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

Juan Rodríguez-Carvajal

Diffraction Group

Institut Laue-Langevin

FRANCE

Outline

➔ Overview of the *Symmetry Analysis* in phase transitions

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

➔ Detailed example: Comparison of CaTiO3 and $LaMnO_3$

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 42**, 820 (2009)

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**.

$$\mathbf{r}(\mu,i) = \mathbf{r_0}(\mu,i) + \mathbf{u}(\mu,i) \qquad \mu = 1,2,\ldots s, \quad i = 1,2,\ldots n_\mu$$

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

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

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

The mode (τ, 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 (τ, 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:

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

Distorted structures in terms of modes

The normalization of the polarisation vectors is chosen to verify:

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

"$mult_{\mu,i}$" 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:

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

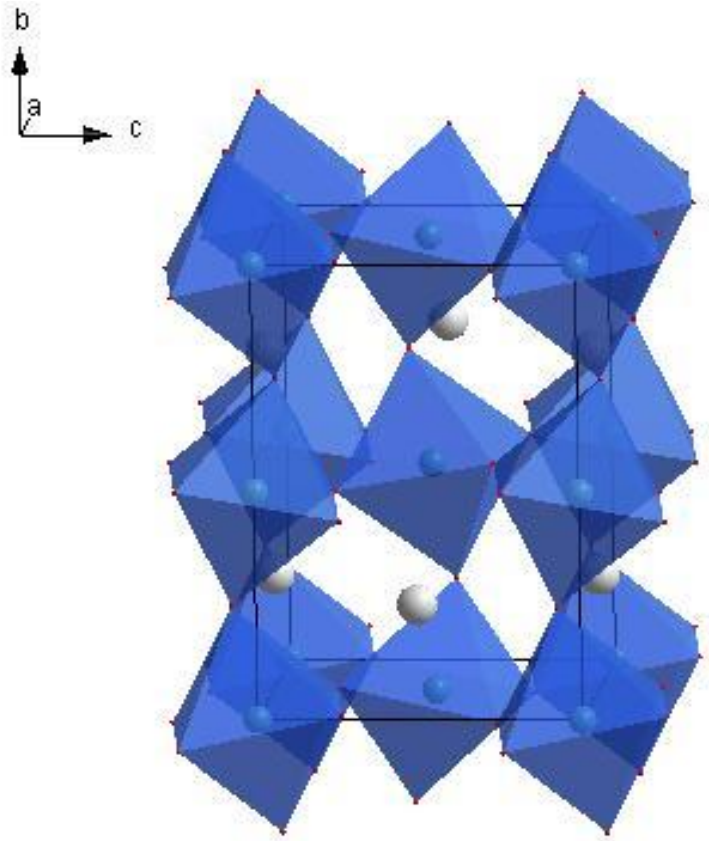
Distorted structures in terms of modes

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**.

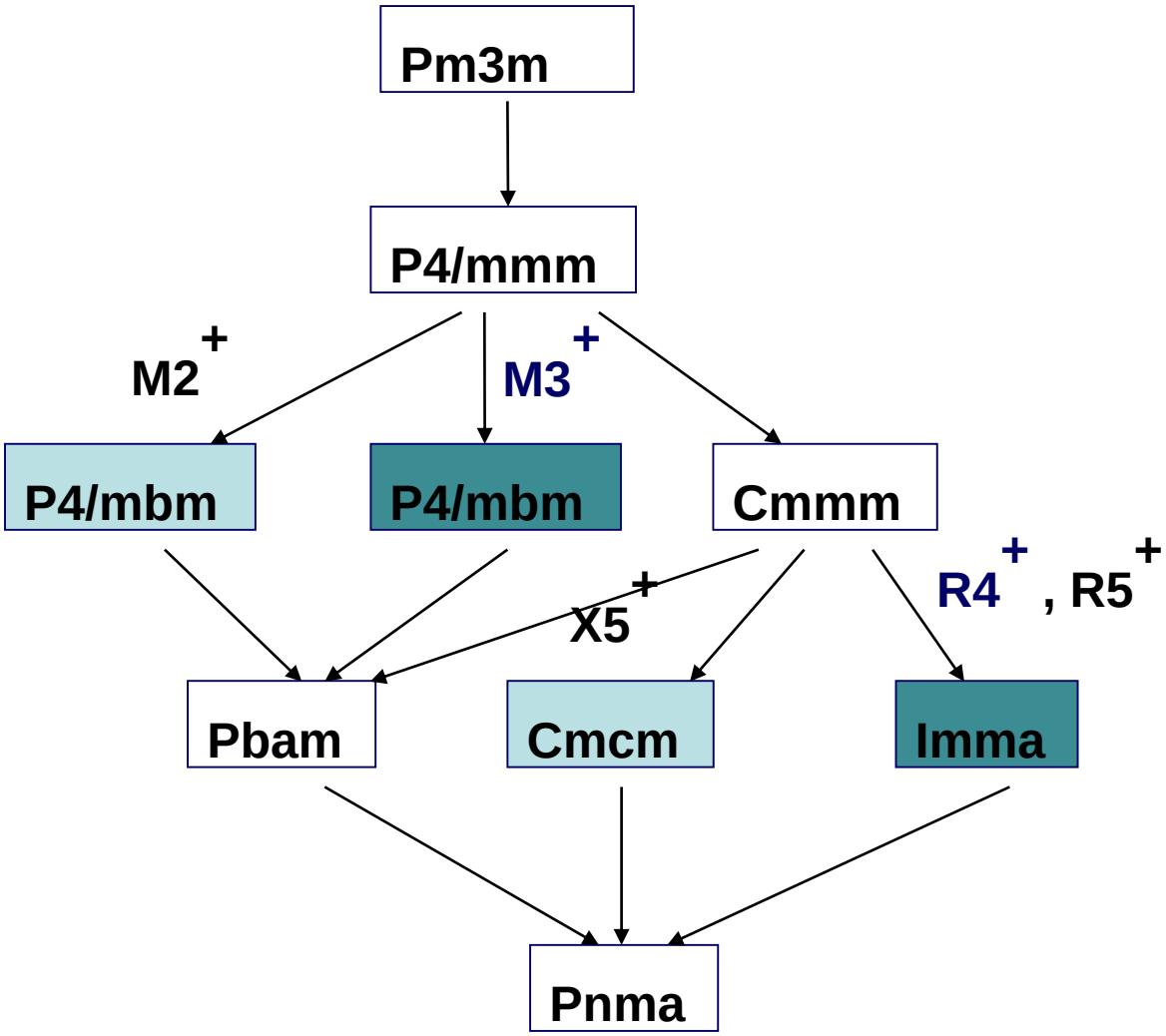
A **primary distortion mode** is sufficient to produce the observed symmetry breaking between **the parent** and **the observed** structure, while **secondary distortion modes** alone would yield **a higher symmetry**.

Distorted perovskite: structure type $GdFeO_3$

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



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



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 example: Comparison of CaTiO3 and $LaMnO_3$

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.

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

The atoms position are calculated from the following formula:

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

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 $LaMnO_3$

```
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
                    0.00                                     .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
```

Symmetry modes option

keyword

Number of polarisation vector modes

Normalisation coefficients

Indices of the modes

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)

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

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 an 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, default of AMPLIMODES)

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.

Outline

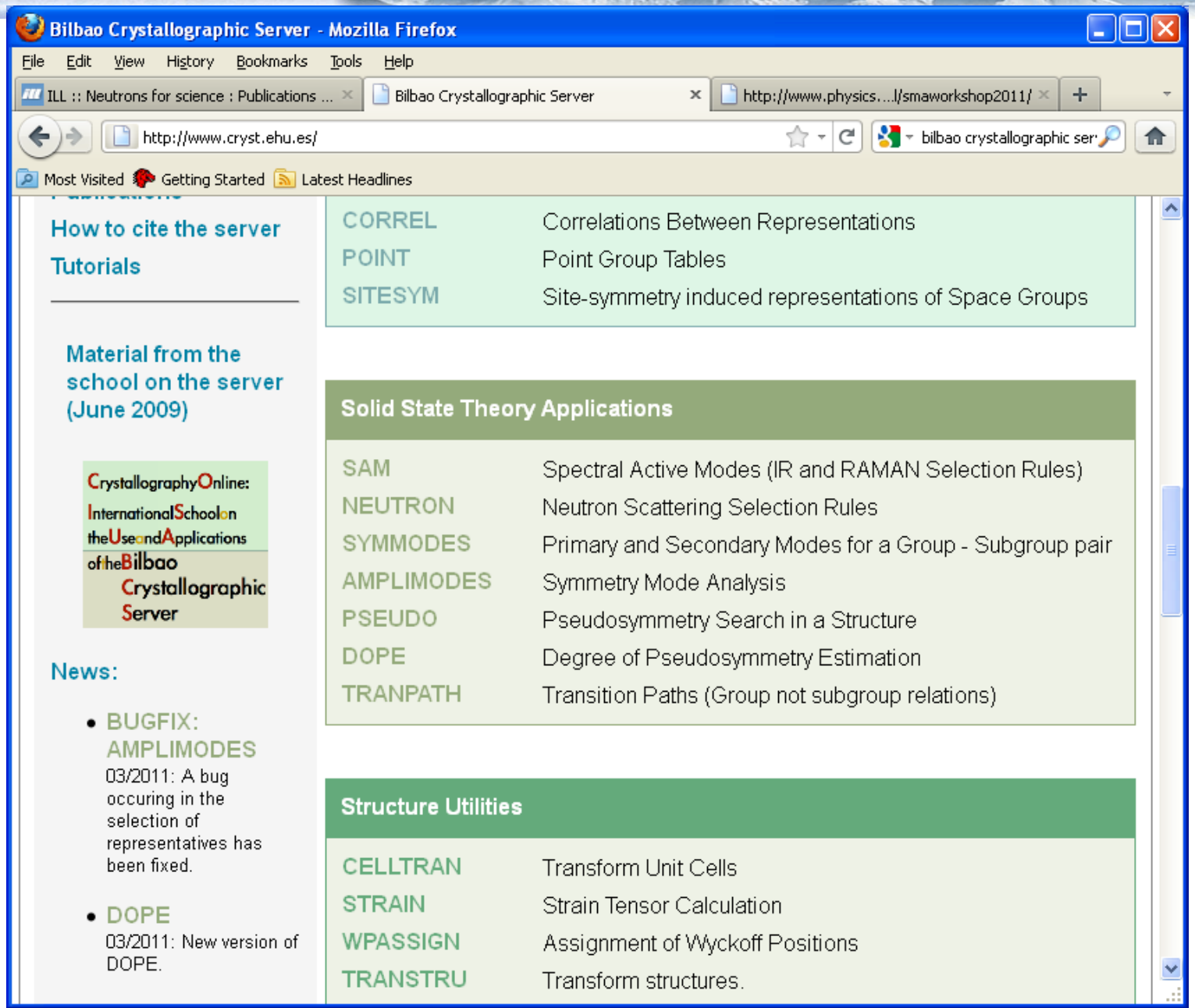
➔ Overview of the *Symmetry Analysis* in phase transitions

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

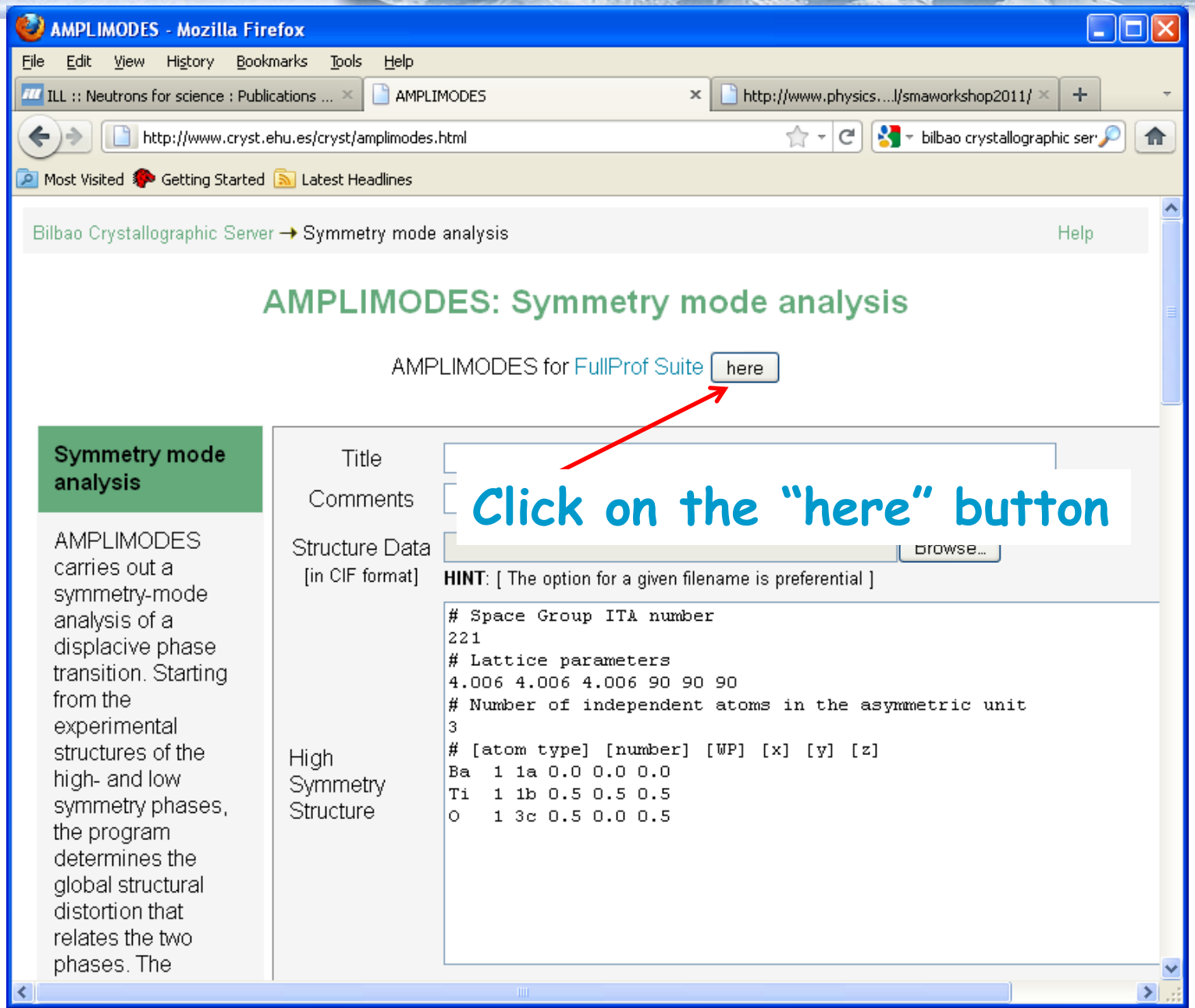
➔ Detailed example: the case of $CaTiO_3$ and comparison with $LaMnO_3$

AMPLIMODES: Bilbao Crystallographic Server

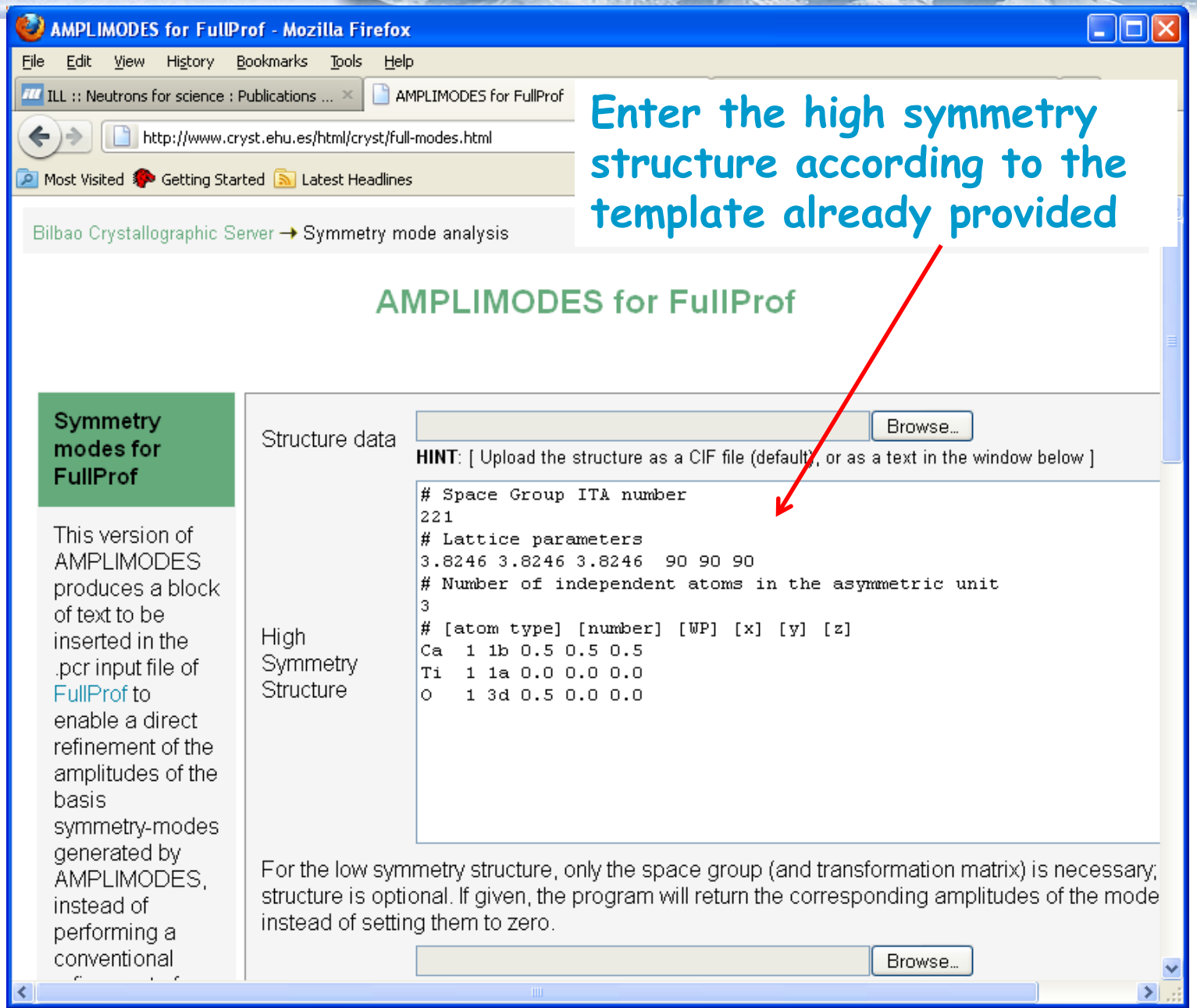
AMPLIMODES: Bilbao Crystallographic Server



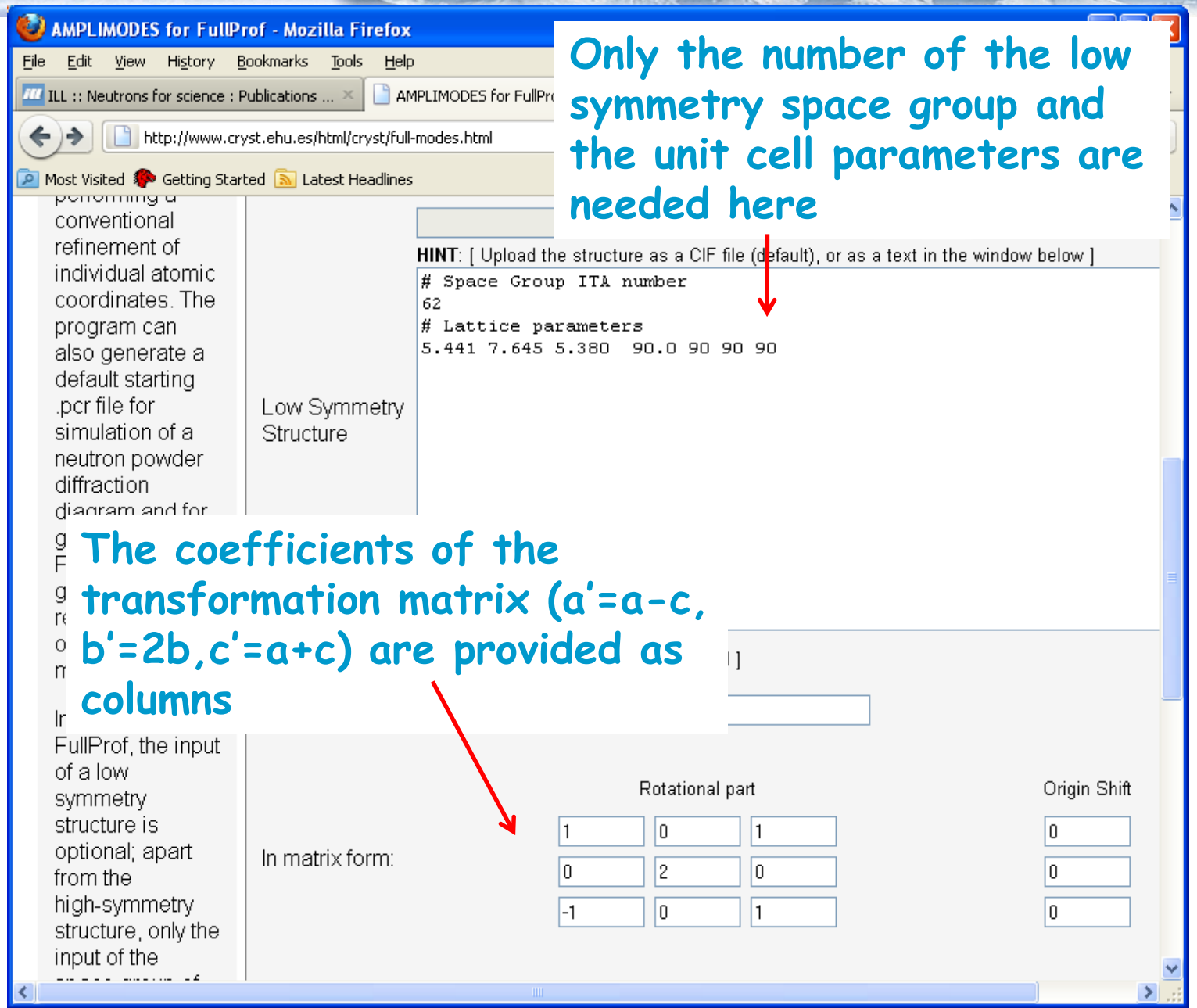
AMPLIMODES: Bilbao Crystallographic Server



