

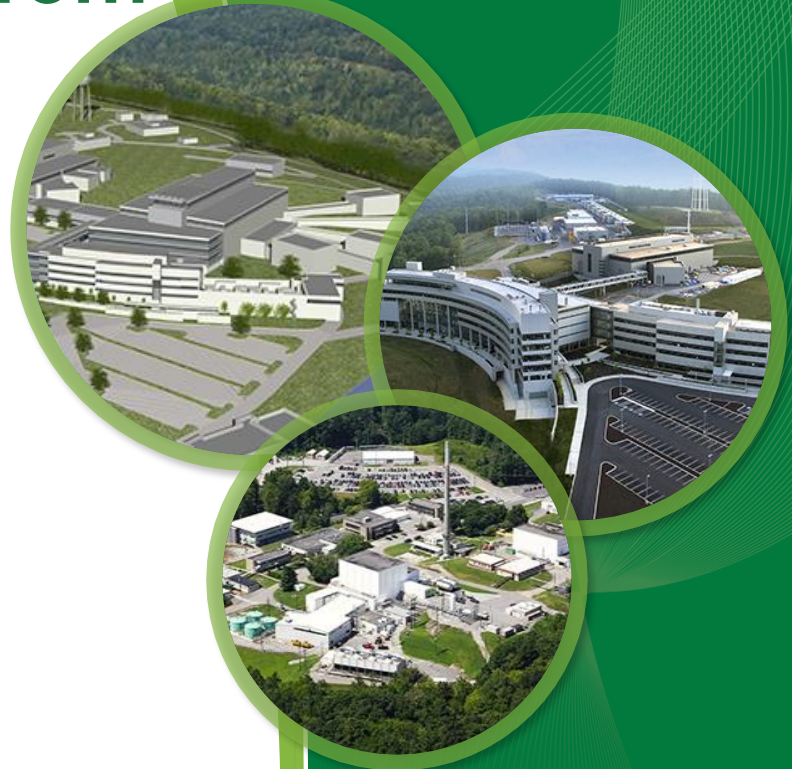
# GSAS-II refinement of commensurate structure from TOF data

**Qiang Zhang**

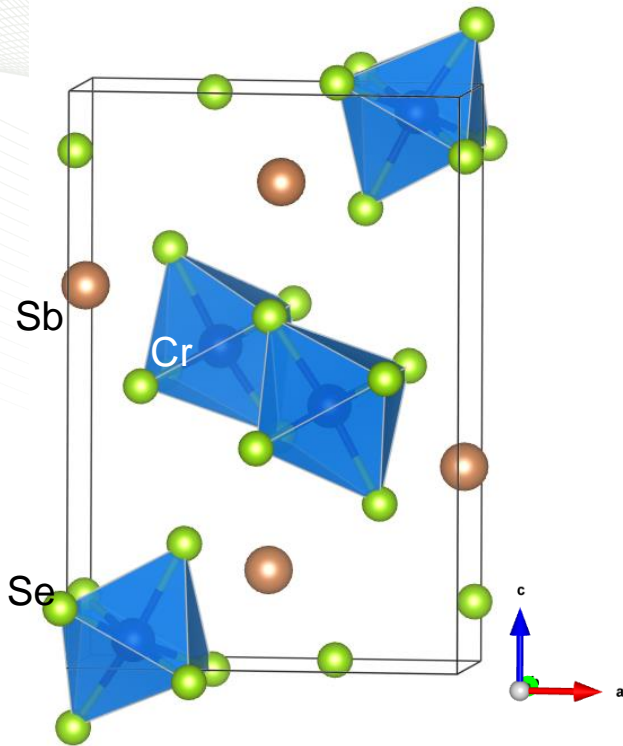
Neutron Scattering Division, ORNL

**Magnetic Structure Determination from Neutron Diffraction Data (MagStr), October 3-7, 2022**

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

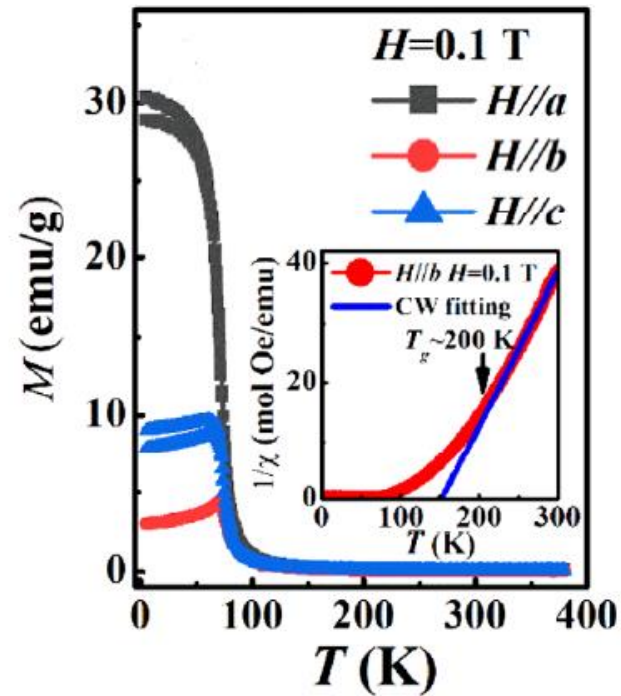


# Basic information on $\text{CrSbSe}_3$



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

- Octahedra  $\text{CrSe}_6$



- 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

CrSbSe<sub>3</sub>.cif

- Final PCR files

CrSbSe3\_N.gpx

CrSbSe3\_1 mag\_3.gpx

- Supporting information

GSAS\_II\_QZhang.PDF (step-by-step instructions)

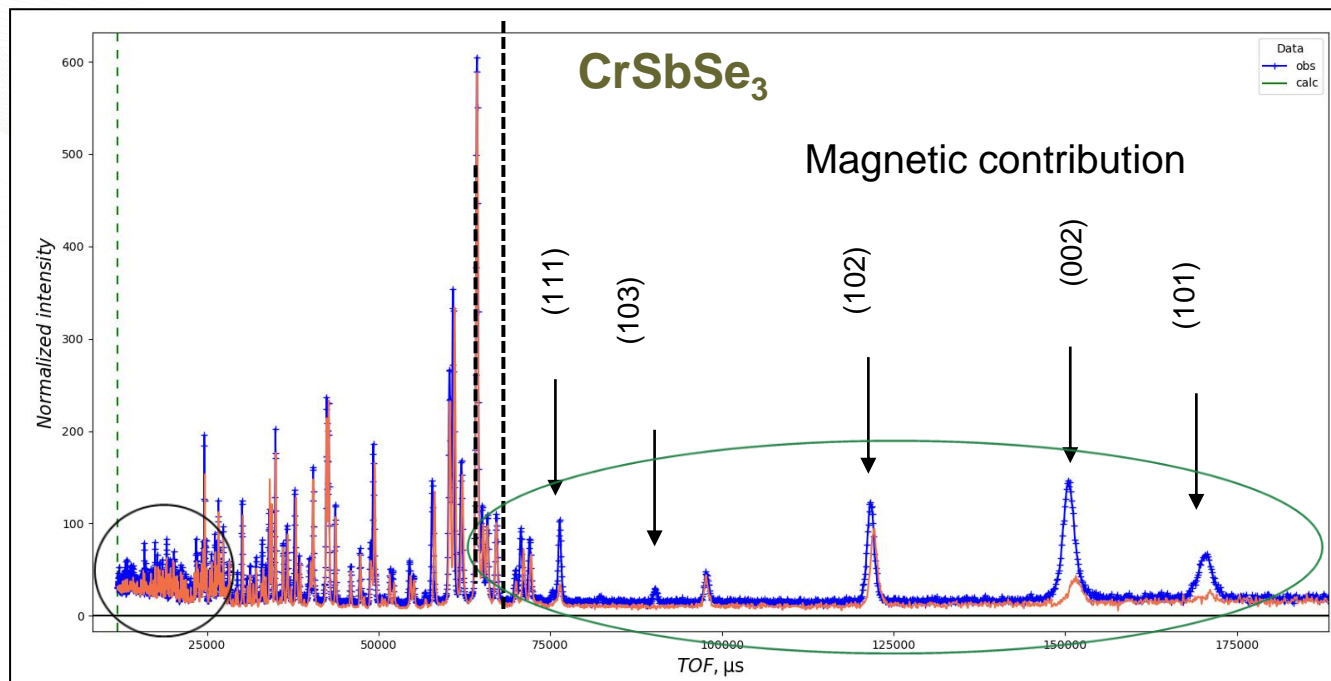
jacs.1c09607.PDF

# Exercise steps

- Identify magnetic peaks in  $\text{CrSbSe}_3$ ;
- Refine the structure of  $\text{CrSbSe}_3$  at 10 K ( $T < T_m$ );
- Refine the magnetic structure of  $\text{CrSbSe}_3$  at 10 K;
- Check if small  $M_z$  (AFM component) is real;
- To publish the magnetic structure and refinement plots;



