OAK RIDGE National Laboratory

Representational analysis with Fullprof and SARAh to refine $MnPSe_3$ data collected on HB2A

Stuart Calder

MagStr, ORNL, 2022

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U.S. DEPARTMENT OF ENERGY

$MnPSe_3$

- *R*-3 space group (148) Setting 1, hexagonal
- *a*=*b*=6.387 Å, *c*=19.996 Å.
- α=90°, β=90°, γ=120°
- Mn^{2+}, *S*=5/2

Solid State Communications, Vol. 40, pp. 1067–1072. Pergamon Press Ltd. 1981. Printed in Great Britain.
0038–1098/81/481067–06$02.00/0

NEUTRON DIFFRACTION STUDY OF THE LAYERED COMPOUNDS $MnPSe_3$ AND $FePSe_3$*

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and

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(*Received* 11 *August* 1981 *by E.F. Bertaut*)

In the insulating compounds $MnPSe_3$ (1) and $FePSe_3$ (2) (sition metal ions form planar honeycomb lattices. A neut study revealed a collinear antiferromagnetic order below (1) and T_N = 119 ± 1 K (2) with the corresponding wavev [0 0 0] (1) and k = [1/2 0 1/2] (2). In $MnPSe_3$ the magne ($m_0 = 4.74\,\mu_B$) lie within the basal plane and in $FePSe_3$ (they are pointing along the *c*-axis. The collinear structures by the dominating intralayer interactions between first (J and third neighbours (J_3) which in $MnPSe_3$ are all antifer whereas in $FePSe_3$ J_1 is ferromagnetic and J_2 and J_3 are a

Originally investigated in 1981. Renewed interest due to quasi-2D van der Waal layered structure.

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Magnetic exchange interactions in the van der Waals layered antiferromagnet $MnPSe_3$

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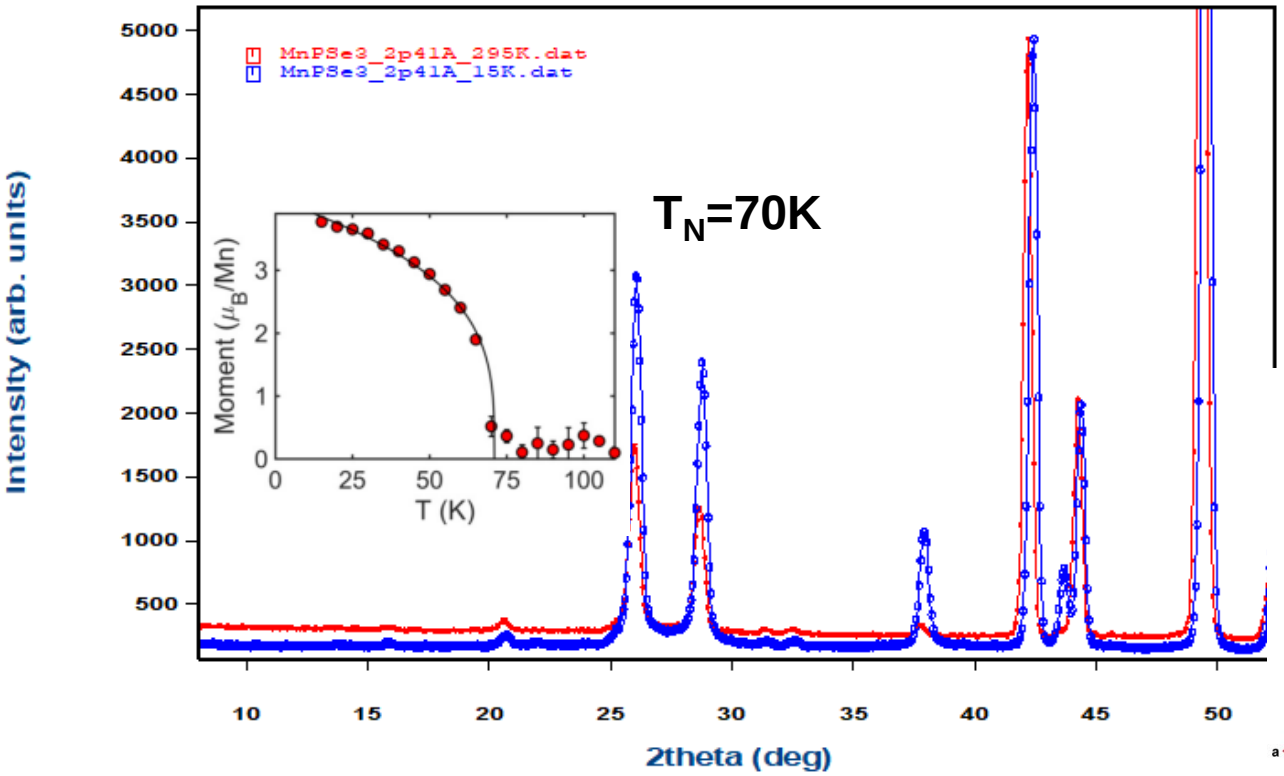
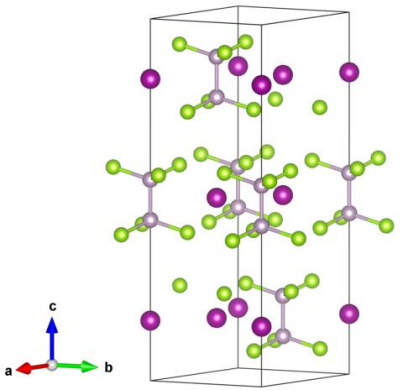
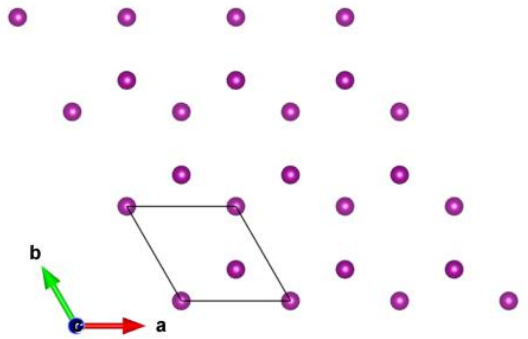
Two-dimensional van der Waals compounds with magnetic ions on a honeycomb lattice are hosts to a variety of exotic behavior. The magnetic interactions in one such compound, $MnPSe_3$, are investigated with elastic and inelastic neutron scattering. Magnetic excitations are observed in the magnetically ordered regime and persist to temperatures well above the ordering temperature, $T_N = 74$ K, consistent with low dimensional magnetic interactions. The inelastic neutron scattering results allow a model spin Hamiltonian to be presented that includes dominant intralayer interactions of $J_{1ab} = 0.45$ meV, $J_{2ab} = 0.03$ meV, $J_{3ab} = 0.19$ meV, consistent with theoretical predictions. Despite the quasi-2D behavior, appreciable interlayer interactions of $J_c = 0.031(5)$ meV are required to model the data. No evidence for anisotropy in the form of a spin gap is observed in the data collected. The measurements on $MnPSe_3$ are contrasted with those on $MnPS_3$ and reveal a large increase in the interlayer exchange interaction in $MnPSe_3$ that may stabilize the similar ordering temperatures in the bulk compounds.

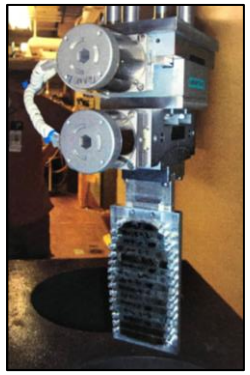
DOI: 10.1103/PhysRevB.103.024414

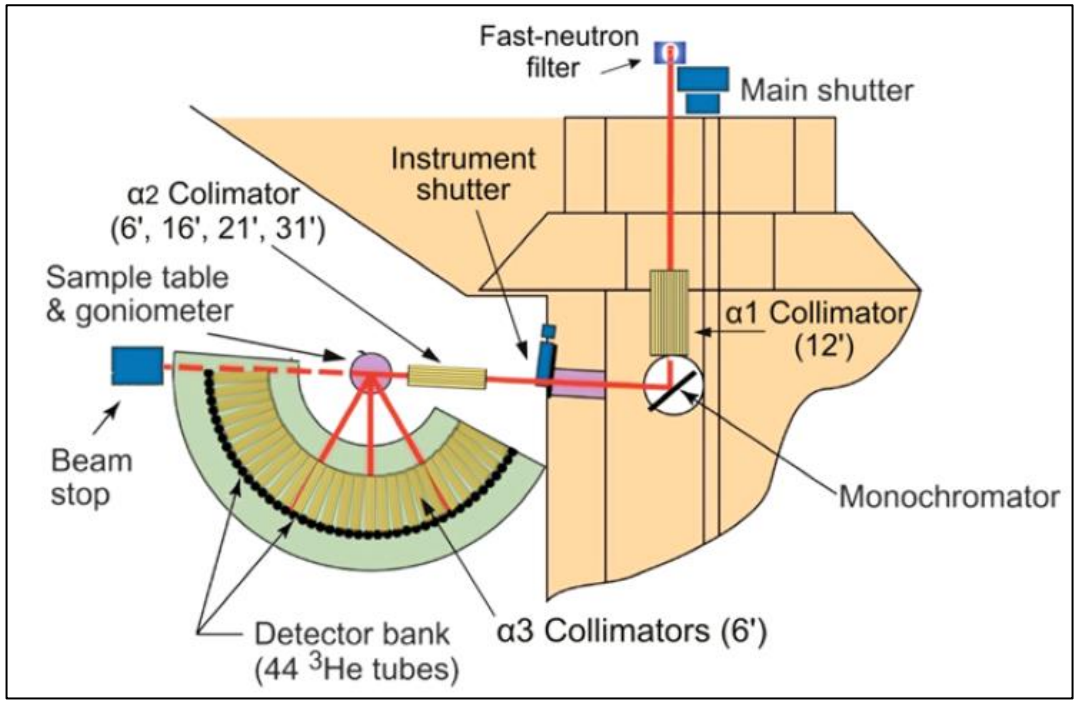






HB-2A: Powder diffractometer at HFIR





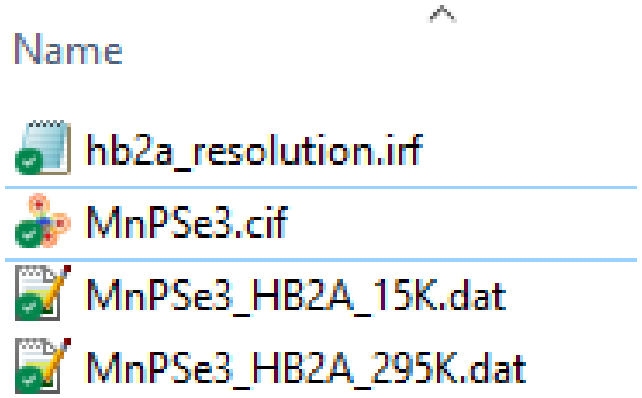
- Constant wavelength
- Germanium monochromator
  - ~90° take off angle for medium-high resolution
  - Variety of complex sample environments: 50mK, 8 Tesla, pressure…
- Detector is an array of 44 individual ^{3}He tubes
  - Low background and robust to magnetic field
  - Covers ~2-150° in 2θ through scanning detector

Ge(hkl)	λ (Å)	d_{max}(Å)	4πsinθ/λ	Flux (n/cm^{2}s)
(113)	**2.41**	**27.6**	**0.2-5.1**	**5 x 10^6**
(115)	**1.54**	**17.6**	**0.35-7.9**	**1 x 10^7**
(117)	1.12	12.8	0.5-10.9	4 x 10^6

https://neutrons.ornl.gov/powder

Details of this $MnPSe_3$ example

- Neutron powder diffraction data collected at HB2A, HFIR
- λ = 2.41 Å. Collimation: open-open-21'
- Data at 15K (**MnPSe3_HB2A_15K.dat**) and 295K (**MnPSe3_HB2A_295K.dat**)
- Sample in a vanadium can
- Instrument resolution file: **hb2a_resolution.irf**
- Crystal structure: **MnPSe3.cif**



$MnPSe_3$

- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
  - Step 3: Create candidate magnetic models using SARAh
  - Step 4: Refine the magnetic model and nuclear phase in Fullprof.
  - Step 5: Visualize the magnetic model

$MnPSe_3$

- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
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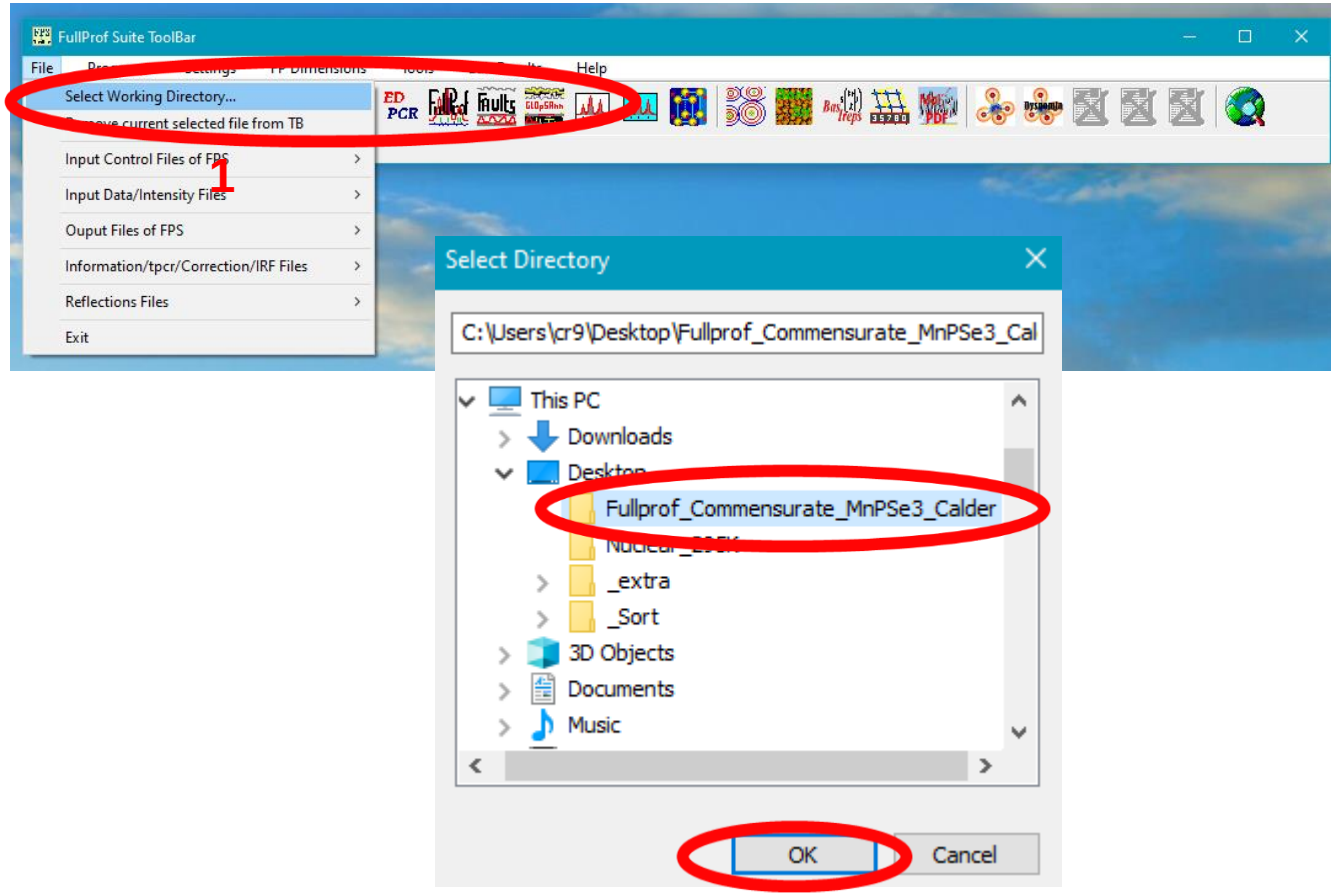
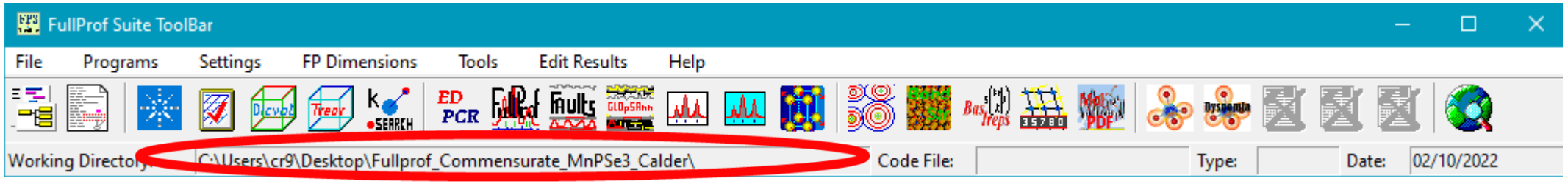
Step 1: Refine the crystal structure using FullProf

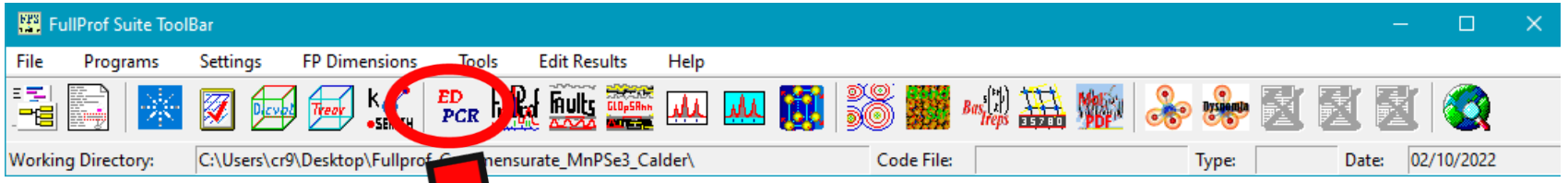
- Open Fullprof Suite toolbar.
  - **1.** Select working directory with data "*File>Select Working directory…*"
  - **2.** Browse to wherever your folder "Ho2Ba2NiO5_MagSpaceGroup" is located on your computer and select "ok"
  - **3.** Path on FP studio toolbar should now be updated. This helps with interacting with other features of Fullprof

