

Cal State Fullerton

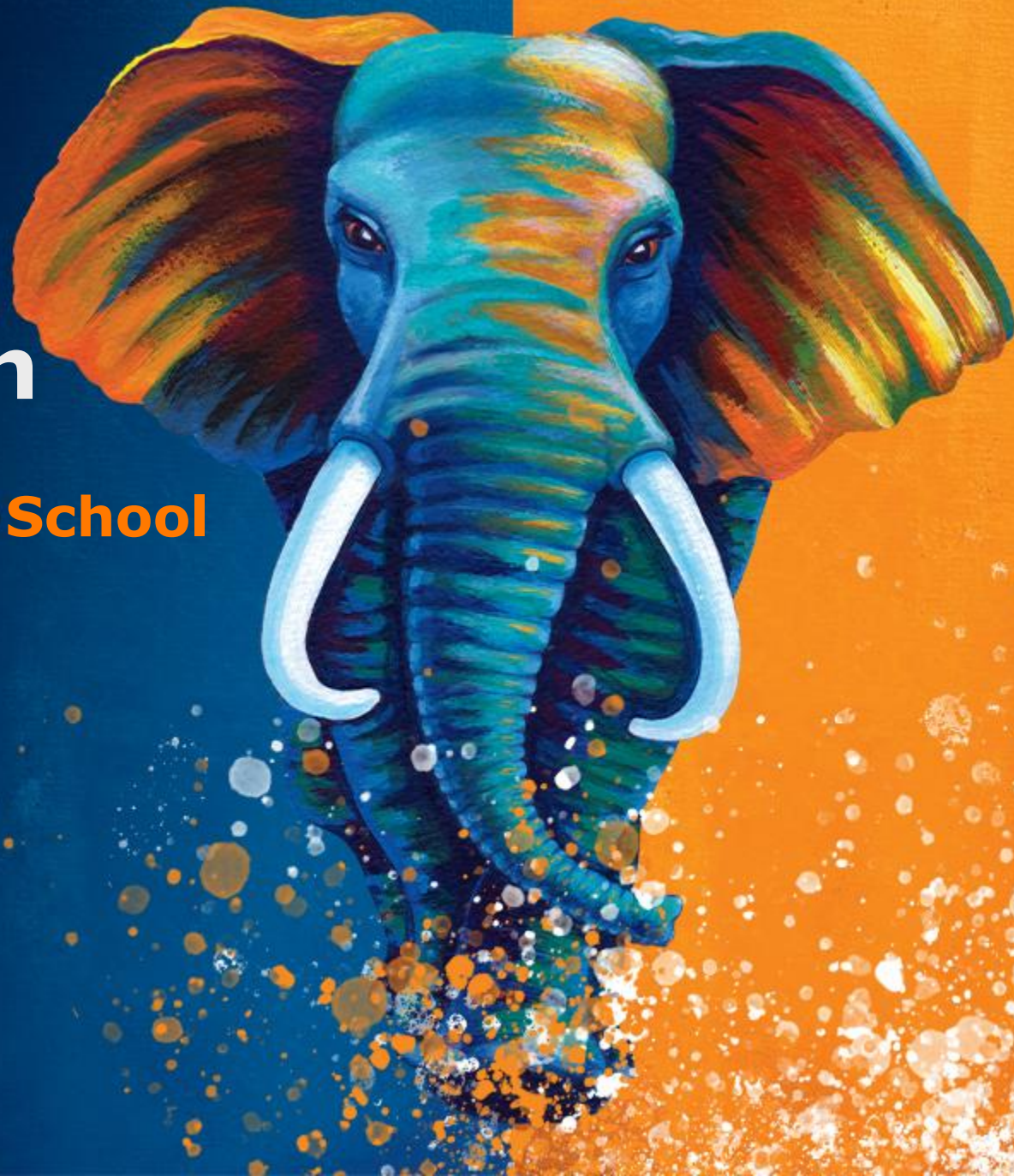
Powder Diffraction

National Neutron Scattering School

Dr. Allyson Fry-Petit

Oak Ridge National Lab

Aug 30, 2026



Blast from the past (2011)



Blast from the past (2011)



Neutron Journey



Bachelors

William Jewell College
Liberal Arts

Neutron Usage

Part of the atom??



PhD

The Ohio State
R01

Neutron Usage

Diffraction: ORNL Mail-in



Post Doc

Johns Hopkins
R01

Neutron Usage

Diffraction: ORNL SNS Mail-in
"Mail-in" NIST and Los Alamos
PDF: ORNL SNS
DyPDF: ORNL SNS



Professor

CSUF
Comprehensive

Neutron Usage

Diffraction: ORNL SNS Mail-in
"Mail-in" NIST and ORNL
HFIR
PDF: ORNL SNS
DyPDF: ORNL SNS
ISIS

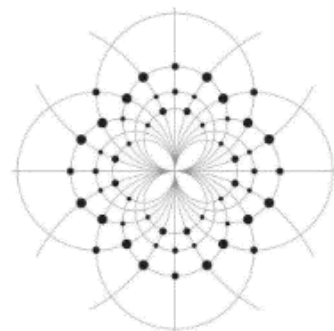
Agenda and Acknowledgements

- Short history of powder diffraction
 - Intro to theory of powder diffraction
 - Neutron powder diffraction applications
- Dr. Ashfia Huq (Molecular Foundry)
 - Dr. Cora Lind-Kovac (U of Toledo)
 - Dr. Saul Lapidus (Advanced Photon Source)
 - Dr. Joshua Goldberg (OSU)
 - Dr. Patrick Woodward (OSU)

Development of X-ray Technology

Discovery of X-rays

Roentgen's groundbreaking discovery in 1895

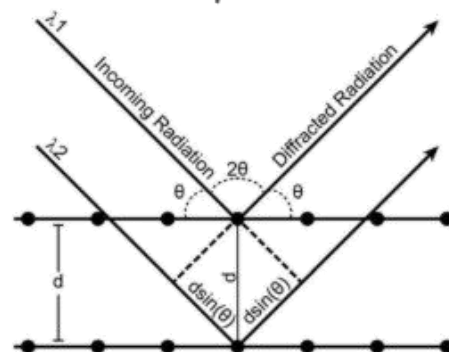


Diffraction of X-rays

von Laue's work on X-ray diffraction in 1912

Bragg's Laws

Bragg & Bragg's formulation of diffraction laws in 1912-1913
Nobel Prize in 1915



Powder Diffraction

Independent development by:
Debye and Scherrer in Germany 1916
Hull in US 1917

First Commercial Diffractometer

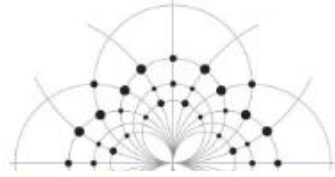
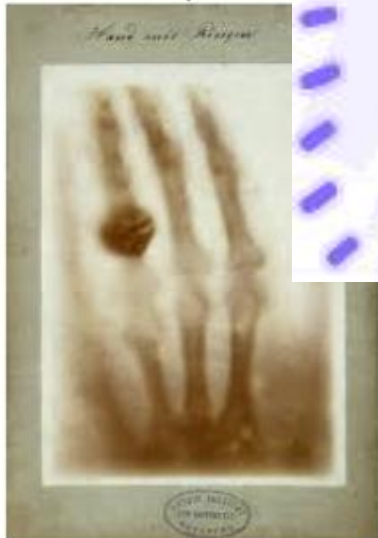
Philips' introduction of the PW1050 in 1947



Development of X-ray Technology

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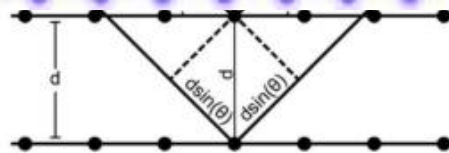
Bragg's Laws

Bragg & Bragg's formulation of

First Commercial Diffractometer

Detectors and optics have improved a lot, but basic design remains similar!

X-ray diffraction in 1912



development by:
Debye and Scherrer in Germany 1916
Hull in US 1917



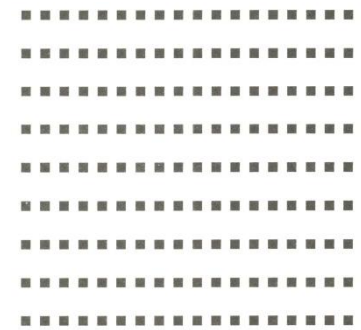
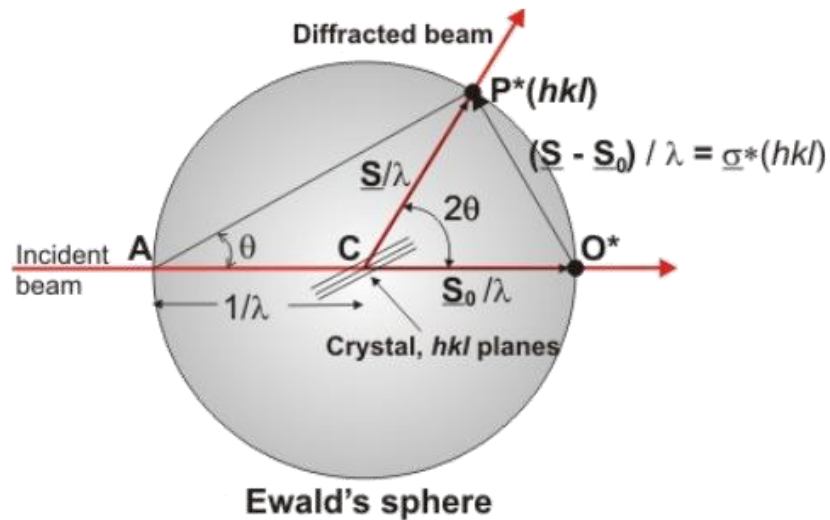
Observations from Single Crystals

Single crystal

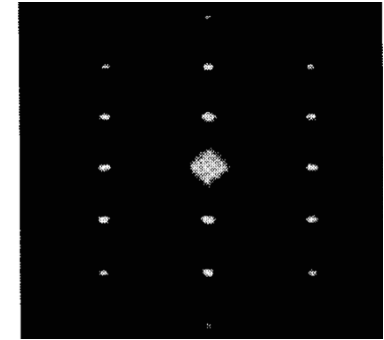
1 orientation in real space

1 orientation of the reciprocal lattice

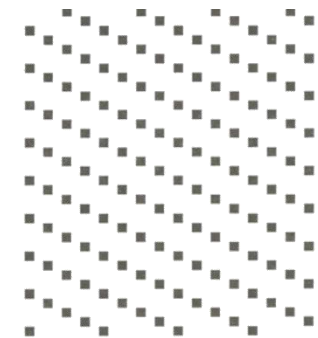
- Rotating the crystal rotates the reciprocal lattice
- Reciprocal lattice points are resolved and will result in diffraction intensity when they touch the Ewald sphere



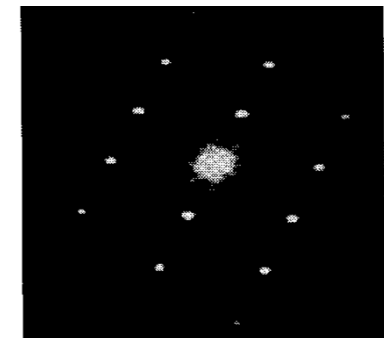
Real space



Reciprocal space



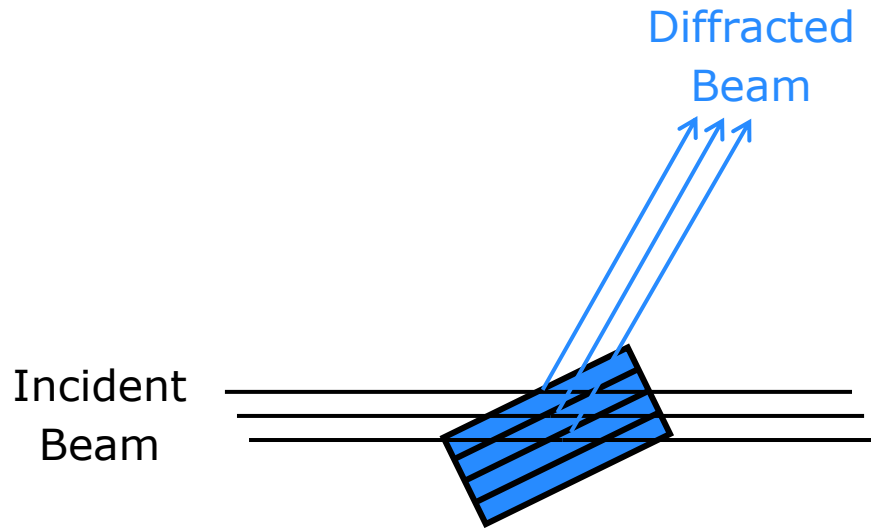
Real space



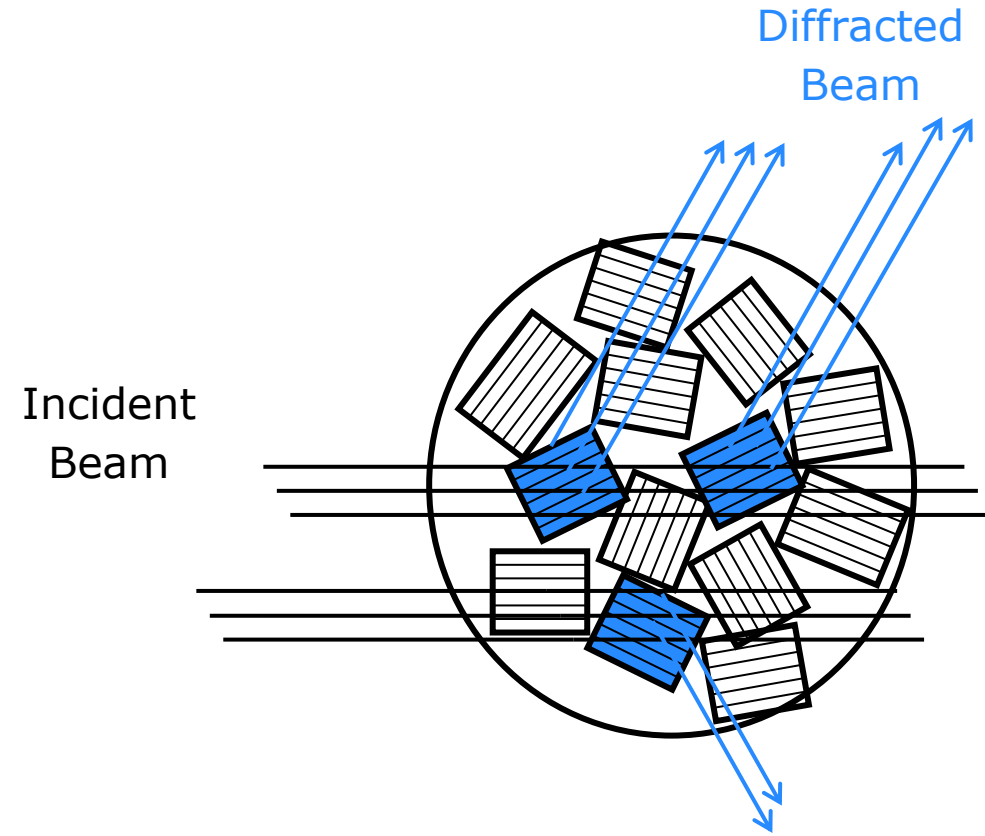
Reciprocal space

Diffraction Samples

Single Crystal Diffraction



Powder Diffraction



Original Powder Setups

- Oldest method: Debye-Scherrer camera
 - Capillary sample surrounded by cylindrical film
 - Simple, cheap setup

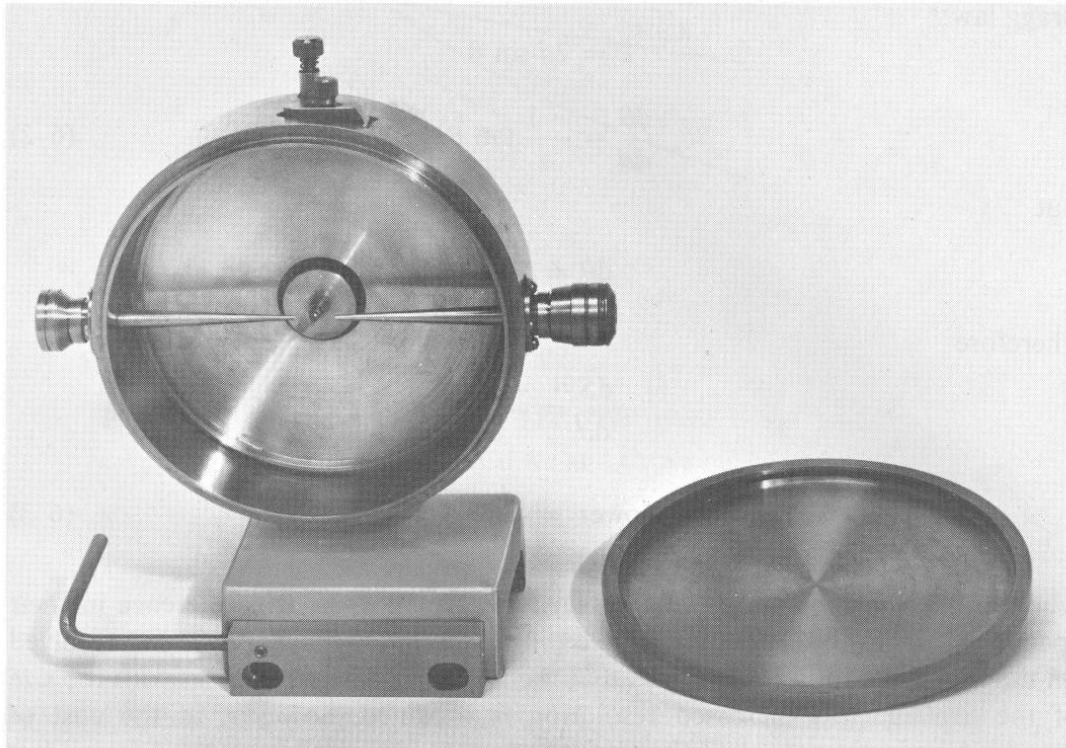


Fig. 6-1 Debye-Scherrer camera, with cover plate removed. (Courtesy of Philips Electronic Instruments, Inc.)

