Example Cr2WO6 (magndata #0.75) commensurate magnetic structure – modulation (propagation) vector: (0,0,0)

Neutron powder data measured at 4K on HB2A at HFIR

\( \lambda = 2.4097 \text{ A} \)

References:
Zhu et al., PRL 113, 076406 (2014)
PHYSICAL REVIEW B 92, 094419 (2015)

Input files: Cr2WO6_T4K.dat (powder profile data)
Cr2WO6.cif (nuclear structure)
Parent space group:

$P4_2/mnm$ (N. 136)

Propagation vector:

$k = (0,0,0)$

Magnetic site:

Cr 4e (0,0,z)
1. **Creating new jobname**

Start Jana2006

“**File → Structure → New**” opens a file manager

Left panel: locate directory with input files

Right panel: double-click at Cr2WO6
2. **Import Wizard**

Select “Magnetic parent structure: nuclear model from CIF”; NEXT

[On the screen: Select input CIF file]

Right panel: select the input file Cr2WO6.cif; OK

3. **Define magnetic propagation vector and form factors**

[On the screen: Define magnetic propagation vector and form factors]

Check “Use non-zero magnetic propagation vector” and fill its value: (0, 0, 0)

For “Atom type” select “Cr”; check “Use as a magnetic atom”

For “Magnetic formfactor <j0>” select Cr3+;

The same for Cr3+; NEXT; FINISH
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 “Cr2WO6_T4K.dat” and the format is “Free format of 2th, l, [sig(l)]”; “Debye-Scherrer Method”, NEXT

Choose OK if the program finds problems with the file format and requests to change the format of the file.

[On the screen: Complete/correct experimental parameters];

For “Wave length” type 2.4097; NEXT; FINISH

[On the screen: Data repository]

Optionally write the data temperature (?)

OK; YES to “Do you want to accept made changes?”;
5. **Refining of profile parameters by 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, b and c parameters;

In the page “Profile” change 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 8

OK; YES to rewrite the changes

“Edit refinement command”; In the page “Basic” change the number of cycles to 20

OK; “Run Refine”;

*The refinement should end with Rp~17.5%.*

“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 of LX; OK; YES to the question about rewriting;

“Run Refine”

*The refinement should converge to Rp~7.2%.*
### Peak-shape function

<table>
<thead>
<tr>
<th>Shape</th>
<th>Cutoff</th>
<th>Width (FWHM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lorentzian</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-Voigt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modified Lorentzian</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Anisotropic particle broadening

- None
- Axial method
- Tensor method

### Anisotropic strain broadening

- None
- Axial method
- Tensor method
“Show powder profile”; Some peaks are observed that should correspond to some impurity. The high Rp is probably due to these unadjustable peaks. Select the region 2θ from 10 to 20 degs – use the button “X exactly”. The peak (0 0 1) has some asymmetry.
QUIT
“Edit profile parameters” -> Asymmetry/Difractometer-> correction by divergence
Activate refinement of HpS/L and HmS /L keeping their default values
OK; YES to save changes
“Run Refine”;
The refinement should end with a similar Rp, but the asymmetry of the peak is well fit
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”;
Fix all parameters for all atoms (“*” for “Atoms/Parameters” textbox ); “Add”; OK; OK;
The command will appear in the panel as “fixed all *”
“Run Refine”
The refinement should converge to Rp~14.4%, R(obs)~6.9%.
NEXT; YES to leave the form for Rietvel refinement
7. Testing different irreps to get the best single irrep model

[On the screen: Information]

NEXT [On the screen: Representation analysis]

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 the screen: List of kernels and epikernels]

NEXT

[On the screen: Select Shubnikov superspace group]

Select the first group in the list, one can see that this group forces cero magnetic moments and therefore is not possible

Select the second group in the list, the spin modulations are forced to be along z. With the Option “details” one gets information about the group and the resulting constraints on the spin modulation parameters.

Use the option “start profile simulation” to observe that the tetragonal groups in the list would not explain some of the magnetic peaks.

“Back”

Select some of the orthorhombic groups, and use the option “Start graphic simulation”, visualize the different models with different orthorhombic MSGs.

