GSAS-II tutorial on crystal and commensurate magnetic structure

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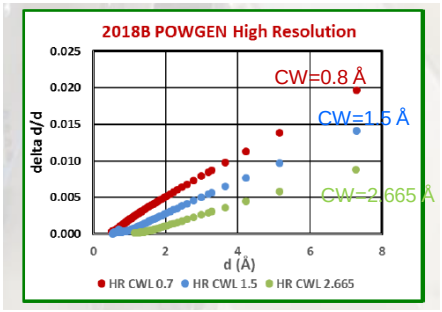
Time-of-flight powder diffractometer POWGEN

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

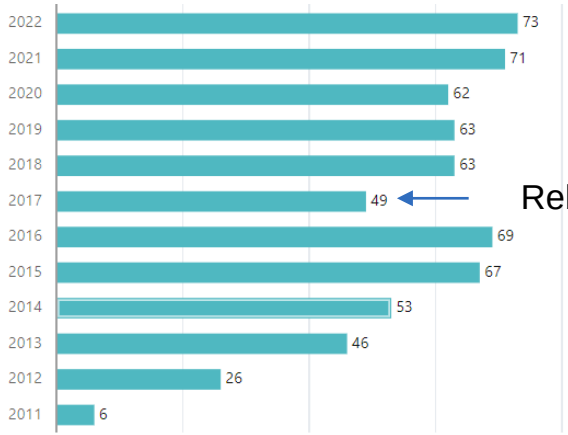
Current Instrument Capabilities (neutron band ~ 1 Å)

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 2theta)



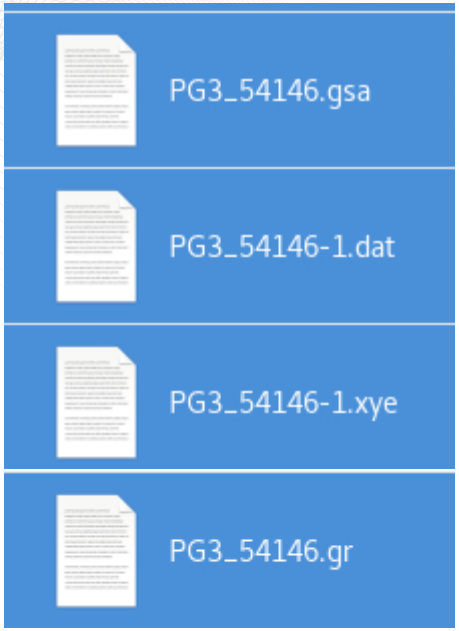
Rebuild POWGEN

> 60 papers/year last 7 years

~ 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

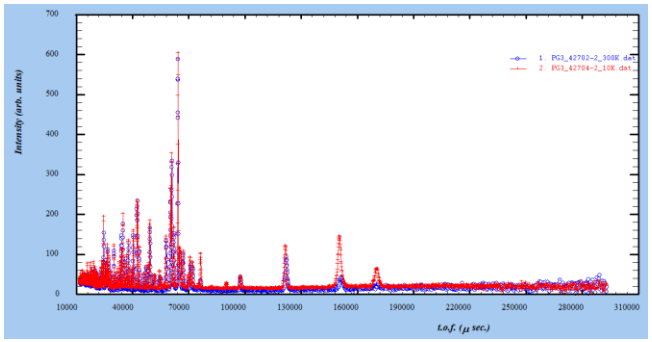


Diffraction data for GSAS-II

Diffraction data for FullProf or JANA

Diffraction data for TOPAS

PDF data



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
```

Ready for Rietveld refinement or PDF analysis

TOF to D spacing (FullProf):

TOF(microseconds) = Zero + Dtt1 * D + Dtt2 * D^2 + 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:

TOF(microseconds) = Zero + Dtt1 * D + Dtt2 * D^2 + 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:

$$\sigma^2 = {\sigma_0}^2 + {\sigma_1}^2 d^2 + {\sigma_2}^2 d^4 + \frac{{\sigma_q}^2}{d^2} \Rightarrow \sigma_q d \text{ GSASII used}$$

$$\gamma = \gamma 1 * d + \gamma 2 * d^2 + \gamma 0$$

- 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;

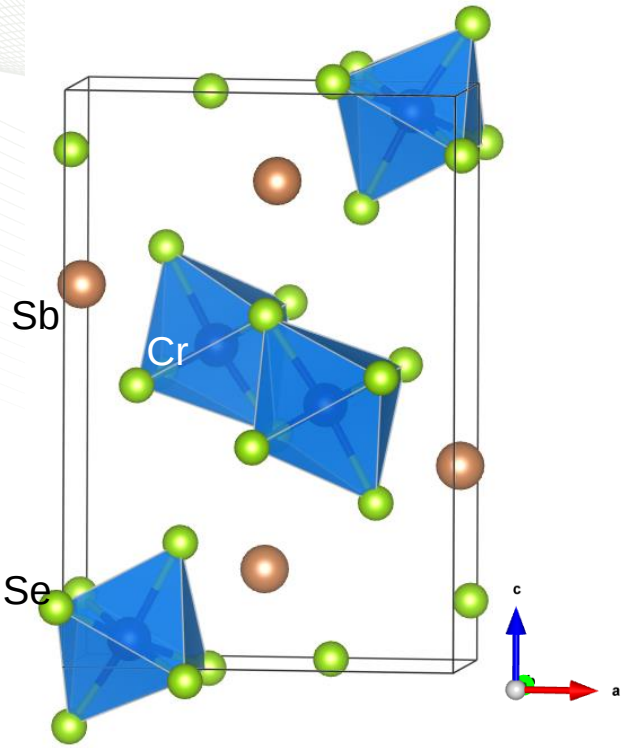
JANA: representation analysis and magnetic space group;

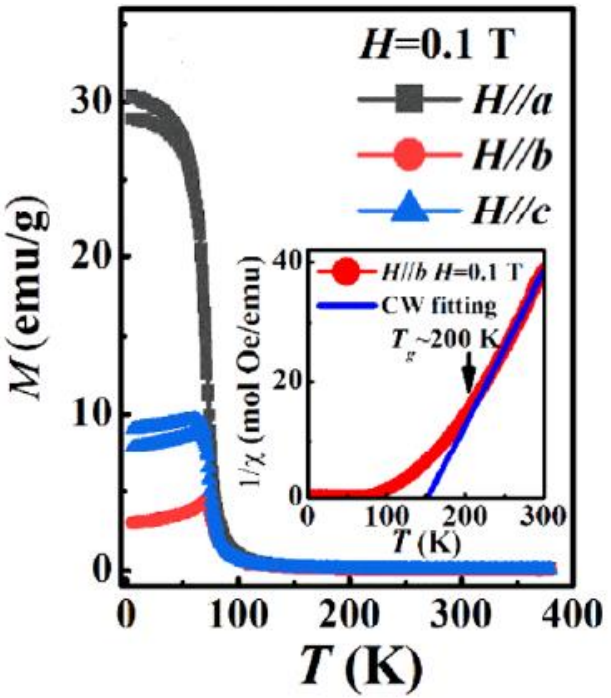
- **Incommensurate magnetic order**

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
  $CrSbSe_3$.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\Temp\Temp1_GSAS_II_QZhang_Thursday.zip\GSAS_II_QZhang_Thursday\2018B_HighRes_60HzB2_1p5.instprm - Notepad++

File Edit Search View Encoding Language Settings Tools Macro Run Plugins Window ?

IR3.mcif.txt | IR3.mcif | bkup_Fe1p16_4K_superSG.pcr | 2018B_HighRes_60HzB2_1p5.instprm | CrSbSe3.mag_3.cif | PG3_42702_300K.gsa | 2018B_HighRes_60HzB2_1p5.instprm

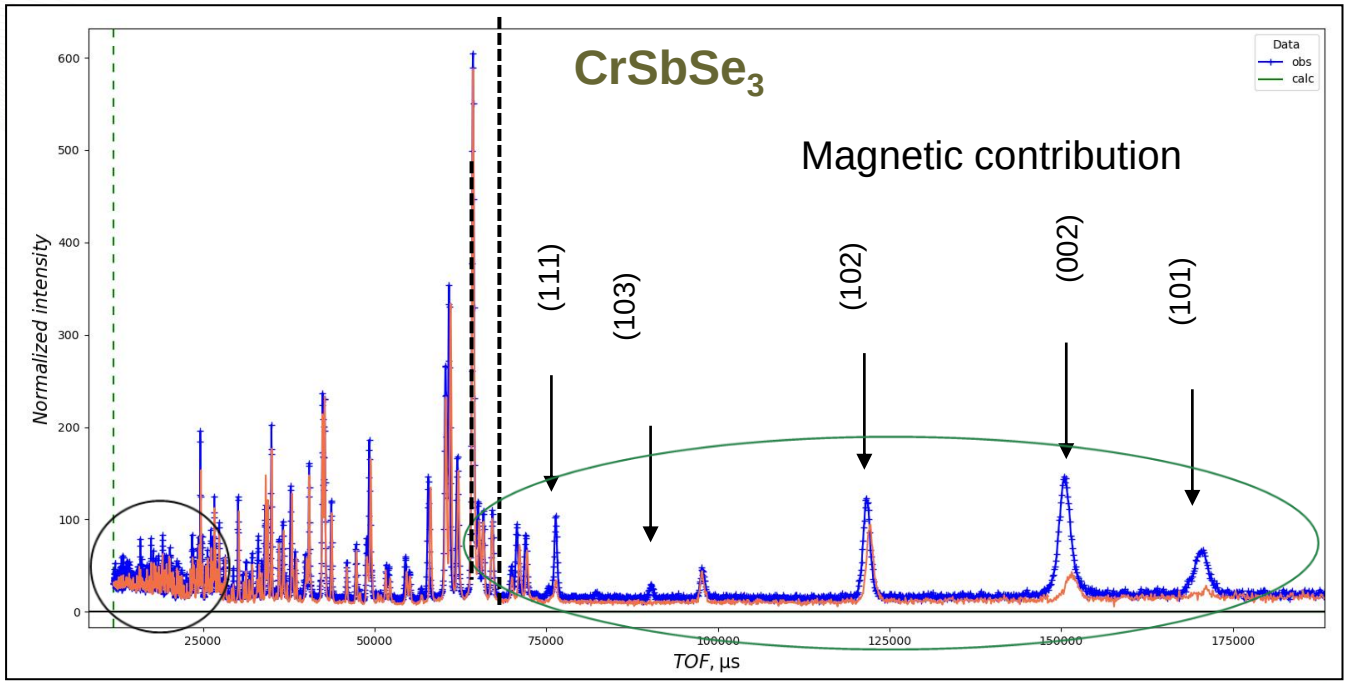
```
1  #GSAS-II instrument parameter file; do not add/delete items POWGEN 2018B!
2  Z:-0.465205938282
3  fltPath:63.183
4  beta-q:0.0
5  Bank:2.0
6  sig-1:-852.163368943
7  2-theta:90.0
8  sig-q:797.184446197
9  sig-0:-203.060186472
10 sig-2:298.195588039
11 Zero:-26.810325593
12 difC:22597.8753723
13 X:-4.50393449632
14 Azimuth:0.0
15 Y:10.9493140839
16 alpha:0.128661555108
17 beta-1:0.00396039253042
18 beta-0:0.100880267005
19 Type:PNT
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<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!

