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Fullprof refinement of commensurate structure from CW powder diffraction data [Fullprof/SARAh]

Stuart Calder, ORNL

MagStr2026

Duke University July 20-24



U.S. DEPARTMENT
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Mn-pyrazinecarboxylate

This example will use Fullprof and SARAh <http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>

- Step 0: Have a well characterized material and good background information
- Step 1: Refine the crystal structure using FullProf
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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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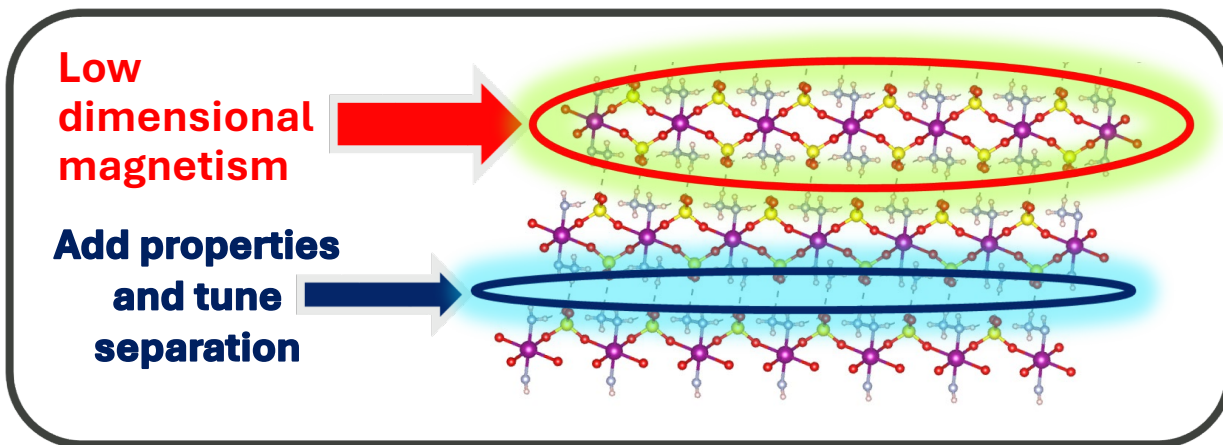
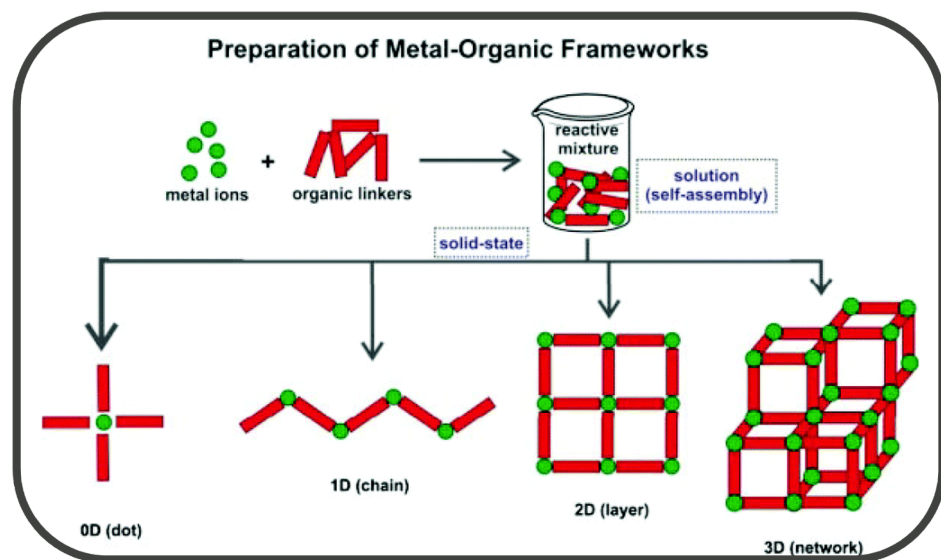
(Received 29 September 2023; revised 8 November 2023; accepted 28 November 2023; published 15 December 2023)

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)

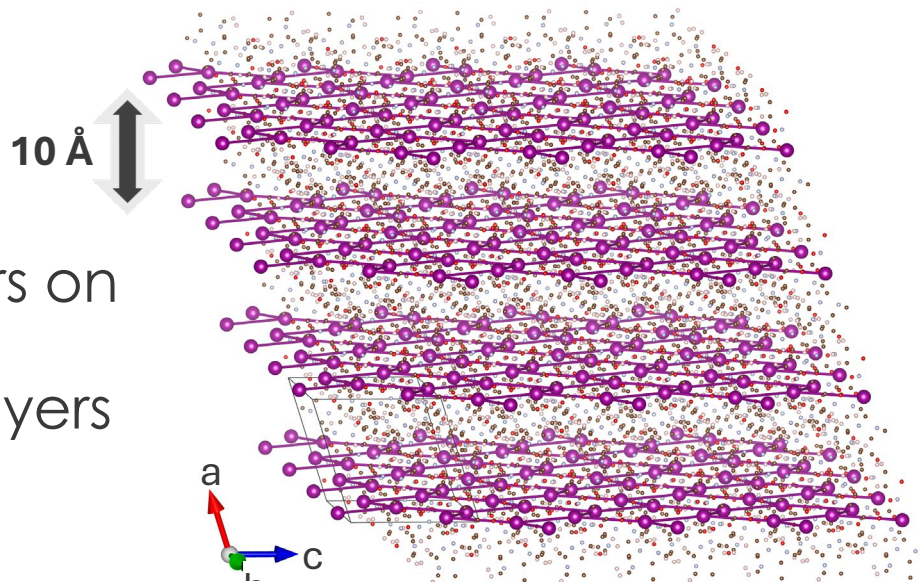
Quantum behavior by design in low dimensional Magnetic MOFs

- 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.

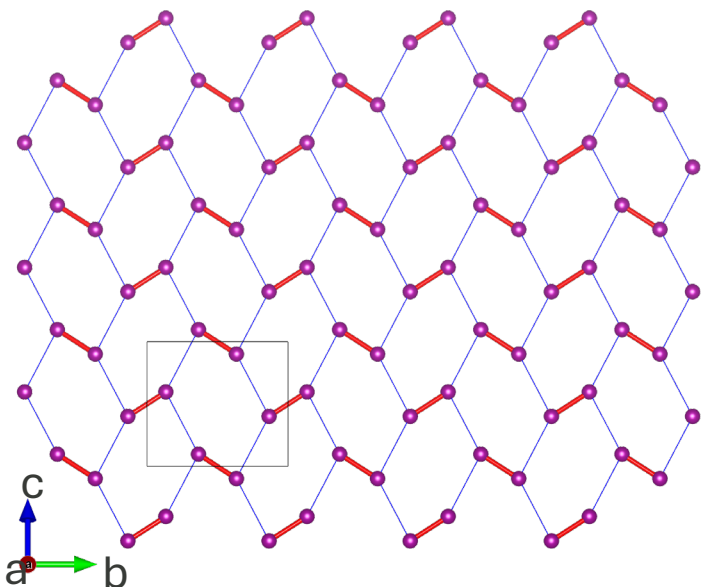


Mn-pyrazinecarboxylate ($\text{Mn}(2\text{-pzc})_2$) $\text{C}_{10}\text{H}_6\text{MnN}_4\text{O}_4$

- 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

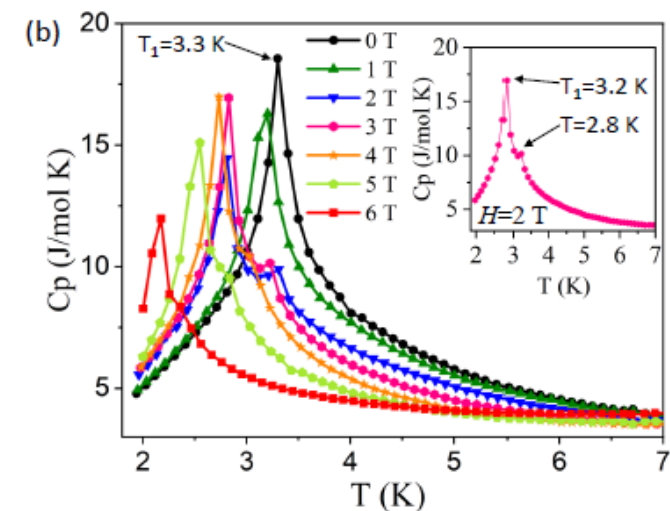
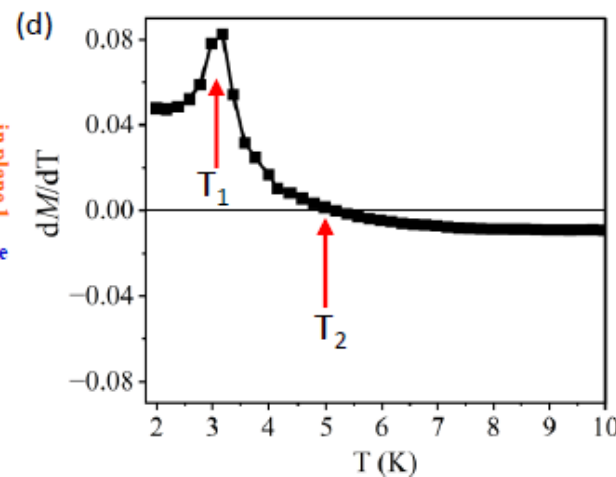
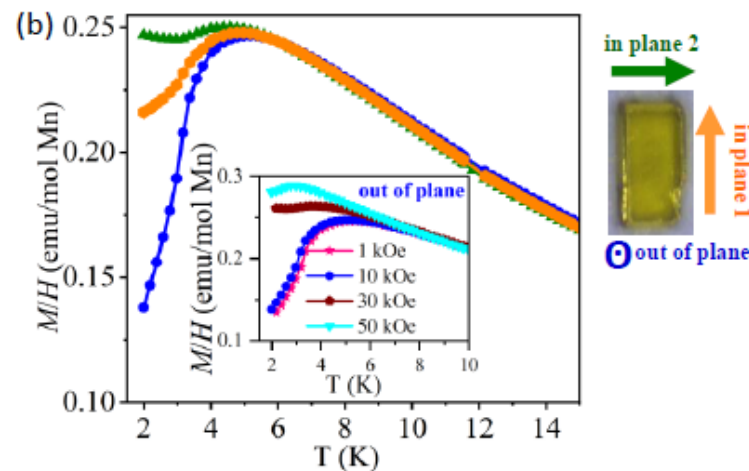
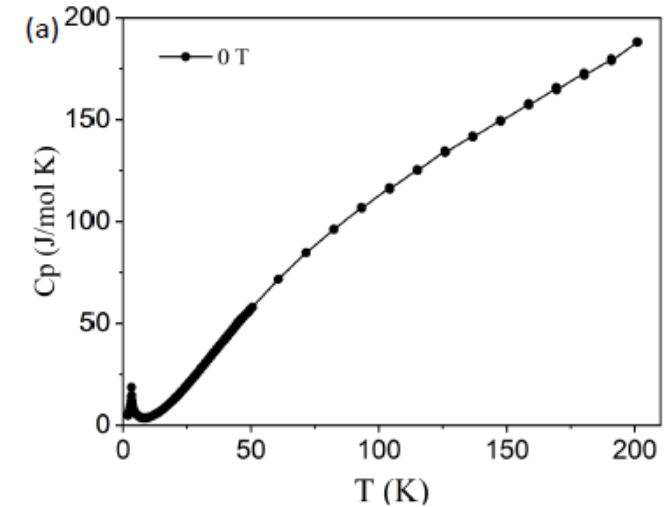
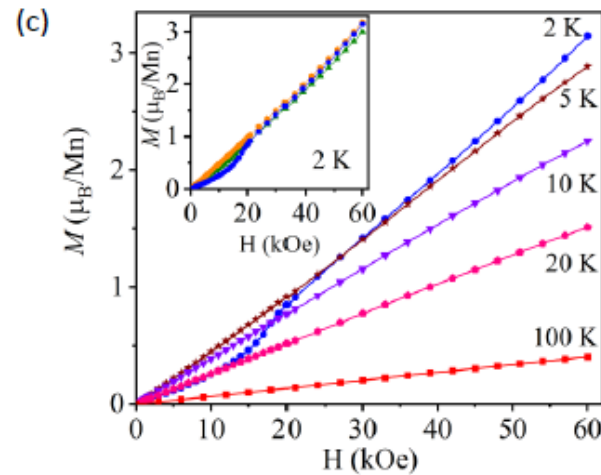
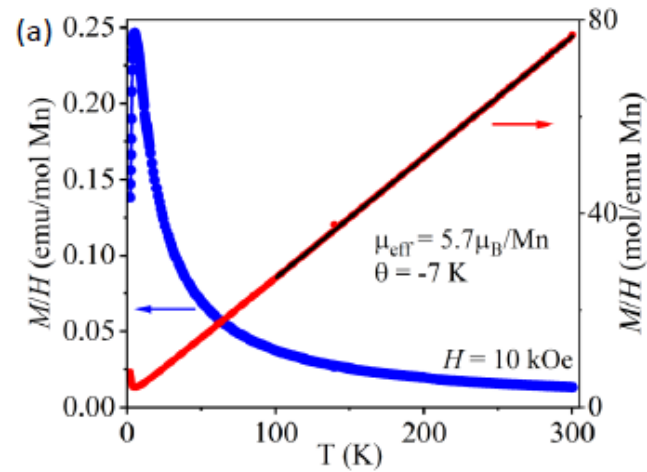
Lattice parameters
a b c alpha beta gamma
10.19000 10.90600 10.11600 90.0000 107.9600 90.0000

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	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	0.024	4e
C	0.471400		0.338300	0.385500	1.000	0.028	4e
C	0.796000		0.262800	0.792500	1.000	0.025	4e
H	0.742540		0.304290	0.837480	1.000	0.037	4e
C	0.933300		0.292500	0.822500	1.000	0.026	4e
H	0.968190		0.356270	0.884090	1.000	0.042	4e
C	0.960400		0.144900	0.676800	1.000	0.035	4e
H	1.015390		0.101040	0.635600	1.000	0.028	4e
C	0.823000		0.116000	0.643000	1.000	0.033	4e
C	0.758100		0.015200	0.540800	1.000	0.034	4e

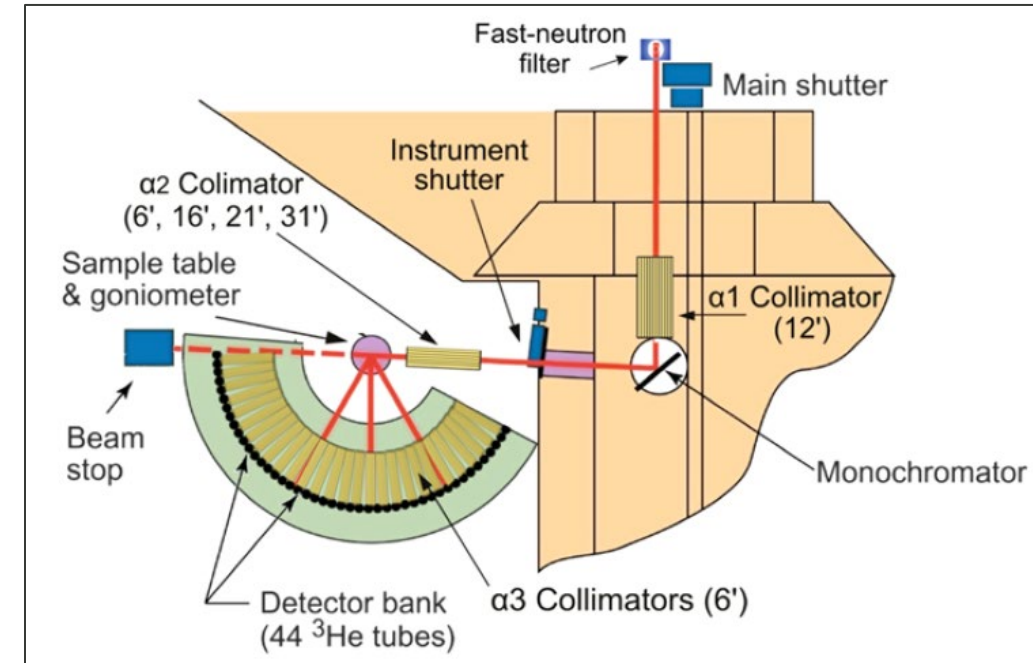
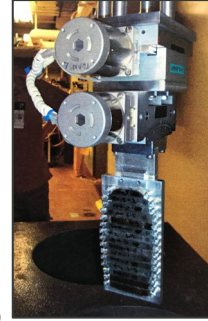
Magnetic susceptibility and heat capacity

- 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 $\sim 2\text{-}150^\circ$ in 2θ by scanning detector
 - **MIDAS detector upgrade coming soon!**



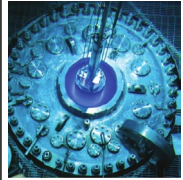
Ge(hkl)	λ (Å)	d_{max} (Å)	Q (Å $^{-1}$)	Flux (n/cm 2 s)
(113)	2.41	27.6	0.2-5.1	5×10^6
(115)	1.54	17.6	0.35-7.9	1×10^7
(117)	1.12	12.8	0.5-10.9	4×10^6



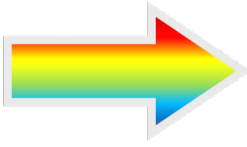
<https://neutrons.ornl.gov/powder>



A typical CS diffractometer (HFIR)



Reactor



Monochromator:

- selects λ .
- Control resolution.

Single wavelength



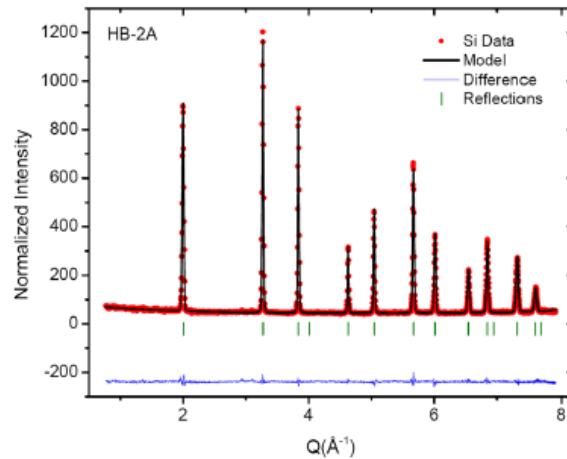
SAMPLE



Detector at 2θ measures single Q

$$\lambda = 2d \sin \theta$$

Q range limit is $4\pi/\lambda$



A typical TOF diffractometer (SNS)

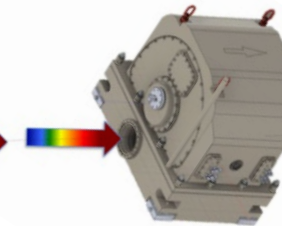
De Broglie wavelength: $\lambda = h/mv = ht/mL$

Bragg's law: $\lambda = 2d \sin \theta = \text{constant} * t$

Target

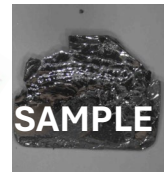


Moderator

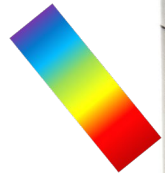


Chopper

Multiple wavelengths

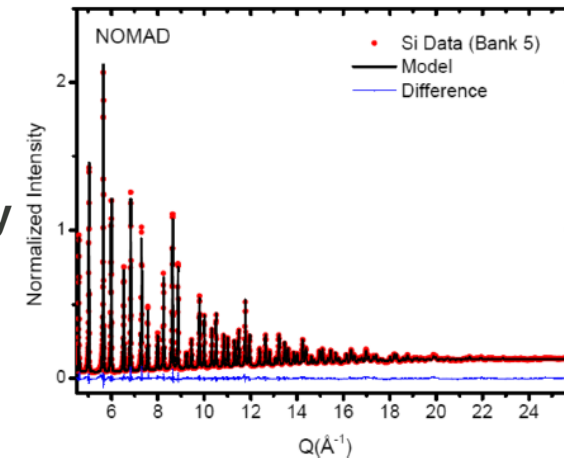


SAMPLE



Resolution depends on moderator and t, L , and 2θ

Q range determined by $\lambda_{\min}$, $\lambda_{\max}$ and 2θ



Detector at 2θ measures multiple Q

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.

