Determination of magnetic structure of $Cu_{1+x}Mn_xO_2$ from time-of-flight data using FullProf Suite

Ovi Garlea
Neutron Scattering Division, ORNL

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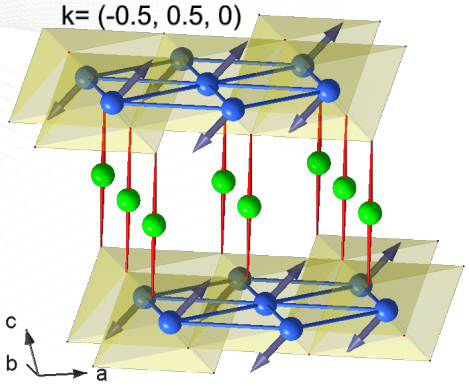
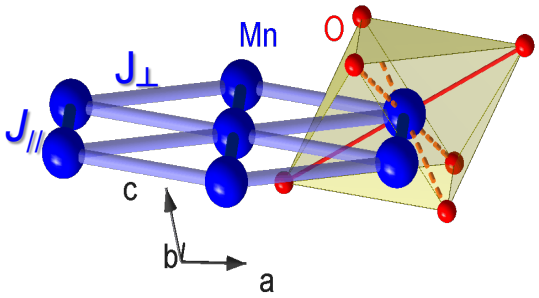
$Cu(Mn_{1-x}Cu_x)O_2$ "Crednerite" : Anisotropic Triangular Lattice

Jahn-Teller distortion of $Mn^{3+}O_6$ ($3d^4$, S=2) ($t_{2g}^3 e_g^1$) Ferro-orbital ordering $d_{3r^2-z^2}$



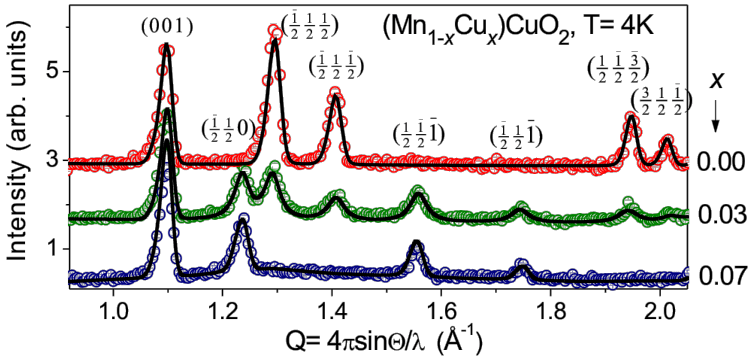


$Cu_{1.07}Mn_{0.93}O_2$

Monoclinic (C2/*m*)

(5.576 Å, 2.880 Å, 5.892 Å
90°, 103.967°, 90°)

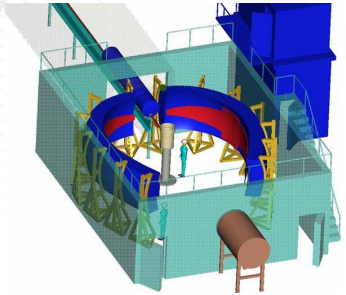
$T_N \approx 65$ K k=(-½, ½, 0)



Doumerc, et al. Eur. J. Solid State Inorg. Chem. 31, 705 (1994)
Trari, et al. J. Solid State Chem. 178, 2751 (2005)
Damay, et al. Phys. Rev. B 80, 094410 (2009)
Vecchini, C. et al. Phys. Rev. B 82, 094404 (2010)
Poienar, et al. Chem. Mater. 23, 85 (2011)
Garlea, Phys. Rev. B 83, 172407 (2011)
Terada, Phys. Rev. B 84, 064432 (2011)
Ushakov, et al. Phys. Rev. B 89, 024406 (2014)

Time-of-flight powder diffraction data from POWGEN

http://neutrons.ornl.gov/powgen



WL center	dmin	dmax	BANK
0.533	0.0000	3.5055	1
1.066	0.2760	5.2582	2
1.333	0.4142	6.1363	3
2.665	1.1038	10.5165	4
3.731	1.6557	14.0220	5

$\lambda = h/mv = ht/mL \rightarrow t_{hkl} \approx \text{const} \cdot L d_{hkl} \sin\theta$

$$T_h = Z_0 + D_1 d_h + D_2 d_h^2$$

Resolution: $\Delta d/d = [(\Delta t/t)^2 + (\Delta L/L)^2 + (\Delta\theta)^2 \cot^2\theta]^{1/2}$

The peak shape for is a convolution of a pseudo-Voigt function with a pair of back-to-back exponentials:

$$\Omega(x) = pV(x) \otimes E(x) = \int_{-\infty}^{+\infty} pV(x-t)E(t)dt$$

Provided files for this tutorial:

- Neutron powder diffraction data (POWGEN) data files measured at 100 K and 9 K with "banks" 2 and 4 (structured in XYSIGMA format):
  PG3_20292-2_100K.dat ; PG3_20274-2_9K.dat
  PG3_20292-4_100K.dat ; PG3_20275-4_9K.dat

- Instrument resolution files:
  2014A_P3_HR60b4_BtB.irf
  2014A_P3_HR60b2_BtB.irf

- CIF files for crystal structure:
  CuMnO2.cif

- Supporting information:
  TOF_FullProf.pdf;
  MnCuO2-PRB-2011.pdf

Exercise Steps:

I. Visualize the data measured at the two temperatures (100 K and 9 K) , for the two configurations (Bank 2 & 4)

II. Import the known crystal structure/instrument parameters to create a PCR file for a single set of data (Bank 4 at T = 9 K)

III. Refine the structural model and the profile parameters

IV. Identify the magnetic reflections and determine the propagation vector (k-search in Winplotr)

V. Perform symmetry analysis to obtained IRs and Basis vectors (using *SARAh or BasIreps*)

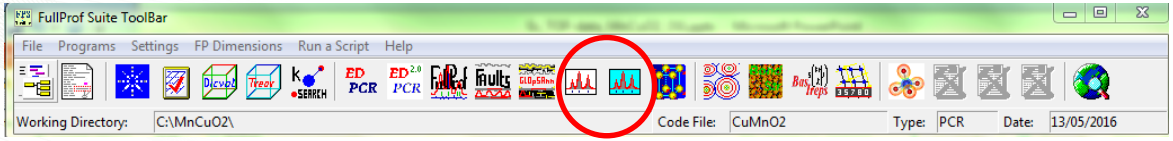
VI. Select a magnetic model and add it as a second phase (magnetic phase) to the existing PCR file

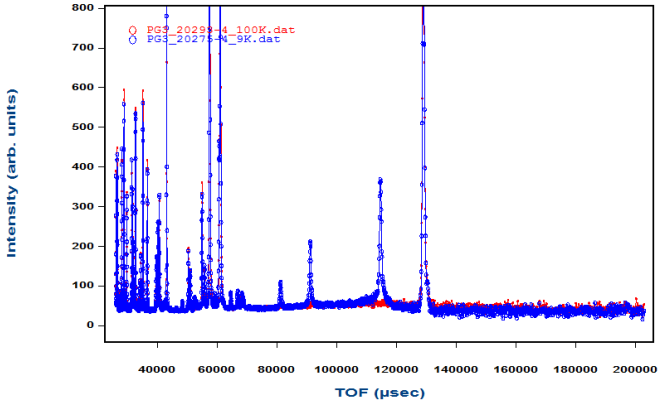
VII. Perform refinement for the magnetic phase

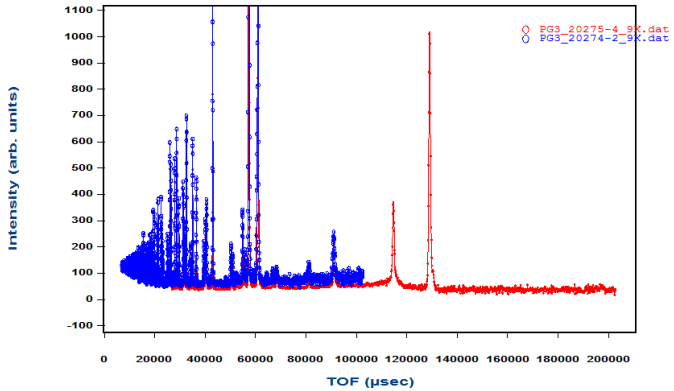
VIII. Display the magnetic structure using *FpStudio or Vesta*

IX. Adding a second data set (Bank 2) to the refinement (reformatting the PCR file for multiple data sets)

I. Observe the differences in the data measured at 100 K and 9 K, and using the two instrument configurations (Bank 2: λ_central = 1.066 A, and Bank 4 : λ = 2.665 A)







The 9 K data contains additional Bragg peaks at low Q (large d-spacing or TOF). The data measured using Bank 4 (larger wavelengths) is more informative with regard to the magnetic scattering .

Note: The crystal structure needs to be well determined before attempting to model the magnetic peaks. This can be done using the high-Q neutron data (Bank 2) or from xray diffraction.