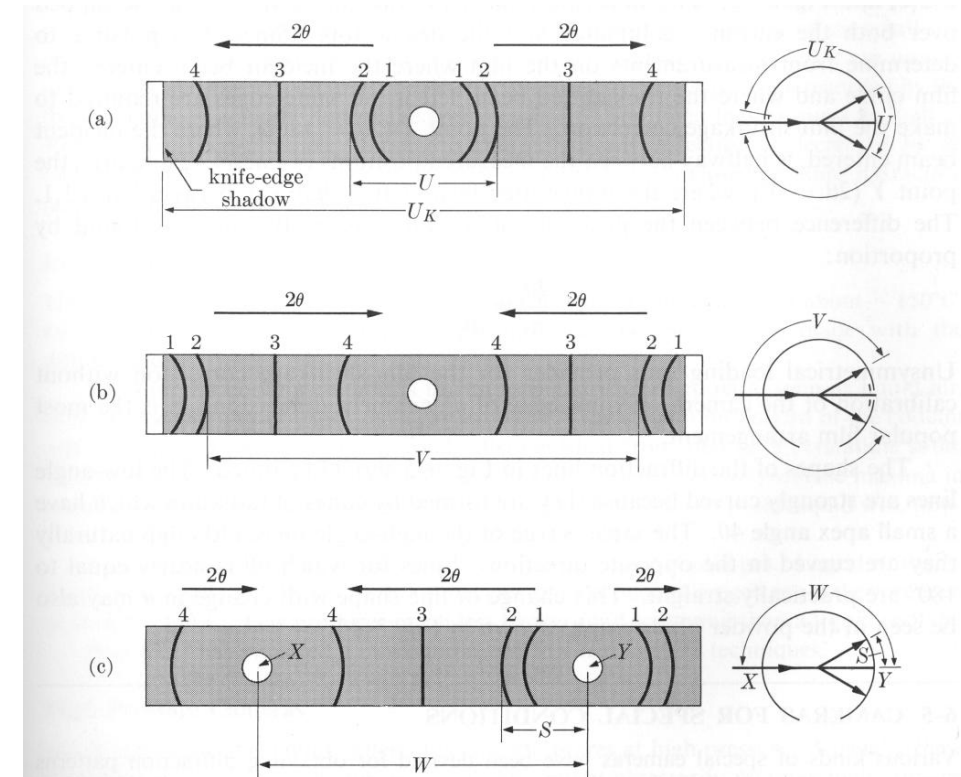
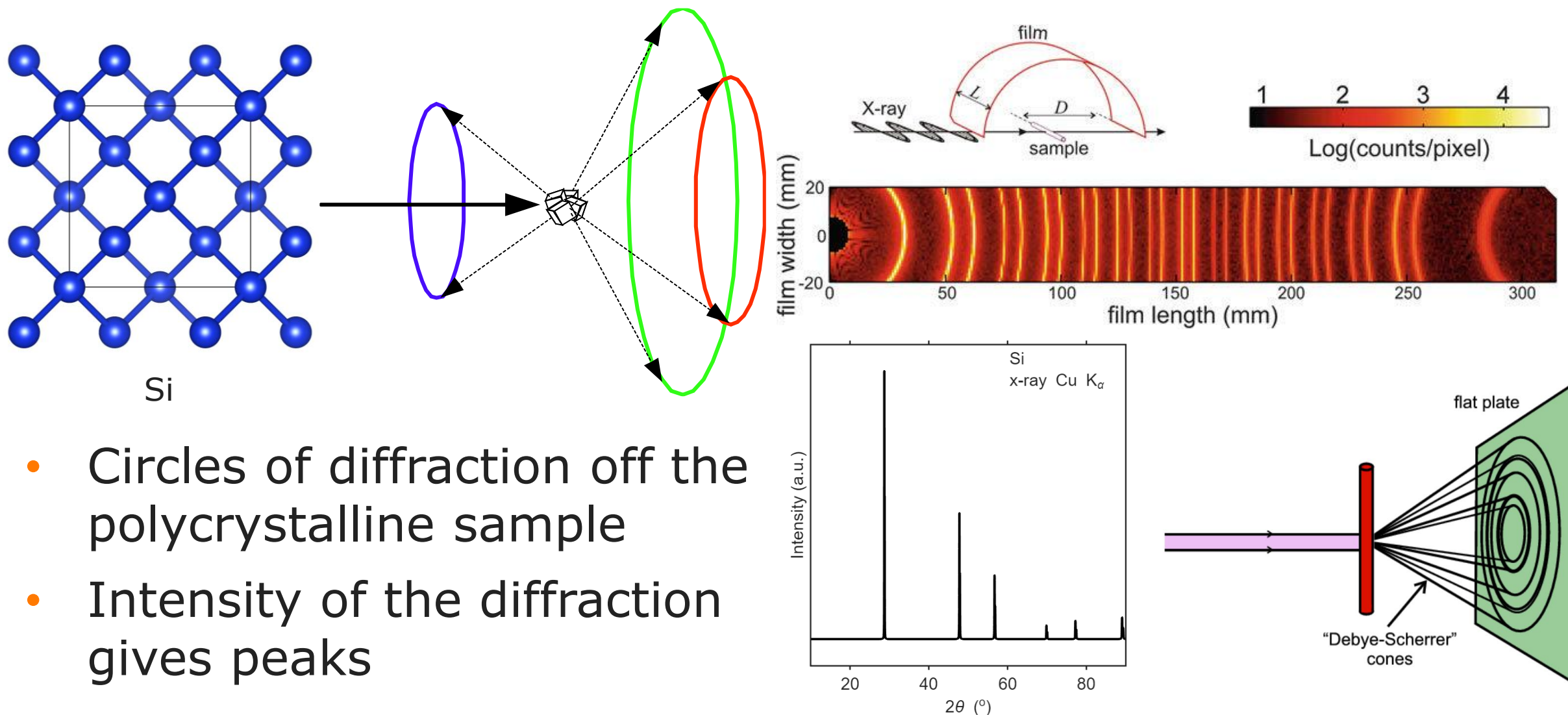
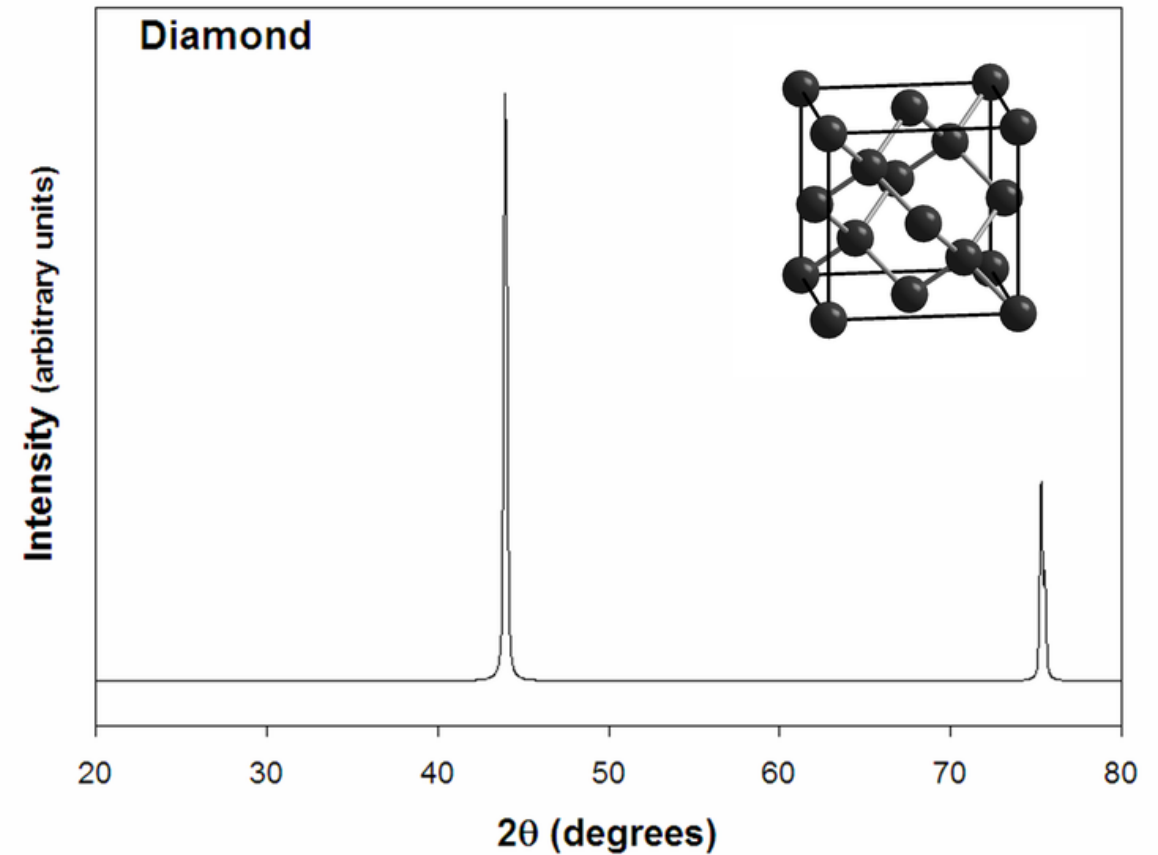
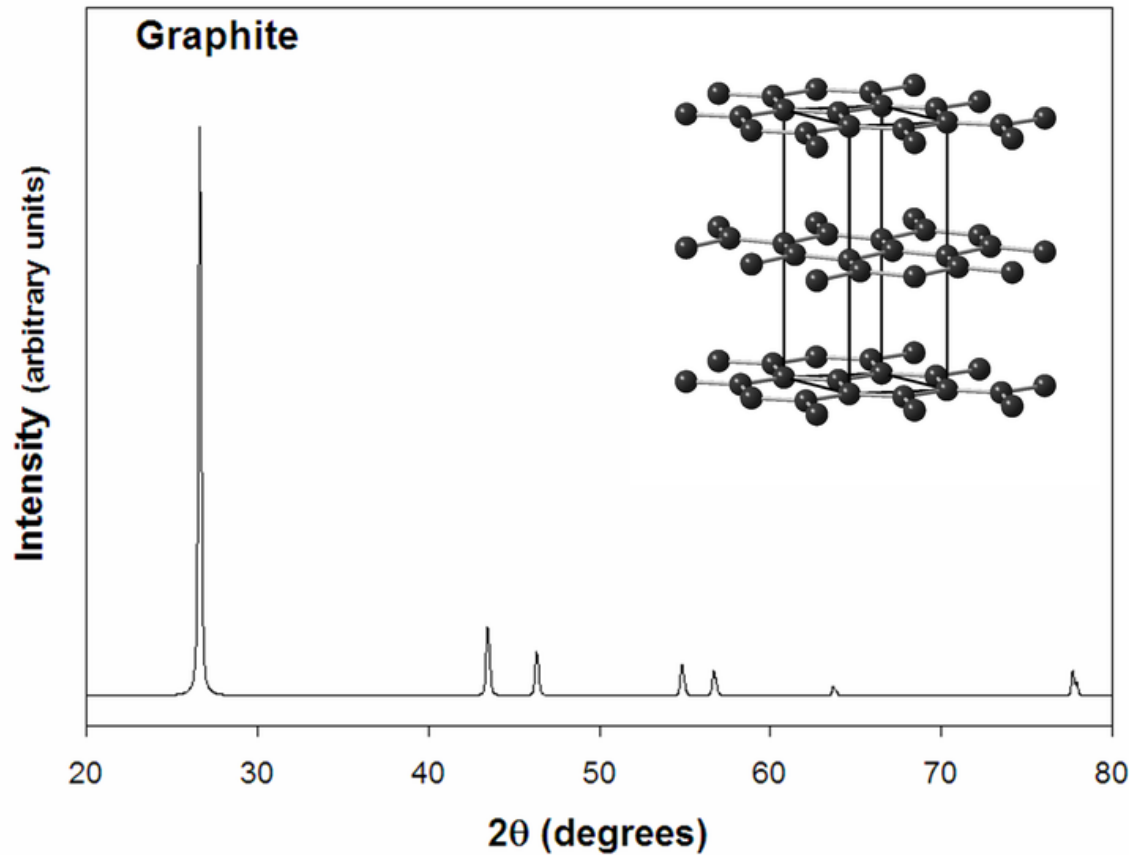


Fig. 6-5 Methods of film loading in Debye cameras. Corresponding lines have the same numbers in all films.

When we measure powders we get peaks?



Diffraction is the fingerprint of the structure

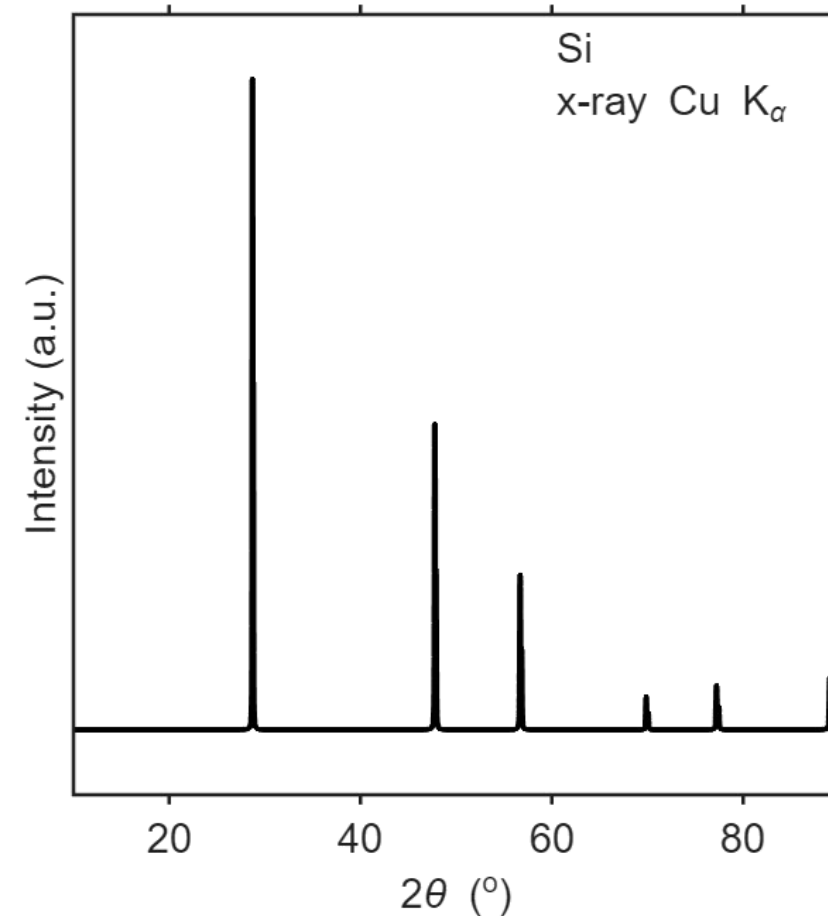


What is in a powder diffraction pattern?

x-Axis = 2θ

This is twice the angle between the incoming beam and the sample. Units are in degrees, as it refers to the angle between the incident beam and the detector.

Other units d (Å), Q (Å⁻¹), and TOF (t)



What is in a powder diffraction pattern?

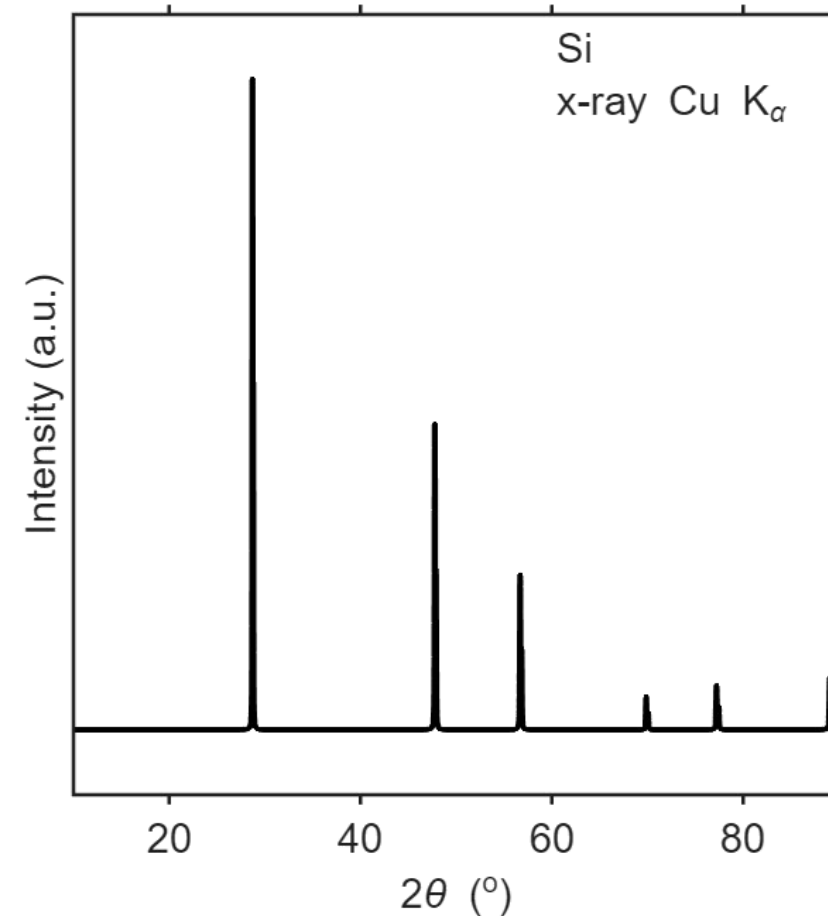
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Other units d (Å), Q (Å⁻¹), and TOF (t)

Peaks

When the angle, θ , and the interplanar spacing, d_{hkl} , satisfy Bragg's Law, constructive interference occurs, and a peak is observed.



