

Example DyMn₆Ge₆ (magndata #1.1.10)

**Incommensurate magnetic structure – modulation (propagation) vectors:
(0, 0, 0.1651) and (0,0,0)**

Neutron powder data measured at 11K on DMC at PSI (Switzerland)

$\lambda = 1.7037 \text{ \AA}$

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.cif (nuclear structure)

1. Creating new jobname

Start Jana2006

“**File → Structure → New**” opens a file manager

Left panel: locate directory with input files

Right panel: double-click at dymn6ge6

2. Import Wizard

Select “**Magnetic parent structure: nuclear model from CIF**”; NEXT

[On the screen: Select input CIF file]

Right panel: select the input file dymn6ge6.cif; OK

3. Define magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors]

Check “**Use non-zero magnetic propagation vector**” and fill its value: **(0, 0, 0.1651)**

For “Atom type” select “Dy”; check “Use as a magnetic atom”

For “Magnetic formfactor <j0>” select Dy3+;

The same for Mn3+; NEXT; FINISH

4. Import the reflection file

[On the screen: Specify type of the file to be imported]

Select “Various CW format”; NEXT

Check that the name of the input file is “dymn6Ge6.dat” and the format is “PSI format”; “Debye-Scherrer Method”, NEXT

[On the screen: Complete/correct experimental parameters];

For “Wave length” type 1.7037 ; NEXT; FINISH

[On the screen: Data repository]

Optionally write the data temperature (?)

OK; YES to “Do you want to accept made changes?”;

5. Refining of profile parameters by le Bail technique.

[On the screen: Information]

NEXT;

[On the screen: Refinement of the powder profile by the le Bail algorithm]

“Show powder profile”

The background is relatively smooth and it can be described without introducing manual background.

“Quit”;

“Edit profile parameters”;

[On the screen: Powder options]

In page “Cell” activate refinement of a, b and c parameters;

In the page “Profile” change the starting value of GW to 50 and activate its refinement;

In the page “Corrections” activate refinement of “shift” parameter and change the number of used Legendre polynomials to 10

OK; YES to rewrite the changes

“Edit refinement command”; In the page “Basic” change the number of cycles to 20

OK; **“Run Refine”;**

The refinement should end with $R_p \sim 4.95\%$.

“Edit profile parameters”;

[On the screen: Powder options]

In the page “Profile” activate refinement of GU and GV; Change the peak-shape function to pseudo-Voigt and activate refinement of LX; OK; YES to the question about rewriting;

“Run Refine”

The refinement should converge to $R_p \sim 2.98\%$.

“Show powder profile”; Select the region 2θ from 30 to 45 degs – use the button “X exactly”.
A couple of peaks are observed that may correspond to some impurity. Also at about $2\theta = 5$, an anomaly in the background is observed. No peaks are possible there.

“Quit”

“Edit profile parameters”;

[On the screen: Powder options]

In page “corrections”, activate **“Define excluded regions”** : from 0 to 7; “Add”, “OK”, “OK”;

“Run Refine”;

The refinement should end with $R_p \sim 2.90\%$.

NEXT; YES to leave the form for le Bail refinement

6. Refinement of the scale parameter for the nuclear structure

[On the screen: Refinement of the nuclear structure by the Rietveld method]

“Edit refinement commands”; On the page **“Various”** select **“Fixed commands”**;

Fix all parameters for all atoms (“*” for “Atoms/Parameters” textbox); “Add”; OK; OK;

*The command will appear in the panel as **“fixed all *”***

“Run Refine”

The refinement should converge to $R_p \sim 11.6\%$, $R(\text{obs}) \sim 7.5\%$.

NEXT; YES to leave the form for Rietvel refinement

7. Testing different irreps to get the best single irrep model

[On the screen: Information]

NEXT

[On the screen: Representation analysis]

This window has an information character. You can see here all irreps leading to Magnetic ordering. The “details” buttons provide more information about an individual irrep and its connection to the kernel magnetic symmetry.

