OAK RIDGE National Laboratory

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

Stuart Calder

MagStr, ORNL, 2024

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

Mn-pyrazinecarboxylate

DOI: 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

S. Calder,[1,*] R. Baral,[1] N. Narayanan,[2] and L. D. Sanjeewa[2,3]
[1]*Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[2]*University of Missouri Research Reactor (MURR), University of Missouri, Columbia, Missouri 65211, USA*
[3]*Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA*

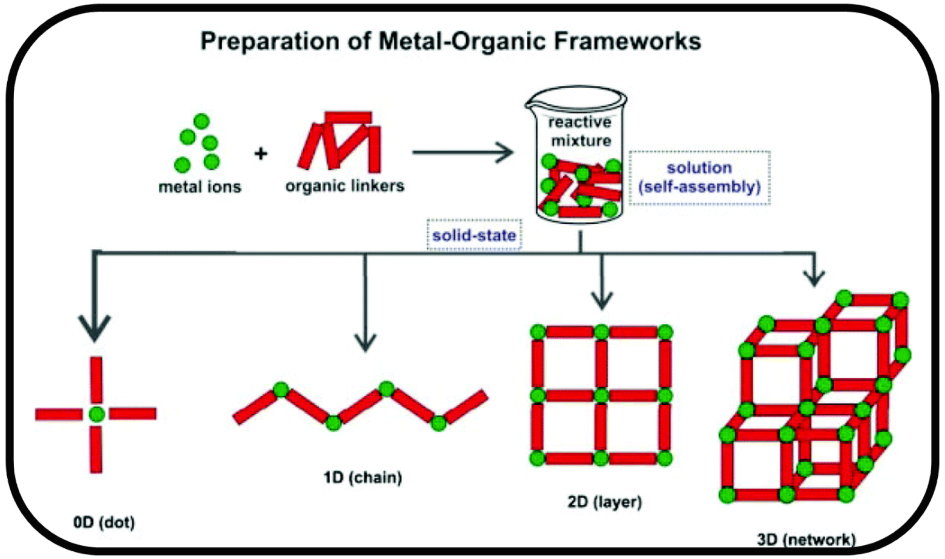
(Received 29 September 2023; revised 8 November 2023; accepted 28 November 2023; published 15 December 2023)

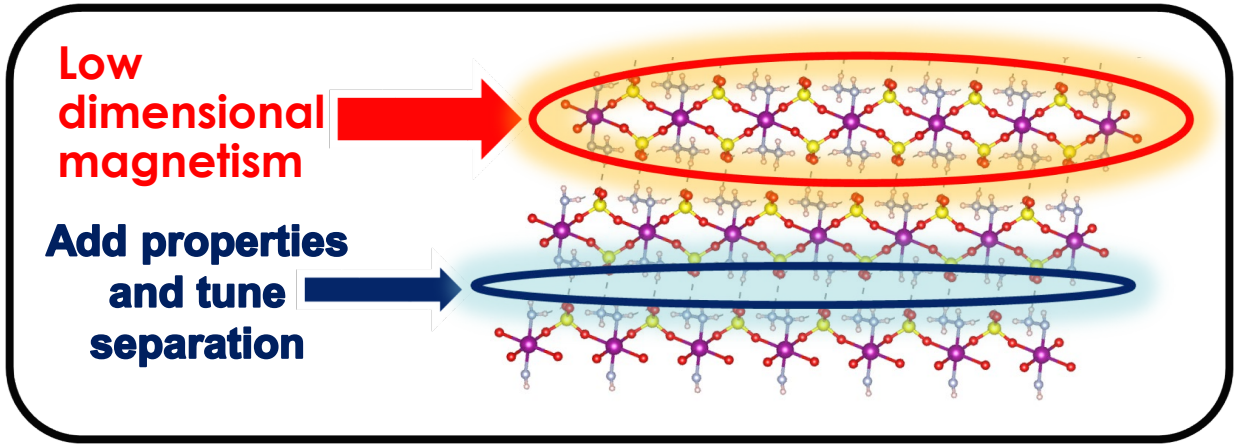
The magnetic properties of $[Mn(pyrazinecarboxylate)_2]_n$, empirical formula $C_{10}H_6MnN_4O_4$, are investigated through susceptibility, heat capacity, and neutron scattering measurements. The structure consists of Mn-Mn dimers linked on a distorted 2D hexagonal structure. The weak out-of-plane interactions 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

Quantum behavior by design in low dimensional Magnetic MOFs

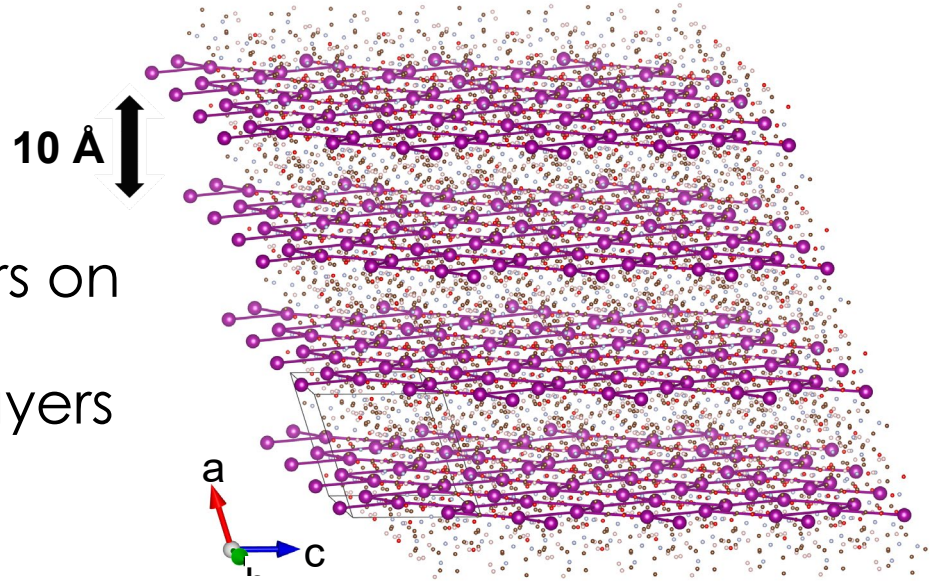
- **Magnetism largely unexplored**
- **Straightforward synthesis to tune low dimensional behavior.**
  - Design quantum behavior on regular lattice.
  - Multifunctionality on magnetic and organic building blocks.
  - Tunable by small pressure, field, strain, light.



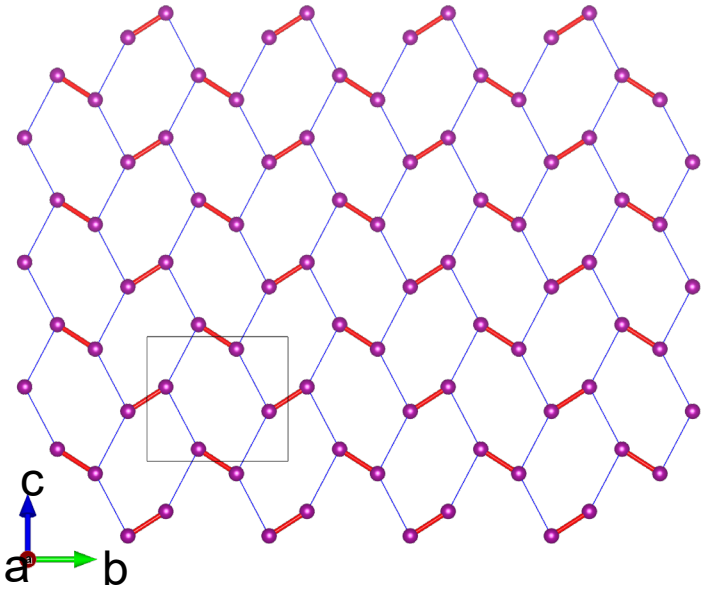


Mn-pyrazinecarboxylate ($Mn(2\text{-}pzc)_2$) $C_{10}H_6MnN_4O_4$

- 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

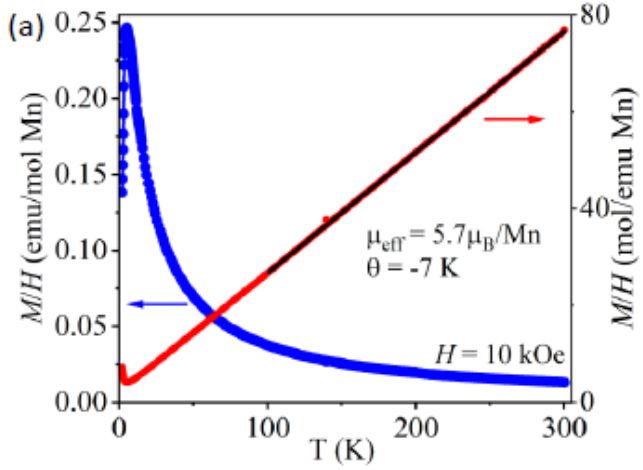
a	b	c	alpha	beta	gamma
10.19000	10.90600	10.11600	90.0000	107.9600	90.0000

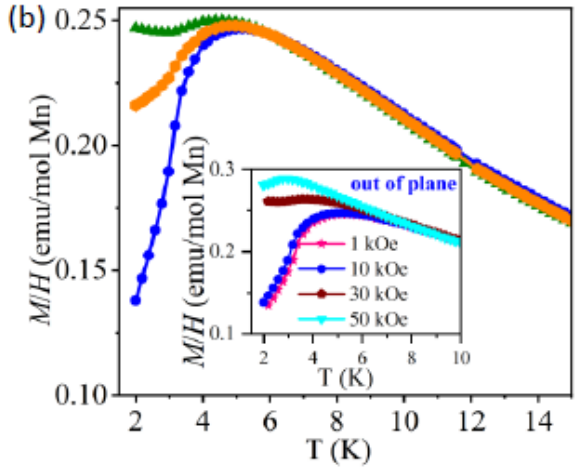
Structure parameters

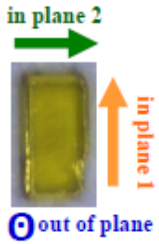
	x	y	z	Occ.	U	Site	
Mn	0.510090	0.134260	0.598000	1.000	0.024	4e	
O	0.541000	0.244300	0.426600	1.000	0.023	4e	
N	0.360600	0.299100	0.562100	1.000	0.031	4e	
C	0.262700	0.325100	0.619200	1.000	0.038	4e	
H	0.254640	0.276940	0.691940	1.000	0.034	4e	
O	0.475200	0.405900	0.287300	1.000	0.041	4e	
N	0.180200	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	0.038	4e	
N	0.738100	0.176100	0.700600	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	0.034	4e	
N	1.018200	0.234100	0.767400	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	

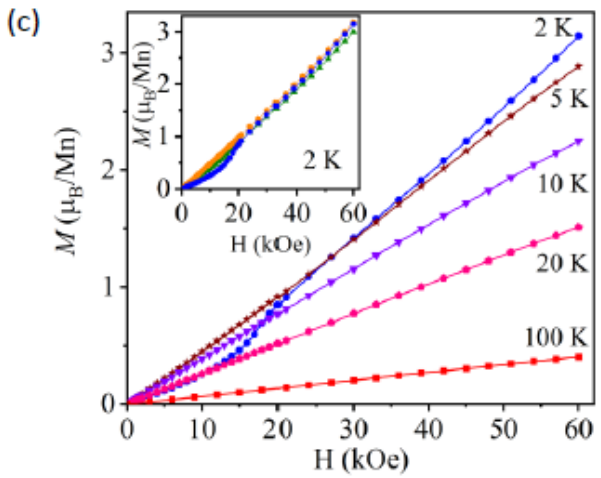
Magnetic susceptibility and heat capacity

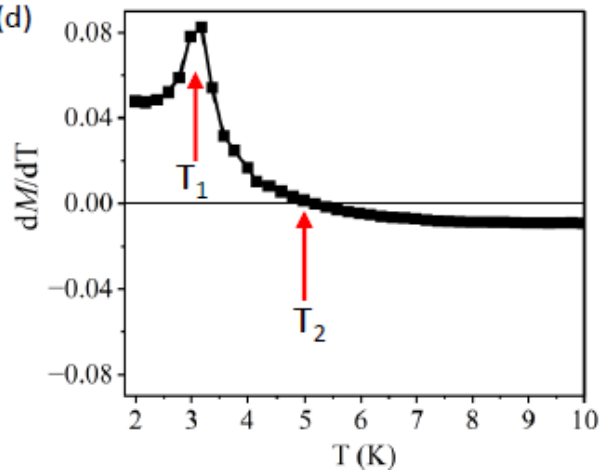
- Two-stage transition T_1=3.3 K and T_2=5 K
- Can fit magnetic susceptibility to dimer models in interactions J = -0.11meV

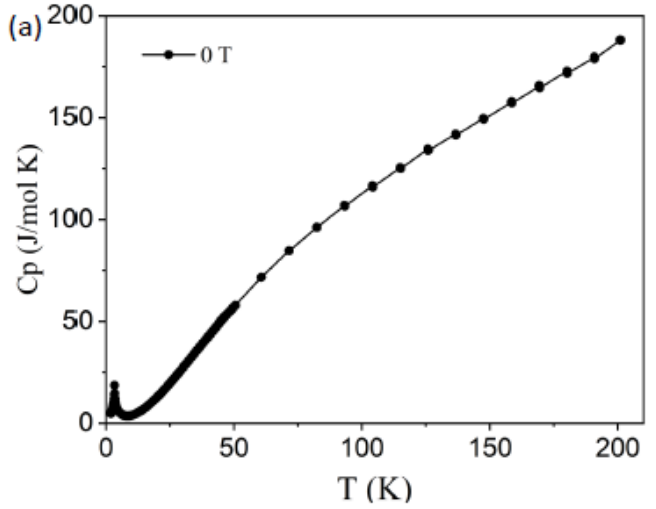


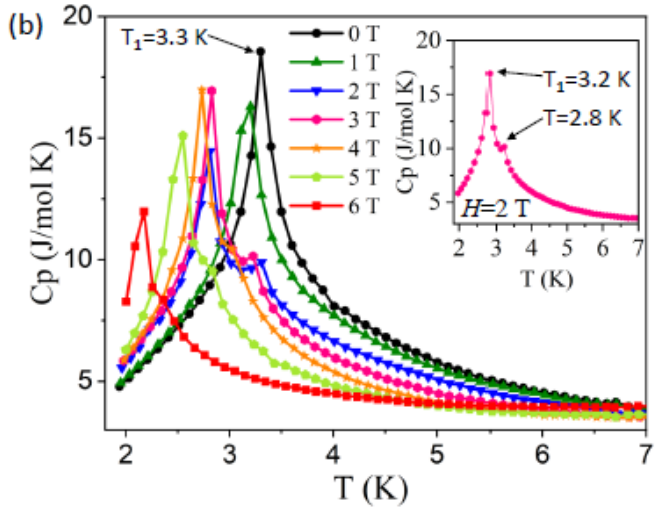






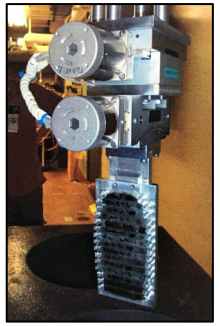


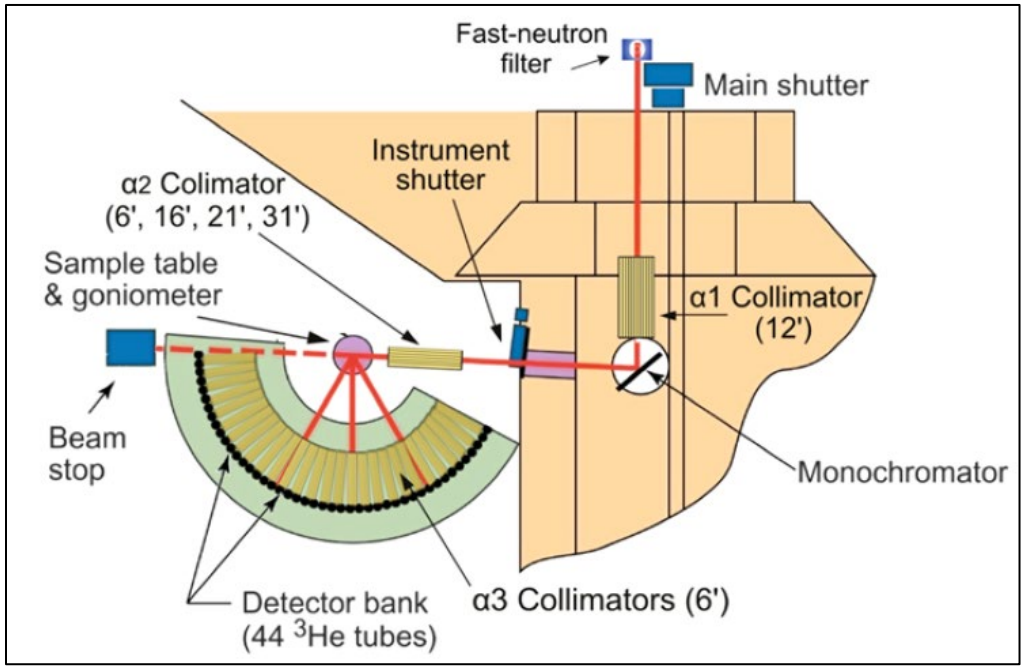




$Cs_2Fe_2(MoO_4)_3$: Neutron measurements on HB-2A, HFIR.

- Constant wavelength
- Germanium monochromator
  - ~90° take off angle for medium-high resolution
  - Variety of complex sample environments: 50mK, 6 Tesla, 2GPa pressure…
- Current detector is an array of 44 individual ^{3}He tubes
  - Low background
  - Covers ~2-150° in 2θ by scanning detector
  - **MIDAS detector upgrade coming soon!**





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

https://neutrons.ornl.gov/powder

S. Calder, MagStr 2024 ORNL

HB-2A instrument resolution and peak shape

MYRESOL.irf

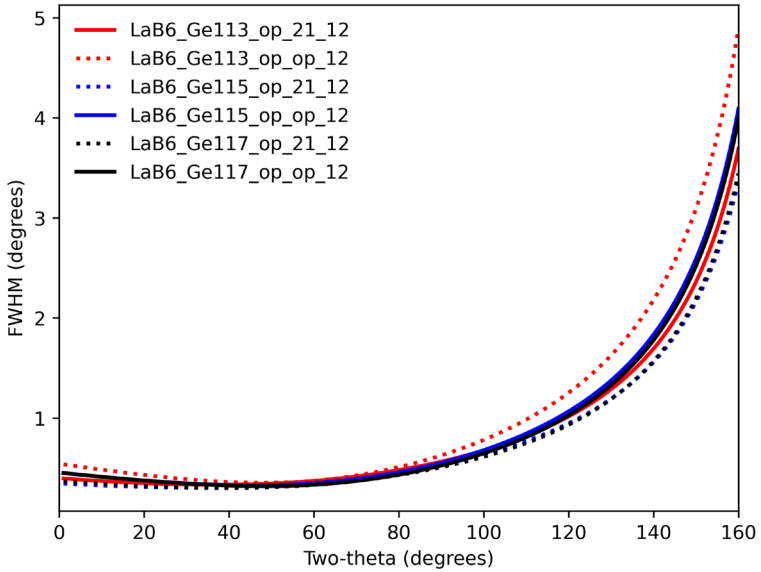
This file is read only when Res≠0. The name of the file is stored in the character variable FILERES= *MYRESOL.irf*. All items are read in free format.

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

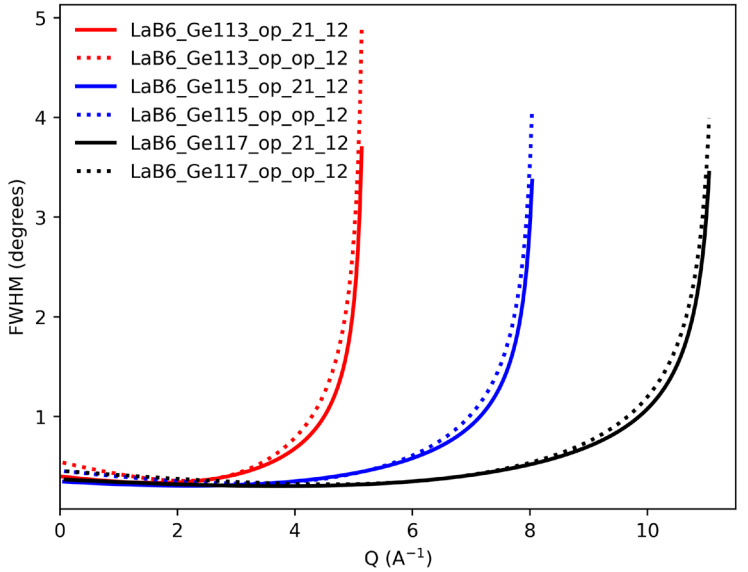
The different types of functions are:

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

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



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



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

DESIGN FOR A CONVENTIONAL HIGH-RESOLUTION NEUTRON POWDER DIFFRACTOMETER

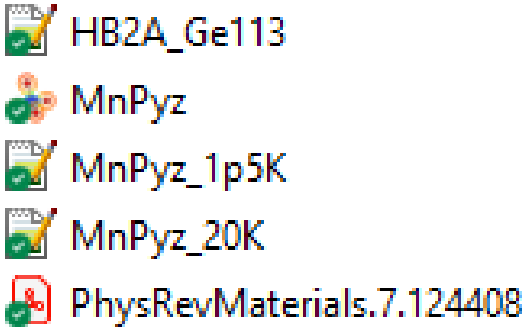
A. W. HEWAT

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

Received 14 April 1975

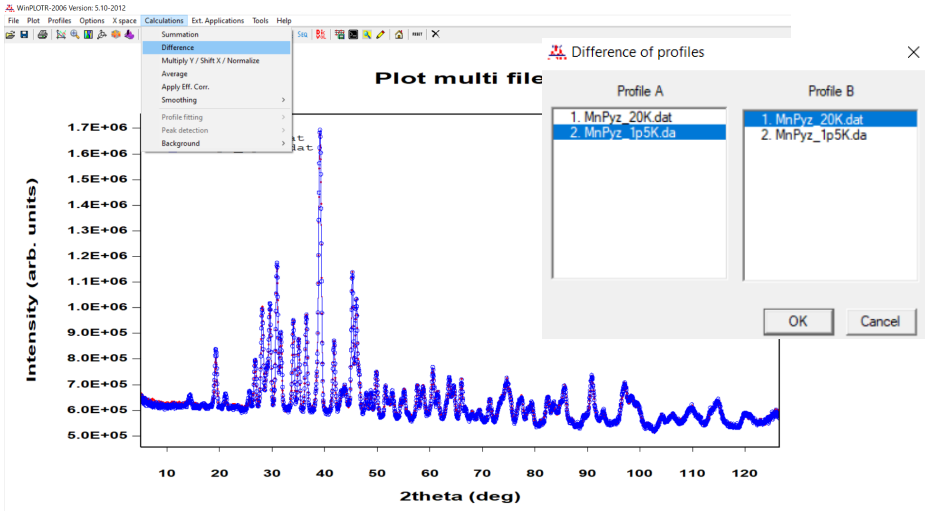
Details of this Mn-pyrazinecarboxylate example

