Teaching Plan

Wednesday 07.03

Lecture 1: Summary + Form Factor

Lecture 2: Structure factor

Friday 09.03

Lecture 1: Evaluation of Structure factor for SC,BCC, FCC

Lecture 2: Crystal structure determination from x-ray diffraction data

Wednesday 14.03

Lecture 1: Consolidation of new knowledge

Lecture 2: Different scattering techniques

Friday 16.03: Exercise Class

Tasks for Next week

(1) Read chapter 3: Crystal Binding (less than 20 pages)

Crystals of Inert Gases
Van der Waals-London Interaction
Repulsive Interaction
Equilibrium Lattice Constants
Cohesive Energy
Ionic Crystals
Electrostatic or Madelung Energy + Evaluation of Madelung Constant
Covalent Crystals
Metals
Atomic Radii + Ionic Crystal Radii

Start Reading chapter 4: Phonons

(2) Refresh your harmonic oscillator knowledge

(3) Solve next exercise sheet

(4) Summary + presentation:

Today’s plan

Recap of the problem

- Powder diffraction

Structure factors

- SC, BCC, FCC, Diamond structure, …

Single crystal diffraction

- Instrumentation
- Laue method

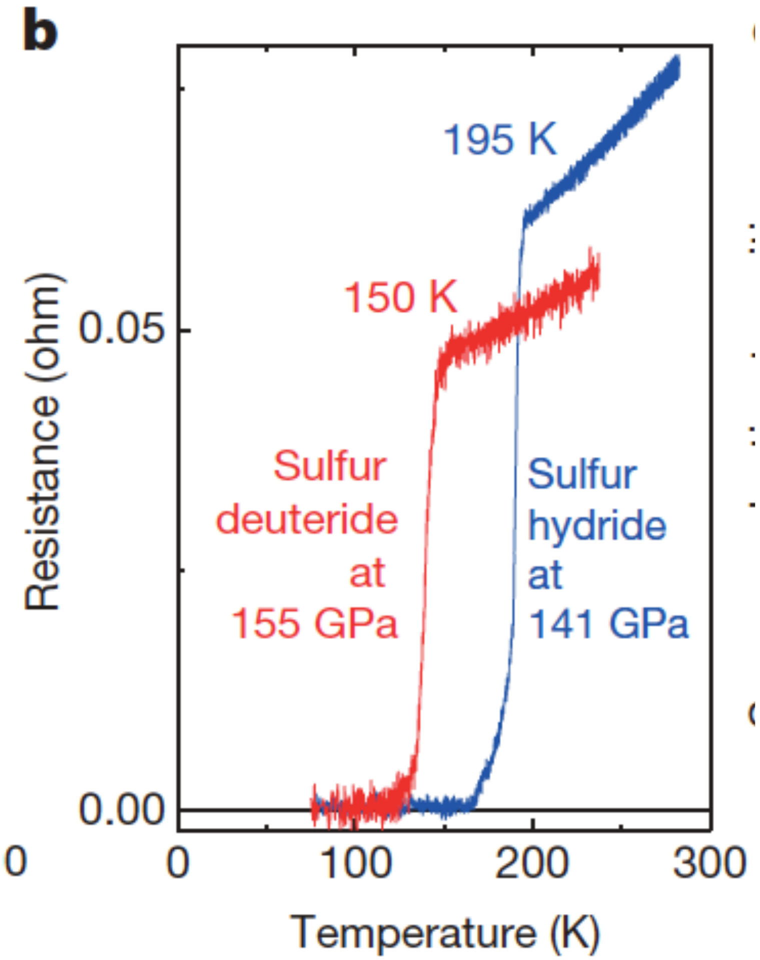
Paul Scherrer Institute

- Neutron diffraction

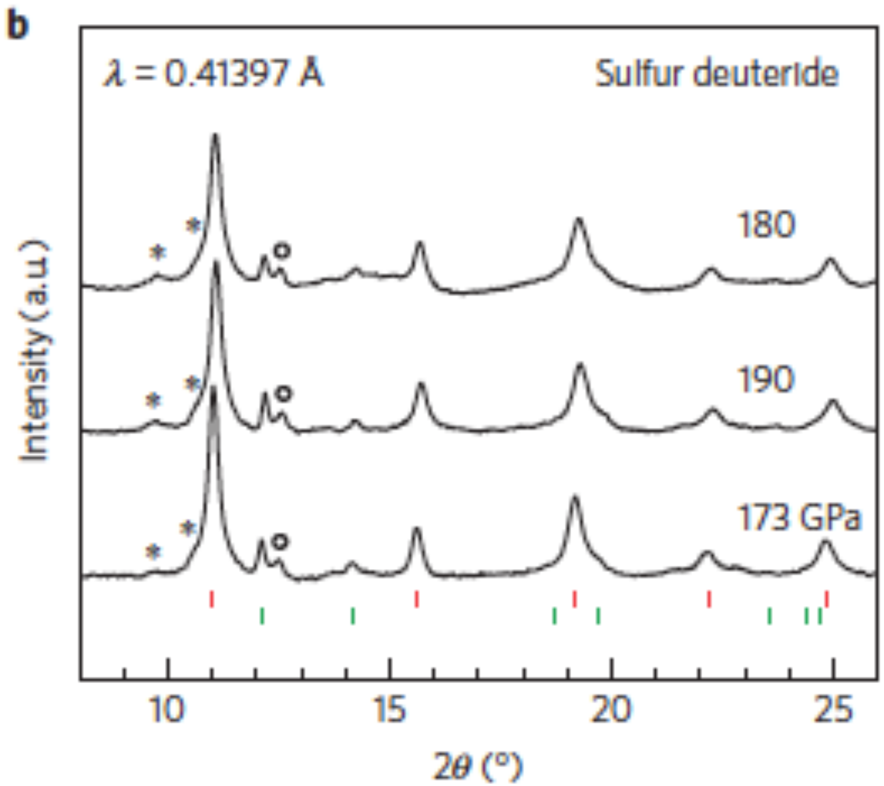
Outlook

- Protein diffraction

H_2S under pressure - A 200 K superconductor



Nature **525**, 73–76 (03 September 2015)



Nature Physics 12, 835–838 (2016)

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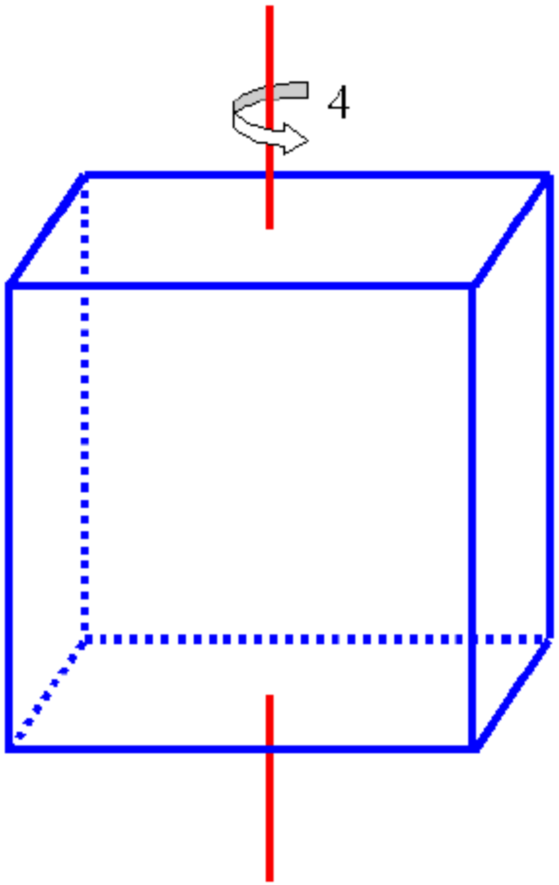
SIMPLE CUBIC

For simple cubic: one atom basis (0,0,0)

$$\mathbf{d}_1 = 0\mathbf{a}_1 + 0\mathbf{a}_2 + 0\mathbf{a}_3$$



$$S_{\mathbf{K}} = e^{i\mathbf{K}\cdot 0} = 1$$

Same result as simple monatomic basis

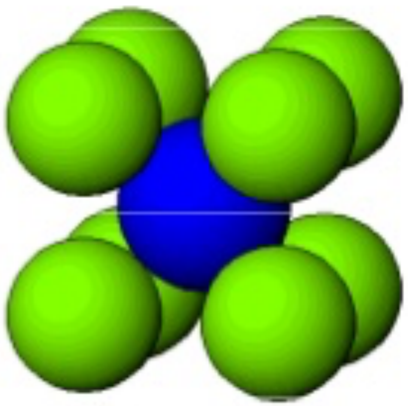
CsCl STRUCTURE

Cesium Chloride is primitive cubic

Cs (0,0,0)

Cl (1/2,1/2,1/2)

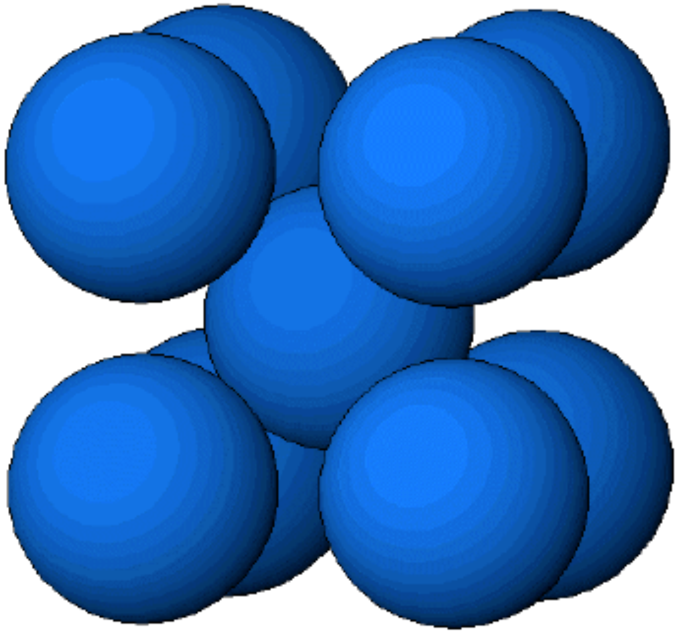
$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$



$$\Phi_{\mathbf{K}} = f_{Cs} + f_{Cl} e^{i\pi(h+k+l)}$$

MONATOMIC BCC

For monoatomic BCC:
we can think of this as SC with two point basis (0,0,0), (½,½,½)



$$S_{\mathbf{K}} = \sum_{j=1}^{2} e^{i\mathbf{K}\cdot \boldsymbol{d}_j} = e^{i\mathbf{K}\cdot 0} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{y}+\vec{z})}$$

For SC, $\mathbf{K} = \dfrac{2\pi}{a}(h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}})$

$$= 1 + e^{i\pi(h+k+l)}$$

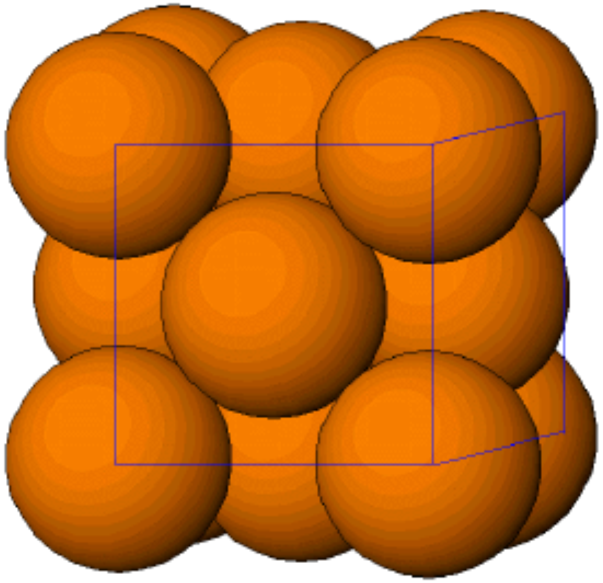
$$= 1 + (-1)^{h+k+l}$$

S = 2, when h + k + l even
S = 0, when h + k + l odd (systematic absences)

MONATOMIC FCC

For monoatomic FCC:

SC with four point basis (0,0,0), (½,½,0), (0,½,½), (½,0,½)