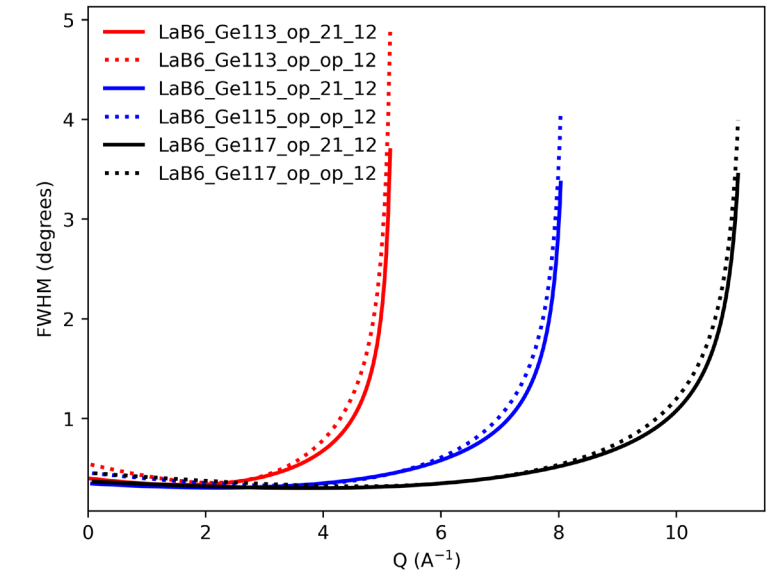
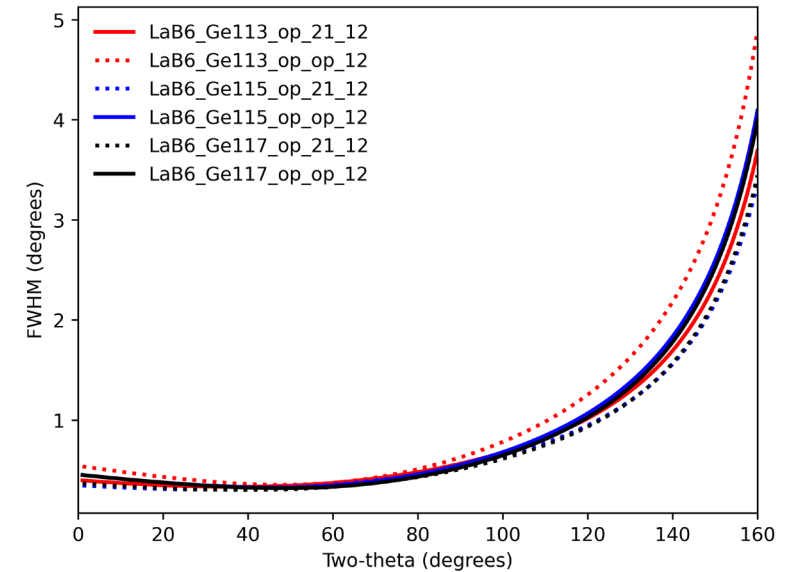
This options works, at present, only for constant wavelength type of data. The profile is assumed to be a Voigt function (Npr=7). 12 parameters or a table determine the resolution function. The parameters are $U_i, V_i, W_i, X_i, Y_i, Z_i$ ($i=1,2$ for λ_1 and λ_2)

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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Institut Laue-Langevin, B.P. N° 156, 38042-Grenoble Cédex, France

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 (this is the wavelength)

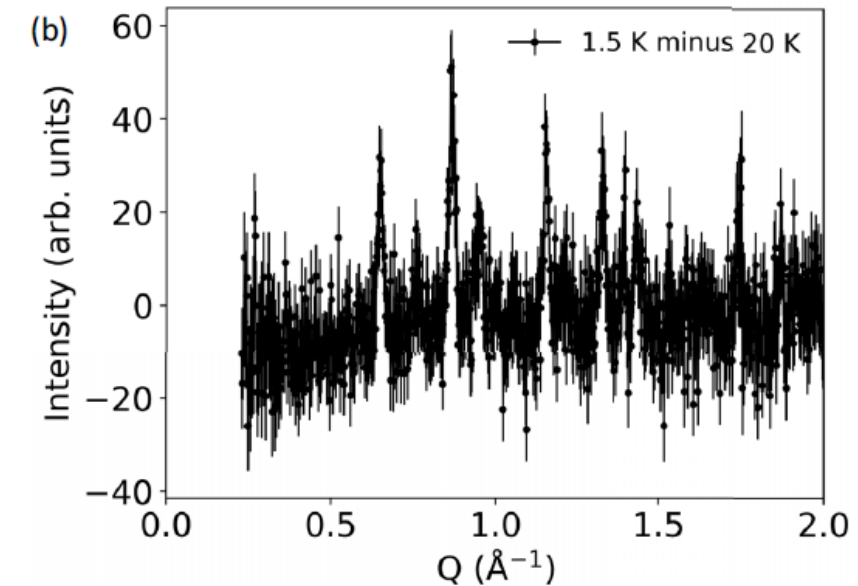
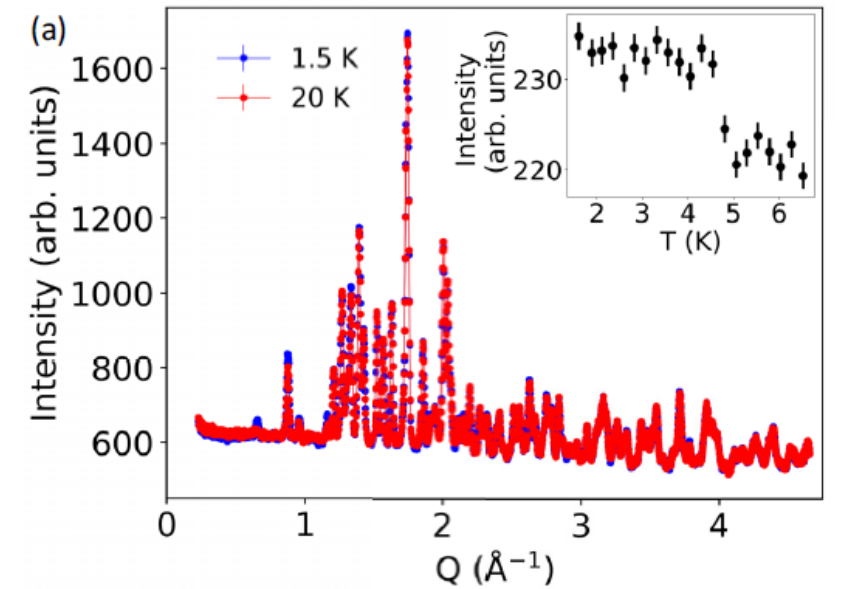
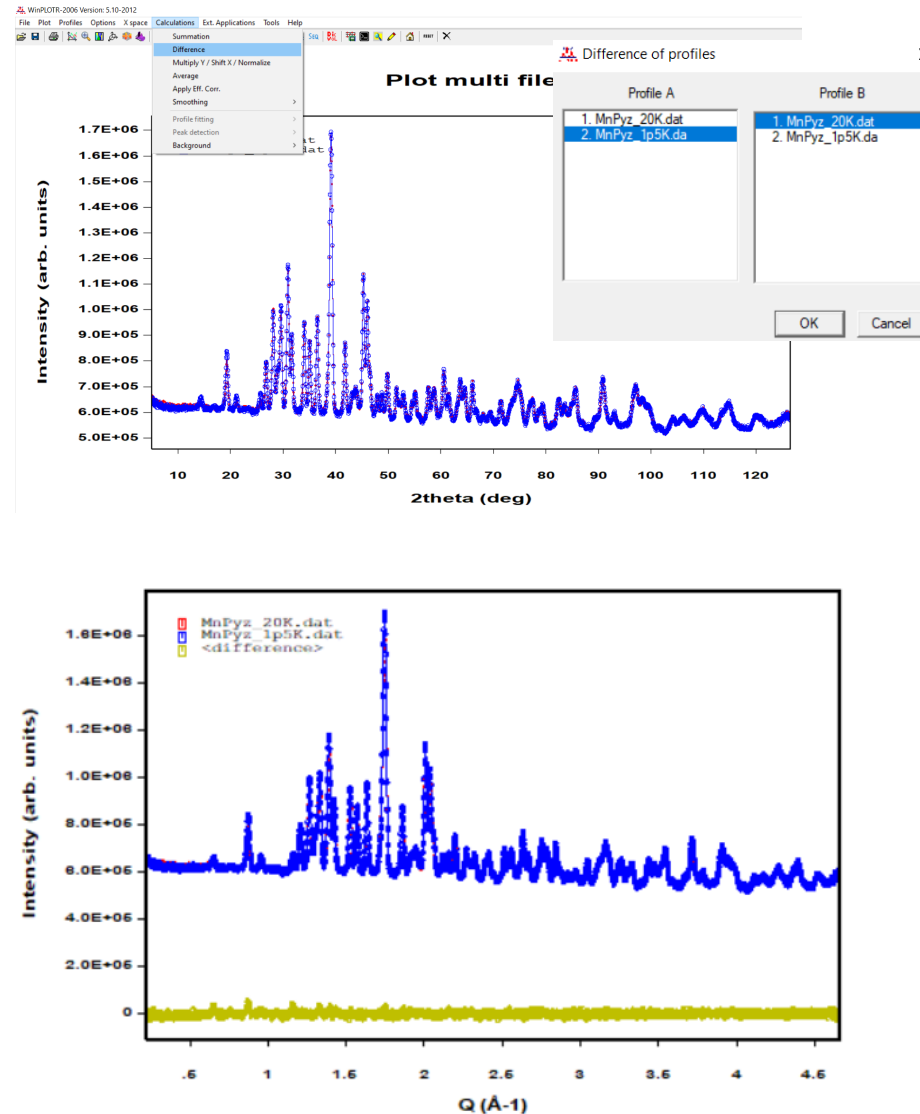


FIG. 5. (a) Neutron powder diffraction data collected at 1.5 K and 20 K. Inset: Intensity at $Q = 0.65 \text{ \AA}^{-1}$ as a function of temperature through the magnetic transition. (b) Difference of intensity at 1.5 K and 20 K in the powder diffraction data.

Mn-pyrazinecarboxylate

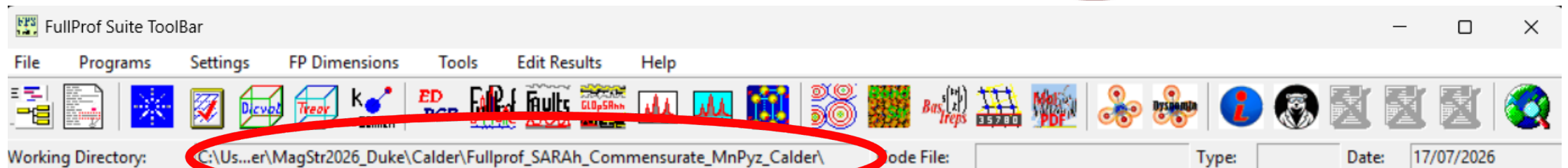
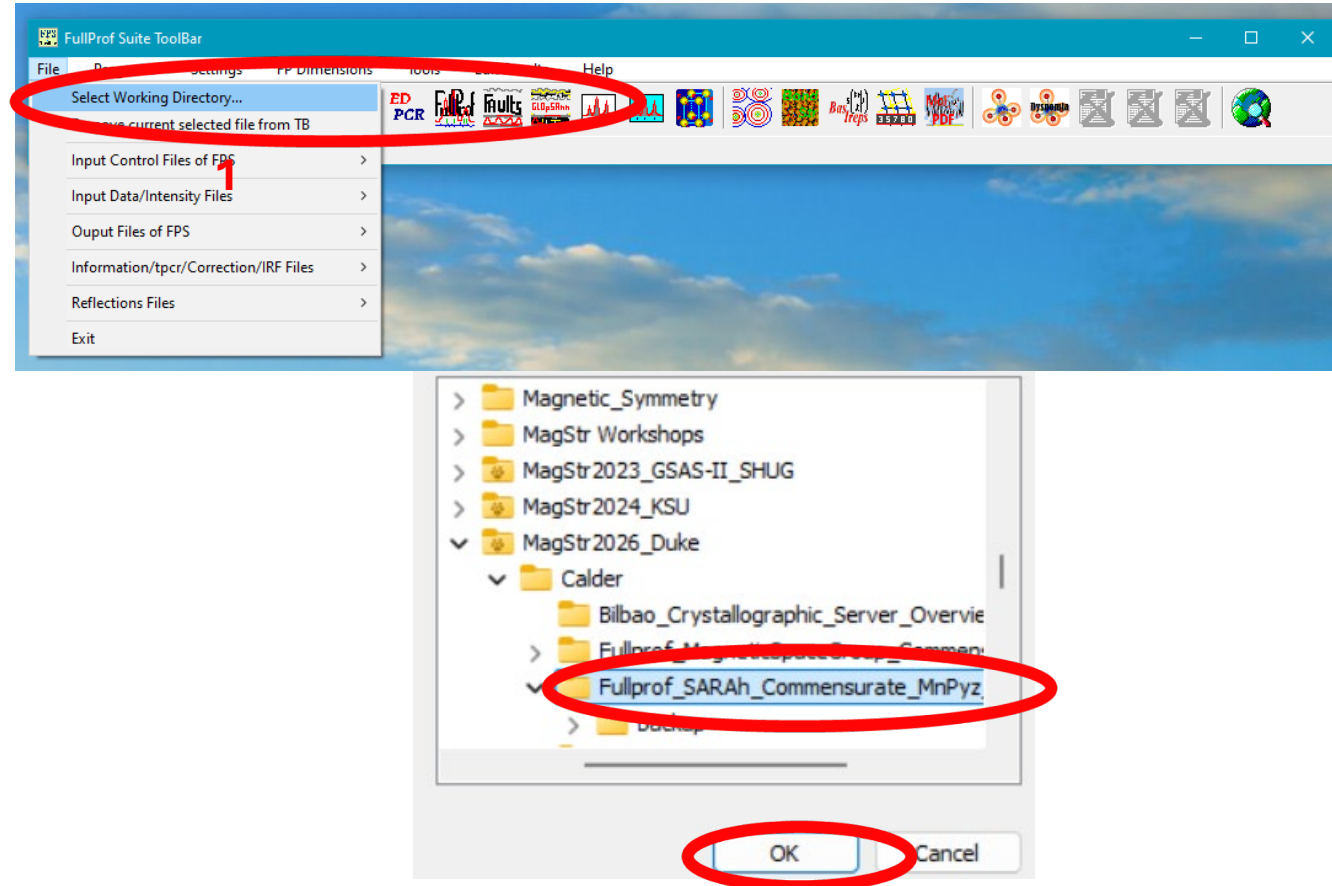
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Step 1: Refine the crystal structure using FullProf

Open Fullprof Suite toolbar.

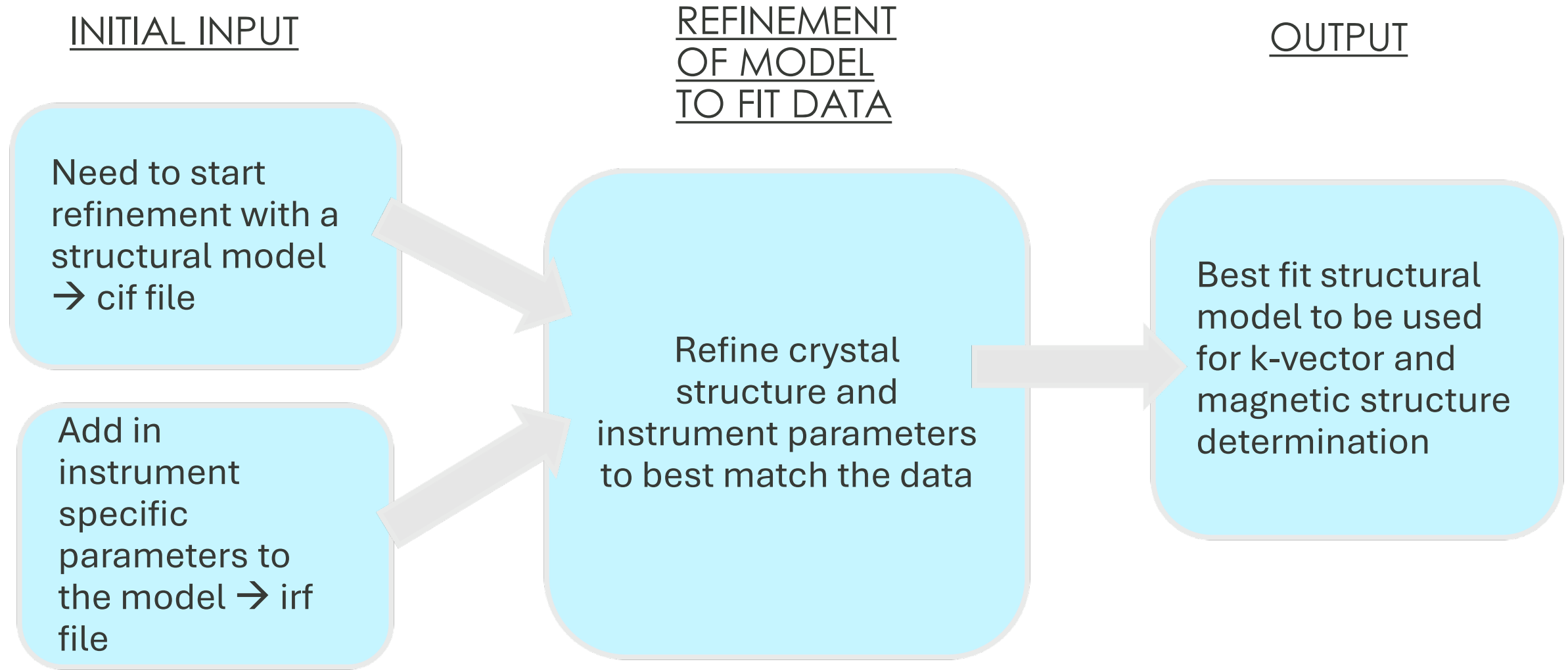
- **1.** Select working directory with data “*File>Select Working directory...*”
- **2.** Browse to wherever your folder “Fullprof_Commensurate_MnPyz_Calder” is located on your computer and select “ok”
- **3.** Path on FP studio toolbar should now be updated. This helps with interacting with other features 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
- Get parameters close
- Then refine this model.

Step 1: Refining the crystal structure using Fullprof

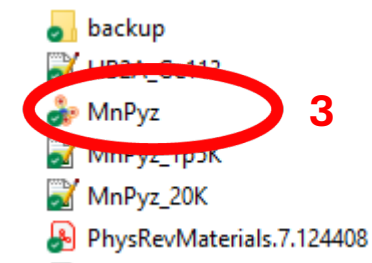
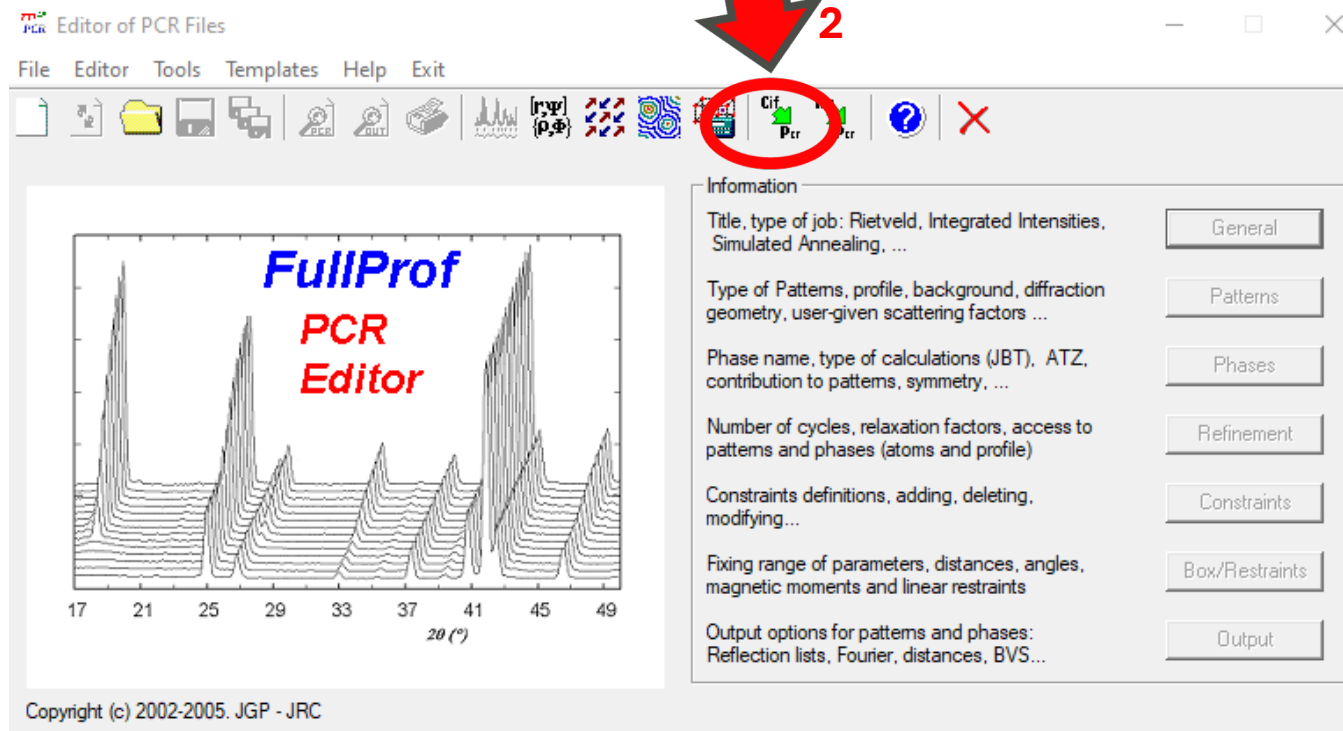
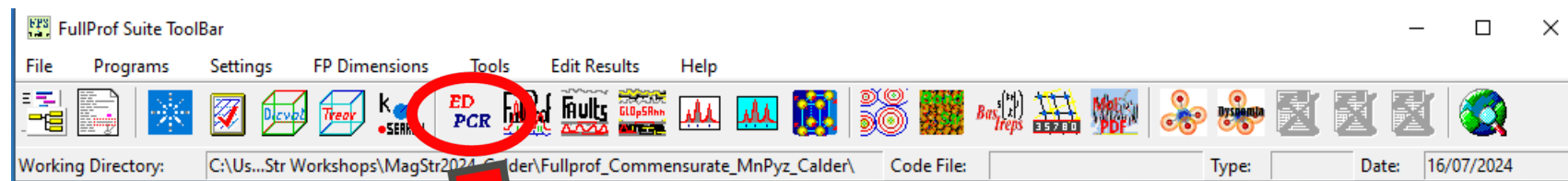


Step 1: Refine the crystal structure using FullProf

1. From FullProf Suite Toolbar open EdPCR.

2. Import crystallographic information file by clicking on “CIF→PCR”

3. Select the file “MnPyz_20K.cif”



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

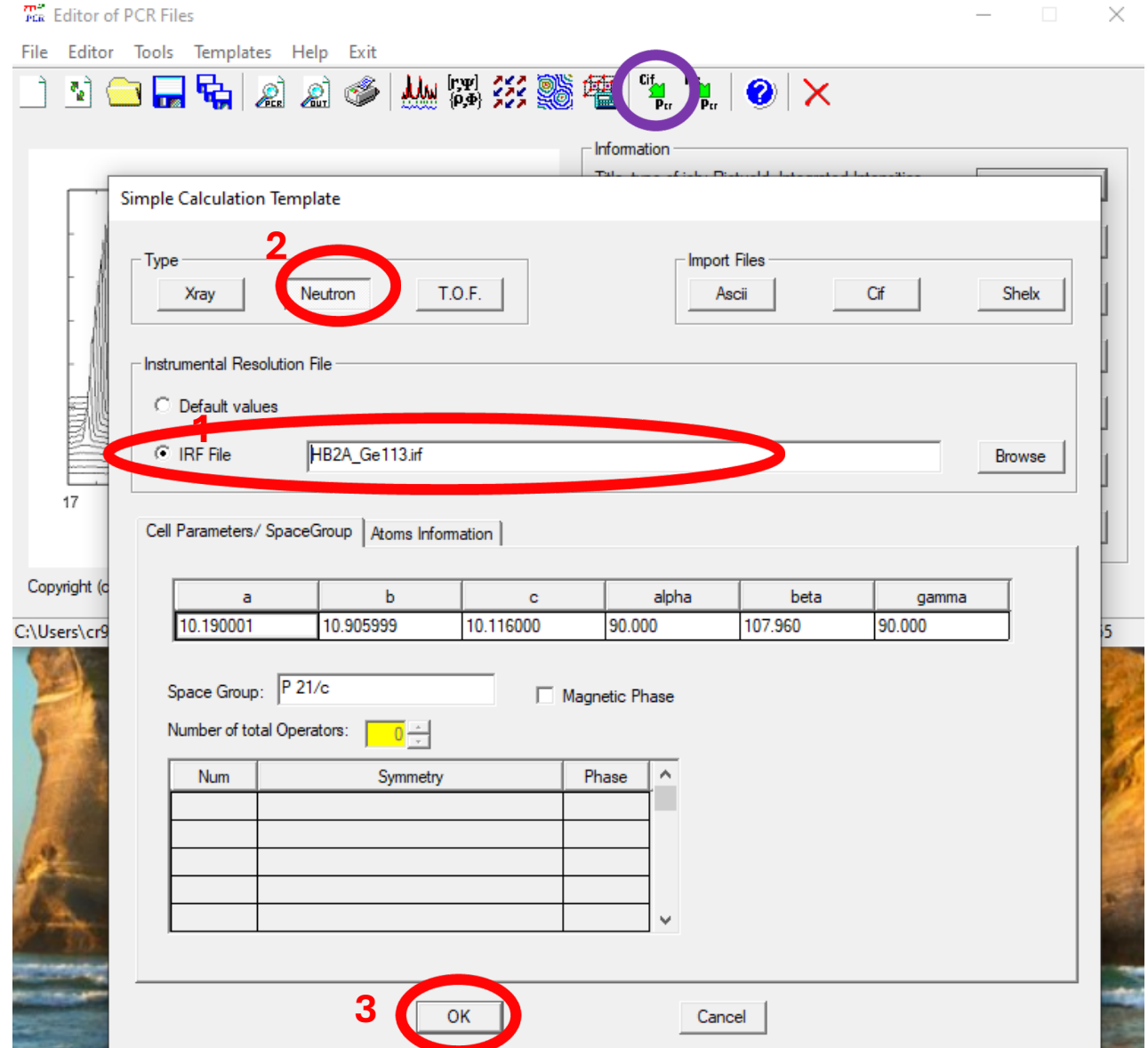
2. Load the instrument resolution file “HB2A_Ge113.irf” (click circle and browse to file).