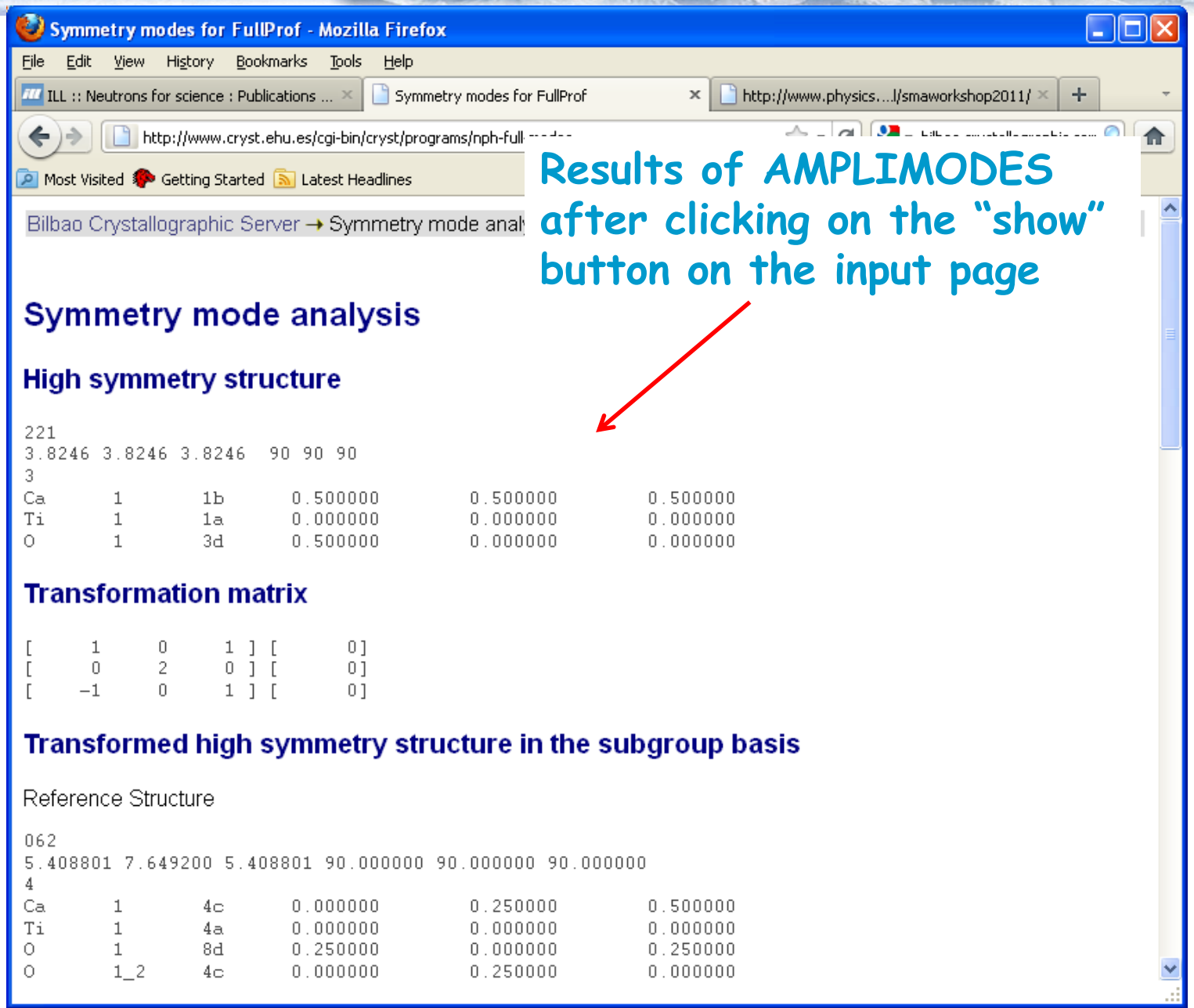
AMPLIMODES for FullProf



AMPLIMODES for FullProf

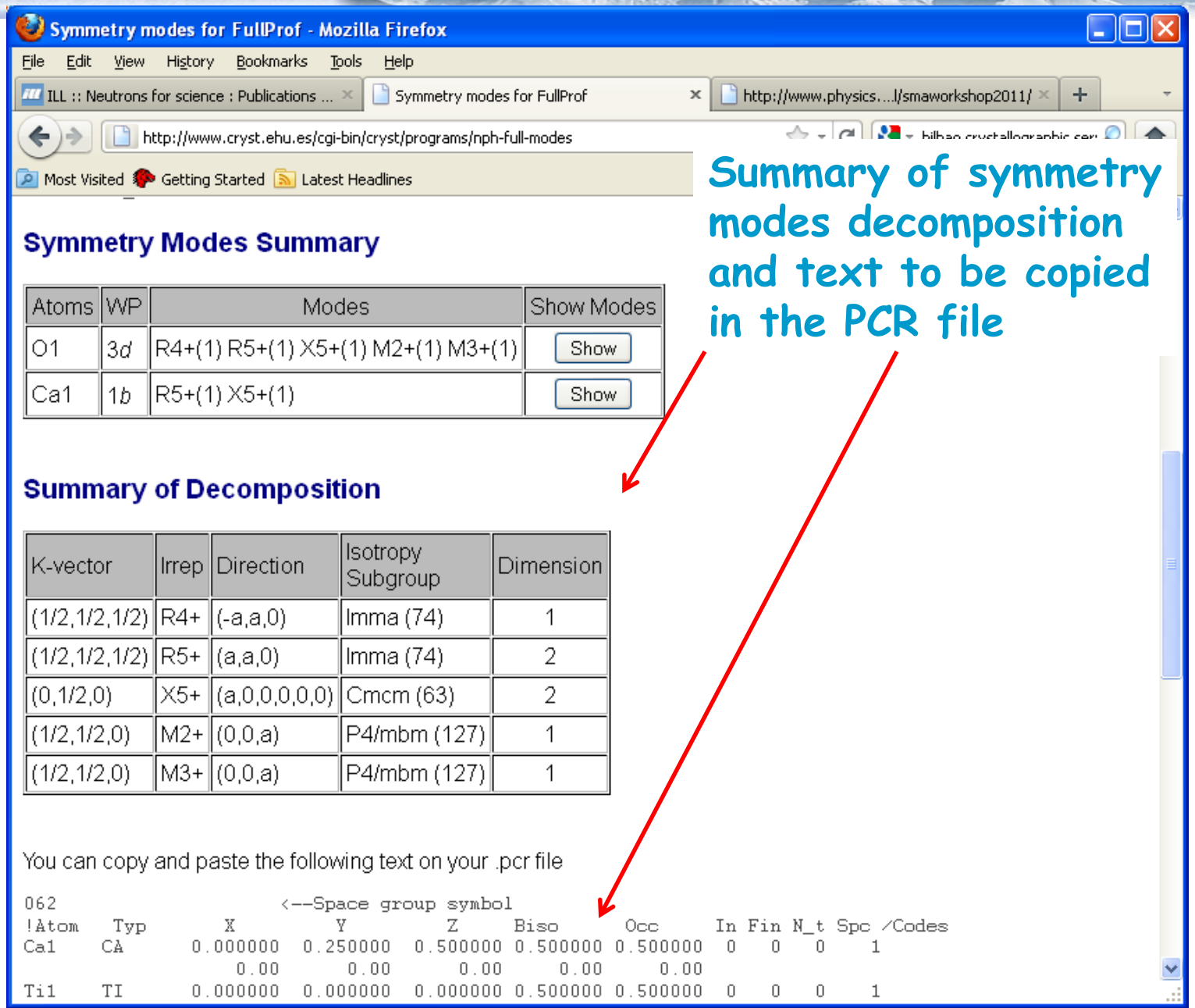


AMPLIMODES for FullProf



Results of AMPLIMODES after clicking on the "show" button on the input page

AMPLIMODES for FullProf



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

Summary of symmetry modes decomposition and text to be copied in the PCR file

Summary of Decomposition

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension
(1/2,1/2,1/2)	R4+	(-a,a,0)	Imma (74)	1
(1/2,1/2,1/2)	R5+	(a,a,0)	Imma (74)	2
(0,1/2,0)	X5+	(a,0,0,0,0,0)	Cmcm (63)	2
(1/2,1/2,0)	M2+	(0,0,a)	P4/mbm (127)	1
(1/2,1/2,0)	M3+	(0,0,a)	P4/mbm (127)	1

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   0.500000 0.500000 0.500000  0   0   0    1
                   0.00       0.00       0.00     0.00     0.00
Ti1     TI      0.000000   0.000000   0.000000 0.500000 0.500000  0   0   0    1
```

AMPLIMODES for FullProf

Symmetry modes for FullProf - Mozilla Firefox

File Edit View History Bookmarks Tools Help

ILL :: Neutrons for science : Publications ... | Symmetry modes for FullProf | http://www.physics...l/smaworkshop2011/

http://www.cryst.ehu.es/cgi-bin/cryst/programs/nph-full-modes

bilbao crystallographic ser

Most Visited Getting Started Latest Headlines

```
062                      <--Space group symbol
!Atom   Typ        X          Y          Z       Biso       Occ      In Fin N_t Spc /Codes
Ca1     CA       0.000000   0.250000   0.500000 0.500000 0.500000  0   0   0    1
                    0.00       0.00       0.00     0.00     0.00
Ti1     TI       0.000000   0.000000   0.000000 0.500000 0.500000  0   0   0    1
                    0.00       0.00       0.00     0.00     0.00
O1      O        0.250000   0.000000   0.250000 0.500000 1.000000  0   0   0    1
                    0.00       0.00       0.00     0.00     0.00
O1_2    O        0.000000   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
  1 O1      R4+      0.000000 -0.032683  0.000000 1.00
  1 O1_2    R4+      0.000000  0.000000  0.065366 1.00
  2 Ca1     R5+      0.000000  0.000000  0.092442 1.00
  3 O1      R5+      0.000000  0.032683  0.000000 1.00
  3 O1_2    R5+      0.000000  0.000000  0.065366 1.00
  4 Ca1     X5+      0.092442  0.000000  0.000000 1.00
  5 O1      X5+      0.000000  0.000000  0.000000 1.00
  5 O1_2    X5+     -0.092442  0.000000  0.000000 1.00
  6 O1      M2+     -0.046221  0.000000 -0.046221 1.00
  6 O1_2    M2+      0.000000  0.000000  0.000000 1.00
  7 O1      M3+      0.046221  0.000000 -0.046221 1.00
  7 O1_2    M3+      0.000000  0.000000  0.000000 1.00
!Amplitudes of Symmetry Modes
A_MODES    7   2
    A1_R4+     0.000000      1.00
    A2_R5+     0.000000      1.00
    A3_R5+     0.000000      1.00
    A4_X5+     0.000000      1.00
    A5_X5+     0.000000      1.00
    A6_M2+     0.000000      1.00
    A7_M3+     0.000000      1.00
```

You can download the full .pcr file for a default neutron simulation [here]

Text to be copied in the PCR file and button "here" to create a template of PCR file for calculations with FullProf

AMPLIMODES for FullProf: Template of PCR file

Mozilla Firefox

File Edit View History Bookmarks Tools Help

ILL :: Neutrons for science : Publications ... | http://www.cryst.eh.../tmp/stru24801.pcr | http://www.physics...l/smaworkshop2011/

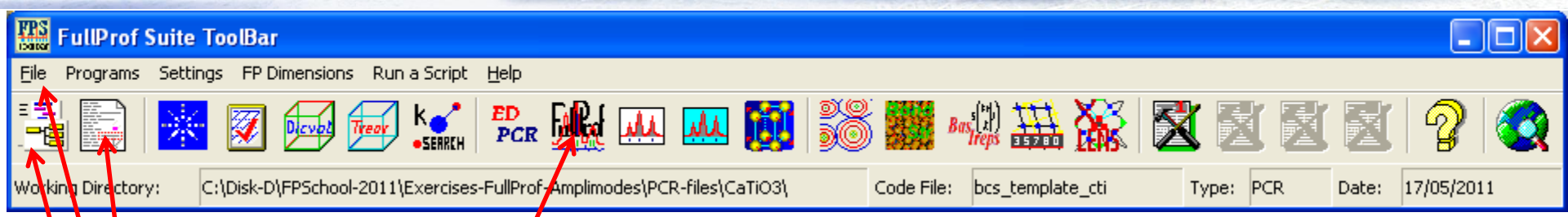
http://www.cryst.ehu.es/tmp/stru24801.pcr

bilbao crystallographic ser

Most Visited Getting Started Latest Headlines

```
COMM  AMPLIMODES for FullProf
! Files => DAT-file: myDAT_file PCR-file: myPCR_file
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
  3   7   1   0   2   0   0   1   0   0   0   0   0   0   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
  0   0   1   0   1   0   4   0   0   3   0   0   0   0   0   0   0
!
! lambda1 Lambda2    Ratio     Bkpos     Wdt     Cthm      muR    AsyLim   Rpolarz ->Patt# 1
1.227200 1.227200  0.0000  50.000 10.0000  0.0000  0.0000  170.00    0.0000
!
!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      1.0000   0.050000   170.0000   0.000   0.000
!
! Excluded regions (LowT  HighT) for Pattern#  1
       0.00        2.00
     170.00      180.00
!
!
7  !Number of refined parameters
!
!  Zero     Code    SyCos     Code   SySin     Code  Lambda     Code MORE ->Patt# 1
 0.00000    0.0  0.00000    0.0  0.00000    0.0 0.000000    0.00    0
!   Background coefficients/codes  for Pattern#  1
 100.00      0.0000      0.0000      0.0000      0.0000      0.0000
      0.000       0.000       0.000       0.000       0.000       0.000
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     0
!-------------------------------------------------------------------------------
AMPLIMODES for FullProf          FIX xyz
!
!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         0.000   0   7   0
062                    <--Space group symbol
!Atom   Typ       X         Y         Z      Biso      Occ      In Fin N_t Spc /Codes
Ca1    CA      0.000000  0.250000  0.500000 0.500000 0.500000  0   0   0    1
```

Running FullProf with the PCR file generated by AMPLIMODES



1: Select, in the "File" menu the working directory

2: Load the PCR file in toolbar (first left button). In our case the file is called: **bcs_template_cti.pcr**

3: The file can be readily edited by clicking on the second button and eventually modified

4: Clicking on the "FullProf" button, the program runs and produces files that may be inspected or used for plotting the calculated diffraction pattern and the crystal structure.

Running FullProf with the PCR file generated by AMPLIMODES

FullProf Suite ToolBar

File Programs Settings FP Dimensions Run a Script Help

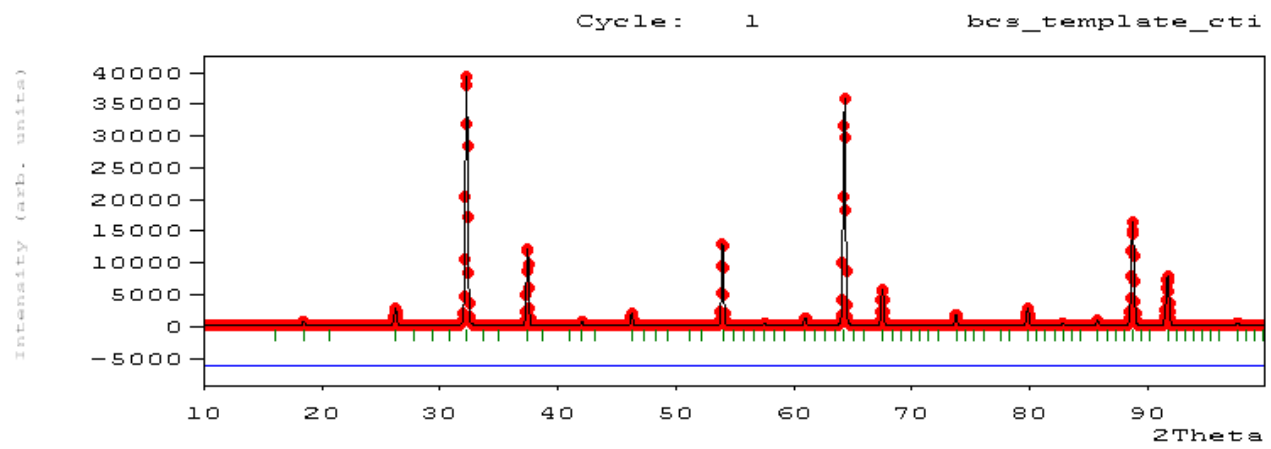
Working Directory: C:\Disk-D\FPSchool-2011\Exercises-FullProf-Amplimodes\PCR-files\CaTiO3\ Code File: bcs_template_cti Type: PCR Date: 17/05/2011

FullProf Program

Load Edit PCR Mode Run Exit

```
    ====================>>> CYCLE:        1

=> Control file *.pcr: bcs_template_cti
=> Pattern:    1  bcs_template_cti
=> Ordering reflections contributing to each point for pattern:        1
=> Calculation of Yi for all points + Normal Matrix & Vector...
=> Calculation for pattern:        1
=> Normal end, final calculations and writing...


=>                CPU Time:      0.375 seconds
=>                               0.006 minutes

=> END    Date:17/05/2011  Time => 08:11:53.923
```

Calculation done for a cubic ideal perovskite described in the low symmetry setting



Running FullProf with the PCR file generated by AMPLIMODES

The calculation is done for a cubic ideal perovskite described in the low symmetry setting. One can edit the file, write the real unit cell parameters and add arbitrary reasonable values to the amplitudes (in angstroms) to see the modification of the powder pattern
(let us call the PCR file: **bcs_modified_cti.pcr**).
For instance, introducing the following values:

```
A1_R4+      0.800000      1.00
A2_R5+     -0.100000      1.00
A3_R5+      0.300000      1.00
A4_X5+      0.700000      1.00
A5_X5+      0.100000      1.00
A6_M2+      0.020000      1.00
A7_M3+      0.100000      1.00
```

a= 5.441Å, *b*=7.645 Å, *c*=5.380 Å

Running FullProf with the PCR file generated by AMPLIMODES and modified by the user

FullProf Suite ToolBar

File Programs Settings FP Dimensions Run a Script Help

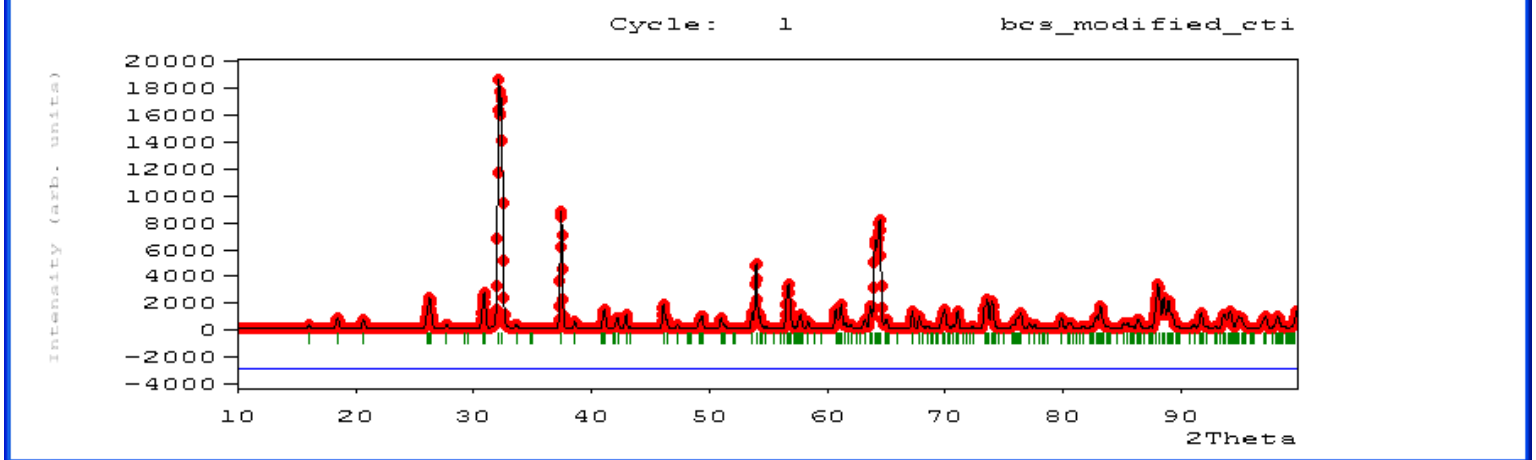
Working Directory: C:\Disk-D\FPSchool-2011\Exercises-FullProf-Amplimodes\PCR-files\CaTiO3\ Code File: bcs_modified_cti Type: PCR Date: 17/05/2011

FullProf Program

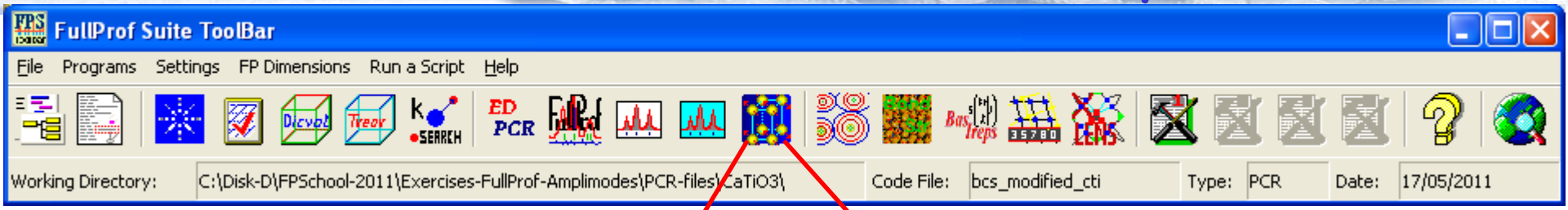
Load Edit PCR Mode Run Exit

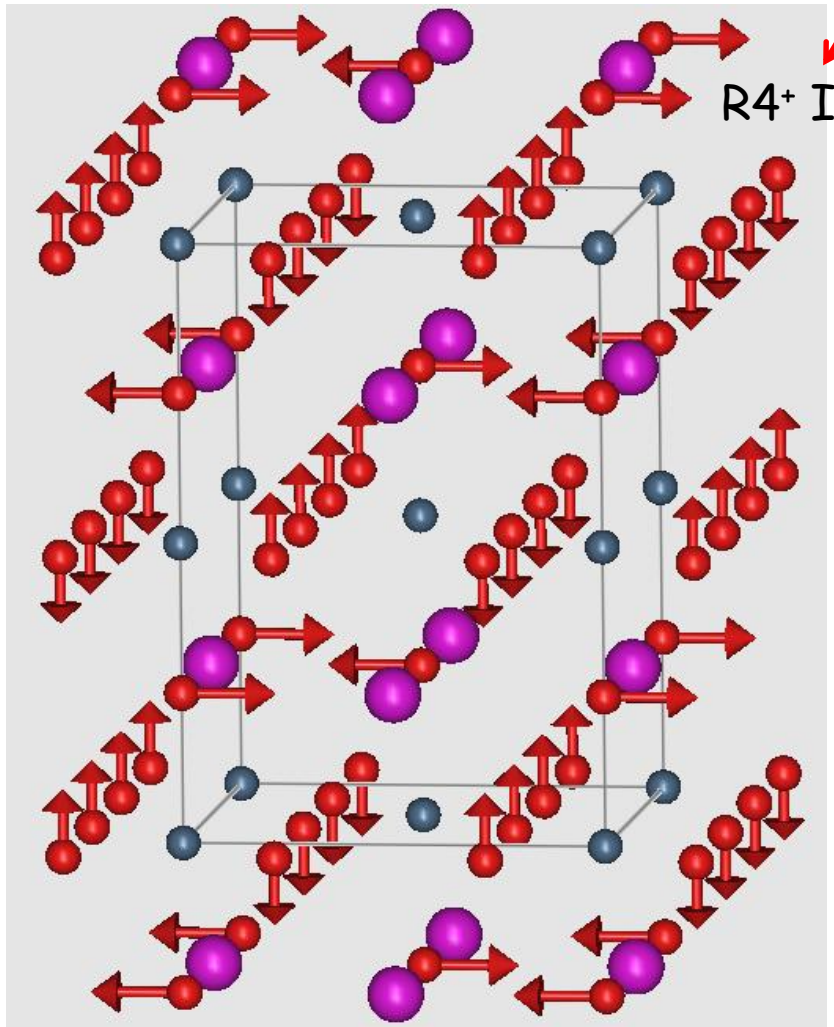
```
    ====================>>> CYCLE:        1

 => Control file *.pcr: bcs_modified_cti
 => Pattern:    1  bcs_modified_cti
 => Ordering reflections contributing to each point for pattern:       1
 => Calculation of Yi for all points + Normal Matrix & Vector...
 => Calculation for pattern:        1
 => Normal end, final calculations and writing...


