Rietveld refinement of complex inorganic materials using FullProf

(Extended version in tutorial form)

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A program for analysis of diffraction patterns: *FullProf*

- A program for :
  - Simulation of powder diffraction patterns
  - Pattern decomposition⇨ integrated intensities
  - Structure refinement
  - Powder and single crystal data
- Crystal and magnetic structures
- Multiple data sets: simultaneous treatment of several powder diffraction patterns (CW X-rays & neutrons, Energy dispersive X-rays, TOF neutron diffraction)
- Combined treatment of single crystal and powder data
- Crystal and magnetic Structure determination capabilities: simulated annealing on integrated intensity data

FullProf Web site

http://www-llb.cea.fr/fullweb/powder.htm

or

ftp://ftp.cea.fr/pub/llb/divers/fullprof.2k

Also from CCP14: http://www.ccp14.ac.uk

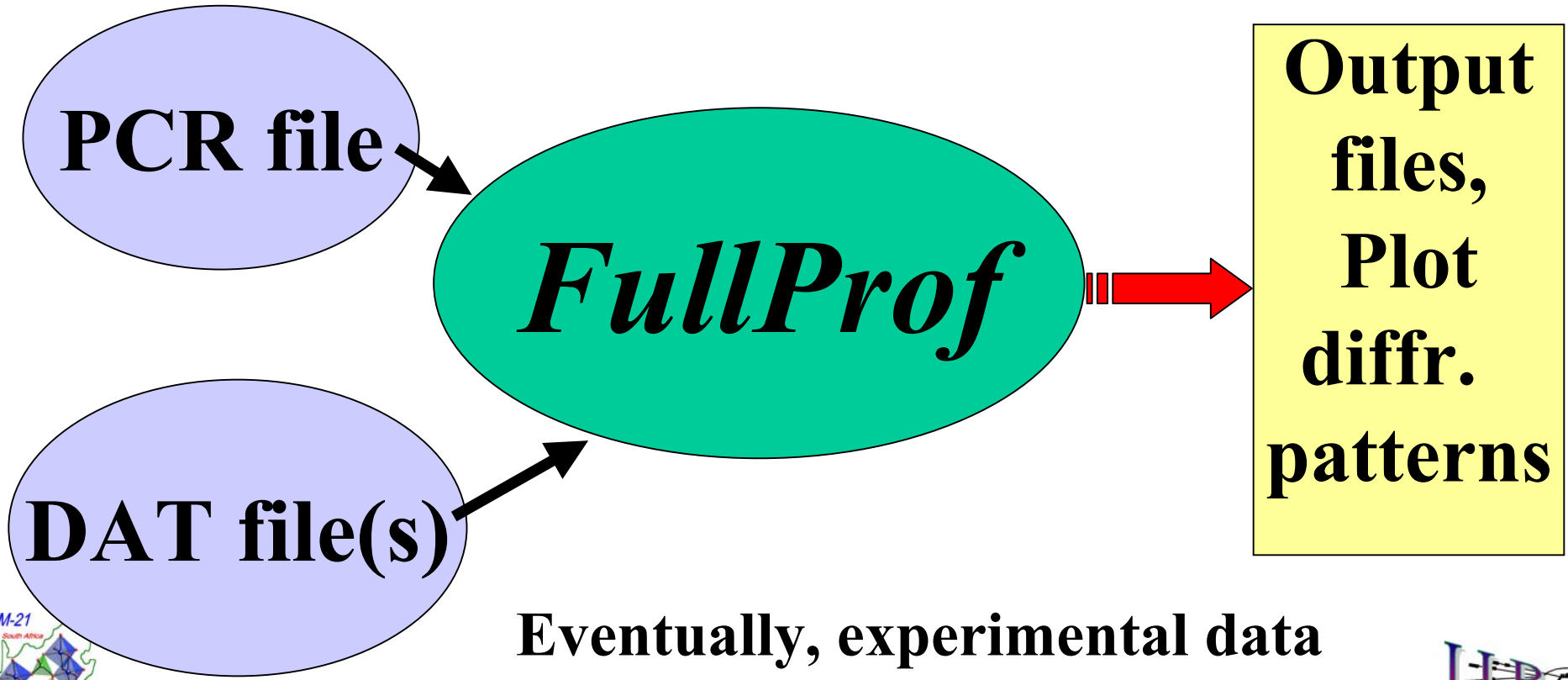
FullProf.2k (Fortran 90 subset ELF90)
Windows , Linux, Solaris, MacOS

How works *FullProf*

Minimal input:

Input control file (extension ' *.pcr* '): PCR-file

Model, crystallographic/magnetic information



Eventually, experimental data

The PCR file: steep learning curve

DAT file(s) → **Format depending on the instrument, usually simple**

PCR file →

- ➔ **Many variables and options**
- ➔ **Complex to handle**
- ➔ **Hint: copy an existing (working) PCR-file and modify it for the user case, or...**
- ➔ **USE the new GUI: EdPCR**

Last minute changes in *FullProf*
Documented in "fp2k.inf"

```
-------------------------------------------------------------------------
  In this file new features, as well as discovered bugs, of FullProf.2k
  are periodically documented. For details consult the manual of FullProf.
  From 10 May 2003, comments on the programs constituting the FullProf suite
  are also provided.
       Juan Rodriguez-Carvajal (Laboratoire Leon Brillouin, Saclay)
  -------------------------------------------------------------------------

---------------
  28 July 2003
---------------
- An updated version of FullProf.2k is now available.
  . . . . . .
- Some changes have been introduced for treating the background:

  (1) The polynomial background of 12 coefficients, for constant wavelength case, has been
      changed so that the last three coefficients correspond to inverse powers of 2theta.
      . . . . . .
  (2) Now there is the possibility to include several previously calculated profiles as
      contributing, through a linear combination, to the background of a powder diffraction
      pattern. The individual profiles are read in input files named "filedat_n.bac". Where
      "filedat" is the code of the data file corresponding to a diffraction pattern and the
      index "n" is the number of the contributing profile. The additional contribution to
      the background is calculated as:
```

Last minute changes in *FullProf*
Documented in "fp2k.inf"

- Reorganization of the TOF peak shapes and derivatives. The refinement of the instrumental parameters is now much more stable. . . . . .

The new peak shape INSTR=13 (thanks to Laurent Chapon!) consisting in the convolution of a pseudo-Voigt function with the Ikeda-Carpenter function is now working.

The TOF peak shapes used in FullProf and the meaning of each refinable parameter is now documented in the note: TOF_FullProf.PDF

Some recent features in *FullProf*

- ➔ New facilities concerning symmetry
- ➔ Automatic mode for handling refinement codes and symmetry constraints
- ➔ The use of distances and angles restraints
- ➔ Changes in the format of the file containing the Instrumental Resolution Function
- ➔ Special form factors
- ➔ Simulated Annealing
- ➔ The treatment of micro-structural effects

New facilities concerning symmetry in *FullProf*

⇒ **The symmetry used within *FullProf* is totally based in the Crystallographic Fortran 95 Modules Library (CrysFML) (Tuesday 26 ⇒ FA3-MS5, Meeting Room 11B)**

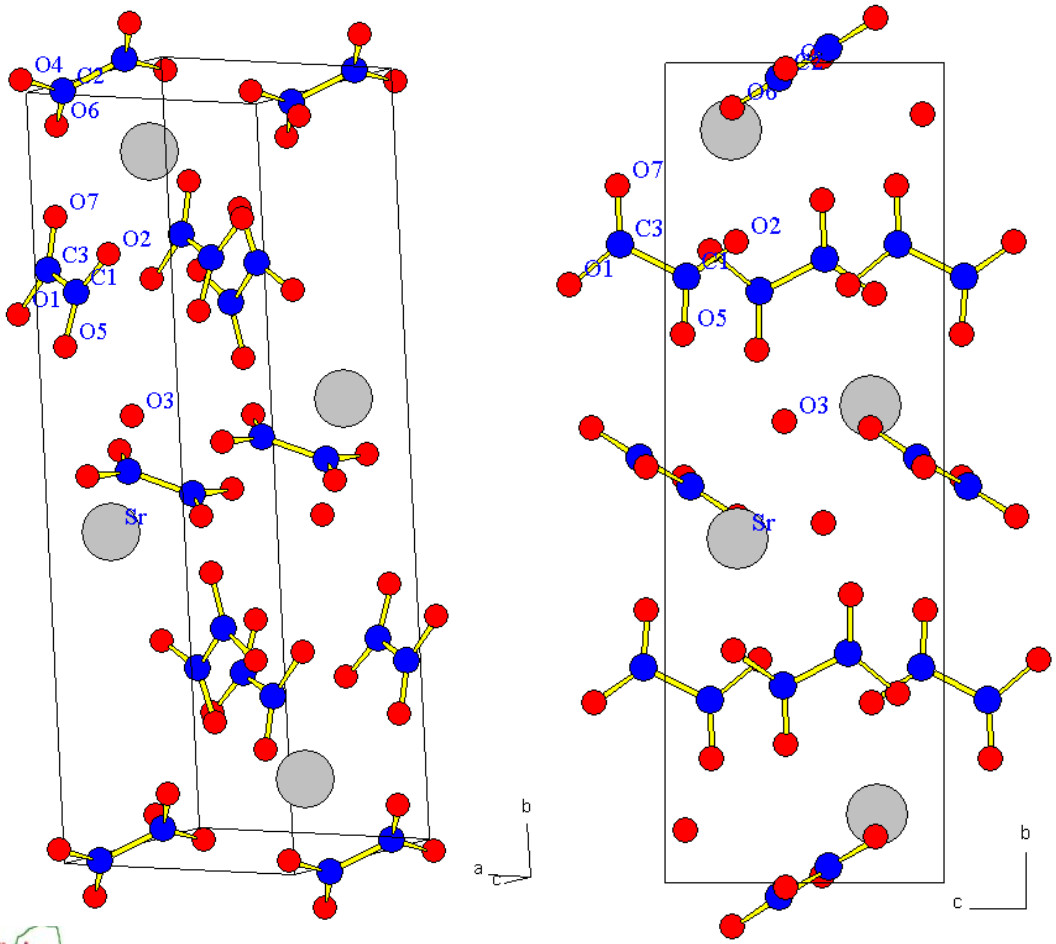
⇒ **These modules provide better crystallographic information to the user of the program. In particular automatic calculation of the multiplicity of each site is now performed after reading the atoms as well as the calculation of the appropriate coefficients for automatic quantitative analysis of mixture of phases.**

⇒ **New output files with full information of crystallographic symmetry are produced (extension: *sym*)**

Simulated Annealing in *FullProf*

The structure of acid strontium oxalate was determined from X-ray powder diffraction G. Vanhoyland *et al.* JSSC 157, 283 (2001)

The raw chemical composition should be: $SrC_3O_7H_3$

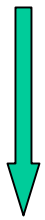


Where are the hydrogen atoms?

Neutron powder diffraction gives you the answer …

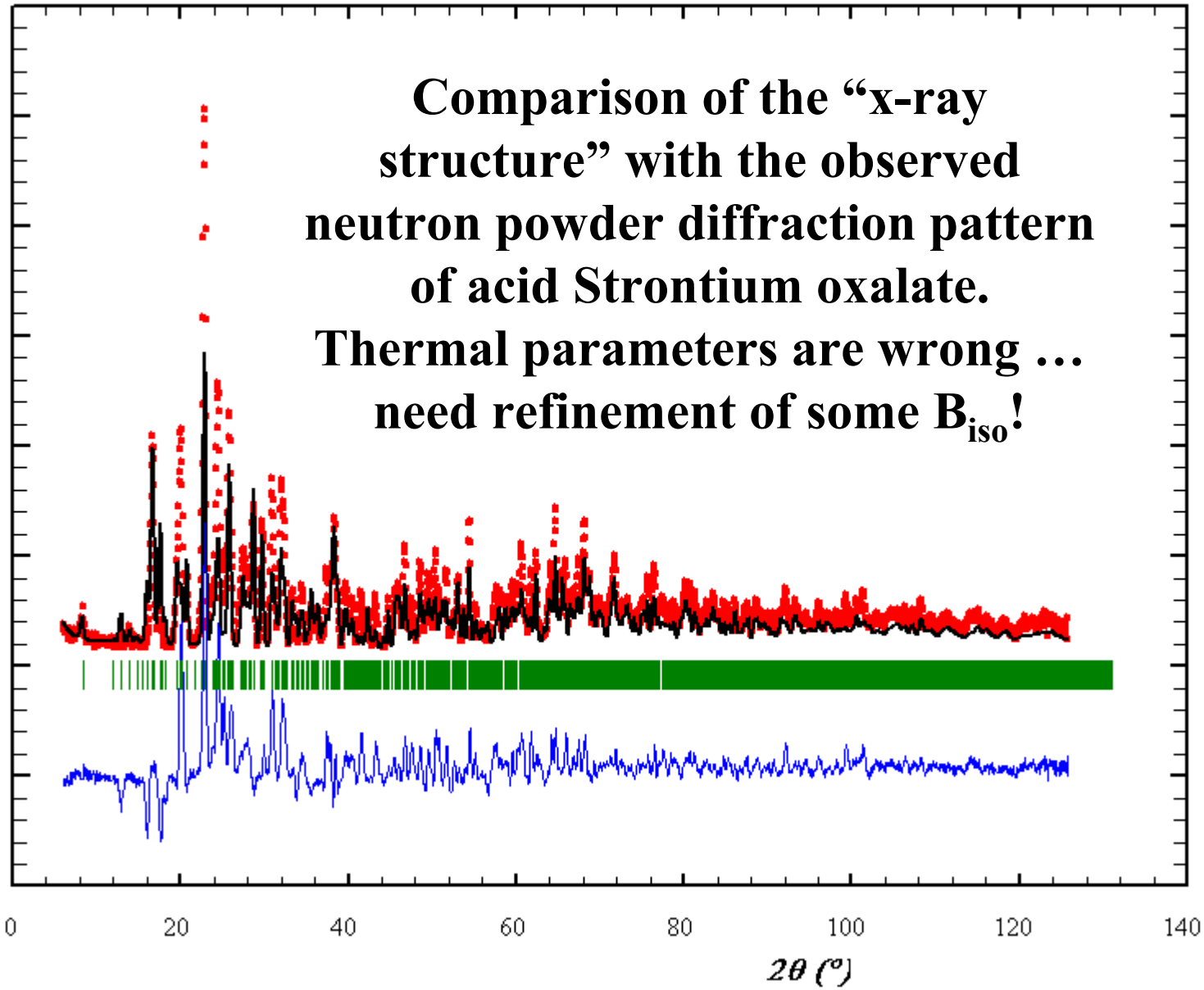
The structure of acid strontium oxalate was determined from X-ray powder diffraction
G. Vanhoyland *et al*. JSSC 157, 283 (2001)

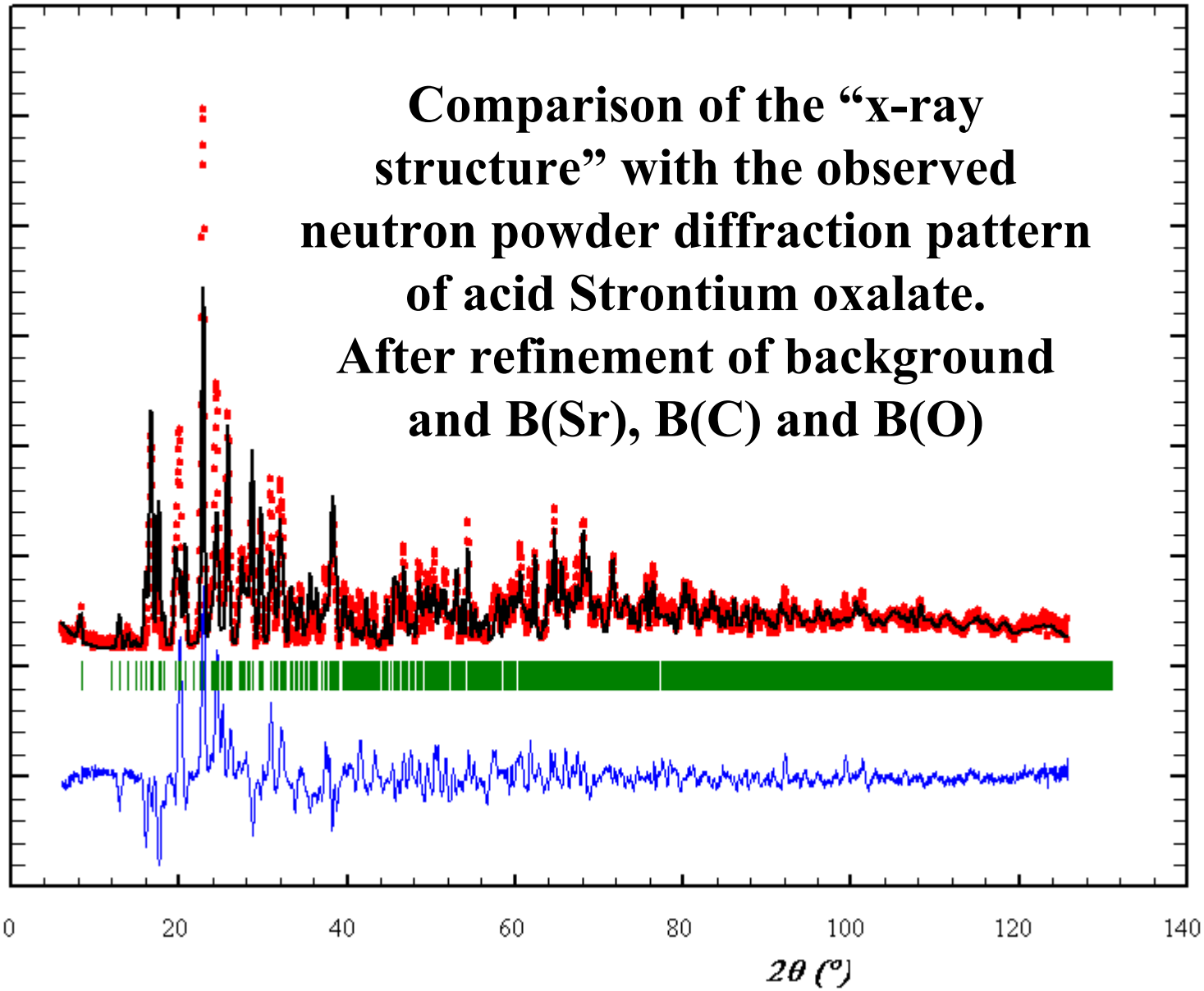
Where are the hydrogen atoms?



