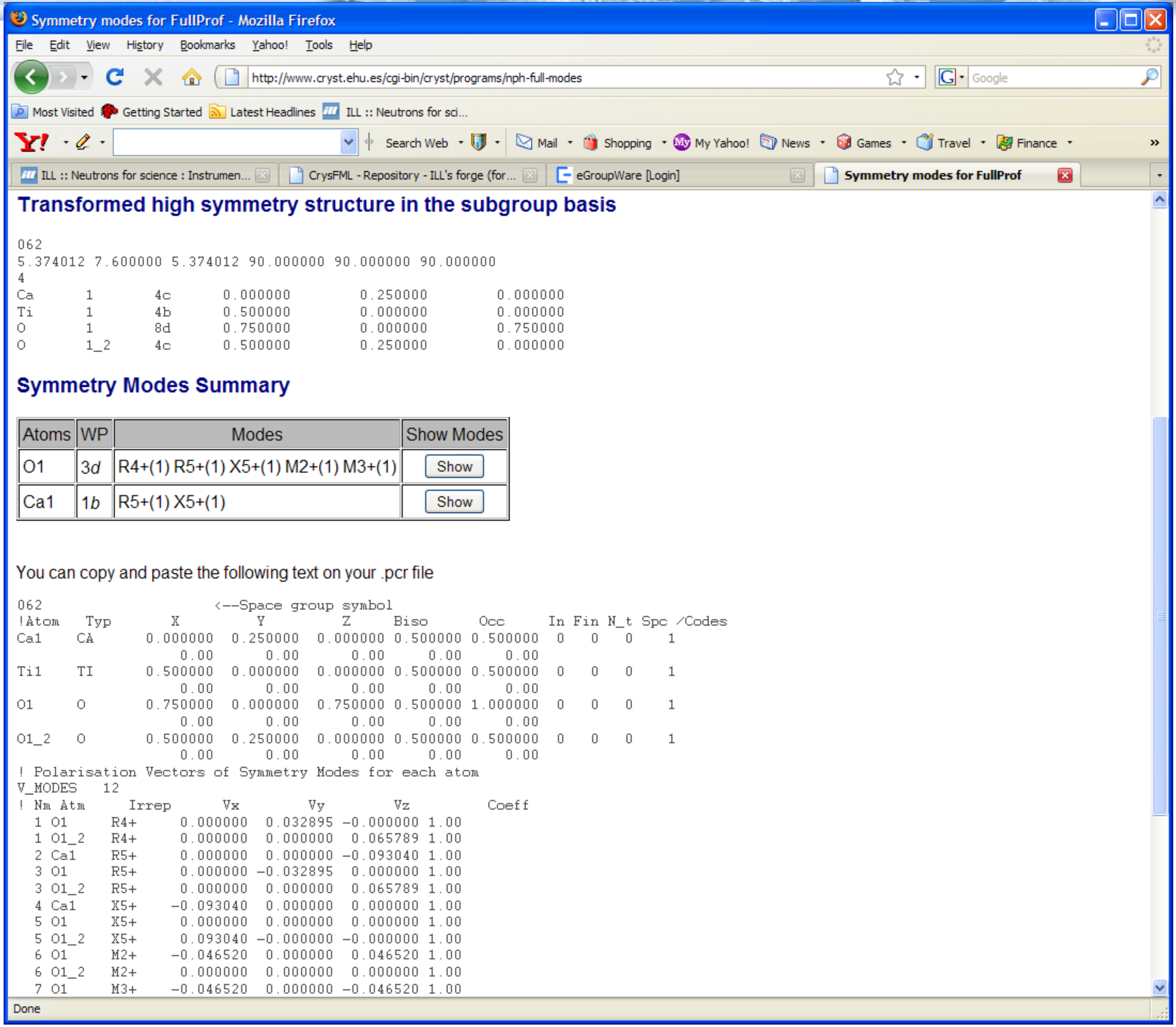
Transformation Matrix

In matrix form:

	Rotational part			Origin Shift
	1	0	-1	0.5
	0	2	0	0
	1	0	1	0.5

[Bilbao Crystallographic Server Main Menu]

AMPLIMODES: Bilbao Crystallographic Server



Transformed high symmetry structure in the subgroup basis

```
062
5.374012 7.600000 5.374012 90.000000 90.000000 90.000000
4
Ca       1       4c       0.000000         0.250000         0.000000
Ti       1       4b       0.500000         0.000000         0.000000
O        1       8d       0.750000         0.000000         0.750000
O        1_2     4c       0.500000         0.250000         0.000000
```

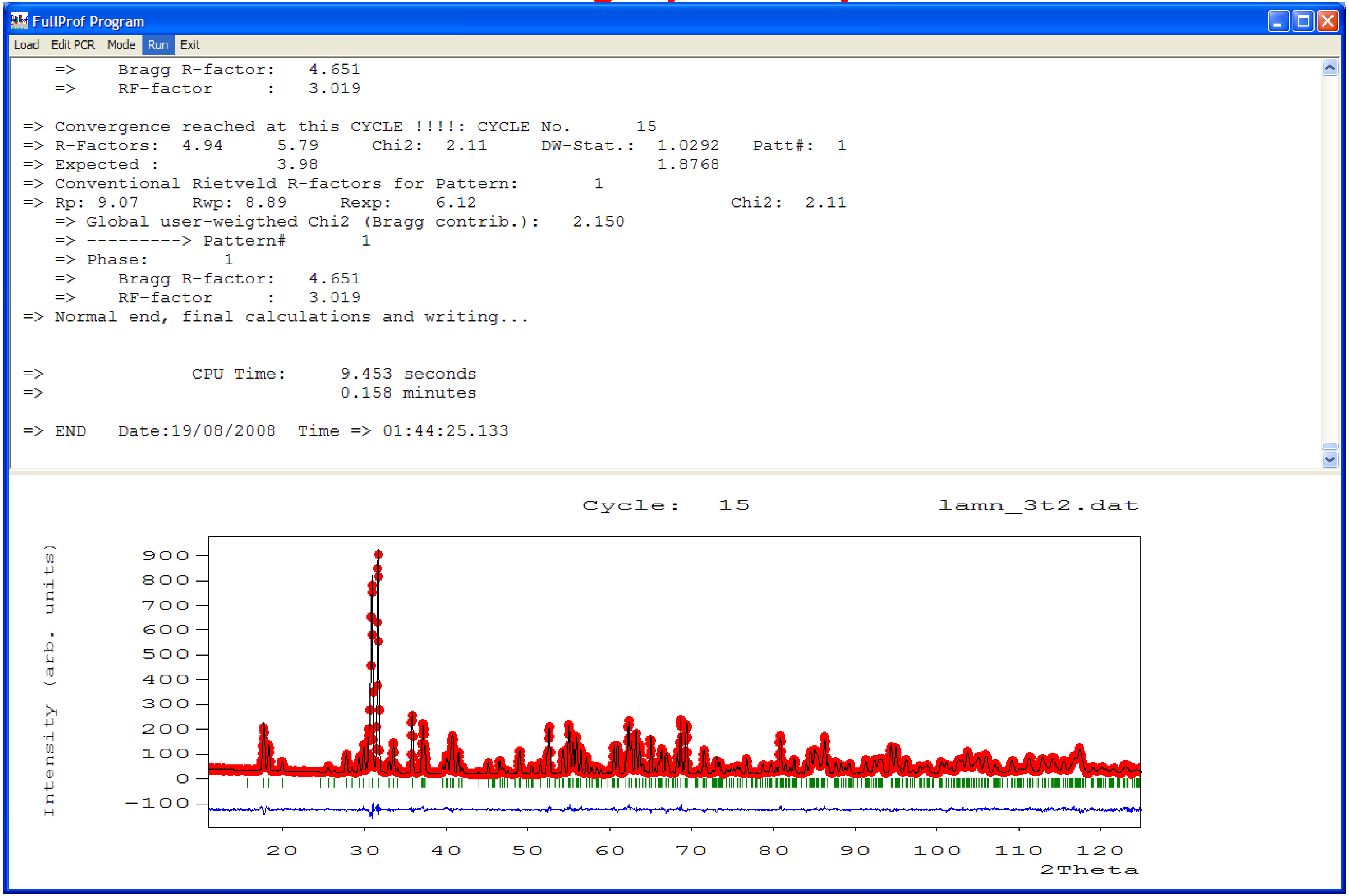
Symmetry Modes Summary

Atoms	WP	Modes	Show Modes
O1	3*d*	R4+(1) R5+(1) X5+(1) M2+(1) M3+(1)	Show
Ca1	1*b*	R5+(1) X5+(1)	Show

You can copy and paste the following text on your .pcr file

```
062                      <--Space group symbol
!Atom   Typ       X          Y          Z      Biso       Occ      In Fin N_t Spc /Codes
Ca1     CA     0.000000   0.250000   0.000000 0.500000 0.500000   0    0    0     1
                   0.00       0.00       0.00      0.00      0.00
Ti1     TI     0.500000   0.000000   0.000000 0.500000 0.500000   0    0    0     1
                   0.00       0.00       0.00      0.00      0.00
O1      O      0.750000   0.000000   0.750000 0.500000 1.000000   0    0    0     1
                   0.00       0.00       0.00      0.00      0.00
O1_2    O      0.500000   0.250000   0.000000 0.500000 0.500000   0    0    0     1
                   0.00       0.00       0.00      0.00      0.00
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES   12
! Nm Atm      Irrep      Vx         Vy         Vz         Coeff
  1 O1      R4+      0.000000   0.032895 -0.000000 1.00
  1 O1_2    R4+      0.000000   0.000000  0.065789 1.00
  2 Ca1     R5+      0.000000   0.000000 -0.093040 1.00
  3 O1      R5+      0.000000 -0.032895  0.000000 1.00
  3 O1_2    R5+      0.000000   0.000000  0.065789 1.00
  4 Ca1     X5+     -0.093040   0.000000  0.000000 1.00
  5 O1      X5+      0.000000   0.000000  0.000000 1.00
  5 O1_2    X5+      0.093040 -0.000000 -0.000000 1.00
  6 O1      M2+     -0.046520   0.000000  0.046520 1.00
  6 O1_2    M2+      0.000000   0.000000  0.000000 1.00
  7 O1      M3+     -0.046520   0.000000 -0.046520 1.00
```

