Bilbao Crystallographic Server and Fullprof refinement of $Cs_2Fe_2(MoO_4)_3$ data

Stuart Calder, ORNL

MagStr 2024 at Kennesaw State University
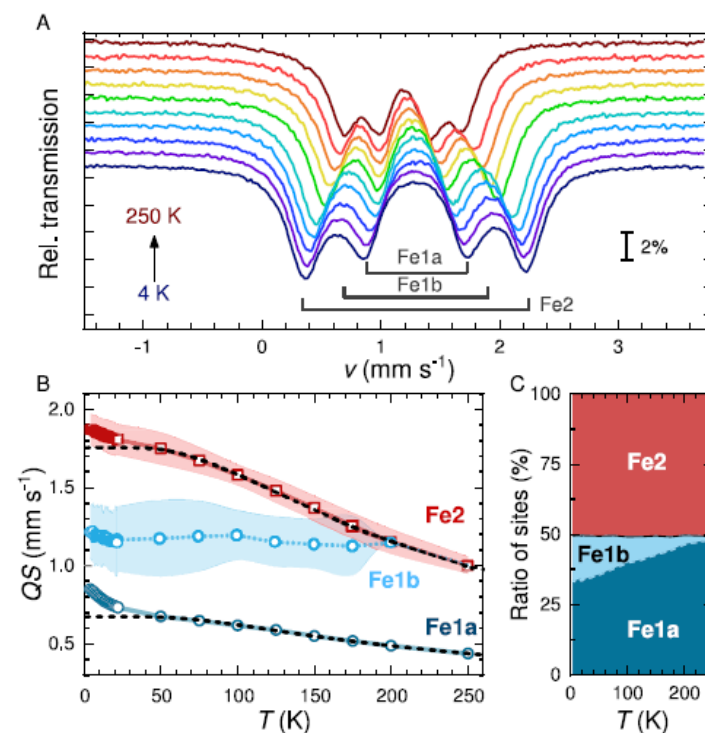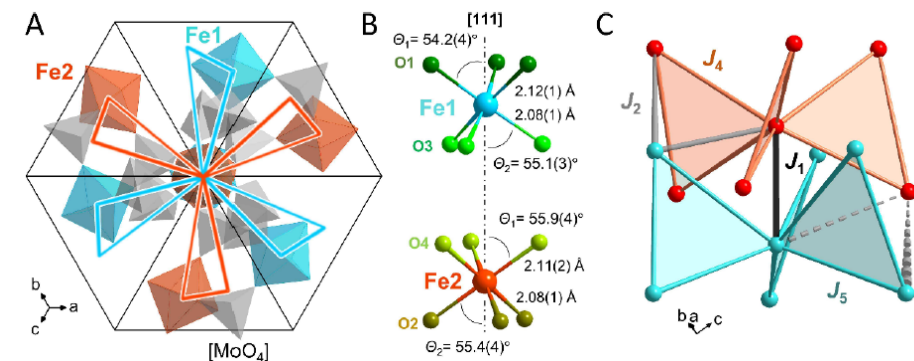
$Cs_2Fe_2(MoO_4)_3$: Background

- Highly frustrated with same space group as FeSi Skyrmion.

- Fe is magnetic ion.
  - Two different Fe sites
  - Indications of distinct ordering of Fe

- Long range order expected below 1 K, with short range order above >20 K


```
Non-centrosymmetric cubic space group P2₁3 (198)

    a         b         c        alpha     beta      gamma
10.91610  10.91610  10.91610   90.0000   90.0000   90.0000


Structure parameters
         x          y          z        Occ.      Site
Cs1   0.17938    0.32062    0.67938    1.000      4a
Mo1   0.30061    0.62363    0.52597    1.000      12b
Fe1   0.33737    0.33737    0.33737    1.000      4a
O1    0.27587    0.48544    0.44750    1.000      12b
Cs2   0.45761    0.95761    0.54239    1.000      4a
Fe2   0.61246    0.61246    0.61246    1.000      4a
O2    0.45432    0.67110    0.51709    1.000      12b
O3    0.25187    0.60297    0.67761    1.000      12b
O4    0.21150    0.73545    0.45198    1.000      12b
```

Goal: Use neutron data to determine the magnetic structure

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

$Cs_2Fe_2(MoO_4)_3$: Neutron measurements on HB-2A, HFIR.

- Constant wavelength

- Germanium monochromator
  - ~90° take off angle for medium-high resolution
  - Variety of complex sample environments: 50mK, 6 Tesla, 2GPa pressure…

- Current detector is an array of 44 individual ^{3}He tubes
  - Low background
  - Covers ~2-150° in 2θ by scanning detector
  - **MIDAS detector upgrade coming soon!**

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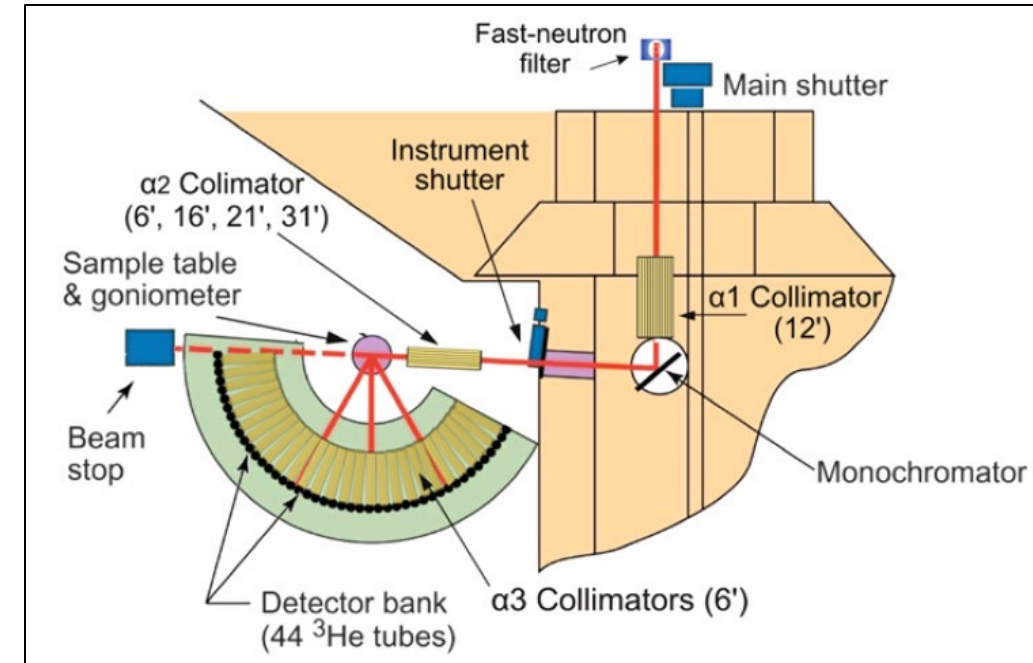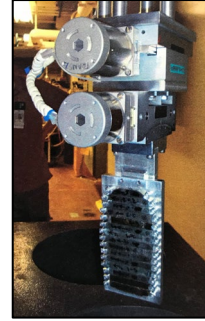
Ge(hkl)	λ (Å)	d_{max}(Å)	Q (Å^{-1})	Flux (n/cm^{2}s)
(113)	**2.41**	**27.6**	**0.2-5.1**	**5 x 10^6**
(115)	**1.54**	**17.6**	**0.35-7.9**	**1 x 10^7**
(117)	1.12	12.8	0.5-10.9	4 x 10^6

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

3

HB-2A instrument resolution and peak shape

MYRESOL.irf

This file is read only when **Res**≠0. The name of the file is stored in the character variable **FILERES**= *MYRESOL.irf*. All items are read in free format.

This options works, at present, only for constant wavelength type of data. The profile is assumed to be a Voigt function (**Npr**=7). 12 parameters or a table determine the resolution function. The parameters are $U_i, V_i, W_i, X_i, Y_i, Z_i$ (i=1,2 for λ_1 and λ_2)

The different types of functions are:

Res =1 $H_G^2 = (U_i \tan\theta + V_i)\tan\theta + Wi$

$$H_L = X_i \tan\theta + \frac{Y_i}{\cos\theta} + Z_i$$

- Caglioti function describes reactor based diffractometers.

- U,V,W parameters in Fullprof.

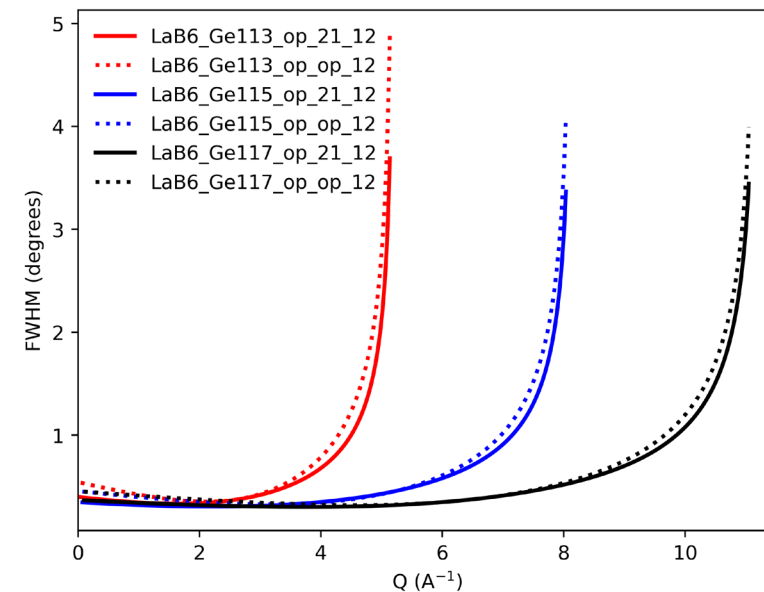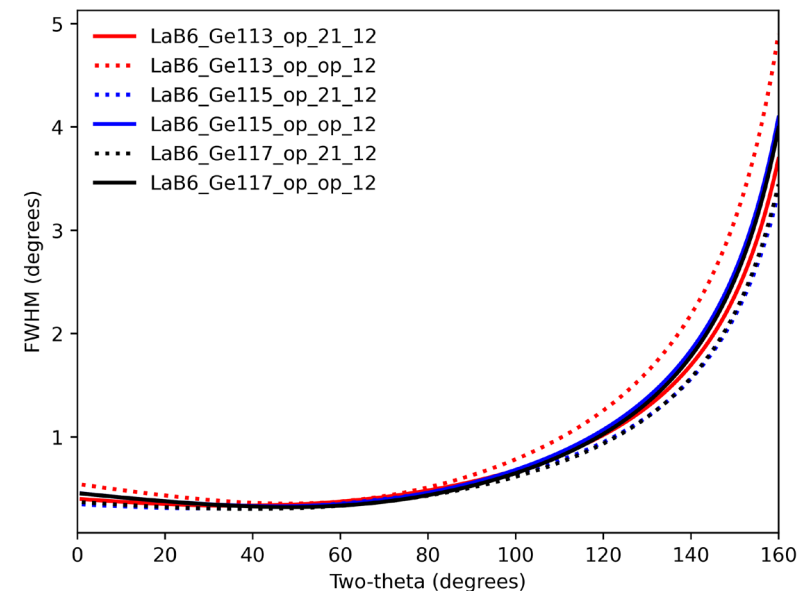- See paper by Hewat for definitions of U,V,W

S. Calder, MagStr 2024

$Cs_2Fe_2(MoO_4)_3$: Low temperature measurements at HB-2A

- Transition temperature of 1 K requires ultra-low temperatures (ULT) sample environments.

- A unique "push-button" ^{3}He sample changer was used that can measure **up to 10 samples** down to millikelvin temperatures of 0.28 K.

- The $Cs_2Fe_2(MoO_4)_3$ powder was contained in an Al can with Cu lid.

  - An overpressure of 10 atm. of helium was added to the can to ensure thermal conduction to millikelvin temperatures.

  - Aluminium has a low background, but adds additional reflections to the diffraction pattern.
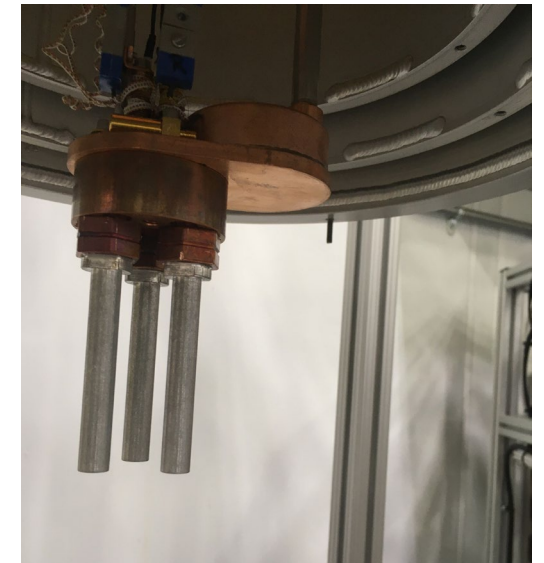
$Cs_2Fe_2(MoO_4)_3$: Files for the example

- Files are in folder
  "**Cs2Fe2(MoO4)3_MagSpaceGroups_Calder2024**"

Filename	Description
CFMO_10K.dat CFMO_300mK.dat	Neutron data from HB2A. Columns are two-theta, intensity, error
ICSD_CollCode422752.cif	Crystal structure information. File obtained from ICSD https://icsd.fiz-karlsruhe.de/search/basic.xhtml
HB2A_Ge113.irf	Instrument parameter file. Instrument specific, download at https://neutrons.ornl.gov/powder/users

- Goal of this exercise is to obtain the magnetic structure at
  300 mK for $Cs_2Fe_2(MoO_4)_3$.

CFMO_10K

CFMO_300mK

hb2a_resolution_Ge113_op_op_12

ICSD_CollCode422752

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

S. Calder, MagStr 2024

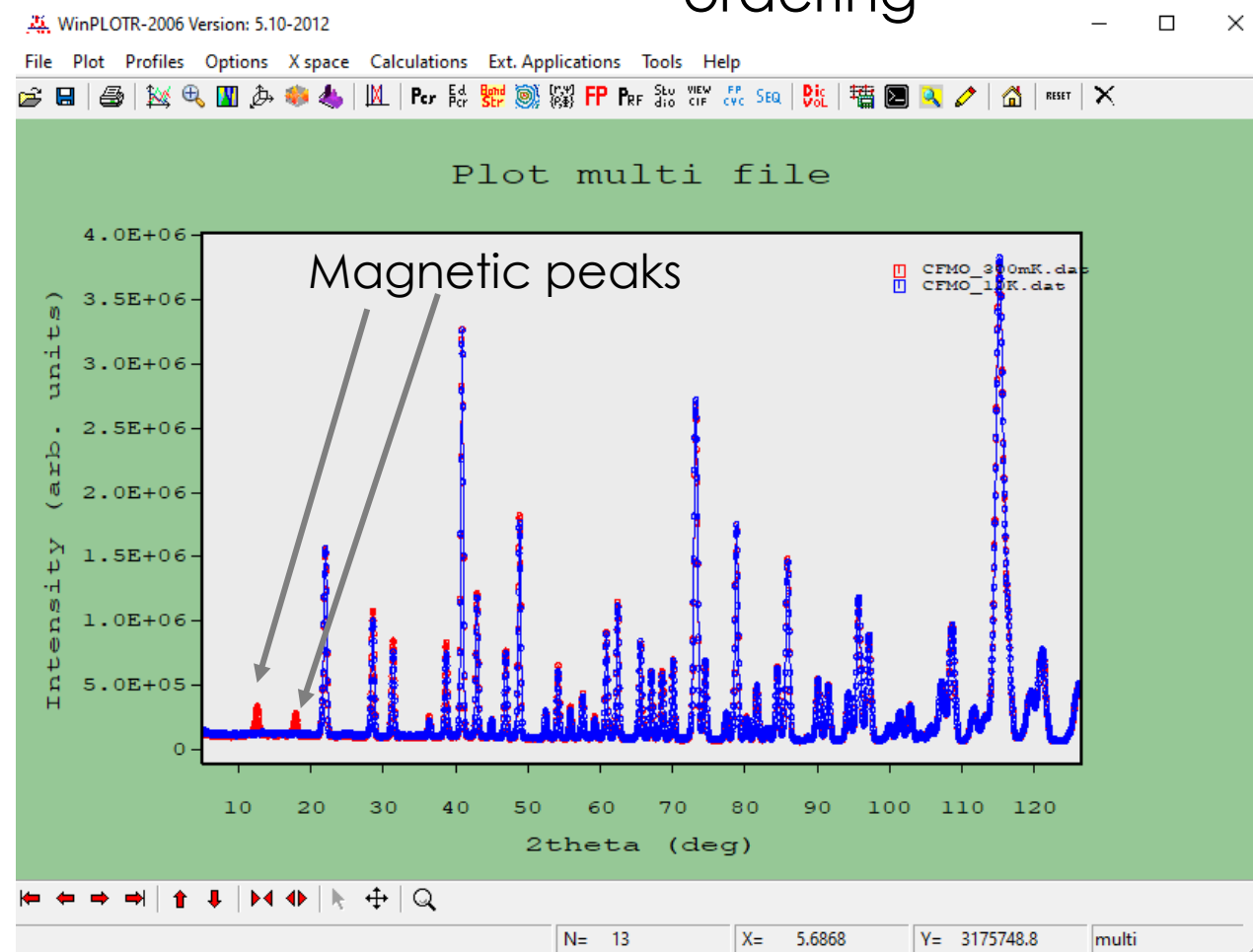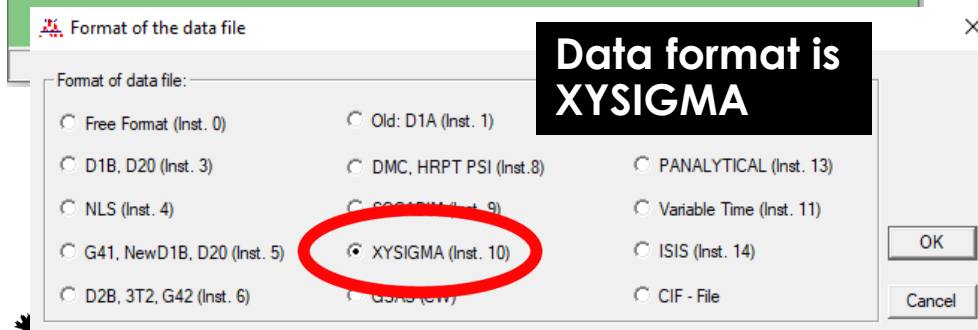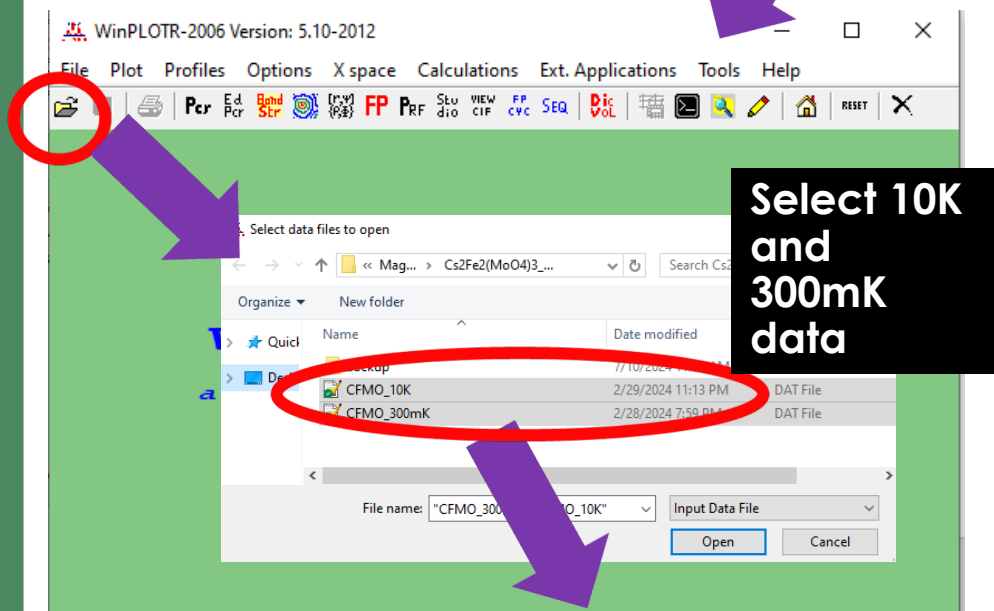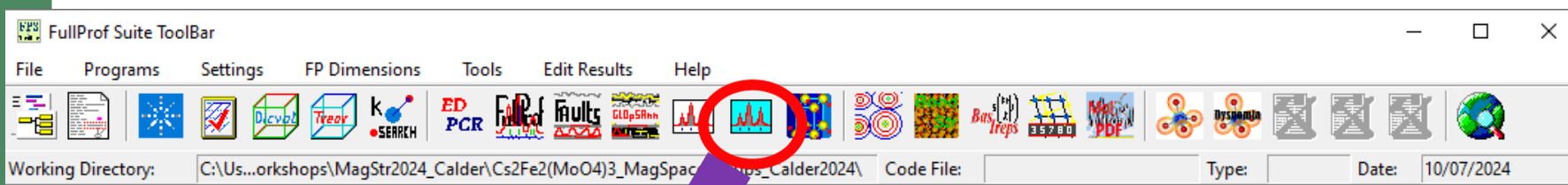# Cs$_2$Fe$_2$(MoO$_4$)$_3$: Set-up Fullprof Suite Toolbar

