Incommensurate magnetic structure of $DyMn_6Ge_6$ determined using Fullprof
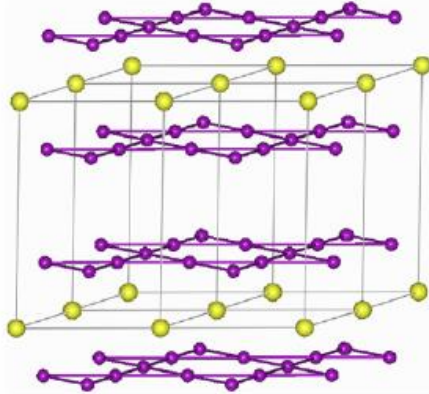
Stuart Calder, ORNL

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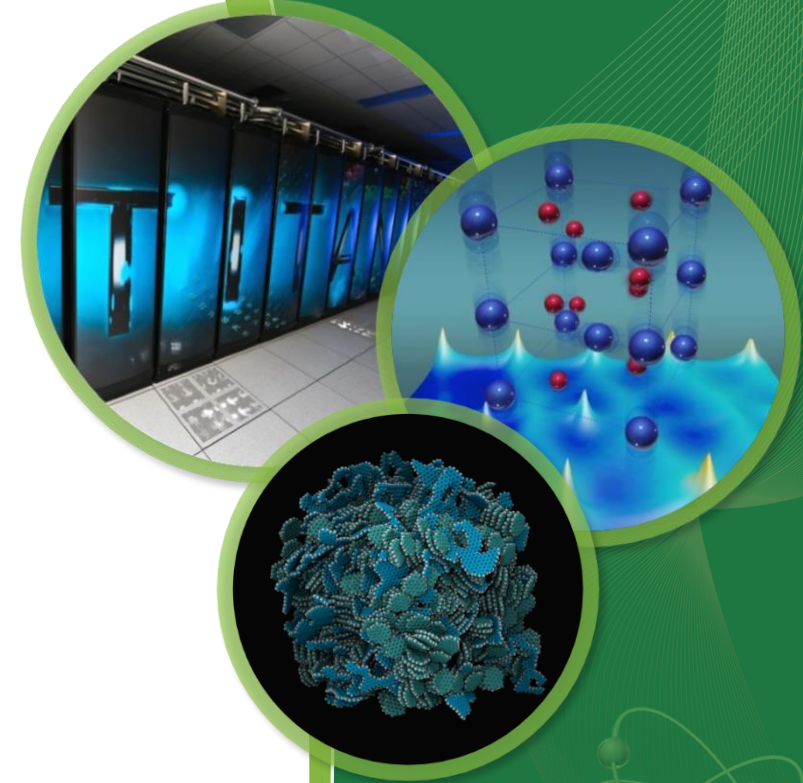
Magnetic phase diagram of DyMn$_6$Ge$_6$

P. Schobinger-Papamantellos et al, Journal of Alloys and Compounds, 203 (1994) 243-250

Atom	X	Y	Z	Wyk
Dy	0	0	0	1b
Mn	1/2	0	0.2504	6i
Ge	1/3	2/3	0	2d
Ge	1/3	2/3	1/2	2c
Ge	0	0	0.345	2e

The compound DyMn$_6$Ge$_6$ crystallizes in the hexagonal HfFe$_6$Ge$_6$-type structure (P6/mmm). It orders antifer-romagnetically at $T_N = 420$ K but there is a second magnetic phase transition near 100 K. Neutron diffraction has shown that the high temperature magnetic structure is a triple flat spiral consisting of ferromagnetic Dy layers and ferromagnetic Mn layers coupled antiparallelly in a three-layer sequence Mn(+), Dy(−), Mn(+). The moment direction is perpendicular to [001] but the direction in the basal plane changes by a constant angle $\phi_s = 2\pi q_z$, on going from one unit cell to another. The wavevector length of the incommensurate structure is temperature dependent and equal to $q_z = 0.184$ at 293 K, which corresponds to $\phi_s = 66°$. Below $T_t = 100$ K the wavevector length remains constant ($q_z = 0.163$) and the magnetic structure is an incommensurate triple-cone structure in which both the Dy and Mn sublattices have a ferromagnetic component along the c axis. These components are antiparallel and lead to a net moment in the c direction of 2.0(5) μ_B per formula unit. The magnetic isotherm at 4.2 K, studied in fields up to 35 T, suggests that below 22 T the cone angle (55° for B=0) gradually decreases. Above 22 T the magnetic isotherm shows a linear behaviour characteristic of bending of the antiparallel rare earth and 3d sublattice moments towards each other. The intersublattice coupling constant derived from the high field slope of the isotherm equals $J_{Dy-Mn}/k = -9.1$ K.

- Hexagonal *P6/mmm*   a=b=5.21Å, c=8.15Å

- Kagome layers of Mn (magenta). Dy atoms (yellow) at origin of unit cell (grey boxes).

- Two magnetic transitions: T_N=420 K and T_N=100 K.

- Exercise will refine 11 K data using an incommensurate propagation vector (k).
  Spin density wave vs canonical (spin spiral)
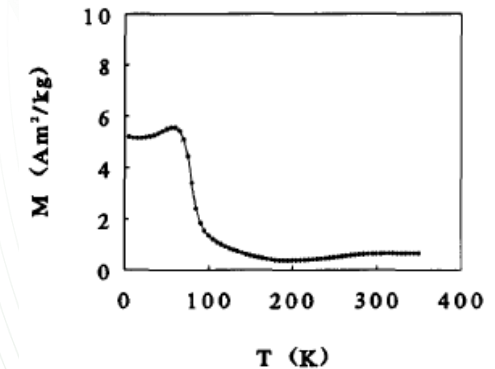 Alternative of two propagation vectors considered as extension to model.

Fig. 1. Temperature dependence of the magnetization of DyMn$_6$Ge$_6$ measured in a field of 0.1 T.

Experimental details of measurements on $DyMn_6Ge_6$

- Neutron powder diffraction collected on DMC at PSI, Switzerland.

- λ=1.7037Å

- Background file: dy_nuc_background.BGR
  This can be created from winplotr, but file is already generated for this example.

- Manually input instrument parameter files U, V, W, asym1 (irf file not needed)

- CIF file obtained for crystal structure from ICSD: dymn6ge6_nuc.cif

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Steps for magnetic structure determination:

1. Import known crystal structure and input instrument parameters to create PCR file for Nuclear phase

2. Refine crystal structure at 11 K (***EdPcr / Winplotr***)

3. Identify magnetic reflections and determine propagation vector **(k-search)**

4. Use crystal structure and propagation vector to perform symmetry analysis to find the allowed irreducible representations (IRs) and Basis vectors (BVs) for magnetic phase. **(*SARAh / Basireps*)**

5. Select a magnetic model and add it as additional phase(s) to the crystal structure refinement **(*EdPcr / SARAh*)**

6. Refine both nuclear phase and magnetic phase(s) (**Fullprof**)

7. Visualize the magnetic structure model (**FpStudio**)

Step 1: Refine the crystal structure of $DyMn_6Ge_6$

- Additional intensity at 11 K compared to 293 K.

- Refine 11 K data to obtain crystal structure and ignore magnetic peaks for now.
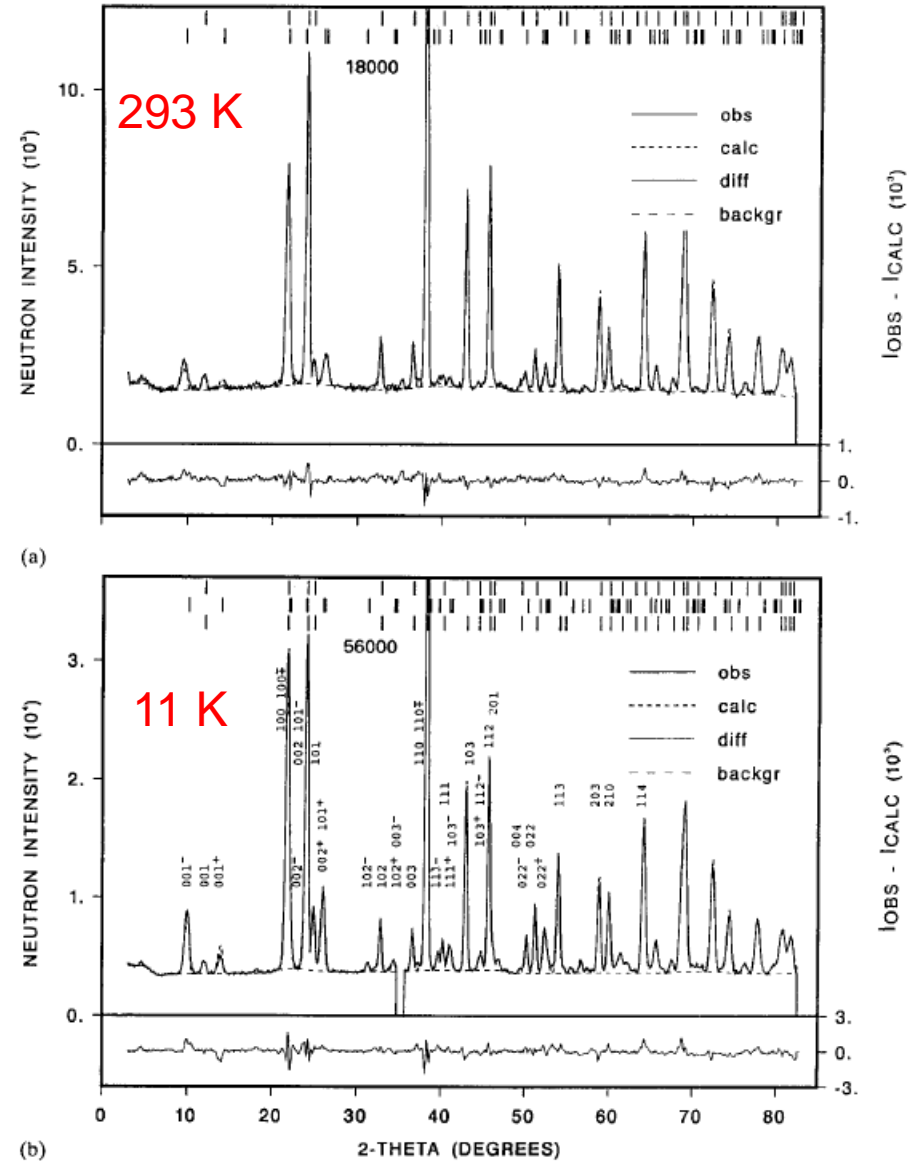
Step 1: Refine the crystal structure of $DyMn_6Ge_6$

Use EdPCR to create the input file for FullProf (.pcr):