Example of *FullProf* running a refinement of LaMnO3 using symmetry modes

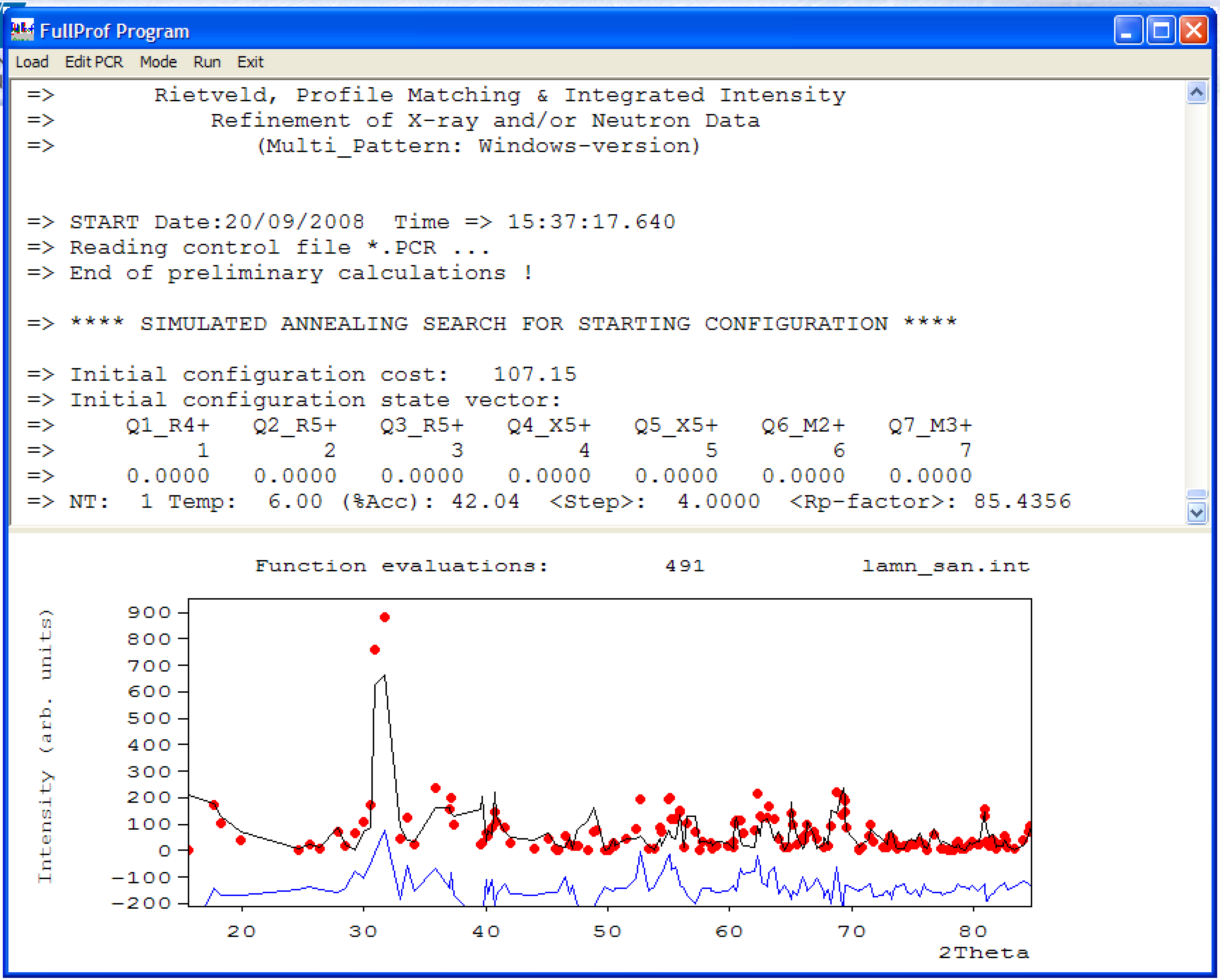


```
    =>     Bragg R-factor:    4.651
    =>     RF-factor      :   3.019

 => Convergence reached at this CYCLE !!!!: CYCLE No.       15
 => R-Factors:  4.94      5.79      Chi2:  2.11      DW-Stat.:  1.0292    Patt#:  1
 => Expected :            3.98                                1.8768
 => Conventional Rietveld R-factors for Pattern:        1
 => Rp: 9.07      Rwp: 8.89      Rexp:     6.12                         Chi2:  2.11
    => Global user-weigthed Chi2 (Bragg contrib.):   2.150
    => ---------> Pattern#        1
    => Phase:        1
    =>     Bragg R-factor:    4.651
    =>     RF-factor      :   3.019
 => Normal end, final calculations and writing...


 =>              CPU Time:      9.453 seconds
 =>                             0.158 minutes

 => END    Date:19/08/2008   Time => 01:44:25.133
```



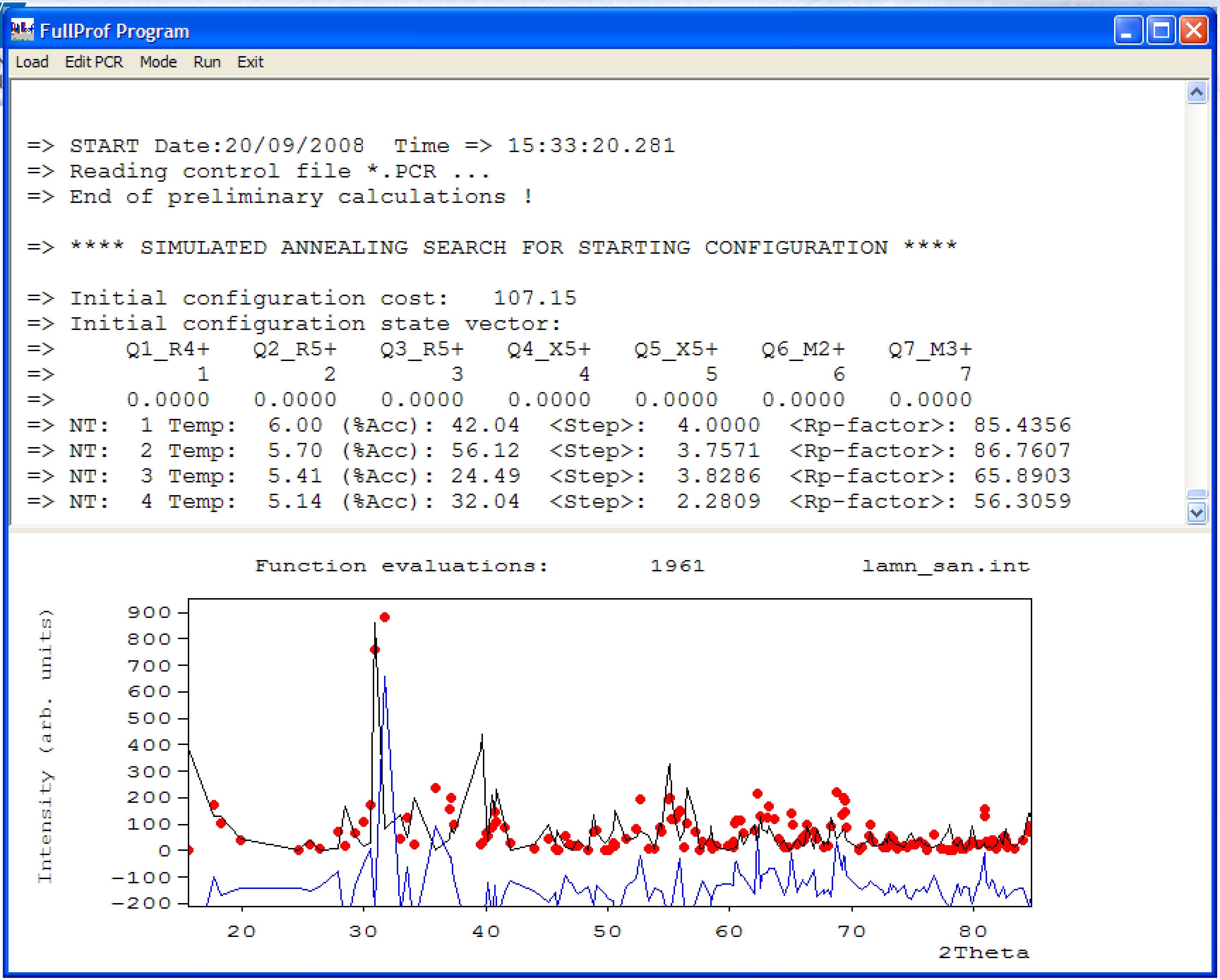
```
=>        Rietveld, Profile Matching & Integrated Intensity
=>            Refinement of X-ray and/or Neutron Data
=>               (Multi_Pattern: Windows-version)


=> START Date:20/09/2008  Time => 15:37:17.640
=> Reading control file *.PCR ...
=> End of preliminary calculations !

=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

=> Initial configuration cost:   107.15
=> Initial configuration state vector:
=>     Q1_R4+    Q2_R5+    Q3_R5+    Q4_X5+    Q5_X5+    Q6_M2+    Q7_M3+
=>          1         2         3         4         5         6         7
=>     0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000
=> NT:  1 Temp:  6.00 (%Acc): 42.04  <Step>:  4.0000  <Rp-factor>: 85.4356
```

```
Function evaluations:        491           lamn_san.int
```

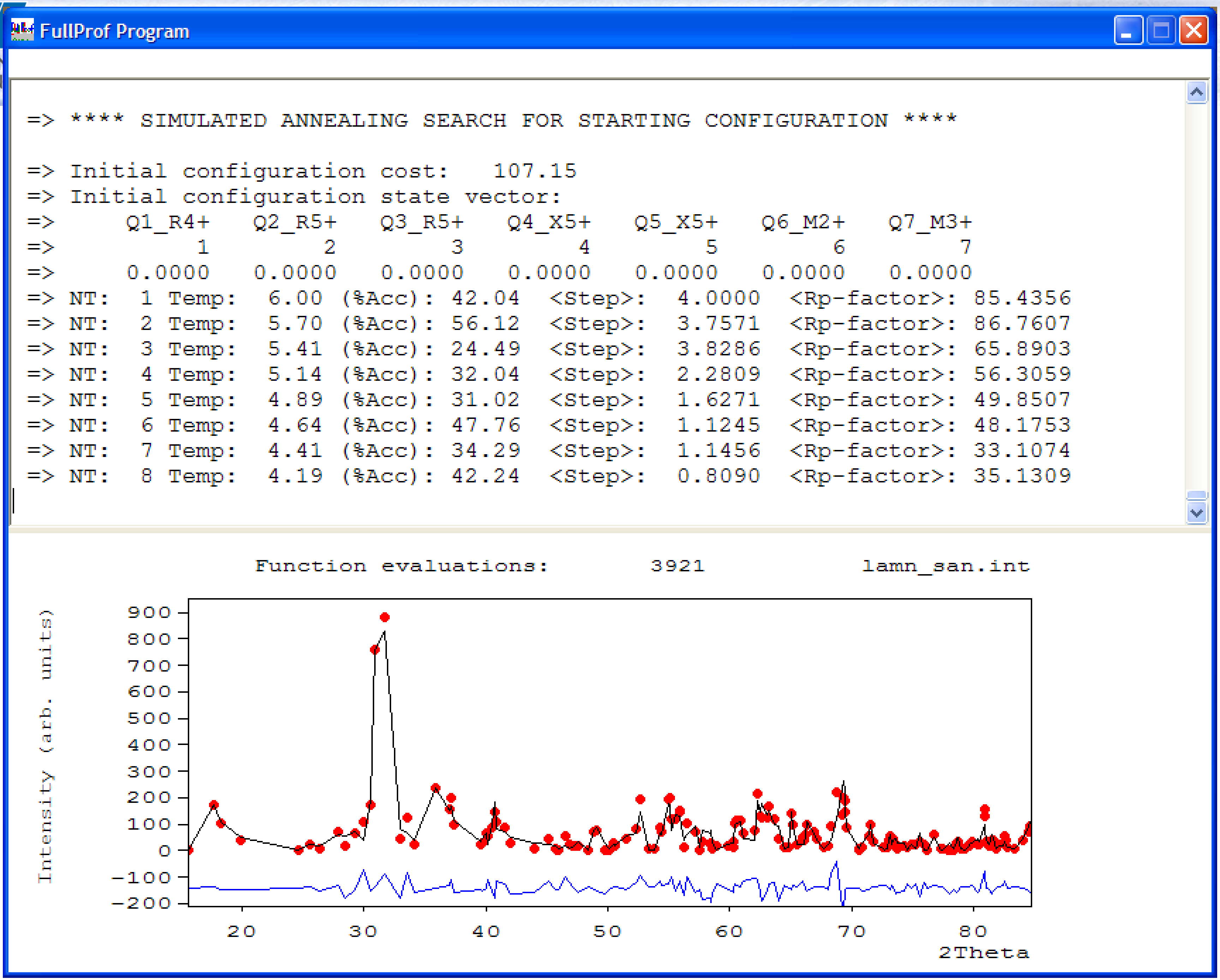


```
=> START Date:20/09/2008  Time => 15:33:20.281
=> Reading control file *.PCR ...
=> End of preliminary calculations !

=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

=> Initial configuration cost:   107.15
=> Initial configuration state vector:
=>     Q1_R4+    Q2_R5+    Q3_R5+    Q4_X5+    Q5_X5+    Q6_M2+    Q7_M3+
=>          1         2         3         4         5         6         7
=>     0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000
=> NT:  1 Temp:  6.00 (%Acc): 42.04  <Step>:  4.0000  <Rp-factor>: 85.4356
=> NT:  2 Temp:  5.70 (%Acc): 56.12  <Step>:  3.7571  <Rp-factor>: 86.7607
=> NT:  3 Temp:  5.41 (%Acc): 24.49  <Step>:  3.8286  <Rp-factor>: 65.8903
=> NT:  4 Temp:  5.14 (%Acc): 32.04  <Step>:  2.2809  <Rp-factor>: 56.3059
```