- *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 $\text{cite/general} = 4/4 = 1$ 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

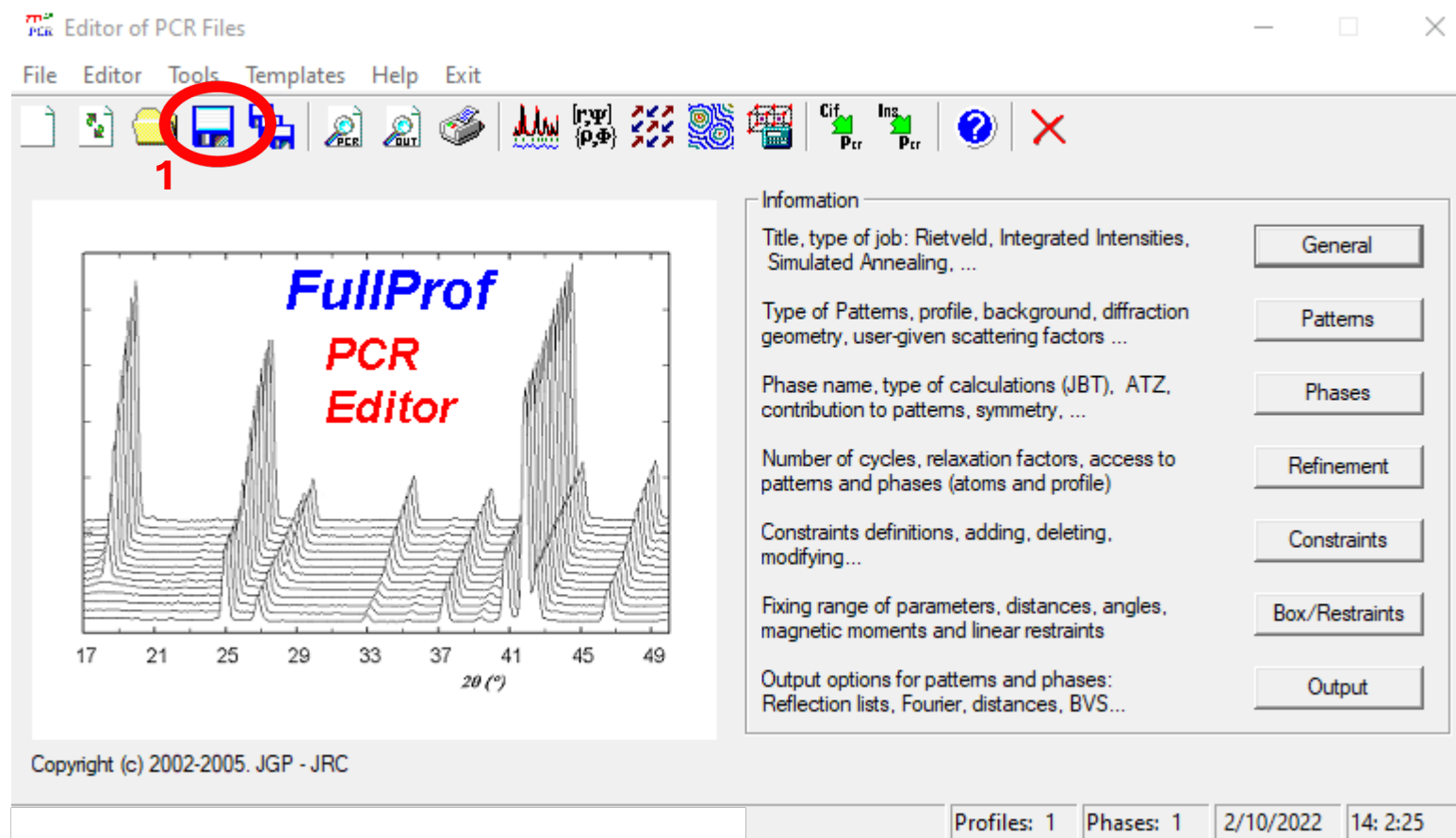
	Rx	Ry	Rz	lx	ly	lz	MPhase
Atom #1							
Atom #2							
Atom #3							
Atom #4							

When finished, hit OK

Step 1: Refine the crystal structure using FullProf

1. Save the changes.

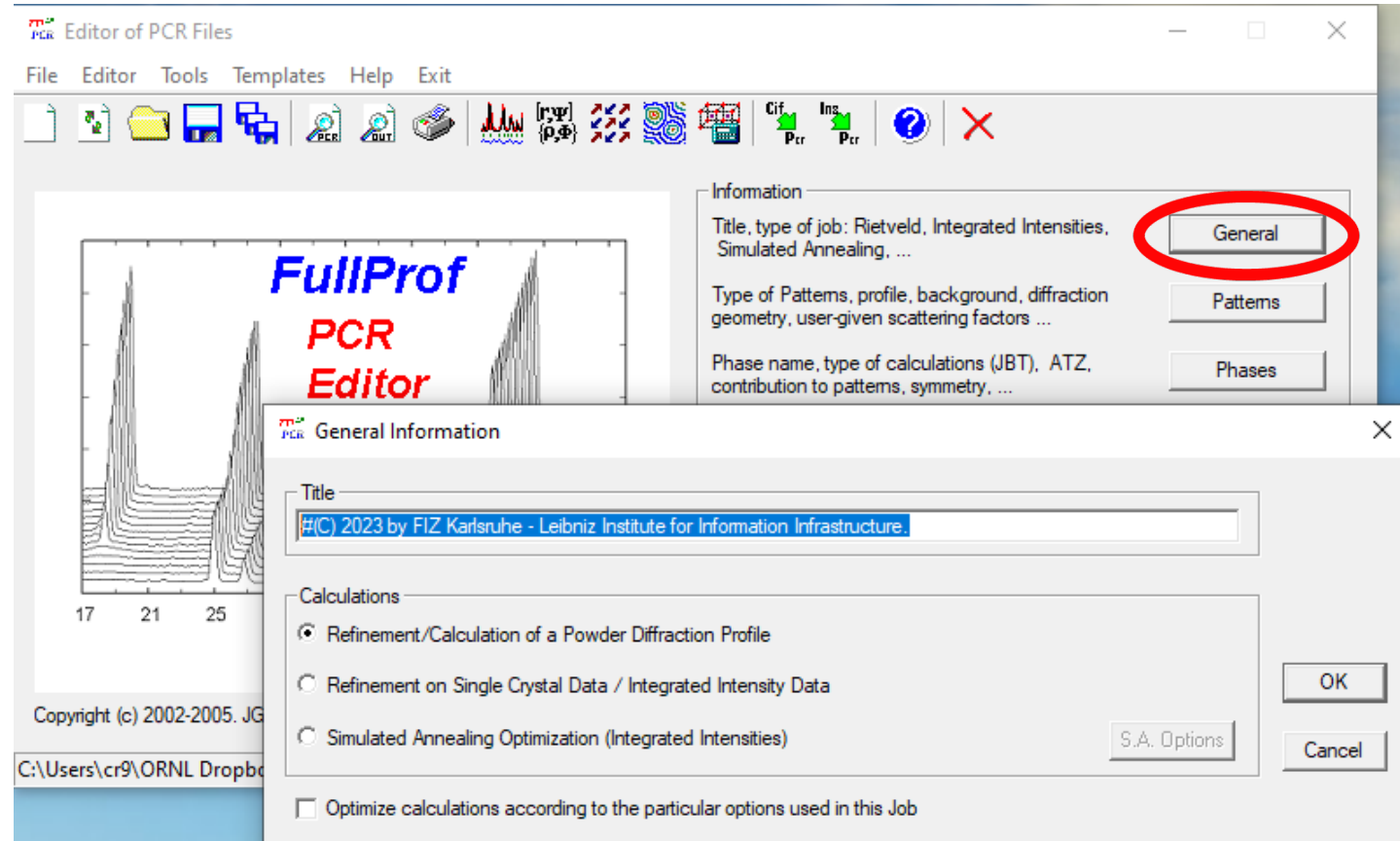
This should be done whenever changes are made in the GUI.



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.

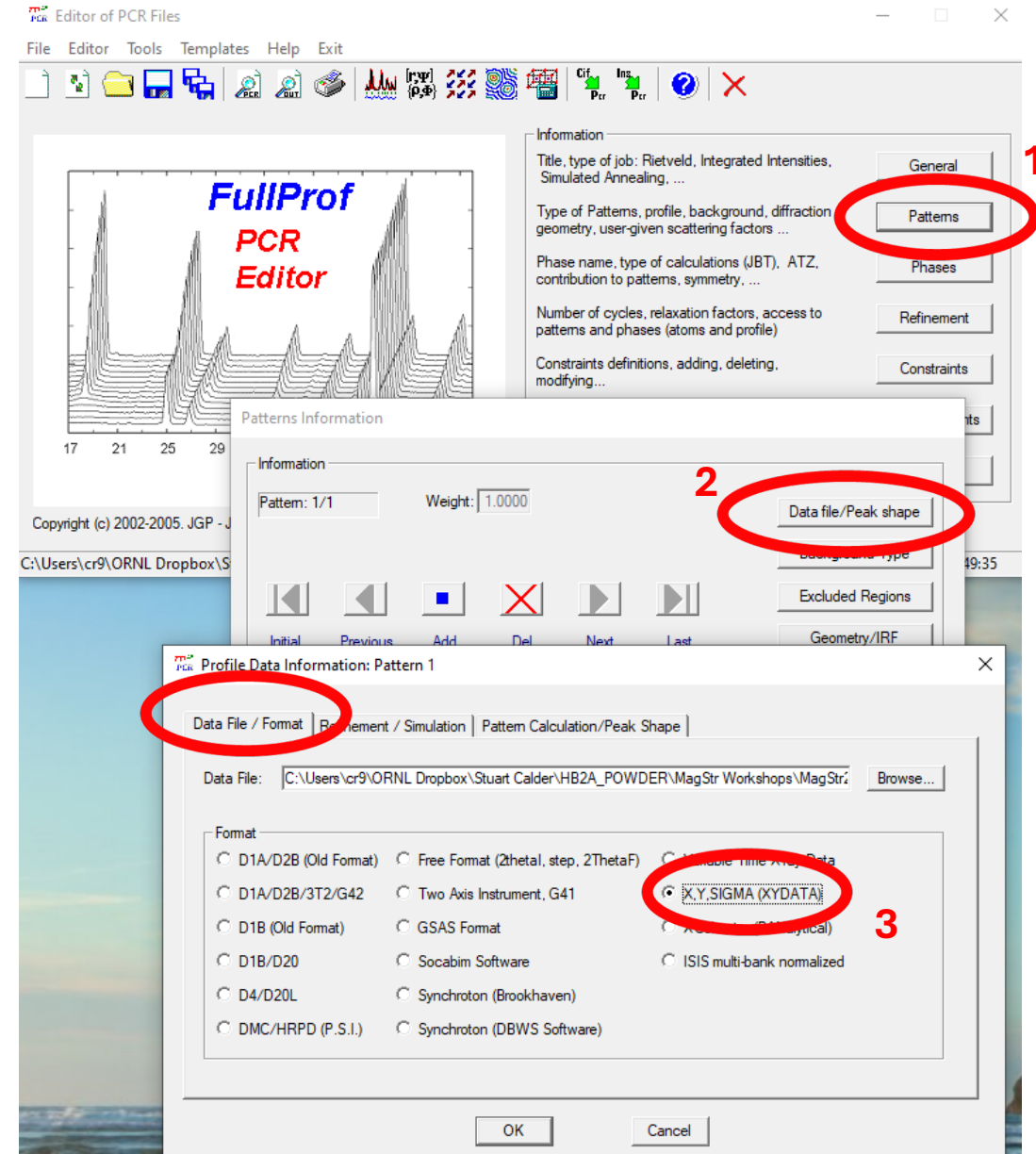
For powder refinements we don’t need to edit this tab



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

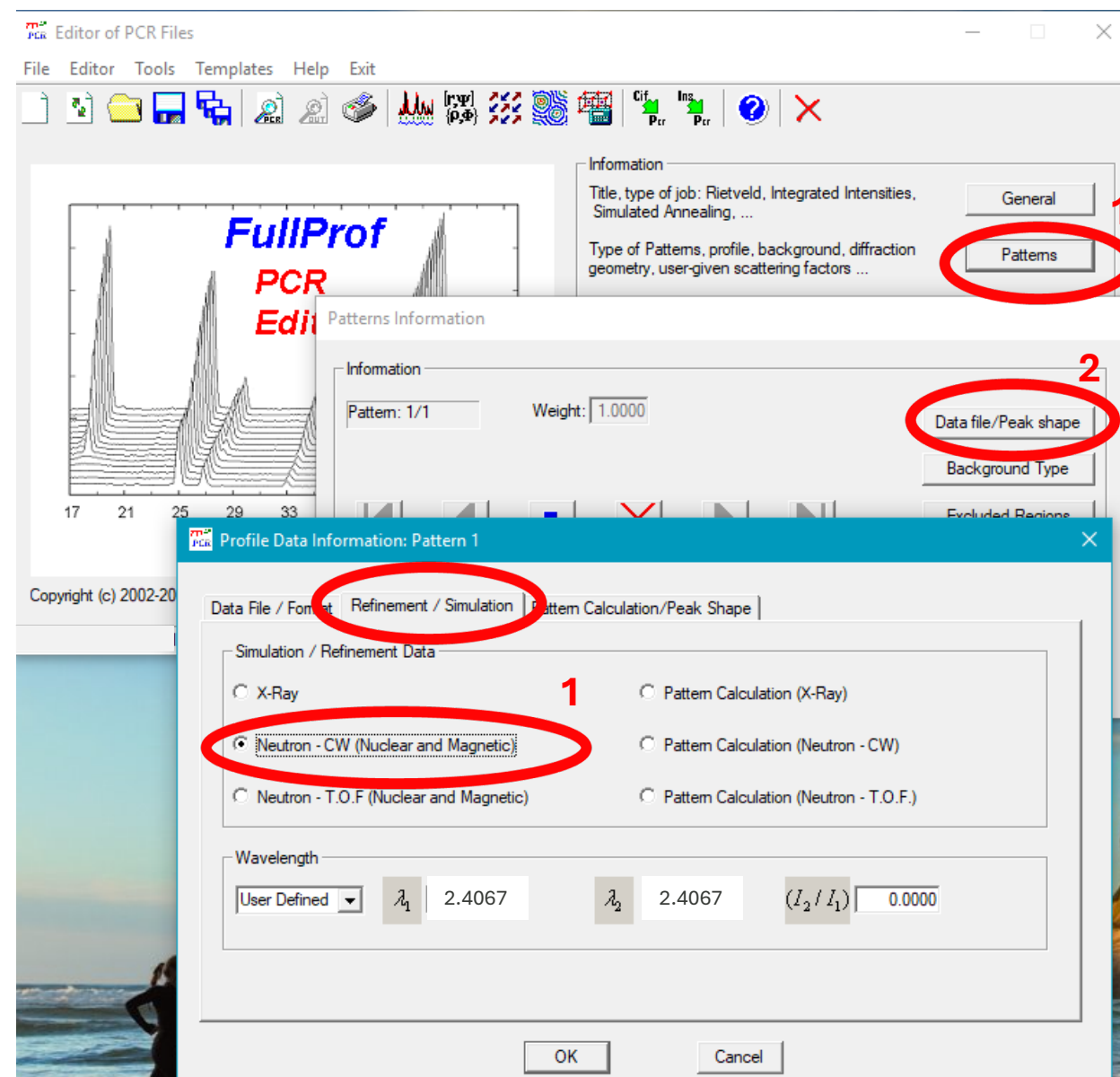


Step 1: Refine the crystal structure using FullProf

Patterns → Data file/Peak Shape
→ Refinement/Simulation

[1] Select Neutron – CW

Wavelength is already set by irf file,
2.4067 in this example.

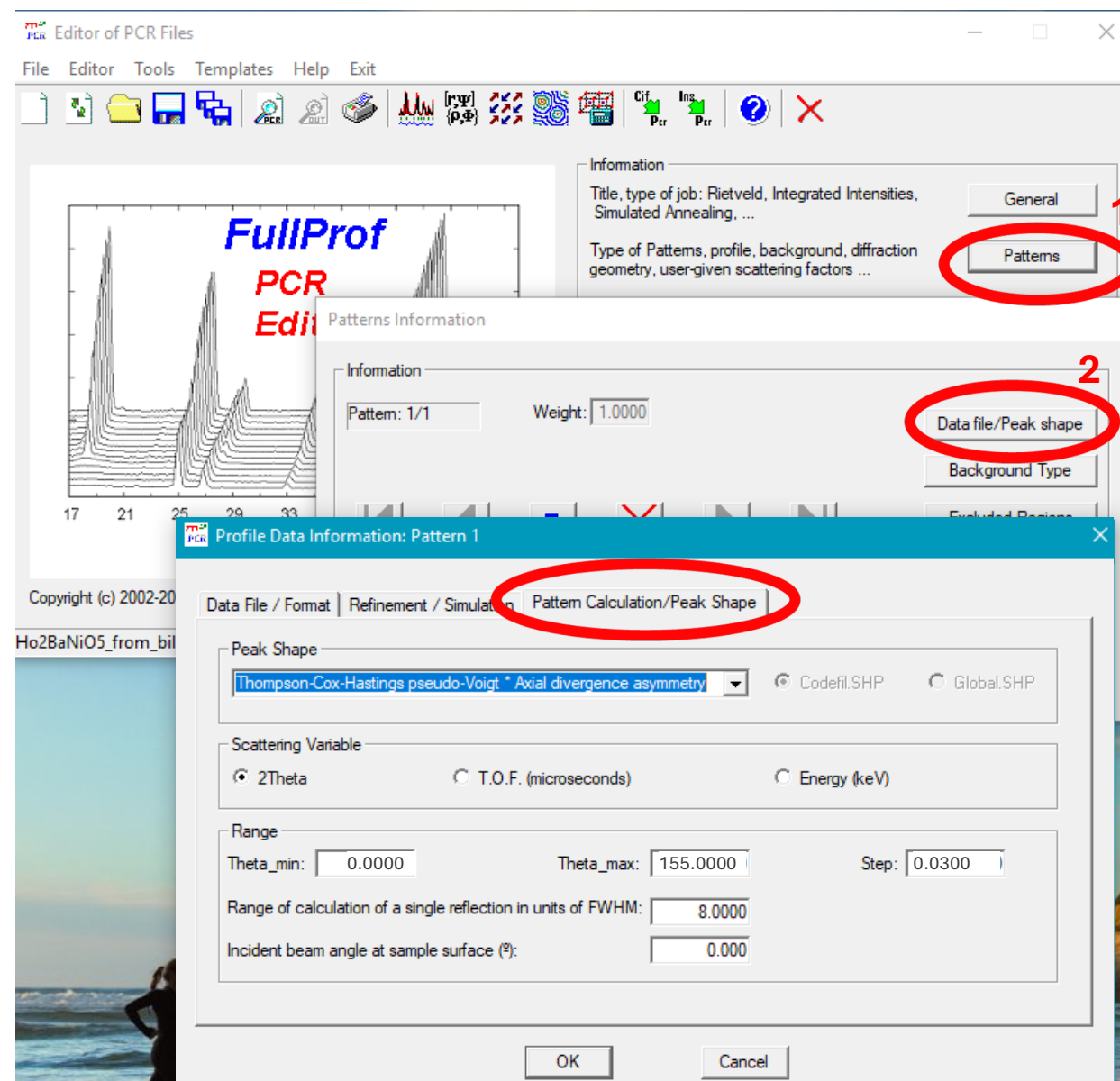


Step 1: Refine the crystal structure using FullProf

Check final tab:

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

Peak shape is already loaded correctly from irf file.



