

PH20017/63 Condensed Matter Physics 1

Dr Simon Crampin

WH 3.41, s.crampin@bath.ac.uk

Course content:

- ▶ Crystal structure
- ▶ Electrons in solids
- ▶ Semiconductors
- ▶ Magnetism
- ▶ Crystal dynamics

These are summary notes. Annotate & expand using supplementary reading. Suggested texts listed at end.

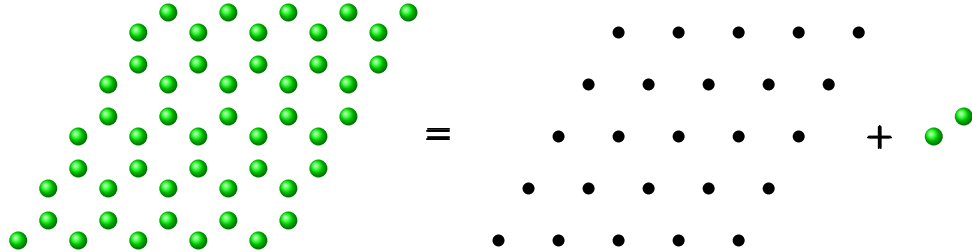
Crystal structure

1. Introduction to crystallography
2. 3D crystal structures
 - Important crystal structures
 - Specifying directions; planes
3. Experimental determination of crystal structure
 - X-rays, neutrons, electrons
 - Bragg's law
 - Rotating crystal, Debye-Scherrer and Laue methods
4. The reciprocal lattice
 - Another view of diffraction
 - Reciprocal lattice
 - Structure factor

What do we mean by crystal structure?

A crystal is a solid material whose constituents (atoms, ions, molecules, ...) are arranged in a highly ordered microscopic structure. ► Amorphous solids

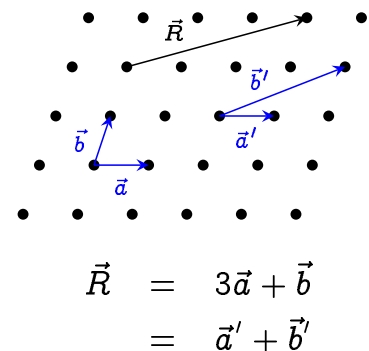
- Crystal structure = lattice + basis (decoration)



- The lattice is determined by translational symmetries.
- Crystals are classified according to the symmetry of lattice+basis.
- The crystal structure strongly influences the physical properties of a material

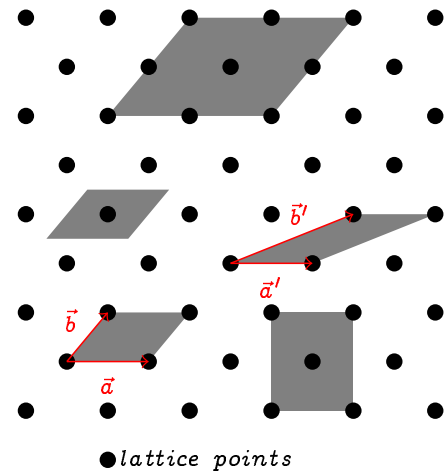
Lattices

- A **lattice** is an infinite array of points in space, each having identical surroundings to the others.
- A lattice is defined by **primitive vectors**. In 2D: \vec{a}, \vec{b} ; in 3D: $\vec{a}, \vec{b}, \vec{c}$.
 - They are not unique.
 - Their *lengths* are called **lattice constants**, or **lattice parameters**.
 - Normally given in nm or Å ($=10^{-10}$ m).
 - Lattice vectors often specified via $a, b, c, \alpha, \beta, \gamma$ (with α the angle between \vec{b} & \vec{c} etc)
- A vector connecting any two lattice points is called a **lattice vector** and can be written $\vec{R} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$ with n_i integer.



Unit cells

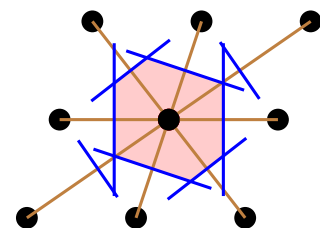
- ▶ a **unit cell** is a region of space which can be repeatedly stacked to assemble the lattice without gaps.
- ▶ a **primitive (unit) cell** is a minimum cell containing a single lattice point.
 - only count the fraction of each lattice point in the cell
 - the primitive lattice vectors span a primitive unit cell.
- ▶ a **conventional (unit) cell** is a cell chosen in preference to the primitive cell e.g. because it is more symmetric.



$$\begin{aligned} 2D : \text{area } A &= |\vec{a} \times \vec{b}| \\ 3D : \text{vol. } V &= |\vec{a} \cdot (\vec{b} \times \vec{c})| \end{aligned}$$

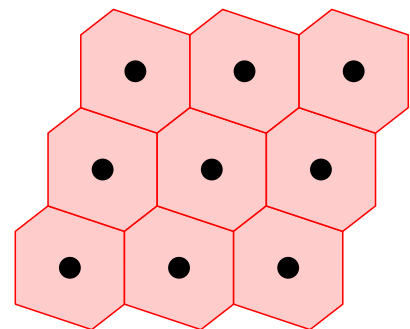
The Wigner Seitz cell

- ▶ The **Wigner-Seitz (primitive unit) cell** contains all space closer to a given lattice point than any other ▶ Wigner
 - it is a unique primitive cell with the symmetry of the lattice



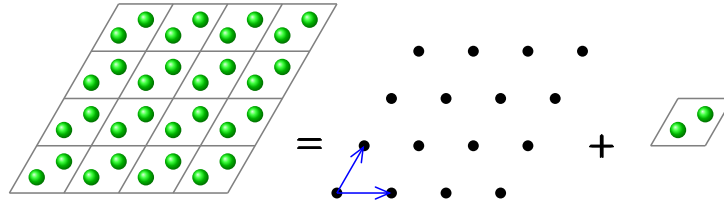
Example: Generating a Wigner-Seitz cell

- ▶ pick a lattice point
- ▶ draw lines to all nearby lattice points
- ▶ draw the perpendicular bisectors of these lines (lines in 2D; planes in 3D)
- ▶ the enclosed region is the Wigner Seitz primitive unit cell



The basis

- ▶ The **basis** is the identical assembly of atoms associated with each lattice point.



- ▶ Positions within the unit cell are normally specified as fractions of the unit cell vectors, with (u, v, w) [or (u, v) in 2D] corresponding to the location $\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}$.

above: ● at $(u,v)=(1/3,1/3)$ and ● at $(u,v)=(2/3,2/3)$.