Data can be converted from TOF to Q by providing the d1,d2 constants (taken from IRFs files) (e.g. d1= 22559 , d2=3.49)

II. Import the known crystal structure/instrument parameters to create a PCR file for a single set of data (Bank 4 at T = 9 K)

- use "Cif →Pcr" button in ***EdPCR*** to import the crystallographic information file CIF (***CuMnO2.cif***) and create the FullProf input file (*.PCR)

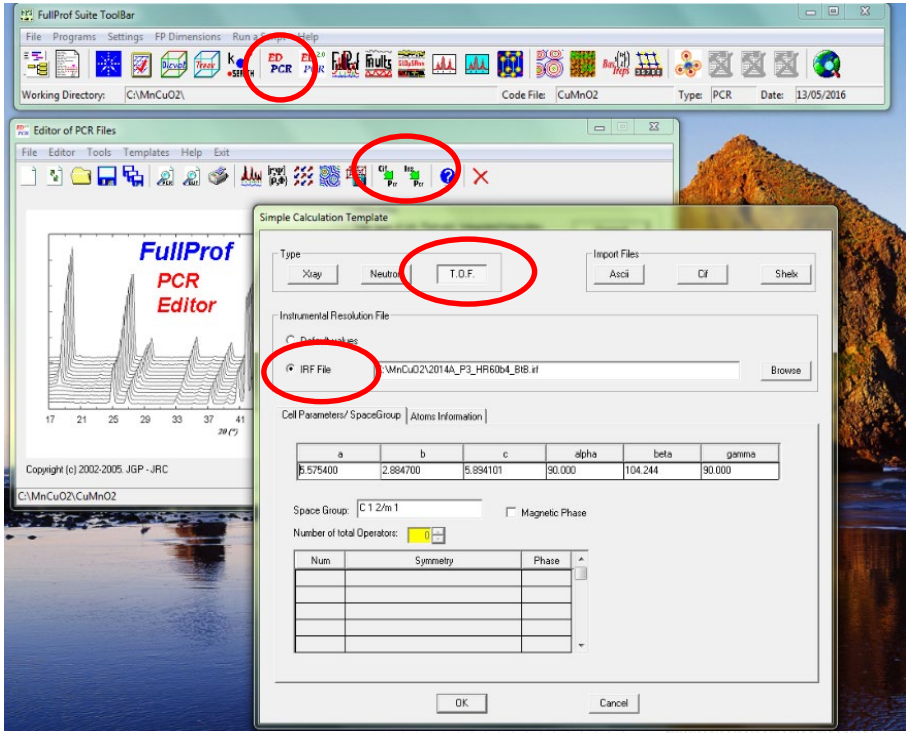
Crystal structure: *C 1 2/m 1*

Atom		x	y	z	occ.
Cu1	2d	0	0.5	0.5	0.25
Mn	2a	0	0	0	0.233
Cu2	2a	0	0	0	0.017
O	4i	0.407	0	0.179	0.5

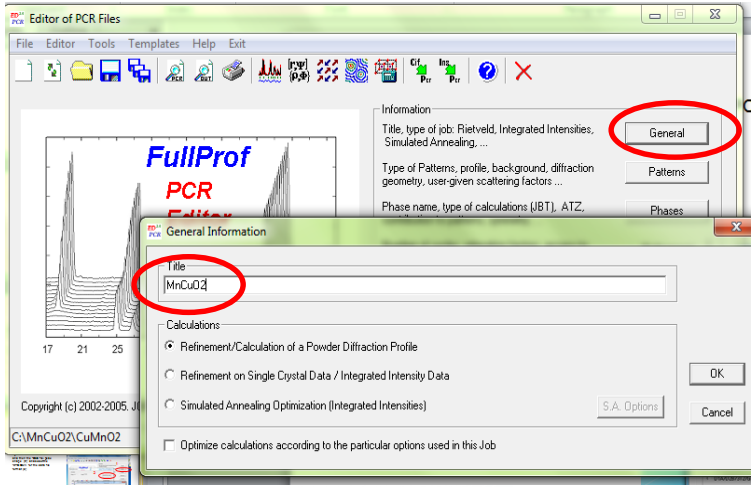
Note: occ = site multip./general multip. Always check if this has been correctly calculated after importing the .cif file.

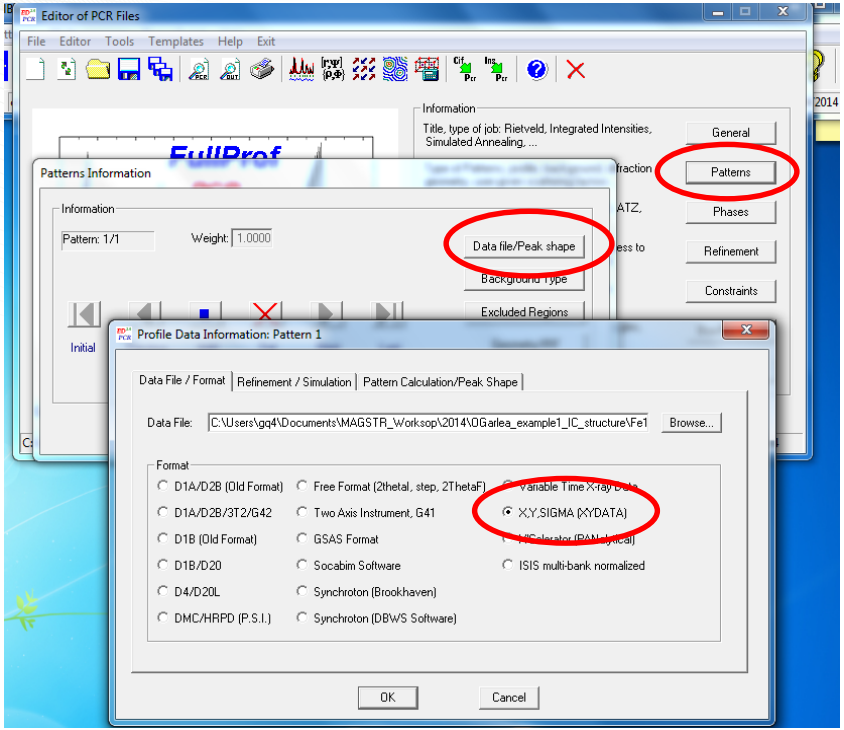
- in the new window, select the "TOF" tab for the type of calculations

- use the "Browse" button to upload the instrument resolution file "IRF" for the bank_4 dataset: ***2014A_P3_HR60b4_BtB.irf***



- In "*General* " tab, you'll see the first option "*Refinement of Powder diffraction*" as the default selection

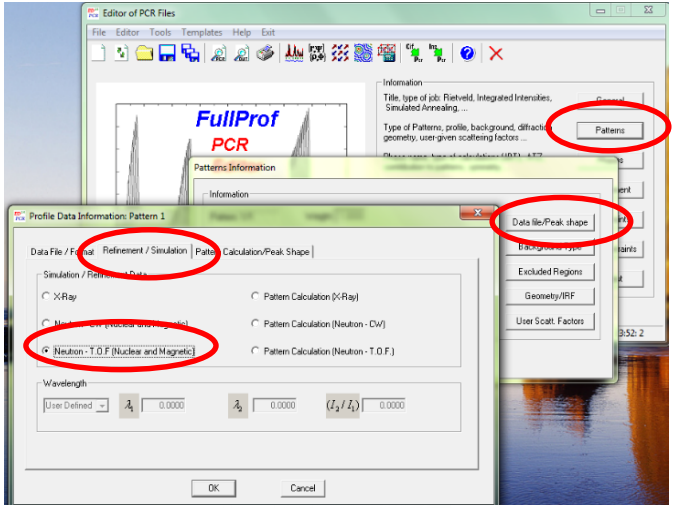


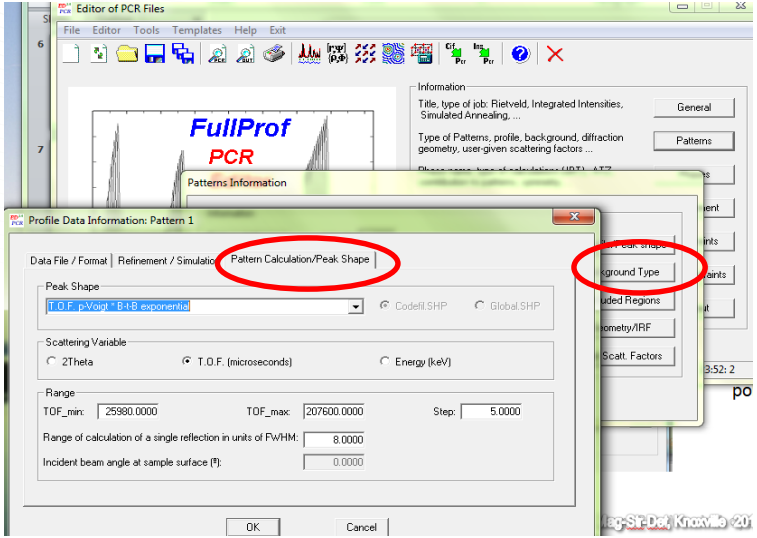


- Open the "Patterns" Tab, and then the "*Data file/ peak shape*" and select the "*XYSIGMA*" for the data file format

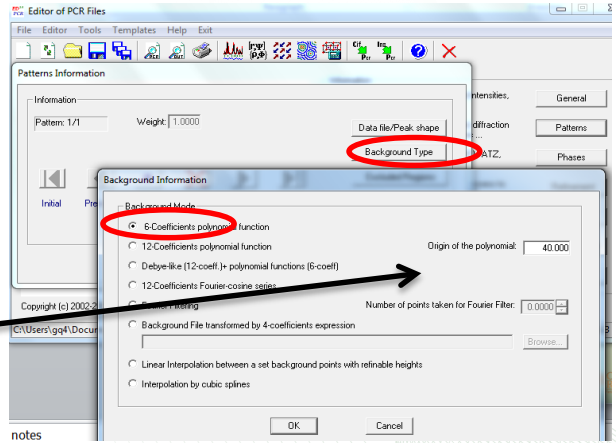
- In the "*Patterns*" & "*Data file/ peak shape*" tabs, select the "Refinement/Simulation", and make sure to select "*Neutron-TOF*"

- In "*Data file/ peak shape*" - "Pattern calculation/Peak Shape" tab, select the "T.O.F. p-Voigt * B-t-B exponential" for the peak shape type

