Yale Course 2018: ‘Advanced Synchrotron and Electron Spectroscopy of Materials’

X-ray Powder Diffraction

Eric Dooryhee Phone: 631-344-2409

Email: dooryhee@bnl.gov

February 08, 2018

Lecture Schedule

Yale Course 2018: Advanced Synchrotron and Electron Spectroscopy of Materials

APHY/ENAS/MENG 450/725, Becton Rm.227, Thursdays, 1:30 - 3:30 PM

Date	Lecturer	Topic	Confirmed
1/18/2018	Qun Shen	Introduction / X-ray Interaction with Matter	Y
1/25/2018	Robert Sweet	X-ray Diffraction & Crystallography	Y
2/1/2018	Timur Shaftan	Synchrotron Radiation	Y
2/8/2018	Eric Dooryhee	X-ray Powder Diffraction	Y
2/15/2018	Anibal Boscoboinik	X-ray Photoelectron Spectroscopy	Y
2/22/2018	Bruce Ravel	X-ray Spectroscopy	Y
3/1/2018	1st Exam		
3/8/2018	Yong Chu	X-ray Microscopy	Y
3/15/2018	Spring Break		
3/22/2018			
3/29/2018	Oleg Gang	Small-Angle & Wide-Angle X-ray Scattering	Y
4/5/2018	Ignace Jarrige	X-ray Emission Spectroscopy & RIXS	Y
4/12/2018	Wah-Keat Lee	X-ray Imaging	Y
4/19/2018	Eric Stach	Transmission Electron Microscopy & EELS	Y
4/26/2018	2nd Exam		
5/3/2018	NSLS-II/CFN tour ?		

My Bio

Education:
- University of Paris, PhD, 1987
- Res. Associate, Synchrotron Radiation Source, Daresbury, UK, 88-89

Professional Experience:
- Assoc. Scientist, Res. Center with Ions and Lasers, France, 90-95
- Scientist, European Synchrotron Radiation Facility, France, 96-00
- Scientist, Neel Institute, CNRS Grenoble, France, 01-09
- Scientist, beamline lead, Brookhaven National Lab., NSLS II, 09-

Background: Materials Science, Irradiation Physics, PD, SR

Current position: ‘Diffraction & In Situ Scattering’ Program Manager

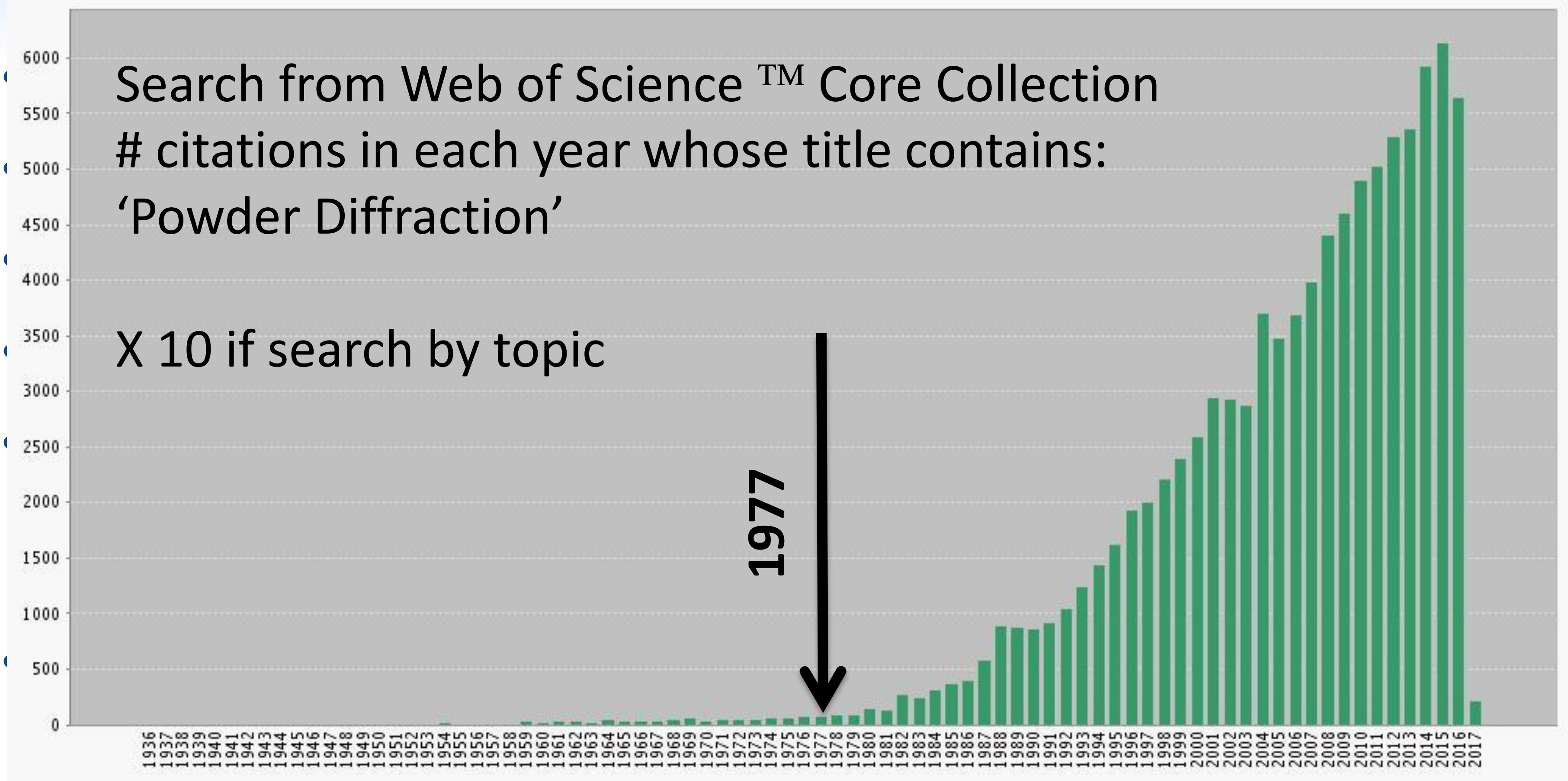
Outline

1. Applications for Powder Diffraction
2. The basics of Powder Diffraction
3. Experimental Methods for collecting PD data
4. Crystal structure Determination
5. Peak Profile Analysis for Microstructural Studies
6. Advanced PD techniques

Short History of Powder Diffraction

- **1895** Discovery of X-rays by Roentgen
- **1912** von Laue demonstrates that X-rays can be diffracted by crystals
- **1935** Le Galley constructs the first X-ray powder diffractometer
- **1947** Phillips introduces the first commercial powder diffractometer
- **1950-60's** Powder diffraction used primarily to study structural imperfections, phase identification, … largely by metallurgists and mineralogists
- **1969** Hugo Rietveld develops a method for whole pattern analysis of neutron powder diffraction data
- **1977** Cox, Young, Thomas and others first apply Rietveld method to laboratory and synchrotron X-ray data

Short History of Powder Diffraction



Search from Web of Science ™ Core Collection
citations in each year whose title contains:
‘Powder Diffraction’

X 10 if search by topic

1977

- **1977** Cox, Young, Thomas and others first apply Rietveld method to laboratory and synchrotron X-ray data

Examples of Powders

Multi-grained
i.e. each grain can
diffract x-rays,
neutrons or electrons
Polycrystalline
materials

Examples of Powders

Wood fiber board

Glass ware

Metal parts

Powdered milk

Cosmetic powder

Gunpowder

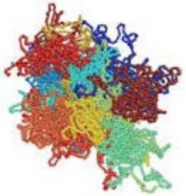
Ground coffee

Powdered sugar

Multi-grained
i.e. each grain can
diffract x-rays,
neutrons or electrons
Polycrystalline
materials

Flour

Polymers



Potassium bromate

Fine snow

Pharmaceuticals

Potassium bromate

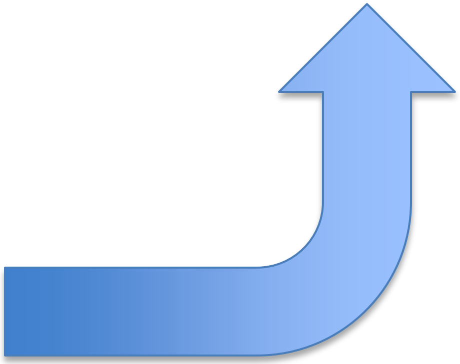
Zymin

Brightening agent

Ceramics

Examples of Powders

Highly disordered
Nanocrystalline
Amorphous



Multi-grained
i.e. each grain can
diffract x-rays,
neutrons or electrons
Polycrystalline
materials

Use of Powder Diffraction

Single Crystal Diffraction is preferred in most cases BUT:

- **the product naturally occurs as a powder**
- **the functionalized (working) form of the product is a powder**
- **a single crystal of sufficient size or quality cannot be synthesized**
- **Lattice parameters and micro-structure**
- **Crystal may shatter during a phase transformation**

Use of Powder Diffraction

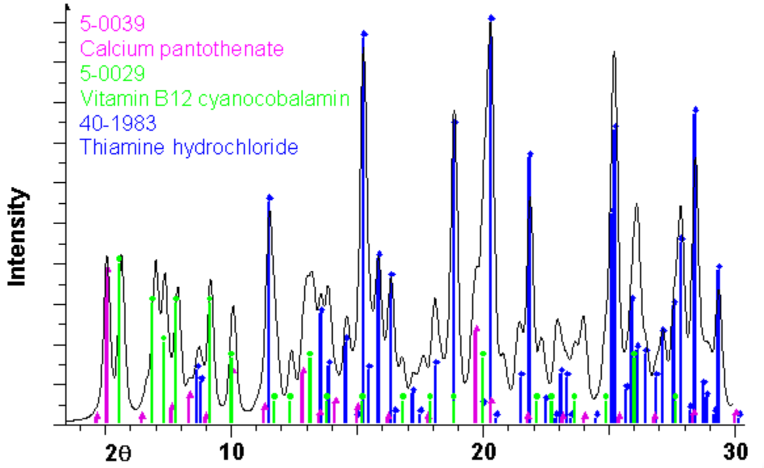
1. **Qualitative Analysis** Phase ID

Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Phase identification

e.g., **Mineralogy:** natural Granodiorite is a mix of Quartz, Feldspar, Albite, Biotite; lesser Clinochlore, Hornblende; traces of Zircon (see webmineral.com)

e.g., **Pharmaceutical :** Mannitol, Sucrose, DL-Valine, Starch, Nizatidine.

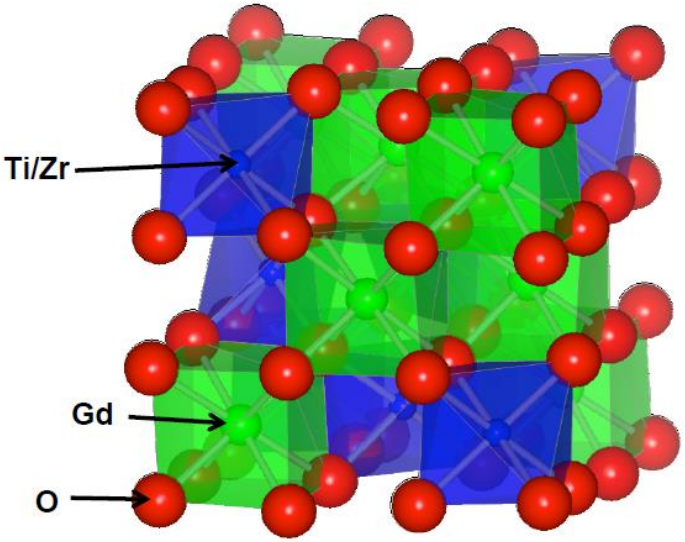


Use of Powder Diffraction

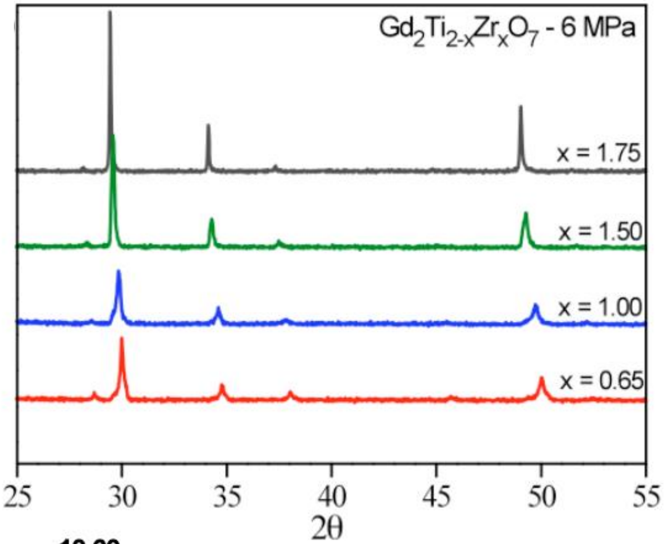
1. **Qualitative Analysis**	Phase ID
2. **Quantitative Analysis**	Lattice parameters (thermal expansivity, compressibility), indexing Phase mass fraction (mixture)

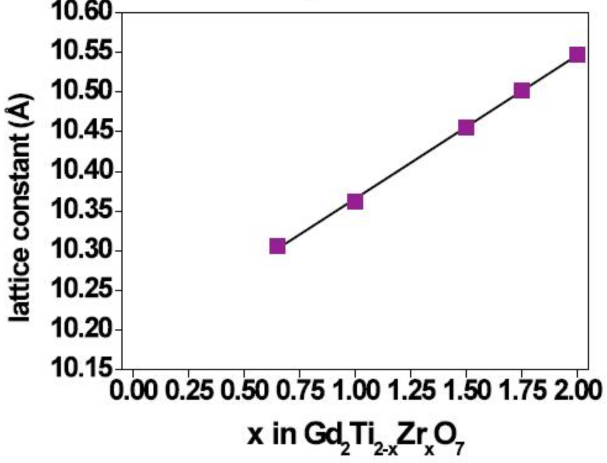
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Effect of substitution



$Gd_2Ti_{2-x}Zr_xO_7$



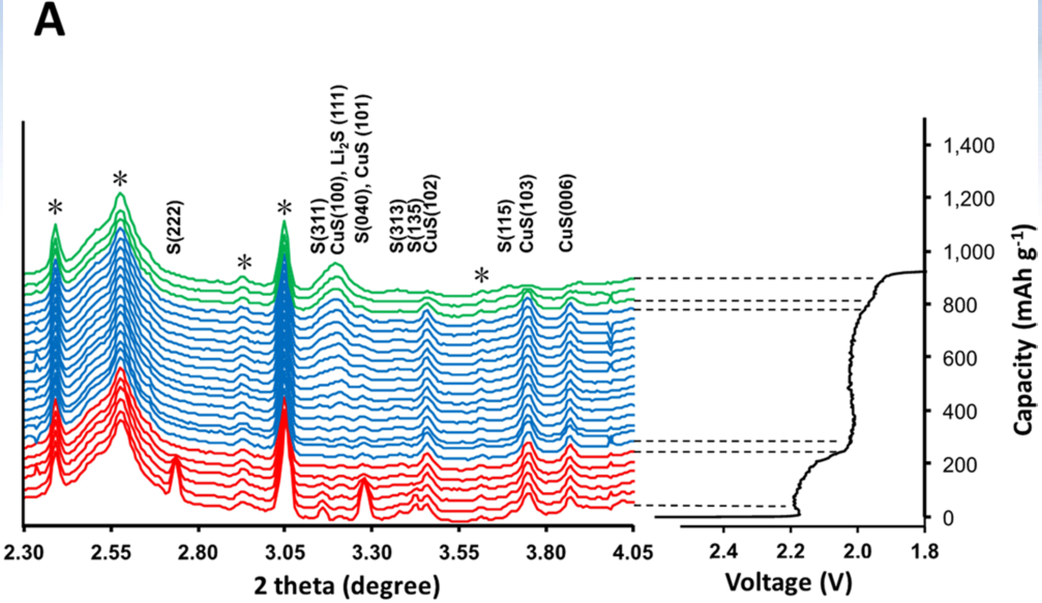


12

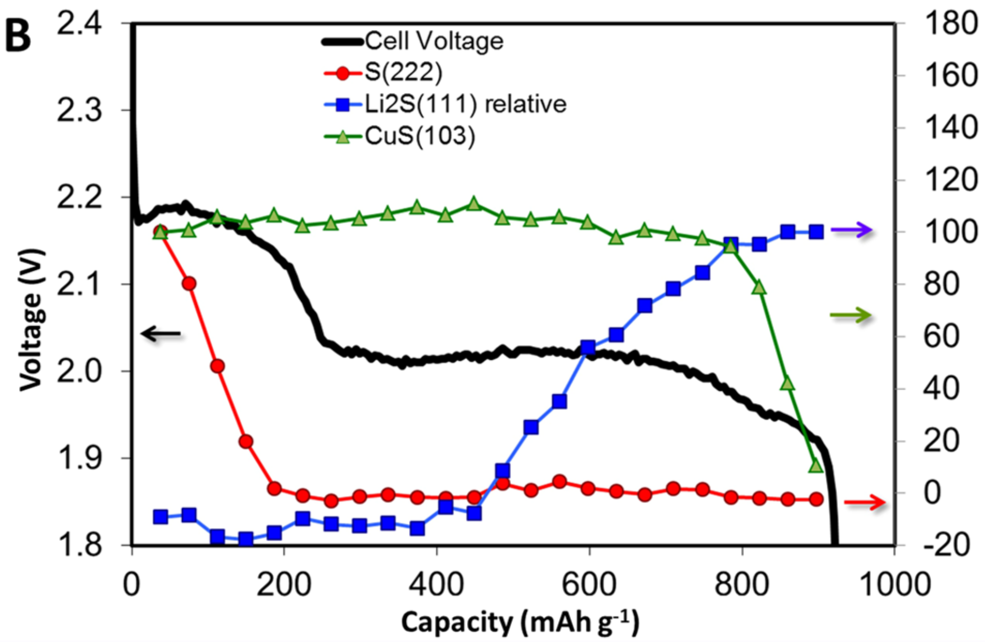
Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Quantitative analysis

- phase content: weight % of each phase inside a mixture
- A + B → A + C + D → A + D
  identify and measure the kinetics: mass fractions f(time)
- follow structural changes and phase transformations as a function of a process variable
- Structural behavior under complex environments



(**A**) *Operando* XPD patterns from the sulfur-CuS hybrid electrode aligned with its electrochemical capacity-voltage profile during lithiation; diffraction peaks from the cell are labelled with "*"



(**B**) Diffracted intensity of S (222), CuS (103), and Li2S (111) are plotted as a function of depth of discharge in comparison with the cell discharge voltage profile (solid black lines)

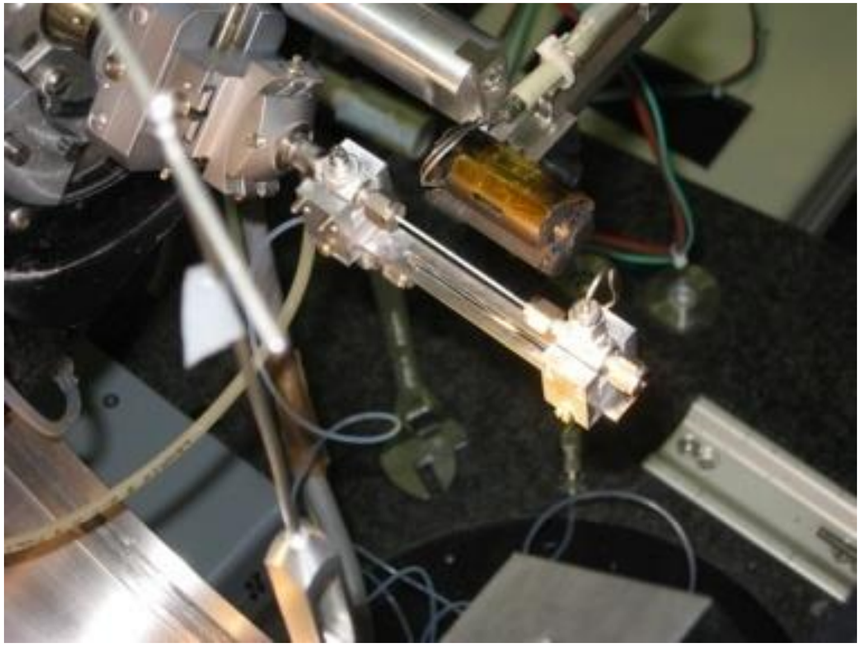
H. Gan et al. Scientific Reports (2017)

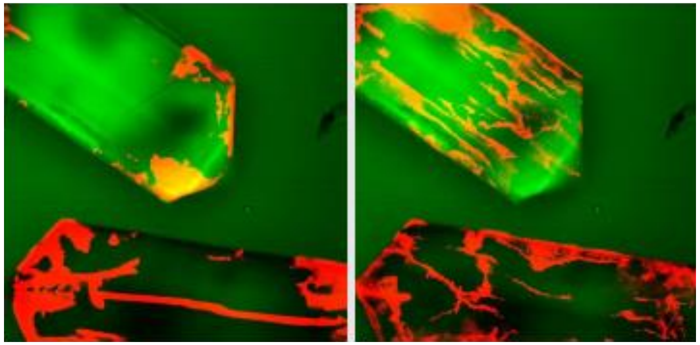
Stabilization of an organic dye in a mesoporous Al-Si mineral.

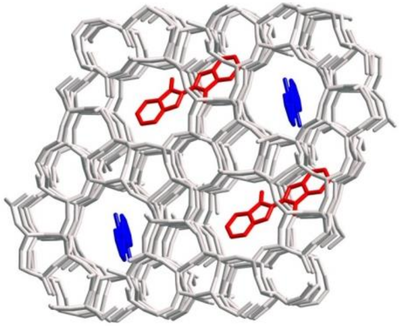
Dejoie, Martinetto, Dooryhee *et al*. Applied Spectroscopy 64 (2010) and Appl. Mater. Interfaces 2 *(*2010)

Design durable, non-toxic hybrid pigments (*e.g*. in replacement of fading paintings): stable color (irradiation, chemical).

In-situ synchrotron diffraction







Use of Powder Diffraction

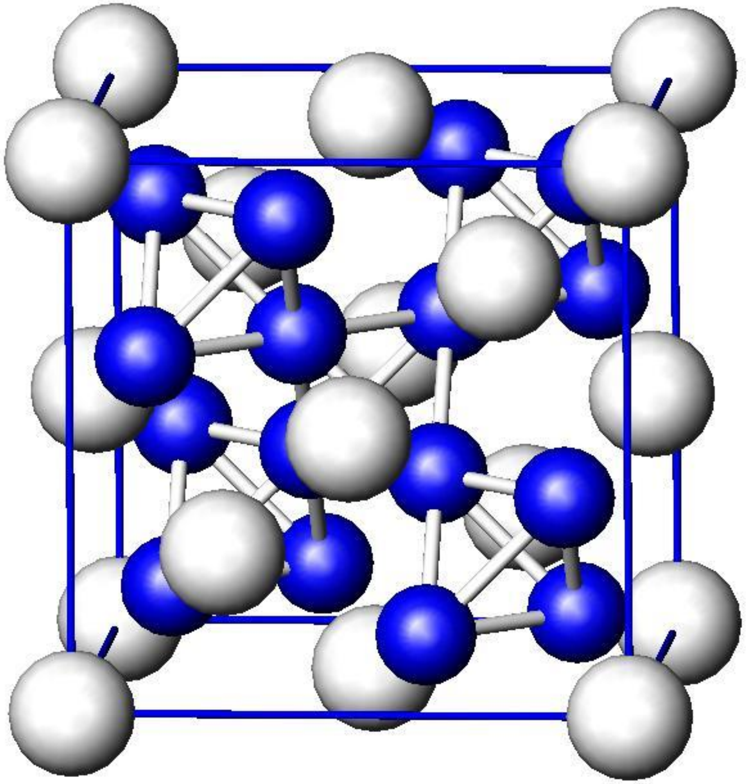
1. **Qualitative Analysis**	Phase ID
2. **Quantitative Analysis**	Lattice parameters (thermal expansivity, compressibility), indexing
	Phase mass fraction (mixture)
3. **Structure Determination**	Reciprocal Space Methods (*ab initio*)
	Real Space Methods

Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Structure determination (crystallography: unit cell and lattice parameters, symmetry, atomic motif)

The entire, ordered and periodic stack of atoms can be generated once the above information is determined from the diffraction data.

The properties of the material are dependent on the crystal structure.



cubic
lattice constant *a*,
space group is *Fd3m,*
atomic motif is $MgCu_2$

Mg in grey, Cu in blue

Use of Powder Diffraction

1. **Qualitative Analysis**	Phase ID
2. **Quantitative Analysis**	Lattice parameters (thermal expansivity, compressibility), indexing
	Phase mass fraction (mixture)
3. **Structure Determination**	Reciprocal Space Methods (*ab initio*)
	Real Space Methods
4. **Structure Refinement**	Rietveld Method (whole pattern)
5. **Microstructure and Texture**	Crystallite Size Distribution
	Preferred Orientation
	Microstrain
	Anti-phase domains, stacking faults,…

Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Texture (orientation) of polycrystalline materials

Powder diffraction essentially assumes crystallites are randomly oriented

IF NOT, diffraction intensities are affected and this can be useful information: **texture, preferred orientation** → found in many engineered materials, and have a great influence on materials properties

Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Large Superconducting cables
(American SuperConductor)

Texture (orientation) of polycrystalline materials

Powder diffraction essentially assumes crystallites are randomly oriented

IF NOT, diffraction intensities are affected and this can be useful information: texture, preferred orientation → found in many engineered materials, and have a great influence on materials properties

e.g., HT superconductor thin films deposited on metallic ribbons (critical currents in $YBa_2Cu_3O_7$)

Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Texture (orientation) of polycrystalline materials

Powder diffraction essentially assumes crystallites are randomly oriented

IF NOT, diffraction intensities are affected and this can be useful information: texture, preferred orientation → found in many engineered materials, and have a great influence on materials properties

e.g., geologic rocks show texture due to their thermo-mechanic history of formation processes

Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

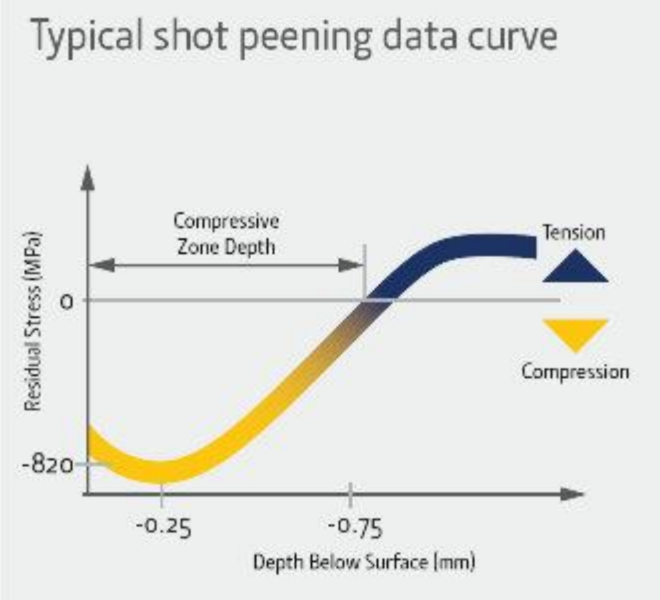
Residual stress analysis

created during the manufacturing process, or it may accumulate in a structure over many years in operation.

stress can have a serious negative effect on a product's quality, durability and lifetime (QA, service)

Applications of Powder Diffraction: Physics, Chemistry, Geology, Industry,…

Peening is a working process to produce a compressive stress at the surface to overcome failure due to metal fatigue, stress corrosion cracking, fretting,…



Residual stress analysis

created during the manufacturing process, or it may accumulate in a structure over many years in operation.

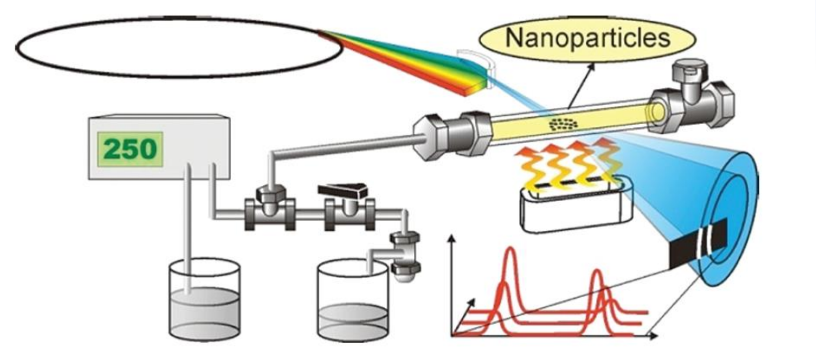
stress can have a serious negative effect on a product's quality, durability and lifetime (QA, service)

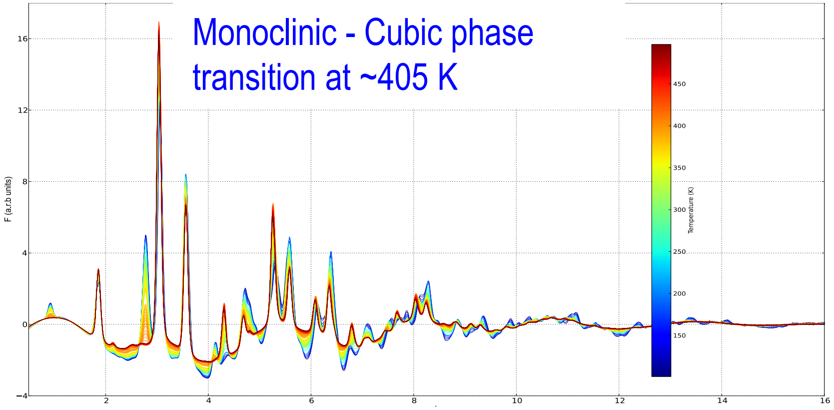
e.g., laser peening in aircraft engine blades

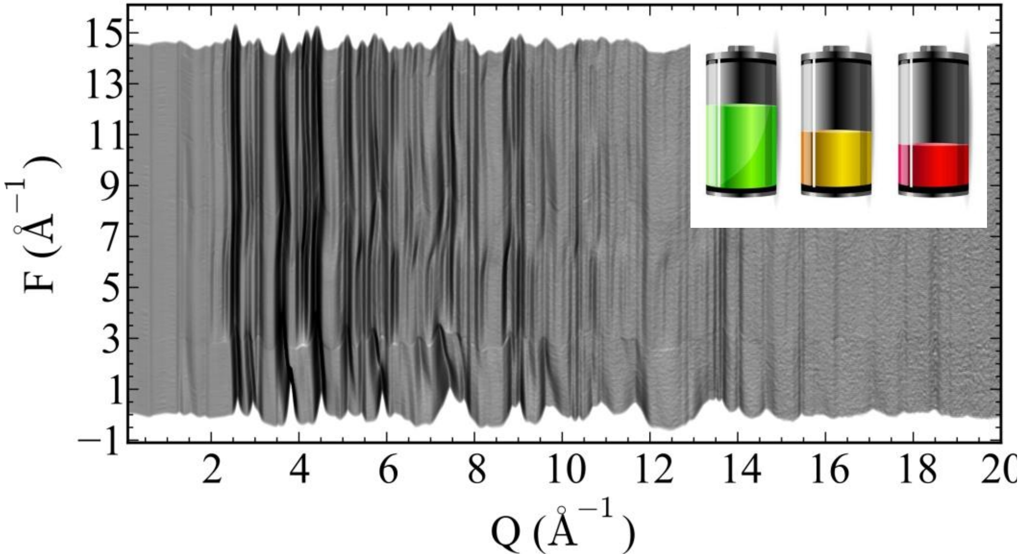
Applications of Powder Diffraction

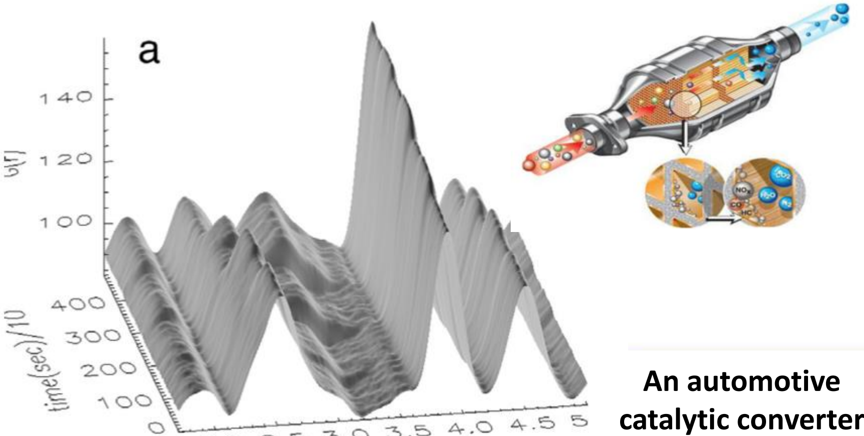
A versatile and powerful technique for time-dependent phase transformations.

- Kinetics and mechanism of how structures form during reversible or irreversible chemical reactions
- How materials work in devices under real working conditions. *e.g.*: batteries, fuel cells.
- Functioning of catalyst during reactions.
- Phase transitions.




Monoclinic - Cubic phase transition at ~405 K



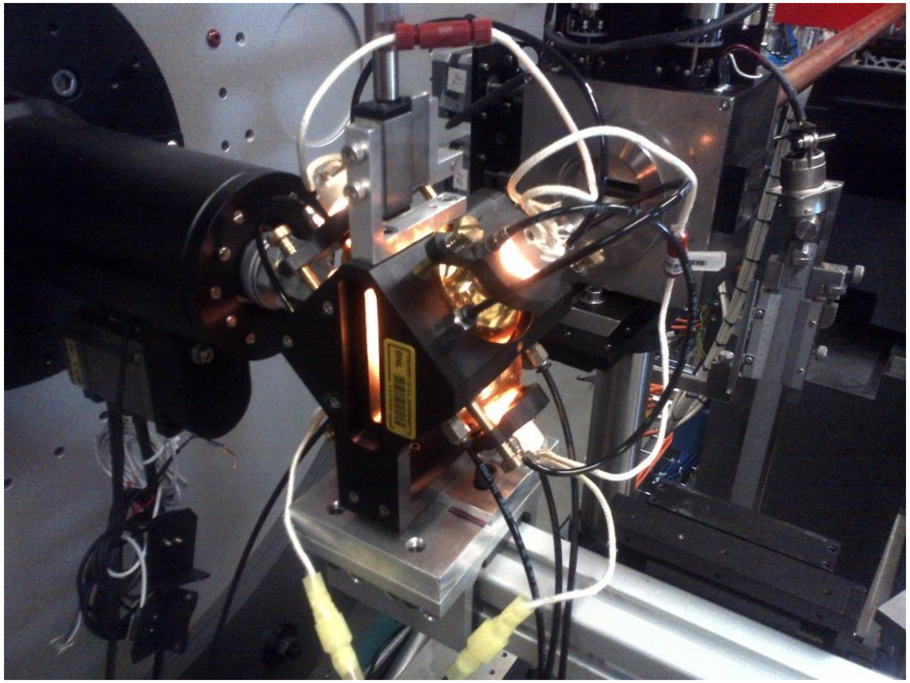


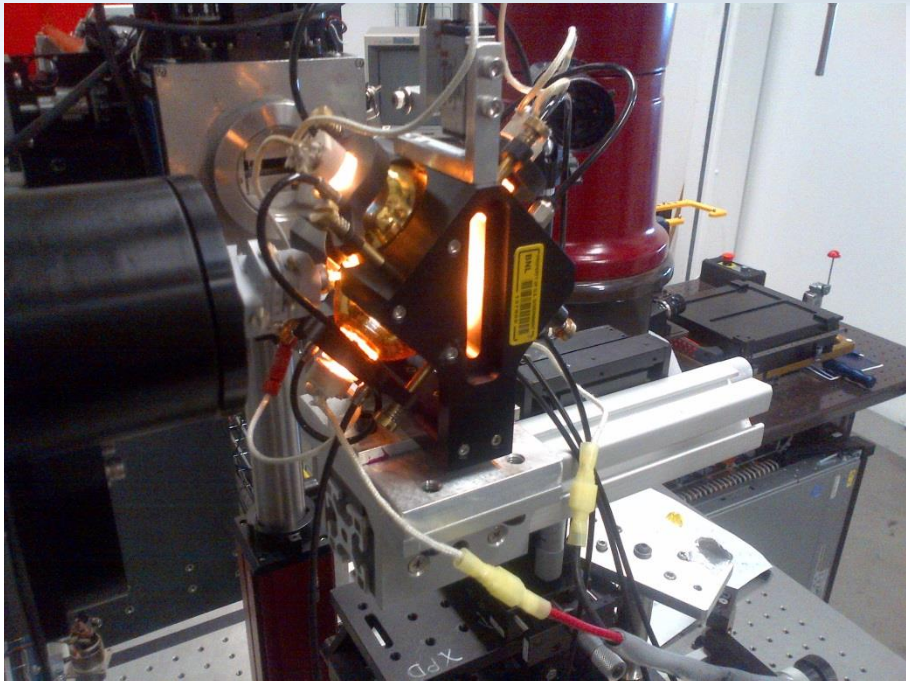
An automotive catalytic converter

Develop oxidation-resistant Ceramics

In-situ, high temperature oxidation studies of HfB_2 composites using a quadrupole lamp furnace.

P. Sarin, Univ. of Oklahoma

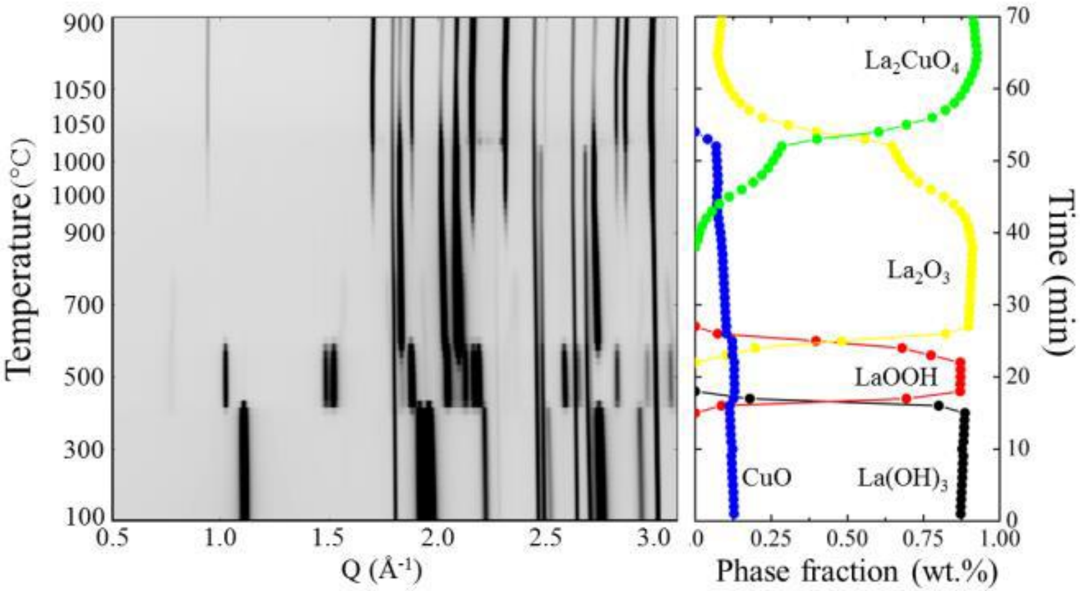




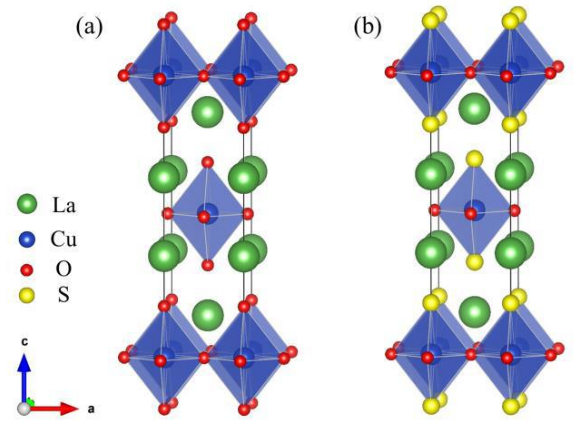
Develop oxidation-resistant HfB_2 and HfB_2-SiC composites as emerging Ultra High Temperature Ceramics for applications beyond 2,000°C (thermal protection for atmospheric re-entry vehicles)

Solid-state syntheses → to accelerate materials discovery. Example: La-Cu-O-S system

- Theory to identify desired materials that are thermodynamically stable *e.g.* La_2CuO_3S and $La_2CuO_2S_2$. However experimental realization of never reported.
- in situ XRD synthesis to pinpoint the feasible synthetic routes.



In situ powder XRD patterns showing how the diffraction peaks (left panel) and phase fractions (right panel) evolve as the temperature changes for synthesis from La2O3+CuO.



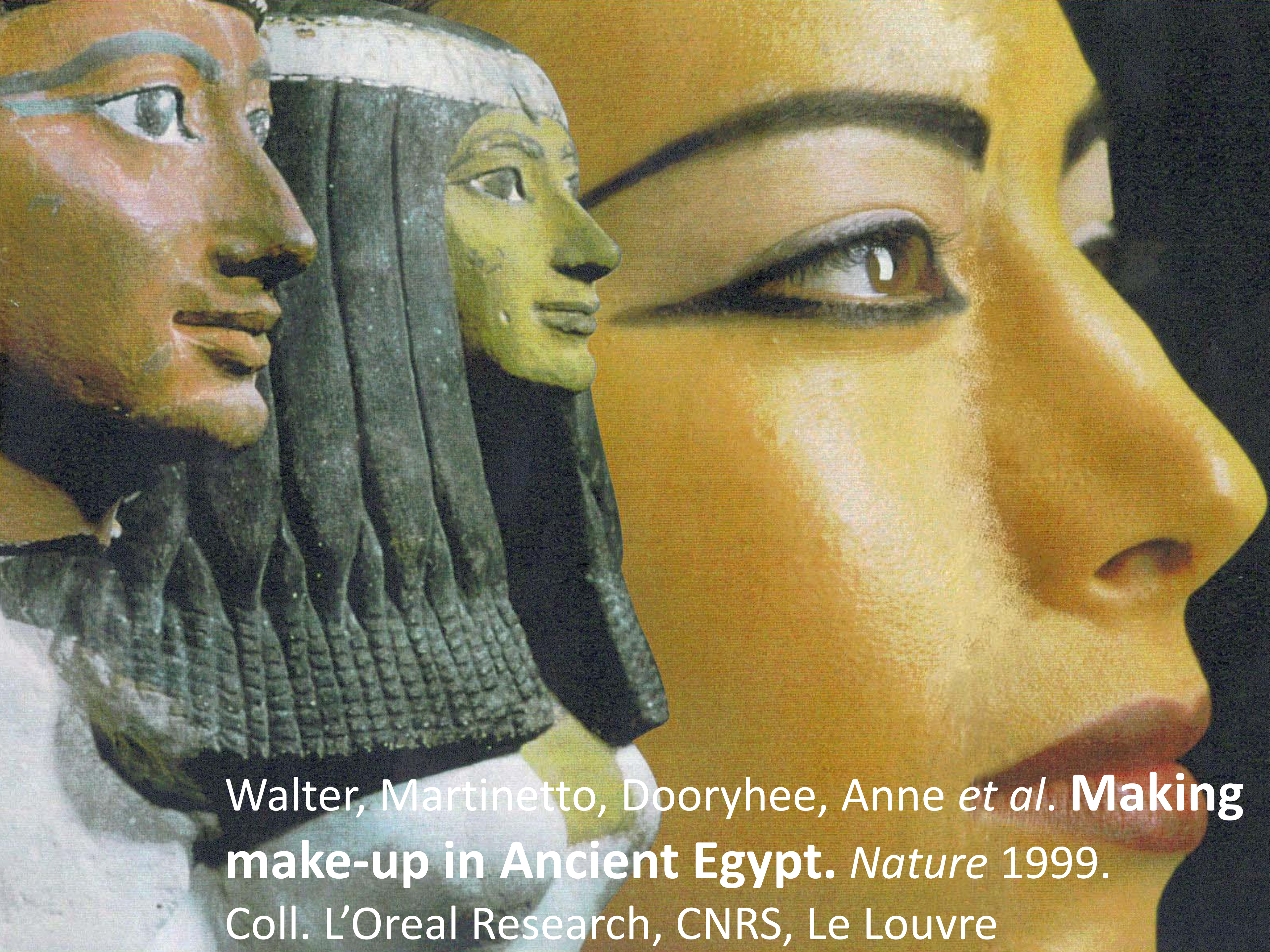
Crystal structures of La2CuO4 (a) and the theoretical compound La2CuO2S2 (b), which is derived by replacing the apical oxygen in La2CuO4 with sulfur.

