

Tutorial: DyMn₆Ge₆

Complex Magnetic Structures: Different approaches within FullProf to handle difficult cases. Incommensurate magnetic structure – modulation (propagation) vector (0, 0, 0.1651) and (0, 0, 0).

DyMn₆Ge₆

Neutron powder data measured at 11K on DMC at PSI (Switzerland) collected at 1.7037Å.

The space group is S.G.= *P6/mmm*, the cell parameters are $a \approx 5.20$ Å, $b \approx 5.20$ Å and $c \approx 8.15$ Å.

U, V, W, X and Y values: 1.682276, -1.301047, 0.380131, 0.000000 and 0.021994

SL and DL = 0.02495 and 0.03168

Cell parameters = 5.208310, 5.208310, 8.152334, 90.0, 90.0 and 120.0.

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

References:

J. Rodríguez-Carvajal & F. Bourée, EPJ Web of Conferences 22, 00010 (2012)

P. Schobinger-Papamantellos et al, Journal of Alloys and Compounds, 203 (1994) 243

Input files:

dymn6ge6.dat (powder profile data)

dymn6ge6_nuclear.cif (nuclear structure)

The format of the data corresponds to $\text{Ins} = 8$ in FullProf.

- 1) **Create a working directory, don't use space or special characters in the path.**
 - a. Copy in this folder all the input files.
- 2) **Create an initial structural PCR file.**
 - a. Open the FullProf toolbar (clicking on the desktop icon)
 - b. Select the working directory. "file > Select working directory..."
 - c. Locate the working directory and click on OK.
 - d. Click on the EdPCR icon, in the FP toolbar.
 - e. Click on the cif_to_pcr icon in the EdPCR.
 - f. Select Neutron as source type, check that the unit cell and the space group correspond with the provided at the beginning of this file. Check in the "atoms information" windows that all is consistent with the provide CIF file. Click on OK to exit.
 - g. Save the PCR file clicking on the "save as" icon. Rename the file with an intuitive name.
- 3) **Modify the PCR file according to the current example.**
 - a. Click on General and modify the name.
 - b. In calculation "Refinement/Calculation of a Powder Diffraction Profile" should be selected.
 - c. Click on OK.
 - d. Click on "patterns"
 - e. Click on Data file/Peak shape > in format select DMC/HRPD which correspond with $\text{Ins} = 8$.
 - f. In "Refinement/simulation" select "Neutron-CW" (CW = constant wavelength).
 - g. In wavelength, roll out the menu and select "user defined" and write the correct wavelength and fix the ratio I_2/I_1 to 1 (or zero, assuming a pure monochromatic neutron beam).
 - h. Click on OK.

- i. Click on Background type and select "Linear Interpolation..." this option allows the user to define a background by clicking on the experimental pattern. We will do it in a further step. Of course other background functions can be used, in particular Chebychev Polynomials give quite stable refinements.
- j. Other parameters Excluded Regions will be changed later after exploring the experimental pattern.
- k. Click on OK.
- l. Click on "Phase", and modify the phase name and check that the calculation is "structural model (Rietveld Method)".
- m. Click on contribution to patterns and select the next options:
- n. Click on OK.
- o. Click on symmetry and check that the selected space group is right.
- p. Click on OK and save the file from the EdPCR windows.
- q. Click on Refinement
- r. Change the number of cycles. Other parameters as Background or Instrumental will be modified later.
The instrumental resolution parameters can be modified clicking on Profile.
- s. Save the file and click on Editor > Input control file (PCR) to see the current PCR file.
- t. Before running this PCR file, we should include a realistic background. To do that we are going to open the experimental data on WinPLOT-2006.
- u. Click on *open* icon or in File > open pattern file (.dat) and select dy.dat. The data are in format $\text{Ins} = 8$.
- v. Click on Calculation > Background > enable and Calculation > Background > Insert point. This allow us define a series of points that could be included into the PCR file. Each background point is included clicking on the left button your mouse. If a wrong point is included, in the same menu you can find "Delete point" which is used in the same way than "Insert point".
In order to increase the accuracy, you can zoom in by clicking on the left button of your mouse and dragging simultaneously. A simple click on the right button reverse the zoom.
- w. The created list of points can be saved clicking on Calculations > Background > save background leave the proposed name "background.bgr" and save.
- x. Now we can include this information in to the PCR file, we can edit the PCR file with a text editor or using the program EdPCR. We are going to use the latter. Click on Refinements > Background > import from background file.
After importing the background, click on OK and save in the main window of EdPCR.