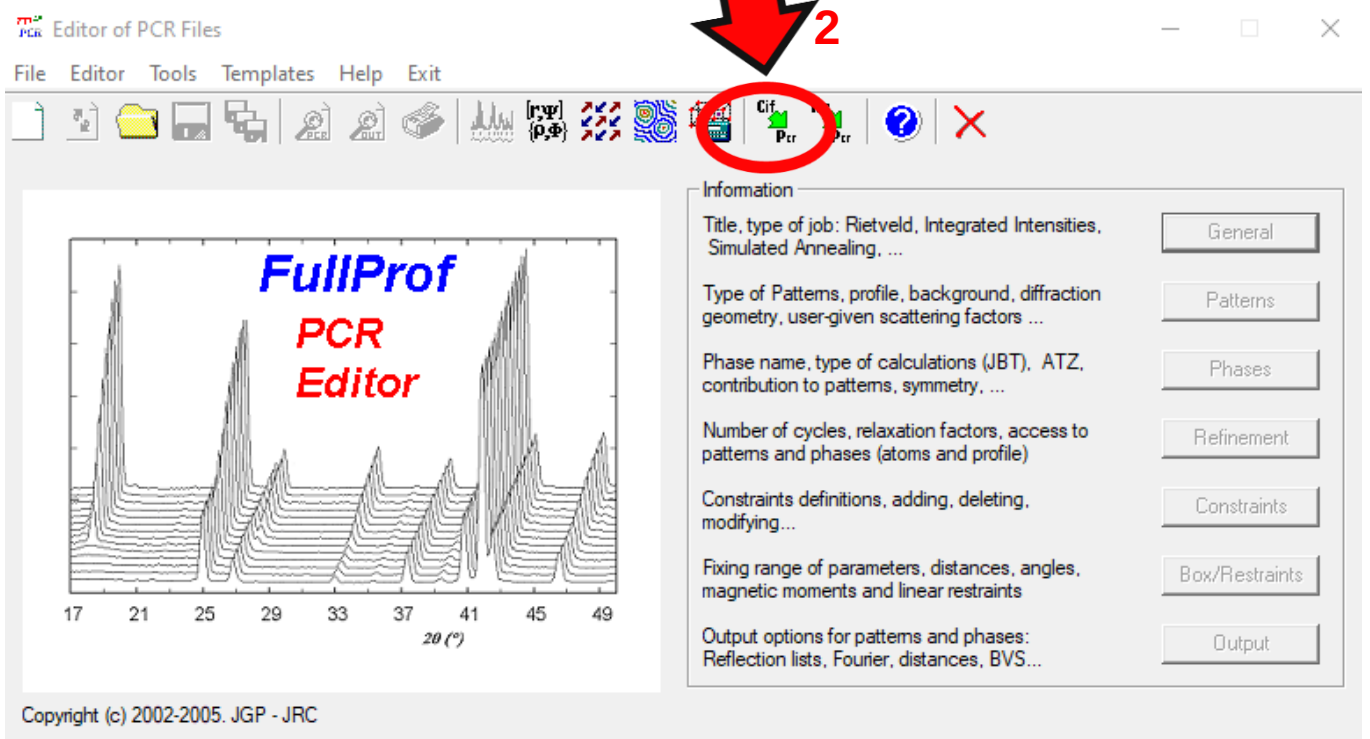




Step 1: Refine the crystal structure using FullProf

- **1.** From FullProf Suite Toolbar open EdPCR.
- **2.** Import crystallographic information file by clicking on "CIF→PCR"
- **3.** Select the file "MnPSe3.cif"

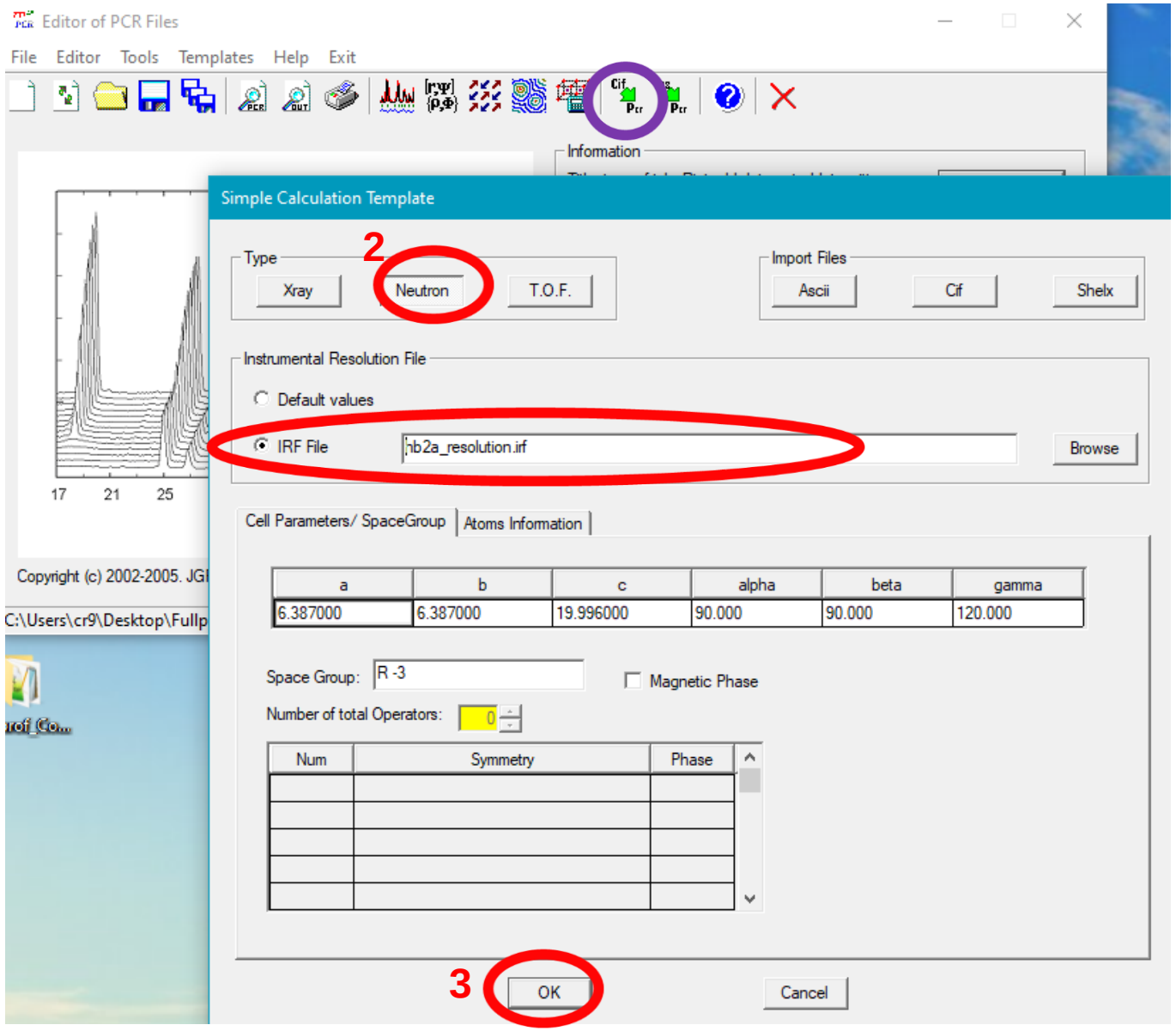




Step 1: Refine the crystal structure using FullProf

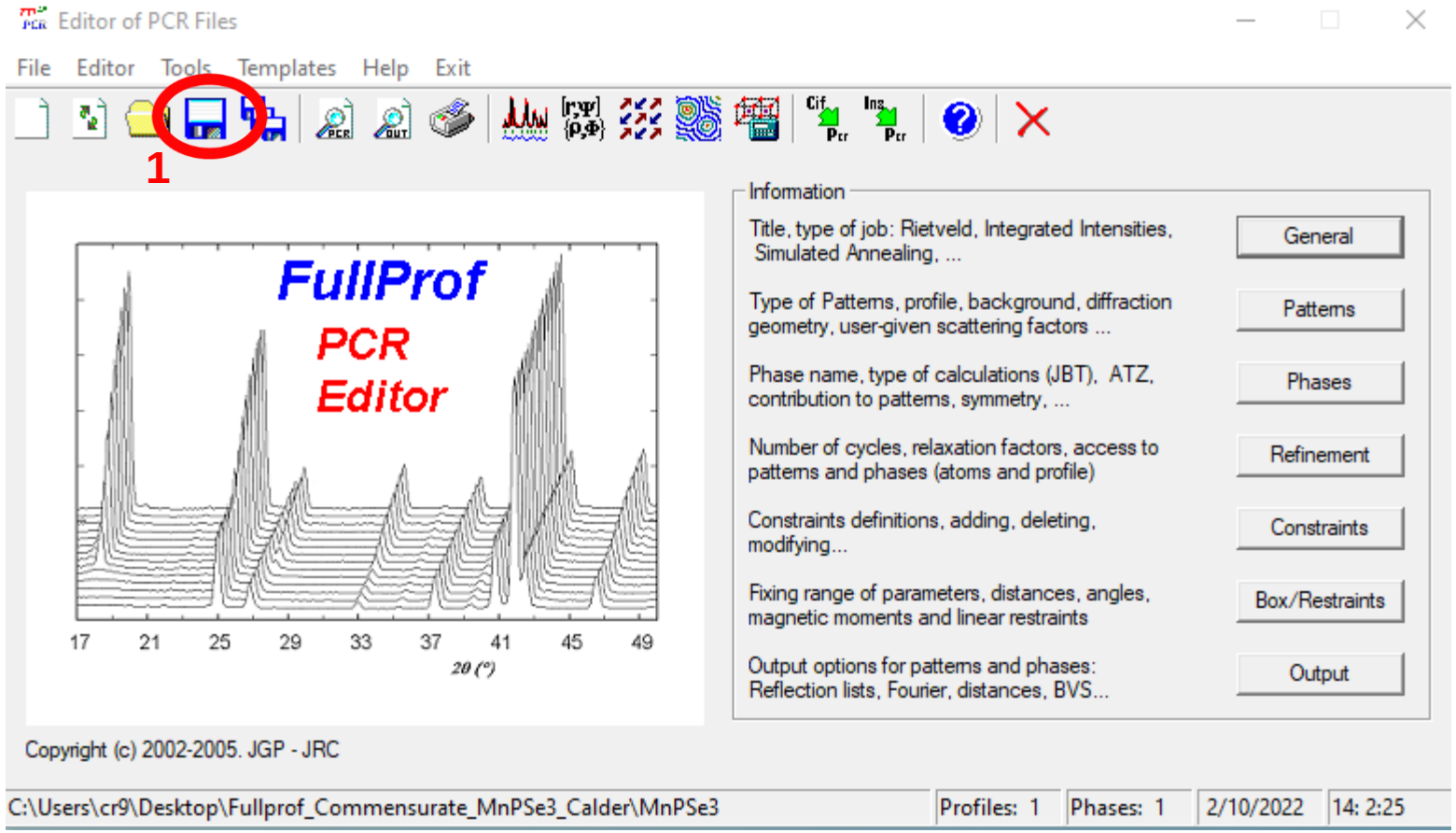
Cif→PCR opens a window to input instrument and show structural info.

- **1.** Load the instrument resolution file "hb2a_resolution.irf". *NOTE: remove the full path to just keep "dib_ill.irf". If you don't and move the pcr file to a different directory (or share the pcr with someone else) it will create problems*
- **2.** Change "Type" to "Neutron" for constant wavelength
- Starting **Cell Parameters**, **Space Group** and **Atoms Information** are now loaded.
- Note: occ = site multip./general multip. Always check this has been correctly calculated after importing the .cif file.
- **3.** Hit "OK"



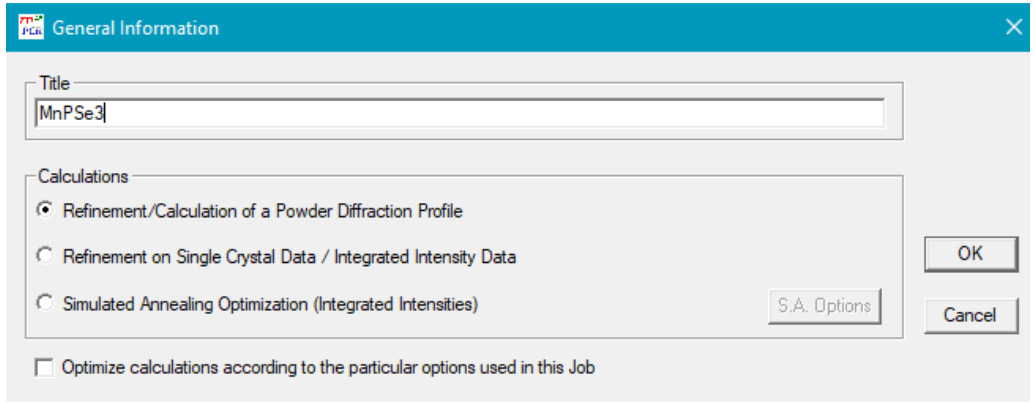
Step 1: Refine the crystal structure using FullProf

- **1.** Save the changes.
- This should be done whenever changes are made in the GUI.



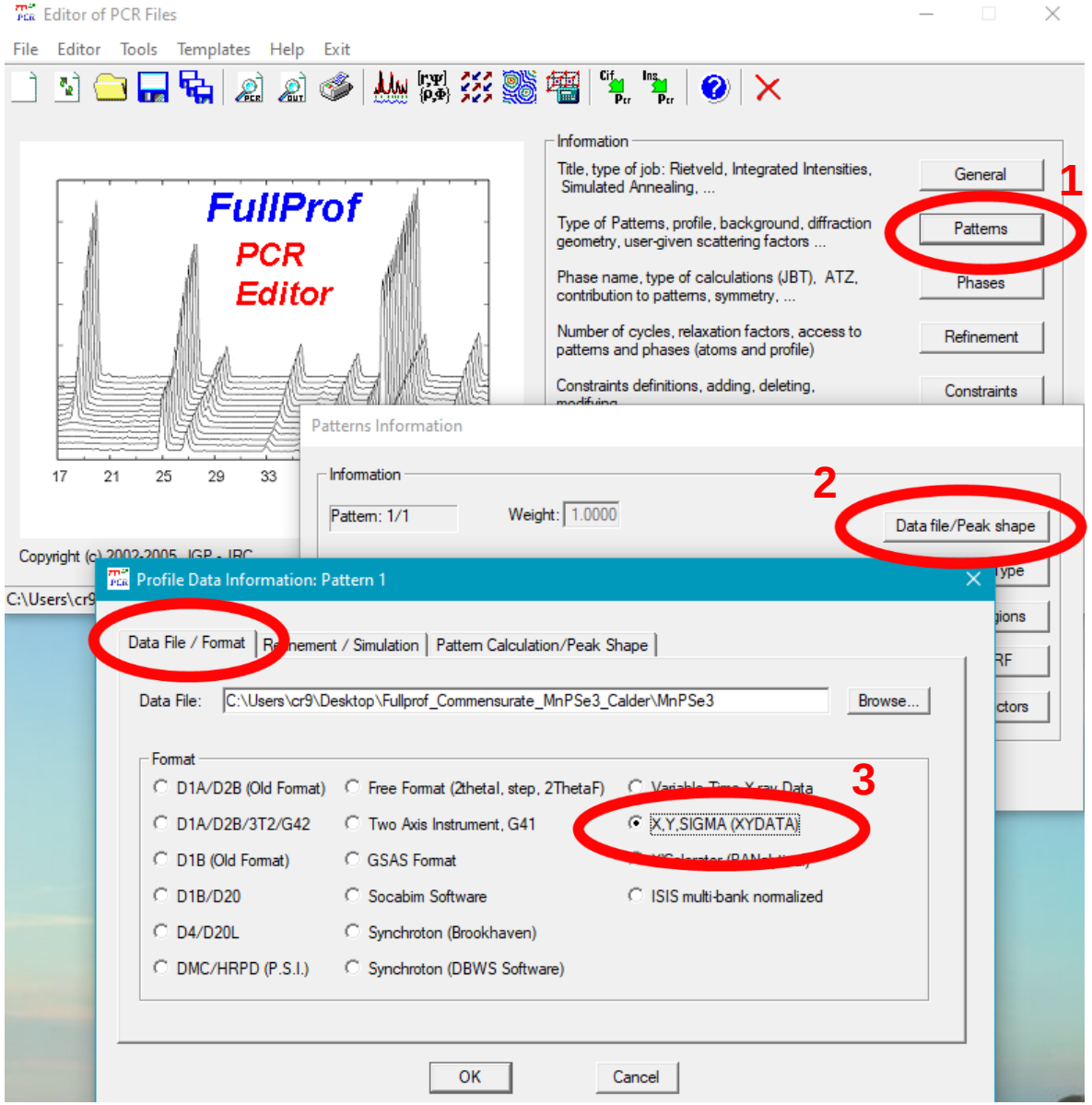
Step 1: Refine the crystal structure using FullProf

"**General**" tab has refinement of powder data as default. Can edit title as wanted.



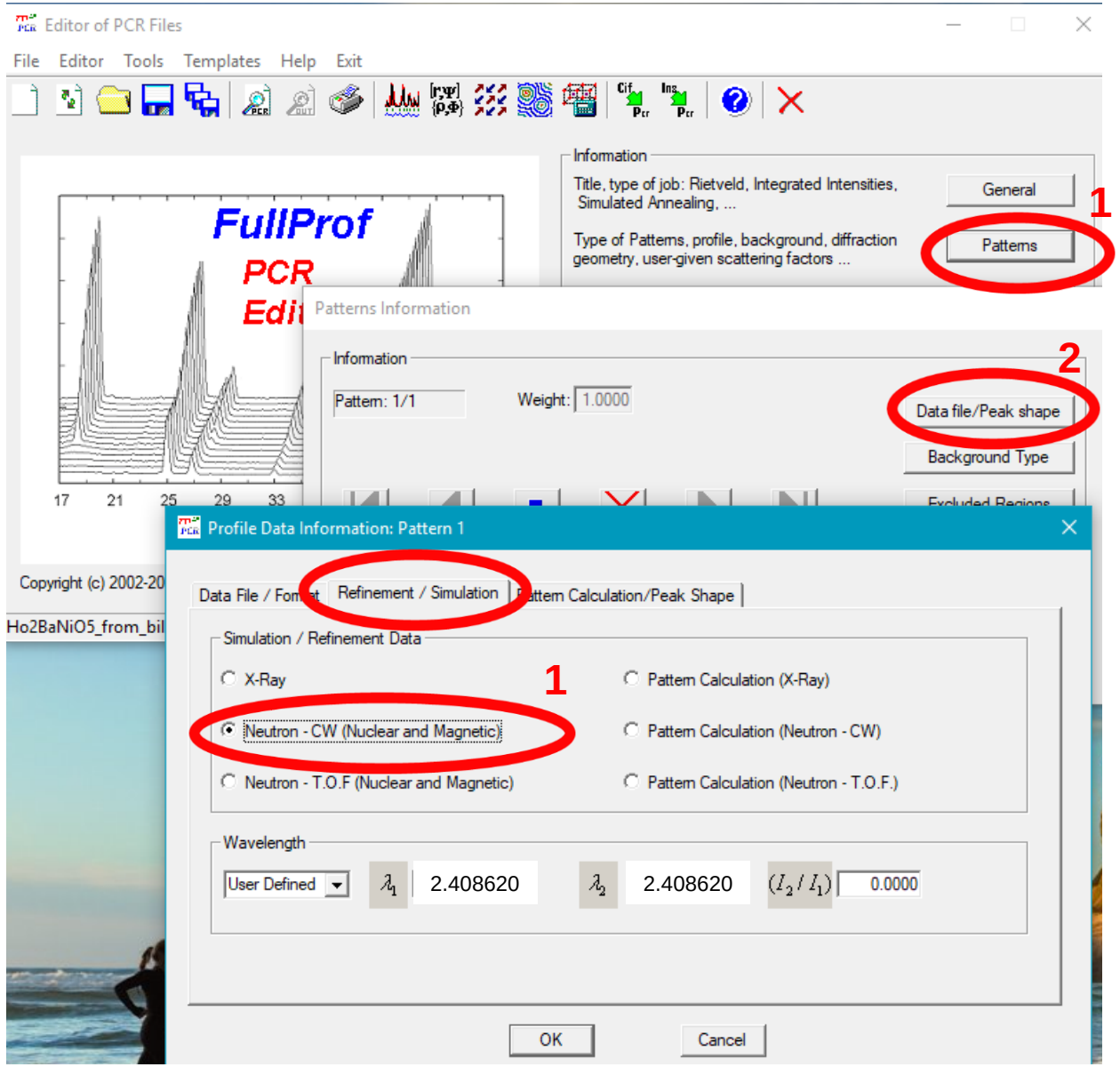
1. "**Patterns**" tab

- 2. Select the format of the data file Fullprof should refine.
- 3. X,YSIGMA (XYDATA).



