

# Tutorial: $\text{Na}(\text{OH}_2)_3\text{Mn}(\text{NCS})_3$

## ***Nuclear and magnetic structure refinement: Single Crystal Multiphase.***

In this tutorial, we present an example of how to work with single crystals in FullProf using a structural model where the description in the PCR file is in terms of two phases. In this particular case the multiphase approach is used to facilitate the refinement of a magnetic structure, characterised by the propagation vector  $\mathbf{k}=(0,0,0)$ , for which the magnetic space group (MSG) splits the atoms in such a way that the full set of new degrees of freedom cannot be properly refined due to the weak magneto-elastic coupling.

### **Compound: $\text{Na}(\text{OH}_2)_3\text{Mn}(\text{NCS})_3$**

Single crystal data obtained at the ILL on the D19 diffractometer with nominal  $\lambda = 1.455669 \text{ \AA}$ .

The space group is S.G. =  $P-3$ .

The initial structural model was determined by single crystal X-ray diffraction using a silver source. The structural parameters required for this tutorial were obtained from the input CIF file (X-ray\_data\_100K.cif).

This compound is a honeycomb antiferromagnet with the following characteristics:

- The compound crystallizes crystallises in a low symmetry trigonal space group ( $P-3$ ) and exhibits an ordering temperature ( $T_N$ ) of 18.1 K.
- Macroscopic magnetic measurements indicate a global antiferromagnetic behaviour, with nearest-neighbour interactions.
- Neutron diffraction experiments confirm the presence of long-range magnetic order.

The structural and magnetic description of  $\text{Na}(\text{OH}_2)_3\text{Mn}(\text{NCS})_3$  can be found in the manuscript presented by Geers *et al.* <https://doi.org/10.1039/d4cp01265h>

### **Input file descriptions**

In this tutorial, we provide two datasets: the first collected at 25 K in the paramagnetic phase, and the second collected at 2 K, well below the Néel temperature ( $T_N$ )

#### Data collected at 25K in the paramagnetic phase:

The reflections were integrated using the following UB matrix, allowing the refinement of the cell parameters based on the strong reflections. The integrated intensities obtained were corrected for absorption due to the experimental setup used.

UB matrix

```
0.003186610  0.026466181  0.155335000
-0.046100520 -0.111142100  0.038448054
0.105338600  0.013364214  0.012127420
```

Refined unit cell parameters:

$a = 10.0384(3)$   $b = 10.0384(3)$   $c = 6.2313(2)$

$\alpha = 90.0000$   $\beta = 90.0000$   $\gamma = 120.0000$

The file containing the integrated reflections in hklf4 format (SHELX format) is included in the distribution of this tutorial under the name '**mn\_25K\_abscan.hkl**'.

Data taken at 25K in the paramagnetic phase:

A similar procedure to that described above was carried out at 2 K. The values obtained after the refinement are shown below.

UB matrix

```
0.003183997  0.026447610  0.155339400
-0.046101250 -0.111171700  0.038412440
0.105366410  0.013376270  0.012112603
```

Refined unit cell parameters:

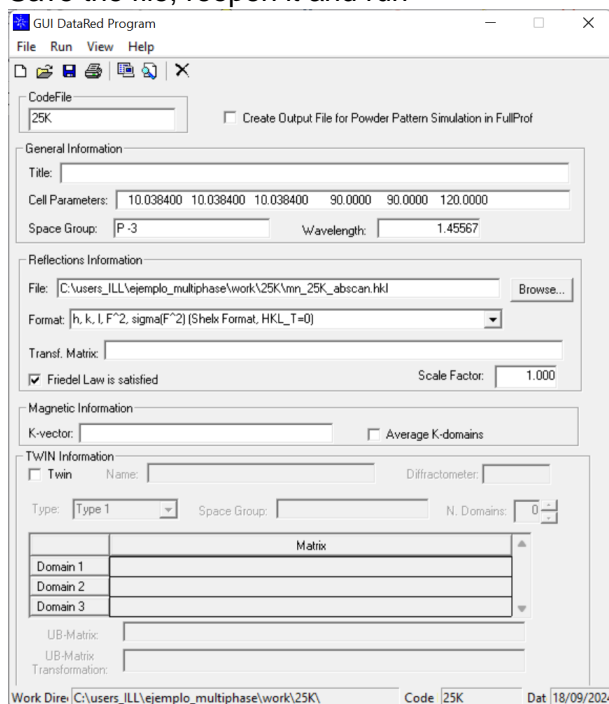
$a = 10.0361 (3)$   $b = 10.0361 (3)$   $c = 6.2315 (2)$

$\alpha = 90.0000$   $\beta = 90.0000$   $\gamma = 120.0000$

The file containing the integrated reflections in hklf4 format (SHELX format) is included in the distribution of this tutorial under the name '**mn\_2K\_abscan.hkl**'.

## Refinement of the nuclear structure at 25 K (paramagnetic phase)

- 1) Open the DataRed program, included in the FullProf toolbar.
  - a. Fill in all the fields including code, cell parameters, space group (P -3, note the space between P and -3), wavelength...
  - b. Include the '**mn\_25K\_abscan.hkl**' file by clicking on Browse
  - c. In Format you should select h,k,l,F<sup>2</sup>...(Shelx format)
  - d. Save the file, reopen it and run



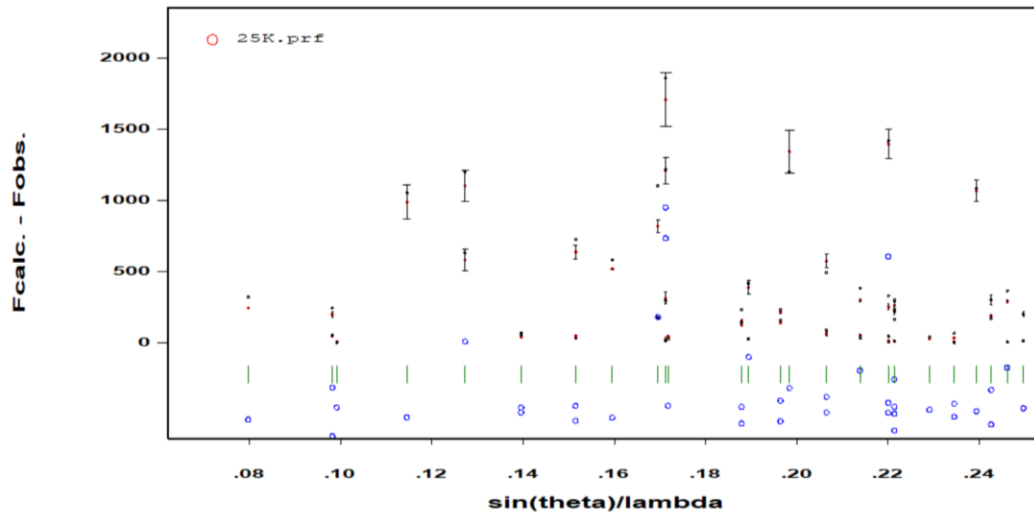
- e. Check the output file. A summary is given below:

=> Number of reflections read:	1942
=> Number of valid independent reflections:	631
=> Number of obs. with equival. reflections:	1803
=> Number of rejected (absences) reflections:	0
=> R-internal for equivalent reflections (%):	5.43
=> R-weighted for equivalent reflections (%):	6.10
=> Average Intensity of reflections:	783.36
=> Average sigma for equivalent reflections:	11.89
- f. Make sure that the program has created a file called 'codefile.int', in our case **25K.int**. This file contains the merged integrated intensities in a format compatible with FullProf.