You can add excluded regions if you think that is needed. Click on Patterns > Excluded Regions and in number of excluded regions increase the number up to 1. Now you can define the lower limit and the higher limit.

- y. The PCR file for refining the nuclear structure is done. We can check the PCR file clicking on Editor > Input control file or opening the file with our favourite text editor.

4) Run FP to refine the 11K data.

- a. Load into the FP toolbar the new PCR file. That can be done clicking on Search Input files icon. Be sure that the PCR file and the data file are in the same folder.
- b. Now you can click on the FullProf icon and run. However, the result is clearly non-satisfactory. Notice that, for the moment, all parameters are fixed.
- c. Let us start refining first the Scale factor (refinement > Profile), the second parameter the zero (refinement > instrumental) and finally the unit cell (refinement > Profile). Refining only these parameters, we obtain a good initial fit.
- d. The sample is absorbing, an effective absorption coefficient ($\mu_R=1.28$) should be included in the PCR file, in the same way an asymmetry correction is applied everywhere ($\text{AsyLim}=180.0$). For neutron diffraction the C_{thm} (square of $\cos(2\Theta - \text{monocromator})$) for polarization correction should be fixed to 0.
The easy way to change these parameters is modifying directly the PCR file as it has been shown in previous exercises.

5) Propagation vector determination.

- Use k-search program to determine the propagation vectors (see details on $\text{Ho}_2\text{BaNiO}_5$ example).

6) Add new phases to check the propagations vectors.

- We are going to use the EdPCR program. 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 Pattern”, and select the options showed here below and click on OK.
The “Satellite reflections are generated automatically from Space group symbol”.

Click on symmetry and add P-1 space group (this is just to generate half-reciprocal space satellite reflections). NB: the space group in FP should be written with a space between elements (P -1, in this particular case). Click on *Symm. Op. Automatic* and on OK and save in the main window of EdPCR.

- Now we need to fill 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 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 the same refinement code.
- Add the first propagation vector.
- Add a new phase and include the incommensurate propagation vector.
- Run FP and check that the full pattern is correctly fitted.

7) Calculation of Irreducible representations.

- You can use the same protocol as in $\text{Ho}_2\text{BaNiO}_5$ example to solve the magnetic structure. Although this method can give you the correct solution, the procedure is quite tedious. You can try to solve the magnetic structure through this method, but in this example, we are going to use a new feature of FullProf using the super-space group formalism. A detailed explanation of this procedure is also described on the next reference; J. Rodríguez-Carvajal & F. Bourée, EPJ Web of Conferences 22, 00010 (2012).

8) Use ISODISTORT to create mcif files

- Open ISOTROPY software suite on the web page and click on ISODISTORT. (<https://stokes.byu.edu/iso/isotropy.php>)
- Upload into the system the structural CIF file and click on OK.
- In the first box “Types of distortions to be considered” select only the magnetic modes for the magnetic atoms (Dy and Mn). After that we can CLICK on Change.

ISODISTORT: search

Space Group: 191 P6/mmm D6h-1, Lattice parameters: a=5.20770, b=5.20770, c=8.15150, alpha=90.00000, beta=90.00000, gamma=120.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Dy1 1a (0,0,0), Ge1 2d (1/3,2/3,1/2), Ge2 2c (1/3,2/3,0), Ge3 2e (0,0,z), z=0.34450, Mn1 6i (1/2,0,z), z=0.25030
Include magnetic Dy Mn distortions

Types of distortions to be considered

Change ?

strain: ☐

Displacive: all ☐ none ☐ Dy ☐ Ge ☐ Mn ☐

Occupational: all ☐ none ☐ Dy ☐ Ge ☐ Mn ☐

Magnetic: all ☐ none ☐ Dy ☒ Ge ☐ Mn ☒

Rotational: all ☐ none ☐ Dy ☐ Ge ☐ Mn ☐

Important: You must click on Change to implement any changes in the above type of distortions to be considered.

- We are going to use the “Method 2: General method - search over specific k points”, here on “Change number of superposed IRs” we should increase the number from 1 to 2, as we have to two propagation vectors. Click on Change. After that, the program shows two set of propagation vectors.
- For the k-vector 1 we select the $\mathbf{k} = (0, 0, 0)$, and the number of incommensurate modulations is fixed to 0.
- For the k-vector 2 we select the $\mathbf{k} = (0, 0, 0.1651)$ [DT (0, 0, g)], and change the number of incommensurate modulations to 1. After that, we click on OK.

