CMP
Lecture 7

School of Physics
The University of Sydney
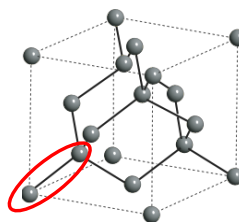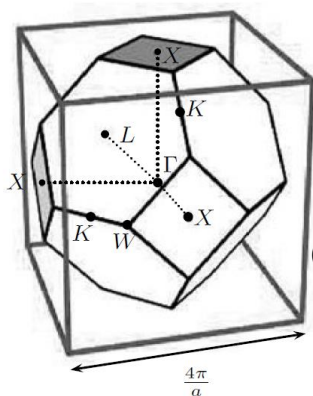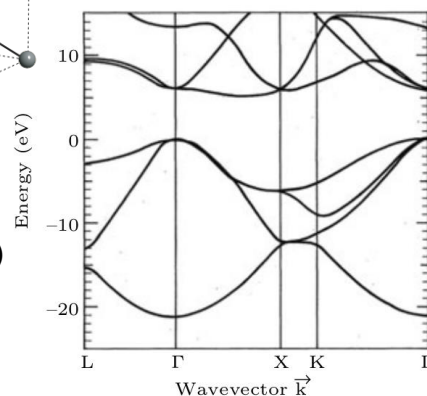
THE UNIVERSITY OF
SYDNEY

Electronic waves in crystals in three dimensions

Recall first Brillouin Zone (BZ)
of FCC lattice

Can plot the dispersion
relation, E($\mathbf{k}$),
("*electronic band structure*")
of diamond which has an
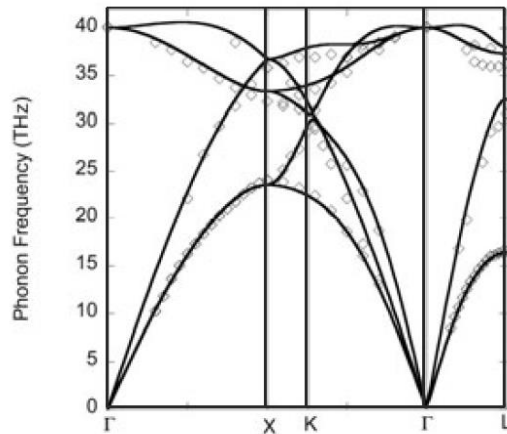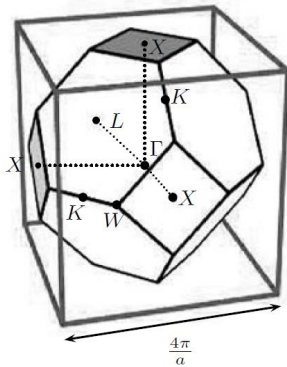fcc lattice with a diatomic
basis.

Displaying a 3D spectrum by plotting several single-line cuts through reciprocal space.

Notice lowest band is quadratic at centre of BZ i.e. $\hbar^2 k^2/(2m^*)$

m^* is the "effective mass" (more on that later)

Recall, for a completely free electron $\epsilon_0(\mathbf{k}) = \dfrac{\hbar^2|\mathbf{k}|^2}{2m}$

Phonon spectrum of diamond

Phonon spectrum of diamond (points are from experiment, solid line is a modern theoretical calculation).

Since diamond has a unit cell with two atoms (fcc with basis of two) there are 6 modes of oscillation per k-point (3 directions of motion times 2 atoms per unit cell). At the Gamma point, there are 3 acoustic modes. Higher one being longitudinal, lower 2 transverse. Other 3 modes at higher energy are the optical modes.

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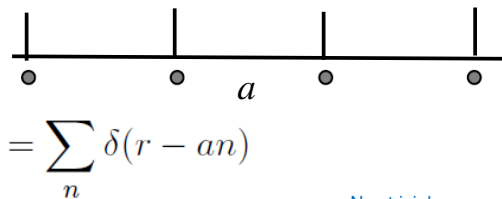# Reciprocal lattice as Fourier transform

Oxford Basics, Ch. 13.1.3

The reciprocal lattice can be thought of as being a Fourier transform of the direct lattice.

