Cal State Fullerton

Powder Diffraction

National Neutron Scattering School

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Oak Ridge National Lab

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Agenda and Acknowledgements

- Short history of powder diffraction
- Intro to theory of powder diffraction
- Neutron powder diffraction applications

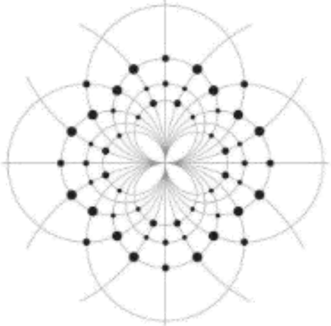
- Dr. Ashfia Huq (Molecular Foundry)
- Dr. Cora Lind-Kovac (U of Toledo)
- Dr. Saul Lapidus (Advanced Photon Source)
- Dr. Joshua Goldberg (OSU)
- Dr. Patrick Woodward (OSU)

Development of X-ray Technology

Discovery of X-rays

Roentgen's groundbreaking discovery in 1895

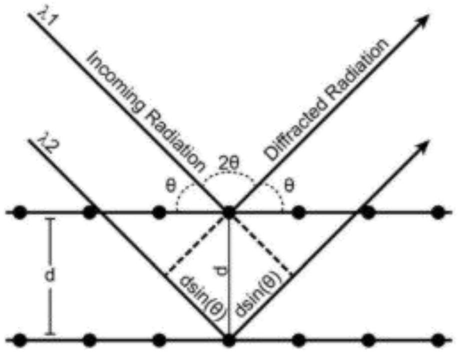
Diffraction of X-rays



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

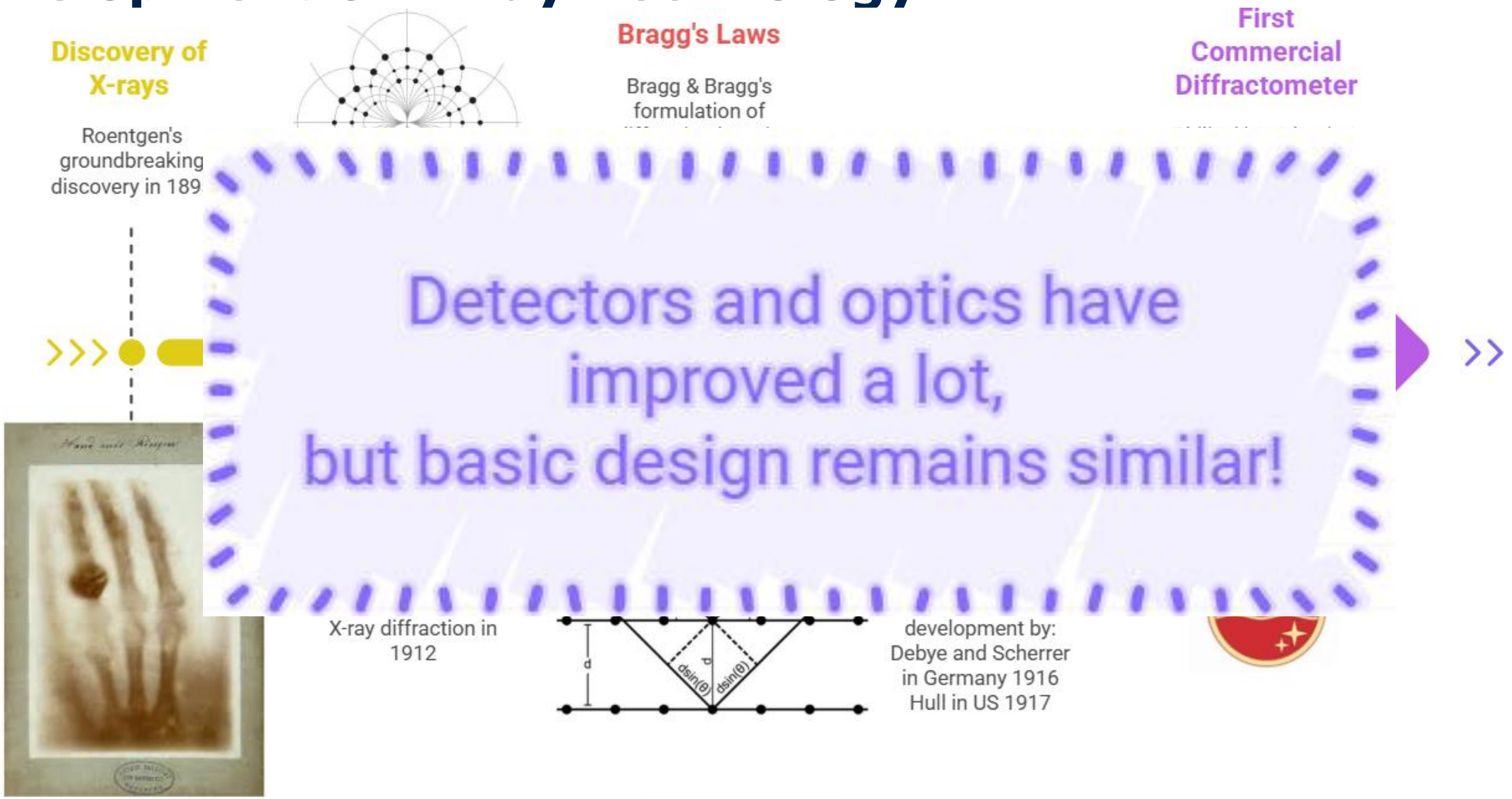
Independent development by:
Debye and Scherrer in Germany 1916
Hull in US 1917

First Commercial Diffractometer

Philips' introduction of the PW1050 in 1947

PHILIPS

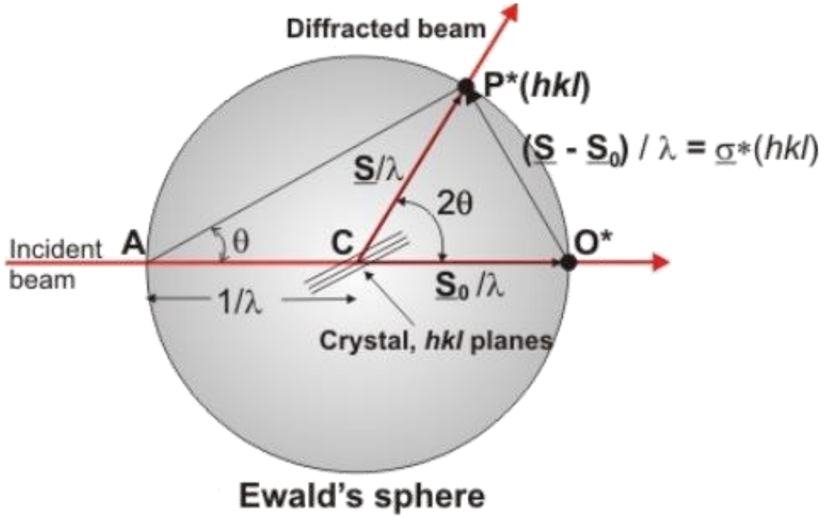
Development of X-ray Technology

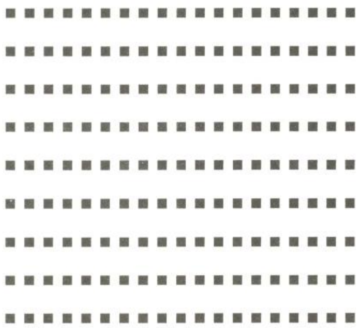


Observations from Single Crystals

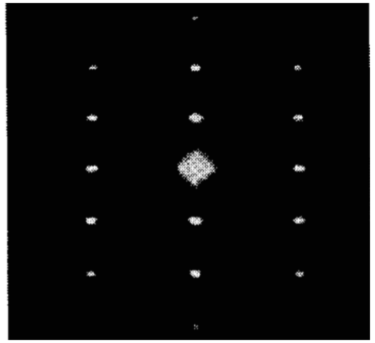
Single crystal → 1 orientation in real space → 1 orientation of the reciprocal lattice

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

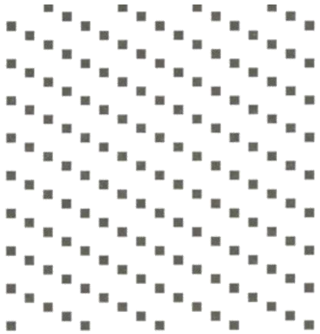




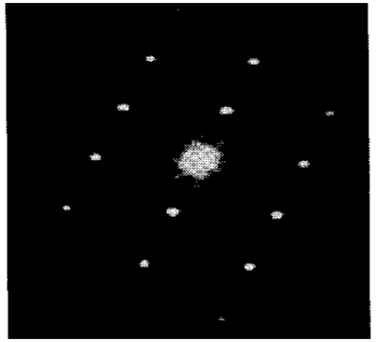
Real space



Reciprocal space



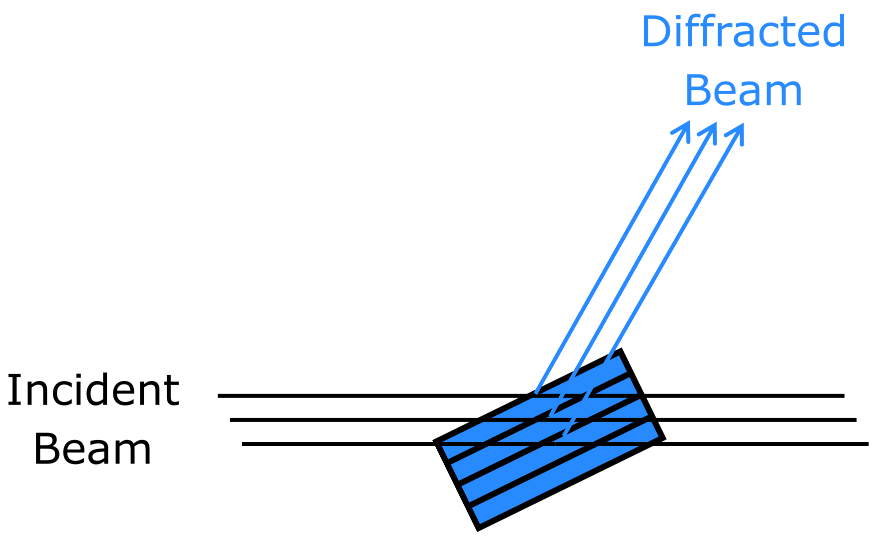
Real space



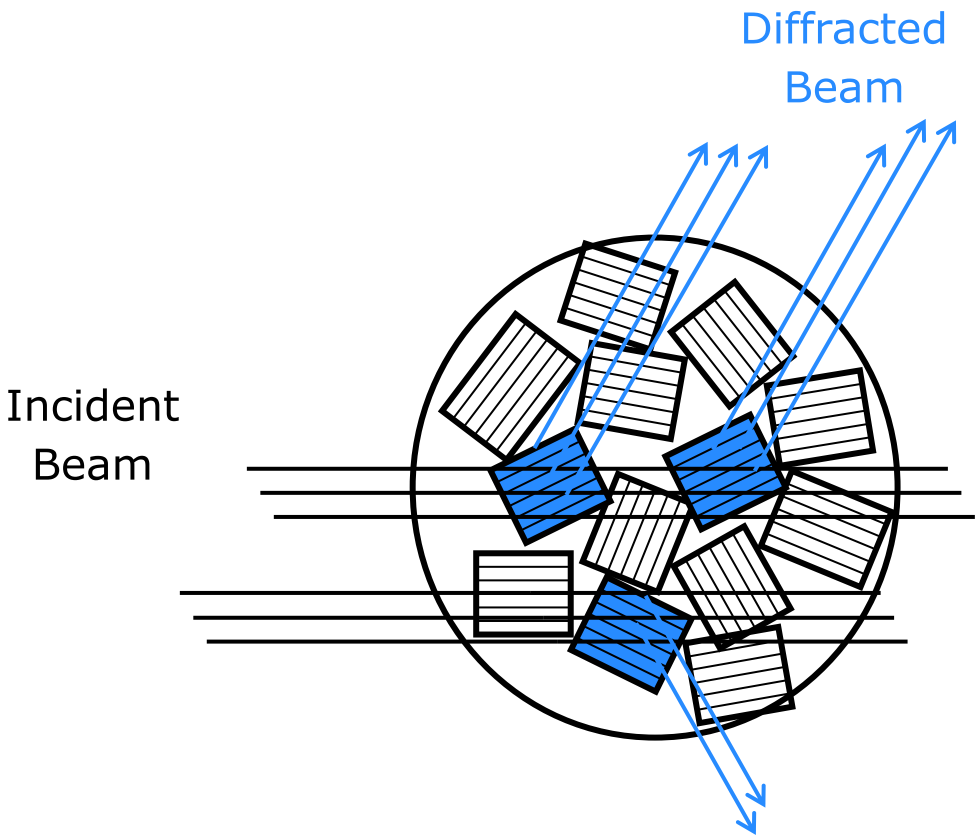
Reciprocal space

Diffraction Samples

Single Crystal Diffraction



Powder Diffraction



Original Powder Setups

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

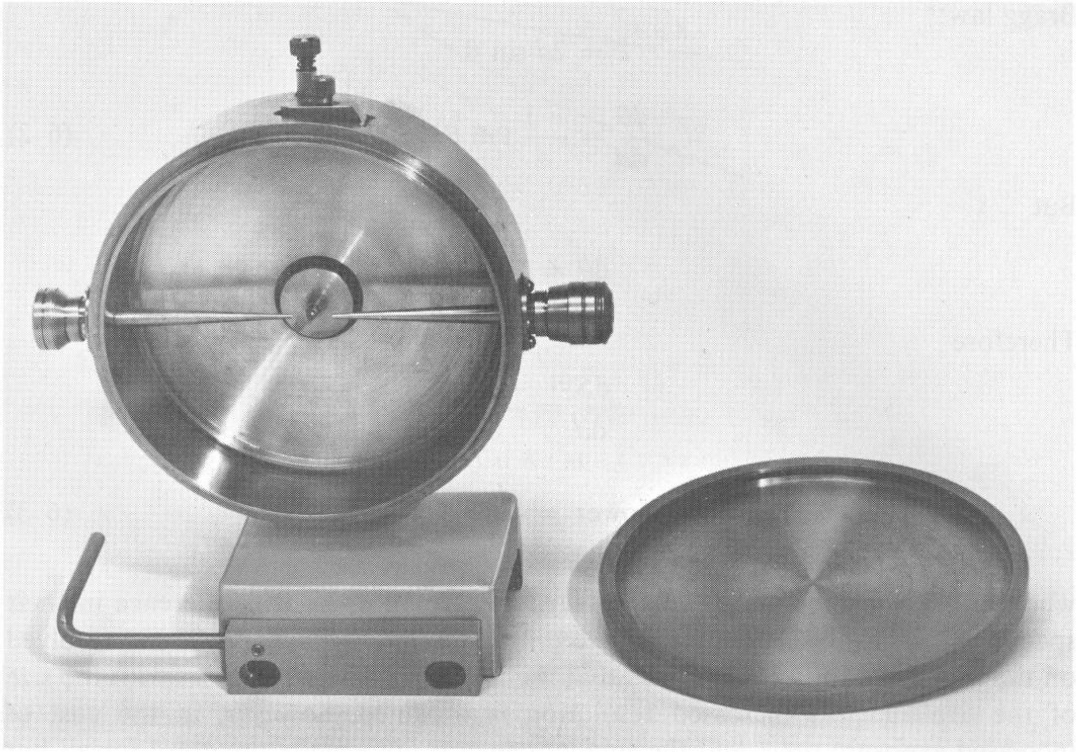


Fig. 6–1 Debye–Scherrer camera, with cover plate removed. (Courtesy of Philips Electronic Instruments, Inc.)