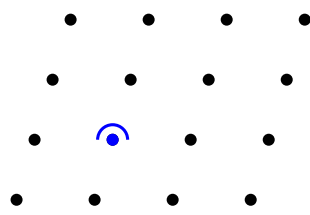
Crystal symmetries

- ▶ Crystal structures are distinguished by their symmetries. These are operations that leave the crystal unchanged.
- ▶ These include
 - translations, by lattice vector \vec{R}
 - inversion, $\vec{r} \rightarrow -\vec{r}$
 - reflection in a mirror plane
 - n -fold rotation, by $360^\circ/n$ about some point
 - combinations:
 - roto-reflection (rotation + refl. in plane \perp to rot. axis) (improper rotation)
 - glide reflection (refl. + transl. \parallel to refl. plane)
 - screw rotation (rot. + transl. \parallel to rot. axis)
- ▶ In 2D, there are only 5 symmetrically distinct **lattices**

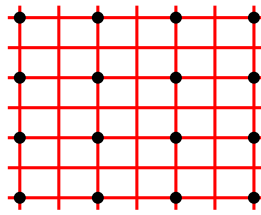
The 5 Bravais space lattices in 2D

The Bravais lattices are symmetrically distinct lattices

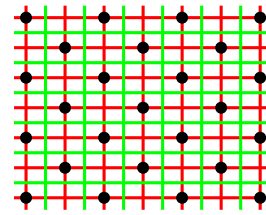
► Bravais



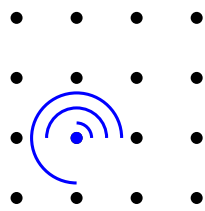
oblique
 $a \neq b, \gamma \neq 90^\circ$
 rotations by 180°



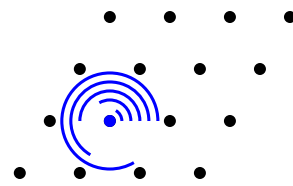
rectangular
 $a \neq b, \gamma = 90^\circ$
 mirror/reflection planes
 rotations by 180°



centered rectangular
 $a = b, \gamma \neq 90^\circ$
 glide-reflection planes
 rotations by 180°



square
 $a = b, \gamma = 90^\circ$
 rotations by $90, 180, 270^\circ$



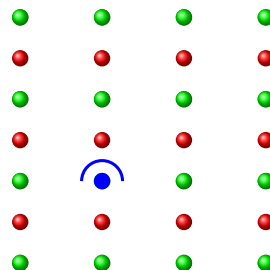
hexagonal
 $a = b, \gamma = 120^\circ$
 rotations by $60, 120, 180, 240, 300^\circ$

► Surface structure

Symmetry classification

The basis of atoms decorating the lattice also affects the symmetry.

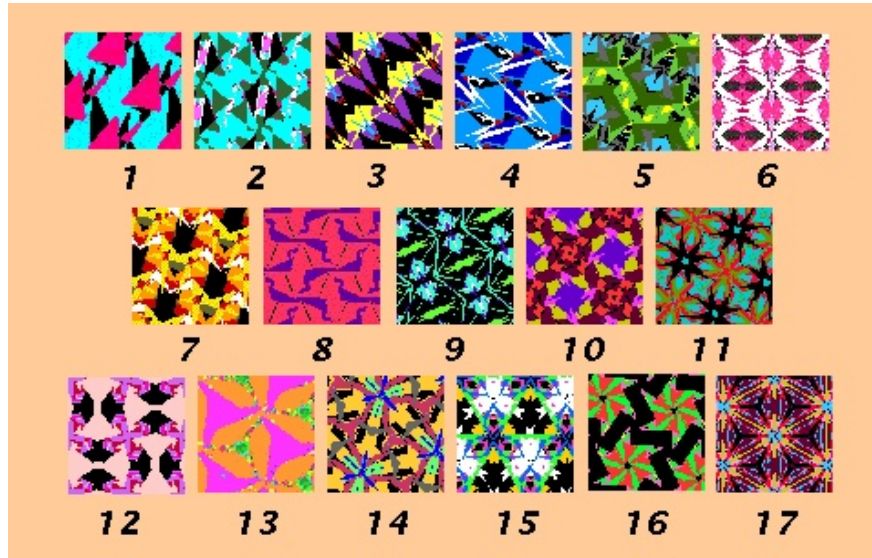
e.g. square lattice with basis: ● at $(u,v)=(0,0)$ and ● at $(u,v)=(0,1/2)$.



— the rotational symmetry is no longer that of the square lattice

Overall, there are 17 symmetrically distinct 2D crystal structures – the so-called wallpaper groups. All 2D crystals can be classified as one of these.

Wallpaper groups (not examinable!)



<http://www2.clarku.edu/~djoyce/wallpaper/>

Homework: Go to Homebase or Rossiters and confirm all wallpaper belongs to one of these groups!

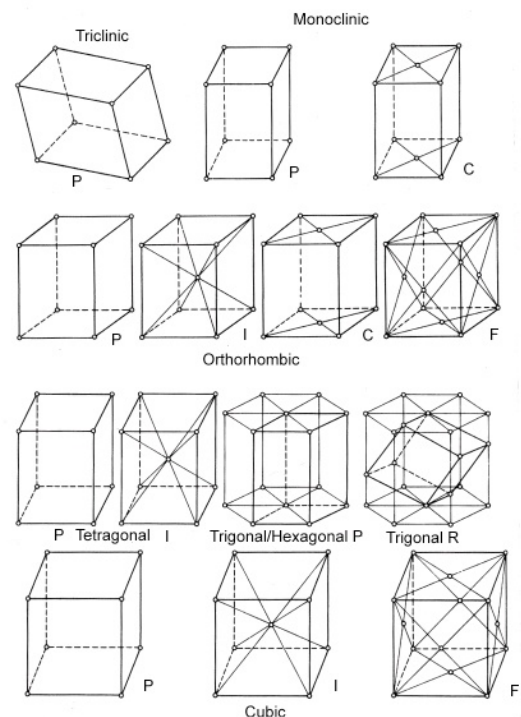
In 3D there are 14 Bravais lattices (not examinable!)

System	Conventional unit cell	Bravais lattice
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	P
Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$	P C
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P C I F
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P I
Trigonal	$a = b = c$ $120^\circ > \alpha = \beta = \gamma \neq 90^\circ$	R
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	P
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	P I F

Notes:

P=primitive, C=base-centered, I=body-centered, F=face-centered, R=rhombohedral primitive

Angles α, β, γ are those between the cell vectors, with α the angle between \vec{b} and \vec{c} etc.



Classification of 3D crystal structure

- ▶ 14 3D Bravais lattices
- ▶ 230 crystallographic groups [lattice + basis]
- ▶ 1651 magnetic groups [lattice + basis + magnetisation]

All crystals in the NIST Crystal Data Base (>170,000 materials) can be assigned to one of the 230 crystallographic groups.

Some structures occur much more frequently than others - see *Crystal Structures* RWG Wyckoff (John Wiley and Sons, NY)

We only aim to become familiar with a few!

