Crystal Structure Refinement

Dr Lucy Clark – School of Chemistry – University of Birmingham

17th Oxford School on Neutron Scattering

7th September 2022

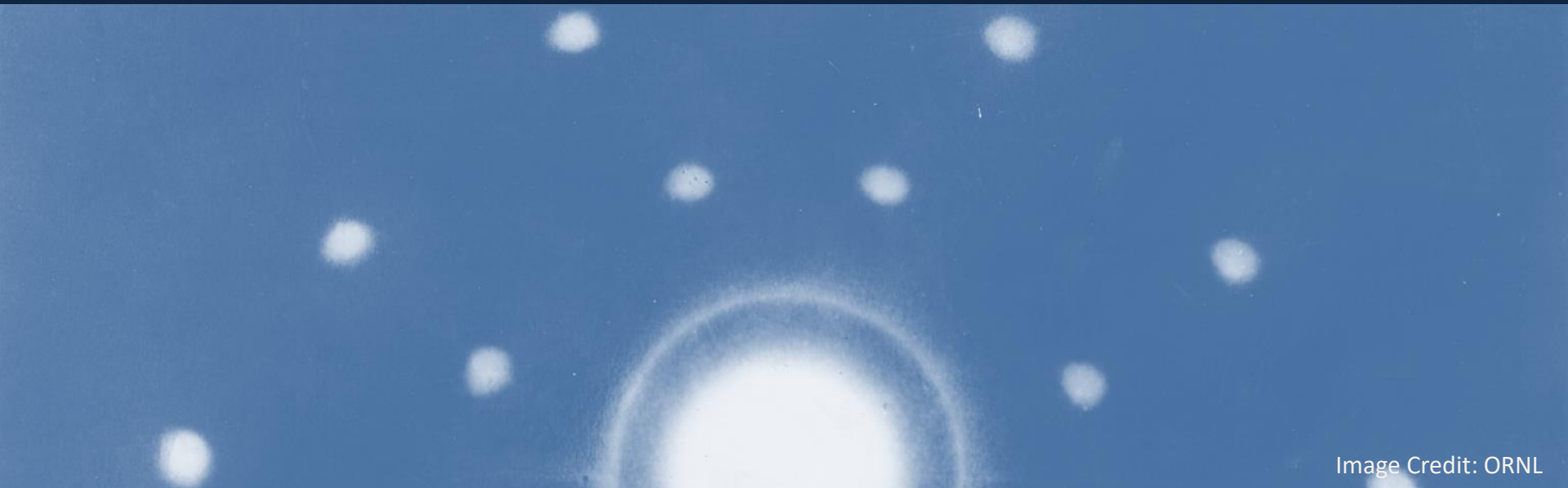


Image Credit: ORNL

Lecture 2 Objectives

In Lecture 2 we will explore:

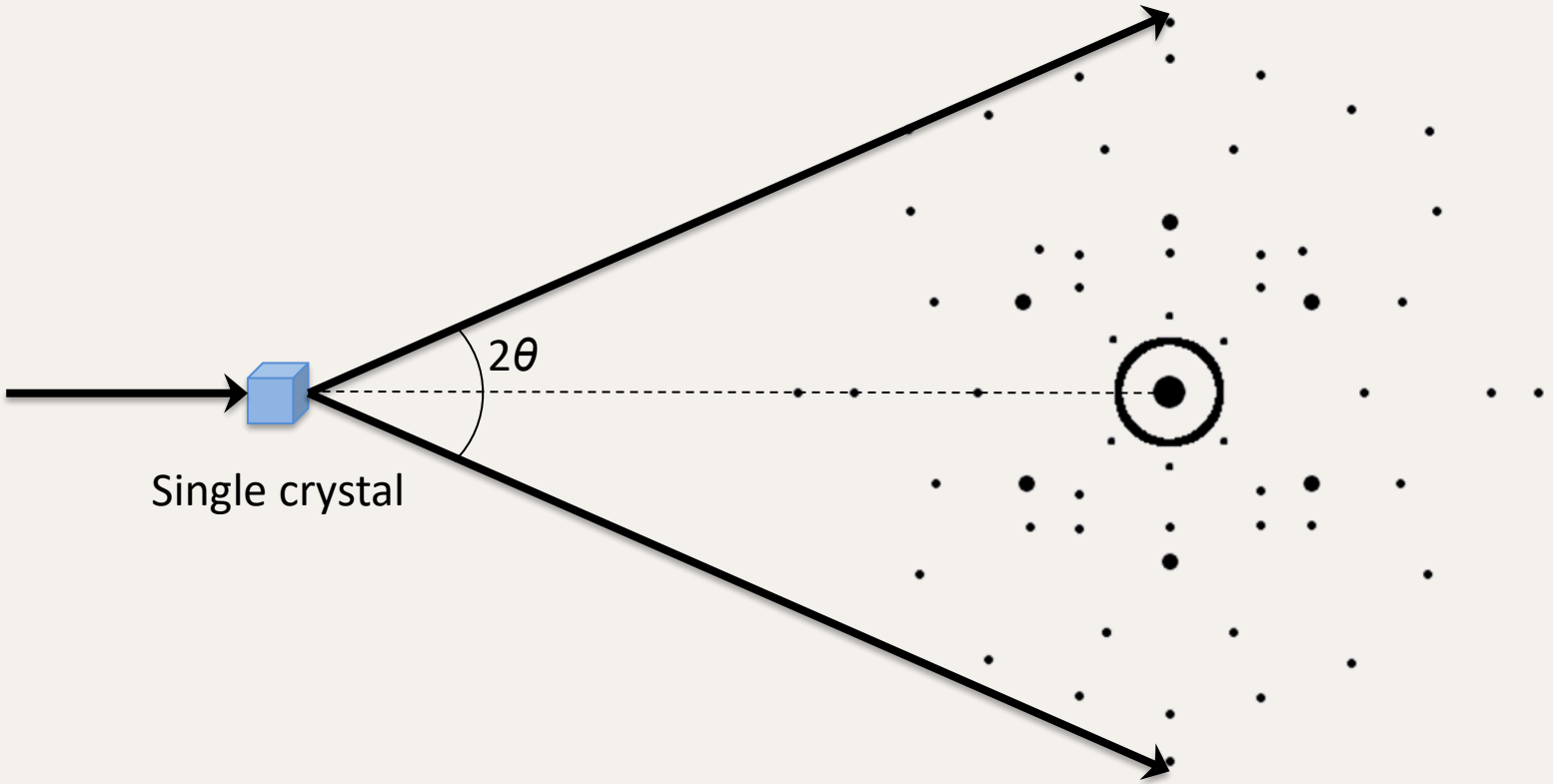
1. Experimental aspects of **single-crystal** and **powder diffraction**,
2. Basic analyses of powder diffraction data, including **phase identification** and **crystallite size determination**,
3. Relationships between the reciprocal lattice, real lattice and diffraction data, and how this allows us to **index a diffraction pattern**,
4. Challenges of peak overlap in powder diffraction and how we may overcome them through **Rietveld analysis** of powder diffraction data,
5. Rietveld refinement softwares and a TOF powder neutron diffraction Rietveld refinement case study.

The material covered in this lecture links to tutorial questions C2 and C3.

Single-Crystal vs. Powder Diffraction

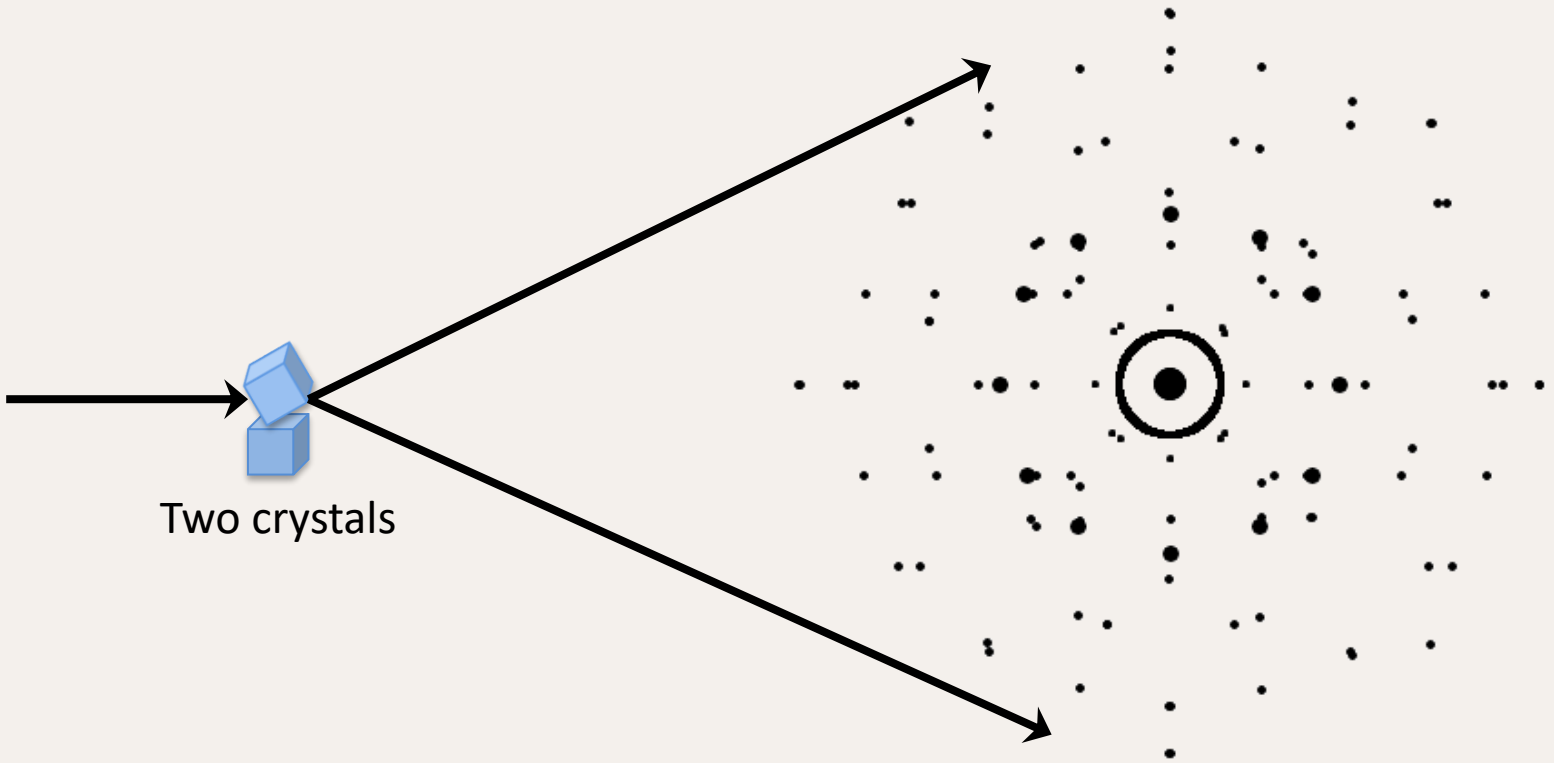
In a single-crystal diffraction experiment, radiation is incident upon a crystal and diffracted through an angle of 2θ by lattice planes that meet the diffraction condition

A sequence of measurements is performed from various crystal, so that all reflections from all of the crystal planes can be collected



Single-Crystal vs. Powder Diffraction

What happens when there is more than one crystal?



