

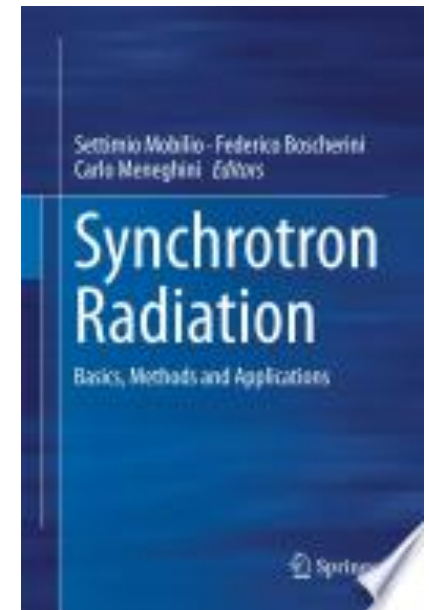
Powder Diffraction with Synchrotron Radiation

Topics

- . What is powder diffraction
- . How do we measure powder diffraction and what do we have to be aware of
- . Instrumentation at synchrotron beamlines for powder diffraction
- . Why perform powder diffraction at synchrotrons
- . Applications of SR-XRPD

Synchrotron Radiation: Basics, Methods and Applications

- Chapter 10:
Powder Diffraction and synchrotron radiation
- Chapter 18:
 - Diffraction from nanocrystalline materials
- Chapter 24:
 - Synchrotron radiation and earth sciences
- Chapter 25:
 - Synchrotron radiation and environmental sciences
- Chapter 26:
 - Synchrotron radiation in art, archeology and cultural heritage
- Chapter 29:
 - Studies of matter at extreme conditions



- Oxford Dictionary:

powder

Pronunciation: [/'paʊdə/](#)

fine, dry particles produced by the grinding, crushing, or disintegration of a solid

solid

Pronunciation: [/'sɒlɪd/](#)

1 a substance or object that is solid rather than liquid or fluid.

2 *Geometry* a body or geometric figure having three dimensions.

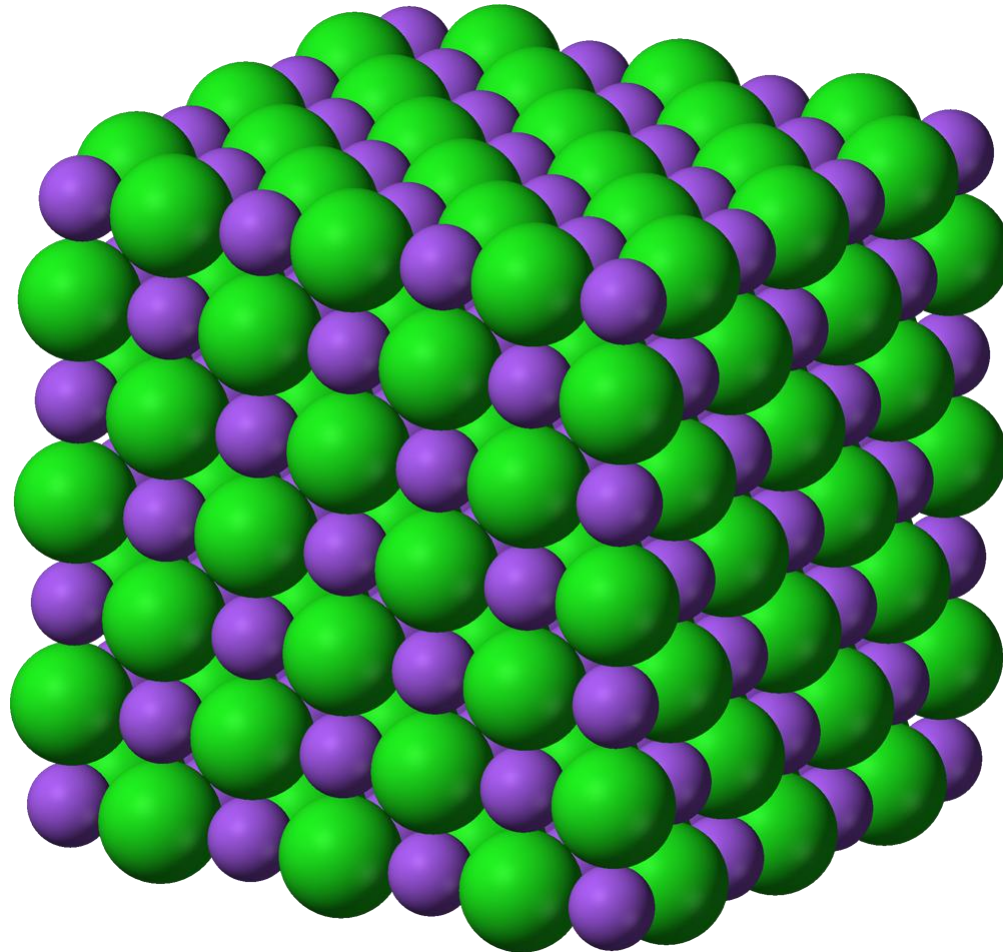
Powder



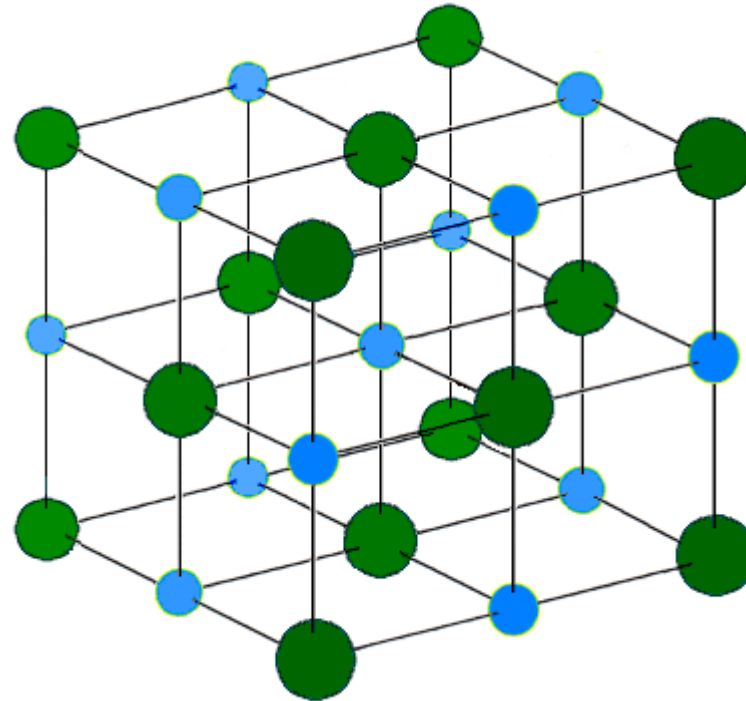
A solid



A solid

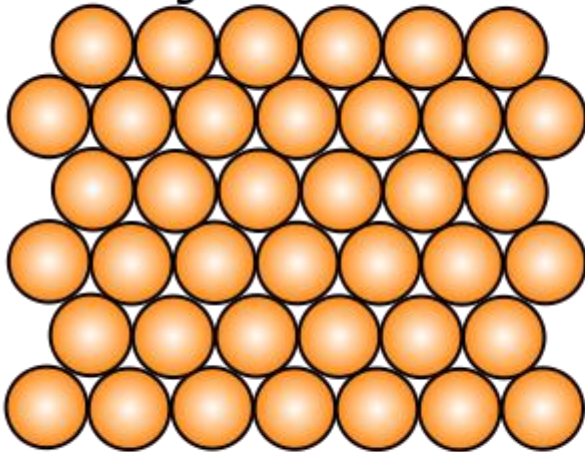


Unit cell

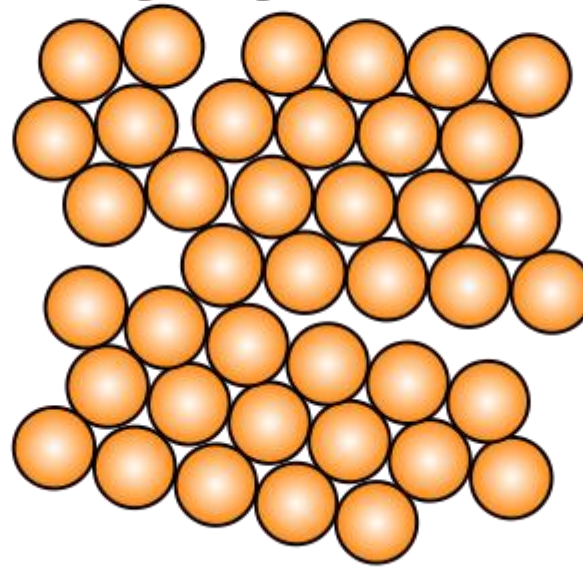


Solids

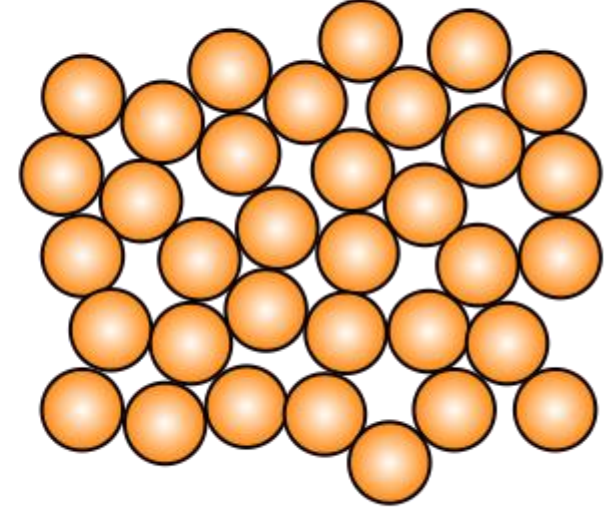
Crystalline



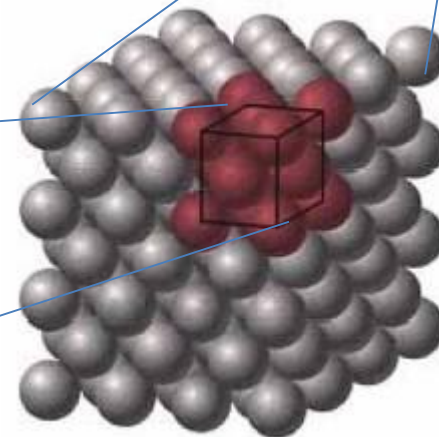
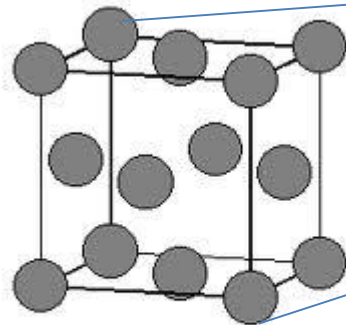
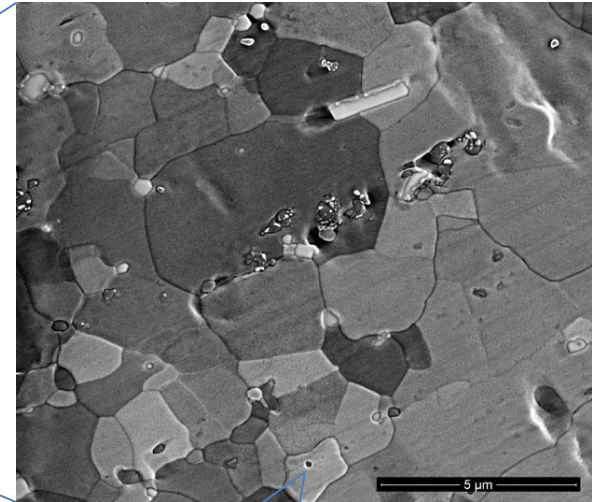
Polycrystalline



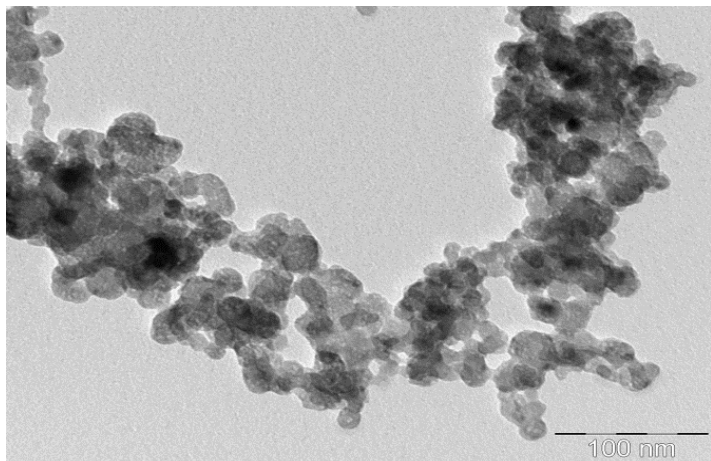
Amorphous



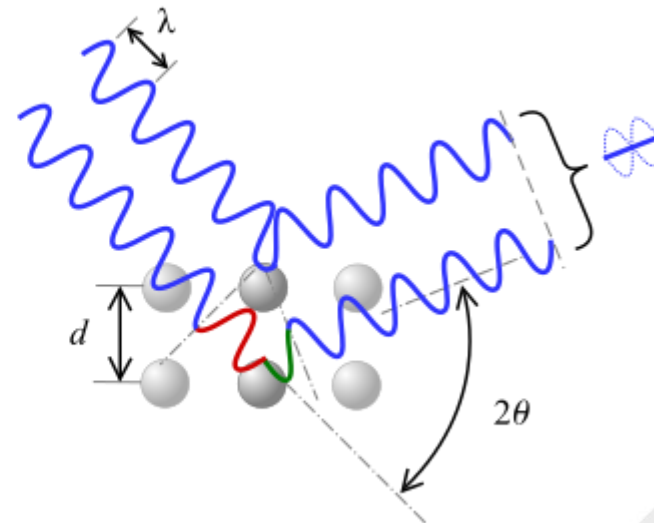
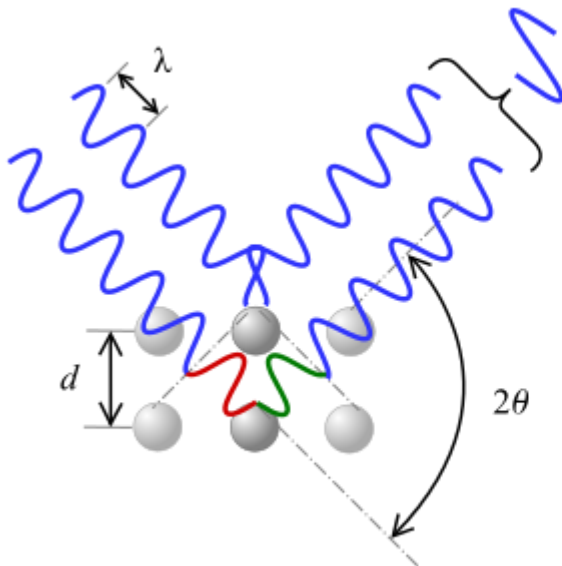
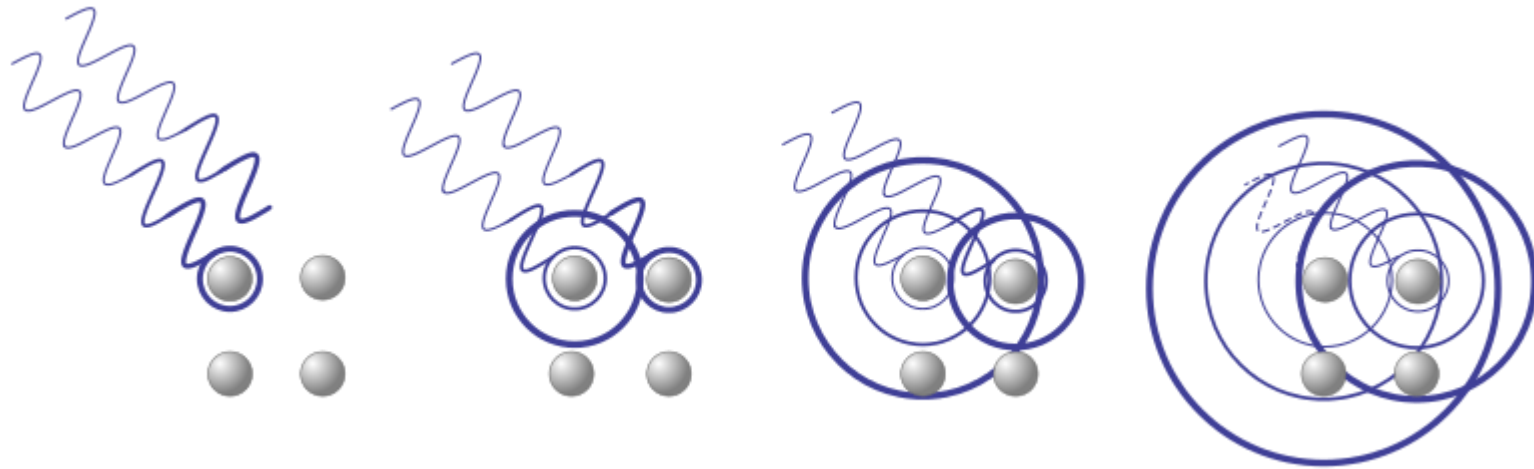
'Powders'



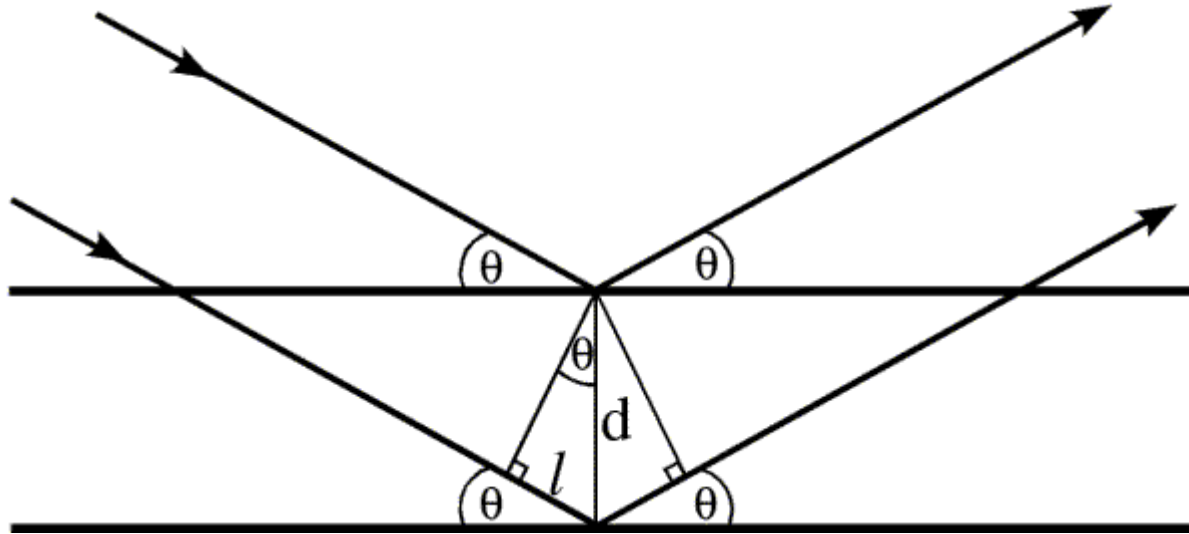
'Powders'



X-ray Diffraction



Bragg's law



The two X-ray beams travel at different distances. This difference is related to the distance between parallel planes

$$2l = d \sin \Theta \qquad n\lambda = 2d \sin \Theta$$

Bragg's law

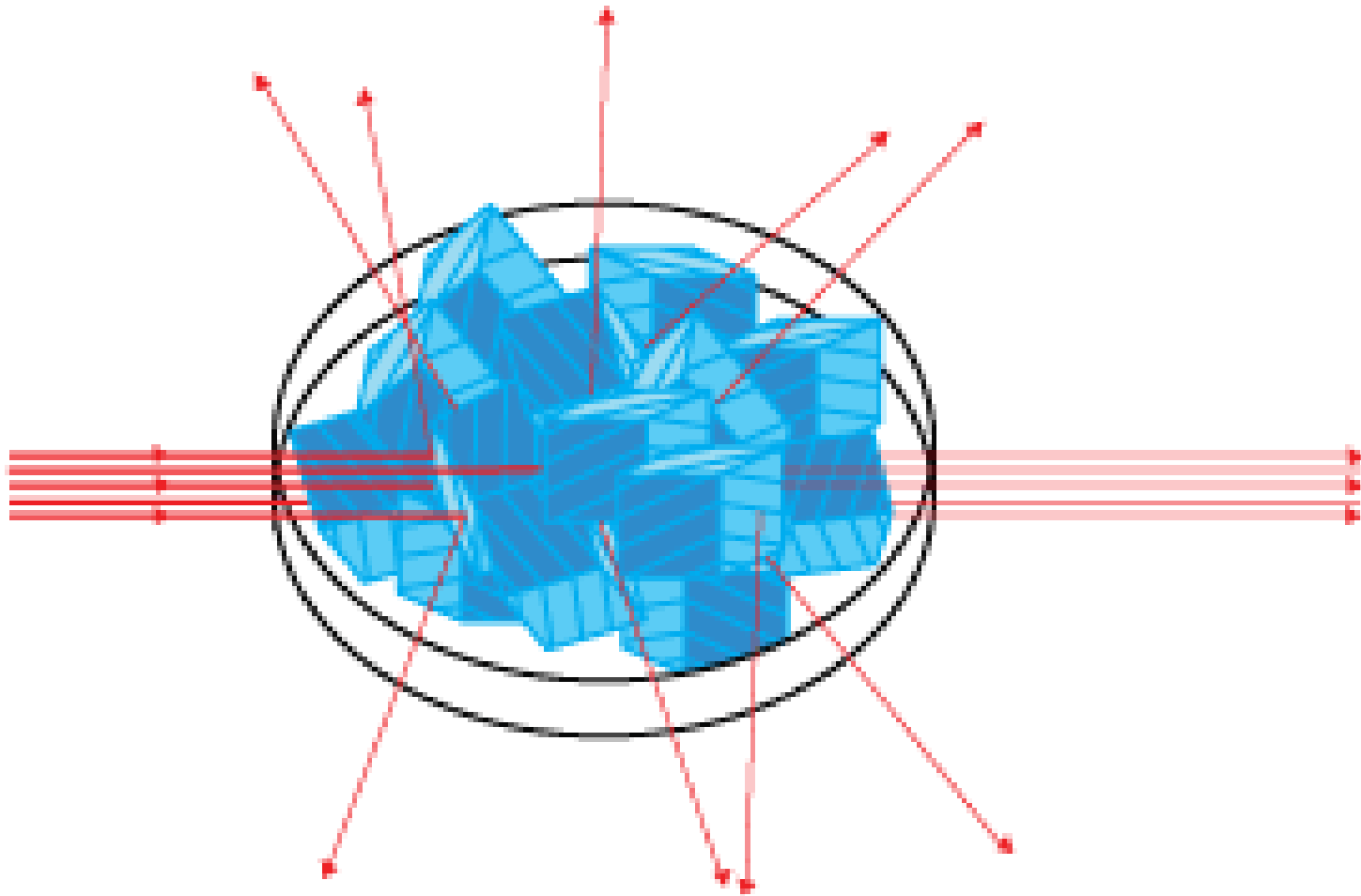
This condition is met when the distance equals an integer multiple of the wavelength, called order of diffraction, n . The final equation is the BRAGG'S LAW

$$n\lambda = 2d \sin \Theta$$

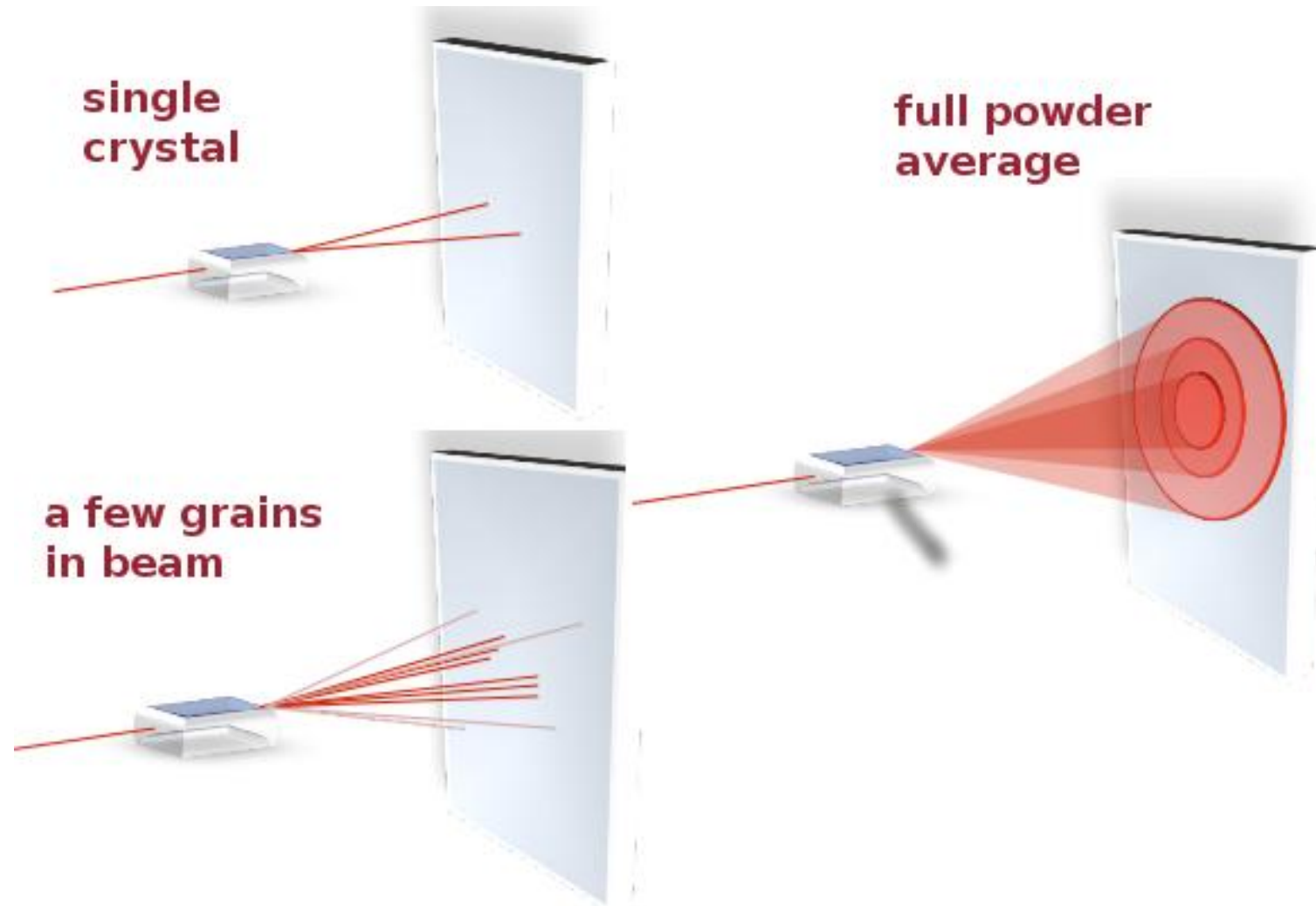
Data are collected by using X-rays of a known wavelength. The sample is rotated so that the angle of diffraction changes

When the angle is correct for diffraction a signal is recorded

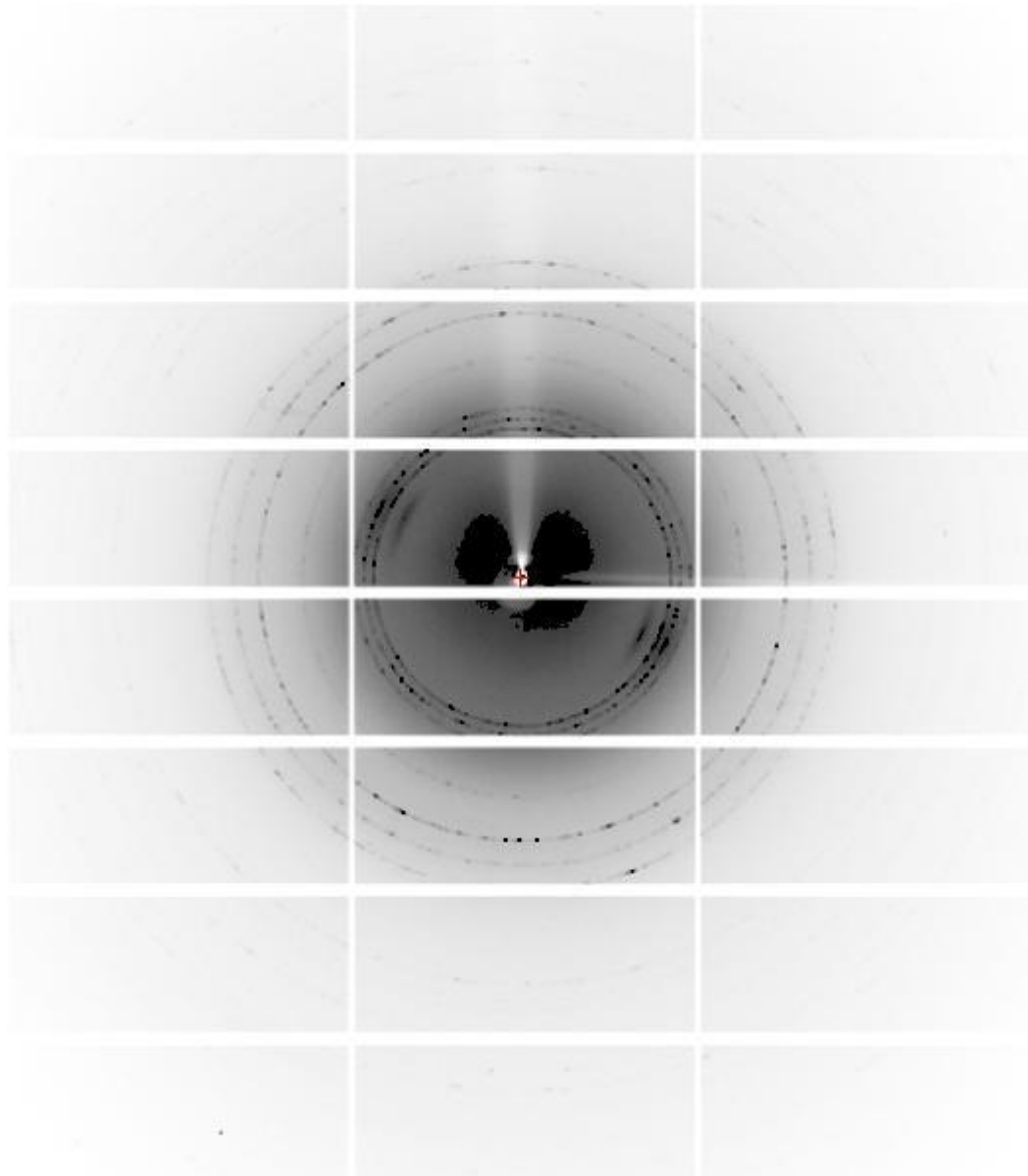
Powder Diffraction



Powder Diffraction

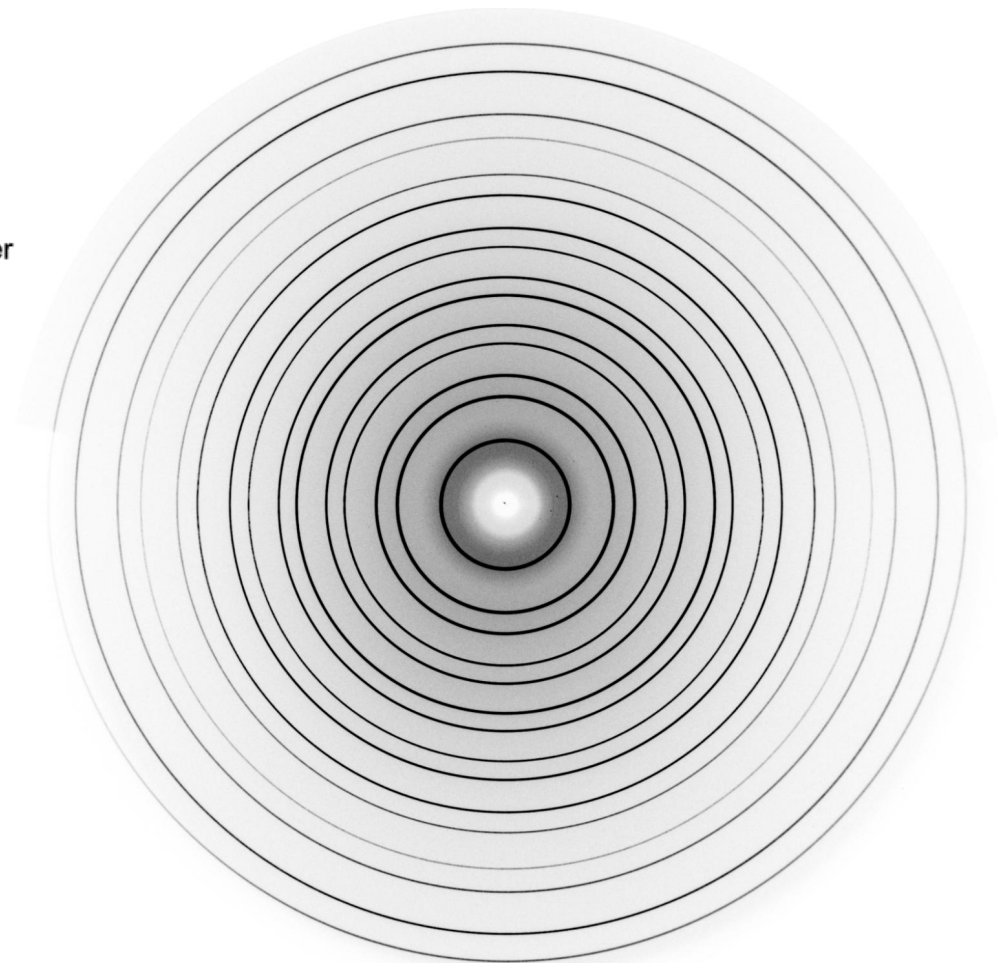
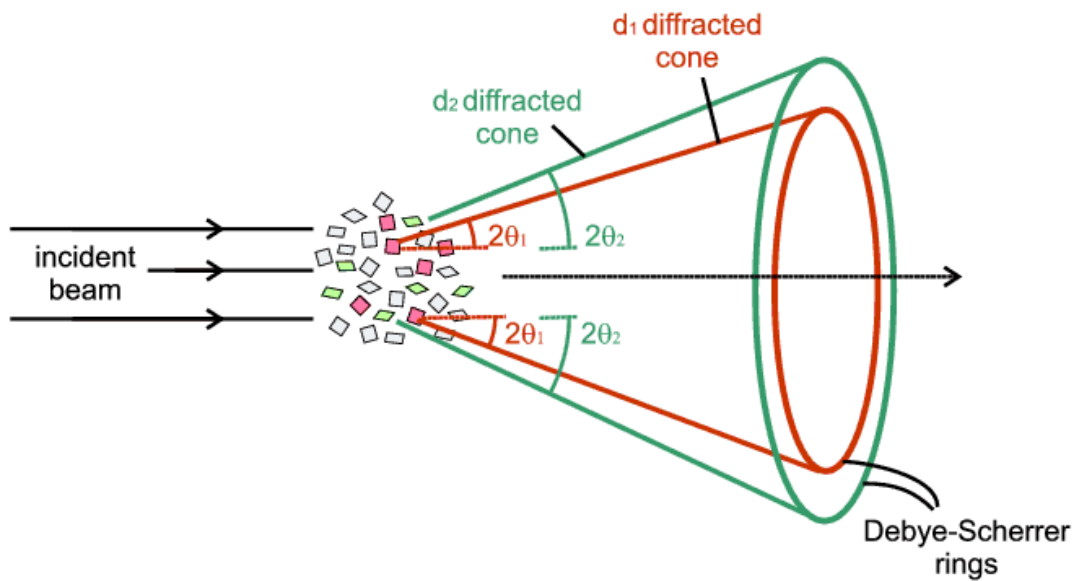


Powder diffraction

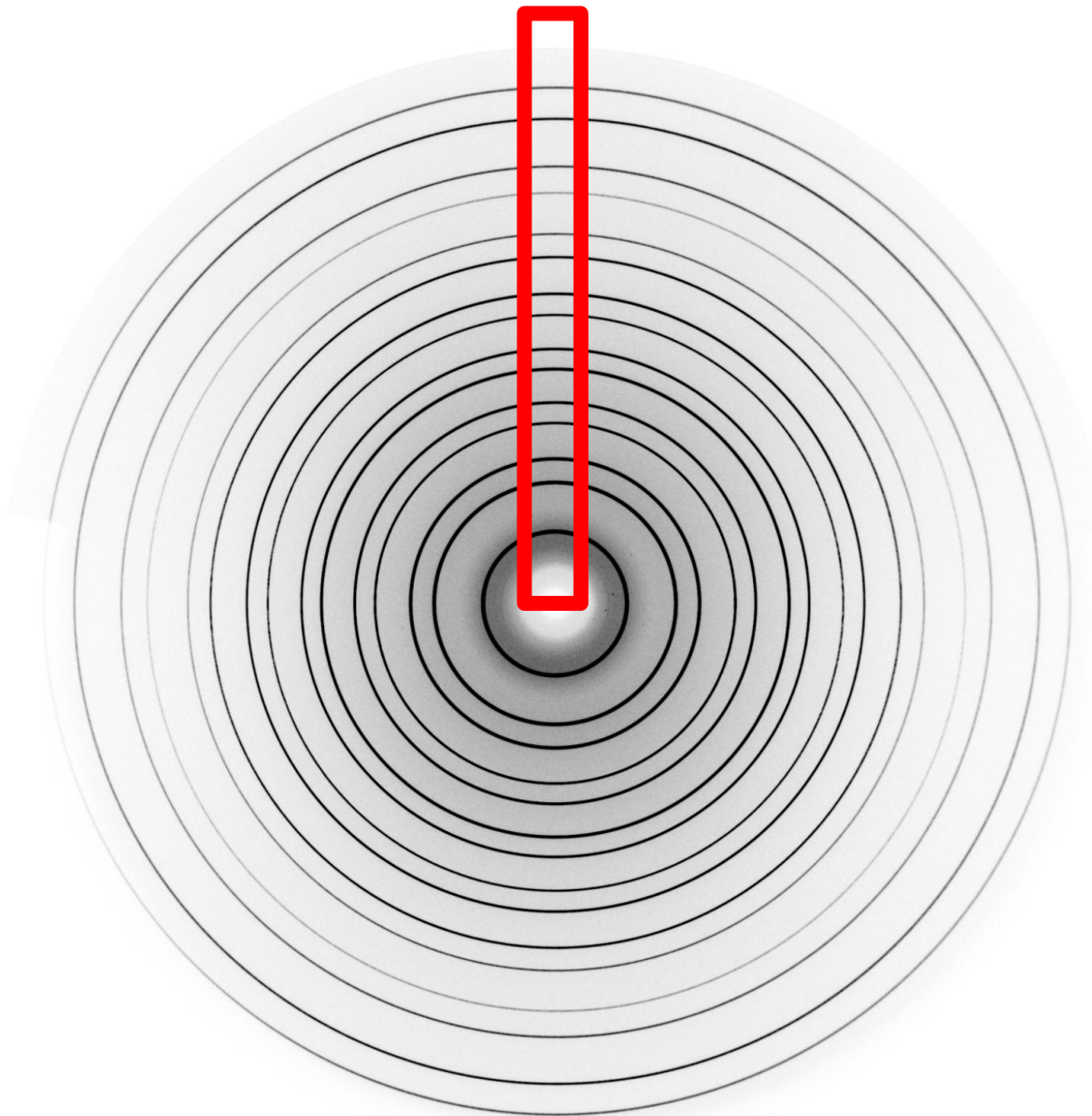




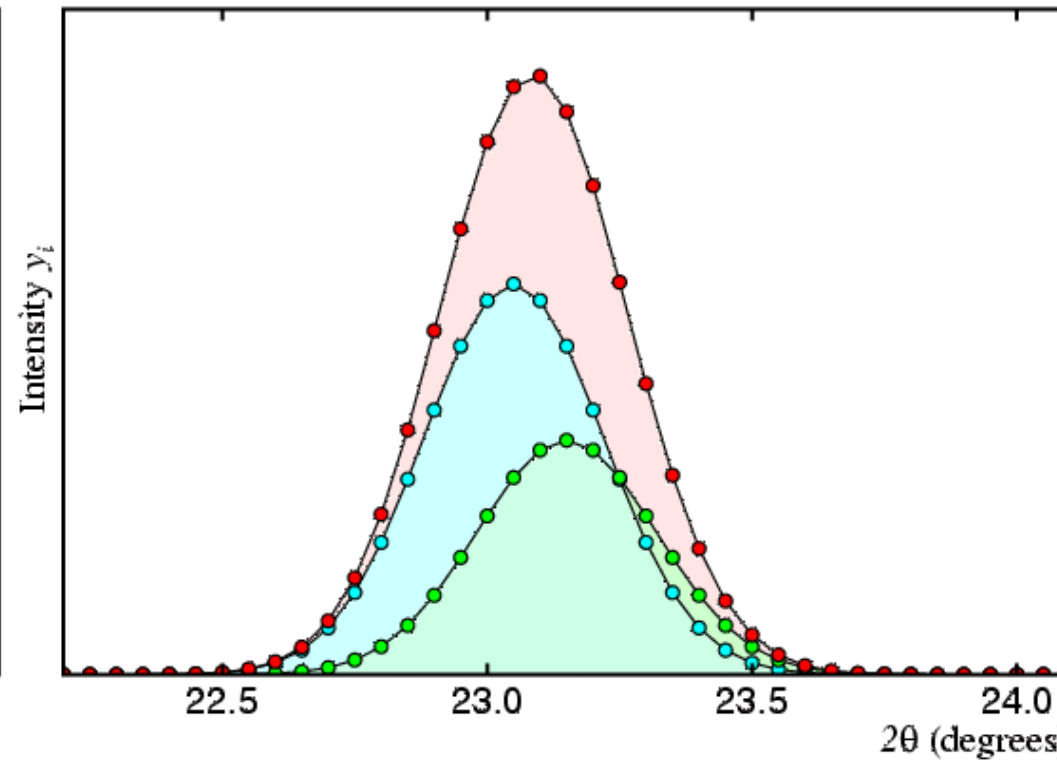
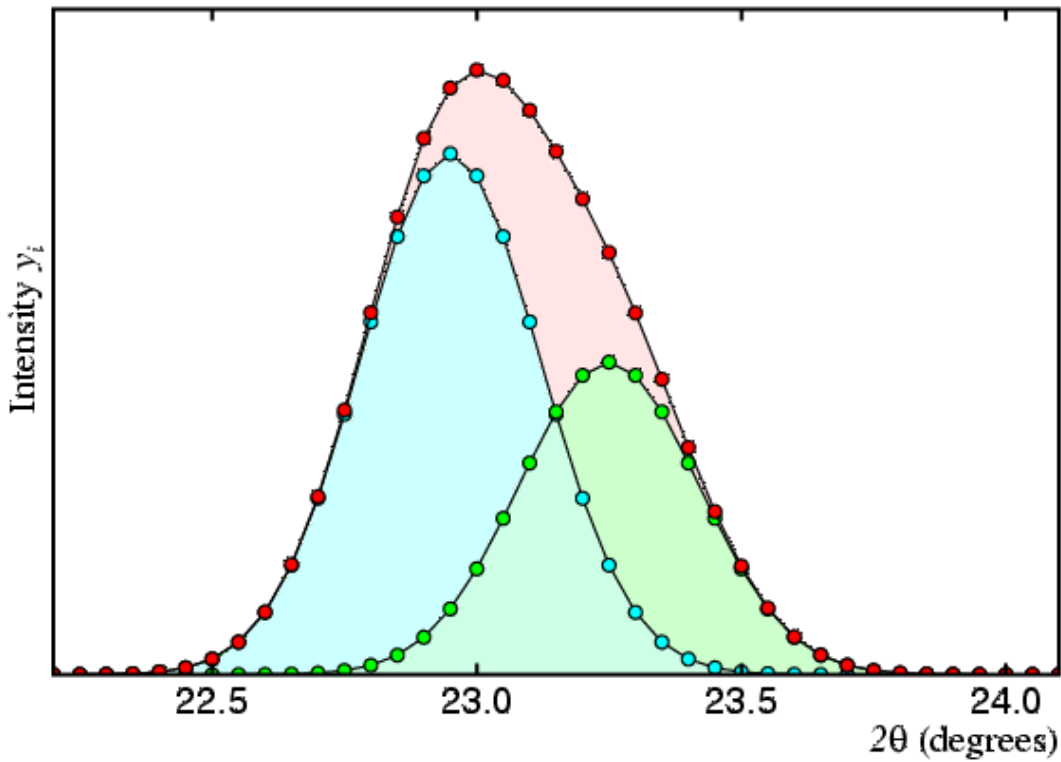
Powder diffraction



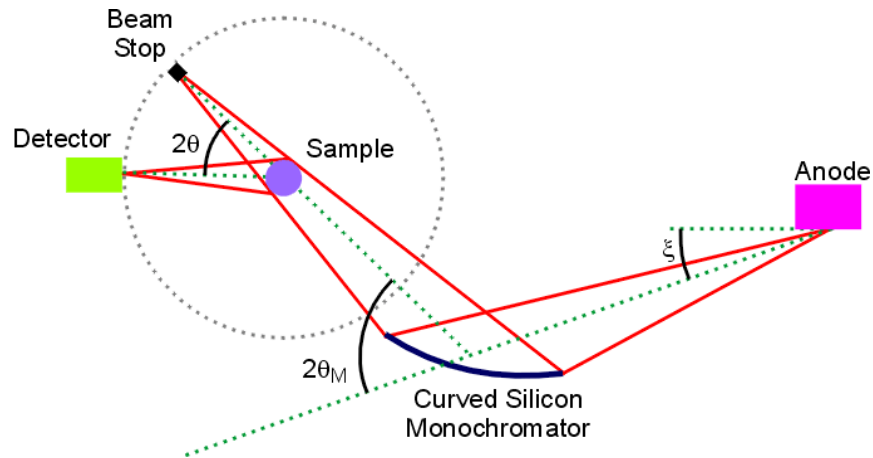
Powder diffraction



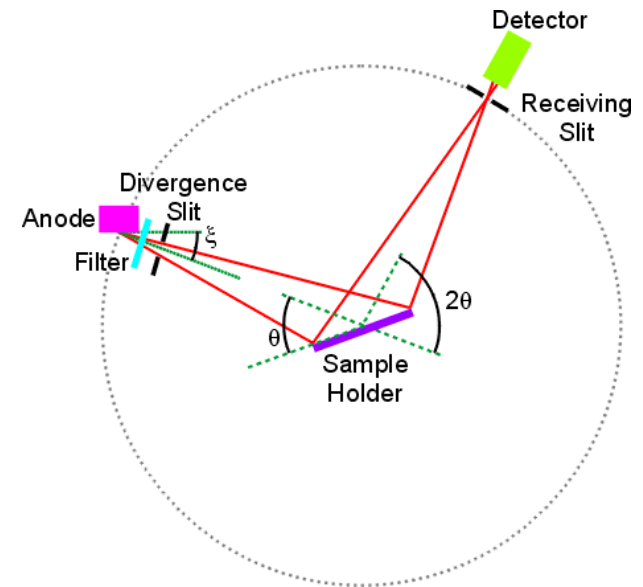
Powder diffraction



Diffraction geometries

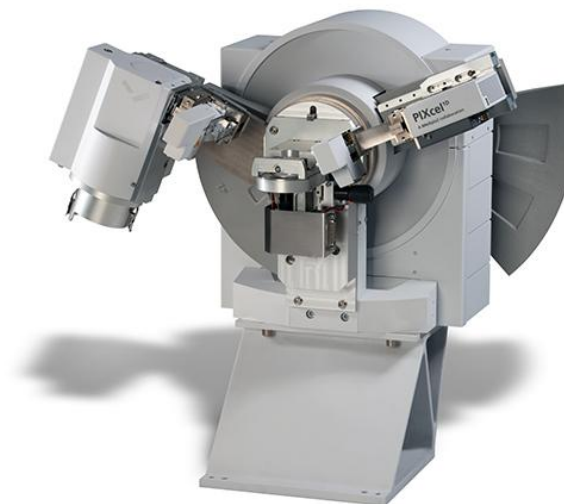
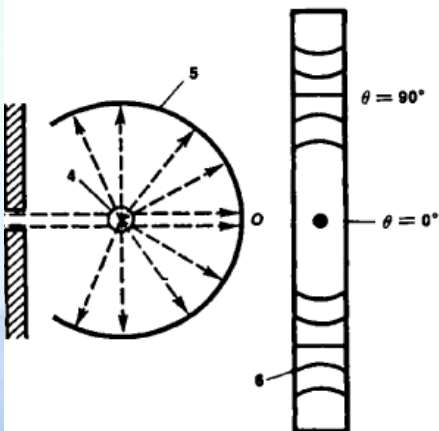
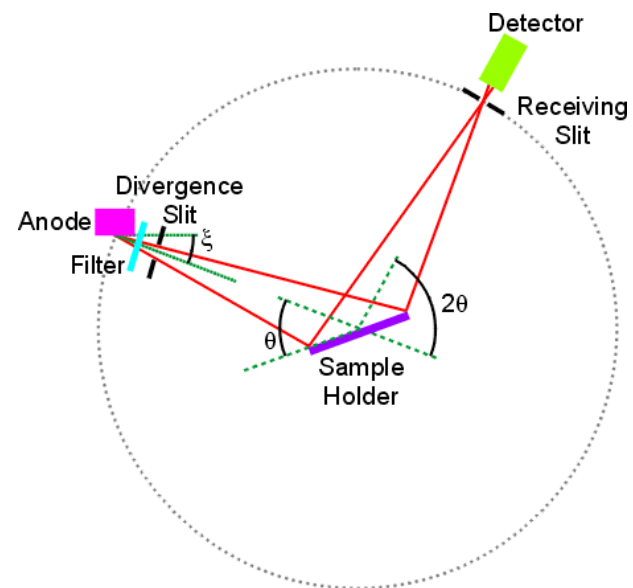
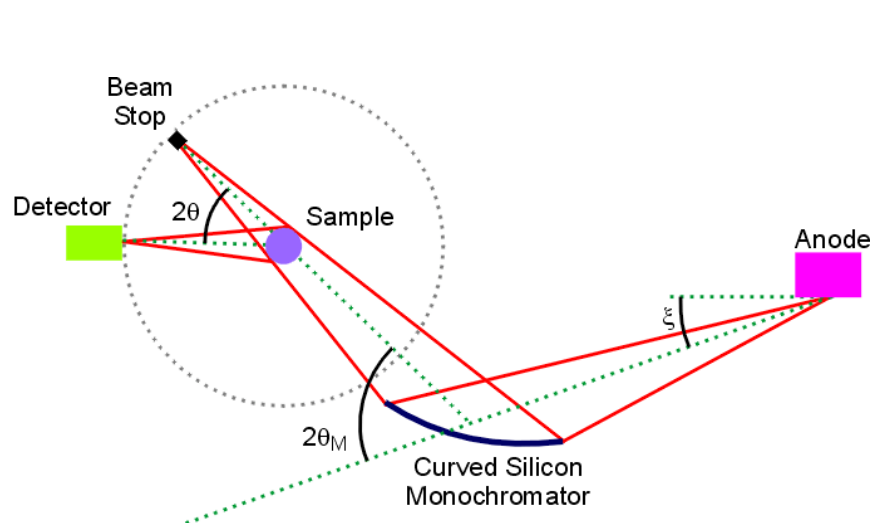


