Defining & Fitting Magnetic Models in GSAS

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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: Mx, My, Mz
  - These are orthogonal spin components:
    - Mx -- along a axis
    - My -- along b* axis (perpendicular to a & c, e.g. direction of a x c)
    - Mz -- in a-c plane and perpendicular to a (direction of a x 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 Mx, My and (or) Mz 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 \textit{Pmmm} for nuclear phase; use \textit{Fmm’’m’} \((2\times2\times2)\) for magnetic phase (2 phases)

2. Use \textit{Fmm’’m’} for nuclear and magnetic scattering (single phase)

3. Use \textit{Pmmm} for nuclear phase; use \textit{P1} \((2\times2\times2)\) for magnetic phase (2 phases)

Other things to try

- List the generated magnetic spin directions with program \textsc{Geometry}

- Visualize spin directions with \textsc{VRSTPLOT} and a VRML viewer
  - You will likely need to install \textsc{VRweb} from key (or other VRML 1.0 viewer like CosmoPlayer)

- Visualize spin directions with \textsc{DRAWxtl} (software on key)