

COMPUTATIONAL WORKFLOWS FOR LARGE DIFFRACTION DATASETS

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Abstract

This report documents the development of a .prm file for the ID4B beamline at CHESS, using previously measured powder patterns from CeO₂. There are some objectives of this project. First of all, learn how to model x-ray diffraction, starting from a description of the crystal structure (the information in a .cif file) and a description of an instrument (the information in a .prm file), using GSAS-II. Second, add automated GSAS-style analysis to existing python-based diffraction workflows for users of the ID4B beamline at CHESS. Finally, generate a technical memo that can be useful to train future remote users of the ID4B beamline for powder diffraction.

Introduction to Powder Diffraction

X-ray diffraction is a technique used for describing crystalline materials, including the atomic and molecular structure of a material. It gives information on determination of unit cell dimensions, on phases, structures, preferred crystal orientations. “XRD peaks are created by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample, where the peak positions are determined by the atomic position.”¹ The atoms in a crystal are positioned in a periodic array, that is why can diffract light. “The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal.”² Diffraction happens only at specific angles, those where Bragg’s Law is satisfied.

▪ Interference of waves

A *wave* can be described as a disturbance that travels through a medium from one location to another location. A wave usually carry energy from one point to another in the form of signals at a well-defined speed which depends on the characteristics of the medium. A *medium* is a substance

¹ <https://www.sciencedirect.com/topics/materials-science/x-ray-diffraction>

² <http://prism.mit.edu/xray/Basics%20of%20X-Ray%20Powder%20Diffraction.pdf>

or material that carries the wave from its source to other locations. Different kinds of waves have a different set of physical characteristics, which depend on the direction of energy and the orientation of particle motion.

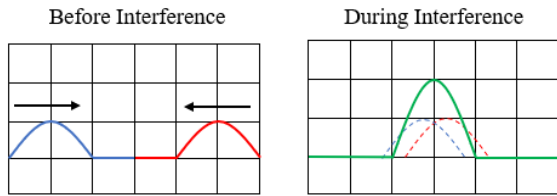


Figure 1: The diagrams illustrate the before and during interference snapshots of the medium for two such pulses. Two pulses moving toward one another experience interference.

In order to analyze the interference of two or more waves, we use the principle of *superposition*, which states that when two or more waves meet at a point, the resultant wave has a displacement which is the algebraic sum of the displacements of each wave.

- **Reflection of light**

Light is a wave in the electromagnetic field. X-rays are a label given to a particular band of the electromagnetic spectrum, where the wavelength is comparable to the size of atoms and the frequency is comparable to the energy that binds electrons to atomic nuclei.

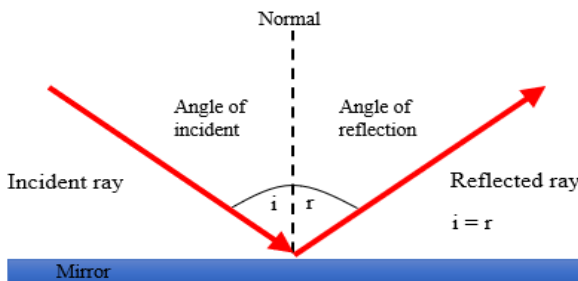


Figure 2: Light reflection happens when waves meet a surface that does not absorb radiation energy and repels the waves away from the surface, where the angle between the incident ray is equal to the reflected angle.

- **Bragg's Law**

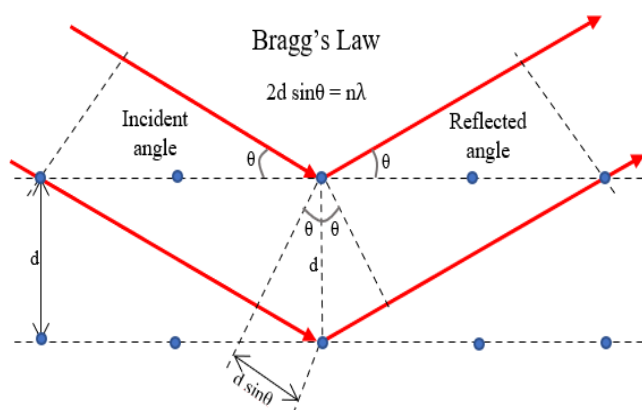
It is difficult to talk about powder diffraction much further without an understanding of Bragg's Law. Scientists have been using x-ray diffraction studies, explained by Bragg's Law, to identify the structures of crystals and molecules. Bragg's law defines the conditions necessary for constructive interference between waves scattered by regular planes of atoms inside a crystalline solid, where the planes are separated by some distance d . Bragg's Law was first proposed by

Lawrence Bragg and his father William Henry Bragg in 1913 in response to their discovery that crystalline solids produced surprising patterns of reflected X-rays.”³

“The law states that when the x-ray is incident onto a set of lattice planes, its angle of incidence, θ , will reflect back with a same angle of scattering, θ . And, when the path difference, d is equal to a whole number, n , of wavelength, a constructive interference will occur. The lower ray travels an additional length of $2d\sin\theta$.”⁴

Bragg's Law, expressed as:

$$2d \sin\theta = n\lambda$$



- d is the spacing of the crystal layers (path difference),
- θ is the incident angle (the angle between incident ray and the scatter plane),
- n is an integer,
- λ is the wavelength of the x-ray.

