Workflow in Neutron TOF Data Reduction for Modulated Crystals

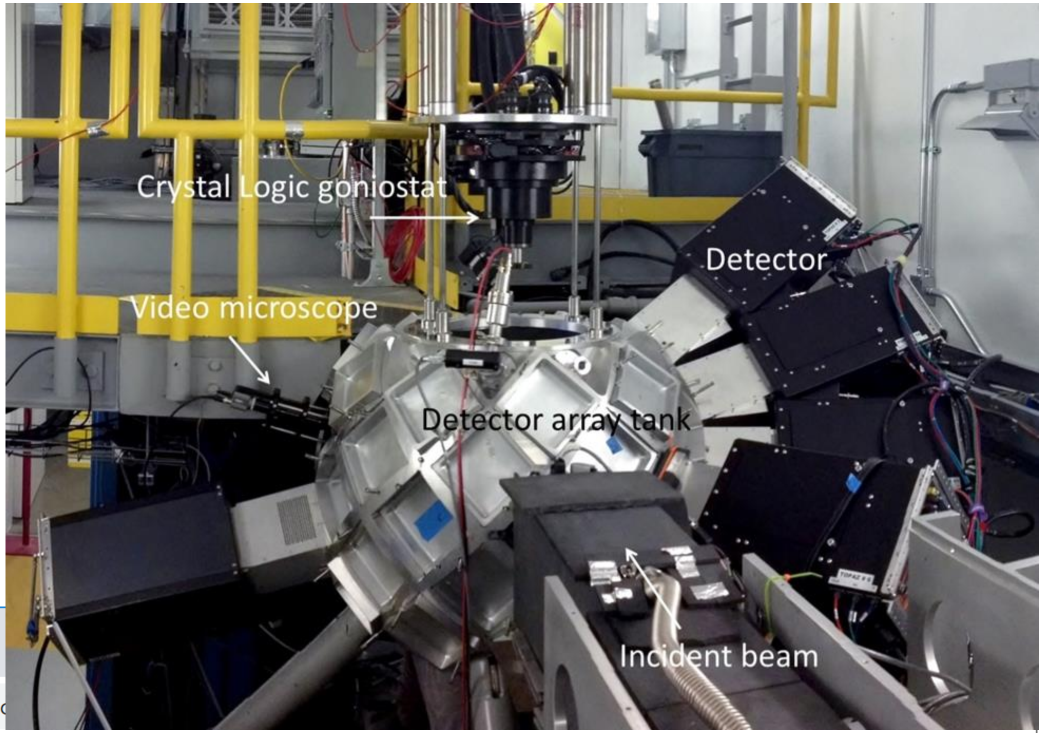
Shiyun Jin

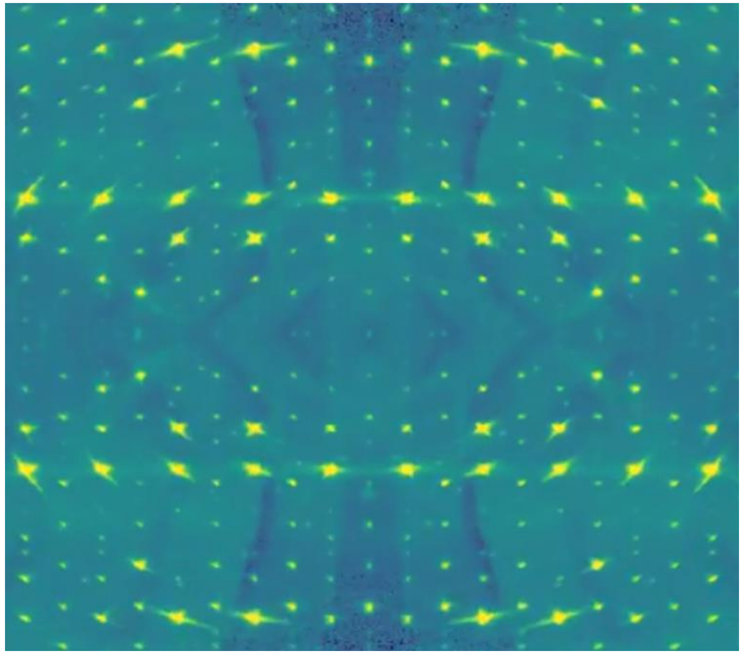
University of Wisconsin-Madison

Acknowledgement

- Graduate Opportunity "GO!" Program at ORNL
- Dr. Xiaoping Wang
- Ms. Vickie E. Lynch
- TOPAZ team at the SNS

J. Appl. Cryst. **47**, 915 (2014)



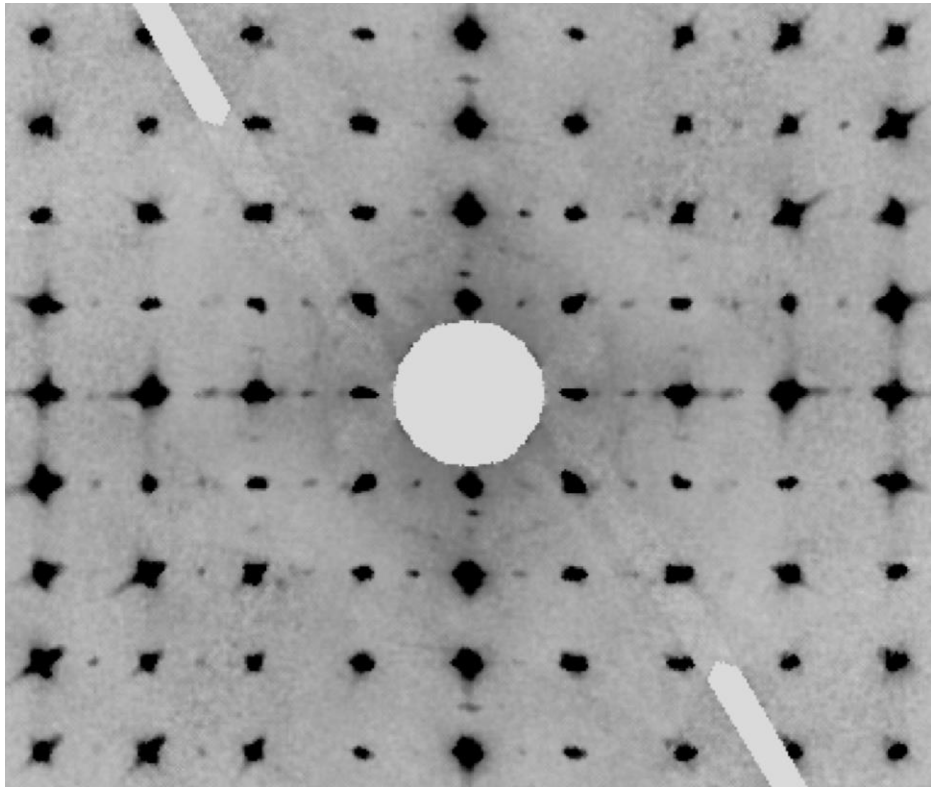


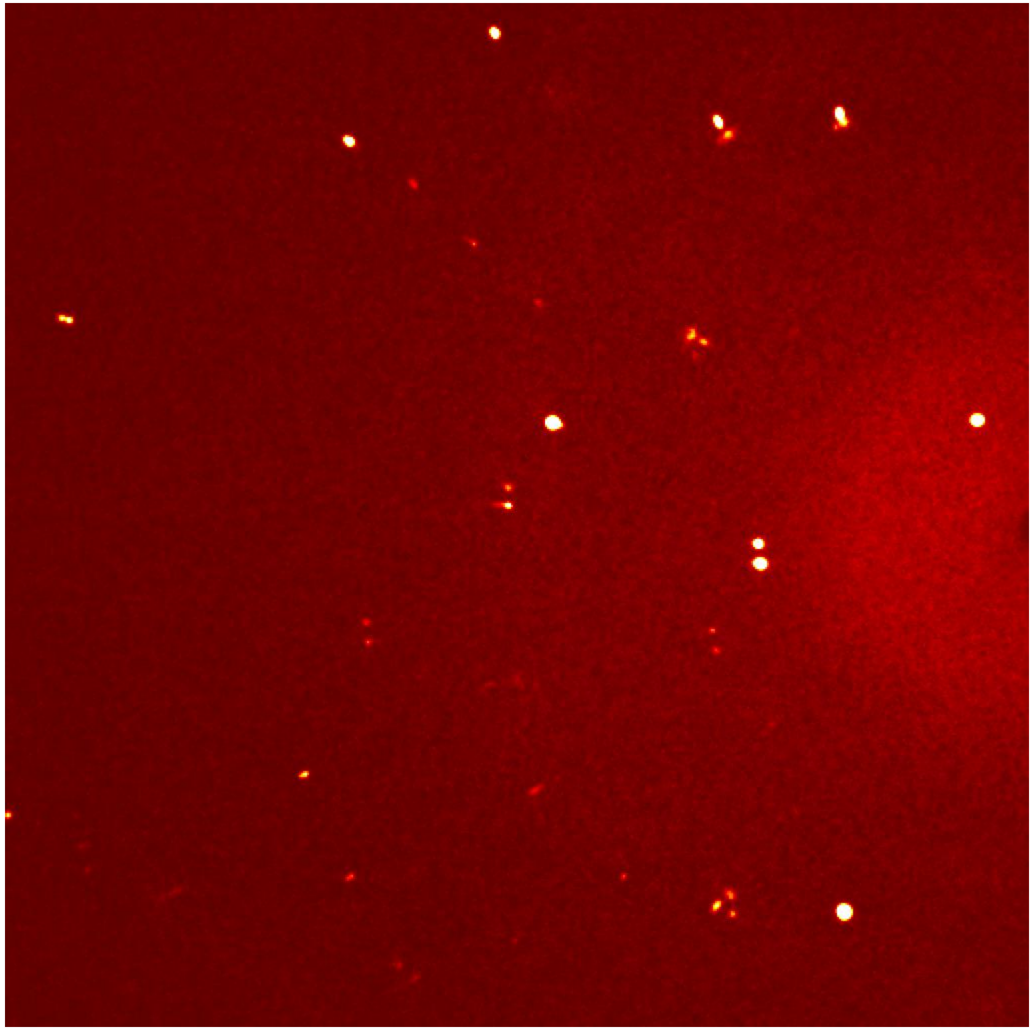
https://neutrons.ornl.gov/topaz

OAK RIDGE National Laboratory | HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE

Single-Crystal Diffraction Experiment

- X-ray diffraction
  - Series of 2D slices
  - Distance, 2θ, ω, φ, χ, λ (Monochromatic)



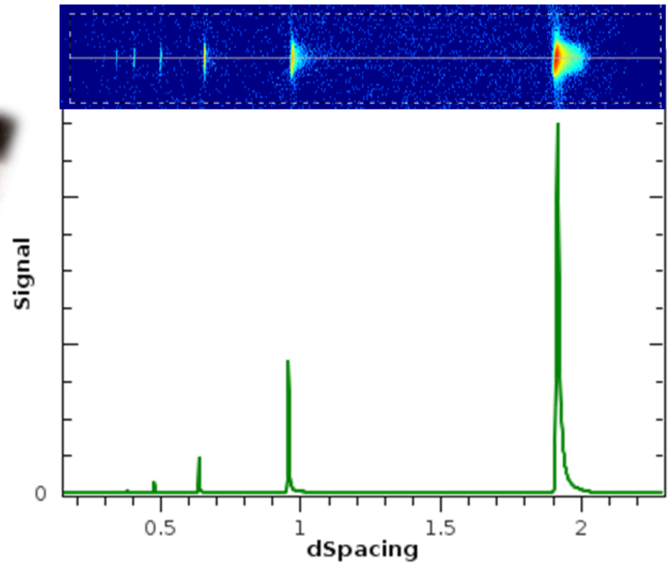


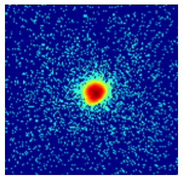
Single-Crystal Diffraction Experiment

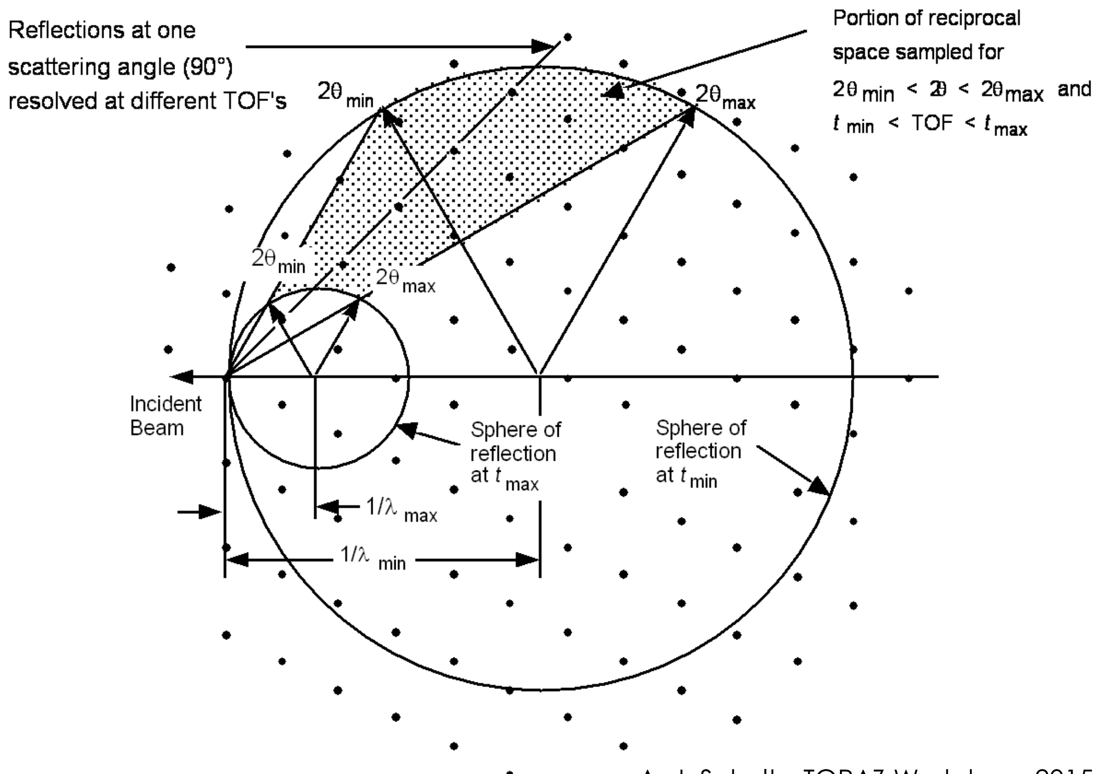
- Neutron TOF Laue diffraction
  - 3D detector
  - TOF Laue diffraction: x, *y*, TOF(*t* or λ)

de Broglie Equation $\lambda = \dfrac{h}{mv} = \dfrac{ht}{m(L_1 + l_2)}$

Anger Camera







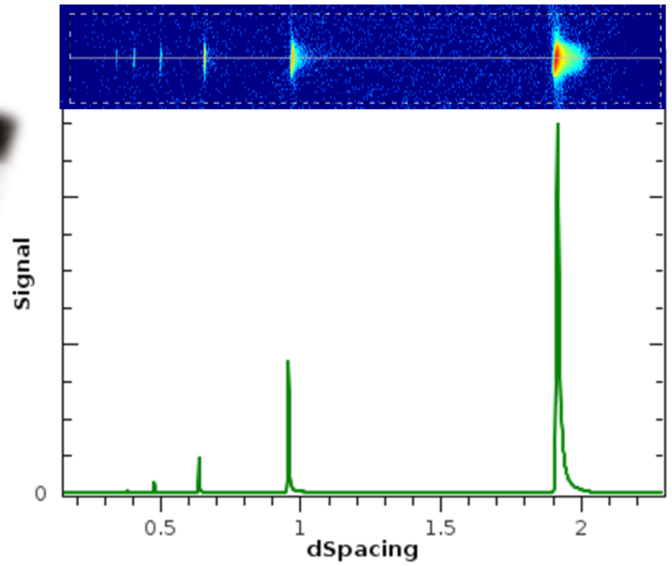
A. J. Schultz, TOPAZ Workshop, 2015

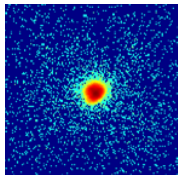
Bragg's Law $d = \dfrac{\lambda}{2\sin\theta_{(x,y)}}$

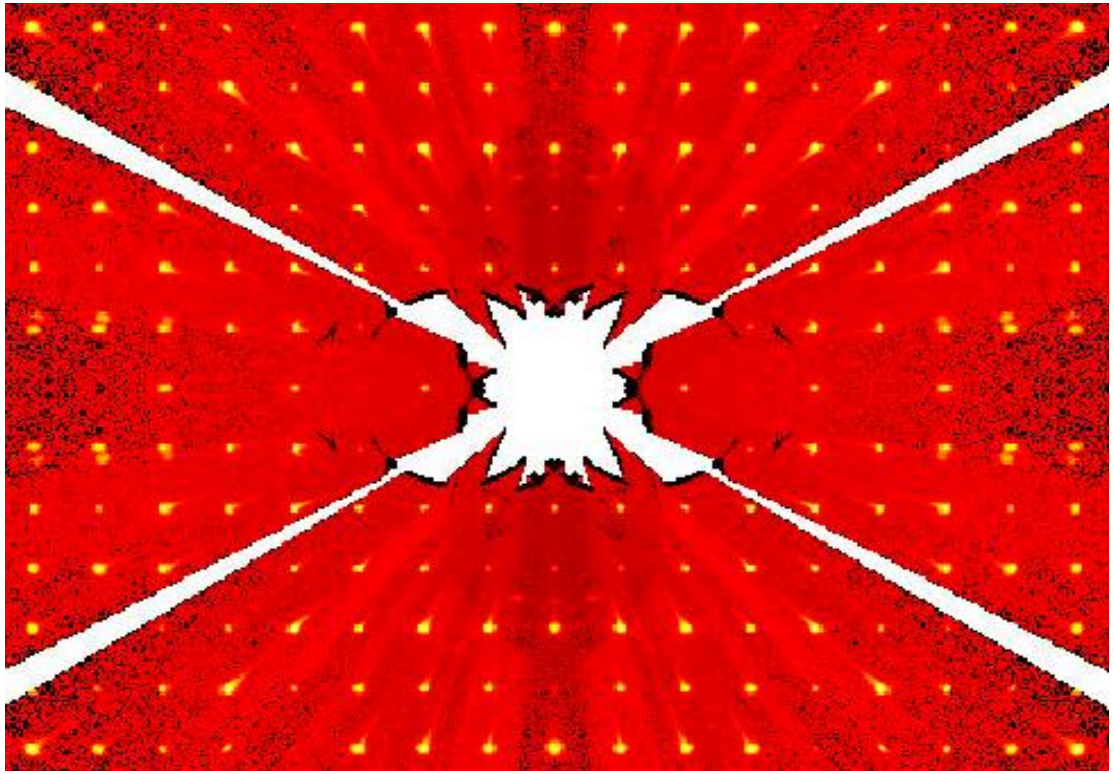
Single-Crystal Diffraction Experiment

- Neutron TOF Laue diffraction
  - 3D detector
  - TOF Laue diffraction: x, y, TOF(λ)