Debye-Scherrer
Transmission

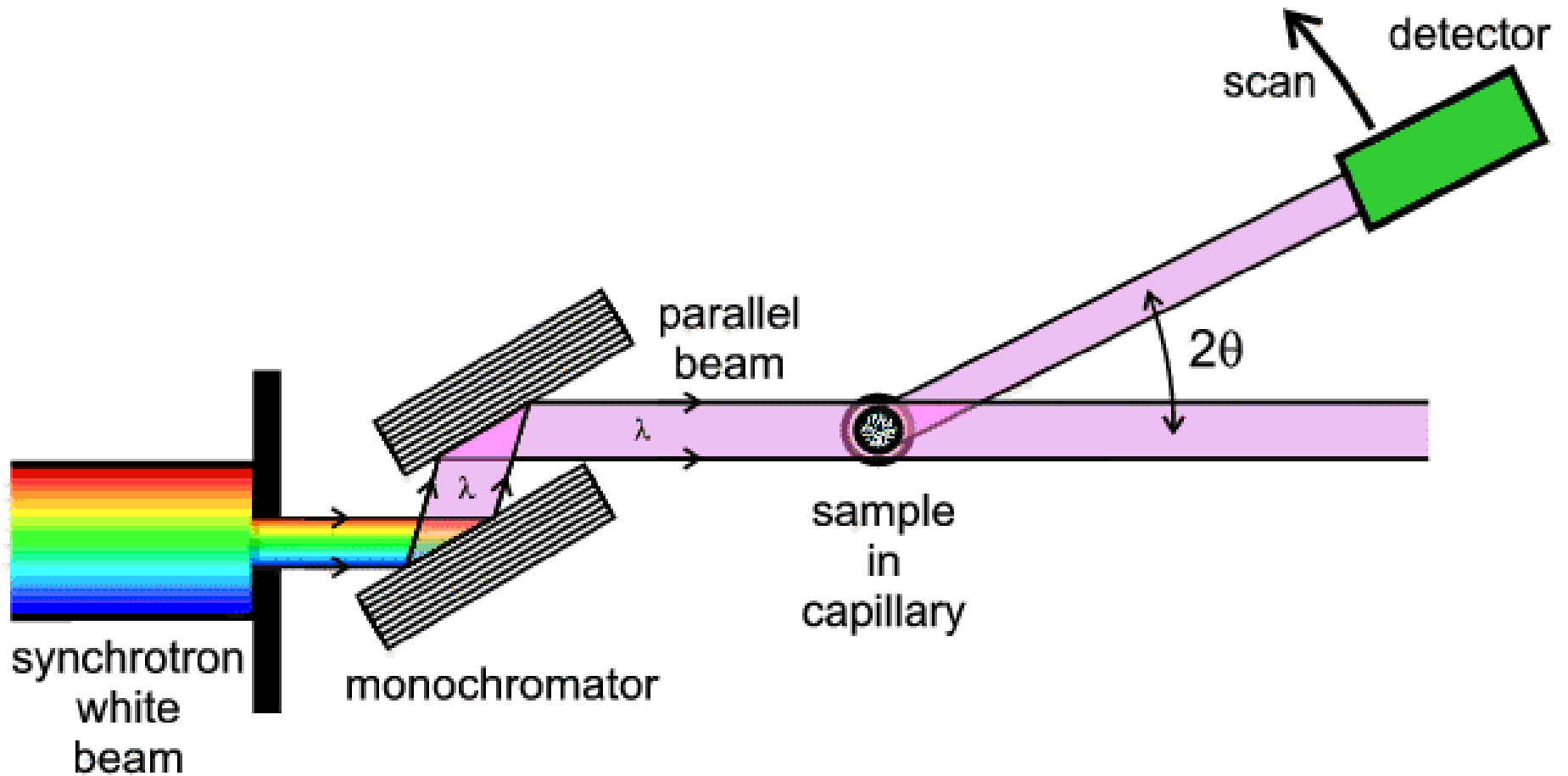


Bragg-Brentano
Reflection

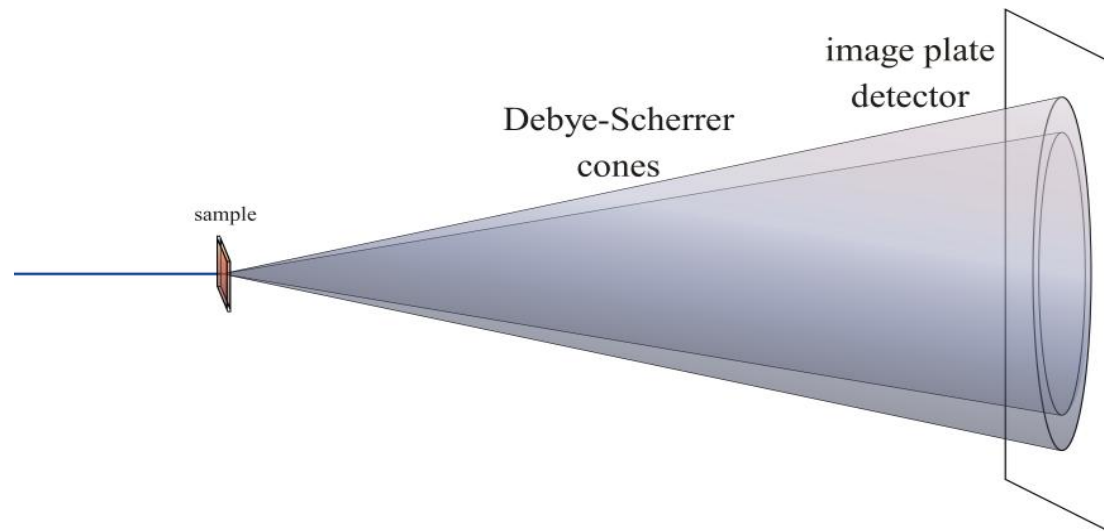
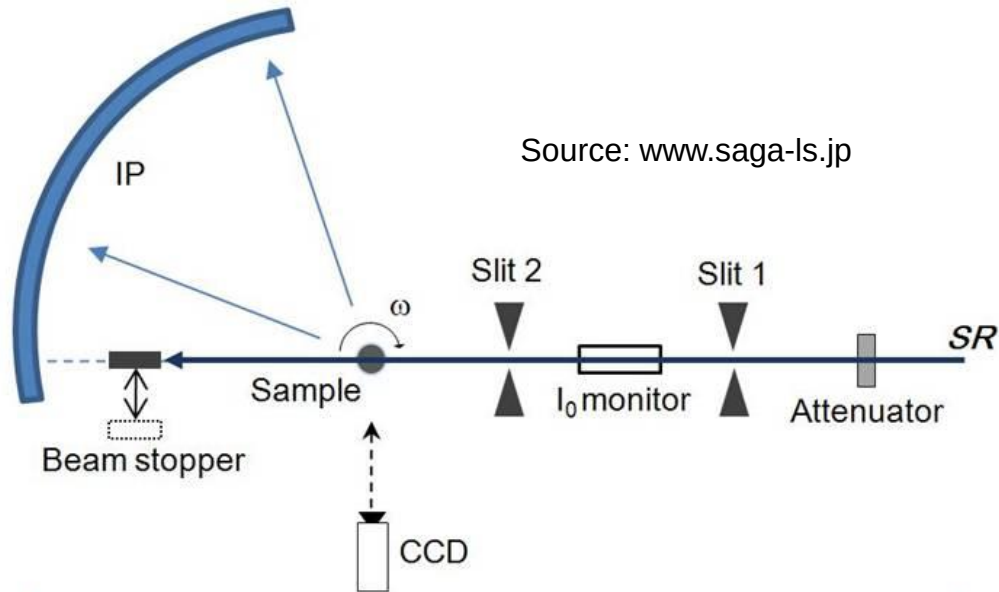
Diffraction geometries



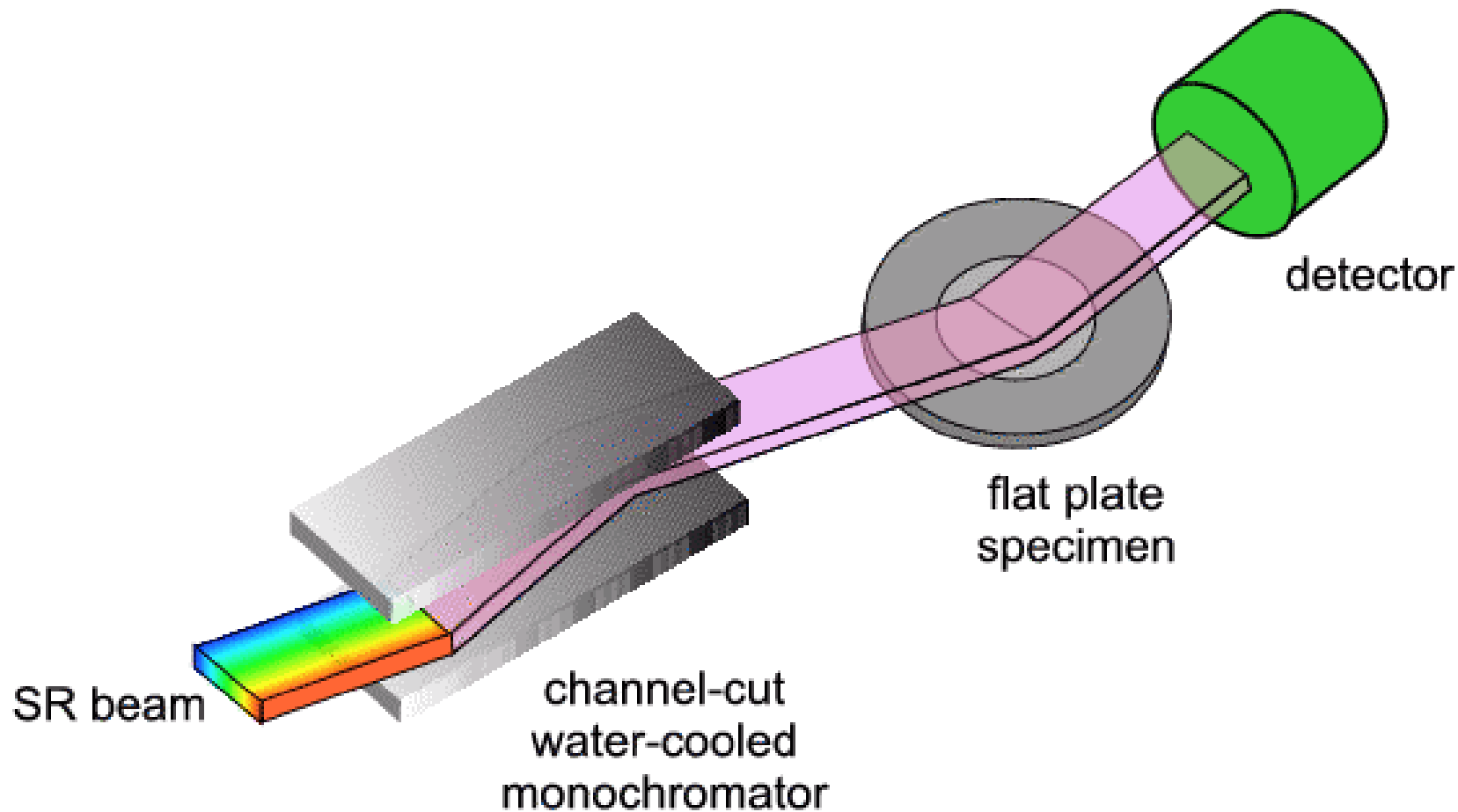
Diffraction geometries in synchrotrons



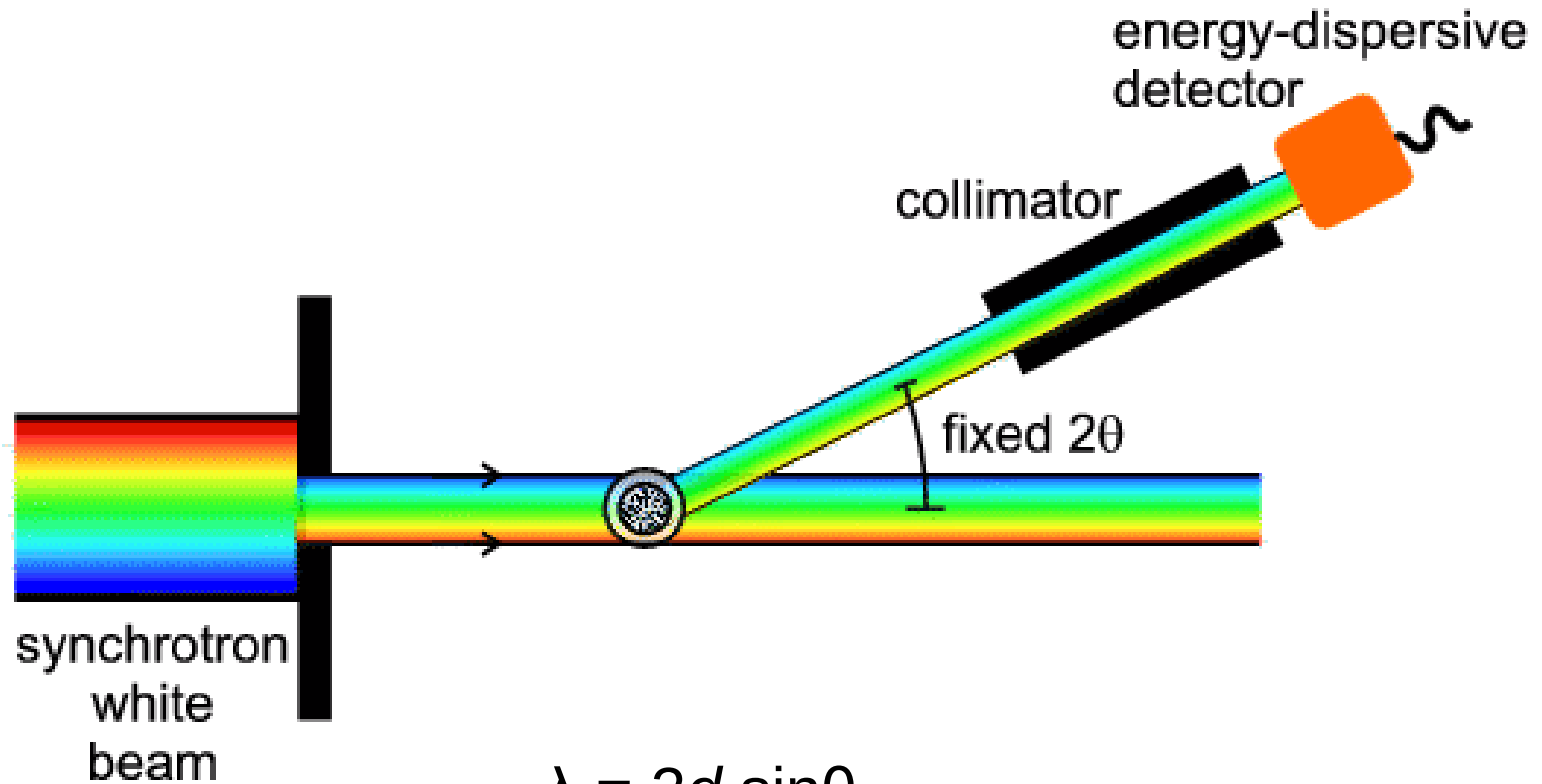
Diffraction geometries in synchrotrons



Diffraction geometries in synchrotrons



Diffraction geometries in synchrotrons



$$\lambda = 2d \sin\theta$$

scanned
variable
(by ED
detector)

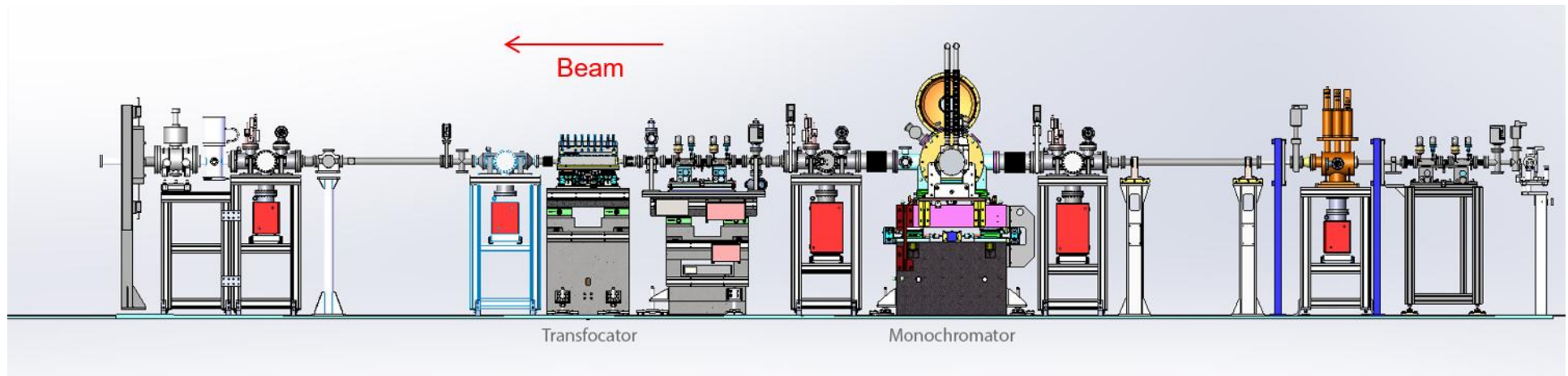
determined
variable

fixed
(by
collimator)

Advantages of XPRD at synchrotrons

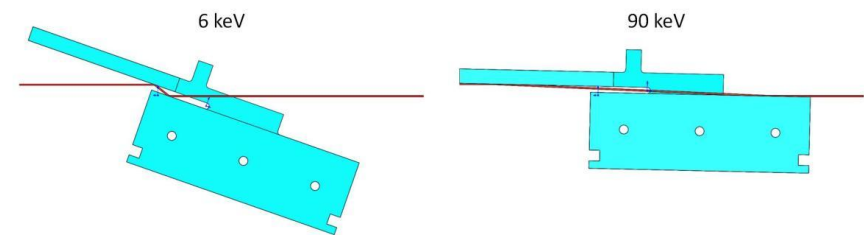
- **High X-ray flux** : Millions count counting statistics in reflection (Bragg-Brentano) as well as in transmission (Debye-Scherrer) modes even with low quantities of powder available
- **Highly collimated photon beam**: angular resolution better due to narrow instrumental profile. FWHM better than $0.01^\circ 2\theta$ obtained with new generation solid state microstrip detectors and down to $0.002^\circ 2\theta$ using multicrystal analyser detectors
- **Tunable photon energy up to high energies:**
 - anomalous scattering experiments
 - collect fluorescence-free XRPD data
 - Extension of d-space that can be probed.
 - depth analysis by varying energy

Instrumentation for X-ray Powder Diffraction at Synchrotrons



Light source:
In vacuum undulator

X-rays at **sample**:
Energy range : 6-80 keV
Beam size can be focused to 50 μm



Elettra - MCX

Light source:

Bending magnet

Critical energy : 3.2keV (2.0) , 5.5keV (2.4)

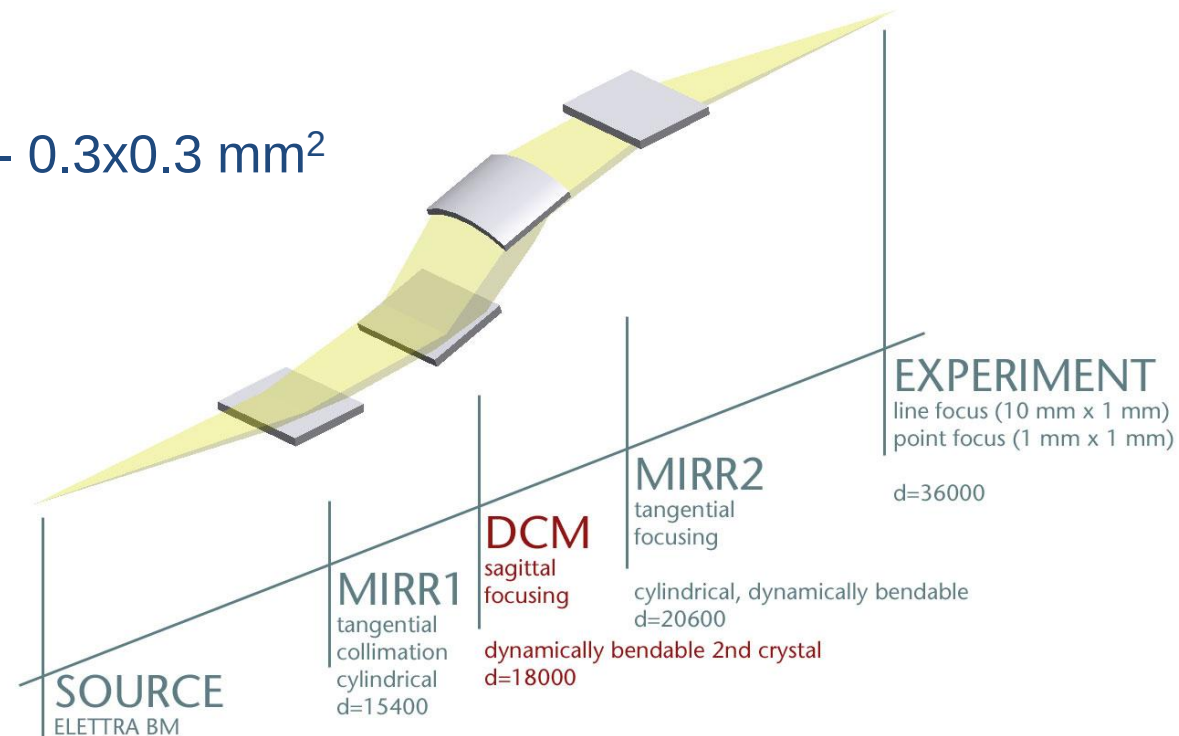
X-rays at sample:

Energy range : 6-21 keV

Photon flux : 10^{11} photons/sec

Beam size at sample : $10 \times 1 \text{ mm}^2$ - $0.3 \times 0.3 \text{ mm}^2$

Energy resolution : $\Delta E/E$ 2×10^{-4}



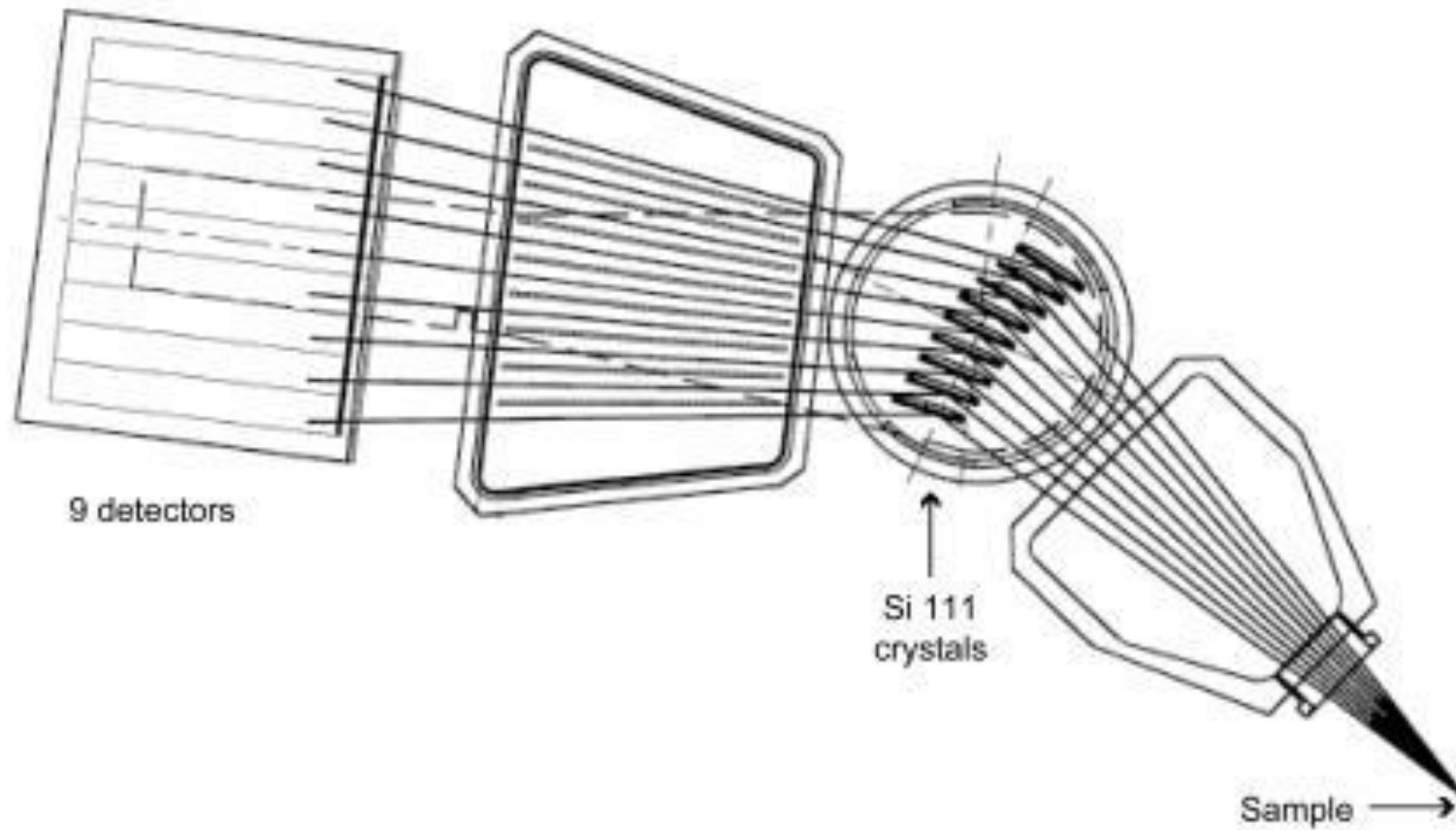
Diffractometer MCX



Diffractometer ID22-ESRF



Diffractometer ID22-ESRF

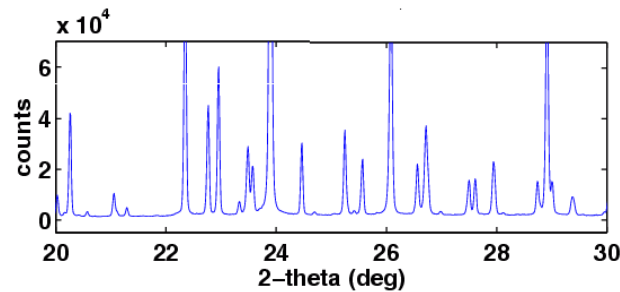


X-ray detectors

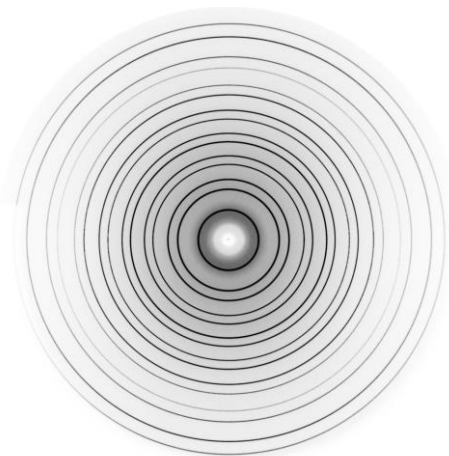
0D – (spot) detectors: Scintillators

N

1D – Line detectors: Gas detectors, Strip



2D -- Area detectors: Image plate, CCD, Pixel



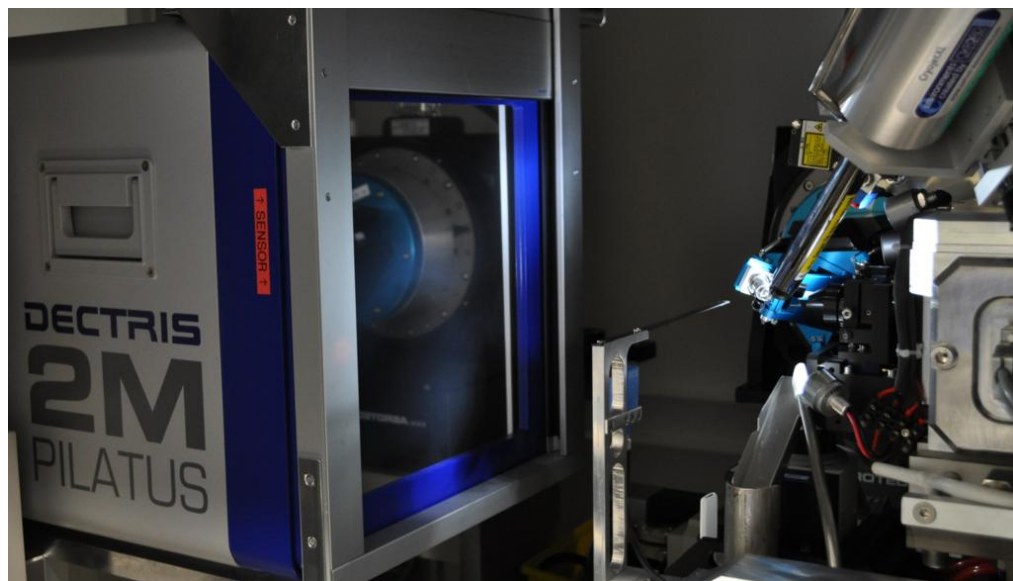
Mythen detector (1D)



Pilatus detector (2D)

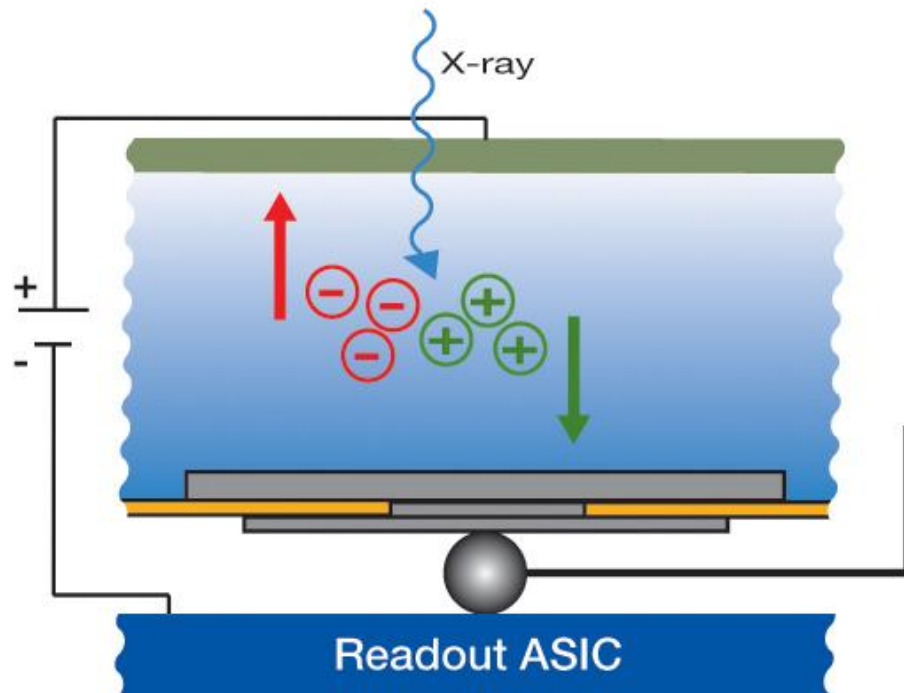
Source: XRD1 - elettra

Source: www.psi.ch



Pilatus detector (2D)

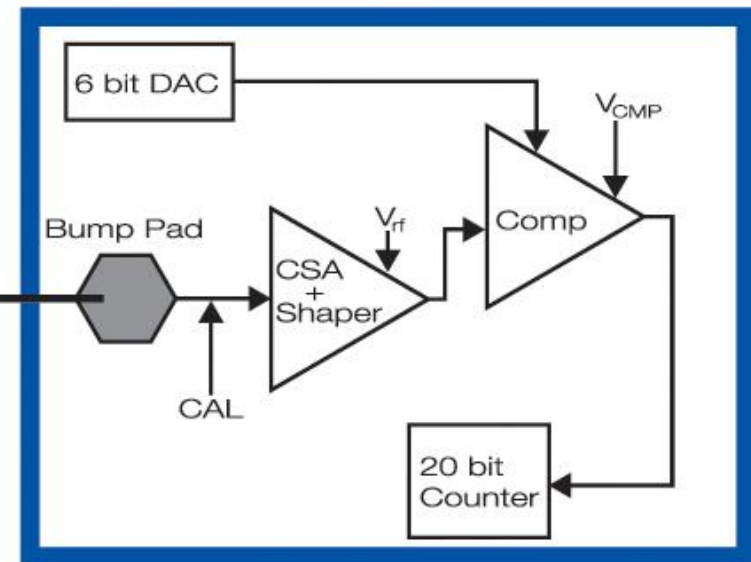
Sensor Pixel



**Direct detection of X-rays
in semiconductor sensor**

→ Point Spread Function 1 pixel

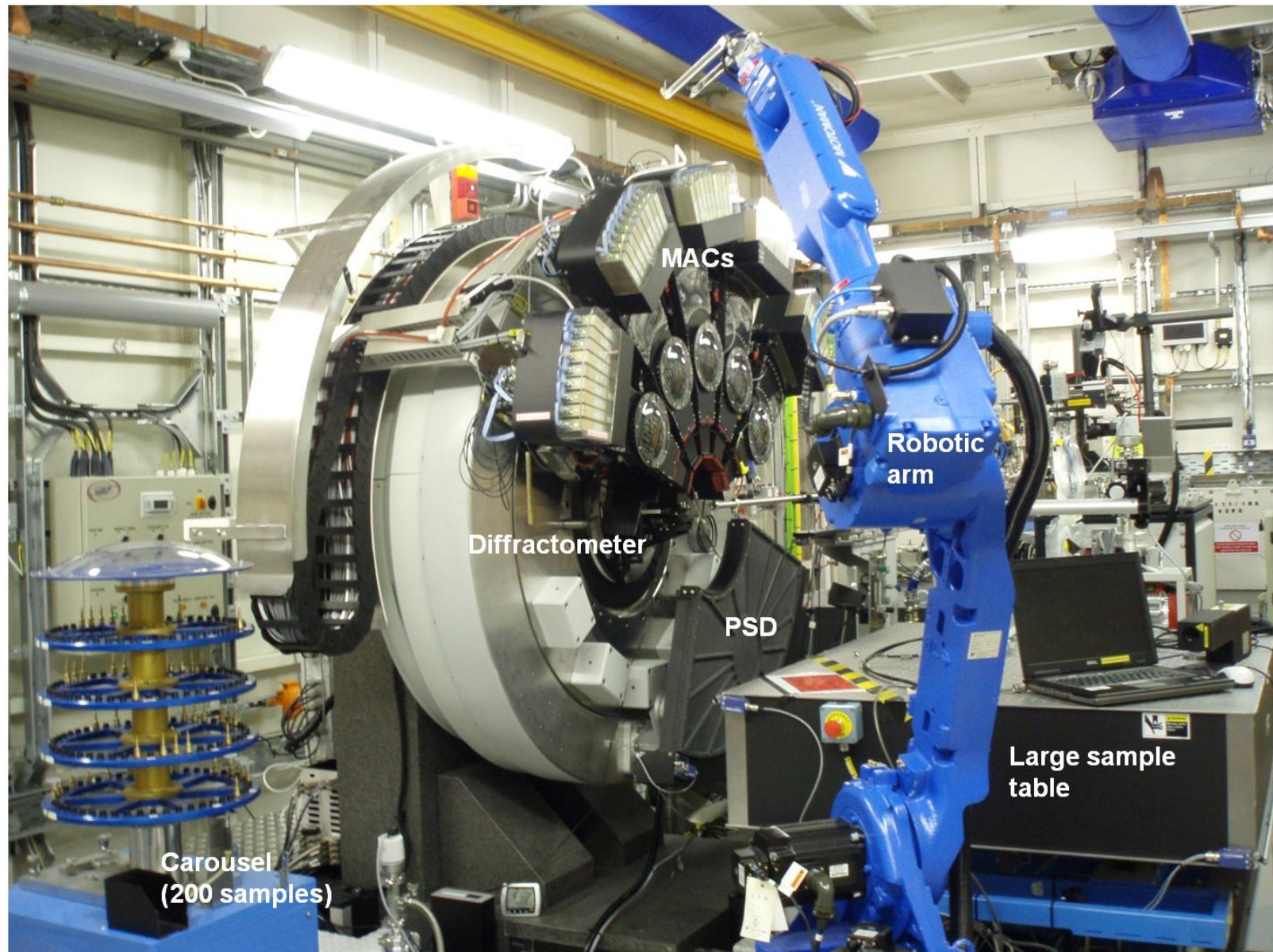
Readout Pixel



Single Photon Counting ASIC

→ No readout noise or dark current
→ High dynamic range (20 bit)
→ Fast readout

Diffractometer I11 - Diamond



Diffractometer MS



Information from Powder Diffraction

Information from powder diffraction

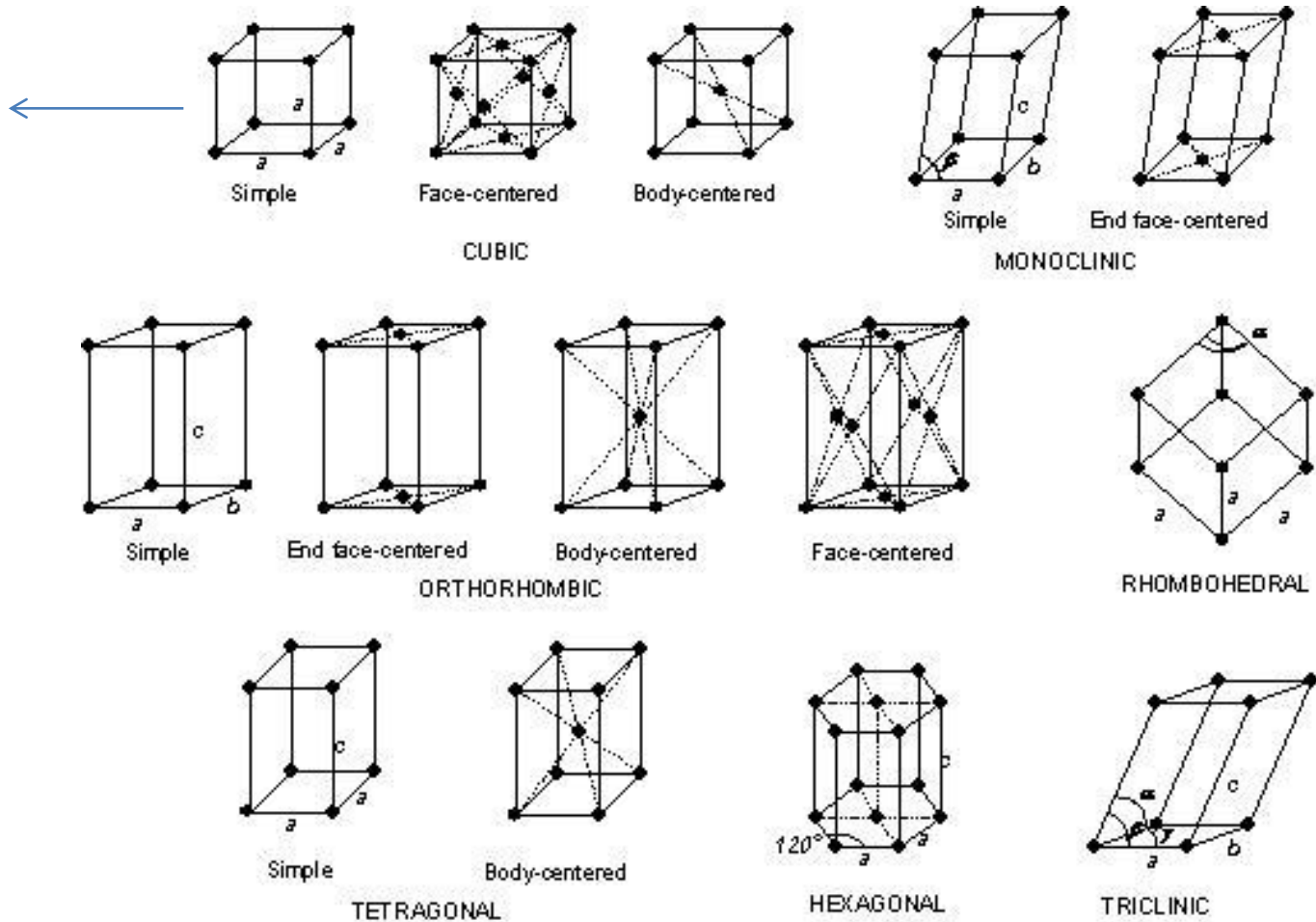
- The diffraction peak positions give information on the size and shape of the unit cell.
- Shifts in peak positions give information about deformation (eg. Residual stress)

$$\lambda = 2d \sin\theta$$

$$\begin{aligned} \frac{1}{d_{hkl}^2} = & h^2 \frac{b^2 c^2 \sin^2 \alpha}{V^2} + k^2 \frac{a^2 c^2 \sin^2 \beta}{V^2} + l^2 \frac{a^2 b^2 \sin^2 \gamma}{V^2} \\ & + 2hk \frac{abc^2 (\cos \alpha \cos \beta - \cos \gamma)}{V^2} + 2kl \frac{a^2 bc (\cos \beta \cos \gamma - \cos \alpha)}{V^2} \\ & + 2lh \frac{ab^2 c (\cos \gamma \cos \alpha - \cos \beta)}{V^2} \end{aligned}$$

Information from powder diffraction

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$



Information from powder diffraction

- The Intensity of a diffracted beam, I_{hkl} is related to an imaginary number called the structure factor, F_{hkl} : $I_{hkl} \propto |F_{hkl}|^2$

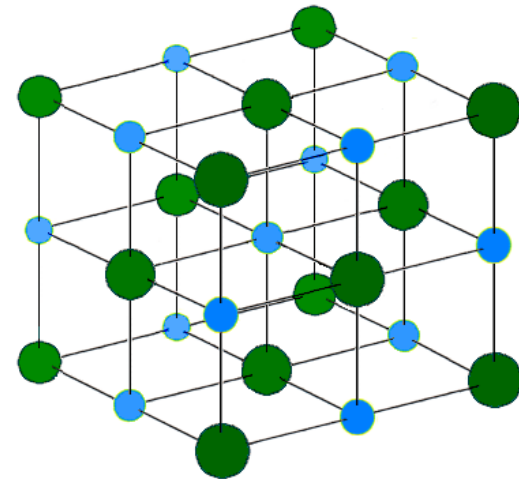
$$F(hkl) = \sum_n f_n N_n e^{2\pi i(hx_n + ky_n + lz_n)} e^{-B \sin^2 \theta / \lambda}$$

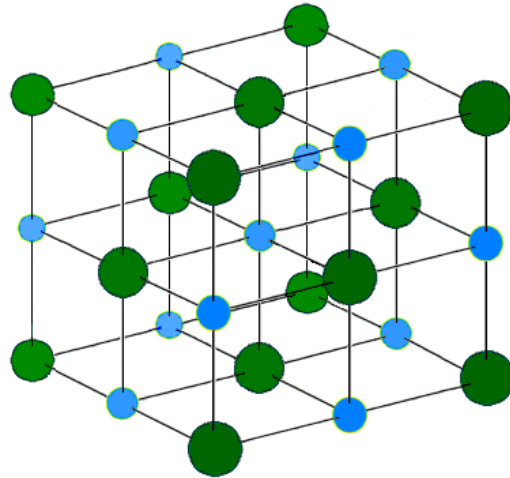
- The Intensity of a diffracted beam gives information on the positions of the atoms in the unit cell and hence the 'atomic structure' of the material
- In case of mixtures the intensities give information on the quantity of various materials in the mixture

Structure determination

- **Steps in structure determination from SR-XRPD:**

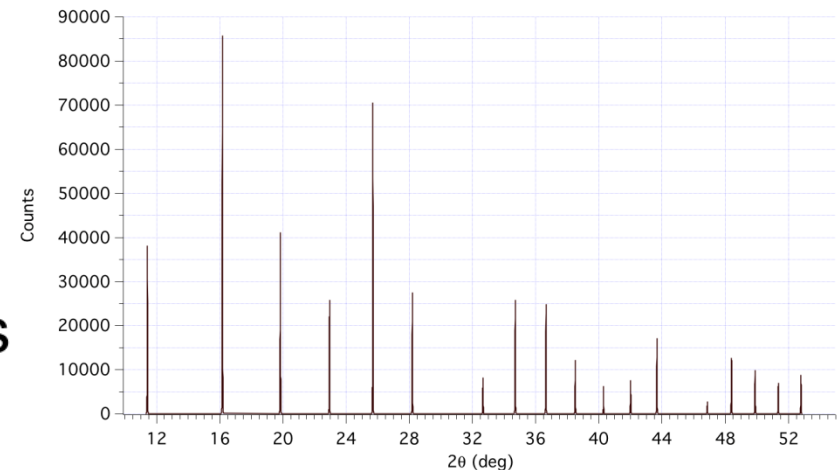
- Indexing (DICVOL ecc.)
- Space group determination
- Finding a model structure
 - Direct methods
 - Simulated annealing etc. (eg. DASH)
 - Model from similar compounds
- Refining the structure (Rietveld)





Structure determination Indexing

- Known parameters: peak positions
- Unknowns:
 - Unit cell $a, b, c, \alpha, \beta, \gamma$
 - Miller indices: h, k, l for each reflection
 - Zero shift ($2\theta_0$)



$$d = \lambda / 2 \sin(\Theta - 2\theta_0/2)$$

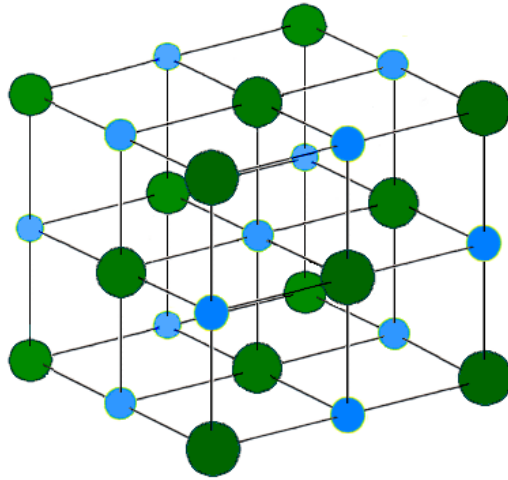
$$\frac{1}{d_{hkl}^2} = h^2 \frac{b^2 c^2 \sin^2 \alpha}{V^2} + k^2 \frac{a^2 c^2 \sin^2 \beta}{V^2} + l^2 \frac{a^2 b^2 \sin^2 \gamma}{V^2}$$

$$+ 2hk \frac{abc^2 (\cos \alpha \cos \beta - \cos \gamma)}{V^2} + 2kl \frac{a^2 bc (\cos \beta \cos \gamma - \cos \alpha)}{V^2}$$