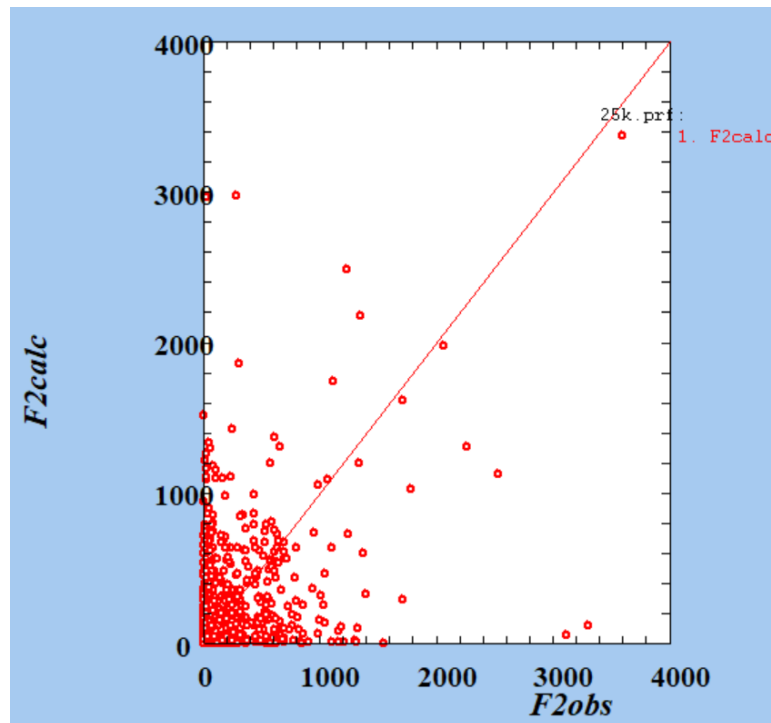
- 2) To refine the crystal structure, you can create a PCR file using the X-ray CIF file as a starting point.



- 3) Try to refine the crystal structure. In the initial stages, you can manually adjust the scale factor to approximate the observations (around 34 is a good number). As shown in the figures, the observed and calculated values appear to be correct, but the difference is surprisingly large.



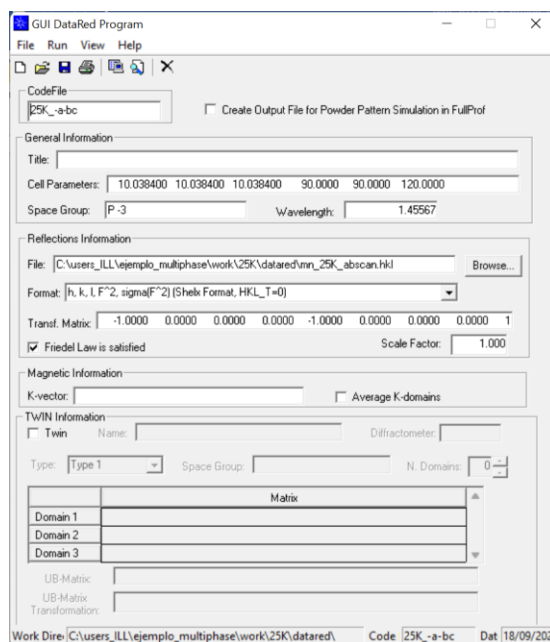
This effect is also observed in the  $F_{2calc}$  vs  $F_{2obs}$ , suggesting that the indexing in both cases (X-rays and Neutrons) has not been integrated using the same unit cell orientation.



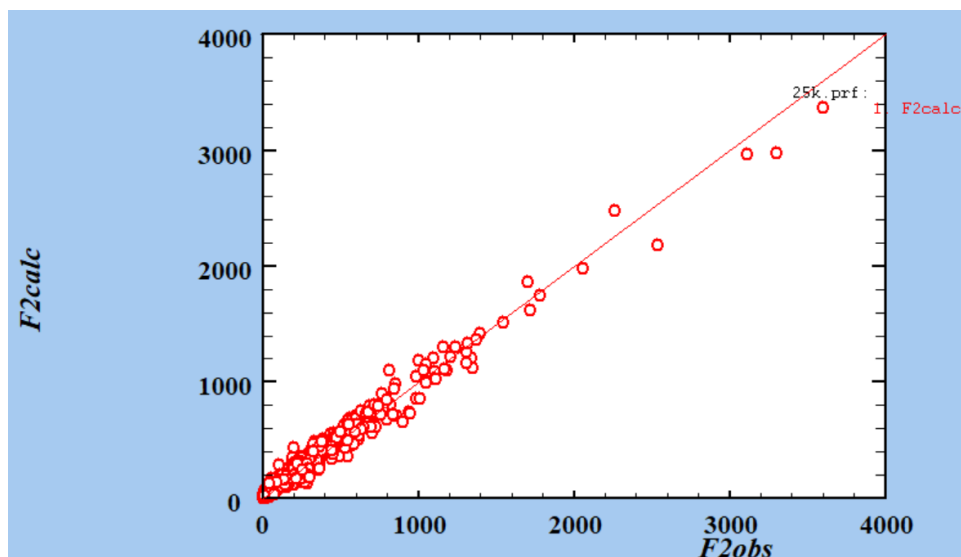
In order to put both in the same orientation, we need to apply the following transformation (-a -b c) to the data we have collected

- 4) Go to point 1 and include in the DataRed the next transformation matrix:

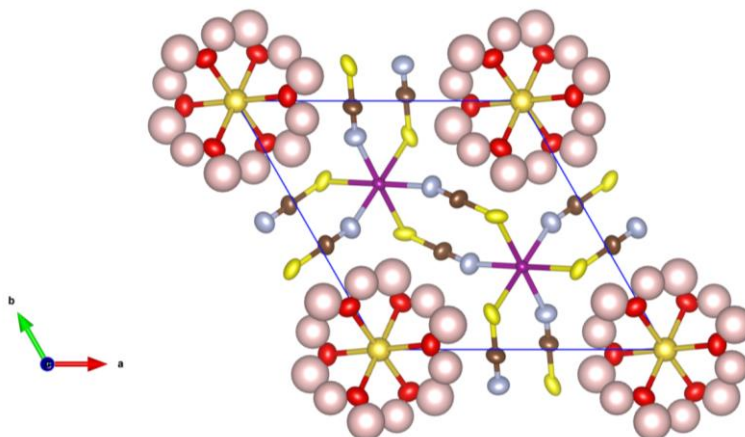
$$T = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