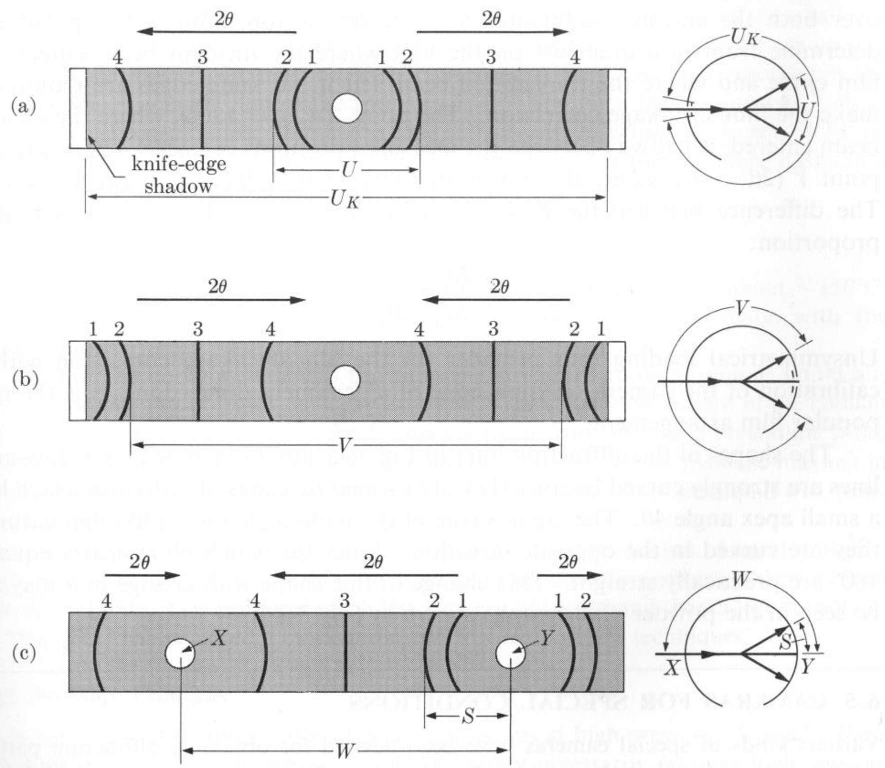
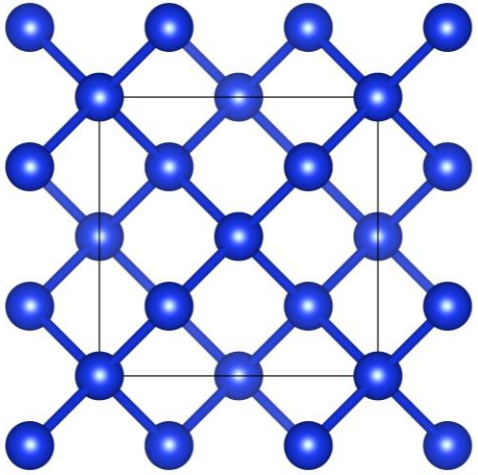
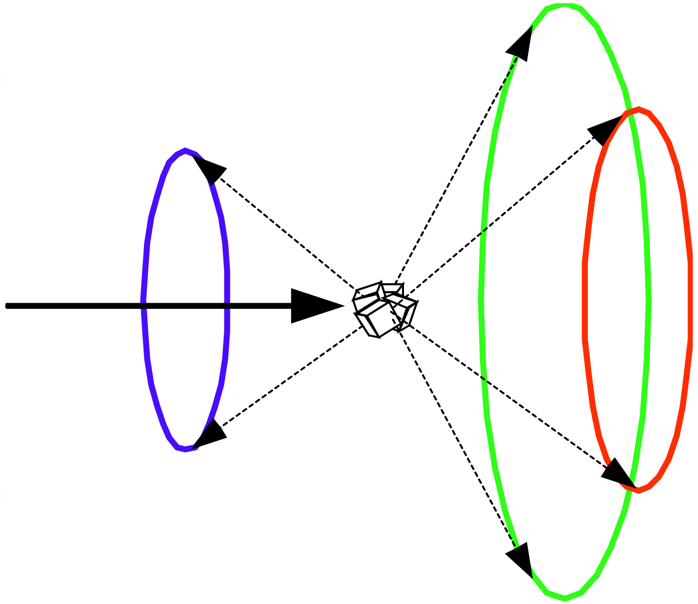
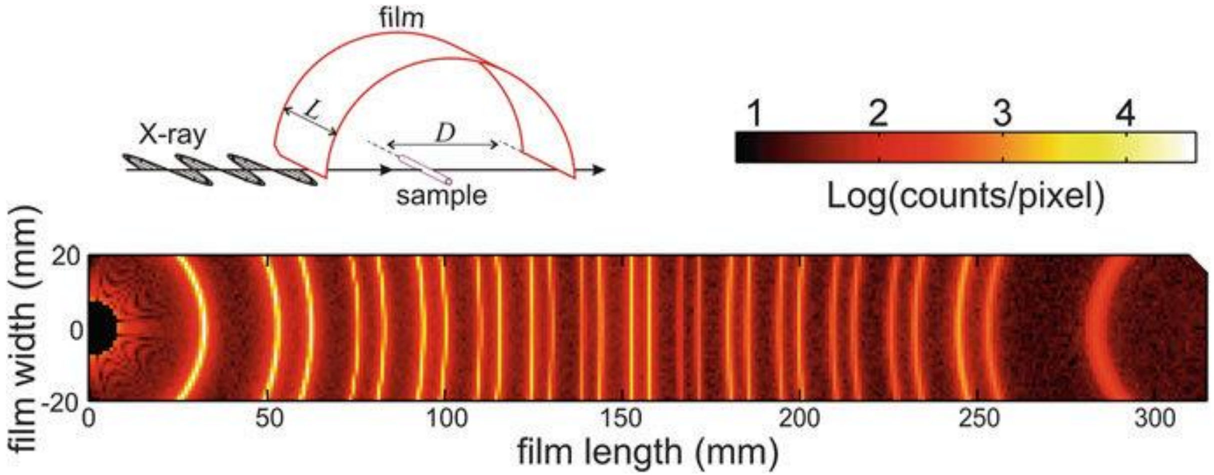


Fig. 6–5 Methods of film loading in Debye cameras. Corresponding lines have the same numbers in all films.

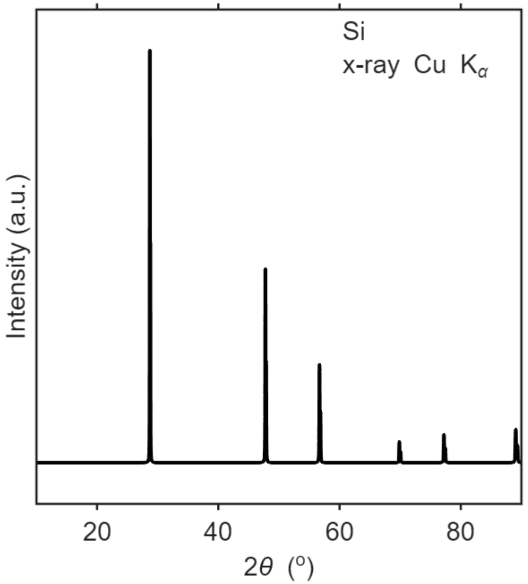
When we measure powders we get peaks?

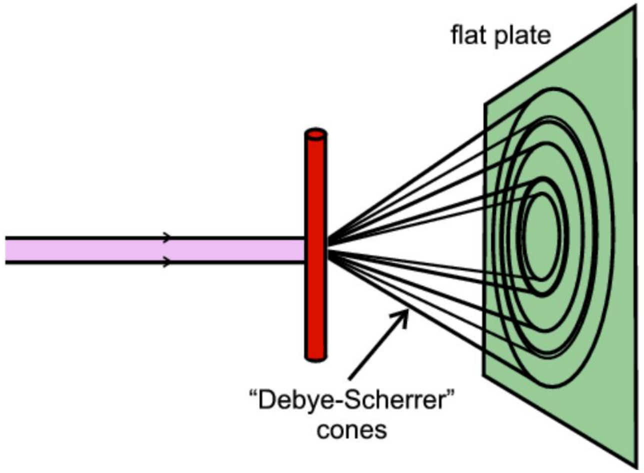






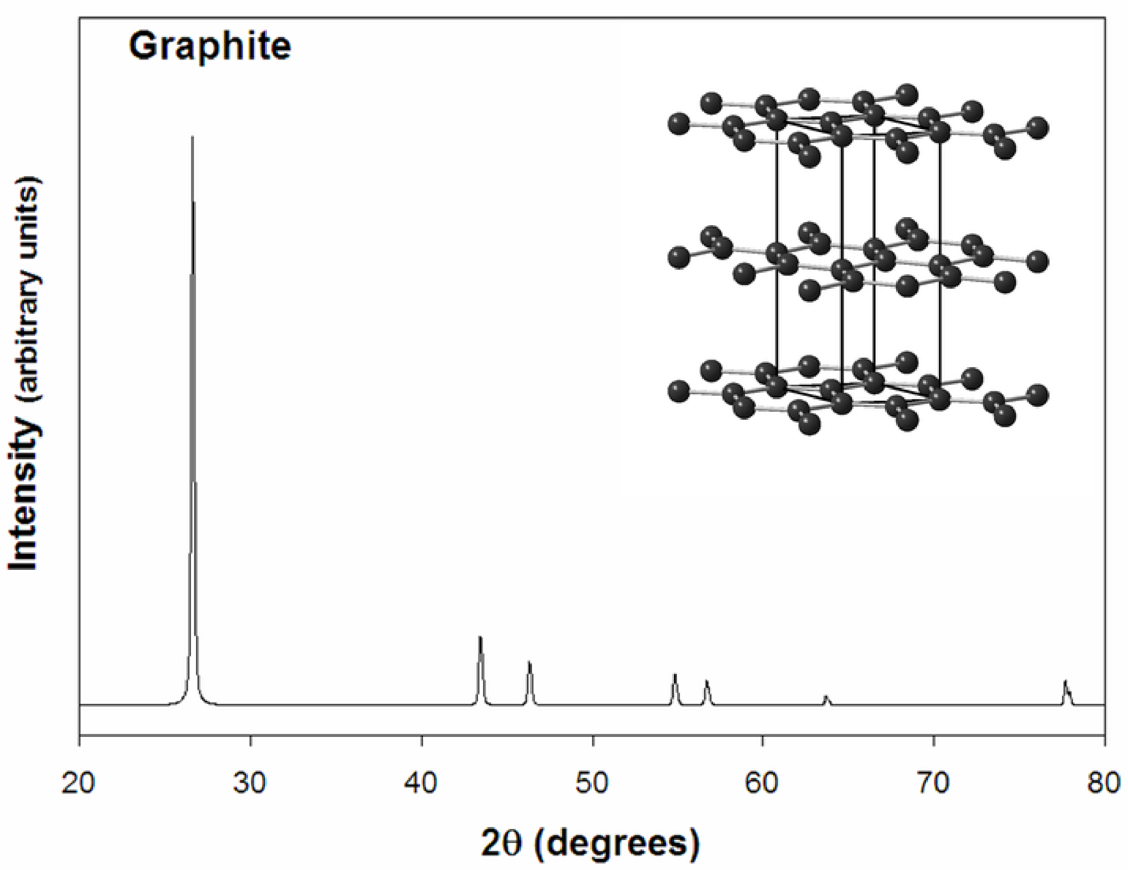
- Circles of diffraction off the polycrystalline sample
- Intensity of the diffraction gives peaks

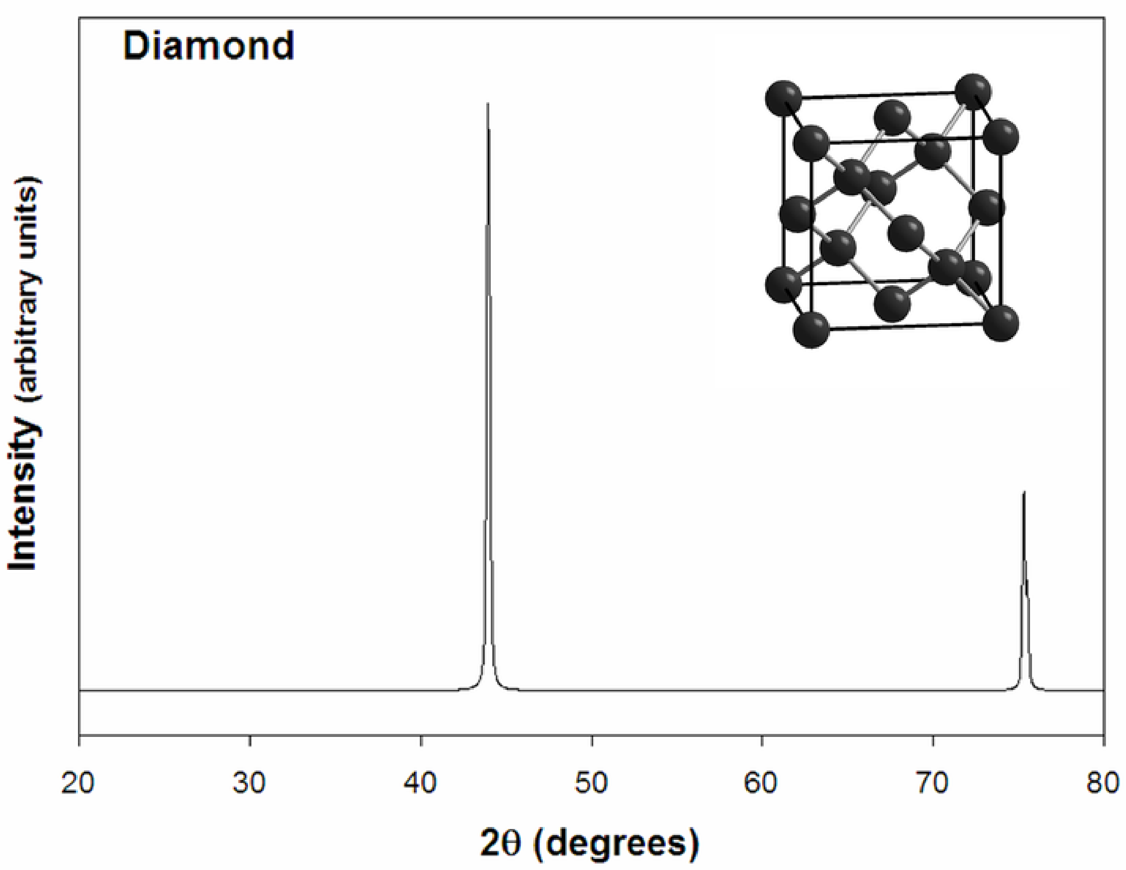




Morelhão, S. L. https://doi.org/10.1007/978-3-319-19554-4_5.
http://pd.chem.ucl.ac.uk/pdnn/inst2/linearea.htm

Diffraction is the fingerprint of the structure



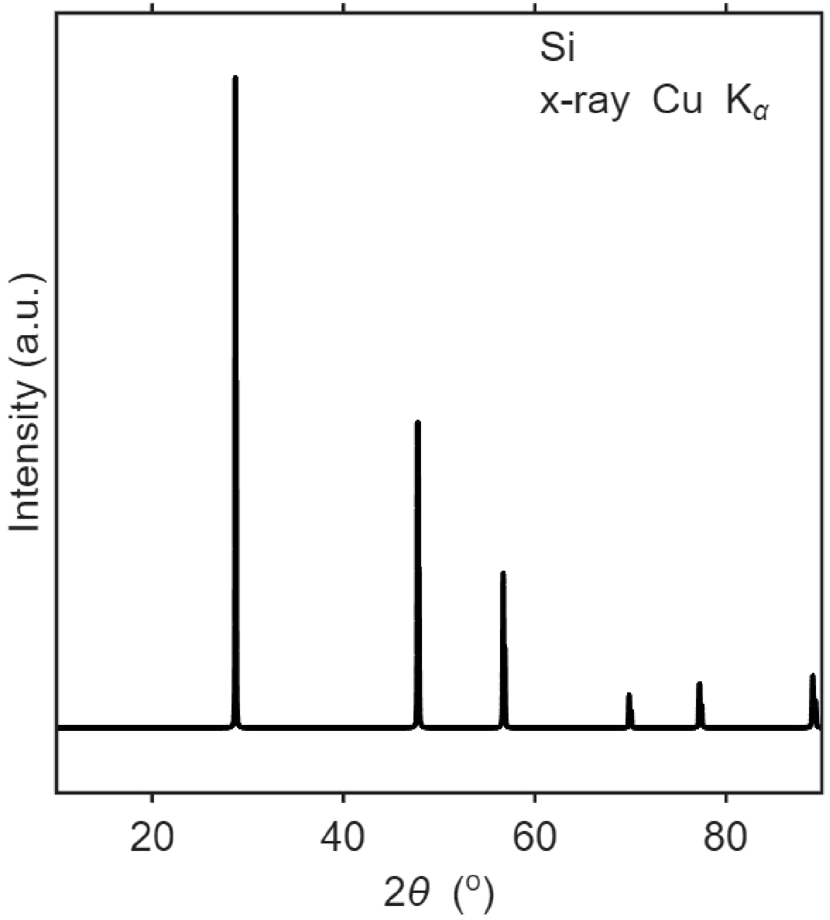


What is in a powder diffraction pattern?