In the original paper hydrogen atoms were determined using Fourier synthesis.

Here we use this published example to illustrate how to use the Simulated Annealing option existing in FullProf

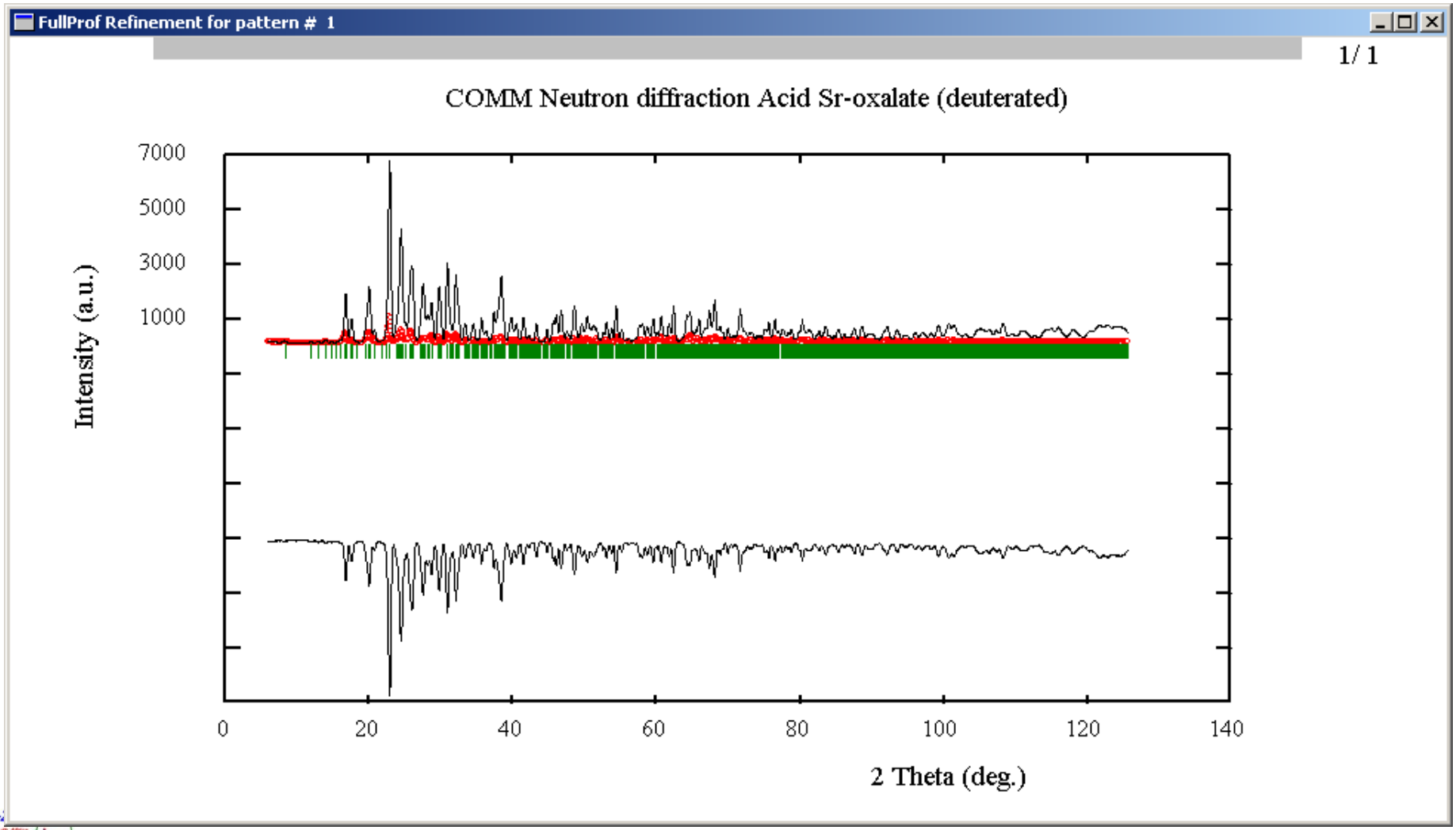

Comparison of the "x-ray structure" with the observed neutron powder diffraction pattern of acid Strontium oxalate. Thermal parameters are wrong … need refinement of some B_{iso}!
0
20
40
60
80
100
120
140
2θ (°)


Comparison of the "x-ray structure" with the observed neutron powder diffraction pattern of acid Strontium oxalate. After refinement of background and B(Sr), B(C) and B(O)
0
20
40
60
80
100
120
140
2θ (°)

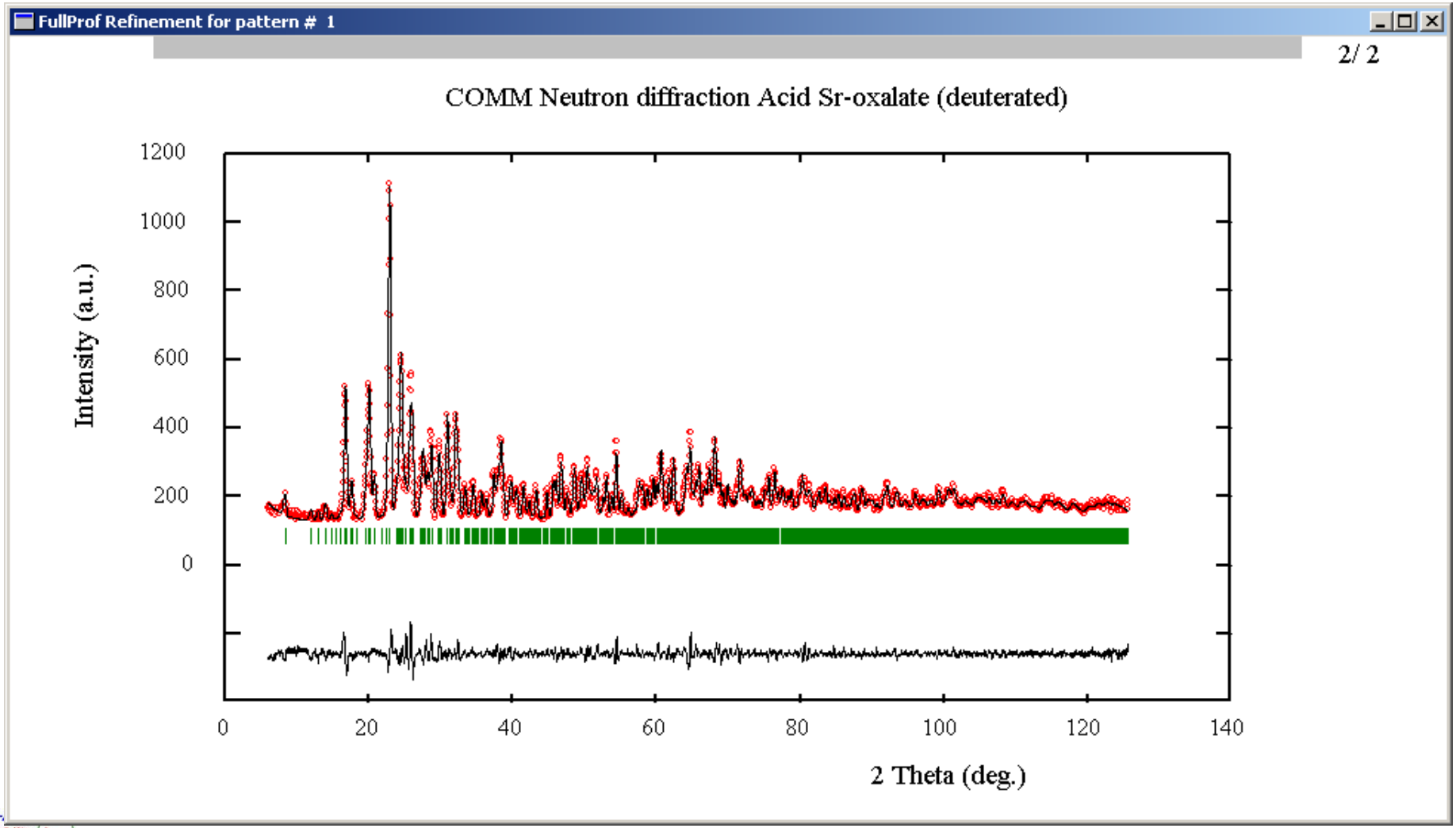
Portion of PCR (Acid Sr-oxalate) file to perform a Le Bail fit with output of an integrated intensity file suitable for Simulated Annealing

```
. . . . . .
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     0.81
!-------------------------------------------------------------------------------
Sr/C/O/D
!
!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        942.600   0   5   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua     RMub     RMuc    Jtyp  Nsp_Ref
  11   0   0   0   0   0  1.0000  0.0000   0.0000   0.0000   1    0
!
P 21/n                    <--Space group symbol
!-------> Profile Parameters for Pattern #  1
!  Scale         Shape1       Bov        Str1       Str2       Str3    Strain-Model
 0.46025E-01    0.23580    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
   0.405860   -0.525900    0.243880    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
   6.330998   16.862967    5.787098   90.000000   97.656639   90.000000
  111.00000   121.00000   131.00000     0.00000   141.00000     0.00000
!  Pref1     Pref2       Asy1      Asy2      Asy3      Asy4
  0.00000   0.00000   0.09150   0.02857   0.00000   0.00000
     0.00      0.00      0.00      0.00      0.00      0.00
```

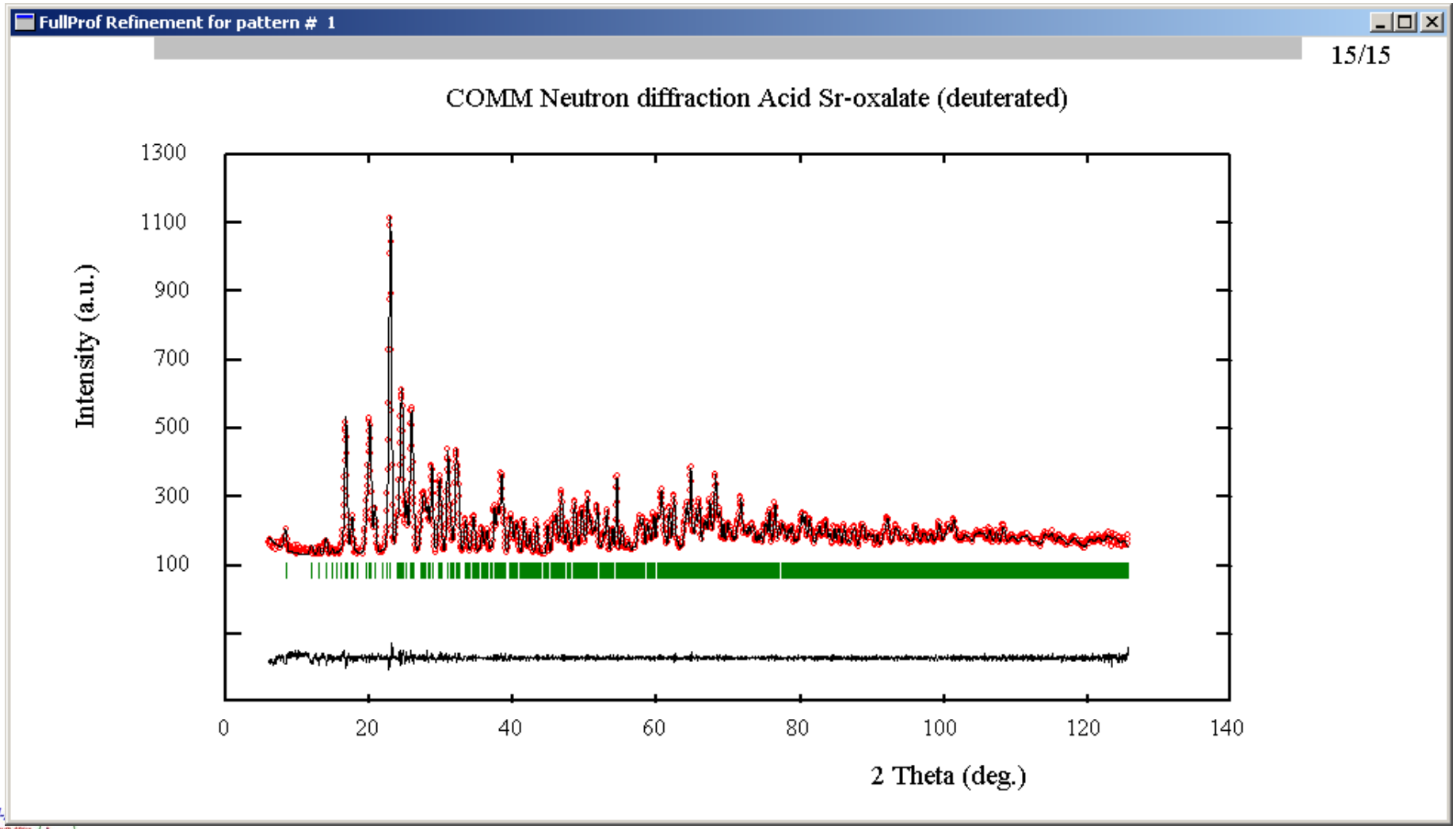
First cycle of Le Bail fit to extract integrated intensities for using Simulated Annealing within FullProf



Second cycle of Le Bail fit to extract integrated intensities for using Simulated Annealing within FullProf