Hua He et al. Submitted to PNAS

Use of Powder Diffraction

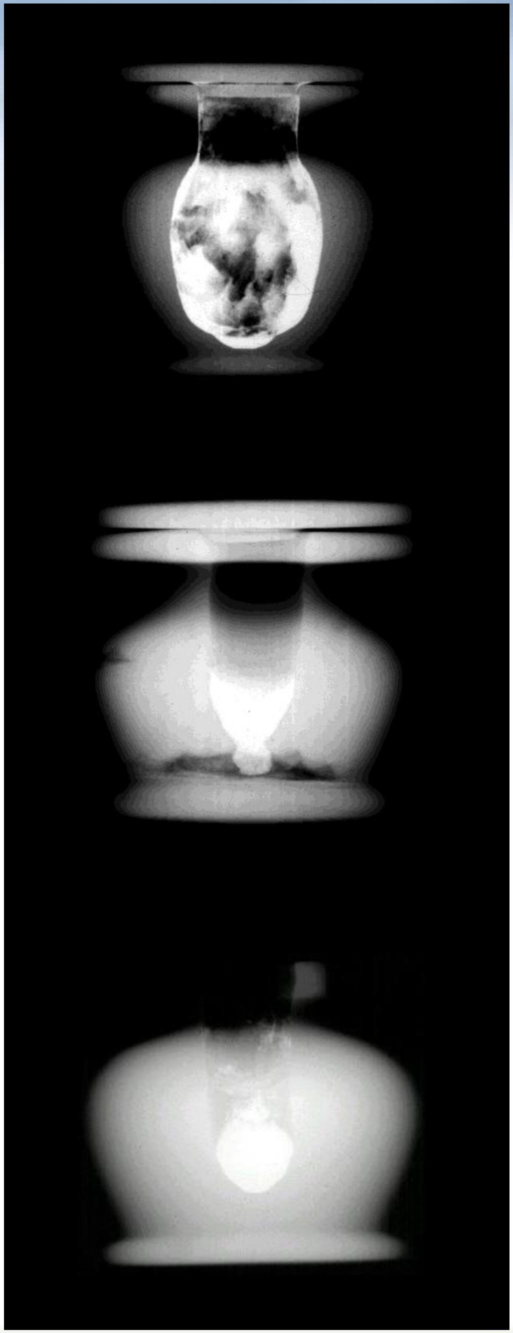
1. **Qualitative Analysis**	Phase ID
2. **Quantitative Analysis**	Lattice parameters (thermal expansivity, compressibility), indexing
	Phase mass fraction (mixture)
3. **Structure Determination**	Reciprocal Space Methods (*ab initio*)
	Real Space Methods
4. **Structure Refinement**	Rietveld Method (whole pattern)
5. **Microstructure and Texture**	Crystallite Size Distribution
	Preferred Orientation
	Microstrain
	Anti-phase domains, stacking faults,…

When Powder Diffraction meets Art



Walter, Martinetto, Dooryhee, Anne *et al*. **Making make-up in Ancient Egypt.** *Nature* 1999.
Coll. L'Oreal Research, CNRS, Le Louvre

Cosmetic, social, and ritual functions of the make-up



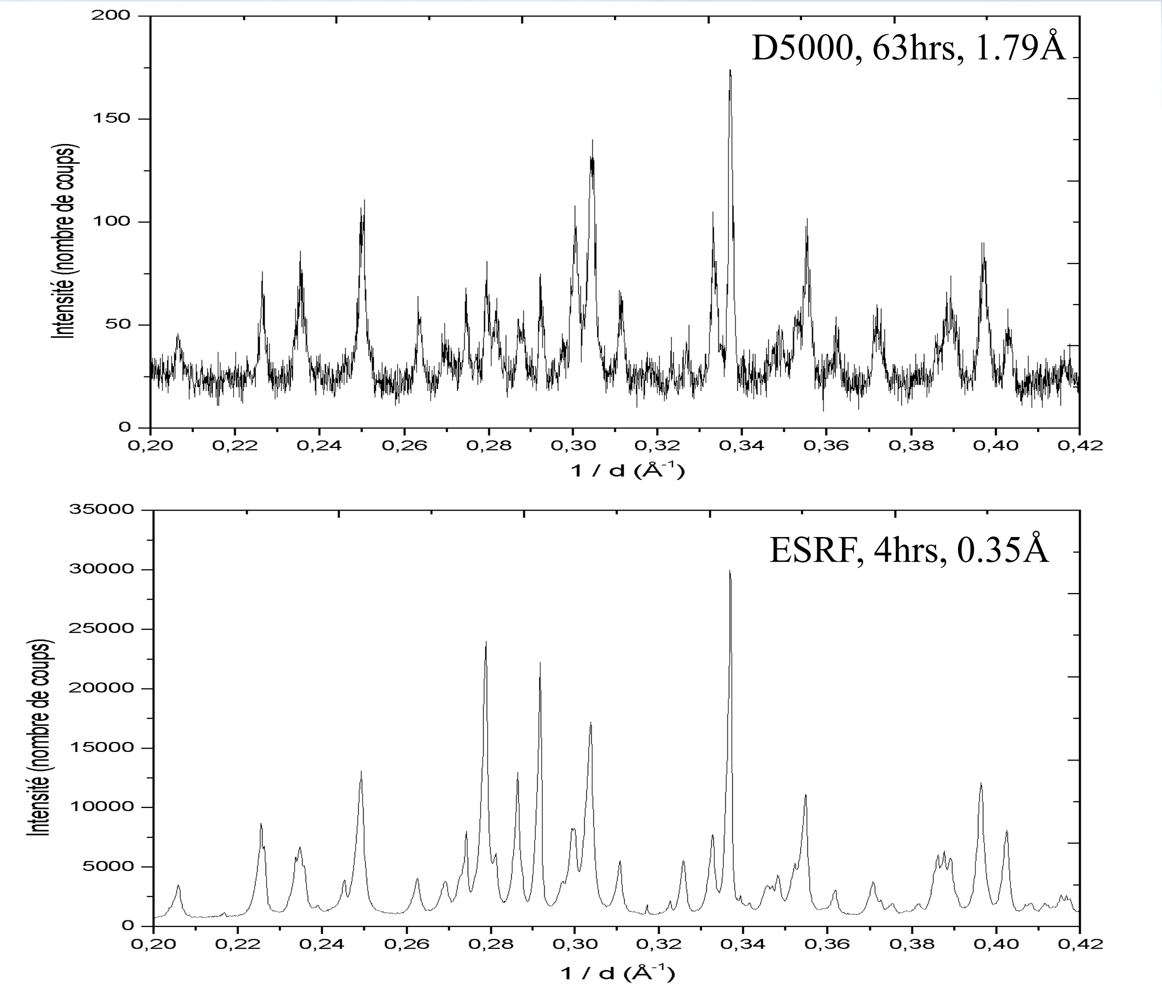
radiographies

Egyptian Cosmetics

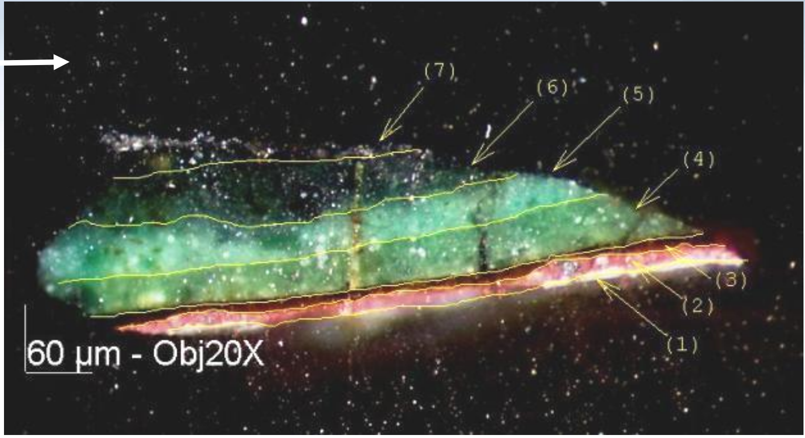
important role in everyday practices and during ritual and burial ceremonies

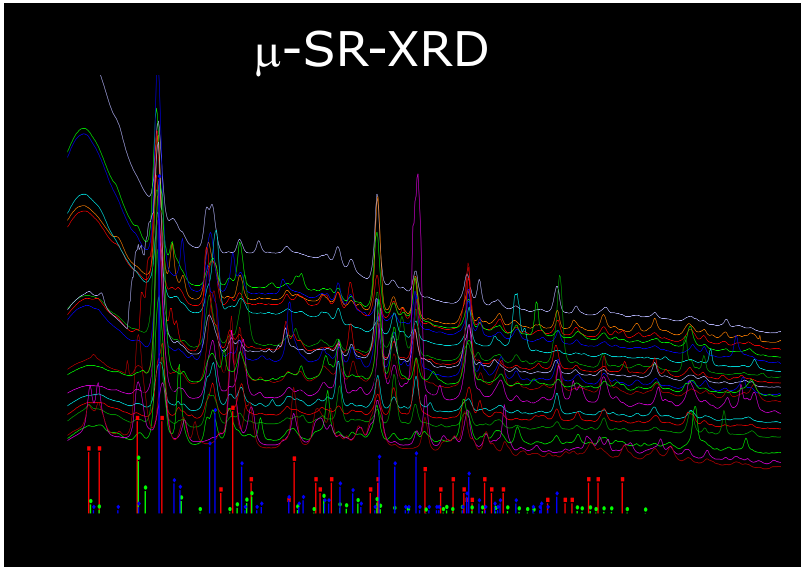
(from P. Martinetto)

Ph. Walter et al. Nature 397 (1999)



High resolution and flux (ESRF) and high energy (Pb-mixtures)





M. Grunewald – German Renaissance

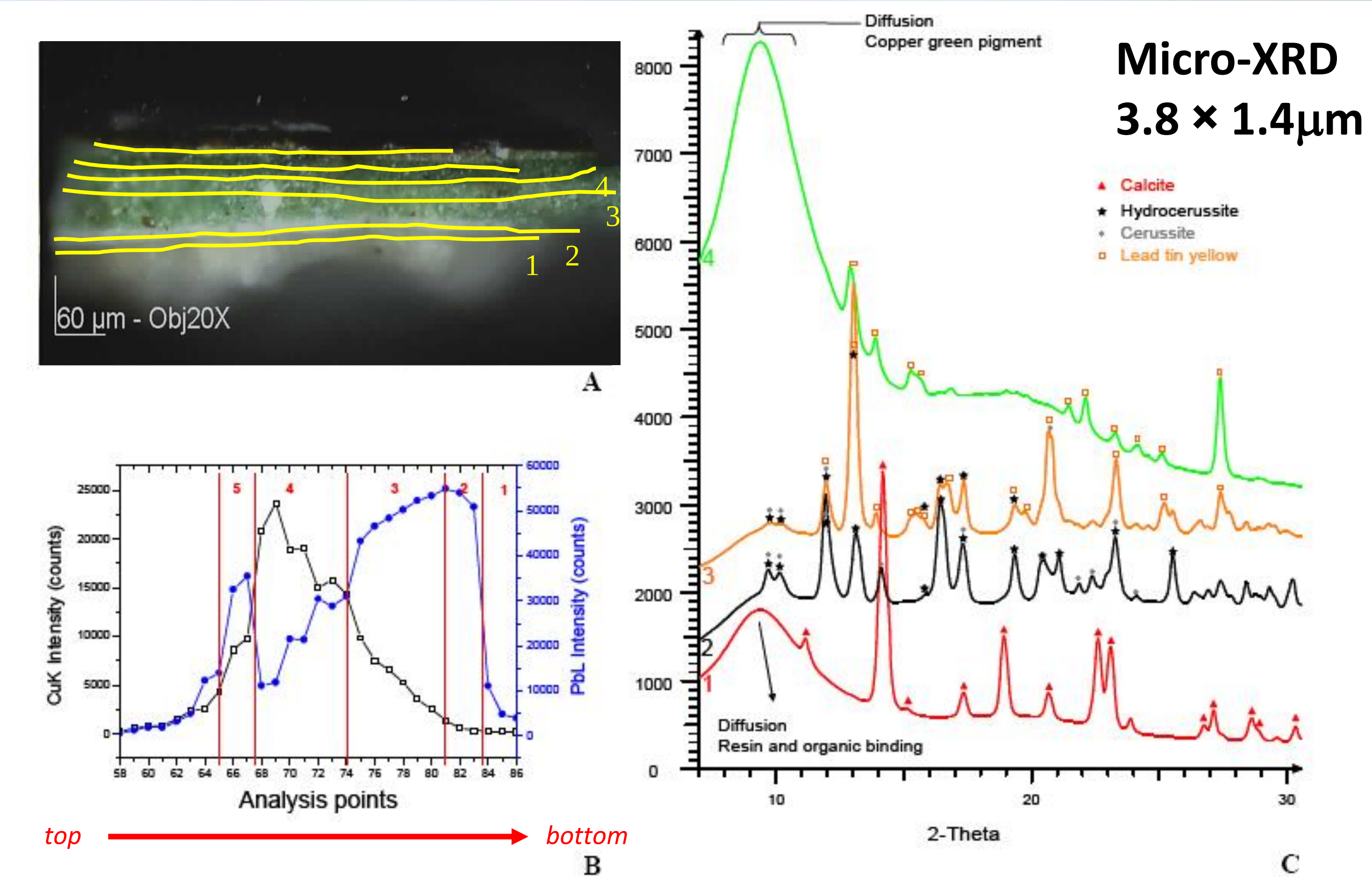
Welcomme E, Walter P, Bleuet P, Hodeau JL, Dooryhee E, Martinetto P, Menu M. Applied Physics A89 (2007)

Synchrotron Analysis of Oil Paintings

top

bottom

Micro-XRF
3.8x1.4µm



Micro-XRD
3.8 × 1.4µm

top → *bottom*

top

bottom

Welcomme, Walter, Dooryhee *et al*. Appl. Phys. A83 (2006)

<u>Layer 1</u>: calcium carbonate preparation layer; <u>Layer 2</u>: priming layer made of lead carbonates (hydrocerussite, cerussite); <u>Layers 3-5</u>: green copper pigments with lead tin yellow $2PbO\text{-}SnO_2$ and lead carbonates; <u>Layer 6</u>: organic, varnish.

Outline

1. Applications for Powder Diffraction
2. The basics of Powder Diffraction
3. Experimental Methods for collecting PD data
4. Crystal structure Determination
5. Peak Profile Analysis for Microstructural Studies
6. Advanced PD techniques

What is a crystal ?

- A **periodic arrangement** of objects (atoms, molecules) repeating in three dimensions
- **Crystal systems**

Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

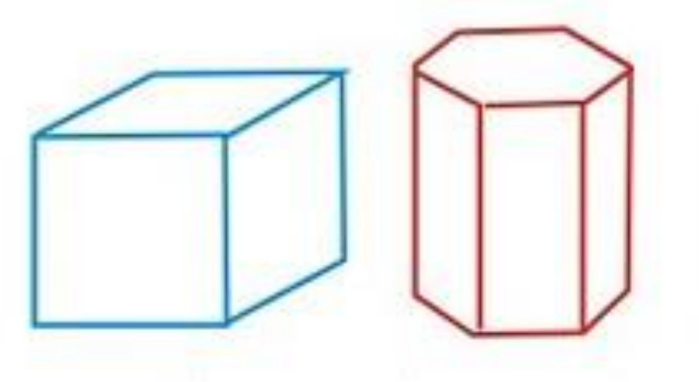
What is a crystal ?

- A **periodic arrangement** of objects (atoms, molecules) repeating in three dimensions
- **Crystal systems**

Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

What is a **crystal** ?

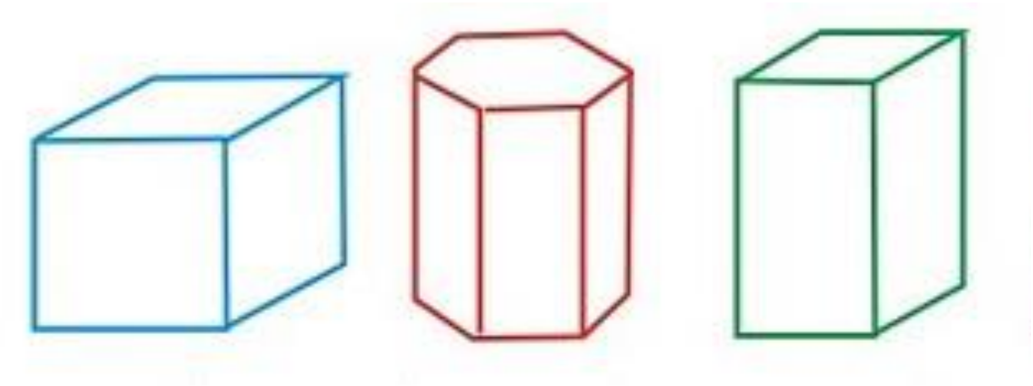
- A **periodic arrangement** of objects (atoms, molecules) repeating in three dimensions
- **Crystal systems**



Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

What is a crystal ?

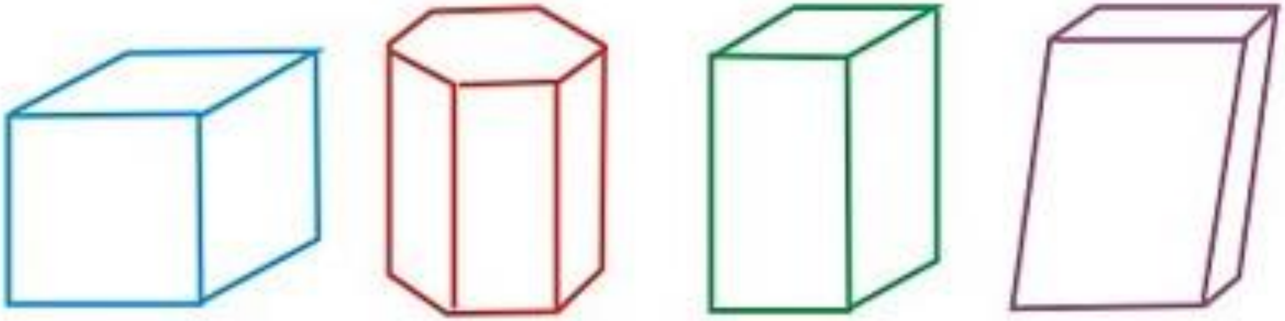
- A **periodic arrangement** of objects (atoms, molecules) repeating in three dimensions
- **Crystal systems**



Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

What is a crystal ?

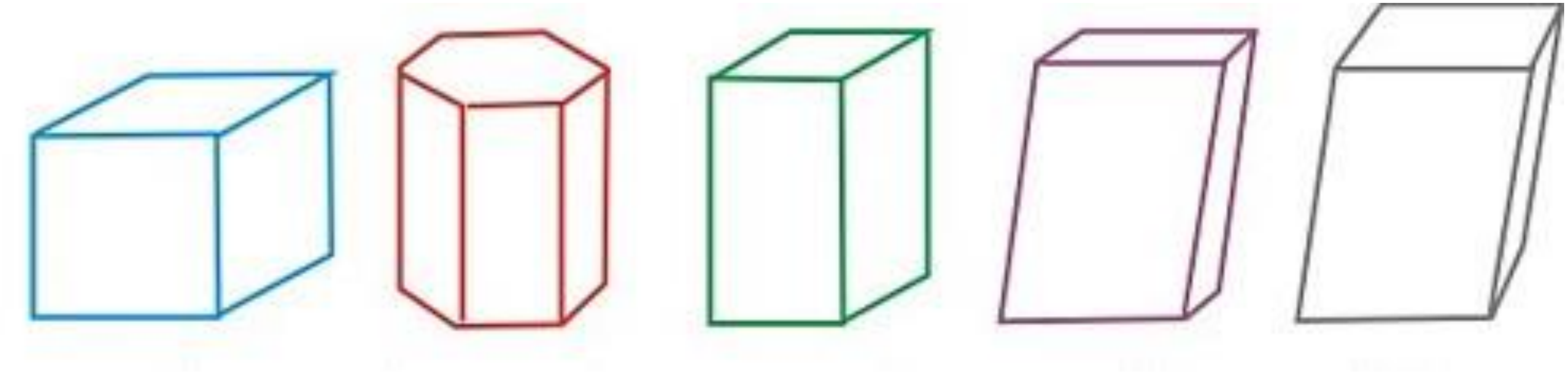
- A **periodic arrangement** of objects (atoms, molecules) repeating in three dimensions
- **Crystal systems**



Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

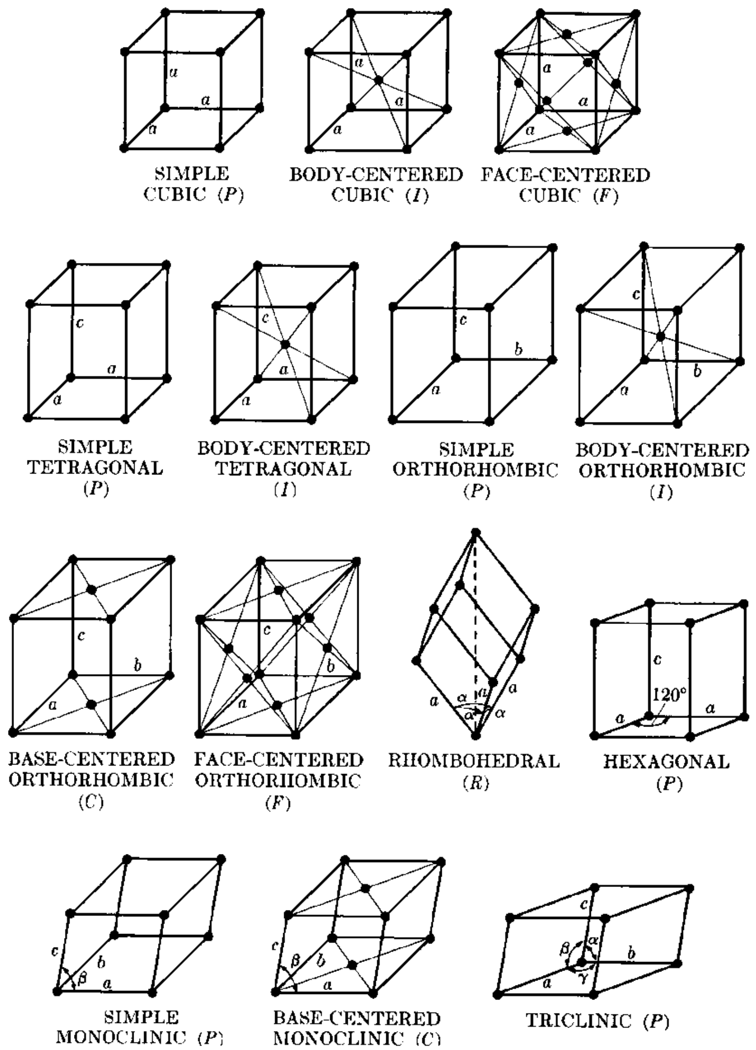
What is a crystal ?

- A **periodic arrangement** of objects (atoms, molecules) repeating in three dimensions
- **Crystal systems (7)**



Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

The 14 Bravais lattices



“Elements of X-ray Diffraction”, Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.

What is a crystal ?

Crystal System	Bravais Types	External Minimum Symmetry	Unit Cell Properties
Triclinic	P	None	a, b, c, al, be, ga,
Monoclinic	P, C	One 2-fold axis, parallel b (b unique)	a, b, c, 90, be, 90
Orthorhombic	P, I, F, C	Three perpendicular 2-folds	a, b, c, 90, 90, 90
Tetragonal	P, I	One 4-fold axis, parallel c	a, a, c, 90, 90, 90
Trigonal	P*, R	One 3-fold axis	a, a, c, 90, 90, 120
Hexagonal	P*	One 6-fold axis	a, a, c, 90, 90, 120
Cubic	P, F, I	Four 3-folds along space diagonal	a, a, ,a, 90, 90, 90

Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

Combining symmetry operations

- An object can possess several symmetry elements
- Not all symmetry elements can be combined arbitrarily
  - for example, two perpendicular two-fold axes imply the existence of a third perpendicular two-fold
- Translational symmetry in 3D imposes limitations
  - only 2, 3, 4 and 6-fold rotation axes allow for space filling translational symmetry
- The allowed combinations of symmetry elements are called point groups
  - there are 32 point groups that give rise to periodicity in 3D

Courtesy of Cora Lind-Kovacs

Space groups

- Crystals are usually described by a *space group*
- Space groups are made up from
  - lattice symmetry (translational)
  - point symmetry (not translational)
  - glide and/or screw axes (some translational component)
- There are 230 space groups

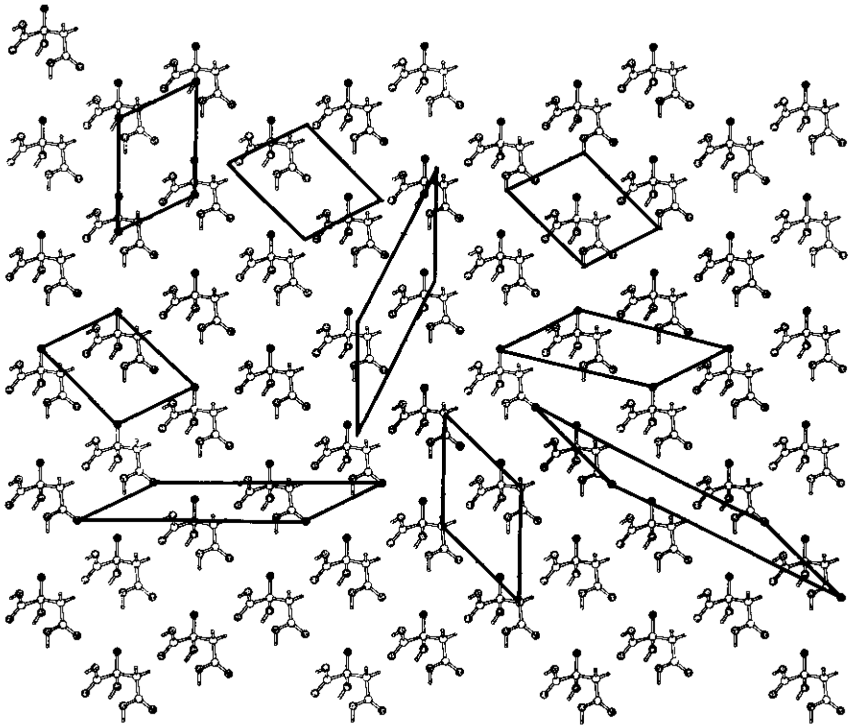
7 crystal systems → 14 Bravais lattices → 32 point groups → 230 space groups

Courtesy of Cora Lind-Kovacs

Lattice symmetry

- Without rules, an infinite number of different unit cells could describe any given lattice

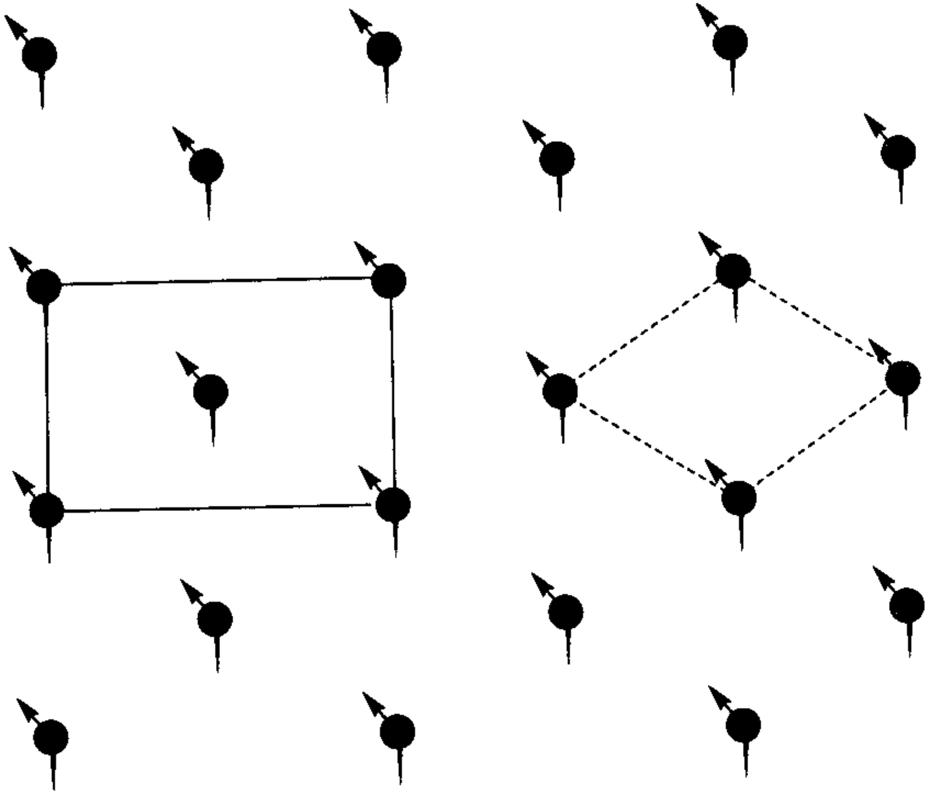
- Choose *smallest cell* with *highest symmetry*
  - Primitive or centered cells



“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

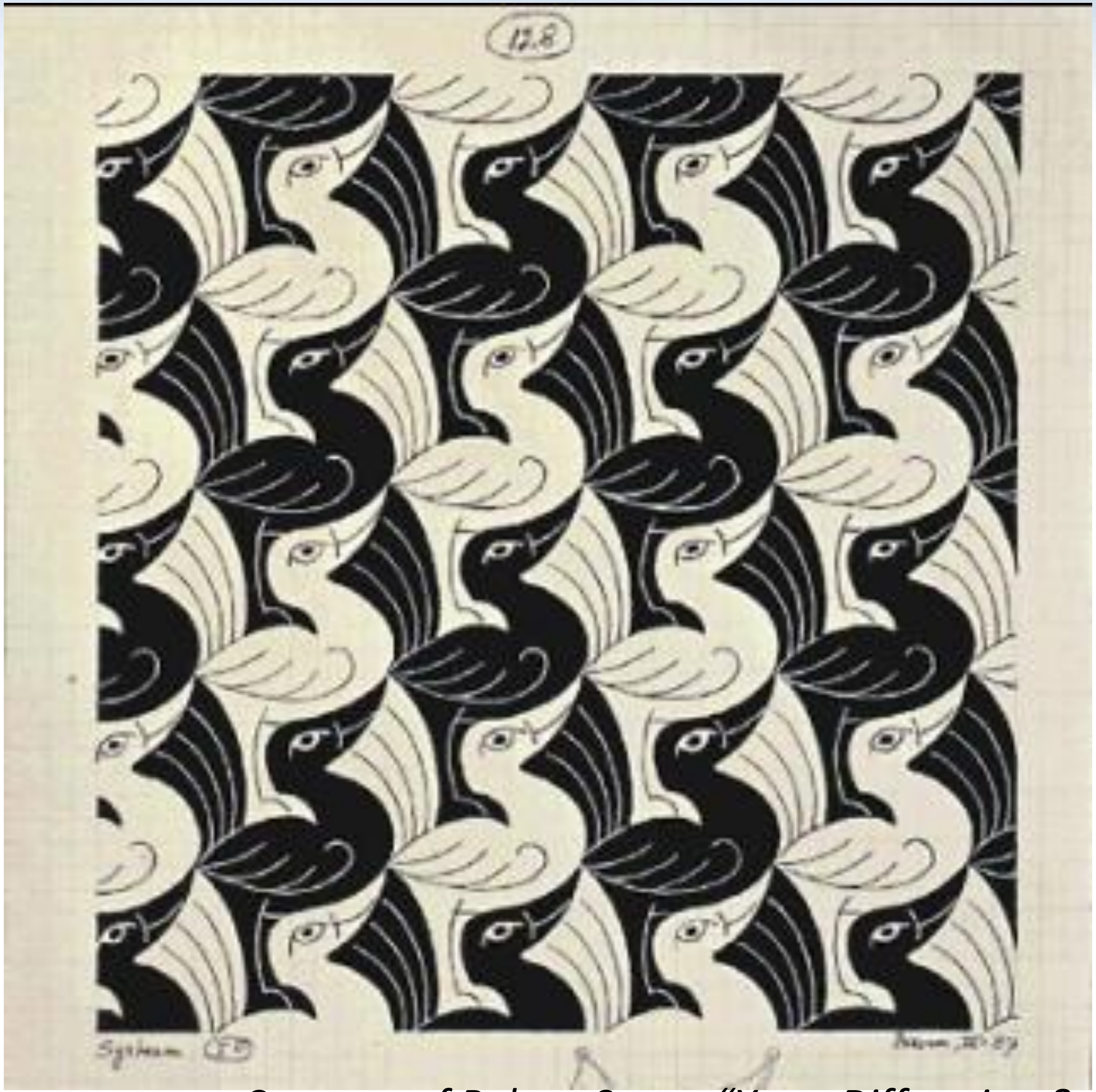
Courtesy of Cora Lind-Kovacs

An example of unit cell choice



◆According to our definitions, the centered cell would be preferred

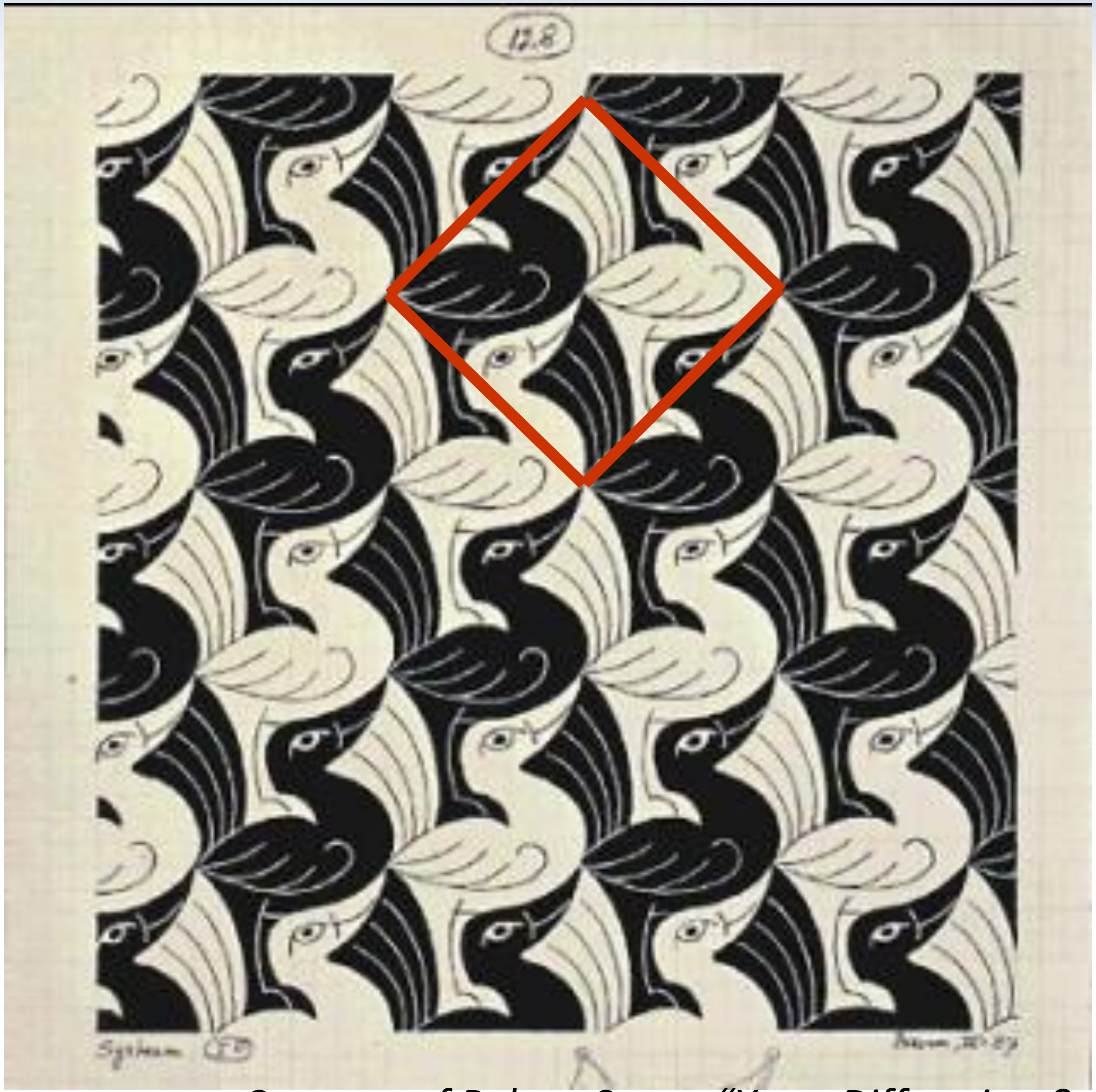
“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.



Courtesy of Robert Sweet “X-ray Diffraction & Crystallography“

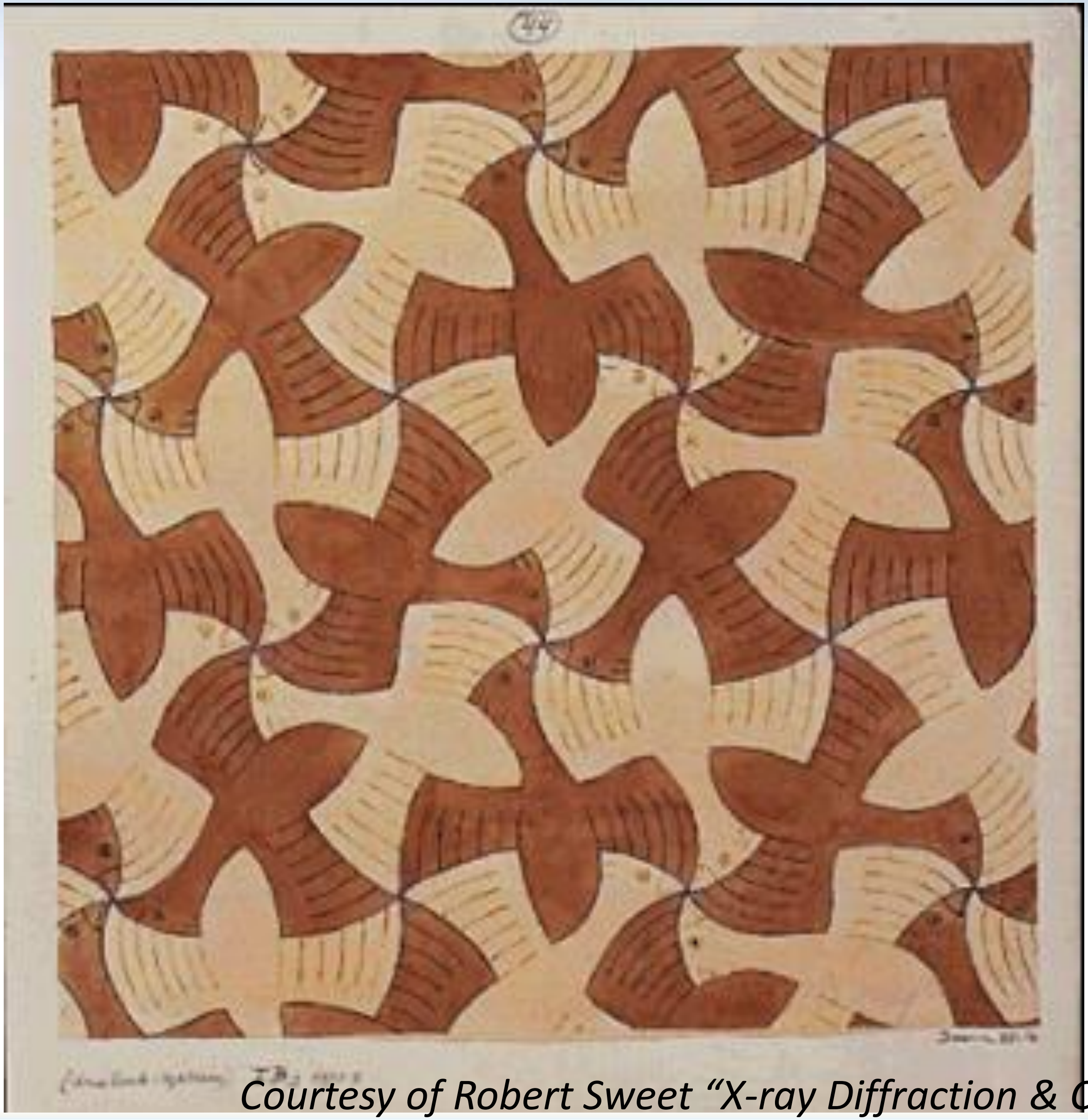
Graphics by M.C. Escher

Translation only.



Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

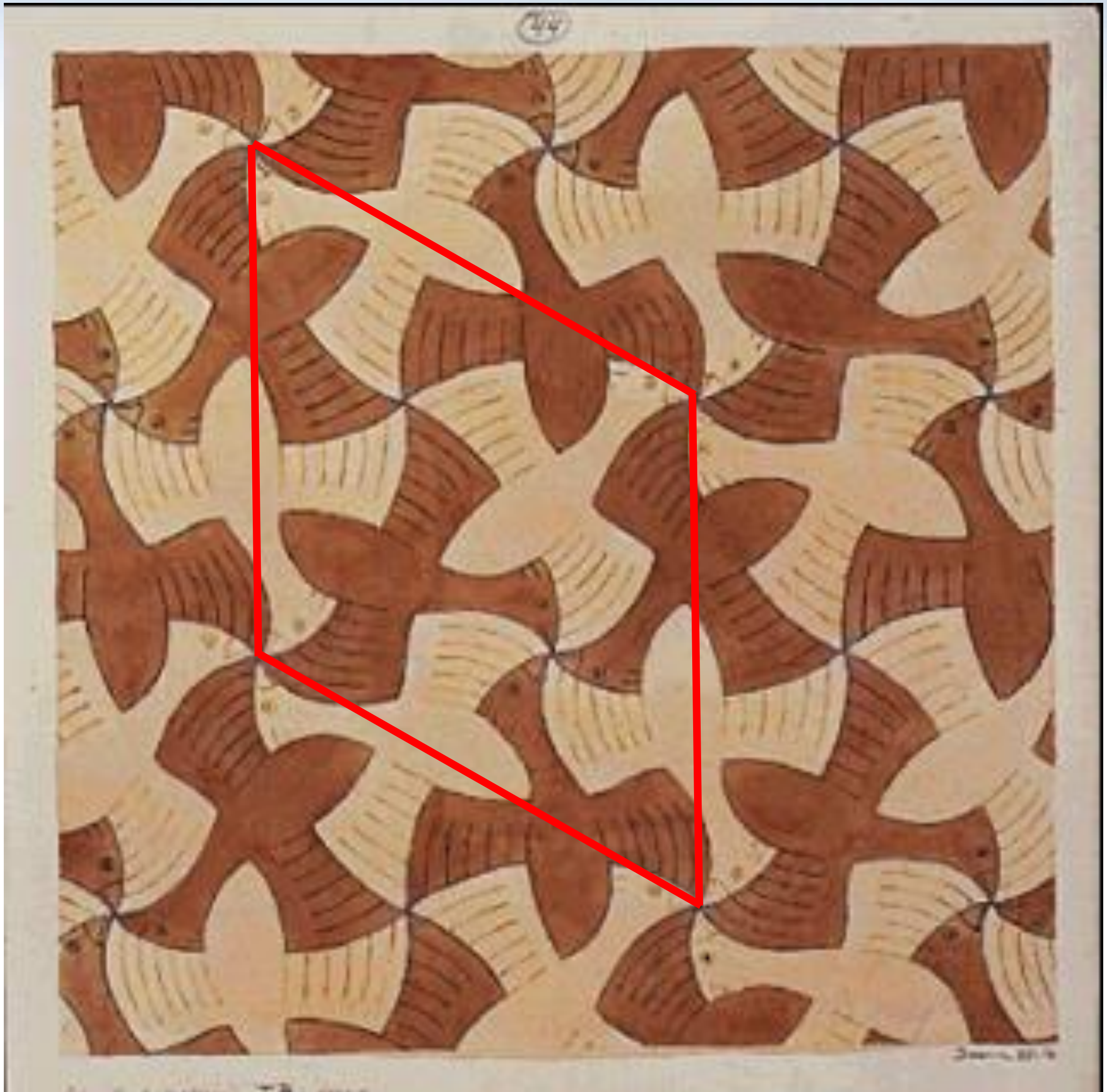
What about here?



Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

Graphics by M.C. Escher

Trigonal symmetry



Notice the two other 3-fold axes in the cell.

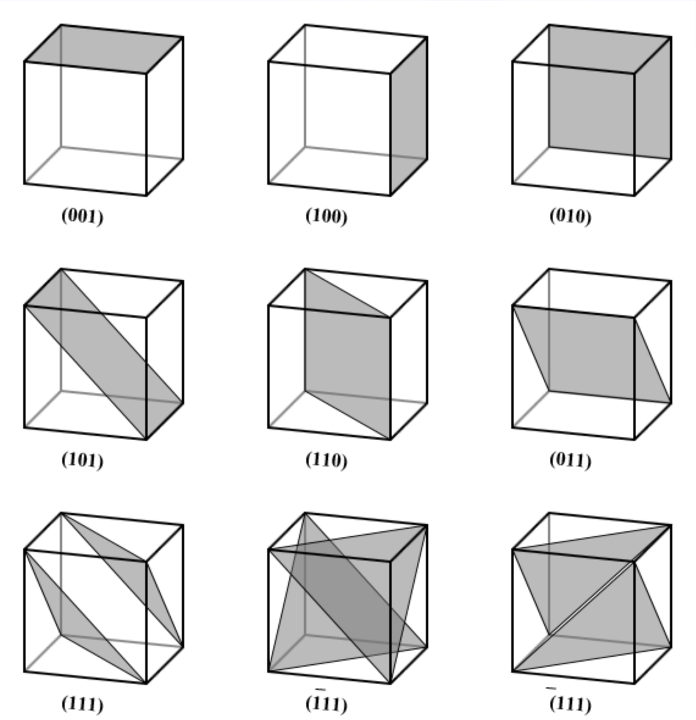
Asymmetric unit is one white and one pink bird.

Order of the group is three.

