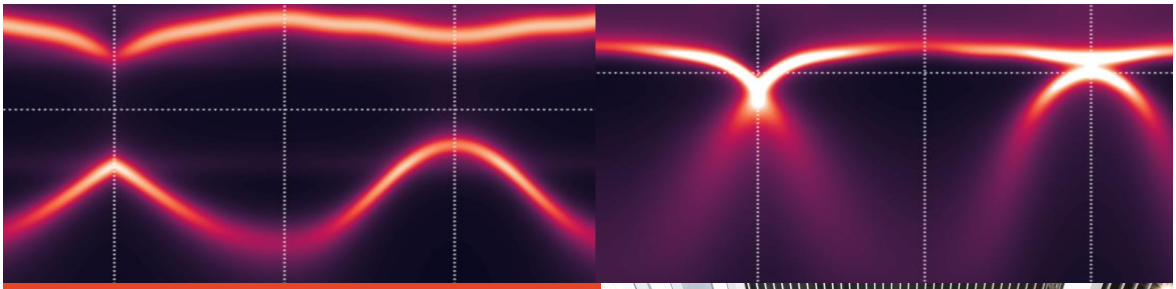
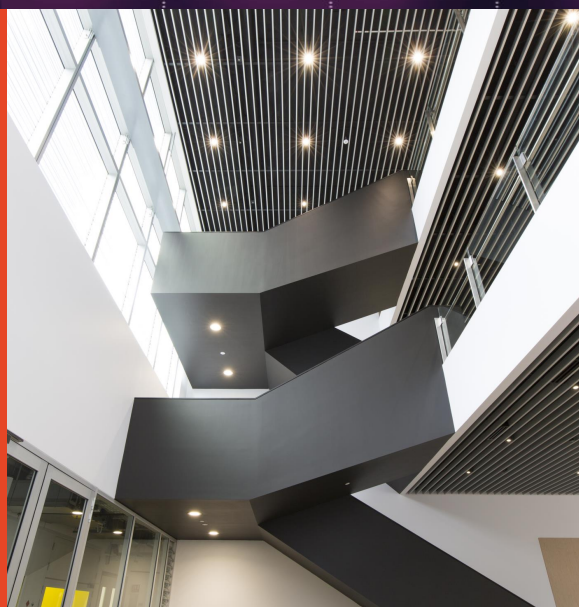


CMP Lecture 8

School of Physics
The University of Sydney

THE UNIVERSITY OF SYDNEY



Structure factor

Ch 14.3 Oxford Basics

Experiments measure the intensity

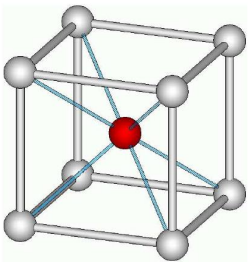
$$I_{(hkl)} \propto |S_{(hkl)}|^2$$

Consider some structure factors

$$S_{(hkl)} = \sum_{\text{atom } j \text{ in unit cell}} f_j \; e^{2\pi i(hx_j+ky_j+lz_j)}$$

f_j form factor

Example 1: Caesium Chloride



Can be described as a simple cubic with a basis given by

Basis for CsCl		
Cs	Position=	$[0,0,0]$
Cl	Position=	$[a/2,a/2,a/2]$

Recall – we found that we will see diffraction spots for all *h,k,l* but a stronger intensity when the *h+k+l* are even as compared to *h+k+l* odd.

$$\begin{aligned} S_{(hkl)} &= f_{Cs} + f_{Cl}\, e^{2\pi i(h,k,l)\cdot[1/2,1/2,1/2]} \\ &= f_{Cs} + f_{Cl}(-1)^{h+k+l} \end{aligned}$$

Systematic absences or selection rules

Example 2: Caesium bcc

Consider pure Cs – simply replace the Cl in CsCl with another Cs atom.
Simple cubic lattice with basis:

(for neutron scattering)

Basis for Cs bcc		
Cs	Position=	$[0,0,0]$
Cs	Position=	$[a/2, a/2, a/2]$

$$S(\mathbf{G}) \sim \sum_{\text{atom } j \text{ in unit cell}} b_j \, e^{i\mathbf{G}\cdot\mathbf{x_j}}$$

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

$$\mathbf{G} = h\,\mathbf{b_1} + k\,\mathbf{b_2} + l\,\mathbf{b_3}$$

$$\begin{aligned} S_{(hkl)} &= f_{Cs} + f_{Cs}\, e^{2\pi i(h,k,l)\cdot[1/2,1/2,1/2]} \\ &= f_{Cs}\left[1 + (-1)^{h+k+l}\right] \end{aligned}$$

Scattering intensity vanishes for *h+k+l* being any odd integer!