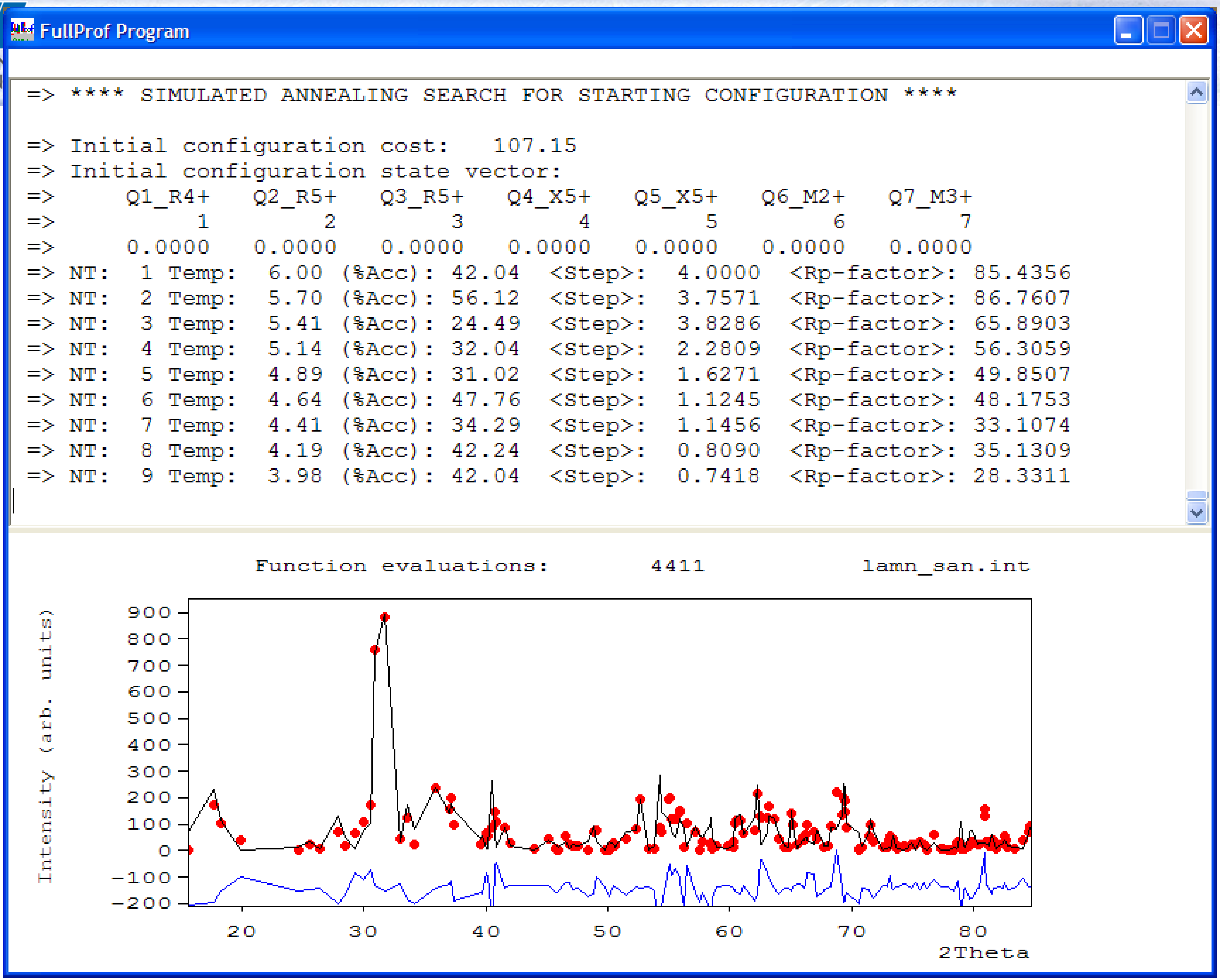
```
Function evaluations:       1961          lamn_san.int
```



```
=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

=> Initial configuration cost:   107.15
=> Initial configuration state vector:
=>      Q1_R4+    Q2_R5+    Q3_R5+    Q4_X5+    Q5_X5+    Q6_M2+    Q7_M3+
=>           1         2         3         4         5         6         7
=>      0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000
=> NT:   1 Temp:   6.00 (%Acc): 42.04  <Step>:   4.0000  <Rp-factor>: 85.4356
=> NT:   2 Temp:   5.70 (%Acc): 56.12  <Step>:   3.7571  <Rp-factor>: 86.7607
=> NT:   3 Temp:   5.41 (%Acc): 24.49  <Step>:   3.8286  <Rp-factor>: 65.8903
=> NT:   4 Temp:   5.14 (%Acc): 32.04  <Step>:   2.2809  <Rp-factor>: 56.3059
=> NT:   5 Temp:   4.89 (%Acc): 31.02  <Step>:   1.6271  <Rp-factor>: 49.8507
=> NT:   6 Temp:   4.64 (%Acc): 47.76  <Step>:   1.1245  <Rp-factor>: 48.1753
=> NT:   7 Temp:   4.41 (%Acc): 34.29  <Step>:   1.1456  <Rp-factor>: 33.1074
=> NT:   8 Temp:   4.19 (%Acc): 42.24  <Step>:   0.8090  <Rp-factor>: 35.1309
```

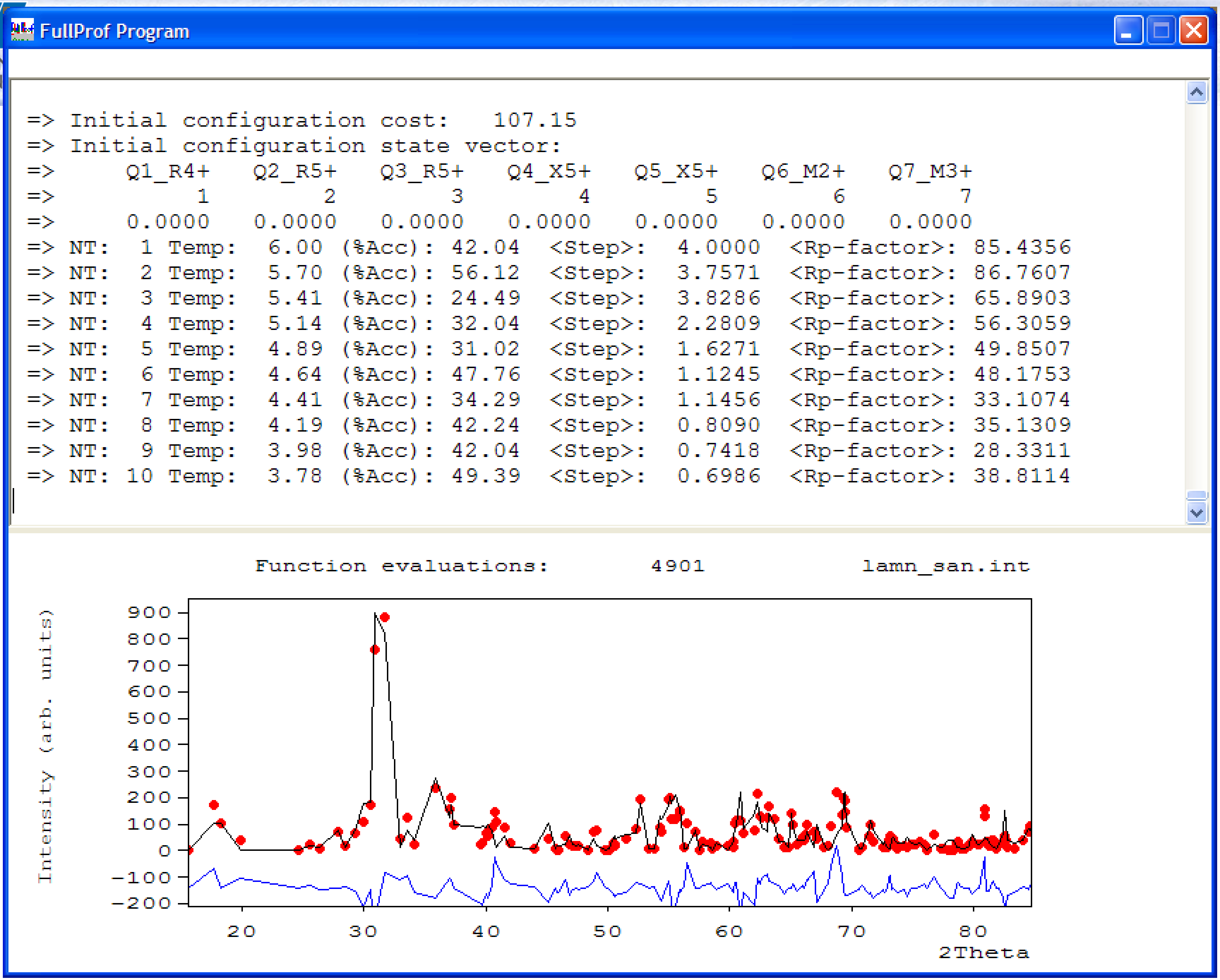
```
Function evaluations:        3921              lamn_san.int
```



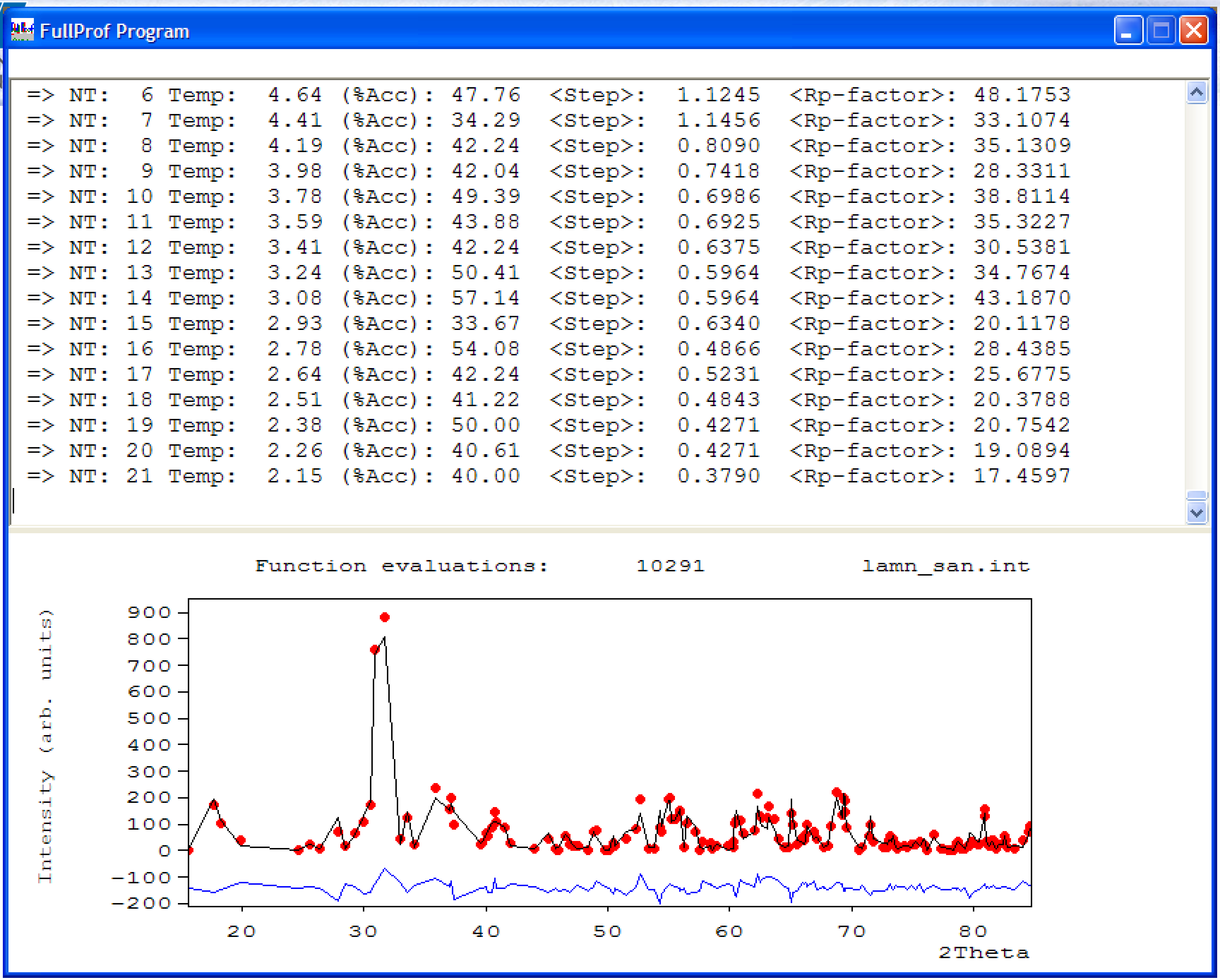
```
=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

=> Initial configuration cost:    107.15
=> Initial configuration state vector:
=>     Q1_R4+    Q2_R5+    Q3_R5+    Q4_X5+    Q5_X5+    Q6_M2+    Q7_M3+
=>          1         2         3         4         5         6         7
=>     0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000
=> NT:   1 Temp:   6.00 (%Acc): 42.04  <Step>:   4.0000  <Rp-factor>: 85.4356
=> NT:   2 Temp:   5.70 (%Acc): 56.12  <Step>:   3.7571  <Rp-factor>: 86.7607
=> NT:   3 Temp:   5.41 (%Acc): 24.49  <Step>:   3.8286  <Rp-factor>: 65.8903
=> NT:   4 Temp:   5.14 (%Acc): 32.04  <Step>:   2.2809  <Rp-factor>: 56.3059
=> NT:   5 Temp:   4.89 (%Acc): 31.02  <Step>:   1.6271  <Rp-factor>: 49.8507
=> NT:   6 Temp:   4.64 (%Acc): 47.76  <Step>:   1.1245  <Rp-factor>: 48.1753
=> NT:   7 Temp:   4.41 (%Acc): 34.29  <Step>:   1.1456  <Rp-factor>: 33.1074
=> NT:   8 Temp:   4.19 (%Acc): 42.24  <Step>:   0.8090  <Rp-factor>: 35.1309
=> NT:   9 Temp:   3.98 (%Acc): 42.04  <Step>:   0.7418  <Rp-factor>: 28.3311
```