# Identify magnetic peaks in CrSbSe<sub>3</sub>



Smaller thermal parameters

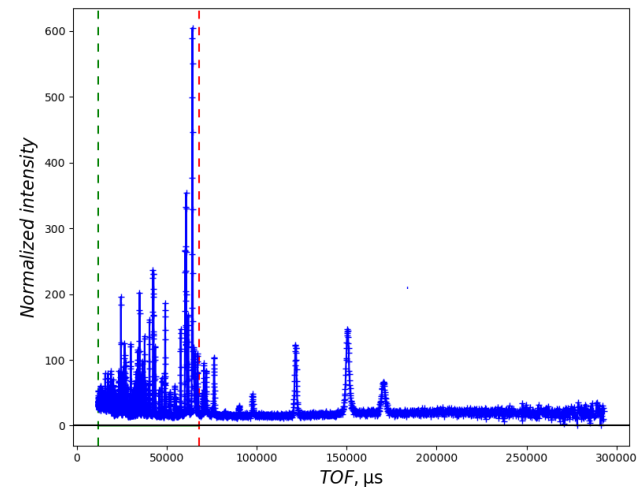
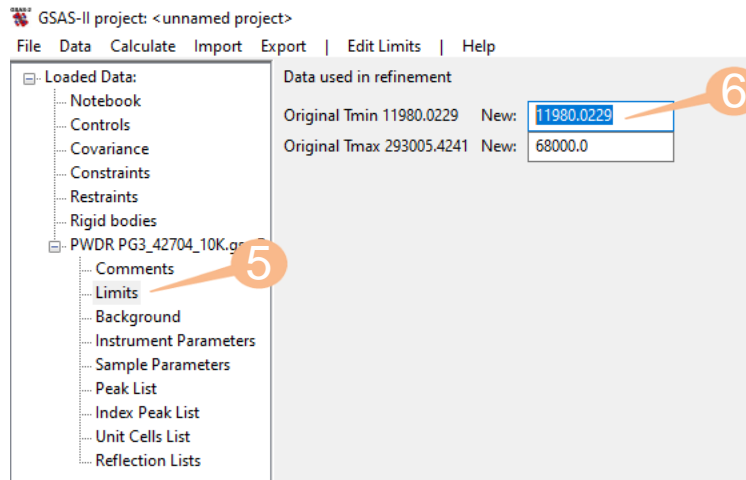
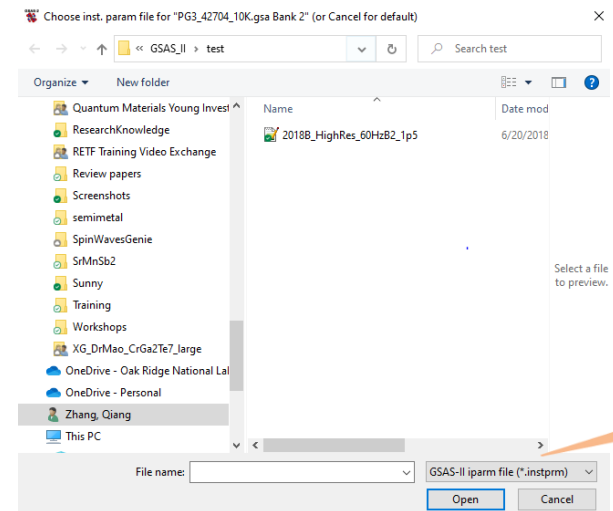
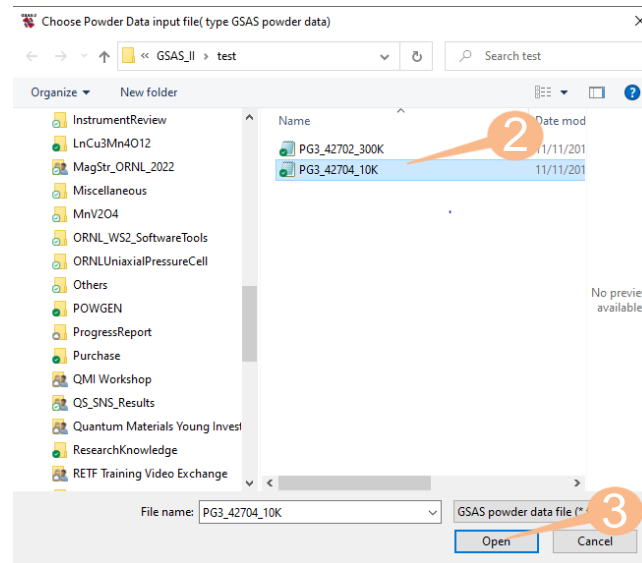
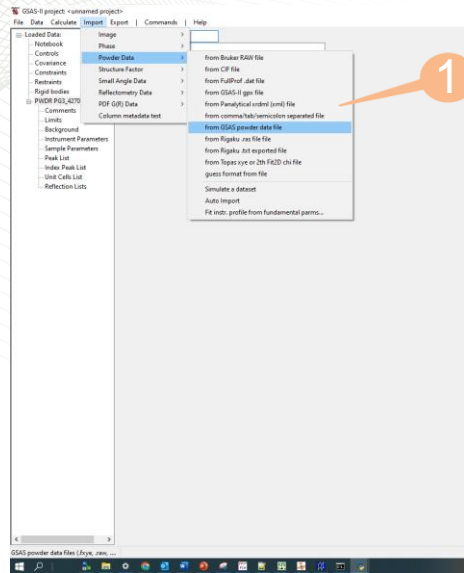
At 10 K, the intensities at high  $d$  part and low  $d$  part both increased: different origins!

**Two ways to determine the structural parameters in  $T < T_N$  (or  $T_C$ ) before refining  $k=0$  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  $\text{TOF} < 68,000 \mu\text{s}$

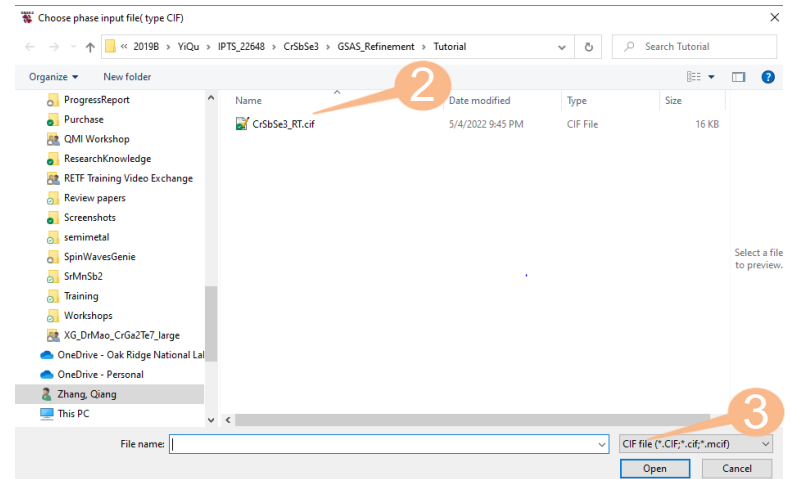
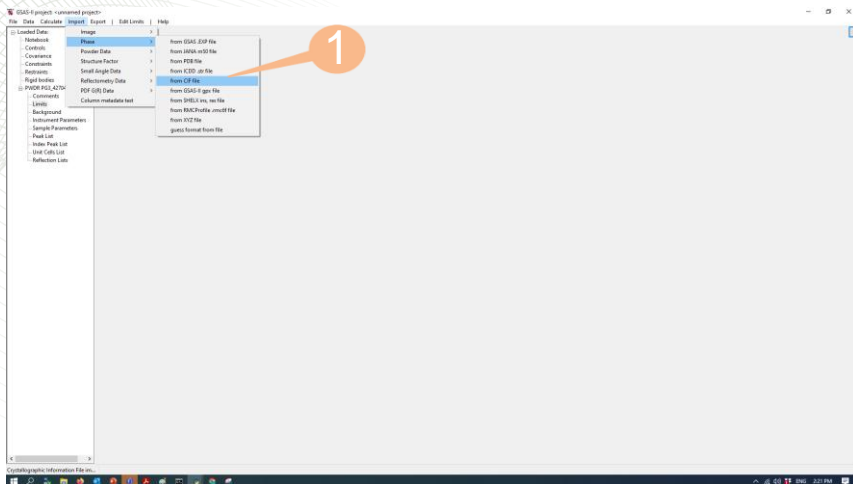
# Refine the structure of $\text{CrSbSe}_3$