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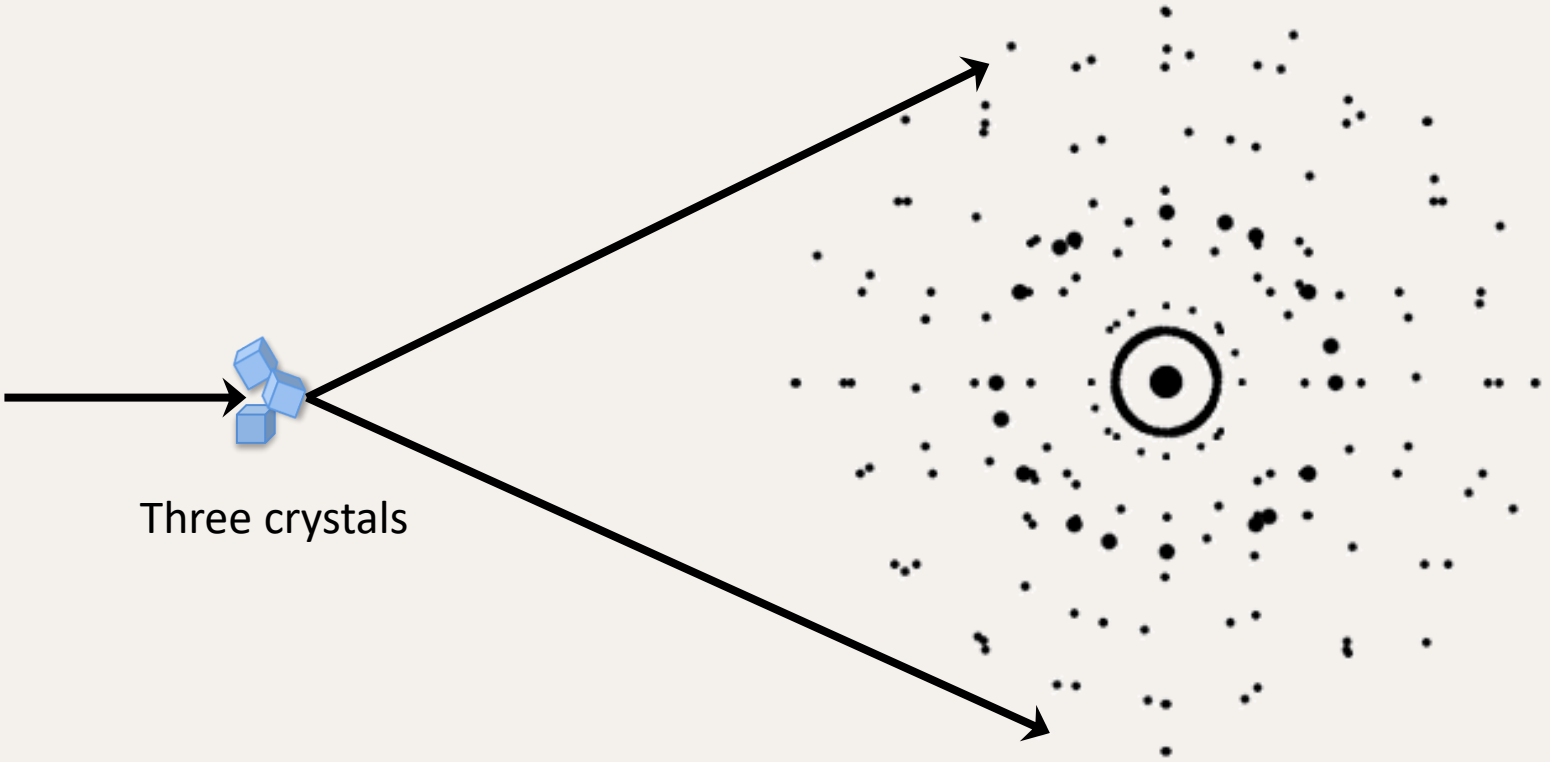

Single-Crystal vs. Powder Diffraction

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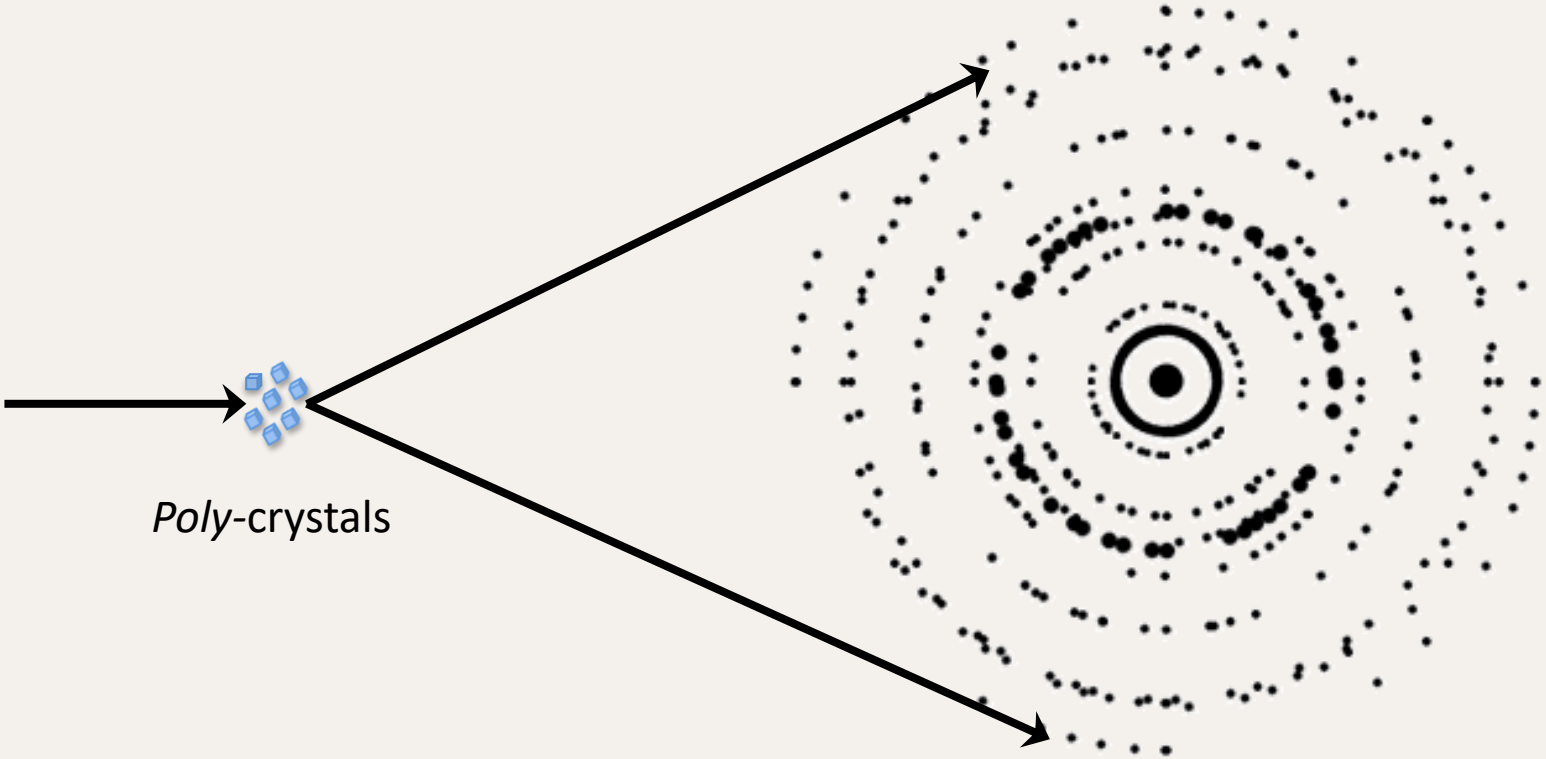
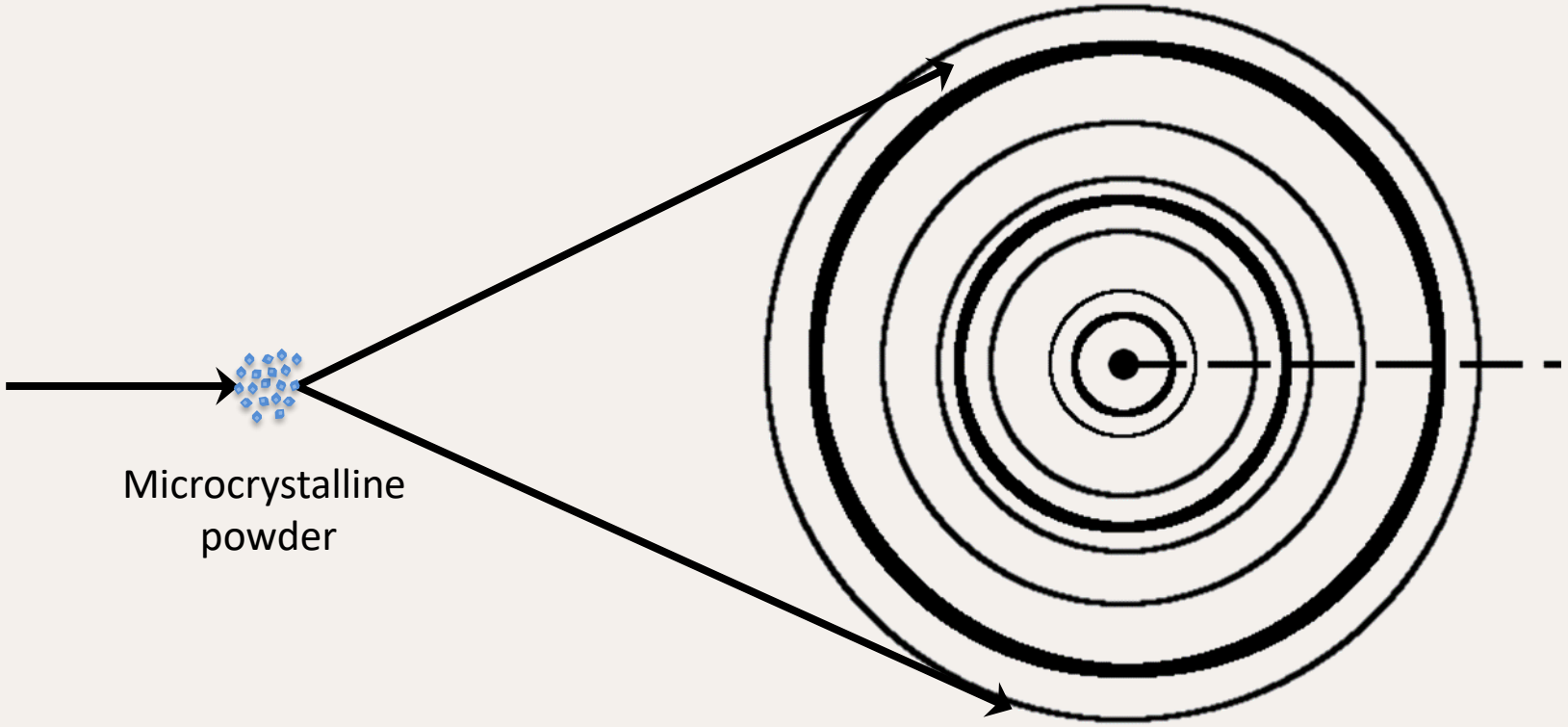