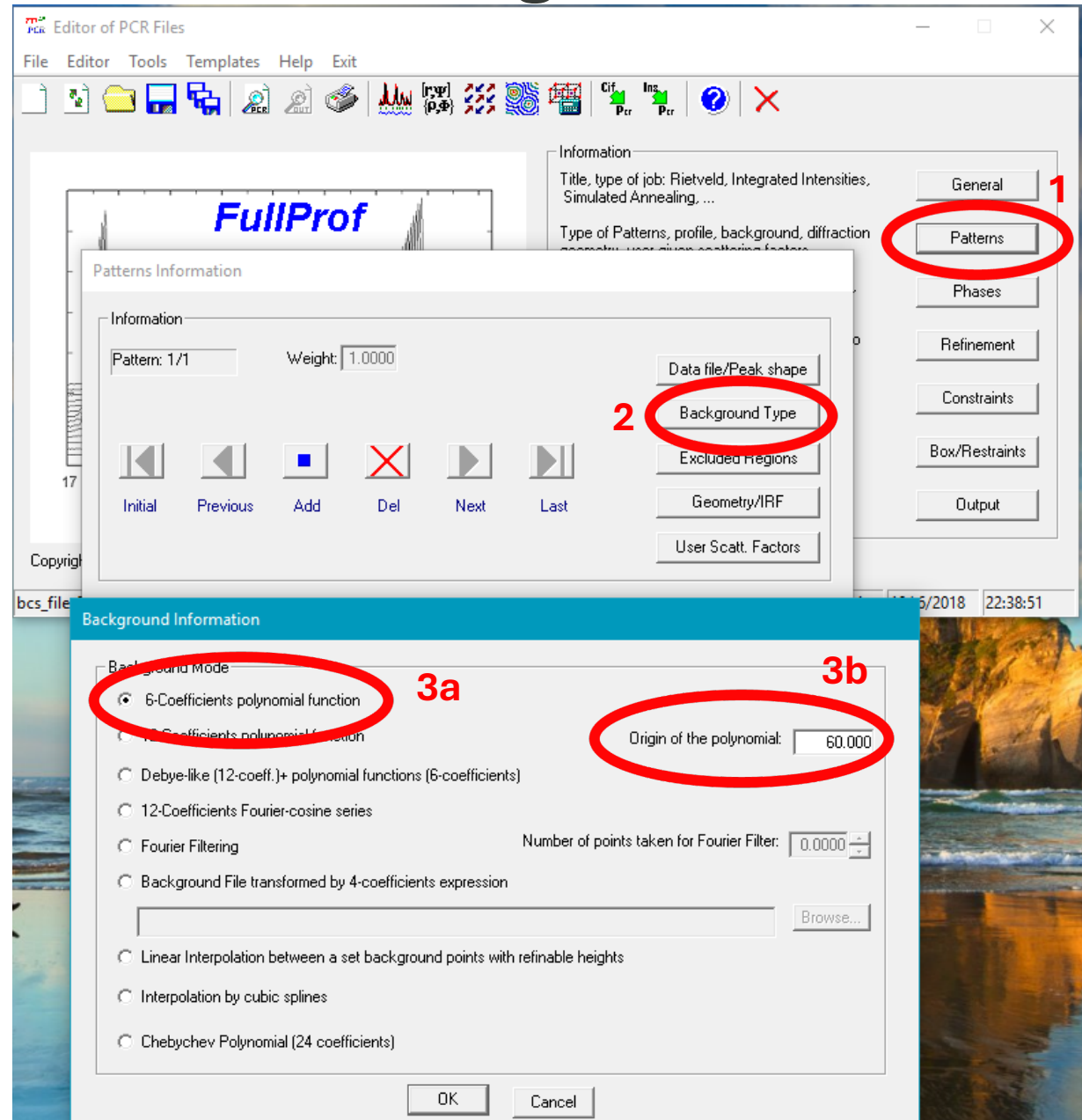
Step 1: Refine the crystal structure using FullProf

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

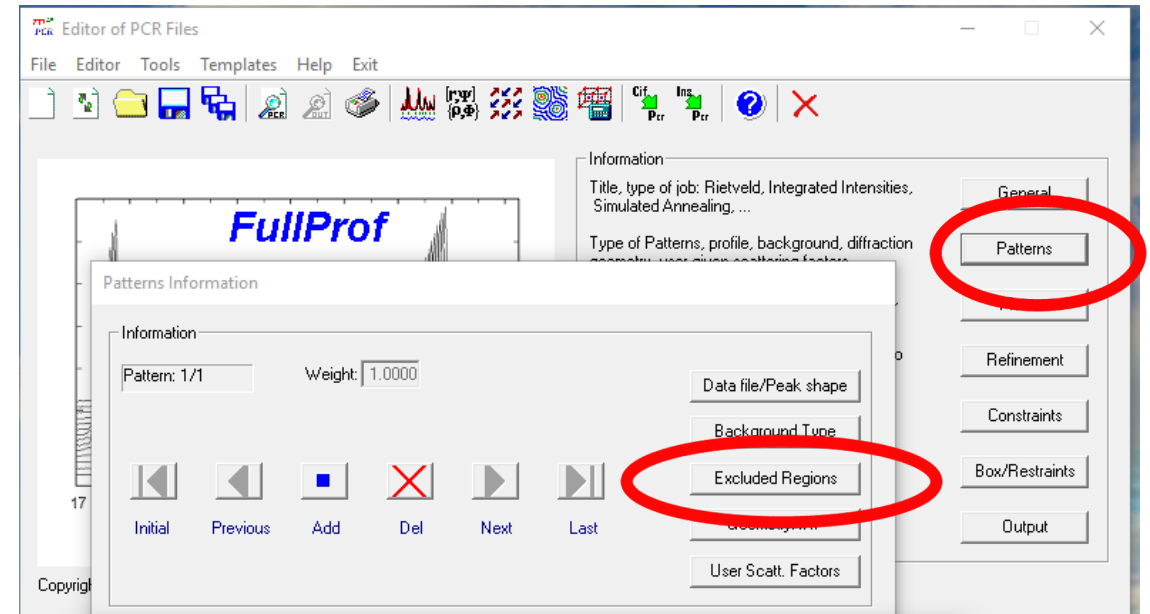
Exclude regions in the data?

We will not exclude any regions of the data

Use with care, but can cut out background.

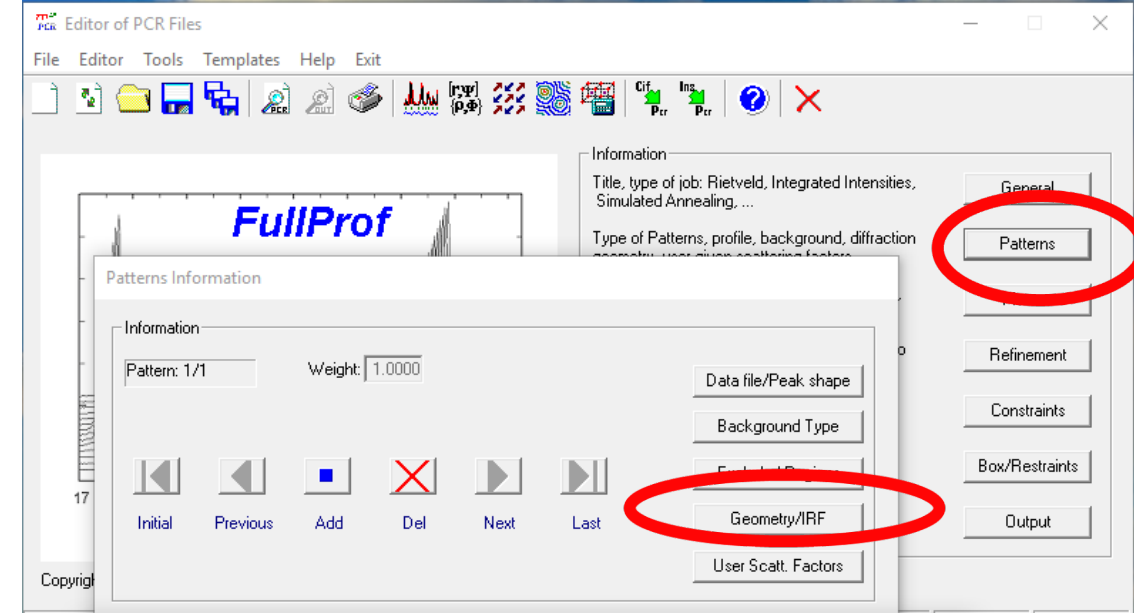
Allow focus of refinement on different regions, e.g. only low Q

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

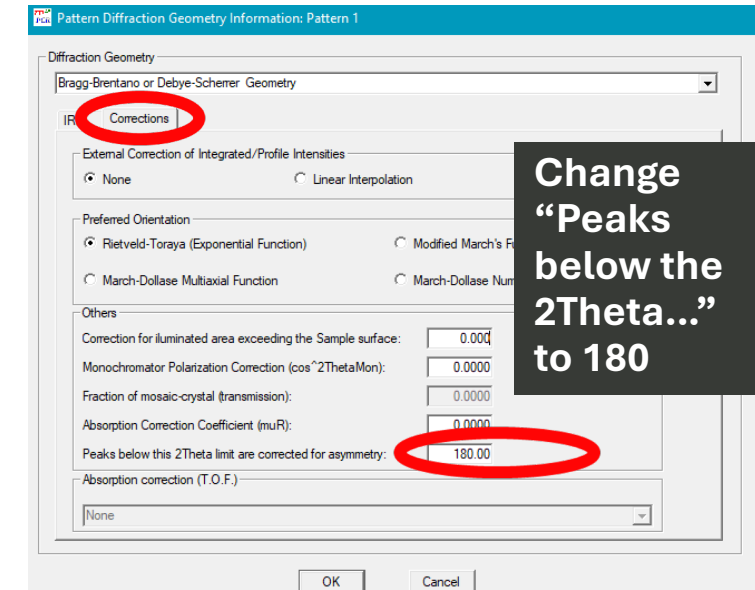
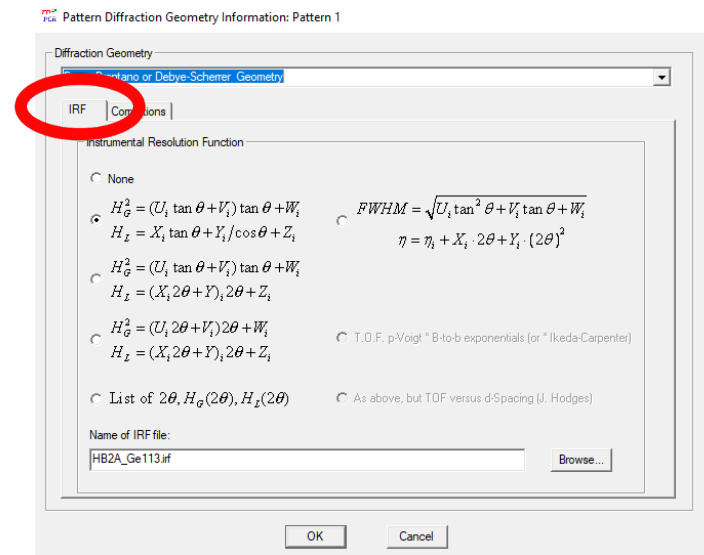


Step 1: Refine the crystal structure using FullProf

- 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!



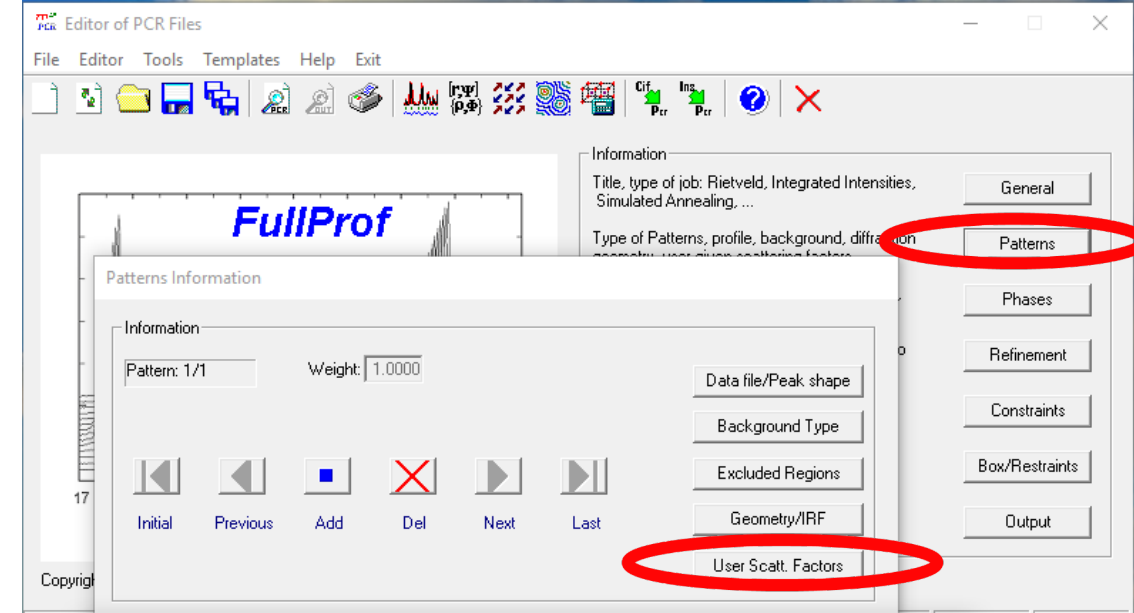
- Can correct for absorption if needed. “muR” is mu (absorption) multiplied by sample radius. Can find mu at NIST website
<https://www.ncnr.nist.gov/resources/activation/>



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

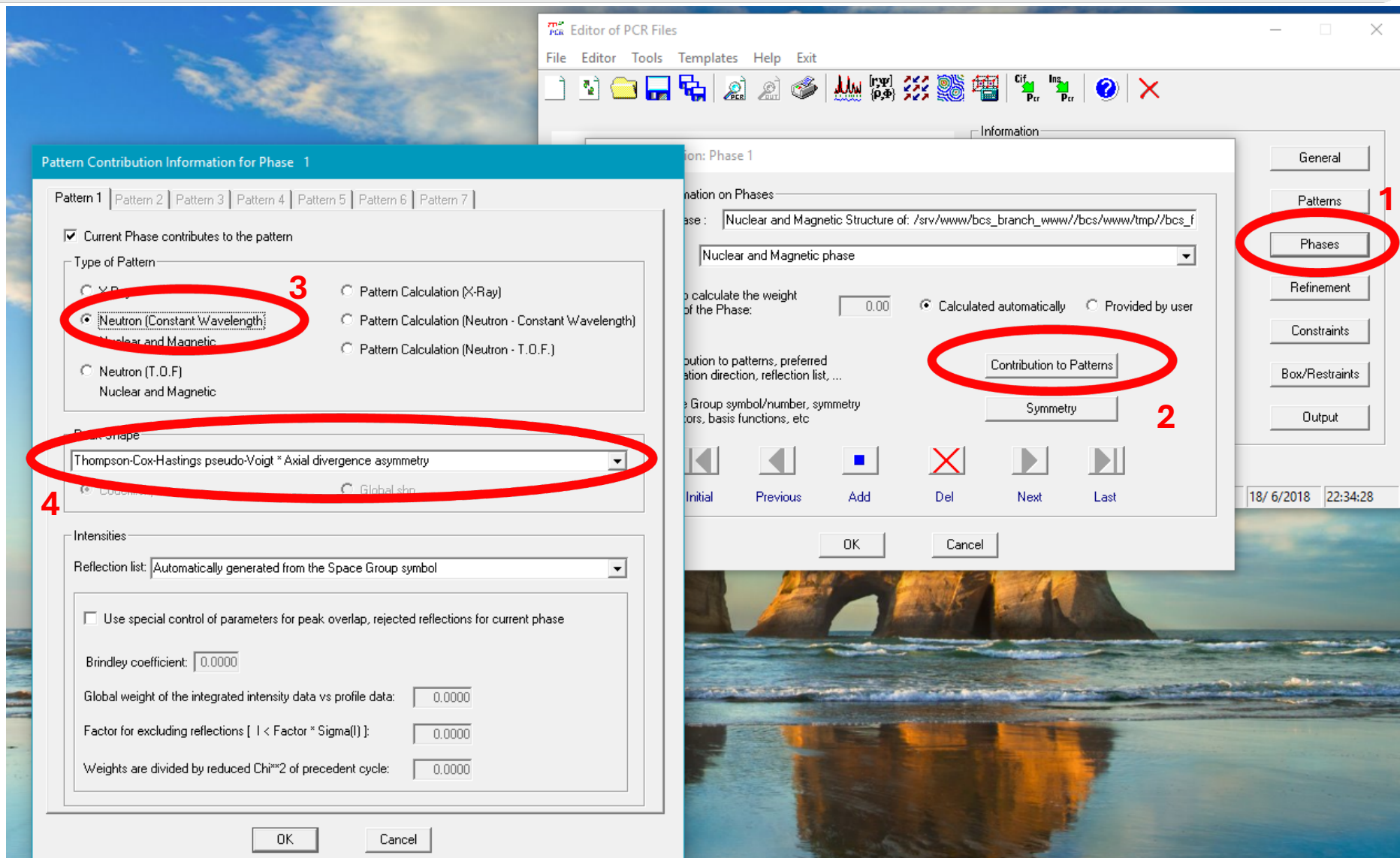
PHASES tab

Make phase contribute to refinement.

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

Set peak shape to “*Thompson-Cox-Hastings pseudo-Voigt*”

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



Step 1: Refine the crystal structure using FullProf

REFINEMENT tab:

Setting starting values for refinements

Starting background value of 600000 (check data)

Editor of PCR Files

File Editor Tools Templates Help Exit

Information

Title, type of job: Rietveld, Integrated Intensities.

General

Patterns

Phases

Refinement

Constraints

Box/Restrains

Output

Refinement Information

Cycles of Refinement: 1

Stop Criterium of Coverage

Forced Termination when shifts < 0.02 x E.S.D.

Others: None

Relaxation Factors for Shifts

Atomic 1.00 Anisotropic 1.00 Profile 1.00 Global 1.00

Reflections ordering

☒ Only at the first cycle ☐ Each cycle

☐ Bragg R-Factor excluding reflections limiting excluded regions

Pattern 1 Pattern 2 Pattern 3 Pattern 4 Pattern 5 Pattern

Phase 1 Phase 2 Phase 3 Phase 4 Phase 5 Phase 6 P

Refinement weighting model

Background

Instrumental

Micro-Absorption

Factor of number of data points: 0

6 Coefficients Polynomial Background: Pattern 1

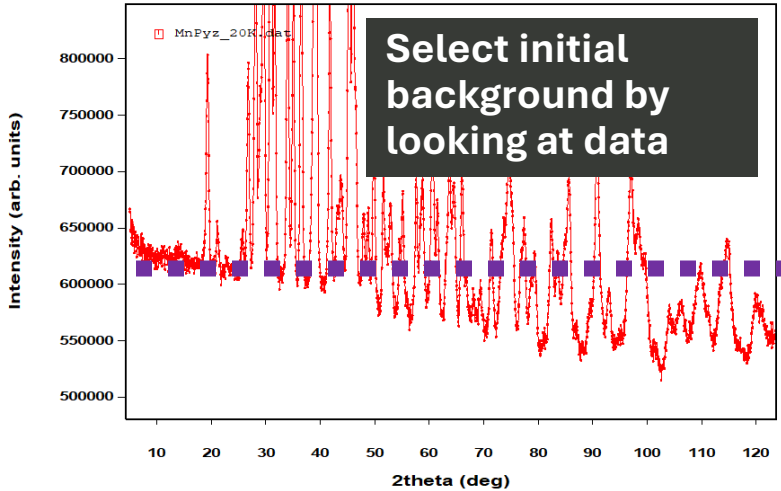
	d_0	d_1	d_2	d_3	d_4	d_5
Coefficients	600000	0.0000	0.0000	0.0000	0.0000	0.0000
	d_6	d_7	d_8	d_9	d_10	d_11
Coefficients						
	d_12	d_13	d_14	d_15	d_16	d_17
Coefficients						
	d_18	d_19	d_20	d_21	d_22	d_23
Coefficients						

Refine All

Fix All

Cancel

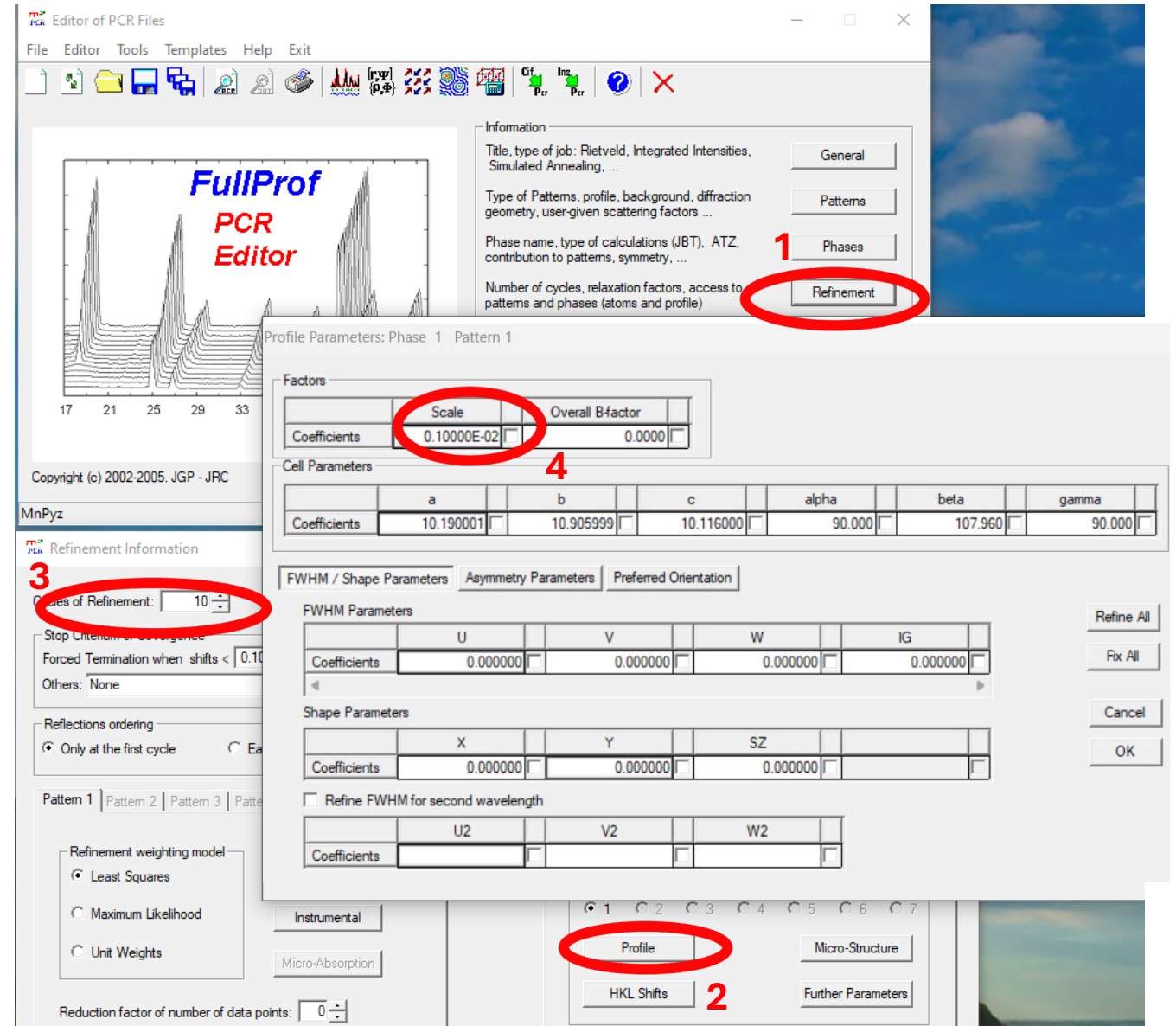
OK



Step 1: Refine the crystal structure using FullProf

1. Select “Refinement” tab again.
Update “Cycle of Refinement” to 10
2. From “Refinement” tab select: Refinement>Profile
3. Change number of cycle refinement will run to 10
4. Scale is a default value
NOTE: You usually have to try different values by hand before refining (see next slides).