- Import the crystallographic information file (CIF) dymn6ge6_nuc.cif

In the new "simple calculation template" window select "Neutron"
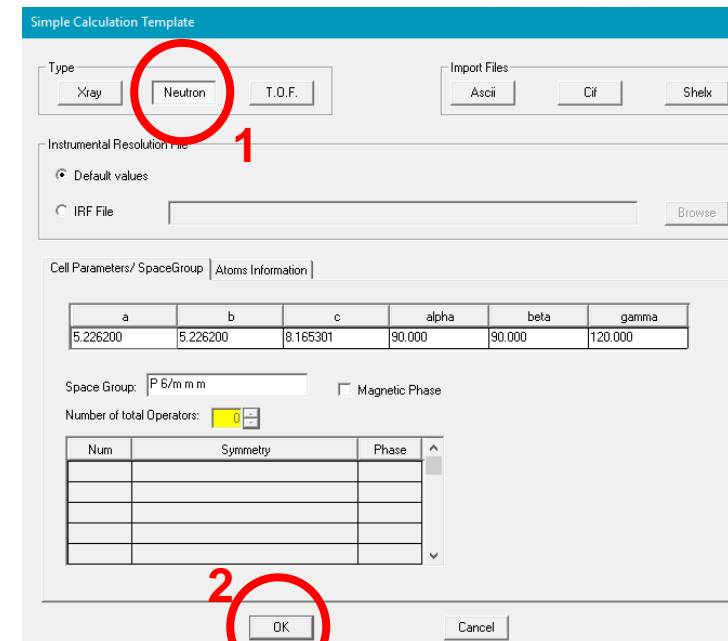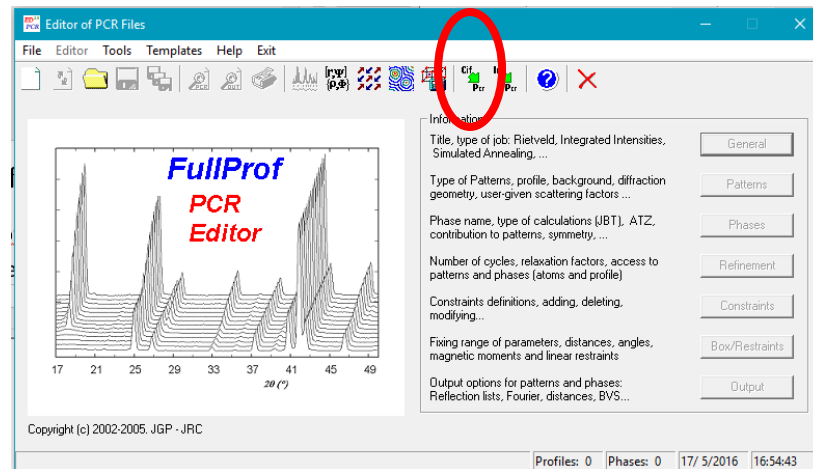
Step 1: Refine the crystal structure of $DyMn_6Ge_6$
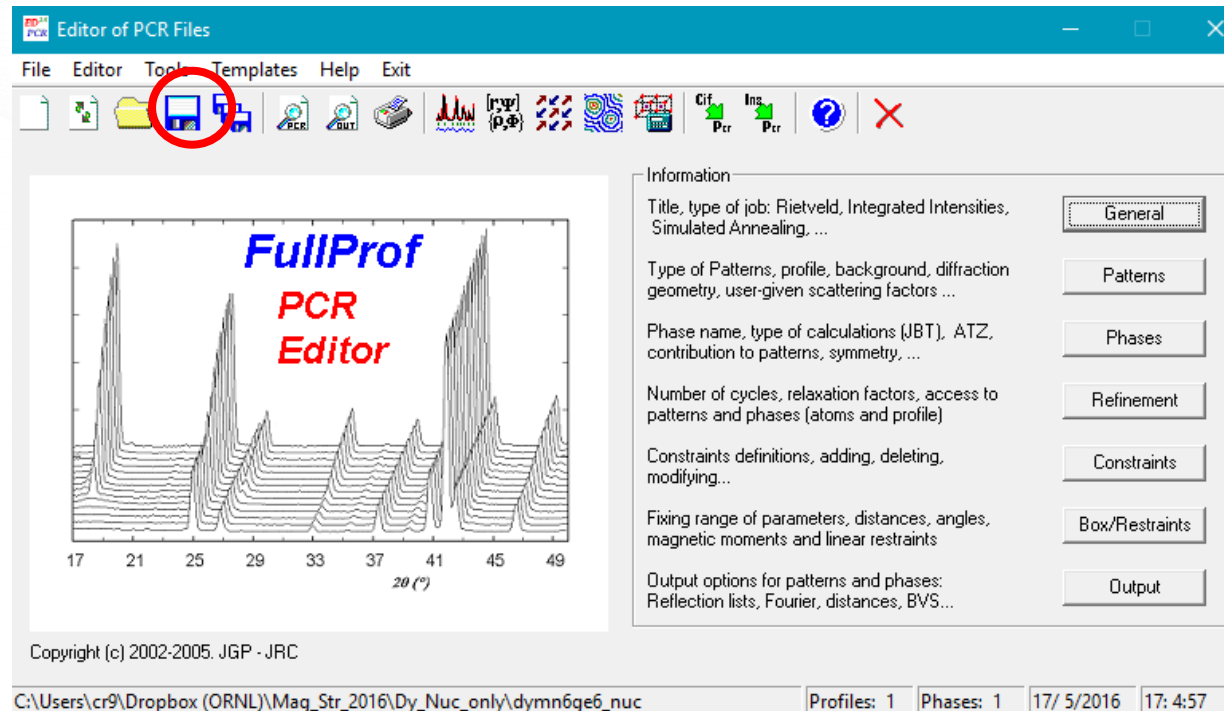
After each step click "OK" to get back to main EdPCR window and save to ensure the changes are accepted.

Step 1: Refine the crystal structure of DyMn$_6$Ge$_6$
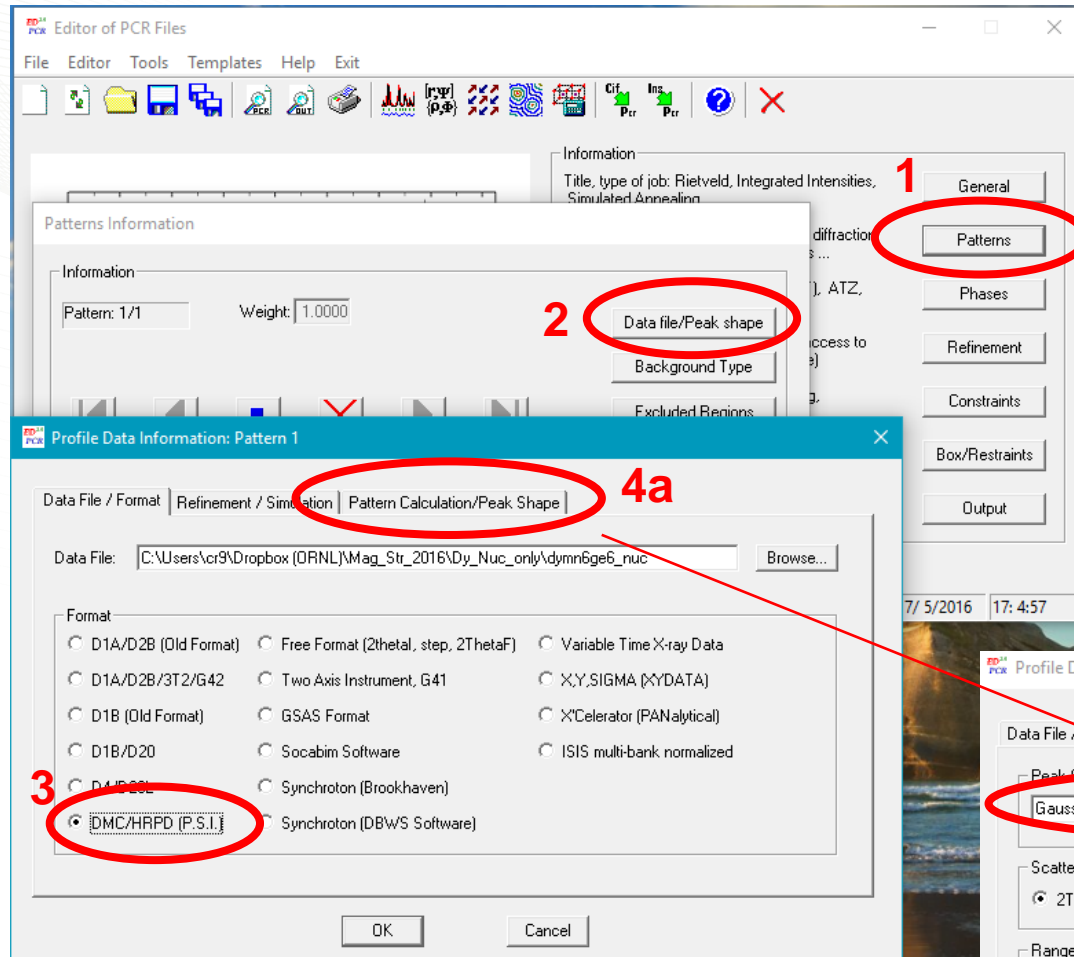
Open tabs "Patterns",
then "DataFile/Peak shape"
and select "DMC/HFPR (P.S.I)"
Steps **1,2,3**
Next select "Pattern
Calculations/Peak Shape" tab and
change peak shape to Gaussian
Steps **4a-4b**
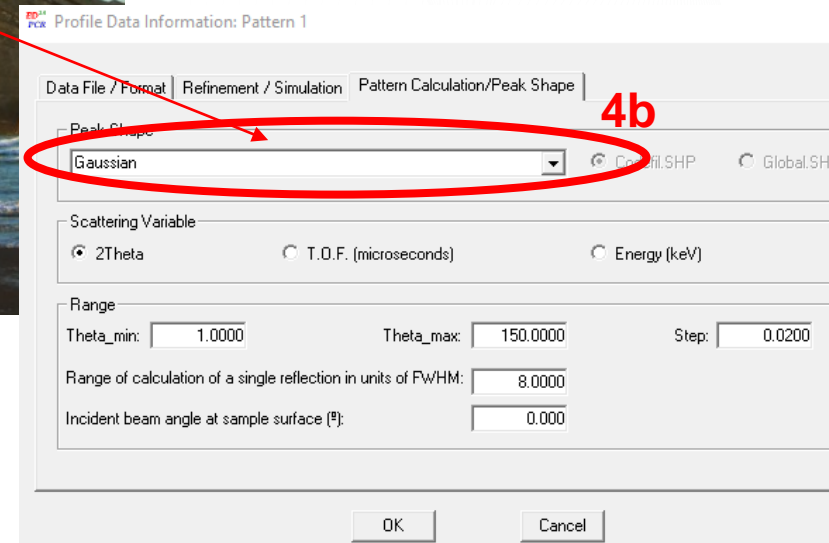
Step 1: Refine the crystal structure of $DyMn_6Ge_6$

