Bilbao Crystallographic Server and Fullprof refinement of LaMnO$_3$ data

Stuart Calder

MagStr 2022, ORNL

LaMnO$_3$

- There is a LaMnO$_3$ example (data/notes) using representation analysis by Juan Rodríguez-Carvajal. See 2014 Magnetic Structure Notes (also in this folder "Tutorial_Magnetic_Structures_LaMnO3_Juan2014.pdf").

- We will start from the same .cif file used in the other example and use the same neutron data set. The k-vector has been previously found using k-search as k= (0,0,0).

WORK THROUGH PREVIOUS EXAMPLE!!

LaMnO$_3$: data format and magnetic peaks

Starting files to find nuclear refinement, magnetic peaks and k-vector

- Nuclear refinement and data for 150 K (no magnetic Bragg peaks):
  LaMn150K_nuclear_only.pcr
  LaMn150K.dat

- Nuclear refinement and data for 150 K (no magnetic Bragg peaks):
  LaMn50K_nuclear_only.pcr
  LaMn50K.dat

Data taken at G4.2 at LLB (λ=2.59 Å)

a=5.53 Å, b=5.75 Å and c=7.68 Å.

Pbnm (62)

	x	y	z	Occ.	B	Site
La1	−0.00630	0.04430	0.25000	1.000	0.800	4c
Mn1	0.50000	0.00000	0.00000	1.000	0.460	4b
O1	0.07250	0.48850	0.25000	1.000	1.000	4c
O2	0.72570	0.30380	0.03780	1.000	0.910	8d
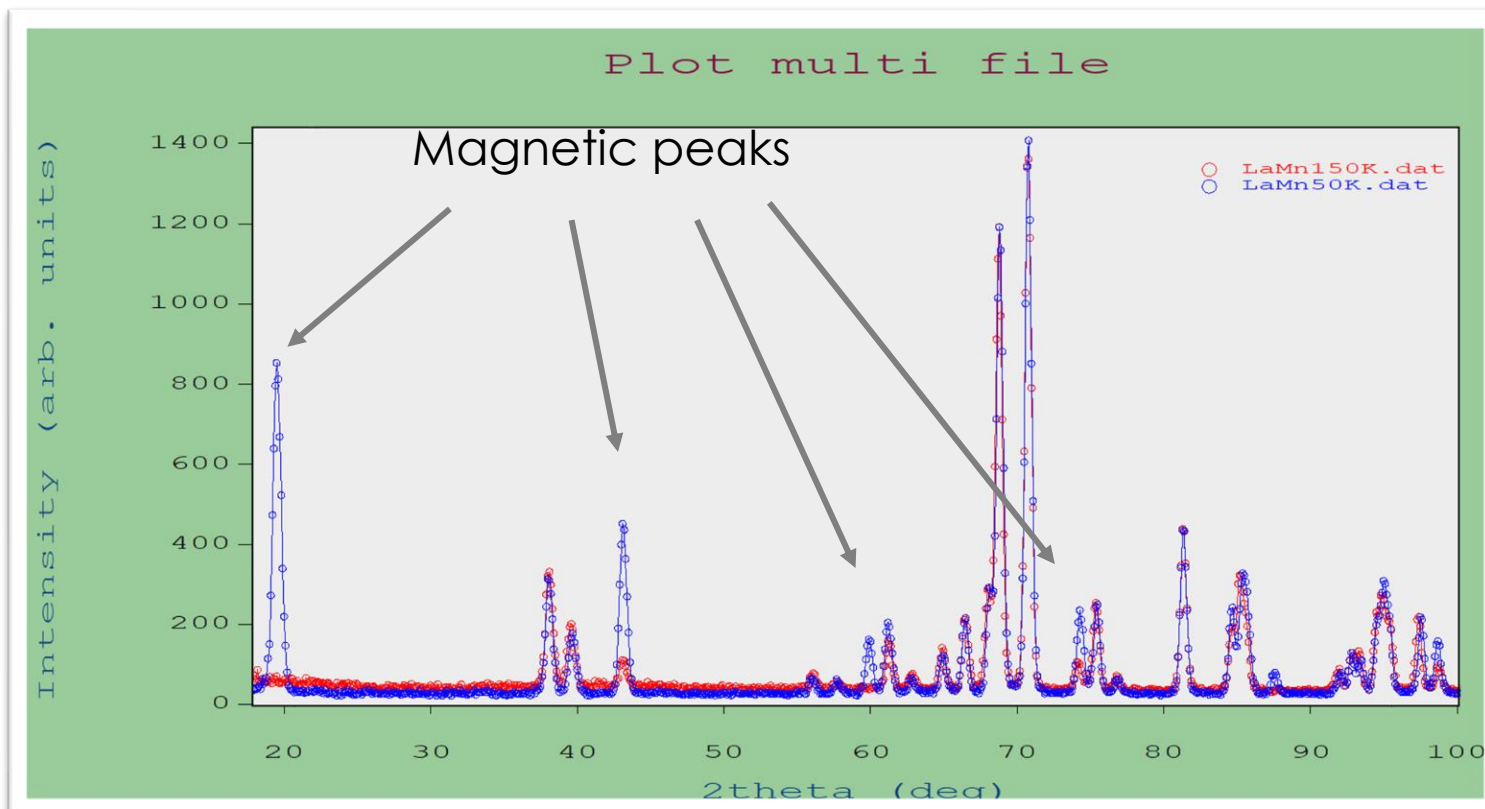
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LaMnO$_3$

- This example will use the Bilbao Crystallographic Server (http://www.cryst.ehu.es/) and follow these steps:

  - Step 1: create an mcif file with MAXMAGN on the Bilbao Crystallographic Server.