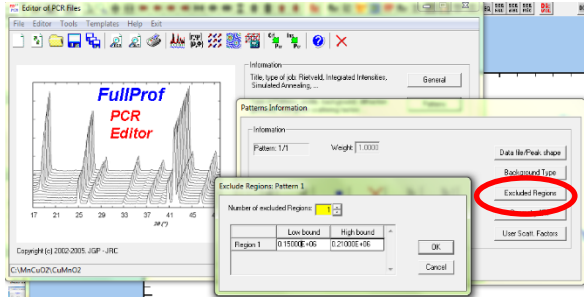


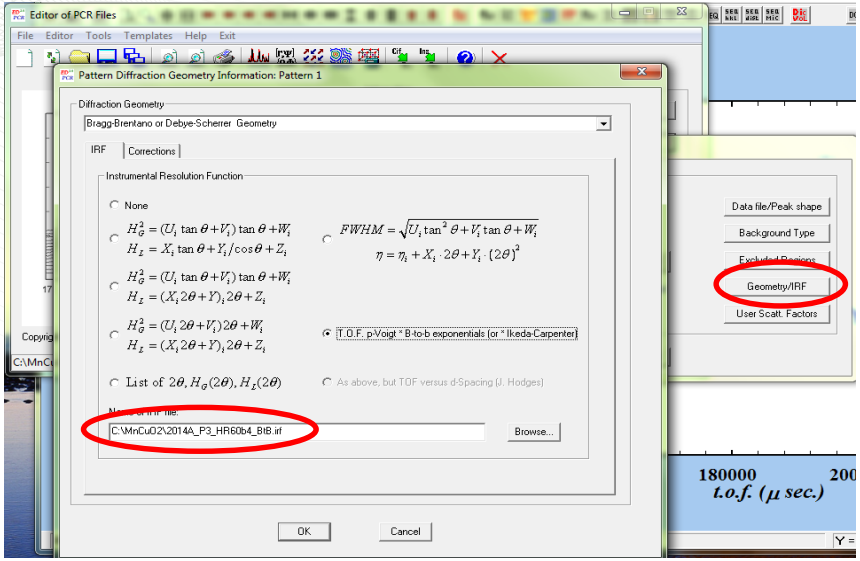


- For the background information, select the "*6-coefficients polynomial function*" and the "*Origin of the polynomial*" at 60000 (μs)



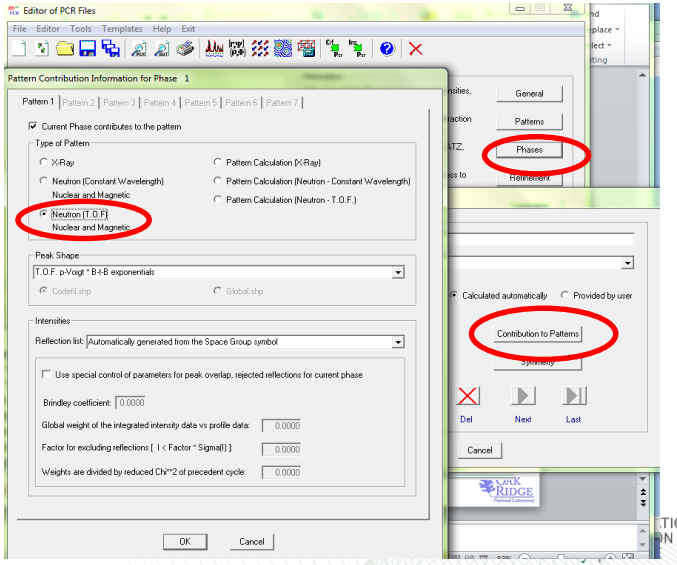
- Add one excluded region with the scattering range 150000 – 210000, as no peaks are present in that range





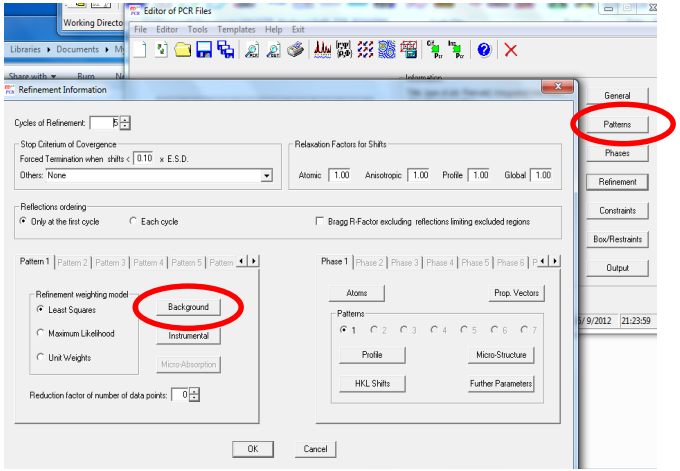
- In the "*Geometry/IRF*" tab, you should see the TOF profile selected and the IRF file that you previously assigned

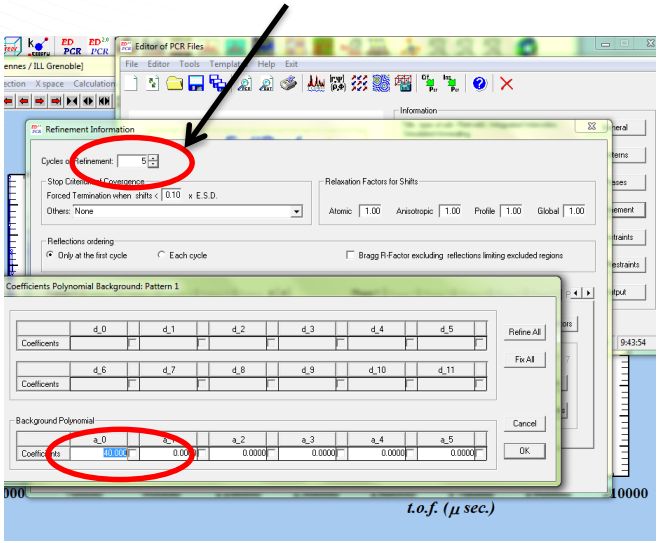
- Open the "*Phases*" tab (1) and then click on the "Contribution to patterns" and select the "current phase contributes to the pattern " and "*Neutron (TOF)*" and "*T.O.F. p-Voigt * B-t-B exponentials*" for the peak shape

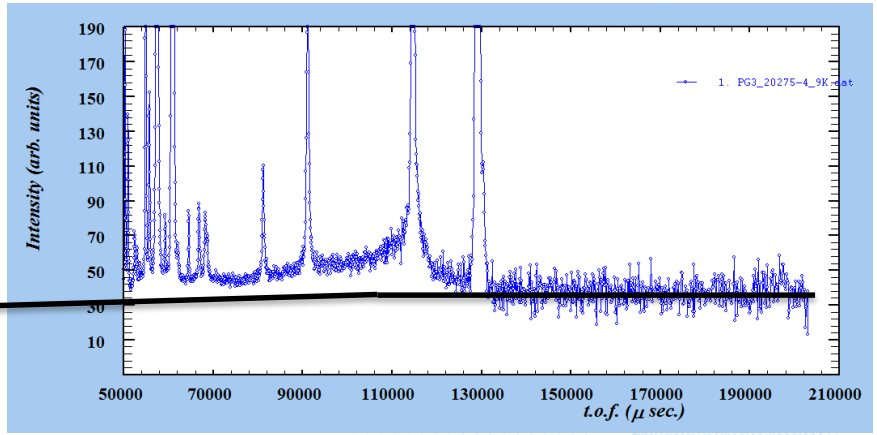


- Open the "*Refinement*" tab and then the "*Background*" and add a value for the "a_o" coefficient that will give a first flat approximation for the background (~ 40, read it from the data file)

- One can also increase the number in the "*Cycles of refinement*" box, to 5 or higher. This only becomes important when we are setting some parameters for being refined.

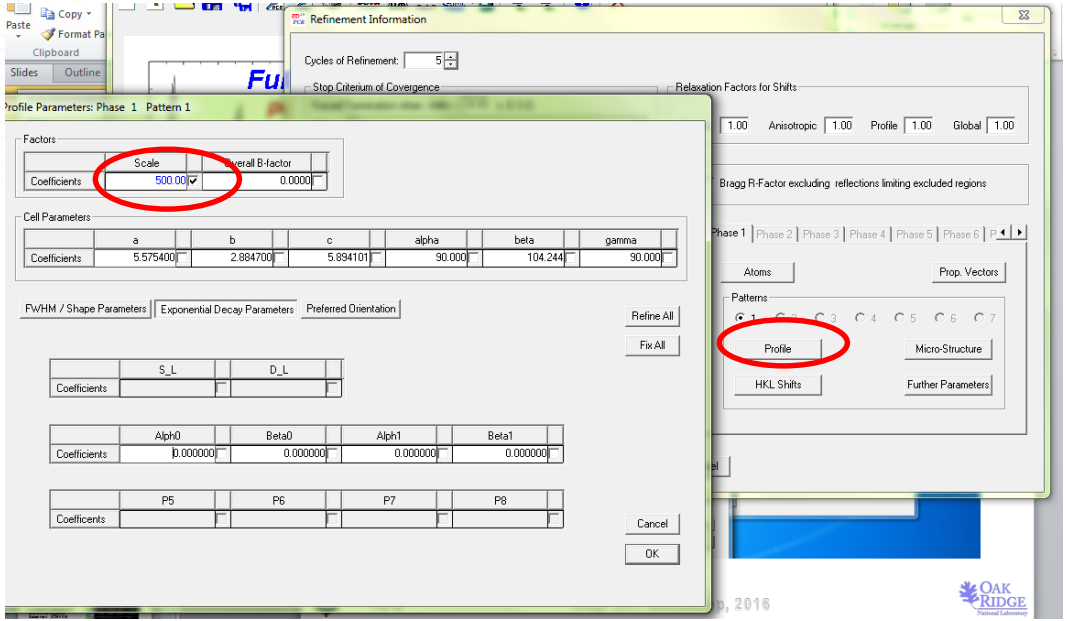




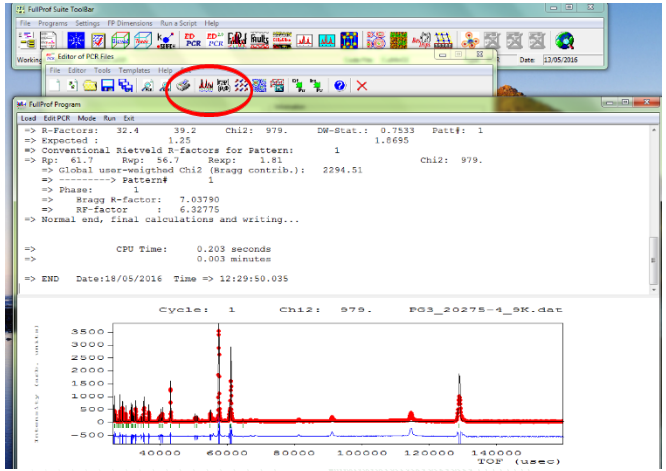


III. Refining the structural and profile parameters

- In the same "*Refinement*" window, click on the "*Profile*" tab and set the number for the "*Scale factor*" to (use 500 for this example). Remember to SAVE the PCR file by clicking the "Save" button, every time a change has been made

