

GSAS-II tutorial on crystal and commensurate magnetic structure

Qiang Zhang

Neutron Scattering Division, ORNL

POWGEN workshop “Getting the Most from Your POWGEN Data”, June 15-17, 2023

ORNL is managed by UT-Battelle
for the US Department of Energy



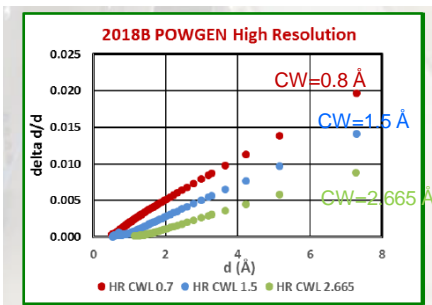
Time-of-flight powder diffractometer POWGEN

- **High resolution** powder diffractometer to study crystal, magnetic and local structure of polycrystalline materials

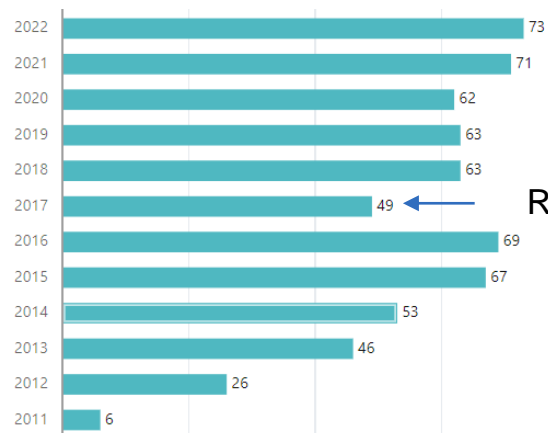
Current Instrument Capabilities (neutron band ~ 1 Å)

Freq (Hz)	WL center	WL min	WL max	dmin	dmax	Qmin	Qmax	Bank
60	0.533	0.15	1.066	0.075	7.50	0.82	83.45	0
60	0.800	0.27	1.333	0.134	8.00	0.76	46.88	1
60	1.500	0.97	2.033	0.485	13.00	0.48	12.95	2
60	2.665	2.13	3.198	1.070	21.00	0.30	5.87	3
60	4.797	4.26	5.33	2.140	38.00	0.17	2.94	4

Resolution: best resolution $\Delta d/d$: 0.8×10^{-3}



Dependent on wavelengths and d (or 2θ)



Rebuild POWGEN

> 60 papers/year last 7 years

Instruments: BL-11A (POWGEN)

[BL-11A Summary](#) [Completed Experiments](#) [Instrument Authors](#) [Publications](#)

★Specially Recognized

Citation Count 20-49 (124)
 Citation Count > 50 (85)
 DOE Highlight (34)
 Editor's Choice (7)
 Journal Cover (4)

Instrument Publications:
698

Instrument H-index:
63

Completed Experiments:
1339

Instrument Authors:
2357

~ 30%: high profile publications: *Nature materials*, *Nature energy*, *Nature physics*, *Nature chemistry*, *PRL*, *Nature Communications*, *PRX*, *Advanced materials*, *Angewandte Chemie International Edition*, *JACS*, etc;

Total publication number and instrument H index of POWGEN are both the **1st place** among all ORNL beamlines;

Autoreduced POWGEN data vs CW neutron data



PG3_54146.gsa

Diffraction data for GSAS-II



PG3_54146-1.dat

Diffraction data for FullProf or JANA



PG3_54146-1.xye

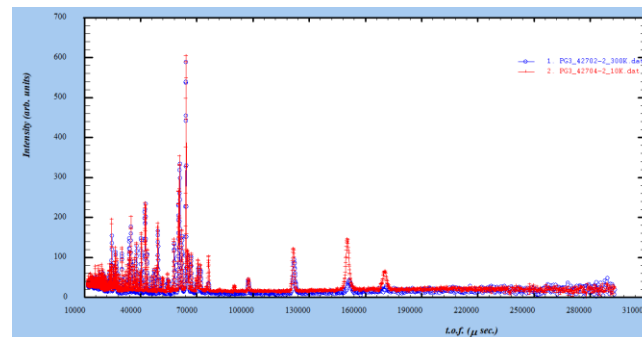
Diffraction data for TOPAS



PG3_54146.gr

PDF data

Ready for Rietveld refinement or PDF analysis



Intensity vs TOF (NOT 2theta!)

```
PG3_42702-2_300K.dat
1 XYDATA
2 # File generated by Mantid, Instrument POWGEN
3 # The X-axis unit is: Time-of-flight, The Y-axis unit
4 # Data for spectra :2
5 # Spectrum 1
6 # Time-of-flight      Y      E
7 14300.17204          28.15968284    0.41506355
8 14311.60584          26.26662343    0.40565232
9 14323.04879          26.17181040    0.40476613
10 14334.50089          25.28546181    0.40012561
```

TOF to D spacing (FullProf):

$$\text{TOF}(\text{microseconds}) = \underline{\text{Zero}} + \underline{\text{Dtt1}} * D + \underline{\text{Dtt2}} * D^2 + \underline{\text{Dtt_1overD}}/D$$

(D in Angstroms)

POWGEN Peak Profile

TOF profile has Convolution of back-to-back exponentials with pseudo-Voigt (a linear combination of Gaussian and Lorentzian)

6 refinable parameters: position, intensity, α , β , σ and γ Position:

$$\text{TOF}(\text{microseconds}) = \text{Zero} + \text{Dtt1} * D + \text{Dtt2} * D^2 + \text{Dtt_1overD}/D$$

Exponentials: Alpha largely affects the sharpness of the leading TOF edge of each peak; larger values mean sharper front edges. Beta terms affect the trailing TOF edge in the same way.

$$\alpha = \alpha_0 + \frac{\alpha_1}{d} + \frac{\alpha_q}{\sqrt{d}} \text{ and } \beta = \beta_0 + \frac{\beta_1}{d^4} + \frac{\beta_q}{d^2}$$

Gaussian and Lorentzian width: Sig terms affect the Gaussian shape component of the peak profiles; larger values result in broader peaks. The coefficients describe the sig and Gamma values as follows:

$$\sigma^2 = \sigma_0^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 + \frac{\sigma_q^2}{d^2} \longrightarrow \sigma_q d \text{ GSASII used}$$
$$\gamma = \gamma_1 * d + \gamma_2 * d^2 + \gamma_0$$

➤ In other TOF instruments, there lack Dtt_1overD , β_q and σ_q .

Overview of the Rietveld softwares to refine magnetic structures

- **Commensurate magnetic order**

FullProf: representation analysis
or magnetic space group;

GSAS-II: magnetic space group
only;

TOPAS: representation analysis or
magnetic space group;

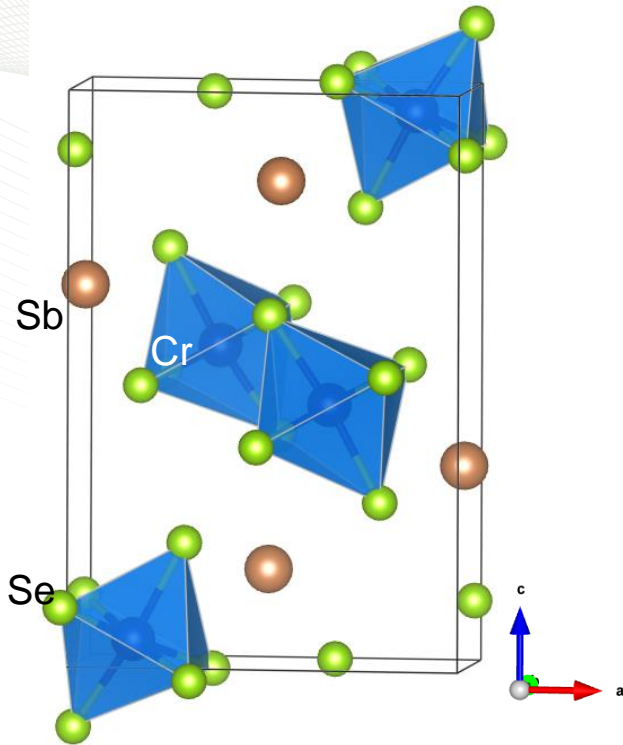
JANA: representation analysis
and magnetic space group;

- **Incommensurate magnetic order**

FullProf: representation analysis or
magnetic superspace group

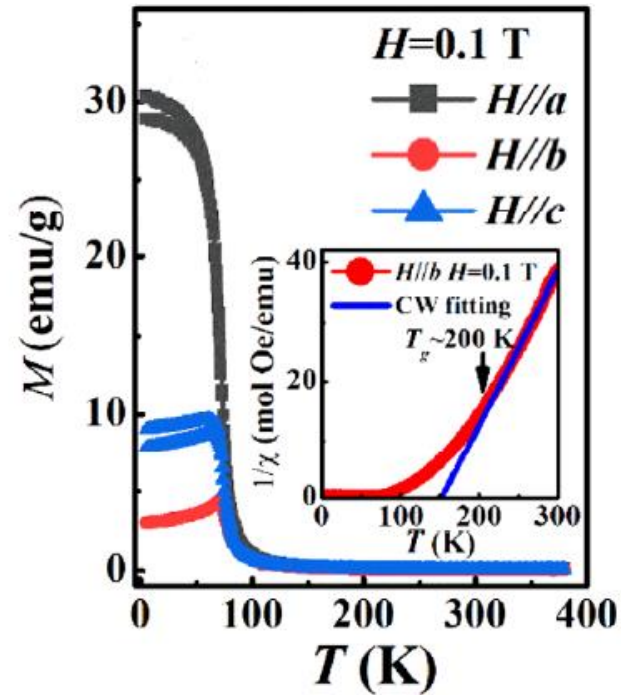
JANA: representation analysis and
magnetic superspace group

Basic information on CrSbSe_3



- Orthorhombic structure: $Pnma$ (No. 62)
 $a=9.143086$, $b=3.784552$,
 $c=13.416915$;

- Octahedra CrSe_6



- Magnetic transition 75 K from the magnetization

Files provided for this tutorial

- Time-of-flight diffraction data at POWGEN:

PG3_42702_300K.gsa

PG3_42704_10K.gsa

- Instrumental resolution file:

2018B_HighRes_60HzB2_1p5

- cif file for crystal structure

CrSbSe₃.cif

- Final PCR files

CrSbSe3_N.gpx

CrSbSe3_1 mag_3.gpx

- Supporting information

GSAS_II_QZhang.PDF (step-by-step instructions)