  - Step 2: convert that mcif file into a .pcr file using mCIF2PCR.

  - Step 3: use the created .pcr file to fit the neutron data using Fullprof to determined the magnetic structure.

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Ho_2BaNiO_5

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Step 1: Creating mCIF file

- Go to Bilboa server: http://www.cryst.ehu.es/

- Select "Magnetic Symmetry and Applications" to open the drop-down menu

Step 1: Creating mCIF file

- Then select "MAXMAGN"

Step 1: Creating mCIF file

- **[1]** Need to have a propagation vector. This can be determined using k-search in fullprof (see other example for $LaMnO_3$). It is (0,0,0).

- **[2]** Input the space group number of the crystal structure (or choose from a list of all space groups)- *Note: if you have a cif file this step is not necessary.*

- **[3]** Check the box "Structure data of the paramagnetic phase will be included". This allows you to input a .cif file.

Step 1: Creating mCIF file

- Choose .cif file (crystal structure only).
  The one for this example is "LaMnO3.cif"

- Then upload the file.

- If you don't have a cif file then have to fill out the details in "Option 2"

Bilbao Crystallographic Server → MAXMAGN - Maximal magnetic space groups

Parent paramagnetic structure cif file

Option 1: Please submit a structure file (CIF format):

Choose File | LaMnO3.cif   Upload the file

No space group provided. The space group indicated in the cif file will be tak

Bilbao Crystallographic Server
http://www.cryst.ehu.es

Step 1: Creating mCIF file

- The paramagnetic phase information is displayed.
  - Select the magnetic atom(s). This case is Cr only.
  - Push Submit. This may take a few seconds to run the calculations…..

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Step 1: Creating mCIF file

- The possible magnetic space groups are displayed in grey.
  White have zero ordered moments.

- To view magnetic structure and export mcif file click on "Show" in last column.

Maximal magnetic space groups for the parent space group *Pnma* (No. 62) and the propagation vector k = (0, 0, 0)

Maximal subgroups which allow non-zero magnetic moments for at least one atom are coloured

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Step 1: Creating mCIF file: **Check #2,3,4,8**

- All magnetic space groups allow spins along either a,b or c.

- Put values for Mx, My, Mz.

- All give unique possible magnetic structures. Since k=000 some are AFM and some are FM.

Step 1: Creating mCIF file: **Check #2**

- We will choose the allowed magnetic structure 2 (*Pn'ma'* (#62.448)) for this example,

- But all should be checked to ensure the solution is uniquely correct or to determine equivalent solutions.

- If none of the shown space groups work → go to a subgroup

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Step 1: Creating mCIF file

- The mcif file is displayed.

- **[1]** This can be downloaded by clicking on "bcs_file.mcif"

- **[2]** Magnetic structure can also be visualized by clicking "Submit to MVISUALIZE"

Step 1: Creating mCIF file

- MVISUALIZE lets you quickly check magnetic structure.

- But we will use the downloaded mcif to fit data using fullprof.