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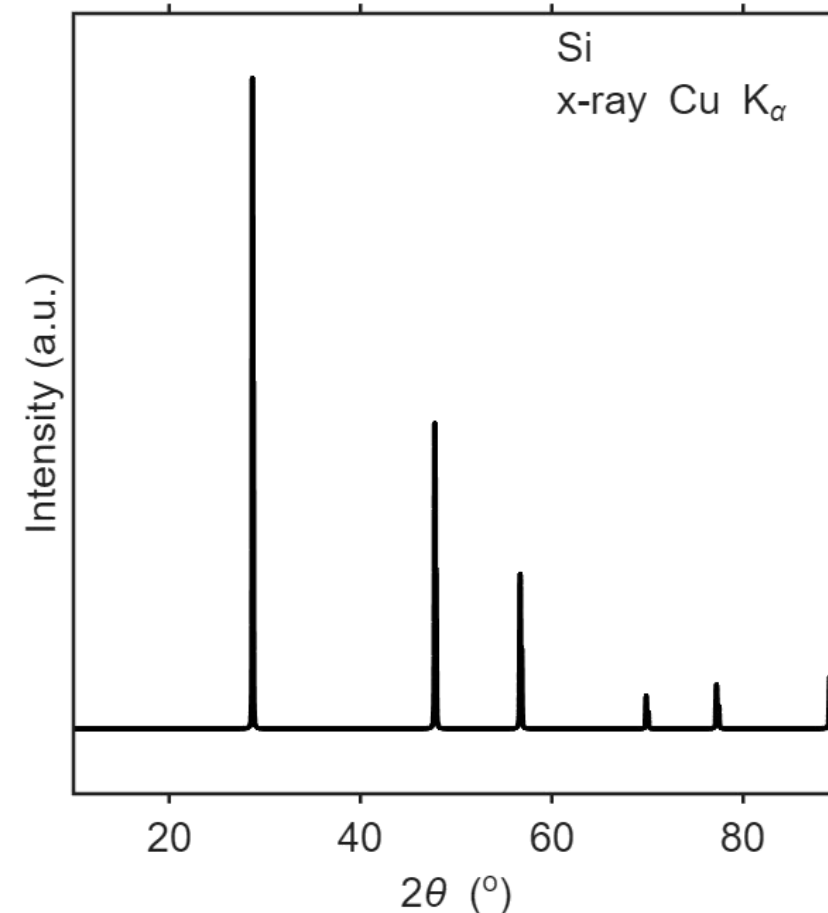
Other units d ($\text{\AA}$), Q ($\text{\AA}^{-1}$), and TOF (t)

Peaks

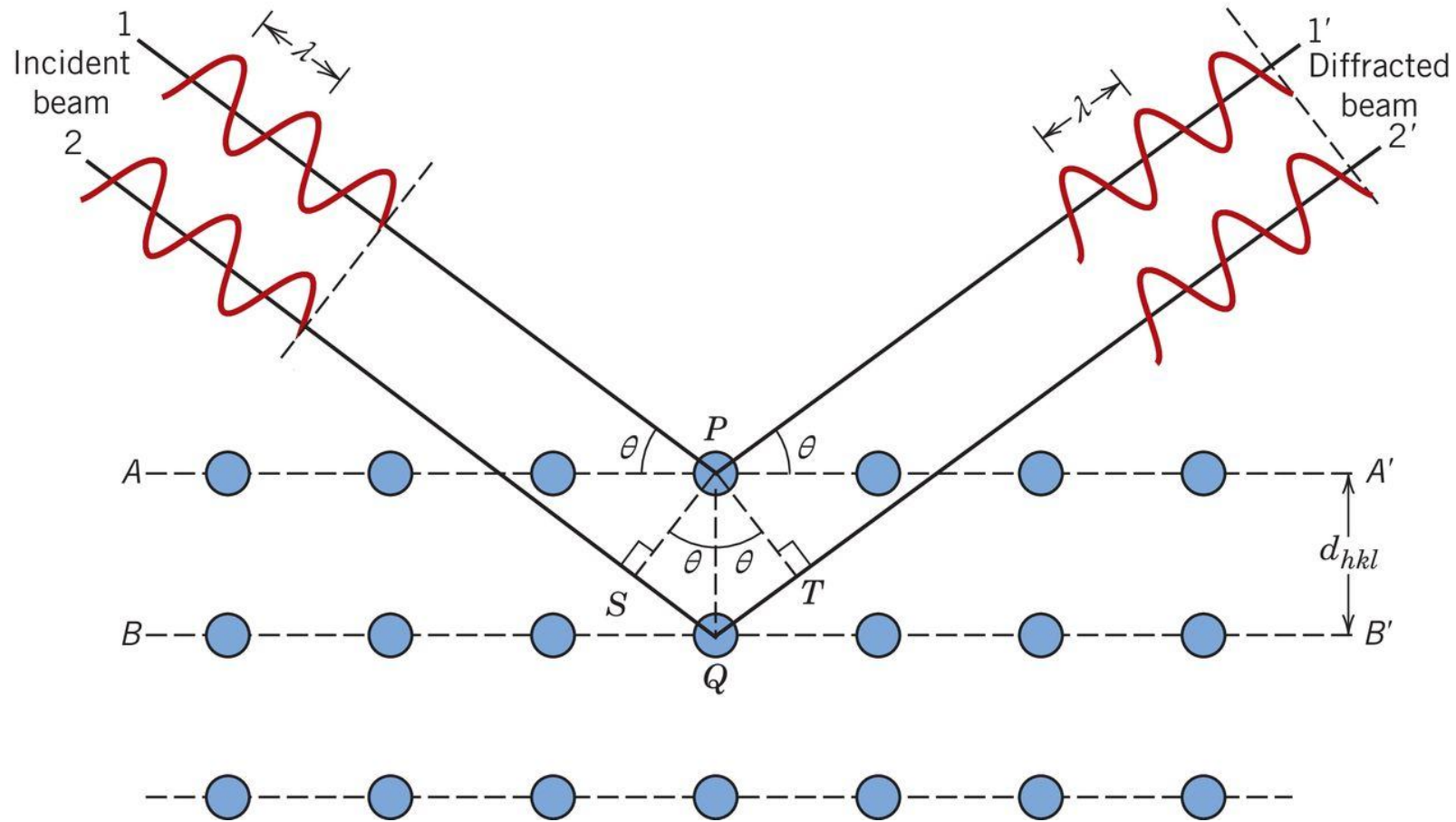
When the angle, θ , and the interplanar spacing, d_{hkl} , satisfy Bragg's Law, constructive interference occurs, and a peak is observed.

y-Axis = Intensity

Proportional to the radiation that reaches the detector and the scattering factor of each atom on the diffracting planes. Units are arbitrary as absolute units are related to the amount of sample and radiation flux.



Braggs' Law



Bragg's law
 $n\lambda = 2d \sin \theta$

*λ must be
similar in size
to the spacing
between the
atoms*

Radiation Sources

X-ray

λ : 10^{-9}m - 10^{-11}m

Source:

- Lab diffractometers
- Synchrotron Sources

Neutron

thermal λ : 1-4 Å

Source:

- Reactors (fission) (e.g. HFIR)
- Spallation Source (e.g. SNS)

Spallation Source – TOF Experiments

- ◆ Neutrons are particles with mass, so wavelength and velocity are correlated (de Broglie)

$$\lambda = \frac{h}{mv} = \frac{ht}{mL} \text{ combine with Braggs Law } \lambda = 2d \sin\theta$$

$$t = \frac{2d \sin\theta mL}{h}$$

- ◆ Data are plotted as a function of t (TOF)

Structure Factor

- ◆ Intensity of diffraction peaks is proportional to $|F(hkl)|^2$

$$F(hkl) = \sum_{j=1}^N f_j \exp(2\pi i (hx_j + ky_j + lz_j)) \cdot \exp \left[-8\pi^2 \langle u^2 \rangle \left(\frac{\sin^2(\theta)}{\lambda^2} \right) \right]$$

Structure Factor

- ◆ Intensity of diffraction peaks is proportional to $|F(hkl)|^2$

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Scattering Factor

- Dependent upon the identity of the atom

Structure Factor

- ◆ Intensity of diffraction peaks is proportional to $|F(hkl)|^2$

$$F(hkl) = \sum_{j=1}^N f_j \exp(2\pi i (hx_j + ky_j + lz_j)) \cdot \exp \left[-8\pi^2 \langle u^2 \rangle \left(\frac{\sin^2(\theta)}{\lambda^2} \right) \right]$$

Exponential Phase Term

- Accounts for atomic positions in the unit cell

Structure Factor

- ◆ Intensity of diffraction peaks is proportional to $|F(hkl)|^2$

$$F(hkl) = \sum_{j=1}^N f_j \exp(2\pi i (hx_j + ky_j + lz_j)) \exp \left[-8\pi^2 \langle u^2 \rangle \left(\frac{\sin^2(\theta)}{\lambda^2} \right) \right]$$

Debye Waller Factor

- Accounts for atomic displacements
- $\langle u^2 \rangle$ mean squared displacement of atoms

Simple Example

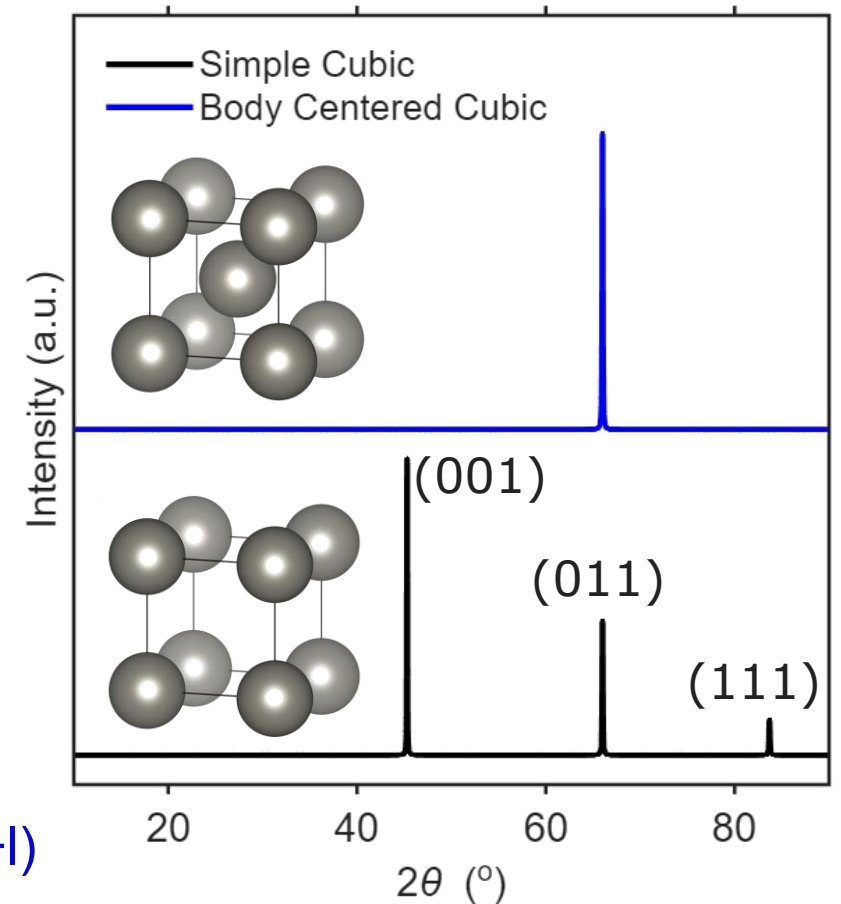
$$F(hkl) = \sum_{j=1}^N f_j \exp(2\pi i (hx_j + ky_j + lz_j))$$

Simple cubic cell with one atom basis at (000)

$$F(hkl) = f_j \exp(2\pi i (h0 + k0 + l0)) = f$$

Body centered cubic cell with atoms at (000) and ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$)

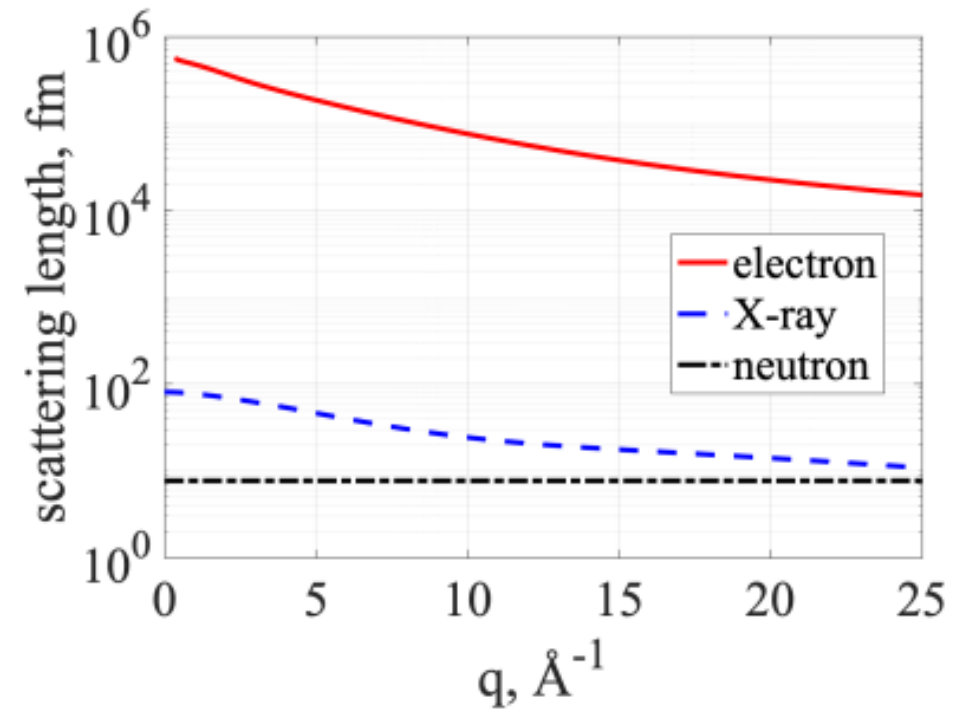
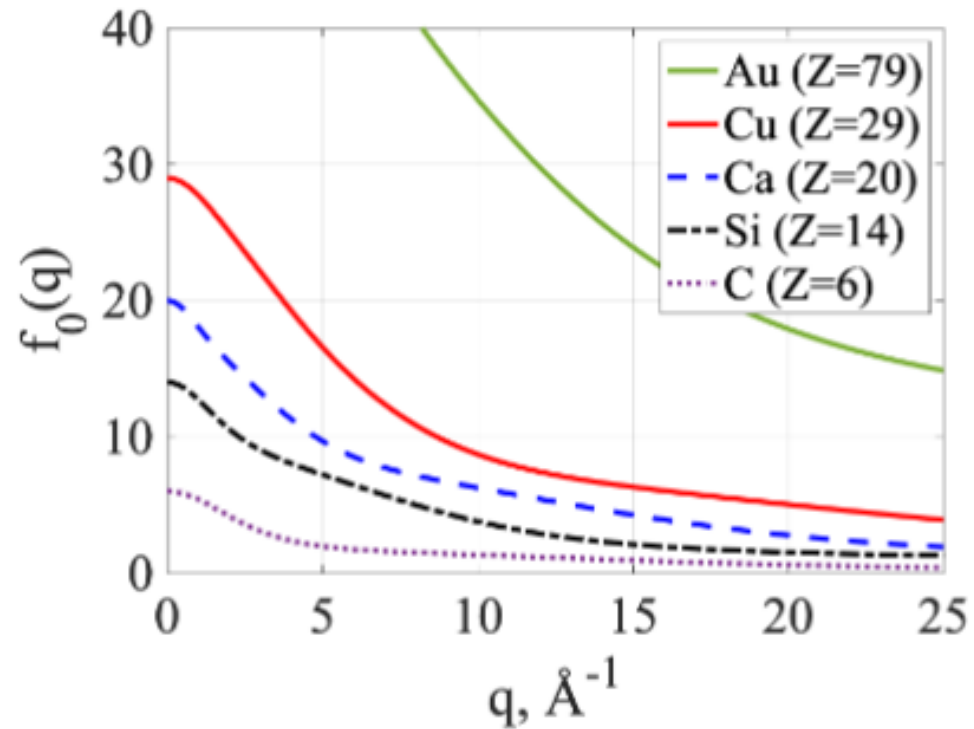
$$F(hkl) = f_j [\exp(2\pi i (h0 + k0 + l0)) + \exp(2\pi i (h + k + l) \frac{1}{2})] = 2f \text{ for even } (h+k+l) \\ = 0 \text{ for odd } (h+k+l)$$