Open tabs "Patterns",
then "DataFile/Peak shape"
and select "DMC/HFPR (P.S.I)"
Steps 1,2,3
Close tabs by selecting OK
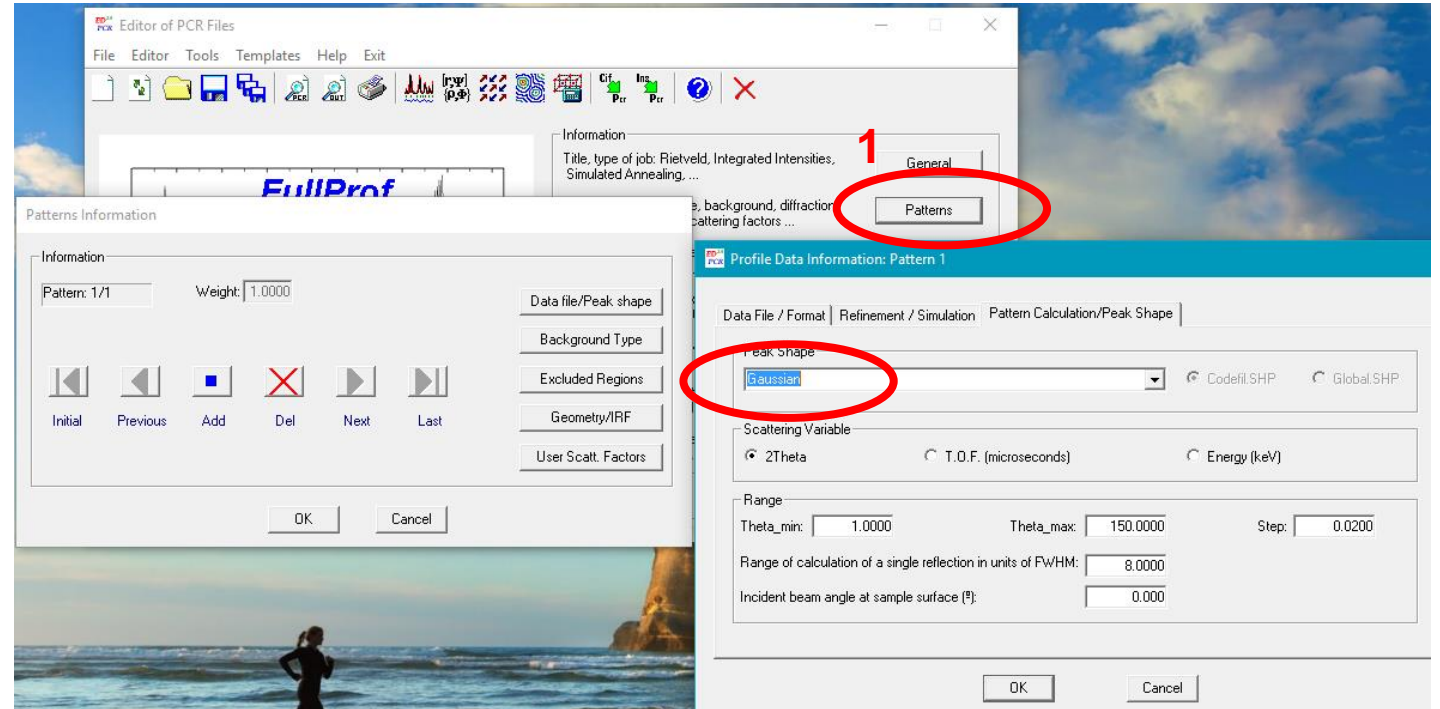
Step 1: Refine the crystal structure of $DyMn_6Ge_6$

- From main window of EdPCR select "Patterns" tab, click on "Data file/Peak shape" and then select "Neutron – CW (Nuclear and Magnetic)"
  Under "Wavelength" from drop-down select "User defined" input 1.7037 for λ_1 and λ_2 and 1 for (I2/I1)
  Steps **1,2,3,4**

- Close tabs (select "OK") and save.
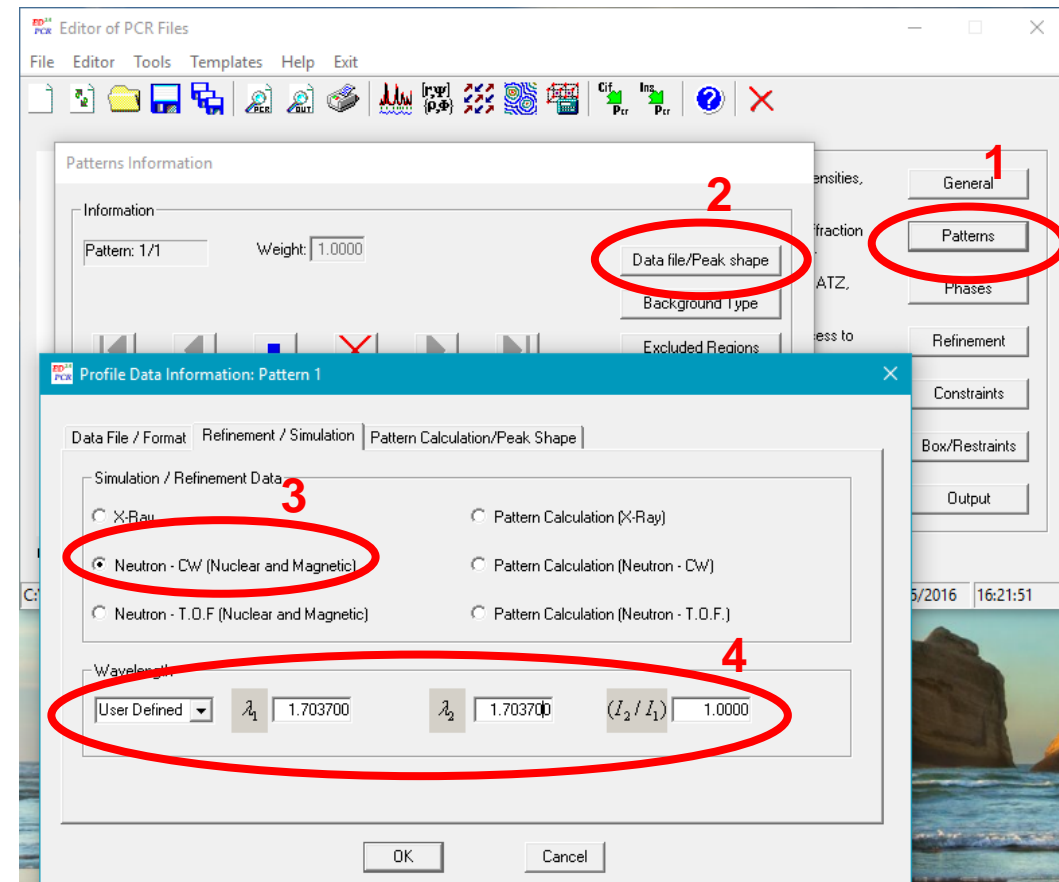
Step 1: Refine the crystal structure of DyMn$_6$Ge$_6$

- From main window of EdPCR select "Phases" tab, click on "Contribution to patterns" and then select "current phase contributes to the pattern"
Steps **1,2,3**
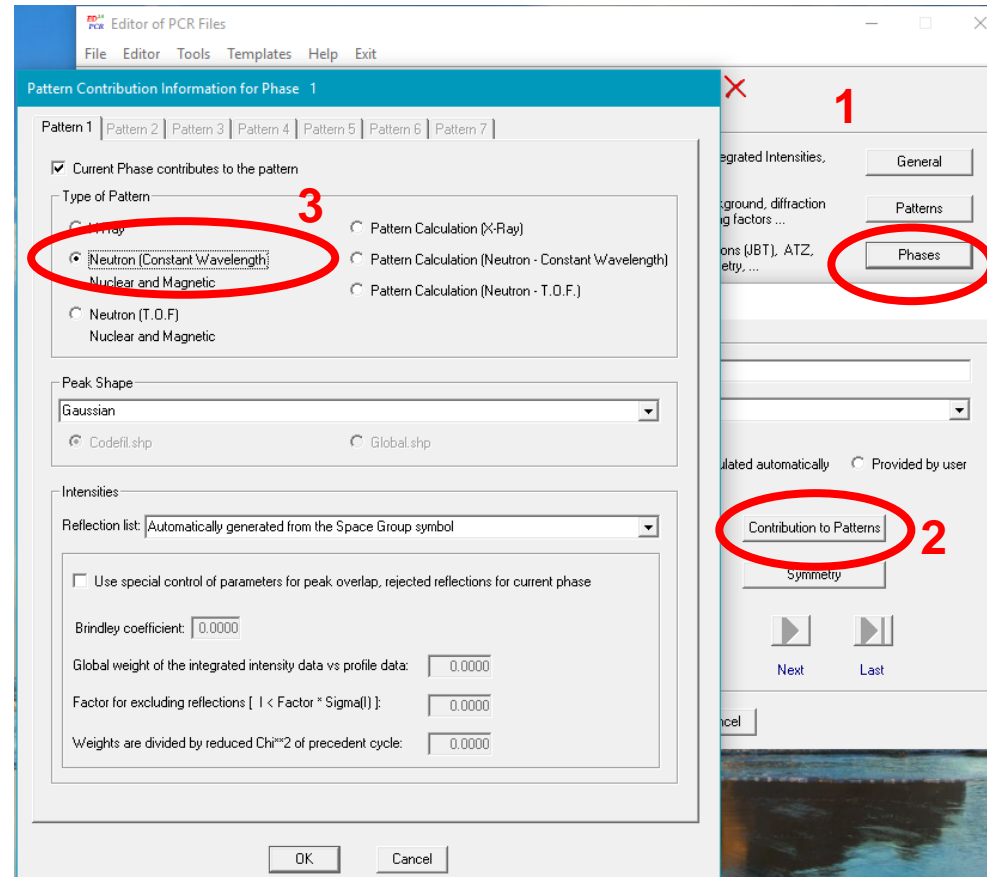
Step 1: Refine the crystal structure of DyMn$_6$Ge$_6$

- From main window of EdPCR select "Patterns" tab, click on "Background type" and then select "Linear Interpolation between a set background points with refinable heights"
Steps **1,2,3**

- Close tabs (select "OK") and save.

- A background file can now be loaded.
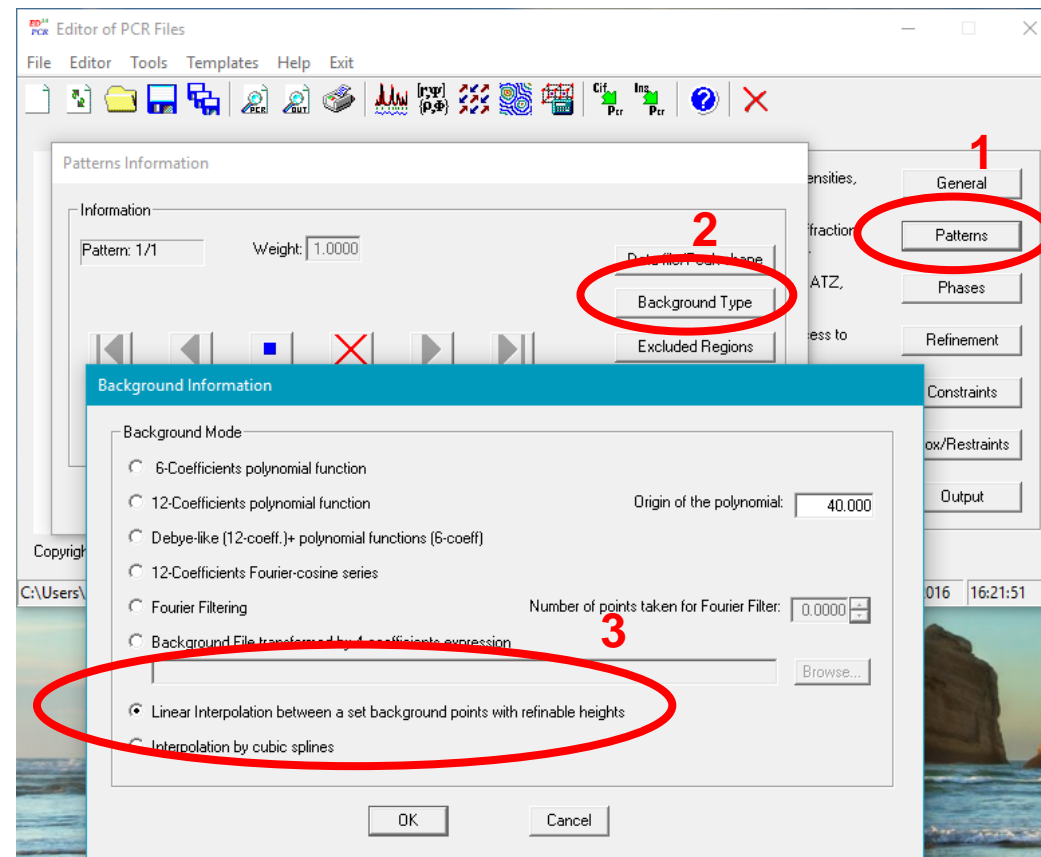
Step 1: Refine the crystal structure of $DyMn_6Ge_6$