We now need to go to Step 2

MVISUALIZE Main Page

Show/Hide File

MVISUALIZE: 3D Visualization of magnetic structures with Jmol
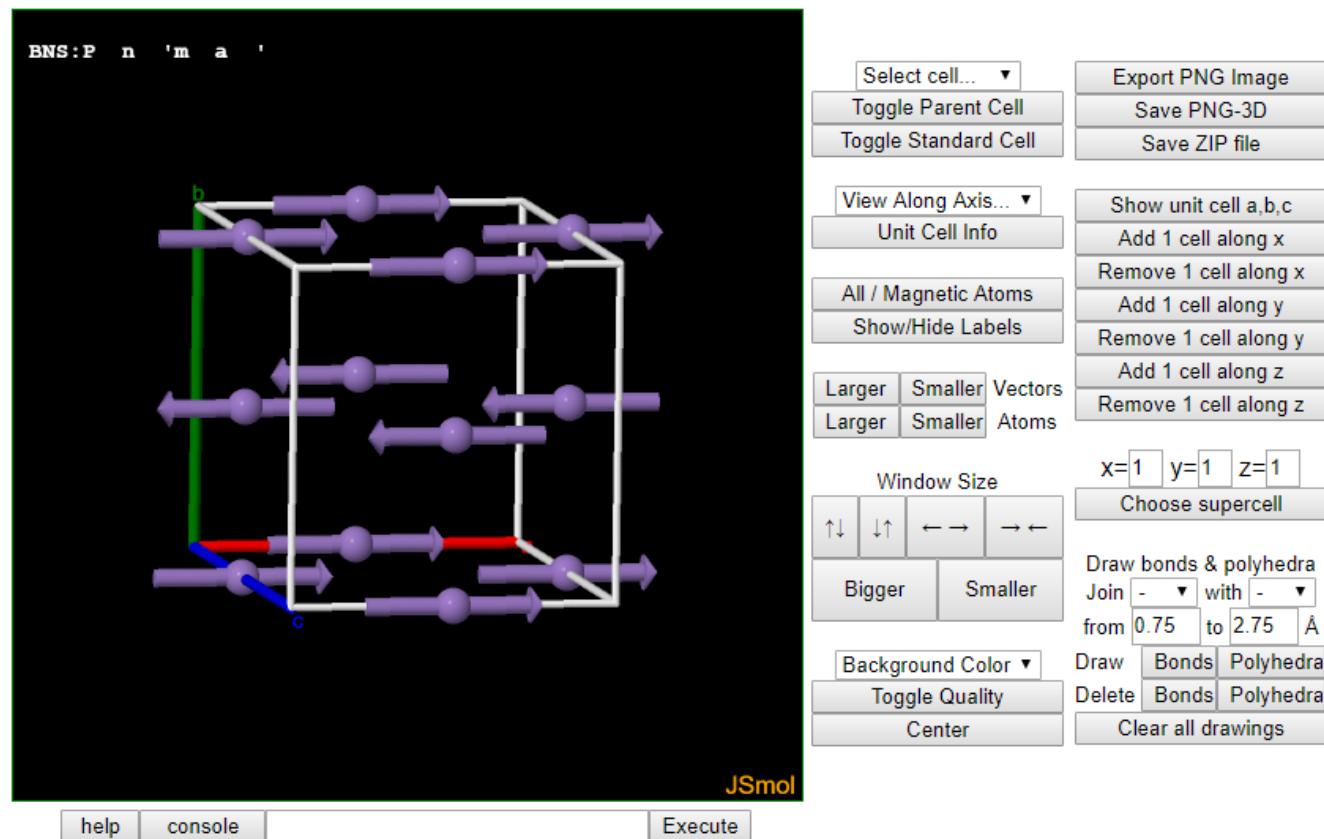
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Step 2: Creating a pcr from an mcif file

- Go back to the main page on server and open mCIF2PCR

Step 2: Creating a pcr from an mcif file

- **[1]** Choose the mcif we just created through MAXMAGN
- **[2]** Click convert

- This will convert the file and "Click to download it" will download the .pcr file
- We will use this .pcr file in <u>Step 3</u>. Put it in the same folder as the data file "LaMn50K.dat"

LaMnO$_3$

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Step 3: Refining the magnetic structure with Fullprof

- Pcr file created contains a single phase with crystal structure and magnetic ions described by a magnetic space group.

- The initial downloaded pcr file calculates the pattern based on default values.

- We need to change the defaults in the .pcr file in the same way as done for the examples created from a .cif file.

- To do this we work down the Tabs in the GUI (General/Patterns/Phases/Refinement) and/or edit the text file.

- The values will depend on the instrument the data was collected on. For this example use values already refined for the nuclear phase (LaMn50K_nuclear_only.pcr)

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Step 3: Refining the magnetic structure with Fullprof

- Open pcr file

- Select the format of the data file Fullprof should refine.