Courtesy of Robert Sweet “X-ray Diffraction & Crystallography“

Graphics by M.C. Escher

Crystal Structure

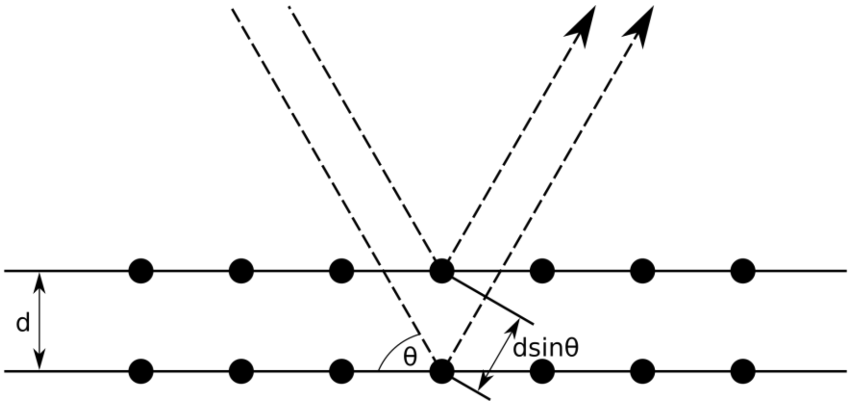


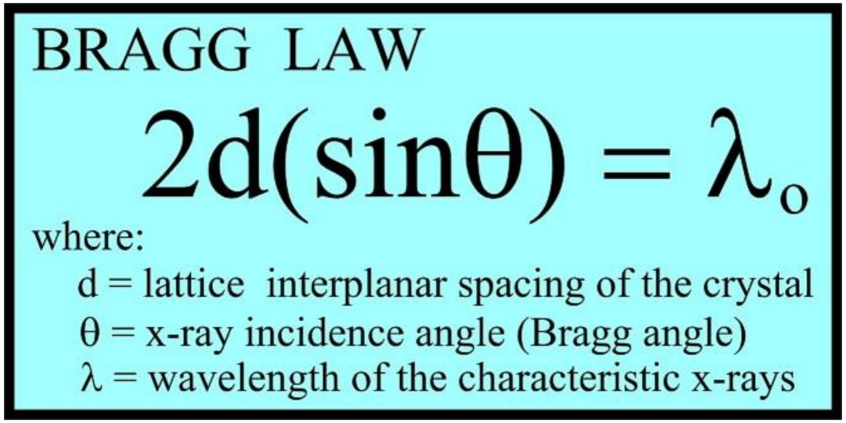
(hkl) indices	d-spacing
(111)	$a/\sqrt{3}$
(200)	$a/2$
(220)	$a/\sqrt{8}$
(311)	$a/\sqrt{11}$
etc	

where *a* is the length of the edge of the cube (lattice parameter)

The crystal structure of a material (the packing of atoms within the crystal) can be described by a discrete set of lattice planes (*hkl*). Lattice planes have specific inter-spacings *d(hkl).*

Bragg Law





BRAGG LAW

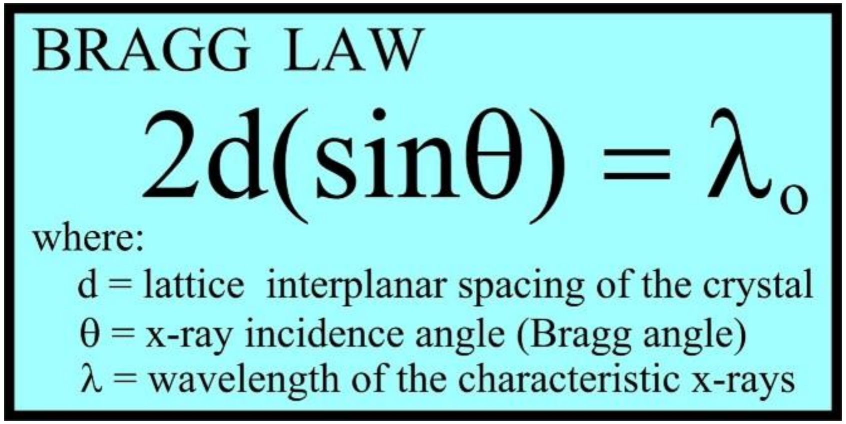
$$2d(\sin\theta) = \lambda_o$$

where:

d = lattice interplanar spacing of the crystal
θ = x-ray incidence angle (Bragg angle)
λ = wavelength of the characteristic x-rays

- Bragg diffraction: constructive interference occurs when the path length difference is equal to an integer multiple of the wavelength of the incident radiation.
- **Translational symmetry and unit cell define the diffraction peak positions (in the 2θ space)**
- **Atomic distribution (atom locations) defines the diffracted peak intensities**

Remember the geometry -- if the **lattice** planes lie at an angle θ w/r to the incident x-ray beam, the **diffraction angle is 2θ (total beam deflection)**. We can make an instrument to exploit that geometry.



BRAGG LAW

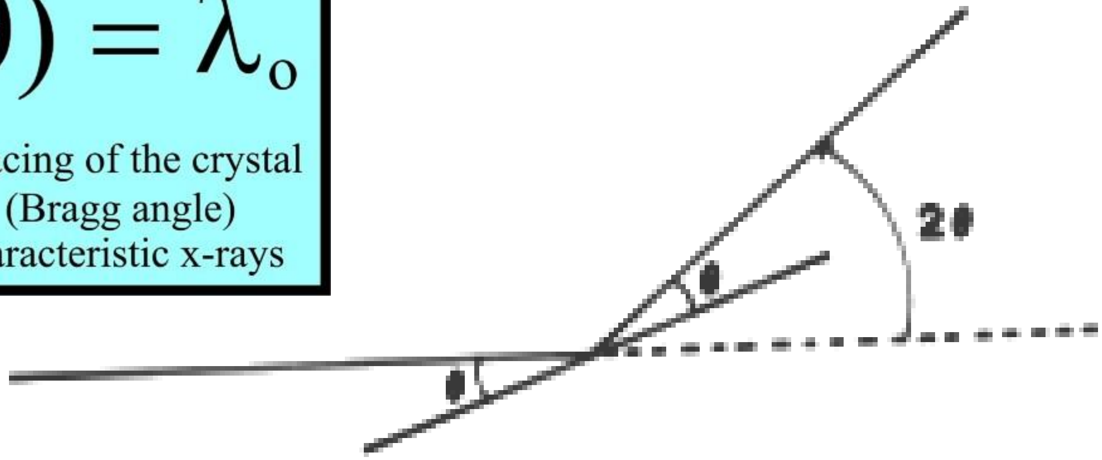
$$2d(\sin\theta) = \lambda_o$$

where:

d = lattice interplanar spacing of the crystal

θ = x-ray incidence angle (Bragg angle)

λ = wavelength of the characteristic x-rays



Courtesy of Robert Sweet “X-ray Diffraction & Crystallography“

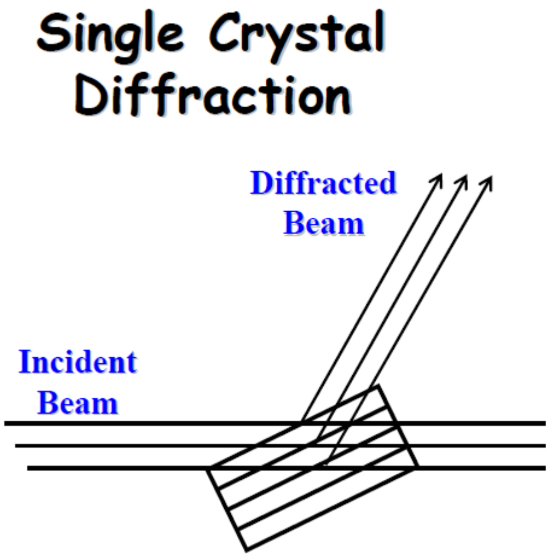
And Remember the objective – We must view the crystal from every direction to recreate a three-dimensional image:

- We must obtain diffraction from **all** (or most) of the **lattice** planes (each set of *h*,*k*,*l* lattice planes produces a diffraction peak at the Bragg angle, extinction rules permitting)

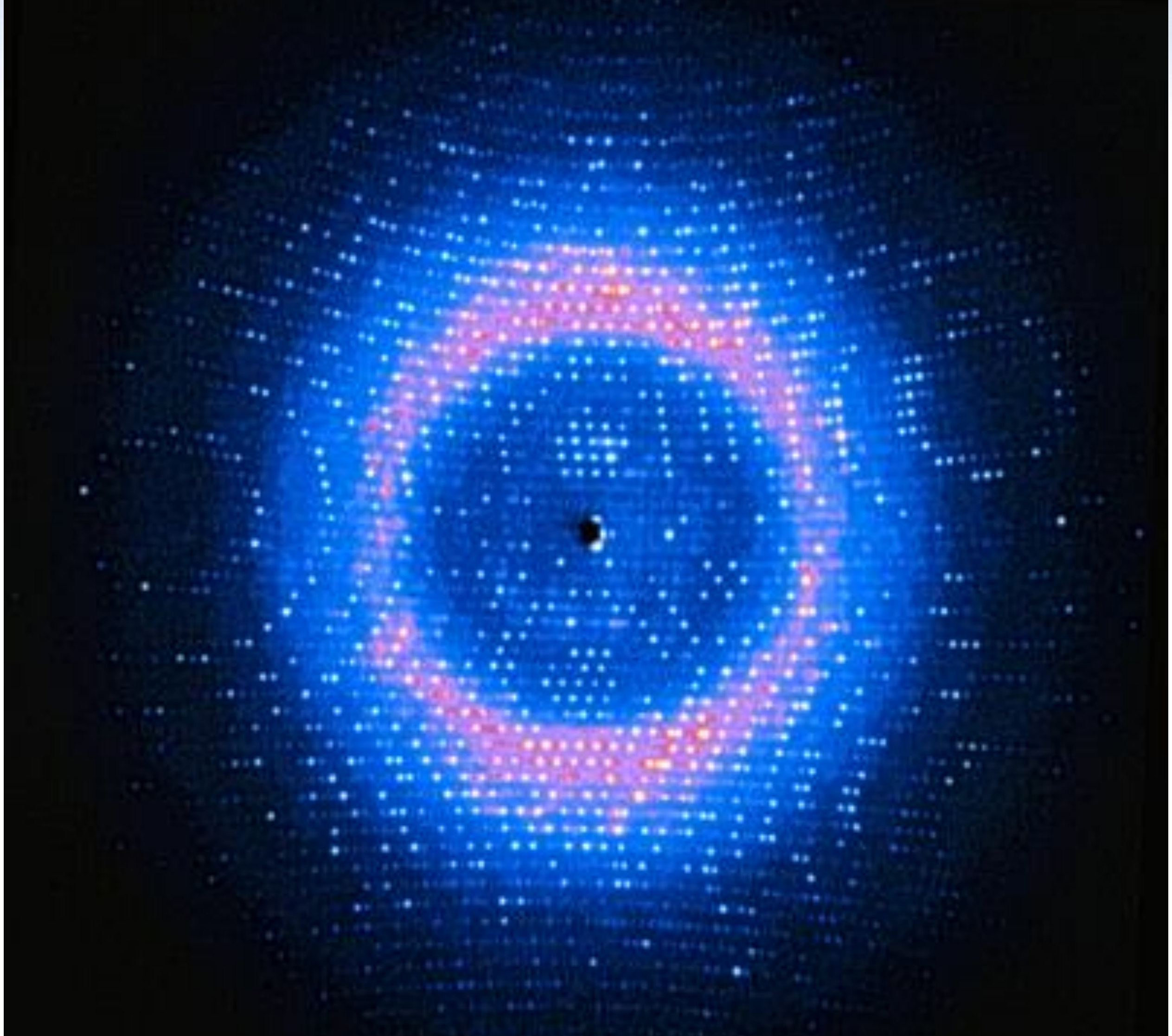
i.e., sample **all** (or most) of the **reciprocal lattice**.

Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

Single Crystal vs. Powder Diffraction



Precess the crystal in all orientations to get diffraction from all lattice planes

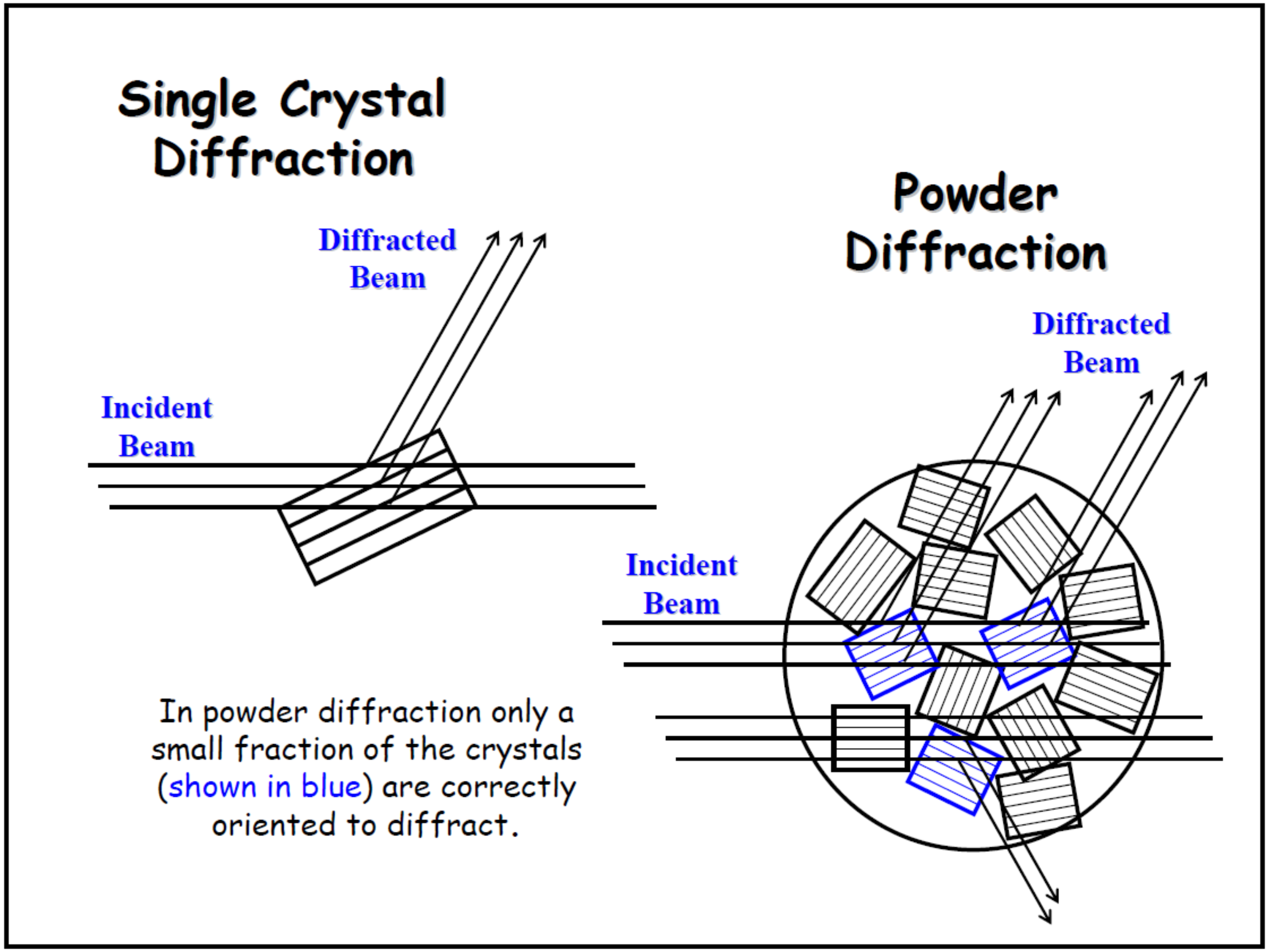


An antique rotation photograph of B-Phyoerythrin -- real x-ray film.

Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

Simple rotation geometry produces a complicated pattern that requires good software to interpret. Modern CCD-based detectors with four-circle diffractometers record such patterns and measure every spot intensity.

Single Crystal vs. Powder Diffraction



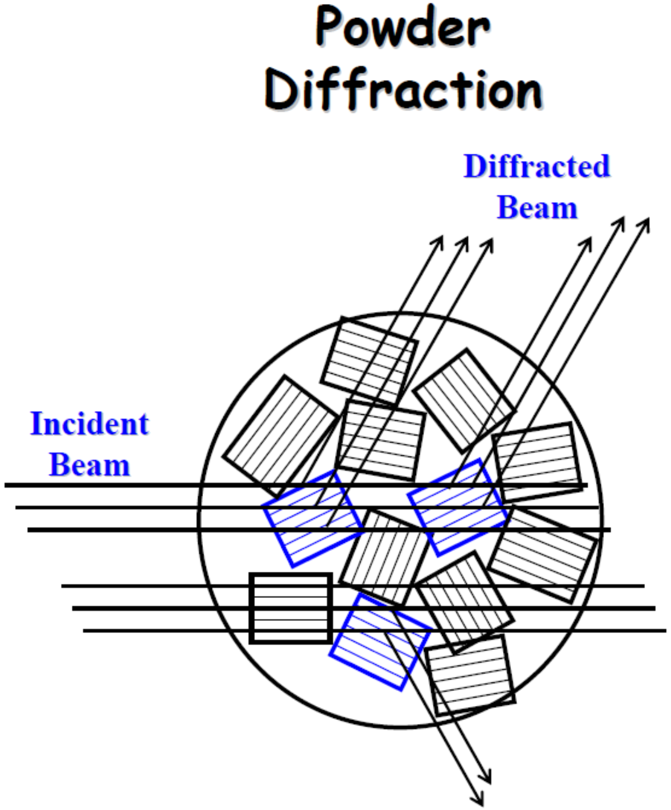
In powder diffraction only a small fraction of the crystals (shown in blue) are correctly oriented to diffract.

Single Crystal vs. Powder Diffraction

At any one diffraction angle, always the same family (or families) of lattice planes contribute(s).

When the sample is spun, different sub-sets of crystallites contribute but from the same family (or families) of lattice planes.

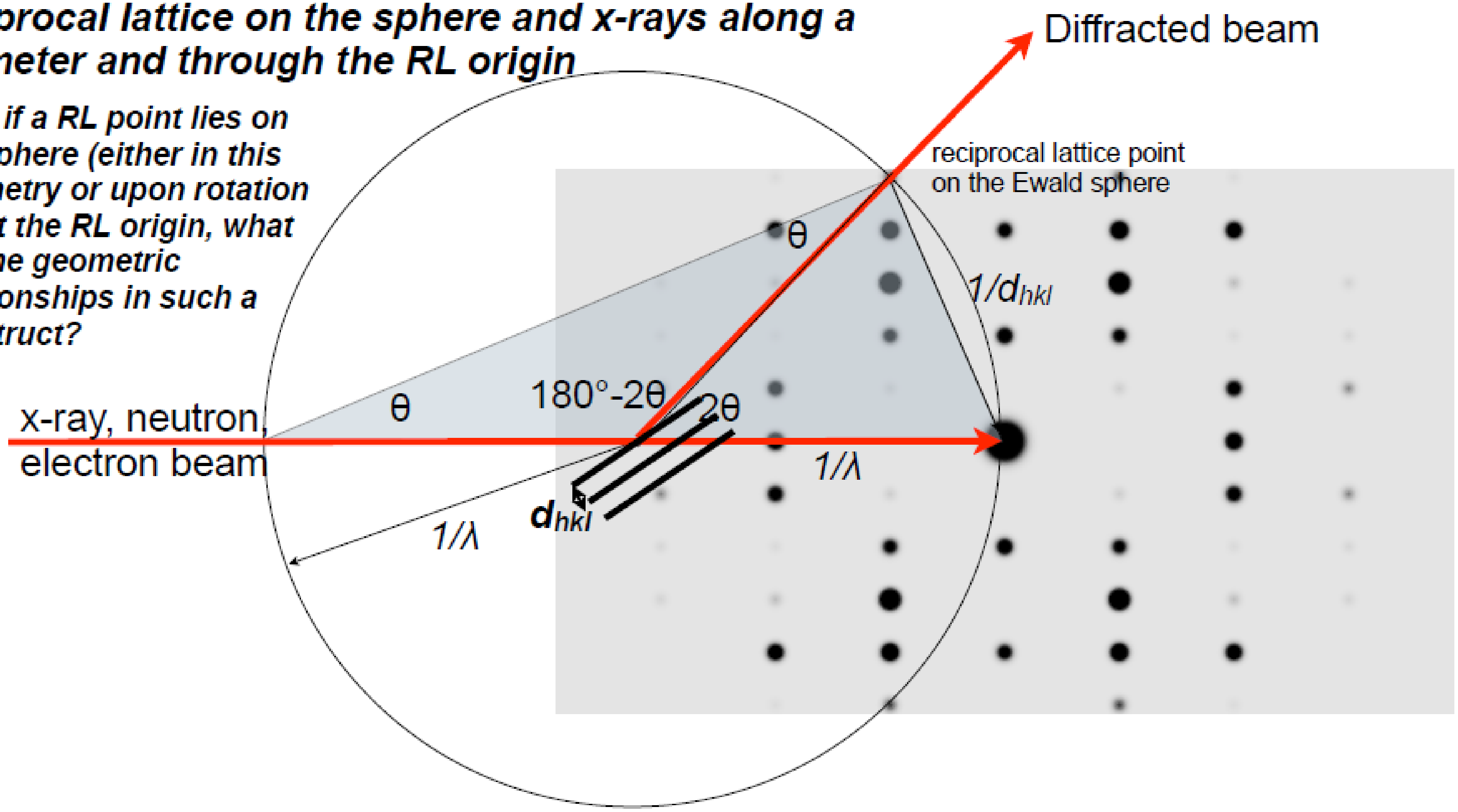
When the diffraction angle is changed, other lattice planes from other crystallites are probed.



The Ewald sphere construction

Construct a sphere of radius 1/λ, with the origin of the reciprocal lattice on the sphere and x-rays along a diameter and through the RL origin

Now, if a RL point lies on the sphere (either in this geometry or upon rotation about the RL origin, what are the geometric relationships in such a construct?

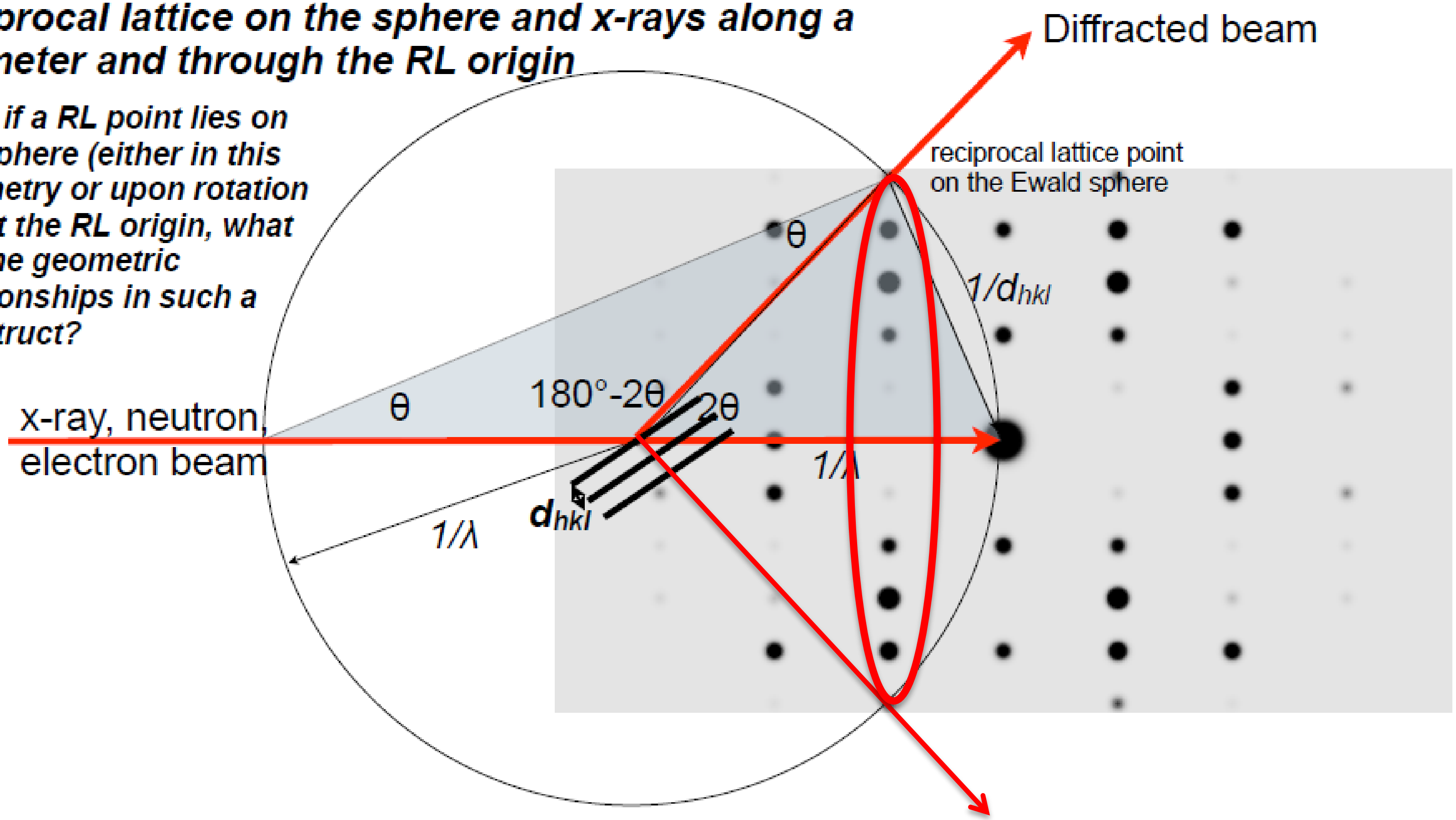


Courtesy of John Parise “Principles of diffraction“

The Ewald sphere construction

Construct a sphere of radius 1/λ, with the origin of the reciprocal lattice on the sphere and x-rays along a diameter and through the RL origin

Now, if a RL point lies on the sphere (either in this geometry or upon rotation about the RL origin, what are the geometric relationships in such a construct?

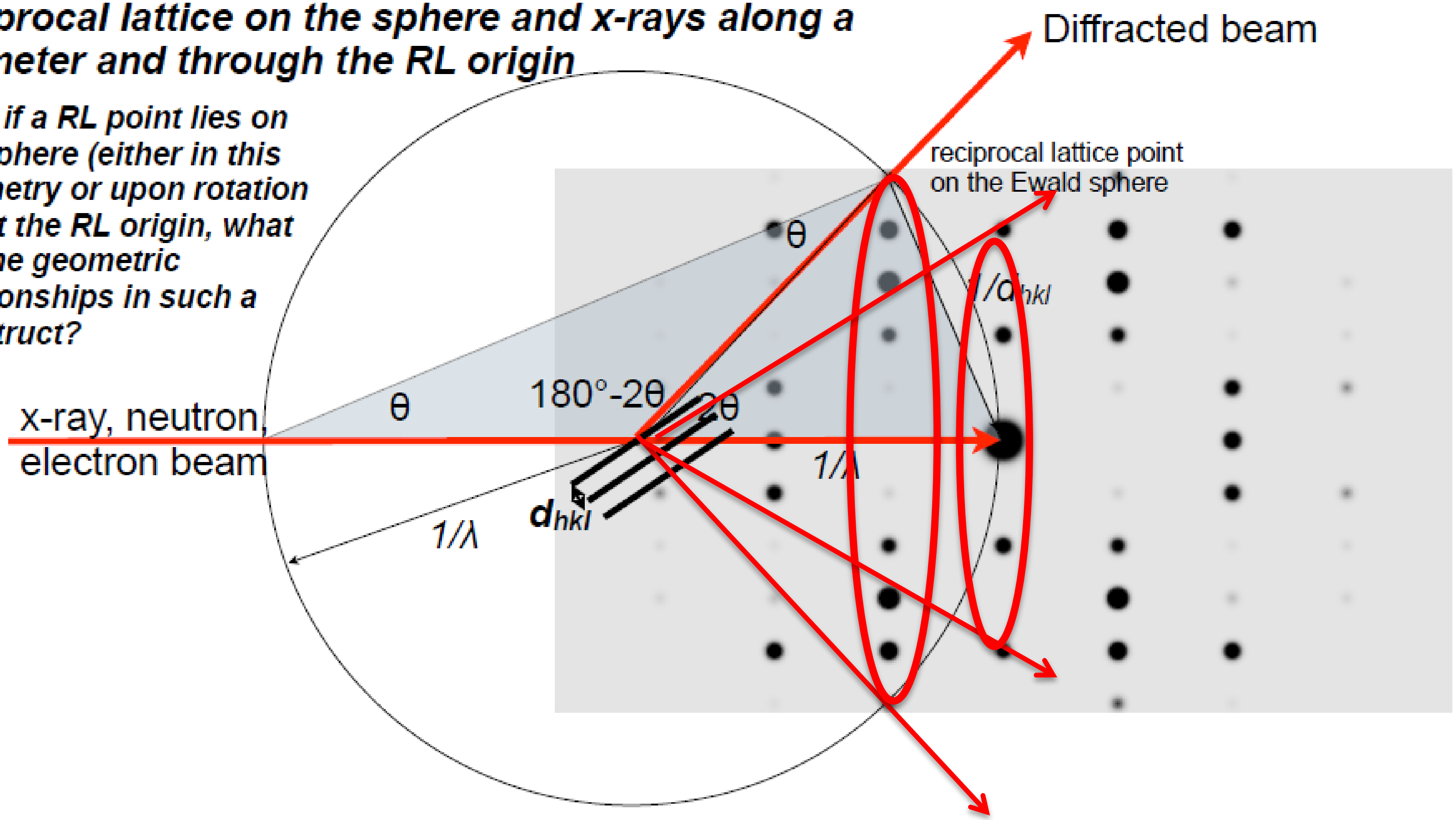


Courtesy of John Parise "Principles of diffraction"

The Ewald sphere construction

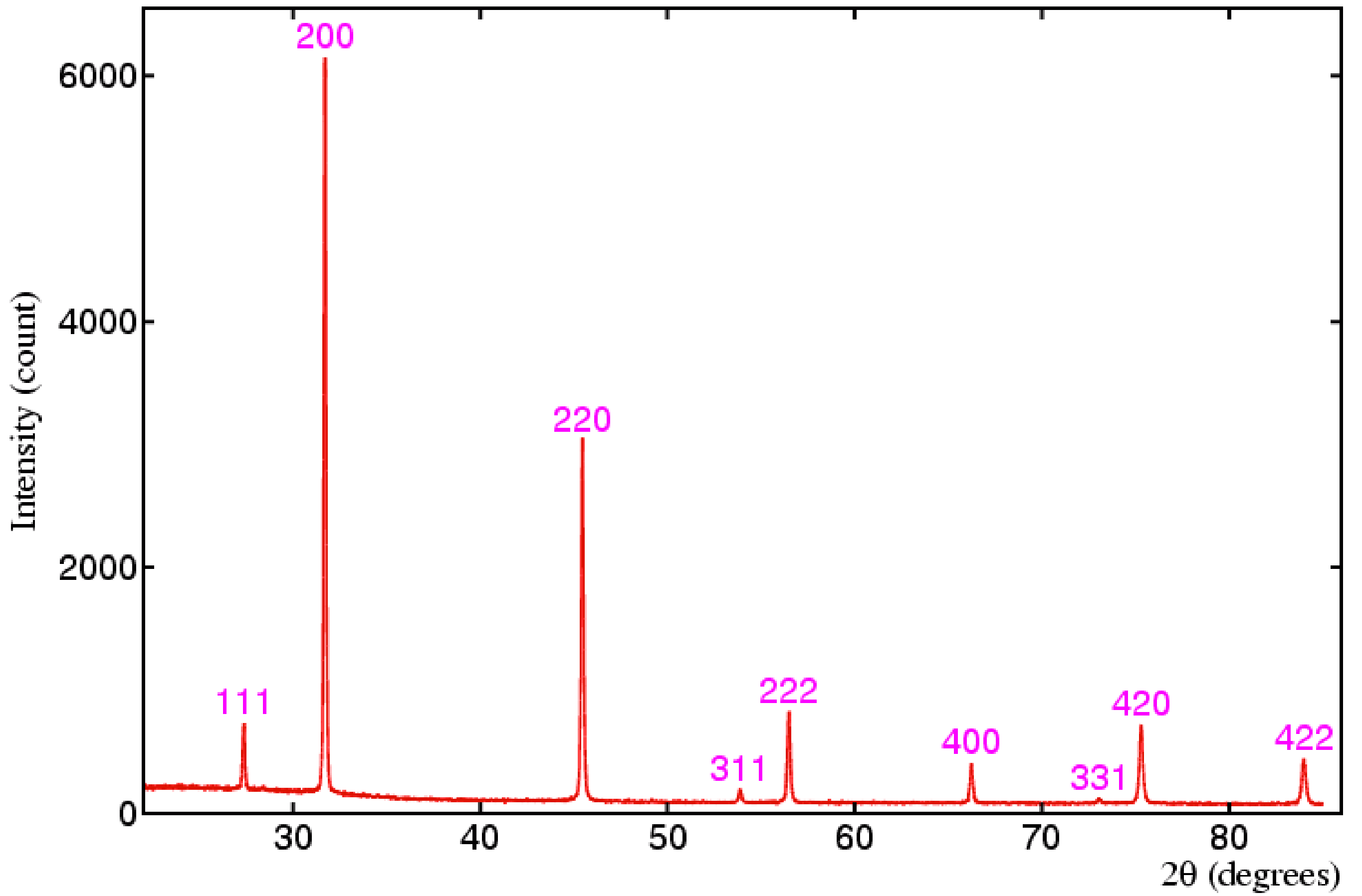
Construct a sphere of radius 1/λ, with the origin of the reciprocal lattice on the sphere and x-rays along a diameter and through the RL origin

Now, if a RL point lies on the sphere (either in this geometry or upon rotation about the RL origin, what are the geometric relationships in such a construct?



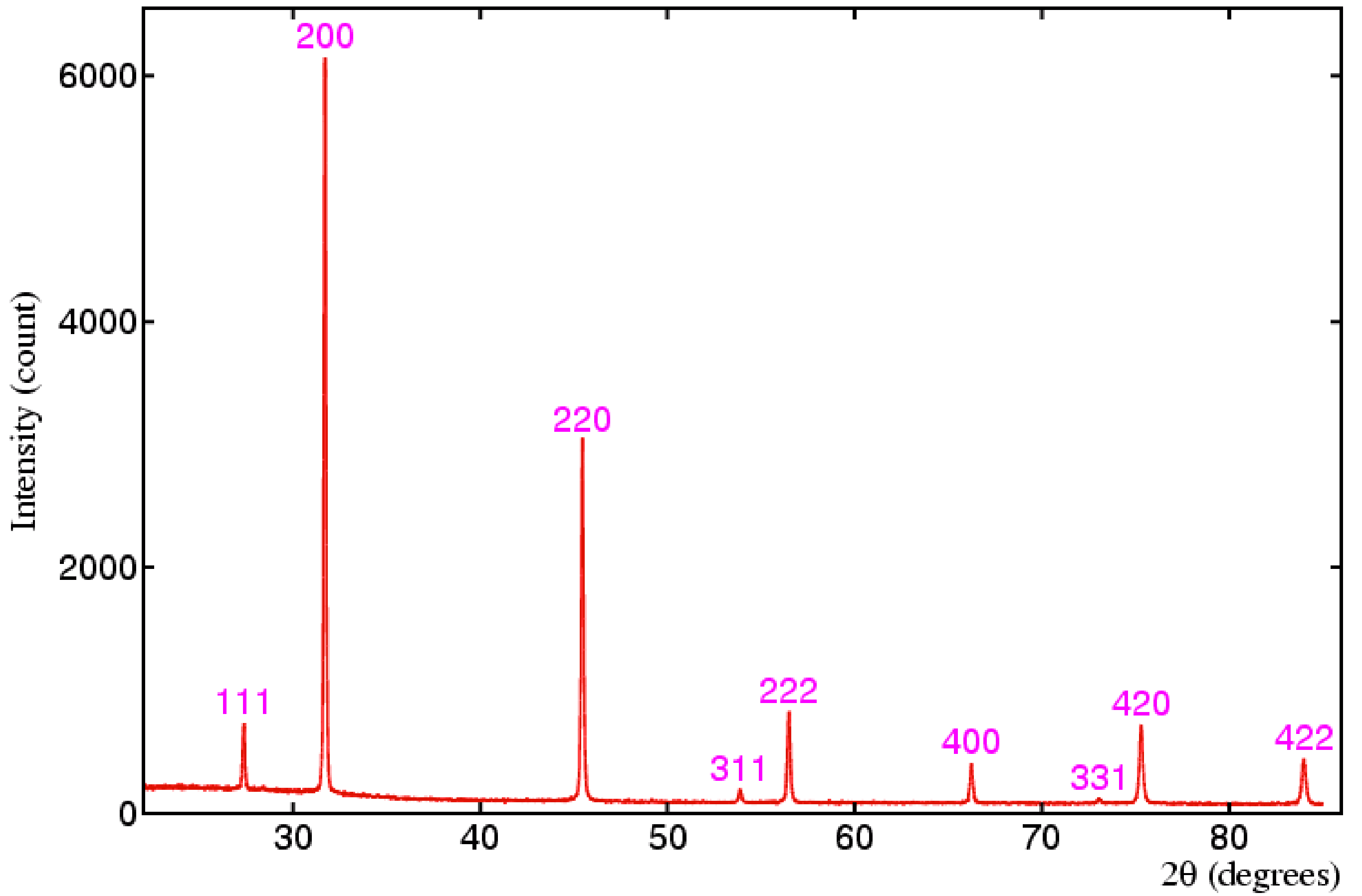
Courtesy of John Parise "Principles of diffraction"

Powder Diffraction Pattern



A series of intensity values (detector photon counts) vs. diffraction angle. Data are compressed into 1D (2θ scale): good and bad!!

Powder Diffraction Pattern



Diffraction pattern (not a spectrum): elastic process

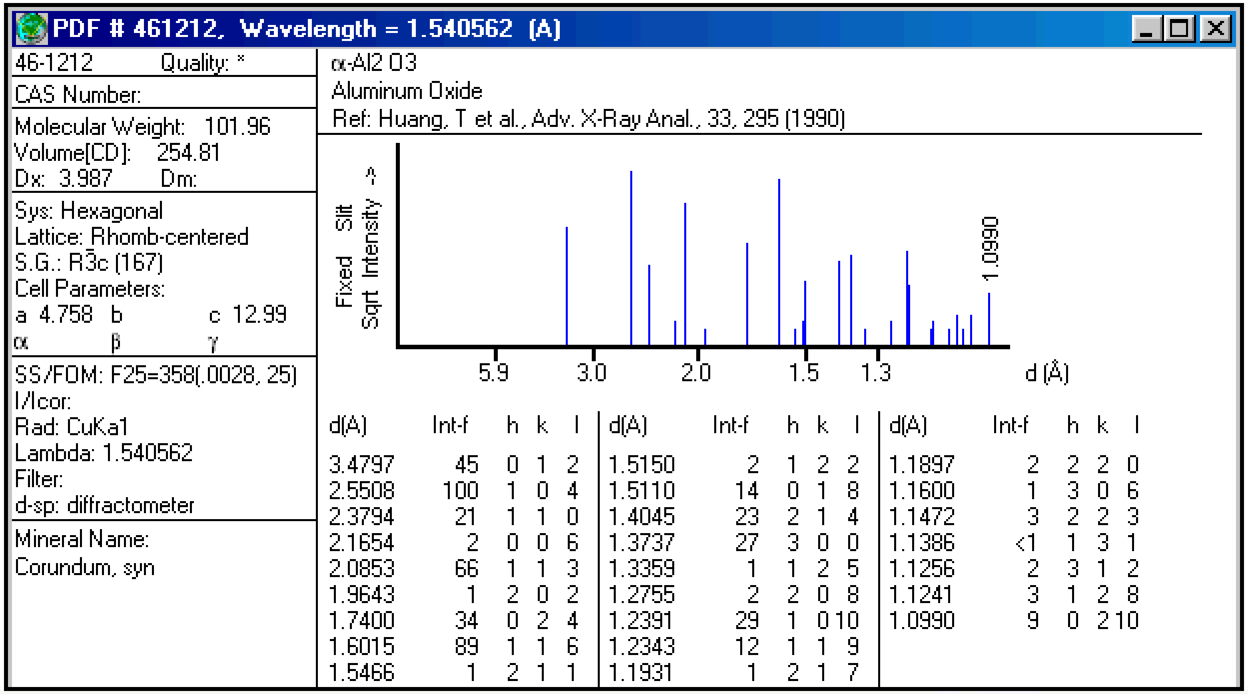
no photon energy change

Qualitative Analysis

Any powder pattern can be used like a fingerprint to see if it matches the powder pattern of an already known compound.

The **International Centre for Diffraction Data (ICDD)** (PA) maintains a database of known powder diffraction patterns (www.icdd.com)

- 365,900 standardized entries
- 42,800 Minerals
- 502,000 Organics



PDF # 461212, Wavelength = 1.540562 (A)

46-1212 Quality: *

CAS Number:

Molecular Weight: 101.96
Volume[CD]: 254.81
Dx: 3.987 Dm:

Sys: Hexagonal
Lattice: Rhomb-centered
S.G.: $R\bar{3}c$ (167)
Cell Parameters:
a 4.758 b c 12.99
α β γ

SS/FOM: F25=358(.0028, 25)
I/Icor:
Rad: CuKa1
Lambda: 1.540562
Filter:
d-sp: diffractometer

Mineral Name:
Corundum, syn

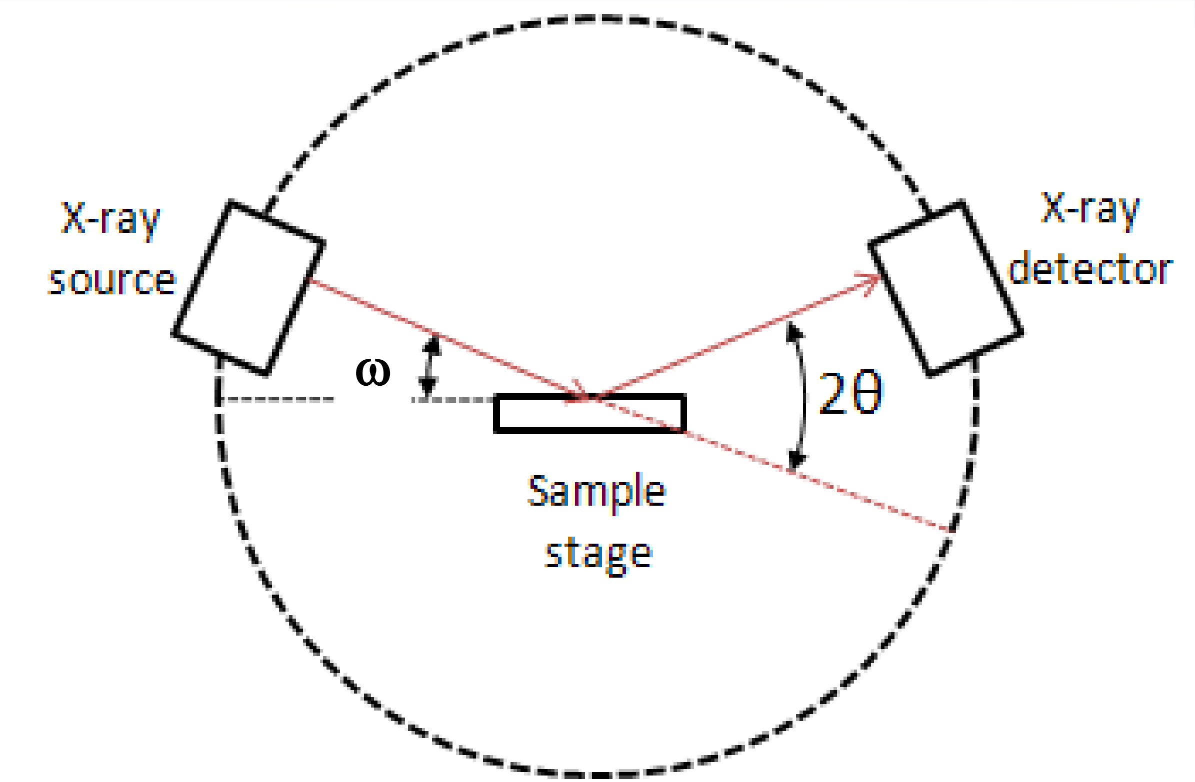
α-Al2 O3
Aluminum Oxide
Ref: Huang, T et al., Adv. X-Ray Anal., 33, 295 (1990)

d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l
3.4797	45	0	1	2	1.5150	2	1	2	2	1.1897	2	2	2	0
2.5508	100	1	0	4	1.5110	14	0	1	8	1.1600	1	3	0	6
2.3794	21	1	1	0	1.4045	23	2	1	4	1.1472	3	2	2	3
2.1654	2	0	0	6	1.3737	27	3	0	0	1.1386	<1	1	3	1
2.0853	66	1	1	3	1.3359	1	1	2	5	1.1256	2	3	1	2
1.9643	1	2	0	2	1.2755	2	2	0	8	1.1241	3	1	2	8
1.7400	34	0	2	4	1.2391	29	1	0	10	1.0990	9	0	2	10
1.6015	89	1	1	6	1.2343	12	1	1	9					
1.5466	1	2	1	1	1.1931	1	2	1	7					

Outline

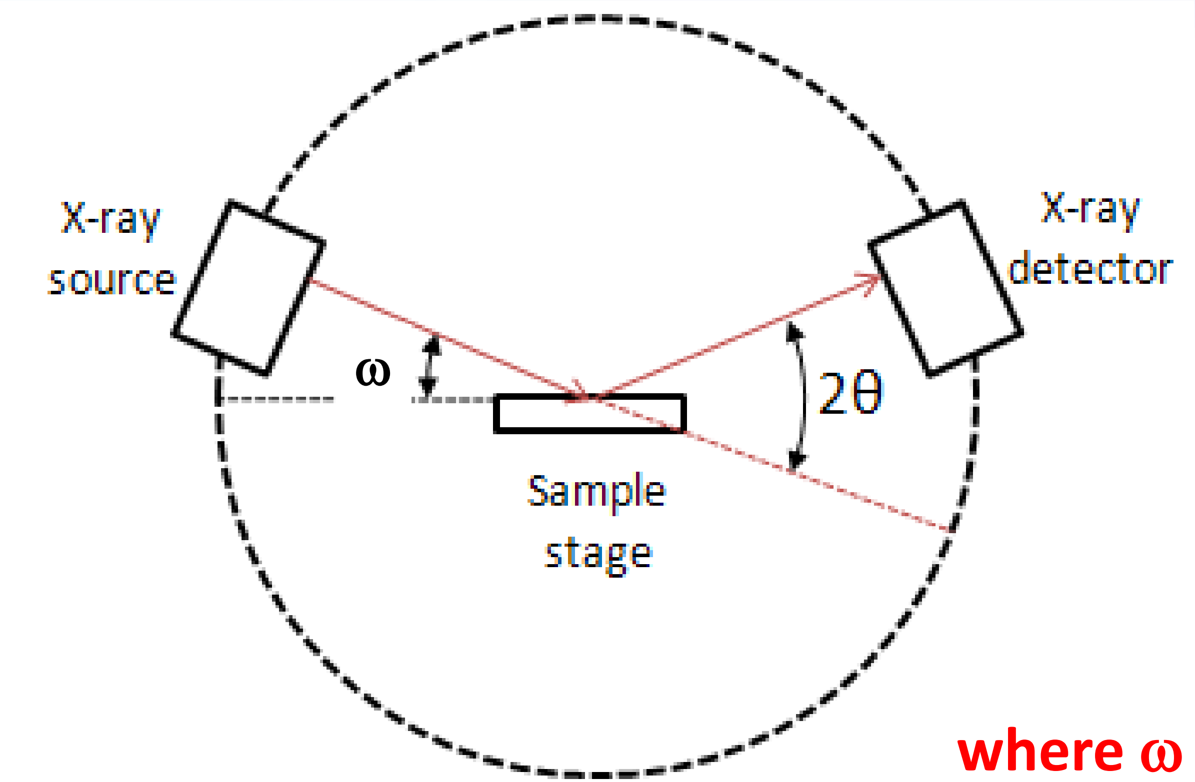
1. Applications for Powder Diffraction
2. The basics of Powder Diffraction
3. **Experimental Methods for collecting PD data**
4. **Crystal structure Determination**
5. **Peak Profile Analysis for Microstructural Studies**
6. **Advanced PD techniques**