Data file for GSAS-II

```
Sample Run: 42702 Vanadium Run: 40506 Wavelength: 1.5 A
Monitor: 1
# PI Y. Qu
# 1 Histograms
# File generated by Mantid:
# Instrument: POWGEN
# From workspace named : PG3_42702
# with Y multiplied by the bin widths.
# Primary flight path 60m
# Sample Temperature: 299.998 K Freq: 60 Hz Guide: -54 mm
#
# Total flight path 63.18m, tth 90deg, DIFC 22585.8
# Data for spectrum : 0
BANK 2 4002 4002 SLOG      11970      293123  0.0007996 0 FXYE
14300.172038374          321.843642162      4.743859049
14311.605842871          300.447453606      4.640002779
14323.048789349          299.602304499      4.633568081
14334.500885116          289.687248340      4.584107965
14345.962137489          289.493223846      4.582999100
14357.432553787          318.844801503      4.723594398
14368.912141338          378.114036161      4.994545340
14380.400907475          410.031405490      5.133395023
14391.898859537          385.574984018      5.024061256
14403.406004869          364.951696099      4.929442215
```

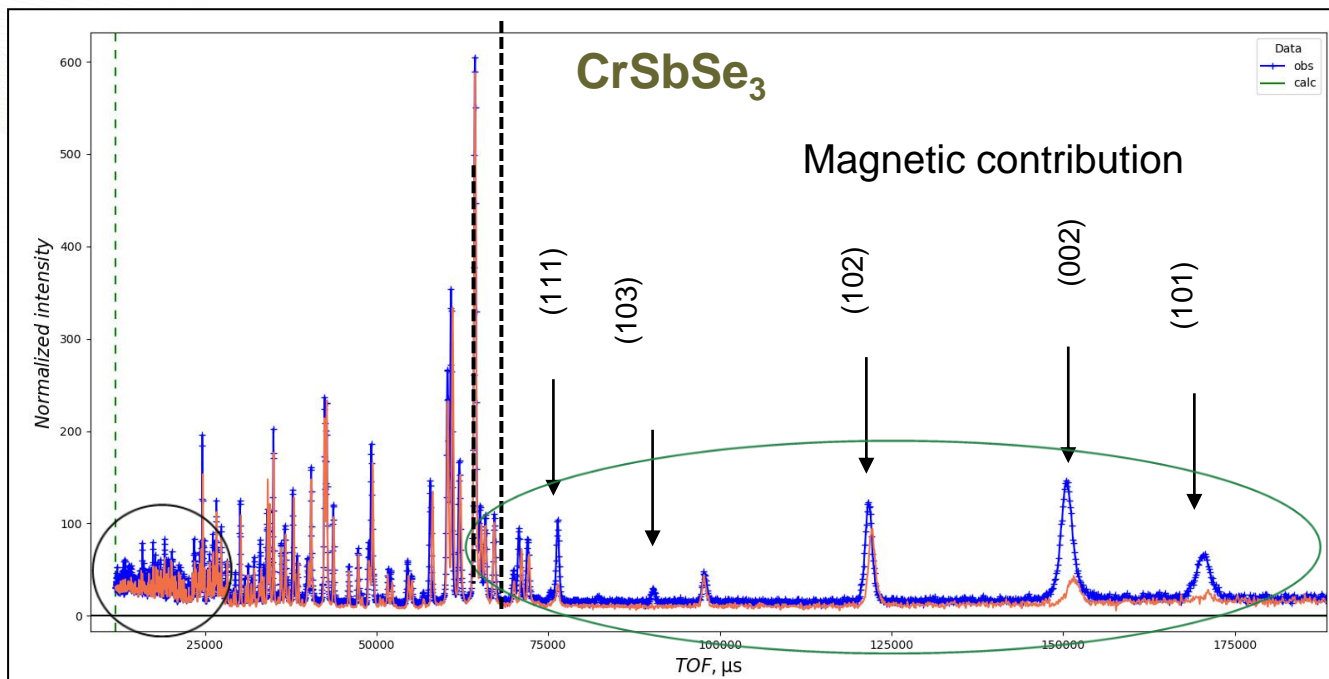
INSTPRM

```
C:\Users\qzg\AppData\Local\Temp1\GSAS_II_QZhang_Thursday.zip\GSAS_II_QZhang_Thursday\2018B_HighRes_60HzB2_1p5.instrpm - Notepad++
File Edit Search View Encoding Language Settings Tools Macro Run Plugins Window ?
IR3.mcf.txt IR3.mcf IR3.mcf backup_Fe1p15_4K_superSG.pcr 2018B_HighRes_60HzB2_1p5.instrpm CrSeSe3.may_3 of PG3_42702_300K.gsa 2018B_HighRes_60HzB2_1p5.instrpm
1 #GSAS-II instrument parameter file; do not add/delete items POWGEN 2018B:
2 Z:-0.465205938282
3 fltPath:63.183
4 beta-q:0.0
5 Bank:2.0
6 sig-1:-852.163368943
7 2-cheta:90.0
8 sig-q:797.184446197
9 sig-0:-203.060186472
10 sig-2:299.195588039
11 Zero:-26.810325593
12 difC:22597.8753723
13 X:-4.50393449632
14 Azimuth:0.0
15 Y:10.94893140839
16 alpha:0.128661555108
17 beta-1:0.00396039253042
18 beta-0:0.100880267005
19 Type:FNT
20 difB:4.70563778582
21 difA:-4.59435624908
22
```


Exercise steps

- Identify magnetic peaks in CrSbSe_3 ;
- Refine the structure of CrSbSe_3 at 10 K ($T < T_m$);
- Refine the magnetic structure of CrSbSe_3 at 10 K;
- Check if small M_z (AFM component) is real;
- To publish the magnetic structure and refinement plots;

Identify magnetic peaks in CrSbSe₃



Smaller thermal parameters

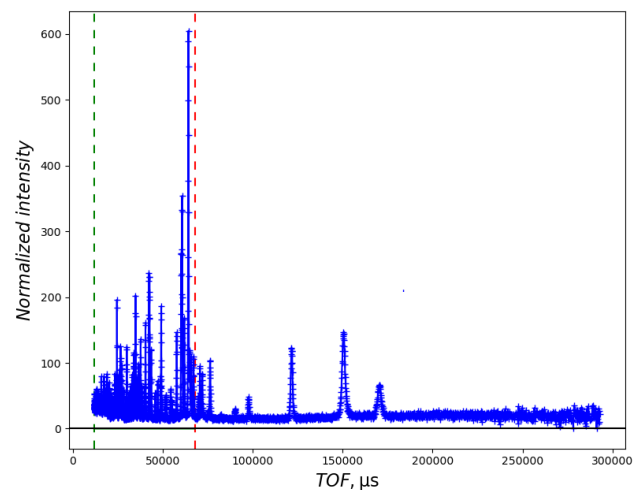
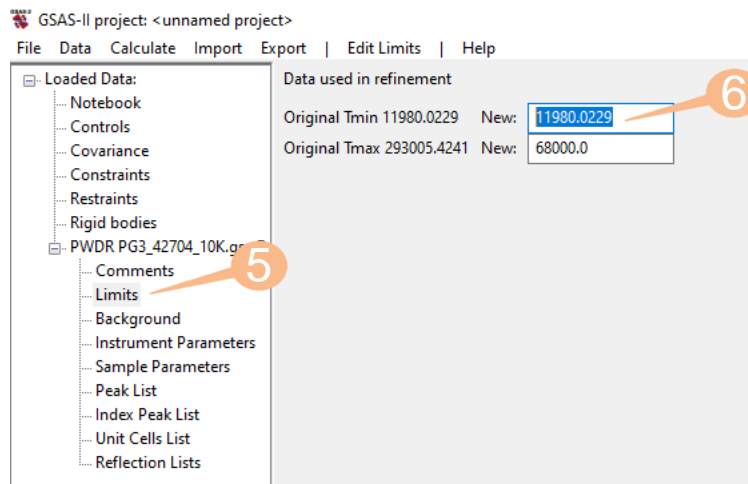
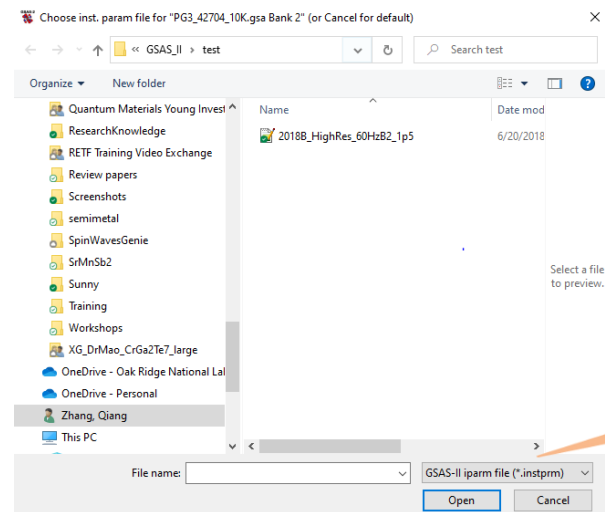
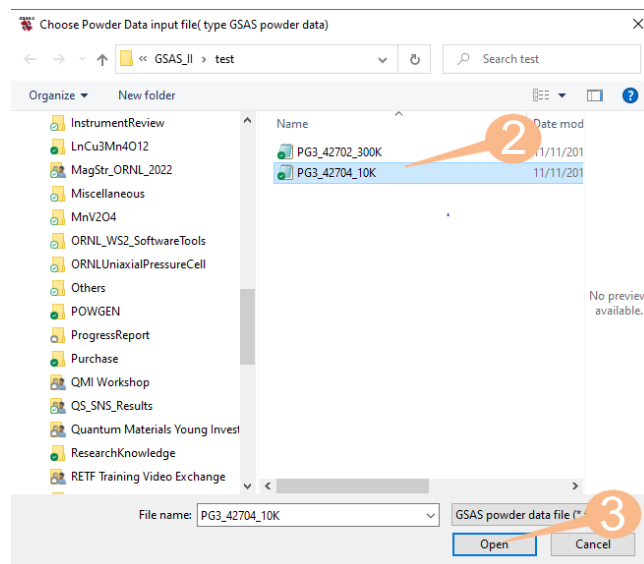
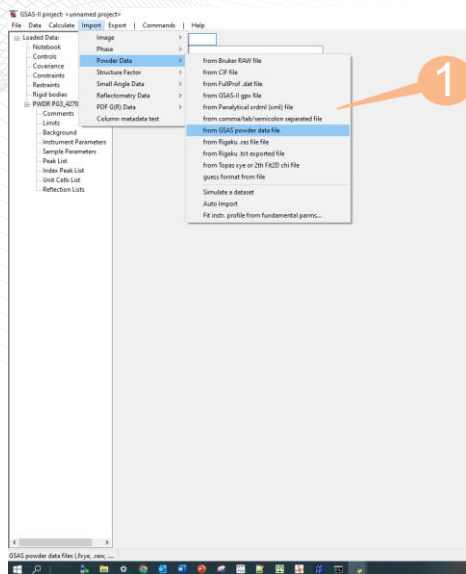
At 10 K, the intensities at high d part and low d part both increased: different origins!