- Consider 1D, direct lattice given as $R_n = an$ with density of lattice points/ atoms represented by delta-function: $\rho(r) = \sum_n \delta(r - an)$

Taking the Fourier transform gives

Non-trivial; known as Poisson resummation formula

$$\mathcal{F}[\rho(r)] = \int dr e^{ikr} \rho(r) = \sum_n \int dr e^{ikr} \delta(r - an) = \sum_n e^{ikan} = \frac{2\pi}{a} \sum_m \delta(k - 2\pi m/a)$$

see $e^{ikan} = 1$ if $k = 2\pi m/a$ i.e. if it is a point on the reciprocal lattice;
if $k \neq 2\pi m/a$ then term oscillates and sum goes to zero.

- In two or three dimensions we have (D represents the dimension):

V = volume of unit cell

$$\mathcal{F}[\rho(\mathbf{r})] = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = \frac{(2\pi)^D}{V} \sum_{\mathbf{G}} \delta^D(\mathbf{k} - \mathbf{G})$$

So FT of real lattice generates the reciprocal lattice

Sum over lattice points of direct lattice   *Sum over points of reciprocal lattice*

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Reciprocal lattice as Fourier transform

δ^D is a D-dimensional delta function, e.g.,

$$\delta^2(\mathbf{r} - \mathbf{r_0}) = \delta(x - x_0)\delta(y - y_0) \text{ where } \mathbf{r} = (x, y)$$

Fourier transform of any periodic function $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R})$
e.g. electron density at point $\mathbf{r}$ in the lattice:

$$\mathcal{F}[\rho(\mathbf{r})] = \int \mathbf{dr}\, e^{i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r})$$

Now, let any point in space $\mathbf{r}$ be written as the sum of a lattice point $\mathbf{R}$ and a vector $\mathbf{x}$ within the unit cell, $\mathbf{r} \rightarrow \mathbf{x} + \mathbf{R}$

$$\mathcal{F}[\rho(\mathbf{r})] = \sum_{\mathbf{R}} \int_{unit-cell} \mathbf{dx}\, e^{i\mathbf{k}\cdot(\mathbf{x}+\mathbf{R})}\rho(\mathbf{x}+\mathbf{R}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int_{unit-cell} \mathbf{dx}\, e^{i\mathbf{k}\cdot\mathbf{x}}\rho(\mathbf{x})$$

$$\mathcal{F}[\rho(\mathbf{r})] = \frac{(2\pi)^D}{V} \sum_{\mathbf{G}} \delta^D(\mathbf{k} - \mathbf{G})S(\mathbf{k})$$

Structure factor
$$S(\mathbf{k}) = \int_{unit-cell} \mathbf{dx}\, e^{i\mathbf{k}\cdot\mathbf{x}}\rho(\mathbf{x})$$
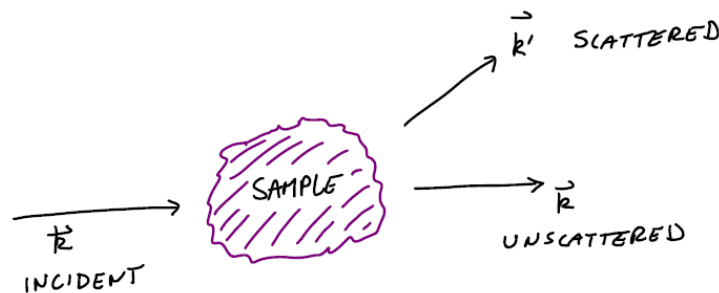
Important for later – scattering!

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Wave scattering by crystals
X-ray diffraction
Neutron diffraction

Generic scattering experiment

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Diffraction of waves by crystals

- The structure of a crystal can be determined by studying the diffraction pattern of a beam of radiation incident on the crystal.

- Beam diffraction takes place only in certain specific directions, much as light is diffracted by a grating.

- By measuring the directions of the diffraction and the corresponding intensities, one obtains information concerning the crystal structure responsible for diffraction.