- Patterns → Data file/Peak Shape → D1A/D2B/3T2/G42

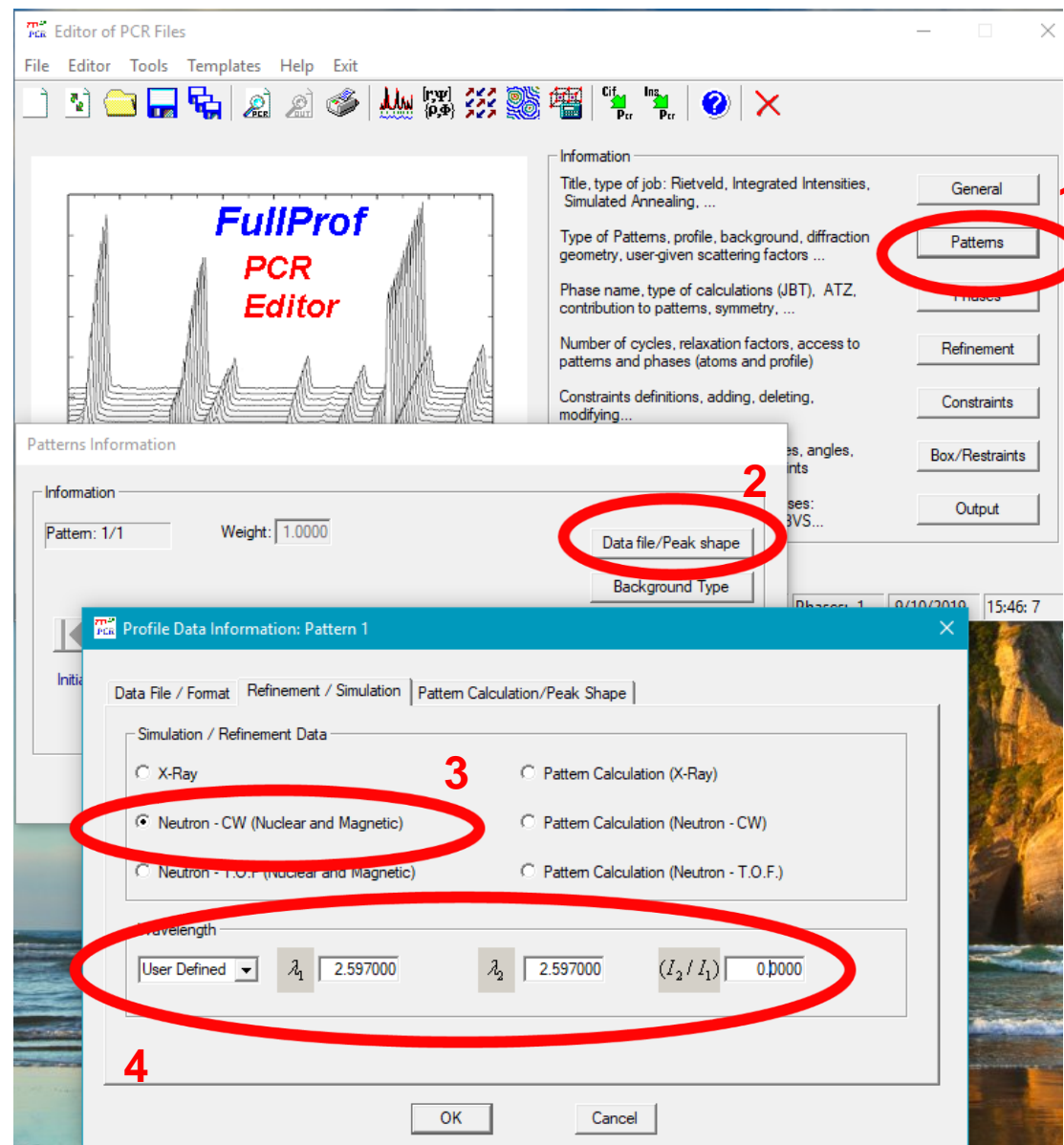S. Calder, MagStr 2022, ORNL
