# Example 12.7: $DyMn_6Ge_6$

## Incommensurate magnetic structure – k=(0,0,0.1651); k=(0,0,0)

Revised: 18 October 2019

### $DyMn_6Ge_6$

Neutron powder data measured at 11K on DMC at PSI (Switzerland)
Available at the Bilbao crystallographic server, database magndata, #1.1.10

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)

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate directory with input files
   Right pane: double-click dymn6ge6

2. ***Import Wizard***
   Select "Magnetic parent structure: nuclear model from CIF"; NEXT
   Right pane: select the input file dymn6ge6_nuclear.cif; OK

3. ***Define magnetic propagation vector and form factors***
   *[On the screen: Define magnetic propagation vector and form factors]*
   Choose the "Number of non-zero magnetic propagation vectors" to '1' and fill its value: 0 0 0.1651
   Select atom type Dy; check "Use as a magnetic atom"; select "Magnetic formfactor <j0>" Dy3+;
   Select atom type Mn; check "Use as a magnetic atom"; select "Magnetic formfactor <j0>" Mn3+;
   NEXT; FINISH
   *The parent structure is created*

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";
   Select "Debye-Scherrer method"
   NEXT
   *[On the screen: Complete/correct experimental parameters];*
   Fill used wavelength 1.7037; Temperature 11; NEXT; FINISH
   *[On the screen: Data repository]*
   OK; YES to "Do you want to accept made changes?"

5. ***Refining of profile parameters by the 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 and c parameters and the third component of the modulation vector – q3;
   In the page "Profile" keep 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 save the changes
   "Edit refinement commands"; In the page "Basic" change the number of cycles to 20; OK
   "Run Refine";
   *The refinement should converge to Rp~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 LX
   OK; YES to save the changes
   "Run Refine"
   *The refinement should converge to Rp~2.98%.*
   "Show powder profile"
   *Select the region 2ϑ from 30 to 45 degs – use the button "X exactly". A couple of observed peaks may correspond to some impurity. Also at about 2ϑ= 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", press button "Define excluded regions" : from 0 to 7; "Add", "OK","OK";
   "Run Refine";
   *The refinement should end with Rp~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";
   *In the case that the fixed command of form is "fixed all *" is already in the panel, do nothing. If not:*
   Fix all parameters for all atoms ("*" for "Atoms/Parameters" textbox); "Add"; OK; OK
   "Run Refine"

*The refinement should converge to Rp=11.6%, R(obs)=7.5%*

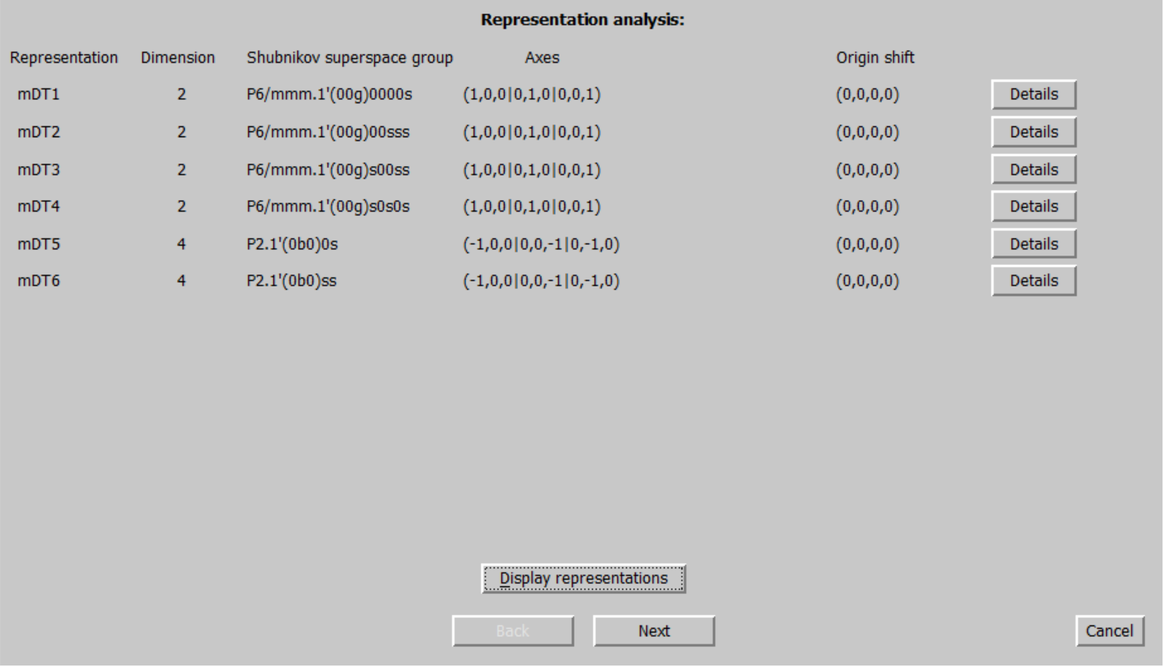
NEXT; YES to leave the for for Rietveld refinement

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

*[On the screen: Information]*

NEXT

*[On the screen: Representation analysis]*



**Representation analysis:**

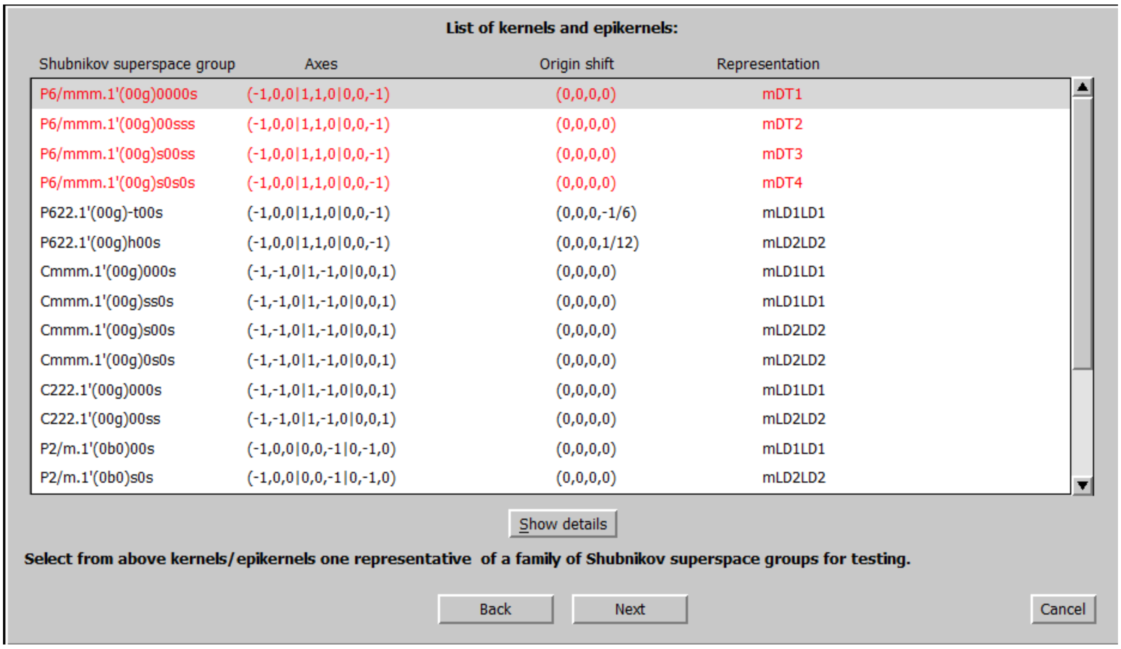
| Representation | Dimension | Shubnikov superspace group | Axes | Origin shift |
|---|---|---|---|---|
| mDT1 | 2 | P6/mmm.1'(00g)0000s | (1,0,0\|0,1,0\|0,0,1) | (0,0,0,0) |
| mDT2 | 2 | P6/mmm.1'(00g)00sss | (1,0,0\|0,1,0\|0,0,1) | (0,0,0,0) |
| mDT3 | 2 | P6/mmm.1'(00g)s00ss | (1,0,0\|0,1,0\|0,0,1) | (0,0,0,0) |
| mDT4 | 2 | P6/mmm.1'(00g)s0s0s | (1,0,0\|0,1,0\|0,0,1) | (0,0,0,0) |
| mDT5 | 4 | P2.1'(0b0)0s | (-1,0,0\|0,0,-1\|0,-1,0) | (0,0,0,0) |
| mDT6 | 4 | P2.1'(0b0)ss | (-1,0,0\|0,0,-1\|0,-1,0) | (0,0,0,0) |

Details
Details
Details
Details
Details
Details
Display representations
Back
Next
Cancel

*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 screen: List of kernels and epikernels]*



