

Representational analysis with Fullprof and SARAh to refine Mn-pyrazinecarboxylate data collected on HB2A

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Magnetic order in the two-dimensional metal-organic framework manganese pyrazinecarboxylate with Mn-Mn dimers

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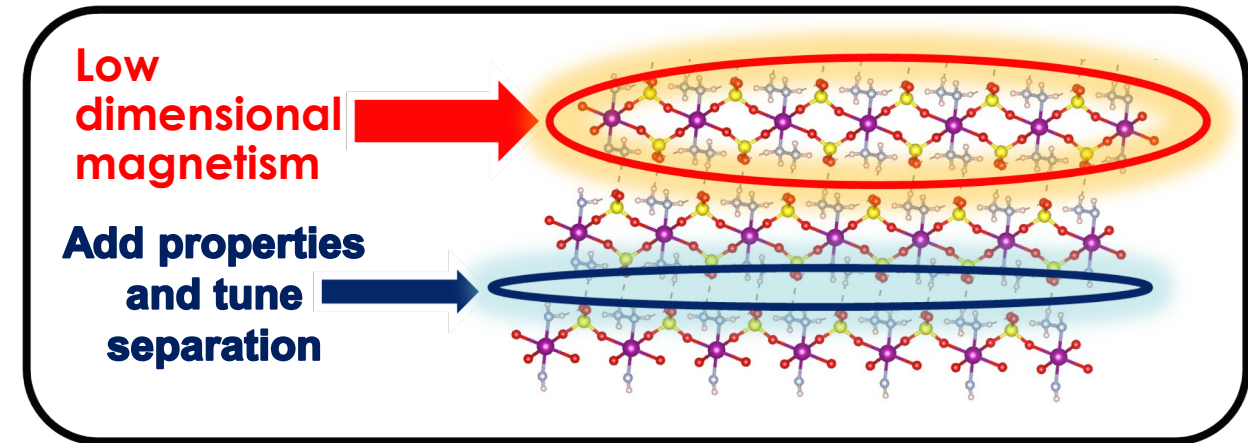
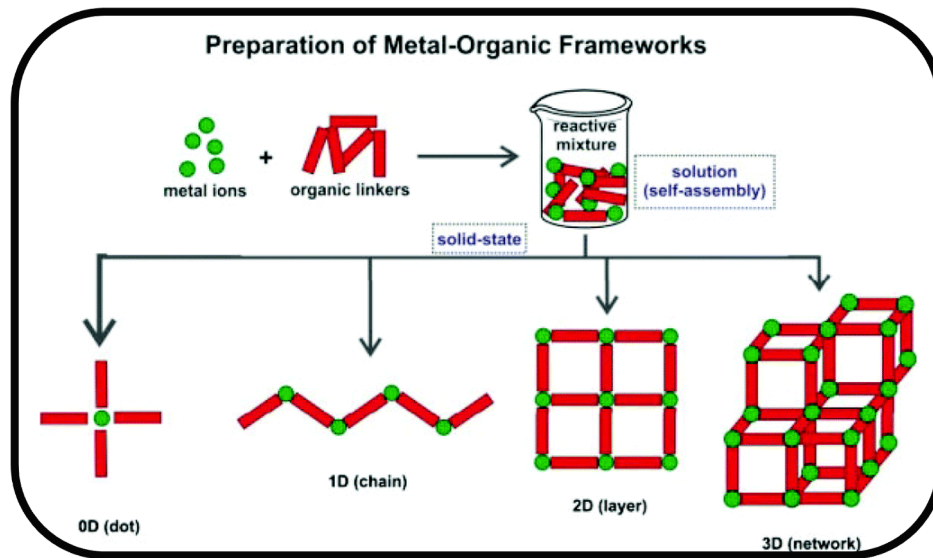
(Received 29 September 2023; revised 8 November 2023; accepted 28 November 2023; published 15 December 2023)

The magnetic properties of $[\text{Mn}(\text{pyrazinecarboxylate})_2]_n$, empirical formula $\text{C}_{10}\text{H}_6\text{MnN}_4\text{O}_4$, are investigated through susceptibility, heat capacity, and neutron scattering measurements. The structure consists of Mn-Mn dimers linked on a distorted 2D hexagonal structure. The weak out-of-plane interactions create a quasi-2D magnetic material within the larger three-dimensional metal-organic framework structure. We show that this material undergoes a two-stage magnetic transition, related to the low dimensionality of the Mn lattice. First, at 5 K, which is assigned to the initial development of short-range order in the 2D layers. This is followed by long-range order at 3.3 K. Applied field measurements reveal the potential to induce magnetic transitions in moderately small fields of ~ 2 T. Neutron powder diffraction enabled the determination of a unique magnetic space group $P2_1'/c$ (No. 14.77) at 1.5 K. This magnetic structure consists of antiferromagnetically coupled Mn-Mn dimers with spins principally along the out-of-plane a axis.

DOI: [10.1103/PhysRevMaterials.7.124408](https://doi.org/10.1103/PhysRevMaterials.7.124408)

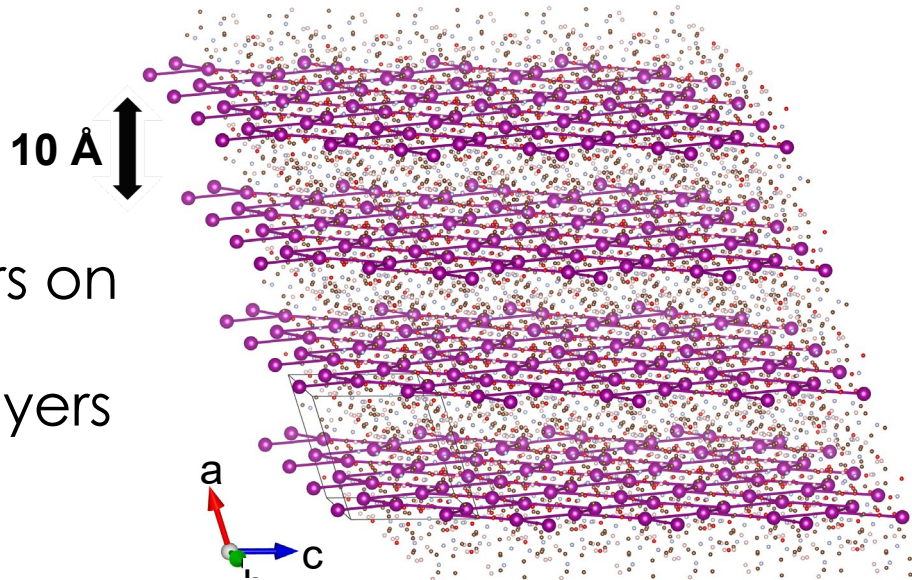
Quantum behavior by design in low dimensional Magnetic MOFs

- **Magnetism largely unexplored**
- **Straightforward synthesis to tune low dimensional behavior.**
 - Design quantum behavior on regular lattice.
 - Multifunctionality on magnetic and organic building blocks.
 - Tunable by small pressure, field, strain, light.

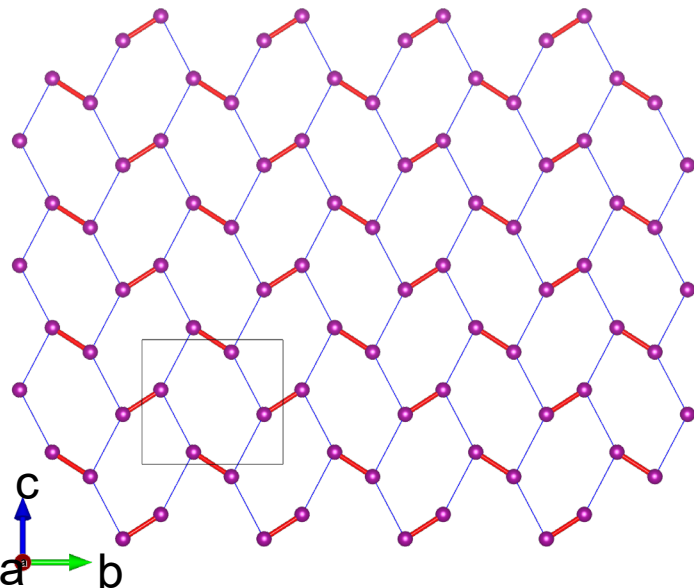


Mn-pyrazinecarboxylate ($\text{Mn}(2\text{-pzc})_2$) $\text{C}_{10}\text{H}_6\text{MnN}_4\text{O}_4$

- Well isolated 2D layers



- Mn-Mn dimers on distorted hexagonal layers



Lots of hydrogen, which creates very large background for neutron powder diffraction. Can we still determine magnetic structure?

Compound

C10 H6 Mn N4 O4

Lattice type

P

Space group name

P21/c

Space group number

14

Setting number

1

Lattice parameters

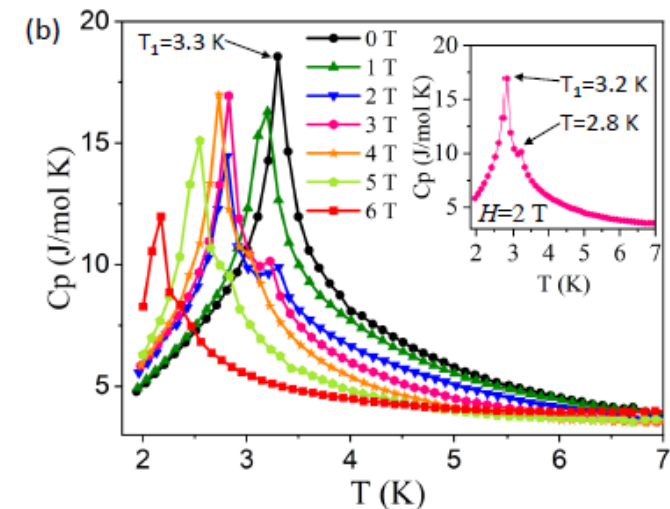
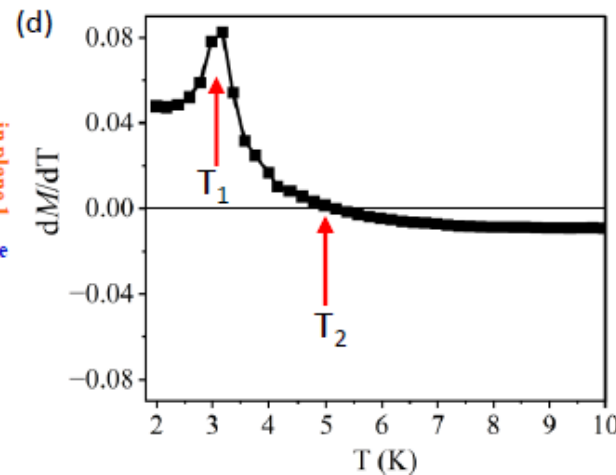
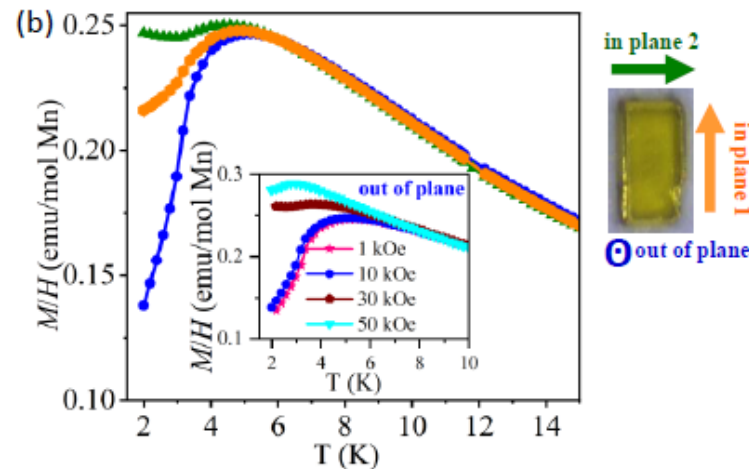
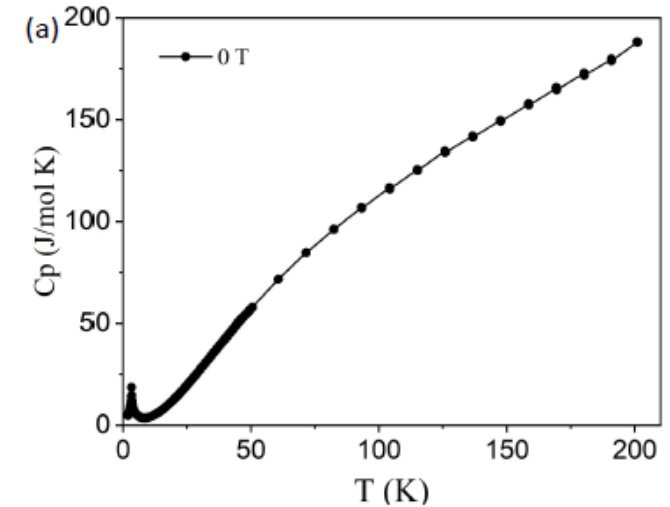
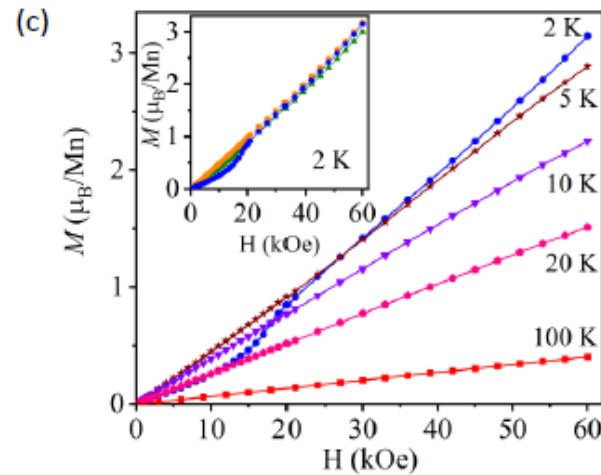
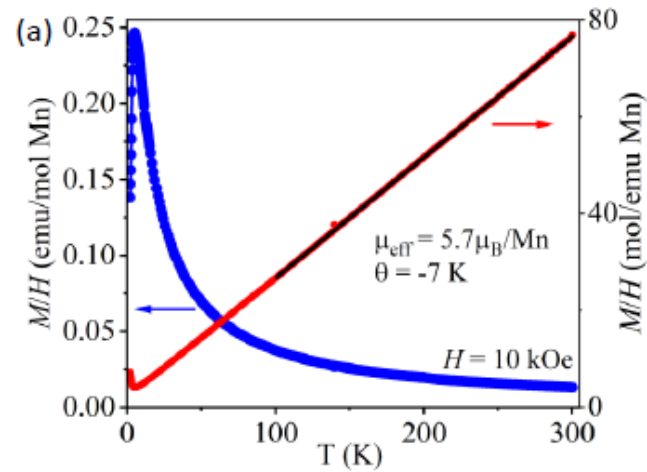
a	b	c	alpha	beta	gamma
10.19000	10.90600	10.11600	90.0000	107.9600	90.0000

Structure parameters

	x	y	z	Occ.	U	Site	
Mn	0.510090		0.134260	0.598000	1.000	0.024	4e
O	0.541000		0.244300	0.426600	1.000	0.023	4e
N	0.360600		0.299100	0.562100	1.000	0.031	4e
C	0.262700		0.325100	0.619200	1.000	0.038	4e
H	0.254640		0.276940	0.691940	1.000	0.034	4e
O	0.475200		0.405900	0.287300	1.000	0.041	4e
N	0.180200		0.495900	0.472800	1.000	0.031	4e
C	0.173100		0.421500	0.573800	1.000	0.037	4e
H	0.105000		0.434840	0.615460	1.000	0.025	4e
O	0.632900	-0.009200	0.533500	1.000	1.000	0.038	4e
N	0.738100	0.176100	0.700600	1.000	1.000	0.046	4e
C	0.277700		0.468700	0.414700	1.000	0.037	4e
H	0.285650	0.517370	0.342340	1.000	1.000	0.045	4e
O	0.824800	-0.033000	0.475000	1.000	1.000	0.034	4e
N	1.018200	0.234100	0.767400	1.000	1.000	0.041	4e
C	0.367000	0.371700	0.457400	1.000	1.000	0.024	4e
C	0.471400	0.338300	0.385500	1.000	1.000	0.028	4e
C	0.796000	0.262800	0.792500	1.000	1.000	0.025	4e
H	0.742540	0.304290	0.837480	1.000	1.000	0.037	4e
C	0.933300	0.292500	0.822500	1.000	1.000	0.026	4e
H	0.968190	0.356270	0.884090	1.000	1.000	0.042	4e
C	0.960400	0.144900	0.676800	1.000	1.000	0.035	4e
H	1.015390	0.101040	0.635600	1.000	1.000	0.028	4e
C	0.823000	0.116000	0.643000	1.000	1.000	0.033	4e
C	0.758100	0.015200	0.540800	1.000	1.000	0.034	4e

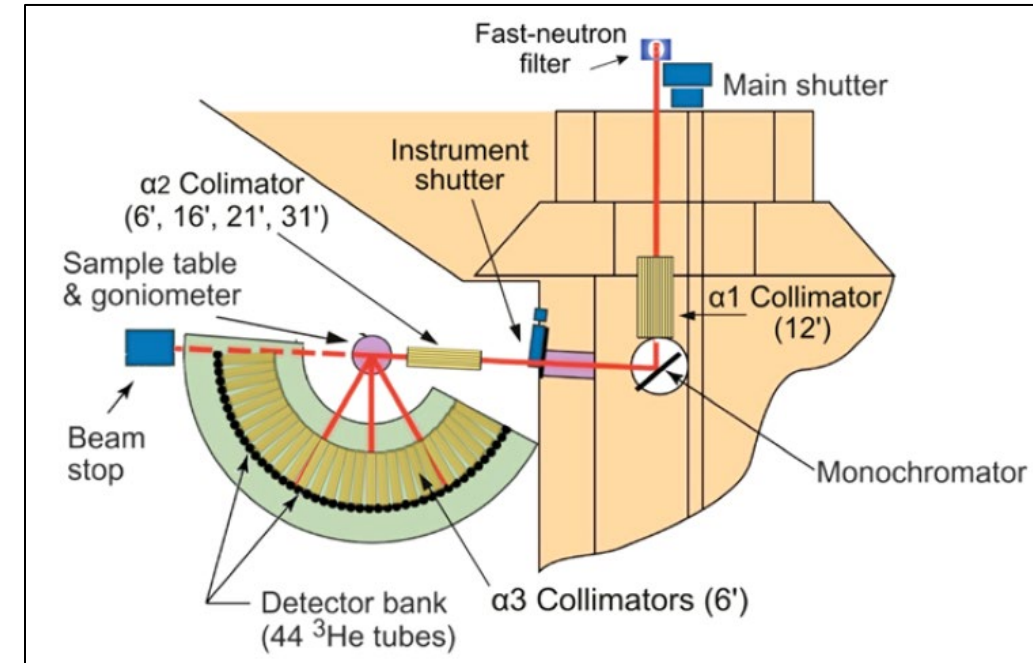
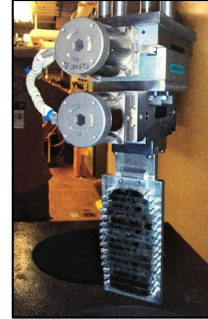
Magnetic susceptibility and heat capacity

- Two-stage transition $T_1=3.3$ K and $T_2=5$ K
- Can fit magnetic susceptibility to dimer models in interactions $J = -0.11$ meV



$\text{Cs}_2\text{Fe}_2(\text{MoO}_4)_3$: Neutron measurements on HB-2A, HFIR.