For *h+k+l* being even, get structure factor = $2\,f_{Cs}$

So if your unknown material is bcc, you can identify it as such due to characteristic missing diffraction spots.

Systematic absences or selection rules

Example 3: Copper fcc

Simple cubic with a basis: $[0,0,0], [1/2,1/2,0], [1/2,0,1/2]$, and $[0,1/2,1/2]$

$$S_{(hkl)} = f_{Cu}\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right]$$

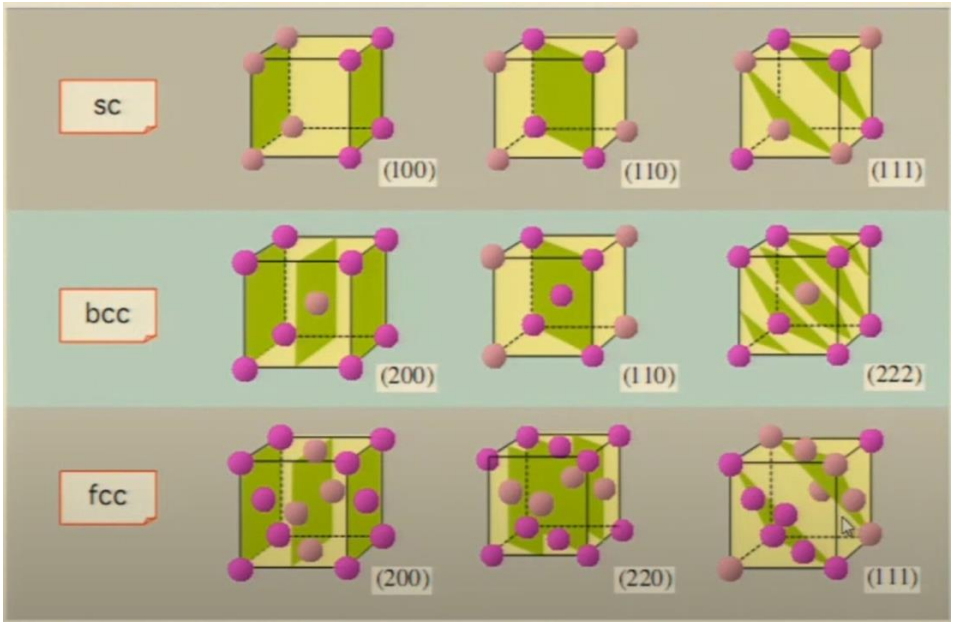
This expression vanishes unless *h, k* and *l* are either all odd or all even.

Systematic Absences of Scattering	
Simple Cubic	all h, k, l allowed
bcc	$h + k + l$ must be even
fcc	h, k, l must be all odd or all even

"selection rules"

So the observed diffraction spots will satisfy these selection rules for a given structure.

Geometric interpretation of selection rules



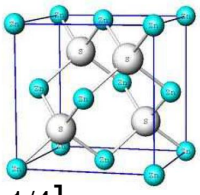
All h,k,l allowed

h+k+l must be even

h,k,l must be either all odd or all even

This is because we are using the conventional cubic unit cell with lattice vectors **a** which are not the primitive lattice vectors for bcc and fcc structures. But it is more convenient to work with orthogonal axes.

Systematic absences



Example 4: Zinc Sulfide = fcc with a basis:

Zincblende structure – fcc with a basis: Zn at [0,0,0], S at [1/4,1/4,1/4].
Consider it as a simple cubic lattice with basis of 8 atoms in the conv. unit cell:

Basis for ZnS						
Zn	Positions=	$[0,0,0]$,	$[1/2,1/2,0]$,	$[1/2,0,1/2]$,	and	$[0,1/2,1/2]$
S	Positions=	$[1/4,1/4,1/4]$,	$[3/4,3/4,1/4]$,	$[3/4,1/4,3/4]$,	and	$[1/4,3/4,3/4]$

$$S_{(hkl)} = f_{Zn}\left[1 + e^{2\pi i(hkl)\cdot[1/2,1/2,0]} + \ldots\right] +$$

$$f_S\left[e^{2\pi i(hkl)\cdot[1/4,1/4,1/4]} + e^{2\pi i(hkl)\cdot[3/4,3/4,1/4]} + \ldots\right]$$

$$S_{(hkl)} = \underbrace{\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right]}_{\text{Same term we found for the fcc crystal}} \underbrace{\left[f_{Zn} + f_S\, e^{i(\pi/2)(h+k+l)}\right]}_{\text{Term associated with ZnS}}$$

In general: $\boxed{S_{(hkl)} = S^{Lattice}_{(hkl)} \times S^{basis}_{(hkl)}}$

(check the above expression is true as exercise)

Scattering intensity – powder diffraction

Powder diffraction: wave scattering on a sample that is not single crystalline, but is powdered – wave can scatter from many small crystals which may be oriented in any possible direction.