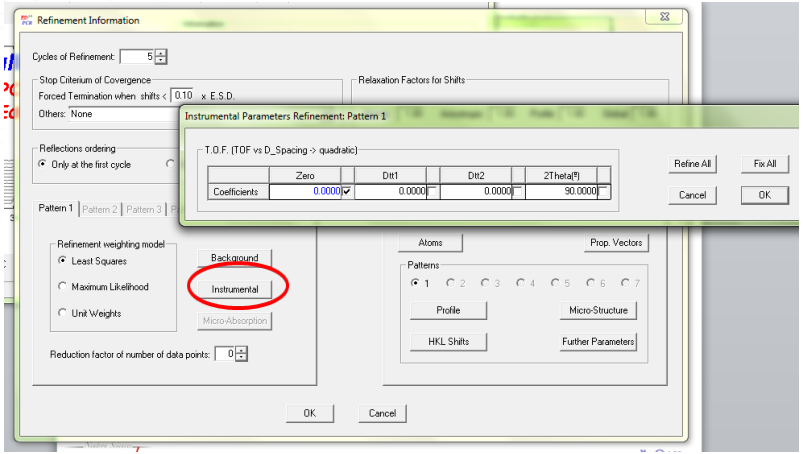


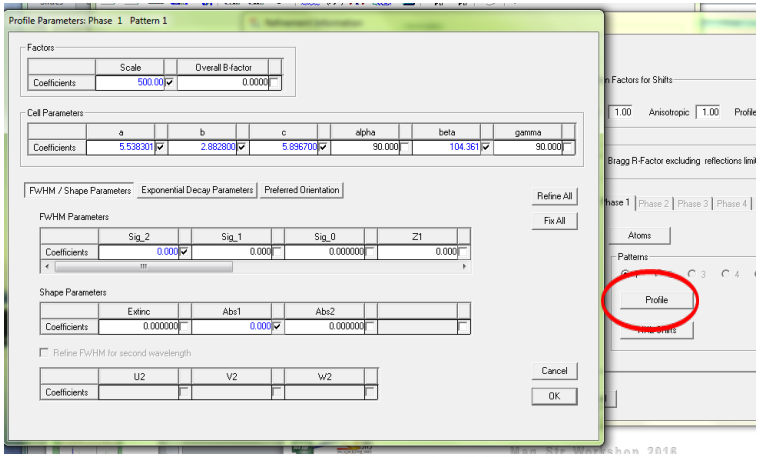
- Run the Fullprof program and select the "***PG3_20275-4_9K.dat*** " file for data.



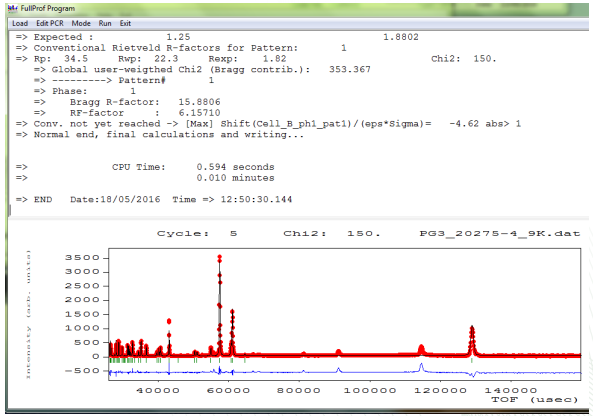
- Refine a number of parameters (e.g.: scale factor, lattice parameters, profile parameters, absorption (abs1), background, 2 theta zero shift) to improve the fit.

Note: For the pseudo-Voight TOF peak profile the biggest contribution comes from sig_2 and gam_1, so only refine these two parameters for start.





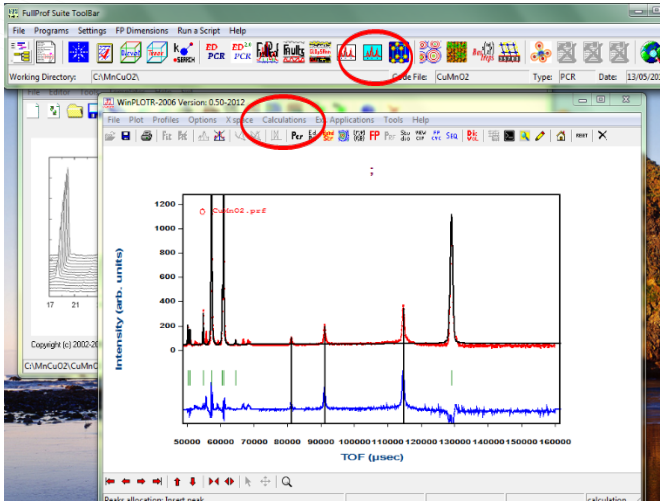
- Run the Fullprof program again to fit the data



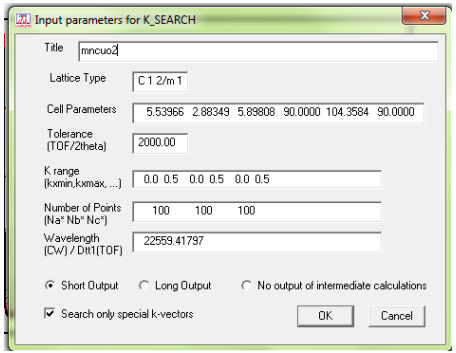
IV. Identify the magnetic reflections and determine the propagation vector (***k***)

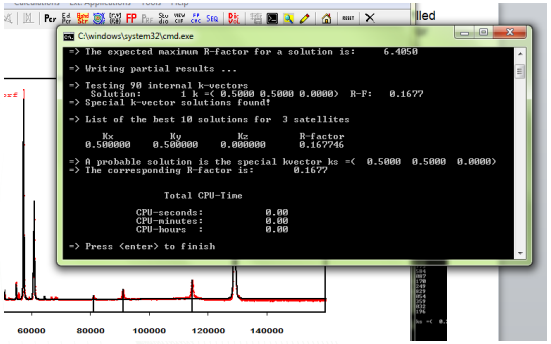
- Open the PFR file (Rietveld plot) with the WINPLOTR-2006 and select the magnetic reflections. Go to "*Calculations – Peak detection – Enable*", followed by *"Calculations – Peak detection – Insert peak"*

- Select three peaks: at tof ~114600 , 91100 , 81150 μs and save them into the "*k-search format*" by doing *"Calculations" – "Peak detection" –"Save peaks"*



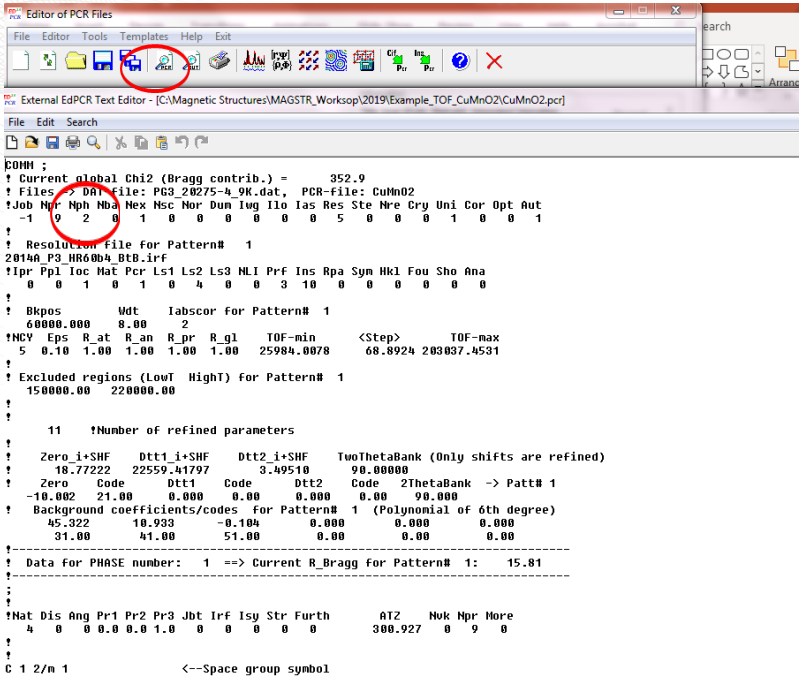
- The "*k-search* "window will display the input parameters that are automatically filled up from the pcr file. One may need to revise the k-range, and to select the box for "search only special k-vectors" if the structure is believed to be commensurate.

