Today's plan

TASKS FOR NEXT WEEK

New Goal: Resolve crystal structure of a new 200 K superconductor!

→ Reciprocal space, reciprocal lattice vectors & units, Brillouin zones
→ Scattering theory

Experiments
Scattering triangle
Scattering probability
Bragg's law
Form factor
Structure factor

→ How to resolve crystal structures from scattering experiments

Tasks for next week

(1) Read chapter 3:

CRYSTALS OF INERT GASES
IONIC CRYSTALS
COVALENT CRYSTALS
METAL BONDS
ATOMIC RADII

YOU CAN SKIP FROM: ANALYSIS OF ELASTIC STRAINS, …

(2) How is summarizing next week?

(3) Install Mathematica (as many of you).

(4) Solve exercise sheet 3

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.

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.

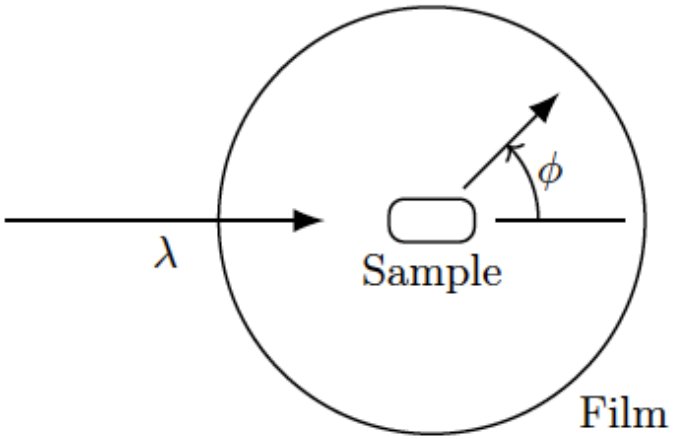

Figure 1: The working principle of a Debye-Scherrer camera.

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?

a) The screened Coulomb potential

$$V(r) = \frac{qQ}{4\pi\epsilon_{\mathrm{r}}\epsilon_0 r} e^{-r/\lambda_{\mathrm{D}}} \tag{1}$$

describes the Coulomb interaction in, for example, an ionic solution. Its typical reach is λ_{D} (the Debye screening length). In cells λ_{D} is very small, which is why biological systems feel essentially no Coulomb force. Calculate the differential scattering cross section

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\omega} = \left| f(\vec{k}, \vec{k}') \right|^2,$$

where

$$f(\vec{k}, \vec{k}') = -\frac{m}{2\pi\hbar^2} \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} V(\vec{r})\, \mathrm{d}^3 r.$$

The result should (hopefully) be:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\omega} = \left(\frac{2mqQ}{\hbar^2 4\pi\epsilon_{\mathrm{r}}\epsilon_0} \right)^2 \frac{1}{[2k^2(1-\cos\Theta) + \lambda_{\mathrm{D}}^{-2}]^2}. \tag{2}$$

b) Derive the scattering cross section for the unscreened Coulomb potential by considering the limit $\lambda \to \infty$ (no screening). (Plug this into equation (2).) Why is it necessary to compute the case for the screened potential first? Why do we not take the unscreened Coulomb potential in equation (1)?

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Paul Scherrer Institute
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Advertisement
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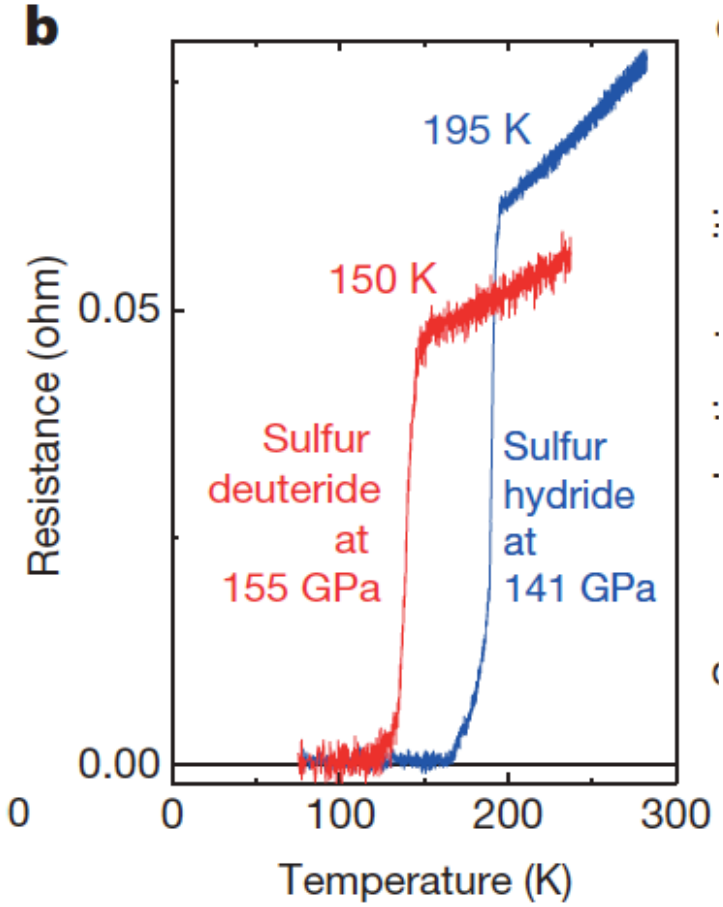
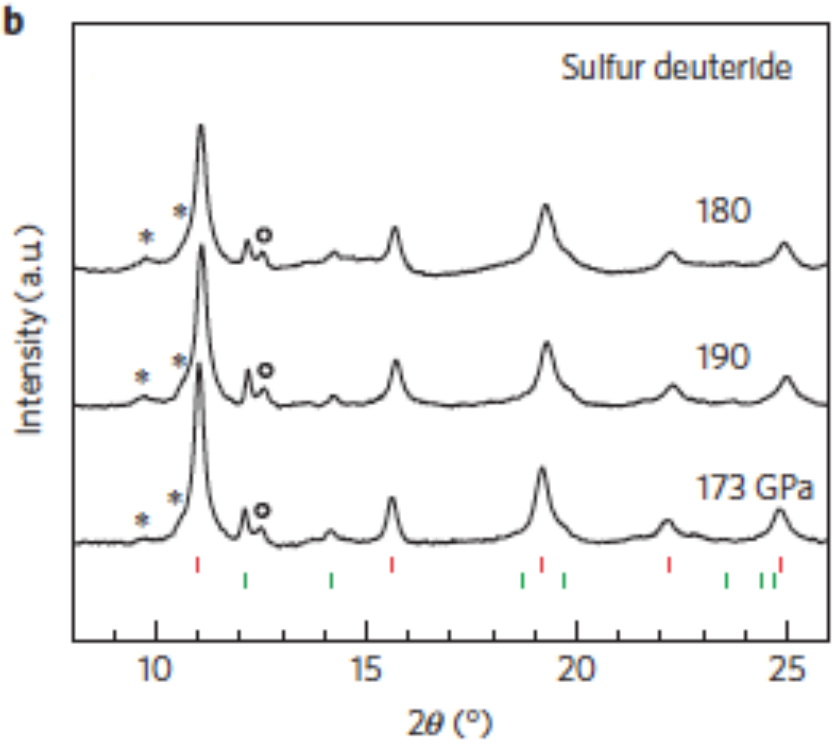
H_2S under pressure - A 200 K superconductor

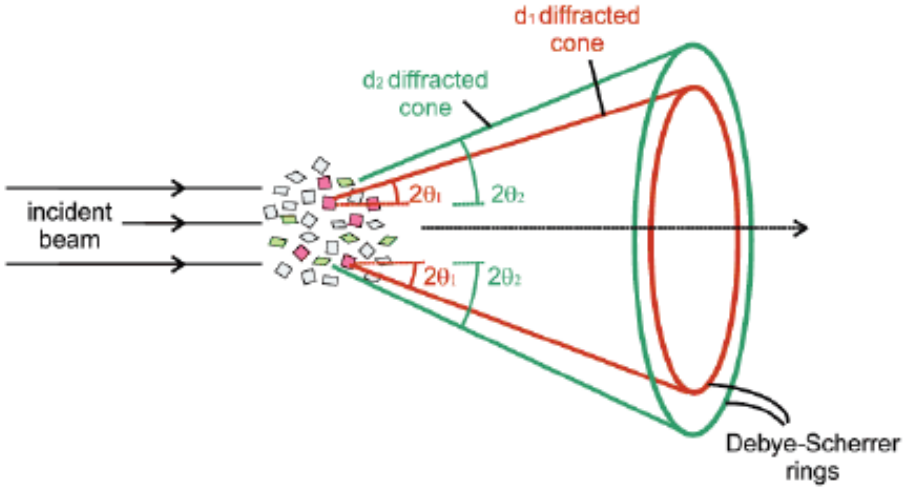




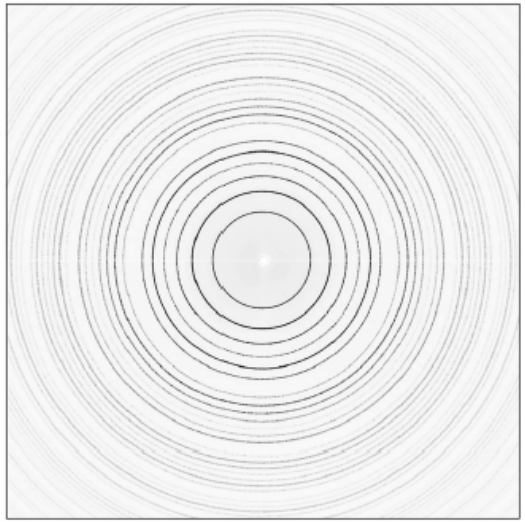
Nature **525**, 73–76 (03 September 2015)