Scheme of a One-Axis Diffractometer



- X-ray source (tube, rotating anode)
- Powder sample (flat plate, capillary)
- X-ray detector (a variety of technologies: direct counting or conversion)
- Diffraction plane (contains the incident and the diffracted beam)

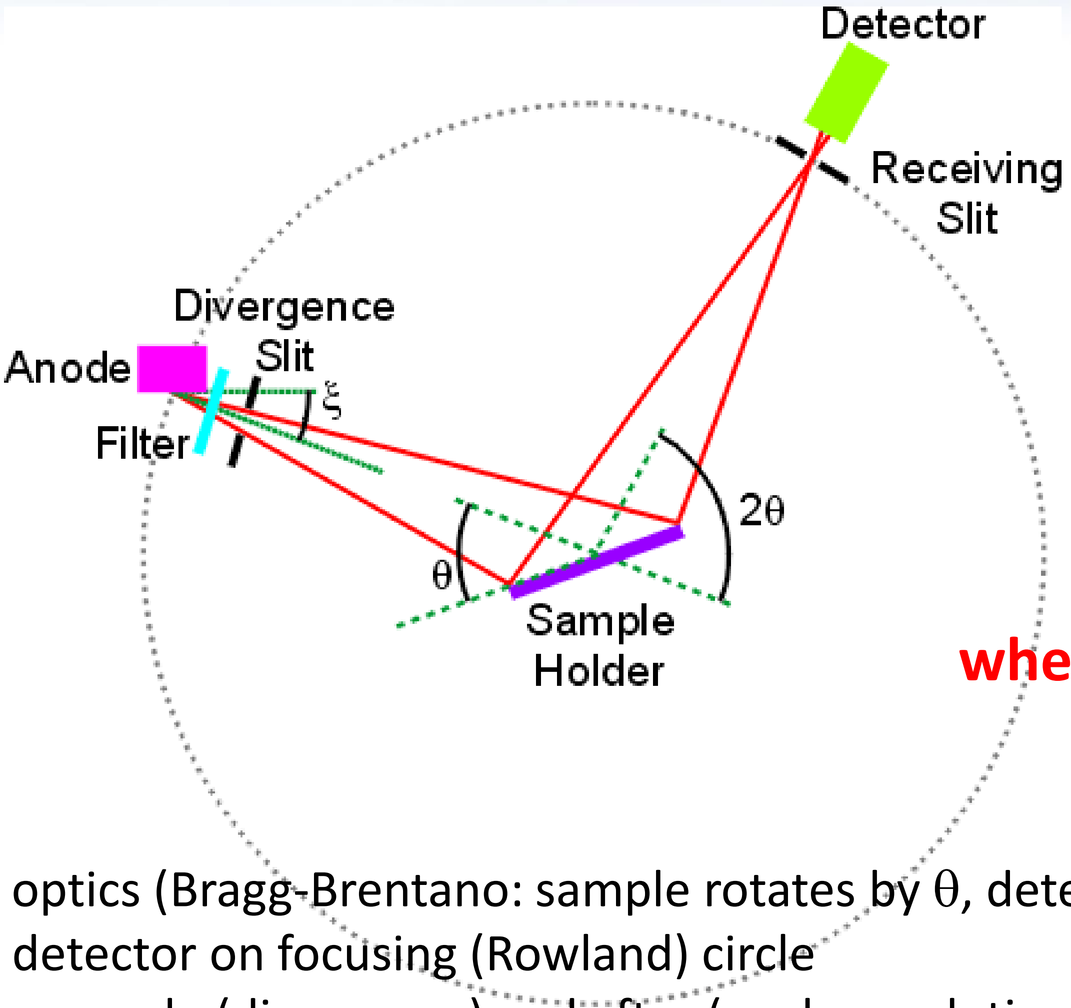
Scheme of a One-Axis Diffractometer



where $\omega \neq 2\theta/2$

- X-ray source (tube, rotating anode)
- Powder sample (flat plate, capillary)
- X-ray detector (a variety of technologies: direct counting or conversion)
- Diffraction plane (contains the incident and the diffracted beam)

Scheme of a Two-Axis Diffractometer



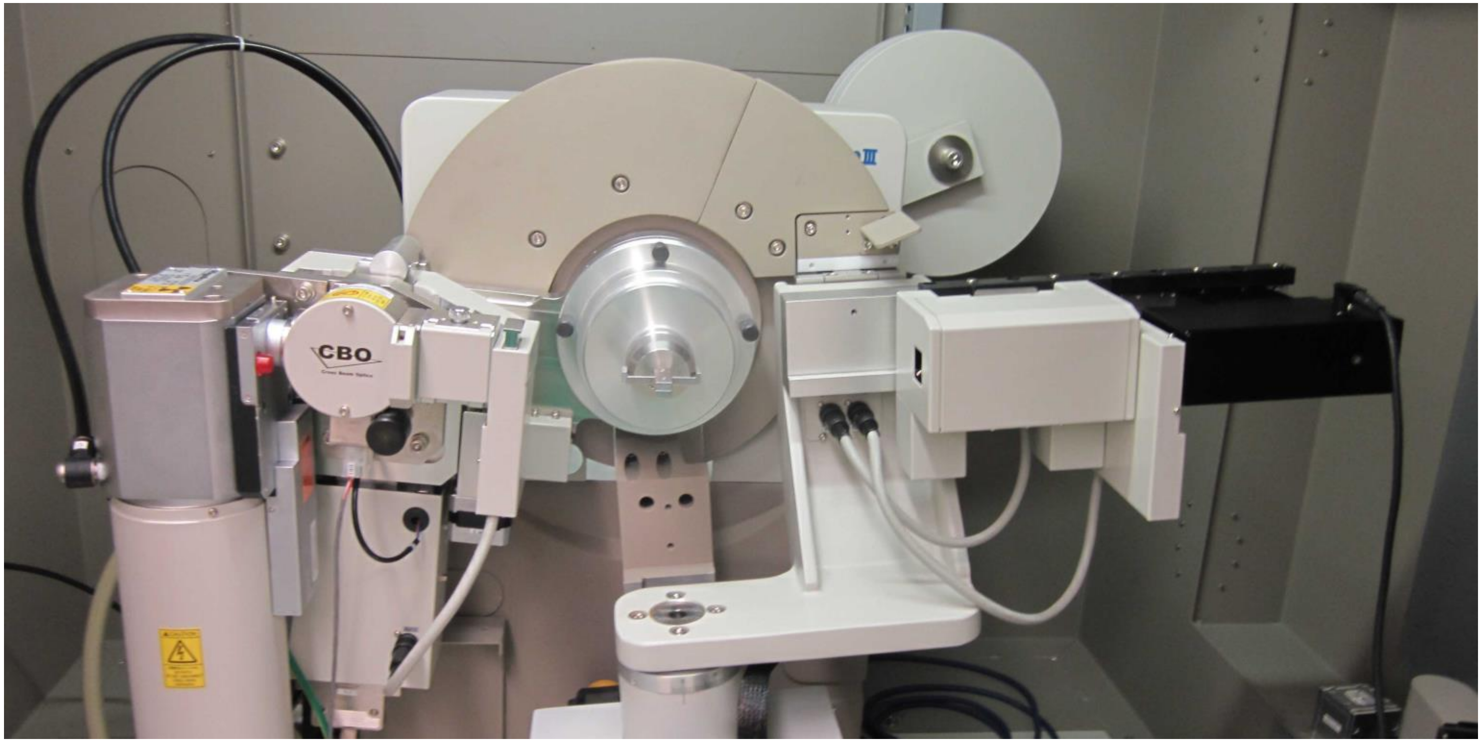
where ω = 2θ/2

Optics:

- Para-focusing optics (Bragg-Brentano: sample rotates by θ, detector rotates by 2θ → to keep detector on focusing (Rowland) circle
- Slits before the sample (divergence) and after (angle resolution Δ2θ)

Scheme of a Three-Axis Diffractometer

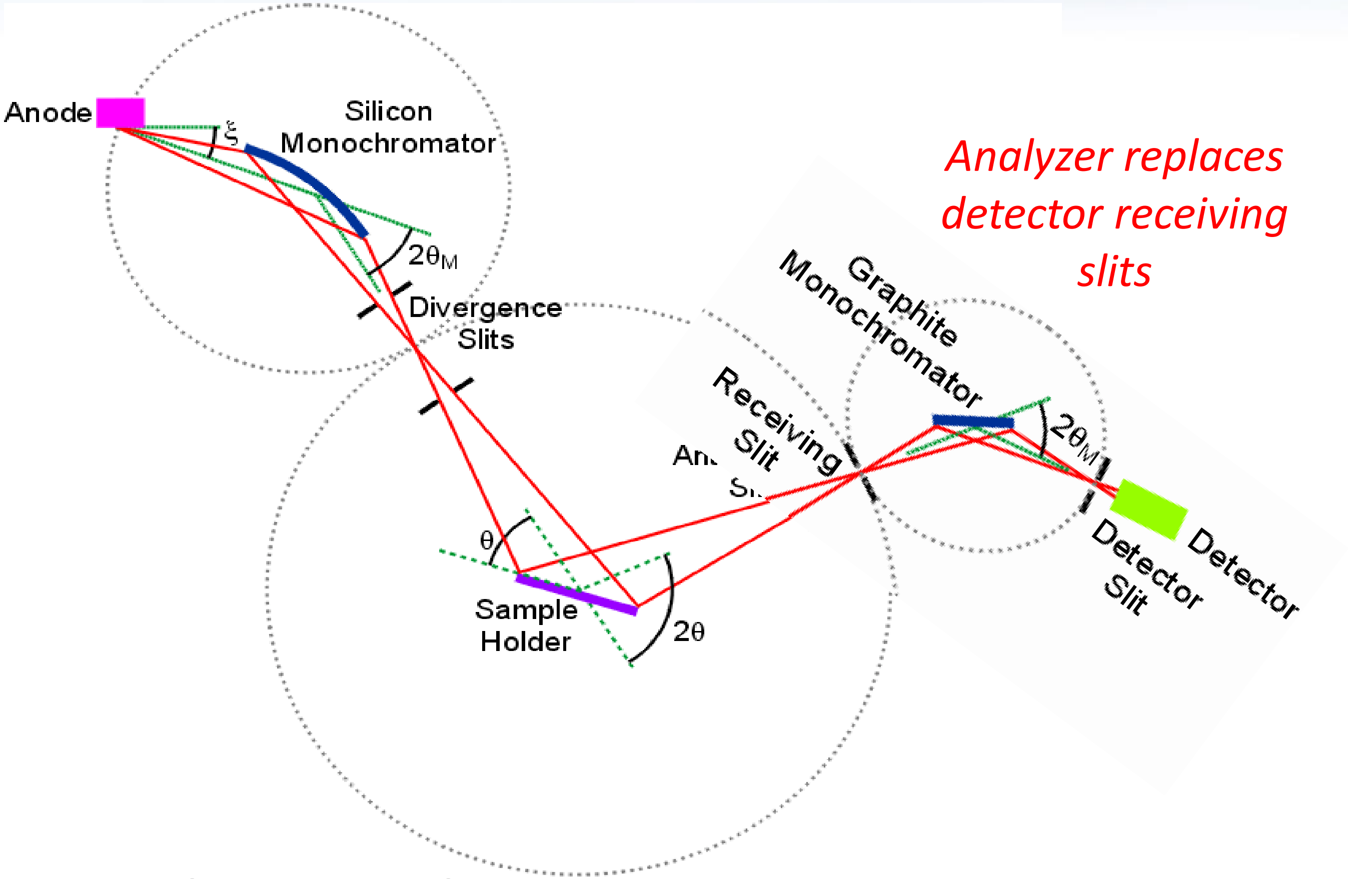
(do you see the additional 3rd circle?)



Spinning sample (in many cases):

- Average: as many crystallites (grains) in the beam as possible
- Randomize: eliminates preferred orientation
- Not an "ideal" powder (texture, poor sampling) → intensities are affected

Scheme of a Four-Axis Diffractometer



Analyzer replaces detector receiving slits

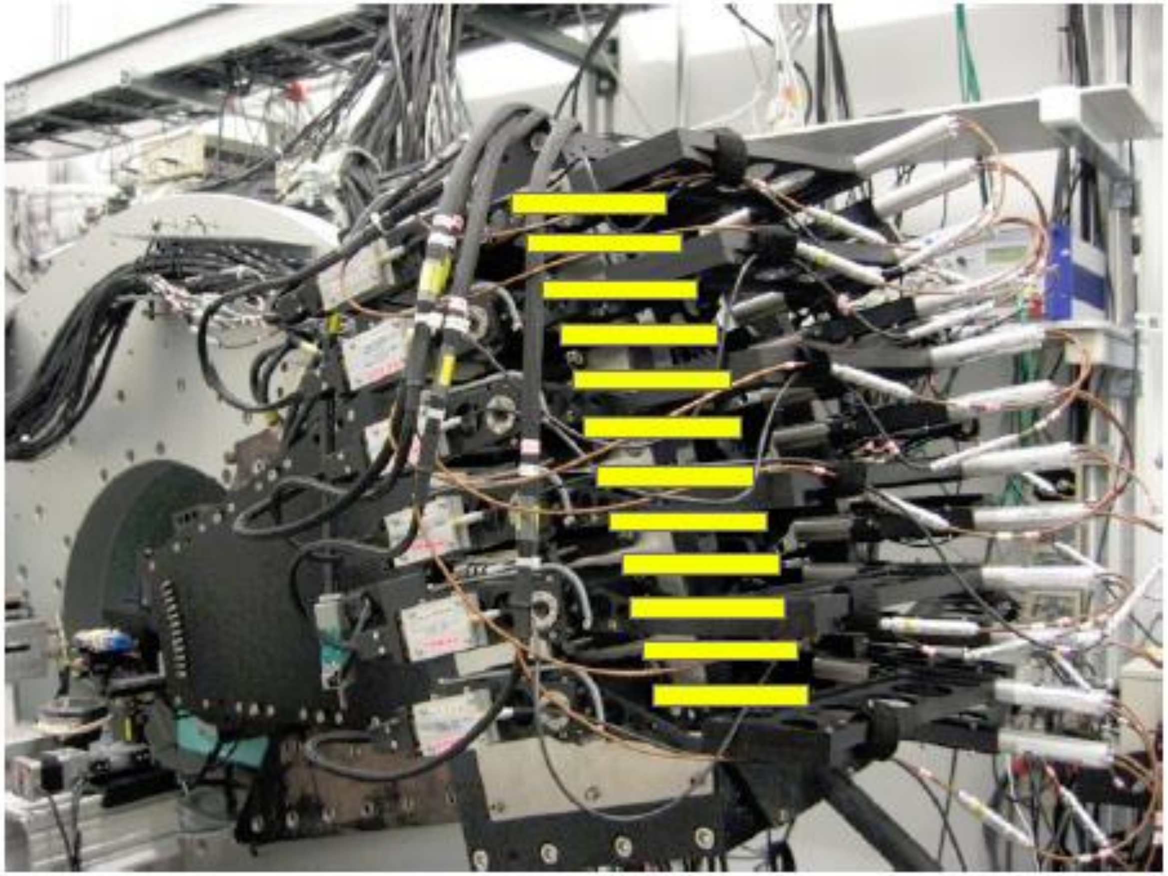
Can you see the 4 circles ?

Multi-Analyzer Crystal detector at Argone (IL)

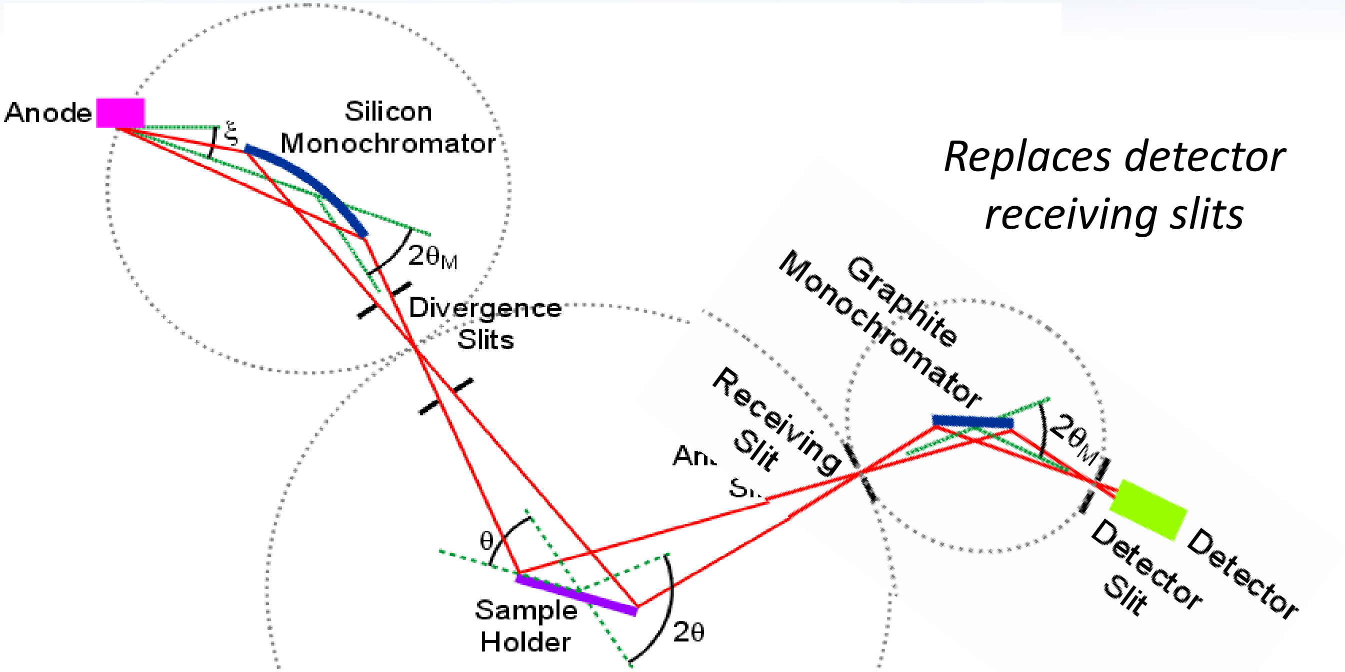
- 12 crystals/detectors
  - Individually adjusted
  - 2° separation
  - Total 2Θ range = 22°
- Si(111) crystals
  - excellent discrimination
  - low background (& yield!)
  - $LaCl_3$ Scintillators

Multiple Observations

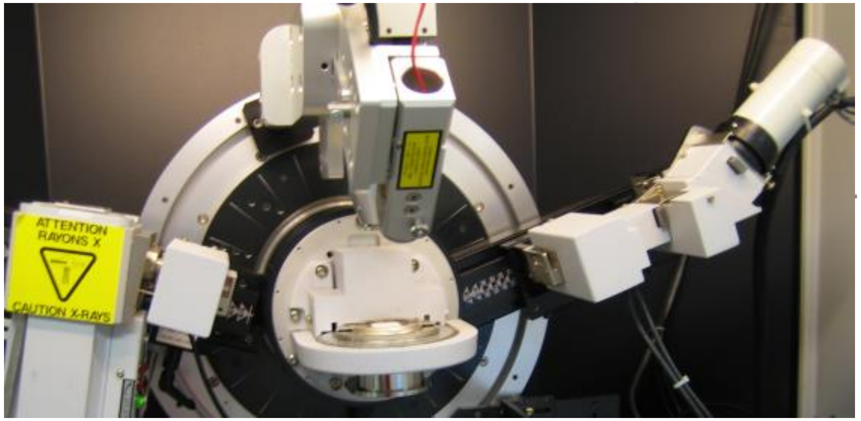
- ➢ **Reduce Collection Time**
- ➢ **Improve Accuracy**



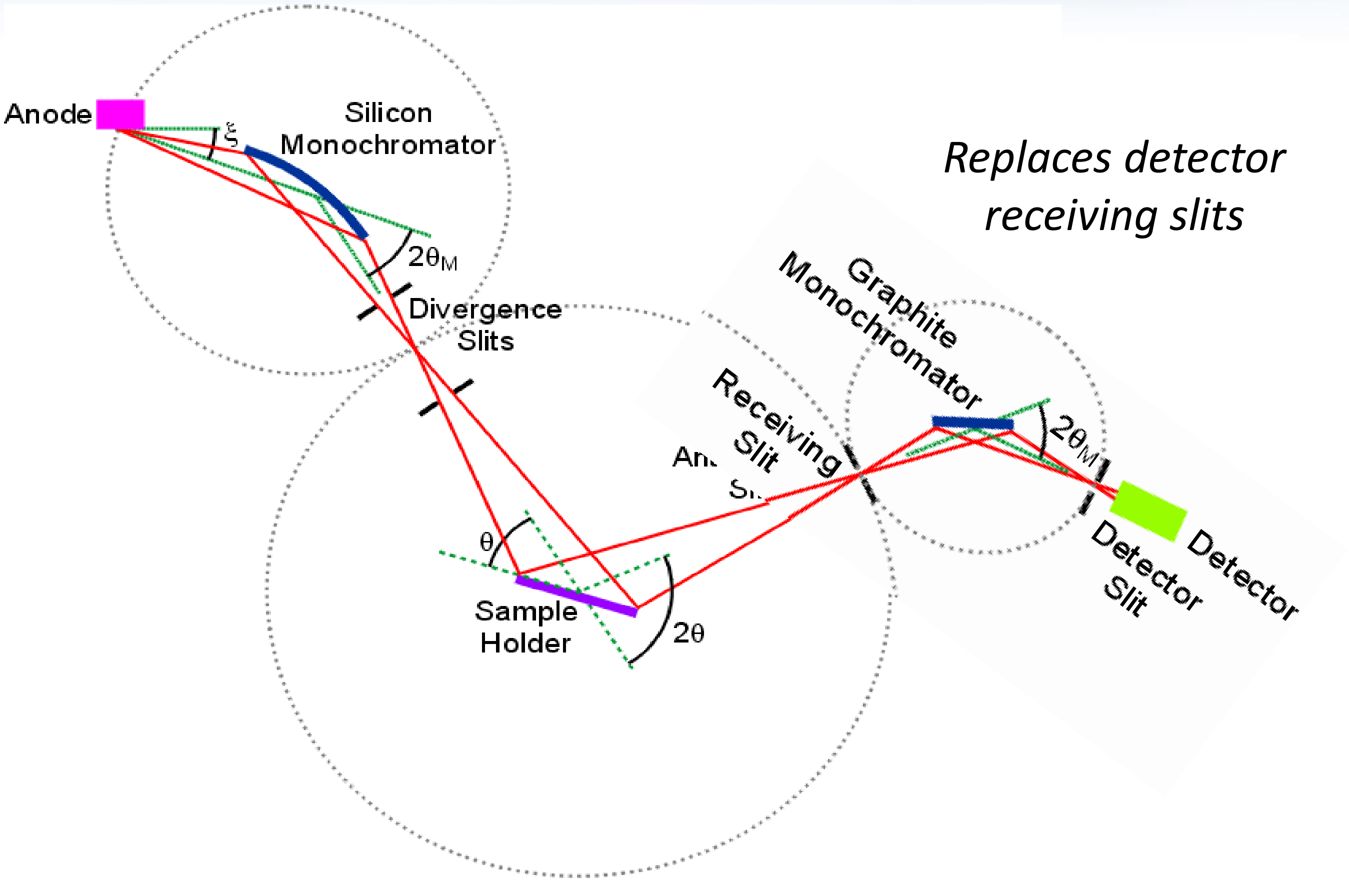
Scheme of a Four-Axis Diffractometer



Replaces detector receiving slits



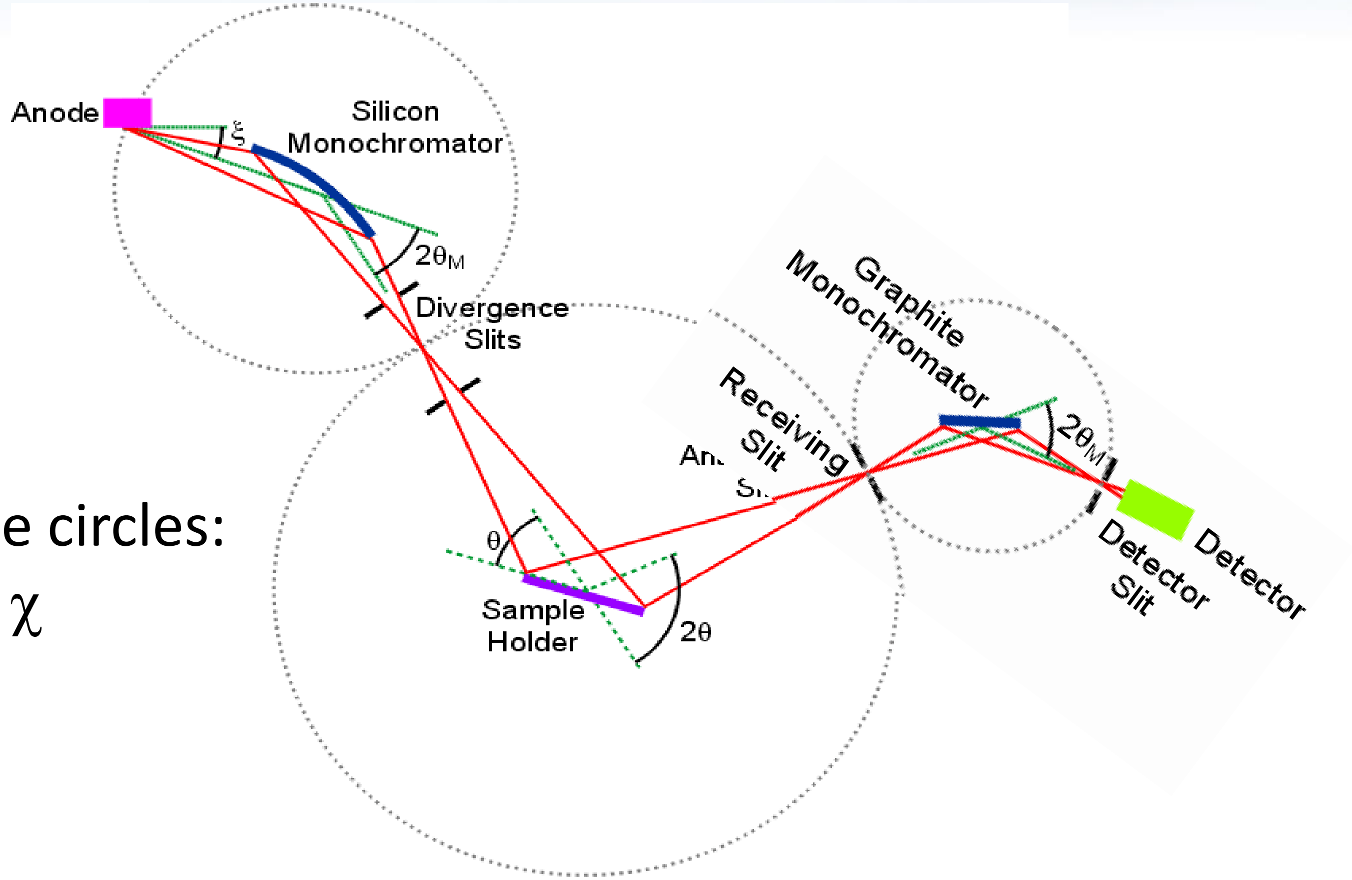
Scheme of a Four-Axis Diffractometer



Replaces detector receiving slits

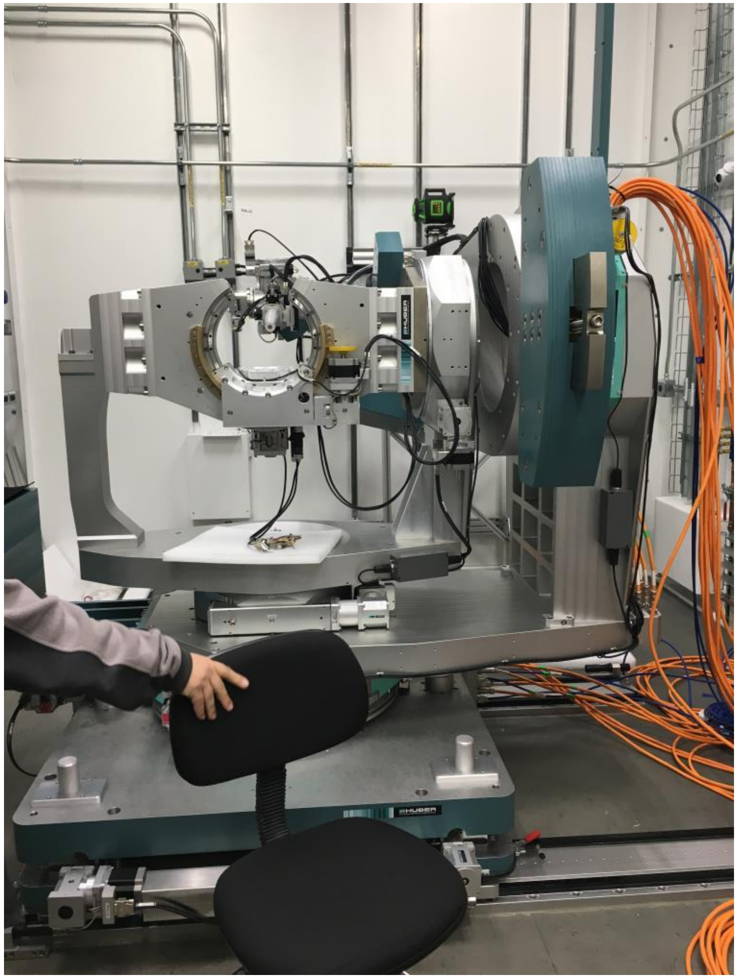
Can you find another 2 circles (not shown) ?

Scheme of a Six-Axis Diffractometer

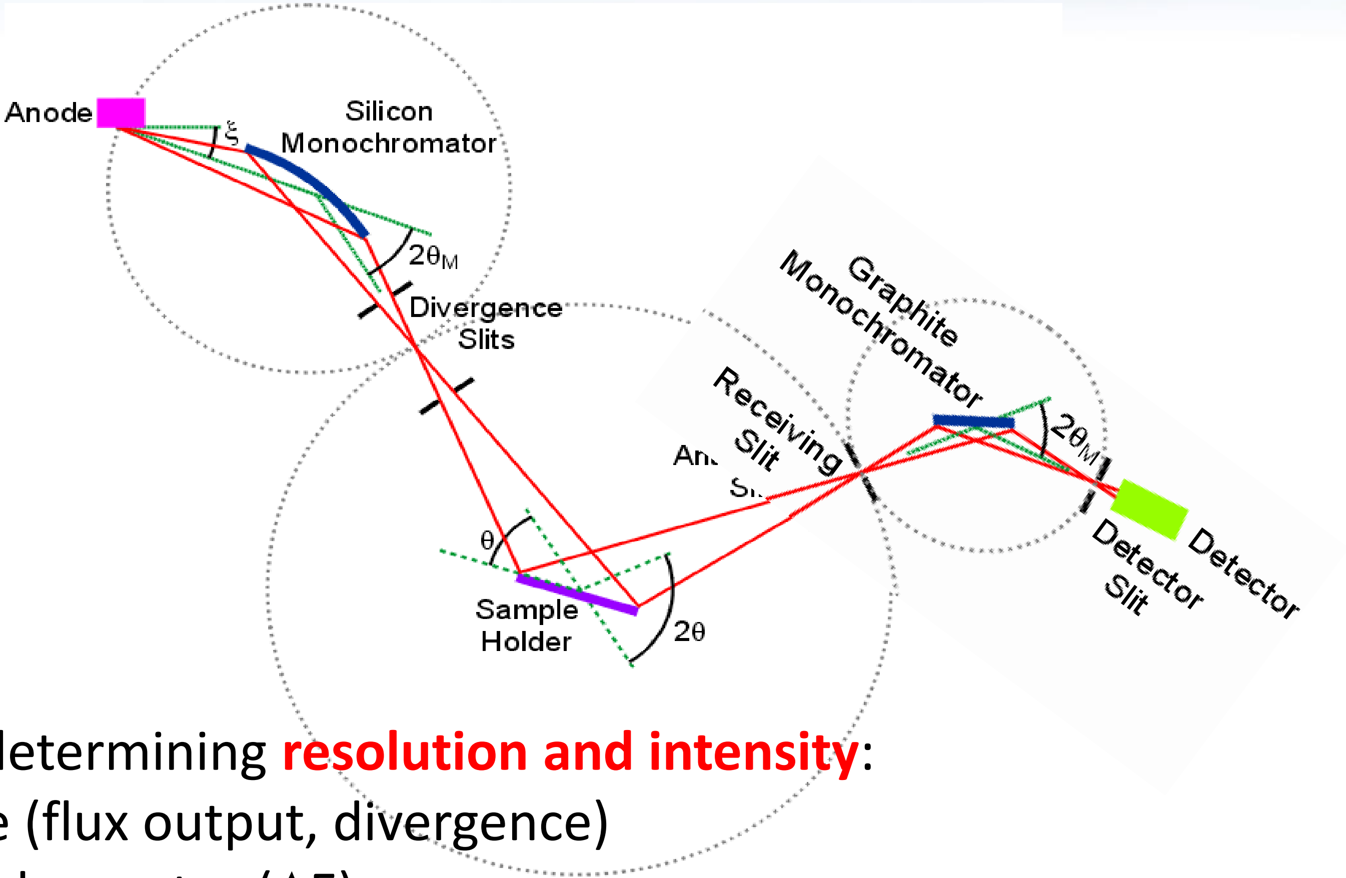


+ 2 sample circles:
ϕ and χ

6-circle diffractometer at the NSLS-II (ISR)



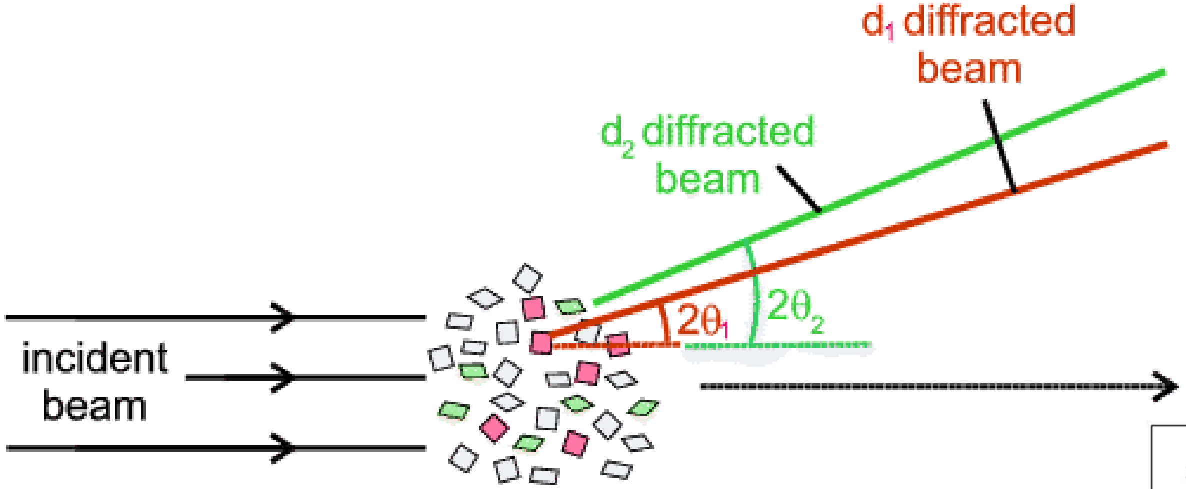
Scheme of a Six-Axis Diffractometer

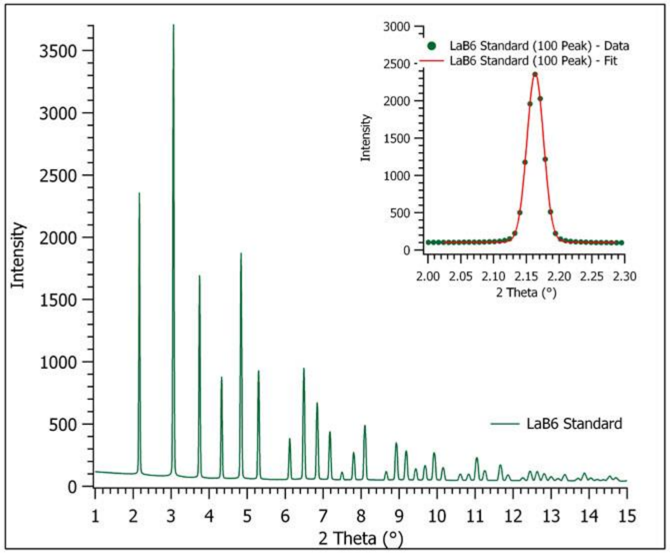


Parameters determining **resolution and intensity**:

- Source (flux output, divergence)
- Monochromator (ΔE)
- Mirror (focusing, parallel)
- Analyzer (discrimination, error immune)

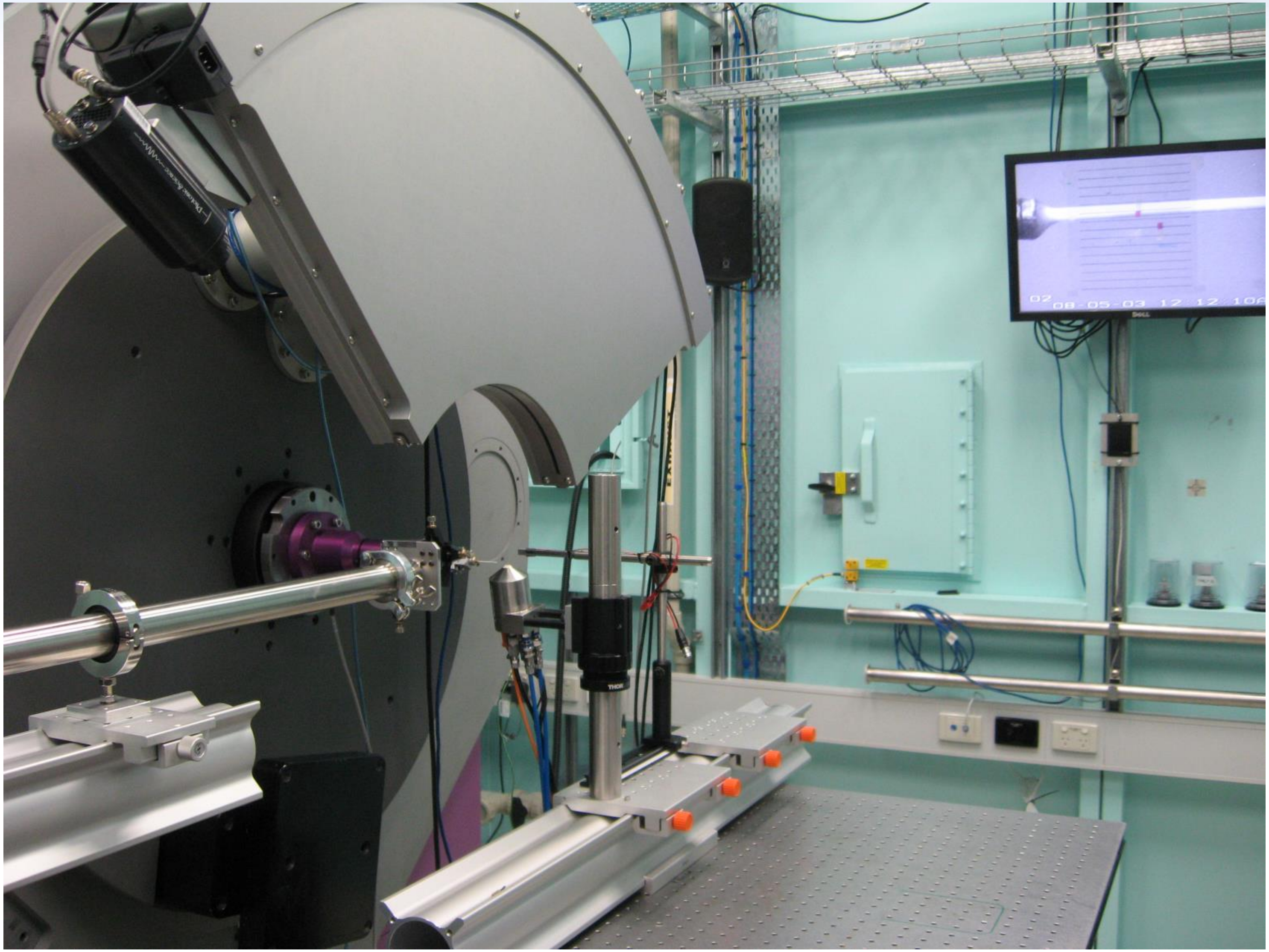
From 0-D Powder Diffraction…



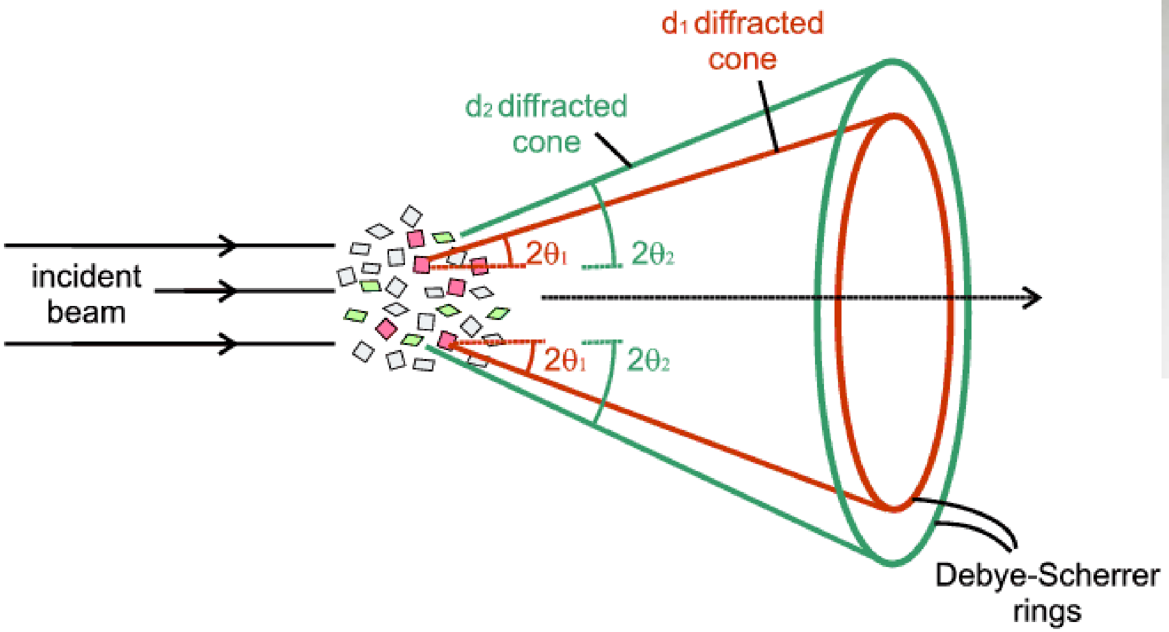


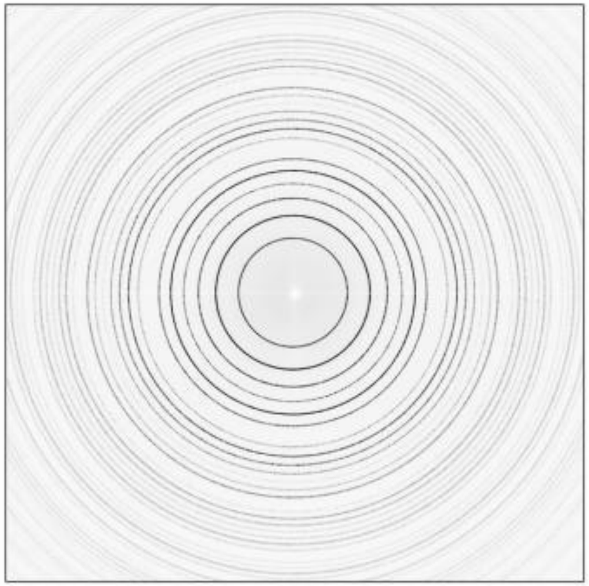
- 0-D (point) detector: scanning (slow and accurate)
- 1-D (line) detector: intercepts all 2θ angles (fast but lower res)