Single-Crystal vs. Powder Diffraction

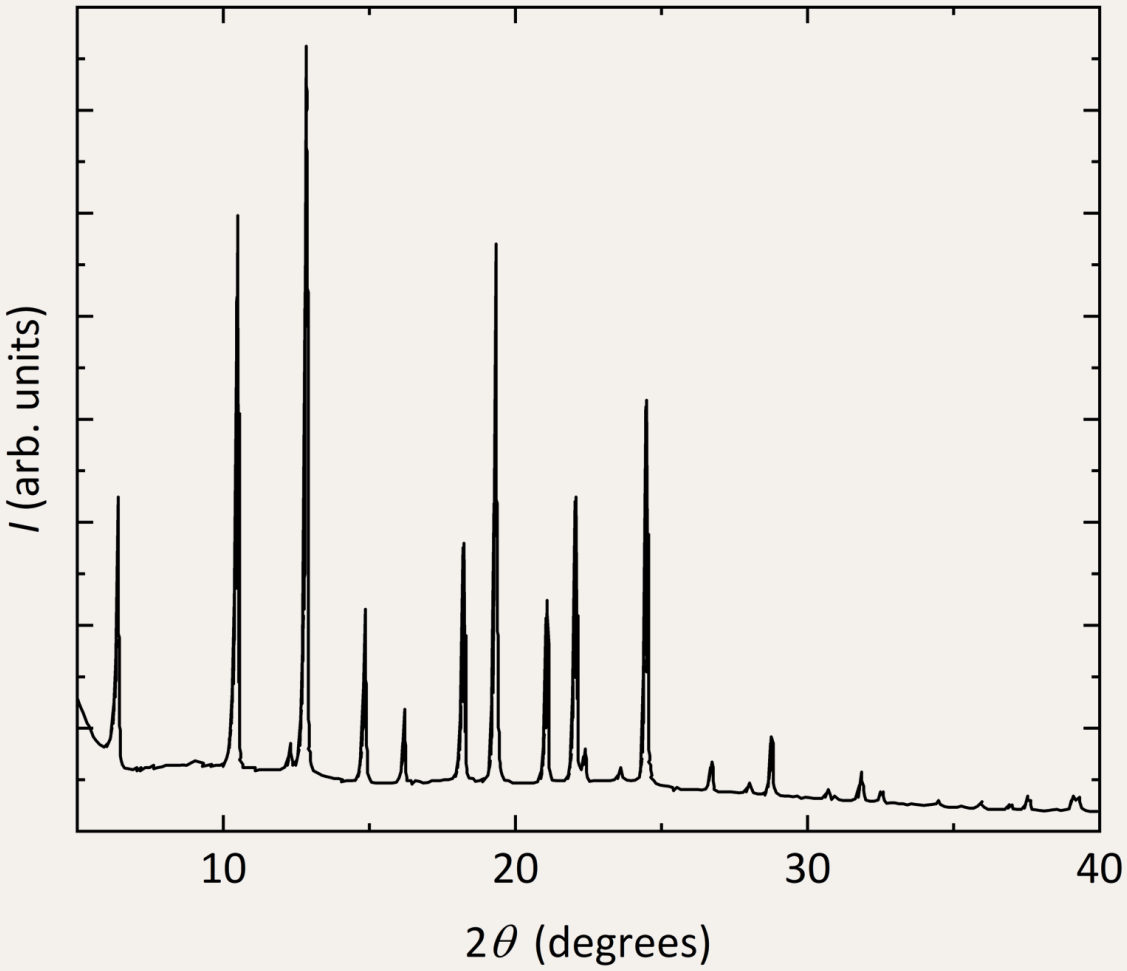
In a powder sample, there is an almost infinite number of randomly oriented crystals



This gives rise to **rings of diffraction intensity** rather than individual spots

Single-Crystal vs. Powder Diffraction

Integrating intensity across the diffraction rings gives a **powder diffraction pattern**



Cons:

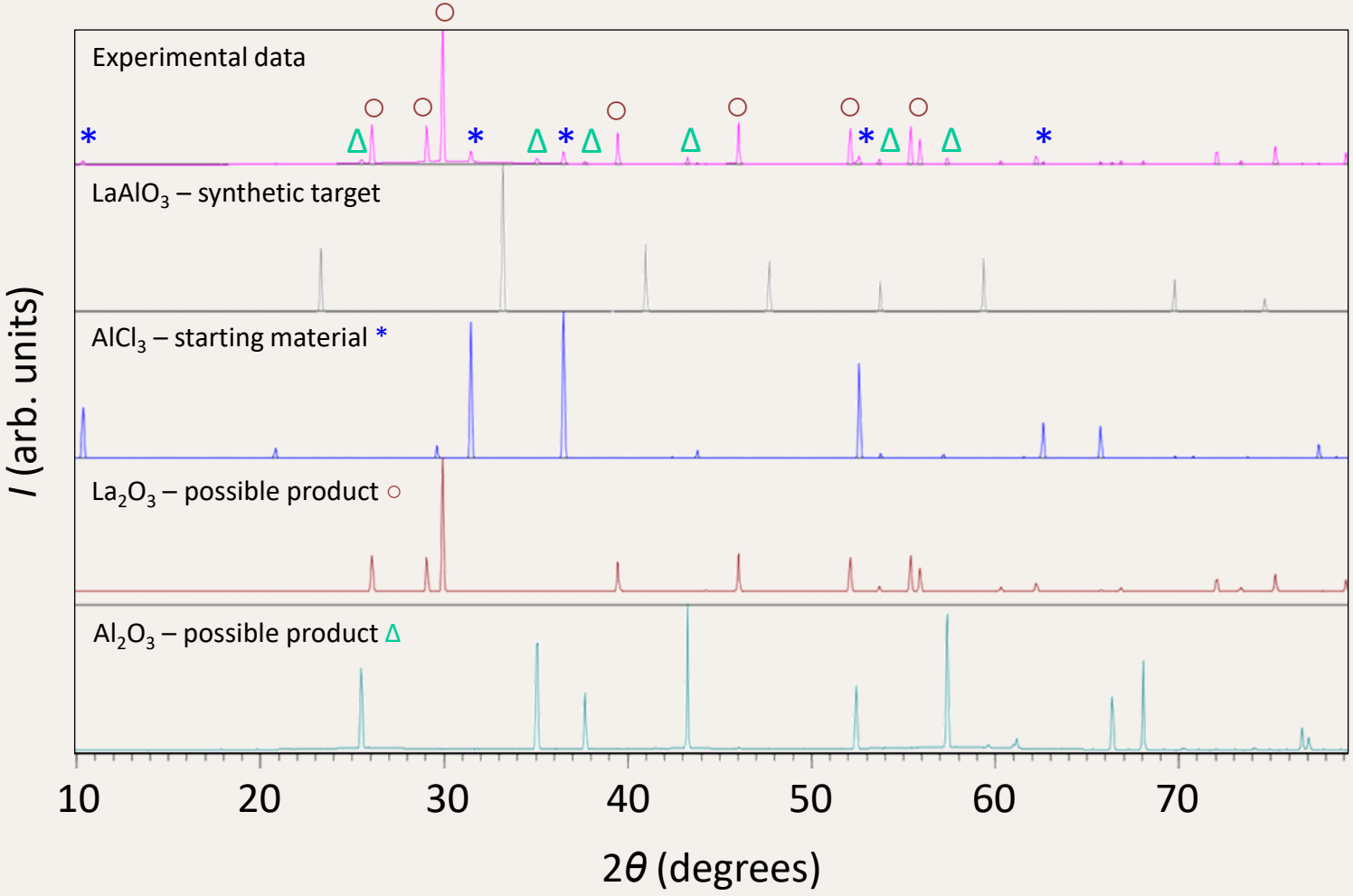
- Data analysis for full structural determination is challenging.