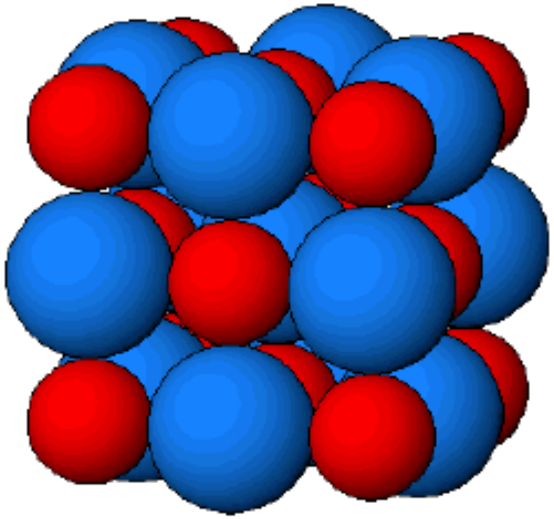
$$S_{\mathbf{K}} = \sum_{j=1}^{4} e^{i\mathbf{K}\cdot \boldsymbol{d}_j} = e^{i\mathbf{K}\cdot 0} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{y})} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{y}+\vec{z})} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{z})}$$

For SC, $\mathbf{K} = \dfrac{2\pi}{a}(h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}})$

$$S_{\mathbf{K}} = 1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)}$$

S = 4 when *h* + *k*, *k* + *l*, *h* + *l* all even (*h*, *k*, *l* <u>all even</u> or <u>all odd</u>)

S = 0 otherwise.



$$\Phi_{\mathbf{K}} = [f_{Na} + f_{Cl} e^{i\pi(h+k+l)}][S_{\mathbf{K},FCC}]$$

$$\Phi_{\mathbf{K}} = [f_{Na} + f_{Cl} e^{i\pi(h+k+l)}][1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(l+k)}]$$

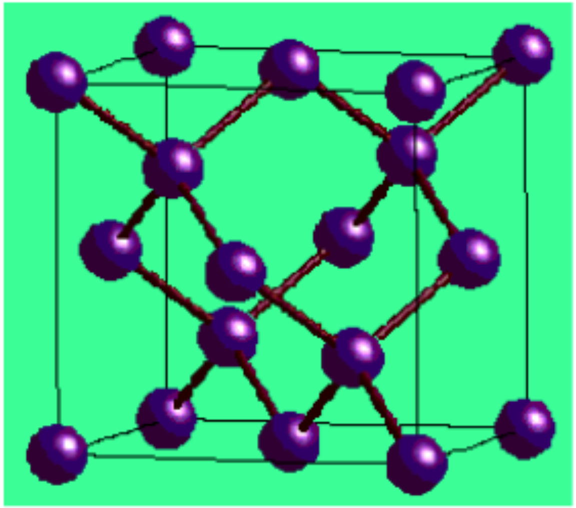
$\Phi = 4(f_{Na} + f_{Cl})$ when *h*, *k*, *l*, all even

$\Phi = 4(f_{Na} - f_{Cl})$ when *h*, *k*, *l* all odd

$\Phi = 0$ otherwise

DIAMOND STRUCTURE

Diamond: FCC lattice with two-atom basis (0,0,0,), (¼,¼,¼)



$$S_{\mathbf{K},diamond} = [e^{iK\cdot 0} + e^{iK\cdot\frac{a}{4}(\vec{x}+\vec{y}+\vec{z})}][S_{\mathbf{K},FCC}]$$

$$= [1 + e^{i(\pi/2)(h+k+l)}][S_{\mathbf{K},FCC}]$$

Only for all even or all odd *hkl* is S ≠ 0. For these unmixed values,

Additional condition:

S = 8	*h* + *k* + *l* twice an even number
S = 4(1 ± i)	*h* + *k* + *l* odd
S = 0	*h* + *k* + *l* twice an odd number

I_{FCC} : all nonvanishing spots have equal intensity.

$I_{diamond}$: spots allowed by FCC have relative intensities of 64, 32, or 0.

SUMMARY OF SYSTEMATIC ABSENCES

crystal structure	condition for peak to occur
SC	any h,k,l
BCC	$h + k + l =$ even
FCC	h,k,l all even or all odd
NaCl	h,k,l all even, or all odd if $f_A \neq f_B$
diamond	h,k,l all even and twice an even #, or all odd
HCP	any h,k,l except when $h + 2k = 3n$ and l is odd

$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

Cubic $$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal $$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic $$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal $$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Monoclinic $$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

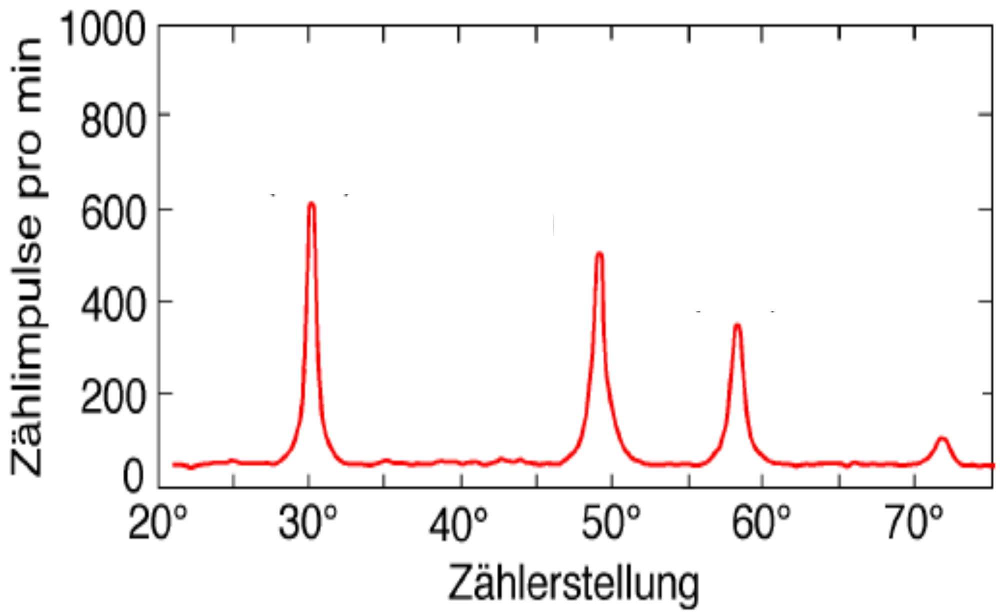
Triclinic $$\frac{1}{d^2} = \frac{1}{V^2}[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta$$

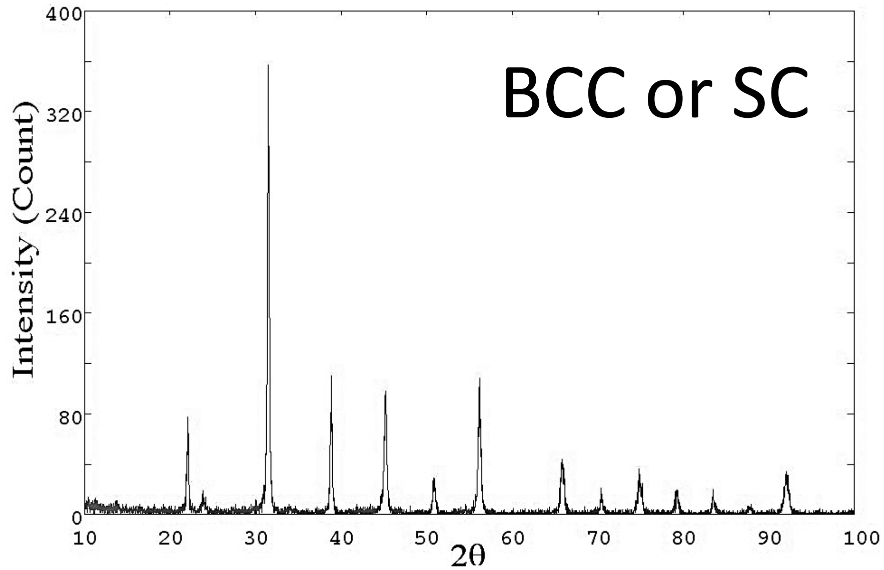
$$+ l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma)$$

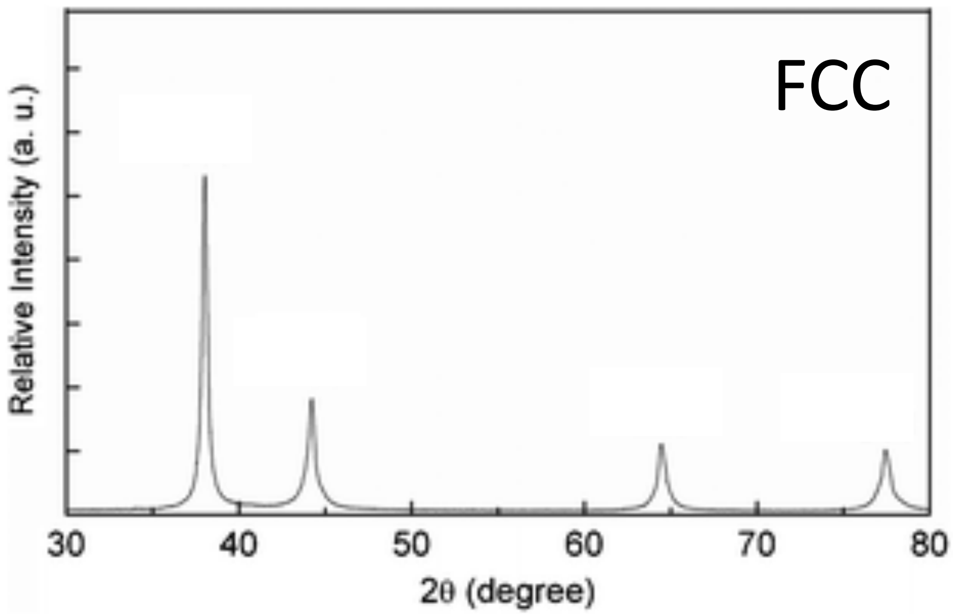
$$+ 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha)$$

$$+ 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)]$$

Quiz: What crystal structure?