Figure 3: Bragg's Law reflection. “Two beams with identical wavelength and phase approach a crystalline solid and are scattered off two different atoms within it. The lower beam traverses an extra length of $2d\sin\theta$. Constructive interference occurs when this length is equal to an integer multiple of the wavelength of the radiation.”¹ When the total path difference $2d \sin\theta$ equals to $n\lambda$, diffraction occurs. Bragg's law allows for the structure of a crystal to be calculated based on the diffraction pattern of X-rays.

“When x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed which correspond to the following conditions: the angle of incidence equals to the angle of scattering; the pathlength difference is equal to an integer number of wavelengths.”⁵

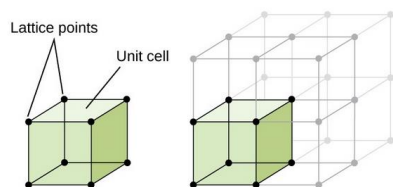
³ https://en.wikipedia.org/wiki/Bragg%27s_law

⁴ [https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_\(Analytical_Chemistry\)/Instrumental_Analysis/Diffraction_Scattering_Techniques/Bragg%27s_Law](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Instrumental_Analysis/Diffraction_Scattering_Techniques/Bragg%27s_Law)

⁵ <http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html>

▪ Crystallography

“*Crystallography* is the science that examines crystals, where crystallographers use the properties and inner structures of crystals to determine the arrangement of atoms and generate knowledge that is used by chemists, physicists, biologists, and others. Crystallographers use X-ray, neutron, and electron diffraction techniques to identify and characterize solid materials.”⁶ In crystallography, a *crystal structure* is an arrangement of atoms, ions, or molecules in a crystal, that are kept together in an ordered, three-dimensional arrangement. It describes the shape of the unit cell. A *crystal* is a solid material whose atoms or group of atoms that are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. Each unit cell is the smallest repeating portion of a crystal lattice. It can be considered as the building block of a crystal that has the same symmetry as the entire crystal. A *crystal lattice* is the arrangement of these atoms, or groups of atoms, in a crystal.



The figure illustrates the crystalline structure that are constructed from repeated arrangements of atoms. It shows the relationship of a unit cell, the smallest repeating unit of a crystal lattice, to the entire crystal lattice.

Figure 4: (from <https://www.askiitians.com/iit-jee-Solid-State/crystal-lattices-and-unit-cells.html>)

When you deal with crystalline materials it is important to specify a crystallographic direction, a line between two points or a vector, within a unit cell. Crystal planes come from the structures known as *crystal lattices*. Crystallographic planes are specified by three *Miller Indices* (hkl), a set of numbers that may be used to identify the plane or surface. A *powder* is a collection of small crystals, or grains, each in a random orientation with respect to the other grains. The *peaks* in the diffraction, "spots" for a single crystal, get smeared out into rings of scattering, with only the scattering Bragg angle (related to d-spacing) remaining well defined. So, a 2D detector will collect a series of rings, all with the same center, and the radius of these rings tells us the spacing between planes of atoms inside the grains of the material we are studying.

⁶ <https://www.acs.org/content/acs/en/careers/college-to-career/chemistry-careers/cystallography.html>

Introduction to GSAS II

“The General Structure Analysis System (GSAS-II) package provides materials and crystallographic analysis for all types of diffraction data. It was initially made available with very limited capabilities, but over much of the last decade the features have been expanded, so that GSAS-II is now a comprehensive tool for nearly all types of structural and material characterization studies. The need to provide materials to teach use of GSAS-II, while the software has been undergoing constant revision and expansion, has required new approaches for documentation. This has included providing tutorials, as each major new capability has been added, and context-sensitive help for each section of the program. Video versions of tutorials were created with animated graphics that make GSAS-II easier to learn and use. GSAS-II provides comprehensive data analysis capabilities for powder and single-crystal diffraction from all types of instruments, including laboratory, synchrotron, and both constant-wavelength and time-of-flight neutron sources.”⁷



Figure 5: Figure illustrates three windows when GSAS-II starts. The window on the right is *Data Window* which has a vertical divider. The left side will contain information about your GSAS-II project as you add data, phases, etc. The right side will contain a display of data depending on your tree item selection, where you can change many of the items in this display depending on how you wish to use GSAS-II. The window in the middle is labeled *GSASII Plots*. This will contain tabbed graphical displays (this may be a crystal structure, powder pattern plot). The third window is the *GSAS-II console*. It will display error messages, some results of calculations.

⁷ http://onlinedigeditions.com/publication/?i=604118&article_id=3435824&view=articleBrowser

Method

▪ 2D detector calibration and integration

In this section, we used CeO₂ a known "standard" material, to calibrate GSAS-II with powder diffraction data collected at the QM2 beamline at CHESS. This data was collected using the large format Pilatus3 6M area detector, with a high-energy undulator x-ray beam. The x-ray wavelength was 0.23843 Angstroms. The distance from sample to detector was about 798 mm. First, we must load a TIF image file to read the data file into the current GSAS-II project. The next step was to edit image parameters, that were added manually. I changed the Max intensity to 50 to make many powder diffraction rings visible above the low background.

The blue X, that you can see inside of the innermost circle in the image below, marks the *beam location*, location where GSAS expects that the beam would strike the detector, if it were not occluded by a tungsten beam stop. In the image below the wavelength was changed to 0.23843 Angstroms, a distance from sample to detector was changed to 798 mm, the *Min calib d-spacing* was changed to 0.7, and CeO₂ SRM674b was set as the material used. These parameters were known, but if they had not been, they could have been refined by GSAS when performing a least-squares fit of the measured pattern. Indeed, after refining, we will discover that the distance is not quite 787mm. Still, it is helpful to give the program a set of starting values which are as close as possible to the truth.