Two ways to determine the structural parameters in $T < T_N$ (or T_C) before refining magnetic structure:

- 1). Refine the data in $T > T_N$ (or T_C) firstly. Then use them as initial parameters and only refine the atomic positions, B factors, and lattice constants in $T < T_N$ (or T_C).
- 2). Exclude the high- d part of data that involves magnetic contribution and only refine low and middle d data on the structural part in $\text{TOF} < 68,000 \mu\text{s}$

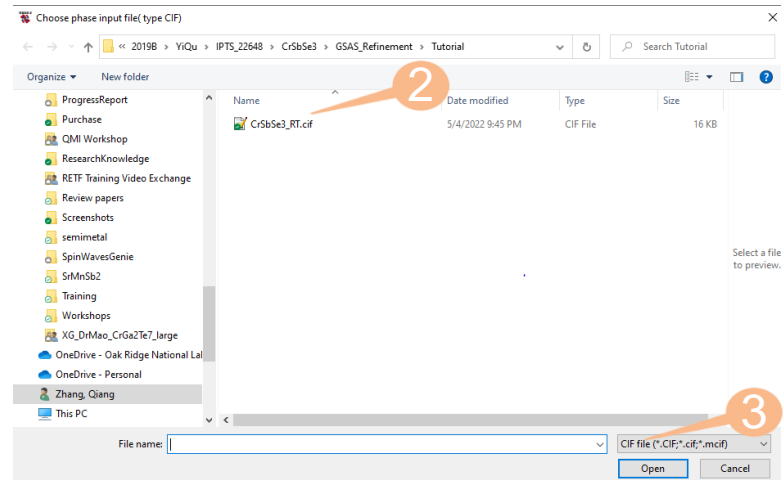
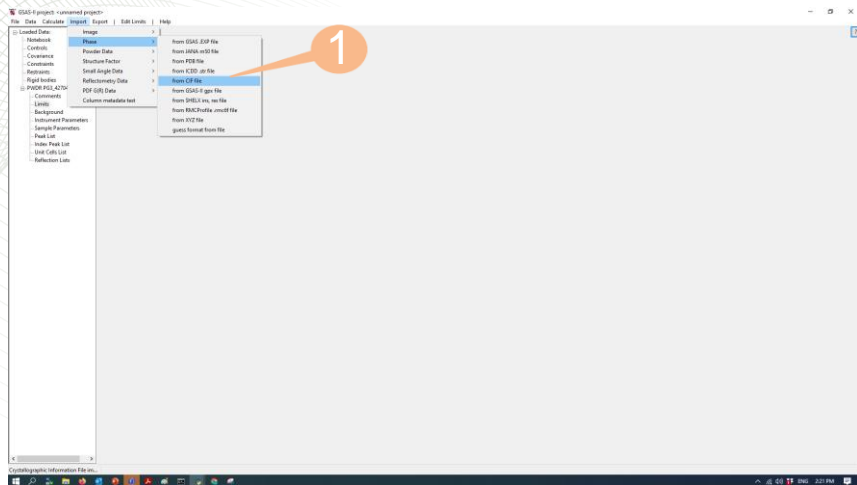
Refine the structure of CrSbSe₃

I. Import datafile and set the limit



File-save project!

II. Import the phase



Is this the file you want?

File C:\Users\qzg\Dropbox
(ORNL)\POWGEN\PTS_users\2019B\YiQu\PTS_22648\CrSbSe3_RT.cif
begins:

```
#####  
#
```

Do you want to read this file?

Yes No

4

Edit phase name

Enter the name for the new phase

CrSbSe3

5

OK

6

Add histogram(s)

Select histogram(s) to add to new phase
CrSbSe3

7

Name Filter:

0) PWDR PG3 42704 10K.gsa Bank 2

Apply stride: 1

Set All

Toggle All

Set Range

OK

8

Cancel

III. Refine background and scale factor

GSAS-II project: CrSbSe3_July6th.gpx

File Data Calculate Import Export | File Fixed Points | Help

Project: C:\Users\qzg\Dropbox (

Background used in refinement

Background function: **log interpolate** Refine?

Number of coeff.: 6

Background coefficients:

32.4298	27.7615	21.03	17.6458	17.2311
---------	---------	-------	---------	---------

14.4897

Debye scattering: Number of terms: 0

Peaks in background: Number of peaks: 0

Fixed background file:

multiplier: 1.0

2

GSAS-II project: CrSbSe3_July6th.gpx

File Data Calculate Import Export | Command | Help

Project: C:\Users\qzg\Dropbox (

Sample and Experimental Parameters

Instrument Name: **Debye Scherrer**

Diffraction type: Debye Scherrer

Histogram scale factor: 1.0

Sample absorption (μ_r/l): 0.0

Goniometer omega: 0.

Goniometer chi: 0.

Goniometer phi: 0.

Detector azimuth: 0.

Clock time (s): 0.

Sample temperature (K): 10.

Sample pressure (MPa): 0.

Sample humidity (%) 0.

Sample voltage (V) 0.

Applied load (MN) 0.

3

4

5

GSAS-II project: N.gpx

File Data Calculate Import Export Help

Project: C:\Users\qzg\Dropbox (

Refinement Controls

Refinement type: **analytic Hessian** λ : 0.001

Max cycles: 10 Initial lambda = 10^{*-3}

SVD zero tolerance: 1e-06

Sequential Settings

Select datasets to switch to sequential refinement: Select datasets

Global Settings

CIF Author (last, first): no name

6

Shipping tool

GSAS-II project: CrSbSe3_July6th.gpx

File Data Calculate Import Export | Command | Help

Project: C:\Users\qzg\Dropbox (

Setup PDFs

Note: View LS parms CRL-L

Cont: **Scale** type: Debye Scherrer

Calc: scale factor: 1.0

Con: Run Profile

Rest: Run Absorb

Rigid Bodies

PWDR PG3_42704_10K.gsa Ba

Scale factor: 1.0

Goniometer omega: 0.

Goniometer phi: 0.

Goniometer chi: 0.

Detector azimuth: 0.

Clock time (s): 0.

Sample temperature (K): 10.

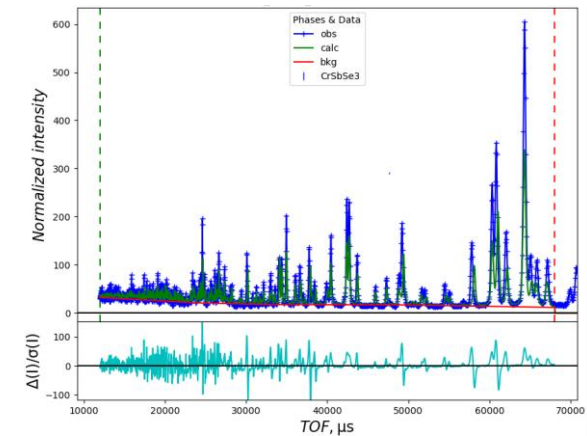
Sample pressure (MPa): 0.

Sample humidity (%): 0.

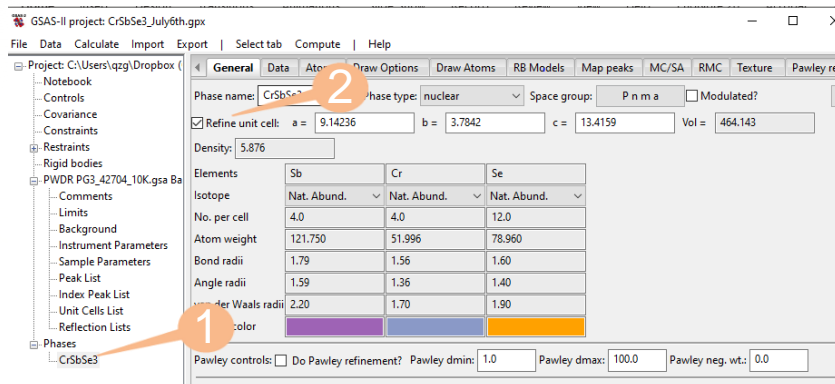
Sample voltage (V): 0.

Applied load (MN): 0.

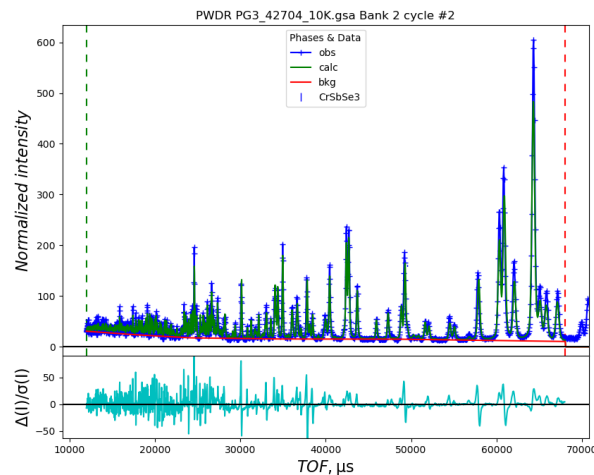
7



IV. Refine lattice constants



Calculate-refine:



Refinement results, $R_w = 18.636$

i Detailed results are in
[C:\Users\qzg\Dropbox \(ORNL\)\POWGEN\...\CrSbSe3_July6th.lst](C:\Users\qzg\Dropbox (ORNL)\POWGEN\...\CrSbSe3_July6th.lst)

Final Reduced χ^2 : 198.776 (before ref: 597.538)

Max shift/sigma=29.109

Load new result?

OK Cancel

V. Refine atomic coordinates and thermal parameters

GSAS-II project: CrSbSe3_July6th.gpx

Project: C:\Users\qzg\Dropbox (...)

Phases

- CrSbSe3

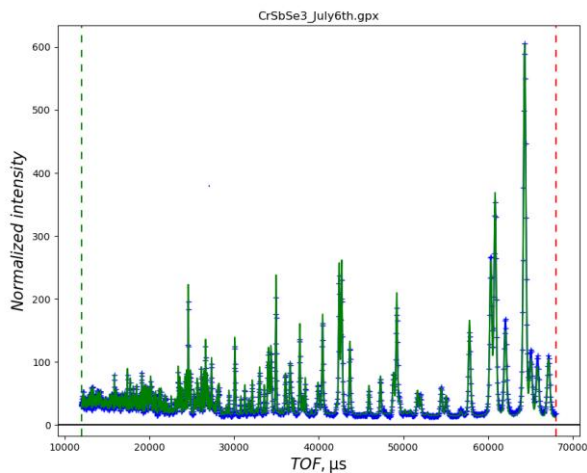
	Name	Type	refine	x	y	z	frac	site sym	mult	I/A	Uso	U11	U22
0	Sb	Sb		0.02930	0.25000	0.65853	1.0000	m(y)	4	I	0.01500		
1	Cr	Cr		0.15670	0.25000	0.04490	1.0000	m(y)	4	I	0.00610		
2	Se3	Se		0.17206	0.25000	0.48457	1.0000	m(y)	4	I	0.01060		
3	Se2	Se		0.28529	0.25000	0.21334	1.0000	m(y)	4	I	0.01060		
4	Se1	Se		0.50254	0.25000	0.60913	1.0000	m(y)	4	I	0.00890		

Refinement controls

Select

- F - site fractions
- X - coordinates
- U - thermal parameters

OK Cancel



Refinement results, $R_w = 8.161$

i Detailed results are in
 C:\Users\qzg\Dropbox
 (ORNL)\POWGEN\I... \CrSbSe3_July6th.lst

Final Reduced χ^2 : 38.383 (before ref: 47.785)

Max shift/sigma=0.827

Load new result?