- Constant wavelength
- Germanium monochromator
 - $\sim 90^\circ$ 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 ^3He tubes
 - Low background
 - Covers ~ 2 - 150° in 2θ by scanning detector
 - **MIDAS detector upgrade coming soon!**



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



<https://neutrons.ornl.gov/powder>



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:

$$\text{Res}=1 \quad H_G^2 = (U_i \tan \theta + V_i) \tan \theta + W_i$$

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

- Caglioti function describes reactor based diffractometers.
- U,V,W parameters in Fullprof.
- See paper by Hewat for definitions of U,V,W

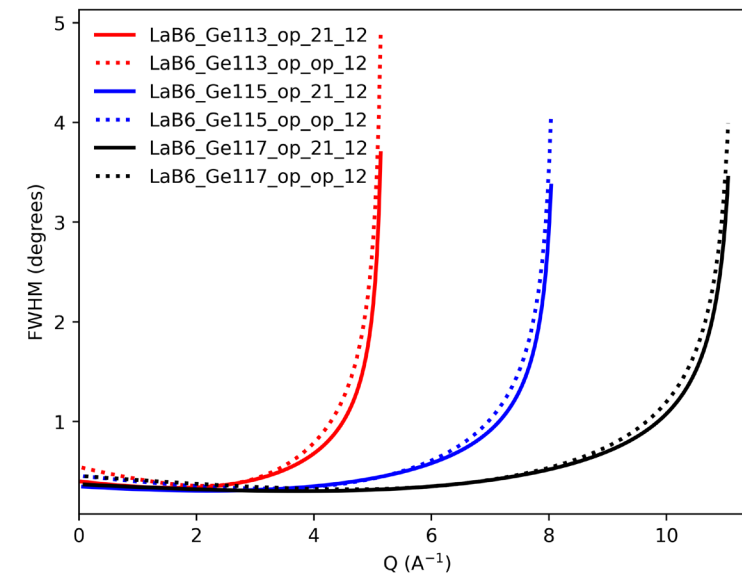
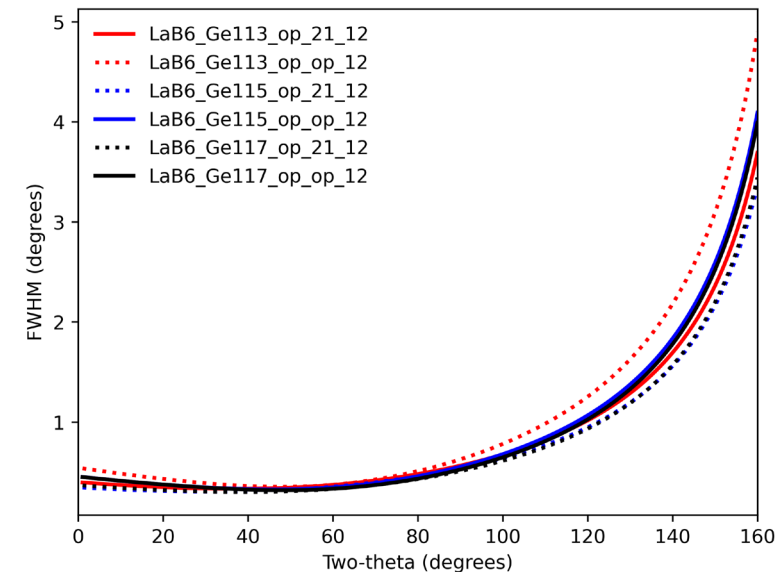
NUCLEAR INSTRUMENTS AND METHODS 127 (1975) 361-370; © NORTH-HOLLAND PUBLISHING CO.

DESIGN FOR A CONVENTIONAL HIGH-RESOLUTION NEUTRON POWDER DIFFRACTOMETER

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Received 14 April 1975



Details of this Mn-pyrazinecarboxylate example

- Neutron powder diffraction data collected at HB2A, HFIR
- $\lambda = 2.41 \text{ \AA}$. Collimation: open-open-21'
- Data at 20K (**MnPyz_20K.dat**) and 1.5K (**MnPyz_1p5K.dat**)
- Sample in a vanadium can
- Instrument resolution file: **hb2a_resolution.irf**
- Crystal structure: **MnPyz.cif**

 HB2A_Ge113

 MnPyz

 MnPyz_1p5K

 MnPyz_20K

 PhysRevMaterials.7.124408

Neutron data from HB-2A

- Plot the 1.5 K and 20 K data using Winplotr
- Take a difference
- Convert to Q. This is the best way to report data
 - “X space” > “Q-space”. Set all to 2.41

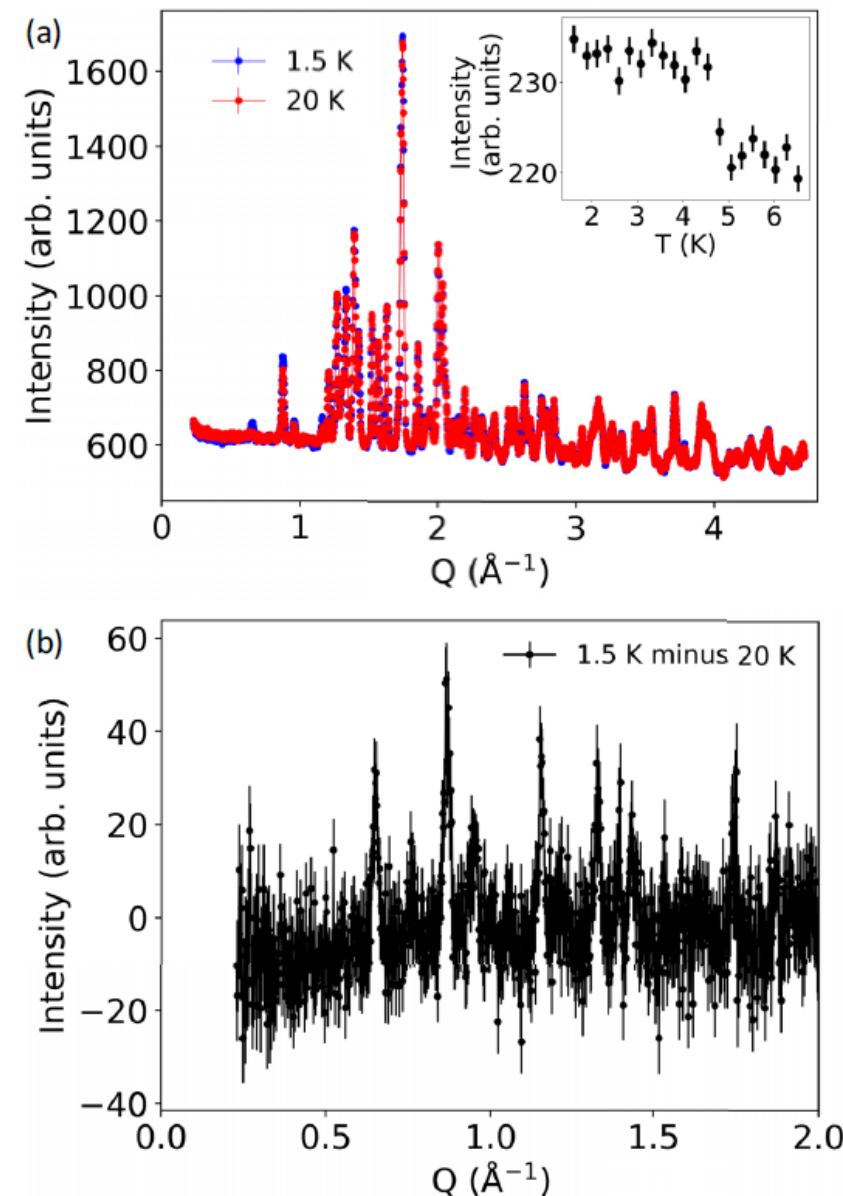
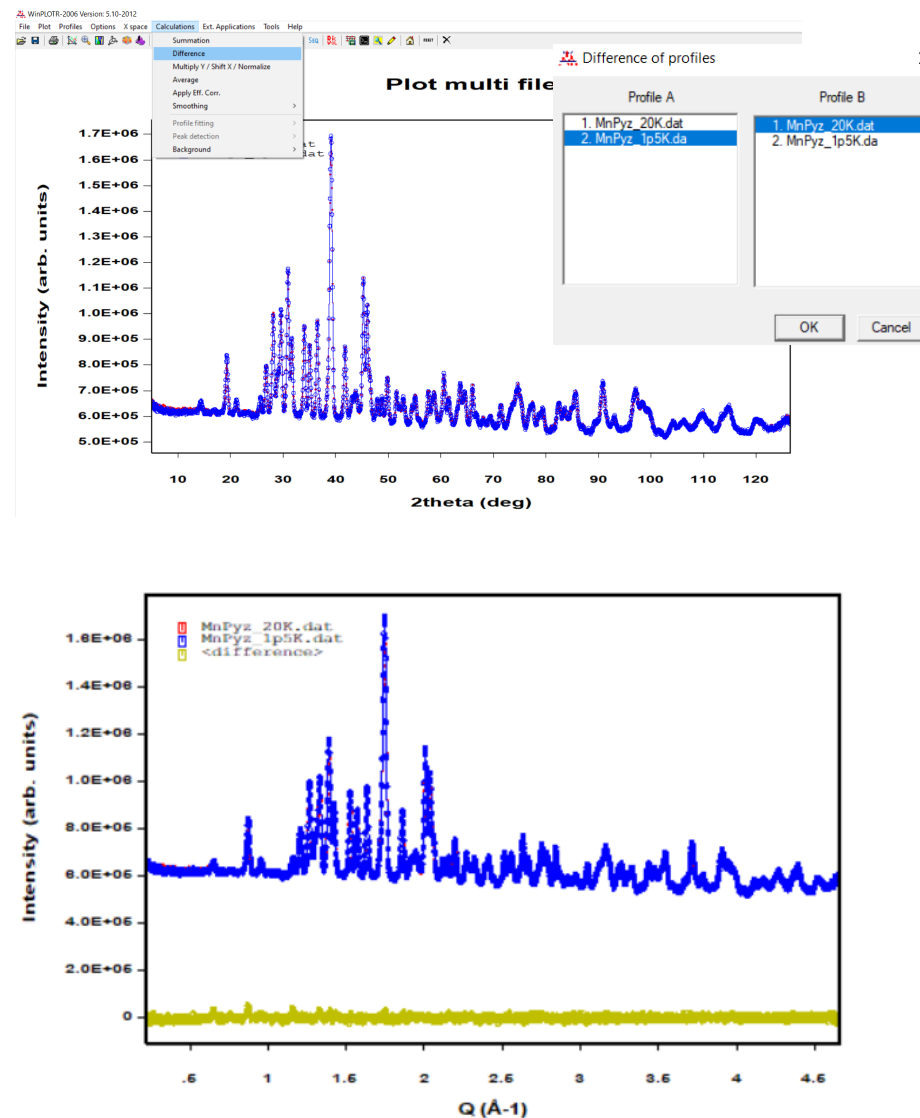


FIG. 5. (a) Neutron powder diffraction data collected at 1.5 K and 20 K. Inset: Intensity at $Q = 0.65 \text{ \AA}^{-1}$ as a function of temperature through the magnetic transition. (b) Difference of intensity at 1.5 K and 20 K in the powder diffraction data.

Mn-pyrazinecarboxylate

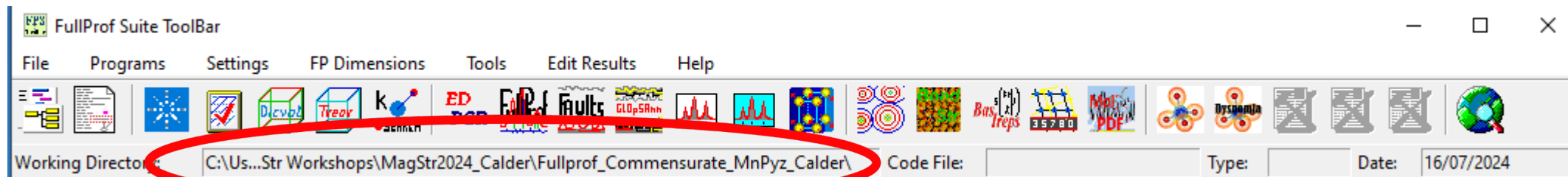
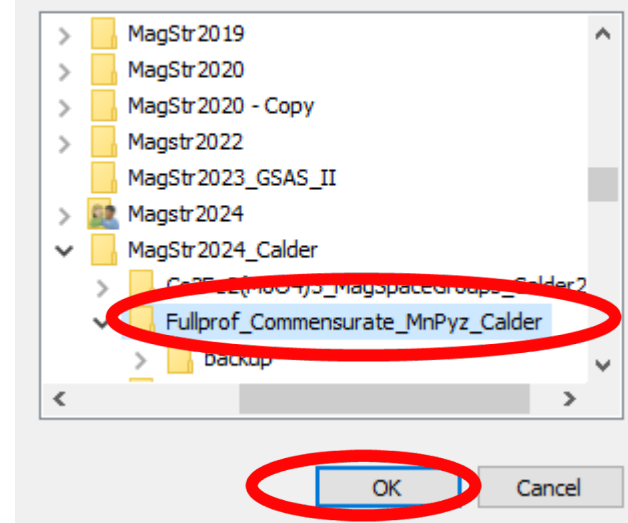
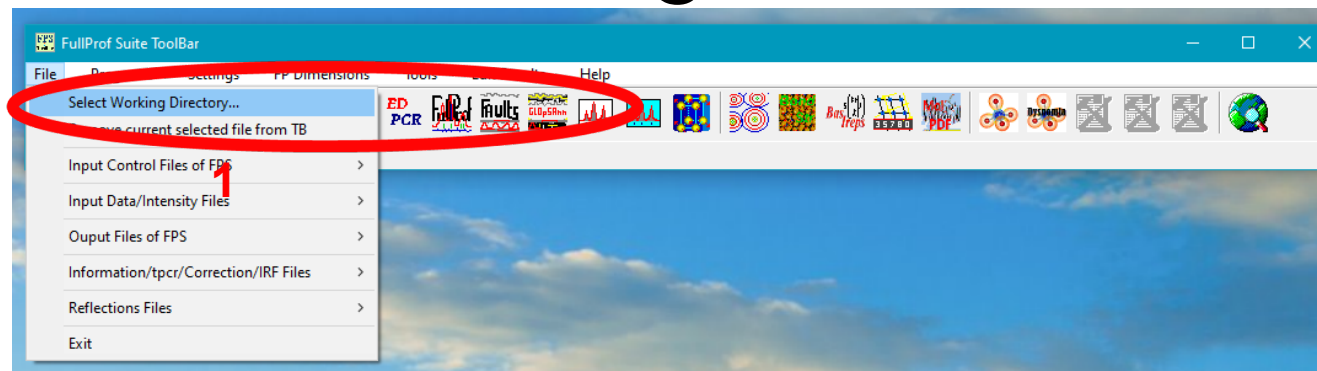
- This example will use Fullprof and SARAh
<http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>
 - Step 1: Refine the crystal structure using FullProf
 - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
 - Step 3: Create candidate magnetic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

Mn-pyrazinecarboxylate

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Step 1: Refine the crystal structure using FullProf

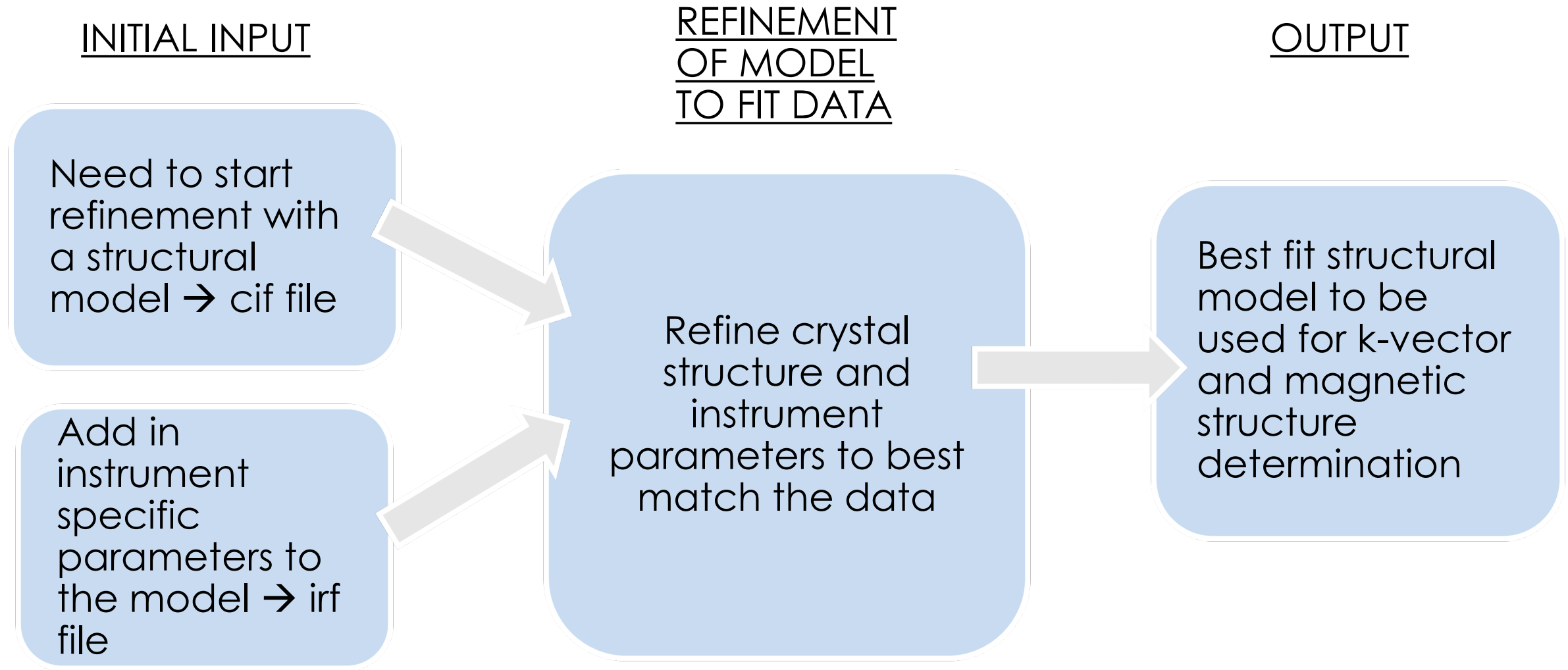
- Open Fullprof Suite toolbar.
 - **1.** Select working directory with data
“File>Select Working directory...”
 - **2.** Browse to wherever your folder
“Fullprof_Commensurate_MnPyz_Calder” is located on your computer and select “ok”
 - **3.** Path on FP studio toolbar should now be updated. This helps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



Step 1: 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.

Step 1: Refining the crystal structure using Fullprof



Step 1: Refine the crystal structure using FullProf

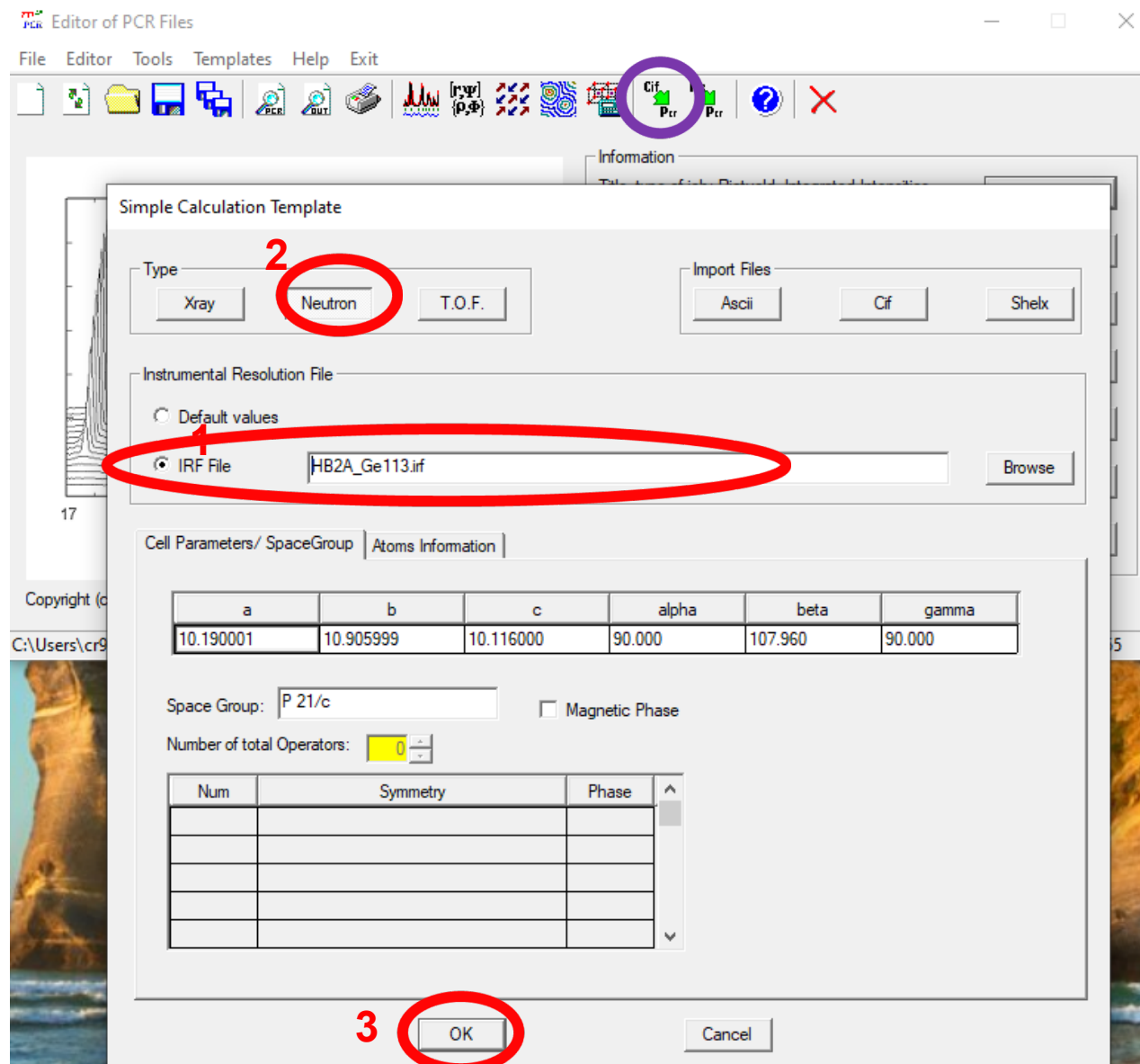
- 1. From FullProf Suite Toolbar open EdPCR.
- 2. Import crystallographic information file by clicking on "CIF→PCR"
- 3. Select the file "MnPyz_20K.cif"

The image shows two screenshots of the FullProf Suite software interface. The top screenshot is the 'FullProf Suite Toolbar' with a red circle around the 'ED PCR' button, labeled with a red '1'. A large red arrow points from this button to the bottom screenshot. The bottom screenshot is the 'Editor of PCR Files' window. In its toolbar, the 'Cif → Pcr' button is circled in red and labeled with a red '2'. To the right of the main editor window, a file explorer shows a list of files: 'backup', 'MnPyz_20K.cif', 'MnPyz', 'MnPyz_1p5K', 'MnPyz_20K', and 'PhysRevMaterials.7.124408'. The 'MnPyz' file is circled in red and labeled with a red '3'. The main editor window displays a plot of intensity versus 2θ (°) with the text 'FullProf PCR Editor' overlaid. The plot shows several sharp peaks. The right sidebar of the editor contains tabs for 'General', 'Patterns', 'Phases', 'Refinement', 'Constraints', 'Box/Restrains', and 'Output', with 'General' currently selected. The 'Information' panel on the right lists various parameters and options.