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X-rays

- X-rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen and were so named because their nature was unknown at the time.

- He was awarded the Nobel prize for physics in 1901.

Wilhelm Conrad Röntgen
(1845-1923)

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X-ray properties

- X-rays are invisible, highly penetrating electromagnetic radiation of much shorter wavelength (higher frequency) than visible light. The wavelength range for X-rays is from about 10^{-8} m to about 10^{-11} m, the corresponding frequency range is from about 3×10^{16} Hz to about 3×10^{19} Hz.
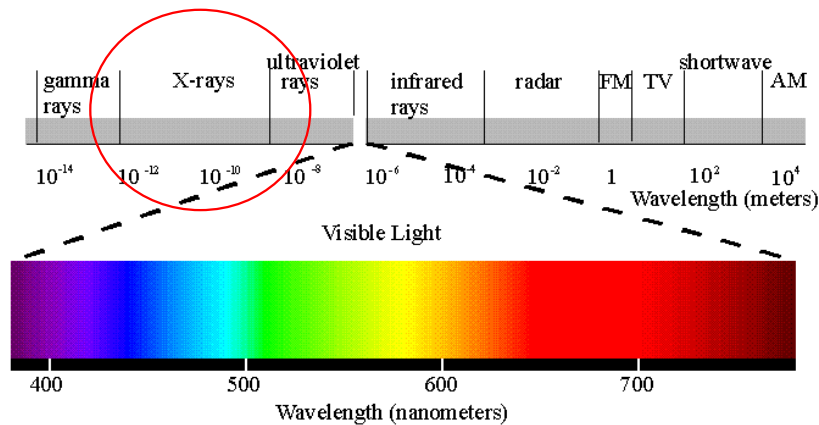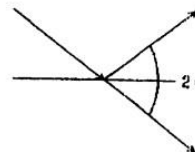
X-ray diffraction

X-ray diffraction peaks are produced by constructive interference of a monochromatic **beam** of **X-rays** scattered at specific angles from each set of lattice planes in a sample.
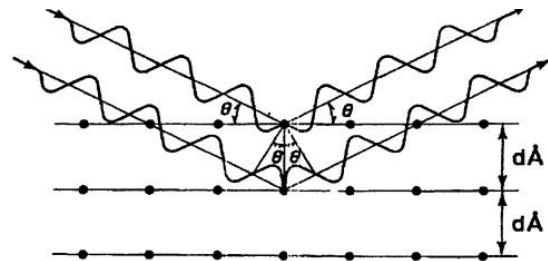
The **X-ray diffraction pattern** is the fingerprint of periodic atomic arrangements in a given material.

The X-rays penetrate deeply and many layers contribute to the reflected intensity The diffracted peak intensities are therefore very sharp (in angle)

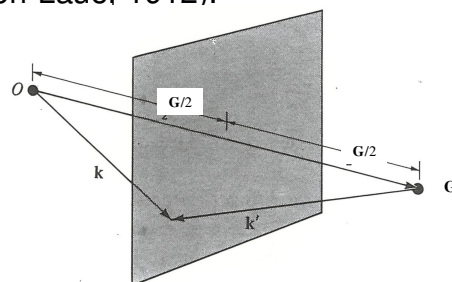Most famous use of X-ray diffraction was in unravelling the structure of the DNA molecule

X-ray diffraction

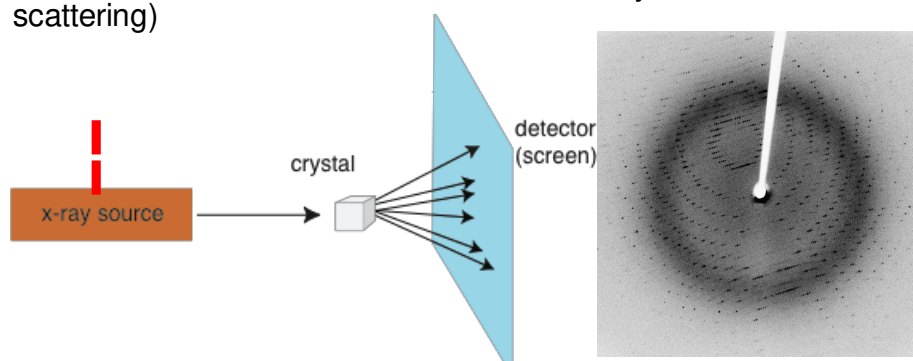- The crystals can be used to diffract X-rays (von Laue, 1912).