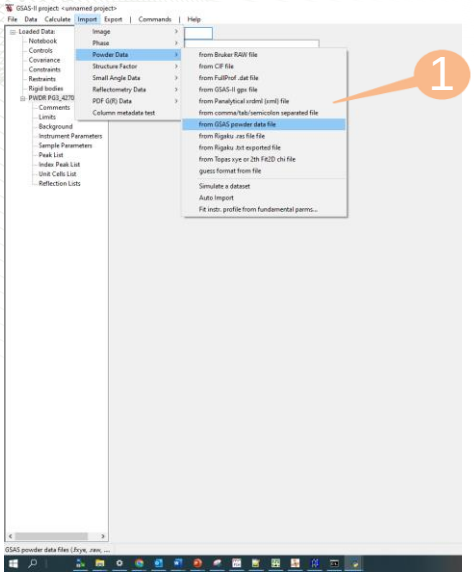
Two ways to determine the structural parameters in $T<T_N$ (or T_C) before refining magnetic structure:

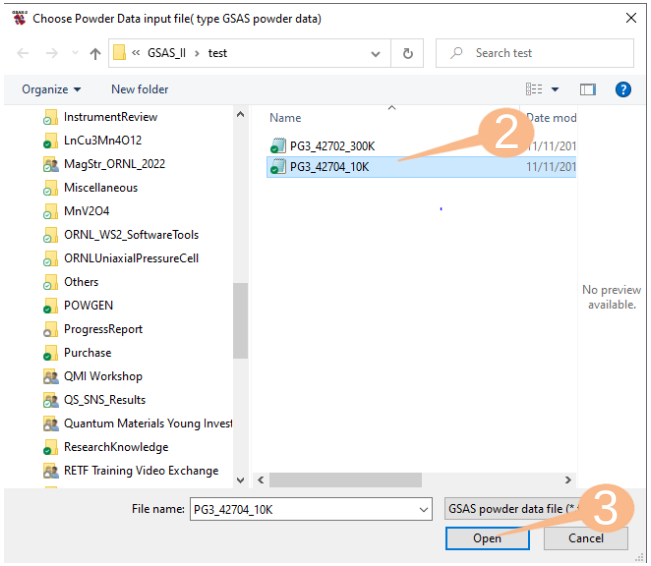
1). Refine the data in $T>T_N$ (or T_C) firstly. Then use them as initial parameters and only refine the atomic positions, B factors, and lattice constants in $T<T_N$ (or T_C).

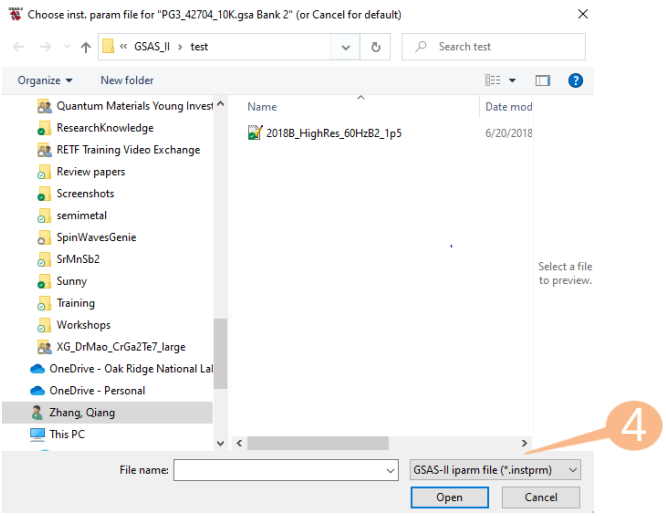
2). Exclude the high-d part of data that involves magnetic contribution and only refine low and middle d data on the structural part in TOF<68,000 μs

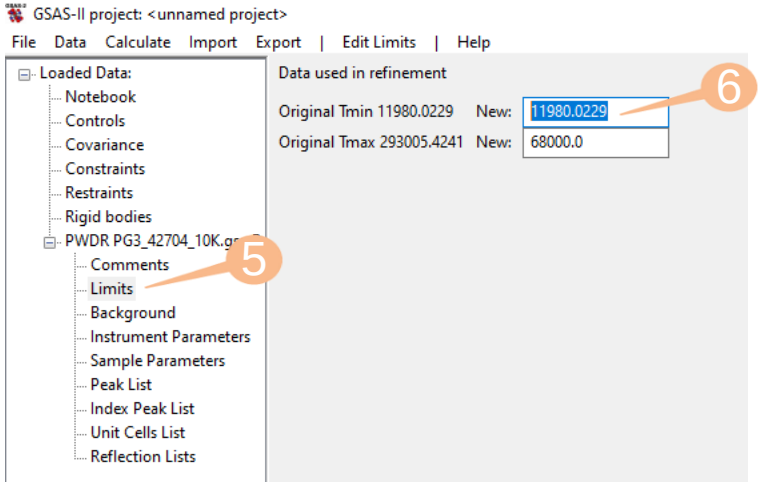
Refine the structure of $CrSbSe_3$

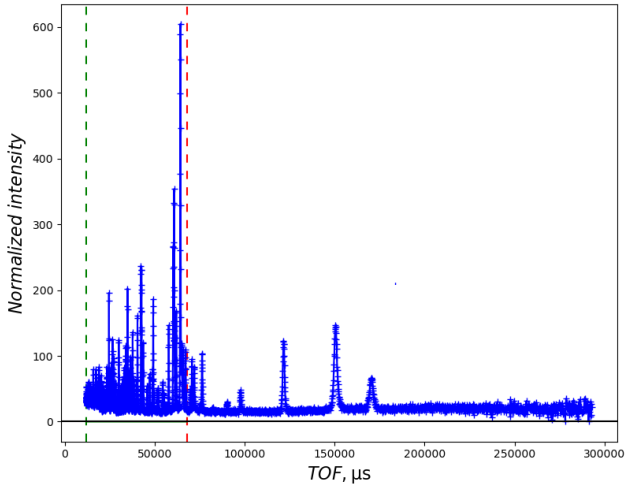
I. Import datafile and set the limit





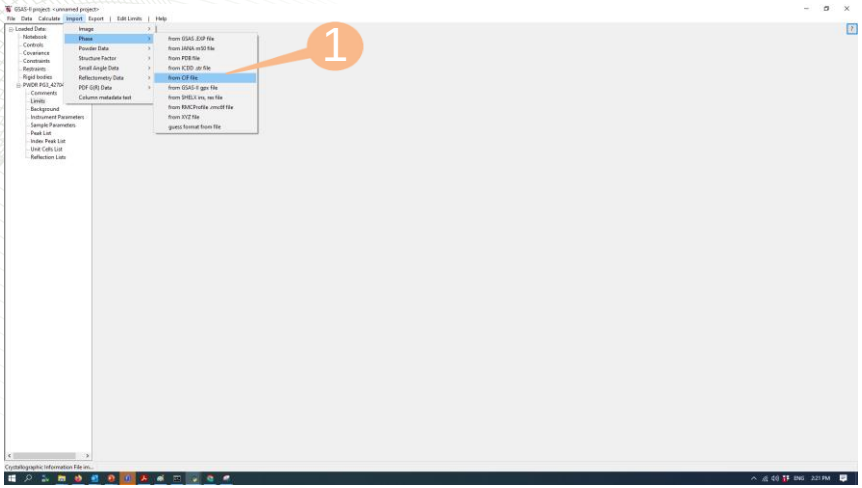


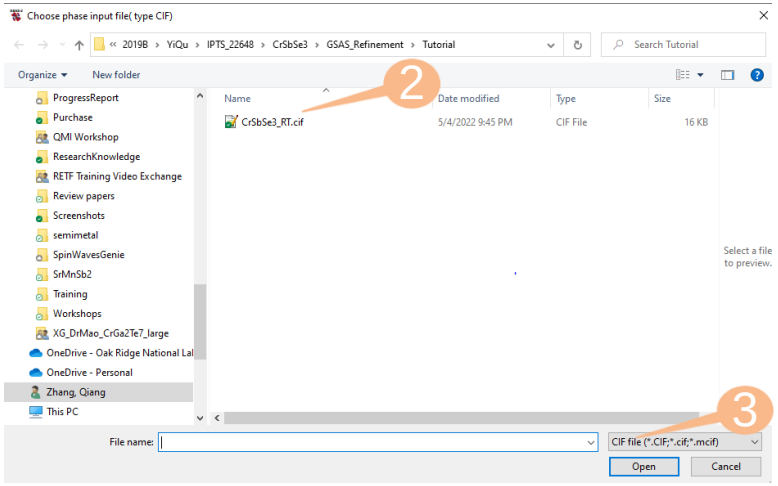


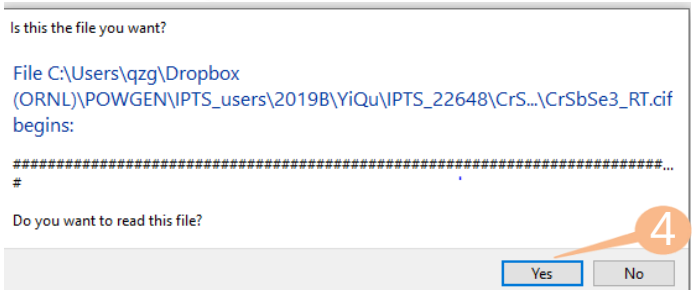


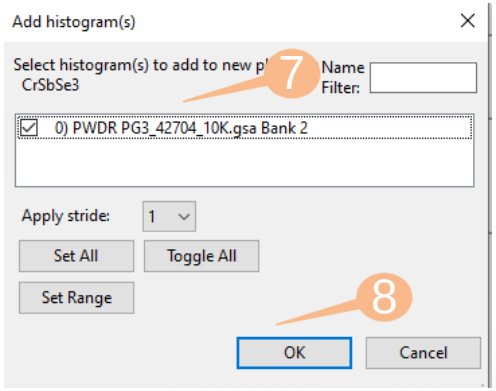
File-save project!

