

FullProf Tutorial

How to work with symmetry modes using FullProf and AMPLIMODES. Two simple examples: CaTiO₃ and LaMnO₃

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We provide in this document an introduction to the use of the program **FullProf** for working with symmetry modes in the description of distorted structures. It is supposed that the reader has already a minimal knowledge of the meaning of symmetry modes. We provide here a summary of the most important concepts and mathematical formulae concerned with the description of distorted structures in terms of symmetry modes. The reader is referred to the literature to get a deeper insight into the method. In particular the recent articles:

AMPLIMODES: Symmetry mode analysis on the Bilbao Crystallographic Server,
D. Orobengoa, C.Capillas, M.I. Aroyo and J.M. Perez-Mato, *J. Appl. Cryst.* **42**, 820 (2009)

Mode crystallography of distorted structures,
J.M. Perez-Mato, D. Orobengoa and M.I. Aroyo, *Acta Cryst.* **A66**, 558 (2010)

Reading these two articles is a pre-requisite for using properly the method we explain here. After the introduction we explain in detail the main characteristics of the input control file intended to work with symmetry modes. We suppose that the reader is not an expert using **FullProf**, so we provide in detail the steps for starting to work without being too much worried with the intricacies of the input control file, called hereafter a PCR file. We give also information to prepare the PCR file for simulated annealing when we want to determine a crystal structure supposed to derive from a more symmetric structure. All the steps are applied to the case of two simple distorted perovskites (CaTiO₃ and LaMnO₃) using neutron powder diffraction. The methods explained in this document can be applied to structures of whatever complexity. Of course when the number of parameters is too high, the amplitudes obtained in the refinement should be carefully and critically analysed because refinement may fall in a local minimum.

Introduction to the symmetry mode analysis of distorted structures

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.

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**.

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.

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

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

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

The indices τ and m label all possible distinct allowed symmetry-adapted distortion modes. The index τ stands for the possible different mode symmetries, while the index m ($m=1,\dots,n_\tau$) enumerates the possible different independent modes of a given symmetry. The mode (τ, m) is defined by the polarisation vectors: $\boldsymbol{\varepsilon}(\tau, m | \mu, i)$

One can refer to the global polarization vector $\boldsymbol{\varepsilon}(\tau, m)$, taking all atoms simultaneously, of the mode (τ, m) . The displacement of an atom (μ', i') related by the symmetry operator $\{\mathbf{R}|\mathbf{t}\}$ to the atom (μ, i) is given directly by:

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

We need only the polarisation vectors of the atoms of the asymmetric unit the rest of information is contained in the symmetry operators of the space group. The normalization of the polarisation vectors is chosen to verify:

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

“ $mult_{\mu, i}$ ” represents the multiplicity in a primitive cell of the space group \mathbf{L} for the Wyckoff position (μ, i) . The following orthogonality relation is verified by the polarization vectors:

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

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

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

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

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

In the output files of **FullProf** after a refinement using symmetry modes all these quantities are calculated together with their standard deviations.

Summary of information for working with symmetry modes in FullProf

Below we provide a part of the file "fp2k.inf" distributed with the **FullProf Suite**, in which all the modifications to the **FullProf** manual are provided. This part concerns the modifications of the PCR file introduced by the use of symmetry modes. The user may skip this section in a first reading because the initial PCR file is automatically provided by **AMPLIMODES**, however it is important to know all the details if one wants to exploit the full functionality of **FullProf** with the symmetry modes option.

```
AMPLIMODES and FullProf: Symmetry modes crystallography
=====
Instructions for working with symmetry modes (from fp2k.inf)
=====
```

All useful comments on this matter in the file "fp2k.inf" have been included below in the opposite sense (from older to newer) of that in the "fp2k.inf" file.

```
Dates of changes in FullProf: 29 August 2008
                             8 October 2008
                             11 January 2009
                             16 January 2009
                             20 May 2010
```

```
-----
>> 29 August 2008: New version of FullProf. Use of symmetry modes with AMPLIMODES.
-----
```

In the present version of FullProf the refinement of a crystal structure can be done in terms of symmetry adapted modes. FullProf uses the output of the program AMPLIMODES from the Bilbao Crystallographic Server (<http://www.cryst.ehu.es/cryst/amplimodes.html>) The free parameters, instead of atom positions, are the amplitudes of symmetry modes. The provided atom positions should not be refined. They are given as a reference of the High Symmetry (HS) phase described in the Low Symmetry (LS) frame.

This option is accessible by putting the variable JBT=6. The input is exactly the same as for JBT=0, except that no refinement codes are allowed for atom positions. This is taken into account by the program when Aut=1 (automatic mode). If Aut = 0 it is the responsibility of the user to nullify the refinement codes of the atom positions. The length of the label of an atom has been increased to 6 characters. This implies a small change in the format of the PCR files that is transparent to the user.

Extra input:

- The number of further parameters should be equal to the number of independent symmetry modes (N_modes). This is, in principle, less or equal to the number of free position parameters allowed to be refined in the conventional description of the low symmetry phase.
- After the conventional atom list (before providing the scale factor, etc ...) the keyword: V_MODES followed by an integer (N_vector_modes) should be given. In general N_vector_modes >= N_modes.
- A set of N_vector_modes lines should be given. In each line one should provide the number of the concerned mode, the atom label (up to 6 characters) to which the vector makes reference (atoms of the asymmetric unit), the label of the irreducible representation to which belong the mode (up to 6 characters), the three components of the polarisation vector referred to the low symmetry conventional crystallographic basis and a numeric coefficient (normally 1.0) used for normalisation purposes.
- The above set of lines must be followed by the keyword A_MODES and the number of effective independent modes (N_modes).
- The integer value N_modes can be optionally followed, in the same line, by a set of

N_{modes} integers, $p_{\text{modes}}(1:N_{\text{modes}})$, of values 0 or 1 for indicating the program to Output files for FullProf Studio of individual modes. If nothing is given the program assumes $p_{\text{modes}}(1:N_{\text{modes}})=0$.

The files contain single modes virtual structures (codefil_n_mode_j.fst for codefil.pcr, n: number of the phase, j: number of the mode when $p_{\text{mode}}(j) = 0$) corresponding to the presence of a single mode. In the case of $p_{\text{mode}}(j)=1$ the codefil_n_mode_j.fst file contain the structure of the high temperature (described in the low symmetry frame) together with an arrow description of the atom displacements corresponding to the single mode j.

- A set of N_{modes} lines containing the name of the amplitude parameter (normally of the form Q_j _Label_Irrep, with $j=1:N_{\text{modes}}$) the value of the amplitude and its refinement code.

FullProf uses this extra information for calculating the effective fractional coordinates of each atom in the asymmetric unit of the LS phase. The component k of the vector position for the atom j, $r_{\text{LS}}(k,j)$, is calculated using the expression:

$$r_{\text{LS}}(k,j) = r_{\text{HS}}(k,j) + U(k,j)$$

$$U(k,j) = \text{Sum}\{m=1,N_{\text{modes}}\} (Q(m) * \text{vect}(k,m,j) * \text{coeff}(m))$$

Where $r_{\text{HS}}(k,j)$ is the k-component of the vector position of atom j given the list of atoms and correspond to the high symmetry phase referred to the low symmetry basis. $Q(m)$ is the amplitude of the mode numbered "m", $\text{vect}(k,m,j)$ in the k component of the polarisation vector of the mode m for the atom j and $\text{coeff}(m)$ is a constant coefficient provided by the user for normalisation purposes.

In the general case $\text{coeff}(m)=1$, but if several symmetry modes, for instance from $m=i+1$ to $m=i+n$, belong to the same representation, D_v , we can define a vector of amplitudes for the form: $V_Q = \{Q(i+1), \dots, Q(i+n)\}$ that may be treated as a single parameter. If one knows the ratios between the amplitudes, so that $V_Q = Q_v \{r_1, r_2, \dots, r_n\}$ and $\{r_1, r_2, \dots, r_n\}$ is normalized to 1.0, the coefficients $\text{coeff}(m)$ can be identified to the ratios. Then using the same amplitude Q_v for all the modes of the representation the coefficients are: $\text{coeff}(i+j) = r_j$.

Of course the values of the refined amplitudes depend on the numerical values used for the components of the polarisation vectors as well as the values provided for $\text{coeff}(m)$. The final displacement vectors $U(k,j)$ in fractional units are independent of the particular values used for $\text{coeff}(m)$ because the amplitude $Q(m)$ will change consequently in order to keep the appropriate product $Q(m)*\text{coeff}(m)$.

The program generates always CFL and FST files containing the conventional description of the final crystal structure together with single mode FST files. The standard deviations of the atoms positions are calculated using the propagation error formula neglecting the correlation between the refined amplitudes of the modes.