- Open Fullprof Suite toolbar.
  - **1.** Select working directory with data
    "File>Select Working directory…"

  - **2.** Browse to wherever your folder
    "Cs2Fe2(MoO4)3_MagSpaceGroups_Calder2024" 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
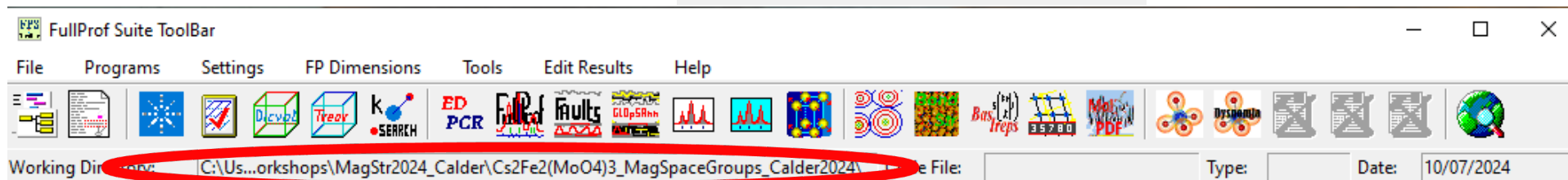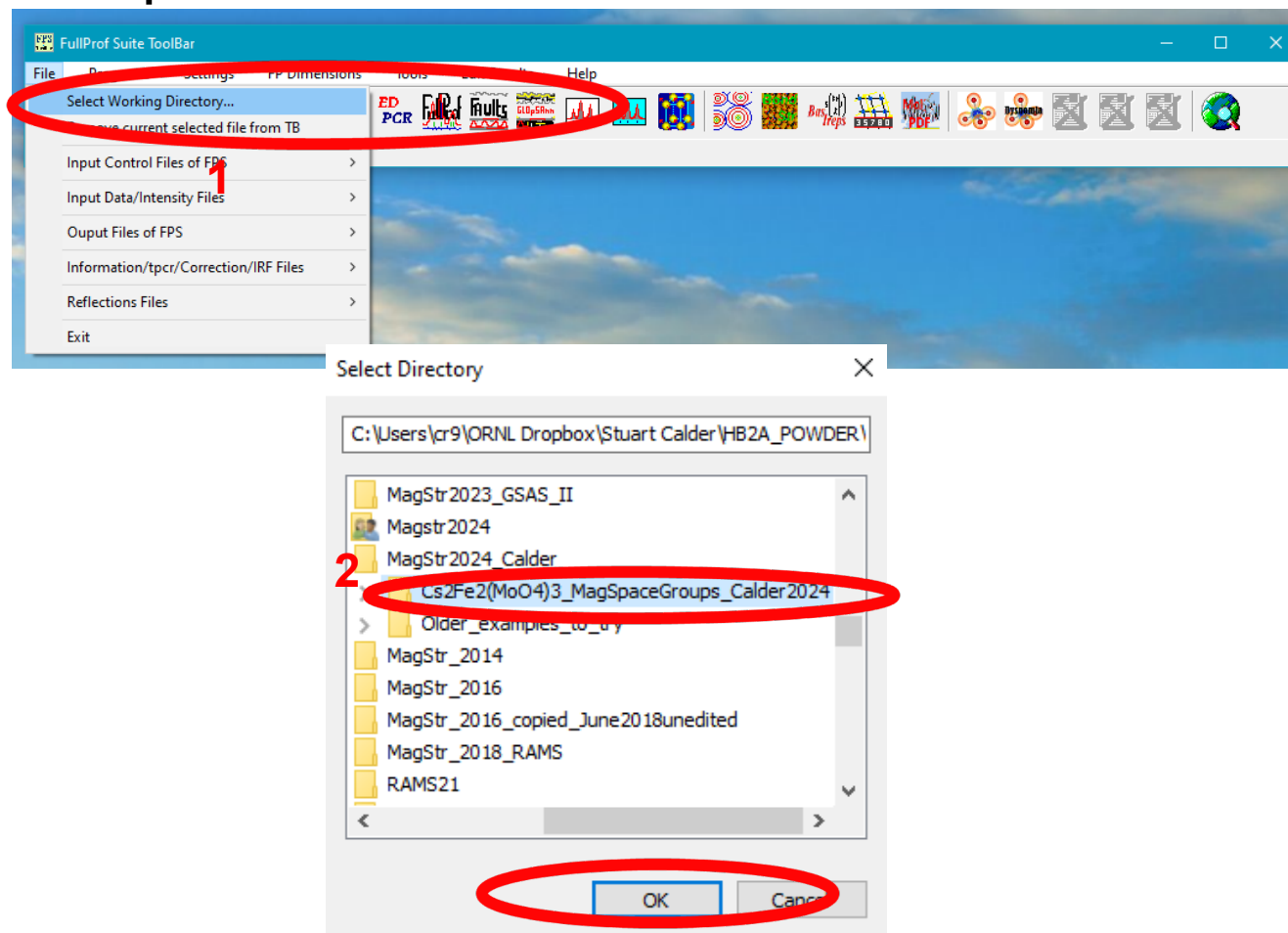
Cs$_2$Fe$_2$(MoO$_4$)$_3$: View Data

- After downloading files open the data with WinPLOTR-2006

- Extra peaks at 300 mK indicate magnetic ordering

Select 10K and 300mK data

Data format is XYSIGMA

Magnetic peaks

S. Calder, MagStr 2024

$Cs_2Fe_2(MoO_4)_3$: Refinement Strategy

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

  - 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 test magnetic space groups using MAXMAGN on the Bilbao Crystallographic Server. Save these as mcif files.

  - Step 4: Convert the mcif file into a .pcr file using mCIF2PCR.

  - Step 5: Use the created .pcr file to fit the nuclear and magnetic neutron data using Fullprof to determined the magnetic structure.

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

$Cs_2Fe_2(MoO_4)_3$: Refinement Strategy

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

  - **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 test magnetic space groups using MAXMAGN on the Bilbao Crystallographic Server. Save these as mcif files.

  - Step 4: Convert the mcif file into a .pcr file using mCIF2PCR.

  - Step 5: Use the created .pcr file to fit the nuclear and magnetic neutron data using Fullprof to determined the magnetic structure.

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

Step 1: Refining the crystal structure using Fullprof

- Need to start refinement with a structural model → **cif file**

- Add in instrument specific parameters to the model → **irf file**

- Then refine this model.

S. Calder, MagStr 2024

Step 1: Refining the crystal structure using Fullprof

<u>INITIAL INPUT</u>

<u>REFINEMENT OF MODEL TO FIT DATA</u>

<u>OUTPUT</u>

Need to start refinement with a structural model → **cif file**

Add in instrument specific parameters to the model → **irf file**

Refine crystal structure and instrument parameters to best match the data

Best fit structural model to be used for k-vector and magnetic structure determination

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

S. Calder, MagStr 2024

Step 1: Refining the crystal structure using Fullprof

Start by putting crystal model into Fullprof

- **1.** From FullProf Suite Toolbar open EdPCR.

- **2.** Import crystallographic information file by clicking on "CIF→PCR"

- **3.** Select the file "ICSD_CollCode422752.cif" when prompted.

S. Calder, MagStr 2024
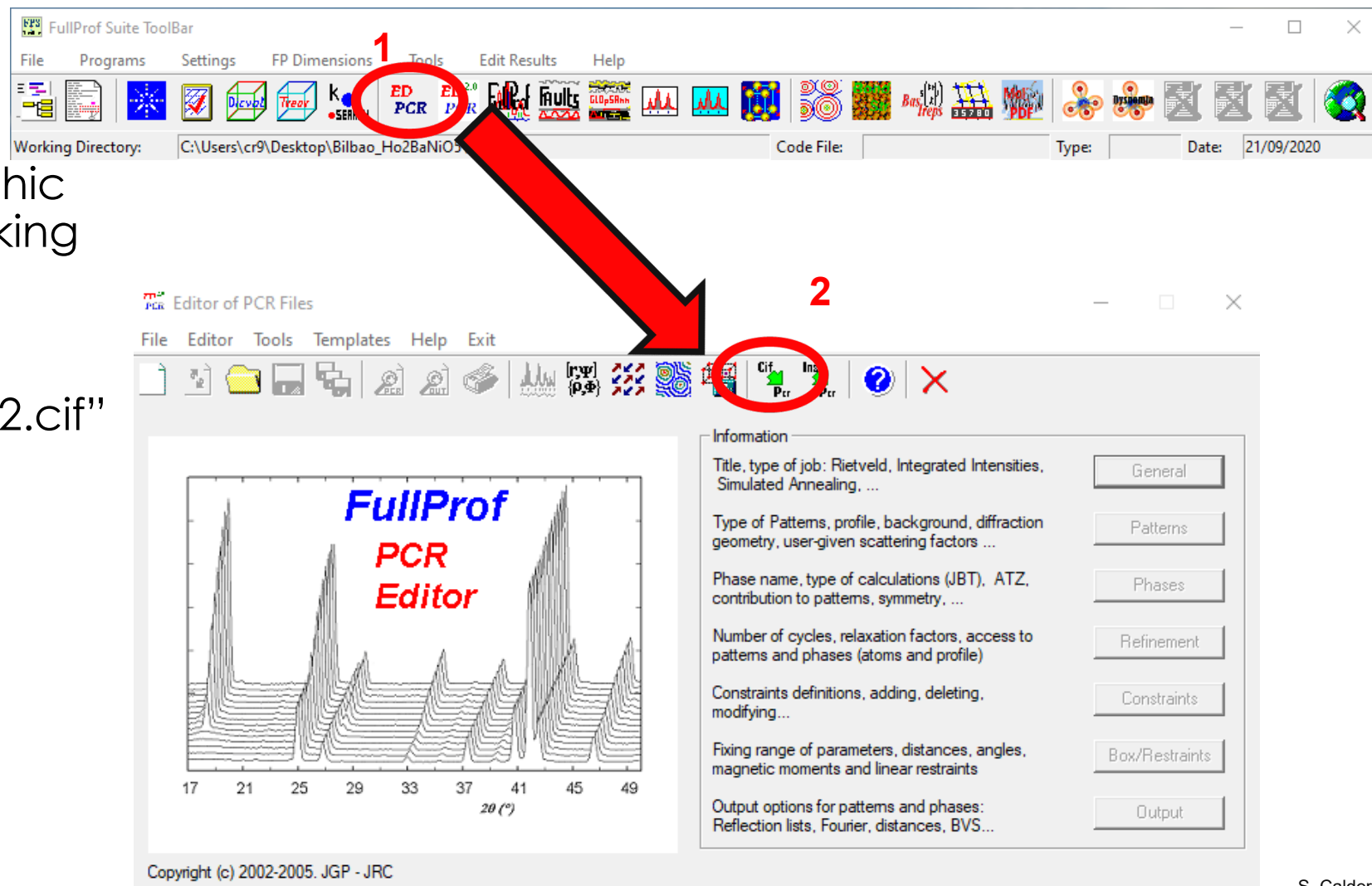
Step 1: Refine the crystal structure using FullProf

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

- **1.** Change "Type" to "Neutron" for constant wavelength

- **2.** Load the instrument resolution file "HB2A_Ge113.irf"
  (click circle and browse to file).

  – *NOTE: remove the full path to just keep "HB2A_Ge113.irf". If you don't it could create problems later if you share file or change folders….*

- Starting **Cell Parameters**, **Space Group** and **Atomic Information** are now loaded.
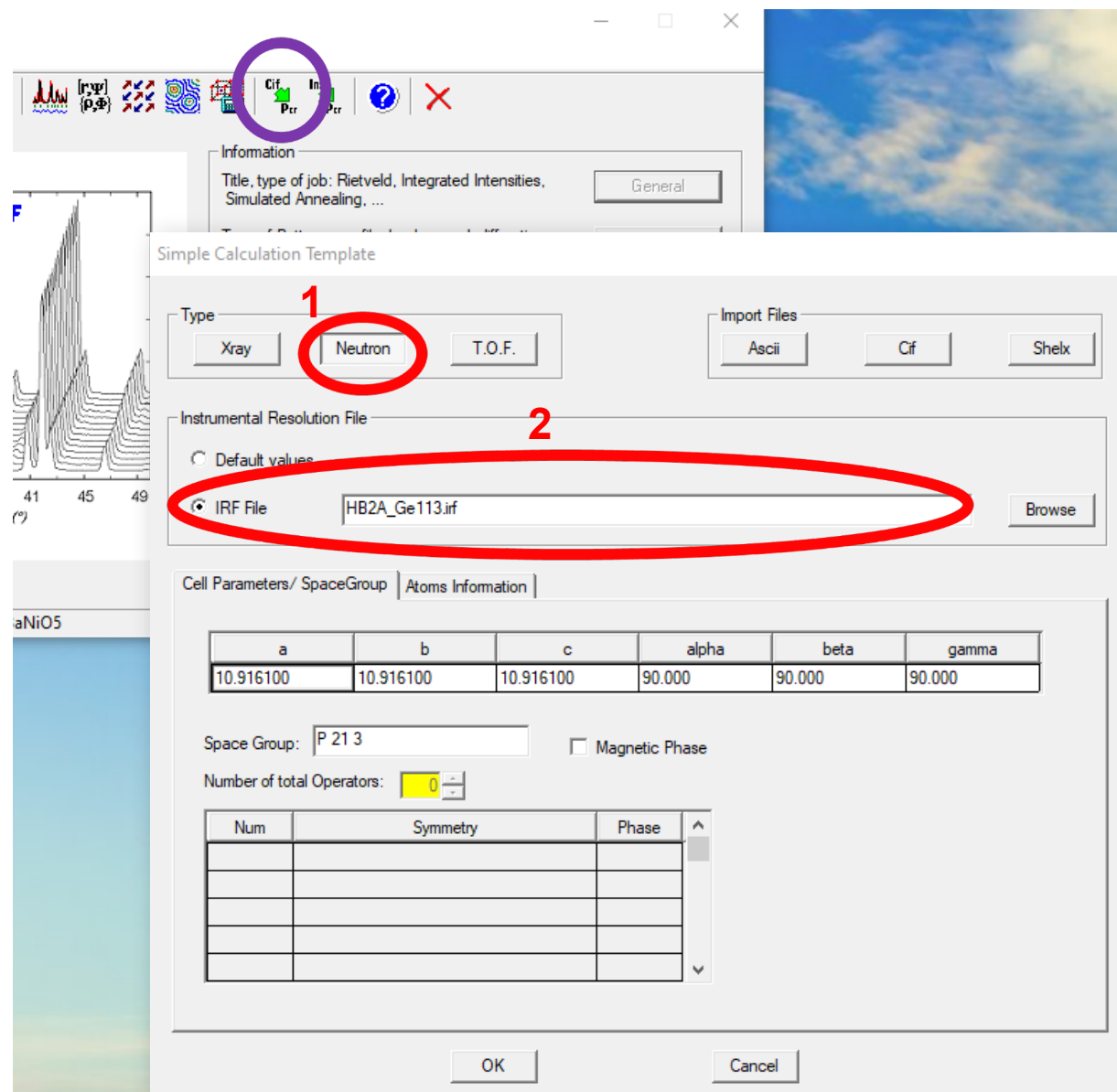
Step 1: Refine the crystal structure using FullProf

- Look in the tab "Atoms Information"
  - Fullprof treats occupancies (Occ) in a particular way related to multiplicities.
  - For example the Cs1 site with Occ=0.333 does not mean that site is deficient or doped.
    In VESTA, GSAS-II etc this would just say "1".
  - **occ = site multip./general multip. Always check this has been correctly calculated after importing the .cif file.**

- Hit "OK" to close the window

Simple Calculation Template

Type: Xray | Neutron | T.O.F.

