

# Tutorial: Ho<sub>2</sub>BaNiO<sub>5</sub>

*Magnetic Structure Determination: Commensurate Magnetic Structure with  $k \neq 0$ .  
Propagation vector determination using the k-search program.*

## Ho<sub>2</sub>BaNiO<sub>5</sub>

Powder data collected at ILL on the diffractometer D1B (old D1B) with  $\lambda = 2.52$  Å.

The space group is S.G. = *Immm*, the cell parameters are  $a \approx 3.754$  Å,  $b \approx 5.732$  Å and  $c \approx 11.271$  Å at RT.

The structural parameters could be obtained from the input CIF file.

The main structural feature is the presence of one-dimensional (1D) chains of NiO<sub>6</sub> octahedra along the *a*-axis. The octahedra are strongly distorted with a very short Ni-O<sub>apical</sub> distance ( $\approx 1.88$  Å), and a longer Ni-O<sub>basal</sub> distance ( $\approx 2.18$  Å). The basal angle O-Ni-O ( $\approx 78^\circ$ ) is also much smaller than expected for a regular octahedron ( $90^\circ$ ).

The magnetic structures of the family of compounds Ho<sub>2</sub>BaNiO<sub>5</sub> have been studied in the past and can be consulted on <https://doi.org/10.1051/epjconf/20122200010>

*Input files:*

hobk.dat (collected below T<sub>N</sub>)

The format of the data corresponds to *Ins* = 3 in FullProf

Instrument resolution parameters: *U* = 1.61, *V* = -1.04, *W* = 0.35.

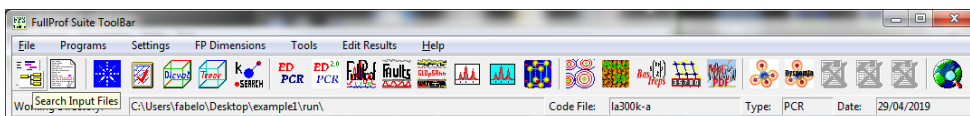
Ho<sub>2</sub>BaNiO<sub>5</sub>.cif

*The standard magnetic structures determination using neutron powder diffraction (NPD) data follow these steps:*

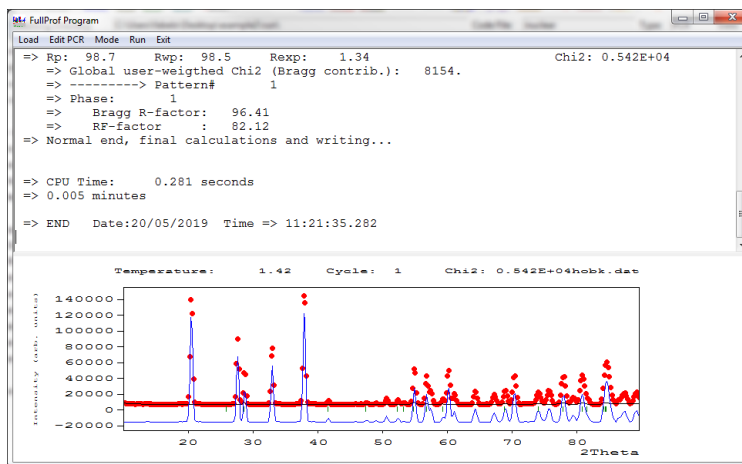
- 1) Plot the NPD pattern above and below the magnetic order temperature.
- 2) Refine the crystal structure, using the collected data, and get all the relevant structural and profile parameters.
- 3) Normally additional magnetic peaks appear in the low temperature diffraction pattern (below order temperature). Index the new reflection to determine the propagation vector. A trial and error method or the K-SEARCH program, included in the FullProf suite, can be used.
- 4) Determine the possible irreducible representations (irreps) of the paramagnetic space group corresponding to the experimentally obtained propagation vector. The program BASIREPS can be used to get the basis vectors of the irreducible representations of the propagation vector group (*G<sub>k</sub>*). The Shubnikov group and the appropriate magnetic symmetry operators, or, alternatively, the basis vectors of the irreps, can be used to refine the experimental data.
- 5) Alternatively simulated annealing refinement can also be done (no information about the magnetic symmetry is needed)

6) Refine against the data the different models and check the output files to discard incompatibilities or inconsistencies.

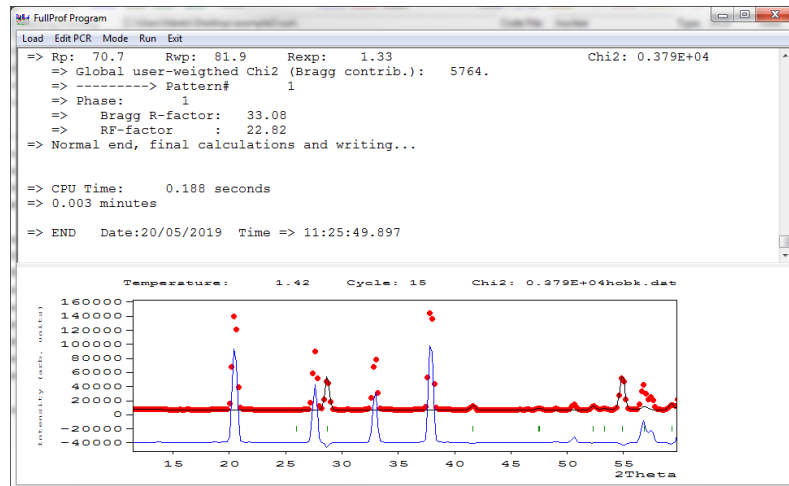
- 1) **Create a working directory; do not use space or special characters in the path.**
  - a. Copy in this folder all the input files.
- 2) **Create an initial PCR file (follow the steps described on  $\text{LaMnO}_3$  example).**
- 3) **Modify the PCR file according to the current example (follow the steps described on  $\text{LaMnO}_3$  example).**
- 4) **Fix all the parameters and compare the experimental data with the initial model.**
  - a. Load into the FP toolbar the created PCR file, in our case “nuclear.pcr”. This can be done by clicking on *Search Input files* icon. Be sure that the PCR file and the data file are in the same folder.



- a.
  - b. Now you can click on the FullProf icon and run. Observe that the result is clearly non-satisfactory. Do not forget that, for the moment, all the parameters are fixed.

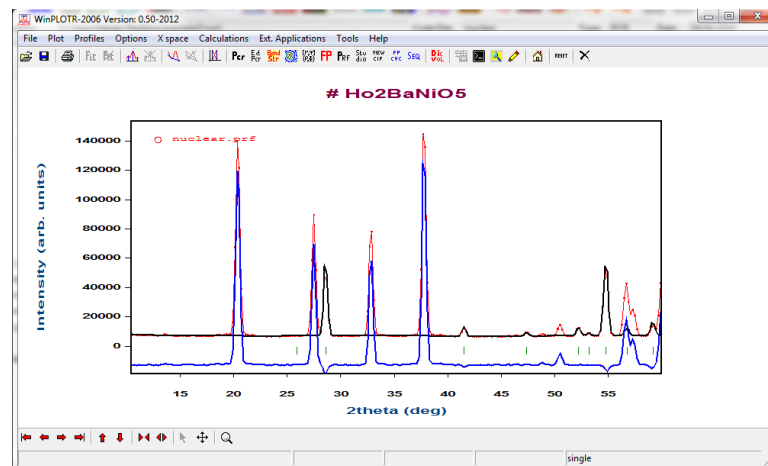


- c. In this example, we will check only the nuclear contribution to the total pattern. Therefore, we refine only the “Scale” factor (*refinement > Profile*). The next parameters will be the zero (*refinement > instrumental*) and the unit cell (*refinement > Profile*). After refining, we can see that only some reflections are nicely fitted. However, there are reflections that are not fitted by the crystallographic model. The unfitted reflections are due to the magnetic contribution.

