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

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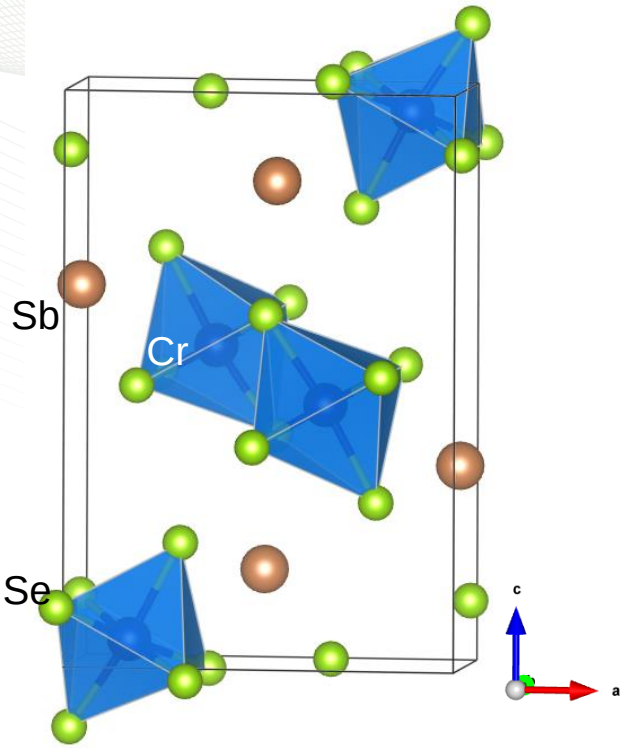
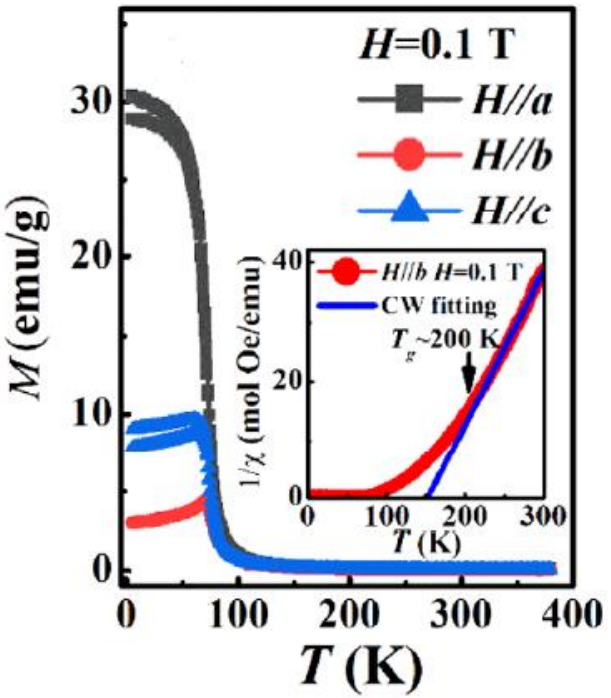
Basic information on $CrSbSe_3$





- 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
  $CrSbSe_3$.cif

- Final PCR files
  CrSbSe3_N.gpx
  CrSbSe3_1 mag_3.gpx

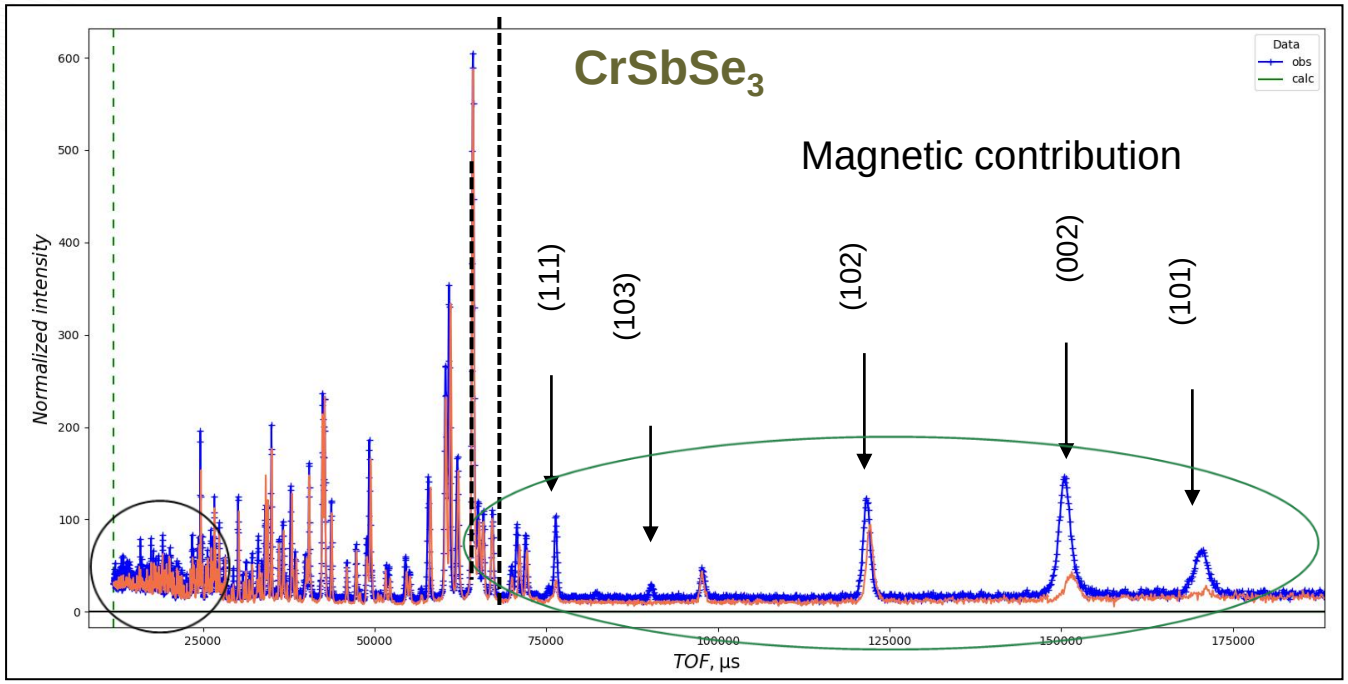
- Supporting information
  GSAS_II_QZhang.PDF (step-by-step instructions)
  jacs.1c09607.PDF

Exercise steps

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

Identify magnetic peaks in $CrSbSe_3$

Smaller thermal parameters



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

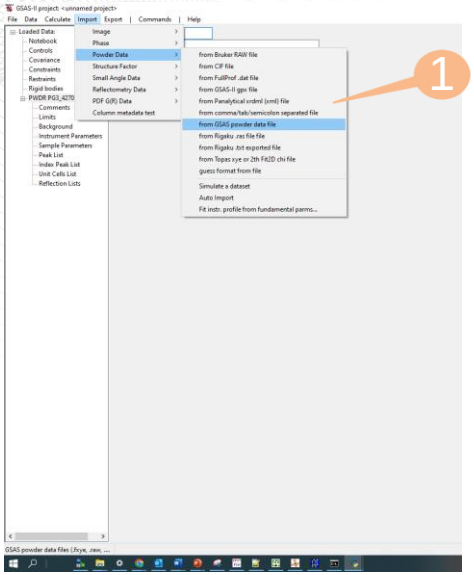
Two ways to determine the structural parameters in $T<T_N$ (or T_C) before refining k=0 magnetic structure:

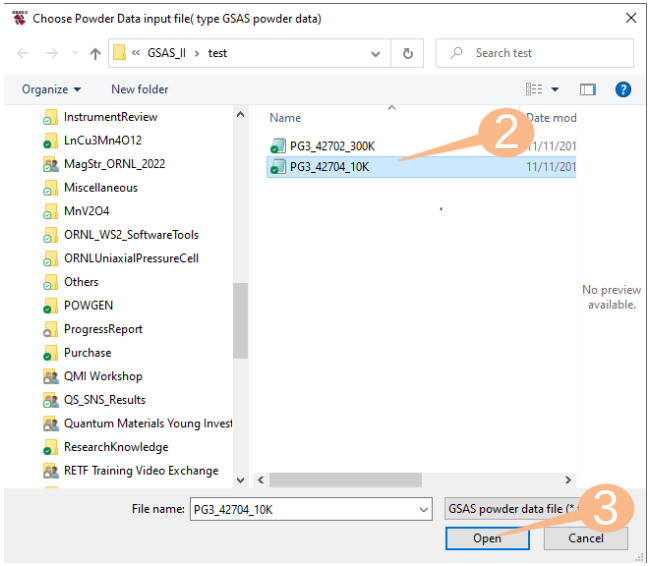
1). Refine the data in $T>T_N$ (or T_C) firstly. Then use them as initial parameters and only refine the atomic positions, B factors, and lattice constants in $T<T_N$ (or T_C).

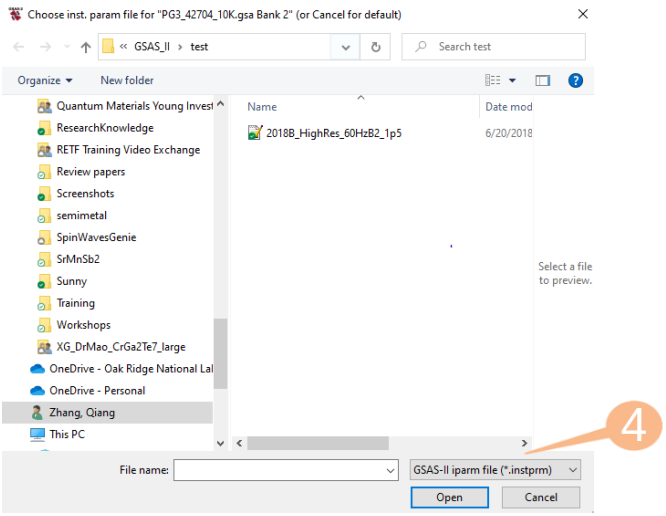
2). Exclude the high-d part of data that involves magnetic contribution and only refine low and middle d data on the structural par in TOF<68,000 μs