- Neutron powder diffraction data collected at HB2A, HFIR
- λ = 2.41 Å. 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**

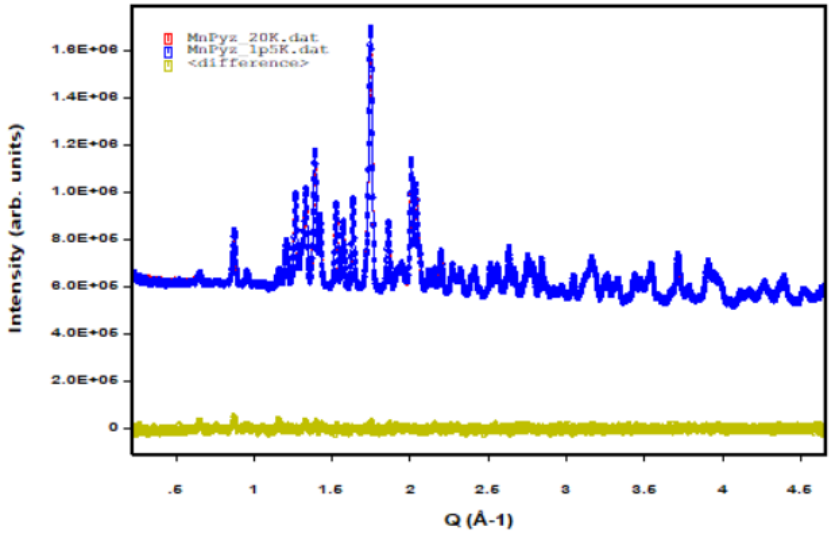


Neutron data from HB-2A

- 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



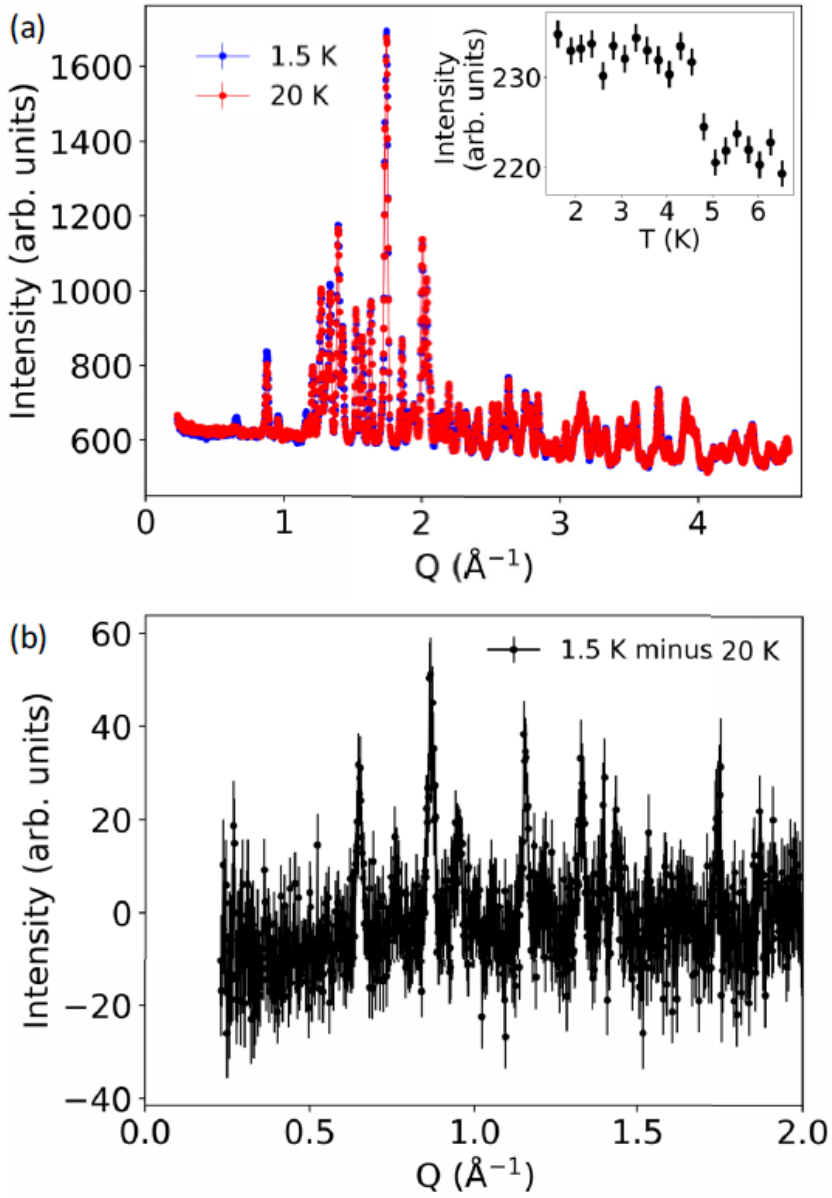


FIG. 5. (a) Neutron powder diffraction data collected at 1.5 K and 20 K. Inset: Intensity at Q = 0.65 Å as a function of temperature through the magnetic transition. (b) Difference of intensity at 1.5 K and 20 K in the powder diffraction data.

Mn-pyrazinecarboxylate

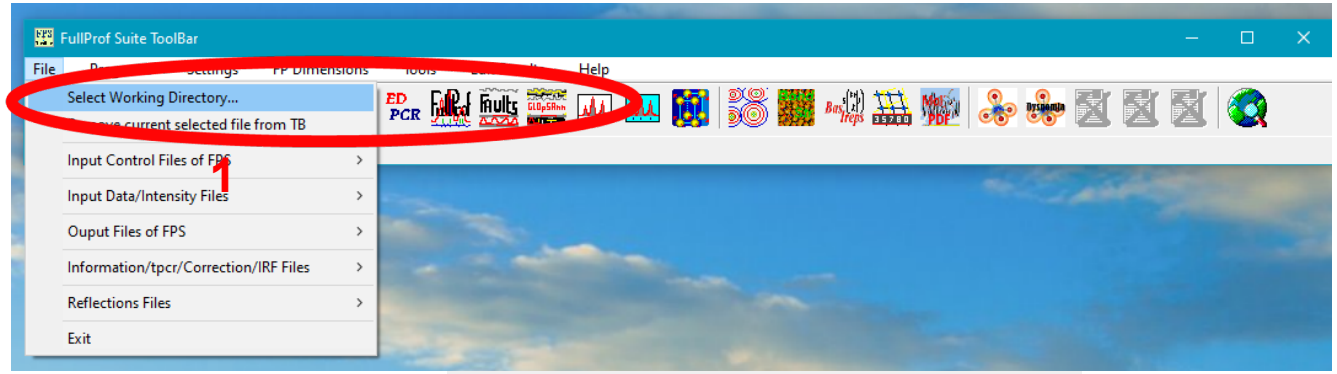
- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
  - Step 3: Create candidate magnetic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

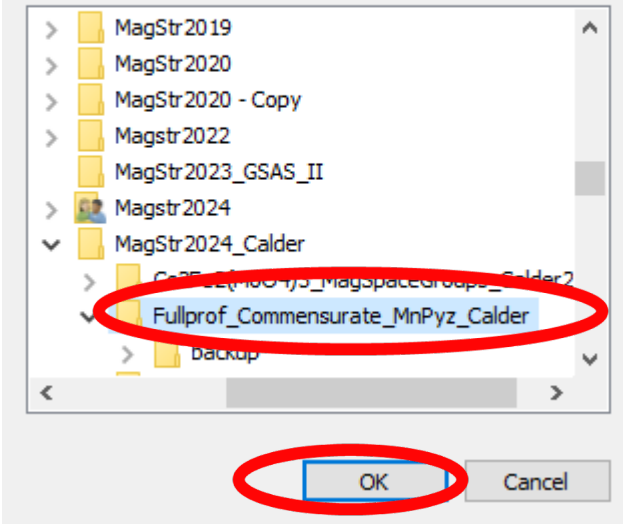
Mn-pyrazinecarboxylate

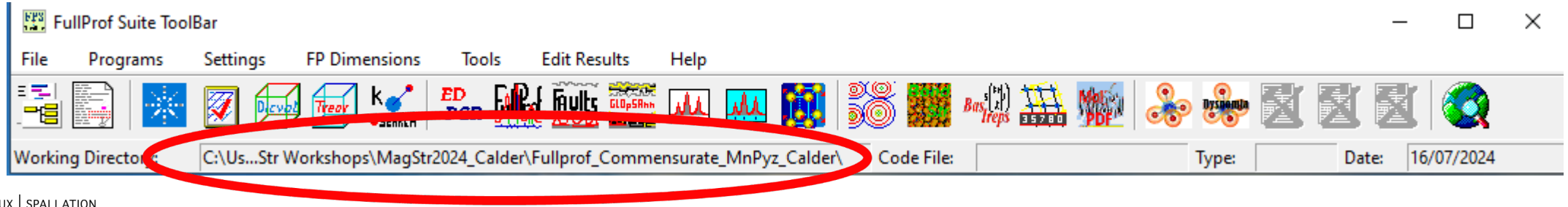
- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - **Step 1: Refine the crystal structure using FullProf**
  - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
  - Step 3: Create candidate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

Step 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







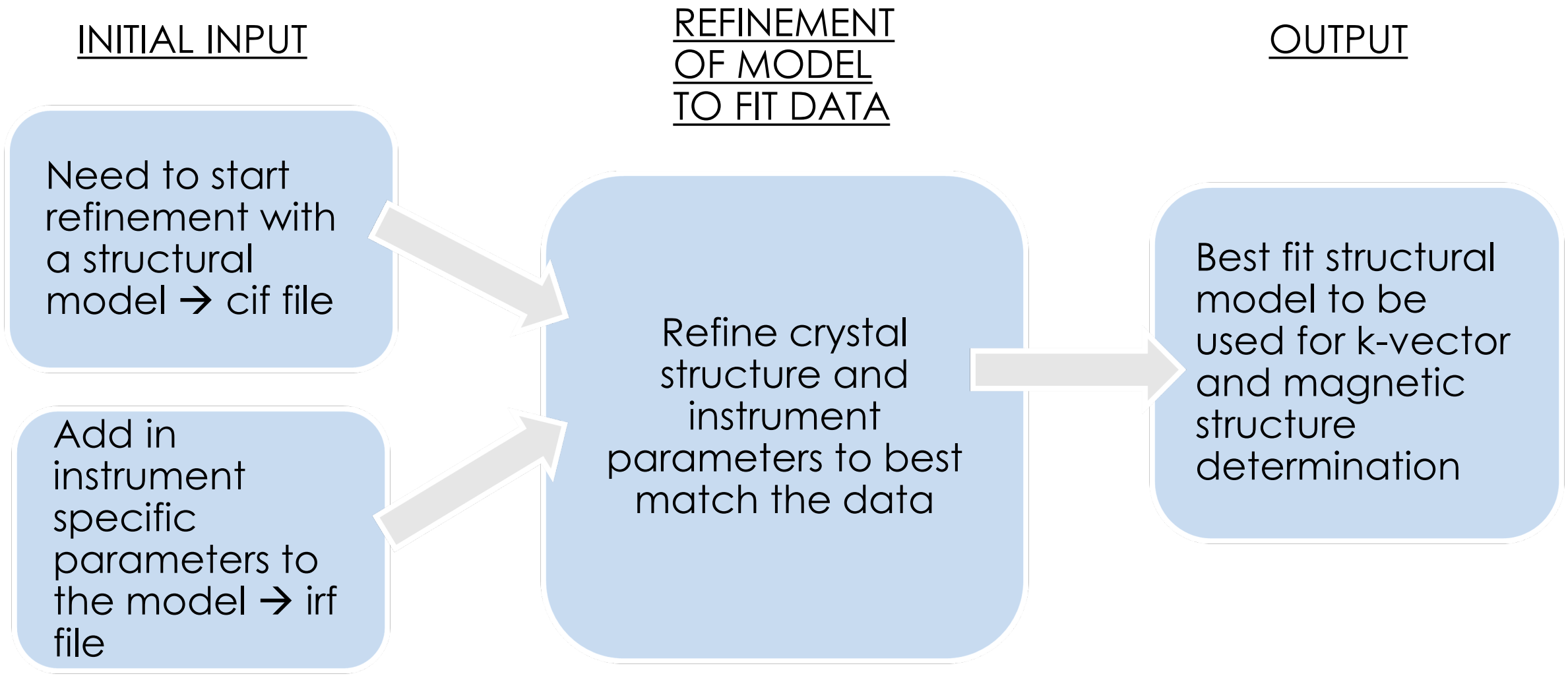
Step 1: Refining the crystal structure using Fullprof

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

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

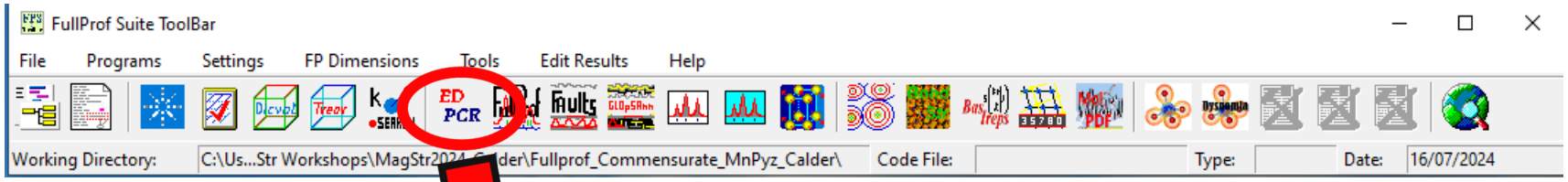
- Then refine this model.

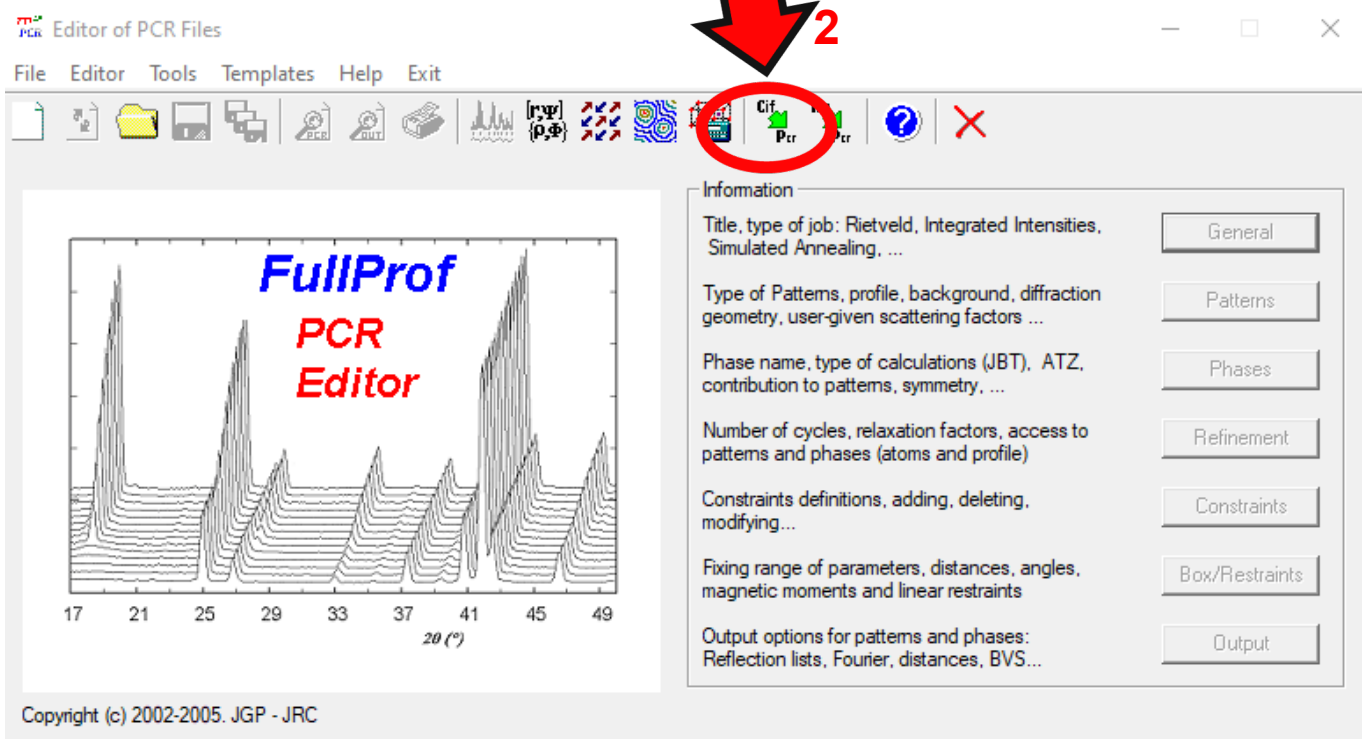
Step 1: Refining the crystal structure using Fullprof

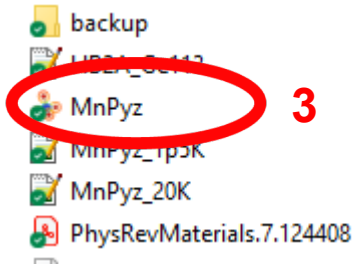


Step 1: Refine the crystal structure using FullProf

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



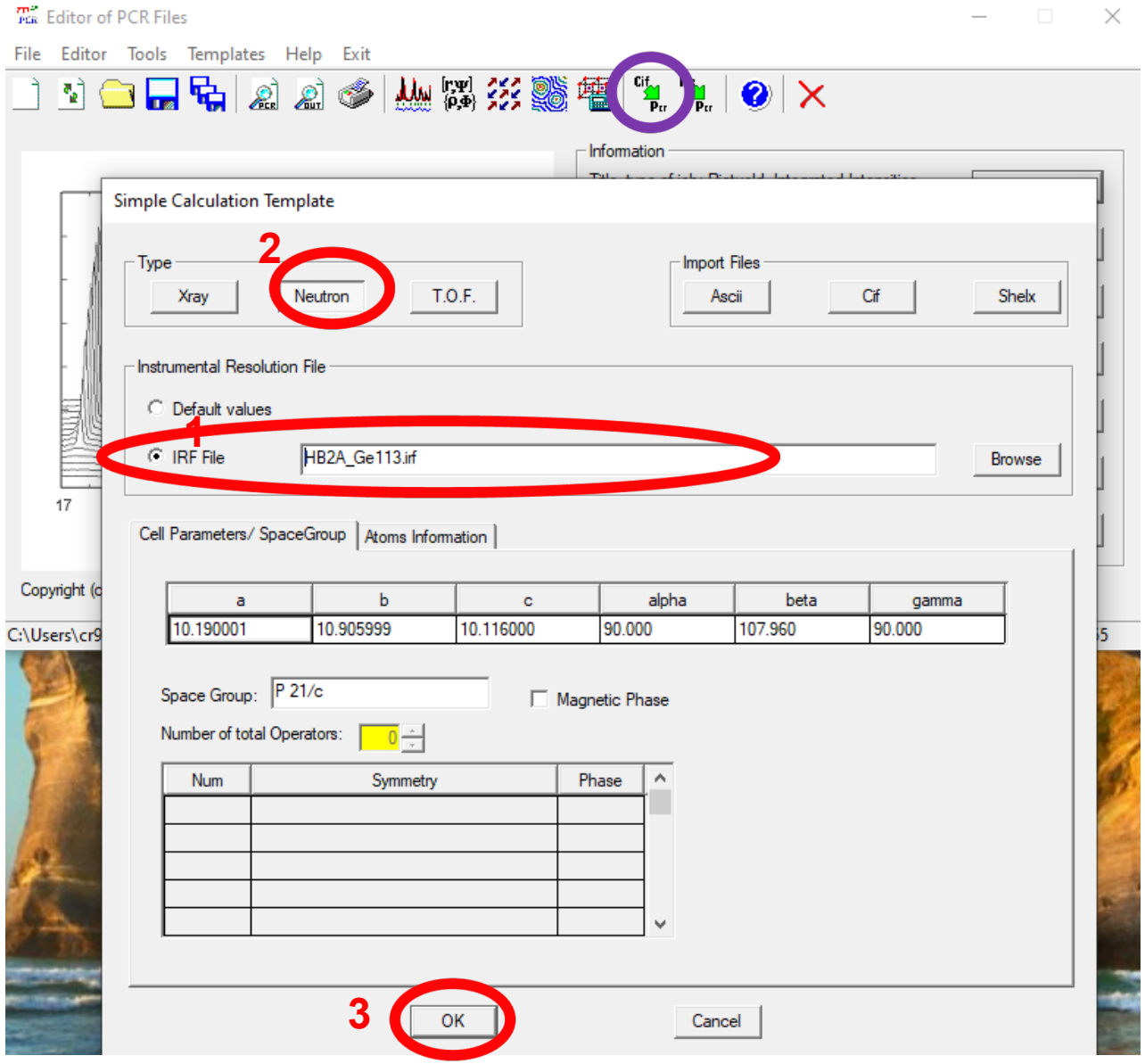




Step 1: Refine the crystal structure using FullProf

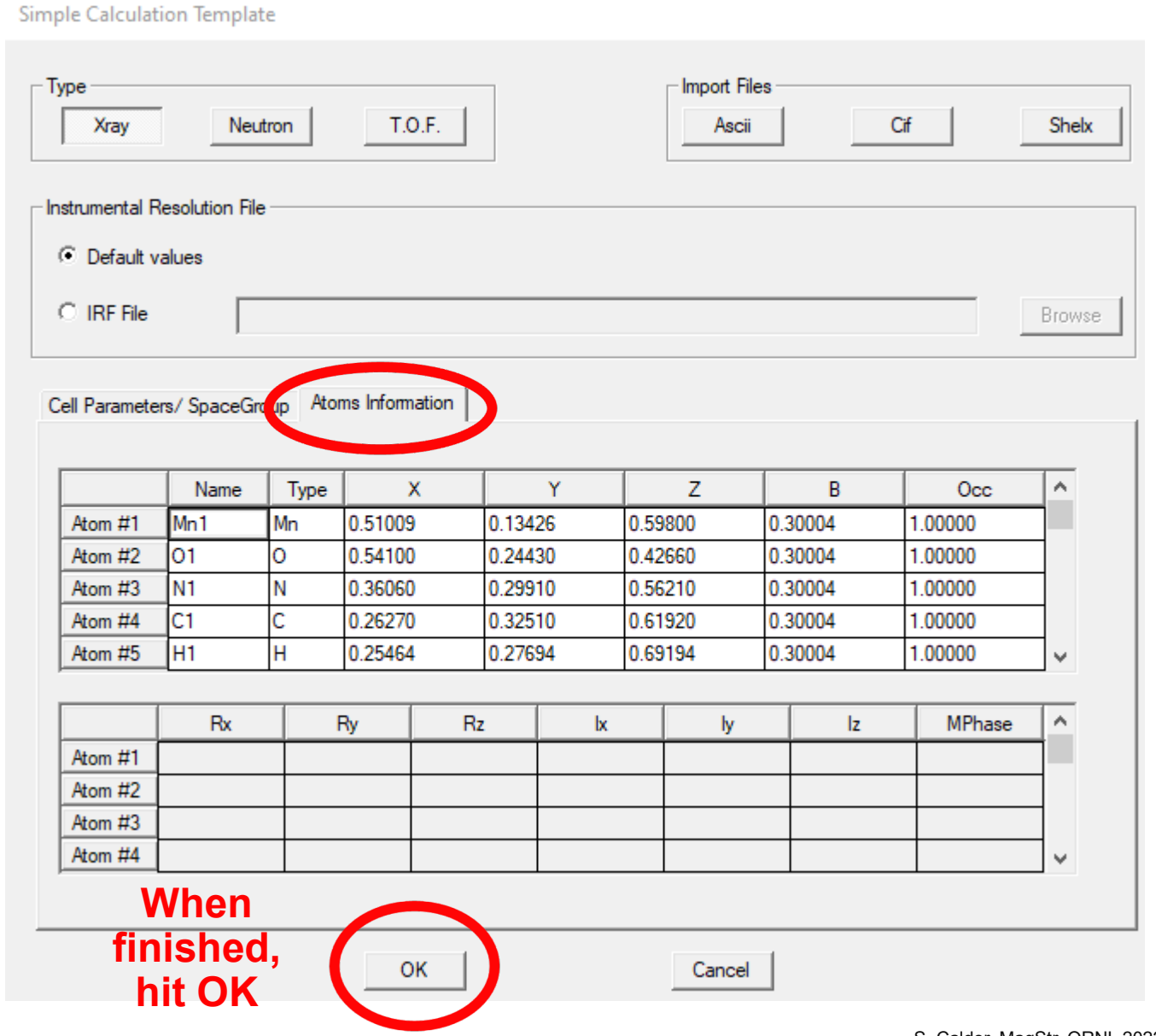
Cif→PCR opens a window to input instrument and shows structural info.