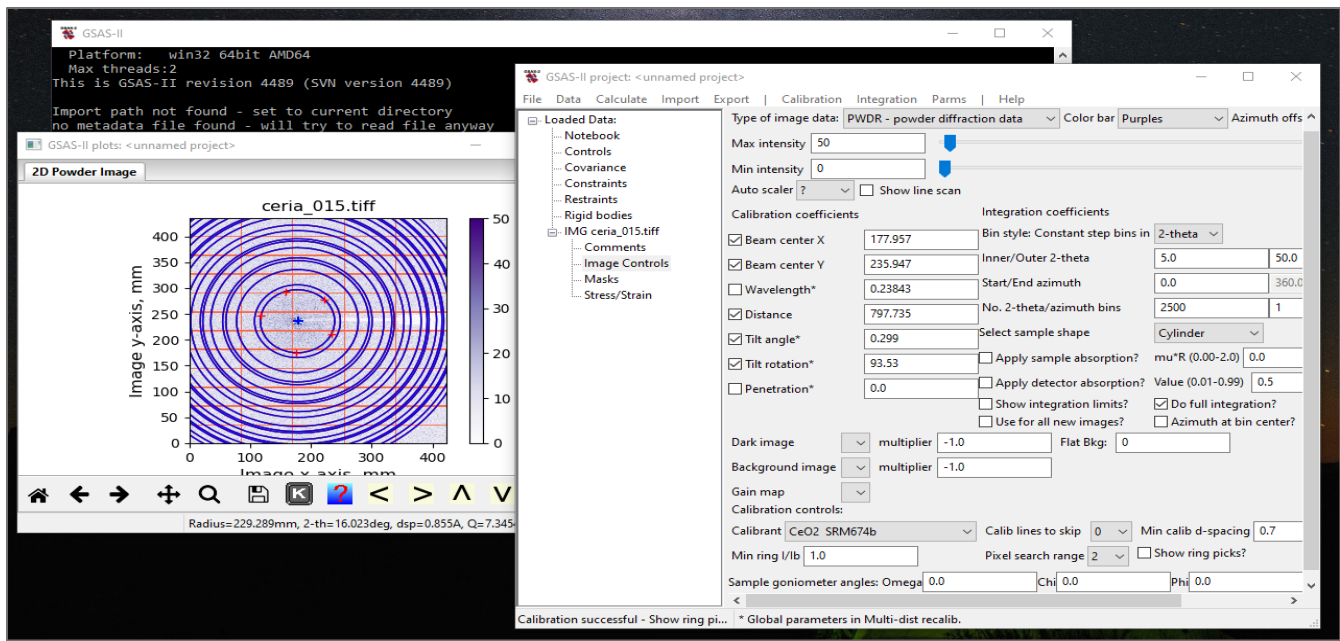


Image 6: This image demonstrates GSAS-II Plots window on the left (contains 2D pattern of a CeO₂ SRM674b powder sample) and Data window on the right (contains all the important data which was measured at the Cornell High Energy Synchrotron Source (CHESS), Ithaca, NY).

To calibrate, using the left mouse button we click on at five locations on the innermost ring, where the points were defined and added to the plot. Note that, you should press the right mouse button well away from the points to perform the calibration. After it is done, select the *Masks* GSAS-II data tree item, change the *Lower/Upper thresholds* to 0 (because the detector uses negative numbers to represent pixels that are not working well) and 20,000 (because it is well above the average count rate observed on the brightest powder ring, and therefore only artifact pixels will read numbers above this).

Enter a frame by pressing the F key and select each corner of the image by pressing on the left mouse button, then close the frame by pressing on the right mouse button. The frame defines the calibration region. Calibration tries to match a calculated set of rings for CeO₂ to the intense rings in your measured data. It varies the position if the detector in real space to get the best fit. If you want, you can change which parameters it can vary by clicking different check boxes. In this example, we allowed distance to vary, but not wavelength. You can also choose a minimum d-spacing (which is equivalent to a maximum scattering angle) for the calibration.

After that go back to the Image controls menu item and recalibrate to get better results. In a case if you want to save a copy of the calibration values, you need to use *Parms/Save Controls*. Notice that several values have changed in the new figure. Calibration found a more accurate distance and determined that the detector was slightly tilted (so the beam is not quite at normal incidence).

After the Calibration of an area detector was performed, we can integrate area detector data into a 1D histogram of intensity vs scattering angle. Before I running the last integration cycle, it is important to adjust the inner and outer 2-theta values with the Inner 2-theta and Outer 2-theta controls and to click on the *Do full integration?* check box and *Show integration limits?* check box. Finally, start the integration.

