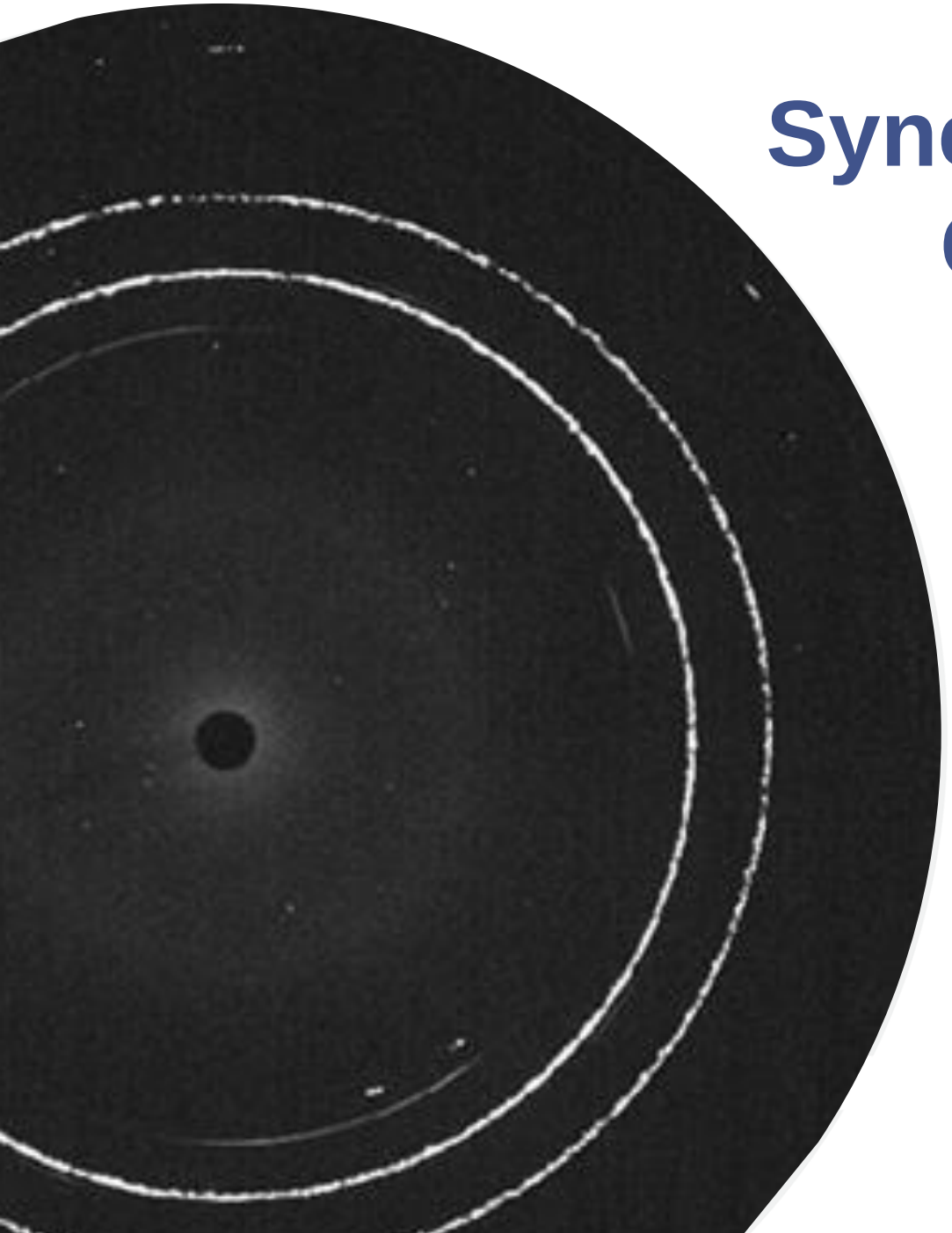
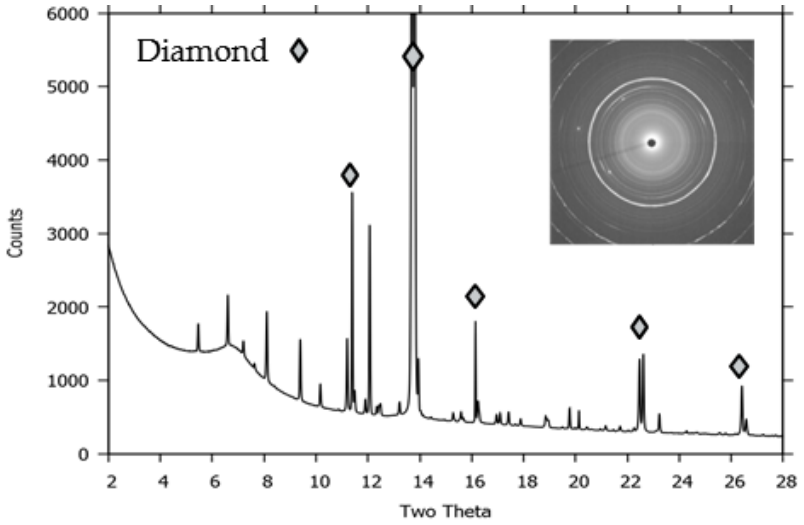


Synchrotron Powder and Single Crystal X-ray Diffraction



Dr Sarah Day

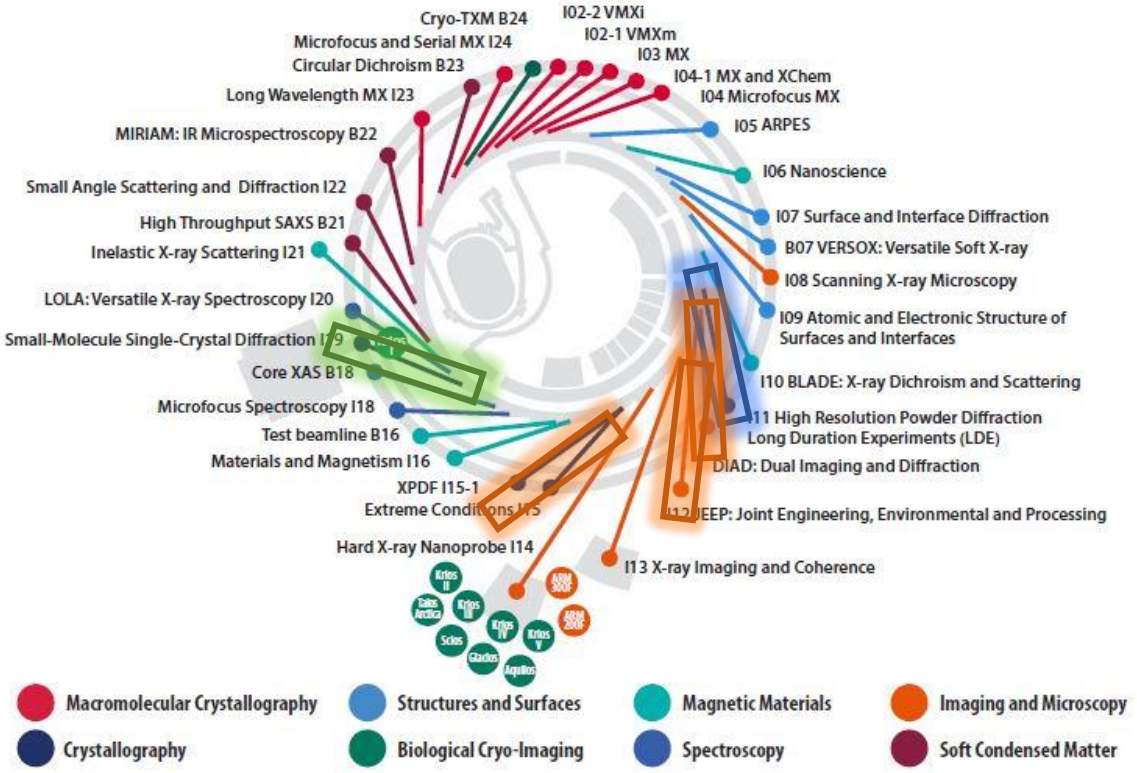
Beamline Scientist - Beamline I11

Diamond Light Source

diamond

Diamond Light Source

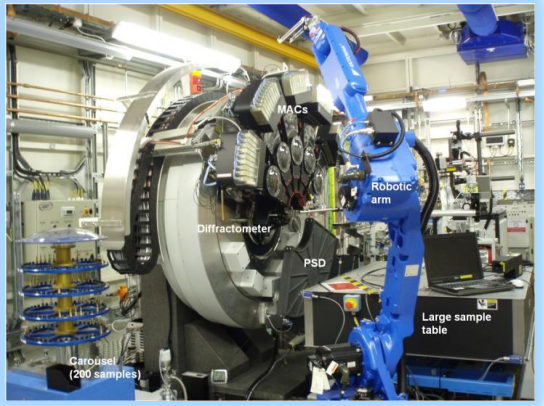




I19



I11



Outline

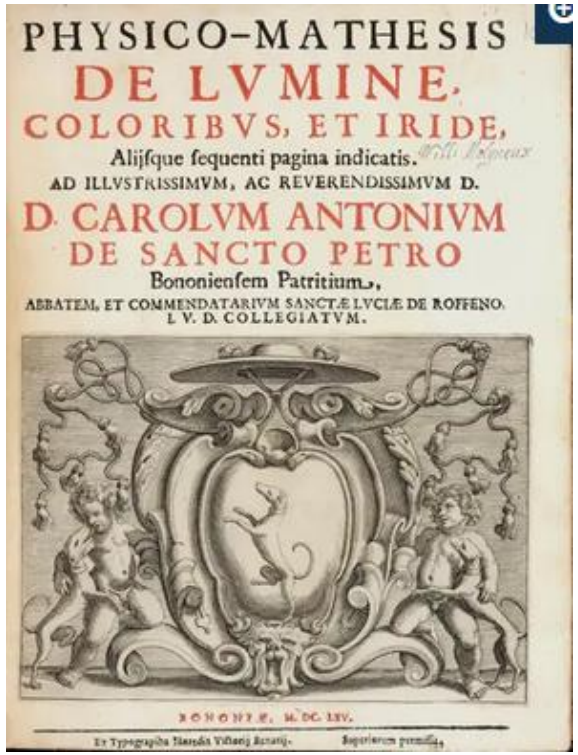
- Introduction to the history and theory of Diffraction
- What does Diffraction tell us: Single Crystal vs Powder
- Why is Synchrotron Radiation so important?
- Capabilities of Synchrotron Powder Diffraction

History and Theory of Diffraction

1665

First recorded observation of diffraction

Francesco Maria Grimaldi


PHYSICO-MATHESIS
DE LVMINE,
COLORIBVS, ET IRIDE,
Aliſque ſequenti pagina indicatis.
AD ILLVSTRISSIMVM, AC REVERENDISSIMVM D.
D. CAROLVM ANTONIVM
DE SANCTO PETRO
Bononienſem Patritium,
ABBATEM, ET COMMENDATARIVM SANCTÆ LVCIÆ DE ROFFENO.
I. V. D. COLLEGIATVM.

First coined the term “diffraction” to describe the behaviour of light by the shape of the light cone after the light passed through a pinhole.

Although Leonardo DaVinci is said to have earlier noted this interaction in code that is now on display in the Museum of Science and Technology in London.

diamond



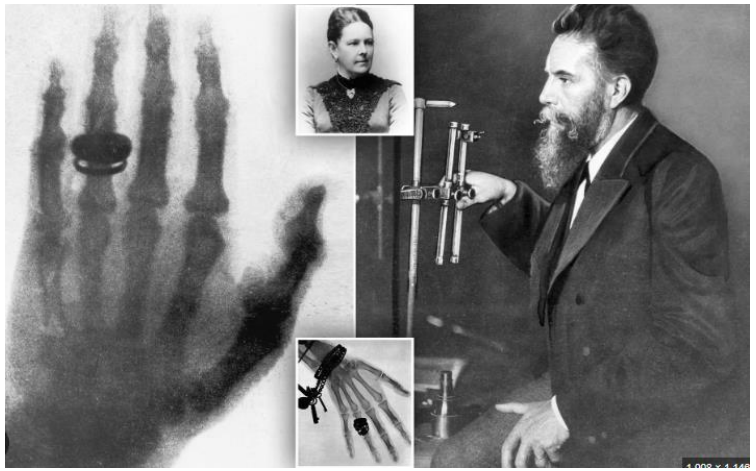
1665
First recorded observation of diffraction

A few centuries later, after many eminent scientists had elucidated the true nature of light in increasing detail, *Wilhelm Conrad Röntgen* made the discovery of his “X-rays” in 1895 while he was experimenting with discharge tubes, which were a hot topic of research at that time.

1895

Discovery of X-rays

Wilhelm Conrad Röntgen





1912

The first Single Crystal Diffraction experiment

Von Laue, Friedrich and Knipping

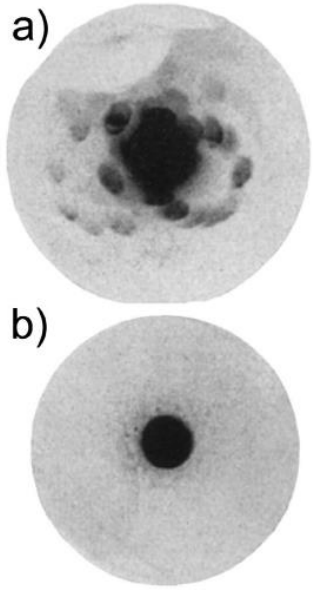
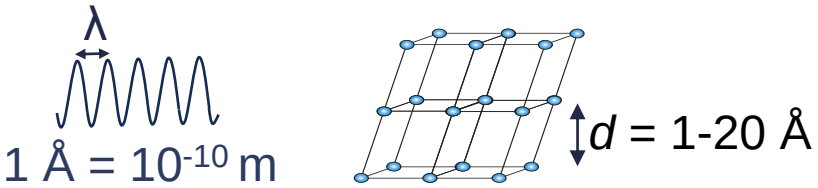
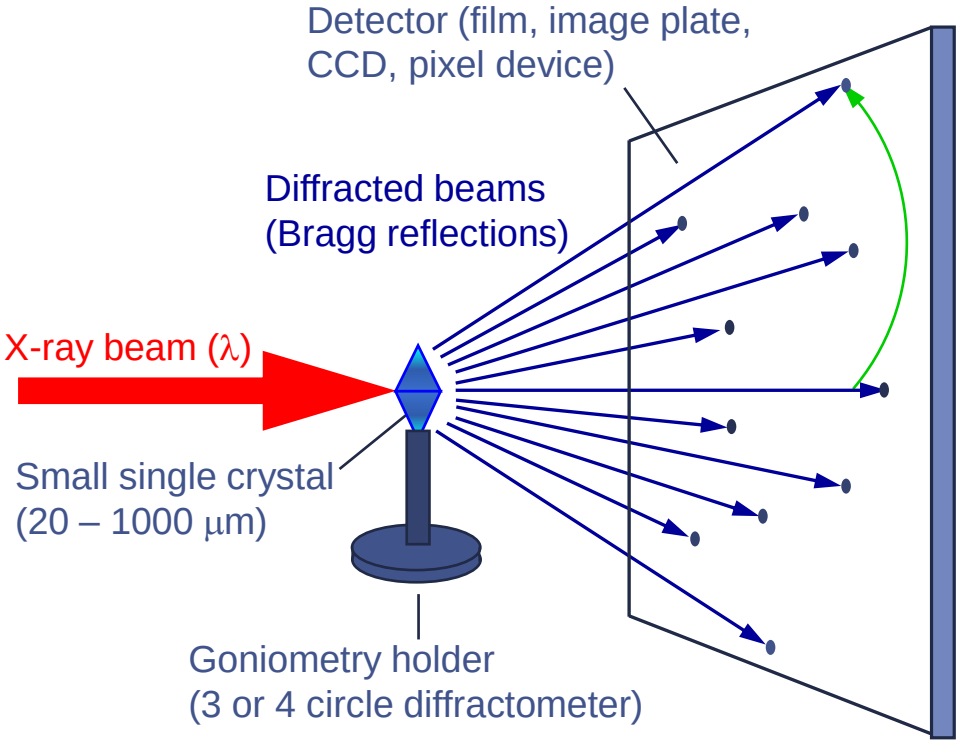


Figure 1. (a) First X-ray diffraction pattern of a copper sulfate single crystal recorded by *Friedrich* and *Knipping*.[13] (b) Subsequent X-ray diffraction pattern of a rough ground copper sulfate crystal.[13]



X-rays 0.1 – 5Å



Crystal structures in materials act as tiny diffraction gratings in 3D

Etter and Dinnebier, Z. Anorg. Allg. Chem. 2014, 3015–3028

diamond

1665
First recorded observation of diffraction

1895
Discovery of X-rays

1912
The first Single Crystal Diffraction experiment

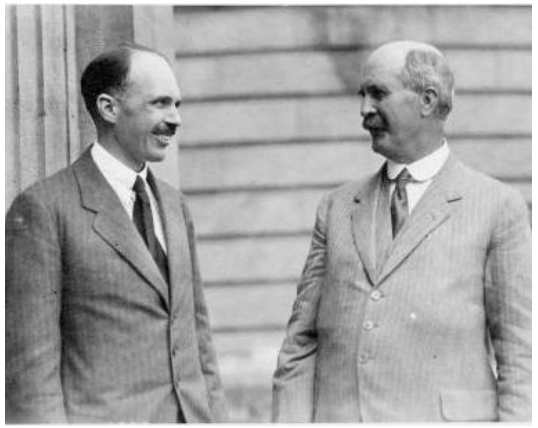
Fundamentally underpins crystallography and diffraction, describing the mechanism by which diffraction works.

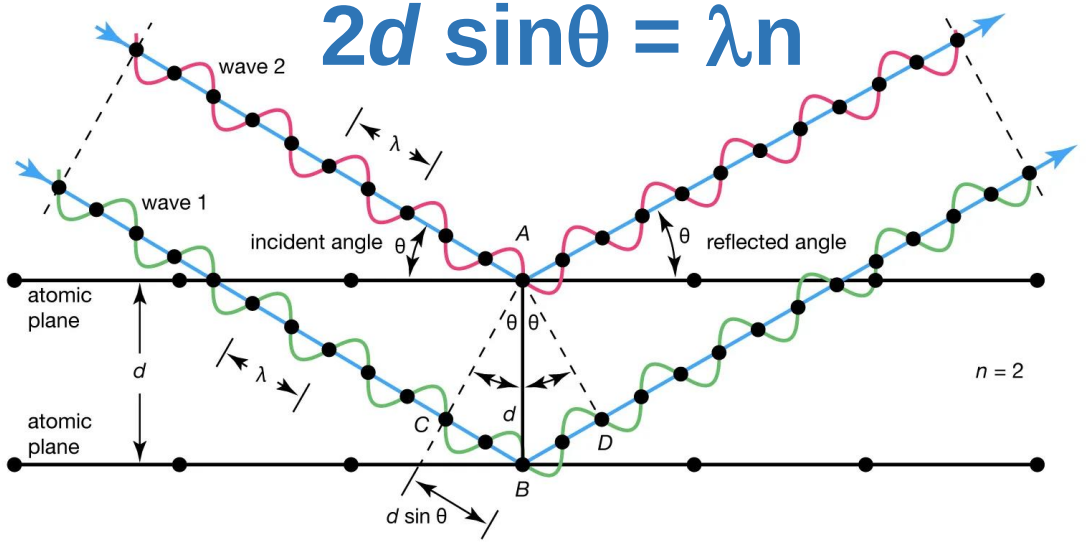
Bragg's law: $2d \sin\theta = \lambda n$

1912

Bragg's Law

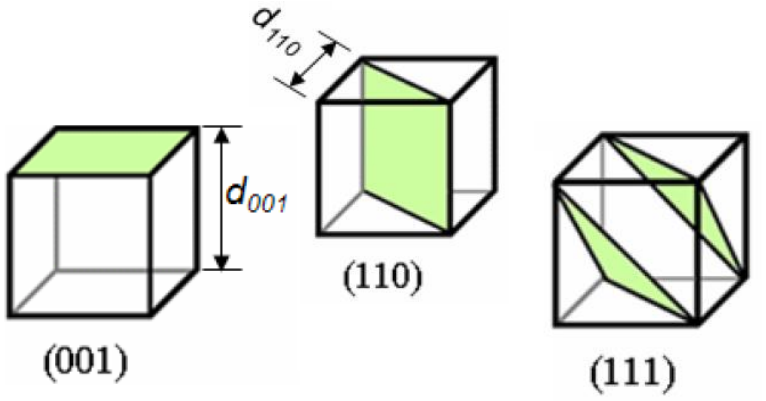
William and Lawrence Bragg





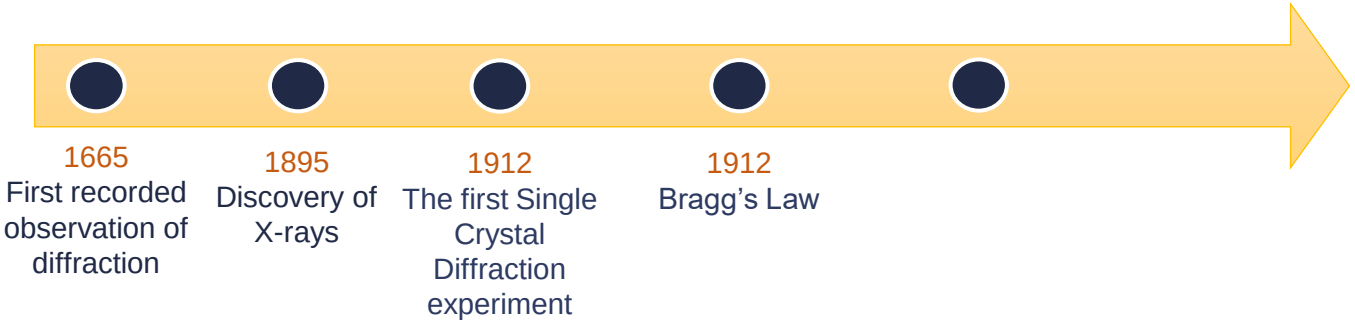
© Encyclopædia Britannica, Inc.

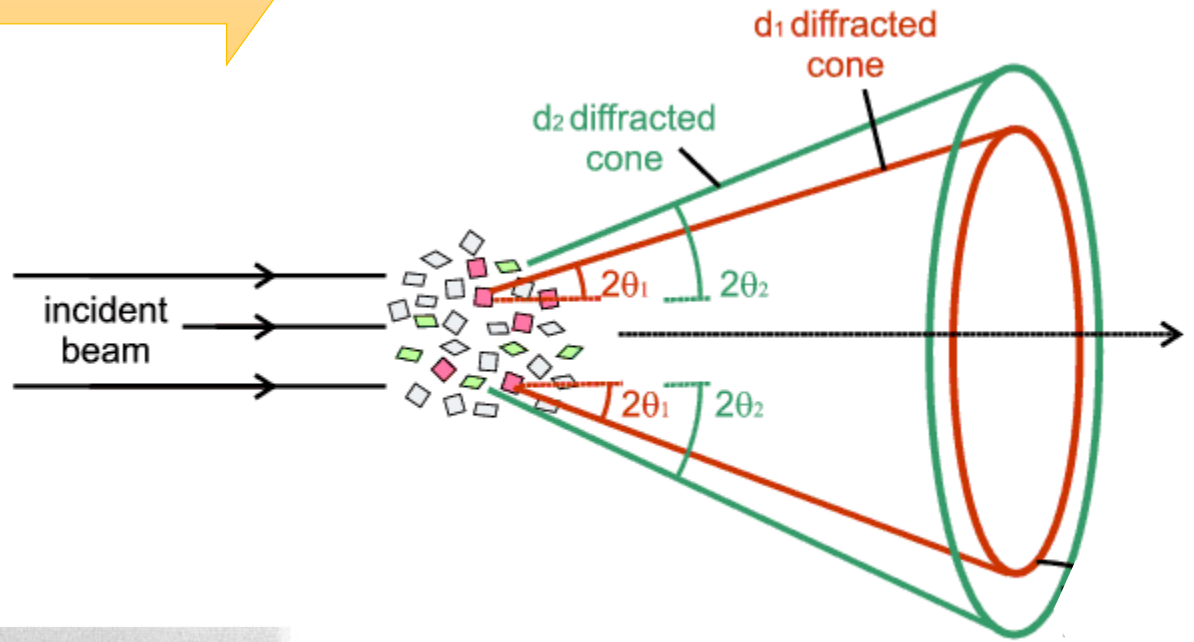
Elastic scattering from e- or atomic nuclei – no energy lost



Constructive interference from equally spaced planes creates peaks at specific 2θ values where path length change of incident beam is an integer value

diamond

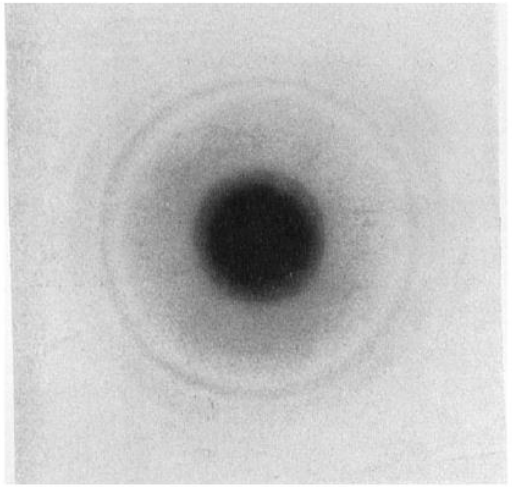




1913

First Powder Diffraction Experiment

Friedrich



Friedrichs first "powder" diffraction rings from white sticky wax.