Crystal structures of the elements

H																			He
Li	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po				

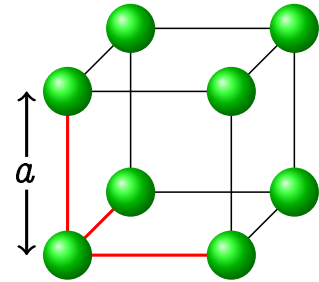
hcp fcc bcc diamond other

A few crystal structures account for a large fraction of the elemental solids

simple cubic (sc)

Primitive cell: cube, side a (the *lattice constant*)

- ▶ primitive vectors $\vec{a} = a\vec{i}$, $\vec{b} = a\vec{j}$, $\vec{c} = a\vec{k}$.
- ▶ Volume: a^3 .
- ▶ Nearest neighbour separation[†]: $R_{nn} = a$
- ▶ Packing fraction[#]: $PF = 0.52$ [▶ packing](#)
- ▶ e.g. Po



[†] $R_{nn}/2$ gives an estimate of the atomic radius

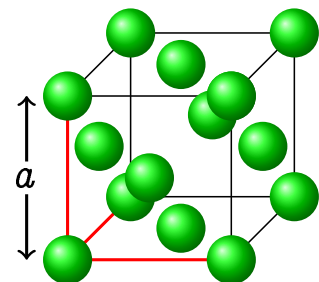
[#] Fraction of space filled by touching spheres.

— This is **NOT** the volume per atom.

face centered cubic (fcc)

Conventional view: simple cubic lattice + 4 atom basis

- ▶ The conventional unit cell is a cube, side a
- ▶ 4 atom basis: $8 \times \frac{1}{8}$ (*corner*) + $6 \times \frac{1}{2}$ (*face*)
- ▶ $(u, v, w) =$
 $(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$
- ▶ $R_{nn} = a/\sqrt{2}$, $PF =$
- ▶ e.g. Cu, Ag, Au, Ni, Pd, Pt [▶ ductility](#)



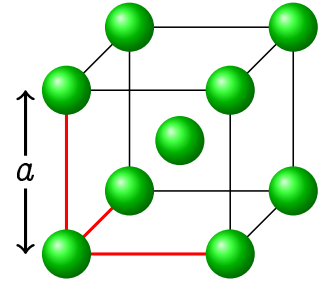
The **primitive** unit cell contains 1 atom: primitive vectors [▶ unit cell](#)

- $\vec{a} = \frac{a}{2}(\vec{i} + \vec{j})$, $\vec{b} = \frac{a}{2}(\vec{i} + \vec{k})$, $\vec{c} = \frac{a}{2}(\vec{j} + \vec{k})$, volume $V = a^3/4$
[\[check!\]](#)

body centered cubic (bcc)

Conventional view: simple cubic lattice + 2 atom basis

- ▶ The conventional unit cell is a cube, side a
- ▶ basis: 2 atoms:
 $8 \times \frac{1}{8}$ (corner) + 1×1 (inside)
- ▶ $(u, v, w) = (0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
- ▶ $R_{nn} = \sqrt{3}a/2, PF =$ ▶ packing
- ▶ e.g. alkali metals, Ba, V, Nb, Ta, W, Mo, Fe



Primitive cell contains 1 atom: primitive vectors

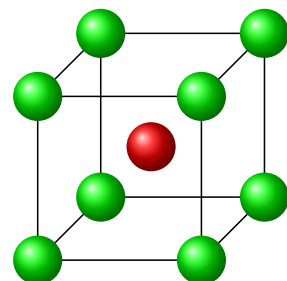
- $\vec{a} = \frac{a}{2}(\vec{i} + \vec{j} - \vec{k}), \vec{b} = \frac{a}{2}(-\vec{i} + \vec{j} + \vec{k}), \vec{c} = \frac{a}{2}(\vec{i} - \vec{j} + \vec{k})$

- ▶ volume $V = |\vec{a} \cdot (\vec{b} \times \vec{c})| = a^3/2$ [check!]

Cesium Chloride, CsCl

simple cubic lattice + 2 atom basis

- ▶ ● at $(u,v)=(0,0,0)$, ● at $(u,v) = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
- ▶ if both atom types the same = bcc
- ▶ e.g. CsCl, CsBr, CsI, TlCl, TlBr, TlI.



zincblende, diamond

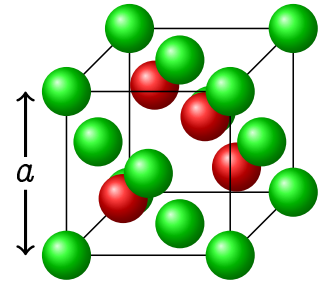
Simple cubic lattice + basis of 8 atoms[#]

► atoms at $(u, v, w) =$

● $(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$

● $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}), (\frac{3}{4}, \frac{1}{4}, \frac{3}{4}), (\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$

$8 \times \frac{1}{8}$ (corner) + $6 \times \frac{1}{2}$ (face) + 4×1 (interior)



► ●: $(0, 0, 0)$, ●: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$

$$R_{nn} = \sqrt{3}a/4, PF =$$

e.g ZnS, GaAs. [Ashcroft & Mermin list 28]

If both atoms the same species = diamond: C, Ge, Si.

Specifying directions in crystals

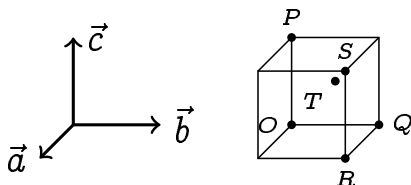
Directions are given in terms of the lattice vectors: $\vec{r} = h\vec{a} + k\vec{b} + \ell\vec{c}$.

The prefactors are scaled to integers with no common denominator.

The integers $h \ k \ \ell$ are known as **Miller indices**.

Notation: The direction of $\vec{r} = h\vec{a} + k\vec{b} + \ell\vec{c}$ is denoted $[h \ k \ \ell]$.

e.g. a cubic structure (could be sc, fcc, bcc, ...)



$$\begin{array}{ll} OP = [0 \ 0 \ 1] & OQ = [0 \ 1 \ 0] \\ OR = [1 \ 1 \ 0] & TS = [2 \ 1 \ 1] \end{array}$$

Notation: • Overbar is used for negative values e.g. $SQ = [\bar{1} \ 0 \ \bar{1}]$

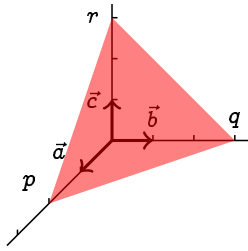
• Set of symmetrically equivalent directions is denoted $\langle h \ k \ \ell \rangle$

e.g. cubic structure: $\langle 1 \ 0 \ 0 \rangle \equiv [1 \ 0 \ 0], [\bar{1} \ 0 \ 0], [0 \ 1 \ 0]$ etc

Specifying atomic planes in crystals

Planes that lattice points lie on are also specified by Miller indices.