de Broglie Equation $\lambda = \dfrac{h}{mv} = \dfrac{ht}{m(L_1 + l_2)}$



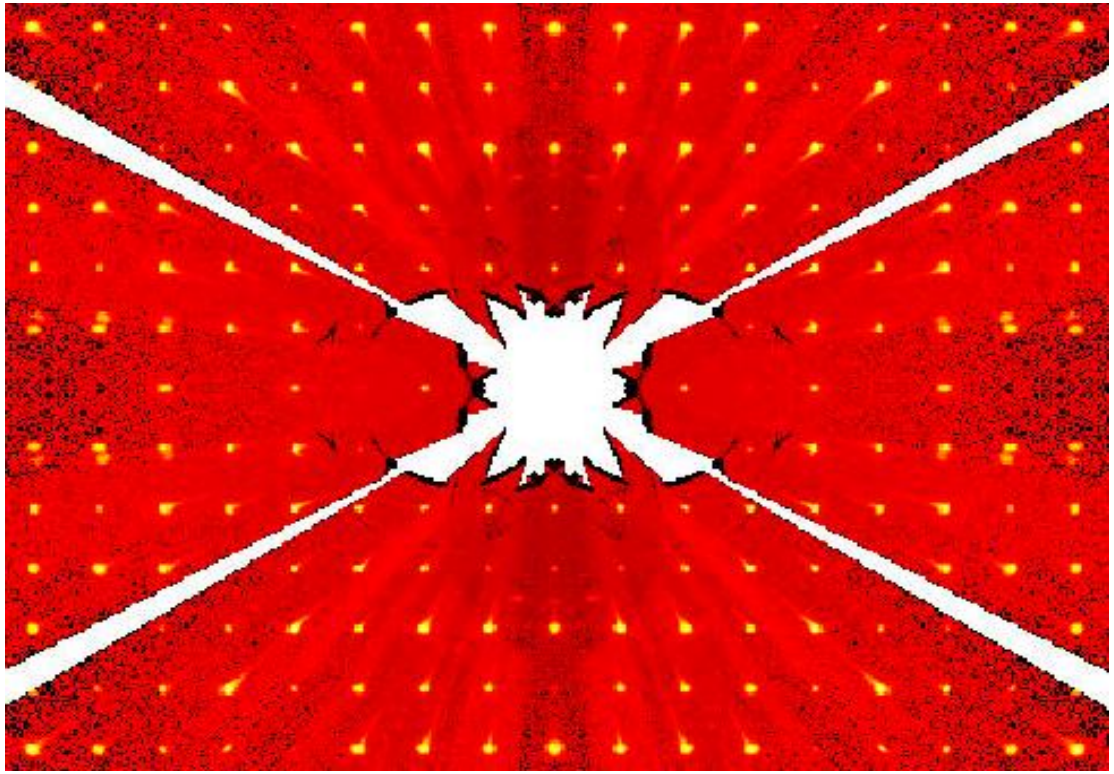




Bragg's Law $d = \dfrac{\lambda}{2\sin\theta_{(x,y)}}$

Single-Crystal Diffraction Experiment

- Neutron TOF Laue diffraction
  - Continuous 3D map of scattered intensity
- Regular 3D periodic structure
  - Discrete list of peak intensities
  - h k l Intensity sig
  - Peak shape, streaking, diffuse scattering are ignored



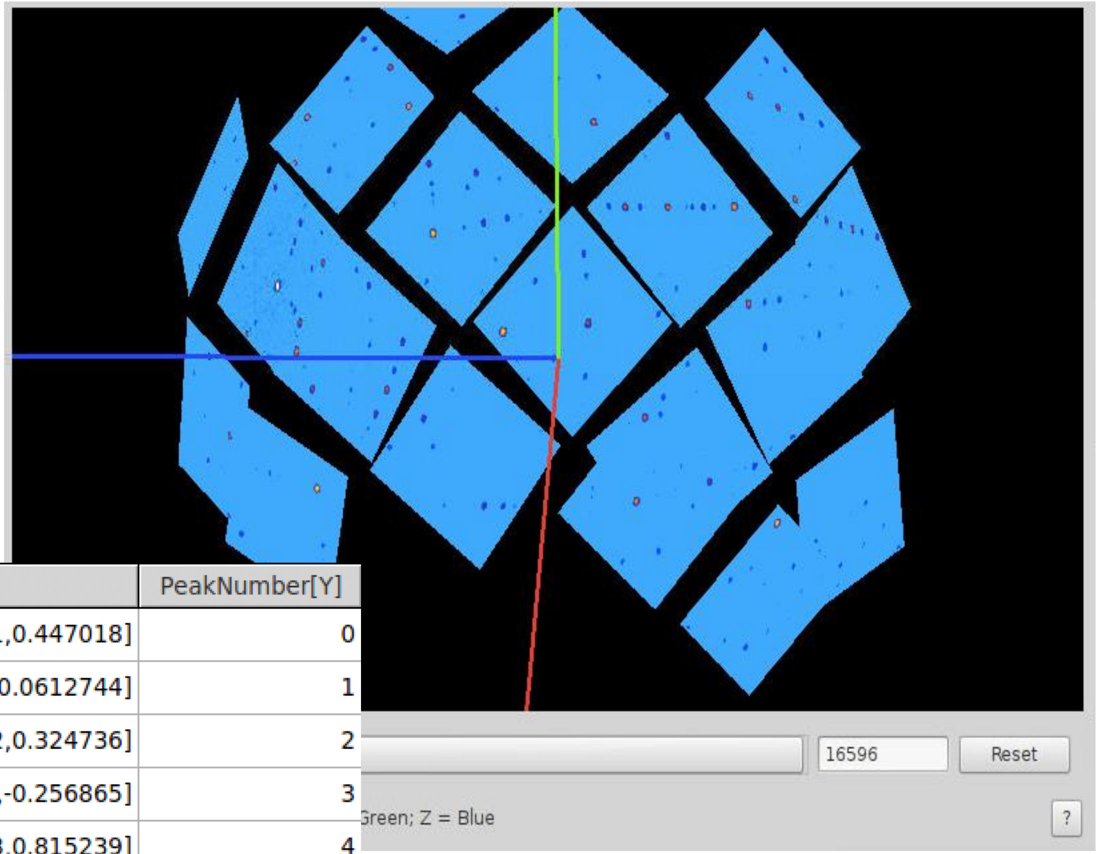
Single-Crystal Diffraction Experiment

- Neutron TOF Laue diffraction
  - Continuous 3D map of scattered intensity
- Regular 3D periodic structure
  - Discrete list of peak intensities
  - h k l Intensity sig
  - Peak shape, streaking, diffuse scattering are ignored

```
-1   0   0 113.223 2.50317
 1   0   0 114.660 3.84132
-2   0   0 66.5458 2.02561
 2   0   0 60.2263 4.60959
-3   0   0 54.4932 2.22779
 3   0   0 56.7562 6.54890
-4   0   0 491.006 8.69669
 4   0   0 470.333 20.2283
-5   0   0 5.22720 1.65361
 5   0   0 1.88785 5.20861
-6   0   0 80.0296 3.32792
 6   0   0 89.4709 8.44958
-7   0   0 95.6262 5.98335
 7   0   0 106.692 14.0558
```

Data Reduction of Single-Crystal Diffraction Experiment

- Regular 3D periodic structure
  - Raw data → peak position in detector space → peak position in reciprocal space (x, y, z)
  - Find lattice and index peaks with *hkl*