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)



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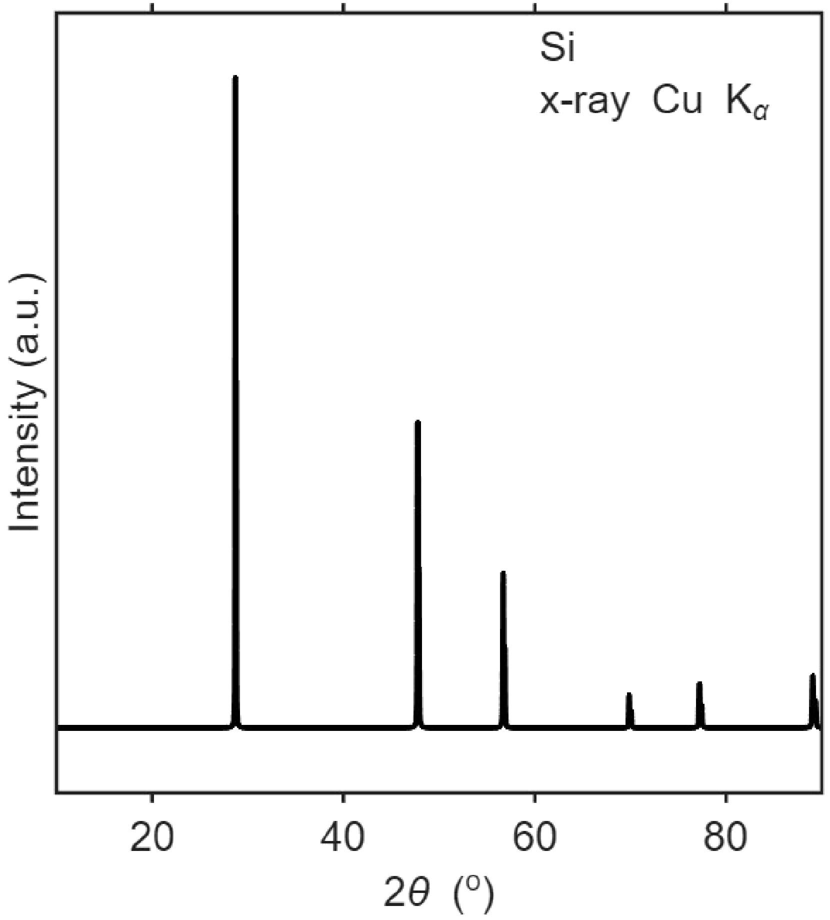
Peaks

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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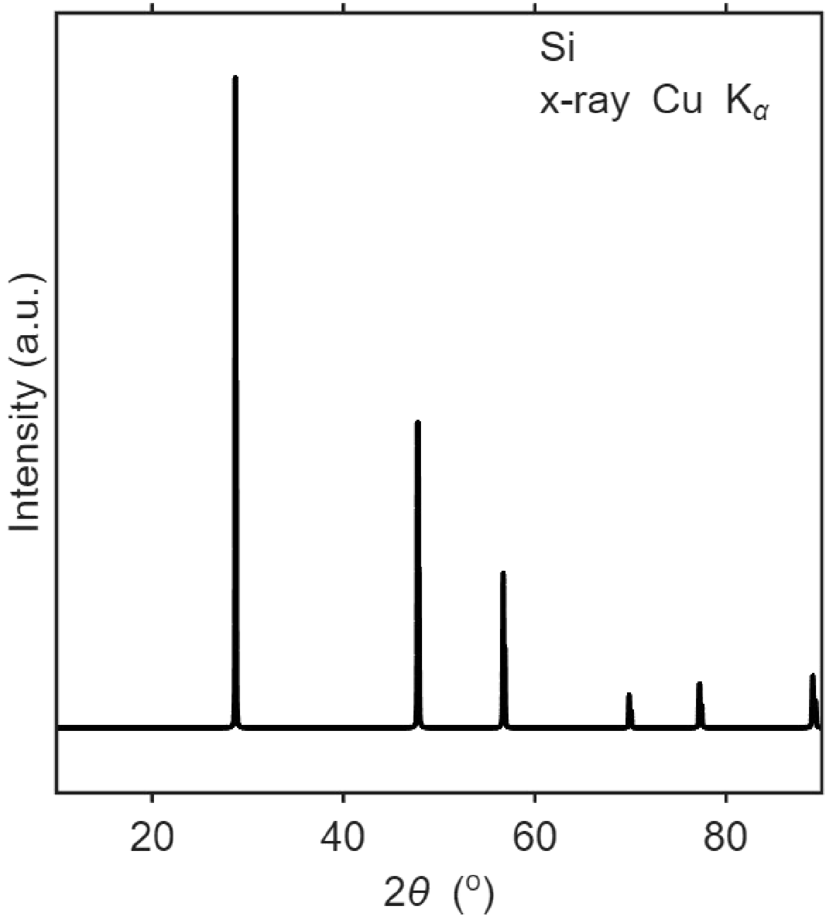
Peaks

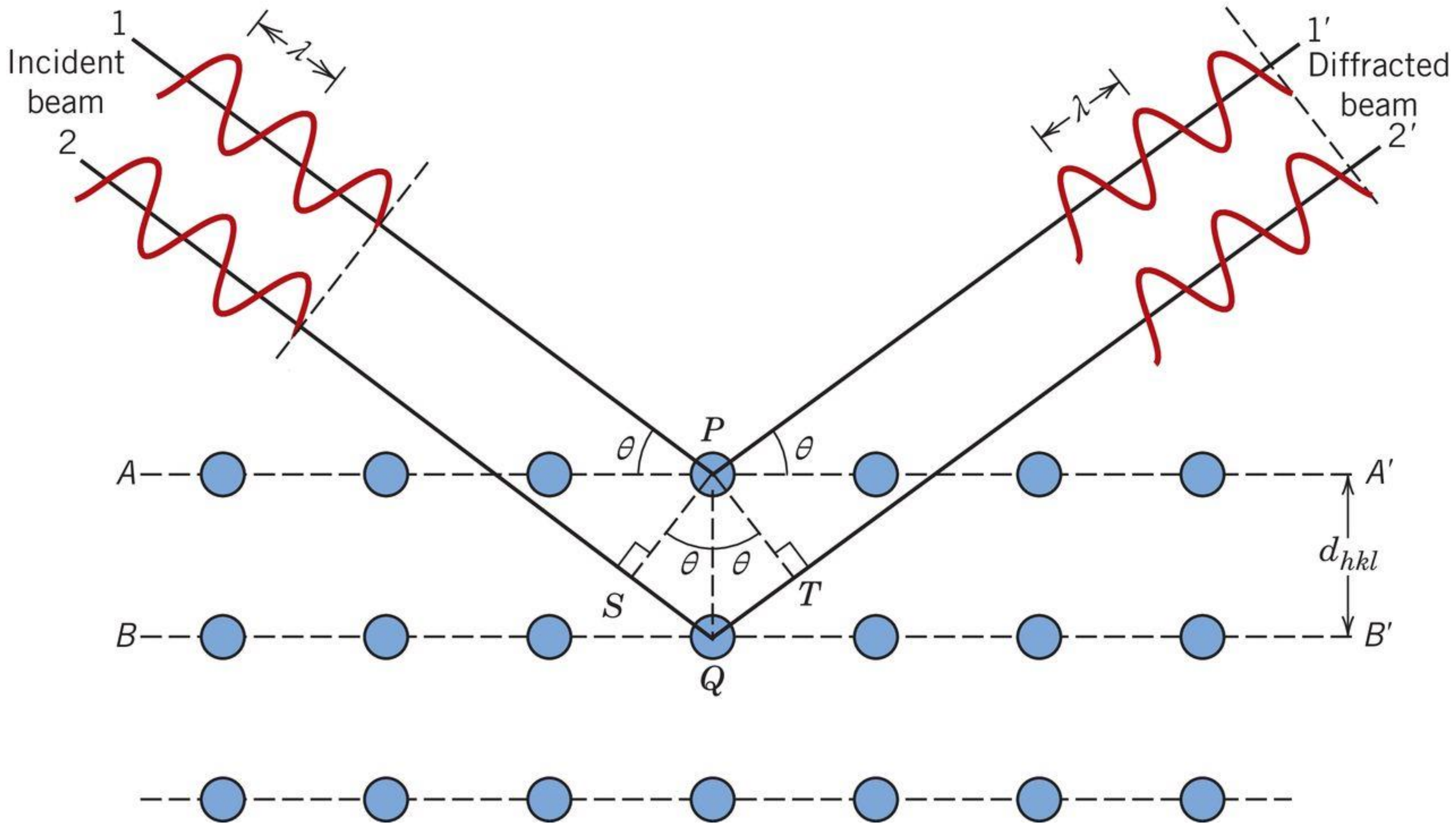
When the angle, θ, and the interplanar spacing, d_{hkl}, satisfy Bragg's Law, constructive interference occurs, and a peak is observed.

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 $|F(hkl)|^2$

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

Structure Factor

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Scattering Factor
- Dependent upon the identity of the atom

Structure Factor

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

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

Exponential Phase Term

- Accounts for atomic positions in the unit cell

Structure Factor

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

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

Debey Waller Factor

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

Simple Example

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

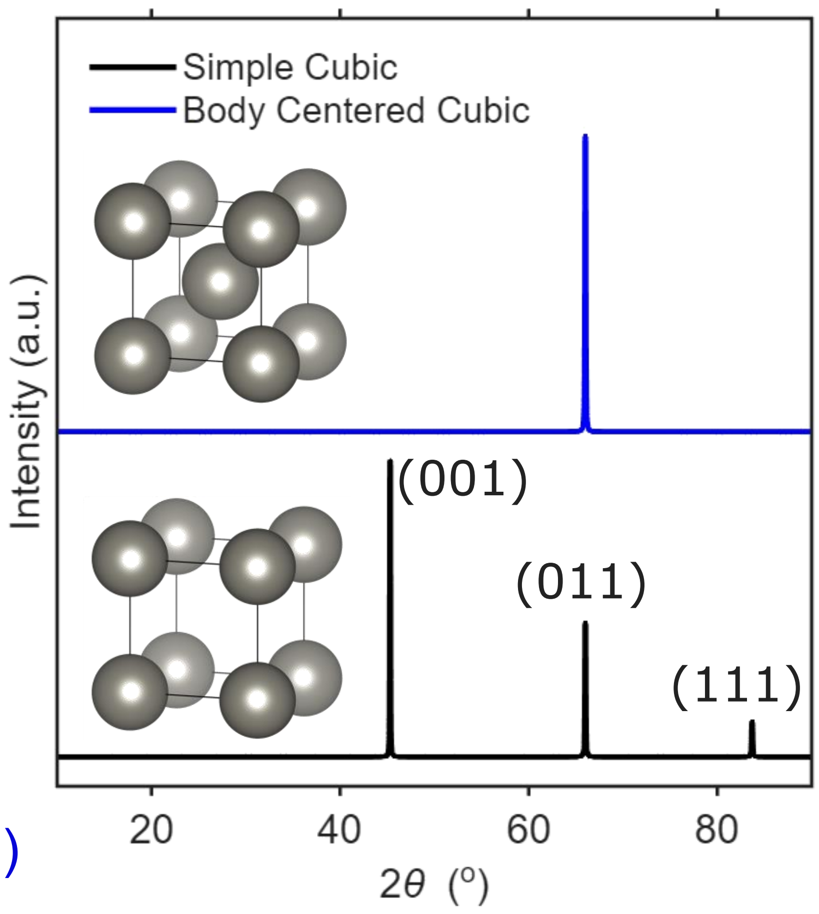
Simple cubic cell with one atom basis at (000)

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

Body centered cubic cell with atoms at (000) and (½ ½ ½)

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

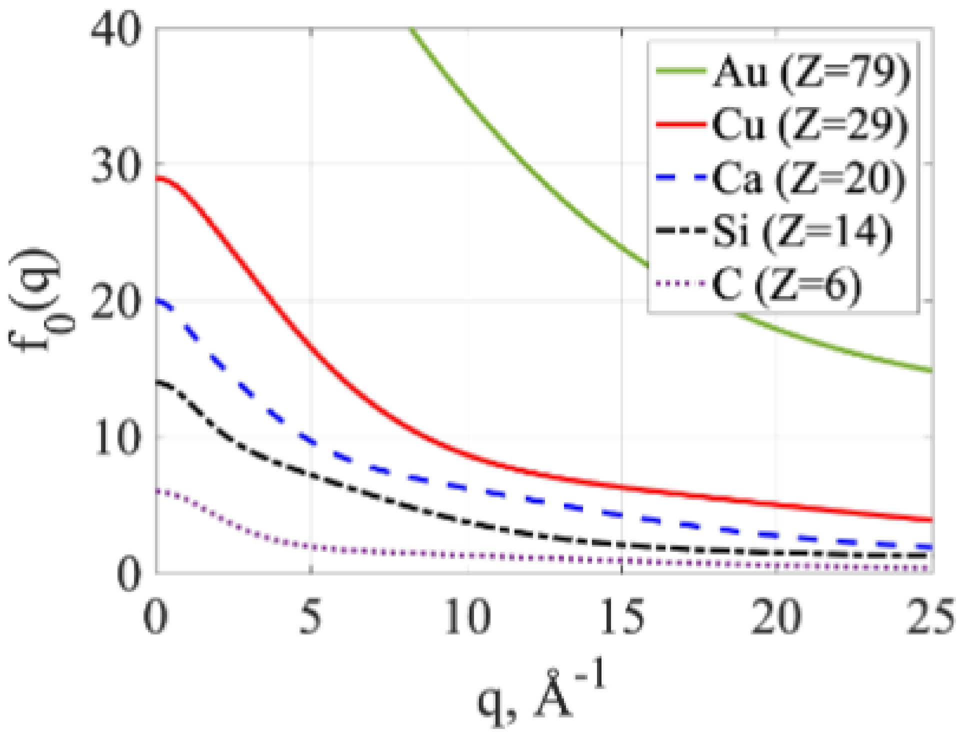
$$= 0 \text{ for odd } (h+k+l)$$

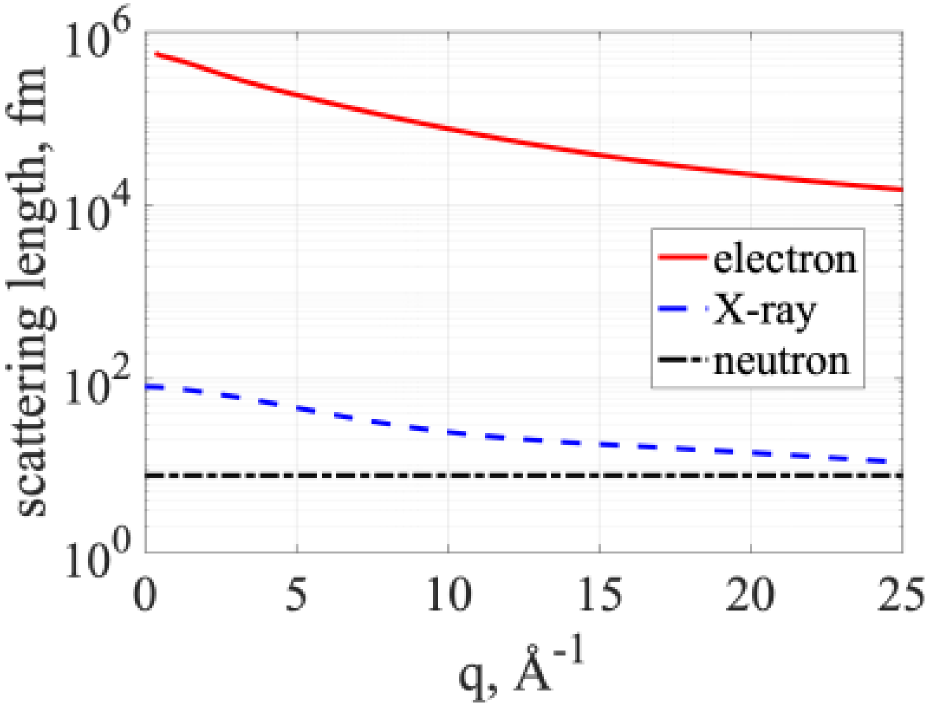


Systematic Absences in Cubic

$(h^2+k^2+l^2)$	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





Zaluzhnyy, I.; Schreiber, F. X-Ray and Neutron Scattering.