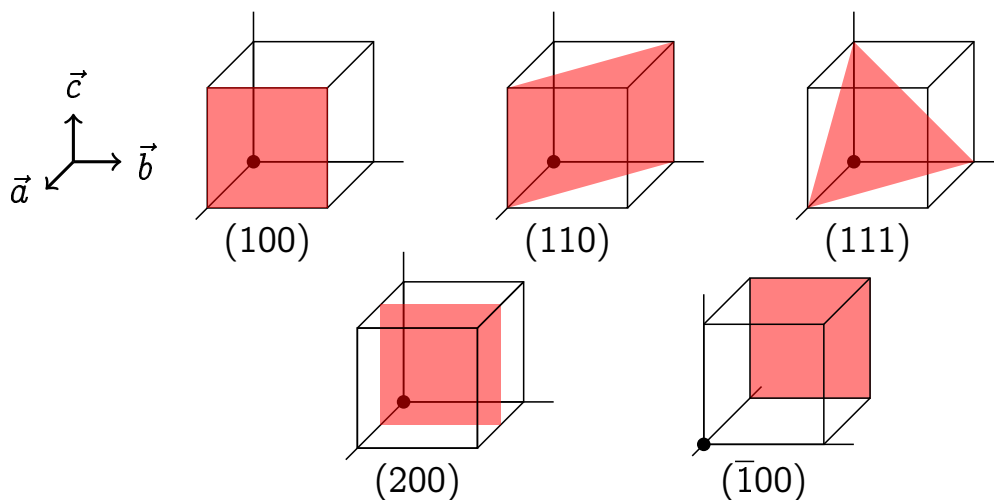
Notation: Planes are denoted by $(h \ k \ \ell)$.



- ▶ Consider a plane crossing the axes at distances p, q, r (could be ∞).
- ▶ Then $h = \alpha a/p$, $k = \alpha b/q$, $\ell = \alpha c/r$ where α (normally) chosen to give integers h, k, ℓ with no common denominator.
- ▶ In the figure, $p, q, r = 2a, 3b, 3c$, so $h = \alpha/2$, $k = \alpha/3$ and $\ell = \alpha/3$. Choosing $\alpha = 6$ gives the plane as (322) .

Notation: Set of symmetrically equivalent planes is denoted $\{h \ k \ \ell\}$
e.g. cubic structure: $\{1 \ 1 \ 1\} \equiv (1 \ 1 \ 1), (\bar{1} \ 1 \ 1), (\bar{1} \ \bar{1} \ \bar{1})$ etc

The most important planes in cubic crystals



Note: (200) parallel to (100) , and to $(\bar{1}00)$.

Experimental determination of crystal structure

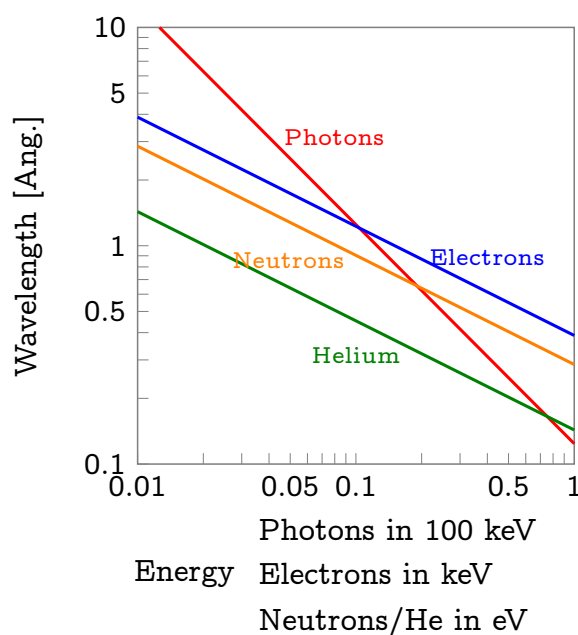
Basic idea:

- ▶ Scatter radiation/particles off sample, and measure results
- ▶ Crystal used as a 3D diffraction grating
- ▶ By analysing the scattered intensity pattern, one can determine:
 - structure, lattice parameters, composition, orientation, ...

Complemented by other specialised techniques

e.g. STM/AFM for determining surface structure

Need de Broglie wavelengths \sim atomic spacings



Prince Louis-Victor Pierre
Raymond de Broglie

Nobel Prize, 1929

*"for his discovery of the wave
nature of electrons"*

Probes

Typical numbers:

	energy E	wavelength λ	scattered by	penetration depth
X-rays	10^4 eV	1.2 \AA	electrons	$\sim \text{cm}$
neutrons	10^{-2} eV	2.8 \AA	nuclei	$\sim \text{cm}$
electrons	$\left\{ \begin{array}{ll} 10\text{-}100 \text{ eV} & \text{LEED} \\ 10^5 \text{ eV} & \text{TEM} \end{array} \right.$	$\left\{ \begin{array}{ll} \sim 1 \text{ \AA} \\ \sim 0.04 \text{ \AA} \end{array} \right.$	$\left\{ \begin{array}{ll} \text{electrons} \\ \text{\& nuclei} \end{array} \right.$	$\left\{ \begin{array}{ll} \sim \text{nm} \\ \sim \mu\text{m} \end{array} \right.$

- Strength of interaction with matter varies with probe
 - can influence choice for specific crystal structure determination

Bragg's Law

Basic analysis follows from Bragg's Law:

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

n - (integer) diffraction order

λ - wavelength of radiation

d - spacing of lattice planes

ϑ - Bragg angle of diffraction.

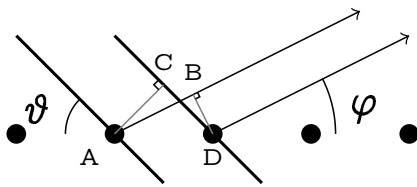
- This is a simple version of diffraction theory - see later.
- "The Bragg derivation is simple but it is convincing only because it reproduces the correct result."

[Kittel, 5th ed. p39]

► The Braggs

“Derivation” : constructive interference of waves

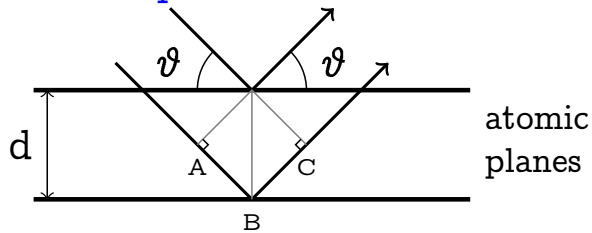
Single plane



To get waves scattered from different atoms in a plane in phase:

$$AB = CD \Rightarrow \vartheta = \varphi, \text{ i.e. reflection}$$

Stack of planes



To get waves scattered from adjacent planes in phase need $ABC = n\lambda$

$$\Rightarrow ABC = 2d \sin \vartheta = n\lambda$$

Using Bragg's Law: $2d \sin \vartheta = n\lambda$

- ▶ Bragg's Law gives the **scattering angle 2ϑ** at which n 'th-order diffraction occurs from a set of *lattice* planes, spacing d .
- ▶ $\sin \vartheta = n\lambda/(2d)$. Solution needs r.h.s. < 1 , so λ cannot be too large i.e. must be comparable to d
- ▶ We measure $\{\vartheta\}$ in experiment, and convert to $\{d\}$
- ▶ Since $\{d\}$ are characteristic of the lattice, this allows the lattice to be identified.

Experimentally exploiting Bragg's law

Satisfying the Bragg condition requires a chance occurrence, with ϑ and λ matching according to the Bragg formula.