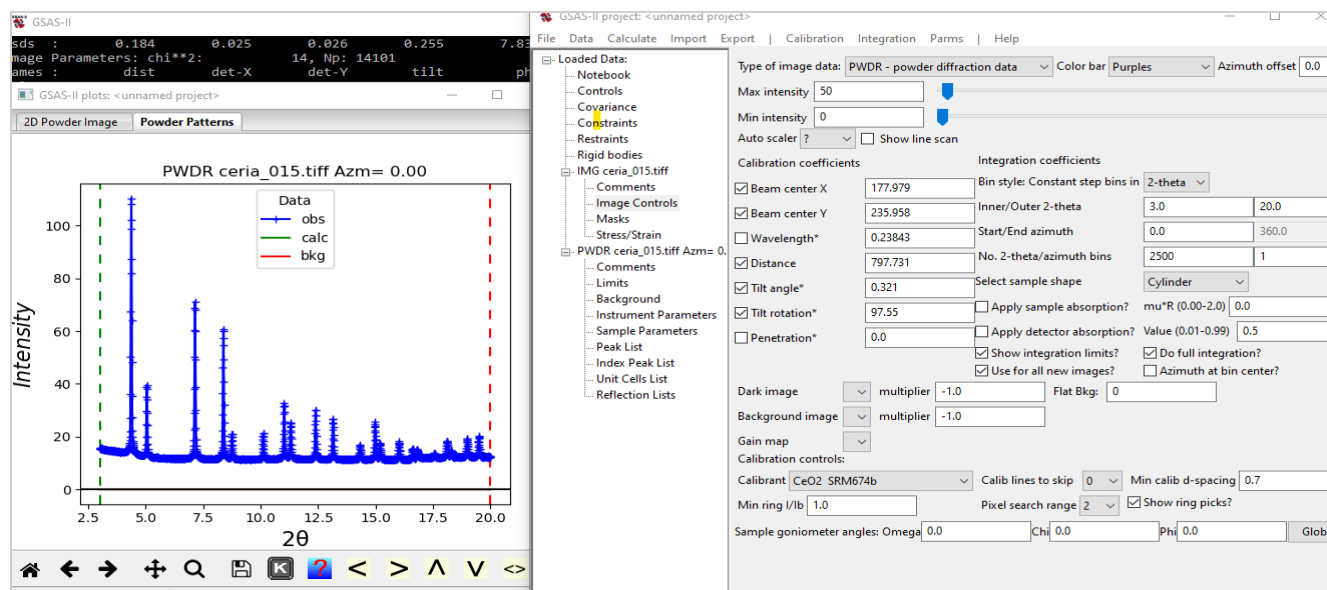


Image 7: This image illustrates GSAS-II Plots window (on the left) that contains the x-ray powder diffraction patterns of CeO₂.

▪ Fitting 1D histograms and instrument parameters

After I performed 2D calibration and integration of the x-ray powder diffraction patterns of CeO₂, we can select individual powder diffraction peaks, fit them, and then index to determine the crystal lattice and possible space group. The powder pattern from the image above has a lot more data that I need, that is why I need to cut down the range by using *Limits*, where I change *Tmin* to 4, and *Tmax* to 27,5. I need to determine manually all the peaks position between the limits by clicking on the *Peak List* item first. The plot window will show all peaks were picked

with a blue vertical line on each one. At this point it is wise to zoom in on the data that will be used for indexing.

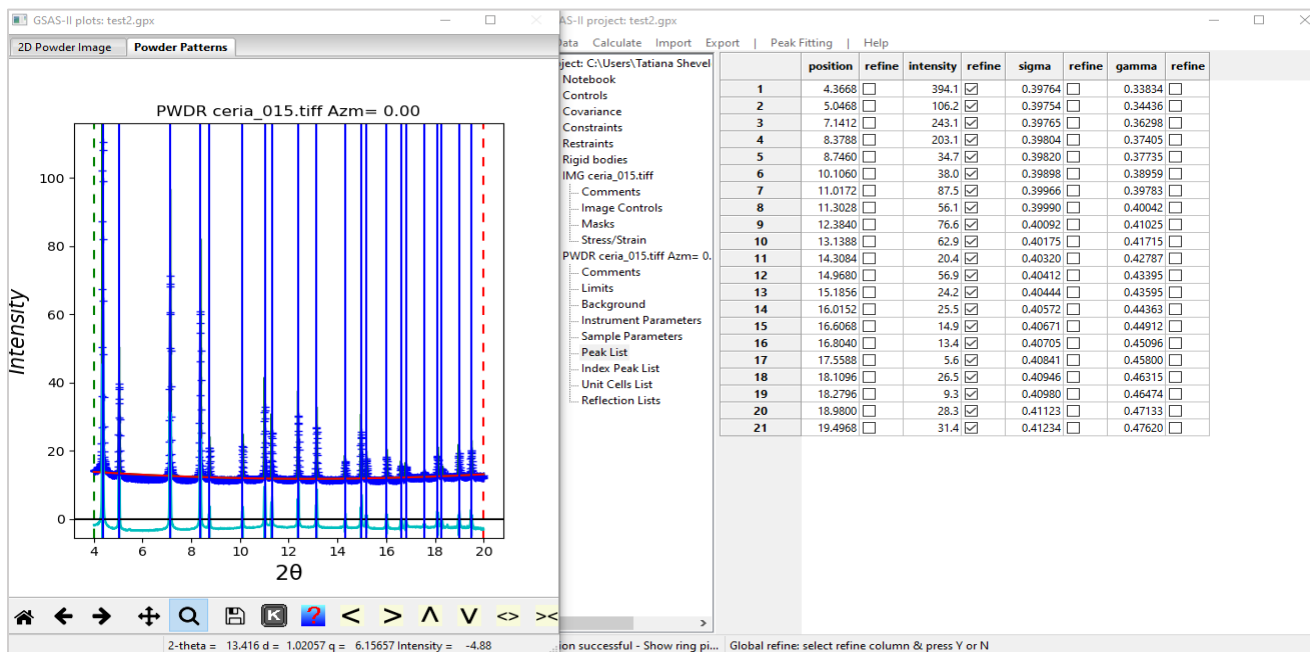


Image 8: It illustrates the Plot window that shows all peaks were picked with a blue vertical line on each one.