Function evaluations: 4411   lamn_san.int

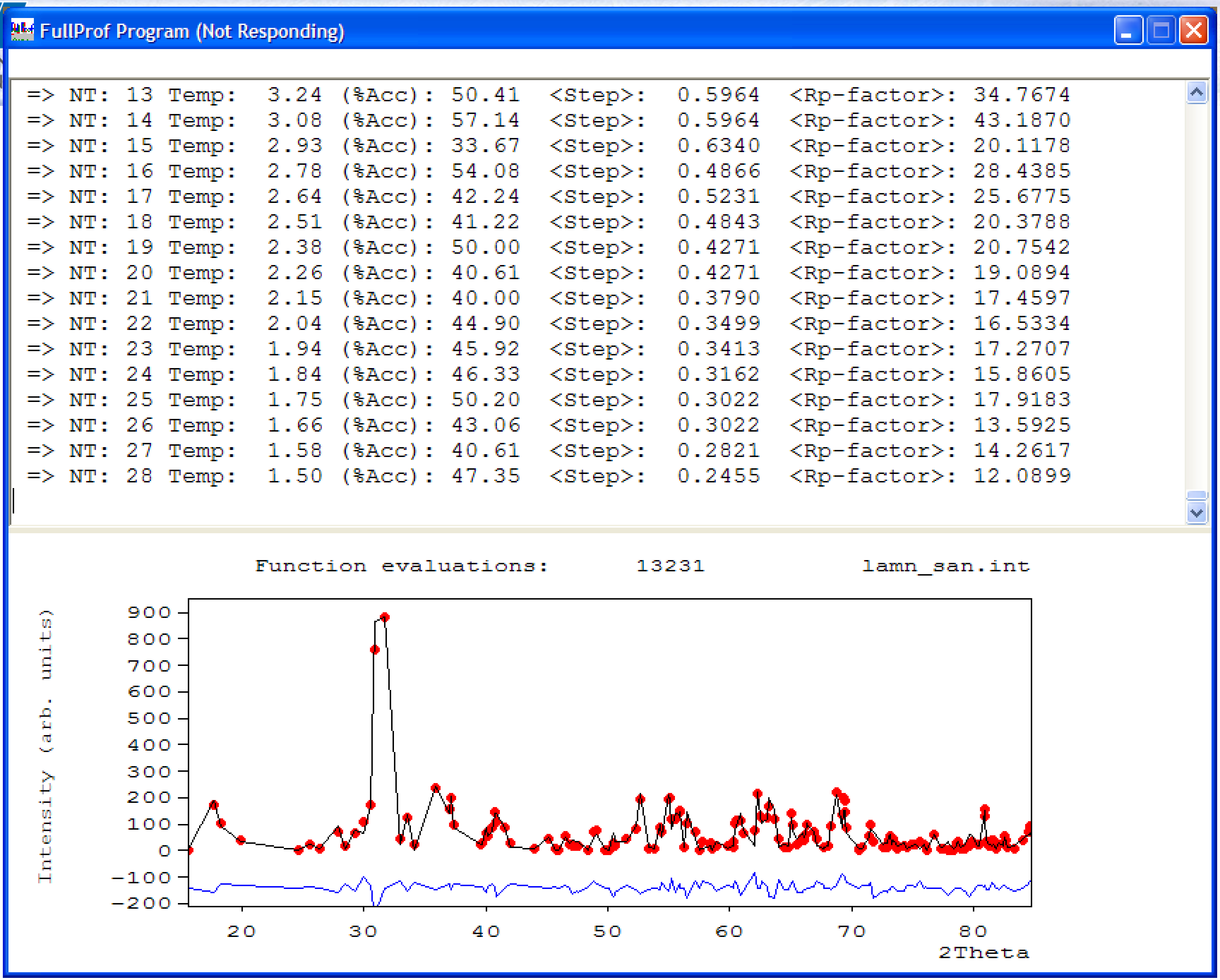


```
=> Initial configuration cost:   107.15
=> Initial configuration state vector:
=>      Q1_R4+    Q2_R5+    Q3_R5+    Q4_X5+    Q5_X5+    Q6_M2+    Q7_M3+
=>           1         2         3         4         5         6         7
=>      0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000
=> NT:  1 Temp:  6.00 (%Acc): 42.04  <Step>:  4.0000  <Rp-factor>: 85.4356
=> NT:  2 Temp:  5.70 (%Acc): 56.12  <Step>:  3.7571  <Rp-factor>: 86.7607
=> NT:  3 Temp:  5.41 (%Acc): 24.49  <Step>:  3.8286  <Rp-factor>: 65.8903
=> NT:  4 Temp:  5.14 (%Acc): 32.04  <Step>:  2.2809  <Rp-factor>: 56.3059
=> NT:  5 Temp:  4.89 (%Acc): 31.02  <Step>:  1.6271  <Rp-factor>: 49.8507
=> NT:  6 Temp:  4.64 (%Acc): 47.76  <Step>:  1.1245  <Rp-factor>: 48.1753
=> NT:  7 Temp:  4.41 (%Acc): 34.29  <Step>:  1.1456  <Rp-factor>: 33.1074
=> NT:  8 Temp:  4.19 (%Acc): 42.24  <Step>:  0.8090  <Rp-factor>: 35.1309
=> NT:  9 Temp:  3.98 (%Acc): 42.04  <Step>:  0.7418  <Rp-factor>: 28.3311
=> NT: 10 Temp:  3.78 (%Acc): 49.39  <Step>:  0.6986  <Rp-factor>: 38.8114
```



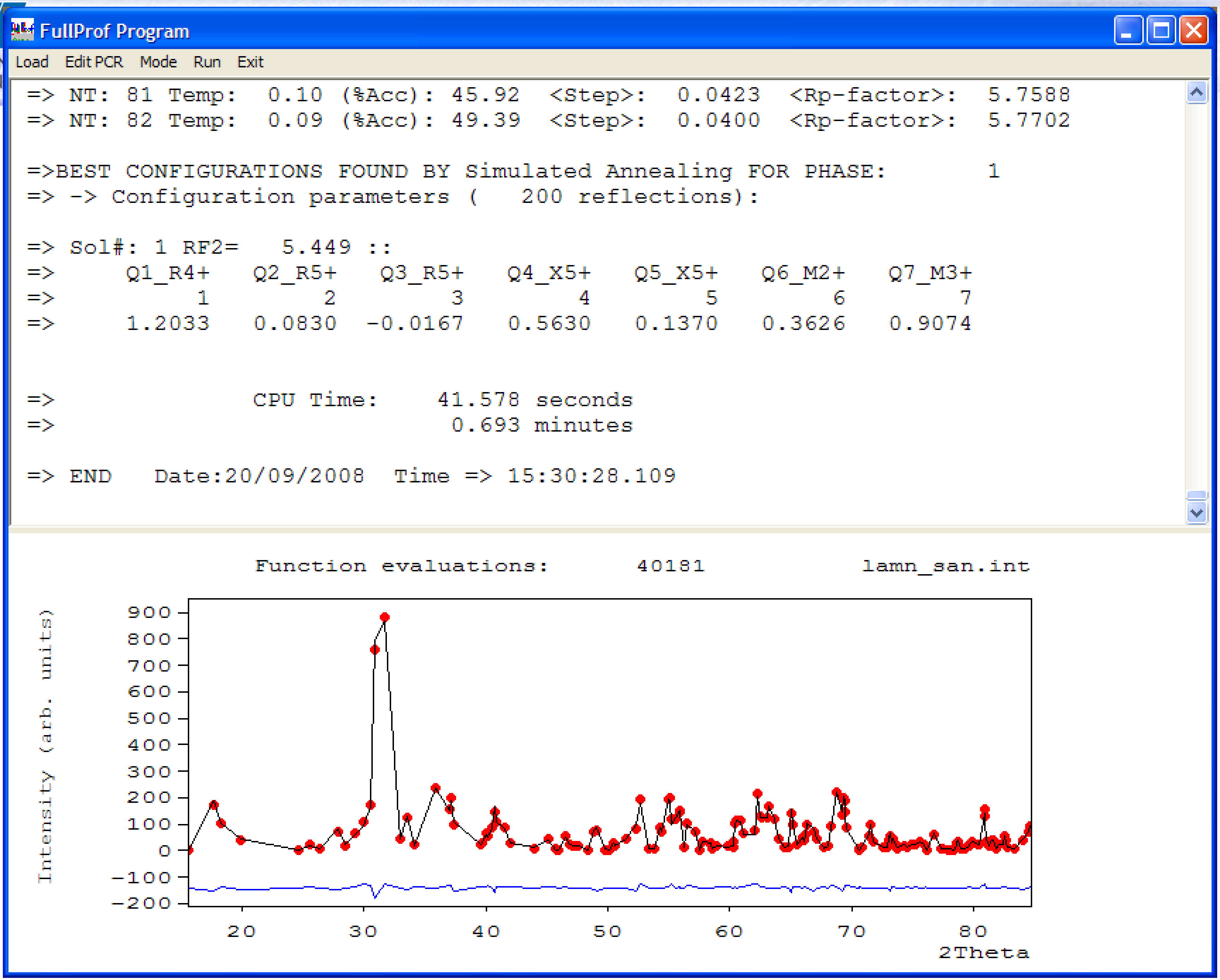
```
=> NT:   6 Temp:   4.64 (%Acc): 47.76  <Step>:   1.1245  <Rp-factor>: 48.1753
=> NT:   7 Temp:   4.41 (%Acc): 34.29  <Step>:   1.1456  <Rp-factor>: 33.1074
=> NT:   8 Temp:   4.19 (%Acc): 42.24  <Step>:   0.8090  <Rp-factor>: 35.1309
=> NT:   9 Temp:   3.98 (%Acc): 42.04  <Step>:   0.7418  <Rp-factor>: 28.3311
=> NT:  10 Temp:   3.78 (%Acc): 49.39  <Step>:   0.6986  <Rp-factor>: 38.8114
=> NT:  11 Temp:   3.59 (%Acc): 43.88  <Step>:   0.6925  <Rp-factor>: 35.3227
=> NT:  12 Temp:   3.41 (%Acc): 42.24  <Step>:   0.6375  <Rp-factor>: 30.5381
=> NT:  13 Temp:   3.24 (%Acc): 50.41  <Step>:   0.5964  <Rp-factor>: 34.7674
=> NT:  14 Temp:   3.08 (%Acc): 57.14  <Step>:   0.5964  <Rp-factor>: 43.1870
=> NT:  15 Temp:   2.93 (%Acc): 33.67  <Step>:   0.6340  <Rp-factor>: 20.1178
=> NT:  16 Temp:   2.78 (%Acc): 54.08  <Step>:   0.4866  <Rp-factor>: 28.4385
=> NT:  17 Temp:   2.64 (%Acc): 42.24  <Step>:   0.5231  <Rp-factor>: 25.6775
=> NT:  18 Temp:   2.51 (%Acc): 41.22  <Step>:   0.4843  <Rp-factor>: 20.3788
=> NT:  19 Temp:   2.38 (%Acc): 50.00  <Step>:   0.4271  <Rp-factor>: 20.7542
=> NT:  20 Temp:   2.26 (%Acc): 40.61  <Step>:   0.4271  <Rp-factor>: 19.0894
=> NT:  21 Temp:   2.15 (%Acc): 40.00  <Step>:   0.3790  <Rp-factor>: 17.4597
```

```
Function evaluations:      10291          lamn_san.int
```



```
=> NT: 13 Temp:   3.24 (%Acc): 50.41  <Step>:   0.5964  <Rp-factor>: 34.7674
=> NT: 14 Temp:   3.08 (%Acc): 57.14  <Step>:   0.5964  <Rp-factor>: 43.1870
=> NT: 15 Temp:   2.93 (%Acc): 33.67  <Step>:   0.6340  <Rp-factor>: 20.1178
=> NT: 16 Temp:   2.78 (%Acc): 54.08  <Step>:   0.4866  <Rp-factor>: 28.4385
=> NT: 17 Temp:   2.64 (%Acc): 42.24  <Step>:   0.5231  <Rp-factor>: 25.6775
=> NT: 18 Temp:   2.51 (%Acc): 41.22  <Step>:   0.4843  <Rp-factor>: 20.3788
=> NT: 19 Temp:   2.38 (%Acc): 50.00  <Step>:   0.4271  <Rp-factor>: 20.7542
=> NT: 20 Temp:   2.26 (%Acc): 40.61  <Step>:   0.4271  <Rp-factor>: 19.0894
=> NT: 21 Temp:   2.15 (%Acc): 40.00  <Step>:   0.3790  <Rp-factor>: 17.4597
=> NT: 22 Temp:   2.04 (%Acc): 44.90  <Step>:   0.3499  <Rp-factor>: 16.5334
=> NT: 23 Temp:   1.94 (%Acc): 45.92  <Step>:   0.3413  <Rp-factor>: 17.2707
=> NT: 24 Temp:   1.84 (%Acc): 46.33  <Step>:   0.3162  <Rp-factor>: 15.8605
=> NT: 25 Temp:   1.75 (%Acc): 50.20  <Step>:   0.3022  <Rp-factor>: 17.9183
=> NT: 26 Temp:   1.66 (%Acc): 43.06  <Step>:   0.3022  <Rp-factor>: 13.5925
=> NT: 27 Temp:   1.58 (%Acc): 40.61  <Step>:   0.2821  <Rp-factor>: 14.2617
=> NT: 28 Temp:   1.50 (%Acc): 47.35  <Step>:   0.2455  <Rp-factor>: 12.0899
```

```
Function evaluations:      13231          lamn_san.int
```



```
=> NT: 81 Temp:  0.10 (%Acc): 45.92  <Step>:  0.0423  <Rp-factor>:  5.7588
=> NT: 82 Temp:  0.09 (%Acc): 49.39  <Step>:  0.0400  <Rp-factor>:  5.7702

=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   200 reflections):

=> Sol#: 1 RF2=   5.449 ::
=>      Q1_R4+    Q2_R5+    Q3_R5+    Q4_X5+    Q5_X5+    Q6_M2+    Q7_M3+
=>           1         2         3         4         5         6         7
=>      1.2033    0.0830   -0.0167    0.5630    0.1370    0.3626    0.9074


=>              CPU Time:    41.578 seconds
=>                            0.693 minutes

=> END   Date:20/09/2008  Time => 15:30:28.109
```

```
Function evaluations:      40181            lamn_san.int
```