The relevant portion of the PCR file corresponding to the default example given in the Web page of the AMPLIMODES program is given below. Notice that the first amplitude (concerning only the Ba atom) is fixed to zero because the origin is floating along z due to the polar nature of the space group.

```

. . . . .
!-----
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 0.79
!-----
BaTiO3                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  5      967.370  0  7  0
!
! A m m 2
!Atom Typ      X      Y      Z      Biso      Occ      In Fin N_t Spc /Codes
Ba1  BA      0.00000  0.00000  0.0000  0.47643  0.25000  0  0  0  1 #color grey conn TI 0 0.0 2.2
      0.00      0.00      0.00      151.00      0.00
Ti1  TI      0.50000  0.00000  0.50000  0.24156  0.25000  0  0  0  2 # color green poly Ti1
      0.00      0.00      0.00      161.00      0.00
O1_2 O      0.00000  0.00000  0.50000  0.58601  0.25000  0  0  0  3 # color cyan
      0.00      0.00      0.00      171.00      0.00
O1   O      0.50000  0.25000  0.25000  0.51687  0.50000  0  0  0  3 # color cyan
      0.00      0.00      0.00      181.00      0.00
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES 8
! Nm Atom Irrep      Vx      Vy      Vz      Coeff
1 Ba1 GM4-      0.000000  0.000000  0.176512  1.00000
2 Ti1 GM4-      0.000000  0.000000  0.176512  1.00000
3 O1  GM4-      0.000000  0.062406  0.062406  1.00000
3 O1_2 GM4-      0.000000  0.000000  0.124813  1.00000
4 O1  GM4-      0.000000 -0.088256  0.088256  1.00000

```

```

 4 O1_2 GM4-    0.000000 0.000000 0.000000 1.00000
 5 O1    GM5-    0.000000 -0.062406 -0.062406 1.00000
 5 O1_2  GM5-    0.000000 0.000000 0.124813 1.00000
! Amplitudes of Symmetry Modes
A_MODES  5      1 1 1 1 1
  Q1_GM4-    0.000000    0.000000
  Q2_GM4-    0.098947    21.000000
  Q3_GM4-   -0.085383    31.000000
  Q4_GM4-   -0.120367    41.000000
  Q5_GM5-   -0.006086    51.000000
!-----> Profile Parameters for Pattern # 1
! Scale      Shape1      Bov      Str1      Str2      Str3      Strain-Model
 4.0008      0.000000    0.00000 0.00000 0.00000 0.00000 0
11.00000    0.000 0.000 0.000 0.000 0.000 0.000
!           U           V           W           X           Y           GauSiz  LorSiz Size-Model
 0.176029 -0.197814 0.091459 0.000000 0.030062 0.000000 0.000000 0
. . . . .

```

>> 8 October 2008: New option for output of symmetry modes

- If the value of p_mode(1)=2 (see note of 29 August 2008) 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 (Irrep). All modes corresponding to a single Irrep are combined in the FST file.

>> 11 January 2009: New options for output of symmetry modes in the FST files

- The size of the labels for irreducible representations has been increased from 6 to 12 characters.
- It is possible to use the initial option putting ALL modes explicitly with 0 for output the distorted structure corresponding to a single symmetry mode or 1 for output of the ideal structure plus arrows indicating the atom displacements. (see note of 29 August 2008)

If no separate output for FST files are asked the user should put just p_mode(1)=-3

If the user asks for output of ALL the modes using arrows only p_mode(1)=N_modes (where N_modes is the total number of modes) has to be given. If true distorted structures are needed then: p_mode(1) = -N_modes.

If the user asks for grouping all the modes of an irreducible representation using arrows then p_mode(1)=2 (see note of 8 October 2008), if the true structures are to be represented then p_mode(1)=-2. In both cases all the irreducible representations are output in separate FST files.

If the user asks for only a set of modes to be represented the items to be provided instead of the integers p_mode(1:N_modes) are as:

```

! Amplitudes of Symmetry Modes
A_MODES  N_modes  Nrm  ip(1)  ip(2)  ip(3)  .....  ip(Nrm)

```

```

Nrm      : Total number of modes to be output in FST files
ip(i)    : Number of the mode to be output (if positive, arrows will be used to mimic
           atom displacements, if negative the true corresponding distorted structure
           is output in the FST file)

```

Examples: (Only the relevant line of the PCR file is given)

```

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
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 0 1 1 0 -> Explicit output of all modes (1: arrows, 0: distorted structure)
A_MODES 7 4 1 3 -4 7 -> Only the 4 modes 1,3,4 and 7 are output in FST files. All of
                        them, except the mode 4, are represented by arrows.

```

>> 16 January 2009: Constraints on amplitudes of symmetry modes

- A new keyword has been introduced in the PCR file in order to globally apply

a box constraint for the amplitudes of symmetry modes. The keyword is "Max_Amplitude" and should appear just below the line defining the number of modes and the output conditions for the FST file. If the keyword does not appear no constraint is applied to the amplitudes unless Nre /= 0 and the box constraints on amplitudes are explicitly described. This last method is needed presently for the simulated annealing mode.

Example:

```

.....
3 011 M4- -0.045281 0.045281 0.000000 1.000000
! Amplitudes of Symmetry Modes
A_MODES 3 2
Max_Amplitude 1.0000
Q1_GM1+ 0.044319 31.000000
Q2_GM1+ -0.158626 41.000000
.....

```

In the above example the amplitudes (in angstroms) of the symmetry modes are limited to values within the interval [-1.0, 1.0]

>> 20 May 2010: New message in FullProf for symmetry modes.

- A stop message is output in FullProf when one uses two phases treated with symmetry modes in case the second phase has more polarisation vectors than the first one. For multiphase diffraction patterns to be treated with symmetry adapted modes, the phase with the greater number of distinct polarisation vectors should be put as the first phase in the list given in the PCR file.

The initial PCR file obtained automatically from AMPLIMODES

We will illustrate the procedure with the case of the perovskite CaTiO_3 . We will consider that we do not know the crystal structure of this material; however we know the unit cell parameters ($a=5.441\text{ \AA}$, $b=7.645\text{ \AA}$, $c=5.380\text{ \AA}$), the number of formula units $Z=4$ in the cell, the space group ($Pnma$, #62) and the matrix and origin translation relating the orthorhombic unit cell with that of the cubic high symmetry phase ($\mathbf{a}-\mathbf{c}$, $2\mathbf{b}$, $\mathbf{a}+\mathbf{c}$: 000). We know that the structure derives from the ideal perovskite ($Pm\bar{3}m$, #221) containing a single formula unit with atoms in positions: Ca 1b-(1/2,1/2,1/2), Ti 1a-(0,0,0), O 3d-(1/2,0,0). The cubic cell parameter of this ideal structure can be obtained from the cell volume of a single formula unit in the orthorhombic phase: $V/4 \approx 223.79/4 \approx 55.95 \rightarrow a_c = (V/4)^{1/3} \approx 3.8246\text{ \AA}$.

To generate a PCR template file one has to connect to the Bilbao Crystallographic Server (BCS) at URL: <http://www.cryst.ehu.es/>

In the home page one has to click on the AMPLIMODES program in the section **Solid State Theory Applications**. Once the page appears one can go directly to the **AMPLIMODES for FullProf Suite** page by clicking on the "here" button. In this page the description of the high symmetry structure should be typed as shown in the figures below:

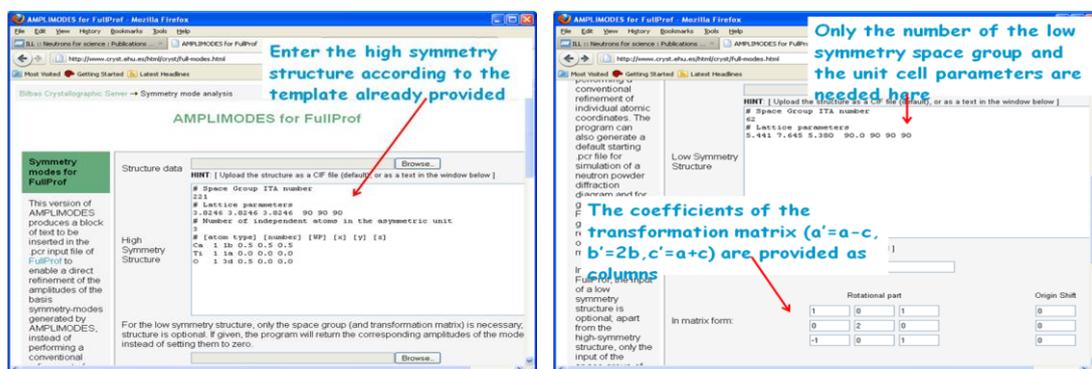


Figure 1: Initial pages of AMPLIMODES for FullProf Suite in the Bilbao Crystallographic Server


```

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 Coeff
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
!
! Scale Shapel Bov Str1 Str2 Str3 Strain-Model
2.00 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0
0.00000 0.000 0.000 0.000 0.000 0.000 0.000
! U V W X Y GauSiz LorSiz Size-Model
0.176020 -0.197809 0.091458 0.000000 0.030039 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
5.408801 7.649200 5.408801 90.000000 90.000000 90.000000 #box -0.15 1.15 -0.15 1.15 -0.15 1.15
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
0.000000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! 2Th1/TOF1 2Th2/TOF2 Pattern # 1
10.000 100.000 1

```

The file above is prepared for the calculation of a neutron diffraction pattern ($J_b t = 3$) similar to those produced by the instrument 3T2 at Laboratoire Léon Brillouin. The above file may be used as a template that should be modified for the particular diffraction measurements done on the sample. We have emphasised in red the variables that have to be eventually modified. Notice that the cell parameters written in the file correspond to the ideal orthorhombic cell deduced from the cubic cell applying the transformation matrix given in the input of **AMPLIMODES** instead of the real cell parameters. This is so because, strictly speaking, the orthogonality of the polarisation vectors is verified exactly only in this cell. In practice one has to write the real cell parameters for refining experimental data.