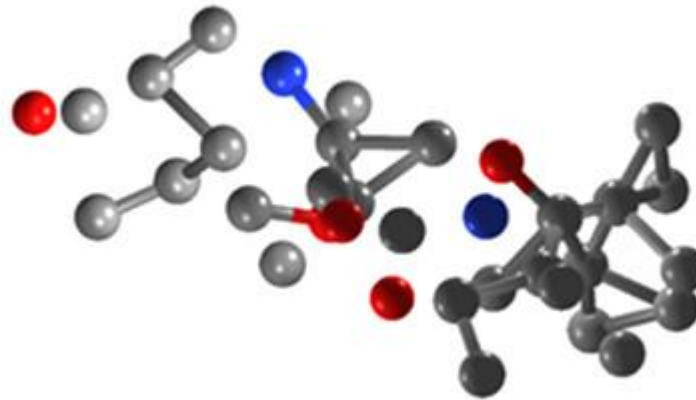
$$+ 2lh \frac{ab^2 c (\cos \gamma \cos \alpha - \cos \beta)}{V^2}$$

Structure determination

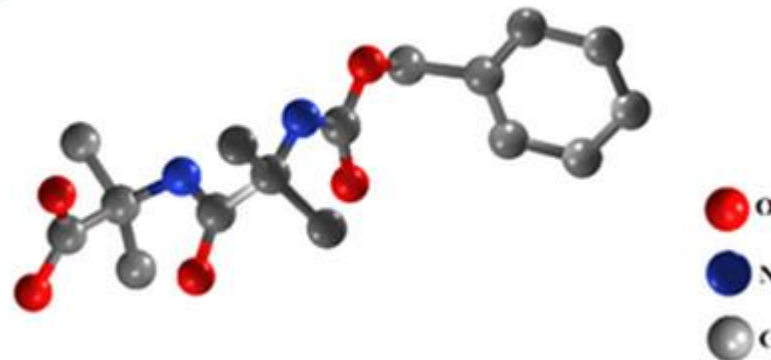
Finding a starting model



a)



b)



Structure Determination



Parameters refined in Rietveld refinement:

- Background (fixed, functions)
- Peak shape (microstructural parameters, functions)
- Lattice constants – Zero point correction – Sample displacement
- Scaling – phase fractions
- Structural parameters (Atoms positions, occupancies, B)
- Preferred orientation
- Absorption

Parameters are adjusted, and a diffraction pattern is calculated until the best fit with the measured pattern is obtained

$$F(hkl) = \sum_n f_n N_n e^{2\pi i(hx_n + ky_n + lz_n)} e^{-B \sin^2 \theta / \lambda}$$

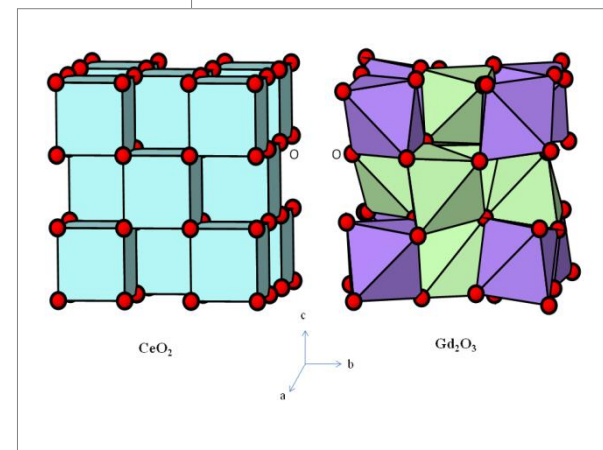
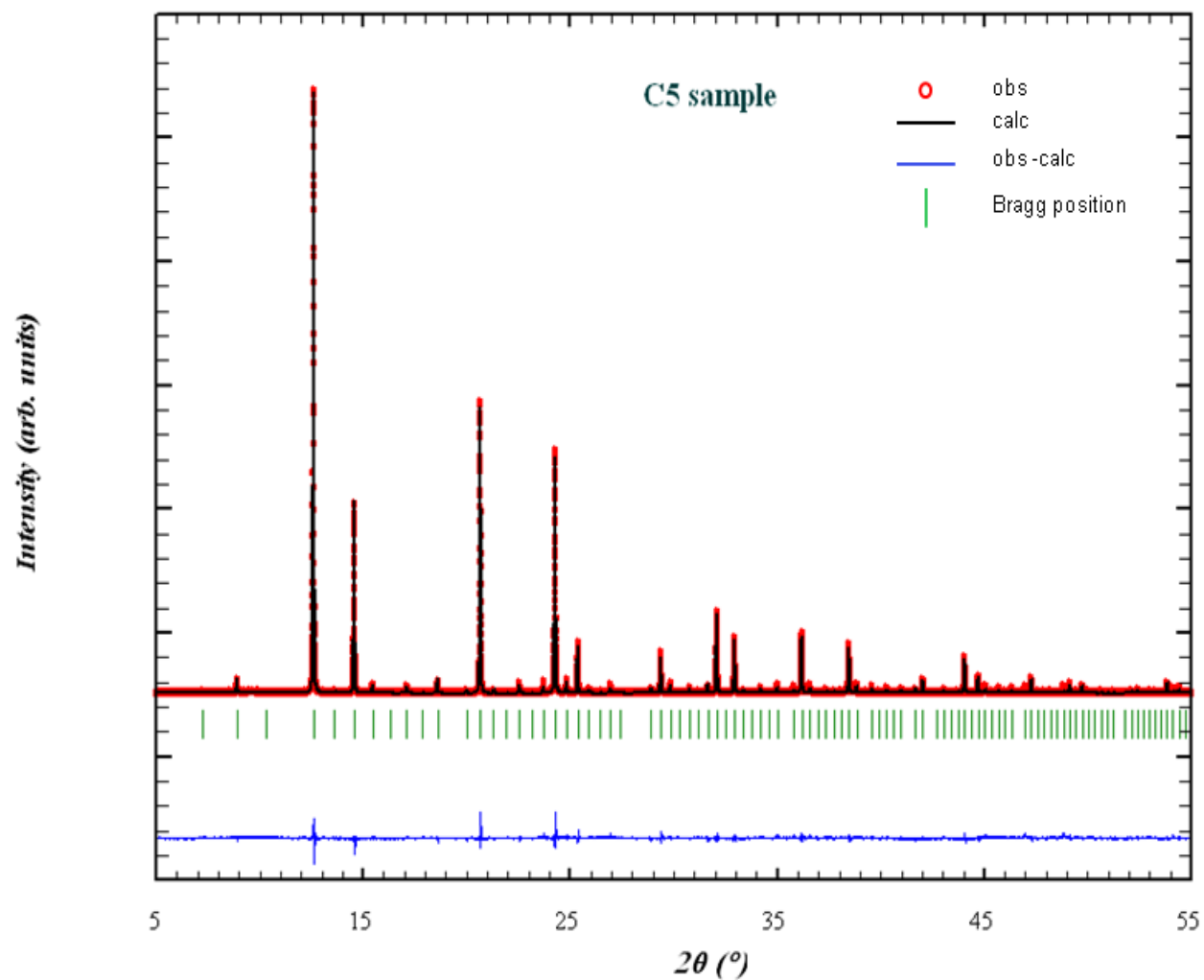
$$I(hkl) \sim |F(hkl)|^2$$

$$y_i = I_k \exp \left[\frac{-4 \ln(2)}{H_k^2} (2\theta_i - 2\theta_k)^2 \right]$$

$$H_k^2 = U \tan^2 \theta_k + V \tan \theta_k + W$$

$$M = \sum_i W_i \left\{ y_i^{obs} - \frac{1}{c} y_i^{calc} \right\}^2$$

Structure determination



Information from powder diffraction

- **1895** Rontgen discovered X-rays
- **1912** Laue measured the first diffraction pattern of crystal
- **1913** Braggs published first crystal structures
- **1918** Paul Scherrer published the Scherrer formula to determine the size of nanocrystals

Information from powder diffraction

$$B(2\theta) = \frac{K\lambda}{L \cos \theta}$$

- Peak width (B) is inversely proportional to the nanocrystal size (L).

P. Scherrer, "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachr. Ges. Wiss. Göttingen* **26** (1918) pp 98-100.

Information from powder diffraction

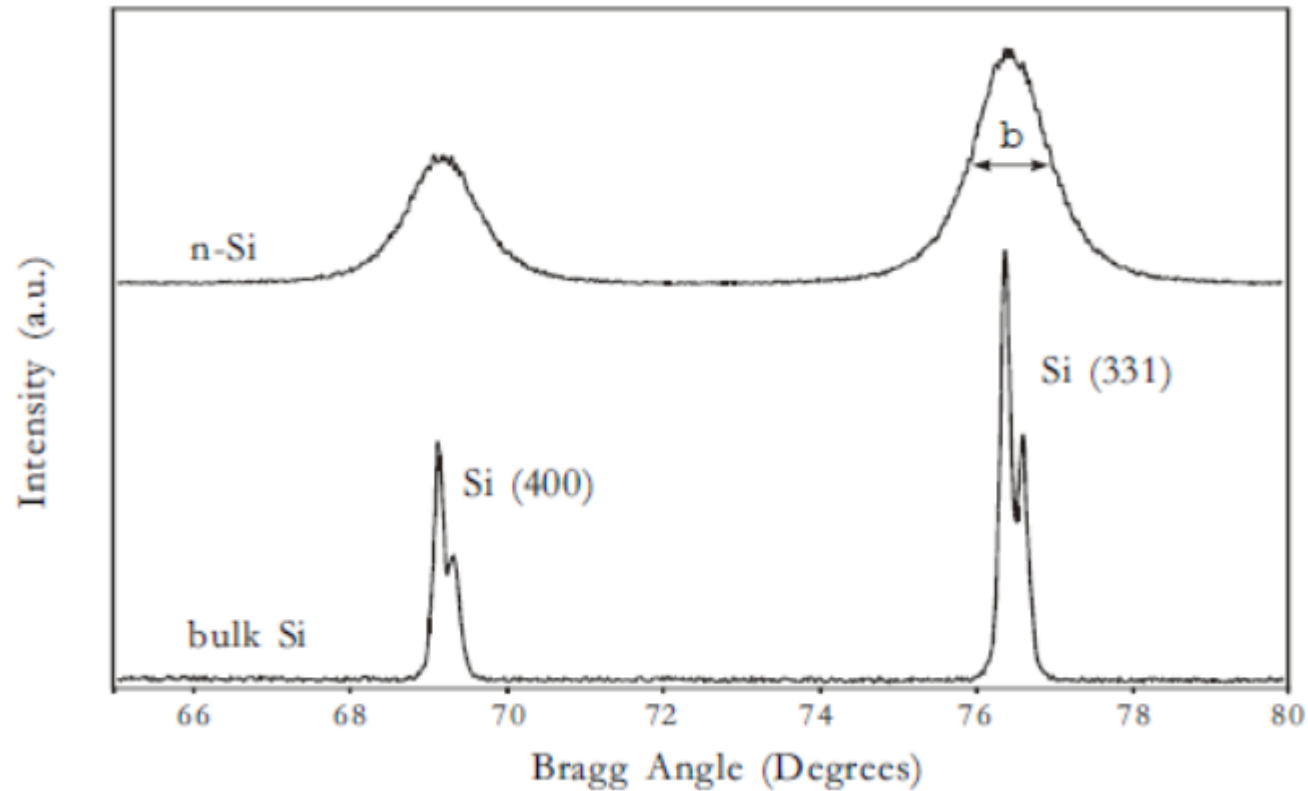
- The shape of the peak give information about the microstructure of the materials

A diffraction peak is a **convolution** () of *profile components* produced by different sources.

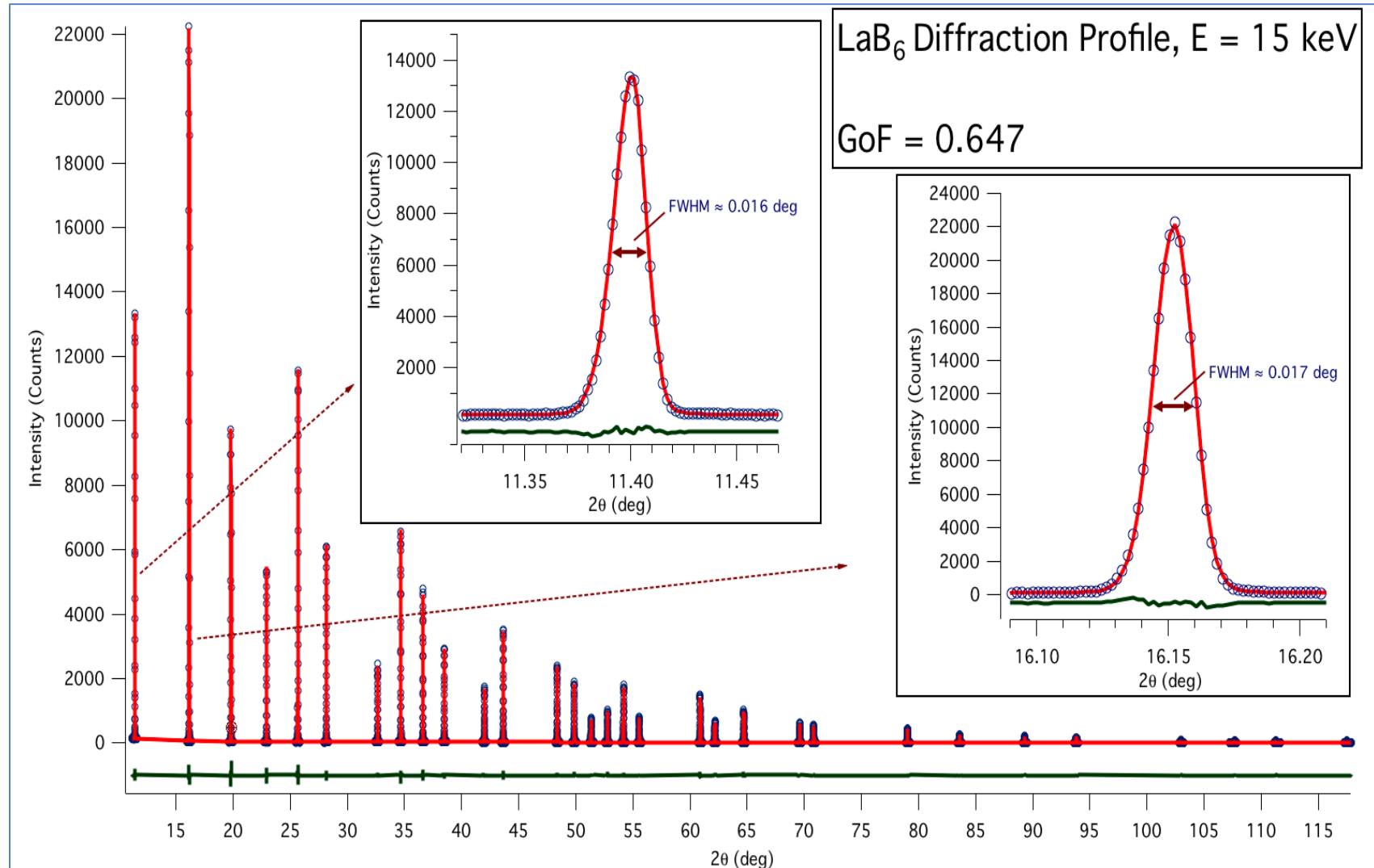
These are instrumental factors (IP) and effects due to domain size (S), microstrain (D), faulting (F), anti-phase domain boundaries (APB), stoichiometry fluctuations (C), grain surfacerelaxation (GSR), etc.

$$I(s) = I_{IP}(s) \otimes I_S(s) \otimes I_D(s) \otimes I_F(s) \otimes I_{APB}(s) \otimes I_C(s) \otimes I_{GRS}(s) \dots$$

Information from powder diffraction



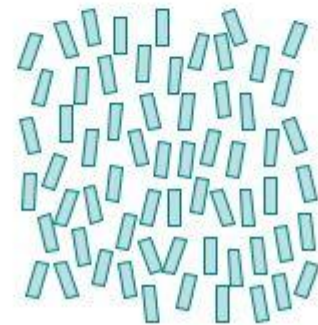
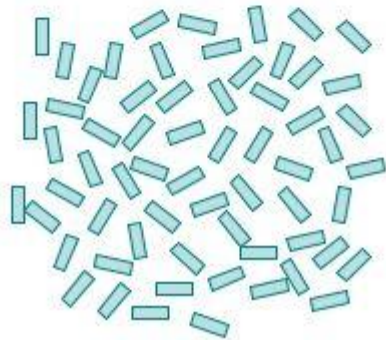
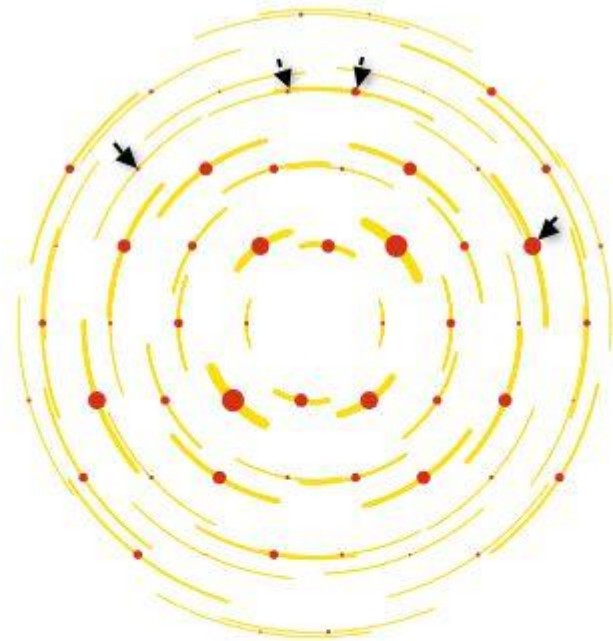
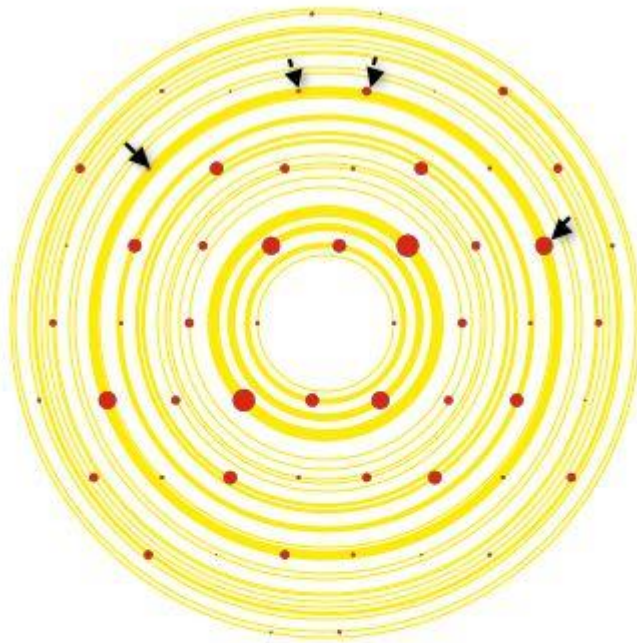
Instrumental profile



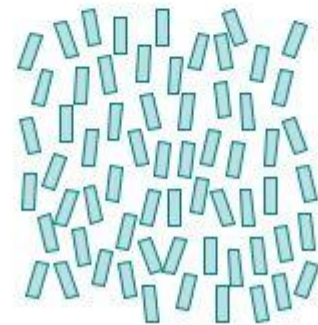
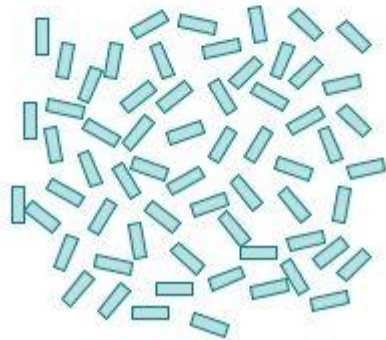
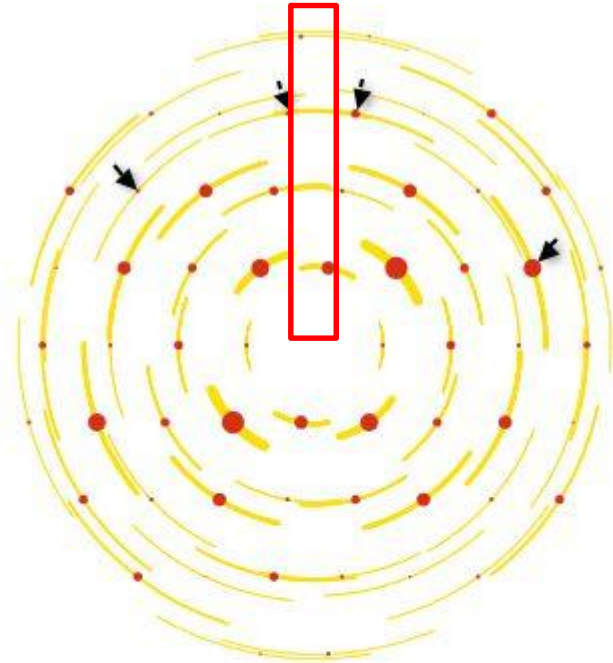
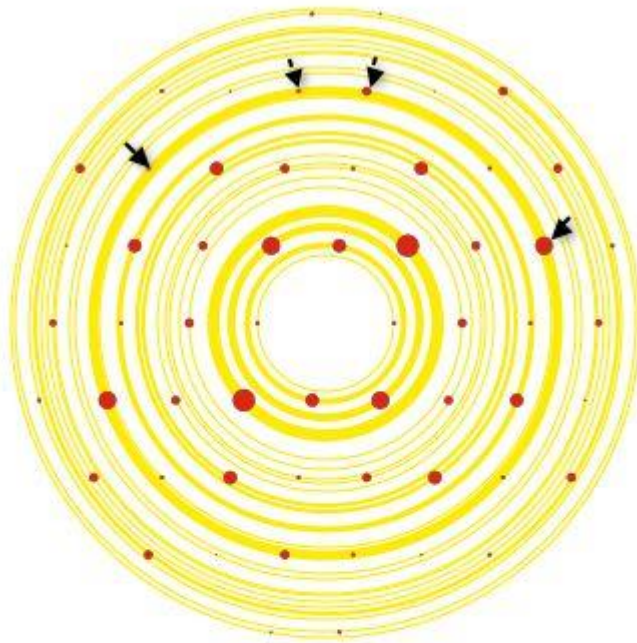
Obtaining information from XRPD

- We want to measure the intensity profile in reciprocal space
 - position of diffraction peaks (d_{hkl})
 - intensity (I_{hkl})
 - peak profile
- **IMPORTANT:** a correct measurement assumes:
 - the homogeneous spatial distribution of the crystallites in the sample
 - the homogeneous probing of the material by the beam
 - the statistically correct measurement of intensity

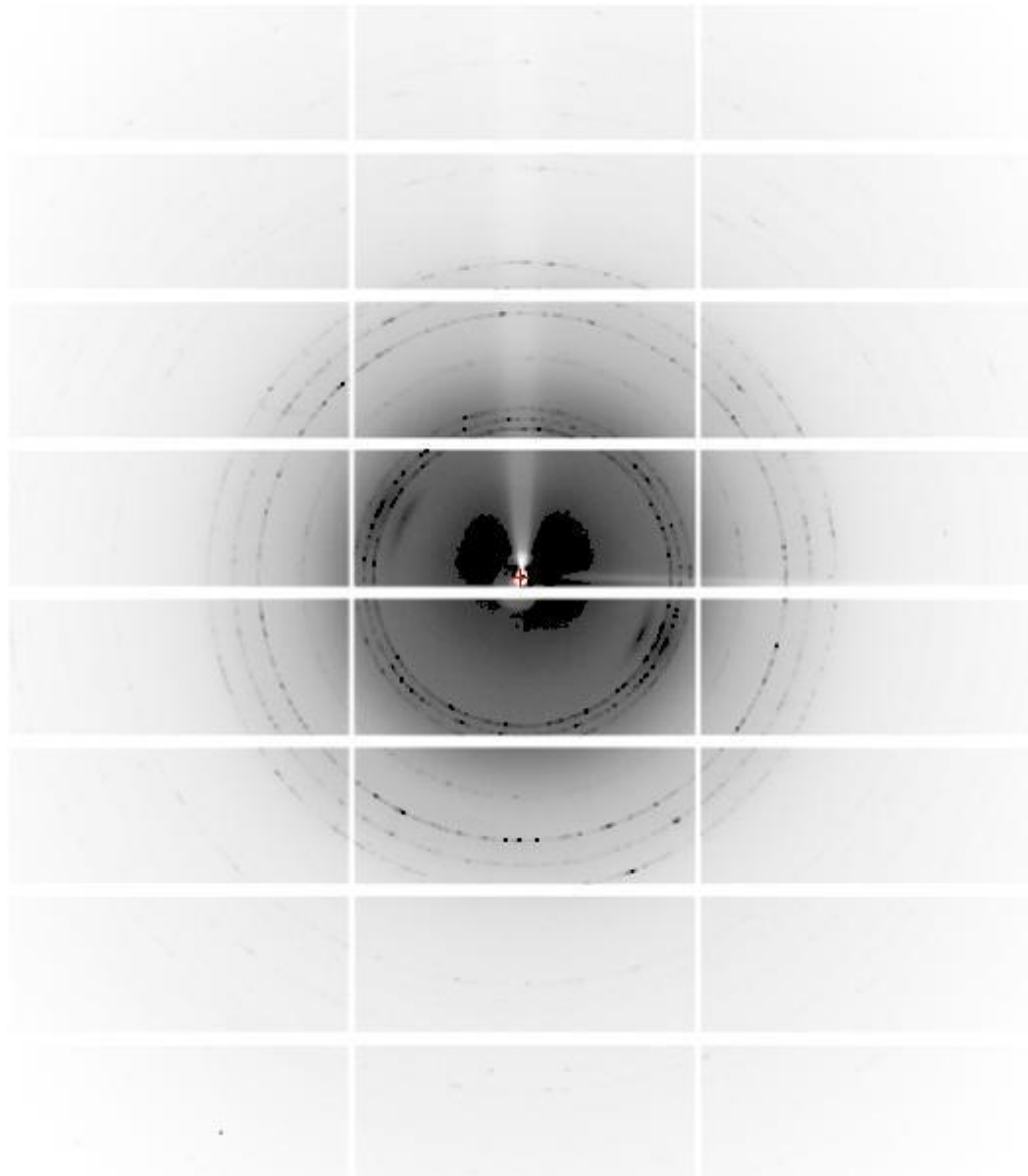
Texture



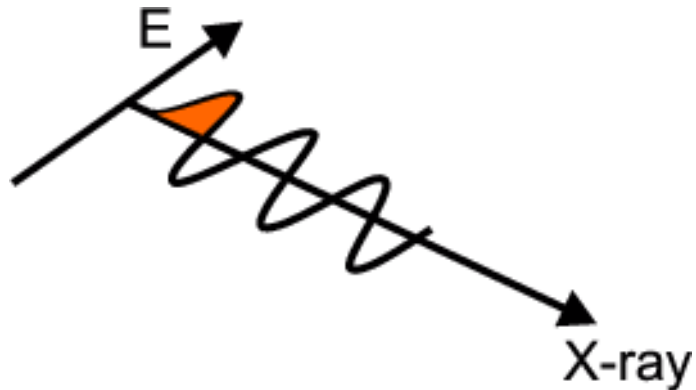
Texture



Few cristallites

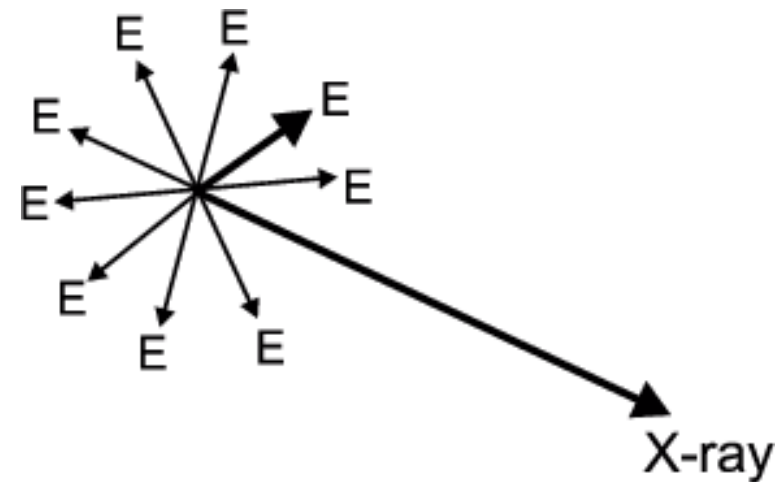


Polarisation



Synchrotron

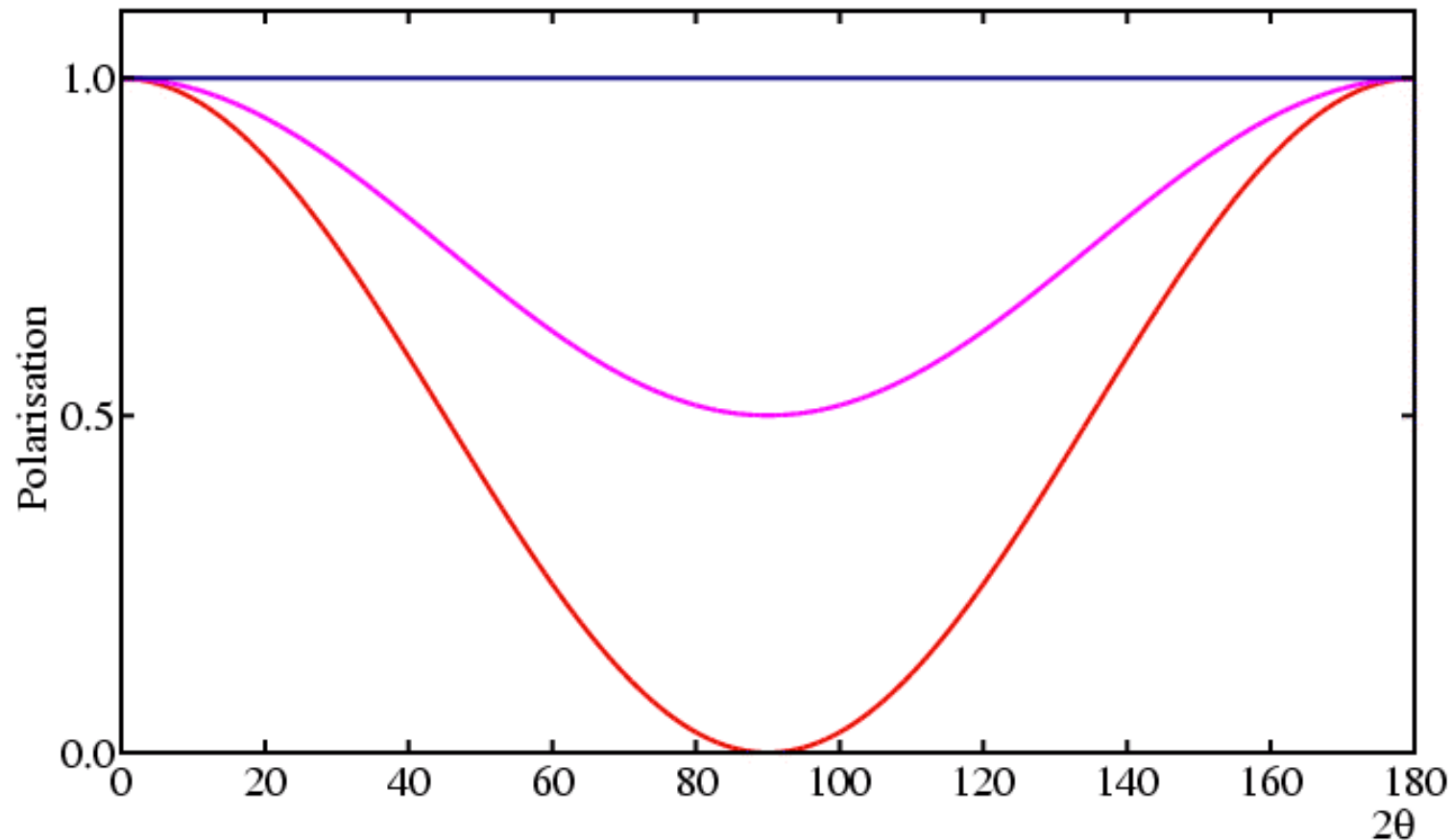
Radiation is horizontally polarised in the plane of the electron orbit



Laboratory source

Unpolarised radiation

Polarisation



Red: Polarisation in plane of scattering

$$P = \cos^2 2\theta$$

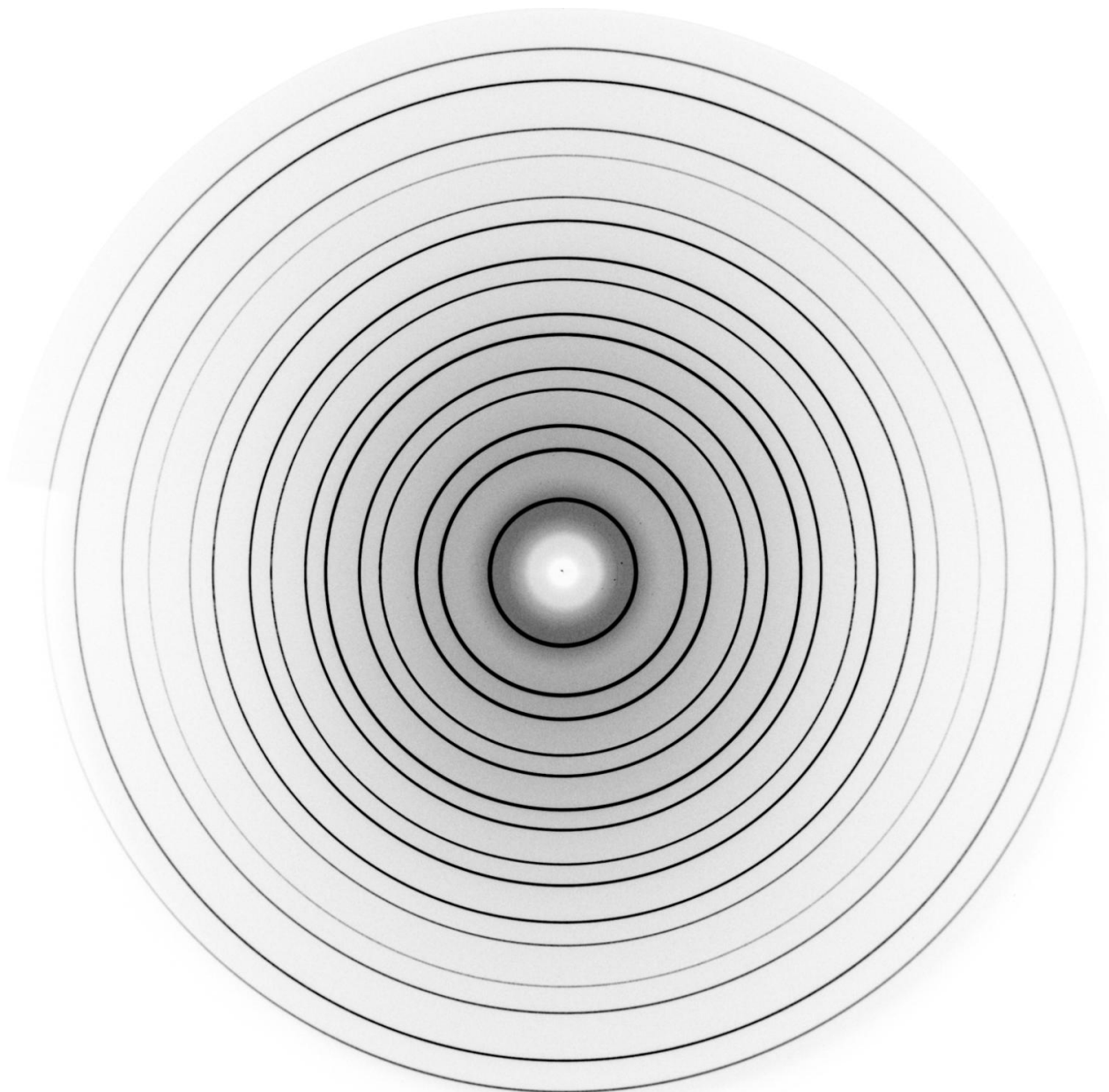
Blue: Polarisation perpendicular to plane of scattering

$$P = 1$$

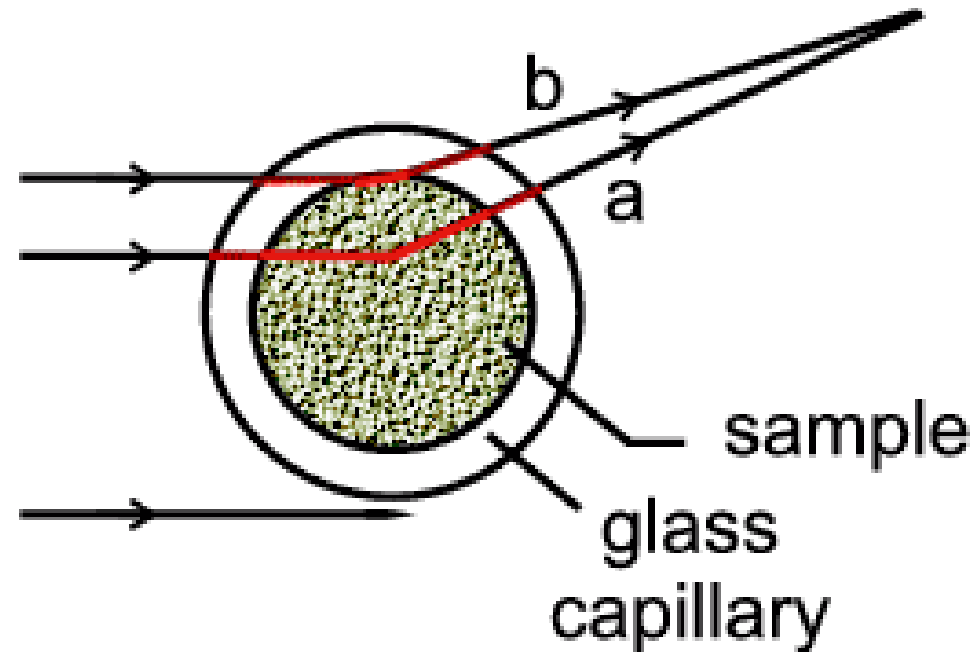
Pink: Unpolarised X-rays

$$P = (1 + \cos^2 2\theta)/2$$

Polarisation

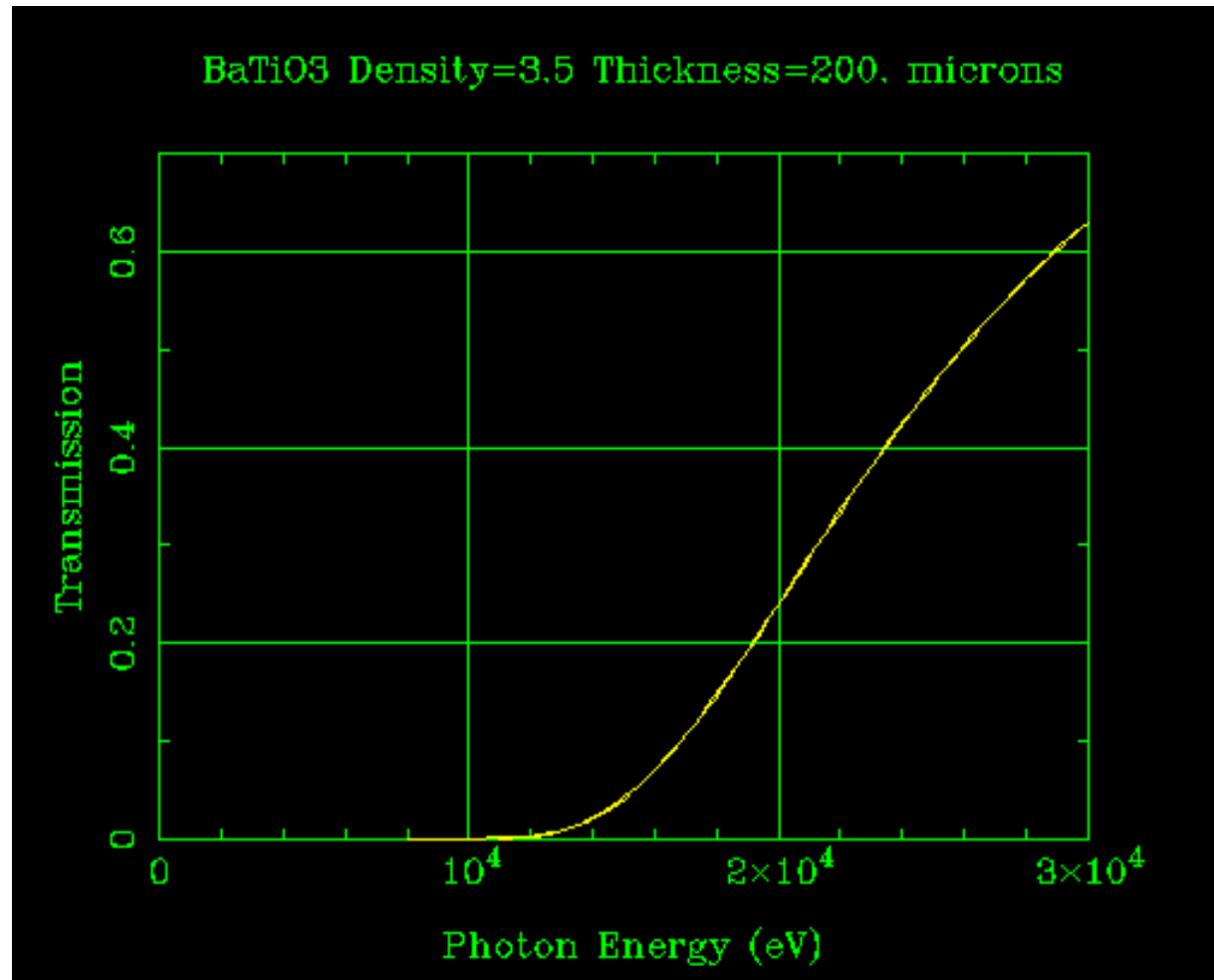


Absorption

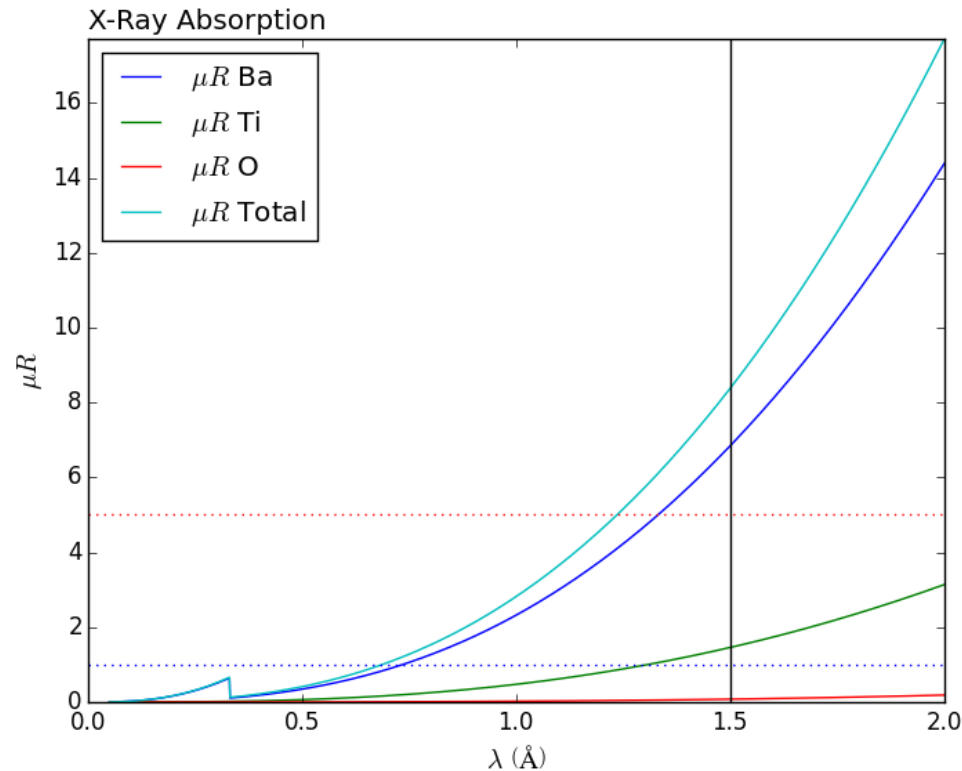


Capillary: The effect is not easy to calculate but the result is satisfying. As the example above illustrates, some paths appear to be like transmission (a) and others like reflection (b). Correction for this effect can be made if the absorption of the sample is not too large.