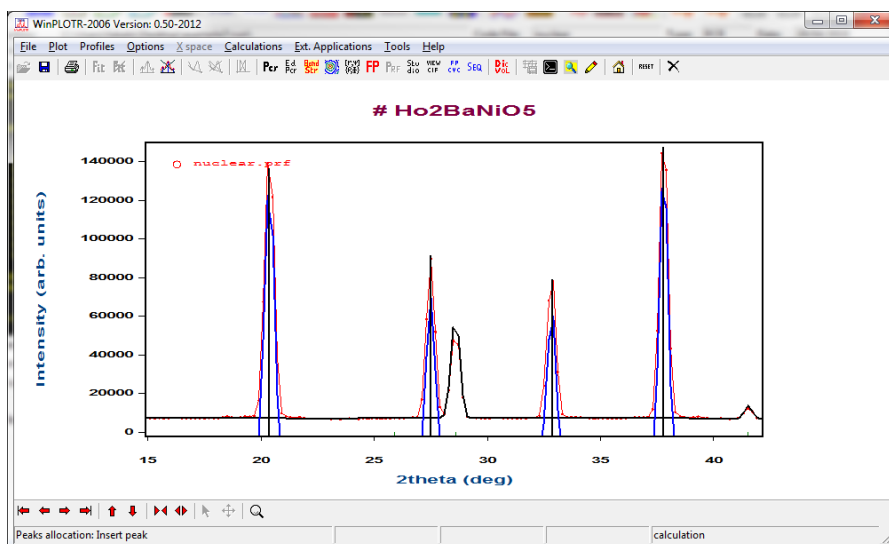


## 5) Propagation vector determination

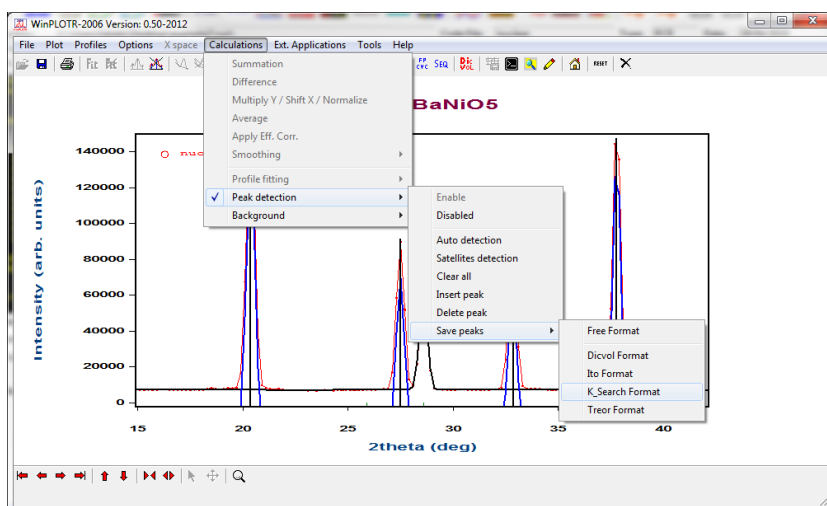
- Open the refined pattern using Winplotr-2006. The blue line (difference between observed and calculated patterns) can be taken as a reference for the determination of magnetic reflections positions.



- Click on *Calculations > Peak detection > Enable*
- Click on *Calculations > Peak detection > Insert Peak* (you can use *satellite detection* for an automatic peak detection)  
Insert a new peak into each non-fitted reflection. You can zoom in/out with the left/right mouse button.



d. Click on *Calculations > Peak detection > Save Peaks > K-search program*



e. The appearing dialog windows is pre-filled, but you can modify some parameters if you think that is needed. NB: In the first run, you can use only special k-vectors (commensurate) and if the program is not able to index the peaks, you can unclic this option to search incommensurate propagation vectors.

- f. Click on OK, save the input file for the k-search program (k\_search.sat) and click on YES to run the program. The program will provide you a list with the best solutions in this particular case 11 satellites have been included on the input file. A detailed output “k\_search.kup” can be consulted for more details.

```

=> Writing partial results ...
=> Testing 90 internal k-vectors
Solution: 1 k =< 0.5000 0.0000 0.5000> R-F: 1.1022
=> Special k-vector solutions found!
=> List of the best 10 solutions for 11 satellites
      Kx      Ky      Kz      R-factor
0.500000  0.000000  0.500000  1.102220
=> A probable solution is the special kvector ks =< 0.5000 0.0000 0.5000>
=> The corresponding R-factor is: 1.1022

      Total CPU-Time
      CPU-seconds: 0.00
      CPU-minutes: 0.00
      CPU-hours   : 0.00

=> Press <enter> to finish

```

- g. From the indexing with k-search, we obtain a propagation vector  $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$ .

## 6) Adding a second phase to fit the magnetic reflections.

- a. We are going to use the EdPCR program for doing this task. Open nucl\_mag1.pcr file and click on *Phases > add* change the *Name of phase* to “magnetic contribution, without model” in *calculation* select “*Profile Matching with constant scale factor*”. Click on *contribution to Patterns*, select the options showed here below and click on OK. The “*Satellite reflections are generated automatically from Space group symbol*” is particularly useful for those magnetic structures with  $\mathbf{k}$  different of 0.

Pattern Contribution Information for Phase 2

Pattern 1 | Pattern 2 | Pattern 3 | Pattern 4 | Pattern 5 | Pattern 6 | Pattern 7

☒ Current Phase contributes to the pattern

Type of Pattern

☐ X-Ray ☐ Pattern Calculation (X-Ray)

☒ Neutron (Constant Wavelength) ☐ Pattern Calculation (Neutron - Constant Wavelength)

☐ Neutron (T.O.F.) ☐ Pattern Calculation (Neutron - T.O.F.)

Nuclear and Magnetic

Peak Shape

Thompson-Cox-Hastings pseudo-Voigt \* Axial divergence asymmetry

☒ Cofeefil.shp ☐ Global.shp

Intensities

Reflection list: Satellite reflections are generated automatically from Space group symbol

☐ Use special control of parameters for peak overlap, rejected reflections for current phase

Brindley coefficient: 0.0000

Global weight of the integrated intensity data vs profile data: 0.0000

Factor for excluding reflections [  $I < \text{Factor} * \text{Sigma}(I)$  ]: 0.0000

Weights are divided by reduced  $\chi^2$  of precedent cycle: 0.0000

OK Cancel

Click on symmetry and add I -1 space group. NB: the space group in FP should be written with a space between elements (I -1, in this particular case). We use the lattice type of the paramagnetic space group and just the triclinic group to generate all possible satellite reflections. Click on *Symm. Op. Automatic* and on OK and save in the main window of EdPCR.

Symmetry Information

Space Group Properties

Symmetry Operators: Generated automatically from the symbol

Spacegroup: I -1

Symm.Op. Automatic

Symmetry operators | Magnetic/Displacement Operators | Irreducible representations

Laue Class: -1 ☒ Centrosymmetric Case

Number of Symmetry Operators: 4

Num	Symmetry	TR	Num	Symmetry	TR
1	x,y,z	<input type="checkbox"/>			<input type="checkbox"/>

TR=Time reversal associated to symmetry operator

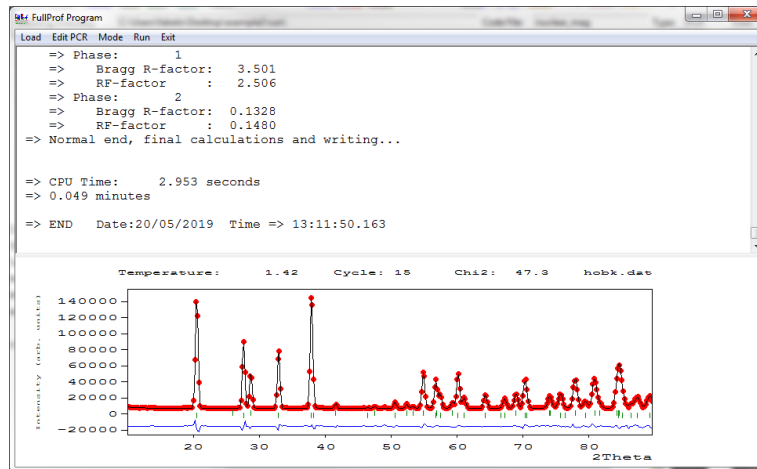
☐ Time Reversal for Inversion operator

OK Cancel

- Now we need to fill in the dialogs for the phase 2, the unit cell the scale, U, V, W, X, Y, SL and DL. You can use the EdPCR or edit the "nucl\_mag1.pcr" file with a text editor and copy the parameters from phase 1 to phase 2.
- Now we can run FP and start to refine parameters. Change AUT from 0 to 1 and be sure that those parameters from phase 1 and phase 2 that should be the same have identical refinement codes.

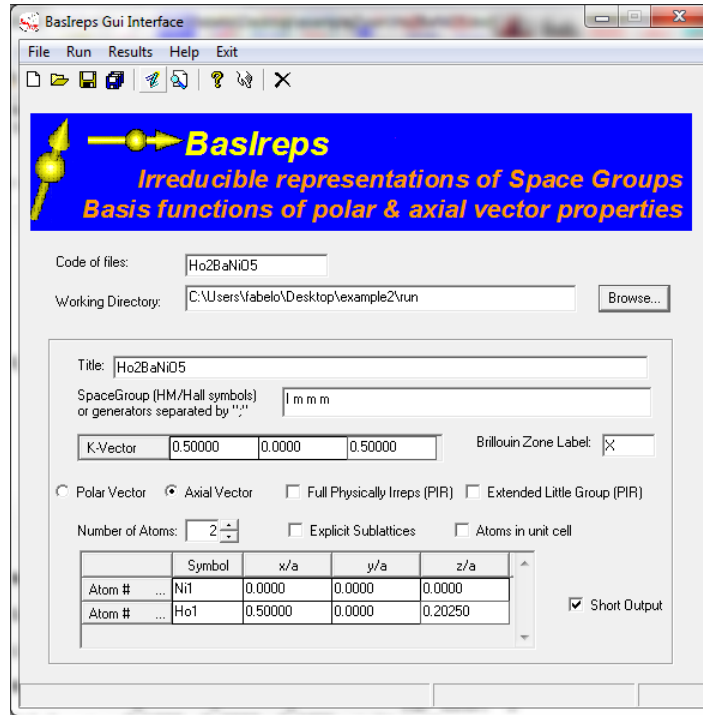
To add constraints you can use the same code into the PCR file (see the next figure as an example) or you can use the EdPCR clicking on *Constraints > Profiles Parameters* (U, V, W, a, b, c, X, Y...). In a first step create a new constraint relation and secondly add a second parameter to constraint. In that case, factor 1 means that if U in phase 1 increase one unit, U in phase 2 increase the same unit. Negative values means that one parameter increase while the second decrease.