Import Files: Ascii | Cif | Shelx

Instrumental Resolution File
- Default values
- IRF File: HB2A_Ge113.irf | Browse

Cell Parameters/ SpaceGroup | **Atoms Information**

	Name	Type	X	Y	Z	B	Occ
Atom #1	Cs1	Cs	0.17938	0.32062	0.67938	0.00000	0.33333
Atom #2	Mo1	Mo	0.30061	0.62363	0.52597	0.00000	1.00000
Atom #3	Fe1	Fe	0.33737	0.33737	0.33737	0.84168	0.33333
Atom #4	O1	O	0.27587	0.48544	0.44750	1.96603	1.00000
Atom #5	Cs2	Cs	0.45761	0.95761	0.54239	2.33317	0.33333

	Rx	Ry	Rz	Ix	Iy	Iz	MPhase
Atom #1							
Atom #2							
Atom #3							
Atom #4							

When finished, hit OK OK | Cancel

Step 1: Refine the crystal structure using FullProf

- **1.** Save the changes.

- This should be done whenever changes are made in the GUI.
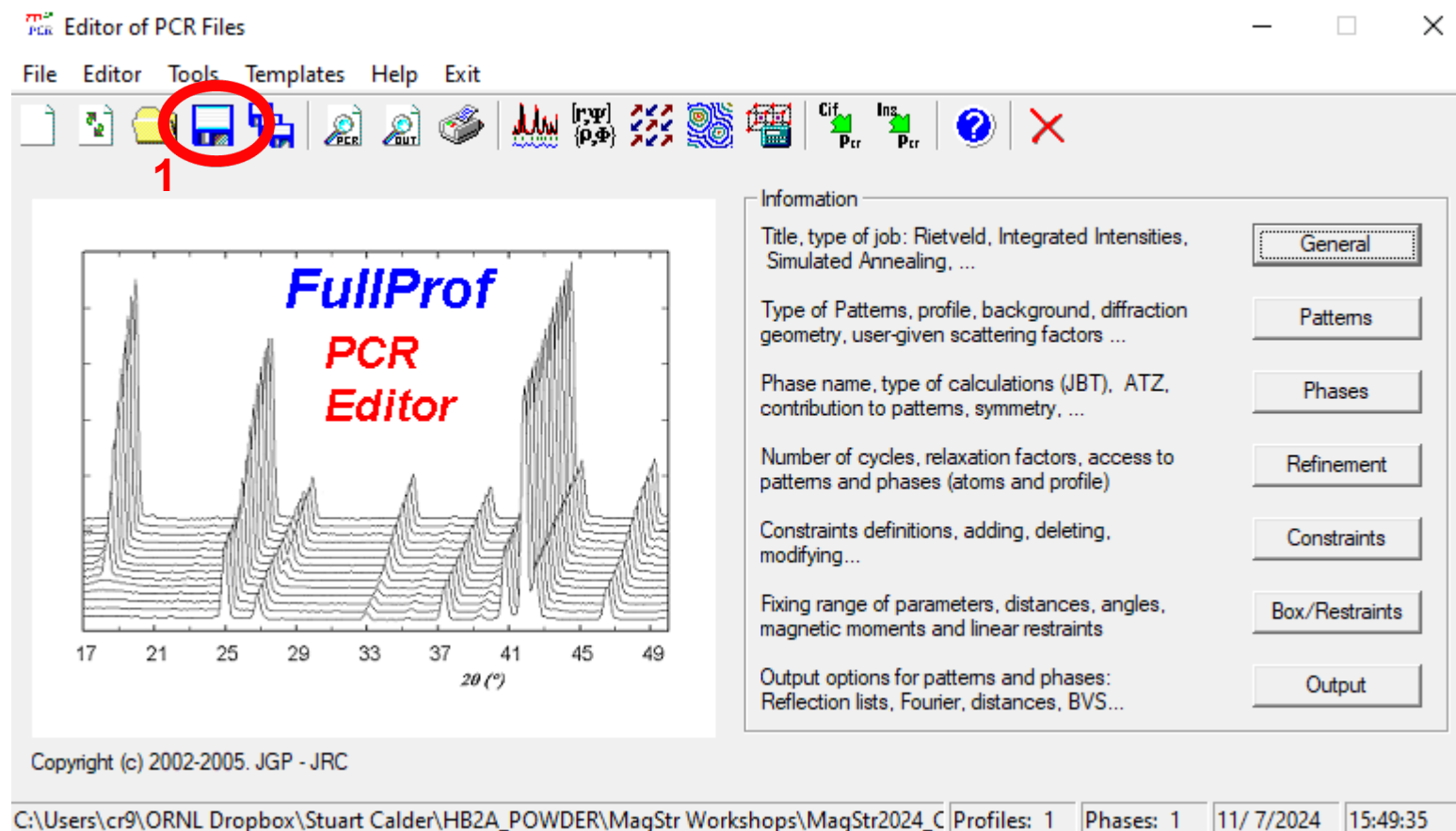
Step 1: Refine the crystal structure using FullProf

- "**General**" tab has refinement of powder data as default. This is what we'll do in this example.

- Can edit title as wanted.

For powder refinements there is no need to edit this tab
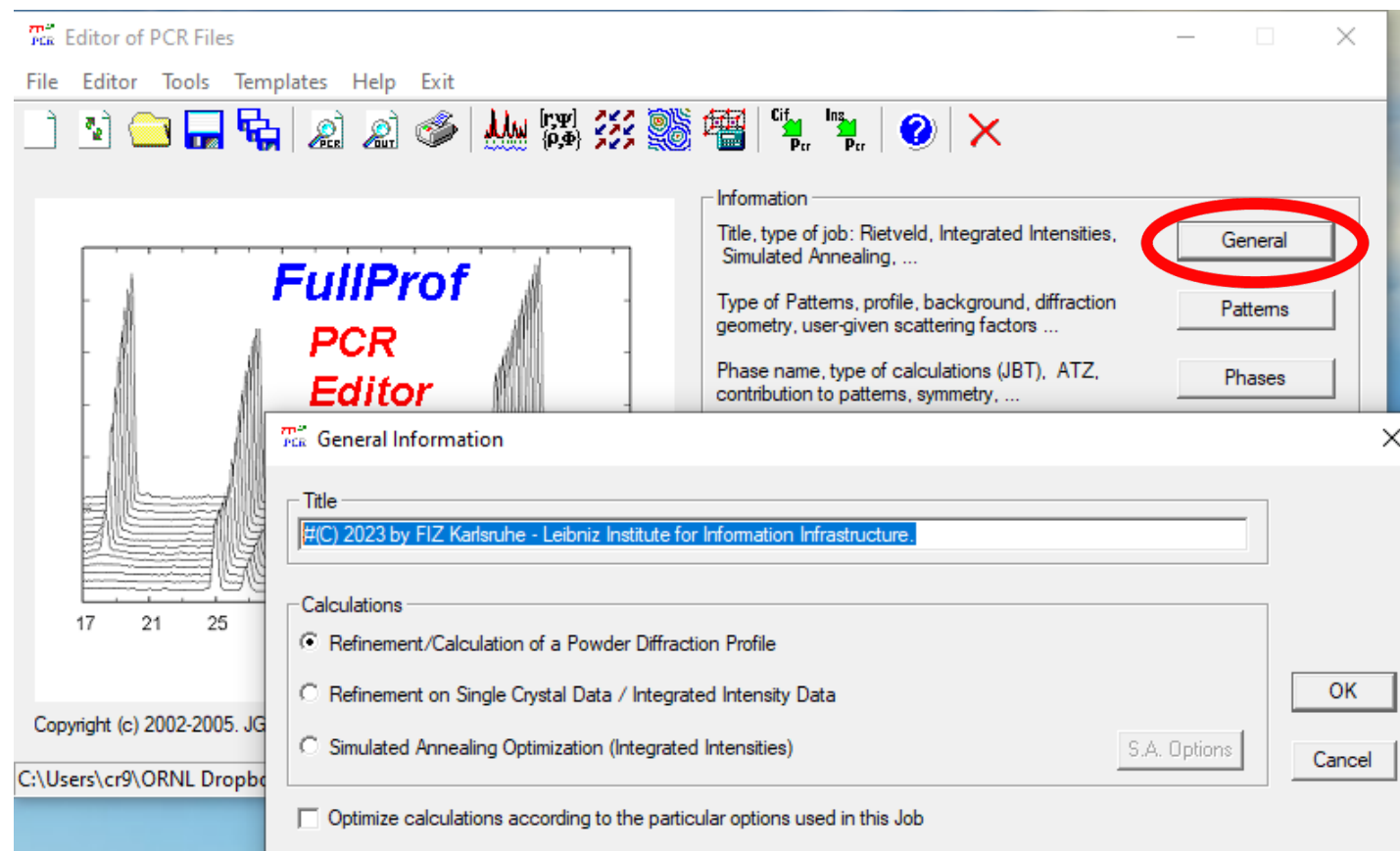
Step 1: Refine the crystal structure using FullProf

1. "**Patterns**" tab

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

- **3.** Patterns → Data file/Peak Shape → X,Y,SIGMA (XYDATA)

Data format from HB-2A is simply three columns with two-theta, Intensity, Intensity Error
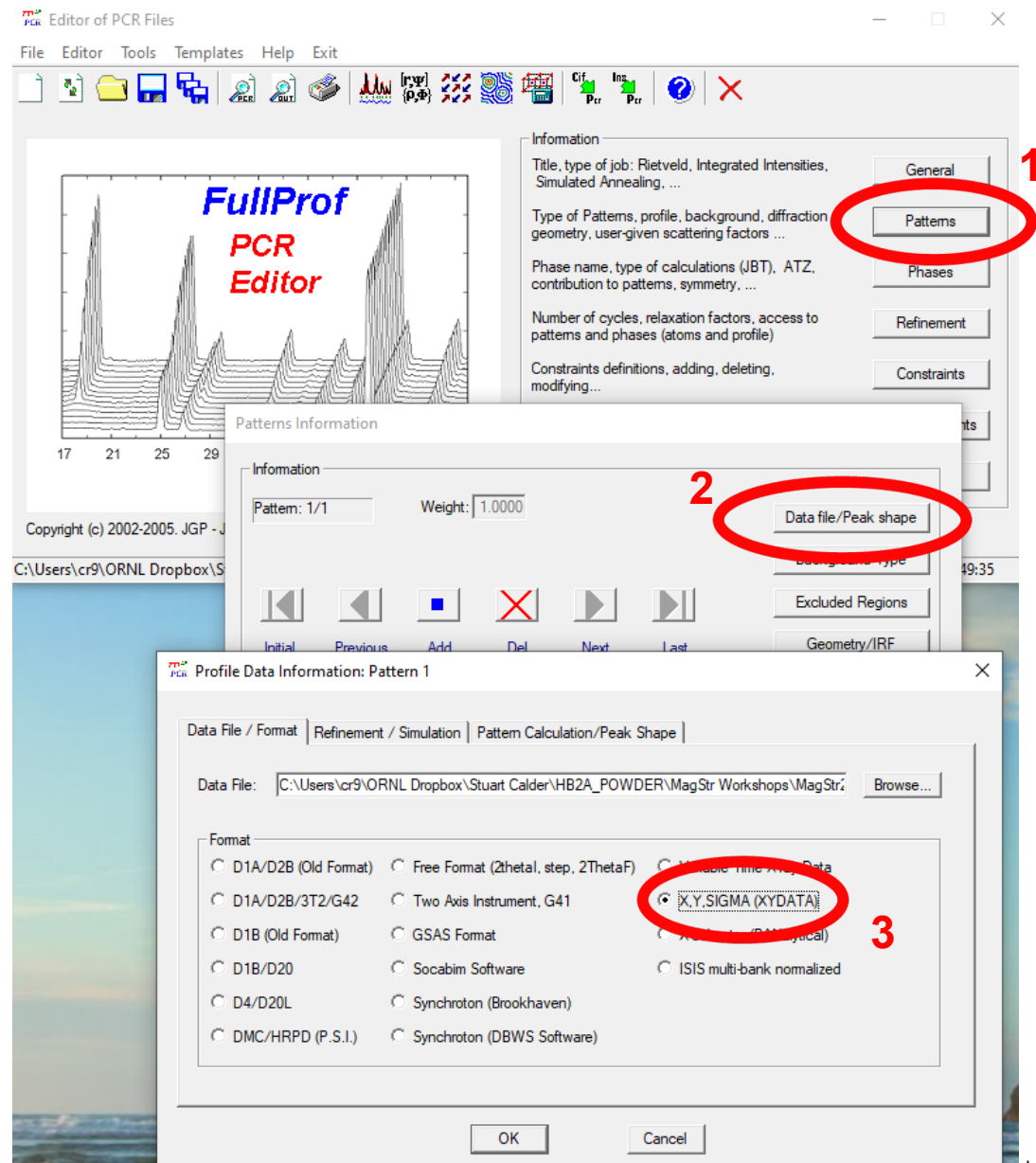
Step 1: Refine the crystal structure using FullProf

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

- **[1]** Select Neutron – CW

- Wavelength is already set by irf file, 2.4067 in this example.
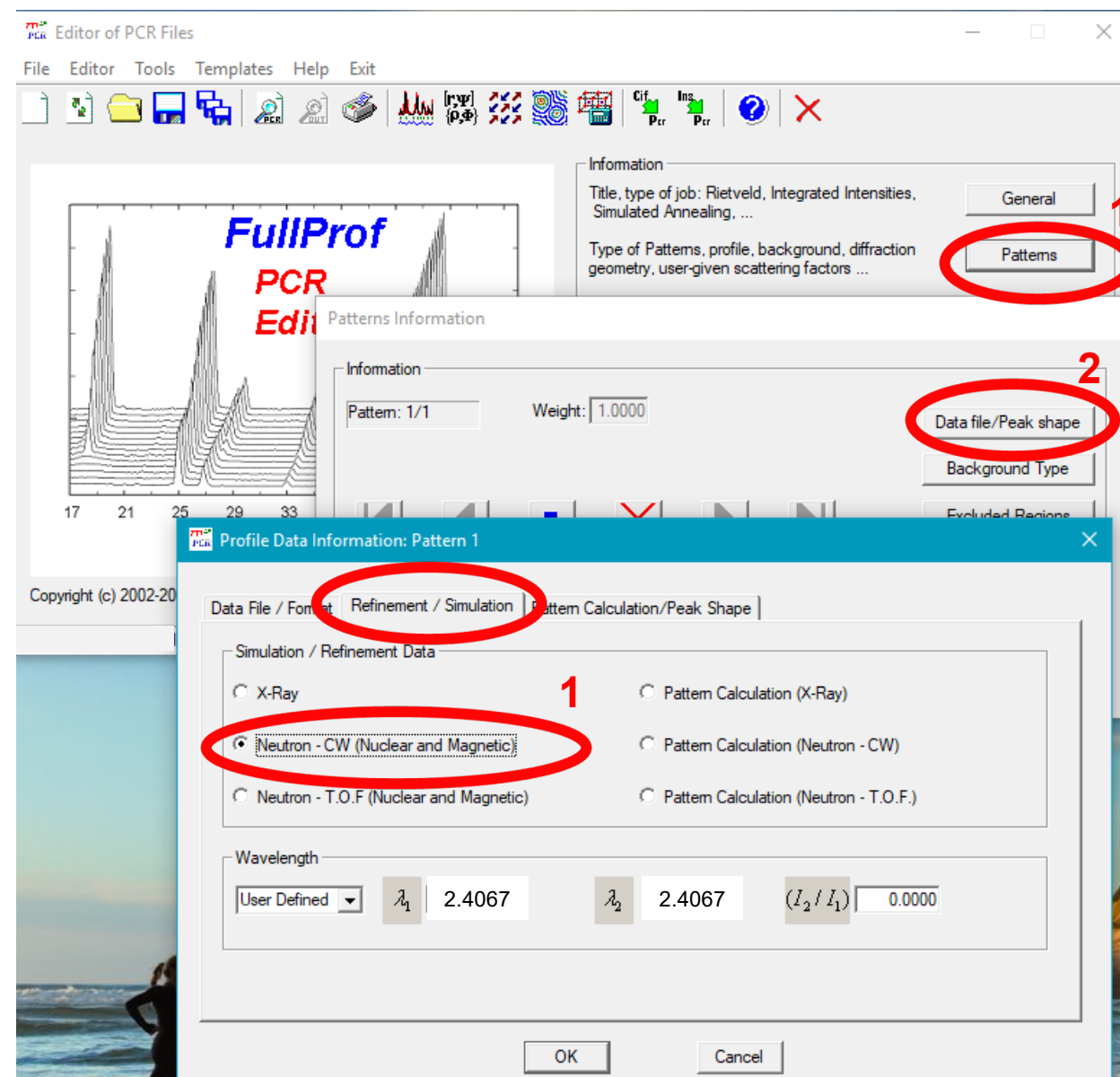
Step 1: Refine the crystal structure using FullProf

- Check final tab:

- Patterns → Data file/Peak Shape →Pattern Calculation/Peak Shape

- Peak shape is already loaded correctly from irf file.