Use also “start profile simulation” to check that the group Pnn’m is a candidate to describe the symmetry of the phase. Select this group, which is one of the possible epikernels of mGM5-, together with Cmm’m. (JANA uses non-standard labels for the MSGs adapted to the basis used)
List of kernels and epikernels:

<table>
<thead>
<tr>
<th>Shubnikov space group</th>
<th>Axes</th>
<th>Origin shift</th>
<th>Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG4M+</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG1M-</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG2M-</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG3M-</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG4M-</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG5M+</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG5M+</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG5M+</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG5M+</td>
</tr>
<tr>
<td>P42/mnm'</td>
<td>(1,0,0)</td>
<td>(0,0,0)</td>
<td>mG5M+</td>
</tr>
</tbody>
</table>

Select from above kernels/epikernels one representative of a family of Shubnikov space groups for testing.
Select Shubnikov space group:

Shubnikov space group

Prnn̅m'  Prnn̅m

Atom  Moment  Global

Cr  (M,M,0)  (0,0,0)

Show details

Start graphic simulation  Start profile simulation

Back  Finish  Cancel

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.
8. Refinement in the superspace group – Pnn’m

[On the screen: Select Shubnikov space group]
Select in the left panel the group Pnn’m; FINISH
YES to the question “Do you want to test structure for the last epikernel?”;

[On screen: Select structure name]
Use the default name i.e. Cr2WO6_01 or any other; OK

Right click on the icon “Refine”; Select the page “Basic” and change the “Number of cycles” to 100 and the “Damping factor” to 0.1;
Select the page “Various”. Use the button “Restrictions”. All atoms are restricted to have identical ADP parameters;
Use button “Fixed commands” and fix all coordinates and delete or disable fixing of ADP’s (if present).
OK; OK; “Yes+start”;
The refinement should end with Rp~8.8% and Bragg R factors R(obs) ~4.5%, 4.7% and 3.1% for all, nuclear and magnetic reflections, respectively. (Edit/View → “View of Refine”)
Use “Tools → Powder → Profile” viewer and check fit of the calculated powder profile:
Select the page of Refine “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~7.4% and Bragg R factors R(obs) ~2.3%, 2.2% and 2.0% for all, main and satellite reflections, respectively. (“View of Refine”).
Go to ”EditProfile” and activate the cell parameter b to be refined. Run Refine. R values
Similar R values...
Edit/View → View of Refine: Mxo= 0.19(15) Myo=2.12(2)
9. **Visualize the refined model with VESTA or MVISUALIZE (Jmol)**

   Tools -> Graphic -> Run Viewer -> Draw+return

   File -> CIF utilities -> make CIF file
   Save the file. It is in magCIF format and includes the list of reflections. With an editor delete this last part of the file, and produce a file with extension .mcif

   This file can be used to visualize the structure with VESTA, Jmol or MVISUALIZE.

10. **The weak canting Mx0 is negligible**

    Edit atoms -> Cr1 -> Edit
    Fix to zero Mx0;
    Right click Refine -> Basic -> desactive “Automatic refinement keys”;
    Refine -> Rp ~7.35, R= 2.19, 2.22, 1.88

    Cr mx,my,0 (0, 2.12(2), 0)

    From FP tutorial of C. Del Cruz: (0, 2.04(2), 0)
K-SUBGROUPSMAG:
Maximal magnetic space groups for the parent space group 136 (P4₂/mnm) and the propagation vector k = (0, 0, 0)

Maximal subgroups which allow non-zero magnetic moments for at least one atom are coloured.

<table>
<thead>
<tr>
<th>N</th>
<th>Group (BNS)</th>
<th>Transformation matrix</th>
<th>General positions</th>
<th>Properties</th>
<th>Magnetic structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P4₂/mnm/m' (#136.503)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>2</td>
<td>P4₂/mnm/m' (#136.502)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>3</td>
<td>P4₂/mnm/m' (#136.501)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>4</td>
<td>P4₂/mnm/m' (#136.500)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>5</td>
<td>P4₂/mnm/m' (#136.499)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>6</td>
<td>P4₂/mnm/m' (#136.498)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>7</td>
<td>P4₂/mnm/m' (#136.497)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>8</td>
<td>P4₂/mnm/m' (#136.496)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>9</td>
<td>Cm'm/m' (#65.486)</td>
<td>(1 1 0 0 0 0 1 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>10</td>
<td>Cm'm/m' (#65.485)</td>
<td>(1 1 0 0 0 0 1 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
<tr>
<td>11</td>
<td>Pmm'm' (#65.384)</td>
<td>(1 0 0 0 0 0 0 1 0 0 0 1 0)</td>
<td>Show</td>
<td>Systematic absences</td>
<td>Show</td>
</tr>
</tbody>
</table>
Magnetic site splits into two independent sites

Two spin parameters to be fit
Only ONE independent magnetic site. But two independent spin components. Spin canting symmetry allowed

Two spin parameters to be fit
Irrep GM5+:

Irrep GM5-:

\[ P_{42}/mn1' \]

2 d.f.
2 basis f.

\[ C_{mm'm'} \]

\[ P_{nn'm'} \]

\[ P_{2'/m} \]

4 degrees of freed.
4 basis functions

\[ P_{42}/mn1' \]

2 d.f.
2 basis f.

\[ C_{m'mm} \]

\[ P_{n'mm} \]

\[ P_{2'/m} \]

4 degrees of freed.
4 basis functions