Method 2: General method - search over specific k points OK ?

k vector 1: GM, k16 (0,0,0) a= b= g= # of independent incommensurate modulations= 0

k vector 2: DT (0,0,g) a= b= g= 0.1651 # of independent incommensurate modulations= 1

Change number of superposed IRs: 2 Change ?

Important: You must click on Change to implement any changes in the number of superposed IRs.

- g. In the next menu, we can combine the irreps obtained from each propagation vector. In the case of $\mathbf{k} = 0$, there are 10 possible magnetic *irreps*. While for the incommensurate vector the number of solutions are only 5.

Now we need to combine the possible *irreps* and sort the Shubnikov magnetic space groups from high to low symmetry.

ISODISTORT: irreducible representation

Space Group: 191 P6/mmm D6h-1, Lattice parameters: a=5.20770, b=5.20770, c=8.15150, alpha=90.00000, beta=90.00000, gamma=120.00000
 Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
 Dy1 1a (0,0,0), Ge1 2d (1/3,2/3,1/2), Ge2 2c (1/3,2/3,0), Ge3 2e (0,0,z), z=0.34450, Mn1 6i (1/2,0,z), z=0.25030
 Include magnetic Dy Mn distortions
 k point: GM, k16 (0,0,0)
 k point: DT (0,0,g), g=0.16510 (1 incommensurate modulation/1 arm)

Choose each superposed IR and OPD (optional):

IR 1: mGM2+, mk16t3 OPD: ?

IR 2: mGM2+, mk16t3 OPD: OK

mGM3+, mk16t5
mGM4+, mk16t7
mGM5+, mk16t11
mGM6+, mk16t9
mGM1-, mk16t2
mGM3-, mk16t6
mGM4-, mk16t8
mGM5-, mk16t12
mGM6-, mk16t10

Choose each superposed IR and OPD (optional):

IR 1: mGM2+, mk16t3 OPD: ?

IR 2: mDT5 OPD: OK

mDT2
mDT3
mDT4
mDT5
mDT6

- h. The combination of mGm2+ with mDT2 gives a list of two possible superspace space groups. The first one corresponding to $P6/mmm'(0,0,g)0000$ and the second one $P6m'm'(0,0,g)000$, in which the inversion centre and a mirror plane disappear.

Finish selecting the distortion mode by choosing an order parameter direction ?

☒ P1-P (a|b,0) 191.1.24.1.m240.1 P6/mmm'(0,0,g)0000, basis={(-1,0,0,0),(0,-1,0,0),(0,0,1,0),(0,0,0,1)}, origin=(0,0,0,1/4), s=1, i=1, k-active= (0,0,0);(0,0,0,165)

☐ P1-C (a|b,c) 183.1.24.1.m189.1 P6m'm'(0,0,g)000, basis={(-1,0,0,0),(0,-1,0,0),(0,0,1,0),(0,0,0,1)}, origin=(0,0,0,0), s=1, i=2, k-active= (0,0,0);(0,0,0,165)