NEXT

[On the screen: List of kernels and epikernels]

NEXT

[On the screen: Select Shubnikov superspace group]

***Select the first group** in the list, one can see that this group forces zero magnetic moments and therefore is not possible*

***Select the second group** in the list, the spin modulations are forced to be along z. With the Option “details” one gets information about the group and the resulting constraints on the spin modulation parameters.*

*Use the option “**start profile simulation**” to observe that the four first groups in the list Would not explain some of the magnetic peaks.*

***Select the group P622.1'(00g)t00s**, one of the possible epikernels of irrep mDT5. With the Simulation of the profile, observe that the first magnetic peak remains unexplained.*

***Select the group P622.1'(00g)-h00s**, one of the possible epikernels of irrep mDT6, and Observe that it can explain the first magnetic peak*

8. Refinement in the superspace group – P622.1'(00g)-h00s

[On the screen: Select Shubnikov space group]

Select the first line in the left panel; **FINISH**

YES to the question “Do you want to continue with the last kernel/epikernel”;

[On screen: Select structure name]

Use the default name i.e. dymn6ge6_01 or any other; **OK**

Right click on the icon “Refine”; Select the page “Basic” and change the “Number of cycles” to 100 and the “Damping factor” to 0.1;

Select the page “**Various**”. Use the button “**Restrictions**”. All atoms are restricted to have identical ADP parameters;

Use button “**Fixed commands**” and fix all coordinates and delete or disable fixing of ADP’s (if present).

OK; OK; “Yes+start”;

*The refinement should end with $R_p \sim 4.7\%$ and Bragg R factors $R(\text{obs}) = 4.9\%$, 4.5% and 5.7% for all, main and satellite reflections, respectively. (“**View of Refine**”)*

Use “**Tools → Powder → Profile**” viewer and check fit of the calculated powder profile :

Observe that some main reflections like (1 0 1 0) around 25 degrees or (2 -1 1 0) at about 40 degrees are poorly fit.

Select the page “Various”. Use the button “**fixed commands**” and **disable the command: “fixed xyz”**. **Run refine** again. Now the atom coordinates will also be refined.

The refinement should end with $R_p \sim 4.7\%$ and Bragg R factors $R(\text{obs}) = 4.8\%$, 4.4% and 5.6% for all, main and satellite reflections, respectively. (“View of Refine”). The improvement is minimal. Some of the main reflections remain poor fit. , systematically with too low Intensity.

9. Refinement in the superspace group – $P62'2'(00g)$ -h00

We try then the possibility that magnetic scattering occurs also at main reflections, i.e. an additional magnetic ordering with $k=(0\ 0\ 0)$ is taking place. In the language of the symmetry group of the phase this implies to lower it, dropping the operation $\{1' | 0001/2\}$ associated with the existence of a single primary incommensurate wave vector.

There are several maximal subgroups without this operation. They can be enumerated, Reducing the list of operations in the list provided by clicking in “EditM50” -> Symmetry.

The generators of the working group until now are:

$$\{6+ | 0\ 0\ 0\ 5/6\}: x_1-x_2, x_1, x_3, x_4+5/6$$

$$\{2_{xy} | 0\ 0\ 0\ 0\}: x_2, x_1, -x_3, -x_4$$

$$\{1' | 0001/2\}: x_1, x_2, x_3, x_4+1/2$$

The possible maximal subgroups will then be generated by:

$P622(00g)$ -h00 (R=4.73, 4.37, 5.39)

$$\{6+ | 0\ 0\ 0\ 5/6\}: x_1-x_2, x_1, x_3, x_4+5/6\ m$$

$$\{2_{xy} | 0\ 0\ 0\ 0\}: x_2, x_1, -x_3, -x_4\ m$$

$P6'22'(00g)t00$ (R=4.83, 4.41, 5.59)

$$\{6+' | 0\ 0\ 0\ 1/3\}: x_1-x_2, x_1, x_3, x_4+1/3\ -m$$

$$\{2_{xy} | 0\ 0\ 0\ 0\}: x_2, x_1, -x_3, -x_4\ m$$

P62'2'(00g)-h00 (R=3.07, 2.44, 4.25)

{6+|0 0 0 5/6}: x1-x2, x1, x3, x4+5/6 m

{2'_xy| 0 0 0 1/2}: x2, x1, -x3, -x4+1/2 -m

P6'2'2(00g)t00 (R=4.83, 4.41, 5.59)

{6+'|0 0 0 1/3}: x1-x2, x1, x3, x4+1/3 -m

{2'_xy| 0 0 0 1/2}: x2, x1, -x3, -x4+1/2 -m

To refine under these four different symmetries, reduce the list of operations to those listed above in M50, and “complete the set”. Then go to “Edit atoms” and set an initial value of 0.1 for Mox, Moy, Moz of Dy and Mn. Check that with “apply site symmetry”, the values of Mox and Moy become again zero, as they are not symmetry allowed.