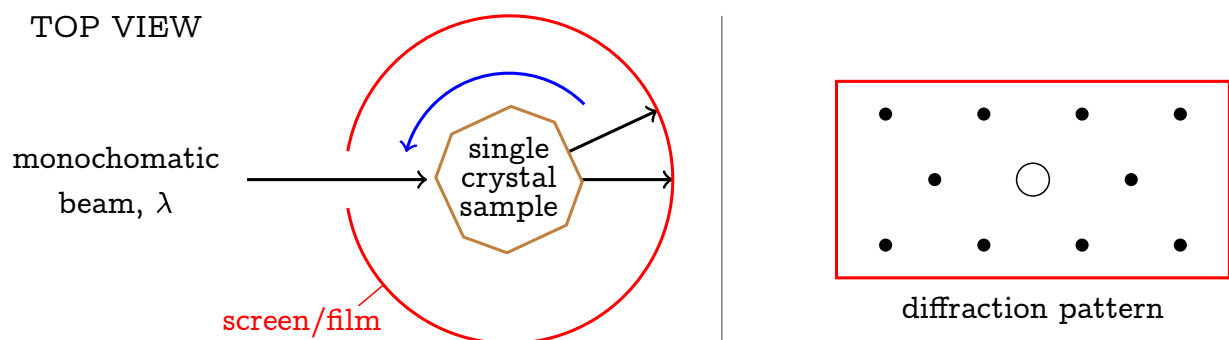
To ensure this happens, experiments scan either ϑ or λ .

We will look at:

- ▶ Rotating crystal method
- ▶ Debye-Scherrer method
- ▶ Laue method

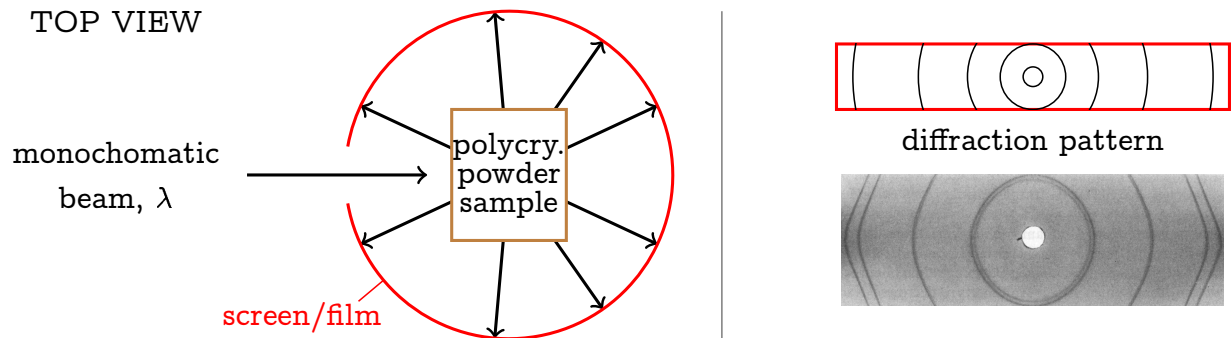
Rotating crystal method

Fixed λ , vary ϑ by rotating crystal



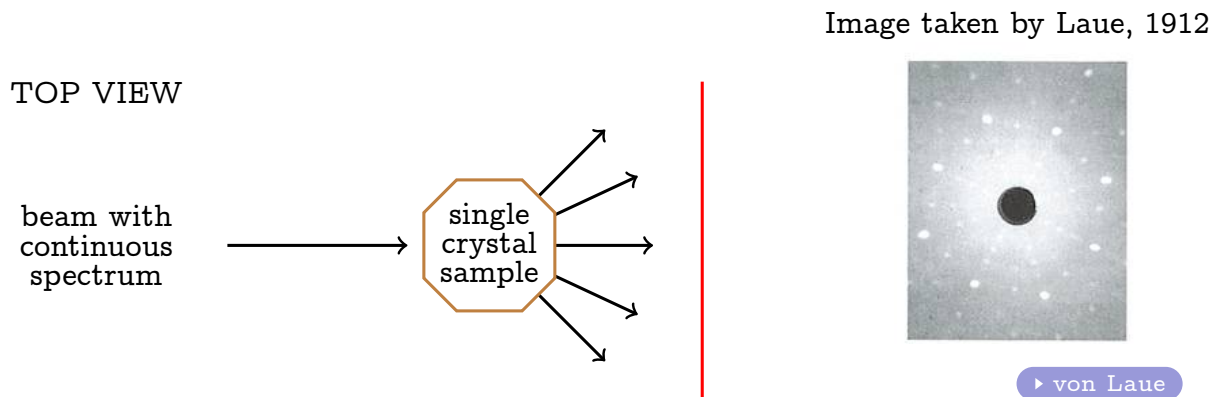
Powder method (Debye-Scherrer)

Finely divided powder target simultaneously presents all orientations of the sample. No need to rotate.



Laue Method

Single crystal on adjustable mount so e.g. sample can be adjusted to present symmetry axis to beam



The λ responsible for a given spot is unknown, so $\{d\}$ cannot be deduced. Full structure determination not possible. Instead, pattern reveals crystal symmetry, useful e.g. for orientating samples.

Example structure determination

In a powder diffraction experiment using 1.5\AA X-rays, the first five diffraction lines are at Bragg angles $\vartheta = 21.65^\circ, 25.22^\circ, 37.06^\circ, 44.96^\circ$ and 47.56° .

Is the crystal fcc, or bcc? What is the lattice constant?

Method. We use the following basic fact: [would be given in exam]

The spacing of planes responsible for diffraction in cubic lattices are given by [problem sheet]

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}} \quad \text{where} \quad \begin{cases} \text{sc} & \text{all } h, k, \ell \text{ allowed} \\ \text{bcc} & \text{only } h + k + \ell \text{ even allowed} \\ \text{fcc} & h, k, \ell \text{ all odd or all even} \end{cases}$$

Note:

This formula includes planes without atoms - e.g. sc (200). However, $n = 1$ diffraction from these planes is equivalent to $n > 1$ diffraction from planes that do contain atoms. We set $n = 1$ in Bragg's Law when using it.

Worked analysis

Inserting into the Bragg equation gives: $\sin^2 \vartheta = \frac{\lambda^2}{4a^2} \times (h^2 + k^2 + \ell^2)$

λ/a constant: the **ratio** of $\sin^2 \vartheta$ values is the **ratio** of $h^2 + k^2 + \ell^2$ values.

From the d_{hkl} expression, we see these are characteristic of the structure.

structure	$h^2 + k^2 + \ell^2$ sequence								ratios
sc	1	2	3	4	5	6	7	8	1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : ...
bcc	.	2	.	4	.	6	.	8	1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : ...
fcc	.	.	3	4	.	.	.	8	1 : 4/3 : 8/3 : ...