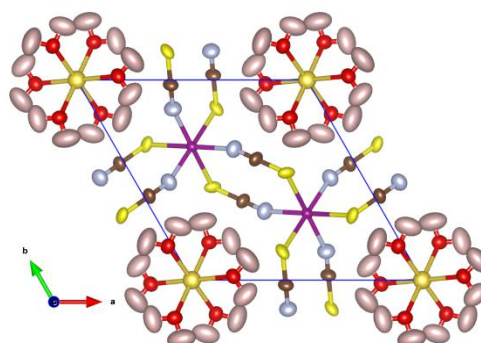
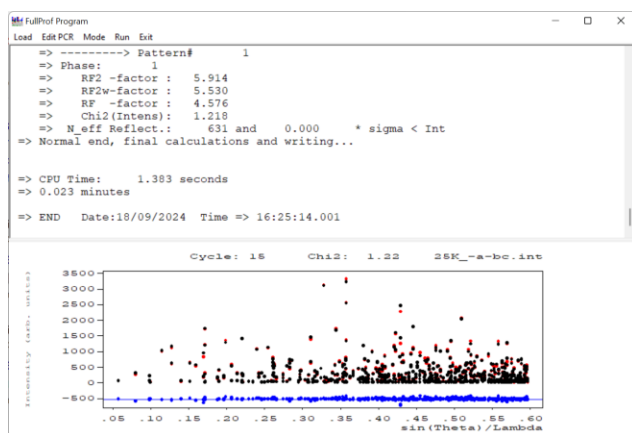
- 5) Now try to refine the crystal structure using the new .int file (**25K\_-a-bc.int**), starting again with the scale factor and compare with the previous fit. (see below the fit refining only the scale factor)



- 6) Include in the pcr the code Rpa ==-1 to generate a CIF file to check the structural model (this step can also be done with EdPCR).  
Below you can see the structural model with all non-hydrogen atoms refined with Atomic Displacement Parameters (ADP) defined anisotropically. As we are using neutron diffraction, the ADP of H1 and H2 can be refined with an anisotropic model.



- 7) After including anisotropic ADPs, the paramagnetic structure is fully defined. The statistics and structural model are shown in the figures below. We rename the PCR file to **nuclear.pcr**.

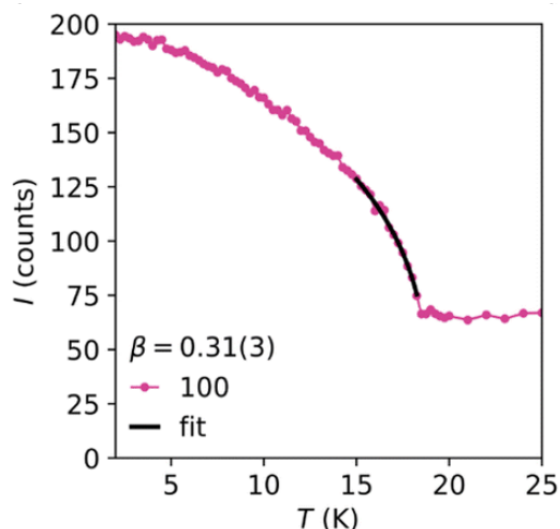


### Determination of possible magnetic space groups and refinement.

The main goal of this section is to generate the list of magnetic space groups (MSG), also called Shubnikov groups, which are compatible with the propagation vector and the parent space group of our compound.

In single-crystal neutron diffraction experiments, the determination of the propagation vector must be done during the experiment, since the region of reciprocal space that is typically measured is only a limited part (due to the size limitations of the detector). Therefore, if an exhaustive search is not conducted, there is a risk of missing magnetic reflections. This procedure is generally performed through Q-scans along specific directions in reciprocal space. In this case, D19 is equipped with a 2D detector covering 120 degrees horizontally and 30 degrees vertically, which cover a large part of reciprocal space. Due to this geometry, omega scans at low temperatures can be used to observe whether new reflections appear ( $\mathbf{k} \neq 0$ ) or whether the main reflections increase in intensity ( $\mathbf{k} = 0$ ), and these can be indexed using the parent cell.

Below, we show the temperature evolution of the (1 0 0) reflection, which has a significant magnetic contribution, fitted to a power law (black line), with  $\beta = 0.31(3)$ . More details about this figure can be found in the reference given at the beginning of the tutorial.



From the comparison of the data measured in the paramagnetic phase and at 2K, it can be concluded that no new reflections appear, and only the nuclear reflections observed at 25K increase in intensity. We can therefore conclude that the propagation vector is of the form  $\mathbf{k} = (0,0,0)$ .

#### 1) PCR file using MSGs.

- a. To determine the possible Shubnikov groups compatible with our system, we can use BaslReps, as demonstrated in previous tutorials. Alternatively, the Bilbao Crystallographic Server/ISODISTORT can be used to compute a list of Shubnikov groups and download the corresponding mcif file (one for each Shubnikov group). The mcif file can then be converted into a PCR format for FullProf using the mCIF\_to\_PCR utility on the FullProf toolbar.
- b. In this tutorial, we will use the Bilbao Crystallographic Server. Open a web browser and write <http://www.cryst.ehu.es/>
- c. Click on Magnetic Symmetry and Applications
- d. Click on k-Subgroupsmag
  - i. Include the parent space group (147)
  - ii. Include the propagation vector
  - iii. Click on Submit



Enter the serial number of the space group of the parent paramagnetic phase:

[Choose an alternative magnetic group](#)

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**Introduce the magnetic wave vector(s)**

(Give the components of the wave vectors in a fractional form, n/m)

$k_{1x}$    $k_{1y}$    $k_{1z}$

[Show the independent vectors of the star](#)

☐ Choose the whole star of the propagation vector

- 2) The program provides a list of possible Shubnikov groups, including those that are subgroups of the parent. You can select the option to include the structural data of the parent phase to generate the mcif files. In this example, we will initially focus on the space groups belonging to the trigonal system. Therefore, we will select the following space groups:  $P\bar{3}'$ ,  $P\bar{3}$ , and  $P3$ .

N	Group Symbol	Transformation matrix	Group-Subgroup Index	Other members of the Conjugacy Class	Irreps	Magnetic structure models (MAGMODELIZE)
1	$P\bar{3}'$ (No. 147.15)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	2=1x2	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>	<input checked="" type="checkbox"/>
2	$P\bar{3}$ (No. 147.13)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	2=1x2	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>	<input checked="" type="checkbox"/>
3	$P3$ (No. 143.1)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	4=1x4	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>	<input checked="" type="checkbox"/>
4	$P\bar{1}'$ (No. 2.6)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	6=1x6	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>	<input type="checkbox"/>
5	$P\bar{1}$ (No. 2.4)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	6=1x6	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>	<input type="checkbox"/>
6	$P1$ (No. 1.1)	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	12=1x12	<input type="button" value="Conjugacy Class"/>	<input type="button" value="Get irreps"/>	<input type="checkbox"/>

☒ Include structure data of the parent phase

NB: To generate a simplified CIF, you can save the refined model from the previous section using VESTA. VESTA generates a CIF that contains only the basic structural information, greatly reducing the risk of reading errors when imported into the BCS. In the BCS folder, you will find a simplified CIF called VESTA.cif containing the refined model at 25K.

- 3) The program will ask for a nuclear CIF file. If there are no errors in your CIF file, the program will ask you to select the magnetic atoms. Select Mn and click "Submit."

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

VESTA.cif

*Note: The space group of the cif file will supersede any previous one.*

**Option 2: Specify structure data by hand:**

Space Group:  $P\bar{3}$  (No. 147)

Lattice parameters (Angstroms and degrees):  
 $a=b=$    $c=$    $\alpha=90$   $\beta=90$   $\gamma=120$

Number of unique atomic positions:

Parent space group: *P*-3 (No. 147)  
 Lattice parameters (Angstroms and degrees): a=10.08120, b=10.08120, c=6.26720, alpha=!