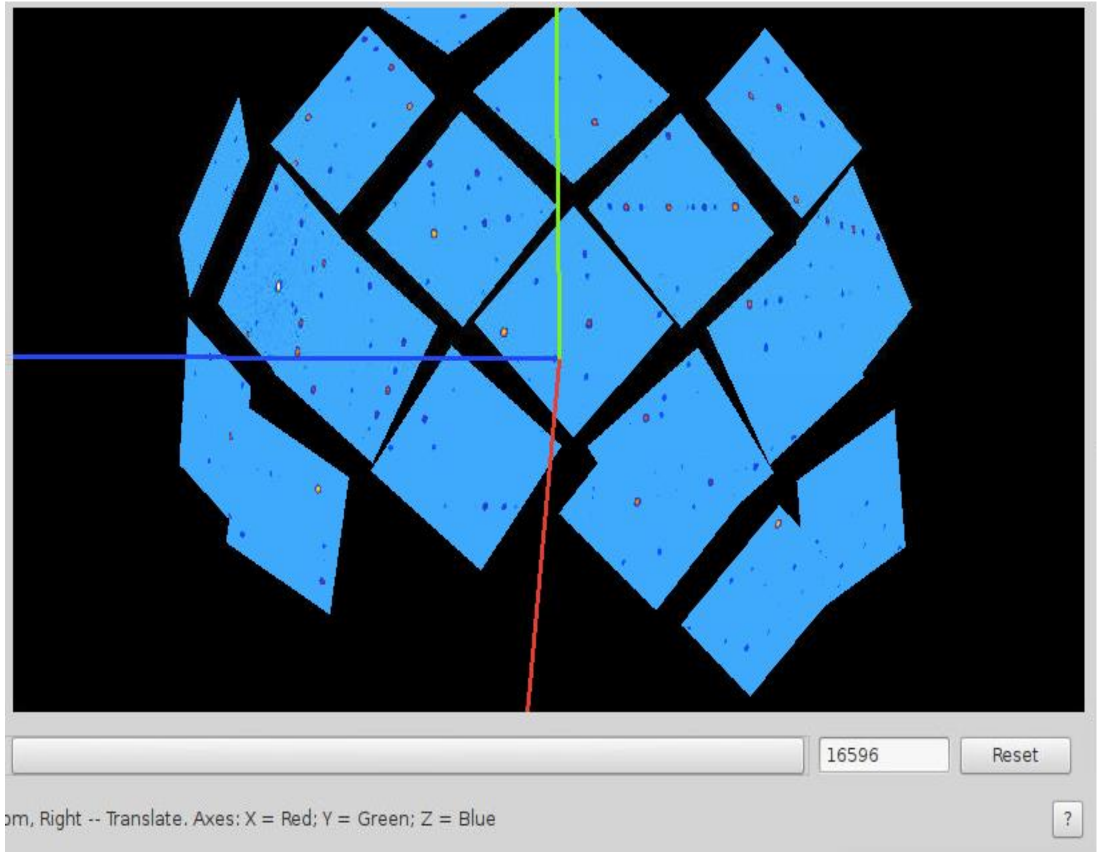
BinCount[Y]	BankName[Y]	Row[Y]	Col[Y]	QLab[Y]	QSample[Y]	PeakNumber[Y]
6699	bank17	25	103	[-2.34476,-2.06202,-4.30599]	[-5.28099,0.45021,0.447018]	0
5027	bank17	164	83	[-1.80961,-1.17719,-2.61117]	[-3.36213,0.413496,-0.0612744]	1
1867	bank17	98	19	[-2.9132,-2.45444,-4.51155]	[-5.82572,0.905952,0.324736]	2
1003	bank17	209	19	[-4.18271,-2.7207,-5.43484]	[-7.26535,1.25834,-0.256865]	3
865	bank17	23	46	[-3.46004,-3.32703,-6.19992]	[-7.7412,0.943053,0.815239]	4
391	bank17	162	85	[-3.60823,-2.35066,-5.22865]	[-6.72346,0.815744,-0.115695]	5
286	bank17	143	220	[-4.99936,-2.65714,-8.13912]	[-9.90404,0.255163,-0.379607]	6
231	bank17	110	162	[-3.04578,-1.97378,-5.01697]	[-6.18064,0.377042,0.0111348]	7

Data Reduction of Single-Crystal Diffraction Experiment

- Regular 3D periodic structure
  - (x, y, z) ↔ *hkl*
  - Reversible relationship by a invertible **3x3 UB matrix** between (x, y, z) and (*hkl*)

$$Q_l = 2\pi R \cdot U \cdot B \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

  - Predict peak position in detector space for a given *hkl* to integrate
  - *hkl* are integer Miller indices, but doesn't have to be.



Data Reduction of Single-Crystal Diffraction Experiment

- Refine UB Matrix and lattice parameters
- (x, y, z) ↔ *hkl*
- List of (x, y, z) and corresponding *hkl*
- round *hkl* to integers
- Least square method for optimal UB

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \mathbf{UB} \times \begin{pmatrix} h_i \\ k_i \\ l_i \end{pmatrix}$$

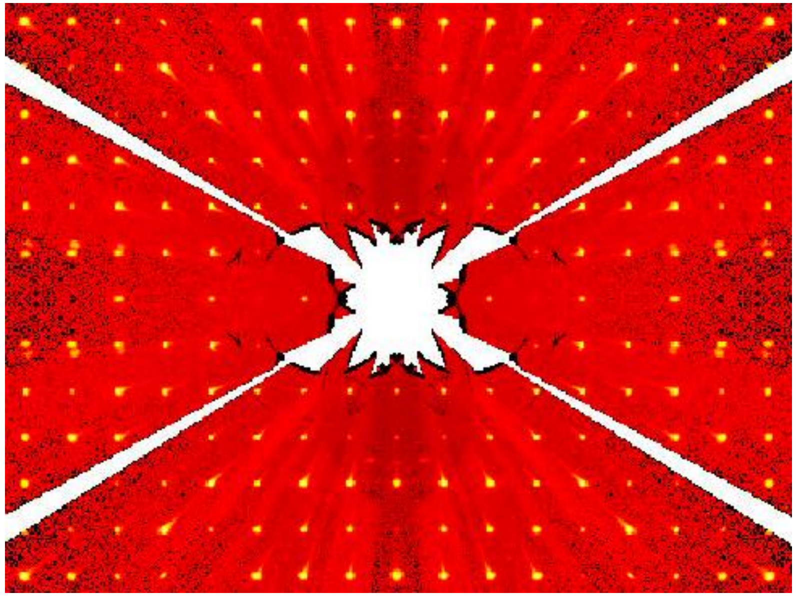
$$\begin{pmatrix} x_1 & x_2 \dots \dots & x_{pc} \end{pmatrix} = \begin{pmatrix} UB_{11} & UB_{12} & UB_{13} \end{pmatrix} \times \begin{pmatrix} h_1 & h_2 & h_3 & & h_{pc} \\ k_1 & k_2 & k_3 & \dots \dots & k_{pc} \\ l_1 & l_2 & l_3 & & l_{pc} \end{pmatrix}$$

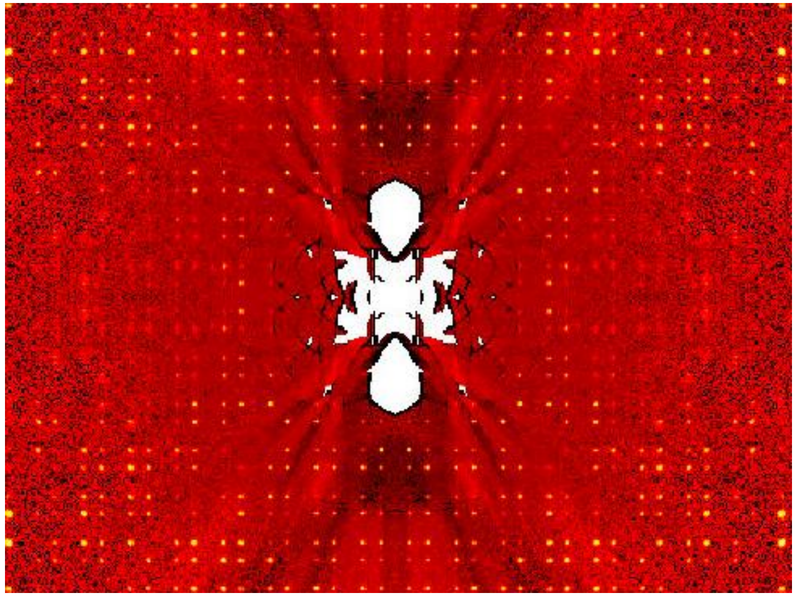
Data Reduction of Single-Crystal Diffraction Experiment

- Incommensurately modulated structures
- Main reflections + satellite reflections
- Main Bragg Peaks:

  (x, y, z) ↔ *hkl* with **UB** matrix
- Satellite Peaks

  (x, y, z) ↔ fractional *hkl* with **UB** matrix



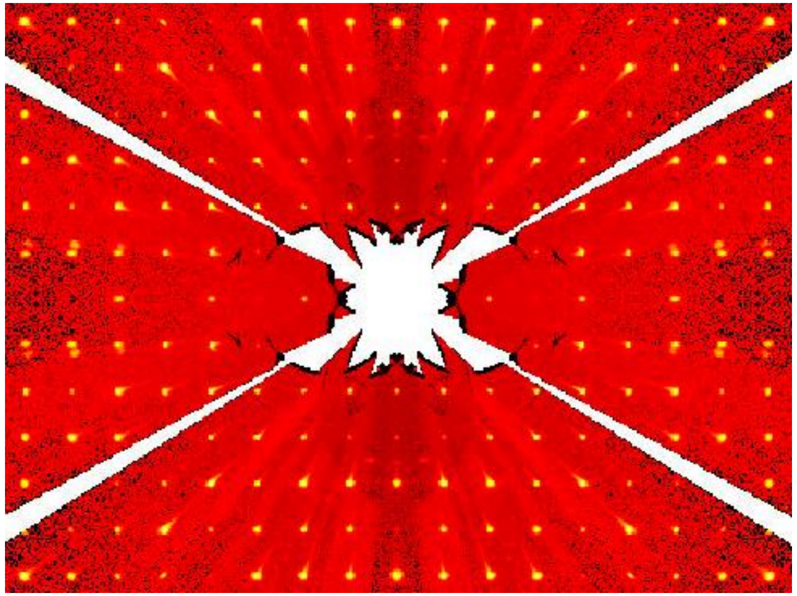


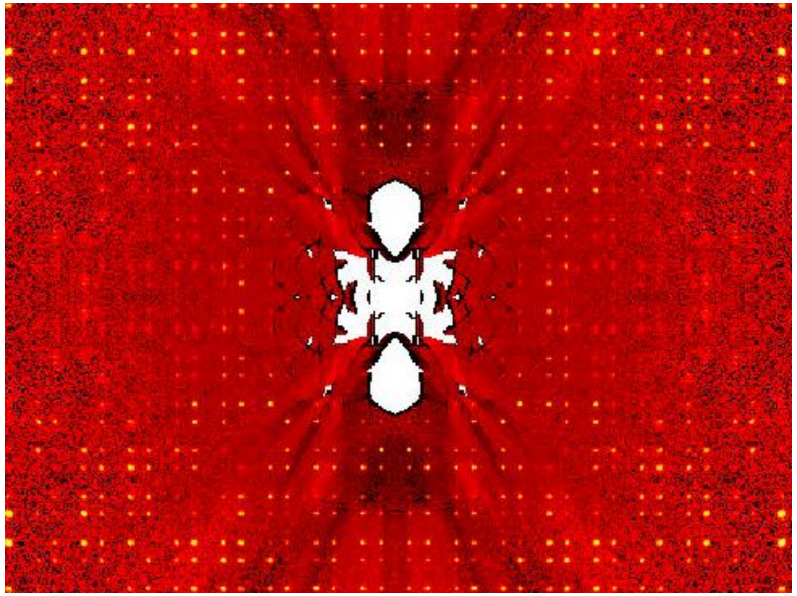
Data Reduction of Single-Crystal Diffraction Experiment

- Incommensurately modulated structures
- Main reflections + satellite reflections
- Main Bragg Peaks:

  (x, y, z) → *hklmnp* (*mnp*=000)
- Satellite Peaks

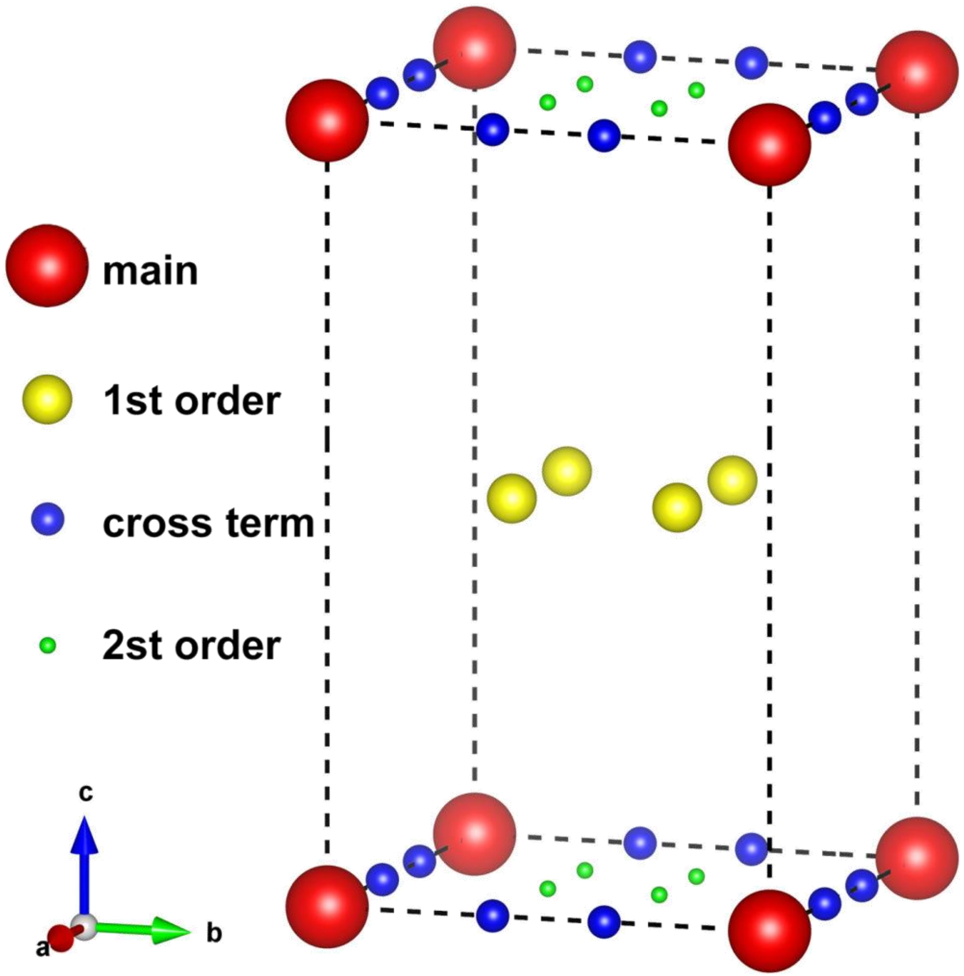
  (x, y, z) → *hklmnp* (*mnp*≠000)





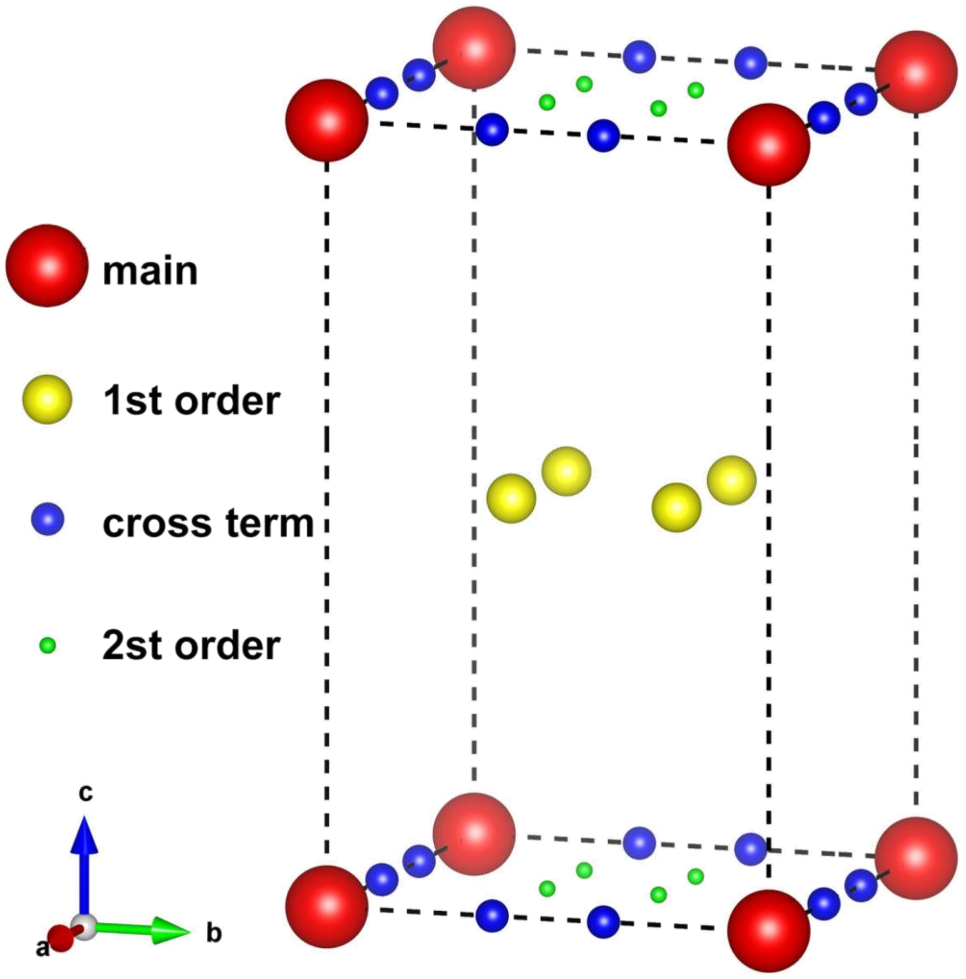
Indexing Satellite Peaks

- How is (x, y, z) → *hklmnp* possible?
- Modulation vectors: ***q*-vectors**
- Only 3 independent bases in 3D space
- Separate Main peaks from Satellites
- Intensities may be useful