Recall that there are equivalent families of planes, e.g. six (for simple cubic)

$$(0\bar{1}0), (00\bar{1})\,(100)\;(010), (001), (\bar{1}00)\; = \{100\}$$

eight:

$$(111), (11\bar{1}), (1\bar{1}1), (1\bar{1}\bar{1}), (\bar{1}11), (\bar{1}1\bar{1}), (\bar{1}\bar{1}1), (\bar{1}\bar{1}\bar{1}) = \{111\}$$

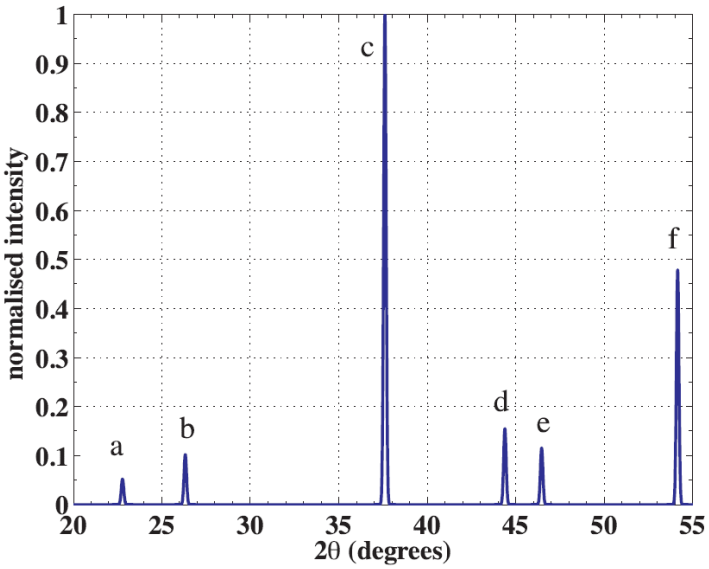
This is called the multiplicity factor, thus more accurately we should write the measured intensity:

$$I_{\{hkl\}} \propto M_{\{hkl\}} |S_{\{hkl\}}|^2$$

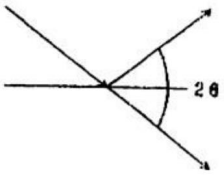
Neutron scattering: powder diffraction from PrO_2

Ch. 14.3 Oxford Basics

Given experimental results see how to determine structure

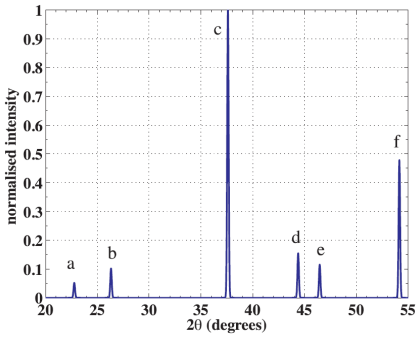


See deflection by 2θ:



Neutron scattering: powder diffraction from PrO_2

Collate a table, reading off the deflection angles, and corresponding distances and possible relationship to Miller indices



$$d_{(hkl)} = \frac{\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

$$\lambda = .123 \text{ nm}$$

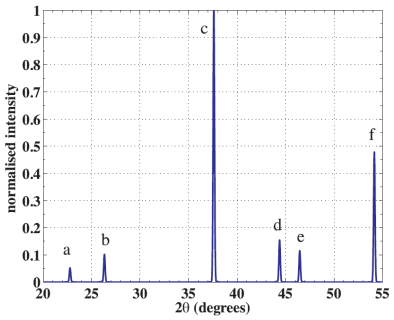
peak	2θ	$d = \lambda/(2\sin\theta)$	d_a^2/d^2	$3d_a^2/d^2$	$N = h^2+k^2+l^2$
a	22.7°	0.313 nm	1	3	3
b	26.3°	0.270 nm	1.33	3.99	4
c	37.7°	0.190 nm	2.69	8.07	8
d	44.3°	0.163 nm	3.67	11.01	11
e	46.2°	0.157 nm	3.97	11.91	12
f	54.2°	0.135 nm	5.35	16.05	16

Working

Neutron scattering: powder diffraction from PrO_2

Calculate the corresponding lattice constant in last column, and average value, find:

$$a = .541 \pm .002 \text{ nm}$$



Find which h,k,l give the N

peak	2θ	$d = \lambda/(2\sin\theta)$	$N = h^2 + k^2 + l^2$	$\{hkl\}$	$a = d\sqrt{h^2 + k^2 + l^2}$
a	22.7°	0.313 nm	3	111	.542 nm
b	26.3°	0.270 nm	4	200	.540 nm
c	37.7°	0.190 nm	8	220	.537 nm
d	44.3°	0.163 nm	11	311	.541 nm
e	46.2°	0.157 nm	12	222	.544 nm
f	54.2°	0.135 nm	16	400	.540 nm