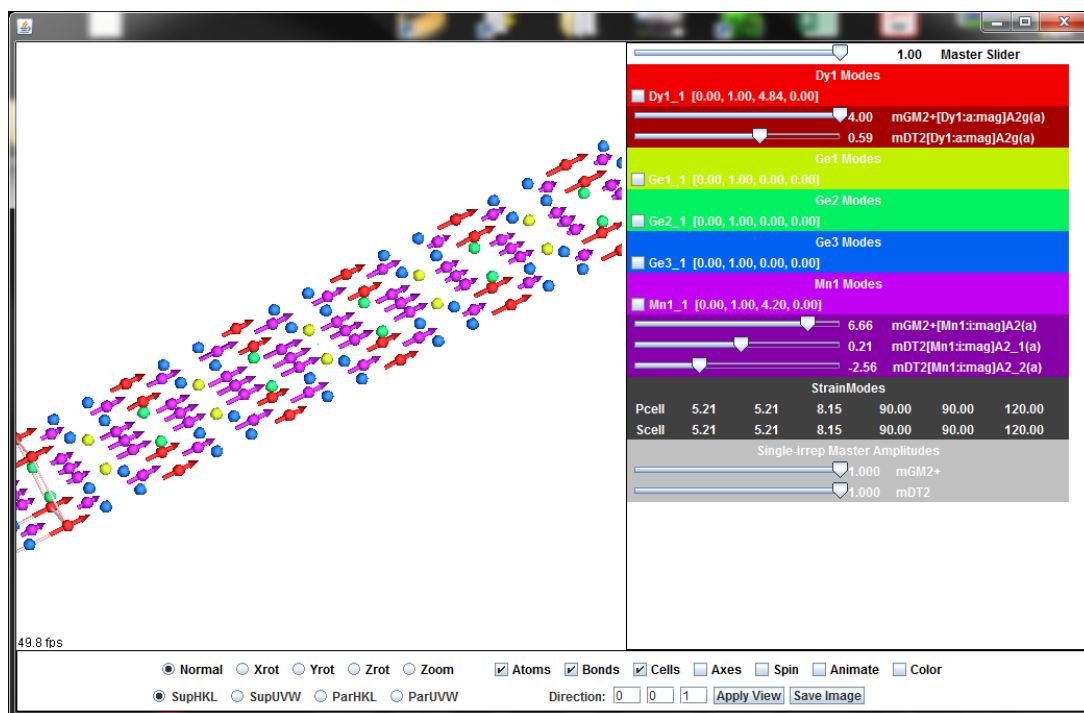
OK

- i. We select the first solution and click on OK. In the next menu we can select "Save interactive distortion" which allows us play with the different modes using the scroll bars of the Isoviz program. The second option is click on CIF file to download a "mcif" file compatible with the FullProf program "mcif_to_pcr".

ISODISTORT: distortion

Space Group: 191 P6/mmm D6h-1, Lattice parameters: a=5.20770, b=5.20770, c=8.15150, alpha=90.00000, beta=90.00000, gamma=120.00000
 Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
 Dy1 1a (0,0,0), Ge1 2d (1/3,2/3,1/2), Ge2 2c (1/3,2/3,0), Ge3 2e (0,0,z), z=0.34450, Mn1 6i (1/2,0,z), z=0.25030
 Include magnetic Dy Mn distortions
 k point: GM, k16 (0,0,0)
 IR: mGM2+, mk16t3
 k point: DT (0,0,g), g=0.16510 (1 incommensurate modulation/1 arm)
 IR: mDT2
 P1-P (a|b,0) 191.1.24.1.m240.1 P6/mmm'(0,0,g)0000, basis={(-1,0,0,0),(0,-1,0,0),(0,0,1,0),(0,0,0,1)}, origin=(0,0,0,1/4), s=1, i=1, k-active= (0,0,0);(0,0,0,165)

☒ Save interactive distortion ? ☐ CIF file ? ☐ Distortion file ? ☐ Modes details ? ☐ Complete modes details ? ☐ IR matrices OK



- j. From the macroscopic measurements we know that the magnetic susceptibility is compatible with the occurrence of ferrimagnetic behaviour, so Isoviz program can help us to reject some models without refining against the experimental data.
- k. Save the PCR file of the $P6/mmm'(0,0,g)0000$ superspace group and use it as input for the mcif_to_pcr program.

9) Create a PCR file compatible with magnetic superspace groups.

- a. A template PCR file compatible with the Shubnikov super-space group can be created in a similar way that was shown on the LaMnO_3 example using the mcif_to_pcr utility from the FullProf toolbar. Alternatively, you can use a previous created template and modify it according with the new magnetic superspace group.
- b. To do the procedure by hand you should only modify the block of the sample data. Here below there is a description of the PCR file for Shubnikov super-space formalism.

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ      Nvk Npr More
   5   0   0 0.0 0.0 1.0   7   0   2   0   0      34495.781   1   7   0
!
P6/mmm'(0,0,g)0000      <-- Magnetic SuperSpace group symbol (not currently used)
genr x1,x2,x3,x4,+1      <-- List of symmetry operators or generators of the group
genr x1-x2,x1,x3,x4,+1
genr -x2,x1-x2,x3,x4,+1
genr -x1,-x2,x3,x4,+1
genr -x1+x2,-x1,x3,x4,+1
genr x2,-x1+x2,x3,x4,+1
genr x1-x2,-x2,-x3,-x4,-1
genr x1,x1-x2,-x3,-x4,-1
genr x2,x1,-x3,-x4,-1
genr -x1+x2,x2,-x3,-x4,-1
genr -x1,-x1+x2,-x3,-x4,-1
genr -x2,-x1,-x3,-x4,-1
genr -x1,-x2,-x3,-x4,+1
genr -x1+x2,-x1,-x3,-x4,+1
genr x2,-x1+x2,-x3,-x4,+1
genr x1,x2,-x3,-x4,+1
genr x1-x2,x1,-x3,-x4,+1
genr -x2,x1-x2,-x3,-x4,+1
genr -x1+x2,x2,x3,x4,-1
genr -x1,-x1+x2,x3,x4,-1
genr -x2,-x1,x3,x4,-1
genr x1-x2,-x2,x3,x4,-1
genr x1,x1-x2,x3,x4,-1
genr x2,x1,x3,x4,-1
```