Pros:

- Simple, fast way to identify new materials, their phase purity and phase behaviour,
- No large single-crystal needed,
- Bulk characterisation method,
- Structure refinement.

Phase Identification

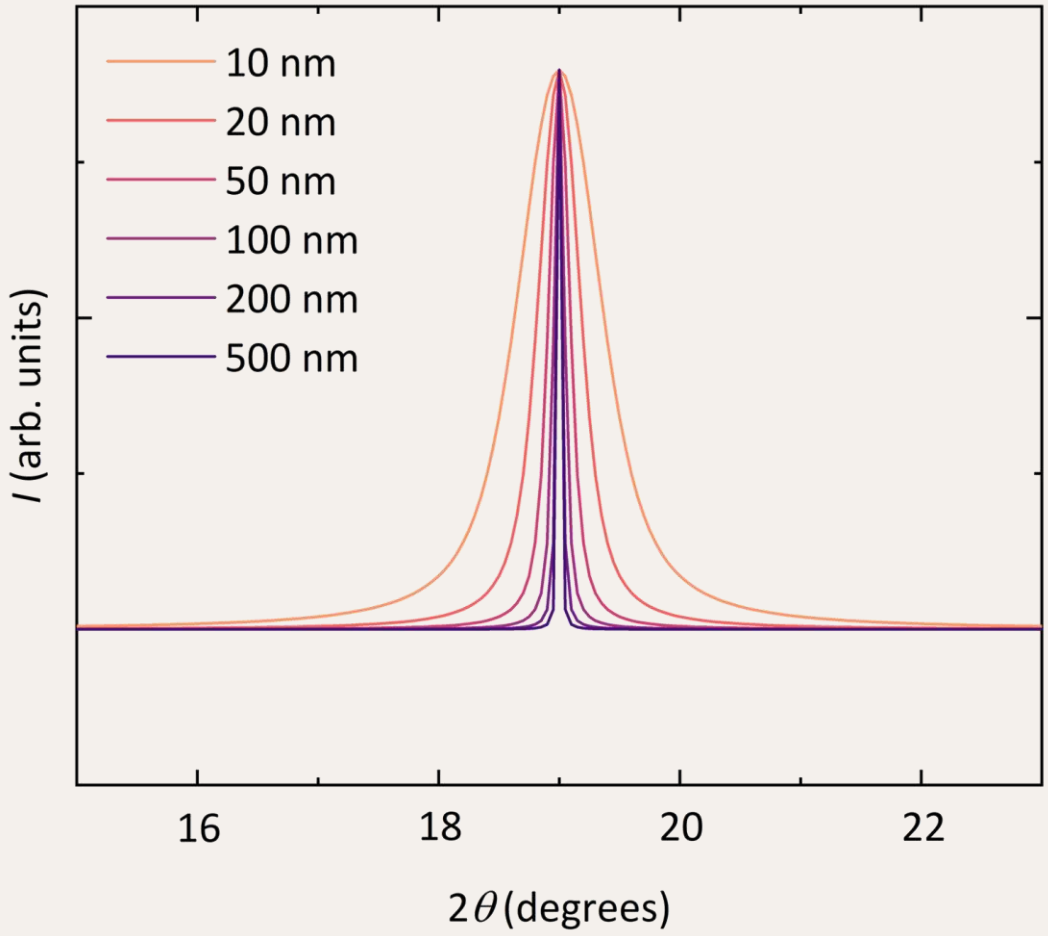
A routine analysis of powder diffraction data is to identify the crystalline phases present within a sample



Crystallite Size Determination

Small crystallites or scattering domains give rise to broadening of diffraction reflections

The **Scherrer equation** approximates crystallite size from the width of a diffraction peak



$$\tau = \frac{0.9\lambda}{\beta \cos\theta}$$

τ = mean crystallite domain size

λ = radiation wavelength

β = diffraction peak FWHM

θ = diffraction angle

Unit Cell Determination

Bragg's law relates θ to the *d*-spacing of the lattice planes (*h, k, l*) of a crystal

It is also possible to **determine the unit cell** parameters of a sample from its powder diffraction pattern through the relationship between d_{hkl} and the unit cell

The process of unit cell determination thus requires a powder diffraction pattern to be **indexed**, *i.e.* for each Bragg peak to be assigned its Miller indices

Crystal system	*d*-spacing in terms of unit cell parameters and Miller indices
Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$

Indexing a Powder Diffraction Pattern

By combining $\lambda = 2d \sin\theta$ with $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$ for a cubic system we get:

$$\sin^2\theta = \underbrace{\frac{\lambda^2}{4a^2}}_{\text{Common factor}}(h^2 + k^2 + l^2)$$

2θ / °	$\sin^2\theta$	Ratio	Miller Indices *(h, k, l)*
22.324	0.03747	1.00	100
31.776			
39.180			
45.555			
51.297			
56.610			
66.394			

From diffraction pattern | Calculate from 2θ | Find an integer value for common factor | Find (*h*, *k*, *l*) that gives integer ratio as sum of squares

Indexing a Powder Diffraction Pattern

By combining $\lambda = 2d \sin\theta$ with $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$, we get:

$$\sin^2\theta = \underbrace{\frac{\lambda^2}{4a^2}}_{\text{Common factor}}(h^2 + k^2 + l^2)$$

2θ / °	$\sin^2\theta$	Ratio	Miller Indices *(h, k, l)*
22.324	0.03747	1.00	100
31.776	0.07494	2.00	110
39.180	0.11242	3.00	111
45.555	0.14989	4.00	200
51.297	0.18736	5.00	210
56.610	0.22483	6.00	211
66.394	0.29978	8.00	220

From diffraction pattern

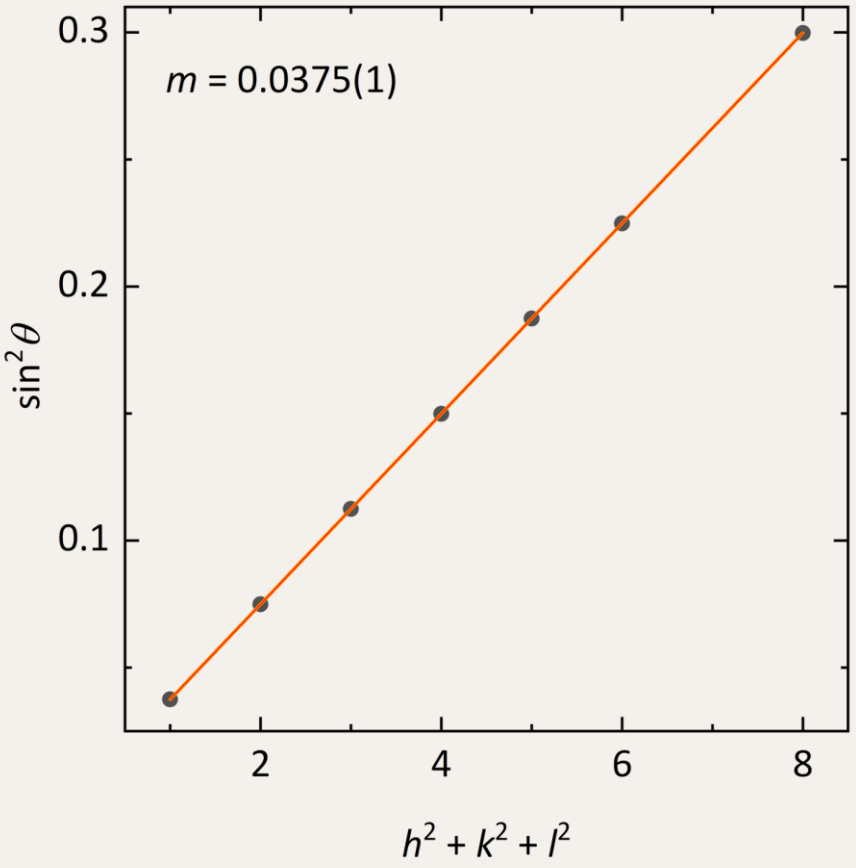
Calculate from 2θ

Find an integer value for common factor

Find (*h*, *k*, *l*) that gives integer ratio as sum of squares

Unit Cell Determination

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$



$\lambda = 0.1594$ nm

$$\frac{\lambda^2}{4a^2} = m = 0.0375(1)$$

$$a = \sqrt{\frac{\lambda^2}{4m}} = 0.412(1) \text{ nm}$$

Rietveld Analysis of Powder Diffraction Data

It is difficult to extract reliable intensities for every reflection observed in a powder diffraction pattern, as reflections often overlap and cannot be fully resolved

This makes structural solution from powder diffraction data challenging

However, if an approximate model of the crystal structure is available, we can vary the model parameters to produce a good match for the experimental data

This process of varying a structural model to fit the whole experimental powder profile is known as **Rietveld refinement**

$$M_{\mathrm{p}} = \sum_i w_i \left(y_i^{\mathrm{obs}} - y_i^{\mathrm{calc}}\right)^2$$

Least-squares minimisation function

$$R_{\mathrm{wp}} = \left(\frac{\sum_i w_i \left(y_i^{\mathrm{obs}} - y_i^{\mathrm{calc}}\right)^2}{\sum_i w_i \left(y_i^{\mathrm{obs}}\right)^2} \right)^{\frac{1}{2}} \times 100\ \%$$

Weighted-profile residual

Softwares for Rietveld Analysis

To perform a Rietveld analysis of a powder diffraction dataset, you will need:

1. Data file for the powder diffraction pattern to be analysed,
2. Crystallographic information file (.cif) for the starting structural model,
3. Instrument parameter file for the diffractometer on which data were collected,
4. Rietveld refinement software.

