Example 12.10: MnWO₄

Last update 19.6.2024

Data Neutron single crystal Topic Commensurate AFM structure Level Intermediate

Input data

Data

Single crystal data collected on DEMAND at HFIR, ORNL neutron source at 5 K

Input files

MnWO4_magneticAF4_5K.int (single crystal data from FullProf) MnWO4_N_5K.cif (nuclear structure)

Additional information

Chemical formula: MnWO4 Antiferromagnetic commensurate: k=(1/2,0,0)

References

F. Ye, S. Chi, J. A. Fernandez-Baca, H. Cao, K.-C. Liang, Y. Wang, B. Lorenz, and C. W. Chu, (2012), Phys. Rev. B 86, 094429.

Highlights

In this example, a single crystal data files from FullProf are imported. Correction for $\lambda/2$ is performed, several type IV Shubnikov groups are tested.

Instructions

1. Data import

Start Jana2020

In the Main menu bar, use "Structure \rightarrow New" and open a new structure MnWO4_AF4_5K in the directory of Example 12.10

[On the screen: Specify type of the file to be imported] Select "Magnetic parent structure: nuclear model from CIF"; NEXT;

	Specify type of the file to be imported
Single crystal:	○ known diffractometer formats
	\bigcirc reflection file corrected for LP and absorption
	\bigcirc start with indexing procedure
Powder data:	🔿 various CW formats
	○ various TOF/ED formats
Structure:	⊖ from SHELX
	◯ from CIF
	○ from SHELX embedded in CIF
	○ from Jana2020 embedded in CIF
	○ from XD
	⊖ from Jana2000
Magnetic parent structure:	O nuclear model interactively
	O nuclear model from SHELX
	Inuclear model from CIF
	O nuclear model from Jana2006/Jana2020

In Windows file explorer: select the input file MnWO4_N_5K.cif; Open

2. Define the magnetic propagation vector and form factors

[On the screen: Define magnetic propagation vector and form factors] Set the "Number of superimposed IRs:" to '1' and select the propagation magnetic vector to be "Y, k13 (1/2,0,0)"

Select "Atom type" Co; check "Use as a magnetic atom" and for "Magnetic formfactor <j0>" select "Co3+";

📶 Data import wizard		×
	Define magnetic propagation vector(s) and form factors	
Number of superimposed IRs:	1 ▲ Y, k13 (1/2,0,0) ∨ Qa 1/2 Qb 0 Qg 0	
Formula - list of atomic types:	Co0.17 Mn0.83 O4 W	
Formula units:	2 Calculate density	
Atom type: Co \sim	Own scattering length for neutrons Use as a magnetic atom	
	O Own form factors Edit	
	Magnetic formfactor <j0> Co3+ V</j0>	
	+ Magnetic formfactor <j2></j2>	
	+ Magnetic formfactor <j4></j4>	
	Magnetic formfactor <j0>+c<j2></j2></j0>	

Repeat for Mn and use Mn3+ for its magnetic form factor.

📕 Data import wizard		×				
Define magnetic propagation vector(s) and form factors						
Number of superimposed IRs:	1 ▲ Y, k13 (1/2,0,0) ∨ Qa 1/2 Qb 0 Qg 0)				
Formula - list of atomic types:	Co0.17 Mn0.83 O4 W					
Formula units:	2 Calculate density					
Atom type: Mn \sim	Own scattering length for neutrons					
	O Own form factors					
	Magnetic formfactor <j0> Mn3+</j0>					
	+ Magnetic formfactor <j2></j2>					
	+ Magnetic formfactor <j4></j4>					
	○ Magnetic formfactor <j0>+c<j2></j2></j0>					

NEXT

[On the screen: Information] The parent structure is now created. NEXT

3. Import of the reflection file

[On the screen: Specify type of the file to be imported] Select "Single crystal: Reflection file corrected for LP and absorption"; NEXT Select the format "From FullProf file"; Check that the name of the input file is "MnWO4_magneticAF4_5K.int"; NEXT [On the screen: Complete/correct experimental parameters]

Check that wavelength is 1.536; Temperature is 5 K.