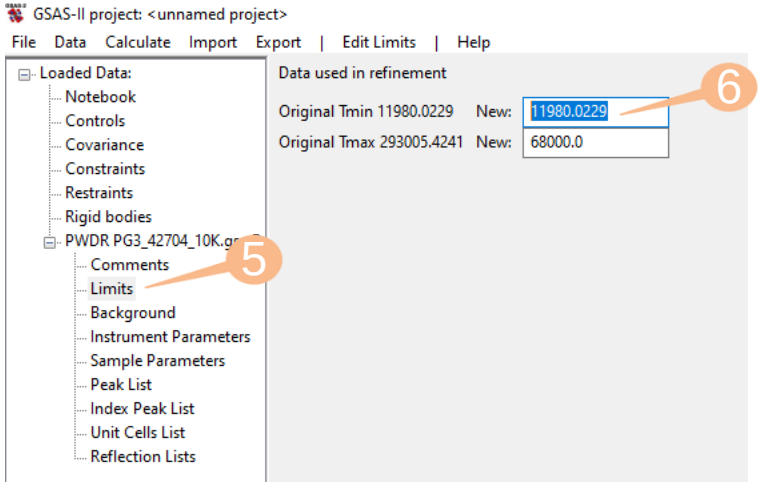
Refine the structure of $CrSbSe_3$

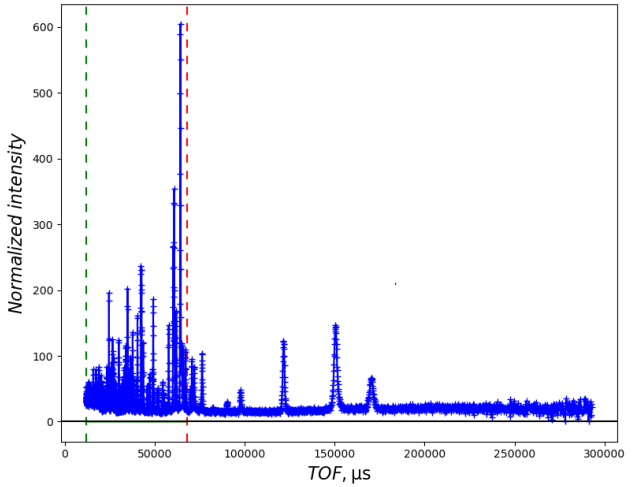
I. Import datafile and set the limit





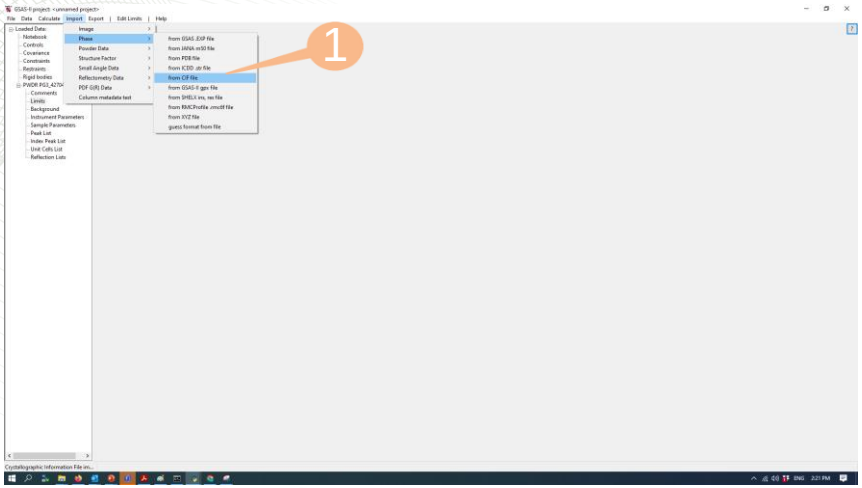


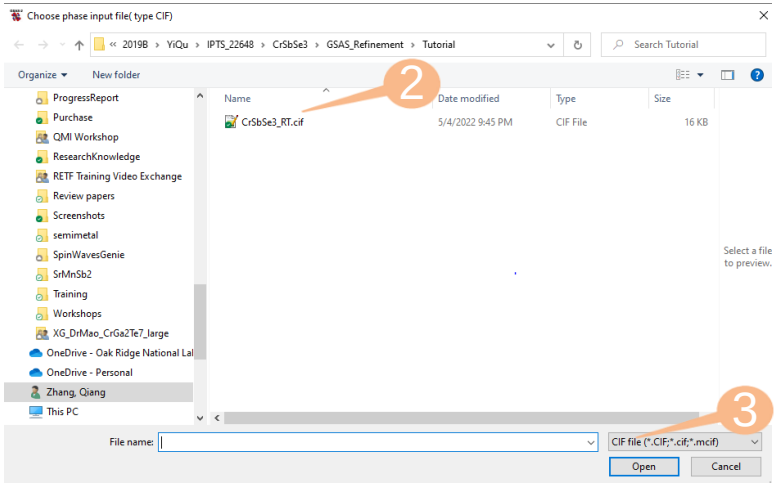


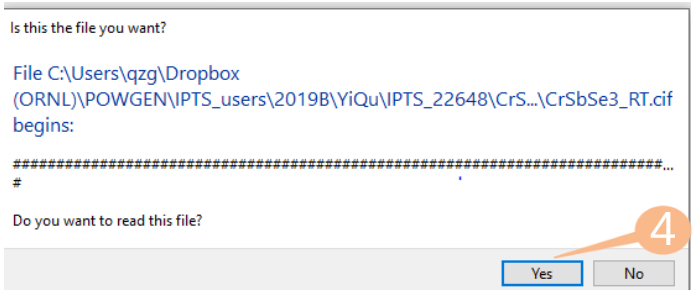


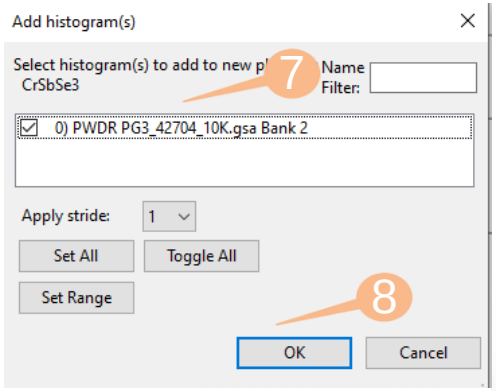
File-save project!