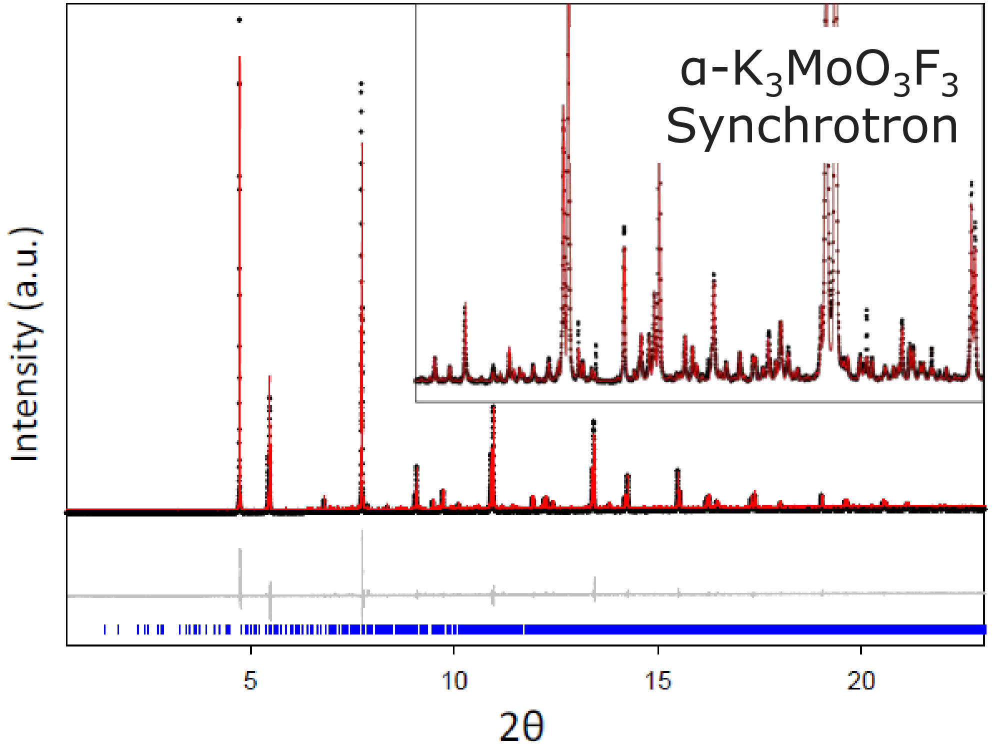
Form Factor Differences

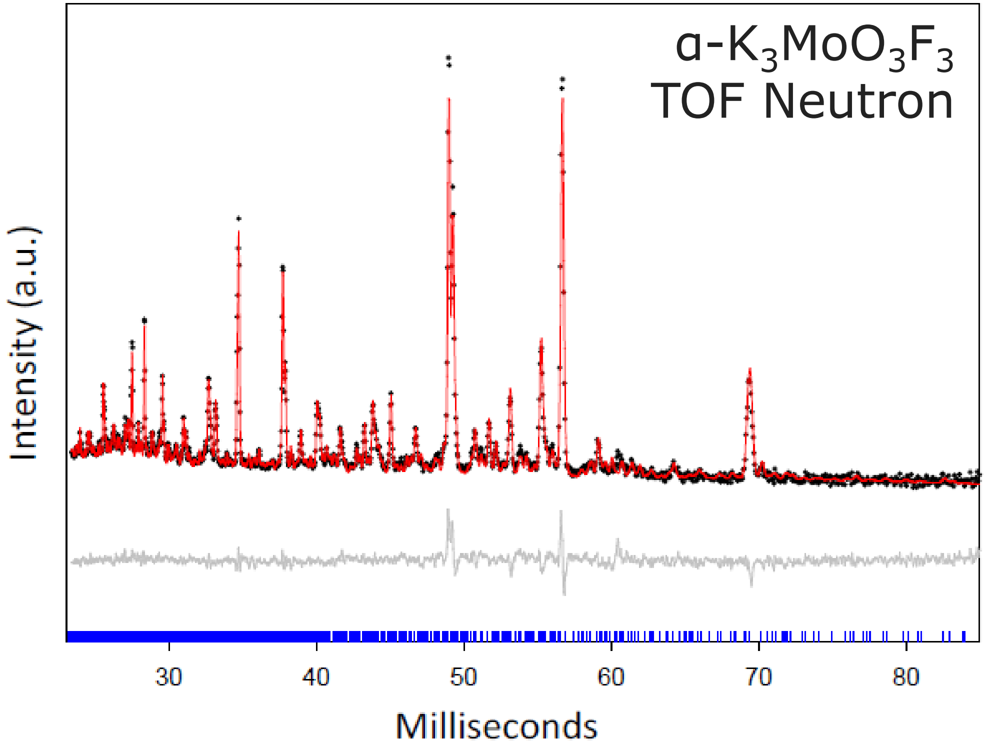
Synchrotron X-ray

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

Neutron

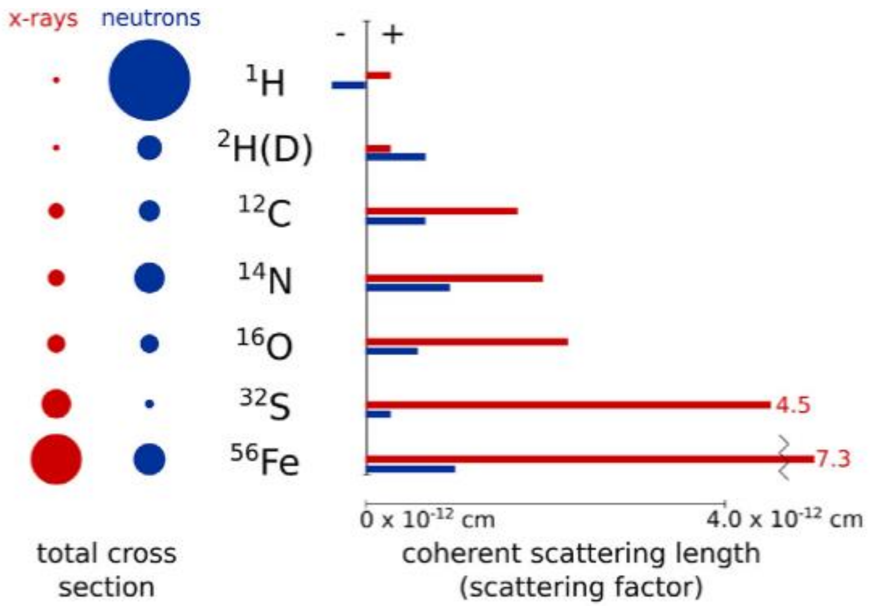
Intensities do not drop off at high angles b/c neutrons are scattered from the nucleus and thus the form factor is not angle dependent

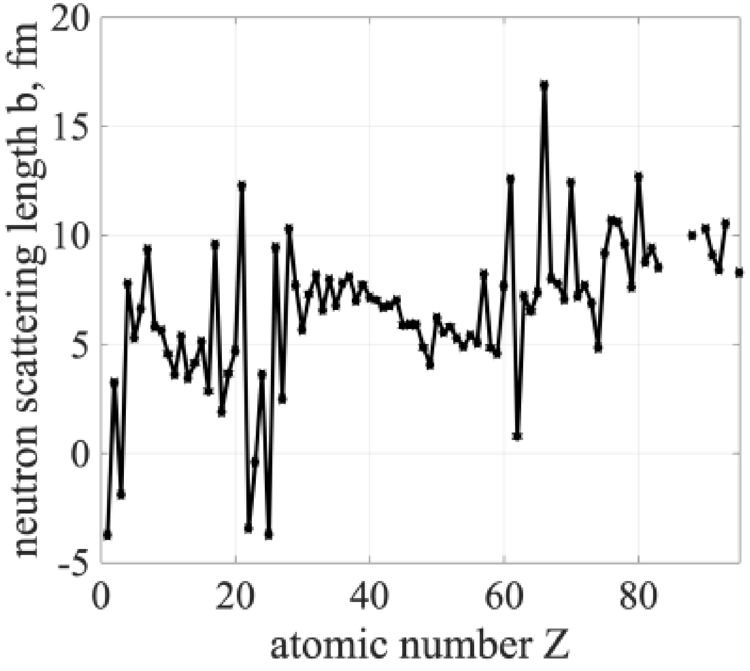


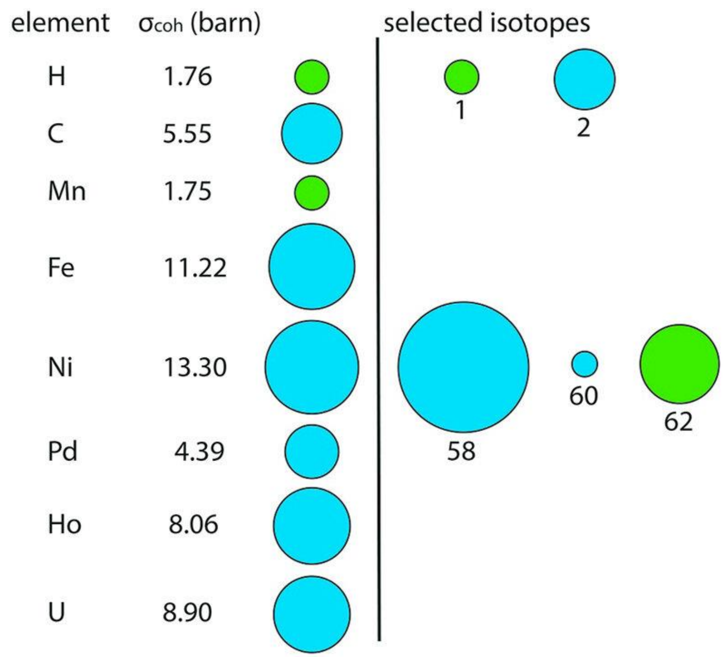


Fry, A. M.; Woodward, P. M. https://doi.org/10.1021/cg401342q.

Differences in scattering

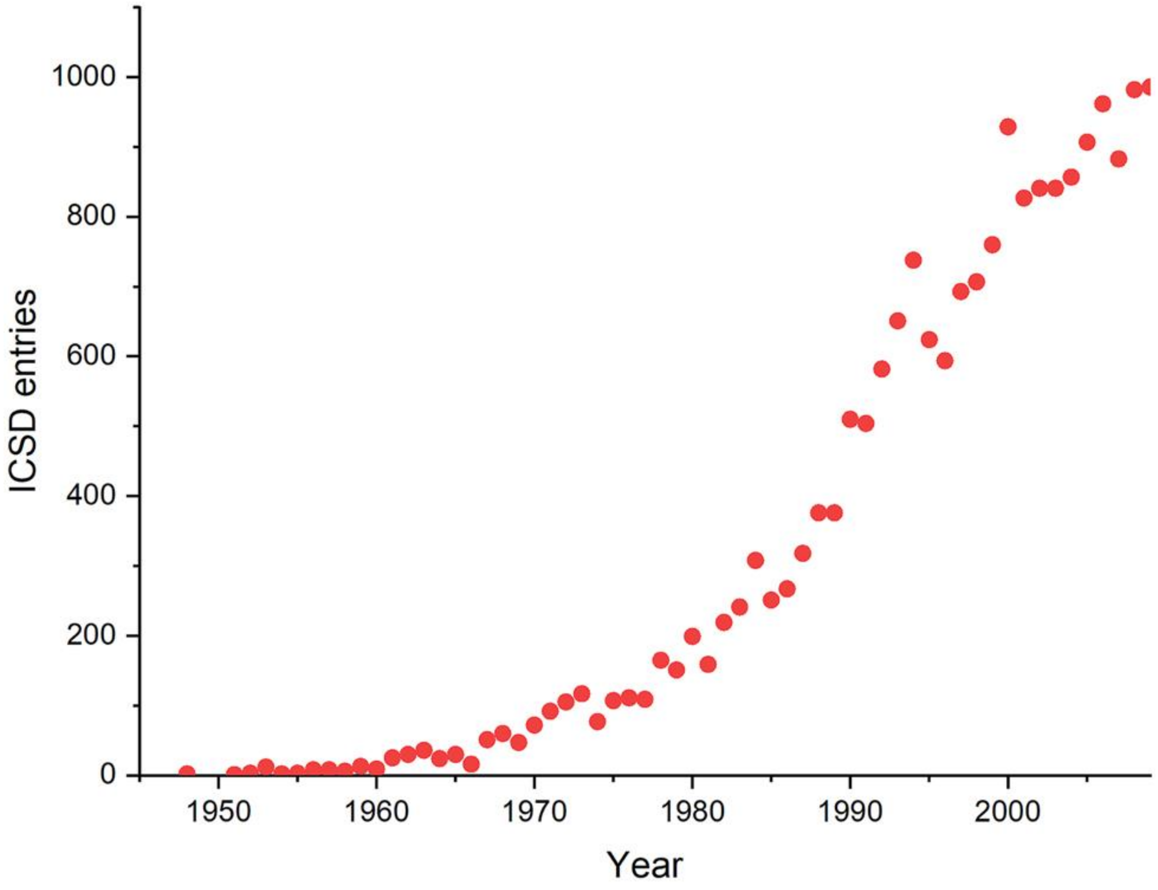






Neutron powder diffraction on the rise

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



Dronskowski, R. *et al*, https://doi.org/10.1515/zkri-2024-0001.

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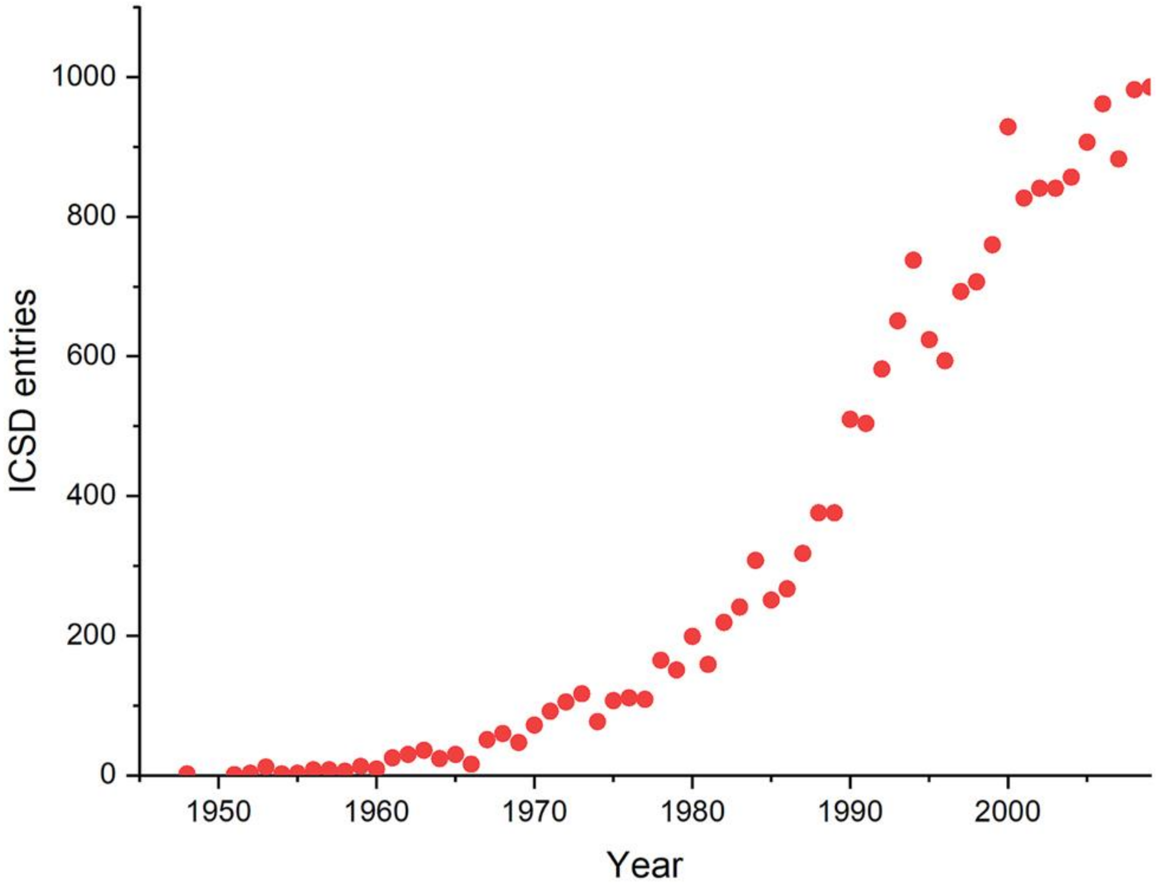

“Powder diffraction is of minimal value in crystal structure analysis and is not discussed in this book.”

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

Dronskowski, R. *et al*, https://doi.org/10.1515/zkri-2024-0001.
Bill David, PSI Powder Diffraction Workshop June 2008

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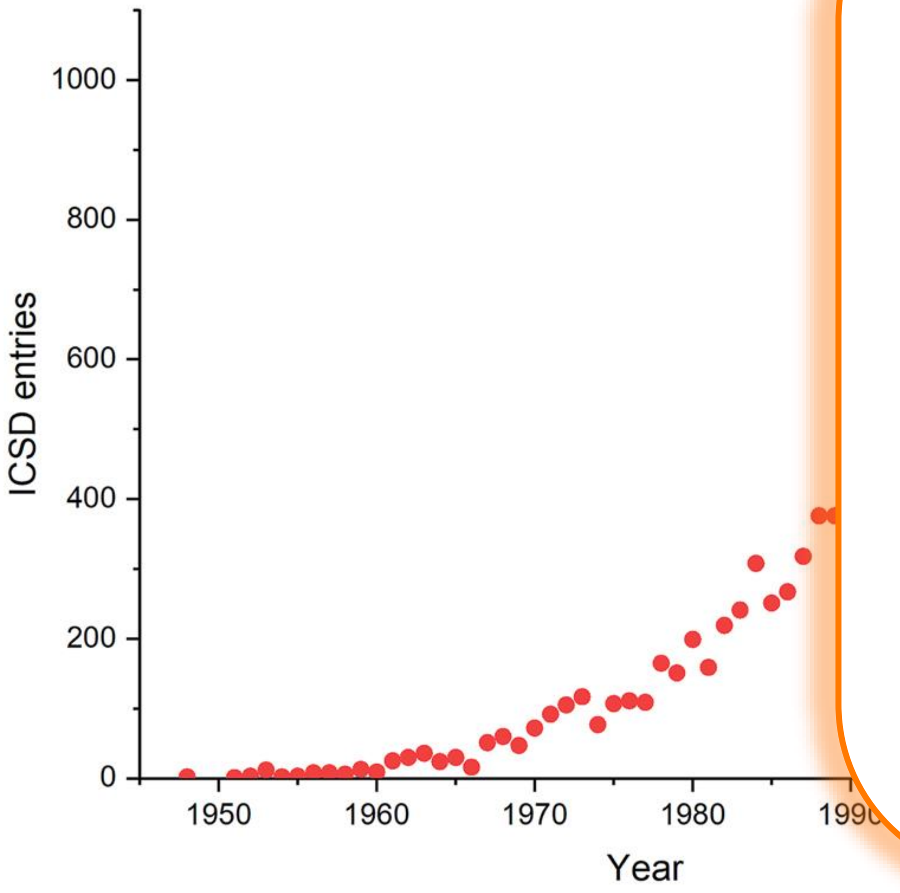
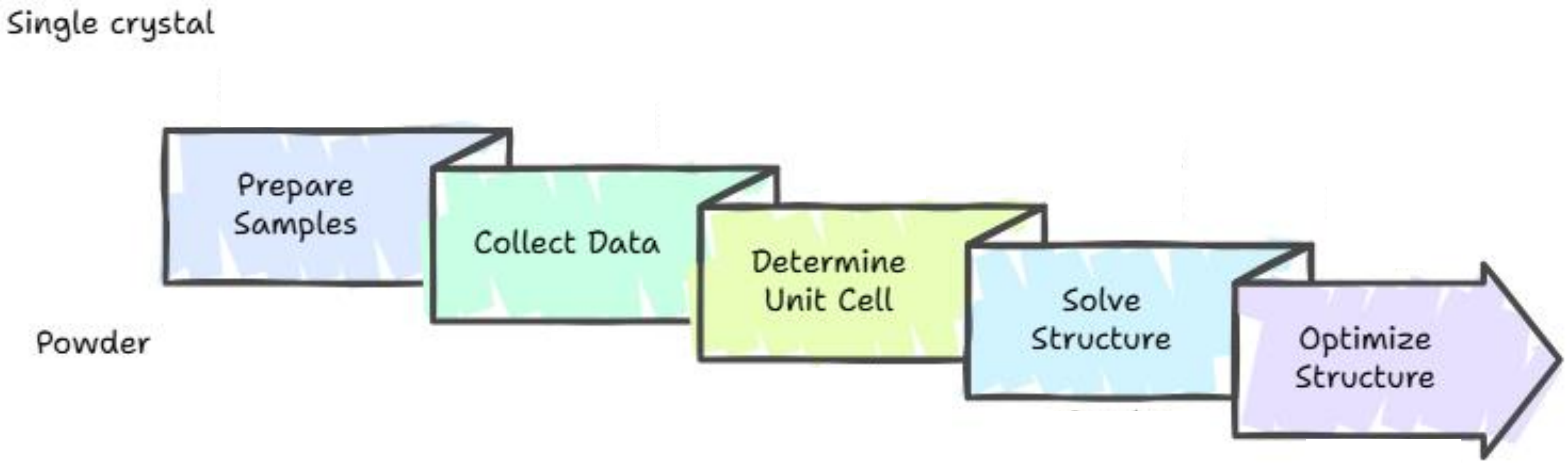


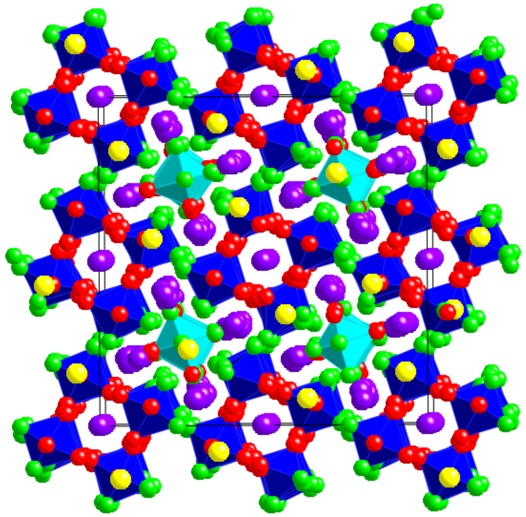
"The main interest in this book is structure determination for which powder methods have, until recent years, been inappropriate, mainly because of the problem of overlap of the X-ray reflections which causes three-dimensional data information to collapse on to a one-dimensional powder record."