OK

Cancel

Calculate-refine:

VI. Refine peak profile coefficients

In "Instrument Parameters" tab:

Histogram Type: PNT Bank: 2
Flight path: 63.183 2-theta: 90.00

Name (default)	Value	Refine?
difC (22597.875):	22597.875	<input type="checkbox"/>
difA (4.594):	4.594	<input type="checkbox"/>
difB (4.706):	4.706	<input type="checkbox"/>
Zero (-26.810):	-26.81	<input type="checkbox"/>
alpha (0.129):	0.129	<input type="checkbox"/>
beta-0 (0.100880):	0.10088	<input type="checkbox"/>
beta-1 (0.003960):	0.00396	<input type="checkbox"/>
beta-q (0.000000):	0.0	<input type="checkbox"/>
sig-0 (-203.060):	-203.06	<input type="checkbox"/>
sig-1 (-852.163):	-852.163	<input type="checkbox"/>
sig-2 (298.196):	298.196	<input type="checkbox"/>
sig-q (797.184):	797.184	<input type="checkbox"/>
X (-4.504):	0.0	<input checked="" type="checkbox"/>
Y (10.949):	0.0	<input type="checkbox"/>
Z (-0.465):	0.0	<input type="checkbox"/>

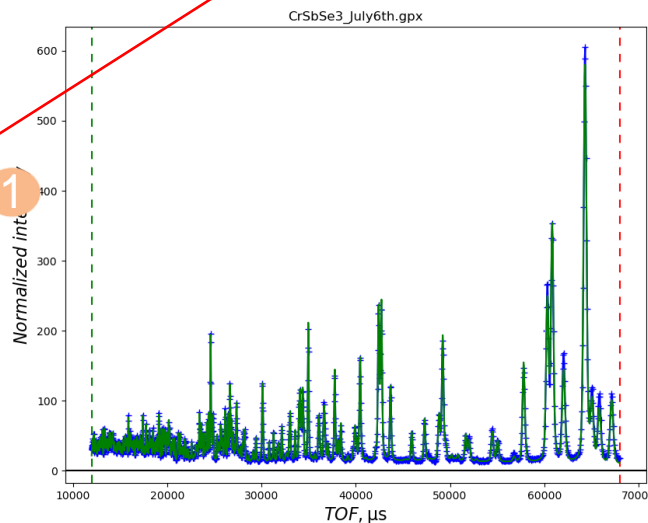
$$TOF = DIFC * d + DIFA * d^2 + ZERO + DIFB/d$$

$$\sigma^2 = \sigma_0^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 + \frac{\sigma_q^2}{d^2} + \sigma_3^3 d^3$$

(Gaussian function)

$$\gamma = X * d + Y * d^4 + Z$$

(Lorentz function)



Refinement results, $R_w = 3.772$

i Detailed results are in
C:\Users\qzg\Dropbox
(ORNL)\POWGEN\...\CrSbSe3_July6th.lst

Final Reduced χ^2 : 8.205 (before ref: 72.633)

Max shift/sigma=0.645

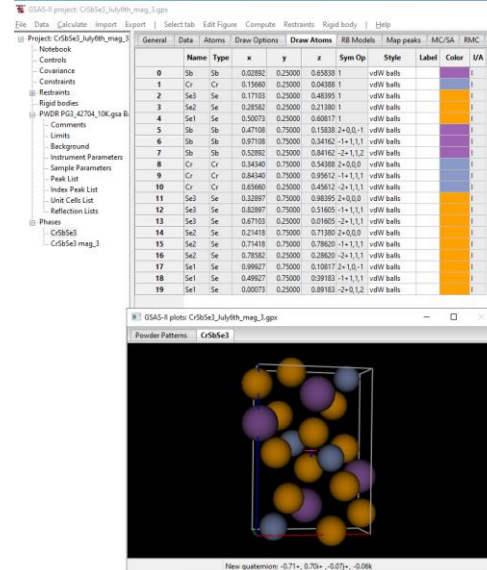
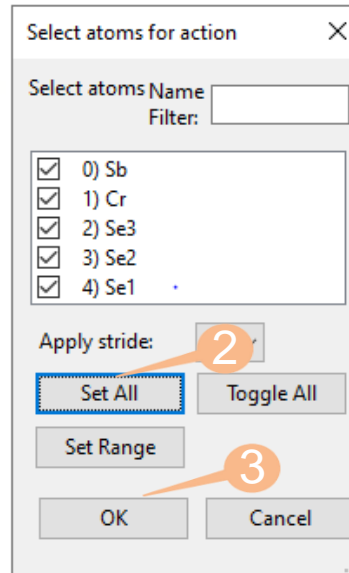
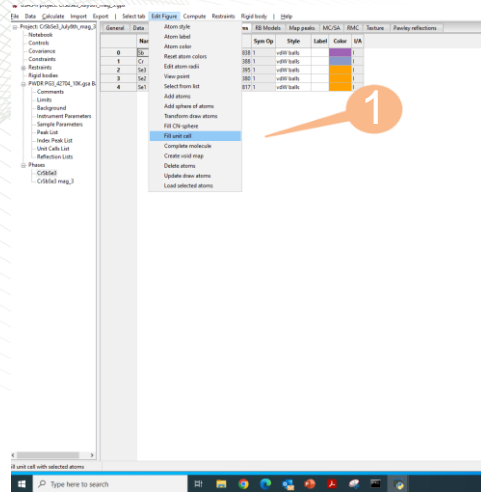
Load new result?

OK **Cancel**

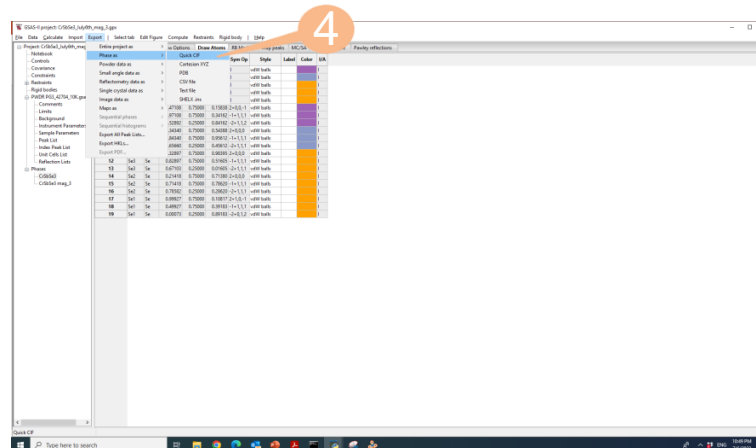
Calculate-refine:

VII. Virtualizing crystal structure

In "Draw Atoms" tab:

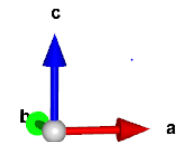
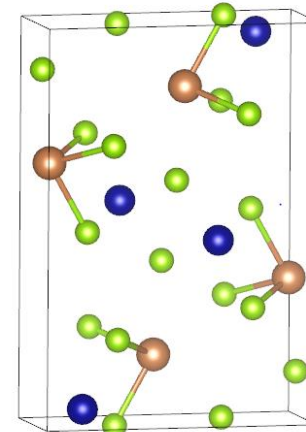


Export cif file:



Use VESTA software (jp-minerals.org/vesta/en/download.html) to open it directly for publication:

Site	r (Å)	C
✓ Sb	1.41	■
Sb	1.41	■
✓ Cr	1.29	■
Cr	1.29	■
✓ Se	1.04	■
Se3	1.04	■
Se2	1.04	■
Se1	1.04	■



Let us add the high-TOF data to refine the magnetic structure!

Refine the magnetic structure of CrSbSe₃

I. Add the high TOF data back and refine background

GSAS-II project: CrSbSe3_N.gpx

File Data Calculate Import Export | Edit Limits | Help

Project: CrSbSe3_N.gpx

- Notebook
- Controls
- Covariance
- Constraints
- Restrains
- Rigid bodies
- PWDR PG3_42704_10K.gsa B:
- Comments
- Limits

Data used in refinement

Original Tmin 11980.0229 New: 14300.0

Original Tmax 293005.4241 New: 2.2e+05

Fix the refinement on the scale, atomic positions, and thermal parameters. *Only refine background, magnetic structure and peak profile coefficient!*

Refinement results, $R_w = 5.548$

Detailed results are in C:\Users\qzg\Dropbox (ORNL)\POWGEN\...CrSbSe3_July6th.lst

Final Reduced χ^2 : 10.720 (before ref: 16.268)

Max shift/sigma=5.673

Load new result?