Absorption

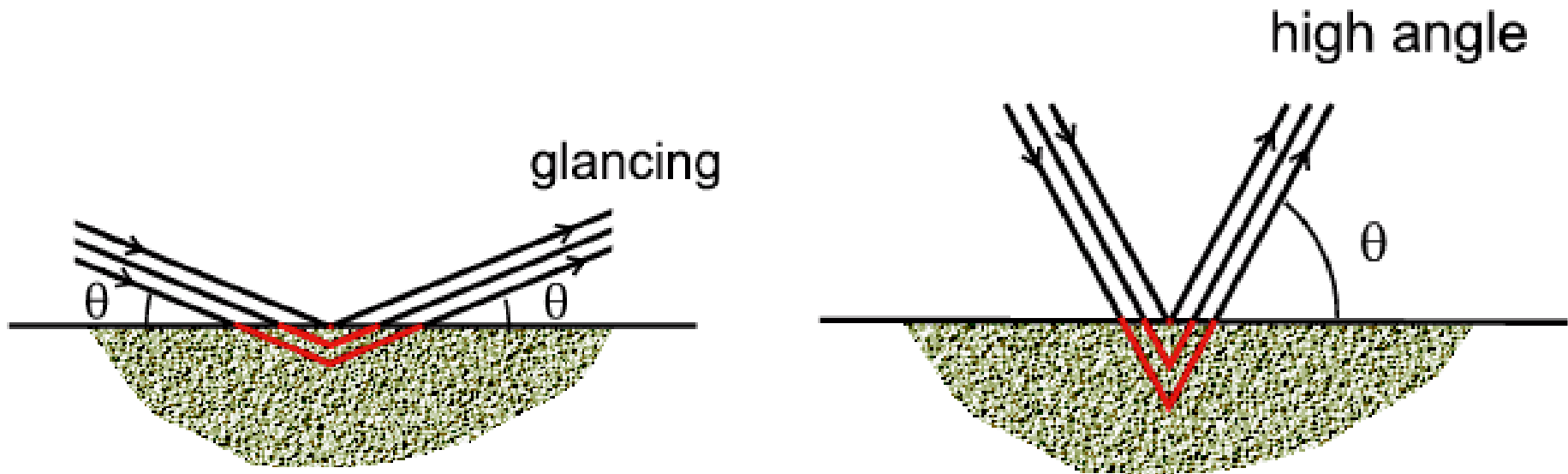


Absorption



The plot above shows the absorption for each input element and for the specified composition as a function of X-ray wavelength/energy. The blue dotted line indicates a μR value of 1. In a capillary (Debye-Scherrer) geometry, it is ideal when μR is 1 or below, as sample absorption is minimal and no correction is usually needed. The red dotted line indicates a μR value of 5. For $\mu R \geq 5$, measurements are generally not possible in a capillary geometry, as there will be very severe levels of absorption and corrections are inaccurate. (source: <http://11bm.xray.aps.anl.gov/absorb/absorb.php>)

Absorption



Bragg-Brentano: The effect might not be so obvious how to calculate but result is that when all the possible path lengths are taken in to account, the net absorption remains constant with θ . This means that the effect of absorption can effectively be ignored in this case since it affects all reflections equally. Therefore this geometry may be an alternative when dealing with strongly absorbing samples

Applications of XRPD

- Phase identification (search match procedures)
- Crystal structure determination (ab initio solution and refinement)
- Quantitative Phase Analysis (QPA)
- Amorphous phase analysis and total Scattering – PDF analysis
- Crystalline domain size/shape and lattice defect analysis (LPA)
- Determination of preferred orientations (Texture Analysis)
- Residual Stress Analysis
- ... and more

Phase identification - example



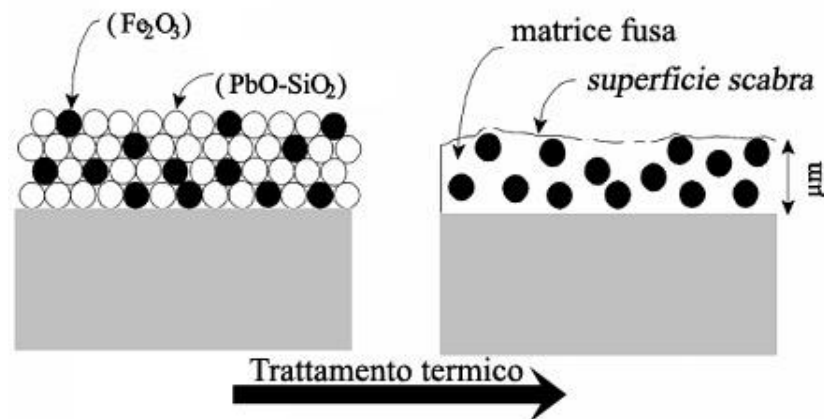
Basilica dei santi Giovanni e
Paolo

XIII-XVI century
End XV large stained glass
windows

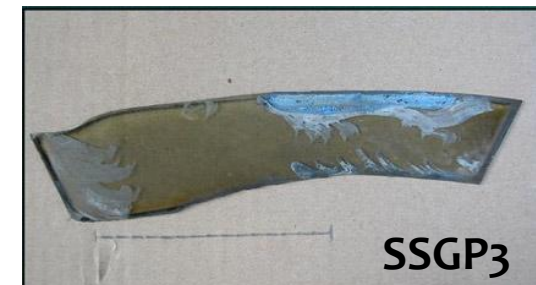
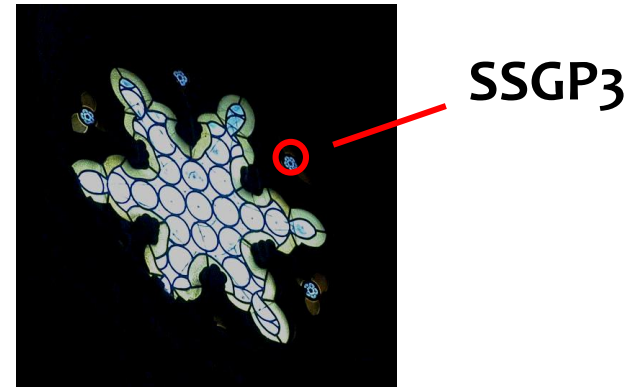
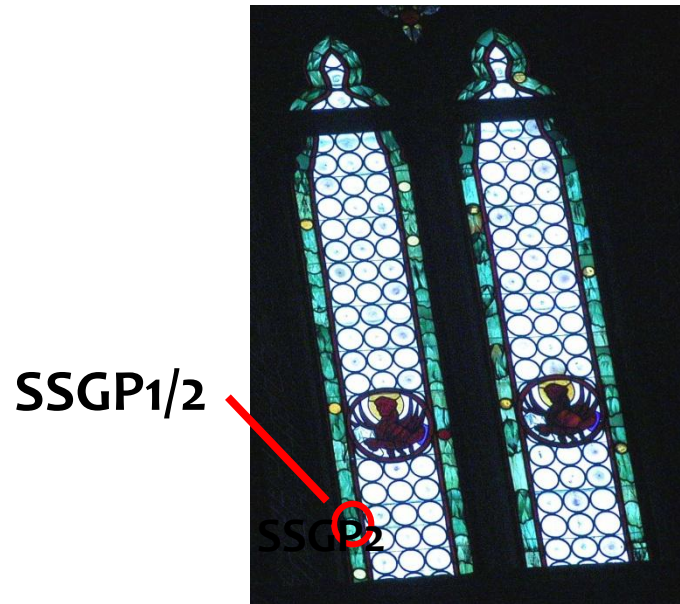
Phase identification - example

Glass samples: Grisaille

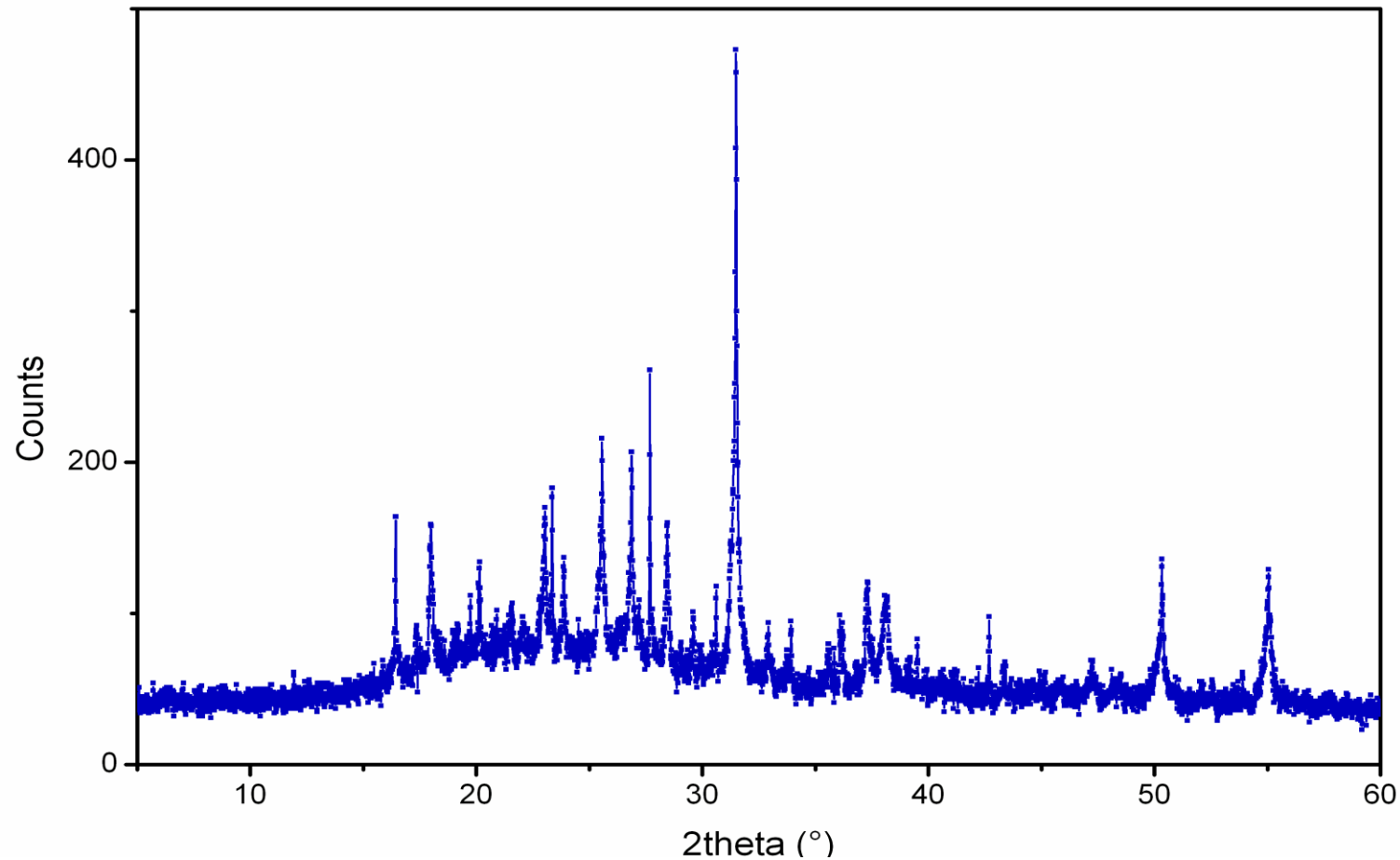
- Low melting glass (SiO_2 , PbO ,)
- Pigment (metal oxides)
- Paint medium (water, vinegar, oil)
- Firing to fuse the grisaille on the glass



Phase identification - example

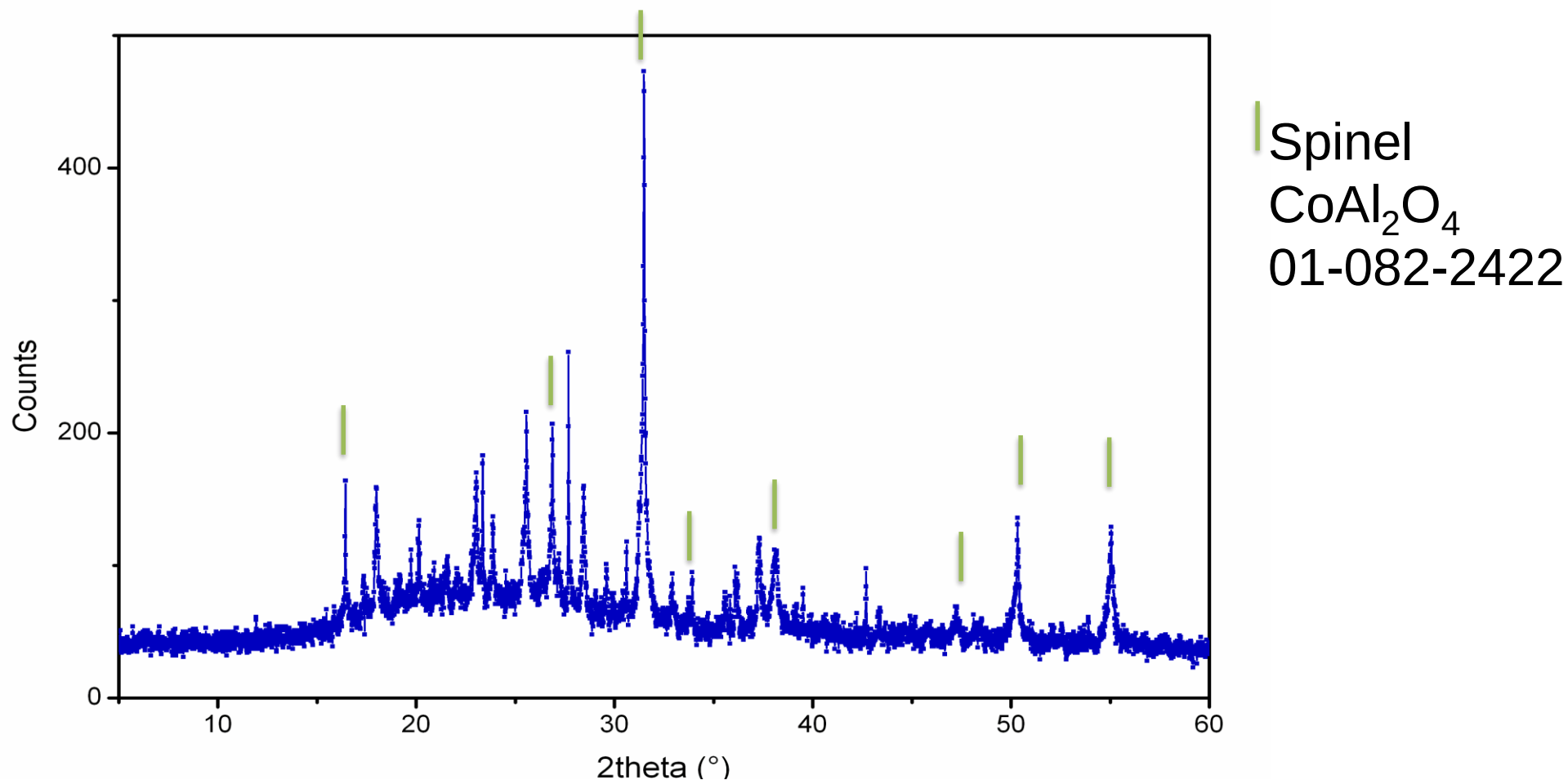


Phase identification - example

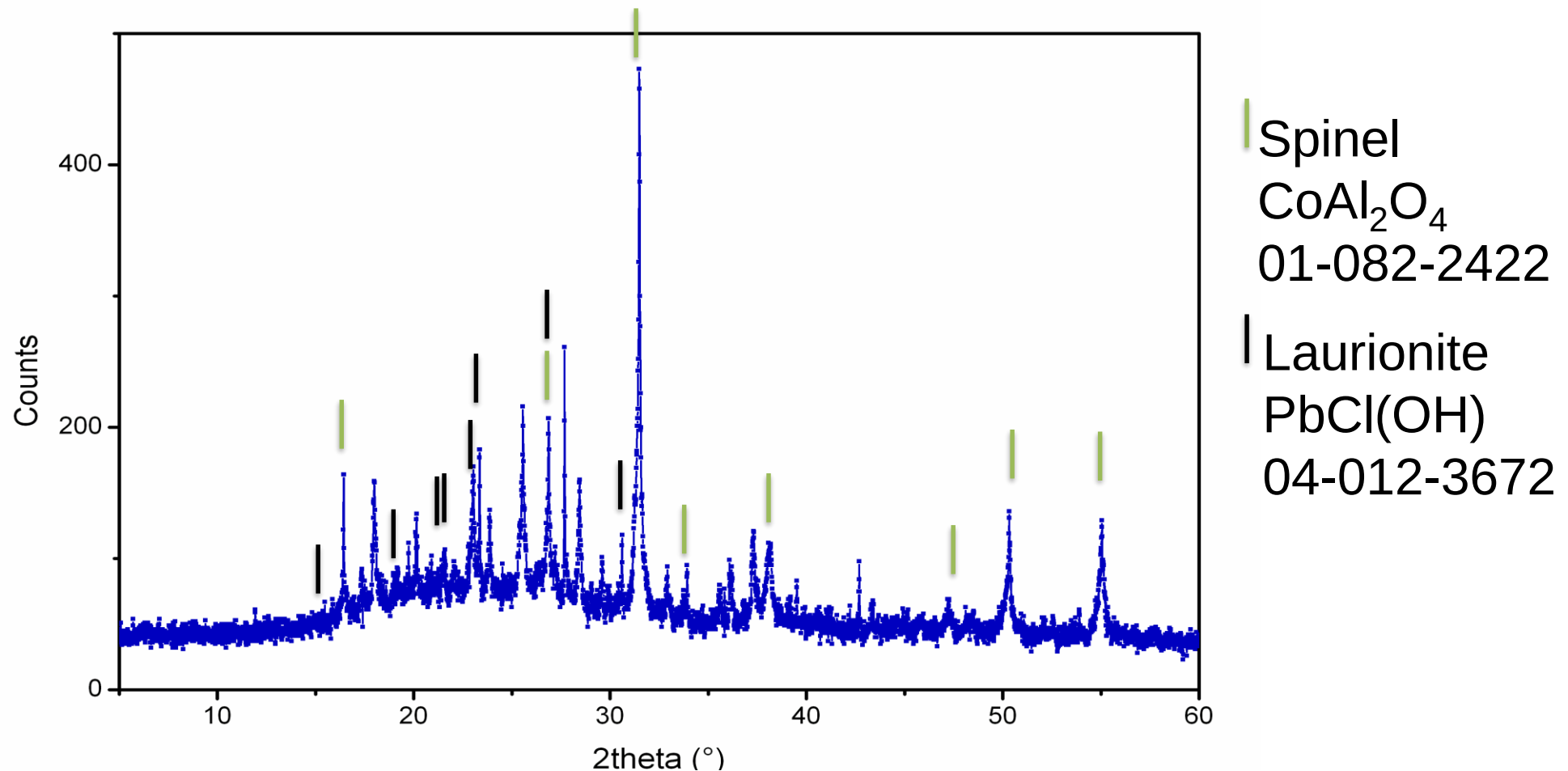


$E = 9.4 \text{ keV}$
 $\lambda = 1.319 \text{ \AA}$

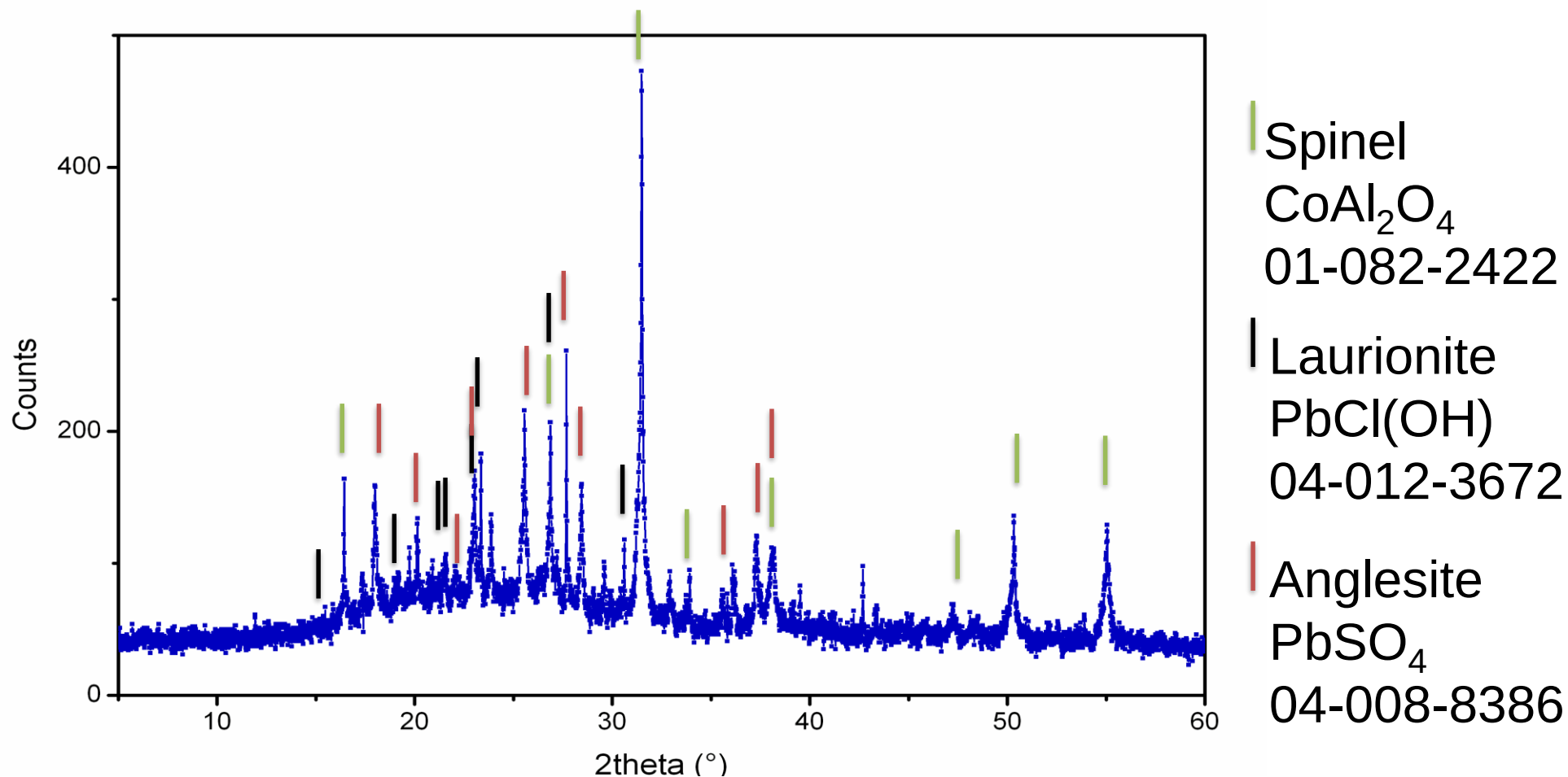
Phase identification - example



Phase identification - example



Phase identification - example



Phase identification - example

GRISAGLIA



CoAl_2O_4 ; PbSO_4 ; $\text{Pb}(\text{OH})\text{Cl}$

PATINA

Amorphous



$\text{Pb}_2\text{Sb}_2\text{O}_7$; PbSO_4 ;
 $\text{CaSO}_4(\text{H}_2\text{O})_2$; $\text{CaAl}_2\text{Si}_2\text{O}_8$

$\text{FeO}(\text{OH})$; $\text{FeSO}_4(\text{OH})(\text{H}_2\text{O})_2$
 PbSO_4 ; $\text{CaSO}_4(\text{H}_2\text{O})_2$;
 $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$



CoAl_2O_4 ; PbSO_4 ;
 $\text{CaPO}_3(\text{OH})_2\text{H}_2\text{O}$

SiO_2 ; PbS ; PbSO_4 ;
 $\text{CaCO}_3(\text{vat})_1$
 $\text{CaPO}_3(\text{OH})_2\text{H}_2\text{O}$

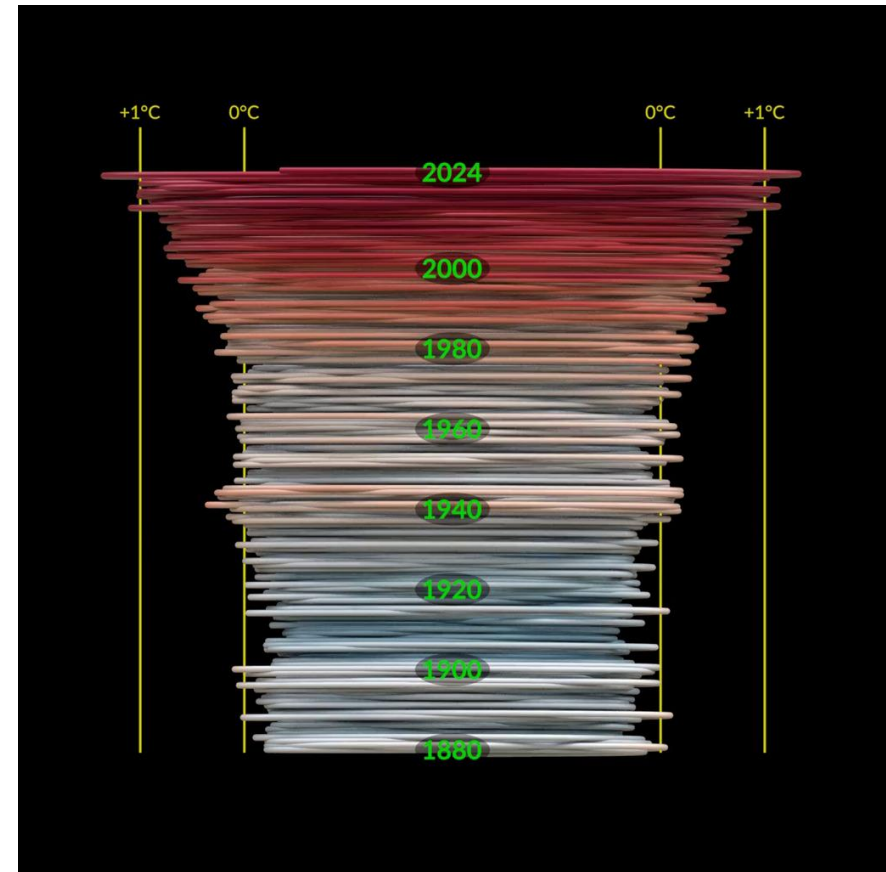
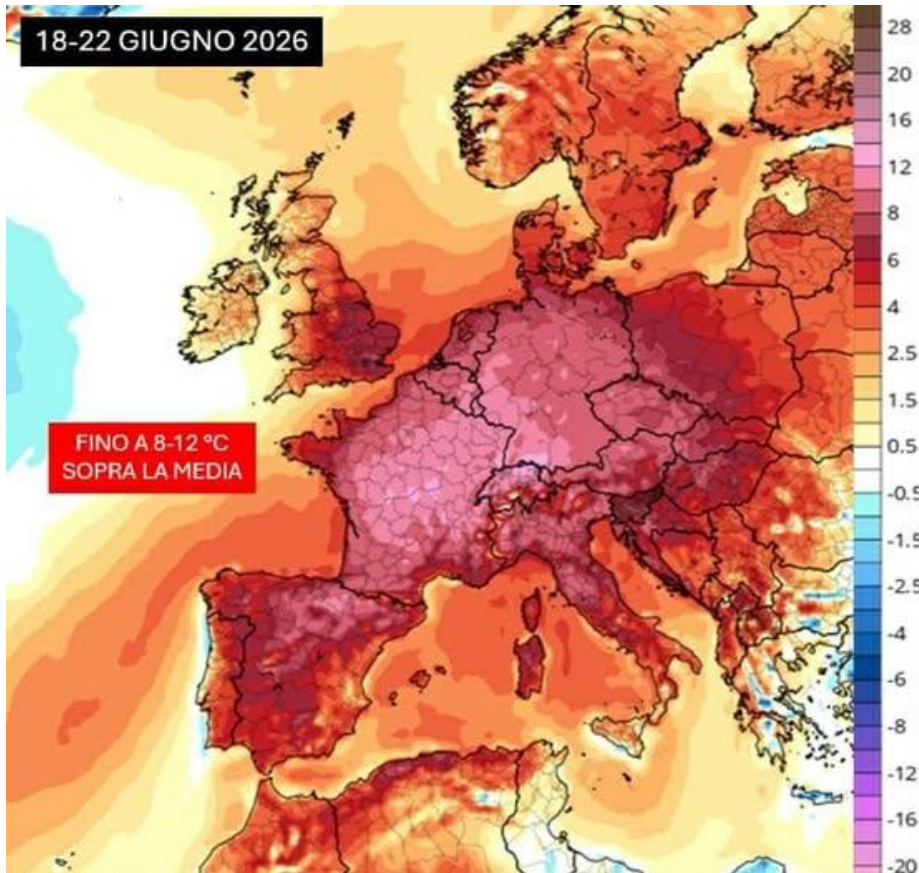
Phase identification - example

- **$\text{Pb}_2\text{Sb}_2\text{O}_7$** : original pigment
- **SO_4^{2-} , S^{2-} , CO_3^{2-}** : alteration product seawater-aerosol , acid rain
- **$\text{FeO}(\text{OH})$; $\text{FeSO}_4(\text{OH})(\text{H}_2\text{O})_2$** : alteration product of original pigments
- **CO_3^{2-} , PO_3^{3-}** : biological origin
- **CoAl_2O_4** : intervention at later date?

Energy transition

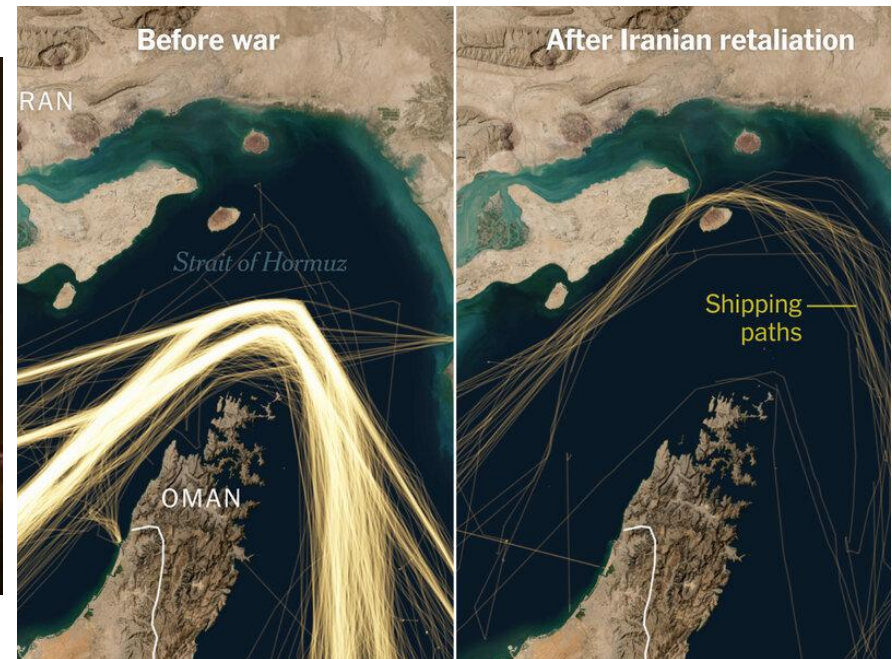


Energy transition



Source:
<https://cicenergigune.com/en/blog/raw-material-shortage-new-big-challenge-battery-industry>

Energy transition



Source:
<https://cicenergigune.com/en/blog/raw-material-shortage-new-big-challenge-battery-industry>

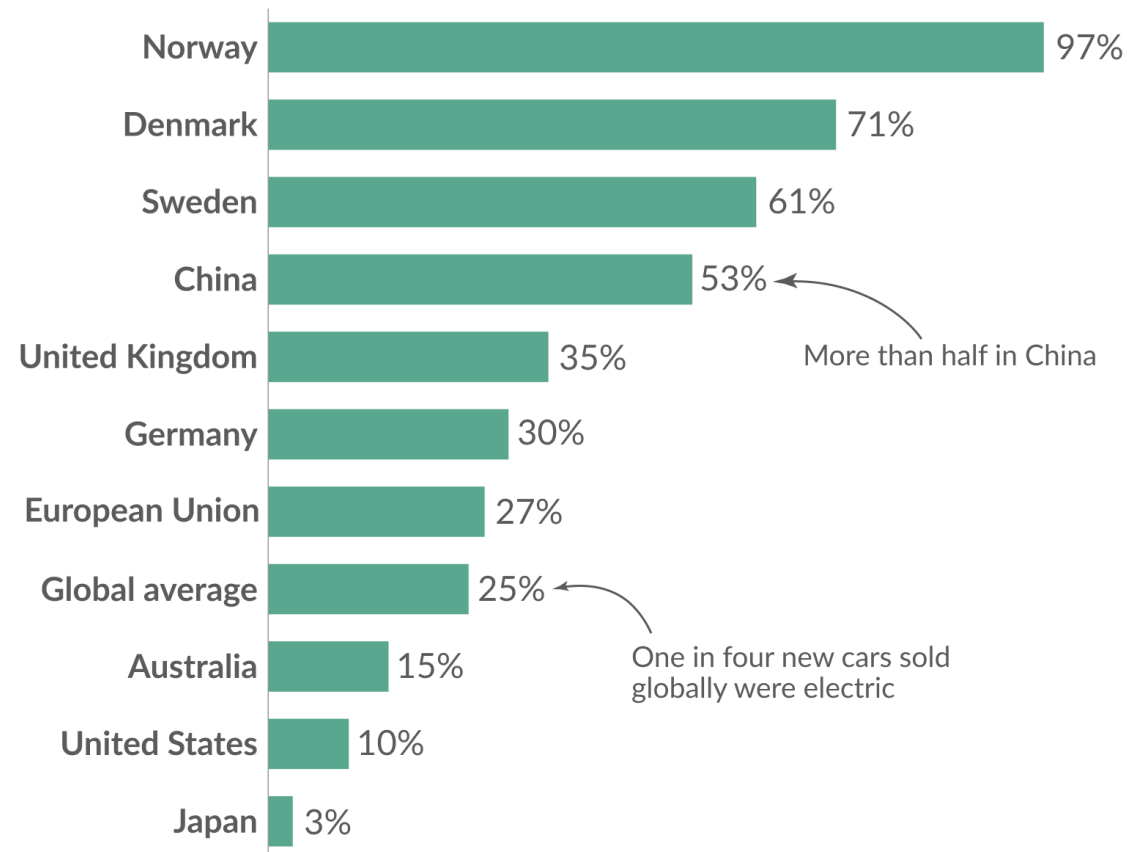
Energy transition



Source:
<https://cicenergigune.com/en/blog/raw-material-shortage-new-big-challenge-battery-industry>

What share of new cars sold in 2025 were electric?

Our World
in Data



Note: Electric cars include fully battery-electric and plug-in hybrids.

Data source: International Energy Agency, Global EV Outlook (2026)

CC BY

Battery applications

Grid energy and industry
Stationary energy storage
Grid energy
Renewable energy
Portable energy storage

Transportation
Cars, buses, bicycles
Forklifts

Consumer electronics and devices
Smartphones, tables, laptops
Power tools
Personal care



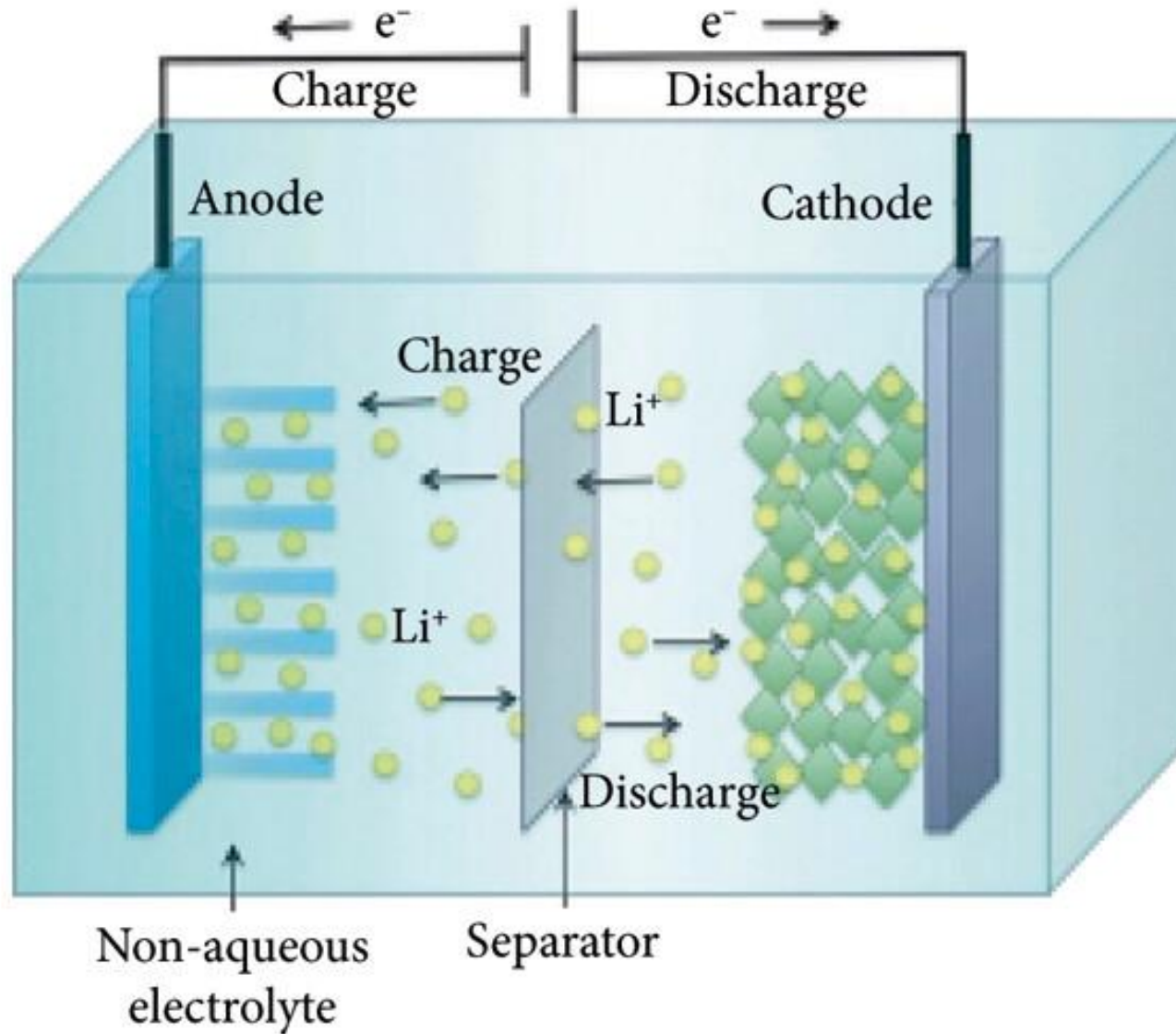


Secondary cells or rechargeable batteries	
- Aluminium-ion battery - Calcium battery^[1] - Flow battery - Iron redox flow battery - Vanadium redox battery - Zinc-bromine battery - Zinc-cerium battery - Hydrogen-bromine battery - Glass battery - Lead-acid battery - Deep-cycle battery - Flooded battery - VRLA battery - AGM battery - Gel battery - UltraBattery - Lithium-ion battery - Lithium-ion lithium cobalt oxide battery (ICR) - Lithium-silicon battery - Lithium-ion manganese iron phosphate battery - Lithium-ion manganese-oxide battery (LMO) - Lithium-ion polymer battery (LiPo) - Lithium-iron-phosphate battery (LFP) - Lithium-nickel-manganese-cobalt oxides (NMC) - Lithium-nickel-cobalt-aluminium oxides (NCA) - Lithium sulfur battery - Lithium-titanate battery (LTO) - Thin-film lithium-ion battery - Lithium-ceramic battery^[2]^[3] - Magnesium-ion battery	- Metal-air electrochemical cells - Lithium-air battery - Germanium-air battery - Calcium-air battery - Iron-air battery - Potassium-ion battery - Silicon-air battery - Zinc-air battery - Tin-air battery - Sodium-air battery - Beryllium-air battery - Microbial fuel cell - Molten-salt battery - Nickel-cadmium battery - Nickel-cadmium battery vented cell type - Nickel-hydrogen battery - Nickel-iron battery (NiFe battery) - Nickel-lithium battery - Nickel-metal hydride battery - Low self-discharge NiMH battery - Nickel-zinc battery - Organic radical battery - Oxygen-ion battery - Polymer-based battery - Polysulfide-bromide battery - Rechargeable alkaline battery - Rechargeable fuel battery - Rechargeable lithium-metal battery - Sand battery - Silver-zinc battery - Silver-calcium battery - Silver-cadmium battery - Sodium-ion battery - Sodium-sulfur battery - Solid-state battery^[4] - Super iron battery - Wet cell - Zinc ion battery

Types of battery



Batteries: How does it work



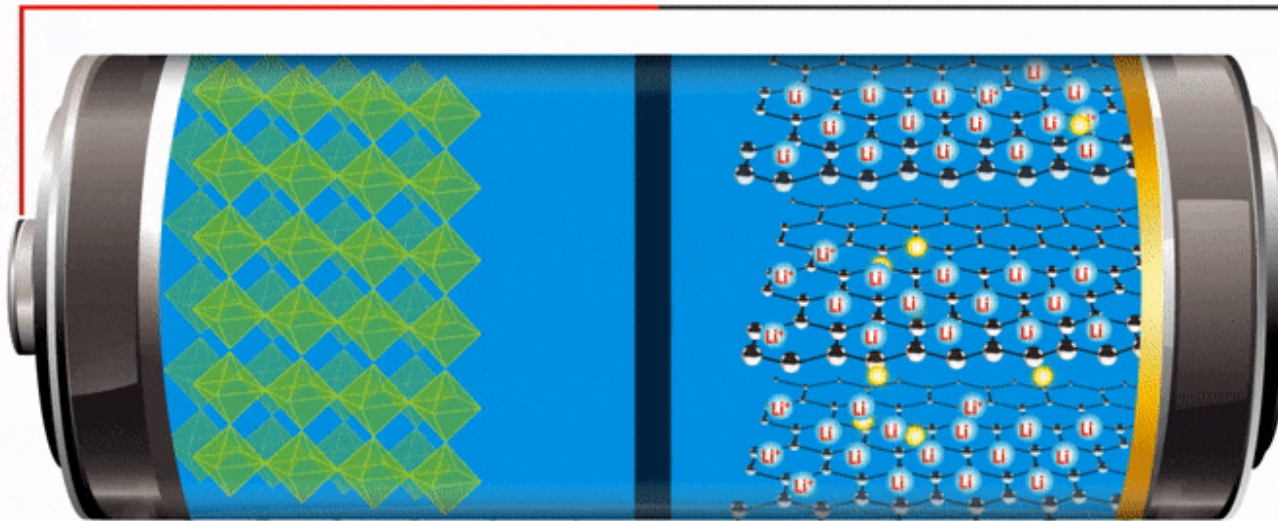
Source:
<https://cicenergigune.com/en/blog/raw-material-shortage-new-big-challenge-battery-industry>

How Lithium-ion Batteries Work

Discharge



Charge
Meter



Source:
<https://scitechdaily.com/science-made-simple-how-do-lithium-ion-batteries-work/>
Scott Minos, U.S. Department of Energy

U.S. DEPARTMENT OF
ENERGY

Office of ENERGY EFFICIENCY
& RENEWABLE ENERGY

Batteries generate electricity through electrochemical (redox) reactions. These processes involve two primary half-reactions that occur simultaneously, converting stored chemical energy into electrical current when the circuit is closed.

Oxidation (Anode): The negative electrode loses electrons. Reduction (Cathode): The positive electrode absorbs those electrons. Electrolyte: The medium that allows ions (charged atoms) to flow between the anode and cathode, keeping the circuit balanced

Lithium-Ion (Rechargeable) Anode (Discharge): $(\text{LiC}_6 \rightarrow 6\text{C} + \text{Li}^+ + \text{e}^-)$ (Lithium ions leave the graphite to enter the electrolyte) Cathode (Discharge): $(\text{CoO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiCoO}_2)$ (Lithium ions and electrons integrate into the metal oxide) How it works: Electrons travel through your device to create power, while the lithium ions move internally through a liquid or solid electrolyte.

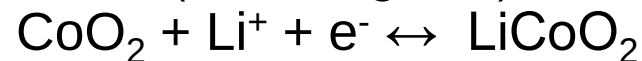
Lithium-Ion Battery (Rechargeable):

Anode (Discharge $\rightarrow$):



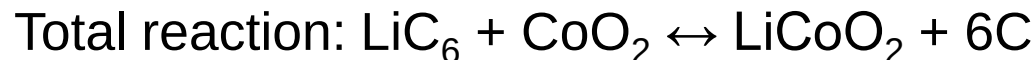
(Lithium ions leave the graphite to enter the electrolyte)

Cathode (Discharge $\rightarrow$):



(Lithium ions and electrons integrate into the metal oxide)

How it works: Electrons travel through your device to create power, while the lithium ions move internally through a liquid or solid electrolyte.



The Underlying Chemistry:

Ion and Electron Flow: When charging lithium ions leave the LiCoO_2 crystal lattice (with Co^{3+}), an equal number of electrons are driven into the external circuit.

Cobalt's Role: The cobalt ions (**Co**) change their oxidation state to balance the charge. When the battery is fully charged and all lithium has been removed (theoretical state), the material exists as CoO_2 , where all cobalt is in the Co^{4+} state.

Structure and Stability: In real-world batteries, extracting too much lithium causes the layered crystal structure of CoO_2 to become highly unstable. Therefore, most standard batteries only utilize about half of the theoretical capacity to prevent irreversible structural damage, oxygen release, and thermal runaway.

Aqueous zinc batteries :

During battery operation, the following fundamental reactions occur at the electrodes:

Anode (Zinc Oxidation/Reduction): At the zinc metal anode, the metal releases electrons to the external circuit during discharge and is oxidized into ions.

During charging, the reverse happens:



Cathode: While the exact cathode reaction depends on the battery type (e.g., Manganese Oxide, Prussian Blue), it generally involves the intercalation or conversion of the zinc ions produced by the anode. ($\text{Zn}^{2+} + 2\text{e}^{-} + \text{Cathode Material} \rightarrow \text{Zn-intercalated Cathode}$)

Unwanted Aqueous Side Reactions: Because water (H_2O) is present in the electrolyte, several simultaneous side reactions naturally occur, which can degrade the battery over time: Hydrogen Evolution Reaction: Water can be reduced at the zinc surface, consuming electrons and releasing hydrogen gas. This causes gassing and depletes water in the electrolyte. ($2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}$)

Lithium Nickel Manganese Cobalt Oxide (NMC) NMC remains the dominant chemistry by market value and demand volume in EVs outside of China.

Composition: Blends nickel (for high energy density), manganese (for thermal stability), and cobalt (for structural integrity).

Variants: Manufacturers have shifted to "Ni-rich" variants like NMC 622 and NMC 811 (using less expensive cobalt and more nickel).

Primary Uses: Standard and premium range electric vehicles.

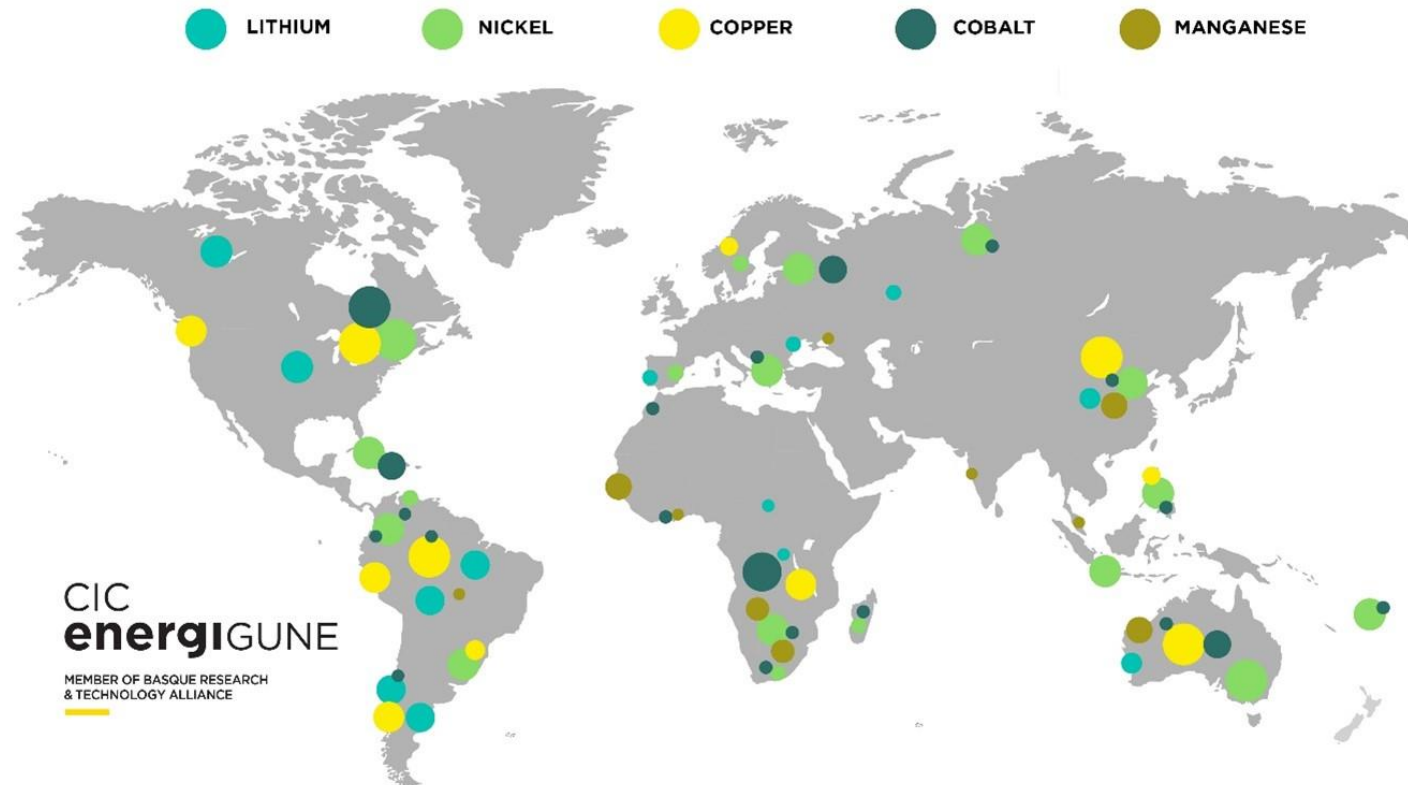
Lithium Iron Phosphate (LFP)

LFP is the fastest-growing cathode material and holds the highest deployment volume globally, capturing a majority of the Chinese and stationary storage markets.

Composition: Uses iron and phosphate instead of scarce, expensive metals like nickel and cobalt. Advantages: Exceptionally long cycle life, highly thermally stable (very low risk of thermal runaway), and cheaper to produce.

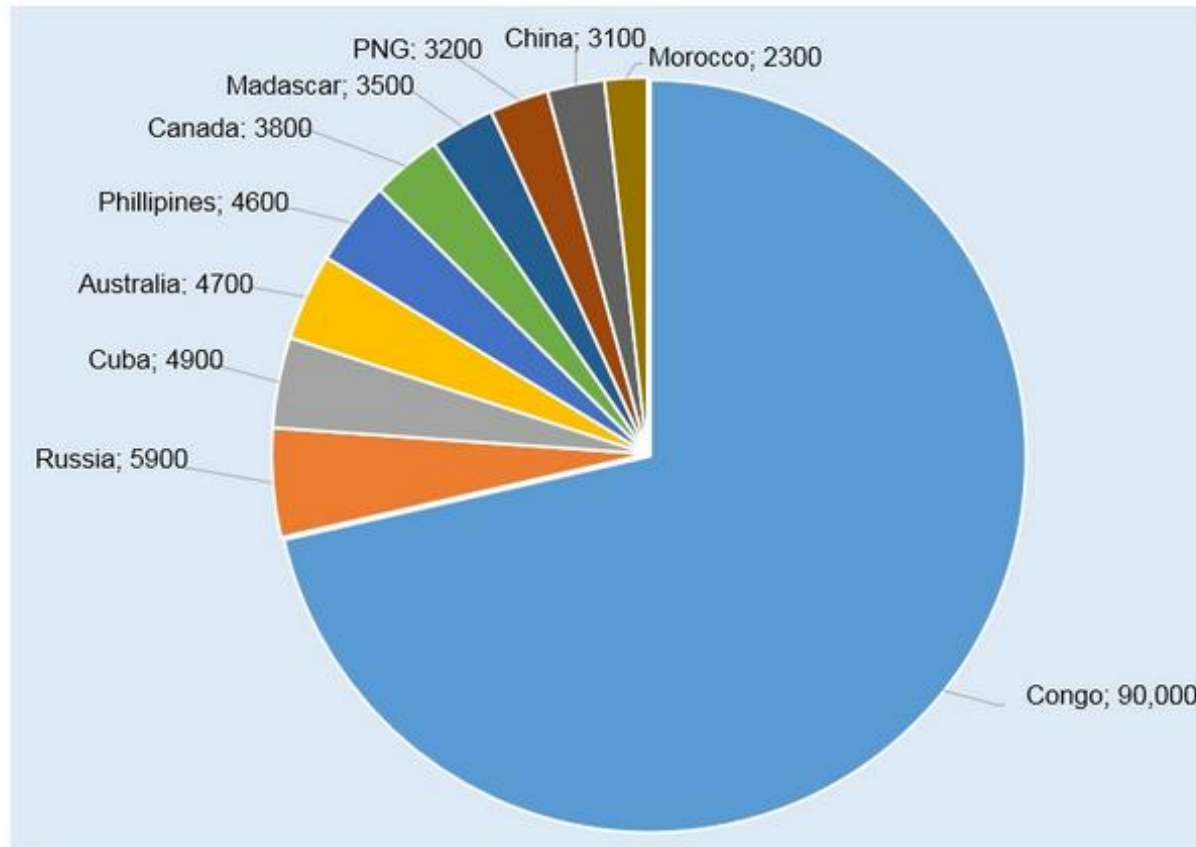
Primary Uses: Standard-range EVs, plug-in hybrids, and large-scale stationary energy storage systems.