 =>                CPU Time:      0.375 seconds
 =>                               0.006 minutes

 => END    Date:17/05/2011   Time => 08:28:21.692
```

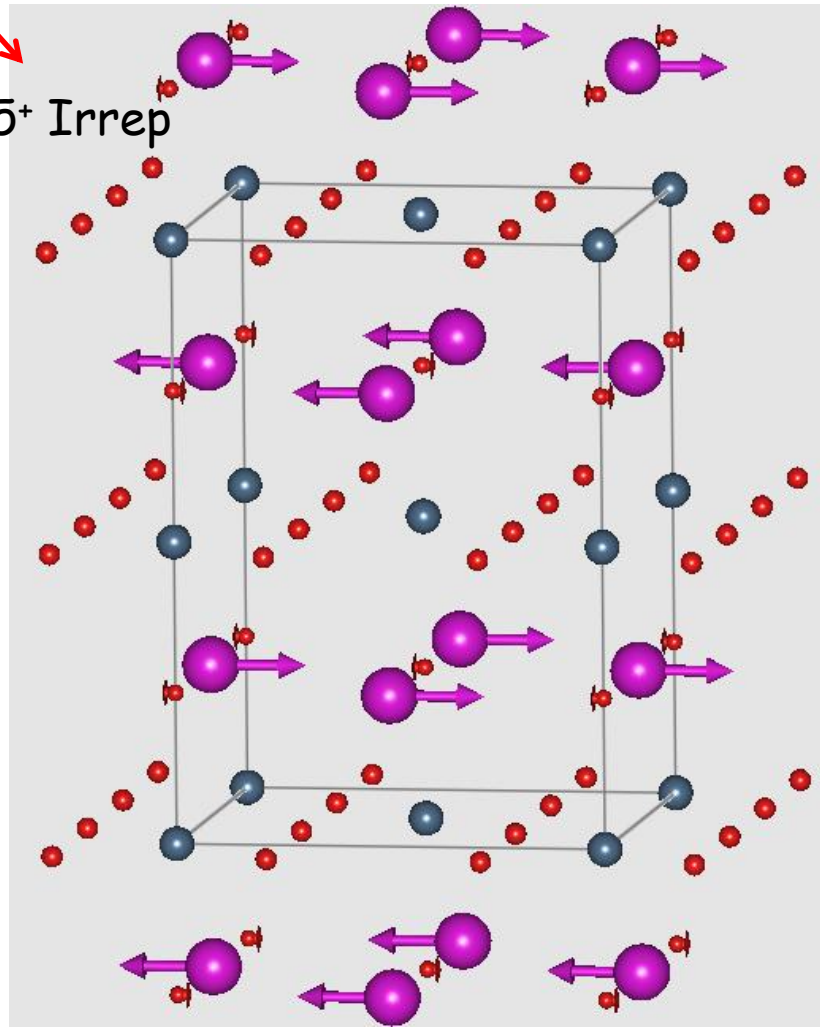
Calculation done for the distorted structure with the amplitudes given above and using the real cell parameters



Using FullProf Studio for visualising the displacements of atoms for individual Irreducible Representations

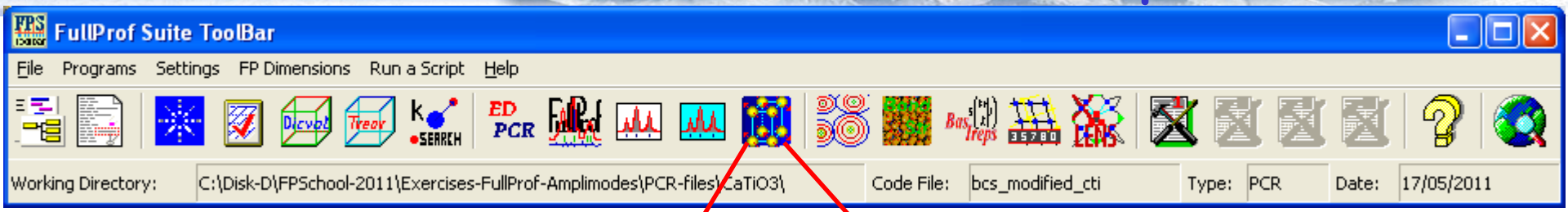


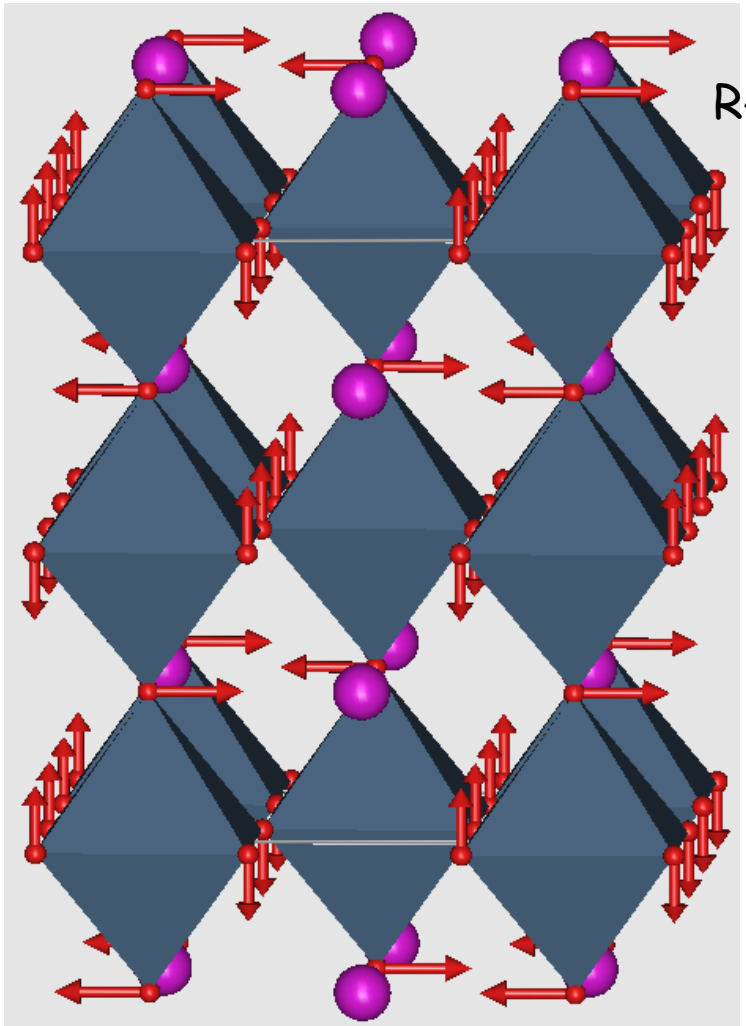




Ca
Ti
O

Using FullProf Studio for visualising the displacements of atoms for individual Irreducible Representations





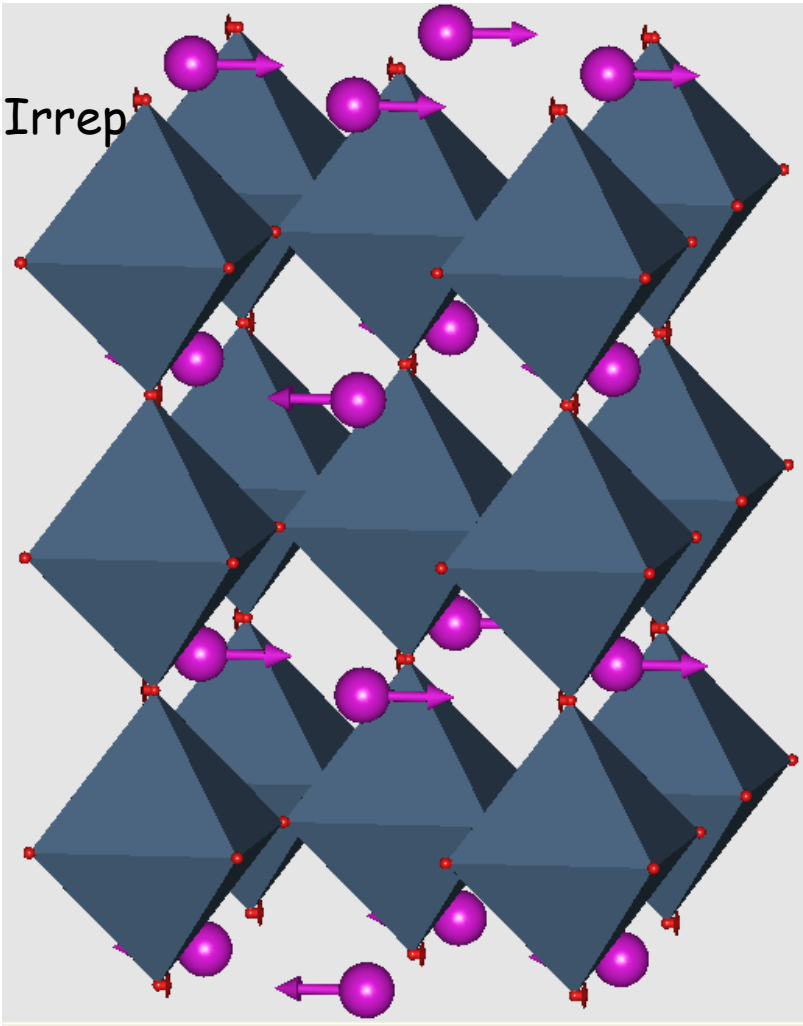
R4⁺ Irrep

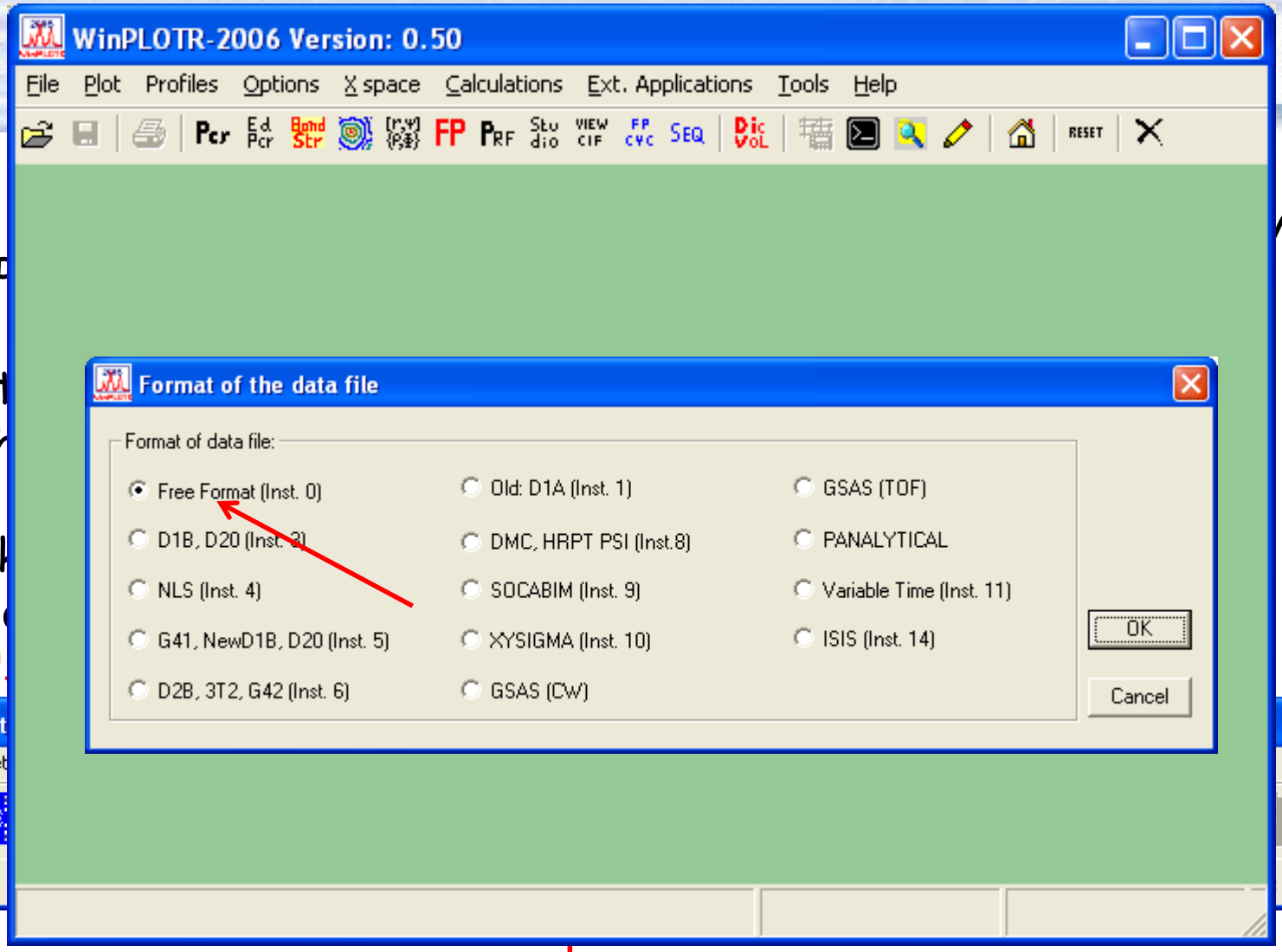
X5⁺ Irrep

Ca

Ti

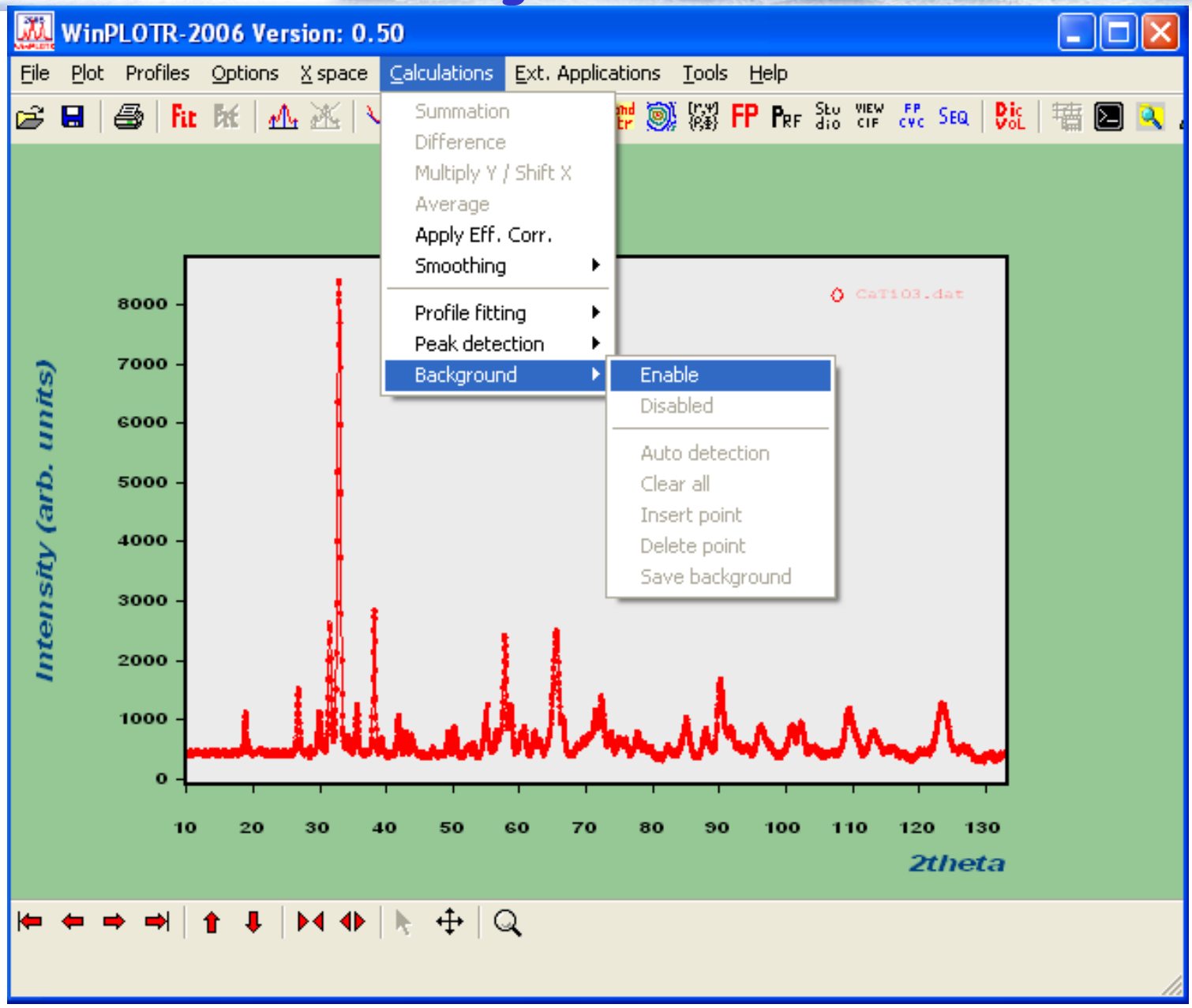
O



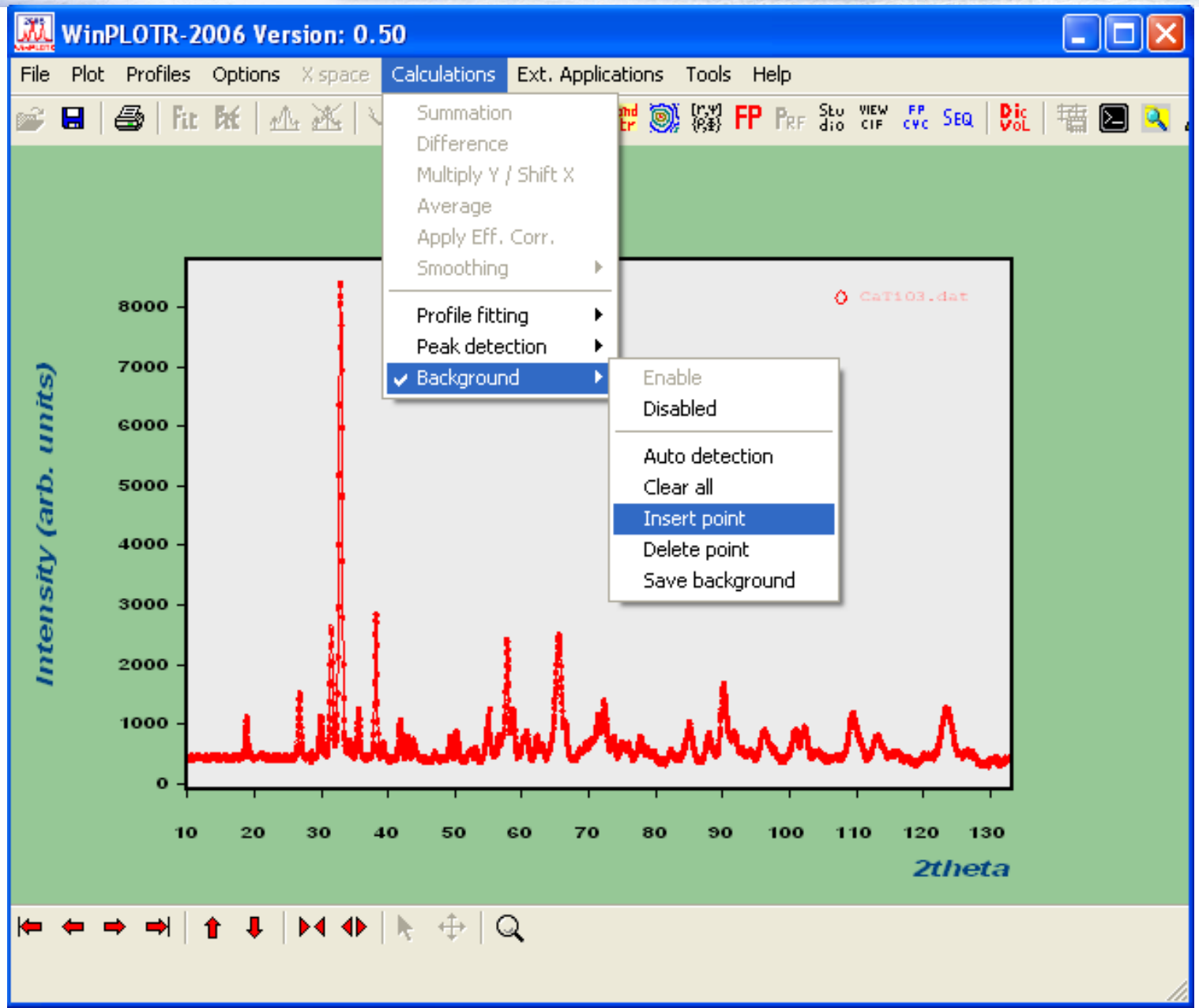


After loading the file into WinPLOTR-2006, the first step is to select background points and save them in a file. The procedure is indicated in the following three slides.

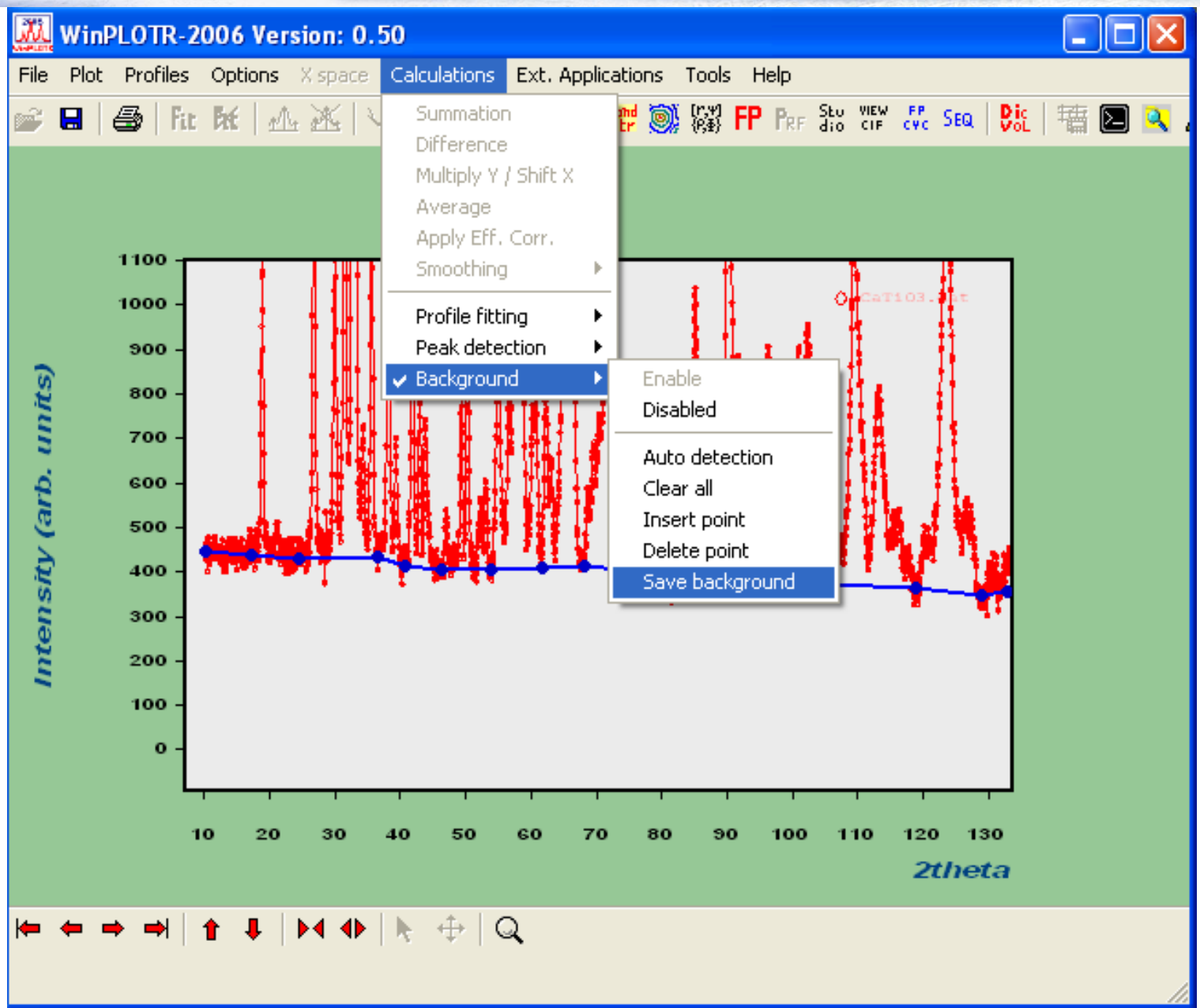
Preparing a PCR file for treating real data: Background selection



Preparing a PCR file for treating real data: Background selection



Preparing a PCR file for treating real data: Background selection



Modifying the file generated by AMPLIMODES to treat real data

Once the background points have been saved in a file, we adapt the file **bcs_modified_cti.pcr** to treat real data by copying it into another file (**CaTiO3ref.pcr**), putting **Job=1** (neutron data), the real wavelength and UVW parameters, etc. We include also the background points as shown below (important items in red):

```
COMM  CaTiO3 Symmetry Modes
! Files => DAT-file: bcs_modified_cti,  PCR-file: bcs_modified_cti
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   7   1  16   2   0   0   0   0   0   0   0   0   0   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   0   3   0   0   0   0   0   0   0
!
! lambda1 Lambda2     Ratio     Bkpos     Wdt     Cthm      muR   AsyLim  Rpolarz ->Patt#1
  1.24900 1.24900 0.00000    50.000 10.0000  0.0000  0.0000  170.00    0.0000
!
!NCY  Eps  R_at  R_an  R_pr  R_gl      Thmin       Step       Thmax     PSD     Sent0
 15  0.10  1.00  1.00  1.00  1.00       1.0000   0.050000   170.0000   0.000    0.000
! Position      Background_value
       10.21211      446.13547
       17.21063      437.90280
       24.48908      429.67017
       36.52652      433.78644
. . . . . . . . . . . . . . . . . . . .
```

Modifying the file generated by AMPLIMODES to treat real data

Notice that the polynomial background parameters have been removed because we have selected the option of linear interpolation between 16 background points