Etter and Dinnebier, Z. Anorg. Allg. Chem. 2014, 3015–3028

Image Credit: Birkbeck College, University of London.
http://pd.chem.ucl.ac.uk/pdnn/diff2/kinemat2.htm

diamond

1665
First recorded observation of diffraction

1895
Discovery of X-rays

1912
The first Single Crystal Diffraction experiment

1912
Bragg's Law

1913
First Powder Diffraction Experiment

1916

Theory of Powder Diffraction

Debye, Scherrer and Hull

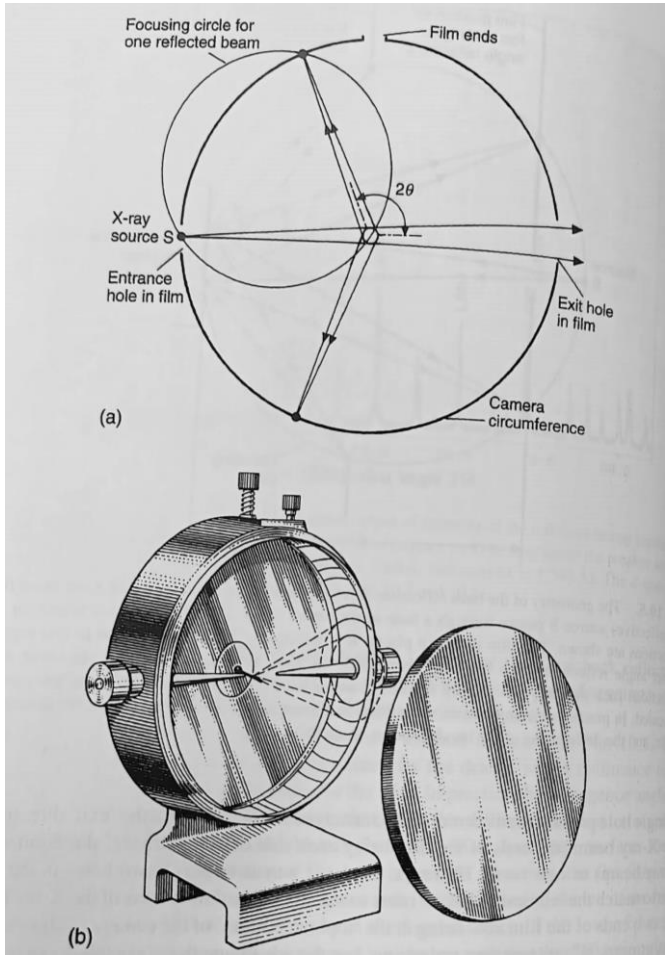
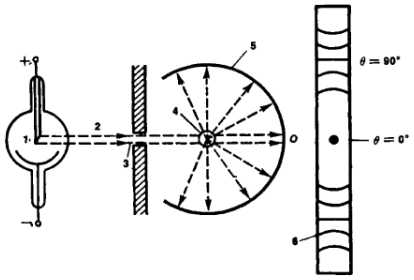
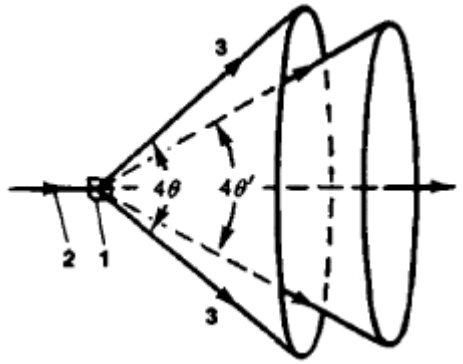


Fig. 10.6. (a) The geometry of the Debye–Scherrer camera; the reflected beams from a cylindrical specimen *tend* towards a focus on the film around the circumference of the camera and the focusing circle for a particular reflected beam is shown. In practice deviations from this idealized situation occur because the reflected beams originate with varying intensities from the whole volume of the specimen and the effective source S may not coincide with the circumference of the camera. (b) The camera with the light-tight lid removed showing the specimen at the centre, the collimator and receiving tube and the (low angle) X-ray diffraction rings on the film. The screws at the top are for locating and fixing the ends of the film (from *Manual of Mineralogy*, 21st edn, by C. Klein and C. S. Hurlbut Jr., John Wiley & Sons Inc., 1993).

Monochromatic radiation
Fine-grained, polycrystalline samples







Etter and Dinnebier, Z. Anorg. Allg. Chem. 2014, 3015–3028

1665 First recorded observation of diffraction

1895 Discovery of X-rays

1912 The first Single Crystal Diffraction experiment

1912 Bragg's Law

1913 First Powder Diffraction Experiment

1916 Theory of Powder Diffraction

Advancements in knowledge of diffraction, crystallography, X-ray sources

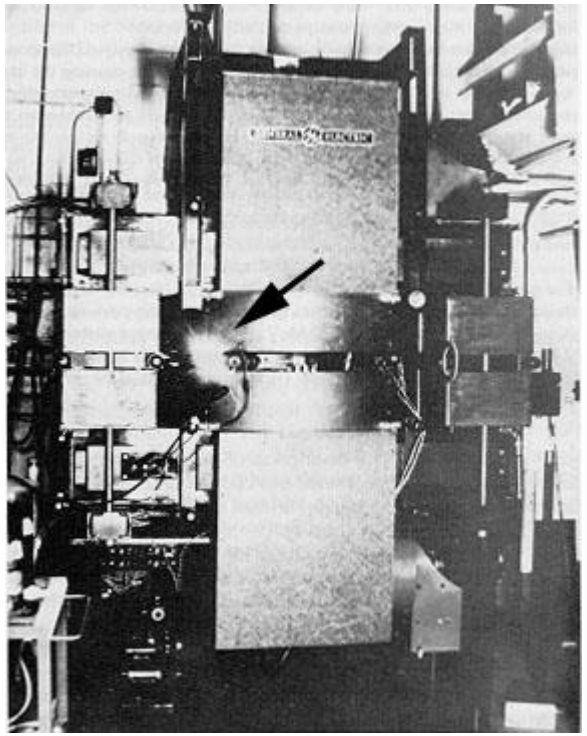
1947 Discovery of Synchrotron radiation

1981 First dedicated Synchrotron facility - Daresbury

1947

Discovery of Synchrotron radiation

General Electric Lab



Synchrotron light from the 70-MeV electron synchrotron at GE.
Image Courtesy of: Arthur L. Robinson (https://xdb.lbl.gov/Section2/Sec_2-2.html)

First dedicated Synchrotron facility was not built until 1981 – SRS at Daresbury, UK!



Etter and Dinnebier, Z. Anorg. Allg. Chem. 2014, 3015–3028

1665
First recorded observation of diffraction

1895
Discovery of X-rays

1912
The first Single Crystal Diffraction experiment

1912
Bragg's Law

1913
First Powder Diffraction Experiment

1916
Theory of Powder Diffraction

Advancements in knowledge of diffraction, crystallography, X-ray sources

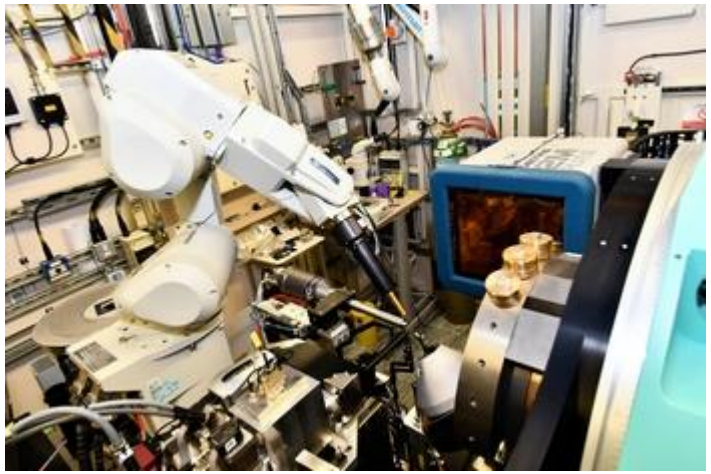
1947
Discovery of Synchrotron radiation

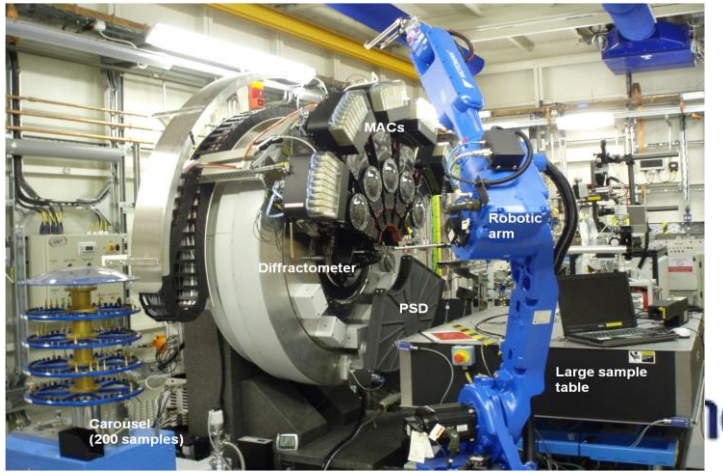
1981
First dedicated Synchrotron facility - Daresbury



Over the following years, the techniques were improved through technological advancements (better x-ray sources), improved understanding of the principles of crystallography, modern software etc…

Now diffraction is a widely used, powerful technique for probing the structure and properties of materials and is readily available in most university labs and synchrotron facilities worldwide!





hond

Sc-XRD Beamlines

I19, Diamond (UK)
12.2.2, ALS (USA)
CRISTAL, SOLEIL (France)
ID27, ESRF (France)
BM01, ESRF (France)
P24, PETRAIII (Germany)
BL02-B1, SPring-8 (Japan)
13-BM-C, APS (USA)
15-ID-C,D, APS (USA)
and others…

Upcoming:

SINCRYS, MAX IV (Sweden)

PXRD Beamlines

BL02-B2, SPring-8 (Japan)
ID22, ESRF (France)
CRISTAL, SOLEIL (France)
X04SA, Swiss Light Source
I11, Diamond (UK)
ID09, SESAME (Jordan)
PD, Australian Synchrotron
MSPD, Alba (Spanish SR)
12.2.2, ALS (USA)
and others…

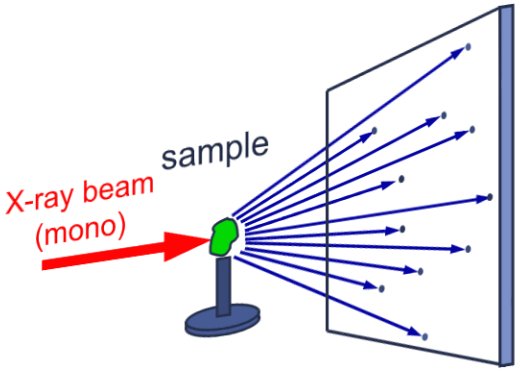
Also offer PXRD:
I15, Diamond (UK)
I12, Diamond (UK)
DIAD, Diamond (UK)

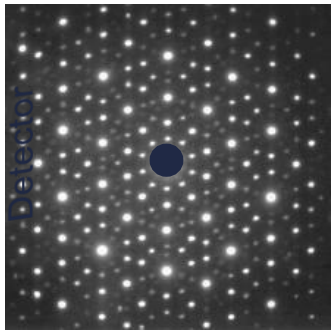
diamond

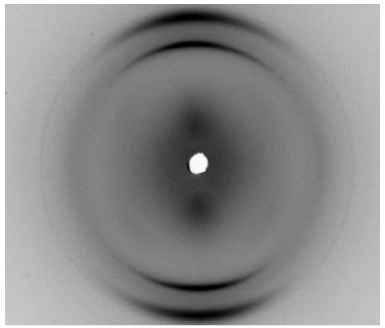
Single Crystal vs Powder Diffraction

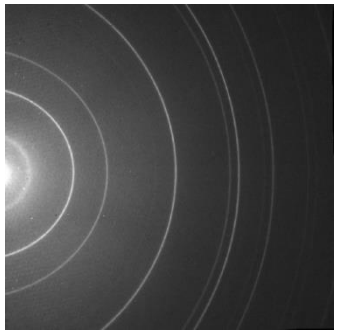
Material Classifications (forms)

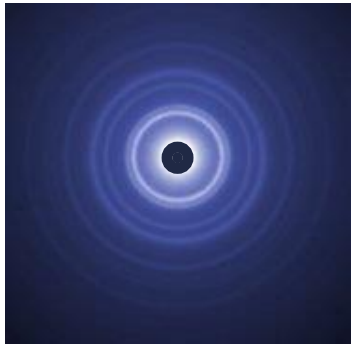
Order → *Disorder*

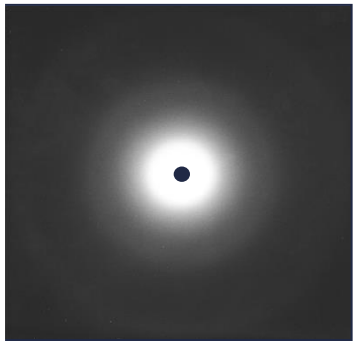




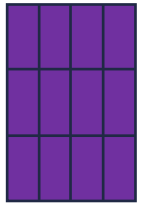






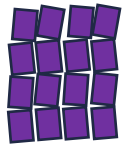


Single crystal



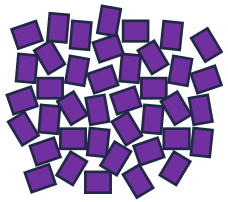
Individual single-crystal

Textured powder (preferred orient.)



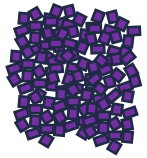
Multiple individual crystallites but not randomly orientated. Preference to one direction

Powder (μ-particle, random)



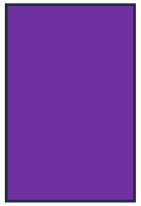
Ideal powder sample, randomly orientated crystallites

Powder (nano-particles)



Crystallites too small, restricted number of atomic planes causes broadening of peaks

Amorphous



No long range order, diffuse scattering – PDF

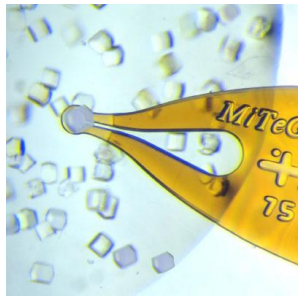
diamond

Single Crystal Diffraction

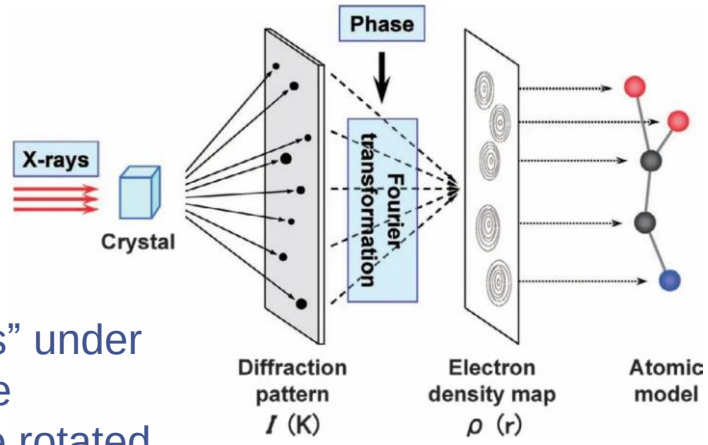


Image Credit: https://www.ncs.ac.uk/

Sc-XRD is a crystallographic method for the determination of structures at the atomic level.



Single crystals are mounted onto “loops” under a microscope and placed onto a 4-circle diffractometer, allowing the crystal to be rotated through all possible angles, with data collected on an area detector collecting frames in 0.1° to 0.3° increments.



The Rigaku Journal, 28(1), 2012

The intensities and positions of the diffracted signals allow us to obtain a three-dimensional map of the electron density in the unit cell of the sample.

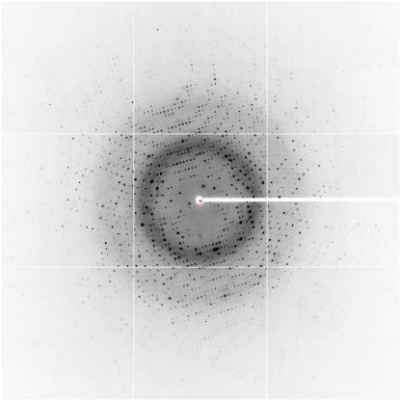
In this map, the positions of the atoms can be located and therefore the molecular structure of the sample determined.

The solved crystal structure enables the study of molecular packing and of non-bonding interactions.

BUT not all materials can form single crystals easily and this doesn’t give a bulk representation of the material being probed so powder diffraction can be used.



Eiger2 4M CdTe detector



diamond

What do we mean by “powder”?



But also









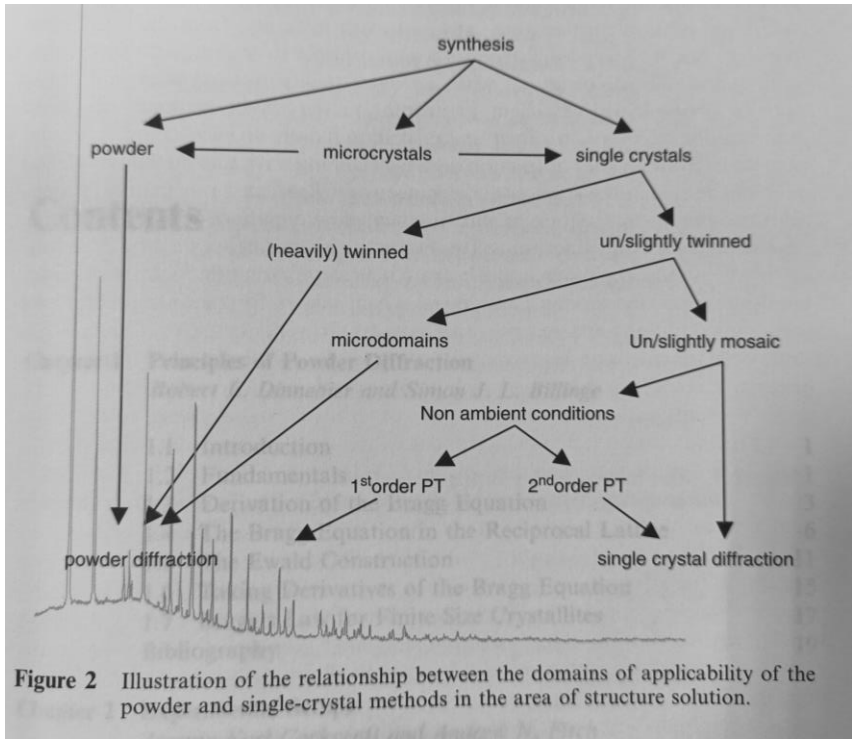


Figure 2 Illustration of the relationship between the domains of applicability of the powder and single-crystal methods in the area of structure solution.

Many important, functional materials are poly-crystalline, not always in typical “powder” form.

Benefits of powder diffraction:

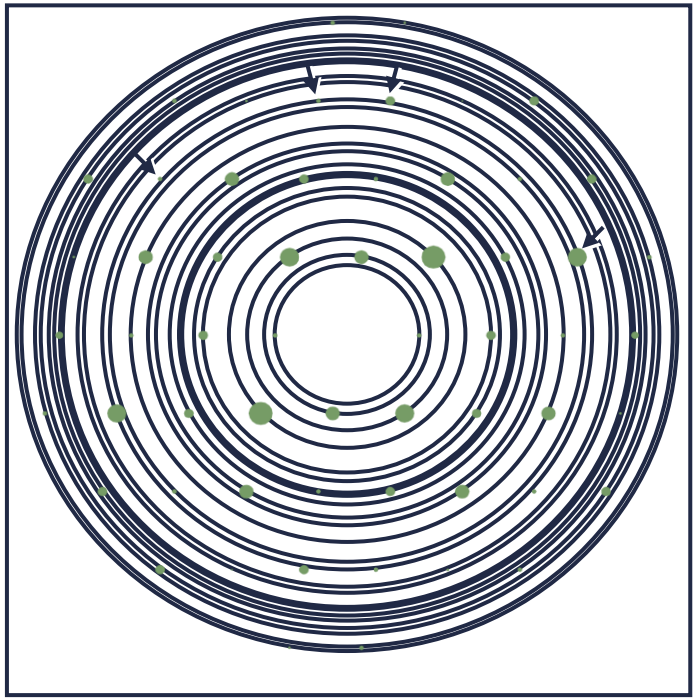
- Bulk representation of material – homogeneity
- Often easier to synthesise and prepare
- Fast data collection
- Very useful for phase ID – database matching
- Can be used for determination of microstructure, stresses

diamond

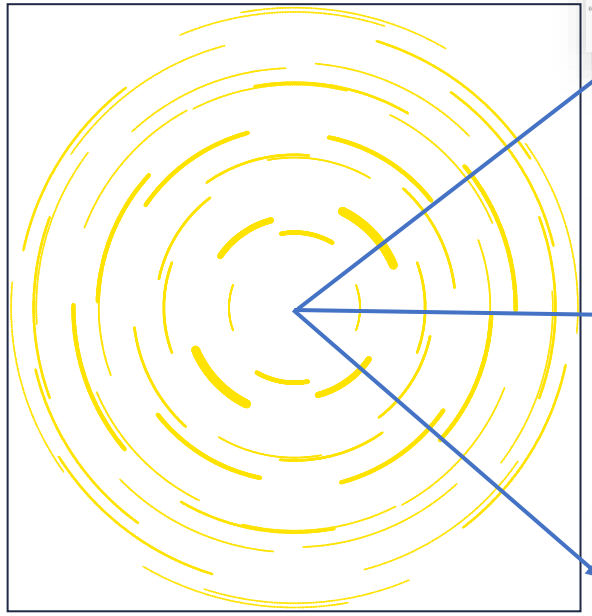
Powder Diffraction: Theory and Practise, Dinnebier and Billinge, 2008