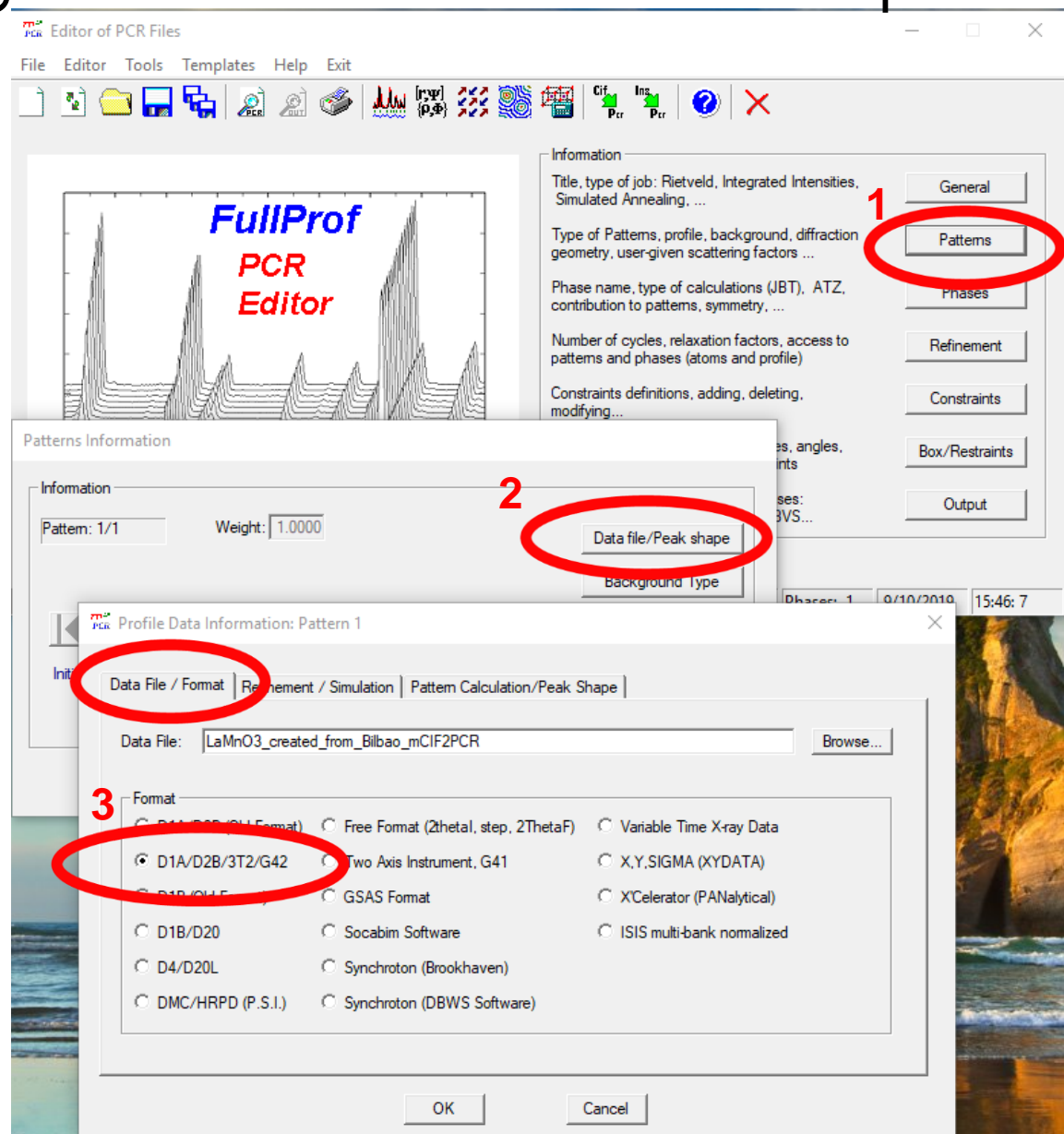
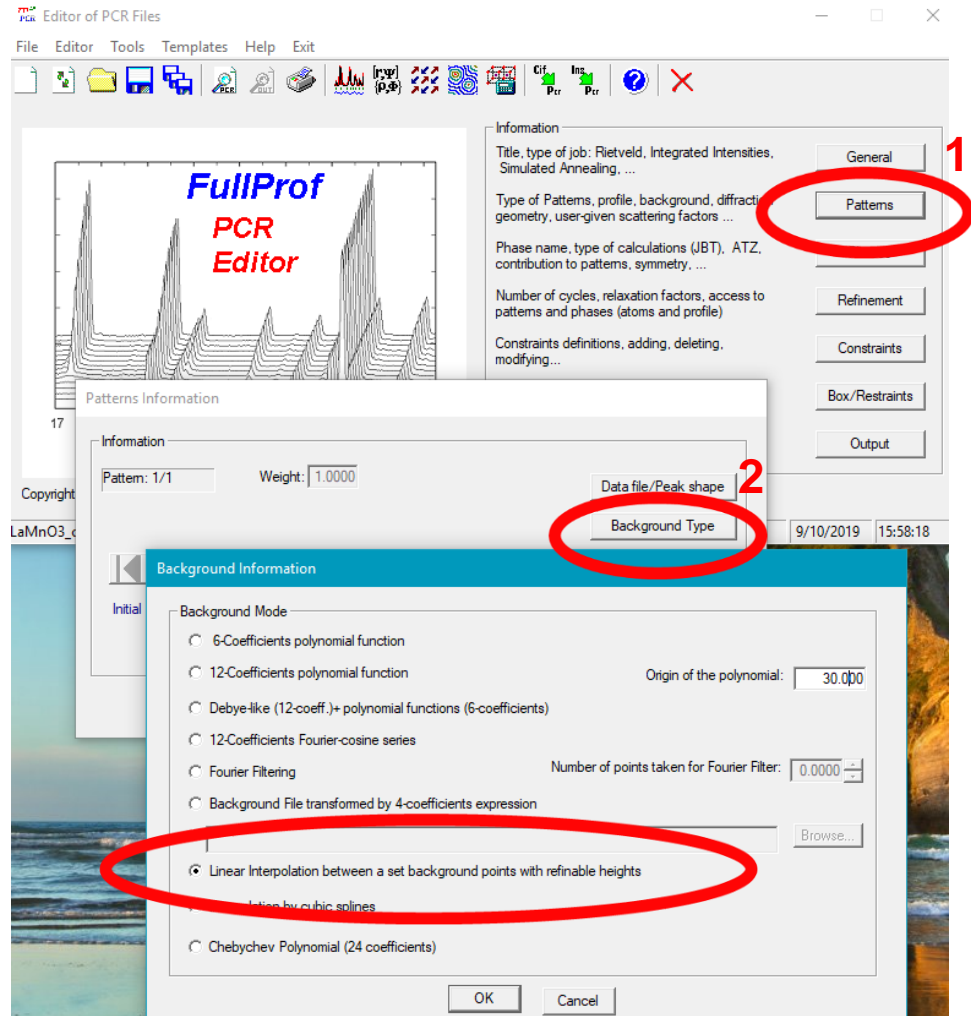# Step 3: Refining the magnetic structure with Fullprof