$$\mathbf{k'} - \mathbf{k} = \mathbf{G}$$

Different direction but same length (elastic scattering)

**Laue condition**/equation or conservation of crystal momentum

The Ewald construction

For an experiment, in this way one can immediately see in which direction one expects to see diffracted X-rays - this is a very exclusive condition!

Laue condition $\quad \mathbf{k'} - \mathbf{k} = \mathbf{G}$ $\qquad$ if **G** is a rec. lat. vec.

- Draw (cut through) the reciprocal lattice.
- Draw a **k** vector corresponding to the incoming X-rays which ends in a reciprocal lattice point.
- Draw a circle around the origin of the **k** vector.
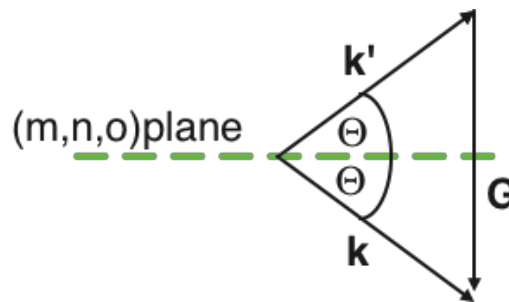- The Laue condition is fulfilled for all vectors **k'** for which the circle hits a reciprocal lattice point.
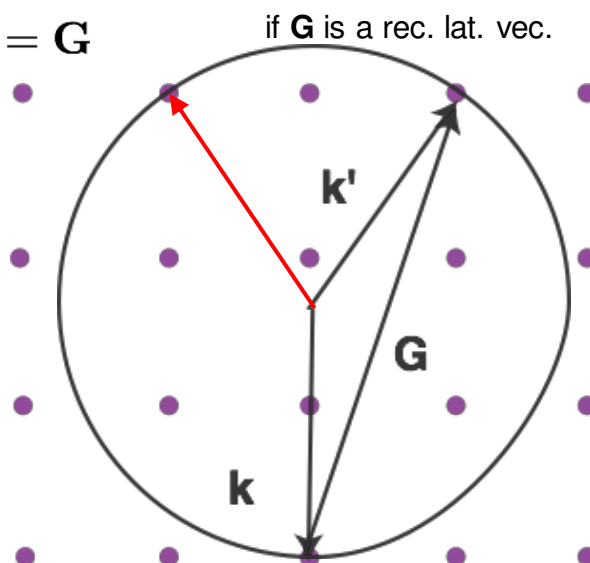
Relation to lattice planes / Miller indices

The vector

$$\mathbf{G} = m\mathbf{b_1} + n\mathbf{b_2} + o\mathbf{b_3}$$

is the normal vector to the lattice planes
with Miller indices (*m,n,o*)

$$\mathbf{k} - \mathbf{k}' = \mathbf{G}$$

Fermi's Golden Rule

Transition rate for particle scattering from $\mathbf{k}$ to $\mathbf{k}'$ due to some potential V is:
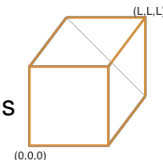
$$\Gamma(\mathbf{k}', \mathbf{k}) = \frac{2\pi}{\hbar} \left| \langle \mathbf{k}' | V | \mathbf{k} \rangle \right|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}})$$

(known from your quantum mechanics)

The matrix element is:

$$\langle \mathbf{k}' | V | \mathbf{k} \rangle = \int \mathbf{dr} \, \frac{e^{-i\mathbf{k}'\cdot\mathbf{r}}}{\sqrt{L^3}} V(\mathbf{r}) \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{L^3}} = \frac{1}{L^3} \int \mathbf{dr} \, e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} V(\mathbf{r})$$

Can see this is just the Fourier transform of the potential.
L is the linear dimension of the sample, and $\sqrt{L^3}$ normalizes the wavefunctions

If the sample is periodic, then $\mathbf{k} - \mathbf{k}'$ is a reciprocal lattice vector.