S. Calder, MagStr 2024
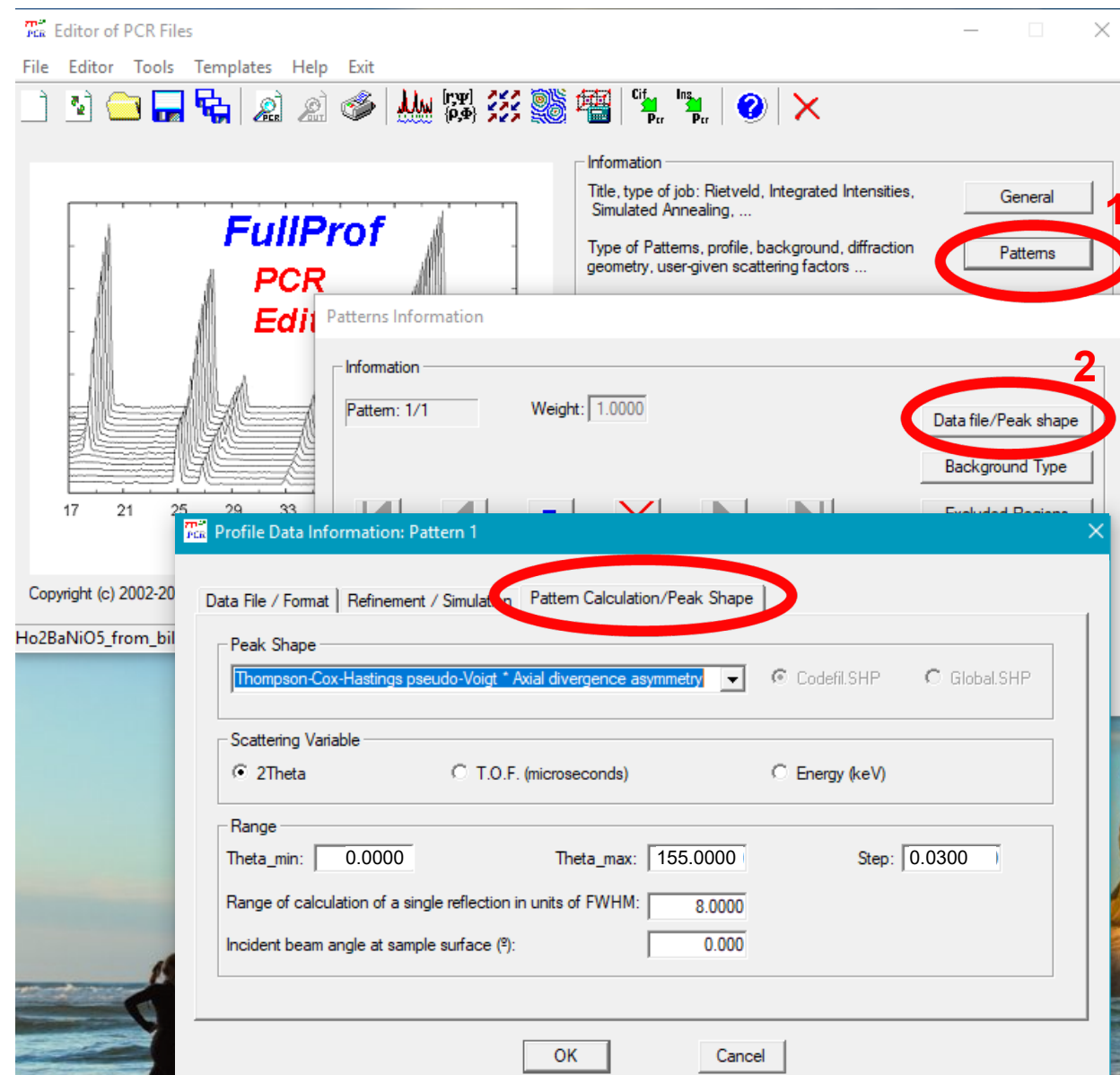
Step 1: Refine the crystal structure using FullProf

- Move to next tab down to select background type

- Patterns→ Background Type Check "6-coefficient"

- Put origin of polynomial at 60 for this example.

Background on HB-2A typically low and featureless so can be captured by simple polynomial function.
But multiple background choices exist in Fullprof.
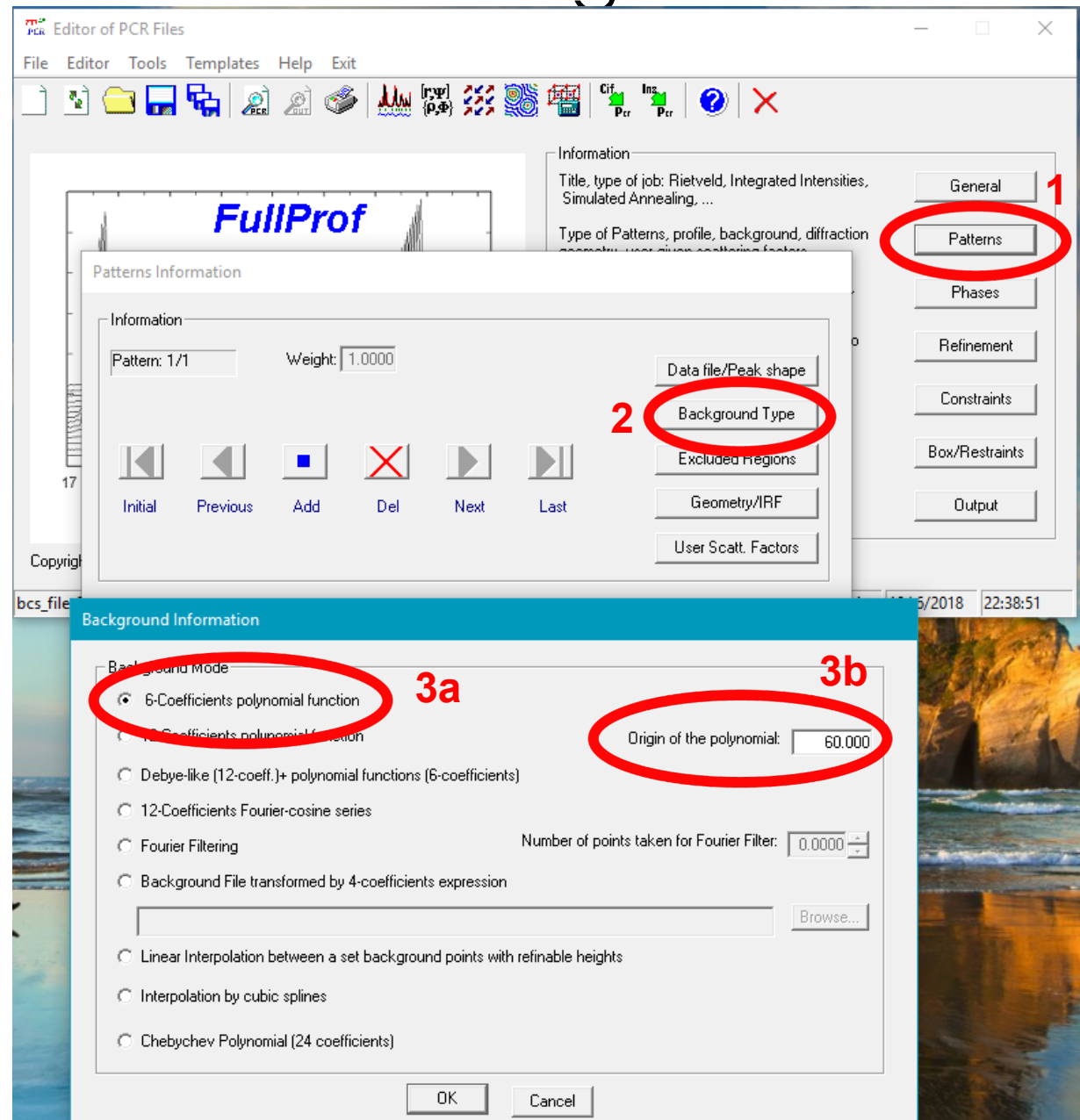
Step 1: Refine the crystal structure using FullProf

Exclude regions in the data?

- For now we will not exclude any regions of the data

- Use with care, but can cut out background.

- Can allow focus of refinement on different regions, e.g. only low Q

- Quick way to remove peaks from sample holder or can → but should try to fit these if possible!

S. Calder, MagStr 2024
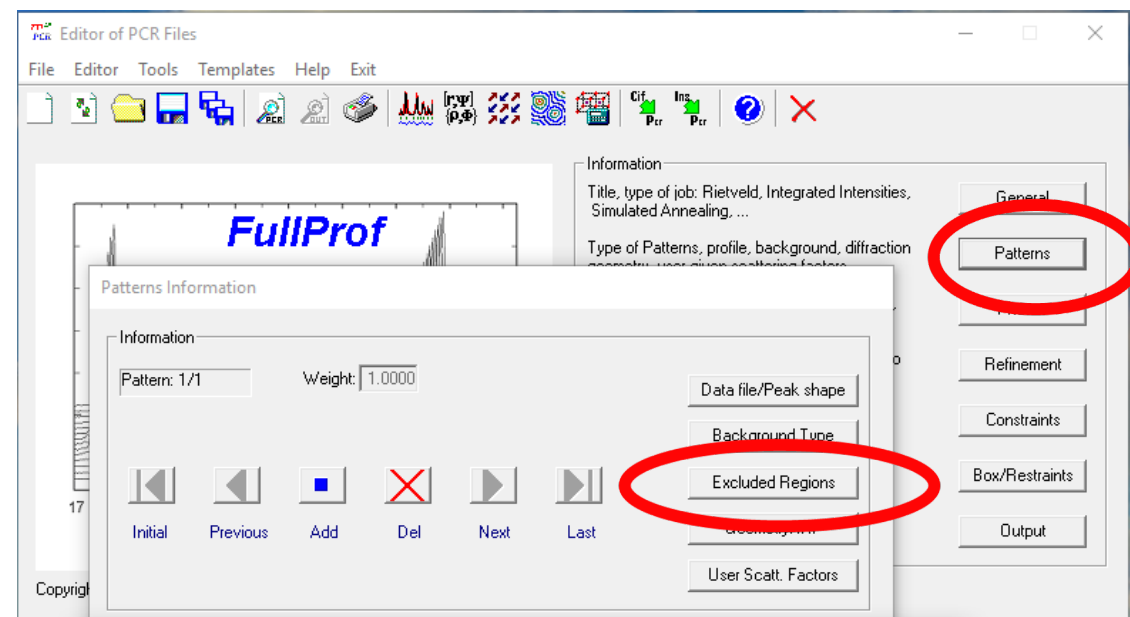
Step 1: Refine the crystal structure using FullProf

– Geometry/IRF
  Populated by irf file.

– Corrections: the instrument layout gives asymmetric peaks, particularly at low angle. These can be corrected.
  Change "Peaks below this 2Theta limit are corrected for asymmetry" to 180. Forgetting to do this, then refining the asymmetry parameters is a common error!
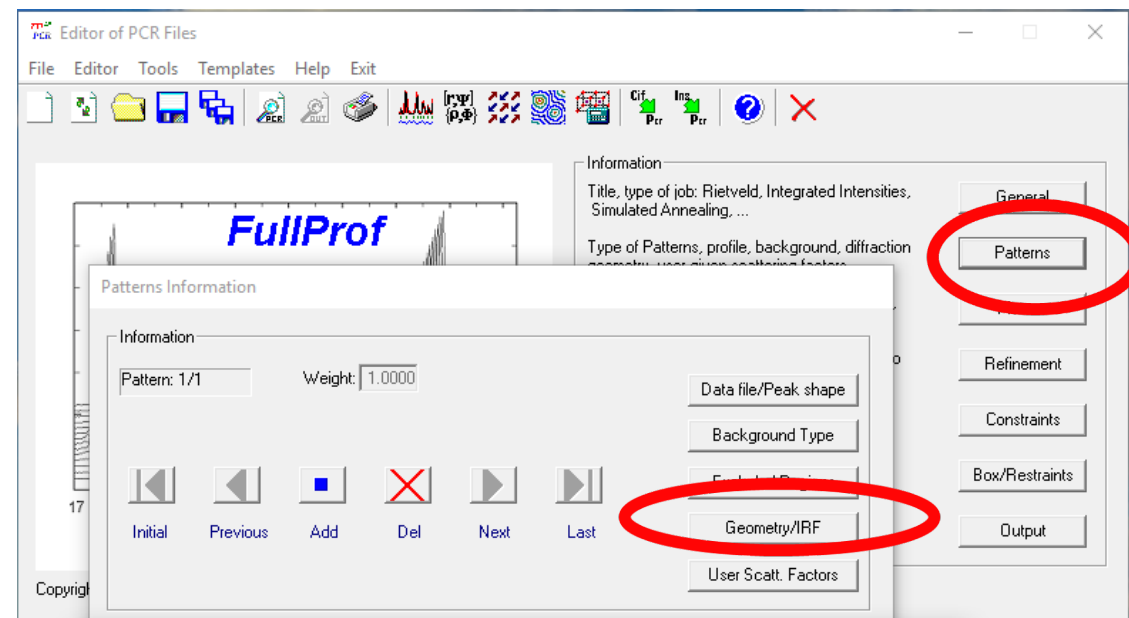
– Can correct for absorption if needed. "muR" is mu (absorption) multiplied by sample radius. Can find mu at NIST website
  https://www.ncnr.nist.gov/resources/activation/

Change "Peaks below the 2Theta…" to 180
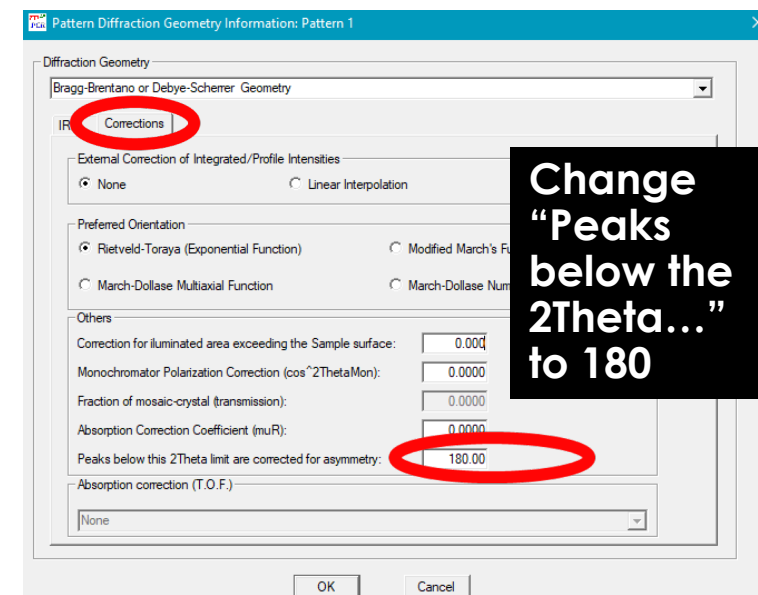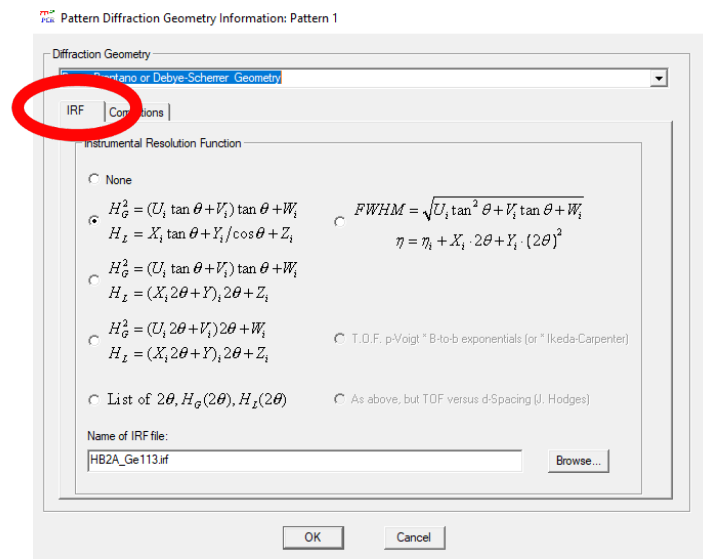
Step 1: Refine the crystal structure using FullProf

- No further editing should be needed of the remaining "Patterns" tab "User Scatt. Factors"

  - This can be used to add e.g. a form factor that isn't tabulated
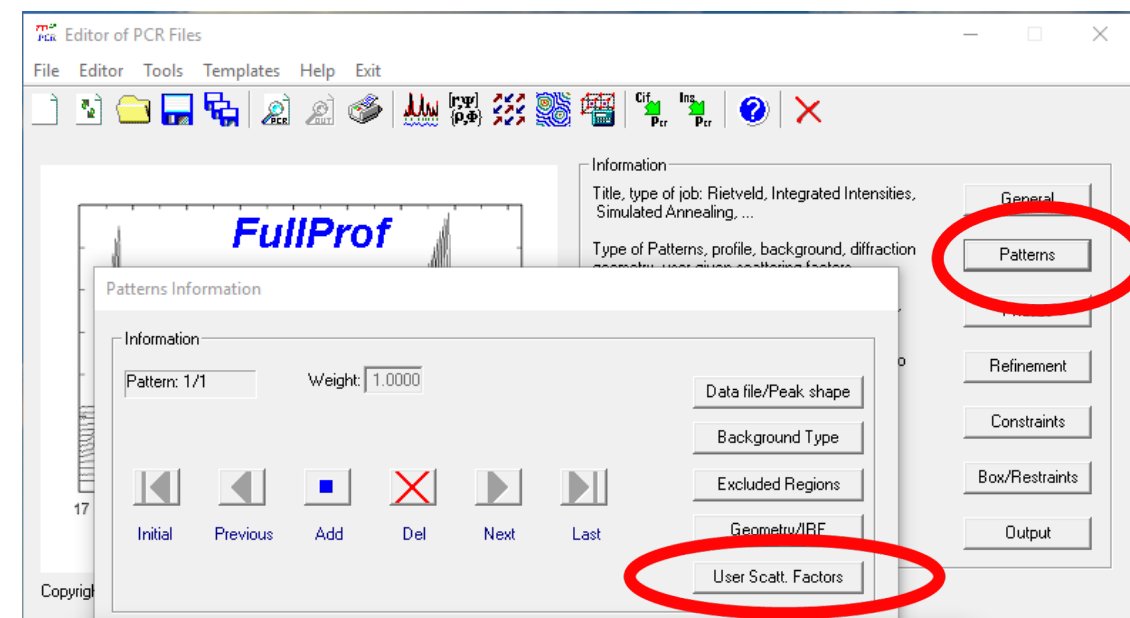
> If the magnetic ion does not have form factor tables tabulated, or you want to test a non-standard form factor, this can be added here. One example would be for 5d ions, such as Ir, Os, etc.

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

Step 1: Refine the crystal structure using FullProf

PHASES tab

Can do a simulation or refinement with data. Select which one here.

- Make phase contribute to refinement.