- d. Run FP and check that all magnetic reflections are properly fitted with the propagation vector  $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$ .



## 7) Calculation of Irreducible representations.

- a. For the *irreps* calculation, we are going to use the Baslreps program. Click on the Baslreps icon on the FP toolbar. Fill the information, code of file, the working directory the paramagnetic space group, the propagation vector (in this case  $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$ ), remember than magnetic moments are axial vectors. The number of atoms within the unit cell can be provided explicitly or the program can calculate the different orbits using the space group symmetry. In this case with *Immm* space group with Ni atoms in the 2a Wyckoff position, forming a single sublattice with the atoms in the (0, 0, 0) and symmetry related positions. The Ho atoms on the 4j Wyckoff positions, forming two sublattices in the primitive cell, the first one at  $(\frac{1}{2}, 0, z)$  and the second at  $(-\frac{1}{2}, 0, -z)$ . As the system is *I*-centred, The other atoms of the conventional unit cell are related to those already given by the centring translation  $\mathbf{t}_I = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .



- b. From the output of Baslreps, we can verify that  $K$  is equivalent to  $-K$  and that the star of  $K$  is formed by two vectors  $\mathbf{k}_1 = (\frac{1}{2}, 0, \frac{1}{2})$  and  $\mathbf{k}_2 = (-\frac{1}{2}, 0, \frac{1}{2})$ .
- c. The list of the irreducible representations (all of them of dimension 1) can be consulted on the output of Baslreps.

<i>irreps</i>	$\{1 000\}$	$\{2_y 000\}$	$\{-1 000\}$	$\{m_y 0$
$\Gamma_1$ ( $A_g$ ) :	1	1	1	1
$\Gamma_2$ ( $A_u$ ) :	1	1	-1	-1
$\Gamma_3$ ( $B_g$ ) :	1	-1	1	-1
$\Gamma_4$ ( $B_u$ ) :	1	-1	-1	1

- d. Check the Baslreps output (filename.fp). As in this example there is two different sites, you should check both independently. In a first approach, we can assume that both sites are ordered at the same moment following the same irrep. The  $\Gamma_{mag}$  reducible representation for the site 1 (Ni) is decomposed in *irreps* as the direct sum:

$$\Gamma_{mag}(Ni) = 1\Gamma_1 \oplus 2\Gamma_3$$

While for the second site (Ho),  $\Gamma_{mag}$  is decomposed in *irreps* as the direct sum:

$$\Gamma_{mag}(Ho) = 1\Gamma_1 \oplus 2\Gamma_2 \oplus 2\Gamma_3 \oplus 1\Gamma_4$$

Where the pre-number is the number or times the *irrep* is contained in  $\Gamma_{mag}$ . This number is related with the number of terms (i.e. number of basis vectors) in this irrep.

So, only  $\Gamma_1$  and  $\Gamma_3$  *irreps* are present in both sites. Now we can combine  $\Gamma_1$  for both sites to create a block to paste into the PCR file.

**Irrep(1) Site 1:**

```
I -1                                <--Space group symbol for hkl generation
! Nsym   Cen   Laue Ireps N_Bas
      1     1     1    -1     1
! Real(0)-Imaginary(1) indicator for Ci
0
SYMM x,y,z
BASR   0  1  0
BASI   0  0  0
```

**Irrep(1) Site 2:**

```
I -1                                <--Space group symbol for hkl generation
! Nsym   Cen   Laue Ireps N_Bas
      2     1     1    -1     1
! Real(0)-Imaginary(1) indicator for Ci
0
SYMM x,y,z
BASR   0  1  0
BASI   0  0  0
SYMM -x,y,-z
BASR   0  1  0
BASI   0  0  0
```

**Irrep(1) both sites:**

```
I -1                                <--Space group symbol for hkl generation
! Nsym Cen Laue Ireps N_Bas
      2         1     1    -2         1 ! the -2 means that each SYMM
have two components
! Real(0)-Imaginary(1) indicator for Ci
0
SYMM x,y,z
BASR  0  1  0      ! BASR and BASI correspond to site 1
BASI  0  0  0
BASR   0  1  0      ! BASR and BASI correspond to site 2
BASI   0  0  0
SYMM -x,y,-z
BASR  0  0  0      ! BASR and BASI correspond to site 1
BASI  0  0  0
BASR   0  1  0      ! BASR and BASI correspond to site 1
BASI   0  0  0
```

The same approach should be done by irrep(3).

**Irrep(3) both sites:**

```
I -1                                <--Space group symbol for hkl generation
! Nsym   Cen   Laue Ireps N_Bas
      2         1     1    -2         2
! Real(0)-Imaginary(1) indicator for Ci
```

```

0 0
SYMM x, y, z
BASR 1 0 0 0 0 1
BASI 0 0 0 0 0 0
BASR 1 0 0 0 0 1
BASI 0 0 0 0 0 0
SYMM -x, y, -z
BASR 0 0 0 0 0 0
BASI 0 0 0 0 0 0
BASR 1 0 0 0 0 1
BASI 0 0 0 0 0 0

```

```

=> Basis functions of Representation IRrep( 3) of dimension 1 contained 2 times in GAMMA
Representation number : 3 for Site: 1
Number of basis functions: 2

----- Block-of-lines for PCR start just below this line
I -1 <---Space group symbol for hkl generation
! Nsym Cen Laue Ireps N_Bas
1 1 1 -1 2
! Real(0)-Imaginary(1) indicator for Ci
0 0
SYMM x,y,z
BASR 1 0 0 0 0 1
BASI 0 0 0 0 0 0
----- End-of-block of lines for PCR
X Y Z for site: 2
-> Ho1_1 : 0.5000 0.0000 0.2025 : (x,y,z)
-> Ho1_2 : -0.5000 0.0000 -0.2025 : (-x,y,-z)

=> Basis functions of Representation IRrep( 1) of dimension 1 contained 1 times in GAMMA
Representation number : 1 for Site: 2
Number of basis functions: 1

----- Block-of-lines for PCR start just below this line
I -1 <---Space group symbol for hkl generation
! Nsym Cen Laue Ireps N_Bas
2 1 1 -1 1
! Real(0)-Imaginary(1) indicator for Ci
0
SYMM x,y,z
BASR 0 1 0
BASI 0 0 0
SYMM -x,y,-z
BASR 0 1 0
BASI 0 0 0
----- End-of-block of lines for PCR

=> Basis functions of Representation IRrep( 2) of dimension 1 contained 2 times in GAMMA

```

## 8) Including the IR into the PCR file (follow the LaMnO<sub>3</sub> example).

- Rename the previous PCR file, in our case nucl\_mag\_bv.pcr (BV corresponding to basic vectors).
- Open the new PCR with the EdPCR and click on *phases* and click NEXT to move to the phase 2. Here you can change the type of calculation from “*Profile Matching with constant scale factor*” to “*Magnetic Phase (Rietveld Method)*” or “*Magnetic Phase with magnetic moments in spherical mode (Rietveld Method)*”. In our case we are going to use the first one. In order to use spherical modes the PCR file should contain MSYM operators instead of basis vectors.

A detail explanation of how derive those MSYM operators from the basis vectors obtained from the Basreps program is included in the Annexe 1.

- Click on symmetry and select “*Basis functions of the irreducible representations of the propagation vector group*”. Here you can add the “*magnetic/displacement*” and the “*irreducible representation*” using the boxes. However, the easy way is to copy this information from the .FP file (Basreps).

In order to create the lines into the PCR file we can add only one basis function and one IR. Click on OK and save from the main window of EdPCR.

**Symmetry Information**

Space Group Properties

Symmetry Operators: Basis functions of the irreducible representations of the propagation vector group

Spacegroup: **I-1** Symm. Op. Automatic

Symmetry operators | Magnetic/Displacement Operators | Irreducible representations

Number of Atomic basis functions: **2**      Number of Irreducible Representations: **2**      ☐ Complex basis functions

Num	Coefficient Ci Type
1	Real
2	Real

	Num	Expression
Real	1	1 0 0 0 0 1
Imag	1	0 0 0 0 0 0
Real	1	1 0 0 0 0 1
Imag	1	0 0 0 0 0 0
Real	2	0 0 0 0 0 0
Imag	2	0 0 0 0 0 0

OK      Cancel

- d. Edit the PCR file and replace the basis vector by the previous created block.
- e. Using EdPCR we need to include the magnetic atoms into the PCR file. Click on "refinements > phase 2 > atoms" add a new atom. Click on OK and save the PCR.