Notice U, V, W, X show 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 (refine), 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

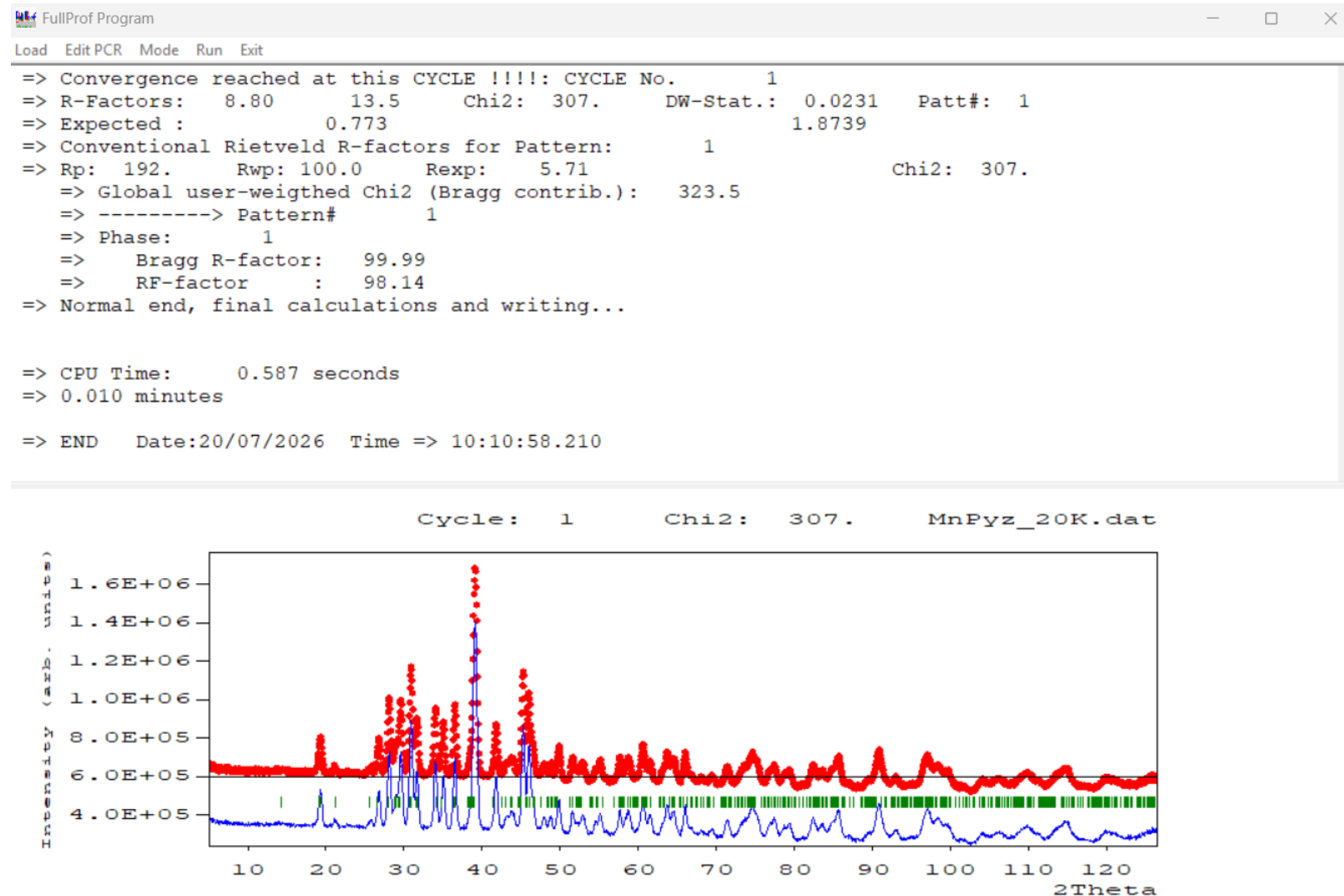
Step 1: Refine the crystal structure using FullProf

The model just shows a flat line.

This indicates the scale is not correct.

The default scale is 0.1×10^{-2} , which is too low for the data scale we have.

Increase this manually to get it close to the data.



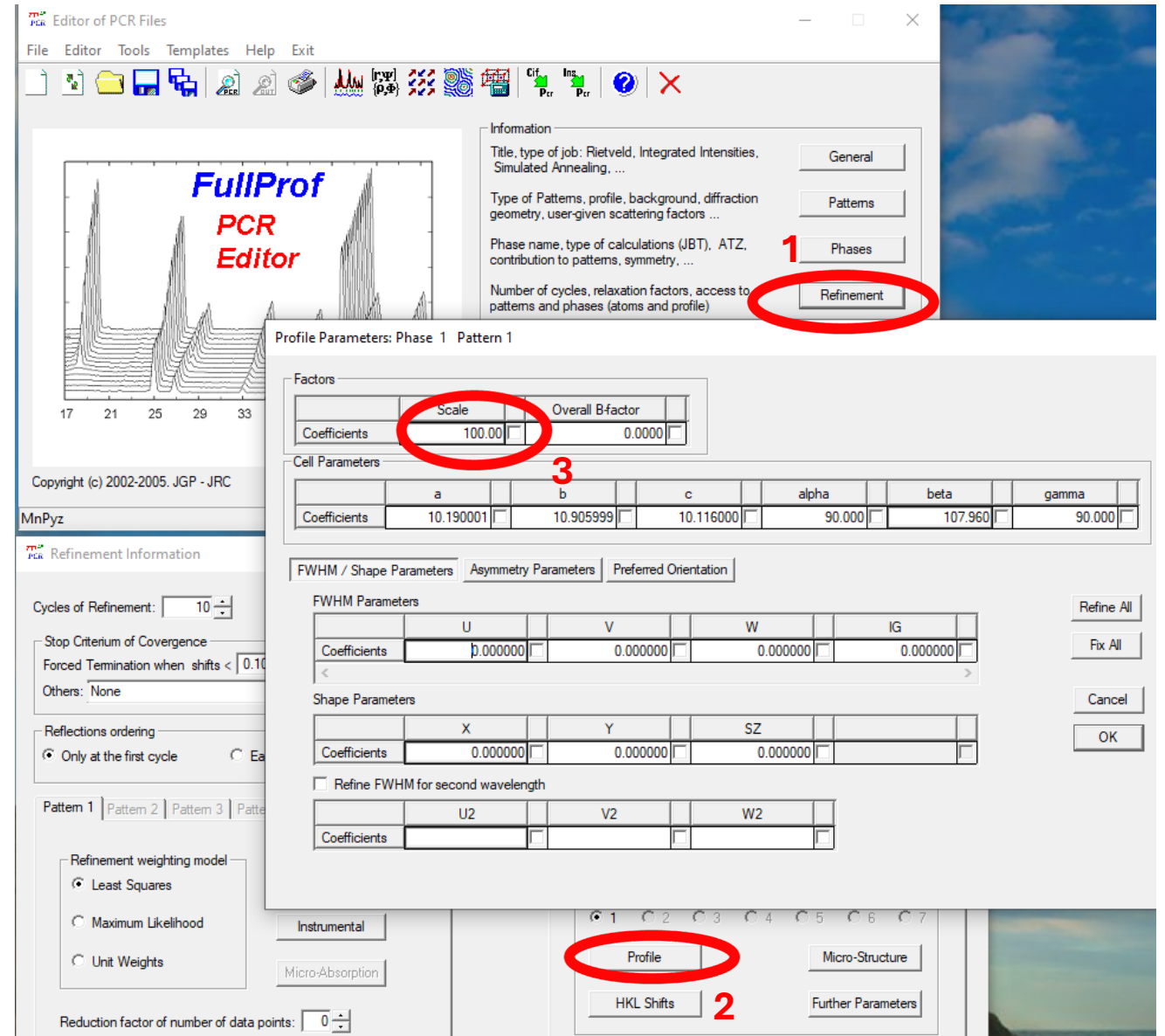
Step 1: Refine the crystal structure using FullProf

1. Select “Refinement” tab again.
Update “Cycle of Refinement” to 10

2. From “Refinement” tab select:
Refinement>Profile

3. Change scale to **100.0**

NOTE: This is a guess, you may have to try different values by hand before refining.



**Re-run refinement, again with
nothing refining**

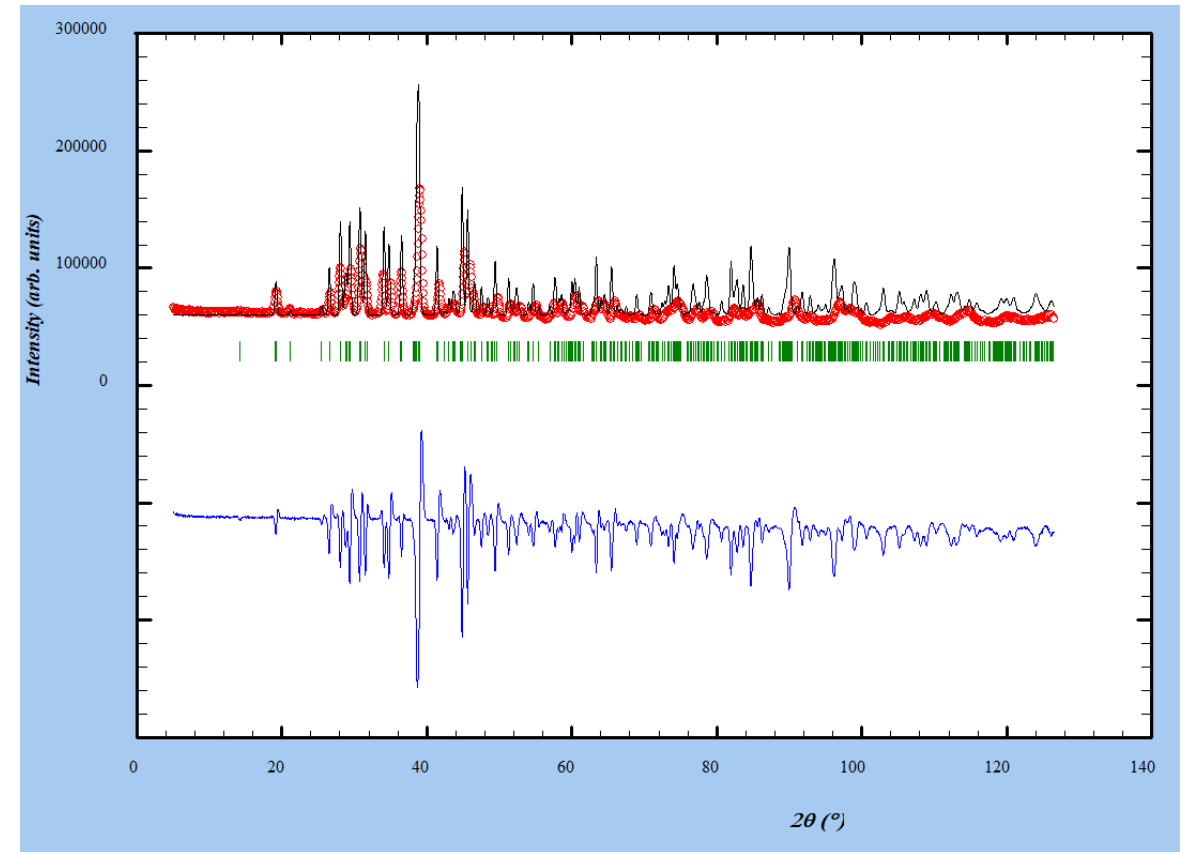
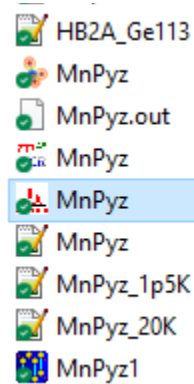
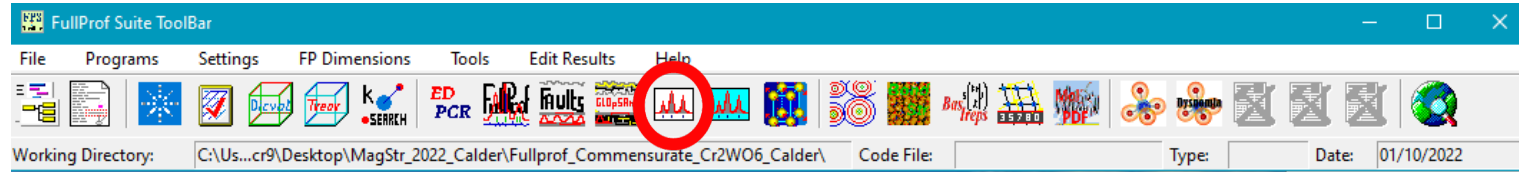
Step 1: Refine the crystal structure using FullProf

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: Always refine lattice constants before peak shape parameters.



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 the 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 ☒
	Overall B-factor
	0.0000 ☐

Cell Parameters											
	a		b		c		alpha		beta		gamma
Coefficients	10.190001 ☒		10.905999 ☒		10.116000 ☒		90.000 ☐		107.960 ☒		90.000 ☐

FWHM / Shape Parameters Asymmetry Parameters Preferred Orientation

FWHM Parameters							
	U		V		W		IG
Coefficients	0.000000 ☐		0.000000 ☐		0.000000 ☐		0.000000 ☐

< >

Shape Parameters

Refine All Fix All Cancel

6 Coefficients Polynomial Background: Pattern 1

	d_0		d_1		d_2		d_3		d_4		d_5
Coefficients	0.60000E+06 ☒		0.0000 ☒		0.0000 ☒		0.0000 ☒		0.0000 ☒		0.0000 ☒

	d_6		d_7		d_8		d_9		d_10		d_11

Refine All Fix All

Instrumental Parameters Refinement: Pattern 1

2_Theta							
	Zero		Displacement		Transparency		Wavelength
Coefficients	0.000000 ☒		0.000000 ☐		0.000000 ☐		0.000000 ☐

Refine All Fix All Cancel OK

Working in text editor and GUI

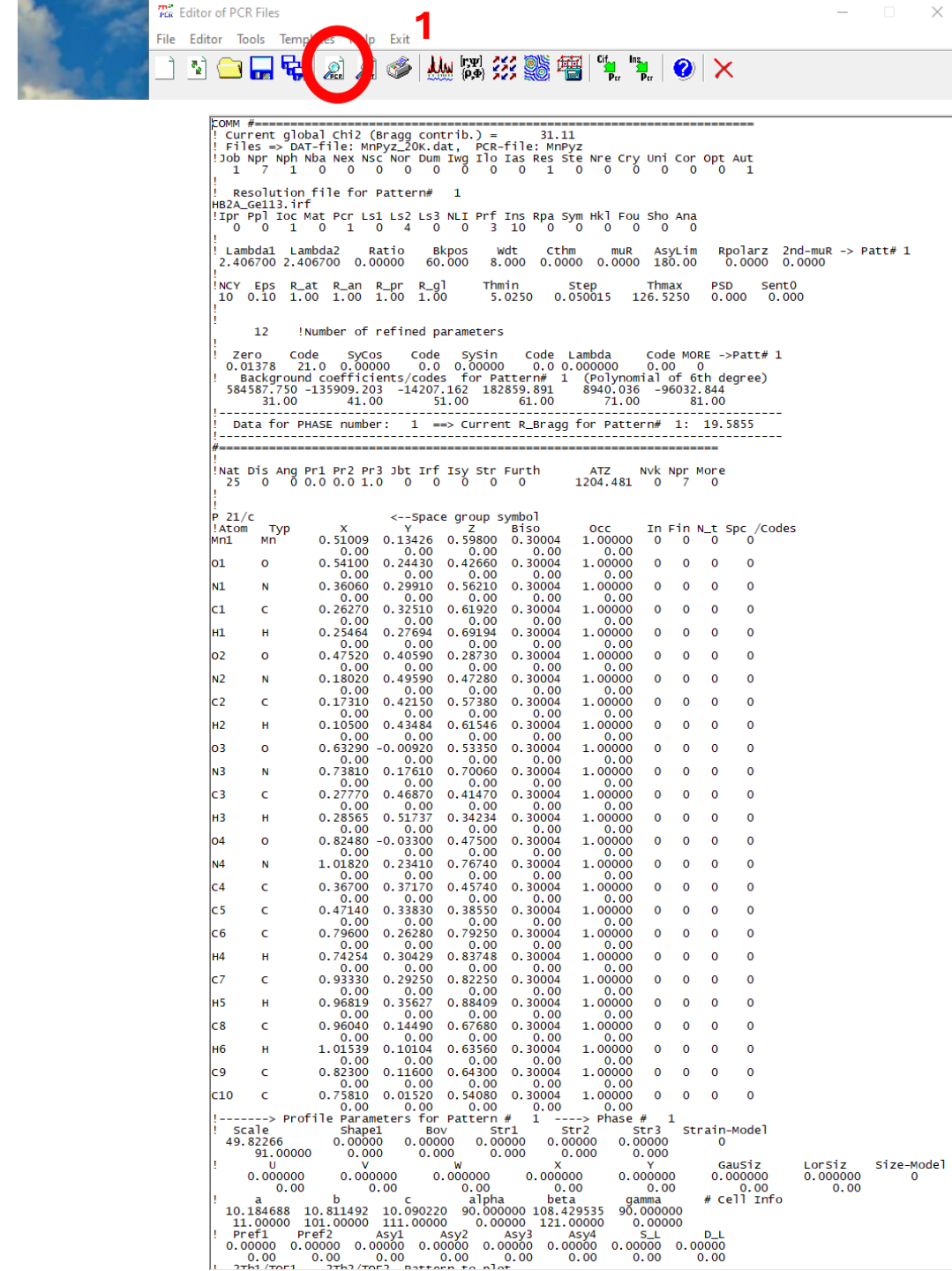
Can use BOTH the GUI and edit the text of the.pcr file.

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

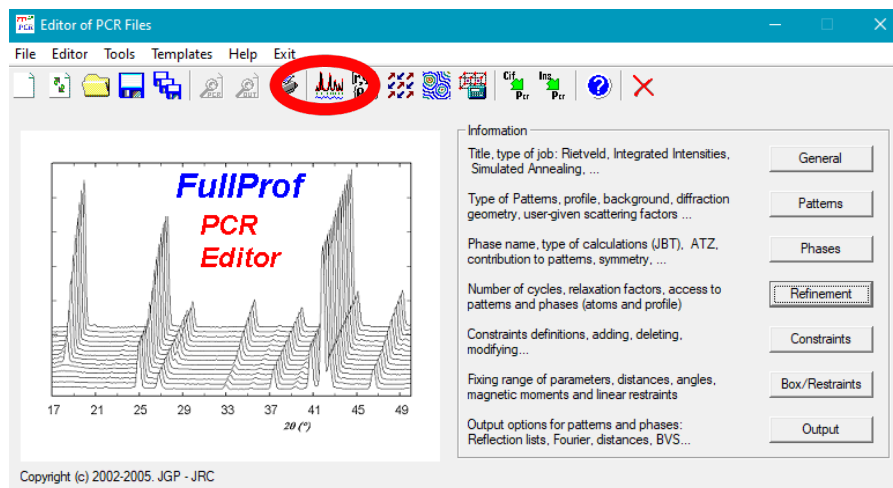
Can quickly see and edit various things quicker than with GUI

- 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.



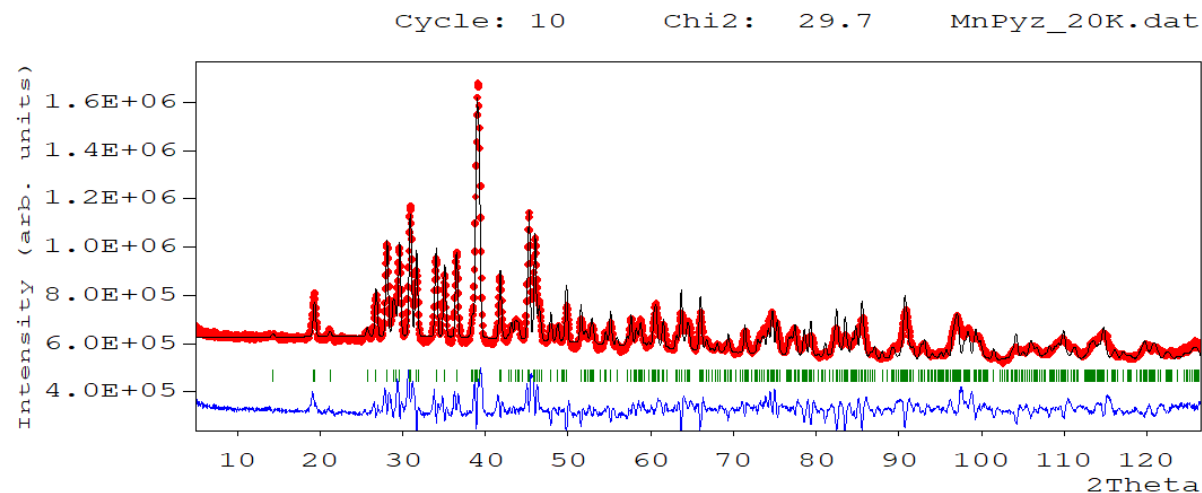
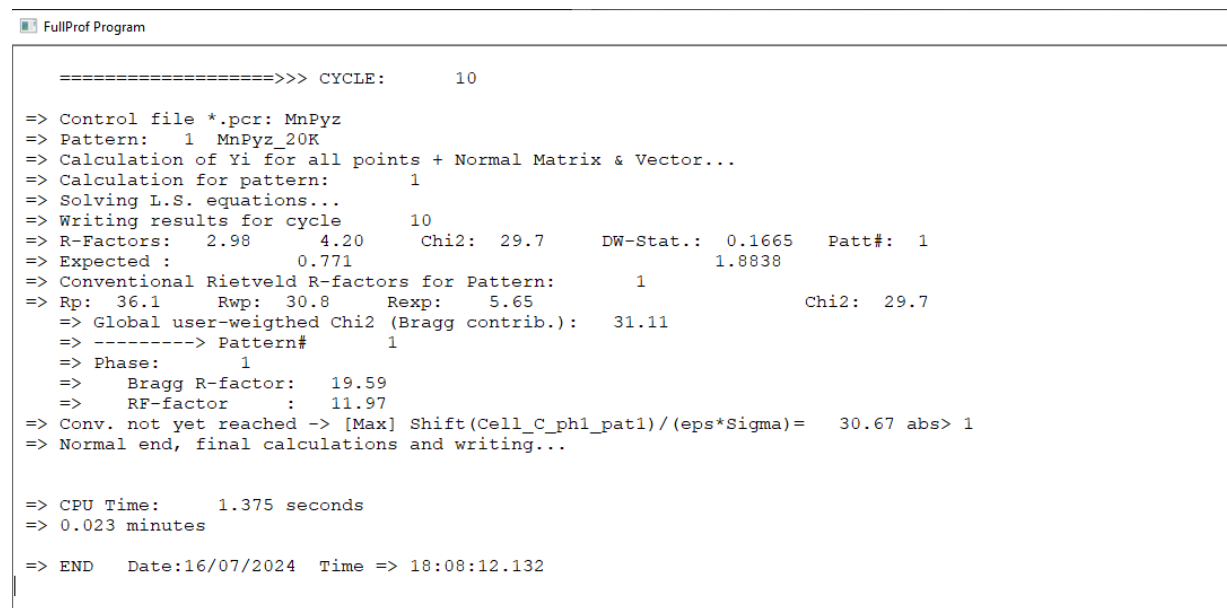
Step 1: Refine the crystal structure using FullProf



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, otherwise the refinement will blow-up



Step 1: Refine the crystal structure using FullProf

Refinement → Profile → Refine U,V,W,X.