**List of kernels and epikernels:**

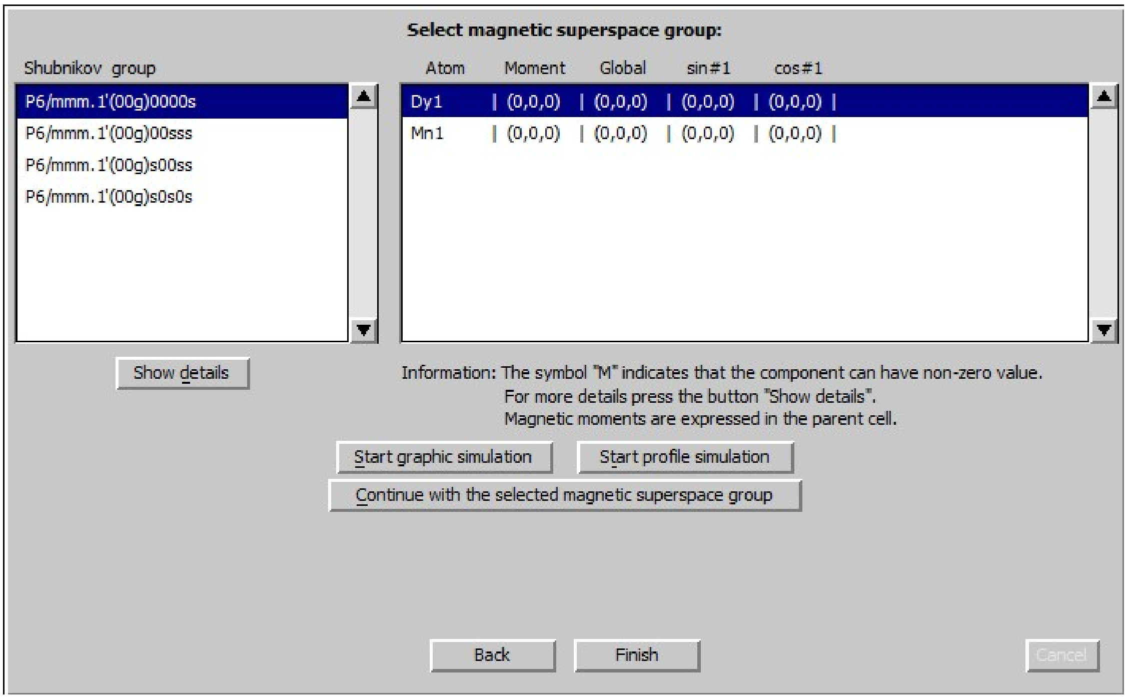
| Shubnikov superspace group | Axes | Origin shift | Representation |
|---|---|---|---|
| P6/mmm.1'(00g)0000s | (-1,0,0\|1,1,0\|0,0,-1) | (0,0,0,0) | mDT1 |
| P6/mmm.1'(00g)00sss | (-1,0,0\|1,1,0\|0,0,-1) | (0,0,0,0) | mDT2 |
| P6/mmm.1'(00g)s00ss | (-1,0,0\|1,1,0\|0,0,-1) | (0,0,0,0) | mDT3 |
| P6/mmm.1'(00g)s0s0s | (-1,0,0\|1,1,0\|0,0,-1) | (0,0,0,0) | mDT4 |
| P622.1'(00g)-t00s | (-1,0,0\|1,1,0\|0,0,-1) | (0,0,0,-1/6) | mLD1LD1 |
| P622.1'(00g)h00s | (-1,0,0\|1,1,0\|0,0,-1) | (0,0,0,1/12) | mLD2LD2 |
| Cmmm.1'(00g)000s | (-1,-1,0\|1,-1,0\|0,0,1) | (0,0,0,0) | mLD1LD1 |
| Cmmm.1'(00g)ss0s | (-1,-1,0\|1,-1,0\|0,0,1) | (0,0,0,0) | mLD1LD1 |
| Cmmm.1'(00g)s00s | (-1,-1,0\|1,-1,0\|0,0,1) | (0,0,0,0) | mLD2LD2 |
| Cmmm.1'(00g)0s0s | (-1,-1,0\|1,-1,0\|0,0,1) | (0,0,0,0) | mLD2LD2 |
| C222.1'(00g)000s | (-1,-1,0\|1,-1,0\|0,0,1) | (0,0,0,0) | mLD1LD1 |
| C222.1'(00g)00ss | (-1,-1,0\|1,-1,0\|0,0,1) | (0,0,0,0) | mLD2LD2 |
| P2/m.1'(0b0)00s | (-1,0,0\|0,0,-1\|0,-1,0) | (0,0,0,0) | mLD1LD1 |
| P2/m.1'(0b0)s0s | (-1,0,0\|0,0,-1\|0,-1,0) | (0,0,0,0) | mLD2LD2 |

**Select from above kernels/epikernels one representative of a family of Shubnikov superspace groups for testing.**

Select one of the hexagonal magnetic superspace groups based on average space group *P6/mmm*; NEXT;

*This will pass all present hexagonal magnetic superspace groups of type P6/mmm to further testing. We assume that both magnetic atoms should have non-zero magnetic moment.*

*[On the screen: Select magnetic space group]*



**Select magnetic superspace group:**

Shubnikov group

P6/mmm.1'(00g)0000s
P6/mmm.1'(00g)00sss
P6/mmm.1'(00g)s00ss
P6/mmm.1'(00g)s0s0s

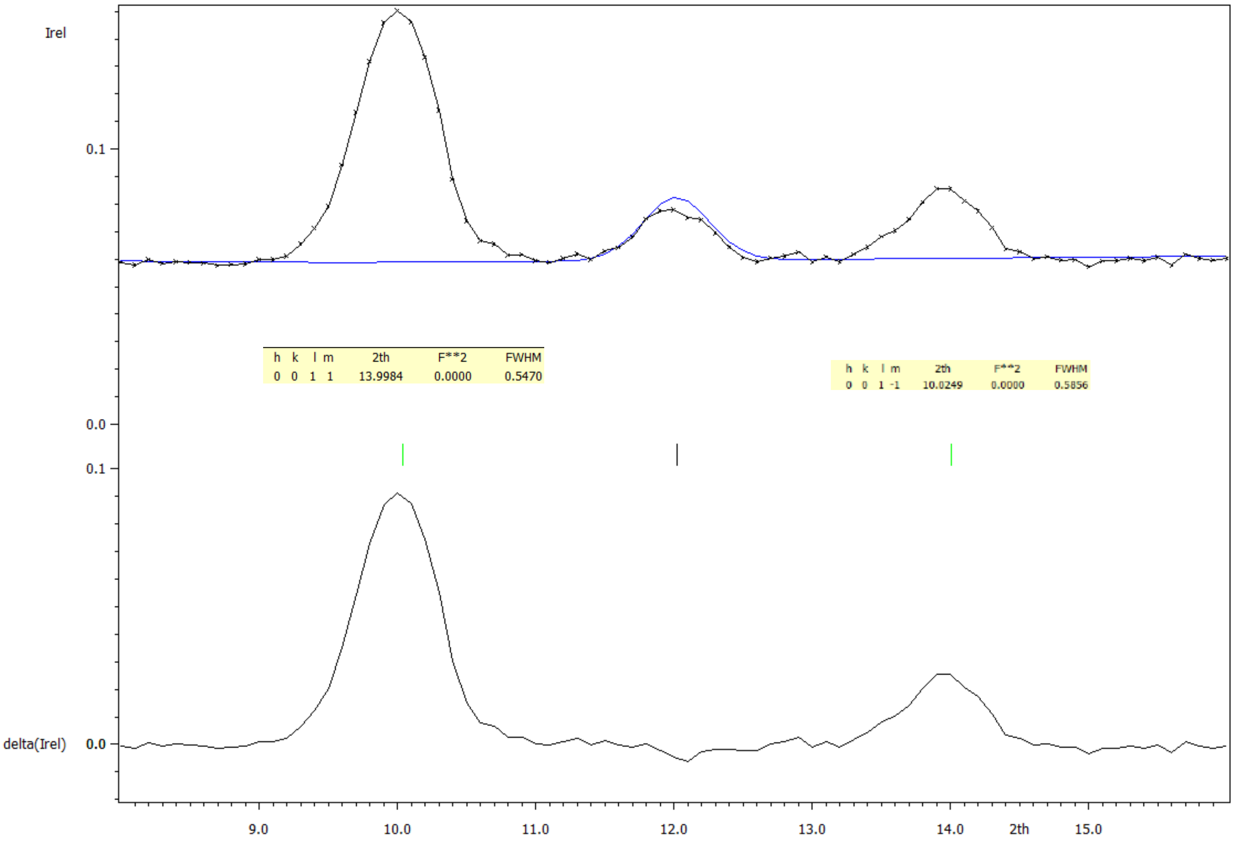
| Atom | Moment | Global | sin#1 | cos#1 |
|---|---|---|---|---|
| Dy1 | (0,0,0) | (0,0,0) | (0,0,0) | (0,0,0) |
| Mn1 | (0,0,0) | (0,0,0) | (0,0,0) | (0,0,0) |

Information: The symbol "M" indicates that the component can have non-zero value.
For more details press the button "Show details".
Magnetic moments are expressed in the parent cell.

*Only the second magnetic superspace group allows for non-zero magnetic moments for Mn and Dy atoms.*

Select the second magnetic superspace group: P6/mmm.1’(00g)00sss and press “Start

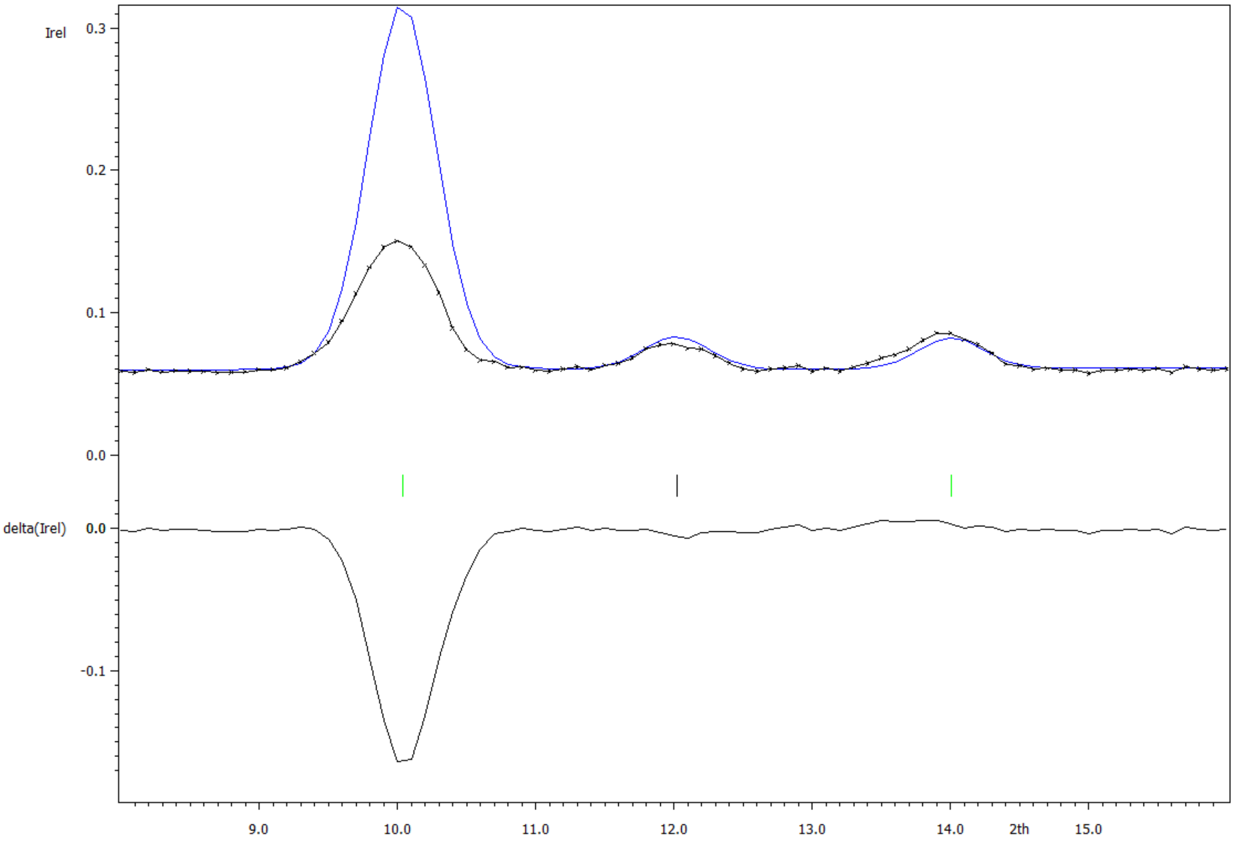
profile simulation”;
Press "X exactly" and focus the region 8-16 degrees; Press “Fit Y”:

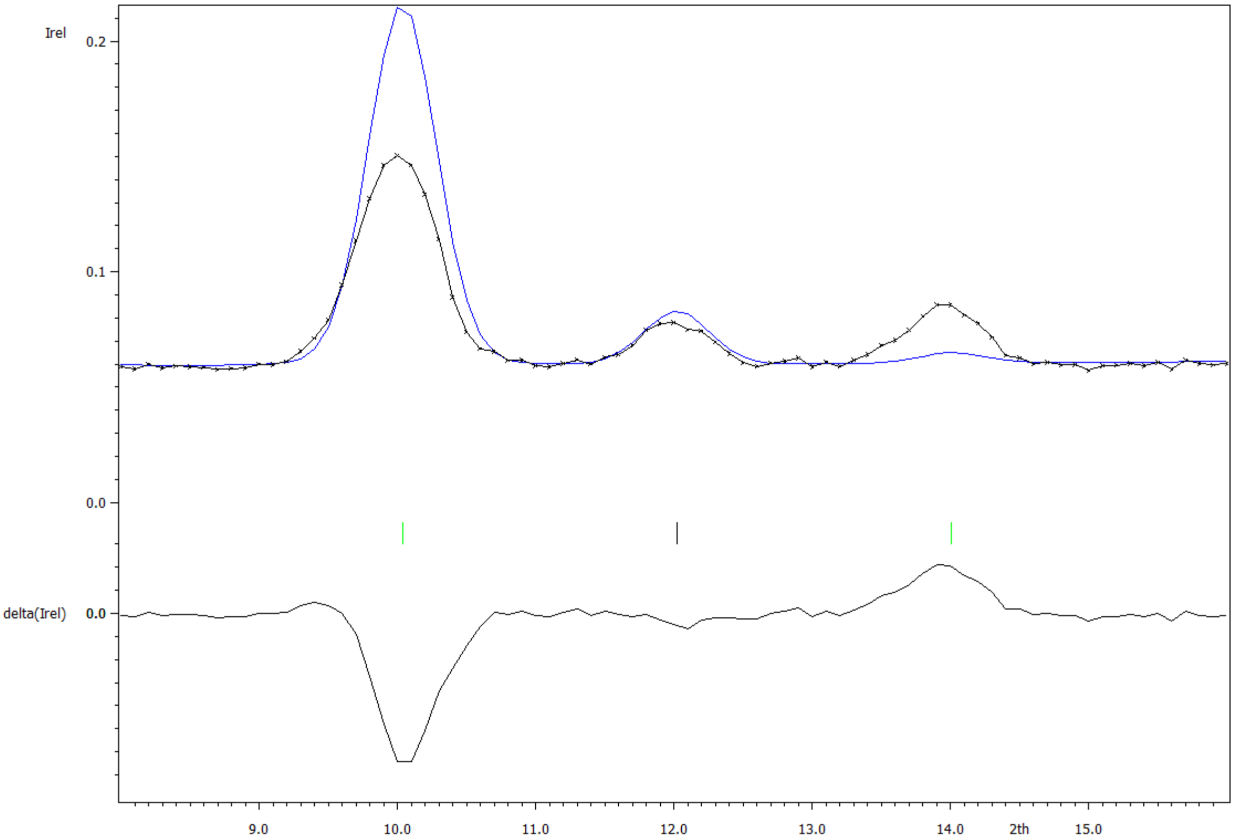


| h | k | l | m | 2th | F**2 | FWHM |
|---|---|---|---|---|---|---|
| 0 | 0 | 1 | 1 | 13.9984 | 0.0000 | 0.5470 |

| h | k | l | m | 2th | F**2 | FWHM |
|---|---|---|---|---|---|---|
| 0 | 0 | 1 | -1 | 10.0249 | 0.0000 | 0.5856 |

*Two dominant magnetic peaks in this region have zero intensity. This means that the tested model does not describe the magnetic ordering correctly. However, in making such conclusion we have to take into account that the simulation procedure uses randomly generated magnetic moments and that the result can be affected by an actual random choice. This is why we recommend repeating the simulation when some doubt exists.*
“Quit”; “Back” and return to the “List of kernels and epikernels” and select one of hexagonal superspace groups based on P622.
*While the first one P622.1’(00g)t00s restricts the magnetic moments of the Dy atom to zero, the second one P622.1’(00g)-h00s allows non-zero magnetic moments for both magnetic atoms. The simulation profiles demonstrate that the intensity of both magnetic peaks in the interval (8-16) degs are generally non-zero:*


Irel
0.3
0.2
0.1
0.0
delta(Irel)
0.0
-0.1
9.0
10.0
11.0
12.0
13.0
14.0
2th
15.0


Irel
0.2
0.1
0.0
delta(Irel)
0.0
9.0
10.0
11.0
12.0
13.0
14.0
2th
15.0

8. ***Refinement of the magnetic structure in – P622.1'(00g)-h00s***

   *[On the screen: Select magnetic superspace group]*
   Select the magnetic superspace group P622.1'(00g)-h00s
   Press 'Continue with the selected magnetic superspace group'
   *[On the screen: Select structure name]*
   Use the default name i.e. dymn6ge6_01 or any other; **OK**
   *[On the screen: Basic window of Jana2006]*
   Right-click the icon of Refine and select the page "Various"
   Use the button "Restrictions" and ensure that all atoms (i.e. *) are restricted to have identical ADP parameters.
   *The restriction "restric * 13" has been set automatically when the program created the testing structure. To see the meaning of the restriction focus it by mouse and press "Load". "Load" opens the restriction for editing. Make sure that "Coordinates" and "Modulations" boxes are cleared and press "Rewrite" to close the editing mode.*
   OK
   Select the page "Fixed commands" and (similarly like in the previous step) ensure that all atomic positions are fixed in their current values ("fixed xyz *").
   OK
   Select the page "Basic" and check if the "Number of cycles" is set to 100 and the "Damping factor" to 0.1; OK; Yes+start;
   *Refinement converges with Rp~5.0%, R(obs)~ 5.0%, 4.6%, 5.7% for all, nuclear and magnetic reflections, respectively.*
   Use "Profile viewer" and check the 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. In order to exclude some additional nuclear effects we can allow the refinement of atomic positions:*
   Right-click the icon of Refine and 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 Rp~5.0% and Bragg R factors R(obs)=4.9%, 4.5% and 5.7% for all, main and satellite reflections, respectively. ("View of Refine"). The improvement is minimal. Some of the main reflections remain poorly fit systematically with too low intensity. This fact can lead to the conclusion that an additional magnetic ordering with k=0 is present.*
9. ***Refinement in the subgroups allowing magnetic wave (0,0,0)***

   *[On the screen: Basic Jana window]*
   *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. Then can be generated by the Jana tool "Tools→Transformations→Go to subgroup structure". As generators for the working group until now can be used:*
   *{6+|0 0 0 5/6}:  x1-x2, x1, x3, x4+5/6*
   *{2_xy| 0 0 0 0}:  x2, x1, -x3, -x4*

*{1’|0001/2} :  x1, x2, x3 , x4+1/2*
*The possible maximal subgroups will then be generated by:*