Step 1: Refine the crystal structure using FullProf

Cif→PCR opens a window to input instrument 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 **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

- Starting **Cell Parameters**, **Space Group** and **Atom Information** are now loaded.
- Look in the tab “Atoms Information”
 - Fullprof treats occupancies (Occ) in a particular way related to site multiplicities.
 - occ = site multip./general multip.**
Always check this has been correctly calculated after importing the .cif file.
 - In this case cite/general = 4/4 = 1 for all atoms. So it looks straightforward. But make sure to check.
- Hit “OK” to close the window

Simple Calculation Template

Type:

Import Files:

Instrumental Resolution File:
☒ Default values
☐ IRF File

Cell Parameters/ SpaceGroup **Atoms Information**

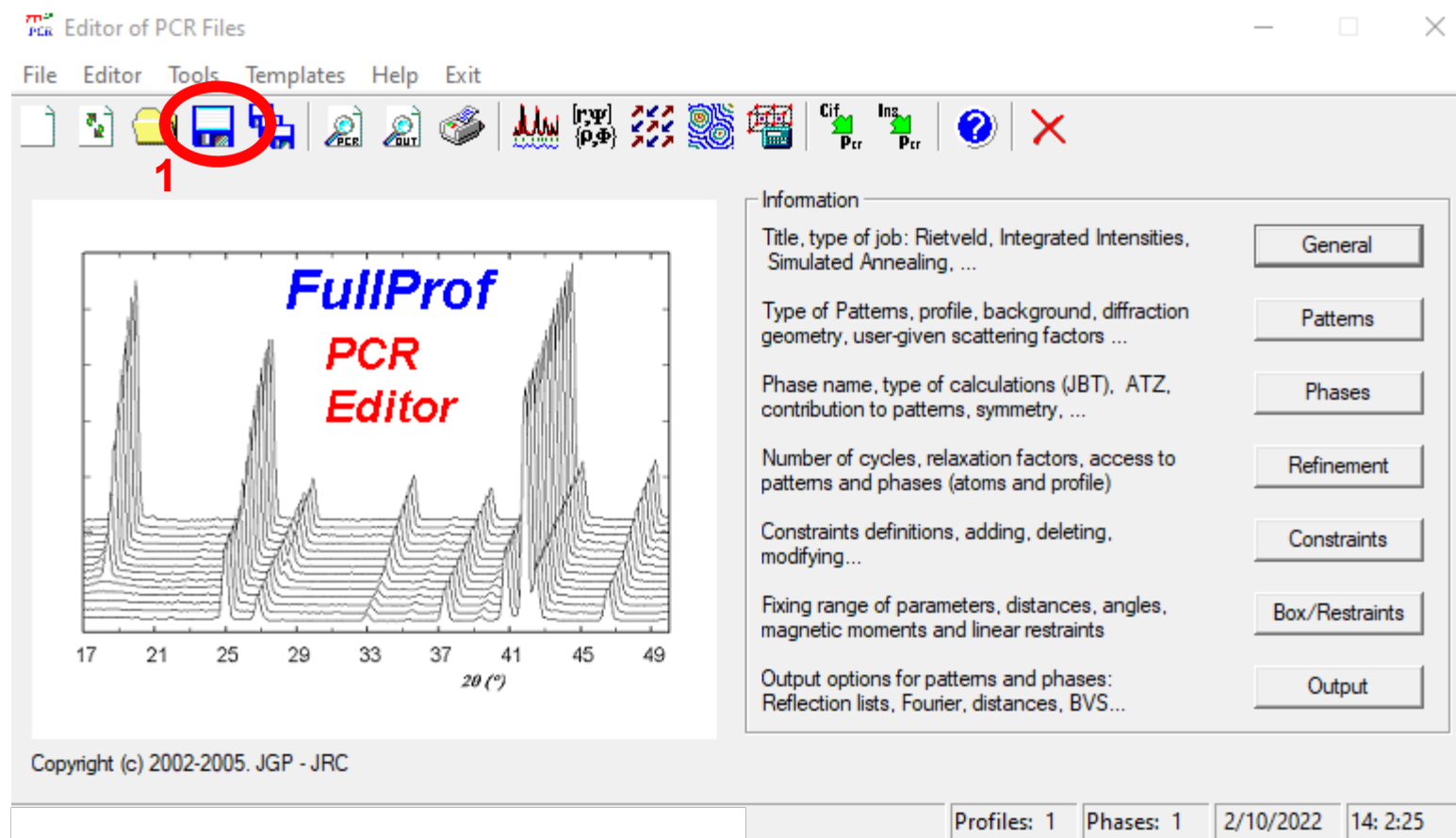
	Name	Type	X	Y	Z	B	Occ
Atom #1	Mn1	Mn	0.51009	0.13426	0.59800	0.30004	1.00000
Atom #2	O1	O	0.54100	0.24430	0.42660	0.30004	1.00000
Atom #3	N1	N	0.36060	0.29910	0.56210	0.30004	1.00000
Atom #4	C1	C	0.26270	0.32510	0.61920	0.30004	1.00000
Atom #5	H1	H	0.25464	0.27694	0.69194	0.30004	1.00000

	Rx	Ry	Rz	lx	ly	lz	MPhase
Atom #1							
Atom #2							
Atom #3							
Atom #4							

When finished, hit OK

Step 1: Refine the crystal structure using FullProf

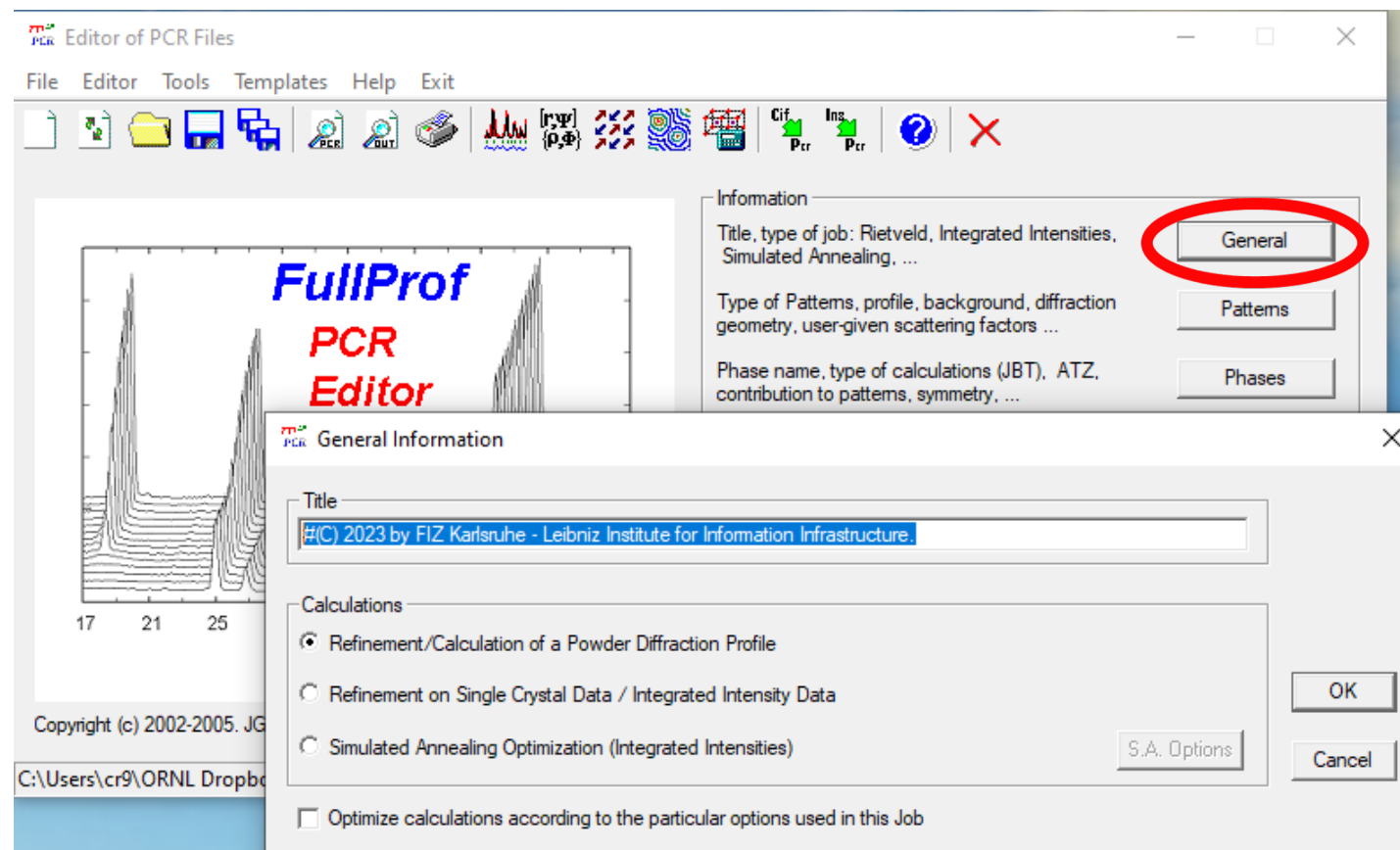
- **1.** Save the changes.
- This should be done whenever changes are made in the GUI.



Step 1: Refine the crystal structure using FullProf

- “**General**” tab has refinement of powder data as default. This is what we’ll do in this example.
- Can edit title as wanted.

For powder refinements don't need to edit this tab

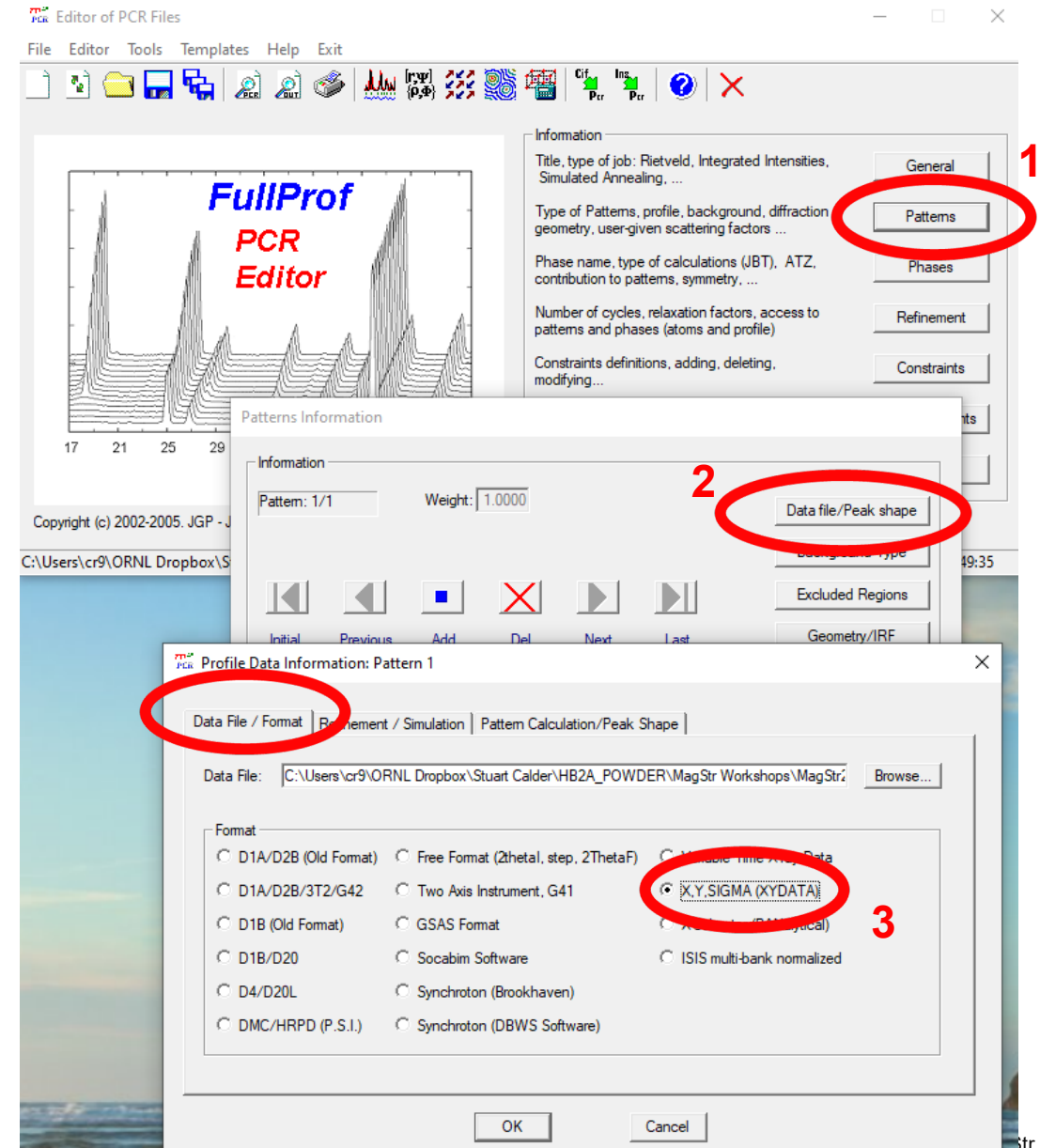


Step 1: Refine the crystal structure using FullProf

1. “Patterns” tab

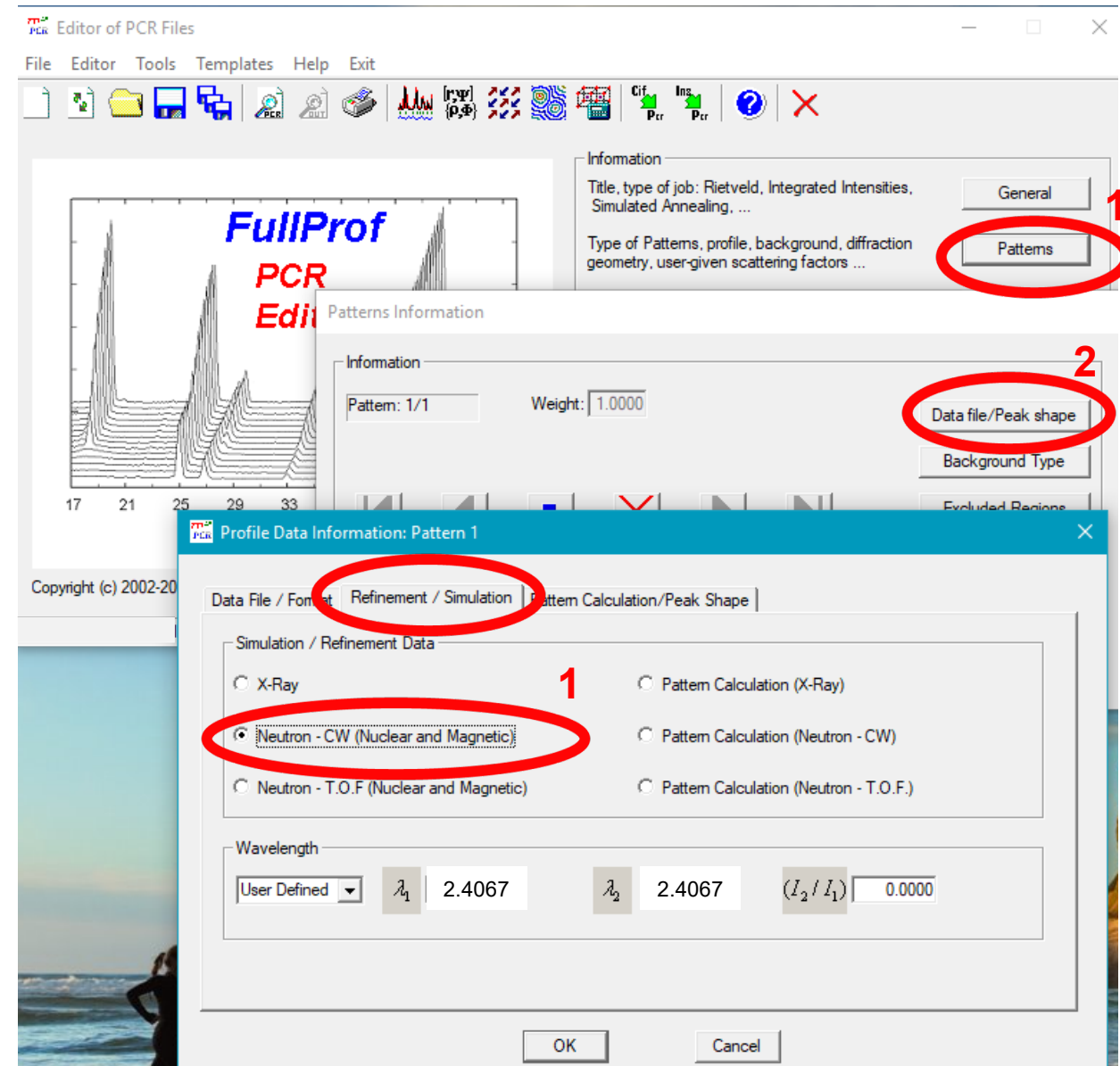
- 2. Select the format of the data file Fullprof should refine.
- 3. Patterns → Data file/Peak Shape → X,Y,SIGMA (XYDATA)

Data format from HB-2A is simply three columns with two-theta, Intensity, Intensity Error



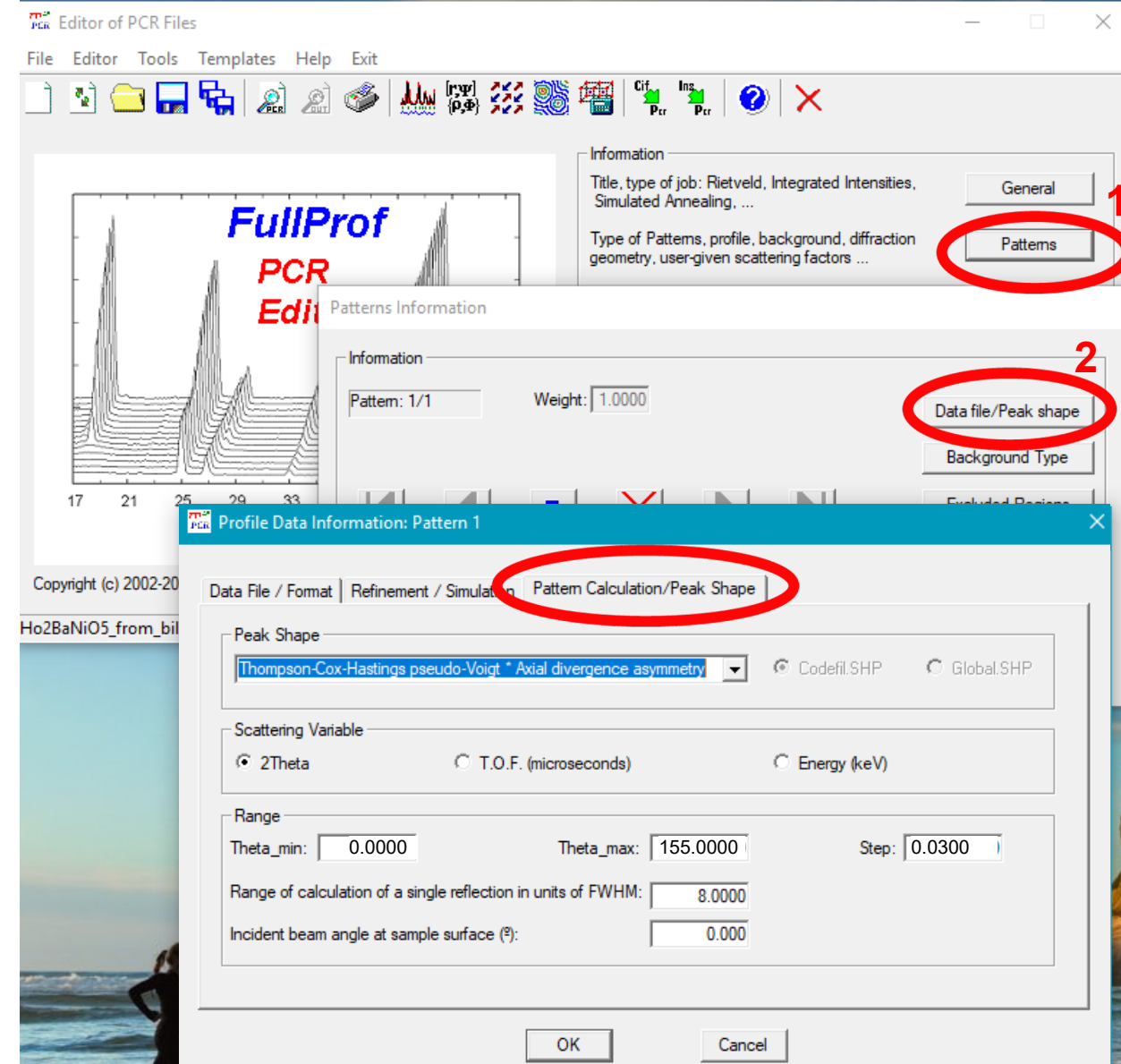
Step 1: Refine the crystal structure using FullProf