Systematic Absences in Cubic

$(h^2+k^2+l^2)$	0	1	2	3	4	5	6	.	8	9	10	11	12	13	14	.	16	17	18	19	20	21	22	.	24
sc																									
bcc																									
fcc																									
diamond																									

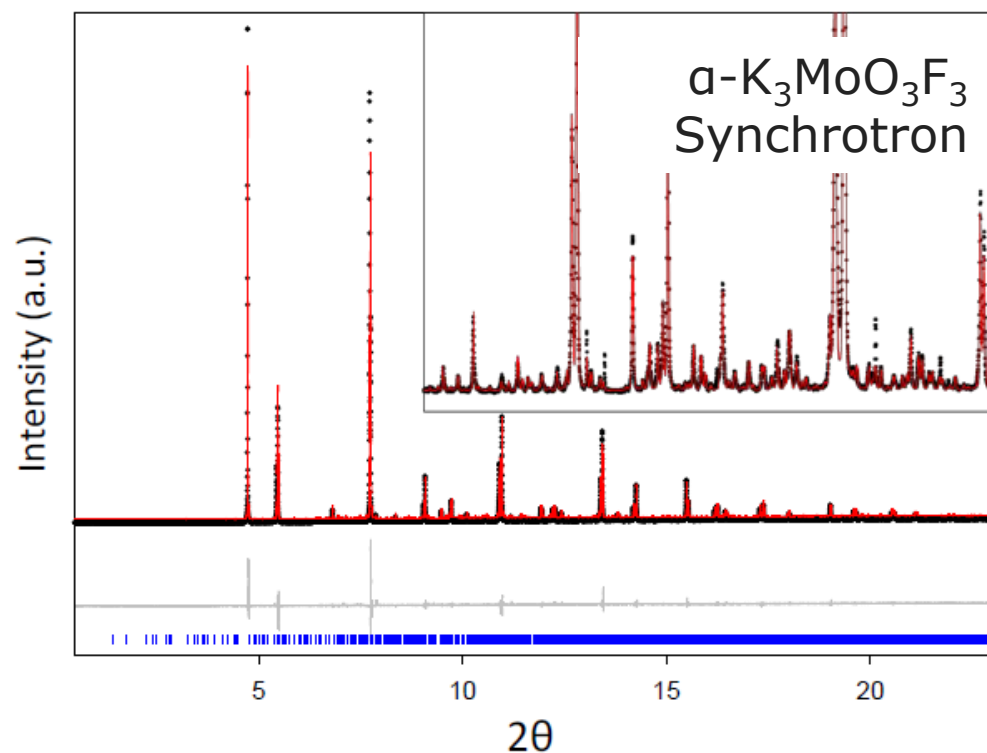
Form Factor Differences



Form Factor Differences

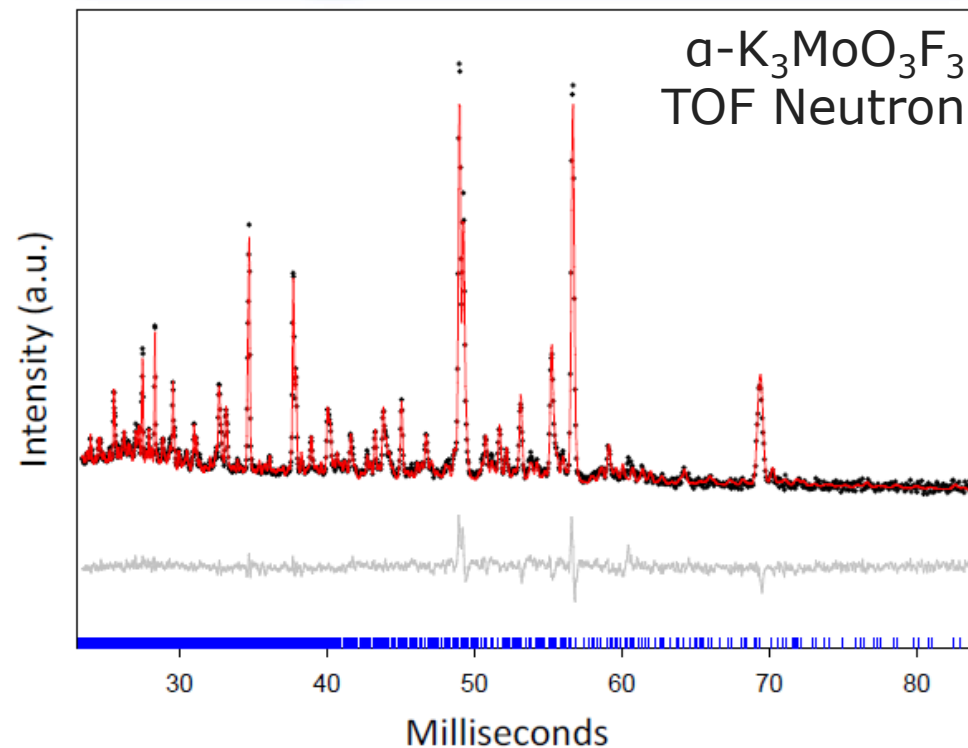
Synchrotron X-ray

Peak intensities drop off at high angles b/c of the decrease in form factor

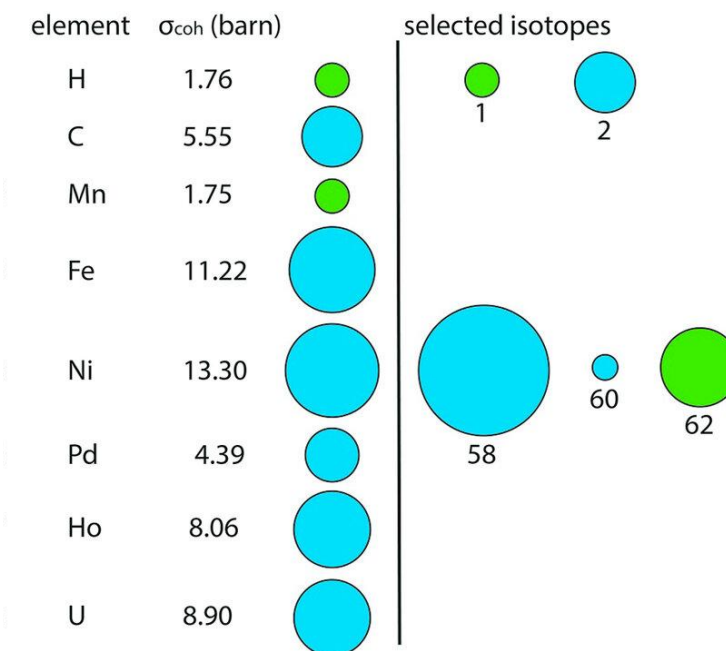
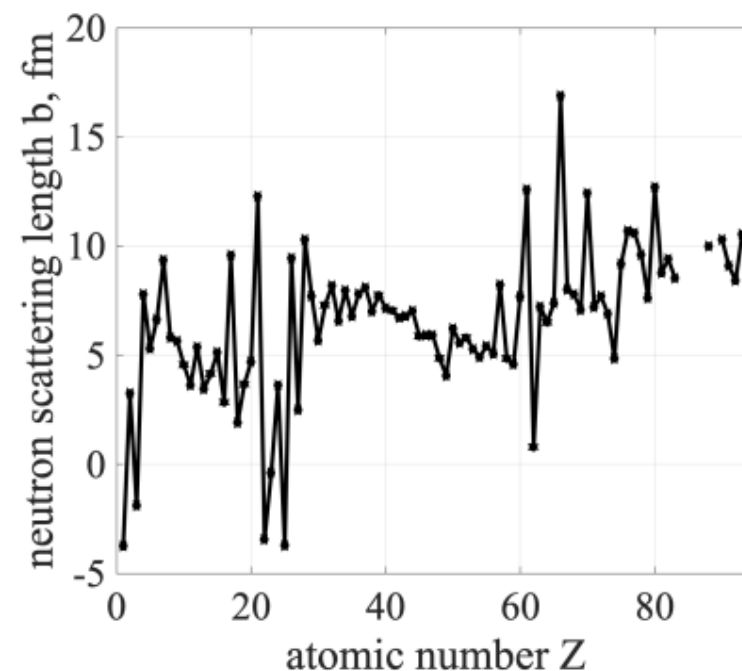
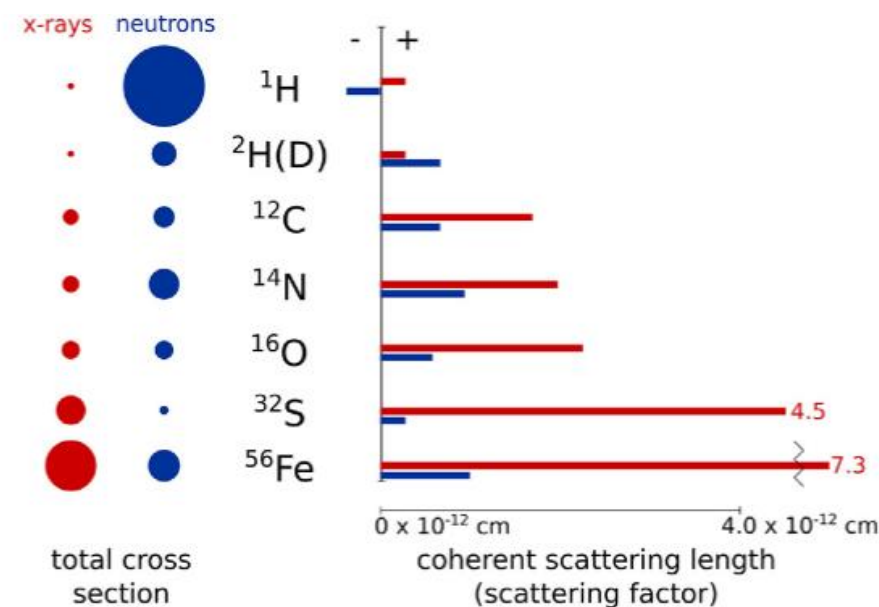


Neutron

Intensities do not drop off at high angles b/c neutrons are scattered from the nucleus and thus the form factor is not angle dependent

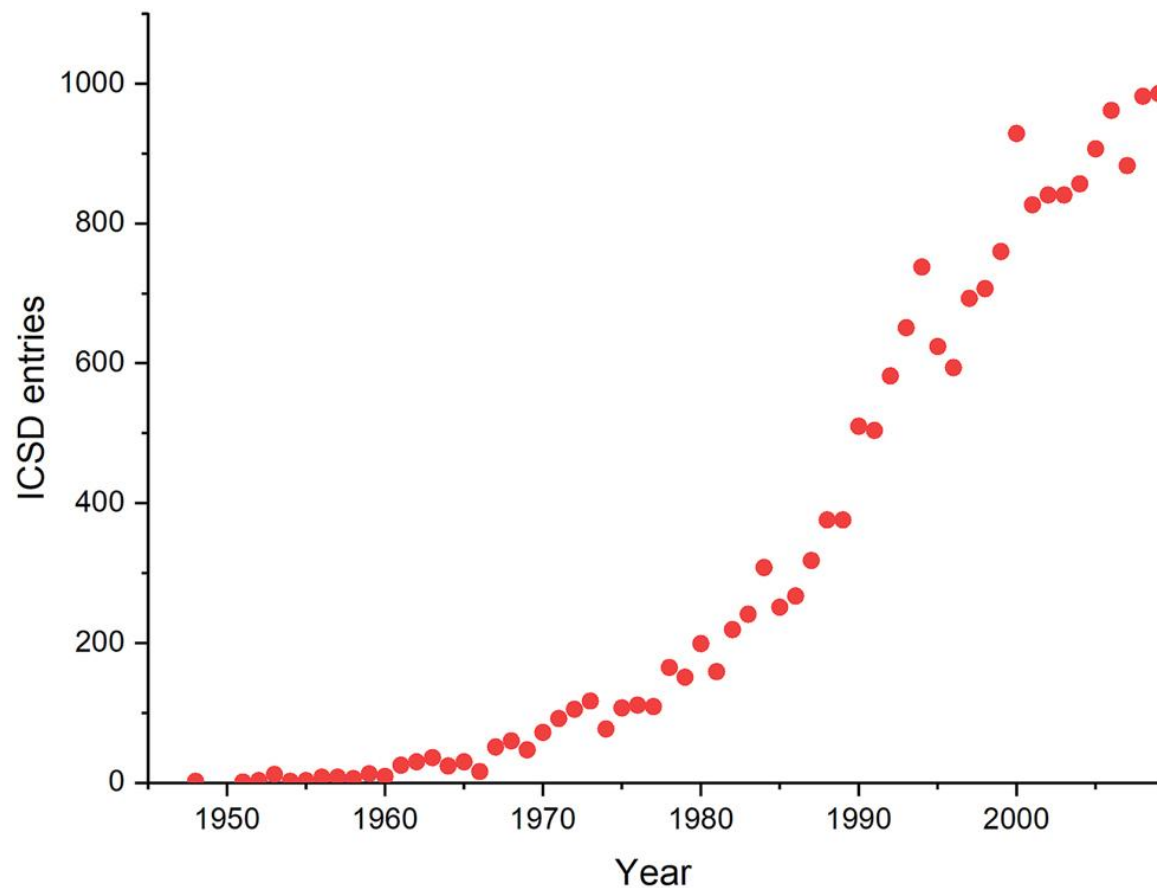


Differences in scattering



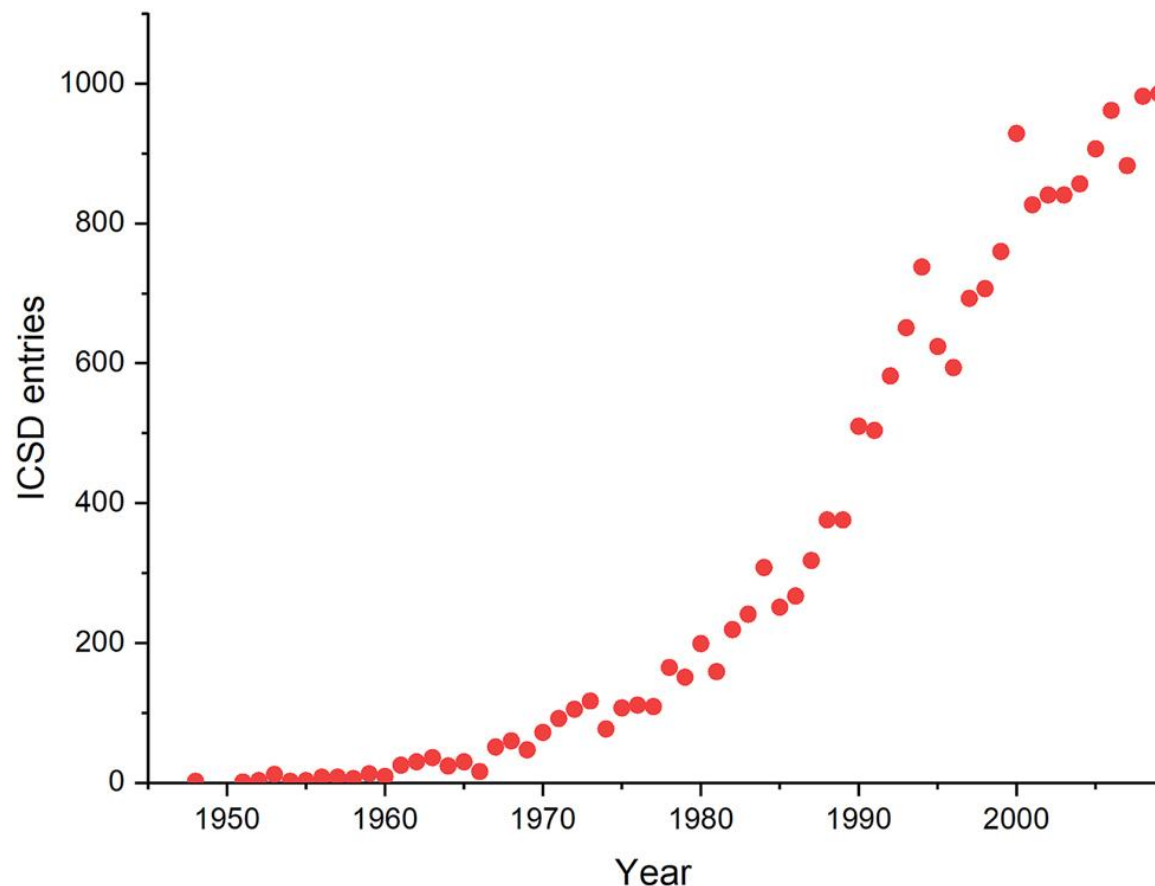
Neutron powder diffraction on the rise

Number of the annual entries in the Inorganic Crystal Structure Database based on neutron powder diffraction data.



Neutron powder diffraction on the rise

Number of the annual entries in the Inorganic Crystal Structure Database based on neutron powder diffraction data.