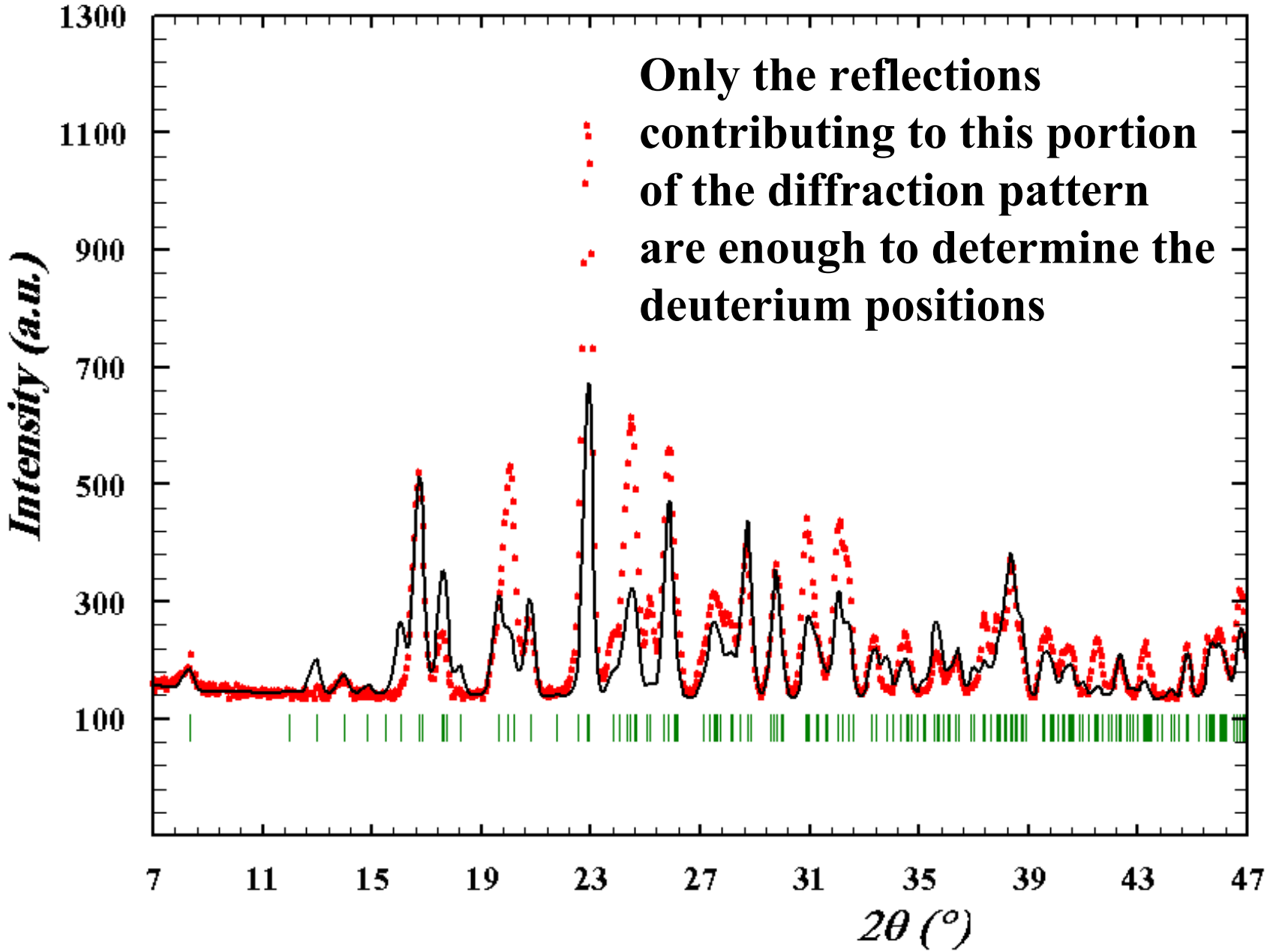


Final Le Bail fit to extract integrated intensities for using Simulated Annealing within FullProf



Intensity file generated after running FullProf with: Jbt=2, More=1, Jvi=11

```
 Phase No:    1 Sr/C/O/D                                  Overlaped reflections re-grouped
(3i4,2f12.2,i4,3f14.4)          <- Format of h,k,l, Int, sigma and non used items
  1.2251    0    2              <- Wavelength, type of data, powder indicator
   0    2    0        31.10        2.79    1         0.0000         0.0000         8.3325
   1    1    0        14.90        1.83    1         0.0000         0.0000        11.9580
   0    1    1        11.94        1.45    1         0.0000         0.0000        12.9544
   1    2    0        25.22        1.58    1         0.0000         0.0000        13.9794
   0    2    1         8.43        1.18    1         0.0000         0.0000        14.8430
  -1    0    1         2.81        0.63    1         0.0000         0.0000        15.4887
  -1    1    1         4.76        0.51    1         0.0000         0.0000        16.0452
   0    4    0        -1.00        1.94    1         0.0000         0.0000        16.7094
   1    3    0       201.31        2.04    1         0.0000         0.0000        16.8261
   0    3    1        -1.00        0.80    1   Negative intensity means that
  -1    2    1        -1.00        0.55    1   the reflection contributes to the
   1    0    1        51.67        0.97    1   next positive observation
   1    1    1         3.53        0.56    1         0.0000         0.0000        18.2075
   1    2    1        -1.00        1.00    1         0.0000         0.0000        19.6075
  -1    3    1        -1.00        1.14    1         0.0000         0.0000        19.9599
   1    4    0       261.17        1.99    1         0.0000         0.0000        20.1632
   0    4    1        62.57        1.26    1         0.0000         0.0000        20.7778
   1    3    1         1.30        0.19    1         0.0000         0.0000        21.7486
   2    0    0        -1.00        0.31    1         0.0000         0.0000        22.5185
  -1    4    1        -1.00        0.85    1         0.0000         0.0000        22.8597
   2    1    0       462.88        3.36    1         0.0000         0.0000        22.9101
  . . . . . .
```


Only the reflections contributing to this portion of the diffraction pattern are enough to determine the deuterium positions
Intensity (a.u.)
1300
1100
900
700
500
300
100
7
11
15
19
23
27
31
35
39
43
47
2θ (°)

How to prepare a Simulating Annealing PCR file?

```
COMM Neutron diffraction Acid Sr-oxalate (deuterated)
!Files => DAT-file: srox-sa,  PCR-file: srox-sa
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   0   1   0   0   0   0   0   0   0   0   0   0   9   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   0   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     5.0000    0.050000    124.900  0.000 0.000
!
!
      9    !Number of refined parameters
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     43.79
!-------------------------------------------------------------------------------
Sr/C/O/D
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
  14   0   0 0.0 0.0 1.0   0   4   0   0   0       966.691   0   5   0
. . . . . . . . .
```

How to prepare a Simulating Annealing PCR file?

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
  14   0   0 0.0 0.0 1.0   0   4   0   0   0        966.691    0   5   0
!
P 21/n                      <--Space group symbol
!Atom Typ        X         Y         Z      Biso       Occ      In Fin N_t Spc /Codes
Sr    SR      0.87930   0.41798   0.73560   1.55853   1.00000    0   0   0     0
                0.00      0.00      0.00      0.00      0.00
C1
C2
C3
O1    O       0.62200   0.22870   0.15700   1.24468   1.00000    0   0   0     0
                0.00      0.00      0.00      0.00      0.00
. . . . . . . . . . .
O7    O       0.69400   0.34880   0.32900   1.24468   1.00000    0   0   0     0
                0.00      0.00      0.00      0.00      0.00
H1    D       0.17449   0.26512   0.31765   2.00000   1.00000    0   0   0     0
                11.00     21.00     31.00     0.00      0.00
H2    D       0.41474   0.05317   0.39374   2.00000   1.00000    0   0   0     0
                41.00     51.00     61.00     0.00      0.00
H3    D       0.14942   0.30371   0.01023   2.00000   1.00000    0   0   0     0
                71.00     81.00     91.00     0.00      0.00
```

Put atoms to be localized in arbitrary general positions.
Avoid starting in special positions unless you want to look for atoms with some fixed coordinates.

How to prepare a Simulating Annealing PCR file?

No profile parameters,
part of the file similar to single crystal format

```
!  Scale Factors
!  Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
 0.3805E-01  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
    6.330226  16.863087    5.787093  90.000000  97.642853  90.000000
     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
```

How to prepare a Simulating Annealing PCR file?

Parameter number

Ranges and steps

Periodic boundary conditions

```
! Limits for selected parameters (+ steps & BoundCond for SA):
   1        0.0000        1.0000        0.0152    1        X_H1
   2        0.0000        1.0000        0.0073    1        Y_H1
   3        0.0000        1.0000        0.0264    1        Z_H1
   4        0.0000        1.0000        0.0279    1        X_H2
   5        0.0000        1.0000        0.0080    1        Y_H2
   6        0.0000        1.0000        0.0323    1        Z_H2
   7        0.0000        1.0000        0.0334    1        X_H3
   8        0.0000        1.0000        0.0087    1        Y_H3
   9        0.0000        1.0000        0.0346    1        Z_H3
! T_ini    Anneal   Accept NumTemps NumThCyc InitConf
   5.000    0.900    0.020       30        0        0
! NCyclM    Nsolu Num_Ref Nscalef  NAlgor
      80        1     106       1       0
```

Number of reflections to consider

Automatic treatment of the scale factor

Corana algorithm
Initial step = range

Random initial configuration

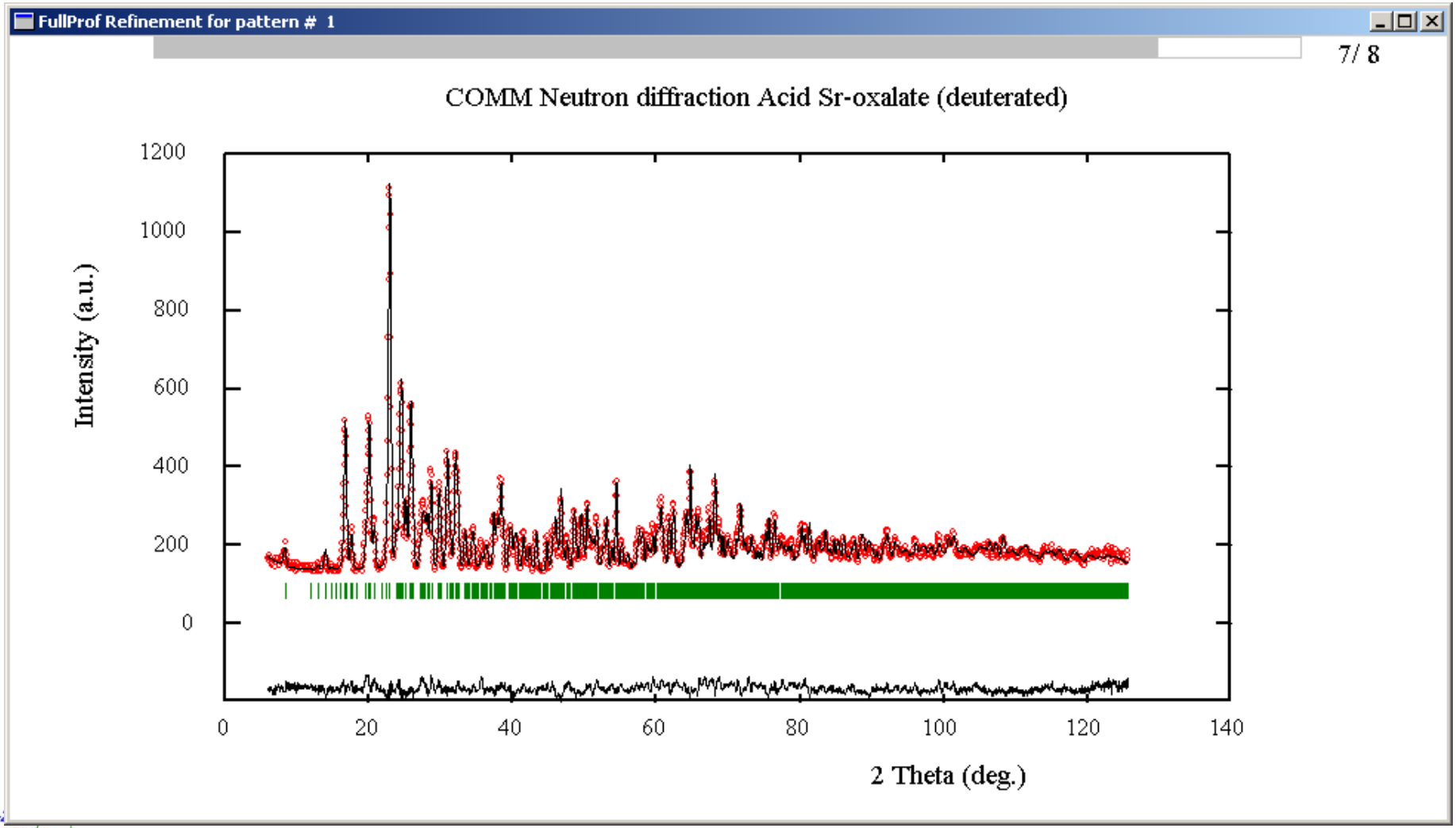
FullProf.2k_Multi_Pattern

```
=>  ************************************************************
=>  ** PROGRAM FullProf.2k (Version 2.45 - Jul2003-LLB JRC) **
=>  ************************************************************
=>                    M U L T I -- P A T T E R N
=>       Rietveld, Profile Matching & Integrated Intensity
=>           Refinement of X-ray and/or Neutron Data
=>              (Multi_Pattern: Windows-version)


=> START Date:24/08/2003  Time => 06:31:25.695
=> Reading control file *.PCR ...
=> End of preliminary calculations !

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

=> Initial configuration cost:     61.57
=> Initial configuration state vector:
=>       X_H1     Y_H1     Z_H1     X_H2     Y_H2     Z_H2     X_H3     Y_H3
=>          1        2        3        4        5        6        7        8
=>     0.5232   0.1764   0.4245   0.2939   0.0887   0.5922   0.7870   0.5707
=>       Z_H3
=>          9
=>     0.2306
=> NT:  1 Temp:  5.00 (%Acc): 54.03  <Step>:  1.0000  <R-factor>: 42.9005
=> NT:  2 Temp:  4.50 (%Acc): 49.44  <Step>:  1.0000  <R-factor>: 40.3423
=> NT:  3 Temp:  4.05 (%Acc): 45.56  <Step>:  0.9935  <R-factor>: 39.4462
=> NT:  4 Temp:  3.64 (%Acc): 40.69  <Step>:  0.9255  <R-factor>: 37.0873
=> NT:  5 Temp:  3.28 (%Acc): 29.31  <Step>:  0.8430  <R-factor>: 32.2989
=> NT:  6 Temp:  2.95 (%Acc): 29.58  <Step>:  0.6034  <R-factor>: 29.5616
=> NT:  7 Temp:  2.66 (%Acc): 29.86  <Step>:  0.4298  <R-factor>: 26.8966
=> NT:  8 Temp:  2.39 (%Acc): 34.44  <Step>:  0.2945  <R-factor>: 28.1128
=> NT:  9 Temp:  2.15 (%Acc): 34.86  <Step>:  0.2103  <R-factor>: 27.0234
=> NT: 10 Temp:  1.94 (%Acc): 39.03  <Step>:  0.1638  <R-factor>: 21.3639
=> NT: 11 Temp:  1.74 (%Acc): 37.64  <Step>:  0.1450  <R-factor>: 15.3967
=> NT: 12 Temp:  1.57 (%Acc): 47.64  <Step>:  0.1243  <R-factor>: 21.4095
=> NT: 13 Temp:  1.41 (%Acc): 45.56  <Step>:  0.1195  <R-factor>: 20.7147
=> NT: 14 Temp:  1.27 (%Acc): 43.61  <Step>:  0.1131  <R-factor>: 19.5571
=> NT: 15 Temp:  1.14 (%Acc): 40.42  <Step>:  0.1024  <R-factor>: 13.4736
=> NT: 16 Temp:  1.03 (%Acc): 44.03  <Step>:  0.0820  <R-factor>: 15.9547
=> NT: 17 Temp:  0.93 (%Acc): 41.11  <Step>:  0.0807  <R-factor>: 17.5574
=> NT: 18 Temp:  0.83 (%Acc): 38.89  <Step>:  0.0746  <R-factor>: 14.2276
=> NT: 19 Temp:  0.75 (%Acc): 41.81  <Step>:  0.0611  <R-factor>:  8.6454
=> NT: 20 Temp:  0.68 (%Acc): 40.97  <Step>:  0.0556  <R-factor>:  9.3925
=> NT: 21 Temp:  0.61 (%Acc): 41.53  <Step>:  0.0511  <R-factor>:  8.0336
=> NT: 22 Temp:  0.55 (%Acc): 45.83  <Step>:  0.0457  <R-factor>:  6.7858
=> NT: 23 Temp:  0.49 (%Acc): 38.75  <Step>:  0.0454  <R-factor>:  6.0588
=> NT: 24 Temp:  0.44 (%Acc): 38.75  <Step>:  0.0379  <R-factor>:  6.0212
=> NT: 25 Temp:  0.40 (%Acc): 43.06  <Step>:  0.0342  <R-factor>:  5.8380
=> NT: 26 Temp:  0.36 (%Acc): 45.14  <Step>:  0.0311  <R-factor>:  4.9175
=> NT: 27 Temp:  0.32 (%Acc): 40.97  <Step>:  0.0296  <R-factor>:  4.5611
=> NT: 28 Temp:  0.29 (%Acc): 42.64  <Step>:  0.0277  <R-factor>:  4.4117
=> NT: 29 Temp:  0.26 (%Acc): 38.06  <Step>:  0.0269  <R-factor>:  4.0134
=> NT: 30 Temp:  0.24 (%Acc): 42.22  <Step>:  0.0240  <R-factor>:  4.4226