🔏 Data import wizard	×
	Complete/correct experimental parameters
Cell parameters:	4.77 5.72 4.92 90 90.9 90
Number of input indices:	4 Info about metrics parameters
1st modulation vector:	1/2 0 0
Radiation:	
○ X-rays	X-ray tube
Neutrons	
Kalpha1/Kalpha2 doub	let
Wavelength #1: 1.53	6
Wavelength #2:	
I(#2)/I(#1):	
Data collection details	
Temperature: 5	

NEXT; NEXT

```
[On the screen: Data repository]
OK
[On the screen: Information]
FINISH
[On the screen: Data repository]
OK
```

4. Testing different irreps to get the best model

[On the screen: Information]

OK

[On the screen: List of irreps and corresponding kernel symmetries]

Representation analyis						
List of irreps and correspoding kernel symmetries:						
Representation	Dimension	Shubnikov space group	Axes	Origin shift		
mY1+	1	P[a]2/c	(2,0,0 0,1,0 0,0,1)	(0,0,0)	Details	
mY2+	1	P[a]2/n	(2,0,0 0,1,0 0,0,1)	(0,0,0)	Details	
mY1-	1	P[a]2/n	(2,0,0 0,1,0 0,0,1)	(1/4,0,0)	Details	
mY2-	1	P[a]2/c	(2,0,0 0,1,0 0,0,1)	(1/4,0,0)	Details	

Notes

This window has an informative 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 screen: List of kernels and epikernels]

T. Representation a	analyis				×
		List of kernels and e	pikernels:		
Shubnikov spa	ace group Axes	Origin shift	Representation	OPD	
P[a]2/c	(2,0,0 0,1,0 0,0,1	(0,0,0)	mY1+	(a)	
P[a]2/n	(2,0,0 0,1,0 0,0,)		mY2+	(a)	
P[a]2/0	(2,0,0 0,1,0 0,0,. (2,0,0 0,1,0 0,0,.	$\begin{array}{c} (1/4,0,0) \\ (1/4,0,0) \end{array}$	mY2-	(a)	

The four monoclinic Shubnikov space groups are selected by default (if not, just click over one of them to select the block); NEXT

Notes

This will pass all the magnetic space groups to further testing.

[On the screen: Select Shubnikov space group]

Shubnikov space group					
0[-10]-	Atom	Moment	Global	sin(2.Pi.x4)	cos(2.Pi.x4)
[a]2/n [a]2/n +(1/4,0,0) [a]2/c+(1/4,0,0)	Mn1 Co1'	(M,0,M) (M,0,M)	(0,0,0) (0,0,0)		
Show details	Information: The syn For more Magneti	bol "M" indicates t details press the l moments are exp	hat the component ca button "Show details". ressed in the parent c	n have non-zero value. ell.	
	Start graphic simulation	Start pro	ofile simulation		
	Continue with the sele	ected Shubnikov sp	ace group		

Notes

For each space group, the components allowed for the magnetic moment of the Co and Mn atoms are indicated in the column 'Moment'. In this case, the y-component is zero, whereas x- and z-components are free.

Select the first Shubnikov group $P_a 2/c$ and press "Show details" for a detailed list of relationships between magnetic moments of individual atoms [On the screen: Details for selected space group structure] Close the window

Refinement in $P_a 2/c$

Press 'Continue with the selected Shubnikov space group' [On the screen: Select structure name] Use the default name i.e. MnWO4_AF4_5K_01; Save Notes

The test runs under the new job name in a new window to keep the parent structure unchanged. The Jana window with the parent structure remains open.

[On the screen: Basic window of Jana2020]

In the Command tree, expand "Refinement" and open "Refinement commands" [On the screen: Refinement commands]

On the basic page, increase the number of cycles to 1000 and the damping factor to 0.0001. Activate "correct for lambda/2 effect";

Main		Refinement commands	×
		Basic Select/Listing Restraints/Constraints Modulation/Twin Powder	
?‰ ፼ 8	Reflection file New Phases Edit structure parameters	Number of cycles 1000 Use Marquart technique Sigma weight Instability factor Damping factor 0.0001 0.001 Fudge factor	
	Structure solution Random search Import Veninement	Use SHELX weighting scheme Use Wilson's modification	
	Refinement commands Run refinement > Distance calculation	Fill it by imported values	
<u></u> B?	> Draw structure > CIF utilities	○ Unit weight	
۳)	> Tools > Edit file > Export structure to Matrix calculator	Use dynamical LS method => if Rw is increased by 10% reduce the damping by a factor 2 After 3 cycles try to enlarge it back.	
	Active phase:	Check for convergence Solution and the solution of the solut	
	Data block:	Automatic refinement keys Apply electroneutrality Correct for lambda/2 effect	
	Delete rejected atoms	Automatic symmetry restrictions	
		Refinements on F(obs)**2 After last cycle call Fourier Calculate only magnetic scatt	ering
		Randomize atomic coordinates Random seed 0 Maximal random displacement in Ang 0.1 Warning: the randomize procedure will be applied just once during the first cycle. 0	