**Atoms Information: Phase 2**

List of Atoms

Number of Atoms: **2**

	Label	Ntyp	Mag. Rot.	Prog. Vec.	X	Y	Z	B	Occ
Atom # 1	Ni1	MNI2	1	1	0.00000	0.00000	0.00000	0.00000	1.00000
Atom # 2	Ho1	JHO3	2	1	0.50000	0.00000	0.20250	0.00000	1.00000

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

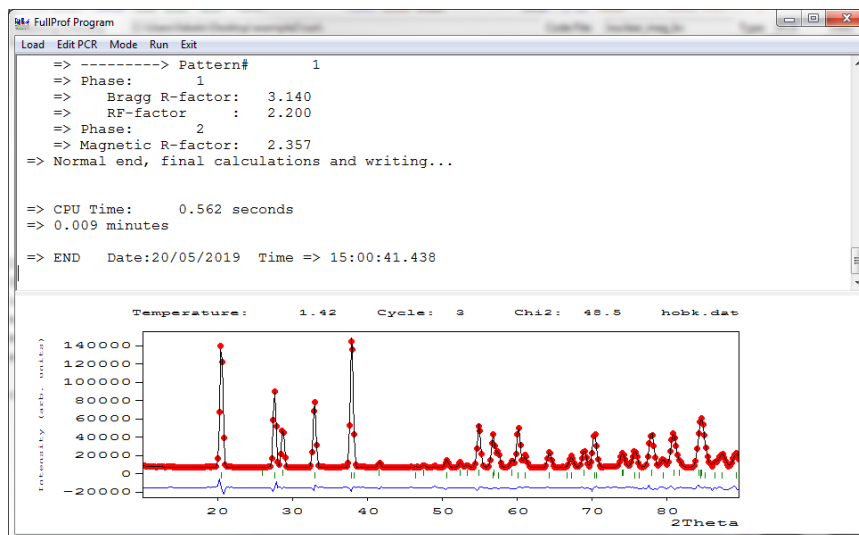
Basis Functions Coefficients

	C1	C2	C3	C4	C5	C6	C7
Atom # 1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Atom # 2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

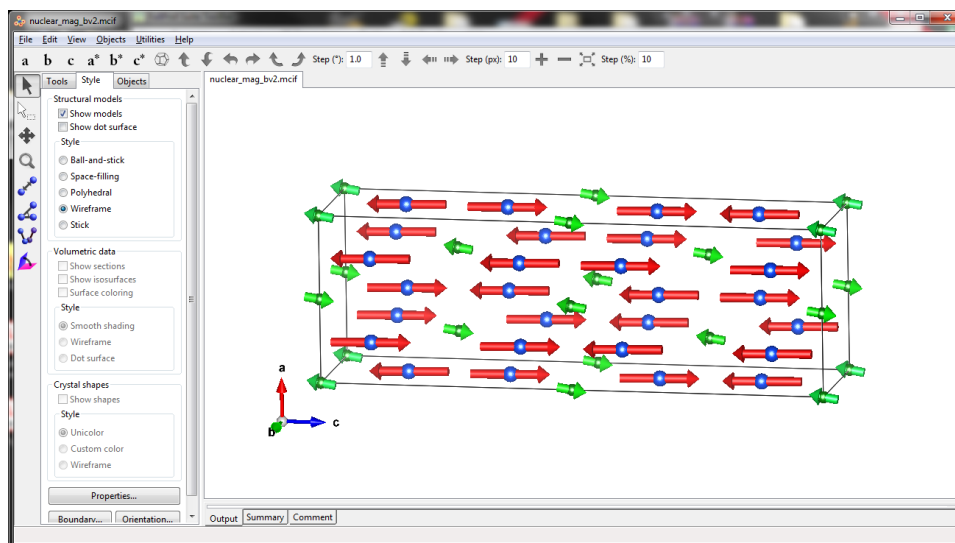
Refine Positions  
Refine B<sub>iso</sub>  
Fix All  
Cancel  
OK

**NB:** The 1 or 2 in the Mag. Rot box is related with the application of the symmetry operators. Each symmetry is applied to a couple of BASR and BASI vectors. If the number is 1, the used vectors are those defined by the first couple (site 1), while if the number is 2, those vectors used correspond to the second couple (site 2).

- f. Now you can run the PCR file. If you want to refine the magnetic structure you can refine from C1 to C2. NB: start with a value close to  $1\mu_B$  from Ni and  $7\mu_B$  to Ho atoms.
- g. Refine the two possible magnetic models, modifying the PCR file, and determine which is the correct. NB: is a good idea rename the PCR file to specify in the name which IR you are using.



- h. After running FullProf, a mcif will be automatically created with the magnetic structure. You can use VESTA program to plot the different magnetic models. NB: Check always the output file from FullProf, there is plenty of useful information that can help you to understand the results.



## 9) PCR file using the Shubnikov magnetic space group.

- a. In order to determine the possible Shubnikov space group compatible with our system we can use the Baslreps as was shown in the previous sections. Using the Bilbao

Crystallographic Server we can create a list of mcif (one for each Shubnikov S.G.), that can be transformed into a PCR file with a single click.

Open a web browser and write <http://www.cryst.ehu.es/>

Click on Magnetic Symmetry and Applications

**bilbao crystallographic server**

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**Space-group symmetry**

**Magnetic Symmetry and Applications**

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

Click on MAXMAGN, fill the boxes and click on submit.

Upload a structural model (cif file). If there is not errors in your cif file the program will ask for the magnetic atoms. Select the Ni and Ho atom and click on submit.

The program gives a list of maximal magnetic space groups compatible with the propagation vector. In addition, the transformation to the standard setting is provided.

### Selected magnetic space subgroup for the parent space group *Immm* (No. 71)

*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>C<sub>c</sub>2/c</i> (#15.90) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 1 & 0 & 2 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$ <a href="#">Alternatives (domain-related)</a>	<a href="#">Show</a>	Systematic absences <a href="#">MAGNEXT</a> Tensor properties <a href="#">MTENSOR</a>	<a href="#">Show</a>
2	<i>C<sub>c</sub>2/m</i> (#12.63) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 1 & 0 & 2 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$ <a href="#">Alternatives (domain-related)</a>	<a href="#">Show</a>	Systematic absences <a href="#">MAGNEXT</a> Tensor properties <a href="#">MTENSOR</a>	<a href="#">Show</a>

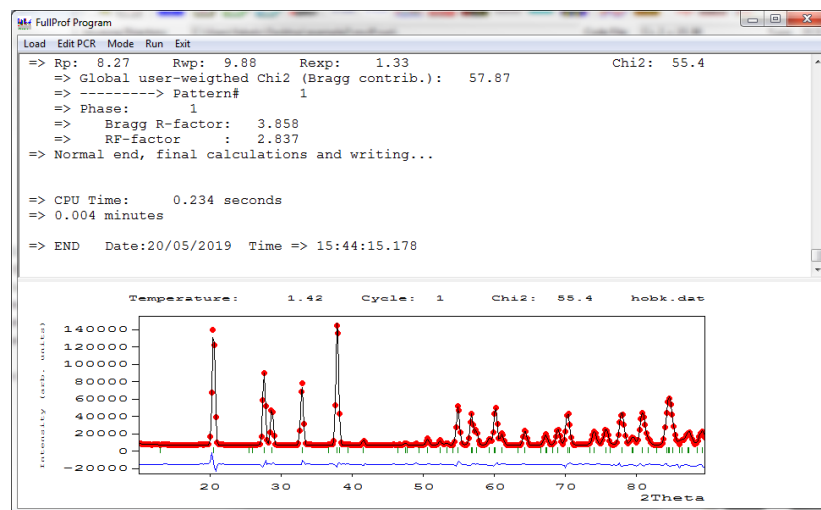
The two proposed space groups correspond to two magnetic structures with the magnetic moments placed perpendicularly one with respect to the other. In the first case *C<sub>c</sub>2/c* (#15.90), the magnetic moment lies on the *ac*-plane for both sites, while in

the second case  $C_{2/m}$  (#12.63) the magnetic moment of both sites are pointing along the  $b$ -axis.

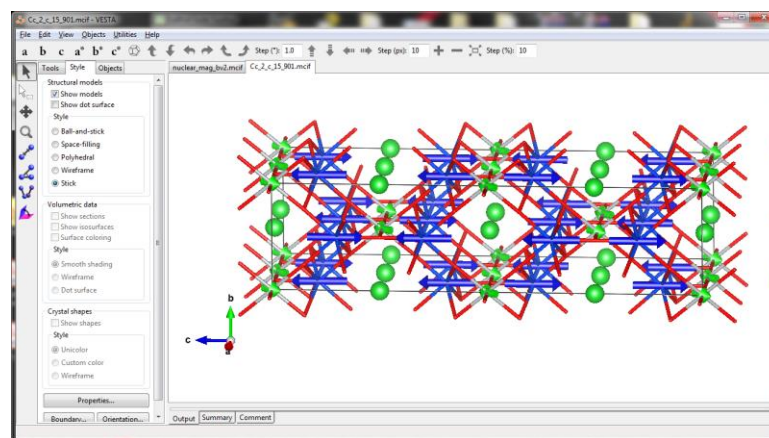
Download the mcif files and create a PCR file for each case (the detailed procedure is described on  $\text{LaMnO}_3$  example).

Change the JOB = 3 to JOB = 1 and include all the information related with your instrument and with the measurements; Lambda, background, muR, zero, U, V, W, unit cell and Scale. All this information can be obtained from the previous PCR file.