To see this, write:

$$\mathbf{r} = \mathbf{R} + \mathbf{x}$$

where $\mathbf{R}$ is a lattice vector position and $\mathbf{x}$ is a position within the unit cell.

Working

Fermi's Golden Rule

And using assumption potential is periodic $V(\mathbf{x} + \mathbf{R}) = V(\mathbf{x})$, we get

Structure factor

$$\langle \mathbf{k'}|V|\mathbf{k} \rangle = \frac{1}{L^3} \left[\sum_{\mathbf{R}} e^{-i(\mathbf{k'}-\mathbf{k})\cdot\mathbf{R}} \right] \left[\int_{unit-cell} \mathbf{dx} \; e^{-i(\mathbf{k'}-\mathbf{k})\cdot\mathbf{x}} \, V(\mathbf{x}) \right]$$

As we found earlier, for such summations of the form $\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}$, if $\mathbf{k}$ is a point of the reciprocal lattice then $e^{i\mathbf{k}\cdot\mathbf{R}}$ is unity, but if $\mathbf{k}$ is not a point of the reciprocal lattice then the summed terms oscillate and sum comes out to be zero.
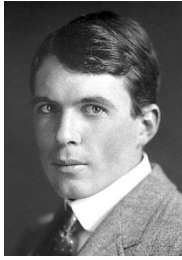
Thus, $\mathbf{k'} - \mathbf{k} = \mathbf{G}$ which is the Laue equation/condition
– statement of the *conservation of crystal momentum.*

When the waves leave
the crystal they should have $|\mathbf{k}| = |\mathbf{k'}|$
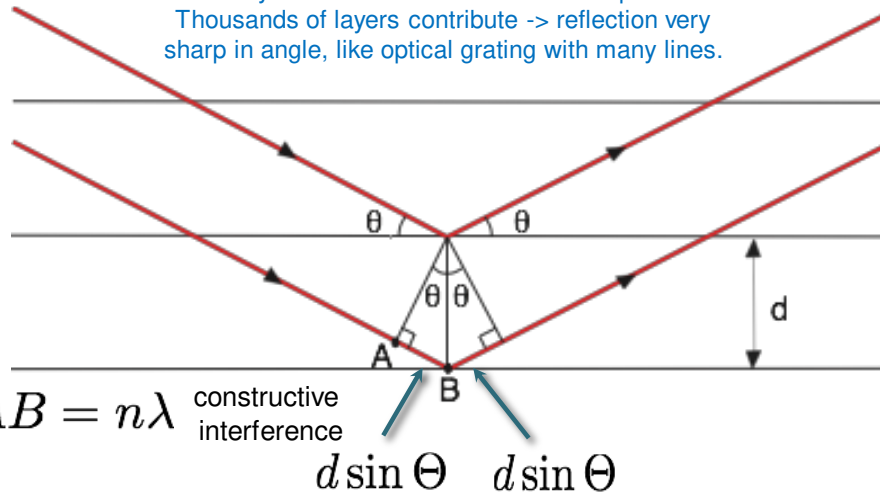which is just the conservation of energy
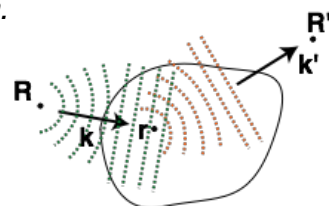
The Bragg description

The crystal is made of reflective lattice planes.
Thousands of layers contribute -> reflection very
sharp in angle, like optical grating with many lines.