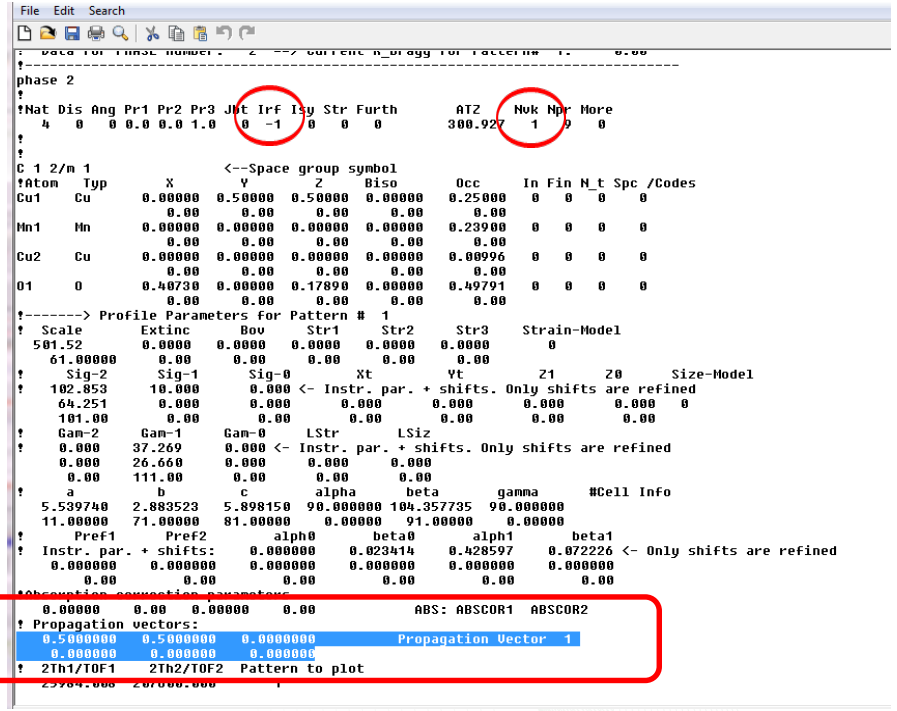




- The results are showed in a command-line window, or they can be found in the output file "k_search.kup"
- A suggested commensurate solution is **k = (0.5, 0.5, 0)**

- Edit the PCR file to add a second phase that produces satellite reflection corresponding to the solution **k** = (0.5, 0.5, 0) (*set the number of phased "Nph" = 2 and create the second phase by Copy/Paste the full information of the first phase)*

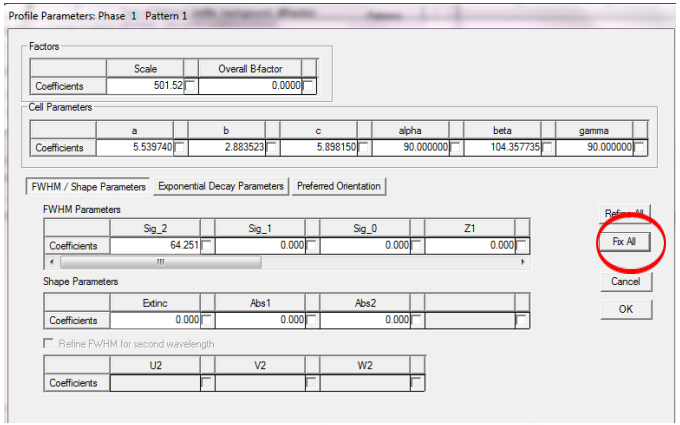




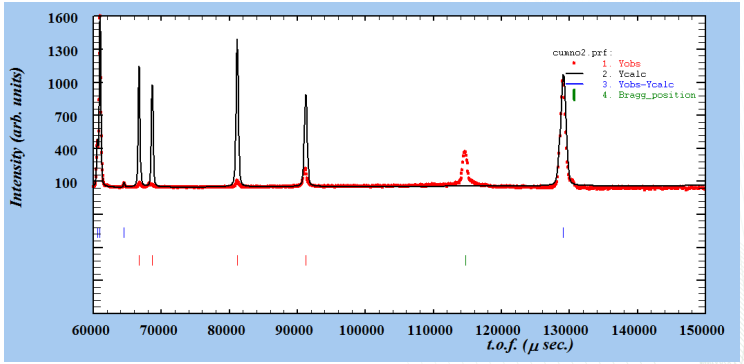
- Edit the new added phase by changing the " Irf " to " -1" (*"Satellite reflections are generated automatically .."*, and "Nvk" to 1 (number of propagation vectors) . The value of the propagation vector must be added at the end of the phased description (as highlighted in the picture above). It is given in the form of two lines, describing the three components of k, 0.5 0.5 0.0 and the corresponding refinement codes : 0.0 0.0 0.0 .
- *VERY IMPORTANT : the line !"2th1/TOF … " giving the range in the PRF plot needs to be at the end*

- Edit the PCR file or, use the EdPcr to fix all the parameters (using “Fix all” button). We do not want the program to perform a refinement at this point. The *“! Number of refined parameter”* must appear as 0.

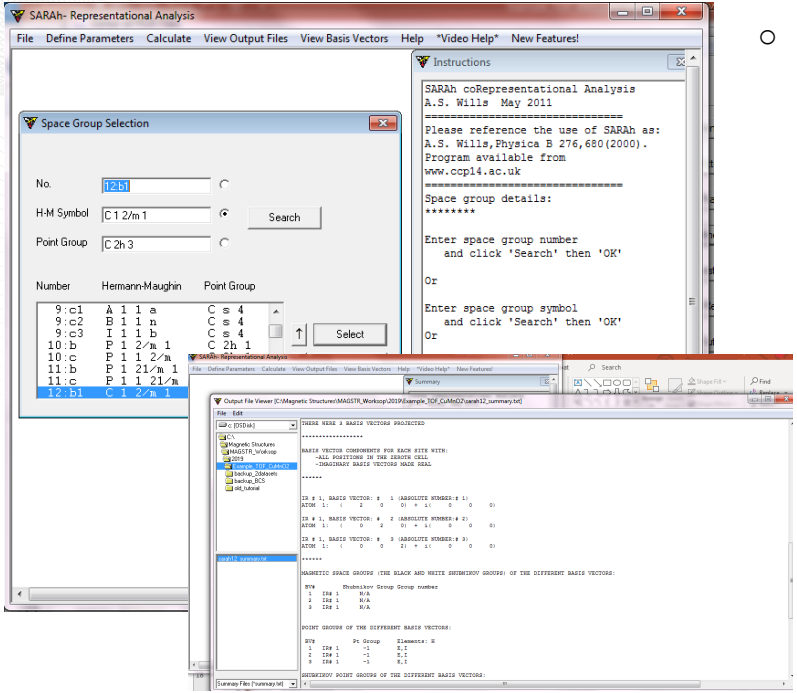
```
  5   0.10   1.00   1.00   1.00   1.00    25984.0078      68.8924 207800.0000
!
! Excluded regions (LowT  HighT) for Pattern#  1
   150000.00   220000.00
!
!
        0    !Number of refined parameters
!
!    Zero_i+SHF    Dtt1_i+SHF    Dtt2_i+SHF    TwoThetaBank (Only shifts are refined)
!      18.77195   22559.41797       3.49510      90.00000
!    Zero    Code      Dtt1    Code      Dtt2    Code   2ThetaBank  -> Patt# 1
   -10.002    0.00     0.000    0.00     0.000    0.00    90.000
!   Background coefficients/codes  for Pattern#  1  (Polynomial of 6th degree)
      45.322      10.933      -0.104       0.000       0.000       0.000
       0.00        0.00        0.00        0.00        0.00        0.00
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     0.00
!-------------------------------------------------------------------------------
;
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   4   0   0 0.0 0.0 1.0   0   0   0   0   0       300.927   0   9   0
!
```



- Run the Fullprof program again to ensure there are no errors in the file formatting and check the calculated profile to see if the satellite peaks corresponding to **k** account for all magnetic reflections.



V. Perform symmetry analysis to get the IRs and basis vectors using *SARAh or BasIreps*



- There is a single IR and 3 BV. Sarah-Refine is used to create the input for Fullprof in a *pcr file: “sarah12.pcr”

- Use Sarah- Representational Analysis to calculate the Irreducible representation and basis vectors associated with space group #12, *C 2/m,* k= (0.5, 0.5, 0), and the magnetic site Mn (0,0,0).

sarah12.pcr - Notepad

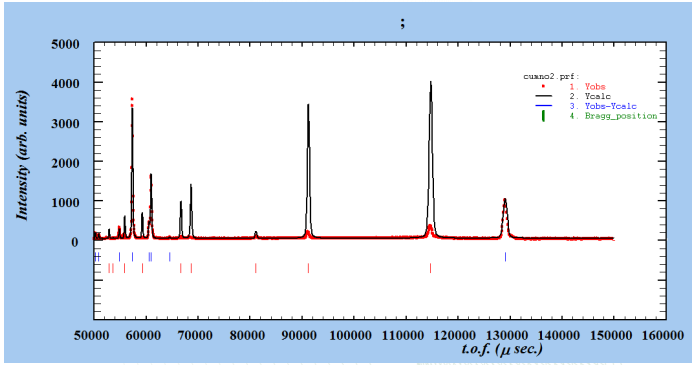
File Edit Format View Help

```
!-------------------------------------------------------------------------------
! Data for PHASE number:  1  ==> Current R_Bragg for Pattern#  1:    1.00
!-------------------------------------------------------------------------------
Magnetic Phase
!
!Nat Dis Mom Pr1  Pr2  Pr3 Jbt Irf Isy Str Furth     ATZ    Nvk Npr More
  1   0   0 0.0 0.0 0.0 1.0   1   0  -2   0   0        0.00   1   0   0
!
C -1                    <--Space group symbol
! Nsym  Cen  Laue Ireps N_Bas
    1    1    1   -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
!
SYMM X, Y, Z
BASR      2      0      0      0      2      0      0      0      2
BASI      0      0      0      0      0      0      0      0      0
!
!Atom Typ  Mag Vek    X      Y      Z      Biso   Occ      C1      C2      C3
!     C4     C5     C6     C7     C8     C9     MagPh
MN1  MMN3 1   0    .00000 .00000 .00000 .30000 1.00000  0.000   0.000   0.000
                  0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00
   0.000  0.000  0.000  0.000  0.000  0.000  0.000  .00000
   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00
!------> Profile Parameters for Pattern #  1
! Scale      Shape1      Bov      Str1      Str2      Str3     Strain-Model
   10.0      0.0000    0.0000    0.0000    0.0000    0.0000       0
    0.00000    0.00      0.00      0.00      0.00      0.00
!     U         V         W         X         Y      GauSiz   LorSiz Size-Model
  1.08239  -0.23233   0.25618   0.00000   0.00000   0.00000  0.00000   0
    0.00      0.00      0.00      0.00      0.00      0.00      0.00
```