Neutron scattering: powder diffraction from PrO_2

$N = h^2 + k^2 + l^2$	$\{hkl\}$
3	111
4	200
8	220
11	311
12	222
16	400

we found

Is it cubic, bcc, fcc? Consider the known selection rules

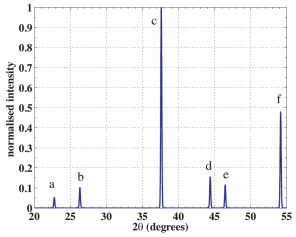
Systematic Absences of Scattering	
Simple Cubic	all h, k, l allowed
bcc	$h + k + l$ must be even
fcc	h, k, l must be all odd or all even

Lattice Plane Selection Rules

$\{hkl\}$	$N = h^2 + k^2 + l^2$	Multiplicity	cubic	bcc	fcc
100	1	6	✓		
110	2	12	✓	✓	
111	3	8	✓		✓
200	4	6	✓	✓	✓
210	5	24	✓		
211	6	24	✓	✓	
220	8	12	✓	✓	✓
221	9	24	✓		
300	9	6	✓		
310	10	24	✓	✓	
311	11	24	✓		✓
222	12	8	✓	✓	✓

FCC!

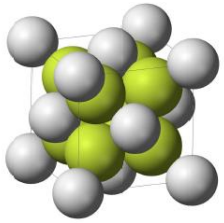
Neutron scattering: powder diffraction from PrO_2



We can also analyse the measured intensities

$$I_{\{hkl\}} \propto M_{\{hkl\}} |S_{\{hkl\}}|^2$$

Calculate the structure factor.

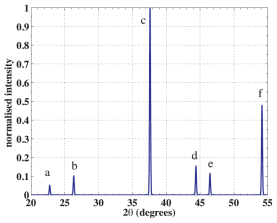


PrO_2: the Pr atoms form the fcc lattice and O atoms fill gaps, the basis is:

$$\text{(Pr) at } [0,0,0]$$
$$\text{(O) at } [1/4,1/4,1/4] \text{ and } [1/4,1/4,3/4]$$

$$S_{(hkl)} = \underbrace{\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right]}_{\text{Structure factor for the fcc lattice, gives 4 for every allowed scattering point}} \underbrace{\left[b_{Pr} + b_O \left(e^{i(\pi/2)(h+k+l)} + e^{i(\pi/2)(h+k+3l)}\right)\right]}_{\text{Structure factor for the basis}}$$

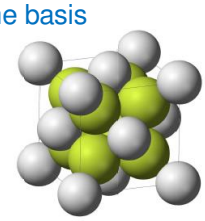
Neutron scattering: powder diffraction from PrO_2



$$I_{\{hkl\}} \propto M_{\{hkl\}} |S_{\{hkl\}}|^2$$

$$S_{(hkl)} = \underbrace{\left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}\right]}_{\text{Structure factor for the fcc lattice}} \underbrace{\left[b_{Pr} + b_O \left(e^{i(\pi/2)(h+k+l)} + e^{i(\pi/2)(h+k+3l)}\right)\right]}_{\text{Structure factor for the basis}}$$

First term will be zero unless *h,k,l* are either all odd or all even (gives value of 4 for each allowed *h,k,l*). Can write:



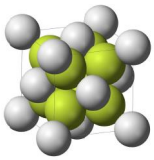
$$I_{\{hkl\}} = CM_{\{hkl\}} \left|b_{Pr} + b_O \left(e^{i(\pi/2)(h+k+l)} + e^{i(\pi/2)(h+k+3l)}\right)\right|^2$$

C is a constant (including the factor of 4^2 for the fcc structure factor)

Neutron scattering: powder diffraction from PrO_2

$$I_{\{hkl\}} = CM_{\{hkl\}} \left| b_{Pr} + b_O \left(e^{i(\pi/2)(h+k+l)} + e^{i(\pi/2)(h+k+3l)} \right) \right|^2$$

Can create a table, predicted intensity and measured



Scattering Intensity			
peak	$\{hkl\}$	$I_{\{hkl\}}/C \propto M\|S\|^2$	Measured Intensity
a	111	$8\,b_{Pr}^2$	0.05
b	200	$6\,[b_{Pr} - 2b_O]^2$	0.1
c	220	$12\,[b_{Pr} + 2b_O]^2$	1.0
d	311	$24\,b_{Pr}^2$	0.15
e	222	$8\,[b_{Pr} - 2b_O]^2$	0.13
f	400	$6\,[b_{Pr} + 2b_O]^2$	0.5