Atoms: Please select the magnetic ones

N	Atom name	Atom type	Wyckoff Position	Coordinates	Magnetic?
1	Mn1	Mn	2d	0.33333 0.66667 0.45660	<input checked="" type="checkbox"/>
2	S1	S	6g	0.67760 0.53560 0.83690	<input type="checkbox"/>
3	Na1	Na	1a	1.00000 1.00000 1.00000	<input type="checkbox"/>
4	Na2	Na	1b	1.00000 1.00000 0.50000	<input type="checkbox"/>
5	O1	O	6g	0.81110 0.98060 0.74320	<input type="checkbox"/>
6	N1	N	6g	0.51068 0.65501 0.63296	<input type="checkbox"/>
7	C1	C	6g	0.58002 0.60457 0.71720	<input type="checkbox"/>
8	H1	H	6g	0.70820 0.89930 0.74260	<input type="checkbox"/>
9	H2	H	6g	0.80520 1.07320 0.75620	<input type="checkbox"/>

Submit

- 4) The program gives a list of maximal magnetic space groups compatible with the propagation vector. It also gives the transformation to the standard setting; in this particular case is the identity.

Selected magnetic space subgroup for the parent space group *P*-3 (No. 147)

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

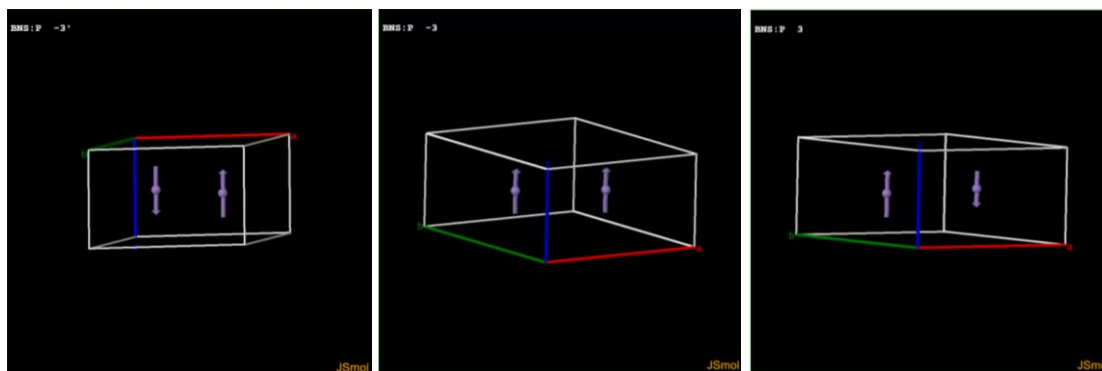
N	Group (BNS)	Transformation matrix	General positions	Properties	Magnetic structure
1	<i>P</i> -3' (#147.15) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
2	<i>P</i> -3 (#147.13) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
3	<i>P</i> 3 (#143.1) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show

mCIFs of the transformed structure in the selected subgroups ('ksubgroupsmag\_mCIFs\_11423.zip')

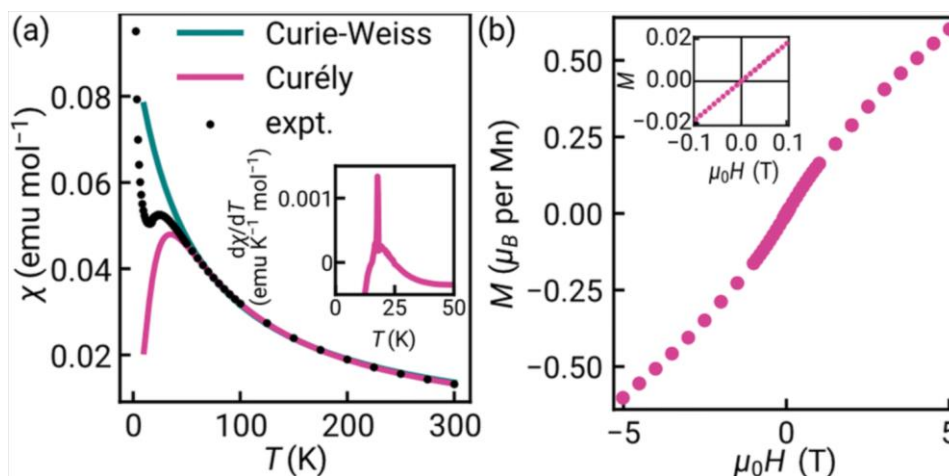
Of the three proposed Shubnikov groups, the *P*-3 MSG allows only collinear ferromagnetic order, which was disregarded as it is inconsistent with our magnetic property measurements. The *P*-3' group only allows for collinear antiferromagnetic order, while *P*3 allows for antiferromagnetic, ferromagnetic, or ferrimagnetic arrangements of the moments as it contains two distinct Mn(II) sites.

To download the three mcif files you can click on the *mCIFs of the transformed structure in the selected subgroups* ('ksubgroupsmag\_mCIFs\_11423.zip') or click on them individually in the Show button. You can visualise the different models by clicking on Show and then on MVISUALIZE.

Here below you can find the 3 magnetic structures:



- 5) As mentioned above, the  $P-3$  model is not compatible with the macroscopic measurements, so we have discarded this model. Below are the magnetometric measurements:



According to these measurements (susceptibility was recorded using a magnetic field of 100 Oe), the system exhibits antiferromagnetic (AF) behaviour with a possible weak ferromagnetic signal at low temperatures, which could be attributed to spin canting or the non-compensation of magnetic moments. Other possible explanations are not discussed at this stage, so as not to provide additional explanations prematurely.

The  $P-3'$  model represents a purely antiferromagnetic structure and therefore cannot explain the increase in susceptibility observed in the magnetic measurements. This magnetic model can be refined following the same steps described in **Tutorial 5**. In this tutorial, we will first explore the  $P3$  model, which appears to be more consistent with the observed magnetic behaviour. However, we also recommend performing refinements using the  $P-3'$  model for a more comprehensive analysis.

- 6) Copy the mcif file generated by BCS for the  $P3$  model into a specific folder (in our case, 2K\Magnetic\_Structure\P3). Use a text editor to check that the file contains the initial magnetic moment.

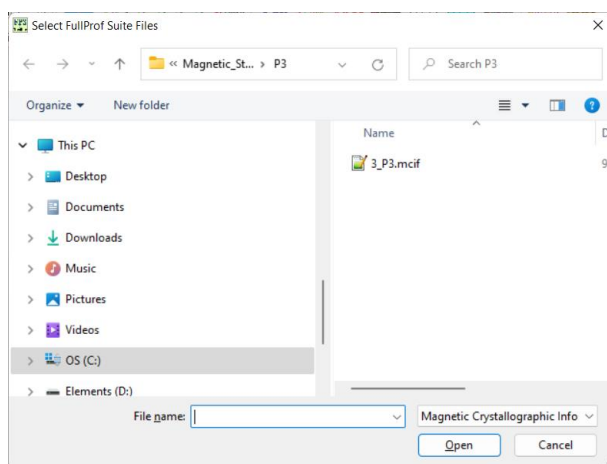
```

loop_
  _atom_site_moment.label
  _atom_site_moment.crystalaxis_x
  _atom_site_moment.crystalaxis_y
  _atom_site_moment.crystalaxis_z
  _atom_site_moment.symmform
Mn1_1 0.00000 0.00000 4.00000 0,0,mz
Mn1_2 0.00000 0.00000 -3.90000 0,0,mz

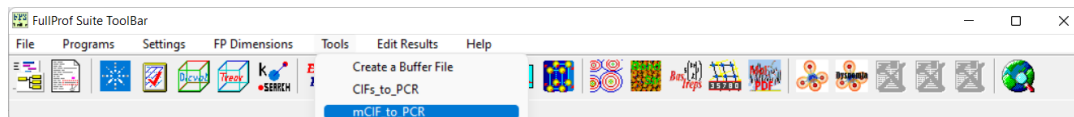
```

In this block, you can see that there are two Mn orbits in the space group  $P3$ , and the magnetic components are symmetrically aligned along the  $c$ -axis. As we need a net ferromagnetic model, we have set slightly different initial values for each site and coupled AF (note the negative sing for Mn1\_2).