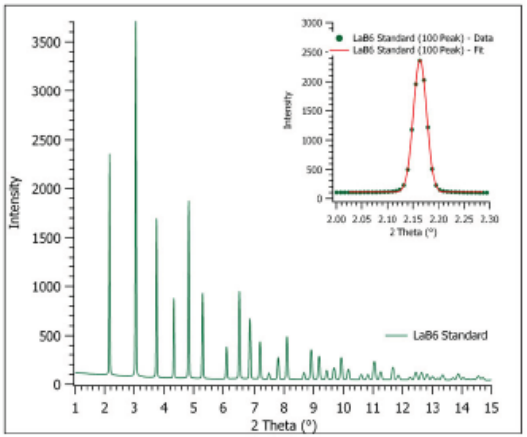
Nature Physics 12, 835–838 (2016)

Powder / poly-crystal diffraction



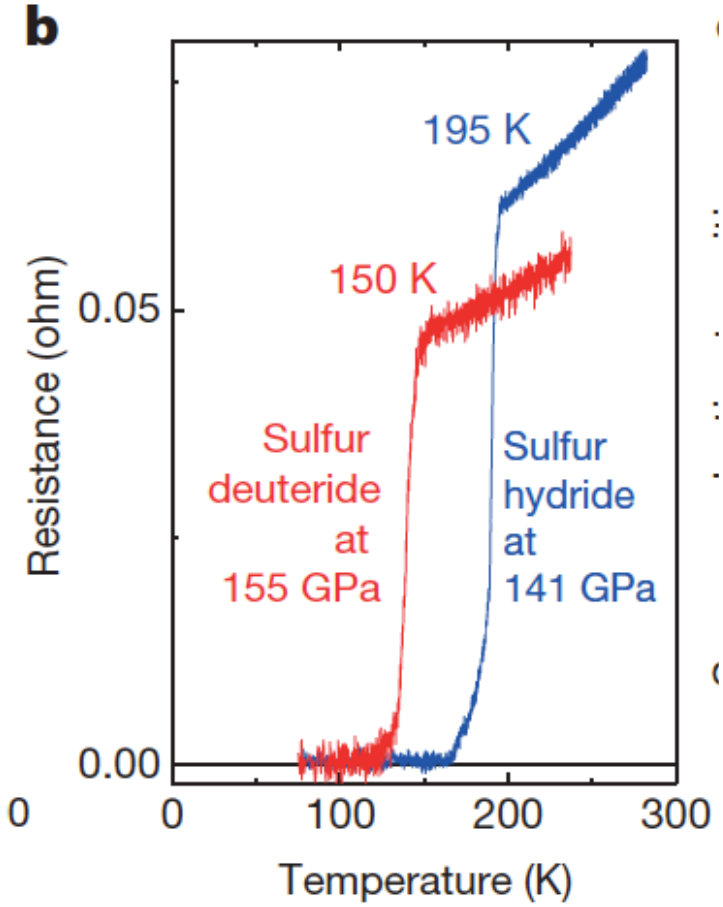
http://pd.chem.ucl.ac.uk/pdnn/diff2/kinemat2.htm

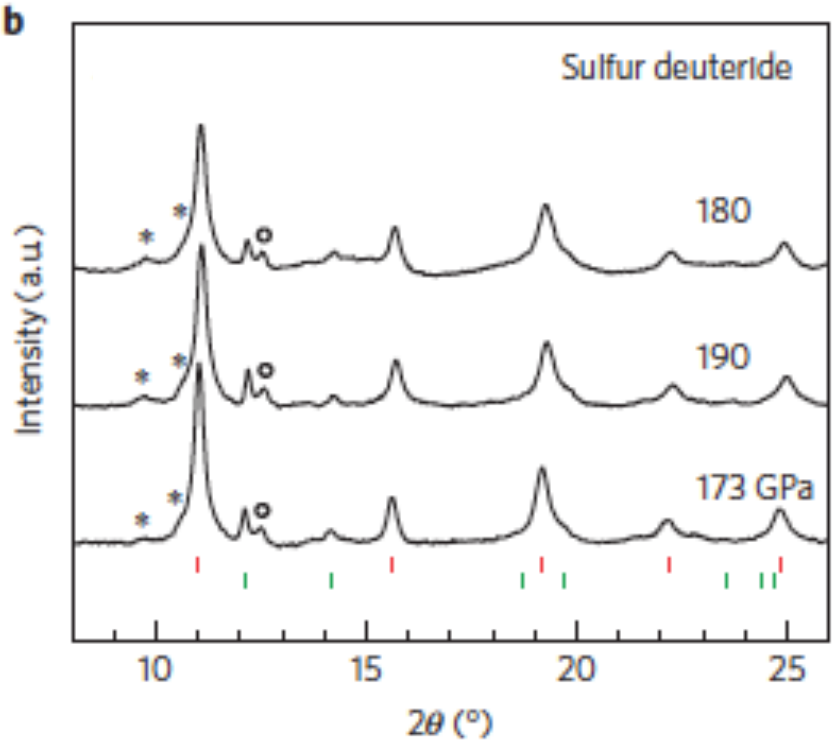




http://www.diamond.ac.uk/Beamlines/Engineering-and-Environment/I12/applications/diffraction.html

H_2S under pressure - A 200 K superconductor





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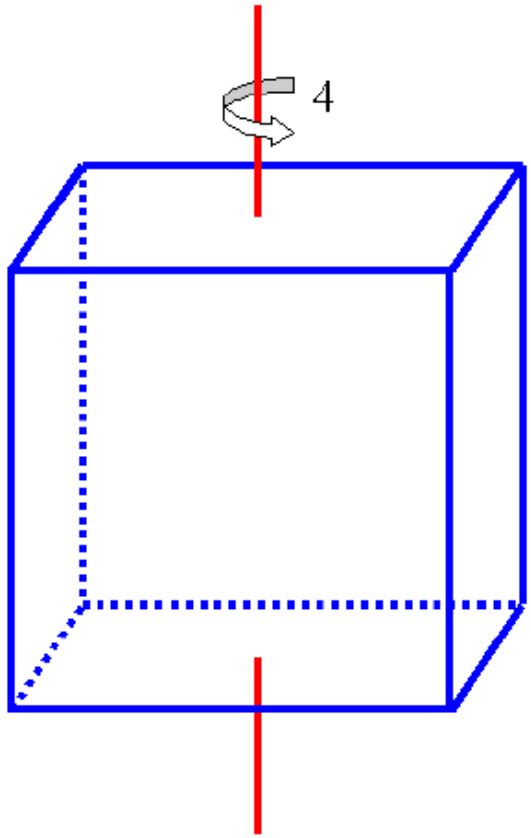
SIMPLE CUBIC

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

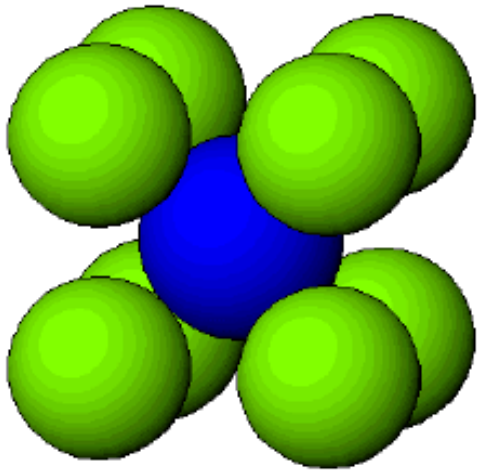
$$\mathbf{d}_1 = 0\mathbf{a}_1 + 0\mathbf{a}_2 + 0\mathbf{a}_3$$



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

Same result as simple monatomic basis

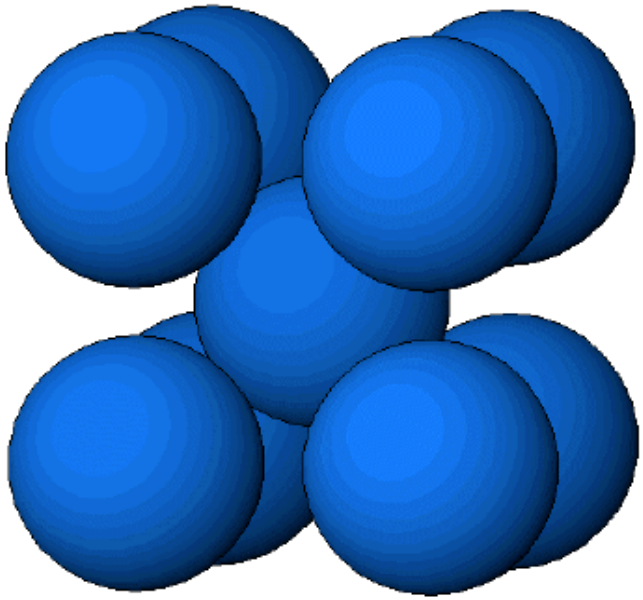
CsCl STRUCTURE



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

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

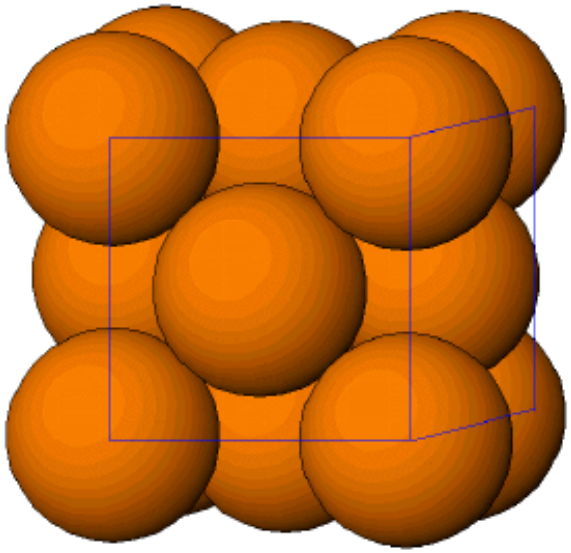
$$= 1 + (-1)^{h+k+l}$$

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)