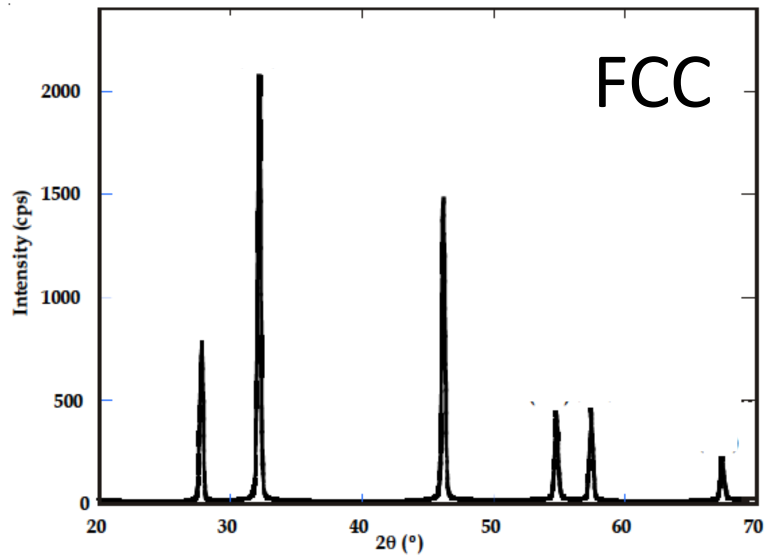
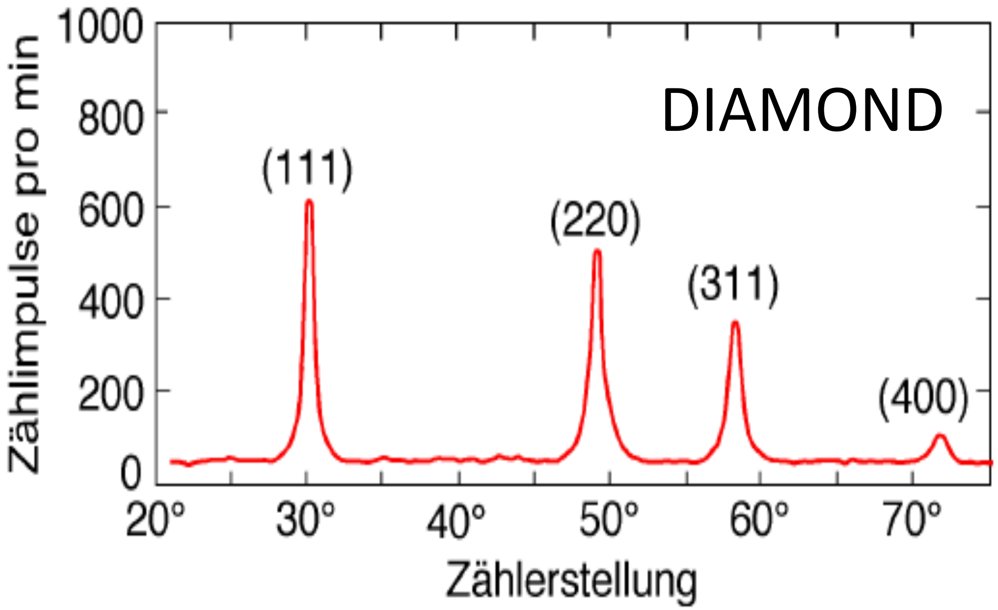
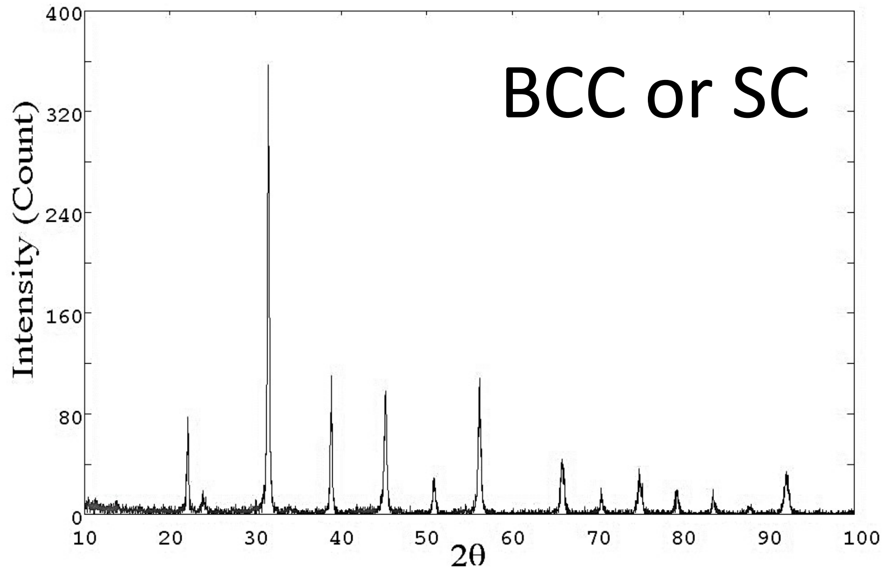
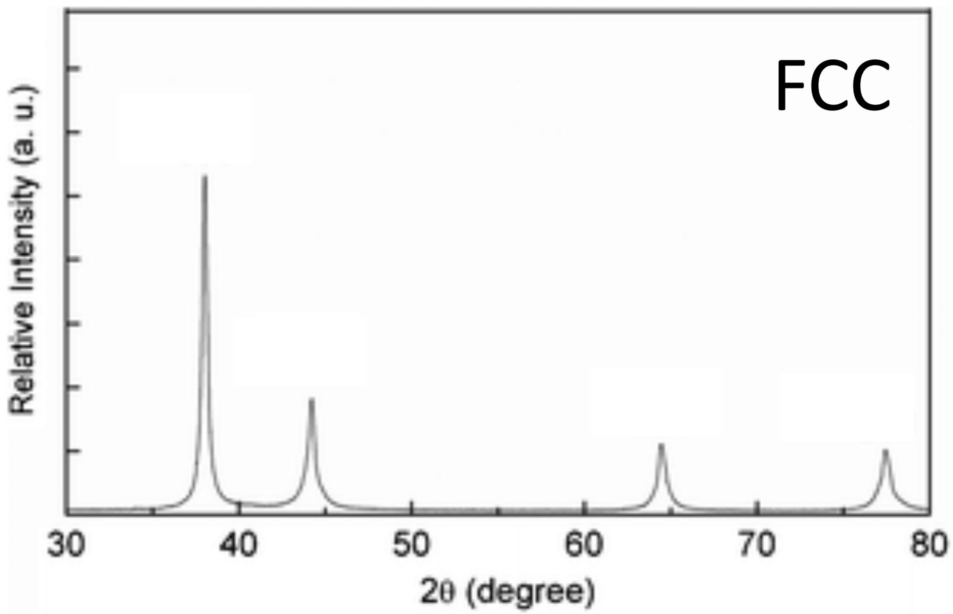


Fig. 9. X-Ray diffraction pattern of silver chloride nanoparticles

Quiz: What crystal structure?







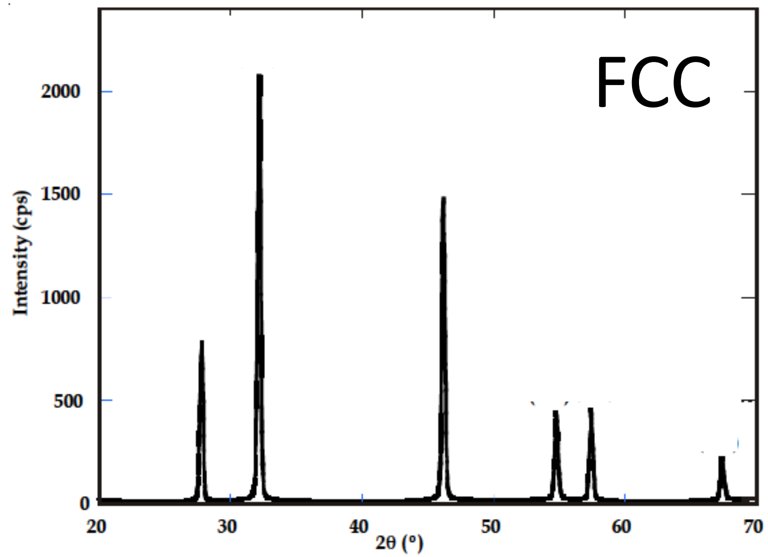


Fig. 9. X-Ray diffraction pattern of silver chloride nanoparticles

Exercise 2 *Debye-Scherrer method*

Powder specimens of three different monoatomic cubic crystals are analysed with a Debye-Scherrer camera. It is known that one sample is face-centred cubic, one is body-centred cubic, and one has the diamond structure. The approximate positions of the first four diffraction rings in each case are given in table 1. The meaning of the angle ϕ is shown in figure 1. Pay attention to the definition of the angle in Bragg's law and the definition of the angle in the figure.

A	B	C
42.2°	28.8°	42.8°
49.2°	41.0°	73.2°
72.0°	50.8°	89.0°
87.3°	59.6°	115.0°

Table 1: The angles ϕ of the diffraction rings in samples A, B, and C.

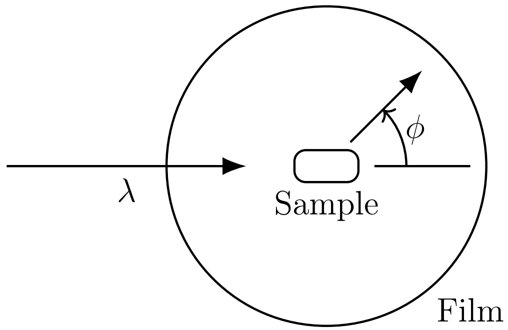
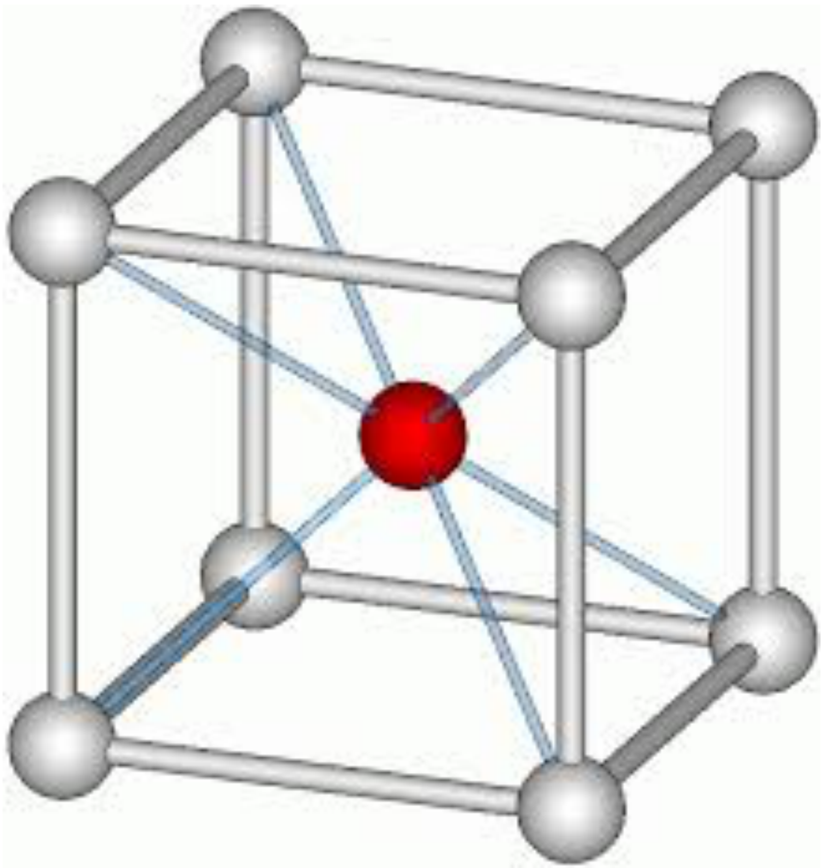


Figure 1: The working principle of a Debye-Scherrer camera.

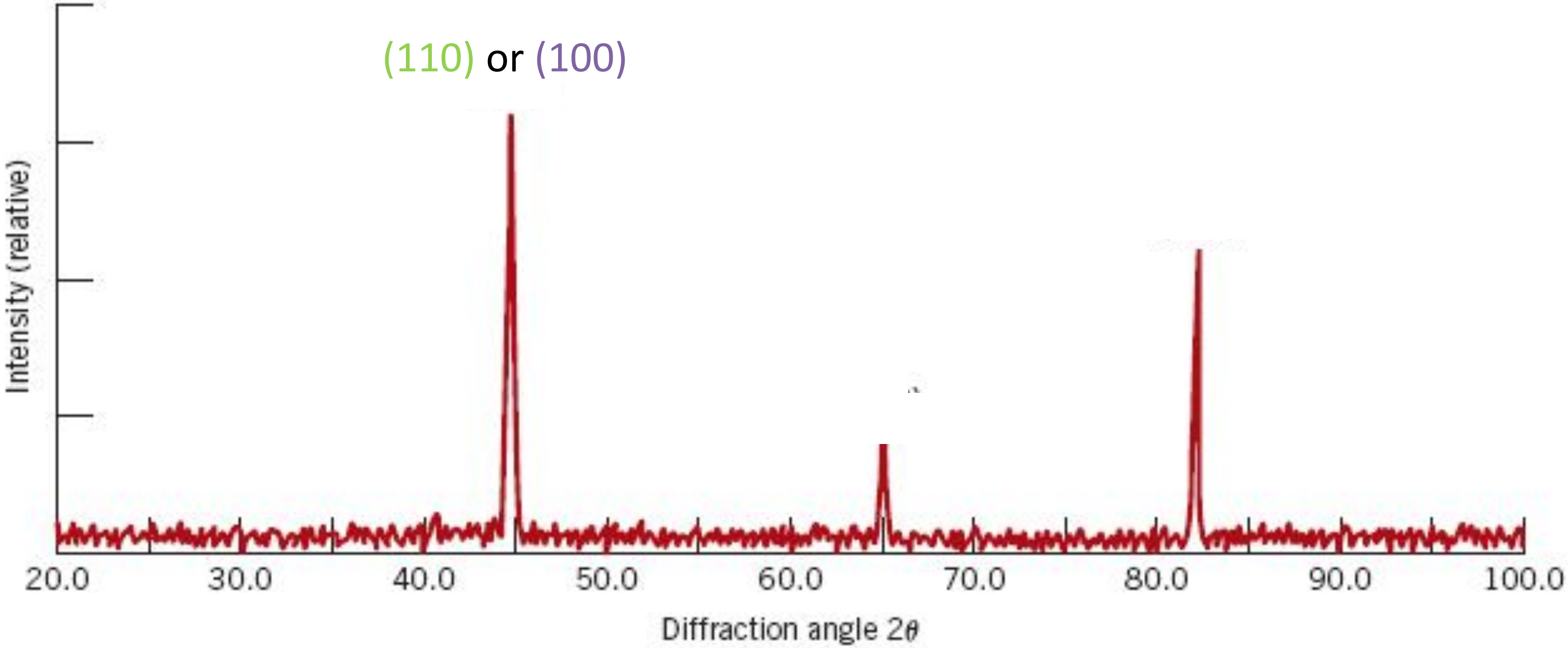
a) Identify the crystal structure of A, B, and C.
b) If the wavelength of the incident X-ray beam is 1.5 Å, what is the length of the side of the conventional cubic cell in each case?
c) If the diamond structure were replaced by a zincblende structure with a cubic unit cell of the same side, at what angles would the first four rings now occur?