BATTERY RAW MATERIAL SOURCES



Source:
<https://cicenergigune.com/en/blog/raw-material-shortage-new-big-challenge-battery-industry>

Batteries: Raw materials



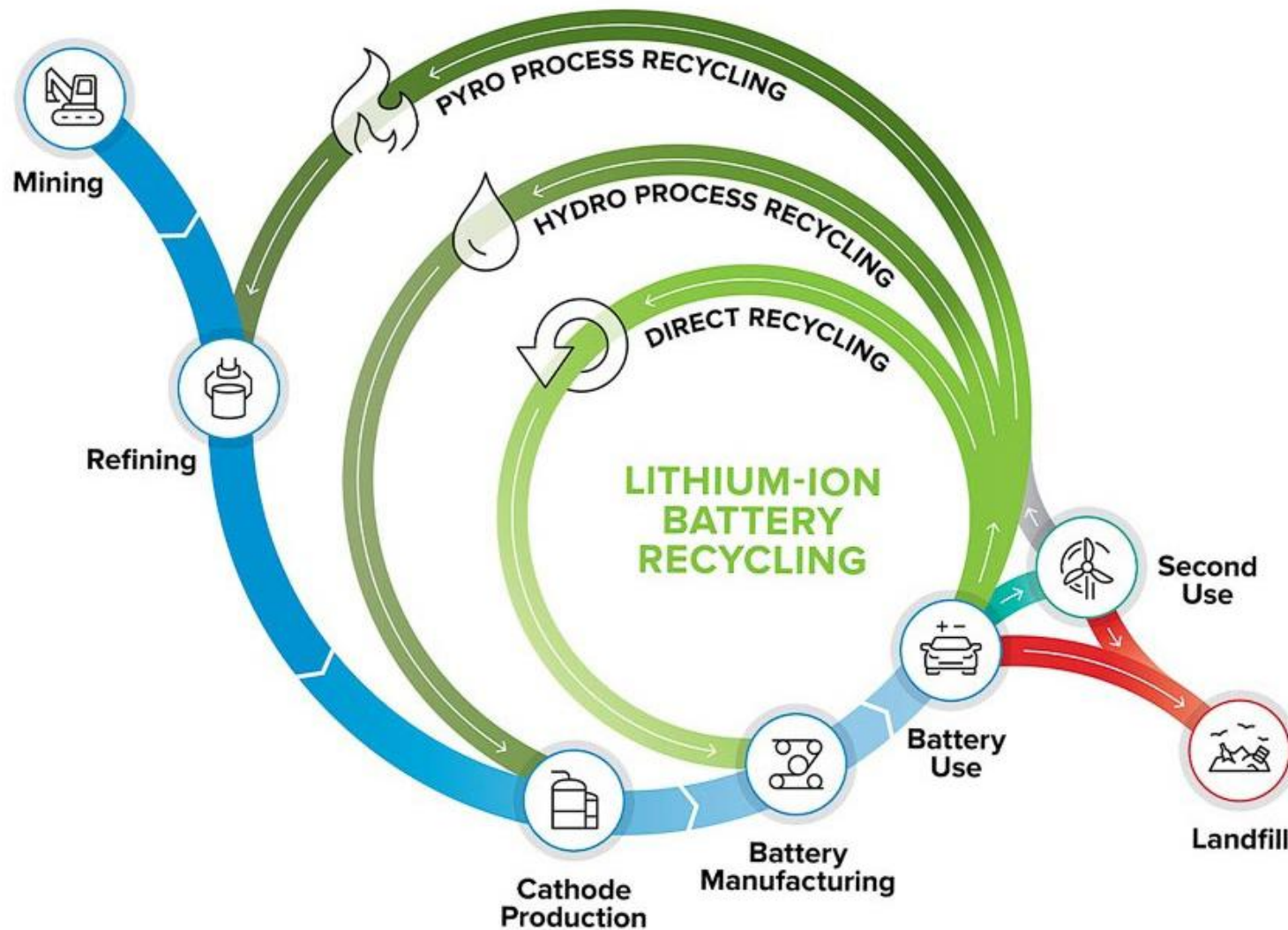
Top 10 cobalt producing countries, metric tonnes by country (2018). Source: US Geological Survey.

Batteries: Safety

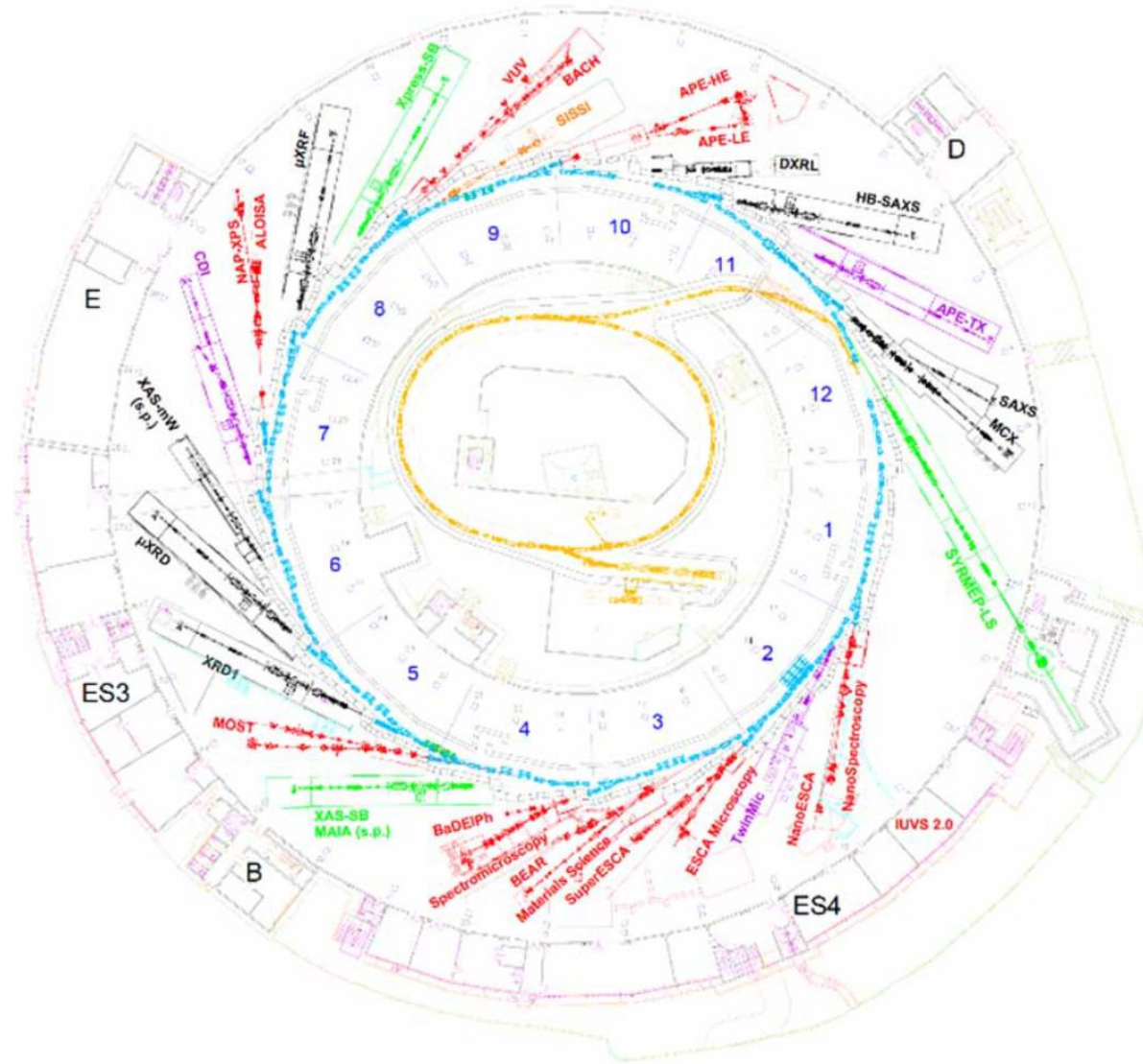


Source:
New York Fire Department

Batteries: Recycling

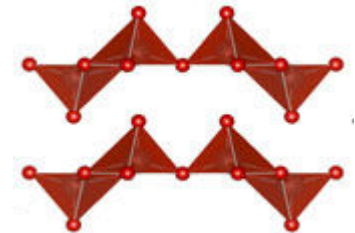
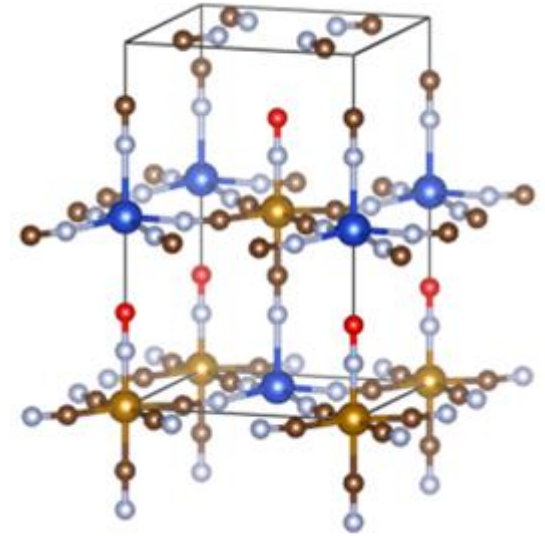
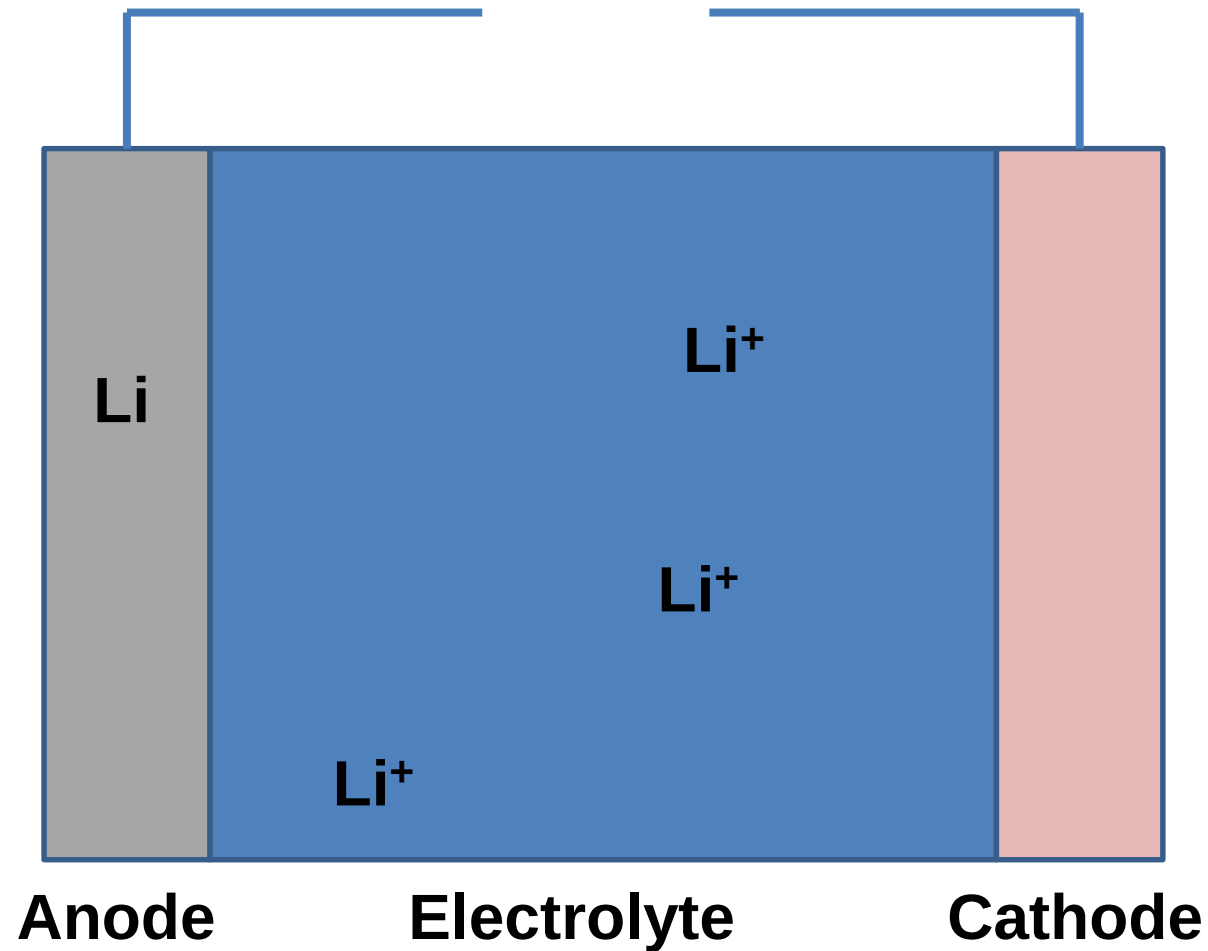


Source:
ReCell Center



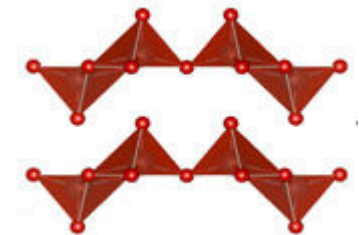
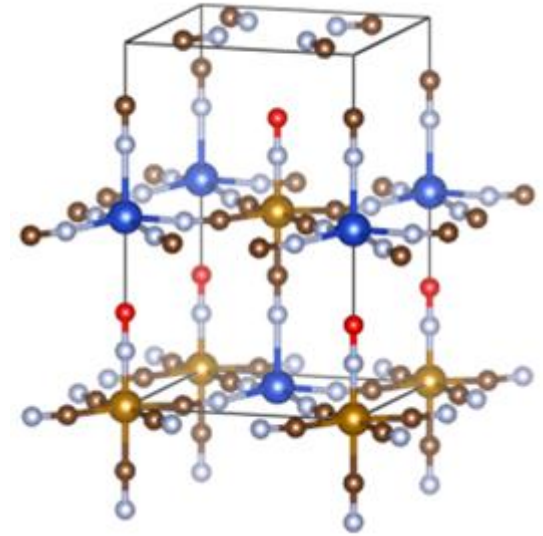
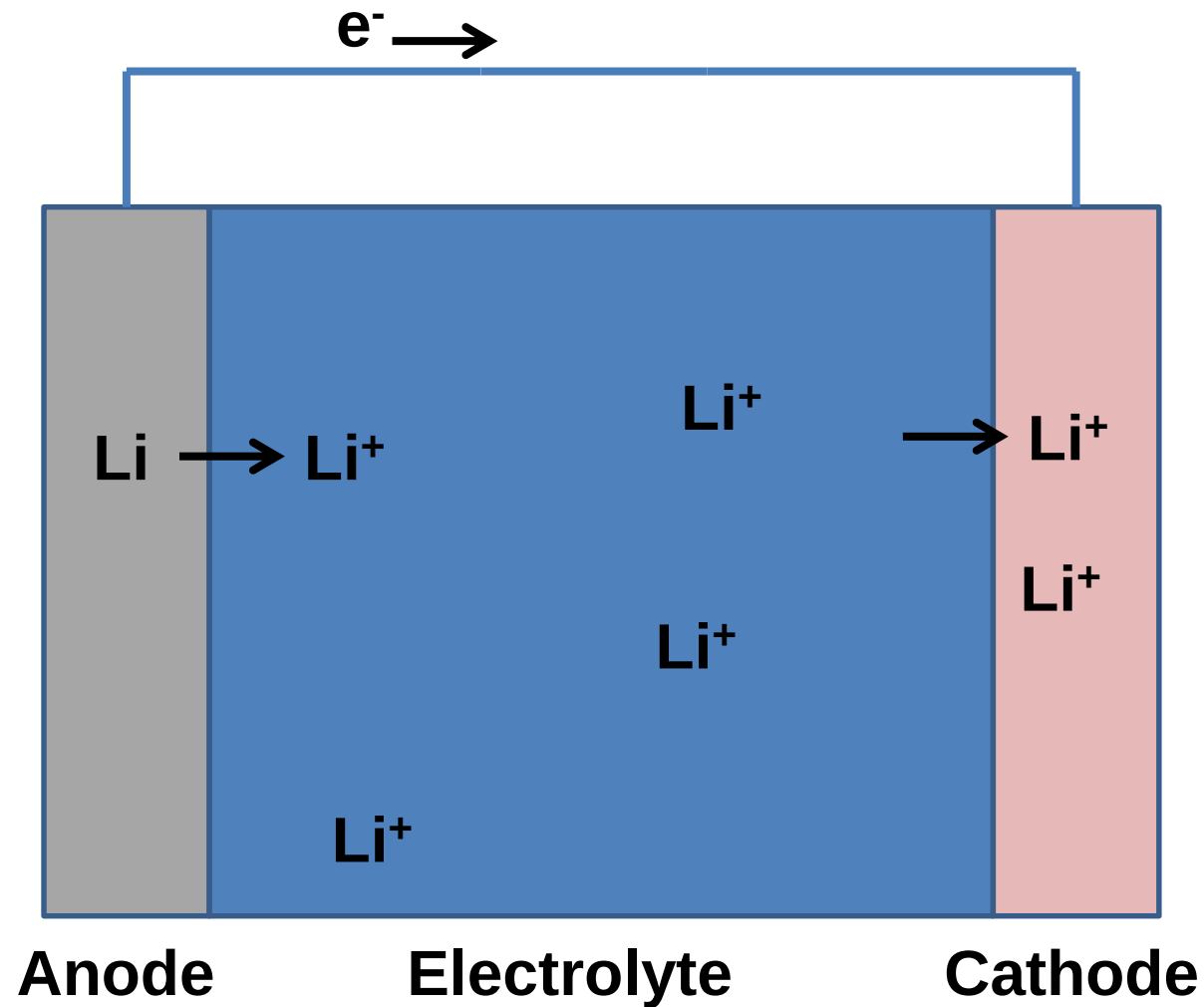
Operando battery studies

- Li batteries



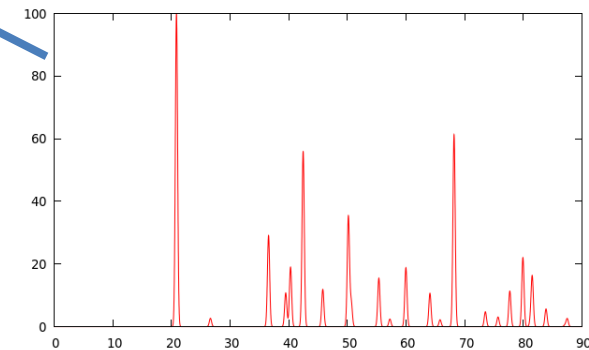
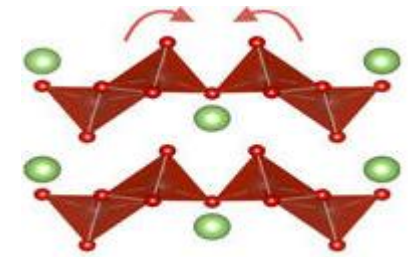
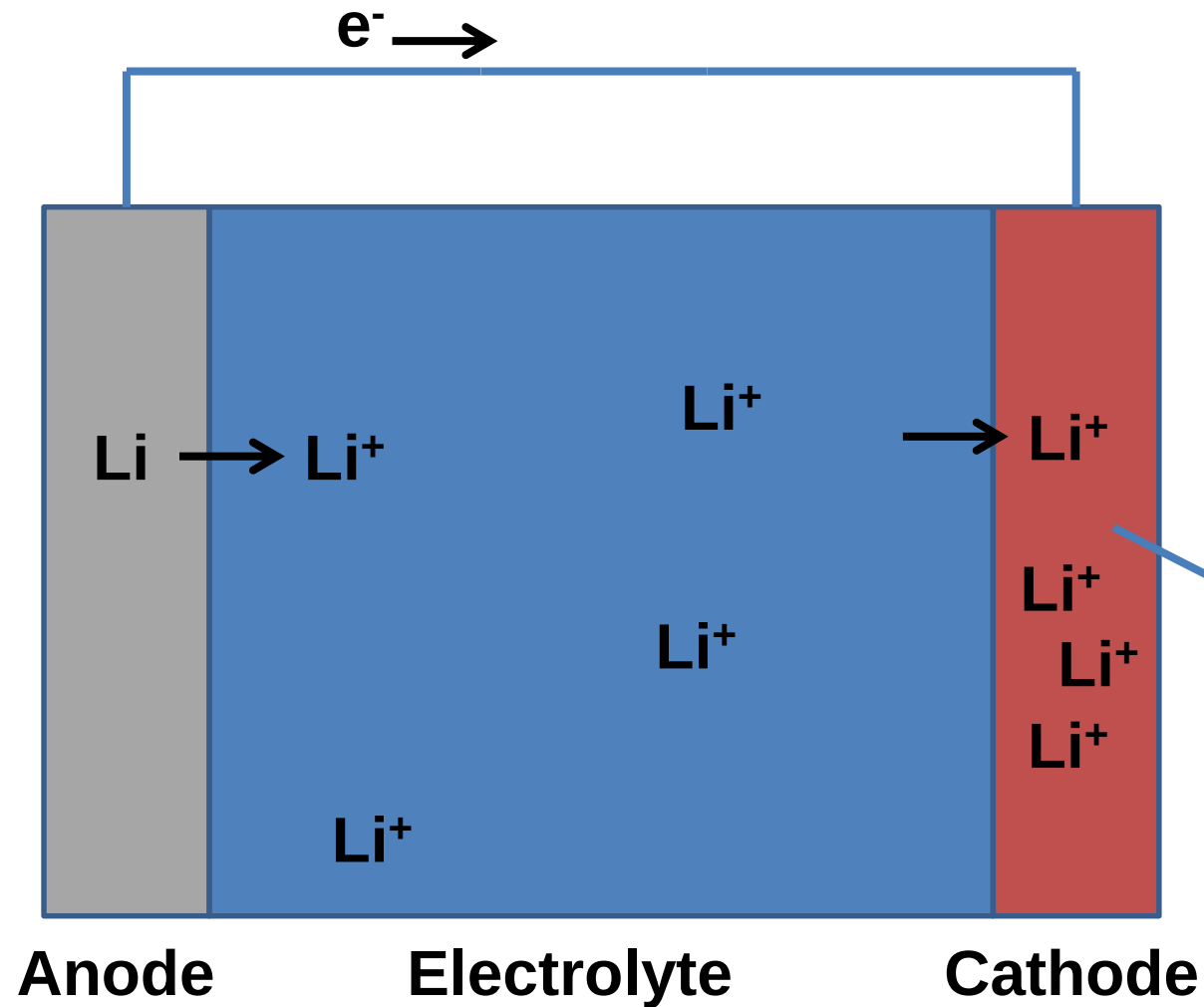
Operando battery studies

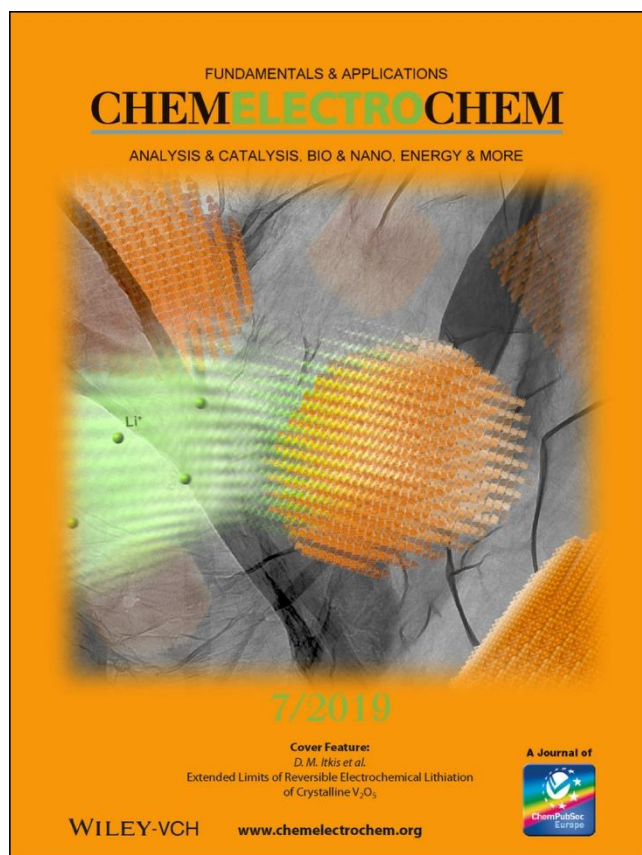
- Li batteries



Operando battery studies

- Li batteries

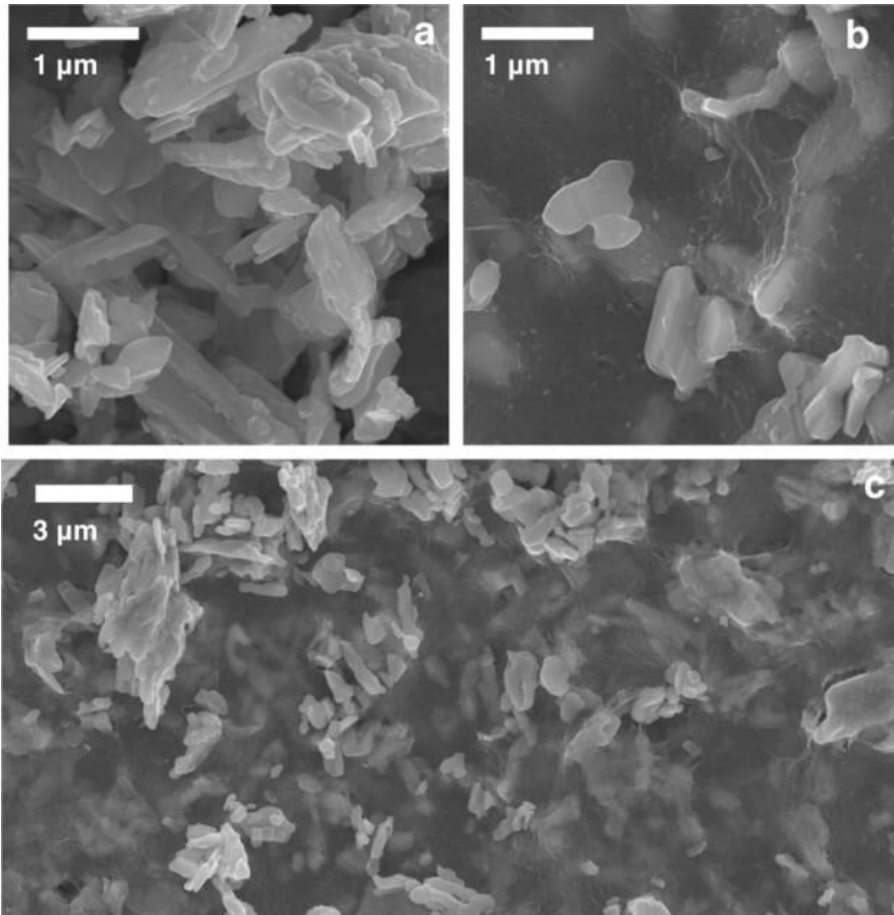




Extended Limits of Reversible Electrochemical Lithiation of Crystalline V₂O₅

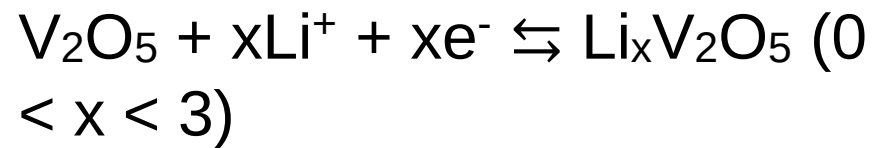
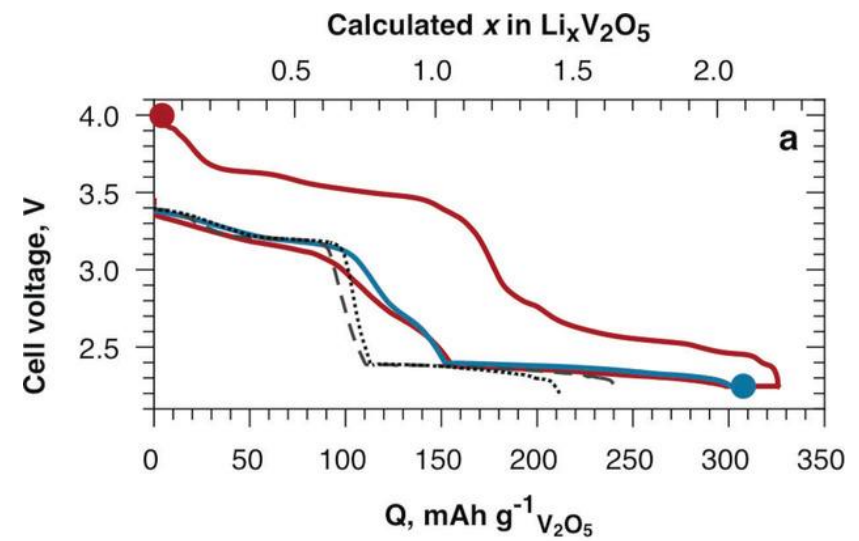
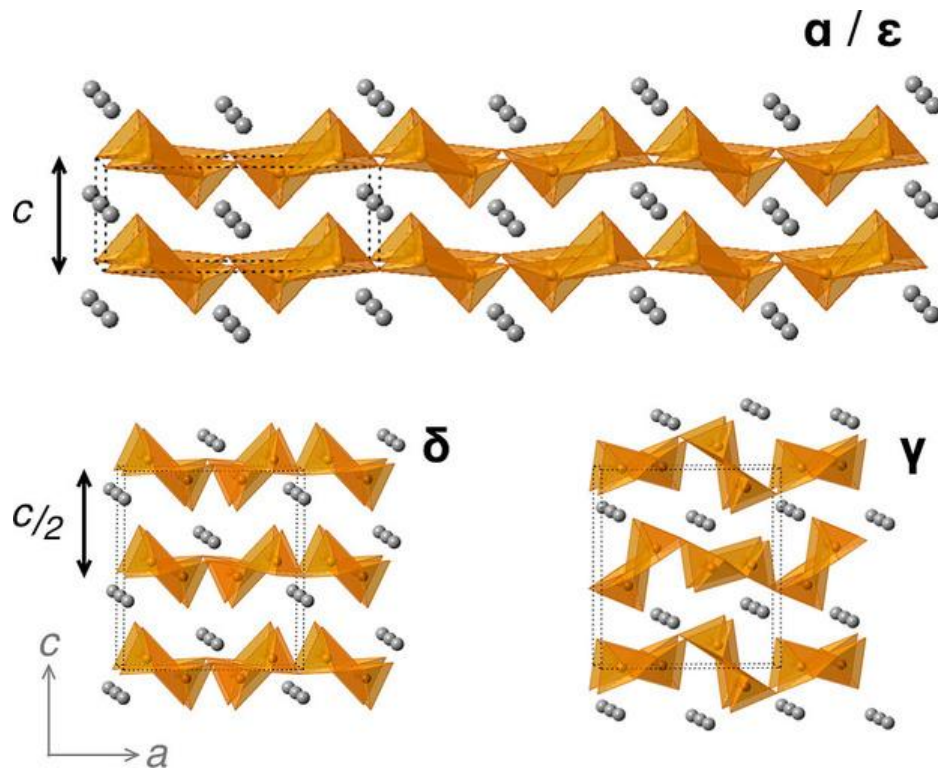
Daniil M. Itkis, Victor A. Krivchenko, Anna Ya. Kozmenkova, Margarita S. Pakhotina, Filipp S. Napolskiy, Lara Gigli, Jasper Plaisier, Nellie R. Khasanova and Evgeny V. Antipov

Lithiation of Crystalline V_2O_5 /RGO

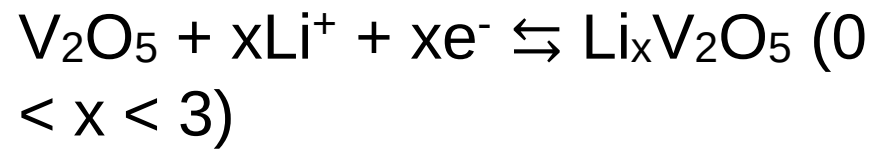
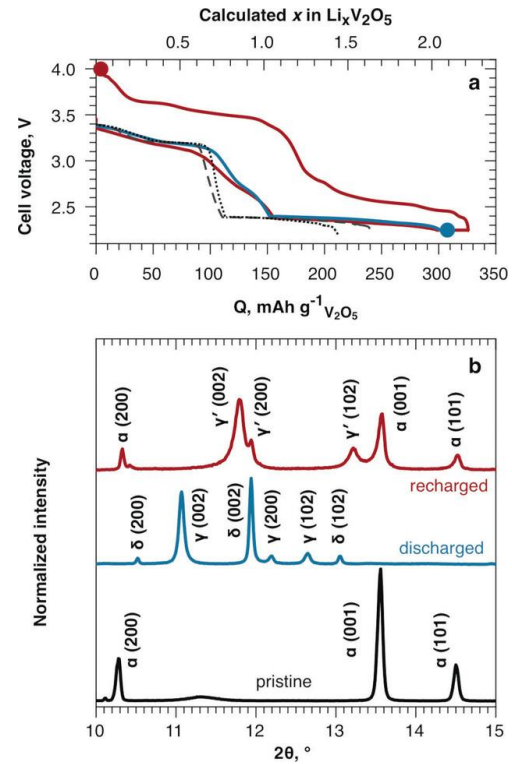
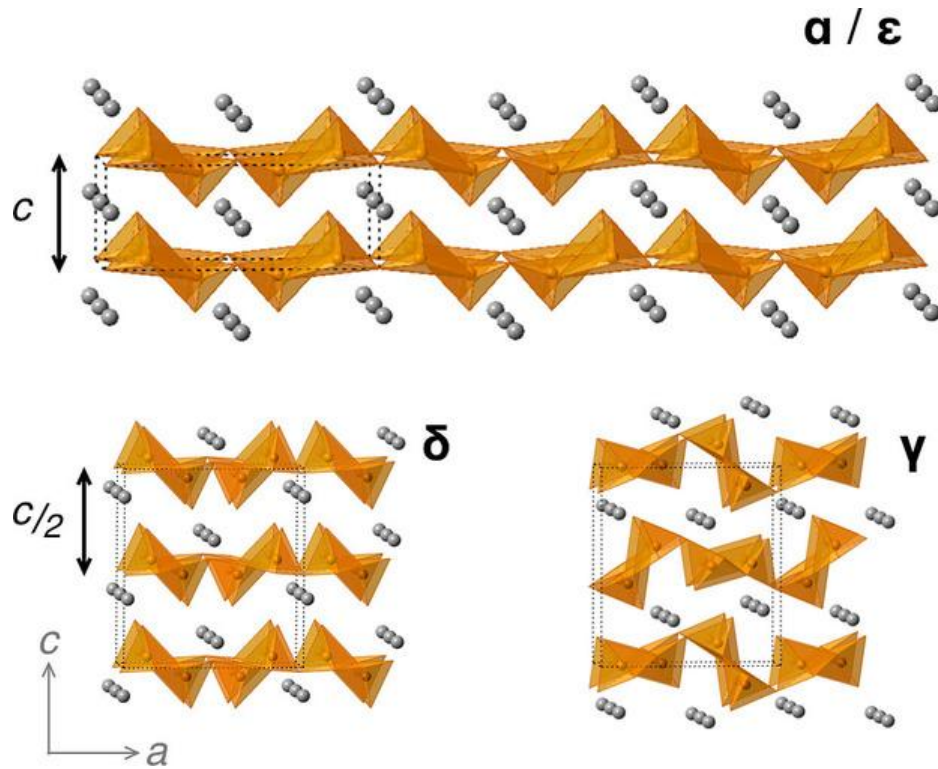


- Vanadium (V) oxide was suggested as an attractive host for electrochemical lithium yet in 1970s due to ability of multielectron redox in layered V_2O_5
- Insertion of extremely high amounts of lithium (up to 3 moles per mole of oxide) is possible, however, it is believed that insertion/extraction of about 1.8 moles of Li^+ can enable sustainable cycling.

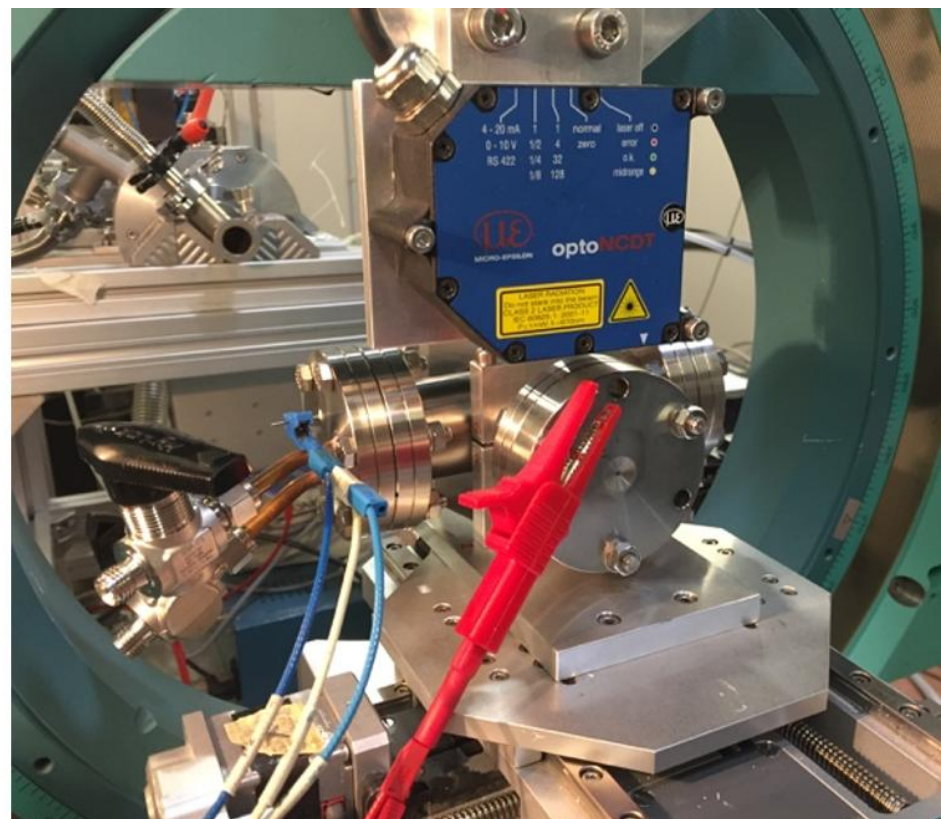
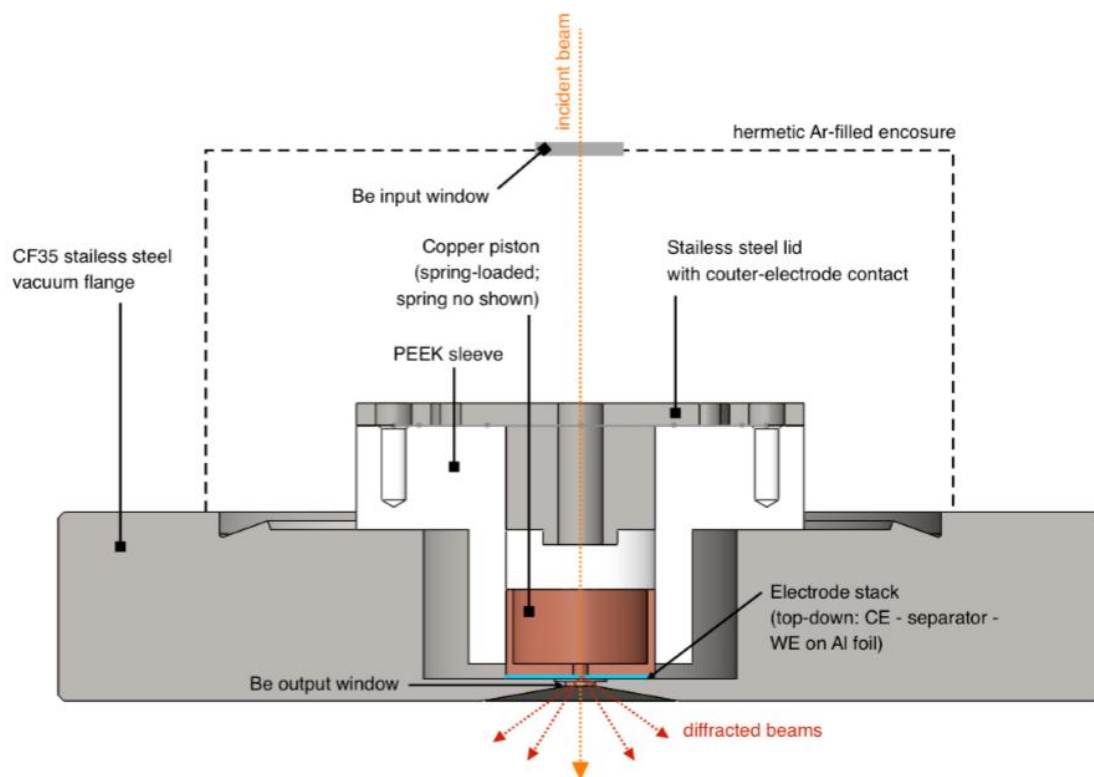
Lithiation of Crystalline V_2O_5 /RGO



Lithiation of Crystalline V₂O₅/RGO



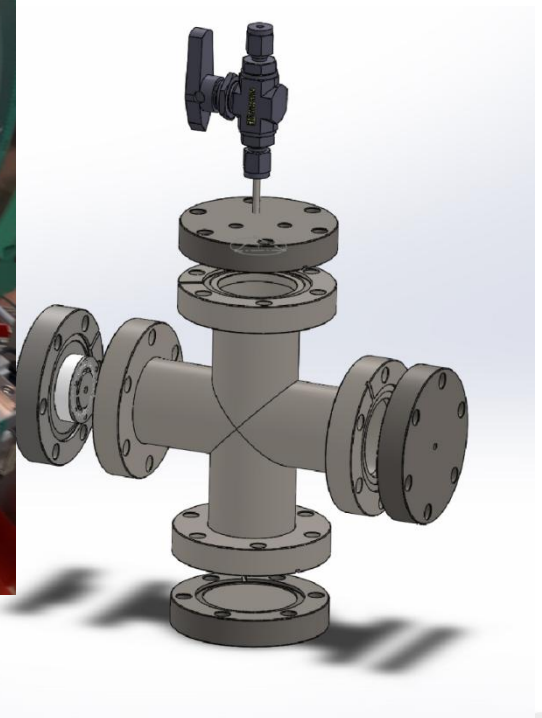
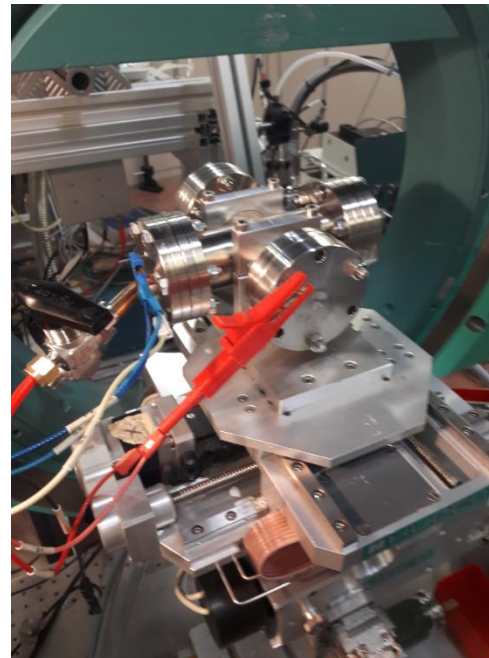
Operando battery studies on V_2O_5 /RGO



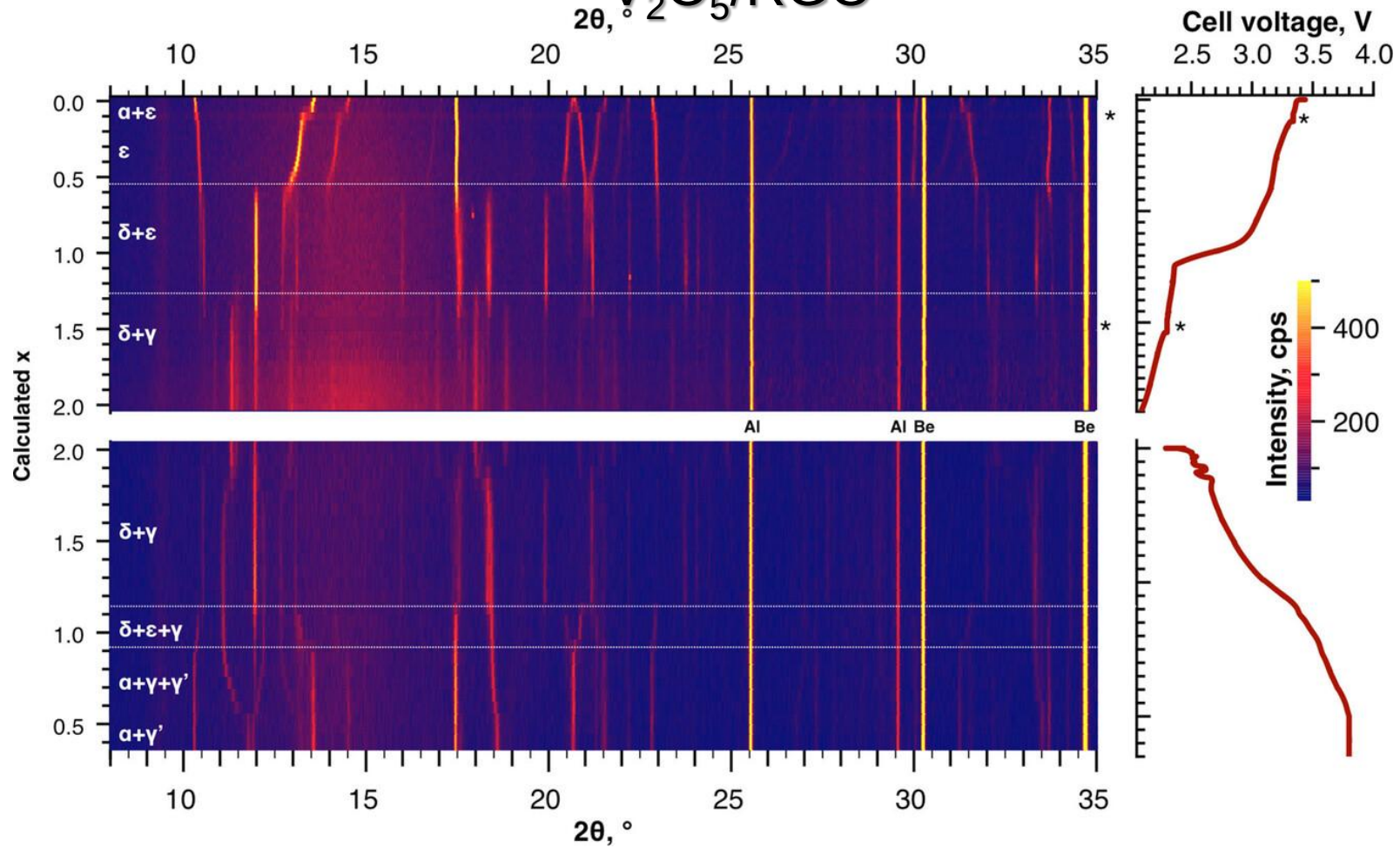
Operando battery studies on V_2O_5 /RGO

The experiment:

- Cathode: Airbrushed slurry of V_2O_5 (85%), RGO (10%) and PVDF (5%) on Al
- Anode: Lithium
- Electrolyte: 1 M $LiClO_4$ in PC/DME
- Wavelength 1.033 Angstrom
- 2θ range 8° to 35° with a 0.01° step
- 0.5 s/point acquisition

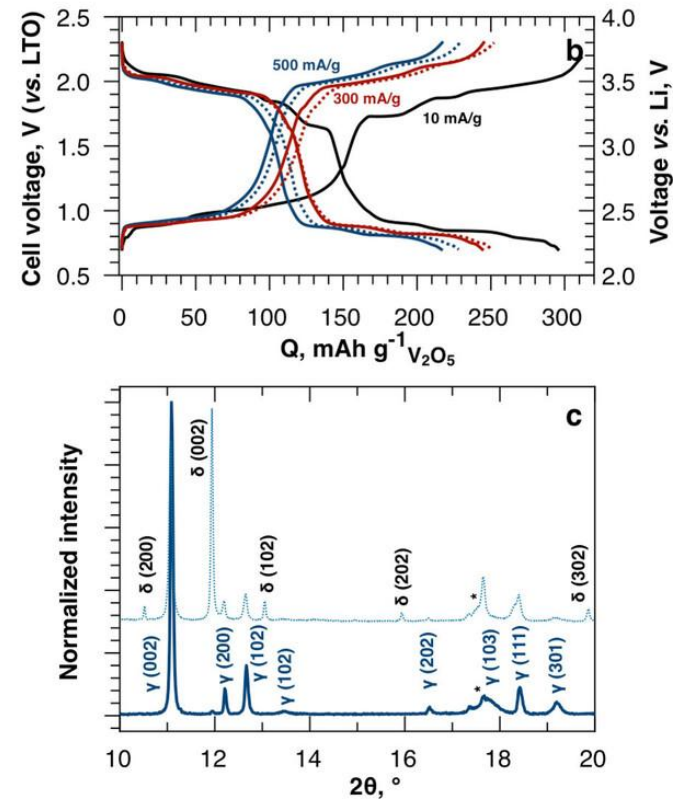
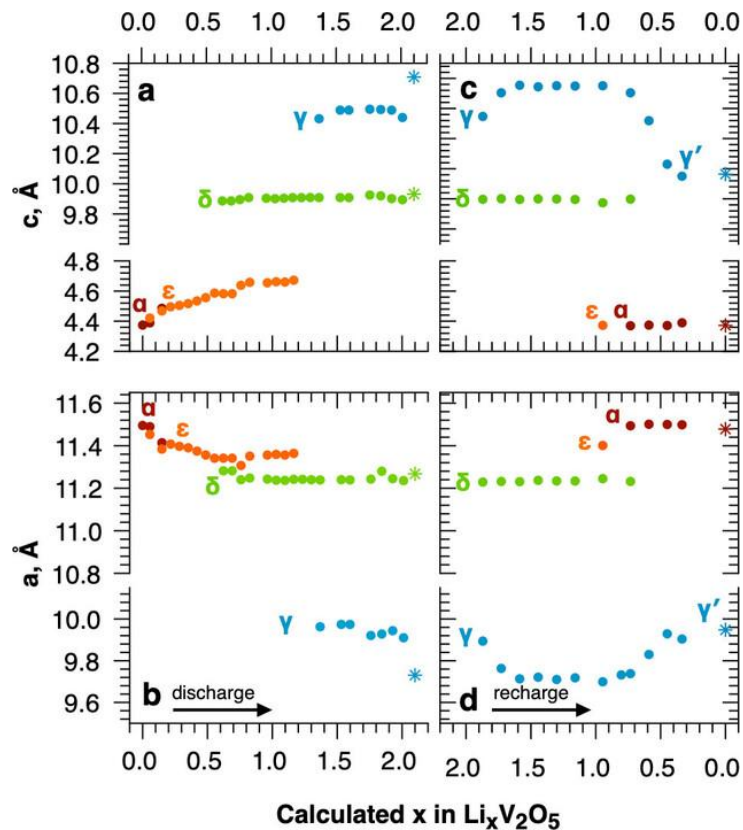


Operando battery studies on V_2O_5 /RGO



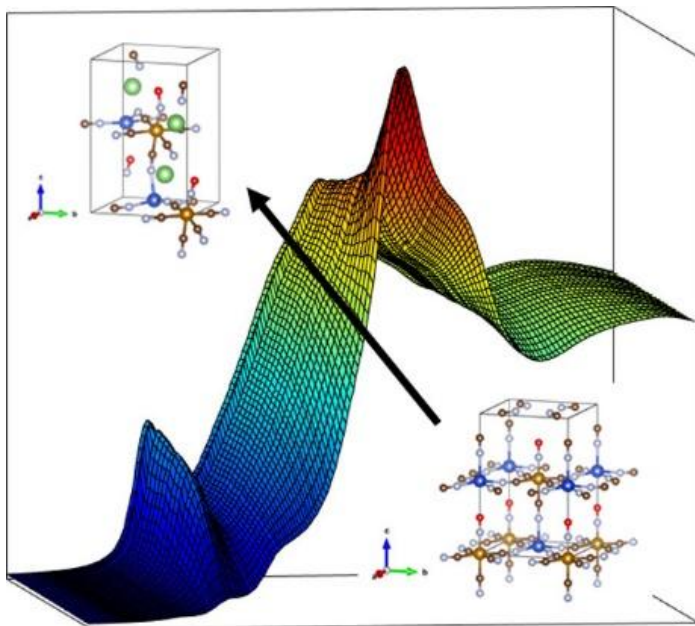
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Operando battery studies on V_2O_5 /RGO



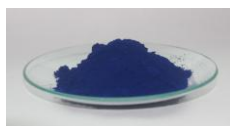
THE JOURNAL OF
**PHYSICAL
CHEMISTRY**

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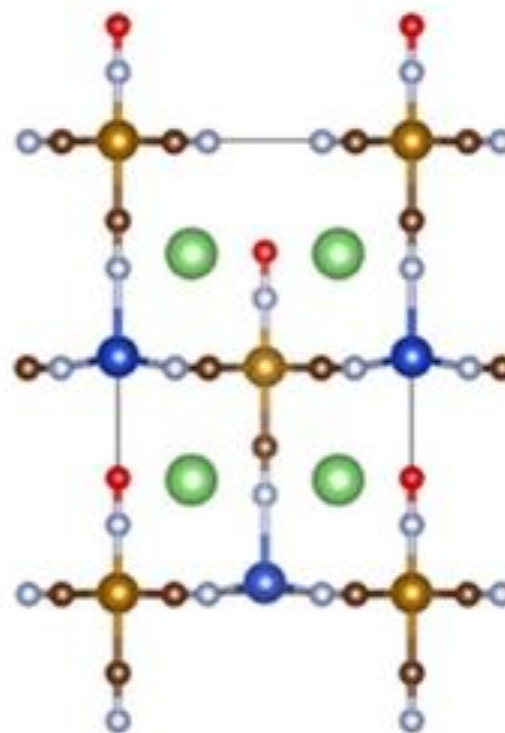
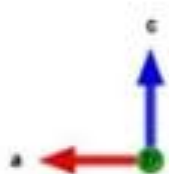
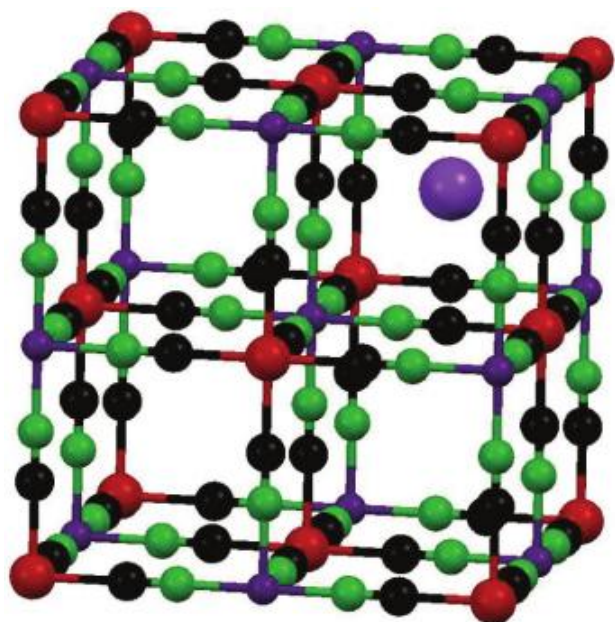


Beyond the Oxygen Redox Strategy in Designing Cathode Material for Batteries: Dynamics of a Prussian Blue-like Cathode Revealed by Operando X-ray Diffraction and X- ray Absorption Fine Structure and by a Theoretical Approach

Angelo Mullaliu, Giuliana Aquilanti, Lorenzo
Stievano, Paolo Conti, Jasper Plaisier, Sylvain
Cristol, Marco Giorgetti



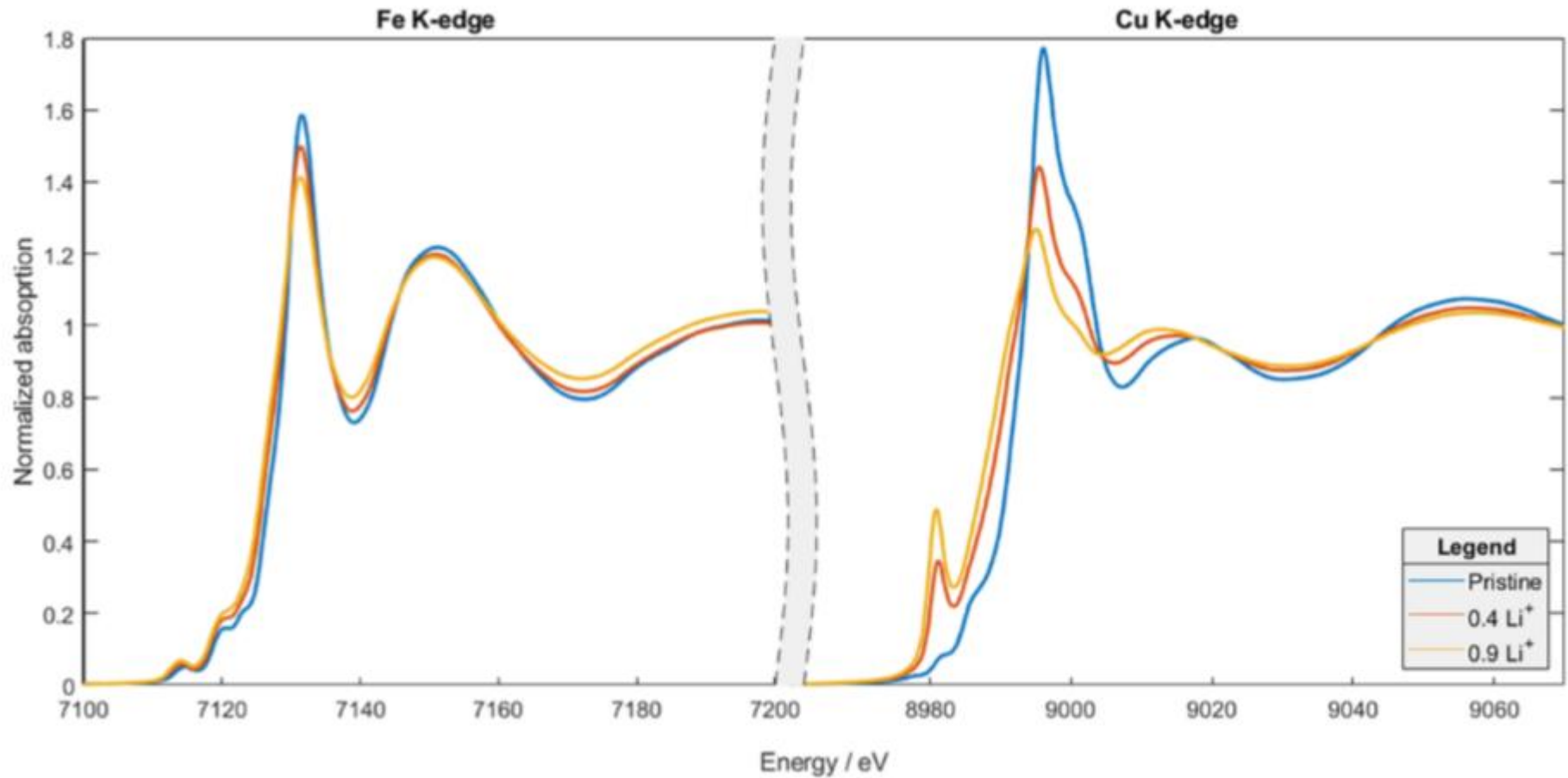
Prussian Blue Analogues: CuNP



**Copper nitroprusside (CuNP),
 $\text{Cu}[\text{Fe}(\text{CN})_5(\text{NO})]$**

•109

Prussian Blue Analogues: XAS

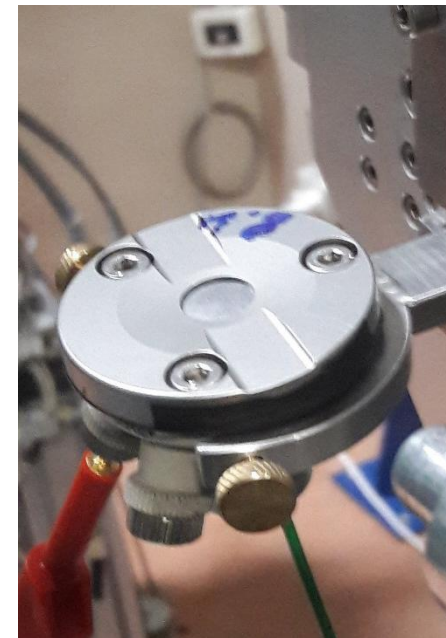


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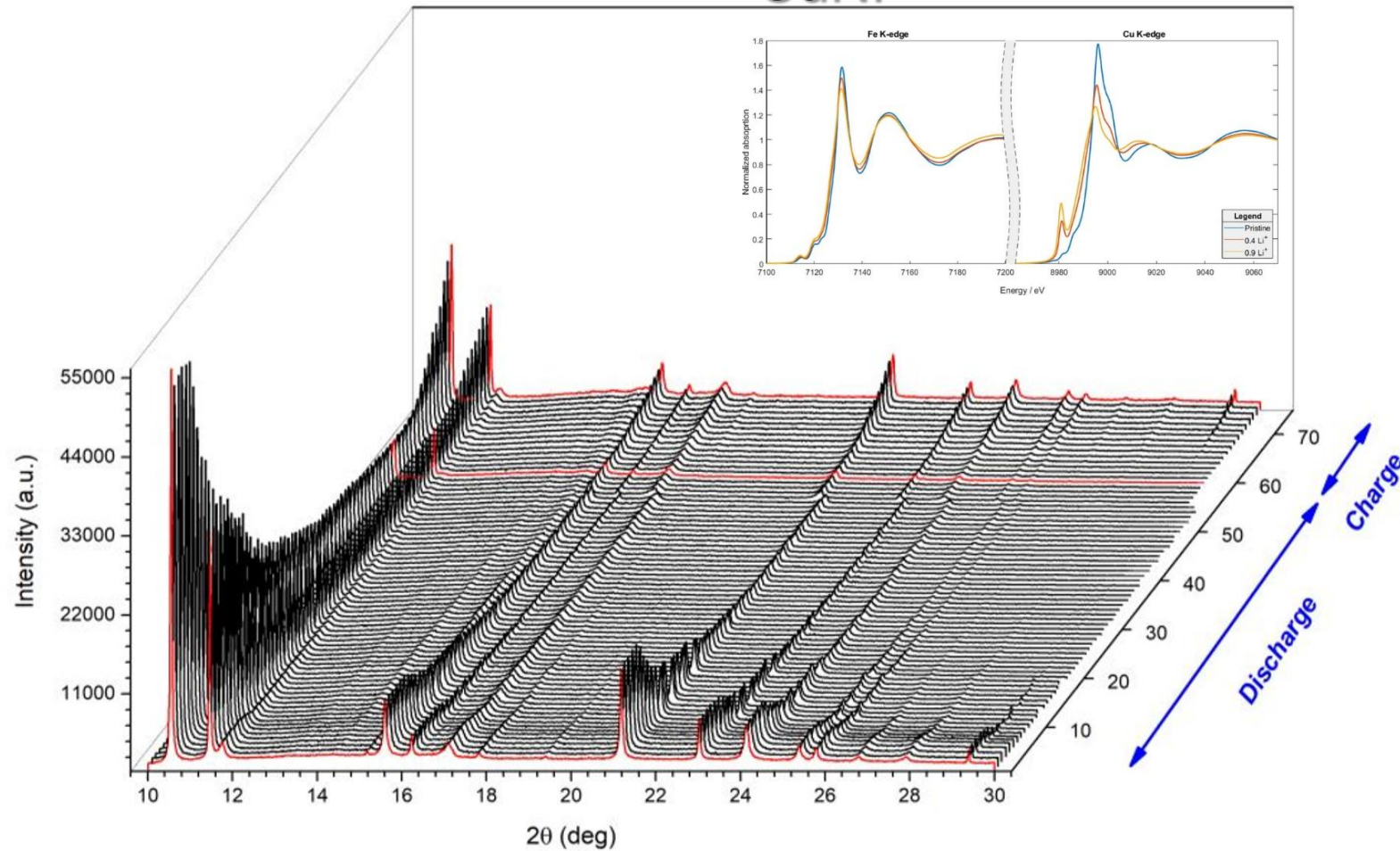
Operando battery studies: CuNP

The experiment:

- Cathode: CuNP (70%), carbon black (10%), vapor-grown carbon fibers-high density (10%) and PTFE (10%)
- Anode: Lithium
- Electrolyte: 1 M LiPF_6 in EC/DC
- Wavelength 1 Angstrom
- 2θ range 10° to 30° with a 0.01° step
- 0.5 s/point acquisition
- Discharge to 1.8 V versus Li^+/Li and subsequent charge to 3.5 V versus Li^+/Li at C/22 current rate

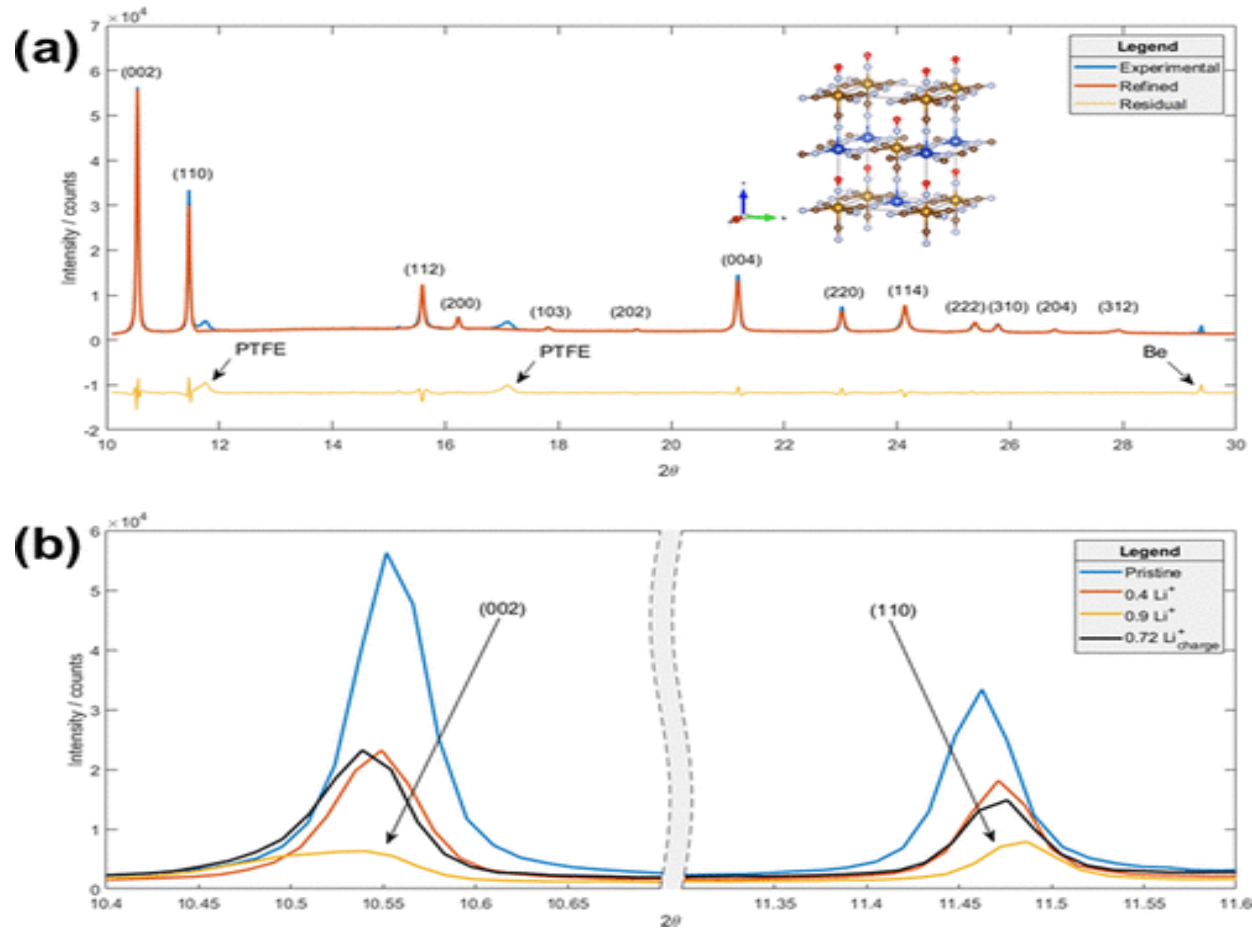


Operando battery studies: CuNP



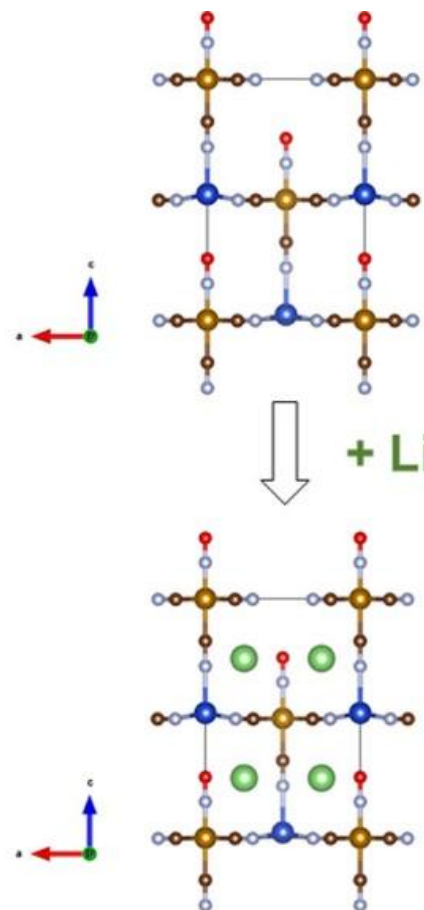
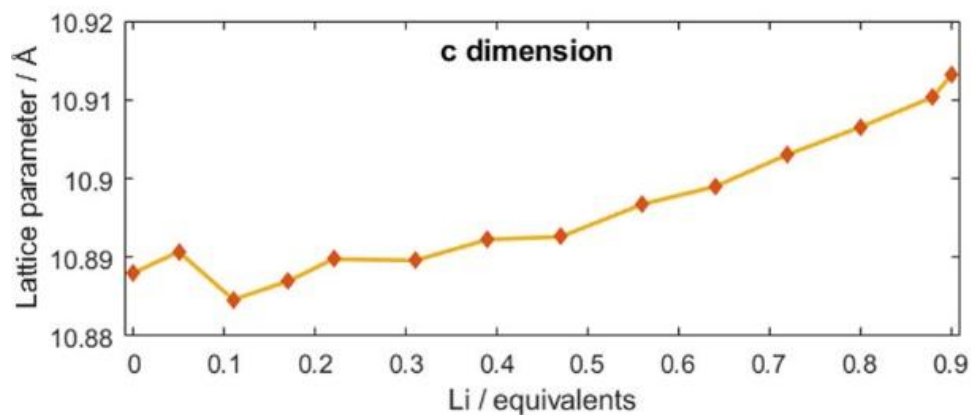
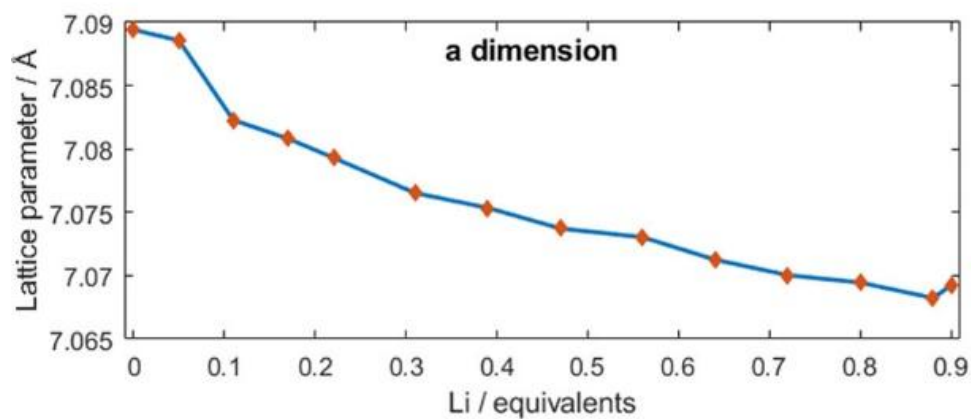
•112

Operando battery studies: CuNP



•113

Operando battery studies: CuNP



Diffraction for stress analysis

- The stresses in a material are the sum of the contributions from any externally applied load (applied stress) and those arising from the interactions between individual grains or components that are not completely relaxed when no external load is present (residual stresses).
- Stresses lead to deformation, the distances between lattice planes changes in the direction where stress is present.
- Measuring how the peak position (related to the lattice plane distance by braggs law) changes, at different orientations of the sample gives us information on the amount of stress

Diffraction for stress analysis

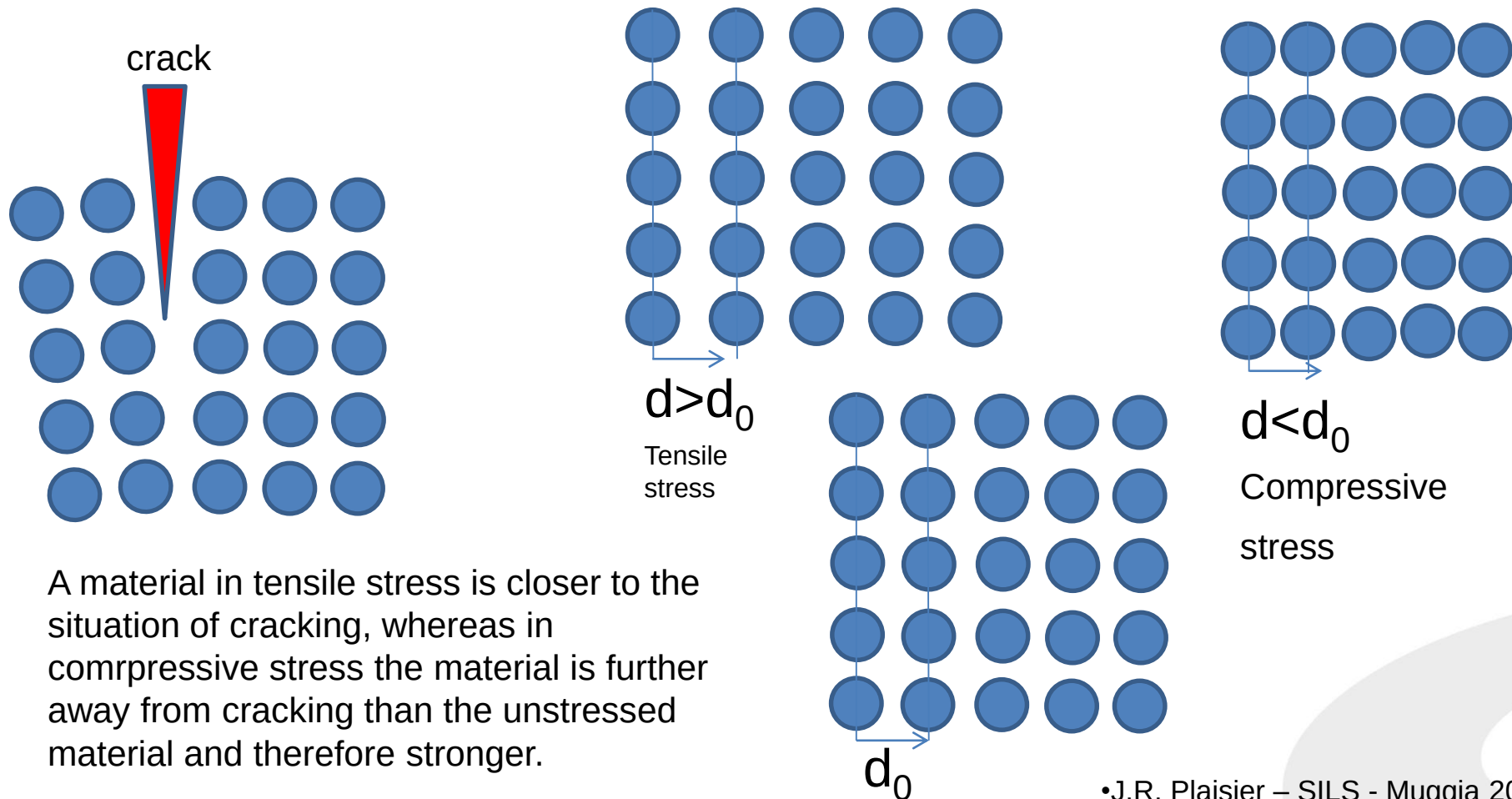
- Not being aware of residual tensile stresses, that make materials weaker can have disastrous consequences in construction for example:



Residual stress is often a cause of premature failure of critical components, and was one factor in the collapse of the suspension bridge at Silver Bridge in West Virginia in December 1967. The eyebar links were castings which showed high levels of residual stress, which in one eyebar, encouraged crack growth. When the crack reached a critical size, it grew catastrophically, and from that moment, the whole structure started to fail in a chain reaction. Because the structure failed in less than a minute, 46 drivers and passengers in cars on the bridge at the time were killed.

Diffraction for stress analysis

- On the other hand residual stresses may be induced in materials on purpose. Compressive residual stress may be induced in order to strengthen it and increase its fatigue life



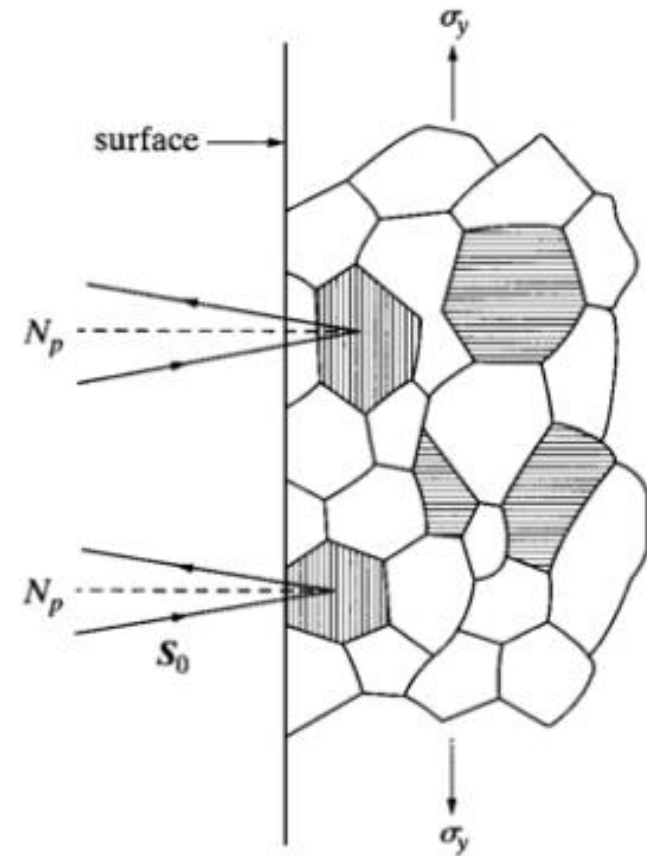
- A material in tensile stress is closer to the situation of cracking, whereas in compressive stress the material is further away from cracking than the unstressed material and therefore stronger.

Diffraction for stress analysis

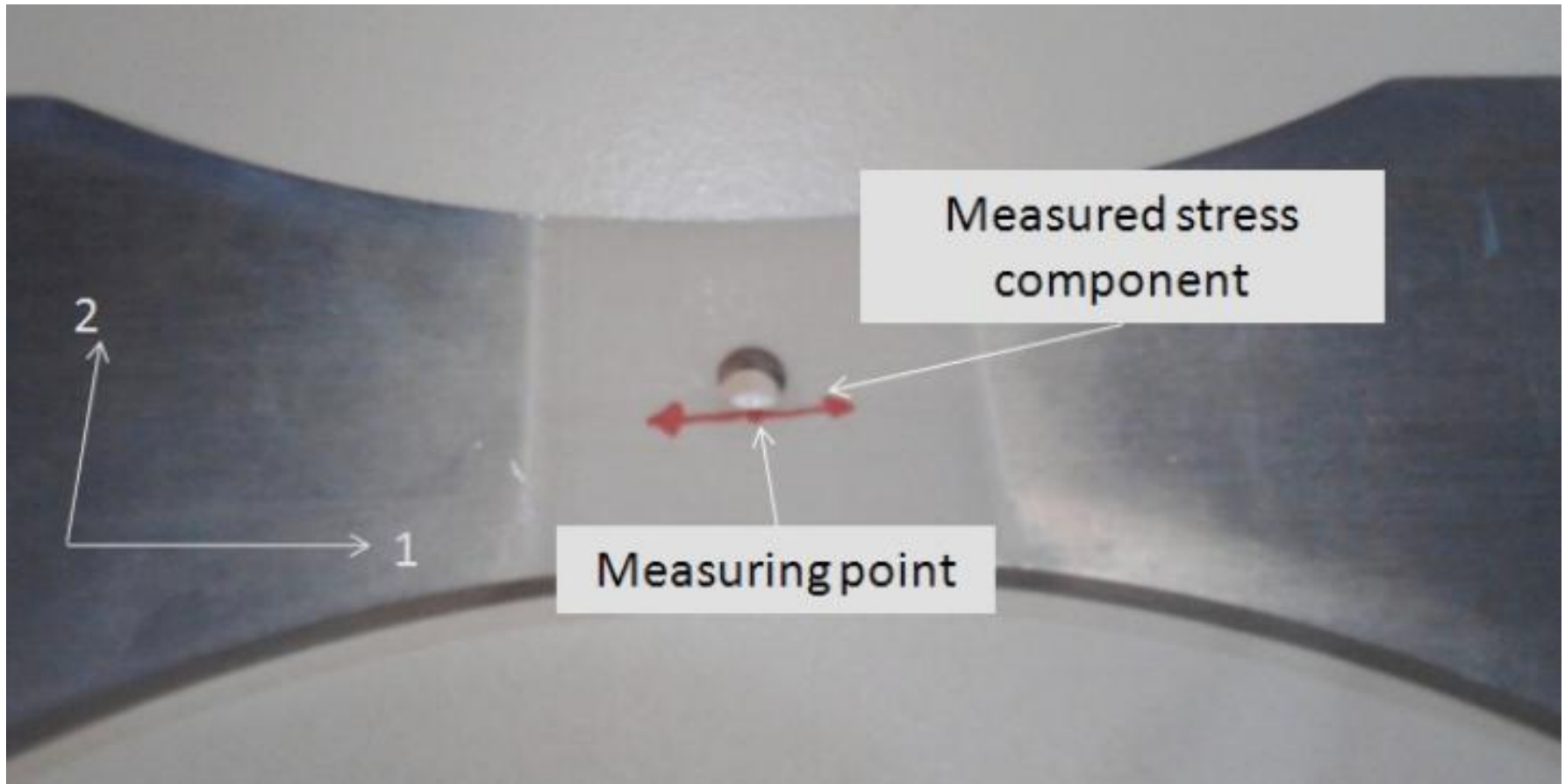
- It is strain that is actually measured: $\Delta d/d_0$
- Residual strain changes interplanar spacings, which shifts the positions of diffraction peaks.
- Strain is resolved differently in different physical directions in the sample.
- Engineering materials are polycrystalline, so some grains are always oriented to diffract enabling stress tensors to be determined.

Diffraction for stress analysis

- When the d-spacing of a reflection is measured, only grains with the planes oriented in a given direction contribute to diffraction. If we change the orientation of the specimen and remeasure the d-spacing we are looking at a different population of grains and we get a different d-spacing due to different stress levels

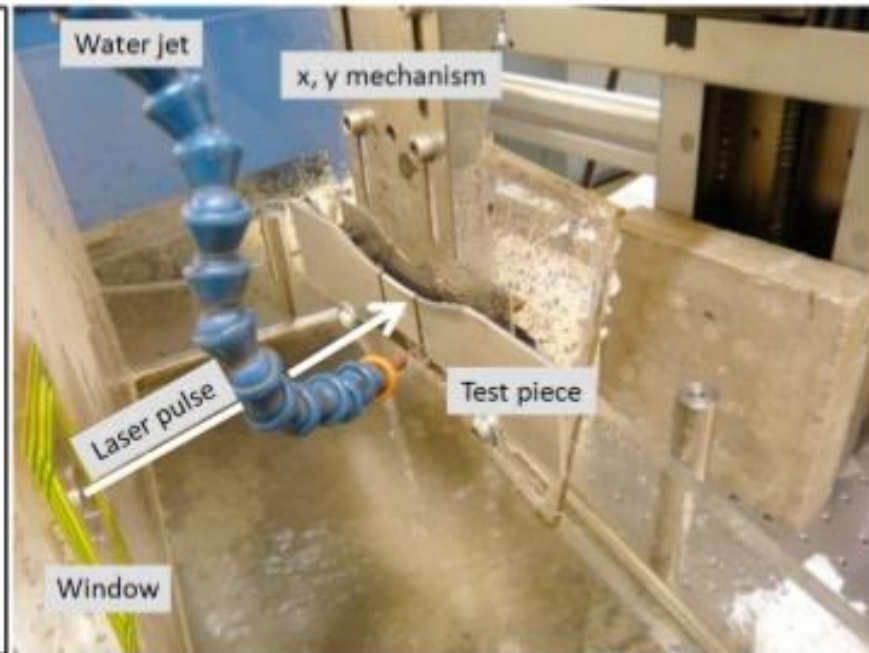
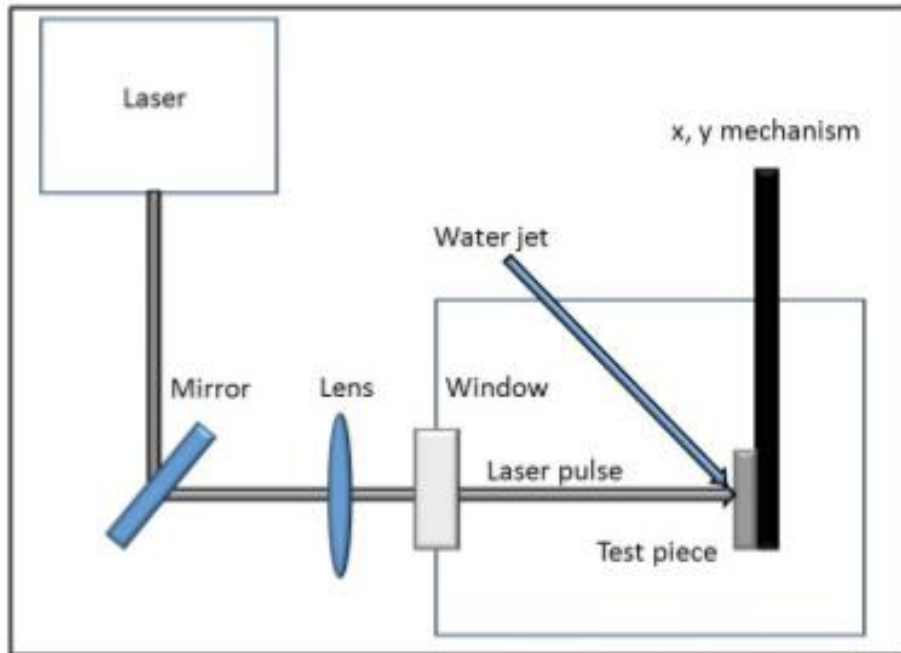


Diffraction for stress analysis



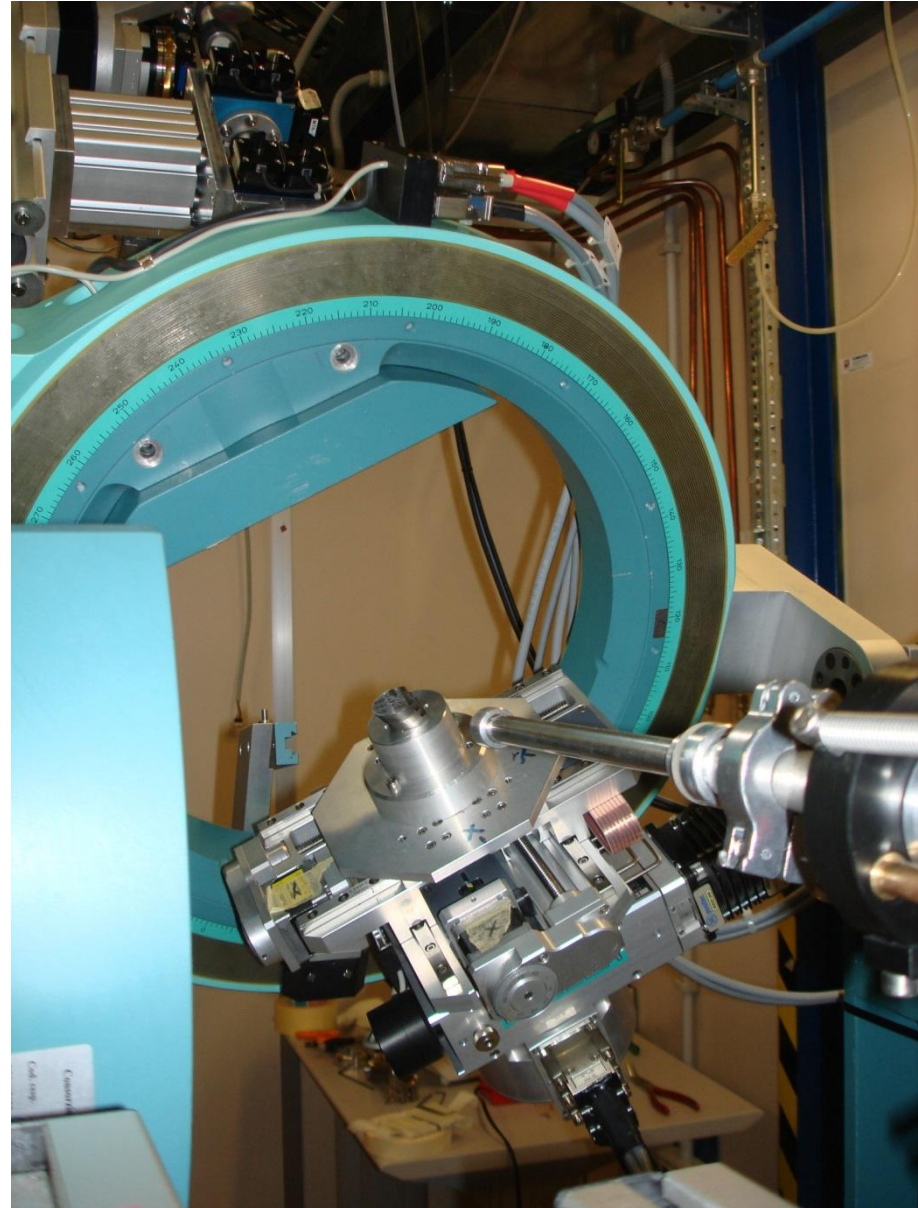
- Alloys of aluminium used in the airplane industry were measured to see the effectiveness of laser peening around a hole.