=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   106 reflections):

=> Sol#:  1 RF2=   2.865 ::
=>       X_H1     Y_H1     Z_H1     X_H2     Y_H2     Z_H2     X_H3     Y_H3
=>          1        2        3        4        5        6        7        8
=>     0.2813   0.4253   0.4885   0.1542   0.2493   0.5134   0.6104   0.1026
=>       Z_H3
=>          9
=>     0.7935


=>              CPU Time:     49.401 seconds
=>                            0.823 minutes
```

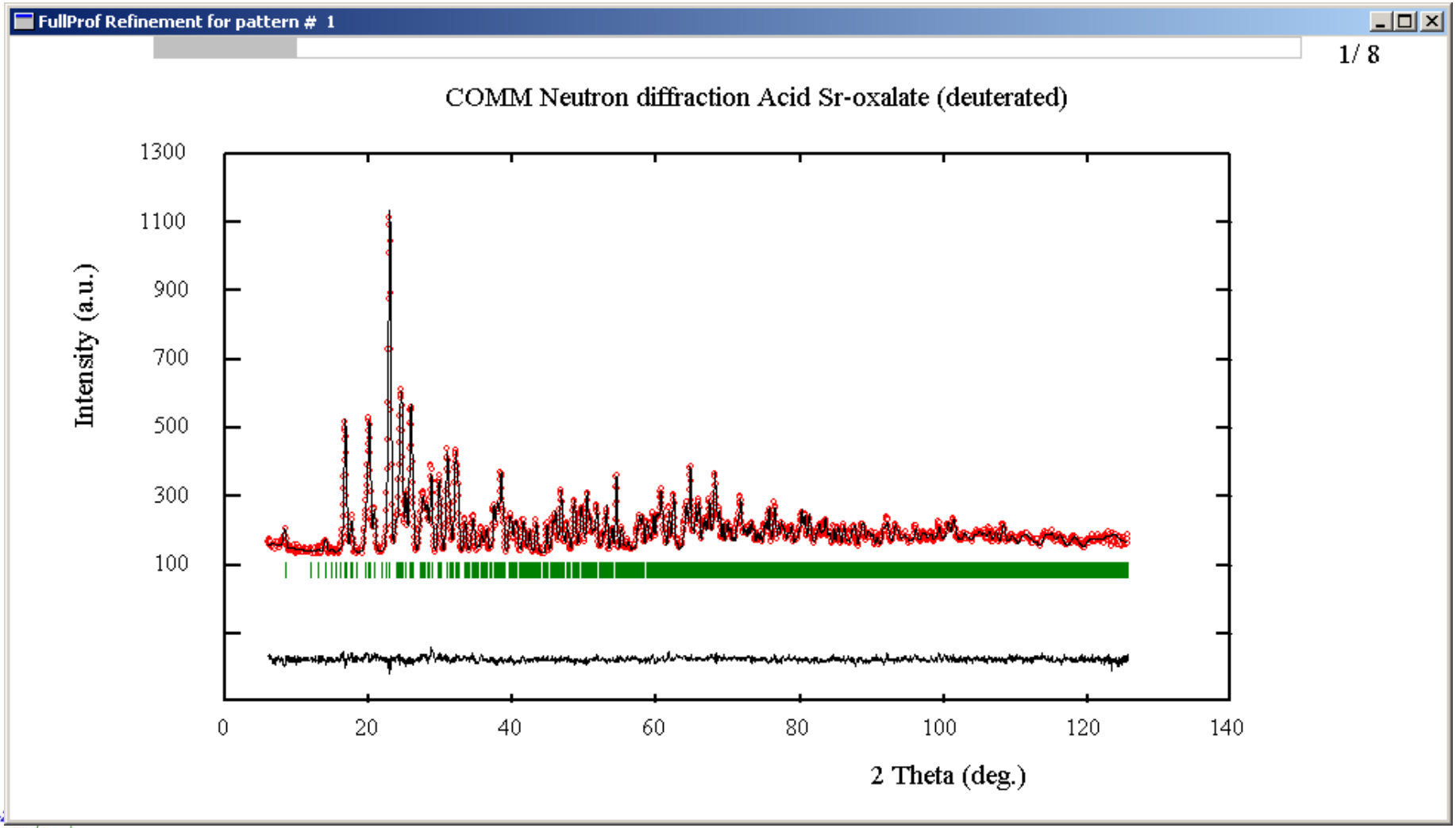
Example of Simulated Annealing run on acid Sr-oxalate

3 hydrogen atoms added to the asymmetric unit that can move freely in the whole unit cell

Refinement of the Simulated Annealing solution (only background and scale factor are refined)

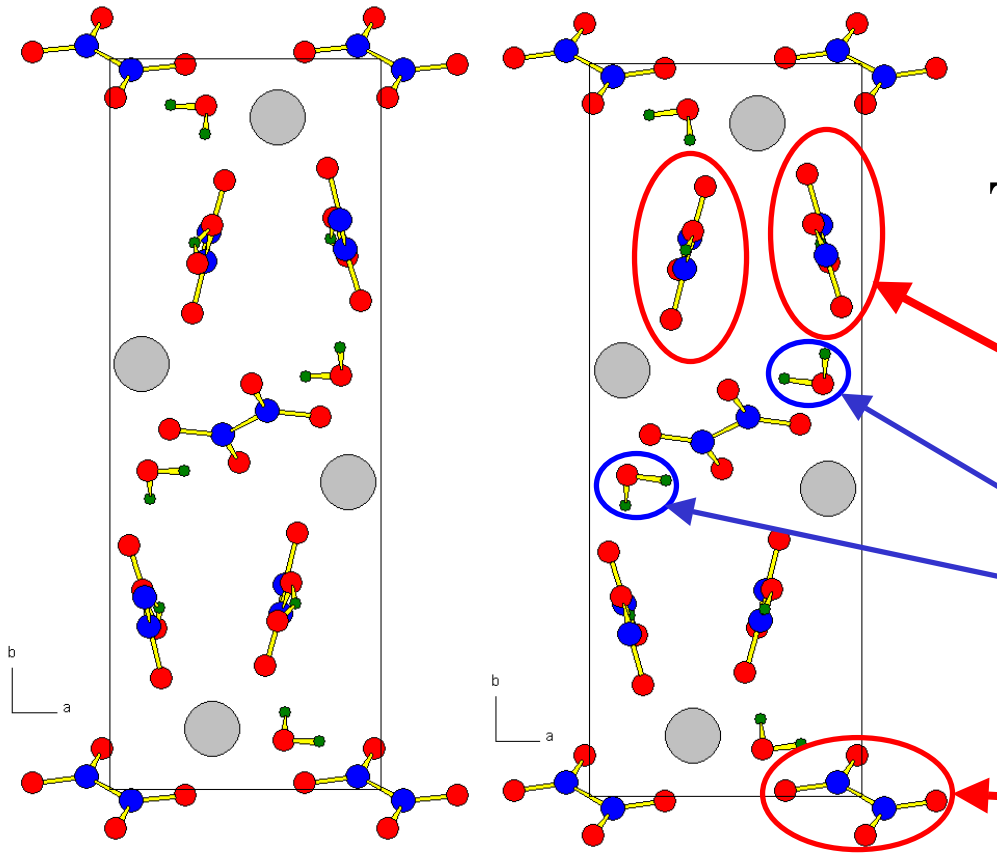


Final Refinement of the Simulated Annealing solution: all structural (56) and profile(19) parameters are refined)



Hydrogen atoms in acid strontium oxalate as determined by Simulated Annealing using FullProf

The chemical formula is $Sr(HC_2O_4).\ ½\ (C_2O_4)\ .\ H_2O$



As found Refined

Where are the hydrogen atoms?

Two types of oxalate groups

Chains along **c**

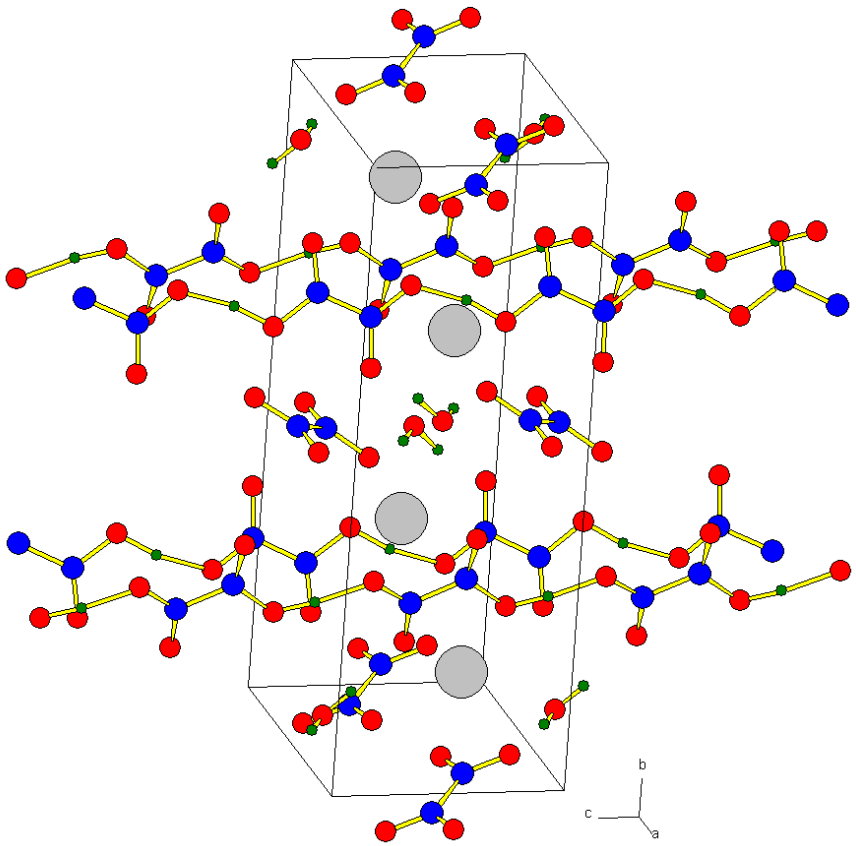
$C_2O_4 \cdots H \cdots C_2O_4 \cdots H \cdots$

And water molecules

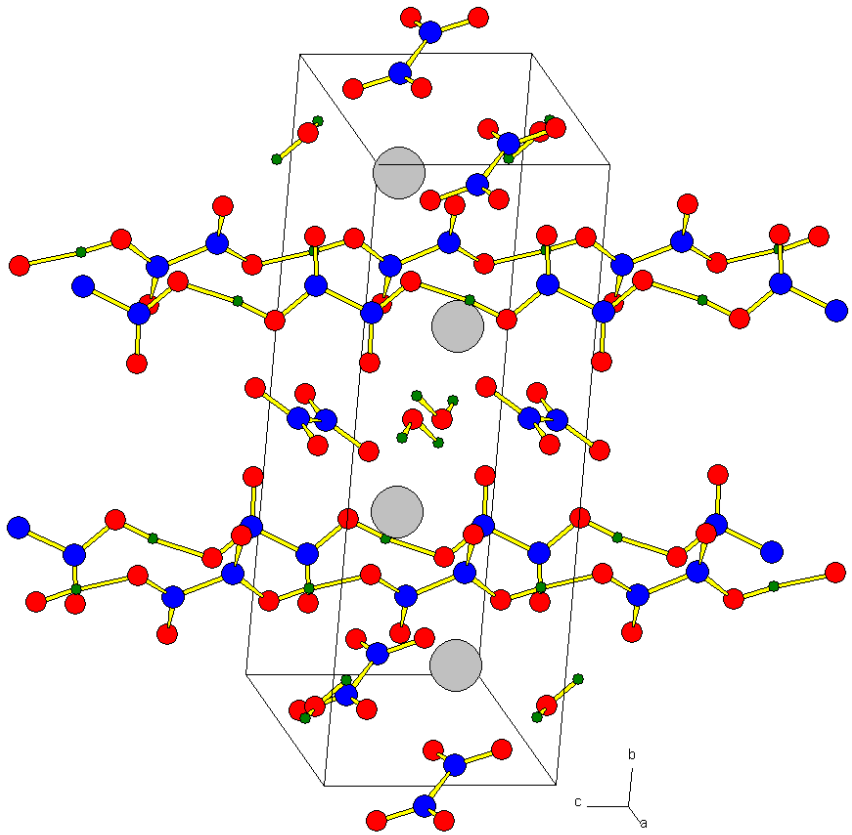
Isolated C_2O_4

Hydrogen atoms in acid strontium oxalate as determined by Simulated Annealing using FullProf

The chemical formula is $Sr(HC_2O_4).\ ½\ (C_2O_4).H_2O$

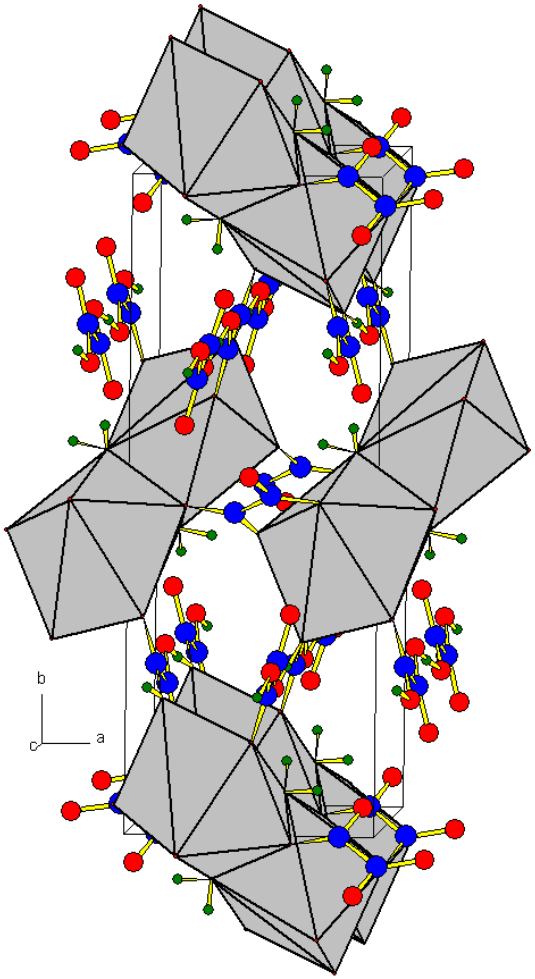


As found



Refined

Hydrogen atoms in acid strontium oxalate as determined by Simulated Annealing using FullProf



$Sr(HC_2O_4)$.½ $(C_2O_4).H_2O$

Sr is coordinated by oxygen atoms belonging to oxalate groups and water molecules

Chains along **c:** ··· C_2O_4 ··· H···C_2O_4 ··· H···

Water molecules

Isolated C_2O_4 (no hydrogen bonding)

The use of distances and angles restraints in *FullProf*

➔ **The calculation of distances and angles, as well as bond valence sums can now be done automatically, without using external programs.**

➔ **Output files with extension *dis* contain all the relevant information for the different phases if the user ask for this option.**

➔ **A byproduct of these calculations is the generation of the output files of names *dconstr*"n".*hlp* (n stands for the number of the phase) containing lines that can be directly pasted to PCR files for soft constraints on distances and angles.**

The use of distances and angles restraints in *FullProf*

Restrains: d(C-C) oxalate=1.5500 ±0.0002

First cycle:

```
=> Distance restraints:        Dobs      Dcalc   diff/sigma

    (C1    - C3   ):          1.55000   1.56618   -80.88648
    (C2    - C2   ):          1.55000   1.53215    89.24484
```

Second cycle:

```
    (C1    - C3   ):          1.55000   1.54243    37.82809
    (C2    - C2   ):          1.55000   1.56776   -88.77576
```

Third cycle:

```
    (C1    - C3   ):          1.55000   1.55625   -31.26800
    (C2    - C2   ):          1.55000   1.55001    -0.06020
```

Convergence at cycle 8:

```
    (C1    - C3   ):          1.55000   1.55004    -0.21458
    (C2    - C2   ):          1.55000   1.54999     0.06676
```

The use of distances and angles restraints in *FullProf*

No restrains