Step 1: Refine the crystal structure using FullProf

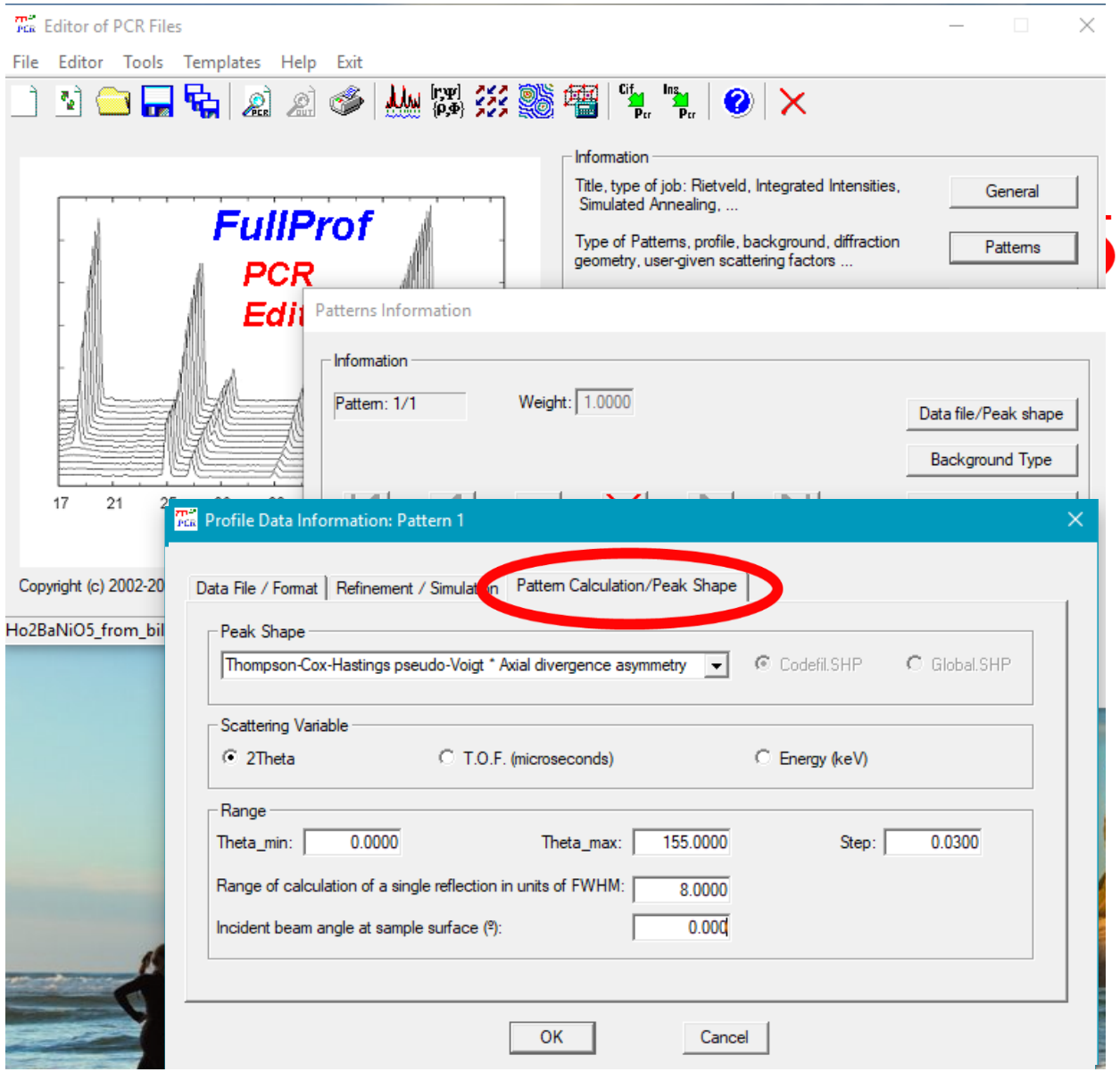
- Patterns → Data file/Peak Shape →Refinement/Simulation
- **[1]** Select "**Neutron – CW (nuclear and Magnetic)**"
- Wavelength is already set by irf file, 2.40862 in this example.



Step 1: Refine the crystal structure using FullProf

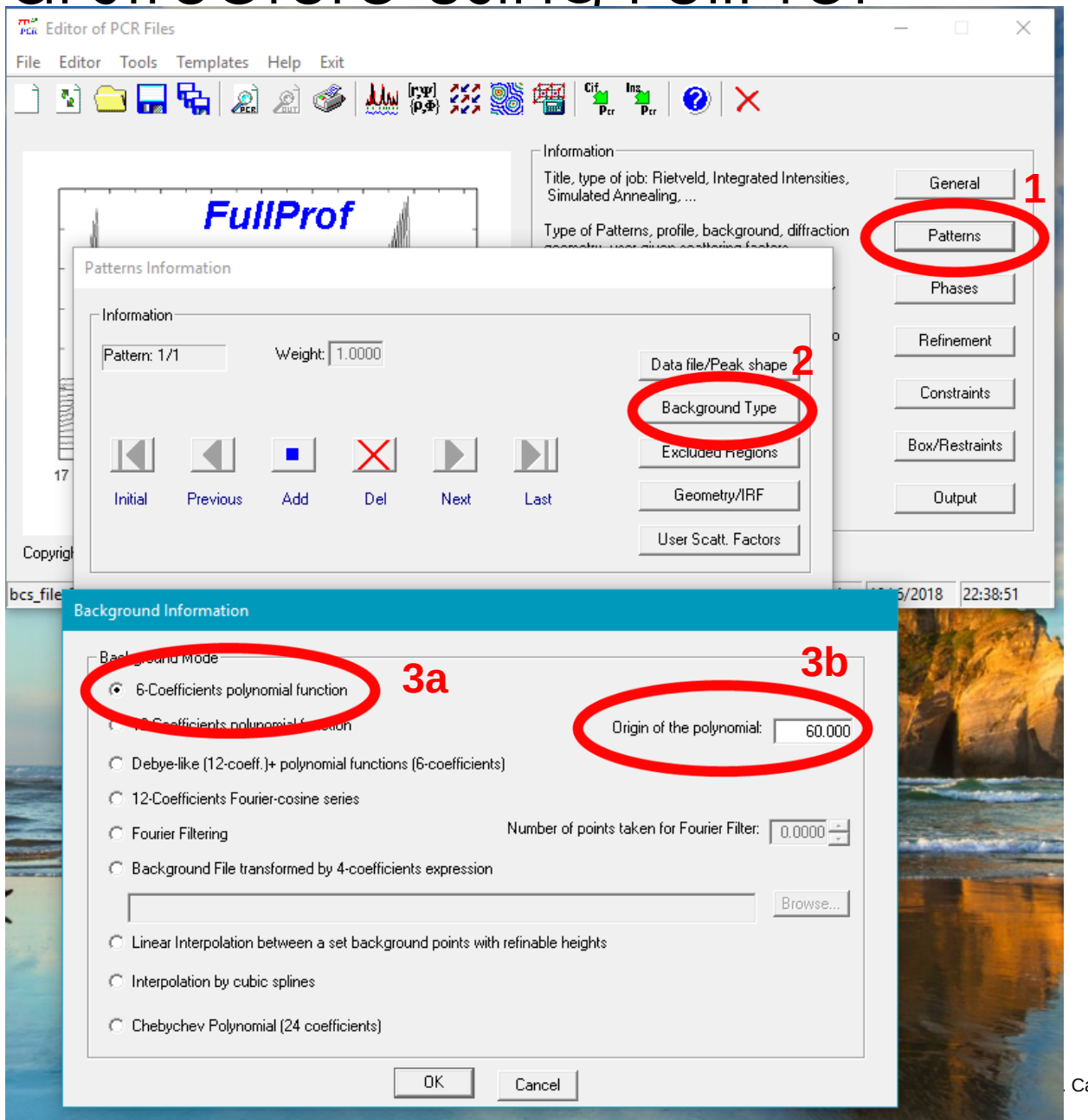
- Check final tab:
- Patterns → Data file/Peak Shape →Pattern Calculation/Peak Shape

- Peak shape is already loaded from irf file.



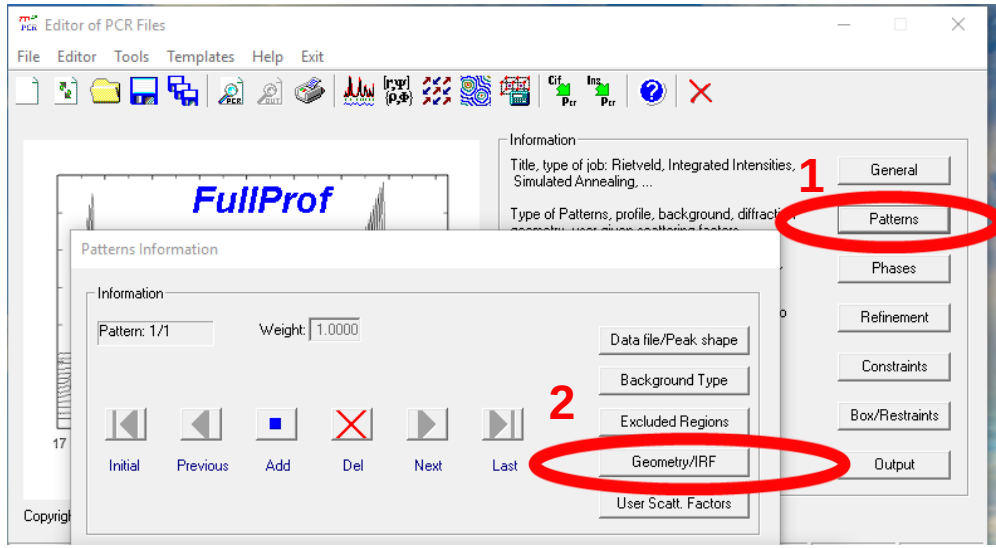
Step 1: Refine the crystal structure using FullProf

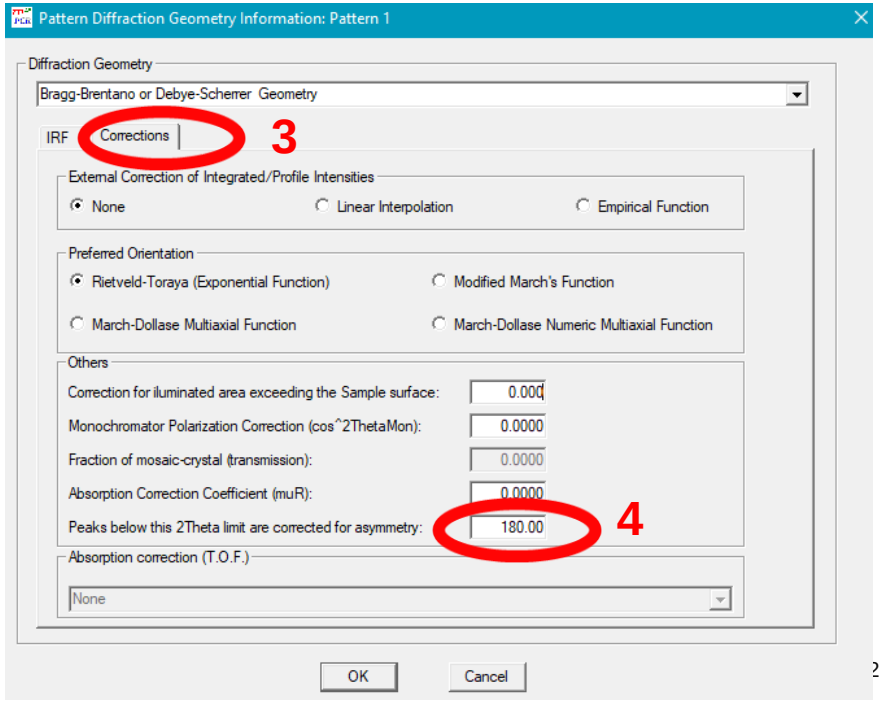
- Move to next tab down to select background type
- Patterns→ Background Type Check "6-coefficient"
- Put origin of polynomial at 60 for this example.



Step 1: Refine the crystal structure using FullProf

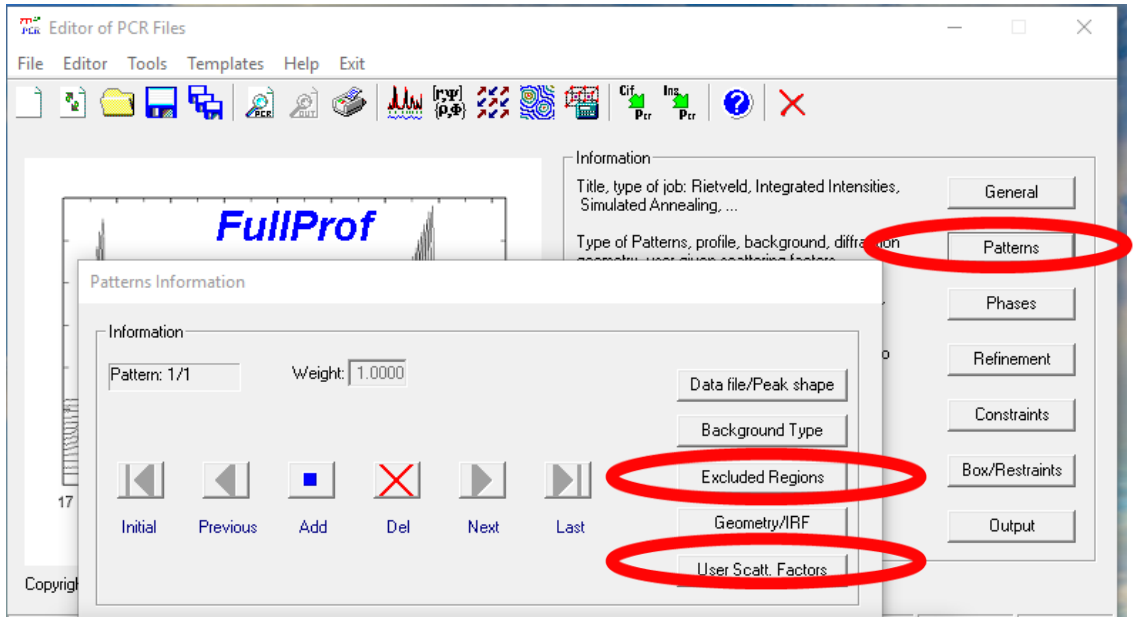
- No further editing should be needed of the remaining "Patterns" → "Geometry/irf":
  - The irf tab is populated since we loaded the file
  - Corrections tab **[3]**
  - **4.** Change asymmetry to 180. If this is kept 0 then you will get errors if you refine asymmetry.
  - *Can add absorption if needed. Check https://www.ncnr.nist.gov/resources/activation/*





Step 1: Refine the crystal structure using FullProf

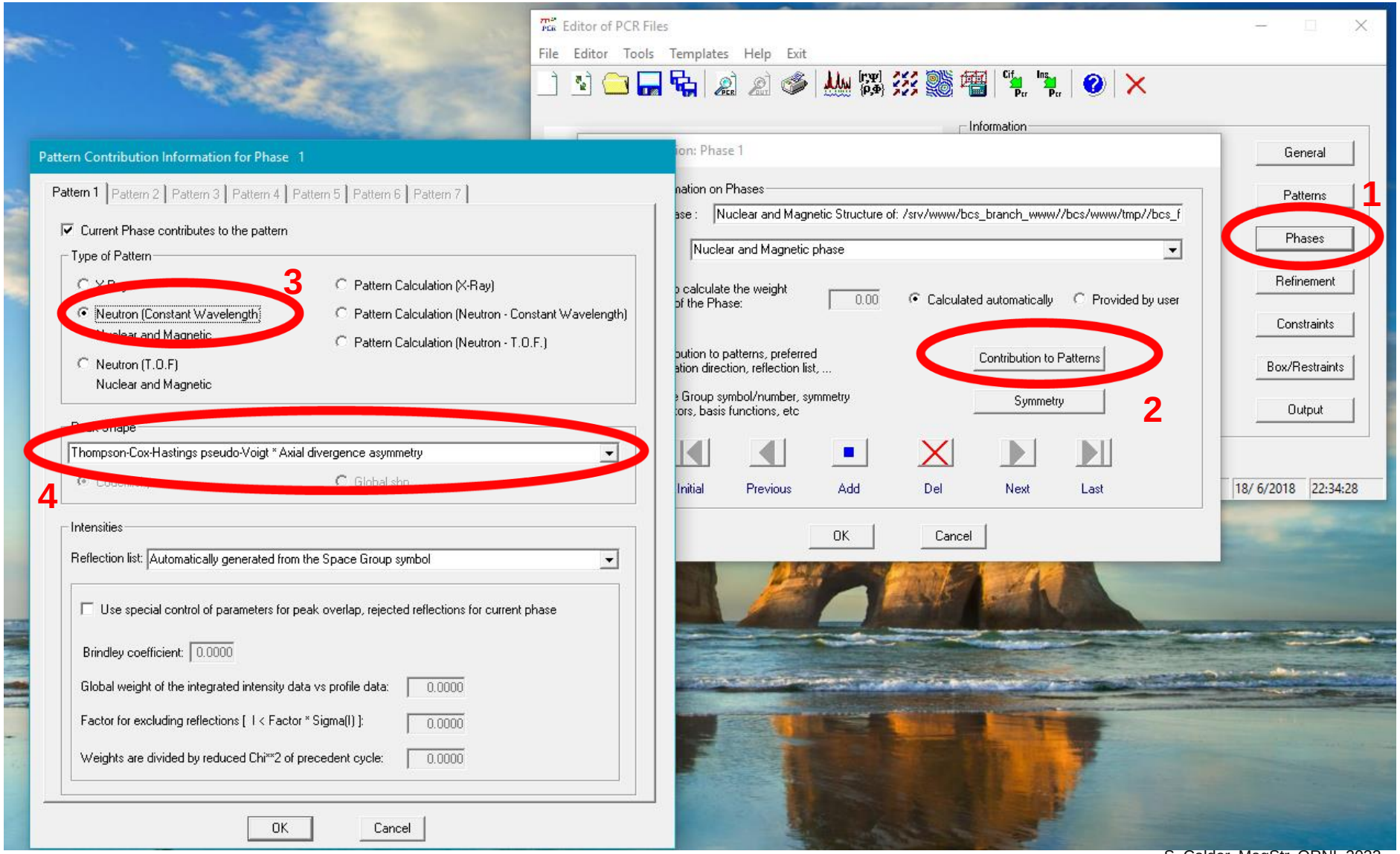
- No further editing should be needed of the remaining "Patterns" tabs:
  - Excluded Region
    Use with care, but can cut out background.
  - User Scatt. Factors
    This can be used to add e.g. a form factor that isn't tabulated