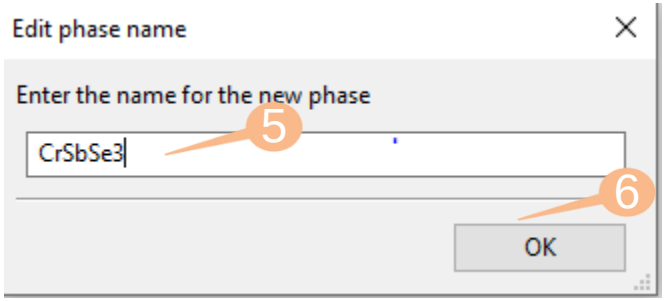
II. Import the phase



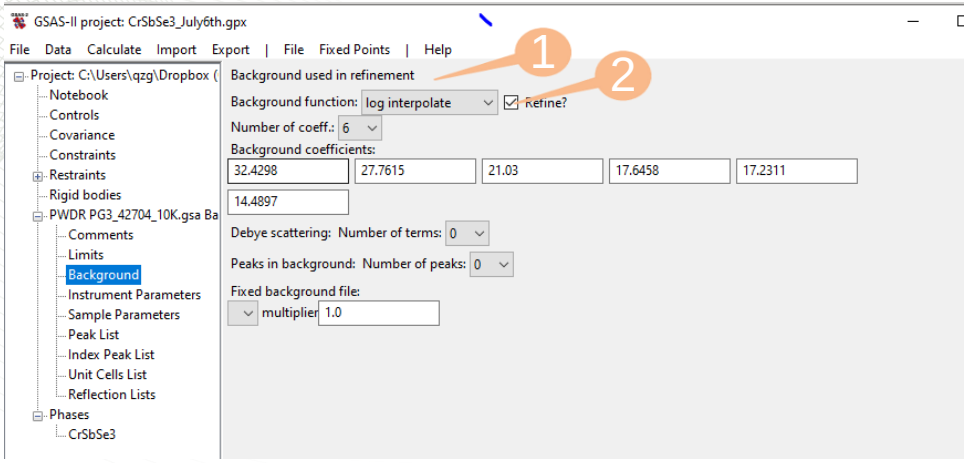


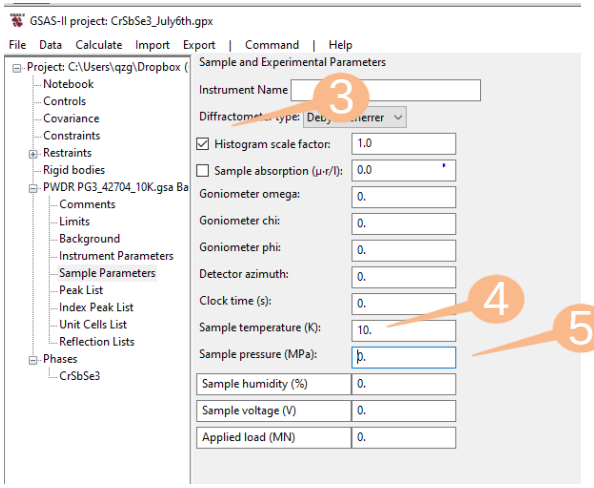


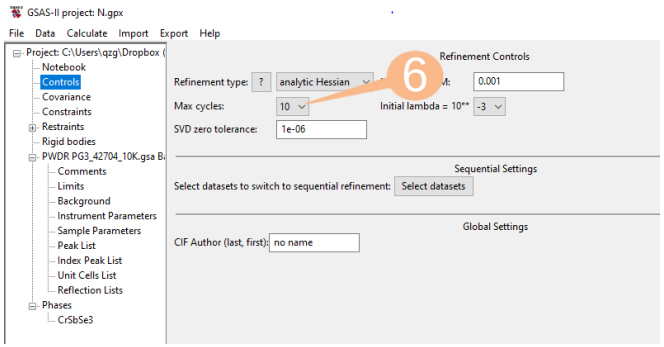


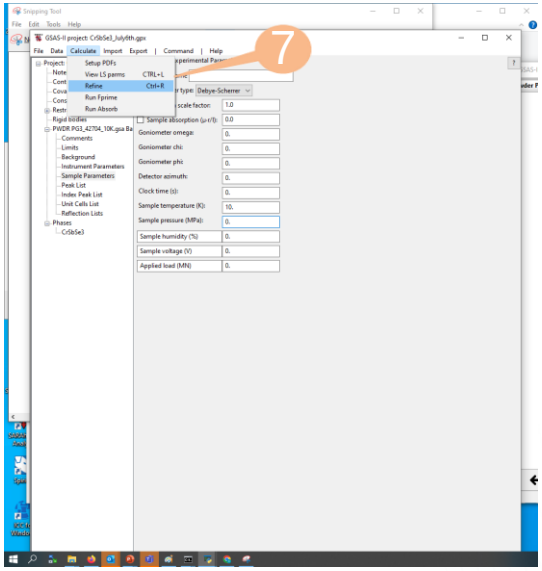


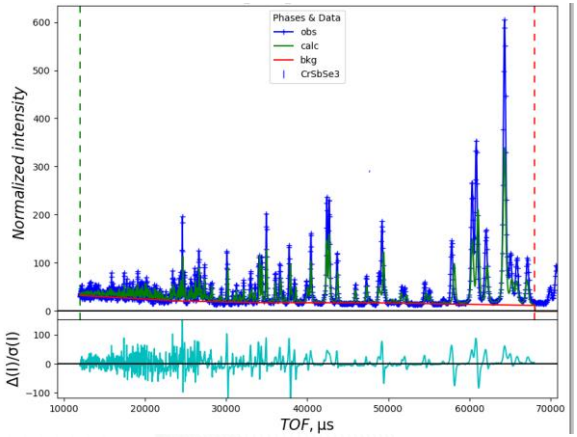
III. Refine background and scale factor



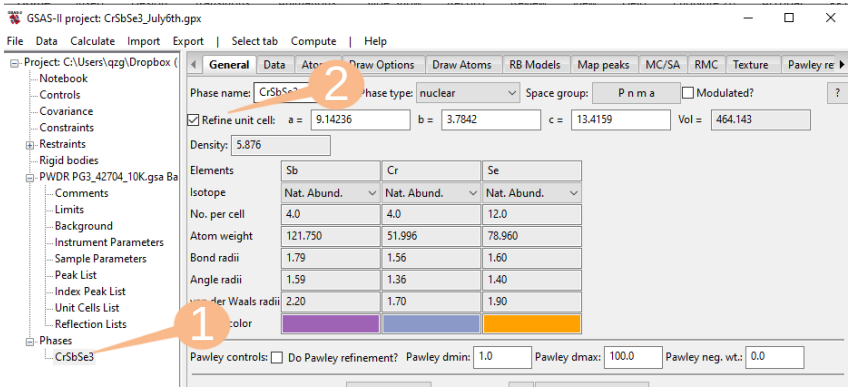




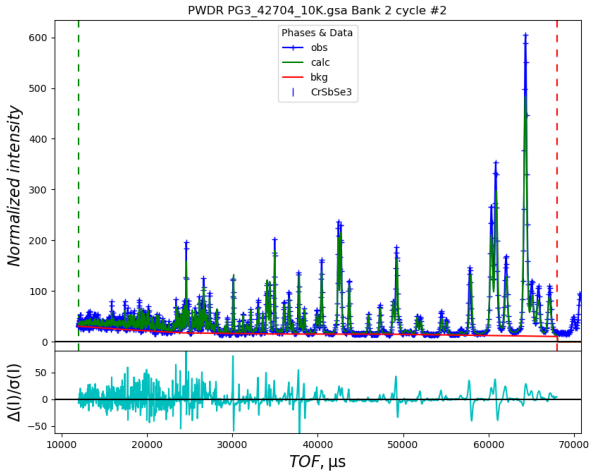


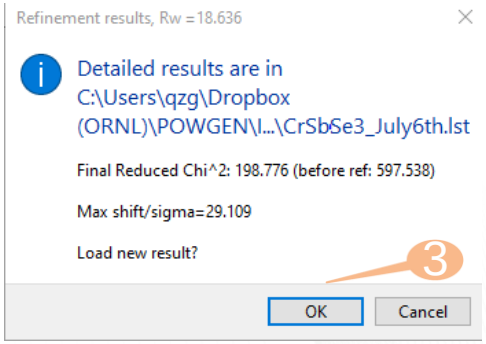


IV. Refine lattice constants

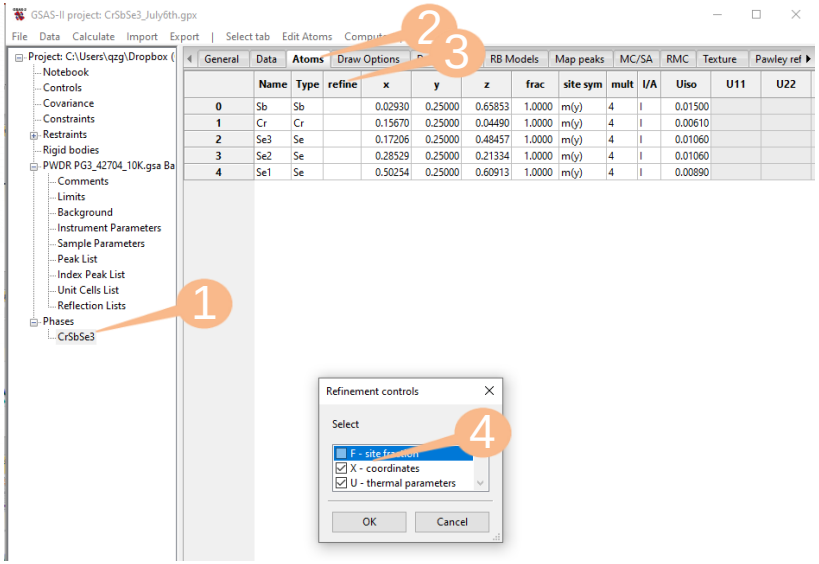


Calculate-refine:

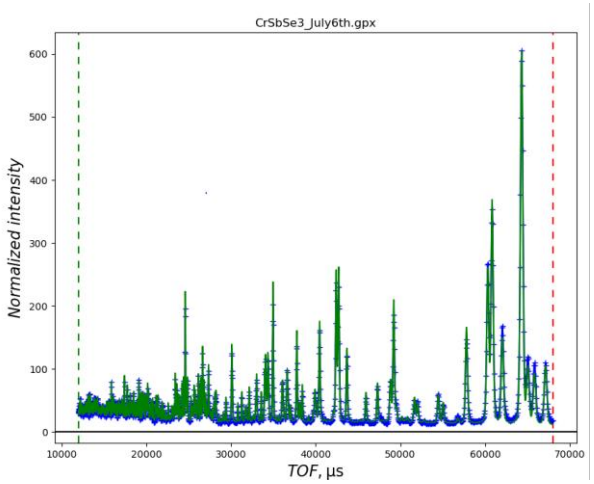


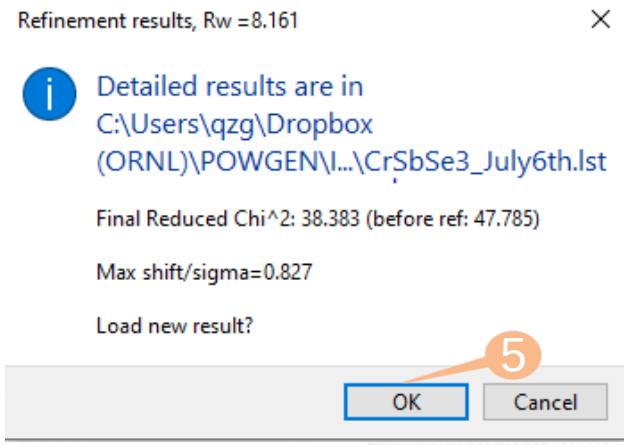


V. Refine atomic coordinates and thermal parameters



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	☐
difA (-4.594):	-4.594	☐
difB (4.706):	4.706	☐
Zero (-26.810):	-26.81	☐
alpha (0.129):	0.129	☐
beta-0 (0.100880):	0.10088	☐
beta-1 (0.003960):	0.00396	☐
beta-q (0.000000):	0.0	☐
sig-0 (-203.060):	-203.06	☐
sig-1 (-852.163):	-852.163	☐
sig-2 (298.196):	298.196	☐
sig-q (797.184):	797.184	☐
X (-4.504):	0.0	☑
Y (10.949):	0.0	☐
Z (-0.465):	0.0	☐

Calculate-refine:

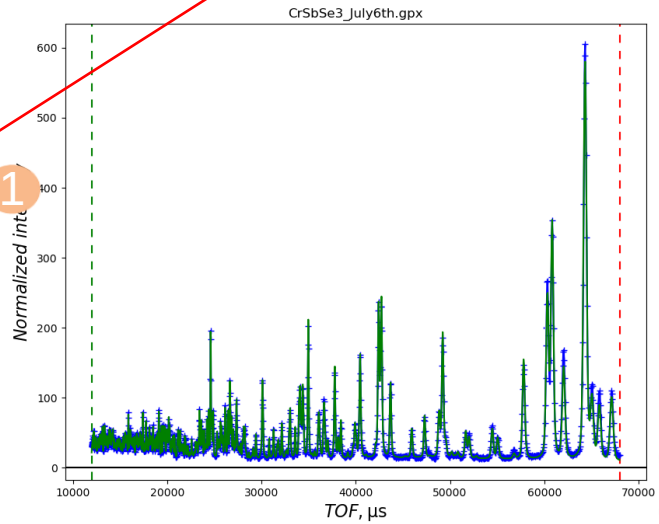
$$TOF = DIFC*d + DIFA*d^2 + ZERO + DIFB/d$$

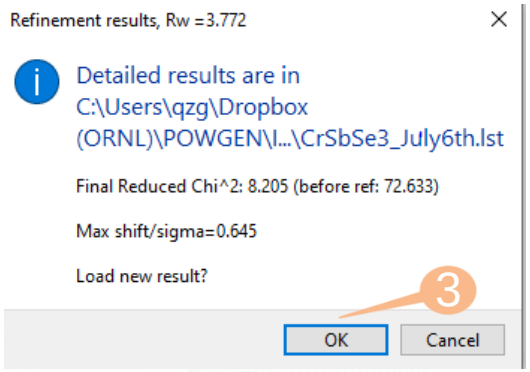
$$\sigma^2 = {\sigma_0}^2 + {\sigma_1}^2 d^2 + {\sigma_2}^2 d^4 + \frac{{\sigma_q}^2}{d^2} + {\sigma_3}^3 d^3$$

(Gaussian function)

$$\gamma = X * d + Y * d^{\prime} + Z$$

(Lorentz function)

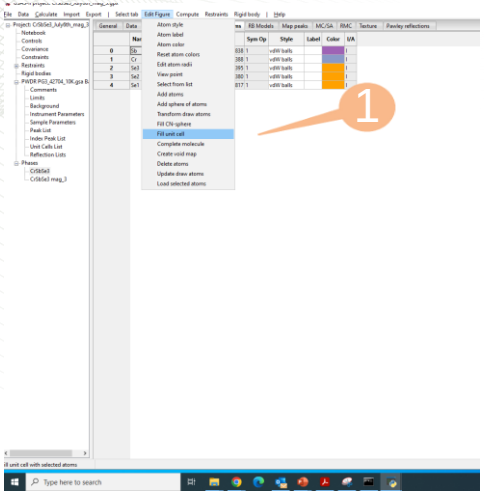


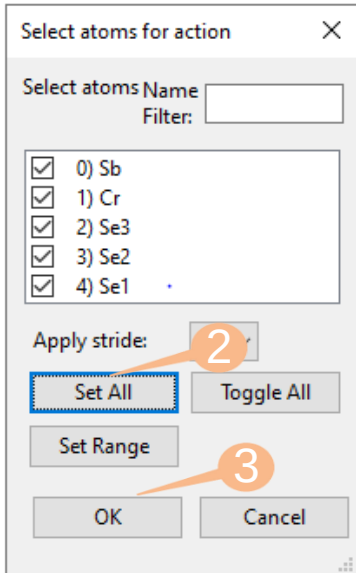


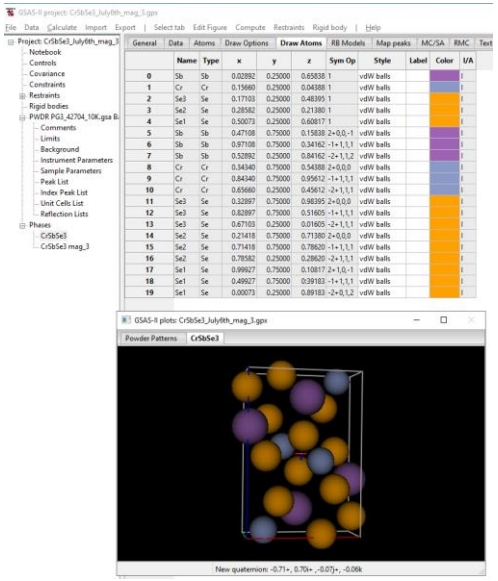
2

VII. Virtualizing crystal structure

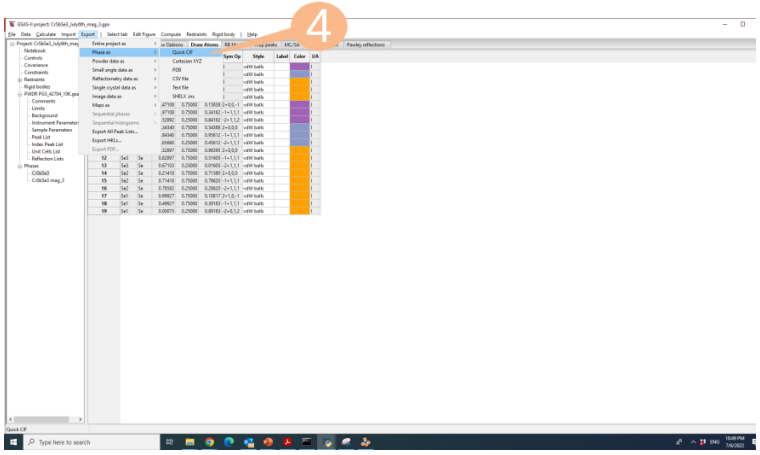
In “Draw Atoms” tab:





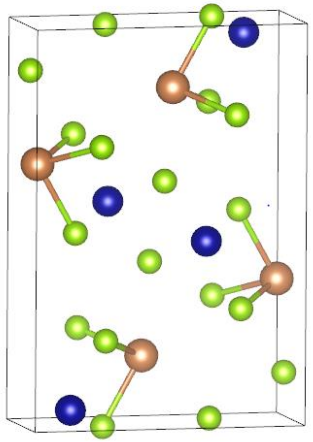


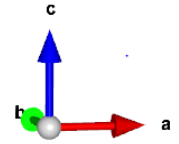
Export cif file:



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	

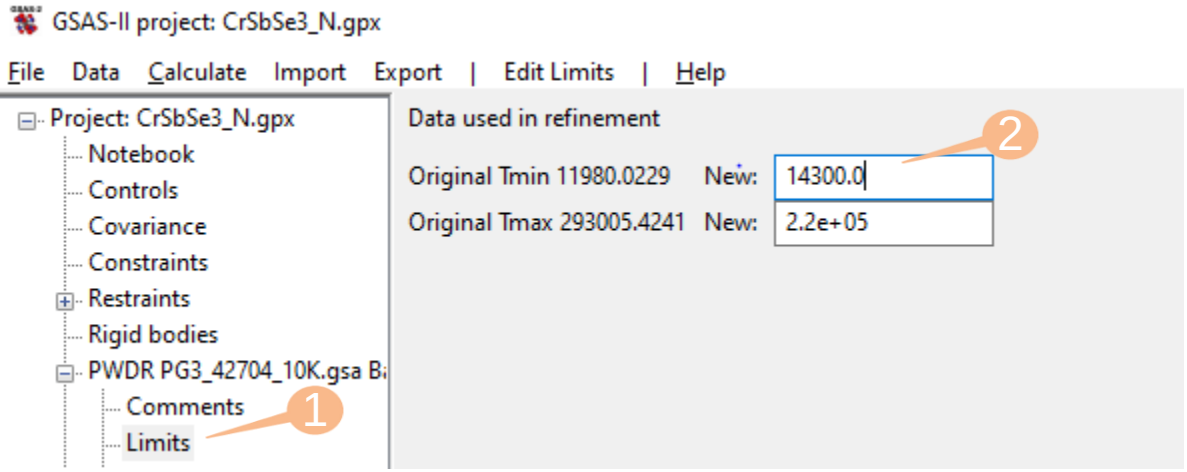




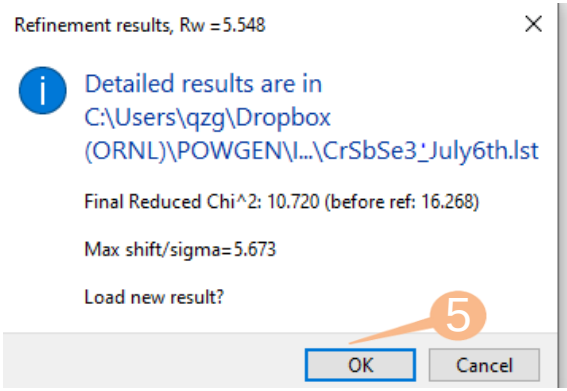
Let us add the high-TOF data to refine the magnetic structure!

Refine the magnetic structure of $CrSbSe_3$

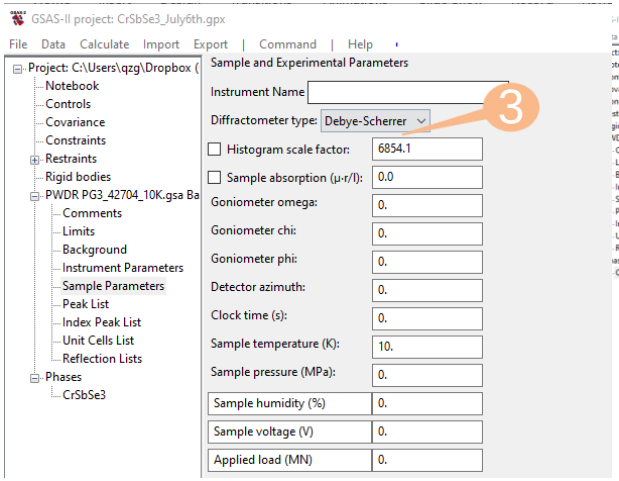
I. Add the high TOF data back and refine background

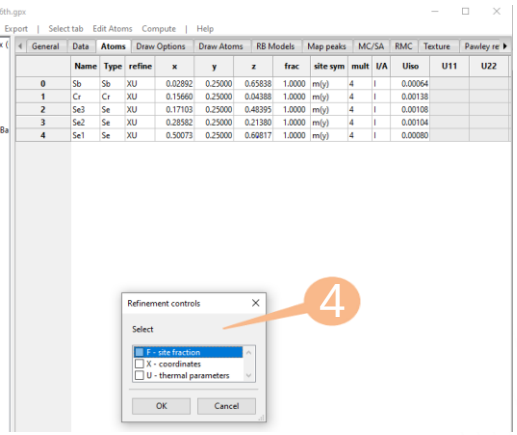


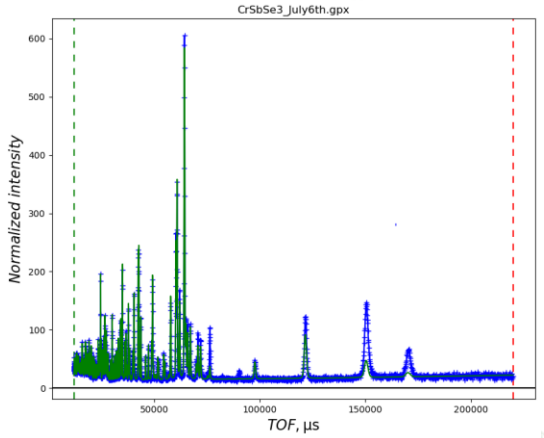
Fix the refinement on the scale, atomic positions, and thermal parameters. *Only refine background and magnetic structure!*



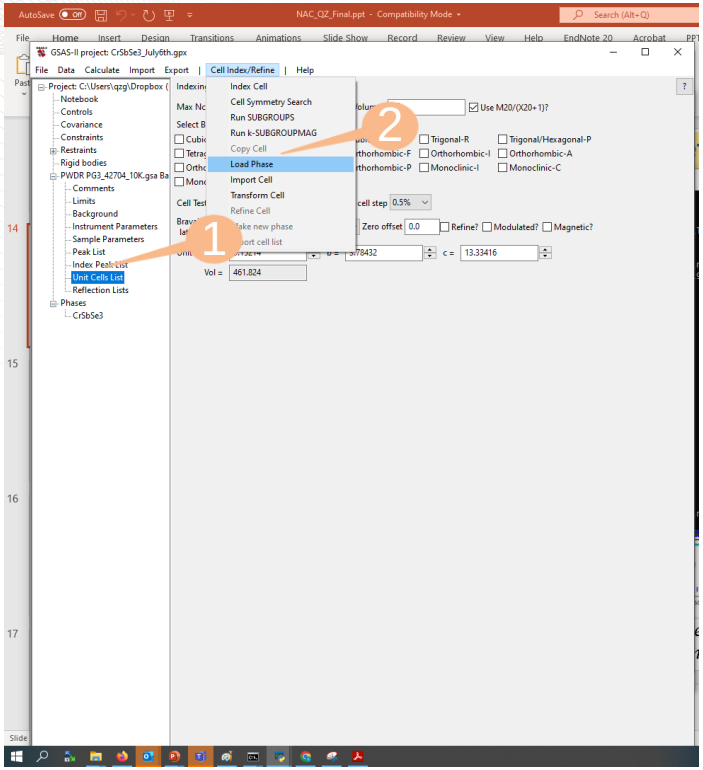
Calculate-refine:

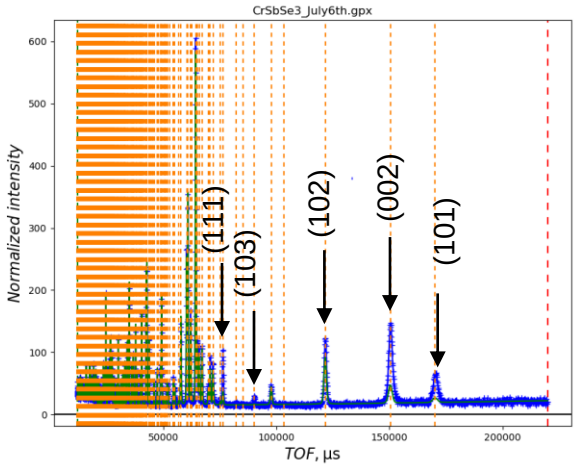






II. Determine the magnetic propagation vector

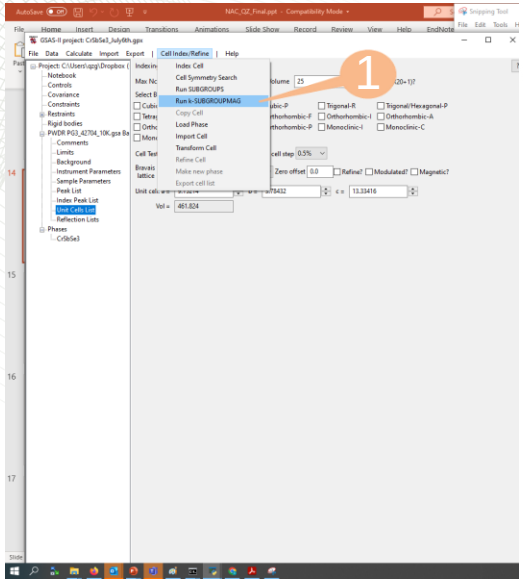


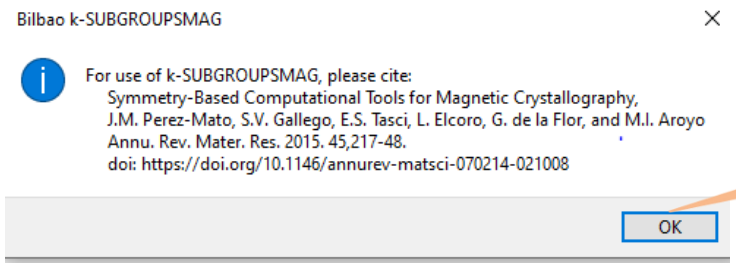


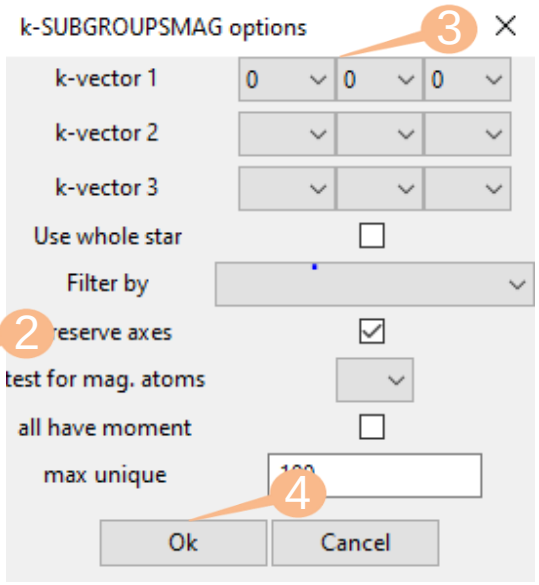
Magnetic peaks sit on the nuclear peak positions!