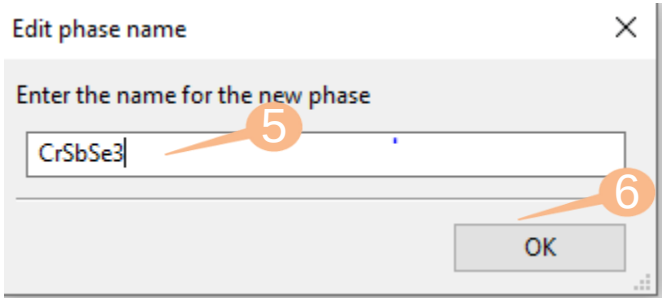
II. Import the phase



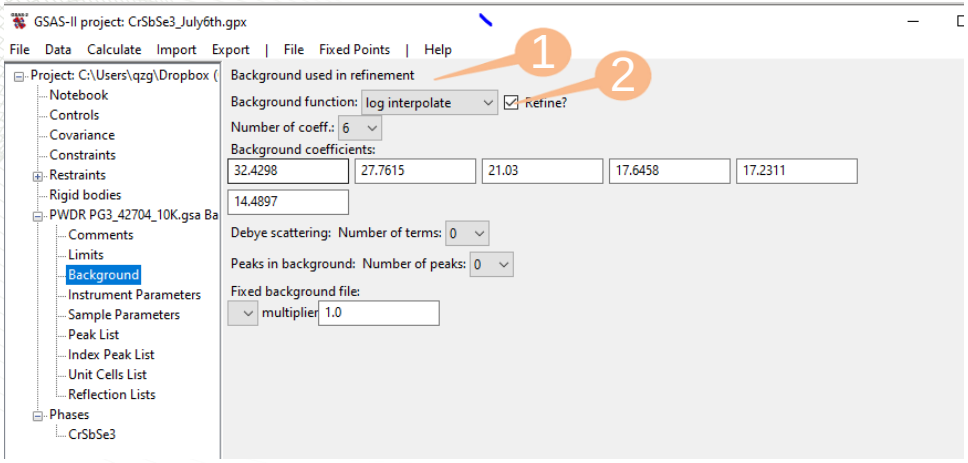


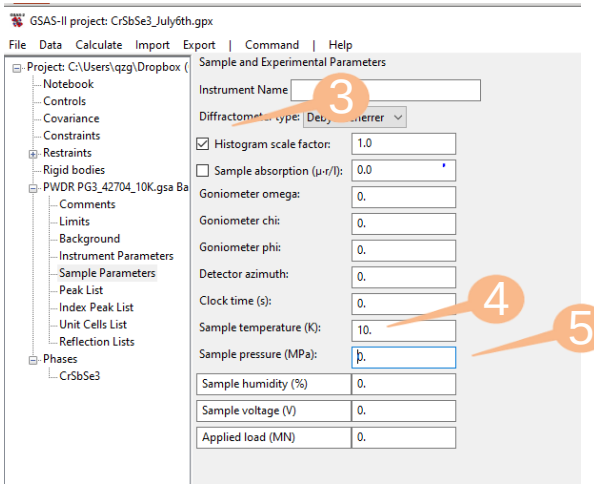


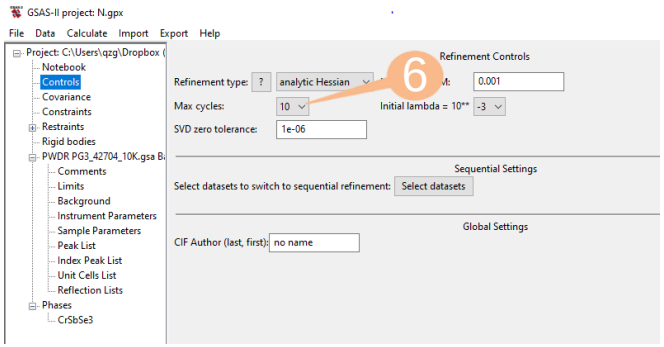


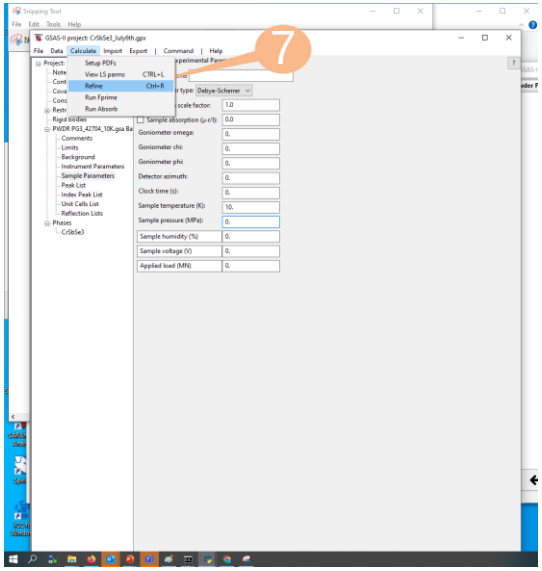


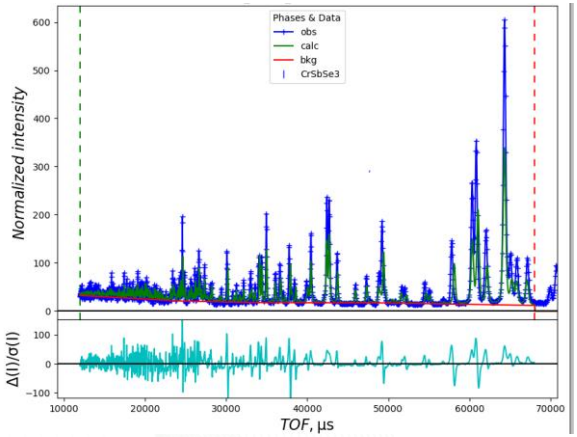
III. Refine background and scale factor



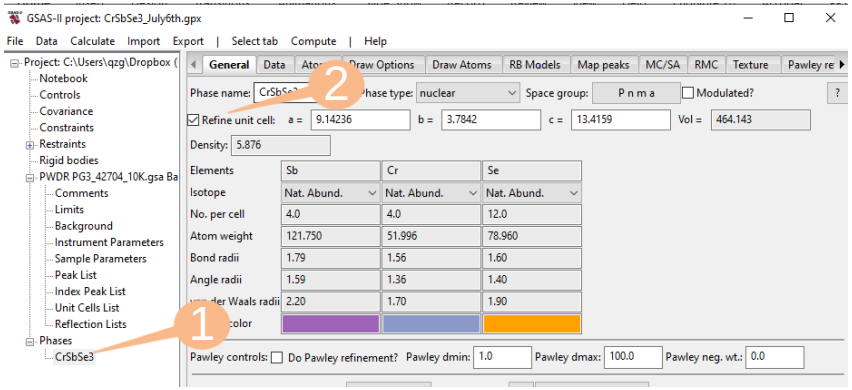




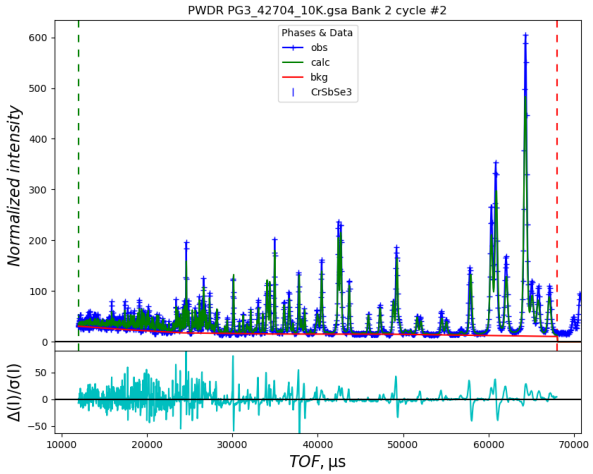


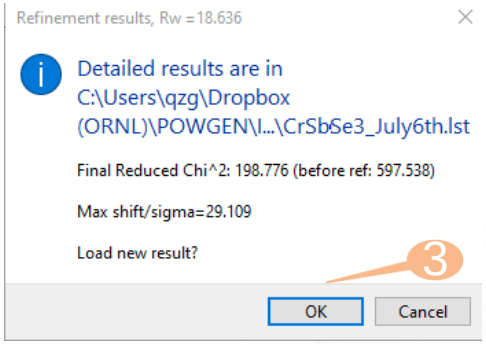


IV. Refine lattice constants

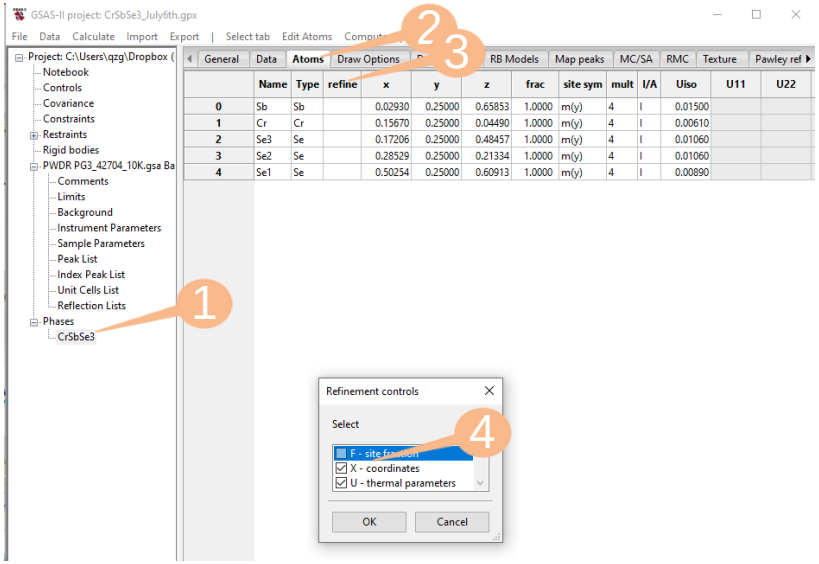


Calculate-refine:

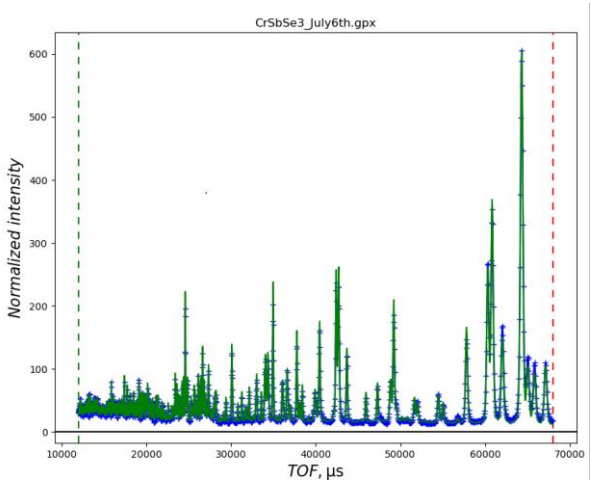


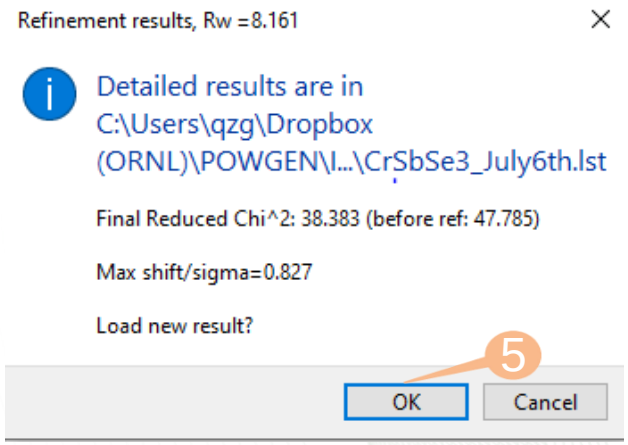


V. Refine atomic coordinates and thermal parameters



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:

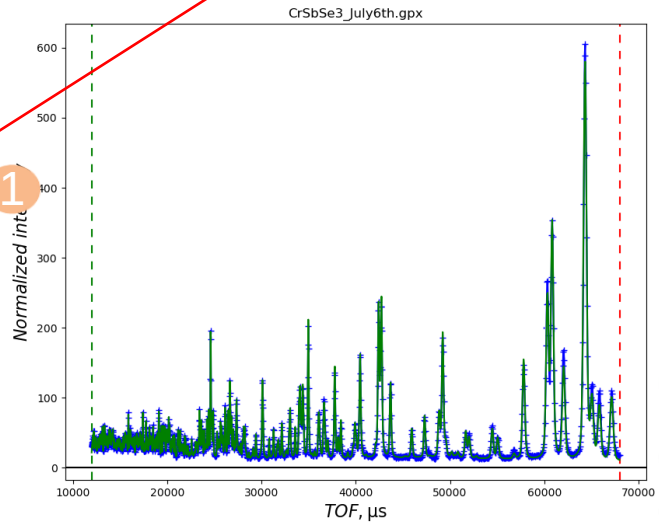
$$TOF = DIFC*d + DIFA*d^2 + ZERO + DIFB/d$$

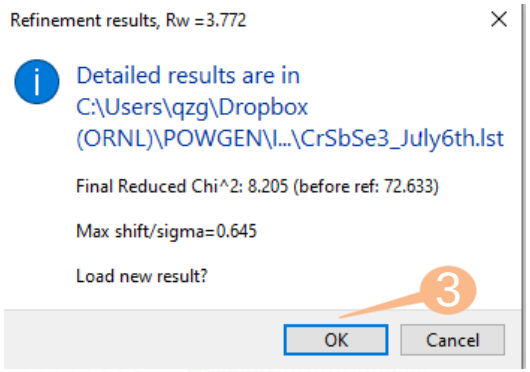
$$\sigma^2 = {\sigma_0}^2 + {\sigma_1}^2 d^2 + {\sigma_2}^2 d^4 + \frac{{\sigma_q}^2}{d^2} + {\sigma_3}^3 d^3$$

(Gaussian function)

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

(Lorentz function)

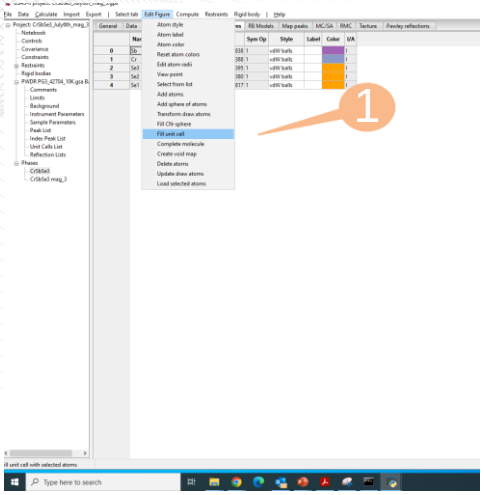


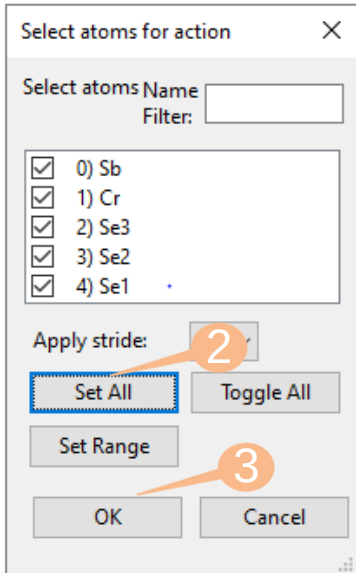


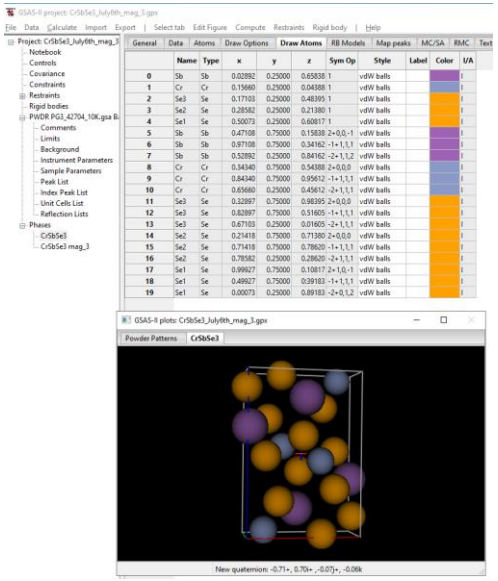
2

VII. Virtualizing crystal structure

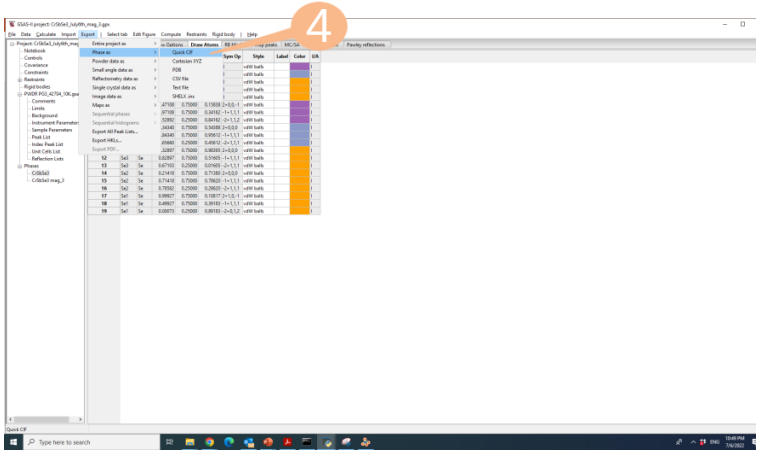
In “Draw Atoms” tab:





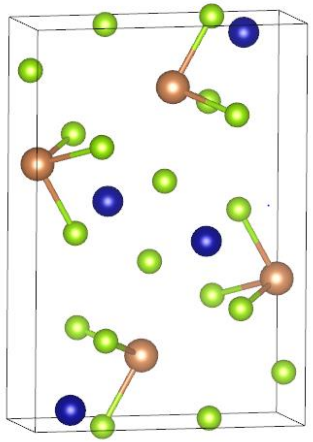


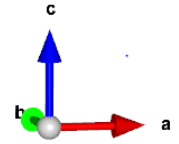
Export cif file:



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	

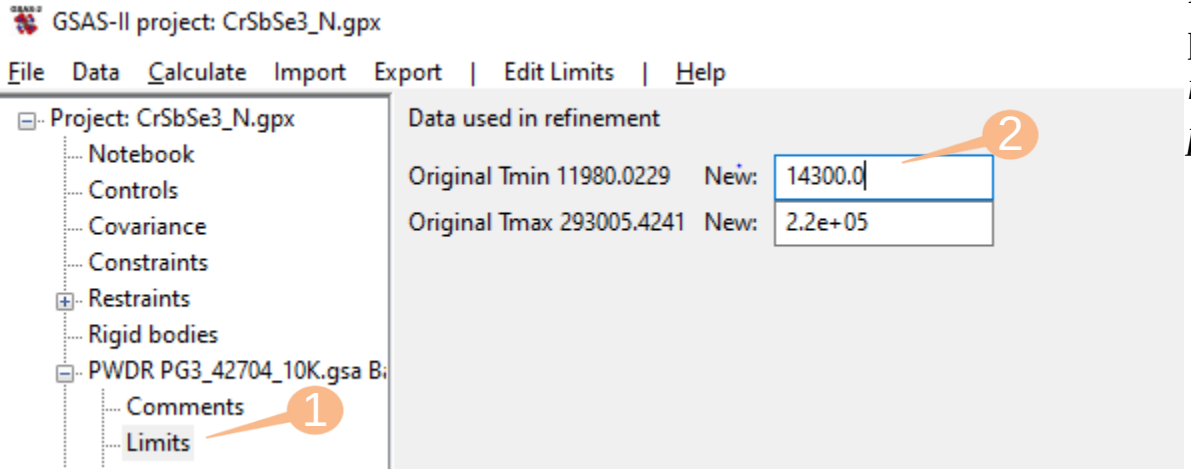




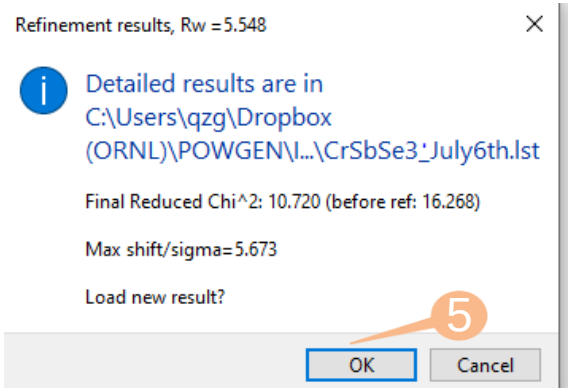
Let us add the high-TOF data to refine the magnetic structure!

Refine the magnetic structure of $CrSbSe_3$

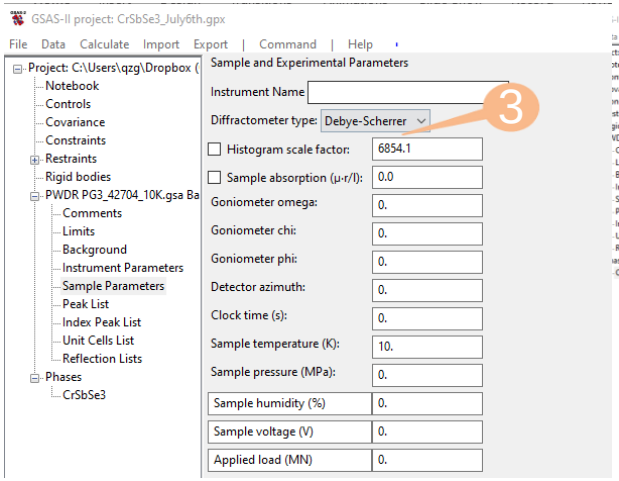
I. Add the high TOF data back and refine background

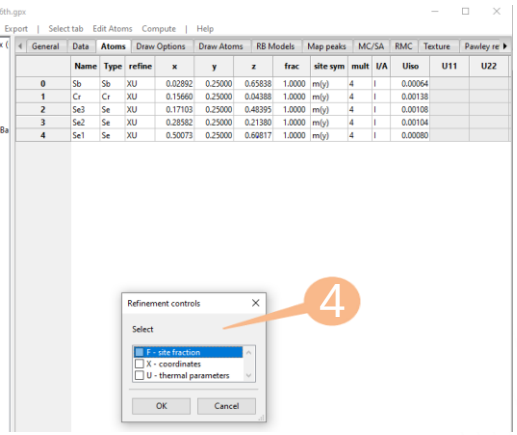


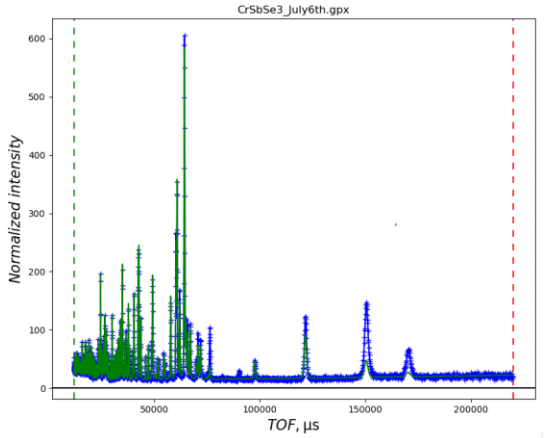
Fix the refinement on the scale, atomic positions, and thermal parameters. *Only refine background, magnetic structure and peak profile coefficient!*



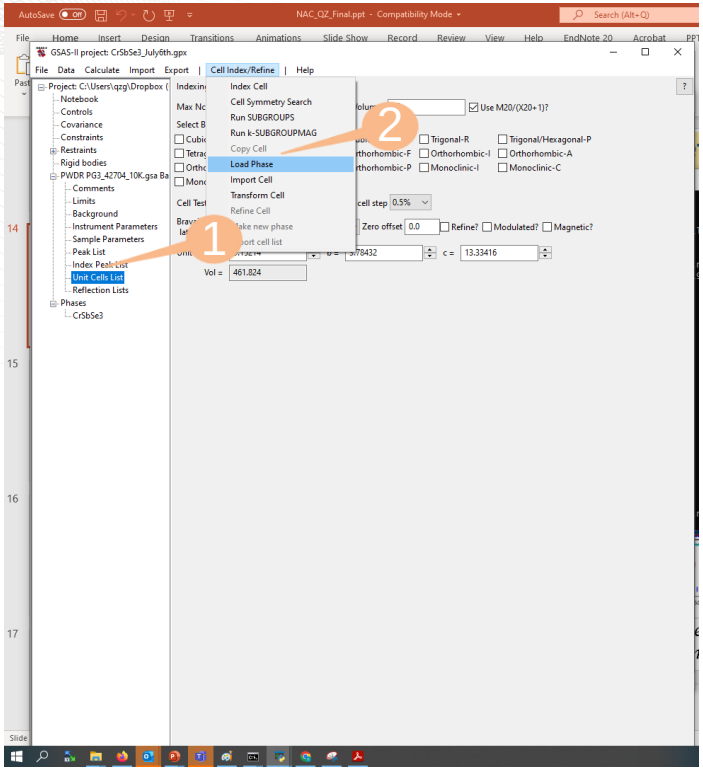
Calculate-refine:

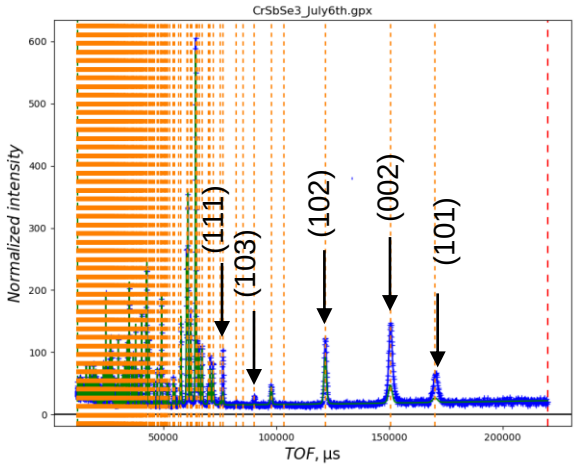






II. Determine the magnetic propagation vector

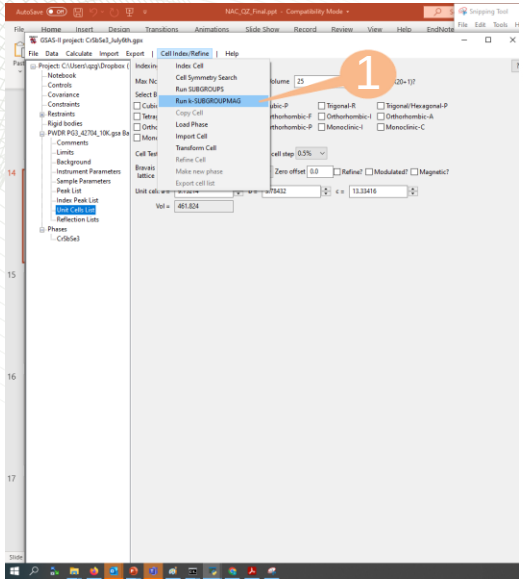


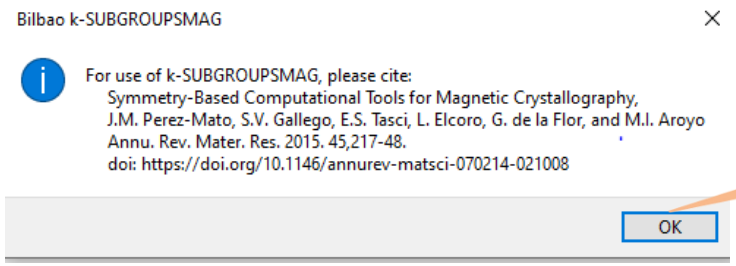


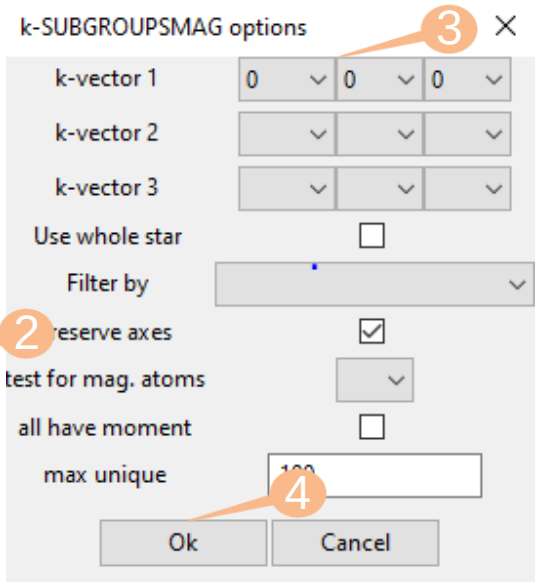
Magnetic peaks sit on the nuclear peak positions!