Step 1: Refine the crystal structure using FullProf

PHASES tab

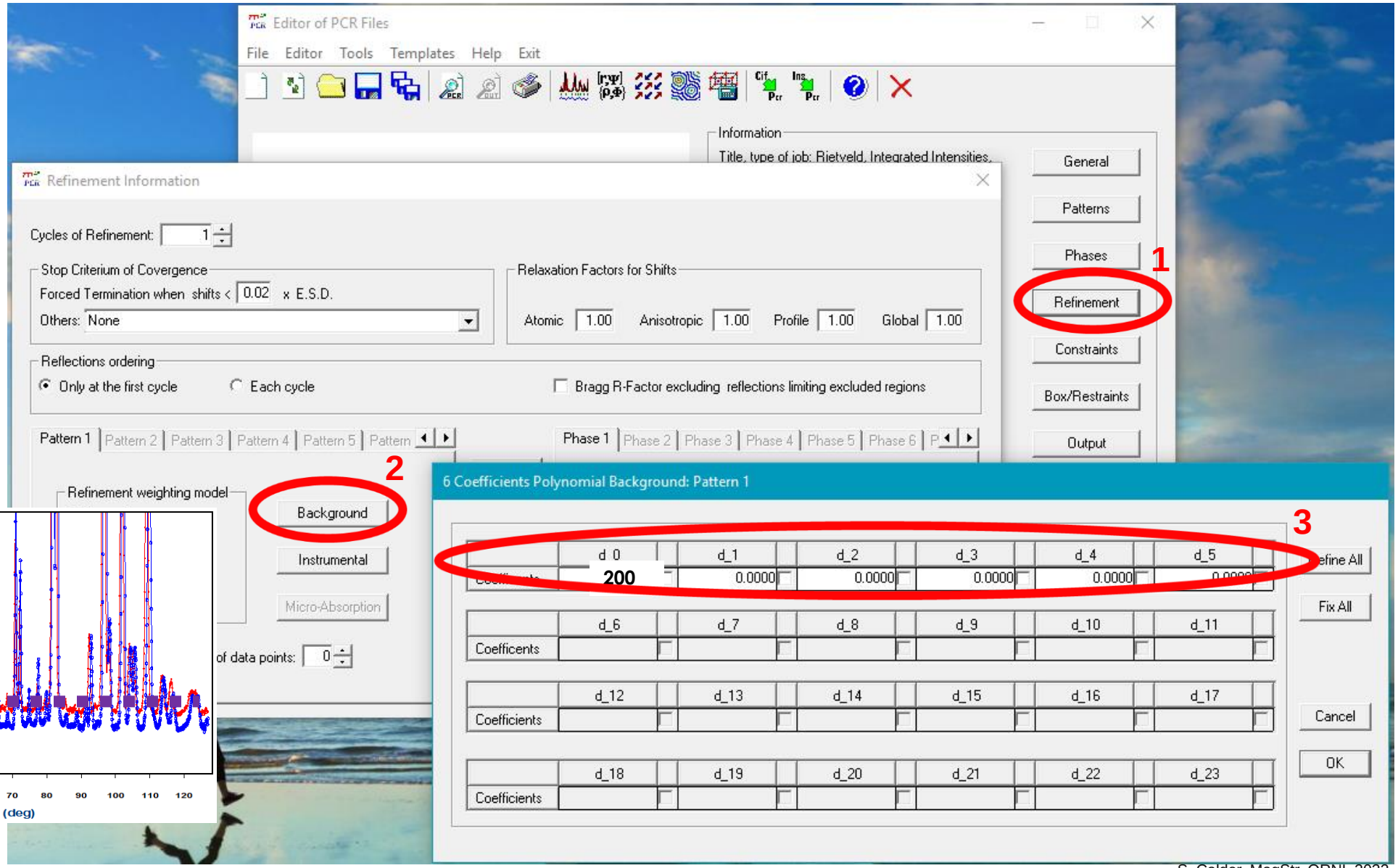
- Make phase contribute to refinement.
- **[1]** Phases→ **[2]** Contribution to Patterns→ **[3]** Neutron (constant wavelength)
- Set peak shape to "***Thompson-Cox-Hastings pseudo-Voigt***"



Step 1: Refine the crystal structure using FullProf

REFINEMENT tab:

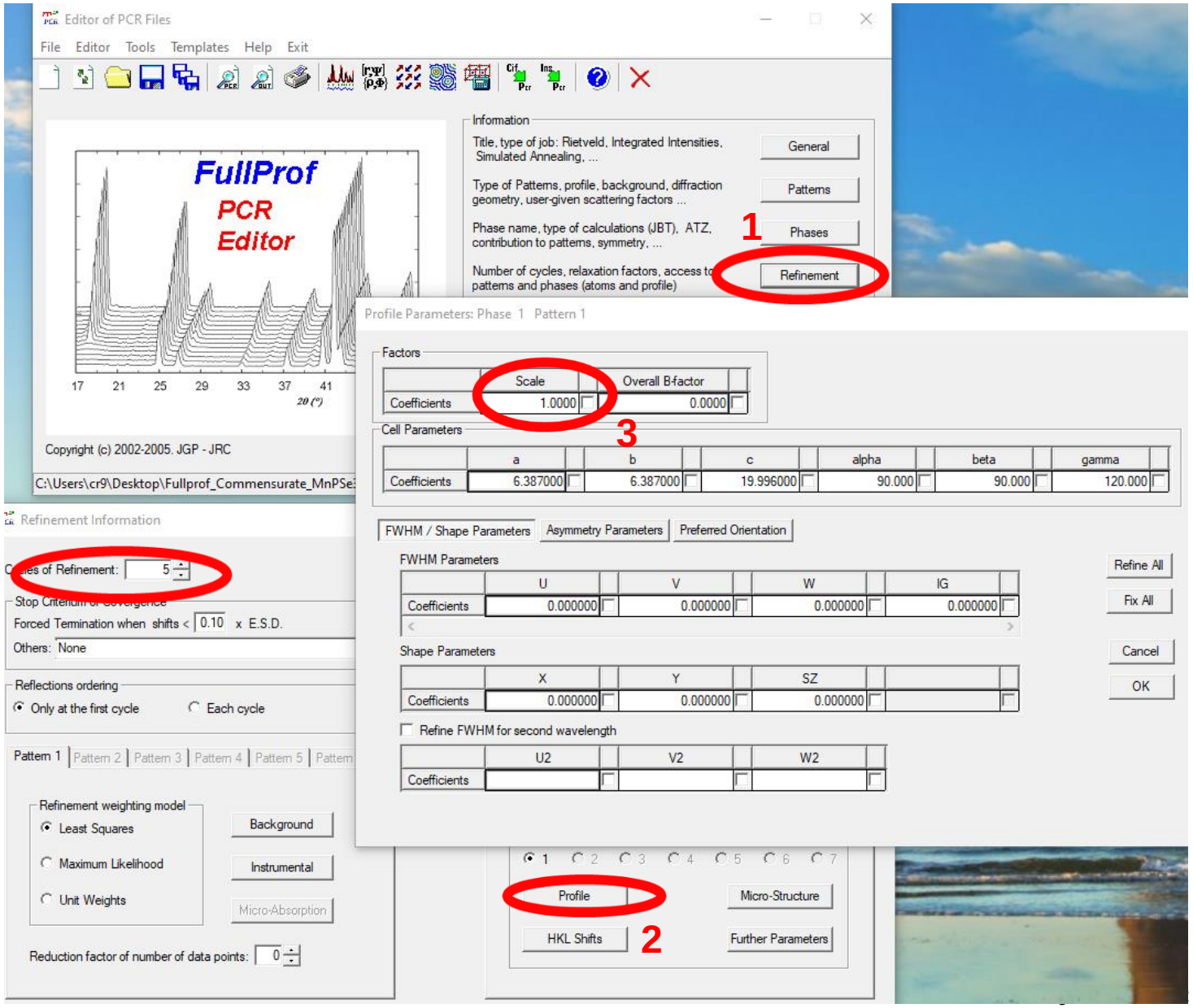
- Setting starting values for refinements
- Starting background value of 200 (check data)



Step 1: Refine the crystal structure using FullProf

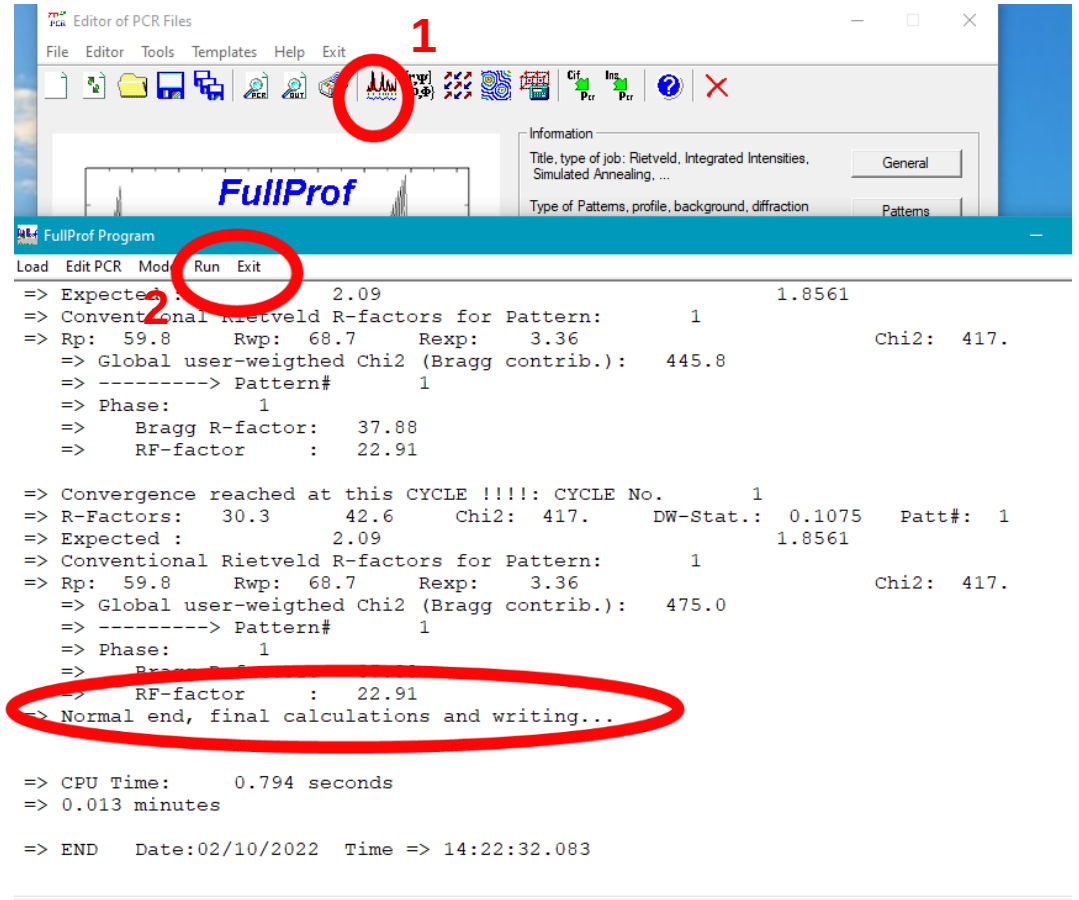
- **1.** Select "Refinement" tab again. Update "Cycle of Refinement" to 5
- From "Refinement" tab select: Refinement>Profile
- Change scale to 1.0

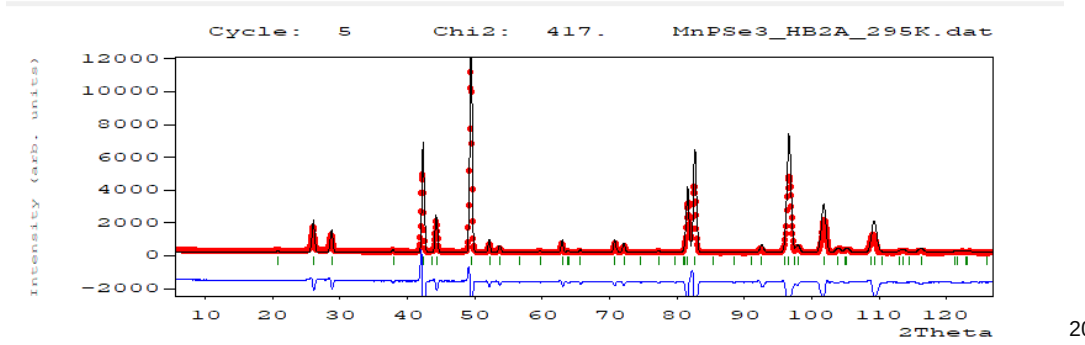
- Note U, V, W, X are set to zero. BUT, the values are being read from the .irf file. So if we refine these then they add on to the irf values.

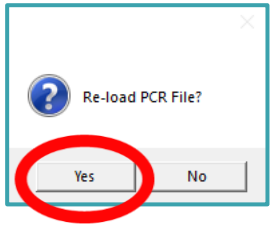


Step 1: Refine the crystal structure using FullProf

- **1.** Can now run the refinement
  Select the "*MnPSe3_HB2A_295K.dat*" data
  - Note: we have not set anything to refine yet. It is good to check your model is close to the data and makes sense before refining.
- **2.** Refinement runs for the number of cycles (in this case 5). You can repeat this by pushing run until "*Normal end, final calculation and writing…" shows rather than "Convergence not reached"*
- Select **yes** to save.
  If you're doing a refinement and the fit gets worse then you can select "no" and the starting values will remain.

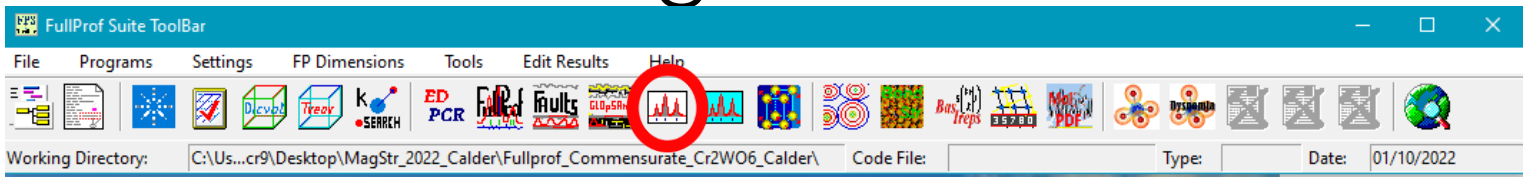


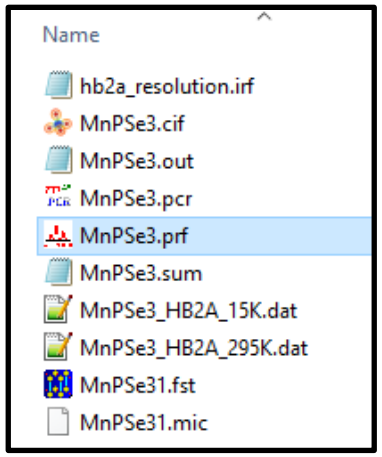


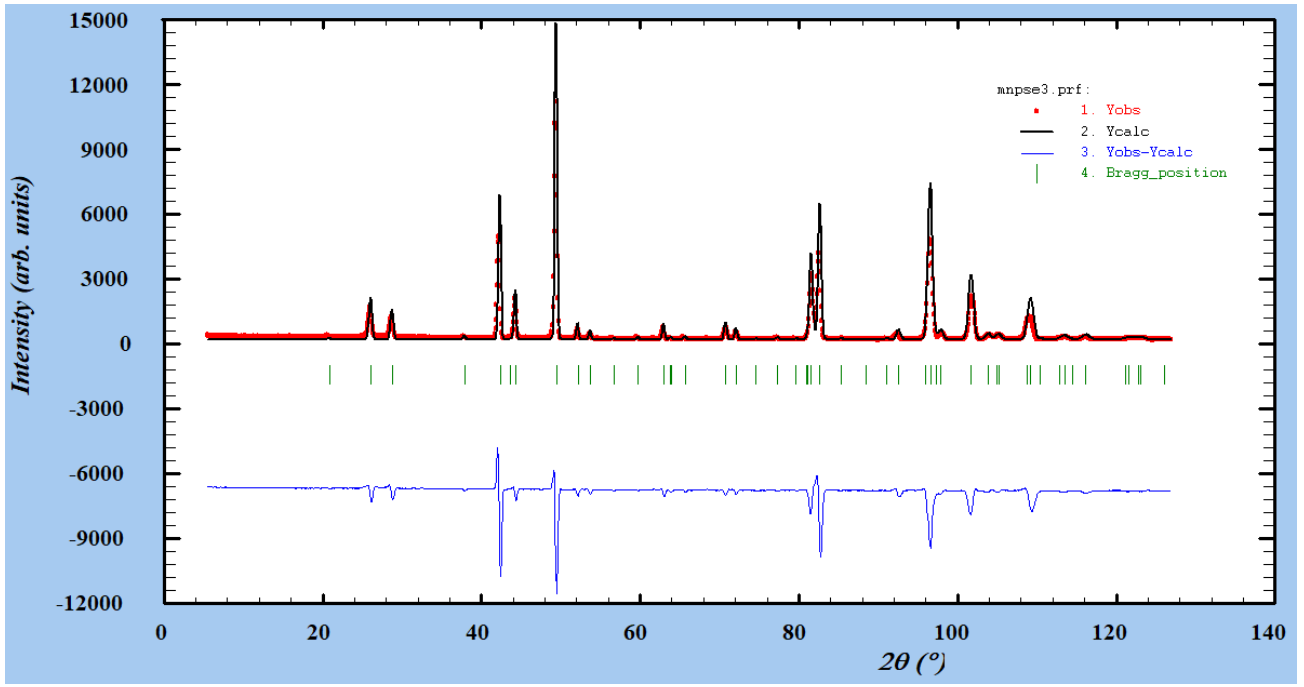


Step 1: Refine the crystal structure using FullProf

- Open the .prf file to check the fit.
- You might have to open the file after clicking on the toolbar. Or open it from the file directly.
- The peaks are fit at slightly different 2theta. So need to refine the lattice constants first. Also scale is a bit off. *NOTE: refine lattice constants before peak shape parameters.*