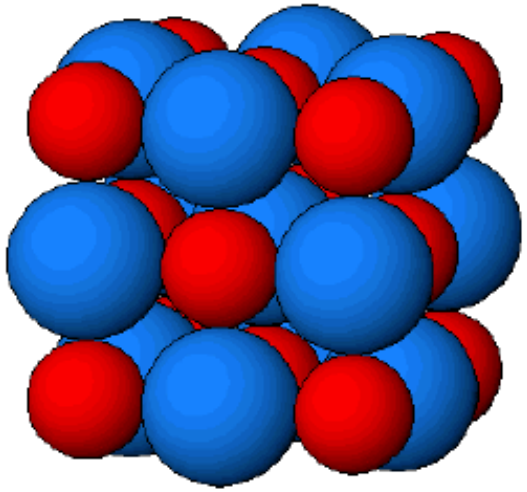
$$S_{\mathbf{K}} = \sum_{j=1}^{4} e^{i\mathbf{K}\cdot\boldsymbol{d}_j} = e^{i\mathbf{K}\cdot 0} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{y})} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{y}+\vec{z})} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{z})}$$

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

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

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.



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

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

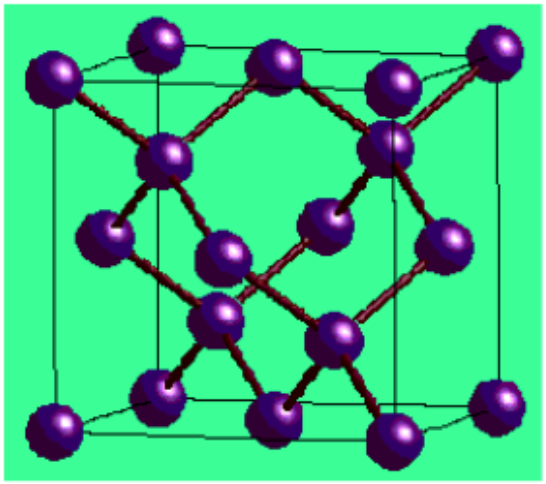
$\Phi = 4(f_{Na} + f_{Cl})$ when h, k, l, all even

$\Phi = 4(f_{Na} - f_{Cl})$ 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.

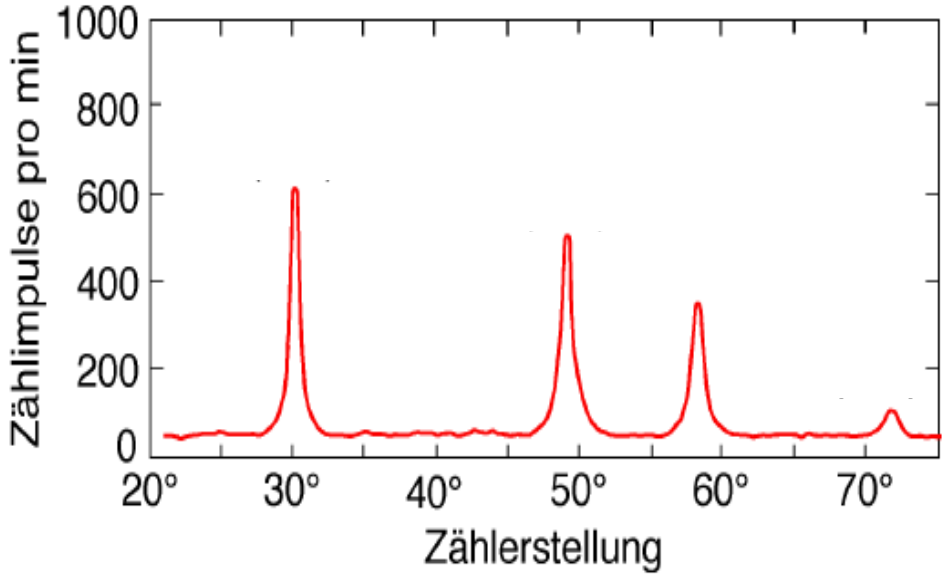
$I_{diamond}$: spots allowed by FCC have relative intensities of 64, 32, or 0.

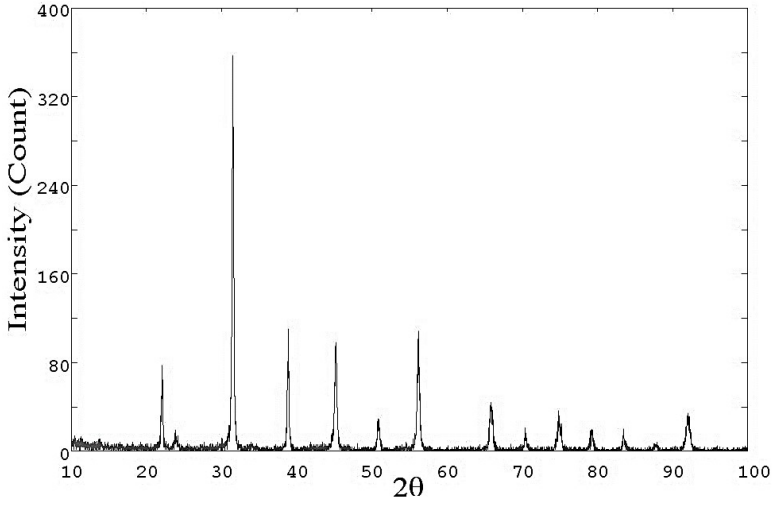
SUMMARY OF SYSTEMATIC ABSENCES

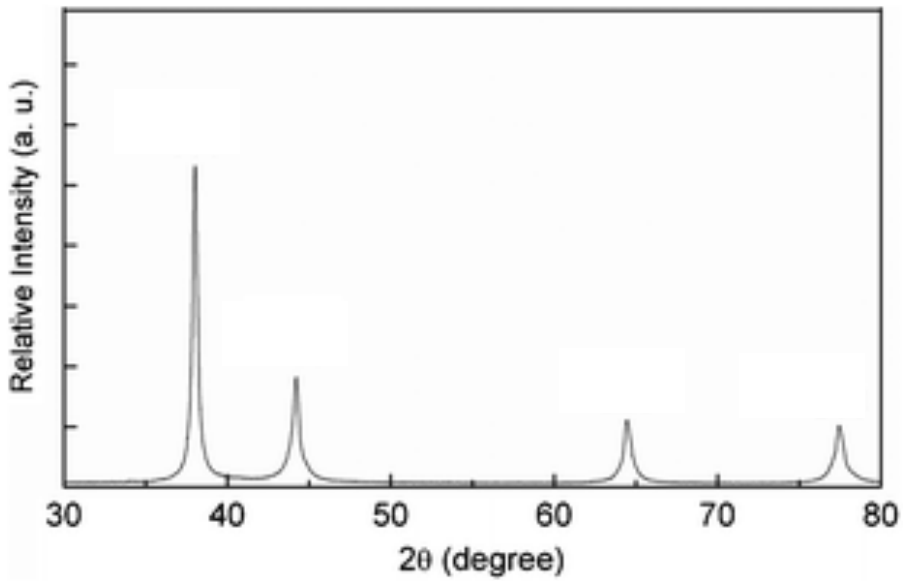
crystal structure	condition for peak to occur
SC	any h,k,l
BCC	$h + k + l$ = even
FCC	h,k,l all even or all odd
NaCl	h,k,l all even, or all odd if $f_A \neq f_B$
diamond	h,k,l all even and twice an even #, or all odd
HCP	any h,k,l except when $h + 2k = 3n$ and l is odd

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

Quiz: What crystal structure?