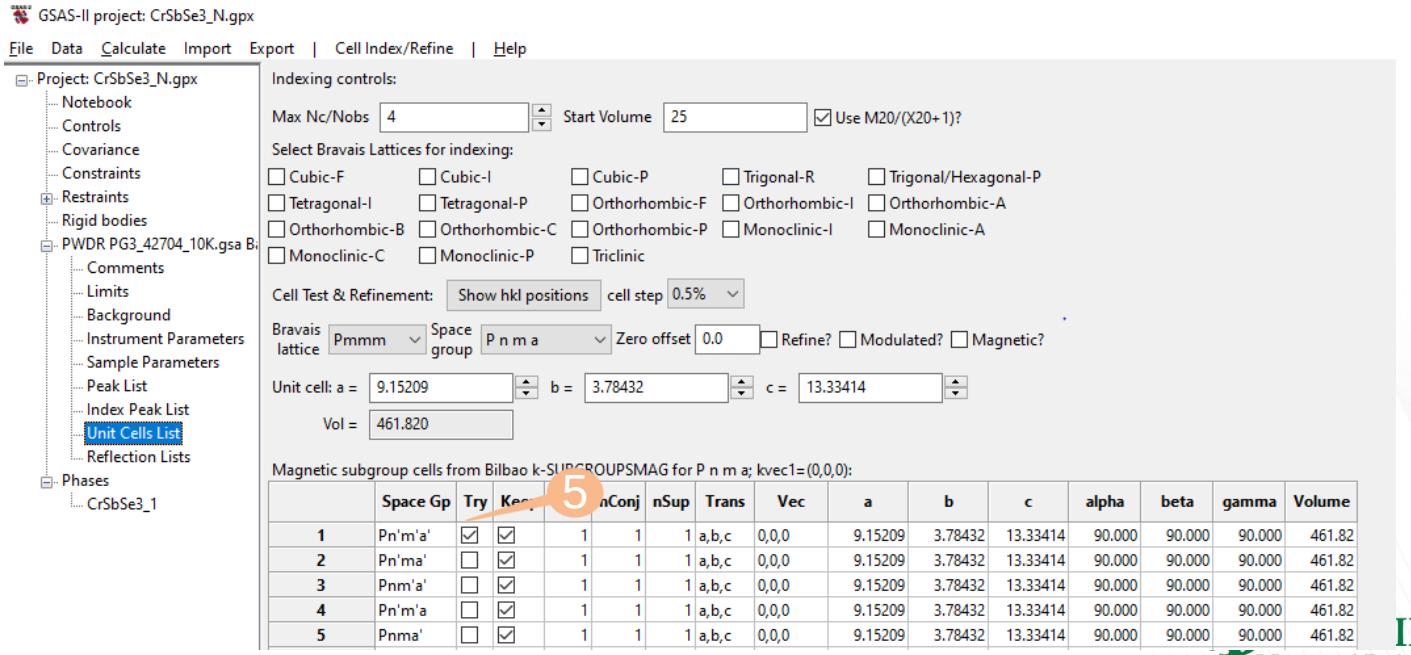
$$\boldsymbol{k} = \boldsymbol{Q}_M - \boldsymbol{Q}_N = 0$$