```
=> Global user-weighted Chi2 (Bragg contrib.):  2.35
=> Phase:  1
=> Bragg R-factor:  4.21        Vol:  612.268( 0.040)  Fract(%):  100.00( 0.91)
=> Rf-factor= 2.38              ATZ:         966.690   Brindley:  1.0000
```

Restrains: d(C-C) oxalate=1.5500 ±0.0002

```
=> Global user-weighted Chi2 (Bragg contrib.):  2.34
=> Phase:  1
=> Bragg R-factor:  4.22        Vol:  612.254( 0.040)  Fract(%):  100.00( 0.91)
=> Rf-factor= 2.43              ATZ:         966.690   Brindley:  1.0000
```

The use of linear restraints in *FullProf*

$$\sum_{i=1,\ldots n} a_i p_i = q \pm \sigma(q)$$

➔ If NLI > 0, the program expect to read at the end of the PCR file the following items:

NLI pairs of lines containing

First line:

Name of the restrain, number of coefficients (n), value(q), sigma

Second line:

Up to n pairs of: coefficient(a_i), parameter number of p_i.

The treatment of micro-structural effects in *FullProf*

Procedure for working with micro-structural effects in *FullProf*

- Characterise the IRF of the diffractometer using a calibrating sample
- Use WinPLOTR for creating an INSTRUMENTAL RESOLUTION FILE (Fit individual peaks through the pattern)
- Use *FullProf* with IRF putting to ZERO all FWHM parameters
- Select a model for microstructure and refine only the parameters related to the sample.
- The program generates a microstructural file and other files for plot

Modeling the Gaussian and Lorentzian components of the profile function in terms of anisotropic microstructural parameters

$$H_G^2 = (U + (1-\xi)^2 D_{ST}^2)\tan^2\theta + V\tan\theta + W + \frac{I_G}{\cos^2\theta}$$

$$H_L = (X + \xi D_{ST})\tan\theta + \frac{[Y + F(S_Z)]}{\cos\theta}$$

Anisotropic strain broadening

Phenomenological model: strains considered as fluctuations and correlation between metric parameters

J. Rodríguez-Carvajal *et al* (J. Phys. Cond. Matt. **3**, 3215 (1991)

$$M_{hkl} = \frac{1}{d_{hkl}^2} = M\left(\alpha_i ; hkl\right)$$

The metric parameters α_i (direct, reciprocal or any combination) are considered as stochastic variables with a Gaussian distribution characterized by :

- the mean $\langle \alpha_i \rangle$ and
- the variance-covariance matrix C_{ij}

The mean and the variance of the function M_{hkl} are given by (JRC *et al* , J. Phys. Cond. Matt. **3**, 3215 (1991) **):**

$$\langle M_{hkl} \rangle = M\left(\langle \alpha_i \rangle; hkl\right)$$

$$\sigma^2\left(M_{hkl}\right) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j}$$

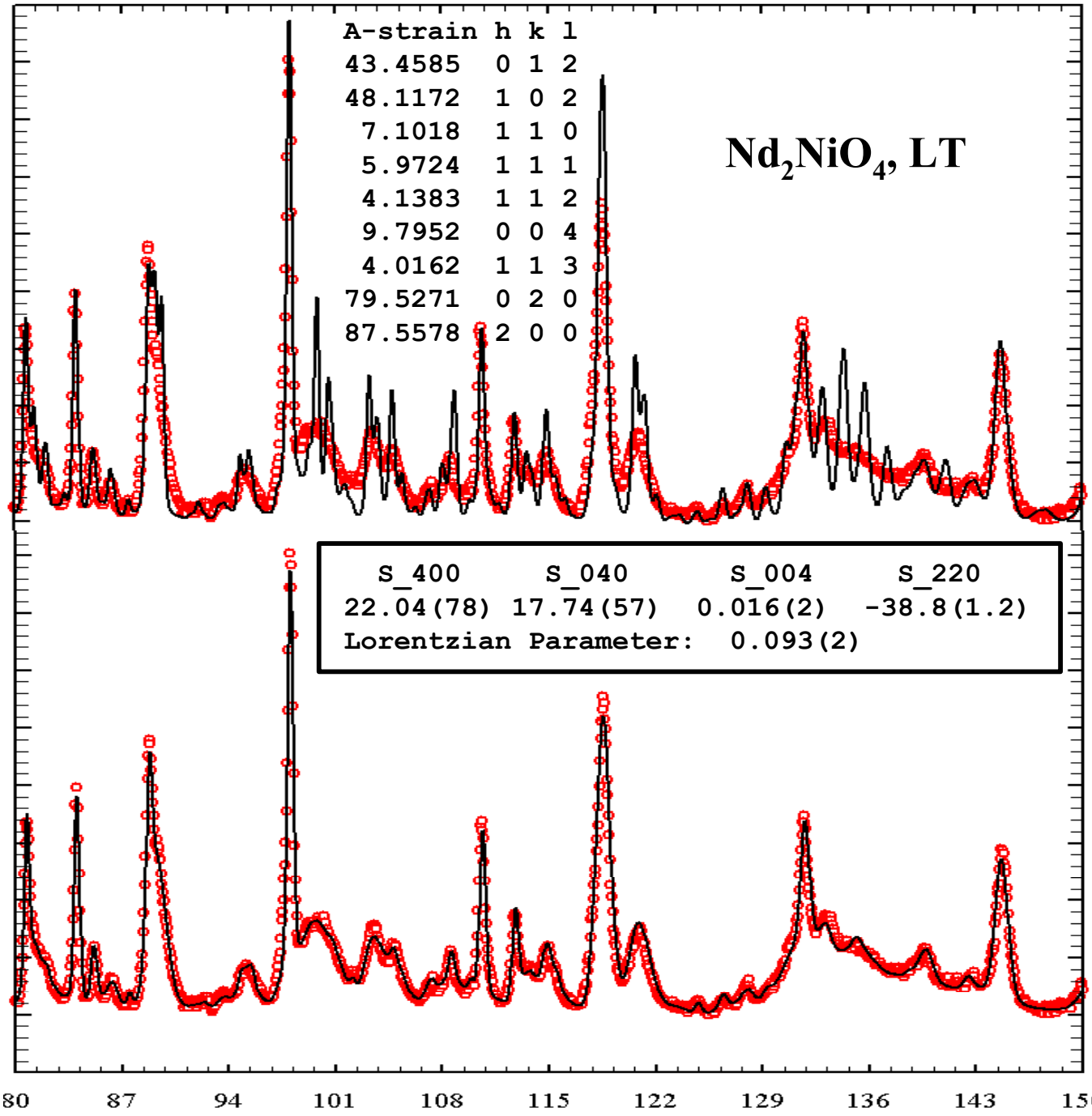
C_{ij} contains 21 parameters, 15 independent

If the metric parameters are taken as the coefficients of the quadratic form: $\frac{1}{d_{hkl}^2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk$

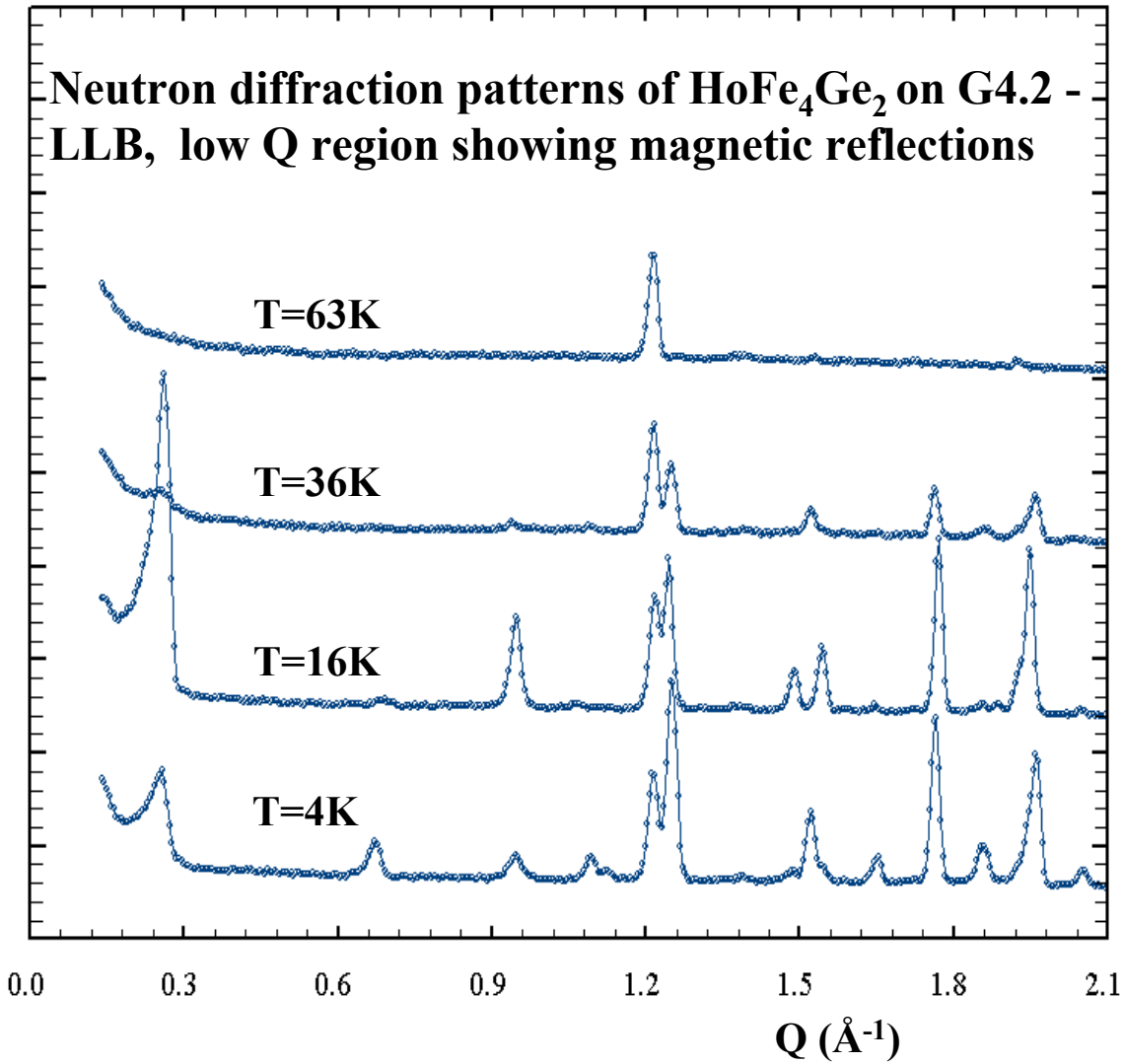
$$\{\alpha_i\} = \{A, B, C, D, E, F\}$$

$$\sigma^2\left(M_{hkl}\right) = \sum_{\substack{HKL \\ \{H+K+L=4\}}} S_{HKL} h^H k^K l^L$$

P. W. Stephens,
J. Appl. Cryst. 32, 281 (1999)

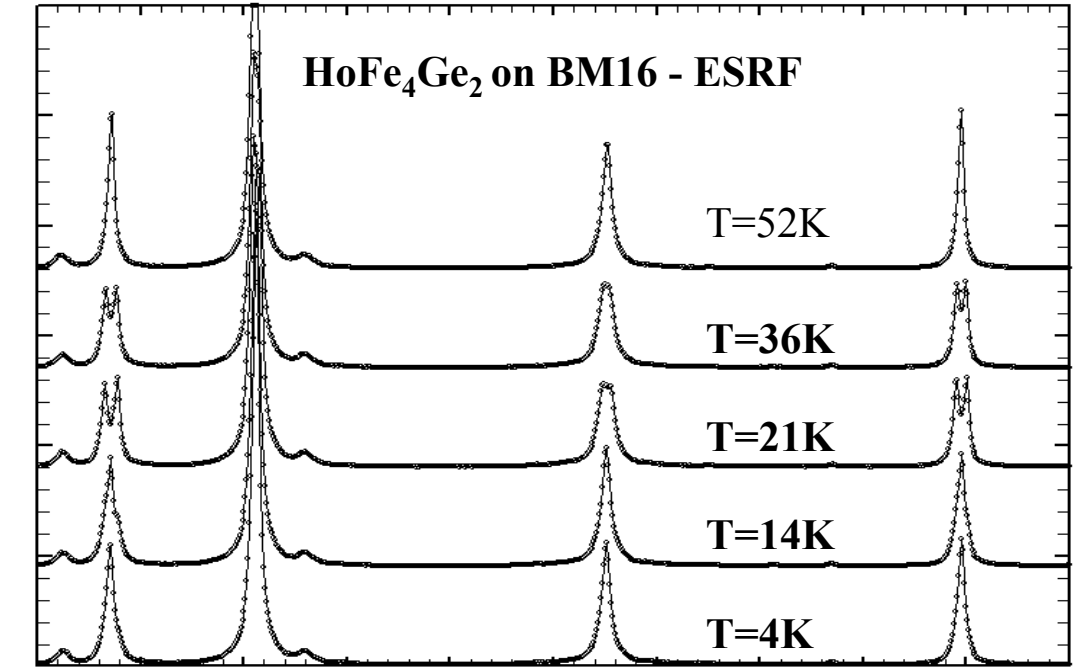

A-strain h k l
43.4585 0 1 2
48.1172 1 0 2
7.1018 1 1 0
5.9724 1 1 1
4.1383 1 1 2
9.7952 0 0 4
4.0162 1 1 3
79.5271 0 2 0
87.5578 2 0 0
Nd2NiO4, LT
S_400 S_040 S_004 S_220
22.04(78) 17.74(57) 0.016(2) -38.8(1.2)
Lorentzian Parameter: 0.093(2)
80 87 94 101 108 115 122 129 136 143 150
2θ (°)

Re-entrant transition in $HoFe_4Ge_2$

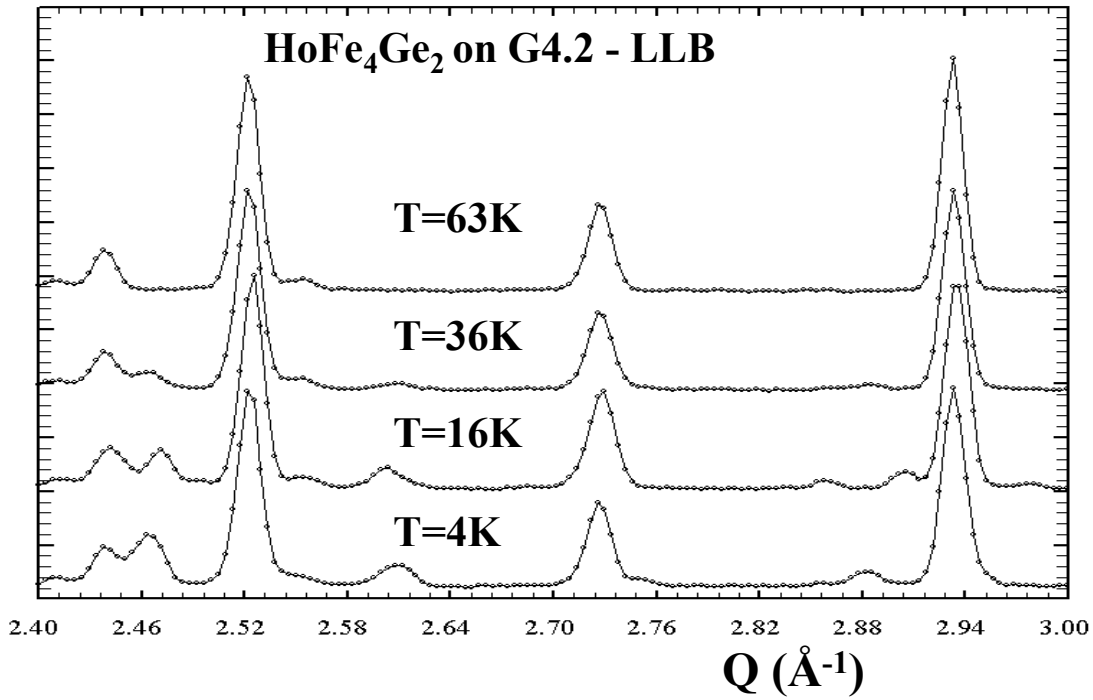


Re-entrant transition in $HoFe_4Ge_2$: RX-vs-N

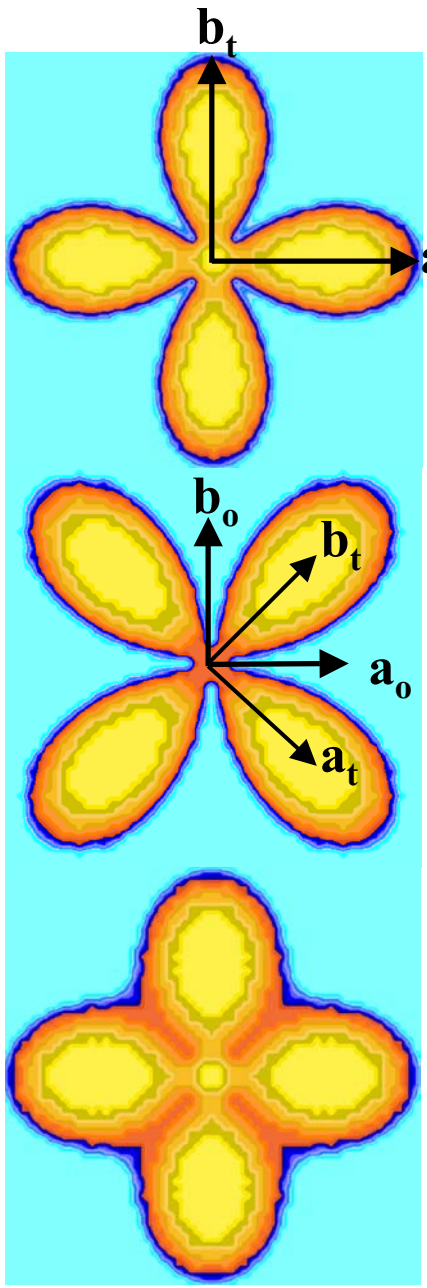
High resolution powder diffraction
X-ray Synchrotron radiation
In the diffraction patterns one can see the re-entrant transition



Neutron powder diffraction
The splitting of nuclear reflections is not seen
Only a subtle broadening can be appreciated by individual refinement of the reflections.
Extra reflections are of magnetic origin.



Microstrain patterns of $HoFe_4Ge_2$

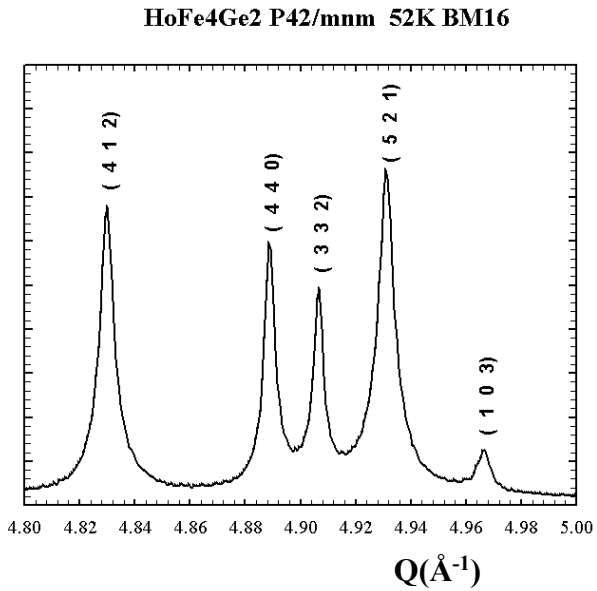


$P4_2/mnm$

Cmmm

$P4_2/mnm$

T=52K, *$P4_2/mnm$*



T=4 K, *Cmmm & $P4_2/mnm$*

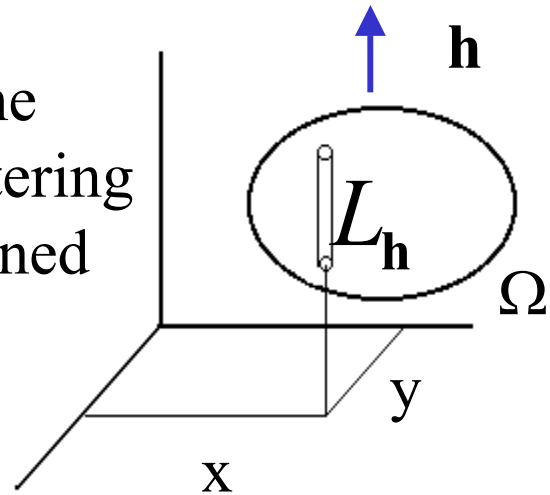
The patterns of microstrains can be visualized putting `Jvi=5` in the PCR file and reading the binary file with GFOURIER. Use projection mode.

Anisotropic broadening due to size effects

The intrinsic profile of a particular reflection due to size effect has an integral breadth β_S, the Scherrer formula:

$$\langle D \rangle_V = \frac{\lambda}{\beta_S \cos\theta} = \frac{1}{\beta_S^*}$$

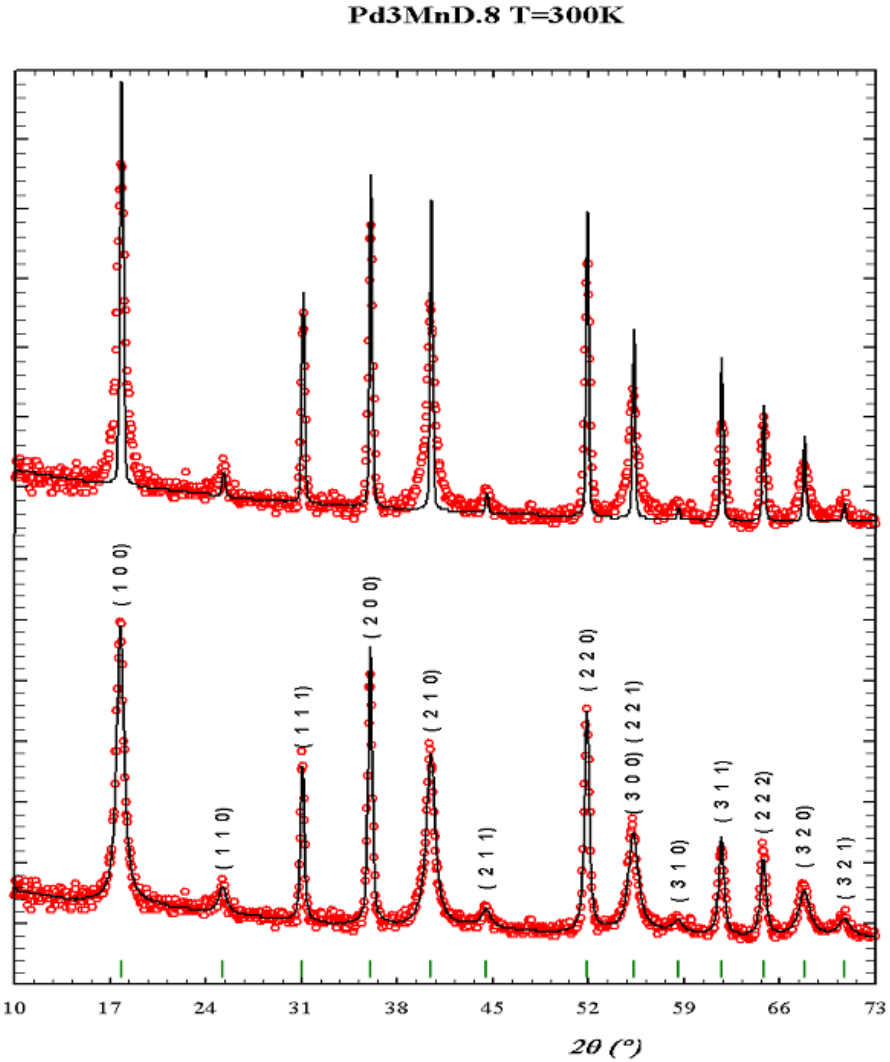
gives the volume-averaged apparent size of the crystallites in the direction normal to the scattering planes. This apparent size has a perfectly defined physical interpretation:



$$\langle D \rangle_V = \frac{1}{N} \sum_{i=1,\ldots N} \frac{1}{V_i} \iiint_{C_i} L_{\mathbf{h}}(x,y)\, d^3\mathbf{r}$$

in terms of the normalized column-length distribution $p_V(L)$:

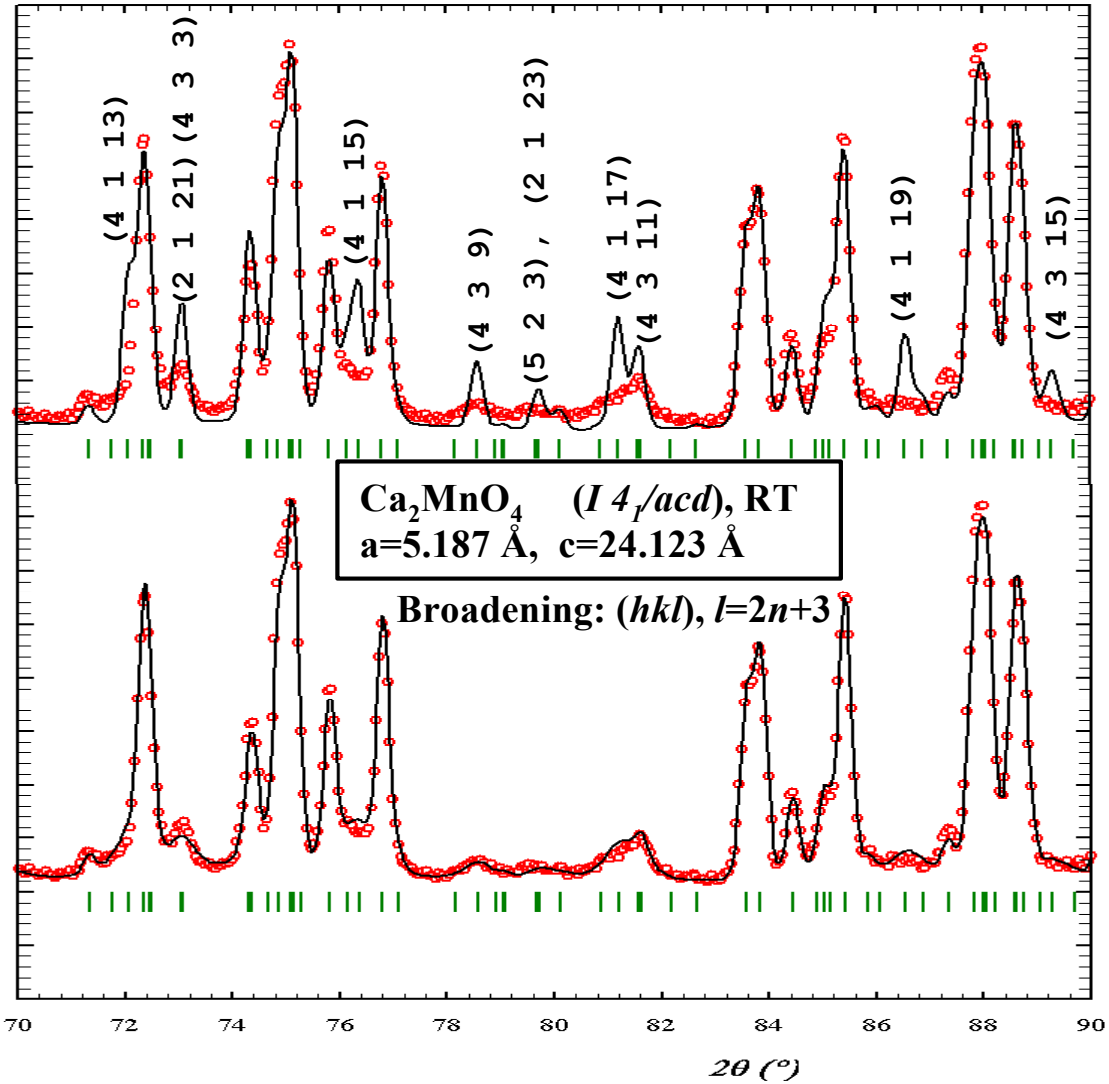
$$\langle D \rangle_V = \int_0^\infty L\ p_V(L) dL$$



Portion of the neutron diffraction pattern of $Pd_3MnD_{0.8}$ at room temperature obtained on 3T2 (LLB, $\lambda = 1.22$ Å). On top, the comparison with the calculated profile using the resolution function of the instrument. Below the fit using **`IsizeModel`** = -14. Notice that only the reflections with indices of different parity are strongly broadened.