path
difference $\quad 2AB = n\lambda \quad$ constructive
interference

$$d \sin \Theta \qquad d \sin \Theta$$

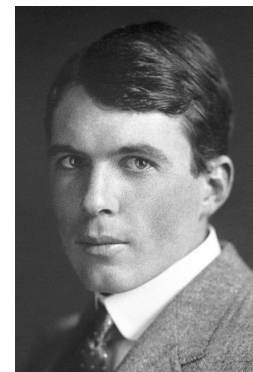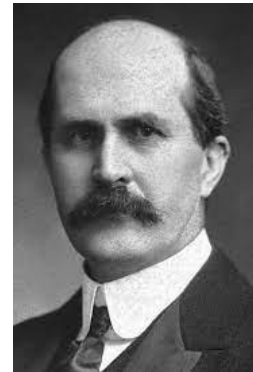$$\boxed{n\lambda = 2d \sin \Theta}$$ and this only works for $\quad \lambda < 2d$

- The Bragg condition for constructive interference holds for any number of layers.

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The Nobel Prize in Physics 1915
was awarded jointly to father
and son:
Sir William Henry Bragg and
William Lawrence Bragg
"for their services in the analysis
of crystal structure by means
of X-rays."

Youngest Nobel Prize Laureate
at 25 years old.

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Equivalence of Laue and Bragg condition
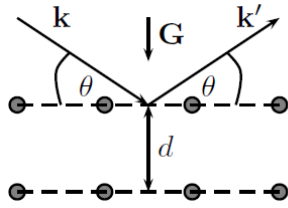
From geometry we have

$$\hat{\mathbf{k}} \cdot \hat{\mathbf{G}} = \sin \theta = -\hat{\mathbf{k}}' \cdot \hat{\mathbf{G}}$$

Suppose Laue condition satisfied: $\mathbf{k} - \mathbf{k}' = \mathbf{G}$, $|\mathbf{k}| = |\mathbf{k}'| = 2\pi/\lambda$
(λ is the wavelength)

Can rewrite Laue condition as:
$$\frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = \mathbf{G}$$

Now dot product with $\hat{\mathbf{G}}$

$$\hat{\mathbf{G}} \cdot \frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = \hat{\mathbf{G}} \cdot \mathbf{G}$$

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Equivalence of Laue and Bragg condition

$$\hat{\mathbf{G}} \cdot \frac{2\pi}{\lambda}(\hat{\mathbf{k}} - \hat{\mathbf{k}}') = \hat{\mathbf{G}} \cdot \mathbf{G}$$

$$\frac{2\pi}{\lambda}(\sin \theta + \sin \theta) = |\mathbf{G}|$$

$$\frac{2\pi}{|\mathbf{G}|}(2 \sin \theta) = \lambda$$

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

Recall: for any family of lattice planes separated by a distance d, there are reciprocal lattice vectors perpendicular to the planes, the shortest of which has a length of G=2π/d.

Laue and Bragg condition equivalent

$$\boxed{n\lambda = 2d \sin \Theta}$$

If there is a reciprocal lattice vector **G**, there is also n**G**; and we would get $n\lambda$ which is for reflecting off the spacing nd .

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Scattering amplitude

Recall we had the transition rate $\Gamma(\mathbf{k'}, \mathbf{k}) = \dfrac{2\pi}{\hbar}\left|\langle\mathbf{k'}|V|\mathbf{k}\rangle\right|^2 \delta(E_{\mathbf{k'}} - E_{\mathbf{k}})$

$$\langle\mathbf{k'}|V|\mathbf{k}\rangle = \left[\frac{1}{L^3}\sum_{\mathbf{R}} e^{-i(\mathbf{k'}-\mathbf{k})\cdot\mathbf{R}}\right]\left[\int_{unit-cell}\mathbf{dx}\; e^{-i(\mathbf{k'}-\mathbf{k})\cdot\mathbf{x}}\, V(\mathbf{x})\right]$$

$$S(\mathbf{G}) = \int_{unit-cell}\mathbf{dx}\; e^{i\mathbf{G}\cdot\mathbf{x}}\, V(\mathbf{x}) \qquad \text{called the } \textit{Structure Factor}$$

have written $\quad\mathbf{G}$ for $(\mathbf{k} - \mathbf{k'})$

Frequently take intensity, I:
$$\boxed{I_{(hkl)} \propto \left|S_{(hkl)}\right|^2}$$

The intensity of scattering off the lattice planes defined by the reciprocal lattice vector (hkl) is proportional to the square of the structure factor at this reciprocal lattice vector.