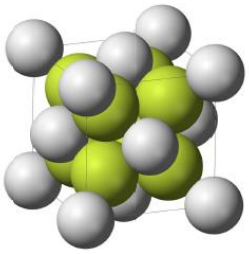
From analytic expressions, predict $I_d = 3I_a$ $I_c = 2I_f$ $I_e = \frac{4}{3} I_b$ Consistent with measured intensities

$$\frac{I_c}{I_a} = \frac{12[b_{Pr} + 2b_O]^2}{8\,b_{Pr}^2} = 20$$

Neutron scattering: powder diffraction from PrO_2

Can solve

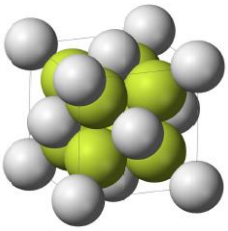
$$\frac{I_c}{I_a} = \frac{12[b_{Pr} + 2b_O]^2}{8\,b_{Pr}^2} = 20$$



to find $b_{Pr}/b_O \approx .75$

Have used the neutron data to experimentally determine the ratio of the nuclear scattering lengths.

Neutron scattering: powder diffraction from PrO_2



Further we can calculate

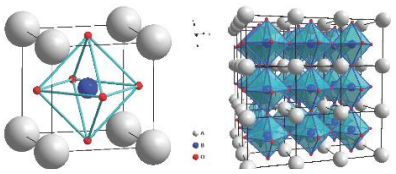
$$\frac{I_b}{I_a} = \frac{6[b_{Pr} - 2b_O]^2}{8\, b_{Pr}^2} = 2$$

which we can solve to give

$$b_{Pr} = .76\, b_O \qquad \text{or} \qquad b_{Pr} = -3.1\, b_O$$

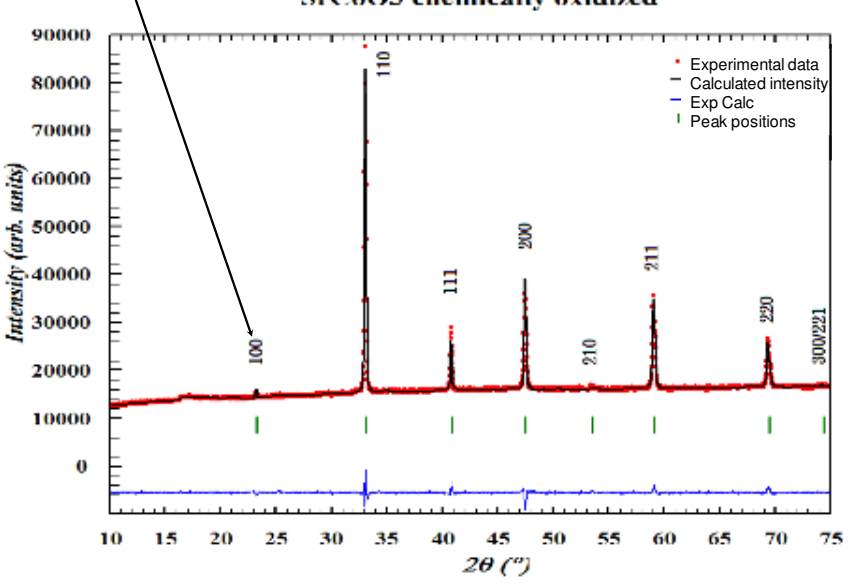
Former is compatible with what was obtained earlier (latter is not).

Powder diffraction



Compare positions with expected positions; calculate intensity and compare intensity.