***P622(00g)-h00***
*{6+|0 0 0 5/6}:  x1-x2, x1, x3, x4+5/6, m*
*{2_xy| 0 0 0 0}:  x2, x1, -x3, -x4, m*

***P6’22’(00g)t00***
*{6+’|0 0 0 1/3}:  x1-x2, x1, x3, x4+1/3, -m*
*{2_xy| 0 0 0 0}:  x2, x1, -x3, -x4, m*

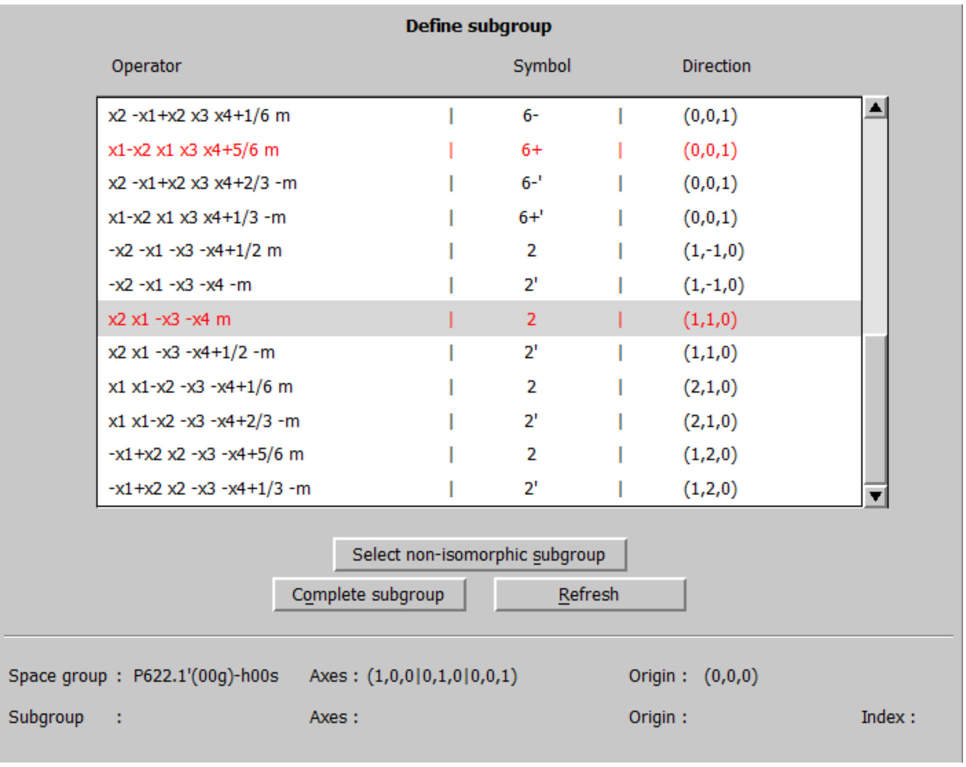
***P62’2’(00g)-h00***
*{6+|0 0 0 5/6}:  x1-x2, x1, x3, x4+5/6, m*
*{2’_xy| 0 0 0 1/2}:  x2, x1, -x3, -x4+1/2, -m*

***P6’2’2(00g)t00***
*{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*

*Make sure that your actual structure is the final refined structure from the previous step.*

“Tools → Transformation → Go to subgroup structure”;
Press the “Refresh” button and select the generators:

x1-x2  x1  x3 x4+5/6 m
x2 x1 -x3 -x4 m

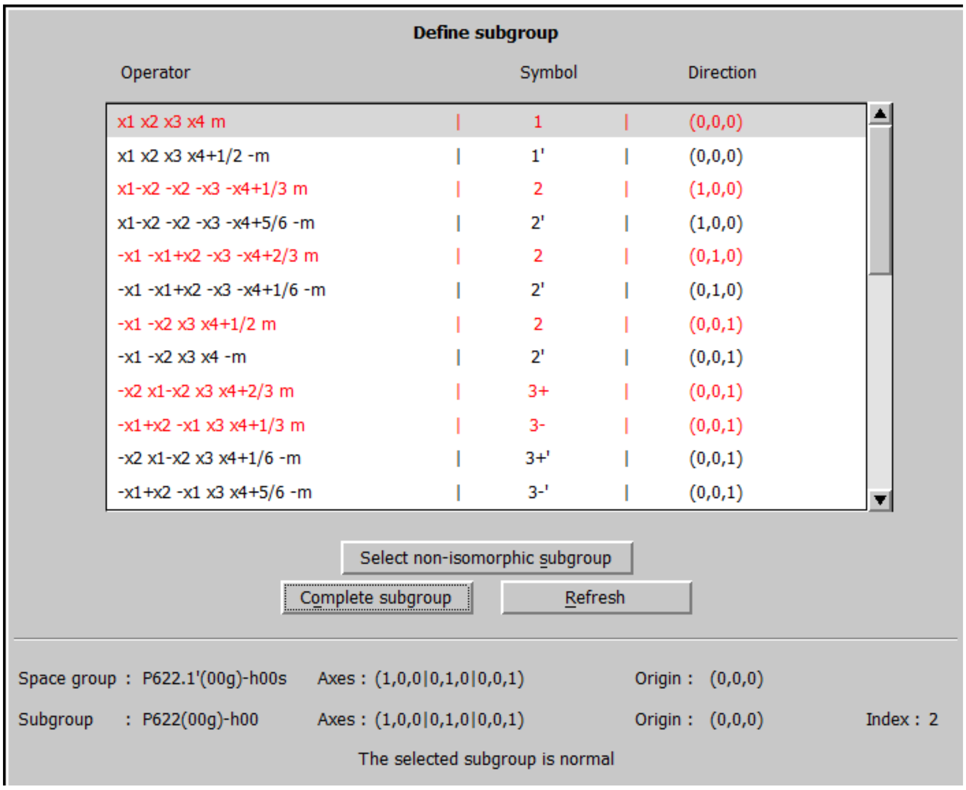


**Define subgroup**

| Operator | Symbol | Direction |
|---|---|---|
| x2 -x1+x2 x3 x4+1/6 m | 6- | (0,0,1) |
| x1-x2 x1 x3 x4+5/6 m | 6+ | (0,0,1) |
| x2 -x1+x2 x3 x4+2/3 -m | 6-' | (0,0,1) |
| x1-x2 x1 x3 x4+1/3 -m | 6+' | (0,0,1) |
| -x2 -x1 -x3 -x4+1/2 m | 2 | (1,-1,0) |
| -x2 -x1 -x3 -x4 -m | 2' | (1,-1,0) |
| x2 x1 -x3 -x4 m | 2 | (1,1,0) |
| x2 x1 -x3 -x4+1/2 -m | 2' | (1,1,0) |
| x1 x1-x2 -x3 -x4+1/6 m | 2 | (2,1,0) |
| x1 x1-x2 -x3 -x4+2/3 -m | 2' | (2,1,0) |
| -x1+x2 x2 -x3 -x4+5/6 m | 2 | (1,2,0) |
| -x1+x2 x2 -x3 -x4+1/3 -m | 2' | (1,2,0) |

Space group : P622.1'(00g)-h00s  Axes : (1,0,0|0,1,0|0,0,1)  Origin : (0,0,0)
Subgroup :  Axes :  Origin :  Index :

Press the button “Complete subgroup”;



**Define subgroup**

| Operator | Symbol | Direction |
|---|---|---|
| x1 x2 x3 x4 m | 1 | (0,0,0) |
| x1 x2 x3 x4+1/2 -m | 1' | (0,0,0) |
| x1-x2 -x2 -x3 -x4+1/3 m | 2 | (1,0,0) |
| x1-x2 -x2 -x3 -x4+5/6 -m | 2' | (1,0,0) |
| -x1 -x1+x2 -x3 -x4+2/3 m | 2 | (0,1,0) |
| -x1 -x1+x2 -x3 -x4+1/6 -m | 2' | (0,1,0) |
| -x1 -x2 x3 x4+1/2 m | 2 | (0,0,1) |
| -x1 -x2 x3 x4 -m | 2' | (0,0,1) |
| -x2 x1-x2 x3 x4+2/3 m | 3+ | (0,0,1) |
| -x1+x2 -x1 x3 x4+1/3 m | 3- | (0,0,1) |
| -x2 x1-x2 x3 x4+1/6 -m | 3+' | (0,0,1) |
| -x1+x2 -x1 x3 x4+5/6 -m | 3-' | (0,0,1) |

Space group : P622.1'(00g)-h00s Axes : (1,0,0|0,1,0|0,0,1) Origin : (0,0,0)

Subgroup : P622(00g)-h00 Axes : (1,0,0|0,1,0|0,0,1) Origin : (0,0,0) Index : 2

The selected subgroup is normal

NEXT; NEXT
*[On the screen: Select one representative of the 2$^{nd}$ coset]*
Select the first operation.
*Generally, all selections would give the same result.*
NEXT;
*[On the screen: Specify the output structure]*
Select “dymn6ge6_01_subgroup_1” or any other
NEXT;FINISH;”Yes” to the question “Do you want to continue with the new structure?”
*[On the screen: Basic window]*
Run “Edit Atoms”; Select atoms Dy1 and Mn1; Press the button “Action”
Select “Reset modulation/magnetic parameters”
Deselect “Magnetic parameters k<>0”
Choose “Reset parameters randomly in the interval (-pmax,pmax)
OK;OK;”Yes” to the question “Do you want to rewrite changed files?”
Run “Refine”;
Repeat the procedure for all subgroups listed above
Use the “File→ Structure → History” to return to the final refined structure in P622.1'(00g)-h00s.