OK Cancel

Calculate-refine:

GSAS-II project: CrSbSe3_July6th.gpx

File Data Calculate Import Export | Command | Help

Project: C:\Users\qzg\Dropbox (ORNL)\POWGEN\...CrSbSe3_July6th.gpx

Sample and Experimental Parameters

Instrument Name: []

Diffractometer type: Debye-Scherrer

Histogram scale factor: 6854.1

Sample absorption (μ_r/l): 0.0

Goniometer omega: 0.0

Goniometer chi: 0.0

Goniometer phi: 0.0

Detector azimuth: 0.0

Clock time (s): 0.0

Sample temperature (K): 10.0

Sample pressure (MPa): 0.0

Sample humidity (%): 0.0

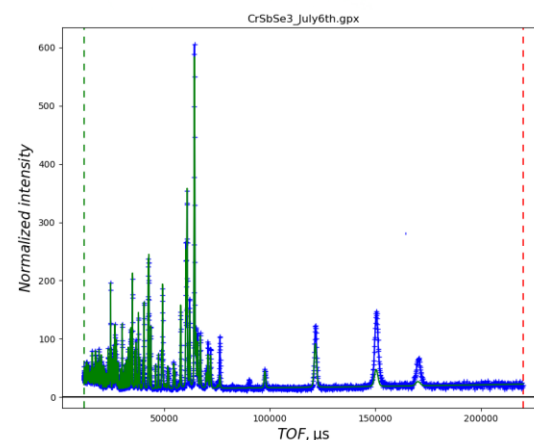
Sample voltage (V): 0.0

Applied load (MN): 0.0

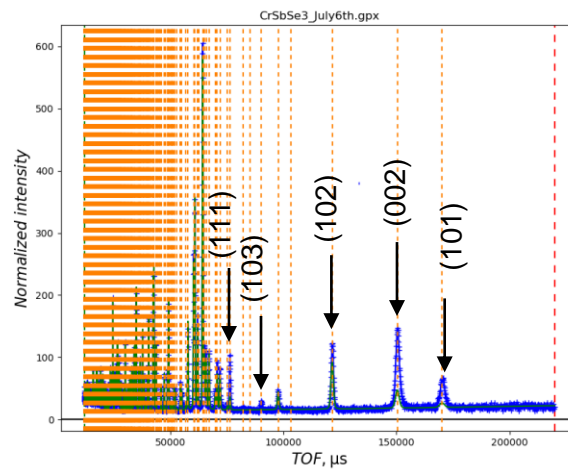
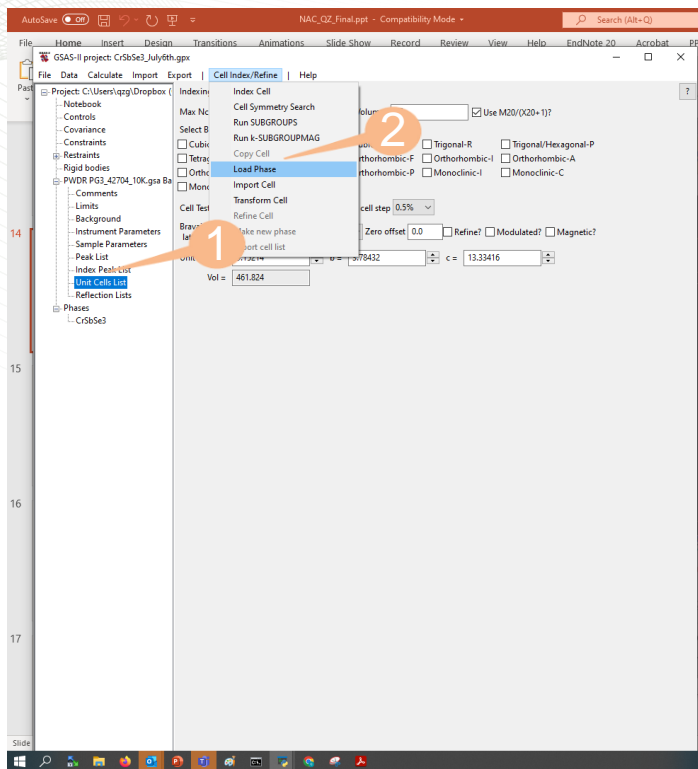
Refinement controls

Select

- F - site fractions
- X - coordinates
- U - thermal parameters



II. Determine the magnetic propagation vector



Magnetic peaks sit on the nuclear peak positions!

$$\mathbf{k} = \mathbf{Q}_M - \mathbf{Q}_N = 0$$

III. Obtain all the possible magnetic models with $k=0$

k-SUBGROUPSMAG options

k-vector 1: 0 0 0

k-vector 2: [dropdown]

k-vector 3: [dropdown]

Use whole star:

Filter by: [dropdown]

reserve axes:

test for mag. atoms: [dropdown]

all have moment:

max unique: 100

Ok Cancel

Bilbao k-SUBGROUPSMAG

For use of k-SUBGROUPSMAG, please cite:
 Symmetry-Based Computational Tools for Magnetic Crystallography,
 J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, and M.I. Aroyo
 Annu. Rev. Mater. Res. 2015. 45,217-48.
 doi: <https://doi.org/10.1146/annurev-matsci-070214-021008>

OK

GSAS-II project: CrSbSe3_N.gpx

Cell Index/Refine | Help

Run k-SUBGROUPSMAG

GSAS-II project: CrSbSe3_N.gpx

File Data Calculate Import Export | Cell Index/Refine | Help

Project: CrSbSe3_N.gpx

Indexing controls:

Max Nc/Nobs: 4 Start Volume: 25 Use M20/(X20+1)?

Select Bravais Lattices for indexing:

Cubic-F Cubic-I Cubic-P Trigonal-R Trigonal/Hexagonal-P

Tetragonal-I Tetragonal-P Orthorhombic-F Orthorhombic-I Orthorhombic-A

Orthorhombic-B Orthorhombic-C Orthorhombic-P Monoclinic-I Monoclinic-A

Monoclinic-C Monoclinic-P Triclinic

Cell Test & Refinement: Show hkl positions cell step 0.5%

Bravais lattice: Pmmm Space group: P n m a Zero offset: 0.0 Refine? Modulated? Magnetic?

Unit cell: a = 9.15209 b = 3.78432 c = 13.33414

Vol = 461.820

Magnetic subgroup cells from Bilbao k-SUBGROUPSMAG for P n m a; kvec1=(0,0,0):

	Space Gp	Try	Keep	nConj	nSup	Trans	Vec	a	b	c	alpha	beta	gamma	Volume	
1	Pn'm'a'	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82
2	Pn'm'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82
3	Pn'm'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82
4	Pn'm'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82
5	Pnma'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82

IV. Select magnetic space group Pn'm'a' for the refinement

GSAS-II project: CrSbSe3_N.gpx

File Data Calculate Import Export Cell Index/Refine Help

Project: CrSbSe3_N.gpx

Indexing controls:
 Max Nc/Nobs: 4 Start Volume: 25 Use M20/(X20+1)?

Select Bravais Lattices for indexing:
 Cubic-F Cubic-I Cubic-P Trigonal-R Trigonal/Hexagonal-P
 Tetragonal-I Tetragonal-P Orthorhombic-F Orthorhombic-I Orthorhombic-A
 Orthorhombic-B Orthorhombic-C Orthorhombic-P Monoclinic-I Monoclinic-A
 Monoclinic-C Monoclinic-P Triclinic

Cell Test & Refinement: Show hkl positions cell step: 0.5%
 Bravais lattice: Pmmm Space group: Pnma Zero offset: 0.0 Refine? Modulated? Magnetic?

Unit cell: a = 9.15209 b = 3.78432 c = 13.33414
 Vol = 461.820

Magnetic subgroup cells from Bilbao k-SUBGROUPS: SMAG for Pnma; kvec1=(0,0,0):

	Space Grp	Try	Keep	nj	nSup	Trans	Vec	a	b	c	alpha	beta	gamma	Volume	
1	Pn'm'a'	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82
2	Pn'm'a'	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82
3	Pnm'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	1	1	1	a,b,c	0,0,0	9.15209	3.78432	13.33414	90.000	90.000	90.000	461.82

Magnetic space group information

Magnetic Space Group: P n ' m ' a '
 The lattice is centrosymmetric primitive orthorhombic
 The Laue symmetry is mmm
 The magnetic lattice point group is m'm'm'
 Multiplicity of a general site is 8
 The inversion center is located at 0,0,0

The equivalent positions are:

- (1) X, Y, Z, (1)
- (2) 1/2-X, 1/2+Y, 1/2+Z, (mx)
- (3) X, 1/2-Y, Z, (my)
- (4) 1/2-X, -Y, 1/2+Z, (2z)
- (5) -X, -Y, -Z, (-1)
- (6) 1/2+X, 1/2-Y, 1/2-Z, (2x)
- (7) -X, 1/2+Y, -Z, (2y)
- (8) X, Y, 1/2-Z, (mz)

OK Print Ops

GSAS-II project: CrSbSe3_July6th.gpx

File Data Calculate Import Export Select/Show Cell Index/Refine Help

Project: C:\Users\ozg\Dropbox\GSAS-II\GSAS-II\CrSbSe3_July6th.gpx

Phase name: CrSbSe3

Space group: Pnma Modulated?

c = 13.33416 Vol = 461.824

Fourier map controls: Map type: Reflection sets: Select reflection sets
 Map grid step: 0.25 Peak cutoff %: 50.0

Charge flip controls: Reflection sets: Select reflection sets Normalizing element: None
 Map grid step: 0.25 k-Factor (0.1-1.2): 0.1 k-Max (>=10.0): 20.0
 Test HKLs: 0 0 2 2 0 0 1 1 1 0 2 0 1 2 3

Monte Carlo/Simulated Annealing controls: Reflection sets from: d-min: 2.8
 MC/SA runs: 1 MC/SA Refine at: 10.0 % of ranges.
 MC/SA schedule: log slope: 0.9
 Annealing schedule: Start temp: 0.7 Final temp: 0.1 No. trials: 250

Make new magnetic phase

Select magnetic space group

- (1) Pn'm'a'; (a,b,c) + (0,0,0)
- (2) Pn'm'a'; (a,b,c) + (0,0,0)
- (3) Pnm'a'; (a,b,c) + (0,0,0)
- (4) Pn'm'a'; (a,b,c) + (0,0,0)
- (5) Pnma'; (a,b,c) + (0,0,0)
- (6) Pnm'a'; (a,b,c) + (0,0,0)
- (7) Pn'm'a'; (a,b,c) + (0,0,0)
- (8) Pnma; (a,b,c) + (0,0,0)
- (9) Pn'21a'; (a,b,c) + (0,0,0)
- (10) Pn21'a'; (a,b,c) + (0,0,0)

OK Cancel

Save as a new gpx file

Magnetic atom selection

For: (1) Pn'm'a'; (a,b,c) + (0,0,0)
 Name, x, y, z, allowed moments, mag. site sym:

Use? Cr_0 0.15649 0.25000 0.04390 (Mx, ---, Mz) m'(y)

Yes No Delete

Choose GSAS-II project file name

File name: CrSbSe3_1_mag_1
 Save as type: GSAS-II project file (*.gpx)

Save Cancel

Refine m_x and m_z , and peak profile coefficient X:

GSAS-II project: CrSbSe3_1_mag_1.gpx

File Data Calculate Import Export | Select tab Edit Atoms Compute | Help

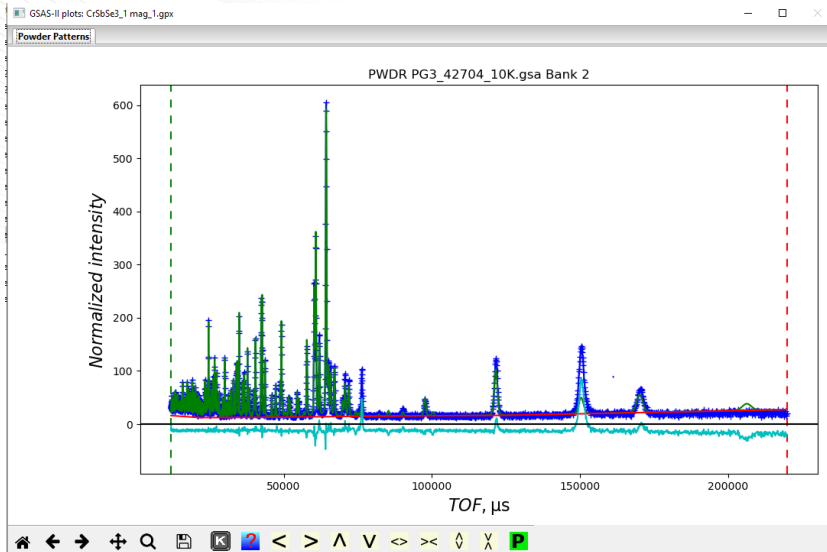
Project: C:\Users\qzg\Dropbox (...)