```

N_qc 1 <-- Number of Q_coeff (harmonics)
Q_coeff <-- List of Q_coeff, 1 coefficient per line
1
!

```

The Jbt indicator should be fix to 7. The Nvk is the number of independent incommensurate vectors. If Nvk is larger than 1, N_qc should have an integer number for each propagation vector as minimum. Q_coeff is used to refine the different harmonics.

The block in blue “genr” can be copied from the mcif file generated by ISODISTORT. The “Magnetic SuperSpace group symbol” is included as information, but is not yet used to obtain the symmetry operators.

```

Dy      JDY3      -1      0.00000  0.00000  0.00000  0.00000  0.25000  1  0
      0.00000  0.00000  0.00000  0.00000  0.00000
MagM0-Moment:  0.00000  0.00000  -5.63530  <- Homogeneous magnetic moment
      0.00000  0.00000  0.00000
Mcos-Msin-1:  0.00000  0.00000  0.97112  0.00000  0.00000  0.00000  <-Mom.Amplitudes
      0.00000  0.00000  51.00000  0.00000  0.00000  0.00000
Ucos-Usin-1:  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  <-Dis. Amplitudes
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
Mn      MMN2      1      0.50000  0.00000  0.25092  0.00000  1.63901  3  0
      0.00000  0.00000  0.00000  0.00000  0.00000  41.00000
MagM0-Moment:  0.00000  0.00000  0.70663  <- Homogeneous magnetic moment
      0.00000  0.00000  0.00000
Mcos-Msin-1:  0.00000  0.00000  3.01341  0.00000  0.00000  3.14535  <-Mom.Amplitudes
      0.00000  0.00000  61.00000  0.00000  0.00000  71.00000
Beta_0(i,j):  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  <-Betas
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
Ge1     GE        0      0.33333  0.66666  0.50000  0.00000  0.50000  0  0
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
Ge2     GE        0      0.33333  0.66666  0.00000  0.00000  0.50000  0  0
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
Ge3     GE        0      0.00000  0.00000  0.34741  0.00000  0.50000  2  0
      0.00000  0.00000  31.00000  0.00000  0.00000  0.00000
Beta_0(i,j):  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  <-Betas
      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000

```

In the structure description there is some extra lines that should be included. The red block correspond with the “homogeneous magnetic moment”, the component described by the commensurate propagation vector $\mathbf{k}=0$.

The green part corresponds to the modulations, the three first terms are the Cosine terms (x, y, z) and the last term are the Sine components (x, y, z). It deserves to be noted that not all these parameter are free, there are symmetry restrictions that should be applied. Fullprof apply automatically the symmetry constrains if the instructions **VARY mxmymz McosMsin** are included on the PCR file after the phase 1 name. The mxmymz allow refine and apply symmetry constrains to the commensurate part while the McosMsin do the same with the cosine and sine amplitudes. If you have problems with the constraints, you can check the selection rules on the mcif file generated by ISODISTORT.

The label after the type of atom (blue 1/-1) is used to include into the PCR file the “Amplitudes of Modulated displacements”, this amplitudes can be seen as structural modulations and can be applied to both, magnetic and non-magnetic atoms. In the current version of FullProf, this option is not yet completely implemented. You can create a PCR file with nuclear amplitudes but for the moment the program only use the average crystal structure.

The purple number (0/1/2/3), is used as in previous PCR files. 0 for only nuclear atoms with isotropic thermal parameters. 1 for nuclear and magnetic atoms, with isotropic thermal factors. 2 nuclear part with anisotropic thermal parameters, and 3 for nuclear and magnetic parts with using anisotropic thermal parameters.

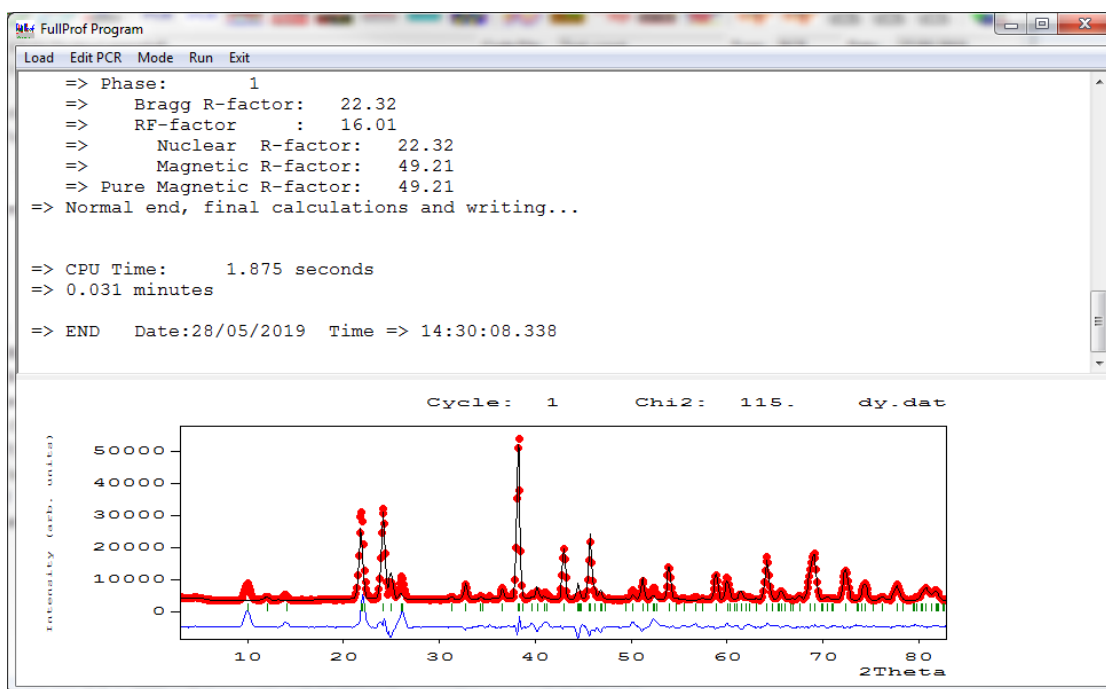
Finally, at the end of the PCR file you should include the “Propagation Vector”, the number of harmonic and a limitation in the satellite calculations “sintl_lim”.