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

Dronskowski, R. *et al*, https://doi.org/10.1515/zkri-2024-0001.

Goal of crystallography?





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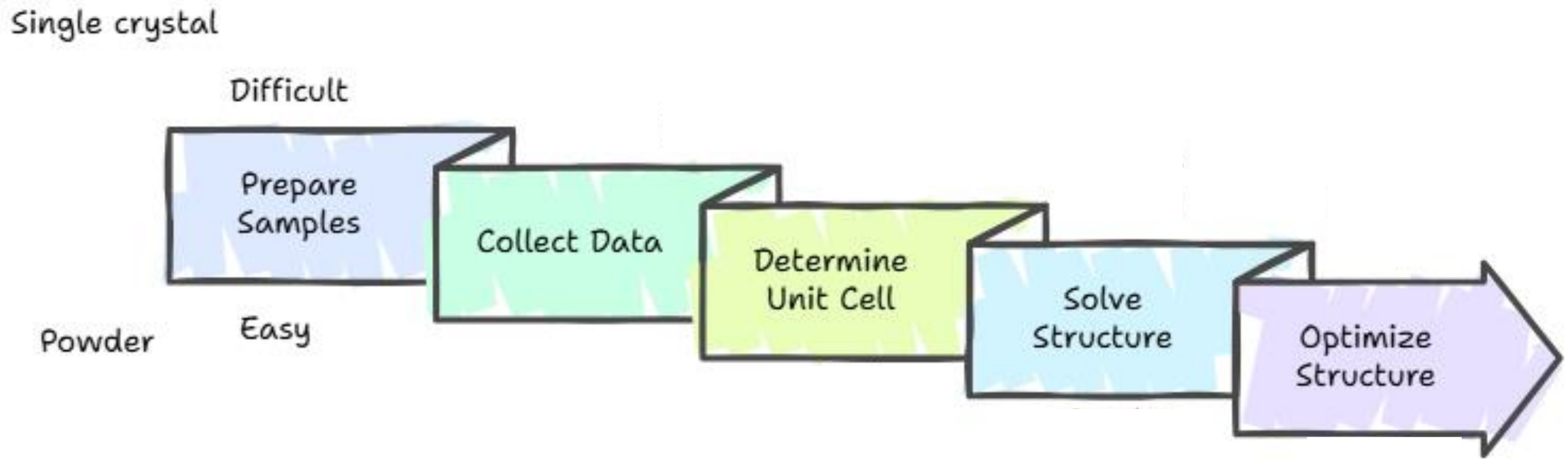

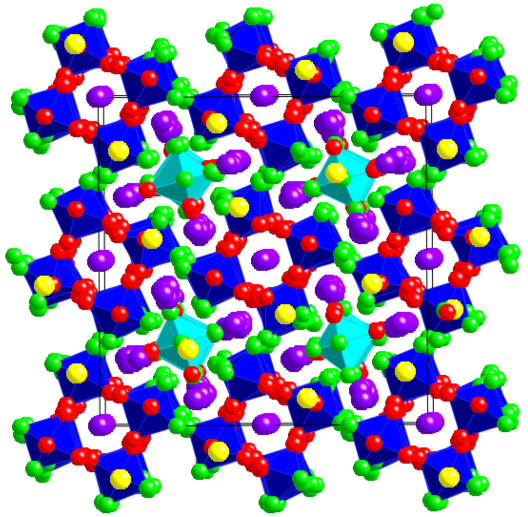

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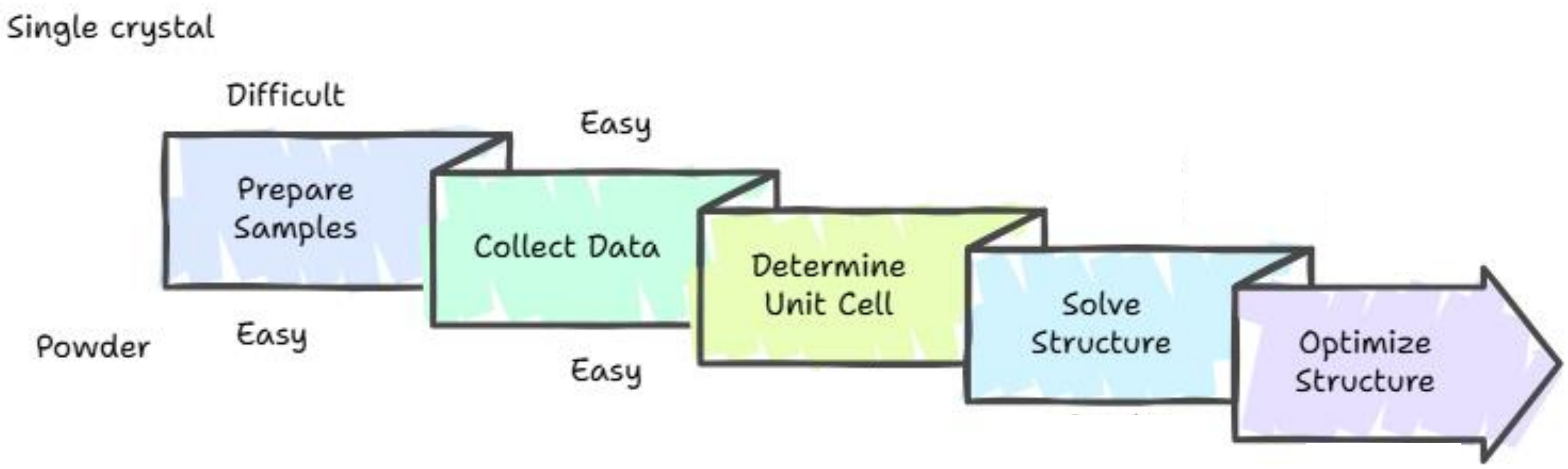

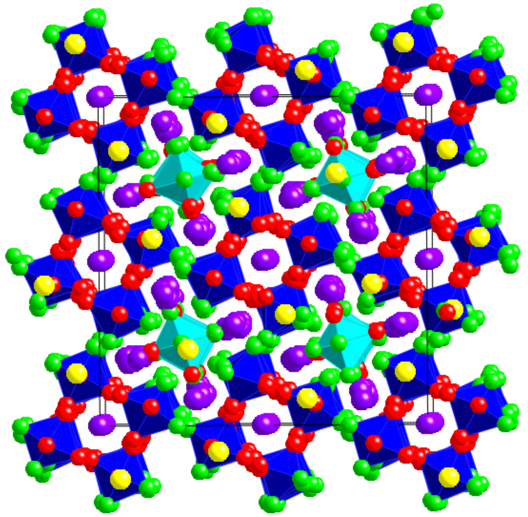

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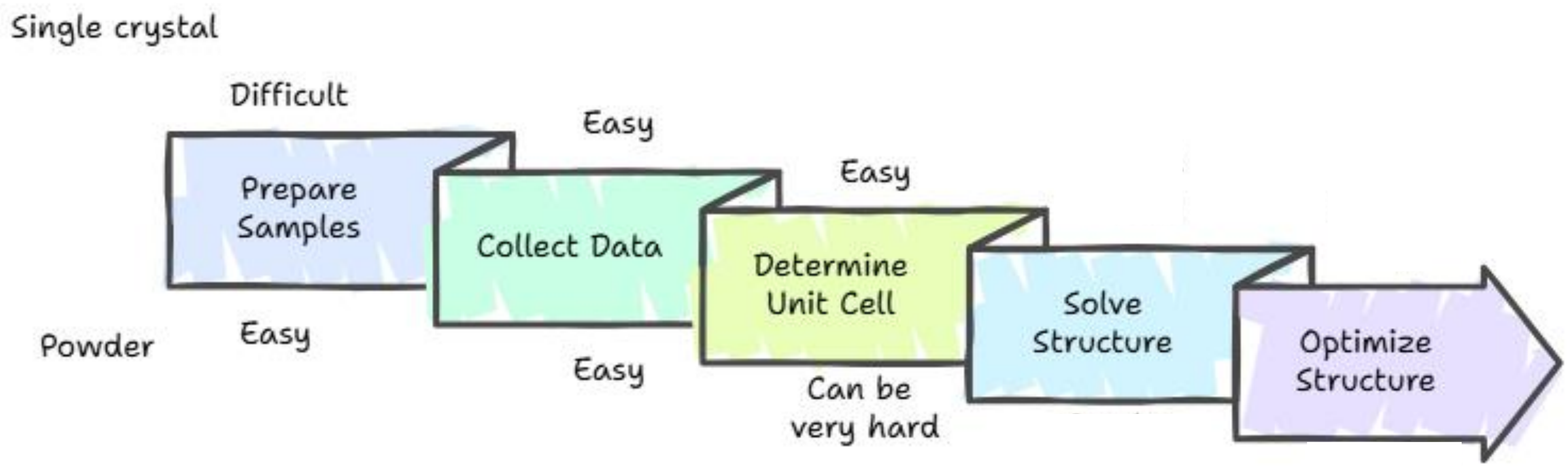

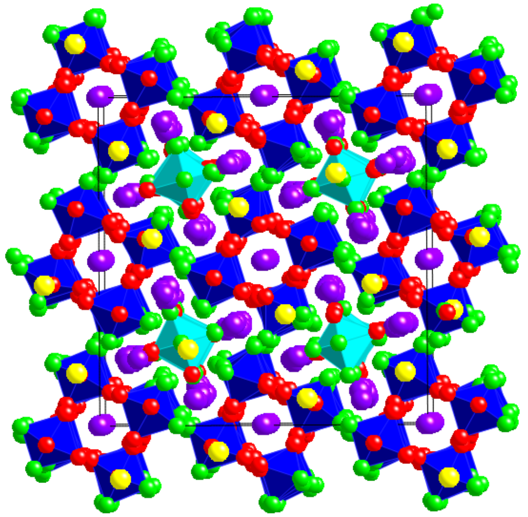

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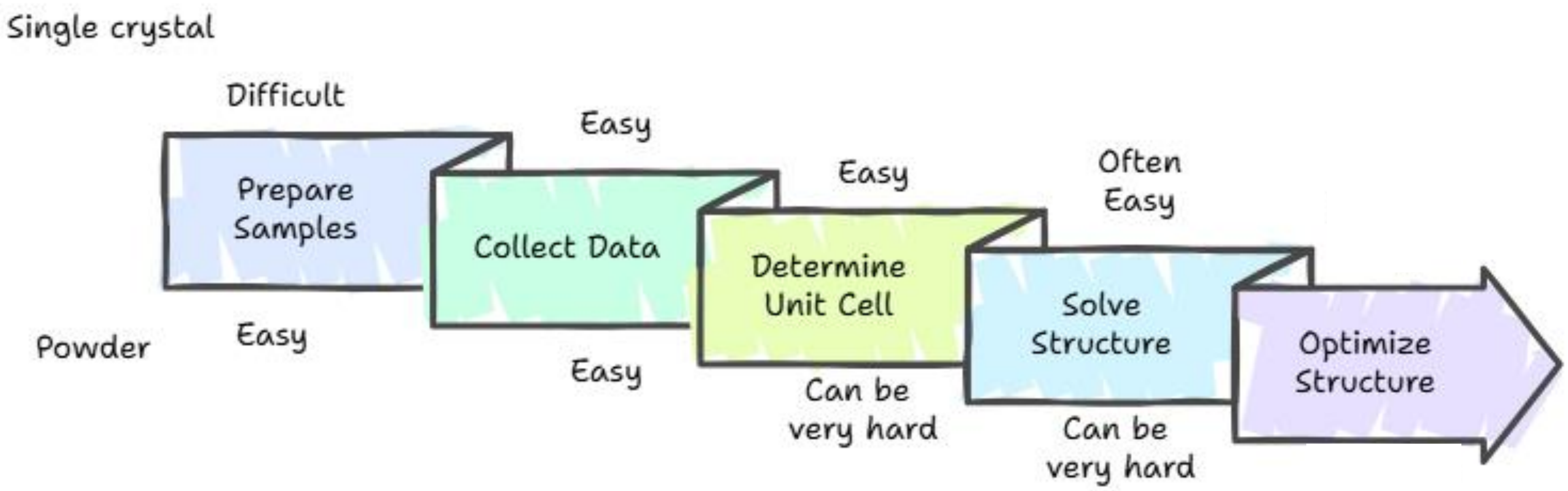