- Notebook
- Controls
- Covariance
- Constraints
- Restraints
- Rigid bodies
- PWDR PG3_42704_10K.gsa B...
- Comments
- Limits
- Background
- Instrument Parameters
- Sample Parameters
- Peak List
- Index Peak List
- Unit Cells List
- Reflection Lists
- Phases
 - CrSbSe3_1
 - CrSbSe3_1_mag_1

General	Data	Atoms	Draw Options	Draw Atoms	RB Models	Map peaks	MC/SA	RMC	Texture	Pawley reflections					
		Name	Type	refl	x	y	z	frac	Mx	My	Mz	site sym	mult	I/A	Uiso
0		Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	1.0000			m'(y)	4	I	0.00176

Visualizing the magnetic structure

In "Draw Atoms" tab:



Poor refinement quality

GSAS-II project: CrSbSe3_1 mag_1.gpx

File Data Calculate Import Export | Select tab Edit Figure Compute Restraints Rigid body | Help

Project: C:\Users\qzg\Dropbox

General	Data	Atoms	Draw Options	Draw Atoms	RB Models	Map peaks	MC/SA	RMC	Texture	Pawley reflections				
		Name	Type	x	y	z	Mx	My	Mz	Sym Op	Style	Label	Color	I/A
		0	Cr1	Cr+3	0.15649	0.25000	0.04390	1.3911	0.0000	-0.4188	1	vdW balls		1

1

Select atoms for action

Select atoms Name

0) Cr_0

Apply stride: 1

Set All Toggle All

Set Range

OK Cancel

2

3

GSAS-II project: CrSbSe3_1 mag_1.gpx

File Data Calculate Import Export | Select tab Edit Atoms Compute | Help

Project: C:\Users\qzg\Dropbox

General	Data	Atoms	Draw Options	Draw Atoms	RB Models	Map peaks	MC/SA	RMC	Texture	Pawley reflections					
		Name	Type	refine	x	y	z	frac	Mx	My	Mz	site sym	mult	I/A	Uiso
		0	Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	1.3911		-0.4188 m(y)	4	1	0.00176

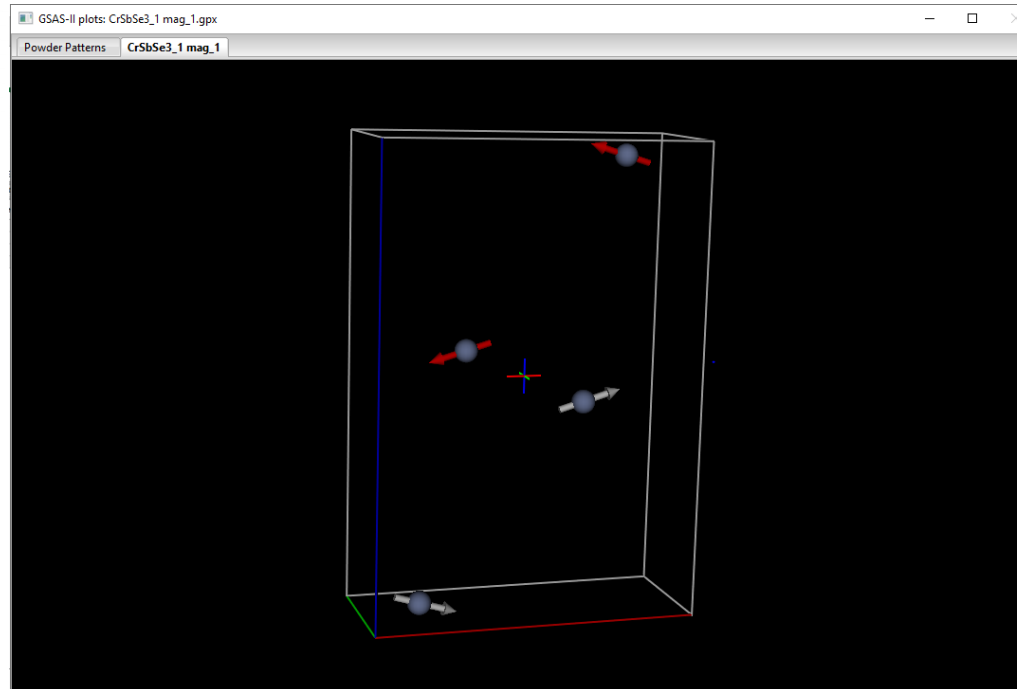
“Draw atom” tab will be updated

GSAS-II project: CrSbSe3_1 mag_1.gpx

File Data Calculate Import Export | Select tab Edit Figure Compute Restraints Rigid body | Help

Project: C:\Users\qzg\Dropbox (...)
Notebook
Controls
Covariance
Constraints
Restraints
Rigid bodies
PWDR PG3_42704_10K.gsa B...

	General	Data	Atoms	Draw Options	Draw Atoms	RB Models	Map peaks	MC/SA	RMC	Texture	Pawley reflections				
			Name	Type	x	y	z	Mx	My	Mz	Sym Op	Style	Label	Color	I/A
0			Cr1	Cr+3	0.15649	0.25000	0.04390	1.3911	0.0000	-0.4188	1	vdW balls			I
1			Cr1	Cr+3	0.34352	0.75000	0.54390	-1.3911	0.0000	-0.4188	2+0,0,0	vdW balls			I
2			Cr1	Cr+3	0.84352	0.75000	0.95610	-1.3911	-0.0000	0.4188	-1+1,1,1	vdW balls			I
3			Cr1	Cr+3	0.65648	0.25000	0.45610	1.3911	-0.0000	0.4188	-2+1,1,1	vdW balls			I



Canted AFM order with magnetic space group $Pn'm'a'$ can be excluded.

V. Select magnetic space group Pnm'n' for the refinement

GSAS-II project: Cr5Se3_July6th.gpx

File Data Calculate Import Export | Cell Index/Refine | Help

Project: C:\Users\jgg\Dropbox\...

Indexing controls: Max Nc/Nobs: 4 Start Volume: 25 Use M20/(X20-1)?

Select Bravais Lattices for indexing:

Cell Test & Refinement: Show hkl positions cell step 0.5%

Bravais lattice: Pmmm Space group: P n m a Zero offset: 0.0 Refine? Modulated? Magnetic?

Unit cell: a = 9.15214 b = 3.78432 c = 13.33416 Vol = 461.824

Magnetic subgroup cells from Bilbao k-SUBGROUPSMAG for P n m a, kvec1=(0,0,0):

Space Gp	Try	Keep	Uniq	nSup	Trans	Vec	a	b	c	alpha	beta
1 Pn'm'a'	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	1	a,b,c	0,0,0	9.15214	3.78432	13.33416	90.000	90.000
2 Pn'm'a'	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	1	a,b,c	0,0,0	9.15214	3.78432	13.33416	90.000	90.000
3 Pnm'a'	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	0	1	a,b,c	0,0,0	9.15214	3.78432	13.33416	90.000
4 Pn'm'a'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	0	1	a,b,c	0,0,0	9.15214	3.78432	13.33416	90.000
5 Pnma'	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	0	1	a,b,c	0,0,0	9.15214	3.78432	13.33416	90.000

Magnetic space group information

Magnetic Space Groups: P n m 'a'

The lattice is centrosymmetric primitive orthorhombic
The Laue symmetry is mmm

The magnetic lattice point group is mm'm'

Multiplicity of a general site is 8

The inversion center is located at 0,0,0

The equivalent positions are:

1	X	Y	Z	(1)	(2)	1/2-X, 1/2+Y, -Z	(ms)
3	X	1/2-Y	Z	(my)	(4)	1/2-X, -Y, -Z	(2s)
5	-X, -Y, -Z	(-1)	(6)	1/2+X, 1/2-Y, -Z	(2b)		
7	-X, 1/2-Y, -Z	(2y)	(8)	1/2-X, -Y, -Z	(mz)		

OK Print Ops

GSAS-II project: Cr5Se3_July6th.gpx

File Data Calculate Import Export | Select tab | Compute | Help

Project: C:\Users\jgg\Dropbox\...

General Data

Fourier map Search map

Charge flipping 4D Charge flipping

Refine unit cell Clear map

Density: 5.906

MC/SA Multi MC/SA Transform Compare

Select magnetic/subgroup phase

Space group: P n m a Modulated? c = 13.33416 Vol = 461.824

Pawley controls: Do Pawley refinement? Pawley dmin: 1.0 Pawley dmax: 100.0 Pawley neg. wt.: 0.0

Fourier map controls: Map type: Reflection sets Select reflection sets

Map grid step: 0.25 Peak cutoff %: 50.0

Charge flip controls: Reflection sets Select reflection sets Normalizing element: None

Map grid step: 0.25 k-factor (0.1-1.2): 0.1 h-Max (h=10.0): 20.0

Test HKL: 0 0 2 2 0 0 1 1 1 0 2 0

Monte Carlo/Simulated Annealing controls: Reflection set from: d-min: 2.8

MC/SA runs: 1 MC/SA Refine at: 10.0 % of ranges.

MC/SA schedule: log slope: 0.9

Annealing schedule: Start temp: 0.7 Final temp: 0.1 No. trials: 250

Make new magnetic phase

Select magnetic space group

- (1) Pn'm'a'; (a,b,c) + (0,0,0)
- (2) Pn'm'a'; (a,b,c) + (0,0,0)
- (3) Pnm'a'; (a,b,c) + (0,0,0)
- (4) Pn'm'a'; (a,b,c) + (0,0,0)
- (5) Pnma'; (a,b,c) + (0,0,0)
- (6) Pnm'a'; (a,b,c) + (0,0,0)
- (7) Pn'm'a'; (a,b,c) + (0,0,0)
- (8) Pnma'; (a,b,c) + (0,0,0)
- (9) Pn'21a'; (a,b,c) + (0,0,0)
- (10) Pn21'a'; (a,b,c) + (0,0,0)

OK

Cancel

Magnetic atom selection

For: (3) Pnm'a'; (a,b,c) + (0,0,0)

Name, x, y, z, allowed moments, mag. site sym:

Use? Cr_0 0.15660 0.25000 0.04388 (Mx, ---, Mz) m'(y)

Yes

No

Delete

Save as a new GSAS-II file!