- 7) Select the working directory in the FullProf toolbar and then, in File>Information/tpcr...>select mCIF(magnetic CIF). In the pop-up windows, select the mCIF from BCS.



After loading the mcif file in the “Code File”/“Type” fields, you can select mcif\_to\_PCR from the Tools menu



You will see a terminal window with some useful information. Check in your working directory for a created PCR file containing the magnetic structure information. The file will have the same name as the mcif. So it is a good idea to rename this file, for this example we will use (**2K\_P3.pcr**).



```

SI_2 S 1 0 0.32240 0.46440 0.16310 0.00000 1.00000 0 0 #
Na1 Na 1 0 0.00000 0.00000 0.00000 0.00000 0.33333 0 0 #
Na2 Na 1 0 0.00000 0.00000 0.50000 0.00000 0.33333 0 0 #
O1_1 O 1 0 0.81110 0.98940 0.74320 0.00000 1.00000 0 0 #
O1_2 O 1 0 0.18890 0.01940 0.25680 0.00000 1.00000 0 0 #
N1_1 N 1 0 0.51048 0.65501 0.63296 0.00000 1.00000 0 0 #
N1_2 N 1 0 0.48932 0.34499 0.36704 0.00000 1.00000 0 0 #
Cl_1 Cl 1 0 0.58002 0.60457 0.71720 0.00000 1.00000 0 0 #
Cl_2 Cl 1 0 0.41998 0.39543 0.28280 0.00000 1.00000 0 0 #
H1_1 H 1 0 0.70820 0.89930 0.74260 0.00000 1.00000 0 0 #
H1_2 H 1 0 0.29180 0.10070 0.25740 0.00000 1.00000 0 0 #
H2_1 H 1 0 0.80520 0.07320 0.75620 0.00000 1.00000 0 0 #
H2_2 H 1 0 0.19480 0.92680 0.24380 0.00000 1.00000 0 0 #
!----- Scale, Extinction and Cell Parameters for Pattern # 1
! Scale Factors
! Sc1 Sc2 Sc3 Sc4 Sc5 Sc6
! 1.000 0.000 0.000 0.000 0.000 0.000
! 0.00 0.00 0.00 0.00 0.00 0.00
! Extinction Parameters
! Ext1 Ext2 Ext3 Ext4 Ext5 Ext6 Ext7 Ext-Model
! 0.1760 -0.1978 0.9145E-01 0.000 0.3008E-01 0.000 0.000 0
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0
! a b c alpha beta gamma #Cell Info
! 10.081201 10.081201 6.267200 90.000000 90.000000 120.000000 #
! x-Lambda/2
! 1.00000
! 0.00
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot
! 2.000 130.000 1

```

Some parameter as:

Job=1 (neutrons + calculation)

NYC (number of cycles) can be changed from 1 to 15.

Extinction parameters, set all to zero, for now.

x-Lambda/2, set to zero

You can set an initial value for Scale other than 1.

It is worth noting that in the mcif file generated by BCS, we have lost the information on the Atomic Displacement Parameters (ADPs). In addition, since we have lost the inversion centre, all the atoms appear duplicated, which means that the parameters to be refined are doubled.

9)

The screenshot shows the 'GUI DataRed Program' window. The 'CodeFile' field contains '2K\_a-bc'. The 'General Information' section includes a 'Title' field, 'Cell Parameters' (10.038400 10.038400 10.038400 90.0000 90.0000 120.0000), 'Space Group' (P 3), and 'Wavelength' (1.45567). The 'Reflections Information' section shows the 'File' path, 'Format' (h, k, l, F<sup>2</sup>, sigma(F<sup>2</sup>)), 'Transf. Matrix' (a 3x3 identity matrix), and 'Scale Factor' (1.000). The 'Magnetic Information' section has a 'K-vector' field and an 'Average K-domains' checkbox. The 'Twin Information' section includes 'Twin' checkbox, 'Name', 'Diffractometer', 'Type' (Type 1), 'Space Group', 'N. Domains' (0), and a 'Matrix' table with three rows (Domain 1, Domain 2, Domain 3) and three columns. The 'UB-Matrix' and 'Transformation' fields are also present. The status bar at the bottom shows 'Work Dir: C:\users\_ILL\ejemplo\_multiphase\work\2K\datared\', 'Code 2K\_a-bc', and 'Dat 19/09/2024'.

- 10) The nuclear and magnetic components are in the same phase ( $JBT = 10$ ), so only one phase is required.
- 11) The code VARY *mxmymz* automatically activates the refinement of the magnetic moment components that are compatible with the symmetry. If the user wishes to fix one component, this code should be removed. As a first step, we recommend removing the VARY code and fixing the magnetic moments to reasonable values (about 4, with one positive and one negative).
- 12) In the FullProf toolbar, select the PCR file and refine.
  - a. In the first refinement, include only the scale factor (if necessary, set a value close to the expected value by hand)
  - b. All thermal parameters are set to zero. Try refining them and see what happens.
  - c. Try applying some constraints to the thermal parameters, using the same code for atoms of the same chemical species.
  - d. If the refinement is stable after the previous step, we can proceed with refining the structural model. Can you predict what might happen next?

Reducing the symmetry from  $P\bar{3}$  to  $P3$  splits the atomic positions due to the loss of the inversion centre. Since the experimental data show no significant difference between reflections with positive and negative hkl, the least-squares method does not converge satisfactorily. In other words, although the system must be described in  $P3$  to explain the magnetic properties, the distortions in the structure are so small that they are not experimentally visible.

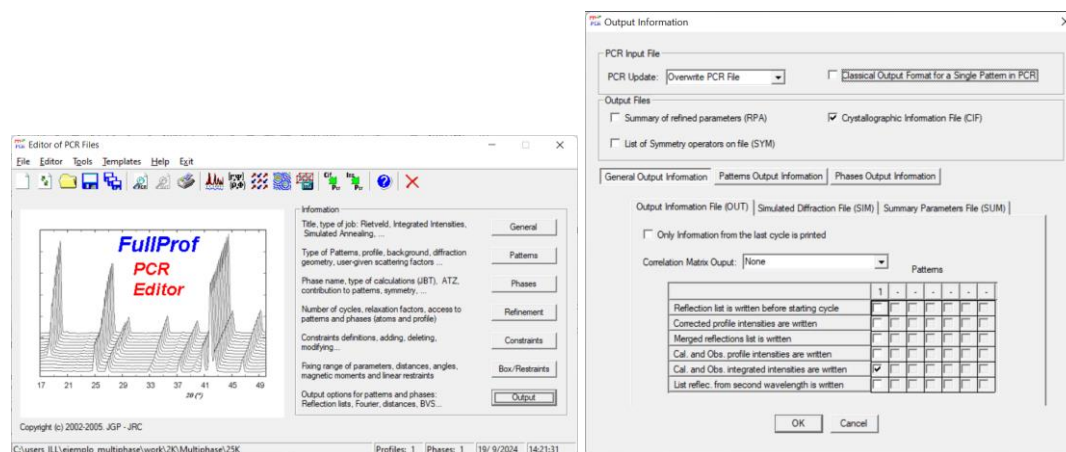
It is relatively easy to describe a structure in  $P\bar{3}$  using the positions in  $P3$ ; one simply has to add the symmetry constraints that are lost when the inversion centre is broken. For example, in the case of the Mn sites, in  $P3$ , we have two orbits, but only one in  $P\bar{3}$ . Therefore, we must make sure that the positions of the two manganese atoms have the same symmetry relationship as in  $P\bar{3}$ . If we look at the z-component of both atoms, their sum is 1. If this relationship is maintained, the description remains in  $P\bar{3}$ , as we are essentially forcing the system to maintain a single orbit by applying additional symmetry constraints. Obviously, this must have been done for all the atoms present in the  $P3$  model.