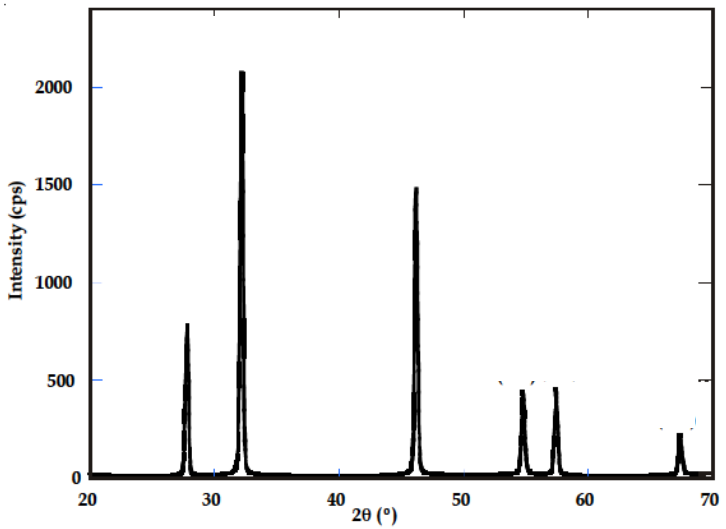


Fig. 9. X-Ray diffraction pattern of silver chloride nanoparticles

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- Powder diffraction

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- Instrumentation
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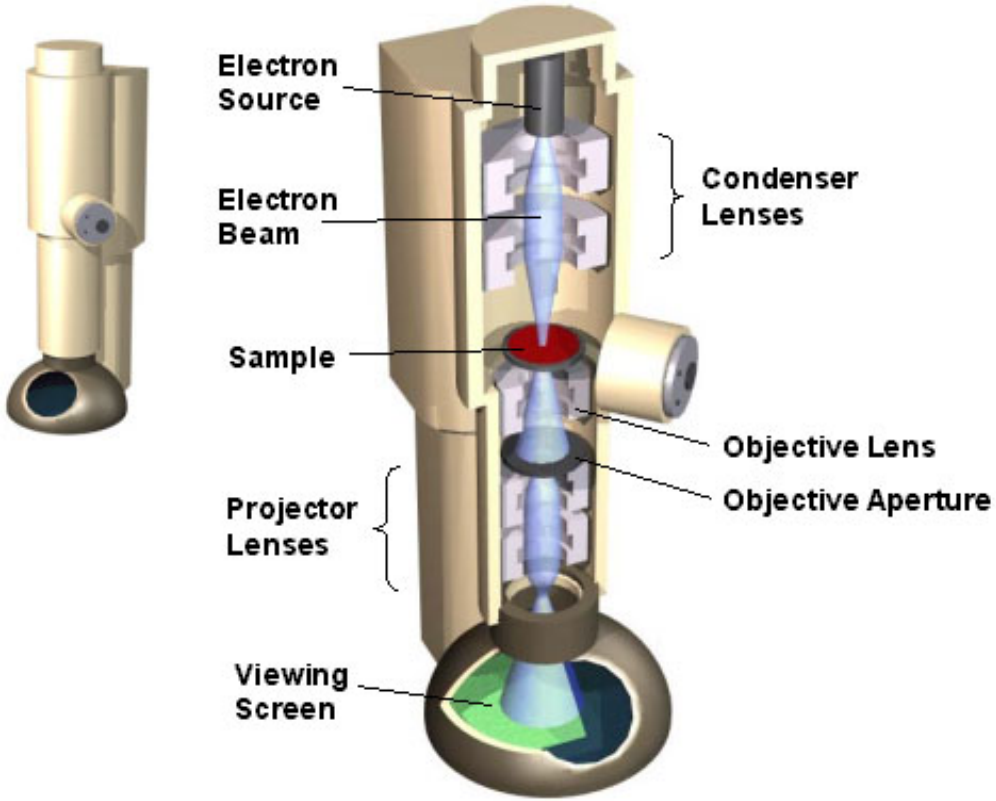
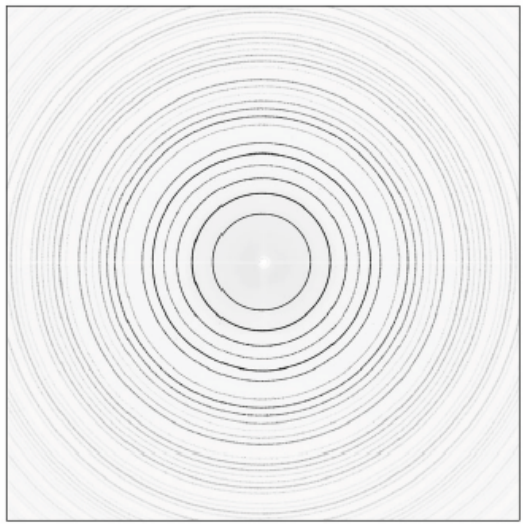
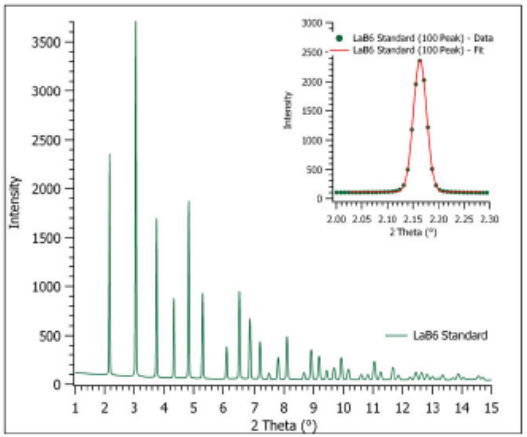
Paul Scherrer Institute
- Neutron diffraction

Advertisement
- Condensed Matter Seminar (next week)

Single crystal diffraction

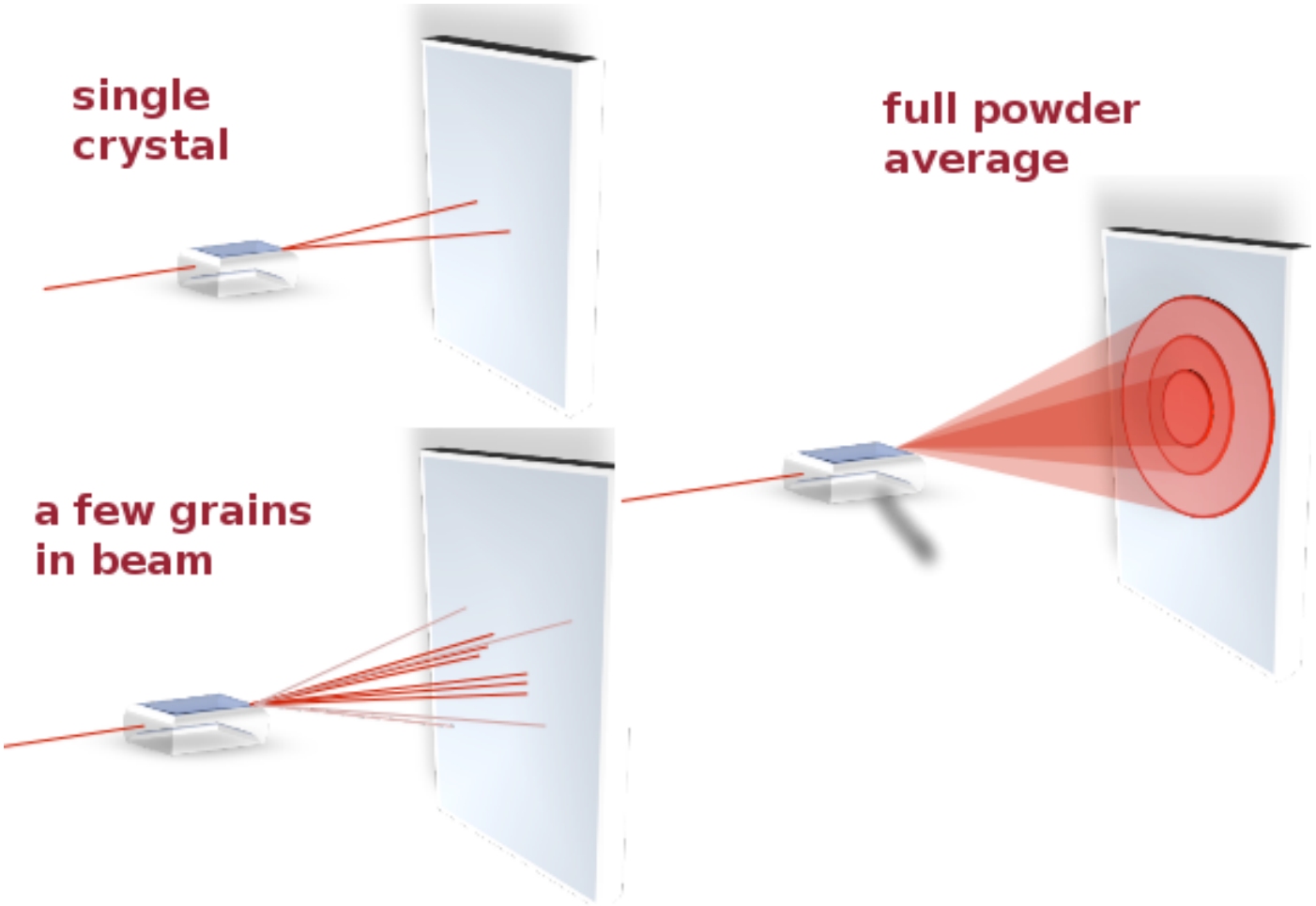






http://www.diamond.ac.uk/Beamlines/Engineering-and-Environment/I12/applications/diffraction.html