- Patterns → Data file/Peak Shape →Refinement/Simulation

- **[3]** Select Neutron – CW

- **[4]** Wavelength is 2.597 Å
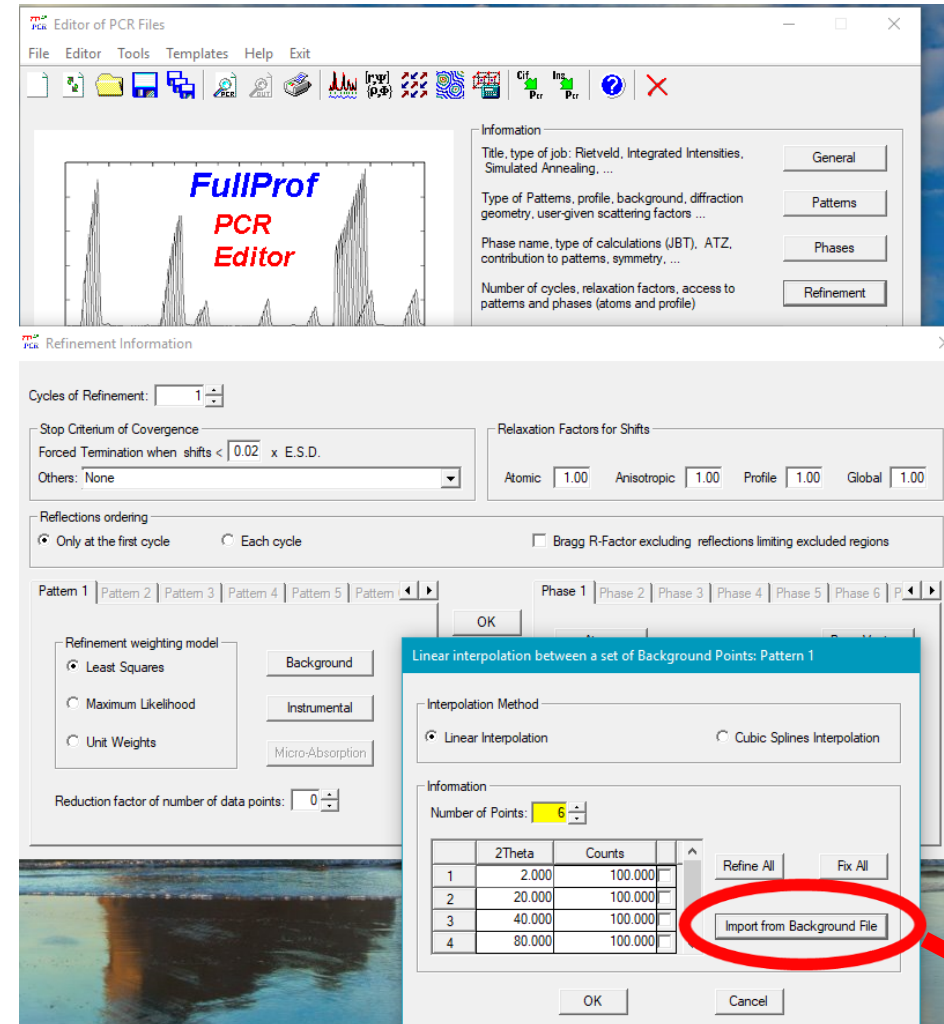
Step 3: Refining the magnetic structure with Fullprof

- Patterns→ Background Type →Linear Interpolation between .....
  THIS IS ALREADY CHOSEN

- Unusual instrument background → Need to import background values **Background.bgr**