In the next process, that includes several steps, I need to refine peak positions.

- Refine the peak intensities and the background by using the menu item *Peak Fitting/Peakfit* and choose a suitable name.
- Add refinement of the peak positions by highlighting the entire column *Refine/Y-vary all*. Next, repeat the refinement using the *Peak Fitting/Peakfit* menu item. Select peak widths for refinement. I click on the *Instrument parameters* item in the data tree, then select U, V, W, X, Y. Then, repeat the refinement using the *Peak Fitting/Peakfit* menu item. GSAS-II assumes a convolution of Gaussian and Lorentzian line shapes for diffraction peaks. Varying these 5 parameters allows significant freedom to match the observed scattering shape, which is determined by the details of the instrument resolution.

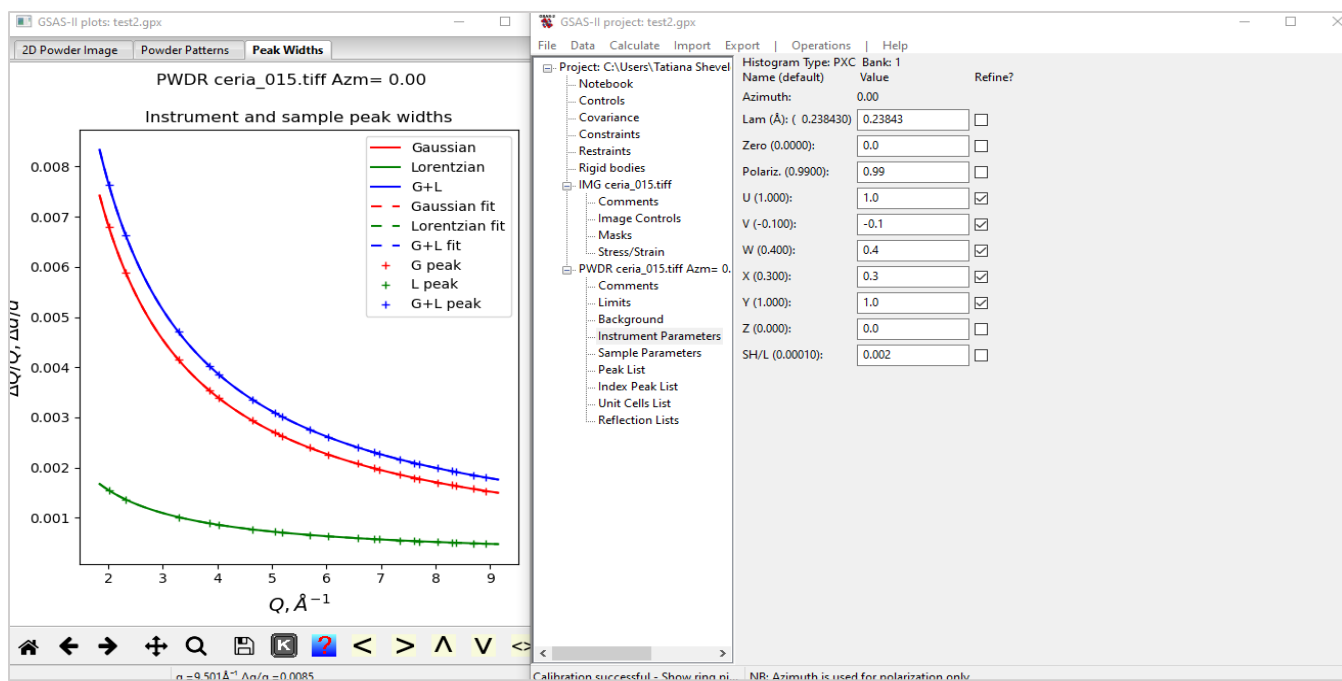


Image 9: The plot window shows “the resolution curves corresponding to the values of the Gaussian U, V, W, Lorentzian X & Y coefficients; ‘+’ marks show the individual values based on the sig & gam values for the peaks in Peak List. Select the refine flag checkbox for Gaussian U, V, W, and Lorentzian X, Y.”⁸

- Refine sigma & gamma individual peaks. To do this, I click on the refinement flags (for both sigma and gamma), then click on the *Y-vary all*. Then, repeat the refinement again.

Prepare *Indexing Peak List* by going to the *Index Peak List//Operations//Load/Reload* to copy the fitted peaks from the peak list. Then I need to *Run autoindexing* by clicking on the Unit Cell List data item, where I need to select *Cubic F*, since CeO₂ has a face-centered cubic crystal structure, after click on the *Cell Index/Refine//Index Cell*.