- 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

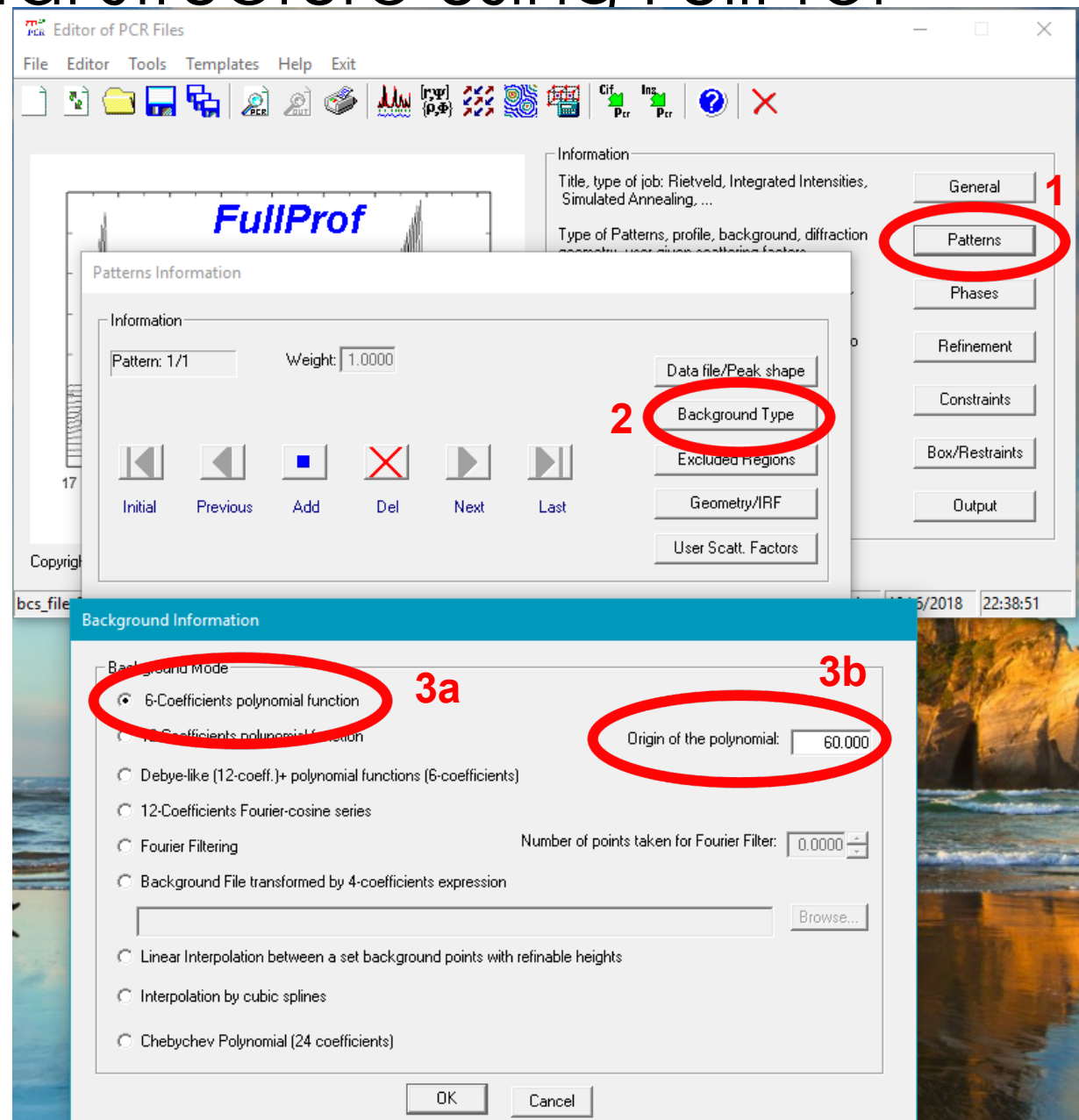
- Check final tab:
- Patterns → Data file/Peak Shape → Pattern Calculation/Peak Shape
- Peak shape is already loaded correctly from irf file.



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.

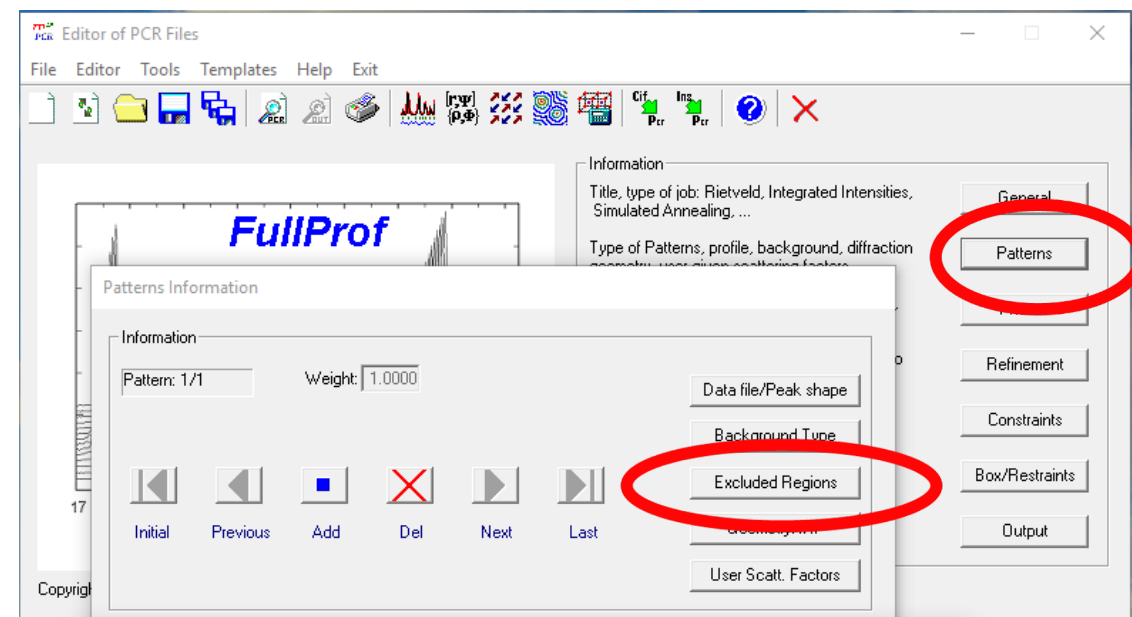
Background on HB-2A typically low and featureless so can be captured by simple function.



Step 1: Refine the crystal structure using FullProf

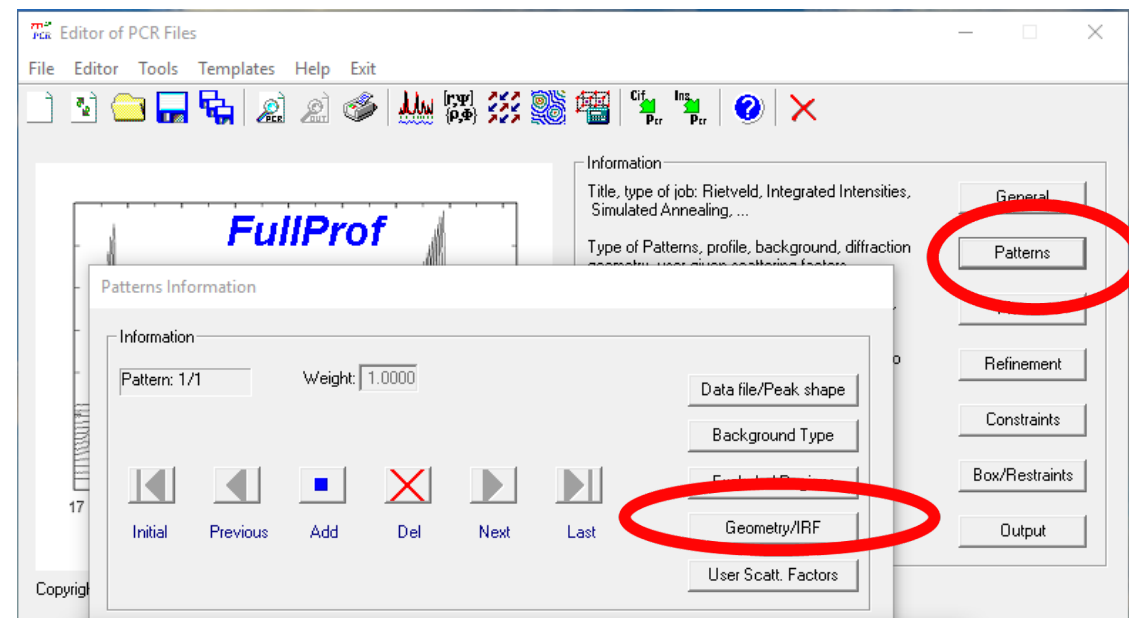
Exclude regions in the data?

- We will not exclude any regions of the data
- Use with care, but can cut out background.
- 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!

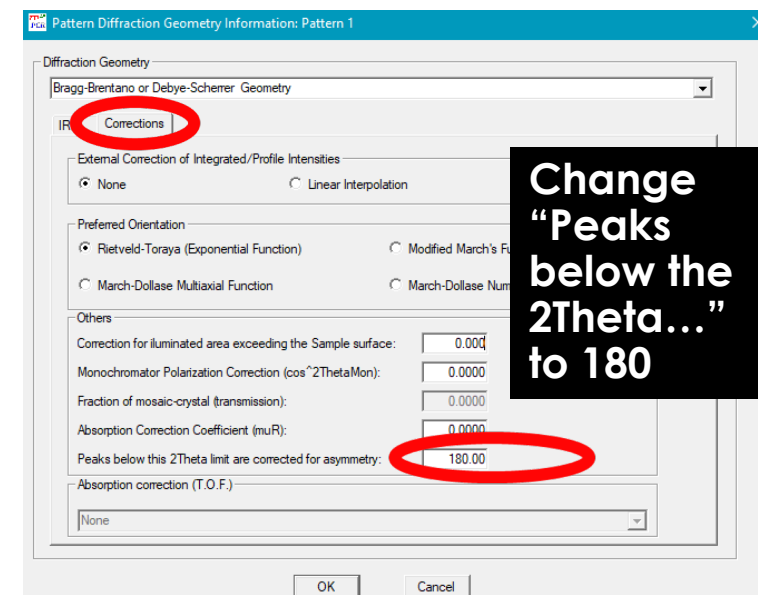
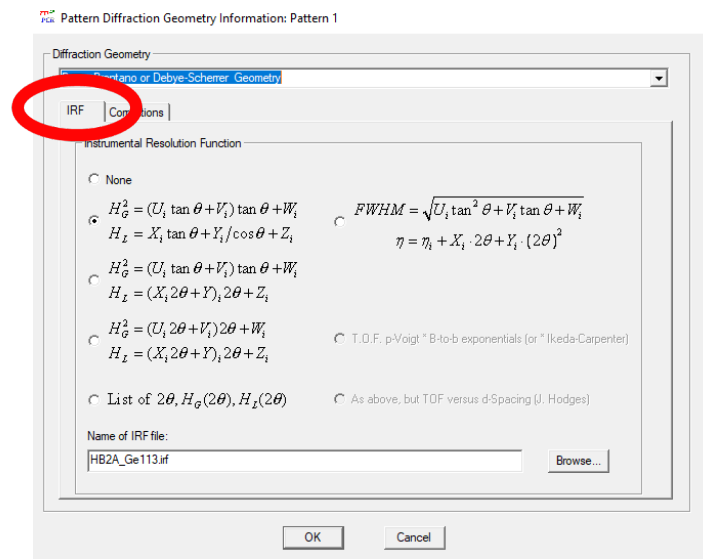


Step 1: Refine the crystal structure using FullProf

- 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!

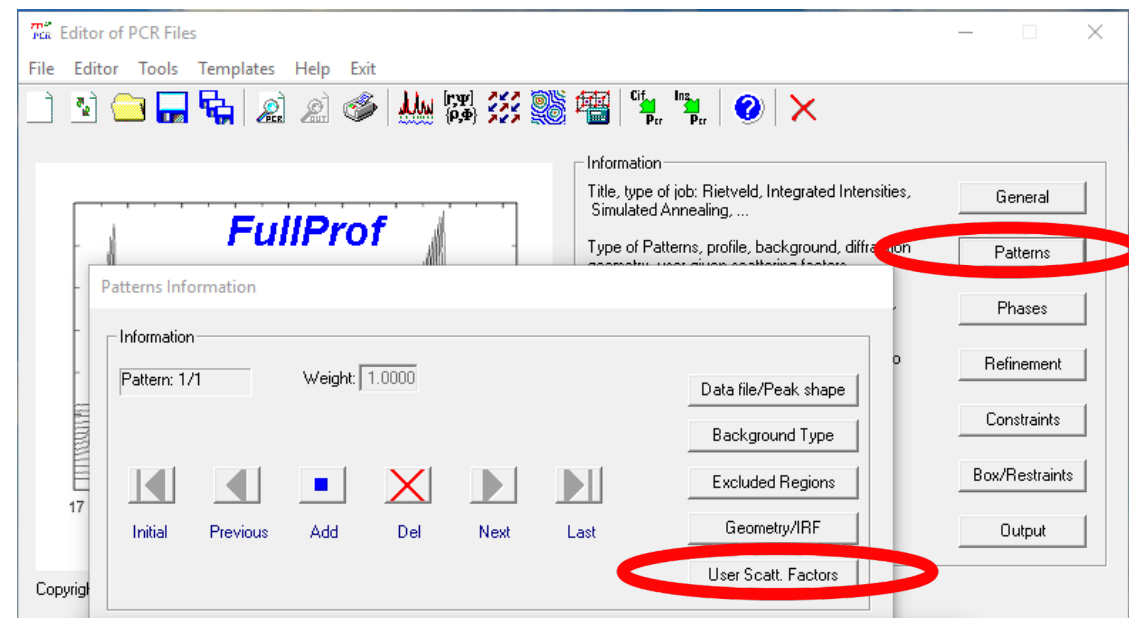


- Can correct for absorption if needed. “muR” is mu (absorption) multiplied by sample radius. Can find mu at NIST website <https://www.ncnr.nist.gov/resources/activation/>



Step 1: Refine the crystal structure using FullProf

- No further editing should be needed of the remaining “Patterns” tabs:
 - User Scatt. Factors
This can be used to add e.g. a form factor that isn't tabulated



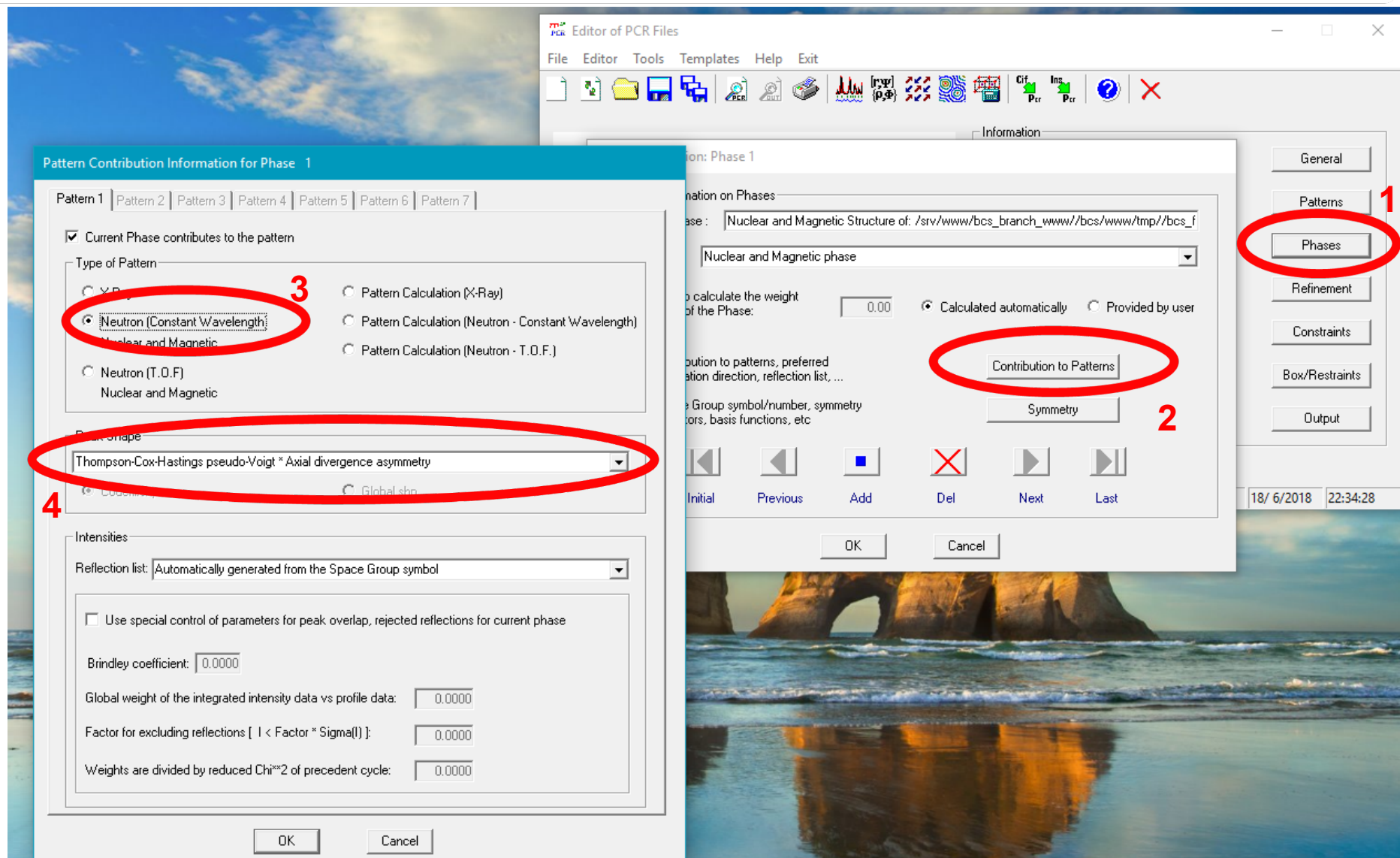
If the magnetic ion does not have form factor tables tabulated, or you want to test a non-standard form factor, this can be added here. One example would be for 5d ions, such as Ir, Os, etc.

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

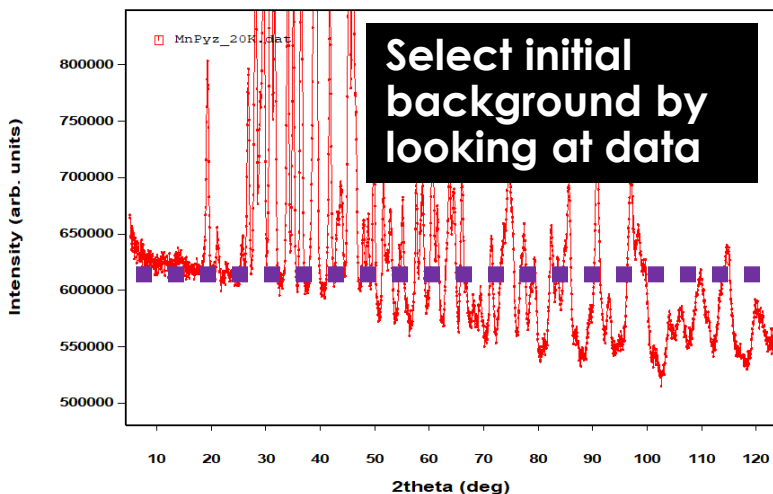
REFINEMENT tab:

- Setting starting values for refinements
- Starting background value of 600000 (check data)

The screenshot displays the FullProf software interface. The main window is titled "Editor of PCR Files" and shows the "Refinement Information" dialog box. The "Refinement" tab is selected in the right-hand sidebar, indicated by a red circle and the number 1. The "Refinement Information" dialog box shows the "Cycles of Refinement" set to 1, the "Stop Criterion of Coverage" set to "Forced Termination when shifts < 0.02 x E.S.D.", and the "Relaxation Factors for Shifts" set to 1.00 for Atomic, Anisotropic, Profile, and Global. The "Reflections ordering" is set to "Only at the first cycle". The "Background" button is circled in red and labeled with a red 2. Below the "Background" button, the "Background" dialog box is open, showing a table of coefficients for a 6 Coefficients Polynomial Background. The coefficient d_0 is set to 600000, which is circled in red and labeled with a red 3. The "Background" dialog box also has "Refine All", "Fix All", "Cancel", and "OK" buttons.