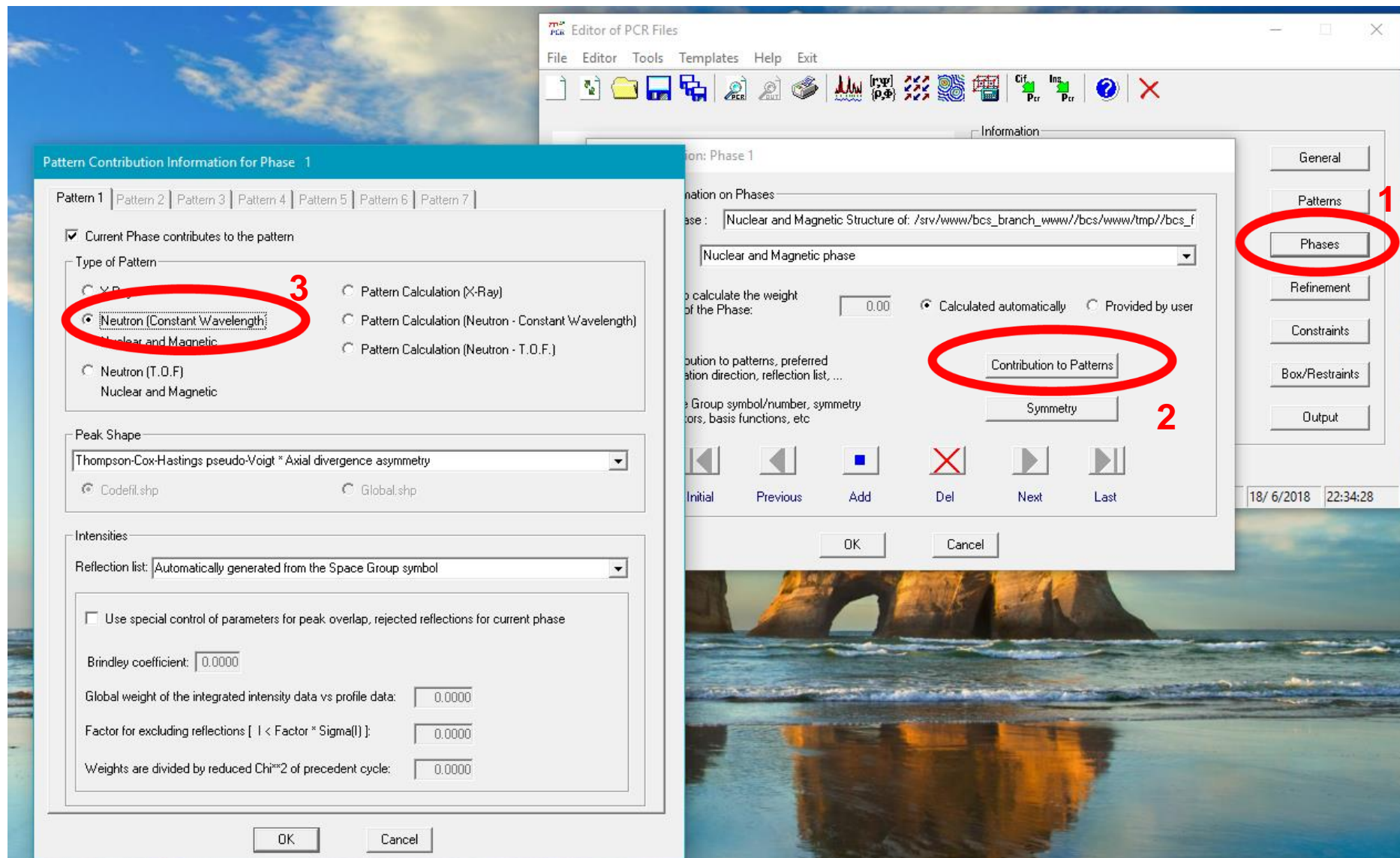# Step 3: Refining the magnetic structure with Fullprof
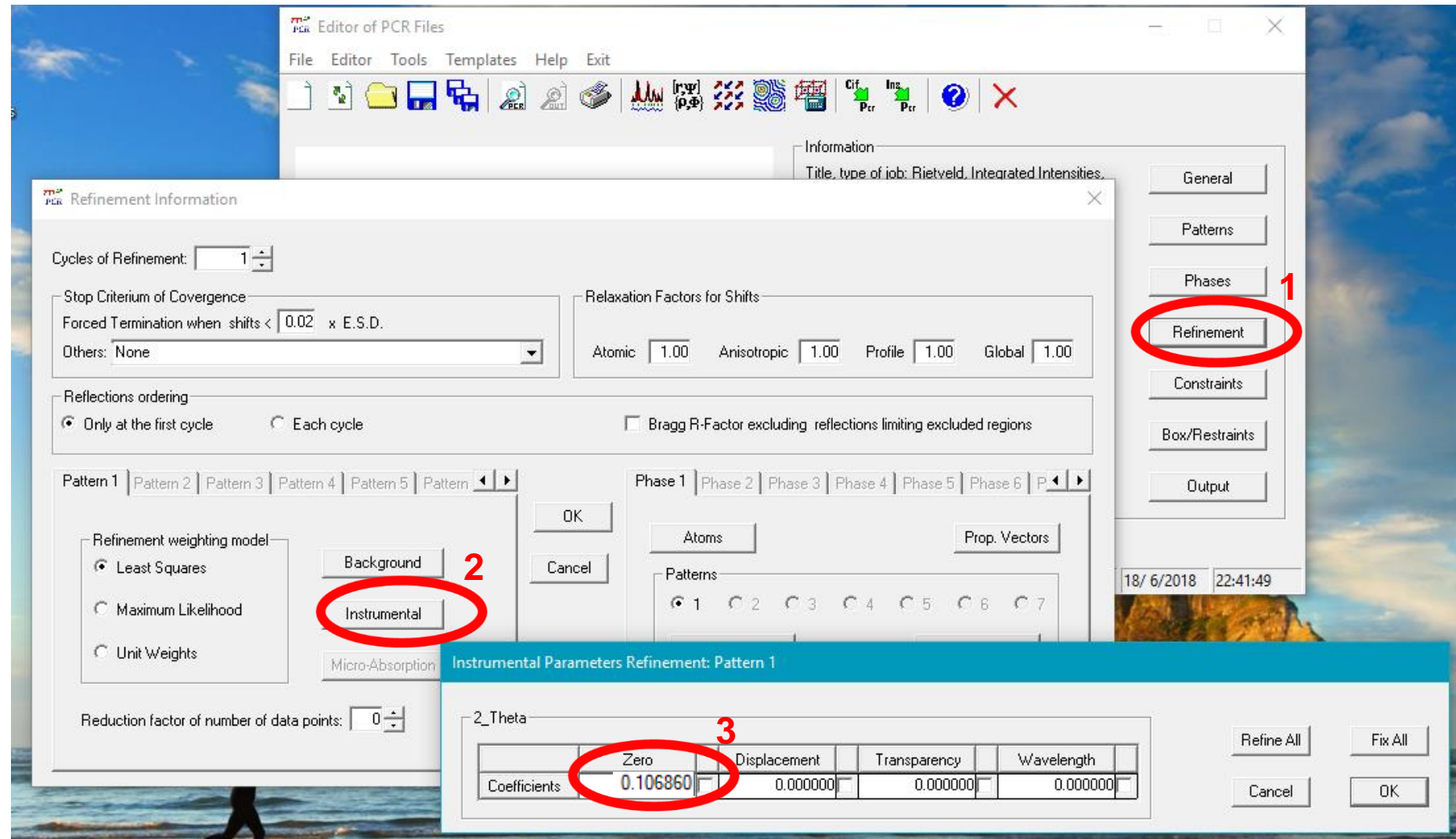
- Add excluded regions (see nuclear pcr)

Step 3: Refining the magnetic structure with Fullprof

- Make phase contribute to refinement.

- **[1]** Phases➔ **[2]** Contribution to Patterns➔ **[3]** Neutron (constant wavelength)

Step 3: Refining the magnetic structure with Fullprof

- Instrumental zero value (See nuclear refinement: 0.10686)

Step 3: Refining the magnetic structure with Fullprof

- Copy values from nuclear pcr for the instrumental profile parameters.