BCC or SC?

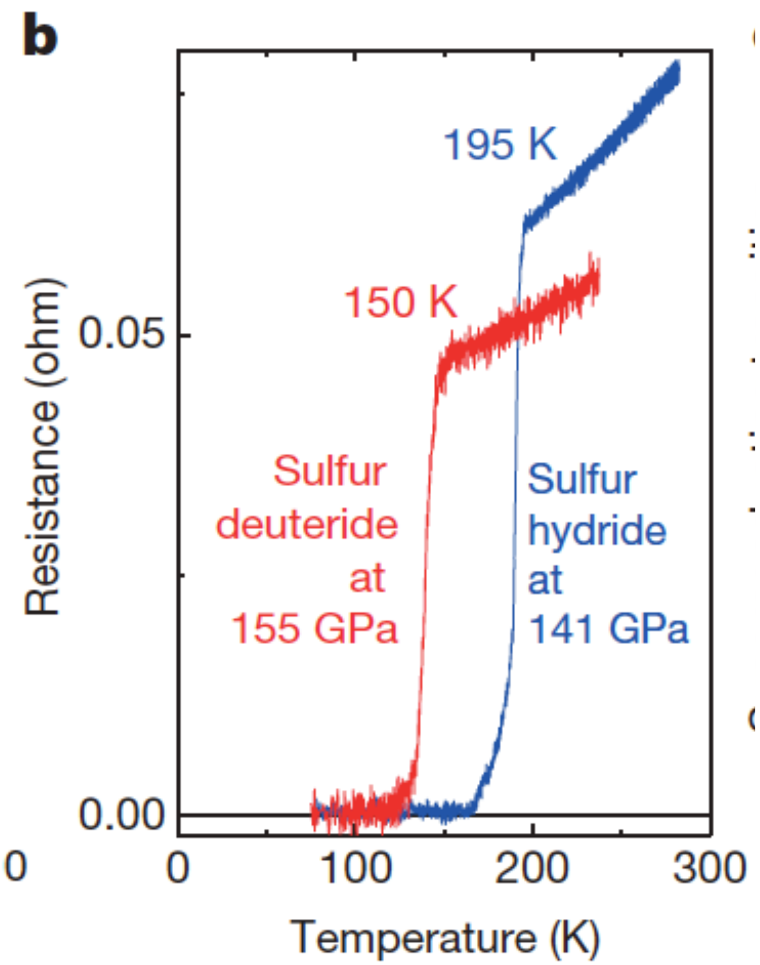


BCC or SC?

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

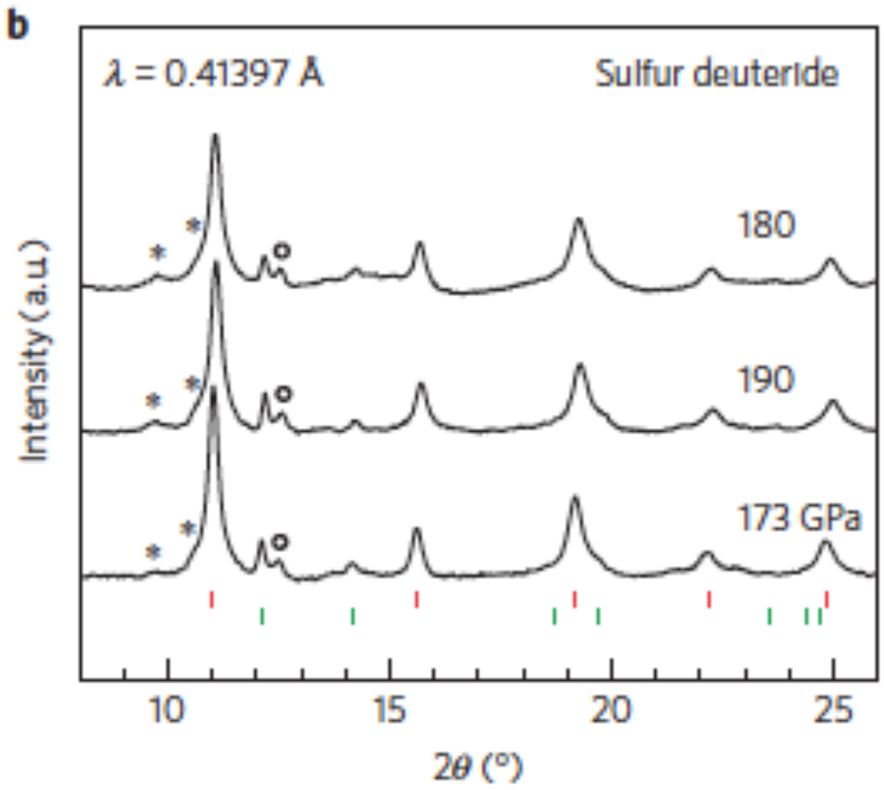


H_2S under pressure - A 200 K superconductor



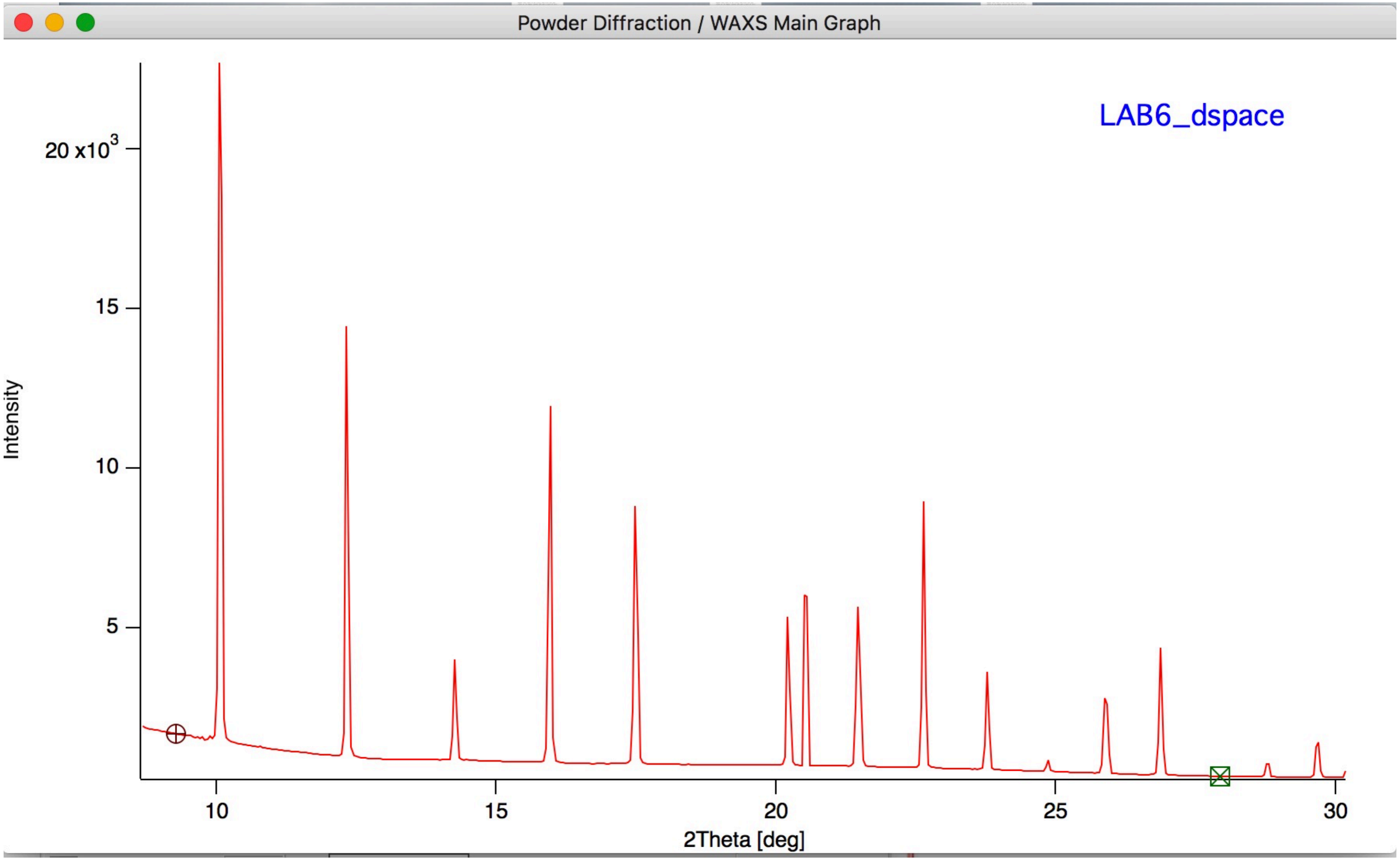
Nature **525**, 73–76 (03 September 2015)

They concluded BCC

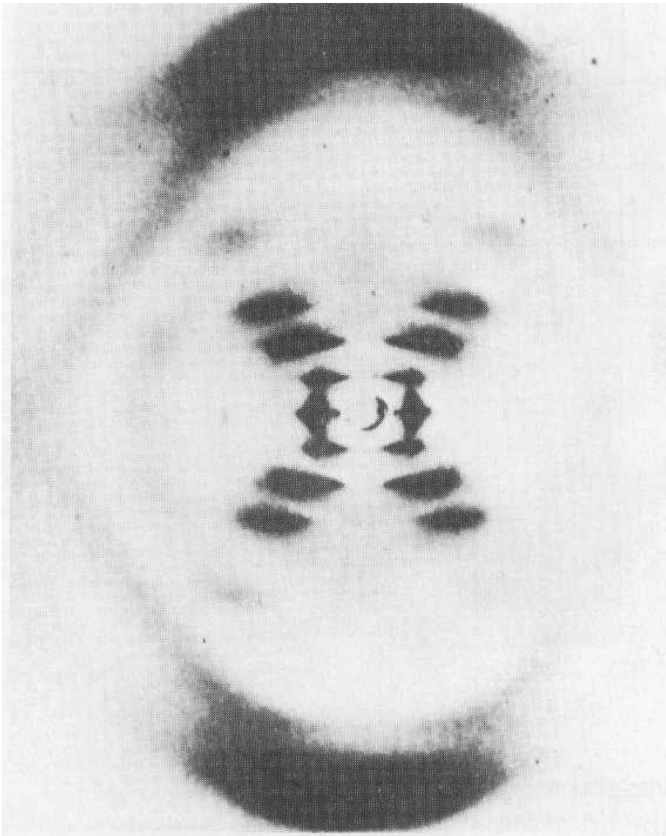


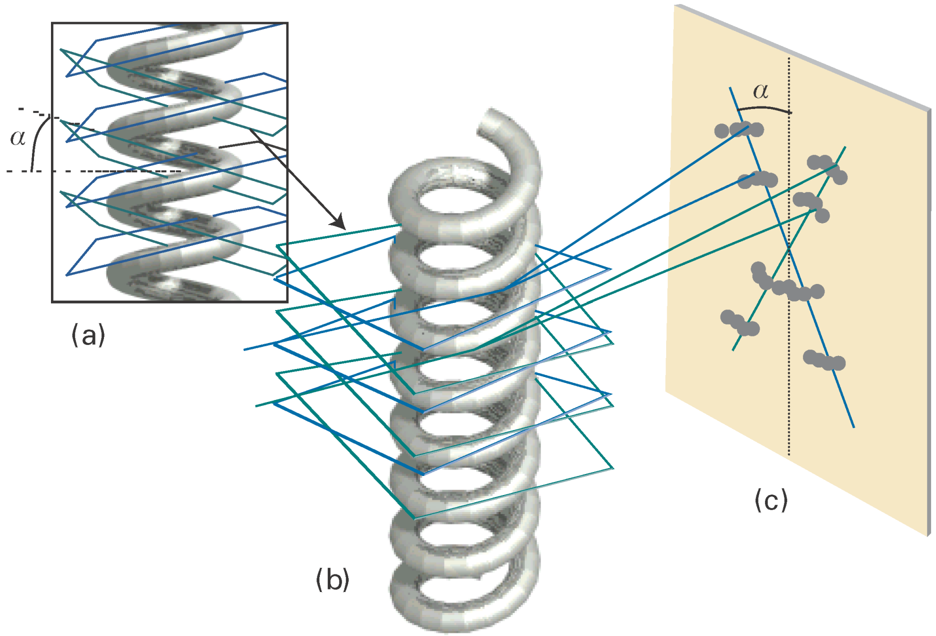
Nature Physics 12, 835–838 (2016)