The file, as produced by **AMPLIMODES**, can be used for making a calculation with **FullProf**. Opening the **FullProf Suite toolbar (FPS toolbar)**, selecting the working directory (File menu), loading the just created PCR file (left button: Search Input Files) and clicking on the **FullProf** button, **FullProf** is launched. The program processes the input data and produces files for further inspection and plotting.

In the following figures one can see the process:

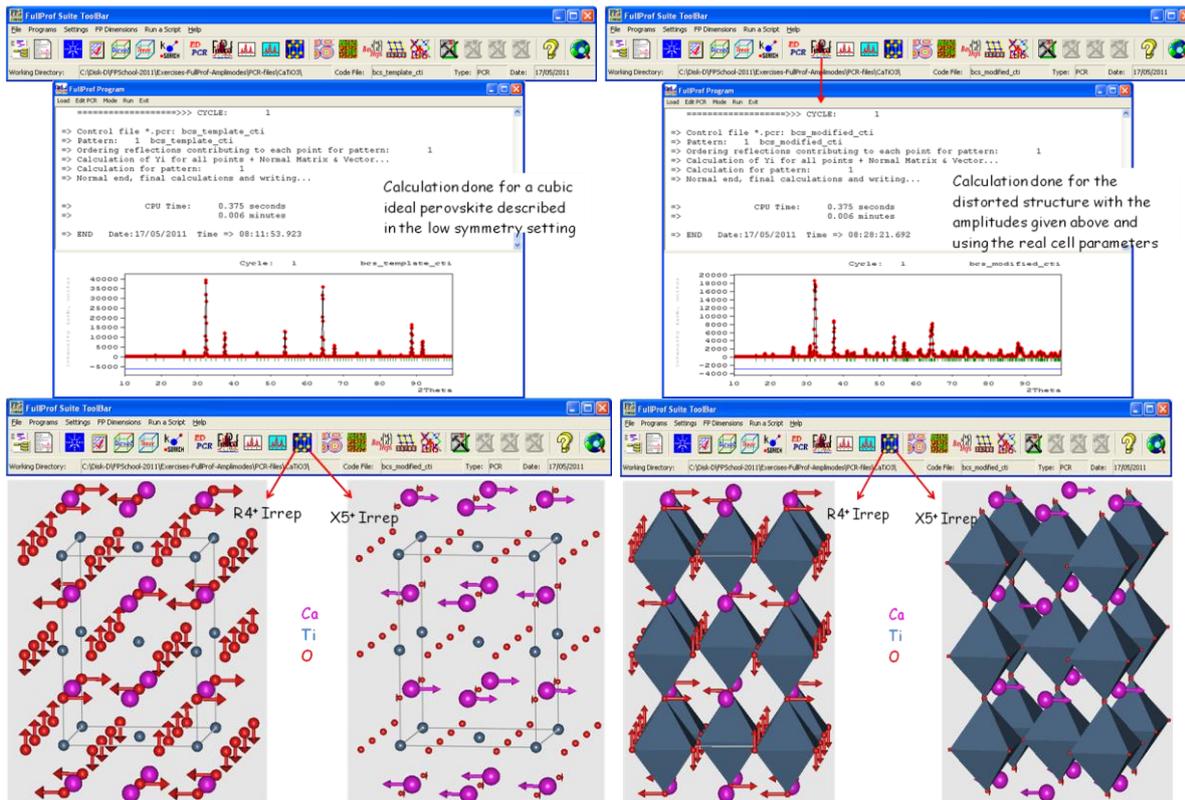


Figure 3: Running **FullProf** with the “as generated” PCR file (ideal cubic CaTiO_3 perovskite, top left panel) and the file modified using real cell parameters and some reasonable arbitrary values for the amplitudes of the modes (top right panel). In the bottom panels, pictures of the atom displacements corresponding to two Irreducible Representations (Irreps) are shown. The pictures of the left panel are produced automatically when open the **FullProf** generated files (*.fst) with **FullProf Studio** by clicking on the button . The bottom right panel showing polyhedral representation are generated by editing the *.fst files and adding the instructions: Conn TI O 0 2.2 and Poly Ti1, after the list of atoms.

The automatically generated PCR-file for CaTiO_3 by **AMPLIMODES** has been called `bcs_template_cti.pcr`, and the manually modified file in which we have introduced the real cell parameters and non-zero reasonable values (lower than 1 \AA) for the amplitudes is called `bcs_modified_cti.pcr`.

```

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  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  0  0  0  0
!
! lambda1 Lambda2 Ratio Bkpos Wdt Cthm muR AsyLim Rpolarz ->Patt# 1
1.227200 1.227200 0.0000 50.0000 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
!
!
      0 !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
!-----
! 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
0 0 0 0.0 0.0 1.0 6 0 0 0 7          0.000 0 7 0
062
! Scale          Shape1          Bov          Str1          Str2          Str3          Strain-Model
2.00          0.00000    0.00000    0.00000    0.00000    0.00000    0
0.00000    0.000    0.000    0.000    0.000    0.000
! U          V          W          X          Y          GauSiz      LorSiz      Size-Model
0.176020    -0.197809    0.091458    0.000000    0.030039    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
5.408801    7.649200    5.408801    90.000000    90.000000    90.000000    #box -0.15 1.15 -0.15 1.15 -0.15 1.15
0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
.....

```

Preparing a PCR file for refining experimental neutron diffraction data

Up to now, the PCR files we have used allow us to make a simulation of a powder diffraction pattern; we have to do some more work for treating real experimental data.

Let us open the provided data file corresponding to CaTiO_3 taken at a medium resolution neutron powder diffractometer, using the wavelength $\lambda=1.249\text{\AA}$. The format of the file corresponds to $\text{Ins}=0$ in **FullProf** and the initial U, V and W parameters controlling the Gaussian part of the FWHM of Bragg peaks are: $U=0.646$, $V=-0.309$ and $W=0.142$.

Using **WinPLOTR-2006** (button  in the **FPS** toolbar) we open the file called **CaTiO3.dat** selecting the free format (default) option and we proceed with the generation of a background file to be pasted in the PCR file. This is illustrated in the following figures (4 and 5):

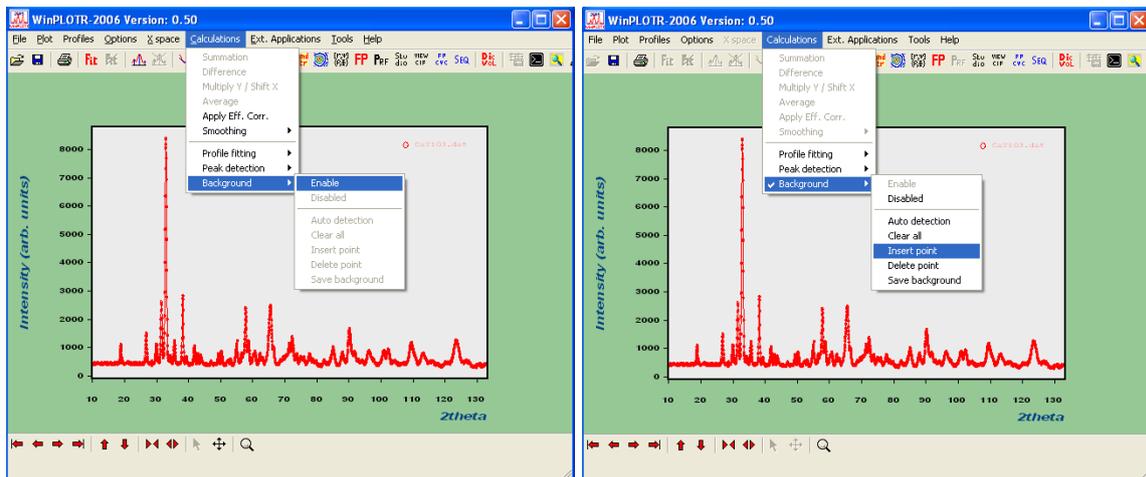


Figure 4: Selecting the Background option in **WinPLOTR-2006** using the manual insertion of points for selecting a linear interpolated background in the PCR file.


```

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
. . . . .
  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
  1.00000    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
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
. . . . .