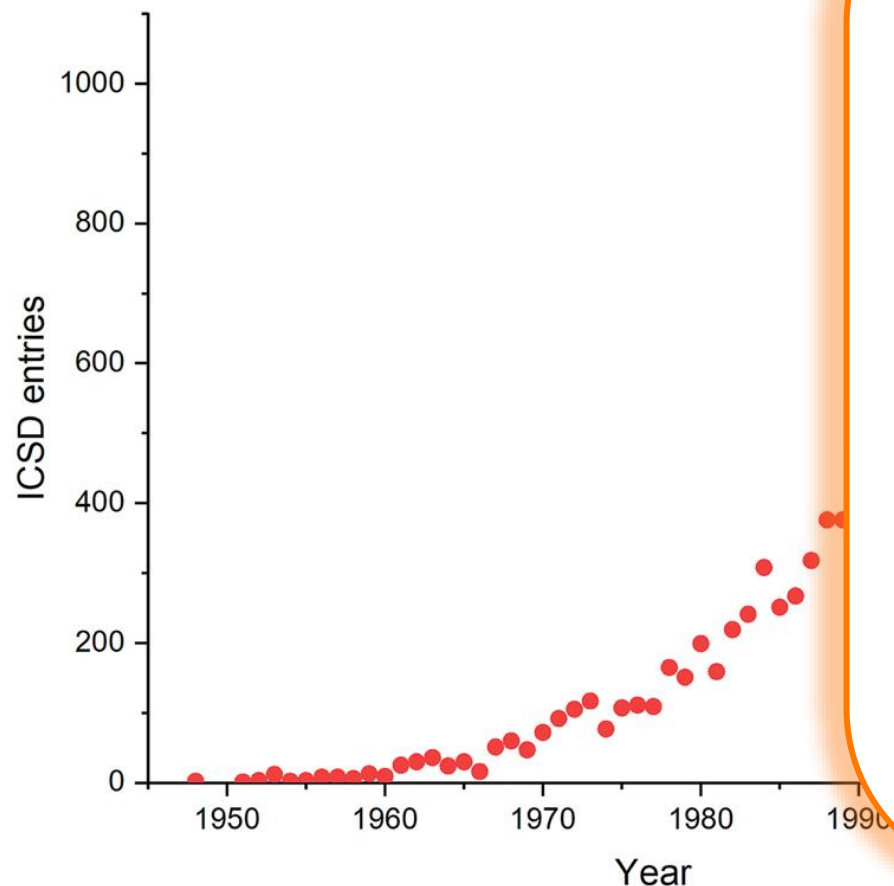


“Powder diffraction is of minimal value in crystal structure analysis and is not discussed in this book.”

Ladd and Palmer in 'Structure determination by X-ray crystallography' Plenum Press (early ed)

Neutron powder diffraction on the rise

Number of the annual entries in the Inorganic Crystal Structure Database based on neutron powder diffraction

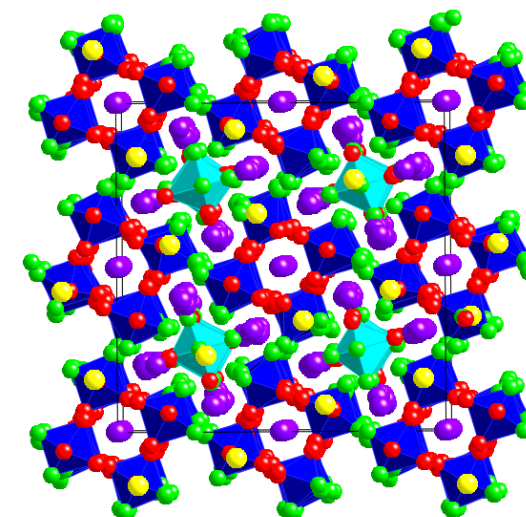
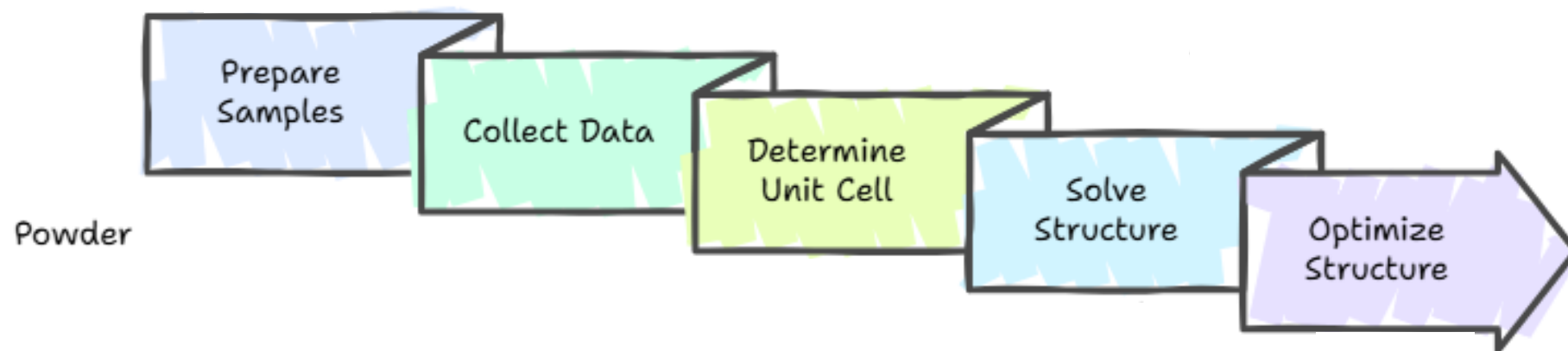


"The main interest in this book is structure determination for which powder methods have, until recent years, been inappropriate, mainly because of the problem of overlap of the X-ray reflections which causes three-dimensional data information to collapse on to a one-dimensional powder record."

Ladd and Palmer in 'Structure determination by X-ray crystallography' Plenum Press (5th ed)

Goal of crystallography?

Single crystal



Goal of crystallography?

Single crystal

Difficult

Prepare
Samples

Collect Data

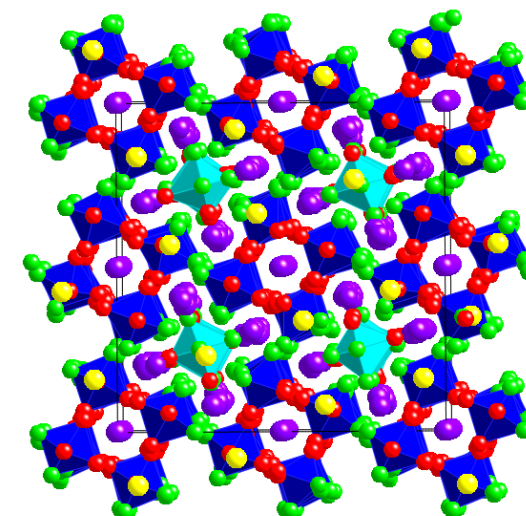
Determine
Unit Cell

Solve
Structure

Optimize
Structure

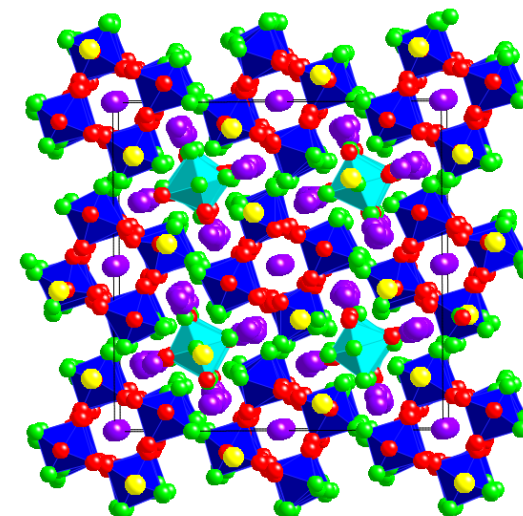
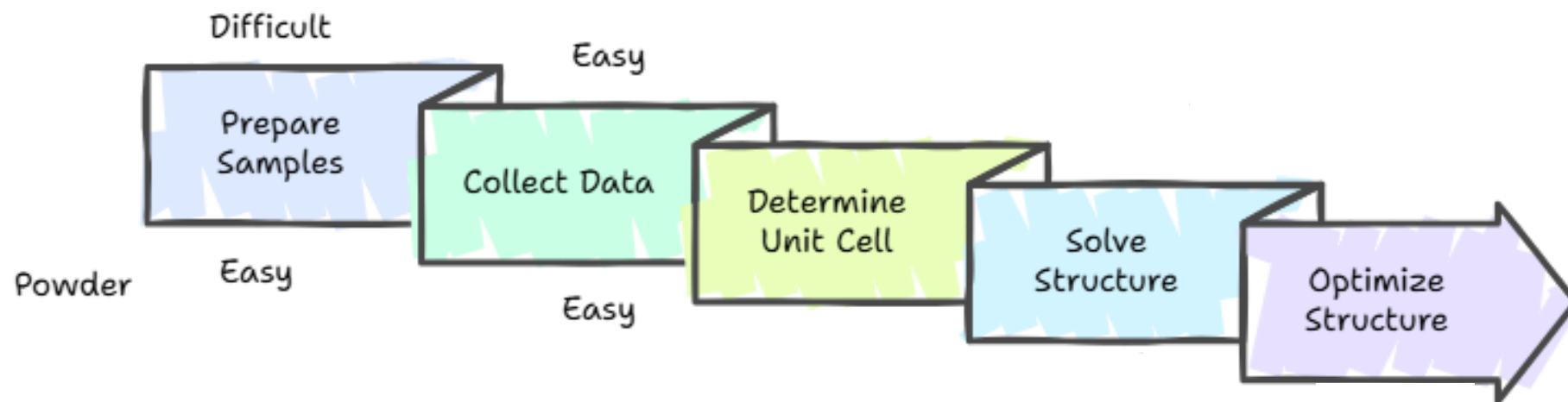
Powder

Easy



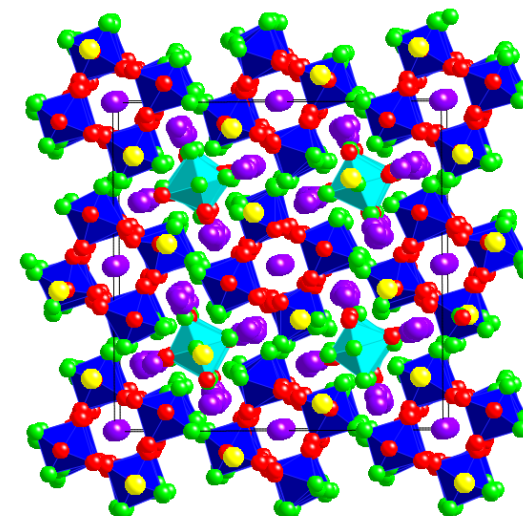
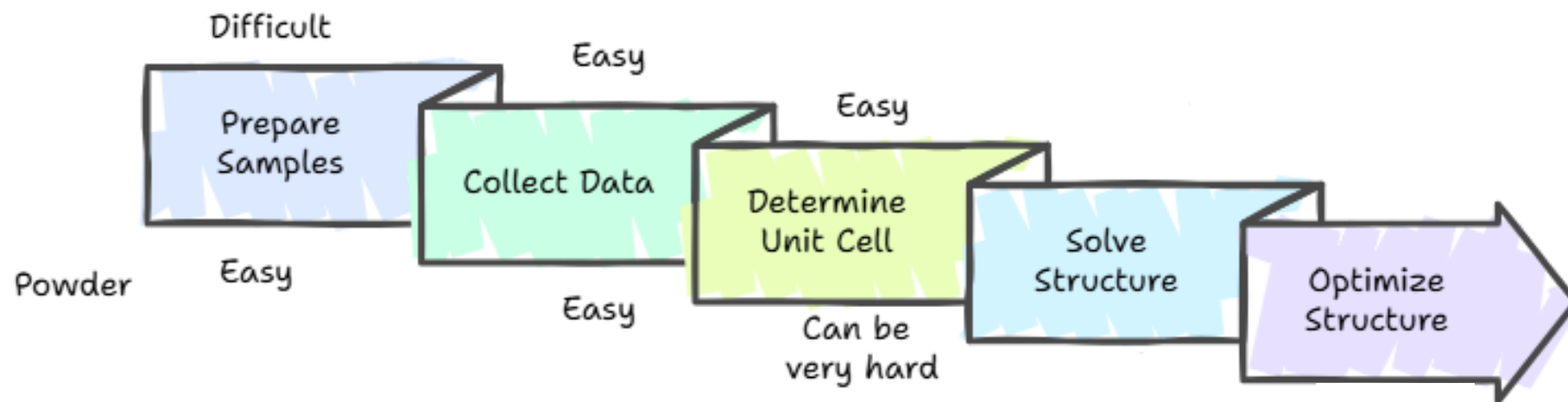
Goal of crystallography?

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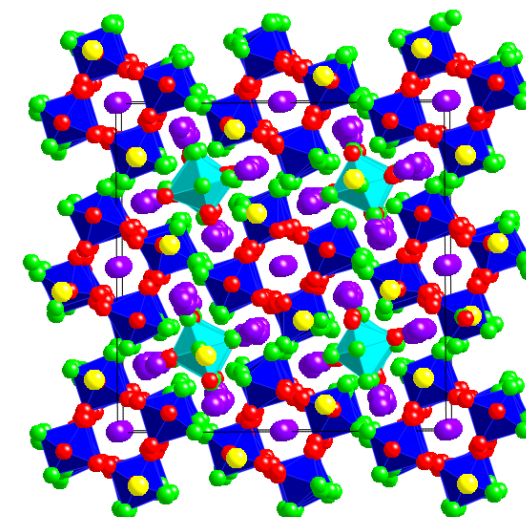
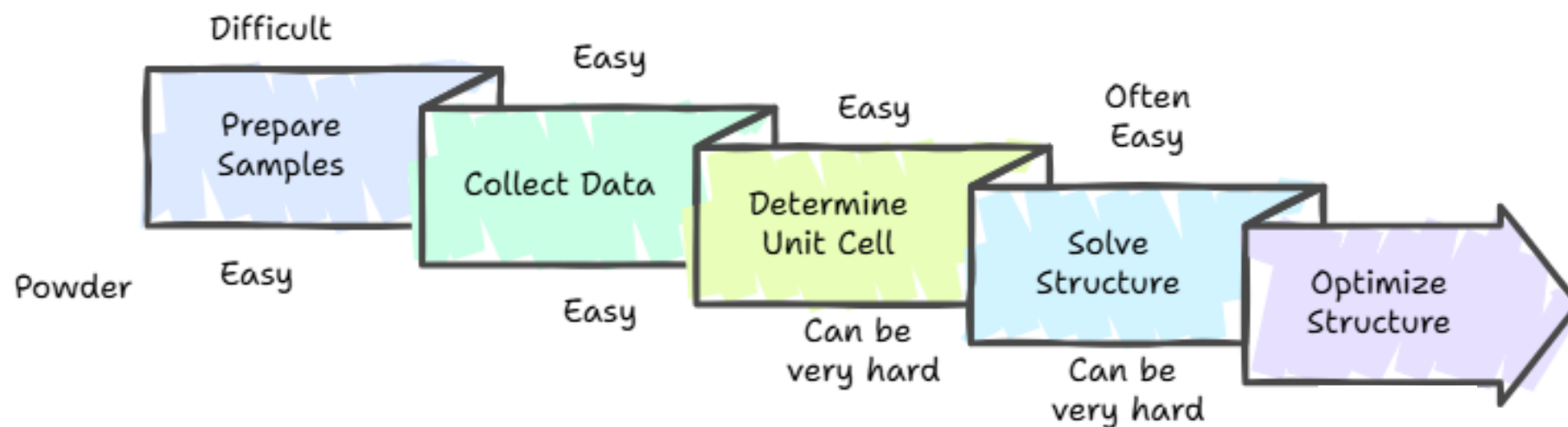
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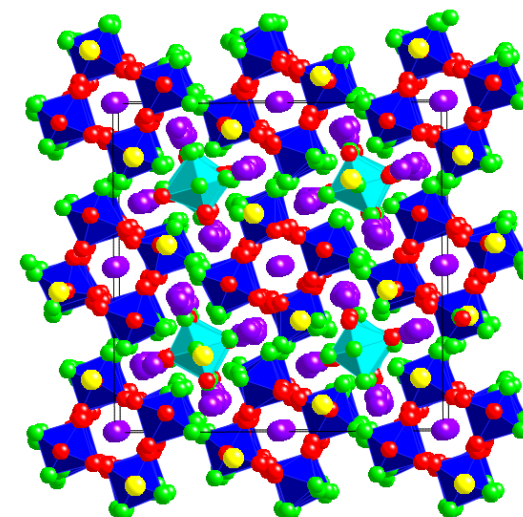
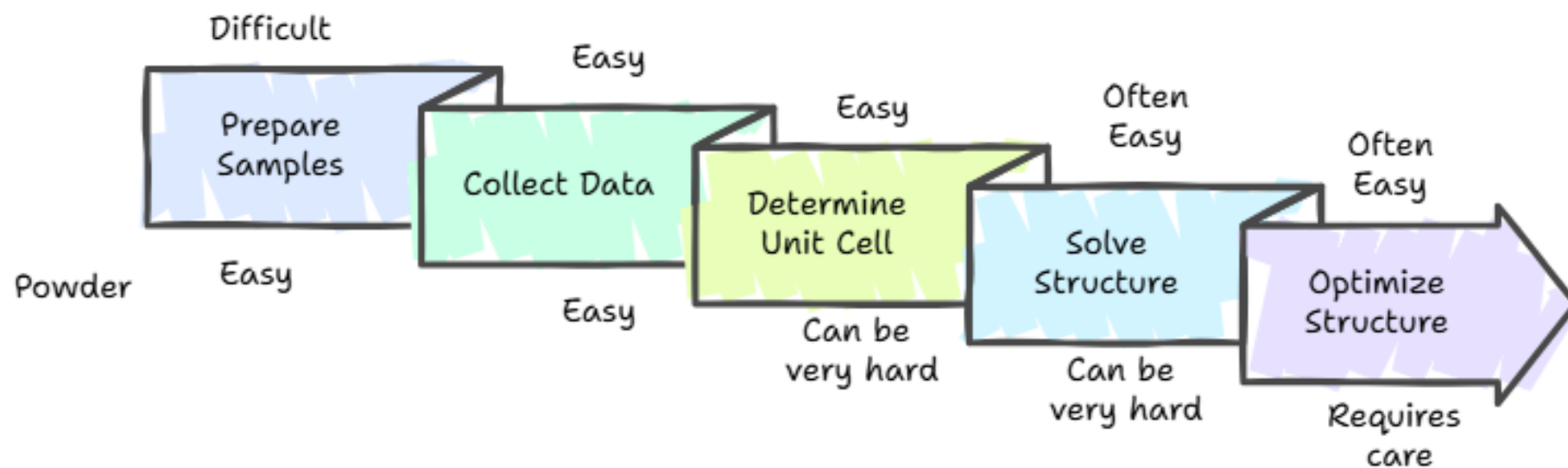
Goal of crystallography?