```

! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.02495 0.03168
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! Propagation vectors:
0.0000000 0.0000000 0.1647532 1 1.0000 <- Propagation Vector, nharm, sintl_lim
0.0000000 0.0000000 0.0000000
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot

```

- c. After doing all these changes, you should be able to refine the created PCR file against the experimental data. The PCR file was created using the $P6/m'm'(0,0,g)0000$ magnetic superspace group. Add some initial values on the component allowed by symmetry and refine.



- d. From data refinement we can conclude that the $P6/m'm'(0,0,g)0000$ Shubnikov superspace group is not able to fit the data. Moreover, the refinement is not stable if all parameters are used during the fit.
- e. Check for lower symmetry solutions, based on the $P6mm$ space group. In this example, we are going to test two different superspace groups. The first one is the $P6m'm'(0,0,g)ss0$, this space group was obtained combining mGM2+ with the mDT4. We can check the solution in Isoviz program or opening the generated mcif with a text editor. Here below we have a small part of the mcif where we can observe that the magnetic moment on the Dy atoms is fixed to zero by symmetry. Therefore, this magnetic space group could not be a solution.

```

_atom_site_moment_Fourier.atom_site_label
_atom_site_moment_Fourier.wave_vector_seq_id
_atom_site_moment_Fourier.axis
_atom_site_moment_Fourier.param.cos
_atom_site_moment_Fourier.param.sin
_atom_site_moment_Fourier.param.cos_symmform
_atom_site_moment_Fourier.param.sin_symmform
Dy1_1 1 x 0.00000 0.00000 0 0
Dy1_1 1 y 0.00000 0.00000 0 0
Dy1_1 1 z 0.00000 0.00000 0 0
Mn1_1 1 x 0.00000 0.00000 0 0
Mn1_1 1 y 0.00000 0.00000 Myc1 Mys1
Mn1_1 1 z 0.00000 0.00000 0 0
Mn1_2 1 x 0.00000 0.00000 0 0
Mn1_2 1 y 0.00000 0.00000 Myc1 Mys1
Mn1_2 1 z 0.00000 0.00000 0 0

```

- f. The same protocol was used with the $P6m'm'(0,0,g)000$ group, this superspace group allows magnetic moments in all magnetic sites. However, by symmetry, only magnetic components along the z-axis are allowed. Here below you can find the used PCR to compare with your result.