- **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"



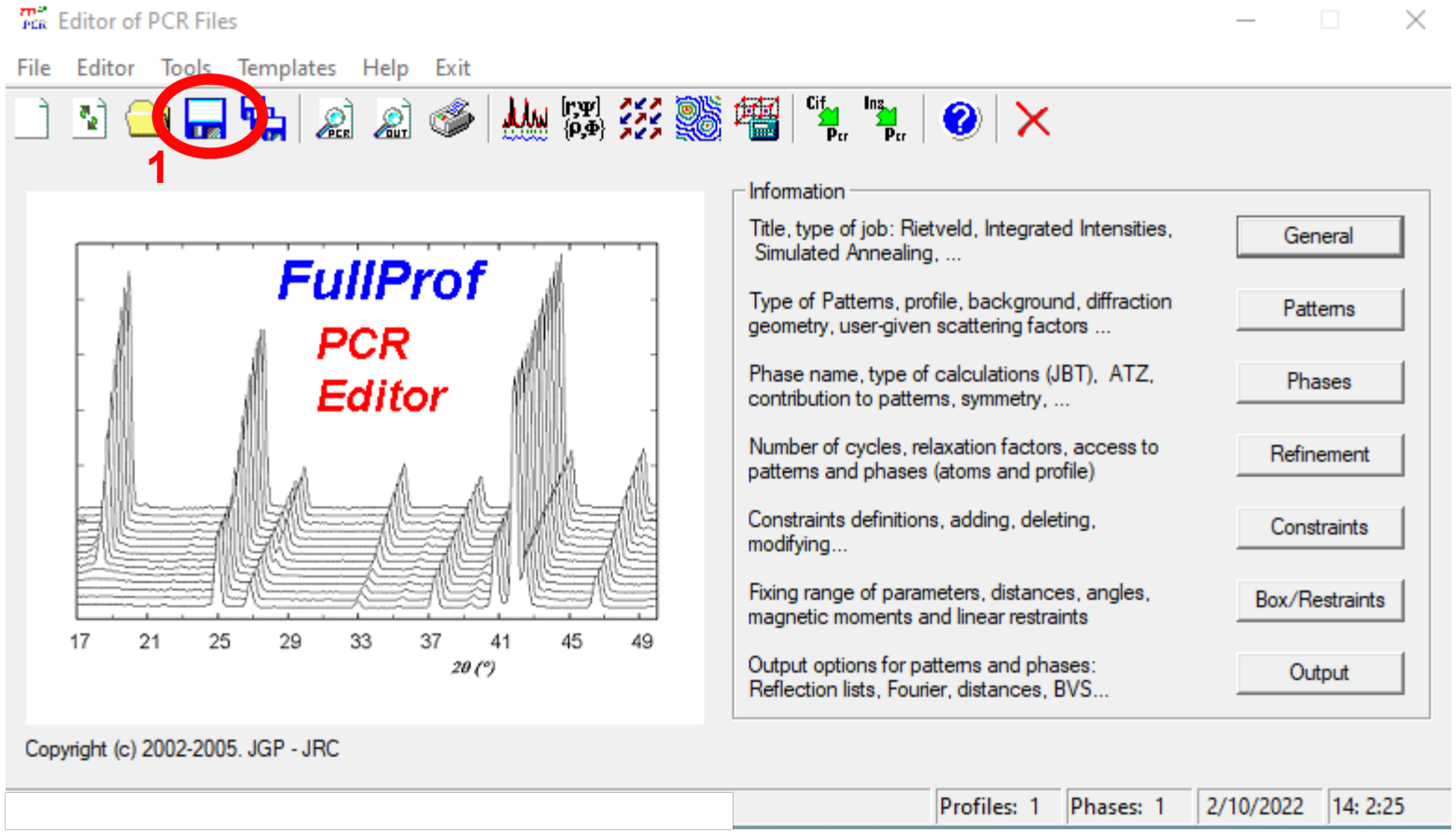
Step 1: Refine the crystal structure using FullProf

- 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



Step 1: Refine the crystal structure using FullProf

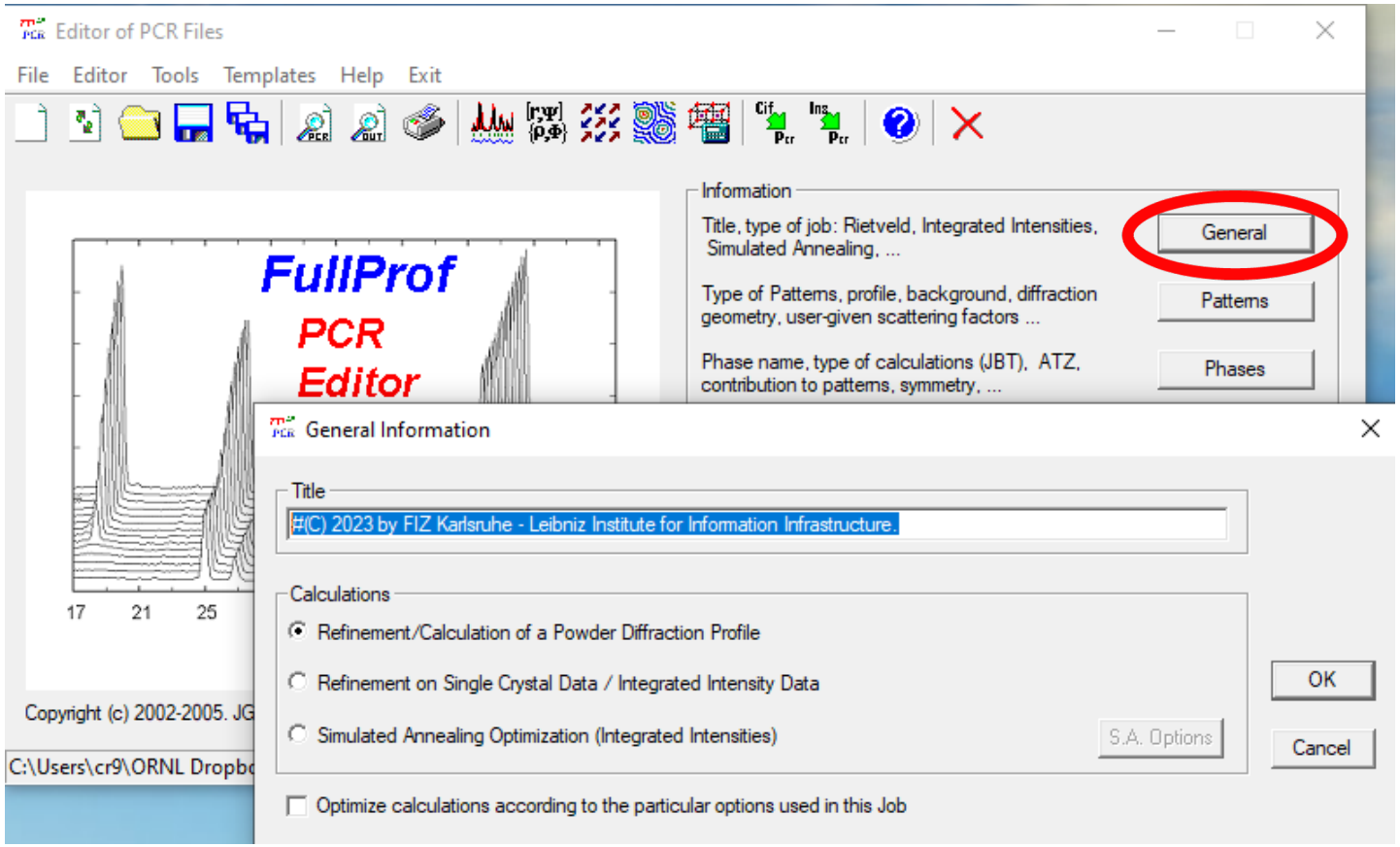
- **1.** Save the changes.
- This should be done whenever changes are made in the GUI.



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.

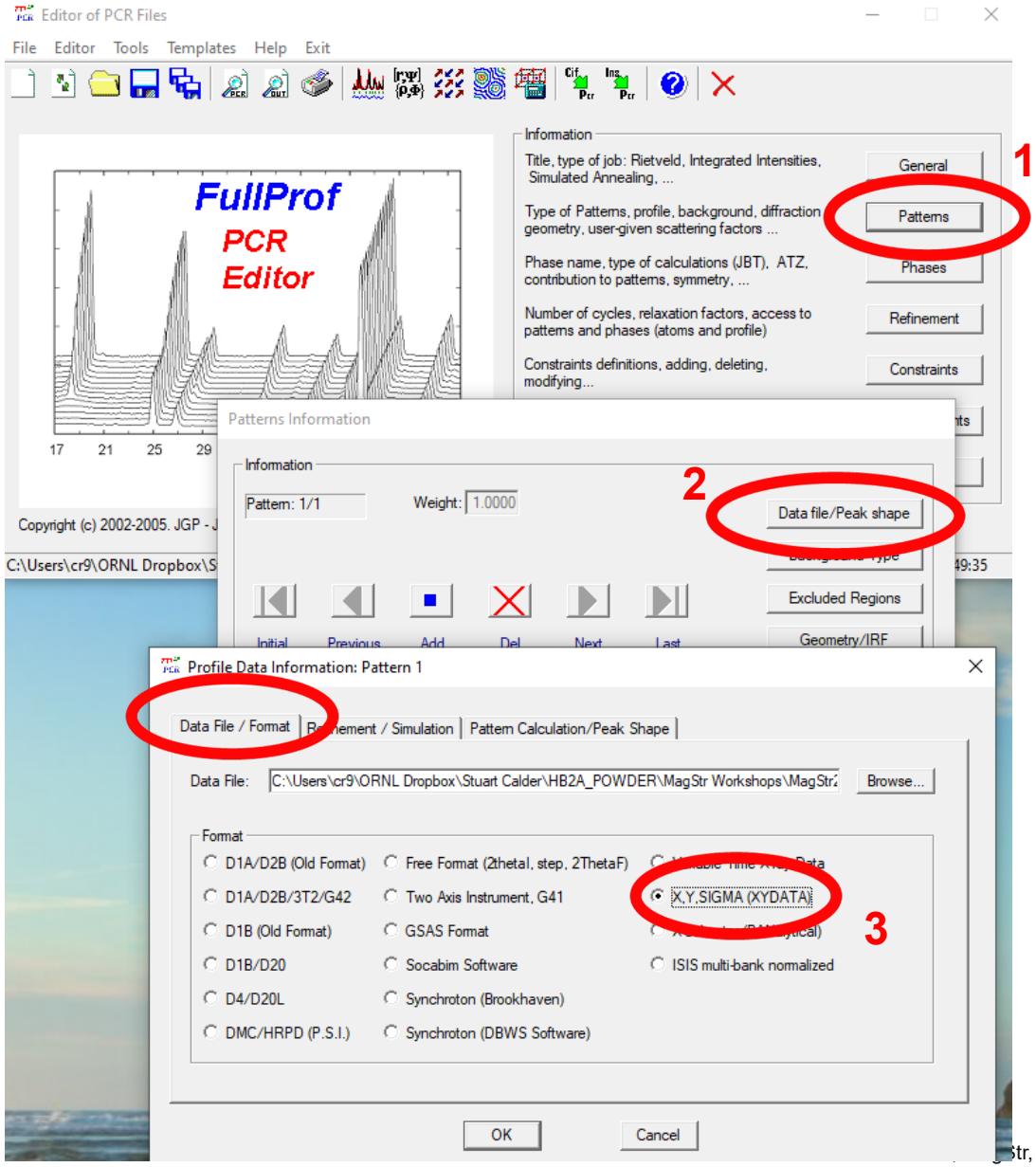
For powder refinements don't need to edit this tab



Step 1: Refine the crystal structure using FullProf

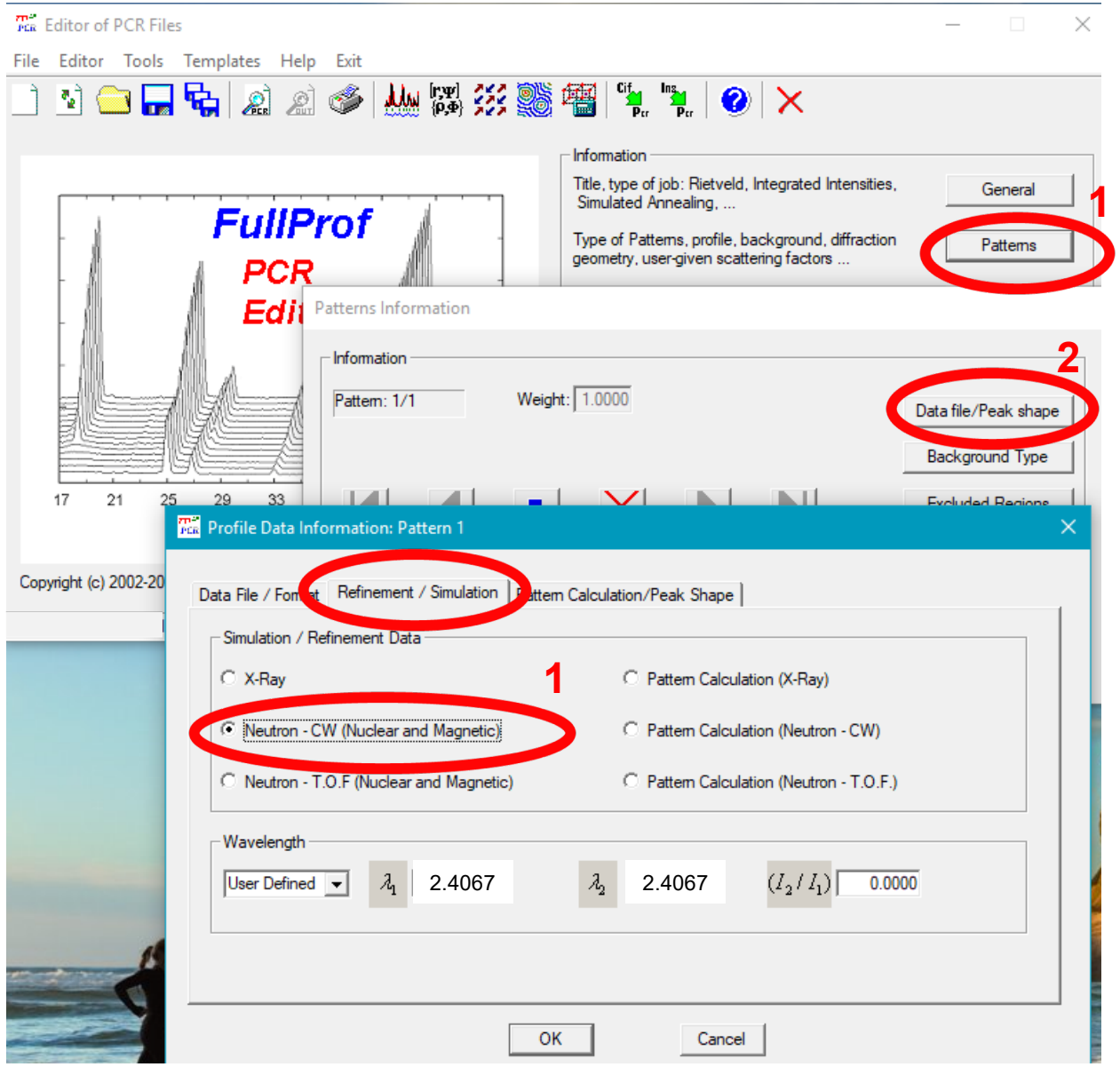
1. "**Patterns**" tab
- 2. Select the format of the data file Fullprof should refine.
- 3. Patterns → Data file/Peak Shape → X,Y,SIGMA (XYDATA)

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



Step 1: Refine the crystal structure using FullProf

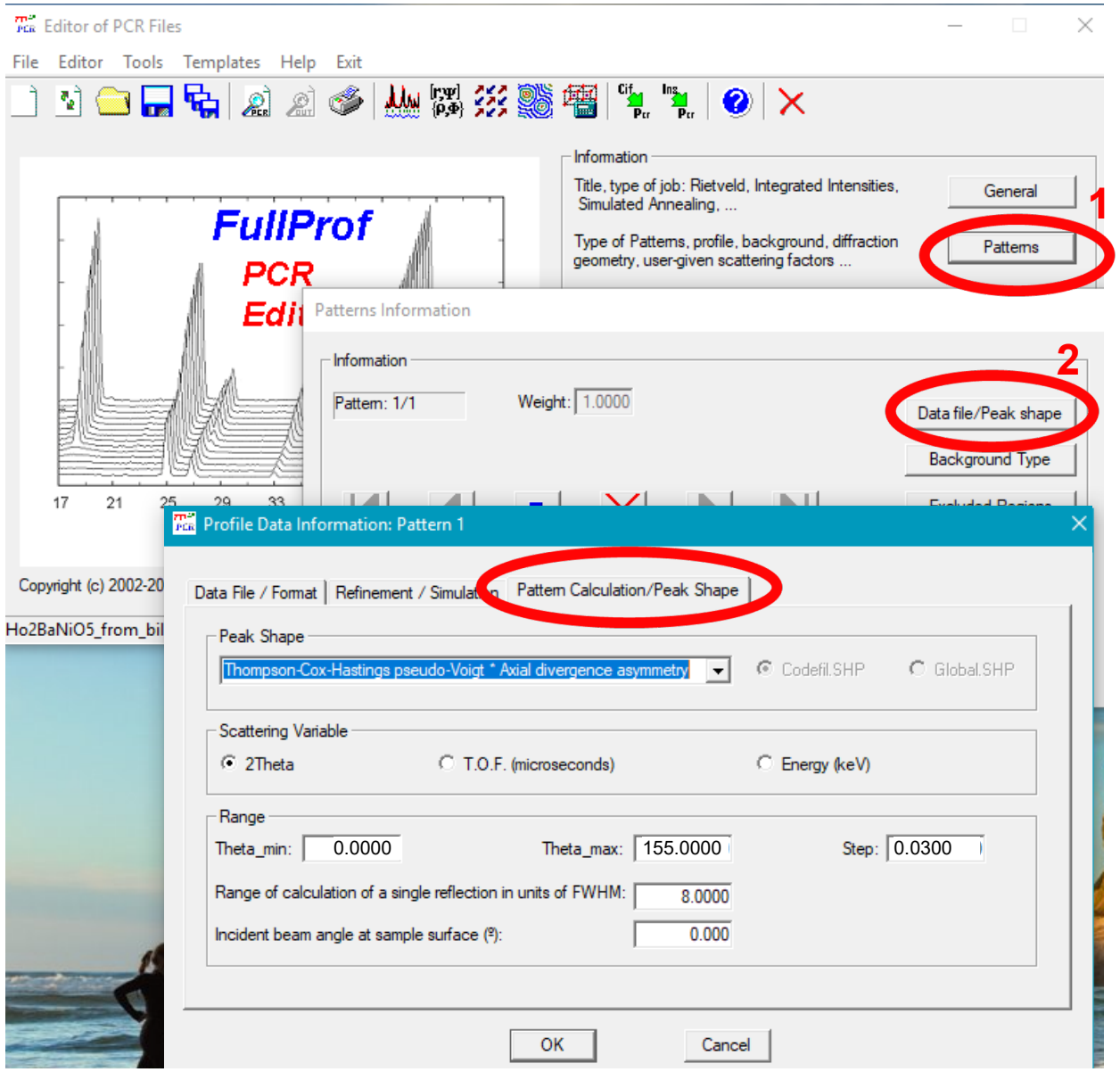
- Patterns → Data file/Peak Shape →Refinement/Simulation
- **[1]** Select Neutron – CW
- Wavelength is already set by irf file, 2.4067 in this example.