Here, $\sin^2 \vartheta = 0.1361, 0.1816, 0.3632, 0.4993, 0.5446$

ratio = 1.000 : 1.334 : 2.668 : 3.668 : 4.001

Comparing with the table, we identify the sequence as **fcc**

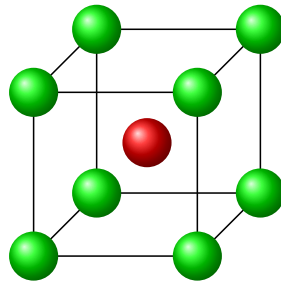
We can now associate h, k, ℓ values to each diffraction angle, and so can find the lattice parameter.

e.g. first angle: $\sin^2 21.65^\circ = 1.5^2 / (4a^2) \times 3 \Rightarrow a = 3.52 \text{\AA}$

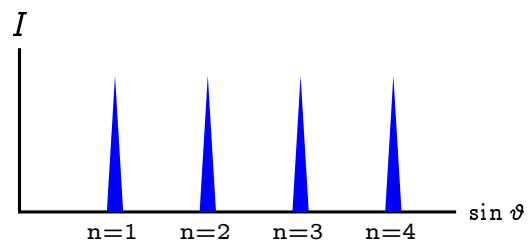
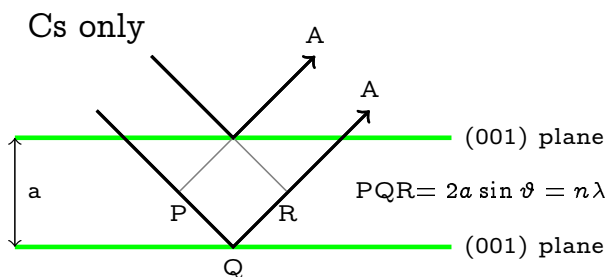
Diffracted intensities – determining the basis structure

- ▶ Different atoms scatter radiation with different amplitudes (see later).
- ▶ This means **the relative intensities of diffraction lines/spots reveal the basis.**

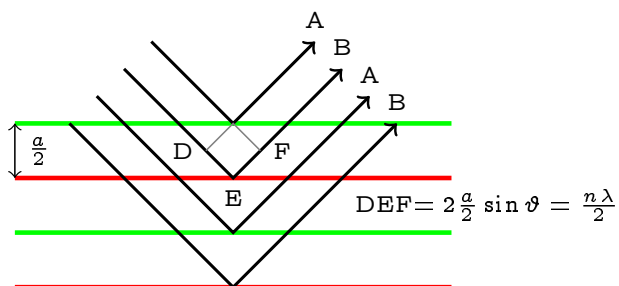
To see how, consider: CsCl



Assume Cs atoms scatter with strength A , and Cl with strength B .

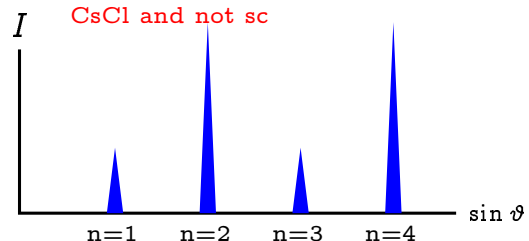


Include Cl



Radiation scattered from Cs & Cl planes is in phase if n is even, and out of phase if n is odd

the relative intensities tell us it is CsCl and not sc



Scattering amplitudes / form factors

The atomic scattering amplitudes are called **form factors**.

X-rays scatter from electrons.

- ▶ $f \sim Z$, the atomic number
- ▶ hard to observe light elements when heavy elements present
- ▶ hard to distinguish elements with similar Z (e.g. $\Delta Z = \pm 1, \pm 2$)

So although relatively cheap and easy to produce, X-rays not always optimum for crystal structure determination.

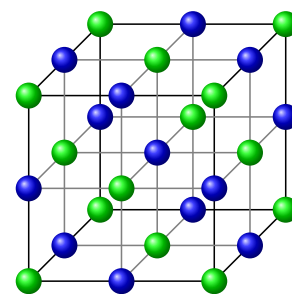
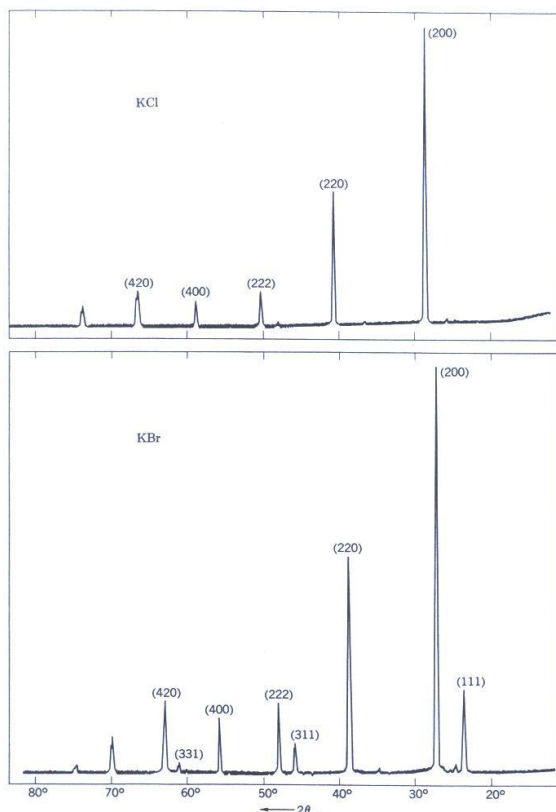


Figure 25 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a . In KBr the form factor of Br^- is quite different than that of K^+ , and all reflections of the fcc lattice are present. (Courtesy of Robert van Nordstrand.)

Neutron form factor

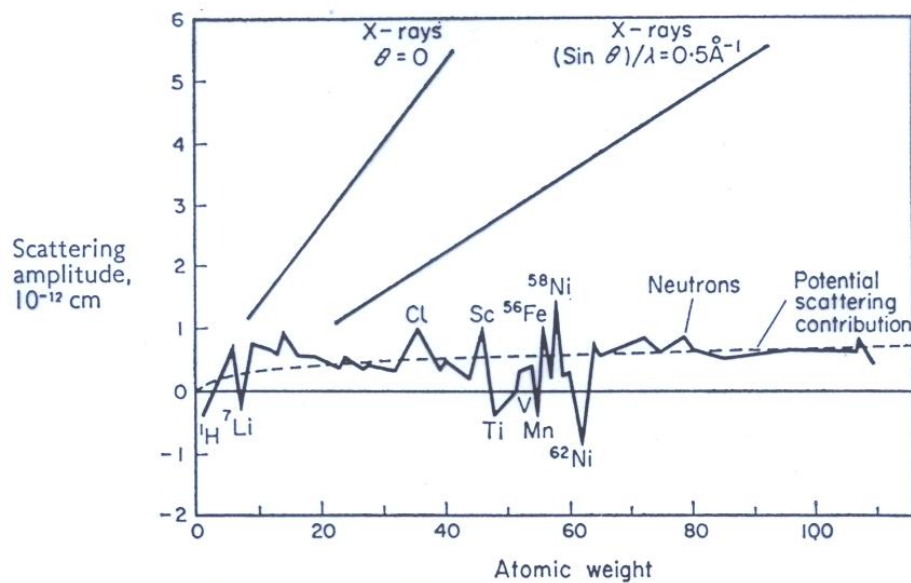


FIG. **N1** The variation of the scattering amplitude of atoms for neutrons, as a function of their atomic weight. The irregular variation is contrasted with the linear relation for X-rays (from *Research*, 1954, **7**, 297).