*P622(00g)-h00*

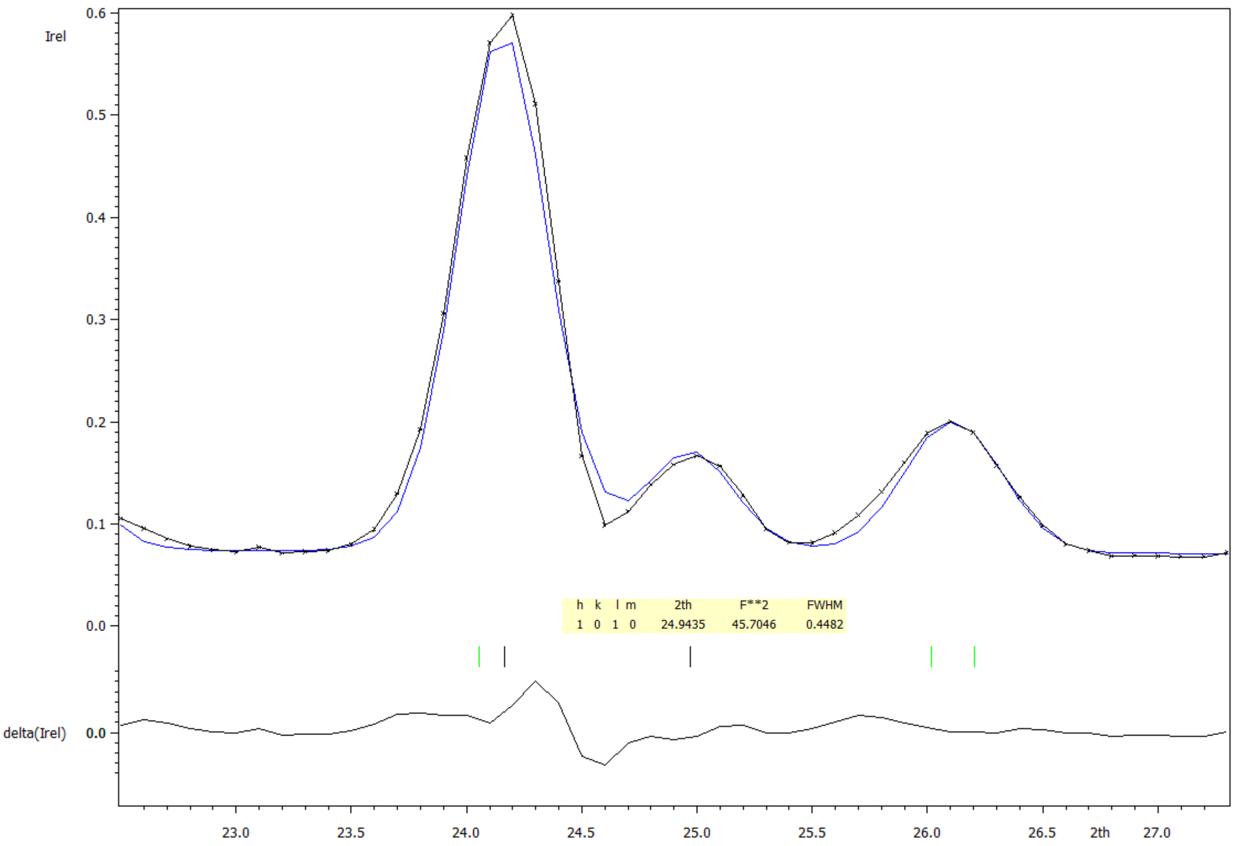
*Rp=4.8%, R(obs)=4.6%,4.2%,5.4% for all, nuclear and magnetic reflections, respectively.*

*P6’22’(00g)t00*
*Rp=4.8%, R(obs)=4.5%,4.0%,5.5% for all, nuclear and magnetic reflections, respectively.*

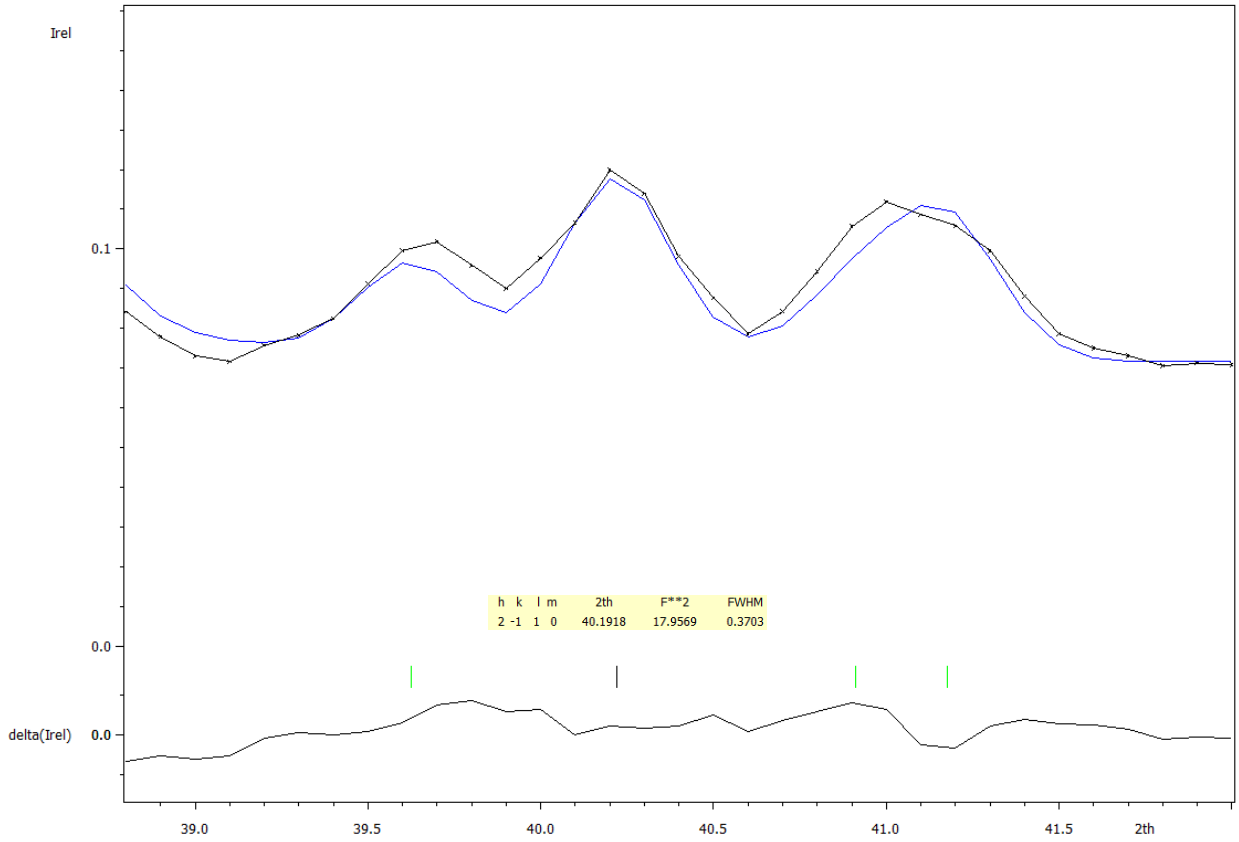
*P62’2’(00g)-h00*
*Rp=4.2%, R(obs)=2.9%,2.3%,4.0% for all, nuclear and magnetic reflections, respectively.*

*P6’2’2(00g)t00*
*Rp=4.8%, R(obs)=4.8%,4.3%,5.5% for all, nuclear and magnetic reflections, respectively.*

*One of the symmetries clearly fits the data better. Observe that the strong misfit of some of the main reflections has disappeared.*



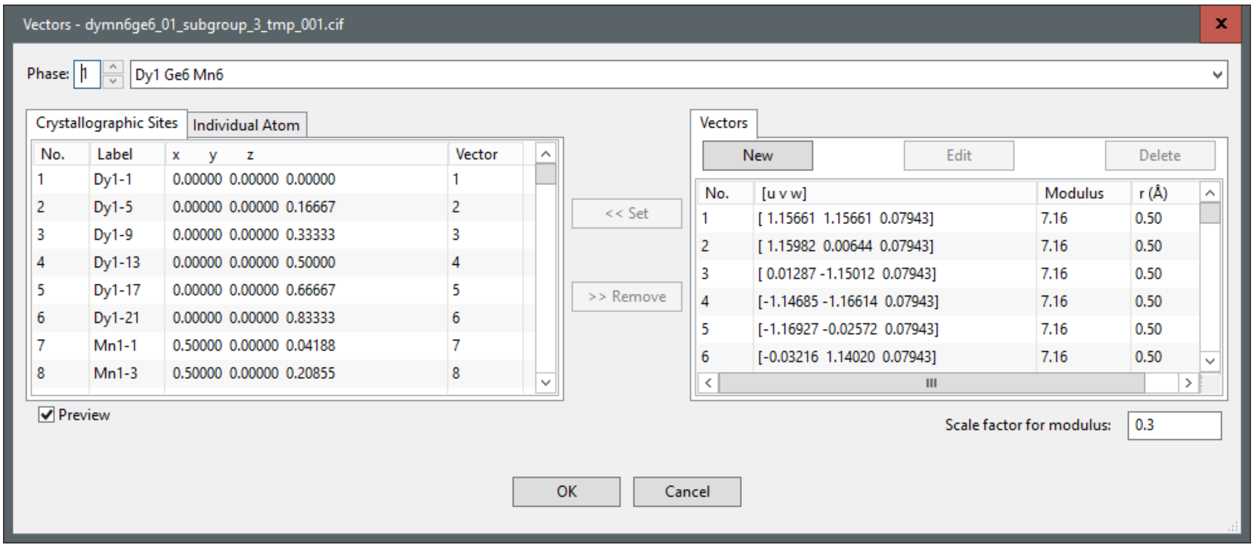
| h | k | l | m | 2th | F**2 | FWHM |
|---|---|---|---|---|---|---|
| 1 | 0 | 1 | 0 | 24.9435 | 45.7046 | 0.4482 |



*The final common Uiso is negative but its absolute value is very small.*
Right-click the icon of Refine and select the page “Various”
Use the button “Fixed commands”
Select “Set individual’; File the edit box by the text “Uiso[*]”; Define value “Set to” zero
Add; OK; OK; Press Button “Yes+start”
*Rp=4.1 %, R(obs)=3.4%,3.2%,3.8% for all, nuclear and magnetic reflections, respectively.*
Run “EditM50”; Go to the page “Magnetic parameters”; Change the magnetic form factor for Dy to <j0>+c<j2> and Dy3+
OK; ”Yes” to the question “Do you want to rewrite M50 file?”
Run “Refine”
*Rp=4.2%, R(obs)=2.9%,2.6%,3.6% for all, nuclear and magnetic reflections, respectively.*

### *10. Visualize the refined model with VESTA*

***[On the screen: Basic window]***
*Double click on the icon “Plot structure”*
*Select “Draw approximant structure”; x from 0 to 1; y form 0 to 1; z from 0 to 6 (c* component of the propagation vector is close to 1/6)*
*Select “Use Vesta to draw the magnetic structure”*
*Press "Draw+return" or "Draw+continue"*
*Select “Edit→Vectors” and modify “Scale factor for modulus” to 0.3*