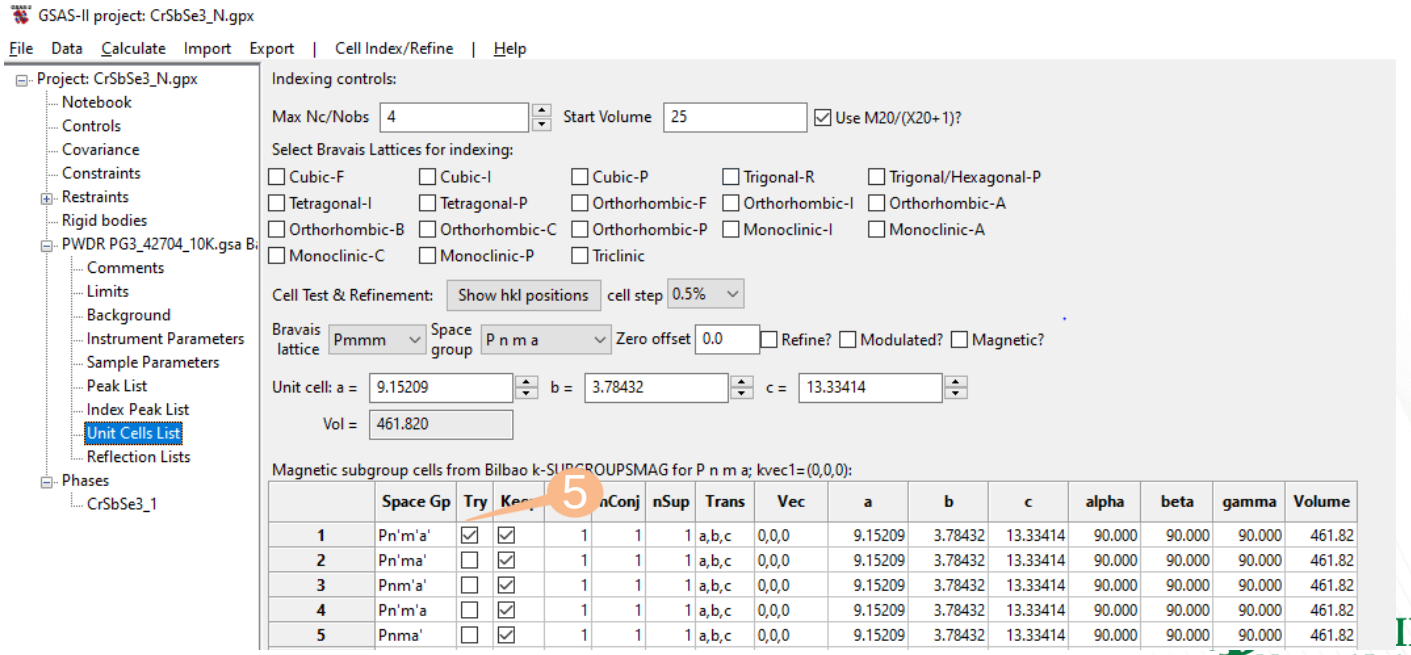
$$\boldsymbol{k} = \boldsymbol{Q}_M - \boldsymbol{Q}_N = 0$$