CIFs of known structures can be downloaded through ISCD or CSD

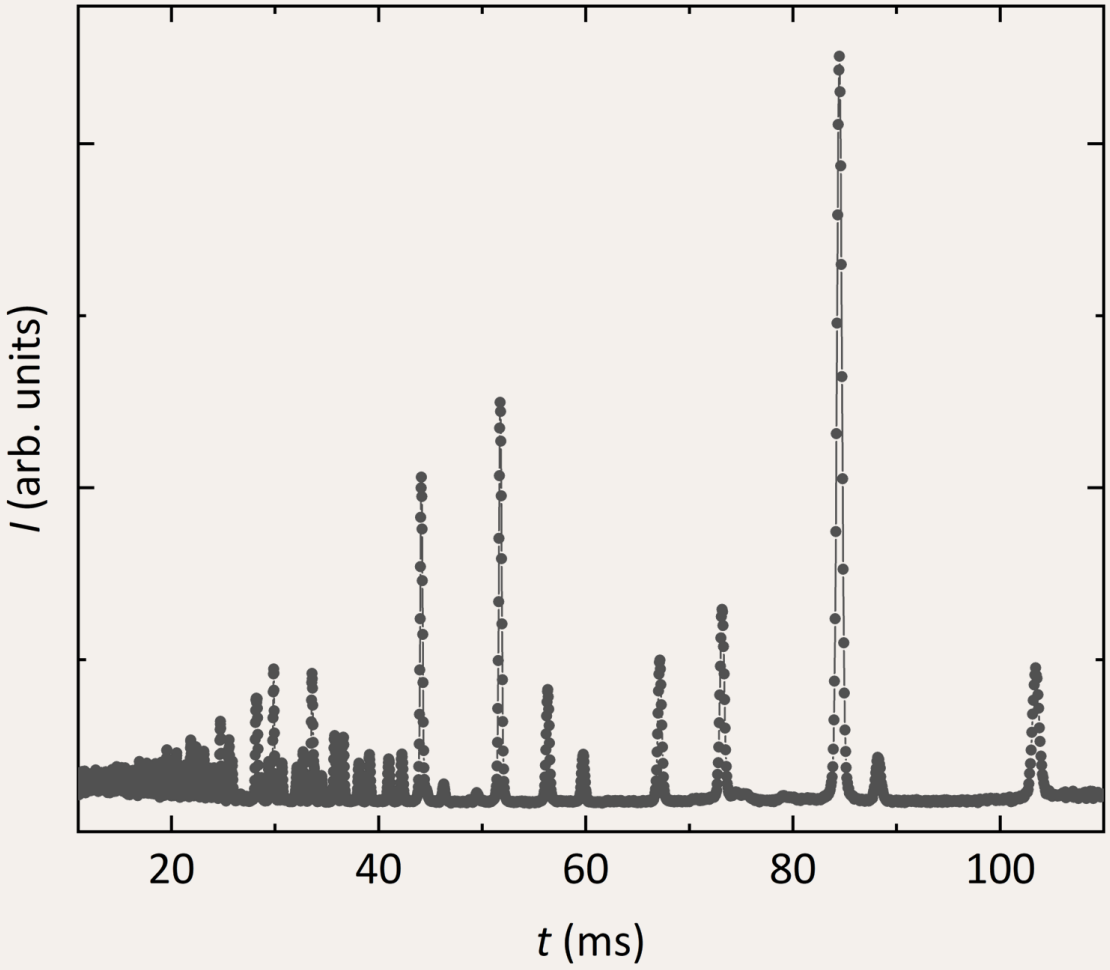
Freely accessible Rietveld refinement softwares include:

- GSAS I: https://subversion.xray.aps.anl.gov/trac/EXPGUI
- GSAS II: https://subversion.xray.aps.anl.gov/trac/pyGSAS/
- FullProf: https://www.ill.eu/sites/fullprof/php/downloads.html
- Mag2Pol: https://www.ill.eu/users/instruments/instruments-list/d3/software
- Jana: http://jana.fzu.cz/

A widely used licensed software is Topas: http://www.topas-academic.net/

A Case Study

Time-of-flight powder neutron diffraction pattern of ZnV_2O_4



Instrumental details:

L = 96 m, $2\theta = 90°$, T = 300 K

Sample details:

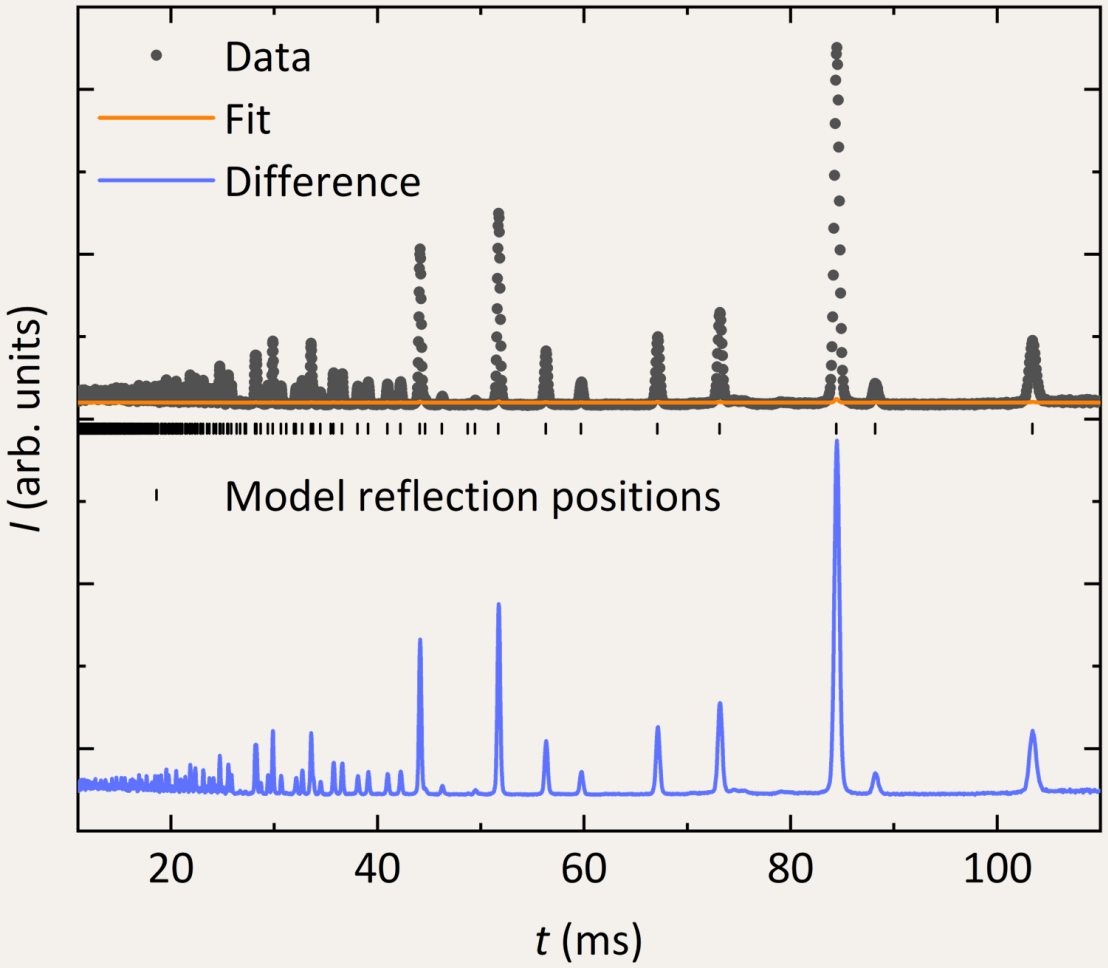
ZnV_2O_4

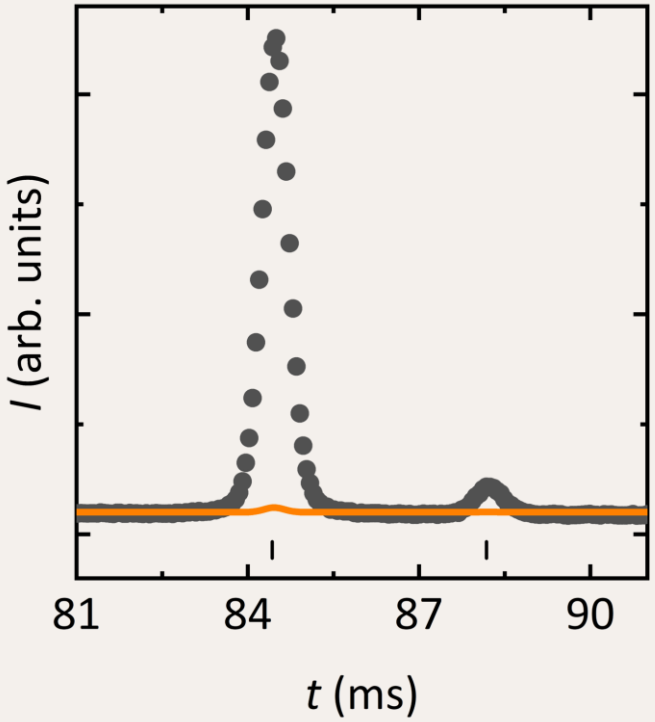
Cubic ($Fd\bar{3}m$)

Zn^{2+}: (0.125, 0.125, 0.125)
V^{4+}: (0.5, 0.5, 0.5)
O^{2-}: (x, x, x)