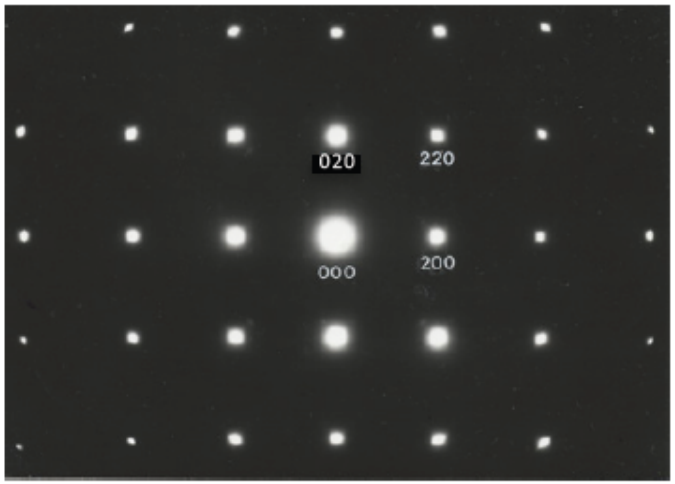
Single crystals, poly-crystals, powder



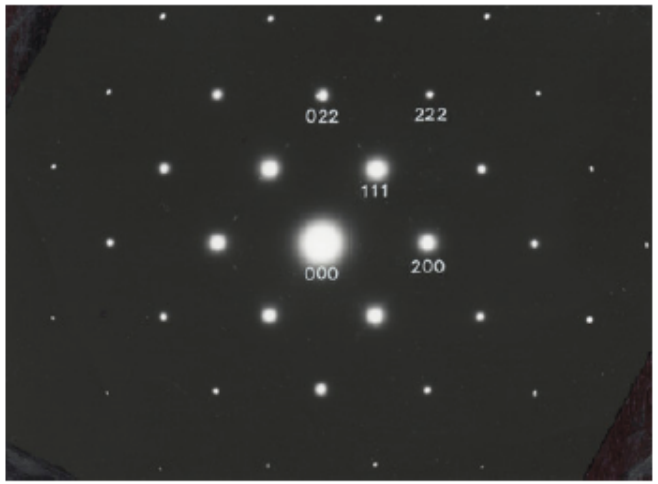
Single crystal diffraction

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

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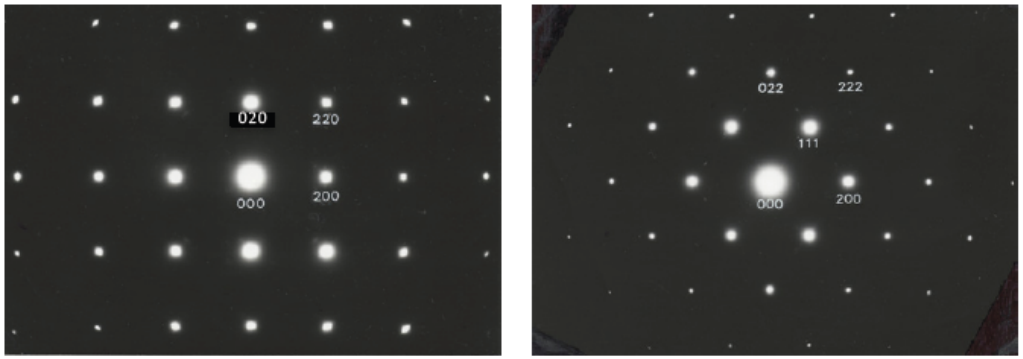

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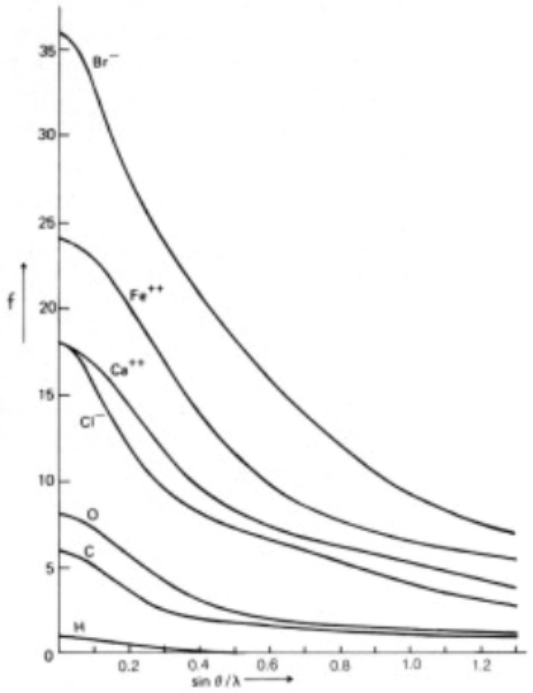
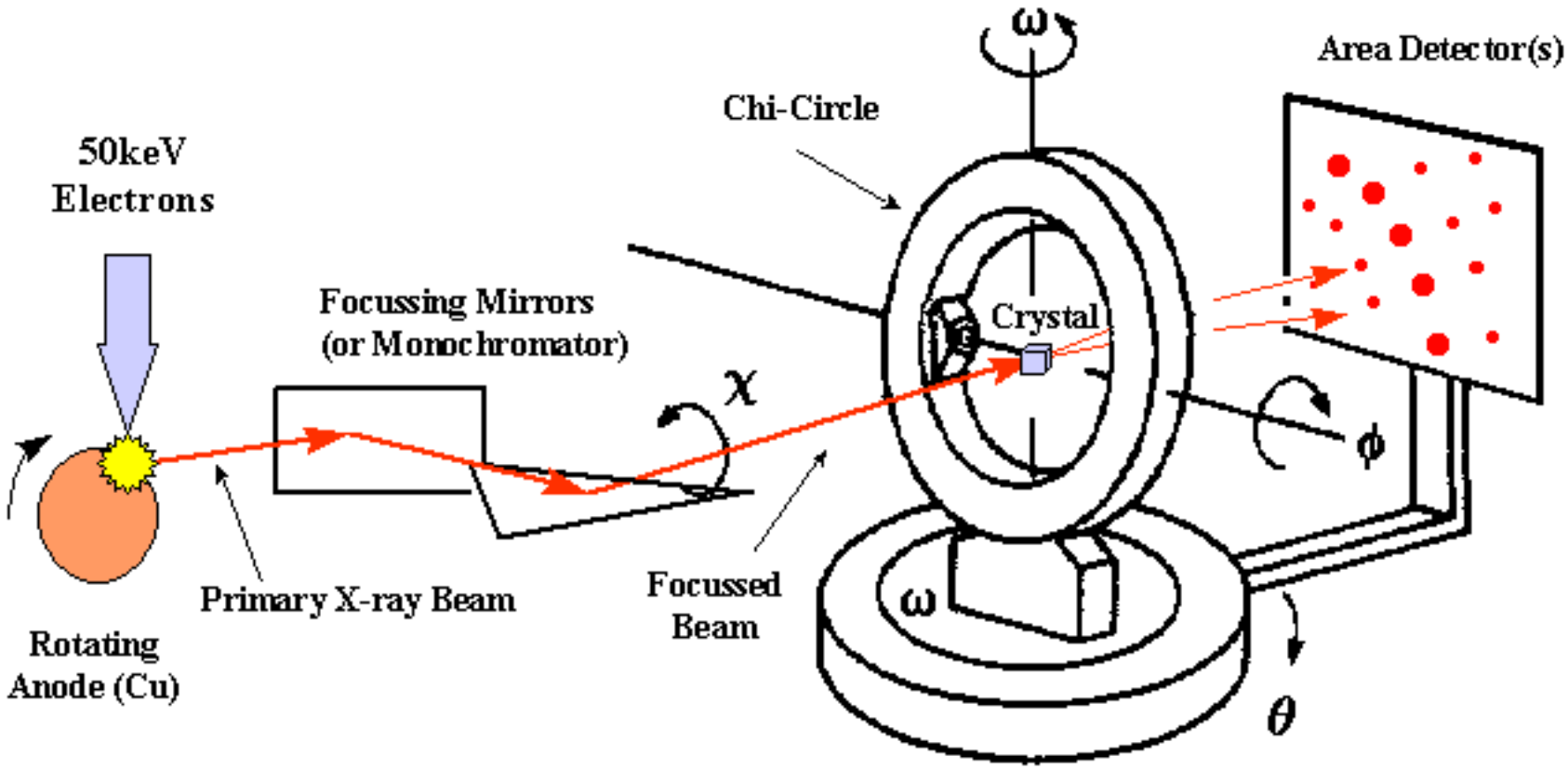
FORM FACTOR



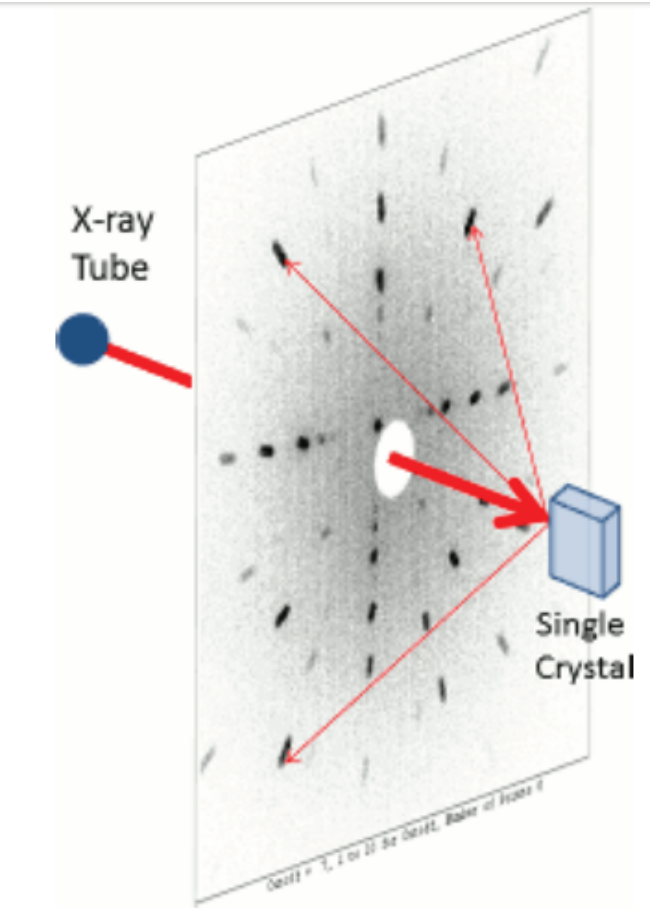
http://www.xtal.iqfr.csic.es/Cristalografia/parte_05-en.html

Single crystal diffraction: x- rays



4-Circle Goniometer (Eulerian or Kappa Geometry)