- Select "Refinement" tab on main EdPCR window. Then "background" and "Import from Background File". Import "dy_nuc_background.BGR"

- Select OK and save.
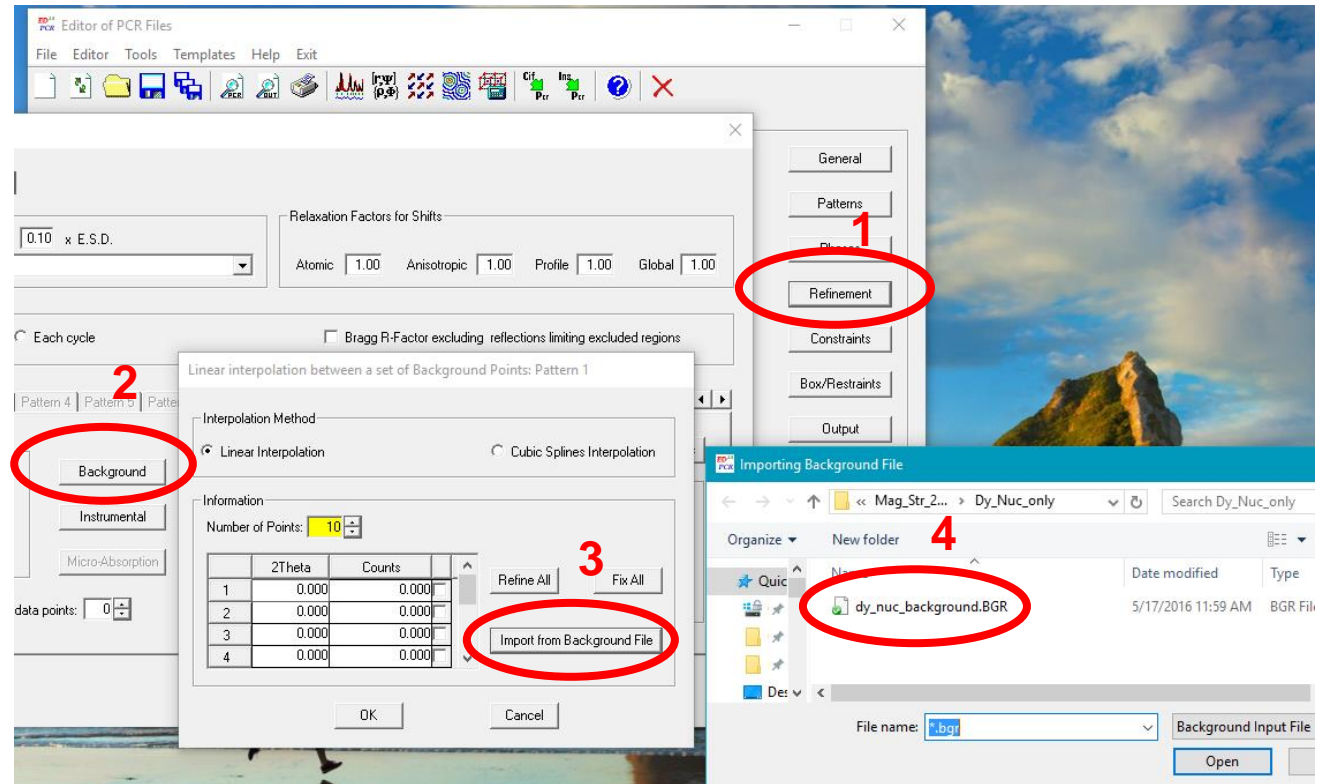
Step 1: Refine the crystal structure of DyMn$_6$Ge$_6$

- Select "Refinement" tab again on main EdPCR window [1]. Increase number "Cycles of refinement" to 6 [2] Then select "Profile" [3] and alter Scale, Overall B-factor, U, V, W and along with a,b,c cell paramaters set them all to refine by checking the boxes (4).

- [5ab]: Select "Asymmetry Paramaters" tab and "Asymm1" to refine

- Select OK and save.

Step 1: Refine the crystal structure of DyMn$_6$Ge$_6$

- Select the PCR button:
- This opens the text for the .pcr file
- Edit the values circled

Step 1: Refine the crystal structure of DyMn$_6$Ge$_6$

- PCR file is set-up for refinement.

- Press circled tab and refinement runs.

- Number of cycles set to 6 in earlier step, more cycles can be performed by pressing "Run" until it reads: "Normal end, final calculations and writing….."
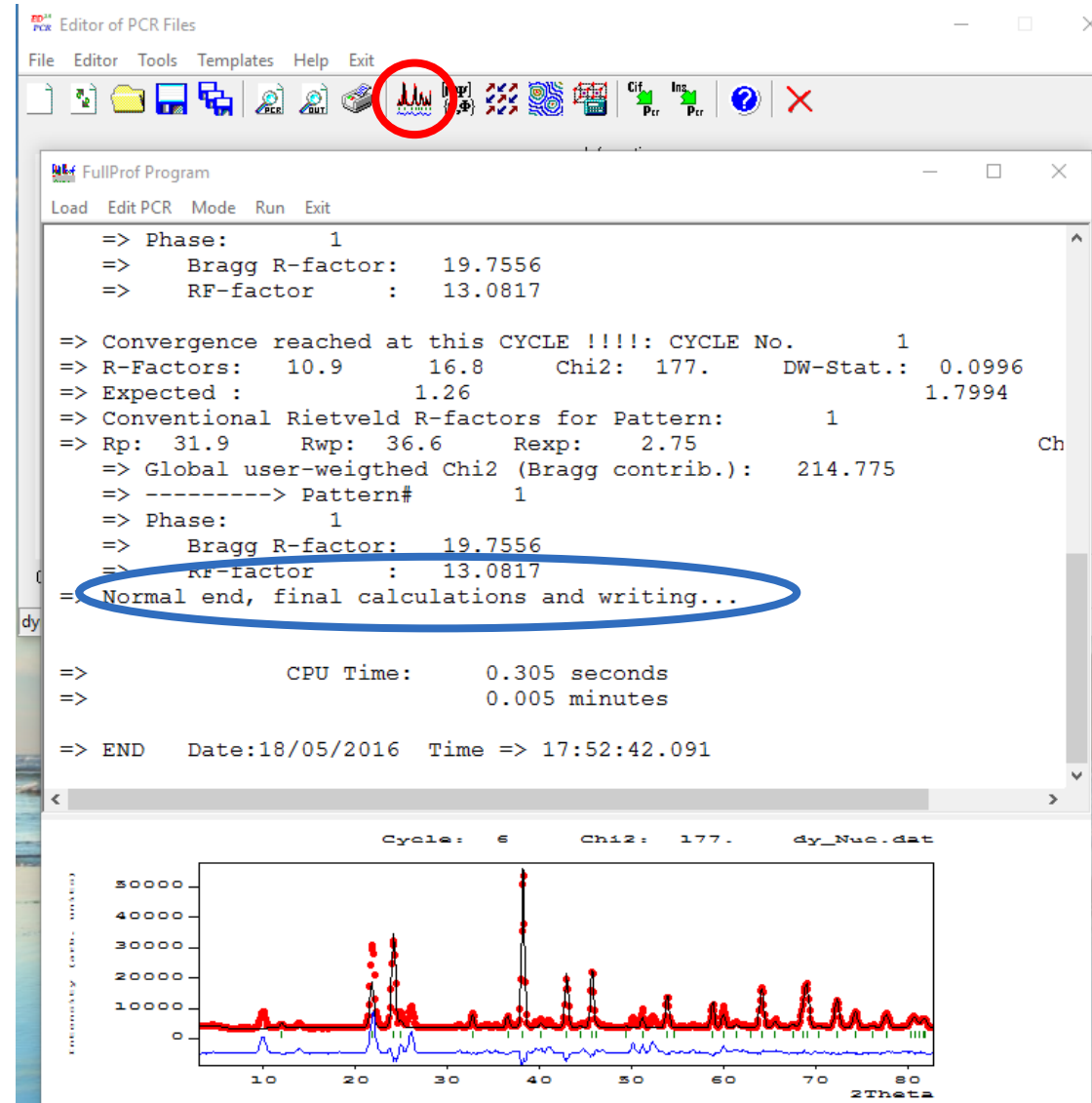
Step 1: Refine the crystal structure of DyMn$_6$Ge$_6$

- Open PRF file created after each refinement.

- Several "extra" peaks or intensity is present. Comparing with high temperature data show these are magnetic.

- The next step is to determine how these magnetic peaks are related to the nuclear peaks.
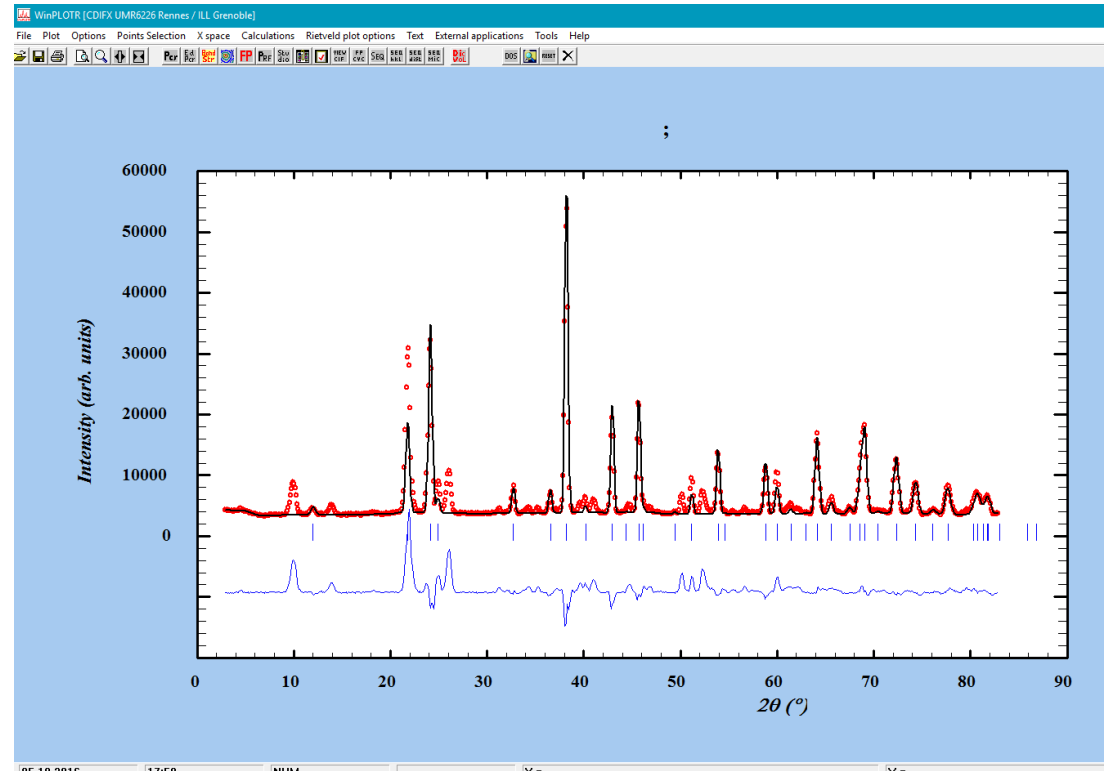
Step 2: Determine the propagation vector (k-wave vector)
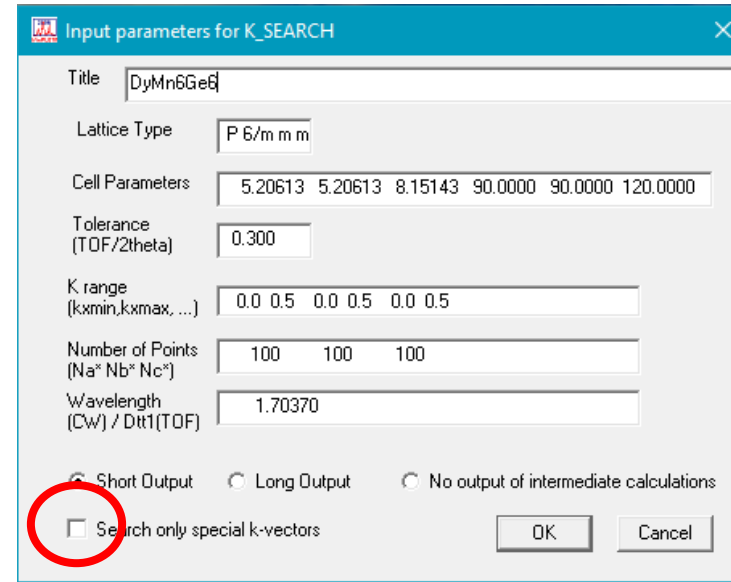
- Open prf with WinPLOTR-2006 from FPtoolbar.
  (Otherwise open WinPLOTR then load the .prf file using
  File→ Open Rietveld/Profile file (.prf))