Although it is "relatively" easy to find the relationships to maintain the description in the parent group for positions, this is much more complex for the ADPs (Atomic Displacement Parameters), and independent refinement is impossible in most cases. Applying direct constraints, as we did in point 12c, is crystallographically incorrect for anisotropically defined ADPs.

Therefore, we can either subtract the nuclear contribution from the reflections in the ordered phase to work exclusively with the magnetic phase, or we can use a recently implemented procedure in FullProf that allows us to work in "multiphase" mode using single crystal data.

## Single crystal Multiphase approach.

- 1) **Create a new working directory**; do not use spaces or special characters in the path (**Multiphase** in our case).
  - a. Copy into this directory the PCR file for 2K (**2K\_P3\_single\_crystal.pcr**), the PCR file for the paramagnetic phase (**25K.pcr**) and the intensity file from 2K (**2K\_-a-bc.int**).
- 2) The first thing we need to do is to convert these two PCR files into the "multiphase" format. The easiest way to do this is by opening both PCR files with EdPCR and saving them in "multiphase" format. This will allow us to copy and paste directly from one file to the other. Load the first PCR file into EdPCR, click on Output and uncheck the box *Classical Output Format for a Single Pattern in PCR*.



Then click on File, save us with a different name in our case **25K\_MP.pcr** and **2K\_P3\_single\_crystal\_MP.pcr**.

The aim is to create a first phase containing the structural information for the paramagnetic phase, based on the data in the **25K\_MP.pcr** file. The second phase should contain the magnetic structure, extracted from the magnetic structure-defining file (**2K\_P3\_single\_crystal\_MP.pcr**), removing all information related to non-magnetic atoms. In addition, the label "*Mag\_Only*" should be added to this second phase to indicate that it will be used only for the calculation of the magnetic structure factors.

- 3) The intensity file should also be modified and included in to the pcr file. This can be done manually or, in the case of  $k=0$  (this procedure can be used by other complex refinements, so the created intensity file is quite general), using the **modify.exe** program distributed with this example.  
Let's have a look at both files, the original and the one needed to perform a multiphase refinement.



### Original file:

```
TITLE
(3i4,2F14.4,i5,4f8.2)
1.45567 0 0
0 0 1 224.1181 16.7878 1 8.32 0.00 0.00 0.00
1 0 0 180.1995 16.3662 1 9.61 0.00 0.00 0.00
```

### Multiphase file:

```
TITLE
dim 3
(3i4,2f14.4,2i4)
lambda 1.45567
0 0 1 -1.0000 0.0000 2 1
0 0 1 224.1181 16.7878 1 1 8.32 0.00 0.00 0.00
1 0 0 -1.0000 0.0000 2 1
1 0 0 180.1995 16.3662 1 1 9.61 0.00 0.00 0.00
```

The file groups reflections into blocks and is very similar to the one used for simulated annealing refinements.

To create this file, simply place the program and the original files in the same folder. Then, from a console (CMD), type:

```
> modify.exe name_original_file.int name_final_file.int
```

In this particular case, the final file was called **2phase\_2K.int**

- 4) In the next step, we will create the PCR by merging the two PCR files that we modified in the previous step.

We will use the 25K\_MP file as a template. Rename this file to a new name and modify it using a text editor (**2phase\_2K.pcr**).

```
data NaMn_taiye_100K_ag_a
NPATT 1 1 <- Flags for patterns (1:refined, 0: excluded)
W PAT 1.000
!Nex Dum Ias Nre Cry Opt Aut
1 0 0 0 0 1 0 0 1
!Job Npr Nba Nex Nsc Nor Iwg Ilo Res Ste Uni Cor Ann Int
1 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 1 !-> Patt#: 1
!
!File names of data(patterns) files
!
!Mat Pcr NLI Rpa Sym Sho
0 1 0 -1 0 0
!Ipr Ppl Ioc Ls1 Ls2 Ls3 Prf Ins Hkl Fou Ana
0 0 1 0 4 0 3 0 0 0 0 0 0 0 0 0 !-> Patt#: 1
!
!NCY Eps R_at R_an R_pr R_gl
15 0.10 1.00 1.00 1.00 1.00
!
!
62 !Number of refined parameters
!
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 0.0000
!
data NaMn_taiye_100K_ag_a VARY xyz b
!
!Nat Dis Ang Jbt Isy Str Furth ATZ Nvk More
9 0 0 0 0 0 0 0 612.4070 0 0
!Contributions (0/1) of this phase to the 1 patterns
1
!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern# 1
4 0 1 0 0
! Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
0.000 0.000 1.000 1.000 1.000 0.000 0.000
!
!
P -3
!Atom Typ X Y Z Biso Occ In Fin N t Spc /Code
```

Nph = 2

Int = 2

Put here the file name: 2phase\_2K.int

In the initial refinements you can fix all parameters.

Change: VARY xyz b by FIX xyz

Irf = 0 (in both phases)

Below the line  $x\text{-lambda}/2$  and above 2th1/TOF1... you need to include phase 2.

```

381.00 361.00 281.00 271.00 261.00 251.00
H1 H 0.70821 0.89930 0.74259 0.00000 1.00000 0 0 2 0
    111.00 101.00 91.00 0.00 0.00
0.00391 0.00702 0.03590 0.00116 0.00004 0.00192
241.00 531.00 621.00 611.00 601.00 591.00
H2 H 0.80525 1.07320 0.75616 0.00000 1.00000 0 0 2 0
    81.00 31.00 21.00 0.00 0.00
0.00849 0.00629 0.02286 0.00529 0.00084 -0.00046
221.00 581.00 571.00 561.00 551.00 541.00
!-----> Scale, Extinction and Cell Parameters for Pattern # 1
! Scale Factors
! Sc1 Sc2 Sc3 Sc4 Sc5 Sc6
32.34 0.000 0.000 0.000 0.000 0.000 0.000
11.00 0.00 0.00 0.00 0.00 0.00 0.00
! Extinction Parameters
! Ext1 Ext2 Ext3 Ext4 Ext5 Ext6 Ext7 Ext-Mod
0.000 0.000 0.000 0.000 0.000 0.000 0.000 1
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! a b c alpha beta gamma #Cell Info
10.081202 10.081202 6.267200 90.000000 90.000000 120.000000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! x-Lambda/2
0.00000
0.00
HERE YOU CAN COPY PHASE 2
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot
0.057 150.000 1

```

From the **2K\_P3\_single\_crystal\_MP.pcr** file, copy the block starting with "Data for phase..." up to the block labeled "x-lambda/2."