```

We have to launch the program **FullProf** after loading the file in the FPS toolbar and using only two free parameters (notice that the amplitudes of the modes have been fixed to arbitrary values): the **scale factor** and the **zero-shift**. For refining these parameters one has to put 1.0 in the place of the corresponding refinement code. We obtain the picture shown in figure 6:

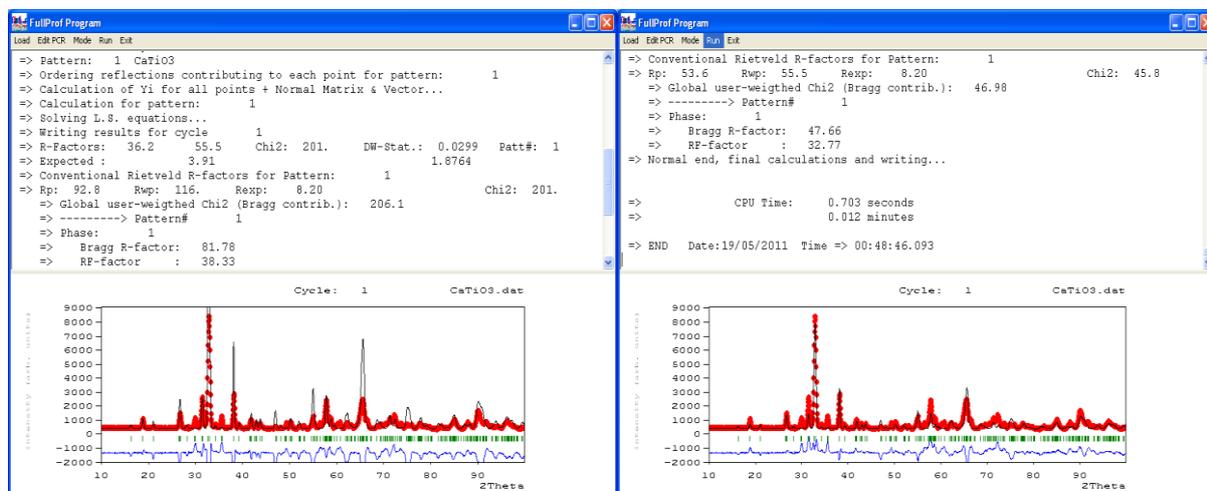


Figure 6: Refinement of the scale factor and zero-shift using fixed arbitrary values for the amplitudes of symmetry modes in CaTiO_3 . Left panel: picture after the first cycle. Right panel: final result after convergence. The amplitudes have to be varied to refine properly the pattern.

The PCR file has been modified automatically by **FullProf** (we put $P_{cr}=1$) at the end of the refinement and now it is prepared for freeing all significant parameters (amplitudes, cell parameters, UVWY, etc). One has to edit the file and add a refinement code to the parameters to be refined. Let us start just with all **amplitudes** and **cell parameters** (keeping free the scale factor and zero-shift).

```

. . . . .
! Amplitudes of Symmetry Modes
A_MODES  7      2
  A1_R4+      0.800000  1.000000
  A2_R5+     -0.100000  1.000000

```

```

A3_R5+          0.300000    1.000000
A4_X5+          0.700000    1.000000
A5_X5+          0.100000    1.000000
A6_M2+          0.020000    1.000000
A7_M3+          0.100000    1.000000
!-----> Profile Parameters for Pattern # 1
! Scale      Shape1      Bov      Str1      Str2      Str3      Strain-Model
0.90509      0.00000      0.00000  0.00000  0.00000  0.00000  0
21.00000     0.000      0.000    0.000    0.000    0.000
! U          V          W          X          Y          GauSiz   LorSiz   Size-Model
0.646000    -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
0.000000    0.000000   0.000000  0.000000  0.000000  0.000000
.....

```

After convergence we obtain a result giving still some important discrepancies in the difference pattern ($y_{\text{obs}} - y_{\text{calc}}$). This is due to the fact that we have used only Gaussian contribution to the profile and fixed values of the UVW parameters. This is shown in the left panel of figure 7.

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 result of the right panel of figure 7.

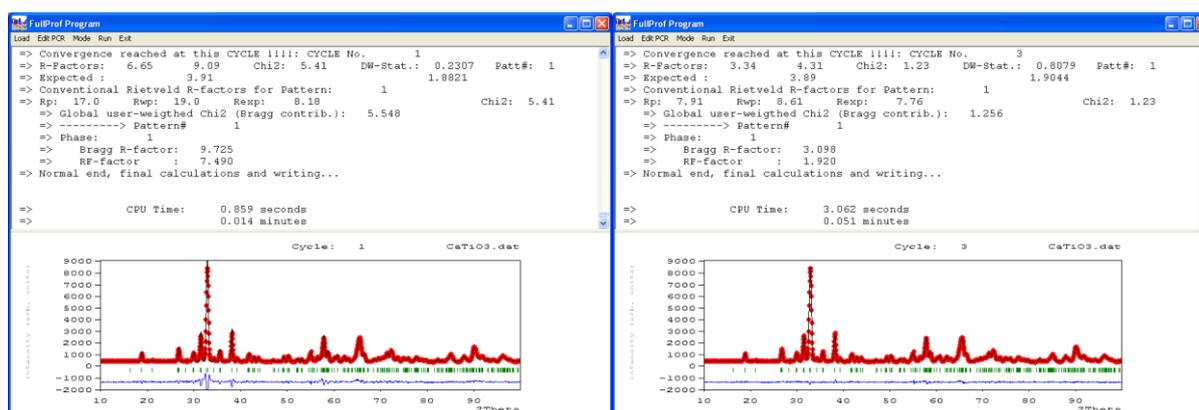


Figure 7: Left panel: picture after refinement of amplitudes. Right panel: final result after convergence, all profile and background parameters have been refined.

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.

In the file `CaTiO3ref.out` all the detailed results are gathered. We show below part of the numerical description of some the individual irreps, corresponding to different isotropy subgroups, as well as the final conventional crystallographic description of the atoms in the asymmetric unit.

```

=====
=== 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

```

The refined amplitudes of the modes at the end of the process, as extracted from file CaTiO3ref.sum are:

```

=> Amplitudes of symmetry modes ==>
      Name           Value           Sigma
A1_R4+           1.109912          0.002517
A2_R5+           0.064669          0.007066
A3_R5+          -0.030927          0.005121
A4_X5+          -0.385523          0.003811
A5_X5+          -0.172907          0.003388
A6_M2+           0.007576          0.003326
A7_M3+           0.852560          0.003616

```

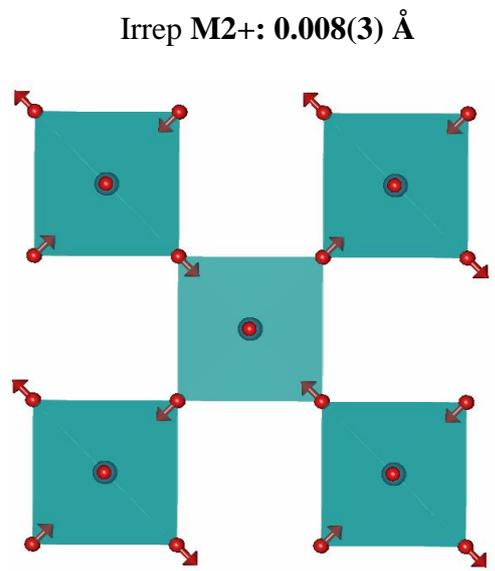
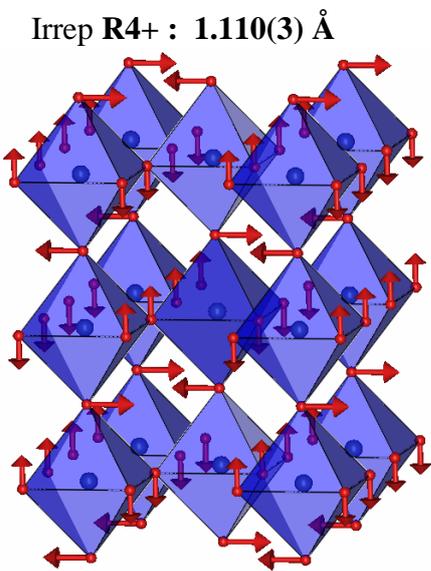
The global amplitudes of the different irreps, ordered from higher to lower, are:

```

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

```

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. Below we display the atom displacements corresponding to the most important mode, R4+ (the b-axis is vertical) and to the nearly negligible M2+ (view along the b-axis).