```
. . . . . .
! Excluded regions (LowT  HighT) for Pattern#  1
        0.00         2.00
      170.00       180.00
!
       2    !Number of refined parameters
!
!  Zero     Code     SyCos     Code    SySin     Code  Lambda      Code MORE ->Patt# 1
  0.00000    1.0   0.00000     0.0   0.00000     0.0 0.000000     0.00    0
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     0.00
!-------------------------------------------------------------------------------
AMPLIMODES for FullProf           FIX xyz
!
!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        543.913   0   7   0
!
062                        <--Space group symbol
!Atom   Typ        X         Y         Z        Biso       Occ      In Fin N_t Spc /Codes
Ca1    CA       0.00000   0.25000   0.50000   0.50000   0.50000    0   0   0     1
                   0.00      0.00      0.00      0.00      0.00
Ti1    TI       0.00000   0.00000   0.00000   0.50000   0.50000    0   0   0     1
                   0.00      0.00      0.00      0.00      0.00
. . .
```

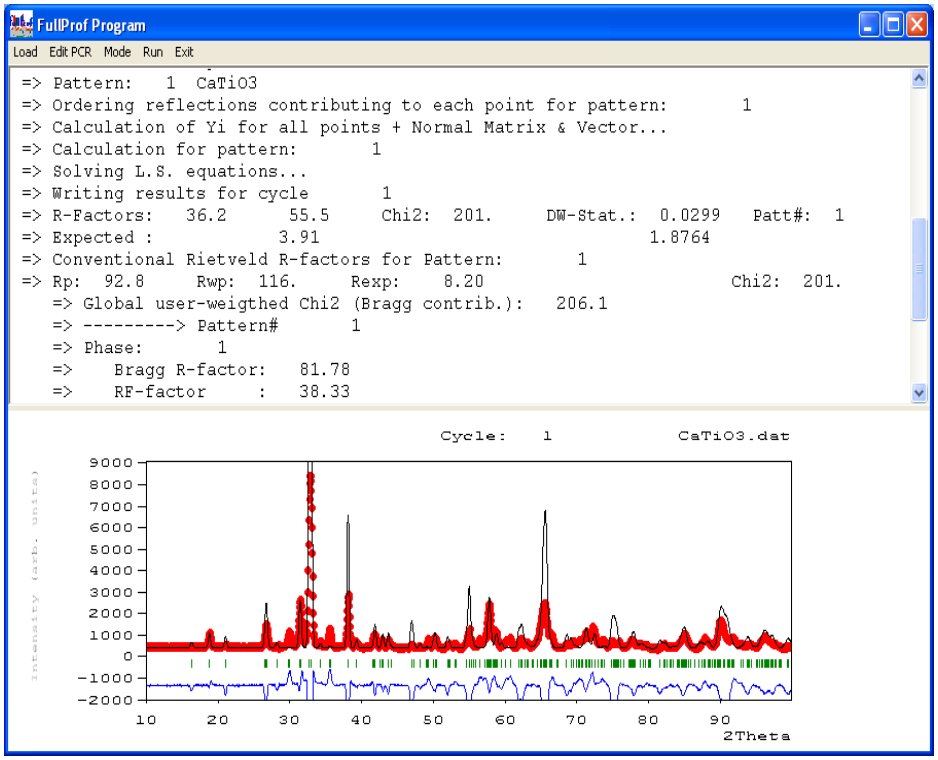
Modifying the file generated by AMPLIMODES to treat real data

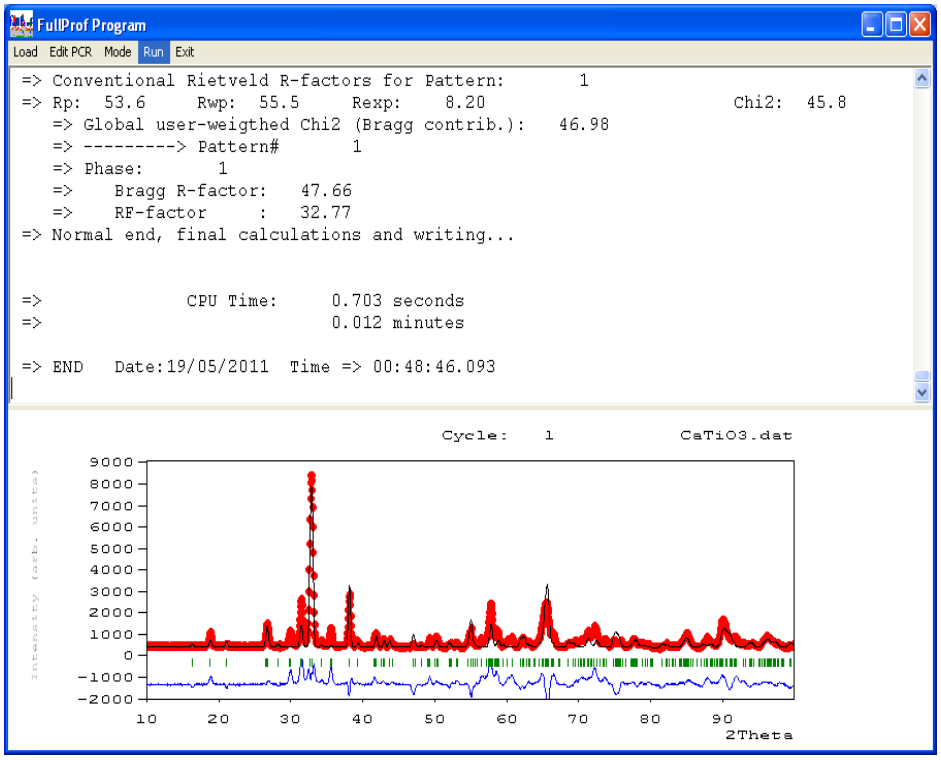
Notice that the Amplitudes of the modes are maintained fixed (zero codes) because the global scale factor and zero-shift have to be refined roughly before starting the full refinement

```
. . . . . .
   7  O1      M3+              0.046221  0.000000 -0.046221    1.000000
   7  O1_2    M3+              0.000000  0.000000  0.000000    1.000000
! Amplitudes of Symmetry Modes
A_MODES    7     2
      A1_R4+               0.800000     .000000
      A2_R5+              -0.100000     .000000
      A3_R5+               0.300000     .000000
      A4_X5+               0.700000     .000000
      A5_X5+               0.100000     .000000
      A6_M2+               0.020000     .000000
      A7_M3+               0.100000     .000000
!-------> Profile Parameters for Pattern #  1
!  Scale        Shape1      Bov       Str1       Str2       Str3   Strain-Model
  1.0000       0.00000   0.00000   0.00000   0.00000   0.00000        0
     1.00000     0.000     0.000     0.000     0.000     0.000
!       U          V          W          X          Y       GauSiz   LorSiz Size-Model
    0.64600  -0.309000   0.142000   0.000000   0.000000   0.000000   0.000000    0
      0.000      0.000      0.000      0.000      0.000      0.000      0.000
!     a          b          c        alpha      beta       gamma      #Cell Info
   5.441000   7.645000   5.380000  90.000000  90.000000  90.000000
    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
. . .
```

Running FullProf to refine the amplitudes of symmetry modes: First refine scale factor and zero shift

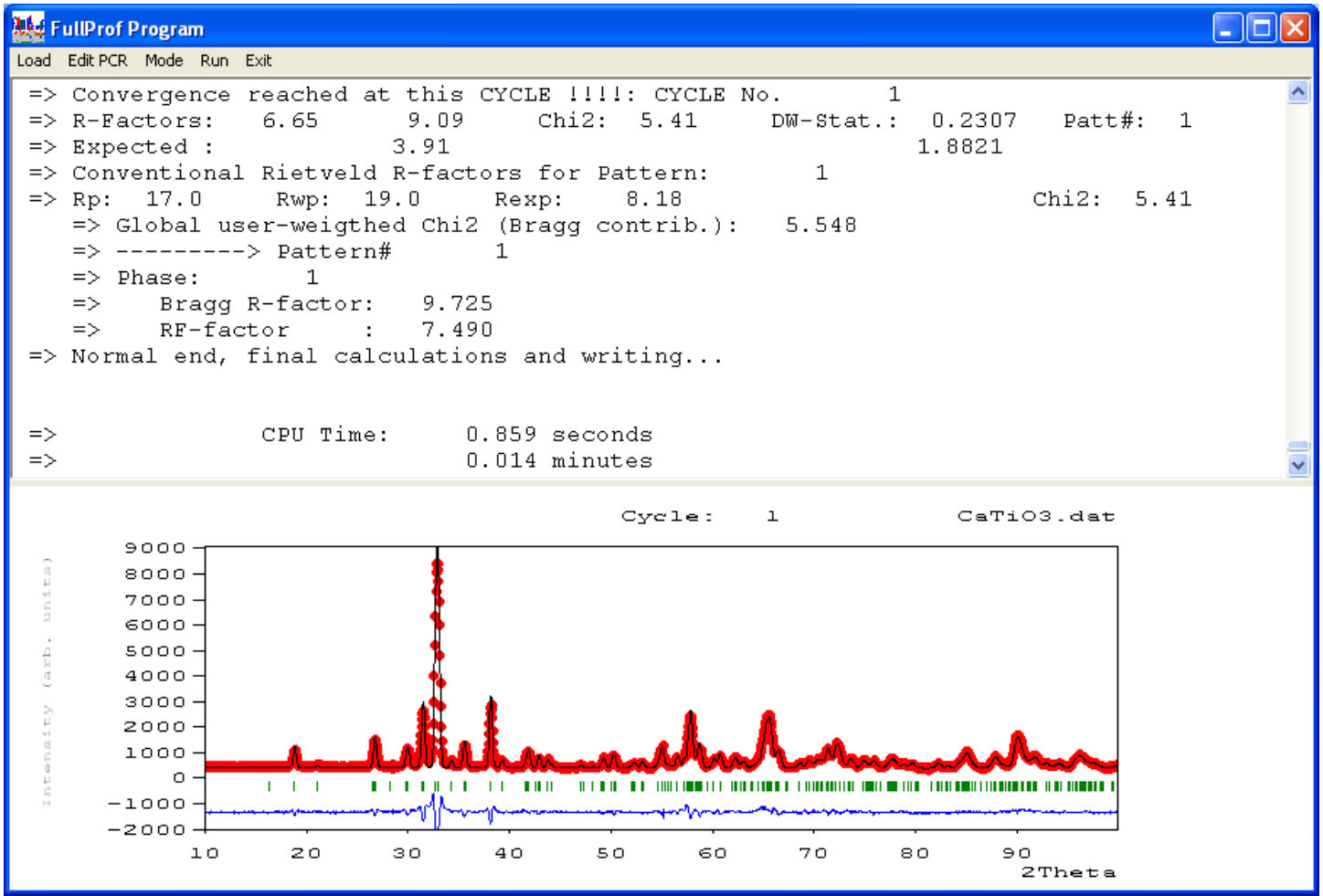
Once the file **CaTiO3ref.pcr** has been completed, we load the file in the FPS toolbar by pressing the button: and the selecting the file.
Clicking on the FullProf button the program launches and executes the refinement only with two parameters: scale factor and zero shift.





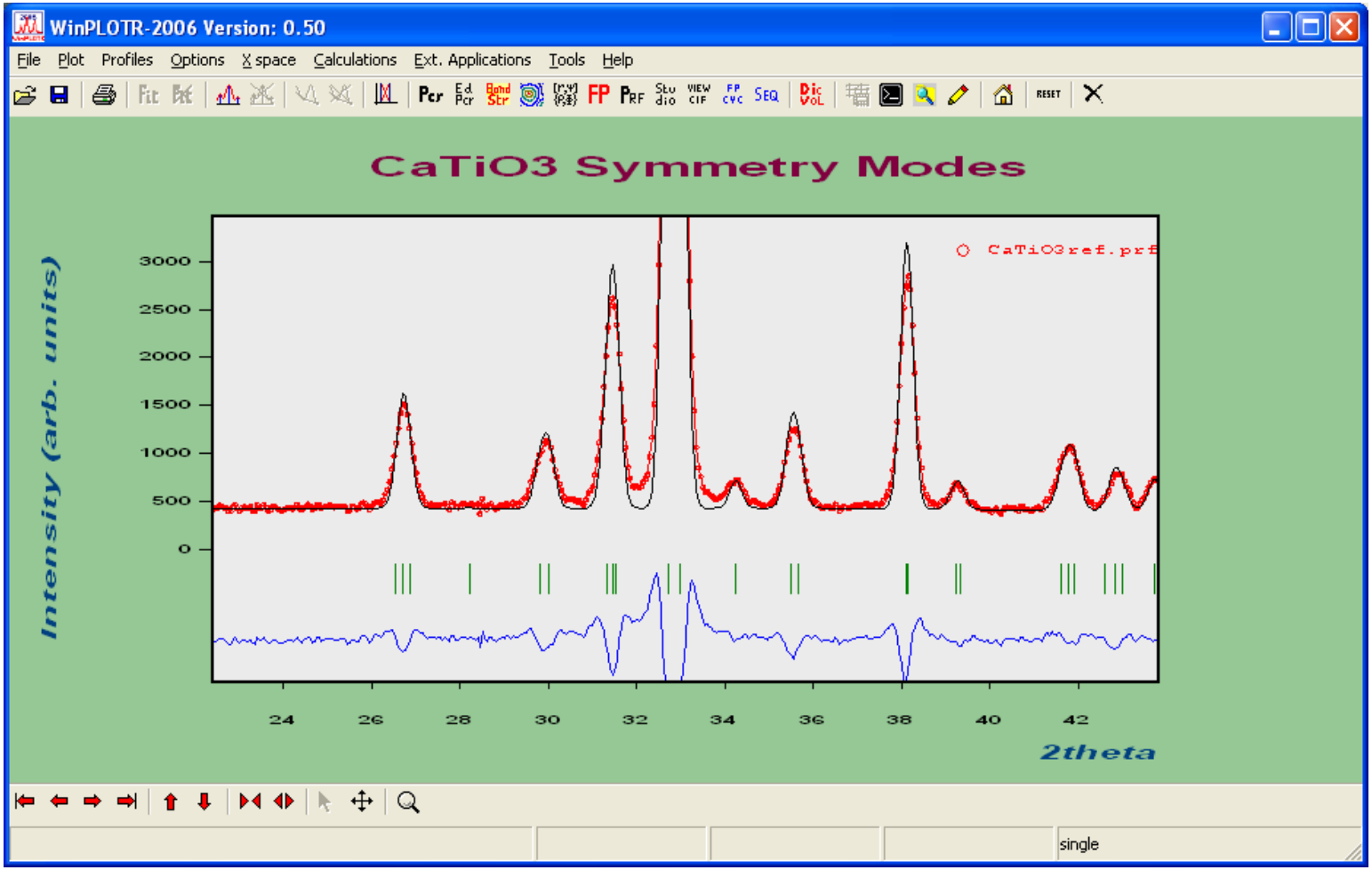
Running FullProf to refine the amplitudes of symmetry modes: varying the amplitudes

Editing again the file **CaTiO3ref.pcr** one can add the variation of amplitudes keeping also the scale factor and zero point as free parameters. After varying freely the amplitudes of the modes we arrive to the following result:



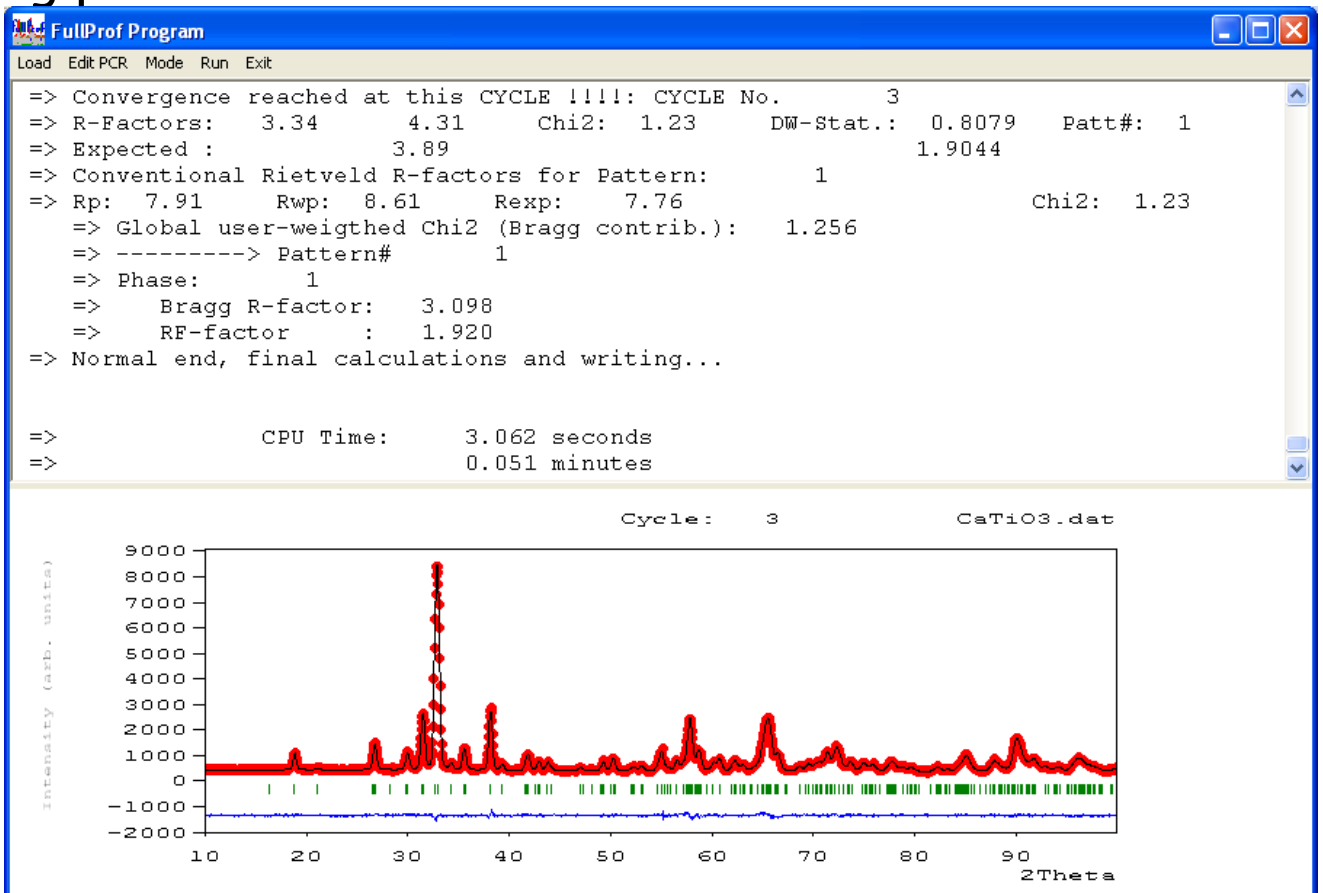
Inspecting the results of FullProf refinement with WinPLOTR-2006

Clicking of the WinPLOTR-2006 button , the program launches and display the observed versus calculated pattern as well as the difference curve and Bragg peaks tick markers. Zooming, one can see the major discrepancy: a Lorentzian component is lacking ...



Modifying the PCR file to perform a full refinement

At the present stage of refinement it is possible to free all parameters. For doing that, one has to add refinement codes to each parameter susceptible of being varied. In our case the remaining parameters are UVWY, height of background points, cell parameters and isotropic temperature factors. After freeing them, we obtain the following picture:



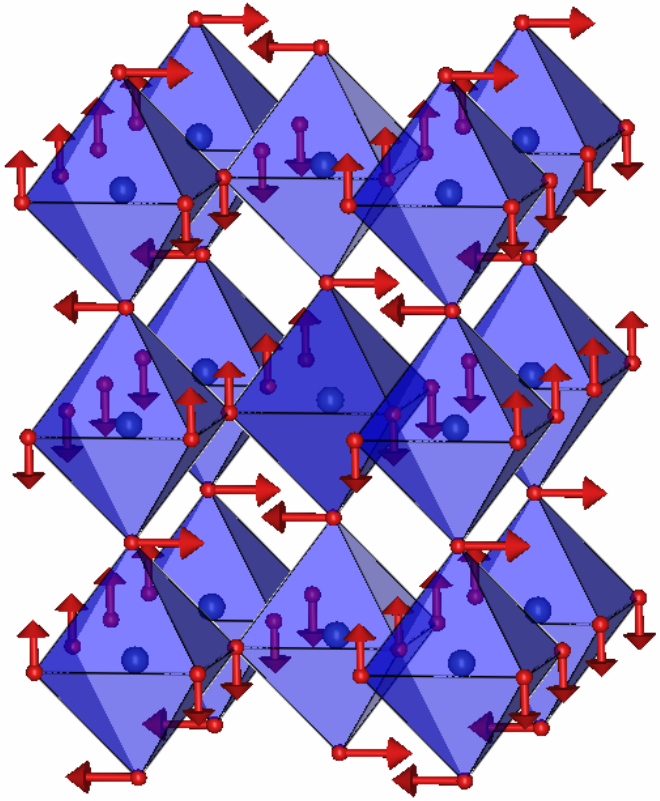
Inspecting the results (files *.out, *.sum) an visualising the symmetry modes (*.fst) with FullProf Studio

After refinement, **FullProf** produces a series of files containing all it is needed to extract physical-chemical information and to allow an analysis of the results by comparison with other cases. Below part of the OUT file .

```
 ================================================================================
 === FINAL ATOMS POSITIONS CALCULATED FROM SYMMETRY MODES FOR PHASE:   1
 ===    Preceded by the structures corresponding to single modes     ===
 ================================================================================


=> Structure corresponding to the single Irreducible representation:R4+
                          X          Y          Z          dx         dy         dz       Dist(A)
   Atom Ca1     CA    0.00000    0.25000    0.50000    0.00000    0.00000    0.00000    0.00000
   Atom Ti1     TI    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
   Atom O1      O     0.25000    0.00000    0.25000    0.00000   -0.03628    0.00000    0.27731
   Atom O1_2    O     0.00000    0.25000    0.00000    0.00000    0.00000    0.07255    0.39029

  => Global Amplitude of Representation R4+          :  1.110(3)


=> Structure corresponding to the single Irreducible representation:R5+
                          X          Y          Z          dx         dy         dz       Dist(A)
   Atom Ca1     CA    0.00000    0.25000    0.50000    0.00000    0.00000    0.00598    0.03216
   Atom Ti1     TI    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
   Atom O1      O     0.25000    0.00000    0.25000    0.00000   -0.00101    0.00000    0.00773
   Atom O1_2    O     0.00000    0.25000    0.00000    0.00000    0.00000   -0.00202    0.01088

  => Global Amplitude of Representation R5+          :  0.072(7)
. . . . . .

=> Final Complete Structure with contribution of all modes
                          X          Y          Z          Biso       Occ        dx         dy         dz       Dist(A)
   Atom Ca1     CA   -0.0356(4)   0.25000    0.5060(7)  0.46(2)    0.50000   -0.03564    0.00000    0.00598    0.19655
   Atom Ti1     TI    0.00000     0.00000    0.00000    0.17(3)    0.50000    0.00000    0.00000    0.00000    0.00000
   Atom O1      O     0.2891(2)  -0.03729(19) 0.2102(2) 0.337(17)  1.00000    0.03906   -0.03729   -0.03976    0.41490
   Atom O1_2    O     0.0160(3)   0.25000    0.0705(4)  0.24(2)    0.50000    0.01598    0.00000    0.07053    0.38926
```

Inspecting the results (files *.out, *.sum) an visualising the symmetry modes (*.fst) with FullProf Studio

The files of type *.fst contain the information for representing the idealised crystal structure decorated with arrows representing atomic displacements. By default **FullProf** produces a number of files equal to the number of different irreducible representations contributing to the global distortion. These files can be edited and modified by the user. For details consult the corresponding manual accessible from the **FPS toolbar**.



Picture of the displacement pattern corresponding to the representation R4+ This irrep involves modes displacing the oxygen atoms is such a way as representing a rotational mode around the a-axis. The global amplitudes of the different irreps are:

```
R4+ :   1.110(3) Å
M3+ :   0.853(4) Å
X5+ :   0.423(4) Å
R5+ :   0.072(7) Å
M2+ :   0.008(3) Å
```

```
Added instructions in the *.fst file to get the picture:
conn TI O 0 2.2
poly Ti1 color 0 0 1 0.5  edges radius 1.5
```

Preparing a PCR file extracting integrated intensity clusters to be used in Simulated Annealing Optimisation

The process we have shown up to now goes directly to the refinement of amplitudes starting with an arbitrary initial set. This works for the case of $CaTiO_3$ because it is a simple structure with only seven degrees of freedom.

In the general case one has to be able to "solve" nearly *ab initio* a crystal structure supposed to derive from another of higher symmetry. For that a global optimisation method (as opposed to least squares, which is local) may be necessary for getting good initial values for the amplitudes.

We discuss below the procedure to extract the integrated intensities using the Le Bail Fit (LBF) with FullProf

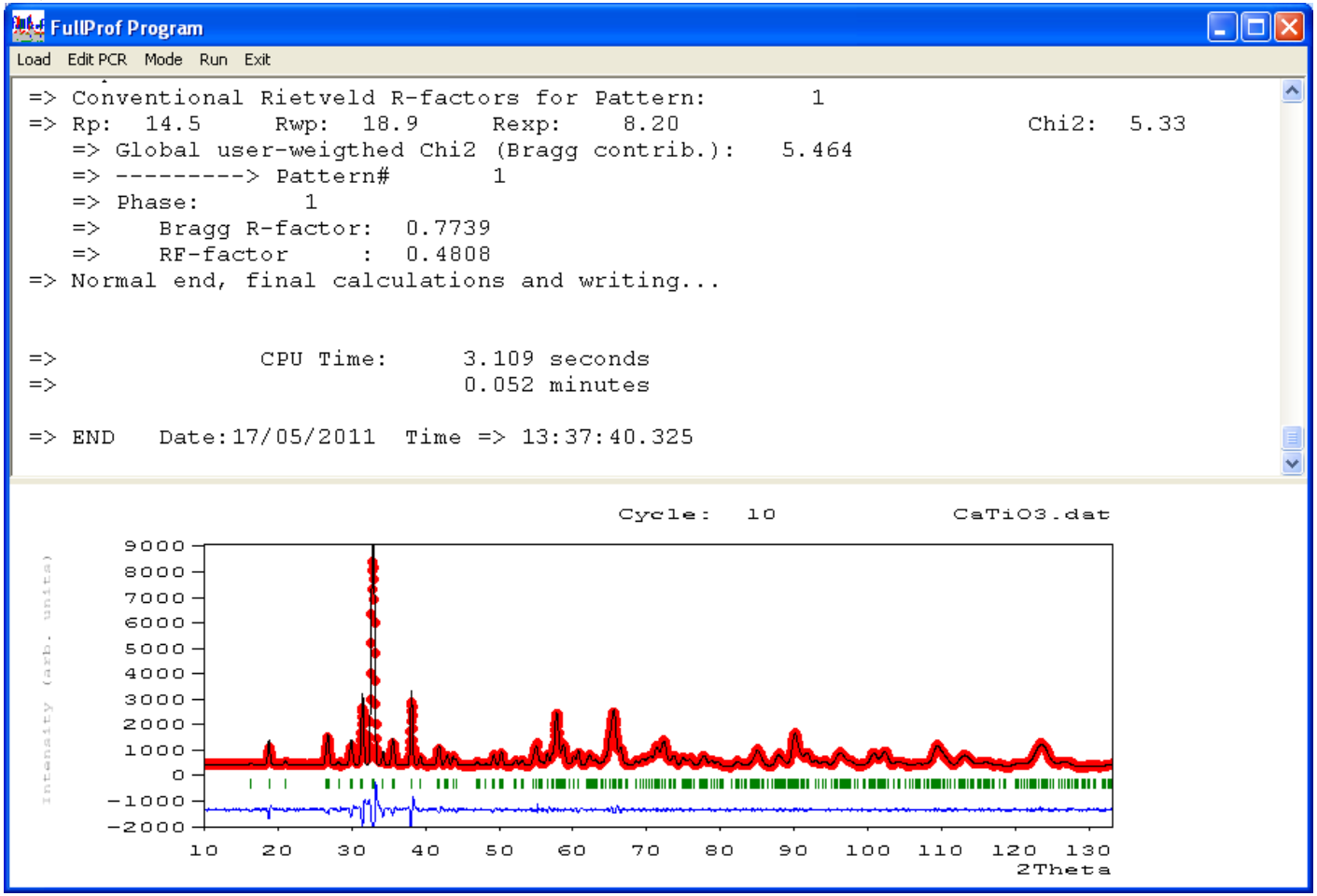
Preparing a PCR file extracting integrated intensity clusters to be used in Simulated Annealing Optimisation

For creating a file with for a LBF the easiest way is to start with a copy of the already available PCR files. For instance we can copy the file **bcs_modified_cti.pcr** into **LBF_cti.pcr**. We proceed by suppressing the atoms block and setting the appropriate flags for doing the LBF (**Nat=0, Jbt=2, Aut=0,** etc). The important sections of the modified PCR file **LBF_cti.pcr** is shown below:

```
.......
.......
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   7   1  16   2   0   0   1   0   0   1   0   0   0   0   0   0   0
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
  -1   0   1   0   1   0   4   0   0   3   0   0   0   0   0   0   0
.......
.......
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   0   0   0 0.0 0.0 1.0   2   0   0   0   0          0.000    0   7   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind    RMua     RMub     RMuc    Jtyp  Nsp_Ref Ph_Shift
  11   0   0   0   0   0  1.0000  0.0000   0.0000   0.0000     1       0       0
!
.......
```

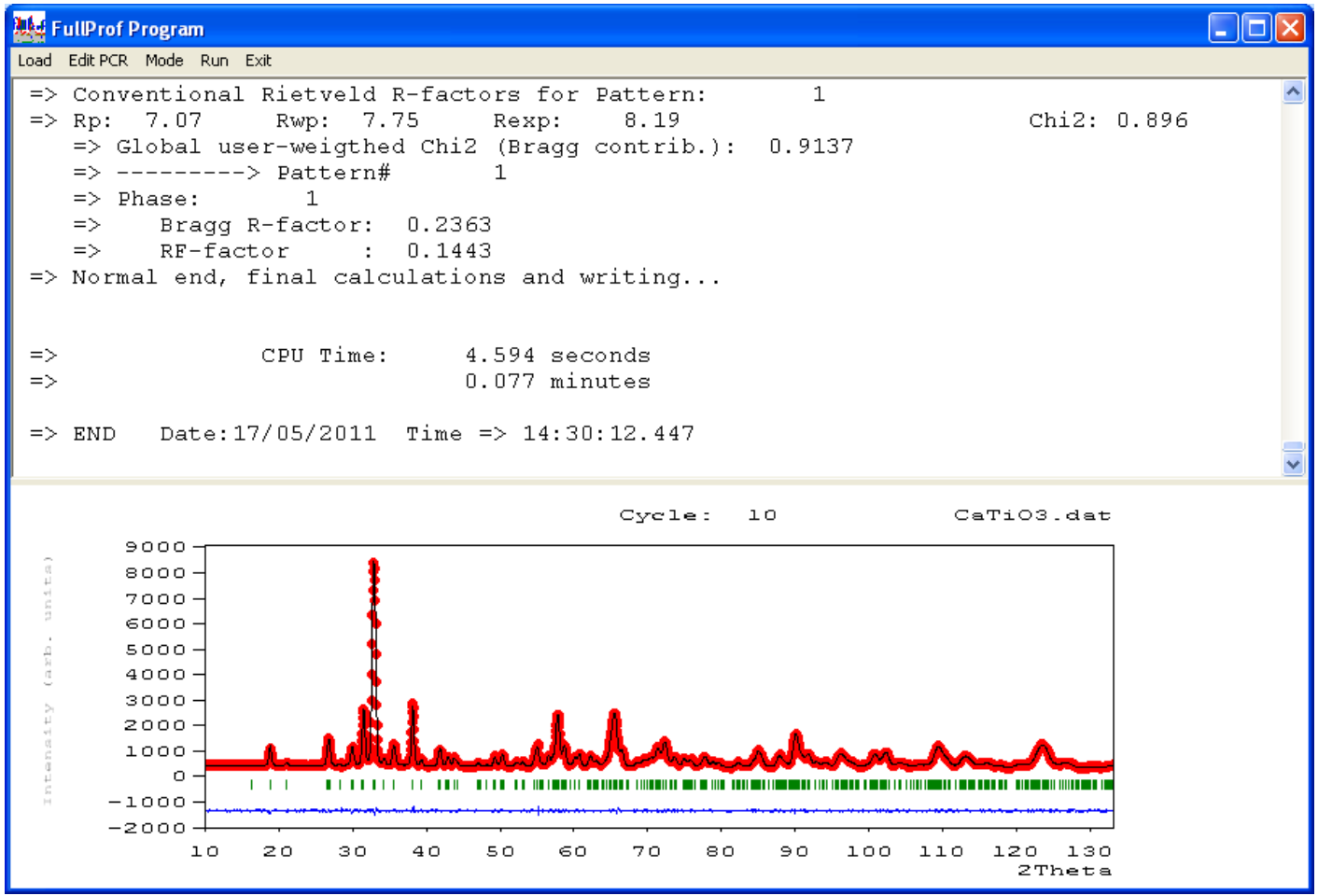
First cycle of a Le Bail Fit to the neutron powder diffraction data on $CaTiO_3$ using Gaussian peaks

Putting **Aut=0** and number of refined parameters equal to zero means that the only parameters to be adjusted are the integrated intensities of the generated peaks for the given unit cell parameters and space group. After doing 10 cycles (**NCY=10**) the run of **FullProf** gives the result below.



Le Bail Fit on $CaTiO_3$ data after convergence. UVWY and cell parameters have been refined

Putting now **Aut=1** and setting to 1 the codes of the parameters to be refined (cell parameters and profile parameters U,V,W and Y) we re-run the program again. After convergence, **FullProf** gives the result below.



Preparing a simulated annealing PCR file for working with integrated intensity clusters of $CaTiO_3$ (1)

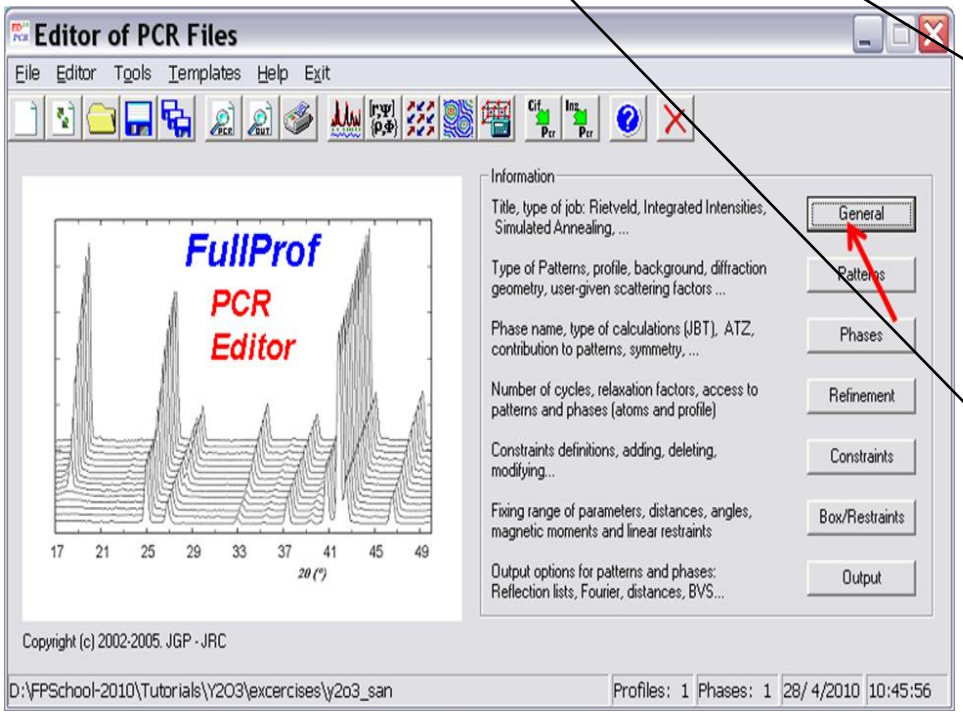
Copy the modified file (with the real cell parameters) from the BCS into another one

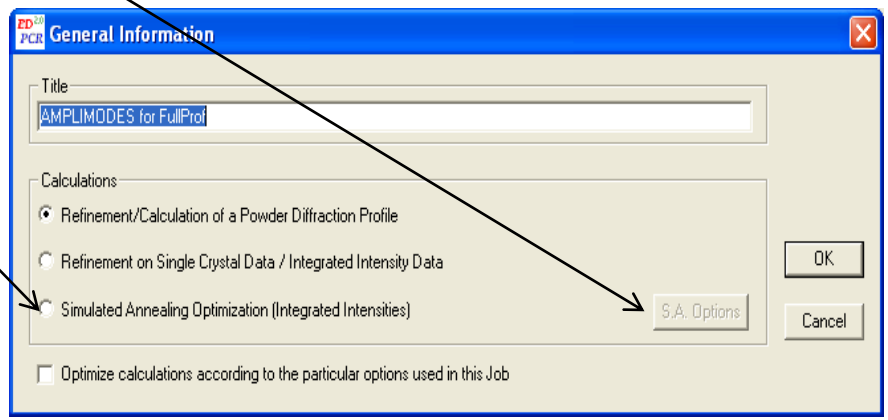
Example.
If the initial file is called **bcs_modified_cti.pcr**
The new file will be called **cti_san.pcr**

Load **cti_san.pcr** in the toolbar and click on **EdPCR** button. The file is loaded into **EdPCR** and we are prepared for modifications.

Preparing a simulated annealing PCR file for working with integrated intensity clusters of $CaTiO_3$ (2)

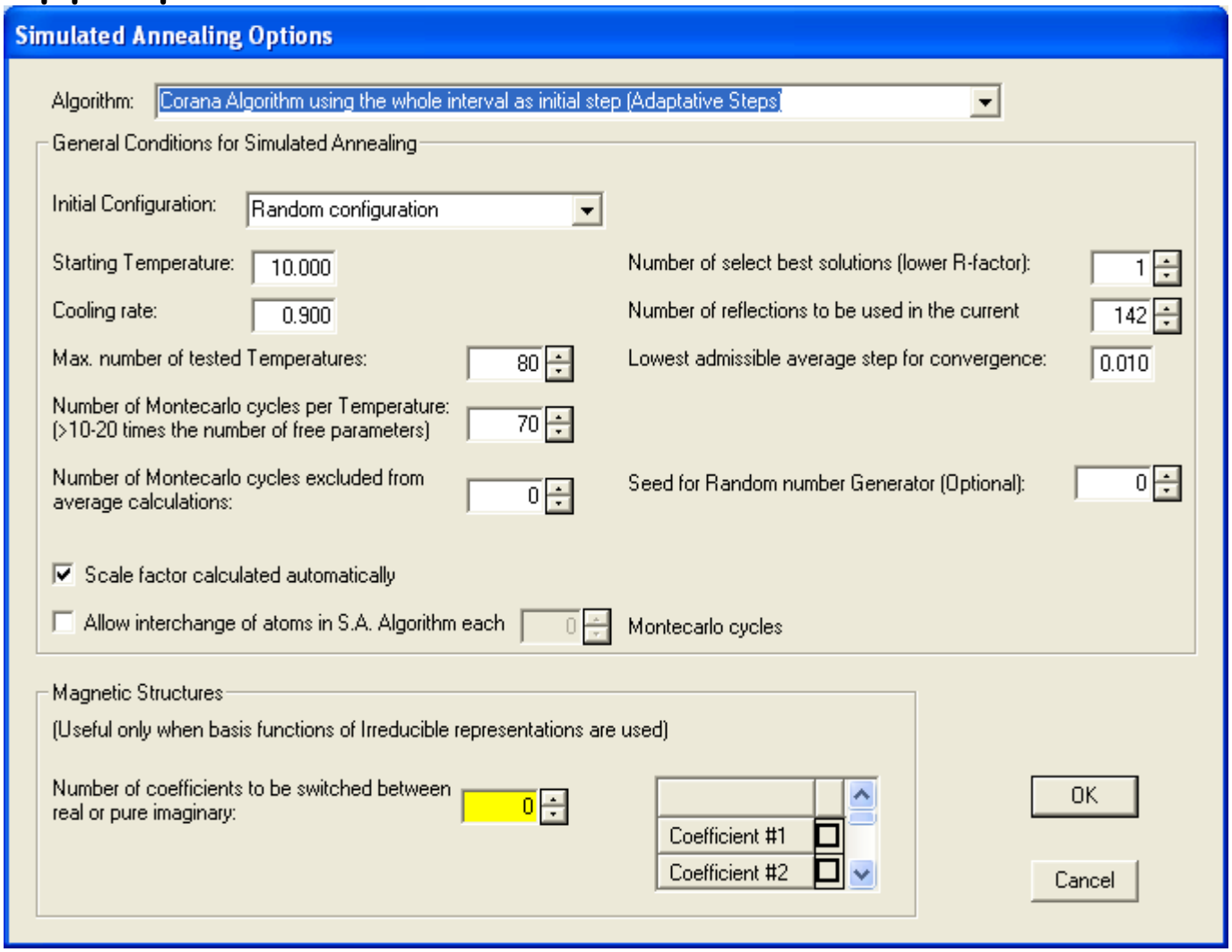
Tick the "Simulated Annealing Optimisation (Integrated Intensities)" item and then click on the "S.A. Options" button.





Preparing a simulated annealing PCR file for working with integrated intensity clusters of $CaTiO_3$ (3)

The following dialog opens and the user has to fill the appropriate boxes. The shown values are OK for $CaTiO_3$ case.



Clicking on OKs returns to the general interface.

Preparing a simulated annealing PCR file for working with integrated intensity clusters of $CaTiO_3$ (4)

Select the menu: Editor → **Unsaved Input File** to open the unsaved.pcr file and change by hand **Job** to **1** (experimental neutron data) and **Irf** to **4** (integrated intensities provided for the phase). Save the file giving it the name **cti_san.pcr** to replace the original and then reopen (clicking on "Yes" button) the changed file into **EdPCR**. Save again to provoke **EdPCR** to generate automatic changes and reopen again the internal editor to continue.

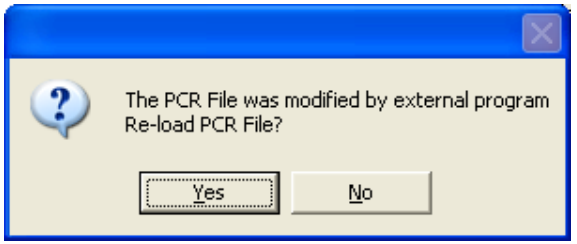
External EdPCR Text Editor - [C:\Disk-D\FPSchool-2011\Exercises-FullProf-Amplimodes\PCR-files\CaTi...

File Edit Search

```
COMM AMPLIMODES for FullProf
! Files => DAT-file: ,  PCR-file: C:\Disk-D\FPSchool-2011\Exercises-FullProf-Amplimodes\PC
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   7   1   0   2   0   0   1   0   0   0   0   0   0   3   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   0   3   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      1.0000   0.050000   170.0000   0.000   0.000
!
!
      7    !Number of refined parameters
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     0.00
!-------------------------------------------------------------------------------
AMPLIMODES for FullProf          FIX xyz
!
!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   4   0   0   7       543.913   0   7   0
!
062                        <--Space group symbol
!Atom   Typ       X         Y         Z      Biso       Occ      In Fin N_t Spc /Codes
Ca1     CA      0.00000   0.25000   0.50000   0.50000   0.50000   0   0   0    1
                  0.00      0.00      0.00      0.00      0.00
Ti1     TI      0.00000   0.00000   0.00000   0.50000   0.50000   0   0   0    1
                  0.00      0.00      0.00      0.00      0.00
O1      O       0.25000   0.00000   0.25000   0.50000   1.00000   0   0   0    1
                  0.00      0.00      0.00      0.00      0.00
O1_2    O       0.00000   0.25000   0.00000   0.50000   0.50000   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                 Ux        Uy        Uz        Coeff
```

Line:20 Col:33 INS

Put **Job=1** and **Irf=4** and save the file giving it the name **cti_san.pcr**



Click yes and re-save the file again for making automatic changes in the file

Preparing a simulated annealing PCR file for working with integrated intensity clusters of $CaTiO_3$ (5)

External EdPCR Text Editor - [C:\Disk-D\FPSchool-2011\Exercises-FullProf-Amplimodes\PCR-fil...

File Edit Search

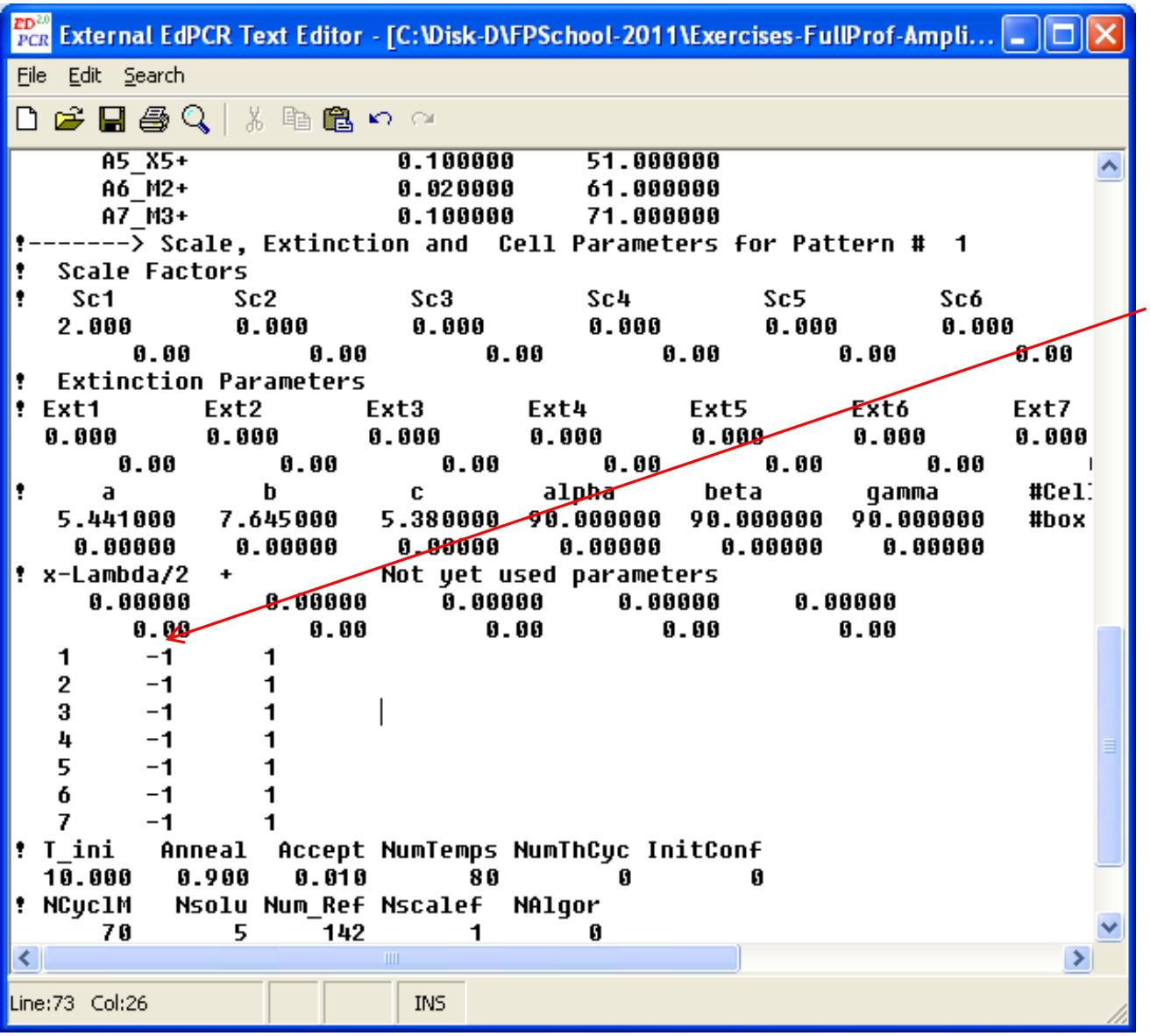
```
   5  01      X5+              0.000000  0.000000  0.000000    1.000000
   5  01_2    X5+             -0.092442  0.000000  0.000000    1.000000
   6  01      M2+             -0.046221  0.000000 -0.046221    1.000000
   6  01_2    M2+              0.000000  0.000000  0.000000    1.000000
   7  01      M3+              0.046221  0.000000 -0.046221    1.000000
   7  01_2    M3+              0.000000  0.000000  0.000000    1.000000
! Amplitudes of Symmetry Modes
A_MODES    7     2
      A1_R4+               0.800000     11.000000
      A2_R5+              -0.100000     21.000000
      A3_R5+               0.300000     31.000000
      A4_X5+               0.700000     41.000000
      A5_X5+               0.100000     51.000000
      A6_M2+               0.020000     61.000000
      A7_M3+               0.100000     71.000000
!-------> Scale, Extinction and  Cell Parameters for Pattern #  1
!  Scale Factors
!   Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
   2.000       0.000       0.000       0.000       0.000       0.000
       0.00        0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7   Ext-Model
 0.1760    -0.1978     0.9146E-01   0.000     0.3004E-01   0.000       0.000        0
       0.00        0.00        0.00        0.00        0.00        0.00        0.00
!     a           b           c         alpha       beta        gamma      #Cell Info
   5.441000    7.645000    5.380000  90.000000  90.000000  90.000000   #box -0.15 1.15
    0.00000     0.00000     0.00000    0.00000    0.00000    0.00000
! x-Lambda/2  +          Not yet used parameters
     0.00000     0.00000     0.00000     0.00000     0.00000
       0.00        0.00        0.00        0.00        0.00
! T_ini   Anneal  Accept NumTemps NumThCyc InitConf
  10.000   0.900   0.010       80        0        0
! NCyclM   Nsolu Num_Ref Nscalef  NAlgor
      70       5     142       1       0
```

Line:1 Col:1 INS

Within EdPCR, accessing the menu : Editor → **Input Control File (.PCR)** Edit the file and delete superfluous items. In particular put to zero all Ext1 items, that were imported from previous U,V,W parameters.

Notice that the amplitudes have now refinement codes. There are 7 free parameters and one has to introduce the box conditions for variations of amplitudes.

Preparing a simulated annealing PCR file for working with integrated intensity clusters of $CaTiO_3$ (6)



Modify the value of **Nre** on top of the file to the value **7** (**Nre=7**), not shown in the figure.

Add seven lines, at the indicated position, starting with the numbers 1, 2 ... 7 and put -1 1 in the same lines to tell the program that the parameter numbered as 1, 2 ... may vary between -1 and 1. We do not allow variations of amplitudes bigger than one angstrom.
Save, re-open the file and save again as before.

Preparing a simulated annealing PCR file for working with integrated intensity clusters of $CaTiO_3$ (7)

External EdPCR Text Editor - [C:\Disk-D\FPSchool-2011\Exercises-FullProf-Amplimodes\PCR-files...

File Edit Search

```
A_MODES    7     2
      A1_R4+              0.800000     11.000000
      A2_R5+             -0.100000     21.000000
      A3_R5+              0.300000     31.000000
      A4_X5+              0.700000     41.000000
      A5_X5+              0.100000     51.000000
      A6_M2+              0.020000     61.000000
      A7_M3+              0.100000     71.000000
!-------> Scale, Extinction and  Cell Parameters for Pattern #  1
!  Scale Factors
!   Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
  2.000       0.000       0.000       0.000       0.000       0.000
       0.00        0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7   Ext-Model
 0.000       0.000       0.000       0.000       0.000       0.000       0.000       0
       0.00        0.00        0.00        0.00        0.00        0.00        0.00
!     a           b           c         alpha       beta        gamma      #Cell Info
   5.441000    7.645000    5.380000   90.000000   90.000000   90.000000   #box -0.15 1.15
    0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
! x-Lambda/2  +          Not yet used parameters
     0.00000     0.00000     0.00000     0.00000     0.00000
       0.00        0.00        0.00        0.00        0.00
! Limits for selected parameters (+ steps & BoundCond for SA):
   1     -1.0000      1.0000      0.0000   0
   2     -1.0000      1.0000      0.0000   0
   3     -1.0000      1.0000      0.0000   0
   4     -1.0000      1.0000      0.0000   0
   5     -1.0000      1.0000      0.0000   0
   6     -1.0000      1.0000      0.0000   0
   7     -1.0000      1.0000      0.0000   0
! T_ini   Anneal  Accept NumTemps NumThCyc InitConf
  80.000   0.900   0.010       80        0        0
! NCyclM   Nsolu Num_Ref Nscalef  NAlgor
      70       1     142       1       0
```

Line:80 Col:33 INS

Within EdPCR, editing again → **Input Control File (.PCR)**

Verify that the aspect of the file is similar to that we have in the picture

Now the file is prepared to run FullProf in simulated annealing mode using Clusters of Integrated Intensities.

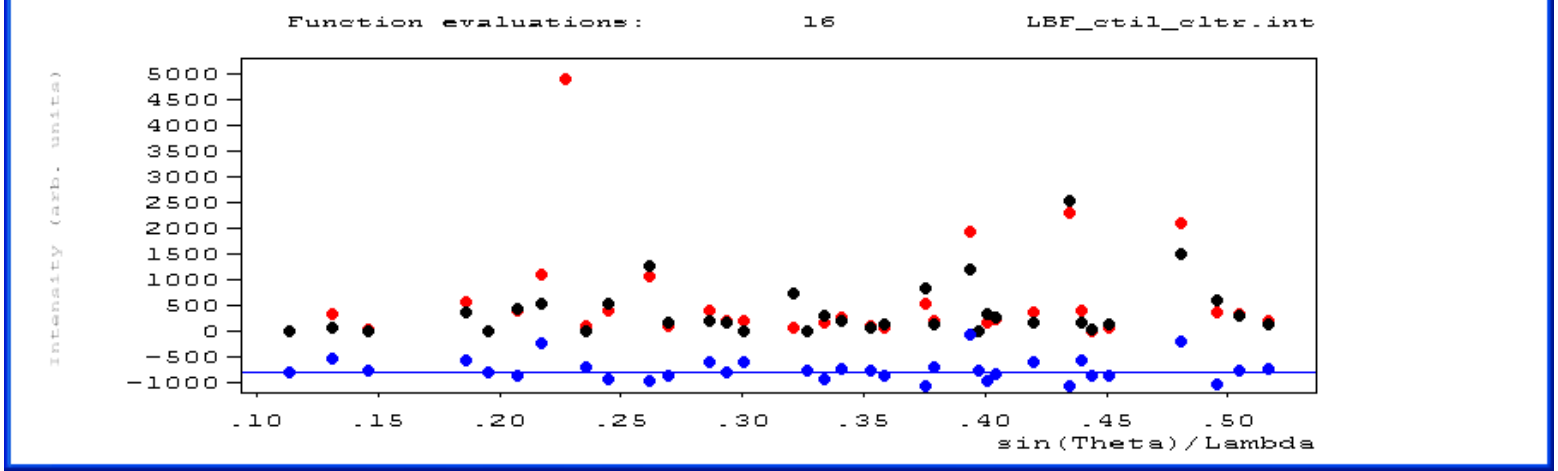
Running a simulated annealing job with integrated intensity clusters of $CaTiO_3$

Having the created file **cti_san.pcr** loaded in the FPS toolbar, one can run FullProf and select as intensity file **LBF_cti1_cltr.int**. The program launches as shown below

FullProf Program

Load Edit PCR Mode Run Exit

```
=>               (Multi_Pattern: Windows-version)


=> START Date:21/05/2011  Time => 12:48:18.343
=> Reading control file *.PCR ...
=> End of preliminary calculations !