The 1-D detector at the Australian Synchrotron

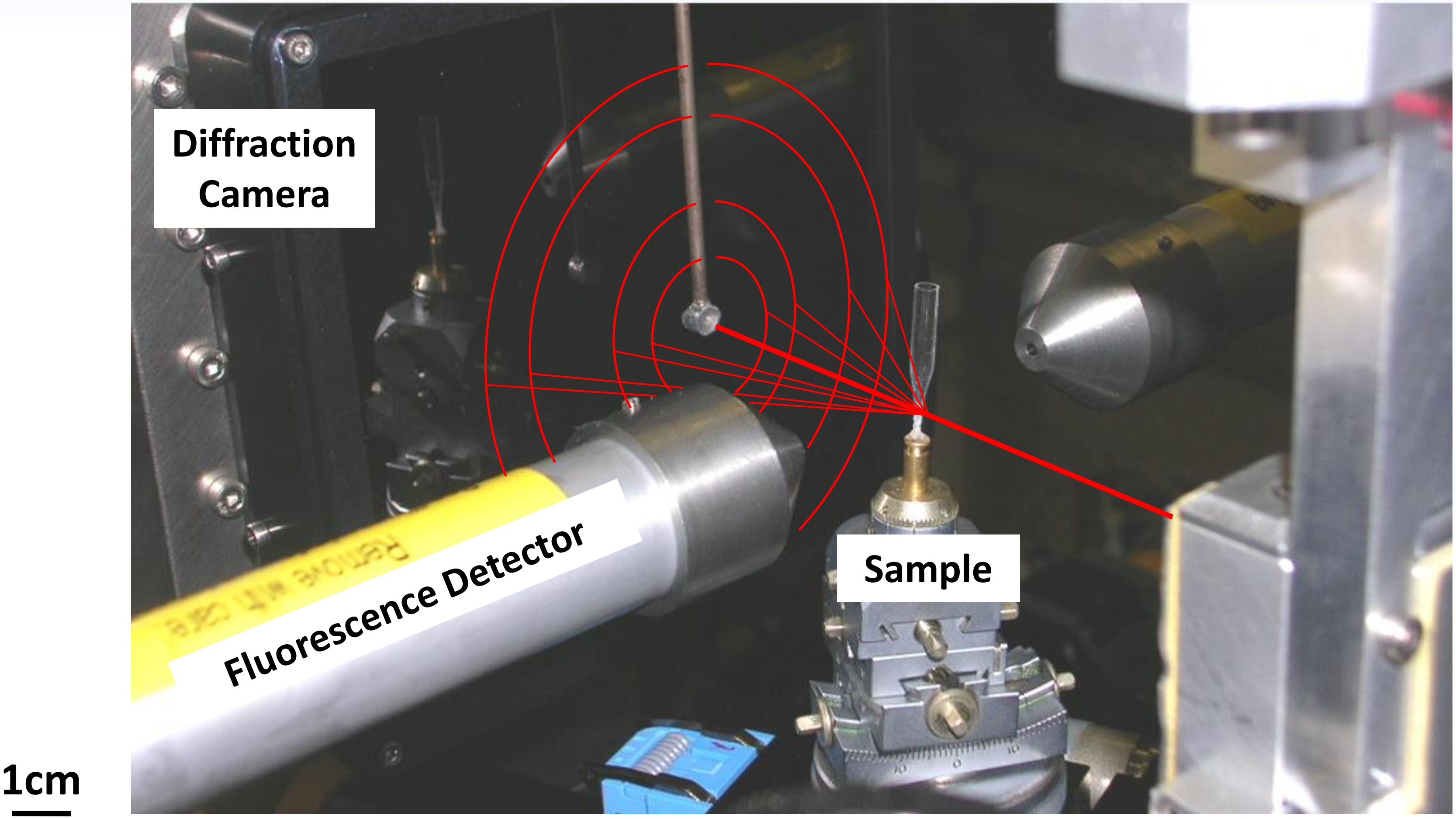


…to 2-D Powder Diffraction

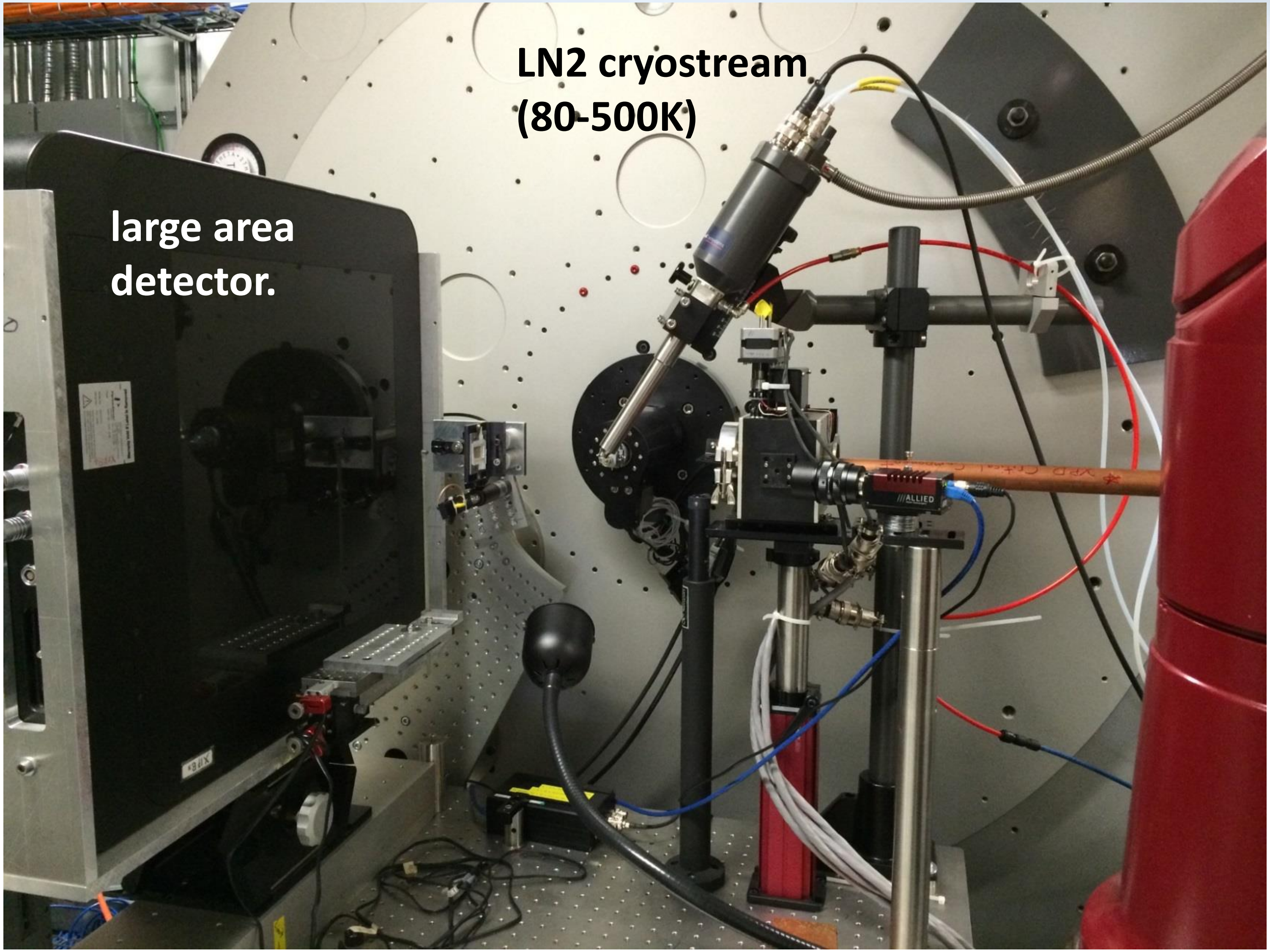




- 2-D (large-area) detector: Debye-Scherrer rings (large field of view in one single shot, background high, low resolution)
- Non-random orientation generates non-uniform or spotty rings (texture, pole figures)


Diffraction Camera
Fluorescence Detector
Sample
1cm

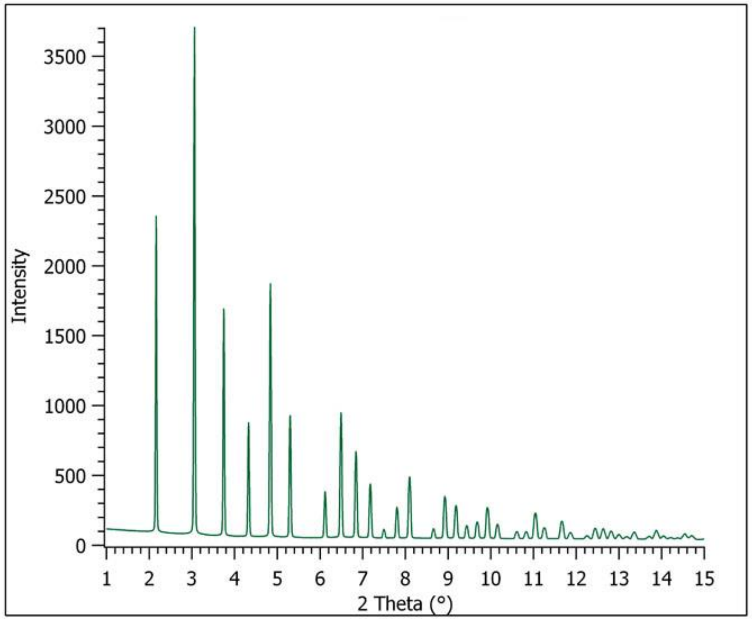
NSLS-II Experimental Set-Up



Comparison of 0D and 2D detection

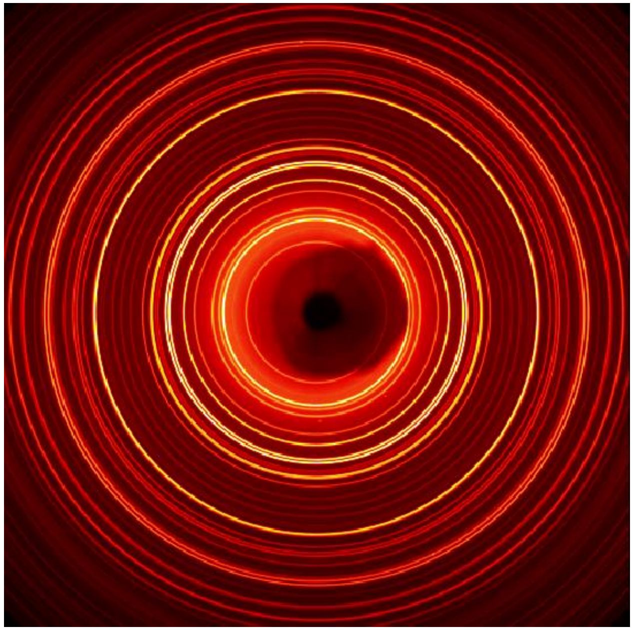
Point Detector

- Angle scanning (slow)
- Higher Resolution (peak shape, peak separation)
- Less Background



Area Detector

- Fixed
- Faster (single shot)
- Higher Statistics (full azimuth)



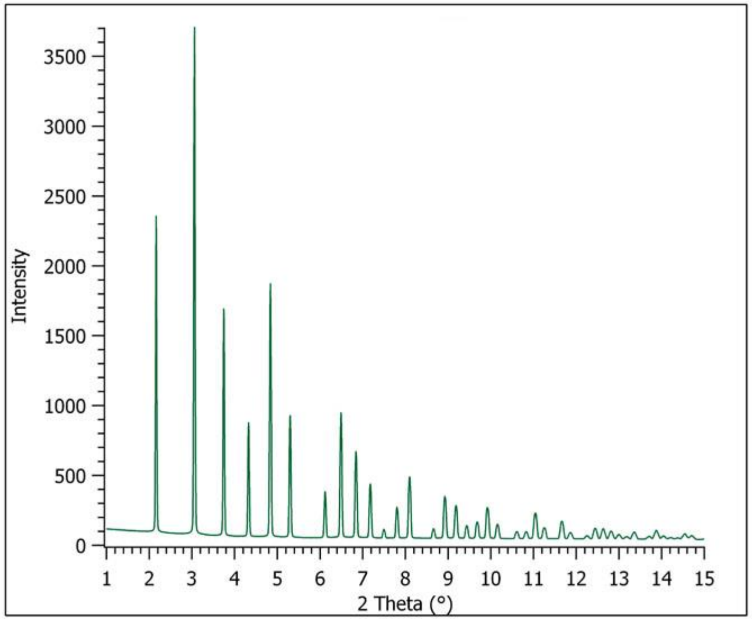
Courtesy of Saul Lapidus, Argonne

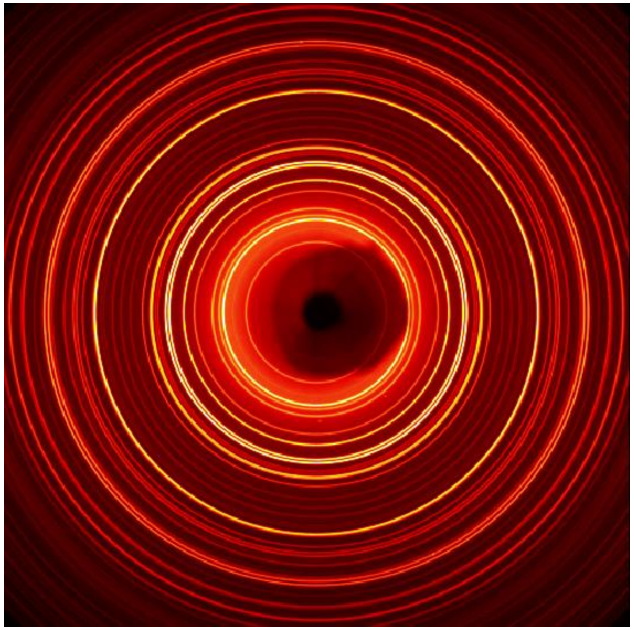
Comparison of 0D and 2D detection

1-D pattern

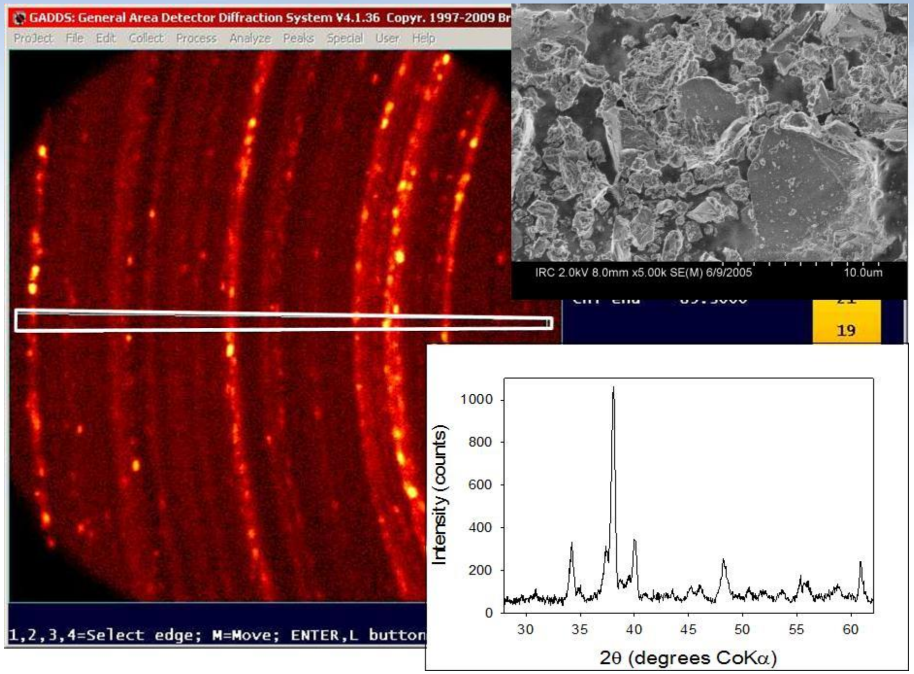
2-D pattern

Radial cross-section
or azimuthal integration

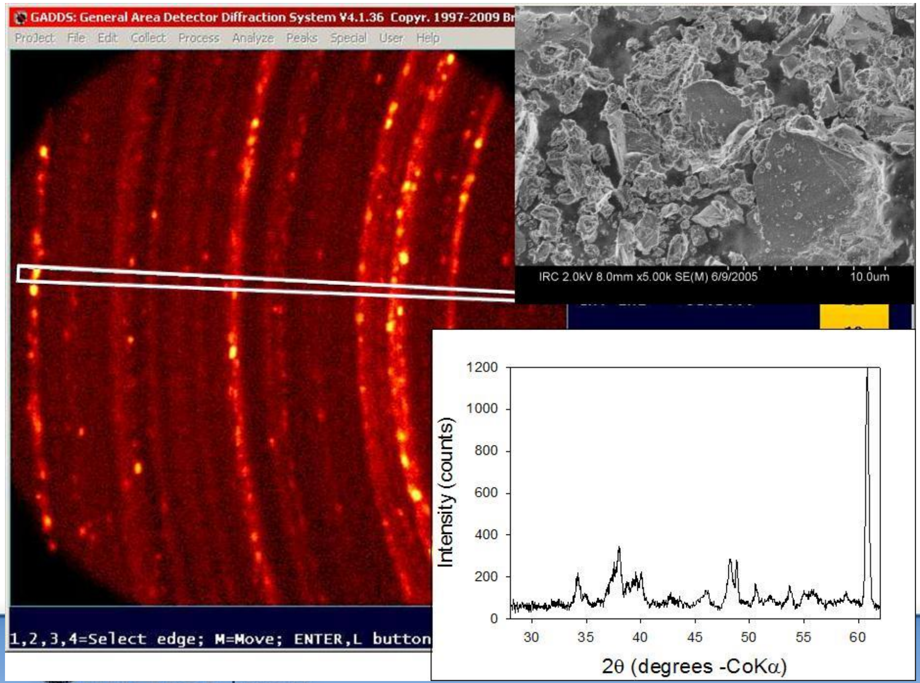




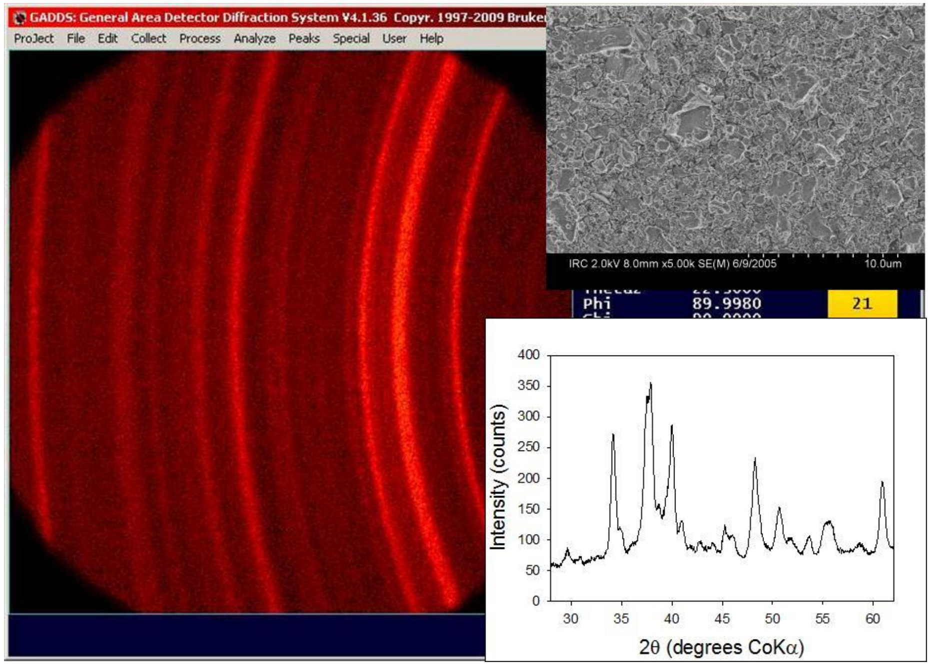
“Seeing” particle statistics



1,2,3,4=Select edge; M=Move; ENTER,L button



1,2,3,4=Select edge; M=Move; ENTER,L button



Courtesy of Pamela Whitfield, Oak Ridge (TN)

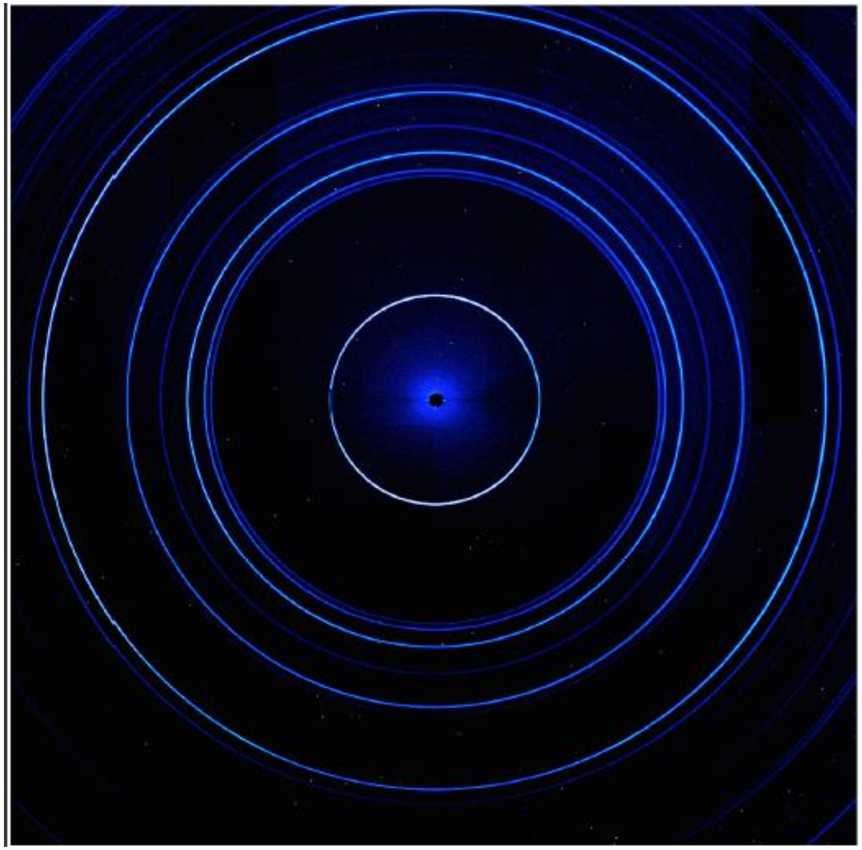
First Dataset at NSLS-II XPD beamline

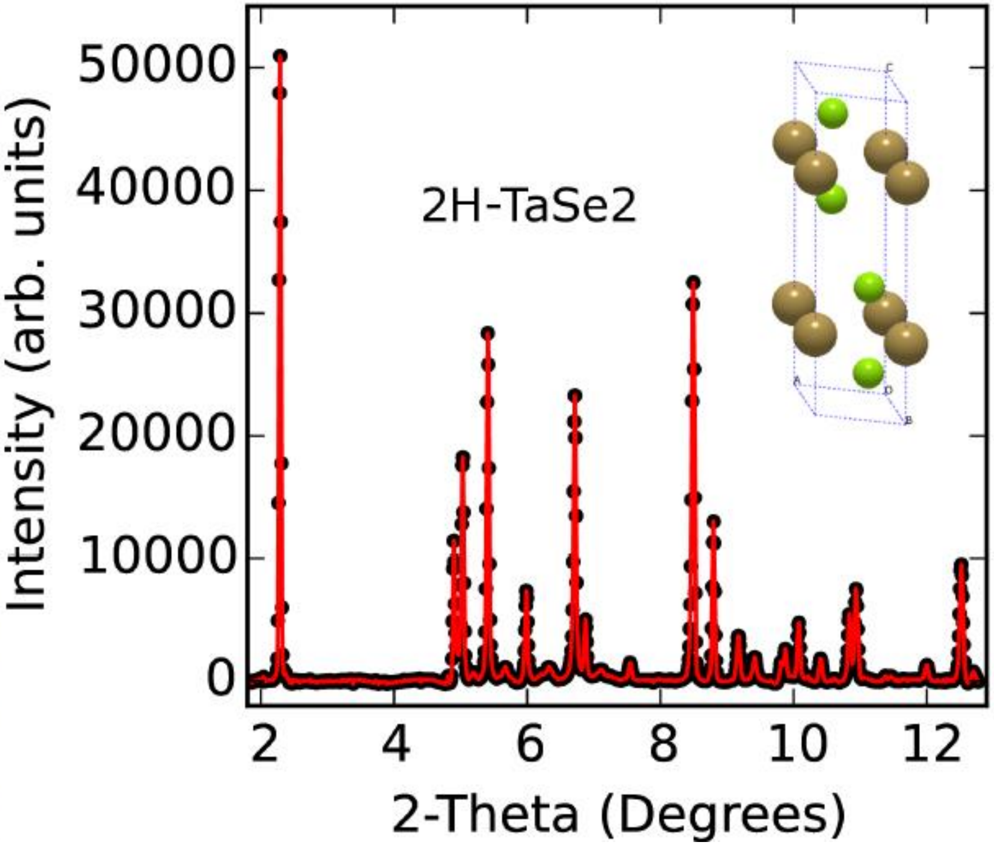
Nov. 2014

"Superconducting Order from Disorder in 2H-TaSe2-xSx"

npj Quantum Materials (2017)

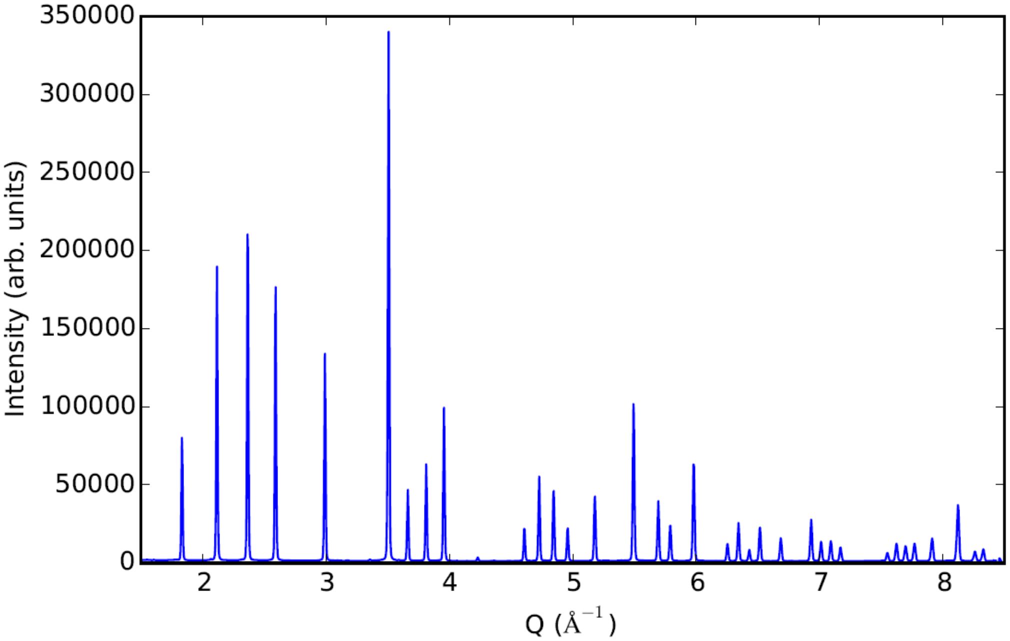
Coll. BNL, APAM Columbia, Rutgers U (NJ), Institute of Solid State Phys. in China.





First Publication at NSLS-II

- 48 keV
- 60 sec acquisition per frame
- Collaboration: S. J. L. Billinge and C. Petrovic, Condensed Matter Physics and Materials Science Department, BNL and APAM Columbia.



APL Materials 3 (2015) 041513. Title: "Enhanced Thermoelectric Power and Electronic Correlations in RuSe2"

Decision Making

	Angle-scanning	Large-area	Comments
Resolution	✓		Positon-resolved. Truly angle-resolved only if an analyzer is used. Crystallography
Acquisition rate		✓	In situ, operando
Statistics		✓	Azimuthal integration
Data quality	✓		Better discrimination of the signal, SNR Energy discrimination, parasitic scattering
Data processing	✓		Spatial distortion, intensity non-uniformity (flat field), parallax, dark image, ghost image, masking
Microstructure		✓	Point detector sees only a tiny portion of the scattering. Ring structure reveals preferred orientation, graininess, texture
Normalization		✓	More immune if beam decays or fluctuates, if sample degrades over time (*e.g.*, radiation damage)

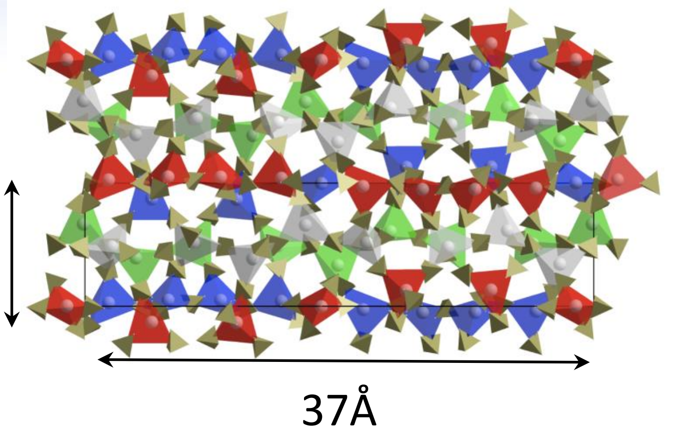
High-Resolution Powder Diffraction

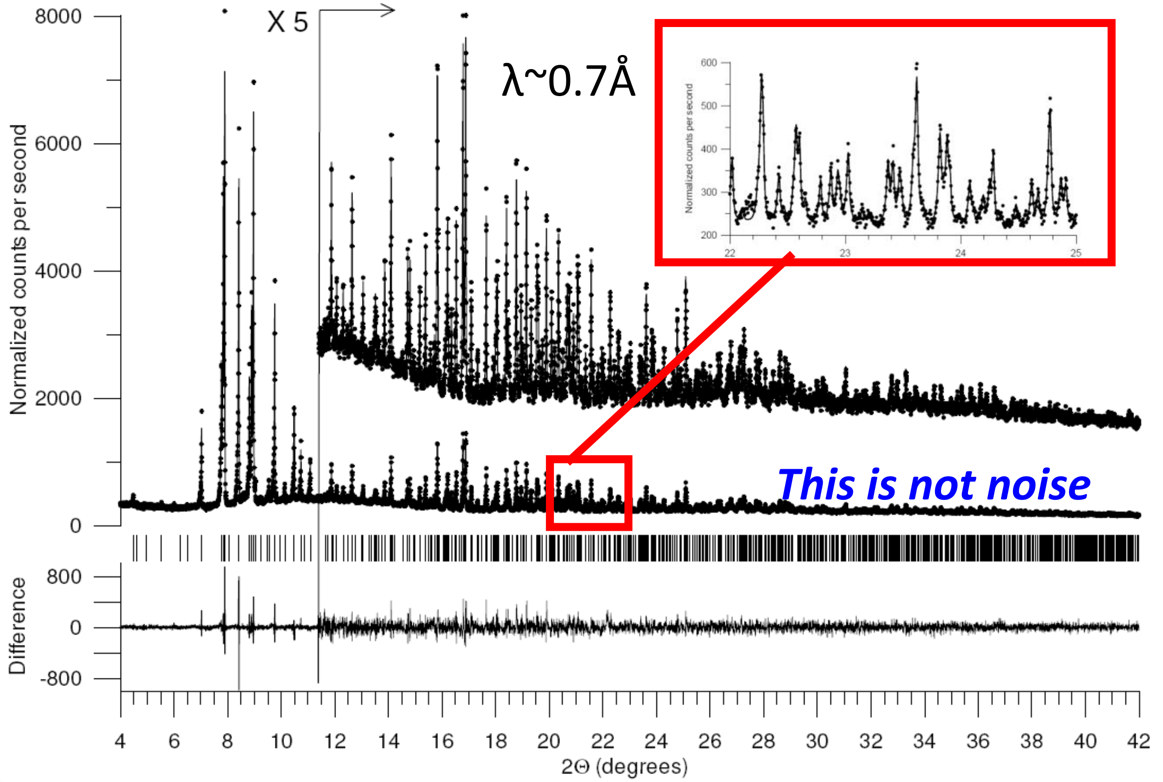
$M + B + 2H_2 \rightarrow MBH_4$ (M = Li, Na, ½Mg, etc)

550 - 700° C; 3 - 15 MPa (≈ 200 atm H2)

Her et al (2007) Acta Crystallog., 63, 561

"Low Temperature" phase of $Mg(BH_4)_2$"





This is not noise

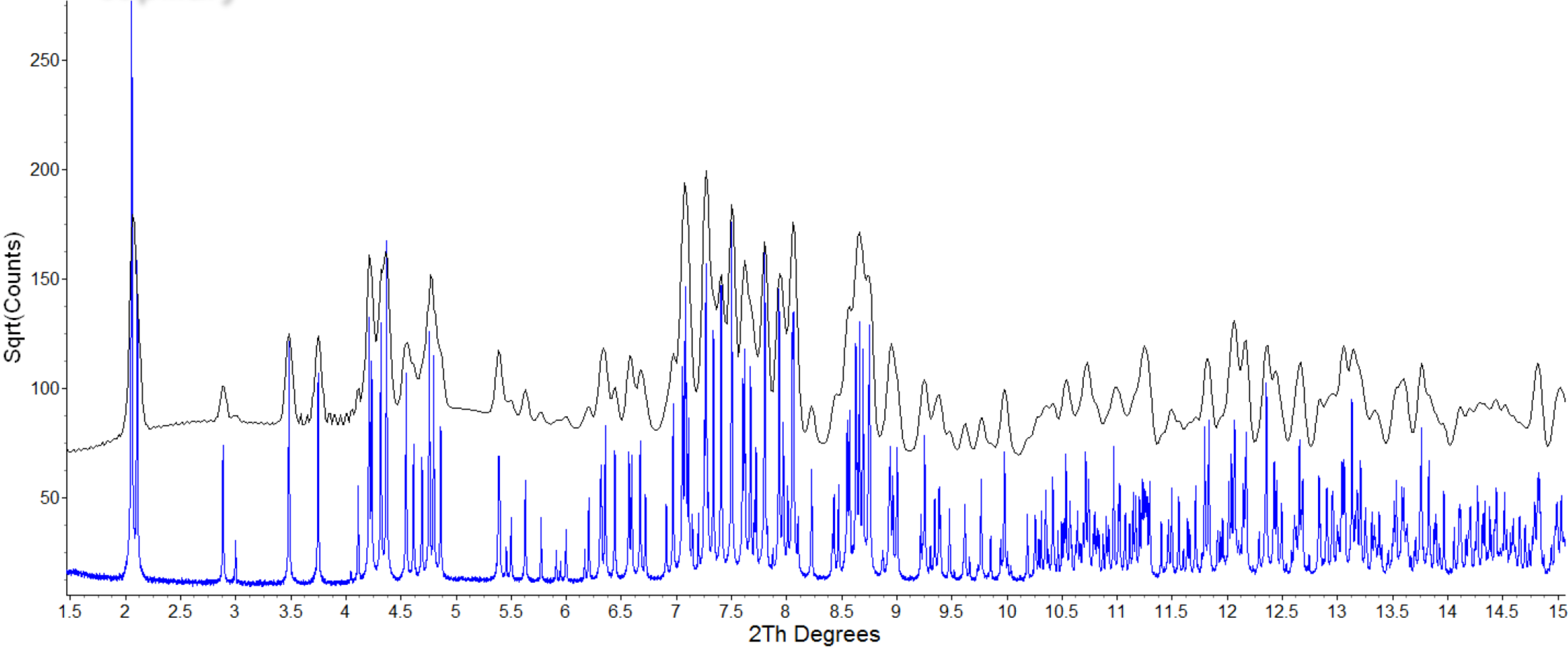
Today's challenge is to achieve this resolution and signal-to-noise performance from sample inside a reactor.

XPD (integrated 2D) vs. 11-BM data (hi-res)

S. Gill (Brookhaven), Greg. Morrison (University of South Carolina)

Gadolinium and Uranium based Salt Inclusion Materials (SIMs) for nuclear waste form applications

In situ ion-exchange of the SIM with NaCl/KCl solution at 90°C in a sealed capillary



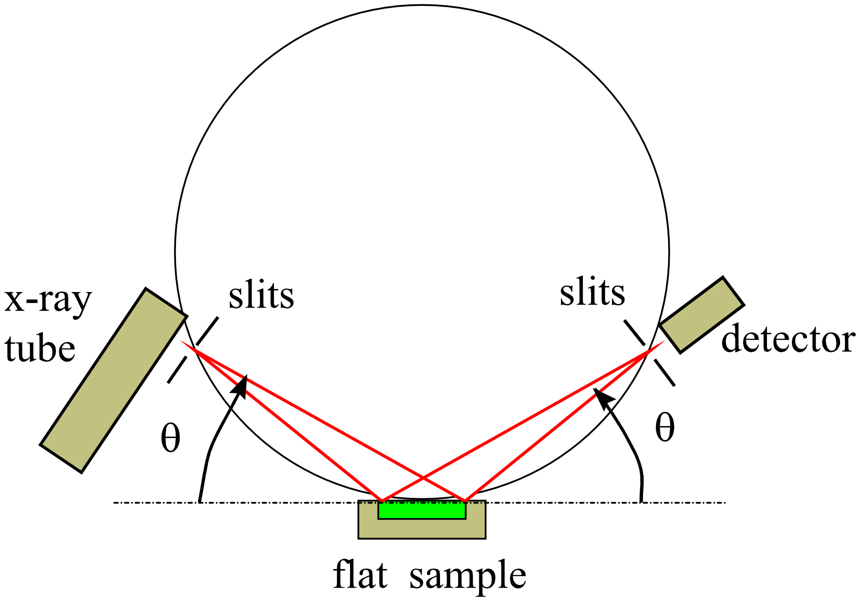
A bit of History

Detectors	Authors	Comments
2D X-ray films	Debye & Scherrer, 1916; Hull, 1917 Guinier, 1939	Debye–Scherrer camera Guinier camera: X-ray optics that focus the scattered beam onto the cylindrical film plane
0D	Brentano, 1925 Parrish, 1949 Cox , 1988 Fitch, 1996 Hodeau & Dooryhee, 1998	A goniometer sweeps a point detector through a range of 2θ angles A crystal analyzer is used with a parallel beam A bank of analyzers
1D PSD	Gabriel & Dupont, 1972 Gobel, 1982 Patterson, 2005	record intensity values as a function of the angular or linear distance along a flat or curved detection strip MYTHEN PSD detector from Dectris
Pixelated 2D	Cernik , 1992; Eikenberry, 2003; Lee, 2007	direct digital readout The intensity sensitivity is more linear than that of film Much larger dynamic range.

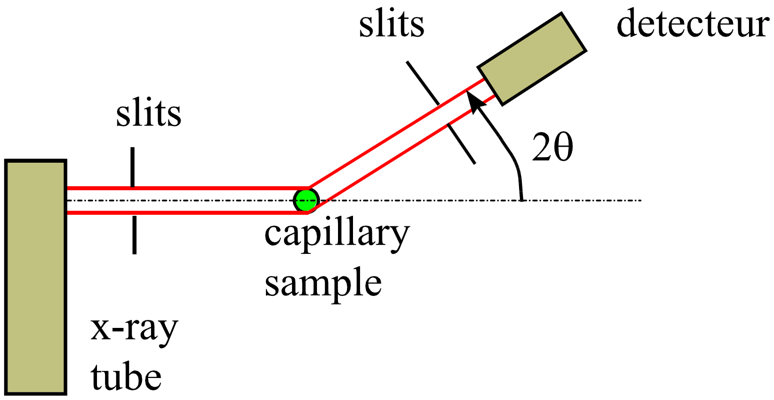
B.H. Toby et al., JAC 46 (2013)

Reflection vs. Transmission

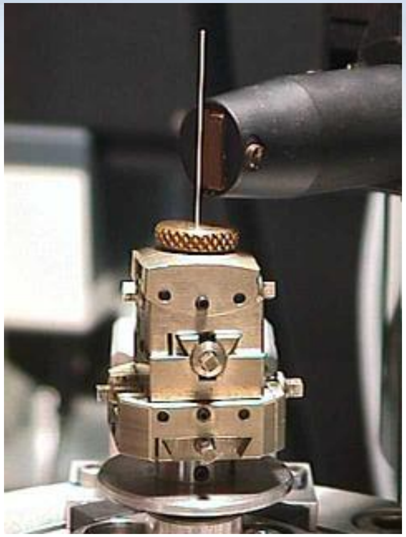
1. Reflection: low energy X-rays, thick or absorbing sample, surface
2. Transmission: high energy X-ray or transparent sample, bulk



Bragg-Brentano parafocusing geometry



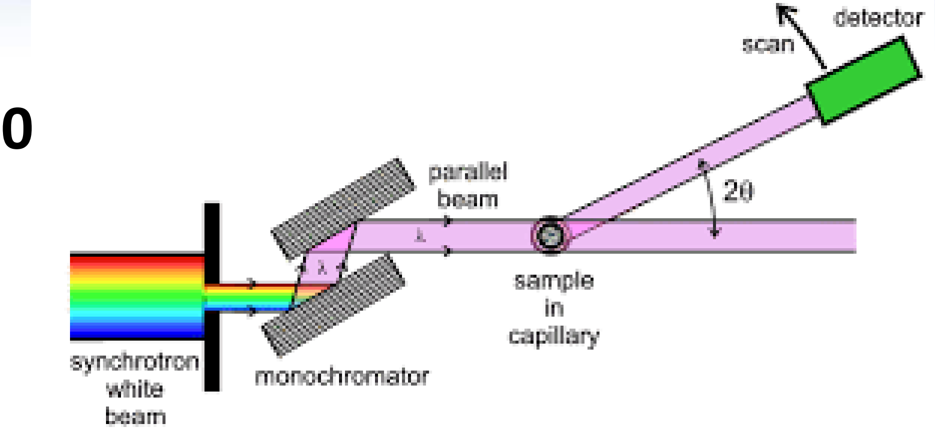
Debye Scherrer geometry



1. Capillary
2. Flat plate

Angle/Energy Dispersive Diffraction

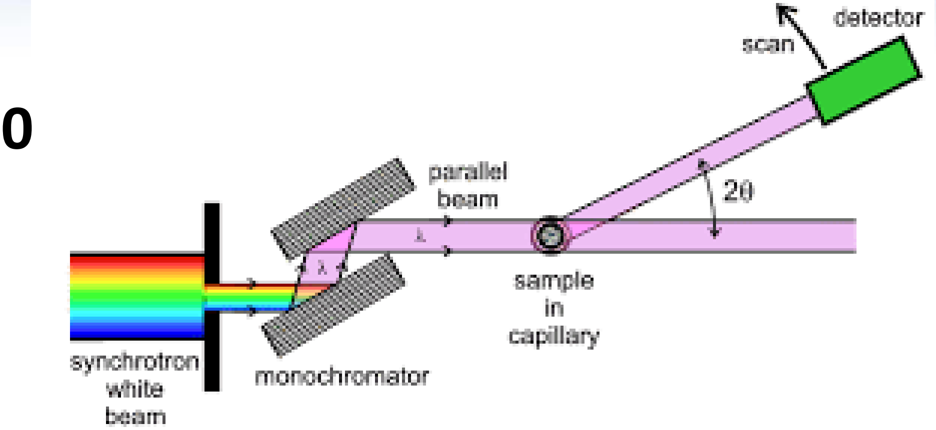
$$2\ d\ \sin\theta = \lambda_0$$



1) Angle Dispersive I(2θ): monochromatic beam and detector is scanned to measure at all possible 2θ angles

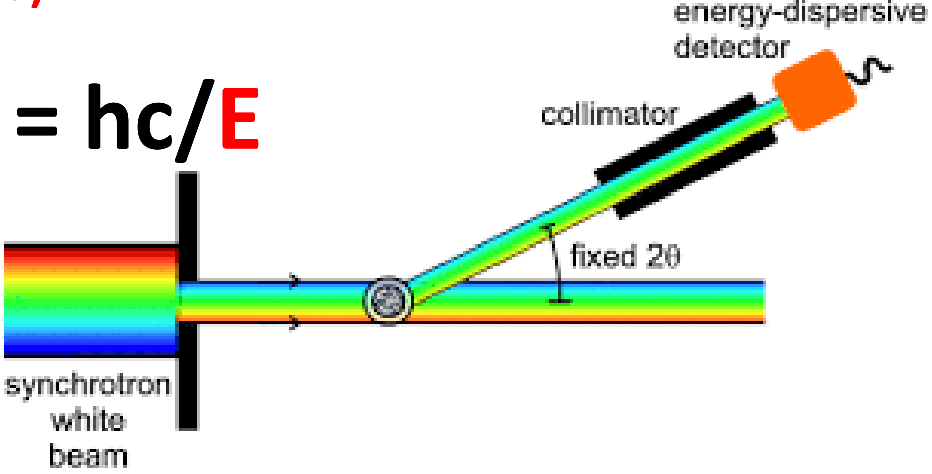
Angle/Energy Dispersive Diffraction

$$2\,d\,\sin\theta = \lambda_0$$



1) Angle Dispersive I(2θ)

$$2\,d\,\sin\theta_0 = \lambda = hc/E$$

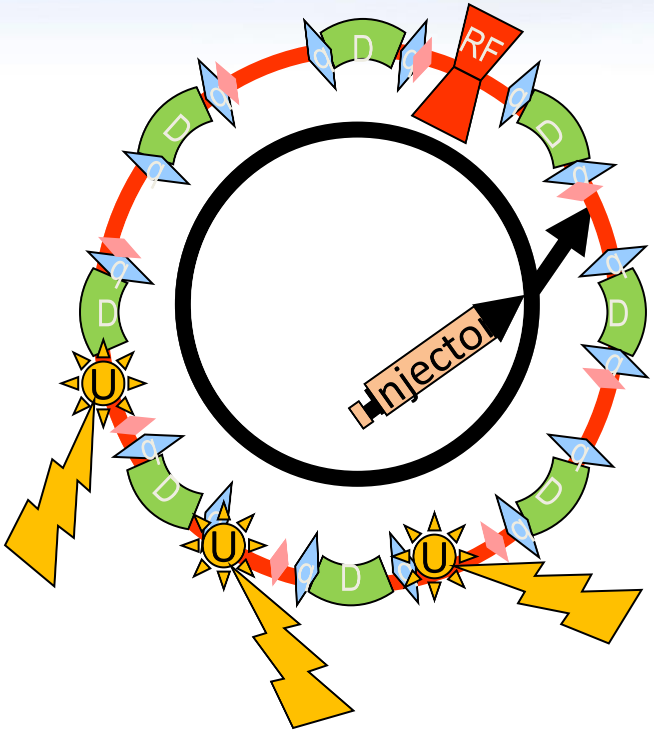


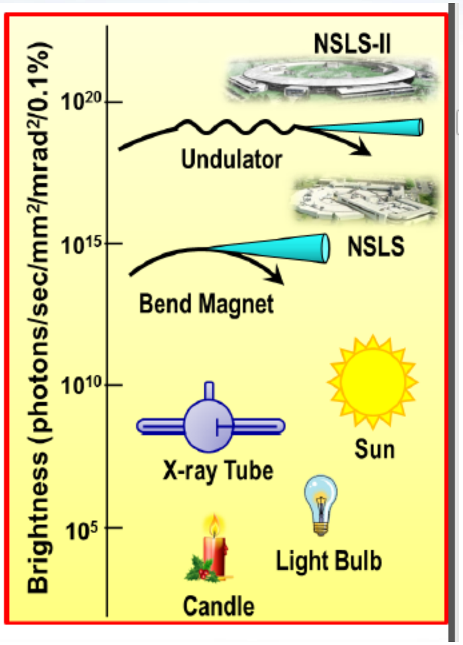
2) Energy Dispersive I(E): polychromatic (white) beam (synchrotron) and detector (SSD with energy discrimination) is at a fixed angle.