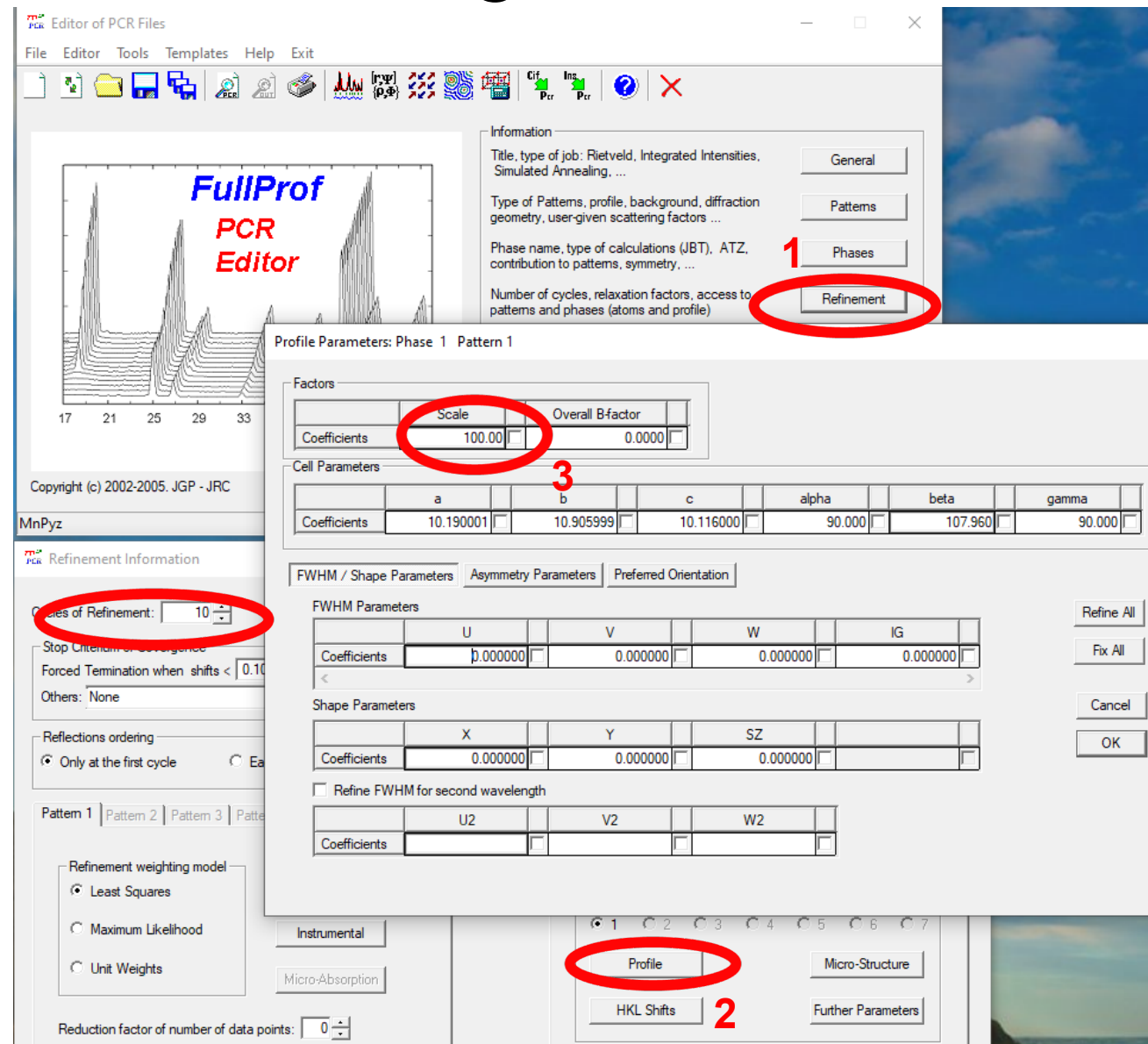
Background Selection Dialog:

	d_0	d_1	d_2	d_3	d_4	d_5
Coefficients	600000	0.0000	0.0000	0.0000	0.0000	0.0000
	d_6	d_7	d_8	d_9	d_10	d_11
Coefficients						
	d_12	d_13	d_14	d_15	d_16	d_17
Coefficients						
	d_18	d_19	d_20	d_21	d_22	d_23
Coefficients						



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.



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

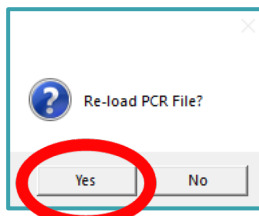
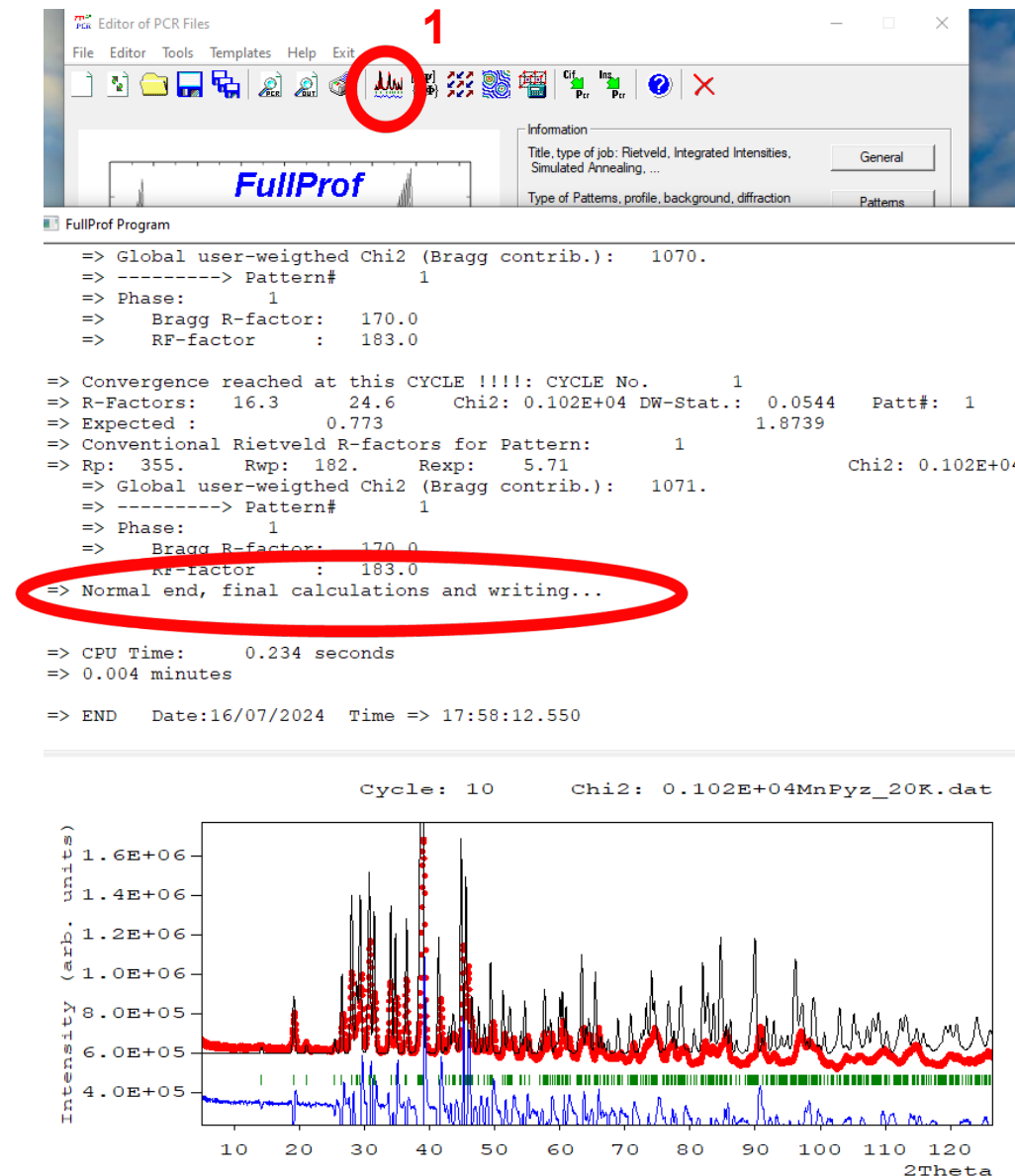
Step 1: Refine the crystal structure using FullProf

- 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 10). You can repeat this by pushing run until “Normal end, final calculation and writing...” shows rather than “Convergence not reached”

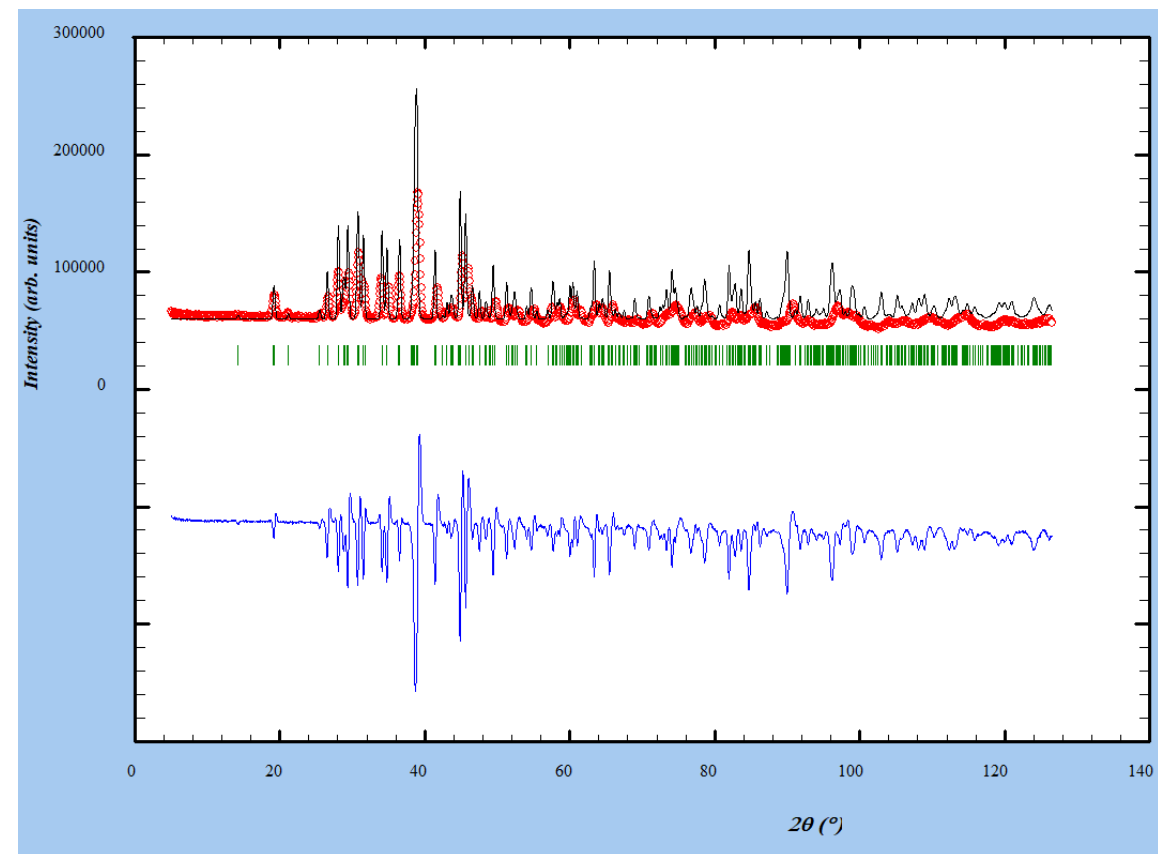
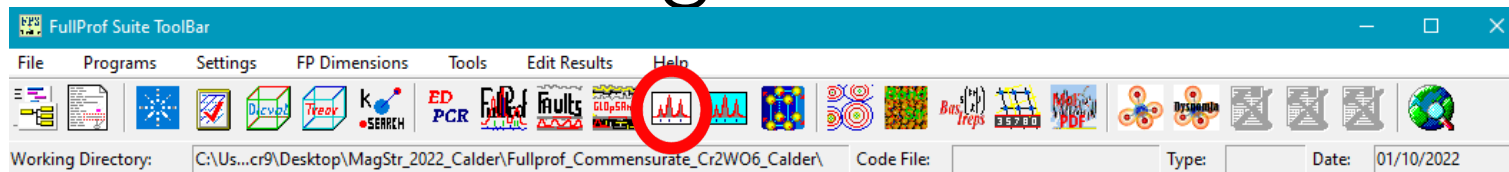
- Select **yes** to save.
If you're doing a refinement and the fit gets worse then you can select “no” and the starting values will remain.



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.*

HB2A_Ge113
MnPyz
MnPyz.out
MnPyz
MnPyz
MnPyz
MnPyz_1p5K
MnPyz_20K
MnPyz1



The model and the data look “close enough” to start refining. We can now we can turn of parameters to refine to try to get he model and data to match.

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*)

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.

Profile Parameters: Phase 1 Pattern 1

Factors	
	Scale
Coefficients	100.00 <input checked="" type="checkbox"/>
	Overall B-factor
	0.0000 <input type="checkbox"/>

Cell Parameters							
	a	b	c	alpha	beta	gamma	
Coefficients	10.190001 <input checked="" type="checkbox"/>	10.905999 <input checked="" type="checkbox"/>	10.116000 <input checked="" type="checkbox"/>	90.000 <input type="checkbox"/>	107.960 <input checked="" type="checkbox"/>	90.000 <input type="checkbox"/>	

FWHM / Shape Parameters	
	U
Coefficients	0.000000 <input type="checkbox"/>
	V
	0.000000 <input type="checkbox"/>
	W
	0.000000 <input type="checkbox"/>
	IG
	0.000000 <input type="checkbox"/>

Shape Parameters	

6 Coefficients Polynomial Background: Pattern 1

6 Coefficients Polynomial Background: Pattern 1						
	d_0	d_1	d_2	d_3	d_4	d_5
Coefficients	0.60000E+06 <input checked="" type="checkbox"/>	0.0000 <input checked="" type="checkbox"/>	0.0000 <input checked="" type="checkbox"/>	0.0000 <input checked="" type="checkbox"/>	0.0000 <input checked="" type="checkbox"/>	0.0000 <input checked="" type="checkbox"/>
	d_6	d_7	d_8	d_9	d_10	d_11

Instrumental Parameters Refinement: Pattern 1

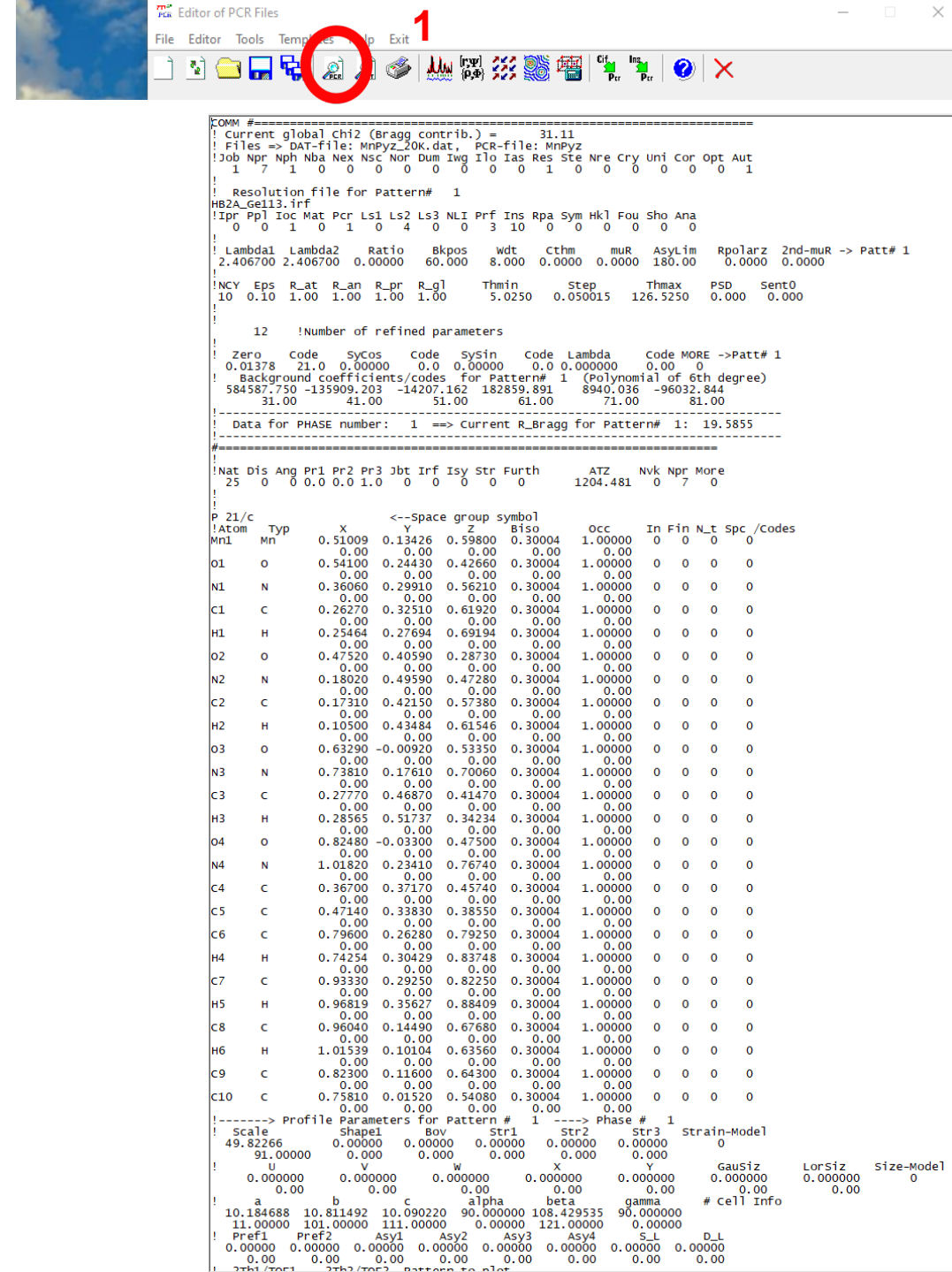
2_Theta			
	Zero	Displacement	Transparency
Coefficients	0.000000 <input checked="" type="checkbox"/>	0.000000 <input type="checkbox"/>	0.000000 <input type="checkbox"/>
	Wavelength		
	0.000000 <input type="checkbox"/>		

Atoms Information: Phase 1

Atoms Information: Phase 1									
List of Atoms									
Number of Atoms: 3									
	Label	Ntyp	X	Y	Z	B	Occ	Therm. Fact.	
Atom # 1	Mn1	Mn	0.00000 <input checked="" type="checkbox"/>	0.00000 <input checked="" type="checkbox"/>	0.16610 <input checked="" type="checkbox"/>	0.00000 <input type="checkbox"/>	0.33333 <input type="checkbox"/>	Isotropic	
Atom # 2	P1	P	0.00000 <input checked="" type="checkbox"/>	0.00000 <input checked="" type="checkbox"/>	0.44430 <input checked="" type="checkbox"/>	0.00000 <input type="checkbox"/>	0.33333 <input type="checkbox"/>	Isotropic	
Atom # 3	Se1	Se	0.33050 <input checked="" type="checkbox"/>	-0.00160 <input checked="" type="checkbox"/>	0.08180 <input checked="" type="checkbox"/>	0.00000 <input type="checkbox"/>	1.00000 <input type="checkbox"/>	Isotropic	