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

=> Initial configuration cost:     41.49
=> Initial configuration state vector:
=>      A1_R4+    A2_R5+    A3_R5+    A4_X5+    A5_X5+    A6_M2+    A7_M3+
=>           1         2         3         4         5         6         7
=>     -0.3520   -0.6724   -0.2551    0.2332   -0.2018    0.9520    0.0596
=> NT:   1 Temp: 80.00 (%Acc):100.00  <Step>:  2.0000  <R-factor(F2)> : 53.1634
```



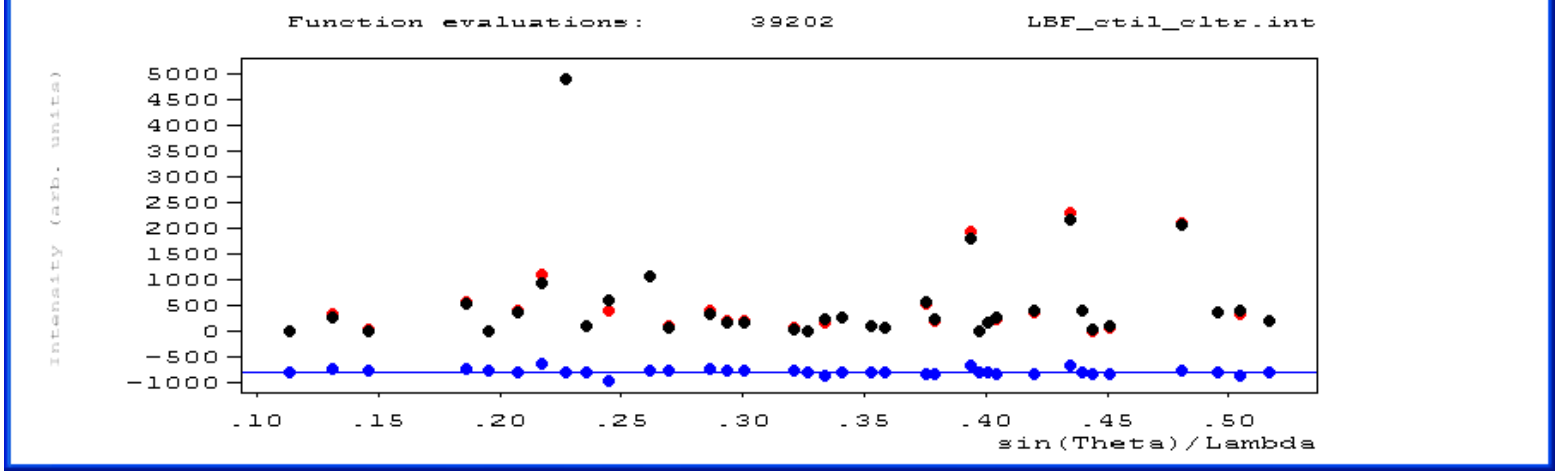
Running a simulated annealing job with integrated intensity clusters of $CaTiO_3$

One can see that one of the amplitudes is blocked at the value 1.0, this means that we have to enlarge the limits in order to allow larger values. We can re-run the program using different conditions.

FullProf Program

Load Edit PCR Mode Run Exit

```
=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   142 reflections):

=> Sol#: 1 <R-factor(F2)>:    6.734 ::
=>     A1_R4+    A2_R5+    A3_R5+    A4_X5+    A5_X5+    A6_M2+    A7_M3+
=>          1         2         3         4         5         6         7
=>     1.0000    0.3313    0.0195   -0.3448   -0.1710    0.0373    0.9614


=>               CPU Time:     19.875 seconds
=>                              0.331 minutes

=> END    Date:21/05/2011  Time => 12:50:05.546
```



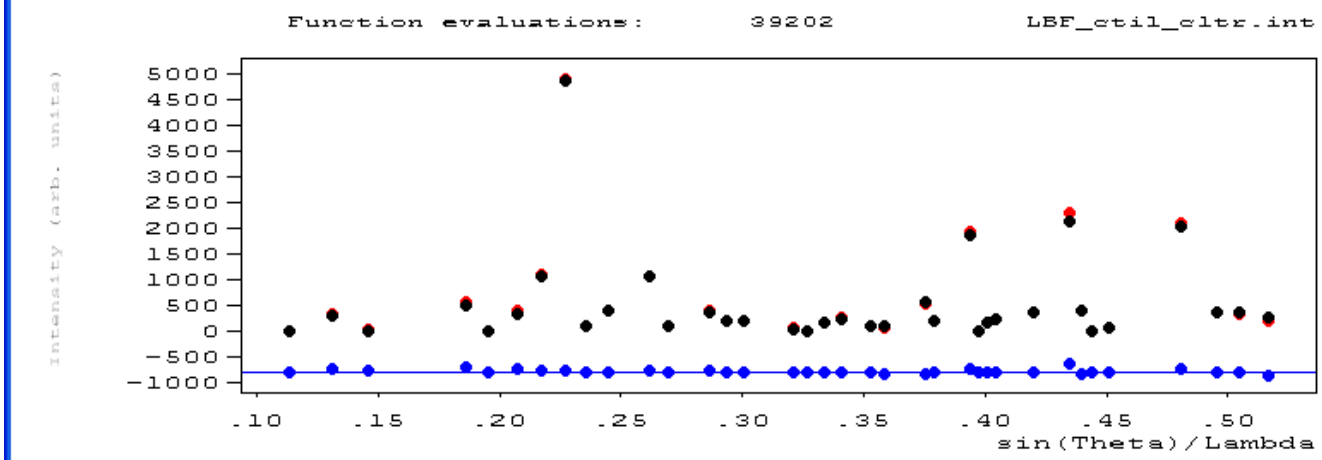
Running a simulated annealing job with integrated intensity clusters of $CaTiO_3$

This is another run in which we have increased the range of amplitudes up to 1.3Å.

FullProf Program

Load Edit PCR Mode Run Exit

```
=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   142 reflections):

=> Sol#: 1 <R-factor(F2)>:    3.452 ::
=>     A1_R4+    A2_R5+    A3_R5+    A4_X5+    A5_X5+    A6_M2+    A7_M3+
=>          1         2         3         4         5         6         7
=>     1.1231    0.0276   -0.0556   -0.3693   -0.2027   -0.0276    0.8433


=>               CPU Time:    20.031 seconds
=>                             0.334 minutes

=> END   Date:21/05/2011  Time => 12:55:40.718
```



Results of the simulated annealing (SAN) run on $CaTiO_3$ data

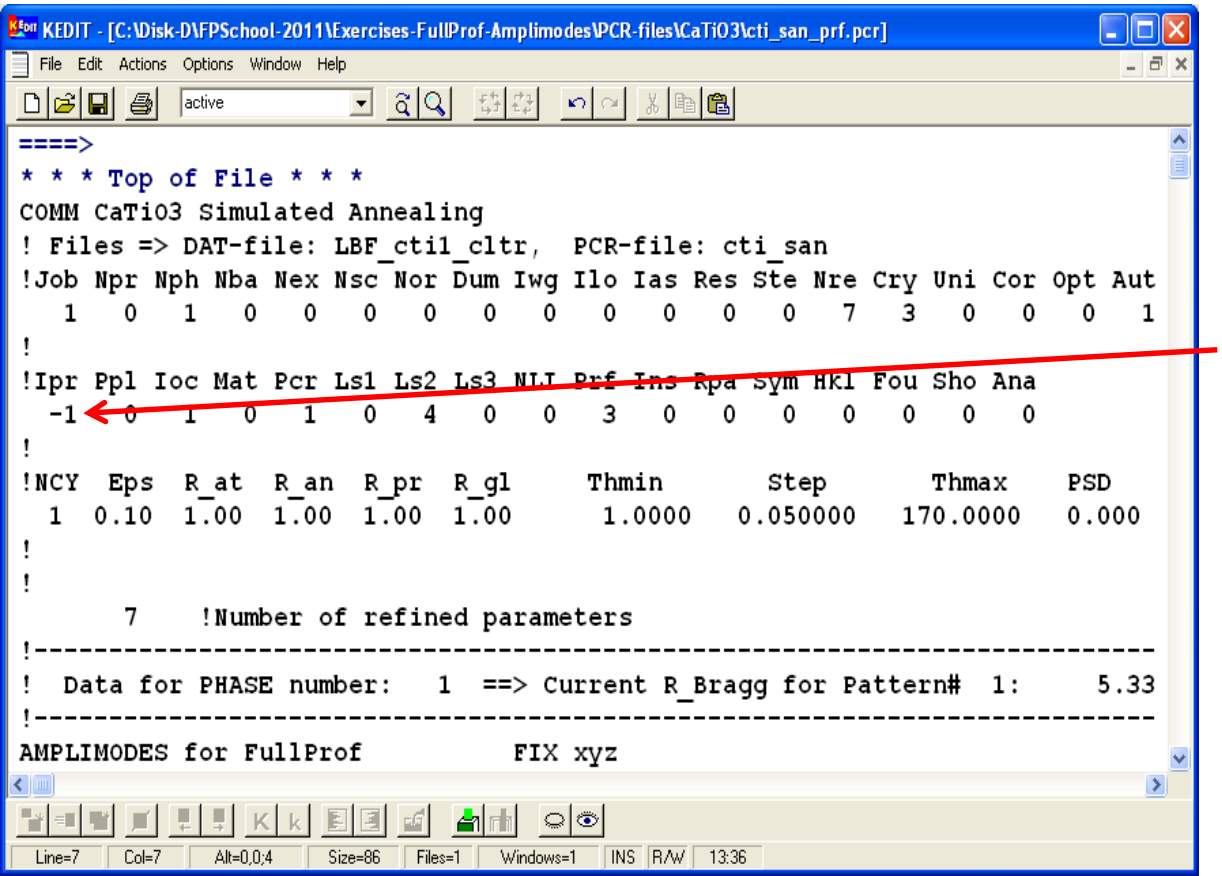
We have seen that the results depend of the constraints. When the maximum amplitude was limited to 1, the results were worse and freeing these conditions the R-factor diminished. When compared with the results of the Least Squares (LSQ) refinement done above, we see that the good order of magnitude is obtained. Keep in mind that we have used only a part of the diagram and clusters of integrated intensities. The SAN method is normally used for solving a structure and get initial values of parameter for a further treatment using LSQ.

Comparison of LSQ and SAN amplitudes

Least squares refinement		Simulated (Integrated
Name	Value	Annealing Intensities)
A1_R4+	1.110(3)	1.1231
A2_R5+	0.065(7)	0.0276
A3_R5+	-0.031(5)	-0.0556
A4_X5+	-0.386(4)	-0.3693
A5_X5+	-0.173(3)	-0.2027
A6_M2+	0.008(3)	-0.0276
A7_M3+	0.853(4)	0.8433

Simulated annealing (SAN) using profile intensities on $CaTiO_3$ data

When the structure is more complex and we need to overcome as much as possible the problem of overlap, one can use the profile intensities instead of integrated intensity clusters. For that it suffices to put **Ipr=-1**, as shown below. Remember that we already prepared the output of the information needed for this option, when we put **Ipr=-1** in the LBF method.



Copy the file **cti_san.pcr** into the file **cti_san_spr.pcr**.

Edit the last file and change to **Ipr=-1**.

Rename the file **LBS_cti.spr** into **cti_san_spr.spr**

Simulated annealing (SAN) using profile intensities on $CaTiO_3$ data

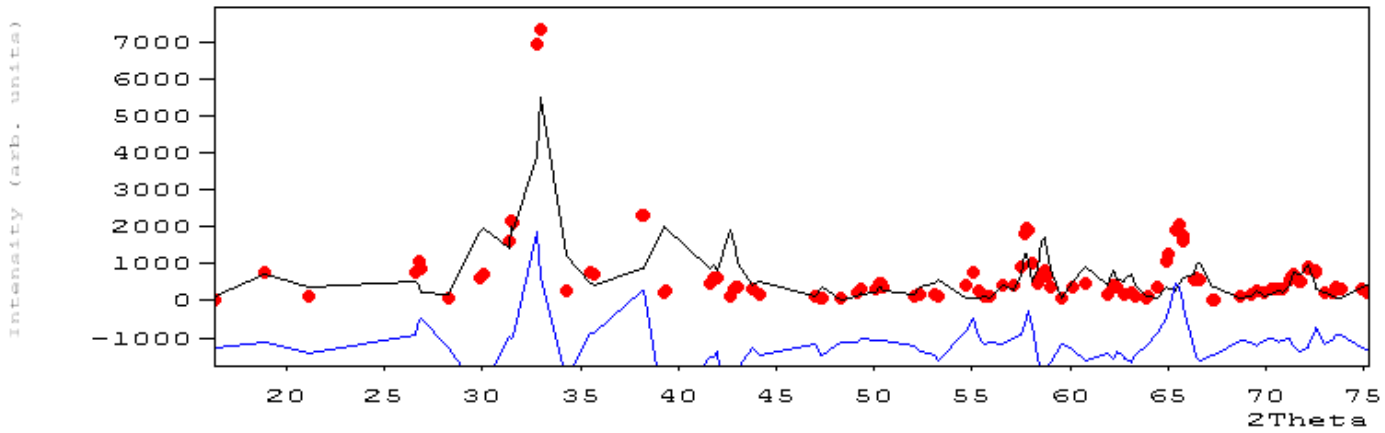
Start of the profile intensity SAN job.
We are still using 142 reflections.

FullProf Program

Load Edit PCR Mode Run Exit

```
=>               (Multi_Pattern: Windows-version)


=> START Date:22/05/2011  Time => 13:46:07.359
=> Reading control file *.PCR ...
=> End of preliminary calculations !

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

=> Initial configuration cost:    58.12
=> Initial configuration state vector:
=>     A1_R4+    A2_R5+    A3_R5+    A4_X5+    A5_X5+    A6_M2+    A7_M3+
=>          1         2         3         4         5         6         7
=>    -0.6484   -0.6086   -0.4897    0.8538    1.2290    0.0450   -0.5371
=> NT:   1 Temp: 80.00 (%Acc): 85.71  <Step>:  2.6000  <Rp-Factor(y)> : 50.8926
```

Function evaluations: 8 LBF_ctil_cltr.int



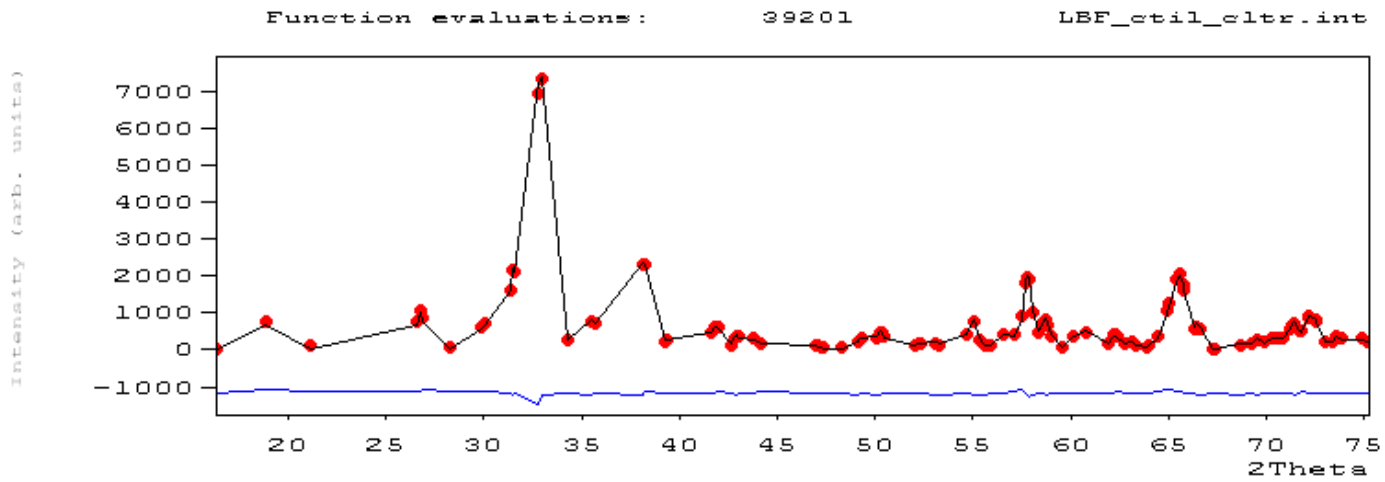
Simulated annealing (SAN) using profile intensities on $CaTiO_3$ data

Final picture of the profile intensity SAN job.
We are still using 142 reflections.

FullProf Program

Load Edit PCR Mode Run Exit

```
=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   142 reflections):

=> Sol#: 1 <Rp-Factor(y)>:     4.380 ::
=>      A1_R4+    A2_R5+    A3_R5+    A4_X5+    A5_X5+    A6_M2+    A7_M3+
=>           1         2         3         4         5         6         7
=>     -1.1054   -0.0694    0.0317    0.3758    0.1609    0.0121    0.8498


=>                CPU Time:     22.469 seconds
=>                               0.374 minutes

=> END    Date:22/05/2011  Time => 13:49:43.390
```

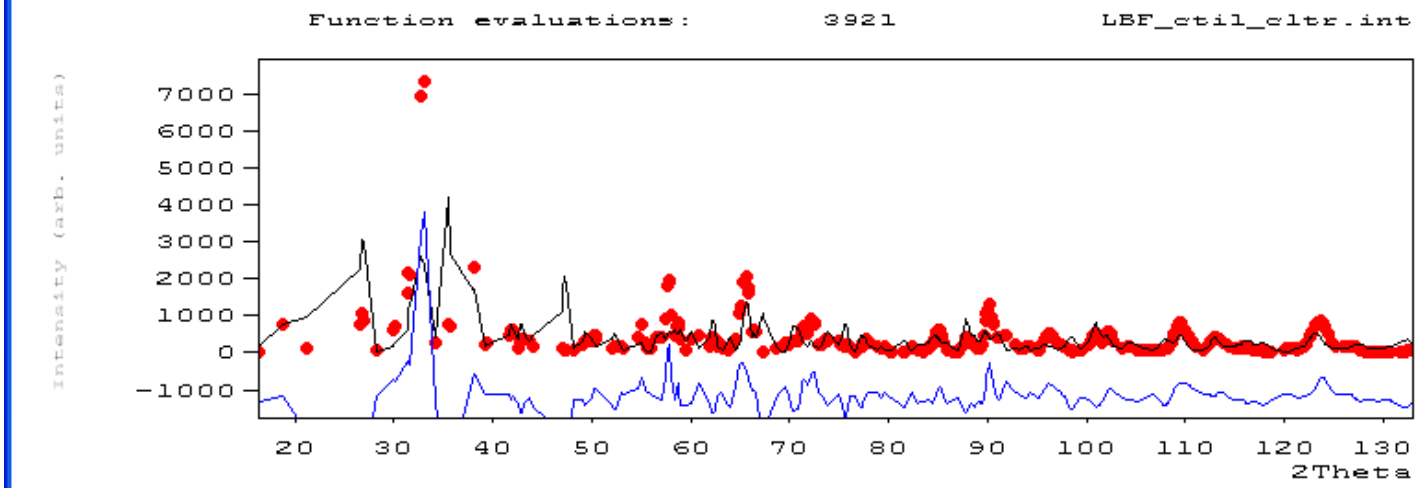


Simulated annealing (SAN) using profile intensities on $CaTiO_3$ data

Starting part of the profile intensity SAN job using the full set of reflections.

FullProf Program

```
=> Initial configuration cost:    76.62
=> Initial configuration state vector:
=>     A1_R4+    A2_R5+    A3_R5+    A4_X5+    A5_X5+    A6_M2+    A7_M3+
=>          1         2         3         4         5         6         7
=>     0.1898   -0.0174    0.1404    0.6903   -0.4554   -0.3432    0.9810
=> NT:   1 Temp:  80.00 (%Acc): 97.96  <Step>:   2.6000  <Rp-Factor(y)> : 73.4473
=> NT:   2 Temp:  72.00 (%Acc): 96.73  <Step>:   2.6000  <Rp-Factor(y)> : 72.8466
=> NT:   3 Temp:  64.80 (%Acc): 97.35  <Step>:   2.6000  <Rp-Factor(y)> : 72.9415
=> NT:   4 Temp:  58.32 (%Acc): 98.16  <Step>:   2.6000  <Rp-Factor(y)> : 74.3033
=> NT:   5 Temp:  52.49 (%Acc): 97.35  <Step>:   2.6000  <Rp-Factor(y)> : 75.1450
=> NT:   6 Temp:  47.24 (%Acc): 96.12  <Step>:   2.6000  <Rp-Factor(y)> : 76.1275
=> NT:   7 Temp:  42.52 (%Acc): 98.37  <Step>:   2.6000  <Rp-Factor(y)> : 73.2831
=> NT:   8 Temp:  38.26 (%Acc): 94.90  <Step>:   2.6000  <Rp-Factor(y)> : 72.5488
```



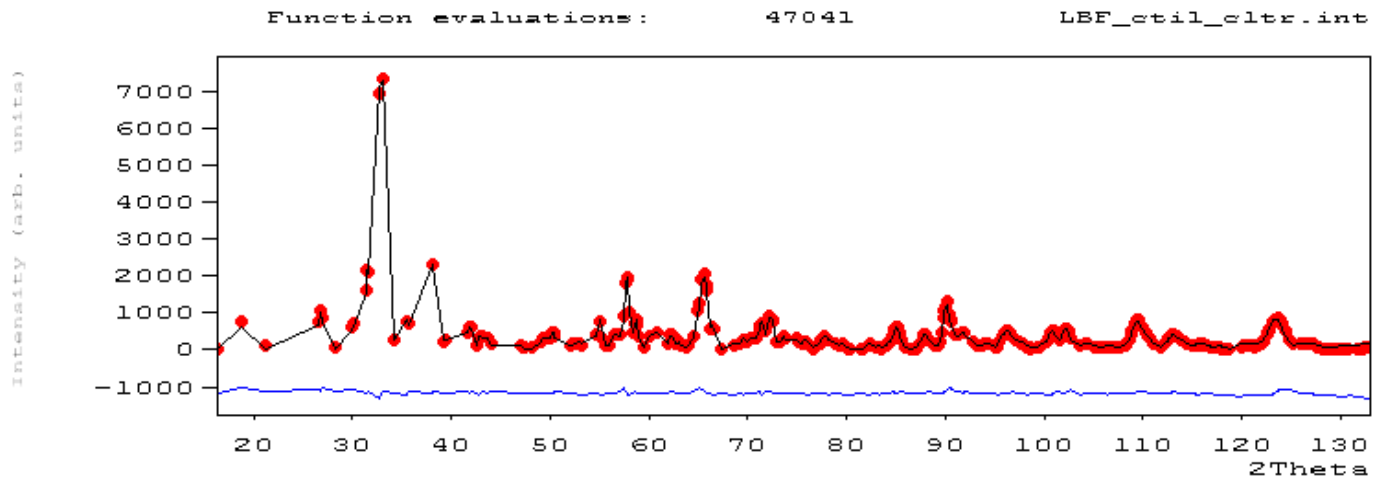
Simulated annealing (SAN) using profile intensities on $CaTiO_3$ data

Final picture of the profile intensity SAN job using the full set of reflections.

FullProf Program

Load Edit PCR Mode Run Exit