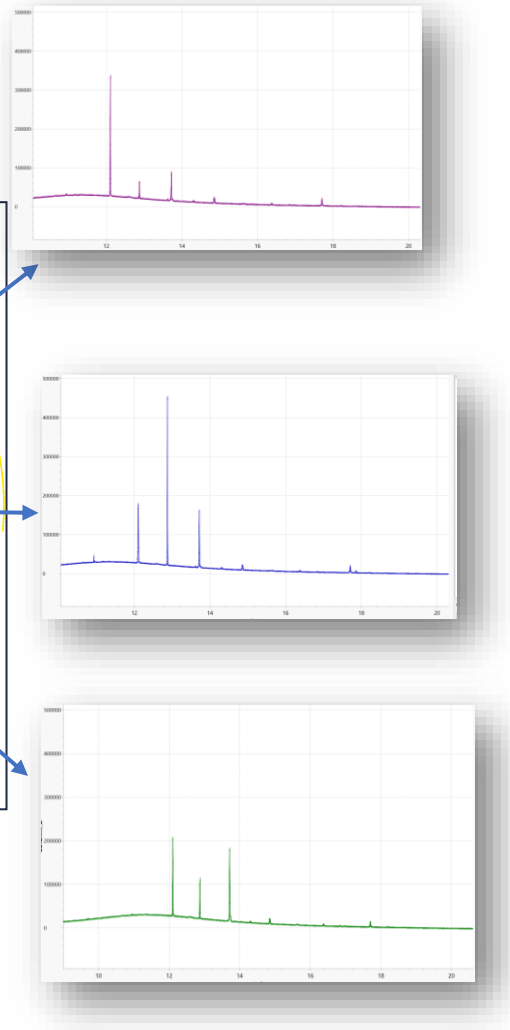
Potential issues in Powder Diffraction

Loss of angular resolution due to overlapping peaks

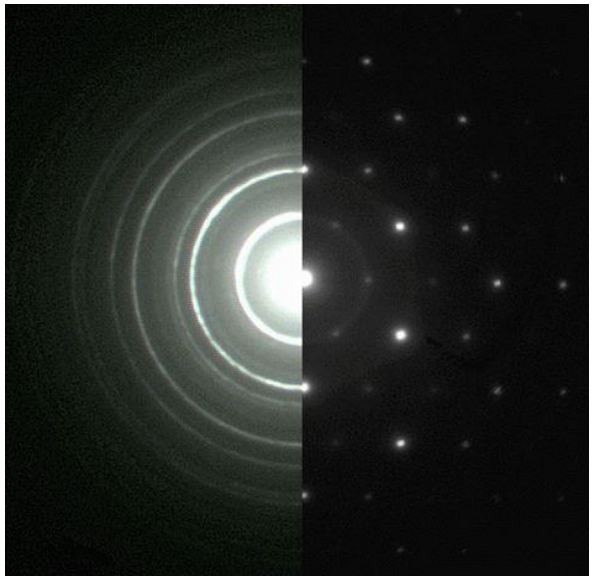


Texture from preferred orientation

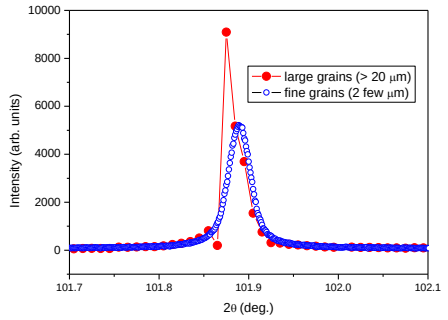




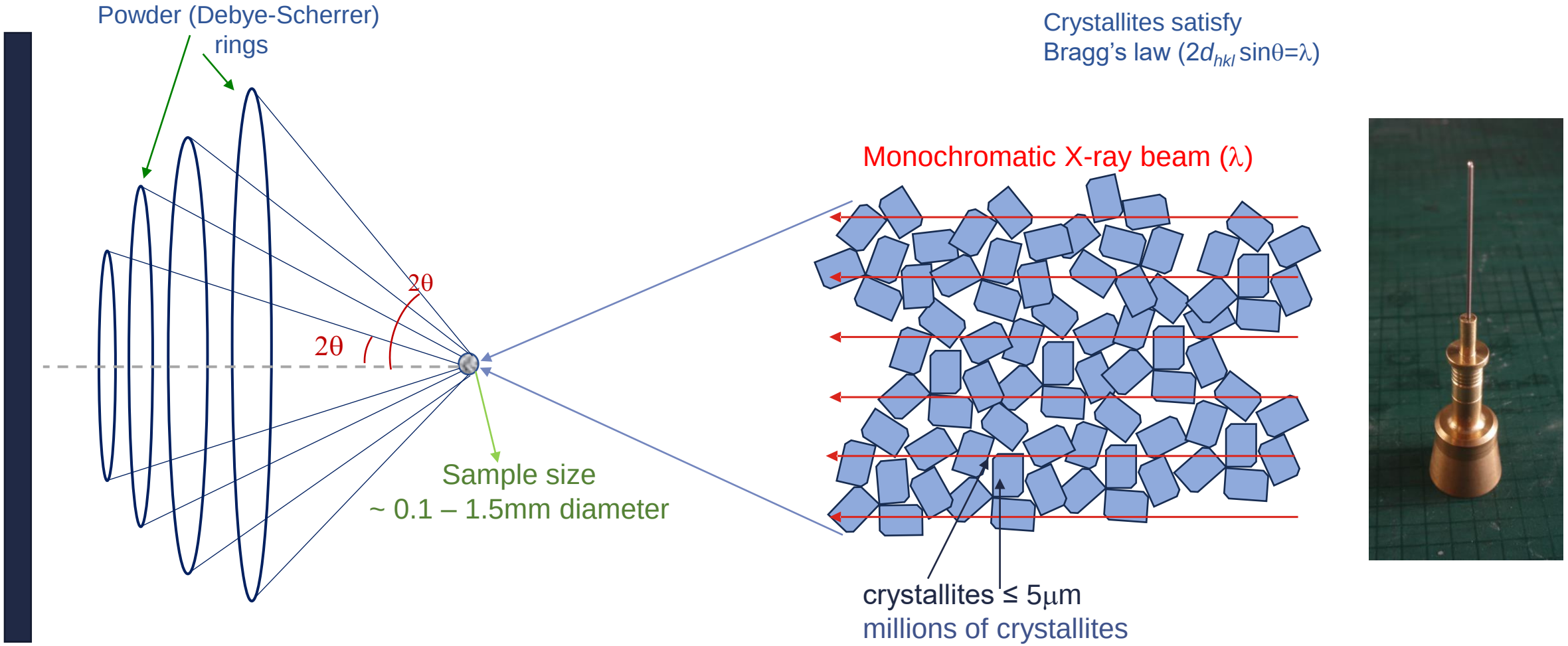
Particle Size



~ few um >20um



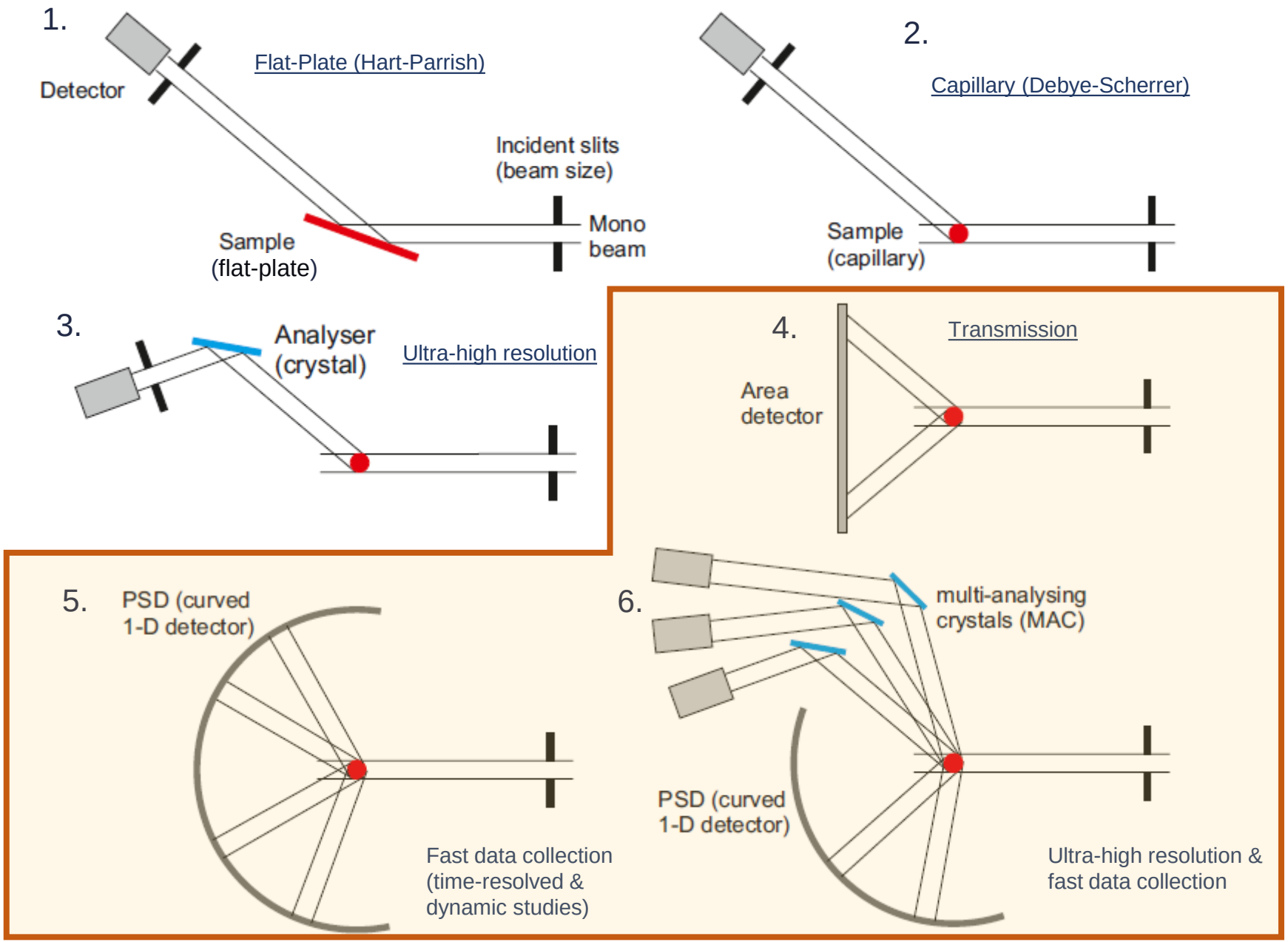
Powder Diffraction



In powder diffraction, the ideal sample consists of a vast number of very tiny crystallites (random orientation)!

diamond

Diffraction Geometries



Area Detectors

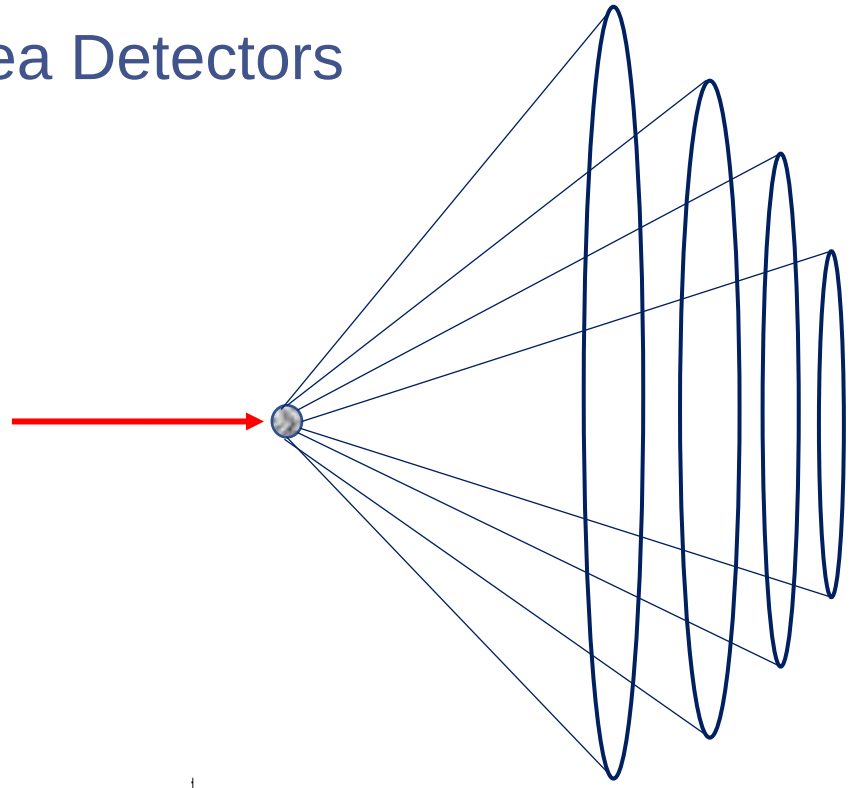
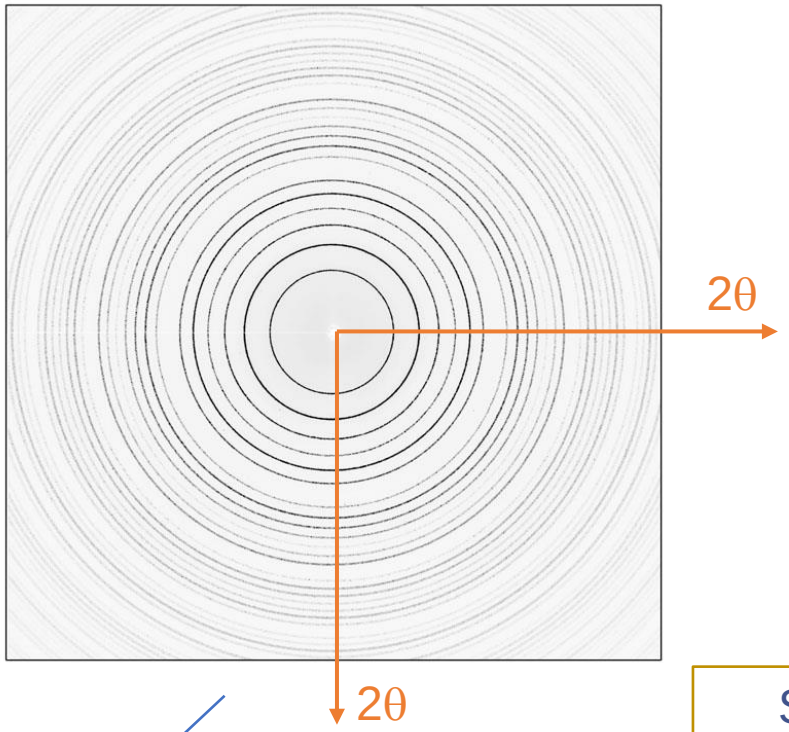


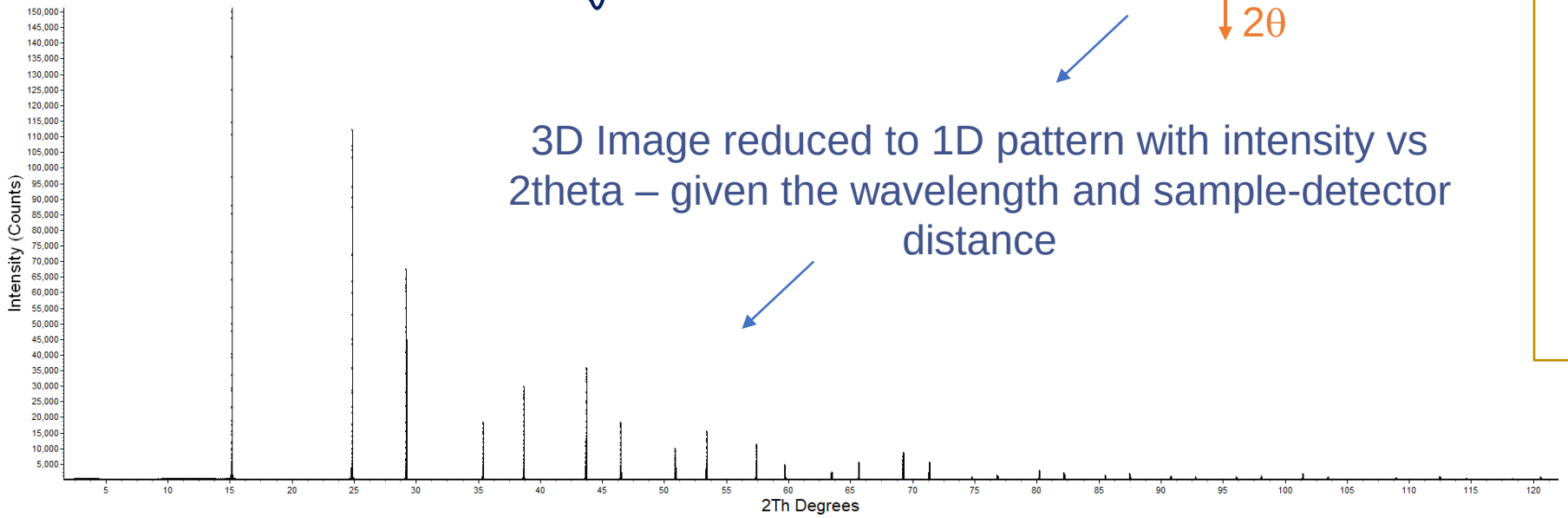
Image plate,CCD



Good resolution dependant on:

- pixel-size
- sample-detector distance
- beam size

Good for observing texture in materials

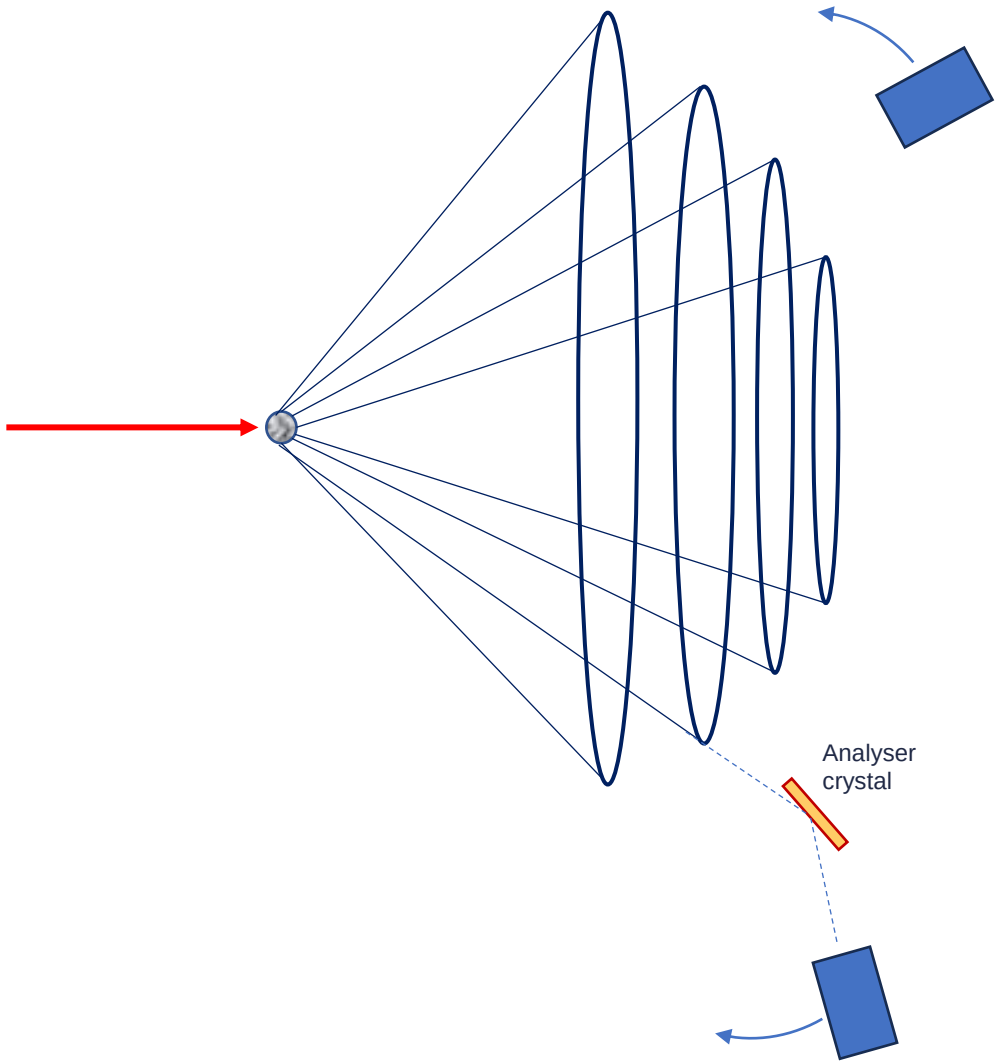


3D Image reduced to 1D pattern with intensity vs 2theta – given the wavelength and sample-detector distance

Sample to Detector distance must be determined accurately, ideally with a standard material (Si, CeO2, LaB6) at the sample position.

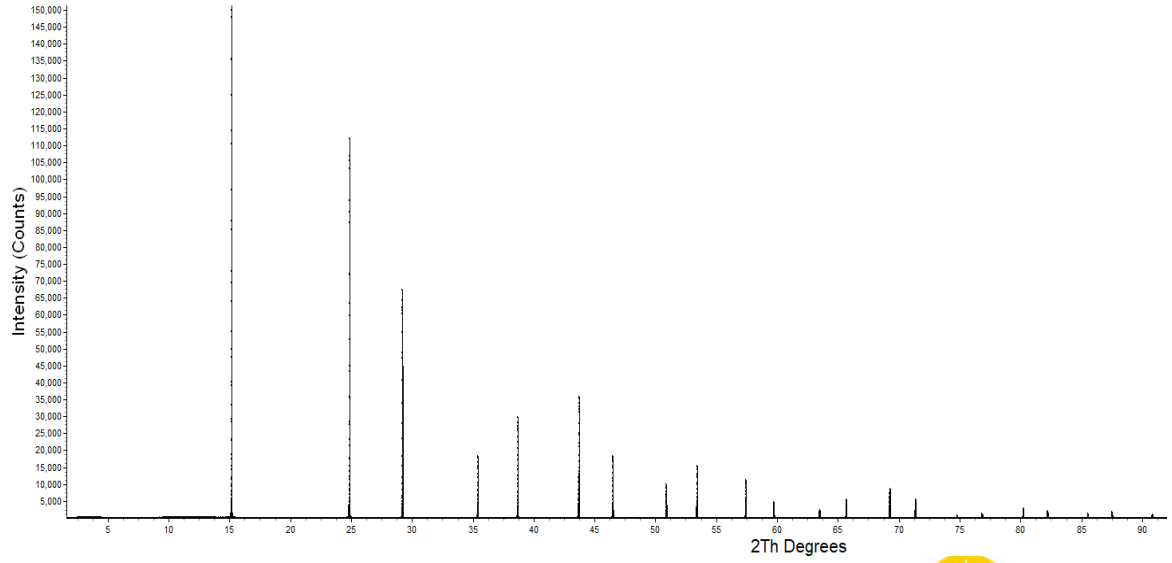
diamond

Point Detectors

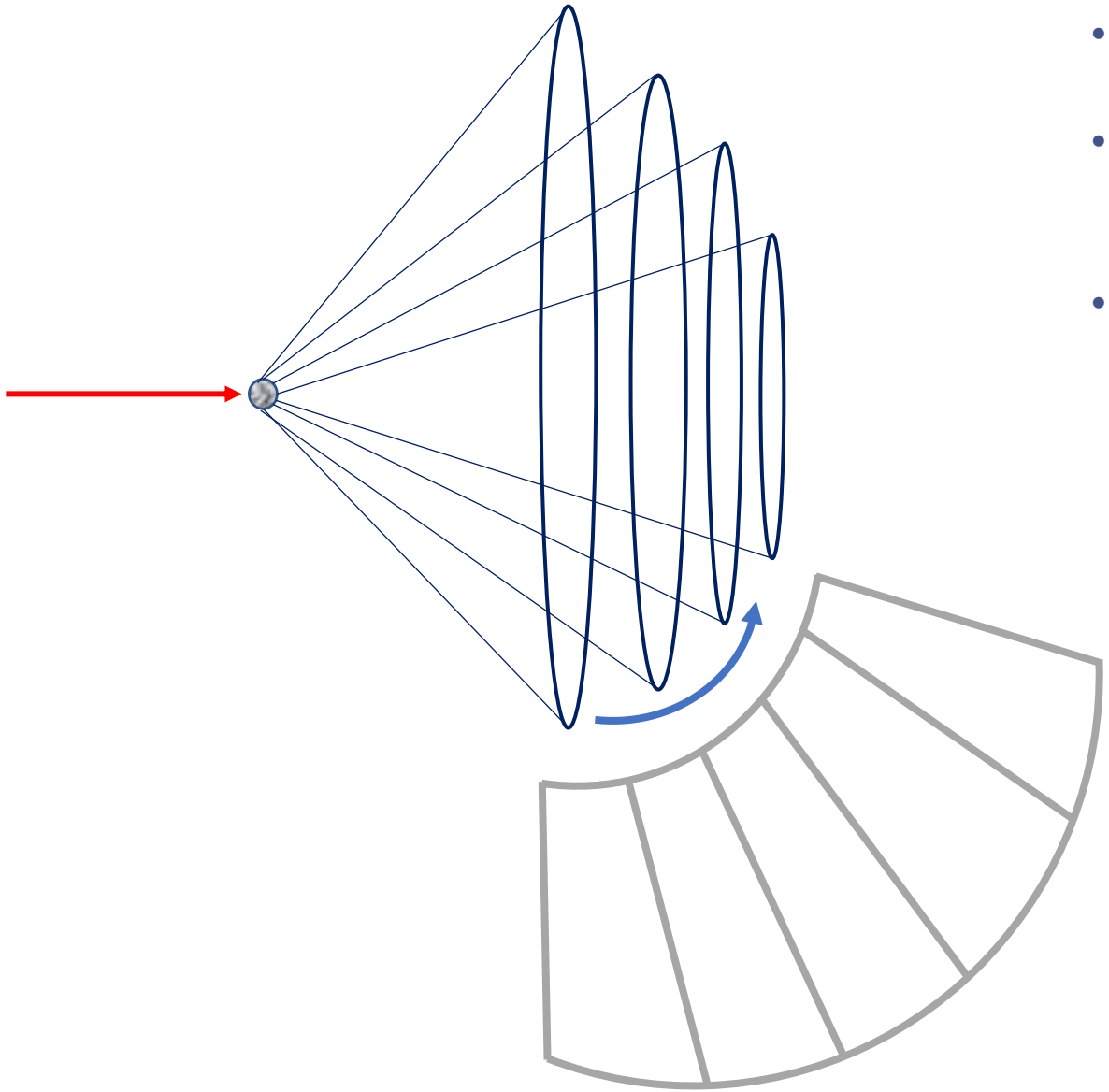


- Must be scanned to measure a diffraction pattern over a certain range
- Easily compatible with other post sample optics, such as slits and analyser crystals which can improve resolution, reduce parasitic scatter and reducing effects of sample misalignment.