LAUE



http://multiwire.com/index.shtml

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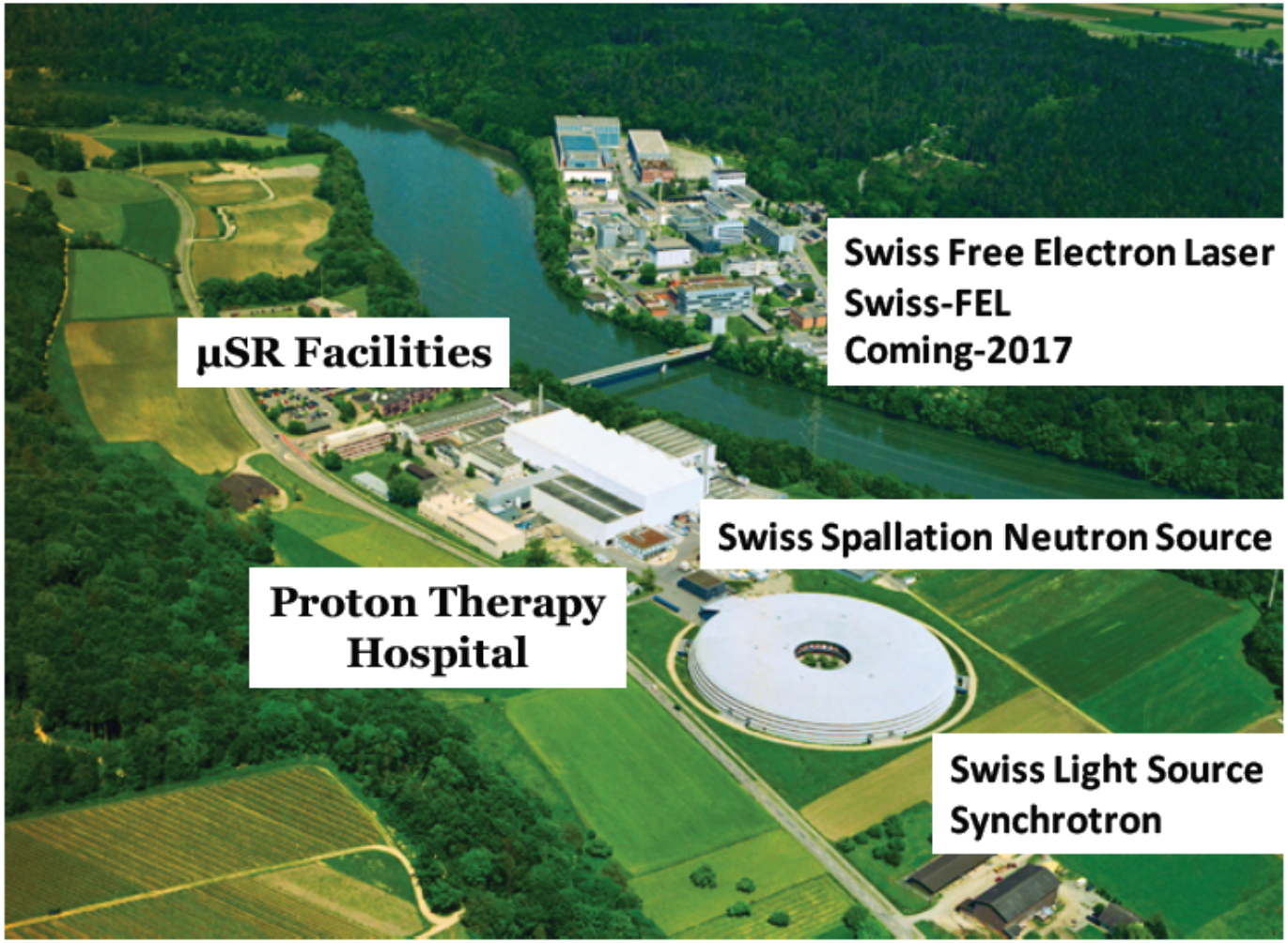
Paul Scherrer Institute

https://www.psi.ch

Paul Scherrer Institute



https://www.psi.ch

Powder diffractometer

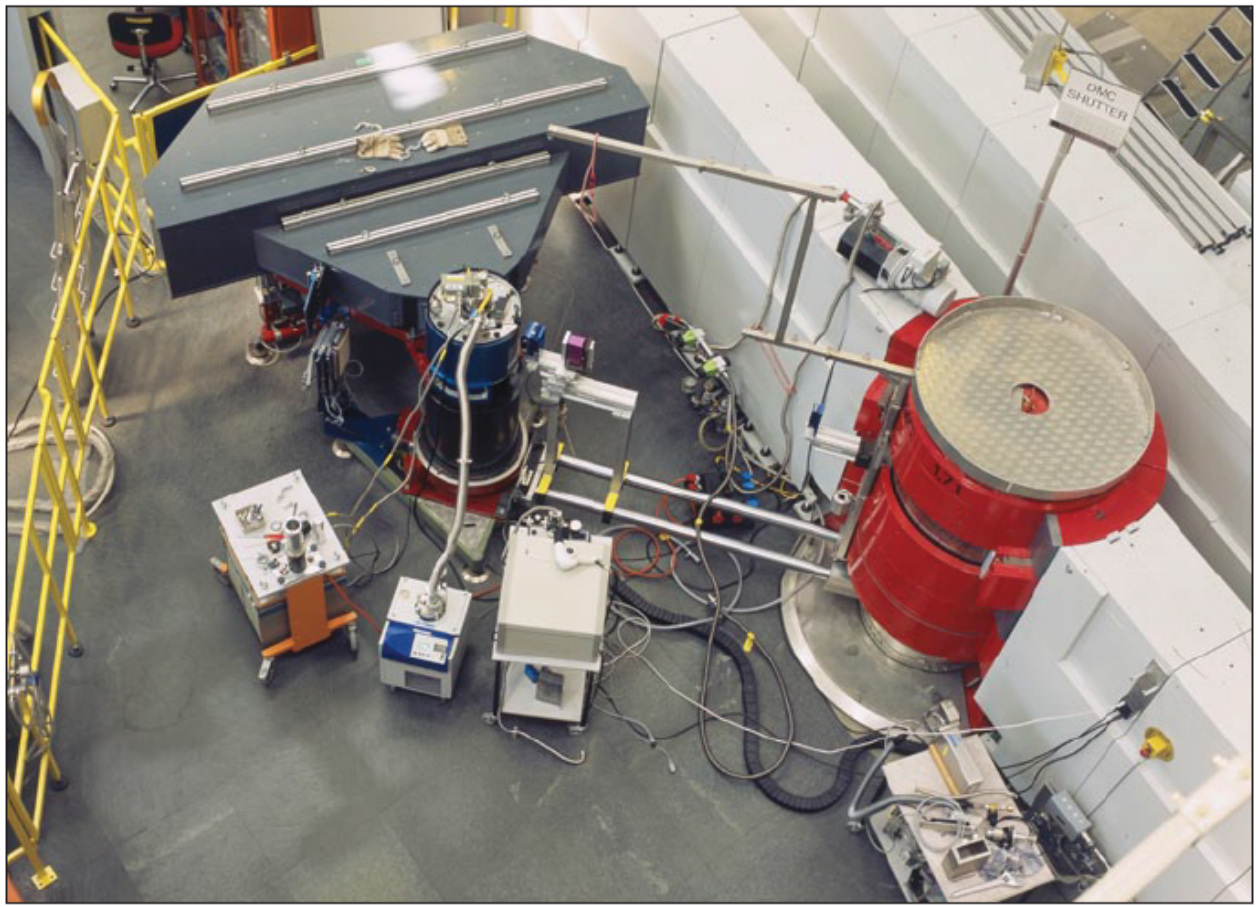
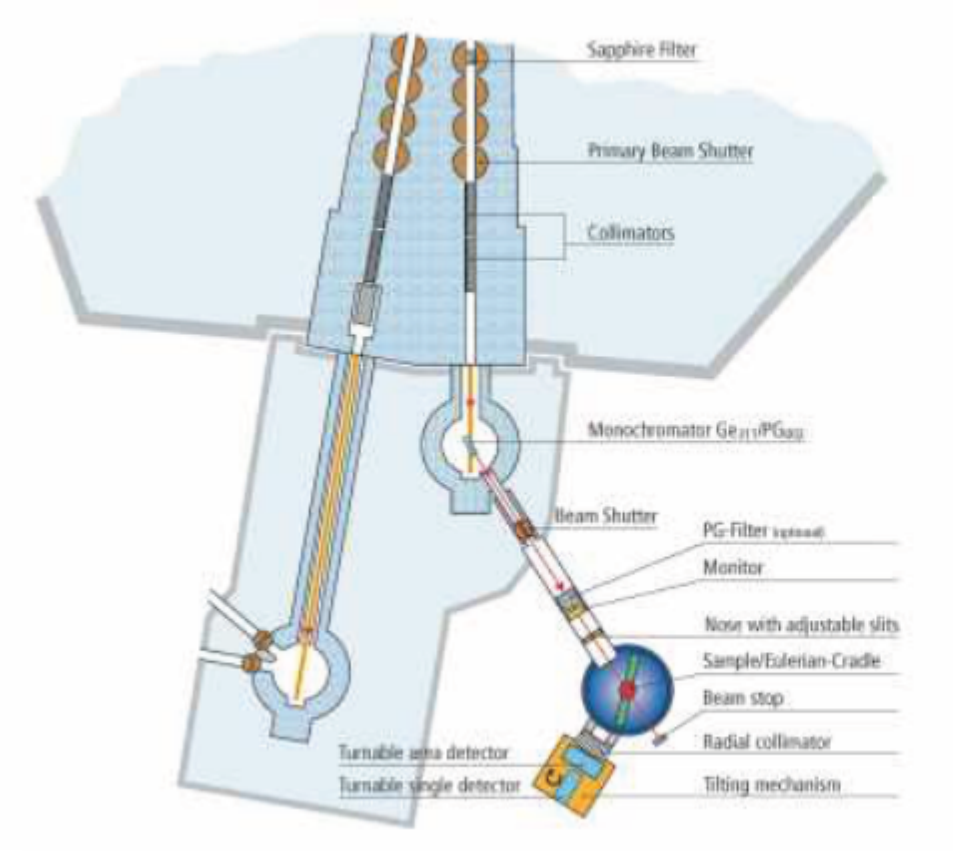
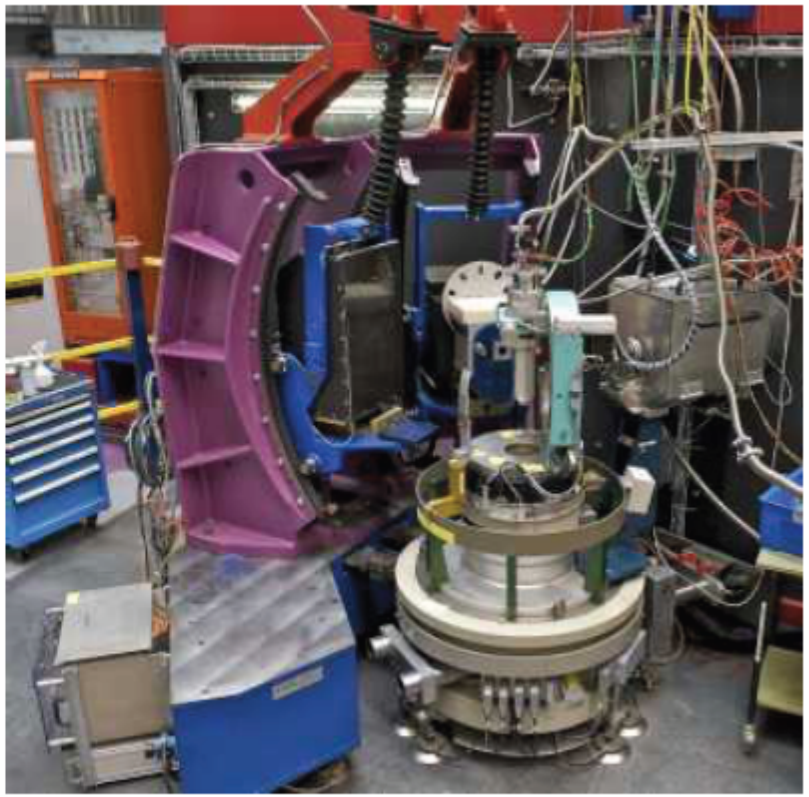