Step 1: Refine the crystal structure using FullProf

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

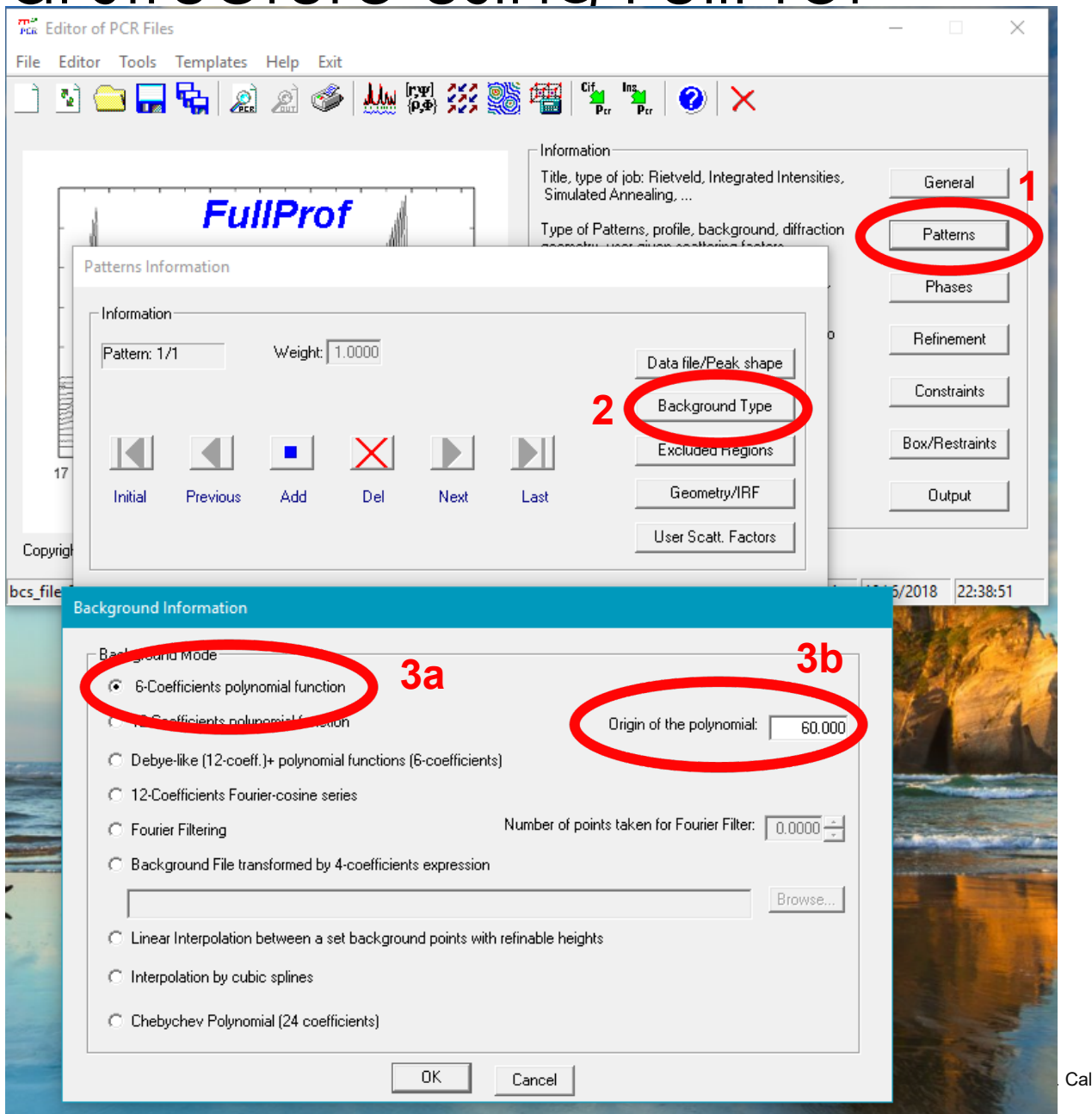
- Peak shape is already loaded correctly from irf file.



Step 1: Refine the crystal structure using FullProf

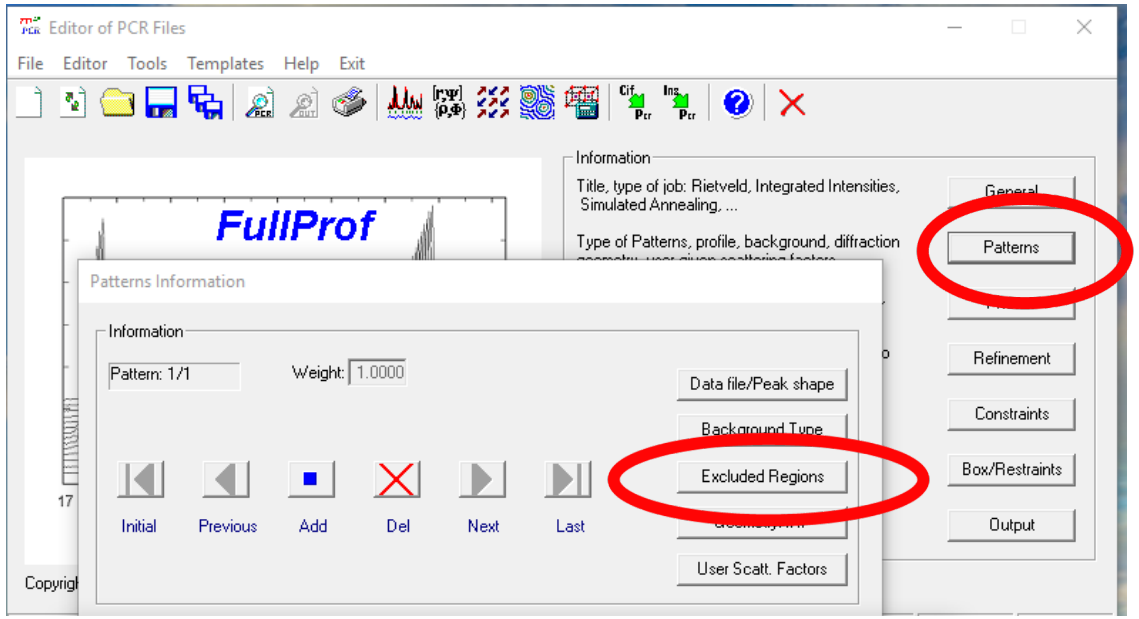
- Move to next tab down to select background type
- Patterns→ Background Type Check "6-coefficient"
- Put origin of polynomial at 60 for this example.

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



Step 1: Refine the crystal structure using FullProf

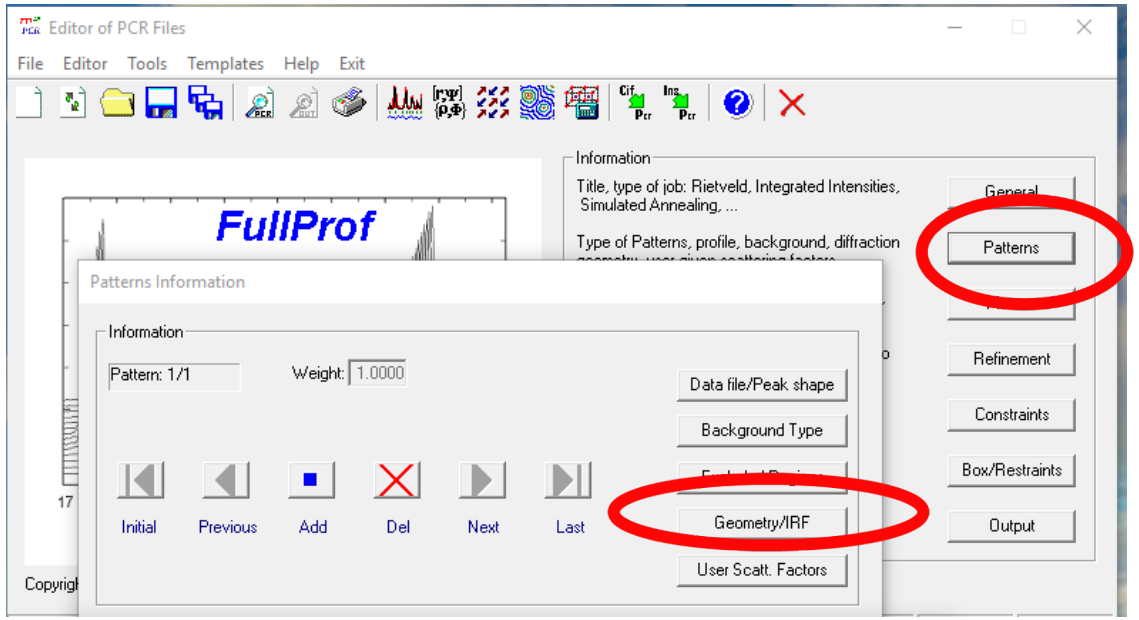
Exclude regions in the data?



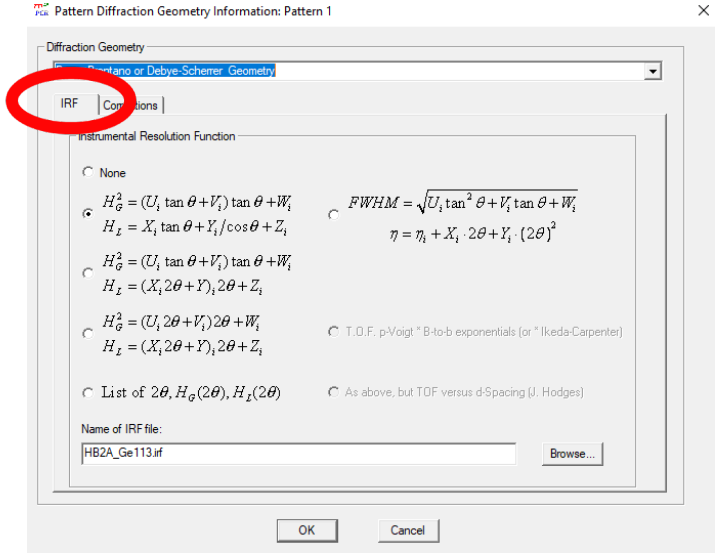
- We will not exclude any regions of the data
- Use with care, but can cut out background.
- Allow focus of refinement on different regions, e.g. only low Q
- Quick way to remove peaks from sample holder or can → but should try to fit these if possible!

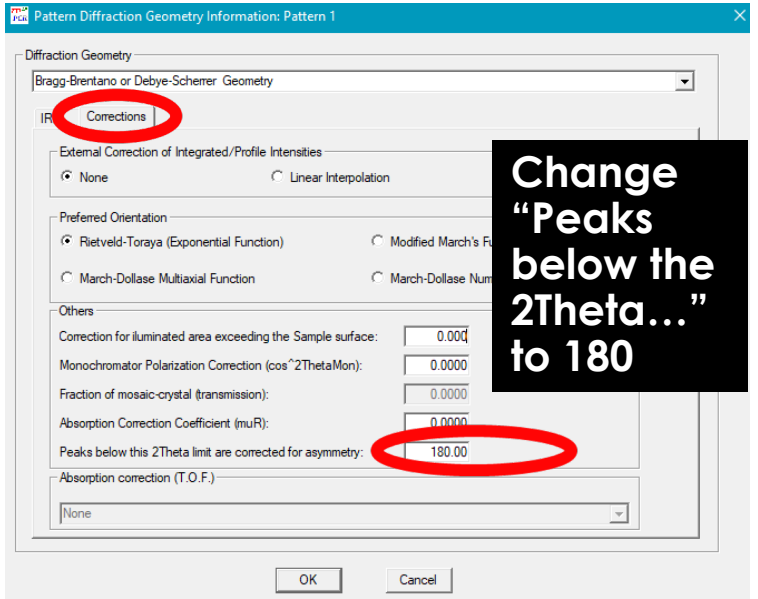
Step 1: Refine the crystal structure using FullProf

- 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/

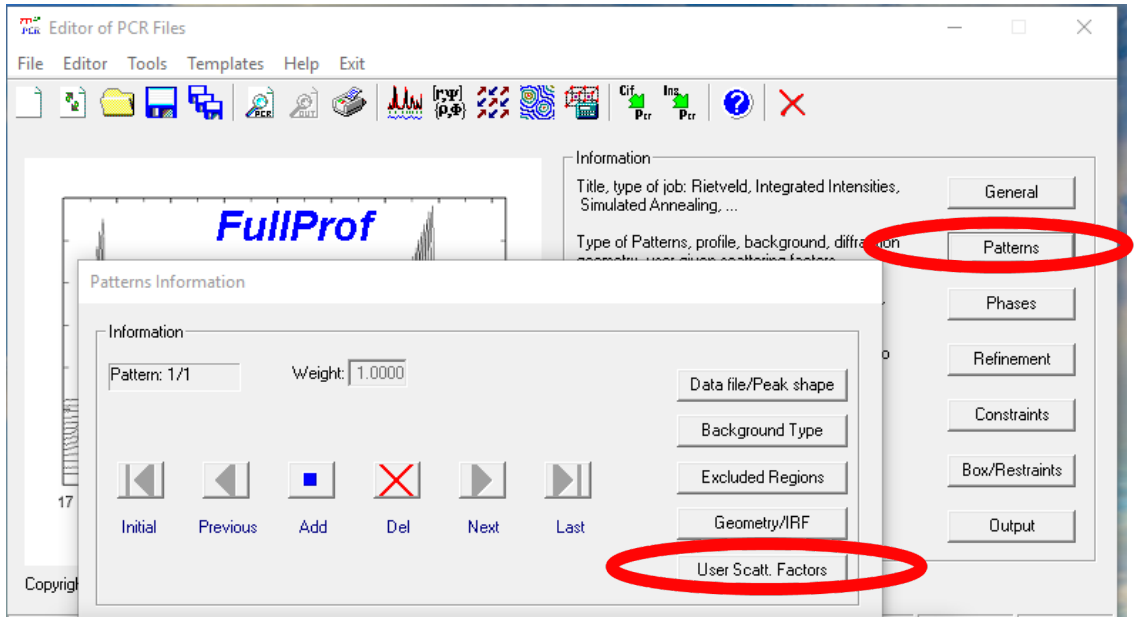




Change "Peaks below the 2Theta…" to 180

Step 1: Refine the crystal structure using FullProf

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



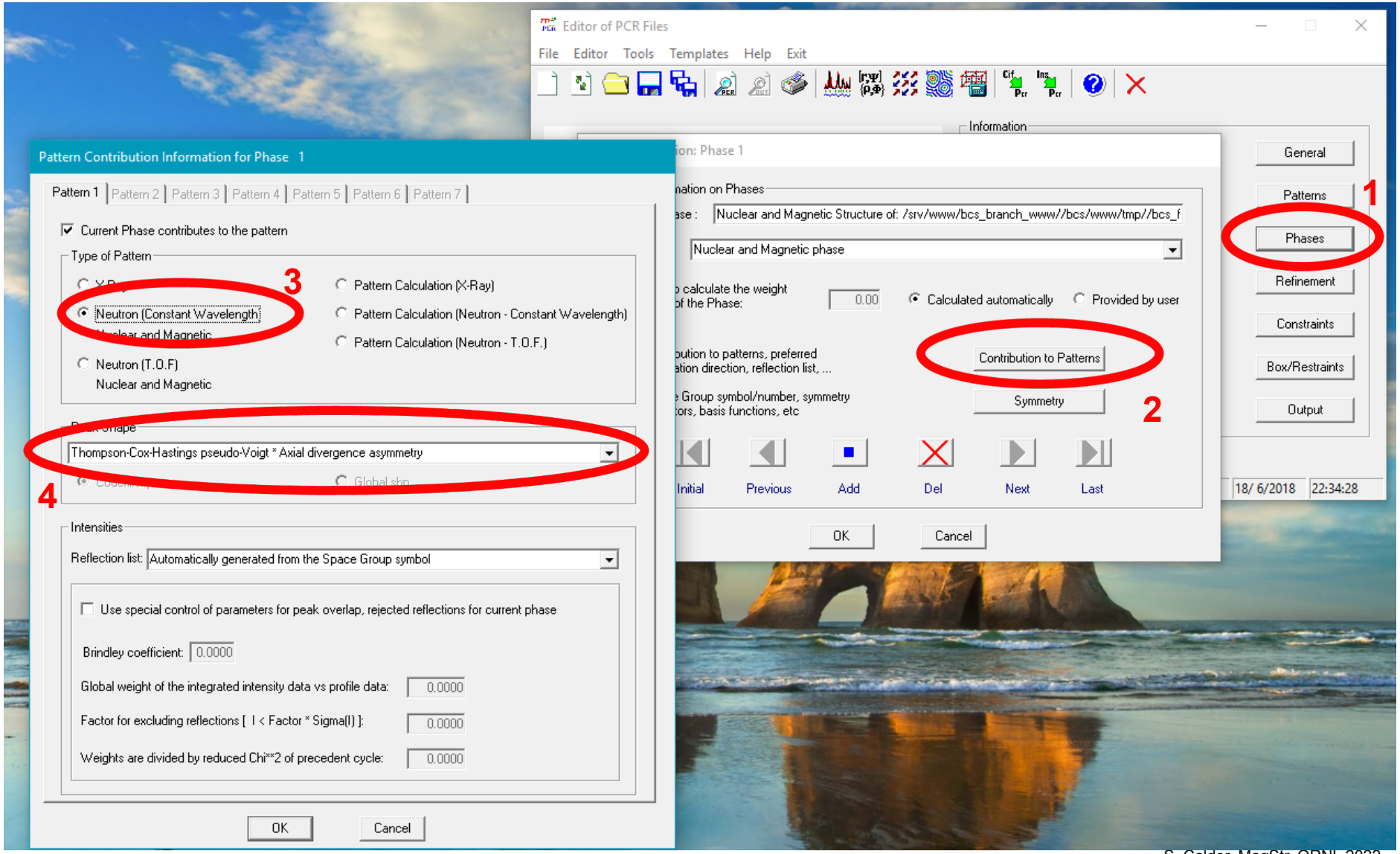
If the magnetic ion does not have form factor tables tabulated, or you want to test a non-standard form factor, this can be added here. One example would be for 5d ions, such as Ir, Os, etc.

Step 1: Refine the crystal structure using FullProf

PHASES tab

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

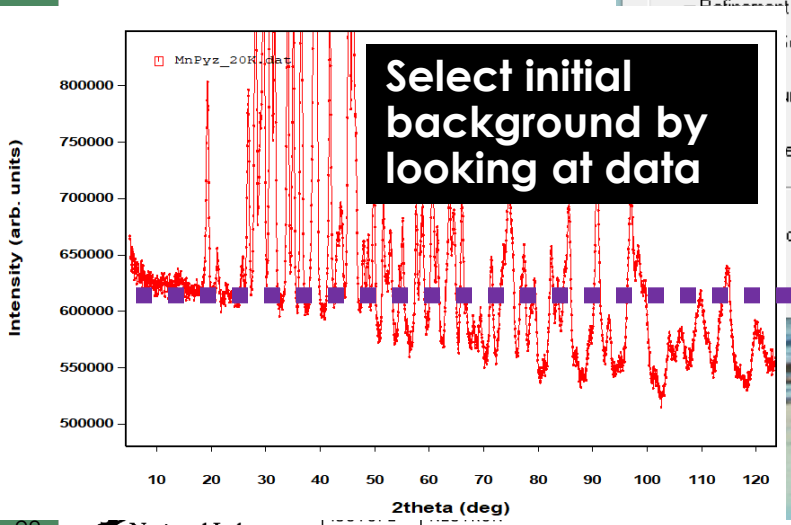
- Make phase contribute to refinement.
- **[1]** Phases→ **[2]** Contribution to Patterns→ **[3]** Neutron (constant wavelength)
- Set peak shape to "***Thompson-Cox-Hastings pseudo-Voigt***"

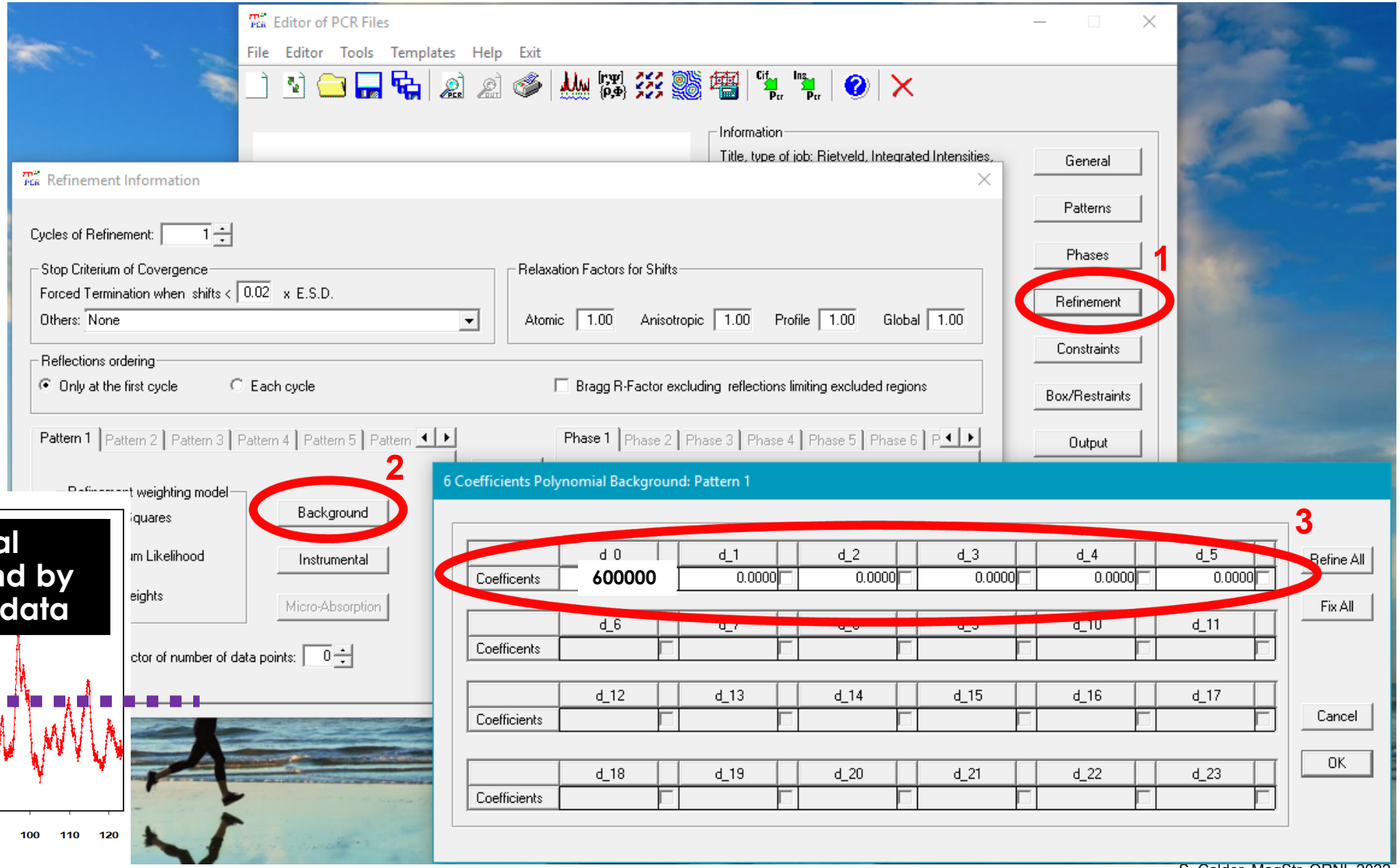


Step 1: Refine the crystal structure using FullProf

REFINEMENT tab:

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

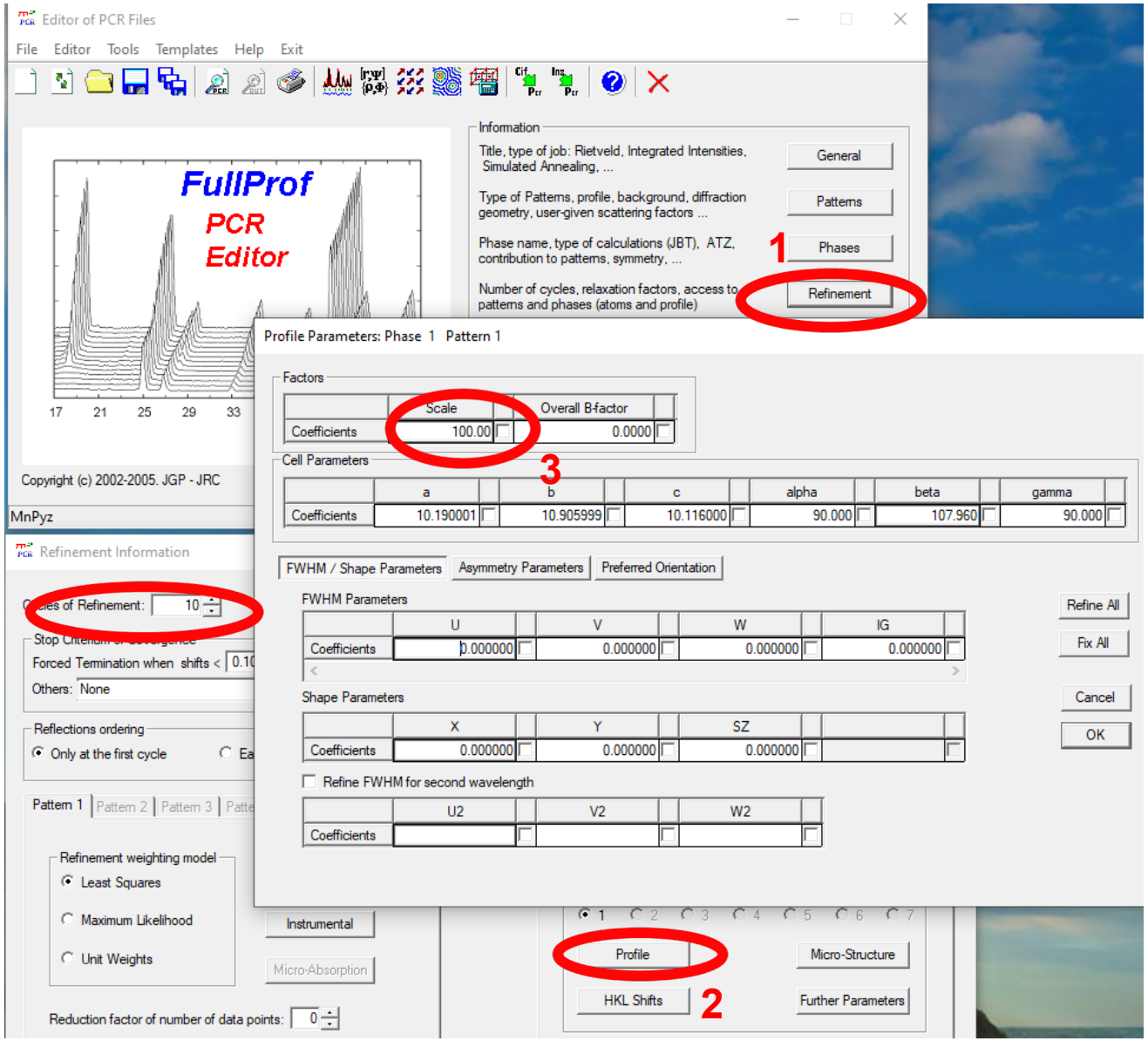




Step 1: Refine the crystal structure using FullProf

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

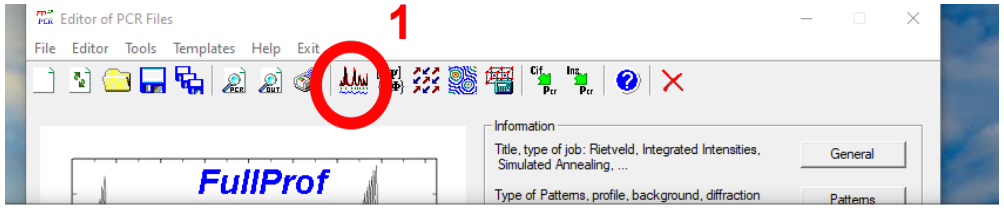
- Note U, V, W, X are set to zero. BUT, the values are being read from the .irf file. So if we refine these then they add on to the irf values.



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

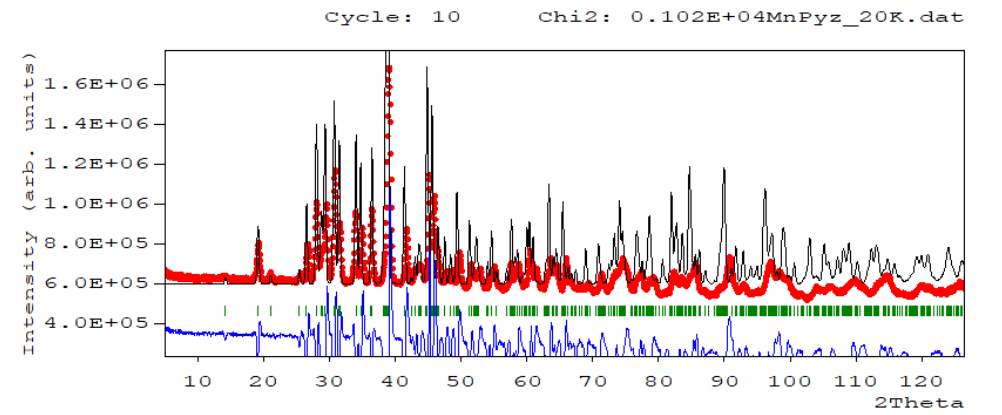
Step 1: Refine the crystal structure using FullProf

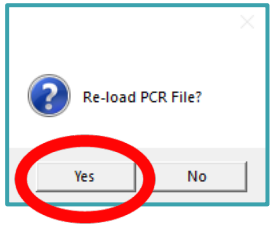
- **1.** Can now run the refinement Select the "*MnPSe3_HB2A_295K.dat*" data
  - **Note: we have not set anything to refine yet. It is good to check your model is close to the data and makes sense before refining.**
- **2.** Refinement runs for the number of cycles (in this case 10). You can repeat this 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.



FullProf Program

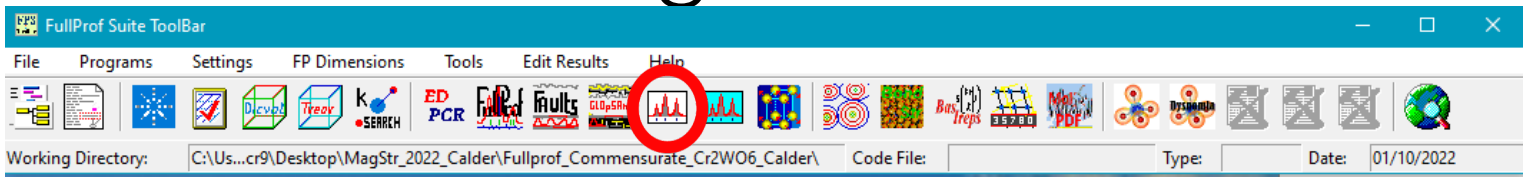
```
   => Global user-weigthed Chi2 (Bragg contrib.):   1070.
   => ---------> Pattern#       1
   => Phase:       1
   =>    Bragg R-factor:   170.0
   =>    RF-factor     :   183.0

=> Convergence reached at this CYCLE !!!!: CYCLE No.       1
=> R-Factors:   16.3      24.6     Chi2: 0.102E+04 DW-Stat.:  0.0544   Patt#:  1
=> Expected :           0.773                                1.8739
=> Conventional Rietveld R-factors for Pattern:       1
=> Rp:  355.     Rwp:  182.     Rexp:    5.71                        Chi2: 0.102E+04
   => Global user-weigthed Chi2 (Bragg contrib.):   1071.
   => ---------> Pattern#       1
   => Phase:       1
   =>    Bragg R-factor:   170.0
   =>    RF-factor     :   183.0
=> Normal end, final calculations and writing...

=> CPU Time:     0.234 seconds
=> 0.004 minutes

=> END   Date:16/07/2024  Time => 17:58:12.550
```

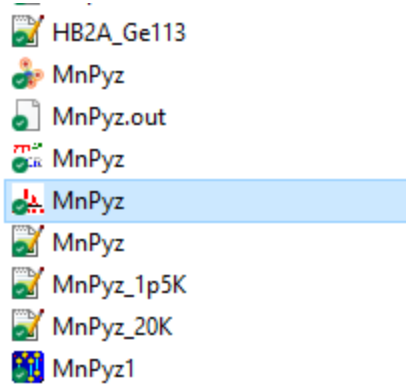


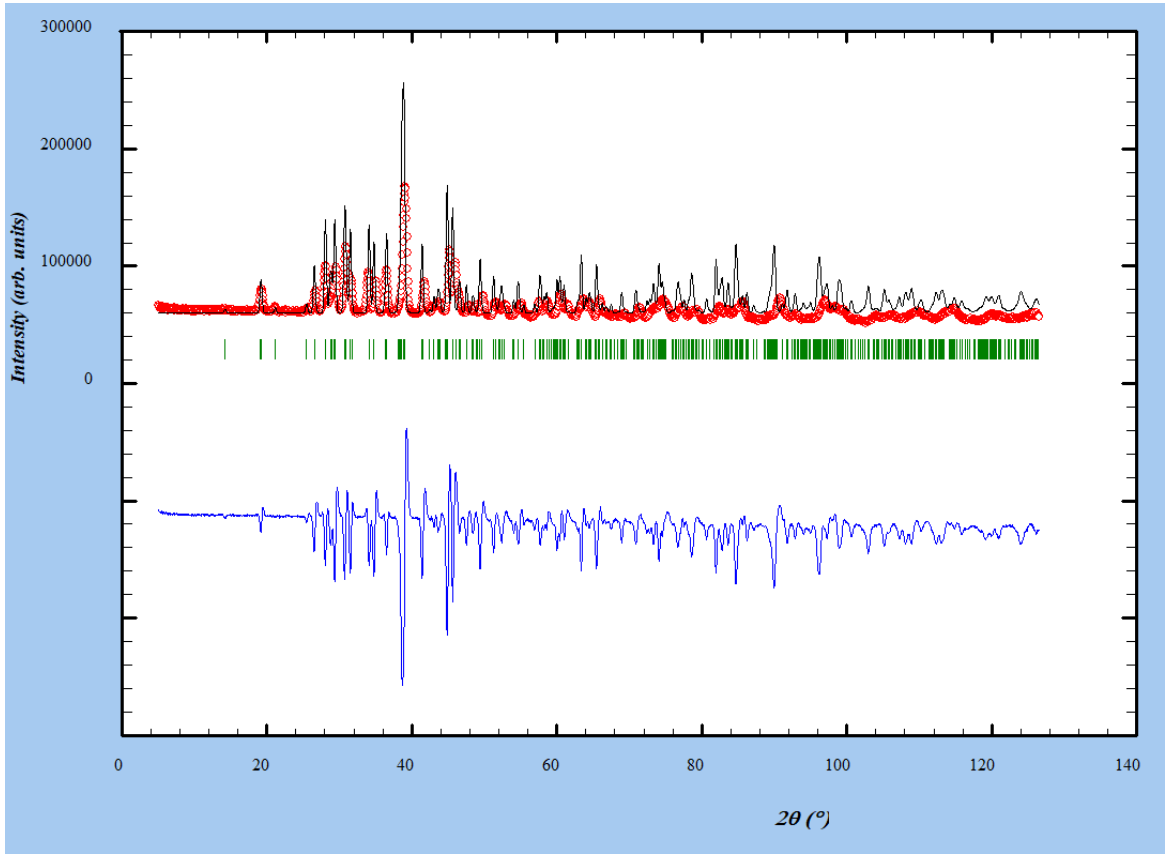


Step 1: Refine the crystal structure using FullProf

- 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.*





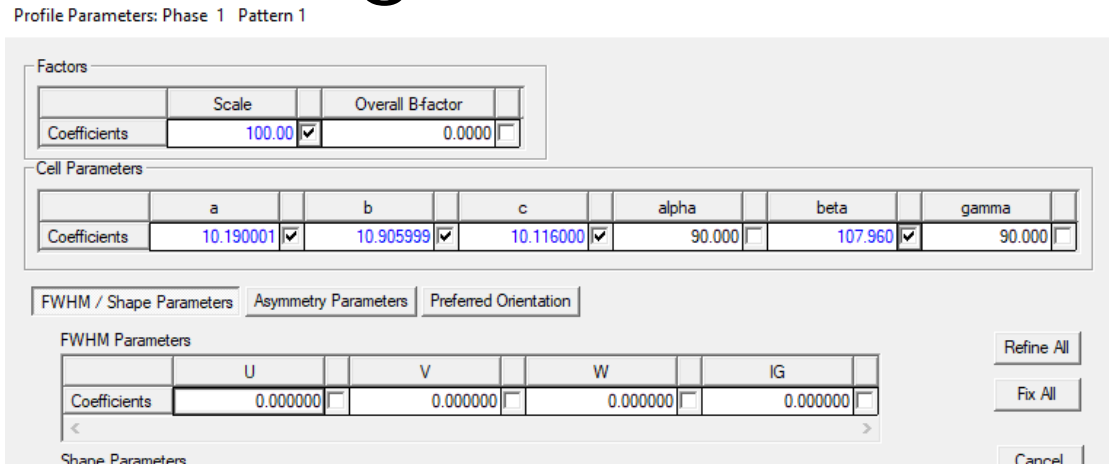


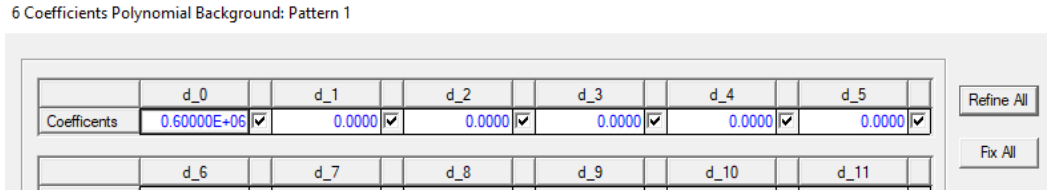
The model and the data look “close enough” to start refining. We can now we can turn of parameters to refine to try to get he model and data to match.

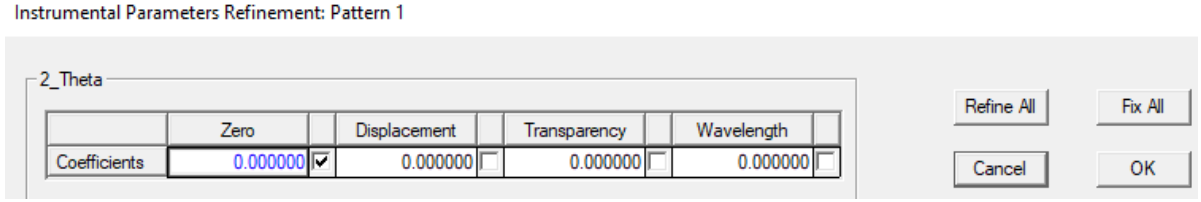
Step 1: Refine the crystal structure using FullProf

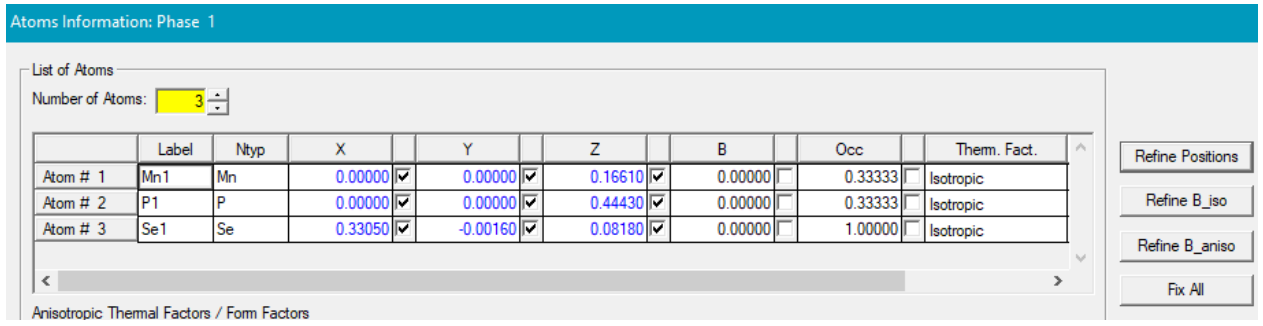
- Now allow the following to refine to fit the nuclear crystal:
  - Scale factor *(Refinement>Profile)*
  - Lattice parameters *(Refinement>Profile)*
  - Background *(Refinement>Background)*
  - 2theta zero. *(Refinement>Instrumental)*

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.





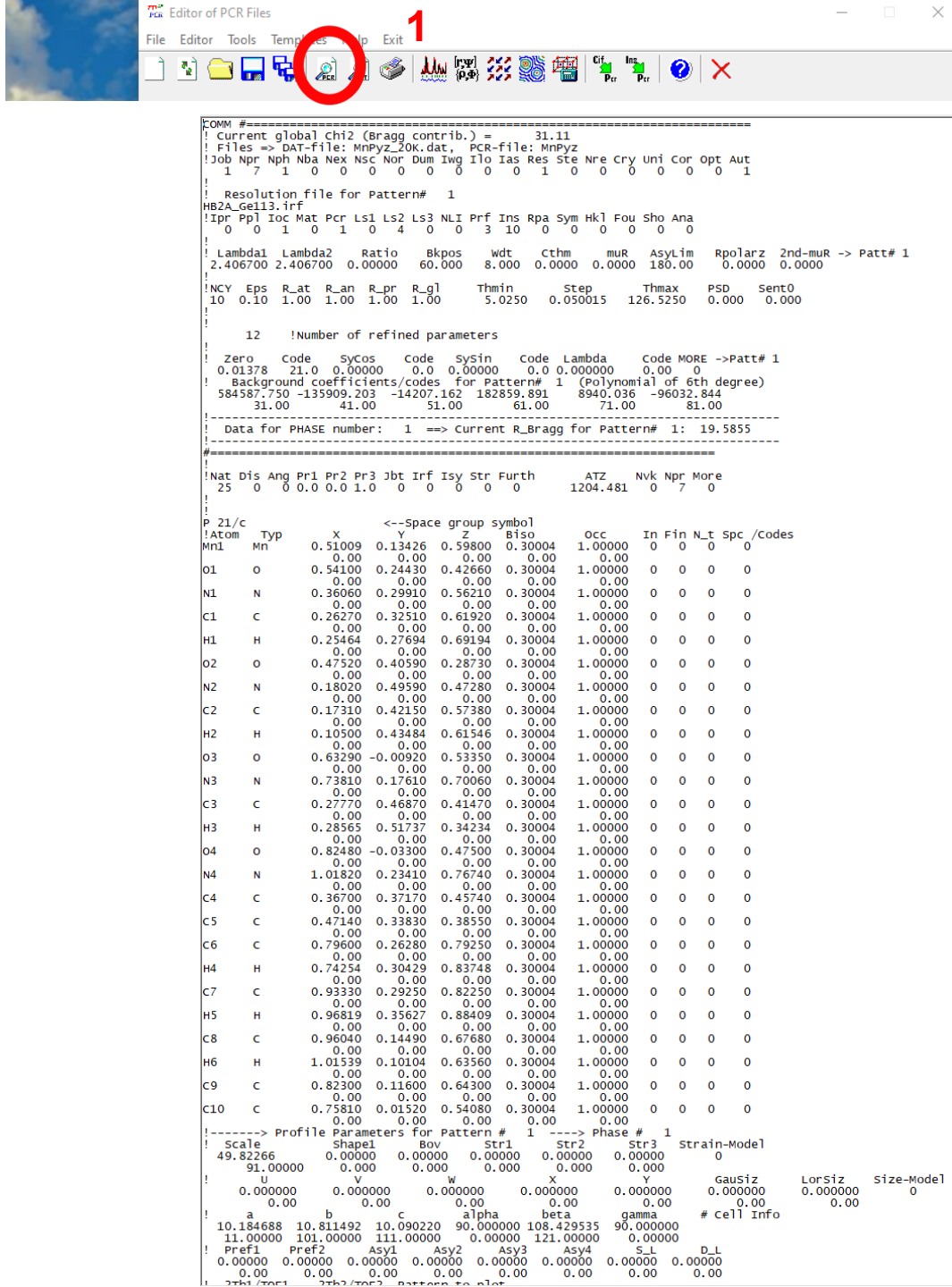




Working in text editor and GUI

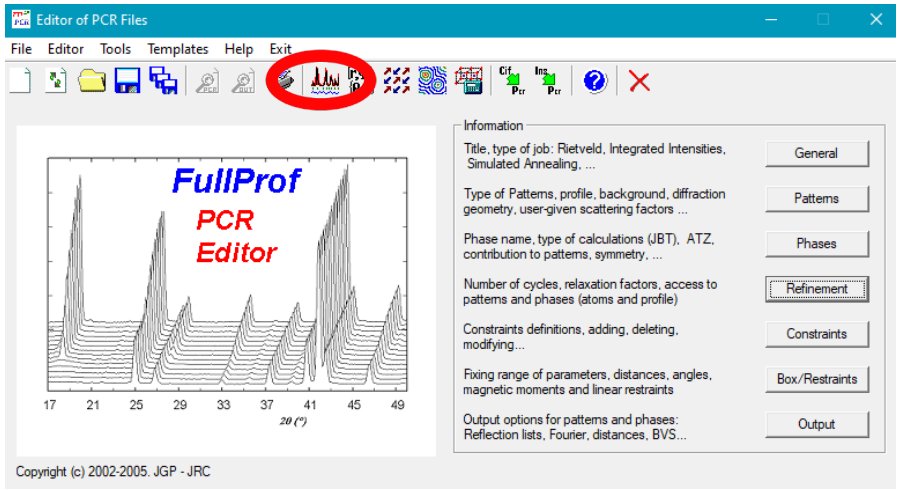
- Can use BOTH the GUI and edit the text of the.pcr file.
- Open text with 1. [pcr and magnifying glass].