VI. Copy the magnetic phase generated with Sarah into the existing PCR file (replacing the second phase)

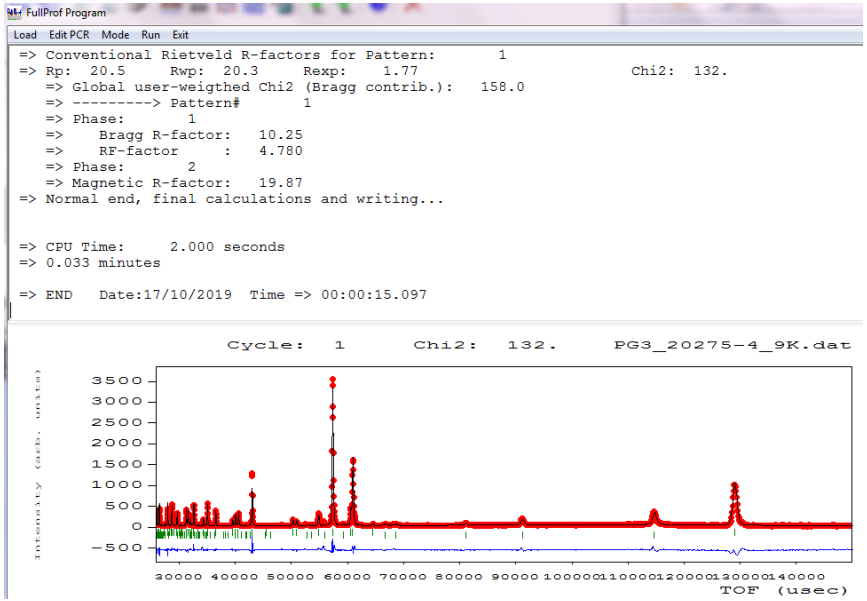
```
!Absorption correction parameters
   0.00000    0.00   0.00000    0.00            ABS: ABSCOR1  ABSCOR2
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:   446.18
!-------------------------------------------------------------------------------
Magnetic Phase
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   0  -2   0   0        0.00  1   0   0
!
C -1                        <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
    1     1     1    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
!
SYMM X, Y, Z
BASR       2       0       0       0       2       0       0       0       2
BASI       0       0       0       0       0       0       0       0       0
!
!Atom Typ  Mag Vek    X       Y       Z       Biso    Occ       C1      C2      C3
!     C4      C5      C6      C7      C8      C9      MagPh
MN1  MN3  1   0    .00000  .00000  .00000 .30000 1.00000    1.000   2.000   3.000
                   0.00    0.00    0.00    0.00    0.00     0.00    0.00    0.00
   0.000   0.000   0.000   0.000   0.000   0.000   .00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
!-------> Profile Parameters for Pattern #  1
!  Scale        Extinc       Bov      Str1      Str2      Str3     Strain-Model
  501.52        0.0000    0.0000    0.0000    0.0000    0.0000        0
     0.00000      0.00      0.00      0.00      0.00      0.00
!     Sig-2       Sig-1       Sig-0        Xt          Yt          Z1       Z0      Size-Model
!   102.853      10.000       0.000 <- Instr. par. + shifts. Only shifts are refined
     64.251       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
!     Gam-2       Gam-1      Gam-0      LStr       LSiz
!     0.000      37.269      0.000 <- Instr. par. + shifts. Only shifts are refined
      0.000      26.660      0.000      0.000      0.000
       0.00        0.00       0.00       0.00       0.00
!     a           b           c          alpha       beta        gamma       #Cell Info
   5.539741    2.883523    5.898150   90.000000 104.357735   90.000000
    0.00000     0.00000     0.00000    0.00000    0.00000     0.00000
!       Pref1       Pref2        alph0       beta0       alph1       beta1
!  Instr. par. + shifts:     0.000000    0.023414    0.428597    0.072226 <- Only shifts are
```

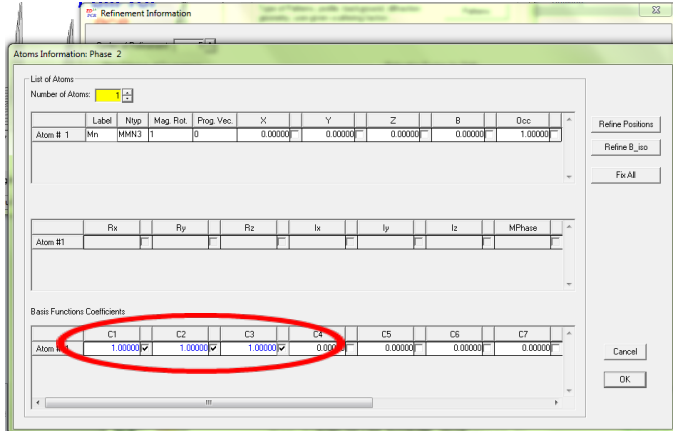
- The section dedicated to the “profile parameters “ of the magnetic phase should remained unchanged. The scale factor and lattice parameters have o be the same as for the nuclear phase. The profile parameters could be allowed to change after finding a good model.
- The c1 , c2 and c3 coefficients to the three existing basis vectors should be initiated to some non-zero values
- Run the Fullprof program and observe the calculated magnetic intensities.



VII. Perform refinement for the magnetic phase

- use the EdPCR and go to Phase 2 / Atoms for to flag the 3 coefficients, C1, C2 and C3 for refinement. *Note: when testing multiple magnetic models it is recommended to keep the the scale factors and profile parameters fixed.*

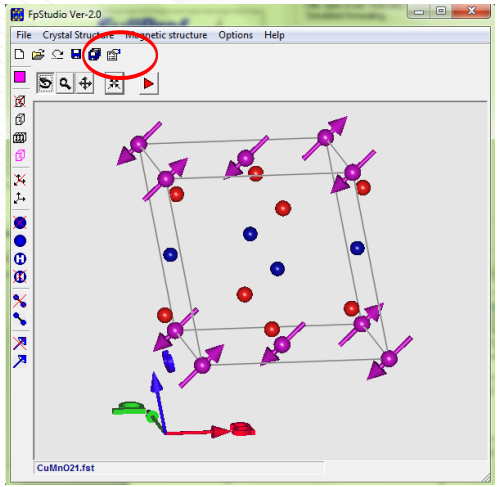


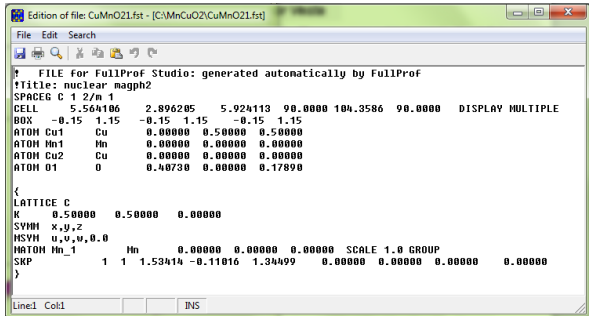


- Run the Fullprof program and inspect the quality of the fit for the magnetic peaks.
- If the result is satisfactory, the fitting can be improved by refining the scale factor, lattice parameters, profile parameter, background and zero offset. Remember to constrain the scale factor and lattice to be the same for both nuclear and magnetic phases.
- The refined moment projections along the three crystal axes are: m_a = 1.6(1) , m_b= -0.1(1) , m_c = 1.4 (1) μB

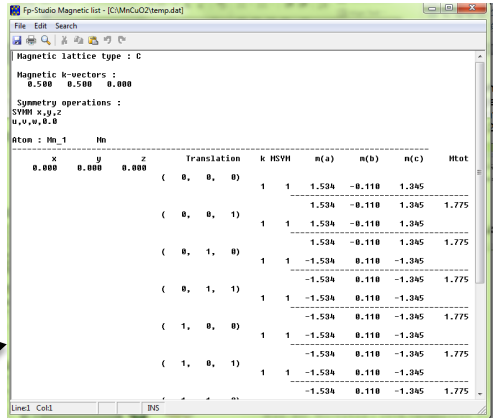
VIII. Display the magnetic structure using *FpStudio* or *Vesta*

- to visualize the magnetic structure one can use ***FpStudio*** program, which reads the *.fst file, generated automatically by Fullprof. Note a different *fst file will get created for each phase in the pcr file. To merge the magnetic and the nuclear phases into a single *fst file, one has to add in the title line for the nuclear phase the code “magph 2”

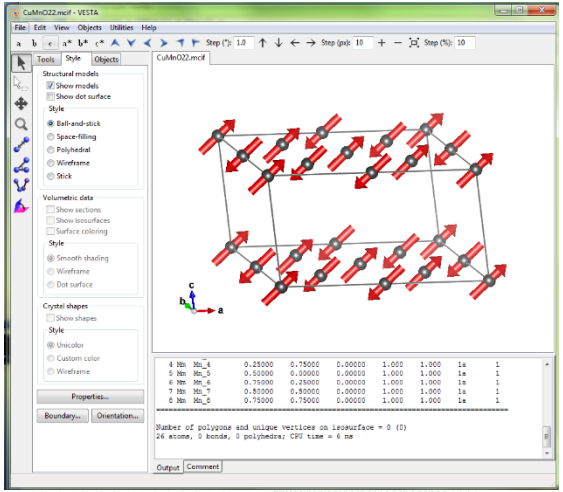




- use FpStudio to see display the magnitude of the magnetic moment for any specific position, by selecting “Magnetic structure” “List magnetic moments”