Measure as many peaks as possible



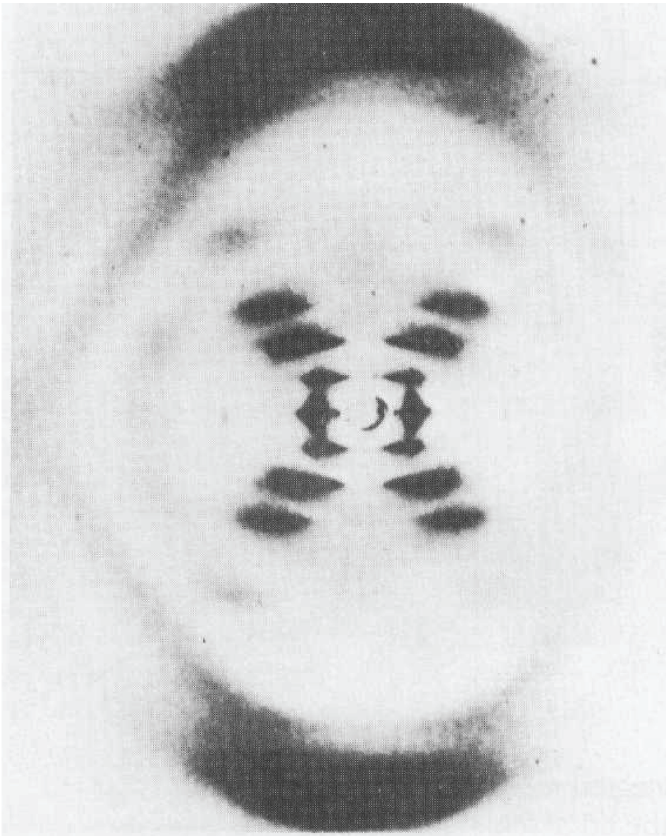
DNA structure: X-ray diffraction

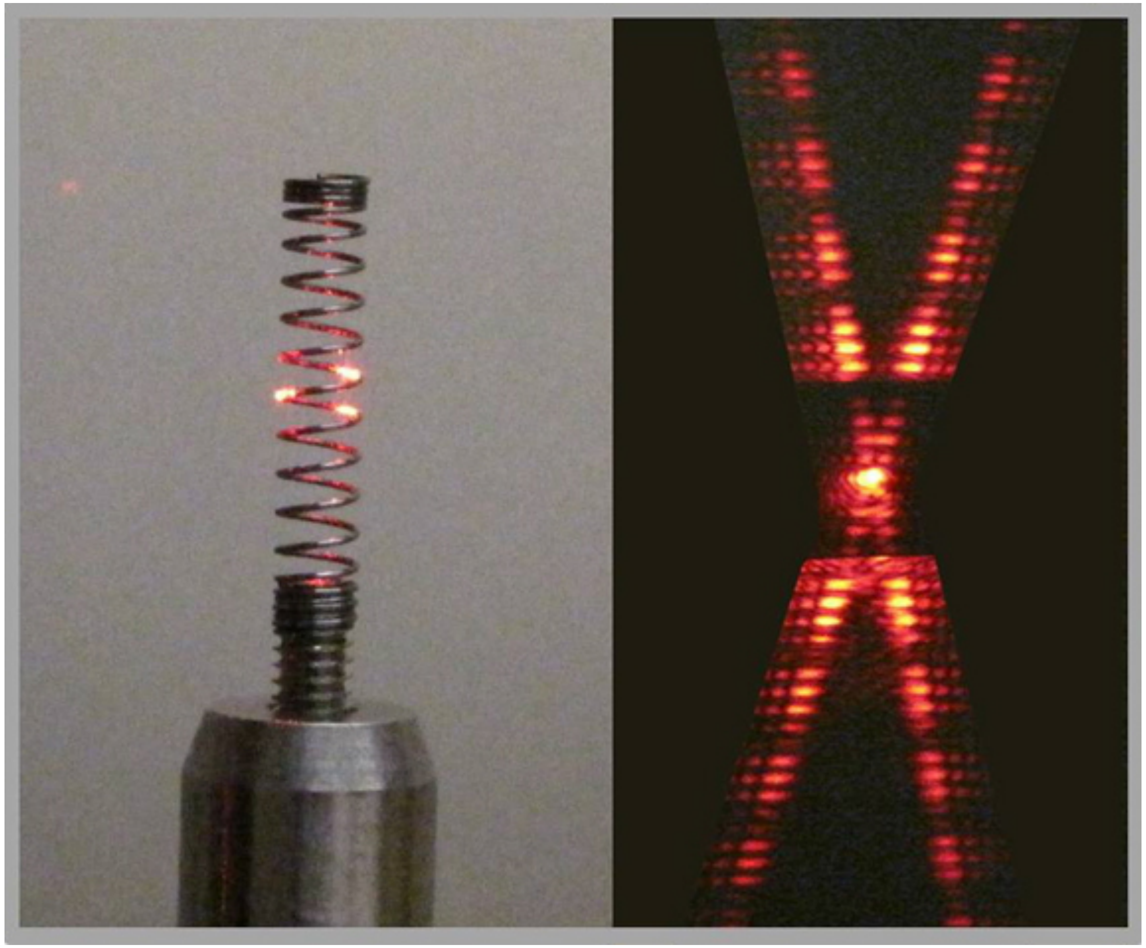




The Nobel Prize in Physiology or Medicine 1962 was awarded jointly to Francis Harry Compton Crick, James Dewey Watson and Maurice Hugh Frederick Wilkins *"for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material"*.

DNA structure: X-ray diffraction





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Paul Scherrer Institute
- Neutron diffraction

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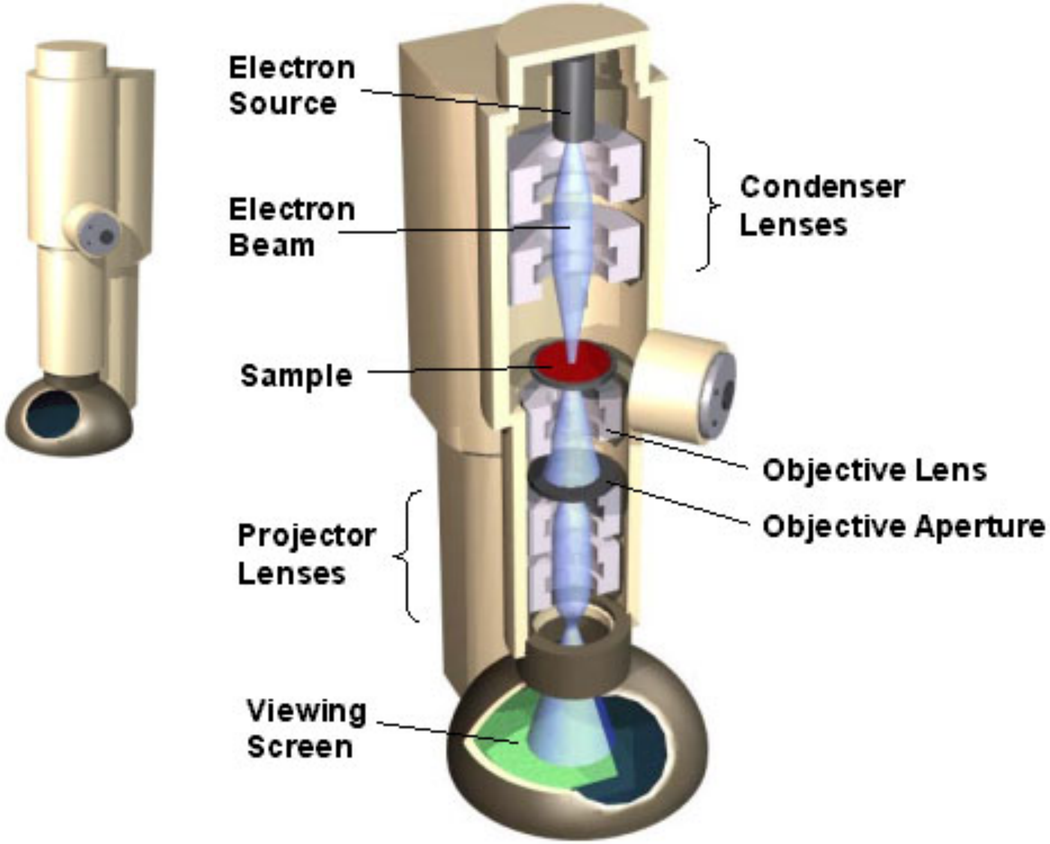
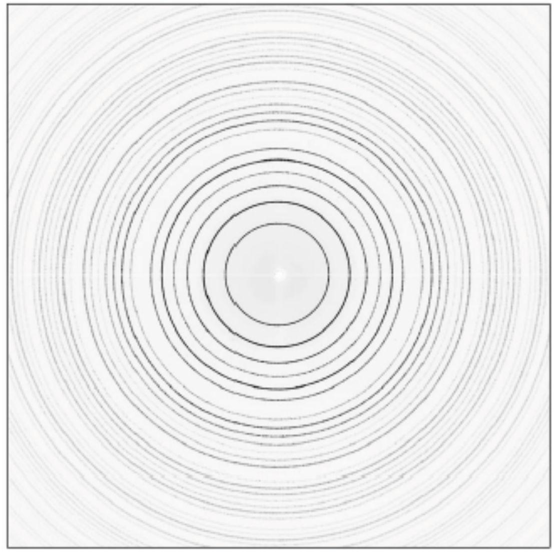
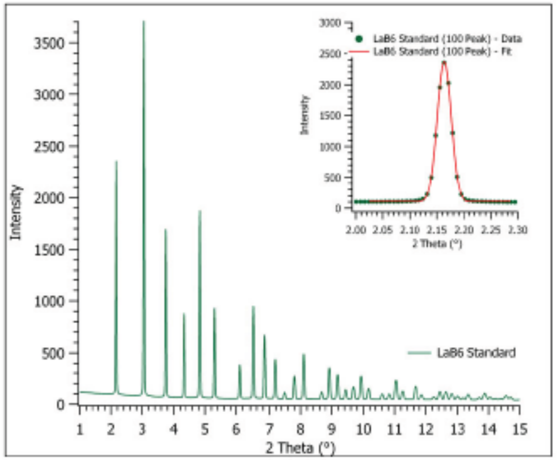
Single crystal diffraction

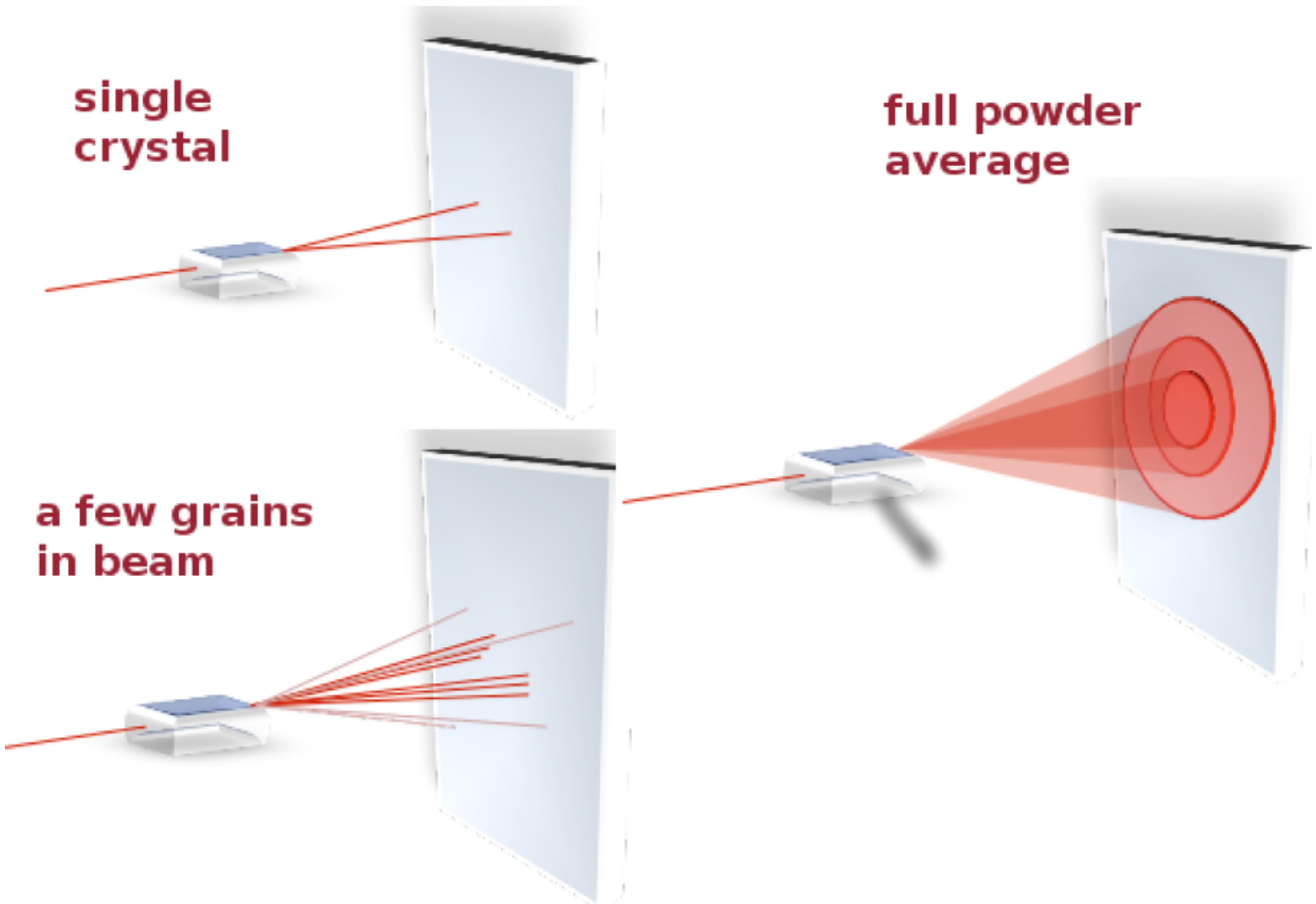






http://www.diamond.ac.uk/Beamlines/Engineering-and-Environment/I12/applications/diffraction.html