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

- Set peak shape to "**Thompson-Cox-Hastings pseudo-Voigt**"
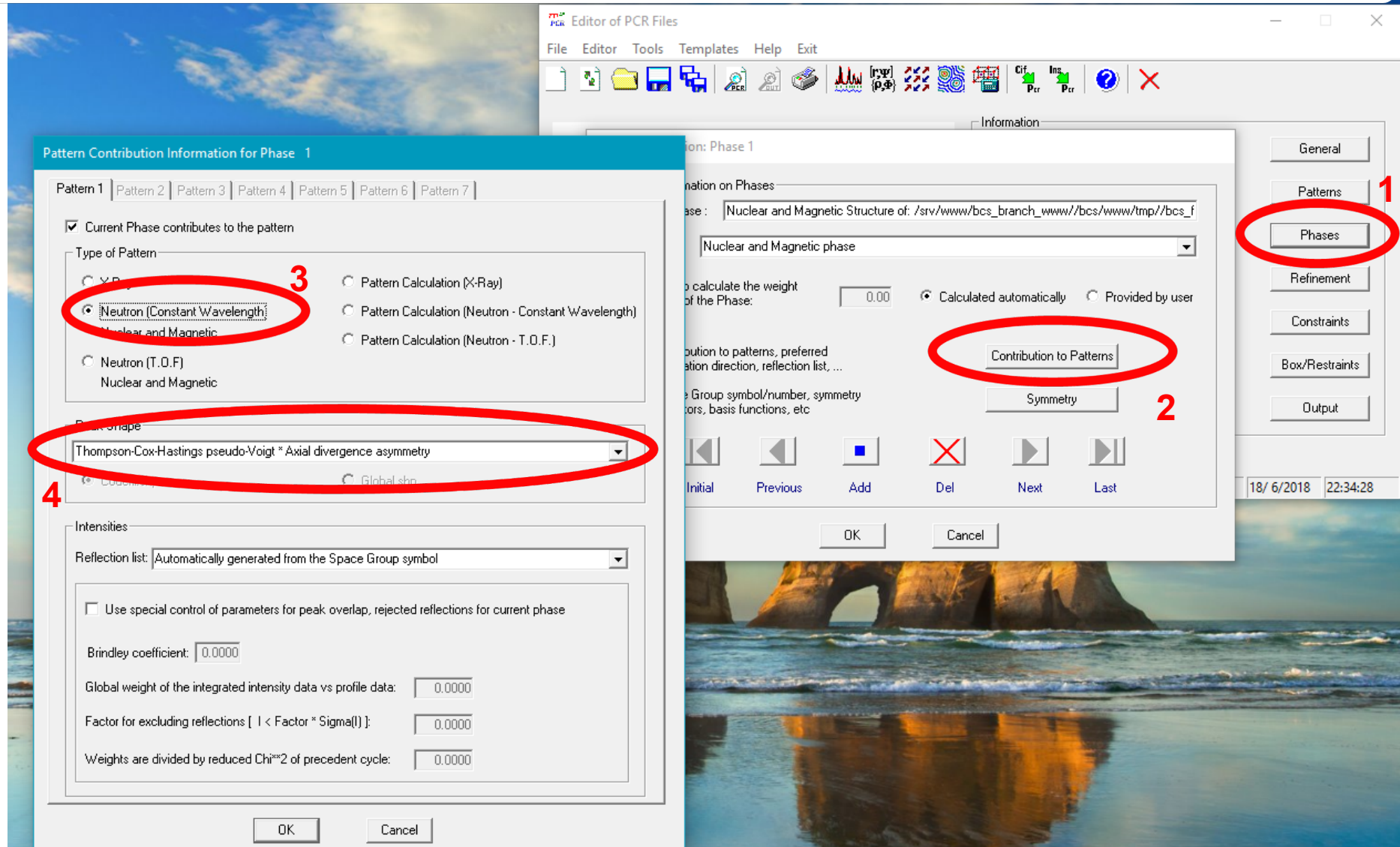
Step 1: Refine the crystal structure using FullProf

REFINEMENT tab:

- Setting starting values for refinements

- Starting background value of 100000 (check data)

National Laboratory | REACTOR | SOURCE

S. Calder, MagStr 2024

Step 1: Refine the crystal structure using FullProf

- Select "Refinement" tab again.

- Update "Cycle of Refinement" to 10

- From "Refinement" tab select: Refinement>Profile

- Change scale to 100.

  - Note – it is often best to run a refinement without anything refining and then adjusting scale manually until it is close.
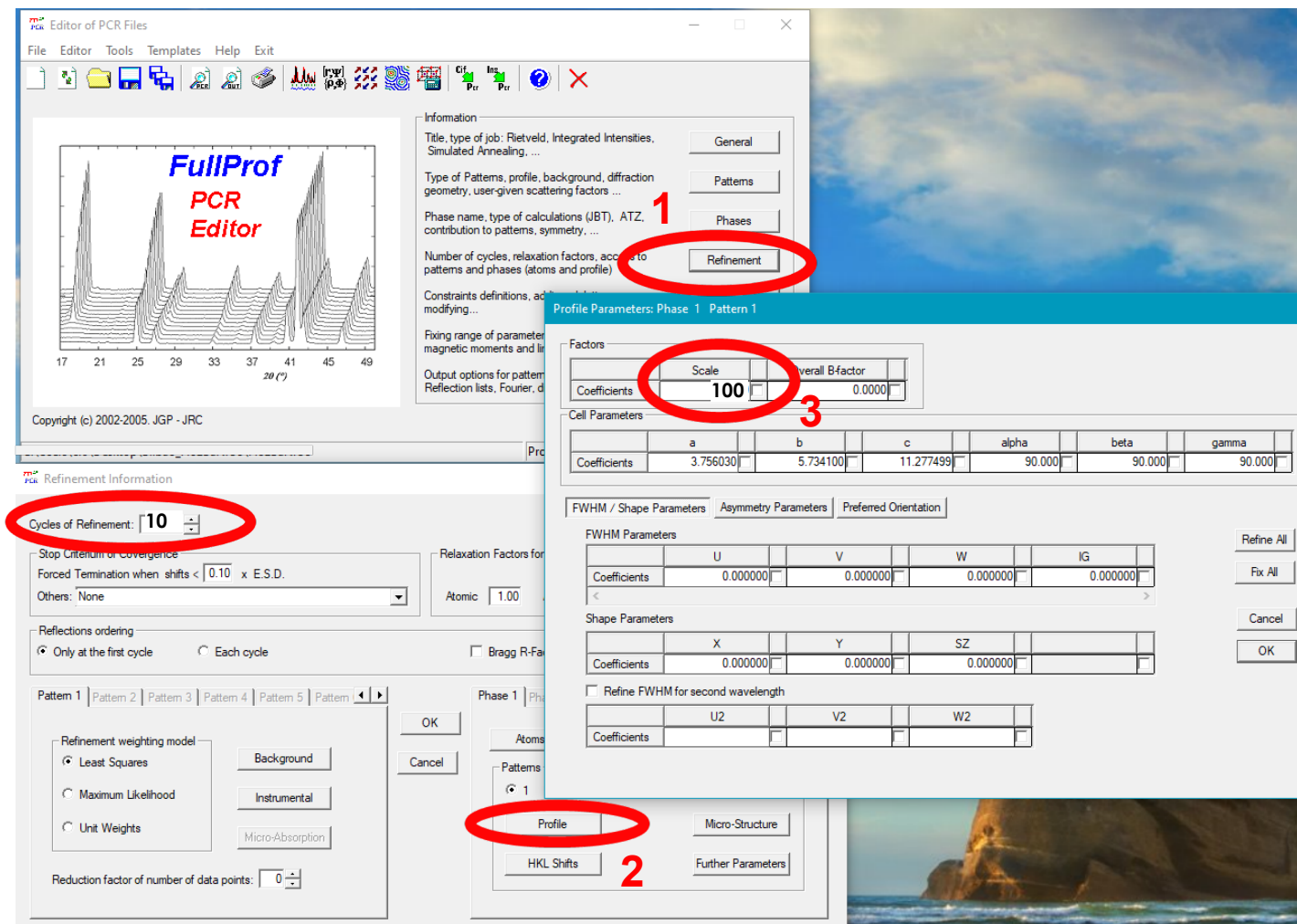
Crystal structure has been added.
Instrument parameters added. We have
checked background.
BEFORE setting anything to vary, run the
refinement with nothing refining.
This lets you see how close you are and if
things have to be manually changed or if
it is close enough to try a refinement

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

Step 1: Refine the crystal structure using FullProf

- 1. Run the refinement
  Select the "*CFMO_10K.dat*" data

- 2. Refinement runs for the number of cycles or until converged.
  Since we're not yet refining anything it just runs for ne cycle.
  You can repeat this by pushing run until
  "Normal end, final calculation and writing…" shows rather than "Convergence not reached"

The residual (blue) shows lots of differences between data (red) and model (black). But scale is close, background is close. Looks mainly like the position of the Bragg peaks are slightly off.
We used a cif file from a database, likely different temperature.
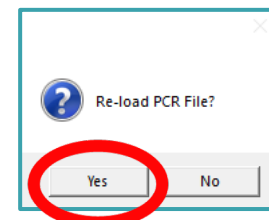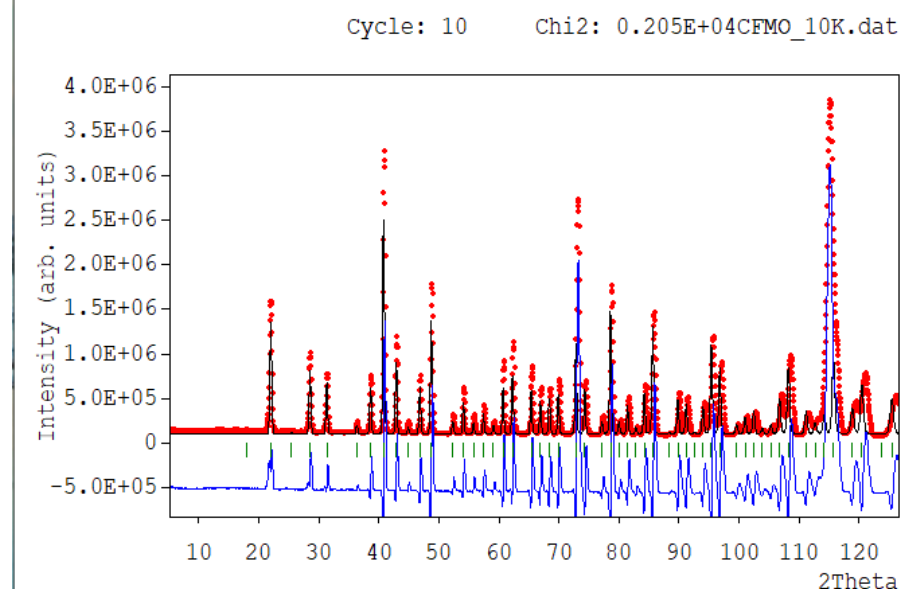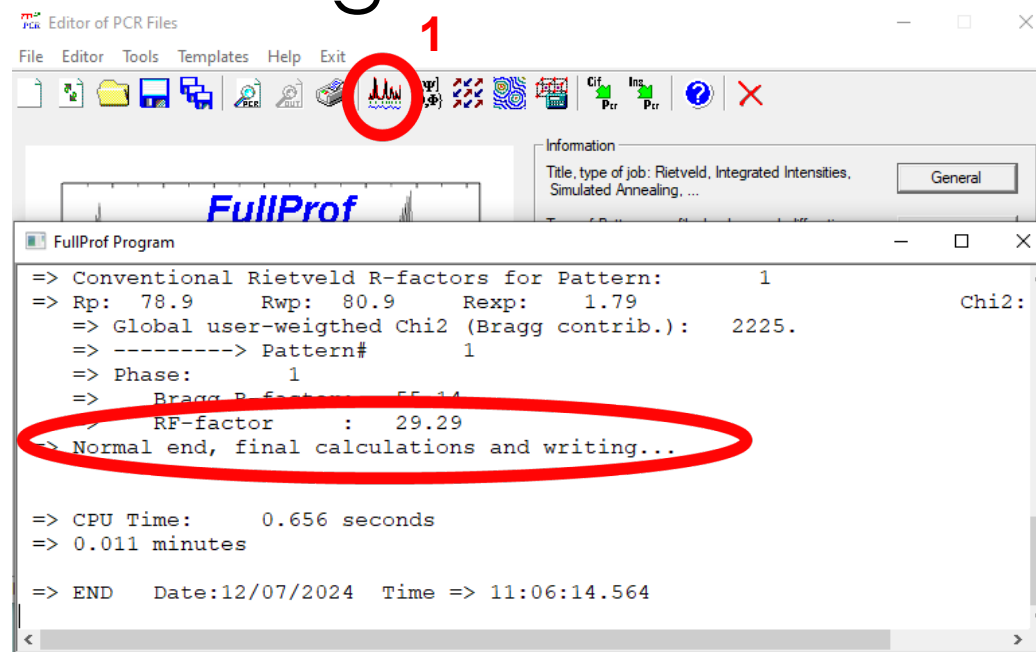
When you first run a refinement several files are created in the same folder as the pcr file. Some by default and others than can be turned on/off using the output tab.
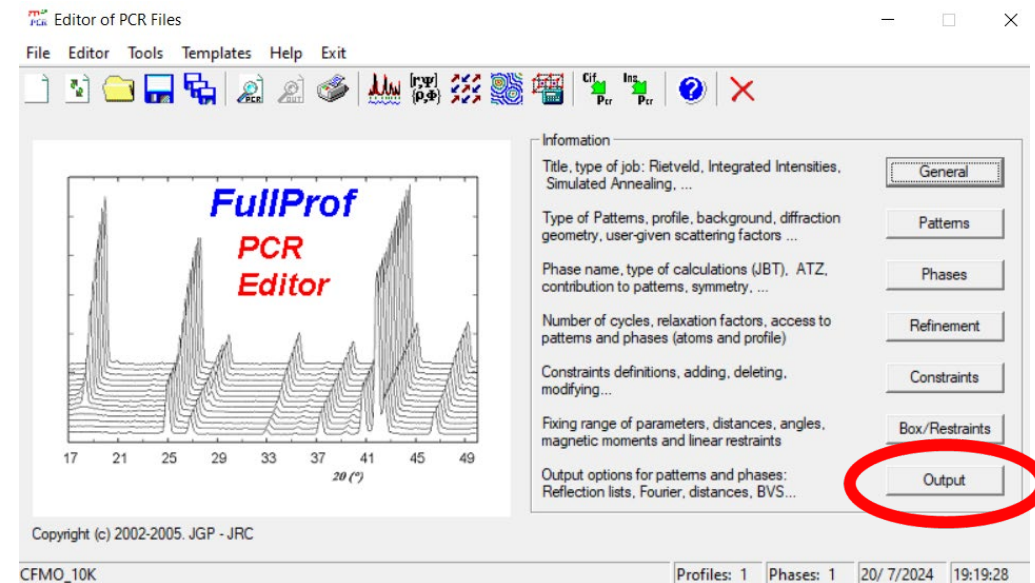
Now we can turn of parameters to refine
to try to get he model and data to match

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

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) Zero corrects for any offset between two-theta in data and actual two-theta, should be small.*

- Can also try to refine atomic parameters (but in this case data may not have enough reflections to be stable): Refinement→Phase tab→Atoms

Profile Parameters: Phase 1 Pattern 1

Factors

	Scale	Overall B-factor
Coefficients	100.00 ☑	0.0000 ☐

Cell Parameters

	a	b	c	alpha	beta	gamma
Coefficients	10.916100 ☑	10.916100 ☑	10.916100 ☑	90.000 ☐	90.000 ☐	90.000 ☐

FWHM / Shape Parameters | Asymmetry Parameters | Preferred Orientation

FWHM Parameters   Refine All   Fix All

	U	V	W	IG
Coefficients	0.000000 ☐	0.000000 ☐	0.000000 ☐	0.000000 ☐

6 Coefficients Polynomial Background: Pattern 1

	d_0	d_1	d_2	d_3	d_4	d_5	Refine All
Coefficents	0.10000E+06 ☑	0.0000 ☑	0.0000 ☑	0.0000 ☑	0.0000 ☐	0.0000 ☐	Fix All

	d_6	d_7	d_8	d_9	d_10	d_11
Coefficents						

Instrumental Parameters Refinement: Pattern 1

2_Theta   Refine All   Fix All

	Zero	Displacement	Transparency	Wavelength	
Coefficients	0.000000 ☑	0.000000 ☐	0.000000 ☐	0.000000 ☐	Cancel OK

List of Atoms

Number of Atoms: 5

	Label	Ntyp	X	Y	Z	B	Occ	Therm. Fact.
Atom # 1	Ho1	Ho	0.50000 ☐	0.00000 ☐	0.20250 ☑	0.00000 ☐	0.25000 ☐	Isotropic
Atom # 2	Ba1	Ba	0.50000 ☐	0.50000 ☐	0.00000 ☐	0.00000 ☐	0.12500 ☐	Isotropic
Atom # 3	Ni1	Ni	0.00000 ☐	0.00000 ☐	0.00000 ☐	0.00000 ☐	0.12500 ☐	Isotropic
Atom # 4	O1	O	0.00000 ☐	0.24140 ☑	0.14950 ☑	0.00000 ☐	0.50000 ☐	Isotropic

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

Refinement parameters in Fullprof

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.
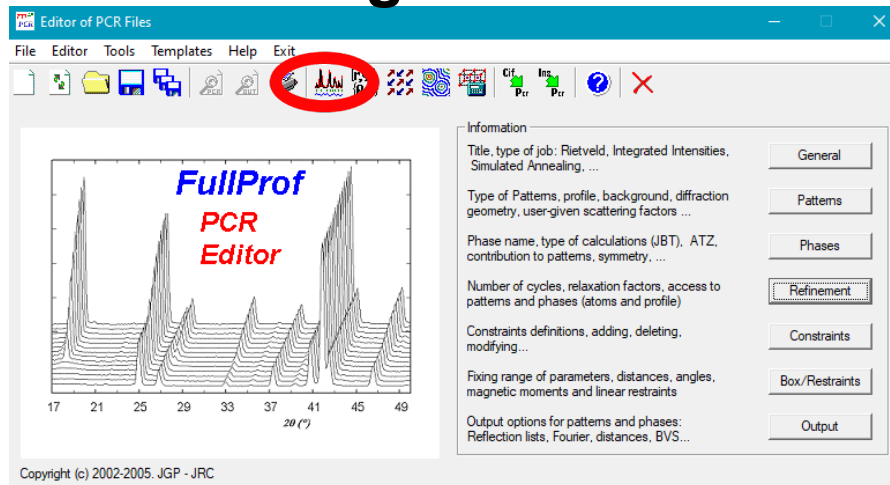Those constrained have the same code e.g. 11 and 11 or 511 and 511.

S. Calder, MagStr 2024

Working in text editor and GUI

- Can use BOTH the GUI and edit the text of the.pcr file.

- Open text with 1. [pcr and magnifying glass].

- Can quickly see and edit varios things quicker than with GUI

  – Anything refining has a number that ends in a 1 (e.g. 11, 21, 31, 811, 641, etc)

  – The scale has a 71, so is refining.

  – The lattice constants (a,b,c) all have a 11 refinement label, so they are constrained.