```
=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   393 reflections):

=> Sol#: 1 <Rp-Factor(y)>:     7.505 ::
=>      A1_R4+    A2_R5+    A3_R5+    A4_X5+    A5_X5+    A6_M2+    A7_M3+
=>           1         2         3         4         5         6         7
=>      1.1006    0.0555   -0.0421   -0.3735   -0.1721   -0.0036    0.8535


=>                CPU Time:     57.941 seconds
=>                               0.966 minutes

=> END    Date:23/05/2011  Time => 11:34:55.255
```



Comparison of Simulated annealing jobs on $CaTiO_3$

We compare below the values of LSQ and different SAN jobs.

Comparison of LSQ and SAN amplitudes for $CaTiO_3$

Least squares refinement Name	Value	Simulated Annealing (Integrated Intensities)	Simulated Annealing (Profile Intensities)
A1_R4+	1.110(3)	1.1231	1.1006
A2_R5+	0.065(7)	0.0276	0.0555
A3_R5+	-0.031(5)	-0.0556	-0.0421
A4_X5+	-0.386(4)	-0.3693	-0.3735
A5_X5+	-0.173(3)	-0.2027	-0.1721
A6_M2+	0.008(3)	-0.0276	-0.0036
A7_M3+	0.853(4)	0.8433	0.8535

Comparing $CaTiO_3$ and $LaMnO_3$

In this tutorial we provide also neutron powder diffraction data of $LaMnO_3$. For this compound we can repeat exactly the same steps as for $CaTiO_3$ and do the symmetry mode analysis in the same way. The most important difference between the two structures is the presence of a strong component of the M2+ mode corresponding to the active Jahn-Teller effect in $LaMnO_3$. In the following we show the value of the amplitudes of the five Irreps in both compounds.

Comparison of LSQ amplitudes of $CaTiO_3$ and $LaMnO_3$

	$CaTiO_3$	$LaMnO_3$
A1_R4+	1.110(3)	1.195(3)
A2_R5+	0.065(7)	0.084(2)
A3_R5+	-0.031(5)	-0.019(3)
A4_X5+	-0.386(4)	-0.546(2)
A5_X5+	-0.173(3)	-0.141(3)
A6_M2+	0.008(3)	-0.363(3)
A7_M3+	0.853(4)	0.904(3)

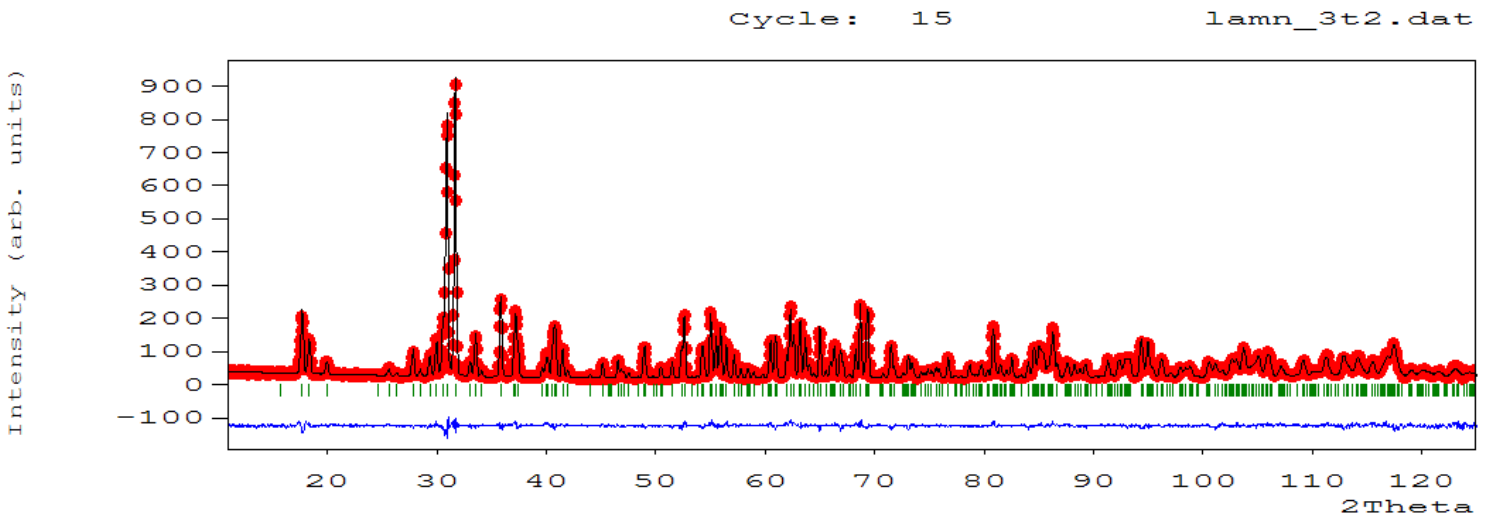
In the following slides we show the running of a LSQ refinement and a profile intensity SAN run for $LaMnO_3$, as well as a series of pictures of the crystal structure and symmetry modes.

Example of *FullProf* running a LSQ refinement of $LaMnO_3$ using symmetry modes

FullProf Program

Load Edit PCR Mode Run Exit

```
    =>     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
```

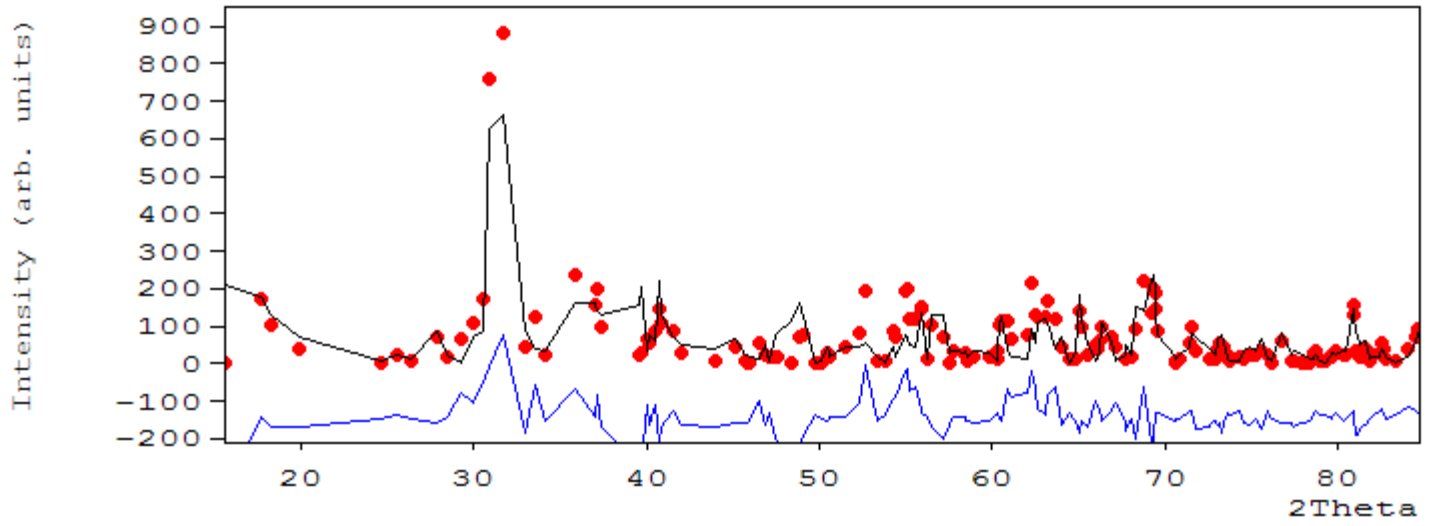


FullProf Program

Load Edit PCR Mode Run Exit

```
=>        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
```

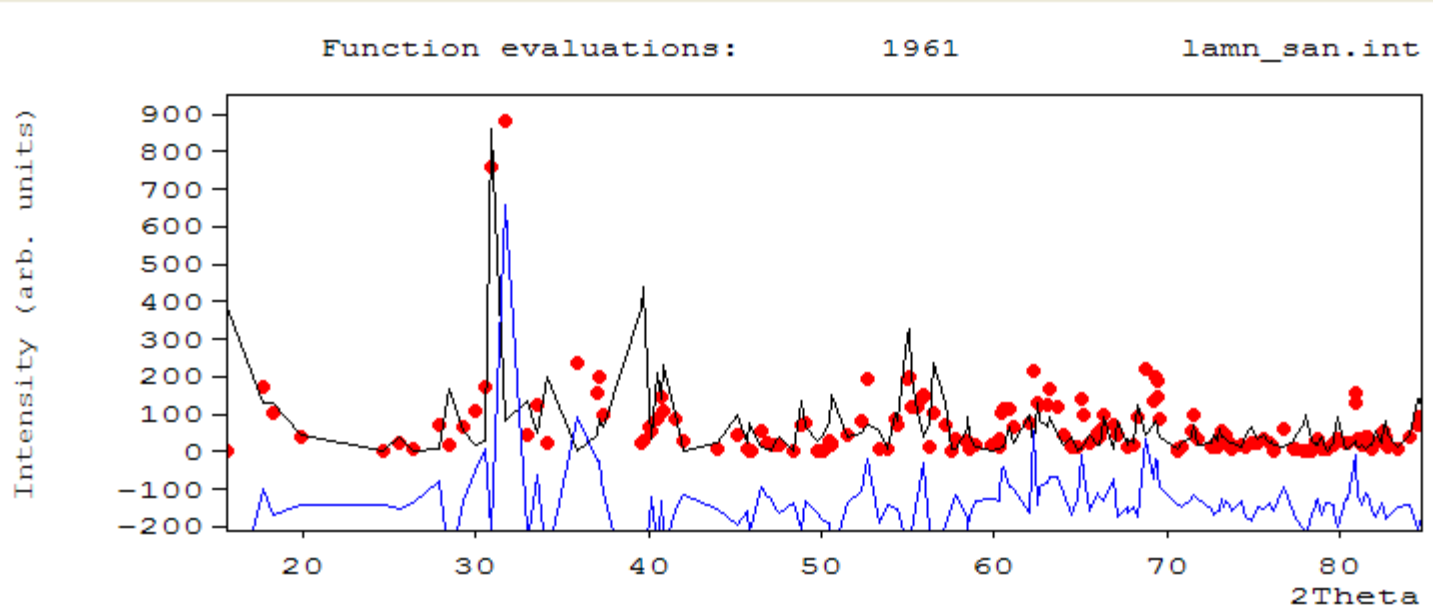
Function evaluations: 491 lamn_san.int



FullProf Program

Load Edit PCR Mode Run Exit

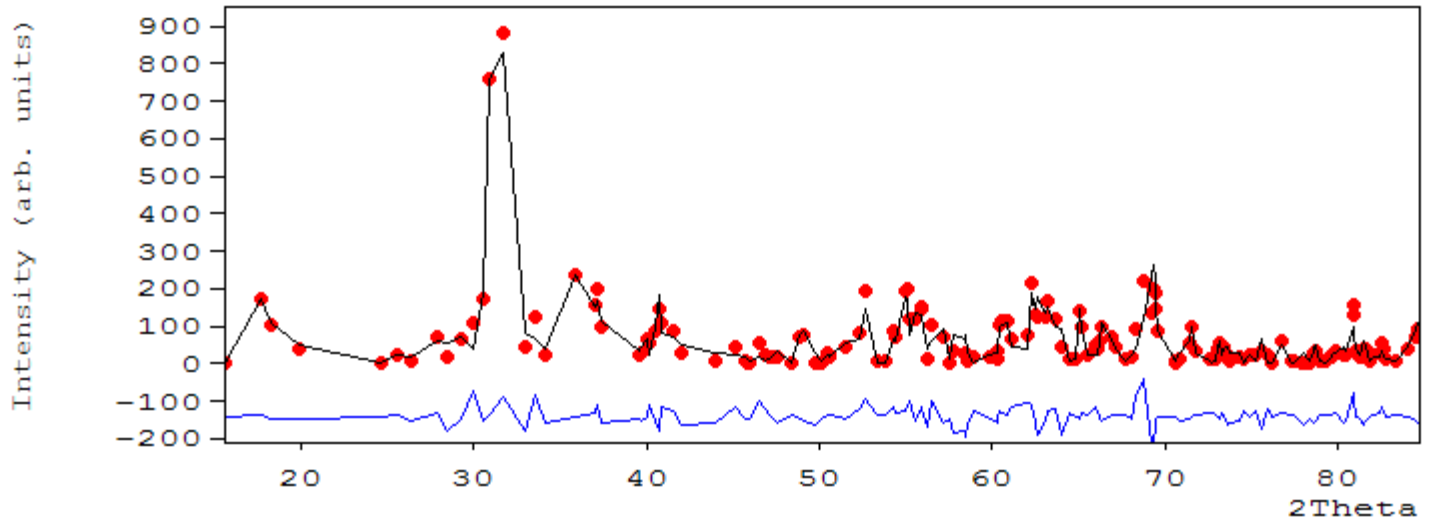
```
=> START Date:20/09/2008  Time => 15:33:20.281
=> Reading control file *.PCR ...
=> End of preliminary calculations !

=> **** 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
```



FullProf Program

```
=> **** 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
```

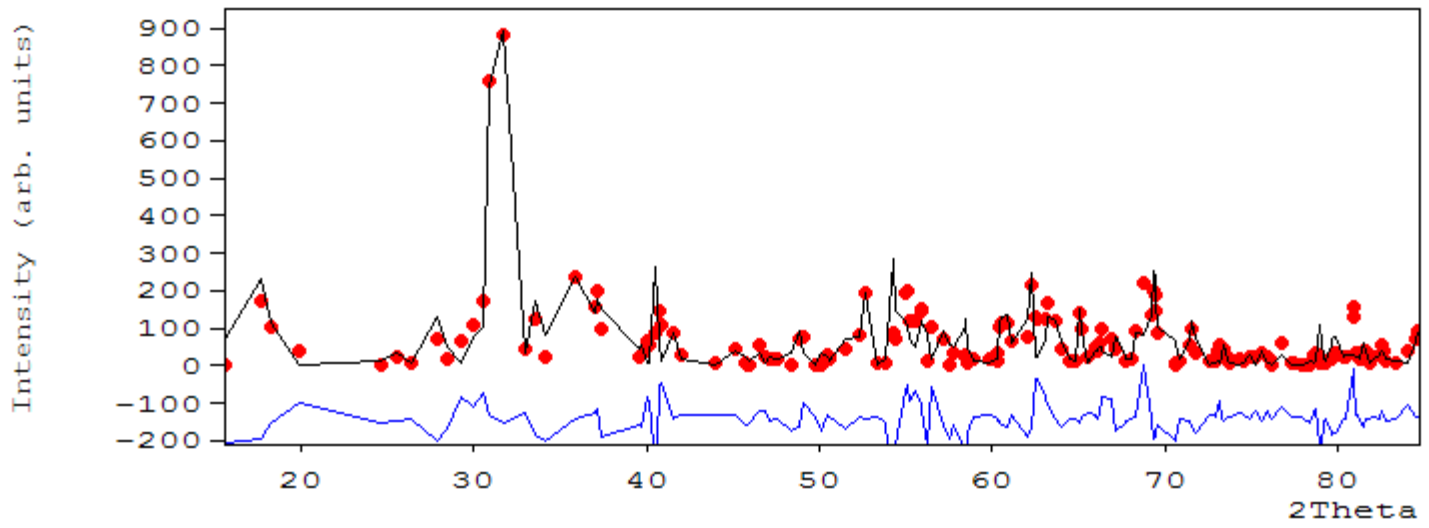
Function evaluations: 3921 lamn_san.int



FullProf Program

```
=> **** 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
```

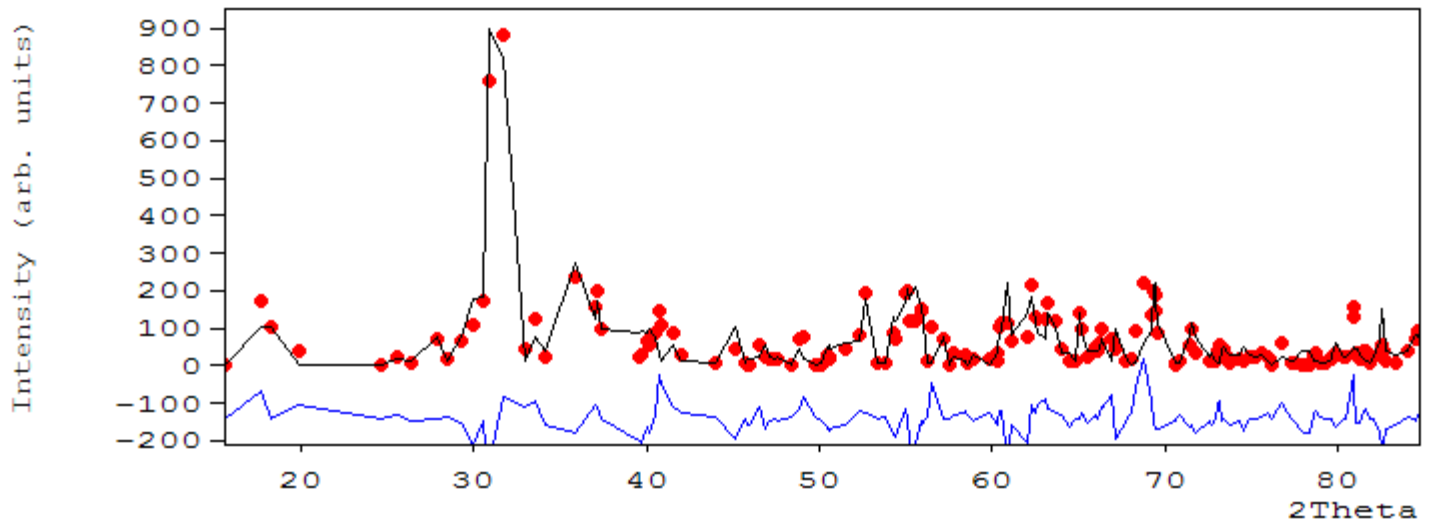
Function evaluations: 4411 lamn_san.int



FullProf Program

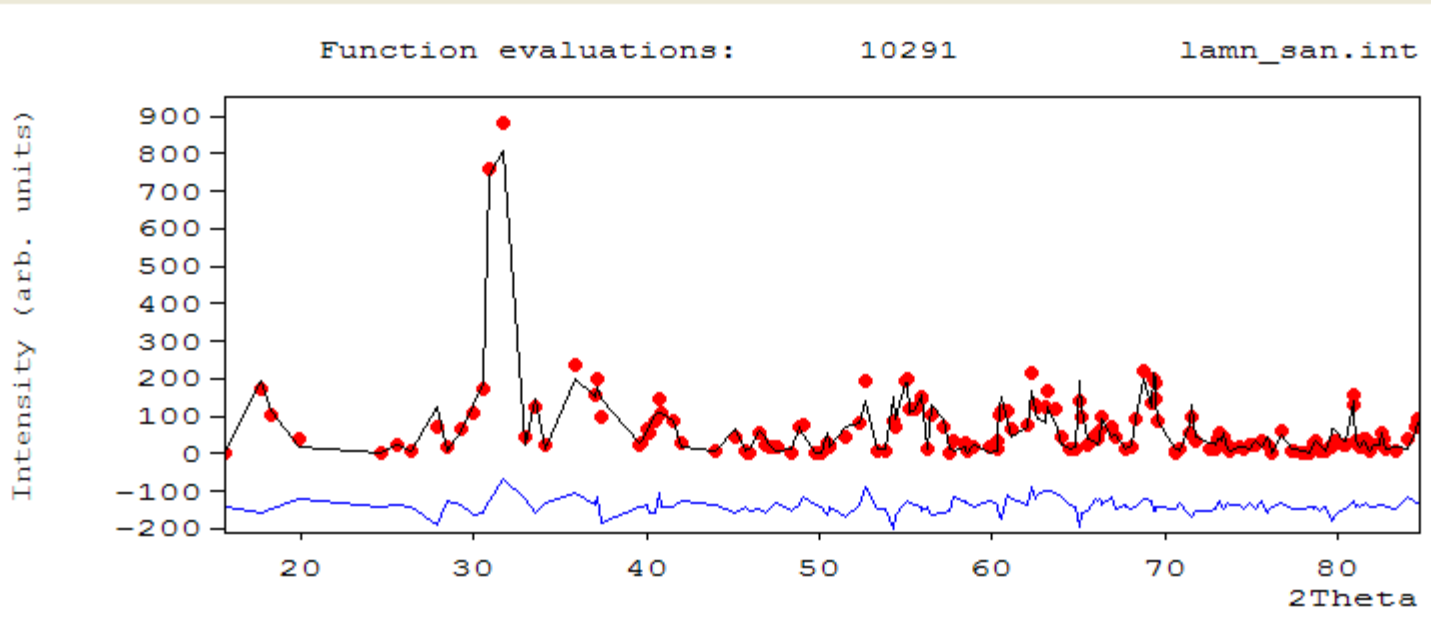
```
=> Initial configuration cost:   107.15
=> Initial configuration state vector:
=>     Q1_R4+    Q2_R5+    Q3_R5+    Q4_X5+    Q5_X5+    Q6_M2+    Q7_M3+
=>          1         2         3         4         5         6         7
=>     0.0000    0.0000    0.0000    0.0000    0.0000    0.0000    0.0000
=> 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
```

Function evaluations: 4901 lamn_san.int



FullProf Program

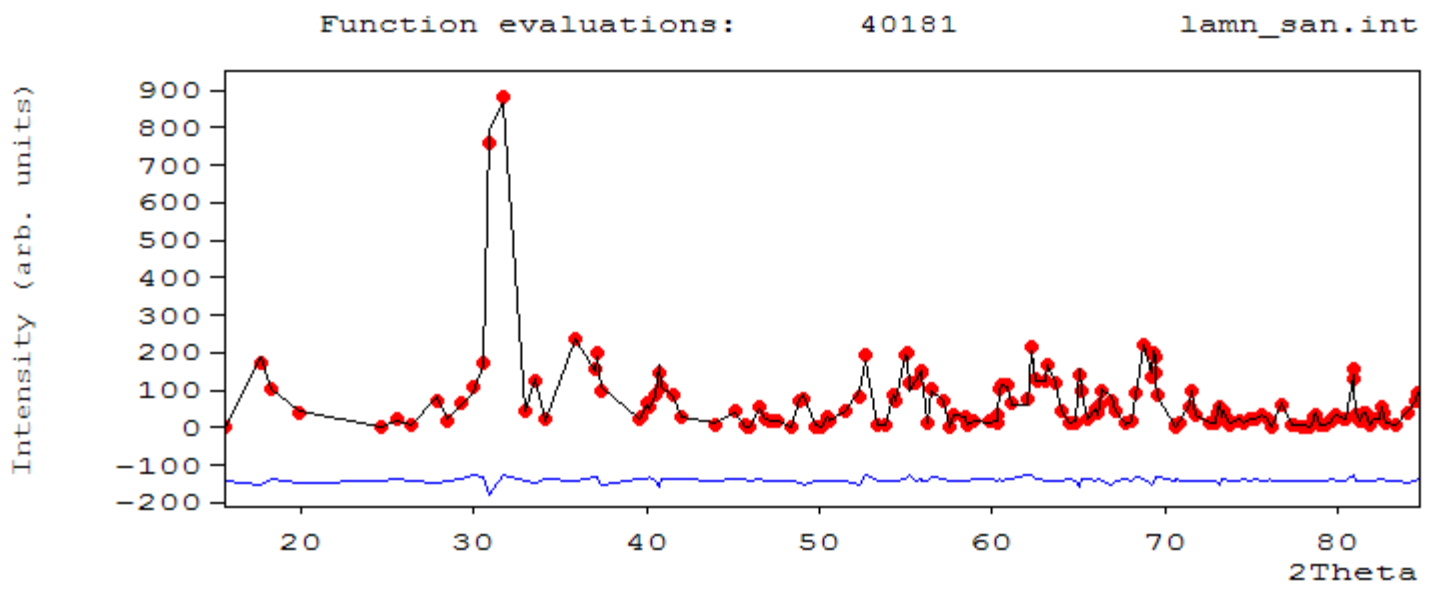
```
=> NT:  6 Temp:  4.64 (%Acc): 47.76  <Step>:  1.1245  <Rp-factor>: 48.1753
=> NT:  7 Temp:  4.41 (%Acc): 34.29  <Step>:  1.1456  <Rp-factor>: 33.1074
=> NT:  8 Temp:  4.19 (%Acc): 42.24  <Step>:  0.8090  <Rp-factor>: 35.1309
=> NT:  9 Temp:  3.98 (%Acc): 42.04  <Step>:  0.7418  <Rp-factor>: 28.3311
=> 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
```



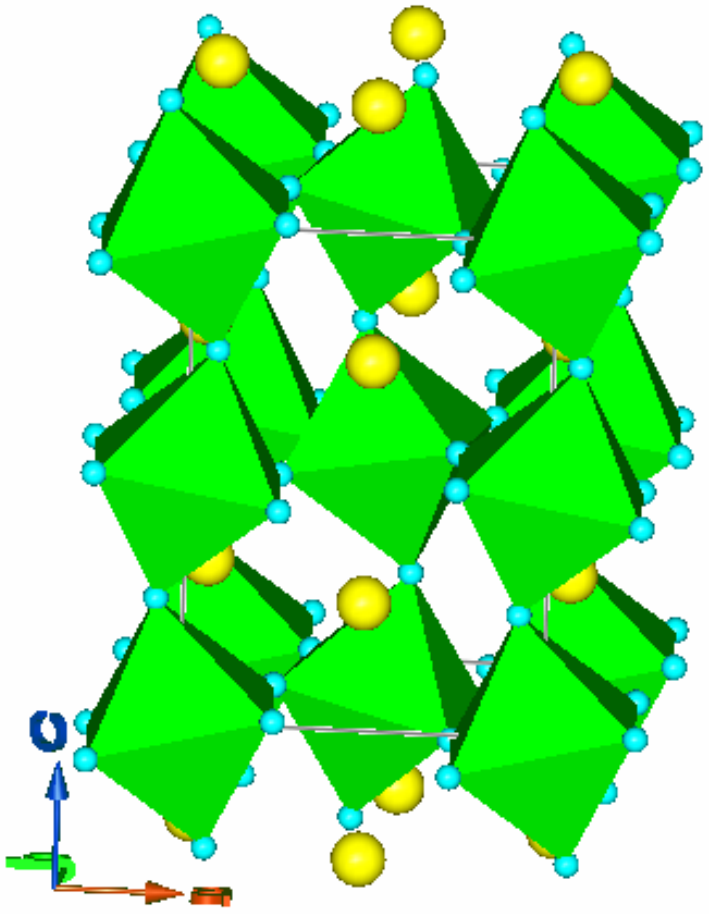
FullProf Program

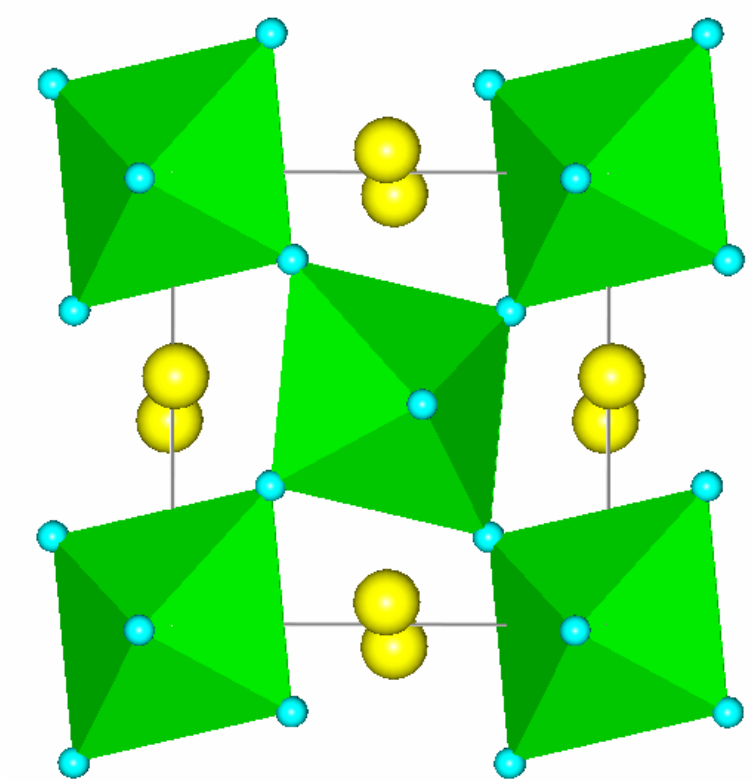
Load Edit PCR Mode Run Exit

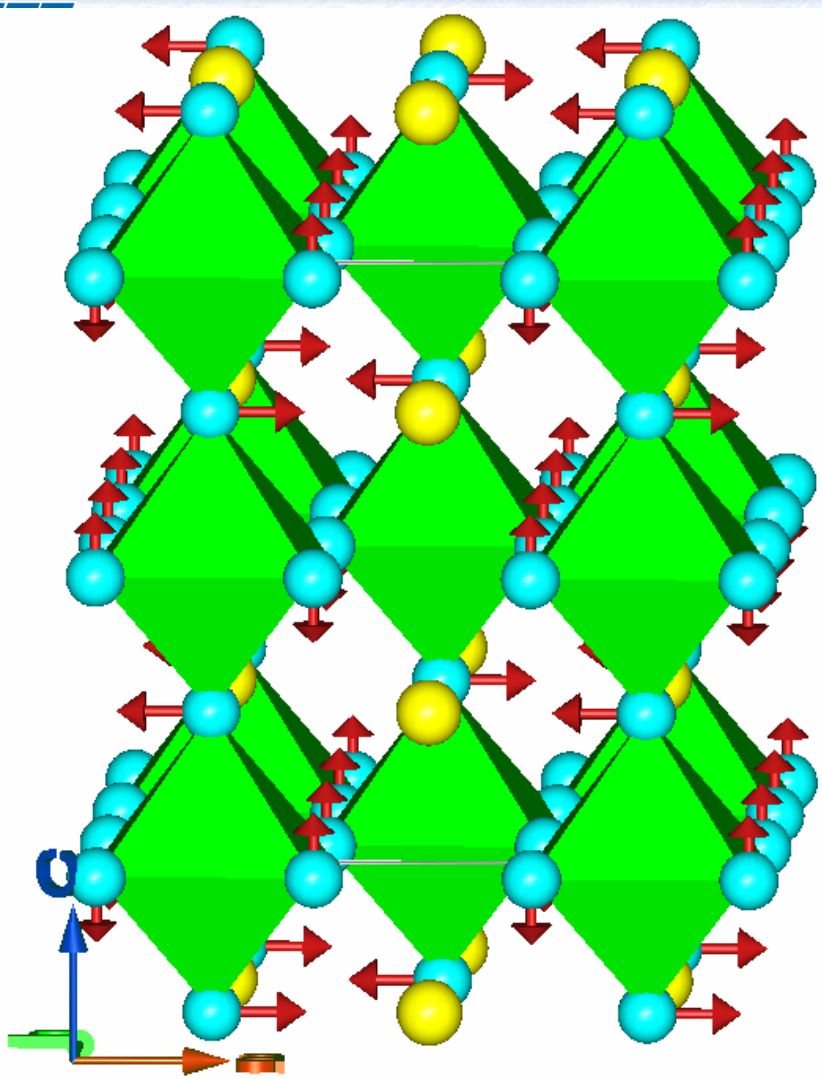
```
=> NT: 81 Temp:   0.10 (%Acc): 45.92  <Step>:   0.0423  <Rp-factor>:   5.7588
=> NT: 82 Temp:   0.09 (%Acc): 49.39  <Step>:   0.0400  <Rp-factor>:   5.7702