## 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

Edit phase name

Enter the name for the new phase

CrSbSe3

OK

Add histogram(s)

Select histogram(s) to add to new phase  
CrSbSe3

Name

Filter:

☒ 0) PWDR PG3 42704 10K.gsa Bank 2

Apply stride:

1

Set All

Toggle All

Set Range

OK

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 (C:\Users\qzg\Dropbox)

- Notebook
- Controls
- Covariance
- Constraints
- Restraints
- Rigid bodies
- PWDR PG3\_42704\_10K.gsa Ba
- Comments
- Limits
- Background
- Instrument Parameters
- Sample Parameters
- Peak List
- Index Peak List
- Unit Cells List
- Reflection Lists
- Phases
- CrSbSe3

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 |
|---------|---------|-------|---------|---------|

Debye scatterings: Number of terms: 0

Peaks in background: Number of peaks: 0

Fixed background file:

multiplier: 1.0

GSAS-II project: CrSbSe3\_July6th.gpx

File Data Calculate Import Export | Command | Help

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

- Notebook
- Controls
- Covariance
- Constraints
- Restraints
- Rigid bodies
- PWDR PG3\_42704\_10K.gsa Ba
- Comments
- Limits
- Background
- Instrument Parameters
- Sample Parameters
- Peak List
- Index Peak List
- Unit Cells List
- Reflection Lists
- Phases
- CrSbSe3

Sample and Experimental Parameters

Instrument Name: **Debye-Scherrer**

Diffractometer type: Debye-Scherrer

☒ Histogram scale factor: 1.0

☐ Sample absorption ( $\mu_r/\lambda$ ): 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.

GSAS-II project: Ngpx

File Data Calculate Import Export Help

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

- Notebook
- Controls
- Covariance
- Constraints
- Restraints
- Rigid bodies
- PWDR PG3\_42704\_10K.gsa Ba
- Comments
- Limits
- Background
- Instrument Parameters
- Sample Parameters
- Peak List
- Index Peak List
- Unit Cells List
- Reflection Lists
- Phases
- CrSbSe3

Refinement Controls

Refinement type: **analytic Hessian**

Max cycles: 10

SVD zero tolerance: 1e-06

Initial lambda =  $10^{-3}$

Select datasets to switch to sequential refinement: **Select datasets**

CIF Author (last, first): no name

GSAS-II project: CrSbSe3\_July6th.gpx

File Data Calculate Import Export | Command | Help

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

- Notebook
- Controls
- Covariance
- Constraints
- Restraints
- Rigid bodies
- PWDR PG3\_42704\_10K.gsa Ba
- Comments
- Limits
- Background
- Instrument Parameters
- Sample Parameters
- Peak List
- Index Peak List
- Unit Cells List
- Reflection Lists
- Phases
- CrSbSe3

Refinement Controls

Refinement type: **analytic Hessian**

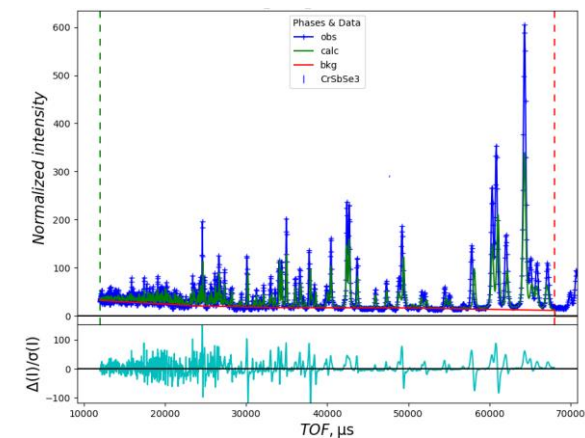
Max cycles: 10

SVD zero tolerance: 1e-06

Initial lambda =  $10^{-3}$

Select datasets to switch to sequential refinement: **Select datasets**

CIF Author (last, first): no name





## IV. Refine lattice constants

GSAS-II project: CrSbSe3\_July6th.gpx

File Data Calculate Import Export | Select tab Compute Help

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

General Data Atoms Draw Options Draw Atoms RB Models Map peaks MC/SA RMC Texture Pawley re

Phase name: CrSbSe3 Phase type: nuclear Space group: P n m a Modulated? ☐

☒ Refine unit cell: a = 9.14236 b = 3.7842 c = 13.4159 Vol = 464.143

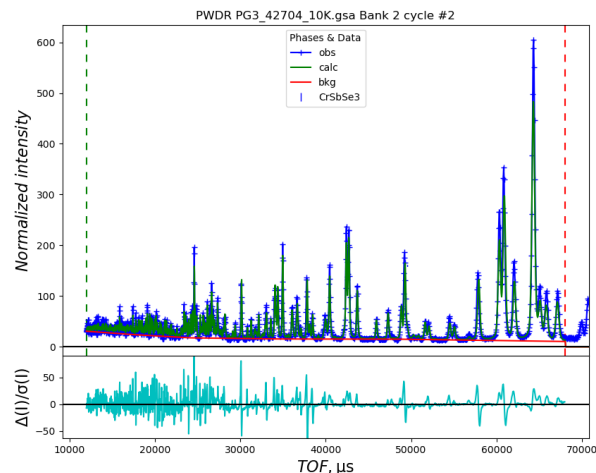
Density: 5.876

| Elements            | Sb          | Cr          | Se          |
|---------------------|-------------|-------------|-------------|
| Isotope             | Nat. Abund. | Nat. Abund. | Nat. Abund. |
| No. per cell        | 4.0         | 4.0         | 12.0        |
| Atom weight         | 121.750     | 51.996      | 78.960      |
| Bond radii          | 1.79        | 1.56        | 1.60        |
| Angle radii         | 1.59        | 1.36        | 1.40        |
| Van der Waals radii | 2.20        | 1.70        | 1.90        |
| Color               |             |             |             |

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

Phases

CrSbSe3



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  $\chi^2$ : 198.776 (before ref: 597.538)

Max shift/sigma=29.109

Load new result?

OK Cancel

Calculate-refine:

# V. Refine atomic coordinates and thermal parameters

GSAS-II project: CrSbSe3\_July6th.gpx

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

1

2

3

|   | Name | Type | refine | x       | y       | z       | frac   | site sym | mult | I/A | Uiso    | 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

4

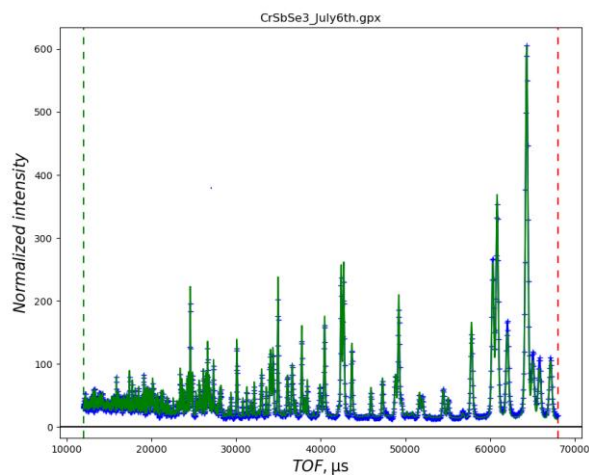
Select

☒ F - site fraction

☒ X - coordinates

☒ U - thermal parameters

OK Cancel



Refinement results,  $R_w = 8.161$



Detailed results are in  
C:\Users\qzg\Dropbox  
(ORNL)\POWGEN\I... \CrSbSe3\_July6th.lst

Final Reduced  $\chi^2$ : 38.383 (before ref: 47.785)

Max shift/sigma=0.827

Load new result?