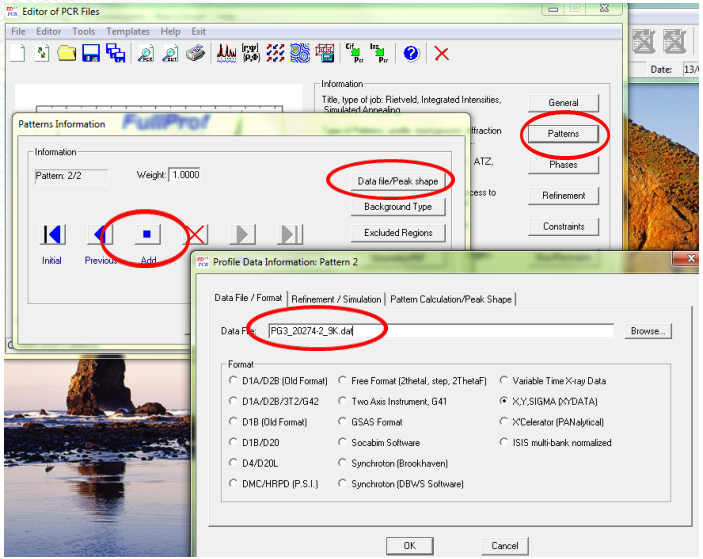


- Alternatively, the magnetic structure could be visualized using the ***VESTA*** program, which reads the *.mcif file.



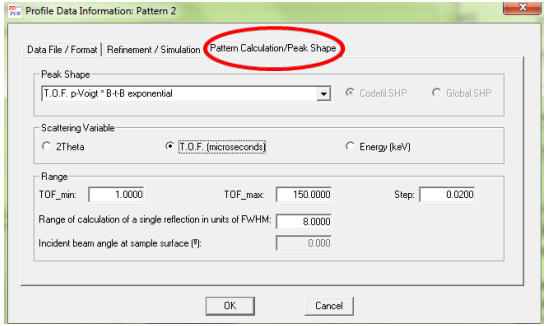
IX. Adding a second data set (Bank 2) to the refinement (reformatting the PCR file for multiple data sets)

- It is recommended to save a copy of your final single bank PCR file before adding the second data set.



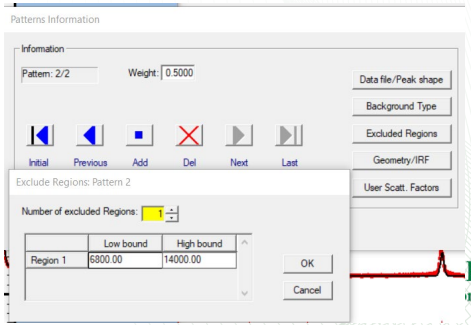
- Open the "Patterns" windows and click on "***Add*** " tab to add a second data set. You will see on the information box "*Patterns 2/2*" From the "*Patterns*" window access the "*DatFile/Format*" tab and browse to the "***PG3_20274-2_9K.dat***" data file. Set the "*Format*" for this file as "*XYSIGMA ".*

- "Peak Shape" needs to be set to the "T.O.F. p-Voigt * B-t-B exponential"

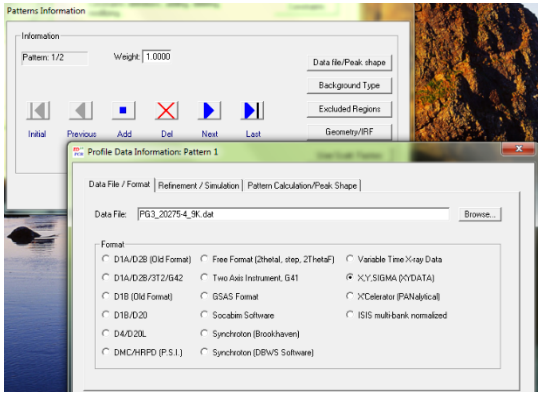


- Repeat the steps shown in pages 8-11 for the first dataset:

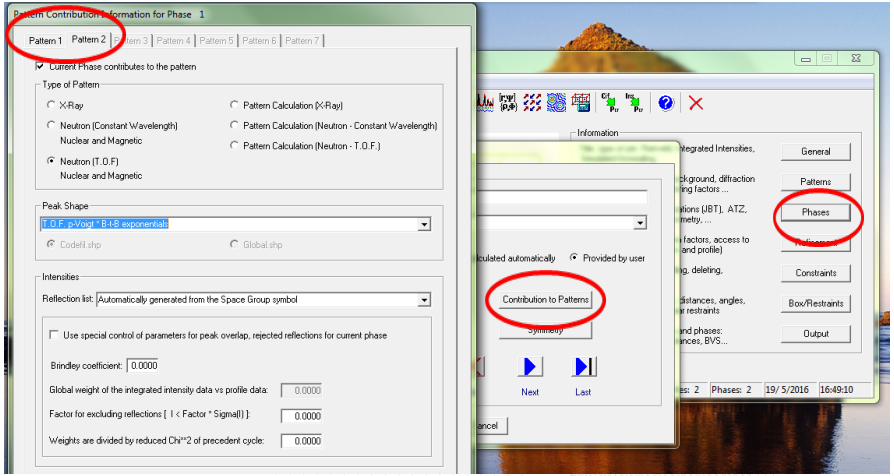
- For the background information, select the "*6-coefficients polynomial function*" and the "*Origin of the polynomial*" at 40000, and for the *"Excluded region"* one can input the 6800 to 14000 range.
- In *"Geometry IRF"* select the *"T.O.F. p-Voigt * B-t-B exponentials"* and set the IRF file to "***2014A_P3_HR60b2_BtB.irf***"
- ! Save the PCR after making the above changes.



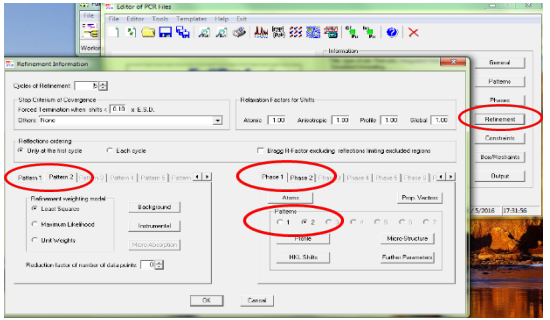
- Before moving to the next step, use the arrow in “Patterns information” to move back to the Pattern 1 and add to the Data file” section the name of the file for this first pattern: “***PG3_20275-4_9K.dat***” . This is needed because in the previous PCR file that was formatted for the single – dataset, the name of the data file was not required. When using multiple data sets, the file name for each data is needed.



- The PCR file contains now **two phases** and **two patterns**. Open the “*Phases*” window and navigate between different phases by using the “next” or “previous” buttons. For **each** phase (nuclear and magnetic) one needs to select both patterns. Select for the Pattern 2 the correct data format (TOF) and the peak shape function.



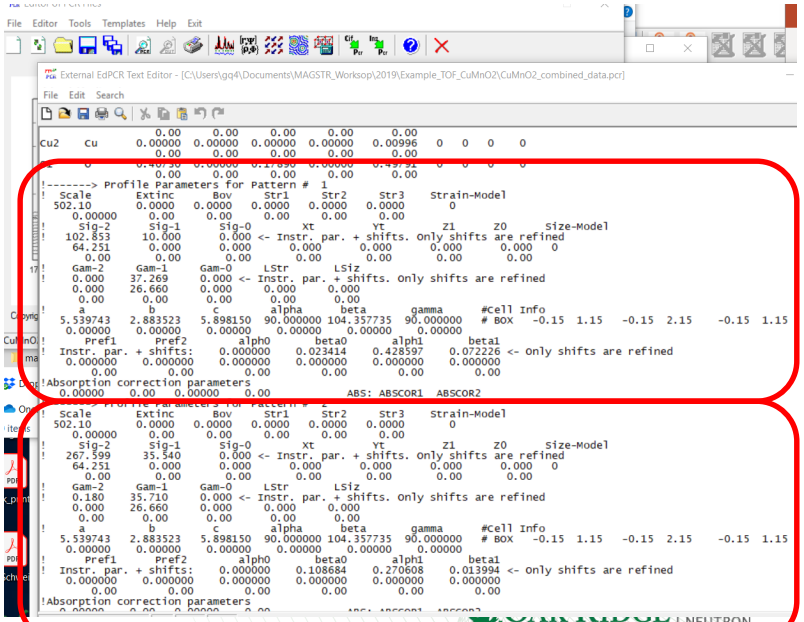
- In the “Refinement” window , one should see that there are two patterns and two phases. One has to be careful to go over all combinations Pattern # - Phase # and revise/initialize all the parameters properly. *Understanding the PCR file and being able to directly edit the PCR input is a big advantage at this point.*



- *! It is useful to fix all the parameters that were refined for a single pattern before starting a new refinement on a multi-pattern setting. If some of the newly introduced profile parameters were not properly initialize that may cause other refined parameters to diverge.*

- *! It is also important to understand which parameters should be constrained to be equal for the two patterns and which should not. For instance, the lattice parameters have to be the same in all phases/patterns but the profile parameters are not. The scale factors will be the same for the two phases but different for the two patterns. Background parameters should be different for each pattern, etc.*

- Open the PCR file in text mode and find the sections corresponding to the profile parameters for *Pattern 2*, for each of the existing phase. You can see that the ***scale factor*** and the ***lattice parameters were not initialized yet***. The easiest way is to copy/paste that “profile section from the pattern 1 to the pattern 2, keeping in mind that the scale factor is will converge to a different value after the refinement.