Rietveld Analysis of Powder Neutron Diffraction Data

Step 1: Read in the data, instrumental details and crystal structure model

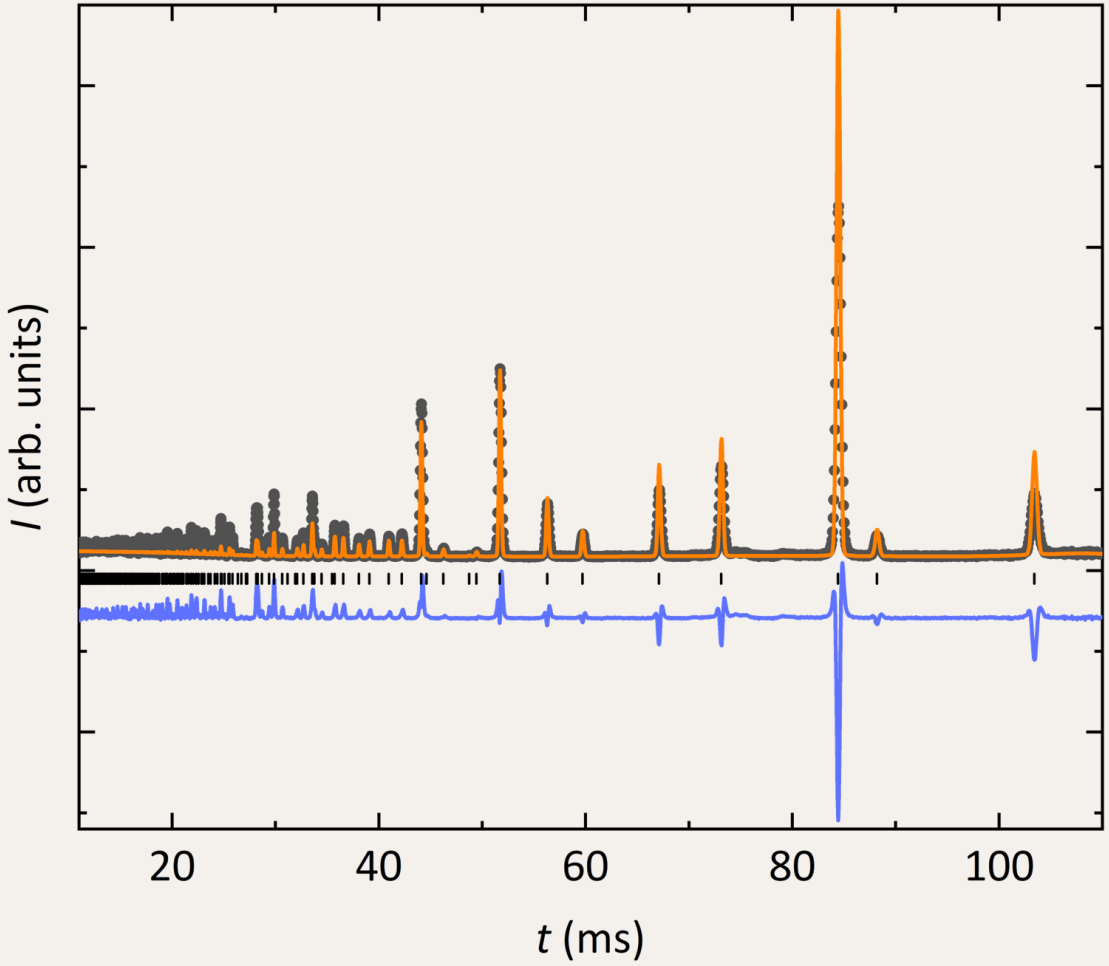


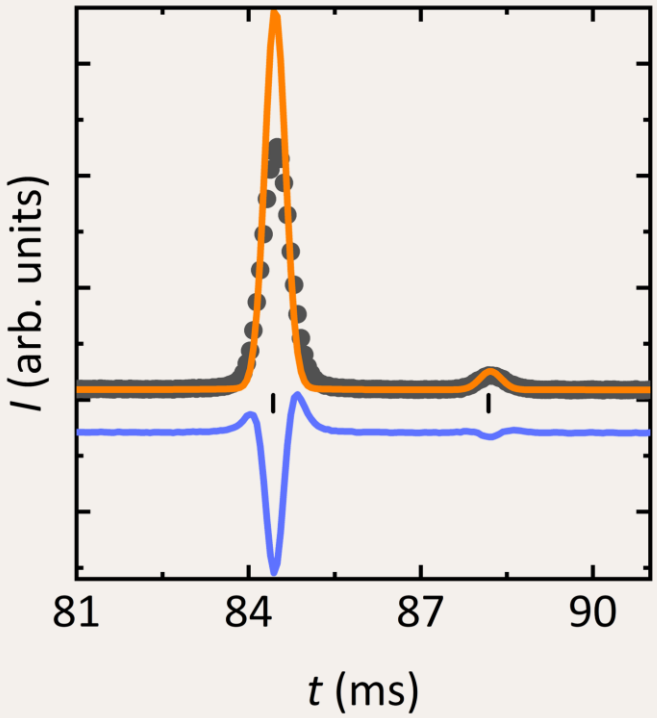


R_{wp} = 45.81 %

Rietveld Analysis of Powder Neutron Diffraction Data

Step 2: Refine the background and the overall scale

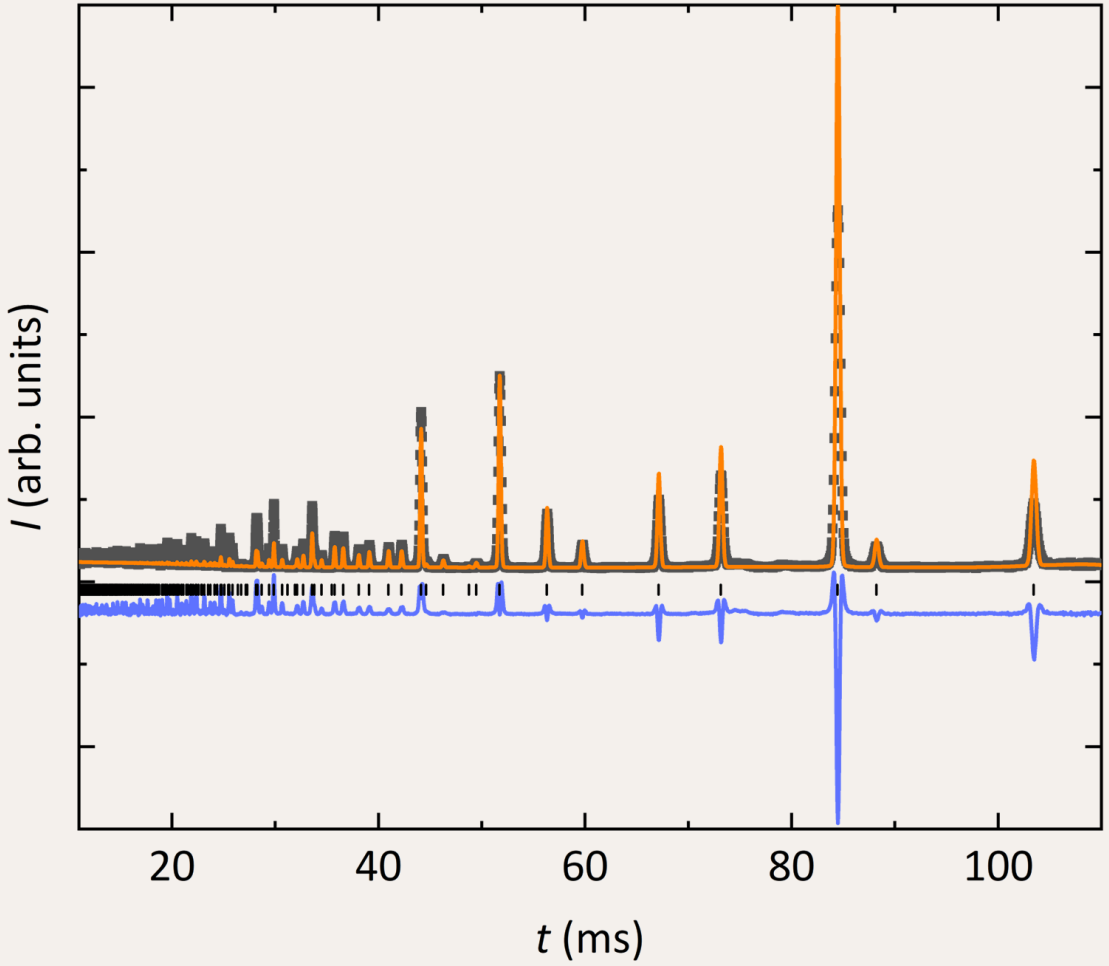


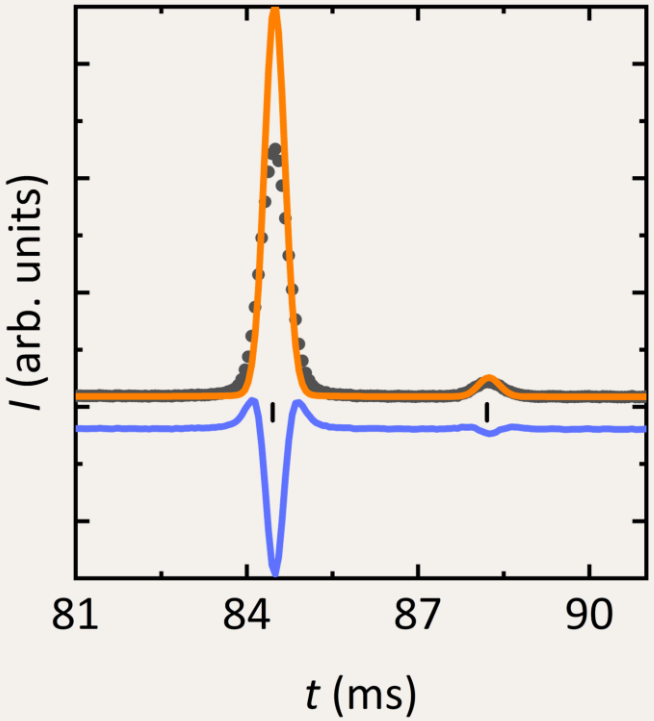


R_{wp} = 20.48 %

Rietveld Analysis of Powder Neutron Diffraction Data

Step 3: Refine the unit cell parameters



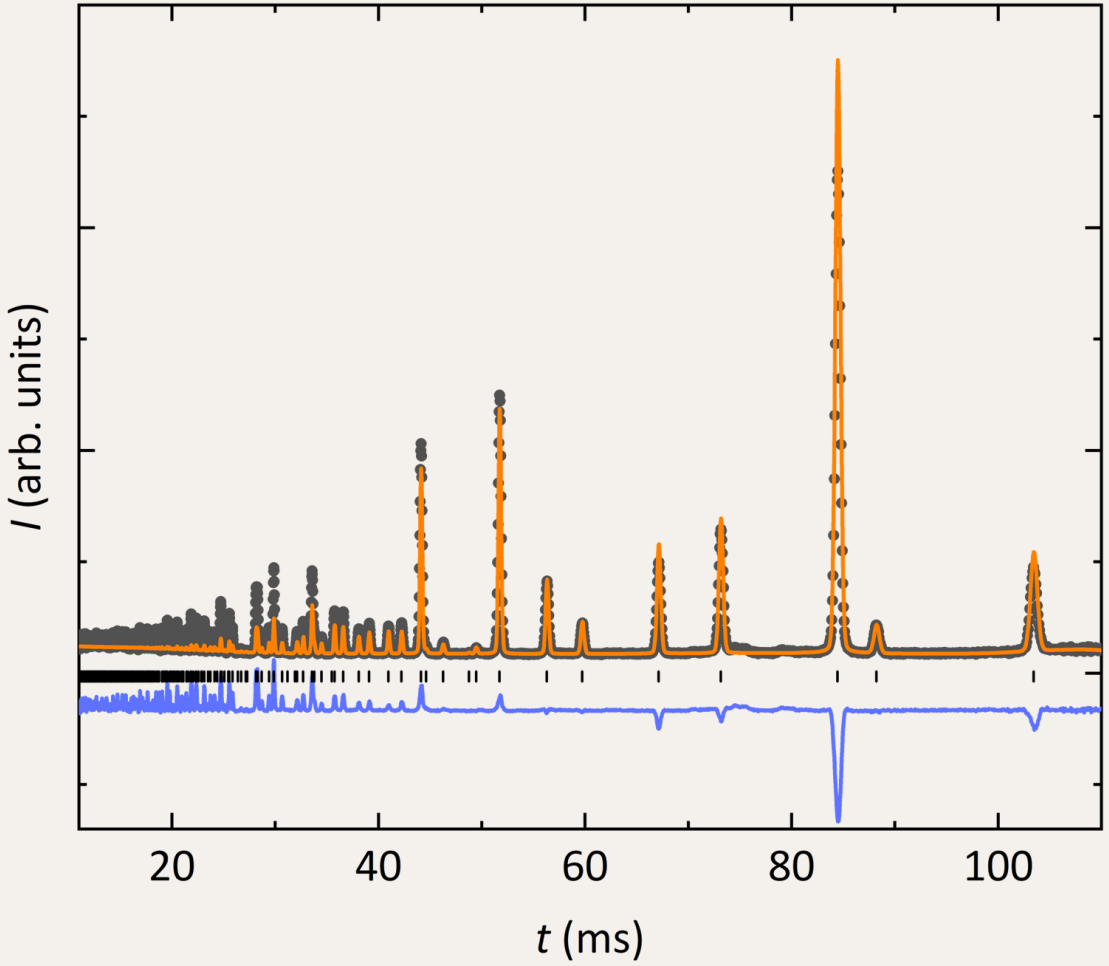


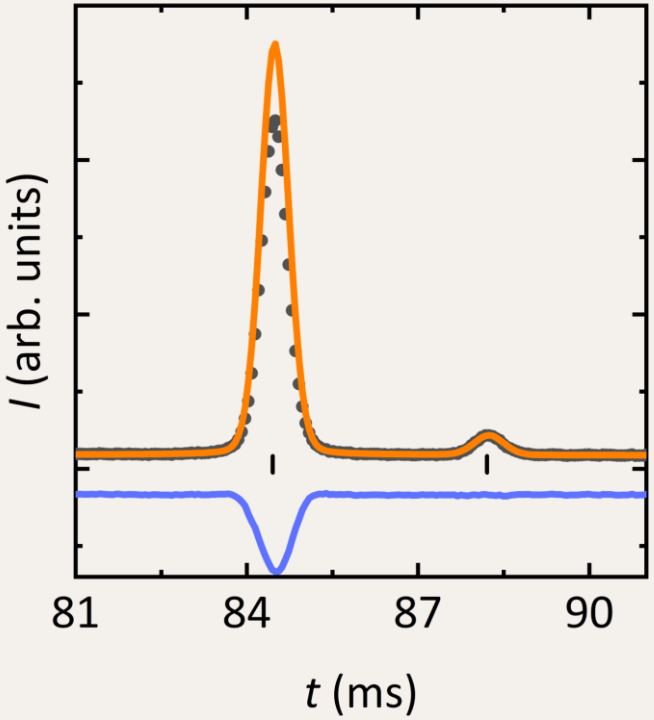
R_{wp} = 19.79 %

a = 0.8950(1) nm