NOTE: Magnetic space groups do not use a propagation vector. Instead the unit cell changes. For k= (0 0 0) there is no change in unit cell.

The orthorhombic space group has b > a > c (converted from Pbnm of nuclear example)

Delete vary mxmymz
This stops the moments automatically refining.
But make sure to keep track of allowed moments.

Step 3: Refining the magnetic structure with Fullprof

- In "Refinement"
→ "atoms" input thermal parameters (0.3). **[1,2,3]**

- Re(x), Re(y), Re(z) can all contribute, so should all be checked.

Step 3: Refining the magnetic structure with Fullprof

Refine scale and lattice constants Set number refinement cycles
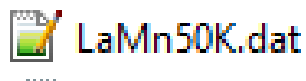
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Step 3: Refining the magnetic structure with Fullprof

- Run the refinement.

- Select the "LaMn50K.dat" neutron data file.

LaMn50K.dat

- Refinement models most of the data well.
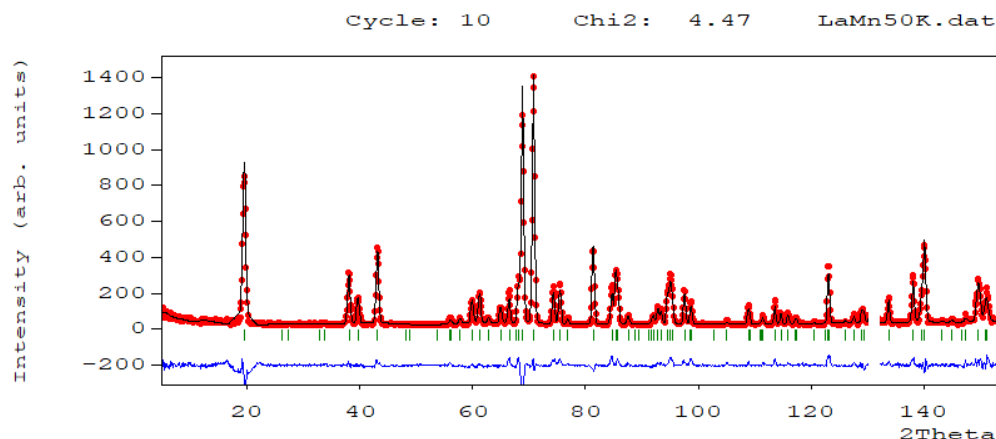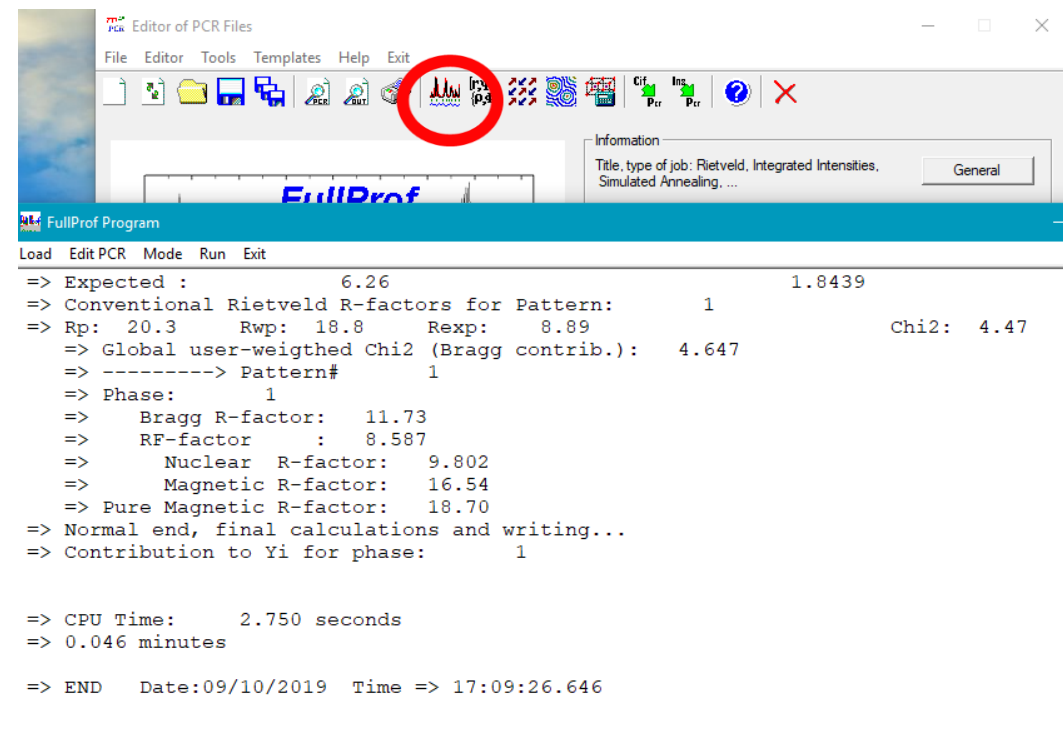
Step 3: Refining the magnetic structure with Fullprof

- List of files output

- Check magnetic structure with .fst file (Fpstudio) or .vesta or .mcif outputs.

- Values with errors in .sum file

  Mn: M_x=3.72(2) μ_B

Moments along My and Mz are allowed, but if refined give small values with large errors.