Visualisation of single modes using FullProf Studio

- A part from the normal FST file generated normally for the final crystal structure, **FullProf** outputs a series of FST files containing
- The “virtual structures” corresponding to single modes

  (e.g.   A_MODES   7   0 0 0 0 0 0 0)
- A representation of the high symmetry phase together with arrows indicating the displacement of atoms in the corresponding mode:

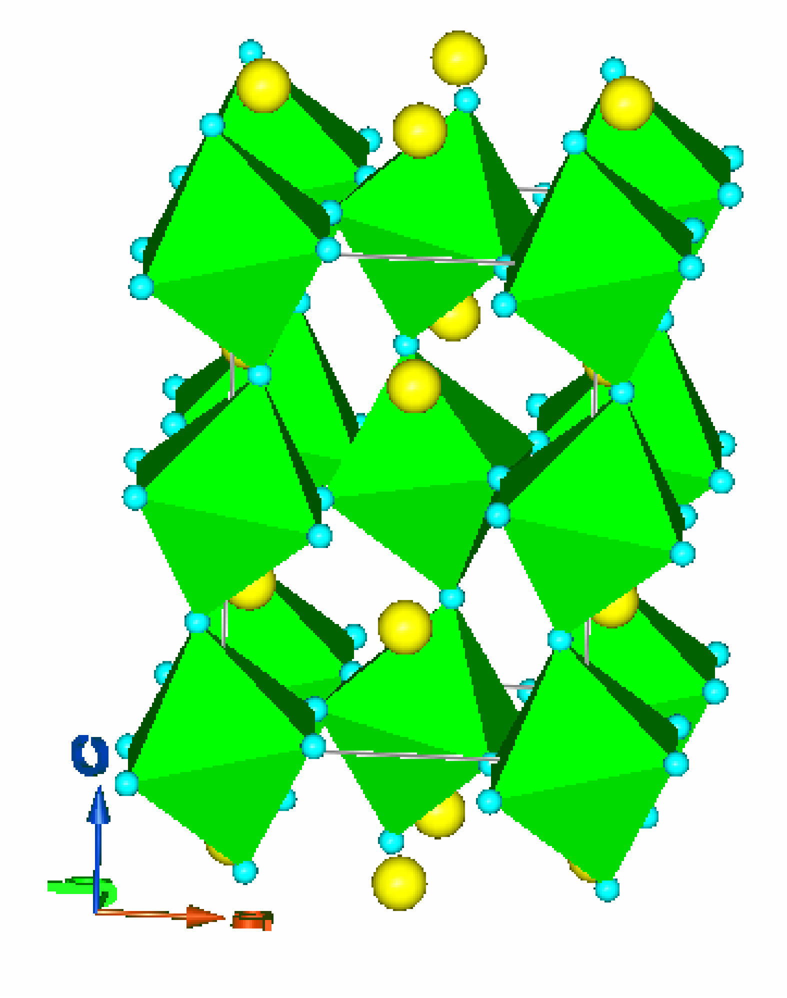
  (e.g.   A_MODES   7   1 1 1 1 1 1 1)
- Both kinds of representations depending on the mode

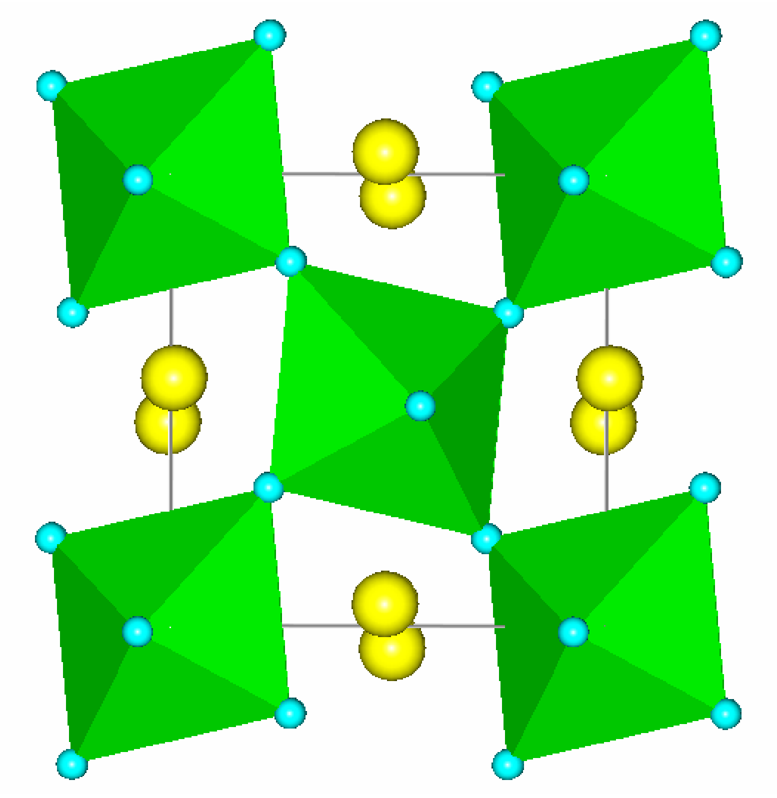
  (e.g.   A_MODES   7   1 0 0 1 1 0 1)

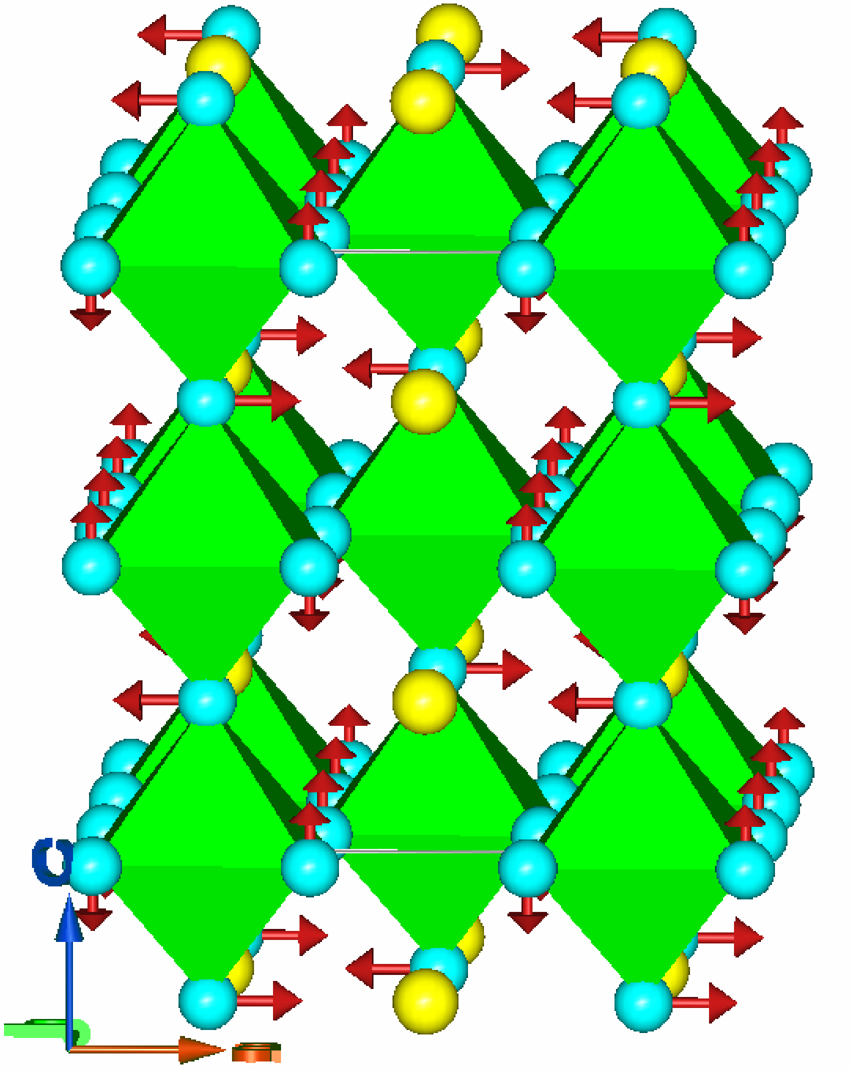
The items after the number of modes are:

p_mode(i)   i=1,... n_modes

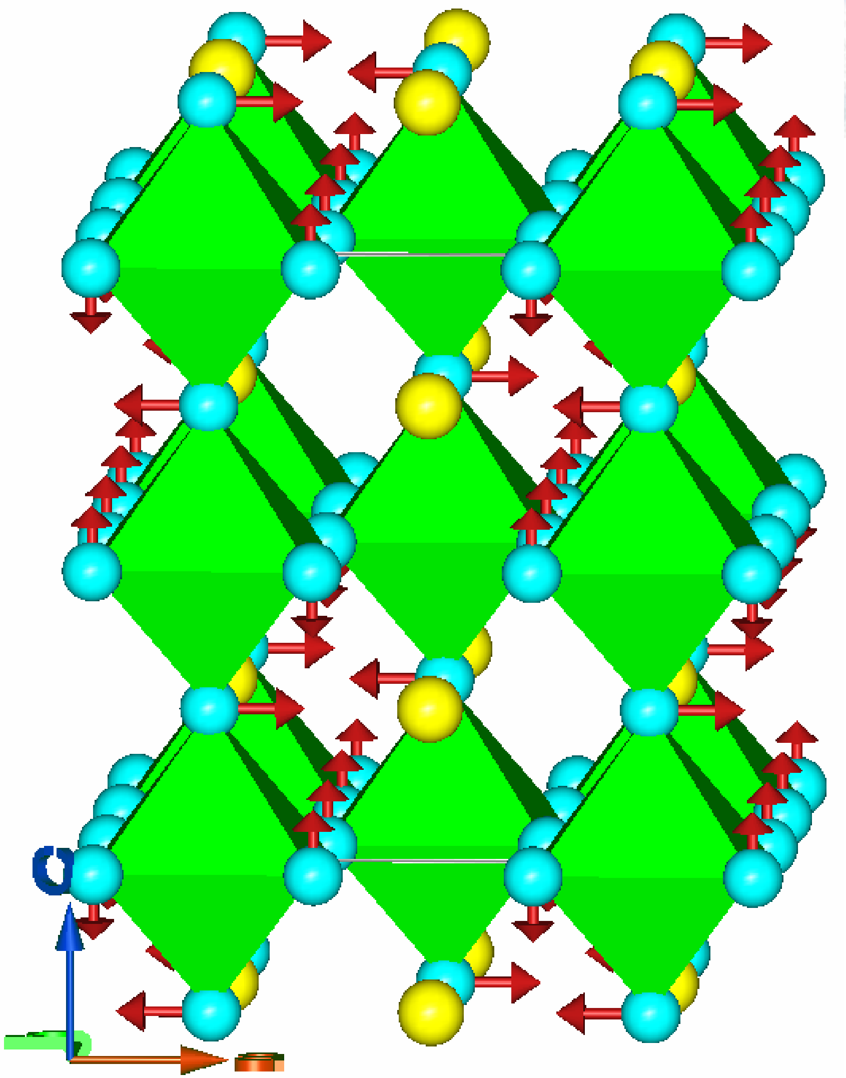
Crystal Structure of $LaMnO_3$



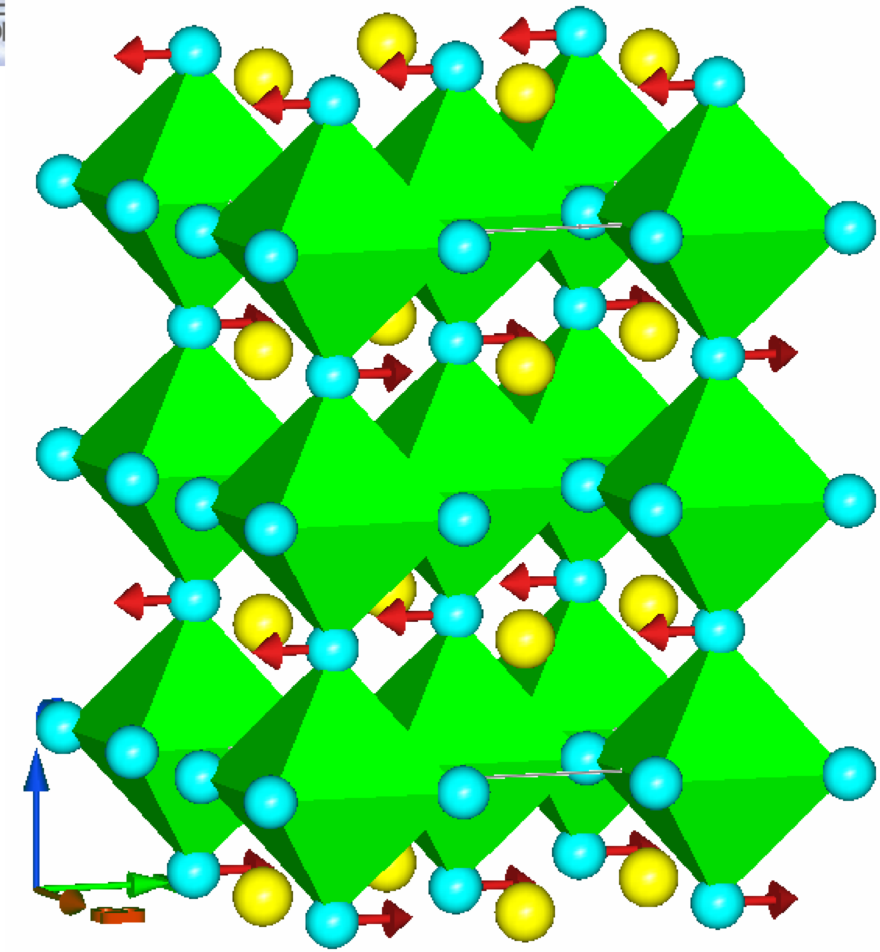


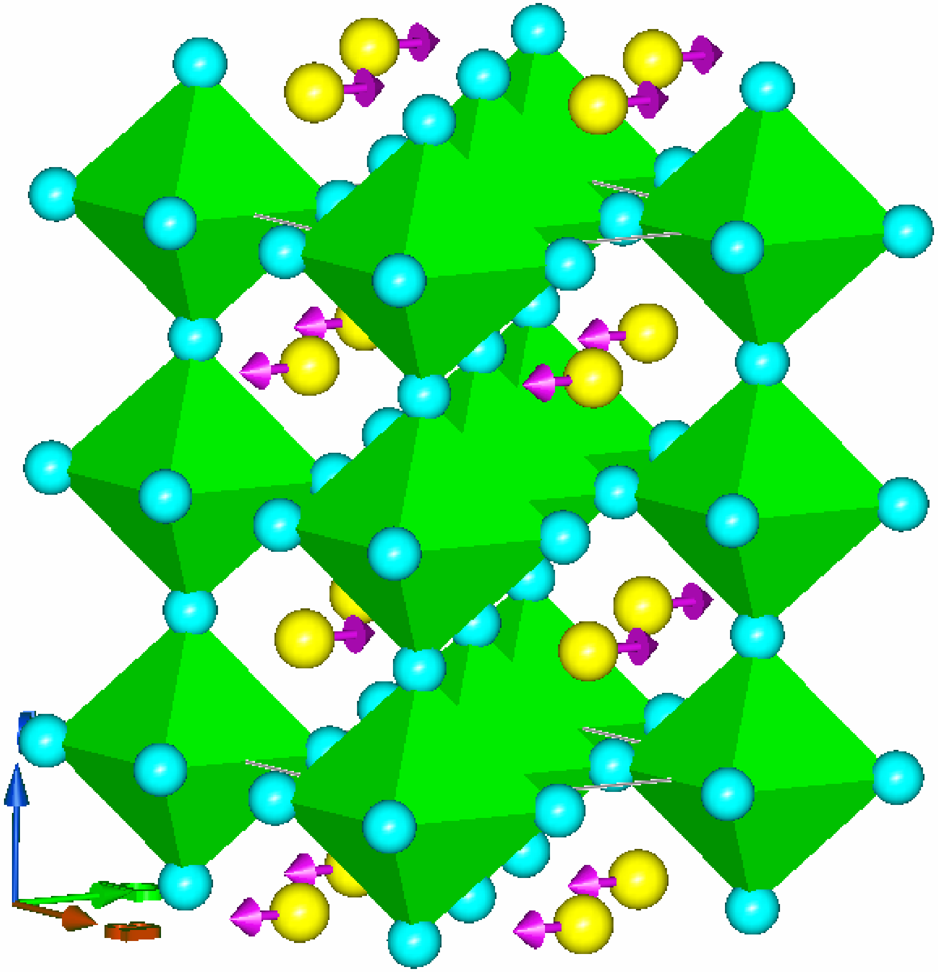


Mode 1, Q1_R4+ = -1.18968
O1 R4+ (0.0, 0.0, 0.031721)
O2 R4+ (0.063442, 0.0, 0.0)



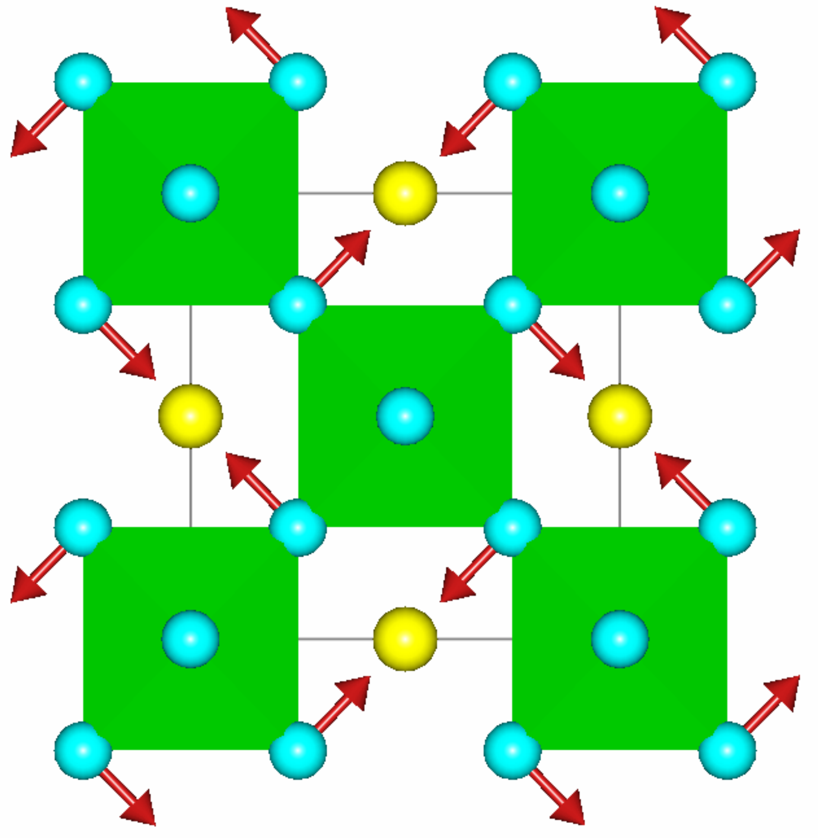
Mode 3, Q3_R5+ = 0.018171
O1 R5+ (0.0, 0.0, -0.031721)
O2 R5+ (0.063442, 0.0, 0.0)



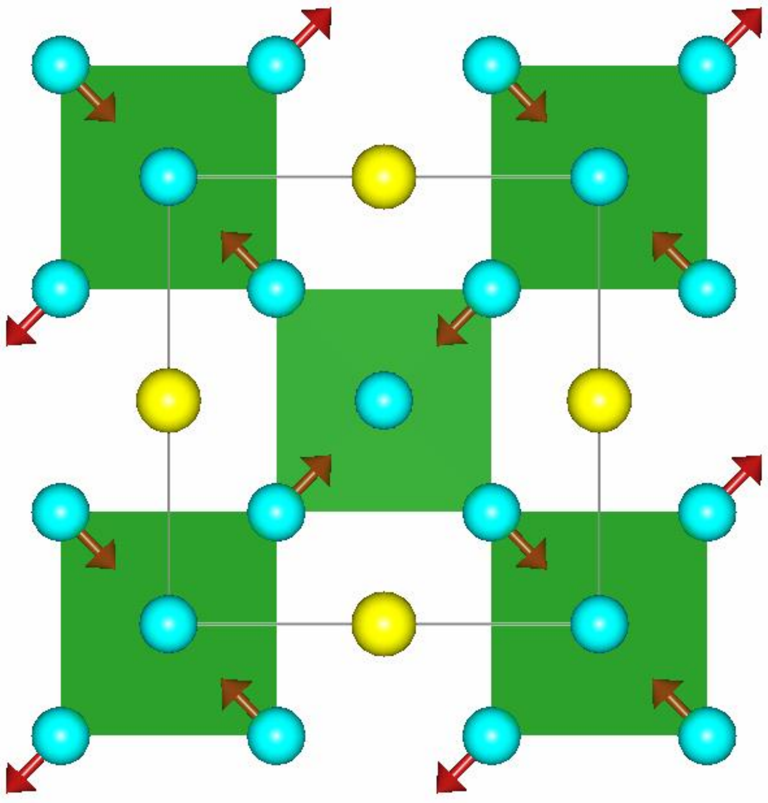


Mode 5, Q5_X5+ = -0.139910
O2 X5+ (0.0, -0.089721, 0.0)

Mode 4, Q4_X5+ = -0.546082
La X5+ (0.0, -0.089721, 0.0)



Mode 7, Q7_M3+ = 0.901264
O1 M3+ (-0.04486, -0.04486, 0.0)



Mode 6, Q6_M2+ = 0.355652
O1 M2+ (0.04486, -0.04486, 0.0)

Visualisation of Irreps modes using FullProf Studio

If the value of **p_mode(1)=2** (see note of 29 August 2008 in **fp2k.inf**) the other values are not needed.