  - Zoom into low 2theta range to observe magnetic scattering.

  - To select peaks for k-search click:
    Calculations→peak detection→enable
     Then:
    Calculations→peak detection→insert peak
    User curser to select peaks at 2theta 9.9,13.9 and 26.1 deg.

  - Run k-search by selecting
    Calculations→peak detection→save peaks→ K_Search Format
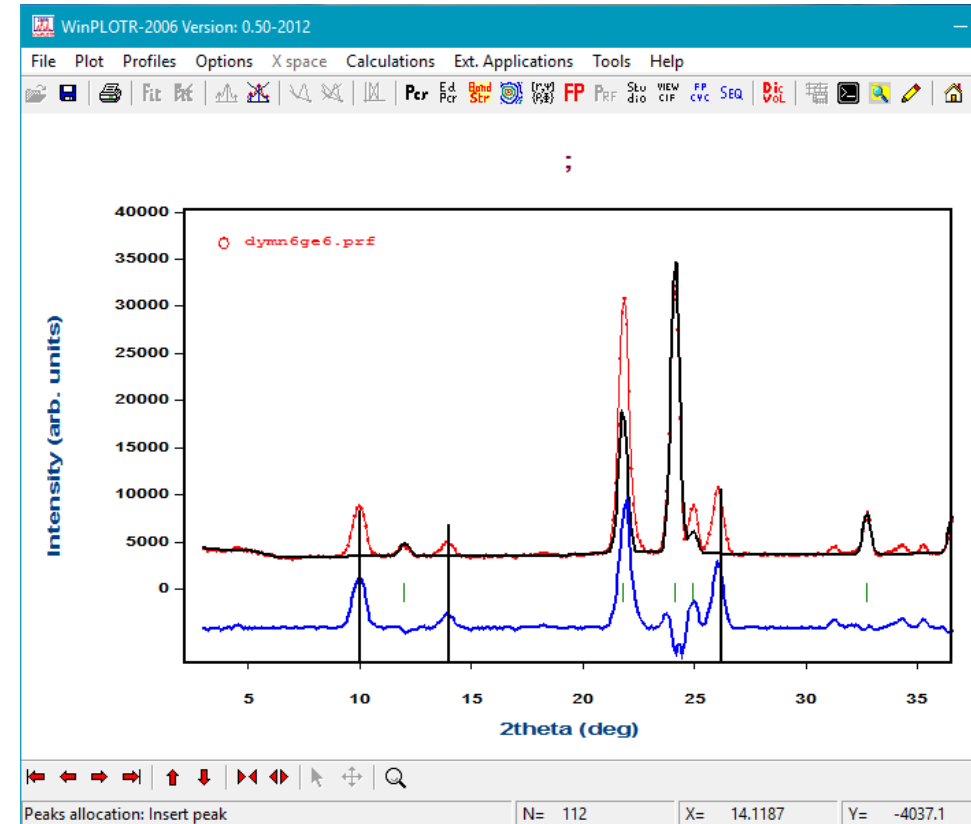
Step 2: Determine the propagation vector (k-wave vector)

- Along with the peak positions the Input parameters for K_SEARCH are loaded from the refinements.

- Run k-search by selecting OK, save .sat file and then "Yes" to run k-search.

- No solution are found with the "Search only special k-vectors" box ticked indicating the solution is not commensurate.

- Uncheck the "Search only special k-vectors" box and rerun k-search

- **k=(0 0 0.165)** appears a good candidate.

- Note – an alternative solution exists for this particular sample with two propagation vectors that goes beyond initial publication in literature.

Note

- Following slides use complex output for SARAh.

- This can make interpreting the BVs potentially more complicated than keeping everything real, but for this example it is the most direct way to a solution.
But the solutions for selecting "yes" or "no" are equivalent and a worked example is shown at the end in Supplemental material.

Step 3: Symmetry analysis

- Use SARAh (or BasIreps) to generate the Irreducible Representations (IRs) and basis vectors (BVs) associated with the propagation vectors, crystal structure and magnetic atom positions.

- Open SARAh- Representational analysis

- Under "Define Parameters" input:
  > "Space group" No. 191 or H_M Symbol P 6/m m m
  > "K-vector" 0 0 0.165
  > "Atoms" Dy   0   0 0
             Mn 0.5 0 0.2504

- Run program using "Calculate" Select directory where the created output files will go (i.e. current directory).

  Some pop windows will appear during calculation. For source of IR select Kovalev and **"No"** so the solution will be complex.

Step 3: Symmetry analysis

- SARAh outputs several files to explain the allowed symmetries.

- From pdf created from .tex file:

IR	BV	Atom	$m_{\|a}$	$m_{\|b}$	$m_{\|c}$	$im_{\|a}$	$im_{\|b}$	$im_{\|c}$
Γ_2	ψ_1	1	0	0	12	0	0	0
Γ_5	ψ_2	1	6	6	0	0	0	0
	ψ_3	1	3.464	-3.464	0	0	0	0

Table 1: Basis vectors for the space group P 6/m m m with $\mathbf{k}_{11} =$ (0, 0, .165). The decomposition of the magnetic representation for the Dy site (0, 0, 0) is $\Gamma_{Mag} = 0\Gamma_1^1 + 1\Gamma_2^1 + 0\Gamma_3^1 + 0\Gamma_4^1 + 1\Gamma_5^2 + 0\Gamma_6^2$. The atom of the primitive basis is defined according to 1: (0, 0, 0).

- Γ_2 and Γ_5 form the common IRs. Both Γ_2 (c-axis) and Γ_5 (ab-plane) will be needed. Note complex BVs.

- The Mn is split into 2 orbits (3 atoms at z=0.2504 and 3 at z=0.7496). For this exercise we will fix both orbits to be the same (in or out of phase). This reduces the free parameters to make the problem more tractable. Moreover for in this kind of compound generally the Mn-Mn interactions are ferromagnetic suggesting constrained orbits.

IR	BV	Atom	$m_{\|a}$	$m_{\|b}$	$m_{\|c}$	$im_{\|a}$	$im_{\|b}$	$im_{\|c}$
Γ_2	ψ_1	1	0	0	4	0	0	0
		2	0	0	4	0	0	0
		3	0	0	4	0	0	0
Γ_3	ψ_2	1	2	0	0	0	0	0
		2	-2	-2	0	0	0	0
		3	0	2	0	0	0	0
Γ_4	ψ_3	1	2	4	0	0	0	0
		2	2	-2	0	0	0	0
		3	-4	-2	0	0	0	0
Γ_5	ψ_4	1	2	2	0	0	0	0
		2	0	1	0	0	-1.732	0
		3	1	0	0	1.732	0	0
	ψ_5	1	2	-2	0	0	0	0
		2	2	1	0	-3.464	-1.732	0
		3	-1	-2	0	-1.732	-3.464	0
	ψ_6	1	0	1	0	0	1.732	0
		2	-2	0	0	0	0	0
		3	-1	-1	0	1.732	1.732	0
	ψ_7	1	-2	-1	0	-3.464	-1.732	0
		2	-2	-4	0	0	0	0
		3	1	-1	0	-1.732	1.732	0
Γ_6	ψ_8	1	0	0	4	0	0	0
		2	0	0	-2	0	0	0
		3	0	0	-2	0	0	0
	ψ_9	1	0	0	0	0	0	0
		2	0	0	3.464	0	0	0
		3	0	0	-3.464	0	0	0

Table 2: Basis vectors for the space group P 6/m m m with $\mathbf{k}_{11} =$ (0, 0, .165). The decomposition of the magnetic representation for the Mn site (.5, 0, .2504) is $\Gamma_{Mag} = 0\Gamma_1^1 + 1\Gamma_2^1 + 1\Gamma_3^1 + 1\Gamma_4^1 + 2\Gamma_5^2 + 1\Gamma_6^2$. The atoms of the nonprimitive basis are defined according to 1: (.5, 0, .2504), 2: (.5, .5, .2504), 3: (0, .5, .2504).

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Step 4: Adding the magnetic phase

- Open SARAh-Refine.

- Under "Fullprof Controls" [1] select "Load SARAh MAT file" and open file created by SARAh (sarah191.mat)

- Under "Common Irreducible Representations" check boxes next to both Γ(2) and Γ(5) and press select to associate all BVs. [2]

- Create the magnetic phase part of the PCR file by selecting "OK" next to "Generate model PCR phase" [3]. This creates a file "sarah191.pcr" that can be copied and pasted into the crystal structure pcr file from Step 1. Note: only open the created "sarah191.pcr" with a text editor and not EdPCR.

Step 4: Adding the magnetic phase

- Open "sarah191.pcr" with a text editor (notepad, notepad++) and open the text of the structural refinement "dymn6ge6.pcr".

- Change the number of phases to 2 since we will now have a nuclear and magnetic phase. [1]

- Copy and paste the created magnetic phase just before line
  !   2Th1/TOF1 [2]

- Make sure there are no blank lines before or after the pasted section.

2→insert magnetic phase

Step 4: Adding the magnetic phase

- The correct profile parameters were refined for the nuclear phase and should be copied into the magnetic phase. Paste in the line before ! Propagation vectors:

- Close and save the Text of the pcr with both the magnetic and nuclear phases.

- To check the phases were added correctly run a refinement. Since no intensity has been added to the coefficients for the magnetic phase this should give the same refinement as for just the nuclear phase, but with a comment to indicate zero intensity is coming from one of the phases.

Copy

Paste

Step 5: Fitting a magnetic model: SDW

- Consider first a real only solution Γ(2) that will yield a spin-density-wave for the incommensurate k-vector.

- As discussed fix MN2 to be proportional to MN3 [1]

- Model with Γ(2) corresponds to C1. Put anti-parallel moments on Dy and Mn as shown in [2].