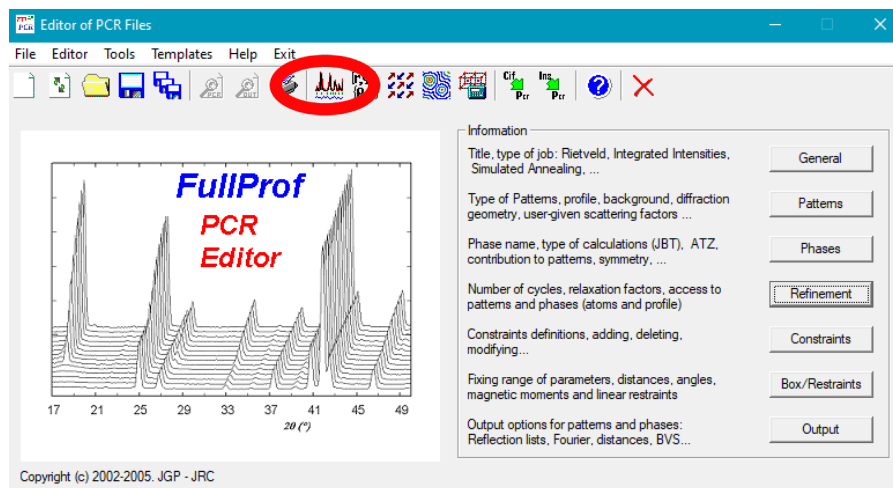
Working in text editor and GUI

- 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 various 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 91, so is refining.
- To turn on any to refine can type a 1, then Fullprof figures out the numbering.



```
=====
! Current global chi2 (Bragg contrib.) = 31.11
! Files => DAT-file: MnPyZ_20K.dat, PCR-file: MnPyZ
! Job Npr Nph Nba Nex NSC Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
! 1 7 1 0 0 0 0 0 0 0 0 0 0 1 0 0 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 Hk1 Fou Sho Ana
! 0 0 1 0 0 1 0 4 0 3 10 0 0 0 0 0 0 0 0
!
! Lambda1 Lambda2 Ratio Bkpos wdt cthm muR AsyLim Rpolaz 2nd-muR -> Patt# 1
! 2.406700 2.406700 0.00000 60.000 8.000 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
! 10 0.10 1.00 1.00 1.00 1.00 5.0250 0.050015 126.5250 0.000 0.000
!
! 12 !Number of refined parameters
!
! Zero Code SyCos Code Sysin Code Lambda Code MORE ->Patt# 1
! 0.01378 21.0 0.00000 0.0 0.00000 0.0 0.000000 0.00 0
! Background coefficients/codes for Pattern# 1 (Polynomial of 6th degree)
! 584587.750 -135909.203 -14207.162 182859.891 8940.036 -96032.844
! 31.00 41.00 51.00 61.00 71.00 81.00
!
! Data for PHASE number: 1 -> Current R_Bragg for Pattern# 1 19.5855
!
!-----
! Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
! 25 0 0 0.0 0.0 1.0 0 0 0 0 0 0 1204.481 0 7 0
!
! P 21/c
! Atom Typ X Y Z Biso Occ In Fin N_t Spc /codes
Mn1 Mn 0.51009 0.13426 0.59800 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
O1 O 0.54100 0.24430 0.42660 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
N1 N 0.36060 0.29910 0.56210 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C1 C 0.26270 0.32510 0.61920 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
H1 H 0.25464 0.27694 0.69194 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
O2 O 0.47520 0.40590 0.28730 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
N2 N 0.18020 0.49590 0.47280 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C2 C 0.17310 0.42150 0.57380 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
H2 H 0.10500 0.43484 0.61546 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
O3 O 0.63290 -0.00920 0.53350 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
N3 N 0.73810 0.17610 0.70060 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C3 C 0.27770 0.46870 0.41470 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
H3 H 0.28565 0.51737 0.34234 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
O4 O 0.82480 -0.03300 0.47500 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
N4 N 1.01820 0.23410 0.76740 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C4 C 0.36700 0.37170 0.45740 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C5 C 0.47140 0.33830 0.38550 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C6 C 0.79600 0.26280 0.79250 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
H4 H 0.74254 0.30429 0.83748 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C7 C 0.93330 0.29250 0.82250 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
H5 H 0.96819 0.35627 0.88409 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C8 C 0.96040 0.14490 0.67680 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
H6 H 1.01539 0.10104 0.63560 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C9 C 0.82300 0.11600 0.64300 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
C10 C 0.75810 0.01520 0.54080 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00 0
!-----> Profile Parameters for Pattern # 1 -----> Phase # 1
! Scale Shape1 Bv Str1 Str2 Str3 Strain-Model
! 49.82266 0.00000 0.00000 0.00000 0.00000 0.00000 0
! 91.00000 0.000 0.000 0.000 0.000 0.000 0
!
! U V W X Y Gauss Lrsiz size-Model
! 0.000000 0.000000 0.000000 0.000000 0.000000 0.00000 0.00000 0
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0
!
! a b c alpha beta gamma # cell Info
! 10.184688 10.811492 10.090220 90.000000 108.429535 90.000000
! 11.00000 101.00000 111.00000 0.00000 121.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
! 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! Pref1 Pref2 Pref3 Pref4 Pref5 Pref6 Pref7 Pref8 Pref9 Pref10
```

Step 1: Refine the crystal structure using FullProf



- The refinement to the 20K data is closer.
- Next can add in refinements to the peak shape, since the sample may add some broadening beyond the parameters loaded in with the irf file.

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

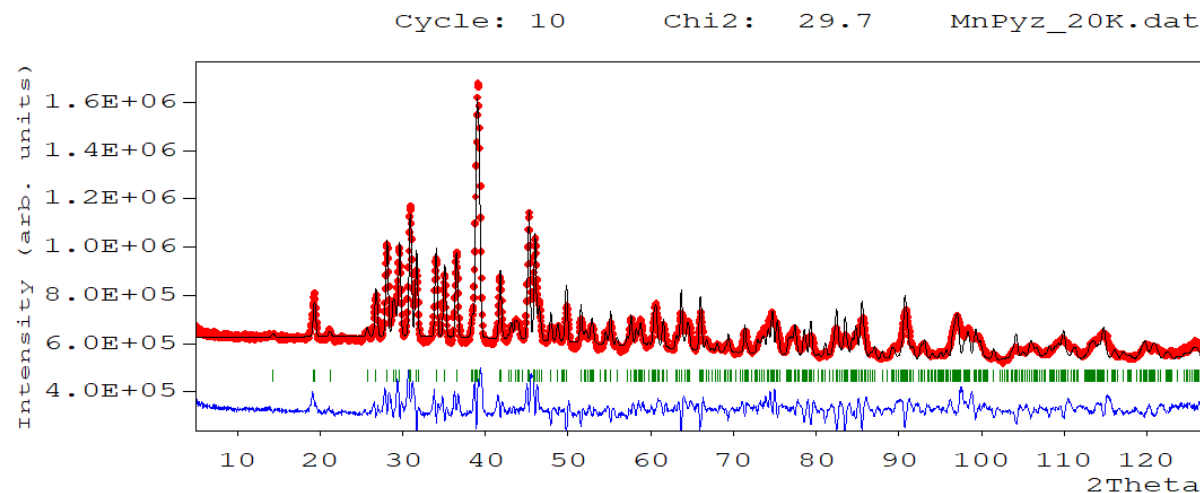
```
FullProf Program

=====>>> CYCLE:      10

=> Control file *.pcr: MnPyz
=> Pattern: 1 MnPyz_20K
=> Calculation of Yi for all points + Normal Matrix & Vector...
=> Calculation for pattern: 1
=> Solving L.S. equations...
=> Writing results for cycle      10
=> R-Factors: 2.98      4.20      Chi2: 29.7      DW-Stat.: 0.1665      Patt#: 1
=> Expected : 0.771      1.8838
=> Conventional Rietveld R-factors for Pattern: 1
=> Rp: 36.1      Rwp: 30.8      Rexp: 5.65      Chi2: 29.7
=> Global user-weighted Chi2 (Bragg contrib.): 31.11
=> -----> Pattern# 1
=> Phase: 1
=> Bragg R-factor: 19.59
=> RF-factor : 11.97
=> Conv. not yet reached -> [Max] Shift(Cell_C_phi_pat1)/(eps*Sigma)= 30.67 abs> 1
=> Normal end, final calculations and writing...

=> CPU Time: 1.375 seconds
=> 0.023 minutes

=> END Date:16/07/2024 Time => 18:08:12.132
```



Step 1: Refine the crystal structure using FullProf

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

Profile Parameters: Phase 1 Pattern 1

Factors

	Scale	Overall B-factor
Coefficients	49.823 ✓	0.0000

Cell Parameters

	a	b	c	alpha	beta	gamma
Coefficients	10.184688 ✓	10.811492 ✓	10.090220 ✓	90.000	108.430 ✓	90.000

FWHM / Shape Parameters | Symmetry Parameters | Preferred Orientation

FWHM Parameters

	U	V	W	IG
Coefficients	0.000 ✓	0.000 ✓	0.000 ✓	0.000000

Shape Parameters

	X	Y	SZ
Coefficients	0.000 ✓	0.000000	0.000000

☐ Refine FWHM for second wavelength

	U2	V2	W2
Coefficients			

Refine All
Fix All
Cancel
OK

Profile Parameters: Phase 1 Pattern 1

Factors

	Scale	Overall B-factor
Coefficients	49.823 ✓	0.0000

Cell Parameters

	a	b	c	alpha	beta	gamma
Coefficients	10.184688 ✓	10.811492 ✓	10.090220 ✓	90.000	108.430 ✓	90.000

FWHM / Shape Parameters | Asymmetry Parameters | Preferred Orientation

S_L D_L

	S_L	D_L
Coefficients	0.000000	0.000000

Asym1 Asym2 Asym3 Asym4

	Asym1	Asym2	Asym3	Asym4
Coefficients	0.000000 ✓	0.000000 ✓	0.000000 ✓	0.000000 ✓

P5 P6 P7 P8

	P5	P6	P7	P8
Coefficients				

Refine All
Fix All
Cancel
OK

Step 1: Refine the crystal structure using FullProf

- Finally the atomic parameters can be refined. This will give a good fit and low chi values. But there are lots of variables, so care should be taken in interpreting these results for the atomic positions.

Atoms Information: Phase 1

List of Atoms

Number of Atoms:

25

	Label	Ntype	X	Y	Z	B	Occ	Therm. Fact.
Atom # 1	Mn	Mn	0.51356	0.12895	0.60217	0.30004	1.00000	Isotropic
Atom # 2	O1	O	0.54868	0.24635	0.42955	0.30004	1.00000	Isotropic
Atom # 3	N1	N	0.36244	0.30105	0.56440	0.30004	1.00000	Isotropic
Atom # 4	C1	C	0.26705	0.31210	0.62293	0.30004	1.00000	Isotropic

<

>

Anisotropic Thermal Factors / Form Factors

	B11/F1	B22/F2	B33/F3	B12/F4	B13/F5	B23/F6	F7
#							
#							

Refine Positions

Refine B_iso

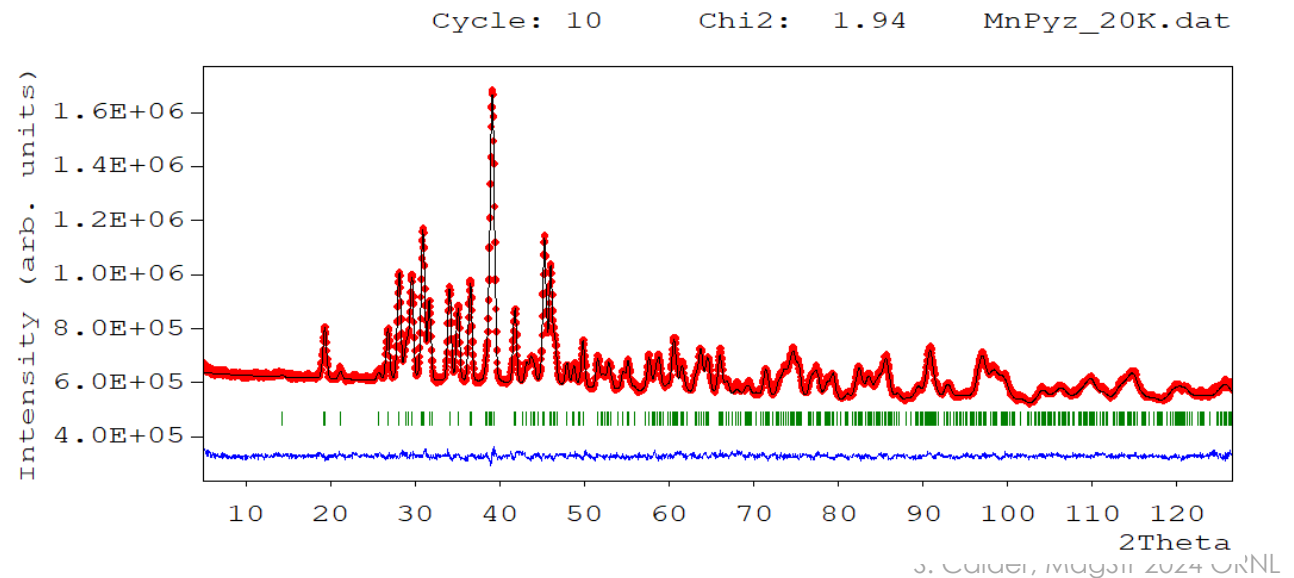
Refine B_aniso

Fix All

Cancel

OK

- Data was collected with a shorter wavelength to cover more reflections that is presented in the paper.



Step 1: Refine the crystal structure using FullProf

- The previous steps were refining the crystal structure at 20K, where there was no long range magnetic order.
- We now want to refine the crystal structure in the magnetically ordered region (1.5K).
- 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

- Refine against the 1.5 K data.
- 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.
- We can now use this to determine the k-vector and then magnetic structure.

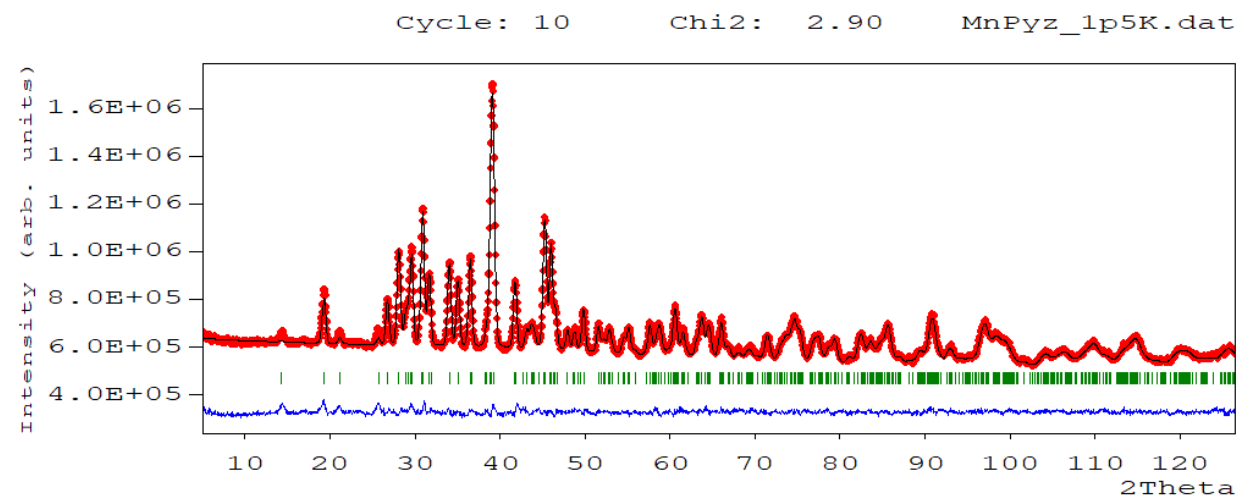
FullProf Program

```
=> Expected :          0.773          1.8739
=> Conventional Rietveld R-factors for Pattern:          1
=> Rp: 8.97   Rwp: 8.31   Rexp: 4.88          Chi2: 2.90
=> Global user-weighted Chi2 (Bragg contrib.): 2.780
=> -----> Pattern#          1
=> Phase:          1
=> Bragg R-factor: 3.428
=> RF-factor      : 1.672

=> Convergence reached at this CYCLE !!!!: CYCLE No.          1
=> R-Factors: 1.02   1.32   Chi2: 2.90   DW-Stat.: 0.7071   Patt#: 1
=> Expected :          0.773          1.8739
=> Conventional Rietveld R-factors for Pattern:          1
=> Rp: 8.97   Rwp: 8.31   Rexp: 4.88          Chi2: 2.90
=> Global user-weighted Chi2 (Bragg contrib.): 3.033
=> -----> Pattern#          1
=> Phase:          1
=> Bragg R-factor: 3.428
=> RF-factor      : 1.672
=> Normal end, final calculations and writing...

=> CPU Time: 0.266 seconds
=> 0.004 minutes

=> END   Date:16/07/2024   Time => 18:27:25.873
```



Step 1: Refine the crystal structure using FullProf

- The background changes slightly between 1.5 K and 20K, these parameters can be refined here or when doing the magnetic phase.

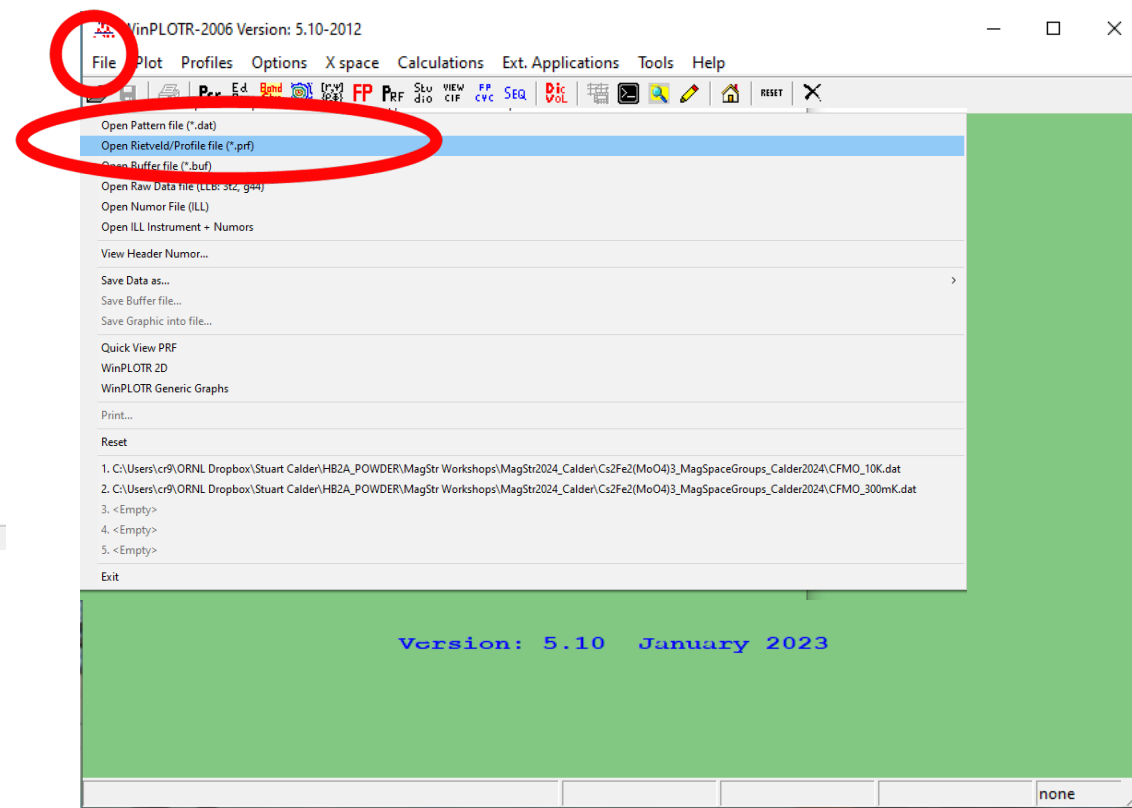
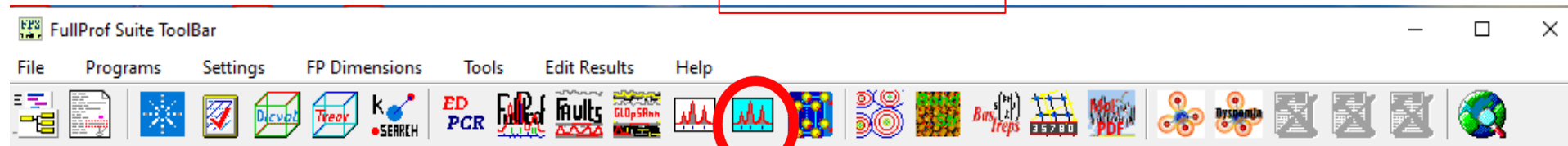
Mn-pyrazinecarboxylate

- 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

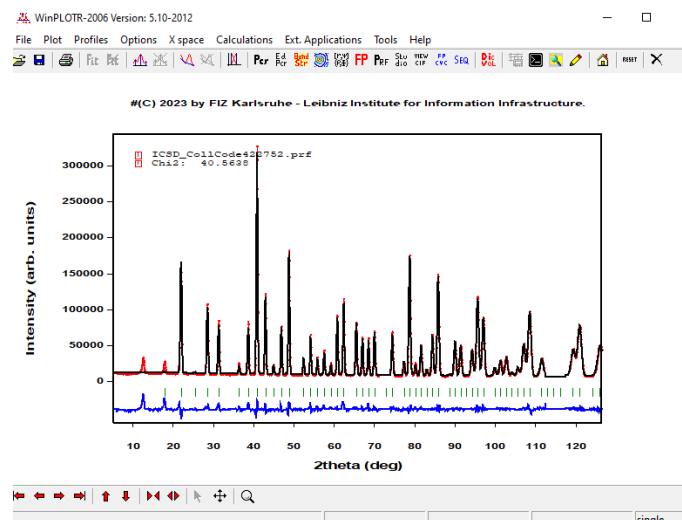
WinPlotr-2006

- k-search is run in WinPlotr-2006.
- Open the .prf file:
 - “File”>”Open Rietveld/Profile file (*.prf)”
 - Select the prf file



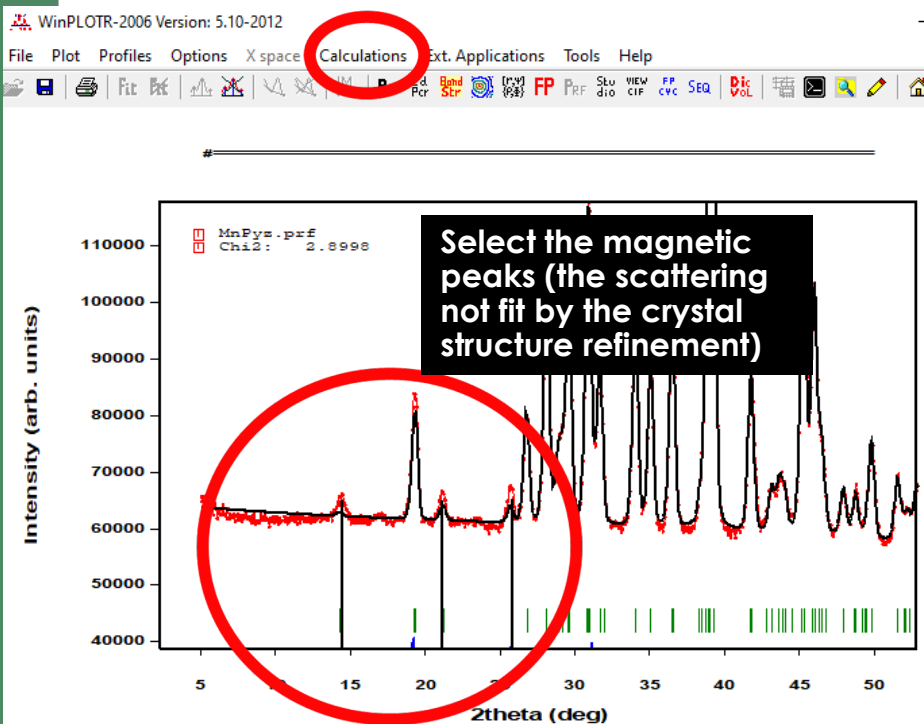
backup
ICSD_CollCode422752

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.