Vectors - dymn6ge6_01_subgroup_3_tmp_001.cif

Phase: 1 Dy1 Ge6 Mn6

Crystallographic Sites

| No. | Label | x y z | Vector |
|---|---|---|---|
| 1 | Dy1-1 | 0.00000 0.00000 0.00000 | 1 |
| 2 | Dy1-5 | 0.00000 0.00000 0.16667 | 2 |
| 3 | Dy1-9 | 0.00000 0.00000 0.33333 | 3 |
| 4 | Dy1-13 | 0.00000 0.00000 0.50000 | 4 |
| 5 | Dy1-17 | 0.00000 0.00000 0.66667 | 5 |
| 6 | Dy1-21 | 0.00000 0.00000 0.83333 | 6 |
| 7 | Mn1-1 | 0.50000 0.00000 0.04188 | 7 |
| 8 | Mn1-3 | 0.50000 0.00000 0.20855 | 8 |

Vectors

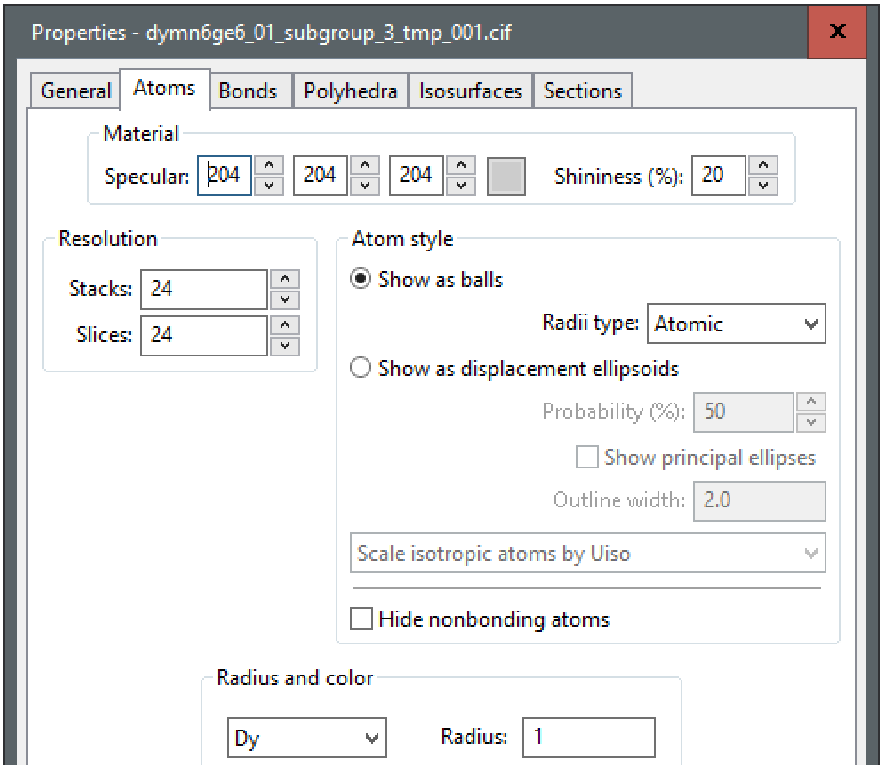
| No. | [u v w] | Modulus | r (Å) |
|---|---|---|---|
| 1 | [ 1.15661 1.15661 0.07943] | 7.16 | 0.50 |
| 2 | [ 1.15982 0.00644 0.07943] | 7.16 | 0.50 |
| 3 | [ 0.01287 -1.15012 0.07943] | 7.16 | 0.50 |
| 4 | [-1.14685 -1.16614 0.07943] | 7.16 | 0.50 |
| 5 | [-1.16927 -0.02572 0.07943] | 7.16 | 0.50 |
| 6 | [-0.03216 1.14020 0.07943] | 7.16 | 0.50 |

☑ Preview

Scale factor for modulus: 0.3

*OK*

*Press button "Properties…"; Go the page "Atoms" and modify "Radius" for all atoms*



Properties - dymn6ge6_01_subgroup_3_tmp_001.cif

Material

Specular: 204 204 204 Shininess (%): 20

Resolution

Stacks: 24

Slices: 24

Atom style

● Show as balls

Radii type: Atomic

○ Show as displacement ellipsoids

Probability (%): 50

☐ Show principal ellipses

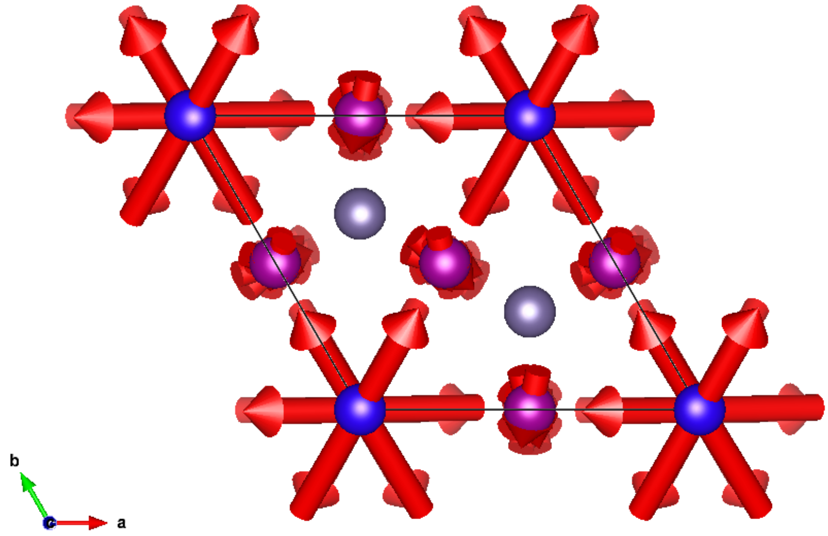
Outline width: 2.0

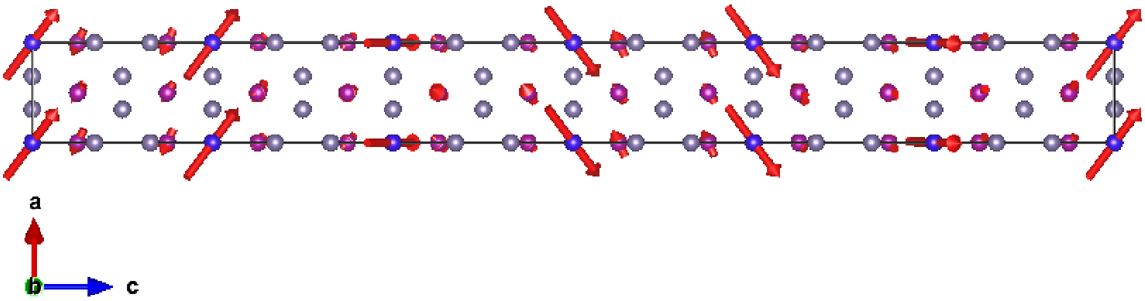
Scale isotropic atoms by Uiso

☐ Hide nonbonding atoms

Radius and color

Dy Radius: 1


b
c
a


a
b
c

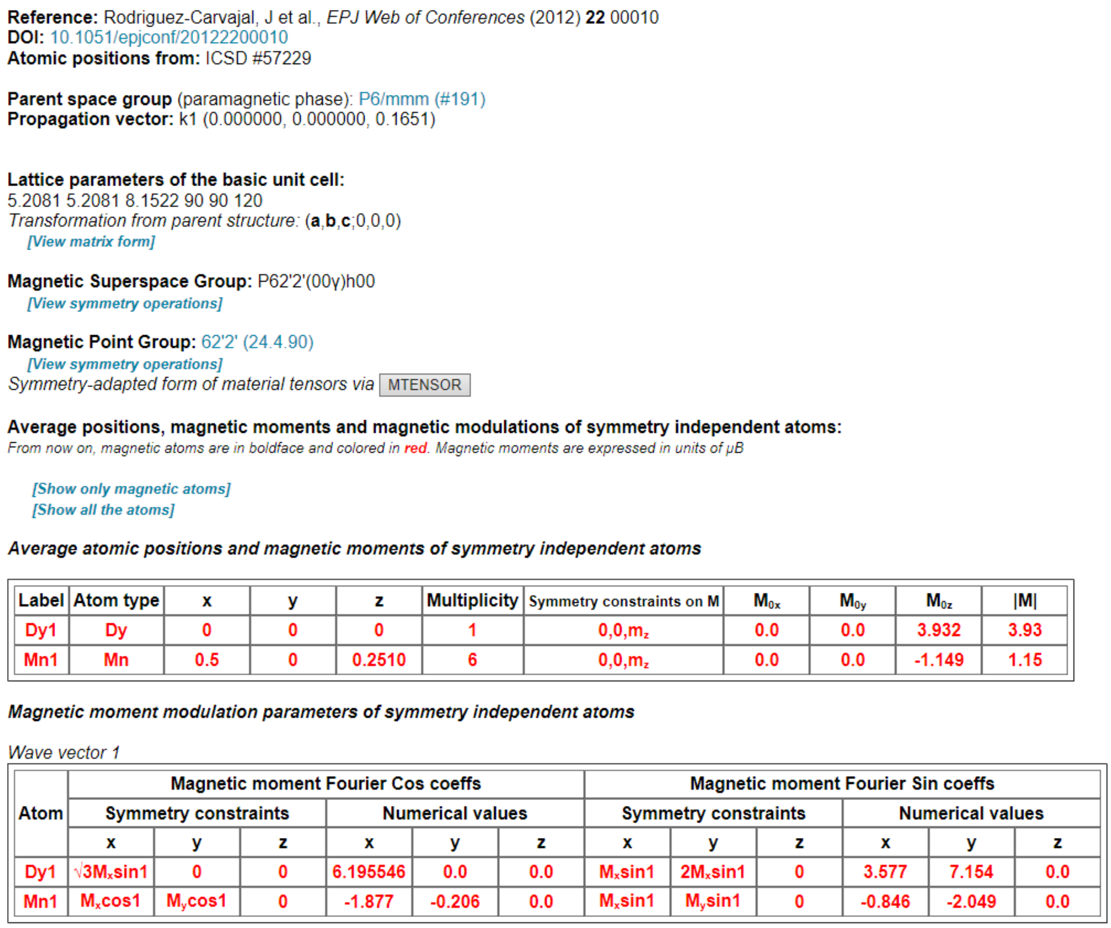
## *11. Transformation to the standard setting as used in MAGNDATA*