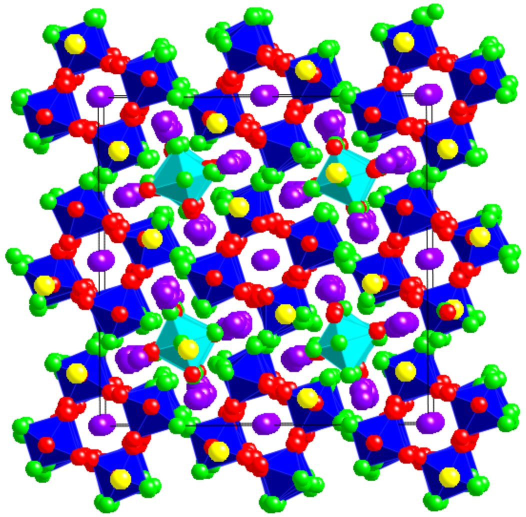

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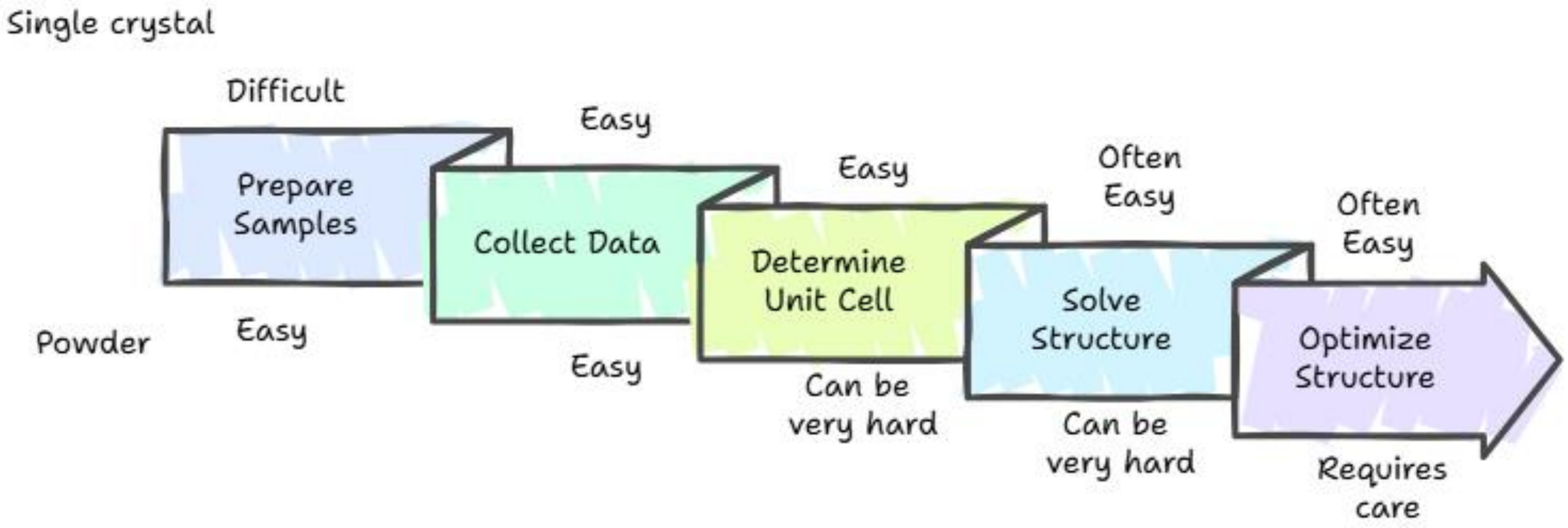
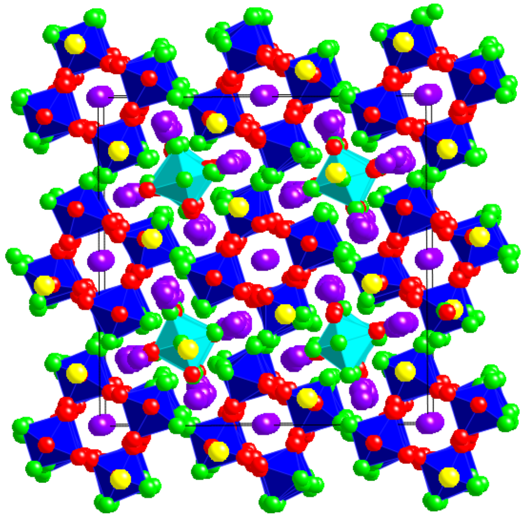
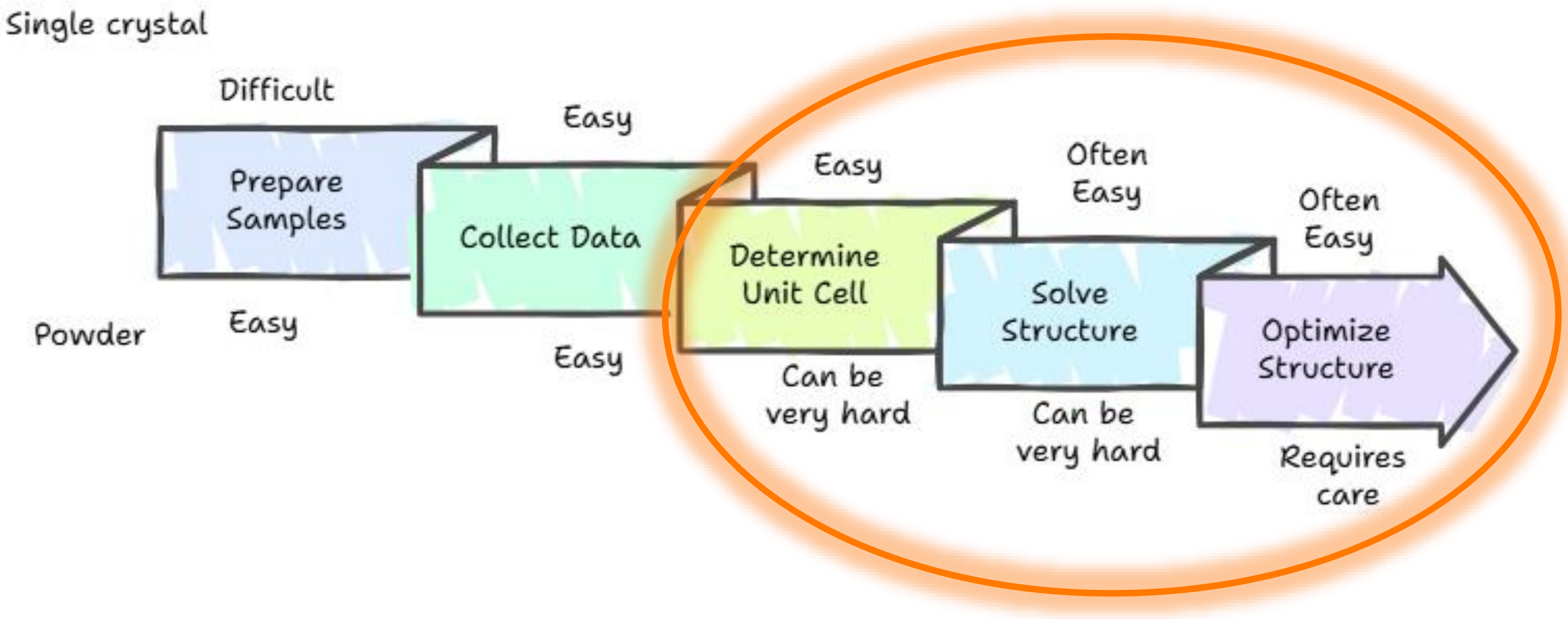
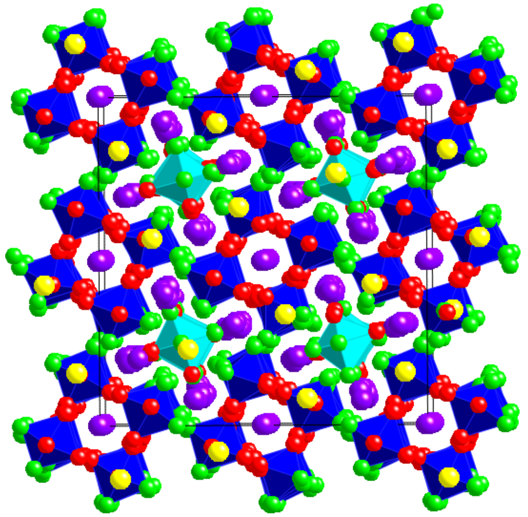




How did we reach the goal?





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."

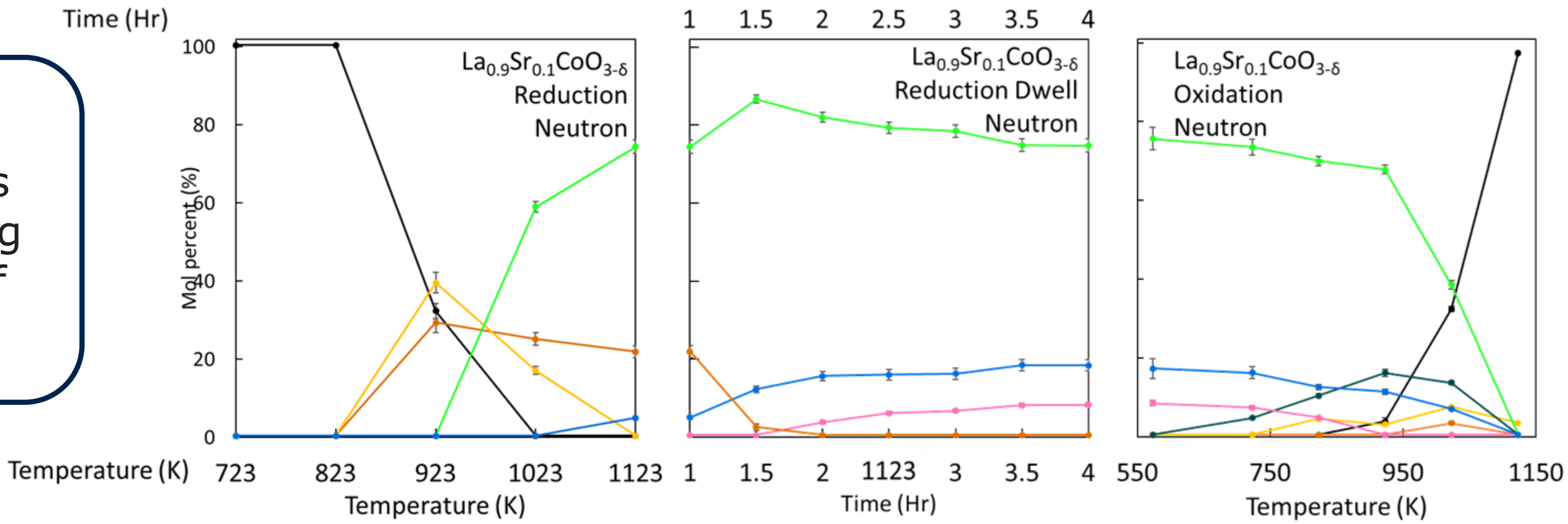
Dr. Rietveld at the neutron powder diffractometer at the High Flux Reactor of the Energy Research Foundation ECN in Petten, The Netherlands. (1987)

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

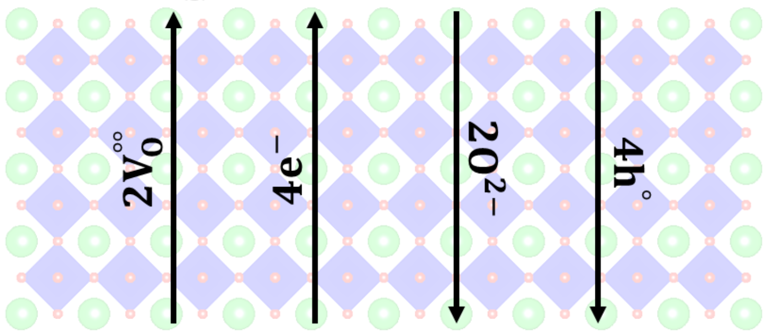
Phase Identification and Phase Fraction Analysis

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



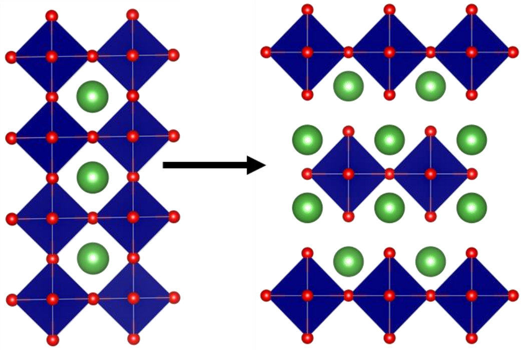
Reduction of oxygen gas and oxidation of OTM

$$O_{2\,(g)} + 2V_O^{\circ\circ} + 4e^- \rightleftharpoons 2O^{2-} + 4h^{\circ}$$



$$2CH_4 + 2O^{2-} + 4h^{\circ} \rightleftharpoons 2CO + 4H_2 + 2V_O^{\circ\circ} + 4e^-$$

Partial oxidation of methane and reduction of OTM



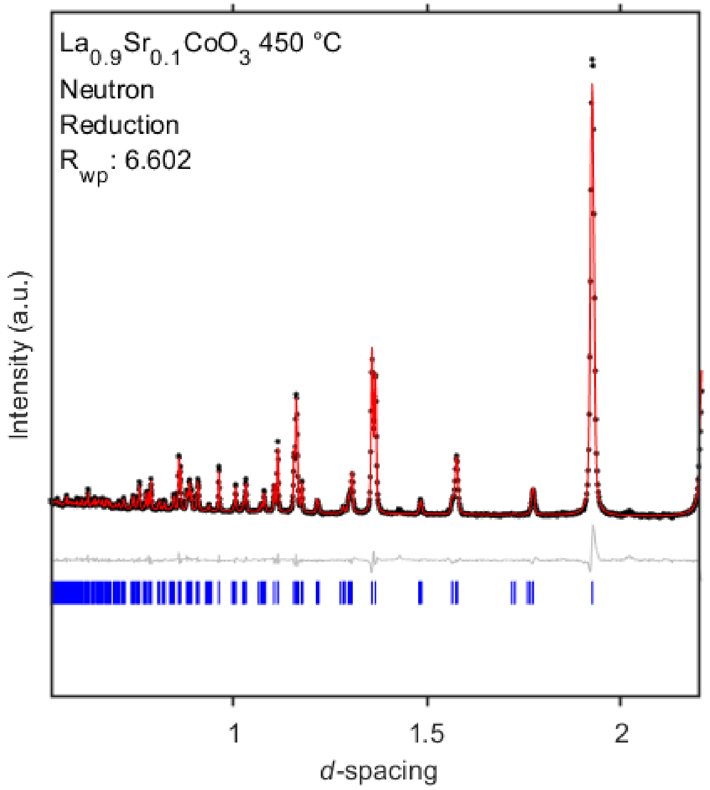
ABO_3 Perovskite

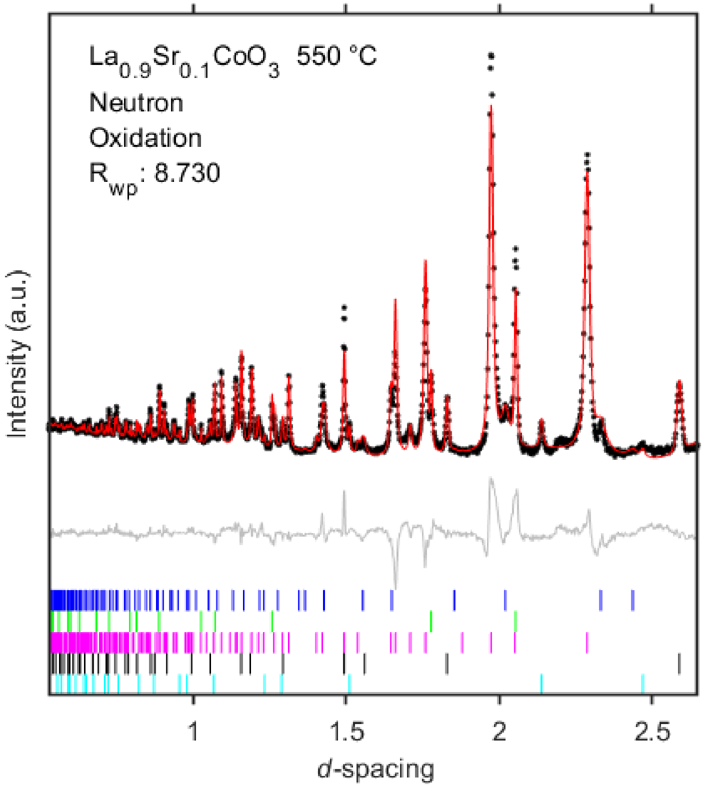
A_2BO_4 (n=1) Ruddlesden-Popper

Role of Neutron Diffraction

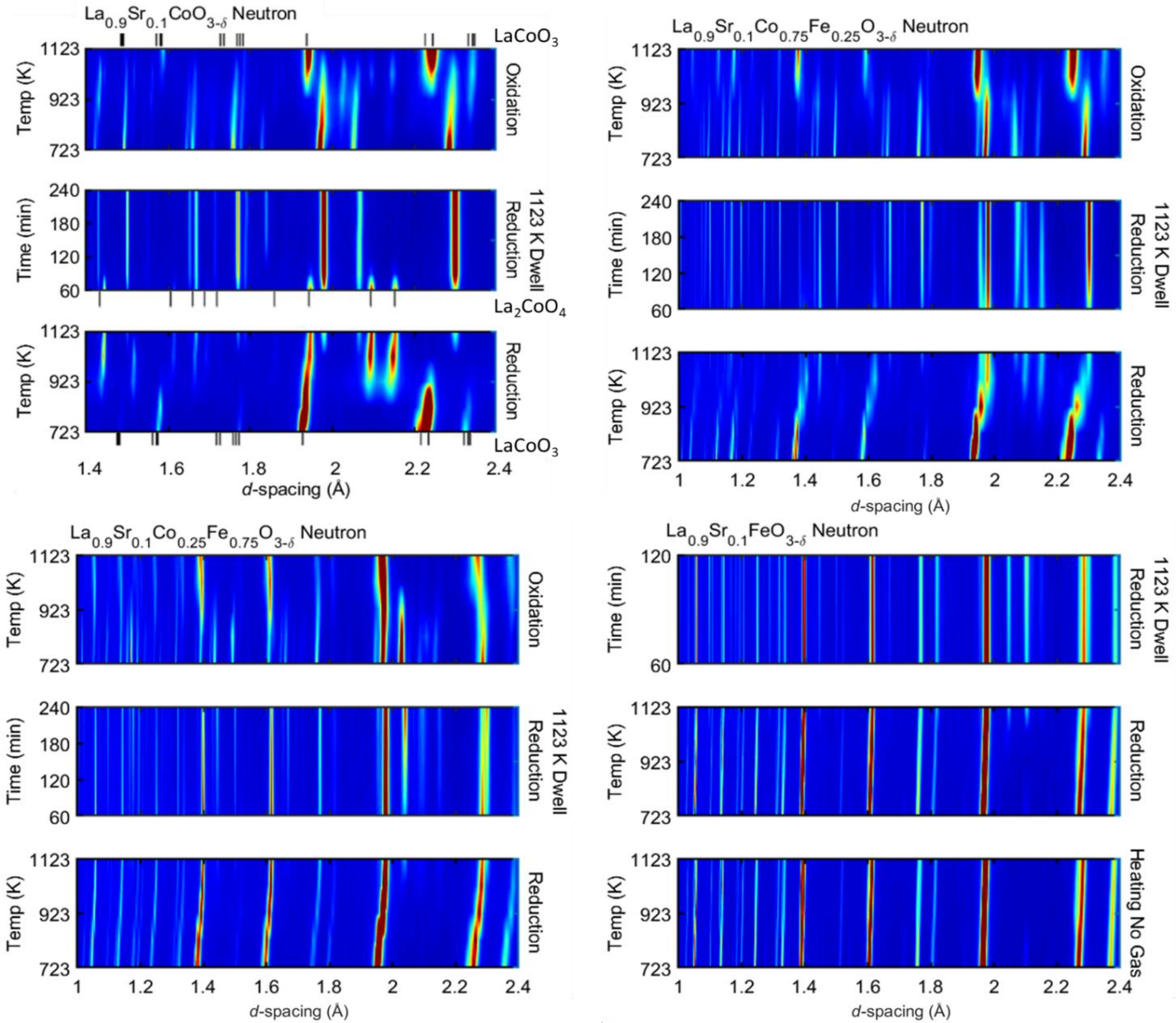
- Phase ID of all phases present
- Determination of catalytically active phases
- Quantification of all phases
- Determination of structural mechanism