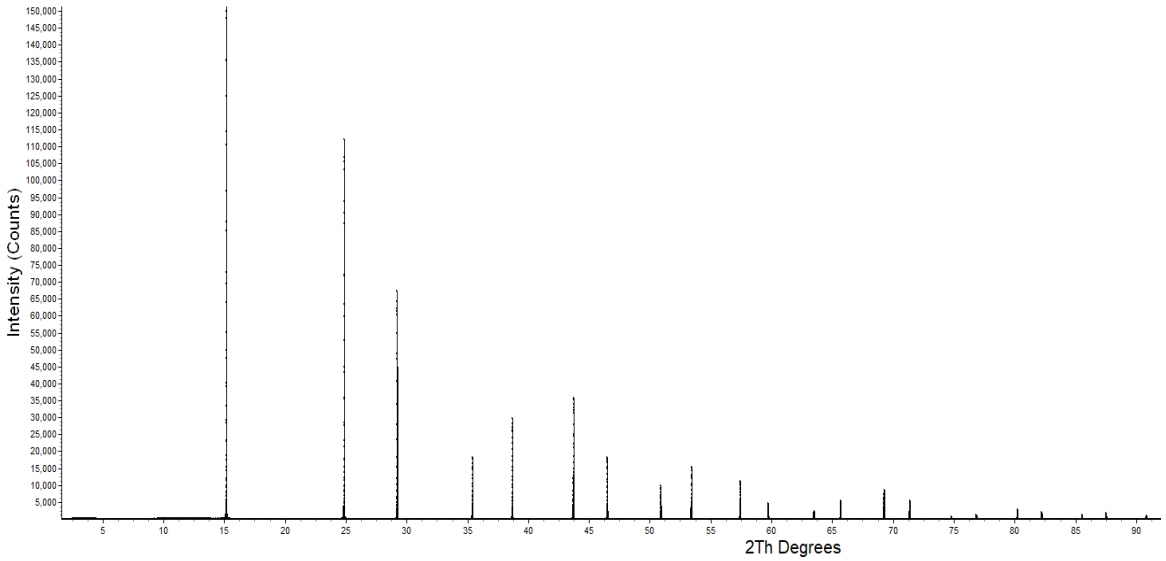
The most common type of detector in the laboratory



Linear Detectors

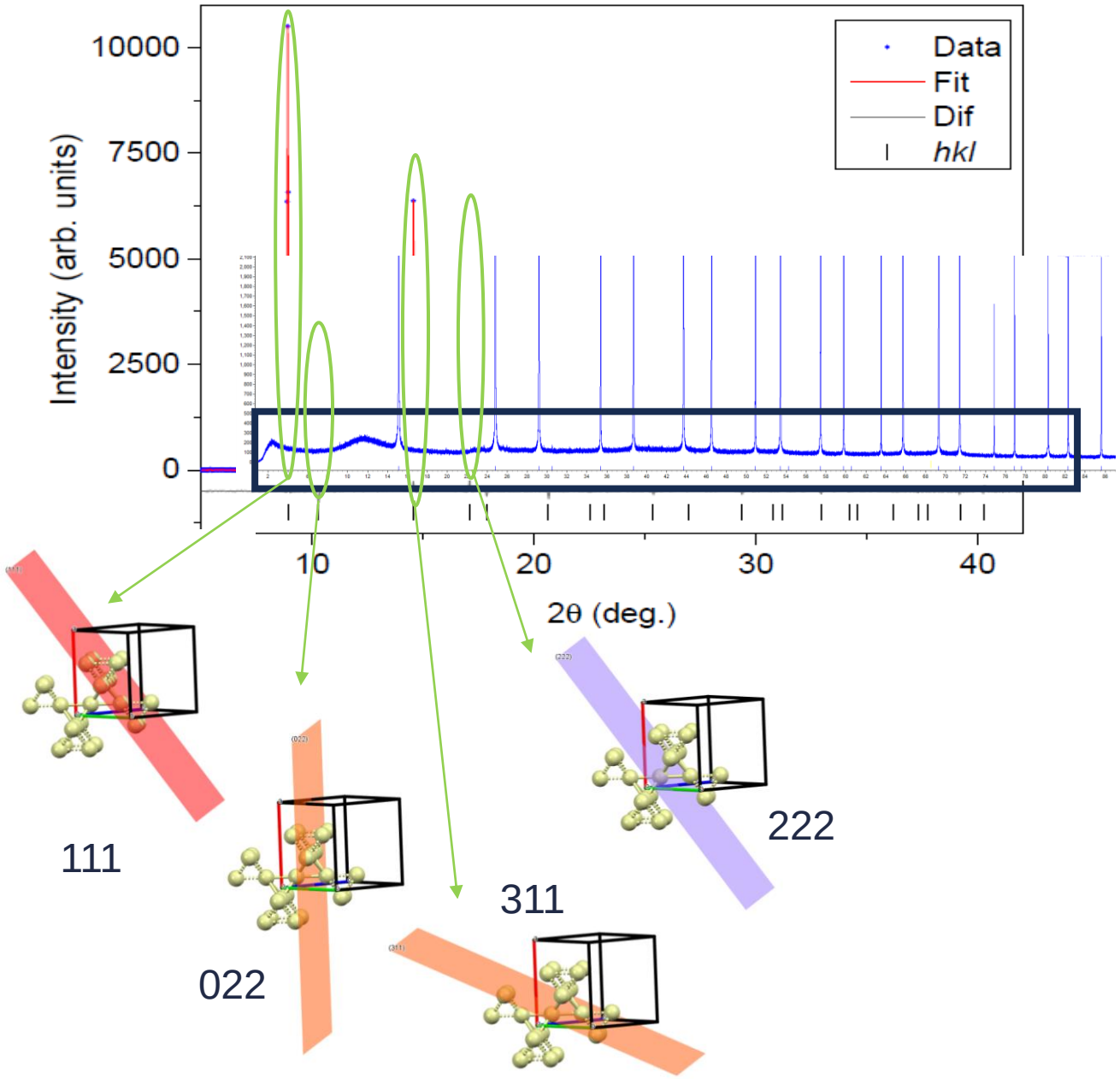


- Used in fixed position, with fixed aperture
- Multiple detection modules (e.g. Mythen)
- Faster than point detectors but more prone to effects of parasitic scatter and sample alignment issues
- Very fast scan times for time-resolved measurements



Breaking down a powder diffraction pattern

– what can it tell us?



Qualitative analysis

Phase identification; “fingerprints” from unique patterns. Compare reflections positions and intensities to power diffraction databases such as CSD, ICDD, COD etc. using search-match software packages

Background

- Scattering from sample holder
- Sample – Diffuse Scattering due to local structure, amorphous components (PDF)

Reflections

- Position – Lattice Parameters, space group: macro-strain, thermal expansion
- Intensity – Crystal structure: Atomic positions, temperature factors, occupancy, texture
- Profile – Instrumental (minimal for synch.), sample broadening due to micro-strain, domain size

Intensity of a diffracted beam

The diffracted beam satisfies Bragg's law: $2d_{hkl}\sin\theta_B = \lambda$

Single Crystal

The intensity (I) of the diffracted beam from a small single crystal:

$I_{hkl} = k\,|\mathbf{F}_{hkl}|^2\,e^{-2M}$

k = scaling constant

$\mathbf{F}_{hkl}$ = structure factor

e^{-2M} = temperature term, where $M = B_n(\sin\theta_B/\lambda)^2$ and B_n is the isotropic temperature factor (Debye-Waller) of atom n.

Powder diffraction

$I_{hkl} = k\,|F_{hkl}|^2\,e^{-2M}\,p\,[LP]\,A(\theta)$

p = multiplicity factor

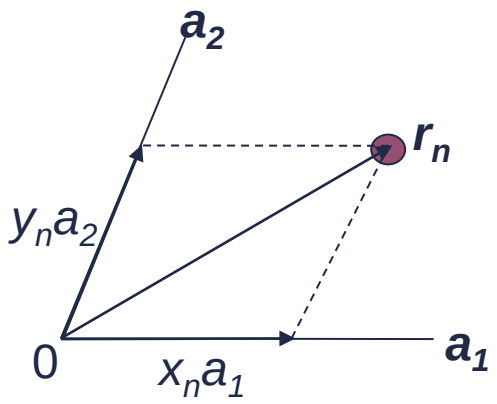
LP = Lorentz-polarisation factor (geometric)

A(θ) = absorption factor

The structure factor, $\mathbf{F}_{hkl}$ depends upon the atomic position (r_n)

$$\boldsymbol{r}_n = x_n\boldsymbol{a}_1 + y_n\boldsymbol{a}_2 + z_n\boldsymbol{a}_3$$

where x_n, y_n and z_n are the fractional coordinates in *a*, *b* and *c* lattice parameters, respectively, and the atomic scattering factor, f_n ($= f_o + f' + if''$).



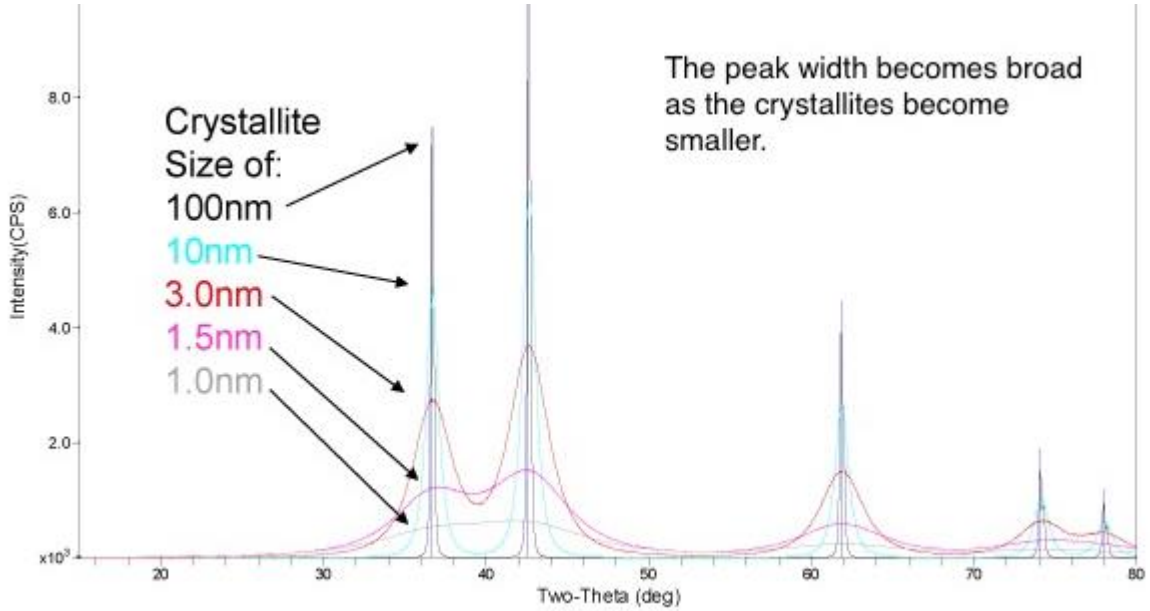
$$F_{hkl} = \sum_n f_n e^{2\pi\cdot i(hx_n+ky_n+lz_n)}$$

Improved contrast or "enhancement" is achieved when λ is tuned to an absorption edge (resonant diffraction), since *f'* can be large (e.g. Cu or Fe K-edge).

diamond

Peak Profile

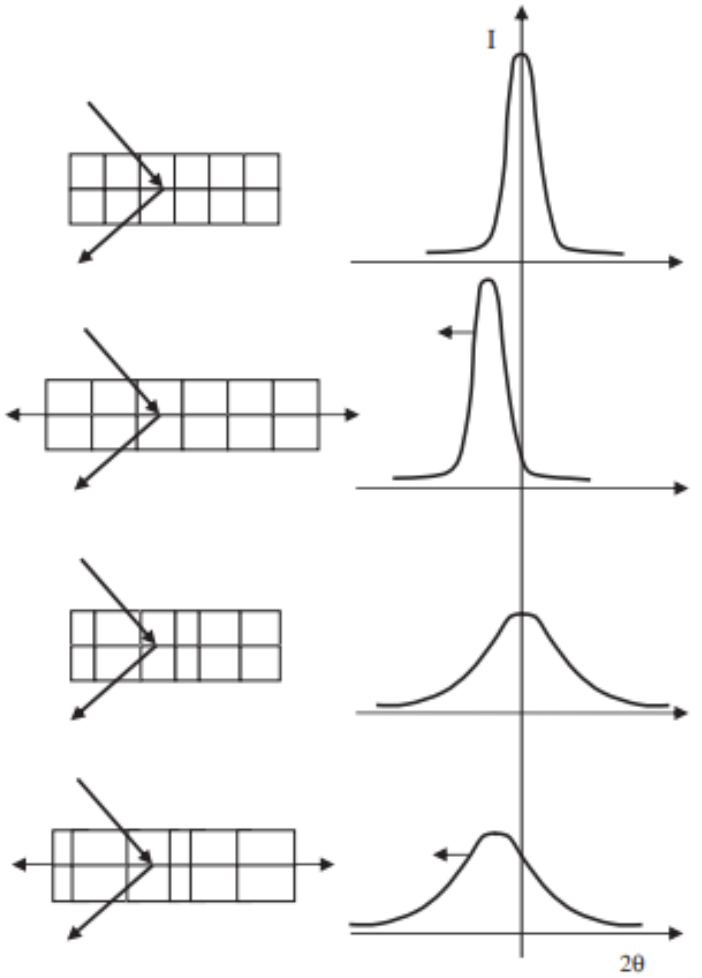
Crystallite Size



$$d = \frac{K\,\lambda}{\beta \cos\theta}$$

Where: λ is the X-ray wavelength
β is the corrected FWHM or IB (in radian),
θ is the Bragg angle (degree)
K is the Scherrer constant

Strain



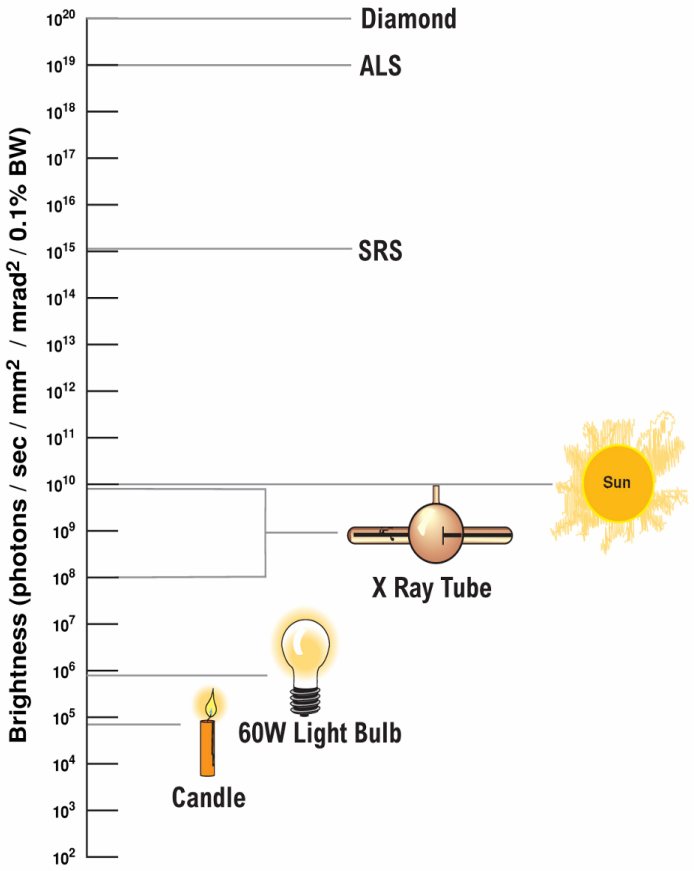
Macro strain	Micro strain
No	No
Yes	No
No	Yes
Yes	Yes

Langford, J. & Louer, D. & Scardi, P.. (2000). Journal of Applied Crystallography. 33. 964-974.

https://www.eag.com/app-note/crystallite-size-determination-using-xrd/

Why is synchrotron radiation so important for Diffraction?

Importance for diffraction:



High Brightness

- High Resolution
- Time-resolved ~ ms – s/pattern
- High spatial resolution (~ mm)

Wavelength tuneability

- Avoid sample absorption
- At absorption edges - Resonant diffraction (elemental tuning)

Large machine → spacious instrument

Non-ambient sample environments, e.g. cryogenic systems and furnaces

Single Crystal

Smaller crystals (~10 - 20 μm)

Poorly diffracting specimens

Time-resolved (high brightness, time structure)

Fast data collection: ~1 hr/sample (~ 1 day on lab machine)

Wavelength tuneability:
(i)high E for absorbing samples
(ii)Resonant diffraction (elemental tuning)

Powder

High brightness (intense and well collimated beam) – high resolution

Poor diffraction specimens

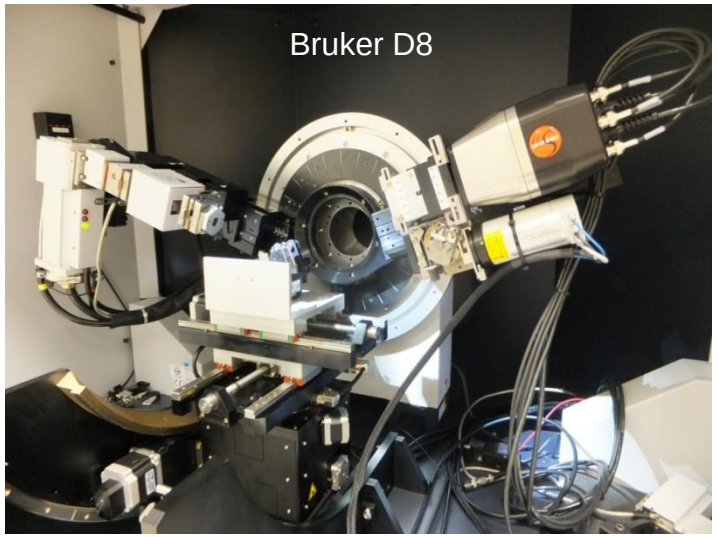
Time-resolved ~ ms – s/pattern

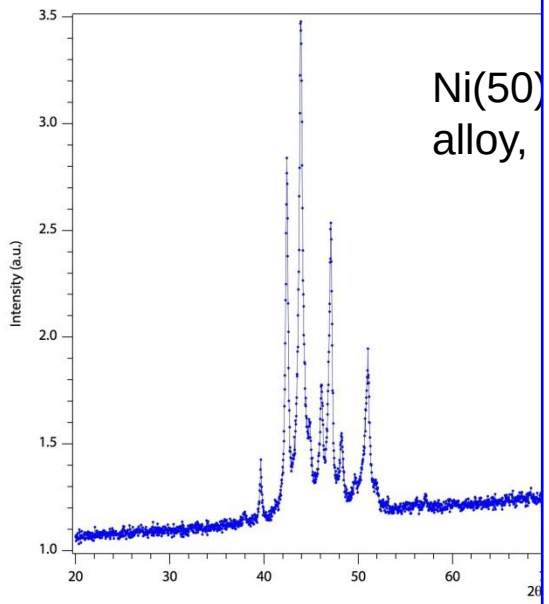
High quality data in short collection time

Wavelength tuneability:
(i)High E for absorbing samples
(ii)Resonant diffraction (elemental tuning)