⁸ <https://subversion.xray.aps.anl.gov/Tutorials/FitPeaks/Fit%20Peaks.htm/pyGSAS/>

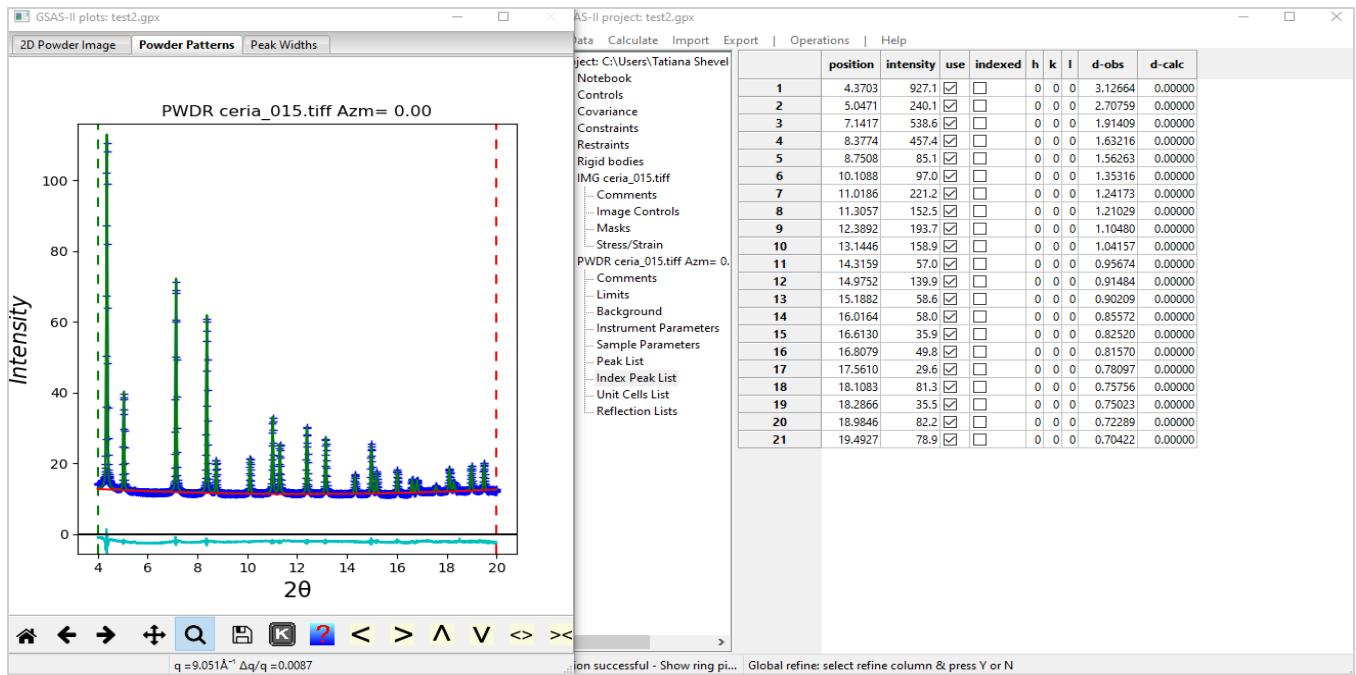


Image 10: It illustrates the console that shows a running list of possible cells as they are found.

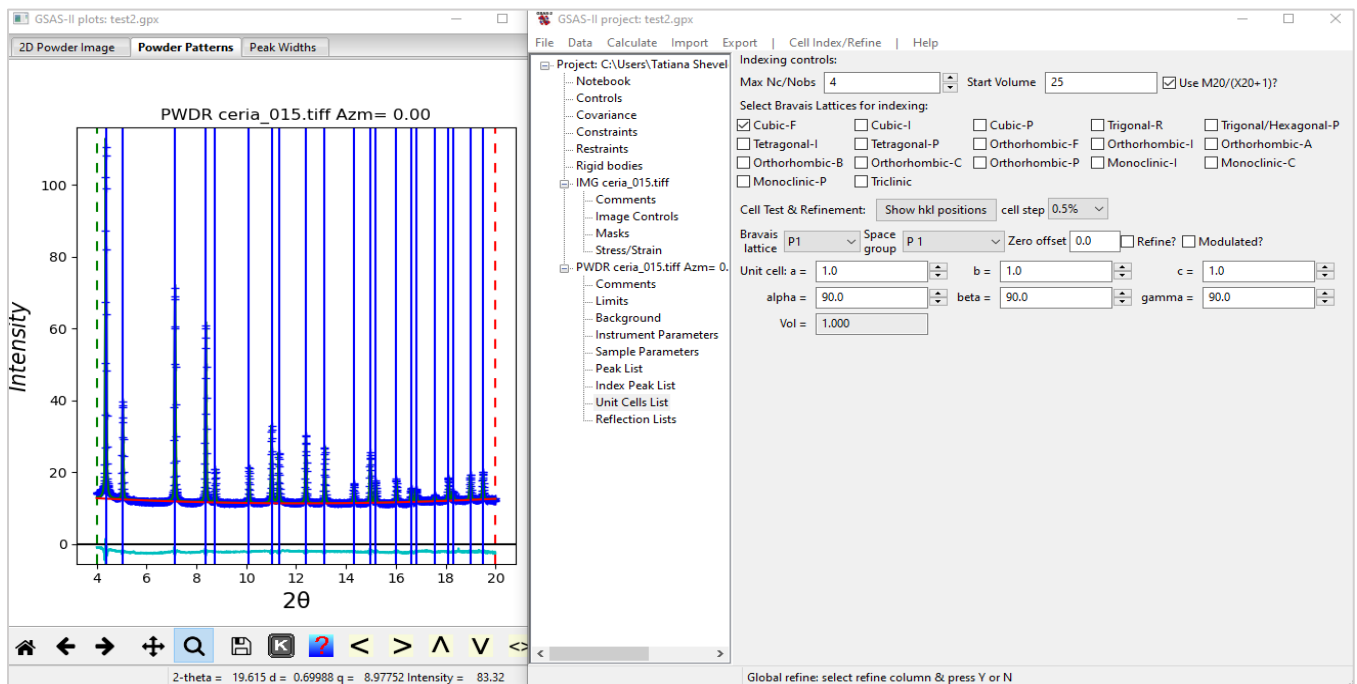


Image 11: This image illustrates a window for indexing and cell refinement options.