Single crystal



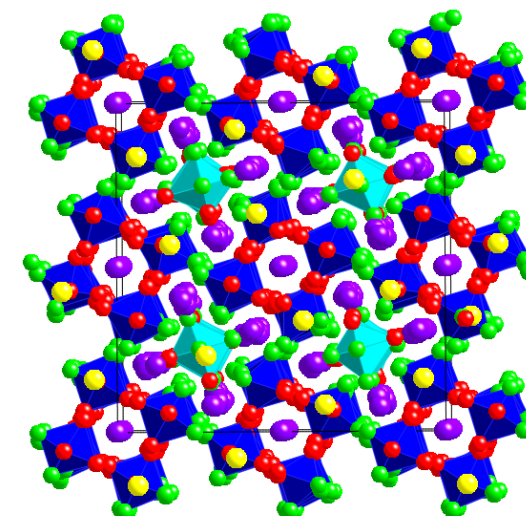
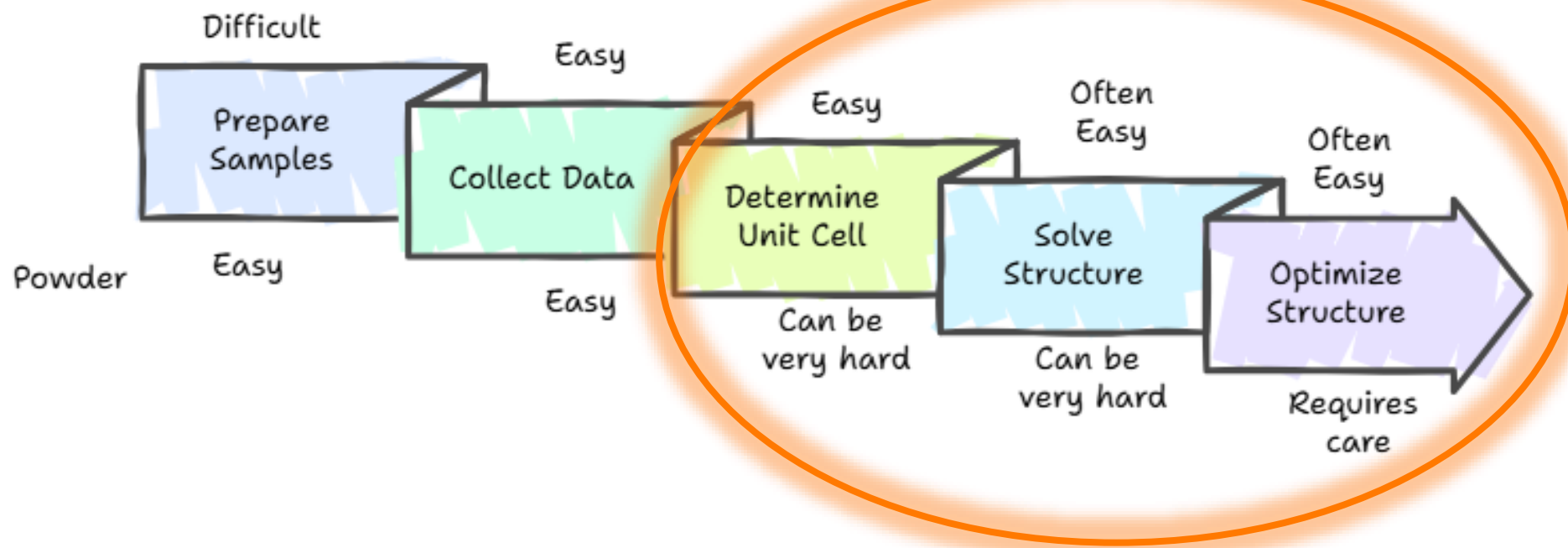
Goal of crystallography?

Single crystal



How did we reach the goal?

Single crystal



Hugo Rietveld

J. Appl. Cryst. 2, 65, 1969

"A structure refinement method is described which does not use integrated neutron powder intensities, single or overlapping, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram. Nuclear as well as magnetic structures can be refined, the latter only when their magnetic unit cell is equal to, or a multiple of, the nuclear cell. The least-squares refinement procedure allows, with a simple code, the introduction of linear or quadratic constraints between the parameters."



Dr. Rietveld at the neutron powder diffractometer at the High Flux Reactor of the Energy Research Foundation ECN in Petten, The Netherlands. (1987)

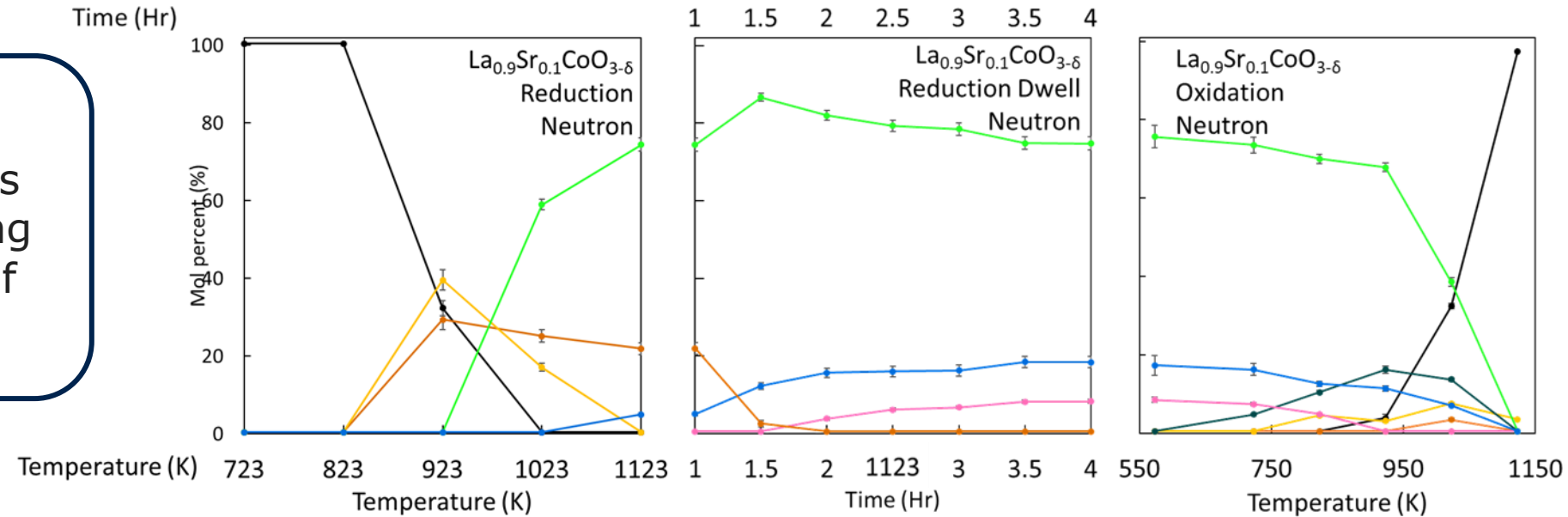
What can we get from powder neutron diffraction?

- ◆ Phase identification (qualitative phase analysis)
- ◆ Phase fraction analysis (quantitative phase analysis)
- ◆ Lattice parameters
- ◆ Rietveld refinement (structural analysis)
- ◆ Structure Solution
- ◆ Magnetic structure determination
- ◆ Phase transition behavior
 - *In situ* diffraction experiments
 - Temperature-induced phase transitions
 - Pressure-induced phase transitions
 - Kinetic studies
 - Studies in different gases
- ◆ Line shape analysis
- ◆ Texture analysis

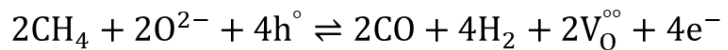
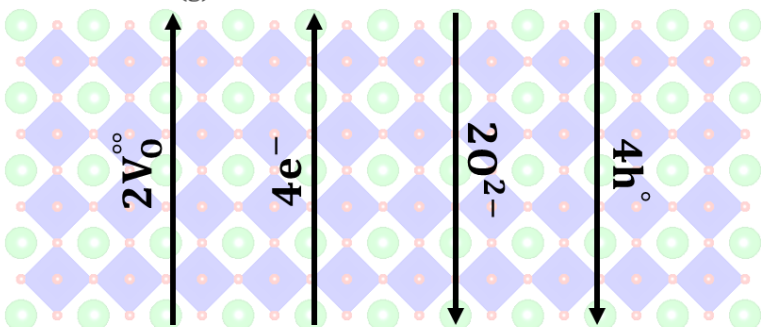
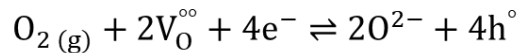
Phase Identification and Phase Fraction Analysis

Research Question

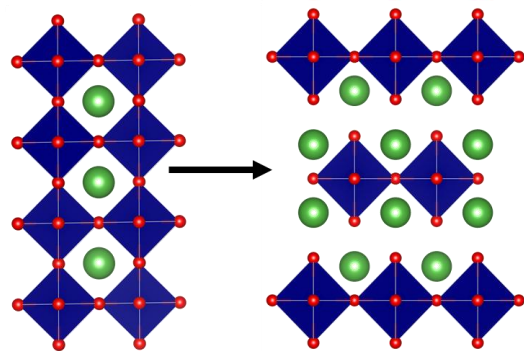
What structural phases does LSCO adopt during the partial oxidation of methane?



Reduction of oxygen gas and oxidation of OTM



Partial oxidation of methane and reduction of OTM



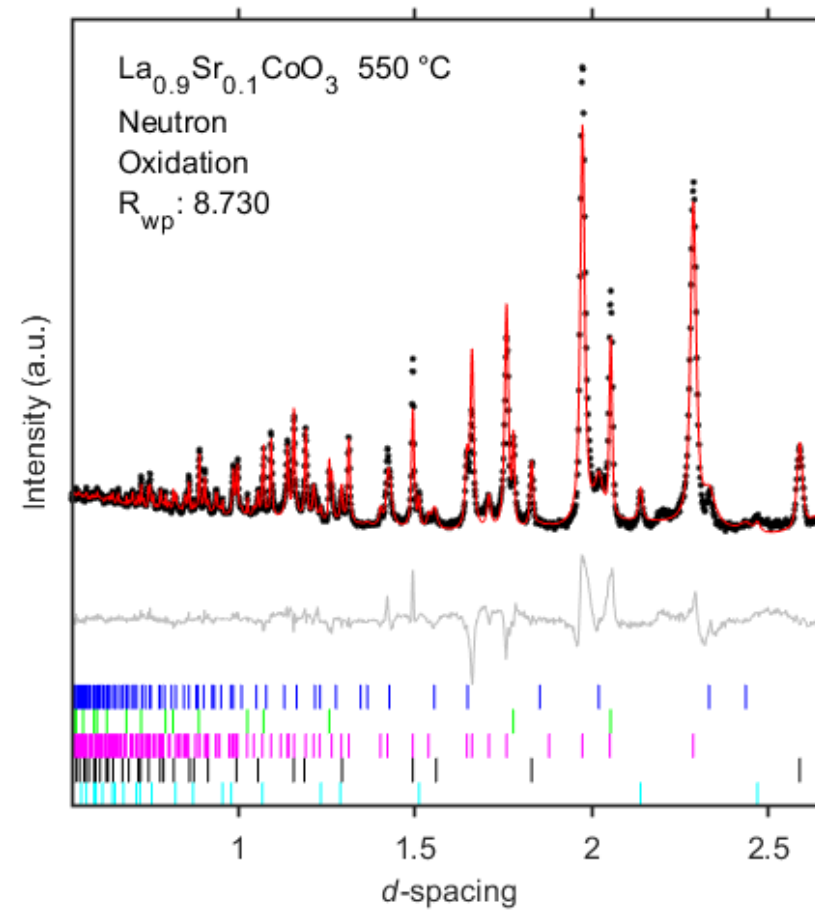
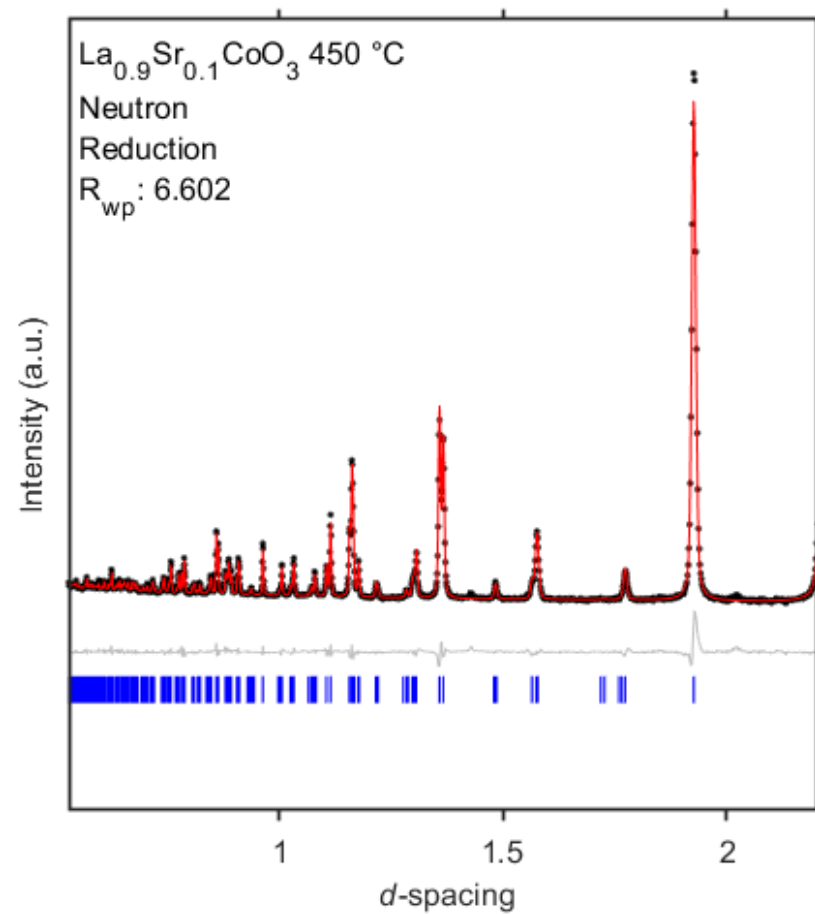
ABO_3
Perovskite