Notes

The atoms Mn1 and Co1' occupy the same position, and therefore, we must restrict their parameters

On the page "Restrains/Constraints", select "Restrictions", focus on the "New command" line. Select make identical coordinates, ADP parameters, and magnetic parameters For occupancies, select "Keep overall sum" In the box "Atoms/molecules" write "Mn1 Co1'"

Define restrictions			
restric * 12 ===> New command <===			Edit
			Delete
			Disable
			EH-
			Enable
			Down Up
			Select all
			Refresh
			Clone
	Rewrite		
		Occupancies	
ike identical:			
Modulations		Modulated complementarily	
ADPs		Keep overall sum	
Magnetic parameters		O Keep identical site occupancies	
Population of valence electrons		○ not restricted	
Карра			
Kappa'			
Multipoles			
toms/molecules: Mp1_Co1'			Browse
ess "Rewrite"	Esc	ОК	
ress "Rewrite"	Esc	OK	
Define restrictions	Esc	OK	
Period Pe	Esc	OK	Edit
Define restrictions restric * 12 restric Mn1 101 Co1' restric Mn2 New command <===	Esc	OK	Edit
Define restrictions estric * 12 estric Mn1 101 Co1' ===> New command <===	Esc	OK	Edit Delete Disable
Define restrictions estric * 12 estric Mn1 101 Co1' ===> New command <===	Esc	ΟΚ	Edit Delete Disable Enable
Define restrictions estric * 12 estric * 12 estric M1 101 Co1' ===> New command <===	Esc	ΟΚ	Edit Delete Disable Enable
Define restrictions estric * 12 estric Mn1 101 Co1' ===> New command <===	Esc	OK	Edit Delete Disable Enable Down Up
Pess "Rewrite" Define restrictions restric * 12 restric Mn1 101 Co1' restric Mn2 New command <===	Esc	OK	Edit Delete Disable Enable Down Up Select al
Define restrictions restric * 12 restric Mn1 101 Co1' restric Mn2 New command <====	Esc	ΟΚ	Edit Delete Disable Enable Down Up Select all Refresh
ress "Rewrite" Define restrictions estric * 12 estric Mn1 101 Co1' ===> New command <===	Esc	ΟΚ	Edit Delete Disable Enable Down Up Select all Refresh
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Define restrictions estric * 12 estric Mn1 101 Co1' ===> New command <===	Esc	ΟΚ	Edit Delete Disable Enable Down Up Select al Refresh Clone
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ress "Rewrite" Define restrictions estric * 12 estric * 12 estric * 11 estric * 11 estric * 11 estric * 11 estric * 12 estric	Esc	OK OK OK OK OK OK	Edit Delete Disable Enable Down Up Select all Refresh Clone
ress "Rewrite" Define restrictions restric * 12 restric Mn1 101 Co1' restric Mn1 101 Co1' restric Mew command <==== Alke identical: Coordinates Modulations ADPs	Esc	OK O	Edit Delete Disable Enable Down Up Select all Refresh Clone
Pefine restrictions Testric * 12 Testric Mn1 101 Co1* Testric Mn1 101 Co1* Testric Mn1 101 Co1* Testric Mn1 101 Co1* Testric Mn1 Co1* Testric	Esc	OK OK OK OCCUPANCIES: Modulated identically Keep overall sum Keep identical ste occupancies	Edit Delete Disable Enable Down Up Select all Refresh Clone
ress "Rewrite" Define restrictions restric * 12 restric Mn1 101 Co1' ===> New command <=== we identical: Coordinates Modulations ADPs Magnetic parameters Population of valence electrons	Rewrite	OK OK OCCUpancies: Modulated identically Keep overall sum Keep identical site occupancies Not complementatily Keep identical site occupancies Not restricted	Edit Delete Disable Enable Down Up Select all Refresh Clone
ress "Rewrite" Define restrictions restric * 12 restric Mn1 101 Co1' ===> New command <=== Ake identical: Coordinates Modulations ADPs Magnetic parameters Population of valence electrons Kappa	Rewrite	OK OCCUpancies: Modulated identically Keep overal sum Keep identical site occupancies Not restricted	Edit Delete Disable Enable Down Up Select all Refresh Clone
ress "Rewrite" Define restrictions restric * 12 restric Mn1 101 Co1' restric Mn1 101 Co1' restric Mn1 101 Co1' restric Mn1 Con' restric Mn1 Co	Rewrite	OK OK OCUPANCIES: Modulated identically Keep overall sum Keep identical site occupancies © not restricted	Edit Delete Enable Down Up Select al Refresh Clone
ess "Rewrite" Define restrictions restric * 12 restric * 11 101 Co1' Restric Mail 101 Co	Esc	OK OCCUPANCIES: Modulated identically Modulated complementarily Keep overall sum Keep identical site occupancies not restricted	Edit Delete Disable Enable Down Up Select al Refresh Clone
ress "Rewrite" Define restrictions restric * 12 restric Mn1 101 Co1' ===> New command <=== Ake identical: Coordinates Modulations ADPs Magnetic parameters Population of valence electrons Kappa Kappa' Multipoles toms/molecules:	Rewrite	OK OCCUPANCIES: Modulated identically Modulated complementarily Keep overall sum Keep identical site occupancies in on restricted	Edit Delete Disable Enable Down Up Select all Refresh Clone
ress "Rewrite" Define restrictions restric * 12 restric Mn1 101 Co1' ===> New command <=== ke identical: Coordinates Modulations ADPs Magnetic parameters Population of valence electrons Kappa Kappa' Multipoles toms/molecules:	Rewrite	OK OCCUpancies: Modulated identically Modulated complementarily Keep overall sum Keep identical site occupancies Ont restricted	Edit Delete Disable Enable Down Up Select all Refresh Clone