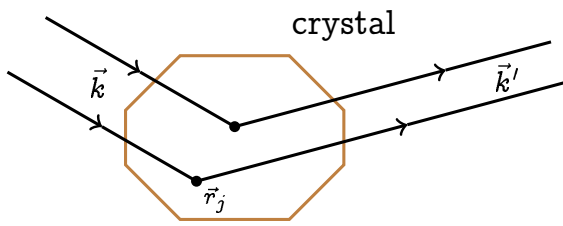
Neutrons as structure probe

Neutrons are scattered by nucleons.

- ▶ f within factor 3 – 4 for all elements
- ▶ neighbouring elements often v. different
 - size vs resonance effect
- ▶ varies with isotope → isotope substitution
- ▶ can be negative → invisible containers
- ▶ sensitive to unpaired spins → magnetic structure

These aspects can override the difficulties of sourcing suitable neutrons

Diffraction from a crystal from an atomic perspective



\vec{k}, \vec{k}' wavevectors of incident and scattered radiation

Film/screen at \vec{R}

$|\vec{R}| \gg \text{crystal dimensions}$

- ▶ Incident radiation $Ae^{i(\vec{k} \cdot \vec{r} - \omega t)}$
– a plane wave, wavelength $\lambda = 2\pi/|\vec{k}|$.
- ▶ Atom at \vec{r}_j scatters radiation towards detector at \vec{R} .
- ▶ Coherent scattering \Rightarrow energy conserved, $|\vec{k}'| = |\vec{k}|$.

Amplitude at detector due to single atom

- ▶ Three-step process

$$A_j = \underbrace{Ae^{i(\vec{k} \cdot \vec{r}_j - \omega t)}}_{\text{ampl. of incident rad. at atom } j} \times \underbrace{f_j}_{\text{atomic scattering amplitude}} \times \underbrace{\frac{e^{ik'|\vec{R} - \vec{r}_j|}}{|\vec{R} - \vec{r}_j|}}_{\text{ampl. at detector of wave emitted by atom}}$$

- ▶ If the detector is a long way from a small crystal, this can be approximated as

$$A_j = A \frac{e^{i(kR - \omega t)}}{R} \times f_j \times e^{-i(\vec{k}' - \vec{k}) \cdot \vec{r}_j}$$

Total amplitude

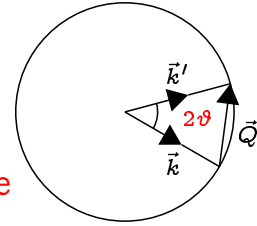
- Amplitude of radiation scattered from all atoms is

$$A_{TOT} = C \sum_j f_j e^{-i\vec{Q} \cdot \vec{r}_j}$$

$$\vec{Q} = \vec{k}' - \vec{k}$$

$$|\vec{Q}| = 2k \sin \vartheta$$

$$\vartheta = \text{Bragg angle}$$



- Consider monatomic crystal: $f_j = f$ and $\vec{r}_j = n\vec{a} + m\vec{b} + \ell\vec{c}$

$$\begin{aligned} A(\vec{Q}) &= Cf \sum_j e^{-i\vec{Q} \cdot \vec{r}_j} \\ &= Cf \sum_{n,m,\ell} e^{-i\vec{Q} \cdot (n\vec{a} + m\vec{b} + \ell\vec{c})} \\ &= Cf \left(\sum_n e^{-in\vec{Q} \cdot \vec{a}} \right) \left(\sum_m e^{-im\vec{Q} \cdot \vec{b}} \right) \left(\sum_\ell e^{-i\ell\vec{Q} \cdot \vec{c}} \right) \end{aligned}$$

What is $\sum_n e^{-in\vec{Q} \cdot \vec{a}}$?

Mathematically:

Let $S(\vartheta) = \sum_n e^{-in\vartheta}$. Then

$$Se^{-i\vartheta} = \sum_n e^{-i(n+1)\vartheta} \stackrel{n' = n+1}{=} \sum_{n'} e^{-in'\vartheta} = S$$

How can $S = Se^{-i\vartheta}$? Either $\vartheta = 2\pi \times \text{integer}$, when $e^{-in\vartheta} = 1$, or $S = 0$.

So

$$\sum_n e^{-in\vec{Q} \cdot \vec{a}} = \begin{cases} N_n & \vec{Q} \cdot \vec{a} = 2\pi h \\ 0 & \text{otherwise} \end{cases}$$

Or, physically:

S is sum of large number waves, each differing in phase by ϑ . They will interfere destructively (cancelling out) unless phase difference is integer number of cycles, in which case they all add constructively in phase.

Laue conditions

Applying to $A(\vec{Q})$,

$$A(\vec{Q}) = \begin{cases} Cf \times N_n \times N_m \times N_\ell = Cf N_{\text{cells}} & \text{if } \begin{cases} \vec{Q} \cdot \vec{a} = 2\pi h \\ \vec{Q} \cdot \vec{b} = 2\pi k \\ \vec{Q} \cdot \vec{c} = 2\pi \ell \end{cases} \\ \simeq 0 & \text{otherwise} \end{cases}$$

Laue conditions - must be satisfied for diffraction to occur

$$\begin{array}{ll} \vec{Q} \cdot \vec{a} = 2\pi h & \vec{Q} = \vec{k}' - \vec{k}, \text{ scattering vector} \\ \vec{Q} \cdot \vec{b} = 2\pi k & \vec{a}, \vec{b}, \vec{c} \text{ primitive lattice vectors} \\ \vec{Q} \cdot \vec{c} = 2\pi \ell & h, k, \ell \text{ integers} \end{array}$$

Note: For cubic crystal $\vec{a} = a\vec{i}$ etc. $\Rightarrow \vec{Q} = (2\pi/a)(h, k, \ell)$.

Then $|\vec{Q}| = 2k \sin \vartheta$ becomes $(2\pi/a)\sqrt{h^2 + k^2 + \ell^2} = 2(2\pi/\lambda) \sin \vartheta$ or $\sin^2 \vartheta = (\lambda/2a)^2 (h^2 + k^2 + \ell^2)$ — as we used before in structure determination

Reciprocal lattice

- ▶ The values of \vec{Q} that satisfy the Laue conditions form a lattice called the **reciprocal lattice**, with lattice vectors \vec{G}_{hkl}
- ▶ Points in the lattice are generated by three **primitive reciprocal lattice vectors** $\vec{A}, \vec{B}, \vec{C}$:

$$\vec{G}_{hkl} = h\vec{A} + k\vec{B} + \ell\vec{C}, \quad (h, k, \ell \text{ integers}).$$

- ▶ The primitive reciprocal lattice vectors are related to the real primitive lattice vectors: (problem sheet)

$$\vec{A} = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \quad \vec{B} = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \quad \vec{C} = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Vectors in the reciprocal lattice have dimensions $[\text{length}]^{-1}$

Real and reciprocal space

We conclude that

- ▶ Every crystal has two lattices: the “real” lattice and the reciprocal lattice.
- ▶ The reciprocal lattice is a lattice in reciprocal space - also called momentum or wave vector space.
- ▶ Diffraction experiments measure the reciprocal lattice (whereas microscopes measure the real lattice).