5

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"/>            |

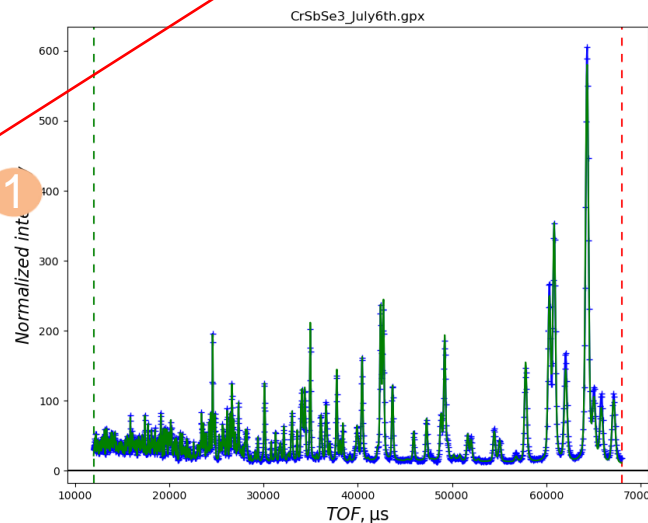
$$\text{TOF} = \text{DIFC} * d + \text{DIFA} * d^2 + \text{ZERO} + \text{DIFB} / d$$

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

(Gaussian function)

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

(Lorentz function)



Refinement results,  $R_w = 3.772$



Detailed results are in  
C:\Users\qzg\Dropbox  
(ORNL)\POWGEN\...\CrSbSe3\_July6th.lst

Final Reduced  $\chi^2$ : 8.205 (before ref: 72.633)

Max shift/sigma=0.645

Load new result?

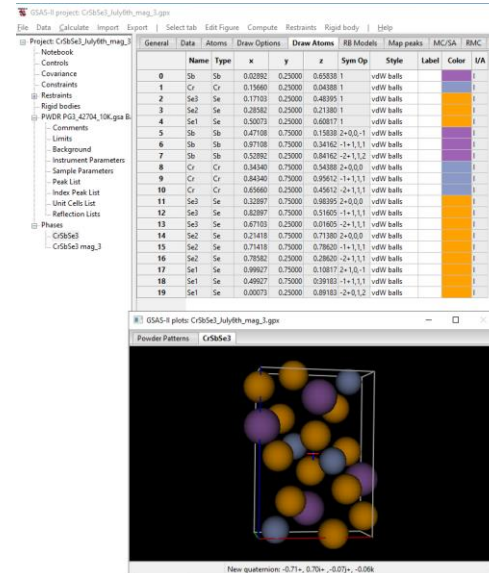
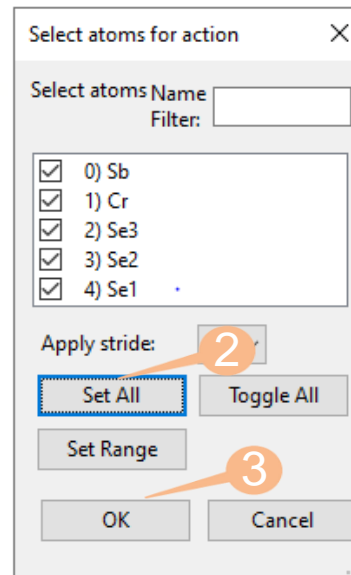
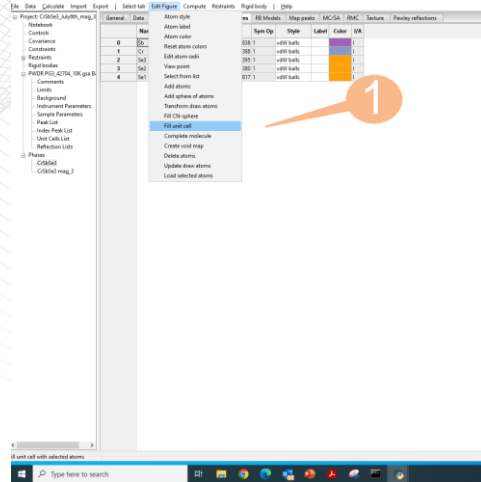
OK

Cancel

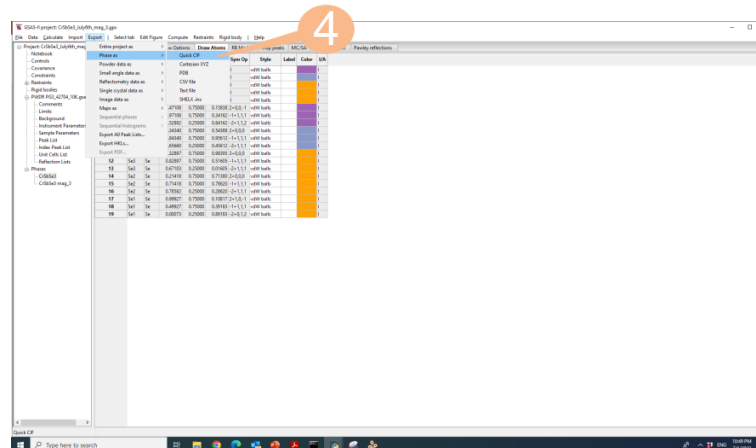
Calculate-refine:

# VII. Virtualizing crystal structure

In "Draw Atoms" tab:

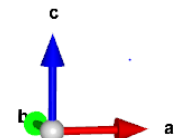
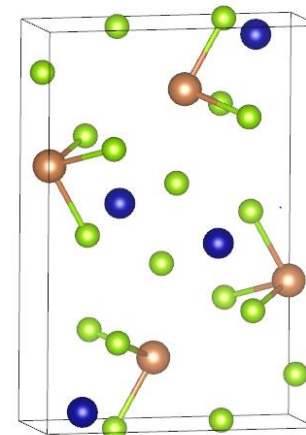


Export cif file:



Use VESTA software ([jp-minerals.org/vesta/en/download.html](http://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 CrSbSe<sub>3</sub>

## I. Add the high TOF data back and refine background

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

GSAS-II project: CrSbSe3\_N.gpx

File Data Calculate Import Export | Edit Limits | Help

Project: CrSbSe3\_N.gpx

Data used in refinement

Original Tmin 11980.0229 New: 14300.0

Original Tmax 293005.4241 New: 2.2e+05

PWDR PG3\_42704\_10K.gsa B

Comments

Limits

Refinement results,  $R_w = 5.548$

Detailed results are in  
C:\Users\qzg\Dropbox  
(ORNL)\POWGEN\...\CrSbSe3\_July6th.lst

Final Reduced  $\chi^2$ : 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

Sample and Experimental Parameters

Instrument Name

Diffractometer type: Debye-Scherrer

☐ Histogram scale factor: 6854.1

☐ Sample absorption ( $\mu \cdot t$ ): 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.

CrSbSe3

File Data Atoms Draw Options Draw Atoms RB Models Map peaks MCSA RMC Texture Pawley re

|   | Name | Type | refine | x       | y       | z       | frac   | site sym | mult | UA | Uiso    | U11 | U22 |
|---|------|------|--------|---------|---------|---------|--------|----------|------|----|---------|-----|-----|
| 0 | Sb   | Sb   | XU     | 0.02892 | 0.25000 | 0.65838 | 1.0000 | m3       | 4    | 1  | 0.00064 |     |     |
| 1 | Cr   | Cr   | XU     | 0.15660 | 0.25000 | 0.04388 | 1.0000 | m3       | 4    | 1  | 0.00138 |     |     |
| 2 | Se   | Se   | XU     | 0.17163 | 0.25000 | 0.48395 | 1.0000 | m3       | 4    | 1  | 0.00108 |     |     |
| 3 | Se   | Se   | XU     | 0.28562 | 0.25000 | 0.21380 | 1.0000 | m3       | 4    | 1  | 0.00104 |     |     |
| 4 | Se   | Se   | XU     | 0.50073 | 0.25000 | 0.69817 | 1.0000 | m3       | 4    | 1  | 0.00080 |     |     |