- To turn on any to refine can type a 1, then Fullprof figures out the numbering.

Step 1: Refine the crystal structure using FullProf

Run refinement again

- Refinement is getting close.

- Peak positions look better. But the peak shape isn't matching
  - Refine peak profiles next

Peak profiles should only be run after the refinement and peak positions are close, others refinement will blow-up

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

Step 1: Refine the crystal structure using FullProf

Run refinement again

Can be easier to look at fit in WINPLOTR which opens the created .prf file.

Set WINPLOTR to always open .prof files. Then don't need to rely on toolbar (which doesn't always work)

Large mismatched peaks are from Al sample can
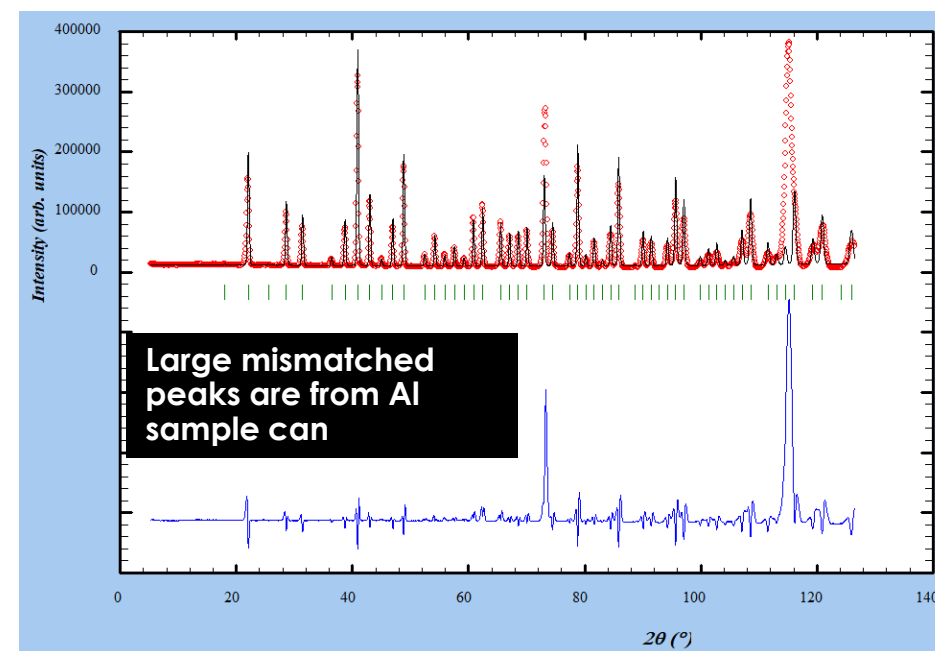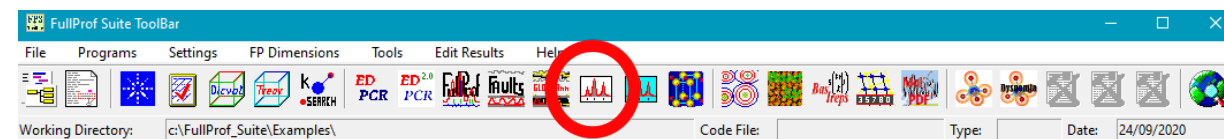
Step 1: Refine the crystal structure using FullProf

Run refinement again (10 K data)

- Refinement getting close.

- Refine peak positions:

- Refinement>profile

- Refine U,V,W.

- These are the Caglioti parameters that define peak shape for reactor based instruments.

These are zero here BUT reading the values from the .irf file. So refining them will add on to the values. This is a way to see how much peak broadening comes from sample. For detailed refinements could use strain, grain size, etc. We don't need this for magnetism

Step 1: Refine the crystal structure using FullProf

Run refinement again (10 K data)

- Now much closer.
  - Do not focus on the chi or other fit values, visually see how close the fit is and what needs improved.

- Two peaks are not fit. These are at 2theta positions consistent with the Al sample can.
  - To save time we will simple exclude the regions around the Al can. But these can and should be fit in final published refinement. But cannot just add an Al phase due to texture. Need to use profile matching to fit each peak separately.

Step 1: Refine the crystal structure using FullProf

Exclude the Al sample holder. This cannot be fit by adding a standard Al phase since it is highly textured, to fit this would need to do profile matching and fit each peak separately.

- Look at data and fit to choose which regions to cut out.

- Patterns>Excluded Regions

Step 1: Refine the crystal structure using FullProf

- Can also try to refine atomic parameters (but in this case data may not have enough reflections to be stable): Refinement→Phase tab→Atoms

- Click "Refine Positions"

- Change all thermal parameters (B) to Isotrpoic in the "Therm. Fact." column.

- Then make all B values 0.3. The maximum Q here is ~4 A. So it is not high enough to refine thermal parameters.

- NOTE: do this for all 9 atoms, use scroll bar.

S. Calder, MagStr 2024

Step 1: Refine the crystal structure using FullProf

- Fit is now very close to the 10 K data.

Step 1: Refine the crystal structure using FullProf

- Can try to refine the asymmetry further.

S. Calder, MagStr 2024

Step 1: Refine the crystal structure using FullProf

- Fit to the 10 K data is now good enough to move on to refine the 0.3 K data and try to determine the magnetic structure.

- Some mismatch could be from short range order that is expected in this material at 10 K.
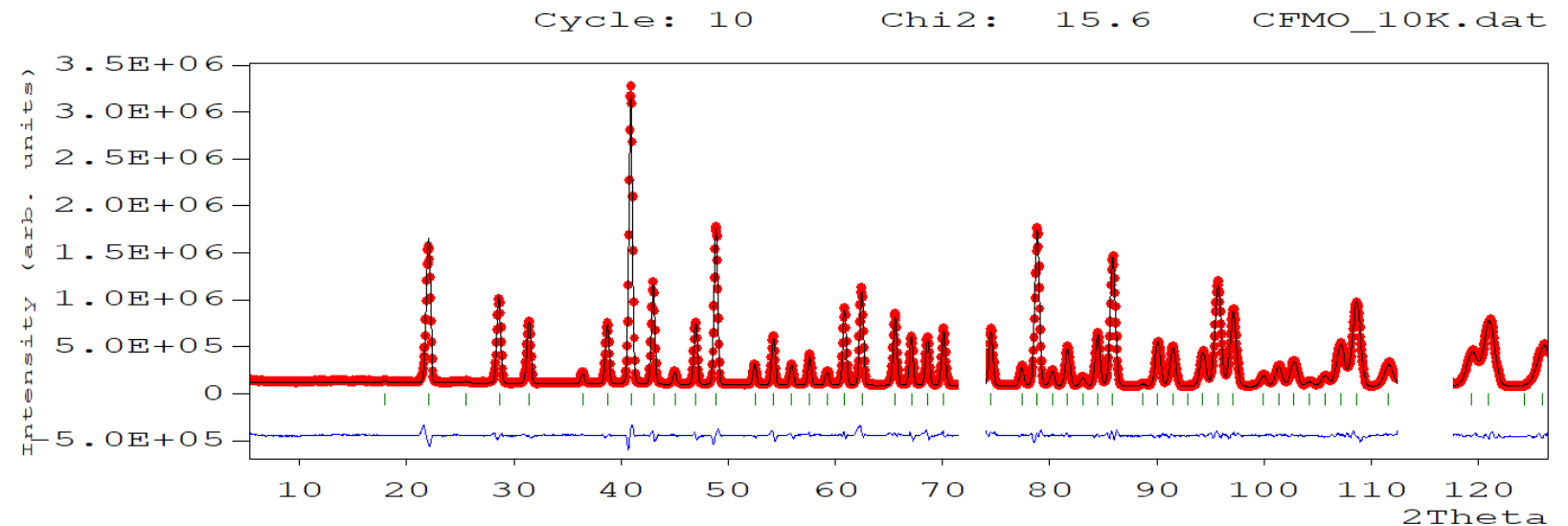


```
 FullProf Program

=> Expected :                1.45                    1.9008
=> Conventional Rietveld R-factors for Pattern:        1
=> Rp:  6.85      Rwp:  8.14     Rexp:    2.06                  Chi2:  15.6
   => Global user-weigthed Chi2 (Bragg contrib.):   16.47
   => ---------> Pattern#       1
   => Phase:       1
   =>    Bragg R-factor:   2.230
   =>    RF-factor     :   1.588

=> Convergence reached at this CYCLE !!!!: CYCLE No.      6
=> R-Factors:    4.16       5.72     Chi2:  15.6    DW-Stat.:  0.2463   Patt#:  1
=> Expected :                1.45                    1.9008
=> Conventional Rietveld R-factors for Pattern:        1
=> Rp:  6.85      Rwp:  8.14     Rexp:    2.06                  Chi2:  15.6
   => Global user-weigthed Chi2 (Bragg contrib.):   16.94
   => ---------> Pattern#       1
   => Phase:       1
   =>    Bragg R-factor:   2.230
   =>    RF-factor     :   1.588
=> Normal end, final calculations and writing...


=> CPU Time:     1.936 seconds
=> 0.032 minutes

=> END    Date:12/07/2024  Time => 12:00:40.582
```

Now refine the 0.3 K data using this model. Before doing this TURN OFF ALL PARAMATERS.

Step 1: Refine the crystal structure using FullProf

- Check everything is turned off in the text file.

Step 1: Refine the crystal structure using FullProf

- Run refinement against the 0.3 K data

- "CFMO_300mK.dat"

- This looks good, with the extra magnetic peaks.

- Could refine lattice constants since the the temperature changed, but fits looks close that this isn't needed yet.


```
FullProf Program
=> Expected :                    1.46                          1.8695
=> Conventional Rietveld R-factors for Pattern:       1
=> Rp: 10.00      Rwp: 13.1      Rexp:    2.05                      Chi2:  40.6
   => Global user-weigthed Chi2 (Bragg contrib.):    29.39
   => ---------> Pattern#        1
   => Phase:       1
   =>     Bragg R-factor:    3.077
   =>     RF-factor     :    1.998

=> Convergence reached at this CYCLE !!!!: CYCLE No.       1
=> R-Factors:     6.10         9.31      Chi2:  40.6      DW-Stat.:  0.1079    Patt#:  1
=> Expected :                    1.46                          1.8695
=> Conventional Rietveld R-factors for Pattern:       1
=> Rp: 10.00      Rwp: 13.1      Rexp:    2.05                      Chi2:  40.6
   => Global user-weigthed Chi2 (Bragg contrib.):    43.97
   => ---------> Pattern#        1
   => Phase:       1
   =>     Bragg R-factor:    3.077
   =>     RF-factor     :    1.998
=> Normal end, final calculations and writing...


=> CPU Time:      0.752 seconds
=> 0.013 minutes

=> END    Date:12/07/2024   Time => 12:09:52.995
```
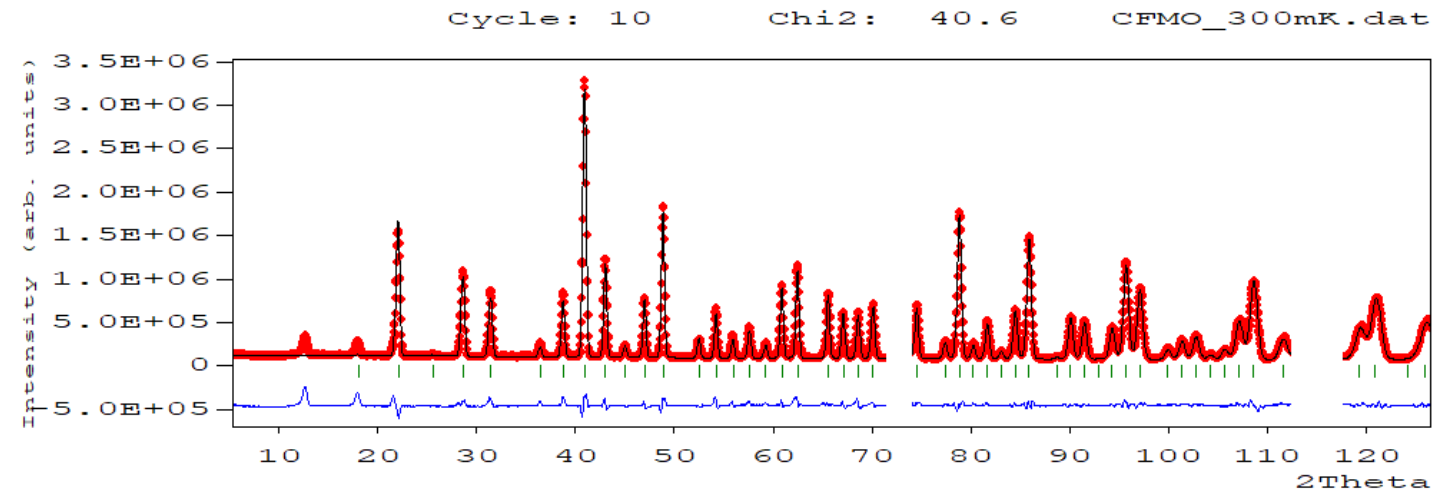
Step 1: Refine the crystal structure using FullProf

- Go into the "Output" tab to create a cif file after each refinement.

- This is a good way to check the structure makes sense.

- We will also use this as the starting point for our magnetic model.

- CHECK your folder to see all the files that are output when you run Fullprof.

- Link this cif file to open with VESTA
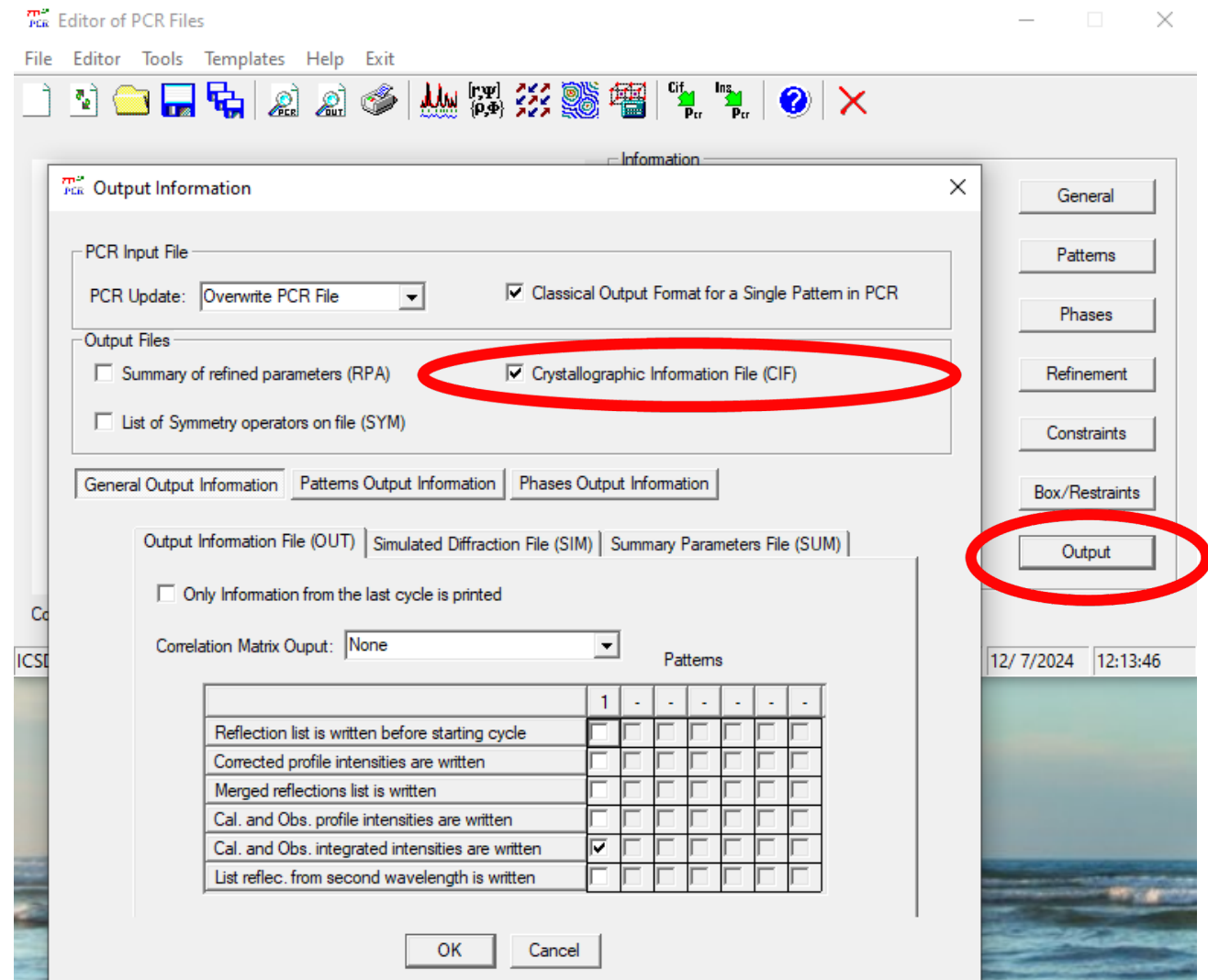
$Cs_2Fe_2(MoO_4)_3$: Refinement Strategy

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

    – 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 test magnetic space groups using MAXMAGN on the Bilbao Crystallographic Server. Save these as mcif files.

    – Step 4: Convert the mcif file into a .pcr file using mCIF2PCR.

    – Step 5: Use the created .pcr file to fit the nuclear and magnetic neutron data using Fullprof to determined the magnetic structure.

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

To determine the k-vector from powder data need to know the crystal structure and then index the magnetic peaks.
We have just refined the crystal structure.
So we will load in this model and use the "k-search" feature in Fullprof

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

Determine the k-vector

- k-search is run in WinPlotr-2006.