The Brillouin zone

The Wigner-Seitz cell of the reciprocal lattice is called the **Brillouin zone**. It can be used to understand diffraction.

From the Laue condition, diffraction occurs if $\vec{Q} = \vec{k}' - \vec{k} = \vec{G}$. This is equivalent to the statement

$$\vec{k} \cdot \vec{G} = \frac{1}{2} G^2 \quad \text{another statement of the condition for diffraction}$$

Aside: To see this, write

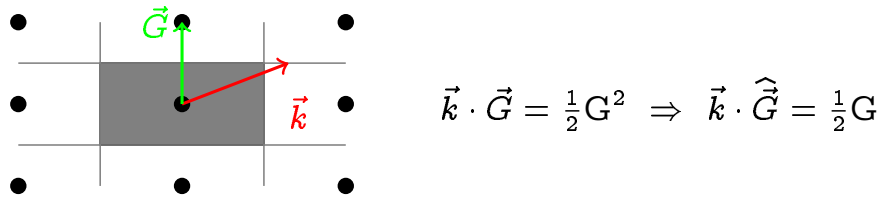
$$\begin{aligned} \vec{k}' \cdot \vec{k}' &= (\vec{k} + \vec{G}) \cdot (\vec{k} + \vec{G}) \\ &= \vec{k} \cdot \vec{k} + 2\vec{k} \cdot \vec{G} + \vec{G} \cdot \vec{G} \end{aligned}$$

Elastic scattering means $|\vec{k}'| = |\vec{k}|$ so $\vec{k}' \cdot \vec{k}' = \vec{k} \cdot \vec{k} \Rightarrow -2\vec{k} \cdot \vec{G} = G^2$

Since if \vec{G} is a reciprocal lattice vector, so too is $-\vec{G}$, we get the result above.

How can we interpret this?

Draw \vec{k} starting at the origin of the reciprocal lattice.



$\vec{k} \cdot \hat{\vec{G}}$ is the component of \vec{k} parallel to \vec{G} . We get diffraction if this is $G/2$. This means \vec{k} lies on the bisector of the line to \vec{G} .

The Wigner Seitz cell is enclosed by such bisectors.

Diffraction occurs when \vec{k} coincides with the surface of the Brillouin zone.

Electrons are also waves. We can expect important diffraction effects for electrons in crystals with wavevectors near the surfaces of the Brillouin zone. [See later in the course.]

Crystals with a basis of atoms

What if there is more than one atom per unit cell.

Crystal with n -atom basis: $j = (J, \mu)$ $J = 1, \dots, N$ labels unit cells

$\mu = 1, \dots, n$ labels basis

$$\vec{r}_j = \vec{R}_J + \vec{r}_\mu$$

$$\begin{aligned} A(\vec{Q}) &= C \sum_{J\mu} f_\mu e^{-i\vec{Q} \cdot (\vec{R}_J + \vec{r}_\mu)} = C \sum_J e^{-i\vec{Q} \cdot \vec{R}_J} \times \sum_\mu f_\mu e^{-i\vec{Q} \cdot \vec{r}_\mu} \\ &= \begin{cases} CN_{\text{cells}} \times S(\vec{Q}) & \text{Laue conditions satisfied} \\ 0 & \text{Laue conditions not satisfied} \end{cases} \end{aligned}$$

Structure factor $S(\vec{Q}) = \sum_\mu f_\mu e^{-i\vec{Q} \cdot \vec{r}_\mu}$ Influences the **relative** intensities of diffraction spots/lines

Structure factor

The Laue conditions mean $\vec{Q} = \vec{G}_{hkl}$ when diffraction occurs.

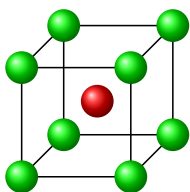
Notation: We denote $S(\vec{Q} = \vec{G}_{hkl})$ as S_{hkl} .

If atomic positions are expressed as $(u, v, w) \equiv u\vec{a} + v\vec{b} + w\vec{c}$, and $\vec{G}_{hkl} = h\vec{A} + k\vec{B} + \ell\vec{C}$, then

$$S_{hkl} = \sum_{\mu} f_{\mu} e^{-2\pi i(hu + kv + \ell w)} \quad \text{Structure factor}$$

The u, v, w values in the exponent are those for atom μ .

Structure factor example: CsCl



$$\vec{a} = a(1, 0, 0), \vec{b} = a(0, 1, 0), \vec{c} = a(0, 0, 1)$$

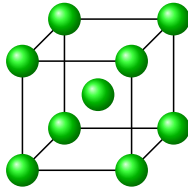
$$\text{Cs at } (0, 0, 0), \text{ Cl at } a(1/2, 1/2, 1/2)$$

$$\begin{aligned} S_{hkl} &= \sum_{\mu} f_{\mu} e^{-2\pi i(hu + kv + \ell w)} \\ &= f_{\text{Cs}} + f_{\text{Cl}} e^{-i(h+k+\ell)\pi} = \begin{cases} f_{\text{Cs}} + f_{\text{Cl}} & h + k + \ell \text{ even} \\ f_{\text{Cs}} - f_{\text{Cl}} & h + k + \ell \text{ odd} \end{cases} \end{aligned}$$

For diffraction from (100) planes: $S_{100} = f_{\text{Cs}} - f_{\text{Cl}}$

(Recall example from last lecture, illustrating how basis affects diffraction spots).

Structure factor example: bcc



If both atoms the same, bcc

$$\begin{aligned} S_{hkl} &= \sum_{\mu} f_{\mu} e^{-2\pi i(hu + kv + \ell w)} \\ &= f \times \left(1 + e^{-i(h+k+\ell)\pi}\right) = \begin{cases} f \times 2 & h + k + \ell \text{ even} \\ f \times 0 & h + k + \ell \text{ odd} \end{cases} \end{aligned}$$

Recall:	structure	sequence							
	sc	1 ₁₀₀	2 ₁₁₀	3 ₁₁₁	4 ₂₀₀	5 ₂₁₀	6 ₂₁₁	·	8 ₂₂₀
	bcc	·	2	·	4	·	6	·	8
	fcc	·	·	3	4	·	·	·	8

The structure factor explains the extinction of certain lines in going from sc to bcc.

Suggested further reading

For alternative descriptions and explanations, often at a different level, plus further problems, see

Crystal Structures

Hook and Hall	p1–19
Myers	p27–44
Kittel (5th ed.)	p3–34
Ibach & Lüth	p15–26
Ashcroft & Mermin	p64–83, p89–93, p112–129

Diffraction

Hook and Hall	p19–28
Myers	p45–58
Kittel (5th ed.)	p35–70
Ibach & Lüth	p27–46
Ashcroft & Mermin	p96–110, p86–89