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Neutrons and X-rays Ch. 14.2 Oxford Basics

Neutrons: uncharged, scatter from nuclei. Scattering potential short-ranged, approximate as a delta-function:

$$V(\mathbf{x}) = \sum_{atom\; j\; in\; unit\; cell} f_j\; \delta(\mathbf{x} - \mathbf{x_j})$$

$\mathbf{x_j}$ position of jth atom in the unit cell

f_j is the atomic form factor, representing scattering strength, and is proportional to the "nuclear scattering length" b_j

Then,
$$V(\mathbf{x}) \sim \sum_{atom\; j\; in\; unit\; cell} b_j\; \delta(\mathbf{x} - \mathbf{x_j})$$

A parameter used in analysing nuclear scattering; radius of a sphere. Depends on nuclear isotope, spin relative to the neutron & nuclear eigenstate

And substituting into the expression for the structure factor we have

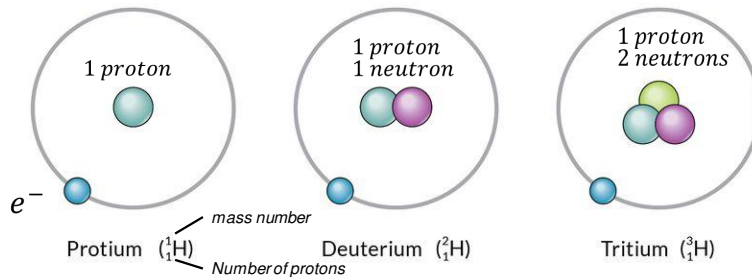$$S(\mathbf{G}) \sim \sum_{atom\; j\; in\; unit\; cell} b_j\; e^{i\mathbf{G}\cdot\mathbf{x_j}}$$

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Neutron scattering

Nuclear scattering lengths

Different for different isotopes:
Isotopes - two or more forms of the same element that contain equal numbers of protons but different numbers of neutrons in their nuclei.

Hydrogen Isotope	Scattering Length b (fm)
^{1}H	-3.7409 (11)
^{2}D	6.674 (6)
^{3}T	4.792 (27)

(1 fm=1×10^{-15} m)

Introduction to Nuclear Scattering Theory:
Roger Pynn, Los Alamos National Laboratory, USA

Neutrons and X-rays

X-rays: scatter from the electrons in a system, take $V(\mathbf{x})$ to be proportional to the electron density:

$$V(\mathbf{x}) \sim \sum_{\text{atom } j \text{ in unit cell}} Z_j \, g_j(\mathbf{x} - \mathbf{x_j})$$

where Z_j is the atomic number of atom j (number of electrons) and g_j is a short-ranged function (few angstroms, size of atom).

Substituting into the expression for the structure factor (effectively taking the Fourier transform) we have:

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

where f_j is the form factor (roughly proportional to Z_j but has some dependence on magnitude of $\mathbf{G}$).

Neutrons and X-rays

- Neutron scattering - can easily detect H atoms, can distinguish atoms with similar atomic numbers (unlike X-ray scattering).

- Neutrons have spin, so can detect whether electrons in the unit cell have spins pointing up or down (unlike X-ray scattering).

- X-rays can have smaller sample sizes - and more facilities around the world to do the experiments compared to neutron scattering facilities.

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Structure factor
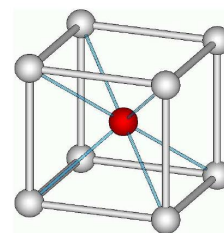
Experiments measure the intensity

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

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=	$[a/2, a/2, a/2]$

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

Let's see

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Working

So, any h,k,l will give a diffracted beam, but when h+k+l odd, will get a smaller structure factor than when h+k+l is even, giving rise to a smaller intensity of the diffraction spots.

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End

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