- Open the .prf file:
  - "File">"Open Rietveld/Profile file (*.prf)"
  - Select the prf file

**NOTE: If the background changes to white this is a good sign. If it stays green, you might have issues with running k-search.
Try running it, if issues then reopen a different way.**

OAK RIDGE
National Laboratory | HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE
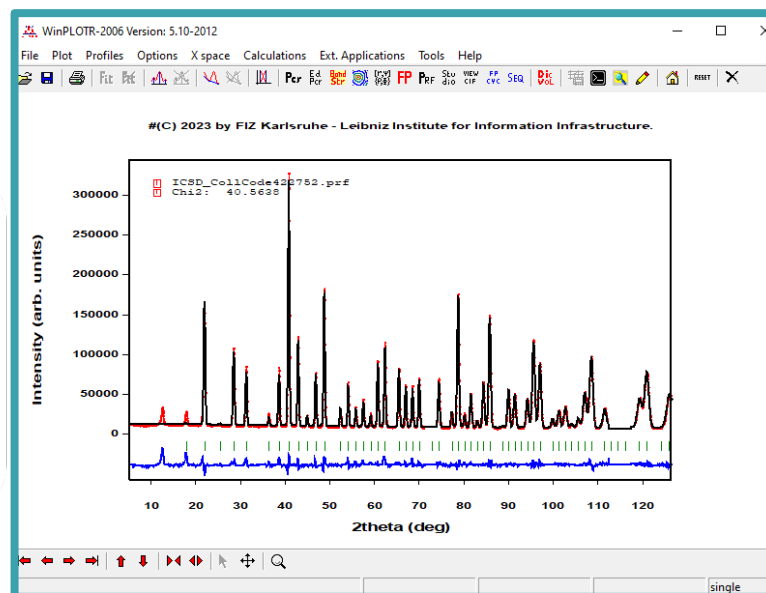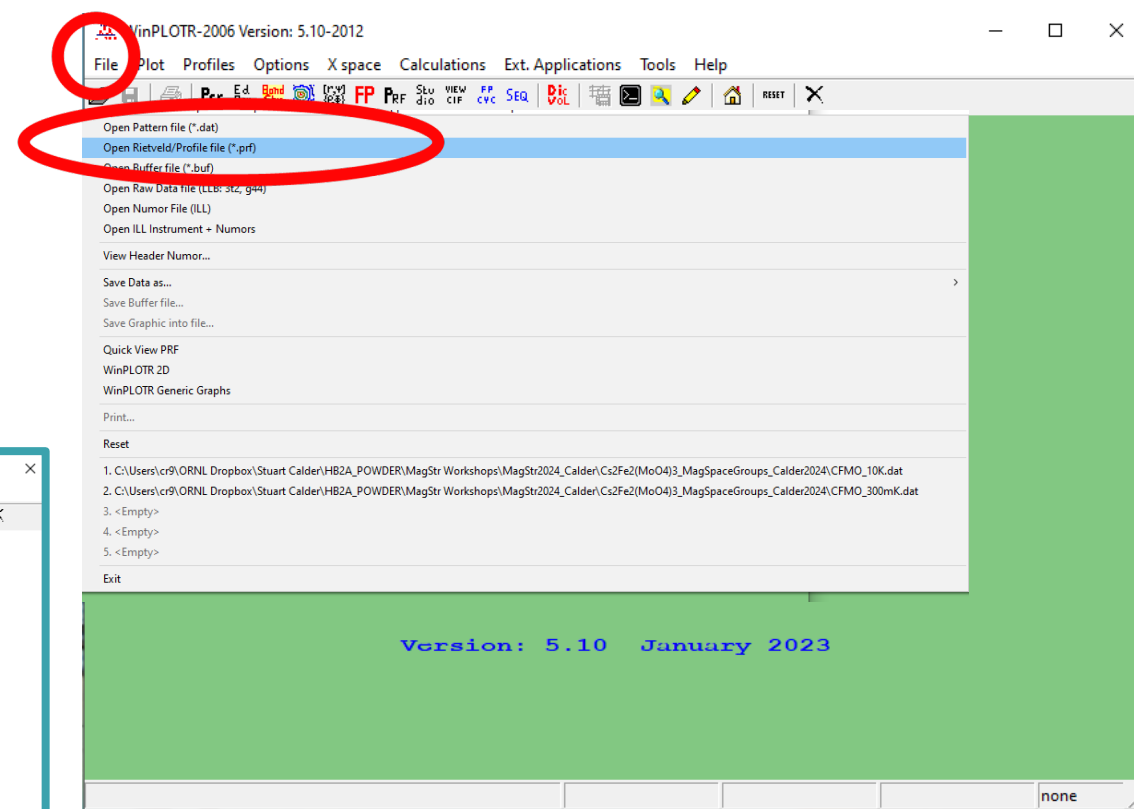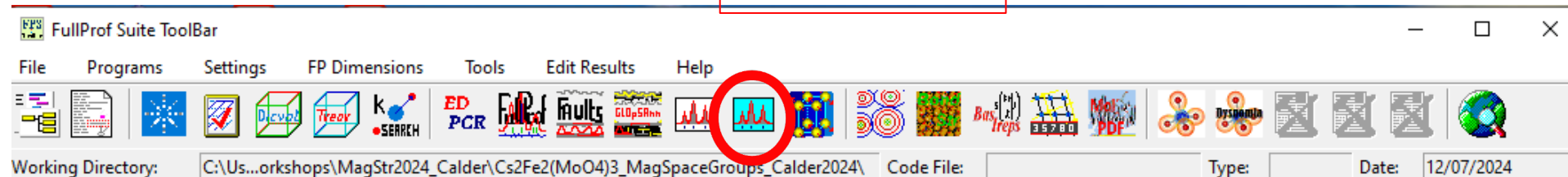
Determine the k-vector

- Now the magnetic peaks need to be indexed to find the propagation vector that defines the magnetic unit cell.

- 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.

Input structural model, this is pulled from prf file

Select the magnetic peaks (the scattering not fit by the crystal structure refinement)

k=(0,0,0)

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

S. Calder, MagStr 2024

Determine the k-vector

A commensurate k-vector was found. If multiple k-vectors seem reasonable, then test them all!
In some cases no solutions are found.
This could indicate an incommensurate structure.
Determine an incommensurate structure uniquely from powders is very challenging.
There is an example later in this workshop that looks at this case.

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

$Cs_2Fe_2(MoO_4)_3$: Refinement Strategy

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

  - 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 test magnetic space groups using MAXMAGN on the Bilbao Crystallographic Server. Save these as mcif files.**

  - Step 4: Convert the mcif file into a .pcr file using mCIF2PCR.

  - Step 5: Use the created .pcr file to fit the nuclear and magnetic neutron data using Fullprof to determined the magnetic structure.

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

Step 3: Creating mCIF file

- Go to Bilbao Crystallographic Server: **http://www.cryst.ehu.es/**
- Select "Magnetic Symmetry and Applications" to open the drop-down menu

Step 3: Creating mCIF file

- Then select "MAXMAGN"

Step 3: Creating mCIF file

- Now the crystal structure and k-vector have been determined the magnetic structure can be found by testing model magnetic space groups.

- This can be done in FullProf by creating a .mcif file from the Bilbao Crystallographic Server.

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

Step 3: Creating mCIF file

- **[1]** Need to have a propagation vector. This was determined using k-search in fullprof (to be (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.*

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

Step 3: Creating mCIF file

- Choose .cif file (crystal structure only).
  The one for this example is the one outputted from Fullprof, so will contain the correct crystal parameters at low temperature.

- Upload the cif file.

Step 3: Creating mCIF file

- The paramagnetic phase information is displayed.
  - Select the magnetic atom(s). This case is there are two Fe ions.
  - Push Submit. This may take a few seconds to run the calculations.....

Bilbao Crystallographic Server → MAXMAGN - Maximal magnetic space groups

Parent phase structure data: Magnetic Atoms

Parent space group: $P2_13$ (No. 198)
Lattice parameters (Angstroms and degrees): a=10.89220, b=10.89220, c=10.89220, alpha=90.0000, beta=90.0000, gamma=90.0000

Atoms: Please select the magnetic ones

N	Atom name	Atom type	Wyckoff Position	Coordinates	Magnetic?
1	Cs1	Cs	4a	0.17935 0.32065 0.67935	☐
2	Mo1	Mo	12b	0.29978 0.62310 0.52710	☐
3	Fe1	Fe	4a	0.33726 0.33726 0.33726	☑
4	O1	O	12b	0.27437 0.48199 0.45051	☐
5	Cs2	Cs	4a	0.45806 0.95806 0.54194	☐
6	Fe2	Fe	4a	0.61176 0.61176 0.61176	☑
7	O2	O	12b	0.45457 0.67094 0.51574	☐
8	O3	O	12b	0.25546 0.60404 0.68066	☐
9	O4	O	12b	0.20847 0.73550 0.45177	☐

Submit

59

Step 3: Creating mCIF file

- The possible maximal magnetic space groups are displayed in grey

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

S. Calder, MagStr 2024

Step 3: Creating mCIF file:
Check #1

Maximal magnetic space groups for the parent space group $P2_13$ (No. 198)
and the propagation vector k = (0, 0, 0)

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

Magnetic Structure

Selected magnetic space group: 1- $P2_13$ (#198.9)

Setting of the parent group

Parent space group $P2_13$ (No. 198)

Lattice parameters: a=10.89220, b=10.89220, c=10.89220, alpha=90.0000, beta=90.0000, gamma=90.0000

[Go to setting standard (**a, b, c** ; 0, 0, 0)]
[Go to an alternative setting]

[Export data to MCIF file/Visualize] [Go to a subgroup]

Atomic positions, Wyckoff positions and Magnetic Moments

N	Atom	New WP	Multiplicity	Magnetic moment	Values of M_x, M_y, M_z
1	Cs1 Cs 0.82065 0.82065 0.82065	$(x,x,x \mid m_x,m_x,m_x)$ $(-x+1/2,-x,x+1/2 \mid -m_x,-m_x,m_x)$ $(-x,x+1/2,-x+1/2 \mid -m_x,m_x,-m_x)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_x,-m_x)$	4	-	-
2	Mo1 Mo 0.29978 0.62310 0.52710	$(x,y,z \mid m_x,m_y,m_z)$ $(-x+1/2,-y,z+1/2 \mid -m_x,-m_y,m_z)$ $(-x,y+1/2,-z+1/2 \mid -m_x,m_y,-m_z)$ $(x+1/2,-y+1/2,-z \mid m_x,-m_y,-m_z)$ $(z,x,y \mid m_z,m_x,m_y)$ $(z+1/2,-x+1/2,-y \mid m_z,-m_x,-m_y)$ $(-z+1/2,-x,y+1/2 \mid -m_z,-m_x,m_y)$ $(-z,x+1/2,-y+1/2 \mid -m_z,m_x,-m_y)$ $(y,z,x \mid m_y,m_z,m_x)$ $(-y,z+1/2,-x+1/2 \mid -m_y,m_z,-m_x)$ $(y+1/2,-z+1/2,-x \mid m_y,-m_z,-m_x)$ $(-y+1/2,-z,x+1/2 \mid -m_y,-m_z,m_x)$	12	-	-
3	Fe1 Fe 0.33726 0.33726 0.33726	$(x,x,x \mid m_x,m_x,m_x)$ $(-x+1/2,-x,x+1/2 \mid -m_x,-m_x,m_x)$ $(-x,x+1/2,-x+1/2 \mid -m_x,m_x,-m_x)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_x,-m_x)$	4	(M_x,M_x,M_x)	$M_x = $ [0.00000]
4	O1 O 0.27437 0.48199 0.45051	$(x,y,z \mid m_x,m_y,m_z)$ $(-x+1/2,-y,z+1/2 \mid -m_x,-m_y,m_z)$ $(-x,y+1/2,-z+1/2 \mid -m_x,m_y,-m_z)$ $(x+1/2,-y+1/2,-z \mid m_x,-m_y,-m_z)$ $(z,x,y \mid m_z,m_x,m_y)$ $(z+1/2,-x+1/2,-y \mid m_z,-m_x,-m_y)$ $(-z+1/2,-x,y+1/2 \mid -m_z,-m_x,m_y)$ $(-z,x+1/2,-y+1/2 \mid -m_z,m_x,-m_y)$ $(y,z,x \mid m_y,m_z,m_x)$ $(-y,z+1/2,-x+1/2 \mid -m_y,m_z,-m_x)$ $(y+1/2,-z+1/2,-x \mid m_y,-m_z,-m_x)$ $(-y+1/2,-z,x+1/2 \mid -m_y,-m_z,m_x)$	12	-	-
5	Cs2 Cs 0.04194 0.04194 0.04194	$(x,x,x \mid m_x,m_x,m_x)$ $(-x+1/2,-x,x+1/2 \mid -m_x,-m_x,m_x)$ $(-x,x+1/2,-x+1/2 \mid -m_x,m_x,-m_x)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_x,-m_x)$	4	-	-
6	Fe2 Fe 0.61176 0.61176 0.61176	$(x,x,x \mid m_x,m_x,m_x)$ $(-x+1/2,-x,x+1/2 \mid -m_x,-m_x,m_x)$ $(-x,x+1/2,-x+1/2 \mid -m_x,m_x,-m_x)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_x,-m_x)$	4	(M_x,M_x,M_x)	$M_x = $ [0.00000]

- The Fe ions have a magnetic moment (M_x,M_x,M_x)

- Shows the moment is constrained to be along 111 direction.

- Makes refinement easier!

Step 3: Creating mCIF file:
Check #2

Maximal magnetic space groups for the parent space group $P2_13$ (No. 198)
and the propagation vector k = (0, 0, 0)

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

N	Group (BNS)	Transformation matrix	General positions	Properties	Magnetic structure
1	$P2_13$ (#198.9) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
2	$P2_1'2_1'2_1$ (#19.27) Go to a subgroup	$\begin{pmatrix} 0 & 0 & 1 & 1/4 \\ 0 & 1 & 0 & 1/4 \\ -1 & 0 & 0 & 1/4 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show

For comments, please mail to
administrador.bcs@ehu.eus

- The Fe ions have a magnetic moment (Mx,My,Mz)

- This time the moments are unconstrained.

Magnetic Structure

Selected magnetic space group: 2- $P2_1'2_1'2_1$ (#19.27)

Setting of the parent group

Parent space group $P2_13$ (No. 198)

Lattice parameters: a=10.89220, b=10.89220, c=10.89220, alpha=90.0000, beta=90.0000, gamma=90.0000

[Go to setting standard (**-c, b, a** ; 1/4, 1/4, 1/4)]
[Go to an alternative setting]

Export data to MCIF file/Visualize   Go to a subgroup

Atomic positions, Wyckoff positions and Magnetic Moments

N	Atom	New WP	Multiplicity	Magnetic moment	Values of M_x, M_y, M_z
1	Cs1 Cs 0.82065 0.82065 0.82065	$(x,x,x \mid m_x,m_y,m_z)$ $(-x+1/2,-x,x+1/2 \mid m_x,m_y,-m_z)$ $(-x,x+1/2,-x+1/2 \mid m_x,-m_y,m_z)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_y,-m_z)$	4	-	-
	Mo1_1 Mo 0.29978 0.62310 0.52710	$(x,y,z \mid m_x,m_y,m_z)$ $(-x+1/2,-y,z+1/2 \mid m_x,m_y,-m_z)$ $(-x,y+1/2,-z+1/2 \mid m_x,-m_y,-m_z)$ $(x+1/2,-y+1/2,-z \mid m_x,-m_y,-m_z)$	4	-	-
2	Mo1_2 Mo 0.52710 0.29978 0.62310	$(z,x,y \mid m_x,m_y,m_z)$ $(z+1/2,-x+1/2,-y \mid m_x,-m_y,-m_z)$ $(-z+1/2,-x,y+1/2 \mid m_x,m_y,-m_z)$ $(-z,x+1/2,-y+1/2 \mid m_x,-m_y,m_z)$	4	-	-
	Mo1_3 Mo 0.62310 0.52710 0.29978	$(y,z,x \mid m_x,m_y,m_z)$ $(-y,z+1/2,-x+1/2 \mid m_x,-m_y,m_z)$ $(y+1/2,-z+1/2,-x \mid m_x,-m_y,-m_z)$ $(-y+1/2,-z,x+1/2 \mid m_x,m_y,-m_z)$	4	-	-
3	Fe1 Fe 0.33726 0.33726 0.33726	$(x,x,x \mid m_x,m_y,m_z)$ $(-x+1/2,-x,x+1/2 \mid m_x,m_y,-m_z)$ $(-x,x+1/2,-x+1/2 \mid m_x,-m_y,m_z)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_y,-m_z)$	4	(M_x,M_y,M_z)	M_x = [0.00000] M_y = [0.00000] M_z = [0.00000]
	O1_1 O 0.27437 0.48199 0.45051	$(x,y,z \mid m_x,m_y,m_z)$ $(-x+1/2,-y,z+1/2 \mid m_x,m_y,-m_z)$ $(-x,y+1/2,-z+1/2 \mid m_x,-m_y,-m_z)$ $(x+1/2,-y+1/2,-z \mid m_x,-m_y,-m_z)$	4	-	-
4	O1_2 O 0.45051 0.27437 0.48199	$(z,x,y \mid m_x,m_y,m_z)$ $(z+1/2,-x+1/2,-y \mid m_x,-m_y,-m_z)$ $(-z+1/2,-x,y+1/2 \mid m_x,m_y,-m_z)$ $(-z,x+1/2,-y+1/2 \mid m_x,-m_y,m_z)$	4	-	-
	O1_3 O 0.48199 0.45051 0.27437	$(y,z,x \mid m_x,m_y,m_z)$ $(-y,z+1/2,-x+1/2 \mid m_x,-m_y,m_z)$ $(y+1/2,-z+1/2,-x \mid m_x,-m_y,-m_z)$ $(-y+1/2,-z,x+1/2 \mid m_x,m_y,-m_z)$	4	-	-
5	Cs2 Cs 0.04194 0.04194 0.04194	$(x,x,x \mid m_x,m_y,m_z)$ $(-x+1/2,-x,x+1/2 \mid m_x,m_y,-m_z)$ $(-x,x+1/2,-x+1/2 \mid m_x,-m_y,m_z)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_y,-m_z)$	4	-	-
6	Fe2 Fe 0.61176 0.61176 0.61176	$(x,x,x \mid m_x,m_y,m_z)$ $(-x+1/2,-x,x+1/2 \mid m_x,m_y,-m_z)$ $(-x,x+1/2,-x+1/2 \mid m_x,-m_y,m_z)$ $(x+1/2,-x+1/2,-x \mid m_x,-m_y,-m_z)$	4	(M_x,M_y,M_z)	M_x = [0.00000] M_y = [0.00000] M_z = [0.00000]
	O2_1 O 0.45457 0.67094 0.51574	$(x,y,z \mid m_x,m_y,m_z)$ $(-x+1/2,-y,z+1/2 \mid m_x,m_y,-m_z)$ $(-x,y+1/2,-z+1/2 \mid m_x,-m_y,-m_z)$ $(x+1/2,-y+1/2,-z \mid m_x,-m_y,-m_z)$	4		

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

Step 3: Creating mCIF file

- MVISUALIZE lets you quickly check magnetic structure.

S. Calder, MagStr 2024

We want to know input the model into Fullprof to see if it fits the data.
To do this we first download an mcif file.
Then convert this mcif into a Fullprof pcr
This is the same way a crystal structure refinement is done.