```
!  MICRO-STRUCTURAL ANALYSIS FROM FULLPROF (still under development!)
!  ===================================================================
!  Pattern No:  1 Phase No:   1 Pd3MnD.8 - CFC
... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ...
!  Integral breadths are given in reciprocal lattice units (1/angstroms)x 1000
!  Apparent sizes are given in the same units as lambda (angstroms) …
!  Apparent strains are given in %% (x 10000) (Strain= 1/2 * beta * d)
!  An apparent size equal to 99999 means no size broadening
!  The following items are output:
... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ...
! The apparent sizes/strains are calculated for each reflection using the formula:
!
!  App-size (Angstroms) =  1/(Beta-size)
!  App-strain (%%) =  1/2 (Beta-strain) * d(hkl)
!
!  (Beta-size) is obtained from the size parameters contributing to the FWHM:
!          FWHM^2 (G-size) = Hgz^2 = IG/cos^2(theta)
!          FWHM   (L-size) = Hlz   = ( Y + F(Sz))/cos(theta)
!(Beta-strain) is obtained from the strain parameters contributing to the FWHM:
!          FWHM^2 (G-strain) = Hgs^2 =   = (U+[(1-z)DST]^2) tan^2(theta)
!          FWHM   (L-strain) = Hls   = (X+ z DST) tan(theta)
!
!   In both cases (H,eta) are calculated from TCH formula and then
!   Beta-pV is calculated from:
!
!            beta-pV= 0.5*H/( eta/pi+(1.0-eta)/sqrt(pi/Ln2))
!
!  The standard deviations appearing in the global average apparent size and
!  strain is calculated using the different reciprocal lattice directions.
!  It is a measure of the degree of anisotropy, not of the estimated error
```

...	betaG	betaL	...	App-size	App-strain	h	k	l	twtet	...
...	1.4817	11.5859	...	93.58	41.6395	1	0	0	17.7931	...
...	2.0954	11.9584	...	93.58	41.6395	1	1	0	25.2665	...
...	2.5664	1.5573	...	99999.00	41.6395	1	1	1	31.0743	...
...	2.9634	1.7982	...	99999.00	41.6395	2	0	0	36.0343	...
...	3.3132	12.6973	...	93.58	41.6395	2	1	0	40.4625	...
...	3.6294	12.8892	...	93.58	41.6395	2	1	1	44.5207	...
...	4.1909	2.5431	...	99999.00	41.6395	2	2	0	51.8786	...
...	4.4451	13.3842	...	93.58	41.6395	3	0	0	55.2849	...
...	4.4451	13.3842	...	93.58	41.6395	2	2	1	55.2850	...
...	4.6855	13.5301	...	93.58	41.6395	3	1	0	58.5562	...
...	4.9142	2.9820	...	99999.00	41.6395	3	1	1	61.7169	...
...	5.1327	3.1146	...	99999.00	41.6395	2	2	2	64.7864	...
...	5.3423	13.9286	...	93.58	41.6395	3	2	0	67.7802	...
...	5.5440	14.0510	...	93.58	41.6395	3	2	1	70.7114	...



Selective size broadening observed by neutron diffraction at room temperature (3T2, LLB) for superstructure reflections in Ca_2MnO_4. (top) Size parameter fixed to zero. (bottom) Single size parameter according to the rule (*hkl*), *l*=2*n*+3.

Spherical harmonics to simulate the average form of crystallites

An arbitrary shape of crystallites can be simulated using spherical harmonics. To access this option in FullProf one needs to select the variable **IsizeModel**= 15 to 22

$$\frac{1}{D_{\mathbf{h}}} = \sum_{lmp} a_{lmp} P_{lm}\left(\cos\Theta_{\mathbf{h}}\right)\begin{Bmatrix}\cos m\Phi_{\mathbf{h}} \\ \sin m\Phi_{\mathbf{h}}\end{Bmatrix}; \qquad p = +/-$$

$\left(\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}}\right)$: Polar angles of reciprocal vector **h** w.r.t. crystal frame

$$FWHM = \frac{k\lambda}{\cos\theta}\sum_{lmp} a_{lmp} P_{lm}\left(\cos\Theta_{\mathbf{h}}\right)\begin{Bmatrix}\cos m\Phi_{\mathbf{h}} \\ \sin m\Phi_{\mathbf{h}}\end{Bmatrix}$$

Spherical harmonic options for size broadening (Lorentzian)