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

Input parameters for K_SEARCH

Title: #

Lattice Type: P 21/c

Cell Parameters: 10.17611 10.80998 10.07803 90.0000 108.4390 90.0000

Tolerance (TOF/2theta): 0.300

K range (xmin, xmax, ...): 0.0 0.5 0.0 0.5 0.0 0.5

Number of Points (Na* Nb* Nc): 100 100 100

Wavelength (CW) / Dtt1(TOF): 2.40670

☒ Short Output ☐ Long Output ☐ No output of intermediate calculations

☒ Search only special k-vectors

OK Cancel

```
*****
*          PROGRAM K_SEARCH          *
*****
(J.R.C. ILL-January 2009)

=> The expected maximum R-factor for a solution is:      4.6089

=> Writing partial results ...

=> Testing 90 internal k-vectors
Solution:  1 k =( 0.0000 0.0000 0.0000) R-F:  0.6544
Solution:  2 k =( 0.3333 0.3333 0.0000) R-F:  1.6619
Solution:  3 k =( 0.0000 0.3333 0.3333) R-F:  1.8539
Solution:  4 k =( 0.1250 0.2500 0.0000) R-F:  1.6127
Solution:  5 k =( 0.0000 0.2500 0.1250) R-F:  2.2418
Solution:  6 k =( 0.5000 0.0000 0.1250) R-F:  1.2668
Solution:  7 k =( 0.1250 0.0000 0.5000) R-F:  1.9448
=> Special k-vector solutions found!

=> List of the best incommensurate 10 solutions for  3 satellites

      Kx      Ky      Kz      R-factor
0.000000  0.000000  0.000000  0.654422
0.500000  0.000000  0.125000  1.266762
0.125000  0.250000  0.000000  1.612743
0.333330  0.333330  0.000000  1.661932
0.000000  0.333330  0.333330  1.853868
0.125000  0.000000  0.500000  1.944756
0.000000  0.250000  0.125000  2.241826

=> The best commensurate solution is the special kvector ks =( 0.0000 0.0000 0.0000)
The corresponding R-factor is:      0.6544 to be compared with incommensurate R-factors

=> Powder diffraction may give wrong results even if the R-factors for the solutions are "good"
The best way to verify the solutions is to perform a full profile fitting and look for mismatches

Total CPU-Time

CPU-seconds:      0.00
CPU-minutes:      0.00
CPU-hours   :      0.00
```

$k=(0,0,0)$

Mn-pyrazinecarboxylate

- 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.
- Use the SARAh webrefine – Fullprof
- <http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>

Wills Group

Magnetism and magnetic materials

HOME

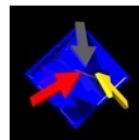
SOFTWARE

WEB SOFTWARE

DOCUMENTS/PAPERS

OTHER FERMAT-E SITES

SARAh – Simulated Annealing and Representation Analysis



News – Feb 2022. The web version of SARAh Refine for FullProf has been released. It reproduces the core features of SARAh Refine for Windows in a browser and has introduces new refinement ideas :

<http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>

(Click icon to download combined install file from Dropbox)

- k search – finding the propagation vector with SARAh
- SARAh – Simulated Annealing and Representation Analysis
 - SARAh Installation Instructions
 - SARAh – Introduction video
 - SARAh with FullProf
 - SARAh with GSAS
- VaList – Bond Valence Calculations and Listing
- Downloads

The SARAh suite is made up of 2 separate programs that perform symmetry calculations and magnetic structure analysis :

SARAh Representational Analysis –

Performs the calculations of Representational Analysis. These allow the determination of atomic displacements or magnetic structures that can accompany a second-order phase transition. Output files includes a tailored summary with cut-and-paste tables written in LaTeX. (Win9x, 2000, Vista and Windows 7) [1]

SARAh Refine –

Is an example of a 'metaprogram'. SARAh refine was developed to add new functionality to the standard Rietveld programs GSAS, FullProf and TOPAS, i.e. to allow them to refine magnetic structures in terms of the basis vectors (symmetry modes) generated by SARAh Representational Analysis and the calculations of group theory. [1]

Step 3: Create candidate magnetic models using SARAh

Help with technical settings and refinement strategies

Technical information: (ASW version Oct 2022 :-)

<http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>

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'

Settings

- You and Google
- Autofill and passwords
- Privacy and security
- Performance
- Experimental AI
- Appearance
- Search engine
- Default browser
- On startup

Languages

Downloads

Accessibility

System

Reset settings

Search settings

Your browser is managed by your organization

Downloads

Location

C:\Users\crl\Desktop

Change

Ask where to save each file before downloading



Show downloads when they're done



Step 3: Create candidate magnetic models using SARAh

- Under “WEB SOFTWARE – NEW APPS!” select “SARAH WEB REFINER - FULLPROF”
- Input the crystal structure information. All we need is the
 - Space group
 - Propagation vector
 - Magnetic ion position

Wills Group

Magnetism and magnetic materials

HOME

WINDOWS SOFTWARE

WEB SOFTWARE- NEW APPS!

VIDEO LECTURES- NEW!

PAPERS/DOCUMENT

SARAh webRefine – FullProf

Two pieces of advice for using SARAh webRefine : 1. change your browser settings to allow you to select where you save downloads (and or <evaluate>, it will look like nothing is happening for a few seconds. Look in the tab '4. Help and Strategies' for more information.

-Andrew (February 2022)



Space group : {14:b1, P 1 21/c 1, C 2h 5} ▾

Propagation vector :

0 0 0

Crystallographic coordinates with each atom on a separate line :

e.g. Cu2 1/2 1/2 -1/2

Mn2 0.51356 0.12895 0.60217

Submit

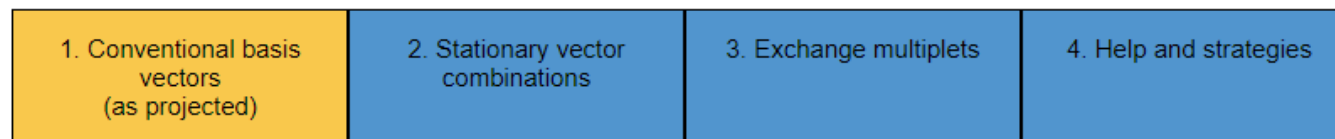
Step 3: Create candidate magnetic models using SARAh

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

SARAh webRefine – FullProf

Two pieces of advice for using SARAh webRefine : 1. change your browser settings to allow you to select where you save downloads (and overwrite files), 2. when you click <evaluate>, it will look like nothing is happening for a few seconds. Look in the tab '4. Help and Strategies' for more information.

-Andrew (February 2022)



Method 1. Conventional analysis - as projected basis vectors

Select command (generate template for magnetic phase for pcr; edit pcr with magnetic phase present):

1. powder format 2. make template pcr

<input type="checkbox"/> Mn2 Γ_1 ψ_1	<input type="checkbox"/> Mn2 Γ_2 ψ_3	<input type="checkbox"/> Mn2 Γ_4 ψ_2
<input type="checkbox"/> Mn2 Γ_1 ψ_2	<input type="checkbox"/> Mn2 Γ_3 ψ_1	<input type="checkbox"/> Mn2 Γ_4 ψ_3
<input type="checkbox"/> Mn2 Γ_1 ψ_3	<input type="checkbox"/> Mn2 Γ_3 ψ_2	
<input type="checkbox"/> Mn2 Γ_2 ψ_1	<input type="checkbox"/> Mn2 Γ_3 ψ_3	
<input type="checkbox"/> Mn2 Γ_2 ψ_2	<input type="checkbox"/> Mn2 Γ_4 ψ_1	

(Your browser should be set to ask for the download location so the pcr file can be overwritten. Please look in '4. Help and strategies' for an explanation/help.)

Submit

Step 3: Create candidate magnetic models using SARAh

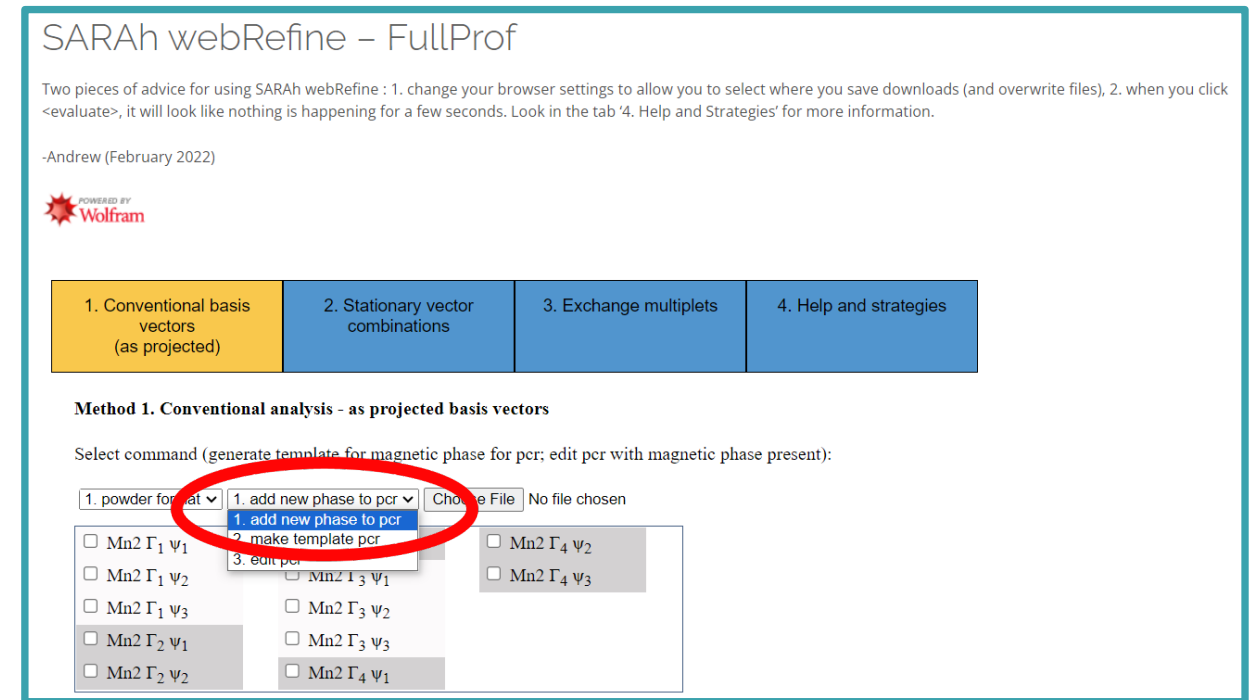
Table. The basis vectors projected from the different IRs :

$\Gamma_1 \psi_1$ Mn2 1) 1. 0. 0. 2) -1. 0. 0. 3) 1. 0. 0. 4) -1. 0. 0.	$\Gamma_1 \psi_2$ Mn2 1) 0. 1. 0. 2) 0. 1. 0. 3) 0. 1. 0. 4) 0. 1. 0.	$\Gamma_1 \psi_3$ Mn2 1) 0. 0. 1. 2) 0. 0. -1. 3) 0. 0. 1. 4) 0. 0. -1.
$\Gamma_2 \psi_1$ Mn2 1) 1. 0. 0. 2) -1. 0. 0. 3) -1. 0. 0. 4) 1. 0. 0.	$\Gamma_2 \psi_2$ Mn2 1) 0. 1. 0. 2) 0. 1. 0. 3) 0. -1. 0. 4) 0. -1. 0.	$\Gamma_2 \psi_3$ Mn2 1) 0. 0. 1. 2) 0. 0. -1. 3) 0. 0. -1. 4) 0. 0. 1.
$\Gamma_3 \psi_1$ Mn2 1) 1. 0. 0. 2) 1. 0. 0. 3) 1. 0. 0. 4) 1. 0. 0.	$\Gamma_3 \psi_2$ Mn2 1) 0. 1. 0. 2) 0. -1. 0. 3) 0. 1. 0. 4) 0. -1. 0.	$\Gamma_3 \psi_3$ Mn2 1) 0. 0. 1. 2) 0. 0. 1. 3) 0. 0. 1. 4) 0. 0. 1.
$\Gamma_4 \psi_1$ Mn2 1) 1. 0. 0. 2) 1. 0. 0. 3) -1. 0. 0. 4) -1. 0. 0.	$\Gamma_4 \psi_2$ Mn2 1) 0. 1. 0. 2) 0. -1. 0. 3) 0. -1. 0. 4) 0. 1. 0.	$\Gamma_4 \psi_3$ Mn2 1) 0. 0. 1. 2) 0. 0. 1. 3) 0. 0. -1. 4) 0. 0. -1.

In this case all irreps have moments in a,b,c direction allowed from the basis vectors. The different BVs, however, will give different magnetic structures and scattering. ALL irreps should be tested. We'll start with Gamma4

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.



Step 3: Create candidate magnetic models using SARAh

- Choose the “MnPyz.pcr” file from STEP 1
- Select the 3 basis vectors for Γ_4 .
- Click submit
- After a few seconds you'll be asked what to name the new file. Call is something instructive, like “MnPyz_Gamma4.pcr” and save to the same folder that has the data and irf file.

Method 1. Conventional analysis - as projected basis vectors

Select command (generate template for magnetic phase for pcr; edit pcr with magnetic phase present):

1. powder format ▼ 1. add new phase to pcr ▼ Choose File MnPyz.pcr

<input type="checkbox"/> Mn2 Γ_1 ψ_1	<input type="checkbox"/> Mn2 Γ_2 ψ_3	<input checked="" type="checkbox"/> Mn2 Γ_4 ψ_2
<input type="checkbox"/> Mn2 Γ_1 ψ_2	<input type="checkbox"/> Mn2 Γ_3 ψ_1	<input checked="" type="checkbox"/> Mn2 Γ_4 ψ_3
<input type="checkbox"/> Mn2 Γ_1 ψ_3	<input type="checkbox"/> Mn2 Γ_3 ψ_2	
<input type="checkbox"/> Mn2 Γ_2 ψ_1	<input type="checkbox"/> Mn2 Γ_3 ψ_3	
<input type="checkbox"/> Mn2 Γ_2 ψ_2	<input checked="" type="checkbox"/> Mn2 Γ_4 ψ_1	

(Your browser should be set to ask for the download location so the pcr file can be overwritten. Please

Submit

Only one IR (Γ_4) will be tested here, but ALL IRs should be tested.

Mn-pyrazinecarboxylate

- 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.**

Nuclear phase

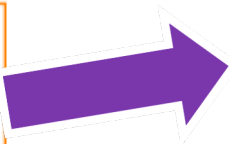
Magnetic phase

```
11.00 21.00 31.00 41.00 51.00 61.00
! Data for PNAOK number: 1 ==> Current_R_Usage for Pattern# 1: 0.0000
!-----
! Unit: Dis Ang Pr1 Pr2 Pr3 Unit Int Int Str North ATZ Nrk Nrk More
! 25 0 0 0 0 0 1.0 0 0 0 0 0 1204.481 0 7 0
!
!
! P 21/c
! Atom Type X Y Z Biso Occ In Fin N.t. Spc /Codea
!-----
! M1 Mn 0.51356 0.12895 0.60217 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C1 O 0.54868 0.24635 0.42955 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! N1 N 0.30244 0.30105 0.56440 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C1 C 0.26705 0.31210 0.62293 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! H1 H 0.24226 0.24571 0.68855 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! O2 O 0.47150 0.40957 0.28321 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! N2 N 0.17238 0.49489 0.41694 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C2 C 0.15921 0.40664 0.56866 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! H2 H 0.10169 0.42860 0.62270 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! O3 O 0.63589 0.00641 0.53074 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! N3 N 0.73160 0.18010 0.70183 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C3 C 0.27027 0.46870 0.41733 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! H3 H 0.27886 0.53942 0.33280 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! O4 O 0.40942 0.02701 0.47011 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! N4 N 1.02037 0.23074 0.77219 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C4 C 0.31122 0.39433 0.46301 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C5 C 0.48774 0.34148 0.39952 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C6 C 0.81776 0.26713 0.79929 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! H4 H 0.72837 0.31267 0.85696 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C7 C 0.93956 0.27897 0.83592 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! H5 H 0.90853 0.33513 0.91943 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C8 C 0.97946 0.13864 0.67951 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! H6 H 1.03201 0.08974 0.64397 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C9 C 0.82851 0.11546 0.64167 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
! C10 C 0.75618 0.02305 0.54995 0.30004 1.00000 0 0 0 0
! 0.00 0.00 0.00 0.00 0.00
!-----
! Profile Parameters for Pattern # 1 ==> Phase # 1
! Scale Shapell Rev Str1 Str2 Str3 Strain Model
! 69.66349 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 GenSix IntSix Size Model
! 0.789266 -0.594567 0.188571 0.247438 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
! 10.116110 10.809982 10.078234 90.000000 108.438995 90.000000
! 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! Pref1 Pref2 Any1 Any2 Any3 Any4 S.L. D.L.
! 0.00000 0.00000 0.11020 0.02420 -0.06668 -0.00207 0.00000 0.00000
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
!-----
! Data for PNAOK number: 2 ==> Current_R_Usage for Pattern# 1: 46.66
!-----
! Template magnetic phase by SARAh - web Representational Analysis
!
! Unit: Dis Ang Pr1 Pr2 Pr3 Unit Int Int Str North ATZ Nrk Nrk More
! 1 0 0 0 0 0 1.0 0 -2 0 0 1204.481 1 7 0
!
!
! P 1
! Atom Type X Y Z Biso Occ C1 C2 C3
!-----
! N1 Mn 0.51356 0.12895 0.60217 0.30004 1.00000 0.000 0.000 0.000
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
!-----
! Profile Parameters for Pattern # 1 ==> Phase # 1
! Scale Shapell Rev Str1 Str2 Str3 Strain Model
! 69.66349 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 GenSix IntSix Size Model
! 0.789266 -0.594567 0.188571 0.247438 0.000000 0.000000 0
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! a b c alpha beta gamma # Cell Info
! 10.116110 10.809982 10.078234 90.000000 108.438995 90.000000
! 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! Pref1 Pref2 Any1 Any2 Any3 Any4 S.L. D.L.
! 0.00000 0.00000 0.11020 0.02420 -0.06668 -0.00207 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

- The basis vectors can be seen in the magnetic phase.
- In this case we loaded three :

$\Gamma_4 \psi_1$	$\Gamma_4 \psi_2$	$\Gamma_4 \psi_3$
Mn2 1) 1. 0. 0.	Mn2 1) 0. 1. 0.	Mn2 1) 0. 0. 1.
2) 1. 0. 0.	2) 0. -1. 0.	2) 0. 0. 1.
3) -1. 0. 0.	3) 0. -1. 0.	3) 0. 0. -1.
4) -1. 0. 0.	4) 0. 1. 0.	4) 0. 0. -1.



- To give these basis vectors magnitude put values in the coefficients C1 and C2