A_2BO_4 (n=1)
Ruddlesden-Popper

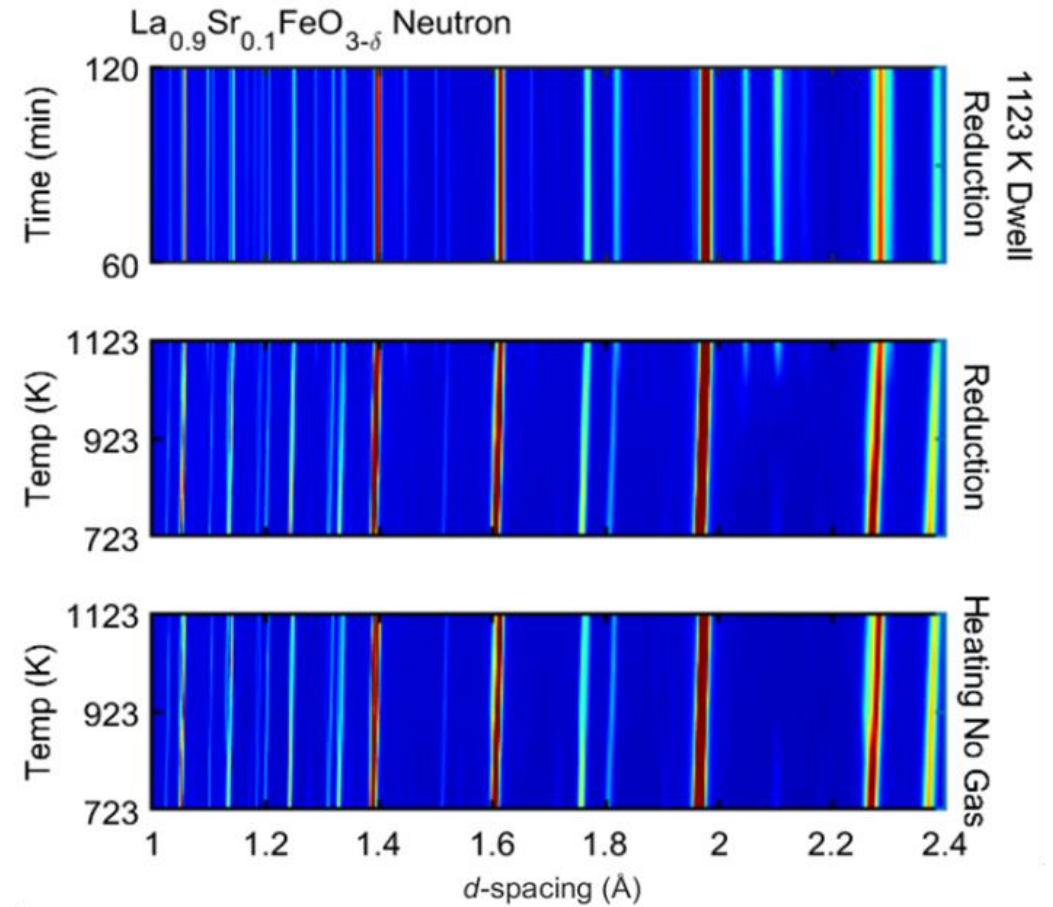
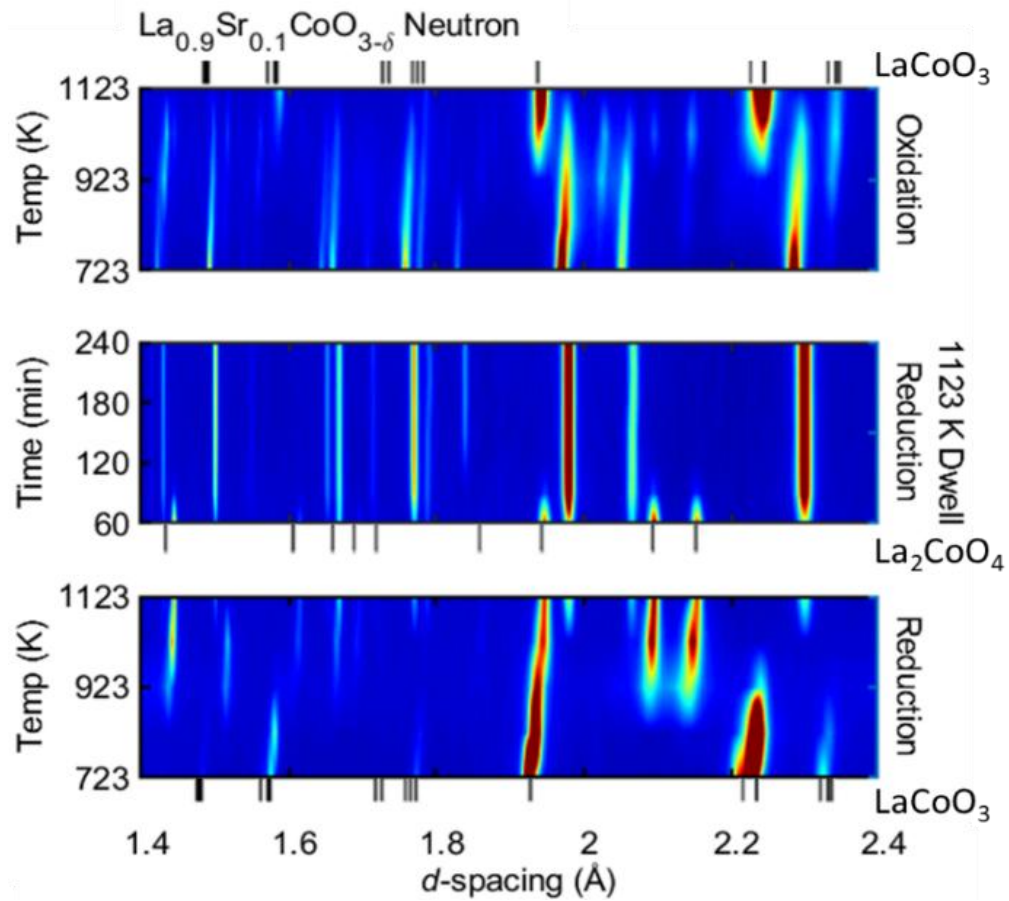
Role of Neutron Diffraction

- Phase ID of all phases present
- Determination of catalytically active phases
- Quantification of all phases
- Determination of structural mechanism

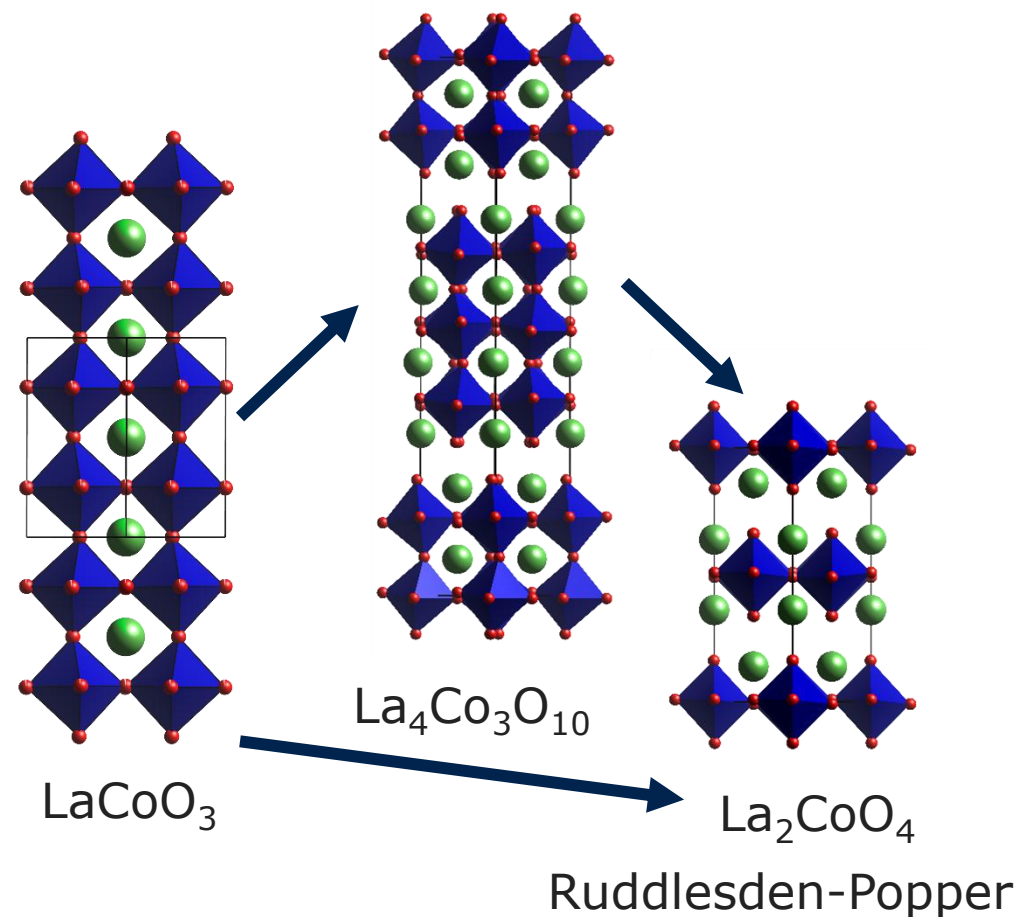
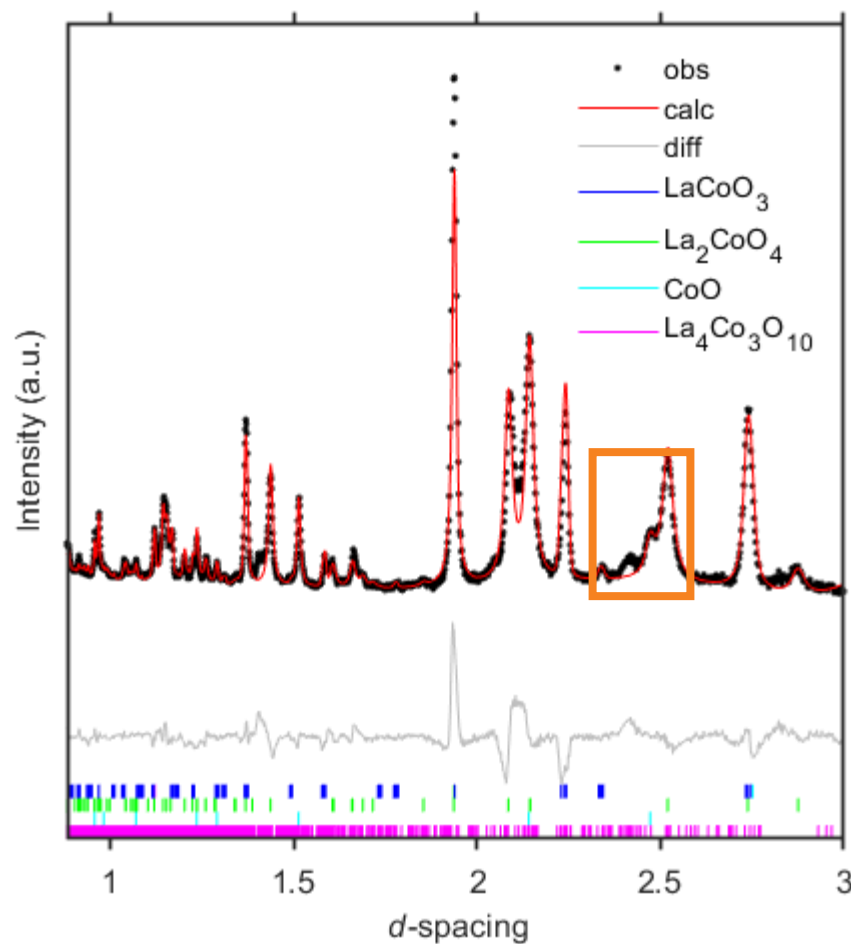
Proof of diffraction



Proof of diffraction



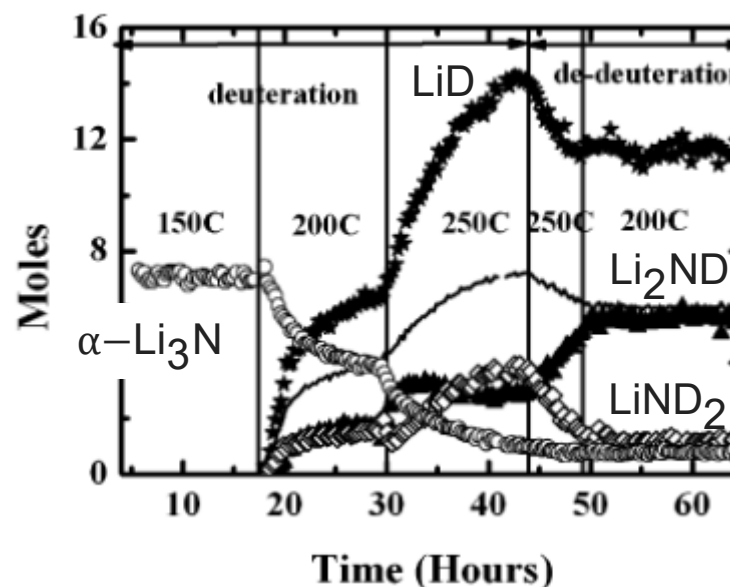
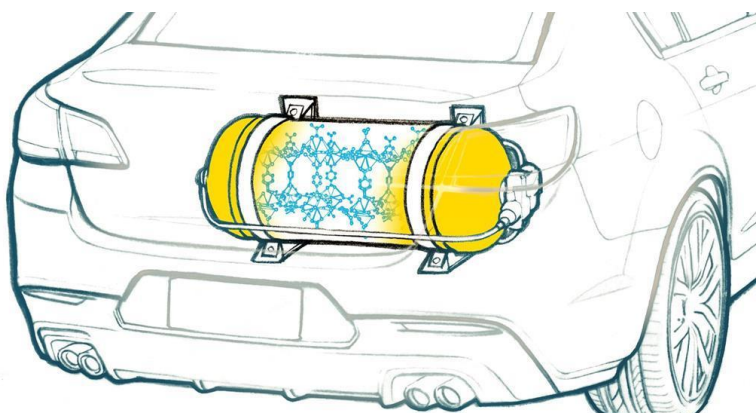
Benefit of neutron: size dependent intermediates



Lattice Parameters

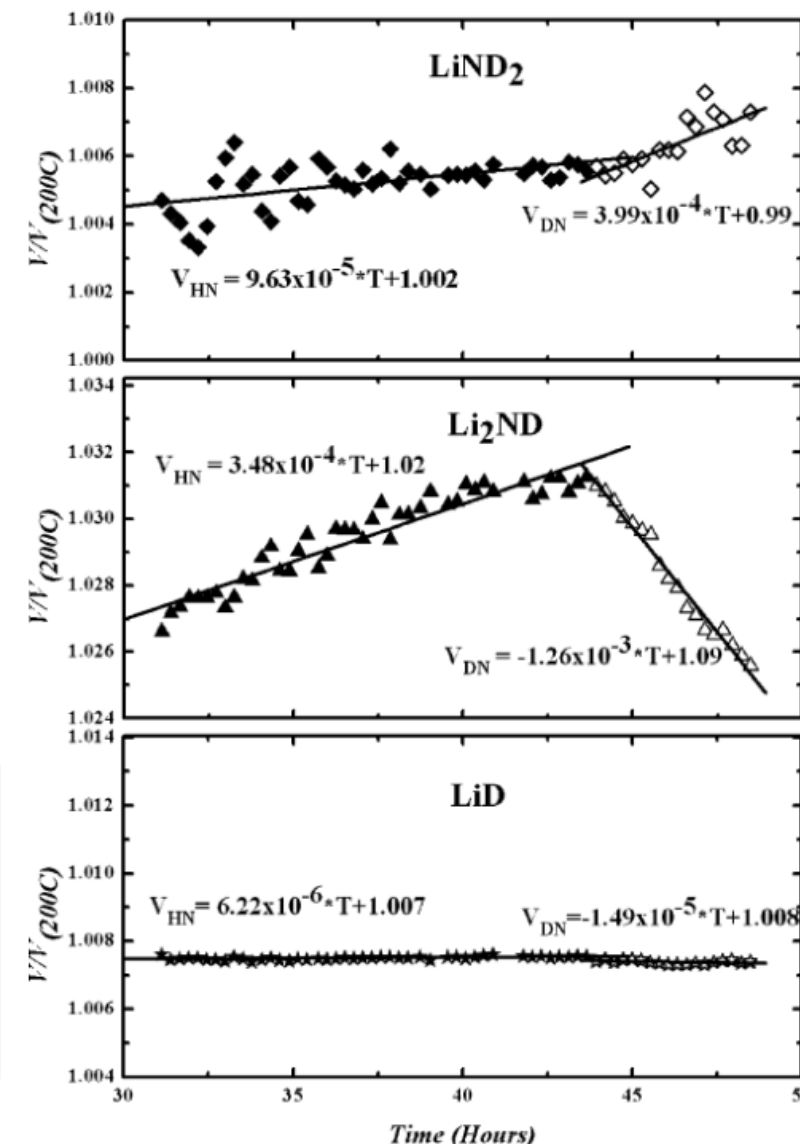
Research Question

What structural changes occur during cycling hydrogenation in hydrogen storage material Li_3N and what can they tell us about the cycling?



Role of Neutron Diffraction

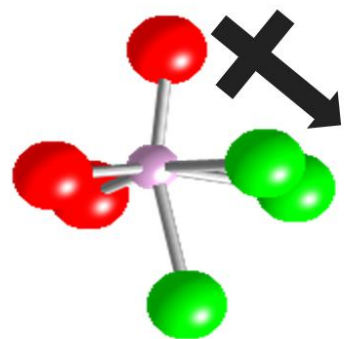
- Quantification of all phases during cycling
- Confirmed rxn mechanism
- Determined the existence of non-stoichiometric phases during hydrogenation from lattice parameters



Rietveld Refinement and Structural Solution

Research Question

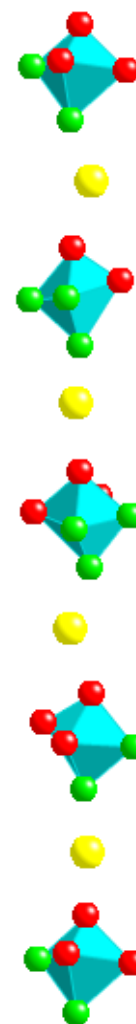
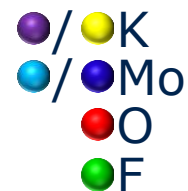
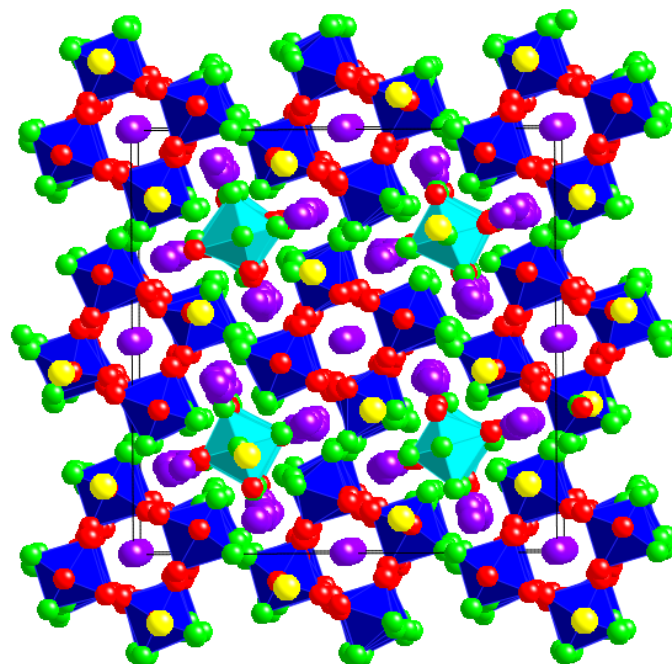
What is the oxygen and fluorine ordering in the ferroelectric α - $\text{K}_3\text{MoO}_3\text{F}_3$ and is the ordering driving ferroelectricity?