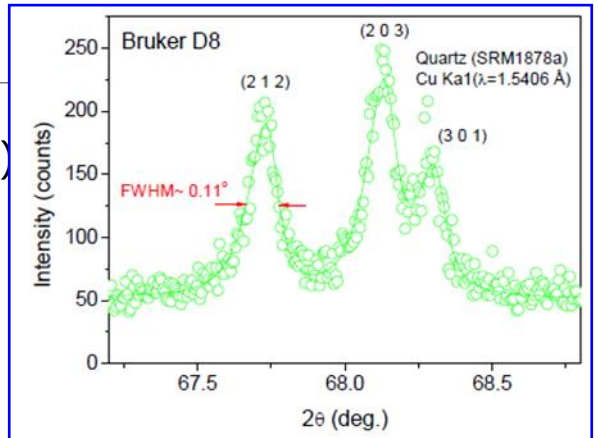
diamond

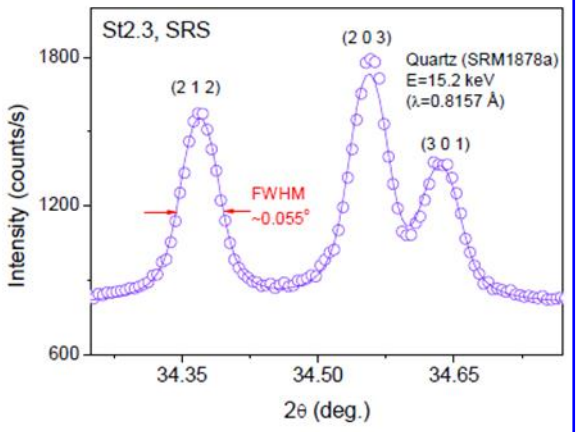
High resolution

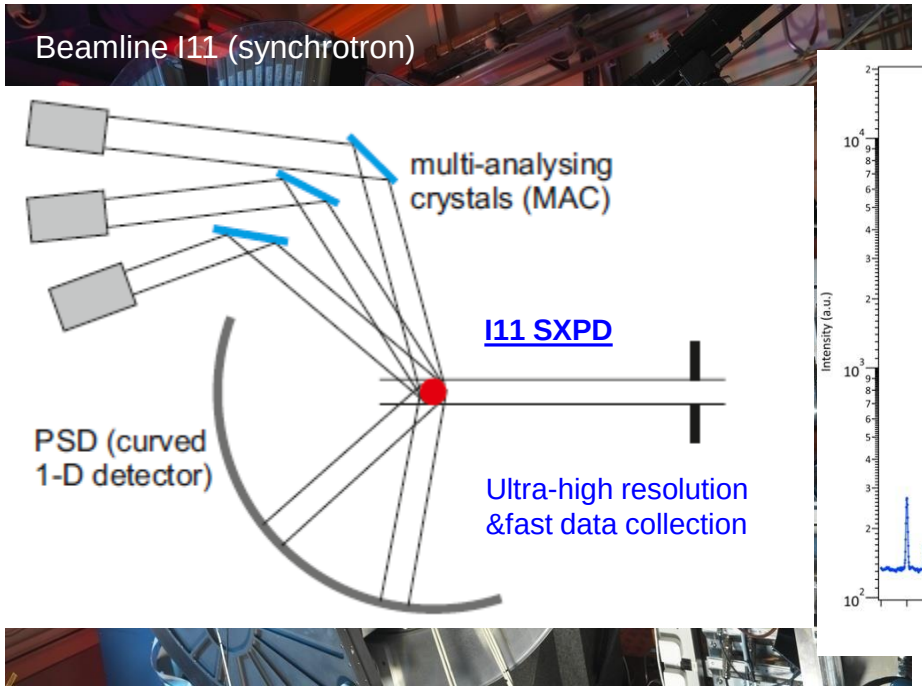




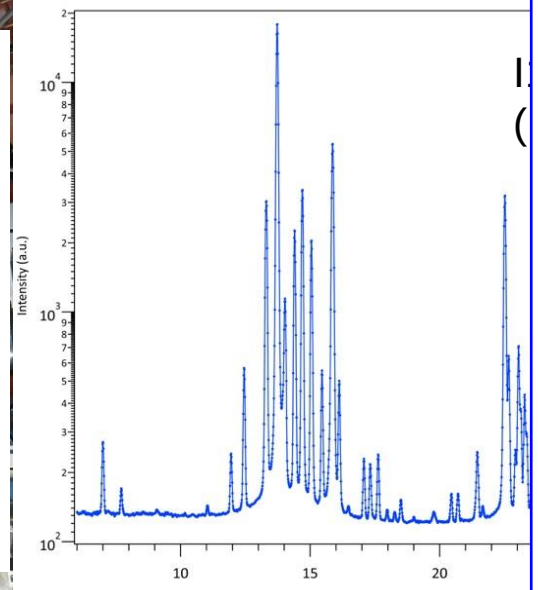
Ni(50)
alloy,

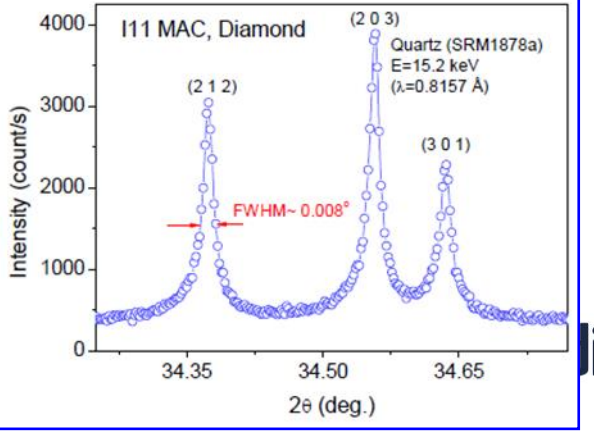






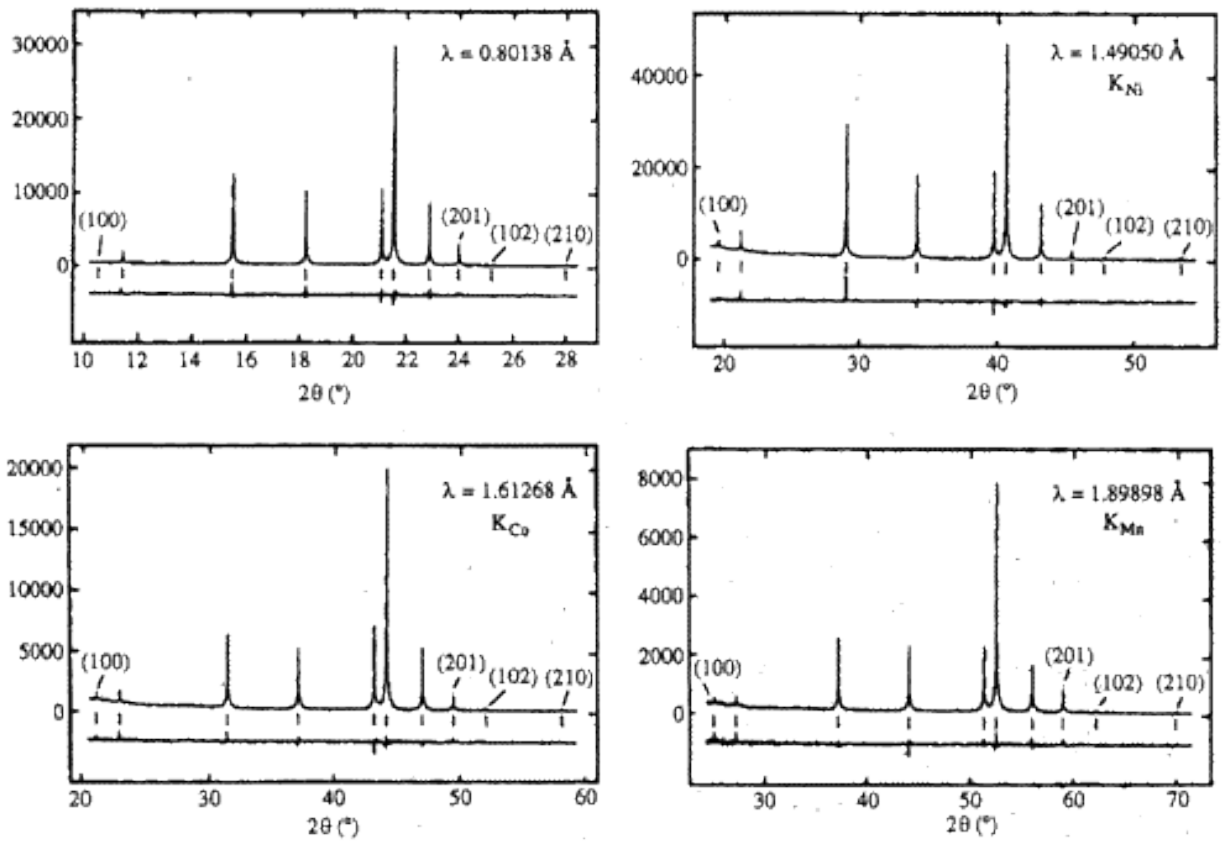
Ultra-high resolution
&fast data collection





Diamond

Resonant Diffraction



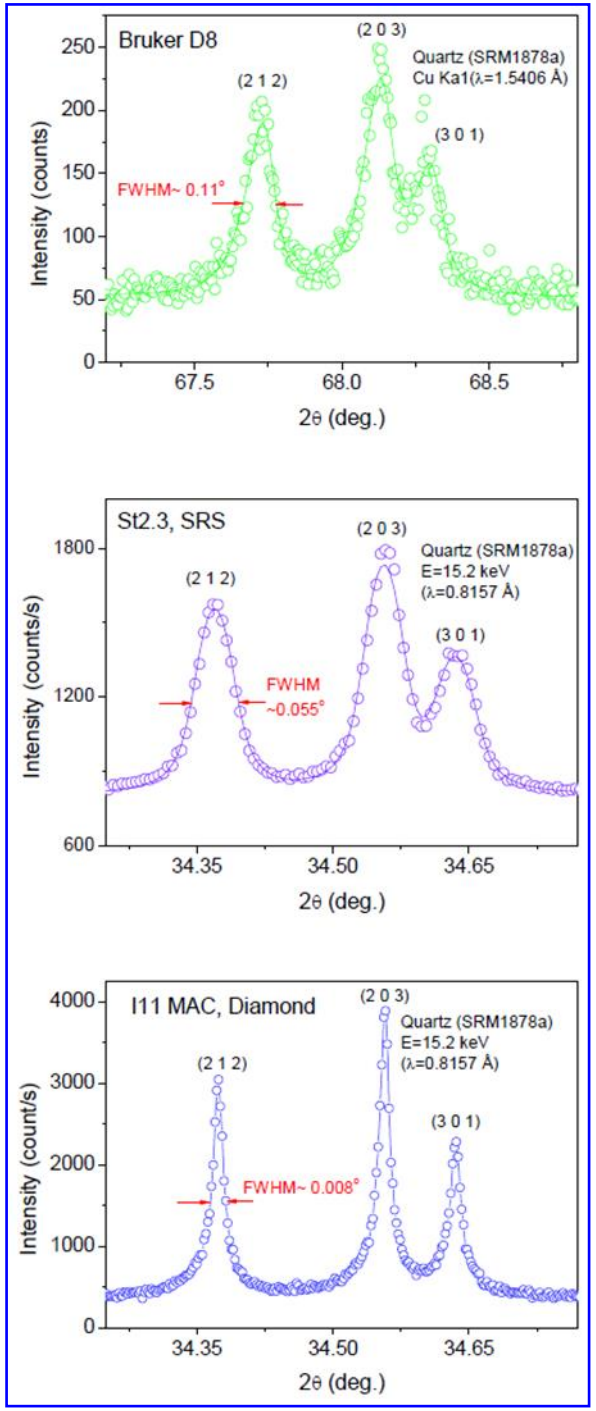
The observed and refined diffraction patterns of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ for wavelengths at the Ni, Co and Mn absorption edges

Wavelength tunability at synchrotron facilities allows for more advance diffraction methods such as resonant diffraction.

Tuning the wavelength of the incident beam to that close to the absorption edges of particular elements allows for enhanced contrast.

This is especially useful when investigating complex substituted systems containing multiple elements with similar atomic numbers, e.g. Ni, Co, Mn as shown in this example.

Joubert, J. M.; Cerny, R.; Latroche, M.; Percheron-Gueguan, A.; Yvon, K. *J. Appl. Crystallogr.* **1998**, *31*, 327.



XRPD (Lab)

Quantitative analysis –
(i) crystallographic cell dimensions and phase fraction determination, (ii) thermal properties, (iii) lattice distortion $\Delta d/d \sim 10^{-2}$ -10^{-4}

Structure refinements - determination of the unknowns

Qualitative analysis – material phase identification; "fingerprints" from unique patterns

Peak profile analysis (position and shape)
(i) strain (applied or residual) and stress
(ii) nano- and micro-features (crystallite size, stress/strain and defects)

SXPD (Synchrotron)

(i) High precision, < 1 wt%
(ii) Small changes and negative expansion
(iii) Subtle effects: bond stretching, tilts, $\Delta d/d \sim 10^{-4}$ -10^{-6}.

Precision refinements: improved solutions and determination of large complex structures

Minor phases in complex material matrices → significant to interpretations

Negligible instrumental contributions → reliable results and modelling

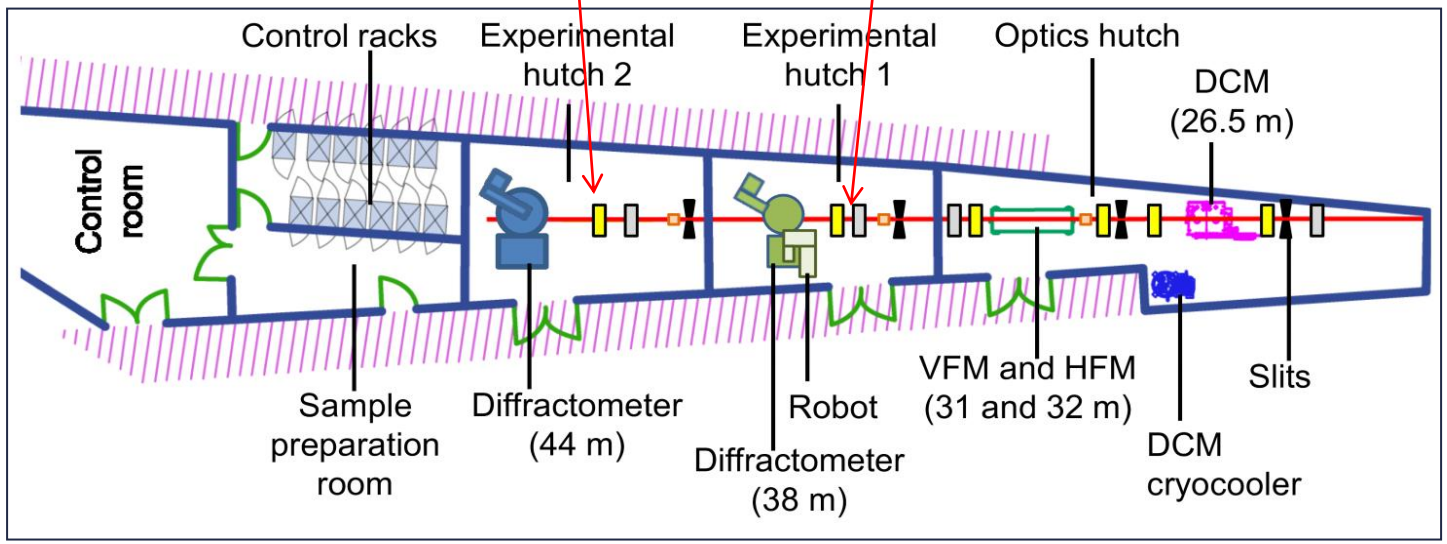
Time-resolved and non-ambient studies (high temp, pressure and reaction, etc.)

diamond

I19 (Sc-XRD) layout

Heavy-duty equipment for non-ambient work

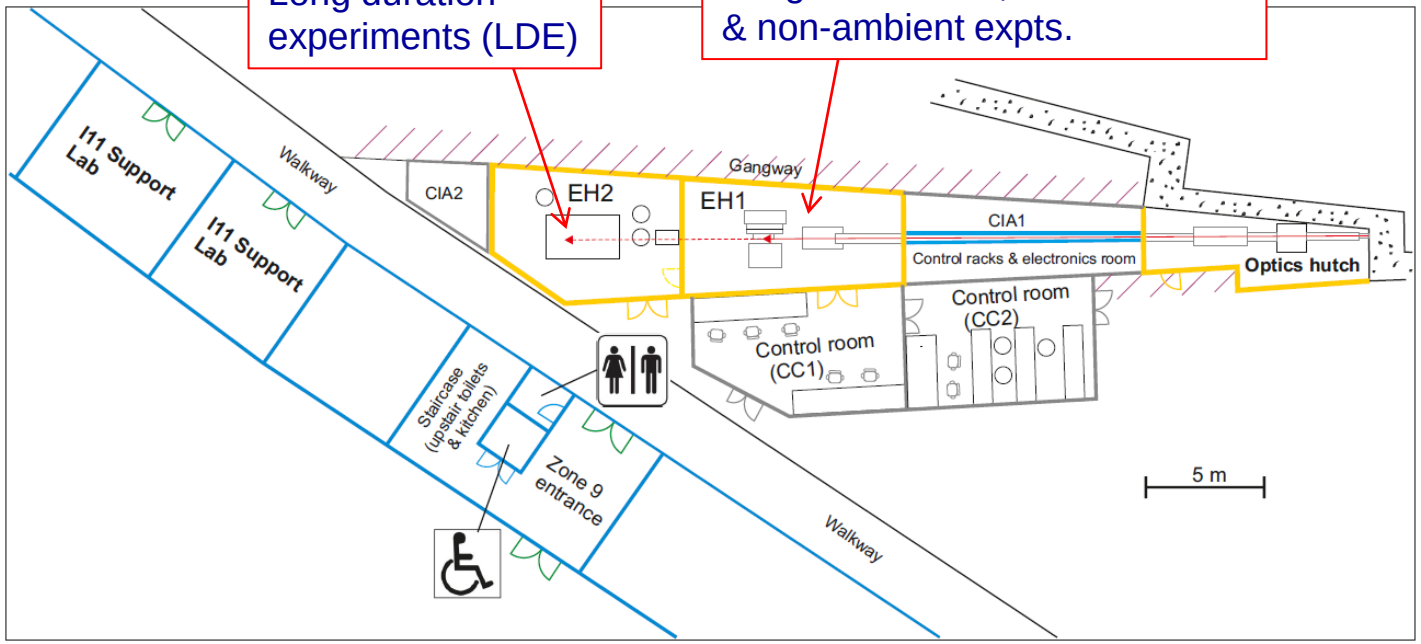
Routine and high throughput expts.



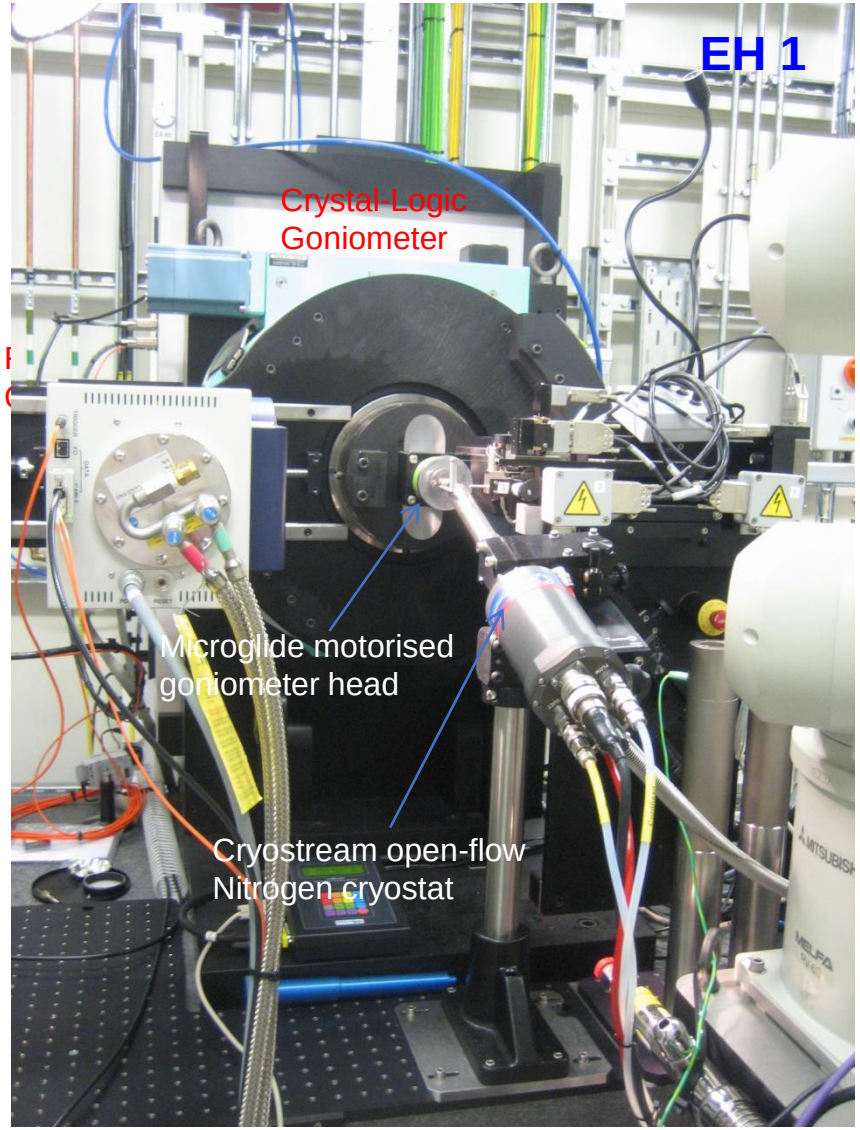
I11 (XRPD) layout

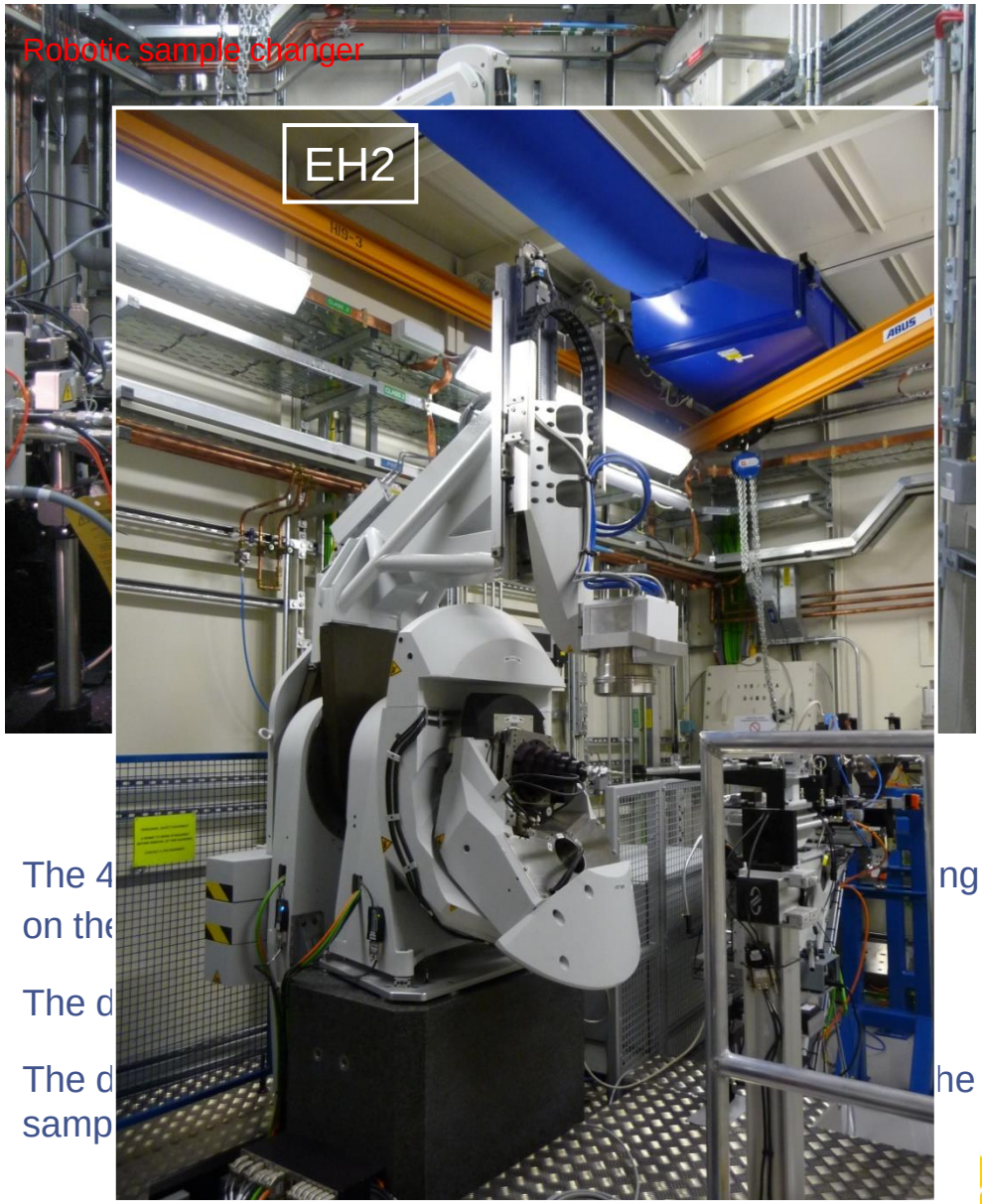
Long duration experiments (LDE)

υ-high resolution, time-resolved & non-ambient expts.