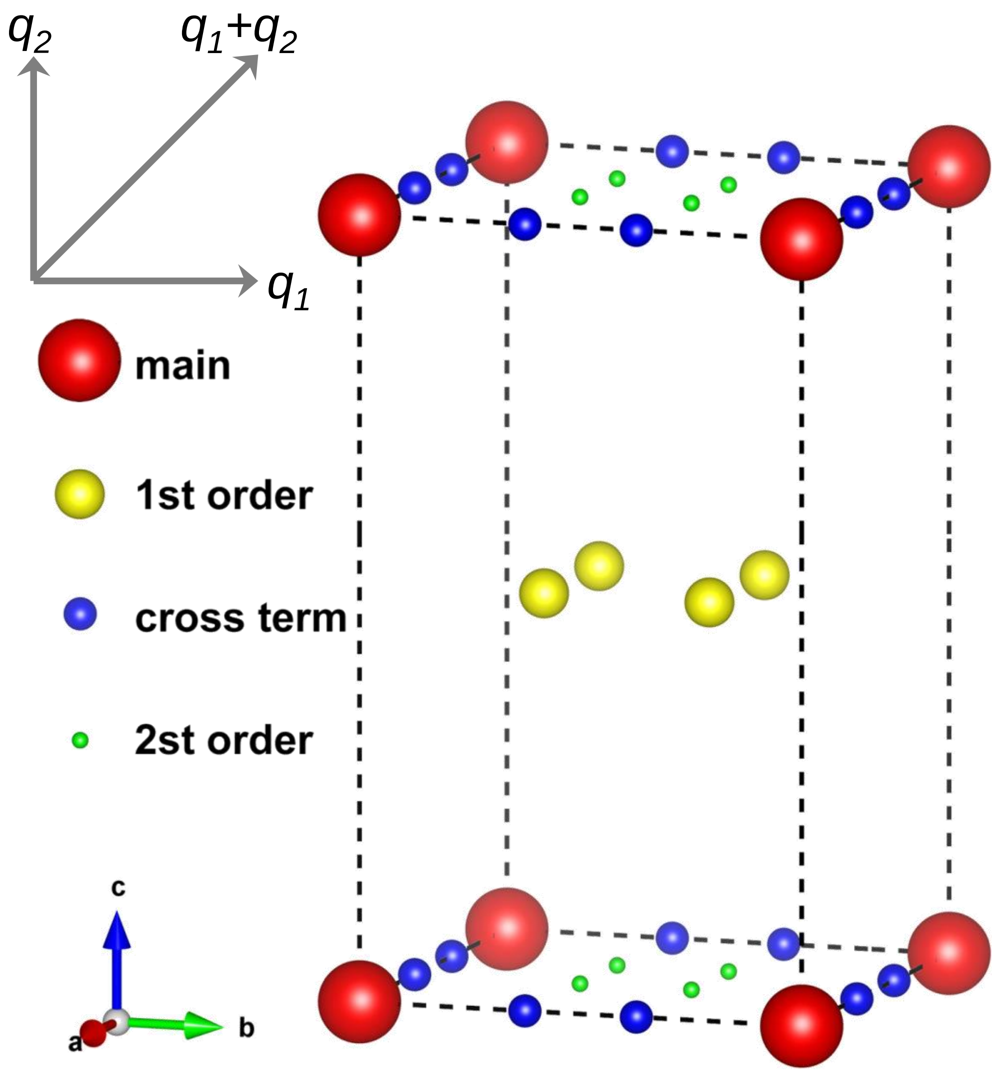
Indexing Satellite Peaks

- How is (x, y, z) → *hklmnp* possible?
- Index main Bragg peaks first
- Identify ***q*-vectors**
- Index satellite peaks
- $hkl_f = hkl_i + m\mathbf{q_1} + n\mathbf{q_2} + p\mathbf{q_3}$



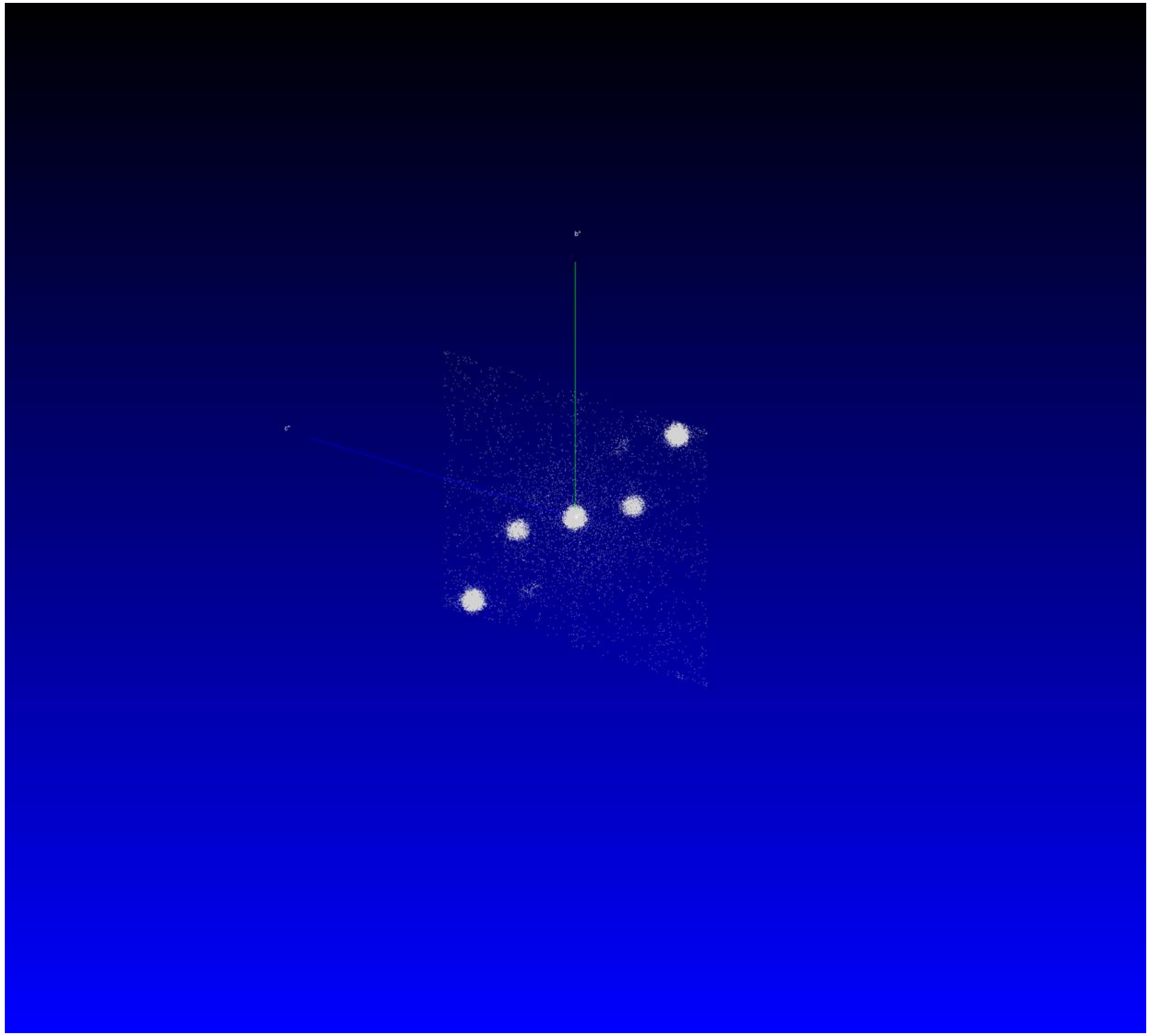
Identifying ***q*-vectors**

- Intensity is the first clue
- ***q*-vector** is not the vector pointing to the closest satellite peak
- ***q*-vector** is the vector pointing to the closest **first-order** satellite peak