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

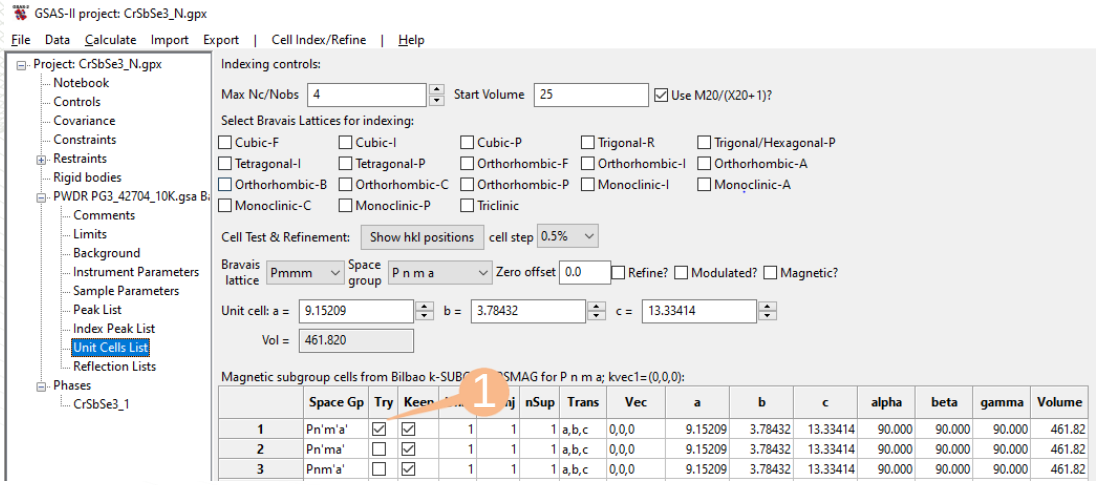


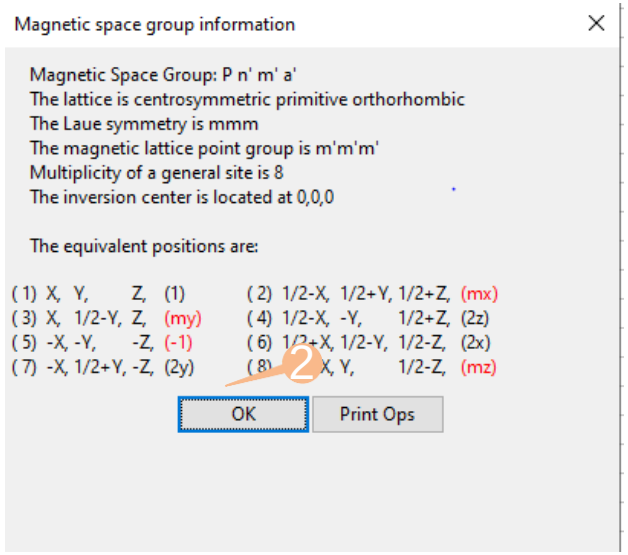


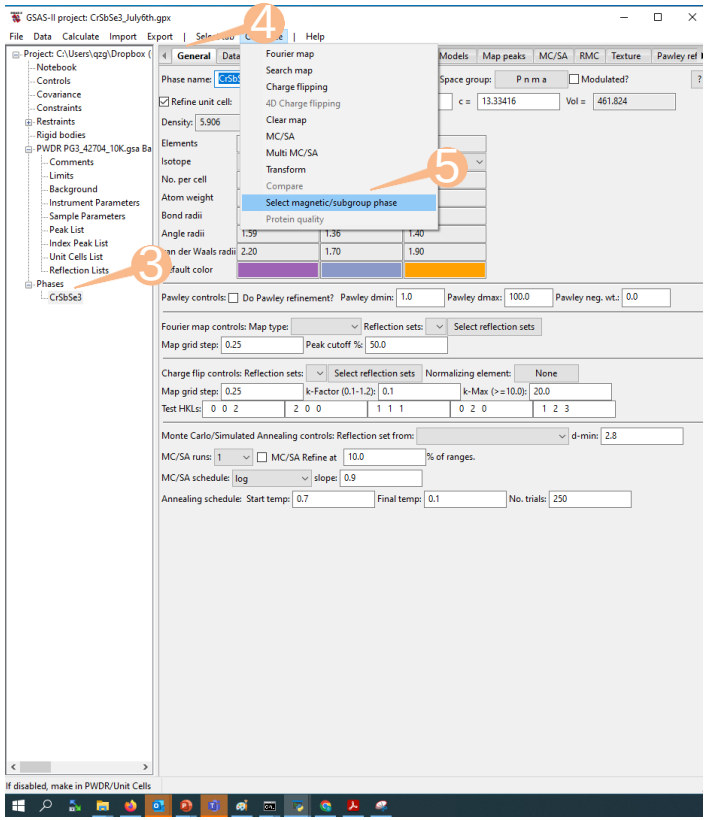


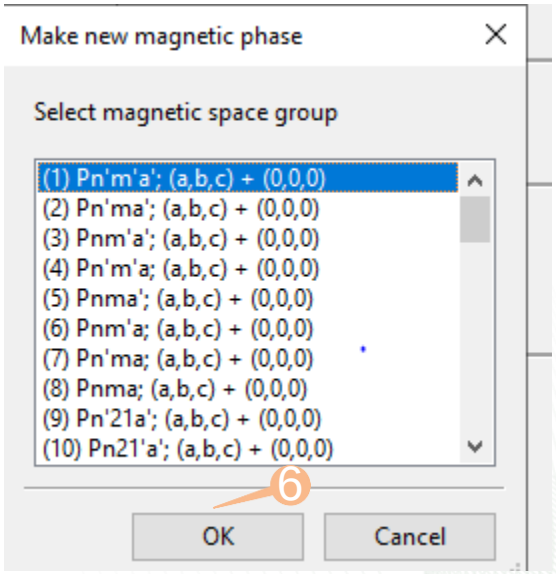


IV. Select magnetic space group Pn’m’a’ for the refinement

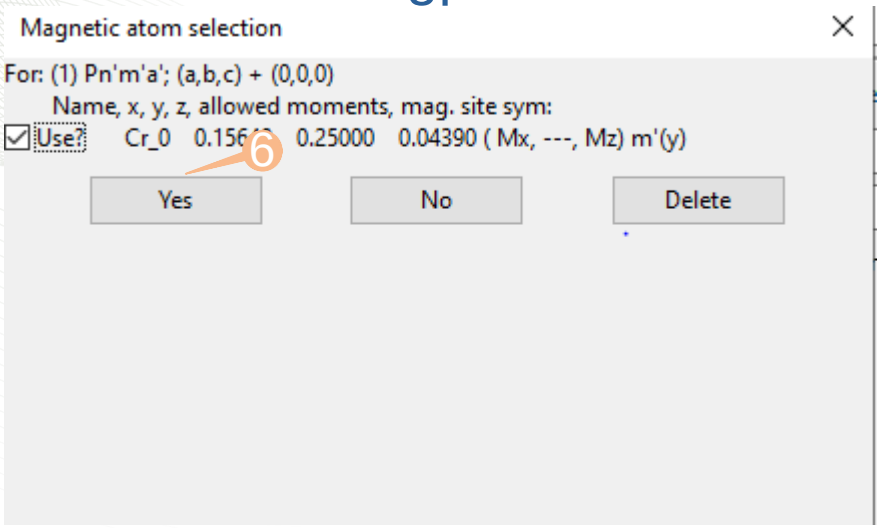


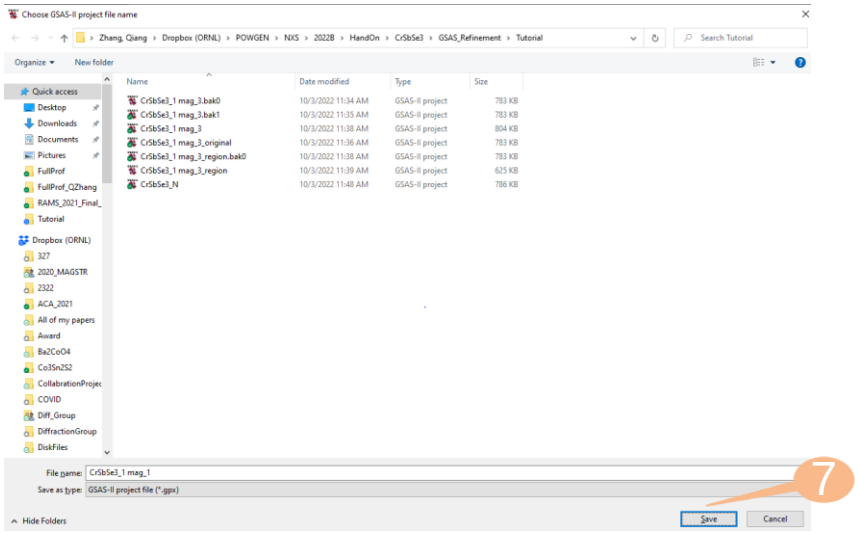




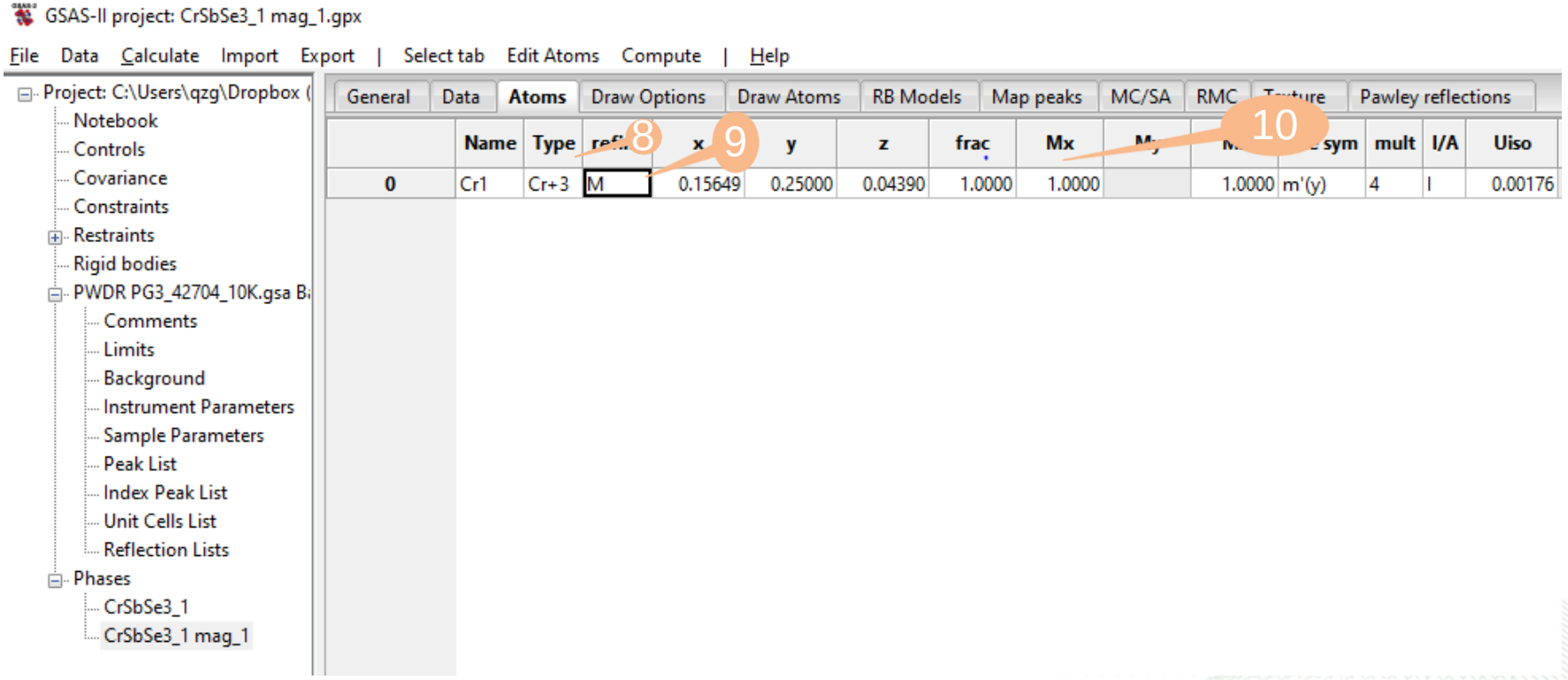


Save as a new gpx file

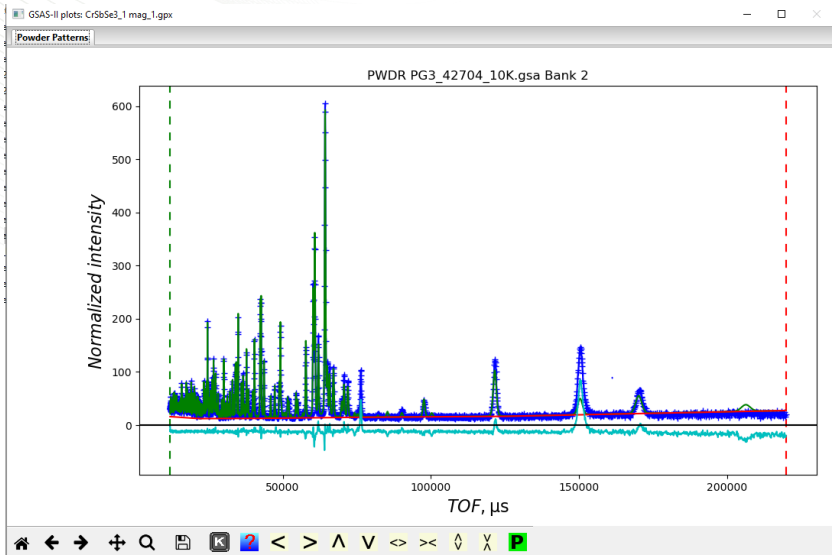




Refine mx and mx:

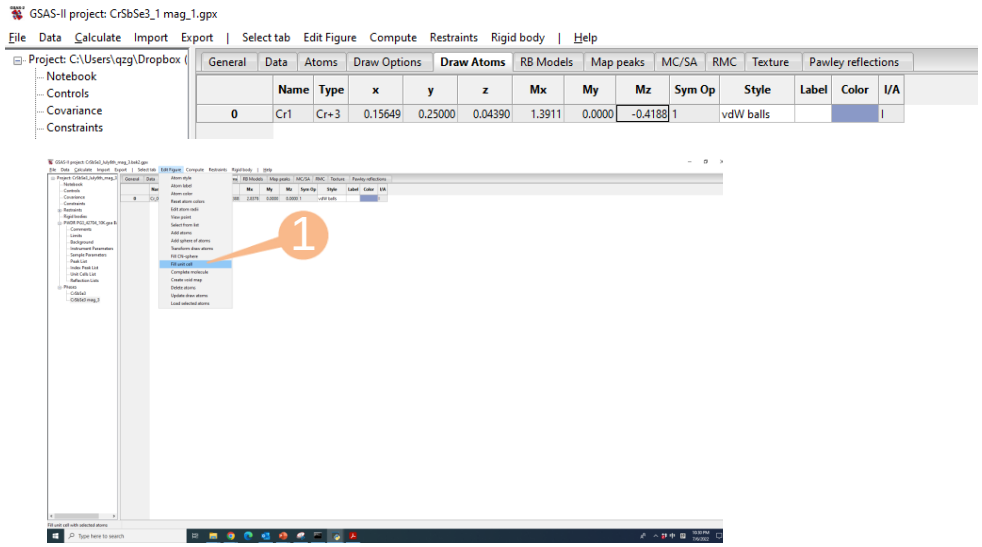


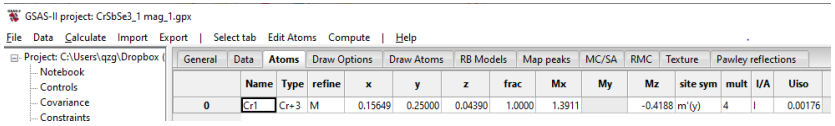
Visualizing the magnetic structure

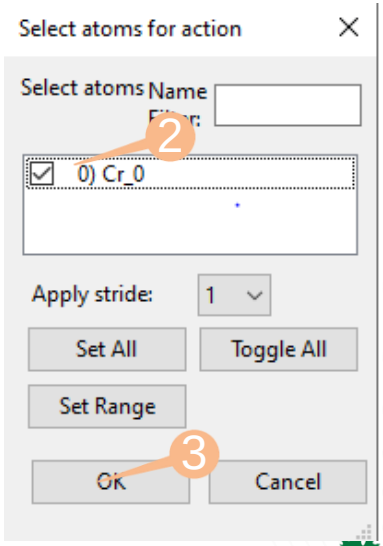


Poor refinement quality

In “Draw Atoms” tab:







“Draw atom” tab will be updated

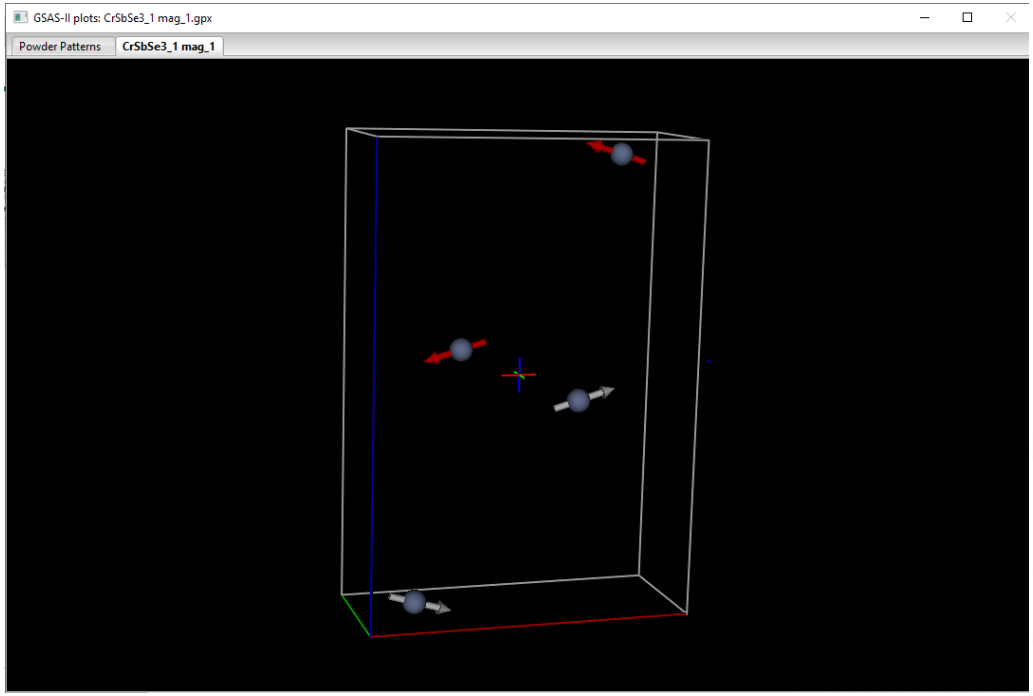
GSAS-II project: CrSbSe3_1 mag_1.gpx

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 Bi

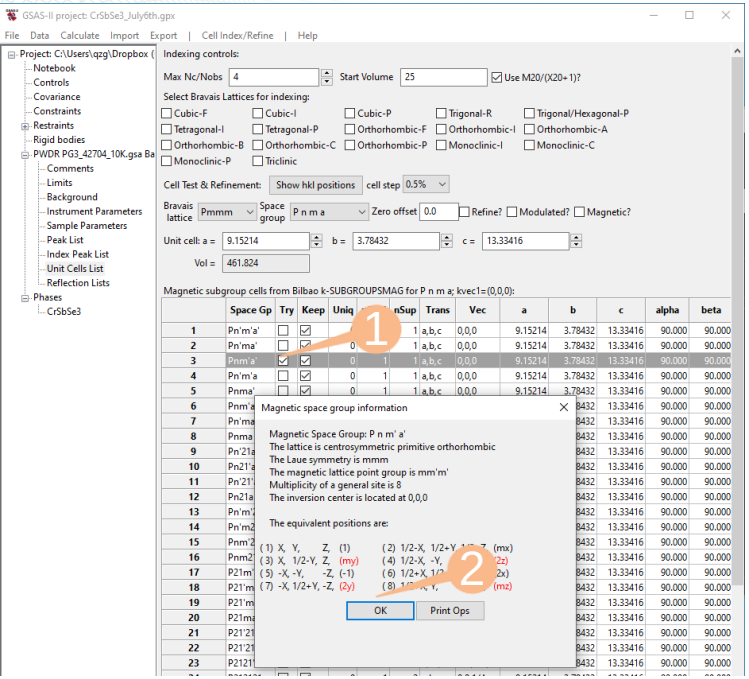
General | Data | Atoms | Draw Options | **Draw Atoms** | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

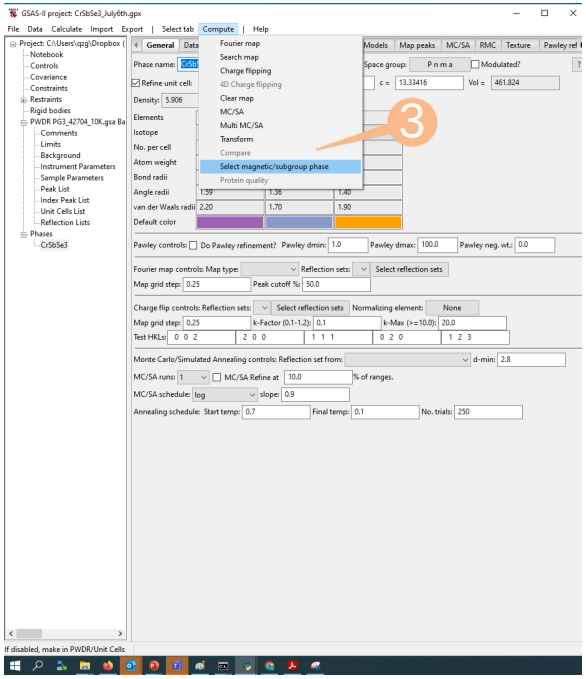
	Name	Type	x	y	z	Mx	My	Mz	Sym Op	Style	Label	Color	I/A
0	Cr1	Cr+3	0.15649	0.25000	0.04390	1.3911	0.0000	-0.4188	1	vdW balls			I
1	Cr1	Cr+3	0.34352	0.75000	0.54390	-1.3911	0.0000	-0.4188	2+0,0,0	vdW balls			I
2	Cr1	Cr+3	0.84352	0.75000	0.95610	-1.3911	-0.0000	0.4188	-1+1,1,1	vdW balls			I
3	Cr1	Cr+3	0.65648	0.25000	0.45610	1.3911	-0.0000	0.4188	-2+1,1,1	vdW balls			I