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

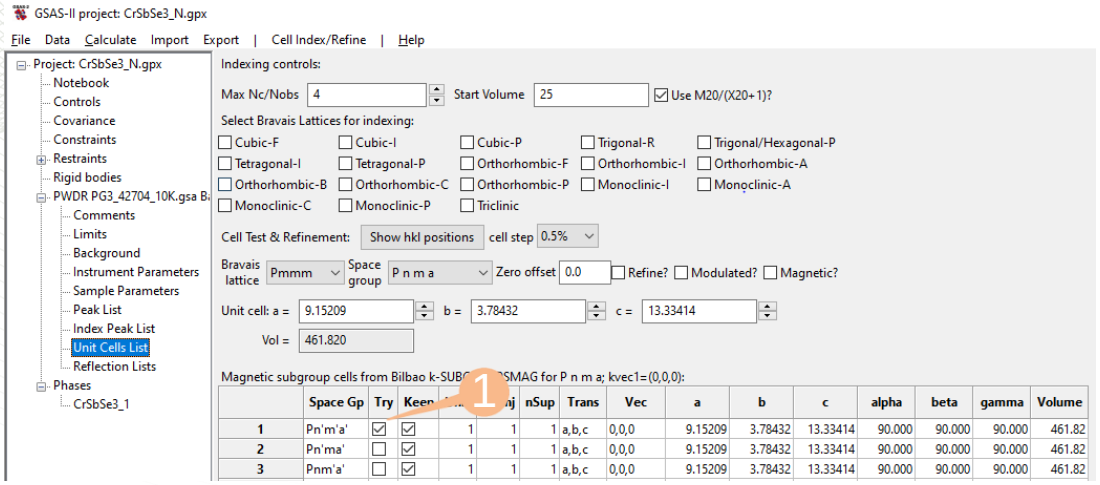


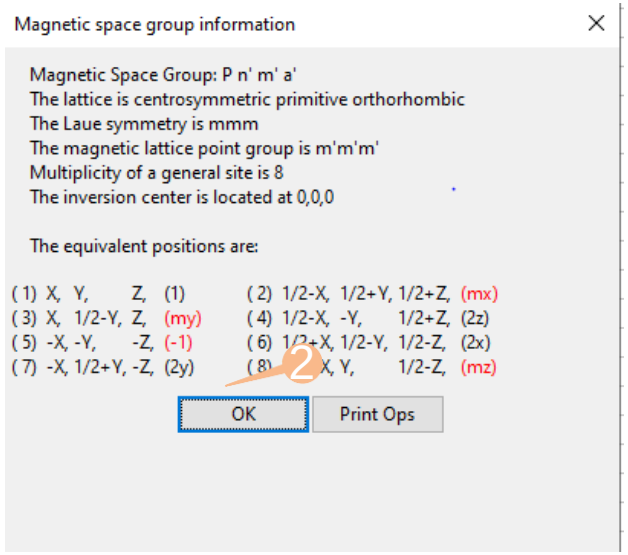


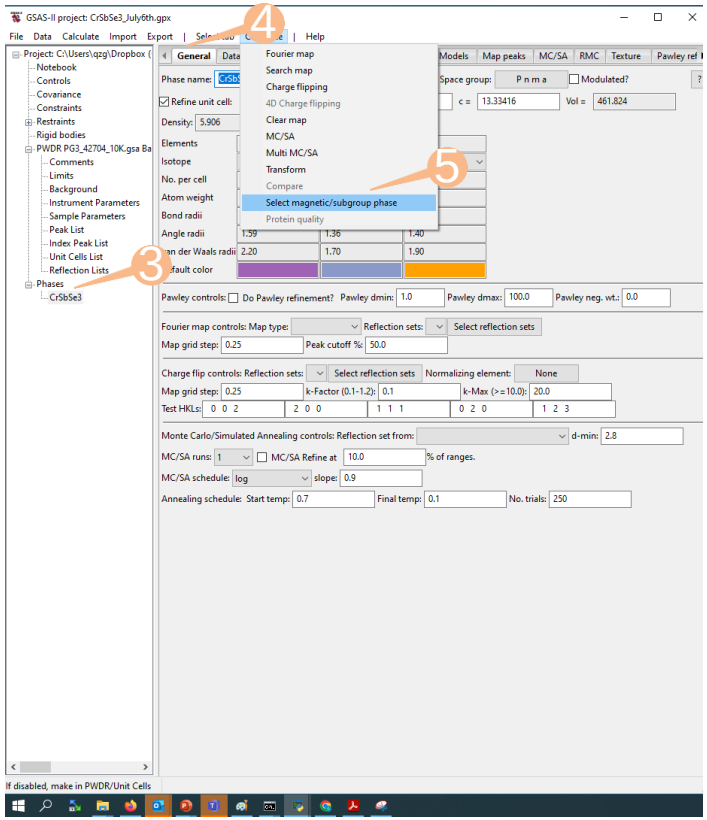


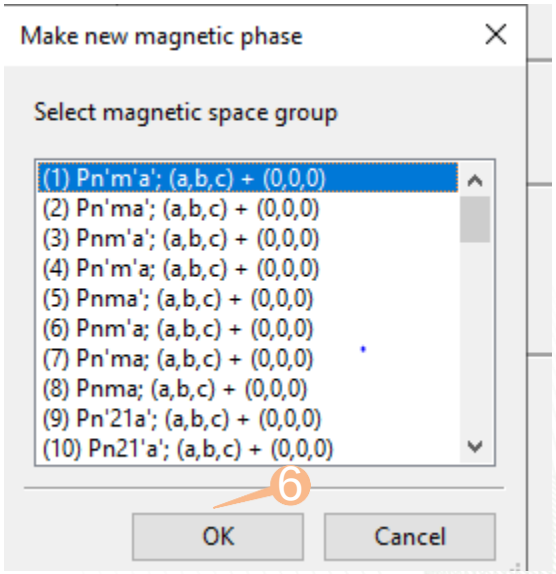


IV. Select magnetic space group Pn’m’a’ for the refinement

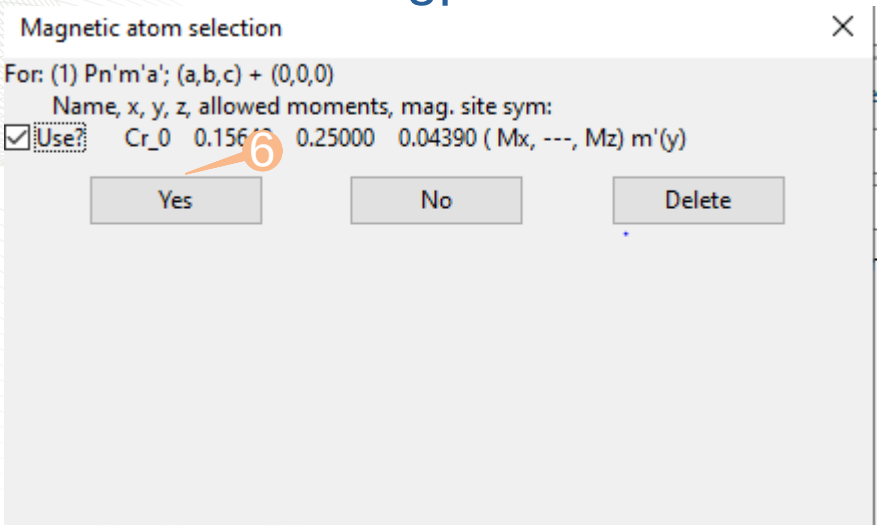


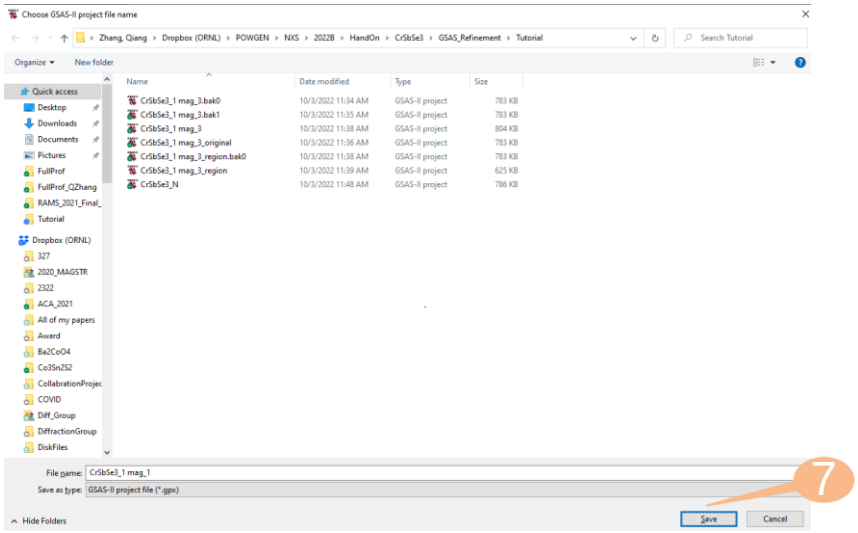




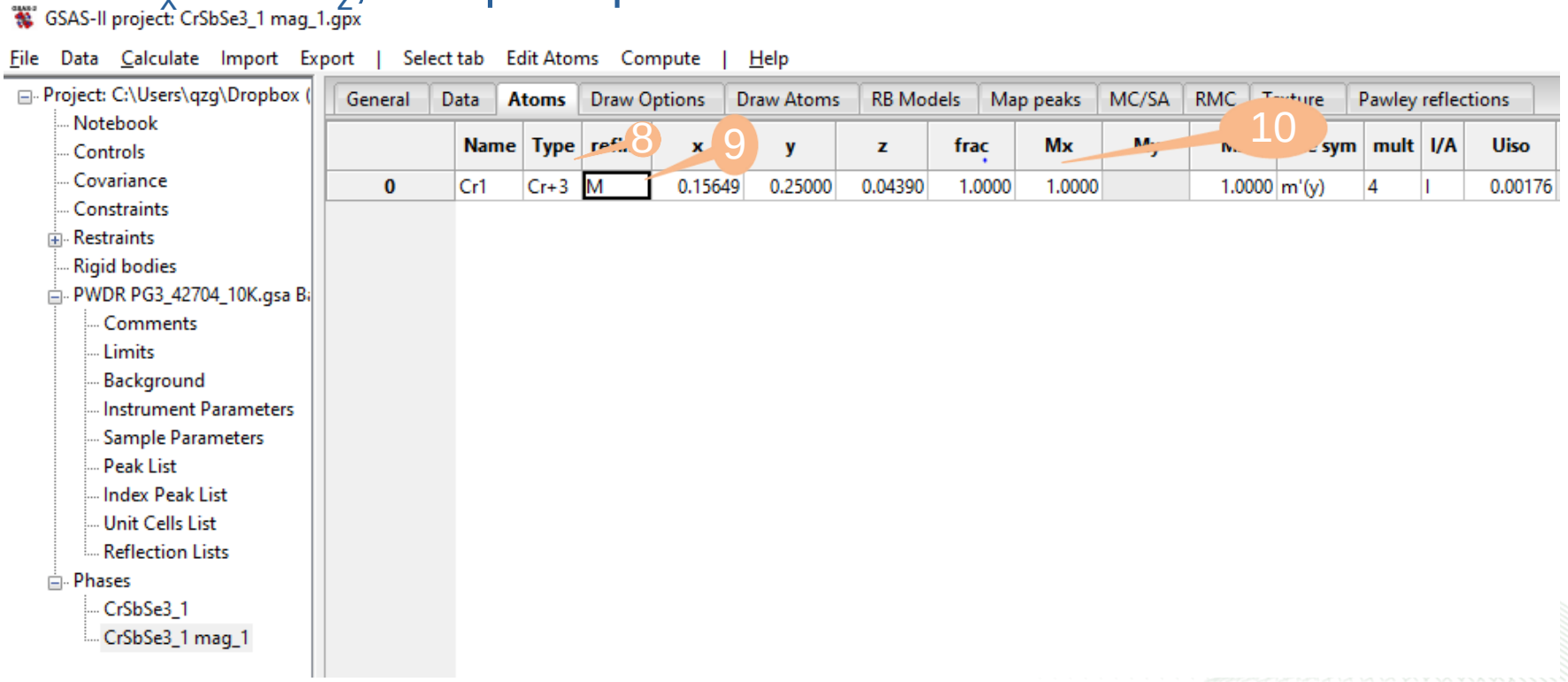


Save as a new gpx file

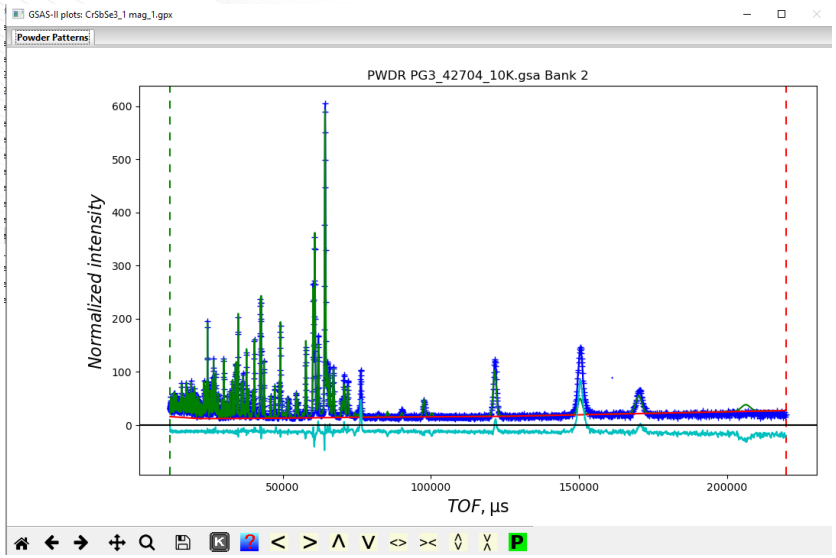




Refine m_x and m_z, and peak profile coefficient X:

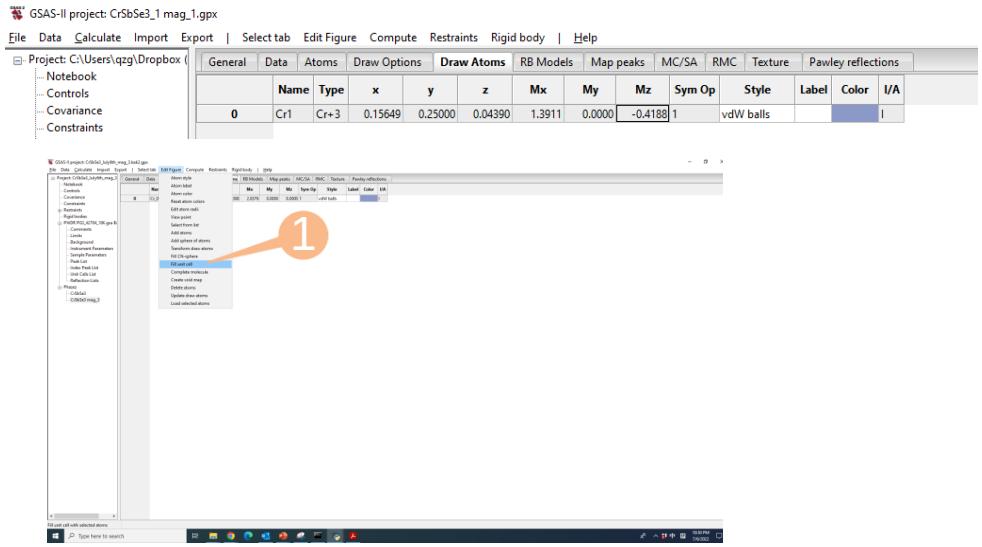


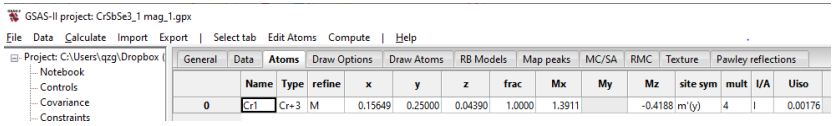
Visualizing the magnetic structure

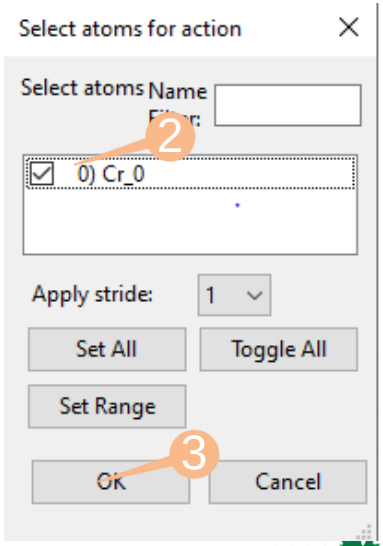


Poor refinement quality

In “Draw Atoms” tab:







“Draw atom” tab will be updated

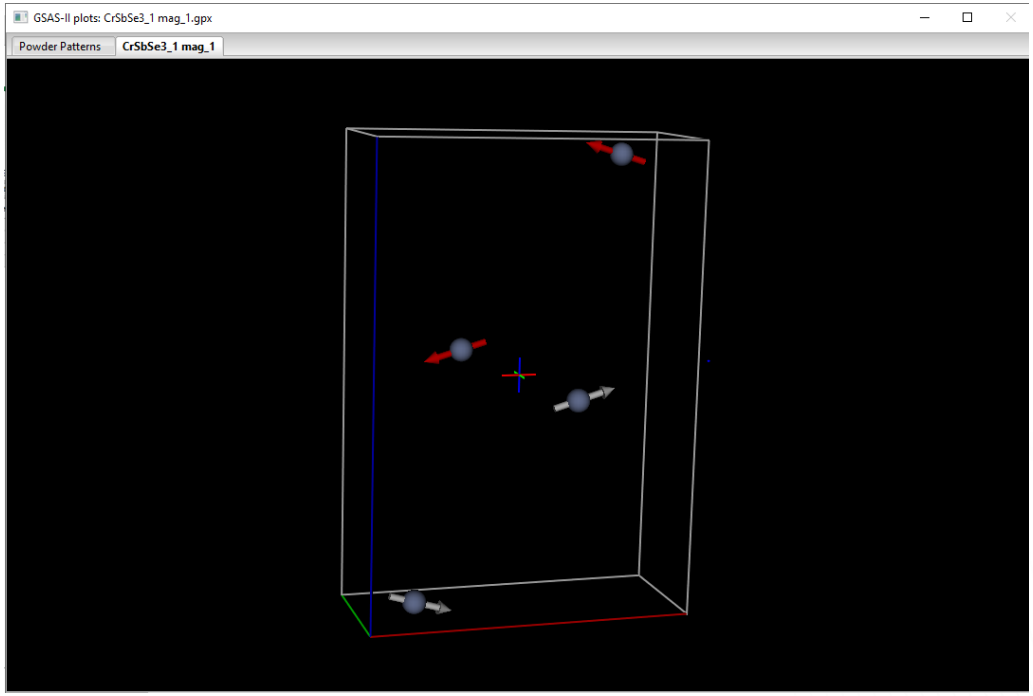
GSAS-II project: CrSbSe3_1 mag_1.gpx

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

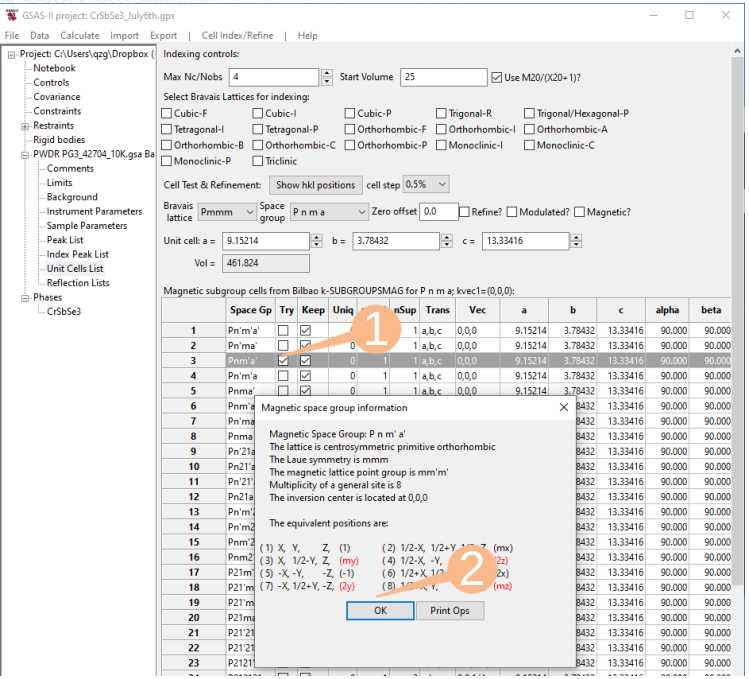
General | Data | Atoms | Draw Options | **Draw Atoms** | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