The program interprets this value as and indication to output in the FST and OUT files the structures corresponding to single irreducible representations (Irreps).

All modes corresponding to a single Irrep are combined in the FST file.

Visualisation of modes using FullProf Studio: Summary

Examples:

A_MODES 7 7 → All the 7 independent modes are represented by displacement vectors (arrows)

A_MODES 7 -7 → All the 7 independent modes are represented by virtual distorted structures

A_MODES 7 -3 → No output of independent modes in FST files

Visualisation of single modes using FullProf Studio

Examples:

A_MODES 7 2 → Modes regrouped in an FST file per irreducible representation (arrows)

A_MODES 7 -2 → Modes regrouped in an FST file per irreducible representation (structures)

A_MODES 7 1 1 1 0 1 1 0 → Explicit output of all modes (1: arrows, 0: distorted structure)

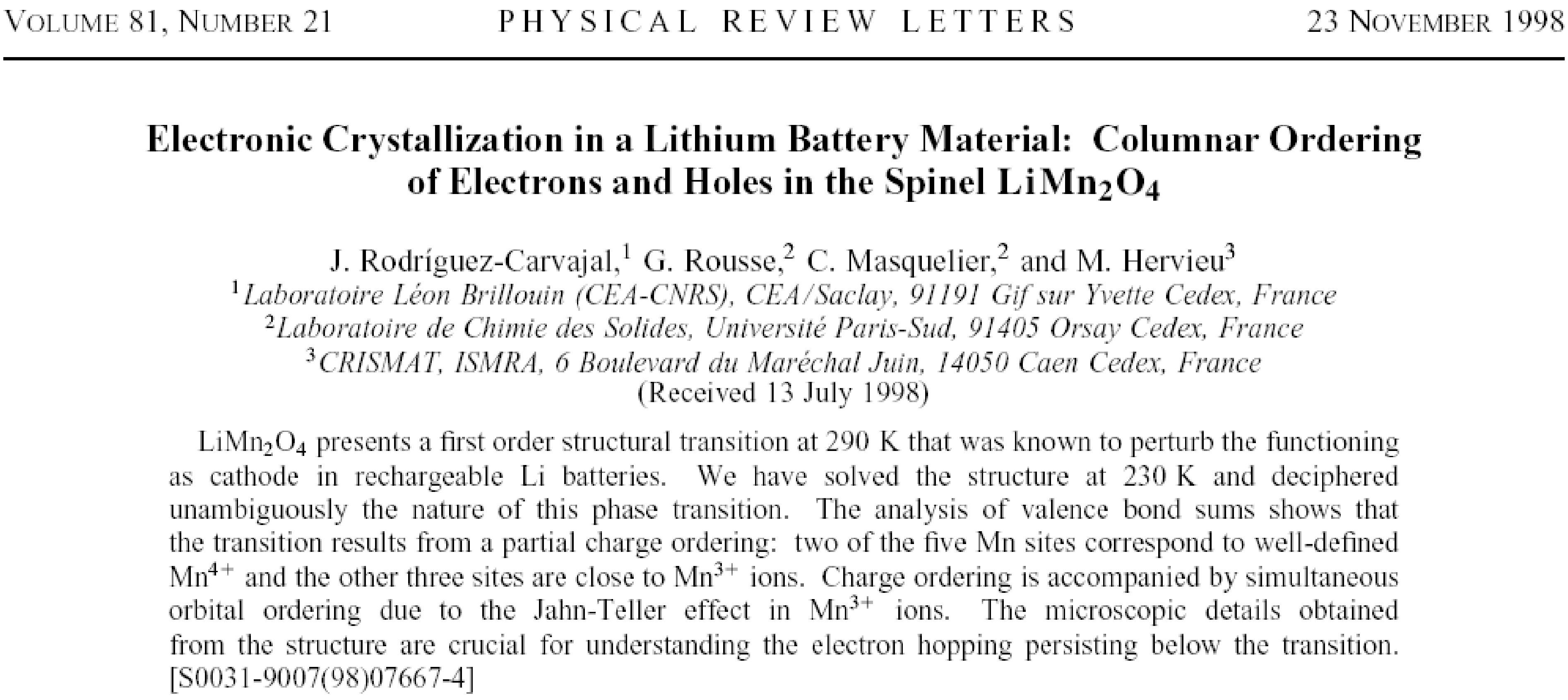
Visualisation of single modes using FullProf Studio

Examples:

A_MODES 7 4 1 3 -4 7 → Only the 4 modes 1,3,4 and 7 are ouput in FST files. All of them, except the mode 4, are represented by arrows.

A more complex case: $LiMn_2O_4$

A complex structure determined and refined with FullProf



VOLUME 81, NUMBER 21 PHYSICAL REVIEW LETTERS 23 NOVEMBER 1998

Electronic Crystallization in a Lithium Battery Material: Columnar Ordering of Electrons and Holes in the Spinel $LiMn_2O_4$

J. Rodríguez-Carvajal,[1] G. Rousse,[2] C. Masquelier,[2] and M. Hervieu[3]
[1] *Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay, 91191 Gif sur Yvette Cedex, France*
[2] *Laboratoire de Chimie des Solides, Université Paris-Sud, 91405 Orsay Cedex, France*
[3] *CRISMAT, ISMRA, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France*

(Received 13 July 1998)

$LiMn_2O_4$ presents a first order structural transition at 290 K that was known to perturb the functioning as cathode in rechargeable Li batteries. We have solved the structure at 230 K and deciphered unambiguously the nature of this phase transition. The analysis of valence bond sums shows that the transition results from a partial charge ordering: two of the five Mn sites correspond to well-defined Mn^{4+} and the other three sites are close to Mn^{3+} ions. Charge ordering is accompanied by simultaneous orbital ordering due to the Jahn-Teller effect in Mn^{3+} ions. The microscopic details obtained from the structure are crucial for understanding the electron hopping persisting below the transition. [S0031-9007(98)07667-4]

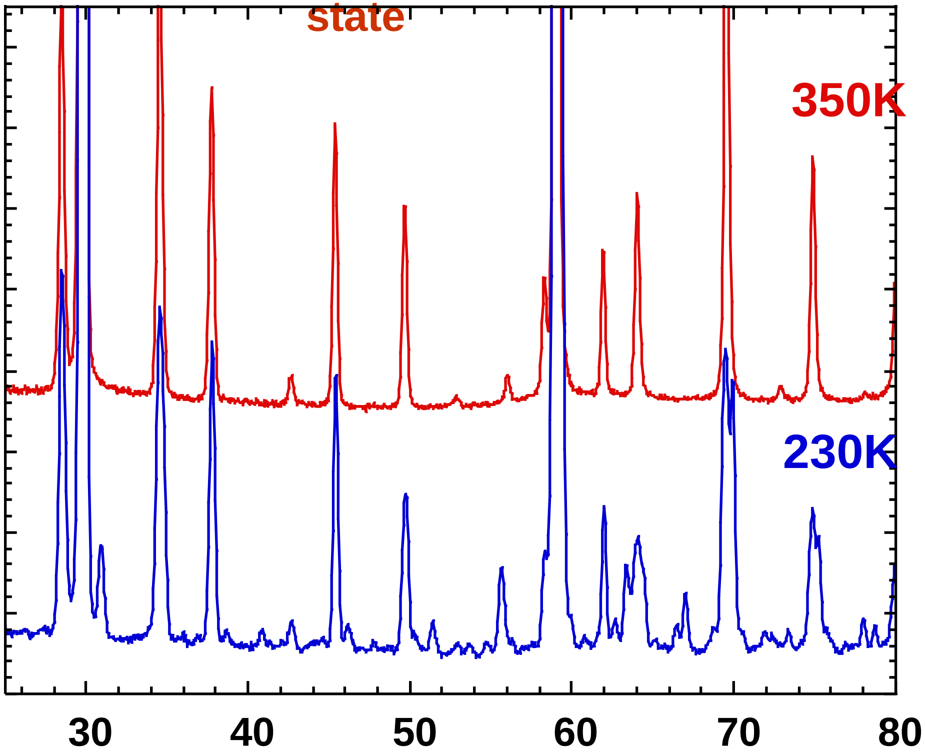
Electronic crystallization in a Li battery material: columnar ordering of electron and holes in the spinel $LiMn_2O_4$

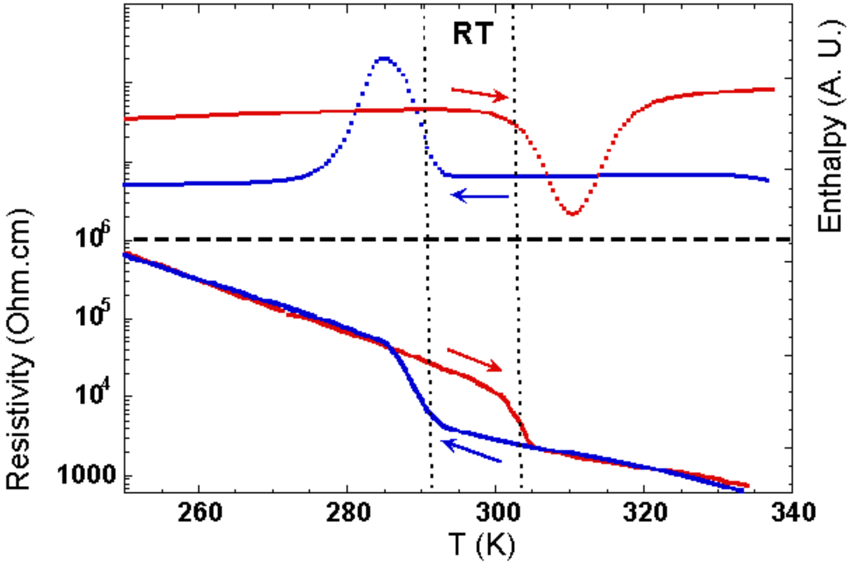
J. Rodríguez-Carvajal, G. Rousse, Ch. Masquelier and M. Hervieu

Physical Review Letters, **81**, 4660 (1998)