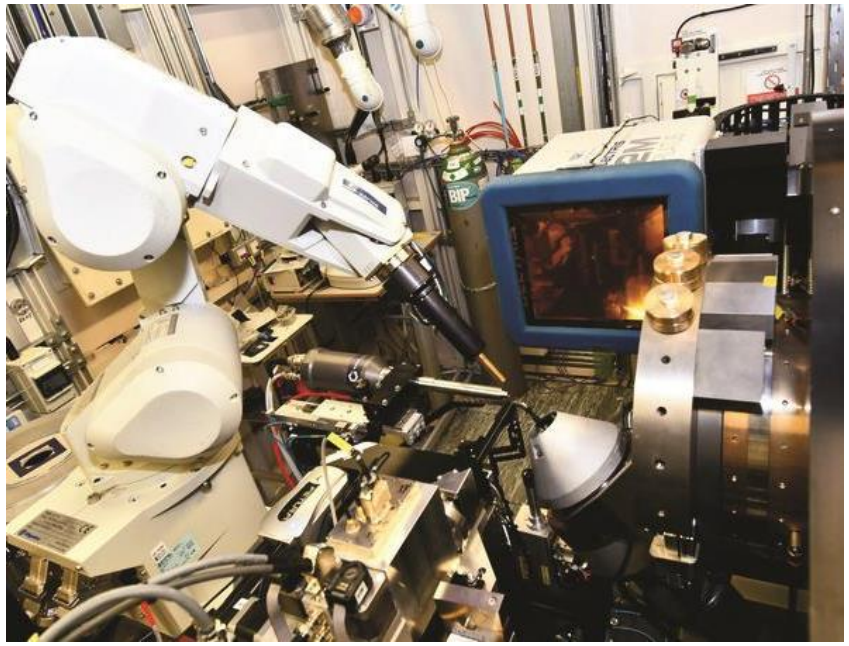
Diamond Beamline I19 – Small Molecule Crystallography





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diamond





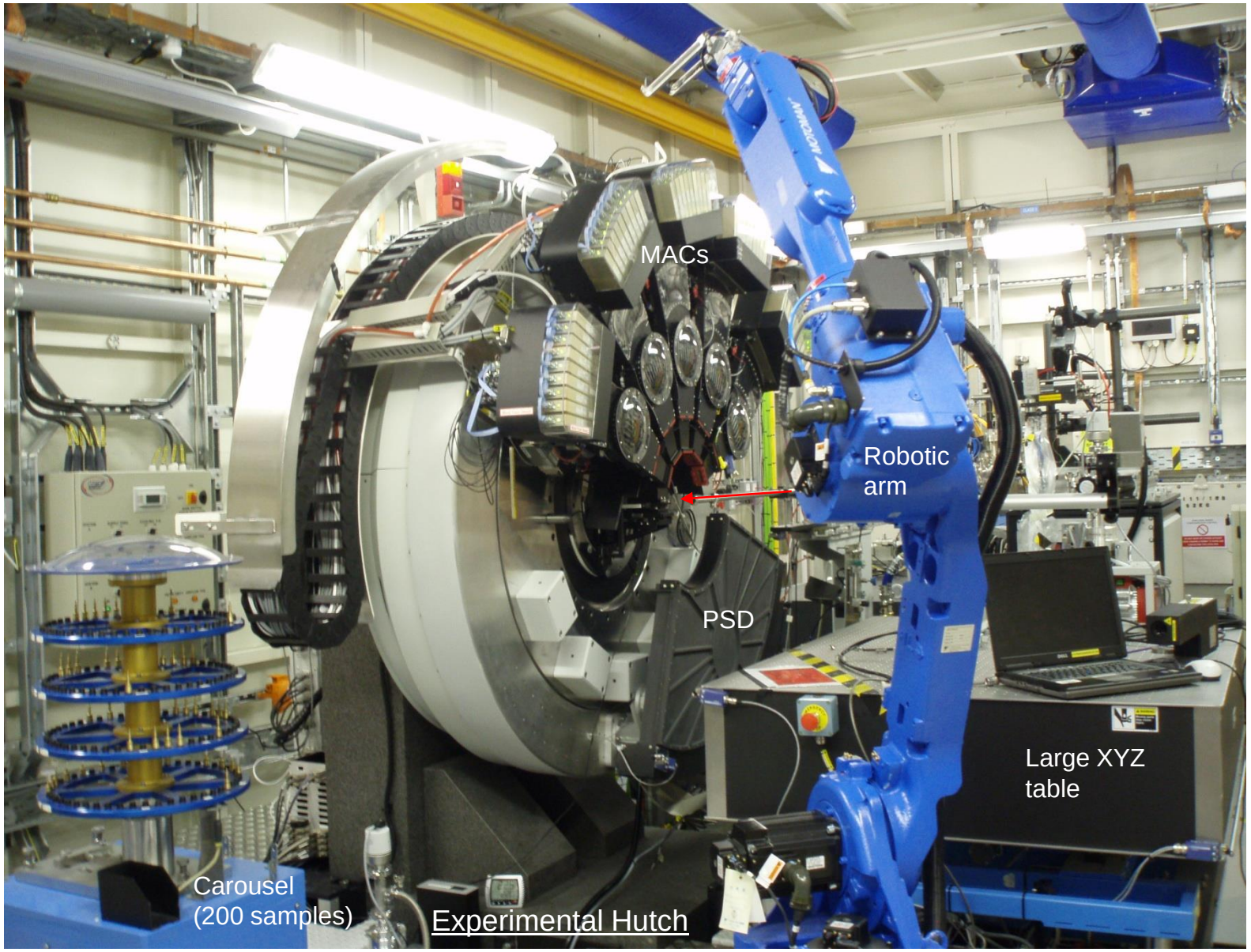
EH1 standard ops

- Microcrystal diffraction
- Robot/remote operation
- Low Temperature (to 30K)

EH2 sample environments

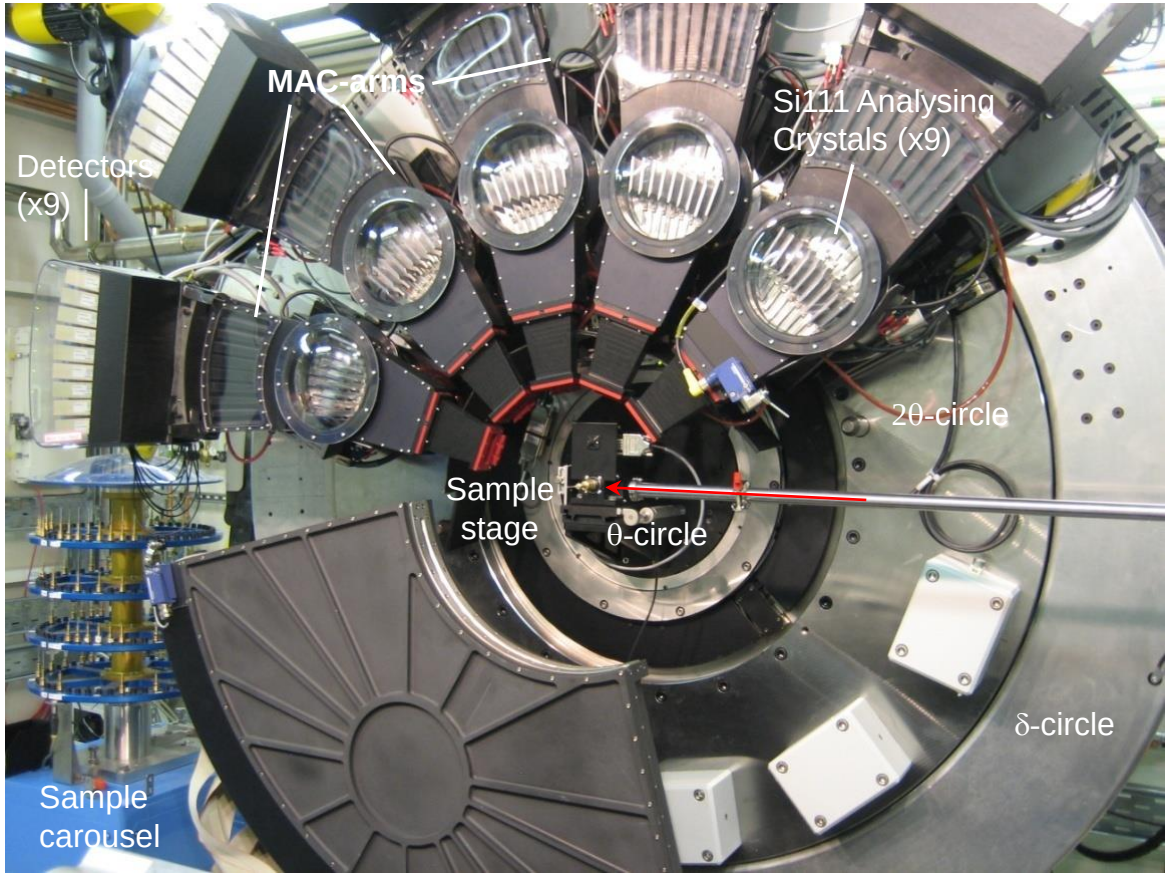
- Gas loading
- High Pressure (DAC)
- Laser excitation

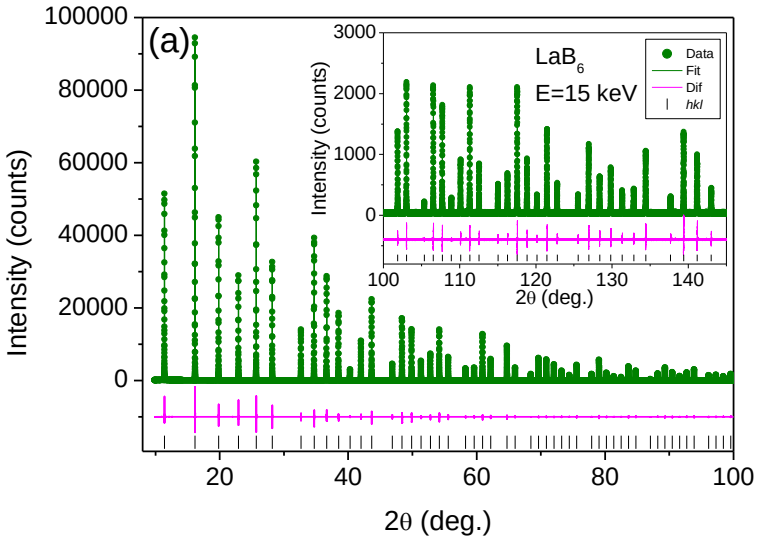
Beamline I11 – High Resolution Powder Diffraction



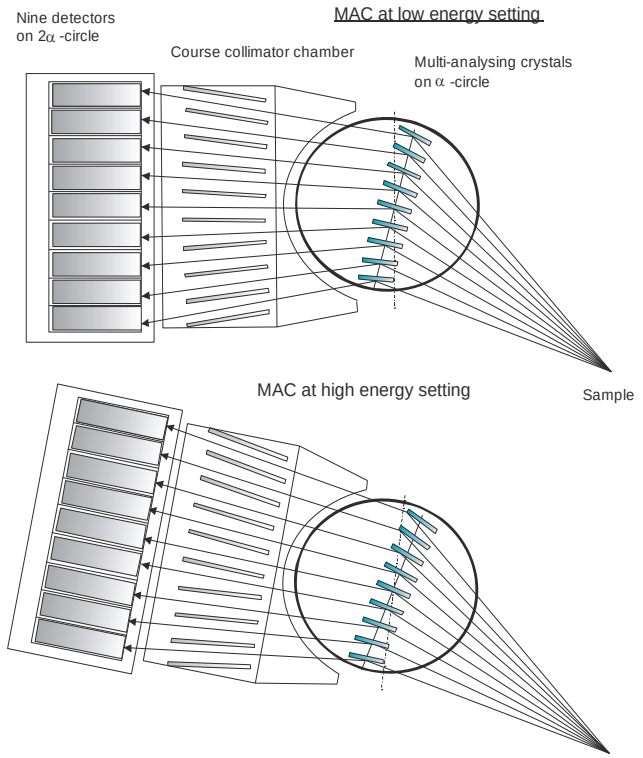
Multi-Analysing Crystals (MAC) for high resolution experiments

45 detectors
Angular resolution: $\Delta 2\theta \sim 0.002°$
Data collection time (scanning) ~ 2 – 60 minutes



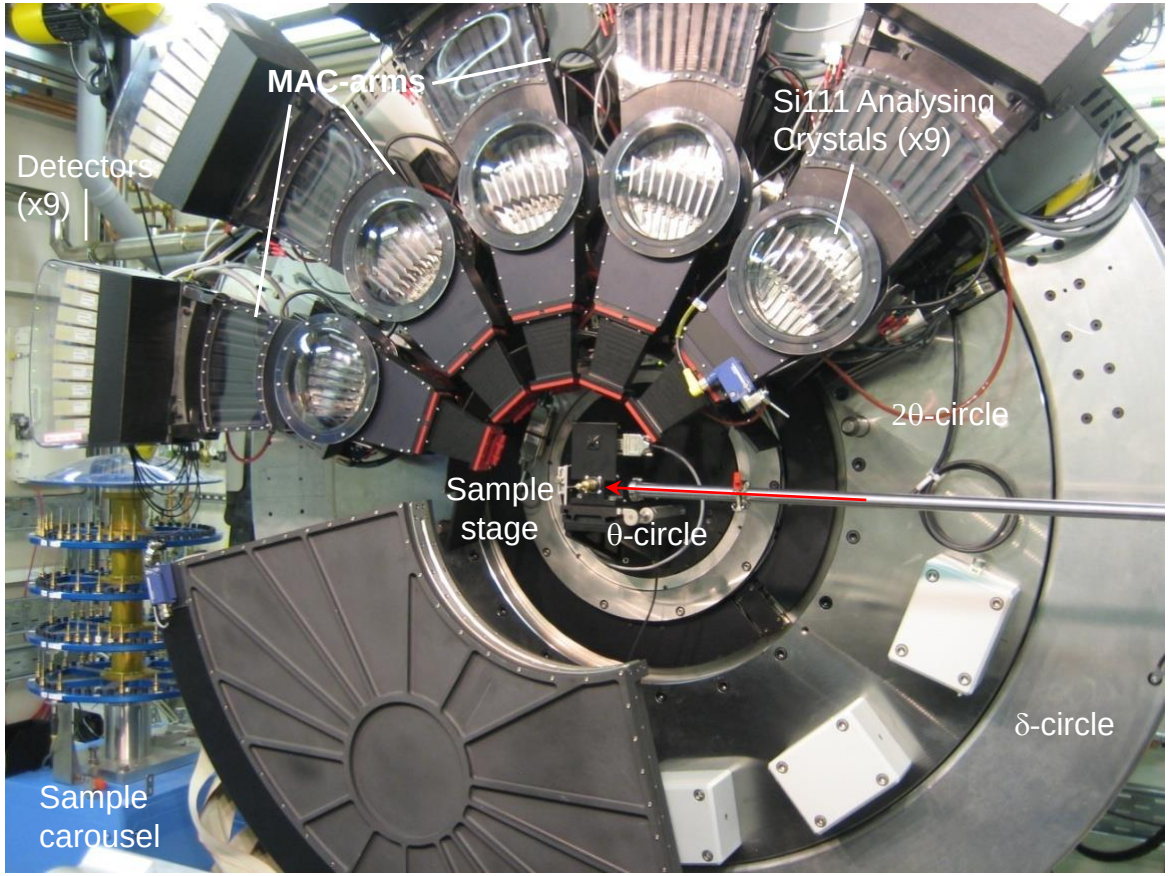


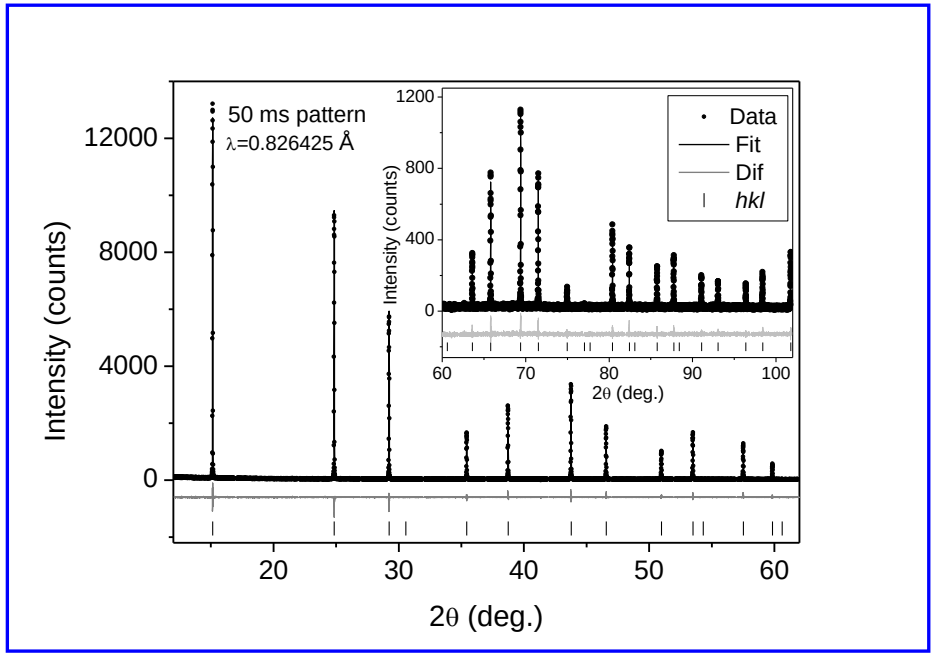
(b) Single-axis MAC stage

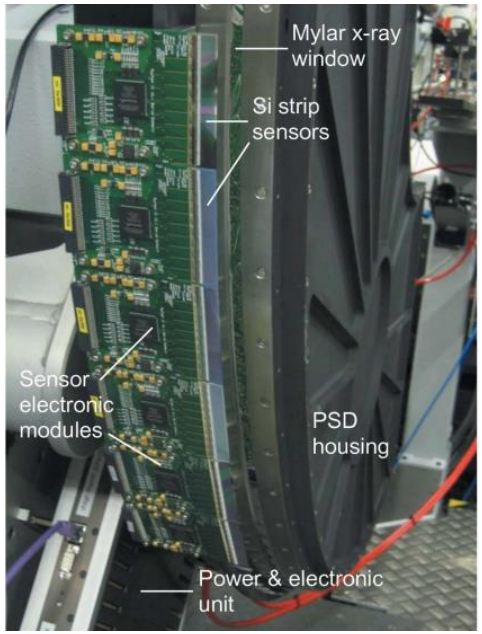


PSD for time Resolved Studies:

Detection elements: Si 50 μm–strip (Mythen2)
Aperture (coverage angle): 90°
Angular resolution : 0.004° (intrinsic) at 700mm
Data collection speed: 50 ms – minutes per pattern

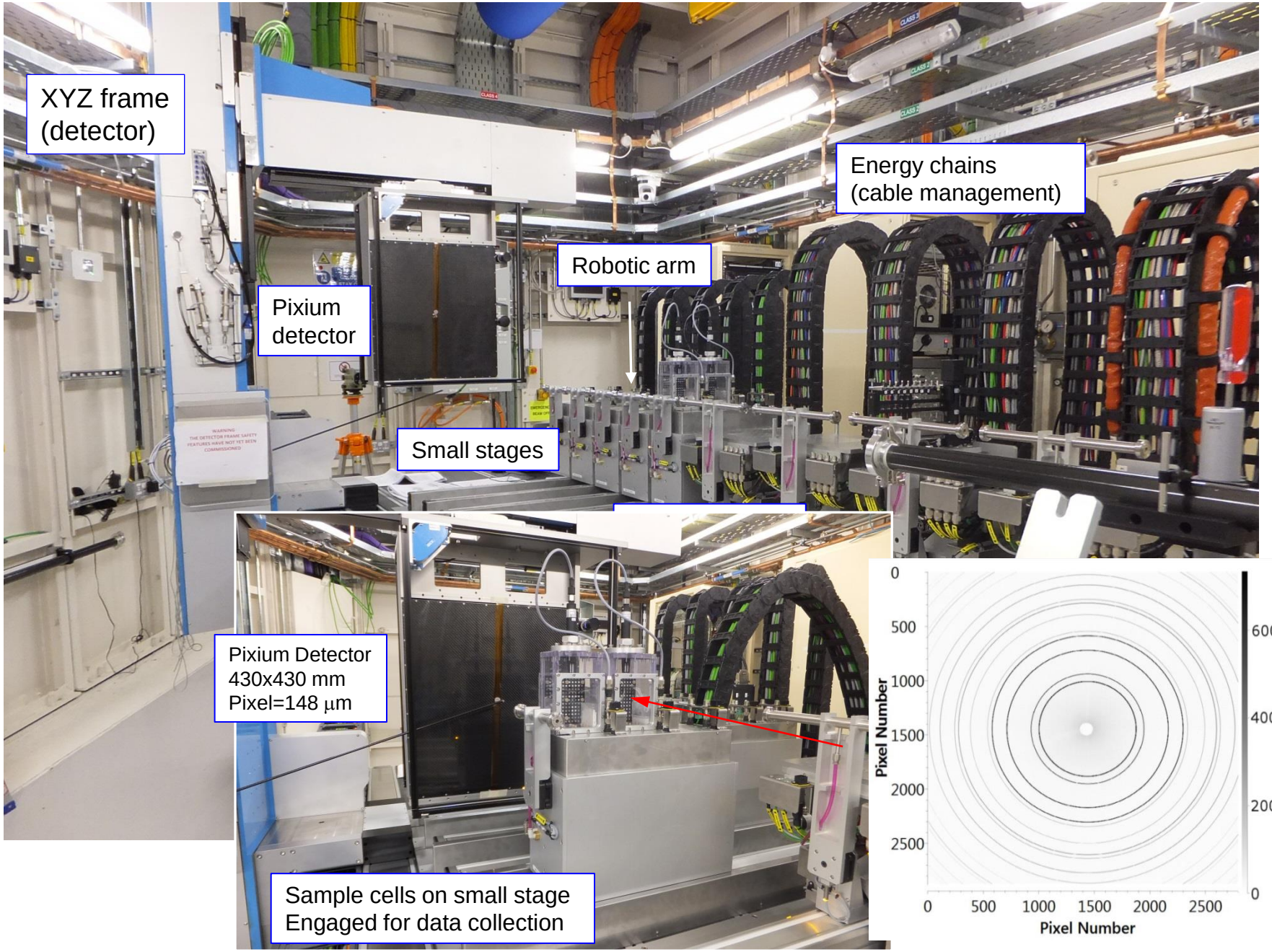




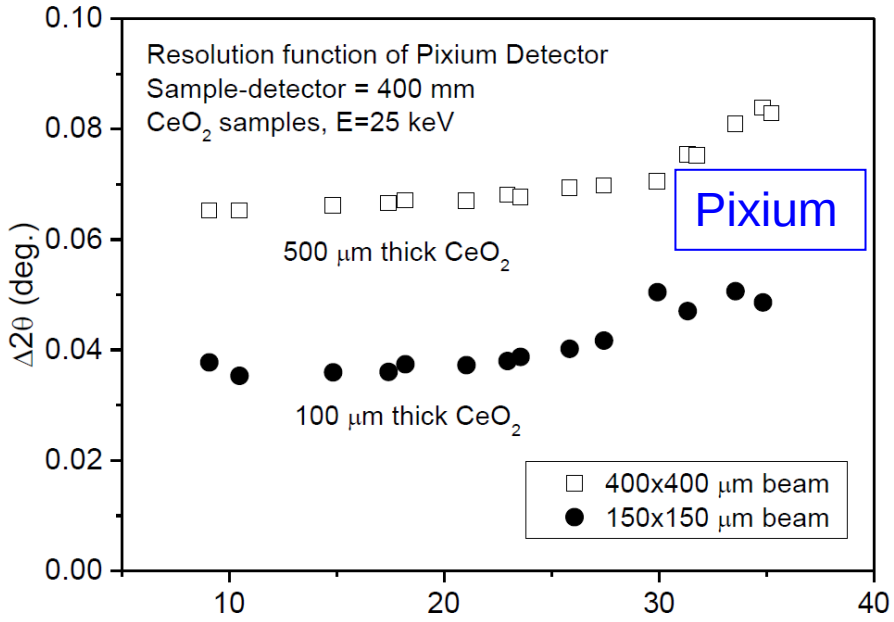


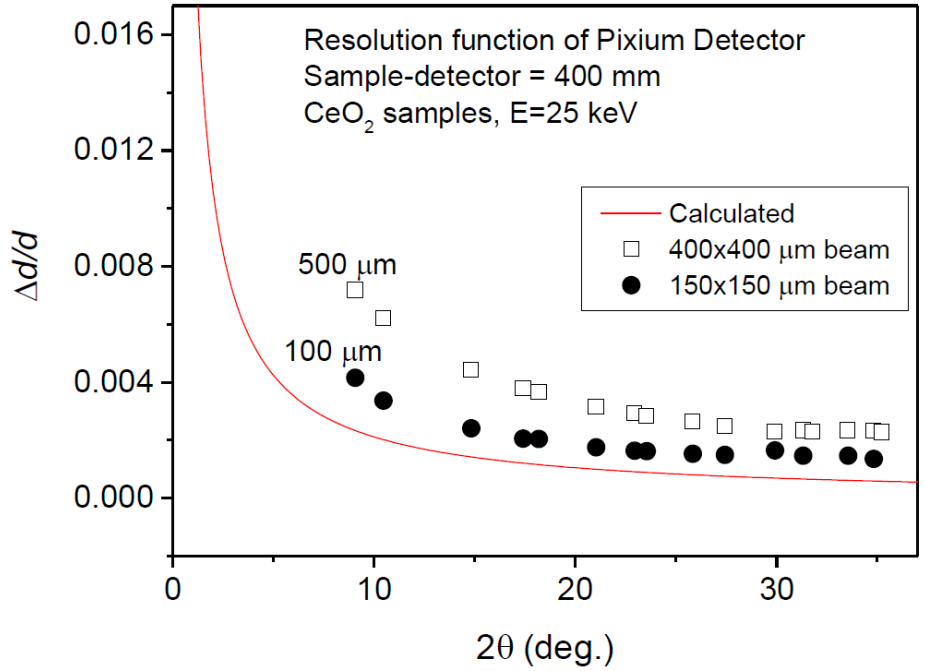
diamond

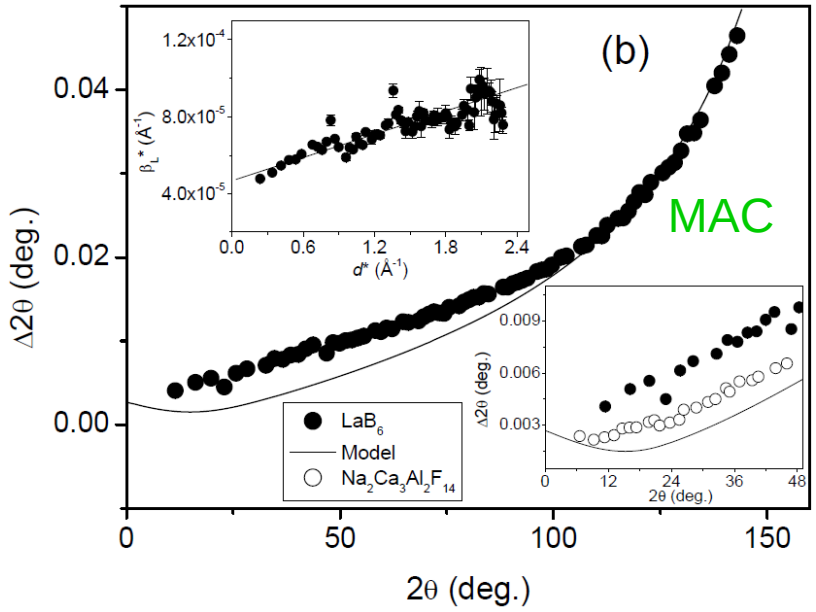
Pixium Area Detector (EH2) -



Detector Resolution Function







Detection width

Detector	Δ2θ	Δd/d	Resolution
Pixium	~ 0.07°	10^{-3}	Medium
PSD	~0.04°	10^{-4}-10^{-5}	High
MAC	< 0.01°	10^{-5}-10^{-6}	υ-High