Figure 3: **The DMC powder diffractometer is also appropriate for the investigation of magnetic phenomena.**

Single crystal diffractometer





European infra-structure

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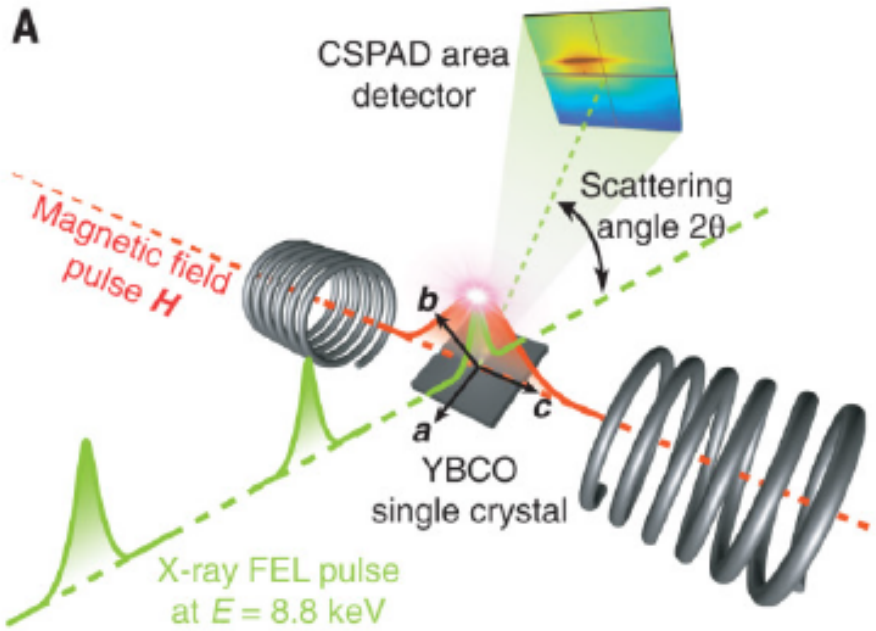
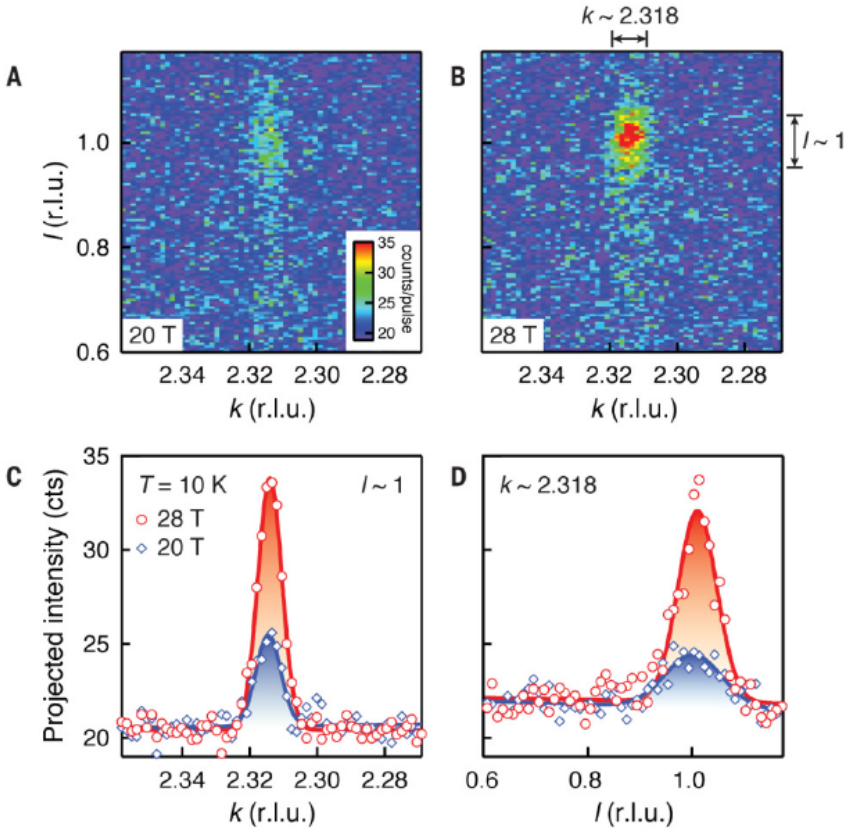
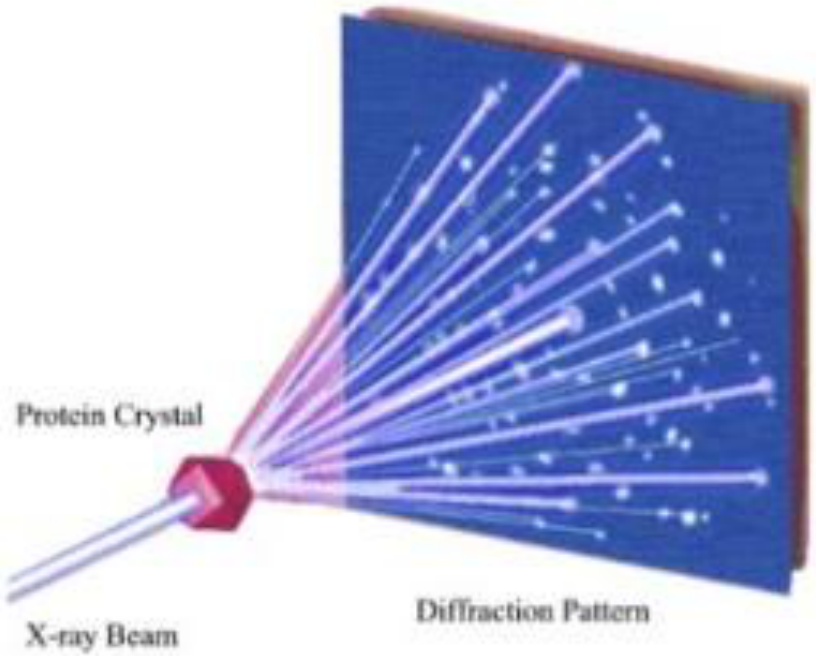
Dr. Simon Gerber (from PSI)
Next Wednesday: 22th March @ 11h15
Condensed Matter Seminar