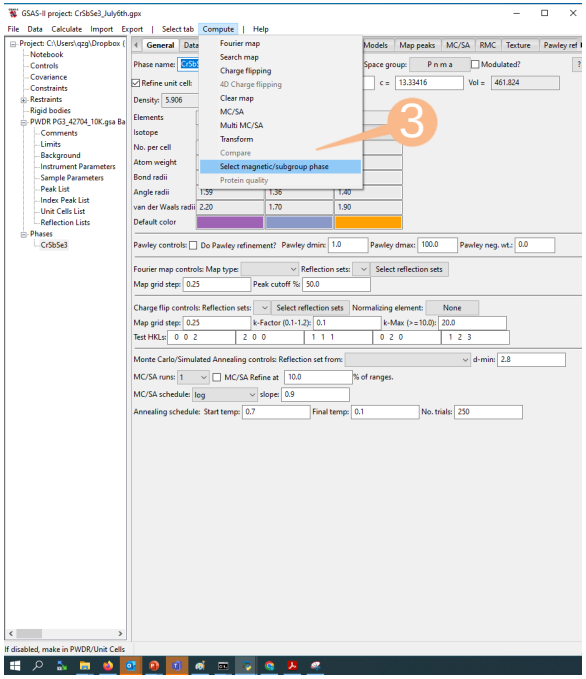
	Name	Type	x	y	z	Mx	My	Mz	Sym Op	Style	Label	Color	I/A
0	Cr1	Cr+3	0.15649	0.25000	0.04390	1.3911	0.0000	-0.4188	1	vdW balls			I
1	Cr1	Cr+3	0.34352	0.75000	0.54390	-1.3911	0.0000	-0.4188	2+0,0,0	vdW balls			I
2	Cr1	Cr+3	0.84352	0.75000	0.95610	-1.3911	-0.0000	0.4188	-1+1,1,1	vdW balls			I
3	Cr1	Cr+3	0.65648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

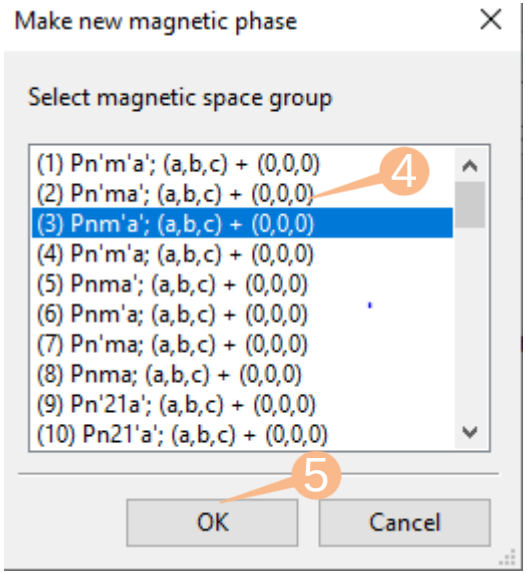


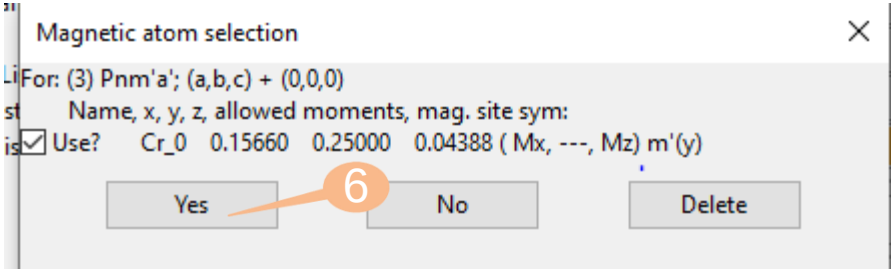
Canted AFM order with magnetic space group *Pn’m’a’* can be excluded.

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

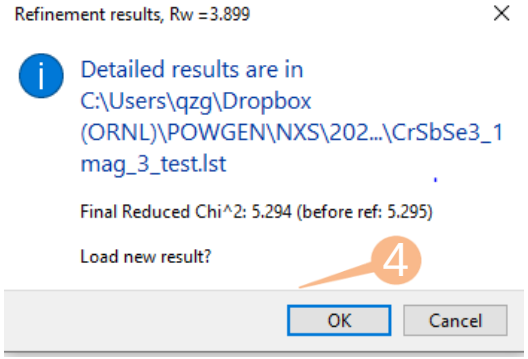
Project: C:\Users\qzg\Dropbox (
- Notebook
- Controls
- Covariance
- Constraints

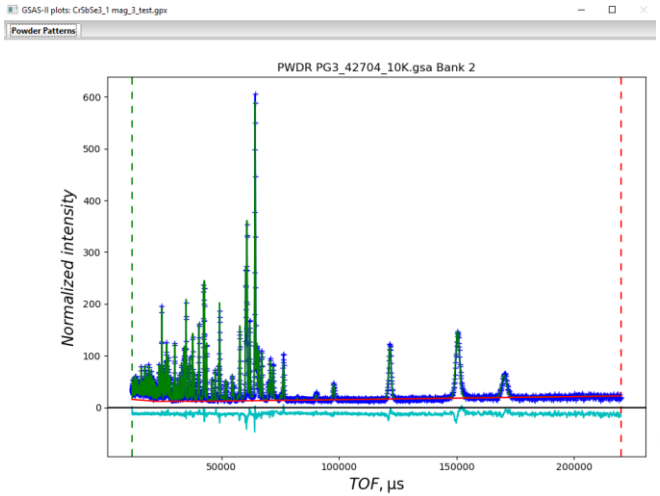
General | Data | **Atoms** | Draw Options | Draw Atoms | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

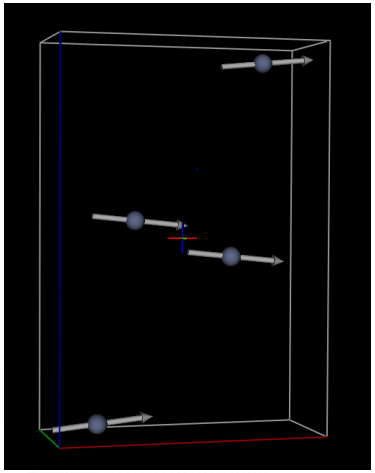
	Name	Type	re		y	z	frac	Mx	y	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15659	0.25000	0.04370	1.0000	1.0000		1.0000	m'(y)	4	I	0.00111

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

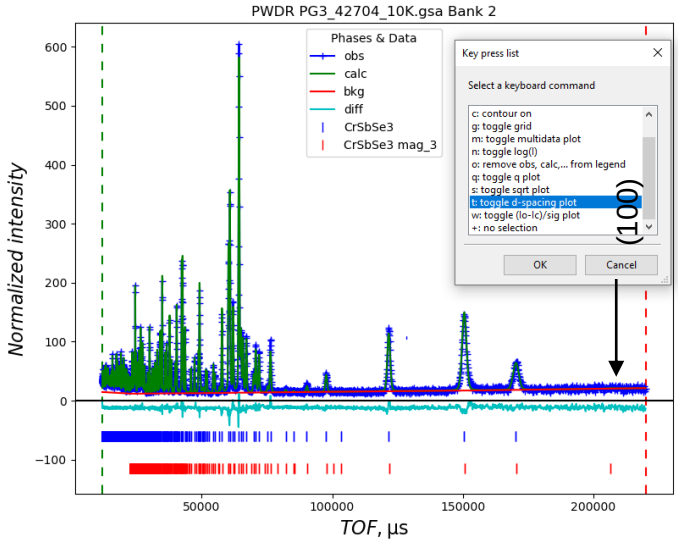
GSAS-II project: CrSbSe3_1 mag_3_test.gpx

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

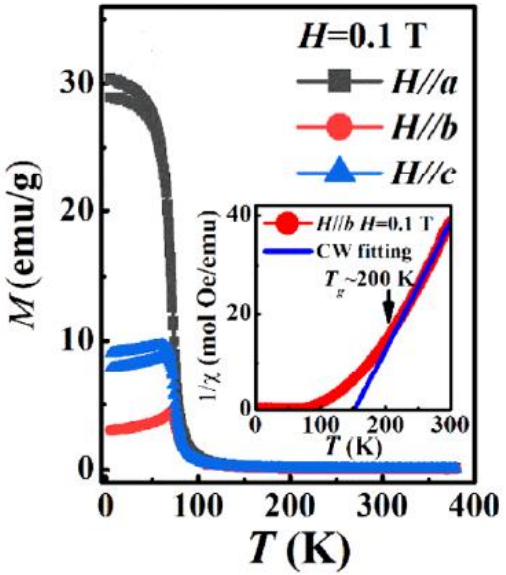
Project: C:\Users\qzg\Dropbox (
- Notebook
- Controls
- Covariance

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.



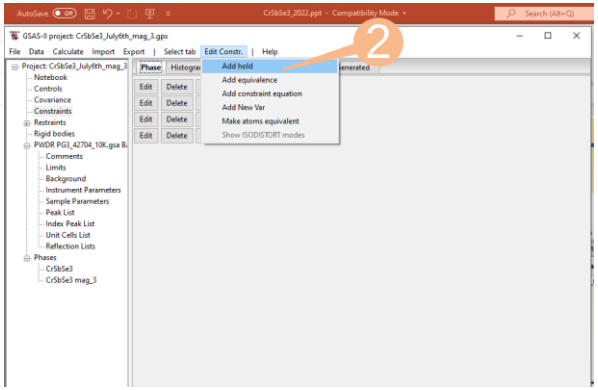
b. Highest magnetization with H//*a*: moment along the *a* axis.

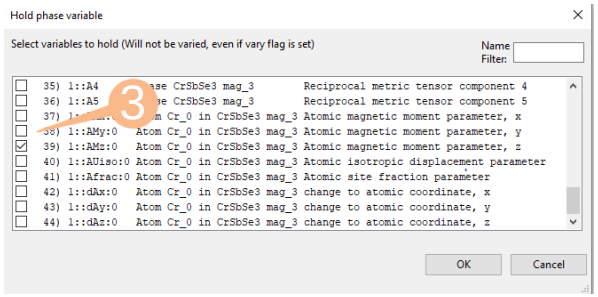
c. Similar refinement quality if Mz=0

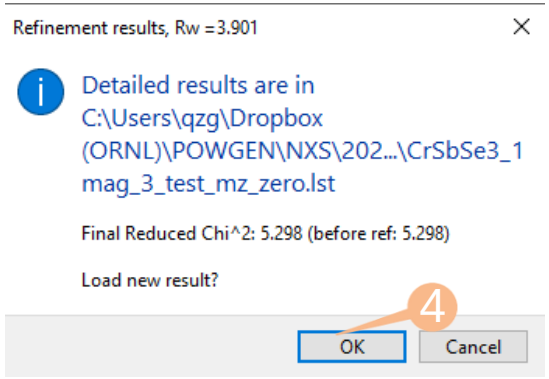
General | Data | **Atoms** | Draw Options | Draw Atoms | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

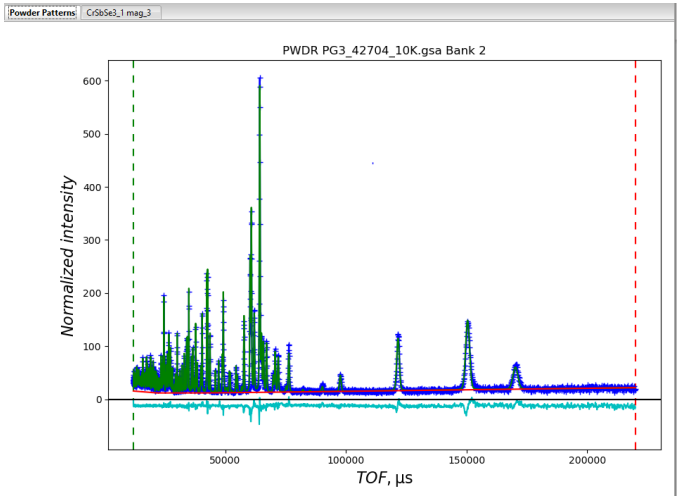
	Name	Type	refine	x	y	z	frac	Mx	Mz	site sym	mult	I/A	Uiso
0	Cr1	Cr+3	M	0.15649	0.25000	0.04390	1.0000	2.6214	0.0000	m'(y)	4	I	0.00176