- The nuclear and magnetic part are in the same phase (JBT = 10), so only one phase is needed.
- The code VARY mxmymz, active automatically the refinement of the magnetic moment components, which are compatible with the symmetry. If the user wants to fix one component this code should be removed.
- In the FullProf toolbar select the PCR file and refine.



- Plot the mcif file using VESTA; in this case as nuclear and magnetic structures were refined in the same phase so both are included into the mcif file.



- f. Repeat the procedure using the second Shubnikov space group and compare the results.
- g. The structure was solved on the  $C_{2/c}$  magnetic space group, which is a subgroup of the orthorhombic paramagnetic space group. Therefore, the final magnetic structure is monoclinic. However, there is an open question, as the system present a  $\mathbf{k}$ -vector formed by a star of two arms  $\mathbf{k}_1=(\frac{1}{2}, 0, \frac{1}{2})$  and  $\mathbf{k}_2=(-\frac{1}{2}, 0, \frac{1}{2})$ , is there a combination of these two vectors providing a higher symmetry multi- $\mathbf{k}$  solution?

#### 10) Multi- $\mathbf{k}$ symmetry analysis

- a. In order to explore this option we are going to use the k-Subgroupsmag utility from the BCS.

([http://www.cryst.ehu.es/cgi-bin/cryst/programs/subgrmag1\\_k.pl](http://www.cryst.ehu.es/cgi-bin/cryst/programs/subgrmag1_k.pl))

- b. We fill the different boxes, clicking on “*Choose the whole star of the propagation vector*” after click, the whole star(s) of the propagation wave-vectors will be used in the calculation of all groups and subgroups.

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

Choose an alternative magnetic group  
Alternatively give the operations of the space group in a non-standard setting

Introduce the magnetic wave vector(s)  
Alternatively give the basis vectors of the supercell  
(Give the components of the wave vectors in a fractional form, n/m)

$k_{1x}$  0.5    $k_{1y}$  0    $k_{1z}$  0.5  
Show the independent vectors of the star  
☒ Choose the whole star of the propagation vector

☐ Include the subgroups compatible with intermediate cells.  
(It is not applied when only the maximal subgroups are calculated)

Optional: refine further the subgroups of the output giving the Wyckoff positions of the atoms  
Give the Wyckoff positions

☐ Optional: Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter).

Optional: refine further the subgroups of the output giving a set of irreps  
Choose the irreps

Optional: possible limitations of the subgroup list  
(Check only one option on the left and the specific value on the right)

☐ Lowest space group to consider  
☐ Lowest point group to consider  
☐ Lowest crystal system to consider  
☒ Only maximal subgroups

1.1

Optional: further limitations considering physical properties of the point groups

☐ Only centrosymmetric / non-centrosymmetric groups  
☐ Only polar / non-polar groups

all  
all

☒ List of subgroups   ☐ Graph of subgroups

- c. Click on submit and, in order to reduce the list of possible magnetic space group, include the structure of the parent phase. From the list of 10 items, we are interested on those of orthorhombic symmetry, the first four; the others are already subgroups of the previously determined magnetic space group ( $C_{2/c}$ ).

# List of subgroups that fulfill the given conditions

Get the subgroup-graph

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	Irreps	Magnetic structure models (MAGMODELIZE)
1	$C_{2v}$ (No. 67.509)	$\begin{pmatrix} 2 & 0 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$	4=4x1	Conjugacy Class	Get irreps	<input checked="" type="checkbox"/>
2	$C_{2v}$ (No. 67.509)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$	4=4x1	Conjugacy Class	Get irreps	<input checked="" type="checkbox"/>
3	$C_{2v}$ (No. 65.489)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$	4=4x1	Conjugacy Class	Get irreps	<input checked="" type="checkbox"/>
4	$C_{2v}$ (No. 65.489)	$\begin{pmatrix} 2 & 0 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$	4=4x1	Conjugacy Class	Get irreps	<input checked="" type="checkbox"/>
5	$P_{21}/c$ (No. 14.82)	$\begin{pmatrix} 1 & 0 & 2 & 1/4 \\ 0 & 1 & 0 & 1/4 \\ -1 & 0 & 0 & 1/4 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	<input type="checkbox"/>
6	$P_{21}/c$ (No. 14.80)	$\begin{pmatrix} 2 & 0 & 1 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	<input type="checkbox"/>
7	$P_{21}/c$ (No. 14.80)	$\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 2 & 0 & 1 & 0 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	<input type="checkbox"/>
8	$P_{21}/c$ (No. 13.70)	$\begin{pmatrix} 2 & 0 & 1 & 1/4 \\ 0 & 1 & 0 & 1/4 \\ 0 & 0 & 1 & -1/4 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	<input type="checkbox"/>
9	$P_{21}/c$ (No. 13.70)	$\begin{pmatrix} 0 & 0 & -1 & 1/4 \\ 0 & 1 & 0 & 1/4 \\ 2 & 0 & 1 & -1/4 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	<input type="checkbox"/>
10	$P_{21}/m$ (No. 11.55)	$\begin{pmatrix} 2 & 0 & -1 & 1/4 \\ 0 & 1 & 0 & 1/4 \\ 0 & 0 & 1 & -1/4 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	<input type="checkbox"/>

Select/Deselect all subgroups

☒ Include structure data of the parent phase

Submit selected subgroups to MAGMODELIZE:

\*Hint: Submit many subgroups to MAGMODELIZE, when the 'include structure' option is selected, may take too long

- Click on submit and upload a cif file. Click on Ni and Ho as magnetic atoms and submit. Four possible magnetic subgroups with at least one site with moment different from zero are shown.

## Selected magnetic space subgroup for the parent space group $Immm$ (No. 71)

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	$C_{2v}$ (#67.509) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 2 & 0 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences [MAGNET] Tensor properties [MTENSOR]	<a href="#">Show</a>
2	$C_{2v}$ (#67.509) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences [MAGNET] Tensor properties [MTENSOR]	<a href="#">Show</a>
3	$C_{2v}$ (#65.489) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences [MAGNET] Tensor properties [MTENSOR]	<a href="#">Show</a>
4	$C_{2v}$ (#65.489) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 2 & 0 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & 0 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences [MAGNET] Tensor properties [MTENSOR]	<a href="#">Show</a>

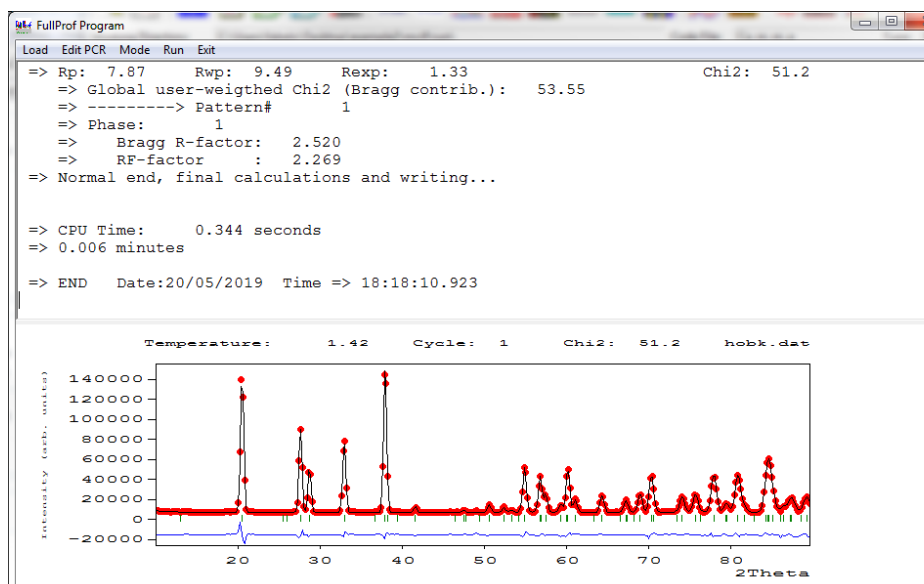
- Click on show on the Magnetic structure box, and verify that both sublattices are different from zero. From the four magnetic space groups only the  $C_{2v}$  (#67.509) magnetic space group allow non-zero magnetic moments on both sublattices. Therefore, this will be the only solution that will be refined against the data. From the symmetry analysis carried out by BCS, we observe that the magnetic moments of Ni and Ho sites, there are two Wyckoff sites for each atom, are perpendicular between them. Therefore, this model is not consistent with the magnetic structure previously solved ( $C_{2v}$ ). However, just to confirm that this magnetic structure

is not correct, we are going to create a PCR file from the mcif of the *C<sub>mma</sub>* (#67.509) magnetic space group.