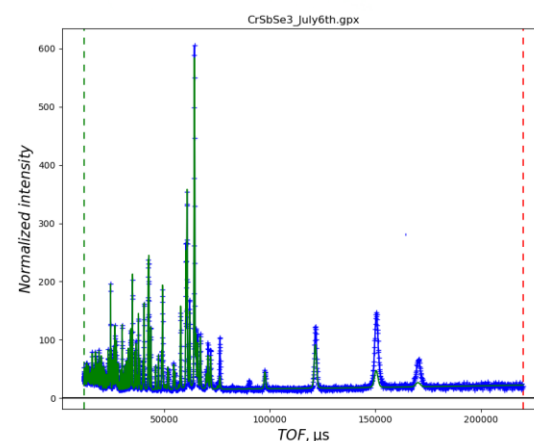
Refinement controls

Select

☒ X - coordinates

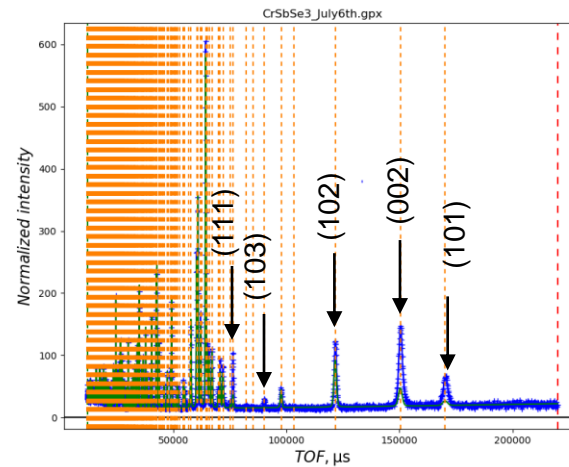
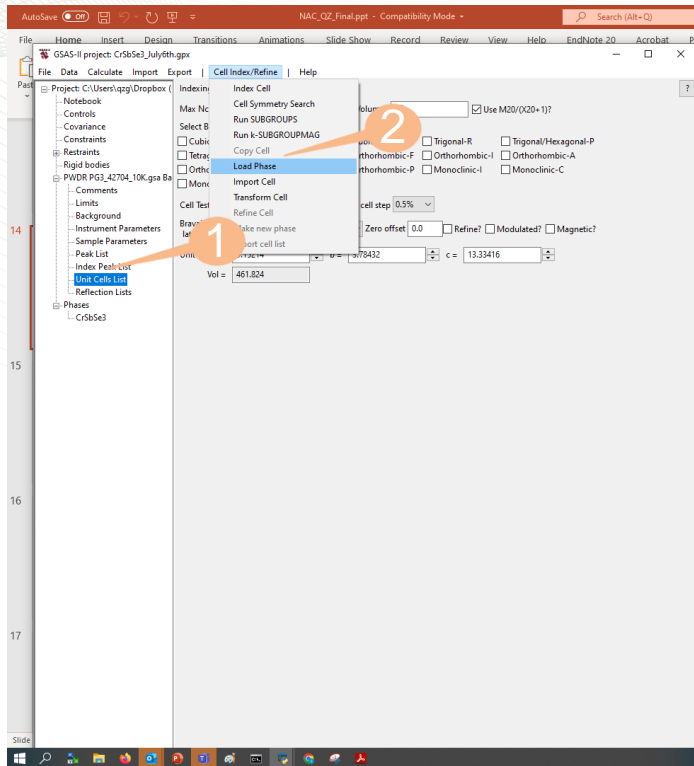
☐ Y - thermal parameters

OK Cancel





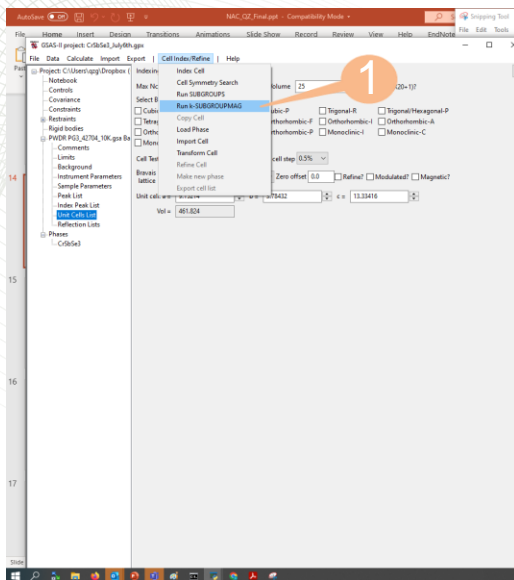
## II. Determine the magnetic propagation vector



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 $k=0$



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.J. Aroyo  
Annu. Rev. Mater. Res. 2015. 45,217-48.  
doi: <https://doi.org/10.1146/annurev-matsci-070214-021008>

OK

k-SUBGROUPSMAG options

k-vector 1 0 0 0

k-vector 2

k-vector 3

Use whole star ☐

Filter by

reserve axes ☒

test for mag. atoms ☐

all have moment ☐

max unique 100

Ok Cancel

GSAS-II project: CrSbSe3\_N.gpx

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

Project: CrSbSe3\_N.gpx

Notebook  
Controls  
Covariance  
Constraints  
Restraints  
Rigid bodies  
PWDR PG3\_42704\_10K.gsa Br  
Comments  
Limits  
Background  
Instrument Parameters  
Sample Parameters  
Peak List  
Index Peak List  
Unit Cells List  
Reflection Lists  
Phases  
CrSbSe3\_1

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    | a,b,c | 0,0,0 | 9.15209 | 3.78432 | 13.33414 | 90.000 | 90.000 | 90.000 | 461.82 |
| 2 | Pn'ma'   | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | 1     | 1    | a,b,c | 0,0,0 | 9.15209 | 3.78432 | 13.33414 | 90.000 | 90.000 | 90.000 | 461.82 |
| 3 | Pmm'a'   | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | 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    | 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    | a,b,c | 0,0,0 | 9.15209 | 3.78432 | 13.33414 | 90.000 | 90.000 | 90.000 | 461.82 |

National Laboratory

IDGE

HIGH FLUX  
ISOTOPE  
REACTOR

SPALLATION  
NEUTRON  
SOURCE

# 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% ☐ Refine? ☐ Modulated? ☐ Magnetic?

Bravais lattice: Pmmm Space group: P n m a Zero offset: 0.0

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

Vol = 461.820

Magnetic subgroup cells from Bilbao k-SUB: 1 SMAG for P n m a; kvec1=(0,0,0):

|   | Space Grp | Try                                 | Keep                                | n | 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 | 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 | 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 | 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 Unit Cells Help

Project: C:\Users\qzq\Dropbox\GSAS-II\CrSbSe3\_July6th.gpx

General Data

Phase name: CrSbSe3

☒ Refine unit cell

Density: 5.906

Elements: Cr, Sb, Se

Isotope: ☐ 54Cr ☐ 121Sb ☐ 78Se

No. per cell: 4

Atom weight: 51.9961, 121.757, 78.96

Bond radii: 1.39, 1.38, 1.40

Van der Waals radii: 2.20, 1.70, 1.90

Unit cell color: ☐ Red ☐ Green ☐ Blue ☐ Yellow ☐ Cyan ☐ Magenta ☐ Black

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

Fourier map controls: Map type: ☐ 2D ☐ 3D 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 HRLs: 0 0 2 2 0 0 1 1 1 0 2 0 1 2 3

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'21'a'; (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

Organize New folder

| Name                        | Date modified      | Type            | Size   |
|-----------------------------|--------------------|-----------------|--------|
| CrSbSe3_1 mag_3.bak0        | 10/9/2022 11:34 AM | GSAS-II project | 783 KB |
| CrSbSe3_1 mag_3.bak1        | 10/9/2022 11:33 AM | GSAS-II project | 783 KB |
| CrSbSe3_1 mag_3             | 10/9/2022 11:38 AM | GSAS-II project | 804 KB |
| CrSbSe3_1 mag_3_original    | 10/9/2022 11:36 AM | GSAS-II project | 783 KB |
| CrSbSe3_1 mag_3_region.bak0 | 10/9/2022 11:38 AM | GSAS-II project | 783 KB |
| CrSbSe3_1 mag_3_region      | 10/9/2022 11:39 AM | GSAS-II project | 625 KB |
| CrSbSe3_N                   | 10/9/2022 11:48 AM | GSAS-II project | 786 KB |

File name: CrSbSe3\_1 mag\_1

Save as type: GSAS-II project file (\*.gpx)

Save Cancel

## Refine mx and my:

GSAS-II project: CrSbSe3\_1 mag\_1.gpx

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

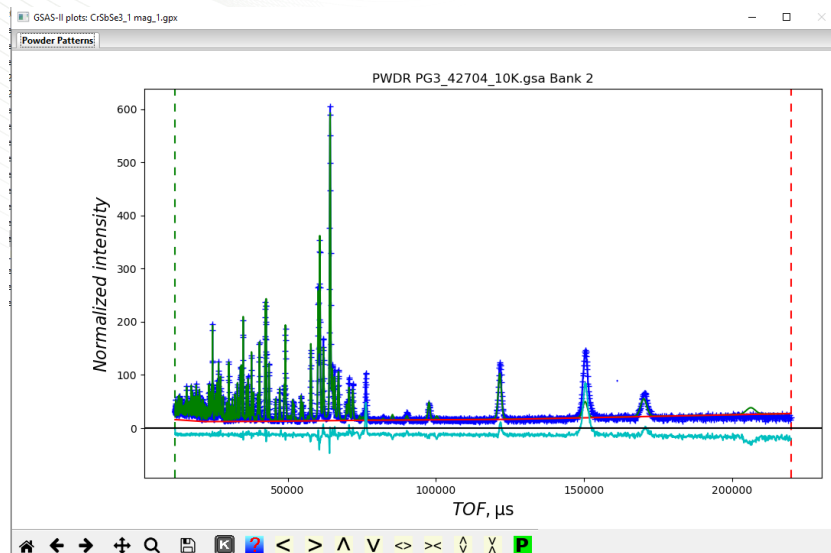
Project: C:\Users\qzg\Dropbox (G...)