- Close and save.

- Run the refinement until it has converged.

Step 5: Fitting a magnetic model: SDW

- Spin structure can be visualized by opening .fst file for magnetic phase (created name ends in 2) with FPStudio.

- Visualized unit cells can be increased to follow the SDW as the magnitude of the moment varies along c-axis.

- Check prf file and fst to see Γ(2) model

- Recall neutrons measure the moment perpendicular to Q. So intensity at these reflections correspond to c-axis spins.

- Zero intensity at 10 and 14 degs corresponding to (001) reflections. Only ab-plane will give intensity.

- The spins form a SDW. To define a helical structure the Real and Imaginary components have to be orthogonal. As an example edit the BVs in the pcr file for the Dy atom to create a helical structure.
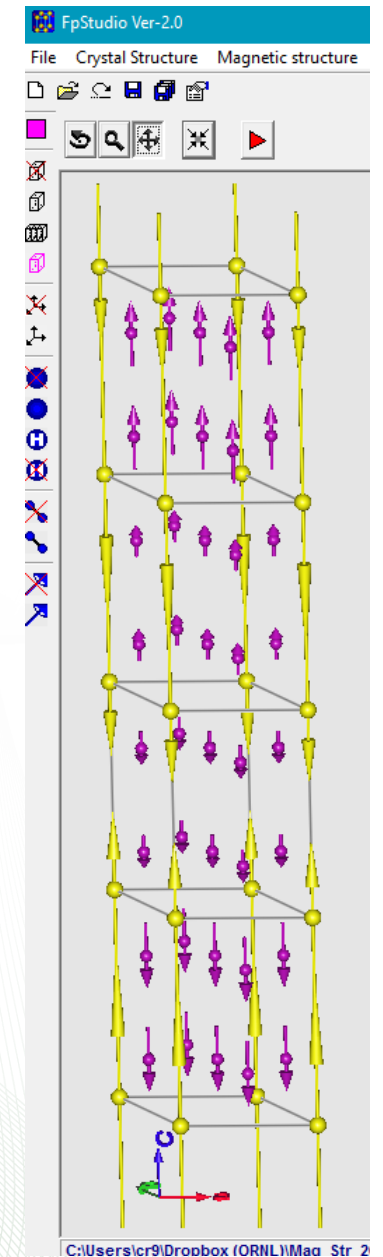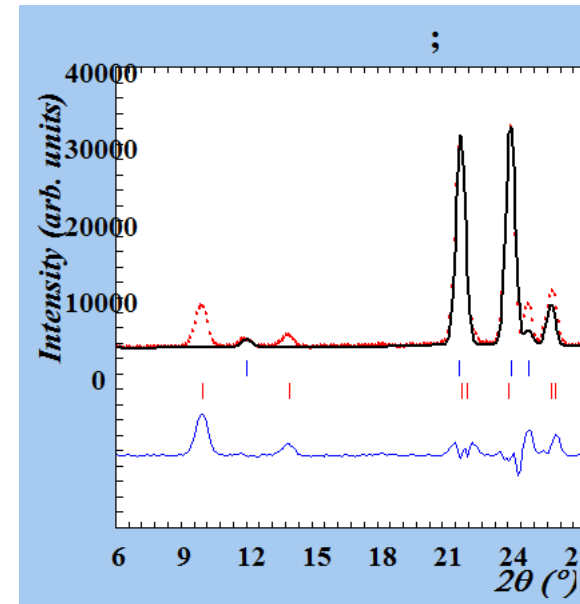
Step 5: Fitting a magnetic model: Helical

- Consider ab-plane spins only Γ(5). Note complex nature.

- Reasonable starting model given knowledge of compound is to have Dy-Dy and Mn-Mn ferromagnetic and Dy-Mn antiferromagnetic.

- This is achieved using BV(1) and BV(2) for Dy (c2,c3 in Fullprof) and BV(3) and BV(5) for Mn (c3,c5 in Fullprof).
  Combining these BVs will give spins for Mn along the b-axis.
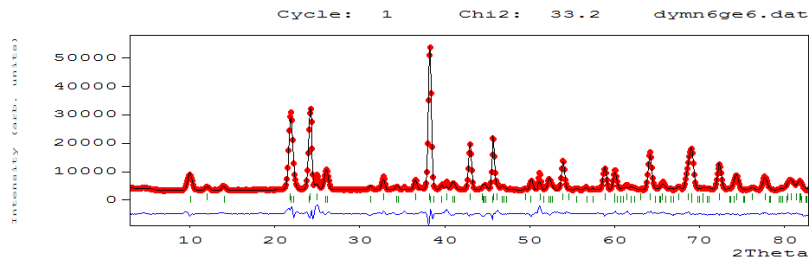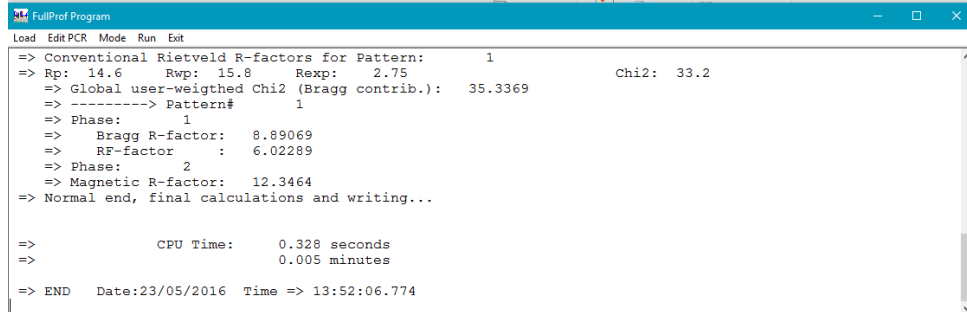
- Save and refine.

Step 5a: Fitting a magnetic model

- Check prf file and fst to see fit for the $\Gamma(5)$ model with chosen BVs.

- Intensity at 10 and 14 degs corresponding to (001) reflections.

- Spin structure can be visualized by opening .fst file for magnetic phase (created name ends in 2) with FPStudio.

- Visualized unit cells can be increased to follow the Helical Mn and SDW Dy.

- To define a helical structure the Real and Imaginary components have to be orthogonal. This occurs for the chosen of BVs of Mn.
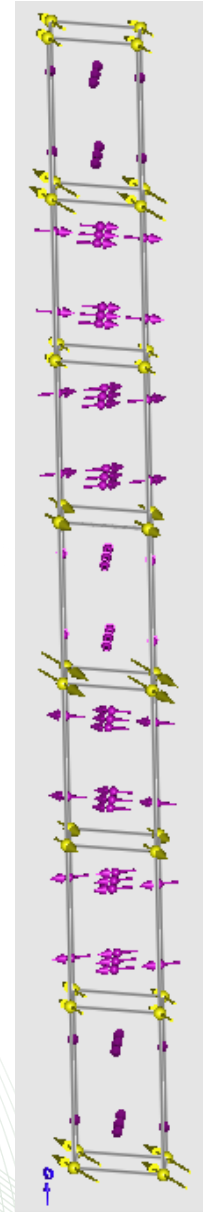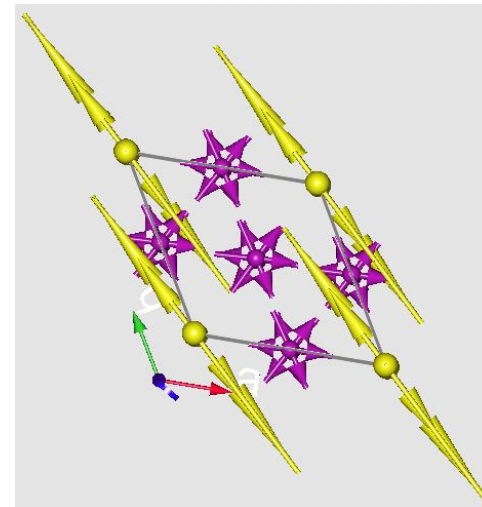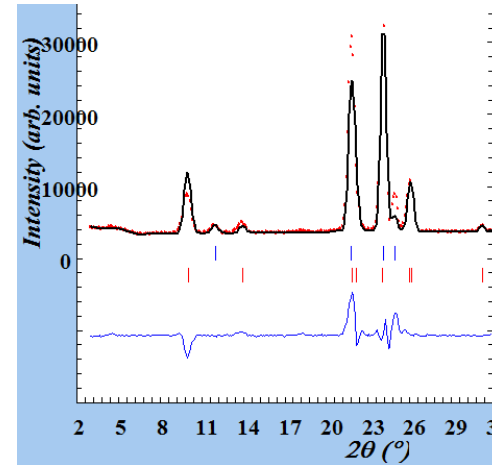
Step 5a: Fitting a magnetic model

- Neither $\Gamma(2)$ or $\Gamma(5)$ alone is a suitable model, so combine both by allowing c1 [$\Gamma(2)$, BV(1)] to refine, along with $\Gamma(5)$.

- The model now gives intensity to all measured peaks.

FullProf Program

Load Edit PCR Mode Run Exit

```
=> Conventional Rietveld R-factors for Pattern:        1
=> Rp:  14.6    Rwp:  15.8    Rexp:   2.75              Chi2:  33.2
   => Global user-weigthed Chi2 (Bragg contrib.):   35.3369
   => ---------> Pattern#    1
   => Phase:      1
   =>    Bragg R-factor:   8.89069
   =>    RF-factor    :   6.02289
   => Phase:      2
   => Magnetic R-factor:  12.3464
=> Normal end, final calculations and writing...

=>          CPU Time:     0.328 seconds
=>                        0.005 minutes

=> END   Date:23/05/2016  Time => 13:52:06.774
```