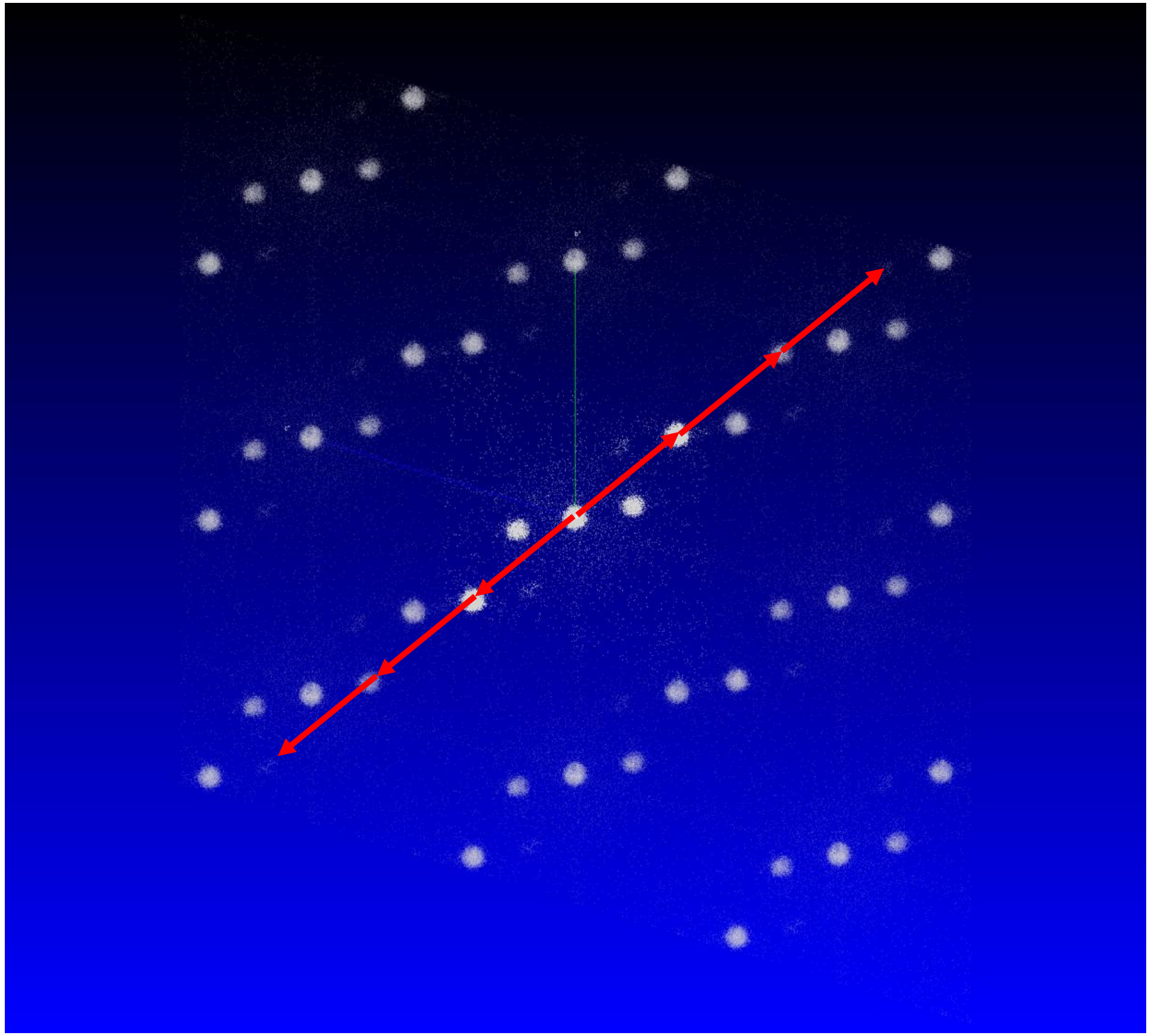
Identifying ***q*-vectors**

- Collapsing the peaks to lattice range in reciprocal space
- Main reflections in the origin



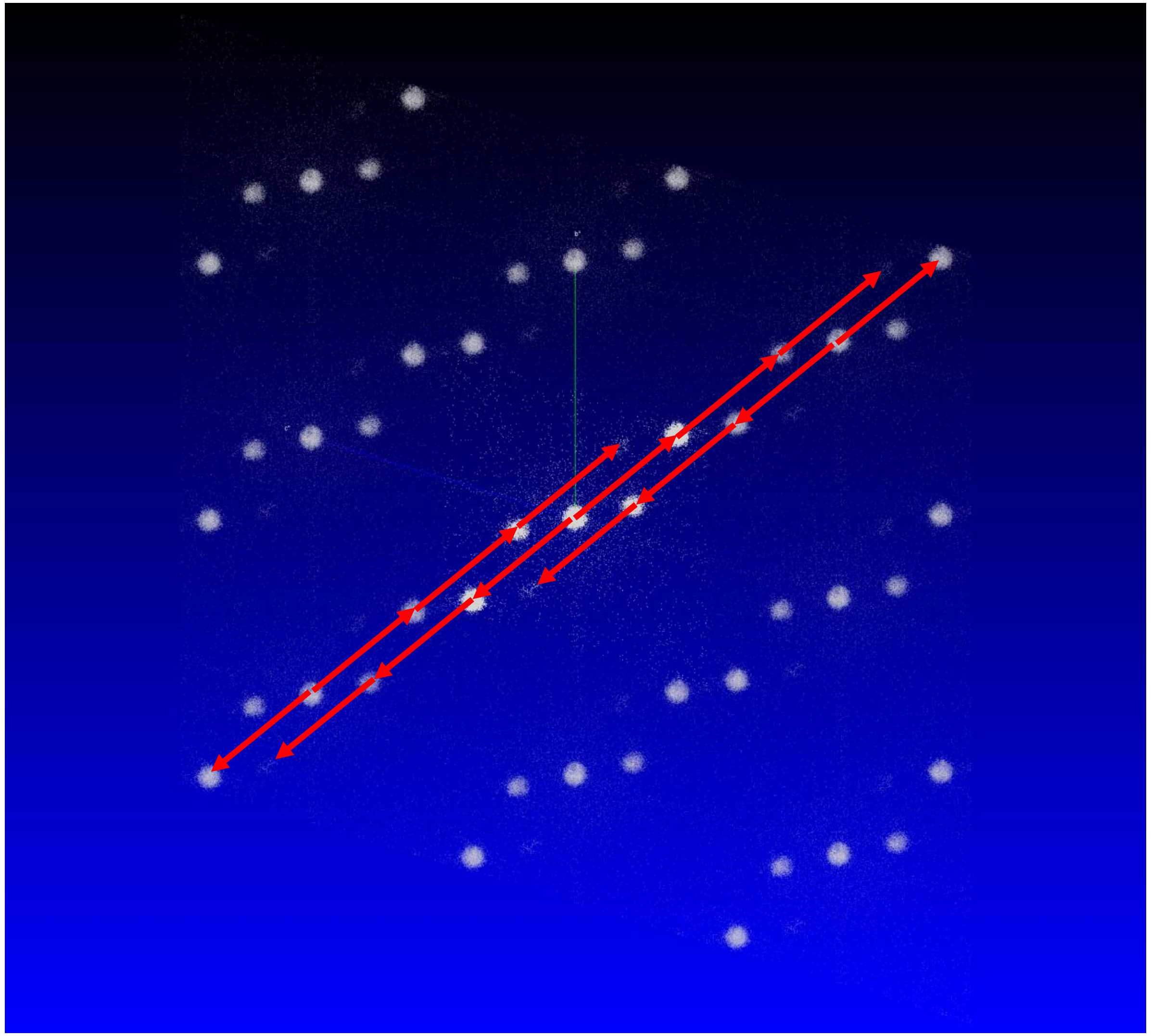
Identifying ***q*-vectors**

- Collapsing the peaks to lattice range in reciprocal space
- Main reflections in the origin
- Expanding the Collapsed image using symmetry