Rietveld Analysis of Powder Neutron Diffraction Data

Step 4: Refine the peak profile parameters



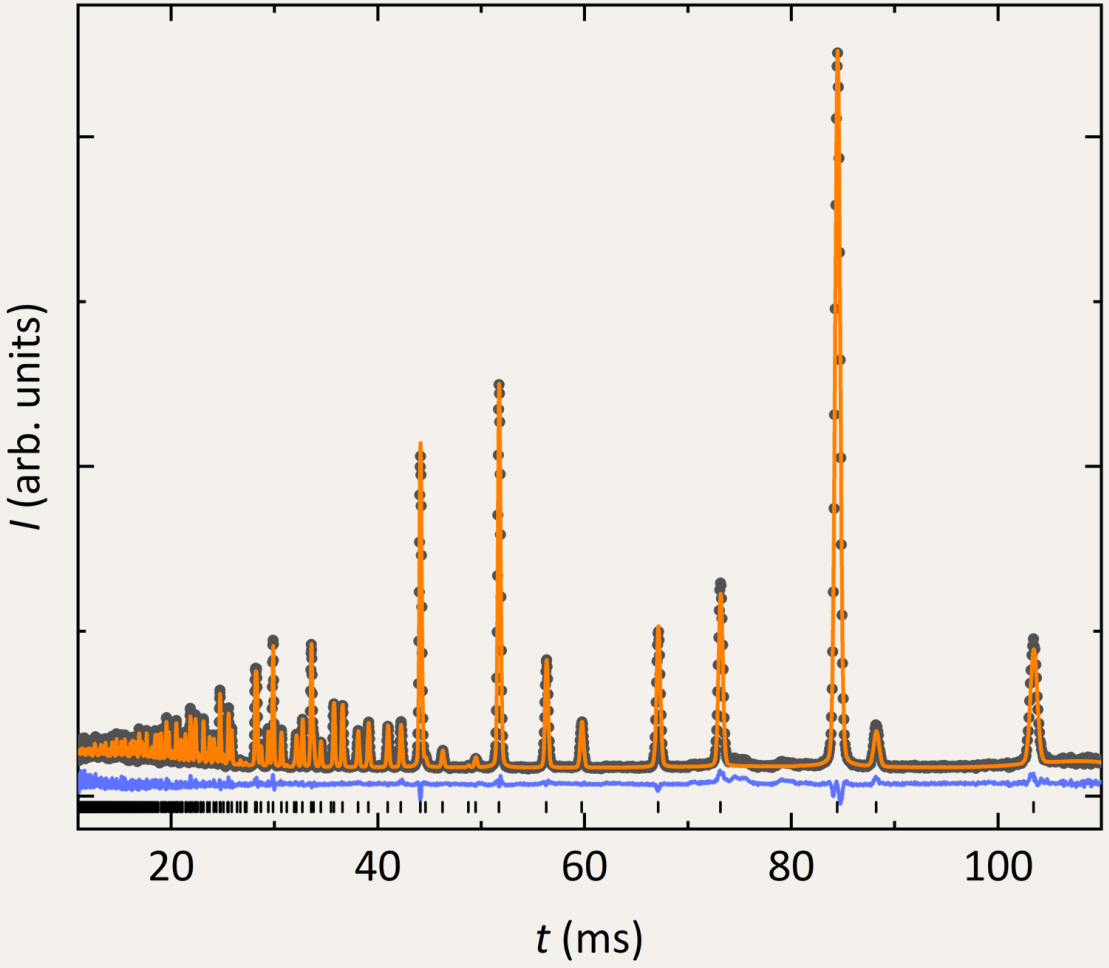


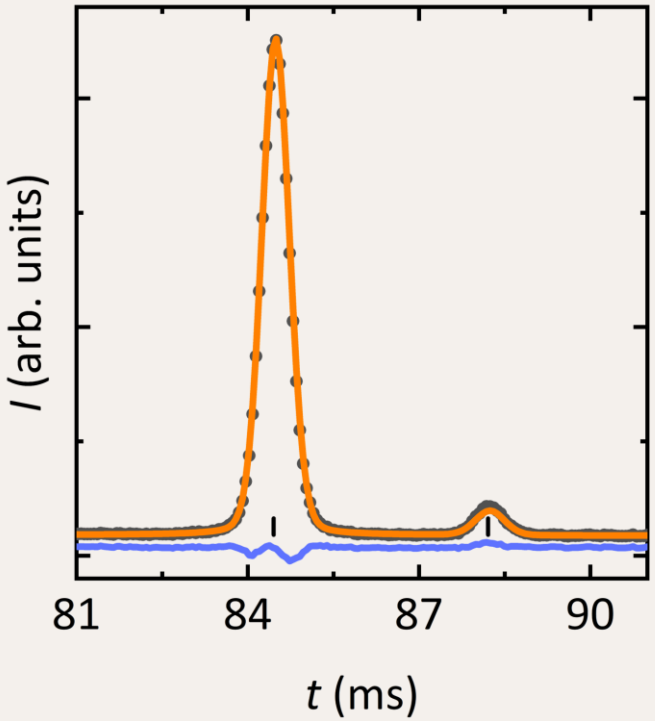
R_{wp} = 14.51 %

G = 46.(5) nm^2, L = 25.4(1) nm

Rietveld Analysis of Powder Neutron Diffraction Data

Step 5: Refine the atom positions and thermal displacements





R_{wp} = 3.69 %

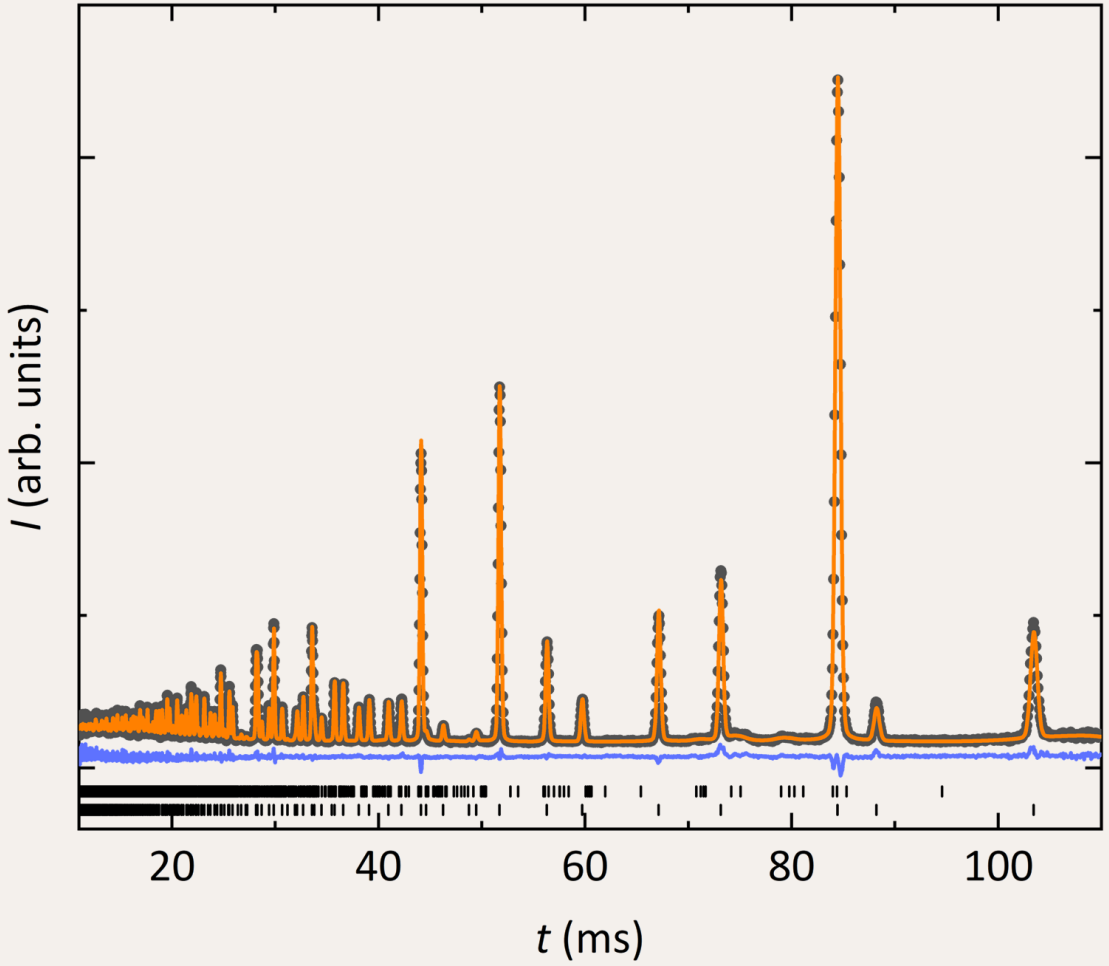
O x = 0.2602(1)

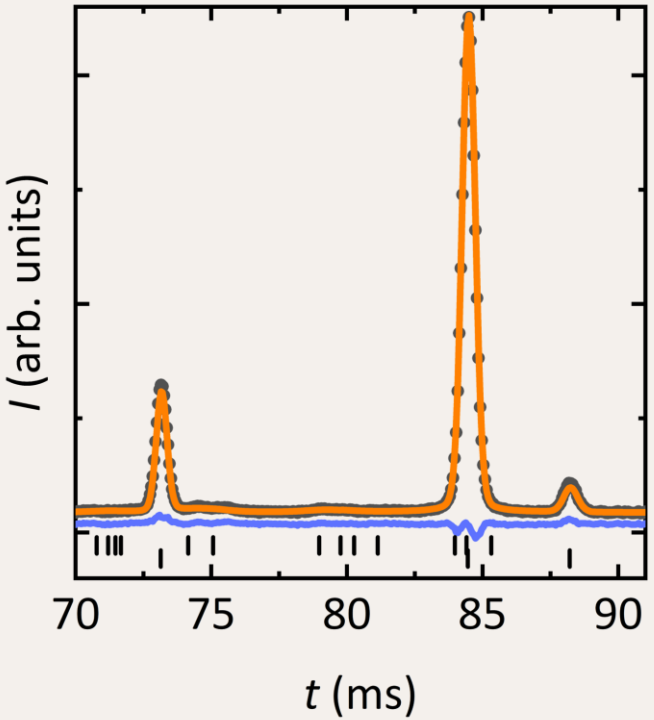
Zn U_{iso} = 2.8(2) × 10^{-5} nm^2

O U_{iso} = 3.8(1) × 10^{-5} nm^2

Rietveld Analysis of Powder Neutron Diffraction Data

Step 6: Add and refine any additional phases as needed

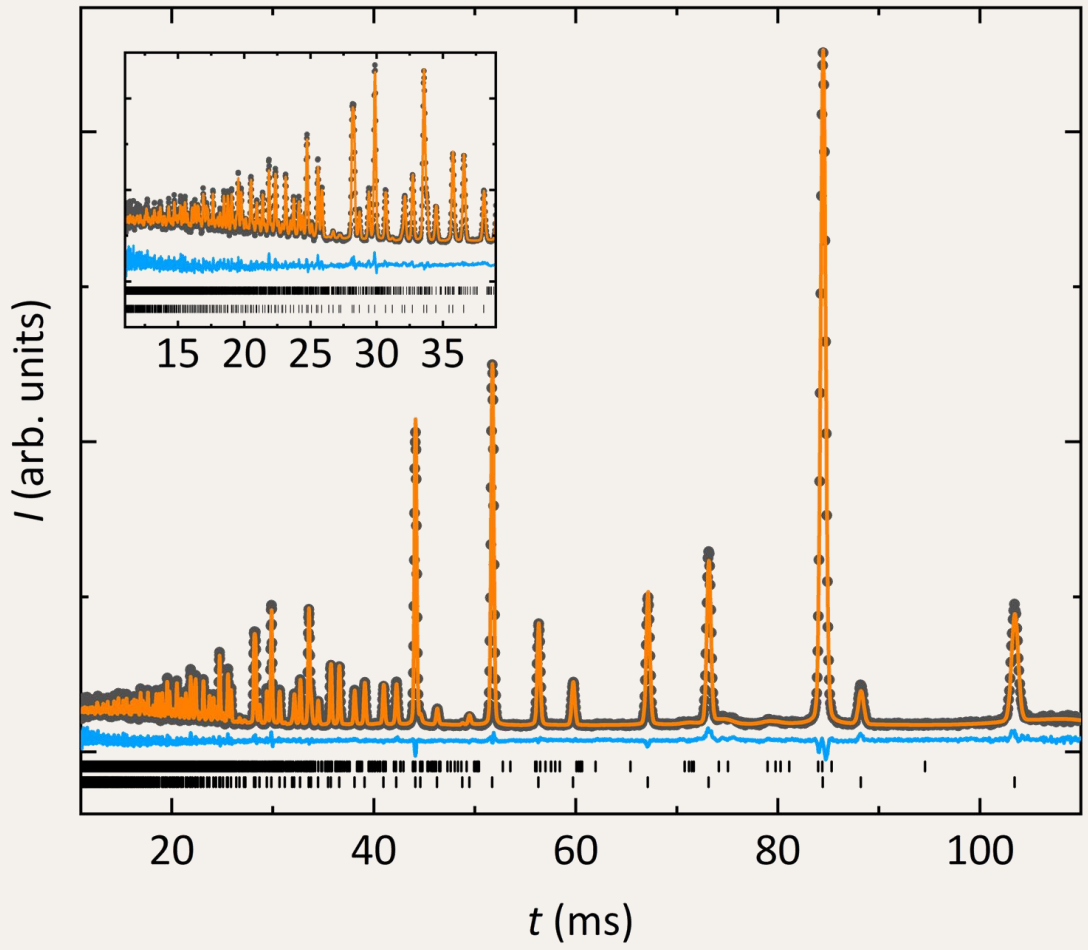




R_{wp} = 3.21 %

V_2O_3 = 2.9(1) %

Publishing a Rietveld Refinement



When reporting a Rietveld refinement, you should include:

- Full details of the data collection, ideally including a link to the diffraction data set(s),
- Rietveld plot of the full fitted profile range, clearly showing any detailed regions of fit,
- Full details of the refined structural model, including space group, refined unit cell parameters, atom positions, thermal parameters and occupancies,
- Fit figures of merit, including $R_{wp,}$
- An exported CIF of the refined structural model, which may be uploaded to a relevant database,
- As much further detail as necessary to ensure the fitting procedure is **reproducible.**