Preparing a PCR file for extracting integrated intensities and generate files to be used by the Simulated Annealing option of FullProf

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.

Extracting integrated intensities or structure factors from powder diffraction data, once we know the unit cell parameters, is straightforward in well crystallised samples; however there are cases where the tasks may be complicated due to the presence of broadening due to micro-structural effects. To avoid, from the beginning, pitfalls due to the handling of full width at half maximum it is convenient to work with instrumental resolution function files. This has as an additional advantage the production of micro-structural files containing information about the size and strain effects of your sample.

The procedure used for extracting the integrated intensities within **FullProf** (profile matching) is currently known as Le Bail fitting [A. LeBail, H. Duroy and J.L. Fourquet, *Mat. Res. Bull.* **23**, 447(1988)]. It does not require any structural information except approximate unit cell and resolution parameters. A similar method developed by Pawley uses traditional least squares with constraints [G.S. Pawley, *J. Applied Cryst.* **14**, 357 (1981)]. A discussion about the profile matching algorithm involved in this kind of refinement may be found in [J. Rodríguez-Carvajal, *Physica B* **192**, 55 (1993)]. This method makes the data input much simpler and enlarges considerably the field of application of powder pattern profile refinement. However the constraints applied to the refinement are far less severe than for Rietveld refinement and profile matching is thereby more prone to instabilities if profile shape parameters or micro-structural parameters are refined.

The Le Bail Fit (LBF) with constant scale factor is accessible by putting ($J_{bt}=2$). In this mode the scale factor is not allowed to vary and integrated intensities are refined individually using iteratively the Rietveld formula for obtaining the integrated *observed* intensity. The recommended procedure is as follows:

- For the first refinement, set $IRF(n)$ of the phase n undergoing profile matching to 0 and the number of refined parameters (MAXS on **line 13**) to zero. Set to 0 the flag controlling the automatic assignment of refinement codes ($A_{ut}=0$). Run **FullProf** for a few cycles (say 10). This will set up the *hkl* 's and intensity file **CODFILn.hkl**.
- If the result of the above step is satisfactory (see plot!), rename the file **CODFIL.new** to **CODFIL.pcr**, or use directly **CODFIL.pcr** if it was automatically updated. Edit the new **CODFIL.pcr** file to select the parameters to refine. The progression of the refinement is very similar to that used for Rietveld refinement: zero-shift of detector, background parameters and lattice constants.

In this mode of refinement **FullProf** cannot calculate *theoretical* integrated intensities and all *hkl* values permitted by the space group are considered and included in the refinement, which sometimes means a lot of reflections! Using this type of refinement one has to bear in mind that the starting cell parameters and resolution function determines to a large extent the obtained intensity parameters. One cannot expect to refine properly the cell parameters of a compound with a severe overlap of reflections if the starting parameters are of poor reliability. It is wise to start with low angle reflections (without refining the FWHM parameters) and progressively increase the angular domain.

In the present case, the easiest way to create a file for a LBF 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 modified PCR file `LBF_cti.pcr` is shown below:

```

COMM Le Bail Fit of CaTiO3 neutron data
! Current global Chi2 (Bragg contrib.) =      411.3
! Files => DAT-file: CaTiO3, PCR-file: LBF_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 1 0 0 1 0 0 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 0 0
!
!lambda1 Lambda2 Ratio Bkpos Wdt Cthm muR AsyLim Rpolarz ->Patt# 1
1.249000 1.249000 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
10 0.10 1.00 1.00 1.00 1.00 10.0000 0.050000 133.2500 0.000 0.000
!
!2Theta/TOF/E (Kev) Background for Pattern# 1
10.2121 446.1355 0.00
17.2106 437.9028 0.00
24.4891 429.6702 0.00
36.5265 433.7864 0.00
40.7256 413.2048 0.00
46.3245 404.9722 0.00
53.8828 404.9722 0.00
61.7212 409.0885 0.00
68.1598 413.2048 0.00
76.8380 400.8558 0.00
80.7571 384.3905 0.00
86.9158 388.5068 0.00
99.2332 376.1579 0.00
118.8291 363.8089 0.00
128.9069 347.3436 0.00
132.8261 355.5762 0.00
!
! Excluded regions (LowT HighT) for Pattern# 1
0.00 2.00
170.00 180.00
!
0 !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
-----
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 122.99
-----
Le Bail Fit of CaTiO3
!
!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 N_Domains
11 0 0 0 0 0 1.0000 0.0000 0.0000 0.0000 1 0 0 0
!
P n m a <--Space group symbol

```

```

!-----> Profile Parameters for Pattern # 1
! Scale      Shape1      Bov      Str1      Str2      Str3      Strain-Model
  1.00000    0.00000    0.00000  0.00000  0.00000  0.00000    0
    0.00000    0.000    0.000    0.000    0.000    0.000
!
  U          V          W          X          Y          GauSiz    LorSiz Size-Model
  0.646000  -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
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
. . . . .

```

All the important flags that we have modified are emphasised in red. The polynomial background parameters have been deleted and replaced by the background points determined with the help of **WinPLOTR-2006**. The flag `Ipr=-1` means that after the LBF a file containing information on profile intensity contributions will be generated (called `LBF_cti.spr`). The flag `Jvi=11` means that a file with integrated intensity clusters is output (`LBF_ctil_cltr.int`). Both files will be used later for doing a simulated annealing search of the amplitudes.

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** looks like the left panel of the Figure 8.

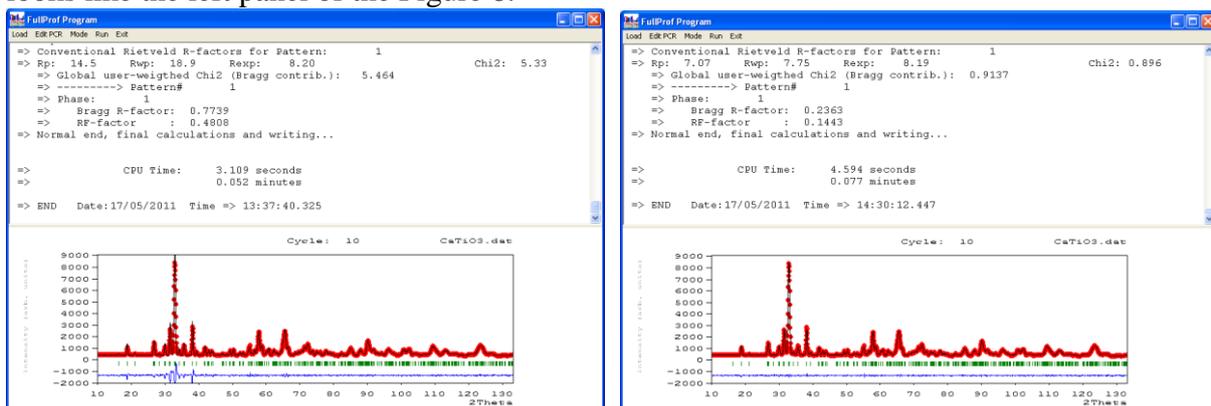


Figure 8: Ten cycles LBF refinement of integrated intensities with fixed profile parameters (left panel). Full LBF varying cell parameters, U, V, W, Y and zero-shift up to convergence (right panel).

No profile parameter has been refined in the run of the left panel. The PCR file is now updated because we wrote `Pcr=1` and the flag `Irf` is put equal automatically to 2 (`Irf=2`), meaning that for the next run the initial integrated intensities are read from the generated file `LBF_ctil.hkl`.

In the next step we have to modify the PCR file putting `Aut=1` and refine U, V, W and the Y -parameter (controlling the Lorentzian isotropic size effect). The zero-shift and cell parameters should also be varied. For refining these parameters one has to set to 1.0 the corresponding refinement code. After running **FullProf** with the modified PCR file up to convergence we obtain the picture of right panel of Figure 8.

The output files after running a Le Bail fit

Primary integrated intensity file: **CODFILn.hkl**, in our case: LBF_ctil.hkl

The format of this file depends on the value of the indicator J_{bt} . For $J_{bt}=2$ the header of the file is similar to the following:

```
Pattern#1 Phase No:1 Le Bail Fit of CaTiO3 Lambda:1.249000 CELL:5.441 7.645 5.382 90 90 90
  393      0      0.00 SPGr: P n m a <-- The number of effective reflections may be lower
  0  1  1  4      1.297      8.159      16.3160      0.3985
  1  0  1  4     122.483      3.803      18.7857      0.3953
  0  2  0  2     230.758      7.133      18.8054      0.3953
  1  1  1  8      48.488      5.673      21.0313      0.3930
  2  0  0  2     111.593      2.965      26.5390      0.3899
  1  2  1  8     273.951      5.656      26.7029      0.3899
  0  0  2  2     204.420      4.372      26.8378      0.3899
  2  1  0  4      19.611      2.832      28.2022      0.3897
  2  0  1  4     171.649      3.333      29.8072      0.3899
```

.....

