Single crystal diffraction

Example: magnetic structures in $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

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Single Crystal Diffractometer

**Advantage:**

- Much more information benefited from the 3D distributed Bragg peaks.
- Less samples – mg VS g
- Larger molecules and unit cells
- Less absorption due to small size, no isotope needed, such as for H, Li, even Eu, Sm, et. al. neutron “block” elements. Intensities corrected by applying the proper absorption correction, similar to the single crystal X-ray
- Fourier coefficients are more accurate – based on integrating well-resolved peaks
- Uniquely characterize non-standard scattering – superlattice or satellite peaks (commensurate and incommensurate), dimensionality of scattering (rods, planes, etc.)
- Extinction, domain, twining issues - FullProf can handle

**Disadvantage:**

- Need to grow a single crystal
- Data collection can be more time consuming

**Always GOOD to combine both X-ray/neutron powder and single crystal diffraction!**
Single Crystal Diffractometer @ ORNL

Small molecular
Unit cell < 20 Å
“Inorganic”

Macromolecular
Unit cell >20 Å
“Organic”
HB3A Four Circle Diffractometer

Monochromator: Vertically fixed and horizontally adjustable focusing silicon

Incident Wavelength: 1.003 Å (133), 1.542 Å (022), 2.525 Å (111)

Scattering angle: 5° < 2θ < 155°

Detector: ³He (single-point)

Crystal size: > 1 mm³, maximum crystal dimension 5mm

Flux at sample: $2.2 \times 10^7$ n/cm²/s

**Capability**

Temperature range 4-450 K

Fixed magnetic field ($H < 1$ T)

High Pressure cell up to 2 GPa.

Electric field option (1100 Volts power supply)

2D detector will be available soon!

Absorption correction!
Magnetic Structures in $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

Phase with both Commensurate AF and Incommensurate AF is selected: 17% Co-doping MnWO$_4$


![Diagram of magnetic structures](image)

- $P\ 1\ 2/c\ 1$
- $a=4.77\ \text{Å}$
- $b=5.72\ \text{Å}$
- $c=4.92\ \text{Å}$
- $\beta=90.9^\circ$

HB3A Four-circle diffractometer @HFIR
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf

Create .pcr file from .cif file

1-load .cif

2-open

3

4-save
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf
Nuclear structure of Mn$_{1-x}$Co$_x$WO$_4$ refined by FullProf
Nuclear structure of Mn$_{1-x}$Co$_x$WO$_4$ refined by FullProf

1. Refine

2. Go back to the scale factor tab (see flag-3) and be sure it is clicked on for refining. And save again.
Nuclear structure of Mn$_{1-x}$Co$_x$WO$_4$ refined by FullProf

Refine

1-select the created .pcr file

2-open
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf

Refine

1-Run Fullprof

2-run until convergent

3-exit

[Image of FullProf software interface showing the refinement process]
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf
Nuclear structure of Mn$_{1-x}$Co$_x$WO$_4$ refined by FullProf

Refine

1-Run Fullprof

2-run until convergent

3-exit
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf

Refine

Run Winplotr

extinction
Nuclear structure of Mn\(_{1-x}Co_xWO_4\) refined by FullProf

Refine
Nuclear structure of Mn$_{1-x}$Co$_x$WO$_4$ refined by FullProf

Refine

1-Run Fullprof

2-run until convergent

3-exit
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf

1-Open .pcr file in text editor

3-occup. refine with constrain

3-lambda/2 refine

4-Save & exit
Nuclear structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ refined by FullProf

Refine

1-Run Fullprof

2-run until convergent

3-exit
Nuclear structure of \( \text{Mn}_{1-x}\text{Co}_x\text{WO}_4 \) refined by FullProf

You also can refine the “anisotropic displacement parameters”, which generally requires to collect more reflections. Here it is good to go for the magnetic structure solution.
Commensurate magnetic structure of Mn$_{1-x}$Co$_x$WO$_4$

Create the magnetic phase using SARAh-Representation Analysis

1-Input str. Inf.

2-calculate
Commensurate magnetic structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

Create the magnetic phase using SARAh-Refine

1. Load SARAh MAT file
2. Generate/Edit .pcr file
3. K-Vector Search
4. Write FPStudio FST file

Generate magnetic phase in sarah13.pcr
We will create the magnetic phase .pcr file from nuclear structure .pcr by inserting the sarah13.pcr
Commensurate magnetic structure of Mn$_{1-x}$Co$_x$WO$_4$

Create the magnetic .pcr

---

<table>
<thead>
<tr>
<th>Data for PHASE number: 1</th>
<th>==&gt; Current R_Bragg for Pattern# 1: 4.43</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnWO4 Nuclear refinement, 12/Co</td>
<td></td>
</tr>
<tr>
<td>Na1 St Ag Pr1 Pr2 Pr3 Jbt Ir1 Isp Str Furth ATZ Nuk Np More</td>
<td></td>
</tr>
<tr>
<td>Co1 0 0 0 0 0 0 0 0 0 605.914 0 0 1</td>
<td></td>
</tr>
<tr>
<td>V1 Z 0 0 0 0 0 0 10000 10000 20000 0.0000 1 0 0 0</td>
<td></td>
</tr>
<tr>
<td>Z1 Z 0 0 0 0 0 0 10000 10000 20000 0.0000 1 0 0 0</td>
<td></td>
</tr>
<tr>
<td>P1 1/2/1 1/2/1 1/2/1</td>
<td></td>
</tr>
</tbody>
</table>