=>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
```



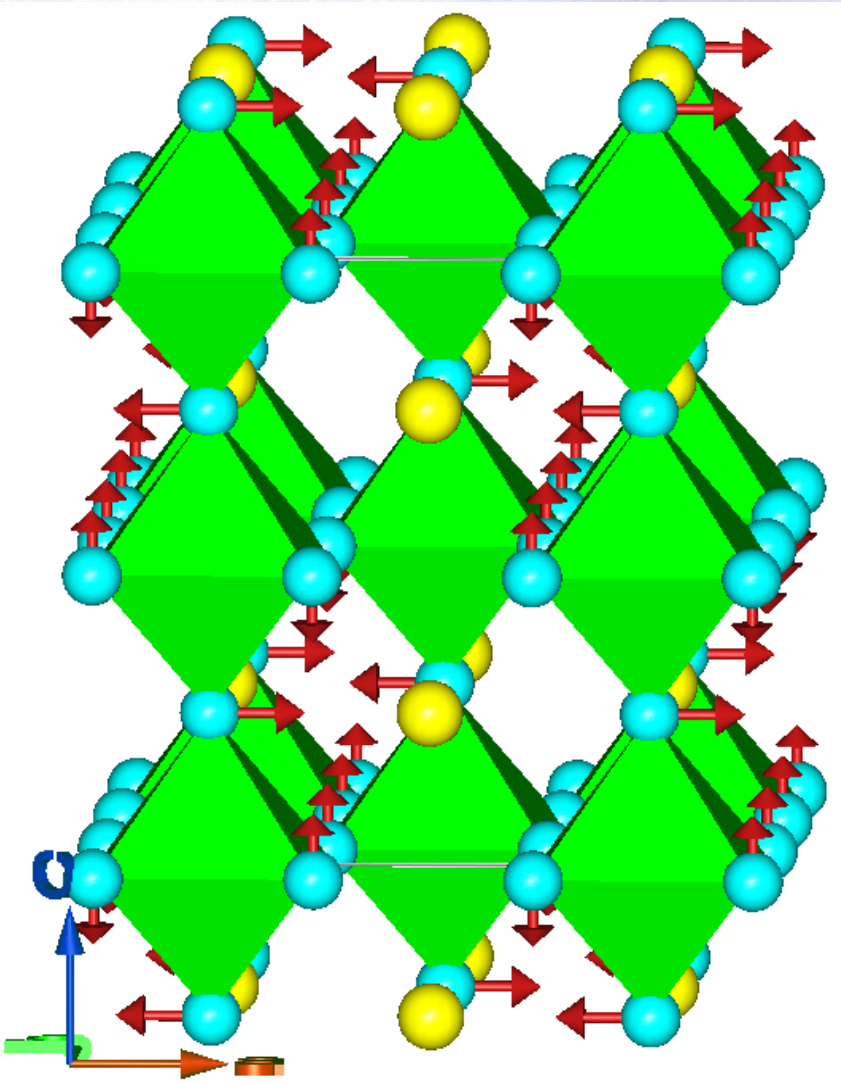
Crystal Structure of $LaMnO_3$



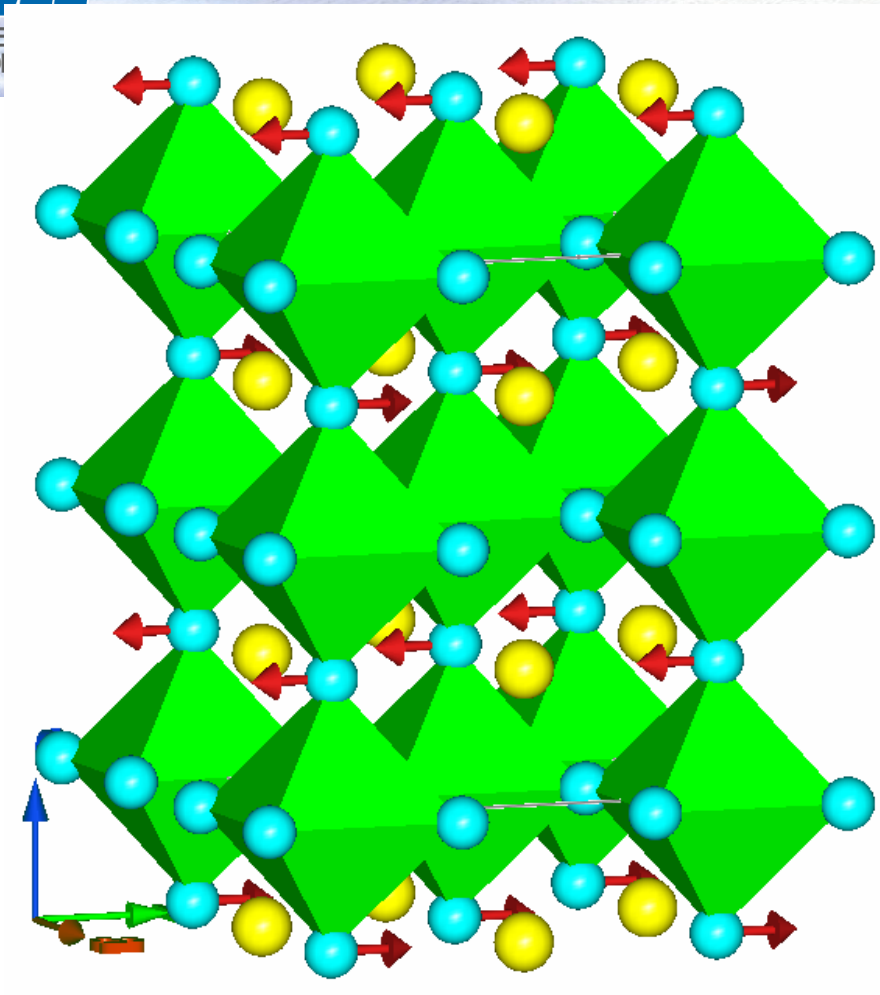




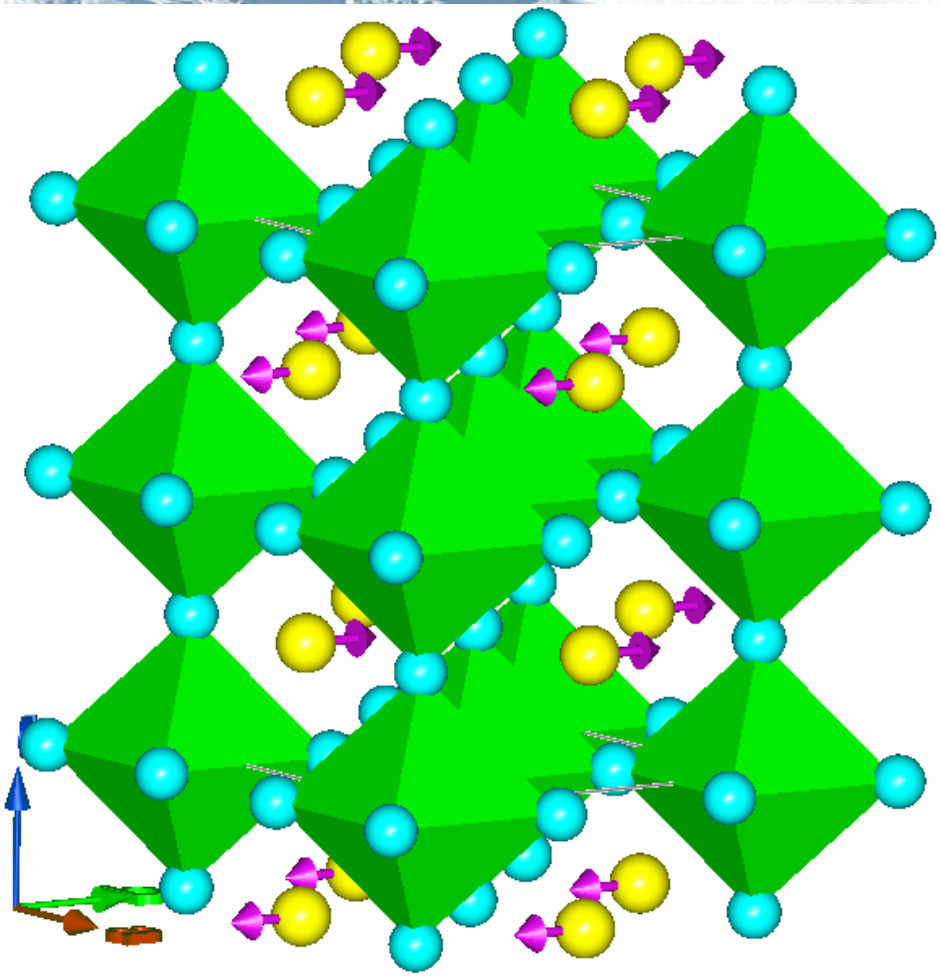
Mode 1, Q1_R4+ = -1.18968
O1 R4+ (0.0, 0.0, 0.031721)
O2 R4+ (0.063442, 0.0, 0.0)



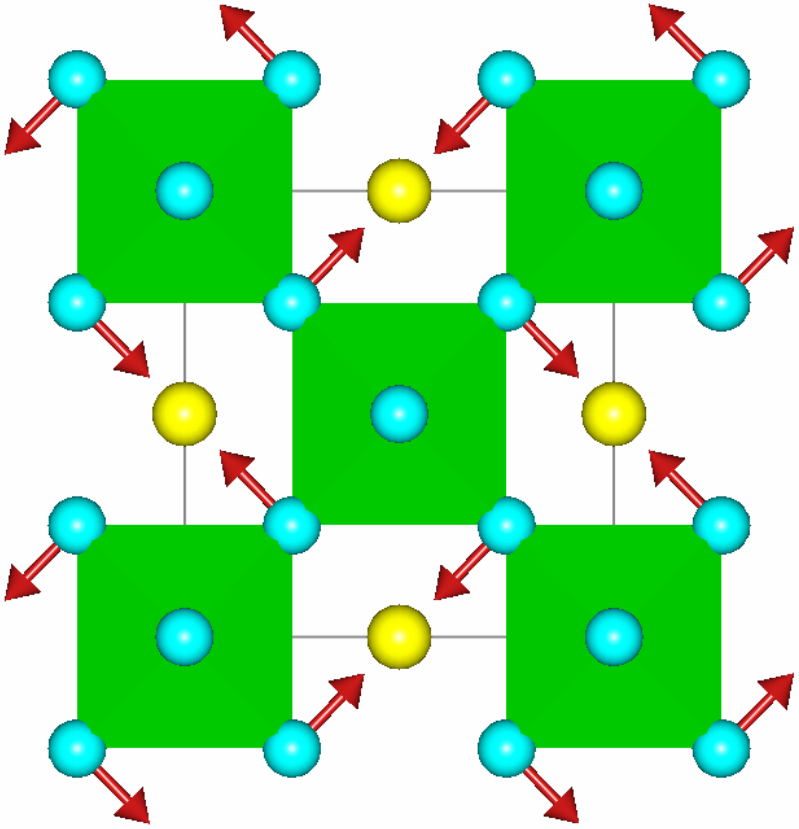
Mode 3, Q3_R5+ = 0.018171
O1 R5+ (0.0, 0.0, -0.031721)
O2 R5+ (0.063442, 0.0, 0.0)



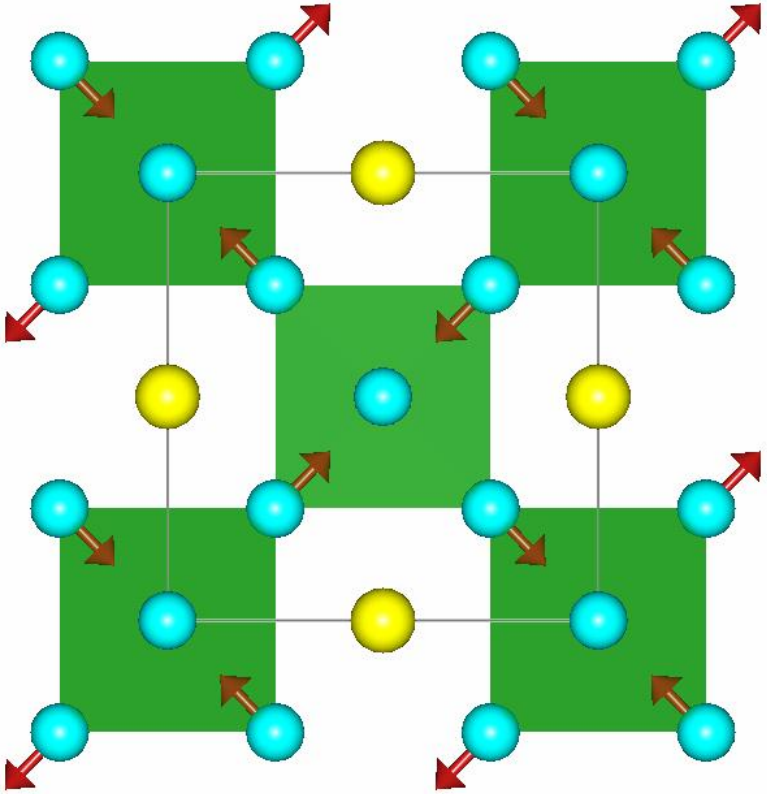
Mode 5, Q5_X5+ = -0.139910
O2 X5+ (0.0, -0.089721, 0.0)



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

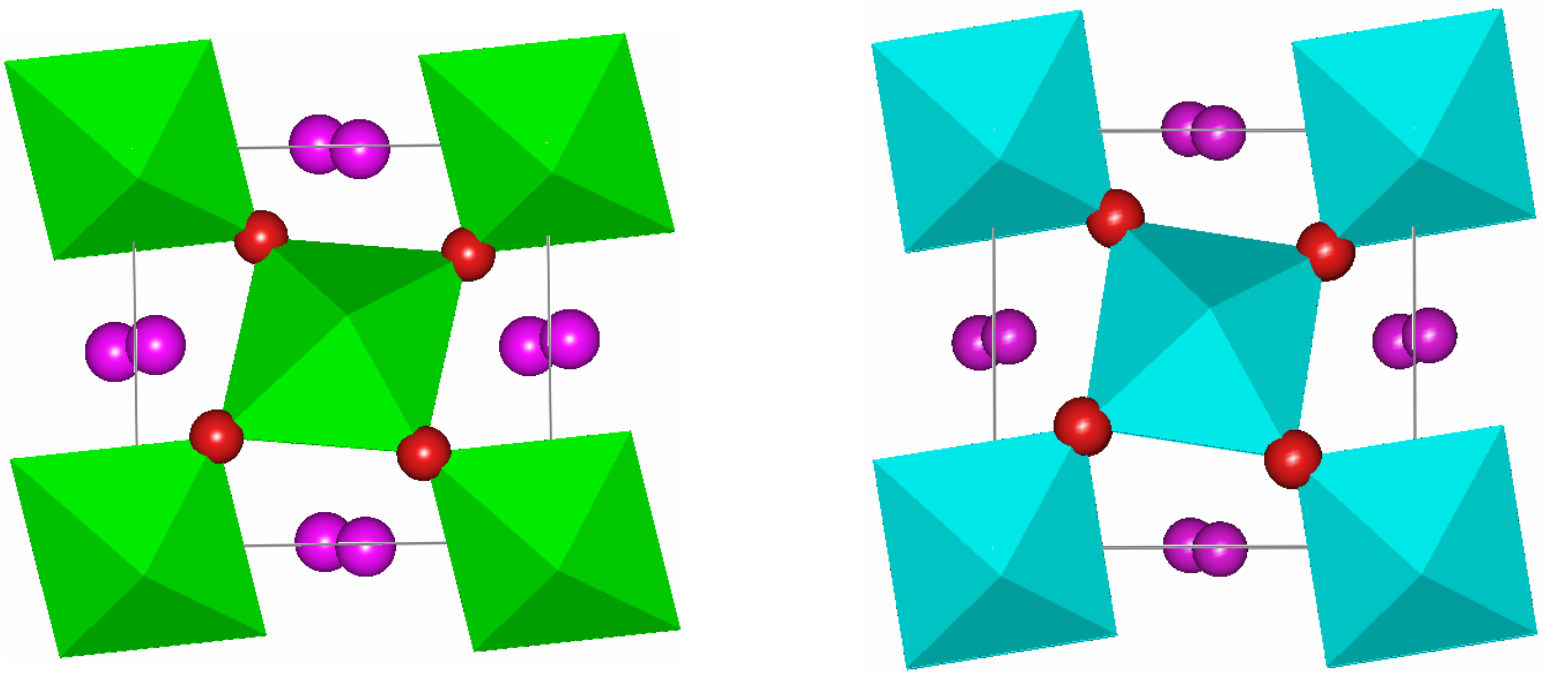


Mode 7, Q7_M3+ = 0.901264
O1 M3+ (-0.04486, -0.04486, 0.0)



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

Comparison of the crystal structures of $LaMnO_3$ and $CaTiO_3$



Pictures (seen along [010]) of the crystal structures of $LaMnO_3$ (left panel) and $CaTiO_3$ (right panel) showing the stronger distortion of MnO_6 octahedra in comparison with TiO_6 octahedra due to the Jahn-Teller effect that is active in $LaMnO_3$. The antiferro-distorsive orbital ordering is clearly seen as an elongation of the occupied d_{z2}-like orbital. This corresponds to a Mn-O distance that is much longer than the others (d_s=1.904(1), d_m=1.969(2), d_l=2.182(1)). The short and long distances are nearly within the shown *ab* plane and a long bond is always connected to the short bond of the adjacent octahedra.