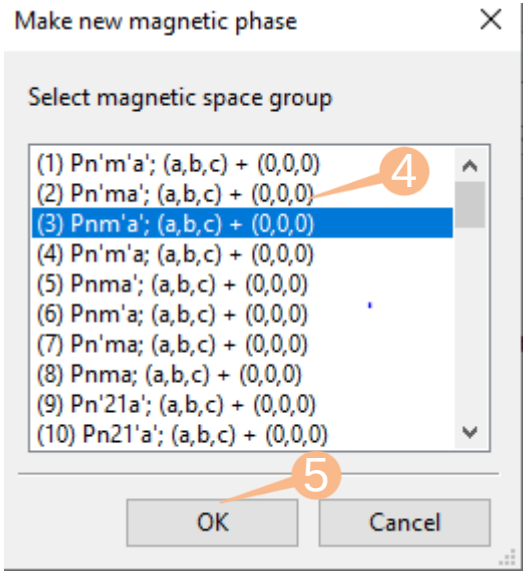


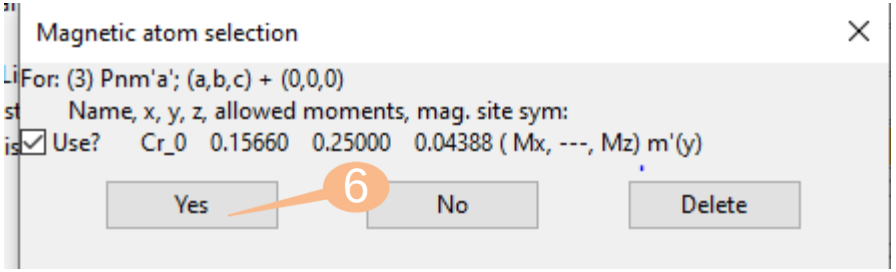
Canted AFM order with magnetic space group *Pn’m’a’* can be excluded.

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









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 C ute | Help

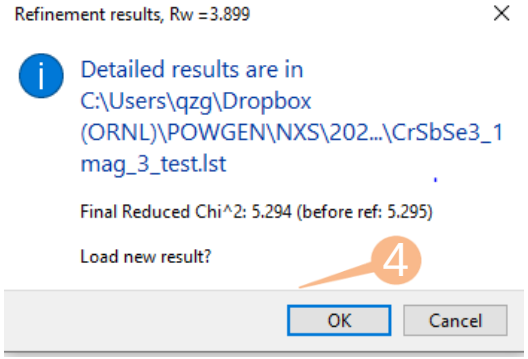
Project: C:\Users\qzg\Dropbox (
- Notebook
- Controls
- Covariance
- Constraints

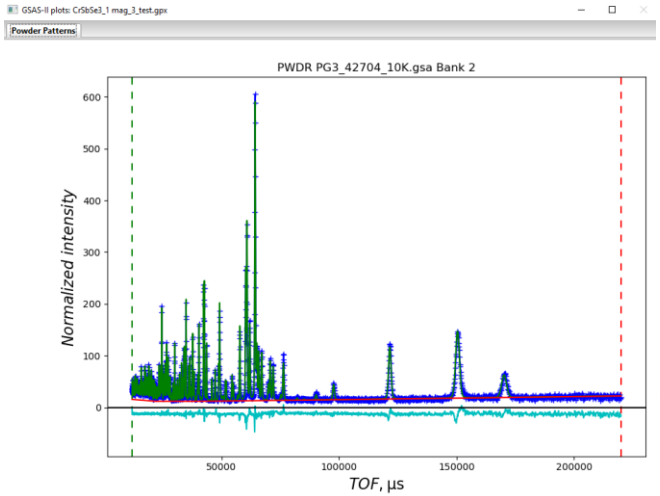
General | Data | **Atoms** | Draw Options | Draw Atoms | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

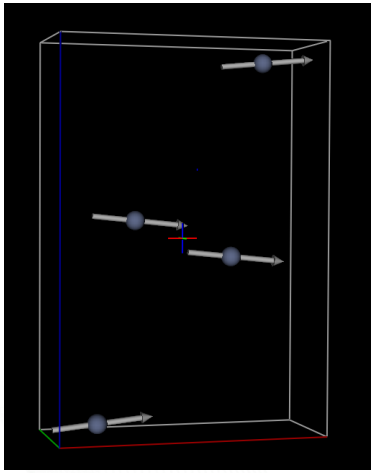
	Name	Type	re		y	z	frac	Mx	y	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15659	0.25000	0.04370	1.0000	1.0000		1.0000	m'(y)	4	I	0.00111

1 2 3

Calculate-refine:







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

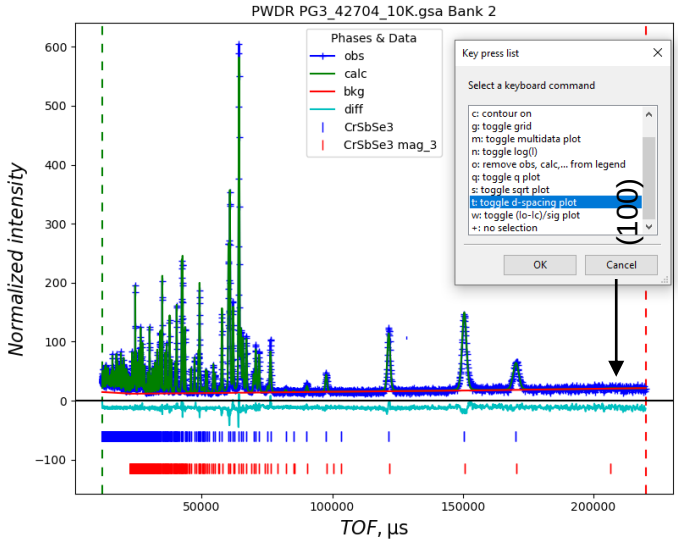
GSAS-II project: CrSbSe3_1 mag_3_test.gpx

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

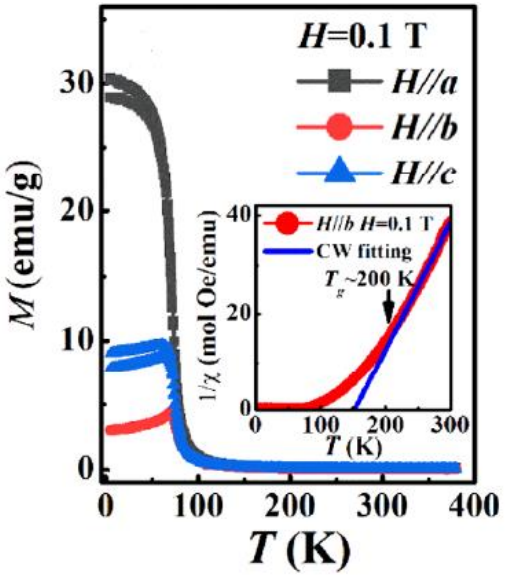
Project: C:\Users\qzg\Dropbox (
- Notebook
- Controls
- Covariance

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	I	0.00176



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



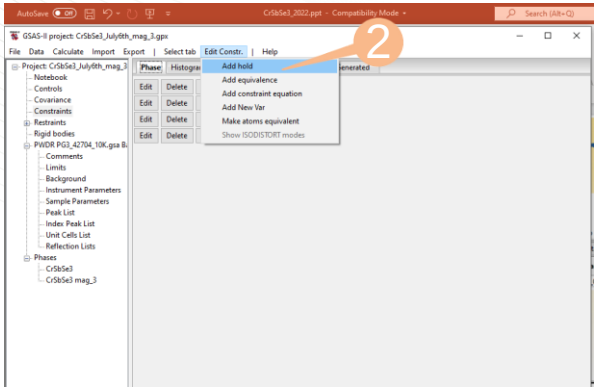
b. Highest magnetization with H//*a*: moment along the *a* axis.

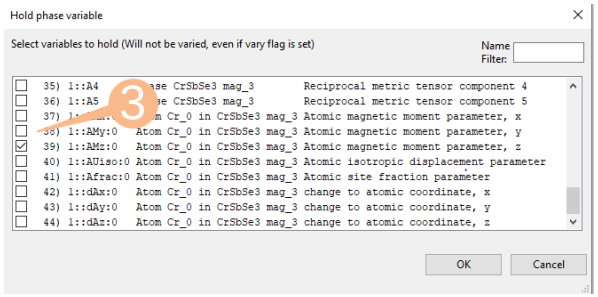
c. Similar refinement quality if Mz=0

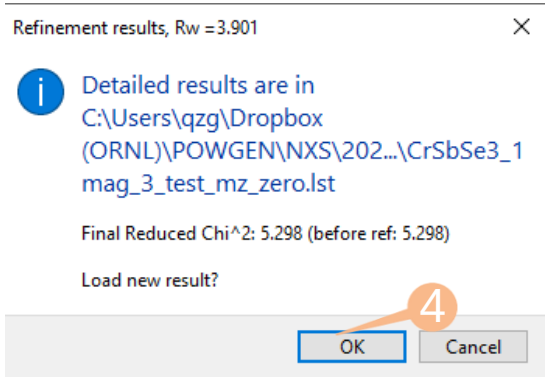
General | Data | **Atoms** | Draw Options | Draw Atoms | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

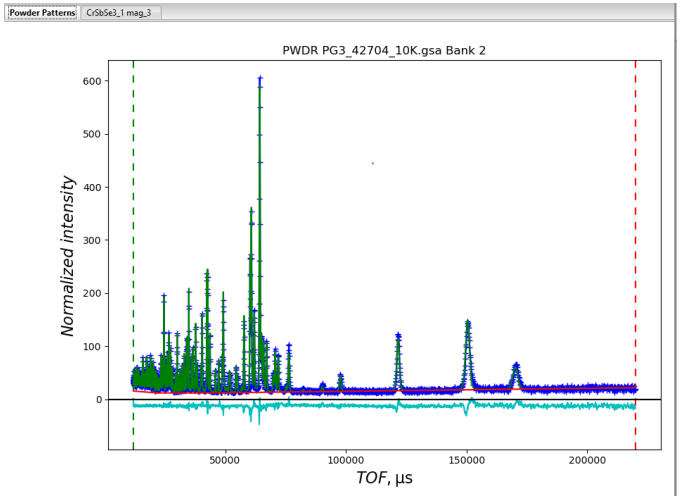
	Name	Type	refine	x	y	z	frac	Mx	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	2.6214	0.0000	m'(y)	4	I	0.00176