From Laboratory Powder Diffraction…

- Flux (weak scatterer, diluted, time-dependent)
- Energy tunability (less absorption, anomalous, white beam)
- Optics (resolution, small beam size)

…to Synchrotron Powder Diffraction





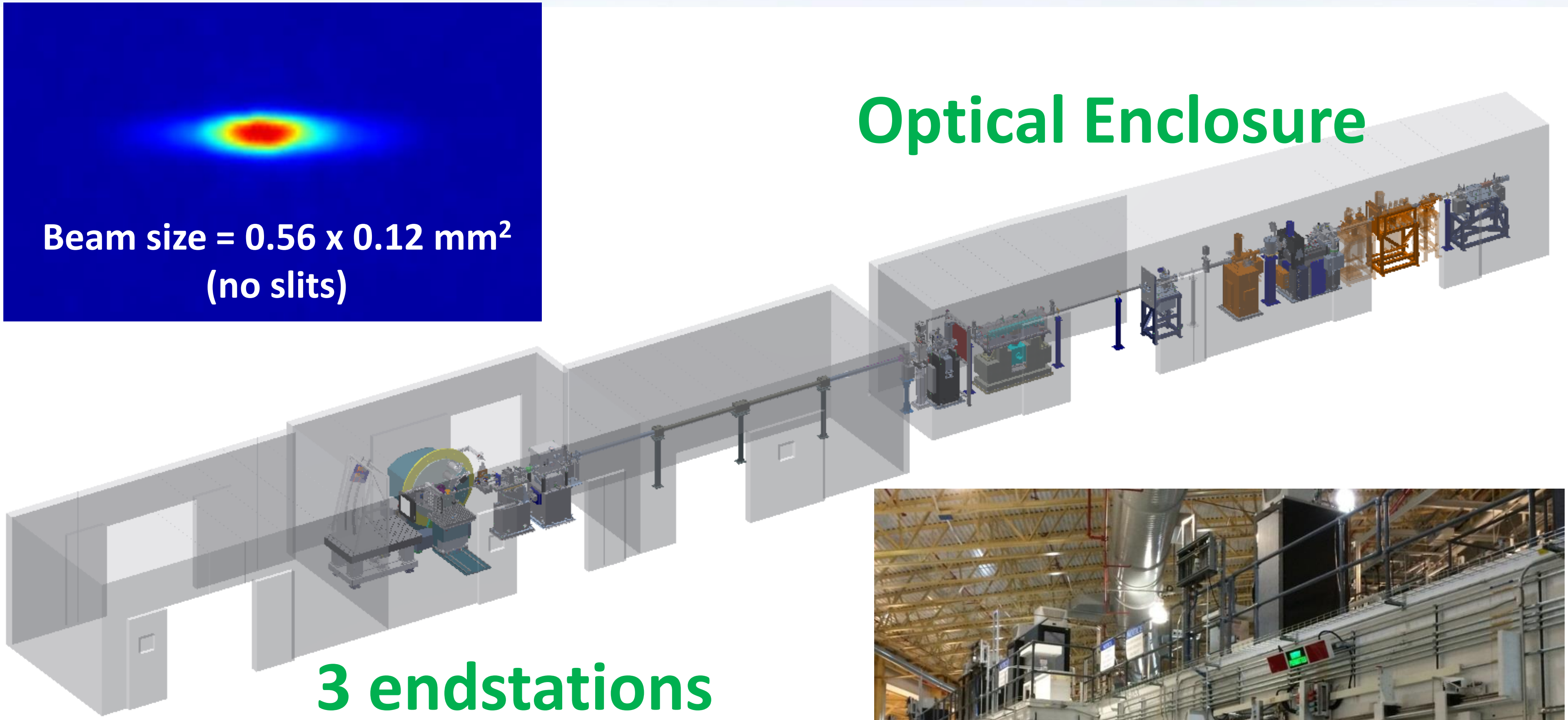
- X-ray source: $ cost and photon flux × 1,000,000
- Capacity of NSLS-2: 60 beamlines

Source and Front End

Damping Wiggler

Front End (shutter , masks, slits)

Powder Diffraction Beamline (XPD)



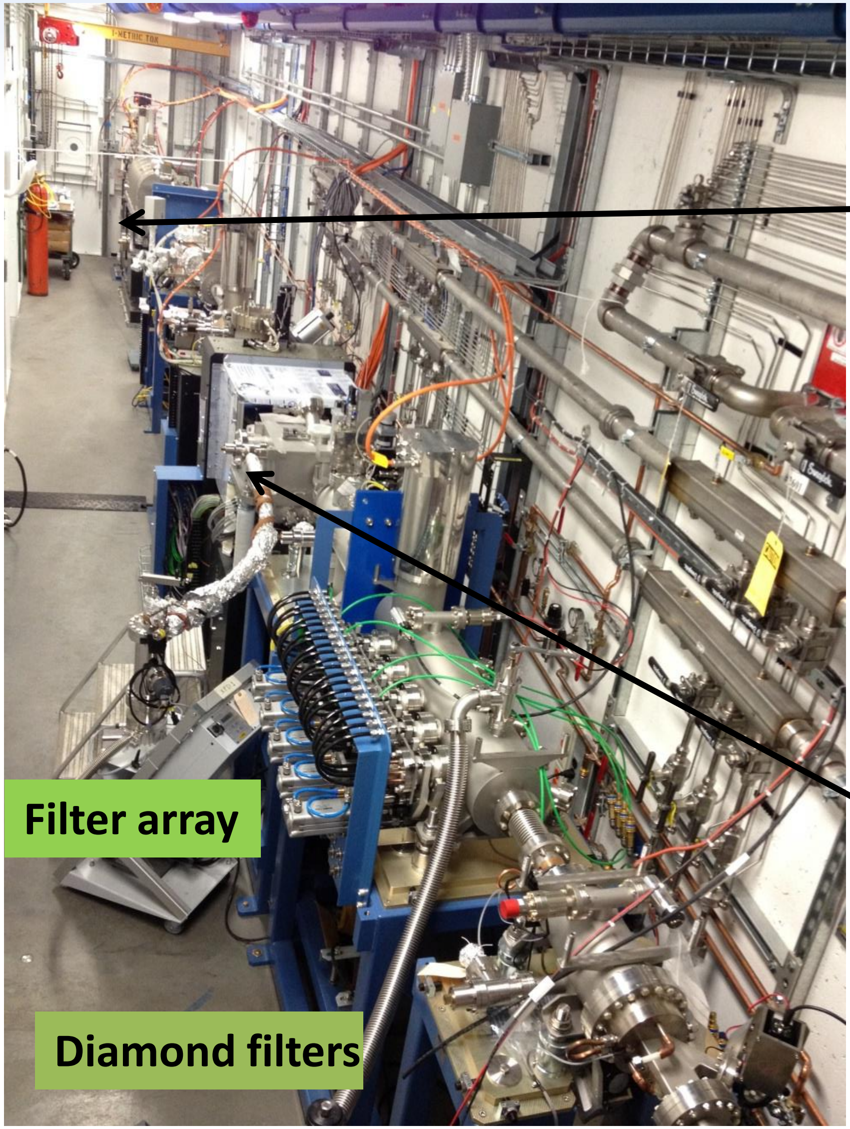
Beam size = 0.56 x 0.12 mm^2
(no slits)

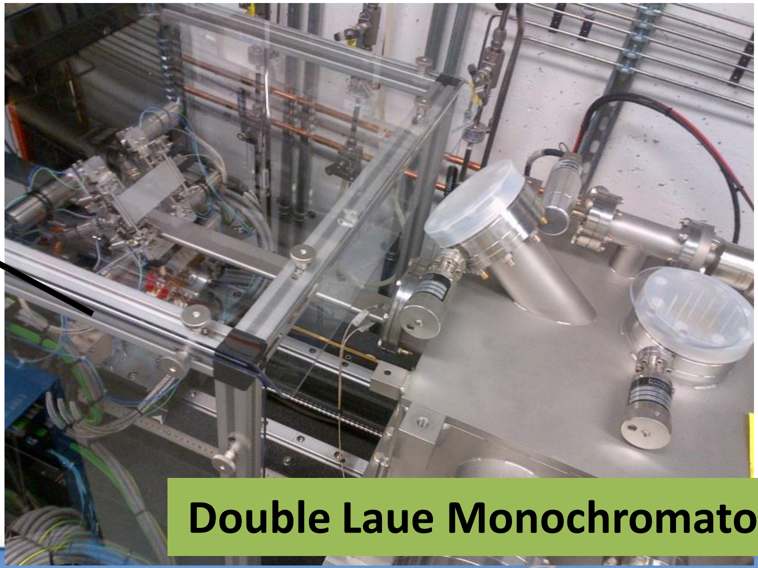
Optical Enclosure

3 endstations

5 years from design to start of operations

XPD OPTICAL ENCLOSURE





VERTICALLY FOCUSING MIRROR

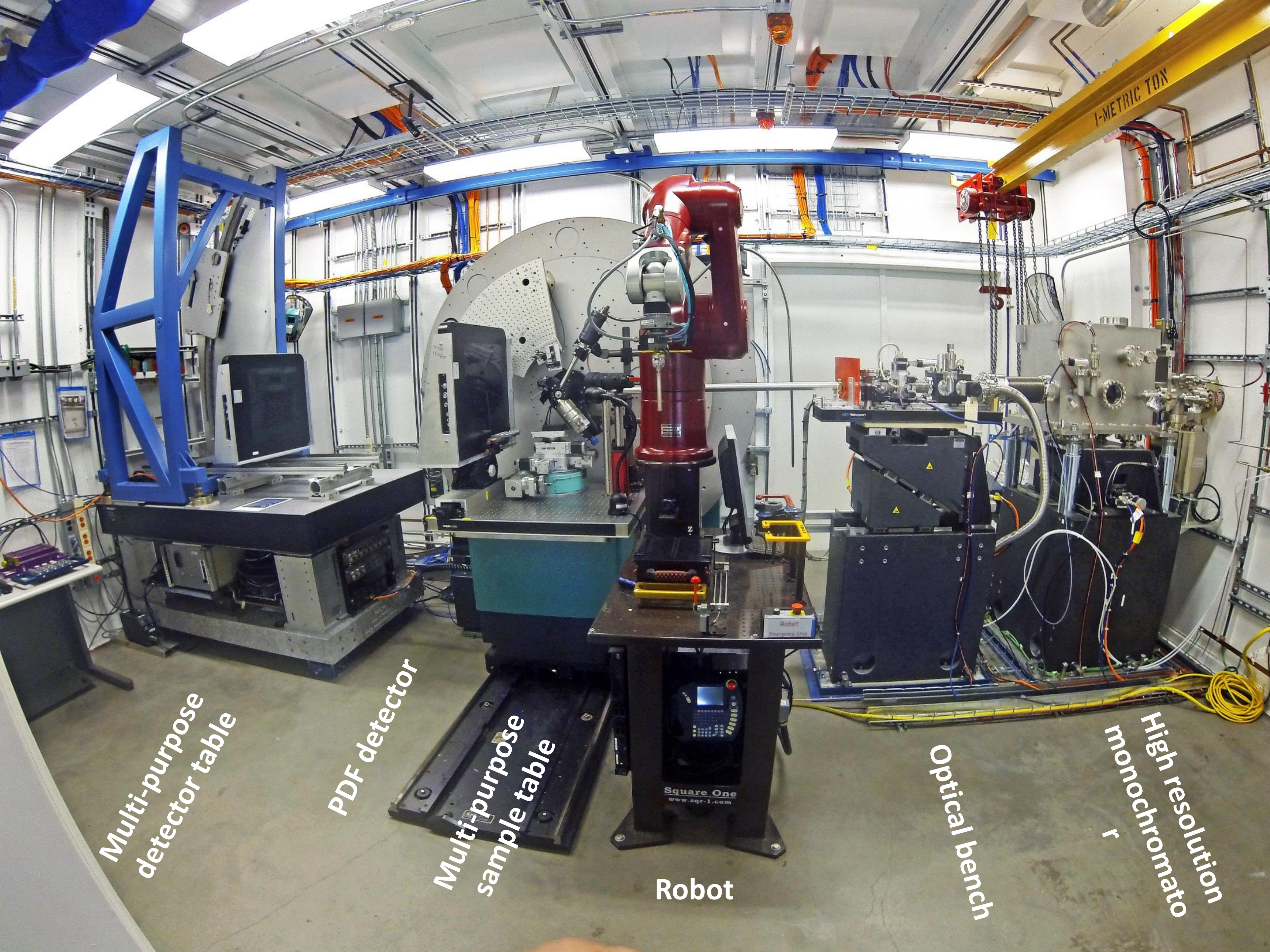
1.4 m long

Roughness
0.3nm rms

Bending 10 km
(anti-sag)

Slope Error:
0.36 microrad
(0.02 mdeg)

At 50 miles ?


1-METRIC TON
Multi-purpose detector table
PDF detector
Multi-purpose sample table
Robot
Robot Emergency Stop
Square One
www.sqr-1.com
Optical bench
High resolution monochromato r

ROBOTIC SAMPLE MANIPULATOR

1. Acquisition of a diffraction image takes seconds.

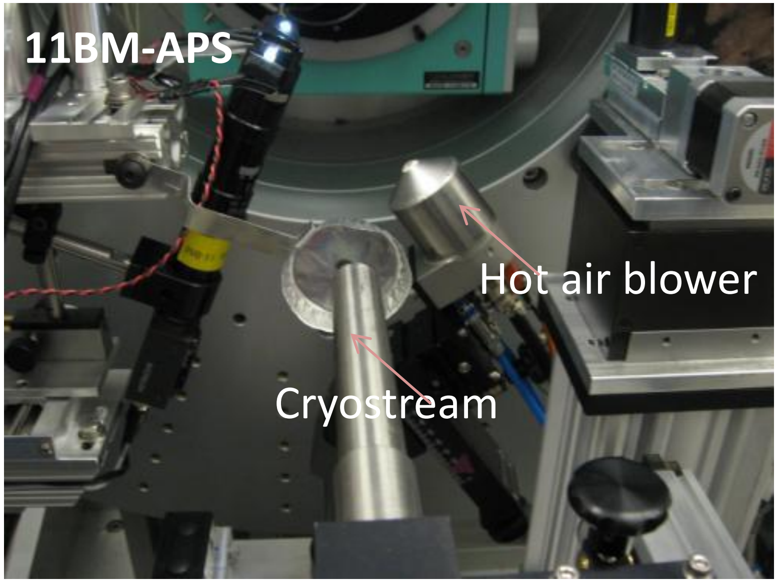
Breaking the interlock system, entering the hutch, changing the sample by hand, exiting the hutch, reactivating the interlock take $\geq$ 5 min.

2. Probability of operator's mistake during sample manipulation

3. Handling of radioactive samples (samples are kept in a shielded box at all times, personnel is never exposed during measurement)

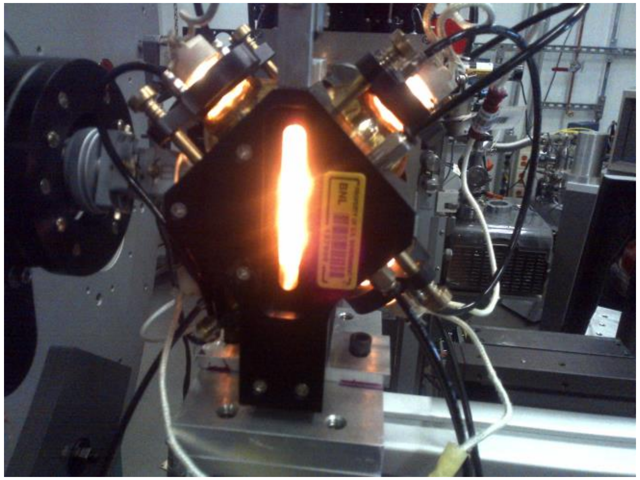
SAMPLE ENVIRONMENTS

LN2 cryostream, LHe cryostat, hot air blower, flat plate heater, quadrupole lamp furnace,…



Capabilities:

- Temperature Range: 80K, Ambient to 2,000˚C
- Sample holder Type: capillary (compatible with robotic sample changer), or flat plate

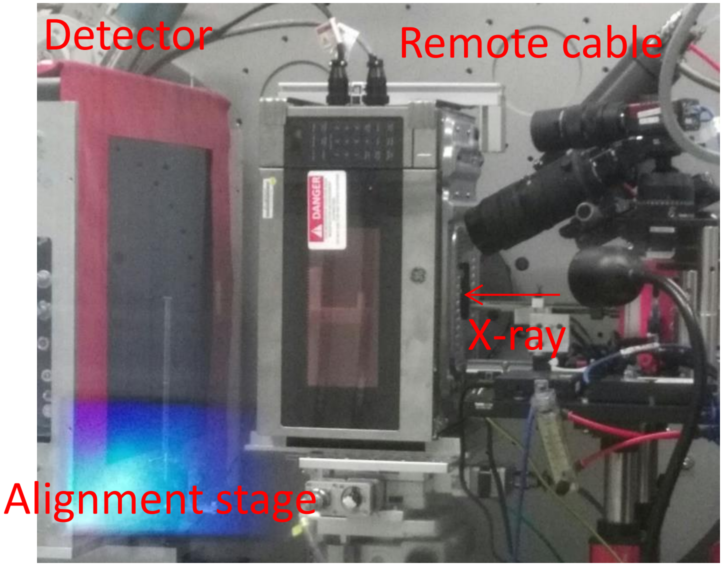


MICROWAVE REACTOR FOR IN SITU DIFFRACTION

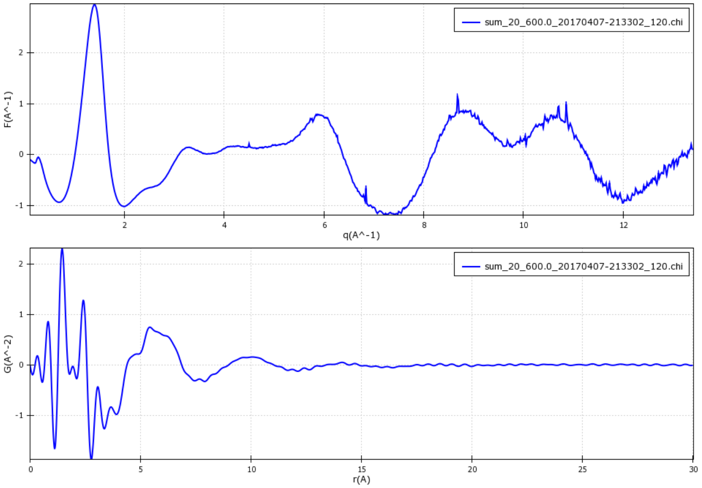
Science motivation: MW assisted materials synthesis is a fast growing field. The MW reactor enabled combined in situ PDF and XRD to study the crystallization process from the stage of nucleation.

Applications: Hydro-Solvolthermal synthesis, solid state synthesis, thin film growing in solution

J. Bai



In Situ MW in operation
with remote control



First in situ PDF measurement during MW assisted Titania (${TiO_2}$) thin film growing @ 28-ID-2 (April 2017)

NEUTRONS vs. SYNCHROTRON

X-rays are scattered by

Neutrons are scattered by

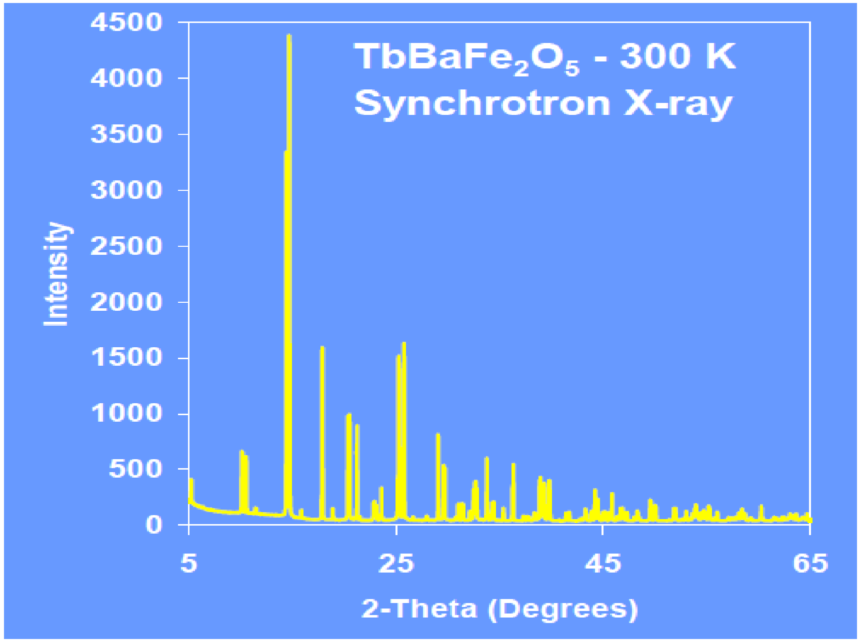
NEUTRONS vs. SYNCHROTRON

X-rays are scattered by the <u>electrons</u> in the atoms

Neutrons are scattered by the <u>nuclei</u>

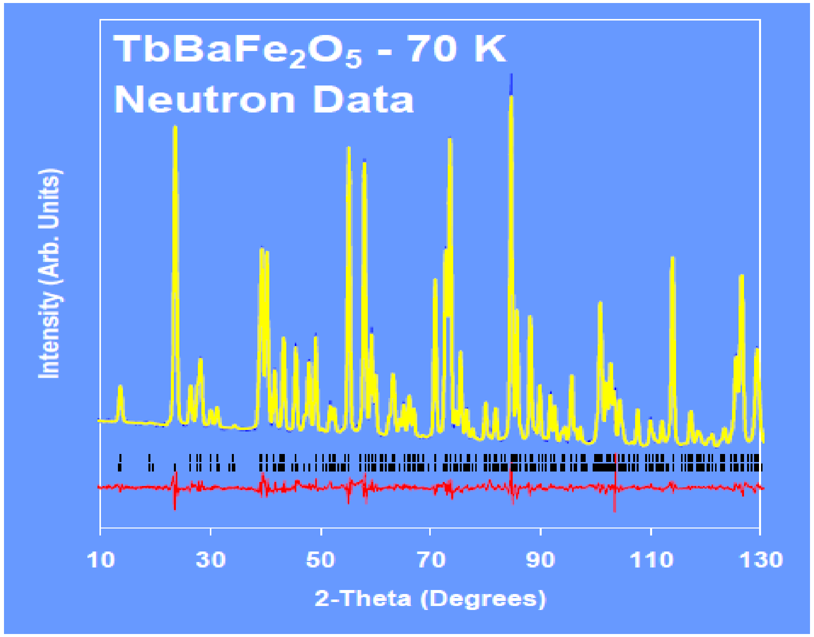
NEUTRONS vs. SYNCHROTRON

Synchrotron X-rays



The peak intensities drop off at high angles in an X-ray diffraction pattern because the form factor decreases

Neutrons



Neutrons are scattered from the nucleus and the form factor is not angle dependent. Intensities do not drop off at high angle.

NEUTRONS vs. SYNCHROTRON

Synchrotron X-rays

- Extremely high resolution
- Subtle distortions
- Indexing and Structure determination
- Anomalous scattering
- Texture effects

Neutrons

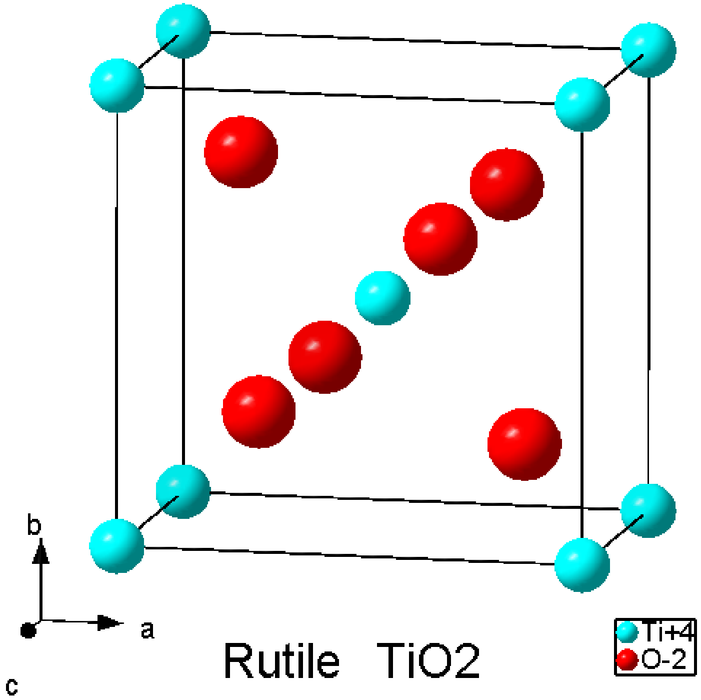
- scattering length contrast
- More sensitive to light elements (H, N, O, F, C, etc.) and isotope distributions
- Low absorption: large samples, easy sample environments
- Magnetic structures
- Moderate resolution

Outline

1. Applications for Powder Diffraction
2. The basics of Powder Diffraction
3. Experimental Methods for collecting PD data
4. Crystal structure Determination
5. Peak Profile Analysis for Microstructural Studies
6. Advanced PD techniques

Crystal Structure: lattice

the unit cell

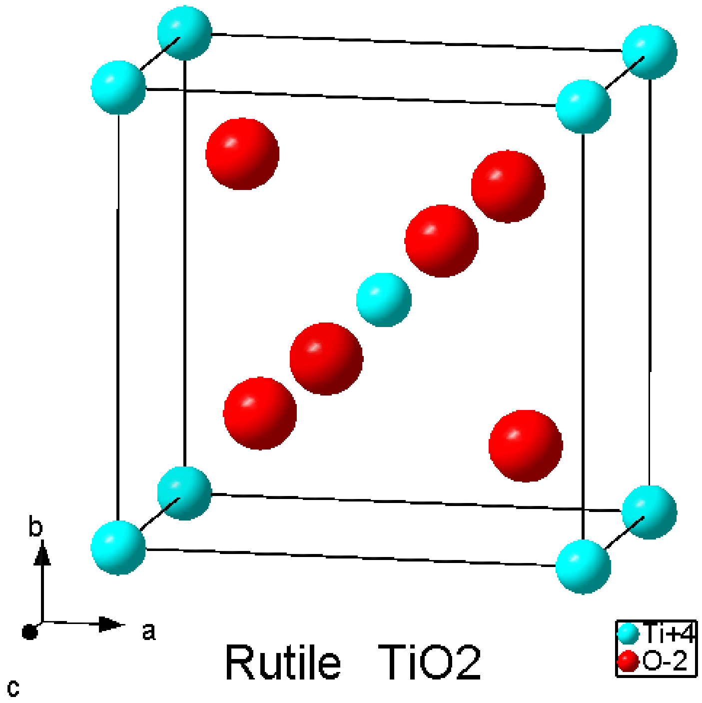


Crystal data

Formula	O2 Ti
Crystal system	**tetragonal**
Space group	*P* 42/m n m (no. 136)
Unit cell dimensions	***a* = 4.5937 Å** **_c_ = 2.9587 Å**
Cell volume	62.40 Å^3
Z	2

Crystal Structure: + symmetry

the unit cell
the space group

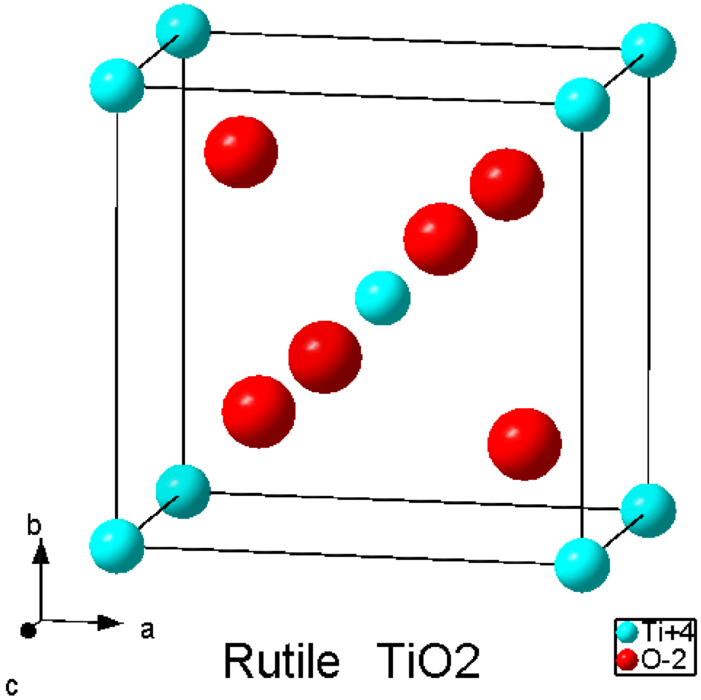


Crystal data

Formula	O2 Ti
Crystal system	tetragonal
Space group	***P*** **42/m n m (no. 136)**
Unit cell dimensions	*a* = 4.5937 Å *c* = 2.9587 Å
Cell volume	62.40 $Å^3$
Z	2

Crystal Structure: + atomic motif

the unit cell
the space group
the asymmetric unit



Crystal data

Formula	O2 Ti
Crystal system	tetragonal
Space group	*P* 42/m n m (no. 136)
Unit cell dimensions	*a* = 4.5937 Å *c* = 2.9587 Å
Cell volume	62.40 Å^3
Z	2

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Ti	+4	2*a*	0	0	0
O	-2	4*f*	0.30469	0.30469	0

Bond lengths, bond angles (Å, °)

Ti—O	1.949(0)	Ti—Ti	2.959
O—O	2.959	Ti—Ti	3.569

Crystal Scattering Amplitude

A crystal = convolution of an atomic motif $M(\vec{r})$ and a lattice $R(\vec{r})$

$$\boxed{C(\vec{r}) = R(\vec{r}) * M(\vec{r})}$$

The scattered amplitude corresponds to the Fourier transform of the scattering object

$$\boxed{C(\vec{h}) = TF\{C(\vec{r})\} = TF\{R(\vec{r}) * M(\vec{r})\} = R(\vec{h}) x F(\vec{h})}$$

The Fourier space is called **reciprocal space**

$R(\vec{h})$ = FT of the (direct) lattice: **Reciprocal Lattice**

$F(\vec{h})$ = FT of the atomic motif: **Structure factor**

Knowing the reciprocal lattice and the structure factors is equivalent to knowing the structure in real space

Real and reciprocal space

CRYSTAL SPACE

DIFFRACTION SPACE

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

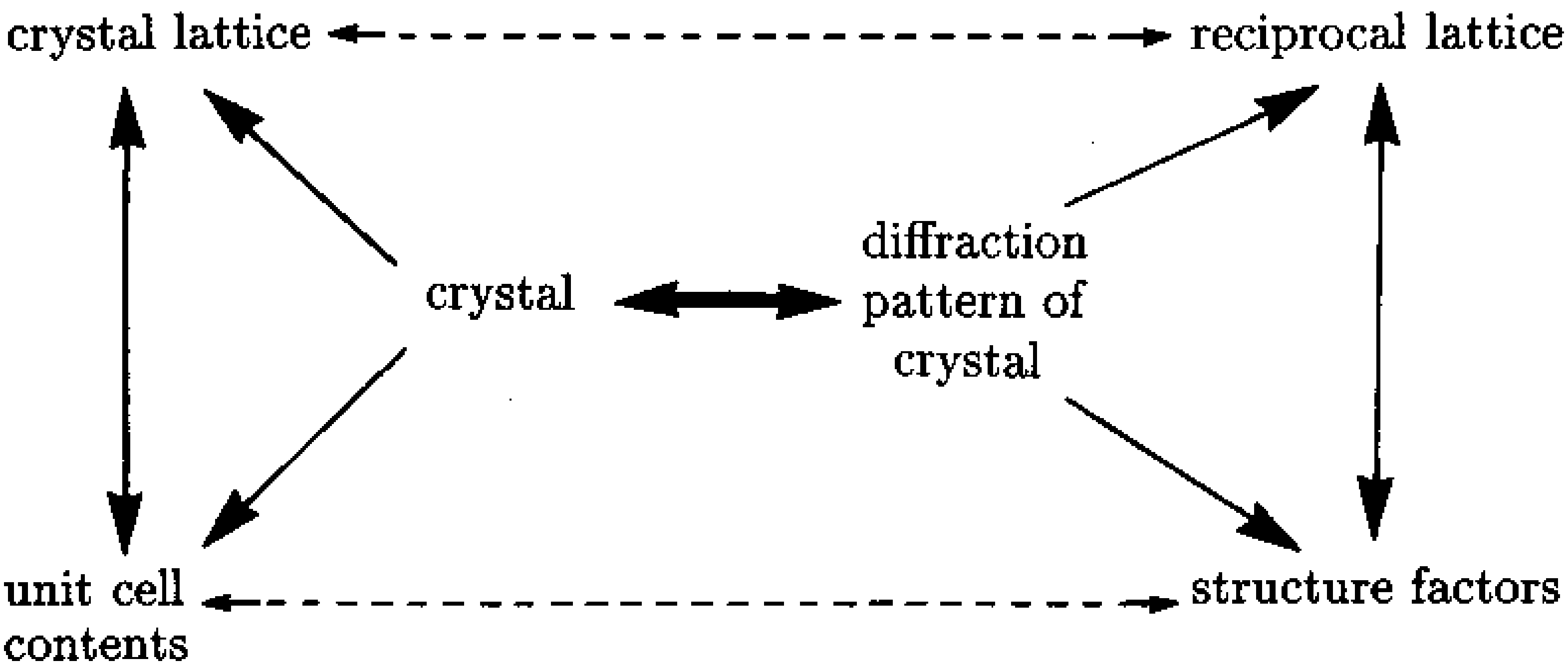


FIGURE 3.11. Relationships between a crystal (in crystal space) and its reciprocal lattice (in diffraction space).

Reciprocal lattice constants

- The mathematical definition of the reciprocal lattice constants is
  - $$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$
  - $$\mathbf{b}^* = \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$
  - $$\mathbf{c}^* = \frac{\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

where $\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) = V$

V = volume of the unit cell

It follows that $|\mathbf{d}| = \dfrac{1}{|\mathbf{d}^*|}$

- Alternative formulation:
  - $$\mathbf{g}_i\cdot\mathbf{h}_j = \delta_{ij}$$

Courtesy of Cora Lind-Kovacs

Reciprocal lattice constants

- The mathematical definition of the reciprocal lattice constants is
  - $$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$
  - $$\mathbf{b}^* = \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$
  - $$\mathbf{c}^* = \frac{\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

where $\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) = V$

V = volume of the unit cell

It follows that $|\mathbf{d}| = \dfrac{1}{|\mathbf{d}^*|}$

- Alternative formulation:
  - $$\mathbf{g}_i \cdot \mathbf{h}_j = \delta_{ij}$$

What is the symmetry of the reciprocal lattice ?

Courtesy of Cora Lind-Kovacs

Crystal Structure Factor

F_{hkl} : structure factor for reflection (hkl) = TF{ $M(\vec{r})$ }, atomic motif

Fhkl : Fourier transform of the scattering (electron) density of the crystal

$$\boxed{F_{hkl} = \sum_{j \subset cell} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j))}$$

f_j : scattering factor for atom j with coordinates (x_j, y_j, z_j). FT of the scattering (electron) density of each individual atom *j* in ONE unit cell.

For x-rays, f_j is the atomic form factor,

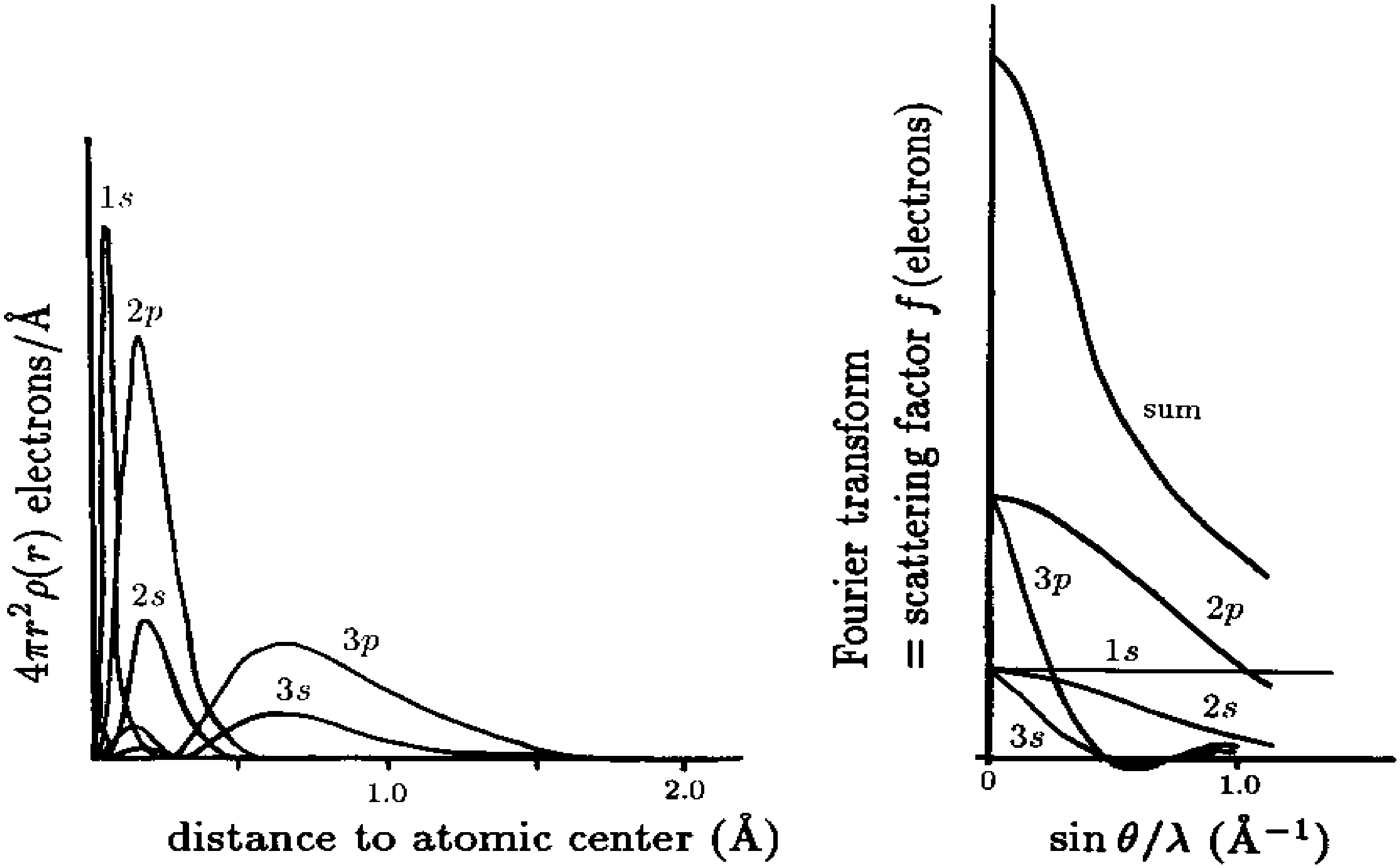
For neutrons, $f_j = b_j$ is the Fermi length.

We can evaluate (compute) this complex number f_j as a trigonometric function:

$$\mathbf{f} = A_o e^{i\varphi} = A_o\{\cos\varphi + i \sin\varphi\}$$

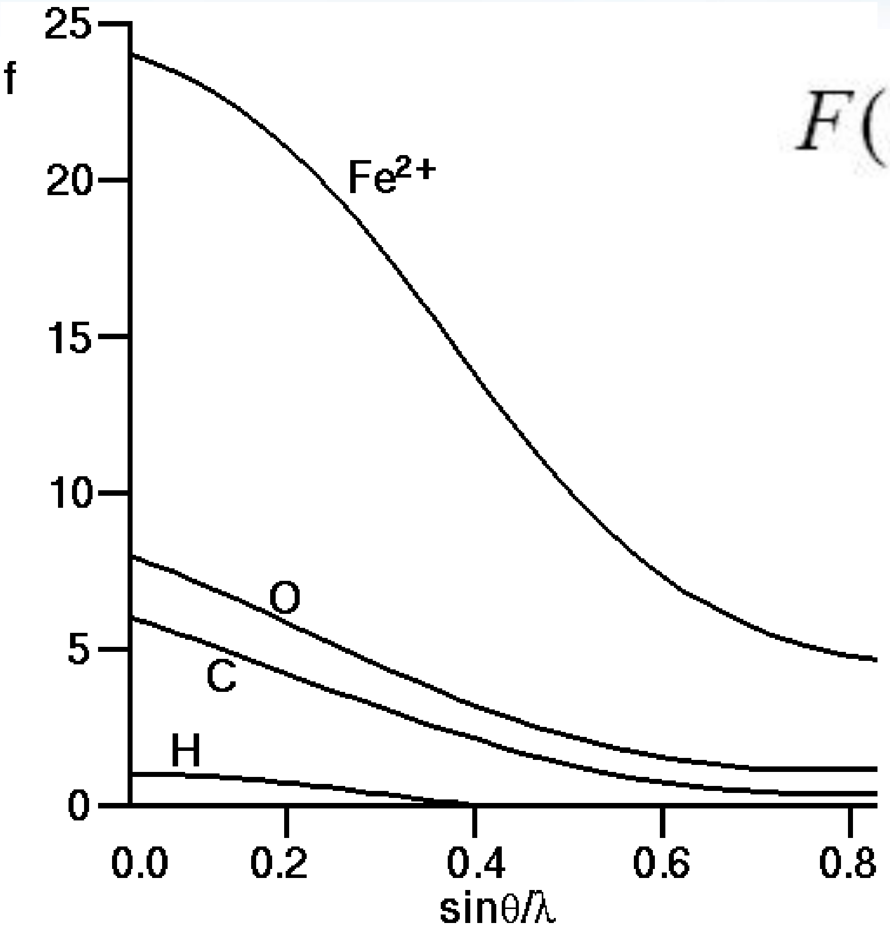
Notice that λ and the unit cell parameters are **NOT** part of this.
F depends only on the hkl of the planes, nature of the atoms *j* and their fractional positions.

The FT relationship between *f* and ρ_{atomic}



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

Atomic Form Factors



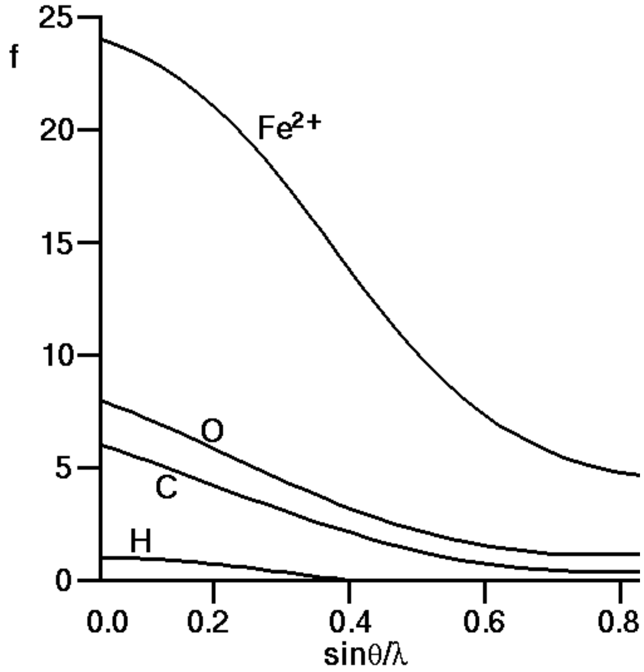
Atomic form factor = scattering amplitude

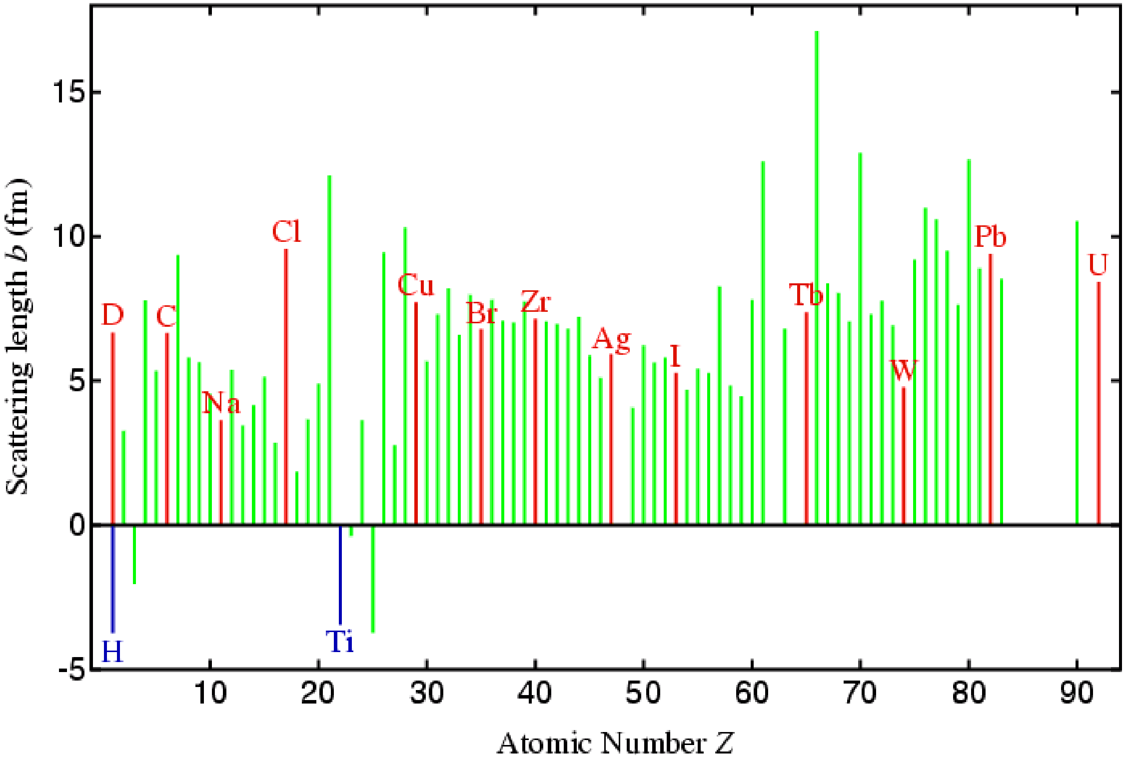
$$F(hkl) = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

Structure factor is the Fourier transform of the electron density. It takes into account the individual scattering ***f*** *of all* ***j*** *atoms contained in the crystal unit cell.*

Notice that data are plotted as a function of sinθ/λ. This is the scattering vector in reciprocal units $Å^{-1}$.