Run “Refine”; *The refinement should end with the values indicated in parenthesis. One of the symmetries clearly fits better the data. Observe that the strong misfit of some of the the main reflections has disappeared.*

*The final common Uiso is negative. Change the form factor of Dy in M50 <jo>+c<j2>
Make Uiso zero and fixed, and refine again for the best model:*

R=2.91, 2.43, 3.76 Rp=3.54

10. Visualize the refined model with MVISUALIZE (Jmol)

File -> CIF utilities -> make CIF file

Save the file. It is in magCIF format and includes the list of reflections. With an editor delete this last part of the file, and produce a file with extension .mcif

Upload the file in MVISUALIZE.

Comparison with FP result transformed to the same parameterization (MAGNDATA 1.1.10):

Dy 0,0,mz 0.0 0.0 3.932
Mn 0,0,mz 0.0 0.0 -1.149

Dy Mcos1: (6.195546 0.0 0.0) Msin1: (3.577 7.154 0.0)
Mn Mcos1: (-1.877 -0.206 0.0) Msin1: (-0.846 -2.049 0.0)

FullProf

Dy 0,0,mz 0.0 0.0 3.885(95)
Mn 0,0,mz 0.0 0.0 -0.937(73)

JANA

Dy Mcos1: (6.00(8) 6.00 0.0) Msin1: (3.47 -3.47 0.0)
Mn Mcos1: (-1.2(1) -1.63(8) 0.0) Msin1: (-0.2(1) -1.65(9) 0.0)

chiral domain 1

Dy Mcos1: (6.00(8) 0 0) Msin1: (3.47(5) 6.93 0.0)
Mn Mcos1: (-1.5(1) -0.62(9) 0.0) Msin1: (-1.30(9) -2.23(9) 0.0)

chiral domain 2

11. Change the refinement to the domain equivalent description

Domain 2 equivalent description is the one used in the published FullProf refinement, this domain is chiral related with the one we have used, and to refine in this description, one only has to change the MSSG to the chiral related one:

P62'2'(00g)-h00 change to \rightarrow P62'2'(00g)h00

This is done by editing M50 file changing the symmetry operations choosing as generators, i.e. changing the 5/6 phase translation of the six-fold operation by 1/6:

$\{6+|0\ 0\ 0\ 1/6\}$: $x_1-x_2, x_1, x_3, x_4+1/6\ m$

$\{2'_{xy}|0\ 0\ 0\ 5/6\}$: $x_2, x_1, -x_3, -x_4+5/6\ -m$

The phase shift of $2'_{xy}$ can be changed and has been chosen so that the origin along x_4 coincides with the one chosen in MAGNDATA for the description of this structure.

12. Use option of polar coordinates for the moments to constraint further the Mn spin to have a circular modulation.

Structure -> save as

Save the refinement as a new case so that the further refinement with polar coordinates produces a different set of files

Parameters -> Magnetic moments in polar coordinates

Activate polar coordinates for Dy1 and Mn1, OK

YES to rewrite

click in Edit atoms icons, click in Dy1, Edit menu. The windows for the magnetic moment parameters have changed to polar coordinates, but the control of the parameters to be refined has not been changed automatically, and must be done manually: for the Mo parameters of Dy1, fix the two polar angles, and leave to refine the modulus (the first one). For the modulation parameters, modify the refinement controls if necessary. Only Mrsin1 parameters should be free, the rest are forced by symmetry. Introduce the symmetry constraint: $Mrcos1 = Mrsin1$ by hand, using Refine -> Various -> equations.

For Mn1, the modulation parameters except the theta angle are symmetry free. In order to force a circular modulation, the constraints must be introduced in Refine -> Various -> equations: $Mrcos1 = Mrsin1$, $Mpcos1 = Mpsin1 - 90$. These equations are only roughly satisfied by the previous refined model, as shown after the transformation.

The refinement converges to about (R=2.93, 2.39, 3.90) Rp=3.60 . The full free refinement (R=2.91, 2.43, 3.76 Rp=3.54) is not much be better!

Dy 0,0,mz 0.0 0.0 3.975

Mn 0,0,mz 0.0 0.0 -1.061

Dy Mcos1: (6.106 0 0) Msin1: (3.525 7.051 0.0)

Mn Mcos1: (-1.777 -0.196 0.0) Msin1: (-0.801 -1.939 0.0)

Dy 0,0,mz 0.0 0.0 3.932

Mn 0,0,mz 0.0 0.0 -1.149

FullProf

Dy Mcos1: (6.195546 0.0 0.0) Msin1: (3.577 7.154 0.0)

Mn Mcos1: (-1.877 -0.206 0.0) Msin1: (-0.846 -2.049 0.0)