1









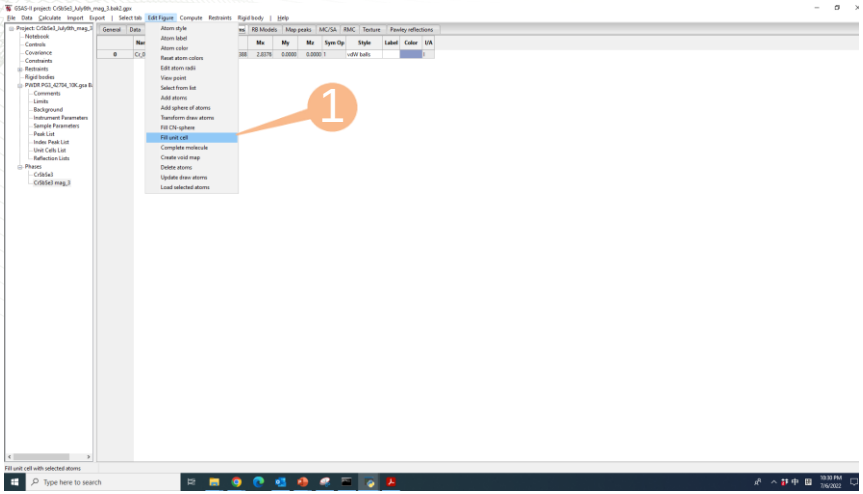
General | Data | **Atoms** | Draw Options | Draw Atoms | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

	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

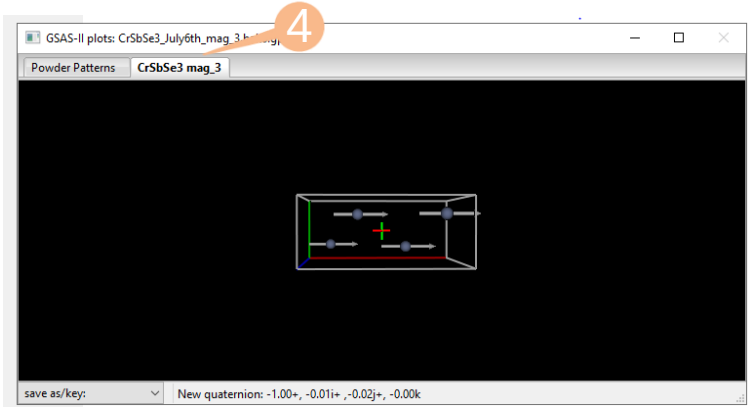
M=(2.64,0,0) μ_B

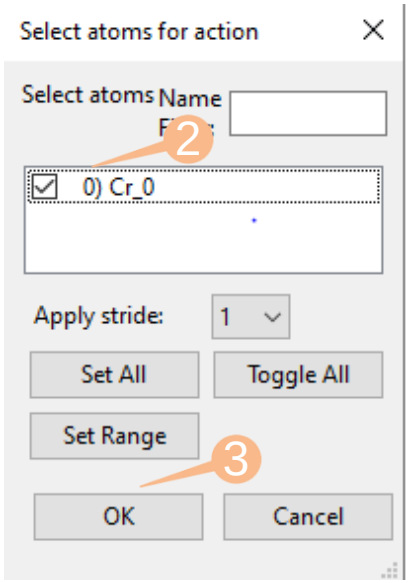
Visualizing the magnetic structure

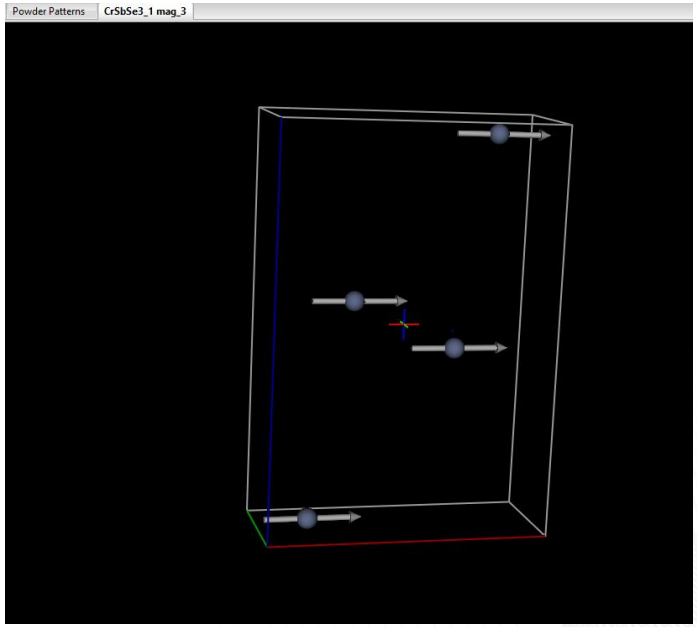
In “Draw Atoms” tab:



Ferromagnetic order



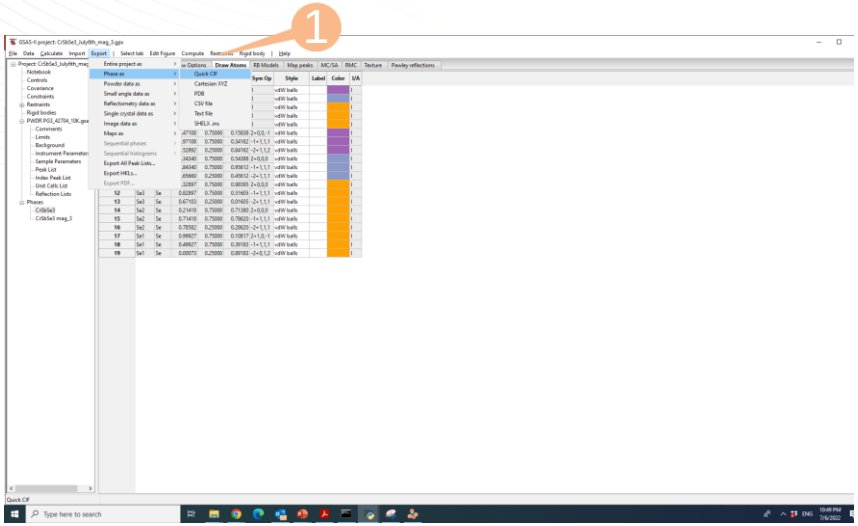


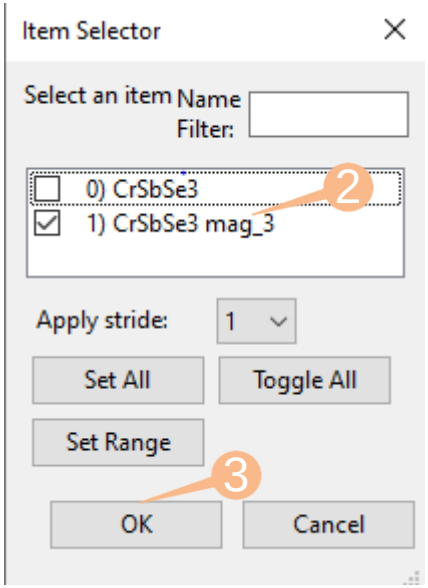


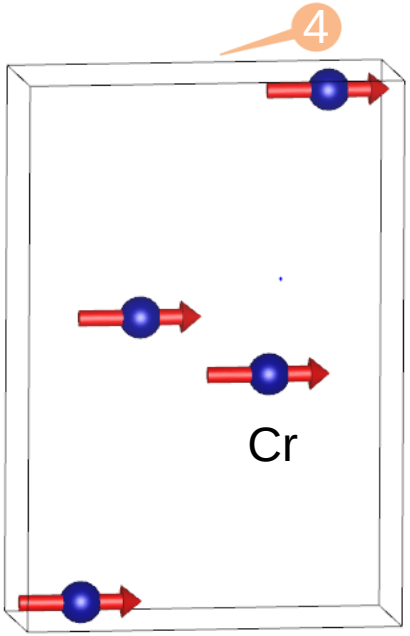
To publish the results

I. 3D magnetic structure

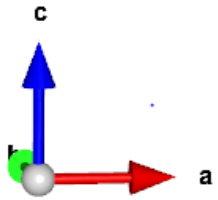
Export to cif file: Export- phase as- quick cif





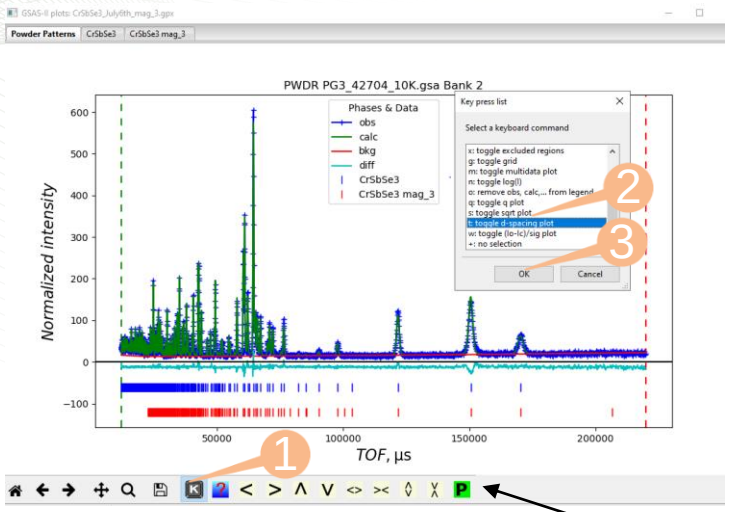


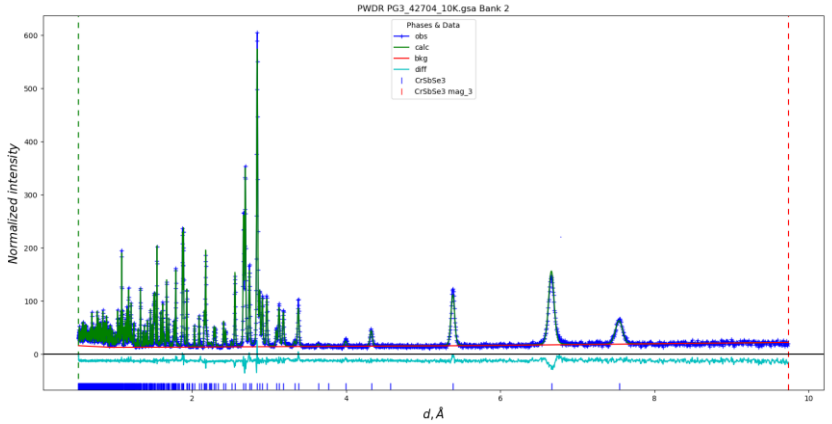
Use VESTA software (jp-minerals.org/vesta/en/download.html) to open it directly for publication:



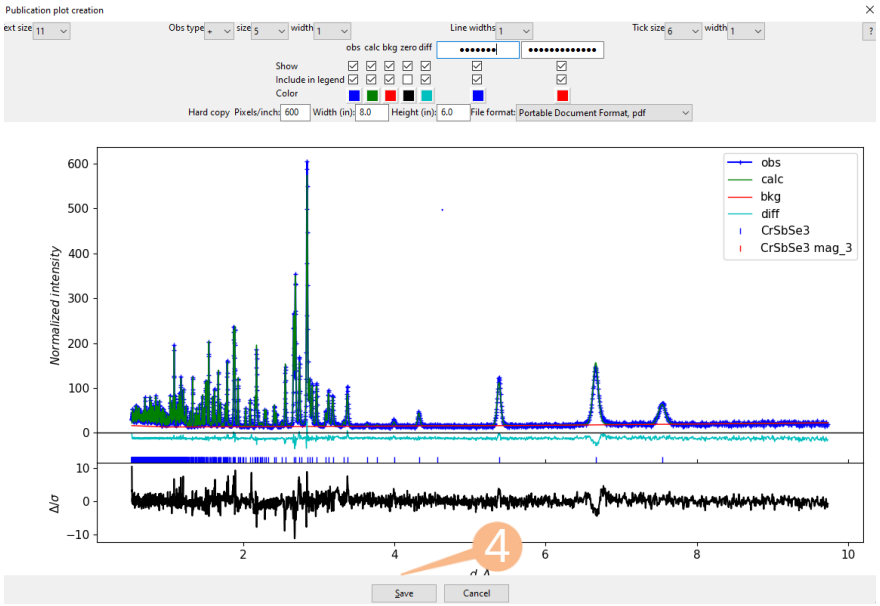
II. Refinement plots

Convert TOF to d





Click P button to open a new window



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!

zhangq6@ornl.gov