As mentioned above, this second phase should contain only the magnetic atoms, so change the number of atoms from 16 to 2. In the block describing the atoms, keep only Mn1\_1 and Mn1\_2 and write Mag\_Only in the phase title line.

After including this second phase, the PCR file should look something like this:

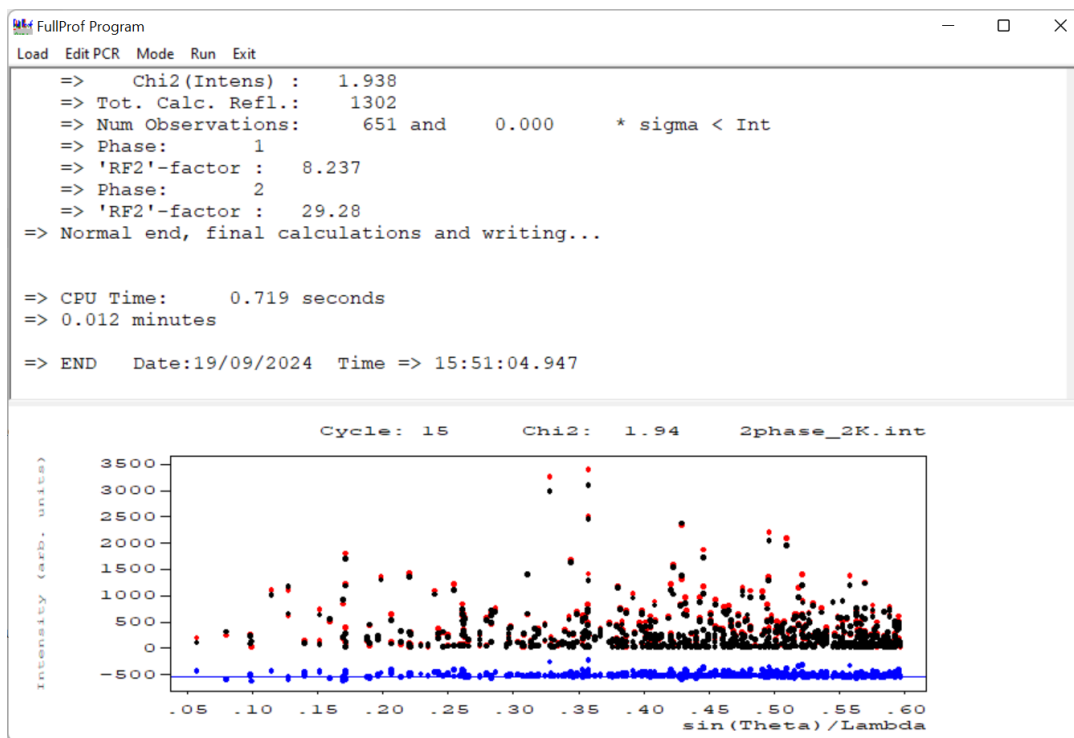
```

! x-Lambda/2
0.00000
0.00
!-----> Scale, Extinction and Cell Parameters for Pattern # 1
! Data for PHASE number: 2 ==> Current Magnetic R-Factor for Pattern# 1: 0.0000
!-----> Scale, Extinction and Cell Parameters for Pattern # 1
Nuclear and Magnetic Structure of: 3 P3 mxmymz Mag_Only
!
!Nat Dis Ang Jbt Isy Str Furth ATZ Nvk More
2 0 0 10 2 0 0 109.8738 0 0
!Contributions (0/1) of this phase to the 1 patterns
1
!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern# 1
0 7 1 0 0
! Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
0.000 0.000 1.000 1.000 1.000 0.000 0.000
!
P3 number:143.1 <--Magnetic Space group symbol (BNS/UNI symbol & number)
Transform to standard: a,b,c;0,0,0
Parent Space Group: P-3 IT_number: 147
Transform from Parent: a,b,c;0,0,0
! Nsym Cen N_Clat N_Ant
3 0 0 0
!
! Symmetry operators
1 x,y,z,+1
2 -y,x-y,z,+1
3 -x+y,-x,z,+1
!
!Atom Typ Mag Vek X Y Z Biso Occ N_type Spc/Fftype /Li
! Rx Ry Rz Ix Iy Iz MagPh / Line below:Codes
! beta11 beta22 beta33 beta12 beta13 beta23 / Line below:Codes
Mn1_1 MMN2 1 0 0.33333 0.66667 0.45765 0.61623 0.33333 1 0 #
0.00000 0.00000 -4.23729 0.00000 0.00000 0.00000 0.00000 <-MagPar
0.00 0.00 11.00 0.00 0.00 0.00 0.00
Mn1_2 MMN2 1 0 0.66667 0.33333 0.54235 0.61623 0.33333 1 0 #
0.00000 0.00000 4.23729 0.00000 0.00000 0.00000 0.00000 <-MagPar
0.00 0.00 -11.00 0.00 0.00 0.00 0.00
!-----> Scale, Extinction and Cell Parameters for Pattern # 1

```

Before trying to use this PCR, make sure that both phases have the same scale, and remove all refinements codes, just to see if there is an error in the PCR.

After modifying the PCR, FullProf operates in multiphase mode, similar to when using powder diffraction patterns. The results of the refinement are shown below, with the scale as the only refined parameter. The program provides detailed information about each phase:



- 5) In the following steps, you can link parameters between the two phases, similar to how it is done when using neutron powder diffraction.
- 6) An interesting aspect is to include a cut in  $\sin(\theta)/\lambda$  in the magnetic phase (phase 2) to prevent the calculation of magnetic reflections in regions of reciprocal space where there should be no magnetic contribution. This not only helps to speed up the refinement, but also eliminates potential errors due to incorrectly assigning intensities at high  $Q$ , which may not fit the structural model, as magnetic intensities.

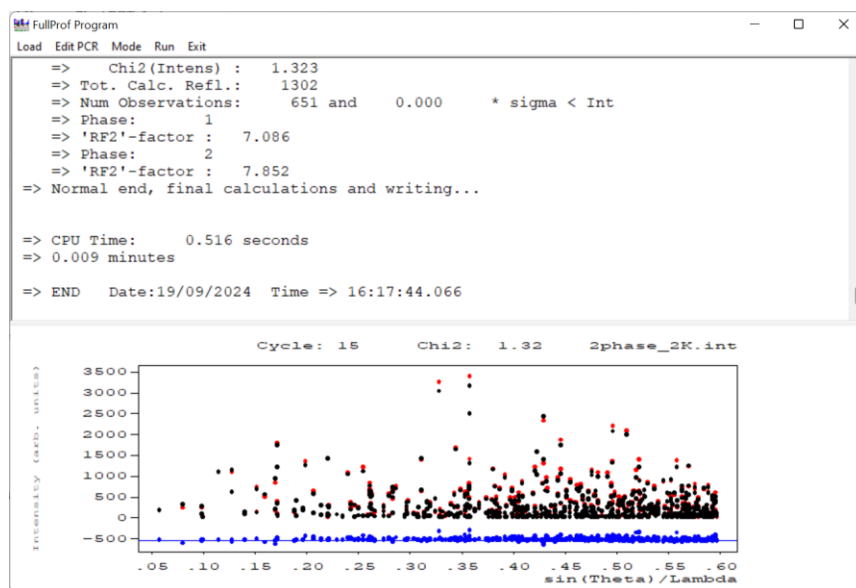
This can be done by including the following commands in Phase 2:

```

!-----
! Data for PHASE number: 2 ==> Current Magnetic R-Factor for Pattern# 1:
!-----
Nuclear and Magnetic Structure of: P3 Mag_Only
!
COMMANDS
MDLIM 1 1.8
END COMMANDS
!Nat Dis Ang Jbt Isy Str Furth      ATZ      Nvk More
  2   0   0  10   2   0   0      109.8738   0   0

```

You can play with the Magnetic D Limits.