How to differentiate
b/t O and F with
diffraction?

$$v_{ij} = \exp \left[R_0 - d_{ij} / 0.37 \right]$$

$$\sum v_{ij} = \text{oxidation state}$$



$$a \approx a_p \sqrt{5} = 19.38613(3) \text{ \AA}$$

$$c \approx 4a_p = 34.86739(8) \text{ \AA}$$

$$V = 13103.93(4) \text{ \AA}^3$$

$$Z = 80$$

104 crystallographically
independent sites

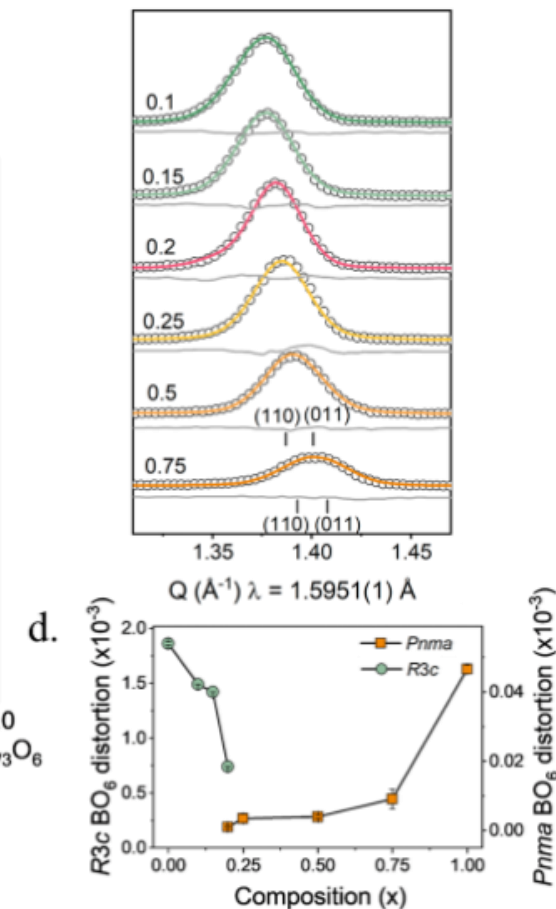
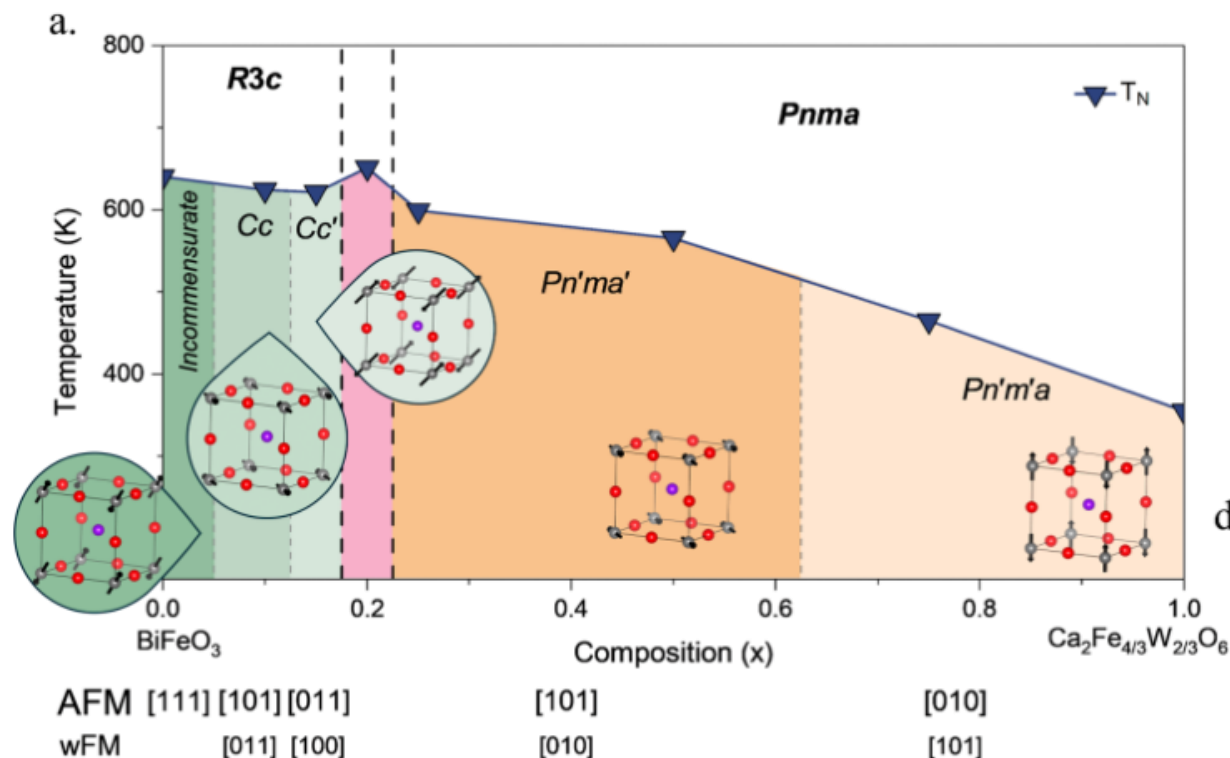
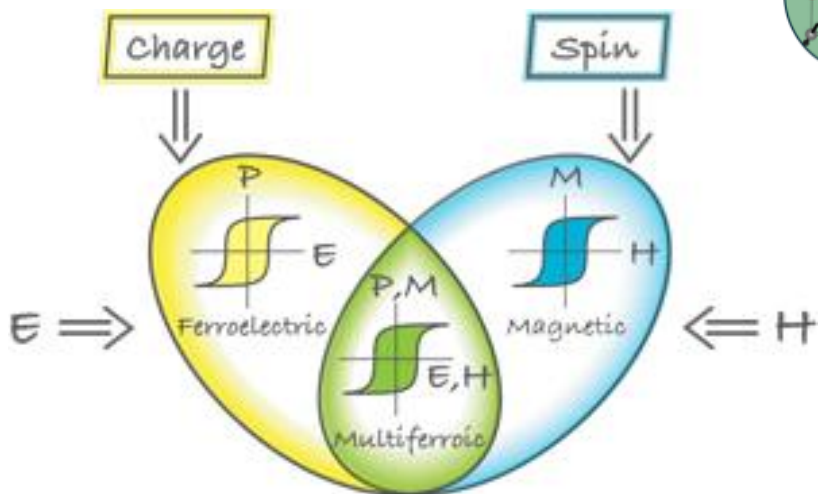
Role of Neutron Diffraction

- Structural solution and refinement of a massive unit cell
- Determination of oxygen and fluorine positions and polarization vector

Magnetic structure determination

Research Question

What is the magnetic structure across the BFO-CFWO solid solution?



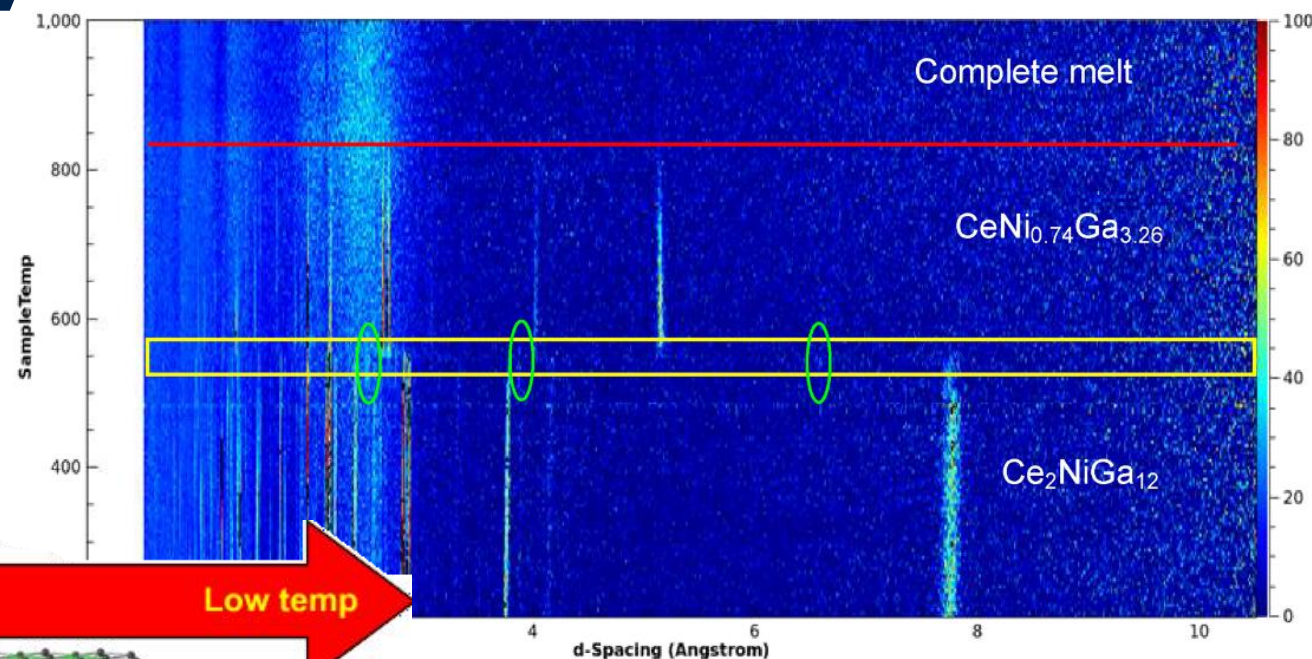
Role of Neutron Diffraction

- Correlation of the nuclear and magnetic structure via precise oxygen positions and magnetic scattering

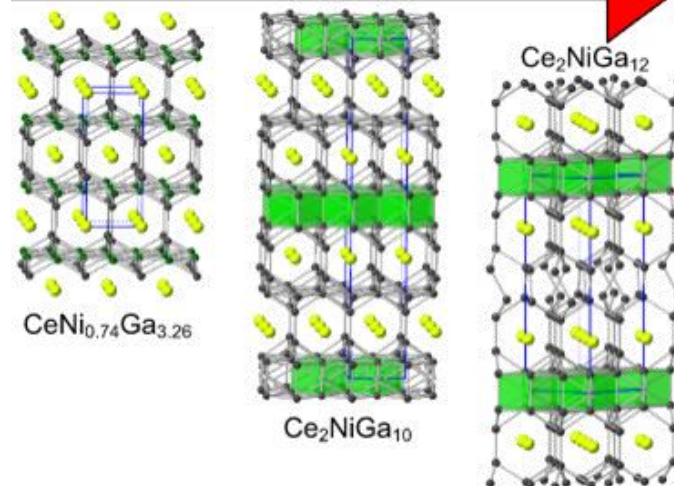
Phase Transitions and Synthesis

Research Question

What phases can be isolated from Ce and Ni in a Ga flux?

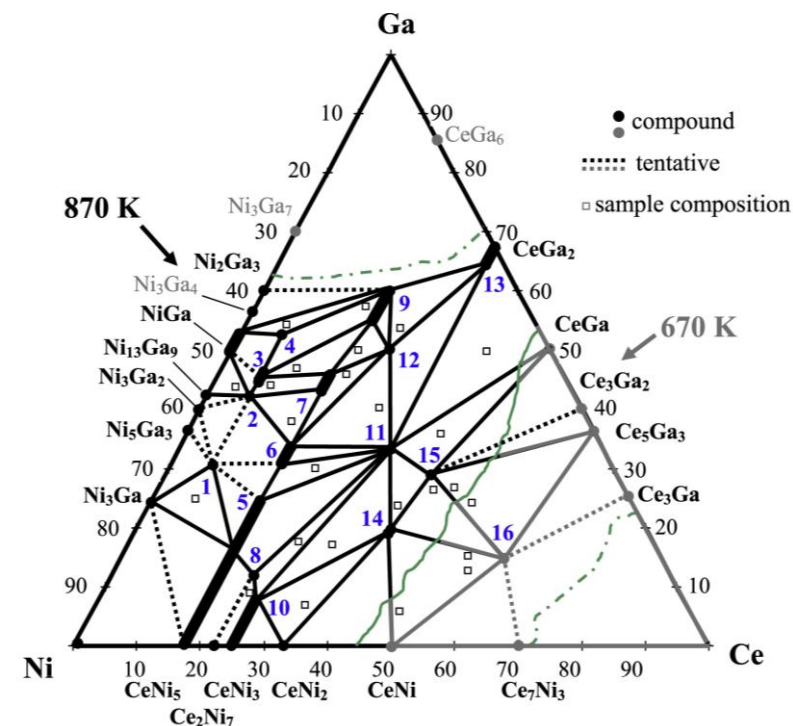


High temp → Low temp



Role of Neutron Diffraction

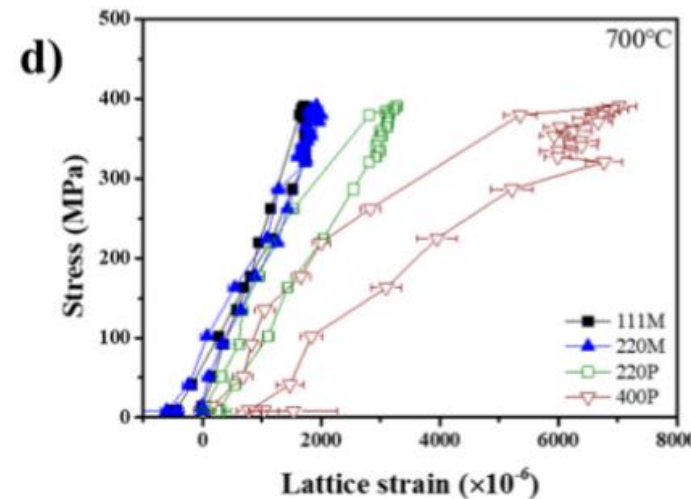
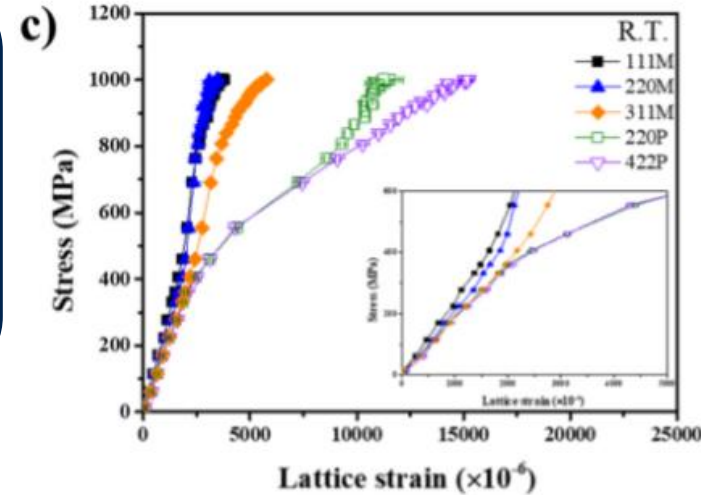
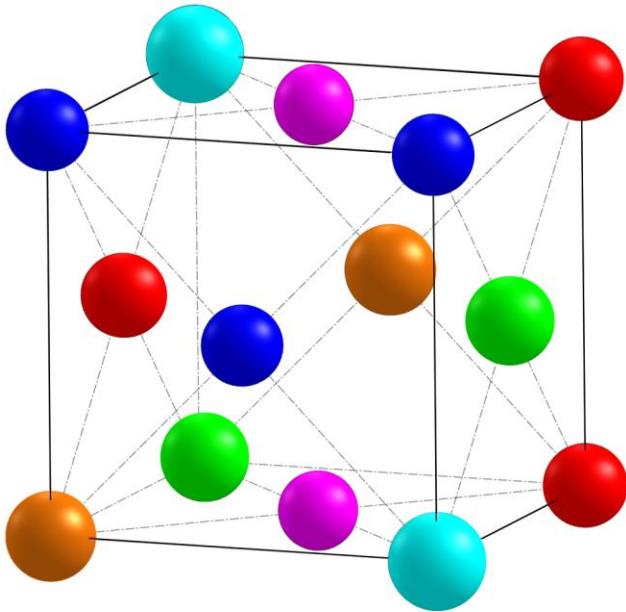
- Determined the temperature for formation of different structures
- Allowed for the *ex situ* isolation of phases that would have been missed otherwise



Line Shape Analysis

Research Question

How mechanical properties change in the high entropy alloy at elevated temperatures relative to RT.



$$\text{Lattice strain: } \varepsilon_{hkl} = \frac{d_{hkl} - d_{hkl,0}}{d_{hkl,0}}$$

Role of Neutron Diffraction

- Determine the lattice strain as a function of temperature and loading
- Determine that load is transferred from the FCC lattice to the precipitate
- Determine that the formation of precipitates may be key in improving mechanical properties at high temp.

Contact me!



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- Powder diffraction is a powerful tool that allows for the determination of the structure under a growing number of stimuli
- Neutron powder diffraction has many strengths that allow for interesting and different problems to be understood

Reciprocal Space

- We do not see the periodic electron density directly during a diffraction experiment
 - We only observe the intensity distribution of X-ray scattering from the crystal(s)
- The diffraction intensity is correlated to the electron density in the crystal by a Fourier transform
 - Often referred to as direct space and reciprocal space
- This means that we sample reciprocal space with our diffraction experiments
 - We can define a reciprocal lattice that corresponds to the direct (crystal) lattice

Time of flight instrument (POWGEN)