- 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                 | sym   | mult | I/A | Uiso    |
| 0       | Cr1  | Cr+3  | M            | 0.15649    | 0.25000   | 0.04390   | 1.0000 | 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    | Cr+3 | 0.15649 | 0.25000 | 0.04390 | 1.3911 | 0.0000 | -0.4188 | 1      | vdW balls |       | I     |     |

1

Select atoms for action

Select atoms Name

From:

☒ 0) Cr:0

Apply stride: 1

Set All Toggle All

Set Range

OK Cancel

3



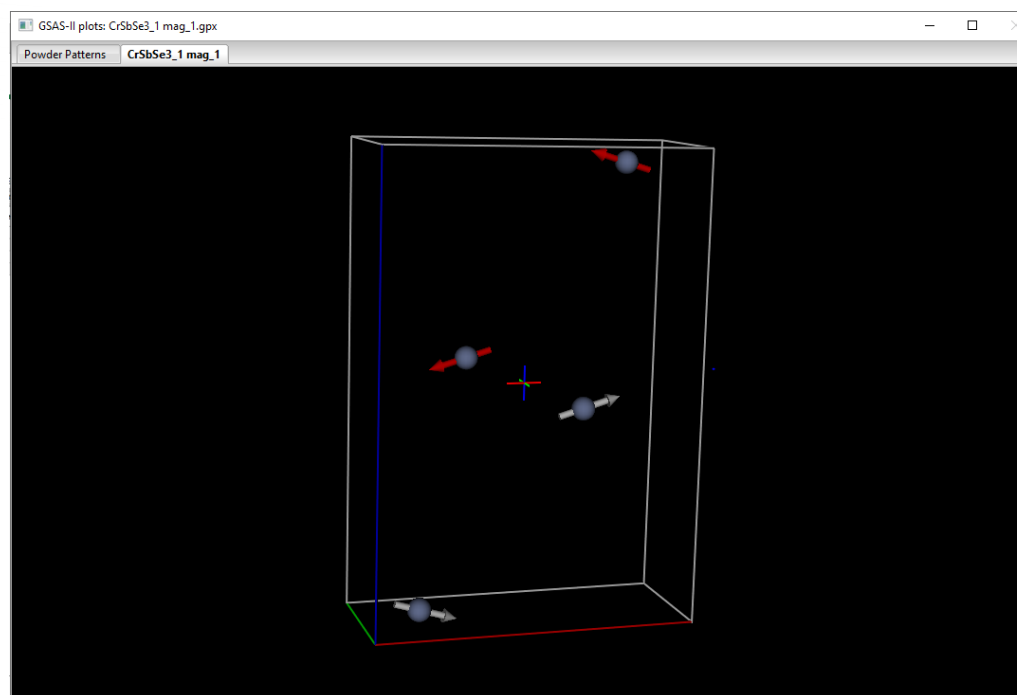
# “Draw atom” tab will be updated

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

|   | 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\agq\Dropbox (C)\GSAS-II\Cr5Se3\_July6th.gpx

Indexing controls:

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

Select Bravais Lattices for indexing:

☐ Cubic-F ☐ 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-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 = 9.15214 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 checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | 0    | 1    | a,b,c | 0,0,0 | 9.15214 | 3.78432 | 13.33416 | 90.000 | 90.000 |
| 2 Pn'm'a' | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | 0    | 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"/> | 0    | 1    | a,b,c | 0,0,0 | 9.15214 | 3.78432 | 13.33416 | 90.000 | 90.000 |
| 4 Pn'm'a' | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | 0    | 1    | a,b,c | 0,0,0 | 9.15214 | 3.78432 | 13.33416 | 90.000 | 90.000 |
| 5 Pnma'   | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | 0    | 1    | a,b,c | 0,0,0 | 9.15214 | 3.78432 | 13.33416 | 90.000 | 90.000 |

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

OK Print Ops

GSAS-II project: Cr5Se3\_July6th.gpx

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

General

Phase name: Cr5Se3

Search map

Charge flipping

4D Charge flipping

Clear map

Density: 5.906

Elements

Isotopes

No. per cell

Multi MC/SA

Transform

Compare

Select magnetic/subgroup phase

Protein quality

Angle radii

Bond radii

van der Waals radii

Default color

Pawley controls: ☐ Do Pawley refinement? Pawley dimin: 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 k-Max (v=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 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

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

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

is ☒ 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** Route | Help

Project: C:\Users\qzg\Dropbox (

- ... Notebook
- ... Controls
- ... Covariance
- ... Constraints

|   | Name | Type | refine <b>2</b> | re <b>3</b> | y       | z       | frac   | Mx <b>3</b> | 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

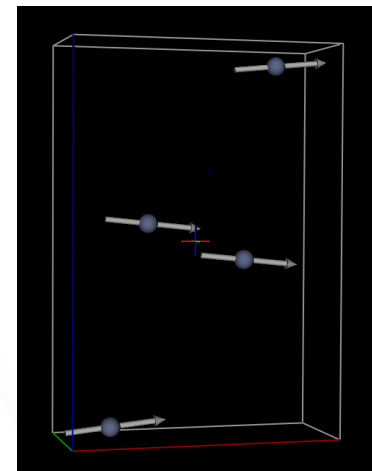
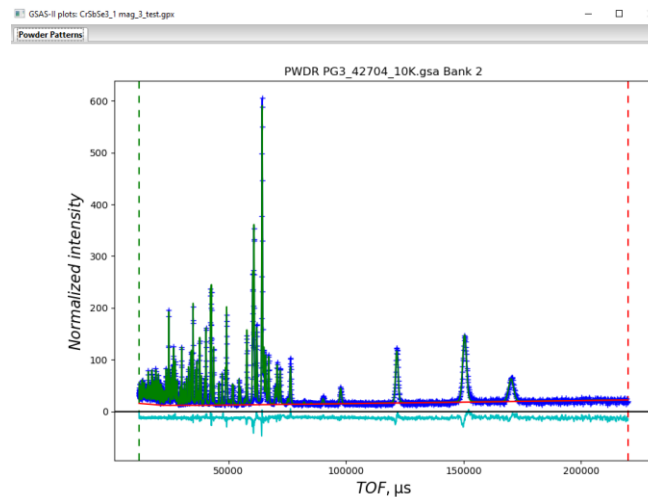
Final Reduced  $\chi^2$ : 5.294 (before ref: 5.295)

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 | 2.6208 |         | 0.1767             | m'(y)    | 4    | I   | 0.00176 |