```

DyMn6Ge6 magnetic VARY McosMsin
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
7 0 0 0.0 0.0 1.0 7 0 2 0 0 133584.188 1 7 0
!
P6m'm' (0,0,g)000 <-- Magnetic SuperSpace group symbol
genr x1,x2,x3,x4,+1
genr x1-x2,x1,x3,x4,+1
genr -x2,x1-x2,x3,x4,+1
genr -x1,-x2,x3,x4,+1

```

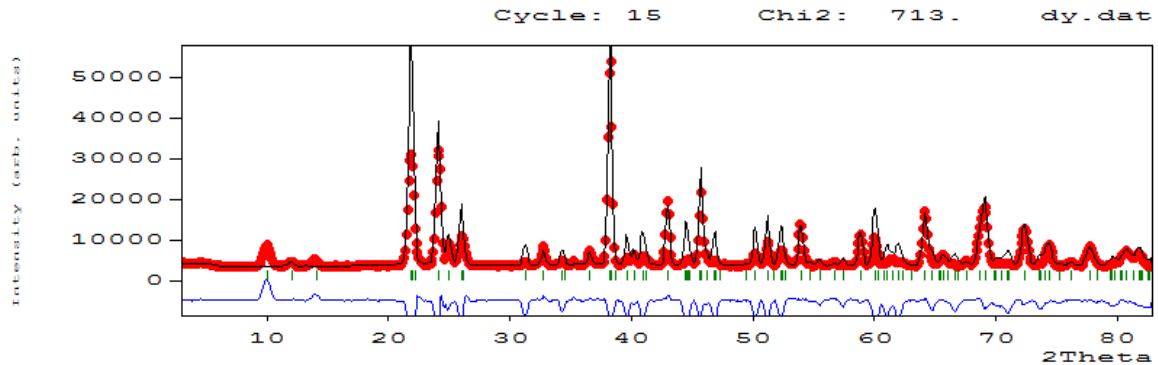


```

genr -x1+x2,-x1,x3,x4,+1
genr x2,-x1+x2,x3,x4,+1
genr -x1+x2,x2,x3,x4,-1
genr -x1,-x1+x2,x3,x4,-1
genr -x2,-x1,x3,x4,-1
genr x1-x2,-x2,x3,x4,-1
genr x1,x1-x2,x3,x4,-1
genr x2,x1,x3,x4,-1
N_qc 1
Q_coeff
1
!
!Atom Typ Max_Qcoeff X Y Z Biso Occ N_type Spc / Line
below:Codes
! Mcosx Mcosy Mcosz Msinx Msiny Msinz / Line
below:Codes
! Ucosx Ucosy Ucosz Usinx Usiny Usinz / Line below:Codes
! beta11 beta22 beta33 beta12 beta13 beta23 / Line
below:Codes
Dy JDY3 1 0.00000 0.00000 0.00000 0.00000 1.00000 1 0
0.00000 0.00000 0.00000 0.00000 0.00000
MagM0-Moment: 0.00000 0.00000 -5.63530 <- Homogeneous magnetic moment
0.00000 0.00000 0.00000
Mcos-Msin-1: 0.00000 0.00000 19.07297 0.00000 0.00000 5.80105 <-
0.00000 0.00000 91.00000 0.00000 0.00000 81.00000
Mn1 MMN2 1 0.00000 0.50000 0.25030 0.00000 3.00000 1 0
0.00000 0.00000 0.00000 0.00000 0.00000
MagM0-Moment: 0.00000 0.00000 2.70663 <- Homogeneous magnetic moment
0.00000 0.00000 0.00000
Mcos-Msin-1: 0.00000 0.00000 -3.06003 0.00000 0.00000 -1.10688 <-
0.00000 0.00000 71.00000 0.00000 0.00000 61.00000
Mn2 MMN2 1 0.00000 0.50000 0.74970 0.00000 3.00000 1 0
0.00000 0.00000 0.00000 0.00000 0.00000
MagM0-Moment: 0.00000 0.00000 2.70663 <- Homogeneous magnetic moment
0.00000 0.00000 0.00000
Mcos-Msin-1: 0.00000 0.00000 -4.15160 0.00000 0.00000 -7.82923 <-
0.00000 0.00000 51.00000 0.00000 0.00000 41.00000
Ge1 GE 0 0.66667 0.33333 0.50000 0.00000 2.00000 0 0
0.00000 0.00000 0.00000 0.00000 0.00000
Ge2 GE 0 0.66667 0.33333 0.00000 0.00000 2.00000 0 0
0.00000 0.00000 0.00000 0.00000 0.00000
Ge3 GE 0 0.00000 0.00000 0.34450 0.00000 1.00000 0 0
0.00000 0.00000 0.00000 0.00000 0.00000
Ge4 GE 0 0.00000 0.00000 0.67258 0.00000 1.00000 0 0
0.00000 0.00000 31.00000 0.00000 0.00000

```

- g. Although this model is compatible with the macroscopic measurements, the resultant magnetic structure is not able to fit properly the experimental data.



- h. In order to allow magnetic structures with magnetic moments out of a single axis we can try with magnetic superspace groups with lower symmetry. So we could decrease the symmetry exploring the $P622$ groups. The combination of mGM2+ with DT5 give rise to the $P62'2'(0,0,g)t00$ magnetic space group while if mGM2+ with DT6 the magnetic space group is $P62'2'(0,0,g)h00$. However, the first magnetic space group can be rejected as the amplitudes of modulated moments of the Dy atoms should be zero by symmetry. Therefore, let check if the $P62'2'(0,0,g)h00$ space group is able to fit the experimental data.
- i. Create a PCR file including the symmetry operator of the $P62'2'(0,0,g)h00$ space group. Here below you can check the list obtained directly from the mcif generated by ISODISTORT.