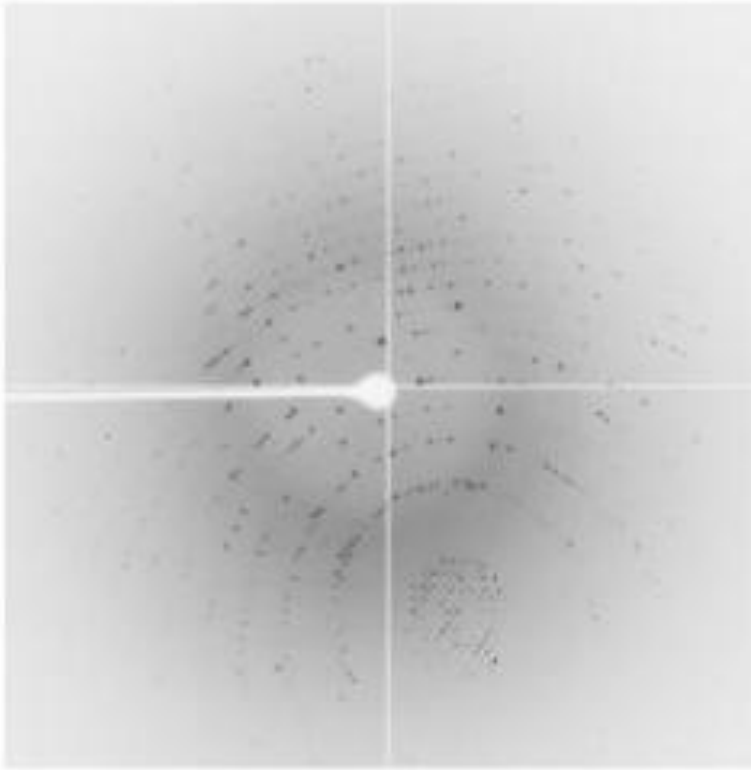


Simon Gerber et al., Science 2015

Synchrotron experiments on proteins

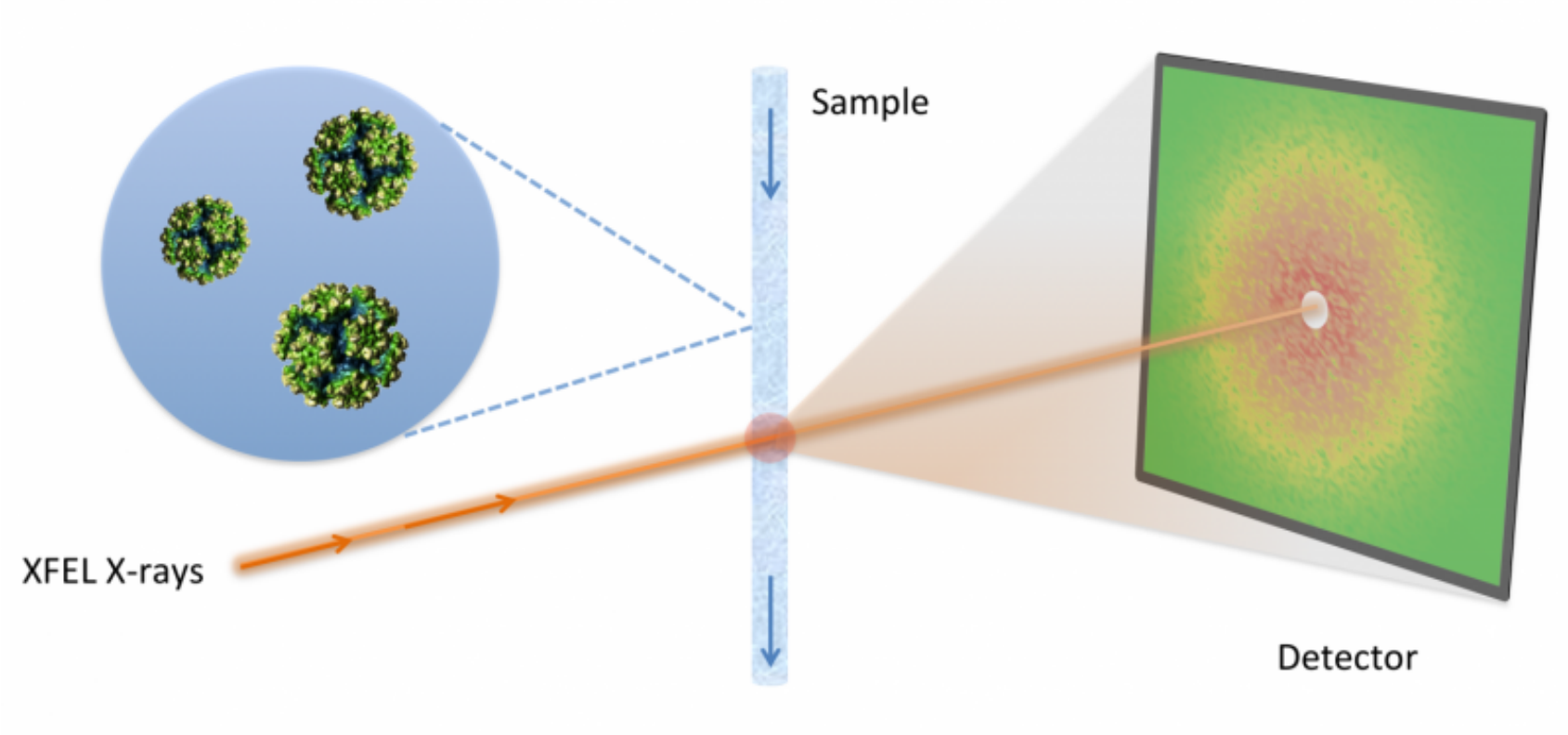


Diffraction Process



Diffraction Pattern from NSLS

X-ray Free Electron Laser experiments on proteins



Reciprocal lattice vectors

2-dimensions

$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$ means

$\mathbf{b}_1 \cdot \mathbf{a}_1 = 2\pi$; $\mathbf{b}_1 \cdot \mathbf{a}_2 = 0$

$\mathbf{b}_2 \cdot \mathbf{a}_1 = 0$; $\mathbf{b}_2 \cdot \mathbf{a}_2 = 2\pi$

3-dimensions

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

$$\mathbf{b}_1 = (2\pi/V)\, \mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{b}_2 = (2\pi/V)\, \mathbf{a}_3 \times \mathbf{a}_1$$

$$\mathbf{b}_3 = (2\pi/V)\, \mathbf{a}_1 \times \mathbf{a}_2$$

$$V = |\, \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$$

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

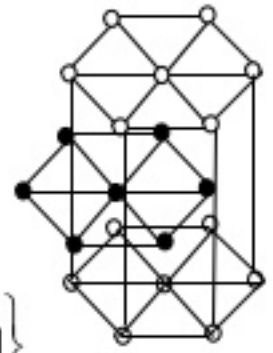
Monoclinic
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic
$$\begin{aligned}\frac{1}{d^2} = \frac{1}{V^2}[&h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta \\ &+ l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma) \\ &+ 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) \\ &+ 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)]\end{aligned}$$

	Direct Lattice	Reciprocal Lattice	
SC	$\begin{cases}\vec{a}_1 = a\hat{x} \\ \vec{a}_2 = a\hat{y} \\ \vec{a}_3 = a\hat{z}\end{cases}$	$\begin{cases}\vec{b}_1 = (2\pi/a)\hat{x} \\ \vec{b}_2 = (2\pi/a)\hat{y} \\ \vec{b}_3 = (2\pi/a)\hat{z}\end{cases}$	SC
FCC	$\begin{cases}\vec{a}_1 = \frac{1}{2}a(\hat{x}+\hat{y}) \\ \vec{a}_2 = \frac{1}{2}a(\hat{y}+\hat{z}) \\ \vec{a}_3 = \frac{1}{2}a(\hat{z}+\hat{x})\end{cases}$	$\begin{cases}\vec{b}_1 = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z}) \\ \vec{b}_2 = \frac{2\pi}{a}(-\hat{x}+\hat{y}+\hat{z}) \\ \vec{b}_3 = \frac{2\pi}{a}(\hat{x}-\hat{y}+\hat{z})\end{cases}$	BCC
BCC	$\begin{cases}\vec{a}_1 = \frac{1}{2}a(\hat{x}+\hat{y}-\hat{z}) \\ \vec{a}_2 = \frac{1}{2}a(-\hat{x}+\hat{y}+\hat{z}) \\ \vec{a}_3 = \frac{1}{2}a(\hat{x}-\hat{y}+\hat{z})\end{cases}$	$\begin{cases}\vec{b}_1 = \frac{2\pi}{a}(\hat{x}+\hat{y}) \\ \vec{b}_2 = \frac{2\pi}{a}(\hat{y}+\hat{z}) \\ \vec{b}_3 = \frac{2\pi}{a}(\hat{z}+\hat{x})\end{cases}$	FCC

Elastic Scattering of Waves by a Crystal

The Structure Factor



For the hexagonal colse-packed structure,

basis of two identical atoms at

$$\vec{r}_1 = 0, \quad \vec{r}_2 = \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c}$$

$$S = f\left\{\exp(i0) + \exp[-i(h\vec{a}^* + k\vec{b}^* + l\vec{c}^*)\cdot(\frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c})]\right\}$$

$$= f\left\{1 + \exp[-i\pi(\frac{4}{3}h + \frac{2}{3}k + l)]\right\} = f\left\{1 + \exp[-i\pi(h + k + l) + \frac{1}{3}(k - h))]\right\}$$

The intensity of diffracted beam is propotional to $|S|^2$

P.11.3

There are four possible value for $|S|^2$ for the case of hcp.

For the diffracted beam of (001), ⇨ S = 0 ⇨ intensity vanishes.

Likewise, some of the possible diffracted beams of $\vec{K} = \vec{G}_{hkl}$ are absent because of destructive interference of the scattering form the two atoms in the basis. This is based on the assumption that both atoms in the basis have identical form factors. Although the atoms are chemically identical, their environments within the crystal are different; electron state within the atoms are distorted slightly by the neighboring atoms and this distortion is reflected in the angular dependence of f. Thus the form factors of the two atoms differ slightly and very weak diffracted beams do occur in the 'forbidden' directions