Diffraction for stress analysis



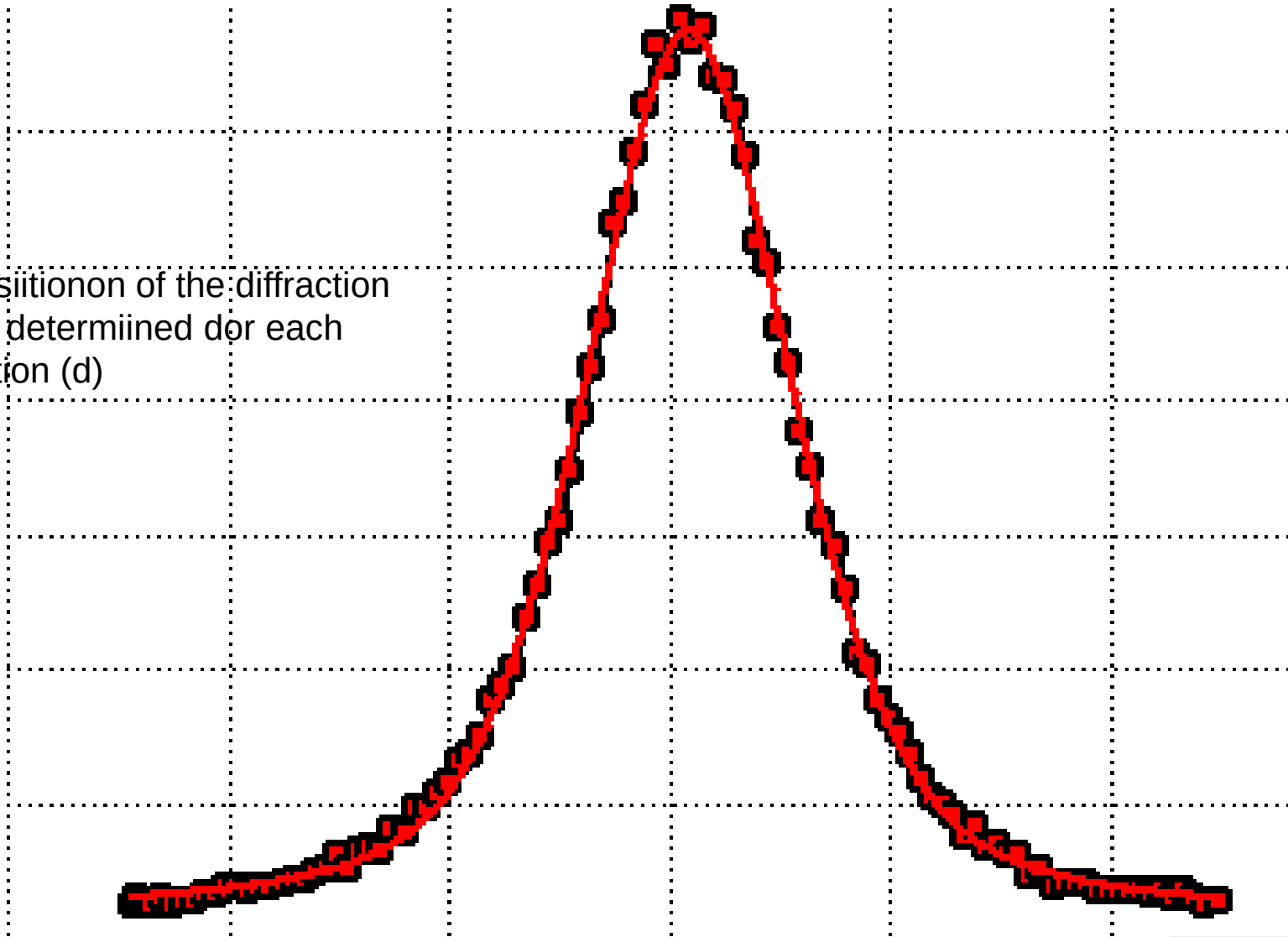
Diffraction for stress analysis

- The same diffraction peak is measured for different orientations of the sample

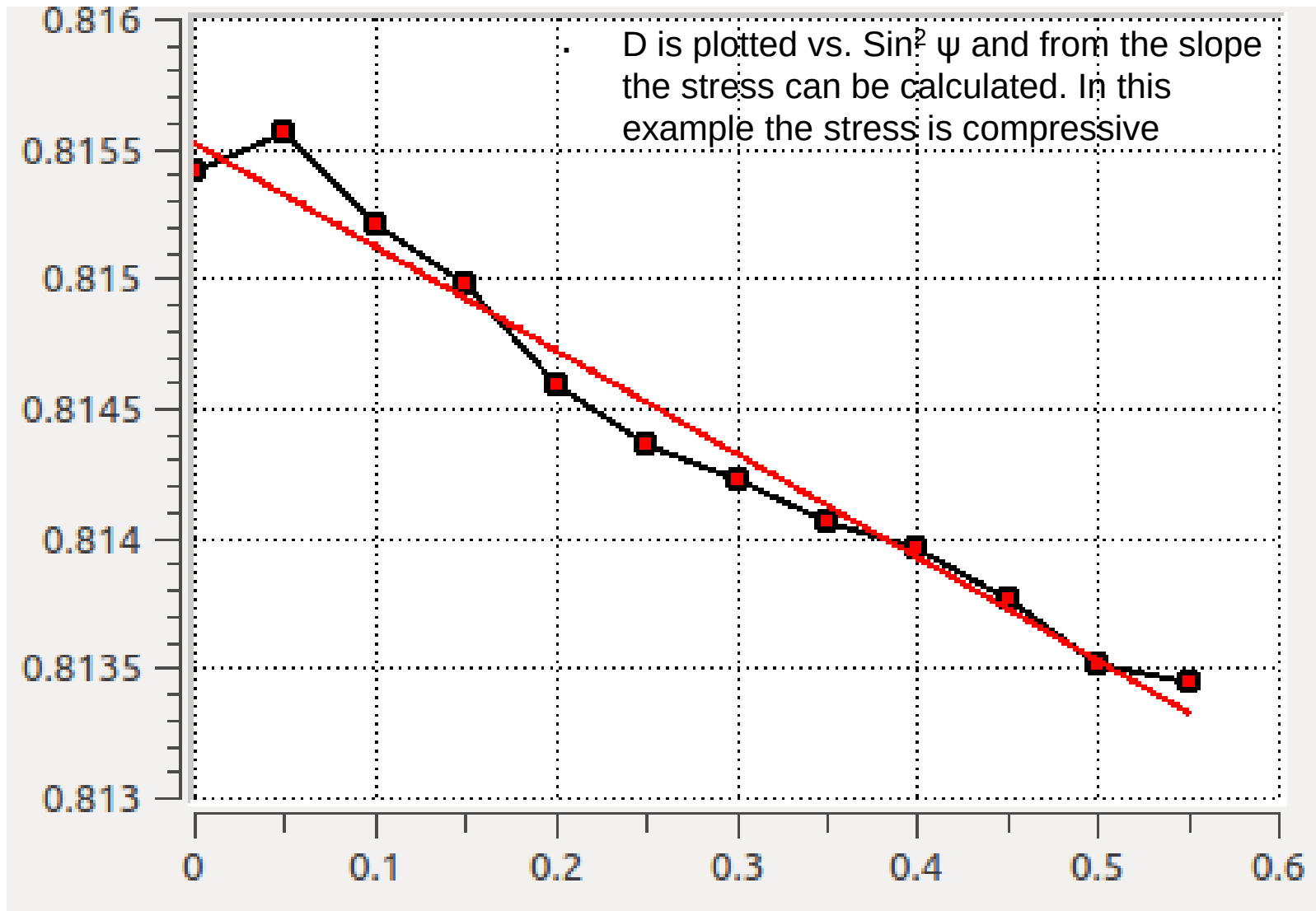


Diffraction for stress analysis

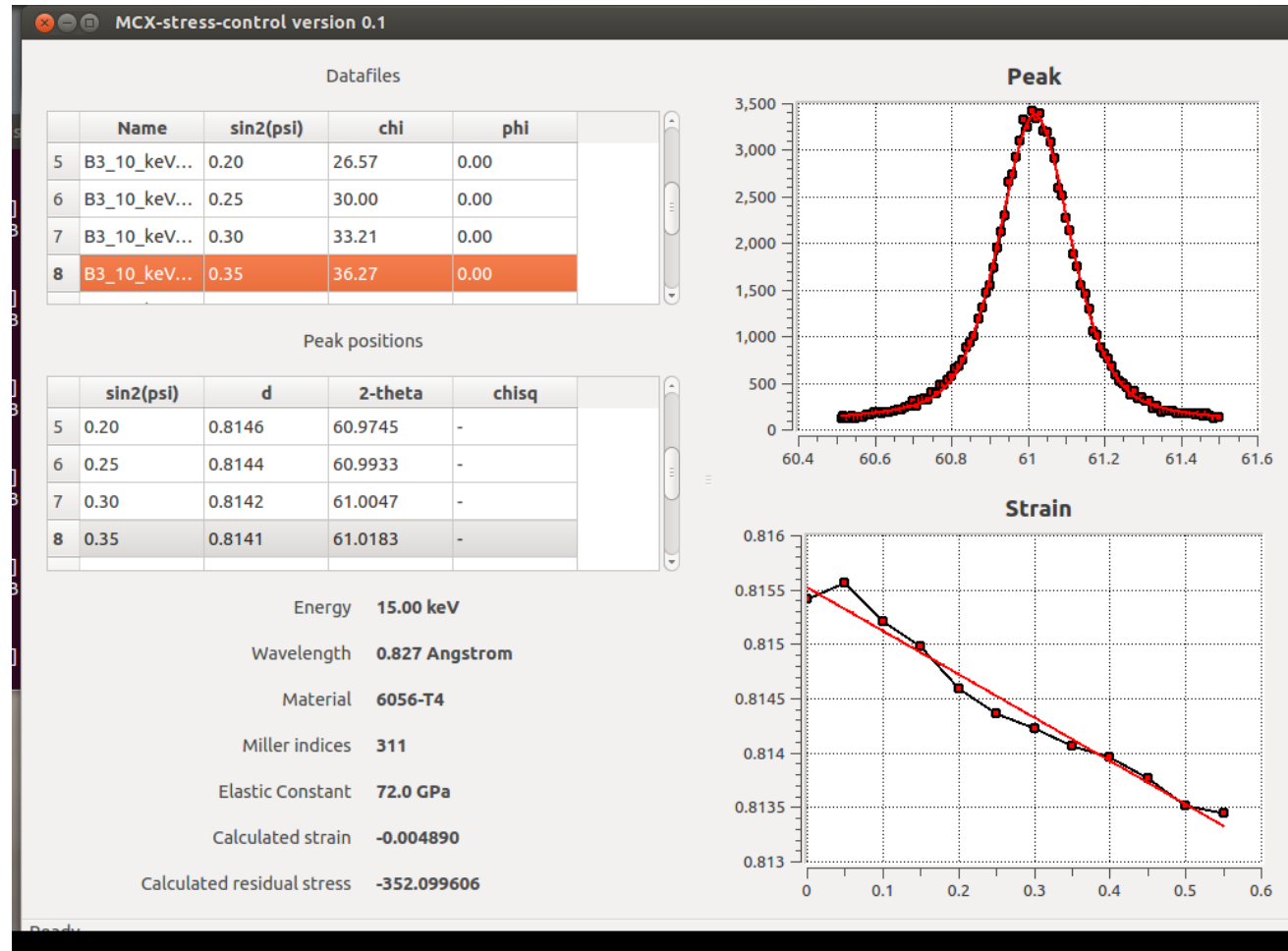
- The position of the diffraction peak is determined for each orientation (θ)



Diffraction for stress analysis

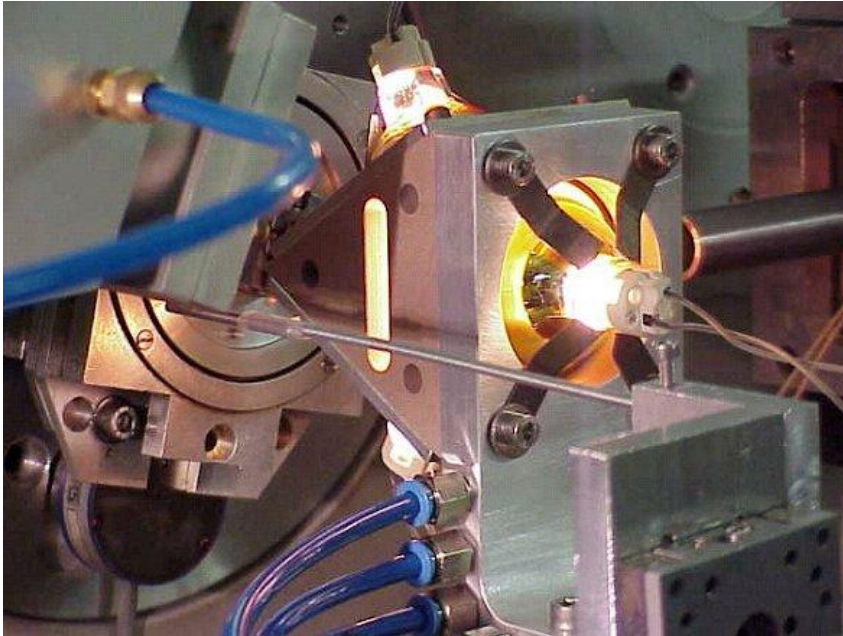


Diffraction for stress analysis

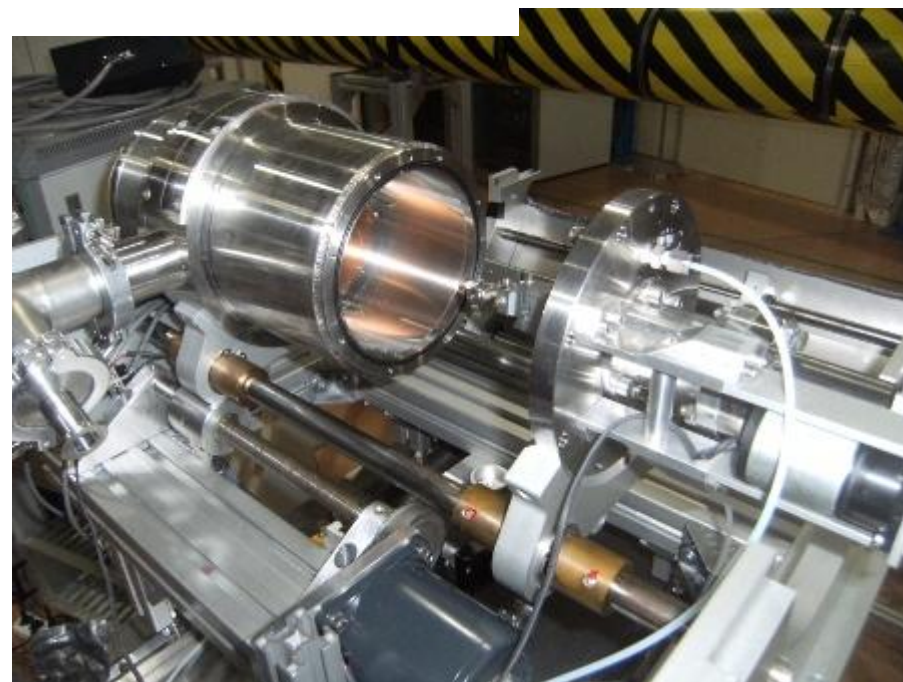
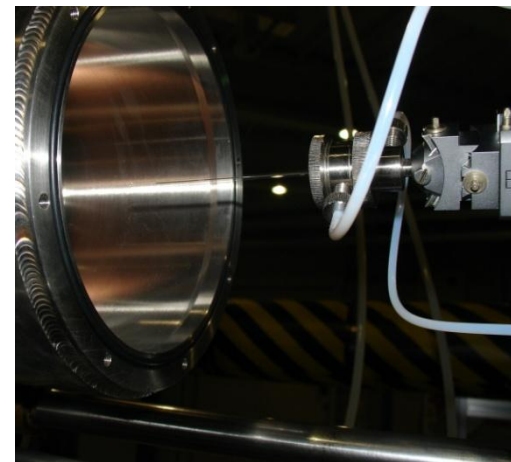
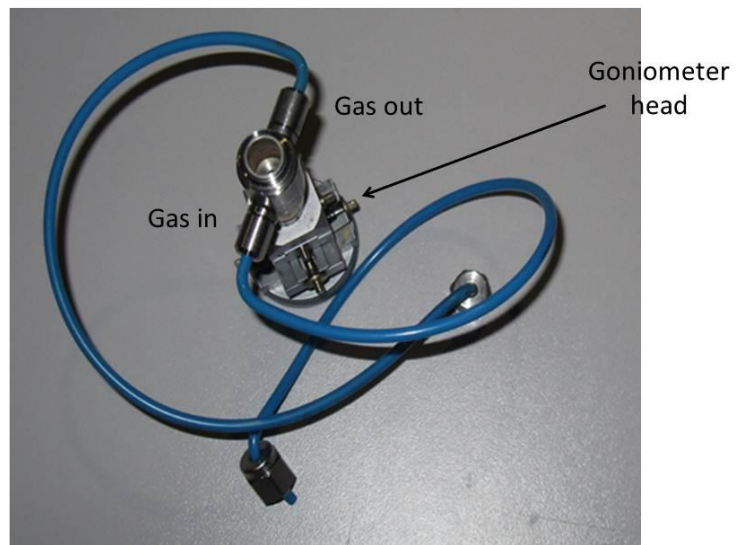
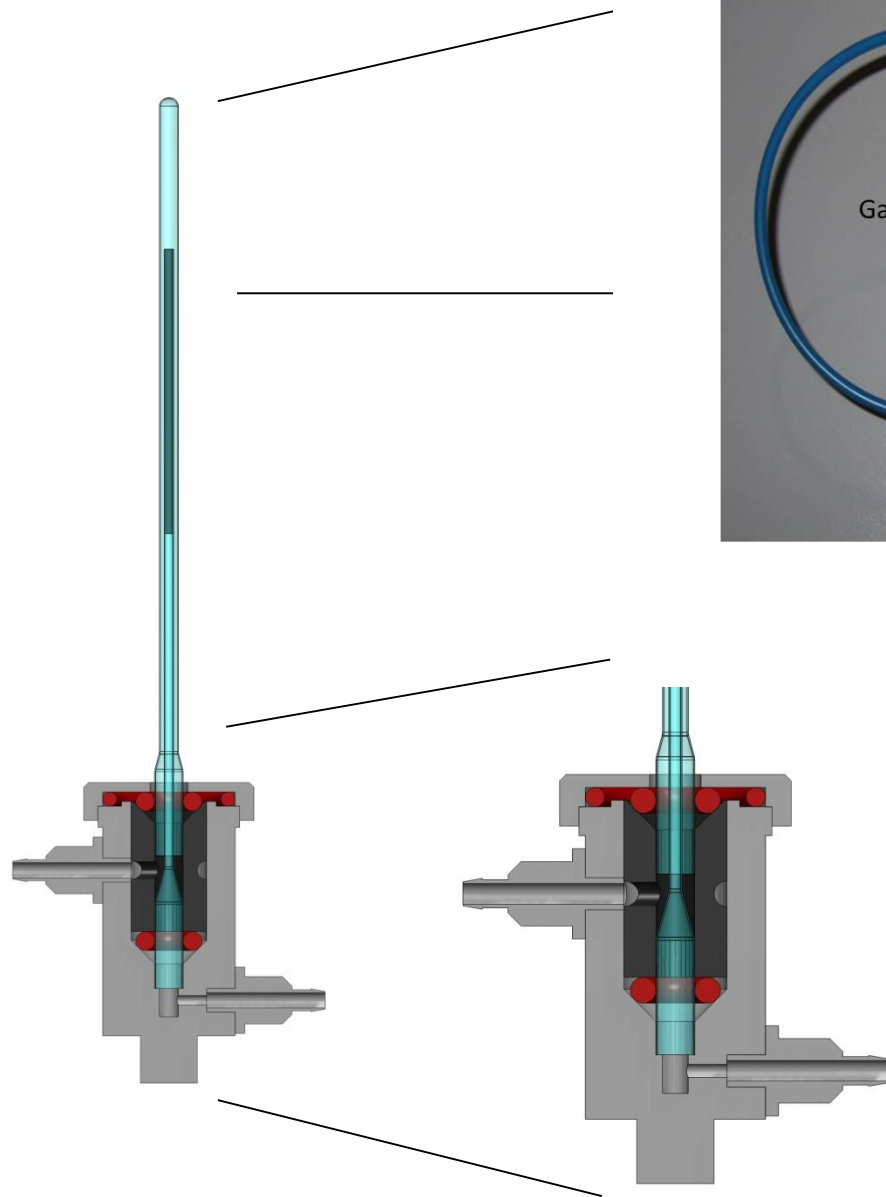


- The result showed that laser peening after drilling the hole actually weakens the material, whereas first applying laser peening and subsequently drilling the hole results in a stronger material

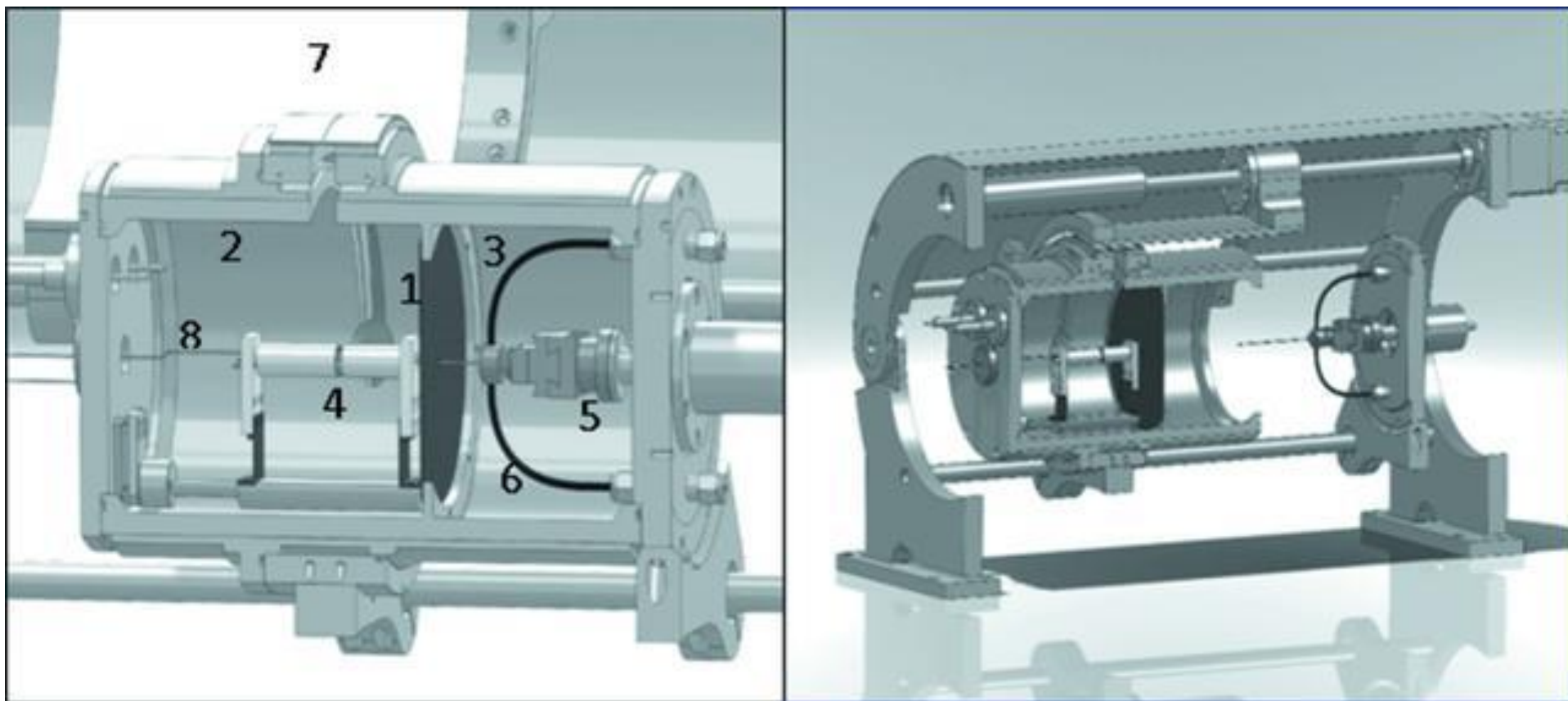
XRPD in non ambient conditions



XRPD in non ambient conditions



Furnace Design

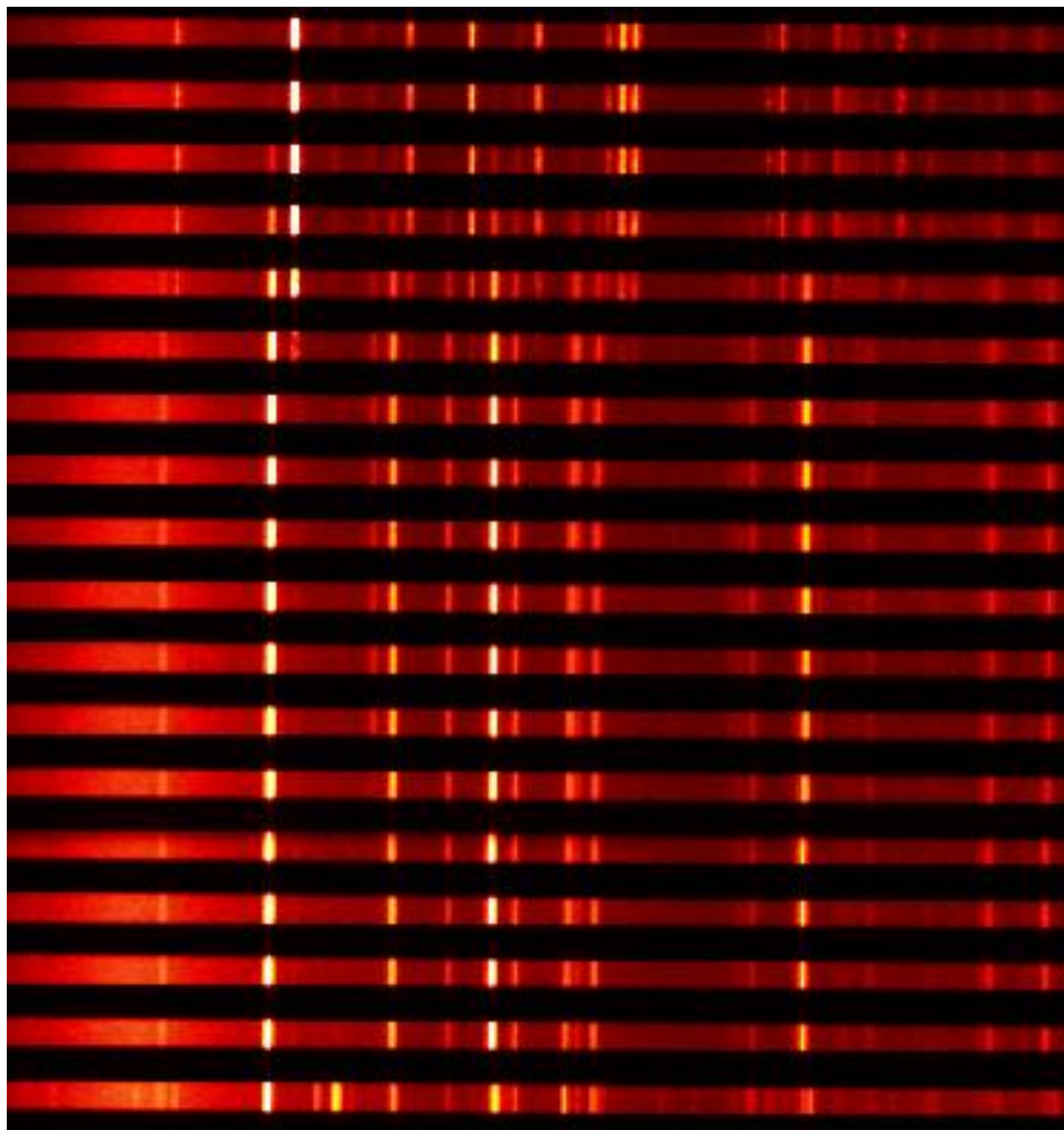


In situ reaction furnace for real-time XRD studies

Riello P., Lausi A., MacLeod J., Plaisier J.R., Zeraushek G., Fornasiero P.

Journal of Synchrotron Radiation, Vol. 20 - 1, pp. 194-196 (2013)

XRPD in non ambient conditions

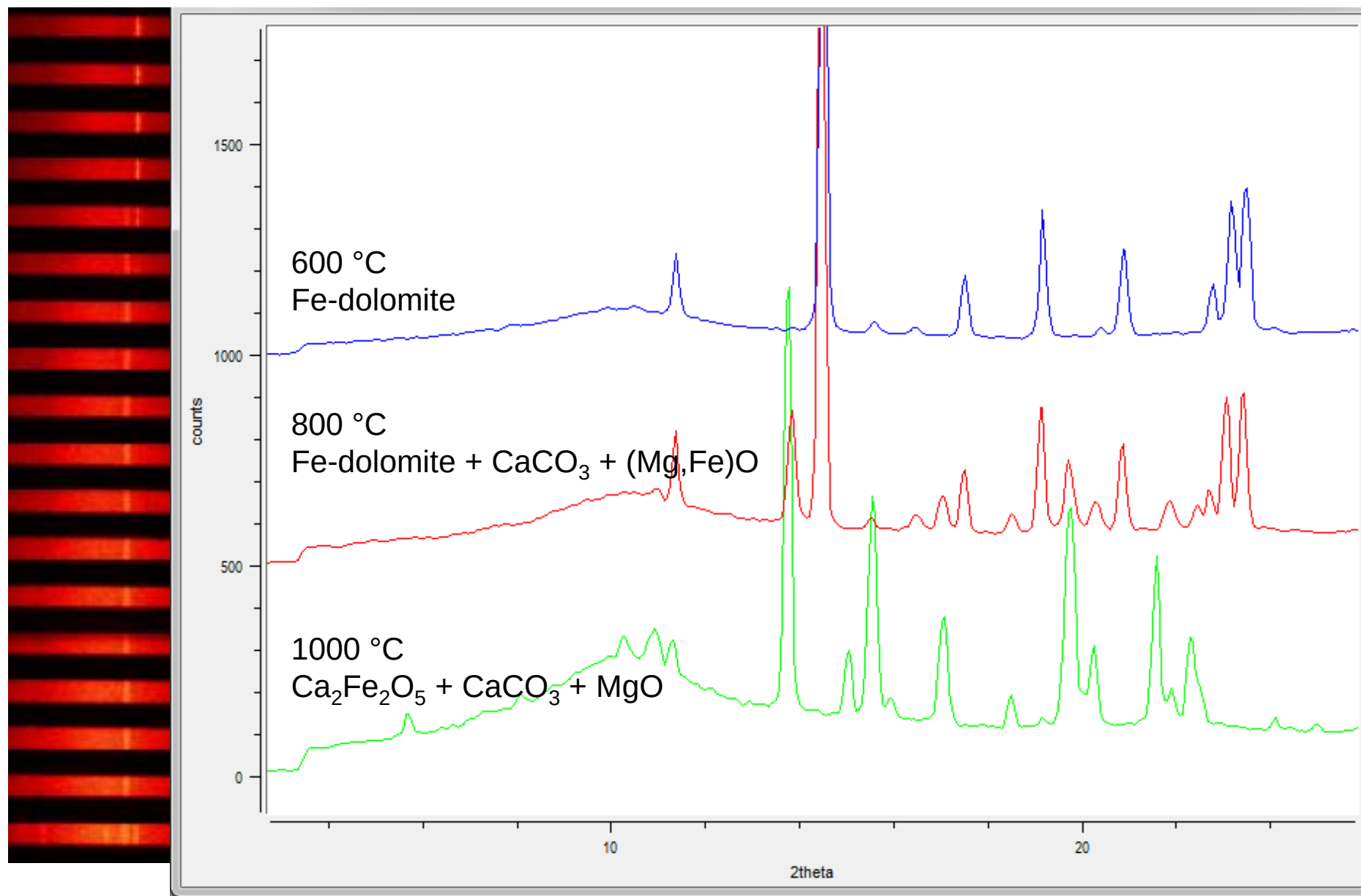


600 °C

800 °C

1000 °C

XRPD in non ambient conditions



2D-3D transition In Cu–TiS₂ system

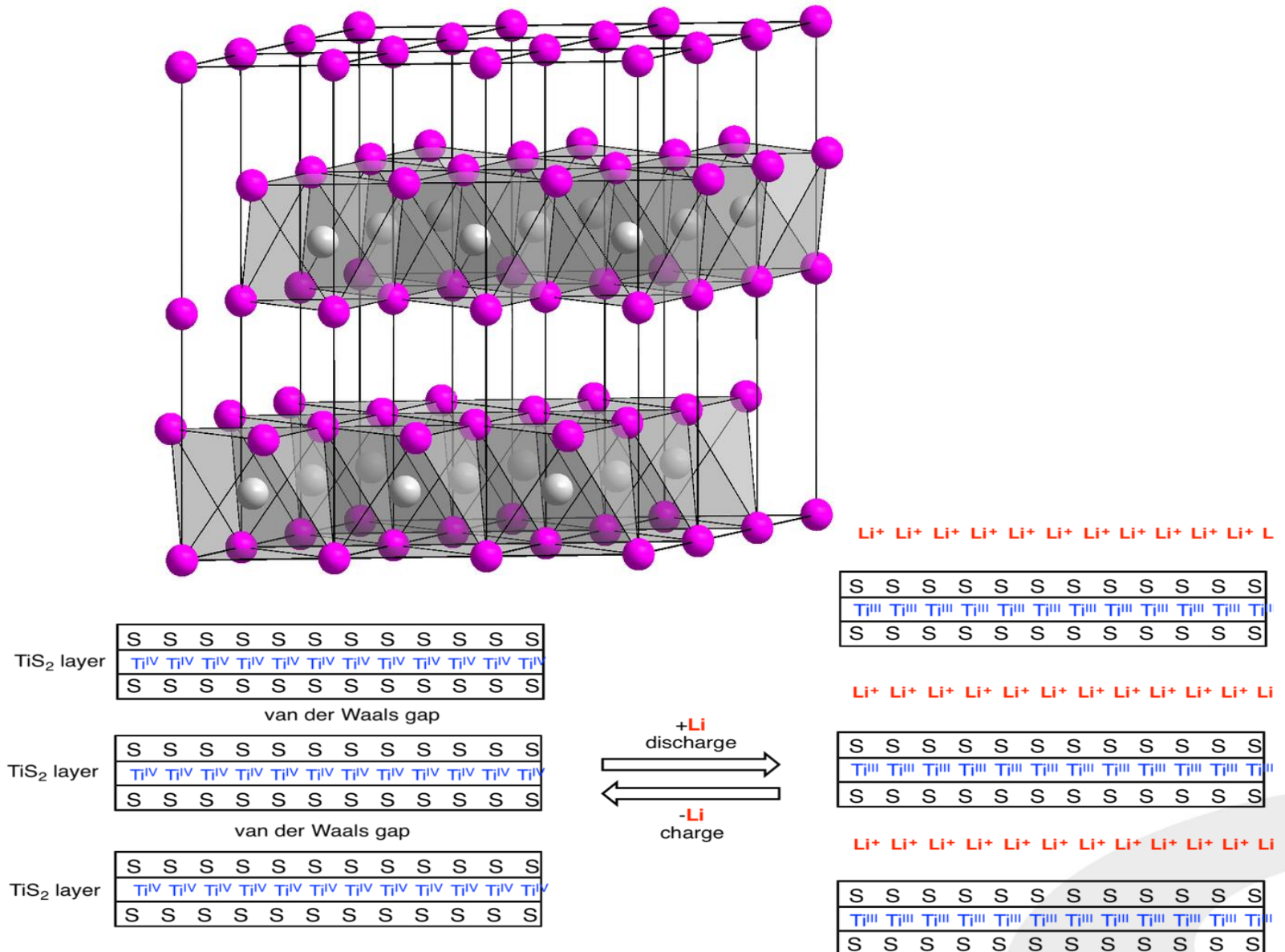
- Phase transitions between 2D (layered) and 3D (cubic) phases in Cu_xTiS₂ (x = 0-0.5) intercalation compounds have been studied *in situ* by the X-ray diffraction technique in the temperature range 20–1000 °C.
- The discovery of CDW (charge density wave) quantum states and superconductivity in the Cu–TiSe₂ system arouses interest to isostructural materials, but known phase transformations to the spinel structure make comparison difficult.
- Samples were prepared by intercalation of Cu at room temperature. All samples had the layered hexagonal structure.

2D-3D transition in Cu–TiS₂ system

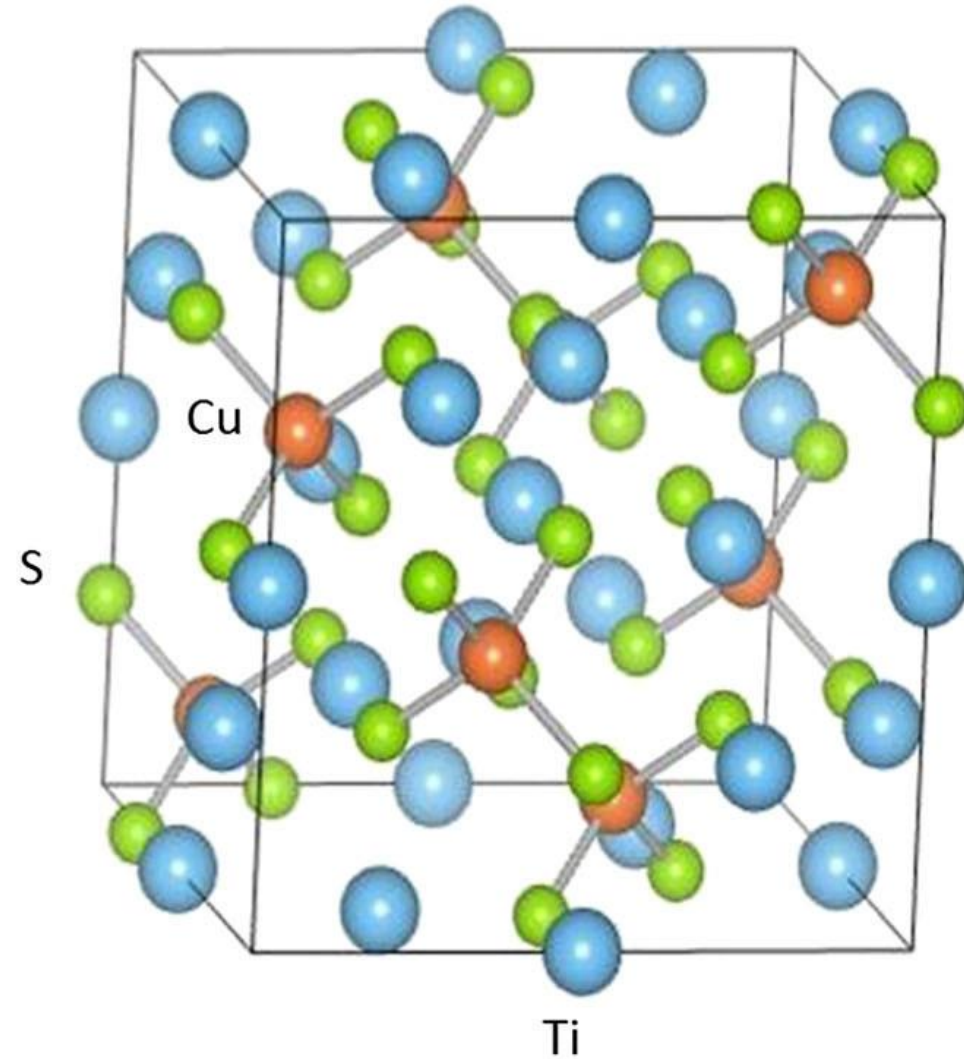
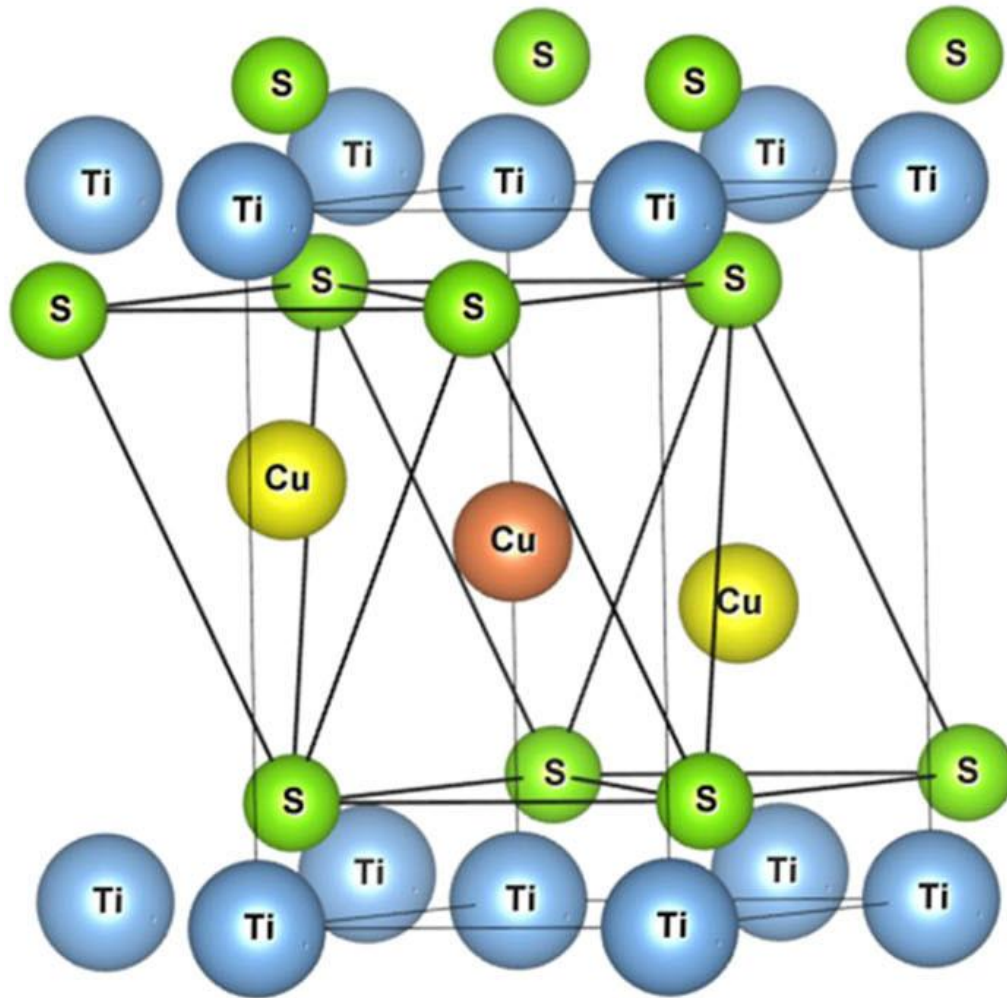
Shkvarina EG, Titov AA, Doroschek AA, Shkvarin AS, Starichenko DV, Plaisier JR, Gigli L, Titov AN.

The Journal of Chemical Physics 147, 044712 (2017)

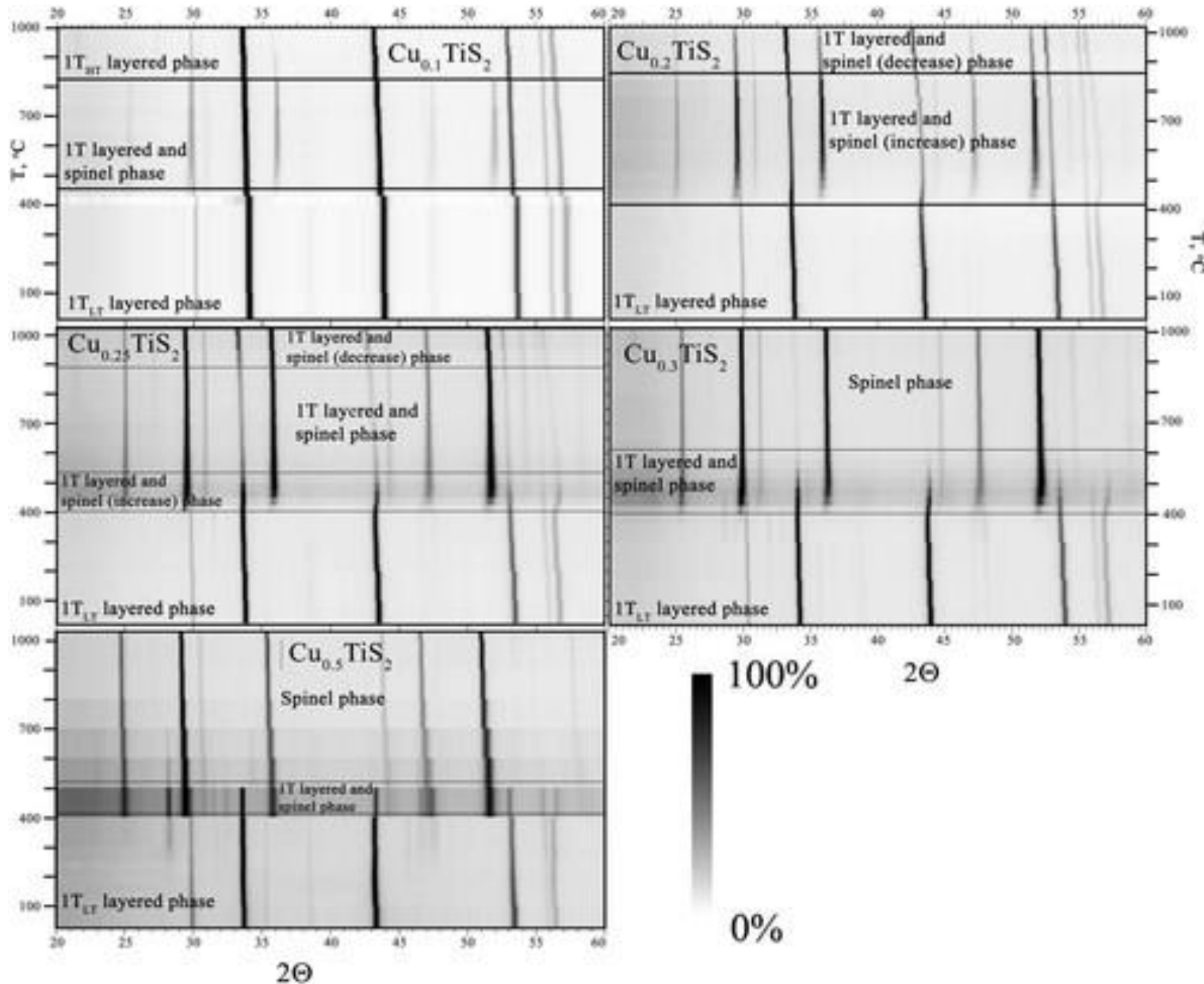
2D-3D transition In Cu-TiS₂ system



2D-3D transition In Cu–TiS₂ system



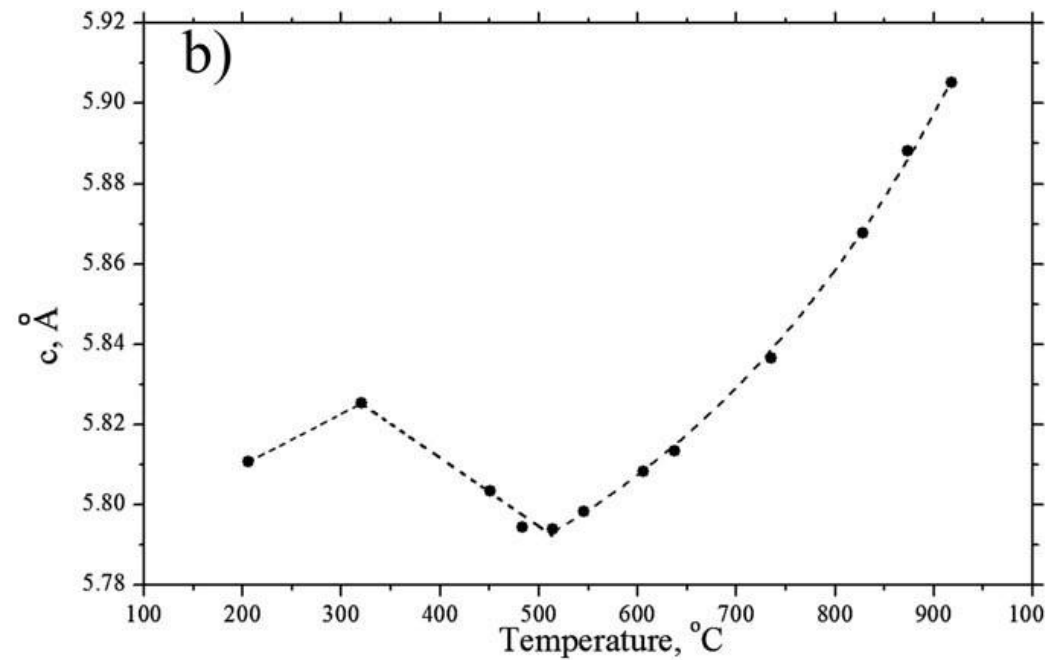
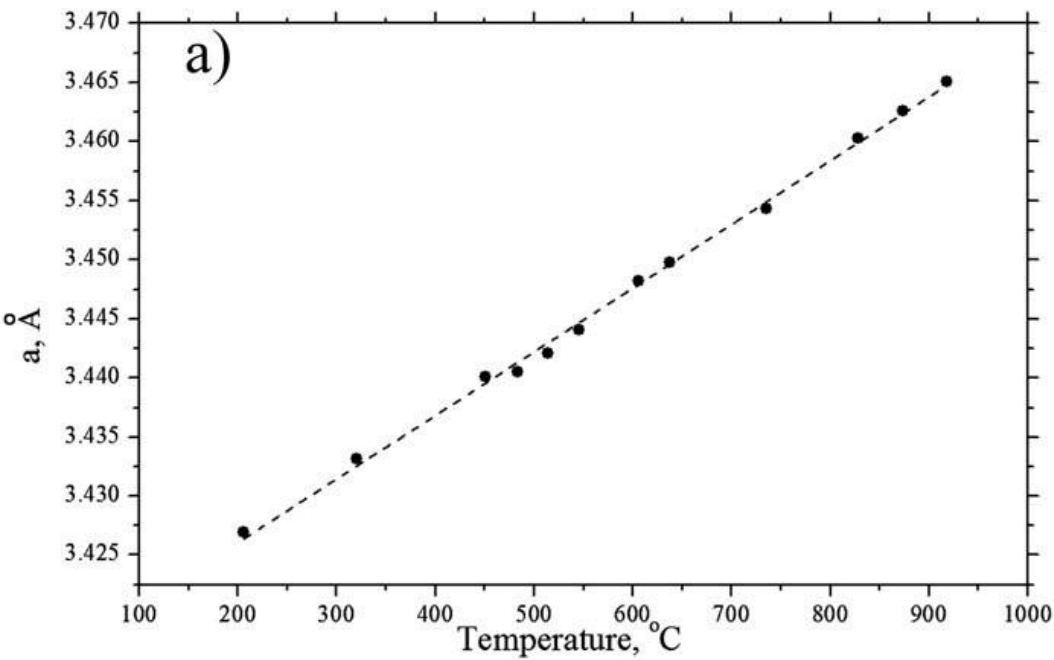
2D-3D transition In Cu-TiS₂ system