1









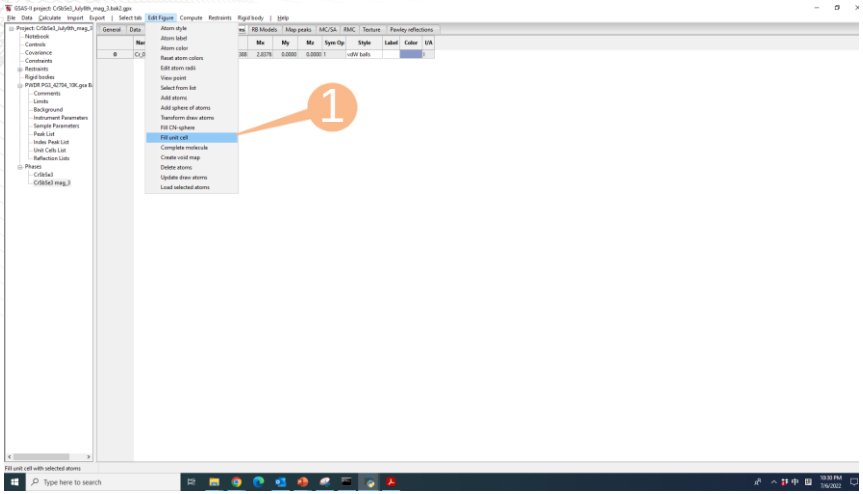
General | Data | **Atoms** | Draw Options | Draw Atoms | RB Models | Map peaks | MC/SA | RMC | Texture | Pawley reflections

	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

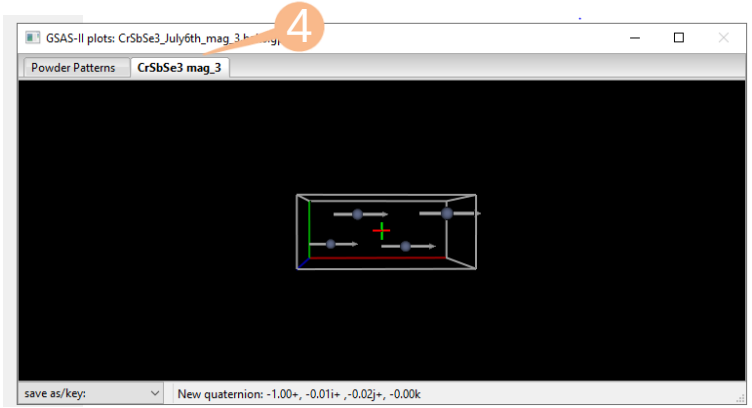
M=(2.64,0,0) μ_B

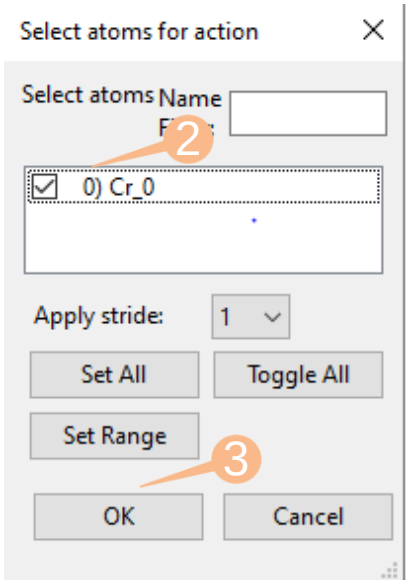
Visualizing the magnetic structure

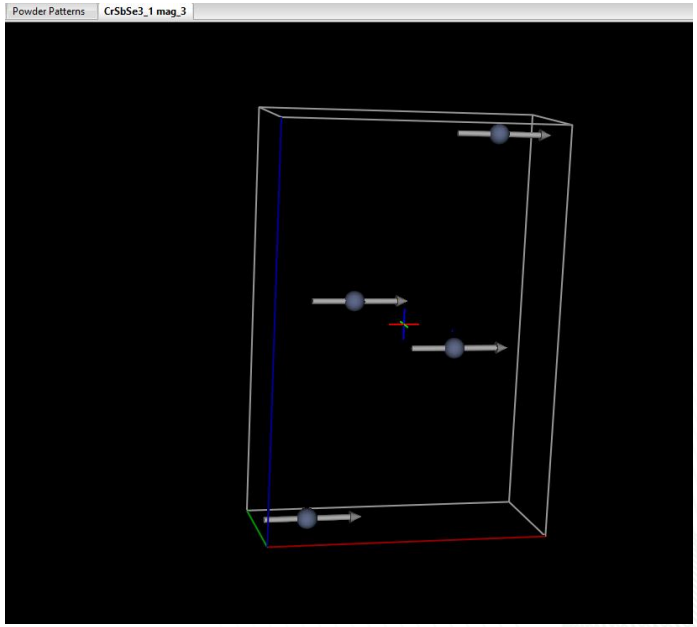
In “Draw Atoms” tab:



Ferromagnetic order



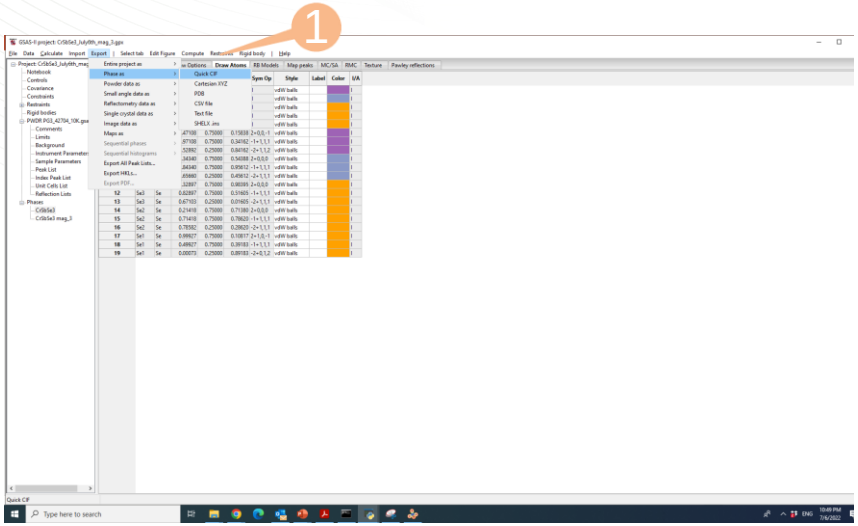


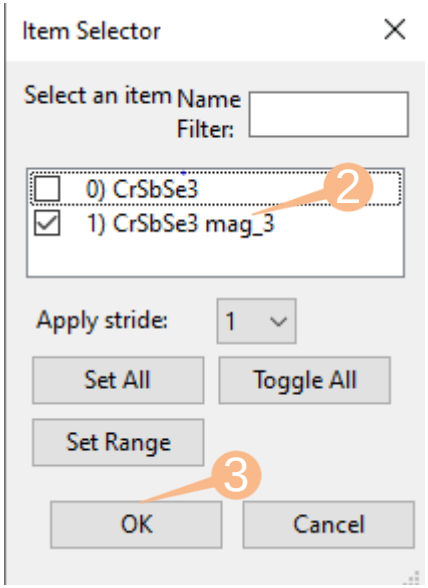


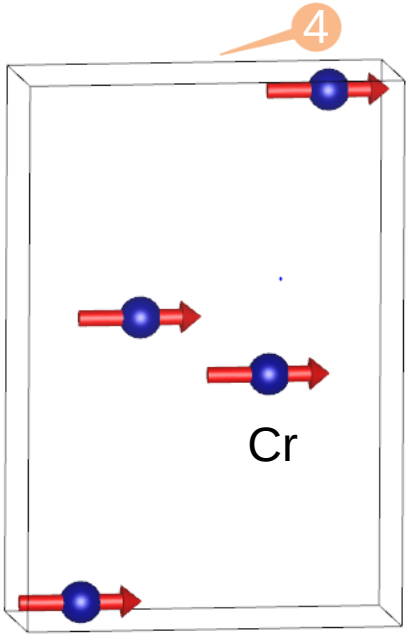
To publish the results

I. 3D magnetic structure

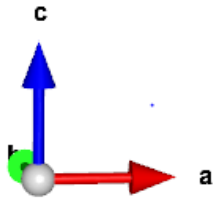
Export to cif file: Export- phase as- quick cif





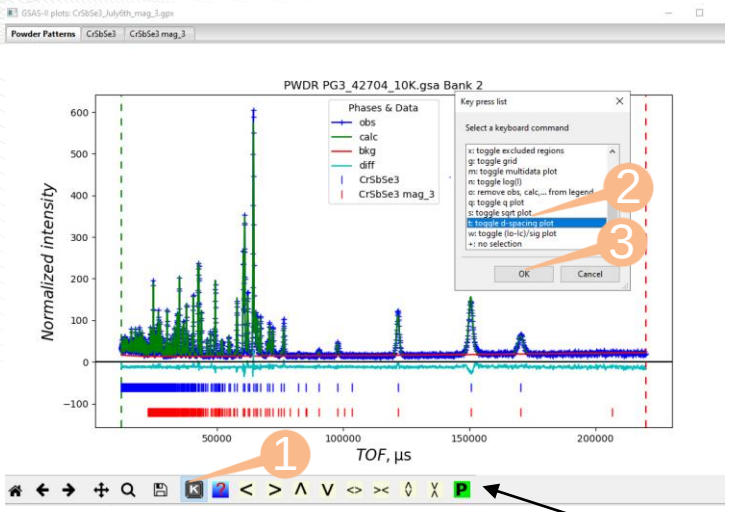


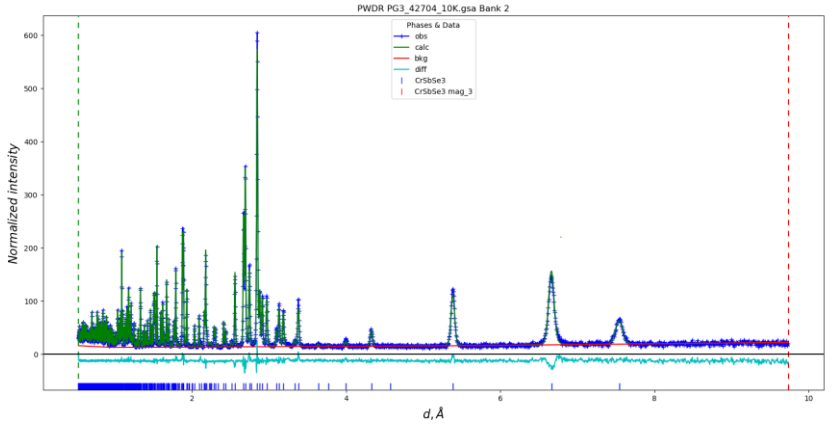
Use VESTA software (jp-minerals.org/vesta/en/download.html) to open it directly for publication:



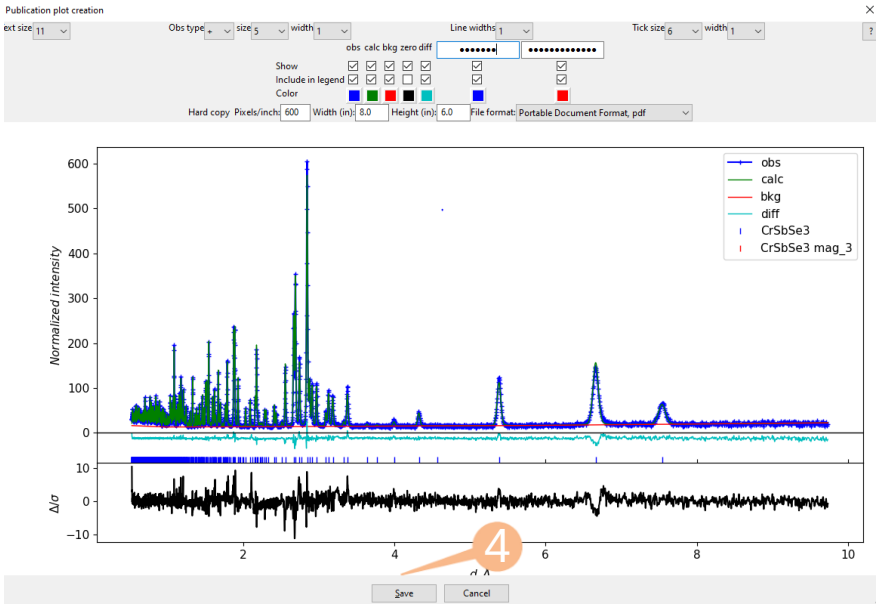
II. Refinement plots

Convert TOF to d





Click P button to open a new window



GSAS-II tutorial on crystal and commensurate magnetic structure

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

zhangq6@ornl.gov