Step 3: Creating mCIF file:

- We will choose the allowed magnetic structure 2 (*P2$_1$3 (#198.9)* 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 maximal magnetic space groups work → go to a subgroup

Step 3: Creating mCIF file

Selected magnetic space group: 1- $P2_13$ (#198.9)

Setting of the parent group

Parent space group $P2_13$ (No. 198)

Lattice parameters: a=10.89220, b=10.89220, c=10.89220, alpha=90.0000, beta=90.0000, gamma=90.0000

1. Input values for magnetic moment

NOTE: In this case Mx(=My=Mz), when we run Fullprof it will constrain them to remain the same.
But if Mx,My,Mz are allowed to be different, as for the second magnetic space group (#19.27) then be careful when adding the moments. If you make them all the same Fullprof will potentially constrain them to always be the same, which is incorrect.
ALWAYS PUT DIFFERENT MOMENT SIZES HERE!

Step 4: Creating a pcr from an mcif file

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

bilbao crystallographic server

Contact us	About us	Publications	How to cite the server

Space-group symmetry

Magnetic Symmetry and Applications

MGENPOS	General Positions of Magnetic Space Groups
MWYCKPOS	Wyckoff Positions of Magnetic Space Groups
MKVEC	The k-vector types and Brillouin zones of Magnetic Space Groups
IDENTIFY MAGNETIC GROUP	Identification of a Magnetic Space Group from a set of generators in an arbitrary setting
BNS2OG	Transformation of symmetry operations between BNS and OG settings
mCIF2PCR	Transformation from mCIF to PCR format (FullProf).
MPOINT	Magnetic Point Group Tables
MAGNEXT	Extinction Rules of Magnetic Space Groups
MAXMAGN	Maximal magnetic space groups for a given space group and a propagation vector
MAGMODELIZE	Magnetic structure models for any given magnetic symmetry
STRCONVERT	Convert & Edit Structure Data (supports the CIF, mCIF, VESTA, VASP formats -- with magnetic information where available)
k-SUBGROUPSMAG	Magnetic subgroups consistent with some given propagation vector(s) or a supercell
MAGNDATA	A collection of magnetic structures with portable cif-type files
MVISUALIZE	3D Visualization of magnetic structures with Jmol
MTENSOR ⚠	Symmetry-adapted form of crystal tensors in magnetic phases
MAGNETIC REP.	Decomposition of the magnetic representation into irreps
Get_mirreps	Irreps and order parameters in a paramagnetic space group- magnetic subgroup phase transition

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

S. Calder, MagStr 2024

$Cs_2Fe_2(MoO_4)_3$: Refinement Strategy

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

    – 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 test magnetic space groups using MAXMAGN on the Bilbao Crystallographic Server. Save these as mcif files.

    – **Step 4: Convert the mcif file into a .pcr file using mCIF2PCR.**

    – Step 5: Use the created .pcr file to fit the nuclear and magnetic neutron data using Fullprof to determined the magnetic structure.

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

Step 4: 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 the next step.

S. Calder, MagStr 2024

$Cs_2Fe_2(MoO_4)_3$: Refinement Strategy

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

  – 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 test magnetic space groups using MAXMAGN on the Bilbao Crystallographic Server. Save these as mcif files.

  – Step 4: Convert the mcif file into a .pcr file using mCIF2PCR.

  – **Step 5: Use the created .pcr file to fit the nuclear and magnetic neutron data using Fullprof to determined the magnetic structure.**

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

Step 5: 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 downloaded pcr file calculates the pattern based on default values.

- We could 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.

BUT, since we already have a working pcr file for the nuclear phase, we can just paste in the magnetic portion of interest

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

Copy the part highlighted in grey in the magnetic pcr file into the part highlighted in blue of the nuclear pcr file.

Nuclear pcr file

Magnetic pcr file created from Bilbao mcif

Paste over blue section

Copy highlighted grey section

NOTE: Here the k-vector is (0,0,0), so the unit cell is unchanged between nuclear and magnetic. If the propagation vector was e.g. *(0.5,0.5,0.5) then the lattice constants would be* doubled (21.78).

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

- The pcr file now contains the magnetic space group and also all the previously refined instrumental parameters.

- Fullprof will now refine a model with both nuclear and magnetic in a single phase (the magnetic space group).

By default the keywords "vary mxmymz" are there. This means Fullprof will always refine the moments. This can be deleted to change this.

It is sometimes convenient to only look at the magnetic scattering, for example when looking at temperature subtracted data. To only model the magnetic scattering add the keyword "Mag_Only". This goes in the line where the VARY mxmymz is contained.

```
COMM #(C) 2023 by FIZ Karlsruhe - Leibniz Institute for Information Infrastructure.
! Files => DAT-file: ,   PCR-file: ICSD_CollCode422752
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   7   1   0   2   0   0   0   0   0   1   0   0   0   0   0   0   1
!
!   Resolution file for Pattern#  1
HB2A_Ge113.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  -1   0   0   0   0   0
!
! Lambda1  Lambda2    Ratio    Bkpos    wdt    Cthm     muR   AsyLim   Rpolarz  2nd-mu
 2.406700 2.406700  0.00000   40.000   8.000  0.0000  0.0000  180.00   0.0000  0.000
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step      Thmax    PSD    Sent0
 10   0.10  1.00  1.00  1.00  1.00   -0.0200    0.030000  155.0000   0.000   0.000
!
! Excluded regions (LowT  HighT) for Pattern#  1
       71.50      74.00
      112.50     117.60
!
!
       2    !Number of refined parameters
!
!  Zero    Code    SyCos     Code    SySin     Code  Lambda      Code MORE ->Patt# 1
  0.03802    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)
  101536.125  -33252.898   12622.551    7347.125  -14217.325    4698.028
     0.00        0.00        0.00        0.00        0.00        0.00
!-------------------------------------------------------------------
!   Data for PHASE number:   1  ==> Current R_Bragg f               0000  Magnet
!-------------------------------------------------------------------
Nuclear and Magnetic Structure of: bcs_file_MSGI p9    VARY mxmymz
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth                       ore
   9   0   0 0.0 0.0 1.0  10   0   2   0   0               0.000   0   7   0
!
P2_13  number:198.9    <--Magnetic Space group symbol (BNS symbol & number)
Transform to standard: a,b,c;0,0,0
Parent Space Group: P2_13      IT_number:  198
Transform from Parent: a,b,c;0,0,0
! Nsym   Cen  N_Clat N_Ant
    12     0    0   0
!
! Symmetry operators
   1 x,y,z,+1
   2 y,z,x,+1
   3 z,x,y,+1
   4 -y+1/2,-z,x+1/2,+1
   5 -z+1/2,-x,y+1/2,+1
   6 y+1/2,-z+1/2,-x,+1
   7 z+1/2,-x+1/2,-y,+1
   8 -x+1/2,-y,z+1/2,+1
   9 -x,y+1/2,-z+1/2,+1
  10 -y,z+1/2,-x+1/2,+1
  11 x+1/2,-y+1/2,-z,+1
  12 -z,x+1/2,-y+1/2,+1
!
!Atom   Typ    Mag Vek     X        Y        Z       Biso     Occ    N_type  Spc/Fftype /Line be
!         RX       Ry      Rz       Ix       Iy       Iz      MagPh  / Line below:Codes
!       beta11   beta22   beta33   beta12   beta13   beta23  / Line below:Codes
Cs1   Cs      1  0   0.82065  0.82065  0.82065  0.00000  0.33333   0    0 #
                    0.00     0.00     0.00     0.00     0.00
Mo1   Mo      1  0   0.29978  0.62310  0.52710  0.00000  1.00000   0    0 #
                    0.00     0.00     0.00     0.00     0.00
Fe1   MFE2    1  0   0.33726  0.33726  0.33726  0.00000  0.33333   1    0 #
                    0.00     0.00     0.00     0.00     0.00
      1.10000  1.10000  1.10000  0.00000  0.00000  0.00000  0.00000 <-MagPar
     21.00    21.00    21.00     0.00     0.00     0.00     0.00
O1    O       1  0   0.27437  0.48199  0.45051  0.00000  1.00000   0    0 #
                    0.00     0.00     0.00     0.00     0.00
Cs2   Cs      1  0   0.04194  0.04194  0.04194  0.00000  0.33333   0    0 #
                    0.00     0.00     0.00     0.00     0.00
Fe2   MFE2    1  0   0.61176  0.61176  0.61176  0.00000  0.33333   1    0 #
                    0.00     0.00     0.00     0.00     0.00
      1.20000  1.20000  1.20000  0.00000  0.00000  0.00000  0.00000 <-MagPar
     11.00    11.00    11.00     0.00     0.00     0.00     0.00
O2    O       1  0   0.45457  0.67094  0.51574  0.00000  1.00000   0    0 #
                    0.00     0.00     0.00     0.00     0.00
O3    O       1  0   0.25546  0.60404  0.68066  0.00000  1.00000   0    0 #
                    0.00     0.00     0.00     0.00     0.00
O4    O       1  0   0.20847  0.73550  0.45177  0.00000  1.00000   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
 152.4438     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
  0.574767   -0.547859    0.173882   0.000000   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
 10.892169 10.892169 10.892169 90.000000 90.000000 90.000000
    0.00000   0.00000   0.00000   0.00000   0.00000   0.00000
! Pref1    Pref2     Asy1    Asy2    Asy3    Asy4     S_L      D_L
  0.00000  0.00000  0.07494  0.05829  0.27161 -0.02522  0.00000  0.00000
    0.00     0.00     0.00     0.00     0.00     0.00     0.00     0.00
!  2Thl/TOF1   2Th2/TOF2  Pattern to plot
     5.325     126.525        1
```

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

S. Calder, MagStr 2024

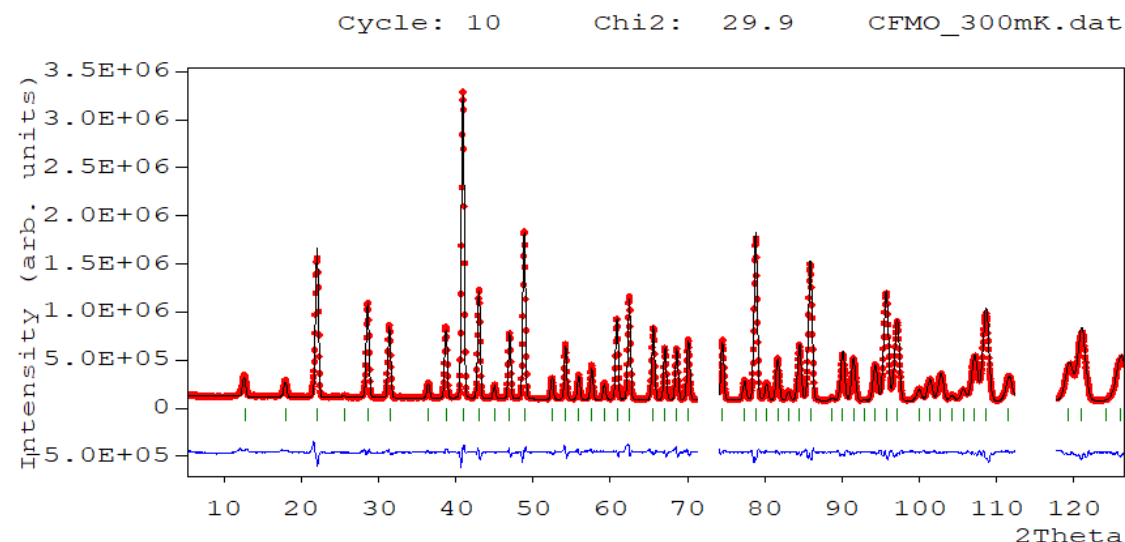# Step 5: Refining the magnetic structure with Fullprof

- Run the refinement.

- The moments vary automatically.

- The fit looks close, with all the new magnetic scattering being captured.

- Refining the background, lattice constants, etc will improve the fit slightly.

- But note the chi2 is fairly high (16 is about the lowest.) This is because of the background. This is likely due to short range magnetic order.

- NOTE: do not just rely on chi2 or Rw values, these are often less important than looking at the fit and understanding why the numbers are what they are.

S. Calder, MagStr 2024

Step 5: Refining the magnetic structure with Fullprof

- This fit captures the magnetic scattering.

- There was another maximal magnetic space group. The same procedure should be done to check how that model works.

- You should find that it is unstable and so we can define P2$_1$3 (#198.9) as the determined magnetic space group

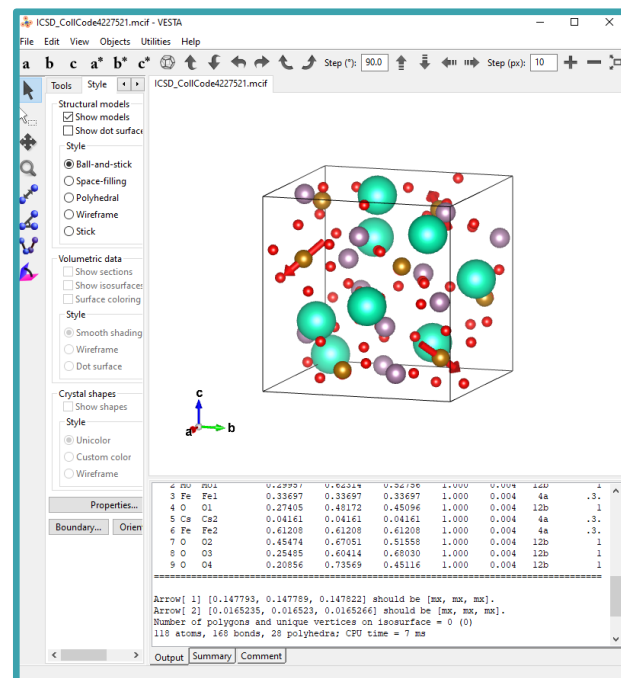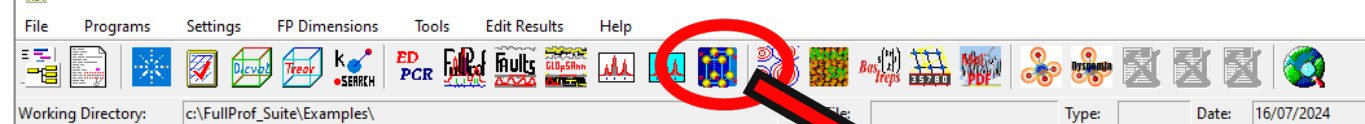# Step 5: Refining the magnetic structure with Fullprof

- From the refinement the moments are predominately only on one site.

- The magnetic structure can be viewed in Fpstudio. The moment sizes can be seen in the drop down menu: "Magnetic structure">"list magnetic moments"

- The mcif file can also be viewed with VESTA.

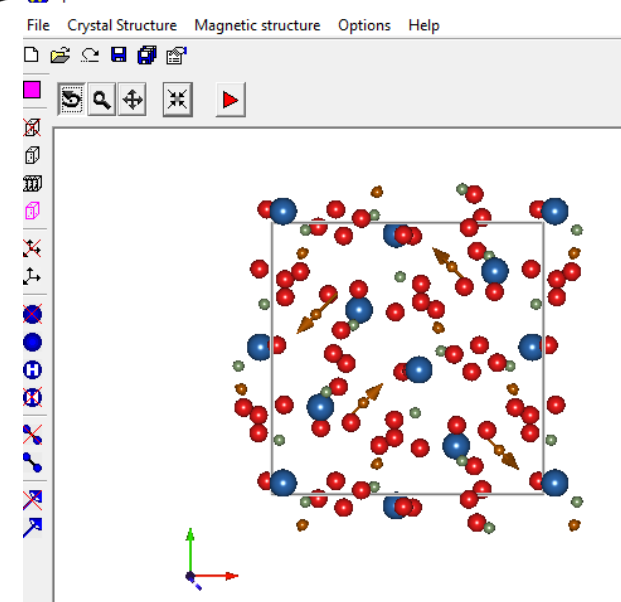**Moment sizes with errors are in the .sum file**

Step 5: Refining the magnetic structure with Fullprof

- Always ask "does this magnetic model make sense?"

- The moment sizes are very different, but within plausible ranges for Fe.

- Look at supporting data and calculations in the manuscript.

- The different Fe moment sizes are expected.

- Therefore we can present this magnetic model as the magnetic structure.

```
==> MAGNETIC MOMENT PARAMETERS:

 Name     Mx    sMx     My    sMy     Mz    sMz        M      sM      MPhas  sMPhas

 Fe1    1.610( 18)   1.610( 18)   1.610( 18)    2.7883( 321)   0.0000(   0)
 Fe2    0.183( 53)   0.183( 53)   0.183( 53)    0.3164( 922)   0.0000(   0)
```

Moment sizes with errors are in the .sum file

Cs$_2$Fe$_2$(MoO$_4$)$_3$—A Strongly Frustrated Magnet with Orbital Degrees of Freedom and Magnetocaloric Properties

Published as part of Chemistry of Materials virtual special issue "In Memory of Prof. Francis DiSalvo".

Lenka Kubíčková, Anna Katharina Weber, Martin Panthöfer, Stuart Calder, and Angela Möller*

Cite This: https://doi.org/10.1021/acs.chemmater.4c01262   Read Online

ACCESS | 📊 Metrics & More | 📑 Article Recommendations | 🆘 Supporting Information

ABSTRACT: We report an in-depth study of the thermodynamic and magnetocaloric properties of a strongly frustrated magnet, Cs$_2$Fe$_2$(MoO$_4$)$_3$. The underlying structure belongs to the double trillium lattice, which consists of two Fe^{II} ($S = 2$) sites with easy-axis and easy-plane single-ion anisotropy. Detailed ^{57}Fe Mössbauer spectroscopic investigations along with ligand-field calculations support the existence of disparate ground states. The antiferromagnetic ordered structure is presented by the propagation vector $k = (0,0,0)$ with noncollinear magnetic moments of 2.97 μ_B (Fe1) and 0.17 μ_B (Fe2), respectively. Strong and disordered magnetic correlations exist in the temperature regime between $T_N \approx 1.0$ K and $|\theta_{CW}| \approx 22$ K. The large degeneracy of the ground state is investigated in terms of its magnetocaloric response. Magnetization and specific heat measurements indicate a significant magnetocaloric cooling efficiency, making this rare-earth-free compound a candidate for cryogenic magnetic refrigeration applications, with refrigeration capacity of 79 J kg^{-1} for $\Delta(\mu_0 H) = 8$ T.

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

S. Calder, MagStr 2024