*[On the screen: Basic window]*

*The structure has been already included into the database "MAGNDATA" in Bilbao Crystallographic Server and you can get originally publish results as follows:*

"Tools → Connect through internet to → Bilbao Crystallographic Server"
Select "MAGNDATA"; Enter the label of the structure "1.1.10"

*In order to make work easier and faster you can skip this point and use the following table directly:*



**Reference:** Rodriguez-Carvajal, J et al., *EPJ Web of Conferences* (2012) **22** 00010
**DOI:** 10.1051/epjconf/20122200010
**Atomic positions from:** ICSD #57229

**Parent space group** (paramagnetic phase): P6/mmm (#191)
**Propagation vector:** k1 (0.000000, 0.000000, 0.1651)

**Lattice parameters of the basic unit cell:**
5.2081 5.2081 8.1522 90 90 120
*Transformation from parent structure:* (**a**,**b**,**c**;0,0,0)
*[View matrix form]*

**Magnetic Superspace Group:** P62'2'(00γ)h00
*[View symmetry operations]*

**Magnetic Point Group:** 62'2' (24.4.90)
*[View symmetry operations]*
*Symmetry-adapted form of material tensors via* MTENSOR

**Average positions, magnetic moments and magnetic modulations of symmetry independent atoms:**
*From now on, magnetic atoms are in boldface and colored in* ***red***. *Magnetic moments are expressed in units of μB*

*[Show only magnetic atoms]*
*[Show all the atoms]*

***Average atomic positions and magnetic moments of symmetry independent atoms***

| Label | Atom type | x | y | z | Multiplicity | Symmetry constraints on M | $M_{0x}$ | $M_{0y}$ | $M_{0z}$ | \|M\| |
|---|---|---|---|---|---|---|---|---|---|---|
| **Dy1** | **Dy** | **0** | **0** | **0** | **1** | **0,0,$m_z$** | **0.0** | **0.0** | **3.932** | **3.93** |
| **Mn1** | **Mn** | **0.5** | **0** | **0.2510** | **6** | **0,0,$m_z$** | **0.0** | **0.0** | **-1.149** | **1.15** |

***Magnetic moment modulation parameters of symmetry independent atoms***

*Wave vector 1*

| Atom | Magnetic moment Fourier Cos coeffs | | | | | | Magnetic moment Fourier Sin coeffs | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Symmetry constraints | | | Numerical values | | | Symmetry constraints | | | Numerical values | | |
| | x | y | z | x | y | z | x | y | z | x | y | z |
| **Dy1** | **$\sqrt{3}M_x$sin1** | **0** | **0** | **6.195546** | **0.0** | **0.0** | **$M_x$sin1** | **$2M_x$sin1** | **0** | **3.577** | **7.154** | **0.0** |
| **Mn1** | **$M_x$cos1** | **$M_y$cos1** | **0** | **-1.877** | **-0.206** | **0.0** | **$M_x$sin1** | **$M_y$sin1** | **0** | **-0.846** | **-2.049** | **0.0** |

*The result as derived step by step from the representation theory is expressed in a different chiral domain than used in MAGNDATA. Therefore, we should transfer it to the equivalent chiral domain.*
*[On the screen: Basic window]*
"Tools → Transformation → Change enantiomorph"
Create a new structure with name e.g. "dymn6ge6_01_subgroup_3_chiral"
OK; Yes to continue with the new structure
Run EdiM50; Go the page "Symmetry"
*Now the superspace group is the same as used in MAGNDATA however there is a non-zero origin shift in $x_4$ equal 1/6.*

ESC

“Tools → Transformation → Origin shift”

Use shift to the point 0 0 0 -1/6

OK

*The last point that has to be checked for a full comparison is if we are using in the same symmetry positions for the magnetic atoms Dy1 and Mn1. The positions of these atoms from 1.1.10 are:*

*Dy1 (0,0,0) and Mn1 (0.5,0,0.251).*

*[On the screen: Basic window]*

Run “Edit atoms”; Double click on Dy1 atom; Go to the page “Edit”

*The coordinates are (1,1,1) and this means that we can just rewrite them to (0,0,0) as such transformation does not change the modulation functions.*

*In the case that the Mz0 is negative change it to positive.*

Move to the atom Mn1

*Its coordinates are (0.5,1,0.749). From the list of symmetry operations we can find that the symmetry operation:* $x_1$-$x_2$,-$x_2$,-$x_3$,-$x_4$+1/2 *combined with the lattice translation (1,1,1,0) makes what is needed.*

OK;

*[On the screen: Select atoms to be used]*

Select the atom Mn1; Press button “Action”; Select “Transform selected atoms”

Use the button “Fill by a symmetry operation”; Select x1-x2 -x2 -x3 -x4+1/2 –m; Modify the translation vector to 1 1 1 1/2

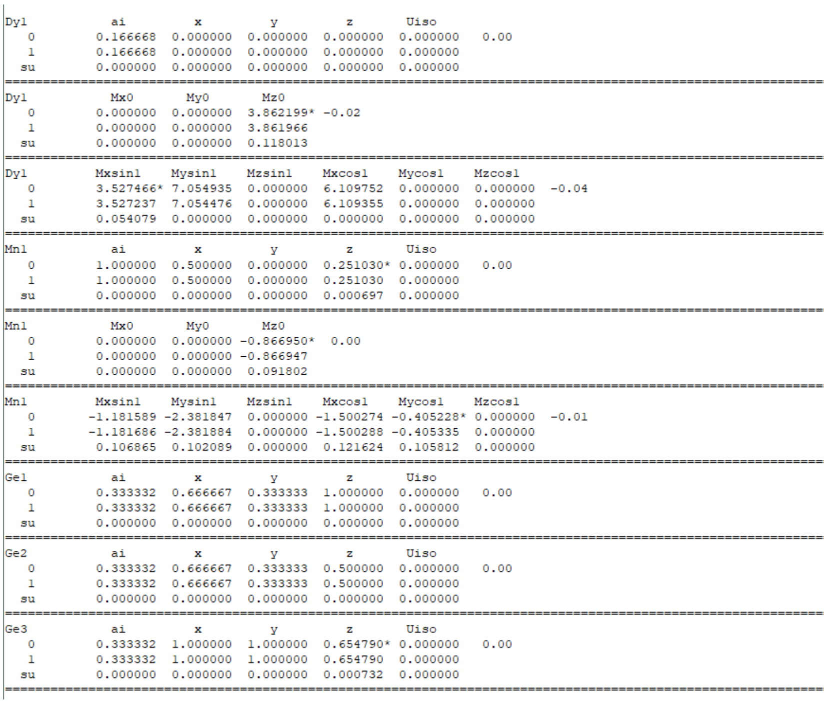
OK; OK; Yes to rewrite files

*[On the screen: Basic window]*

Run “Refine” to check that all transformation did not change the solution

*[On the screen: Basic window]*

“Edit/View → View of Refine”; Press “Go to” and select “Changes overview”



```
Dy1          ai         x          y          z         Uiso
   0       0.166668  0.000000  0.000000  0.000000  0.000000    0.00
   1       0.166668  0.000000  0.000000  0.000000  0.000000
  su       0.000000  0.000000  0.000000  0.000000  0.000000
================================================================================================
Dy1          Mx0        My0        Mz0
   0       0.000000  0.000000  3.862199* -0.02
   1       0.000000  0.000000  3.861966
  su       0.000000  0.000000  0.118013
================================================================================================
Dy1        Mxsin1     Mysin1     Mzsin1     Mxcos1     Mycos1     Mzcos1
   0       3.527466* 7.054935  0.000000  6.109752  0.000000  0.000000  -0.04
   1       3.527237  7.054476  0.000000  6.109355  0.000000  0.000000
  su       0.054079  0.000000  0.000000  0.000000  0.000000  0.000000
================================================================================================
Mn1          ai         x          y          z         Uiso
   0       1.000000  0.500000  0.000000  0.251030* 0.000000    0.00
   1       1.000000  0.500000  0.000000  0.251030  0.000000
  su       0.000000  0.000000  0.000000  0.000697  0.000000
================================================================================================
Mn1          Mx0        My0        Mz0
   0       0.000000  0.000000 -0.866950*  0.00
   1       0.000000  0.000000 -0.866947
  su       0.000000  0.000000  0.091802
================================================================================================
Mn1        Mxsin1     Mysin1     Mzsin1     Mxcos1     Mycos1     Mzcos1
   0      -1.181589 -2.381847  0.000000 -1.500274 -0.405228* 0.000000  -0.01
   1      -1.181686 -2.381884  0.000000 -1.500288 -0.405335  0.000000
  su       0.106865  0.102089  0.000000  0.121624  0.105812  0.000000
================================================================================================
Ge1          ai         x          y          z         Uiso
   0       0.333332  0.666667  0.333333  1.000000  0.000000    0.00
   1       0.333332  0.666667  0.333333  1.000000  0.000000
  su       0.000000  0.000000  0.000000  0.000000  0.000000
================================================================================================
Ge2          ai         x          y          z         Uiso
   0       0.333332  0.666667  0.333333  0.500000  0.000000    0.00
   1       0.333332  0.666667  0.333333  0.500000  0.000000
  su       0.000000  0.000000  0.000000  0.000000  0.000000
================================================================================================
Ge3          ai         x          y          z         Uiso
   0       0.333332  1.000000  1.000000  0.654790* 0.000000    0.00
   1       0.333332  1.000000  1.000000  0.654790  0.000000
  su       0.000000  0.000000  0.000000  0.000732  0.000000
================================================================================================
```

| | | $M_{0x}$ | $M_{0y}$ | $M_{0z}$ | $\|M\|$ |
|---|---|---|---|---|---|
| Dy1 | MAGNDATA | 0.0 | 0.0 | 3.93 | 3.93 |
| | Jana | 0.0 | 0.0 | 3.86(12) | 3.86(12) |
| Mn1 | MAGNDATA | 0.0 | 0.0 | -1.15 | 1.15 |
| | Jana | 0.0 | 0.0 | -0.87(9) | 0.87(9) |

| | | cos | | | sin | | |
|---|---|---|---|---|---|---|---|
| | | $M_x$ | $M_y$ | $M_z$ | $M_x$ | $M_y$ | $M_z$ |
| Dy1 | MAGNDATA | 6.20 | 0.0 | 0.0 | 3.58 | 7.15 | 0.0 |
| | Jana | 6.11 | 0.0 | 0.0 | 3.53(5) | 7.05 | 0.0 |
| Mn1 | MAGNDATA | -1.88 | -0.21 | 0.0 | -0.85 | -2.05 | 0.0 |
| | Jana | -1.50(12) | -0.41(10) | 0.0 | -1.18(11) | -2.38(10) | 0.0 |

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

*[On the screen: Basic window]*

"File → Structure → Save as"; Use e.g. "dymn6ge6_01_subgroup_3_final"

OK; No to the question "Do you want to continue with the new structure?"