Atomic positions, Wyckoff positions and Magnetic Moments

N	Atom	New WP	Multiplicity	Magnetic moment	Values of M <sub>x</sub> , M <sub>y</sub> , M <sub>z</sub>
1	Ho1_1 Ho 0.25000 0.00000 0.10125	(1/4,0,z   m <sub>x</sub> ,0,0) (1/4,0,-z   -m <sub>x</sub> ,0,0) (1/4,0,z+1/2   -m <sub>y</sub> ,0,0) (1/4,0,-z+1/2   m <sub>x</sub> ,0,0) (3/4,0,z   -m <sub>y</sub> ,0,0) (3/4,0,-z   m <sub>x</sub> ,0,0) (3/4,0,z+1/2   m <sub>x</sub> ,0,0) (3/4,0,-z+1/2   -m <sub>x</sub> ,0,0)	8	(M <sub>x</sub> ,0,0)	M <sub>x</sub> = 0.0000
	Ho1_2 Ho 0.00000 0.50000 0.35125	(0,1/2,z+1/4   0,0,m <sub>z</sub> ) (0,1/2,-z+1/4   0,0,-m <sub>z</sub> ) (0,1/2,z+3/4   0,0,-m <sub>z</sub> ) (0,1/2,-z+3/4   0,0,m <sub>z</sub> ) (1/2,1/2,z+1/4   0,0,-m <sub>z</sub> ) (1/2,1/2,-z+1/4   0,0,m <sub>z</sub> ) (1/2,1/2,z+3/4   0,0,m <sub>z</sub> ) (1/2,1/2,-z+3/4   0,0,-m <sub>z</sub> )	8	(0,0,M <sub>z</sub> )	M <sub>z</sub> = 0.0000
2	Ba1_1 Ba 0.25000 0.50000 0.00000	(1/4,1/2,0   0,0,0) (1/4,1/2,1/2   0,0,0) (3/4,1/2,0   0,0,0) (3/4,1/2,1/2   0,0,0)	4	-	-
	Ba1_2 Ba 0.00000 0.00000 0.25000	(0,0,1/4   0,0,0) (0,0,3/4   0,0,0) (1/2,0,1/4   0,0,0) (1/2,0,3/4   0,0,0)	4	-	-
3	Ni1_1 Ni 0.00000 0.00000 0.00000	(0,0,0   0,0,m <sub>z</sub> ) (0,0,1/2   0,0,-m <sub>z</sub> ) (1/2,0,0   0,0,-m <sub>z</sub> ) (1/2,0,1/2   0,0,m <sub>z</sub> )	4	(0,0,M <sub>z</sub> )	M <sub>z</sub> = 0.0000
	Ni1_2 Ni 0.25000 0.50000 0.25000	(1/4,1/2,1/4   m <sub>x</sub> ,0,0) (1/4,1/2,3/4   -m <sub>x</sub> ,0,0) (3/4,1/2,1/4   -m <sub>x</sub> ,0,0) (3/4,1/2,3/4   m <sub>x</sub> ,0,0)	4	(M <sub>x</sub> ,0,0)	M <sub>x</sub> = 0.0000
4	O1_1 O 0.00000 0.24140 0.07475	(0,y,z   0,m <sub>y</sub> ,m <sub>z</sub> ) (0,-y,z   0,-m <sub>y</sub> ,m <sub>z</sub> ) (0,y,-z   0,-m <sub>y</sub> ,m <sub>z</sub> ) (0,-y,-z   0,m <sub>y</sub> ,m <sub>z</sub> ) (0,y,z+1/2   0,-m <sub>y</sub> ,m <sub>z</sub> ) (0,-y,z+1/2   0,m <sub>y</sub> ,m <sub>z</sub> ) (0,y,-z+1/2   0,m <sub>y</sub> ,m <sub>z</sub> ) (0,-y,-z+1/2   0,-m <sub>y</sub> ,m <sub>z</sub> ) (1/2,y,z   0,-m <sub>y</sub> ,m <sub>z</sub> ) (1/2,-y,z   0,m <sub>y</sub> ,m <sub>z</sub> ) (1/2,y,-z   0,m <sub>y</sub> ,m <sub>z</sub> ) (1/2,-y,-z   0,-m <sub>y</sub> ,m <sub>z</sub> ) (1/2,y,z+1/2   0,m <sub>y</sub> ,m <sub>z</sub> ) (1/2,-y,z+1/2   0,-m <sub>y</sub> ,m <sub>z</sub> ) (1/2,y,-z+1/2   0,-m <sub>y</sub> ,m <sub>z</sub> ) (1/2,-y,-z+1/2   0,m <sub>y</sub> ,m <sub>z</sub> )	16	-	-
	O1_2 O 0.25000 0.74140 0.32475	(1/4,y+1/2,z+1/4   m <sub>x</sub> ,0,0) (1/4,-y+1/2,z+1/4   m <sub>x</sub> ,0,0) (1/4,y+1/2,-z+1/4   m <sub>x</sub> ,0,0) (1/4,-y+1/2,-z+1/4   m <sub>x</sub> ,0,0) (1/4,y+1/2,z+3/4   -m <sub>x</sub> ,0,0) (1/4,-y+1/2,z+3/4   -m <sub>x</sub> ,0,0) (1/4,y+1/2,-z+3/4   -m <sub>x</sub> ,0,0) (1/4,-y+1/2,-z+3/4   -m <sub>x</sub> ,0,0) (3/4,y+1/2,z+1/4   -m <sub>x</sub> ,0,0) (3/4,-y+1/2,z+1/4   -m <sub>x</sub> ,0,0) (3/4,y+1/2,-z+1/4   -m <sub>x</sub> ,0,0) (3/4,-y+1/2,-z+1/4   -m <sub>x</sub> ,0,0) (3/4,y+1/2,z+3/4   m <sub>x</sub> ,0,0) (3/4,-y+1/2,z+3/4   m <sub>x</sub> ,0,0) (3/4,y+1/2,-z+3/4   m <sub>x</sub> ,0,0) (3/4,-y+1/2,-z+3/4   m <sub>x</sub> ,0,0)	16	-	-
5	O2_1 O 0.00000 0.50000 0.25000	(0,1/2,1/4   0,0,0) (0,1/2,3/4   0,0,0) (1/2,1/2,1/4   0,0,0) (1/2,1/2,3/4   0,0,0)	4	-	-
	O2_2 O 0.25000 0.00000 0.00000	(1/4,0,0   0,0,0) (1/4,0,1/2   0,0,0) (3/4,0,0   0,0,0) (3/4,0,1/2   0,0,0)	4	-	-

- f. Download the mcif of the *C<sub>mma</sub>* (#67.509) magnetic space group and create a PCR. Change the JOB = 3 to JOB = 1 and include all the information related with your instrument and with the measurements; Lambda, background, zero, U, V, W, unit cell and Scale. All this information can be obtained from the previous PCR file.
- g. Refine the data and check the convergence.  
In order to avoid problems during the refinement, refine only the scale and the magnetic moments.



- h. The values of the Bragg R-factor and RF-factor are comparable, even slightly better, than those values obtained with the  $C_c2/c$  magnetic space group. This is an example of the degeneracy of solutions that is common in magnetic structure determination and refinement using neutron powder diffraction. However, if we check the output file we can observe that the refined values of the different atomic orbits are quite different, moreover some of those parameters are physically inconsistent. The magnetic moment of Ho(III) should not be larger than  $10 \mu_B$  and based on the nuclear structure there is no reason to think that one orbit is close to zero while the other (with the same environment) have a magnetic moment above  $10 \mu_B$ .

$$\begin{aligned}
 R_x &= \text{Ni}(1) = 0.8(2) \mu_B \\
 R_z &= \text{Ni}(2) = 1.81(7) \mu_B \\
 R_x &= \text{Ho}(1) = -0.21(9) \mu_B \\
 R_z &= \text{Ho}(2) = -12.61(8) \mu_B
 \end{aligned}$$

Moreover, if we try to refine the atomic positions of the oxygen atoms, the refinement does not converge, while with the  $C_c2/c$  the refinement is stable even if the oxygen positions are refined.

## Annexe 1.

### Some simple rules for using MSYM operators instead of basis vectors in magnetic refinements of commensurate structures with FullProf

The use of spherical components for describing the orientation of magnetic moments (or Fourier components of magnetic moments) is done simply by changing the sign of the indicator JBT in the PCR file. If we use directly the basis vectors as output by Baslreps, we cannot use spherical components. For that, you have to provide MSYM operators. This is not done directly in Baslreps,

however you can obtain these operators in cases you have Fourier coefficients of the form:  $Sk(1) = (u, v, w)$  in Baslreps, because the coefficients of the linear combination of basis vectors like

$$Sk(1) = u(1,0,0) + v(0,1,0) + w(0,0,1) = (u, v, w) \text{ and}$$

$$Sk(2) = u(1,0,0) + v(0,-1,0) + w(0,0,-1) = (u, -v, -w)$$

can also be interpreted as rotational operators and in the above case you can write two rotational operators acting on the Fourier coefficient  $Sk(1)$ . The first one is the identity  $MSYM\ u,v,w,0.0$  and the second one is  $MSYM\ u,-v,-w,0.0$ . The phase 0.0 has only a sense for incommensurate magnetic structures.

In Baslreps, the operators are not explicitly given but they can be easily constructed. If for instance you have provided a special position for an atom you may obtain something like:  $Sk(i) = (u, -u, 0)$ . Of course, this is only valid for an atom in a special position and this is NOT the expression of a  $MSYM$  operator. You should run Baslreps for an atom in a general position to obtain no constraint in the Fourier coefficients  $Sk$ , and only when you describe in the PCR file the components of the Fourier coefficients you can put the constraints using codes like 191.0 -191.0 0.0 for the three components of the Fourier coefficients.