$Li_{Td}\,[Mn_2]_{Oct.}O_4$: $Mn^{3.5+}$

High temperature: mixed valence state

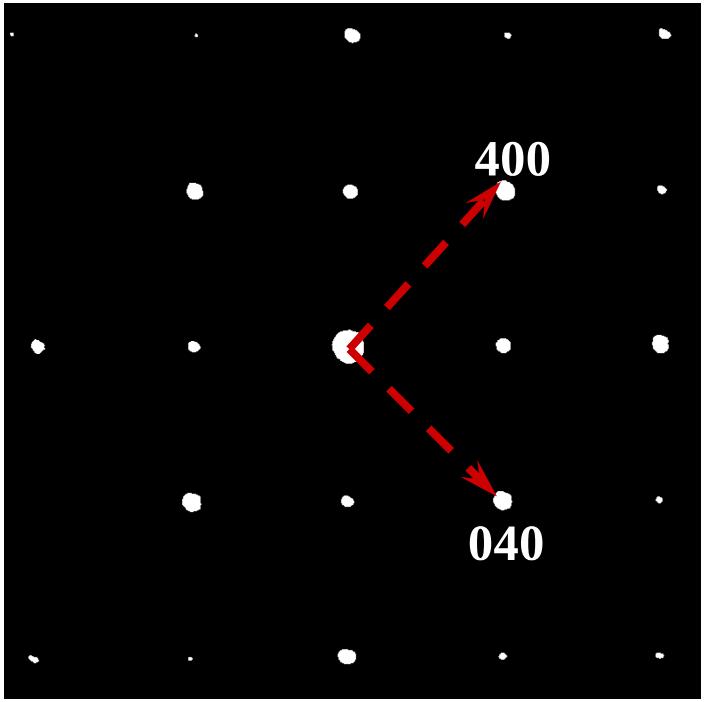




Orthorhombic Distortion
Superstructure reflections

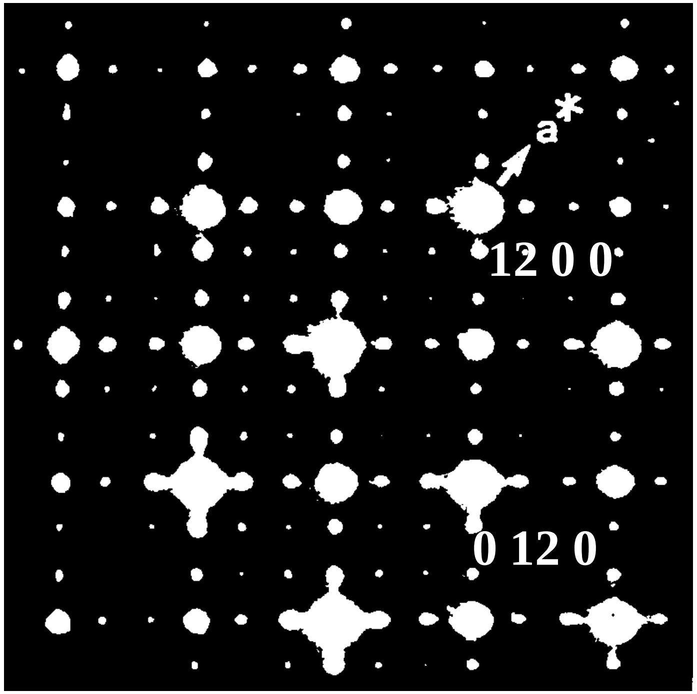
$LiMn_2O_4$: Electron Diffraction

320 K



Cubic Fd$\bar{3}$m
a = 8,248 (1) Å

230 K

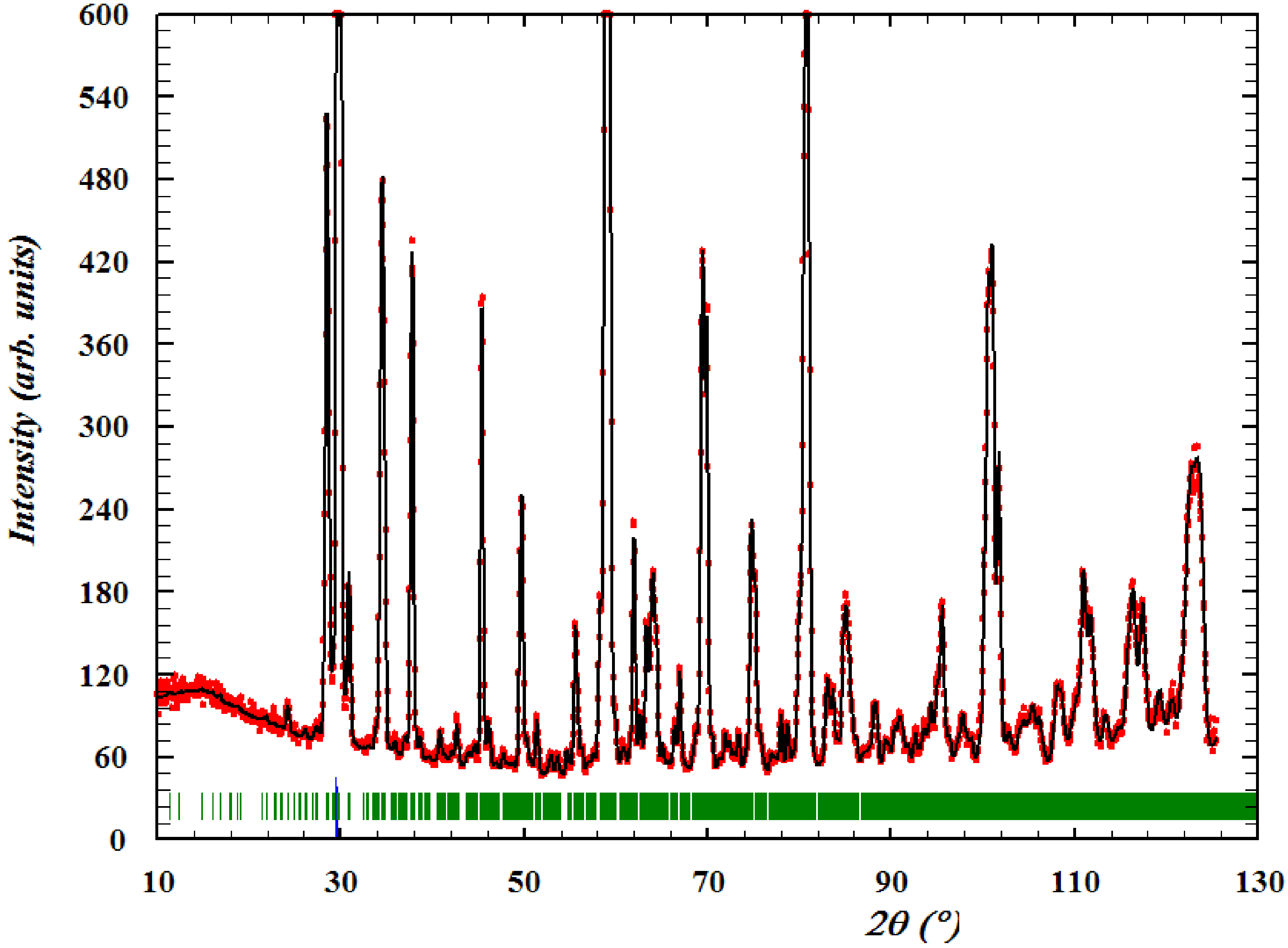


x 9 →

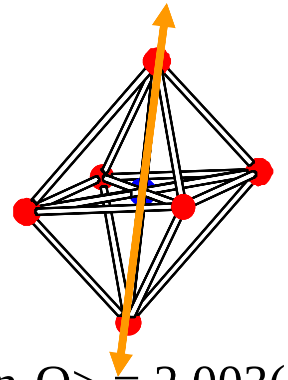
Orthorhombic Fddd
a = 24.7435(5) Å
b = 24.8402(5) Å
c = 8.1989(1) Å

J. Rodríguez-Carvajal *et al*, *PRL*, **81**, 4660 (1998)

Refinement of the charge-ordered phase



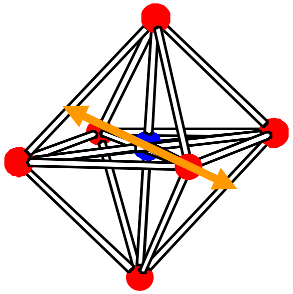
$LiMn_2O_4$: Partial Charge Ordering



<Mn-O> = 2,003(2) Å

Mn(1) = **3.20+**

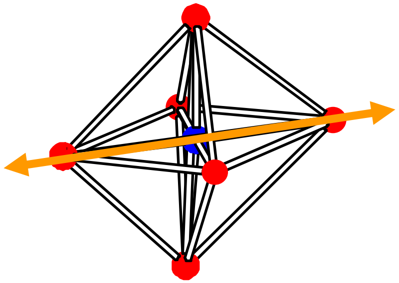
Δ = 20.6



<Mn-O> = 1,996(4) Å

Mn(2) = **3.27+**

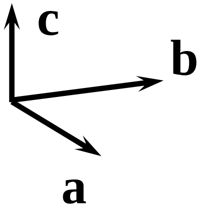
Δ = 19.4

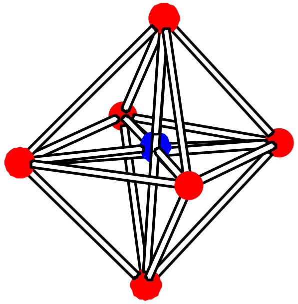


<Mn-O> = 2,020(5) Å

Mn(3) = **3.12+**

Δ = 36.6



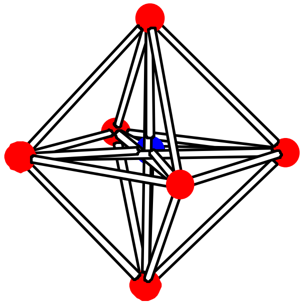


<Mn-O> = 1,903(4) Å

Mn(4) = **4.02+**

Δ = 4.6

64 « Mn^{4+} »
80 « Mn^{3+} -like»
8 delocalised holes

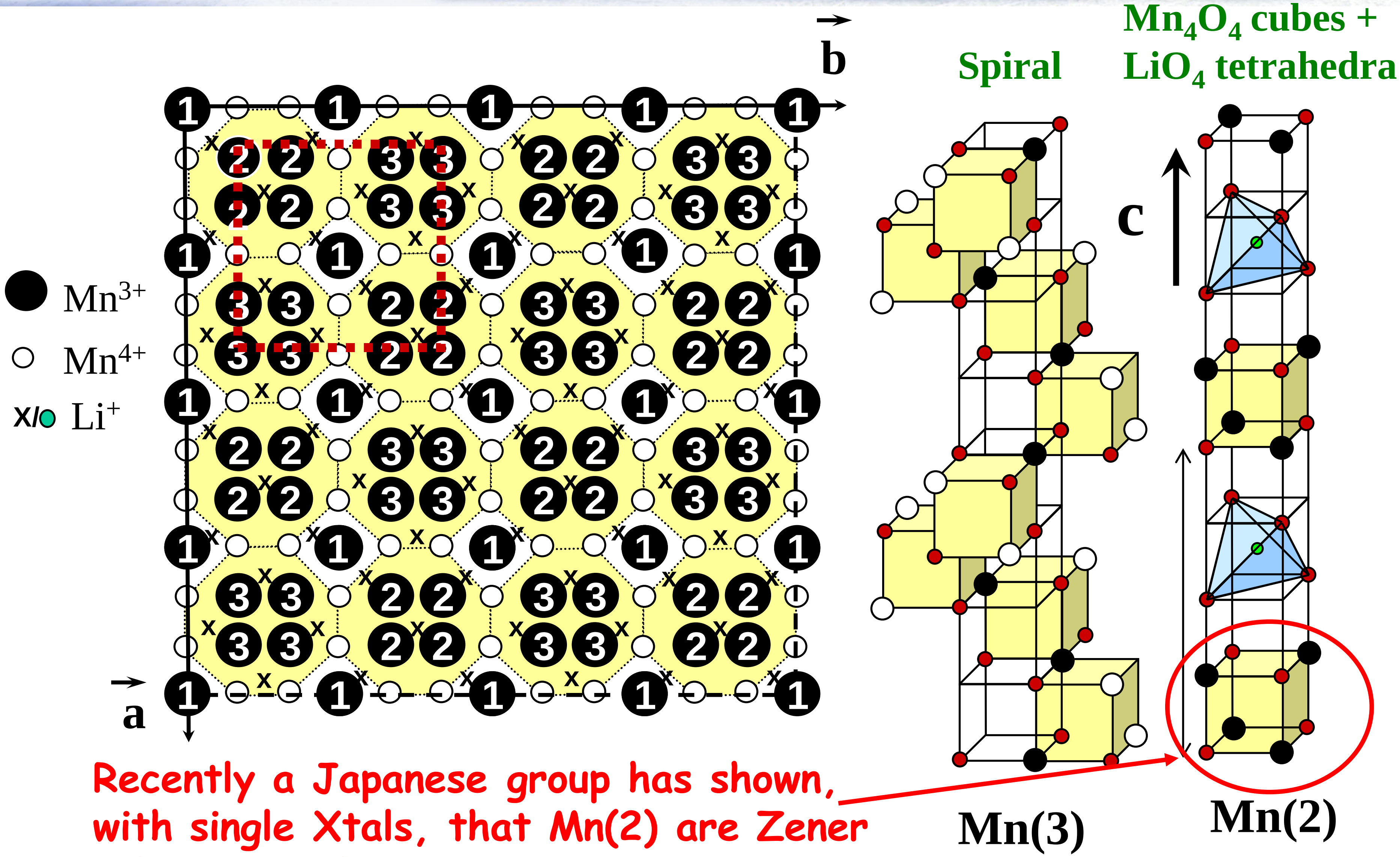


<Mn-O> = 1,915(4) Å

Mn(5) = **3.90+**

Δ = 6.1

Distribution of Mn^{3+} and Mn^{4+} in the cell



Recently a Japanese group has shown, with single Xtals, that Mn(2) are Zener Polarons involving 4Mn