Refine the components Mx and Mz of magnetic moment

GSAS-II project: CrSbSe3 mag_3.gpx

File Data Calculate Import Export | Select tab Edit Atoms **1** Compute | Help

Project: C:\Users\qzg\Dropbox (...)

Notebook
Controls
Covariance
Constraints

	Name	Type	refine 2	x	y 3	z	frac	Mx 3	My	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15659	0.25000	0.04370	1.0000	1.0000		1.0000	m'(y)	4	I	0.00111

Calculate-refine:

Refinement results, $R_w = 3.899$



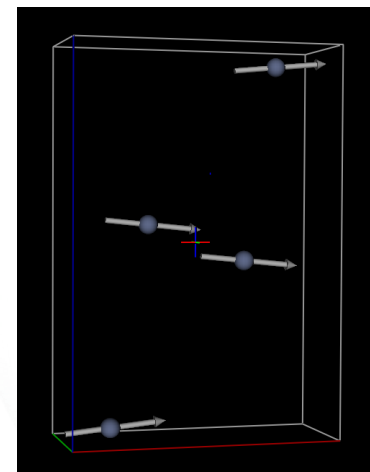
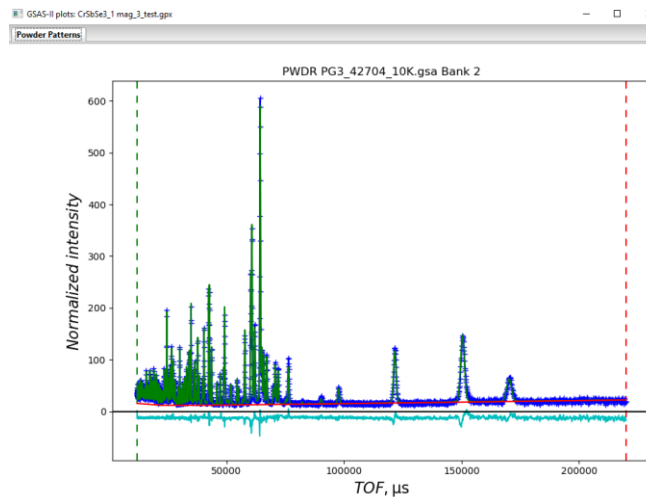
Detailed results are in
C:\Users\qzg\Dropbox
(ORNL)\POWGEN\NXS\202...\CrSbSe3_1
mag_3_test.lst

Final Reduced χ^2 : 5.294 (before ref: 5.295)

Load new result?

4

OK Cancel



	Name	Type	refine	x	y	z	frac	Mx	My	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	2.6208		0.1767	m'(y)	4	I	0.00176

*FM alignment along the a axis;
AFM alignment along the c axis.*

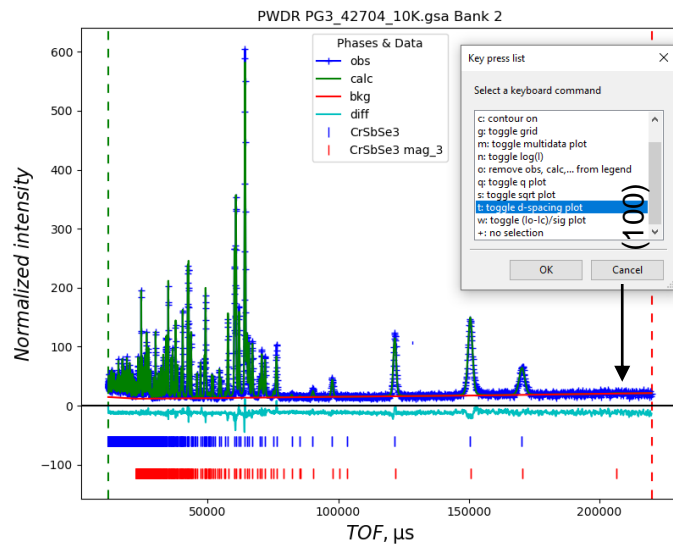
Check if small Mz is real

GSAS-II project: CrSbSe3_1 mag_3_test.gpx

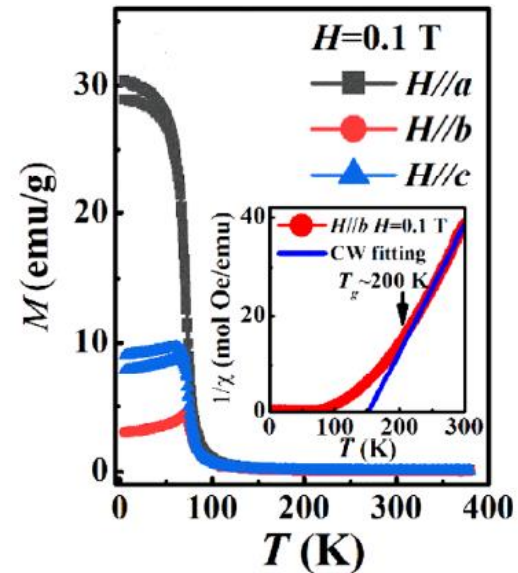
File Data Calculate Import Export | Select tab Edit Atoms Compute | Help

Project: C:\Users\qzg\Dropbox (...)
 Notebook
 Controls
 Covariance
 Constraints

General	Data	Atoms	Draw Options	Draw Atoms	RB Models	Map peaks	MC/SA	RMC	Texture	Pawley reflections					
		Name	Type	refine	x	y	z	frac	Mx	My	Mz	site sym	mult	I/A	Uiso
		0	Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	2.6208	0.1669	m (y)	4	1	0.00176



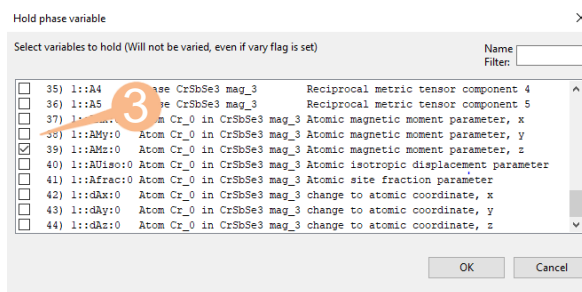
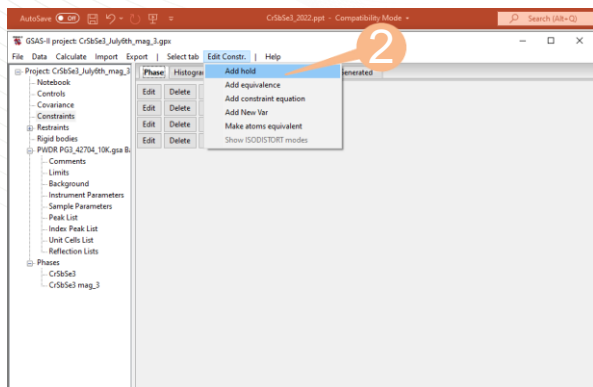
a. Zero (100) magnetic peak:
 moment along the *a* axis.



b. Highest magnetization with
 $H//a$: moment along the *a* axis.

c. Similar refinement quality if Mz=0

General	Data	Atoms	Draw Options	Draw Atoms	RB Models	Map peaks	MC/SA	RMC	Texture	Pawley reflections			
	Name	Type	refine	x	y	z	frac	Mx	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	2.6214	0.0000	m'(y)	4	I	0.00176



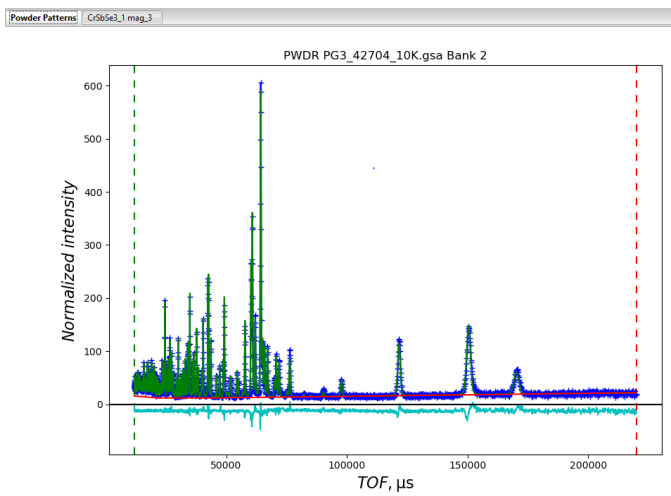
Refinement results, $R_w = 3.901$

i Detailed results are in C:\Users\qzg\Dropbox\ORNL\POWGEN\NXS\202...\CrSbSe3_1_mag_3_test_mz_zero.lst

Final Reduced χ^2 : 5.298 (before ref: 5.298)

Load new result?

4 OK Cancel

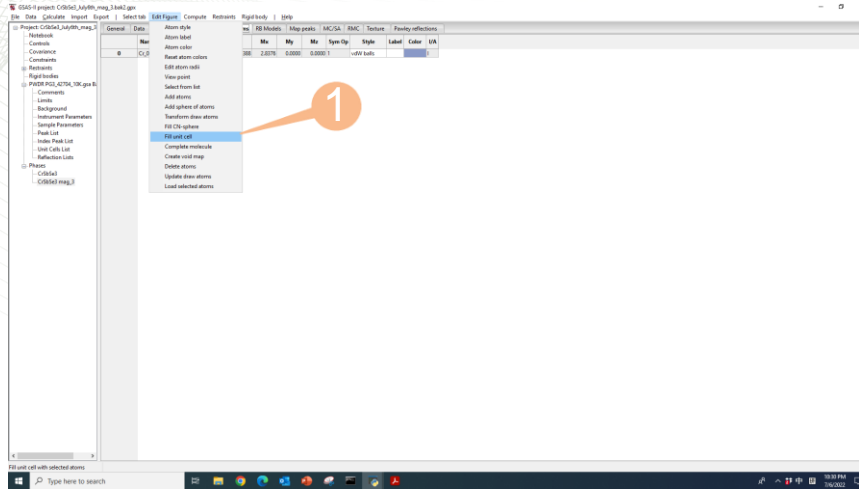


General	Data	Atoms	Draw Options	Draw Atoms	RB Models	Map peaks	MC/SA	RMC	Texture	Pawley reflections				
	Name	Type	refine	x	y	z	frac	Mx	My	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	2.6360		0.0000	m'(y)	4	I	0.00176