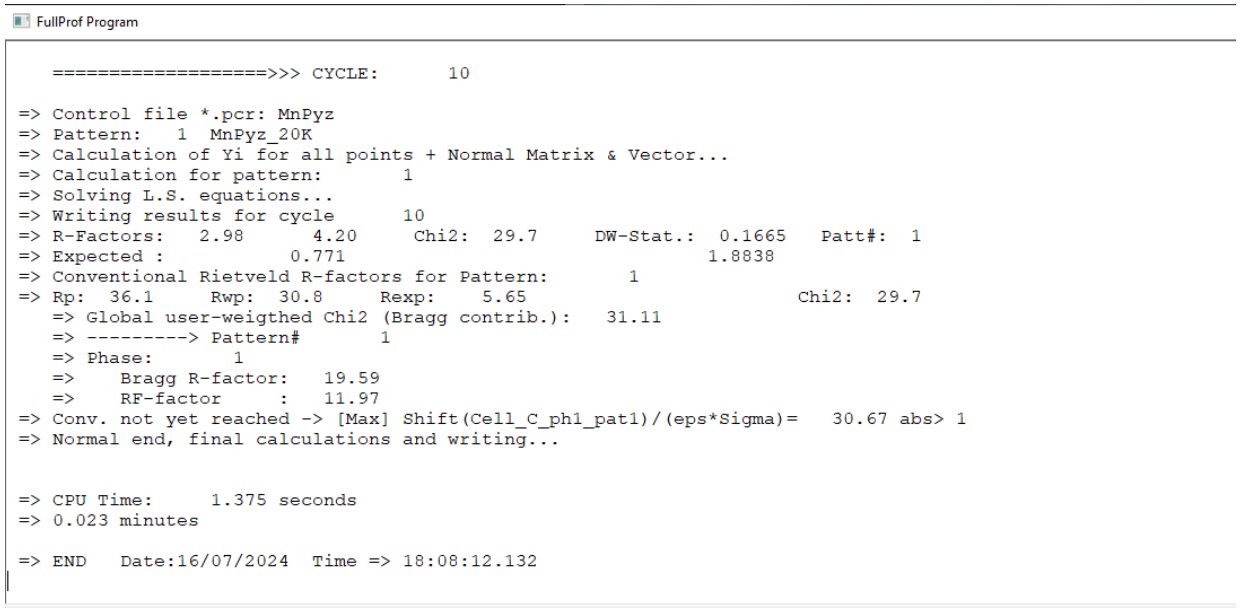
- Can quickly see and edit varios things quicker than with GUI
  - Anything refining has a number that ends in a 1 (e.g. 11, 21, 31, 811, 641, etc)
  - The scale has a 91, so is refining.
- To turn on any to refine can type a 1, then Fullprof figures out the numbering.




```
!COMM #=================================================================
! 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   1   0   0   0   0   0   0   1
!
!  Resolution file for Pattern#   1
HB2A_Ge113.irf
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   0   3  10   0   0   0   0   0   0
!
! Lambda1  Lambda2     Ratio     Bkpos     Wdt     Cthm      muR   AsyLim   Rpolarz  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       1204.481   0   7   0
!
!
P 21/c                 <--Space group symbol
!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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
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
!-------> Profile Parameters for Pattern #   1  ----> Phase #   1
!  Scale          Shape1       Bov        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
!      U          V          W          X          Y        GauSiz     LorSiz     Size-Model
    0.000000   0.000000   0.000000   0.000000   0.000000   0.000000   0.000000        0
         0.00       0.00       0.00       0.00       0.00       0.00       0.00
!       a          b          c        alpha       beta       gamma      # Cell Info
  10.184688  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
! 2Th1/TOF1   2Th2/TOF2   Pattern to plot
```

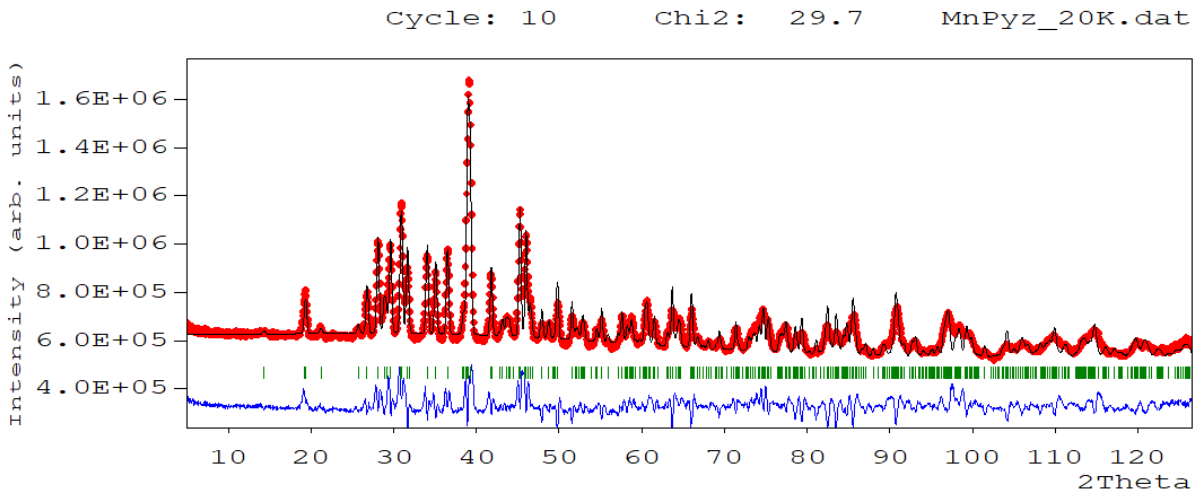
Step 1: Refine the crystal structure using FullProf





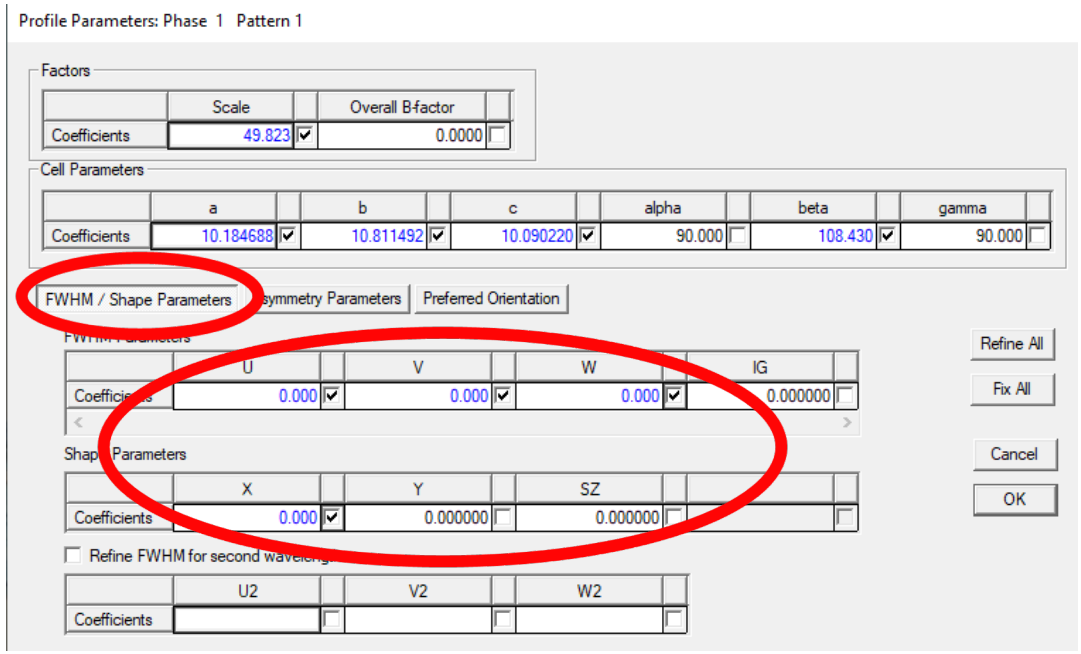
- The refinement to the 20K data is closer.
- Next can add in refinements to the peak shape, since the sample may add some broadening beyond the parameters loaded in with the irf file.

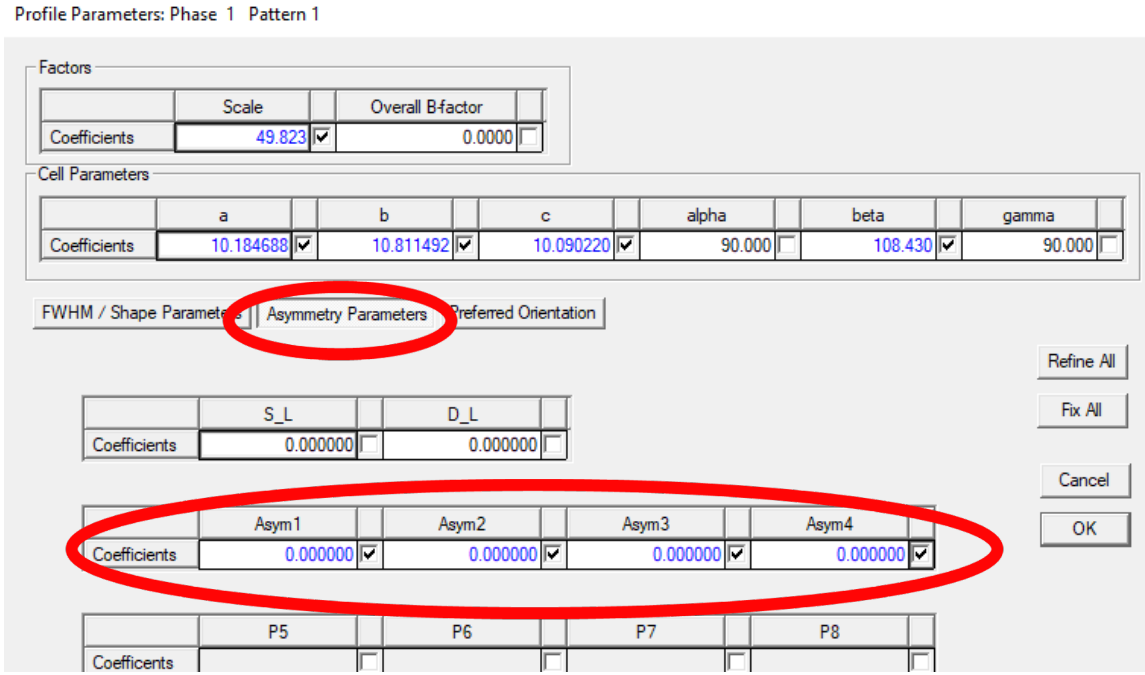
Peak profiles should only be run after the refinement and peak positions are close, others refinement will blow-up



Step 1: Refine the crystal structure using FullProf

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

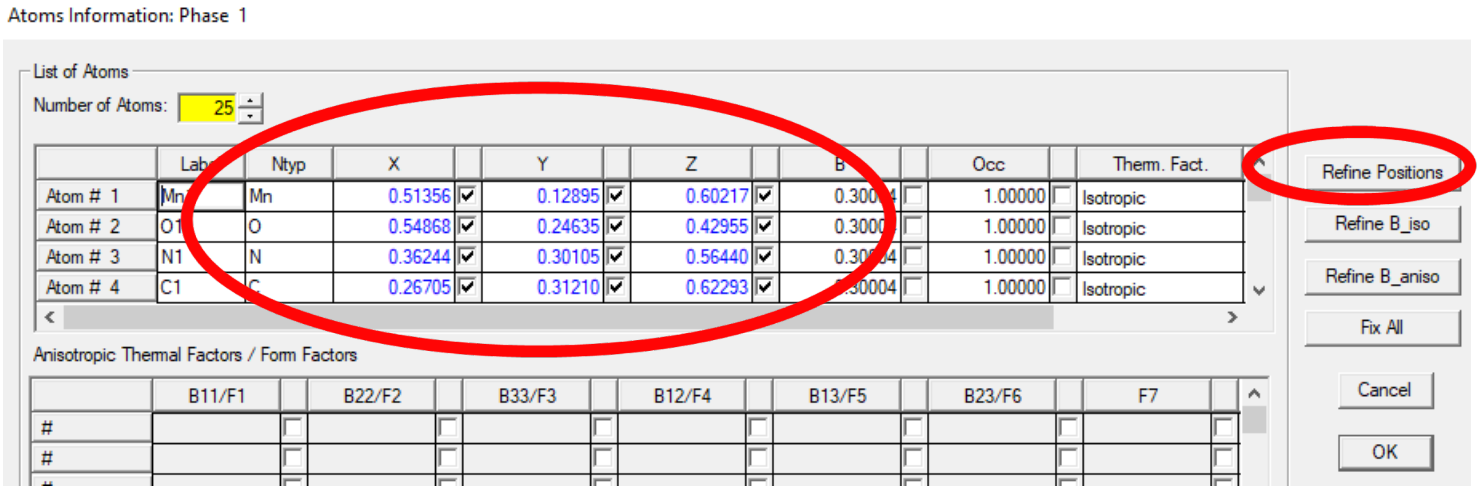


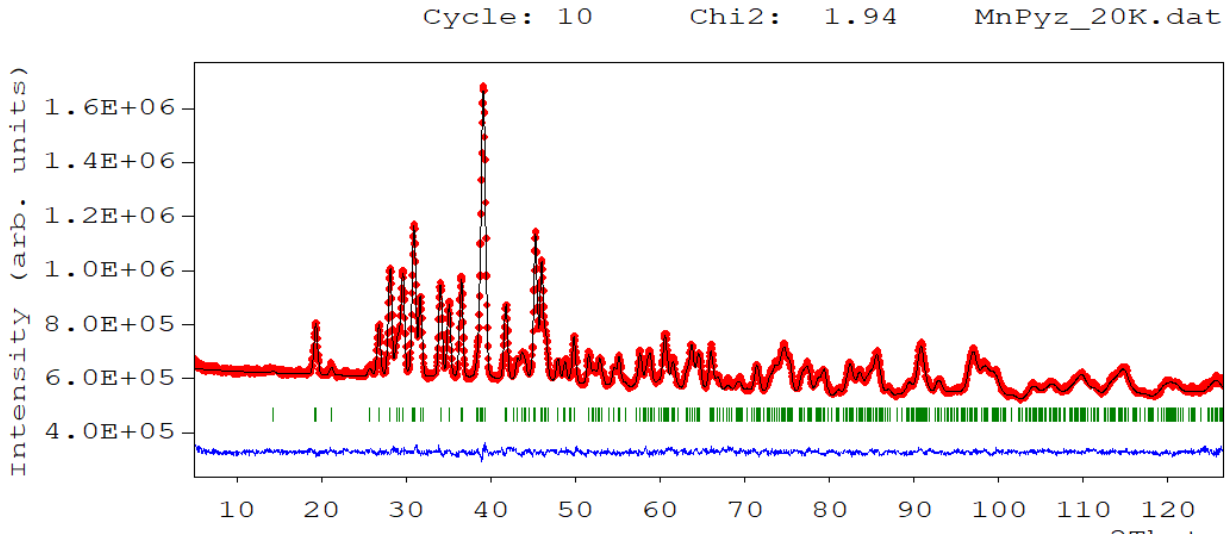


Step 1: Refine the crystal structure using FullProf

- 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.

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





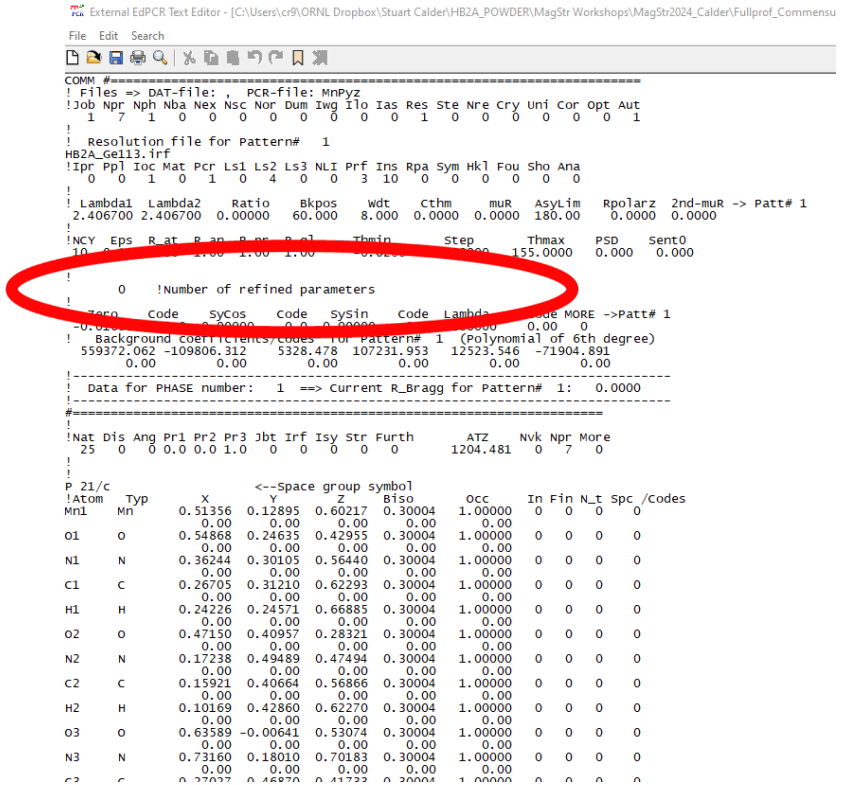
Step 1: Refine the crystal structure using FullProf

- 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

- Before refining the 1.5 K data **FIRST TURN OFF ALL PARAMETERS**.
  The peak shapes should not change with temperature (we're measuring the same sample on the same instrument!)
  - The lattice constants and structural parameters vary with temperature, but the temperature change here is small. We can refine as needed.

Check in text file that nothing is refining.

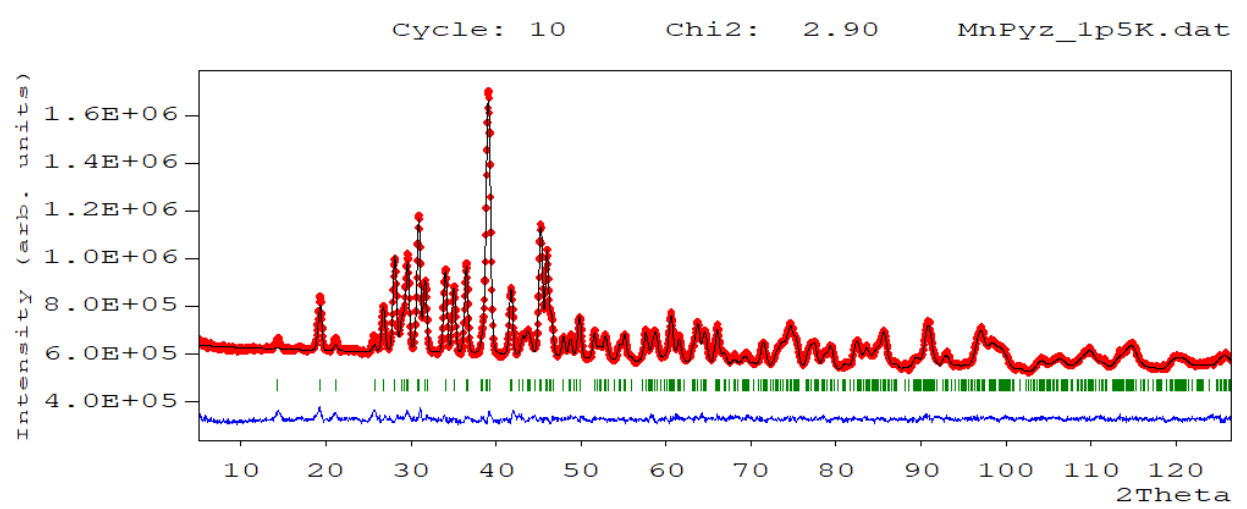


Step 1: Refine the crystal structure using FullProf

- 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-weigthed 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-weigthed 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

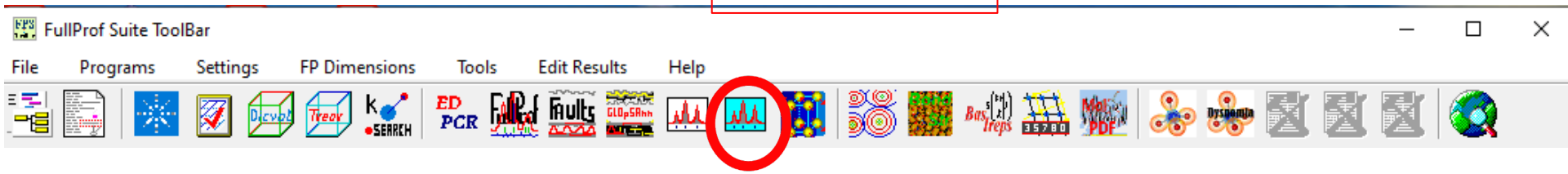
- The background changes slightly between 1.5 K and 20K, these parameters can be refined here or when doing the magnetic phase.