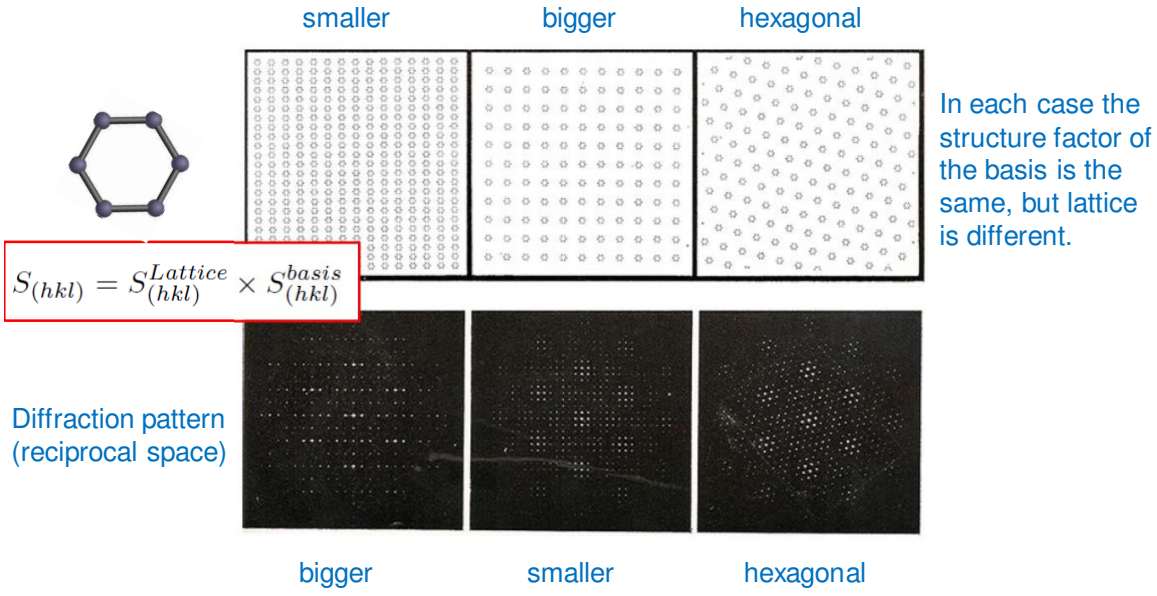
reciprocal lattice



X-ray/neutron diffraction in practice

Example of “benzene crystal” in 2D

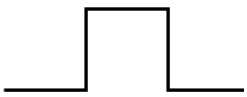
A crystal is a convolution of a basis with a Bravais lattice, therefore the Fourier transform is a product of a reciprocal Bravais lattice and the transform of the basis (structure factor).



In each case the structure factor of the basis is the same, but lattice is different.

Shape function

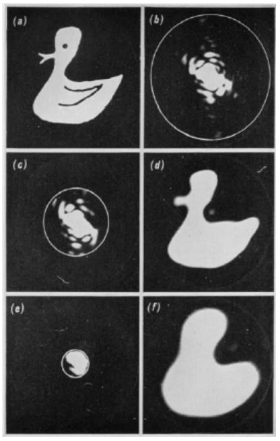
The Fourier transform of a direct lattice is only a lattice of points if the direct lattice is infinite. A finite lattice is an infinite lattice multiplied by a '**shape function**' which is unity inside the sample and zero elsewhere ('top hat function').
The Fourier transform of the finite lattice is the convolution of the infinite lattice and the transform of the shape function.
This means that each reciprocal lattice point is broadened or **smeared out**.



Small crystals therefore do not have sharp diffraction peaks.

The converse effect is seen when the diffraction pattern is transformed back to give the object.

This shows how finite collection of data in a diffraction experiment limits the information recoverable.



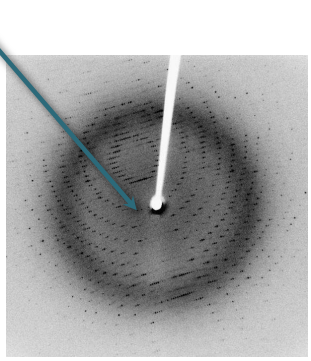
Optical Transforms
Taylor and Lipson

Advanced X-ray diffraction

- The position of the spots gives information about the reciprocal lattice and thus the Bravais lattice.
- An intensity analysis can give information about the basis.
- Even the structure of a very complicated basis can be determined (proteins...)

every spot $I(\mathbf{K} = \mathbf{G}) \propto |\rho_{\mathbf{G}}|^2$

crystallize protein →



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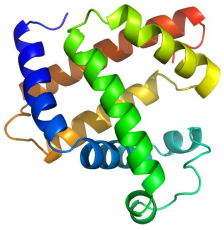


Why so many spots for a protein? – real space is big, so reciprocal space tiny!

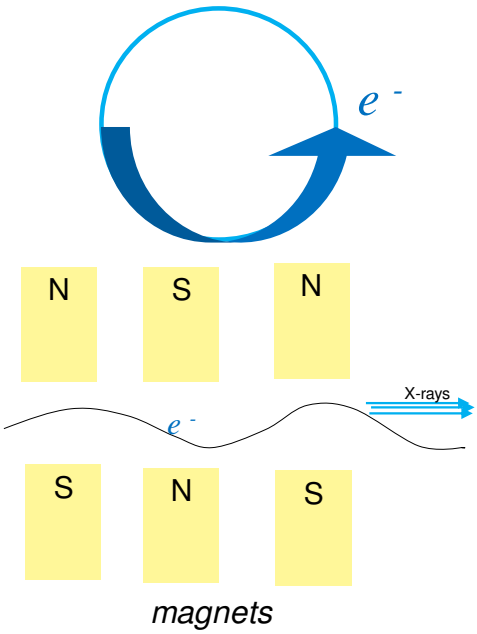
Advanced X-ray sources: synchrotron radiation

SPring-8, Japan

Australian synchrotron

- A highly collimated and monochromatic beam is needed for protein crystallography.
- This can only be provided by a synchrotron radiation source.