```
ISizeModel = 15:  Monoclinic with unique b-axis up to 4th-order Ylm's:
                :  Y00,Y22+,Y22-,Y20,Y44+,Y44-,Y42+,Y42-,Y40
                :  Spacegroups 3-15 (Laue class 2/m)

ISizeModel = 16:  Trigonal with hexagonal setting, unique axis c
                :  Spacegroups 149-167(Laue class -3 m)
                :  Ylm's up to 6th order: Y00,Y20,Y40,Y43-,Y60,Y63-,Y66+

ISizeModel = 17:  Cubic - x,y,z along a,b and c.
                :  No restriction for spacegroups 195-206 (Laue class  m -3)
                :  For spacegroups 207-230 coefficient of K62=0 (Laue class  m -3 m)
                :  Cubic harmonics Klm's up to 8th order: K00,K41,K61,K62,K81

ISizeModel = 18:  Orthorhombic - Spacegroups 16-74 (Laue class mmm)
                :  Ylm's up to 4th order: Y00,Y20,Y22+,Y40,Y42+,Y44+

ISizeModel = 19:  Hexagonal - Spacegroups 168-194
                :  For spacegroups 177-194,coefficient of Y66=0 (Laue class 6/mmmm).
                :  No restriction for spacegroups 168-176 (Laue class 6/m )
                :  Spherical harmonics Ylm's up to 6th order: Y00,Y20,Y40,Y60,Y66+,Y66-

ISizeModel = 20:  Trigonal with hexagonal setting, unique axis c
                :  Spacegroups 143-148 (Laue class -3)
                :  Ylm's up to 4th order: Y00,Y20,Y40,Y43-,Y43+

ISizeModel = 21:  Tetragonal - Spacegroups 75-142
                :  For spacegroups 89-142 coefficients of Y44-=0, Y64=0 (Laue class 4/mmm)
                :  No restriction for spacegroups 75-88 (Laue class 4/m)
                :  Ylm's up to 6th order: Y00,Y20,Y40,Y44+,Y44-,Y60,Y64+,Y64-

ISizeModel = 22:  Triclinic
                :  Spacegroups 1-2 (Laue class -1)
                :  Ylm's up to 2th order: Y00,Y20,Y21+,Y21-,Y22+,Y22-
```

Example: Simulated data of anisotropic size effects using Spherical Harmonics (based in unpublished real data)

```
 Simulated data for an Al-oxide (ex. spherical harmonics)
! Current global Chi2 (Bragg contrib.) =      93.78
NPATT      1
W_PAT   1.000
!Nph Dum Ias Nre Cry Opt Aut
   1   0   0   0   0   0   1
!Job Npr Nba Nex Nsc Nor Iwg Ilo Res Ste Uni Cor
   0   7   0   1   0   1   0   0   1   0   0   0
!File names of data(patterns) files
siz-sph.dat
!
!  Resolution file for Pattern#   1
xray-res.irf
!Mat Pcr NLI Rpa Sym Sho
   0   1   0   0   1   1
!Ipr Ppl Ioc Ls1 Ls2 Ls3 Prf Ins Hkl Fou Ana
   0   0   1   0   4   0   3   0   0   0   0
  . . . . . . . . .
```

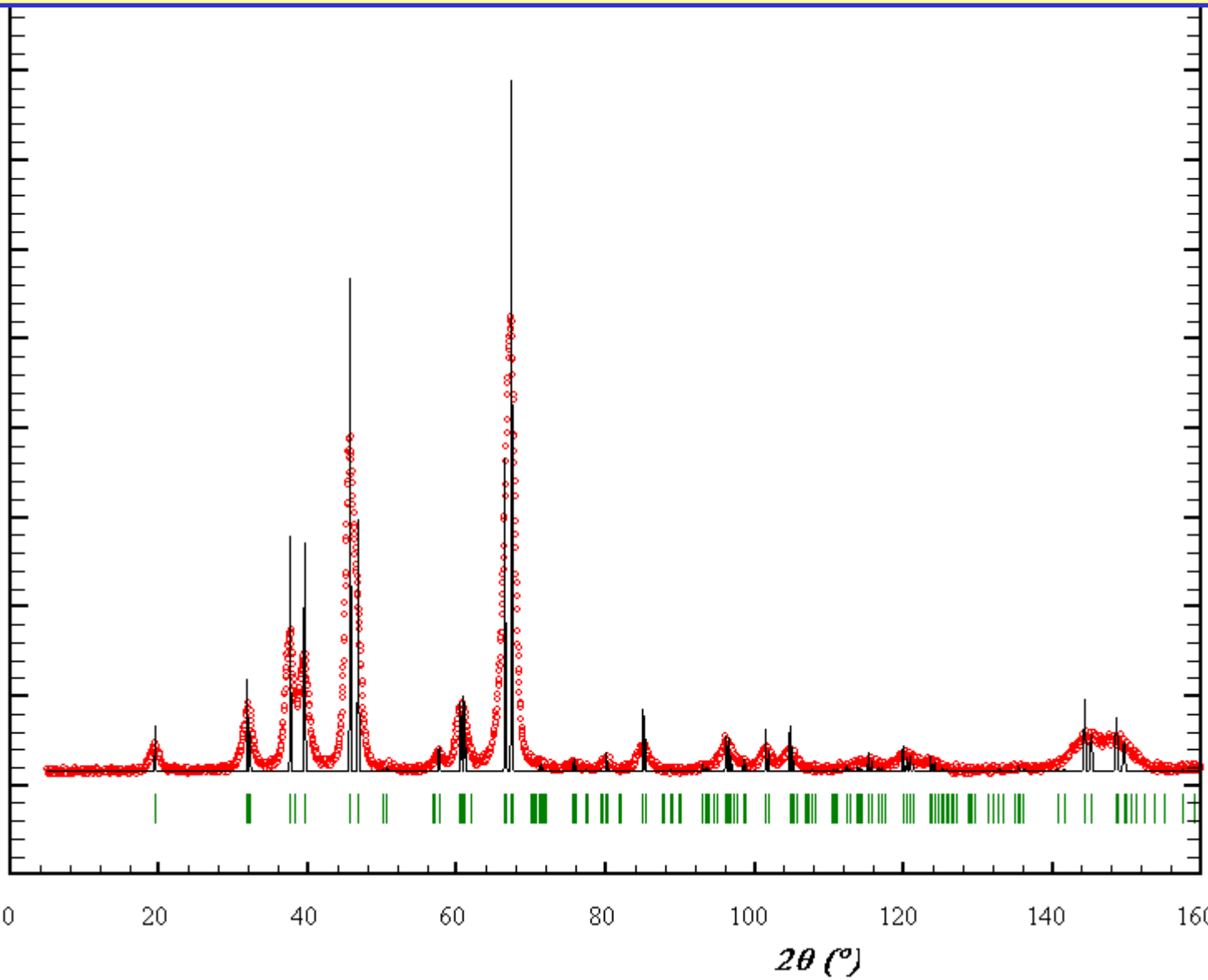
Simple example of a file containing the Instrumental Resolution Function in form a Caglioti-like parameters

This is the file: **xray-res.irf**

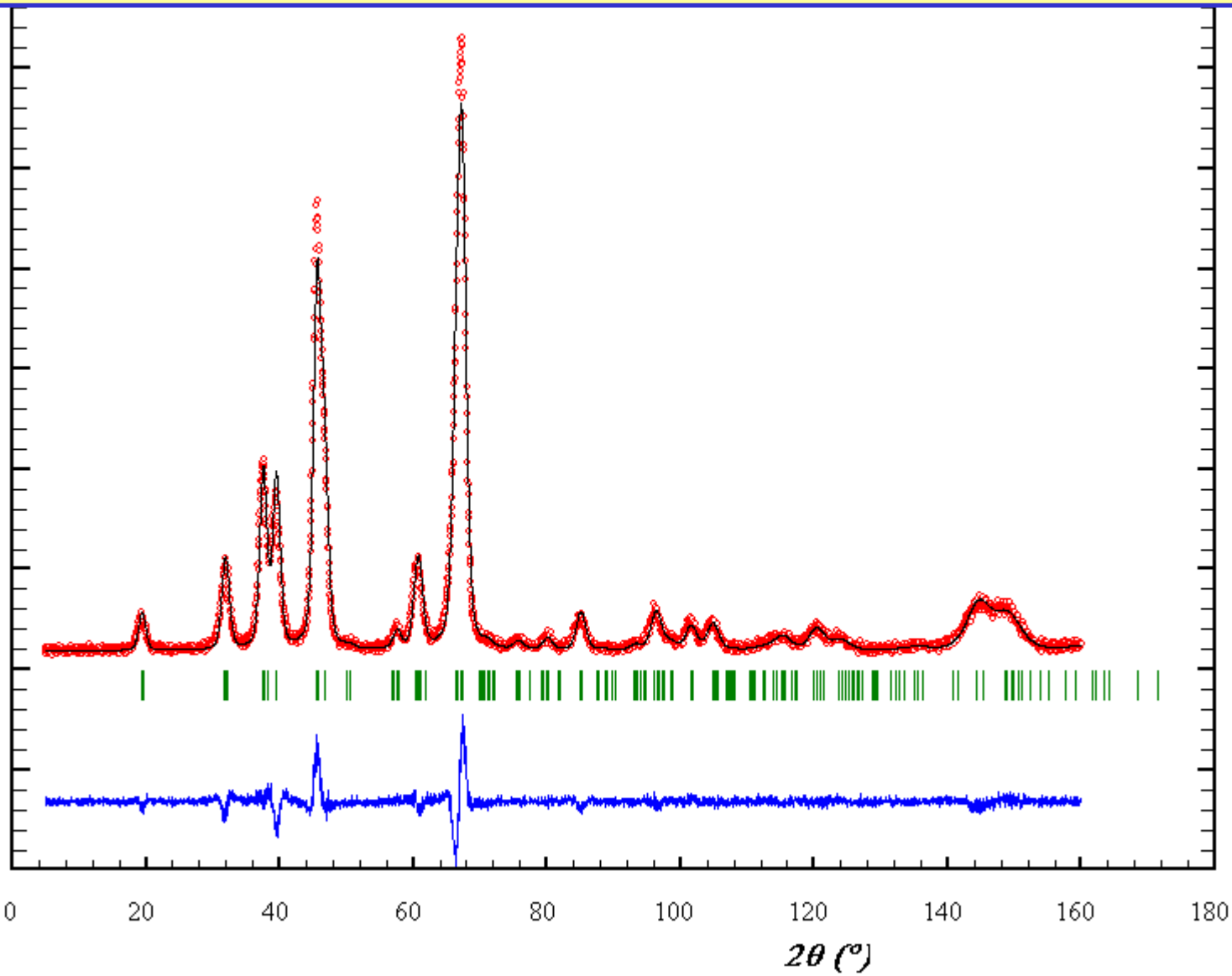
```
Approximate resolution function of a conventional
! X-ray diffractometer with CuKalpha1,2
!    Uins       Vins          Wins       Xins       Yins       Zins
   0.007621  -0.008895    0.010214    0.003352     0.0        0.0
   0.007621  -0.008895    0.010214    0.003352     0.0        0.0
```

Running the program without refining the profile parameters gives you an idea of the peak broadening

Comparison of the experimental pattern with the resolution function of the diffractometer



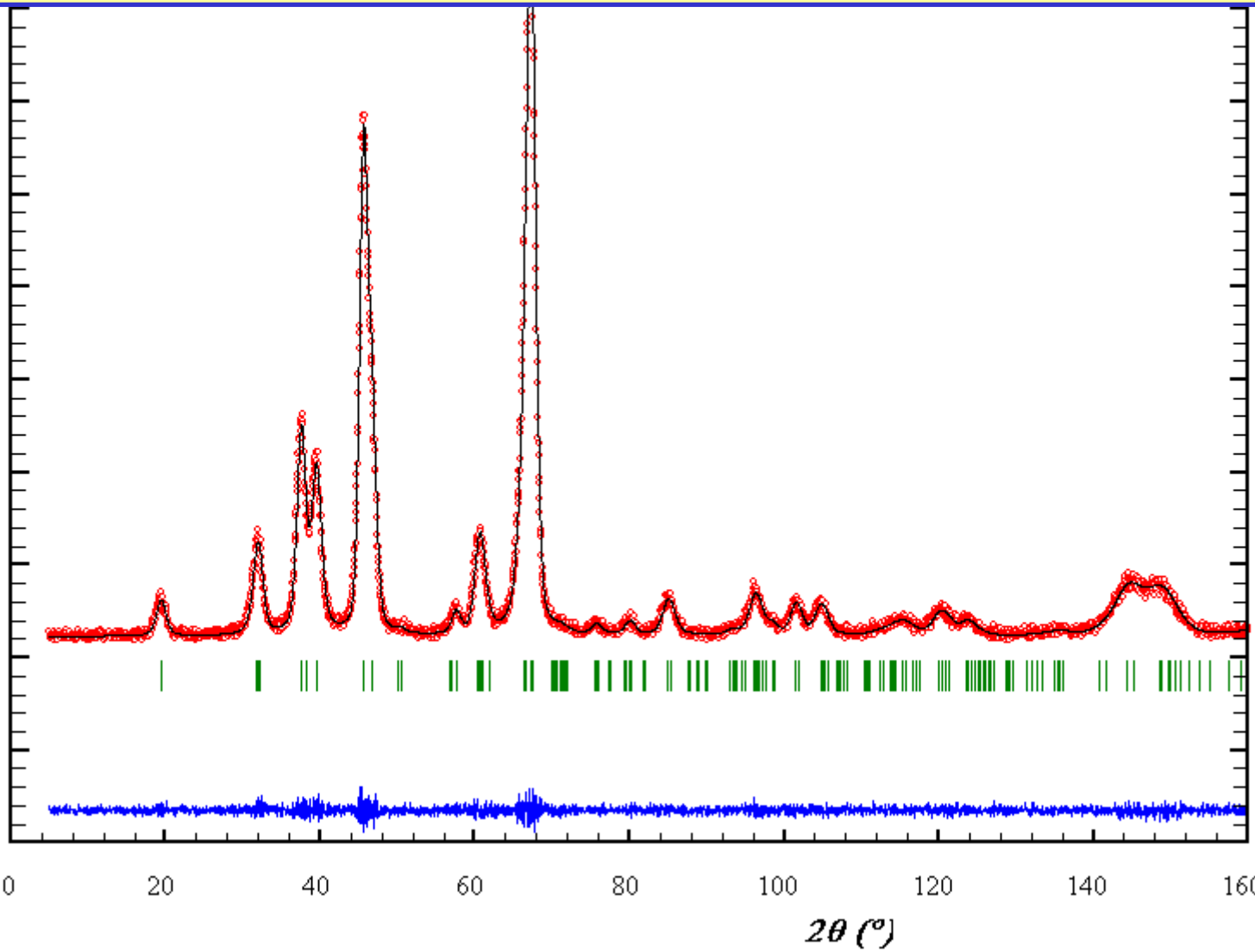
Refinement using isotropic Lorentzian and Gaussian parameters: Average crystallite size 58.3 Å



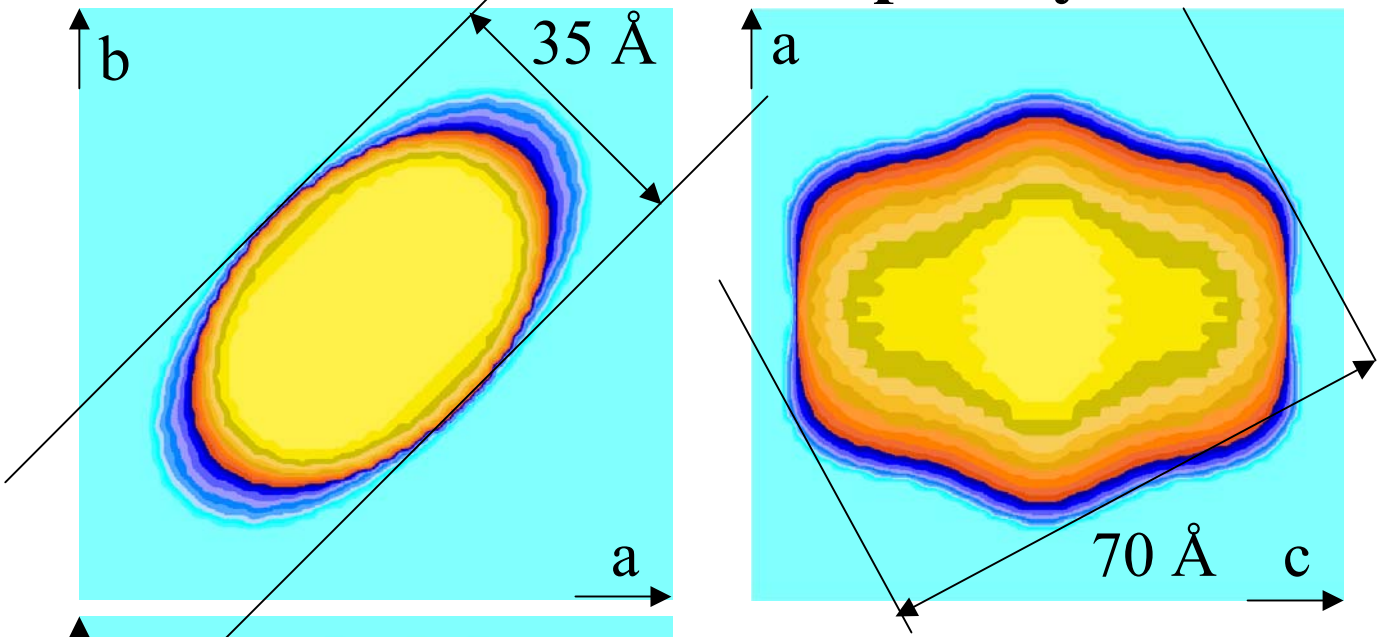
PCR-file treating anisotropic size effects using Spherical Harmonics

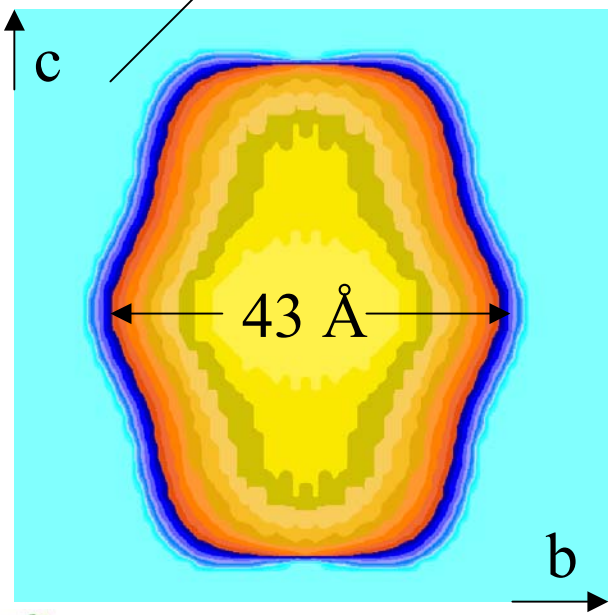
```
.................
I 41/a m d                  <--Space group symbol
!Atom Typ        X         Y         Z      Biso       Occ      In Fin N_t Spc /Codes
16h  o-2      0.00000   0.02789   0.25409   1.88354   0.50000    0   0   0     0
                0.00      0.00      0.00      0.00      0.00
. . . . . . . . . . . . . . . . . . . . .
16g  al+3     0.21293   0.46293   0.87500   0.66821   0.11416    0   0   0     0
                0.00      0.00      0.00      0.00      0.00
!-------> Profile Parameters for Pattern #  1
!  Scale          Shape1       Bov        Str1       Str2       Str3    Strain-Model
 0.15556E-01    0.00000    0.00000    0.00000    0.00000    0.00000         0
    11.00000      0.000      0.000      0.000      0.000      0.000
!       U          V          W          X          Y        GauSiz    LorSiz Size-Model
   0.000000   0.000000   0.000000   0.000000   0.000000   0.905546   0.000000   21
      0.000      0.000      0.000      0.000      0.000    101.000      0.000
!     a          b          c        alpha      beta       gamma
   5.627625   5.627625   7.782376  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
  1.00000   0.00000   0.00096   0.00144   0.00000   0.00000   0.02907   0.02907
     0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00
!   Y00         Y20         Y40         Y44+        Y44-        Y60
  11.372407  -5.957819  -0.839027   2.933409   0.000000   3.458423
      51.00      61.00      71.00      81.00       0.00      91.00
!   Y64+        Y64-+
   0.000000   0.000000
       0.00       0.00
```

Refinement using isotropic Lorentzian and Gaussian parameters: Average crystallite size (anisotropy): 56.31 (7.74)

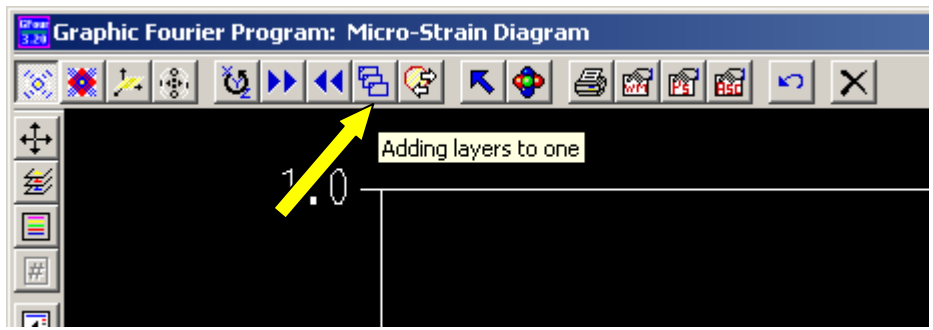


Anisotropic crystallite size

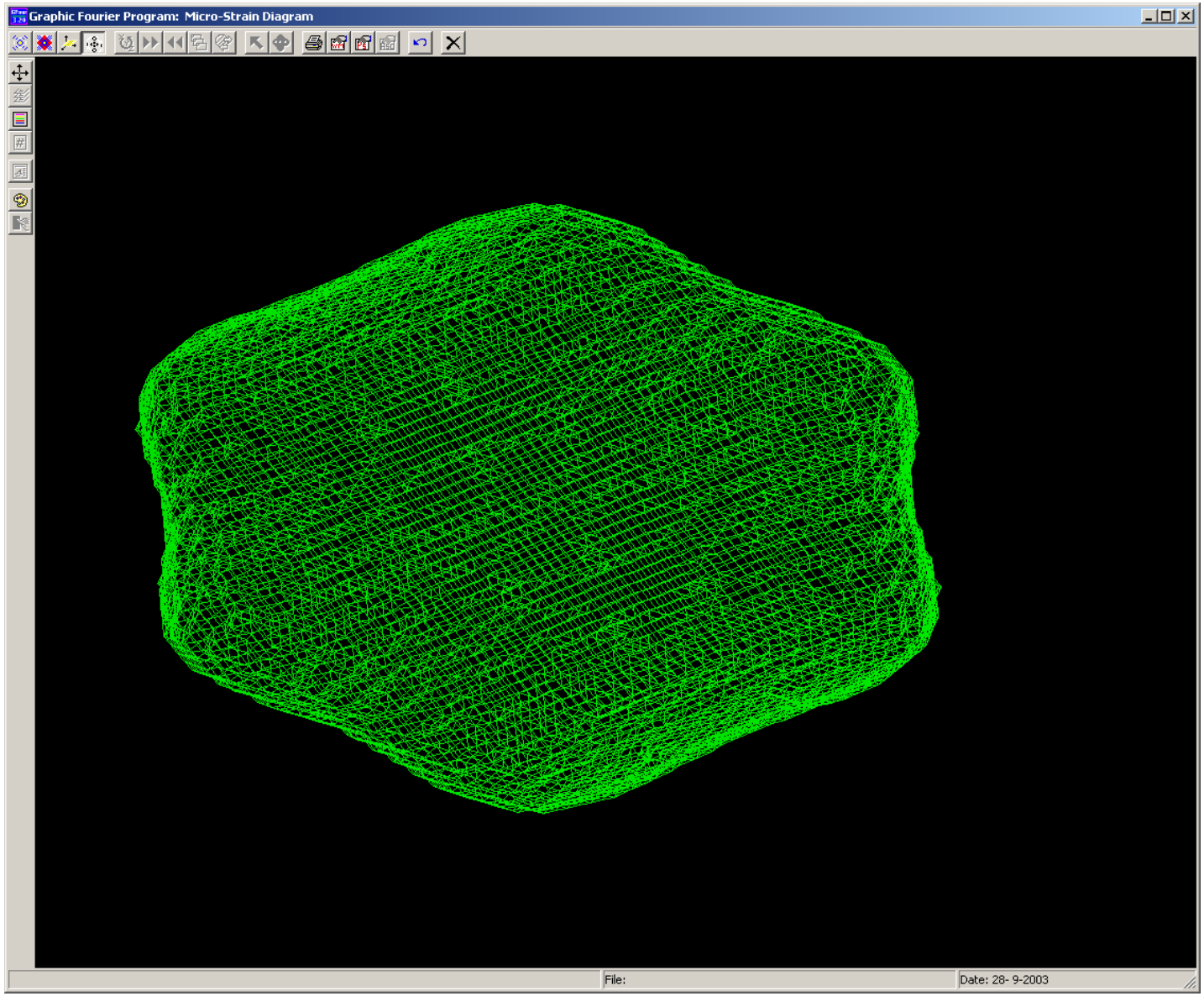




The visualization of the average crystallite shape is done by using **GFOURIER** to read the binary file: **myPCR_size_n.bin** generated when an IRF file is used and **Jvi=5**



3D visualization of the average crystallite shape



New option to relax some profile parameters of special reflections

This option works with Constant Wavelength and Time of Flight diffraction patterns.

The user may select few reflections from the pattern to treat them in a special manner: an additional Gaussian and Lorentzian broadening with respect to the values calculated with the resolution parameters, as well as the shift with respect to the calculated position (from cell parameters) can be fitted.

This situation may be found in cases of defective materials for which the law governing the shifts and broadening is not known in advance, or in cases of instrumental defects (slight change of wavelength across the pattern, etc).

At present 50 reflections per phase and per pattern is the maximum allowed.

New option to relax some profile parameters of special reflections

The program expect to read a list Nspec_ref lines containing:

`h k l nvk D-HG^2 Cod_D-HG^2 D-HL Cod_D-HL Shift Cod_Shift`

The list starts at the end of the profile parameters for a given pattern.

The Gaussian `FWHM^2` for a special reflections is calculated as:

```
FWHM^2 =  FWHM^2(resolution parameters) + D-HG^2      (CW)
Sigma^2= Sigma^2(resolution parameters) + D-HG^2      (TOF)
```

`D-HG^2` is treated as a free parameter.

The Lorentzian `FWHM` for a special reflections is calculated as:

```
FWHM =  FWHM(resolution parameters) + D-HL      (CW)
Gamma = Gamma(resolution parameters) + D-HL     (TOF)
```

`D-HL` is treated as a free parameter.

The position of a special reflections is calculated as:

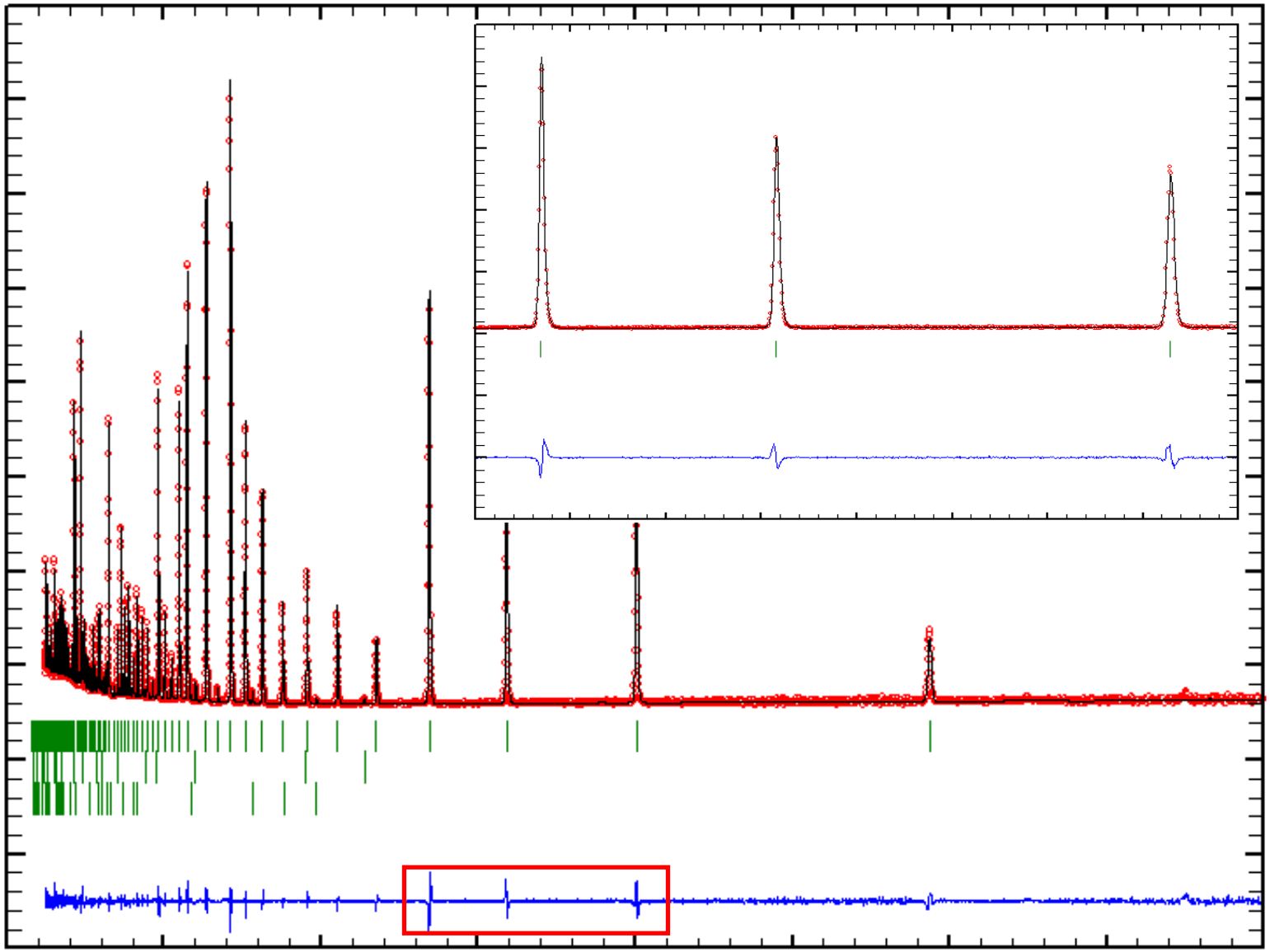
```
2Theta(degrees) =  2Theta(cell parameters,zero,etc.)        + Shift
TOF(micro-scnds) = TOF(cell parameters,zero,dtt1,dtt2,etc.) + Shift
```

`Shift` is treated as a free parameter.

New option to relax some profile parameters of special reflections (Example)

```
!-------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern# 1:  1.06
!-------------------------------------------------------------------------
 Myphase
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
   6   0   0 0.0 0.0 1.0   0   0   0   0   0     5050.20    0   7   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind    RMua     RMub     RMuc    Jtyp  Nsp_Ref
   0   0   0   0   0   0  1.0000  0.0000   0.0000   0.0000    1    3
!
P 3 1 c                  <--Space group symbol
. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
!  Pref1    Pref2      Asy1     Asy2     Asy3     Asy4      S_L      D_L
  0.00000  0.00000   0.07373  0.01902  0.00000  0.00000  0.00000  0.00000
     0.00     0.00    251.00   241.00     0.00     0.00     0.00     0.00
! Special reflections:
!  h   k   l  nvk   D-HG^2    Cod_D-HG^2  D-HL    Cod_D-HL    Shift   Cod_Shift
   1   0   1    0  0.00000       0.000  0.04417   551.000  -0.01236    561.000
   2   0   0    0  0.00000       0.000  0.03056   571.000  -0.00274    581.000
   3   0   1    0  0.00000       0.000  0.00759   591.000  -0.00119    601.000
```

$Na_2Ca_3Al_2F_{14}$: shifts of peaks due to complex T.O.F. versus d-spacing



$Na_2Ca_3Al_2F_{14}$: shifts of peaks due to complex T.O.F. versus d-spacing. Effect of relaxing some peak positions