Suppose that you have an Fe-atom occupying the position (0.0, 0.23456, 0.5) in the space group Cmc<sub>2</sub>m and you obtain a magnetic structure with propagation vector  $k = (0,0,0)$ . When you run Baslreps, you obtain 8 irreps of dimension 1. For instance for irrep=2 you obtain in the \*.bsr file the following basis vectors:

```

=====
=> Basis functions of Representation IRrep( 2) of dimension 1 contained 2 times in GAMMA
=====
          SYMM  x,y,z  -x,-y,z+1/2  -x,y,-z+1/2  x,-y,-z
          Atoms:  Fe_1          Fe_2          Fe_3          Fe_4
BsV( 1, 1: 4):Re ( 0  1  0) ( 0  -1  0) ( 0  1  0) ( 0  -1  0)
BsV( 2, 1: 4):Re ( 0  0  1) ( 0  0  1) ( 0  0  -1) ( 0  0  -1)

The general expressions of the Fourier coefficients Sk(j) of the atoms non-related
by lattice translations are the following:

SYMM x,y,z                      Atom: Fe_1      0.0000  0.2346  0.5000
Sk(1): (0,u,v)

SYMM -x,-y,z+1/2                Atom: Fe_2      0.0000 -0.2346  1.0000
Sk(2): (0,-u,v)

SYMM -x,y,-z+1/2                Atom: Fe_3      0.0000  0.2346  0.0000
Sk(3): (0,u,-v)

SYMM x,-y,-z                     Atom: Fe_4      0.0000 -0.2346 -0.5000
Sk(4): (0,-u,-v)

```

Of course, the expression of the Fourier coefficients cannot be converted to proper operators, but if you run another time Baslreps for the same case but putting the Fe-atom in an arbitrary general position you obtain for the same irrep:

```

          SYMM  x,y,z  -x,-y,z+1/2  -x,y,-z+1/2  x,-y,-z
          Atoms:  Fe_1          Fe_2          Fe_3          Fe_4
BsV( 1, 1: 4):Re ( 1  0  0) ( -1  0  0) ( -1  0  0) ( 1  0  0)
BsV( 2, 1: 4):Re ( 0  1  0) ( 0  -1  0) ( 0  1  0) ( 0  -1  0)
BsV( 3, 1: 4):Re ( 0  0  1) ( 0  0  1) ( 0  0  -1) ( 0  0  -1)

          SYMM  -x,-y,-z  x,y,-z+1/2  -x,y,z+1/2  -x,y,z
          Atoms:  Fe_5          Fe_6          Fe_7          Fe_8
BsV( 1, 5: 8):Re ( -1  0  0) ( 1  0  0) ( 1  0  0) ( -1  0  0)
BsV( 2, 5: 8):Re ( 0  -1  0) ( 0  1  0) ( 0  -1  0) ( 0  1  0)
BsV( 3, 5: 8):Re ( 0  0  -1) ( 0  0  -1) ( 0  0  1) ( 0  0  1)

```

The general expressions of the Fourier coefficients  $Sk(j)$  of the atoms non-related by lattice translations are the following:

SYMM $x, y, z$ Sk(1): $(u, v, w)$	Atom: Fe_1	0.1230	0.2346	0.4560
SYMM $-x, -y, z+1/2$ Sk(2): $(-u, -v, w)$	Atom: Fe_2	-0.1230	-0.2346	0.9560
SYMM $-x, y, -z+1/2$ Sk(3): $(-u, v, -w)$	Atom: Fe_3	-0.1230	0.2346	0.0440
SYMM $x, -y, -z$ Sk(4): $(u, -v, -w)$	Atom: Fe_4	0.1230	-0.2346	-0.4560
SYMM $-x, -y, -z$ Sk(5): $(-u, -v, -w)$	Atom: Fe_5	-0.1230	-0.2346	-0.4560
SYMM $x, y, -z+1/2$ Sk(6): $(u, v, -w)$	Atom: Fe_6	0.1230	0.2346	0.0440
SYMM $x, -y, z+1/2$ Sk(7): $(u, -v, w)$	Atom: Fe_7	0.1230	-0.2346	0.9560
SYMM $-x, y, z$ Sk(8): $(-u, v, w)$	Atom: Fe_8	-0.1230	0.2346	0.4560

Here you can put all this information in form of MSYM operators and write the PCR file for a magnetic phase as:

```
!-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern#
!-----
Test artificial structure with C m c m space group, k=0 and Fe at (0.0, 0.23456, 0.5)
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
1 0 0 0.0 1.0 1.0 1 0 -1 0 0 0.000 0 5 0
!
C -1 <--Space group symbol for hkl generation
!Nsym Cen Laue MagMat
8 1 3 1
!
SYMM x,y,z
MSYM u,v,w,0.0
SYMM -x,-y,z+1/2
MSYM -u,-v,w,0.0
SYMM -x,y,-z+1/2
MSYM -u,v,-w,0.0
SYMM x,-y,-z
MSYM u,-v,-w,0.0
SYMM -x,-y,-z
MSYM -u,-v,-w,0.0
SYMM x,y,-z+1/2
MSYM u,v,-w,0.0
SYMM x,-y,z+1/2
MSYM u,-v,w,0.0
SYMM -x,y,z
MSYM -u,v,w,0.0
!Atom Typ Mag Vek X Y Z Biso Occ Rx Ry Rz
! Ix Iz beta11 beta22 beta33 MagPh
Fe MFE3 1 0 0.00000 0.23456 0.50000 0.00000 0.50000 0.000 1.200 3.400
0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000
!-----> Profile Parameters for Pattern # 1
! Scale Shapel Bov Str1 Str2 Str3 Strain-Model
1.308 0.000000 0.0000 0.00000 0.00000 0.00000 0
. . . . .
```

With this formulation, only two parameters are refinable: Ry and Rz. The atom position of Fe is the Wyckoff site 8f, so Occ=0.5 because we provide all the symmetry operators. The lattice centring is given in the symbol to generate reflections. The magnetic space group is easily obtained in this case because  $\mathbf{k}=0$  and the representations are of dimension 1, just looking at the table of the representations we have just to associate the time inversion with an operator when the character is -1. The irrep 2 corresponds to the magnetic space group  $Cm'c'm'$ .

If you want to use spherical components, you should keep in mind that magnetic moments are given with respect to the Cartesian system related to the crystallographic basis. In this case is trivial  $x//a$ ,  $y//b$  and  $z//c$ . Therefore, in spherical components, the constraint (0, Ry, Rz) means that the “Phi” angle should be fixed to 90° and “Theta” and the modulus of the moment are free. The only changes are: JBT should be put equal to -1 to select spherical components and the ordering of parameters is: Moment, Phi and Theta, so the changes to be applied are put in bold is the new version of the PCR file:

```
!-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern#
!-----
Test artificial structure with C m c m space group, k=0 and Fe at (0.0, 0.23456, 0.5)
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
1 0 0 0.0 1.0 1.0 -1 0 -1 0 0 0.000 0 5 0
!
C -1 <---Space group symbol for hkl generation
!Nsym Cen Laue MagMat
8 1 3 1
!
SYMM x,y,z
MSYM u,v,w,0.0
SYMM -x,-y,z+1/2
MSYM -u,-v,w,0.0
SYMM -x,y,-z+1/2
MSYM -u,v,-w,0.0
SYMM x,-y,-z
MSYM u,-v,-w,0.0
SYMM -x,-y,-z
MSYM -u,-v,-w,0.0
SYMM x,y,-z+1/2
MSYM u,v,-w,0.0
SYMM x,-y,z+1/2
MSYM u,-v,w,0.0
SYMM -x,y,z
MSYM -u,v,w,0.0
!Atom Typ Mag Vek X Y Z Biso Occ Rm Rphi Rtheta
! Im Iphi Itheta beta11 beta22 beta33 MagPh
Fe MFE3 1 0 0.00000 0.23456 0.50000 0.00000 0.50000 3.605 90.000 19.440
0.000 0.000 0.00 0.00 0.00 0.00 0.00 1.00 0.00 1.00
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00000
!-----> Profile Parameters for Pattern # 1
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
1.308 0.000000 0.0000 0.00000 0.00000 0.00000 0
. . . . .
```

In cases of representations with  $\dim > 1$ , the situation is more complicated because what Baslreps outputs is the most general (lower symmetry) case for Fourier coefficients. There is no correspondence between *one irrep* and *one magnetic group*, for  $\dim > 1$  there are many possible magnetic groups. The different symmetries are obtained by making zero some of the coefficients of the linear combinations of basis vectors. Let us use the following example: Fe-atom in a general position of the group  $Pmma$  and propagation vector  $\mathbf{k}=(1/2,1/2,0)$ . In this case, there are two 2D irreps and the output of Baslreps for the first irrep is:

```
+++++
=> Basis functions of Representation IRrep( 1) of dimension 2 contained 6 times in GAMMA
+++++
```