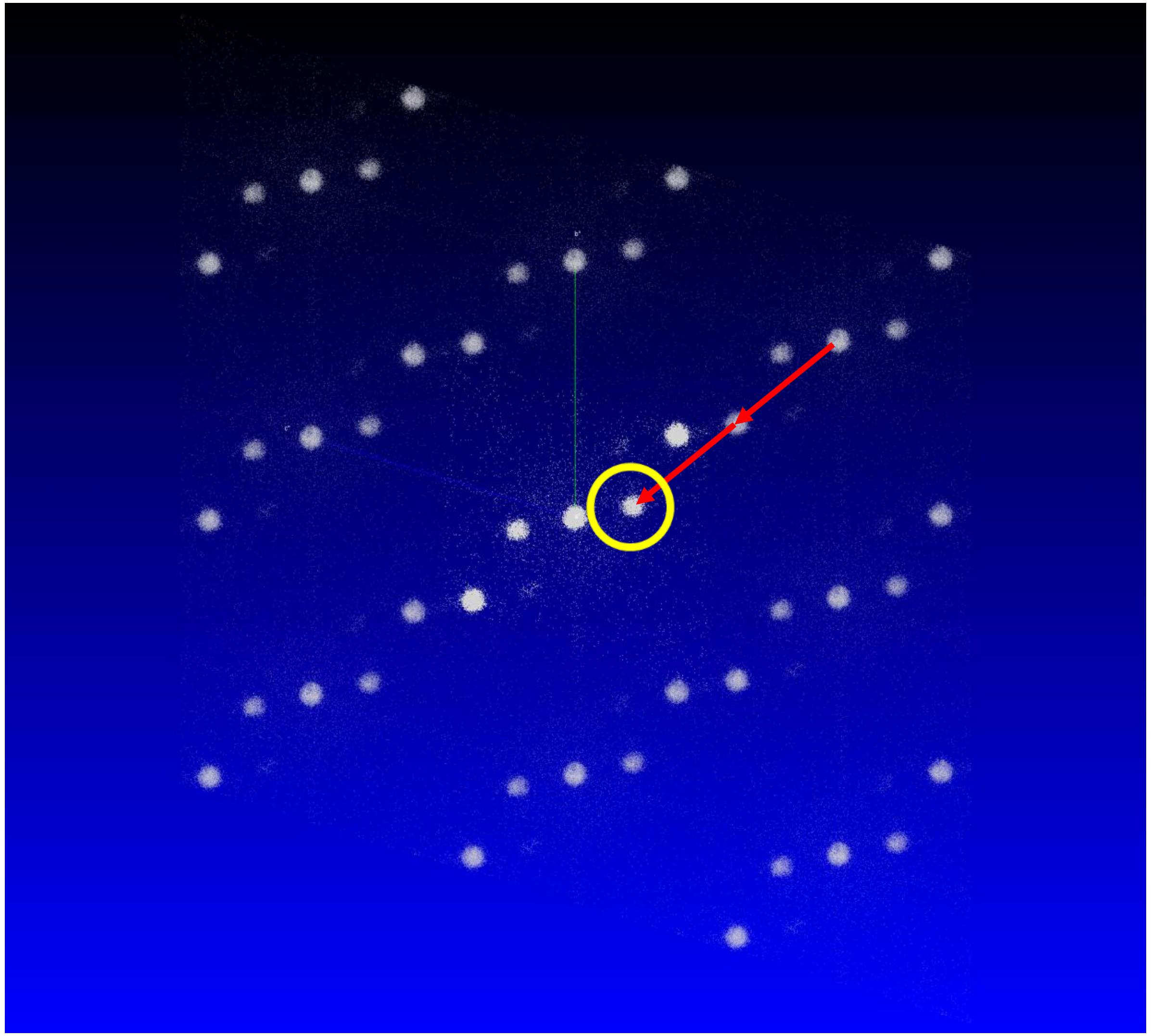
Identifying ***q*-vectors**

- Make sure all the peaks are accounted for by the ***q*-vectors**
- Number of ***q*-vectors**, maximum order of satellite, cross terms (if more than one ***q*-vector**)



Identifying ***q*-vectors**

- Fractional index for satellite peaks cannot be rounded to the nearest integer
- *3.4 5.2 7.8 ≠ 358m*



Indexing Satellite Peaks

- *hklmnp* → (x, y, z) is trivial
- $h_f = (h + m\delta h_1 + n\delta h_2 + p\delta h_3)$
- $k_f = (k + m\delta k_1 + n\delta k_2 + p\delta k_3)$
- $l_f = (l + m\delta l_1 + n\delta l_2 + p\delta l_3)$
- $h\mathbf{a^*} + k\mathbf{b^*} + l\mathbf{c^*} + m\mathbf{q_1} + n\mathbf{q_2} + p\mathbf{q_3}$
- With indexed peaks, lattice parameters and modulation vectors can be refined

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} \mathbf{a}^* & \mathbf{b}^* & \mathbf{c}^* & \mathrm{MV}_\mathbf{1} & \mathrm{MV}_\mathbf{2} & \mathrm{MV}_\mathbf{3} \end{pmatrix} \times \begin{pmatrix} h_i \\ k_i \\ l_i \\ m_i \\ n_i \\ p_i \end{pmatrix}$$

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} \mathrm{UB}_{11} & \mathrm{UB}_{12} & \mathrm{UB}_{13} & \mathrm{MV}_{11} & \mathrm{MV}_{12} & \mathrm{MV}_{13} \\ \mathrm{UB}_{21} & \mathrm{UB}_{22} & \mathrm{UB}_{23} & \mathrm{MV}_{21} & \mathrm{MV}_{22} & \mathrm{MV}_{23} \\ \mathrm{UB}_{31} & \mathrm{UB}_{32} & \mathrm{UB}_{33} & \mathrm{MV}_{31} & \mathrm{MV}_{32} & \mathrm{MV}_{33} \end{pmatrix} \times \begin{pmatrix} h_i \\ k_i \\ l_i \\ m_i \\ n_i \\ p_i \end{pmatrix}$$

$$(x_1 \quad x_2 \ldots \ldots x_{pc}) = (UB_{11} \;\; UB_{12} \;\; UB_{13} \;\; MV_{11} \;\; MV_{12} \;\; MV_{13}) \times \begin{pmatrix} h_1 & h_2 & & h_{pc} \\ k_1 & k_2 & & k_{pc} \\ l_1 & l_2 & \ldots\ldots & l_{pc} \\ m_1 & m_2 & & m_i \\ n_1 & n_2 & & n_i \\ p_1 & p_2 & & p_i \end{pmatrix}$$

Integration and Absorption Correction

- Integration only need the peak position in detector space
- Absorption is only a function of the diffraction geometry, doesn't matter the reflection type
- These process are not affected by the modulated structure

Summary of the Process

1. Harvest strong main Bragg Peaks
2. Find 3D UB for average structure
3. Harvest all the peaks in the data
4. Index all the peaks with found UB
5. Collapse all index peaks to lattice range in reciprocal space
6. Identify the satellite peaks from the clusters, and find modulation vectors
7. Index satellite (and main) peaks with the modulation vector
8. Refined the modulation vectors and save UB for data reduction

Mantid Documentation

Shiyun Jin, Xiaoping Wang and Vickie Lynch

https://docs.mantidproject.org/nightly/concepts/ModulatedStructure.html

Home Download Documentation Contact Us Search

Modulated Structure

Data reduction for single-crystal neutron diffraction on (3+d) dimension modulated structure with Mantid

Modulated Structures cannot be described by only three hkl indices, so additional dimensions must be added to standard reduction of Bragg reflections for these structures. More explanation can be found in Acta Crystallographica Section B About modulated structures.

The general procedure for reducing data collected on a modulated structure should be as follows:

1. Harvest strong peaks from the data collected and find the basic unit cell and corresponding UB matrix;
2. Harvest more peaks to include the weaker satellites;
3. Index all the harvested peaks based on the UB found for the basic unit cell, with fractional Miller indices (h, k, l) allowed;
4. Collapse all the indexed peaks to lattice range by calculating *h-floor(h)*, *k-floor(k)*, *l-floor(l)*, and visualize all the peaks by making a 3d-plot of all the collapsed peaks. Find the clusters of the collapsed peaks, and calculate the coordinates of the centers of the clusters in HKL space, save them as options for modulation vectors;
5. It is up to the user to identify the best options for modulation vectors, and the maximum order of satellite peaks for each modulation vector. Up to three modulation vectors are allowed; (This task is can be really complicated to realize with an algorithm due to the countless number of special cases to consider, but should be effortless for a human mind in most cases with necessary knowledge of modulated structures. The rule of thumb is to use least number of modulation vectors to account for most satellite peaks, if not all.)
6. Use the identified modulation vectors together with the basic unit cell to index all the harvested peaks, both main and satellites, with a reasonable tolerance set by user. One extra index is introduced (m, n, p) for each modulation vector identified;
7. Recalculate the UB matrix together with the modulation vectors using indexed peaks; (Step 7 and 8 can be iterated several times with smaller tolerances to refine the UB matrix and modulation vectors.)
8. Predict all the main and satellite peaks that hit the detector with the refined UB matrix and modulation vectors;
9. Integrate the predicted peaks and save them. Scale the integrated peaks for scattering angles and correct for absorption.

For processing the data from modulated structures, new member ModUB is added to the OrientedLattice class:

$$ModUB = \begin{pmatrix} \mathrm{MV}_{11} & \mathrm{MV}_{12} & \mathrm{MV}_{13} \\ \mathrm{MV}_{21} & \mathrm{MV}_{22} & \mathrm{MV}_{23} \\ \mathrm{MV}_{31} & \mathrm{MV}_{32} & \mathrm{MV}_{33} \end{pmatrix}$$

$$ModulationVector_i = \begin{pmatrix} \mathrm{MV}_{1i} \\ \mathrm{MV}_{2i} \\ \mathrm{MV}_{3i} \end{pmatrix}$$

In other words, the coordinates of Modulation Vector i (i=1,2,3) in Q space is $(\mathrm{MV}_{1i}, \mathrm{MV}_{2i}, \mathrm{MV}_{3i})$. If the structure is not modulated, ModUB=0. Correspondingly, new members ModHKL and errorModHKL are added to UnitCell class.

$$ModHKL = \begin{pmatrix} \mathrm{dh}_1 & \mathrm{dh}_2 & \mathrm{dh}_3 \\ \mathrm{dk}_1 & \mathrm{dk}_2 & \mathrm{dk}_3 \\ \mathrm{dl}_1 & \mathrm{dl}_2 & \mathrm{dl}_3 \end{pmatrix}$$

$$errorModHKL = \begin{pmatrix} \mathrm{errdh}_1 & \mathrm{errdh}_2 & \mathrm{errdh}_3 \\ \mathrm{errdk}_1 & \mathrm{errdk}_2 & \mathrm{errdk}_3 \\ \mathrm{errdl}_1 & \mathrm{errdl}_2 & \mathrm{errdl}_3 \end{pmatrix}$$

In this case, $(\mathrm{dh}_i, \mathrm{dk}_i, \mathrm{dl}_i)$ is the modulation vector i (i=1,2,3) in HKL space. And the relation between ModUB and ModHKL is:

$$ModUB = UB \times ModHKL$$

or

$$ModHKL = \mathrm{UB}^{-1} \times ModUB$$

ModUB is added to OrientedLattice class and ModHKL and ModVec are added to UnitCell class. Value for ModHKL in UnitCell is set when the function setModUB is used in OrientedLattice. Some of the values can be set from python.

Demo