Notice that the wavelength, cell parameters and space group symbol are provided in order to be used by other programs. The first three items in the second line are: Number of lines, “numor” (number related to the use of ILL database, which is of no interest here) and temperature of the sample.

The items of the rest of lines are:

```
h, k, l, mult, Intensity, Pseudo-sigma, 2theta/T.O.F./Energy, FWHM
```

Here the intensity contains all geometrical and physical factors multiplying the square of the structure factors. The units are counts \times degrees or counts \times micro-seconds or counts \times keV, depending of the scattering variable units.

In the case of $J_{bt}=-2$ the header of the file is as before except that in the place of the integrated intensity the structure factors are written. Of course they are not in absolute units because no information about the structure has been provided.

Exercise: Modify J_{bt} and put $I_{rf}=0$ in the previous PCR files to see what happens.

If the user wants **FullProf** to use integrated intensities for making a simulated annealing work for solving or completing the structure, the indicator J_{vi} , appearing when $More=1$ in the line containing the number of atoms, that follows immediately after the mentioned line should be put equal to 11 ($J_{vi}=11$). In such a case the program generates an additional file called **CODFILn_cltr.int** in which the integrated intensities of overlapped clusters of reflections are written. The header of this file (in our case LBF_ctil_cltr.int) is like:

```
! Phase No: 1 Le Bail Fit of CaTiO3 Overlapped reflections re-grouped -> Obs = j LP F^2
(3i4,2f16.5,i4,3f14.4)
  1.24900  0  2  0.0000
  0  1  1      1.29664      8.15944  1      0.0000      0.0000      16.3160
  1  0  1     -1.00000      3.80302  1      0.0000      0.0000      18.7857
  0  2  0     353.24097      8.08370  1      0.0000      0.0000      18.8054
  1  1  1     48.48777      5.67258  1      0.0000      0.0000      21.0313
  2  0  0     -1.00000      2.96528  1      0.0000      0.0000      26.5390
  1  2  1     -1.00000      5.65601  1      0.0000      0.0000      26.7029
  0  0  2     589.96399      7.73956  1      0.0000      0.0000      26.8378
  2  1  0     19.61056      2.83157  1      0.0000      0.0000      28.2022
```

2	0	1	-1.00000	3.33281	1	0.0000	0.0000	29.8072
1	0	2	399.24738	5.05503	1	0.0000	0.0000	30.0091
2	1	1	-1.00000	3.22797	1	0.0000	0.0000	31.3112
0	3	1	-1.00000	1.17173	1	0.0000	0.0000	31.4644
1	1	2	1100.58142	6.09536	1	0.0000	0.0000	31.5043
.....								
.....								

A negative value of the intensity means that the corresponding reflection contributes to the first positive reflection following in the list. For instance the reflections (2 0 0), (1 2 1) and (0 0 2) contribute altogether with an intensity of 589.96 to a single observation. The degree of overlap can be controlled by the user modifying the parameters `RMub` and `RMuc` (see the **FullProf** manual).

In our case we have run the program putting `Ipr=-1`, so the file `LBF_cti.spr` has also been generated. The content of this file is too long to be explained here. It is used when the profile intensities (instead of peak clusters) are considered in the simulated annealing option. This is slightly slower than using intensities but it is equivalent to the Rietveld method on selected profile points with a robust global optimisation.

Determining the amplitudes of the symmetry modes of CaTiO_3 Illustration of the use of simulated annealing with FullProf

We have already determined the amplitudes of the symmetry modes of CaTiO_3 using least squares. This is not always possible when the crystal structure is too complex. The simulated annealing option is an alternative for getting the values of the amplitudes. We use the same data to illustrate the use of simulated annealing in **FullProf**.

For using the option of simulated annealing we have to transform the PCR file `bcs_modified_cti.pcr` into another one able to work with the regrouped integrated intensities stored in the file `LBF_cti1_cltr.int`. We will use the program **EdPCR** (together with some manual editing) to modify `bcs_modified_cti.pcr`. First we copy this file into another with the name `cti_san.pcr`. Now we should follow strictly the steps below for transforming the PCR file in order make it adapted to simulated annealing.

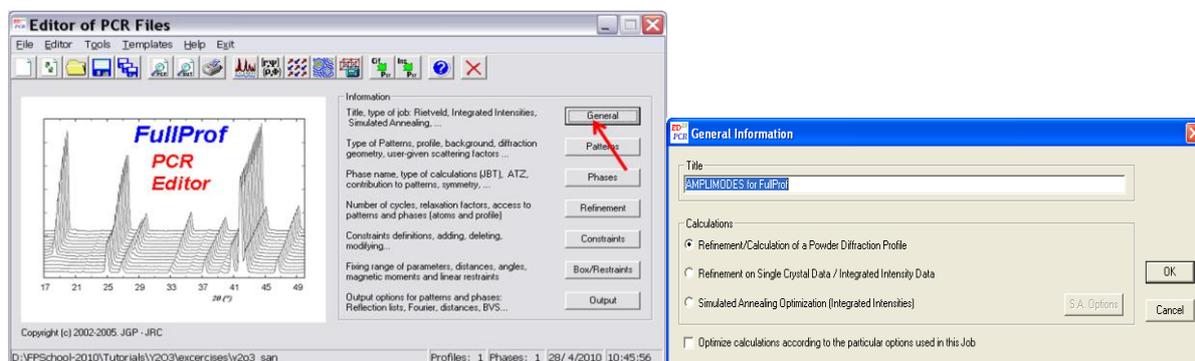
Notice that the results of simulated annealing jobs may give slightly different results because by default the seed of the random number generator is obtained also randomly. This behaviour can be changed by the user by providing explicitly the seed as a big odd integer (see, for instance the file `pb_san.pcr` in the **Examples** directory of the **FullProf Suite** distribution).

Steps for transforming a PCR file into another appropriate for simulated annealing

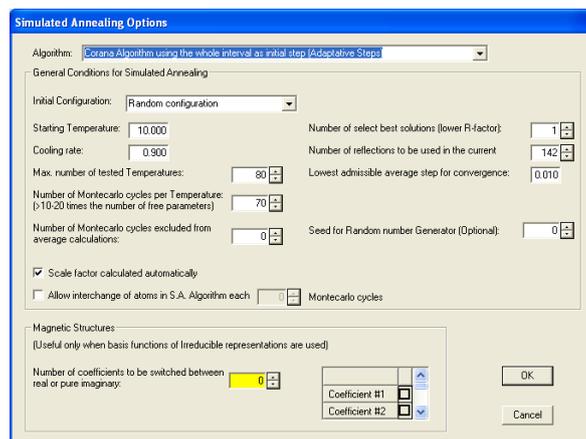
We shall describe below the steps for preparing a PCR file appropriate for simulated annealing. The experienced **FullProf** user can directly go to edit an example of PCR file for simulated annealing (as those provided in the **FullProf Suite** distribution) and adapt it to the present purpose.

Step 1: Load `cti_san.pcr` into the **FPS** Toolbar and open **EdPCR** by clicking in the corresponding icon.

Step 2: Click on the **General** button



Step 3: Select **Simulated Annealing Optimization (Integrated Intensities)** and click on the button **S.A. Options**. If you wish, you may change also the content of the **Title** box.



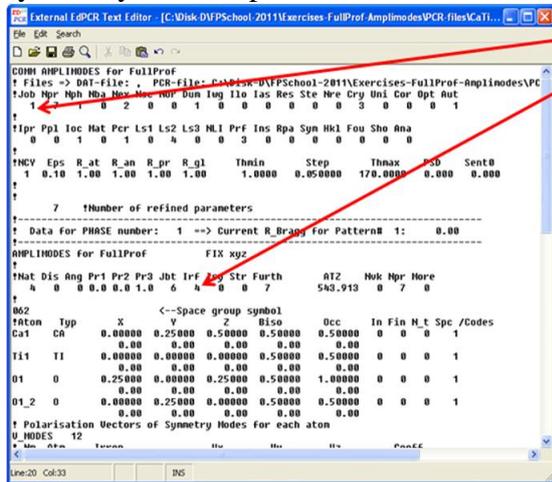
Step 4: In the **Simulated Annealing Options (Integrated Intensities)** dialog (shown on the right) change the **Starting Temperature**, the **Cooling rate**, etc, as shown below (do not forget ticking the **Scale factor calculated automatically** checkbox). If we leave the **Number of reflections to be used in the current job** equal to zero, the program will use all reflections existing in the file `LBF_ctil_cltr.int`. Notice that, in our case, we have selected 142 reflections that correspond to an angle of approximately 80 degrees in 2θ . The overlap in this low resolution pattern is too high to use the whole set of reflections.