diamond

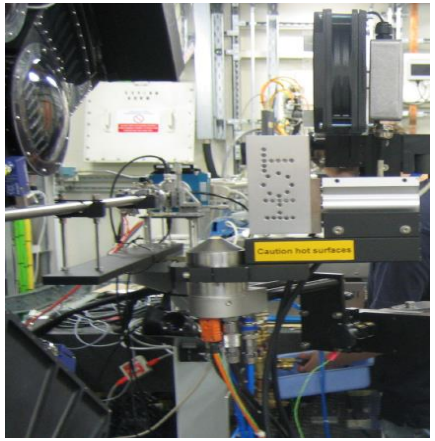
Optimising data quality for Synchrotron Powder Diffraction:

- Spinning sample for powder averaging – wherever possible. If not spinning, rocking.
- Careful alignment of sample at centre of rotation for every sample/stage/cell – for each experiment
- Calibrate λ and 2θ zero point and optimize DCM crystal pitch - every few days or after energy change
- MAC: measure angular offsets between all 45 detectors and all 5 arms - a few times per run
- MAC: Calibrate all 45 detectors (pmt voltage & window threshold, alpha and 2alpha positions) for each λ used – when energy is changed
- PSD: measure flat field (each λ) - detector exposed to uniform intensity across all channels – for new energies and refreshed every year or so.

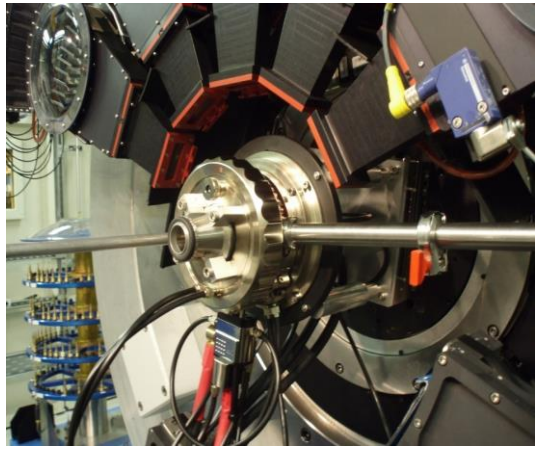


Capabilities of Synchrotron Powder Diffraction

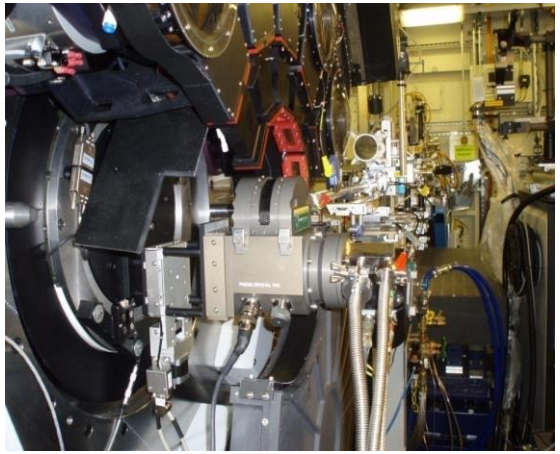
Variable Temperature



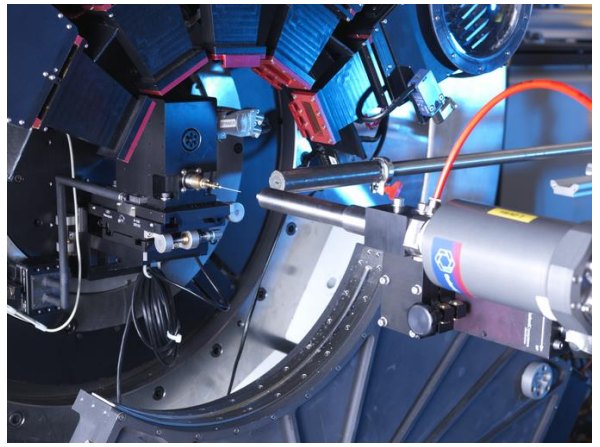
Hotair blower
(RT – 1000°C)



MRI furnace
(RT – 1700 C)



Phenix Cryostat
(11K – 300K)



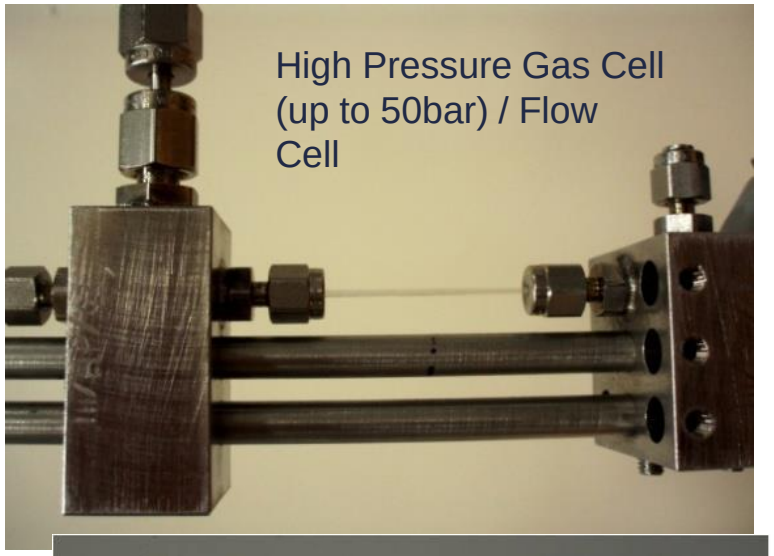
Cryostream
(80K – 500K)

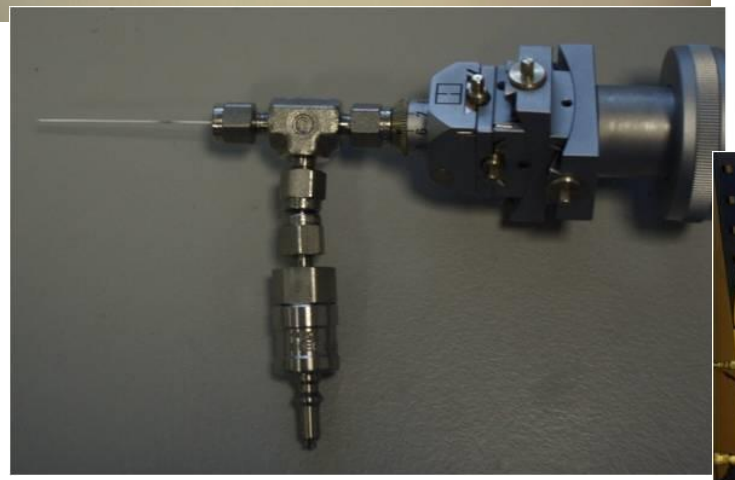
Due to the space available in synchrotron experimental hutches, many more sample environments for non-ambient conditions can be explored than on lab machines and faster data collections allow for the monitoring of rapidly changing systems during heating or cooling.

A combination of the time-resolved PSD and high-resolution MAC detectors can be utilised to provide enhanced results.

diamond

Gas Work





Low Pressure Gas Cell (up to 50bar)

In-Situ gas loading of samples:

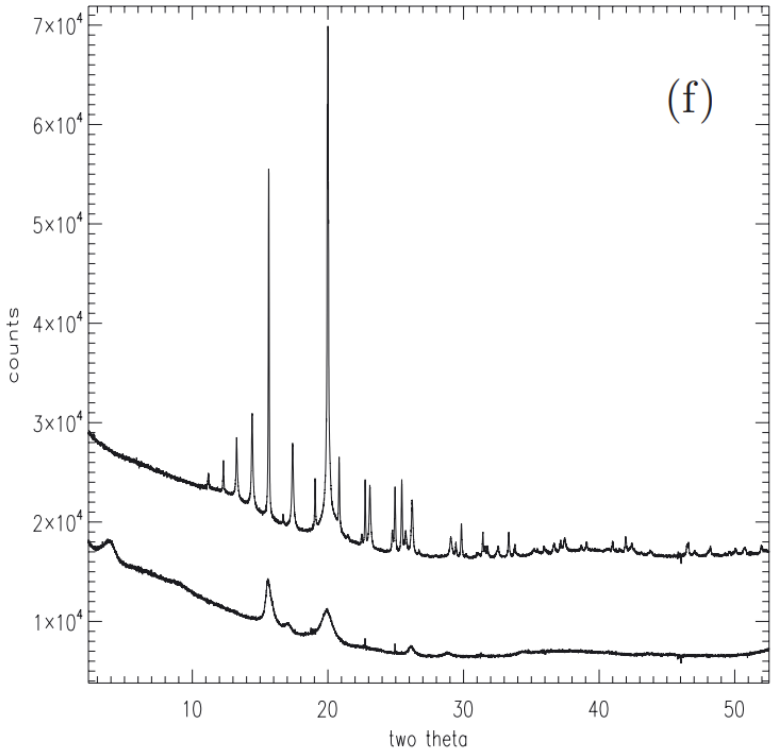
- ❑ Ambient flow
- ❑ Low Pressure (0-50bar)
- ❑ High pressure (50 – 150bar)

Compatible with HAB and Cryostream for VT experiments

Mounted via goniometer for sample alignment



Gas Delivery Panel



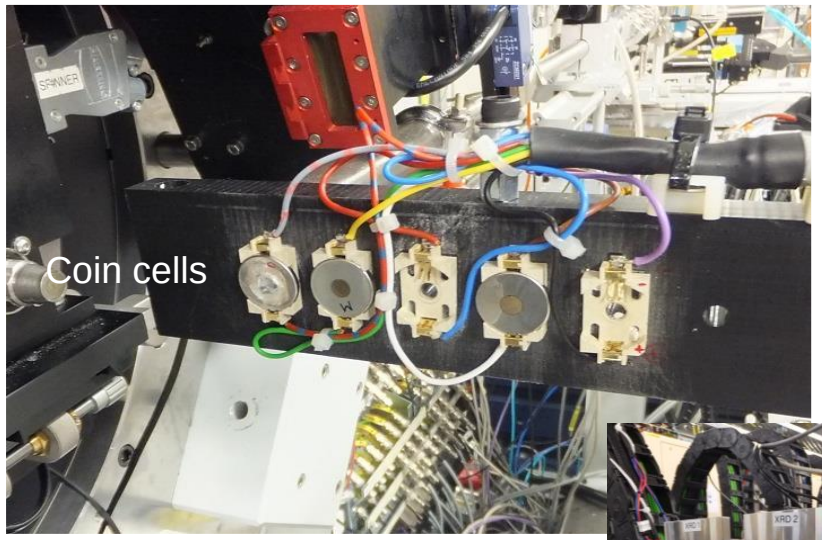
Showing the formation of crystalline calcium carbonate (CaCO3, top pattern) following the reaction of CO2 gas with amorphous CaSiO3 silicate grains – simulating circumstellar environments

Thompson, Day et. al. 2012. EAS Publications Series. 58. 225-229.

diamond

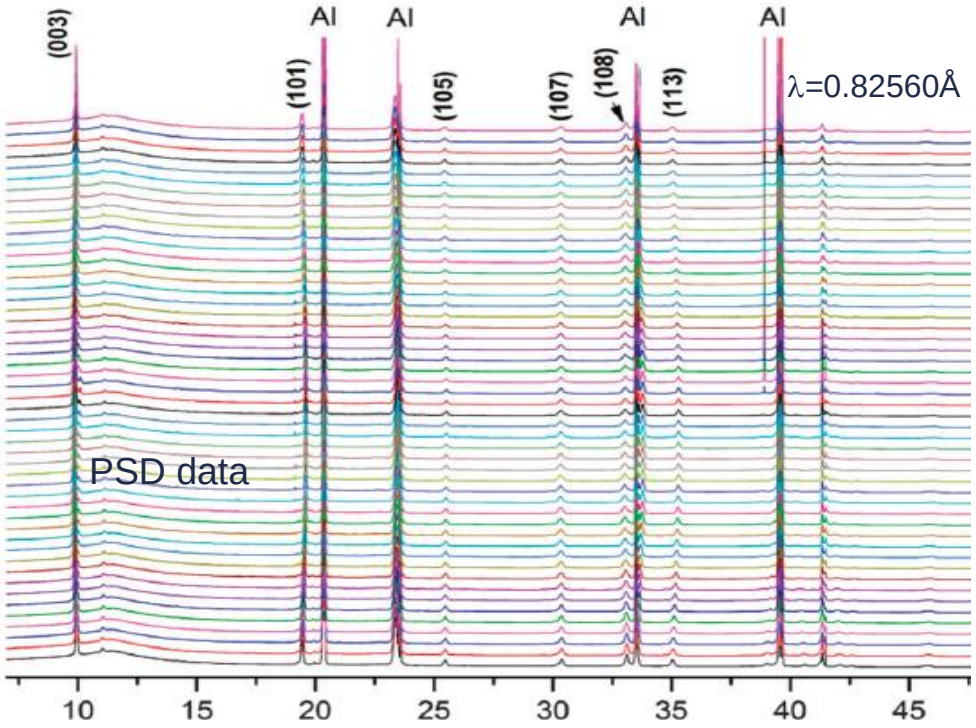
Battery Cycling Facility

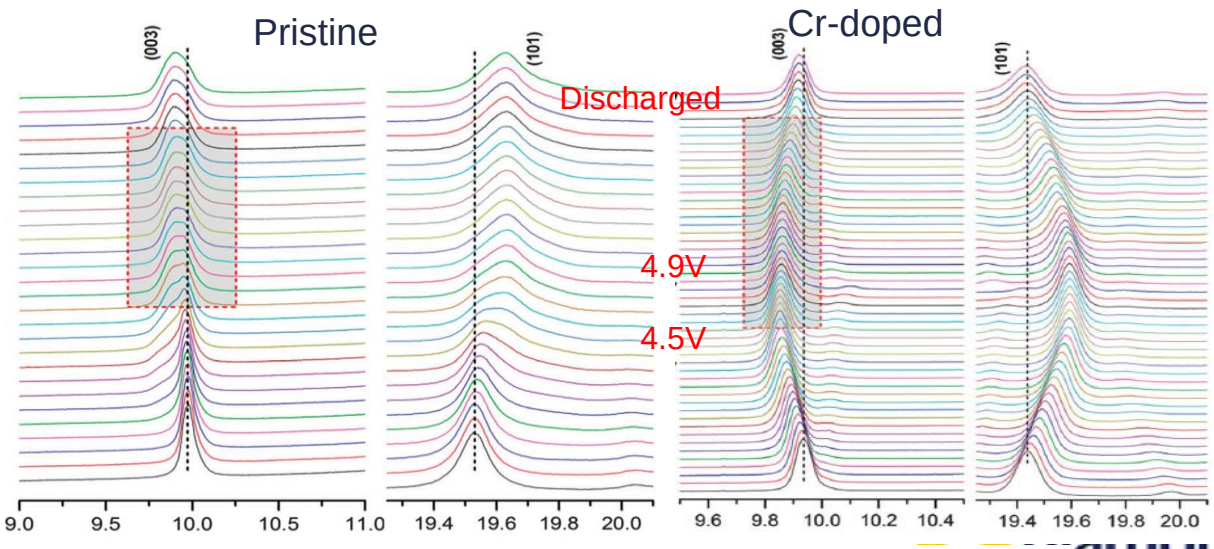
- In operando coin cells: modified CR2032 battery stainless steel casing), ampix-style, pouch cells.
- Glove box for battery cells assembly
- Potentiostats for offline and online cycling
- Data and time resolution that cannot be achieved in a lab



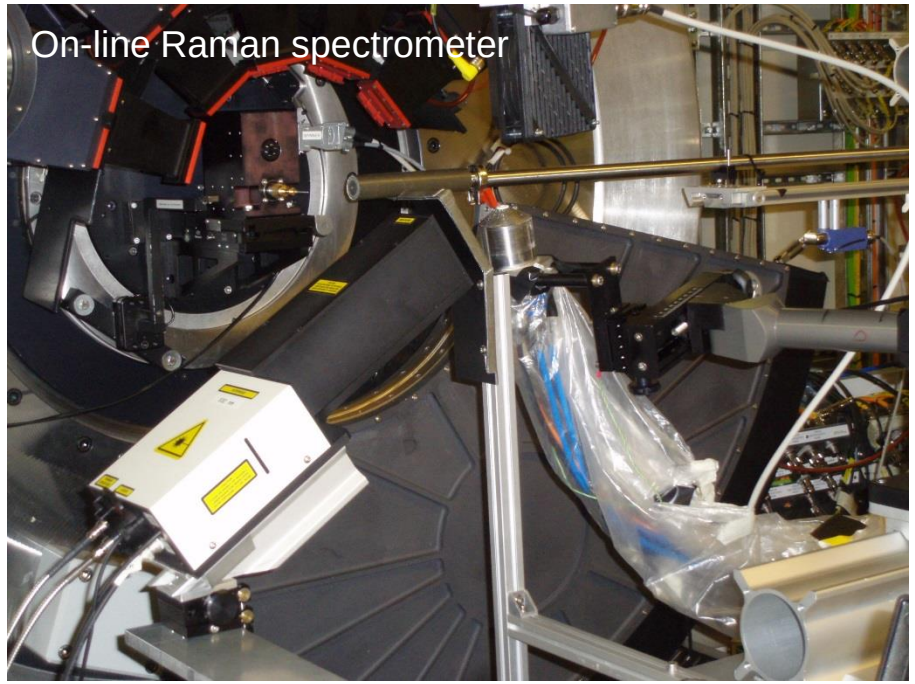


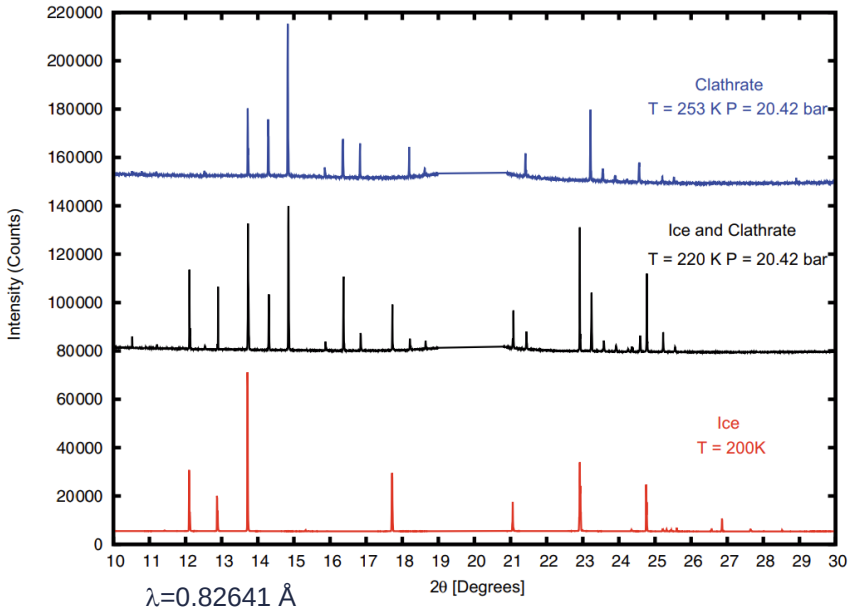
$Li(Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.03}Cr_{0.10})O_2$ and Cr-doped



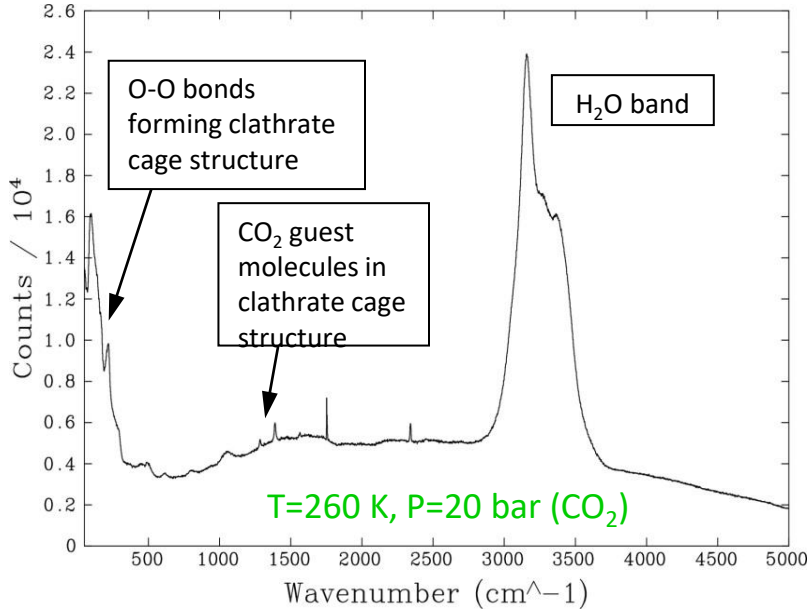


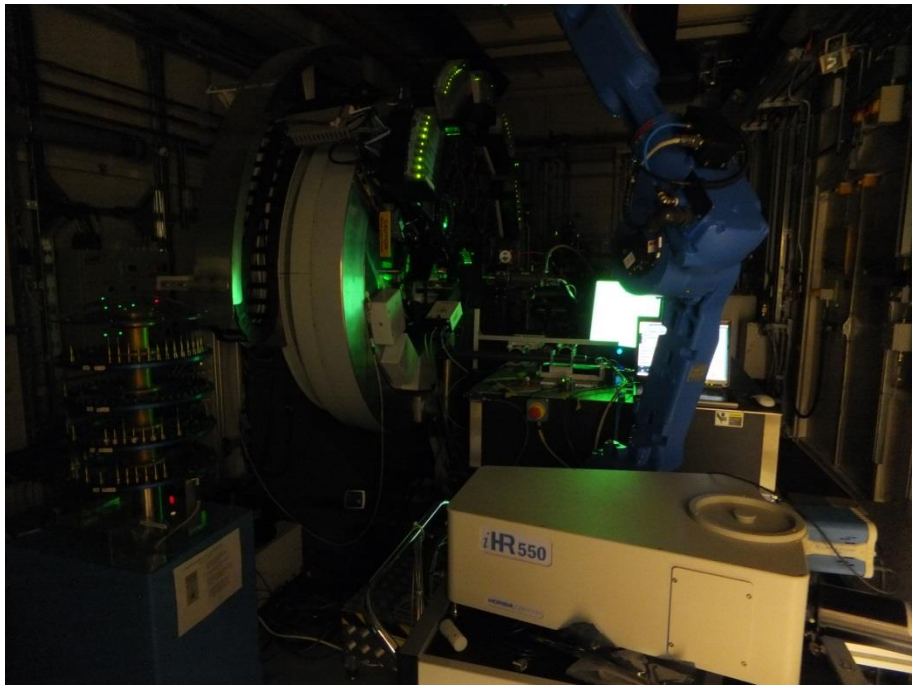
Song et al. (2016), *Phys. Chem. Chem. Phys.*18, 4745