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

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

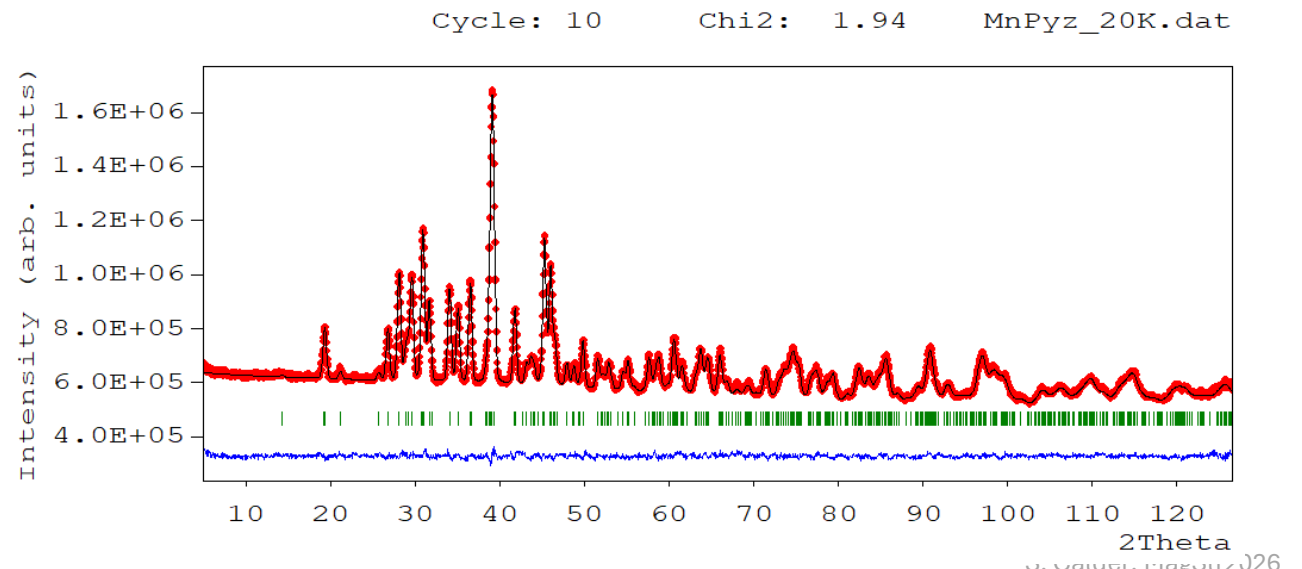
	Label	Ntype	X	Y	Z	B	Occ	Therm. Fact.
Atom # 1	Mn	Mn	0.51356	0.12895	0.60217	0.300	1.00000	Isotropic
Atom # 2	O1	O	0.54868	0.24635	0.42955	0.3000	1.00000	Isotropic
Atom # 3	N1	N	0.36244	0.30105	0.56440	0.30004	1.00000	Isotropic
Atom # 4	C1	C	0.26705	0.31210	0.62293	0.30004	1.00000	Isotropic

Anisotropic Thermal Factors / Form Factors

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

Buttons: Refine Positions, Refine B_iso, Refine B_aniso, Fix All, Cancel, OK

- Other data was collected with a shorter wavelength (1.54 Å) to cover more reflections. This is presented in the paper.



Step 1: Refine the crystal structure using FullProf

Up to now we have been 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

Before refining the 1.5 K data **FIRST TURN OFF ALL PARAMETERS.**

The peak shapes should not change with temperature since we are measuring the same sample on the same instrument!

- The lattice constants and structural parameters will vary with temperature, but the temperature change here is small. We can refine as needed.

Check in text file that nothing is refining.

```
File Edit PCr Text Editor - [C:\Users\cyr9\OneDrive\Desktop\Stuart Calder\HBZA_MQD\MagStr Workshops\MagStr2024_Calder\Fulprof_Commons
```

```
File Edit Search  
[Icons]  
=====  
COMM #=====  
! Files ==> DAT-file:      PCR-file: MnPzy  
Job Npr Nph Nba Nex Nsc Nor Dum Ing Ilo Tas Res Ste Nre Cry Uni Cor Opt Aut  
1   7   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0  
  
! Resolution file for Pattern# 1  
HBZA_Ge113.irf  
Ipr Ppl Ioc Mat Pcr Lsl Ls2 Ls3 NLI Prf Ins Rpa Sym Hk1 Fou Sho Ana  
0   0   0   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0  
  
! Lambda1 Lambda2 Ratio Bkpos wdt cthm mur AsyLim Rpolzar 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_3D R_5R R_6L TbmIn Step Thmax PSD Sent0  
10 0.0000 1.000 1.000 1.000 0.0000 155.000 0.000 0.000  
  
!  
! 0 !Number of refined parameters  
  
! Code Sycos Code SysIn Code Lambda Code MORE ->Patt# 1  
0.0000 0.0000 0.0000 0.0000 0.0000 0.0000  
Background coefficients/Codes for Pattern# 1 (Polynomial of 6th degree)  
559372.062 -109806.312 5328.478 107231.953 12523.546 -71904.891  
0.00 0.00 0.00 0.00 0.00 0.00  
  
-----  
Data for PHASE number: 1 ==> Current_R_Bragg for Pattern# 1: 0.0000  
-----  
#=====  
Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Mvk Npr More  
25 0 0 0 0 0 0 0 0 0 0 0 0 1204.481 0 7 0 0  
  
!  
P 21/c <---Space group symbol  
Atom Typ X Y Z Biso Occ In Fin N_t Spc /Codes  
Mn1 Mn 0.51356 0.12895 0.60217 0.30004 1.00000 0 0 0 0  
O1 O 0.0000 0.0000 0.0000 0.0000 1.00000 0 0 0 0  
N1 N 0.36244 0.30105 0.56440 0.30004 1.00000 0 0 0 0  
C1 C 0.0000 0.0000 0.0000 0.0000 1.00000 0 0 0 0  
H1 H 0.26705 0.31210 0.62293 0.30004 1.00000 0 0 0 0  
C2 C 0.24226 0.24571 0.66885 0.30004 1.00000 0 0 0 0  
O2 O 0.0000 0.0000 0.0000 0.0000 1.00000 0 0 0 0  
N2 N 0.47150 0.40957 0.28321 0.30004 1.00000 0 0 0 0  
C3 C 0.17238 0.49489 0.47494 0.30004 1.00000 0 0 0 0  
H2 H 0.15921 0.40664 0.56866 0.30004 1.00000 0 0 0 0  
C4 C 0.10169 0.42860 0.62270 0.30004 1.00000 0 0 0 0  
O3 O 0.0000 0.0000 0.0000 0.0000 1.00000 0 0 0 0  
N3 N 0.63580 0.00641 0.53074 0.30004 1.00000 0 0 0 0  
C5 C 0.73160 0.18010 0.70183 0.30004 1.00000 0 0 0 0  
H3 H 0.0000 0.0000 0.0000 0.0000 1.00000 0 0 0 0
```

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.

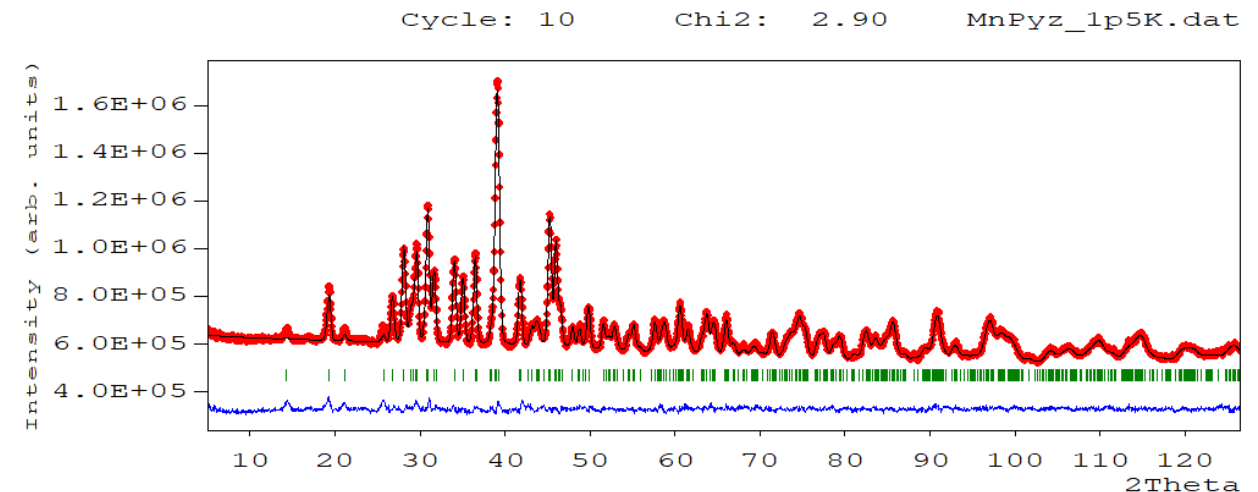
We can now use this to determine the k-vector and then magnetic structure.

```
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.

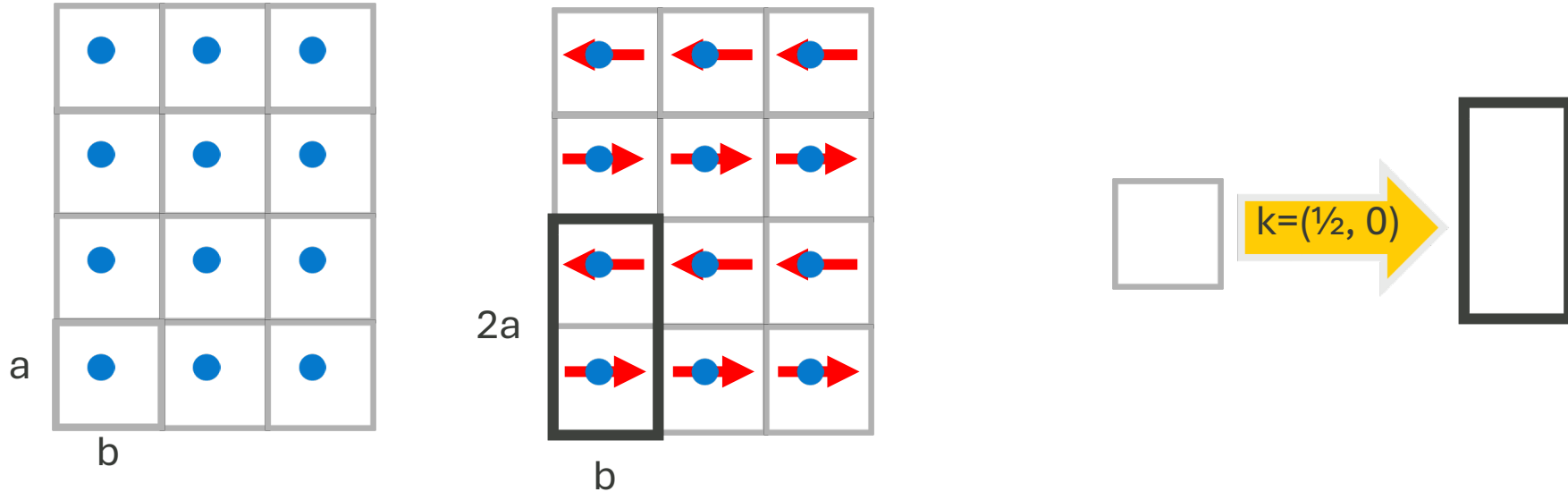
Mn-pyrazinecarboxylate

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

Magnetic propagation vector: k-vector

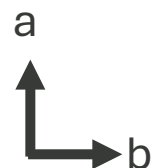
- **Crystal** and **magnetic** unit cells are not necessarily the same size.
- **k-vector** describes the relation between the crystallographic and magnetic unit cells
 - Determine with neutron diffraction



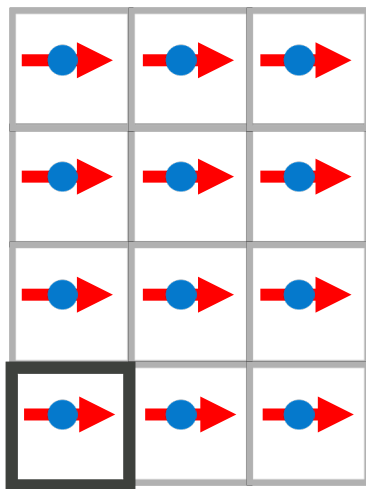
Magnetic propagation vector: k-vector

Reciprocal
space: k-vector

Real space:
crystal and
magnetic
unit cells

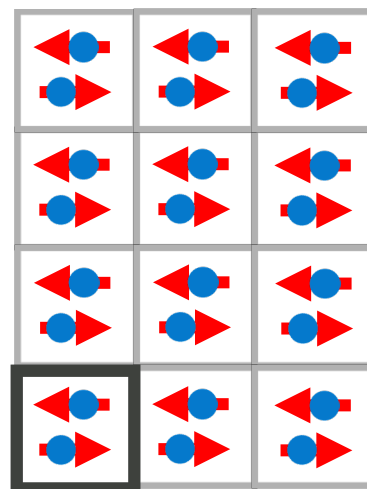


$k=(0,0)$



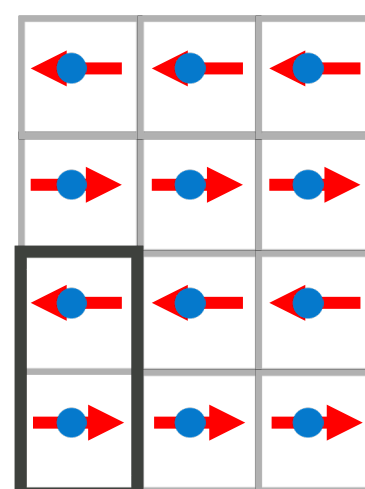
FM

$k=(0,0)$



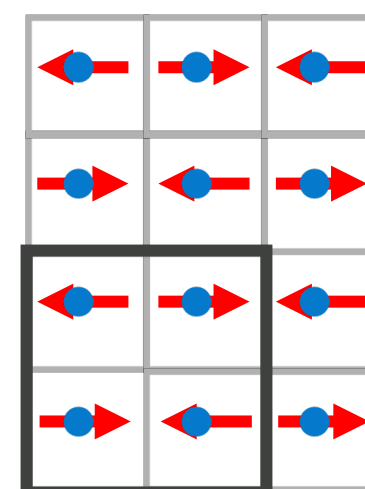
AFM

$k=(\frac{1}{2},0)$



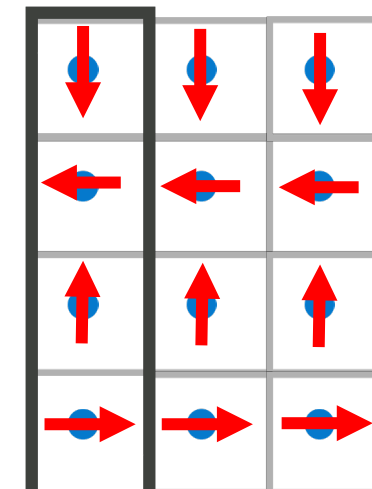
AFM

$k=(\frac{1}{2}, \frac{1}{2})$



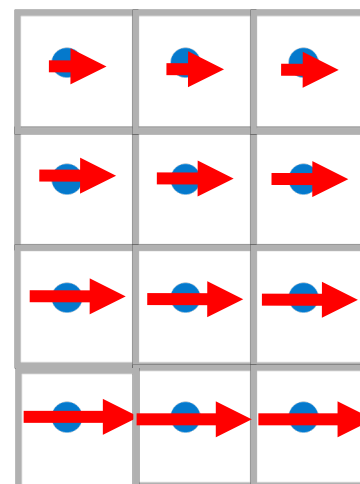
AFM

$k=(\frac{1}{4},0)$

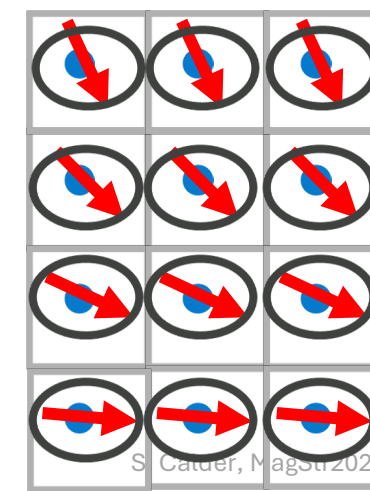


AFM

Incommensurate
spin density wave
structure with
 $k_1=(\delta,0)$



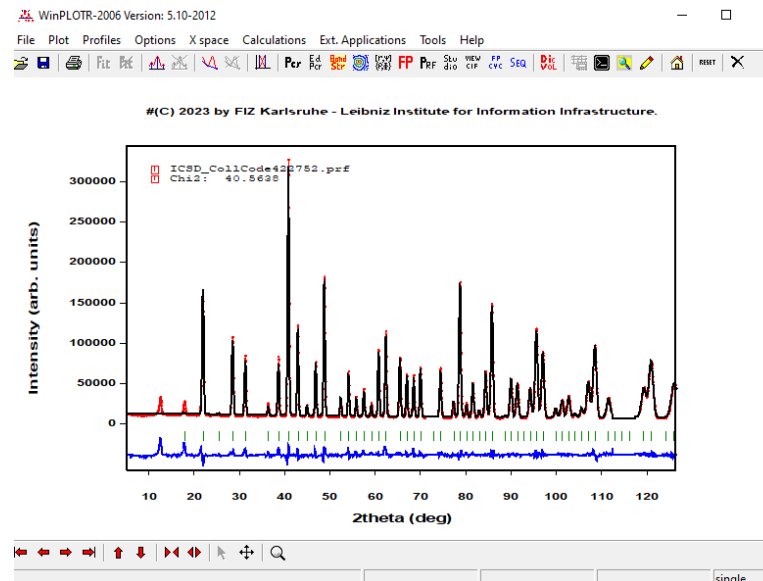
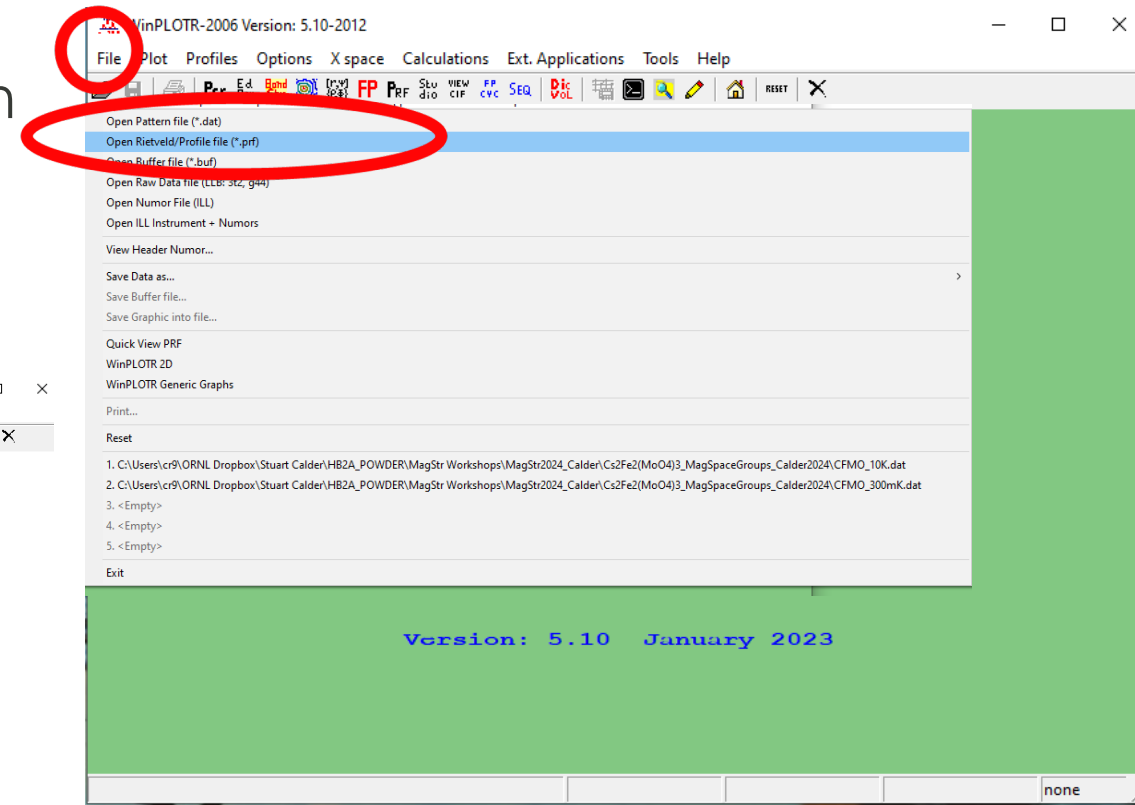
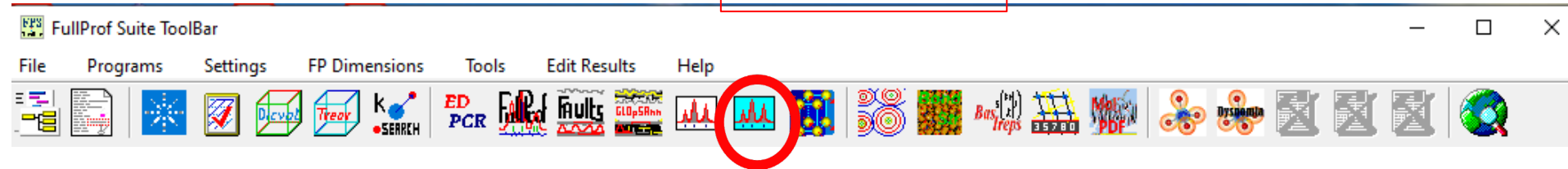
Incommensurate
Helical structure
with
 $k_1=(\delta,0)$



Determine the k-vector

WinPlotr-2006

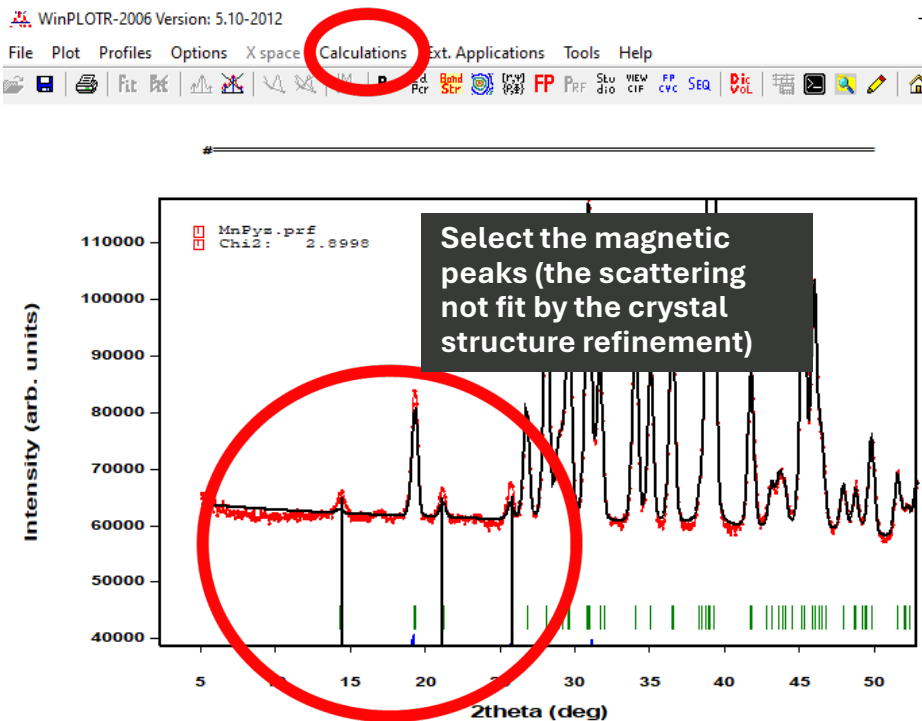
- k-search is run in WinPlotr-2006.
- Open the .prf file. Clicking on icon may open it automatically, if not follow these steps:
 - “File”>”Open Rietveld/Profile file (*.prf)”
 - Select the prf file



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

```
C:\windows\SYSTEM32\cmd.exe

*****
*          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  0.250000  0.500000  1.944756
0.500000  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

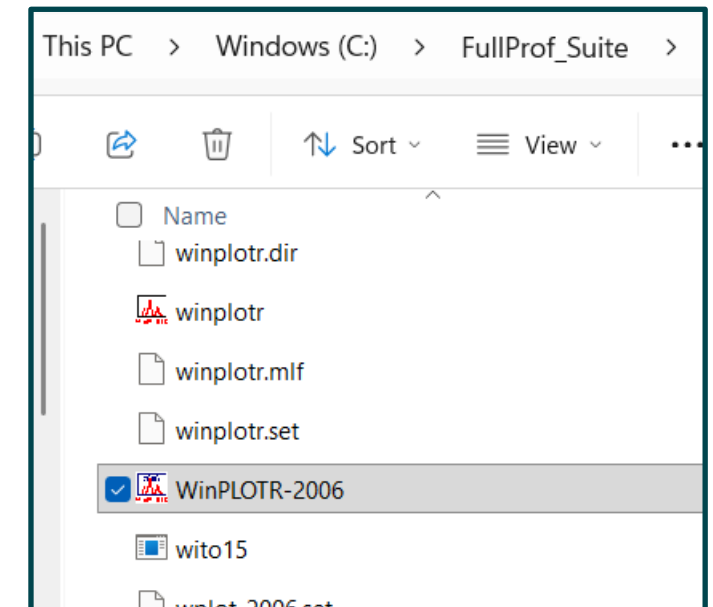
=> Powder diffraction may give wrong results even if the R-factors for the solutions are "good"
The best way to verify the solutions is to perform a full profile fitting and look for mismatches

Total CPU-Time

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

k=(0,0,0)

- NOTE: Depending on your set-up, k-search may not run exactly the same as on the previous slides.
 - You may not see the results shown in the black terminal when you run k-search (it might flash for a second then close)
 - Look in the folder where the .prf file is located for a “.kup” file. This can be opened with any text editor and has all the details.
- FIXES if you still cannot see the k-search results:
 - First try opening WinPlotr-2006 from the toolbar then follow previously slides.
 - If that does not work try opening WinPlotr-2006 directly from the Fullprof program location
 - Classic Fullprof is usually C:\FullProf_Suite\
 - New Fullprof is wherever you put it



- The determined k-vector is $k=000$
- With the k-vector and paramagnetic crystal structure we have all the information needed to start to determine the magnetic structure.