X-ray vs. neutron Scattering Length





The neutron scattering length does not vary with sinθ/λ. It varies with Z and isotope number.

Crystal Structure Factor

F_{hkl} : structure factor for reflection (hkl) = TF{ $M(\vec{r})$ }, atomic motif

Fhkl : Fourier transform of the scattering density of the crystal

$$\boxed{F_{hkl} = \sum_{j\subset cell} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j))}$$

f_j : scattering factor for atom j with coordinates (x_j, y_j, z_j). FT of its scattering density of each individual atom *j*.

For x-rays, f_j is the atomic form factor,

For neutrons, $f_j = b_j$ is the Fermi length.

The amplitude of scattering depends on the electron density (atoms).
The phase depends on the fractional distance of the atoms to the lattice plane.

T_j = **Debye-Waller** factor related to atomic displacements (thermal, positional,…).

The atomic "Temperature" factor

Can we describe the **vibration** of an individual atom?

If the vibration is harmonic, the probability distribution will be Gaussian with a form exp(-a•x^2). The diffraction pattern of a Gaussian is another Gaussian, where the argument is related to 1/d-spacing

We usually use this in the Structure Factor expression:

$$\mathbf{T} = \exp(-B_j\, \mathbf{Q}^2) = \exp(-B_j \sin^2\theta / \lambda^2)$$

where $B = 8\pi^2\langle u^2\rangle$ where **u** is the r.m.s. displacement of a scattering center, and <...> denotes time averaging.

We call B the **"Temperature factor"** because it rises with the temperature of the crystal. You see that it's more properly a measure of mean square displacement, whatever the temperature. → Anisotropic Displacement Factor

Courtesy of Robert Sweet "X-ray Diffraction & Crystallography"

Crystal Diffracted Intensity

The diffracted intensity is the quantity accessible in a diffraction experiment (proportional to the number of diffracted photons/particles reaching the detector)

In the kinematic approximation (neglecting double diffraction), one has :

$$\boxed{I_{hkl} = S.C_{hkl}.\left|F_{hkl}\right|^2}$$

S : scale factor (amount of sample, count time, incident flux,…)

C_{hkl} : experimental corrections

instrument *(Lorentz, polarization, diffraction geometry…)*

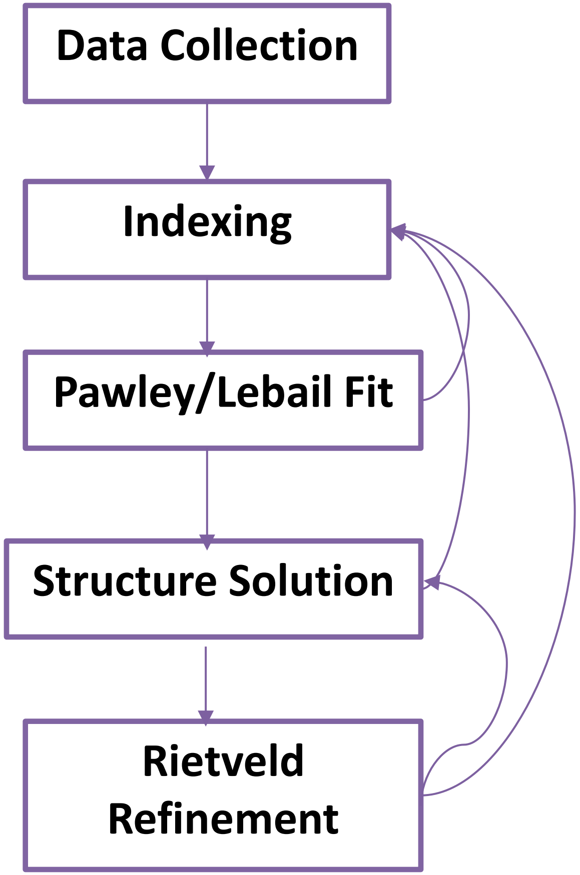
sample *(multiplicity, absorption, preferred orientation, extinction…)*

$$\boxed{F_{hkl} = \sum_{j \subset cell} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j))}$$

F_{hkl} : complex number => **phase of F_{hkl} not measured**. Information is incomplete

To solve the structure, one must retrieve the phases of F_{hkl} , one way or another…

Flowchart illustrating crystal structure determination from powder diffraction.



Data Collection

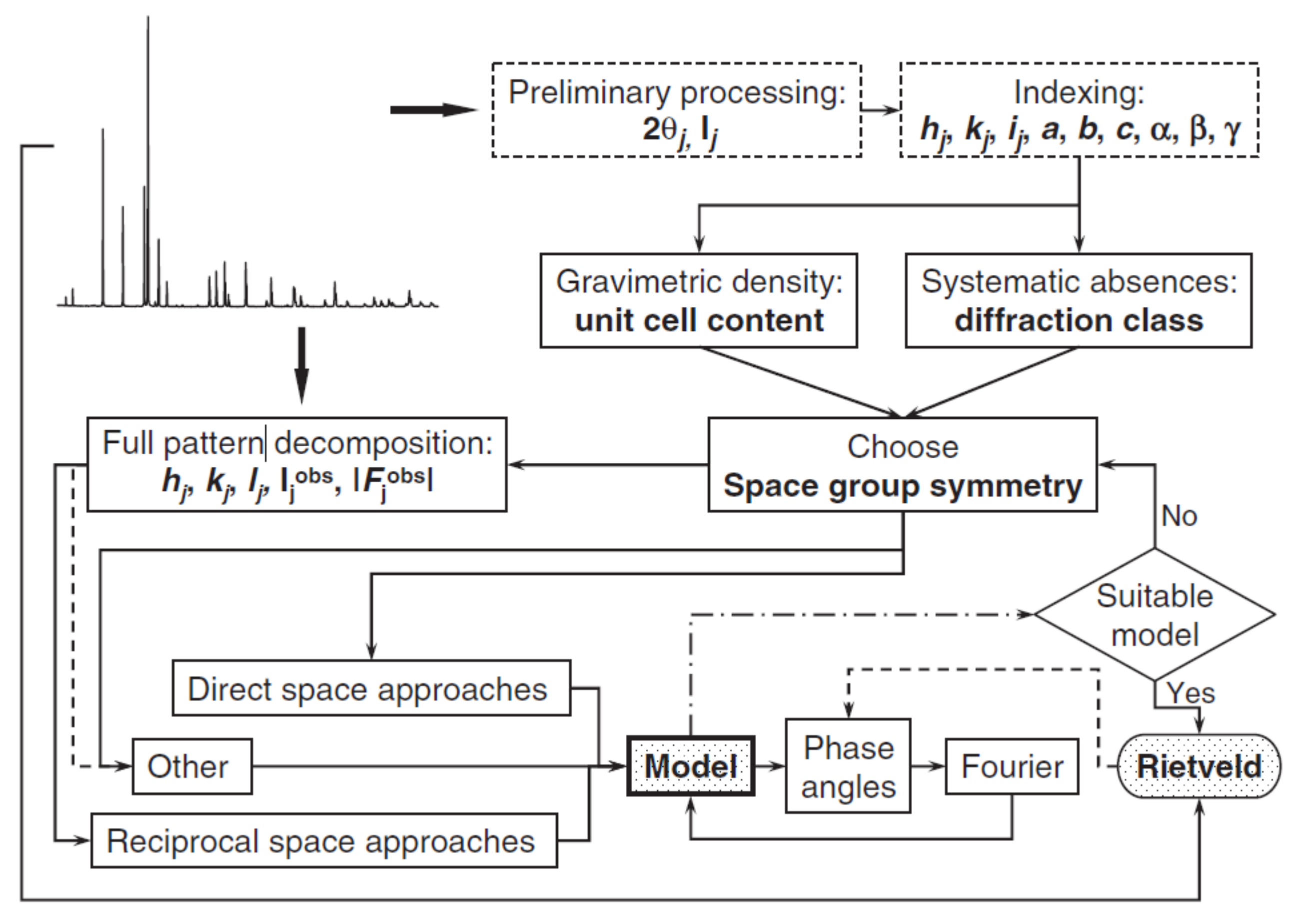
Indexing

Pawley/Lebail Fit

Structure Solution

Rietveld Refinement

Flowchart illustrating crystal structure determination from powder diffraction.



Preliminary processing:
$2\theta_j, I_j$

Indexing:
$h_j, k_j, l_j, a, b, c, \alpha, \beta, \gamma$

Gravimetric density:
unit cell content

Systematic absences:
diffraction class

Full pattern decomposition:
$h_j, k_j, l_j, I_j^{obs}, |F_j^{obs}|$

Choose
Space group symmetry

No

Suitable model

Yes

Direct space approaches

Other

Reciprocal space approaches

Model

Phase angles

Fourier

Rietveld

Source: V.K. Pecharsky, P.Y. Zavalij, *Fundamentals of Powder Diffraction and Structural Characterization of Materials,* © Springer Science 2009

Ab Initio Structure Solving

1) Needs a high quality sample already well characterized (composition, density, …)

2) Carry out one or more *well adapted* diffraction experiments
   Optimize the data quality (low background, low peak overlapping,…)
   (x-rays and/or neutrons and/or electrons, choice of resolution, wavelength, *etc*…)

Ab Initio Structure Solving

1) Needs a high quality sample already well characterized (composition, density, …)

2) Carry out one or more *well adapted* diffraction experiments
Optimize the data quality (low background, low peak overlapping,…)
(x-rays and/or neutrons and/or electrons, choice of resolution, wavelength, *etc*…)

3) Find unit cell and index Bragg reflections (Dicvol, Treor, Ito, etc…). See www.ccp14.ac.uk/solution/indexing/. See 'Peter W. Stephens (SBU): *Indexing Powder Diffraction Data*' tutorial on youtube.

also see '*Discussion of the indexing algorithms within TOPAS*'. A. Coelho & A. Kern (2005) CPD Newsletter No. 32, 43-45

→ finding the unit cell symmetry and dimensions that best describe the position of the diffraction peaks on the powder pattern

Ab Initio Structure Solving

1) Needs a high quality sample already well characterized (composition, density, …)

2) Carry out one or more *well adapted* diffraction experiments
Optimize the data quality (low background, low peak overlapping,…)
(x-rays and/or neutrons and/or electrons, choice of resolution, wavelength, *etc*…)

3) Find unit cell and index Bragg reflections (Dicvol, Treor, Ito, etc…). See www.ccp14.ac.uk/solution/indexing/. See 'Peter W. Stephens: *Indexing Powder Diffraction Data*' tutorial on youtube.

4) Obtain intensities of Bragg reflections and determine the space group
(LeBail technique + CheckGroup)

Systematic absences (extinctions)

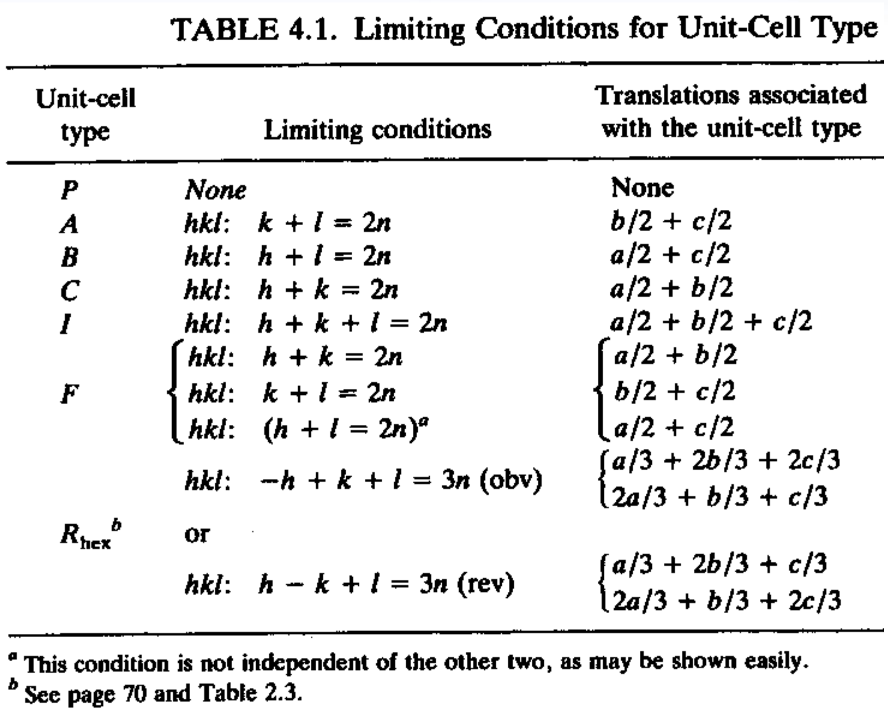


TABLE 4.1. Limiting Conditions for Unit-Cell Type

Unit-cell type	Limiting conditions	Translations associated with the unit-cell type
P	*None*	None
A	hkl: $k + l = 2n$	$b/2 + c/2$
B	hkl: $h + l = 2n$	$a/2 + c/2$
C	hkl: $h + k = 2n$	$a/2 + b/2$
I	hkl: $h + k + l = 2n$	$a/2 + b/2 + c/2$
F	hkl: $h + k = 2n$	$a/2 + b/2$
	hkl: $k + l = 2n$	$b/2 + c/2$
	hkl: $(h + l = 2n)^a$	$a/2 + c/2$
$R_{hex}{}^b$	hkl: $-h + k + l = 3n$ (obv)	$a/3 + 2b/3 + 2c/3$ $2a/3 + b/3 + c/3$
	or	
	hkl: $h - k + l = 3n$ (rev)	$a/3 + 2b/3 + c/3$ $2a/3 + b/3 + 2c/3$

---

[a] This condition is not independent of the other two, as may be shown easily.

[b] See page 70 and Table 2.3.

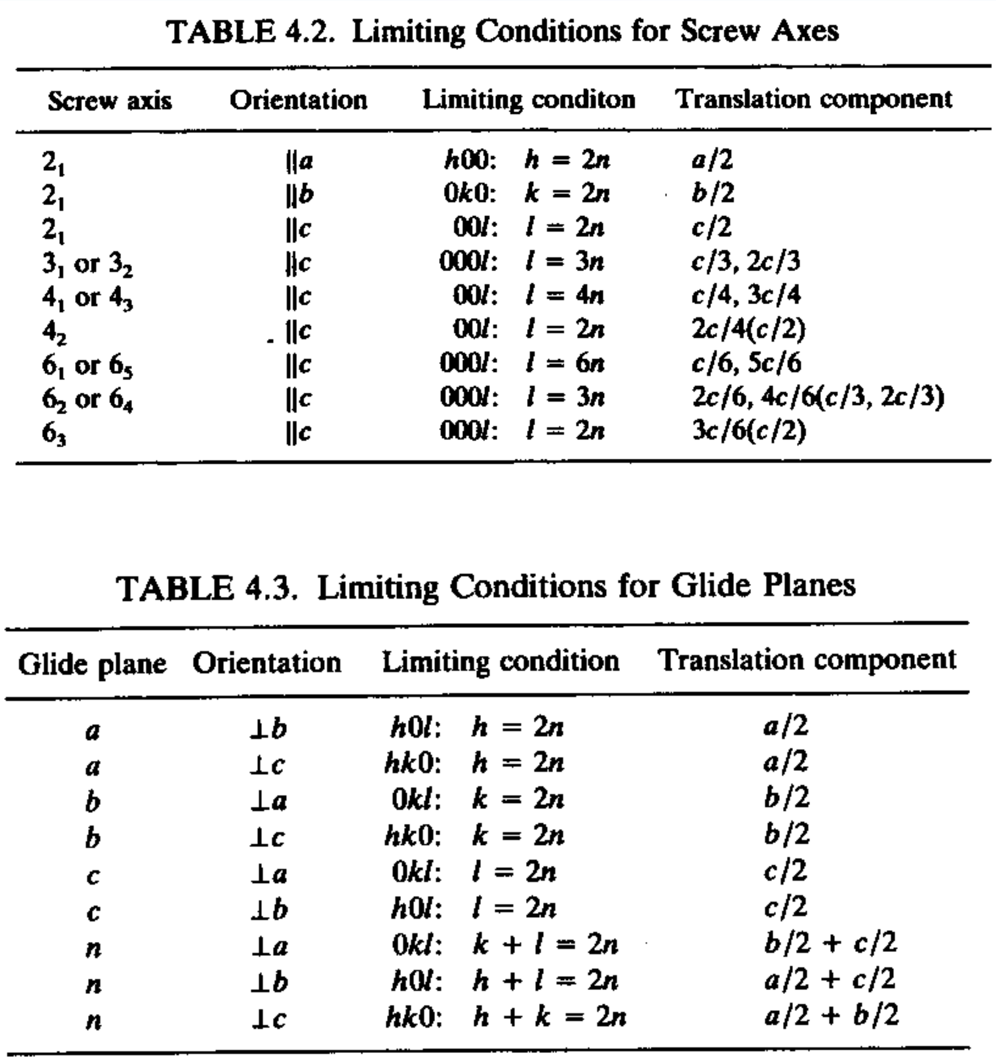


TABLE 4.2. Limiting Conditions for Screw Axes

Screw axis	Orientation	Limiting conditon	Translation component
2_1	$\parallel a$	$h00$: $h = 2n$	$a/2$
2_1	$\parallel b$	$0k0$: $k = 2n$	$b/2$
2_1	$\parallel c$	$00l$: $l = 2n$	$c/2$
3_1 or 3_2	$\parallel c$	$000l$: $l = 3n$	$c/3, 2c/3$
4_1 or 4_3	$\parallel c$	$00l$: $l = 4n$	$c/4, 3c/4$
4_2	$\parallel c$	$00l$: $l = 2n$	$2c/4(c/2)$
6_1 or 6_5	$\parallel c$	$000l$: $l = 6n$	$c/6, 5c/6$
6_2 or 6_4	$\parallel c$	$000l$: $l = 3n$	$2c/6, 4c/6(c/3, 2c/3)$
6_3	$\parallel c$	$000l$: $l = 2n$	$3c/6(c/2)$

TABLE 4.3. Limiting Conditions for Glide Planes

Glide plane	Orientation	Limiting condition	Translation component
a	$\perp b$	$h0l$: $h = 2n$	$a/2$
a	$\perp c$	$hk0$: $h = 2n$	$a/2$
b	$\perp a$	$0kl$: $k = 2n$	$b/2$
b	$\perp c$	$hk0$: $k = 2n$	$b/2$
c	$\perp a$	$0kl$: $l = 2n$	$c/2$
c	$\perp b$	$h0l$: $l = 2n$	$c/2$
n	$\perp a$	$0kl$: $k + l = 2n$	$b/2 + c/2$
n	$\perp b$	$h0l$: $h + l = 2n$	$a/2 + c/2$
n	$\perp c$	$hk0$: $h + k = 2n$	$a/2 + b/2$

“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.

Ab Initio Structure Solving

1) Needs a high quality sample already well characterized (composition, density, …)

2) Carry out one or more *well adapted* diffraction experiments
Optimize the data quality (low background, low peak overlapping,…)
(x-rays and/or neutrons and/or electrons, choice of resolution, wavelength, *etc*…)

3) Find unit cell and index Bragg reflections (Dicvol, Treor, Ito, etc…). See www.ccp14.ac.uk/solution/indexing/. See 'Peter W. Stephens: *Indexing Powder Diffraction Data*' tutorial on youtube.

4) Obtain intensities of Bragg reflections and determine the space group
(LeBail technique + CheckGroup)

5) Find approximate structural model *ab initio* using Direct Methods (reciprocal space) or Heavy Atom (Patterson) Methods, or methods in direct space.

also use Difference Fourier analysis to locate missing atoms

Ab Initio Structure Solving by Direct Methods

1) It requires preliminary determination of the diffraction intensity of the individual reflections (as accurately as possible), which is done using profile fitting or full pattern decomposition methods (G. S. Pawley: J. Appl. Cryst. (1981), or A. Le Bail: Mat. Res. Bull. (1988)).

2) Any substantial overlapping of the reflections lowers the quality and makes the true solution less distinguishable.

3) The same programs that are used to solve single crystal structures are used to solve structure from the powder diffraction data, *e.g.*, SHELXS or EXPO

Ab Initio Structure Solving in Direct Space

Plausible structure models are randomly generated by moving atoms or groups of atoms in crystal coordinates within the pre-determined unit cell. The calculated diagram is compared to the observed one.

- Trial-and-error approach, that can be computer-intensive and can be guided by prior chemical or crystallographic knowledge and structural database mining (*e.g.*, search for isostructural or analogous compounds)
- In case of overlapping reflections, the direct space search, *e.g.*, global optimization method, becomes much more advantageous.
- Prior to simulations, eliminate experimental biases, *e.g.*, huge preferred orientation or absorption effects, and other factors that decrease intensity or increase broadening of the peaks.
- Avoid a priori impossible configurations (too small distances, unrealistic angles, *etc*.) *e.g.*, apply "common" chemical sense, check the calculated density (Z x M/V)
- Avoid to get blocked in a local minimum

Ab Initio Structure Solving in Direct Space

Plausible structure models are randomly generated by moving atoms or groups of atoms in crystal coordinates within the pre-determined unit cell. The calculated diagram is compared to the observed one.

One possible method: **simulated annealing** (FOX, PowderSolve)
For each configuration, one calculates a ***cost function***, based on a pseudo-potential energy to minimize, and on the agreement between experiment and model :

$$C = \alpha\, Epot + (1-\alpha)\, R$$

Epot may depend on the bond type (ionic, covalent, intermetallic…), Lennard-Jones, Coulomb, …

$$R = 100 \sum_{2\theta} \left| I_{\exp}(2\theta) - I_{calc}(2\theta) \right| / \sum_{2\theta} I_{\exp}(2\theta)$$

One goes from config. Ci to Ci+1 following a **Monte-Carlo** type algorithm:
If Ci+1 < Ci, move accepted
If Ci+1 > Ci, move accepted with probability : ***exp[-(Ci+1-Ci)/K]***
K ≈ temperature, decreases slowly during search.

And more…

Complexity of the materials, and hence the data, increases…

Performance of the measuring methods increases…

Effectiveness of numerical data processing techniques increases…

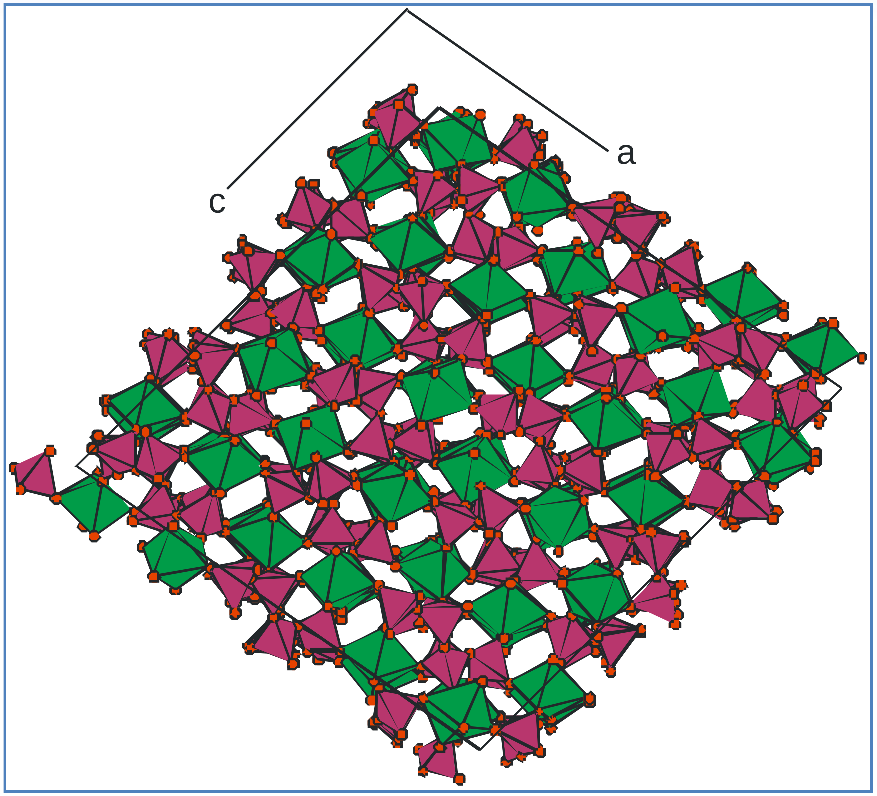
- Maximum Entropy (1996)
- Maximum Likelihood (1998)
- Genetic Algorithm (1999)
- Simulated Annealing (2000)
- Parallel Tempering (2002)
- Charge Flipping (2008) (truly ab initio; no information about atom types, composition, charge, *etc*. is required; starting symmetry can be kept as low as P1)

Structure Determination of $Mo_2P_4O_{15}$

One of the largest structures solved with TOPAS (simulated annealing)

Single crystal data
(Bruker AXS SMART 6000)

- SG: Pn (7)
- a = 24.1134(6) Å
- b = 19.5324(5) Å
- c = 25.0854(6) Å
- ß = 100.015(1)°
- V = 4450.9 $Å^3$
- 441 atoms in asymmetric unit



Lister et al., Chem. Commun., 2004, 2540

Ab Initio Structure Solving

1) Needs a high quality sample already well characterized (composition, density, …)

2) Carry out one or more *well adapted* diffraction experiments
   Optimize the data quality (low background, low peak overlapping,…)
   (x-rays and/or neutrons and/or electrons, choice of resolution, wavelength, *etc*…)

3) Find unit cell and index Bragg reflections (Dicvol, Treor, Ito, etc…). See www.ccp14.ac.uk/solution/indexing/. See 'Peter W. Stephens: *Indexing Powder Diffraction Data*' tutorial on youtube.

4) Obtain intensities of Bragg reflections and determine the space group
   (LeBail technique + CheckGroup)

5) Find approximate structural model *ab initio* using Direct Methods (reciprocal space) or Heavy Atom (Patterson) Methods, or methods in direct space.

6) Rietveld refinement and Fourier recycling to obtain a complete and accurate structure using Fullprof or GSAS

Pattern Refinement

- ✓ cell dimensions define the position of the peaks
- ✓ atomic parameters (the only parameters optimized in the single crystal refinement) determine the diffraction intensities
- ✓ microstructural parameters drive the shape of the diffraction peaks (*e.g.*, crystallite size, defects)
- ✓ Instrumental parameters affect the diffracted intensity (*e.g.*, preferred orientation and absorption) and the peak shape

Pattern Refinement

The method consists of refining a crystal (and/or magnetic) structure by minimizing the weighted squared difference between the observed y_i and the calculated y_{ci} intensities at all diffraction angles $1 \leq i \leq n$.

$$\boxed{\chi^2 = \sum_{i=1}^{n} w_i \{y_i - y_{ci}(\beta)\}^2}$$

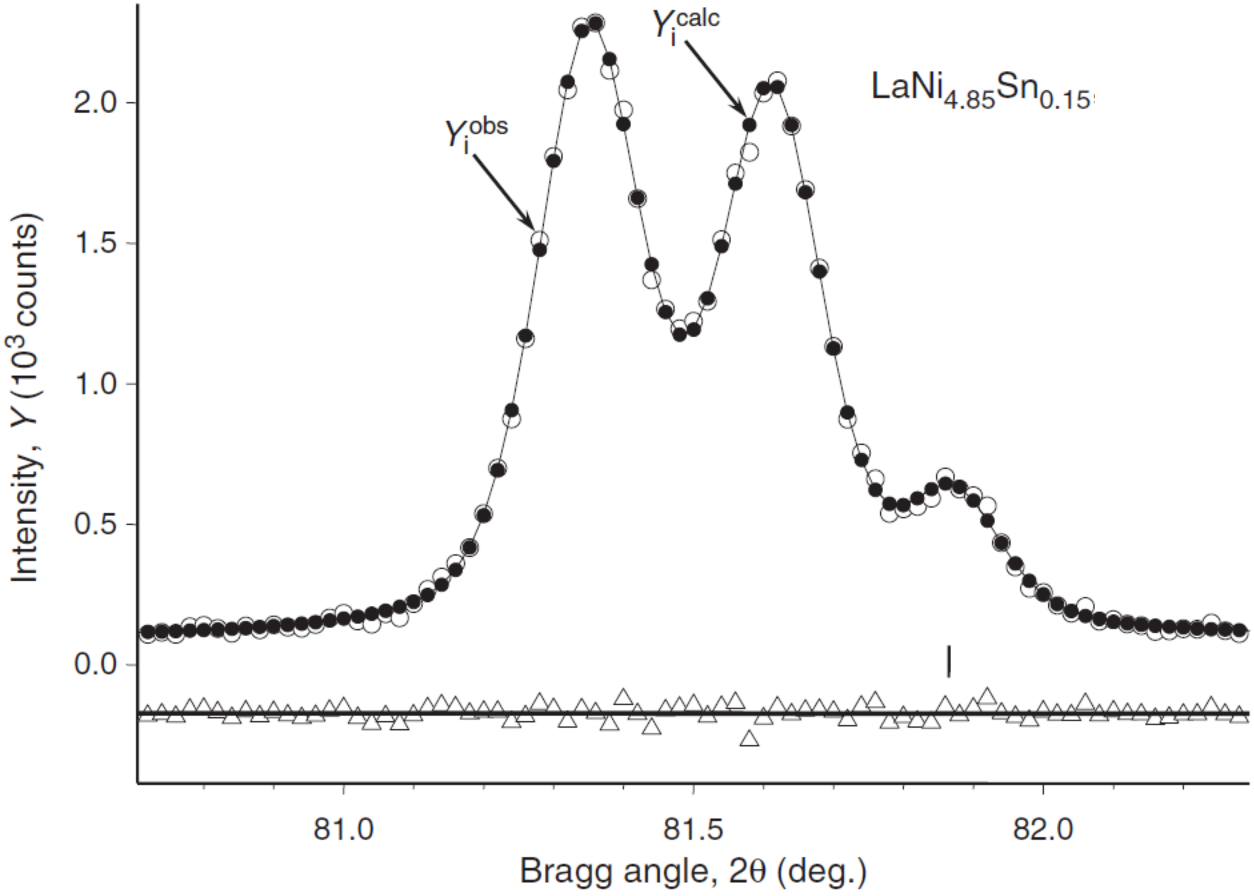
$$\boxed{w_i = \frac{1}{\sigma_i^2}}$$

σ_i^2: **is the variance of the "observation"** y_i

The model to calculate a powder diffraction pattern is:

$$y_{ci} = \sum I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$T = 2\theta$
diffraction angle



Pattern Refinement

The model to calculate a powder diffraction pattern is:

$$y_{ci} = \sum_{\mathbf{h}} \boxed{I_{\mathbf{h}}}\,\Omega(T_i - T_{\mathbf{h}}) + b_i$$

T = 2θ
diffraction angle

y_{ci} is the calculated diffraction intensity at the diffraction angle T_i

***I(h)* is the diffracted intensity from a particular set of planes (*h*).**
***I(h)* is driven by the atomic motif *i.e.*, by the structure factor *F(h)*.**

Several peaks *h* - *I(h)*, angle T_h - might contribute to the measured intensity at any particular T_i (diffraction) angle.

***I(h)* is distributed over a range of T_i (diffraction) angles around T_h.**

Pattern Refinement

The model to calculate a powder diffraction pattern is:

$$y_{ci} = \sum_{\mathbf{h}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

T = 2θ
diffraction angle

$$\int_{-\infty}^{+\infty} \Omega(x)dx = 1$$

Profile function characterized by its full width at half maximum (FWHM=*H*) and *shape* parameters (η, m, ...)

$$\Omega(x) = g(x) \otimes f(x) = instrumental \otimes intrinsic\,profile$$

Pattern Refinement

The model to calculate a powder diffraction pattern is:

$$y_{ci} = \sum_{\mathbf{h}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

T = 2θ
diffraction angle

$$\int_{-\infty}^{+\infty} \Omega(x)dx = 1$$

Profile function characterized by its full width at half maximum (FWHM=*H*) and *shape* parameters (η, m, ...)

$$\Omega(x) = g(x) \otimes f(x) = instrumental \otimes intrinsic\,profile$$

- **Profile refinement**: pattern matching is constrained by peak positions (symmetry, unit cell) and peak profile (instrument, microstructure). Each *I(h)* is not constrained by the atomic motif but is a free parameter.

Rietveld Refinement

The model to calculate a powder diffraction pattern is:

$$y_{ci} = \sum_{\mathbf{h}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

T = 2θ
diffraction angle

$$\int_{-\infty}^{+\infty} \Omega(x)dx = 1$$

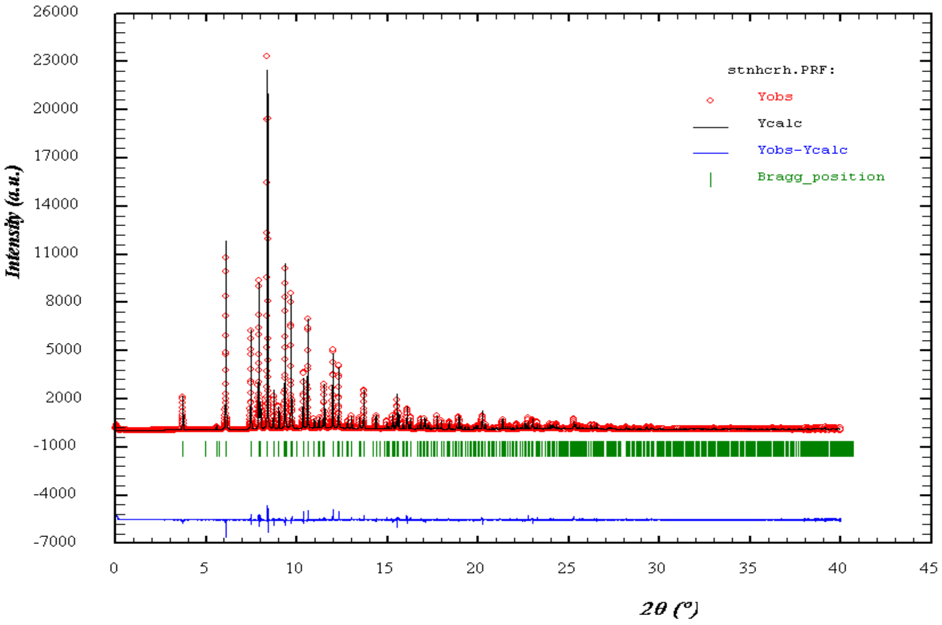
Profile function characterized by its full width at half maximum (FWHM=*H*) and *shape* parameters (η, m, ...)

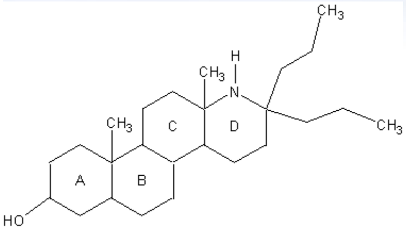
$$\Omega(x) = g(x) \otimes f(x) = instrumental \otimes intrinsic\, profile$$

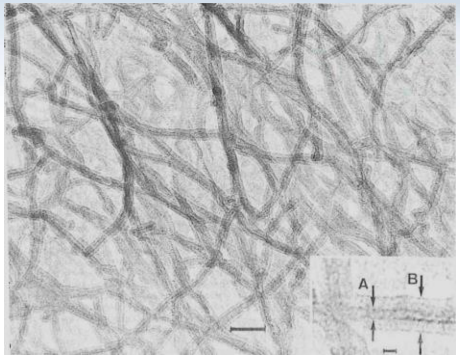
- Rietveld refinement: diffraction peak intensities are driven by the atomic model (atom coordinates within the unit cell). Each *I(h)* is constrained by the atomic motif *i.e., F(h)*

see for example "The Rietveld Method", R.A. Young (IUCr Monograph no.5) - 1994

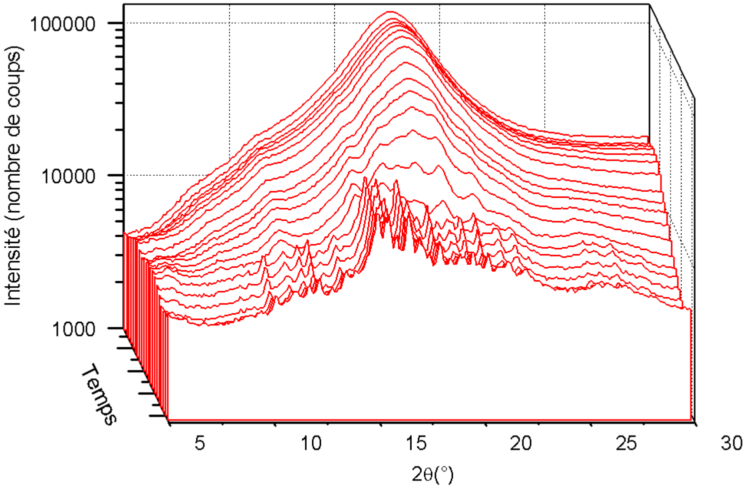
Rietveld Structure refinement

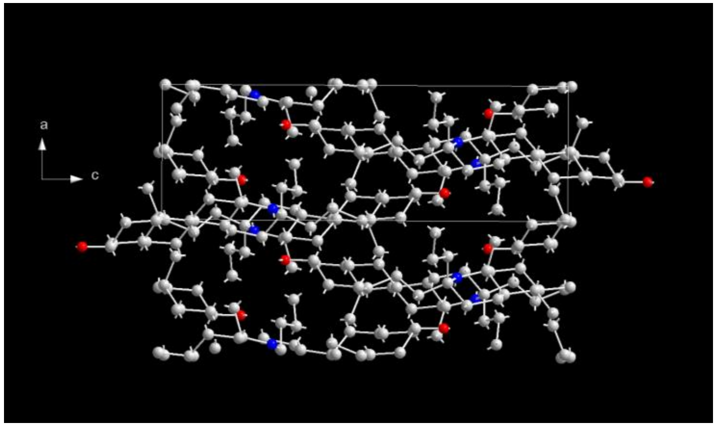






a = 6,5358 Å
b = 17,6040 Å
c = 19,7070 Å
$P\ 2_1\ 2_1\ 2_1$
$\chi^2 = 1{,}73$



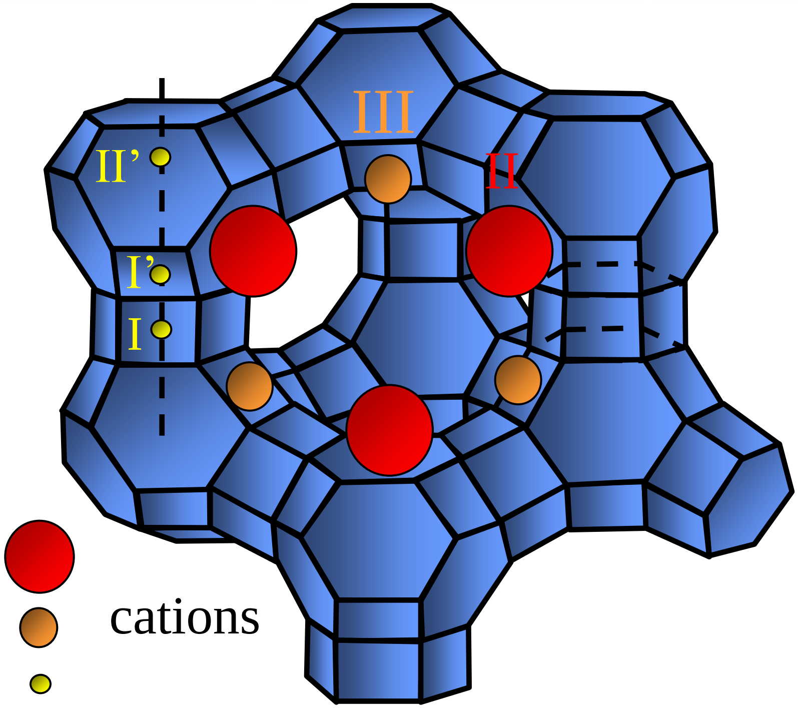


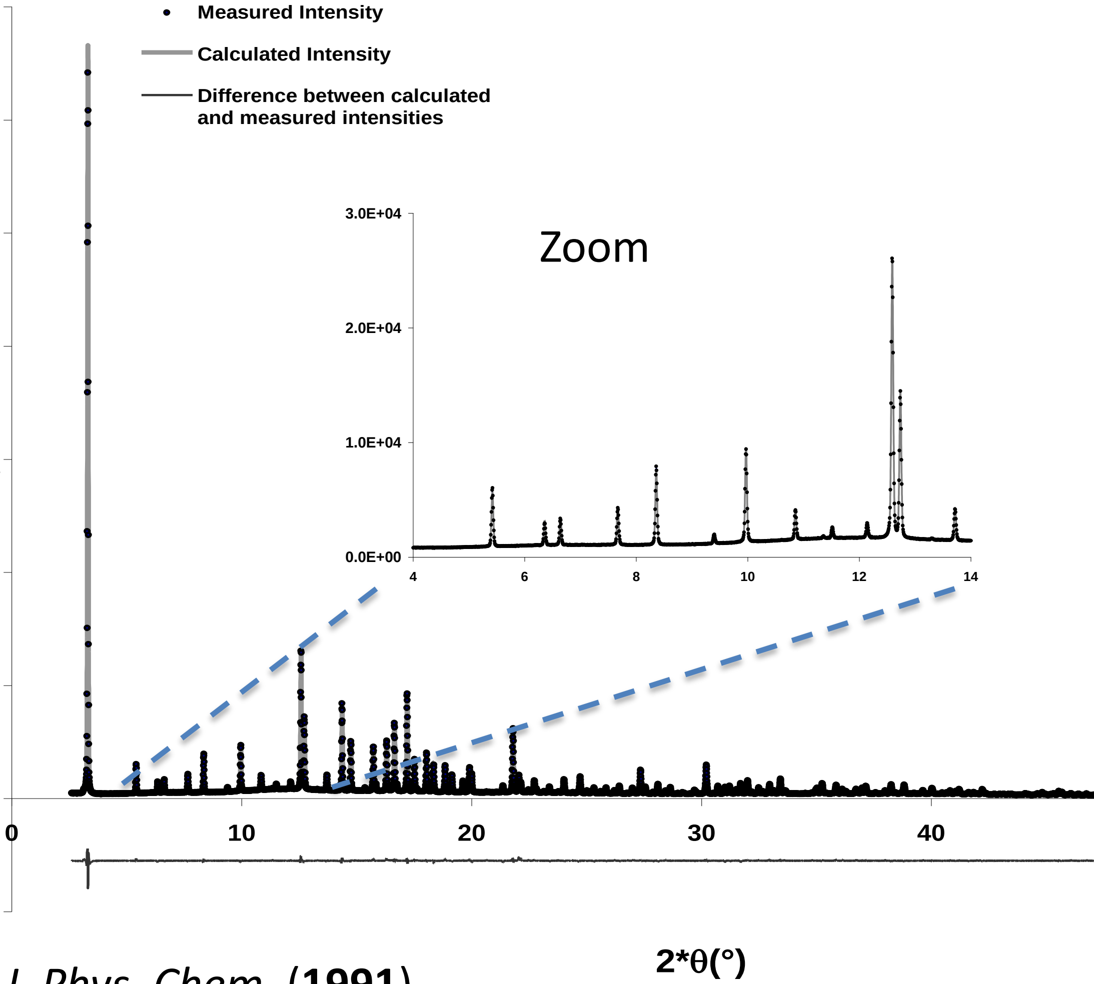
Hydrogen linked network

J. of Physical Chemistry **(2006)**

Rietveld Structure refinement

Cation sorption in a zeolite (filter, membrane, trap)





Formula: $Si_{110}Al_{84}O_{384}, nH_2O$

Space Group: F d -3 m

Unit cell parameter: 25 Å

J. Phys. Chem. (**1991**)

Rietveld Refinement

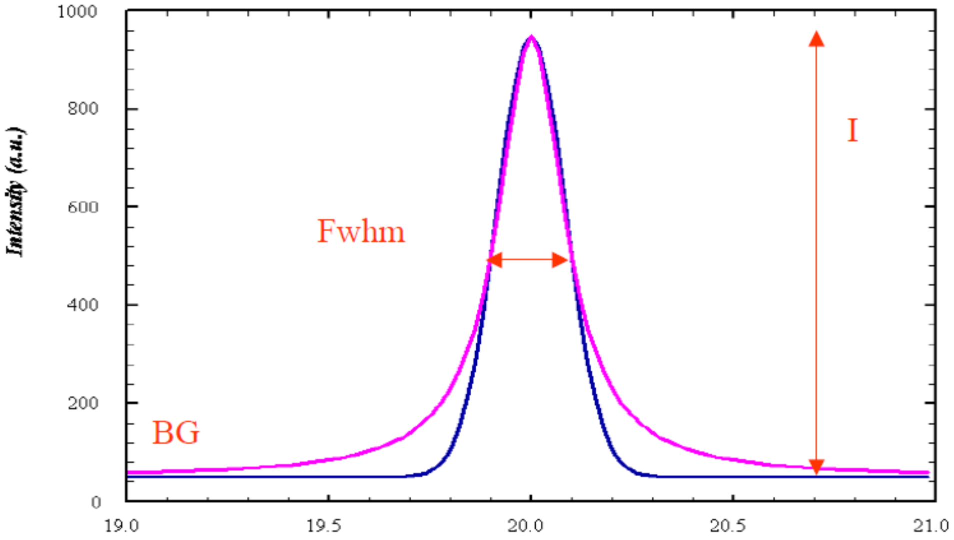
1) Peak position fitting: **unit cell parameters** (thermal expansivity, macroscopic strain)

2) Intensity fitting of individual reflections to extract the structure factors: they contain the phase fractions (**quantitative analysis**) and the structural parameters (**crystal structure**: atomic positions)

3) Isotropic or anisotropic temperature or displacement factors

4) **Peak shape fitting** of individual from the perfect crystal
   - crystallite size
   - shape (needle, platelet,…)
   - microstrain

Peak broadens when crystallite size decreases



Rietveld Refinement

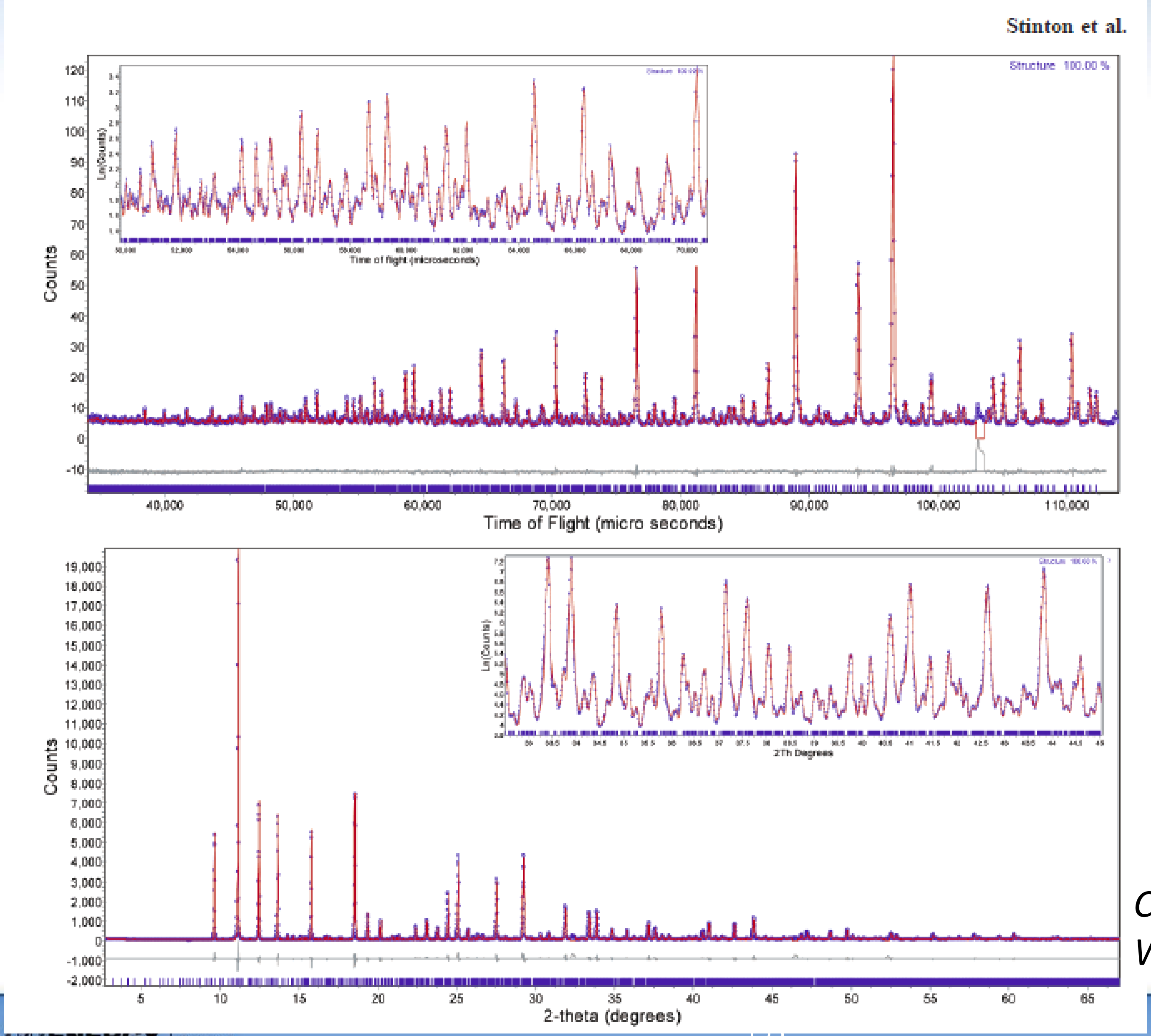
L.B. McCusker, et al, "*Rietveld Refinement Guidelines*", J. Appl. Cryst. (1999), 32, 36-50

see Peter W. Stephens (SBU): '*Rietveld Refinement*': https://www.youtube.com/watch?v=YF5EHwMGJFc

Technique played major role in every 'hot' material in solid-state chemistry in past 30 years, *e.g.*, high Tc, C60, giant magnetoresistance, batteries, fuel cells, *etc*

Programs: TOPAS, GSAS, FullPROF, …

ZrP_2O_7 – a 'peak-fest'



TOF neutron data
(HRPD, ISIS)
21195 reflections

Synchrotron data
(X7A, NSLS, 0.8Å)
22015 reflections

Courtesy of Pamela Whitfield, Oak Ridge (TN)

Outline

1. Applications for Powder Diffraction
2. The basics of Powder Diffraction
3. Experimental Methods for collecting PD data
4. Crystal structure Determination
5. **Peak Profile Analysis for Microstructural Studies**
6. **Advanced PD techniques**

Peak Profile Fitting

- 3 contributions into each individual peak profile:

1. Instrument
2. Crystallite size
3. Lattice strain

E. J. Mittemeijer, P. Scardi (eds.)
Diffraction Analysis of the Microstructure of Materials, Springer Verlag, Heidelberg 2004.