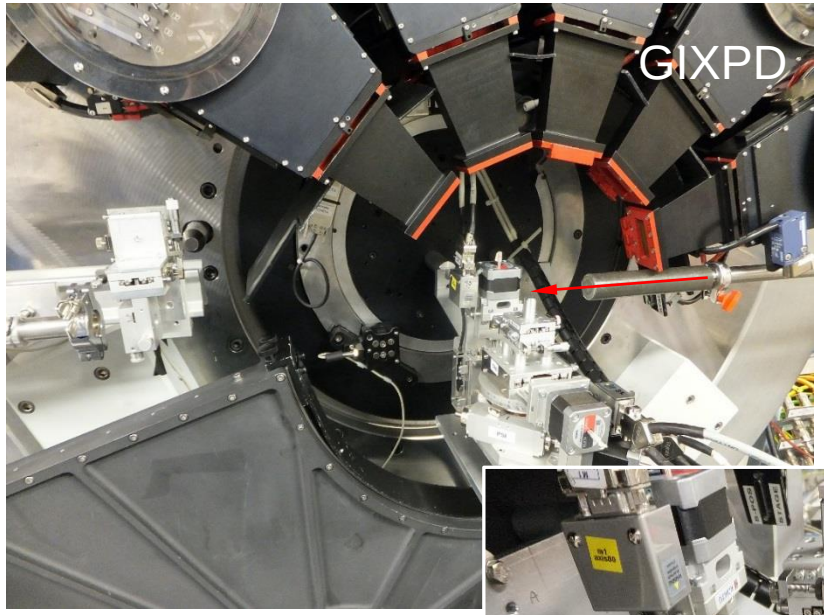


Formation of CO_2 gas hydrate structures in ice *(Day et al. 2015, Astron. & Astrophy. **574**, A91)*





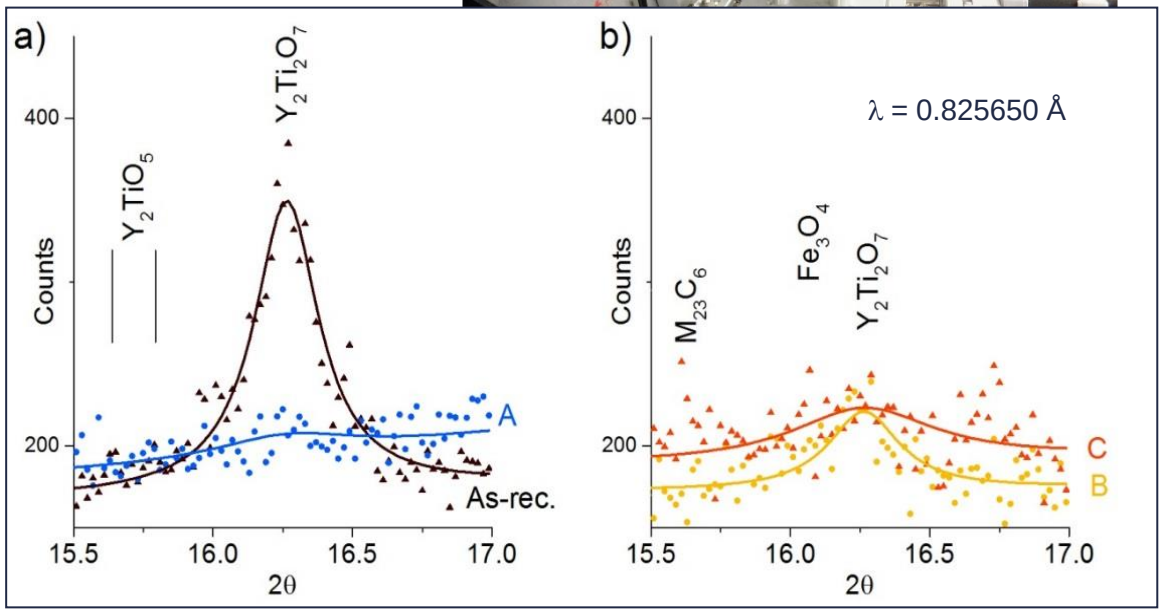
diamond

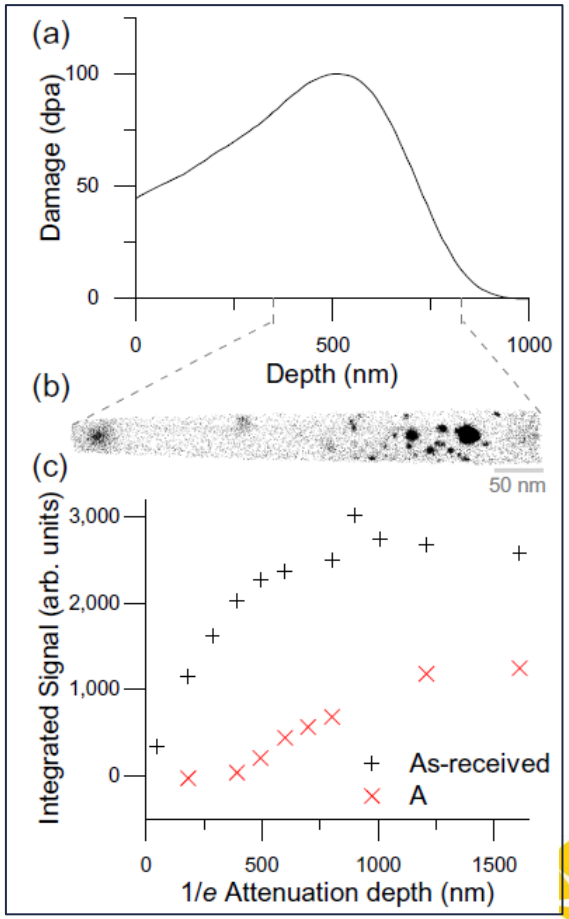




GIXPD experiments to study surface damage by ion-beam radiation

Sample area ~ 3 x 5 mm
Beam size=100 μm x 2 mm
Damage thickness ~ a few microns
Low angle of incident beam=0.2 – 2.0°





London et al (2017), *Scripta Materialia 110, 24-27 (2016)*

diamond

Long Duration Experiments

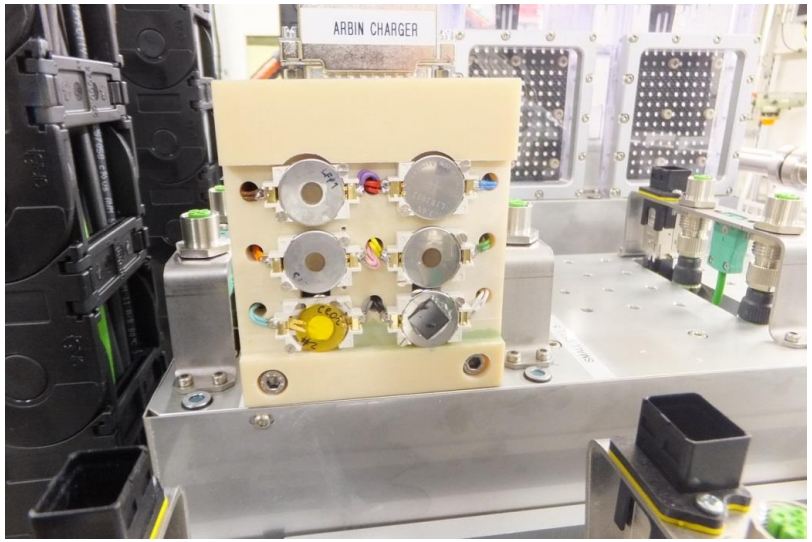
- Slow dynamics in natural systems, engineering processes and energy materials
- Important information on the development of phases over time cannot be obtained via *ex-situ* methods
- Use LDE to periodically monitor the experiment *in-situ* over longer timescales (weeks, months, years...)

Areas of Scientific Interest

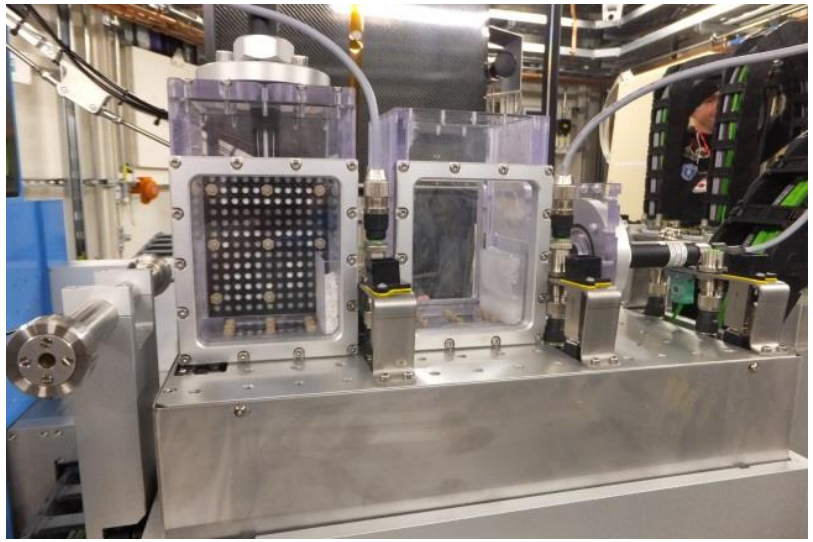
- ❑ Energy
- ❑ Catalysis
- ❑ Environmental
- ❑ Pharmaceutical
- ❑ Metallurgy and alloys
- ❑ Gas storage systems
- ❑ Corrosion
- ❑ Others

Data collection schedule – once a week (every Monday)

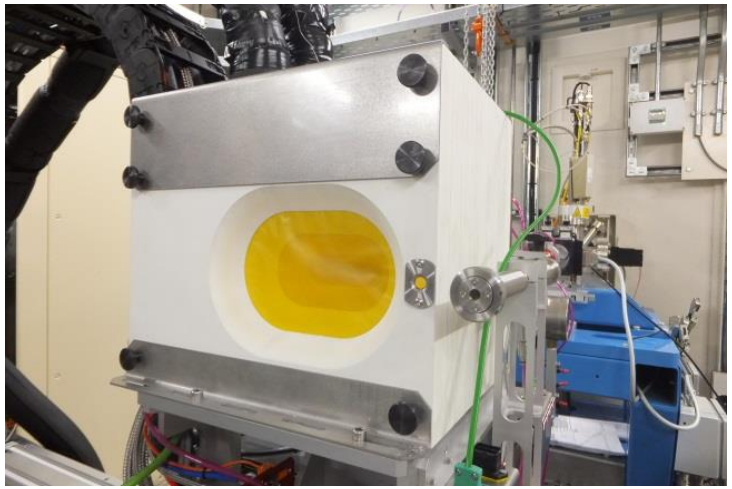




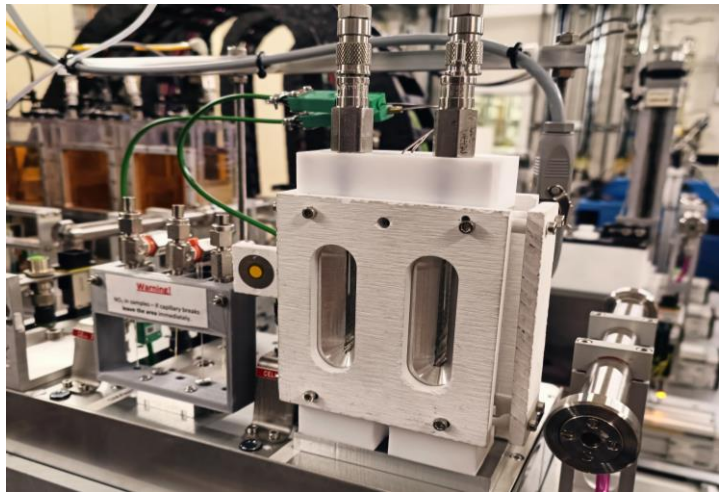
Li-ion battery coin cells and charger



Humidity chambers

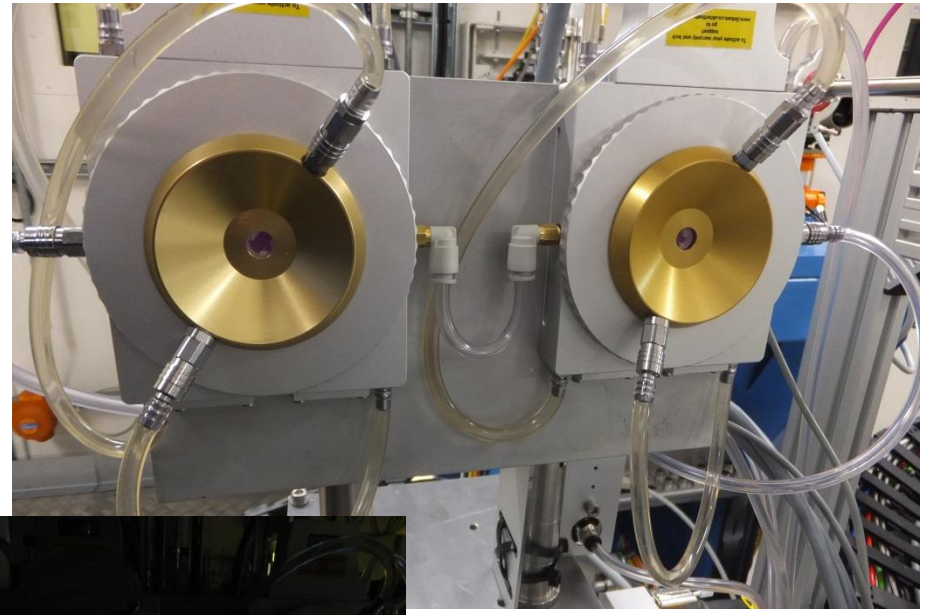


Cold mineralisation cell (-30°)



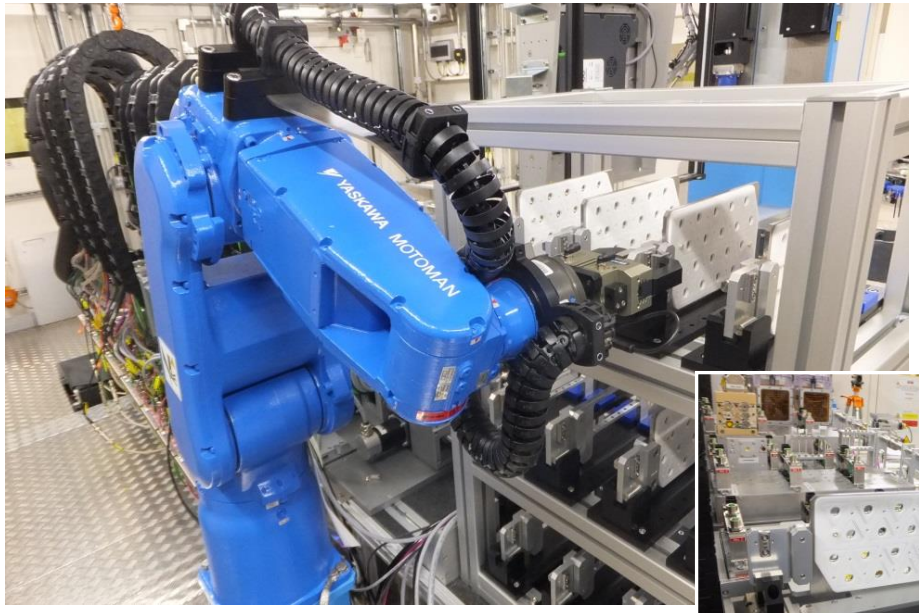
Gas cycling/dosing

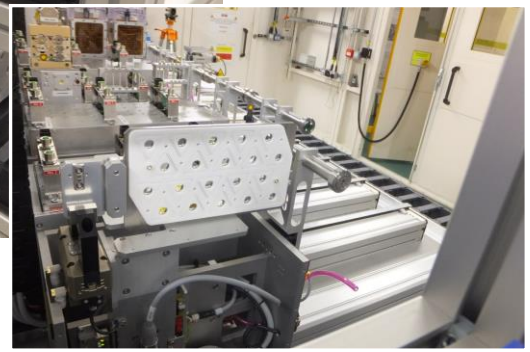
Linkam furnaces (RT – 1500°C)



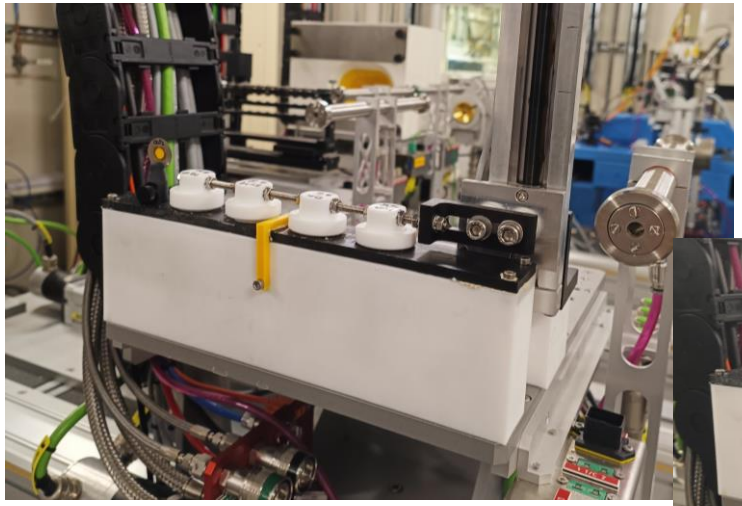


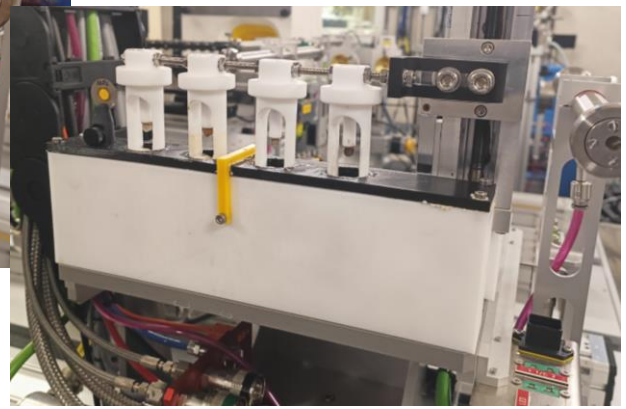
Ni-Cr-Co alloys at 800°C





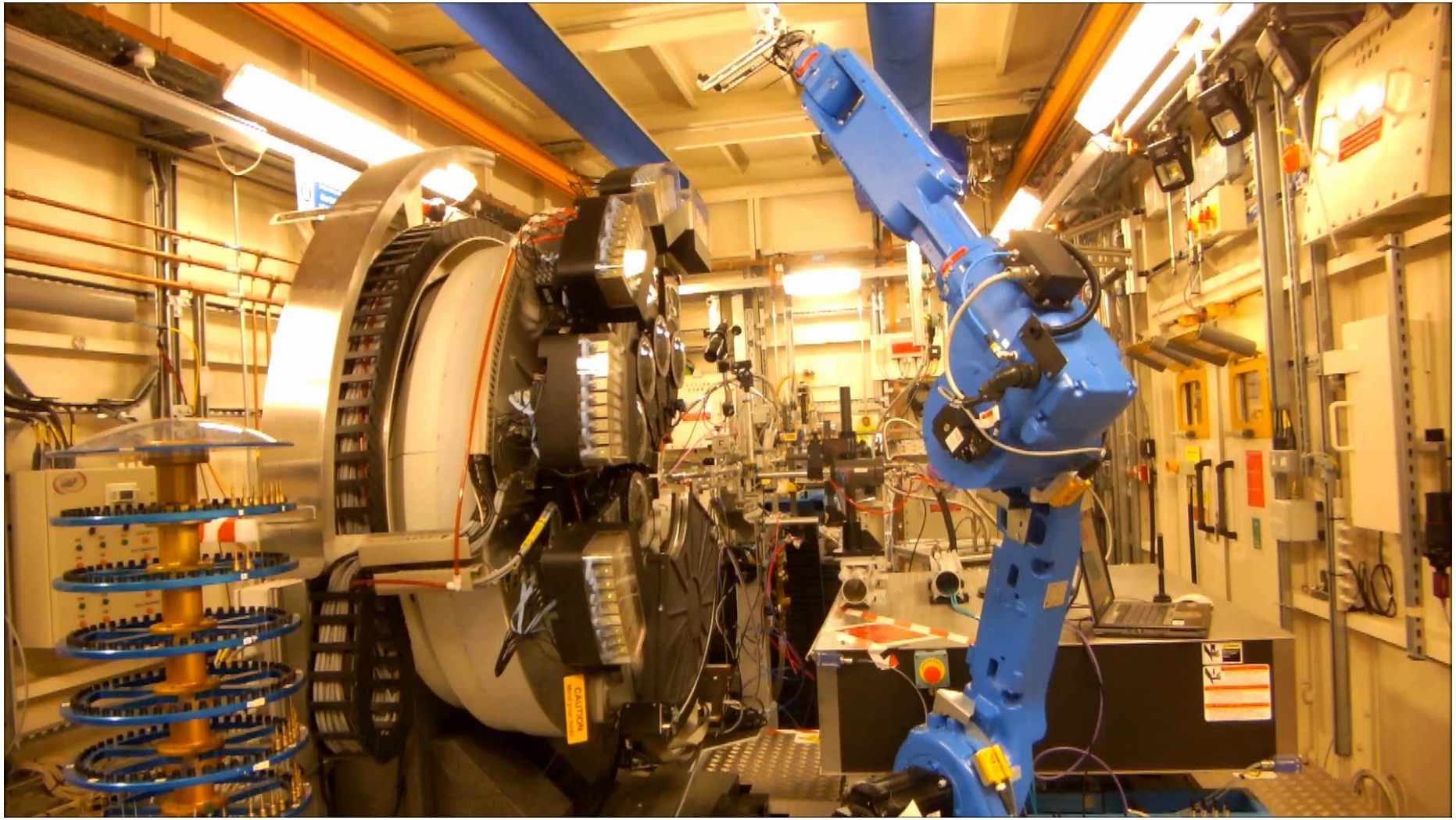
Robotic arm for additional non-ambient samples and high-throughput screening





Submersion stage – interactions with solutions over time

diamond



Filmed & directed by Annabelle Baker
Robot trained by Tom Cobb, Ronaldo Mercado

diamond



Filmed & directed by Annabelle Baker
Robot trained by Tom Cobb, Ronaldo Mercado