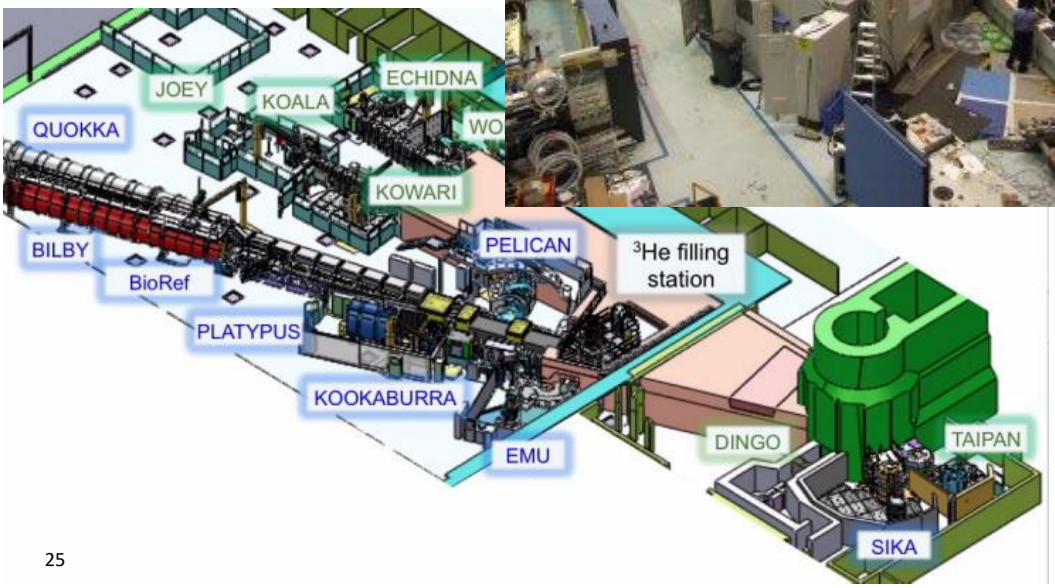
Producing X-rays at a synchrotron



Electrons accelerated around the ring at energy in the GeV range.
To get X-rays, electron beam is passed through a series of magnets, called an “undulator” or a “wiggler”
These accelerate the electrons so that they emit radiation that is highly collimated and well defined in frequency.

If want to specify the frequency (wavelength) more precisely, then the X-rays are diffracted off a known crystal that will pick out particular wavelengths, called a “diffraction grating”.

ANSTO: Australian Centre for Neutron Scattering



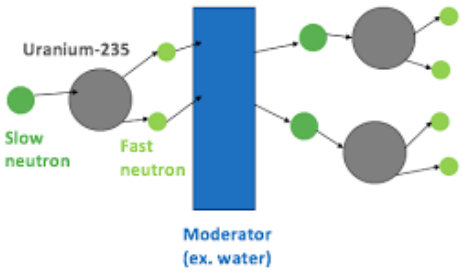
Diamond synchrotron light source

ISIS spallation neutron facility

Rutherford-Appleton Lab in Oxfordshire UK

Producing neutrons

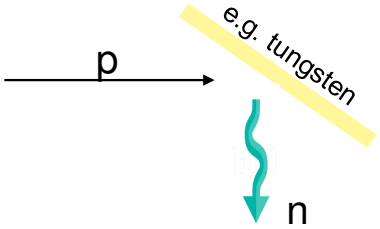
Nuclear reactor



A nuclear reactor is driven by the splitting of atoms, a process called fission, where a particle (a 'neutron') is fired at an atom, which then fissions into two smaller atoms and some additional neutrons

When a slow neutron collides with a fissile material like Uranium-235, it produces fast neutrons. The moderator will then slow these fast neutrons, and produce more slow neutrons to continue the nuclear chain reaction. When this process is repeated the fissile events are doubled each time