Click on **OK** buttons to accept the changes in the current dialog and in the previous one for coming back to the general interface of **EdPCR**. Click on the **Save Data** button of the general **EdPCR** interface to save the modified file.

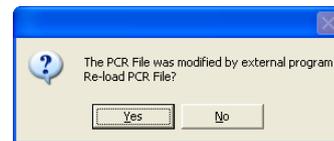
Step 5: Select the menu: Editor → **Unsaved Input File** to open the `unsaved.pcr` file and change by hand **Job** to **1** (experimental neutron data) and **Irf** to **4** (integrated intensities provided for the phase). Save the file giving it the name `cti_san.pcr` to replace the original and then 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.

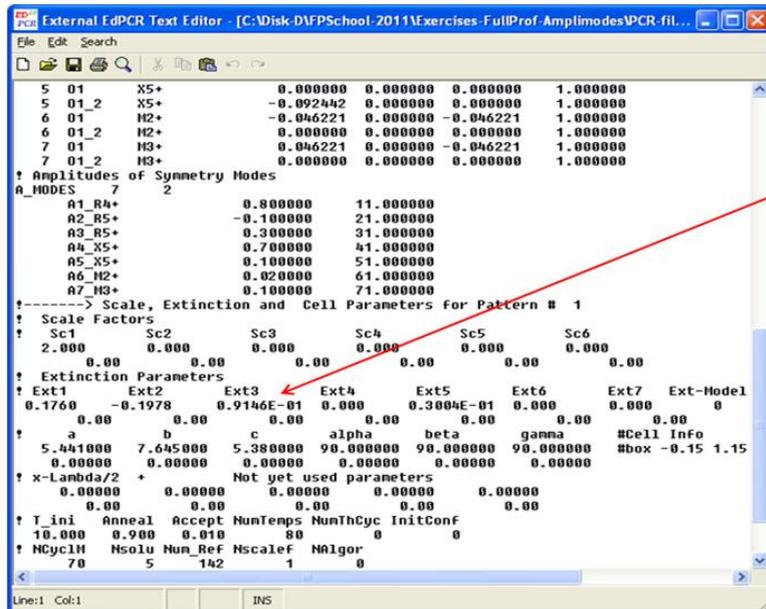
(The reason of doing that by hand is that is that **EdPCR** has a bug when going to select the symmetry modes option with the interface; however the major part of the work is done)



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



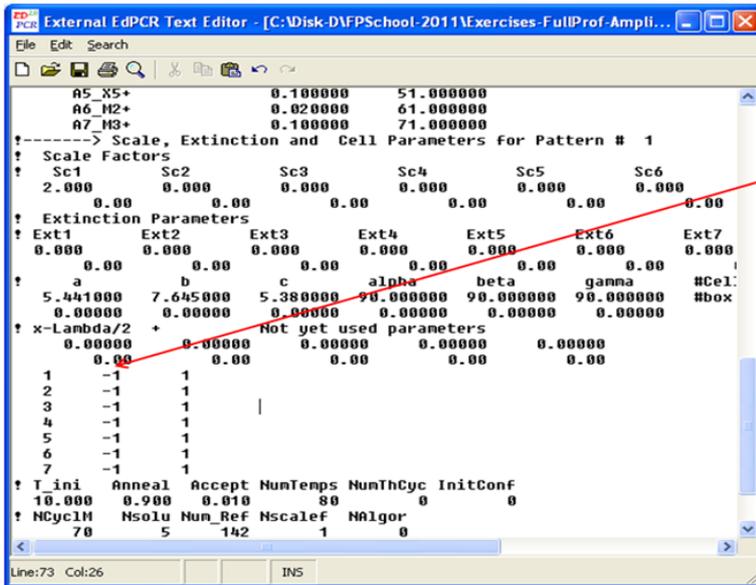
Step 6: In the Editor menu select the item: Input Control File (.PCR). The modified PCR-file is reloaded into the internal editor and we follow the indications of the panel below.



Edit the already created 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.

Step 7: Follow the indications of the panel below.



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 and reopen the file as before.

Now the file is prepared to be used as a simulated annealing job. Click again on the save button  (or select **File** → **Save** in the menu) of **EdPCR** in order to save all changes and get the file prepared for running **FullProf**.

The reason of saving the file repeatedly is that **EdPCR** is analysing the modifications and writes the PCR file according to the rules needed for running **FullProf**. If for some reason a mistake appears one can always come back and properly redo the modifications.

Running a simulated annealing job with integrated intensity clusters

If we run **FullProf** from the toolbar, it will take automatically the charged PCR file `cti_san.pcr` as input and the toolbar will ask immediately for the intensity file. One must select the file `LBF_cti1_cltr.int`. When **FullProf** is launched the simulated annealing (SAN) job starts and we observe the evolution of the observed and calculated set of integrated intensity clusters as in figure 9.

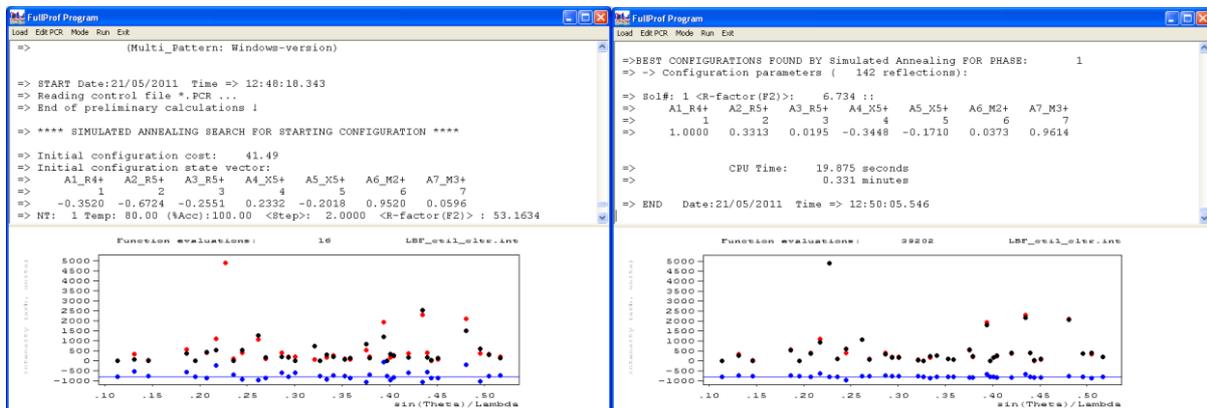


Figure 9: Starting (left panel) and final (right panel) of a simulated annealing run using integrated intensity clusters obtained from a previous LBF on CaTiO_3 neutron powder diffraction data. Notice that in the right panel the value of the amplitude $A1_R4+$ has attained its maximum of 1\AA . The final R-factor(F2) is equal to 6.73%.

The first SAN job has shown that the maximum amplitude for one of the modes (R4+) is attained. This indicates that the constraint we put of limiting the amplitudes to a maximum of 1Å is not supported by the data. We can free this condition and rerun the same job; we immediately see the improvement of the results as shown in figure 10.

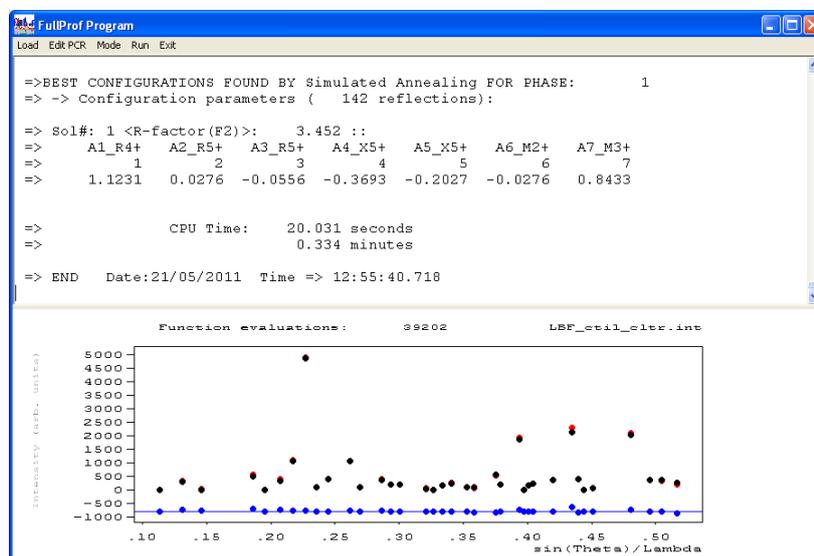


Figure 10: Final picture of a SAN run using integrated intensity clusters as in figure 9 but freeing the restriction of maximum amplitude limited to 1Å. The final R-factor(F^2) has dropped from 6.73% to 3.45%.

We can see that the results depend of the constraints. When the maximum amplitude is limited to 1 Å, the results are 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 (only 142 reflections out of the 393 contributing reflections). The SAN method is normally used for solving a structure and to get initial values of parameter for a further treatment using LSQ.