Proof of diffraction

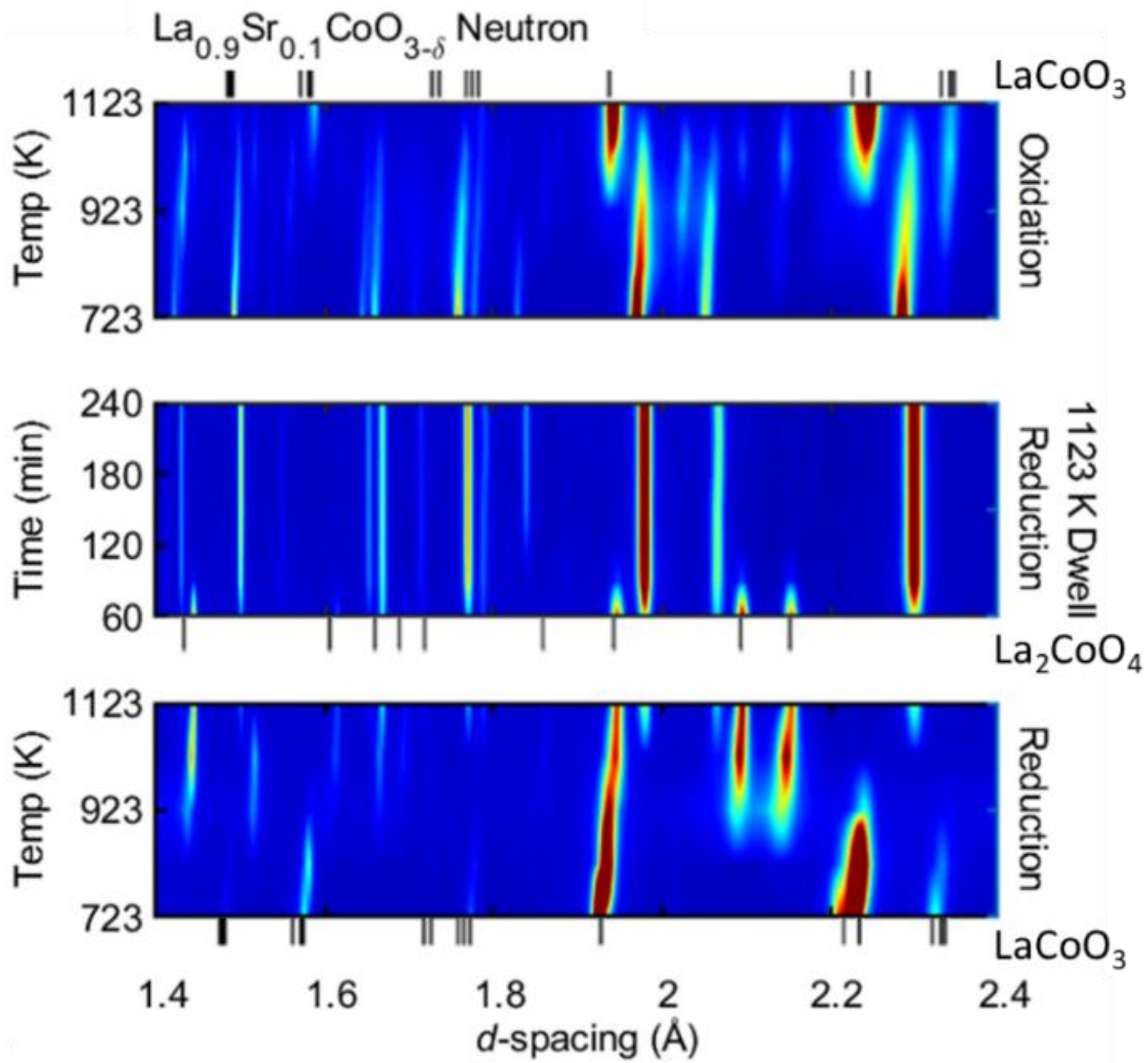




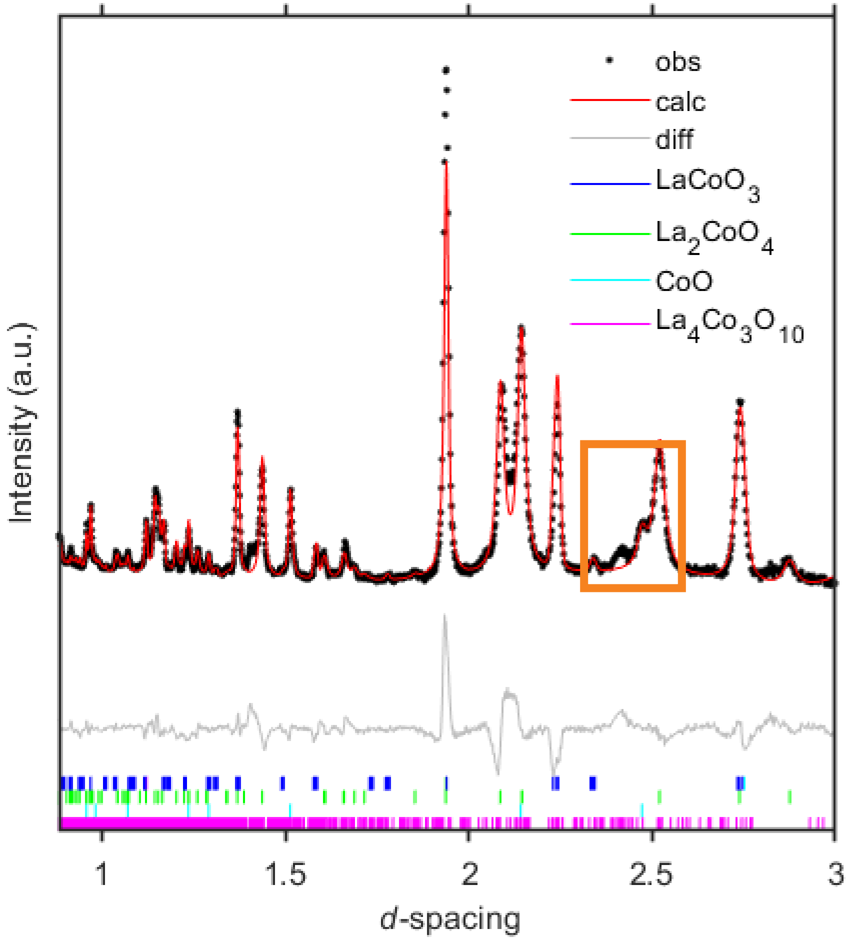
Proof of diffraction



Proof of diffraction

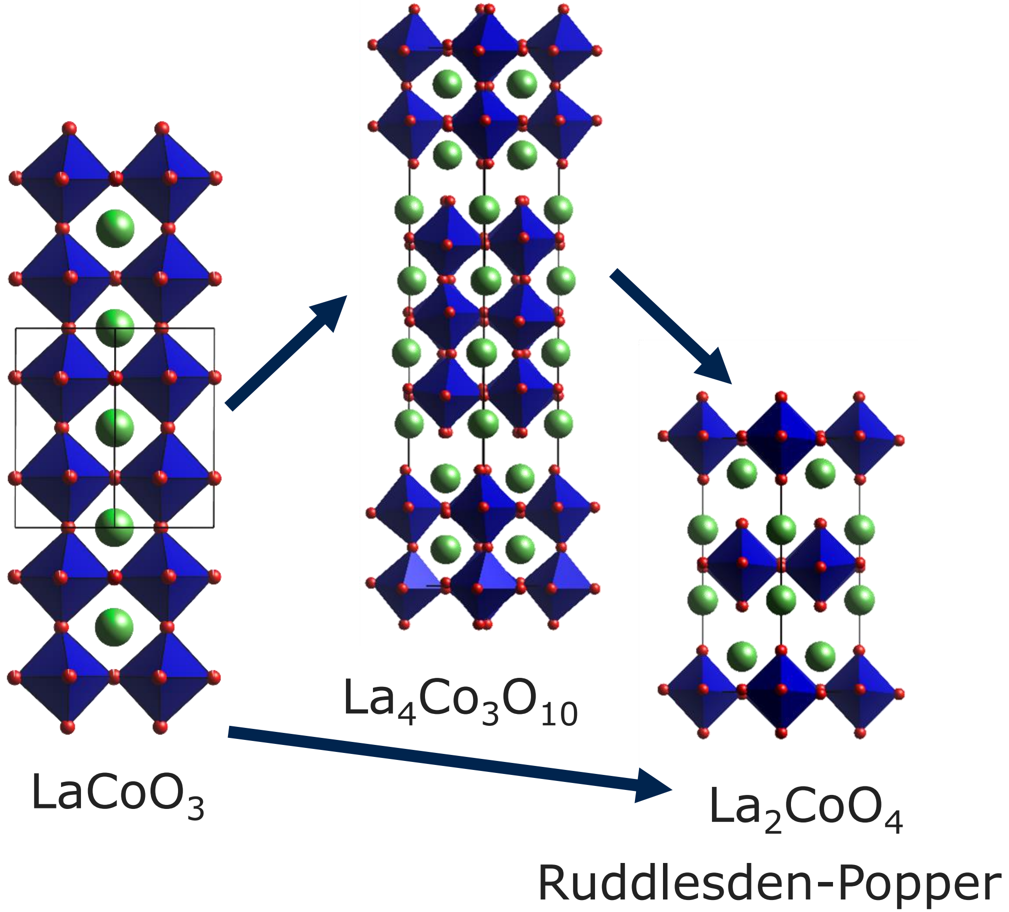


Benefit of neutron: size dependent intermediates



$8LaCoO_3 \rightarrow 2La_4Co_3O_{10} + 2CoO + O_2$

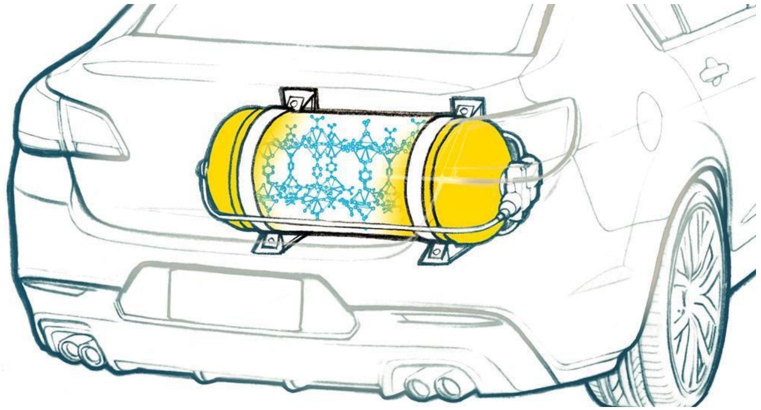
$La_4Co_3O_{10} \rightarrow La_2CoO_4 + La_2O_3 + CoO + O_2$

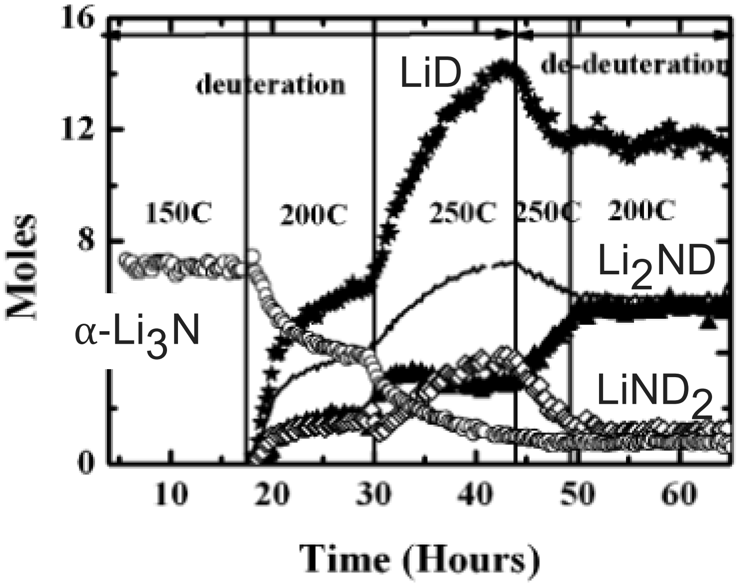


Lattice Parameters

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

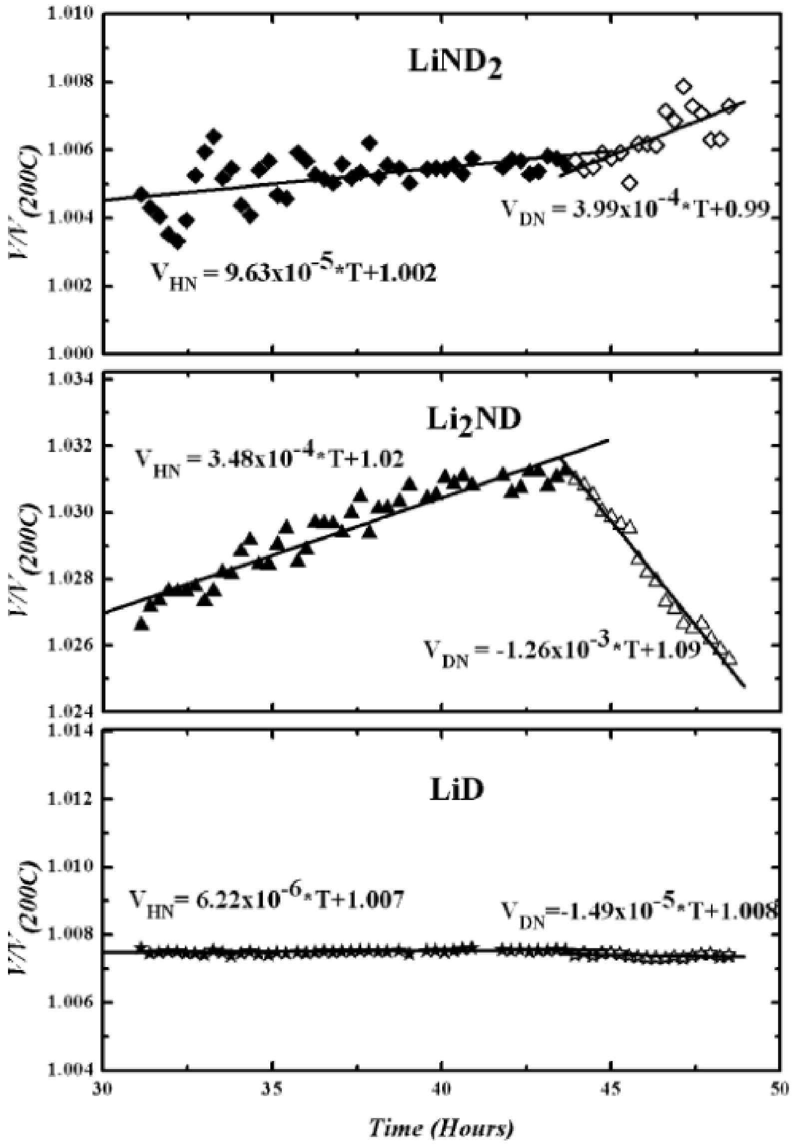
$Li_3N + 2H_2 \rightarrow Li_2NH + LiH + 2H_2 \leftrightarrow LiNH_2 + 2LiH$





Role of Neutron Diffraction

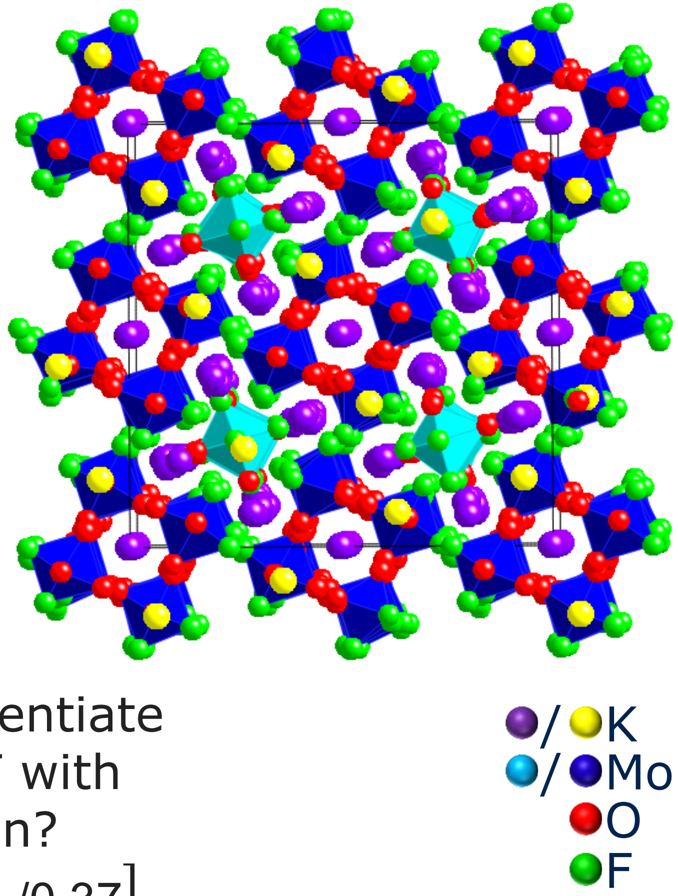
- Quantification of all phases during cycling
- Confirmed rxn mechanism
- Determined the existence of non-stoichiometric phases during hydrogenation from lattice parameters

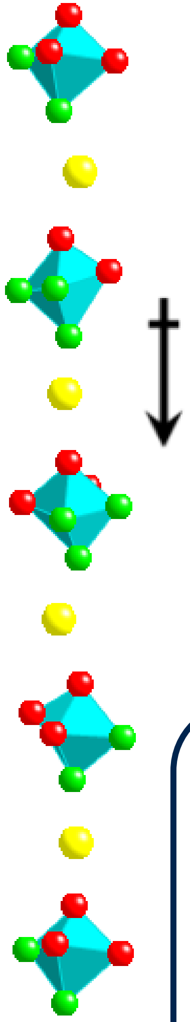


Huq, A. *et al*. https://doi.org/10.1021/jp070026d.
http://chemistryworld.com/features/hydrogen-storage-gets-real/3010794.article

Rietveld Refinement and Structural Solution

Research Question
What is the oxygen and fluorine ordering in the ferroelectric α-$K_3MoO_3F_3$ and is the ordering driving ferroelectricity?