Finally, I need to *Select/Refine Cell*, where I should Import the cell information using the *Cell Index/Refine/Copy Cell* menu option. Then optimize the cell by refining the lattice parameters and the two-theta zero: click on the *Refine?* checkbox next to the Zero offset value and then the *Cell Index/Refine/Refine Cell* menu option. In the final step I need to create a *.prm file*, a parameter file used in programming that stores data parameters with descriptions.

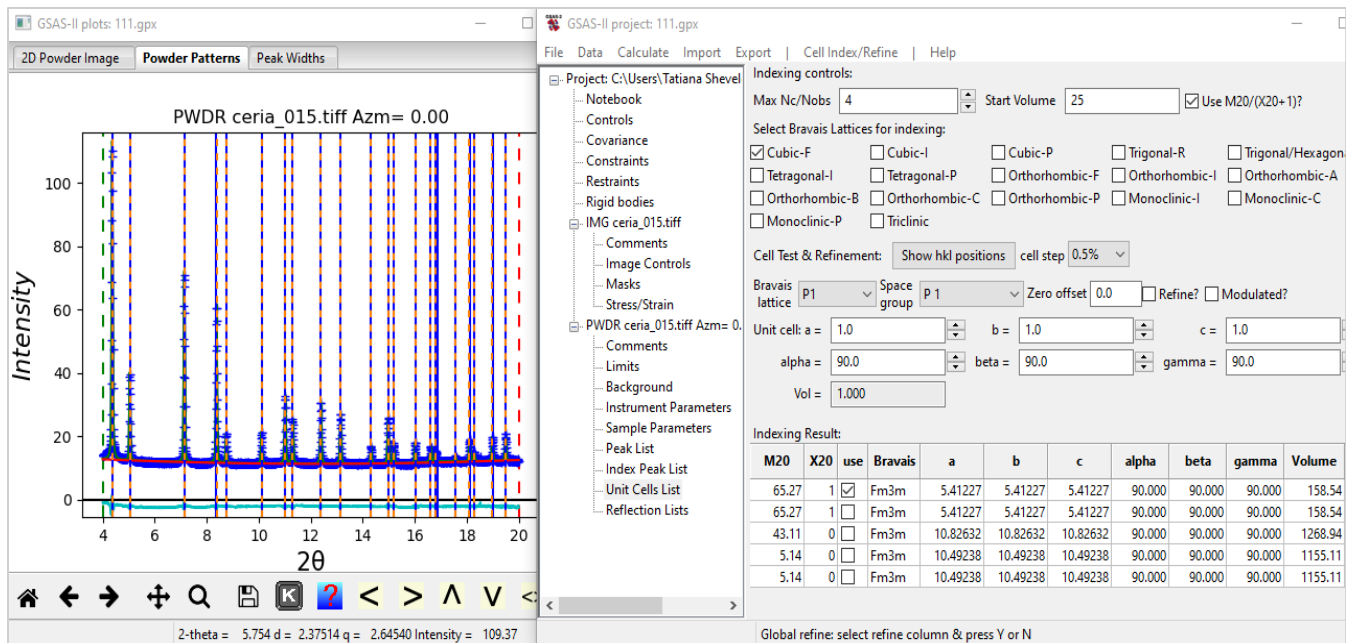


Image 12: This image illustrates the real cell for CeO₂ is known to have a lattice constant of 5.412 Angstroms. Here, we can tell that the selected cell is correct.