*[On the screen: Basic window]*

Run "Edit atoms"

*[On the screen: Select atoms to be used]*

Double click on the atom Dy1; Activate option "in spherical coordinates";

Go the "Edit" page;

*For the magnetic moment **k=0** only Mr0-amplitude is a free parameter. Both angles Mp0-φ angle and Mt0-ϑ angle are fixed by symmetry.*

Uncheck the refine flags for angular components if active.

Press the button "Magnetic" to magnetic modulation waves.

*The only free parameter is the amplitude Mrsin1. The φ angle is fixed for cos wave to 90 and for sin wave to 0. This means that the circular modulation is fully induced by the symmetry.*

Uncheck the refine flags for angular components if active.

Go to the atom Mn1 and activate option "in spherical coordinates";

Go the "Edit" page;

*For the magnetic moment **k=0** only Mr0-amplitude is a free parameter. Both angles Mp0-φ angle and Mt0-ϑ angle are fixed by symmetry.*

Uncheck the refine flags for angular components if active.

Press the button "Magnetic" to magnetic modulation waves.

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

Right click on the “Refine” icon; Select the page Various; Click on the button “Equations”;

Define the equations mentioned above:

Mp0[Dy1]=0
Mt0[Dy1]=0
Mrcos1[Dy1]=Mrsin1[Dy1]
Mpsin1[Dy1]=90
Mpcos1[Dy1]=0
Mtsin1[Dy1]=90
Mtcos1[Dy1]=90
Mp0[Mn1]=0
Mt0[Mn1]=180
Mrcos1[Mn1]=Mrsin1[Mn1]
Mpcos1[Mn1]= Mpsin1[Mn1]-90
Mtsin1[Mn1]=90
Mtcos1[Mn1]=90
*You can do either one by one or you can use pre-prepared file “Equations-circular.txt”. For the former method:*
Press the button “Edit” and use the copy-paste method from the file “Equations-circular.txt”.

OK;OK; Yes+start
*Rp=3.83%, R(obs)=2.93%,2.43%,3.82% for all, nuclear and magnetic reflections, respectively. Which means that it is not significantly worse than the full refinement – see point 9.*

| | | $M_{0x}$ | $M_{0y}$ | $M_{0z}$ | \|M\| |
|---|---|---|---|---|---|
| Dy1 | MAGNDATA | 0.0 | 0.0 | 3.93 | 3.93 |
| | Jana | 0.0 | 0.0 | 3.96(11) | 3.96(11) |
| Mn1 | MAGNDATA | 0.0 | 0.0 | -1.15 | 1.15 |
| | Jana | 0.0 | 0.0 | -1.00(8) | 1.00(8) |

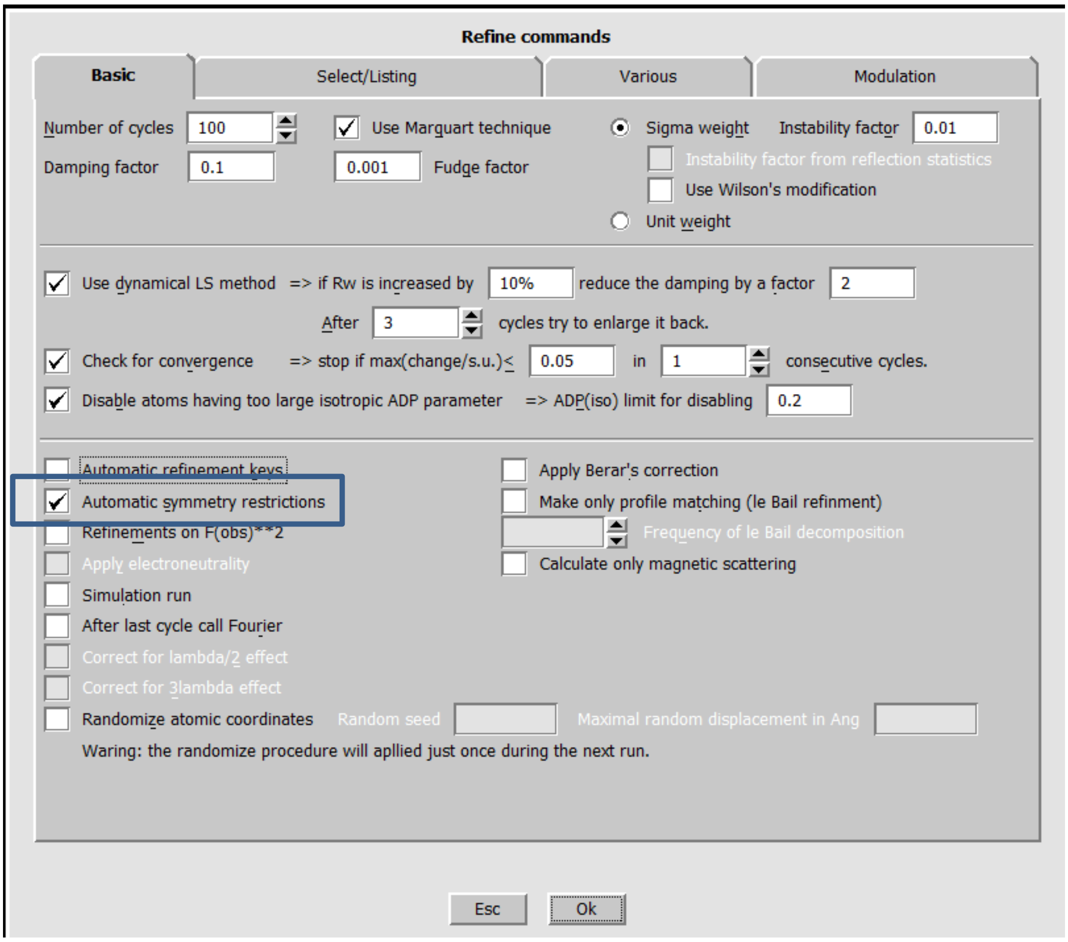
After transforming from polar to crystallographic coordinates

| | | cos | | | sin | | |
|---|---|---|---|---|---|---|---|
| | | $M_x$ | $M_y$ | $M_z$ | $M_x$ | $M_y$ | $M_z$ |
| Dy1 | MAGNDATA | 6.20 | 0.0 | 0.0 | 3.58 | 7.15 | 0.0 |
| | Jana | 6.18 | 0.0 | 0.0 | 3.57(5) | 7.13 | 0.0 |
| Mn1 | MAGNDATA | -1.88 | -0.21 | 0.0 | -0.85 | -2.05 | 0.0 |
| | Jana | -1.88(10) | -0.20(9) | 0.0 | -0.86(9) | -2.06(8) | 0.0 |

***General note: Two different strategies for handling refinement keys in Jana2006***
*From Petříček, V., Dušek, M. & Palatinus, L. (2014) Z.Kristallogr.* ***229****, 345-352.*

*"All refinable parameters are divided into two groups: automatic and user-controlled ones. The automatic parameters are those which can be usually refined without numerical problems: scale factors and extinction parameters; parameters describing position, ADP and their modulation for individual atoms as well as for molecules; background parameters of the powder profile; magnetic parameters. The user-controlled parameters are twin/phase volume fractions, atomic or molecular site occupancies, parameters of crenel modulation functions, parameters of multipole refinement and powder profile parameters for individual Bragg reflections.*
*The automatic parameters are activated by default at the beginning of the refinement process while the user-controlled ones must be always explicitly activated by the user. The program always fixes the parameters which cannot be refined due to symmetry restrictions. In order to fix other automatic parameters the user is provided with a range of special fixing commands. This way is very useful for most cases because it minimizes mistakes in setting refinement flags. However, the program also allows switching to a completely manual mode, where all parameters are to be activated explicitly by the user, analogically to other refinement programs such as FullProf [29]."*

***Handling of symmetry restrictions of magnetic moments in polar coordinates would be easier for most of users if the non-automatic procedure is used:***



Number of cycles 100

☑ Use Marquart technique

● Sigma weight

Instability factor 0.01

☐ Instability factor from reflection statistics

☐ Use Wilson's modification

○ Unit weight

Damping factor 0.1

0.001 Fudge factor

☑ Use dynamical LS method => if Rw is increased by 10% reduce the damping by a factor 2

After 3 cycles try to enlarge it back.

☑ Check for convergence => stop if max(change/s.u.)≤ 0.05 in 1 consecutive cycles.

☑ Disable atoms having too large isotropic ADP parameter => ADP(iso) limit for disabling 0.2

☐ Automatic refinement keys

☑ Automatic symmetry restrictions

☐ Refinements on F(obs)**2

☐ Apply electroneutrality

☐ Simulation run

☐ After last cycle call Fourier

☐ Correct for lambda/2 effect

☐ Correct for 3lambda effect

☐ Randomize atomic coordinates Random seed Maximal random displacement in Ang

Waring: the randomize procedure will apllied just once during the next run.

☐ Apply Berar's correction

☐ Make only profile matching (le Bail refinment)

Frequency of le Bail decomposition

☐ Calculate only magnetic scattering