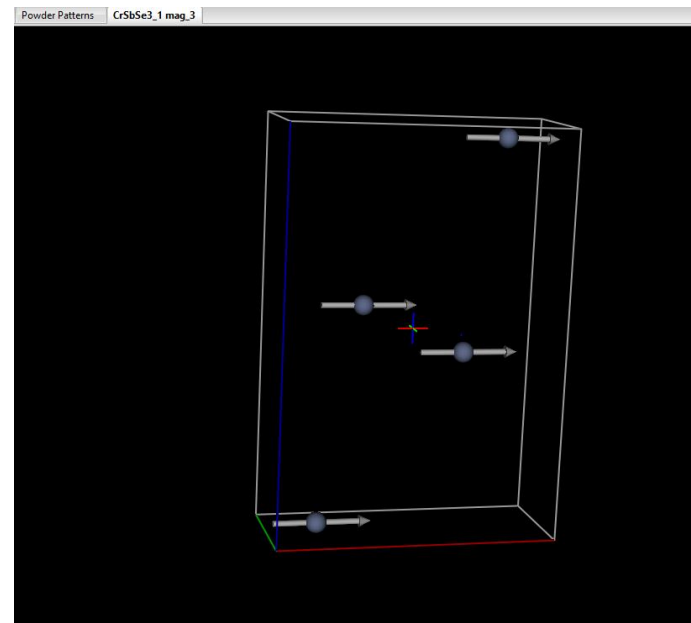
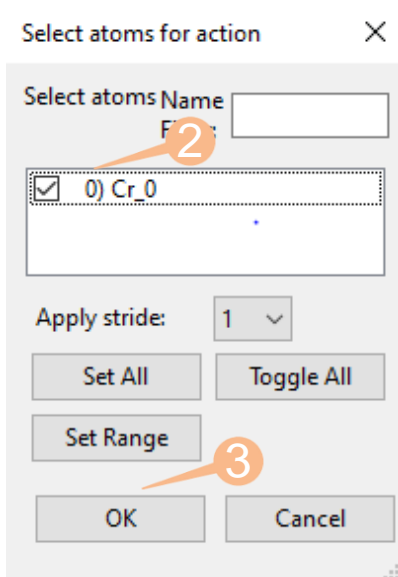
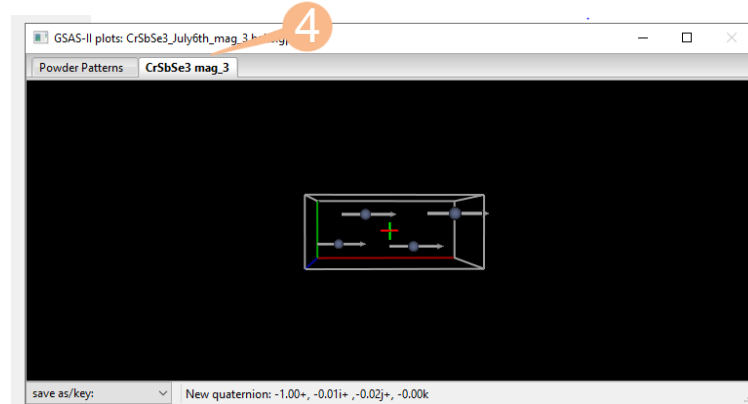
$$\mathbf{M} = (2.64, 0, 0) \mu_B$$

Visualizing the magnetic structure

In "Draw Atoms" tab:



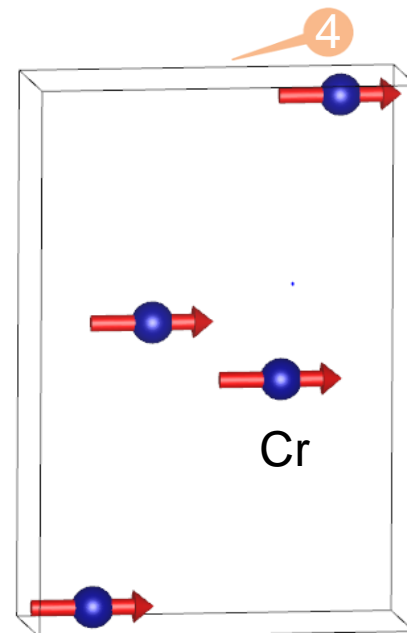
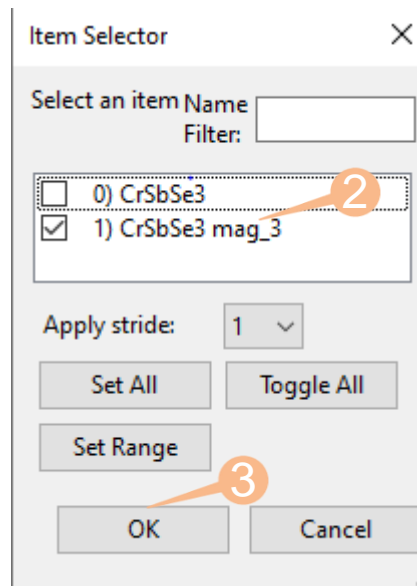
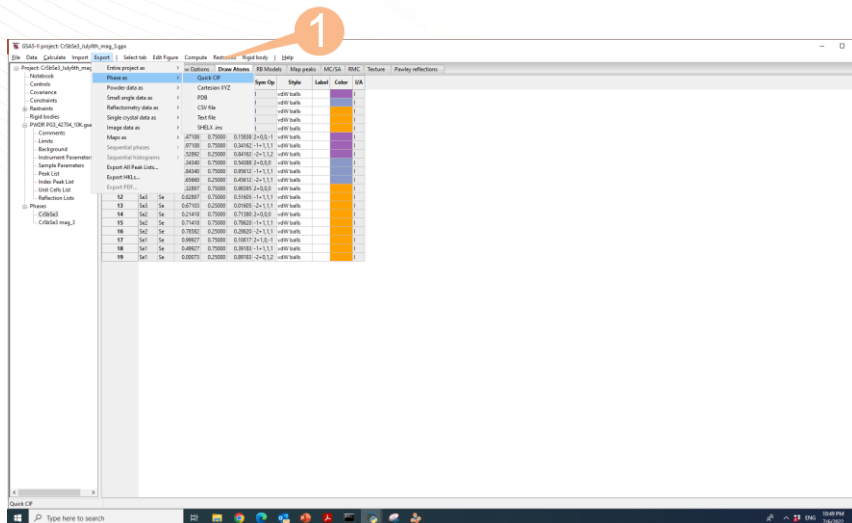
Ferromagnetic order



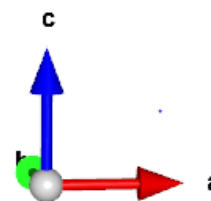
To publish the results

I. 3D magnetic structure

Export to cif file: Export- phase as- quick cif

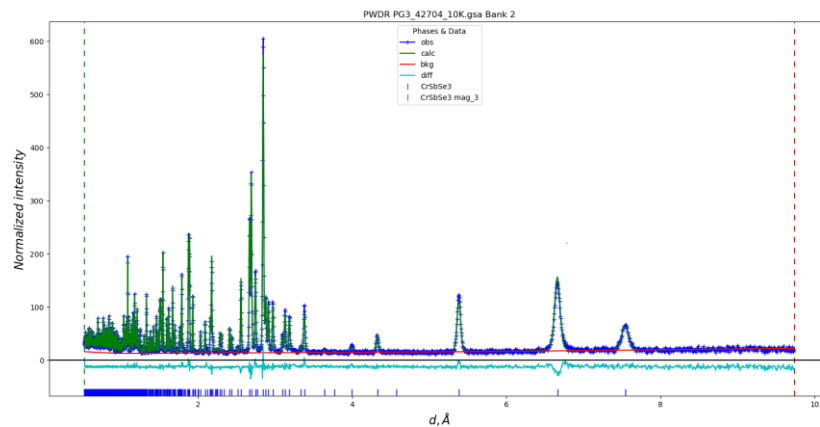
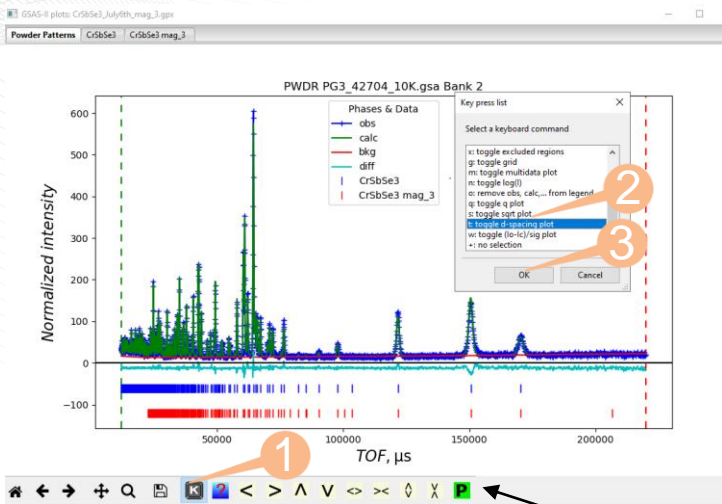


Use VESTA software (jp-minerals.org/vesta/en/download.html) to open it directly for publication:

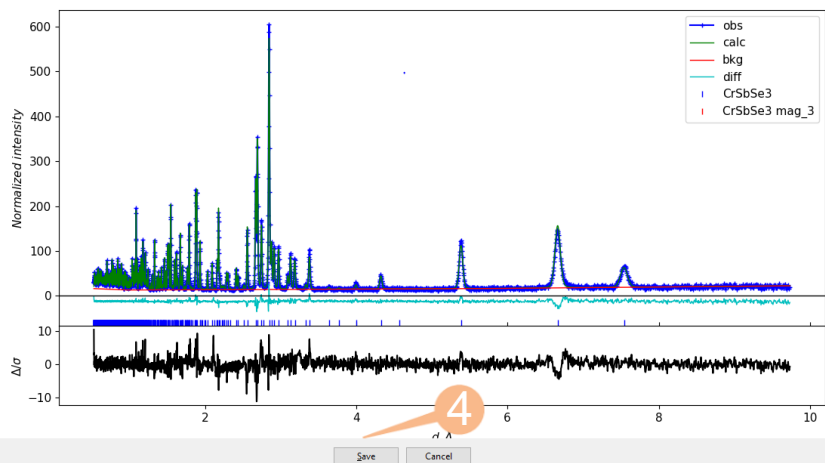
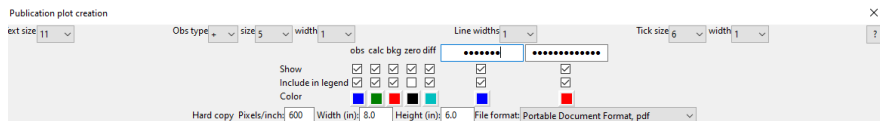


II. Refinement plots

Convert TOF to d



Click P button to open a new window



GSAS-II tutorial on crystal and commensurate magnetic structure

Please contact me if you have any question or comments. Thanks!

zhangq6@ornl.gov