- 7) In the next steps, you can refine the atomic coordinates, ADPs, the magnetic moment components of each magnetic atom...

Mn(II) is  $S=5/2$ , so the magnetic moments can be limited from -5 to 5  $\mu_B$ . This task can be done using EdPCR or by hand adding Nre = 2 and the next lines below the x-lambda/2 block.

```

!
!Atom Typ Mag Vek X Y Z Biso Occ N_type Spc/Fftype /Line bel
! Rx Ry Rz Rx Ry Rz Iz MagPh / Line below:Codes
! betall beta22 beta33 beta12 beta13 beta23 / Line below:Codes
Mn1_1 MMN2 1 0 0.33333 0.66667 0.45765 0.00000 0.33333 3 0 #
0.00000 0.00000 -4.94870 0.00000 0.00000 0.00000 0.00000 <-MagPar
0.00 0.00 11.00 0.00 0.00 0.00 0.00 0.00
0.00211 0.00211 0.00453 0.00106 0.00000 0.00000 <-Betas
0.00 0.00 0.00 0.00 0.00 0.00
Mn1_2 MMN2 1 0 0.66667 0.33333 0.54235 0.00000 0.33333 3 0 #
0.00000 0.00000 3.07618 0.00000 0.00000 0.00000 0.00000 <-MagPar
0.00 0.00 31.00 0.00 0.00 0.00 0.00 0.00
0.00211 0.00211 0.00453 0.00106 0.00000 0.00000 <-Betas
0.00 0.00 0.00 0.00 0.00 0.00
!-----> Scale, Extinction and Cell Parameters for Pattern # 1
! Scale Factors
! Sc1 Sc2 Sc3 Sc4 Sc5 Sc6
33.31 0.000 0.000 0.000 0.000 0.000
21.00 0.00 0.00 0.00 0.00 0.00
! Extinction Parameters
! Ext1 Ext2 Ext3 Ext4 Ext5 Ext6 Ext7 Ext-Model
0.000 0.000 0.000 0.000 0.000 0.000 0.000 1
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! a b c alpha beta gamma #Cell Info
10.036100 10.036100 6.231500 90.000000 90.000000 120.000000 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! x-Lambda/2
0.00000
0.00
! Limits for selected parameters:
1 -5.0000 5.0000 0.0000 0 Rz_Mn1_1_ph2
3 -5.0000 5.0000 0.0000 0 Rz_Mn1_2_ph2
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot
2.000 130.000 1

```

- 8) It is always a good idea to check the output files. Below, you can see the refined values of the magnetic moments along with their associated error bars.

Rz\_Mn1\_1\_ph2 -4.9487000 ( +/- 0.14856574)

```

Rz_Mn1_2_ph2      3.0761755      ( +/-      0.15929686)
=> Pattern:      1
=> RF2 -factor    :    6.549
=> RF2w-factor    :    6.985
=> RF -factor     :    4.416
=> Chi2(Intens)   :    1.436
=> Tot. Calc. Refl.:    1302
=> Num Observations:    651 and    0.000      * sigma < Int
=> Phase:        1
=> 'RF2'-factor   :    6.530
=> Phase:        2
=> 'RF2'-factor   :    8.328

```

Although the fit is quite good and the errors in the magnetic moments are acceptable, the difference between the two magnetic moments is substantial. According to the magnetisation curves, the ferromagnetic signal should be below 0.1  $\mu_B$ , making it difficult to distinguish using unpolarised neutrons.

We can constrain the two magnetic moments to differ by 0.1  $\mu_B$  and compare the quality of the fit.

```

!Atom  Typ  Mag Vek  X  Y  Z  Biso  Occ  N_type  Spc/Fftype /Line below:Codes
!      Rx      Ry      Rz  Ix  Iy  Iz  MagPh / Line below:Codes
!      beta11 beta22 beta33 beta12 beta13 beta23 / Line below:Codes
Mn1_1  MMN2  1  0  0.33333  0.66667  0.45765  0.00000  0.33333  3  0  #
      0.00000  0.00000  -4.10970  0.00000  0.00000  0.00000  0.00000  <-MagPar
      0.00  0.00  11.00  0.00  0.00  0.00  0.00  0.00
      0.00211  0.00453  0.00106  0.00000  0.00000  <-Betas
      0.00  0.00  0.00  0.00  0.00  0.00
Mn1_2  MMN2  1  0  0.66667  0.33333  0.54235  0.00000  0.33333  3  0  #
      0.00000  0.00000  4.00970  0.00000  0.00000  0.00000  0.00000  <-MagPar
      0.00  0.00  -11.00  0.00  0.00  0.00  0.00  0.00
      0.00211  0.00453  0.00106  0.00000  0.00000  <-Betas
      0.00  0.00  0.00  0.00  0.00  0.00
!-----> Scale, Extinction and Cell Parameters for Pattern # 1
! Scale Factors
! Sc1 Sc2 Sc3 Sc4 Sc5 Sc6
! 33.34 0.000 0.000 0.000 0.000 0.000
! 21.00 0.00 0.00 0.00 0.00 0.00
! Extinction Parameters
! Ext1 Ext2 Ext3 Ext4 Ext5 Ext6 Ext7 Ext-Model
! 0.000 0.000 0.000 0.000 0.000 0.000 0.000 1
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! a b c alpha beta gamma #Cell Info
! 10.036100 10.036100 6.231500 90.000000 90.000000 120.000000 #
! 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! x-Lambda/2
! 0.00000
! 0.00
! Limits for selected parameters:
! 1 -5.0000 5.0000 0.0000 0 Rz_Mn1_1_ph2
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot
! 2.000 130.000 1

```

```

=> Pattern:      1
=> RF2 -factor    :    6.548
=> RF2w-factor    :    6.987
=> RF -factor     :    4.437
=> Chi2(Intens)   :    1.434
=> Tot. Calc. Refl.:    1302
=> Num Observations:    651 and    0.000      * sigma < Int
=> Phase:        1
=> 'RF2'-factor   :    6.531
=> Phase:        2

```

=> 'RF2'-factor : 8.183

As can be seen, there is no significant change in the statistics, and the value of the magnetic moment lies between the two observed values when no constraints are applied.

Rz\_Mn1\_1\_ph2 -4.1097045 ( +/- 0.11370224)

With the current data, we cannot distinguish between a magnetic model with two sites that have a very small difference ( $P3$ ) and a model with a single site that gives a strictly antiferromagnetically coupled model ( $P-3'$ ). This example, therefore, illustrates a case where neutron diffraction cannot solve a magnetic structure unambiguously. To confirm whether the magnetic model can be described in  $P3$ , we have carried out optical measurements of second harmonic generation. In the case of non-centrosymmetric groups, this measurement would give a signal. However, no signal was observed in these measurements, suggesting that the magnetic space group is likely to have a centre of symmetry, indicating that it should be  $P-3'$ . Therefore, the observed increase in susceptibility measurements is likely due to paramagnetic impurities.