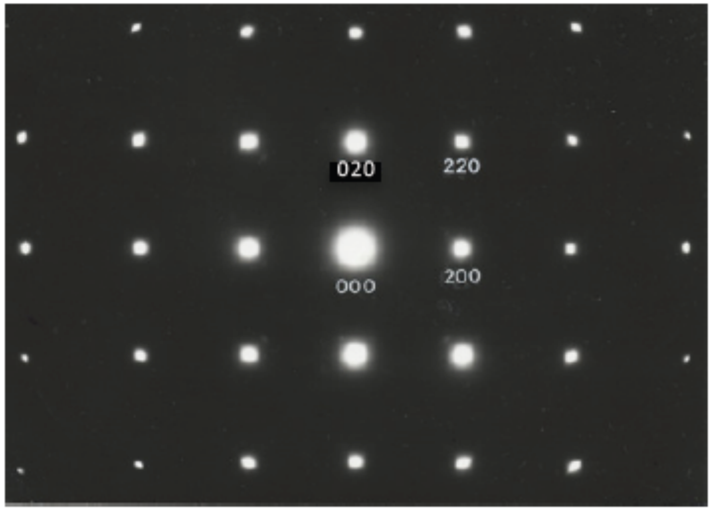
Single crystals, poly-crystals, powder



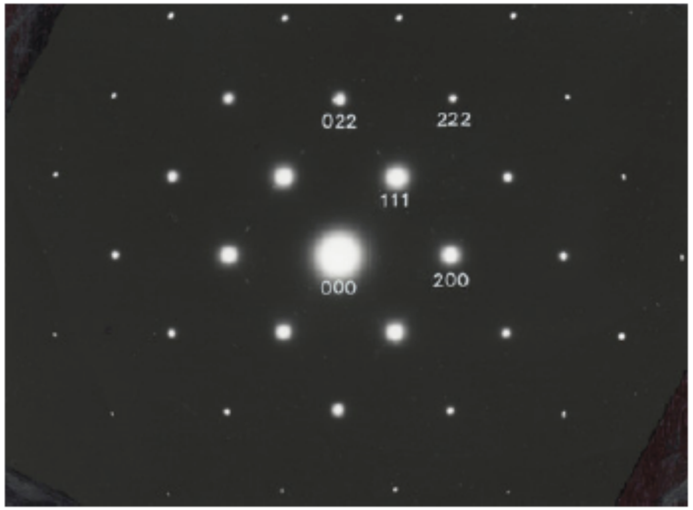
Single crystal diffraction

TEM diffraction patterns of a gold-film

Gold film



Scattering plan: (100) & (010)



Scattering plan: (100) & (011)

(a) and (b) are [001] and [110] incidence of the electron beam.

http://www.k5.dion.ne.jp/~inos1936/shozoHP1E.html

Single crystal diffraction

TEM diffraction patterns of a gold-film

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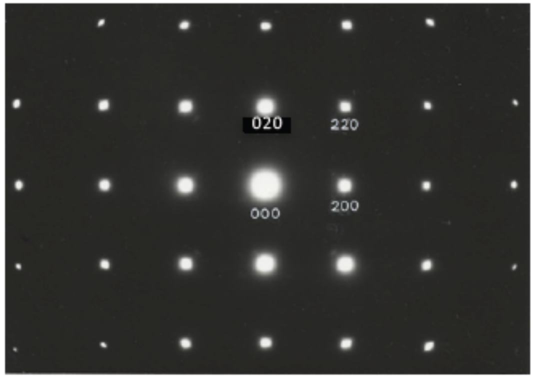

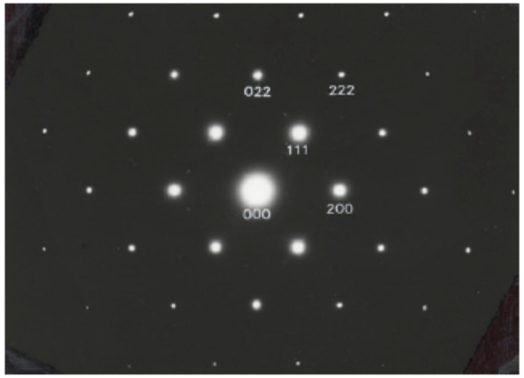

Scattering plan: (100) & (010)   Scattering plan: (100) & (011)

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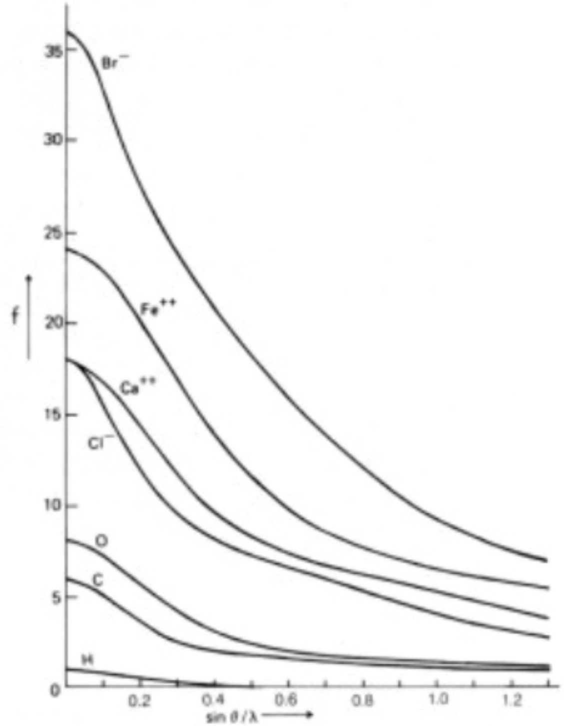
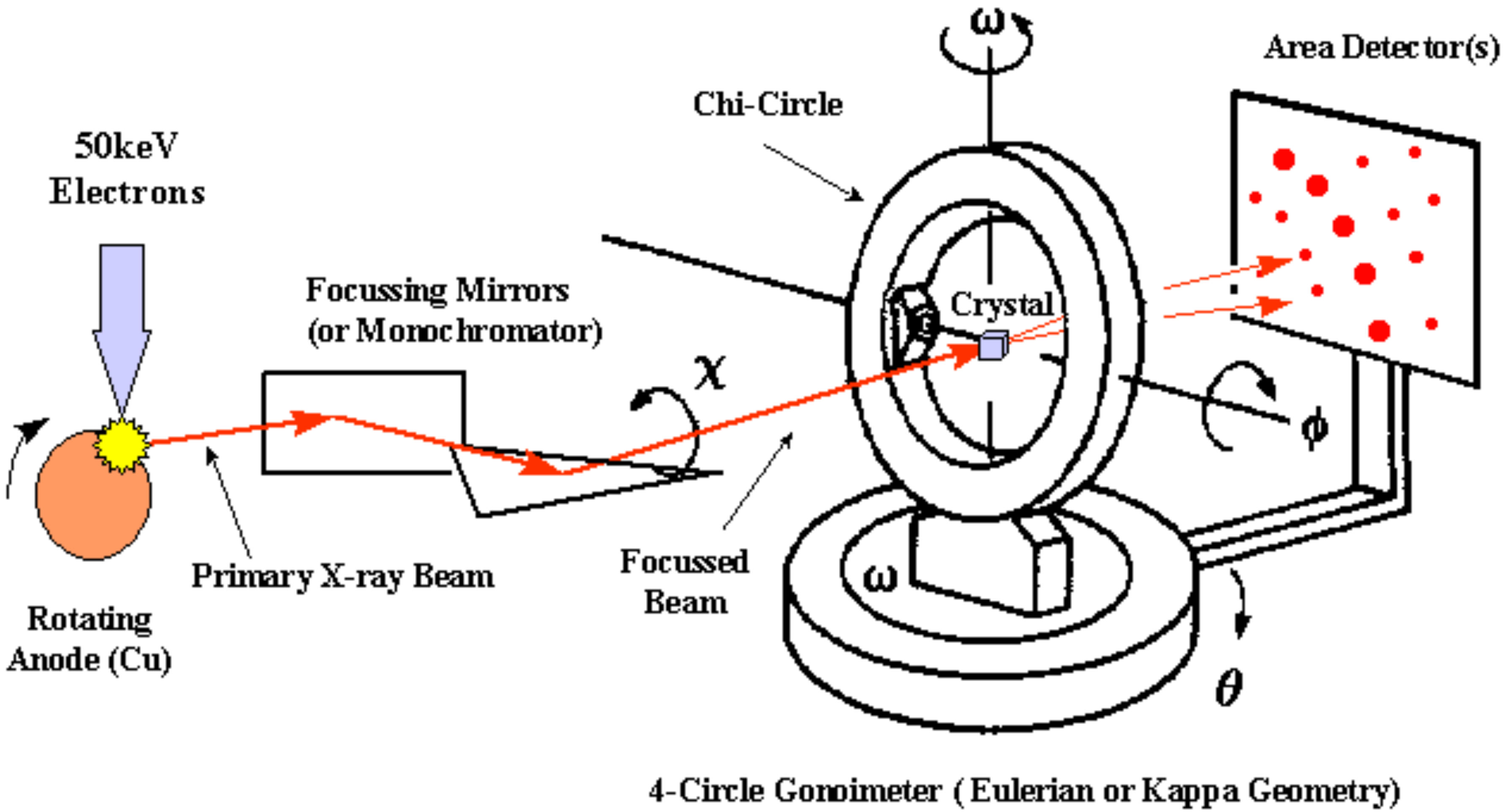
FORM FACTOR



http://www.xtal.iqfr.csic.es/
Cristalografia/parte_05-en.html

Single crystal diffraction: x- rays

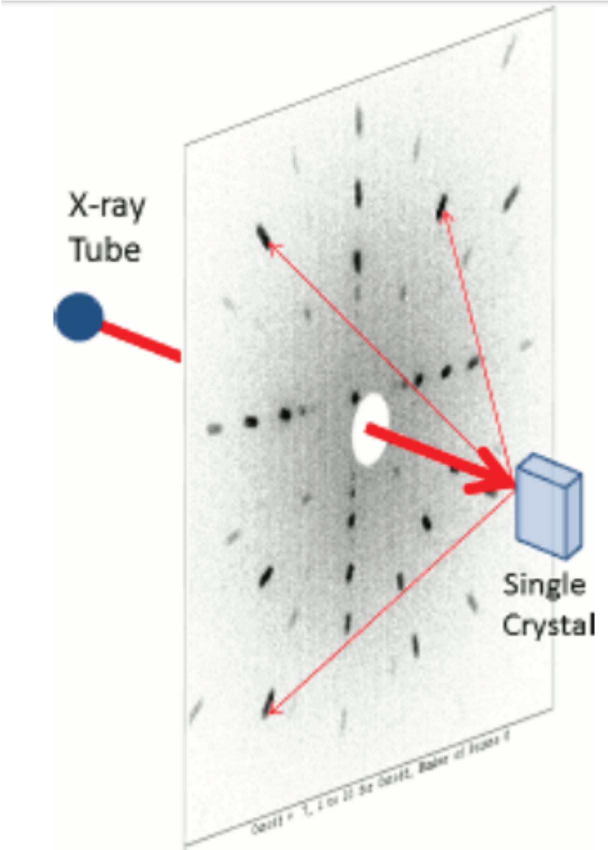


Single crystal diffraction: x- rays

https://www.dectris.com/products/specific-solutions/diffraction

Dectris prize for best physics master thesis

LAUE



http://multiwire.com/index.shtml

Exercise 1 *Laue method*

Estimate the maximal possible number of interference maxima of a Laue recording. Assume that the voltage of the X-ray tube is 60 kV and the crystal is simple cubic with a lattice constant of 0.2 nm. The X-ray tube produces a continuous spectrum of Bremsstrahlung.

