Neutron Training Course.

Powder Diffraction - Example of a magnetic structure refinement: MnF_2

In the simplest case, the magnetic scattering can be calculated by entering a second crystalline phase containing the magnetic Mn atoms only.

Phase 1 (non-magnetic): Space group P 4_2/m n m : Mn on (0, 0, 0); F on (0.307, 0.307, 0)

Phase 2 (magnetic): Space group P 1 : Mn1 on (0, 0, 0); Mn2 on (0.5, 0.5, 0.5)

- set Uiso = 0.005 for all atoms in both phases

- when entering the Mn atoms for the magnetic phase 2 use **I 1** (insert atom with sequence number 1) to insert the first atom, instead of **I N**, otherwise the sequence numbering assumed below when adding atom parameter constraints will not be correct.

Insert second phase (phase name, space group and lattice parameters may be entered from EXPGUI). Press EXPEDT button.

> **P** (Powder data preparation)
> **P** (Phases - lattice and space group)
> **I** (insert new phase)
> Enter identifying name> **MnF2 magnetic**
> Enter Space group> **P 1**
> Enter real lattice parameters (Å and °)> **4.87, 4.87, 3.31, 90.0, 90.0, 90.0**
>
> **M 2** (modify phase type flag for phase 2)
> **C** (magnetic structure only)
> **X** - exit to previous menu
> **X** -   "   "   "
> **X** - exit to main EXPEDT menu

On the VMS system, **M 2** above will toggle the phase as magnetic and you will be prompted for two more options. At the first of these answer **Y** (generate only magnetic reflections for phase 2) followed by **N** (none of the lattice constants are doubled in the magnetic cell).

Edit Mn form factors (to set magnetic form factor coefficients for Mn^{2+})

> **L** (Least squares refinement setup)
> **F** (edit atom form factors)
> **M** (edit magnetic form factor info - note: ALWAYS update (**U**) before exiting this menu)
>
> Enter atom type> **Mn**
>
> **C** - change values of coefficients
>
> A(1) and B(1): **0.422   17.684**
> A(2) and B(2): **0.5948   6.005**
> A(3) and B(3): **0.0043   -0.609**
> A(4) and B(4): **0.0   0.0**
> C: **-0.0219**
>
> DO NOT modify <j2> values (answer **N** when prompted)
>
> - as a check, the value of mff(0) output to the screen should be very close to 1.0.
>
> **U** - update experiment file (MUST DO THIS, or new coefficients will not be saved!)

X - exit to previous menu
X -   "   "   "
X - exit to main EXPEDT menu

Fix / Constrain lattice parameters between two phases

L O L (Least squares - Overall parameters - Lattice parameters)
P 2 (select phase 2)
F (fix specific reciprocal metric tensor elements) - the α, β and γ angles
I (insert a hold parameter)
  rm12
I
  rm13
I
  rm23
X - exit to previous menu

K (set constraints among reciprocal metric tensor elements)
I (insert constraint) - first the **a** unit cell edge
   1 rm11 1.0
   1 rm22 1.0 - should happen automatically, but won't do any harm to include explicitly
   2 rm11 1.0
   2 rm22 1.0
   <return>
I (insert constraint) - then the **c** unit cell edge
   1 rm33 1.0
   2 rm33 1.0
   <return>
X - exit to previous menu
X -   "   "   "
X -   "   "   "
X - exit to main EXPEDT menu

Fix / Constrain Atom parameters between two phases

L A (Least squares - Atom parameters)
P 2 (phase 2)
F (fix specific atom parameters) - components of moment in xy plane and coordinates
I (insert a hold parameter) - fix atom 1 mx, my, x, y and z
  1 (atom sequence number 1)   *** ensure sequence numbers are correct ***
  mx (component of moment in x direction will be fixed = 0.0)
I
  1
  my (component of moment in y direction will be fixed = 0.0)
I
  1
  x
I
  1
  y
I
  1
  z
- repeat these inserts (**I**) for atom 2 mx, my, x, y and z
X - exit to atom parameters menu

(note: because the Mn atoms are on special positions (0,0,0) and (½,½,½) in the nuclear structure we will not refine their x,y,z and the fixes are not strictly necessary. Nevertheless it is good practice to fix them in case you inadvertently try to refine them later...)

K (Set atom parameter constraints)
I (Enter a new constraint) - Mn UISOs in nuclear and magnetic phases
  1 uiso 1 1.0   ** *ensure sequence numbers are correct* **
  2 uiso 1:2 1.0
  <return>
I (Enter a new constraint) - both Mn MZs in magnetic phase
  2 mz 1 1.0
  2 mz 2 -1.0   (note minus sign - moment at (½,½,½) is in
                                          opposite direction to moment at (0,0,0))

  <return>
X (exit to atom editing menu)

M (edit magnetic moment data)
M 1 (modify moment on atom 1)   ** *ensure sequence numbers are correct* **
Enter magnetic moment component 1> **0.0 0.0 1.5**
M 2 (modify moment on atom 2)
Enter magnetic moment component 1> **0.0 0.0 -1.5 (note minus sign)**
X - exit to atom parameters menu

Set Refinement Flags for magnetic moments

L A (Least squares - Atom parameters) *- not needed, already in L A menu*
P 2 - phase 2 (the magnetic atoms) *- not needed, already selected P 2*
V 1:2 m (modify refinement flags) - refine moments for atoms 1 and 2
D 1:2 m 5 (atom damping factors) - put 50% damping on moments

Finally, due to the way GSAS operates, you also need to enter the spin flip model menu and then leave it again, without changing any parameters, otherwise on your first attempt at least squares you will get an error message saying *ISAM record with key "CRS2   SPNFLP" has problems*.

M (edit magnetic moment data)
S (modify the spin flip model)
L (list the current spin flip info)
X - exit to previous menu
X -   "   "   "
X - exit to main EXPEDT menu
X - exit from EXPEDT

You can now use **POWPREF** and **GENLES** to refine the magnetic structure in an identical fashion to refining nuclear structures. When using **POWPLOT** to examine the fit, an additional set of reflection markers will be displayed to show the positions of the magnetic reflections.