On the page "Restrains/Constraints", select "Fixed commands" and ensure that all atomic positions are fixed in their current values ("fixed xyz *"). OK; OK; YES+START

Notes

After several cycles, when the refinement converges, you can modify the damping parameters:

On the "R-factors overview", press "Parameters" [On the screen: Modify refinement options] Change the "Damping factor" to 0.1

RFactors ov	verview	
R factors : GOF(obs)= R(obs)= R factors f	[25=21+4/4], Damping factor: 0.0001 = 19.22 GOF(all)= 17.20	97.86
R(obs)= Last wR2(a Maximum o	Number of cycles: 1000	97.86
	Use Marquart method Fudge factor 0.001	
	Make these settings permanent	
	Refining procedure - cycle 783/1000	
	End Parameters Cancel	

ОК

Notes R factors : [25=21+4/5] GOF(obs)~17.0 GOF(all)~15.2 R(obs)~55.7 wR2(obs)~83.7 R(all)~60.8 wR2(all)~84.6 R factors for magnetic reflections : [25=21+4] R(obs)~55.7 wR2(obs)~83.7 R(all)~60.8 wR2(all)~84.6

Now we shall test the remaining Shubnikov apce groups on the list.

Close the window of the structure MnWO4_AF4_5K_01. YES to the question "Do you want to quit Jana2020?" [On the screen: (Parent structure) Select Shubnikov space group:]

Refinement in $P_a 2/n$

Select the second Shubnikov group P_a 2/n. Press "Continue with the selected Shubnikov space group". [On the screen: Select structure name] Use the default name i.e. MnWO4_AF4_5K_02; Save [On the screen: Basic window of Jana2020] Repeat the same procedure as for the previous space group. Notes

R factors : [25=21+4/4] GOF(obs)~16.9 GOF(all)~15.8 R(obs)~62.3 wR2(obs)~85.5 R(all)~69.1 wR2(all)~89.2 R factors for magnetic reflections : [25=21+4] R(obs)~62.3 wR2(obs)~85.5 R(all)~69.1 wR2(all)~89.2

Close the window of the structure MnWO4_AF4_5K_02. YES to the question "Do you want to quit Jana2020?"

[On the screen: (Parent structure) Select Shubnikov space group:]

Refinement in *P*_a 2/*n* +(1/4,0,0)

Select the third Shubnikov group $P_a 2/n + (1/4,0,0)$. Press "Continue with the selected Shubnikov space group". [On the screen: Select structure name] Use the default name i.e. MnWO4 AF4 5K 03; Save

Notes

For the space groups with origin shift, the program offers a transformation to the standard setting. While the matrix doubling the a-cell parameter is always applied (BNS notation), the origin shift is optional. Skipping this point will keep the atoms in all models at the same positions.