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Paul Scherrer Institute
- Neutron diffraction

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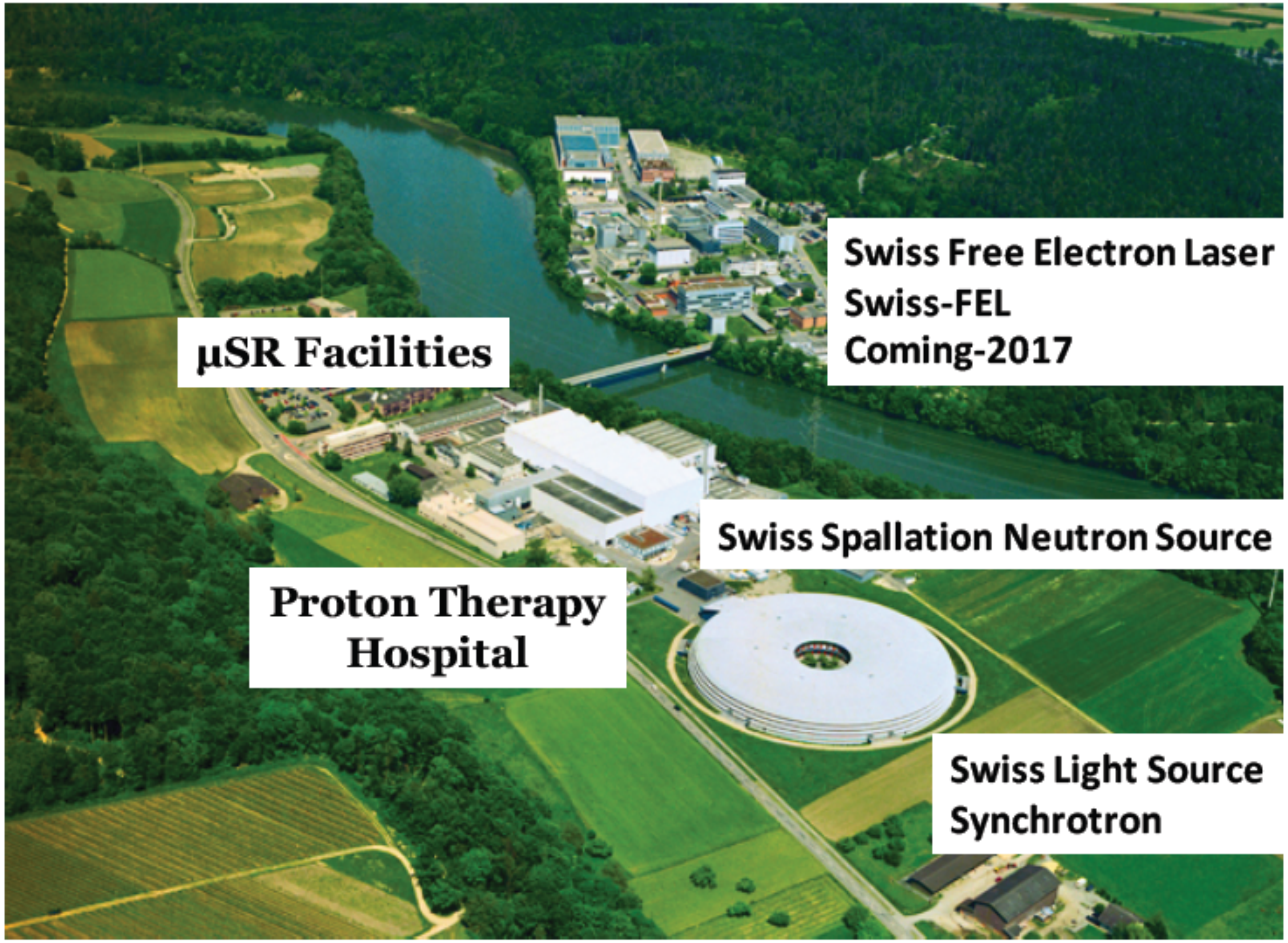
Paul Scherrer Institute

https://www.psi.ch

Paul Scherrer Institute



https://www.psi.ch

Powder diffractometer

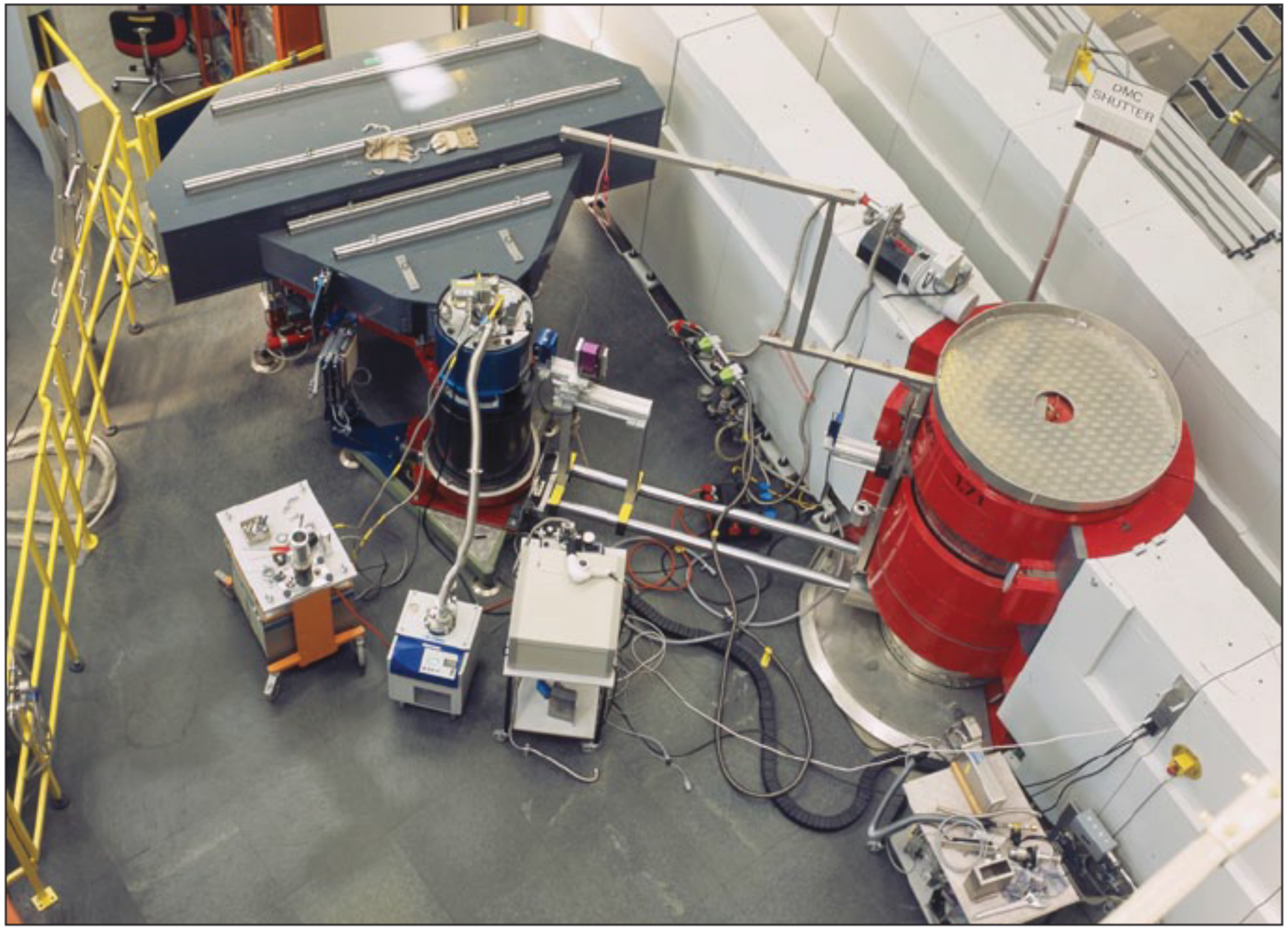
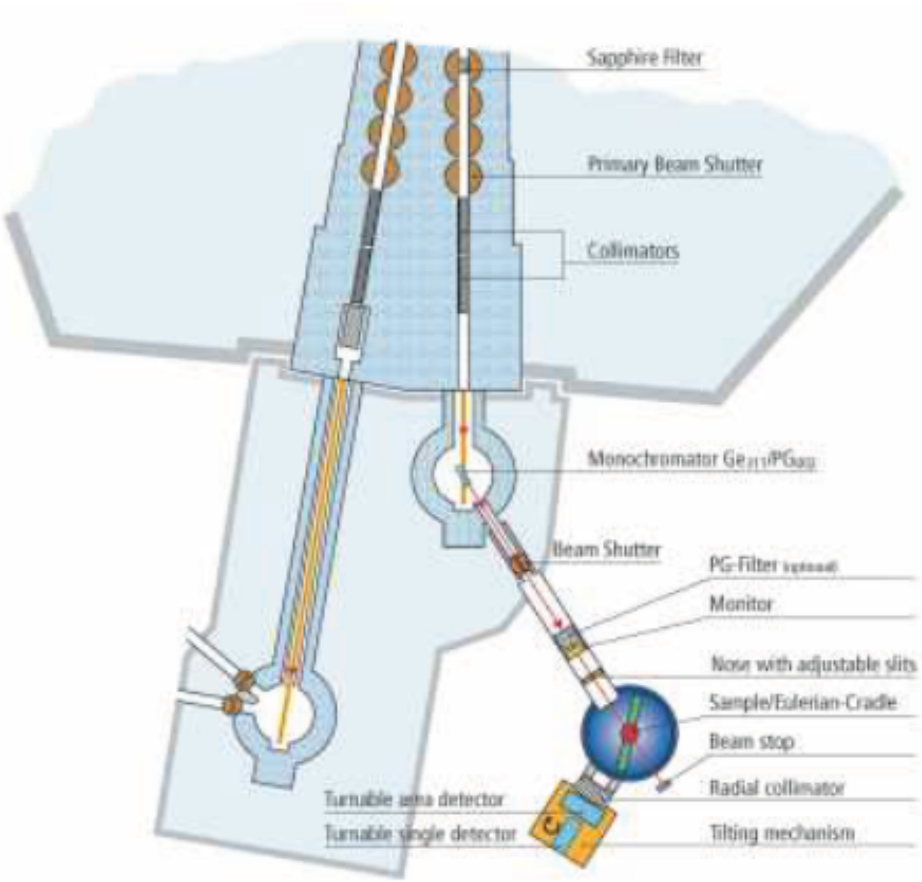
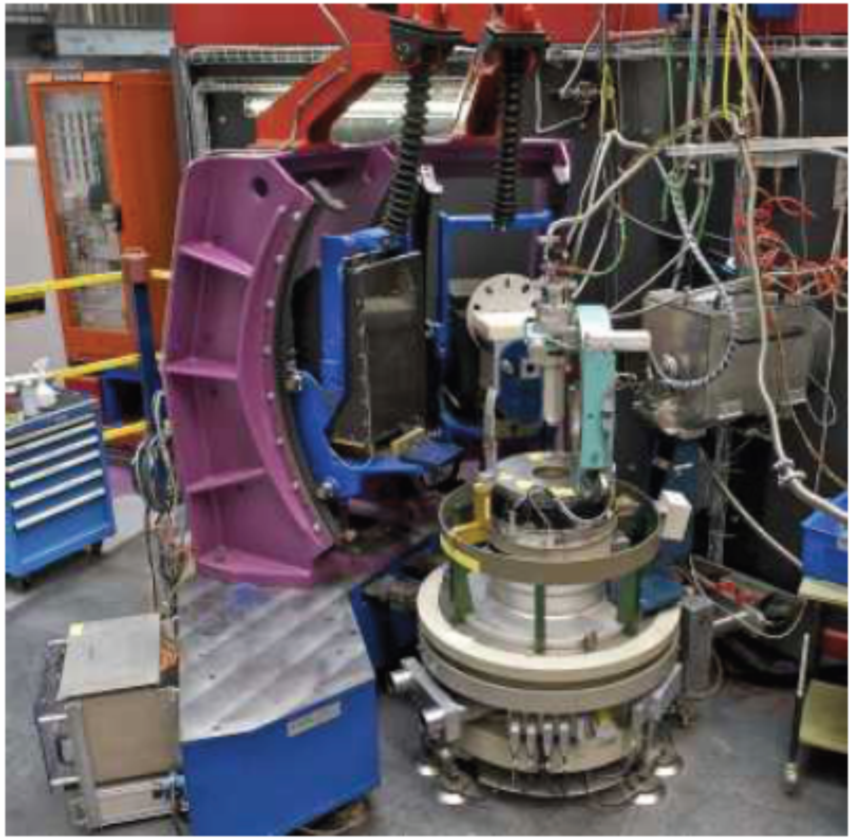