Mn-pyrazinecarboxylate

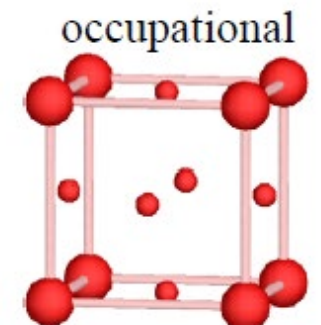
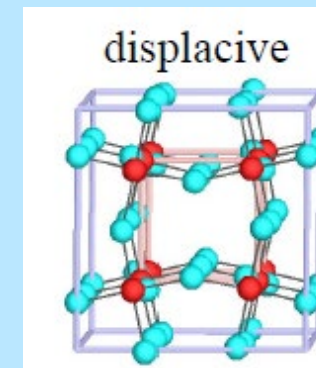
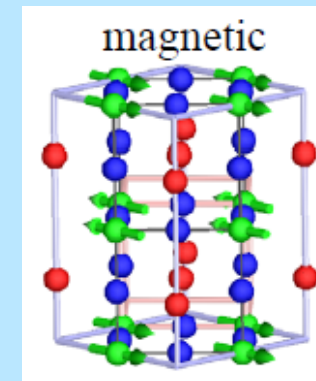
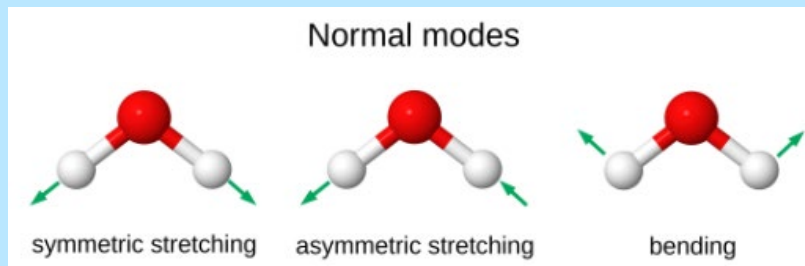
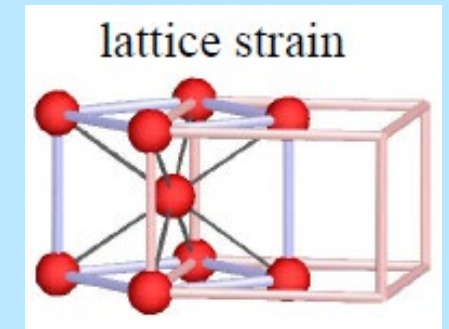
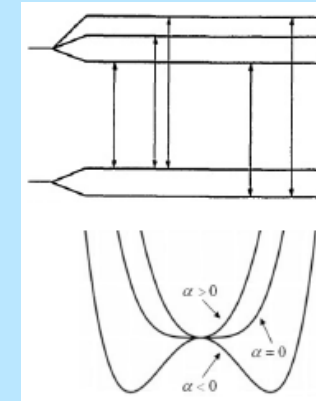
This example will use Fullprof and SARAh <http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>

- 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

Why Representation analysis?

- Provides the smallest (IRREDUCIBLE) building blocks to construct all possible magnetic structures based on the crystal symmetry and k-vector
→ greatly simplifies determination of magnetic structures

- A general symmetry-based approach to parameterize any “distortion” or deviation from previous symmetry
 - Molecular vibrations
 - Hybridized and molecular orbitals
 - Crystal-field splitting
 - Crystal band structure



Representational analysis is, first of all, a tool for finding magnetic structures

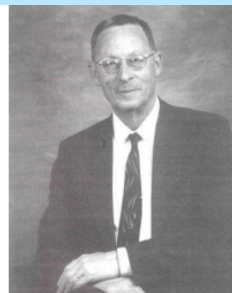
Acta Cryst. (1968). **A24**, 217

Representation Analysis of Magnetic Structures

BY E. F. BERTAUT

*Laboratoire d'Électrostatique et de Physique du Métal, C.N.R.S., B.P. 319 et
Laboratoire de Diffraction Neutronique, C.E.N.G., B.P. 269, Grenoble 38, France*

(Received 20 July 1967)



In the analysis of spin structures a 'natural' point of view looks for the set of symmetry operations which leave the magnetic structure invariant and has led to the development of magnetic or Shubnikov groups. A second point of view presented here simply asks for the transformation properties of a magnetic structure under the classical symmetry operations of the 230 conventional space groups and allows one to assign irreducible representations of the actual space group to all known magnetic structures. The superiority of representation theory over symmetry invariance under Shubnikov groups is already demonstrated by the fact proven here that the only invariant magnetic structures describable by magnetic groups belong to real one-dimensional representations of the 230 space groups. Representation theory on the other hand is richer because the number of representations is infinite, *i.e.* it can deal not only with magnetic structures belonging to one-dimensional real representations, but also with those belonging to one-dimensional complex and even to two-dimensional and three-dimensional representations associated with any $\mathbf{k}$ vector in or on the first Brillouin zone.

We generate from the transformation matrices of the spins a representation Γ of the space group which is reducible. We find the basis vectors of the irreducible representations contained in Γ .

The basis vectors are linear combinations of the spins and describe the structure. The method is first applied to the $\mathbf{k}=0$ case where magnetic and chemical cells are identical and then extended to the case where magnetic and chemical cells are different ($\mathbf{k}\neq 0$) with special emphasis on $\mathbf{k}$ vectors lying on the surface of the first Brillouin zone in non-symmorphic space groups. As a specific example we

cor
ass C 1 - 470

E. F. BERTAUT

matical difficulties when one is not willing to impose cyclic boundary conditions ». As far as I understand, cyclic boundary conditions are the mathematical trick to handle infinite groups (translation and space groups) on the same footing as finite groups and have led to the success of space group theory. I am not willing to abandon these achievements if there is no better theory available.

As far as usefulness is concerned I still think that C 2 gives more immediate information than C 1'. There is no difficulty in using both descriptions jointly and, as a common practice, I indicate the Shubnikov group (except P 1) in my writings.

Conclusion. — Representation analysis is, first of all, a tool for finding magnetic structures. The description of a magnetic structure by basis vectors of irreducible representations is certainly useful.

Finally the construction of an effective spin hamil-

tonian using *all* the symmetry elements of the irreducible representation becomes possible. Of course, physicists did not wait for the theory presented here to build their hamiltonian in the helimagnetic case. But when minimizing the isotropic part of the hamiltonian, say $J_1 \cos \pi l + J_2 \cos 2\pi l$ in the case of say the dysprosium or AuMn_2 -helix, they may have got some feeling from this lecture that their hamiltonian is invariant under the wave vector group $\mathbf{G}_k (= P 6_3 m c)$ with $\mathbf{k} = [0 0 l]$ and that the helical spin configuration may belong to a two-dimensional representation of $\mathbf{G}_k$ [10].

Thus we reach this final conclusion. When the spin arrangement belongs to an irreducible representation of order higher than one or to a complex representation, the effective spin hamiltonian has a symmetry higher than the symmetry (Shubnikov-symmetry) which leaves the magnetic structure invariant.

JOURNAL DE PHYSIQUE

Colloque C 1, supplément au n° 2-3, Tome 32, Février-Mars 1971, page C 1 - 462

MAGNETIC STRUCTURE ANALYSIS AND GROUP THEORY

E. F. BERTAUT

C. N. R. S. and C. E. N.-G., rue des Martyrs, Grenoble

Introduction. — Representation analysis of a magnetic structure is not only *a)* labelling or classifying a structure, but consists mainly of *b)* the search for the structure before it is known and of *c)* the discussion of the interactions which might explain the final structure model. Professor Opechowski has not evaluated the merits of representation analysis for *b)* and *c)*. Thus I shall answer his criticism at the end of my lecture.

Neutron-diffraction studies of magnetic structures of crystals

Yu. A. Izyumov

*Institute of Metal Physics of the Ural Scientific Center of the Academy of Sciences of the USSR, Sverdlovsk
Usp. Fiz. Nauk 131, 387-422 (July 1980)*

The contemporary state of neutron diffraction of magnetic structures is analyzed from the standpoint of the theory of symmetry of crystals. It is shown that the varied and numerous structures determined in neutron-diffraction studies can be classified and described by the theory of representations of space groups of crystals. This approach is based on expanding the spin density of the crystal in terms of basis functions of the irreducible representations of its space group. Thus the magnetic structure can be specified by the mixing coefficients of the basis functions. Analysis of a large number of different kinds of magnetic structures shows that they arise in the overwhelming majority of cases, in accord with Landau's hypothesis, from a phase transition that follows a single irreducible representation. This means that the number of parameters that fully fix the magnetic structure of an arbitrarily complex crystal is small and equal to the dimensionality of the responsible irreducible representation. This offers great advantages in employing the symmetry approach in deciphering neutron-diffraction patterns of a crystal under study. This is because it reduces the problem of determining a large number of magnetic-moment vectors of the crystal to finding a small number of mixing coefficients. This review presents the fundamentals of such a symmetry analysis of magnetic structures and methods of determining them from neutron-diffraction data.

Neutron-diffraction studies of magnetic structures of crystals

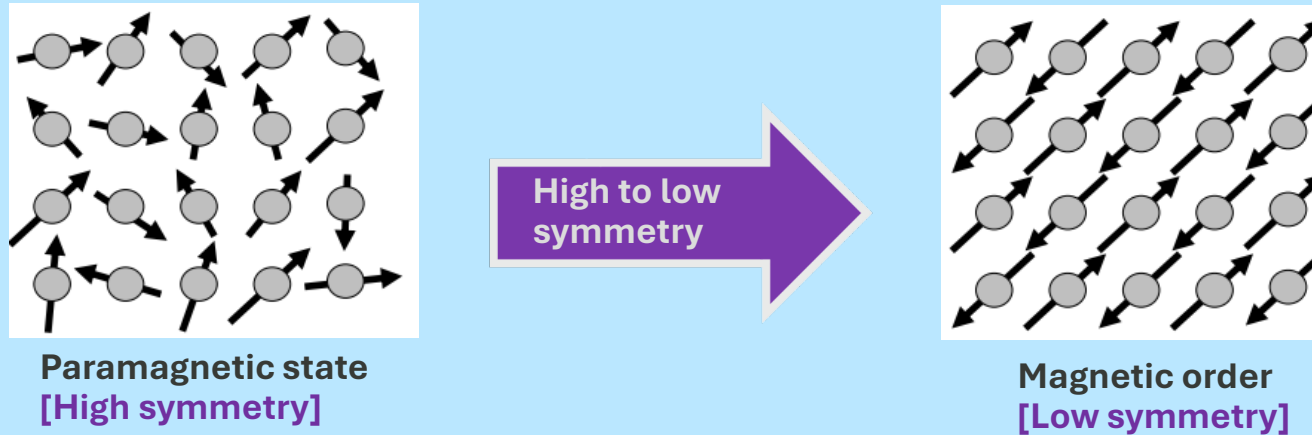
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Magnetic structures, phase transitions and symmetry

- In magnetic neutron diffraction experiments we typically measure materials with phase transitions and want to find the magnetic structure.



- Phase transitions involve symmetry breaking
 - High symmetry (paramagnet) to low symmetry (antiferromagnet)
 - Loss of some symmetry operation (rotation, translation, time-reversal, etc)
 - Transition can be 1st order (discontinuous) or 2nd order (continuous)
 - 2nd order transitions follow Landau theory

Space groups describe the symmetry

- Start by considering symmetry of the non-magnetic crystallographic space group (G).

Properties of a group (G)

- A group contains a set of elements A,B,C... that make up the group that satisfy the requirements:
 - **Closure:** Product of two elements of a group is also a member of the group $AB \in G$
 - **Associativity:** $A(BC)=(AB)C$ for all $ABC \in G$
 - **Identity (E):** There is an identity element (E) satisfying $EA=AE=A$ if $A \in G$
 - **Inverse:** There must be an inverse of each element. $AA^{-1}=A^{-1}A=E$
- Order of a group (h) is the number of elements in the group (can be finite or infinite).



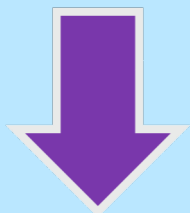
Representational analysis

- A **representation** of any group G is a mapping of the elements of G to a set of $n \times n$ matrices, $\Gamma = \{ \Gamma(g) \mid g \in G \}$, which have the same group structure under matrix multiplication.
 - e.g. $\Gamma(g_1 g_2) = \Gamma(g_1) \Gamma(g_2)$
- Two matrices are equivalent if there is a similarity transformation U between them common to all matrices: $\Gamma'(g) = U \Gamma(g) U^{-1}$

Representational analysis for magnetic structures

- Start with **k**-vector and crystal space group (*G*).
- Select in the crystal space group *G* the symmetry operators *g* that leaves **k** invariant
 - Little group $G_{\mathbf{k}}$ (subgroup of *G*) = $\{g \in G \mid \alpha \mathbf{k} = \mathbf{k} + \mathbf{H}\}$ with $g = \{\alpha \mid \mathbf{t}_\alpha\}$
 - This group $G_{\mathbf{k}} = \{a, b, c, \dots\}$ can have magnetic representation $\Gamma = \{\Gamma(a), \Gamma(b), \Gamma(c), \dots\}$
- Find a similarity transformation *U* that converts all matrices to the same block-diagonal form
 → obtain an equivalent representation that can be decomposed: $\Gamma(g) = U\Gamma(g)U^{-1}$
- **Irreducible Representation (IRs)** are those representations that cannot be reduced further.

Representation



Irreducible representations:

$\Gamma(g) =$

$$\begin{pmatrix} A_{11} & A_{12} & 0 & 0 & 0 & 0 & 0 \\ A_{21} & A_{22} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & B_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & B_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{11} & C_{12} & C_{13} \\ 0 & 0 & 0 & 0 & C_{21} & C_{22} & C_{23} \\ 0 & 0 & 0 & 0 & C_{31} & C_{32} & C_{33} \end{pmatrix}$$

$$= A(g) + 2B(g) + C(g)$$

Matrices $A(g), B(g)$ and $C(g)$ are all representations of the group **G**.

$$\begin{aligned} \Gamma^1 &= \{A(a), A(b), A(c), \dots\} \\ \Gamma^2 &= \{B(a), B(b), B(c), \dots\} \\ \Gamma^3 &= \{C(a), C(b), C(c), \dots\} \end{aligned}$$

Each IR has a set of basis vector → magnetic spin directions

Basis vectors and mixing coefficient

$$\Gamma = \sum_{\oplus \nu} n_{\nu} \Gamma^{\nu} = n_1 \Gamma^1 \oplus n_2 \Gamma^2 \oplus \dots \oplus n_m \Gamma^m$$

- The IRs ($\Gamma^1, \Gamma^2, \dots$) consist of Basis Vectors (BVs) that describe the spin directions which create the symmetry allowed magnetic structures.

For magnetic structures:

$$\mathbf{m}_j = \sum_{\mathbf{k}} \Psi_j^{\mathbf{k}} e^{-2\pi i \mathbf{k} \cdot \mathbf{R}}$$

$\mathbf{k}$: propagating vector
 ν : reference to irrep Γ_{ν}

$$\Psi_j = \sum_{\nu} C_{\nu} \psi_{\nu}$$

Mixing coefficient:
parameters that are varied to
determine the magnetic structure

Basis vector:
Allowed spin direction

Irreducible representation: Notation

$$\Gamma_{\text{mag}} = 1\Gamma_1^{(1)} \oplus 1\Gamma_2^{(2)}$$

- Superscript $\rightarrow$ order of the IR (how many basis vectors of a certain type)
- Subscript $\rightarrow$ just an index or label
- Γ_{mag} contains IR number 1, of order 1, once and IR number 2, of order 2, once.
 - One basis vector associated with Γ_1
 - Two basis vectors associated with Γ_2
- $\oplus \rightarrow$ symmetry spaces are joined (direct sum)

Irreducible representation: Simplification of problem

$$\Gamma = \sum_{\oplus \nu} n_{\nu} \Gamma^{\nu} = n_1 \Gamma^1 \oplus n_2 \Gamma^2 \oplus \dots \oplus n_m \Gamma^m$$

- Can have several IRs describing several possible magnetic structures.

Landau theory: In a second order phase transition, a single symmetry mode is involved
→ **Only one IR needed to determine magnetic structure**

Using representational analysis: don't panic, lots of tools!

Determine
crystal
structure

Fullprof,
JANA,
TOPAS,
(GSAS-II)

Find k-vector

Fullprof

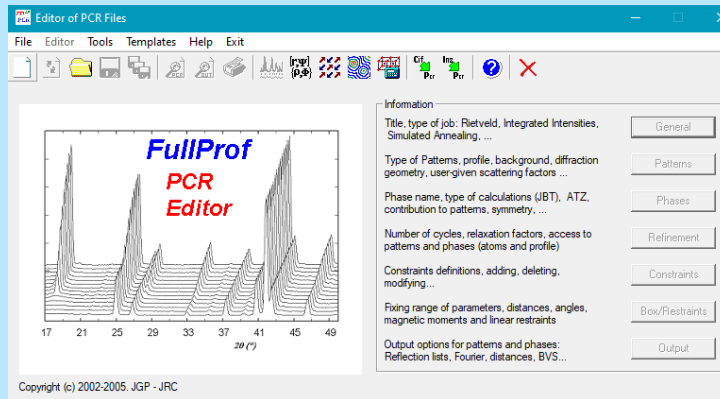
Find irreducible
representations
(IR) and Basis
vectors (BV)

SARAh
ISODISTORT
Basireps

Refine
coefficients
for BVs

Fullprof,
JANA,
TOPAS

Magnetic
structure



Wills Group

Magnetism and magnetic materials

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SOFTWARE

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DOCUMENTS/PAPERS

OTHER

SARAh – web Representational Analysis

ISODISTORT SUITE HELP

ISODISTORT

Version 6.11.1, Jan 2022

Harold T. Stokes, Branton J. Campbell, and Dorian M. Hatch, Department of Physics and Astro

Description: ISODISTORT is a user-friendly internet-based tool for exploring the structural dist one to visualize and interactively manipulate the modes generated in ISODISTORT.

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/>

The goal is to use symmetry to produce distinct allowed magnetic structures, that can then be tested against the neutron data to find the most likely magnetic structure(s),

Wills Group

Magnetism and magnetic materials

HOME

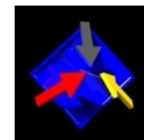
SOFTWARE

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 introduced 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
- ValList – 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\crd\Downloads
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 REFINE - 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 irreps and 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)



1. Conventional basis vectors (as projected)	2. Stationary vector combinations	3. Exchange multiplets	4. Help and strategies
---	-----------------------------------	------------------------	------------------------

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 ▾

☐ Mn2 Γ_1 ψ_1	☐ Mn2 Γ_2 ψ_3	☐ Mn2 Γ_4 ψ_2
☐ Mn2 Γ_1 ψ_2	☐ Mn2 Γ_3 ψ_1	☐ Mn2 Γ_4 ψ_3
☐ Mn2 Γ_1 ψ_3	☐ Mn2 Γ_3 ψ_2	
☐ Mn2 Γ_2 ψ_1	☐ Mn2 Γ_3 ψ_3	
☐ Mn2 Γ_2 ψ_2	☐ 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

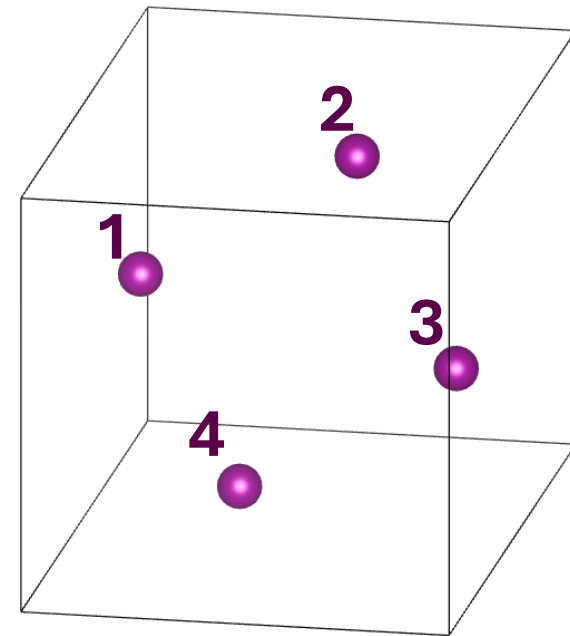
Appendix 1. Input used in the calculations and for reporting in articles :

Space group : P 1 21/c 1
k vector (input, user setting) : {0., 0., 0.}
k vector (used, user setting) : {0., 0., 0.}
k vector (primitive, Kovalev's tables): {0, 0, 0} = {k7, {0, 0, 0}}
Mn2 {0.51042, 0.1262, 0.60077}

Symmetry related positions used to define the basis vectors (these coordinates should always be given when listing basis vectors) :

Mn2	1:	0.51042	0.1262	0.60077
	2:	0.48958	0.6262	0.89923
	3:	0.48958	0.8738	0.39923
	4:	0.51042	0.3738	0.10077

Four Mn magnetic ions per unit cell



Step 3: Create candidate magnetic models using SARAh

$\Gamma_1 \psi_1$	$\Gamma_1 \psi_2$	$\Gamma_1 \psi_3$
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.