Comparison of LSQ and SAN amplitudes

Least squares refinement		Simulated Annealing (Integrated Intensities)
Name	Value	
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

Running a simulated annealing job with profile intensities

As we stated in the paragraph dedicated to the Le Bail Fit, it was possible to generate a file containing information for making a profile intensity SAN run. The option `Ipr=-1` was used

for output the file LBF_cti.spr. If we copy the file cti_san.pcr into the file cti_san_spr.pcr we can transform it easily to run SAN jobs using profile intensities.

We need only to change the value of I_{pr} to -1. We need also to rename the file LBF_cti.spr to cti_san_spr.spr in order to run **FullProf** with the PCR file named as cti_san_spr.pcr

The program will still need the file of integrated intensities LBF_cti1_cltr.int but it uses the file just for getting the Miller indices of the reflections.

We need now to load the modified cti_san_spr.pcr file into the **FPS** toolbar. If we now run **FullProf** from the toolbar, it will take automatically the loaded PCR file as input. The program asks for the intensity file and the user must select still the file LBF_cti1_cltr.int. The program will use the content of this file and that of the file cti_san_spr.spr for optimising the profile intensities. Notice that only selected points of the profile are used. In figure 11 we can see the pictures of such a run.

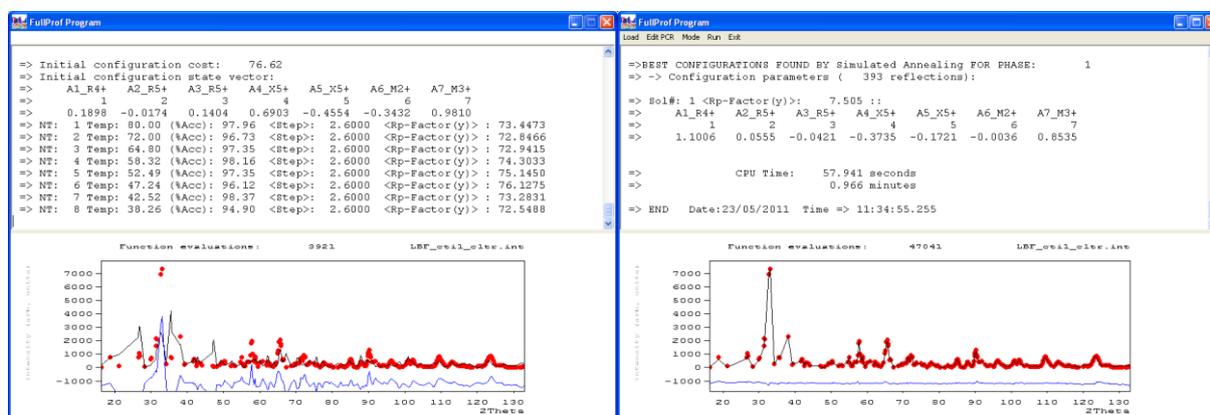


Figure 11: Starting and final pictures of a SAN run using profile intensities.

We can compare the obtained amplitudes in this case with the previous results as shown in the pane below:

Comparison of LSQ and SAN amplitudes for CaTiO₃

Least squares refinement		SAN	SAN
Name	Value	(Integrated Intensities)	(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

It is clearly seen that the SAN using profile intensities and a larger Q-range is much closer to the final result that it is obtained using LSQ.

Notice that the A6_M2+ amplitude in SAN jobs has a changed sign with respect to the LSQ result. Changing the sign of an amplitude value, means a change in the direction of atomic

displacements related to the mode concerned with this amplitude. In some cases this gives rise to another structure that may correspond to a local minimum. In our case the concerned amplitude is very small. The sign of the amplitudes is an issue that should be studied in detail because both LSQ and SAN may be trapped in a local minimum.

The case of LaMnO₃

We provide also neutron powder diffraction data corresponding to LaMnO₃, another perovskite with the same structure as that of CaTiO₃. The data were taken on the diffractometer 3T2 at LLB. The input file LaMnO3.dat (the format of the file corresponds to $I_{NS}=6$) was collected with a wavelength $\lambda=1.229\text{\AA}$, the unit cell parameters in this case are $a=5.747\text{\AA}$, $b=7.693\text{\AA}$ and $c=5.536\text{\AA}$. The UVW parameters of 3T2 are approximately: $U=0.177$, $V=-0.199$ and $W=0.0925$. With this information, the user should be able to redo the same process described for CaTiO₃ in the above paragraphs. In practice the template generated by AMPLIMODES has the proper values of the UVW parameters; however the unit cell must be adapted to be closer to the real cell. Let us just give the final results we obtained after refining the data of LaMnO₃ by LSQ as extracted from the file LaMnO3ref.sum.

=> Amplitudes of symmetry modes

Name	Value	Sigma
A1_R4+	1.194835	0.002608
A2_R5+	0.083992	0.002215
A3_R5+	-0.019105	0.002860
A4_X5+	-0.545605	0.001912
A5_X5+	-0.141112	0.002648
A6_M2+	-0.363314	0.002912
A7_M3+	0.904234	0.002523

==== FINAL ATOMS POSITIONS CALCULATED FROM SYMMETRY MODES FOR PHASE: 1

```
=> Global Amplitude of Representation R4+      : 1.195(3)
=> Global Amplitude of Representation R5+      : 0.086(2)
=> Global Amplitude of Representation X5+      : 0.5636(20)
=> Global Amplitude of Representation M2+      : 0.363(3)
=> Global Amplitude of Representation M3+      : 0.904(3)
```

	X	Y	Z	B-iso	Occ
Atom La1	-0.04895(17)	0.25000	0.50754(20)	0.355(15)	0.50000
Atom Mn1	0.00000	0.00000	0.00000	0.24(3)	0.50000
Atom O1	0.30686(17)	-0.03851(12)	0.22573(17)	0.434(16)	1.00000
Atom O1_2	0.0127(2)	0.25000	0.0746(2)	0.51(2)	0.50000

Notice that the data taken on LaMnO₃ at 3T2 are of higher resolution than those of CaTiO₃ so that the standard deviations are smaller.

Both structures are quite similar concerning the most important rotational modes R4+ and M3+. The main difference comes from the value of the amplitude corresponding to the Jahn-Teller mode M2+.

In the panel below we compare directly the refined amplitudes in angstroms for 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)

The Jahn-Teller mode M2+ is clearly active in LaMnO_3 , in which Mn^{3+} is a d^4 ion presenting orbital degeneracy, whereas it is negligible in CaTiO_3 .

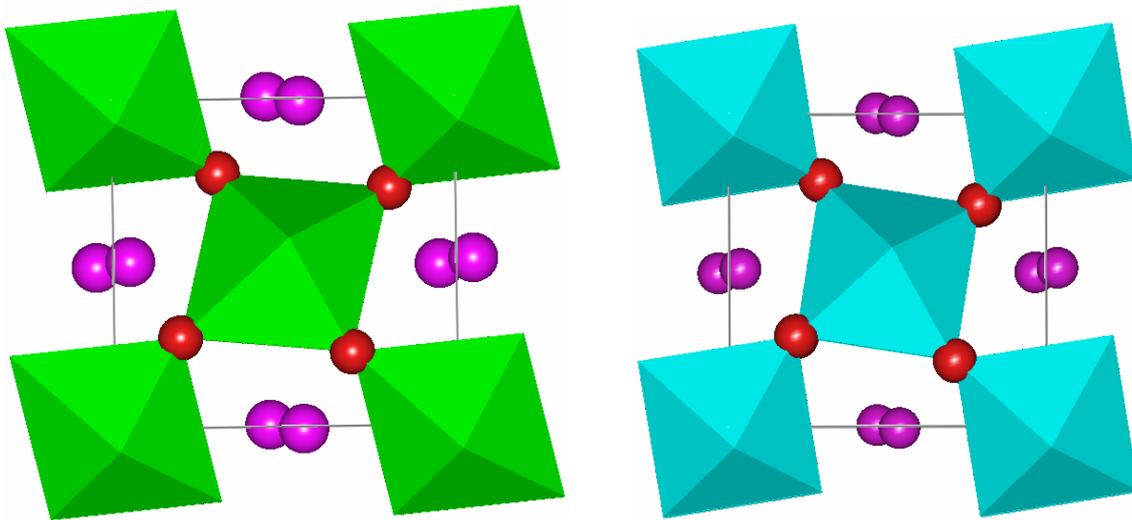


Figure 12: Pictures (seen along [010]) of the crystal structures of LaMnO_3 (left panel) and CaTiO_3 (right panel) showing the stronger distortion of MnO_6 octahedra in comparison with TiO_6 octahedra due to the Jahn-Teller effect that is active in LaMnO_3 . The antiferro-distorsive orbital ordering is clearly seen as an elongation of the occupied d_{z^2} -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.