Mn-pyrazinecarboxylate

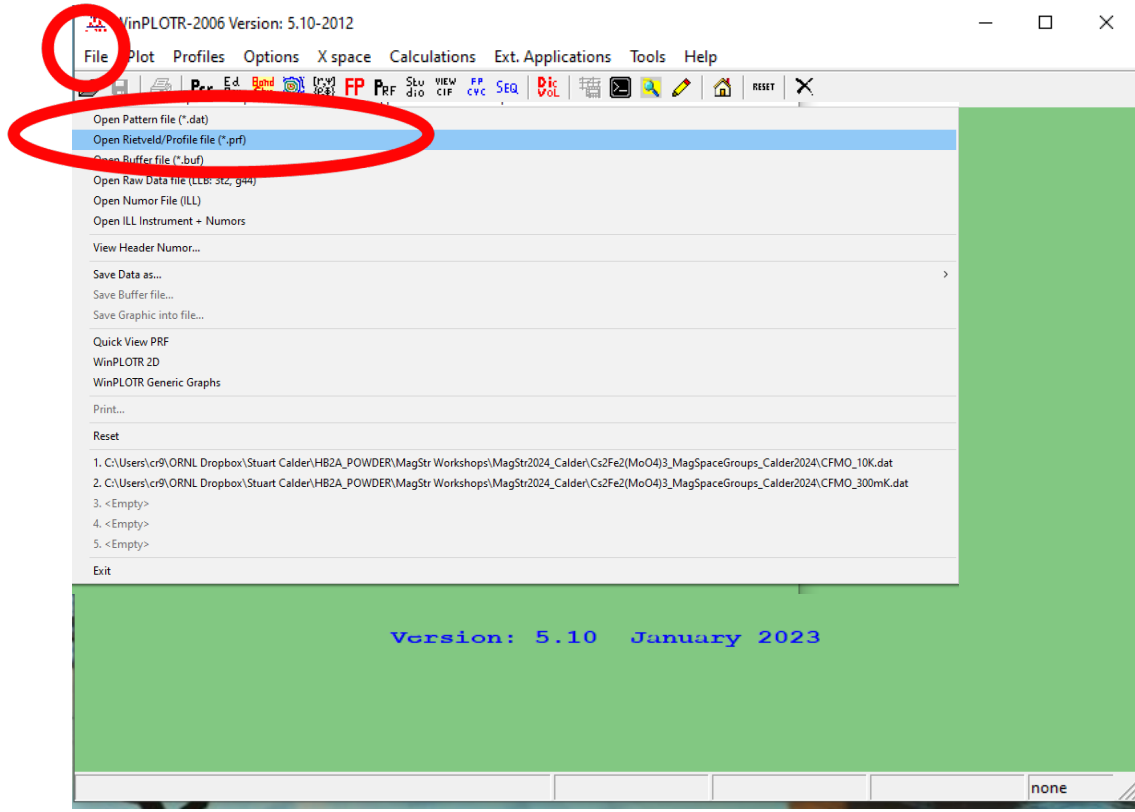
- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - **Step 2: Determine the k-vector by indexing the magnetic reflections using k-search**
  - Step 3: Create candidate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

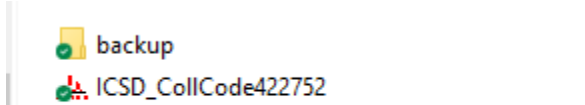
Determine the k-vector

WinPlotr-2006

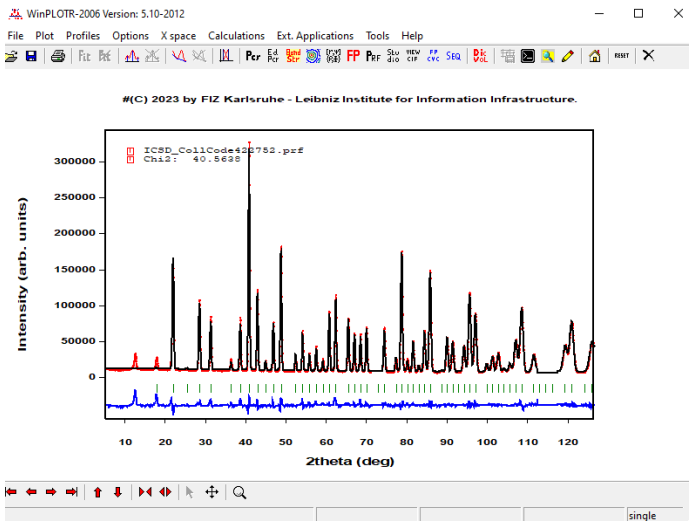


- k-search is run in WinPlotr-2006.
- Open the .prf file:
  - "File">"Open Rietveld/Profile file (*.prf)"
  - Select the prf file



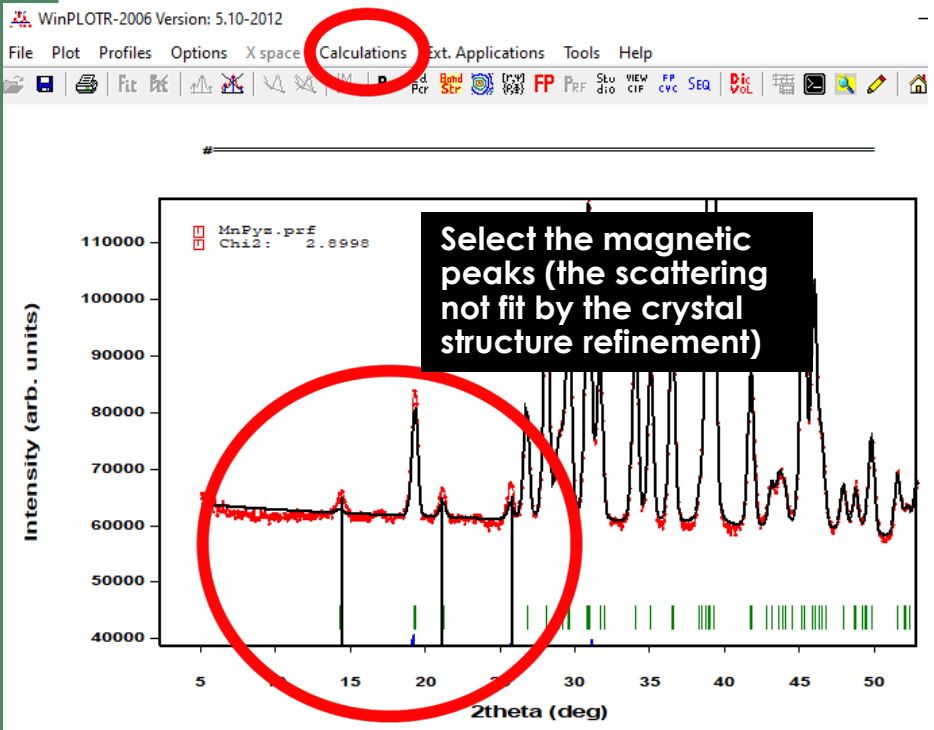


NOTE: If the background changes to white this is a good sign. If it stays green, you might have issues with running k-search.
Try running it, if issues then reopen a different way.

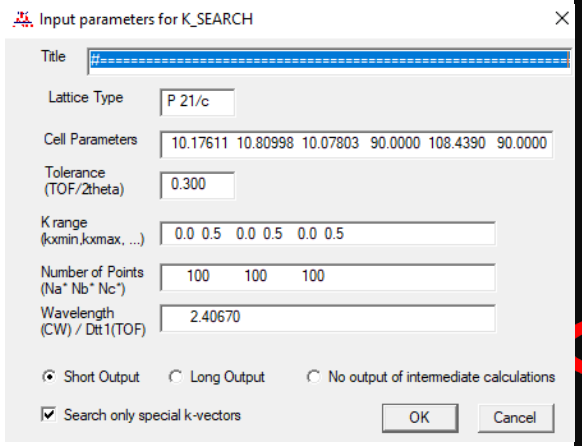


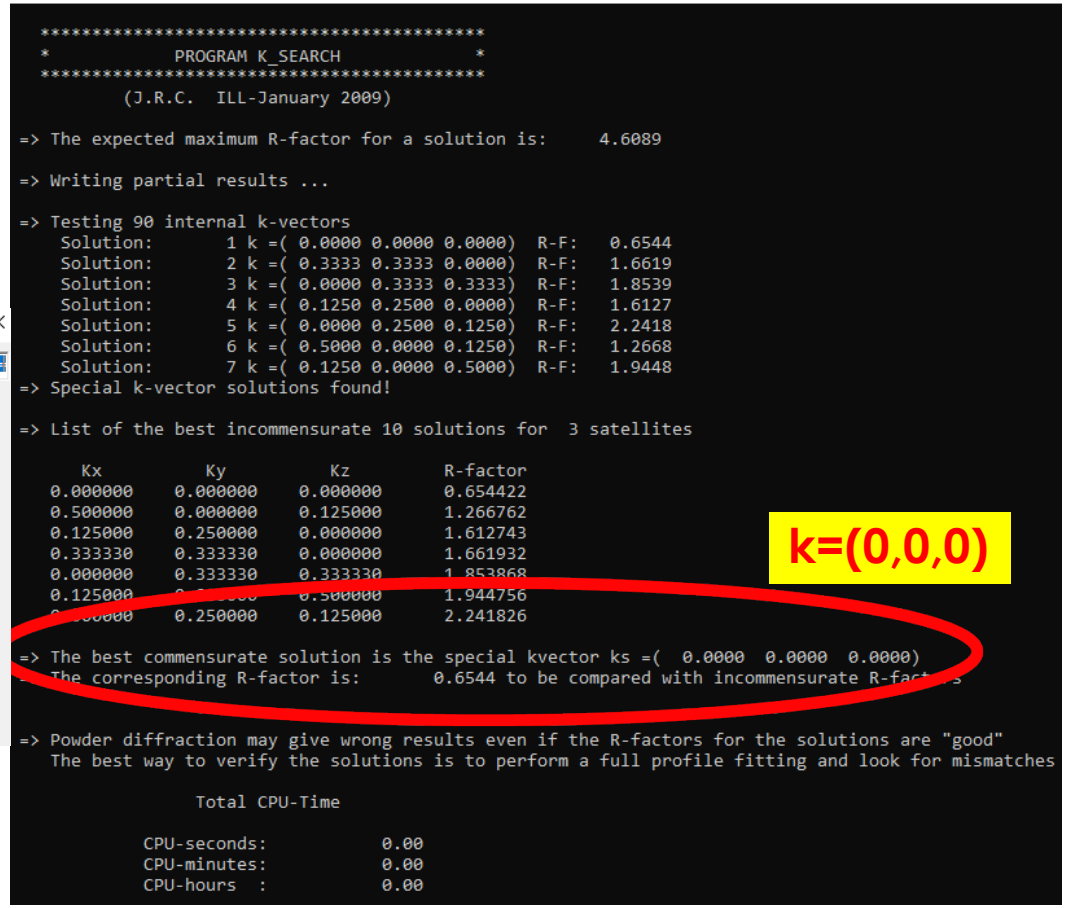
Determine the k-vector

- 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





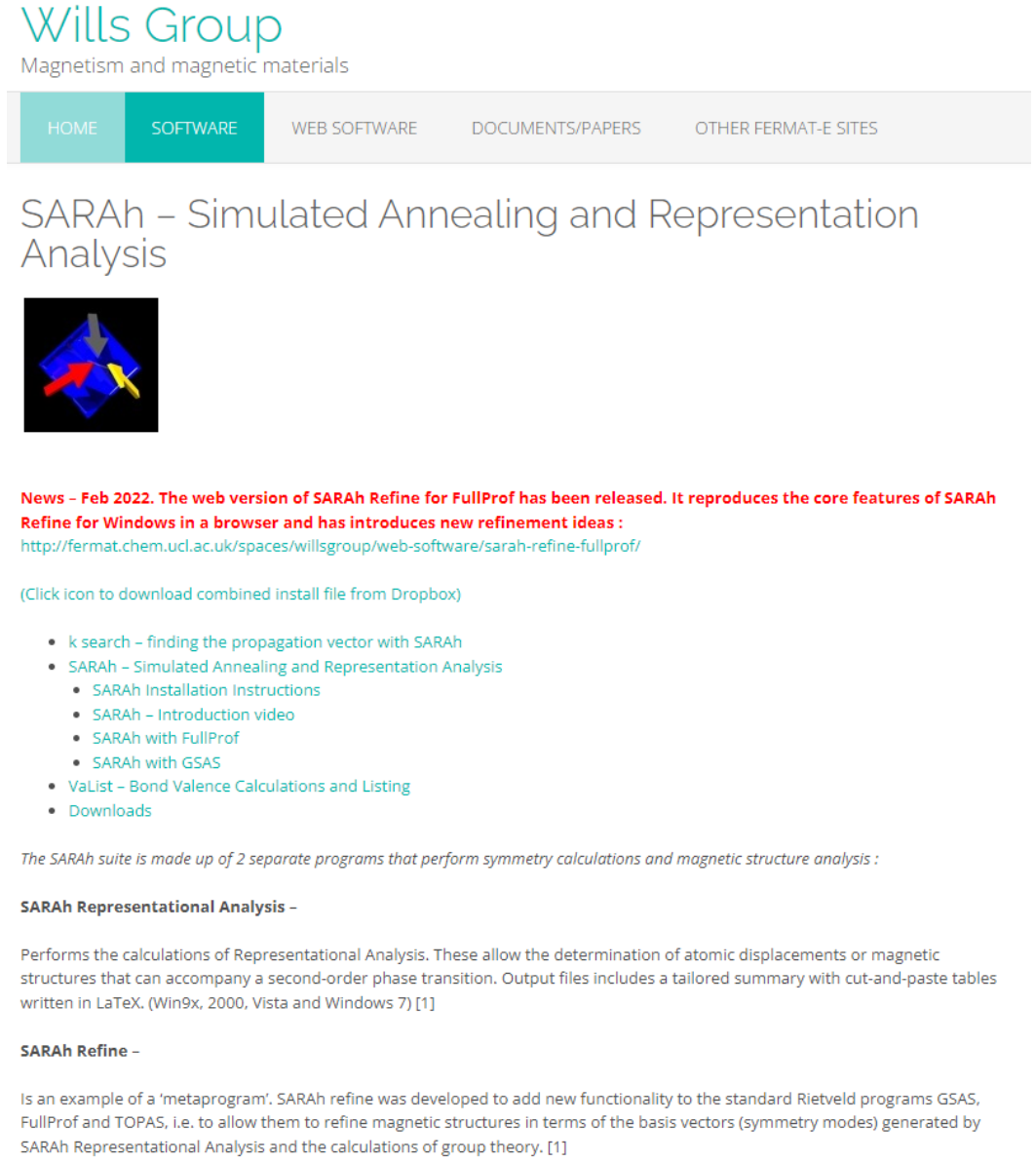
k=(0,0,0)

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.

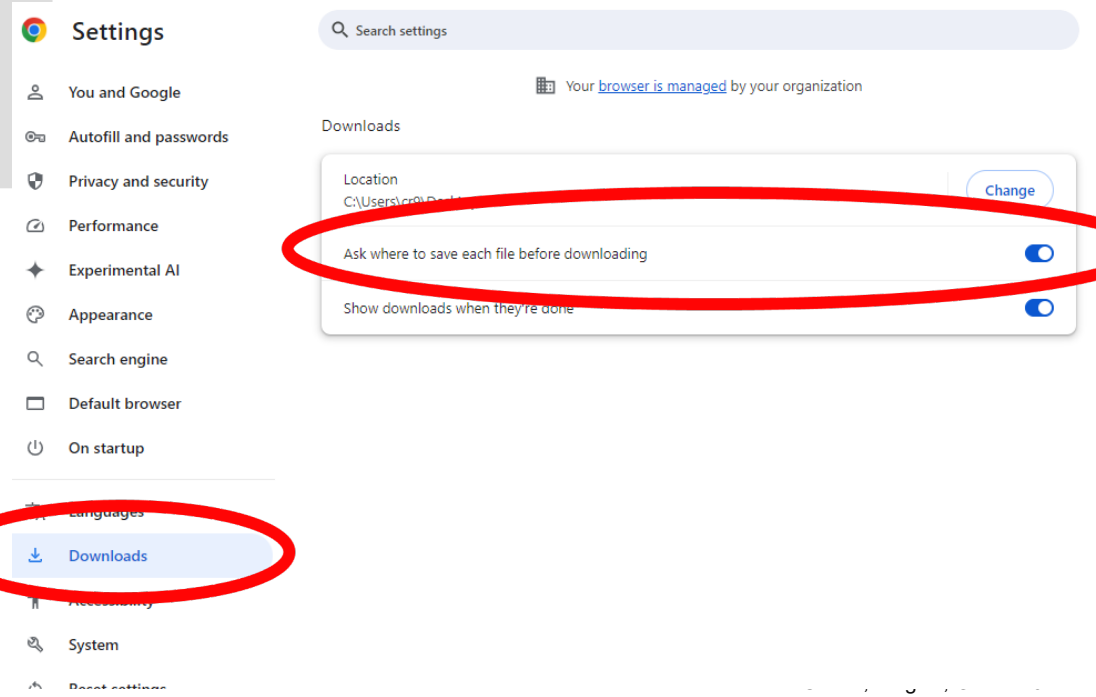
Below are some settings for common browsers that turn on 'Ask where to save each file before downloading':

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'

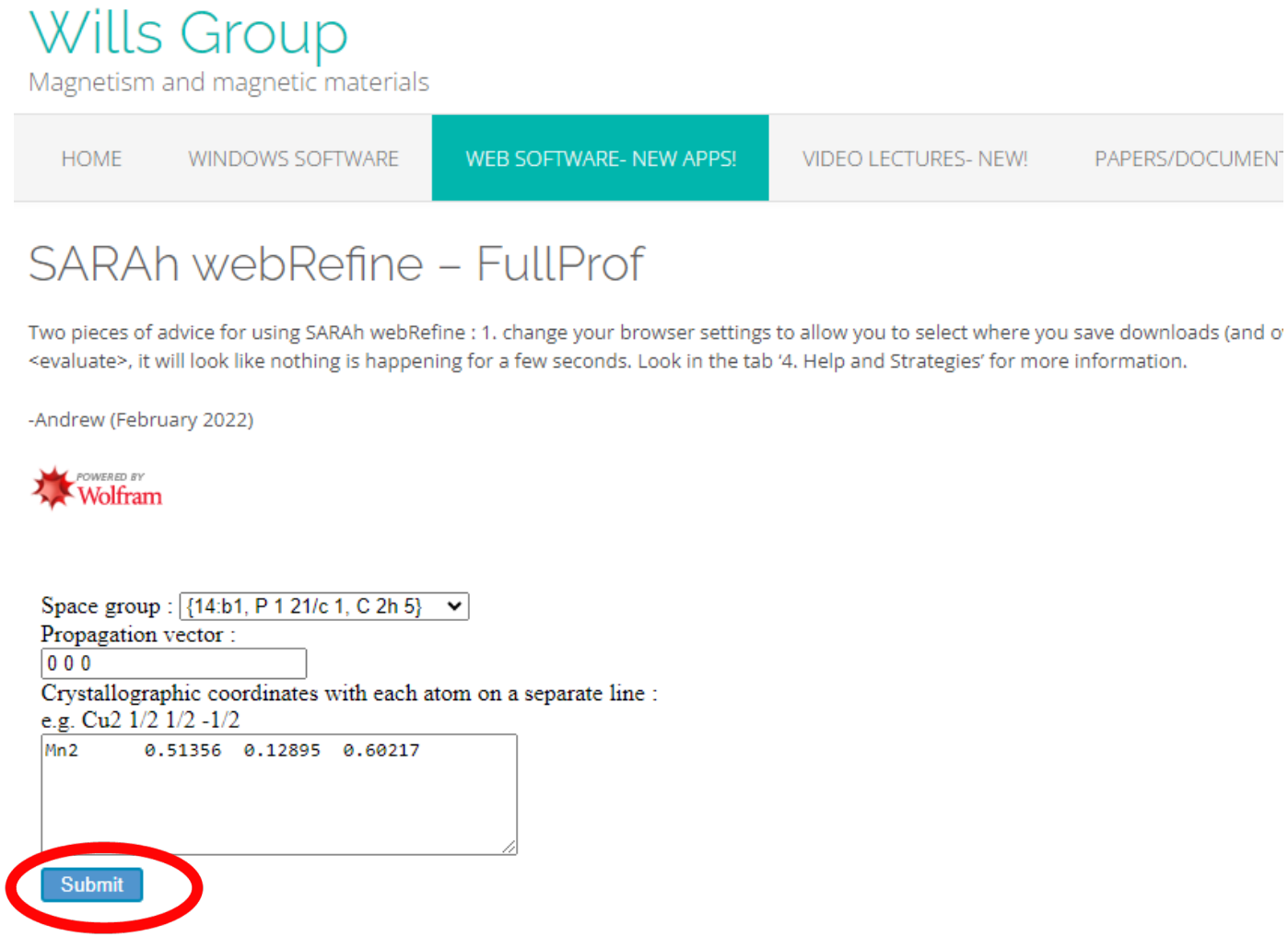
Firefox - Windows 11: 1) Click the menu button (the 3 line burger button) and select 'Settings'. 2) In the General panel scroll down to 'Files and Applications'. 3) In Downloads select 'Always ask where to save files'

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'



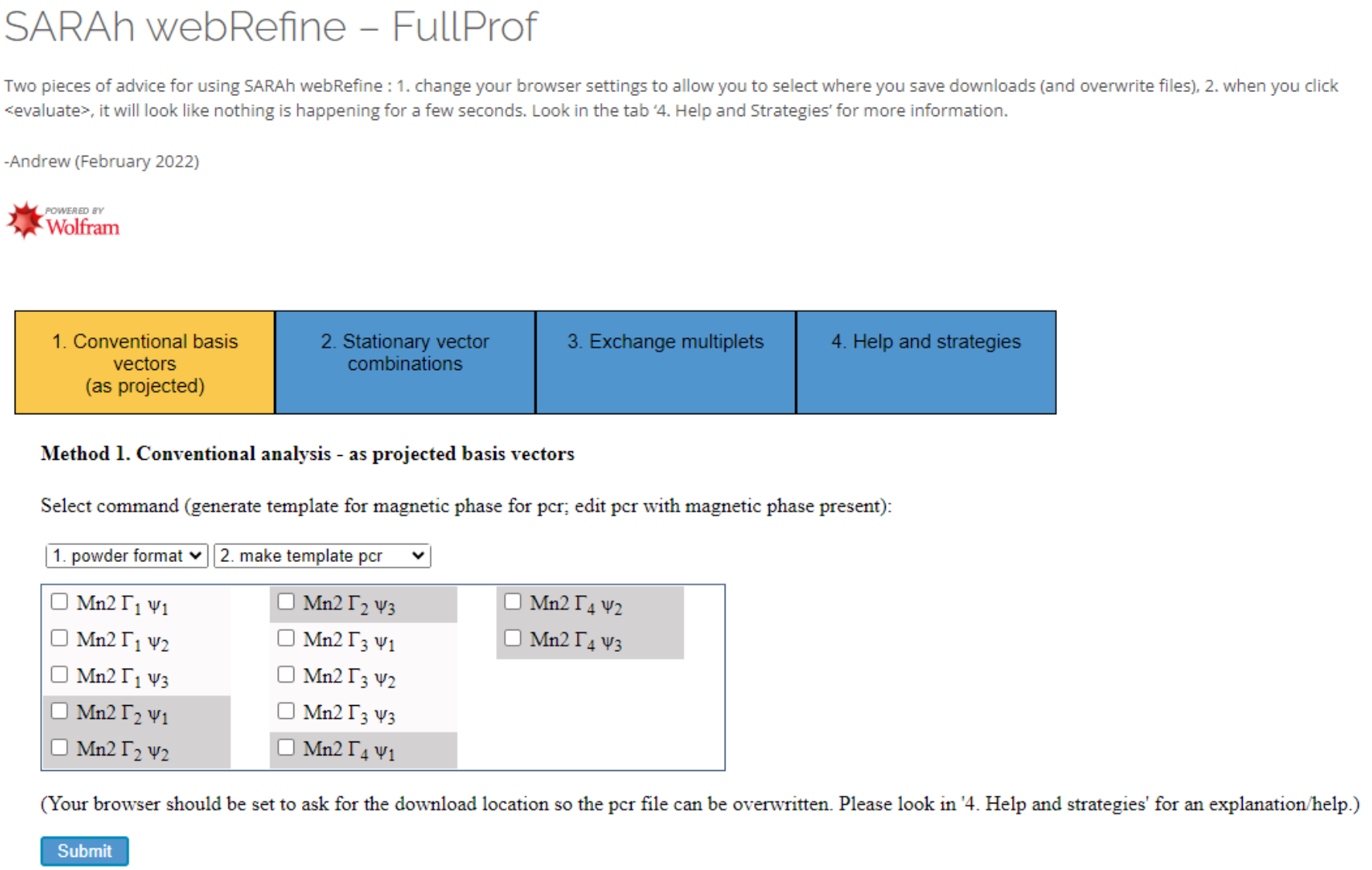
Step 3: Create candidate magnetic models using SARAh

- 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



Step 3: Create candidate magnetic models using SARAh

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



Step 3: Create candidate magnetic models using SARAh

Table. The basis vectors projected from the different IRs :

Γ_1 ψ_1	Γ_1 ψ_2	Γ_1 ψ_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.

Γ_2 ψ_1	Γ_2 ψ_2	Γ_2 ψ_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.