$\Gamma_2 \psi_1$	$\Gamma_2 \psi_2$	$\Gamma_2 \psi_3$
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.

$\Gamma_3 \psi_1$	$\Gamma_3 \psi_2$	$\Gamma_3 \psi_3$
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.

$\Gamma_4 \psi_1$	$\Gamma_4 \psi_2$	$\Gamma_4 \psi_3$
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.

- In this case all irreps can 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

- The terms IR, irreps, Gamma all typically refer to the same thing: the irreducible representations (Γ).
- The basis vectors, BVs describe the specific spin directions of the irreps.

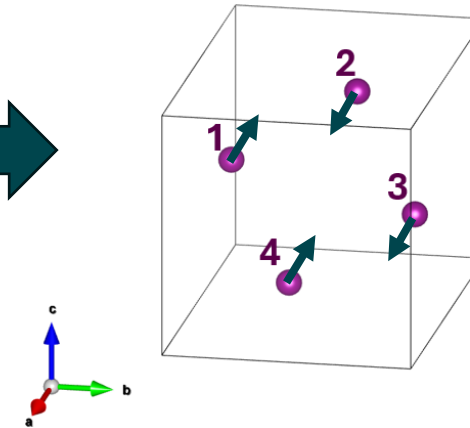
Step 3: Create candidate magnetic models using SARAh

Consider first IR (Γ_1)

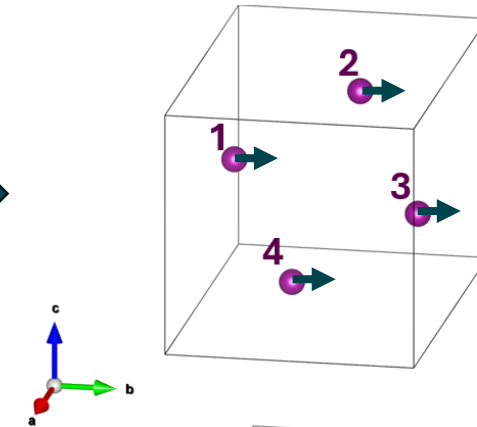
Table. The basis vectors projected from the different IRs :

$\Gamma_1 \psi_1$ 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.

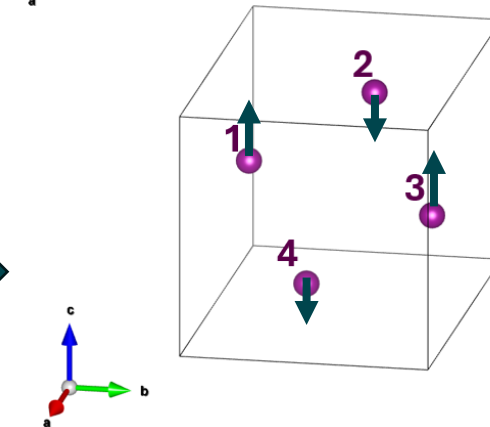
$\Gamma_1 \psi_1$
Mn2 1) 1. 0. 0.
2) -1. 0. 0.
3) 1. 0. 0.
4) -1. 0. 0.



$\Gamma_1 \psi_2$
Mn2 1) 0. 1. 0.
2) 0. 1. 0.
3) 0. 1. 0.
4) 0. 1. 0.



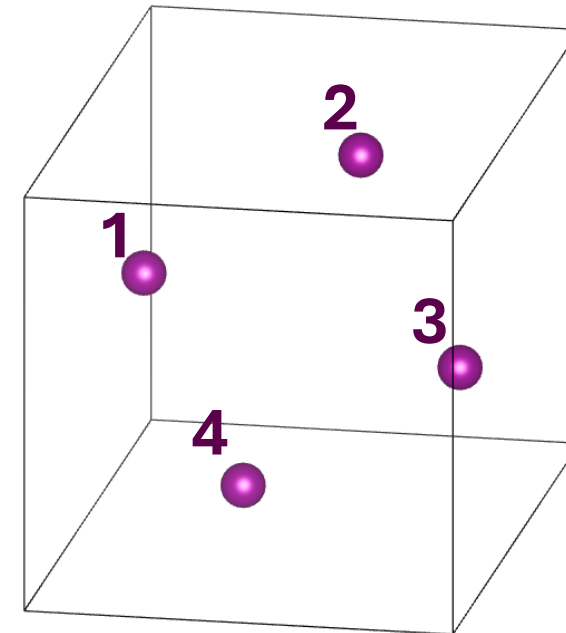
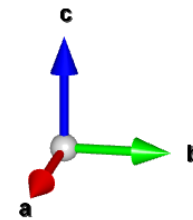
$\Gamma_1 \psi_3$
Mn2 1) 0. 0. 1.
2) 0. 0. -1.
3) 0. 0. 1.
4) 0. 0. -1.



Step 3: Create candidate magnetic models using SARAh

You can do this for all the IRs to see what possible magnetic structures are.

$\Gamma_1 \psi_1$ 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.



Step 3: Create candidate magnetic models using SARAh

- Now we have the potential models (4 IRs, each with 3 basis vectors) we can start to test the models against our data using Fullprof.
- **We need to create a magnetic phase in Fullprof.**

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.

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)

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 Wolfram

1. Conventional basis vectors (as projected)	2. Stationary vector combinations	3. Exchange multiplets	4. Help and strategies
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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 for fit No file chosen

☐ Mn2 $\Gamma_1 \psi_1$ ☐ Mn2 $\Gamma_3 \psi_1$ ☐ Mn2 $\Gamma_4 \psi_2$

☐ Mn2 $\Gamma_1 \psi_2$ ☐ Mn2 $\Gamma_3 \psi_2$ ☐ Mn2 $\Gamma_4 \psi_3$

☐ Mn2 $\Gamma_1 \psi_3$ ☐ Mn2 $\Gamma_3 \psi_3$

☐ Mn2 $\Gamma_2 \psi_1$ ☐ Mn2 $\Gamma_4 \psi_1$

☐ Mn2 $\Gamma_2 \psi_2$

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

☐ Mn2 Γ_1 ψ_1

☐ Mn2 Γ_1 ψ_2

☐ Mn2 Γ_1 ψ_3

☐ Mn2 Γ_2 ψ_1

☐ Mn2 Γ_2 ψ_2

☐ Mn2 Γ_2 ψ_3

☐ Mn2 Γ_3 ψ_1

☐ Mn2 Γ_3 ψ_2

☐ Mn2 Γ_3 ψ_3

☒ Mn2 Γ_4 ψ_1

☒ Mn2 Γ_4 ψ_2

☒ Mn2 Γ_4 ψ_3

(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 on these slides, but ALL IRs should be tested.
- All were tested for the paper (and some are actually close).

Mn-pyrazinecarboxylate

This example will use Fullprof and SARAh <http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>

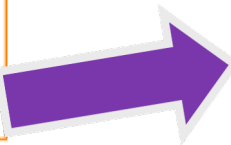
- Step 1: Refine the crystal structure using FullProf
- Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
- Step 3: Create candidate magnetic models using SARAh
- **Step 4: Refine the magnetic model and nuclear phase in Fullprof.**
- Step 5: Check the magnetic model

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

The 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.



```
!-----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 C1 C2 C3
! C4 C5 C6 C7 C8 C9 MagPh
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 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
```

To give these basis vectors magnitude put values in the coefficients C1 and C2 an C3

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

Turn on C1,C2,C3 to refine in the pcr text file. This will give moment along the a-axis.

Also update the Mn ion to MMN2 (this is magnetic Mn^{2+}). The form factor is selected by the valence 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 Irep 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 MMN2 5 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 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
! 0.00000 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.

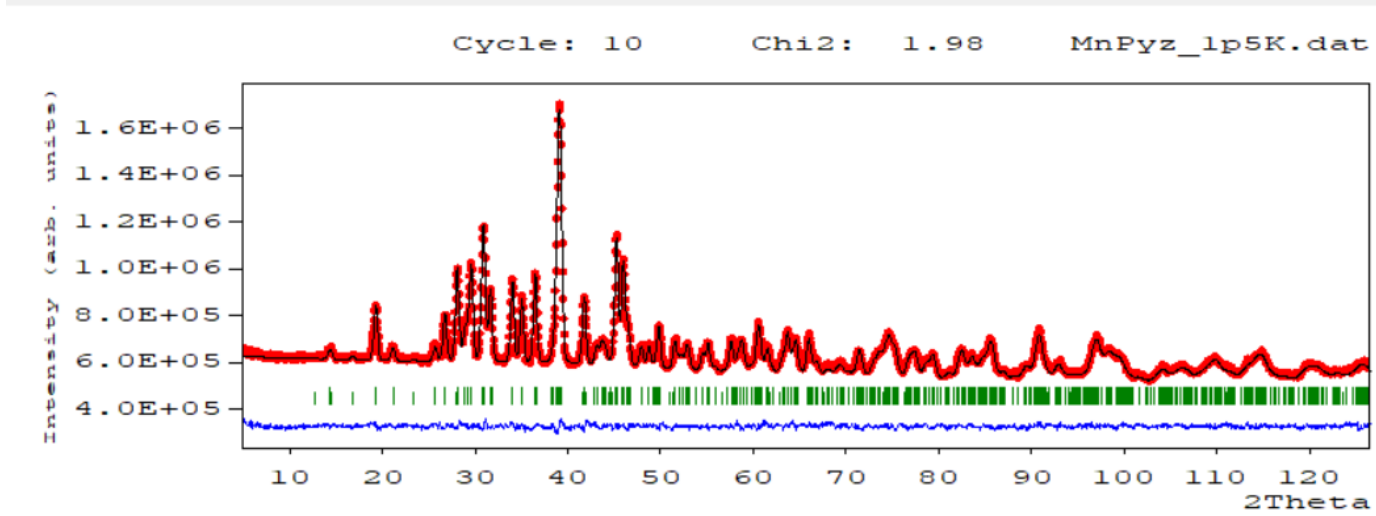
Check if all basis vectors are needed by setting C1, C2 or C3 to zero.

To improve the fit, try refining the peak shapes, background, atom positions, lattice constants, etc

```
FullProf Program
=> Expected :          0.772          1.8813
=> Conventional Rietveld R-factors for Pattern:          1
=> Rp:  7.36      Rwp:  6.72      Rexp:   4.77          Chi2:  1.98
=> Global user-weighted Chi2 (Bragg contrib.):   2.045
=> -----> Pattern#          1
=> Phase:          1
=>   Bragg R-factor:   2.211
=>   RF-factor       :   1.331
=> Phase:          2
=> Magnetic R-factor:   7.732
=> Normal end, final calculations and writing...

=> CPU Time:       5.922 seconds
=> 0.099 minutes

=> END   Date:16/07/2024   Time => 23:01:11.971
```



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

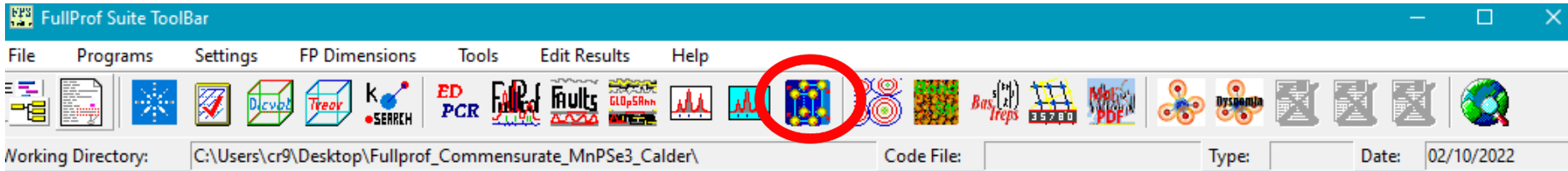
This example will use Fullprof and SARAh <http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/>

- 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

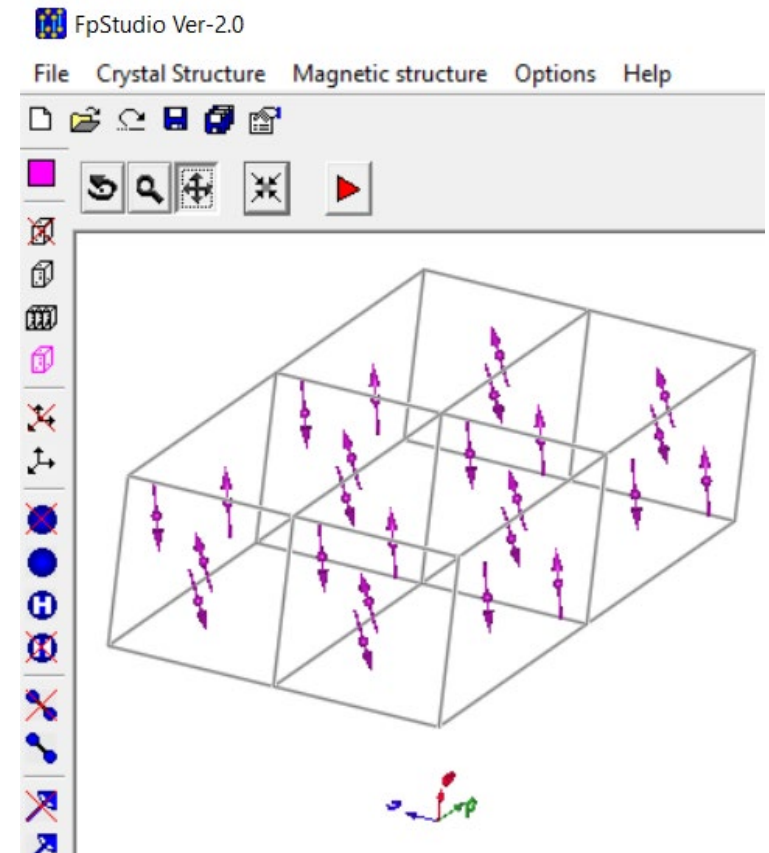
The model can be checked in FPStudio

MnPyz_Gamma4
MnPyz_Gamma4
MnPyz_Gamma4
MnPyz_Gamma41
MnPyz_Gamma41.mic
MnPyz_Gamma42
MnPyz_Gamma42
MnPyz_Gamma42



- 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									
Atom : Mn2_1 Mn									



Step 5: Check the magnetic model

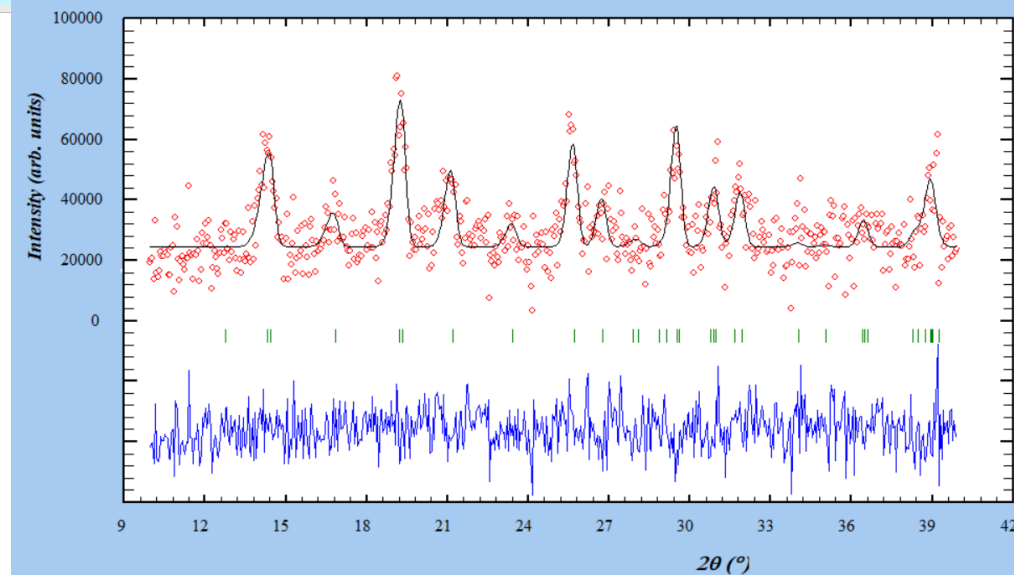
There is a dataset

“diff_1p5Kminus20K_offset_so_no_negative_intensities.dat”. This is the difference between the 1.5 K data and the 20 K data. This can be treated as the magnetic only scattering.

In the pcr file remove the nuclear phase1 and just keep the magnetic phase. Then try refining this to the data.

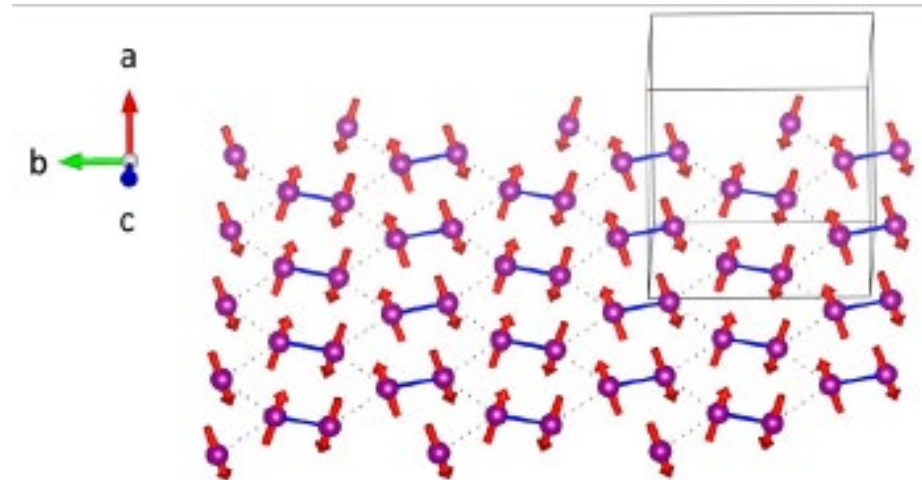
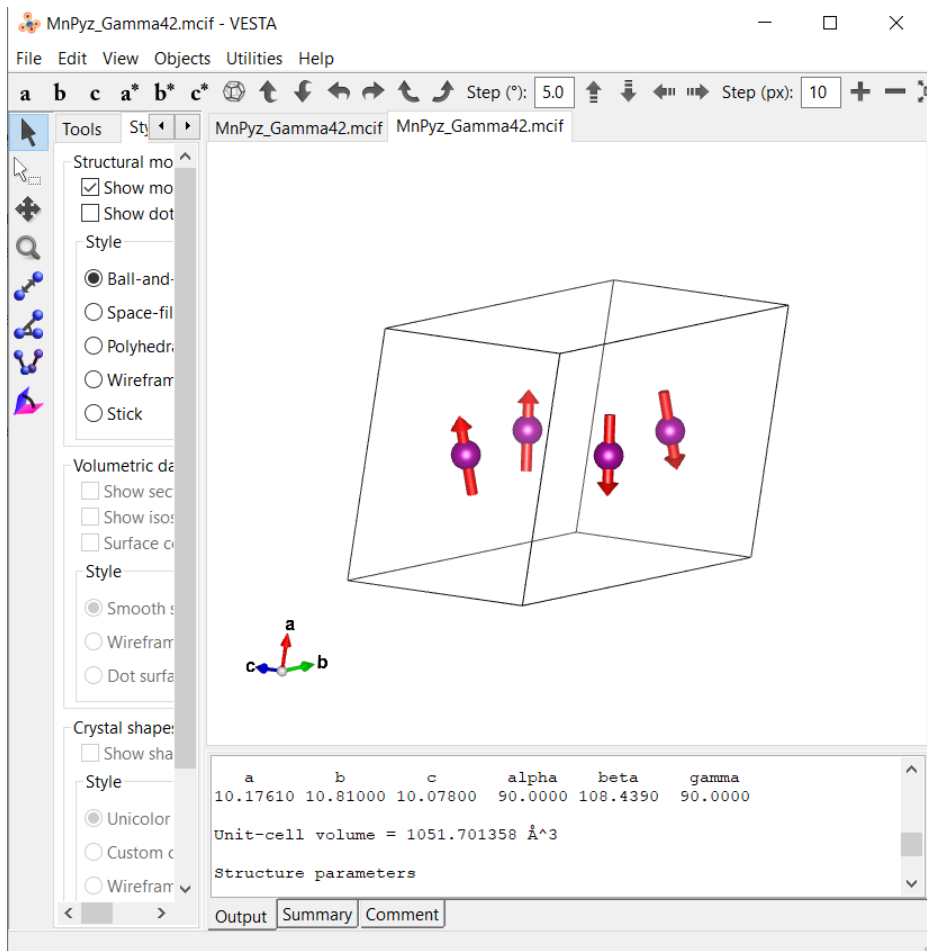
Examples are in the backup folder.

This will help to convince you of the best fit magnetic structure.



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

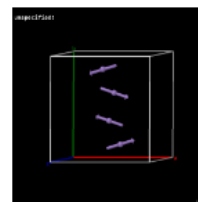
MAGNDATA: A Collection of magnetic structures with portable cif-type files

Log

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

To upload any published structure click [HERE](#)

Enter the label of the structure:



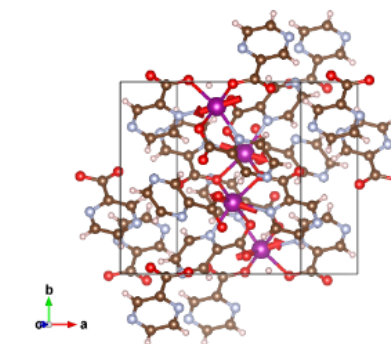
$\text{C}_{10}\text{H}_6\text{MnN}_4\text{O}_4$ (#0.1010)

[view in Jmol](#)

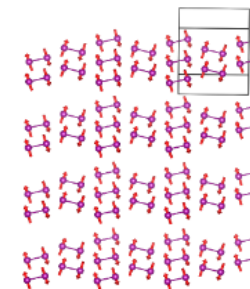
[Download mcif file](#)

[Download vesta file \(all atoms\)](#)

[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)