Figure 3: **The DMC powder diffractometer is also appropriate for the investigation of magnetic phenomena.**

Single crystal diffractometer





European infra-structure

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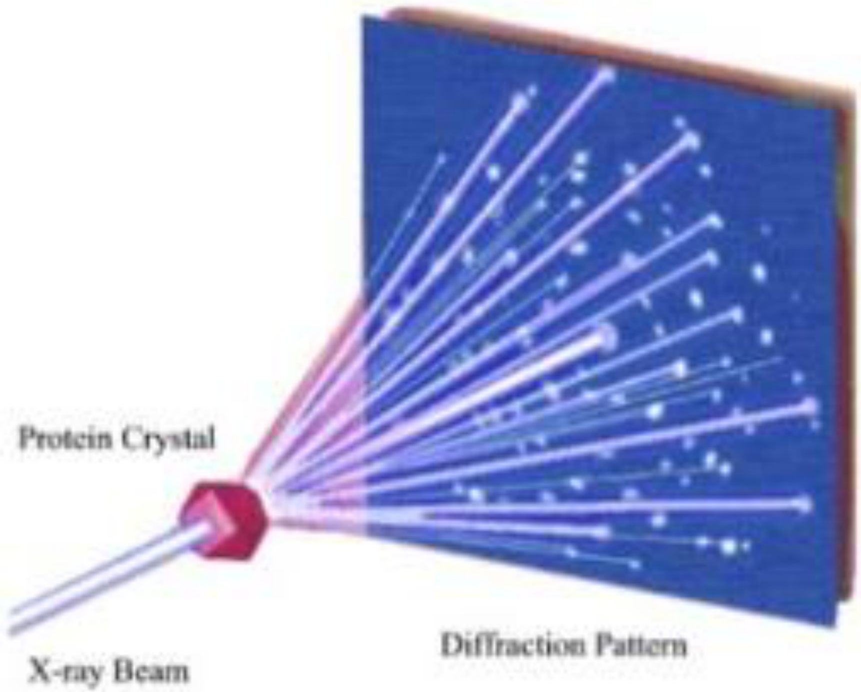
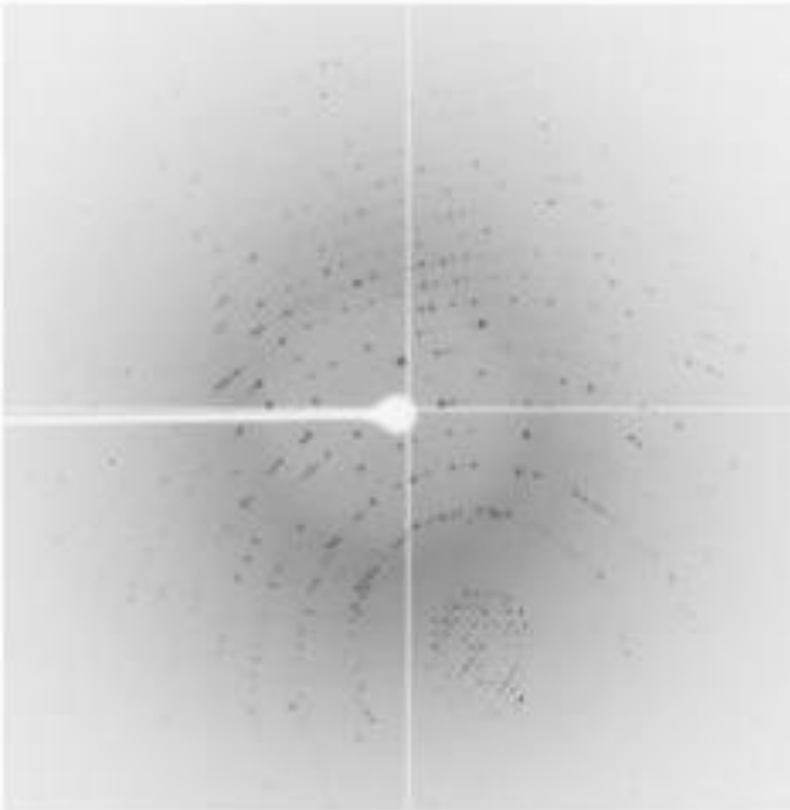
Synchrotron experiments on proteins



Diffraction Process



Diffraction Pattern from NSLS

SwissFEL

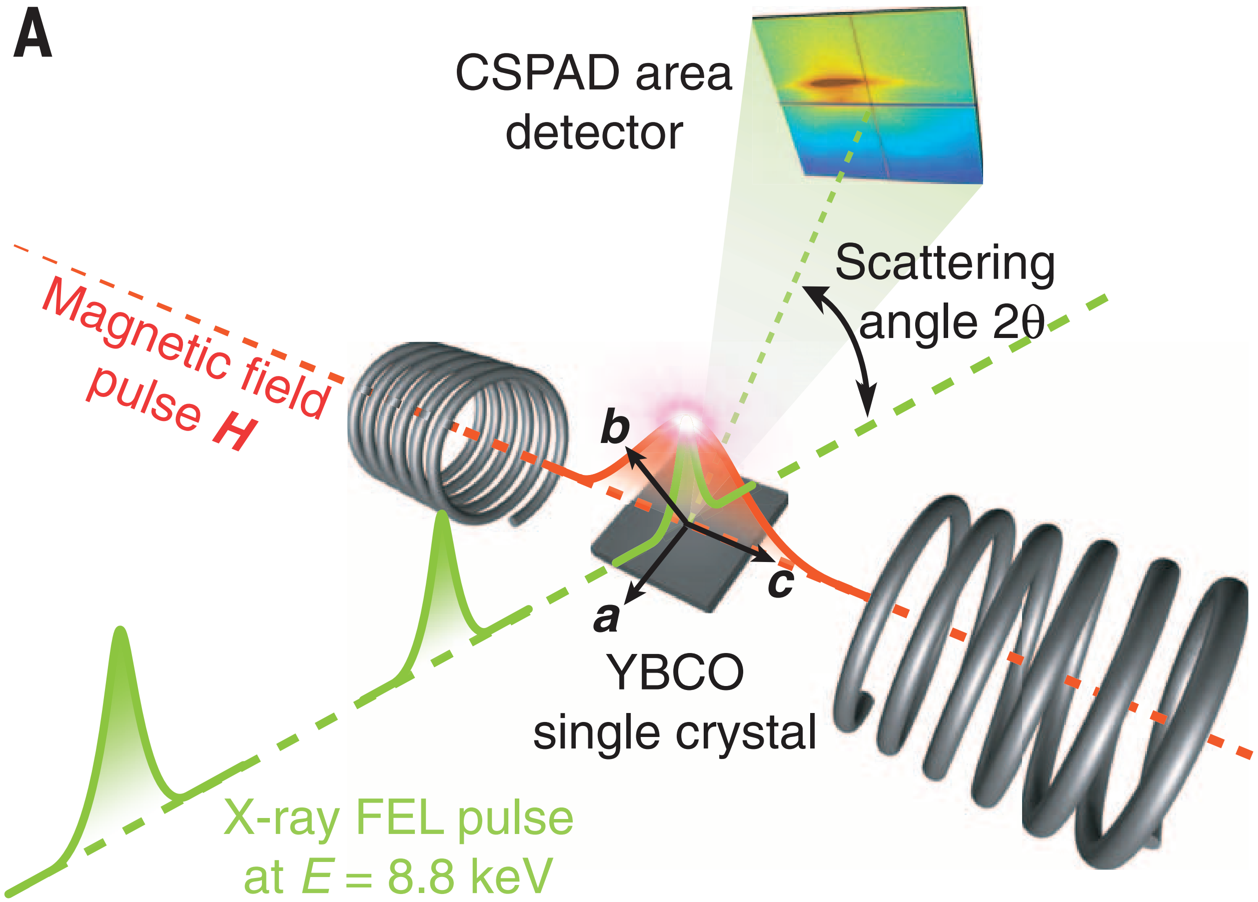
Swiss Free Electron Laser

SwissFEL

Swiss Free Electron Laser

SwissFEL – 2018 Commissioning phase

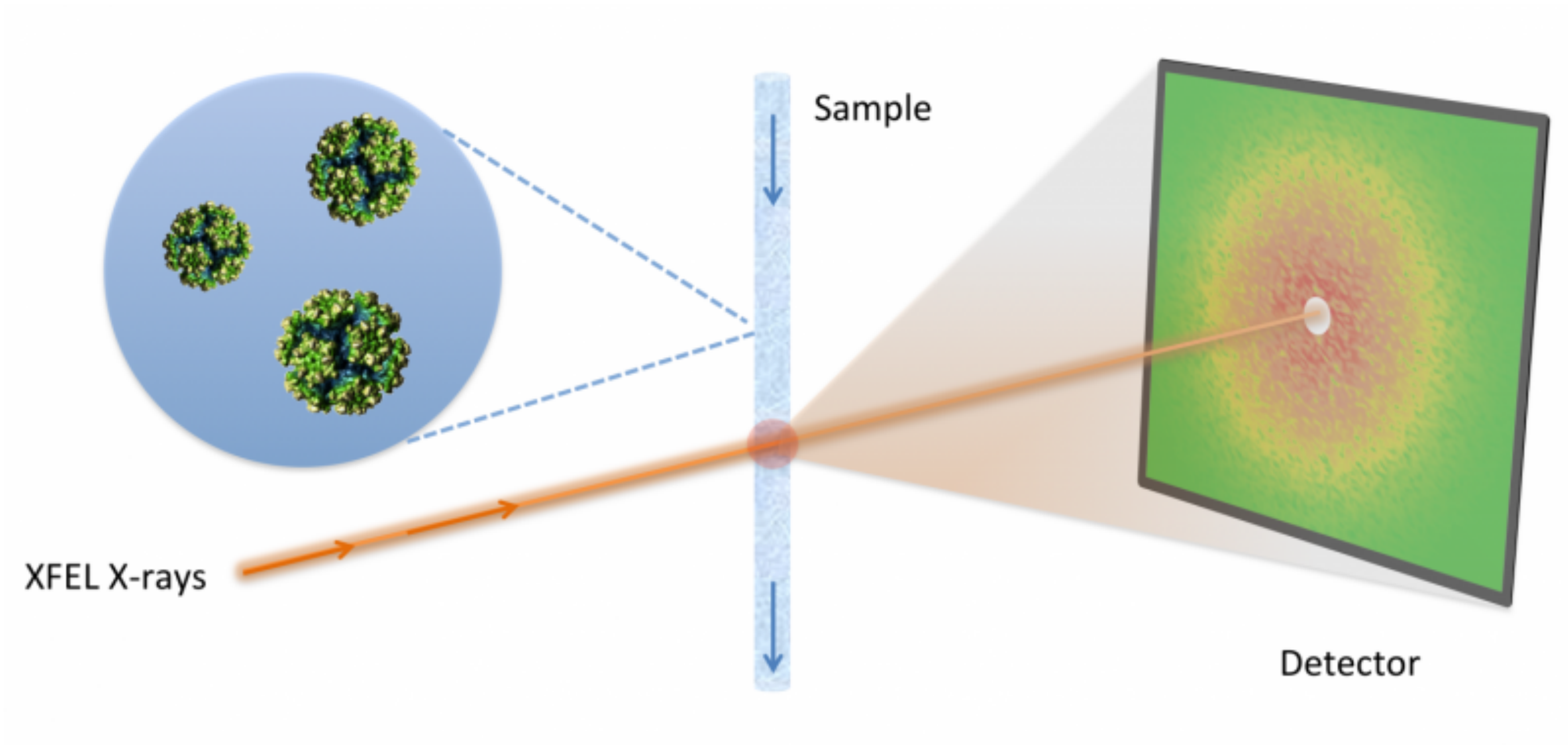
Free Electron Laser



Femto-second pulses ($1x10^{-15}$ s)

photon/ pulse = synchrotron-#photons/sec

X-ray Free Electron Laser experiments on proteins



Protein structure determinations