Peak Profile Fitting

- 3 contributions into each individual peak profile:

1. Instrument
2. Crystallite size
3. Lattice strain

- XRD Crystallite Size using the Scherrer Formula
  http://www.d.umn.edu/~bhar0022/dpcalculator

$$D = \frac{K\lambda}{\beta \mathrm{Cos}\,\theta}$$

β is the FWHM of the Bragg peak after correction for instrumental broadening

The Scherrer formula applies if strain broadening if negligible.

Peak Profile Fitting

- Modeling the Gaussian an Lorentzian components of the Bragg profile function: provides microstructural parameters

$$H_G^2 = (U + (1-\xi)^2 D_{ST}^2)\tan^2\theta + V\tan\theta + W + \frac{I_G}{\cos^2\theta}$$

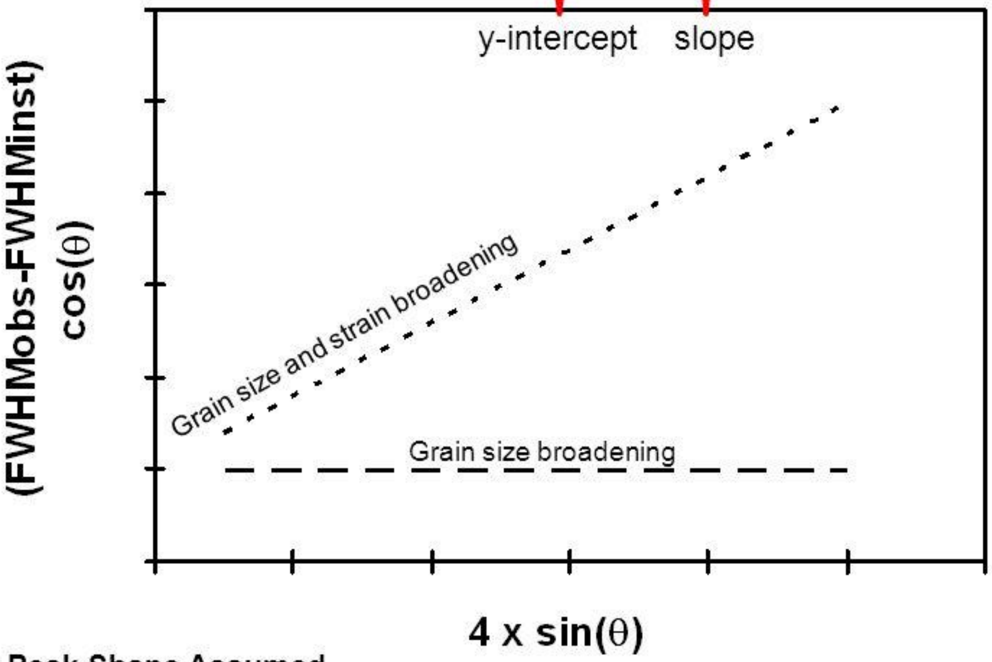
$$H_L = (X + \xi D_{ST})\tan\theta + \frac{[Y + F(S_Z)]}{\cos\theta}$$

***Microstructure Analysis** from Diffraction* Edited by R. L. Snyder, H. J. Bunge, and J. Fiala, International Union of Crystallography, 1999

Size and Strain in Reciprocal Space

Size and strain may be separated in favorable cases by measuring several peaks (*i.e.*, over a portion of the reciprocal space)

$$FWHM \times \cos(\theta) = \underbrace{\frac{K \times \lambda}{Size}}_{\text{y-intercept}} + \underbrace{Strain}_{\text{slope}} \times 4 \times \sin(\theta)$$



Gausian Peak Shape Assumed

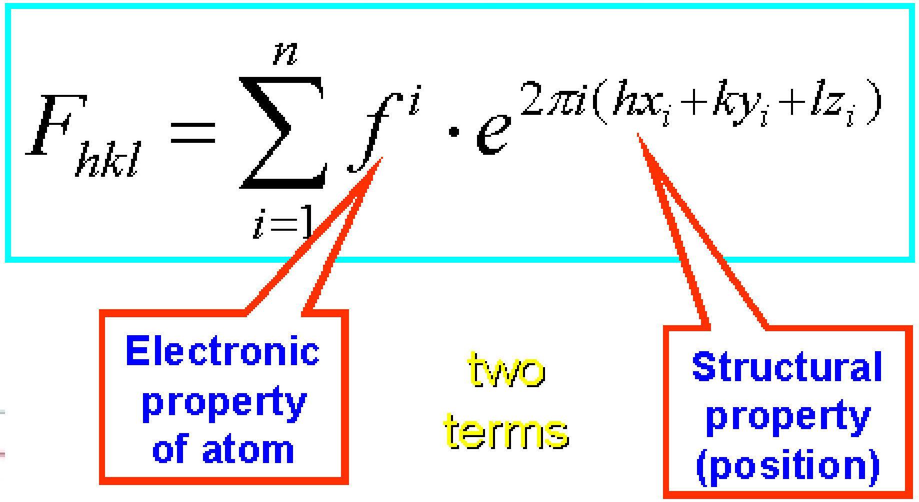
K≈0.94

grain (actual particle of matter) ≠ crystallite (coherent domain)

Outline

1. Applications for Powder Diffraction
2. The basics of Powder Diffraction
3. Experimental Methods for collecting PD data
4. Crystal structure Determination
5. Peak Profile Analysis for Microstructural Studies
6. **Advanced PD techniques**

Anomalous Powder Diffraction

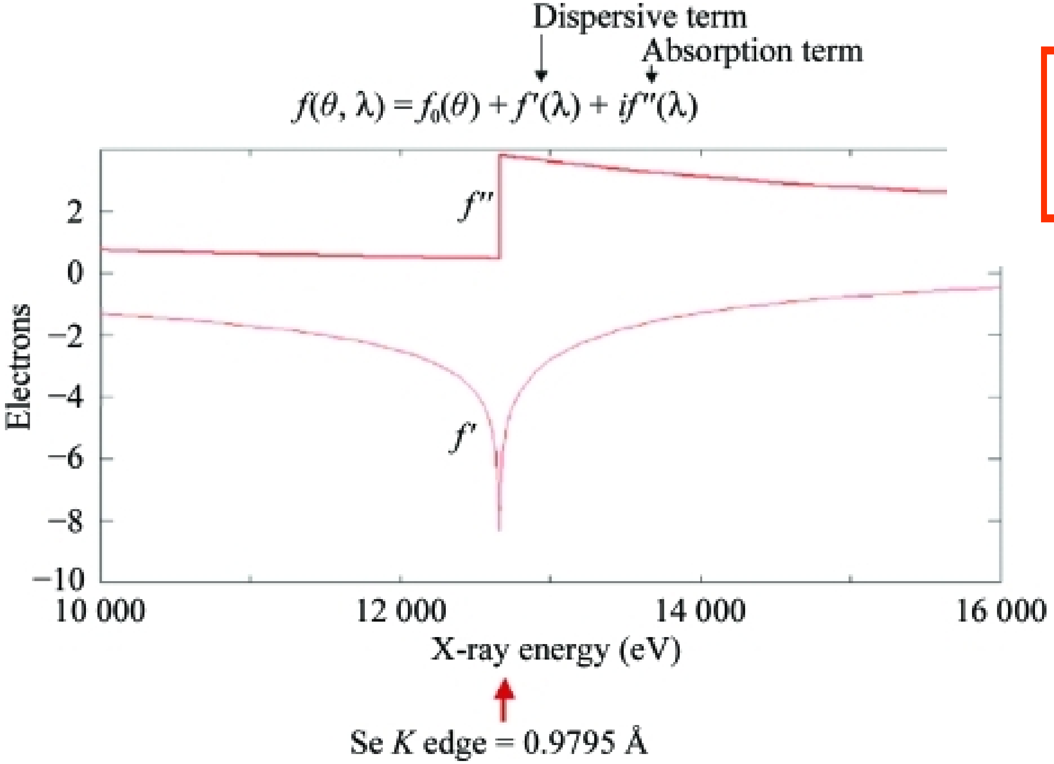


$$F_{hkl} = \sum_{i=1}^{n} f^{i} \cdot e^{2\pi i(hx_i + ky_i + lz_i)}$$

Electronic property of atom

two terms

Structural property (position)



Dispersive term

Absorption term

$$f(\theta,\lambda) = f_0(\theta) + f'(\lambda) + if''(\lambda)$$

Se K edge = 0.9795 Å

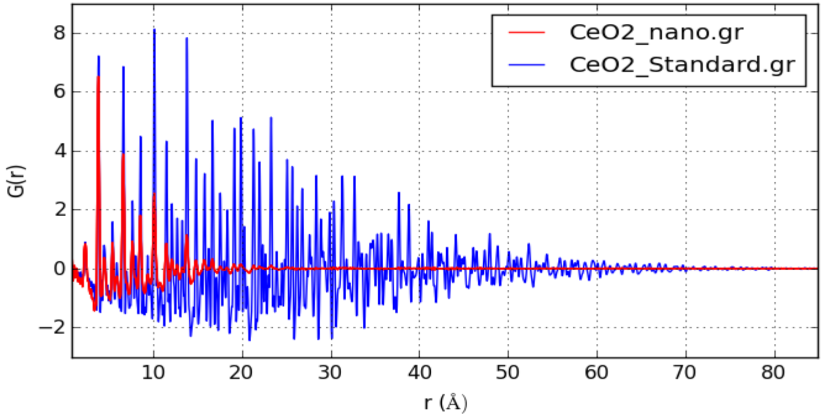
See Q. Shen's lecture

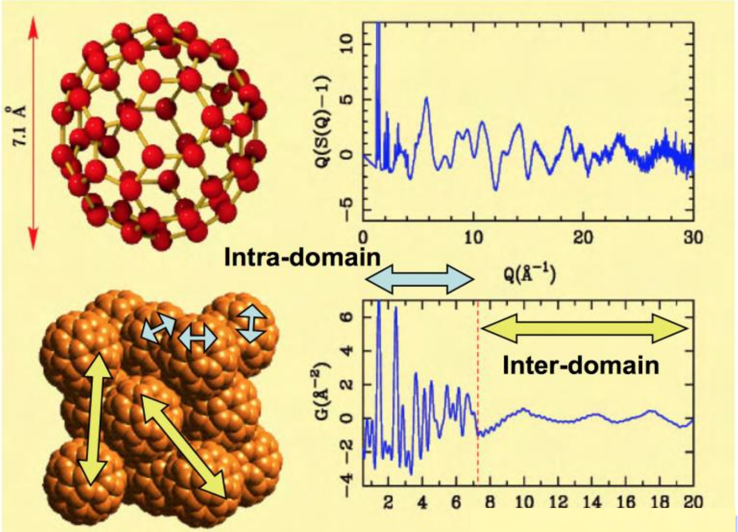
Total Scattering

- “Conventional” powder diffraction data analysis is insufficient or fails in particular for non crystalline materials (disorder, defects) and nanomaterials (short structural coherence length, broad Bragg peaks)
- PD patterns of complex materials often shows diffuse scattering smeared in the reciprocal under the Bragg peaks.

Total Scattering

- "Conventional" powder diffraction data analysis is insufficient or fails in particular for non crystalline materials (disorder, defects) and nanomaterials (short structural coherence length, broad Bragg peaks)
- PD patterns of complex materials often shows diffuse scattering smeared in the reciprocal under the Bragg peaks.
- FT of the total powder diffraction data (Bragg + diffuse) gives the PDF.

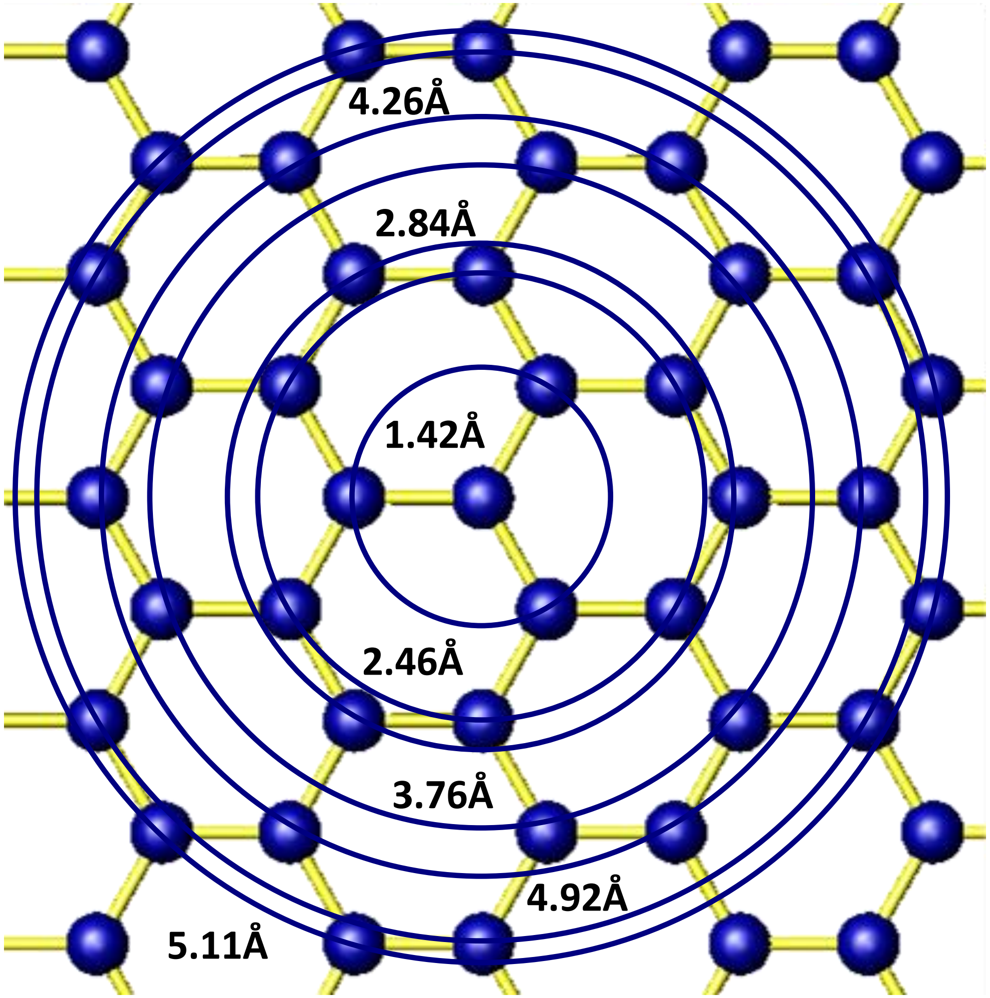




Carbon buckyballs

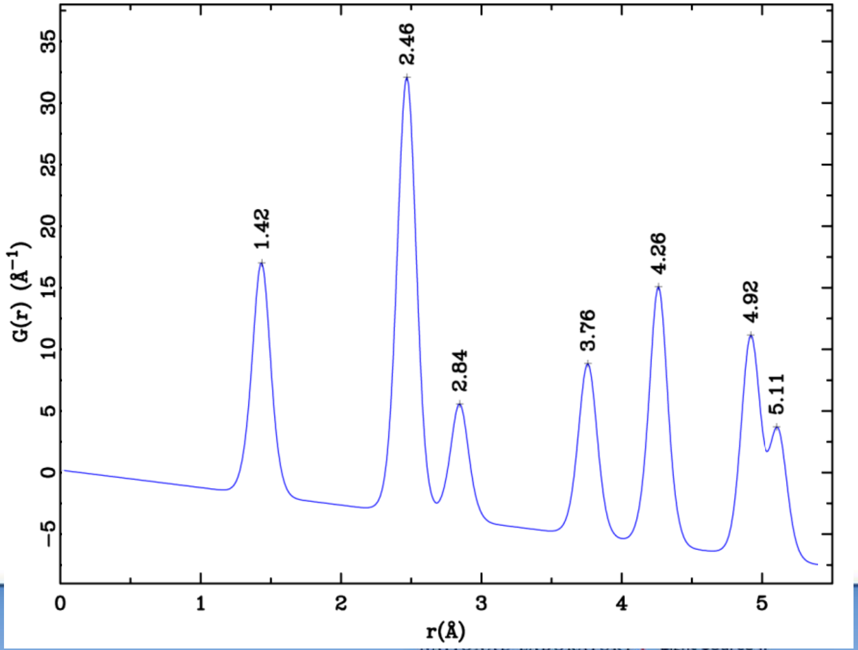
Schematic representation of the PDF

$$Q = 4\pi \sin(\theta)/\lambda$$

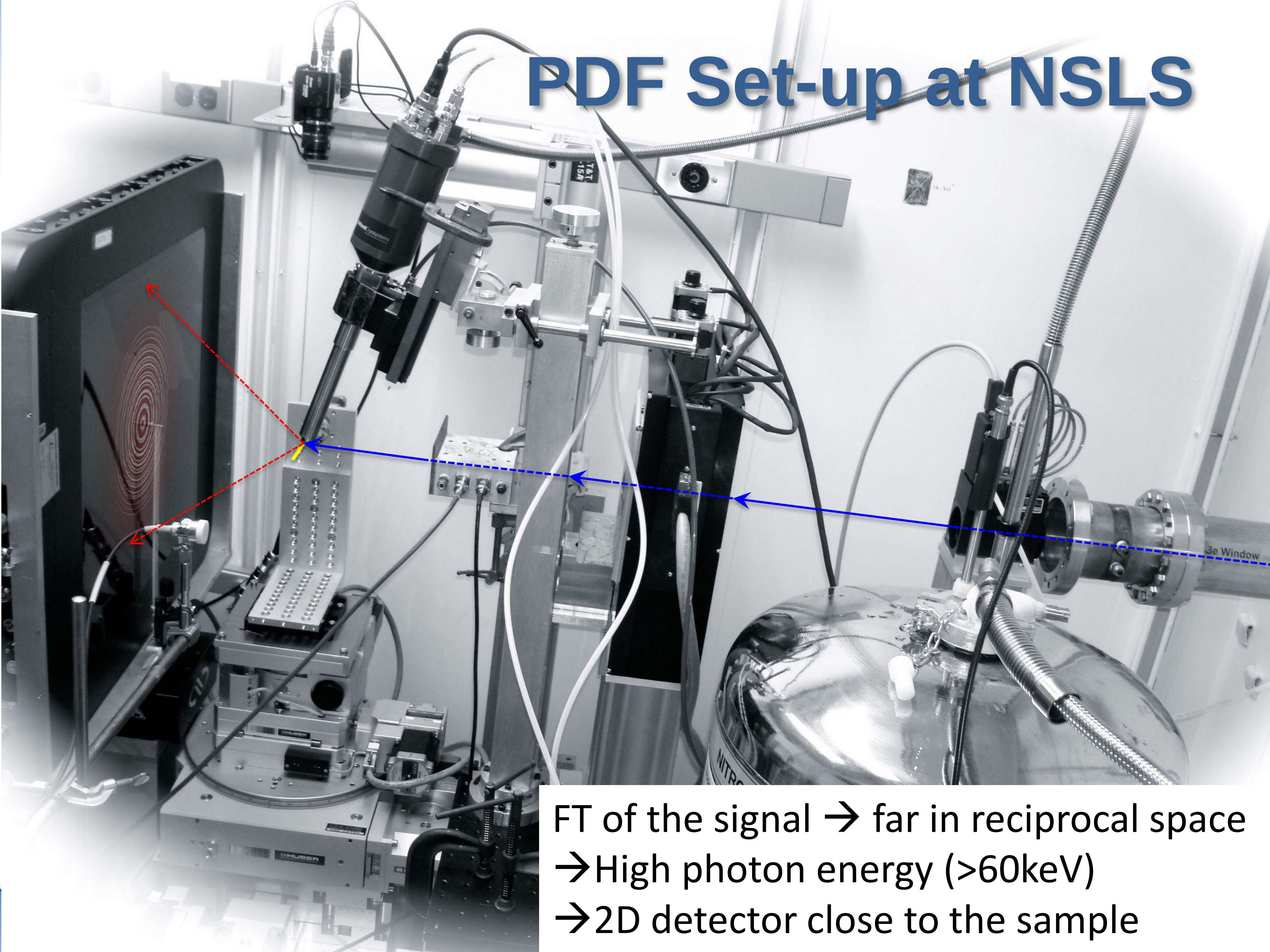


Pair distribution function (PDF) gives the probability of finding a neighbor atom at a distance "r" from a given atom.

$$G(r) = (2/\pi)\int_{Q_{\min}}^{Q_{\max}} Q[S(Q)-1]\sin(Qr)\,dQ$$



PDF Set-up at NSLS

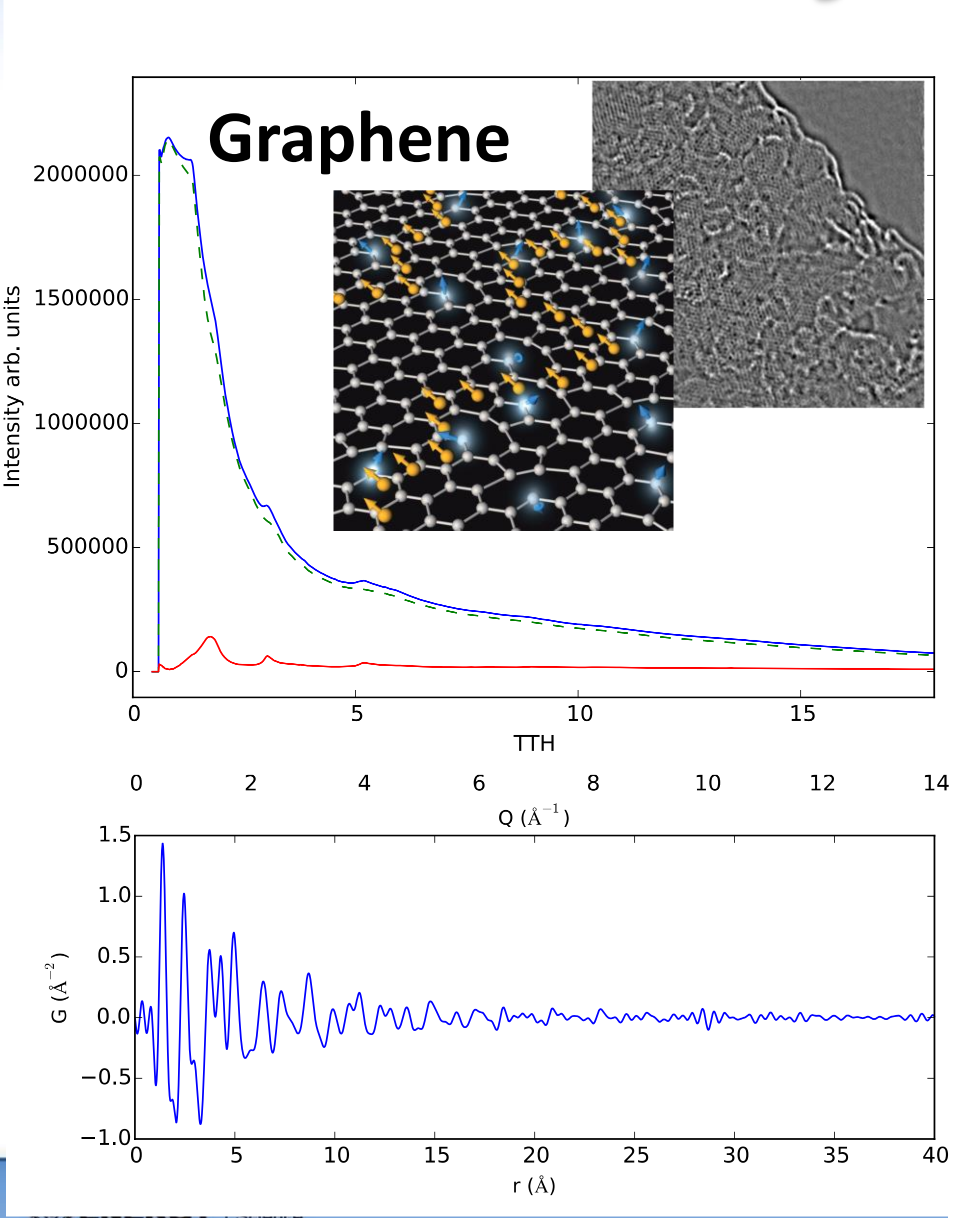


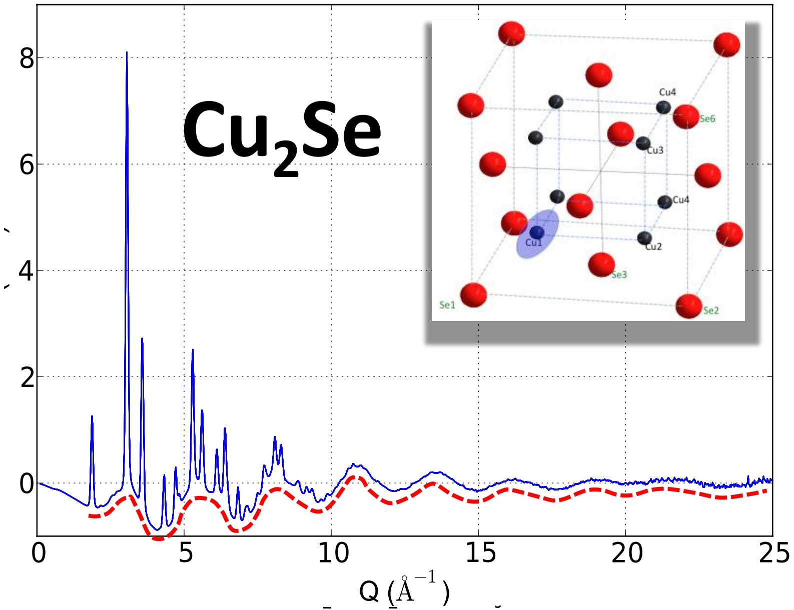
FT of the signal → far in reciprocal space

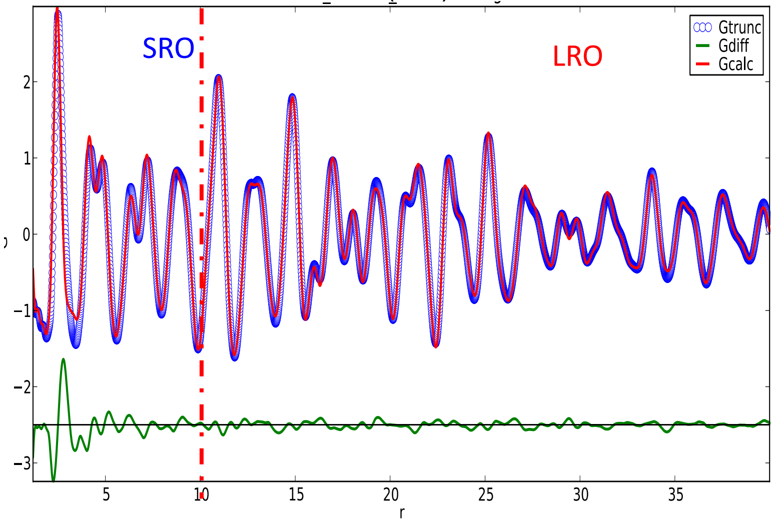
→High photon energy (>60keV)

→2D detector close to the sample

PDF Analysis Examples





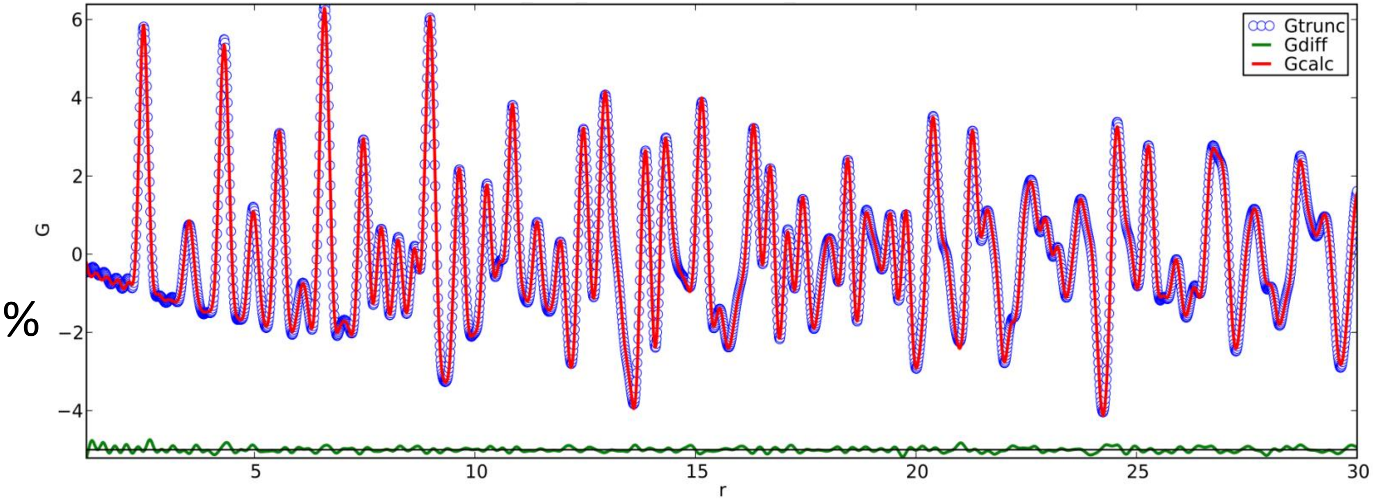


PDF Benchmarking NSLS-II (Columbia, BNL)

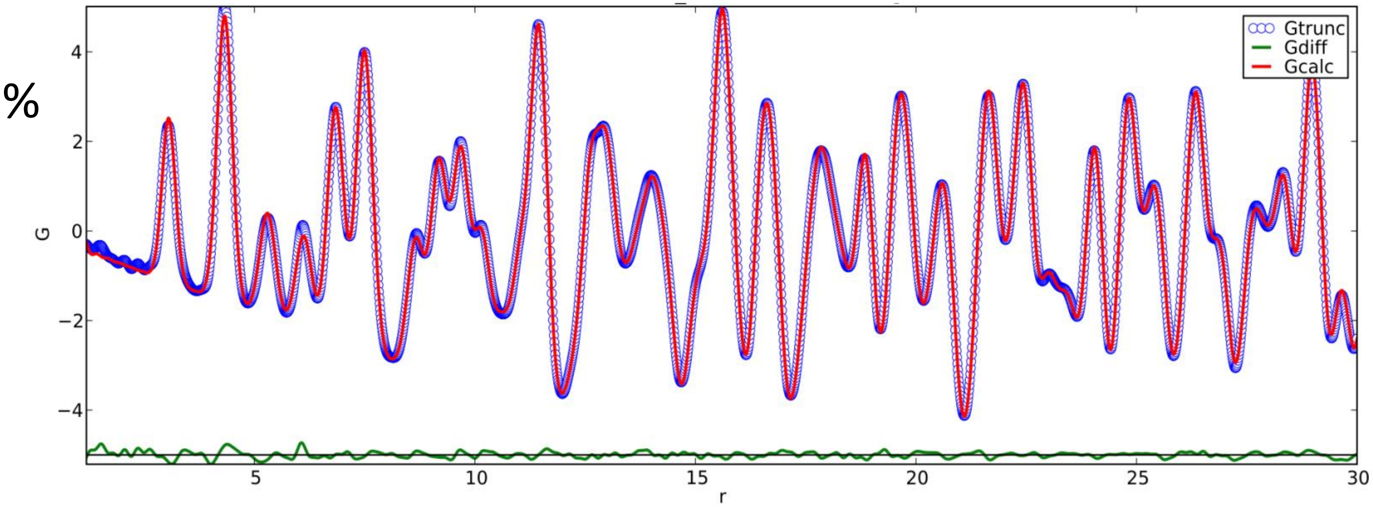
65.7 keV (300μm)^2
1 min @ 25mA

Measured (blue) and calculated (red) Pair Distribution Functions. Green curve shows the difference.

Ni Standard
Qmax = 25 Ǻ$^{-1}$, Rw = 3.6%



PbSe
Qmax = 25 Ǻ$^{-1}$, Rw = 3.8%



Total Scattering

- “Conventional” Powder Diffraction is applied to crystalline materials (**long range order**) with limited disorder. PD only looks at the Bragg peaks, background is treated as a baseline that is subtracted.
- Pair Distribution Function extends the PD technique over to non-crystalline materials, materials that contain a high degree of disorder and defects, and nanomaterials (**short range order**). PDF treats the signal that is contained both in the Bragg peaks and in the background.

‘Underneath the Bragg Peaks: Structural Analysis of Complex Materials’ (Pergamon Materials Series) 2nd Edition, by. Takeshi Egami and Simon J.L. Billinge.

Total Crystallography

Applies to samples that contain too many crystallites for “conventional” single crystal diffraction and too few for powder diffraction (randomization is insufficient).

This is a recurrent issue as probing beams get smaller and smaller. Software is being developed (see FABLE project) to manage this case.

TIME TO CONCLUDE…

My hope is that you will leave with a sense of why or how powder XRD might be applicable to your research.

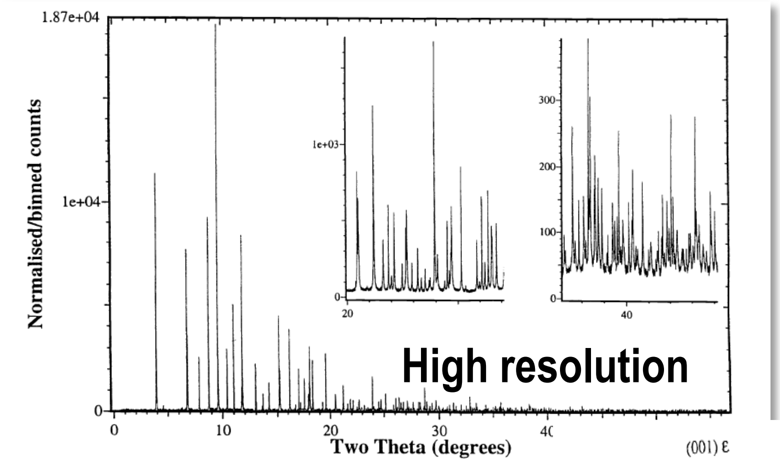
Where is the information in powder data?

1. **Peak positions** *(easy to measure, interpret)*
   - *Lattice parameters determination*
   - *Thermal expansivity or compressibility*
   - *Macro-stress*
2. **Peak widths and shapes** *(easy to measure / hard to interpret)*
   - *Microstructure (crystallite size, stacking faults, etc)*
3. **Peak intensities** *(challenging to measure, interpret)*
   - *Identification of fully occupied sites*
   - *Quantification of vacancies / mixed sites*
   - *Accurate DPs / ADPs*
   - *Structure solution*
4. **Between the Bragg peaks (PDF)** *(even more challenging)*
   - *Short range order*

- All problems are affected by quality of data
  - Ask yourself how many parameters contribute to intensity of peaks
  - A light atom may contribute 1% of total peak intensity (small vs. noise)
  - Data quality ~ number of independent peaks, and esds in their intensities

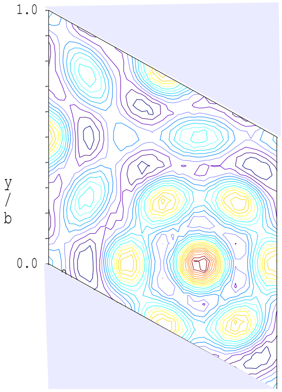
Summary of the Scientific Scope

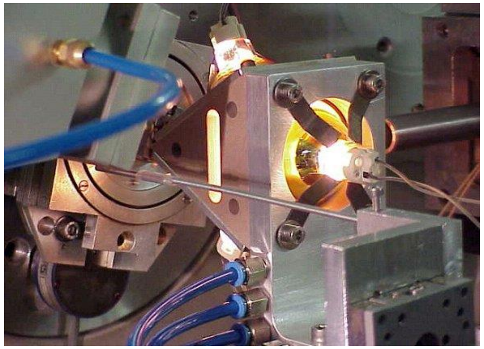
Powder Diffraction addresses a wide range of topics from Fundamental (*incl*. metallurgy, physics, chemistry, biology *etc.)* to Applied Research → <u>controlling complexity</u> (real devices, heterogeneous)



High resolution

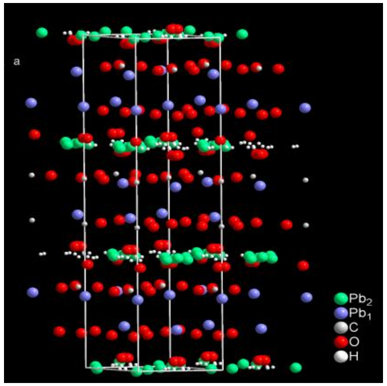
Crystallography

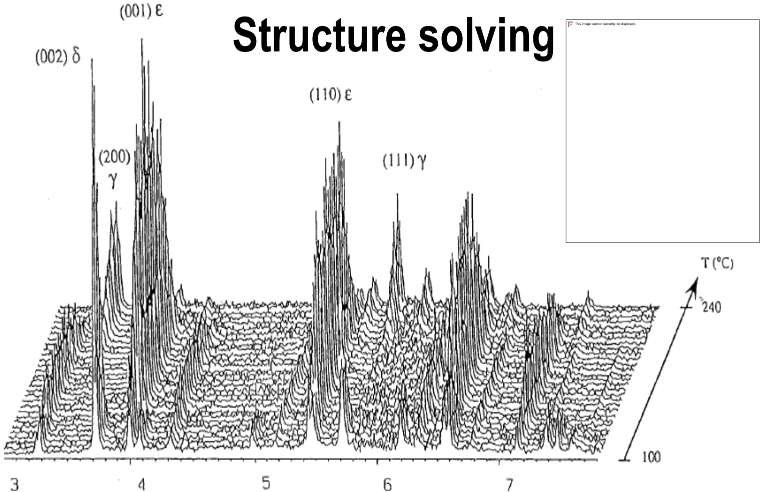




Extreme environments (T, P, gas, *B*, *E*)

Structure solving





Kinetics / time-resolved

High throughput

In situ

Operando

Current Trends in Powder Diffraction

Complex materials:

- Photovoltaics with improved efficiency – *Nanoparticles in the light collecting layer*
- High energy density batteries – *Electrodes, Electrolytes*
- Fuel cells – *Electrodes, Electrolytes*
- Catalysts – *Higher-order oxides, graphitic carbon, nanoparticles*
- Hydrogen storage – *MOF's*
- Carbon sequestration – *Functionalized mesoporous materials*
- Strongly correlated materials – *Materials doped with impurities*

Complexity: *Defects, Surfaces, Interfaces, Nano and multi-scale structures, heterogeneities, nanoscale disorder and surface relaxation etc.*

***Properties** in relation with LRO (average) and SRO (deviations)*

Current Trends in Powder Diffraction

- **Real materials** ≠ lab prepared (synthetic)
- **Real conditions** (*in situ*, operando) ≠ room T, P
- **Real time** ≠ static observation

Powder Diffraction Resources

- Commission on Powder Diffraction*:* http://www.iucr.org/iucr-top/comm/cpd/
- http://11bm.xray.aps.anl.gov/resources.html Instructional Resources, Software and Tools, Textbooks & Journal Articles, PD Beamlines.
- http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography/ This page references a series of demos and lectures that introduce Rietveld analysis techniques, incl. Flash movie presentations.
- Modern Methods in Rietveld Refinement and Structural Analysis https://sites.google.com/a/stonybrook.edu/mmrrsa_2016/home
- http://www.ccp14.ac.uk/mirror/mirror.htm Collaborative Computational Project Number 14 Tutorials and Program Repository.
- http://www.lightsources.org/ news and science highlights from each facility, as well as photos and videos, education and outreach resources, a calendar of conferences and events
- https://www.bnl.gov/ps/beamlines/beamline.php?r=28-ID-2 XPD at NSLS-II

Powder Diffraction Software Packages

Structure Refinement Software (Rietveld, Le Bail etc)

- GSAS-EXPGUI
- FullProf
- JANA
- TOPAS Professional
- TOPAS Academic
- MAUD
- BGMN

Structure Solution from Powder Diffraction Software

- FOX/ObjCryst++
- EXPO2009
- DIFFRACplus (TOPAS)
- Superflip (JANA)

Crystal structure drawing & visualization software

- DRAWxtl
- ATOMS
- VESTA
- CrystalMaker
- Diamond
- Mercury

And many more…

International Tables for Crystallography

- Home page = http://it.iucr.org/

A. Space-group symmetry
Symmetry relations between space groups

B. Reciprocal space

C. Mathematical, physical and chemical tables

D. Physical properties of crystals

E. Subperiodic groups

F. Crystallography of biological macromolecules

G. Definition and exchange of crystallographic data

H. Powder Diffraction (new: 50 chapters, 800 pages)
    1. Introduction to the principles of powder diffraction.
    2. Instrumentation for laboratory X-ray studies, synchrotron, neutron and electron diffraction, 2D diffraction, and special environments (temperature, pressure, magnetic fields, reaction cells).
    3. Different methodologies used in powder diffraction.
    4. Structure determination and validation.
    5. Defects, texture and microstructure: stress and strain, grain size and thin films.
    6. Review of available software.
    7. Applications to: macromolecules, zeolites, mining, ceramics, cement, forensic science, archaeology and pharmaceuticals.

I. X-ray Absorption Spectroscopy

Acknowledgments

This presentation uses material from:

- Robert M. Sweet (BNL)
- Patrick M. Woodward (Columbus, OH)
- Saul Lapidus (Argonne National laboratory, IL)
- Pierre Bordet (Neel Institute, France)
- Juan Rodríguez-Carvajal (Institut Laue-Langevin, France)
- Milinda Abeykoon (BNL)
- Cora Lind-Kovacs (U. Toledo, OH)
- Pamela Whitfield (Oak Ridge National Laboratory, TN)
- John Parise (Stony Brook and BNL, NY)

Thank you for your attention