	SYMM	$x, y, z$	$-x+1/2, -y, z$	$-x, y, -z$	$x+1/2, -y, -z$							
	Atoms:	Fe <sub>1</sub>		Fe <sub>2</sub>		Fe <sub>3</sub>		Fe <sub>4</sub>				
BsV( 1, 1: 4):Re (		1	0	0	(	-1	0	0	(	0	0	0)
BsV( 2, 1: 4):Re (		0	1	0	(	0	-1	0	(	0	0	0)
BsV( 3, 1: 4):Re (		0	0	1	(	0	0	1	(	0	0	0)
BsV( 4, 1: 4):Re (		0	0	0	(	0	0	0	(	-1	0	0)
BsV( 5, 1: 4):Re (		0	0	0	(	0	0	0	(	0	1	0)
BsV( 6, 1: 4):Re (		0	0	0	(	0	0	0	(	0	0	-1)
BsV( 7, 1: 4):Re (		0	0	0	(	0	0	0	(	-1	0	0)
BsV( 8, 1: 4):Re (		0	0	0	(	0	0	0	(	0	1	0)
BsV( 9, 1: 4):Re (		0	0	0	(	0	0	0	(	0	0	1)
BsV(10, 1: 4):Re (		1	0	0	(	1	0	0	(	0	0	0)
BsV(11, 1: 4):Re (		0	1	0	(	0	1	0	(	0	0	0)
BsV(12, 1: 4):Re (		0	0	1	(	0	0	-1	(	0	0	0)

	SYMM	$-x, -y, -z$	$x+1/2, y, -z$	$x, -y, z$	$-x+1/2, y, z$							
	Atoms:	Fe <sub>5</sub>		Fe <sub>6</sub>		Fe <sub>7</sub>		Fe <sub>8</sub>				
BsV( 1, 5: 8):Re (		0	0	0	(	0	0	0	(	1	0	0)
BsV( 2, 5: 8):Re (		0	0	0	(	0	0	0	(	-1	0	0)
BsV( 3, 5: 8):Re (		0	0	0	(	0	0	0	(	0	1	0)
BsV( 4, 5: 8):Re (		-1	0	0	(	1	0	0	(	0	0	0)
BsV( 5, 5: 8):Re (		0	-1	0	(	0	1	0	(	0	0	0)
BsV( 6, 5: 8):Re (		0	0	-1	(	0	0	-1	(	0	0	0)
BsV( 7, 5: 8):Re (		-1	0	0	(	-1	0	0	(	0	0	0)
BsV( 8, 5: 8):Re (		0	-1	0	(	0	-1	0	(	0	0	0)
BsV( 9, 5: 8):Re (		0	0	-1	(	0	0	1	(	0	0	0)
BsV(10, 5: 8):Re (		0	0	0	(	0	0	0	(	1	0	0)
BsV(11, 5: 8):Re (		0	0	0	(	0	0	0	(	0	-1	0)
BsV(12, 5: 8):Re (		0	0	0	(	0	0	0	(	0	0	-1)

The general expressions of the Fourier coefficients  $Sk(j)$  of the atoms non-related by lattice translations are the following:

SYMM $x, y, z$ Sk(1): $(u+d, v+e, w+f)$	Atom: Fe <sub>1</sub>	0.1230	0.2346	0.4560
SYMM $-x+1/2, -y, z$ Sk(2): $(-u+d, -v+e, w-f)$	Atom: Fe <sub>2</sub>	0.3770	-0.2346	0.4560
SYMM $-x, y, -z$ Sk(3): $(-p-a, q+b, -r-c)$	Atom: Fe <sub>3</sub>	-0.1230	0.2346	-0.4560
SYMM $x+1/2, -y, -z$ Sk(4): $(p-a, -q+b, -r+c)$	Atom: Fe <sub>4</sub>	0.6230	-0.2346	-0.4560
SYMM $-x, -y, -z$ Sk(5): $(-p-a, -q-b, -r-c)$	Atom: Fe <sub>5</sub>	-0.1230	-0.2346	-0.4560
SYMM $x+1/2, y, -z$ Sk(6): $(p-a, q-b, -r+c)$	Atom: Fe <sub>6</sub>	0.6230	0.2346	-0.4560
SYMM $x, -y, z$ Sk(7): $(u+d, -v-e, w+f)$	Atom: Fe <sub>7</sub>	0.1230	-0.2346	0.4560
SYMM $-x+1/2, y, z$ Sk(8): $(-u+d, v-e, w-f)$	Atom: Fe <sub>8</sub>	0.3770	0.2346	0.4560

There are 12 basis vectors so in total 12 coefficients:  $u, v, w, p, q, r, a, b, c, d, e, f$ .

Obviously, for each atom we need a maximum of three coefficients. We can construct MSYM operators by systematically nullifying coefficients and regrouping atoms. Remember that the symmetry operators are referred to the standard basis of the parent group *Pmma*. If we group the atoms having the coefficients  $u, v$  and  $w$  nullifying all the others ( $d, e, f$ ) we obtain:

```

SYMM  $x, y, z$ 
Sk(1):  $(u, v, w)$ 
SYMM  $-x+1/2, -y, z$ 
Sk(2):  $(-u, -v, w)$ 
SYMM  $x, -y, z$ 
Sk(7):  $(-u, v, -w)$ 
SYMM  $-x+1/2, y, z$ 
Sk(8):  $(u, -v, -w)$ 

```

If we group the rest of atoms, we see that in all of them there are the coefficients  $p, q, r$ . Let us nullify the accompanying coefficients ( $a, b, c$ ). We obtain:

```

SYMM -x,y,-z
Sk(3): (-p,q,-r)
SYMM x+1/2,-y,-z
Sk(4): (p,-q,-r)
SYMM -x,-y,-z
Sk(5): (p,q,r)
SYMM x+1/2,y,-z
Sk(6): (-p,-q,r)

```

It is easy to see that the operators are the same as above changing  $-x,-y,-z \rightarrow x,y,z$ . If we apply the centre of inversion and re-order the above list we obtain:

```

SYMM -x,-y,-z      SYMM x,y,z
Sk(5): (p,q,r)      Sk(5): (p,q,r)
SYMM x+1/2,y,-z     SYMM -x+1/2,-y,z
Sk(6): (-p,-q,r)    → Sk(6): (-p,-q,r)
SYMM -x,y,-z        SYMM x,-y,z
Sk(3): (-p,q,-r)    Sk(3): (-p,q,-r)
SYMM x+1/2,-y,-z    SYMM -x+1/2,y,z
Sk(4): (p,-q,-r)    Sk(4): (p,-q,-r)

```

The right part is identical to the first list of operators if we replace  $p, q, r$  by  $u, v, w$ . This particular selection of coefficients of the linear combination of basis vectors gives rise to a splitting of the Fe atoms in two independent sites so the relevant part of the PCR file corresponding to this case in spherical coordinates is:

```

!-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern#
!-----
Test artificial structure with Pmma k=(1/2,1/2,0) space group and Fe at (0.0, 0.23456, 0.5)
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
2 0 0 0.0 1.0 1.0 -1 -1 -1 0 0 0.000 1 5 0
!
P -1 <--Space group symbol for hkl generation
!Nsym Cen Laue MagMat
4 1 3 1
!
SYMM x,y,z
MSYM u,v,w,0.0
SYMM -x+1/2,-y,z
MSYM -u,-v,w,0.0
SYMM x,-y,z
MSYM -u,v,-w,0.0
SYMM -x+1/2,y,z
MSYM u,-v,-w,0.0
!
!Atom Typ Mag Vek X Y Z Biso Occ Rm Rphi Rtheta
! Im Iphi Itheta betall beta22 beta33 MagPh
Fe1 MFE3 1 0 0.1230 0.2346 0.4560 0.00000 0.50000 3.605 23.000 19.440
0.00 0.00 0.00 0.00 0.00 0.00 0.00 41.00 1.00 1.00
0.000 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 0.00
Fe2 MFE3 1 0 -0.1230 -0.2346 -0.4560 0.00000 0.50000 3.605 47.000 19.440
0.00 0.00 0.00 0.00 0.00 0.00 0.00 41.00 1.00 1.00
0.000 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 0.00
!-----> Profile Parameters for Pattern # 1
! Scale Shapel Bov Str1 Str2 Str3 Strain-Model
1.308 0.000000 0.0000 0.00000 0.00000 0.00000 0
. . . . .
0.5 0.5 0.0 <- Propagation vector
0.0 0.0 0.0
. . . . .

```

We have explicitly used a constraint not coming from symmetry: the equality of moments  $m(\text{Fe1})=m(\text{Fe2})$ . In principle, the magnetic moment of the atoms Fe1 and Fe2 are independent because the initial site is split in two independent atoms.

Using other ways of selecting the coefficients one obtains other symmetries. For instance a more symmetric solution is obtained imposing  $p=u$ ,  $q=v$  and  $r=w$  and nullifying all the other coefficients. In such a case, one have a single site

In cases like this, it may be easier to use directly Shubnikov groups (magnetic space groups). For such cases it is convenient to use the Bilbao Crystallographic Server that provides the possible Shubnikov groups for a given space group and propagation vector (using the programs MAXMAGN or K-SUBGROUPSMAG). These programs can generate mCIF files that can be converted to PCR files by the program mCIF\_to\_PCR. The description in terms of Shubnikov groups does not consider the concept of propagation vector, instead the magnetic unit cell with a crystallographic description (symmetry operators associated or not with time inversion) of atom positions and magnetic moment is used.