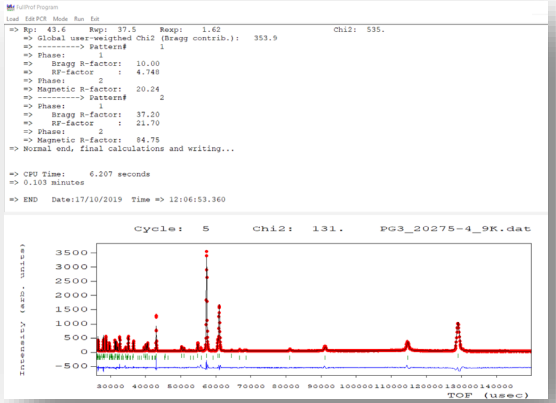


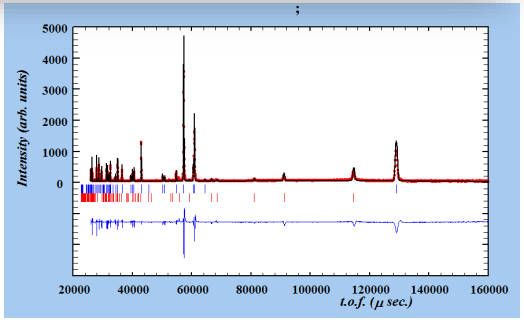
- The PCR file must look like in the screen caption, shown in the right:
  It should to contain two datasets and two Irf files. All parameters should be fixed for the first refinement (see: “0 ! Number of refined parameters”.

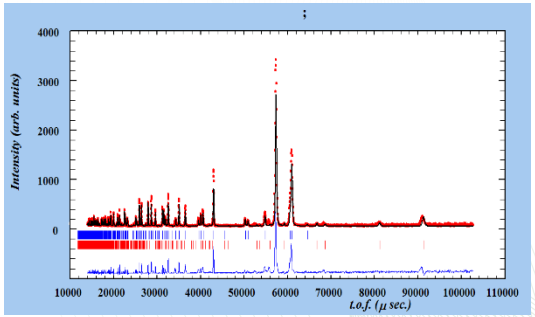
- By running the refinement, you will notice that there is no popup dialog window asking about the data file. The program will automatically use the two data files you selected. Each dataset will produce a separate PRF file (Rietveld profile files).

- The PRF profile plots for bank 4 and bank 2 data, obtained without fitting any parameters, should look like here:

```
NPATT      2       1 1 <- Flags for patterns (1:refined, 0: excluded)
W_PAT   0.500 0.500
!Nph Dum Ias Nre Cry Opt Aut
   2   0   0   0   0   0   1
!Job Npr Nba Nex Nsc Nor Iwg Ilo Res Ste Uni Cor Anm Int
  -1   9   0   1   0   0   0   0   5   0   1   0   0   0  !-> Patt#: 1
  -1   9   0   1   0   0   0   0   5   0   1   0   0   0  !-> Patt#: 2
!
!File names of data(patterns) files
PG3_20275-4_9K.dat
PG3_20274-2_9K.dat
!
!  Resolution file for Pattern#   1
2014A_P3_HR60b4_BtB.irf
!  Resolution file for Pattern#   2
2014A_P3_HR60b2_BtB.irf
!Mat Pcr NLI Rpa Sym Sho
   0   1   0   0   0   0
!Ipr Ppl Ioc Ls1 Ls2 Ls3 Prf Ins Hkl Fou Ana
   0   0   1   0   4   0   3  10   0   0   0  !-> Patt#: 1
   0   0   1   0   0   0   3  10   0   0   0  !-> Patt#: 2
!
!  Bkpos        Wdt    Iabscor for Pattern#  1
   60000.000    8.00     2
!  Bkpos        Wdt    Iabscor for Pattern#  2
   40000.000    8.00     2
!NCY  Eps  R_at  R_an  R_pr  R_gl
  5  0.10  1.00  1.00  1.00  1.00
!    TOF-min       <Step>        TOF-max  -> Patt#: 1
  25984.0078     68.8924 207600.0000
!    TOF-min       <Step>        TOF-max  -> Patt#: 2
   6775.0000      5.0000 104000.0000
!
! Excluded regions (LowT  HighT) for Pattern#  1
   150000.00   220000.00
!
! Excluded regions (LowT  HighT) for Pattern#  2
     6800.00     9000.00
!
!
      0    !Number of refined parameters
!
```

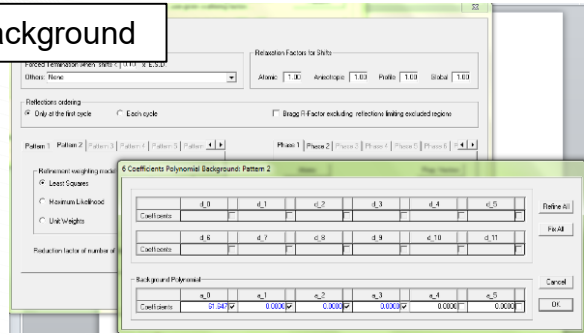




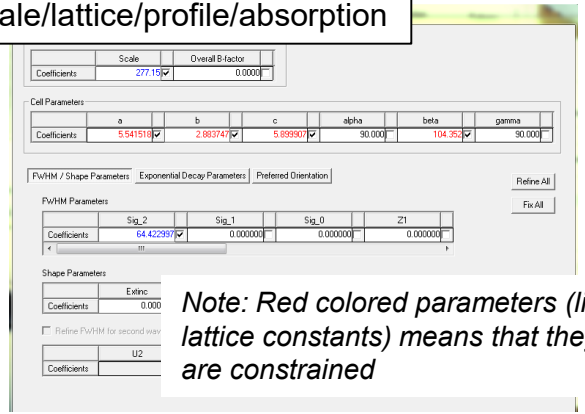


- We can start at this point refining different profile and structural parameters to improve the fit. For starting, one can vary the *background coefficients for pattern 2*, *lattice parameters* (those have to be the same for all patterns & phases), *Scale factor* (remember that the scale for nuclear and magnetic phases have to be equal, but not the same for different patterns), *profile* (Sig_2 & Gam_1)

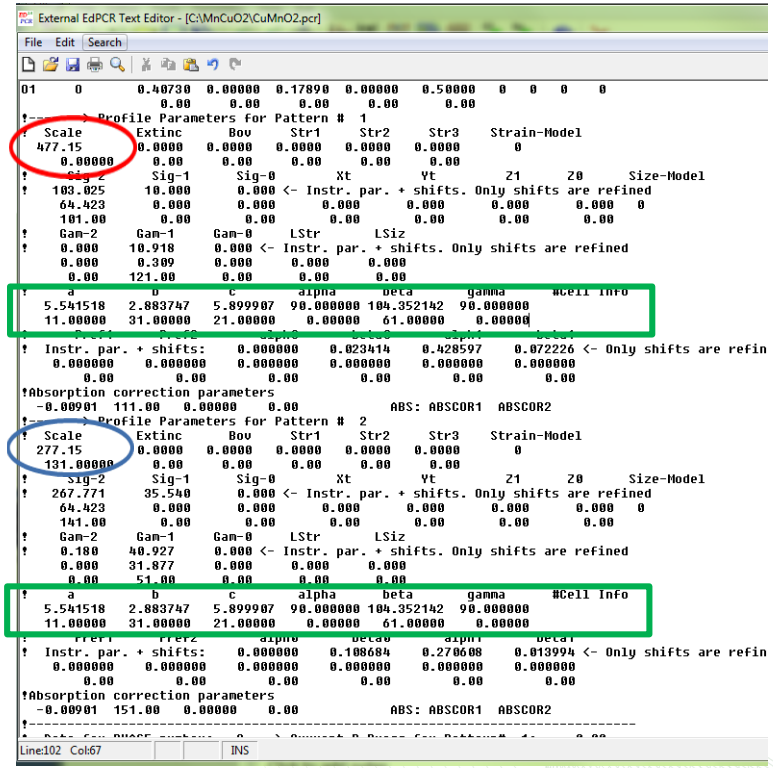
refining background



refining scale/lattice/profile/absorption

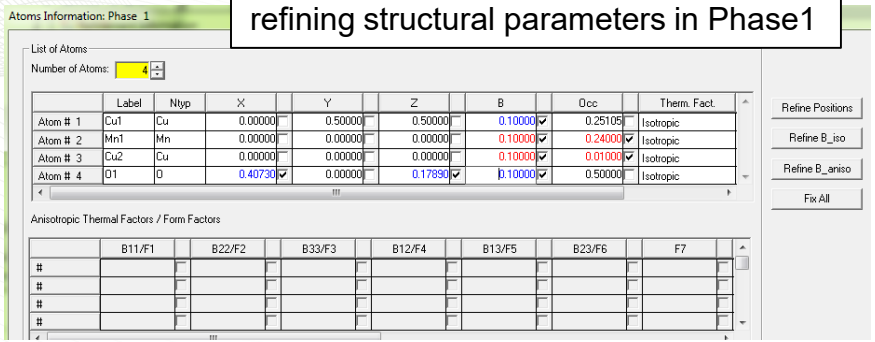


Note: Red colored parameters (like lattice constants) means that they are constrained



- Once we have a good control on the refinement and more experimental data at higher Q, from adding the pattern 2, we can also refine the structure parameters (atom positions, thermal parameters, occupancy) and the magnitude of the moments.

refining structural parameters in Phase1



- The thermal parameters of the atoms sharing the same site should be constrained to be equal, and the total occupancy of the "*2a*" site to be 0.25 (fully occupied = 2/8).
- The final refinement should give you a reasonable fit for both patterns.

refining BV coefficients Phase2