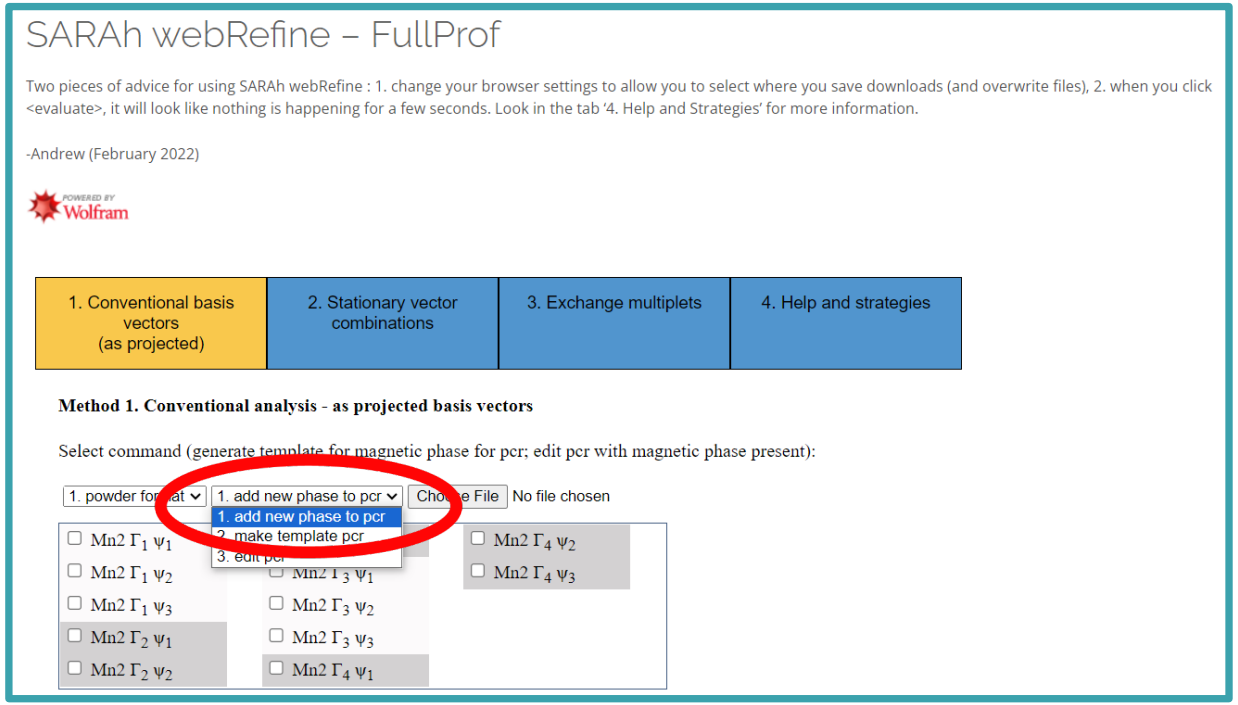
Γ_3 ψ_1	Γ_3 ψ_2	Γ_3 ψ_3
Mn2 1) 1. 0. 0.	Mn2 1) 0. 1. 0.	Mn2 1) 0. 0. 1.
2) 1. 0. 0.	2) 0. −1. 0.	2) 0. 0. 1.
3) 1. 0. 0.	3) 0. 1. 0.	3) 0. 0. 1.
4) 1. 0. 0.	4) 0. −1. 0.	4) 0. 0. 1.

Γ_4 ψ_1	Γ_4 ψ_2	Γ_4 ψ_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 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

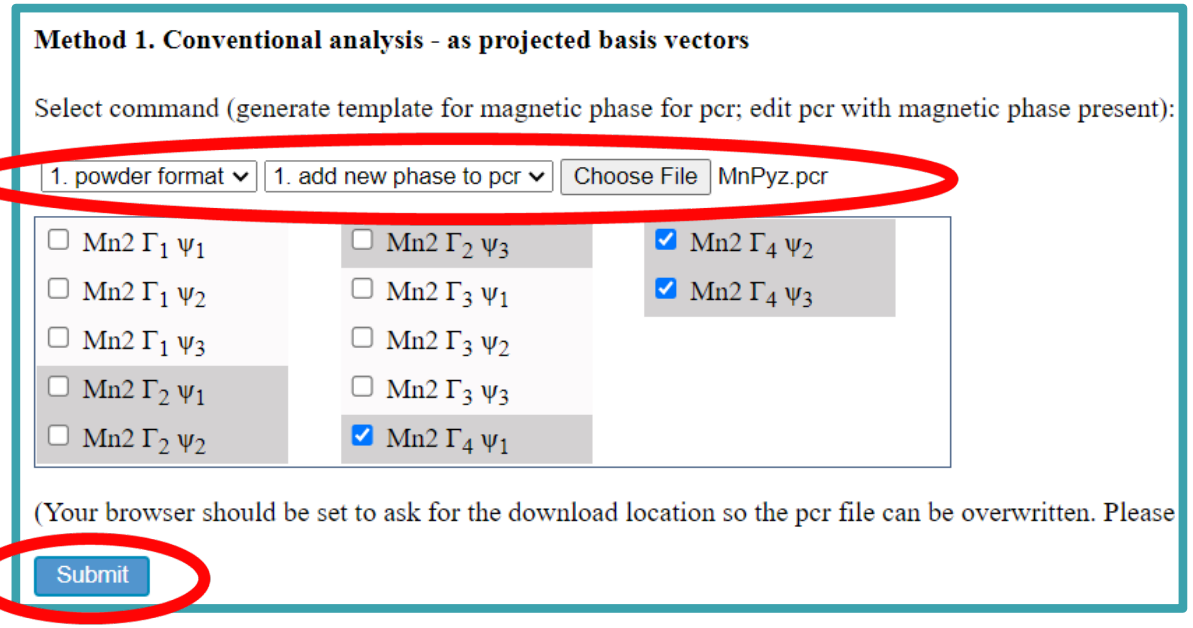
Step 3: Create candidate magnetic models using SARAh

- 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.



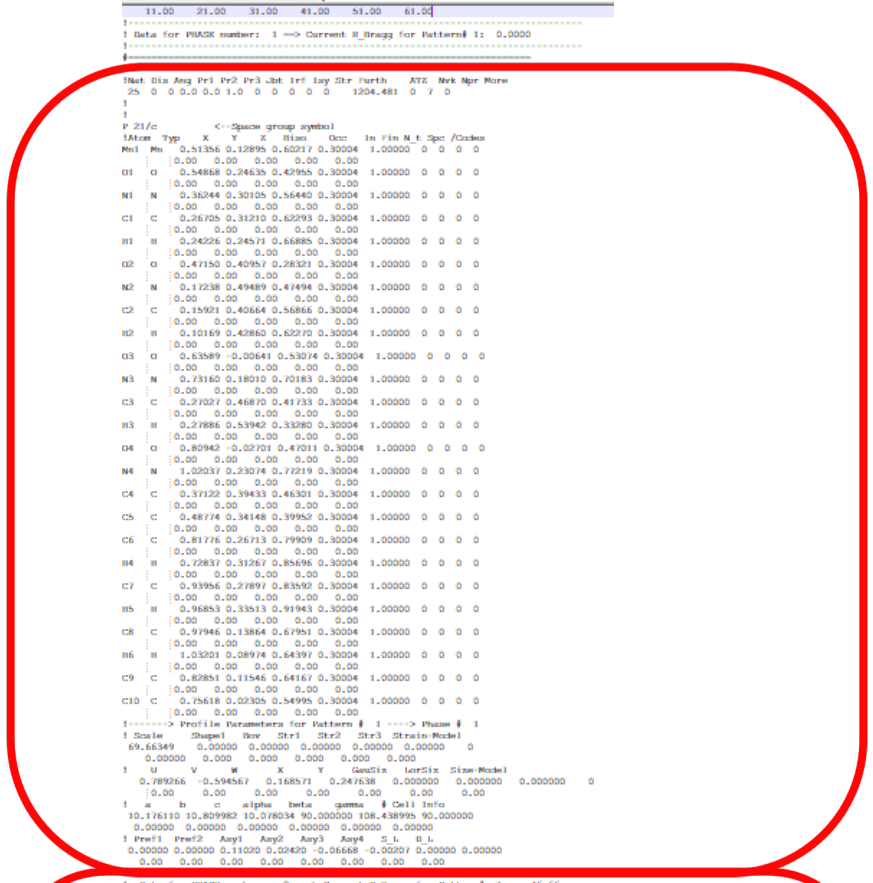
Only one IR (Γ_4) will be tested here, but ALL IRs should tested.

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

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                                <--Space group symbol
! 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.
BASI 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.
BASI 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.
BASI 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.
BASI 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
                     0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00
     0.000     0.000     0.000     0.000     0.000     0.000     0.00000
     0.00      0.00      0.00      0.00      0.00      0.00      0.00
!-------> Profile Parameters for Pattern #  1 ----> Phase #  1
! Scale      Shape1    Bov       Str1      Str2      Str3   Strain-Model
 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.      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.

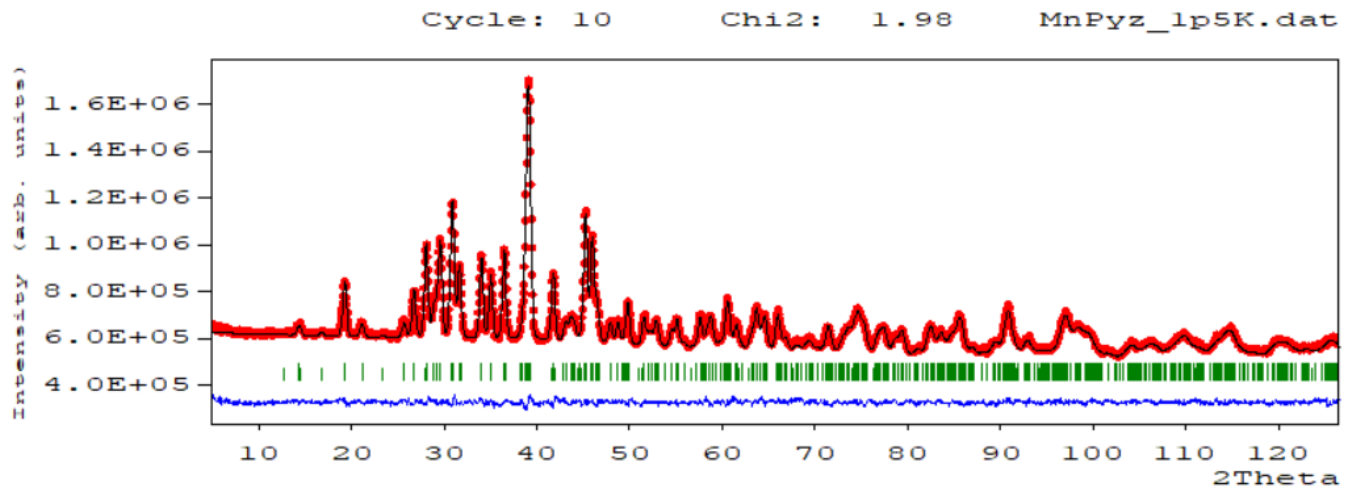
```
!------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:   0.0000
!------------------------------------------------------------------------------
Template magnetic phase by SARAh - web Representational Analysis
!
!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.
BASI 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.
BASI 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.
BASI 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.
BASI 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  0.51356 0.12895 0.60217 0.30000  1.00000   1.000   1.000   1.000
                        0.00    0.00    0.00    0.00     0.00     71.00   81.00   91.00
       0.000   0.000   0.000   0.000   0.000   0.000   0.00000
        0.00    0.00    0.00    0.00    0.00    0.00     0.00
!-------> Profile Parameters for Pattern #   1  ----> Phase #   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:
    0.0000000   0.0000000   0.0000000          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-weigthed 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
```



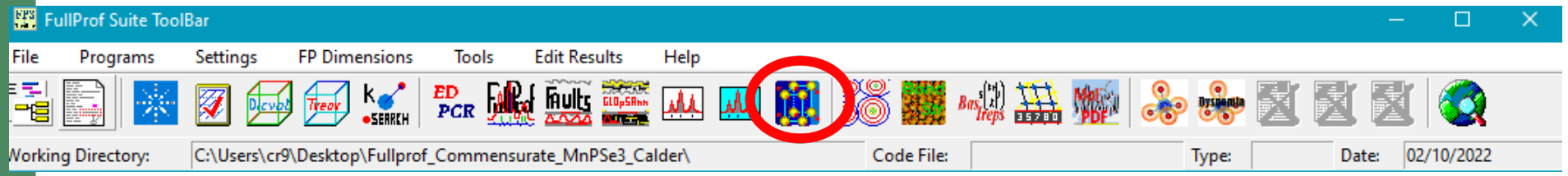
Try to refine the other IRs (Γ_1, Γ_2 and Γ_3). The fit is close, but some magnetic scattering is not captured.

Mn-pyrazinecarboxylate

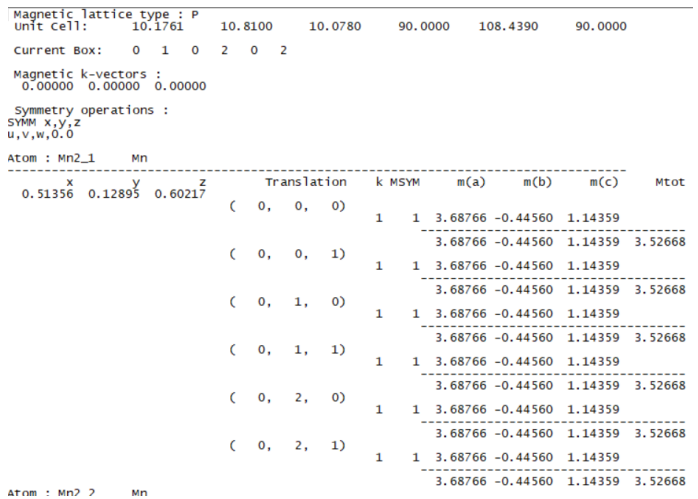
- This example will use Fullprof and SARAh http://fermat.chem.ucl.ac.uk/spaces/willsgroup/web-software/sarah-refine-fullprof/
  - Step 1: Refine the crystal structure using FullProf
  - Step 2: Determine the k-vector by indexing the magnetic reflections using k-search
  - Step 3: Create candidate magnetic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

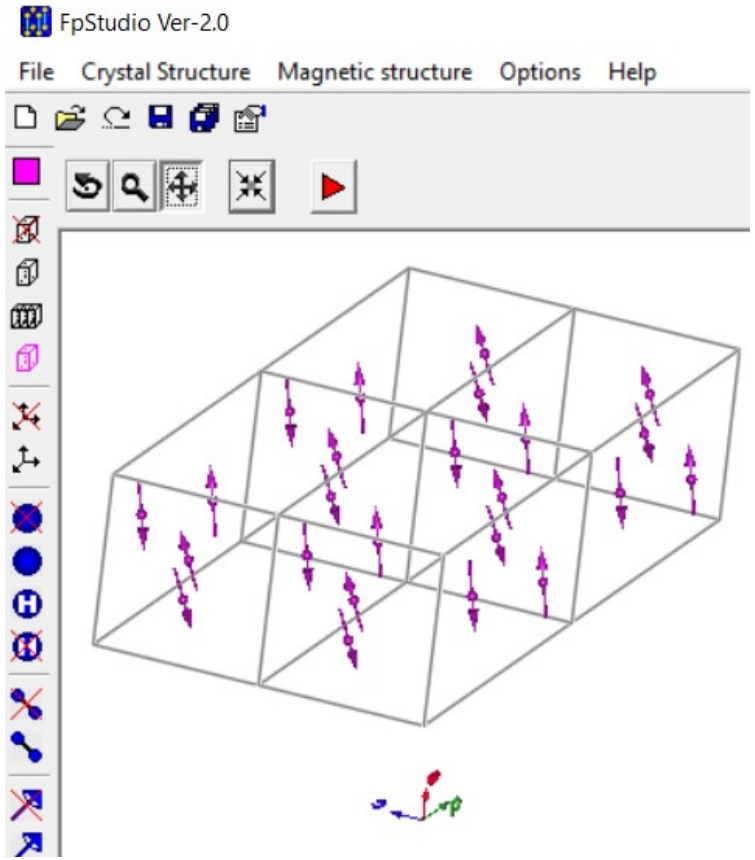
- The model can be checked in FPStudio



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

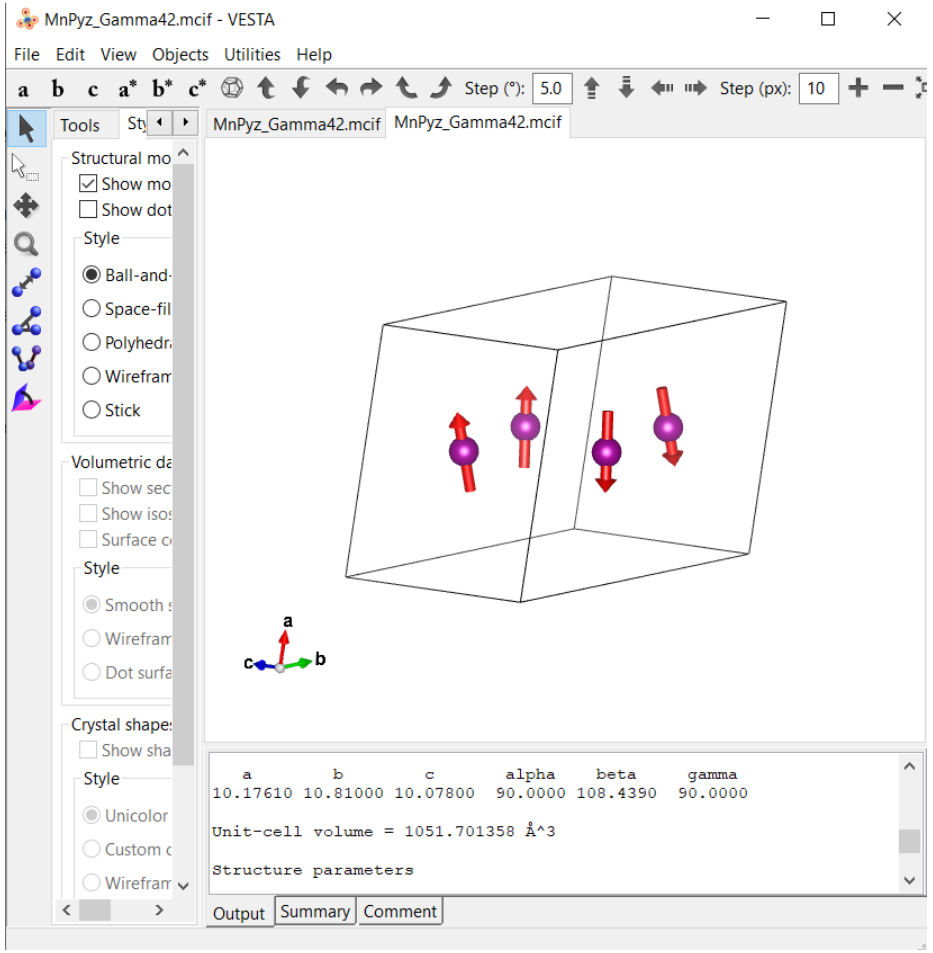


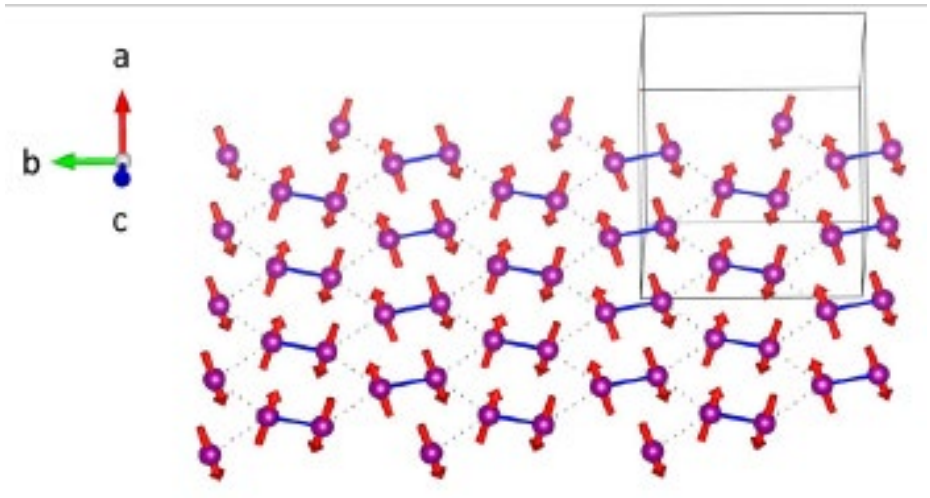
```
Magnetic lattice type : P
Unit Cell:      10.1761     10.8100     10.0780     90.0000    108.4390     90.0000

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_2     Mn
```



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

PHYSICAL REVIEW MATERIALS 7, 124408 (2023)

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

S. Calder,[1,*] R. Baral,[1] N. Narayanan,[2] and L. D. Sanjeewa[2,3]
[1]*Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[2]*University of Missouri Research Reactor (MURR), University of Missouri, Columbia, Missouri 65211, USA*
[3]*Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA*

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

The magnetic properties of $[Mn(pyrazinecarboxylate)_2]_n$, empirical formula $C_{10}H_6MnN_4O_4$, 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

The magnetic structure is in the MAGNDATA database

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

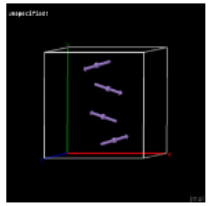
Log

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

To upload any published structure click HERE

Enter the label of the structure: Submit

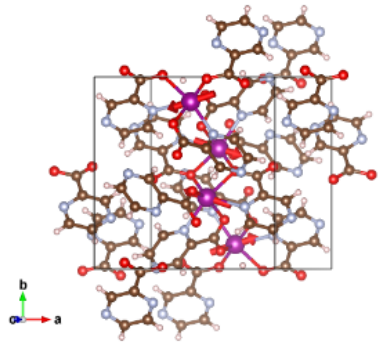
Previous entry Next entry



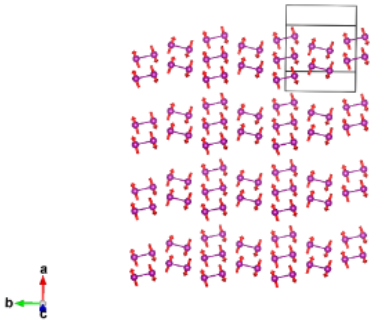
$C_{10}H_6MnN_4O_4$ (#0.1010)

view in Jmol
Download mcif file
Download vesta file (all atoms)
Download vesta file (magnetic atoms only)

submit to STRCONVERT



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
Atomic positions from: Cai

Parent space group (paramagnetic phase): $P2_1/c$ (#14)
Propagation vector: k1 (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)

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