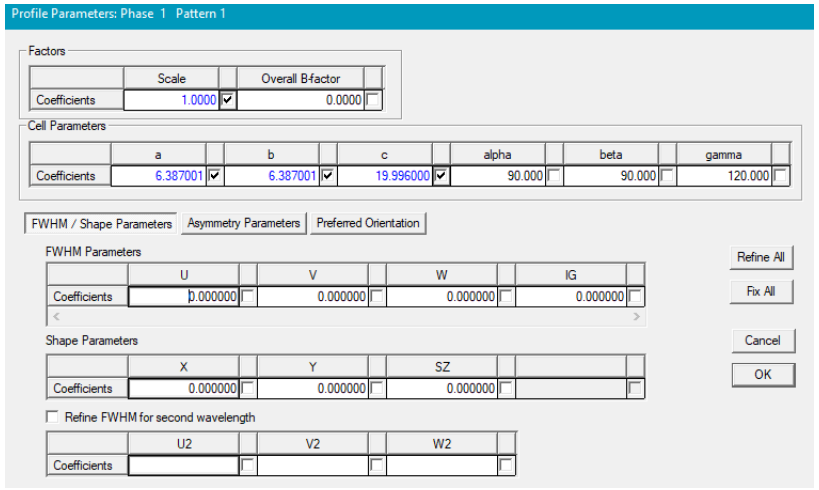


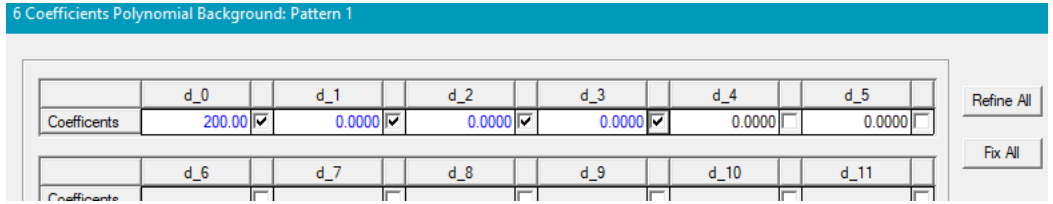
Step 1: Refine the crystal structure using FullProf

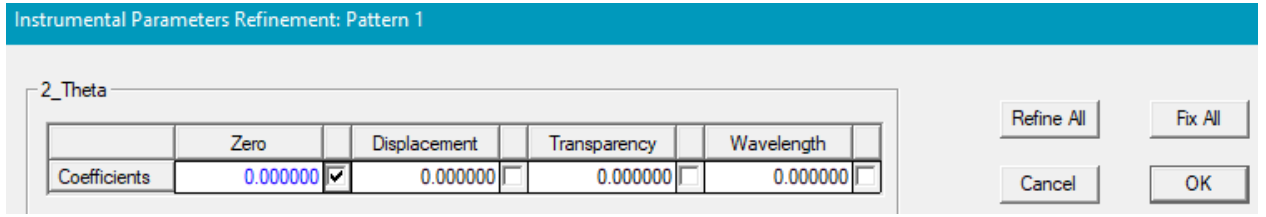
- Now allow the following to refine to fit the nuclear crystal:
  - Scale factor *(Refinement>Profile)*
  - Lattice parameters *(Refinement>Profile)*
  - Background *(Refinement>Background)*
  - 2theta zero. *(Refinement>Instrumental)*

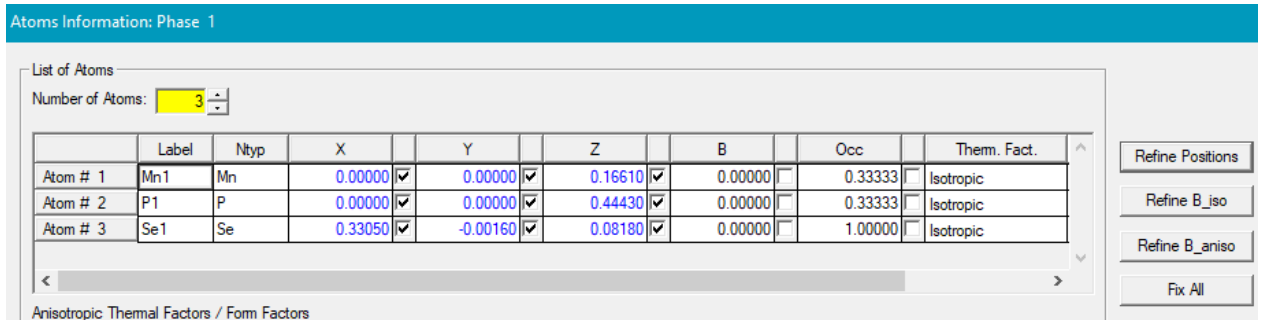
- Can also try to refine atomic parameters Refinement→Phase tab→Atoms
- If B is 0 in atom information, put in 0.3

Checking the box turns the number **blue** to show they are set to refine.
If they are **red** then they are constrained to refine with another parameter.
Looking in the text of the pcr file shows refined parameters by codes ending in 1.
Those constrained have the same code e.g. 11 and 11 or 511 and 511.









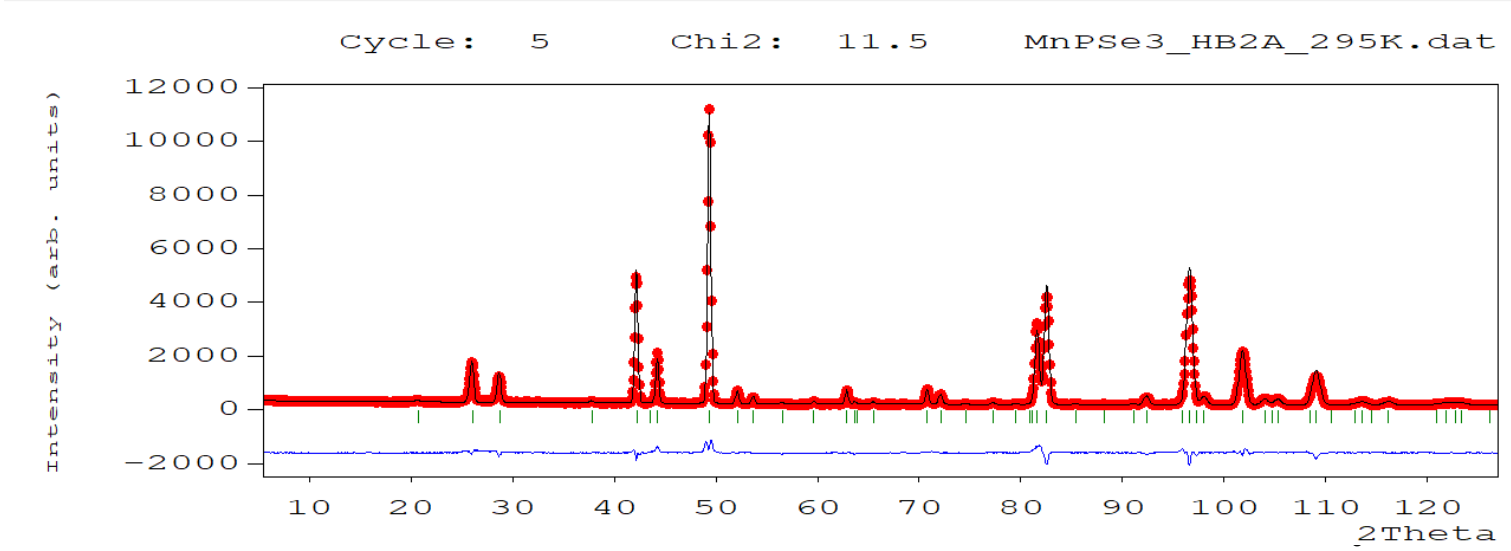
Step 1: Refine the crystal structure using FullProf

- The refinement to the 295K data is now close.
- You can add in refinements to the peak shape, since the sample may add some broadening beyond the parameters loaded in with the irf file.

FullProf Program

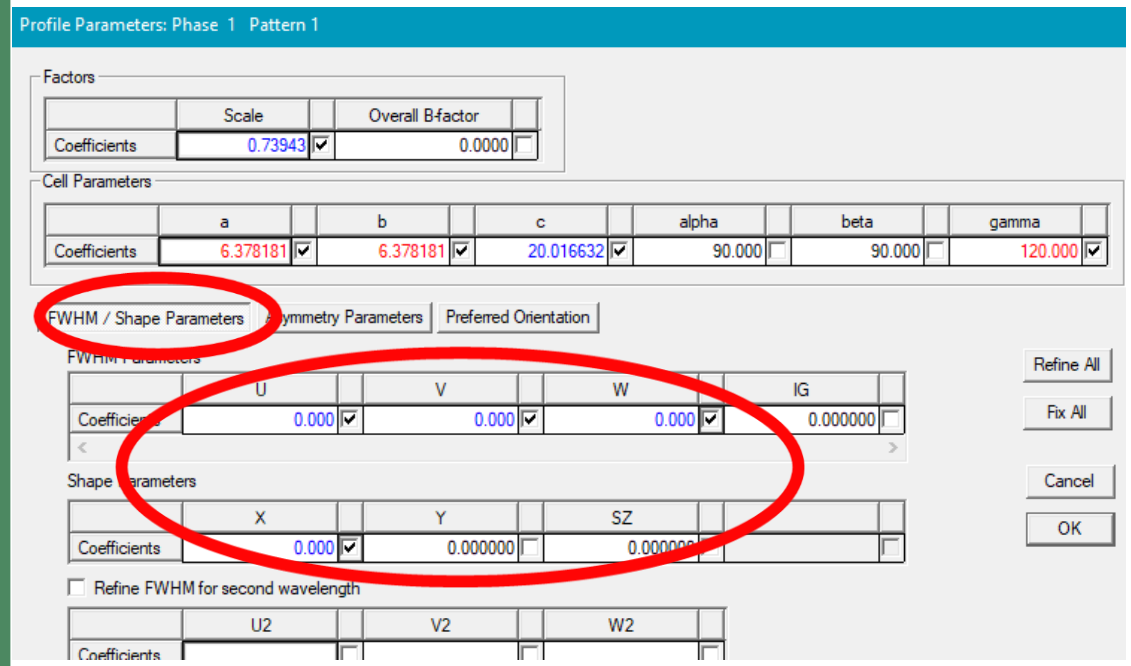
Load Edit PCR Mode Run Exit

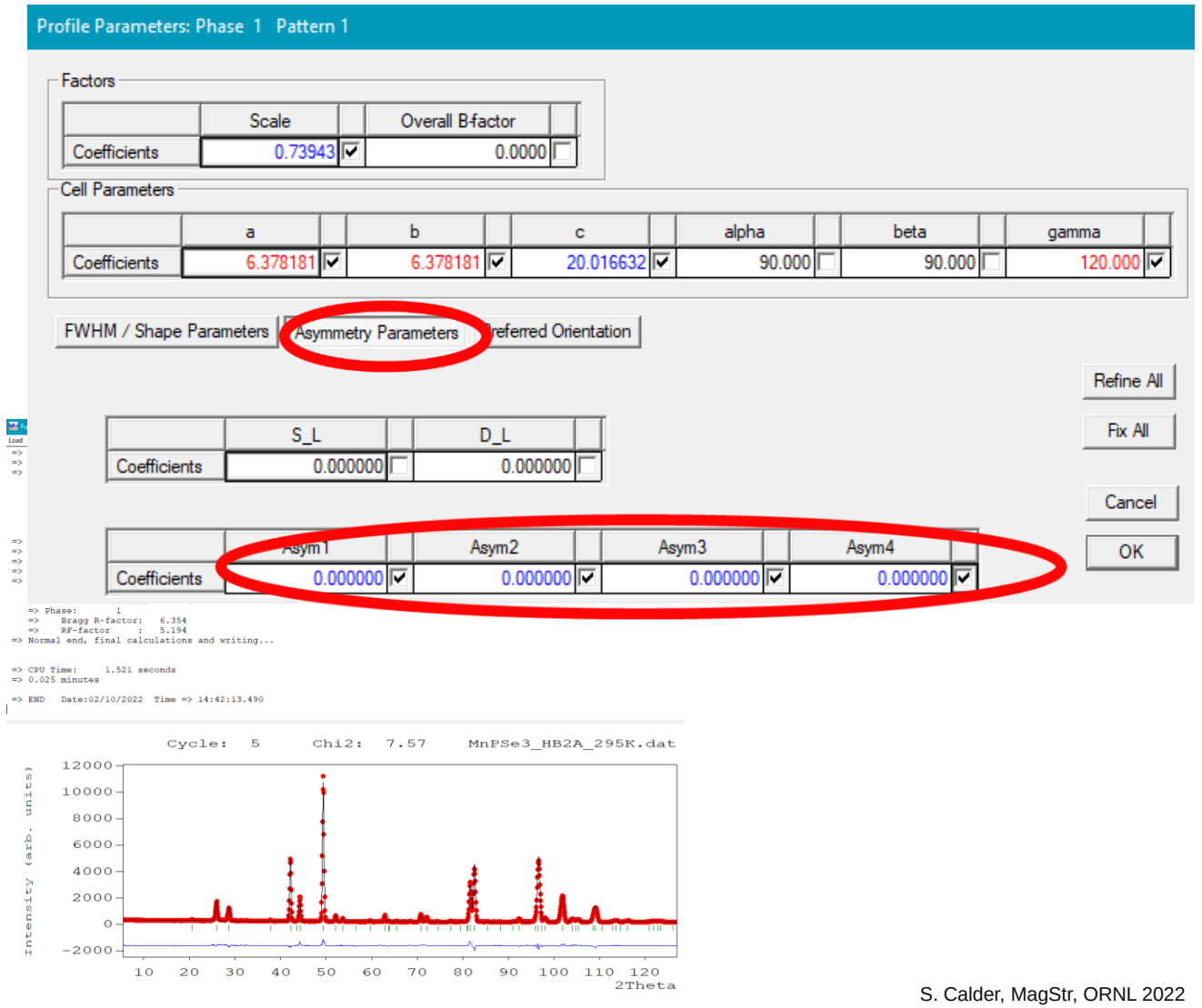
```
=> Expected :            2.08                                1.8701
=> Conventional Rietveld R-factors for Pattern:       1
=> Rp:  12.3     Rwp:  11.8     Rexp:    3.49                        Chi2:  11.5
   => Global user-weigthed Chi2 (Bragg contrib.):   12.73
   => ---------> Pattern#       1
   => Phase:       1
   =>    Bragg R-factor:   7.624
   =>    RF-factor     :   6.833

=> Convergence reached at this CYCLE !!!!: CYCLE No.       2
=> R-Factors:   5.21      7.04     Chi2:  11.5     DW-Stat.:  0.1937   Patt#:  1
=> Expected :            2.08                                1.8701
=> Conventional Rietveld R-factors for Pattern:       1
=> Rp:  12.3     Rwp:  11.8     Rexp:    3.49                        Chi2:  11.5
   => Global user-weigthed Chi2 (Bragg contrib.):   13.06
   => ---------> Pattern#       1
   => Phase:       1
   =>    Bragg R-factor:   7.624
   =>    RF-factor     :   6.833
=> Normal end, final calculations and writing...


=> CPU Time:     1.136 seconds
=> 0.019 minutes

=> END   Date:02/10/2022  Time => 14:37:37.528
```



Step 1: Refine the crystal structure using FullProf

- Refinement →Profile→ Refine U,V,W,X. Also refine asymmetry parameters.





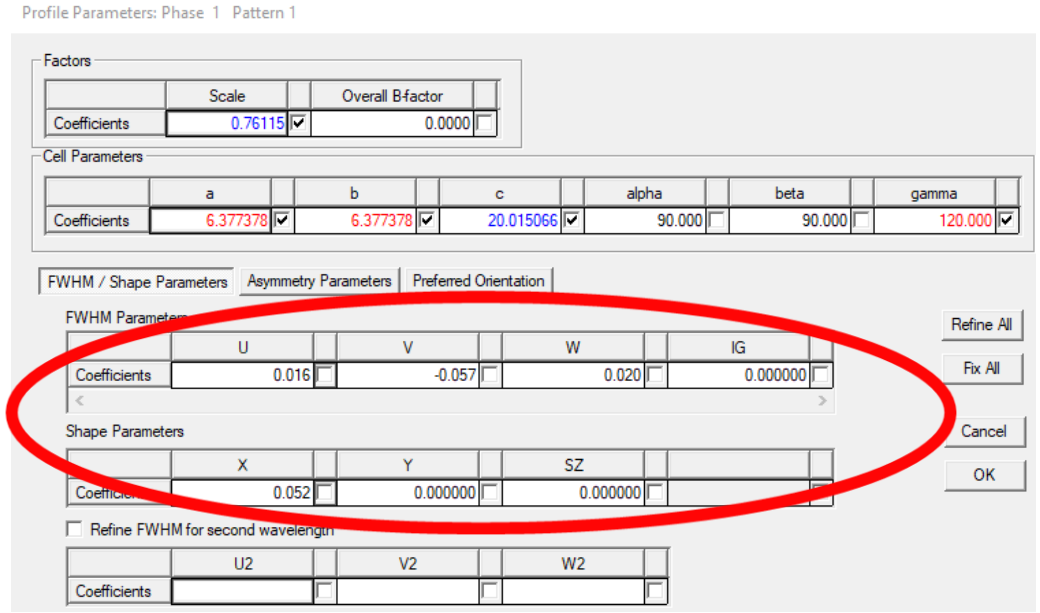
- The refinement to the 295K data is now very close.
- At this point you should copy the pcr file or rename it so you can go back to this point if the refinement crashes or you have issues.

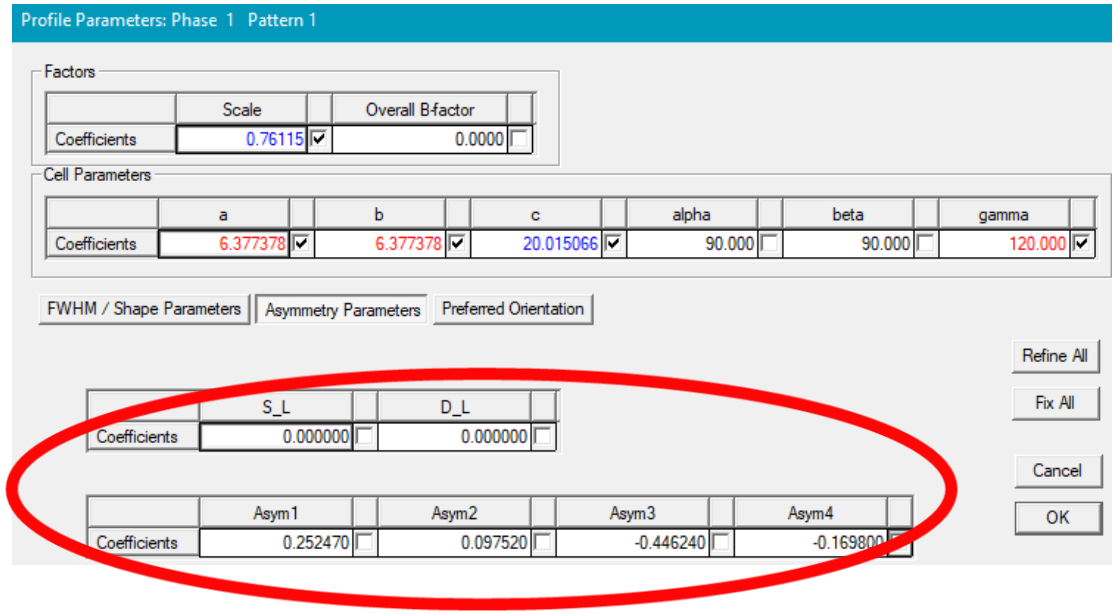
Step 1: Refine the crystal structure using FullProf

- The previous steps were refining the crystal structure at 295K, where there was no long range magnetic order.
- We now want to refine the crystal structure in the magnetically ordered region (15K).
- Then we will add on the magnetic phase based on that refinement in steps 2 and 3.