$A_2BB'O_3F_3$

$I4_1$

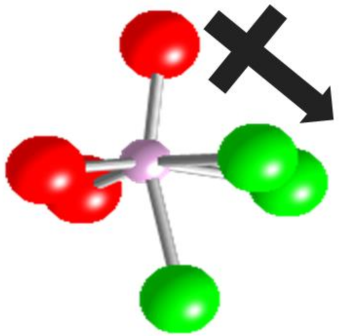
$a \approx a_p\sqrt{5}=19.38613(3)$Å

$c \approx 4a_p=34.86739(8)$Å

V= 13103.93(4) $Å^3$

Z=80

104 crystallographically independent sites



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

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

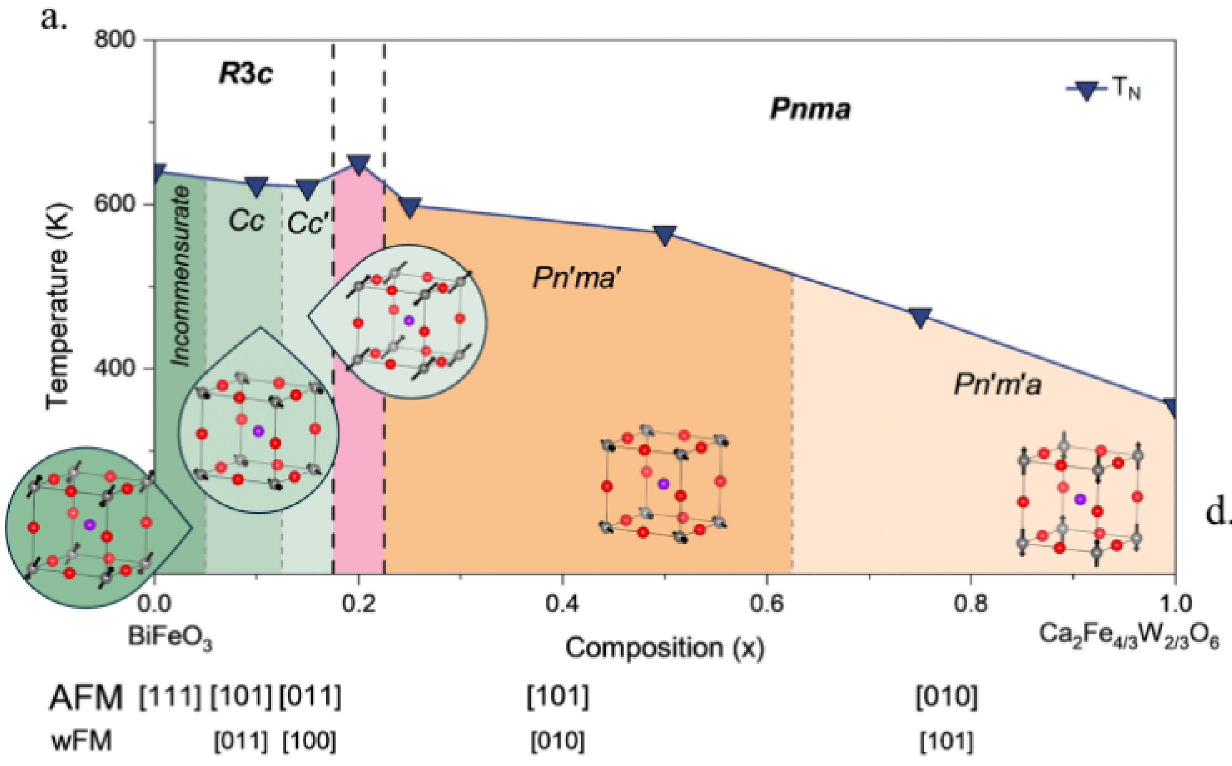
$$\sum v_{ij}=\text{oxidation state}$$

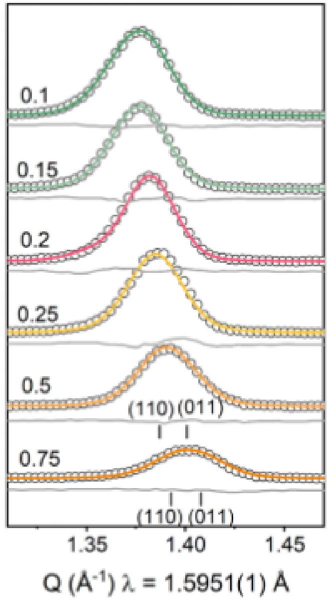
Role of Neutron Diffraction

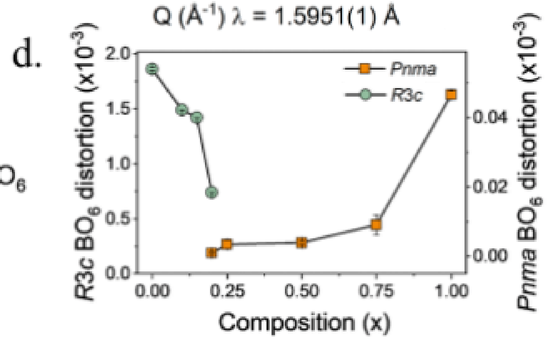
- Structural solution and refinement of a massive unit cell
- Determination of oxygen and fluorine positions and polarization vector

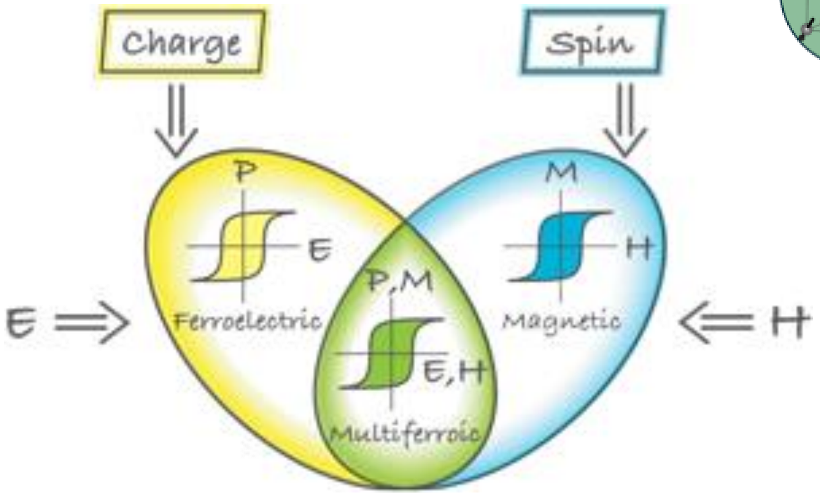
Magnetic structure determination

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







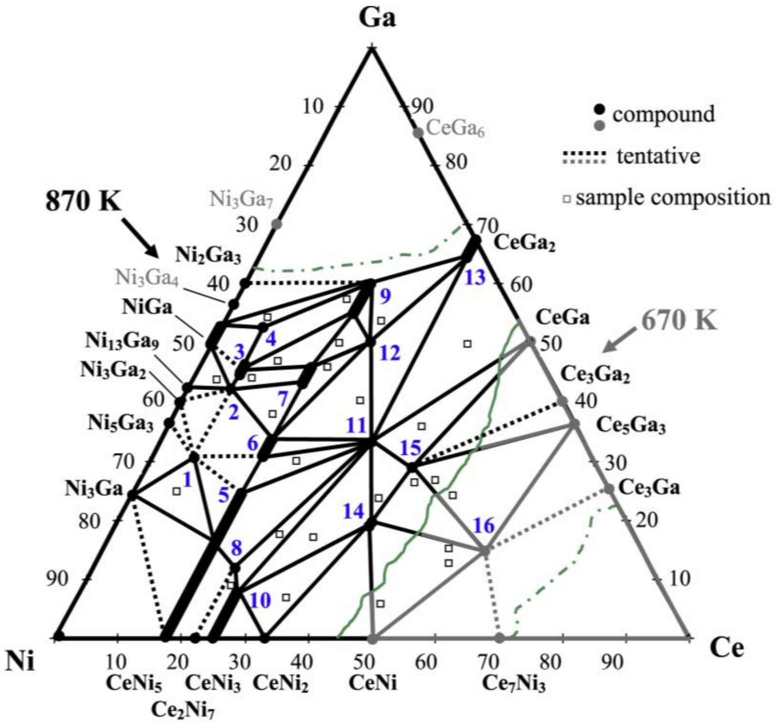


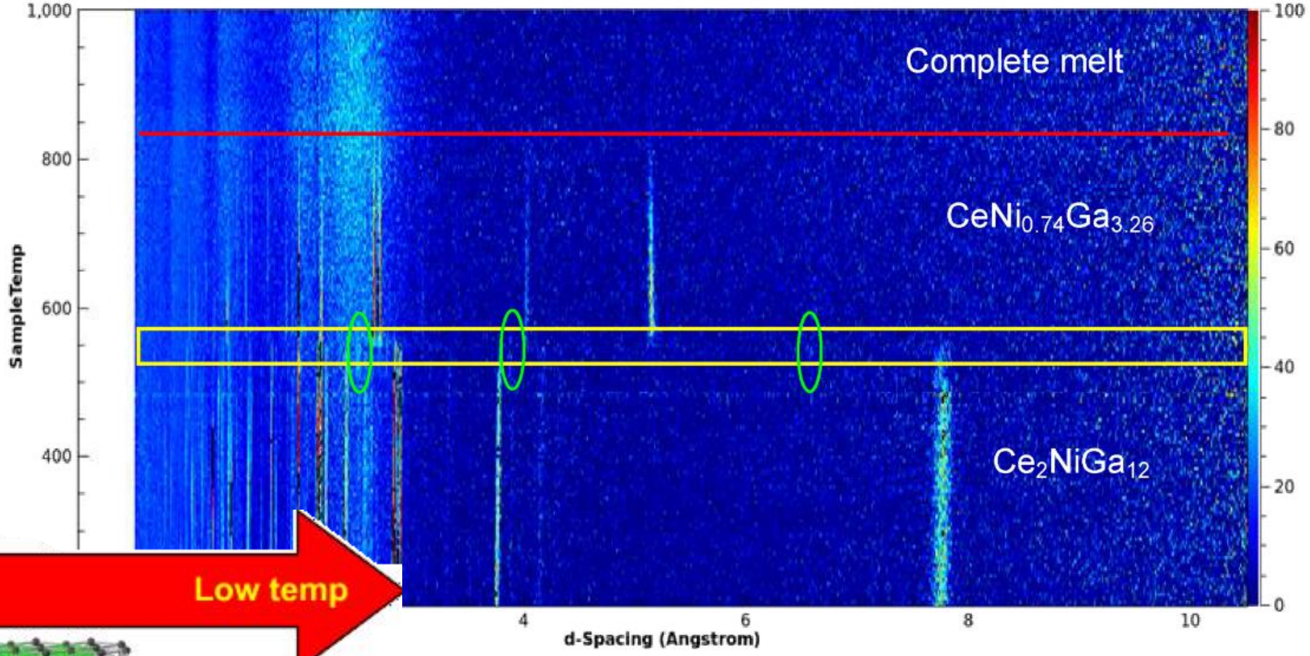
Role of Neutron Diffraction

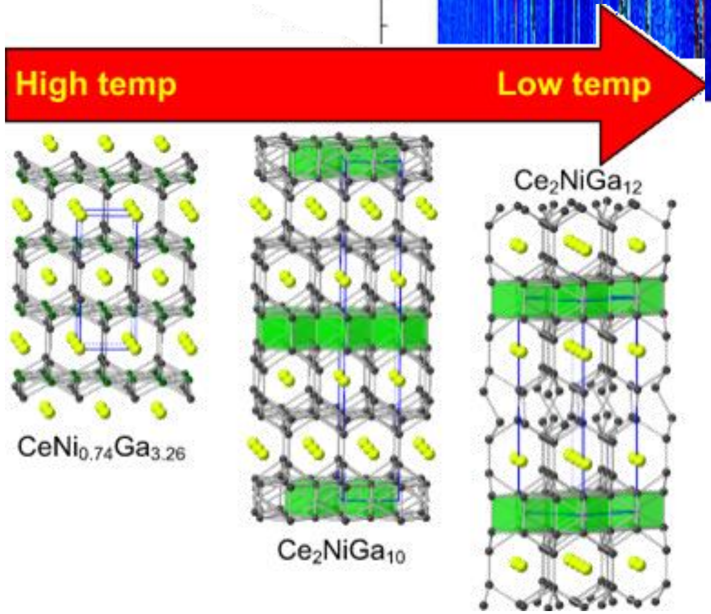
- Correlation of the nuclear and magnetic structure via precise oxygen positions and magnetic scattering

Phase Transitions and Synthesis

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







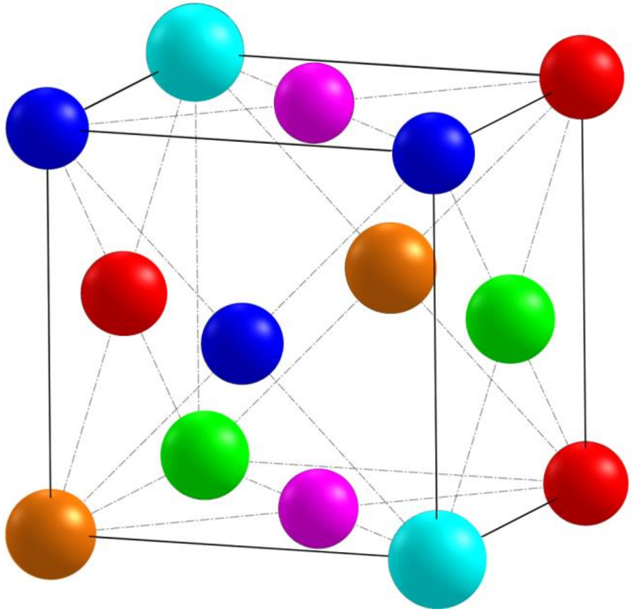
Role of Neutron Diffraction

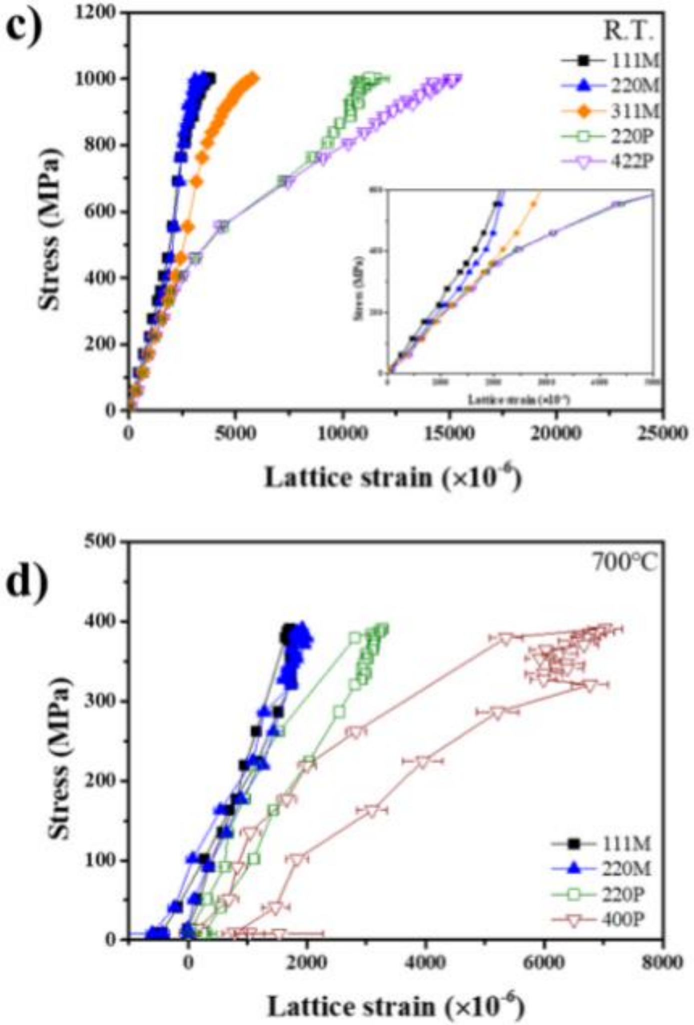
- Determined the temperature for formation of different structures
- Allowed for the *ex situ* isolation of phases that would have been missed otherwise

Haddock, J. W.et al. https://doi.org/10.1021/acs.inorgchem.2c02588.
Yao, J. et al. https://doi.org/10.1016/j.jssc.2020.121895.

Line Shape Analysis

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





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)