---

MnWO4 Nuclear refinement, 12/Co

| AtCom Typ X Y Z Bis0 OrgC C1 C3 C3 |
| Mn1 MN 0.50000 0.60491 0.25000 0.63149 0.41661 0 0 0 0 |
| Co1 Co 0.50000 0.60491 0.25000 0.63149 0.00339 0 0 0 0 |
| V1 V 0.0000 0.1000 0.25000 0.76664 0.5000 0 0 0 0 |

---

Insert/replace sarah13.pcr MnWO4_nuclear_5K.pcr

---

Save as commag.pcr
Commensurate magnetic structure of \( \text{Mn}_{1-x}\text{Co}_x\text{WO}_4 \)
Commensurate magnetic structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

Commag.pcr

1-select the created .pcr file

2-open
Commensurate magnetic structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

**Commag.pcr**

1. Open .pcr file

2. Click on selection

3. Contribution to Patterns

4. Click on option

5. 2sigma
Commensurate magnetic structure of Mn$_{1-x}$Co$_x$WO$_4$

Commag.pcr

1. FullProf PCR Editor
2. Click on and initial values
3. 3-click on and initial values
4. 4. Click to finalize
5. 5. Reduce factors
6. 6-save
7. 7-close
Commensurate magnetic structure of Mn$_{1-x}$Co$_x$WO$_4$

Commag.pcr

1-Run Fullprof

2-Select the data

3
Commensurate magnetic structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

Commag.pcr

Run until convergent

1-run until convergent

2-exit

3-FPStudio
Incommensurate magnetic structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$
Results

1-Results

=> Basis functions of Representation IRrep( 1) of dimension 1 contained 3 times in GAMMA
  Representation number : 1 for Site: 1
  Number of basis functions: 3

----- Block-of-lines for PCR start just below this line
P -1 

--Space group symbol for hkl generation

! Nsym Cen Laue Irep N_Bas
  2 1 1 -1 3

! Real(0)-Imaginary(1) indicator for Ci
  0 0 0

SYMM x,y,z
BASR 1 0 0 0 1 0 0 0 1
BASI 0 0 0 0 0 0 0 0 0

SYMM x,y,z+1/2
BASR -0.1253 0.0000 0.0000 0.0000 0.1253 0.0000 0.0000 0.0000 -0.1253
BASI -0.9921 0.0000 0.0000 0.0000 0.9921 0.0000 0.0000 0.0000 -0.9921

----- End-of-block of lines for PCR

=> Basis functions of Representation IRrep( 2) of dimension 1 contained 3 times in GAMMA
  Representation number : 2 for Site: 1
  Number of basis functions: 3

----- Block-of-lines for PCR start just below this line
P -1 

--Space group symbol for hkl generation

! Nsym Cen Laue Irep N_Bas
  2 1 1 -1 3

! Real(0)-Imaginary(1) indicator for Ci
  0 0 0

SYMM x,y,z
BASR 1 0 0 0 1 0 0 0 1
BASI 0 0 0 0 0 0 0 0 0

SYMM x,y,z+1/2
BASR 0.1253 0.0000 0.0000 0.0000 -0.1253 0.0000 0.0000 0.0000 0.1253
BASI 0.9921 0.0000 0.0000 0.0000 -0.9921 0.0000 0.0000 0.0000 0.9921

----- End-of-block of lines for PCR

3-Copy Gamm2

**k-vector:** (0.217 0.5 -0.46)
Incommensurate magnetic structure of Mn\textsubscript{1-x}Co\textsubscript{x}WO\textsubscript{4}

Incommag.pcr

1) Open “commag.pcr” file in text editor
2) Replace the symmetry part with Gamm2 generated from BasIreps
3) Change the “Nvк” value from 1 to -1, i.e. “-k” is included.
4) Change the propagation vector from (0.5 0 0) to (0.217 0.5 -0.46)
4) Save as “incommag.pcr”
1) Open “incommag.pcr” file in text editor
2) Change the indicator for C2 from Real “0” to Imaginary “1” and also have to change the 2nd BASI vector of site-2 from “0 -0.9921 0” to “0 0.9921 0” to keep the vector invariant.
3) Refine the parameter C3 by put code 31 for both Mn and Co
4) Save
Incommensurate magnetic structure of Mn$_{1-x}$Co$_x$WO$_4$
Incommensurate magnetic structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

incommag.pcr
Incommensurate magnetic structure of Mn$_{1-x}$Co$_x$WO$_4$

incommag.pcr

1-run until convergent

2-exit

3-FPStudio
Incommensurate magnetic structure of Mn$_{1-x}$Co$_x$WO$_4$
Incommensurate magnetic structure of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

incommag.fst
What is the magnetic structure at 5 K?

Combine two magnetic structures together
Single crystal diffraction

Thanks!

If you follow each step but still have problems or have any suggestions, please email me!

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