```

P62'2'(0,0,g)h00          <-- Magnetic SuperSpace group symbol
genr x1,x2,x3,x4,+1
genr x1-x2,x1,x3,x4+1/6,+1
genr -x2,x1-x2,x3,x4+1/3,+1
genr -x1,-x2,x3,x4+1/2,+1
genr -x1+x2,-x1,x3,x4+2/3,+1
genr x2,-x1+x2,x3,x4+5/6,+1
genr x1-x2,-x2,-x3,-x4+1/3,-1
genr x1,x1-x2,-x3,-x4+1/2,-1
genr x2,x1,-x3,-x4+2/3,-1
genr -x1+x2,x2,-x3,-x4+5/6,-1
genr -x1,-x1+x2,-x3,-x4,-1
genr -x2,-x1,-x3,-x4+1/6,-1

```

- j. In the atoms block we add some initial values for the homogeneous magnetic moment, $2 \mu_B$ for the Dy atom and $1.5 \mu_B$ for the Mn. Some initial values have to be included in the modulated amplitudes. It deserves to be noted that we expect much larger magnetic moments on the Dy atoms than on the Mn atoms, so the initial values are larger for Dy than Mn. Due to the least squares refinement, sometimes the refinement is anchored in a local minima, if you think that your refinement converges to a false minimum you can modify the initial values, including changing the signs of some components.

```

DyMn6Ge6 magnetic VARY   mxmymz McosMsin
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ      Nvk Npr More
   5   0   0 0.0 0.0 1.0   7   0   2   0   0      133584.188    1   7   0
.
.
!Atom  Typ  Max_Qcoeff   X       Y       Z       Biso      Occ  N_type Spc / Line below:Code
!      Mcosx      Mcosy      Mcosz      Msinx      Msiny      Msinz      / Line below:Codes
!      beta11      beta22      beta33      beta12      beta13      beta23      / Line below:Codes
Dy      JDY3      1              0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  1.00000  1   0
      MagM0-Moment:    0.00000  0.00000  2.00000  <- Homogeneous magnetic moment
                      0.00000  0.00000  1.00000
      Mcos-Msin-1:    4.000000  4.000000  0.00000  0.00000  4.00000  0.00000  <-
                      1.00000  1.00000  0.00000  0.00000  1.00000  0.00000
Mn1      MMN2      1              0.00000  0.50000  0.25030  0.00000  0.00000  6.00000  1   0
                      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
      MagM0-Moment:    0.00000  0.00000  1.50000  <- Homogeneous magnetic moment
                      0.00000  0.00000  1.00000
      Mcos-Msin-1:    1.50000  1.50000  0.00000  1.50000  1.50000  0.00000  <-
                      1.00000  1.00000  0.00000  1.00000  1.00000  0.00000
Ge1      GE        0              0.66667  0.33333  0.50000  0.00000  0.00000  2.00000  0   0
                      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
Ge2      GE        0              0.66667  0.33333  0.00000  0.00000  0.00000  2.00000  0   0
                      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
Ge3      GE        0              0.00000  0.00000  0.34450  0.00000  0.00000  2.00000  0   0
                      0.00000  0.00000  0.00000  0.00000  0.00000  0.00000

```

- k. After including all this modifications into the PCR file, you can run FullProf and check the quality of the refinement. Check also the output files, there is plenty of interesting information that can help you to understand the results!!