Step 1: Refine the crystal structure using FullProf

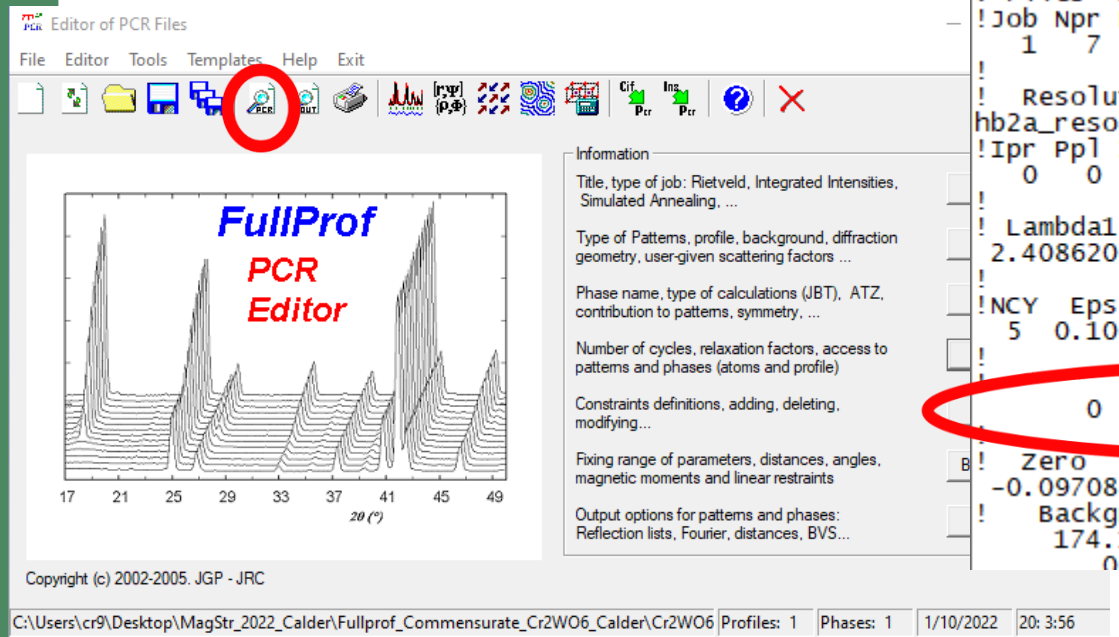
- Before refining the 4K data **FIRST TURN OFF PEAK SHAPE REFINEMENTS**. Since the peaks shift with temperature, refining both the lattice constants and peak shape may become unstable if all done at the same time.
  - The peak shapes should not change with temperature (we're measuring the same sample on the same instrument!)
  - The lattice constants and structural parameters would be expected to vary with temperature.

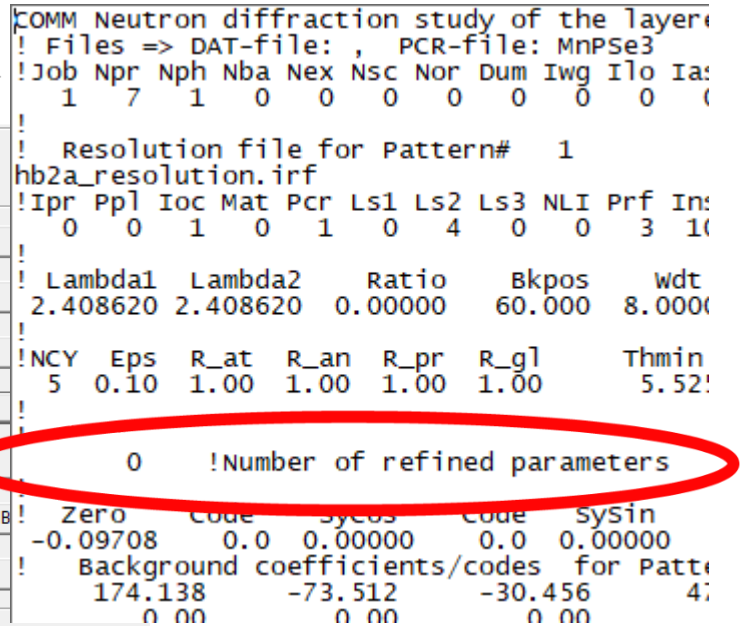


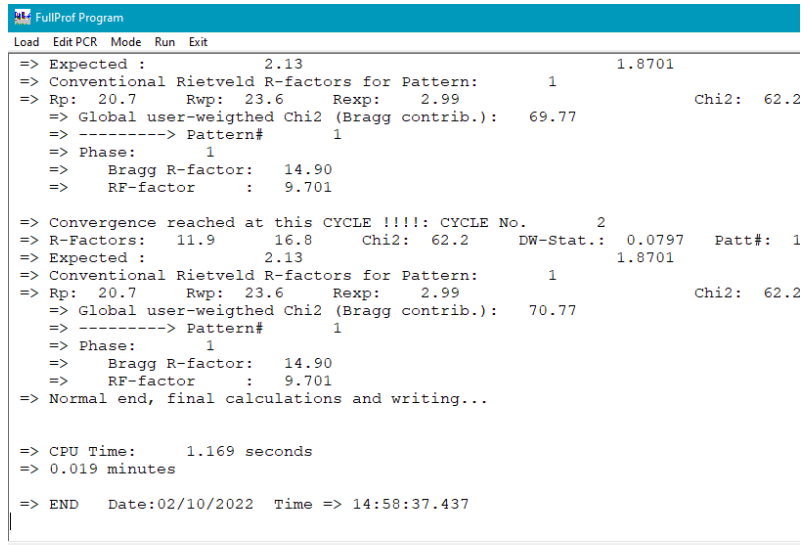


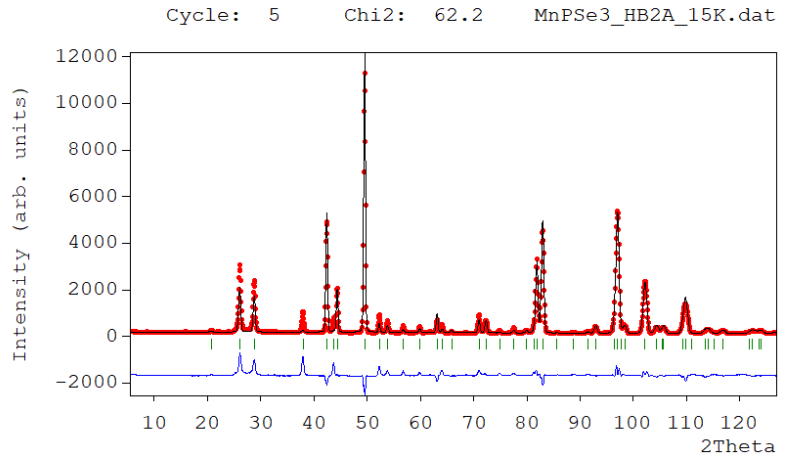
Step 1: Refine the crystal structure using FullProf

- Now refine the 4K data (**MnPSe3_HB2A_295K.dat**).
- NOTE: New peaks are present at low angle. These are the magnetic peaks. The structural model still captures the high angle peaks indicating there is no observable structure phase transition.
- So the poor fit is due to the magnetism, which we will fit in the following steps!
- **TURN OFF ALL THE REFINEMENT PARAMATERS.**
  *****Check in pcr text*****





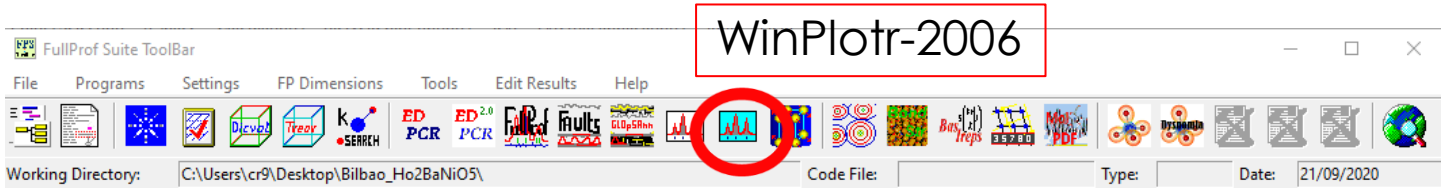




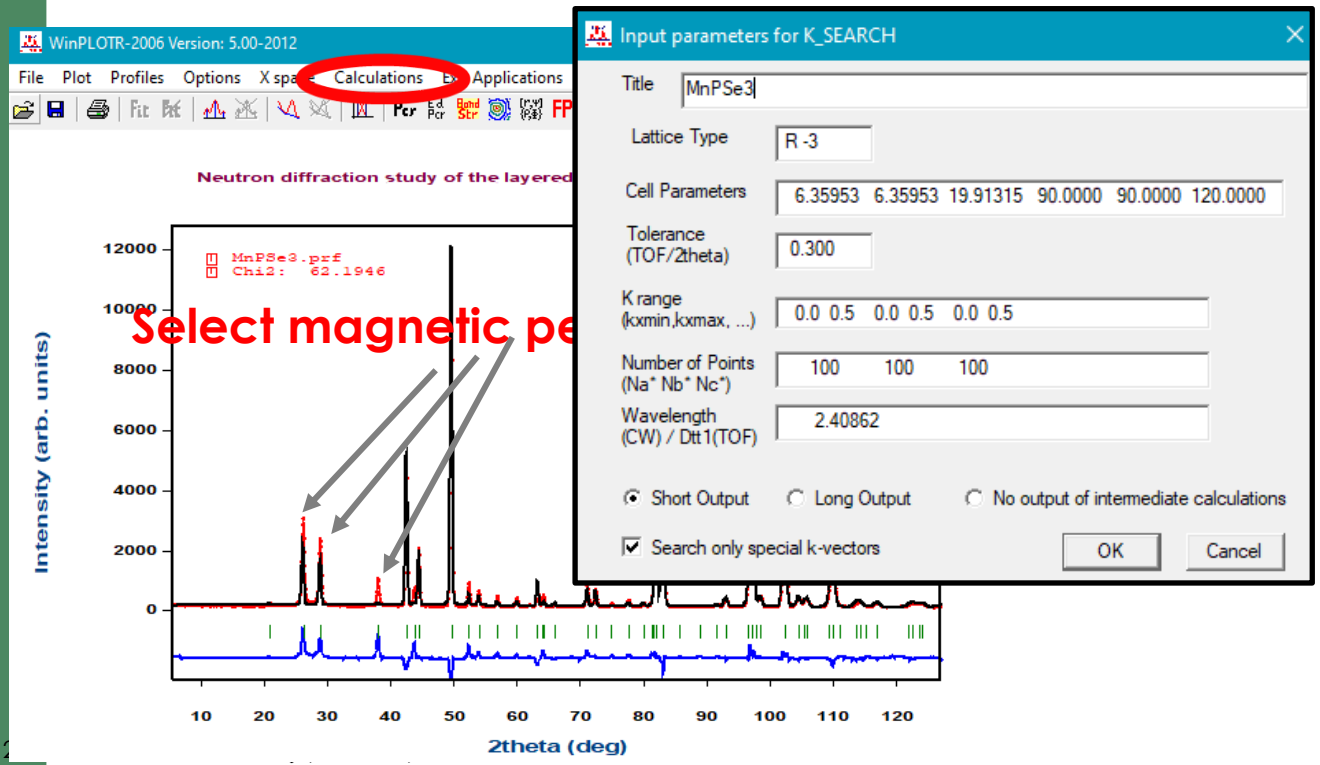
$MnPSe_3$

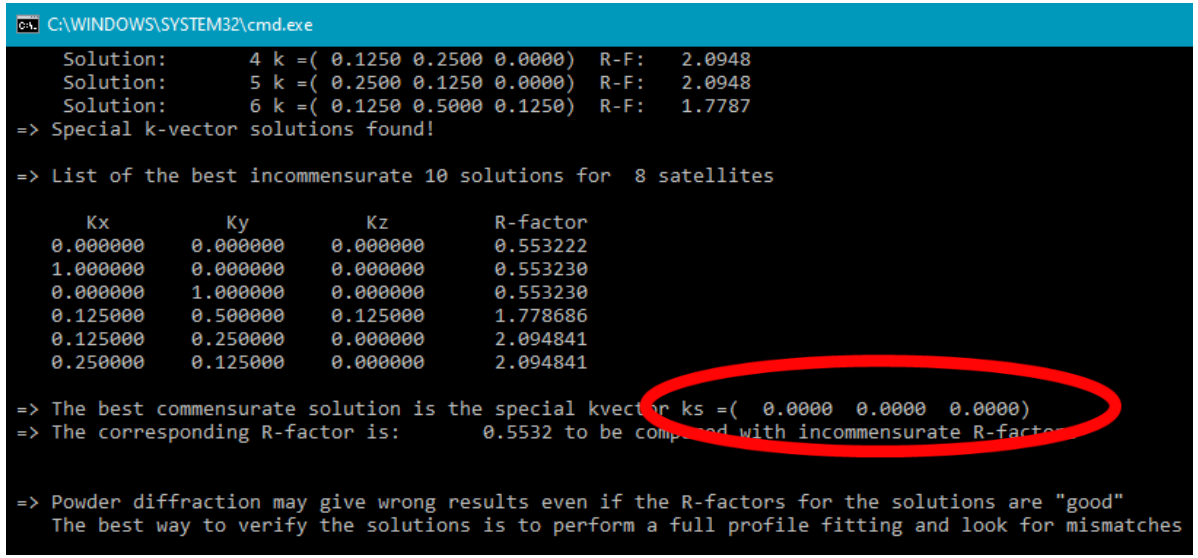
- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - **Step 2: Determine the k-vector by indexing the magnetic reflections using k-search**
  - Step 3: Create candidate magnetic models using SARAh
  - Step 4: Refine the magnetic model and nuclear phase in Fullprof.
  - Step 5: Check the magnetic model

Determine the k-vector



- Now the magnetic peaks need to be indexed to find the propagation vector that defines the magnetic unit cell.
- Open the refinement .prf file using **WinPlotr-2006 > File > Open Rietveld/Profile (*.prf)**
- Select “Calculations”> “peak detection”>”enable” . After enabling, go again to “Calculations”> “peak detection” > “insert peak”. After clicking on magnetic peaks, go to “save peaks” to save them as “K-search format”. Run k-search.





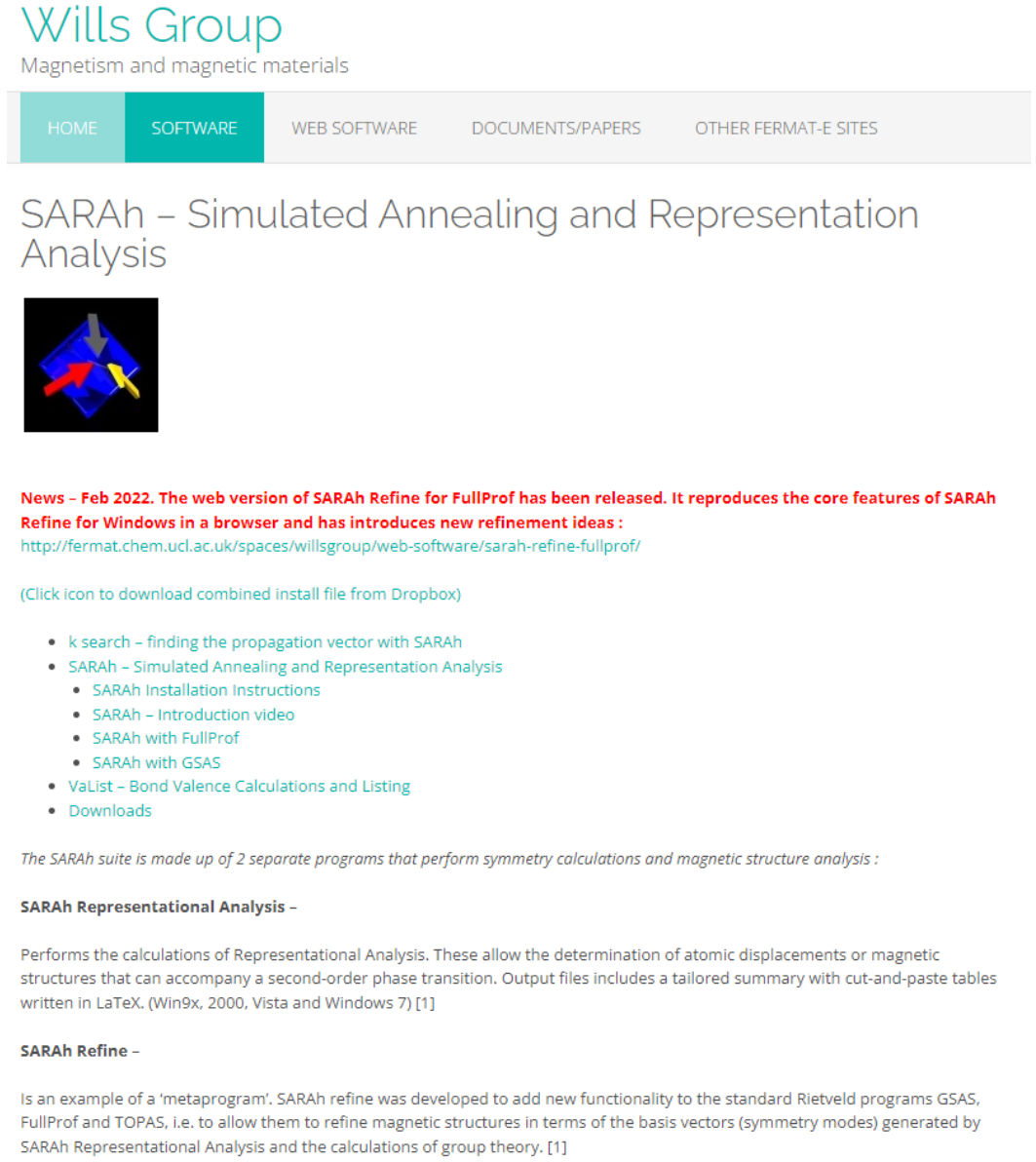
k=(0,0,0)

$MnPSe_3$

- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
  - **Step 3: Create candidate magnetic models using SARAh**
  - Step 4: Refine the magnetic model and nuclear phase in Fullprof.
  - Step 5: Visualize the magnetic model

Step 3: Create candidate magnetic models using SARAh

- We will use the SARAh software that is web based.
- There is an example of refininf Cr_2WO_6 using the stand alone software.
- Use the SARAh webrefine – Fullprof
- http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/



Step 3: Create candidate magnetic models using SARAh

Help with technical settings and refinement strategies http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/

Technical information: *(ASW version Oct 2022 :-)*

Open information about browser settings (this is really important!) –

Most browsers have a default directory where they save files. webSARAh-Refine works best if you can select the location for each download. This will enable you to save the template magnetic phase .pcr file to your current refinement directory or to edit a file by replacing it. If you use more than one browser, perhaps for compatibility or as part of your internet security, it may be easiest to have one set to using a default folder and another that asks each time for the download location.