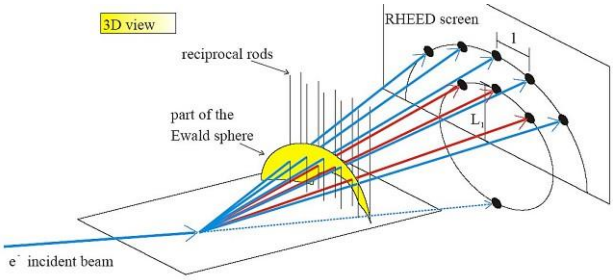
Spallation facility

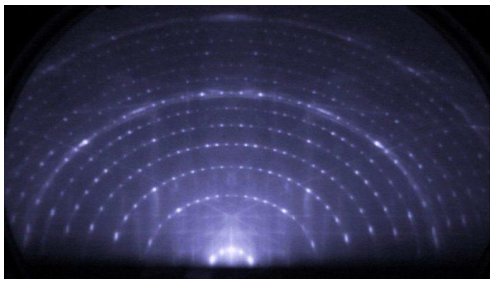


Protons are accelerated at GeV energies and hit a target knocking out neutrons.

A modern facility could produce about 10^{16} neutrons/(s cm^2) (the flux or brightness).

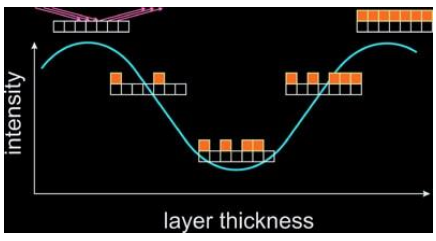
Reflection High Energy Electron Diffraction (RHEED)

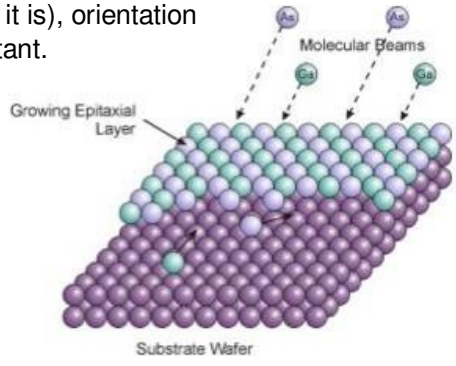




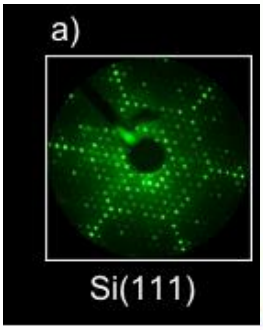
4-50 keV electrons "grazing incidence", angle 1-4°

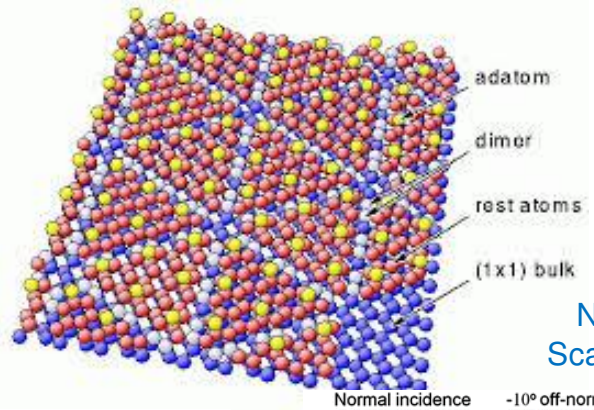
Used to characterize the surface of a crystalline material, e.g., growing GaAs – can monitor growth *in situ* and measure how many layers you have (thickness) and quality of surface (how rough it is), orientation of crystal, lattice constant.





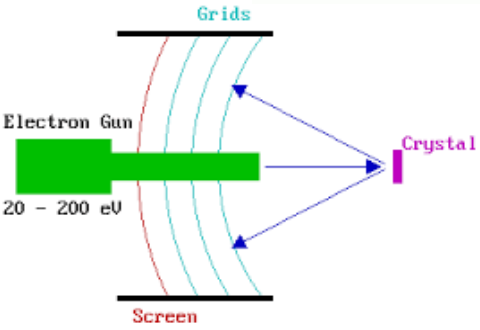
Low Energy Electron Diffraction (LEED)

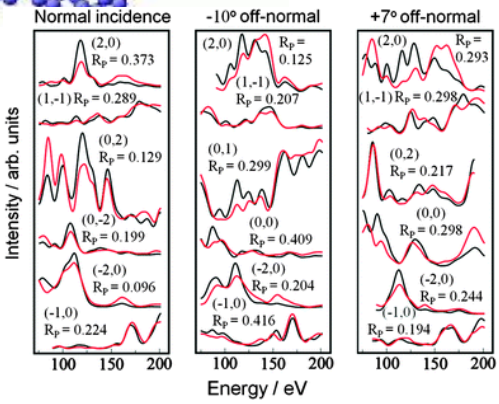




Si(111)-7x7

Need Multiple Scattering Theory





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End

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