Cycle: 1   Chi2:   33.2   dymn6ge6.dat

```
P -1                    <--Space group symbol for hkl generation
! Nsym   Cen  Laue  Ireps  N_Bas
    5      1   10     -3     5
! Real(0)-Imaginary(1) indicator for Ci
   0  0  0  0  0
!
SYMM  X, Y, Z
BASR   0   0  12    6    6    0  3.46 -3.5   0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASR   0   0   4    2    2    0    2   -2    0    0    1    0   -2   -1    0
BASI   0   0   0    0    0    0    0    0    0  1.73   0  -3.5 -1.7   0
BASR   0   0   4    2    2    0    2   -2    0   -2    0    0   -2   -4    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
SYMM -Y, X-Y, Z
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASR   0   0   4    1    0    0   -1   -2    0   -1   -1    0    1   -1    0
BASI   0   0   0  1.73   0    0  -1.7 -3.5   0  1.73 1.73    0  -1.7 1.73   0
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
SYMM -X+Y+1, -X+1, Z
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASR   0   0   4    0    1    0    2    1    0   -2    0    0   -2   -4    0
BASI   0   0   0    0  -1.7   0  -3.5 -1.7   0    0    0    0    0    0    0
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
SYMM -Y+1, X-Y+1, Z
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASR   0   0   4    1    0    0   -1   -2    0    0    1    0   -2   -1    0
BASI   0   0   0  1.73   0    0  -1.7 -3.5   0    0  1.73   0  -3.5 -1.7   0
SYMM -X+Y, -X, Z
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASR   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASI   0   0   0    0    0    0    0    0    0    0    0    0    0    0    0
BASR   0   0   4    0    1    0    2    1    0   -1   -1    0    1   -1    0
BASI   0   0   0    0  -1.7   0  -3.5 -1.7   0  1.73 1.73    0  -1.7 1.73   0
!
!Atom  Typ  Mag Vek    X        Y        Z        Biso     Occ       C1      C2      C3
!       C4       C5       C6       C7       C8       C9      MagPh
DY1    MDY3  1  0  0.00000  0.00000  0.00000  0.30000  1.00000    1.000   0.363  -1.490
                      0.00     0.00     0.00     0.00     0.00   911.00  101.00   21.00
       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
MN2    MMN3  2  0  0.50000  0.00000  0.25040  0.30000  1.00000   -1.000   0.000   0.736
                      0.00     0.00     0.00     0.00     0.00   911.00    0.00   11.00
       0.000    0.736    0.000    0.000    0.000    0.000  0.00000
       0.00    11.00     0.00     0.00     0.00     0.00    0.00
MN3    MMN3  2  0  0.00000  0.50000  0.74960  0.30000  1.00000   -1.000   0.000   0.736
                      0.00     0.00     0.00     0.00     0.00   911.00    0.00   11.00
       0.000    0.736    0.000    0.000    0.000    0.000  0.00000
       0.00    11.00     0.00     0.00     0.00     0.00    0.00
```
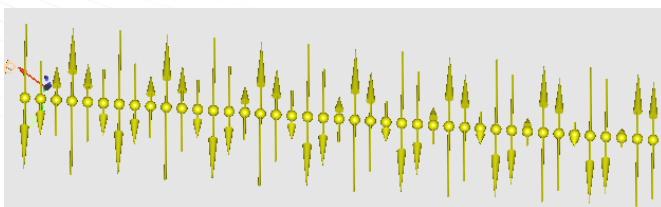
HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE
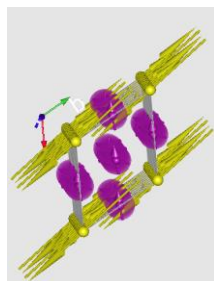
Step 5b: Fitting a magnetic model (visualize)
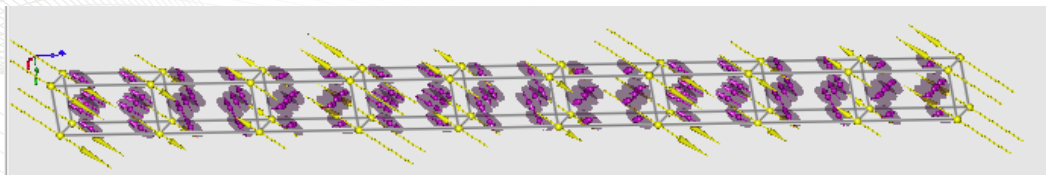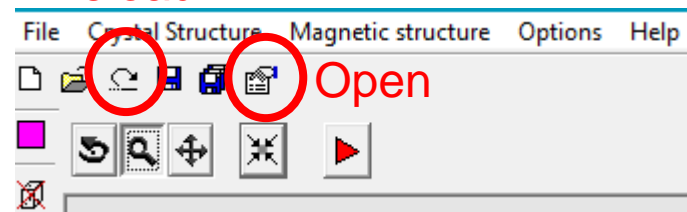
- Fst file can be edited to show envelope.

SDW for Dy

Helical for Mn

- Pitch of the rotation can be altered and unfixed from the real components to create a cycloidal structure, but this doesn't improve the fit.

- The magnitude of the magnetic moment size at any specific position can be seen with Fpstudio under:
  "Magnetic structure"→"list moments

Reload

Open

Alternative solution with two k-vectors

- While the magnetic fit to SDW or Helical is good, it is not the final solution.

- An alternative solution is to use two propagation vectors, k1=(0,0,0) and k2=(0,0,0.165).

  Rodriguez-Carvajal & Bouree EPJ 22, 00010 (2012)

Figure 19. Powder diffraction pattern of $DyMn_6Ge_6$ at 11 K taken at DMC (PSI) with $\lambda = 2.425$ Å. The first propagation vector is $k_1 = (0, 0, 0)$ and the second one is $k_2 = (0, 0, \delta)$ with $\delta \approx 0.1651(4)$, quite close to $\delta = 1/6$. The calculated nuclear diffraction pattern is shown as a continuous line.

- Check with SARAh the solutions for k=(0,0,0).

→The same IRs are solutions as previously used.

- The physics tells us k=(000) is the FM c-axis.

- Γ(2) corresponds to k1 and Γ(5) corresponds to k2.

- This solution is included in the folders, but can be readily produced by following the previous steps in this example.
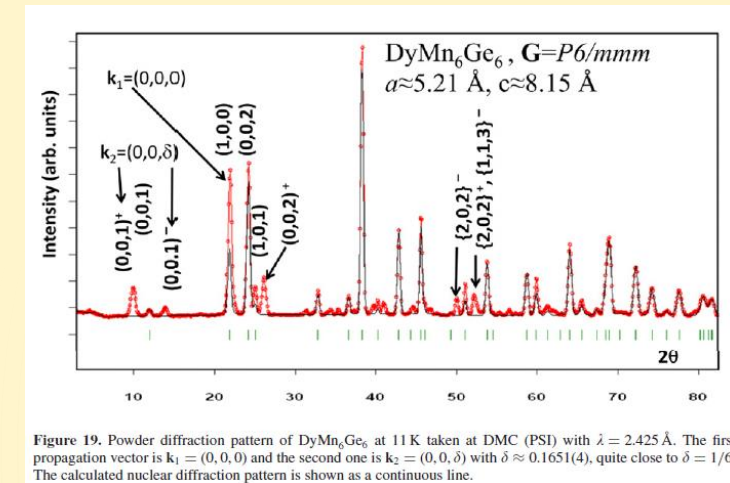
Alternative solution with two k-vectors

- Change number of phases to 3.

- Create the 3rd magnetic phase by copying and pasting the current magnetic phase.

- Alter the propagation vector of phase 2 to k=(0,0,0) and make all coefficients apart from C1 zero. i.e. k=(0,0,0) corresponds only to $\Gamma(2)$.

- For phase 3 make C1 values zero i.e k=(0,0,0.165) corresponds only to $\Gamma(2)$.

- Refinement now is improved further.
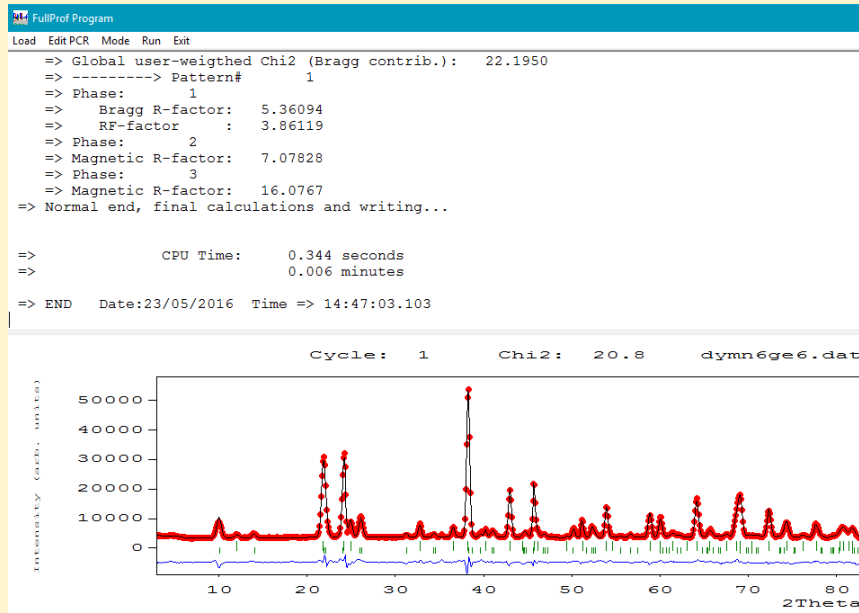
COMM ;
! Files > DAT-file: ...., PCR-file: dymn6ge6
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni
   1   3   38   0   0   0   0   0   0   0   0   0   0   0   0

!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho
   0   0   1   0   1   0   4   0   0   3   8   0   0   0   0

! Lambda1 Lambda2   Ratio   Bkpos   Wdt   Cthm   muR   Asy
  1.703700 1.703700 1.00000 40.000 5.000 0.0000 1.2800 18

!NCY Eps R_at R_an R_pr R_gl   Thmin   Step   Thm
  6 0.50 1.00 1.00 1.00 1.00   3.0000   0.100000 82.9

!2Theta/TOF/E(Kev)   Background   for Pattern# 1

BASR   0   0   0   0   0   0   0   0   0   0   0   0
BASI   0   0   0   0   0   0   0   0   0   0   0   0
SYMM -Y+1, X-Y+1, Z
BASR   0   0   0   0   0   0   0   0   0   0   0   0
BASI   0   0   0   0   0   0   0   0   0   0   0   0
BASR   0   0   0   0   0   0   0   0   0   0   0   0
BASI   0   0   0   0   0   0   0   0   0   0   0   0
BASR   0   0   4   1   0   0 -1 -2   0   1   0 -2 -1
BASI   0   0   0 1.73   0 -1.7 -3.5   0 1.73   0 -3.5 -1.7
SYMM -X+Y, -X, Z
BASR   0   0   0   0   0   0   0   0   0   0   0   0
BASI   0   0   0   0   0   0   0   0   0   0   0   0
BASR   0   0   0   0   0   0   0   0   0   0   0   0
BASI   0   0   0   0   0   0   0   0   0   0   0   0
BASR   0   0   4   1   0   2   1   0 -1 -1   0   1 -1
BASI   0   0   0 -1.7   0 -3.5 -1.7 0 1.73 1.73 0 -1.7 1.73

!Atom Typ Mag Vek X   Y   Z   Biso Occ   C1   C2   C3
!   C4   C5   C6   C7   C8   C9   MagPh
DY1 MDY3 1 0 0.00000 0.00000 0.00000 0.30000 1.00000 0.411 0.000 0.000
              0.00   0.00   0.00   0.00   0.00 111.00   0.00   0.00
  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
MN2 MMN3 2 0 0.50000 0.00000 0.25040 0.30000 1.00000 -0.288 0.000 0.000
              0.00   0.00   0.00   0.00   0.00 101.00   0.00   0.00
  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
MN3 MMN3 2 0 0.00000 0.50000 0.74960 0.30000 1.00000 -0.288 0.000 0.000
              0.00   0.00   0.00   0.00   0.00 101.00   0.00   0.00
  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
!-------> Profile Parameters for Pattern # 1
! Scale   Shape1   Bov   Str1   Str2   Str3   Strain-Model
  95.044   0.00000 0.96612 0.00000 0.00000 0.00000   0
  51.00000   0.00   0.000   0.000   0.000   0.000
!   U   V   W   X   Y   GauSiz LorSiz Size-Model
  1.932143 -1.589736 0.469940 0.000000 0.000000 0.000000 0.000000 0
  61.000   71.000   81.000   0.000   0.000   0.000   0.000
!   a   b   c   alpha   beta   gamma   #Cell Info
  5.206095 5.206095 8.149457 90.00000 90.00000 120.000000
  41.00000 41.00000 91.00000 0.00000 0.00000 41.00000
! Pref1   Pref2   Asy1   Asy2   Asy3   Asy4
  0.00000 0.00000 0.01425 0.00000 0.00000 0.00000
   0.00   0.00   31.00   0.00   0.00   0.00
! Propagation vectors:
  0.0000000 0.0000000 0.0000000   Propagation Vector 1
   0.000000   0.000000   0.000000
!--
! Data for PHASE number: 3 ==> Current R_Bragg for Pattern# 1:   0.00
!--
Magnetic Phase
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth   ATZ   Nvk Npr More
  3   0   0 0.0 0.0 1.0   1 -1 -2   0   0   0.000 -1   0   0

P -1   <--Space group symbol for hkl generation
! Nsym Cen Laue Ireps N_Bas
   5   1   10   -3   5

FullProf Program
Load Edit PCR Mode Run Exit
    => Global user-weigthed Chi2 (Bragg contrib.):   22.1950
    => ---------> Pattern#   1
    => Phase: 1
    =>   Bragg R-factor: 5.36094
    =>   RF-factor   :   3.86119
    => Phase: 2
    => Magnetic R-factor: 7.07828
    => Phase: 3
    => Magnetic R-factor: 16.0767
 => Normal end, final calculations and writing...