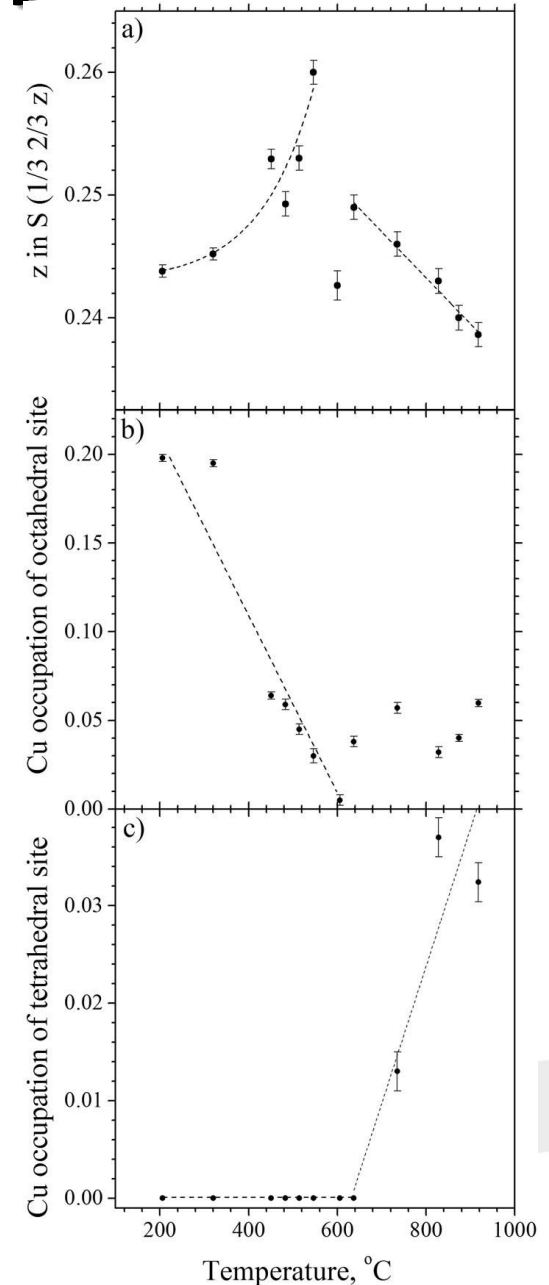
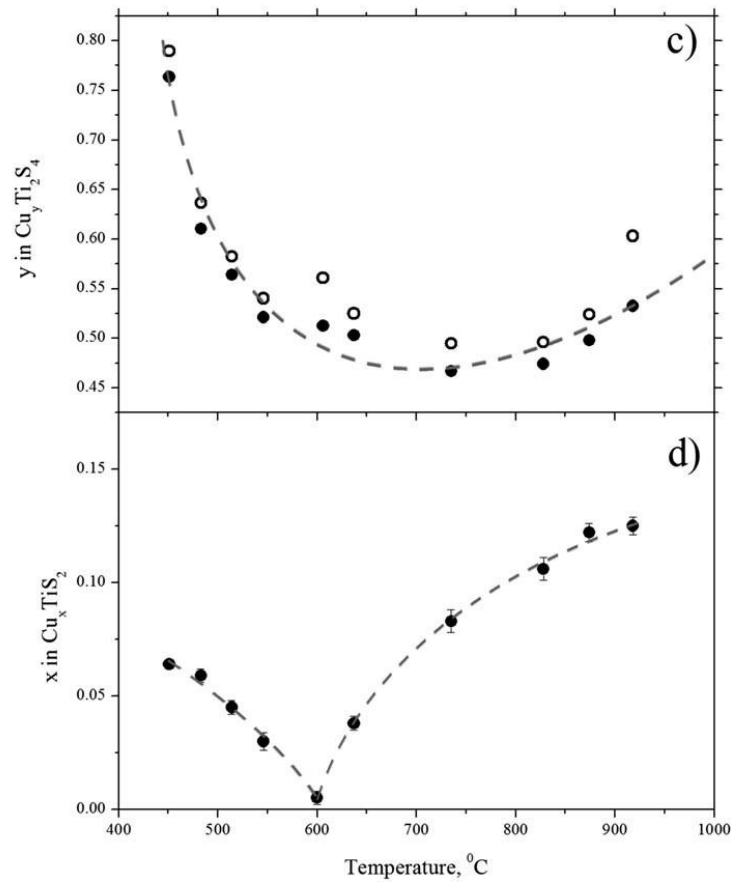
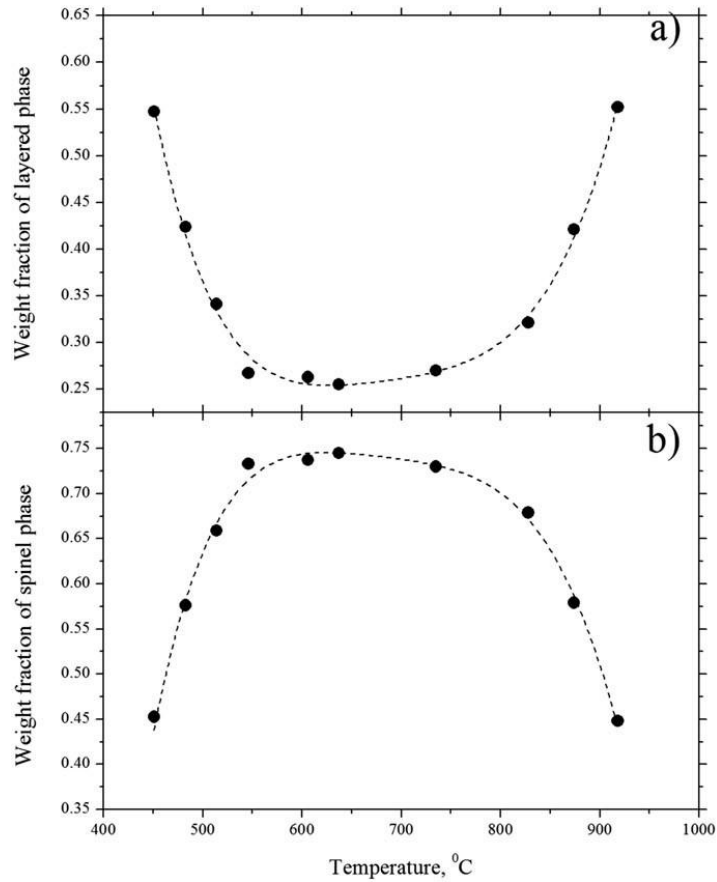
2D-3D transition In Cu–TiS₂ system

T (°C)	1T layered phase							Cubic spinel phase			R _F ² (%)	χ ²
	a	c	S (1/3 2/3 z)	Cu (0 0 1/2)	Cu (1/3 2/3 z)		Ti (0 0 1/2)	a	Cu (1/8 1/8 1/8)	S (x x x)		
			z	Occupation	z	Occupation	Occupation		Occupation	x		
Cu _{0.2} TiS ₂												
206	3.4269(1)	5.8106(2)	0.2438(5)	0.198(2)	...	...	...	...	...	...	5.96	1.880
320	3.4331(1)	5.8252(2)	0.2452(5)	0.195(2)	...	...	...	...	...	...	6.44	1.688
451	3.4401(1)	5.8037(2)	0.2593(8)	0.064(2)	...	...	0.005(3)	9.9816(4)	0.763(8)	0.2502(5)	3.90	1.123
483	3.4405(1)	5.7942(3)	0.249(1)	0.059(3)	...	...	...	9.9631(3)	0.611(5)	0.2526(3)	2.89	1.136
514	3.4421(1)	5.7937(3)	0.253(1)	0.045(3)	...	...	0.017(4)	9.9592(2)	0.564(4)	0.2530(2)	3.18	1.064
546	3.4441(1)	5.7982(4)	0.260(1)	0.030(4)	...	...	0.018(5)	9.9604(2)	0.521(3)	0.2529(3)	2.78	1.138
606	3.4482(1)	5.8083(4)	0.243(1)	0.005(3)	...	...	0.074(6)	9.9642(1)	0.512(3)	0.2536(2)	4.55	1.107
637	3.4498(1)	5.8133(4)	0.249(1)	0.038(3)	...	...	0.018(5)	9.9660(1)	0.503(3)	0.2532(1)	1.86	1.105
735	3.4543(1)	5.8365(4)	0.246(1)	0.057(3)	0.45(3)	0.013(2)	0.020(5)	9.9726(1)	0.467(3)	0.2538(2)	2.89	1.565
828	3.4603(1)	5.8677(3)	0.243(1)	0.032(3)	0.454(7)	0.037(2)	0.029(4)	9.9846(1)	0.474(3)	0.2536(2)	2.72	1.296
874	3.4626(1)	5.8881(2)	0.240(1)	0.040(2)	0.431(6)	0.041(2)	0.031(4)	9.9908(1)	0.498(4)	0.2535(2)	2.92	1.770
918	3.4654(1)	5.9051(3)	0.239(1)	0.060(2)	0.445(8)	0.032(2)	0.001(4)	9.9662(4)	0.533(6)	0.2540(3)	4.12	2.410
Cu _{0.1} TiS ₂												
525	3.4422(1)	5.7990(2)	0.2460(6)	0.044(2)	0.35(2)	0.013(2)	0.024(3)	9.9701(8)	0.66(2)	0.2547(8)	8.16	5.921
647	3.4494(1)	5.8129(2)	0.2448(6)	0.038(2)	0.37(2)	0.015(2)	0.023(4)	9.9690(4)	0.50(2)	0.2544(6)	7.05	5.813
918	3.4650(1)	5.8691(2)	0.2428(7)	0.055(2)	0.42(2)	0.020(3)	0.002(4)	...	...	...	9.65	10.47
Cu _{0.25} TiS ₂												
918	3.4664(2)	5.9140(8)	0.236(2)	0.009(6)	0.46(1)	0.052(4)	...	10.0075(1)	0.512(4)	0.2531(2)	6.42	10.81

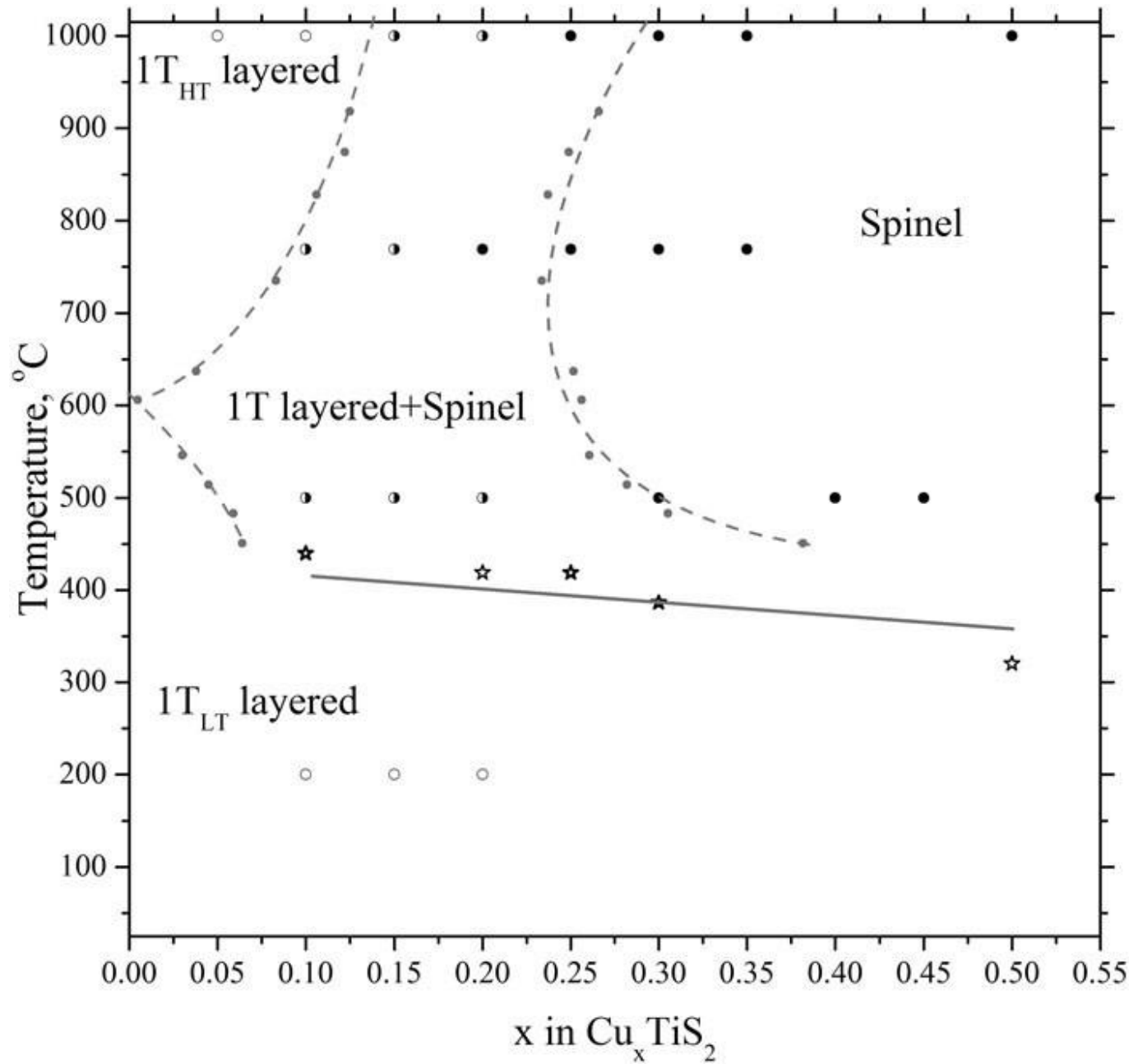
2D-3D transition In Cu-TiS₂ system



2D-3D transition In Cu-TiS₂ system



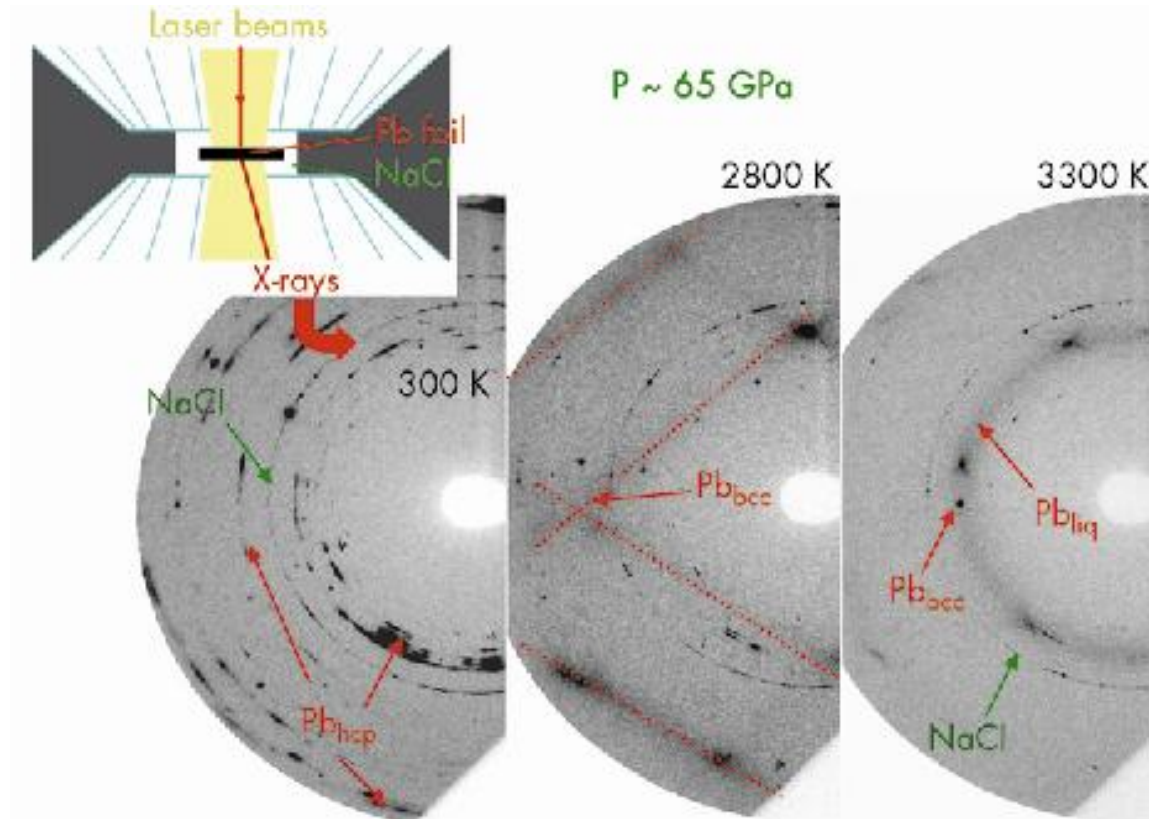
2D-3D transition In Cu-TiS₂ system



2D-3D transition In Cu–TiS₂ system

- It has been found that the stability of the layered phase is determined by the distribution of copper atoms between the octahedral and tetrahedral crystallographic sites.
- The occupation of octahedral sites dominates at low temperatures.
- Upon heating, tetrahedral site occupation is limited and the layered phase becomes unstable and transforms to the spinel.
- Further heating allows the distribution of copper between octahedral and tetrahedral sites; the layered phase becomes stable again.

XRPD in non ambient conditions



Source: www.esrf.eu

Line profile analysis - example

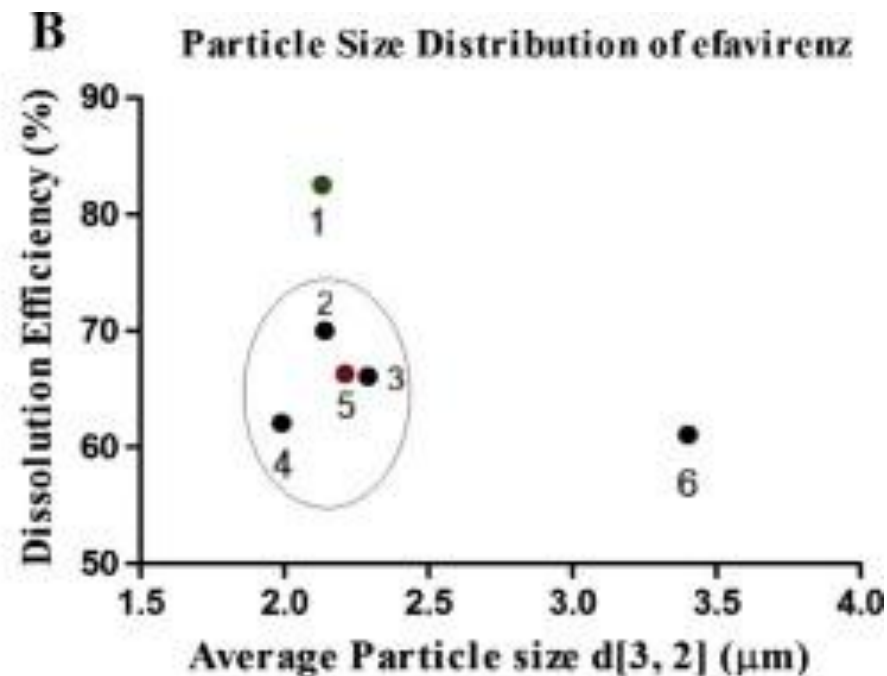
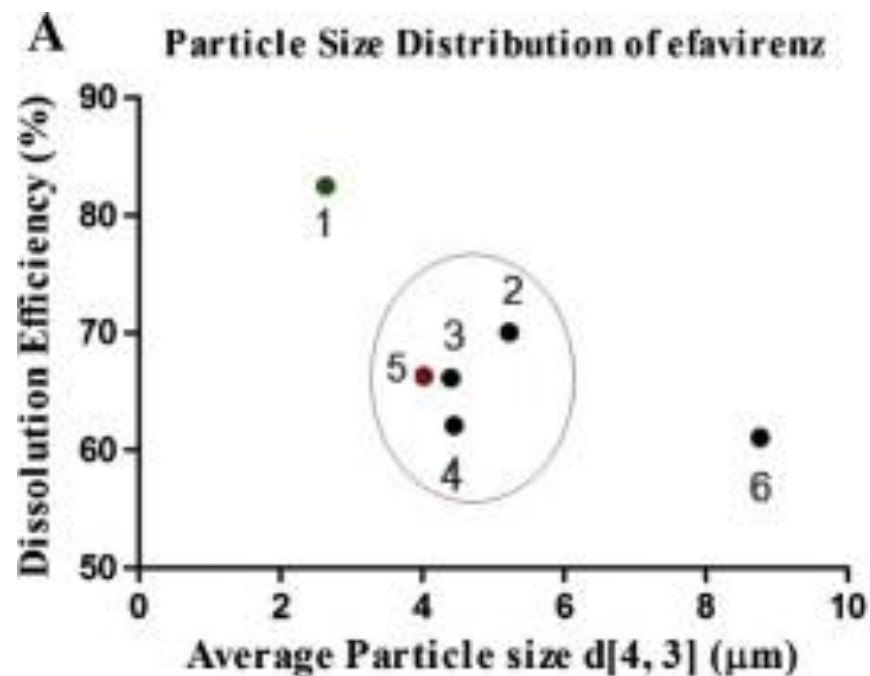
- Correlation between microstructure and bioequivalence in Anti-HIV Drug Efavirenz, C. Fandaruff *et al.*, **European Journal of Pharmaceutics and Biopharmaceutics** 91, 52-58 (2015)



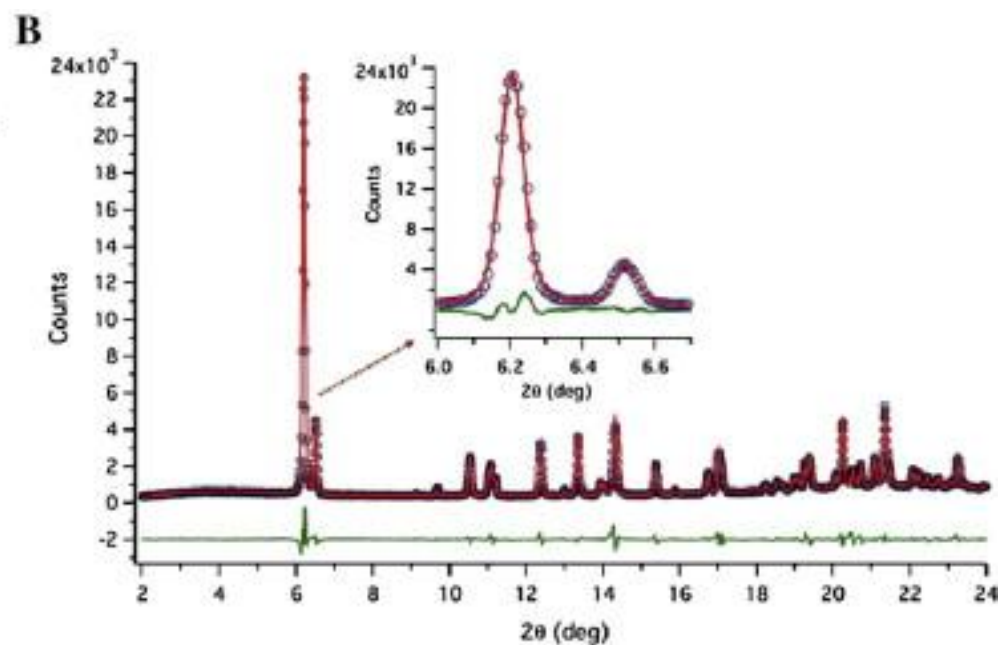
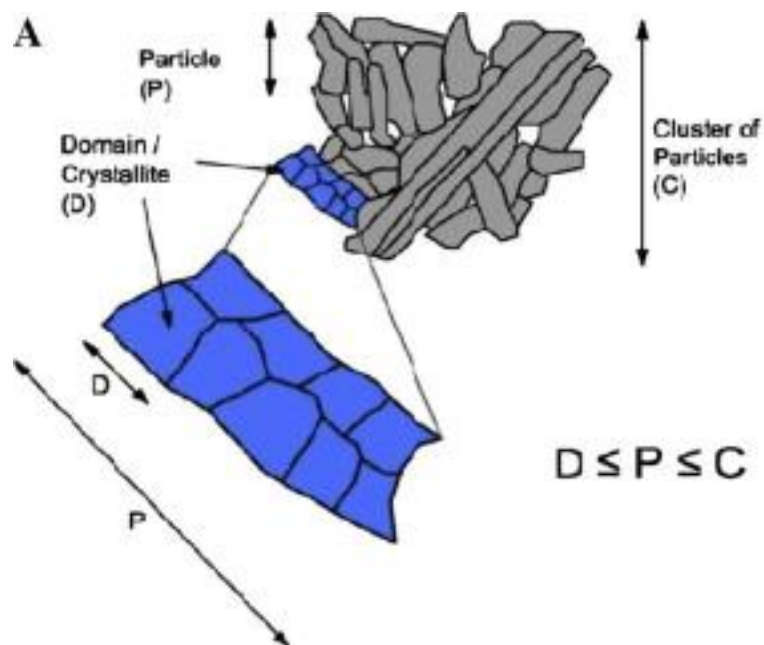
Line profile analysis - example

- Polymorphism and particle size distribution can impact the dissolution behaviour and, as a consequence, bioavailability and bioequivalence of poorly soluble drugs, such as Efavirenz (EFV).
- The aim of this work was to study microstructure, a solid-state property of current interest in the pharmaceutical area, in order to find an explanation for the dissolution and bioequivalence behaviour.
- The microstructure of EFV raw materials was studied by Whole Powder Pattern Modelling (WPPM) of X-ray powder diffraction data.

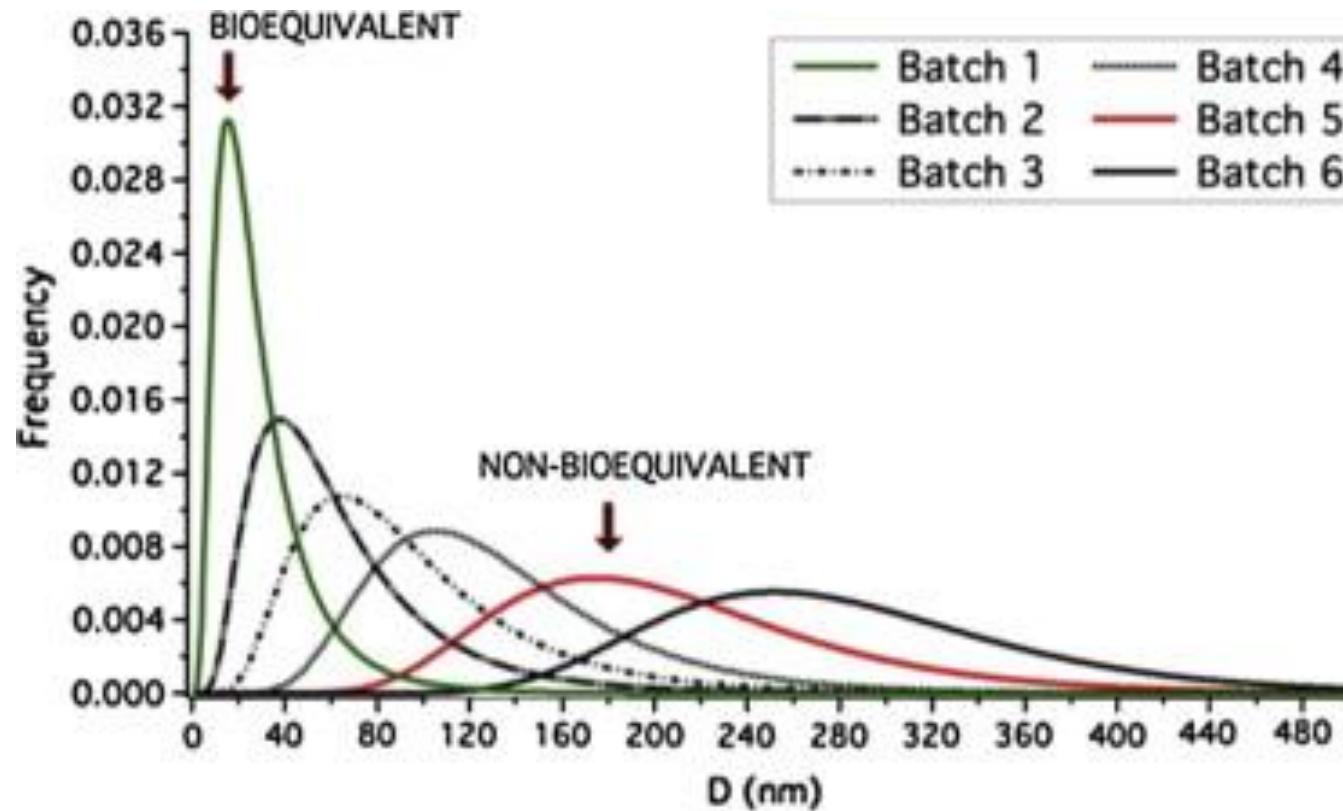
Line profile analysis - example



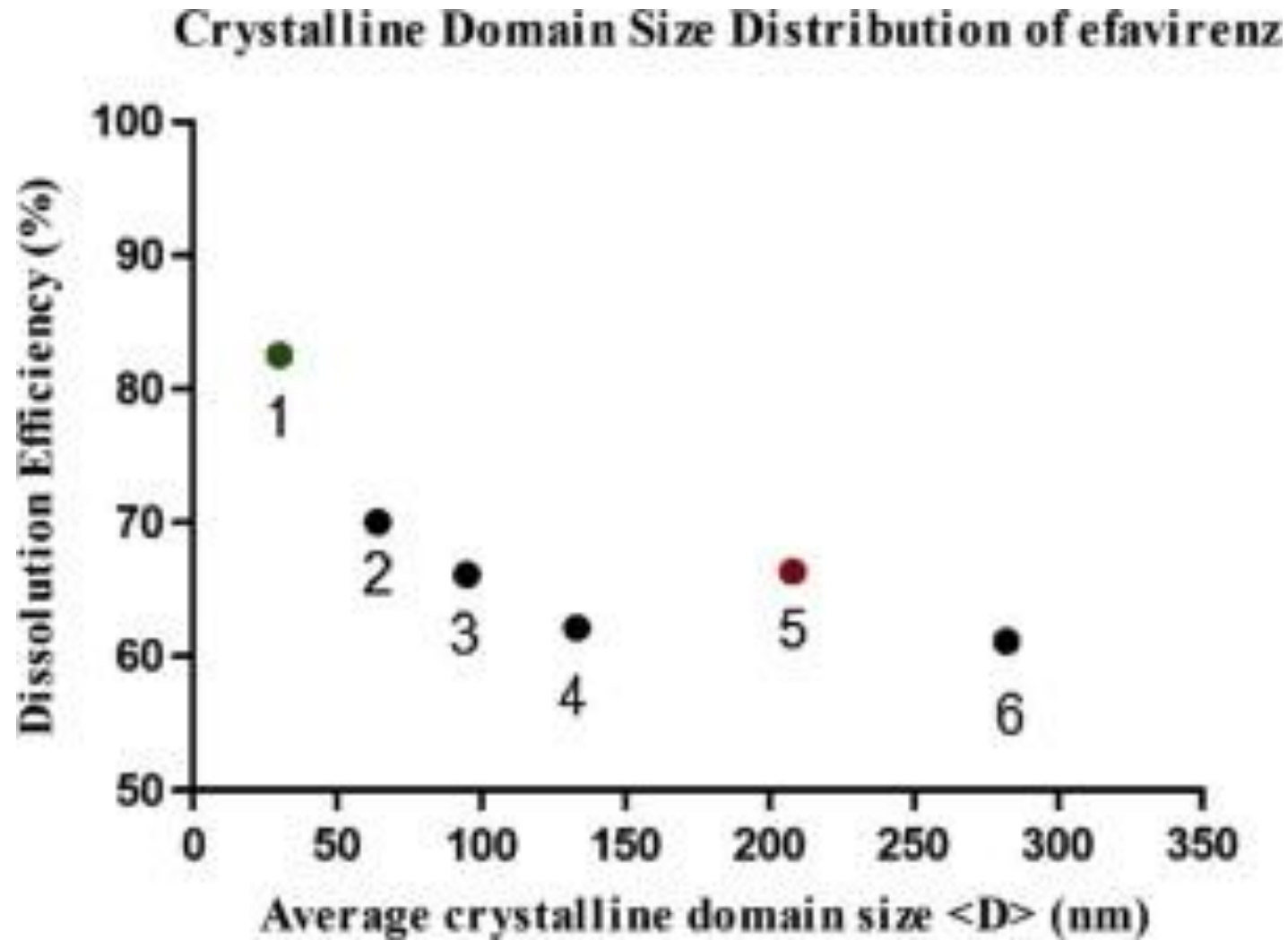
Line profile analysis - example



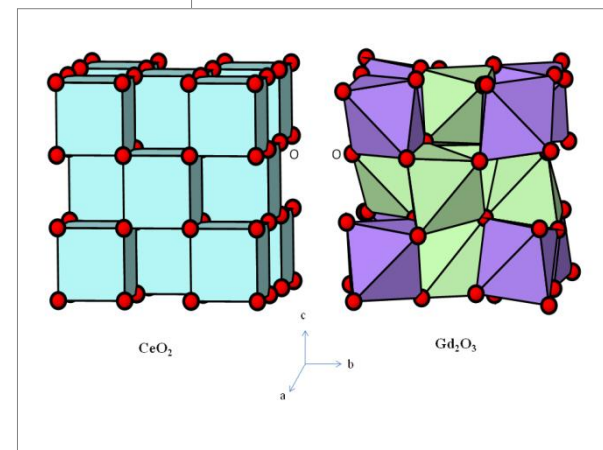
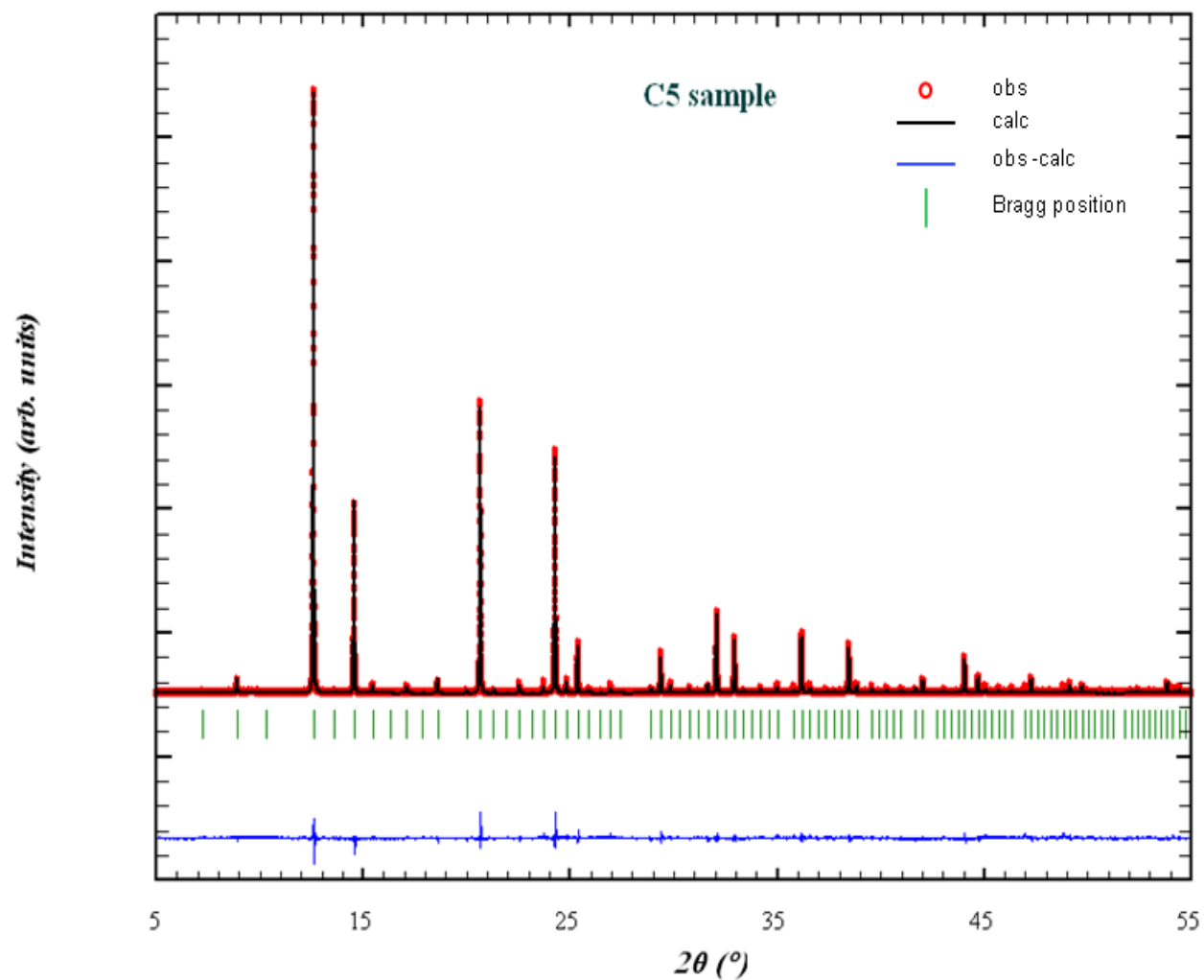
Line profile analysis - example



Line profile analysis - example

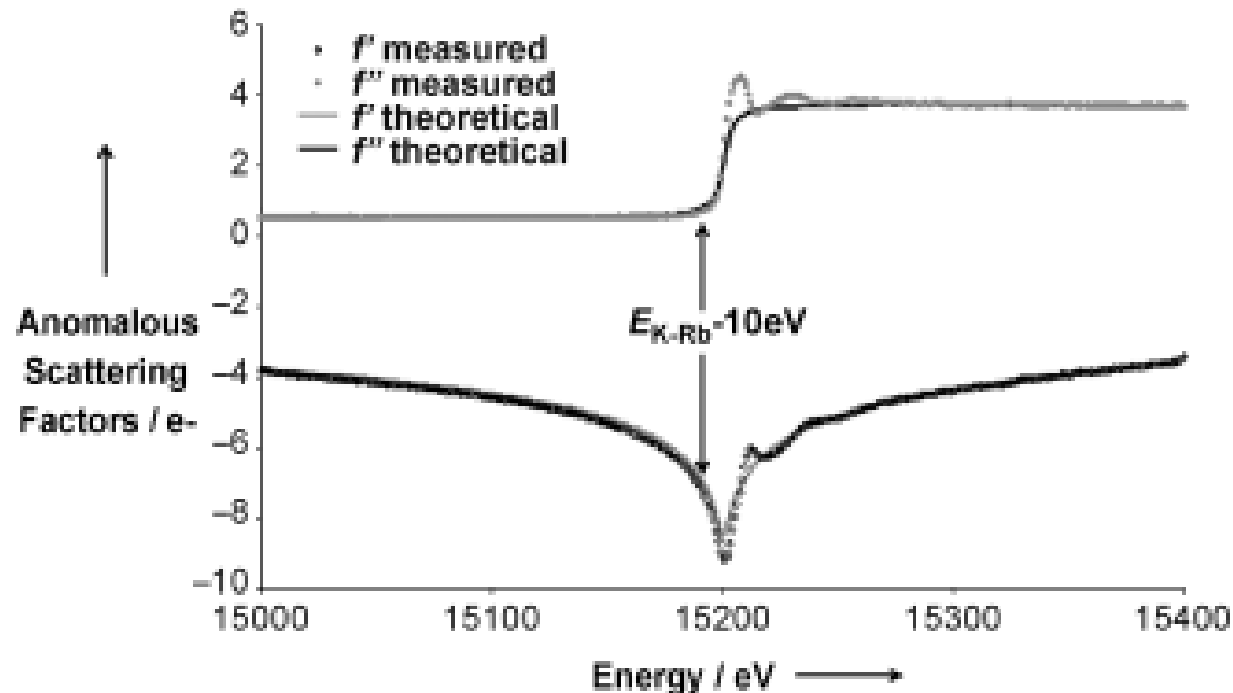


Structure determination



Structure determination - example

- Direct localization of atoms in mixed-occupancy powders by resonant contrast diffraction, M.K. Panda *et al.*, H. Palancher *et al.*, *Angew. Chem. Int. Ed.*, **44**, 1725-1729 (2005)

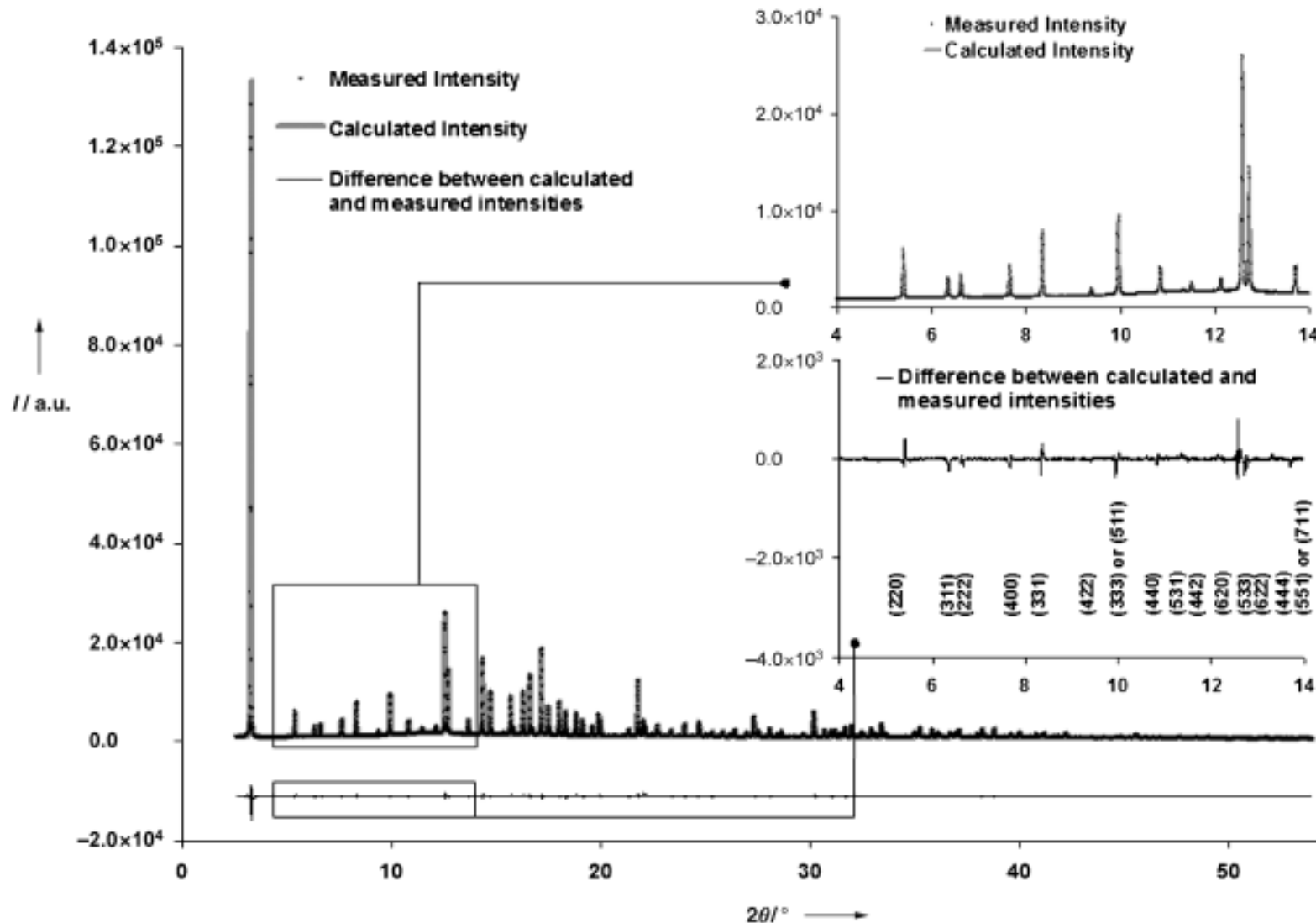


$$f = f_0 + \Delta f' + i \Delta f''$$

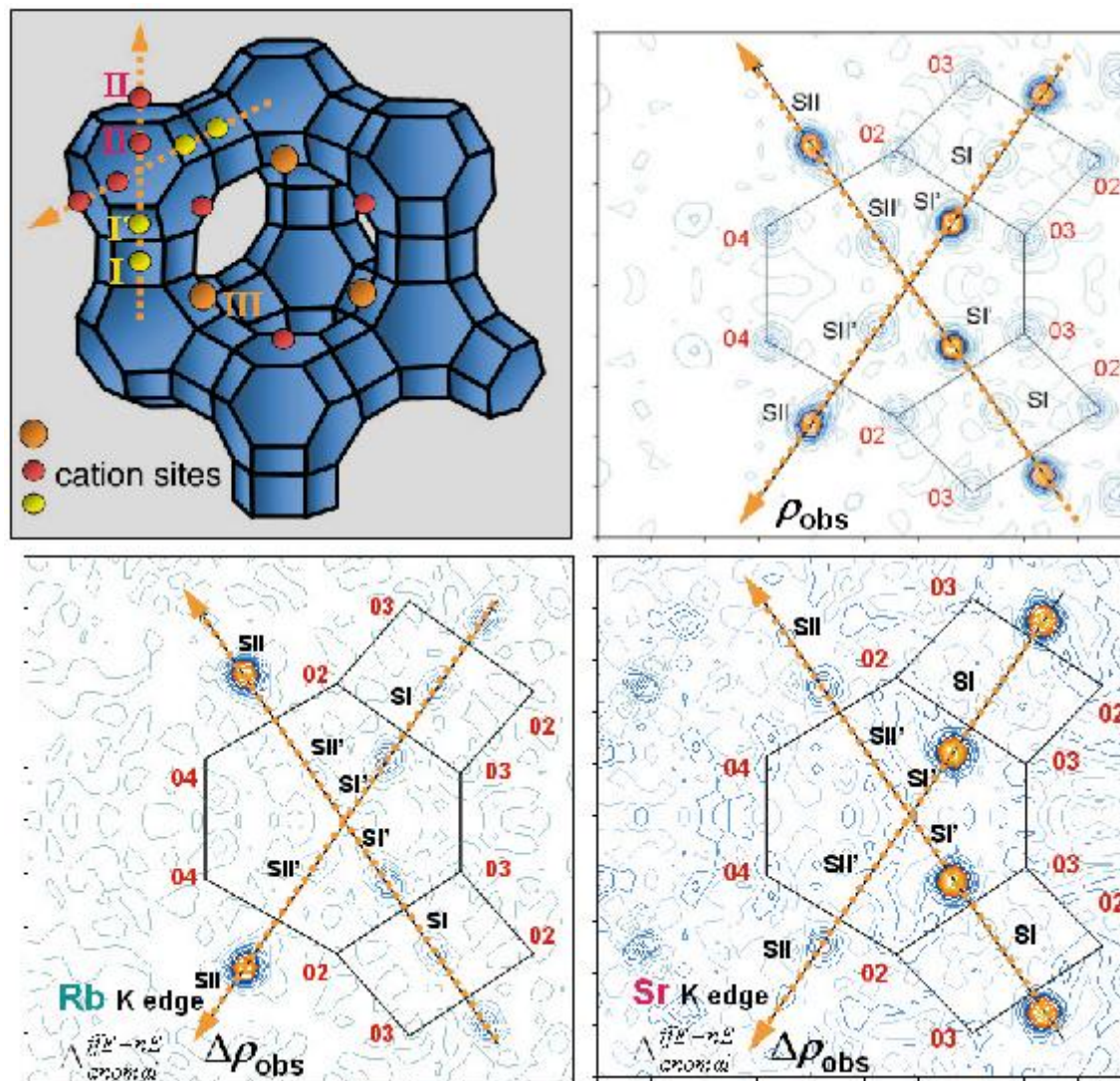
Structure determination - example

- Resonant scattering variations near an absorption edge provide chemical sensitivity and are used to extract the contribution of a single element to each crystallographic site.
- The method was demonstrated for highly-crystalline solids of industrial interest: bicationic X zeolites to determine Sr^{2+} and Rb^+ cation distributions in SrRbX
- Since Sr^{2+} and Rb^+ have the same number of electrons and similar neutron scattering lengths ($b_{\text{Sr}} = 0.702 \times 10^{-12} \text{ cm}$; $b_{\text{Rb}} = 0.709 \times 10^{-12} \text{ cm}$) this is a particularly difficult case for conventional X-ray or neutron diffraction

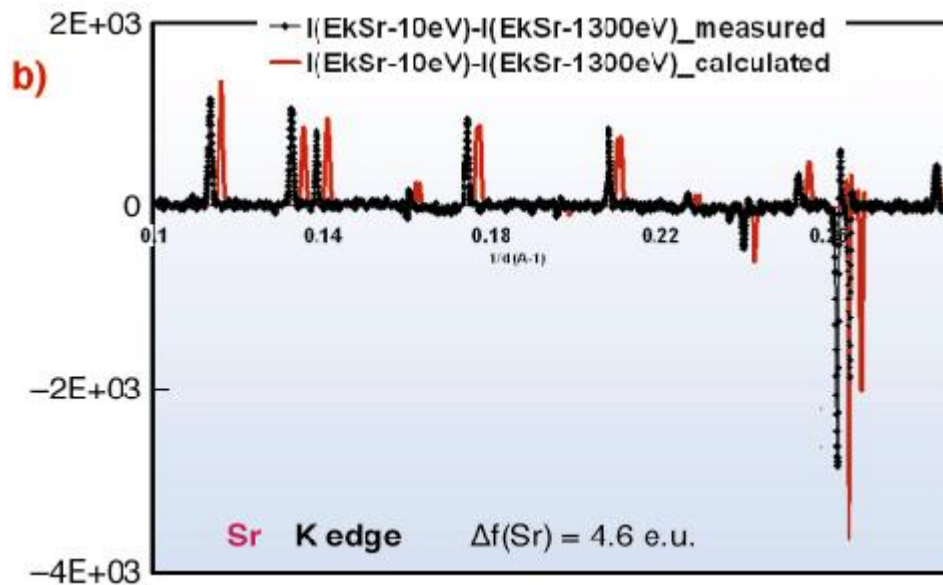
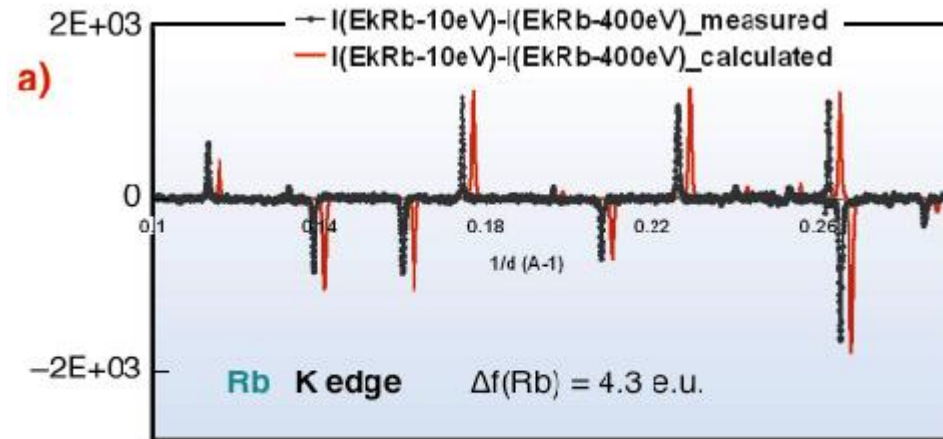
Structure determination - example



Structure determination - example



Structure determination - example



Thank you!



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