```
!-----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 1204.481 1 7 0
!-----
! P -1
! Nsym Cen Laue Ireps N_Bas
4 1 1 -1 3
! Real(0)-Imaginary(1) indicator for Ci
0 0 0
!-----
SYMM X Y Z
BASR 1. 0 0 0 1. 0 0 0 1.
BASR 0 0 0 0 0 0 0 0 0
SYMM 1 - X, 1/2 + Y, 1/2 - Z
BASR 1. 0 0 0 -1. 0 0 0 1.
BASR 0 0 0 0 0 0 0 0 0
SYMM 1 - X, 1 - Y, 1 Z
BASR -1. 0 0 0 -1. 0 0 0 -1.
BASR 0 0 0 0 0 0 0 0 0
SYMM X, 1/2 - Y, -1/2 + Z
BASR -1. 0 0 0 1. 0 0 0 -1.
BASR 0 0 0 0 0 0 0 0 0
!Atom Typ Mag Vek X Y Z Biso Occ MagPh
! C4 C5 C6 C7 C8 C9
Mn2 MMN5 1 0 0.51356 0.12895 0.60217 .30000 1.00000
0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000
!-----> Profile Parameters for Pattern # 1 -----> Phase # 1
! Scale shape1 Bv Str1 Str2 Str3 Strain-Model
69.66349 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
0.789266 -0.594567 0.168571 0.247638 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
10.176110 10.809982 10.078034 90.000000 108.438995 90.000000
0.000000 0.000000 0.000000 0.000000 0.000000 0.000000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
0.000000 0.000000 0.11020 0.02420 -0.06668 -0.00207 0.000000 0.000000
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
```

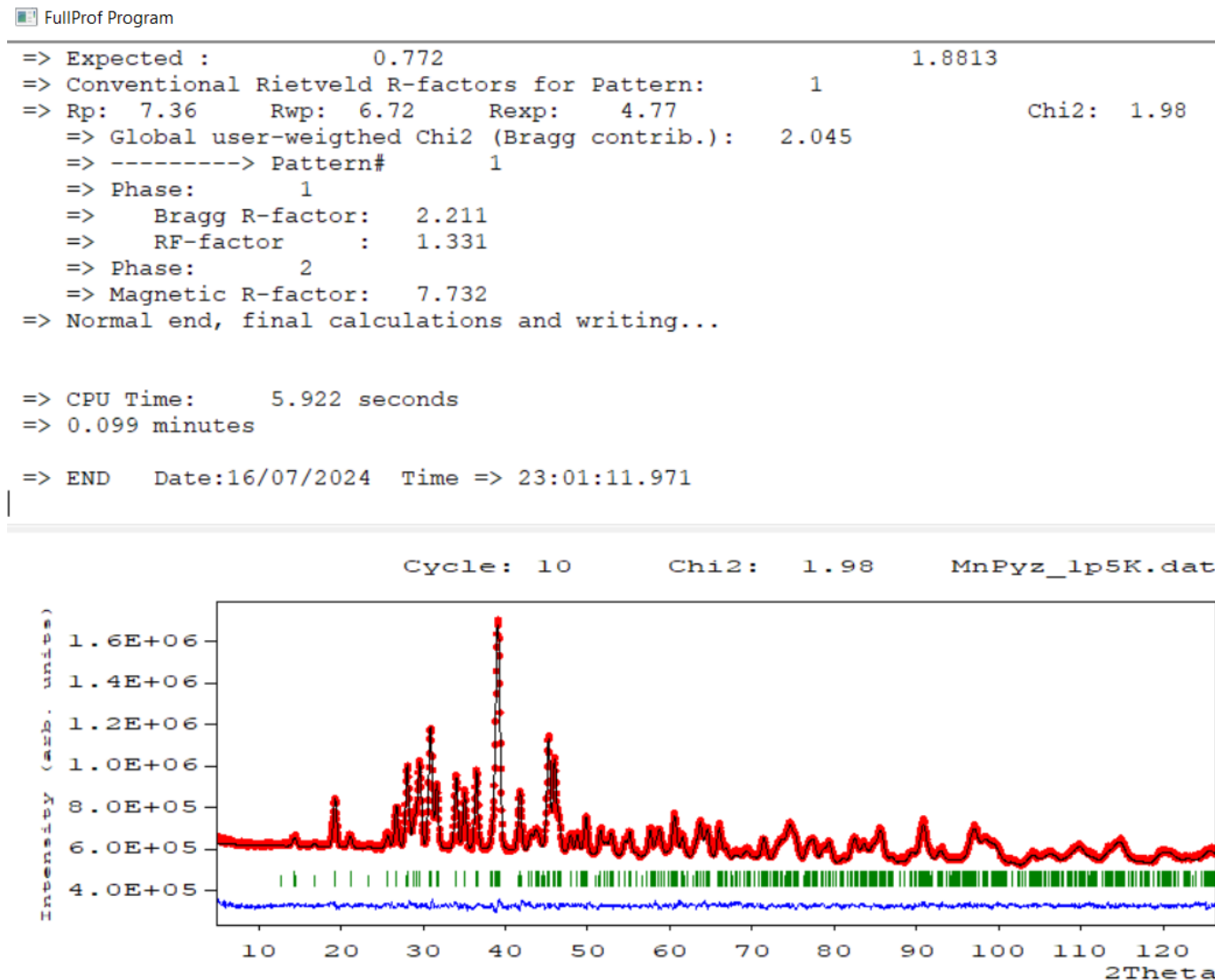
Step 4: Refine the magnetic model and nuclear phase in Fullprof

- 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 valance state, so might vary slightly if the valence label is wrong.

```
!-----Data for PHASE number: 2 ==> Current R_Bragg for Pattern# 1: 0.0000
!-----
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 -1 -2 0 0 1204.481 1 7 0
!
! P -1 <--Space group symbol for hkl generation
! Nsym Cen Laue Ireps N_Bas
! 4 1 1 -1 3
! Real(0)-Imaginary(1) indicator for ci
! 0 0 0
!
SYMM X , Y , Z
BASR 1. 0 0 0 1. 0 0 0 1.
BASR 0 0 0 0 0 0 0 0 0
SYMM 1 - X , 1/2 + Y , 3/2 - Z
BASR 1. 0 0 0 -1. 0 0 0 1.
BASR 0 0 0 0 0 0 0 0 0
SYMM 1 - X , 1 - Y , 1 - Z
BASR -1. 0 0 0 -1. 0 0 0 -1.
BASR 0 0 0 0 0 0 0 0 0
SYMM X , 1/2 - Y , -1/2 + Z
BASR -1. 0 0 0 1. 0 0 0 -1.
BASR 0 0 0 0 0 0 0 0 0
!
!Atom Typ Mag vek X Y Z Biso Occ C1 C2 C3
! C4 C5 C6 C7 C8 C9 MagPh
Mn2 MMN5 0 0.51356 0.12895 0.60217 0.30000 1.00000 1.000 1.000 1.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 71.00 81.00 91.00
0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000
!-----> Profile Parameters for Pattern # 1 <----> Phase # 2
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
! 69.66349 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 Lorziz size-Model
! 0.789266 -0.594567 0.168571 0.247638 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
! 10.176110 10.809982 10.078034 90.000000 108.438995 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 0.11020 0.02420 -0.06668 -0.00207 0.00000 0.00000
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! Propagation vectors:
! 0.000000 0.000000 0.000000 Propagation vector 1
! 0.000000 0.000000 0.000000
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot
! -0.020 155.000 1
```

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

- Refine the 1.5K data.
- This captures the magnetic peaks well.
- Check if all basis vectors are needed by setting C1, C2 or C3 to zero.
- *To improve the fit, try refining the peak shapes, background, atom positions, lattice constants, etc*



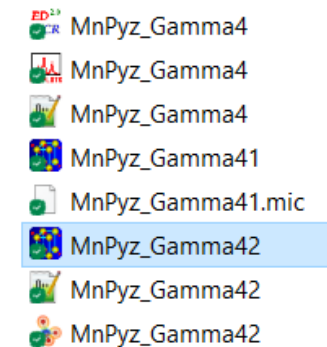
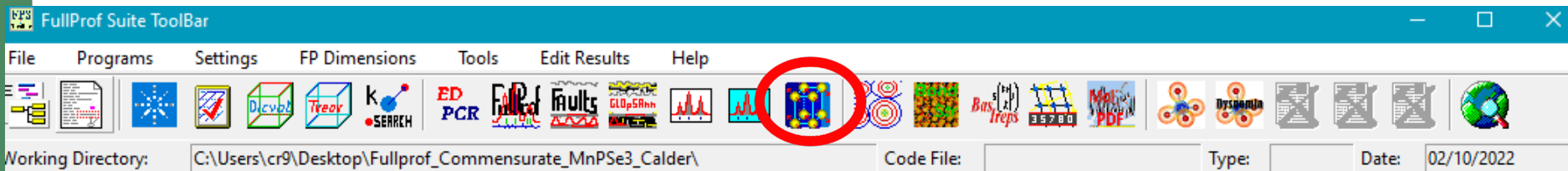
Try to refine the other IRs (Γ_1 , Γ_2 and Γ_3).
The fit is close, but some magnetic
scattering is not captured.

Mn-pyrazinecarboxylate

- 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**

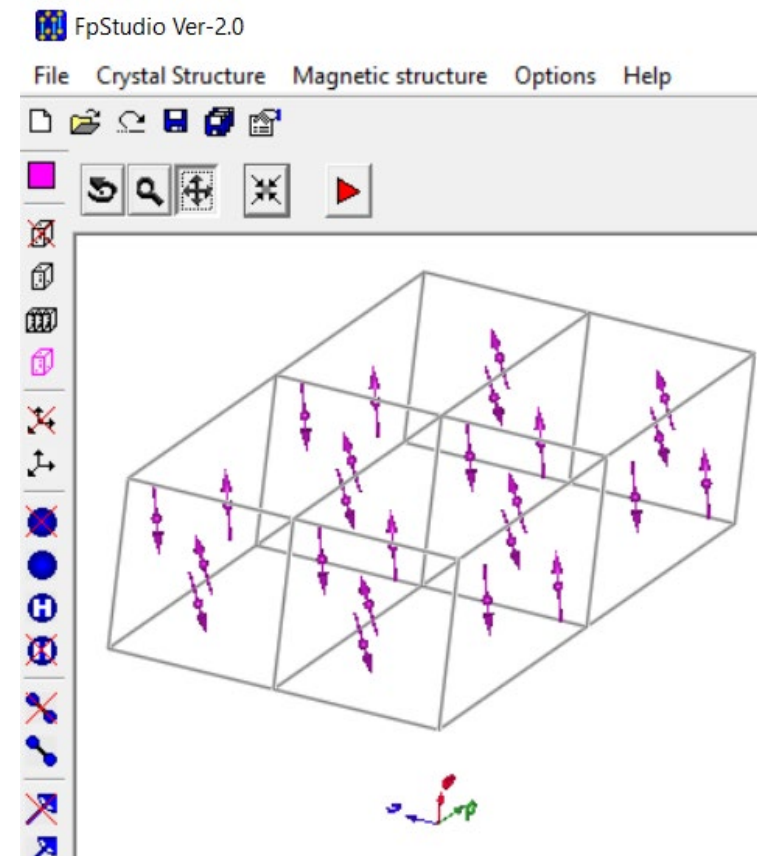
Step 5: Check the magnetic model

- The model can be checked in FPStudio



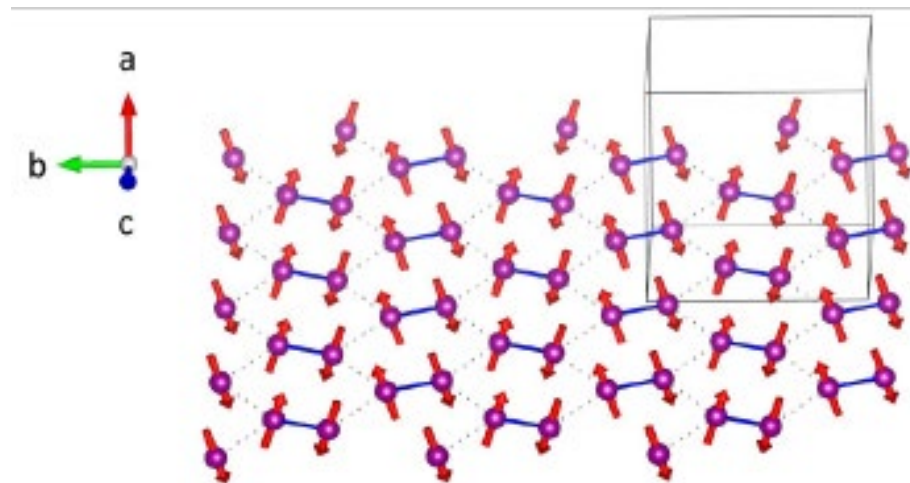
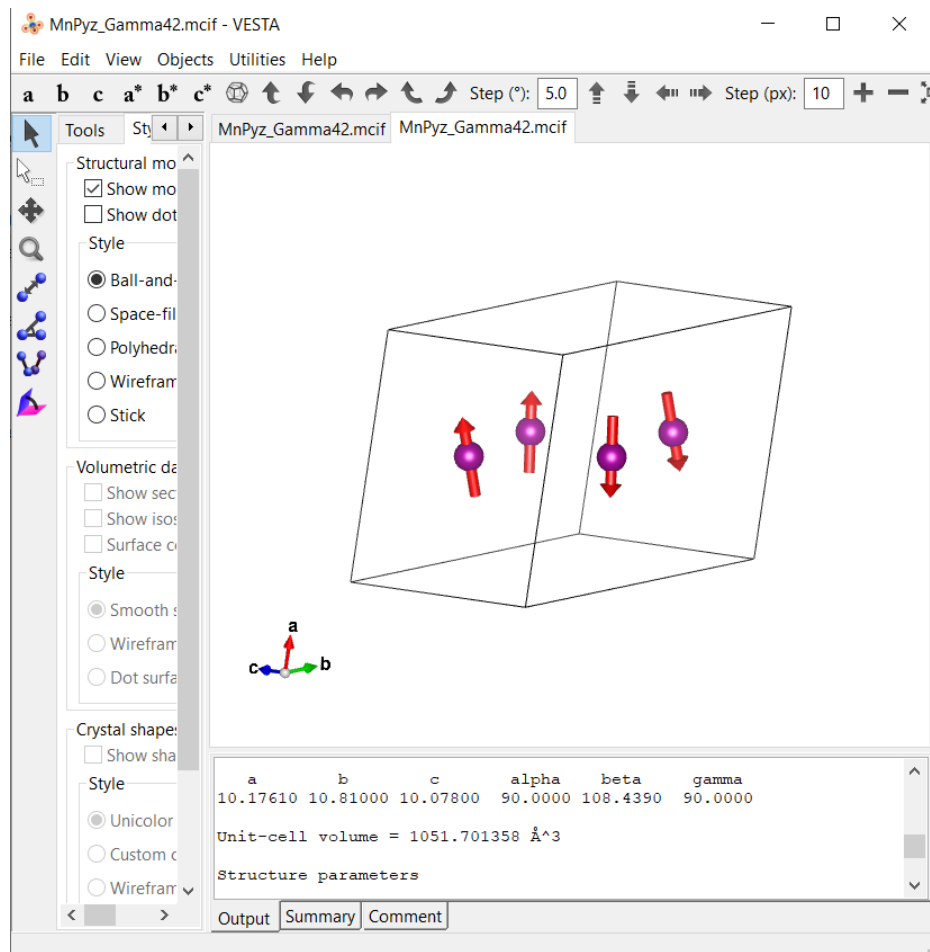
- There are two .fst files, these are for the 2 phases. Open the magnetic phase (file ending in 2.fst)
- In Fpstudio click on the drop-down menu "Magnetic Structure" and select "List magnetic moments"

Magnetic lattice type : P									
Unit Cell: 10.1761 10.8100 10.0780 90.0000 108.4390 90.0000									
Current Box: 0 1 0 2 0 2									
Magnetic k-vectors :									
0.00000 0.00000 0.00000									
Symmetry operations :									
SYMM x,y,z									
u,v,w,0.0									
Atom : Mn2_1 Mn									
	x	y	z	Translation	k MSYM	m(a)	m(b)	m(c)	Mtot
0.51356	0.12895	0.60217	(0, 0, 0)	1	1	3.68766	-0.44560	1.14359	
						3.68766	-0.44560	1.14359	3.52668
			(0, 0, 1)	1	1	3.68766	-0.44560	1.14359	
						3.68766	-0.44560	1.14359	3.52668
			(0, 1, 0)	1	1	3.68766	-0.44560	1.14359	
						3.68766	-0.44560	1.14359	3.52668
			(0, 1, 1)	1	1	3.68766	-0.44560	1.14359	
						3.68766	-0.44560	1.14359	3.52668
			(0, 2, 0)	1	1	3.68766	-0.44560	1.14359	
						3.68766	-0.44560	1.14359	3.52668
			(0, 2, 1)	1	1	3.68766	-0.44560	1.14359	
						3.68766	-0.44560	1.14359	3.52668



Step 5: Check the magnetic model

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



The mcif in this case ONLY has the magnetic atoms.
The method of creating IRs and using SARAh splits the nuclear and magnetic phases.

Mn-pyrazinecarboxylate

- Full details can be found in DOI:
[10.1103/PhysRevMaterials.7.124408](https://doi.org/10.1103/PhysRevMaterials.7.124408)

PHYSICAL REVIEW MATERIALS 7, 124408 (2023)

Magnetic order in the two-dimensional metal-organic framework manganese pyrazinecarboxylate with Mn-Mn dimers

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The magnetic properties of $[\text{Mn}(\text{pyrazinecarboxylate})_2]_n$, empirical formula $\text{C}_{10}\text{H}_6\text{MnN}_4\text{O}_4$, are investigated through susceptibility, heat capacity, and neutron scattering measurements. The structure consists of Mn-Mn dimers linked on a distorted 2D hexagonal structure. The weak out-of-plane interactions create a quasi-2D magnetic material within the larger three-dimensional metal-organic framework structure. We show that this material undergoes a two-stage magnetic transition, related to the low dimensionality of the Mn lattice. First, at 5 K, which is assigned to the initial development of short-range order in the 2D layers. This is followed by long-range order at 3.3 K. Applied field measurements reveal the potential to induce magnetic transitions in moderately small fields of ~ 2 T. Neutron powder diffraction enabled the determination of a unique magnetic space group $P2_1'/c$ (No. 14.77) at 1.5 K. This magnetic structure consists of antiferromagnetically coupled Mn-Mn dimers with spins principally along the out-of-plane a axis.

DOI: [10.1103/PhysRevMaterials.7.124408](https://doi.org/10.1103/PhysRevMaterials.7.124408)

The magnetic structure is in
the MAGNDATA database

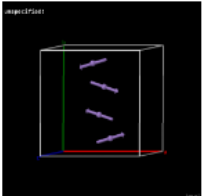
MAGNDATA: A Collection of magnetic structures with portable cif-type files

Log

Element search (separate with space or comma): AND OR Search [View Full Database](#) [Advanced Search](#)

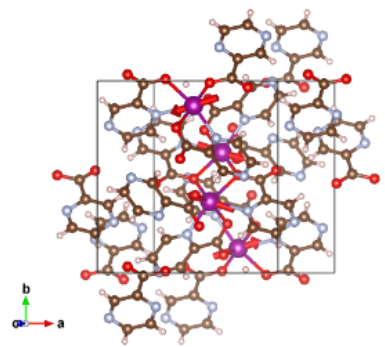
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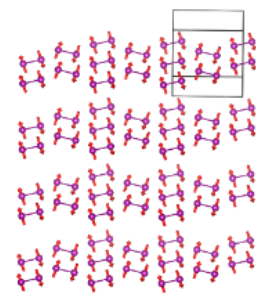
Enter the label of the structure:



$\text{C}_{10}\text{H}_6\text{MnN}_4\text{O}_4$ (#0.1010)

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[Download vesta file \(magnetic atoms only\)](#)


Magnetic structure with all atoms


Magnetic structure with only magnetic atoms

Reference: S. Calder, R. Baral, N. Narayanan, L. D. Sanjeewa, *PHYSICAL REVIEW MATERIALS* (2023) 7 124408
DOI: [10.1103/PhysRevMaterials.7.124408](https://doi.org/10.1103/PhysRevMaterials.7.124408)
Atomic positions from: Cai

Parent space group (paramagnetic phase): $P2_1/c$ (#14)
Propagation vector: k_1 (0, 0, 0)

Transition Temperature: 3.3 K
Experiment Temperature: 1.5 K

Lattice parameters of the magnetic unit cell:
10.2078(4) 10.8444(4) 10.1095(4) 90.00 108.429 90.00
Transformation from parent structure: (a,b,c;0,0,0)
[\[view matrix form\]](#)

BNS Magnetic Space Group: $P2_1'/c$ (#14.77) (standard setting)
[\[view symmetry operations\]](#)
Transformation to a standard setting: (a,b,c;0,0,0)