Below are some settings for common browsers that turn on 'Ask where to save each file before downloading':

Google Chrome : 1) Click the menu icon (aka 3 dots) in the upper right corner of the Chrome window. 2) Select 'Settings'. 3) Scroll down and click 'Show Advanced Settings'. 4) Scroll down to the 'Downloads' section and click 'Ask where to save each file before downloading'

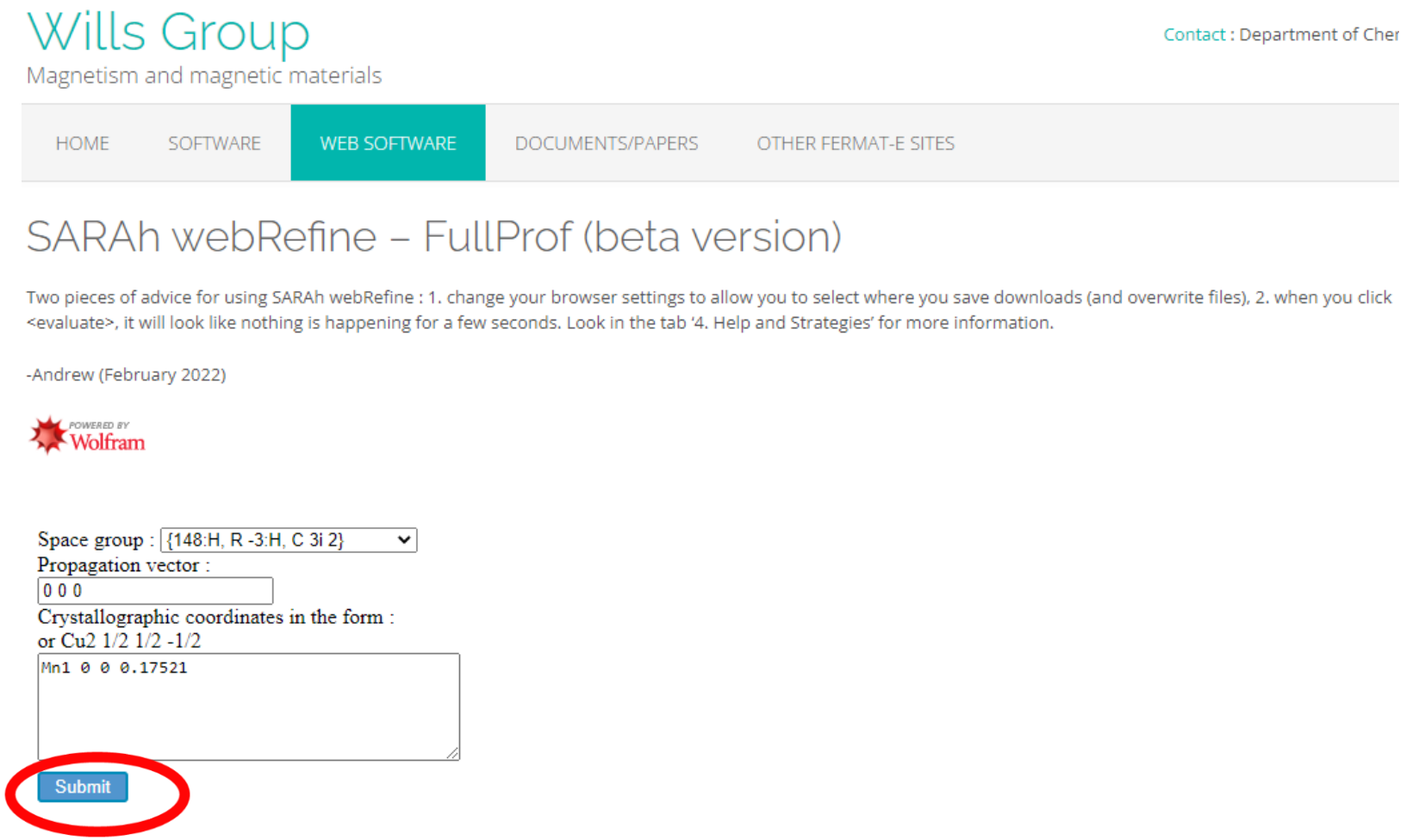
Firefox - Mac: 1) Select 'Firefox' → 'Preferences' from the menu bar. 2) In the General panel scroll down to 'Files and Applications'. 3) In Downloads select 'Always ask where to save files'

Firefox - Windows 11: 1) Click the menu button (the 3 line burger button) and select 'Settings'. 2) In the General panel scroll down to 'Files and Applications'. 3) In Downloads select 'Always ask where to save files'

Safari - Mac: 1) Select 'Safari' → 'Preferences' from the menu bar. 2) In the General tab, click the dropdown menu next to 'File download location'. 3) Select 'Ask for Each Download'

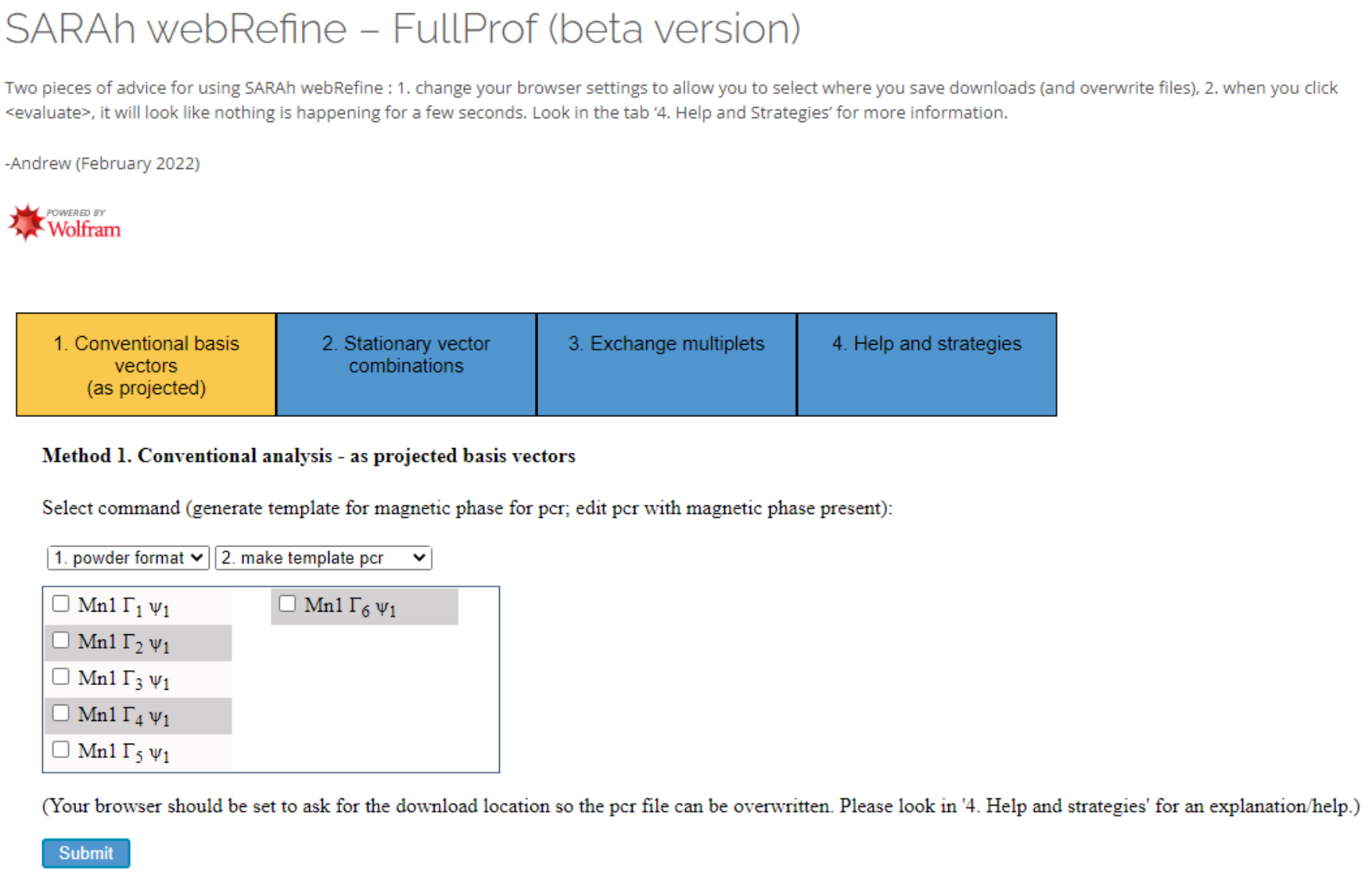
Step 3: Create candidate magnetic models using SARAh

- Input the crystal structure information. All we need is the
  - Space group
  - Propagation vector
  - Magnetic ion position

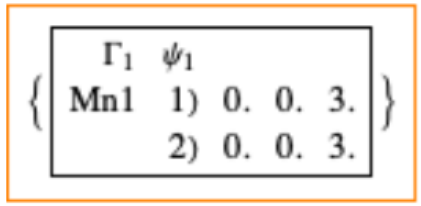


Step 3: Create candidate magnetic models using SARAh

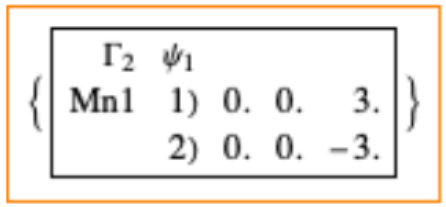
- SARAh produces the basis vectors.
- These can be viewed on the webpage
- See next slide for details



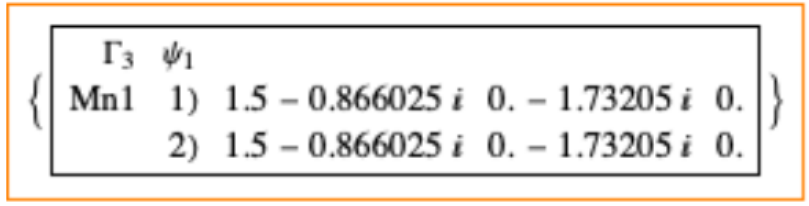
Step 3: Create candidate magnetic models using SARAh



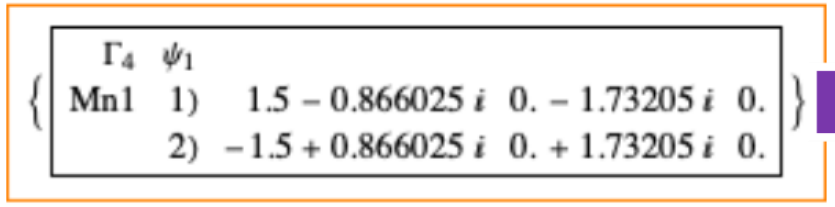
Γ_1: c-axis moment (FM)



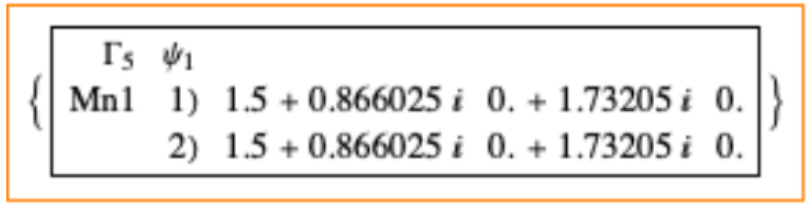
Γ_2: c-axis moment (AFM)



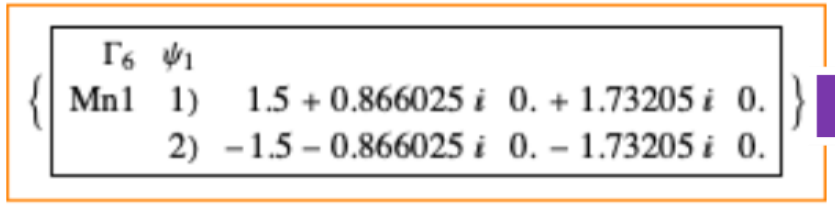
Γ_3: ab-plane moment (FM)



Γ_4: ab-plane moment (AFM)



Γ_5: ab-plane moment (FM)



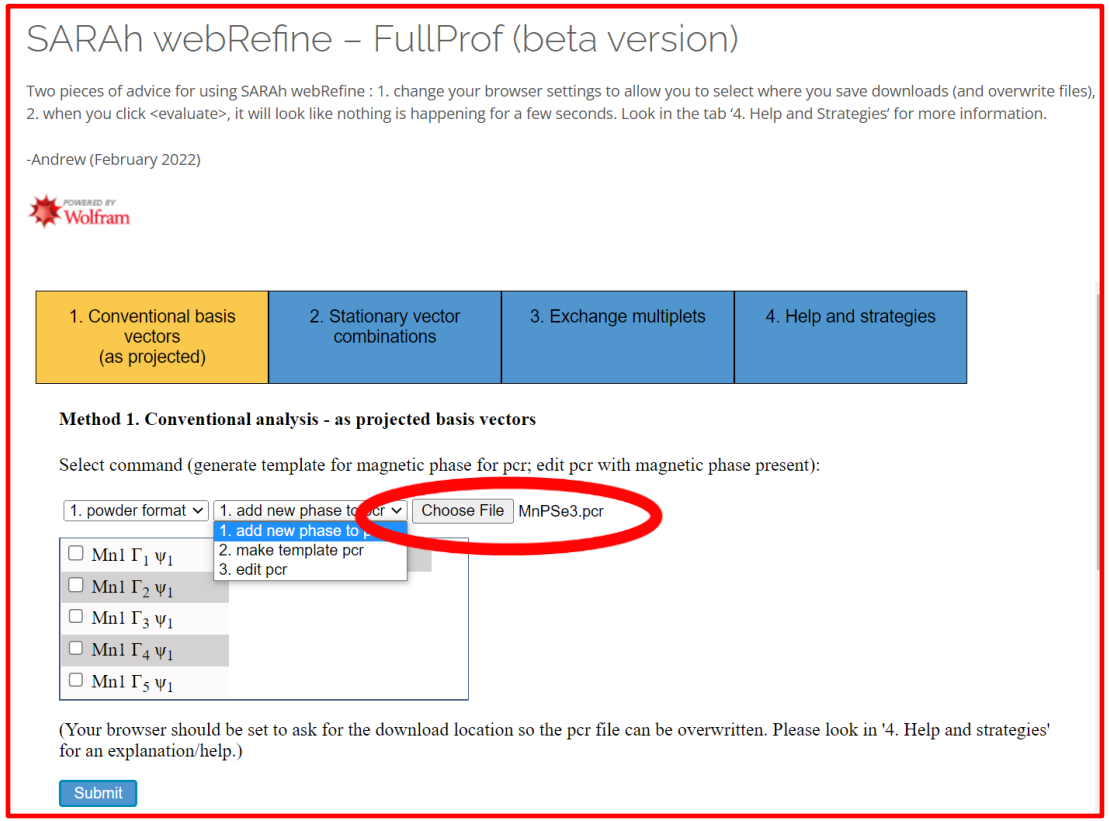
Γ_6: ab-plane moment (AFM)

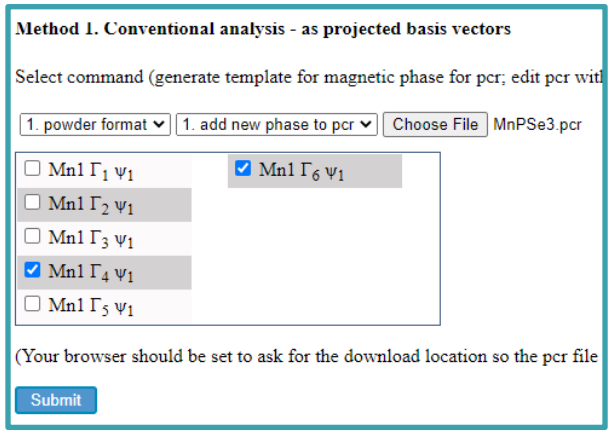
Most reflections have zero h or k. No change at (110). This suggests spins in ab-plane. Bulk measurements indicated AFM and no FM.

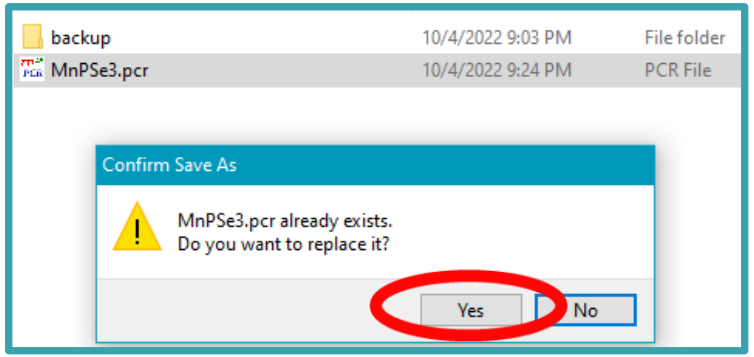
So try Γ_4 and Γ_6 first, but all should be checked.