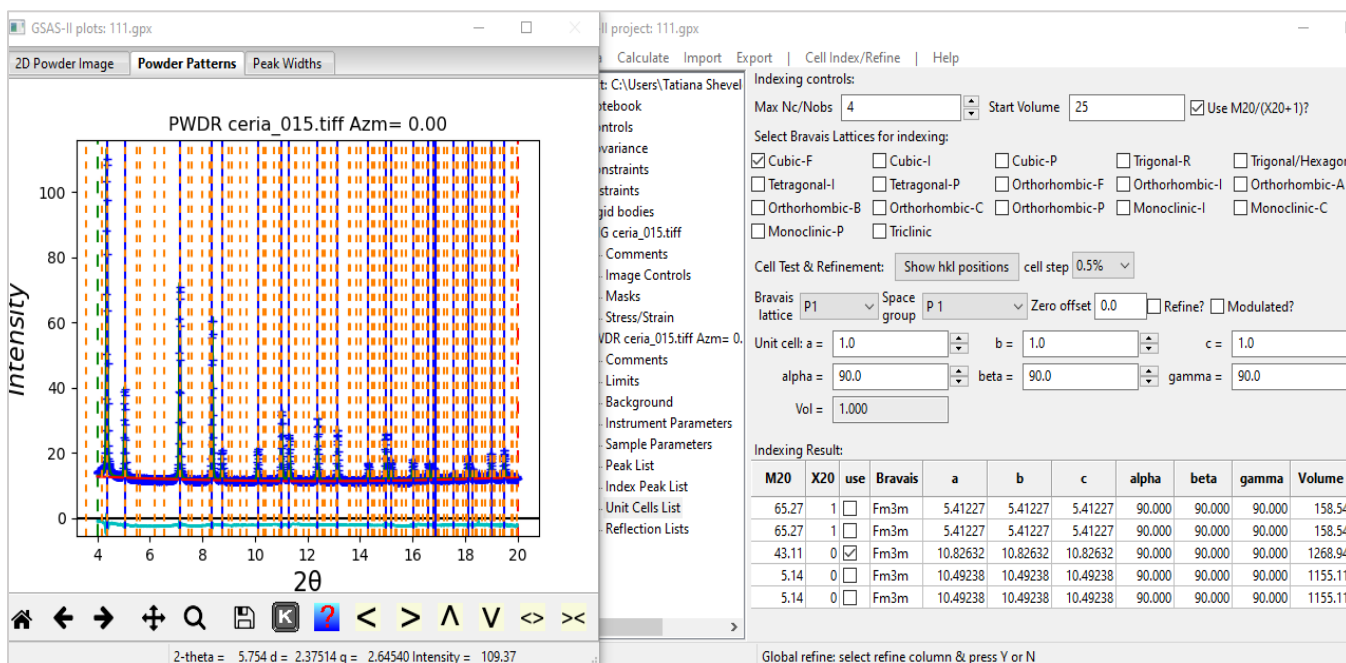


Image 13: This image illustrates (on the left) the peaks we selected marked in blue, and the peaks that GSAS calculates based on the refined cell in orange. Here, we can tell that the selected cell (with lattice constant 10.82 Angstroms) is not correct, because GSAS predicts several peaks that are not observed.

• Python script for CeO₂

Now that we have defined an instrument parameter file for the ID4B beamline, we are able to use GSAS-II to simulate what the scattering would look like, for any material that we have a .cif file for. While it is possible to do this using the GSAS-II GUI, we decided to write a simple python script to simulate powder diffraction for any material on ID4B, using the python API. The script is included here, along with a simulation of CeO₂.

```
import os,sys
sys.path.insert(0,os.path.expanduser("/Users/bryan/gsas2full/GSASII/"))
import GSASIIscriptable as G2sc
import matplotlib.pyplot as plt
%matplotlib notebook
gpx = G2sc.G2Project(newgpx='MyProjectName.gpx') # create a project
# step 1, add a phase to the project
phase0 = gpx.add_phase("ceria.cif",phasename="ceria",fmthint='CIF')
# step 2, link a simulated histogram to the phase (name,prm,min,max,step,phase)
hist1 = gpx.add_simulated_powder_histogram("ceo2 sim","ceo2.instprm",5.,120.,0.01,phases=gpx.phases())
# Step 3: Set the scale factor to adjust the y scale
hist1.SampleParameters['Scale'][0] = 1000000.
# step 4, compute: turn off parameter optimization and calculate pattern
gpx.data['Controls']['data']['max cyc'] = 0 # refinement not needed
gpx.do_refinements([{}])
gpx.save()
# step 5, retrieve results & plot
plt.figure()
x = gpx.histogram(0).getdata('x')
y = gpx.histogram(0).getdata('ycalc')
import matplotlib.pyplot as plt
plt.plot(x,y)
plt.show()
```

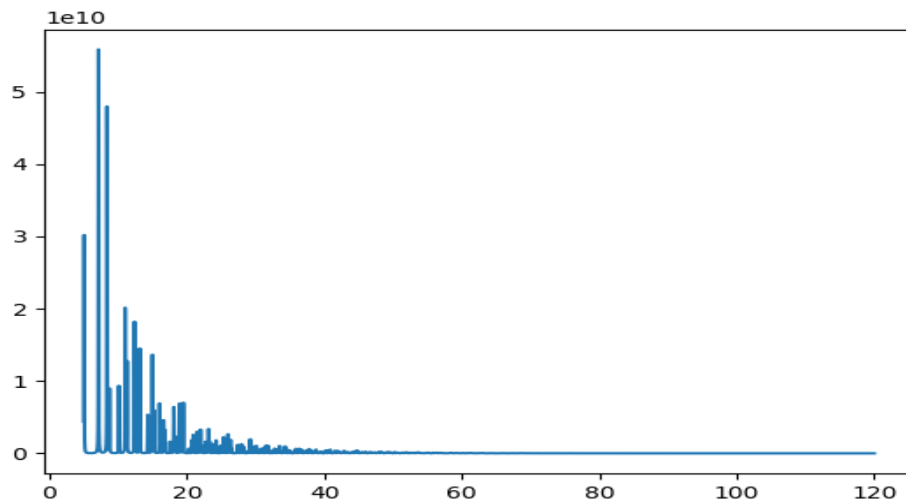


Image 14: This image illustrates a histogram for CeO₂ created in Jupyter Notebook.

Summary

This document is an instructional guide in the use of 2D Image Processing (including 2D detector calibration and integration, using powder X-ray diffraction (XRD)) and Fitting 1D histograms and instrument parameters. The General Structure Analysis System (GSAS-II) program was used to generate a .prm file for the ID4B beamline at CHESS, using previously measured powder patterns from CeO₂.

Acknowledgments

I would like to thank my mentor, Jacob Ruff for providing continuous guidance in every step of the process. Special thanks to the Cornell High Energy Synchrotron Source for supporting the summer research for community college students (SRCCS).