	Select S	Shubnikov space group	:		
Shubnikov space group	Atom	Moment	Global	sin(2.Pi.x4)	cos(2.Pi.x4
P[a]2/c P[a]2/n P[a]2/n+(1/4,0,0) P[a]2/c+(1/4,0,0)	Mn1 Co1'	(M,0,M) (M,0,M)	(0,0,0) (0,0,0)		
2.	The following transformation	can bring the structure to	o the standard settin	× a:	
	a' 2	0 0	a	y.	
	b' = 0 c' 0	1 0 0 1	* b c	_	
Show details	O	igin shift: (0.25,0,0)		on-zero value.	
	Do you wan	t to apply this transformat	tion?		
	· · · · ·	/es No			
				_	

NO to the question "Do you want to apply this transformation?"

[On the screen: Basic window of Jana2020]

Repeat the same procedure as for the previous space groups.

Notes

R factors : [25=21+4/5] GOF(obs)~1.7 GOF(all)~1.6 R(obs)~3.7 wR2(obs)~9.1 R(all)~4.6 wR2(all)~9.4 R factors for magnetic reflections : [25=21+4] R(obs)~3.7 wR2(obs)~9.1 R(all)~4.6 wR2(all)~9.4

Close the window of the structure MnWO4_AF4_5K_03. YES to the question "Do you want to quit Jana2020?"

[On the screen: (Parent structure) Select Shubnikov space group:]

Refinement in $P_a 2/c + (1/4,0,0)$

Select the fourth Shubnikov group $P_a 2/c + (1/4,0,0)$. Press 'Continue with the selected Shubnikov space group' [On the screen: Select structure name] Use the default name i.e. MnWO4_AF4_5K_04; Save NO to the question "Do you want to apply this transformation?" [On the screen: Basic window of Jana2020] Repeat the same procedure as for the previous space groups.

Notes

R factors : [25=21+4/4] GOF(obs)~14.7 GOF(all)~13.2 R(obs)~49.5 wR2(obs)~75.2 R(all)~53.4 wR2(all)~75.7 R factors for magnetic reflections : [25=21+4] R(obs)~49.5 wR2(obs)~75.2 R(all)~53.4 wR2(all)~75.7

Clearly the best group is $P_a 2/n + (1/4,0,0)$.

On the main menu, Go to "Structure" \rightarrow History and choose MnWO4_AF4_5K_03; OK Change the focus to JanaDraw in the icon

Structure Transformations Settings Tools Help



[On the screen: JanaDraw window]

On the lower menu panel choose to fill the unit cell. Then on the upper menu select "Build" \rightarrow "Filter" \rightarrow "Filter atomic types" [On the screen: Build atomic types] Deselect O and W

Build atom	types:		>
☑ Co ☑ Mn			
0			
W			
	Esc	ОК	

ОК

On the menu "Build" \rightarrow "Fill" \rightarrow "Supercell" [On the screen: Define the supercell] Write "z to:" 2; OK

On the lower menu panel deselect D to hide the unit cell lines the unit cell.

Go to ^{CC}; Change "Bonds between atoms derived from atomic radii and typical distances expanded by:" to 20%

JanaDraw options	×
☑ Display coordinate system	Background:
 Direct coordinate system Reciprocal coordinate system 	 ○ White ● Light blue ○ Black
Bonds between atoms derived from atomic radii and typical distances expanded by: 20 %	
Don't draw bonds being shorter than 50 % of distance derived from atomic radii and typical distances	
Define/modify typical distances	
Atom radius [Ang]: 0.3 Bond thickness [An	g]: 0.12 Atom label shift [Ang]: 0.4
Draw only atoms with site occupancy greater than: 0 Reduce atomic radii by occupancy factor	
Bohr to angstroem ratio: 1 Magnetic vector from the center of the atom, otherwise the two centers are at one point	
Filling extension of the cell or supercell [Ang]: 0.01	
Delay time for drawing atom labels and visualization of selected atoms: 0 milliseconds	
Note: For most graphic cards this delay can be 0. In case of problems try to find the smallest value.	
Limits for H-bond	
Maximal distance D-H: 1.4 Maximal distance H	IA: 2.5 Minimal angle D-HA: 110
Shine: 0.70	Gloss: 0.00
Esc Ok	

OK; choose view along a and slightly rotate the structure, by dragging it with the mouse or by rotate the y axis on the right menu;



Notes

This is the best model refined in $P_a 2/n + (1/4,0,0)$ for MnWO4.