Step 3: Create candidate magnetic models using SARAh

- There are different options for the magnetic phase output
  - 1. add new phase to pcr
  - 2. make template pcr
    This is similar to the older stand alone SARAh that creates the magnetic phase in a text file that needs to be pasted into the pcr. See other examples for this.
  - 3. edit pcr
- We'll use 1. to add the new magnetic phase directly to the pcr file.
- Choose the "MnPSe3.pcr" file from STEP 1
- Click submit and again choose the "MnPSe3.pcr" file to overwrite it
- "MnPSe3.pcr" should now contain the additional magnetic phase







OAK RIDGE National Laboratory | HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE

S. Calder, MagStr, ORNL 2022

$MnPSe_3$

- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
  - Step 3: Create candidate magnetic models using SARAh
  - **Step 4: Refine the magnetic model and nuclear phase in Fullprof.**
  - Step 5: Check the magnetic model

Step 4: Refine the magnetic model and nuclear phase in Fullprof

- The SARAh web interface directly adds the magnetic phase.
  - For representational analysis there are two phases
    - Nuclear
    - Magnetic
- *NOTE: The scale for nuclear and magnetic phase should always be kept the SAME.*

```
COMM Neutron diffraction study of the layered compounds Mn P Se3 and Fe P Se3
! Files => DAT-file: , PCR-file: MnPSe3
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
  1  7  2  0  0  0  0  0  0  0  1  0  0  0  0  0  0  1
!
! Resolution file for Pattern#  1
hb2a_resolution.irf
!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 10  0  0  0  0  0  0
!
! Lambda1 Lambda2  Ratio  Bkpos  Wdt  Cthm   muR  AsyLim  Rpolarz 2nd-muR -> Patt# 1
 2.408620 2.408620 0.00000  60.000 8.0000 0.0000 0.0000 180.00  0.0000 0.0000
!
!NCY Eps R_at R_an R_pr R_gl   Thmin    Step    Thmax  PSD  Sent0
 5 0.10 1.00 1.00 1.00 1.00   5.5250  0.064983  155.0000  0.000  0.000
!
!
    0  !Number of refined parameters
!
! Zero  Code  SyCos  Code  SySin  Code Lambda   Code MORE ->Patt# 1
 -0.09708  0.0 0.00000  0.0 0.00000  0.0 0.000000  0.00  0
!  Background coefficients/codes for Pattern# 1 (Polynomial of 6th degree)
   174.138   -73.512   -30.456   47.759    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:  0.0000
!-------------------------------------------------------------------------------
Neutron diffraction study of the layered compounds Mn P Se3 and Fe P Se3
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth    ATZ  Nvk Npr More
  3  0  0 0.0 0.0 1.0  0  0  0  0  0    1936.726  0  7  0
!
!
R -3          <--Space group symbol
!Atom  Typ    X     Y     Z    Biso    Occ   In Fin N_t Spc /Codes
Mn1  Mn   0.00000 0.00000 0.17521 0.30000  0.33333  0  0  0  0
          0.00    0.00    0.00    0.00    0.00
P1   P    0.00000 0.00000 0.44848 0.30000  0.33333  0  0  0  0
          0.00    0.00    0.00    0.00    0.00
Se1  Se   0.32983 -0.01193 0.08193 0.30000  1.00000  0  0  0  0
          0.00    0.00    0.00    0.00    0.00
!-------> Profile Parameters for Pattern #  1 ----> Phase #  1
! Scale      Shape1   Bov   Str1   Str2   Str3  Strain-Model
 0.8798522    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
   0.015521  -0.057189   0.020187   0.052448   0.000000   0.000000   0.000000    0
     0.00      0.00      0.00      0.00      0.00      0.00      0.00
!    a        b        c      alpha    beta     gamma    #Cell Info
  6.359528  6.359528 19.913155 90.000000 90.000000 120.000000
  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
! Pref1  Pref2   Asy1   Asy2   Asy3   Asy4   S_L   D_L
 0.00000 0.00000 0.25247 0.09752 -0.44624 -0.16980 0.00000 0.00000
   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00
!
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:    46.66
!-------------------------------------------------------------------------------
Template magnetic phase by SARAh - web Representational Analysis
!
!Nat Dis Ang 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    1936.726  1  7  0
!
!
R -1                      <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
    2    1    1    -1    2
! Real(0)-Imaginary(1) indicator for Ci
  0 0
!
SYMM X , Y , Z
BASR  1.5      0      0       1.5     0      0
BASI  0.866    1.732  0      -0.866  -1.732  0
SYMM 4/3 - X , 2/3 - Y , 2/3 - Z
BASR -1.5      0      0      -1.5     0      0
BASI -0.866   -1.732  0       0.866   1.732  0
!Atom Typ Mag  Vek     X       Y       Z       Biso    Occ     C1      C2      C3
!      C4      C5      C6      C7      C8      C9      MagPh
Mn1  MMN5  1   0          0       0 0.17521 .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   0.00000
     0.00    0.00    0.00    0.00    0.00    0.00    0.00
!-------> Profile Parameters for Pattern #  1 ----> Phase #  1
! Scale      Shape1   Bov   Str1   Str2   Str3  Strain-Model
 0.8798522    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
   0.015521  -0.057189   0.020187   0.052448   0.000000   0.000000   0.000000    0
     0.00      0.00      0.00      0.00      0.00      0.00      0.00
!    a        b        c      alpha    beta     gamma    #Cell Info
  6.359528  6.359528 19.913155 90.000000 90.000000 120.000000
  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
! Pref1  Pref2   Asy1   Asy2   Asy3   Asy4   S_L   D_L
 0.00000 0.00000 0.25247 0.09752 -0.44624 -0.16980 0.00000 0.00000
   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00
! Propagation vectors:
0.     0.     0.          Propagation Vector  1
0.000000    0.000000    0.000000
```

Nuclear phase

Magnetic phase

Step 4: Refine the magnetic model and nuclear phase in Fullprof

- The basis vectors can be seen in the magnetic phase.
- In this case we loaded two: ☑ Mn1 Γ_4 ψ_1 ☑ Mn1 Γ_6 ψ_1
- To give these basis vectors magnitude put values in the coefficients C1 and C2

Magnetic phase

Mn1 Γ_4 ψ_1

Mn1 Γ_6 ψ_1

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:    46.66
!-------------------------------------------------------------------------------
Template magnetic phase by SARAh - web Representational Analysis
!
!Nat Dis Ang 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    1936.726  1  7  0
!
!
R -1                          <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
     2     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0 0
!
! MM  X , Y , Z
  R  1.5      0      0        1.5     0      0
  T  0.866  1.732    0       -0.866  -1.732  0
! MM  4/3 - X , 2/3 - Y , 2/3 - Z
BASR -1.5      0      0       -1.5     0      0
BASI -0.866  -1.732   0        0.866   1.732  0
!Atom Typ Mag_Vek    X        Y        Z        Biso      Occ      C1       C2       C3
!     C4      C5      C6       C7       C8       C9       MagPh
Mn1  MMN5  1   0          0        0 0.17521  .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    0.00000
    0.00    0.00    0.00     0.00     0.00     0.00     0.00
!-------> Profile Parameters for Pattern #  1 ----> Phase #  1
! Scale      Shape1     Bov     Str1     Str2     Str3   Strain-Model
 0.879852    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
   0.015521  -0.057189   0.020187   0.052448   0.000000   0.000000   0.000000    0
     0.00      0.00      0.00       0.00       0.00       0.00       0.00
!    a        b        c      alpha    beta     gamma    #Cell Info
  6.359528  6.359528 19.913155 90.000000 90.000000 120.000000
  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
! Pref1  Pref2   Asy1    Asy2    Asy3    Asy4    S_L     D_L
 0.00000 0.00000 0.25247 0.09752 -0.44624 -0.16980 0.00000 0.00000
   0.00    0.00    0.00    0.00    0.00    0.00    0.00    0.00
! Propagation vectors:
0.      0.      0.          Propagation Vector  1
0.000000    0.000000    0.000000
```

Step 4: Refine the magnetic model and nuclear phase in Fullprof

- Turn on C1 to refine in the pcr text file.
- Also update the Mn ion to MMN2 (this is magnetic Mn^{2+}).
  The form factor is selected by the valaence state, so might vary slightly if the valence label is wrong.

```
!------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:    46.66
!------------------------------------------------------------------------------
Template magnetic phase by SARAh - web Representational Analysis
!
!Nat Dis Ang 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    1936.726  1   7   0
!
!
R -1                        <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
     2     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0 0
!
SYMM X , Y , Z
BASR  1.5       0       0        1.5     0      0
BASI  0.866   1.732     0       -0.866  -1.732  0
SYMM 4/3 - X , 2/3 - Y , 2/3 - Z
BASR -1.5       0       0       -1.5     0      0
BASI -0.866  -1.732     0        0.866   1.732  0
!Atom Typ Mag  Vek     X       Y       Z       Biso    Occ       C1        C2        C3
!     C4      C5      C6      C7      C8      C9      MagPh
Mn    MMN2      0       0       0 0.17521 .30000  1.000 0    2    0.000    0.000
                0.00    0.00    0.00    0.00    0.00     1    0.00     0.00
    0.000   0.000   0.000   0.000   0.000   0.000   0.00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
!-------> Profile Parameters for Pattern #  1 ----> Phase #  1
! Scale      Shape1    Bov    Str1    Str2    Str3  Strain-Model
 0.8798522    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
   0.015521  -0.057189   0.020187   0.052448   0.000000   0.000000   0.000000    0
     0.00      0.00      0.00      0.00      0.00      0.00      0.00
!    a       b       c     alpha    beta     gamma    #Cell Info
  6.359528  6.359528 19.913155 90.000000 90.000000 120.000000
  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
! Pref1  Pref2   Asy1   Asy2   Asy3   Asy4   S_L    D_L
 0.00000 0.00000 0.25247 0.09752 -0.44624 -0.16980 0.00000 0.00000
   0.00   0.00   0.00   0.00   0.00   0.00   0.00   0.00
! Propagation vectors:
0.      0.      0.          Propagation Vector  1
0.000000    0.000000    0.000000
```

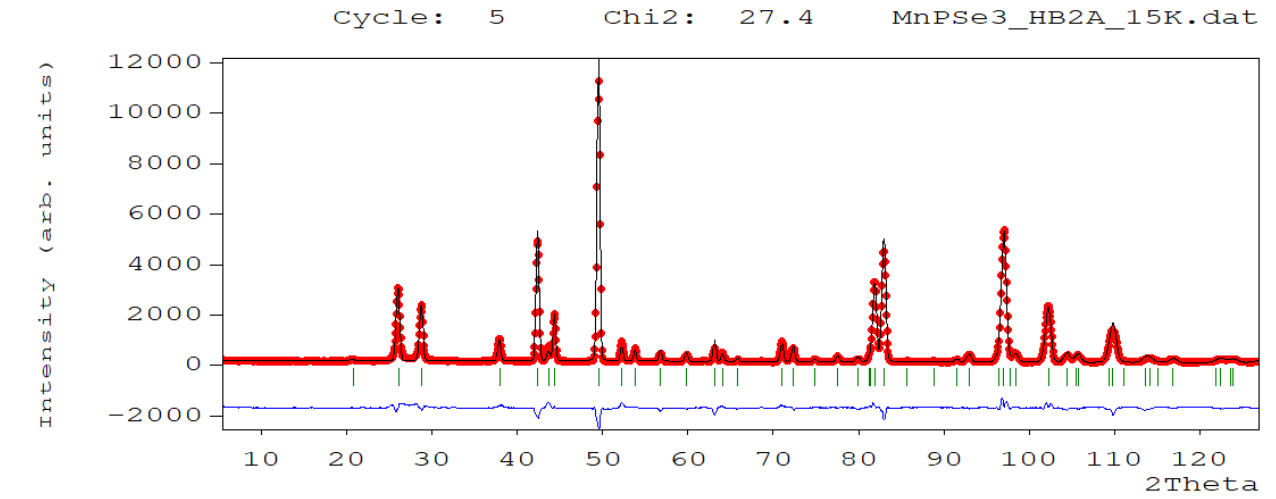
Step 4: Refine the magnetic model and nuclear phase in Fullprof

- Refine the 15K data.
- This captures the magnetic peaks well.
- Put the C1 back to zero and refine C2. The fit is identical.
- These are related solutions.
- Try refining C1 and C2 (with the constraint that they are equal).
- *To improve the fit, try refining the peak shapes, background, atom positions, thermal parameters, etc*

FullProf Program

Load Edit PCR Mode Run Exit

```
    => ---------> Pattern#       1
    => Phase:       1
    =>    Bragg R-factor:   9.407
    =>    RF-factor     :   6.532
    => Phase:       2
    => Magnetic R-factor:   18.65

 => Convergence reached at this CYCLE !!!!: CYCLE No.       4
 => R-Factors:   8.59      11.2     Chi2:  27.4     DW-Stat.:  0.1143   Patt#:  1
 => Expected :           2.13                              1.8572
 => Conventional Rietveld R-factors for Pattern:       1
 => Rp:  14.9     Rwp:  15.7     Rexp:    3.00                    Chi2:  27.4
    => Global user-weigthed Chi2 (Bragg contrib.):   31.12
    => ---------> Pattern#       1
    => Phase:       1
    =>    Bragg R-factor:   9.407
    =>    RF-factor     :   6.532
    => Phase:       2
    => Magnetic R-factor:   18.65
 => Normal end, final calculations and writing...


 => CPU Time:     2.662 seconds
 => 0.044 minutes

 => END   Date:02/10/2022  Time => 16:25:16.376
```

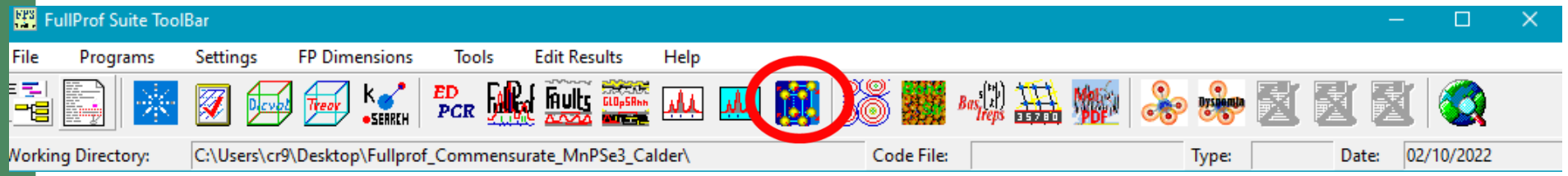


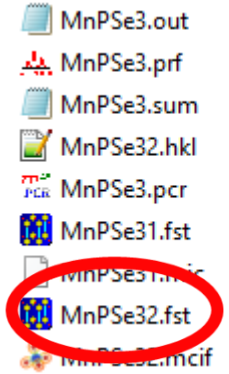
$MnPSe_3$

- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
  - Step 3: Create candidate magnetic models using SARAh
  - Step 4: Refine the magnetic model and nuclear phase in Fullprof.
  - **Step 5: Check the magnetic model**

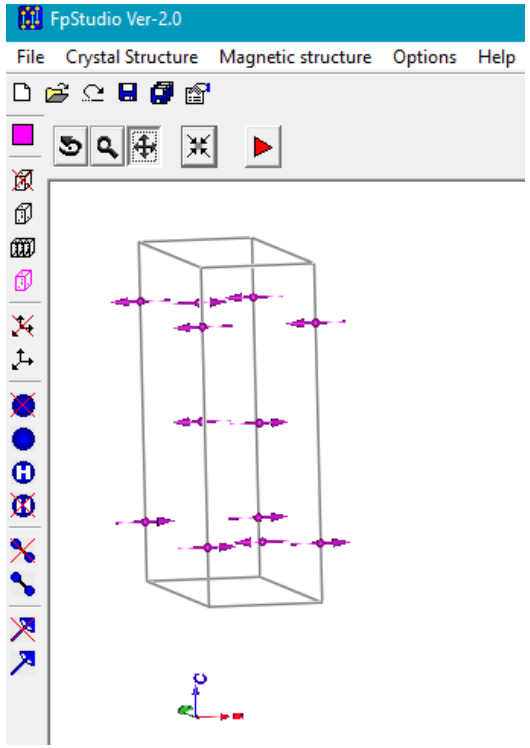
Step 5: Check the magnetic model

- The model can be checked in FPStudio





- There are two .fst files, these are for the 2 phases. Open the magnetic phase (file ending in 2.fst)
- In Fpstudio click on the drop-down mend "Magnetic Structure" and select "List magnetic moments"

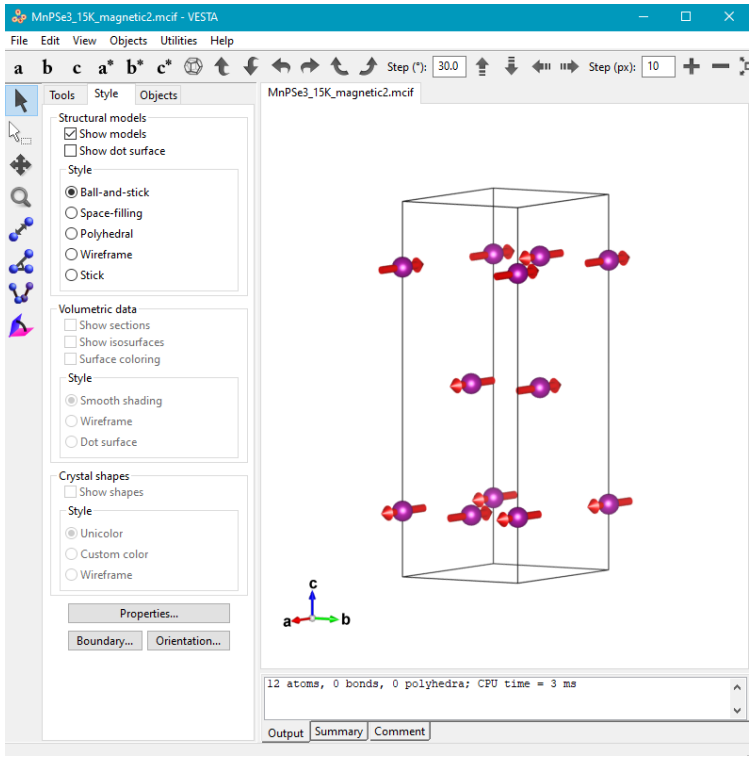


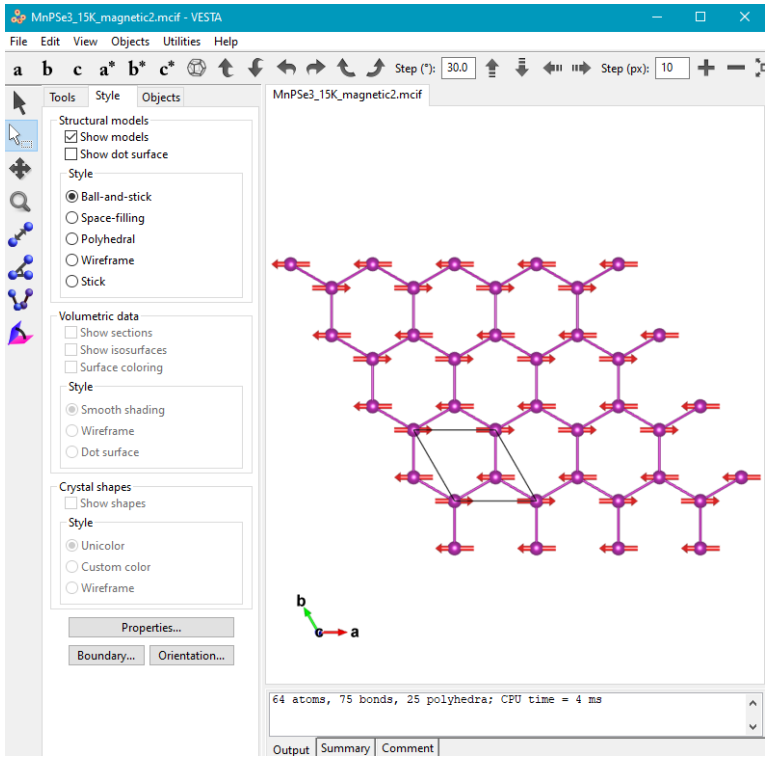

```
Magnetic lattice type : R
Unit Cell:       6.3595      6.3595     19.9132     90.0000     90.0000    120.0000

Current Box:     0   1    0   1    0   1

Magnetic k-vectors :
 0.00000  0.00000  0.00000

 Symmetry operations :
SYMM x,y,z
u,v,w,0.0

Atom : Mn1_1     Mn
------------------------------------------------------------------------------
        x        y        z        Translation    k MSYM     m(a)      m(b)      m(c)     Mtot
  0.00000  0.00000  0.17521
                                  (  0,   0,   0)
                                                 1    1  3.34510  0.00000  0.00000
                                                           3.34510  0.00000  0.00000  3.34510
                                  (  0,   1,   0)
                                                 1    1  3.34510  0.00000  0.00000
                                                           3.34510  0.00000  0.00000  3.34510
                                  (  1,   0,   0)
                                                 1    1  3.34510  0.00000  0.00000
```

Note the assignment of moments along the a-axis is arbitrary. Symmetry allows for any direction in the *ab*-plane. c-axis moment should also be checked.

Step 5: Check the magnetic model

- The .mcif file output by Fullprof can be used to visualize the magnetic structure in vesta





- This is the published magnetic structure.