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

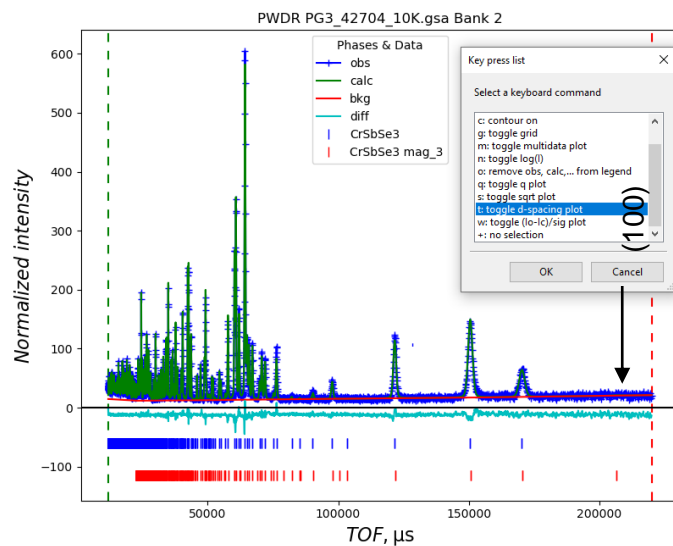
# Check if small Mz is real

GSAS-II project: CrSbSe3\_1 mag\_3\_test.gpx

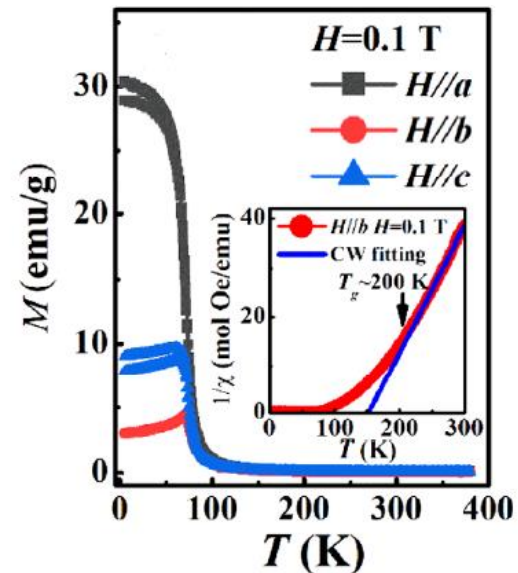
File Data Calculate Import Export Select tab Edit Atoms Compute Help

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 |



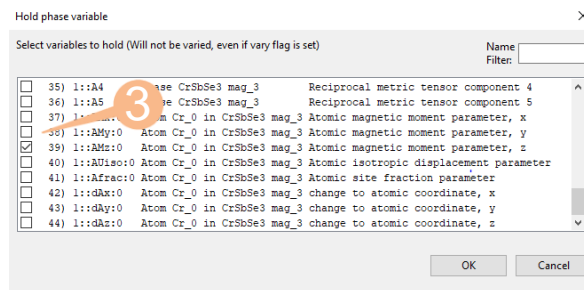
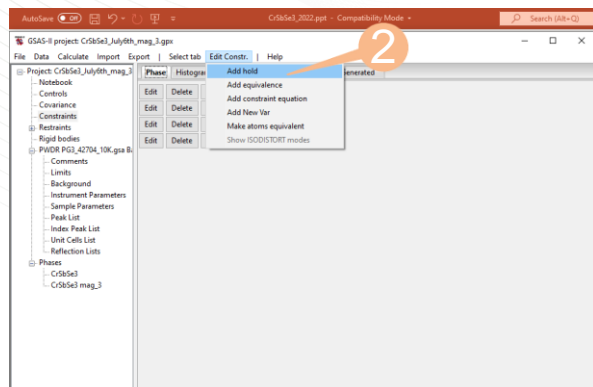
a. Zero (100) magnetic peak: moment along the  $a$  axis.



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 |



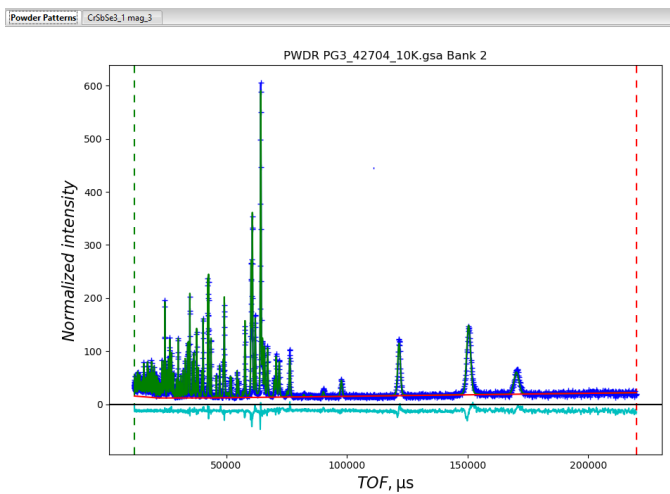
Refinement results,  $R_w = 3.901$

**i** Detailed results are in [C:\Users\qzg\Dropbox\ORNL\POWGEN\NXS\202...\CrSbSe3\\_1\\_mag\\_3\\_test\\_mz\\_zero.lst](C:\Users\qzg\Dropbox\ORNL\POWGEN\NXS\202...\CrSbSe3_1_mag_3_test_mz_zero.lst)

Final Reduced  $\chi^2$ : 5.298 (before ref: 5.298)

Load new result?

OK Cancel



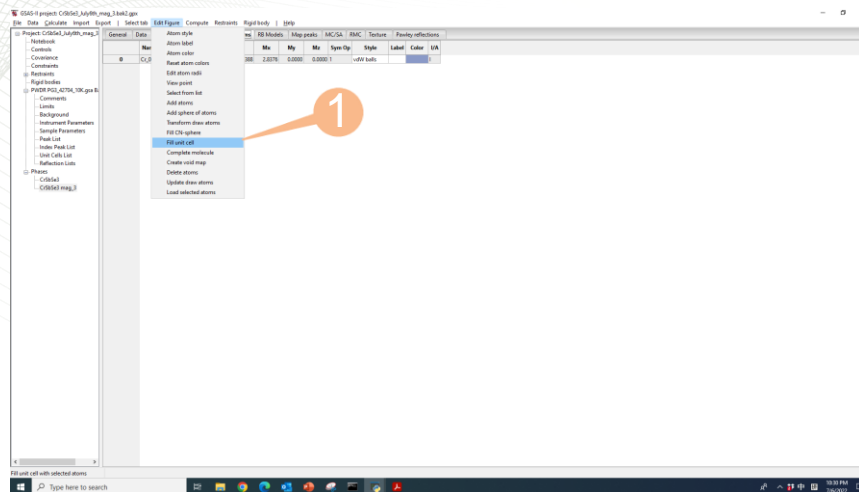
| General | Data | Atoms | Draw Options | Draw Atoms | RB Models | Map peaks | MC/SA  | RMC    | Texture | Pawley reflections |          |      |     |         |
|---------|------|-------|--------------|------------|-----------|-----------|--------|--------|---------|--------------------|----------|------|-----|---------|
|         | 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 |

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

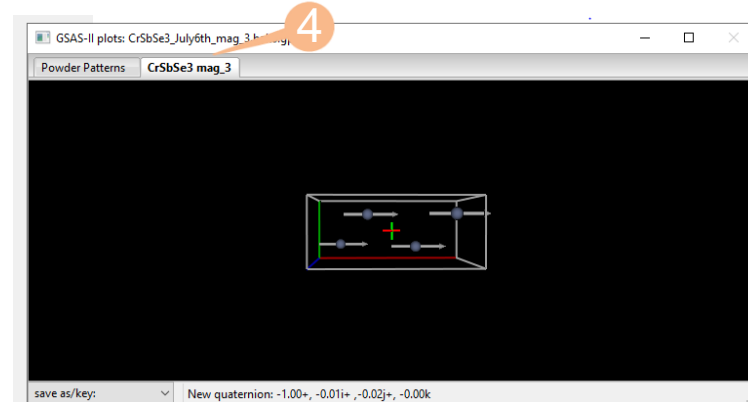


# Visualizing the magnetic structure

In “Draw Atoms” tab:



Ferromagnetic order

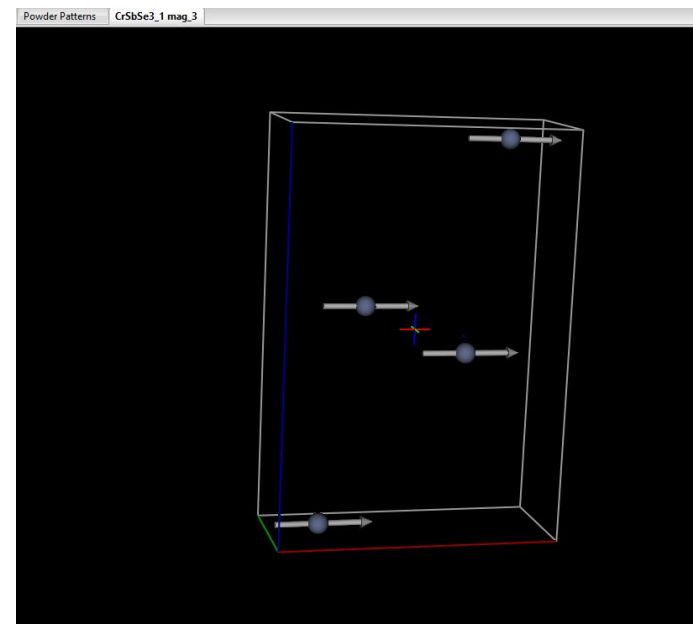


Select atoms for action

Select atoms Name

☒ 0) Cr\_0

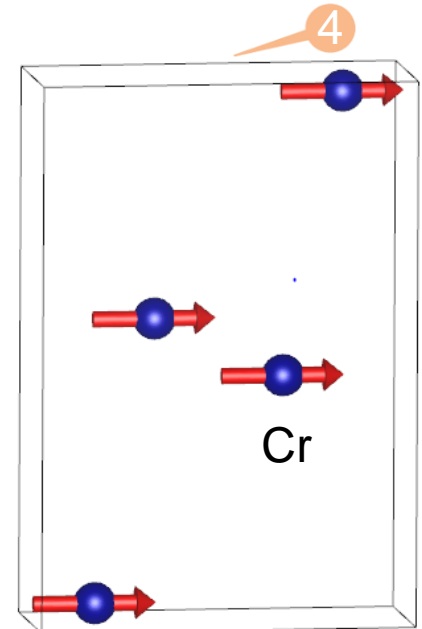
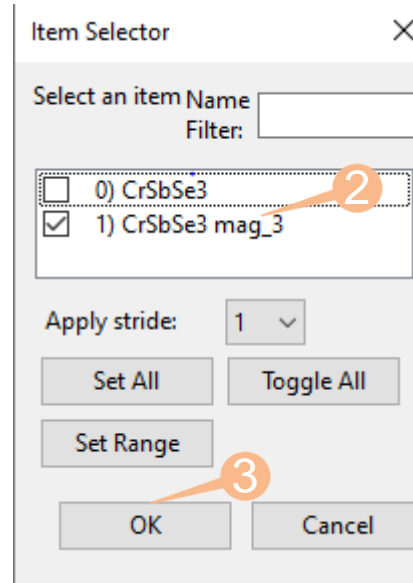
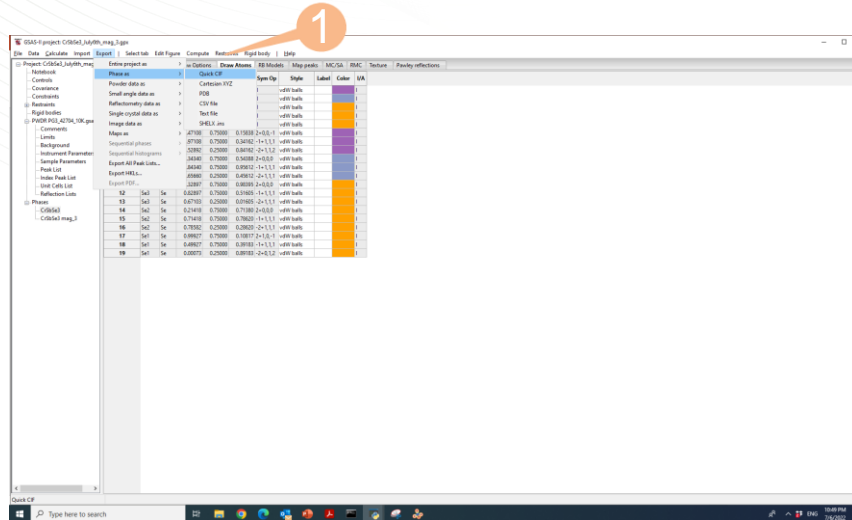
Apply stride:



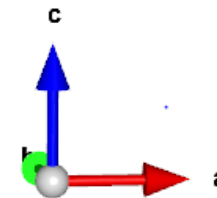
# To publish the results

## I. 3D magnetic structure

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

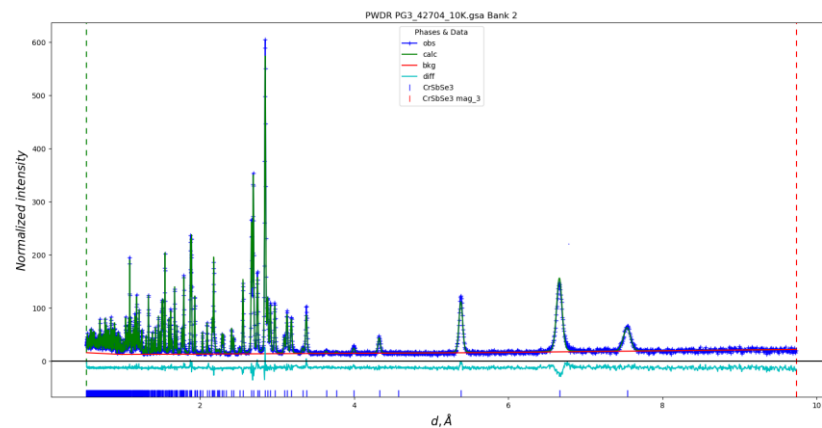
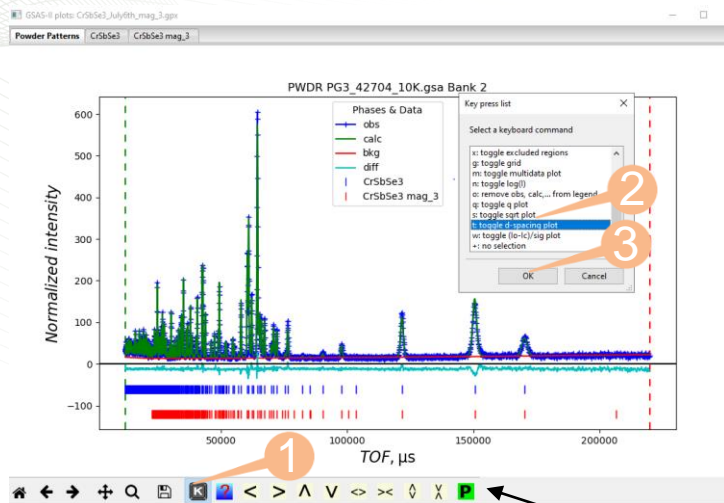


Use VESTA software ([jp-minerals.org/vesta/en/download.html](http://jp-minerals.org/vesta/en/download.html)) to open it directly for publication:

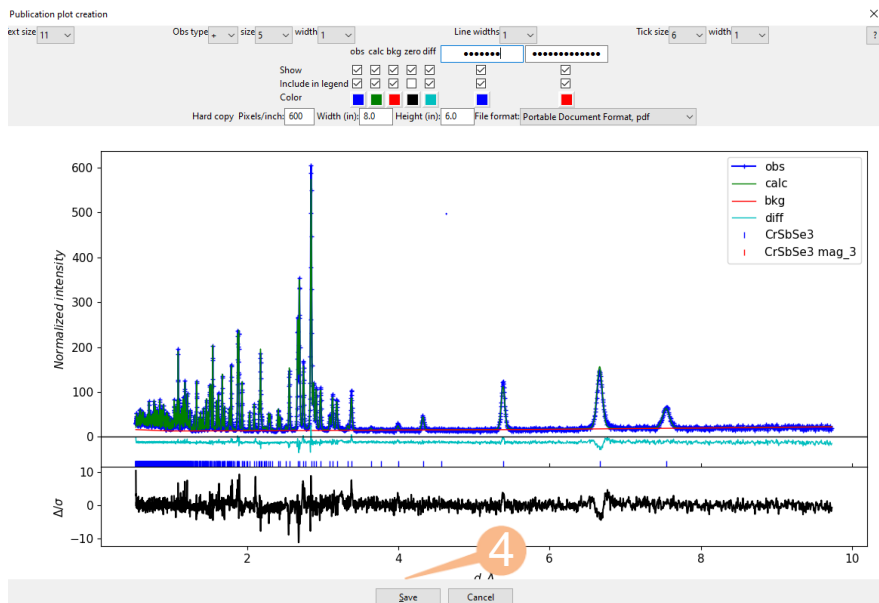


# II. Refinement plots

Convert TOF to d



Click P button to open a new window



# Magnetic Structure Determination from Neutron Diffraction Data (MagStr), October 3-7, 2022

Tutorial example for GSAS-II refinement of commensurate structure from TOF data

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

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