 =>   CPU Time: 0.344 seconds
 =>   0.006 minutes

 => END   Date:23/05/2016 Time => 14:47:03.103

Cycle: 1   Chi2: 20.8   dymn6ge6.dat

Supplemental Material:

- Fit solution using only real BVs outputted from SARAh Representational Analysis

- More intuitive, but requires knowledge of system.

- Makes BVs for commensurate and SDW easier to interpret.

- Imaginary component can be added to create e.g. Helical, BUT care should be taken to make sure it is appropriate (loose symmetry constraints).

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Step 3(Real IRs): Symmetry analysis

- Use SARAh (or BasIreps) to generate the Irreducible Representations (IRs) and basis vectors (BVs) associated with the propagation vectors, crystal structure and magnetic atom positions.

- Open SARAh- Representational analysis

- Under "Define Parameters" input:
  "Space group" No. 191 or H_M Symbol P 6/m m m
  "K-vector" 0 0 0.165
  "Atoms" Dy   0   0 0
             Mn 0.5 0 0.2504

- Run program using "Calculate"
  Select directory where the created output files will go (i.e. current directory).
  Some pop windows will appear during calculation. For source of IR select Kovalev and "Yes" so the solution will be easier to interpret, although not imaginary.

Step 3(Real IRs): Symmetry analysis

- SARAh outputs several files to explain the allowed symmetries.

- From pdf created from .tex file:

IR	BV	Atom	$m_{\parallel a}$	$m_{\parallel b}$	$m_{\parallel c}$	$im_{\parallel a}$	$im_{\parallel b}$	$im_{\parallel c}$
Γ_2	ψ_1	1	0	0	12	0	0	0
Γ_5	ψ_2	1	0	3	0	0	0	0
	ψ_3	1	3.464	1.732	0	0	0	0

Table 1: Basis vectors for the space group P 6/m m m with $\mathbf{k}_{11}$ = (0, 0, .165).The decomposition of the magnetic representation for the Dy site (0, 0, 0) is $\Gamma_{Mag} = 0\Gamma_1^1 + 1\Gamma_2^1 + 0\Gamma_3^1 + 0\Gamma_4^1 + 1\Gamma_5^2 + 0\Gamma_6^2$. The atom of the primitive basis is defined according to 1: (0, 0, 0).

- Γ_2 and Γ_5 form the common IRs.
  Both Γ_2 (c-axis) and Γ_5 (ab-plane) will be needed.

- The Mn is split into 2 orbits (3 atoms at z=0.2504 and 3 at z=0.7496). For this exercise we will fix both orbits to be the same (in or out of phase). This reduces the free parameters to make the problem more tractable. Moreover for in this kind of compound generally the Mn-Mn interactions are ferromagnetic suggesting constrained orbits.

IR	BV	Atom	$m_{\parallel a}$	$m_{\parallel b}$	$m_{\parallel c}$	$im_{\parallel a}$	$im_{\parallel b}$	$im_{\parallel c}$
Γ_2	ψ_1	1	0	0	4	0	0	0
		2	0	0	4	0	0	0
		3	0	0	4	0	0	0
Γ_3	ψ_2	1	2	0	0	0	0	0
		2	-2	-2	0	0	0	0
		3	0	2	0	0	0	0
Γ_4	ψ_3	1	2	4	0	0	0	0
		2	2	-2	0	0	0	0
		3	4	2	0	0	0	0
Γ_5	ψ_4	1	2	3	0	0	0	0
		2	-2	1	0	0	0	0
		3	0	-1	0	0	0	0
	ψ_5	1	0	-3	0	0	0	0
		2	0	-3	0	0	0	0
		3	0	-3	0	0	0	0
	ψ_6	1	0	1.732	0	0	0	0
		2	0	-1.732	0	0	0	0
		3	3.464	1.732	0	0	0	0
	ψ_7	1	-3.464	-1.732	0	0	0	0
		2	-3.464	-1.732	0	0	0	0
		3	-3.464	-1.732	0	0	0	0
Γ_6	ψ_8	1	0	0	3	0	0	0
		2	0	0	-3	0	0	0
		3	0	0	0	0	0	0
	ψ_9	1	0	0	1.732	0	0	0
		2	0	0	1.732	0	0	0
		3	0	0	-3.464	0	0	0

Table 2: Basis vectors for the space group P 6/m m m with $\mathbf{k}_{11}$ = (0, 0, .165).The decomposition of the magnetic representation for the Mn site (.5, 0, .2504) is $\Gamma_{Mag} = 0\Gamma_1^1 + 1\Gamma_2^1 + 1\Gamma_3^1 + 1\Gamma_4^1 + 2\Gamma_5^2 + 1\Gamma_6^2$. The atoms of the nonprimitive basis are defined according to 1: (.5, 0, .2504), 2: (.5, .5, .2504), 3: (0, .5, .2504).

Step 4(Real IRs): Adding the magnetic phase

- Open SARAh-Refine.

- Under "Fullprof Controls" [1]
  select "Load SARAh MAT file"
  and open file created by SARAh
  (sarah191.mat)

- Under "Common Irreducible
  Representations" check boxes
  next to both Γ(2) and Γ(5) and
  press select to associate all BVs. [2]

- Create the magnetic phase part of the PCR file by selecting "OK" next to
  "Generate model PCR phase" [3]. This creates a file "sarah191.pcr" that
  can be copied and pasted into the crystal structure pcr file from Step 1.
  Note: only open the created "sarah191.pcr" with a text editor and not
  EdPCR.

Step 4(Real IRs): Adding the magnetic phase

- Open "sarah191.pcr" with a text editor (e.g. notepad++) and open the text of the structural refinement "dymn6ge6.pcr" (either from EdPCR or text editor).

- Change the number of phases to 2 since we will now have a nuclear and magnetic phase. [1]

- Copy and paste the created magnetic phase just before line
  !   2Th1/TOF1 [2]

- Make sure there are no blank lines before or after the pasted section.

2→insert magnetic phase

Step 4(Real IRs): Adding the magnetic phase

- The correct profile parameters were refined for the nuclear phase and should be copied into the magnetic phase. Paste in the line before ! Propagation vectors:

- Close and save the Text of the pcr with both the magnetic and nuclear phases.

- To check the phases were added correctly run a refinement. Since no intensity has been added to the coefficients for the magnetic phase this should give the same refinement as for just the nuclear phase, but with a comment to indicate zero intensity is coming from one of the phases.

Copy

Paste

Step 5a(Real IRs): Fitting a magnetic model: SDW

- Consider first a solution that will yield a spin-density-wave for the incommensurate k-vector. (BVs real)

- As discussed fix MN2 to be proportional to MN3 [1]

- Start model with Γ(2). There is only one BV, corresponding to coefficients C1 in Fullprof. There is evidence for a ferrimagnetic component along the c-axis so put anti-parallel moments on Dy and Mn as shown in [2].

- Close and save.

- Run the refinement until it has converged.

Step 5a(Real IRs):
Fitting a magnetic model: SDW

- Check prf file and fst to see fit for the Γ(2) model.

- Recall neutrons measure the moment perpendicular to Q. So intensity from Γ(2) at reflections with H or L equal to zero, e.g around 2θ=22°.

- Zero intensity at 10 and 14 degs corresponding to (001) reflections. Only ab-plane spins will give intensity for these reflections.

- Spin structure can be visualized by opening .fst file for magnetic phase (created name ends in 2) with FPStudio.

- Visualized unit cells can be increased to follow the SDW.
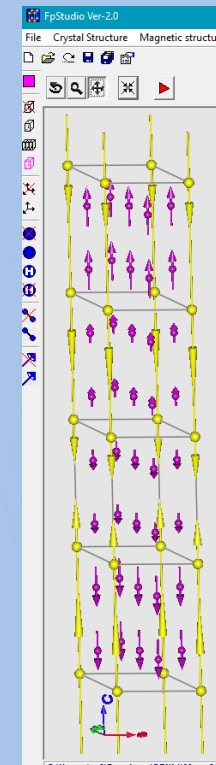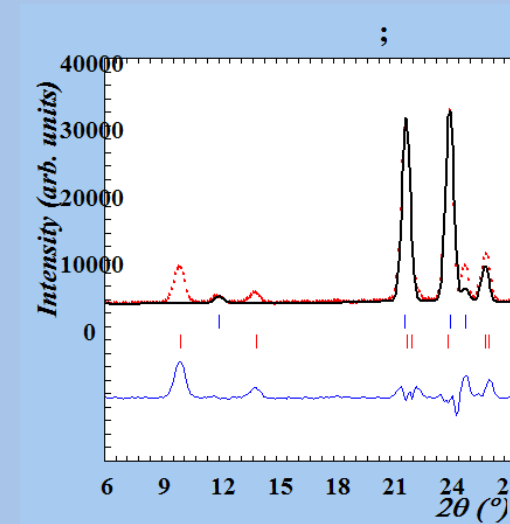
Step 5a(Real IRs): Fitting a magnetic model: SDW

- Consider ab-plane spins only Γ(5).

- Reasonable starting model given knowledge of compound is to to have Dy-Dy and Mn-Mn ferromagnetic and Dy-Mn antiferromagnetic.

- This is achieved using BV(1) for Dy (c2 in Fullprof) and BV(3) for Mn (c3 in Fullprof).

- Save and refine.

Step 5a(Real IRs): Fitting a magnetic model: SDW

- Check prf file and fst to see fit for the Γ(5) model with chosen BVs.

- Intensity at 10 and 14 degs corresponding to (001) reflections.

- Spin structure can be visualized by opening .fst file for magnetic phase (created name ends in 2) with FPStudio.

- Visualized unit cells can be increased to follow the SDW.

- Neither Γ(2) or Γ(5) alone is a suitable model, so combine both by allowing c1 [Γ(2), BV(1)] to refine.

- The model now gives intensity to all measured peaks.

SDW

- The magnitude of the magnetic moment size at any specifc position can be seen with Fpstudio under: "Magnetic structure"→"list moments"

Model can be slightly improved by adding equal and opposite components to C5

Step 5b(Real IRs): Fitting a magnetic model: Helical

- An alternative to a SDW (varying spin magnitude) is rotating spins forming a helical or cycloidal structure.

- To define a helical structure the Real and Imaginary components have to be orthogonal. This dictates the choice of BVs.

- Copy and paste C2-C5 and make these new coefficients (C6-C9) imaginary by adding 1s to the circled indicator.

- Alter N_bas to 9

Copy highlighted   **Paste**

Step 5b(Real IRs): Fitting a magnetic model: Helical

- Refining the imaginary BVs of C5 yields the same solution as purely real.

- Instead need to refine orthogonal BVs. Try C9 with equal value to C3. For Dy refine C7 equal to C2

Step 5b(Real IRs): Fitting a magnetic model: Helical

- Fst file can be edited to show envelope.