

Defining & Fitting Magnetic Models in GSAS

Brian Toby APS

GSAS Implementation of Magnetism

- GSAS allows 4 types of structural models (phases)
 - 1) Nuclear (no magnetism)
 - 2) Magnetic only (no nuclear scattering)
 - 3) Combined Nuclear & Magnetic
 - 4) Macromolecular (no magnetism, duh!)
- GSAS does not implement edge centering
 - Must use a doubled cell instead
 - This leads to challenges in coupling magnetic and nuclear symmetry
- Almost no magnetism implementation in EXPGUI
 - must use EXPEDT

Input of Magnetic Symmetry

- Define a [normal] Hermann-Mauguin space group
- Designate phase as magnetic
- In appropriate submenu, designate which of the unique operators will be red (antisymmetry). Default is black.
 - Note that not all combinations are allowed in GSAS because of group theory rules, but don't count on GSAS to prevent use of invalid input

Input Parameters for Magnetic Atoms

- Atoms in magnetic phases can be flagged as magnetic
- Magnetic atoms have three extra parameters: M_x , M_y , M_z
 - These are orthogonal spin components:
 - M_x -- along a axis
 - M_y -- along b^* axis (perpendicular to a & c , e.g. direction of $a \times c$)
 - M_z -- in a - c plane and perpendicular to a (direction of $a \times b^*$)
 - For non-orthogonal systems, can use program GEOMETRY to see components computed in other directions
- GSAS will constrain components according to color symmetry
- Magnetic atoms will have an additional refinement flag, M
 - M varies M_x , M_y and (or) M_z as allowed by color symmetry

Other magnetism input for GSAS

- You must use the magnetic symmetry menu in GSAS even if you do not need to toggle any symmetry to red --- otherwise magnetic intensities are not computed
- Magnetic form factors: GSAS has a table with form factors from the "ILL Blue Book"
 - This does not include all possible magnetic ions
 - Make sure to enter the magnetic ions with the right valence (e.g. FE+3 not FE) or you will get the wrong form factor.
 - To see what is defined in GSAS, check for magnetic form factors in file c:\GSAS\DATA\ATMDATA.DAT
 - Look for lines that begin "XX+n M" and "XX+n N"

Strategies - 1

Since magnetic symmetry can be lower than that of the nuclear structure, how does one perform a fit?

1. Use two phases with different symmetry
 - Constrain cell lengths between phases
 - Constrain magnetic atom positions to be the same between phases
 - Constrain magnetic atoms to special positions for the higher symmetry
2. Use a single phase with the lower magnetic symmetry, but constrain crystallographically identical atoms to move together and stay on special sites

Strategies - 2

- GSAS does not implement all magnetic space groups directly (no edge centers)
 - Increase size of magnetic unit cell
 - Decrease phase fraction by $V_{\text{nuclear}}/V_{\text{magnetic}}$ (or refined moments will be incorrectly scaled)
 - Manually constrain moments of non-unique atoms

This is not automatic, it takes thought and sometimes some trial and error.

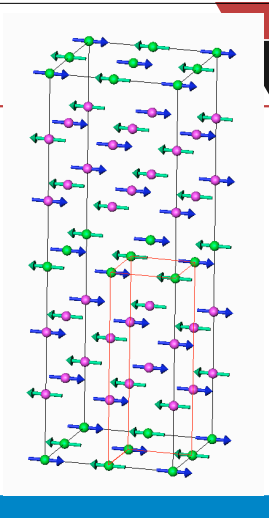
Strategies - 3

- Some people prefer to not deal with magnetic symmetry at all
 - Use magnetic cell with $P1$ symmetry (see 3rd example)
 - Easy to build a model; hard to do refinements (lots of constraints)
 - OK for simpler structures, but use care to get it right

Self-guided exercises

Same structure worked three ways

1. Use $Pmmm$ for nuclear phase; use $Fmm'm'$ ($2 \times 2 \times 2$) for magnetic phase (2 phases)
2. Use $Fmm'm'$ for nuclear and magnetic scattering (single phase)
3. Use $Pmmm$ for nuclear phase; use $P1$ ($2 \times 2 \times 2$) for magnetic phase (2 phases)



Other things to try

- List the generated magnetic spin directions with program GEOMETRY
- Visualize spin directions with VRSTPLOT and a VRML viewer
 - You will likely need to install VRweb from key (or other VRML 1.0 viewer like CosmoPlayer)
- Visualize spin directions with DRAWxtl (software on key)