

# PH20017/63 Condensed Matter Physics 1

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Class hours:	Tuesday	12.15-13.05	Edge Theatre
	Wednesday	12.15-13.05	Edge Theatre
	Thursday	12.15-13.05	3WN 2.1

Check Moodle for latest schedule, announcements and course materials

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

# Crystal structure

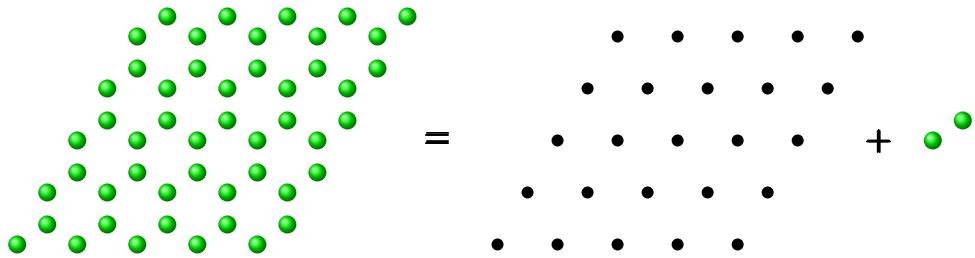
1. Introduction to crystallography
2. 3D crystal structures
  - Important crystal structures
  - Specifying directions; planes
3. Experimental determination of crystal structure
  - X-rays, neutrons, electrons
  - Bragg's law
  - Rotating crystal, Debye-Scherrer and Laue methods
4. The reciprocal lattice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

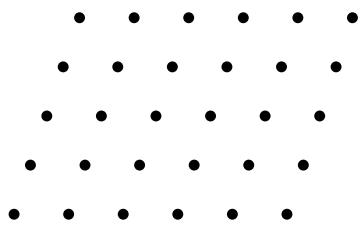
- ▶ Crystal structure = lattice + basis (decoration)



- ▶ 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:  $\vec{a}, \vec{b}, \vec{c}$ .

- *not uniq*

- *lengths = lattice const / parameter*

-  $\text{nm} / \text{\AA} (10^{-10} \text{m})$

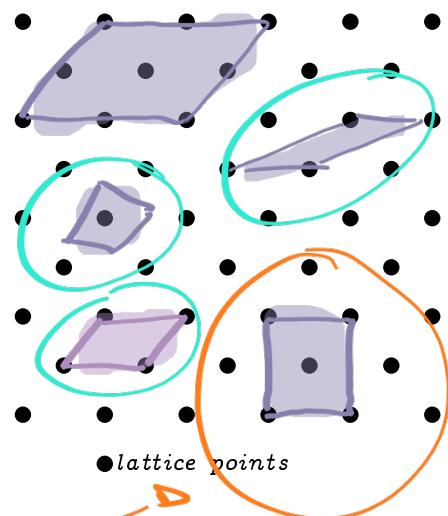
- *lattice vectors often specified with  
 $\alpha, \beta, \gamma, \alpha, \beta, \gamma, \dots$*

- ▶ 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. **not uniq**
- ▶ a **primitive (unit) cell** is a minimum cell containing a single lattice point. **primitive**
  - 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.

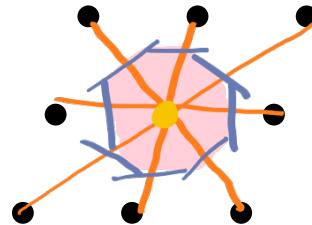


$$2D \text{ area: } A = |\vec{a} \times \vec{b}|$$

$$3D \text{ vol: } V = |\vec{a} \cdot (\vec{b} \times \vec{c})|$$

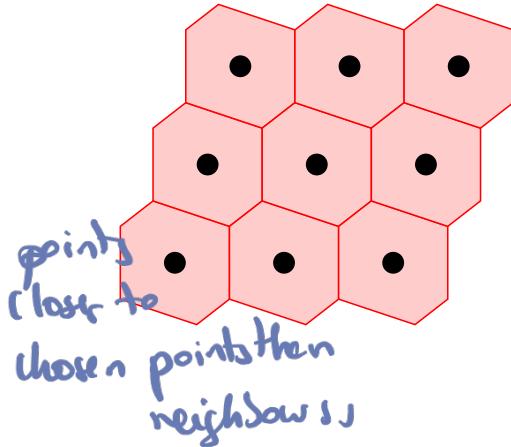
# The Wigner Seitz cell *uniquely def*

- 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



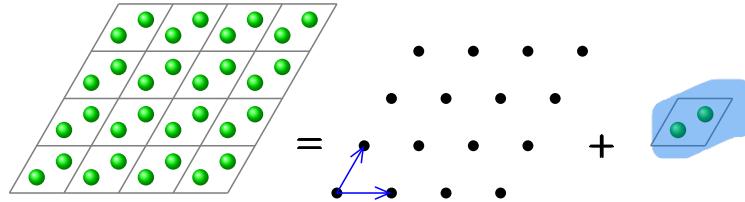
Example: Generating a Wigner-Seitz cell

- pick a lattice point
- draw lines to all nearby lattice points
- draw the perpendicular bisectors of these lines (lines in 2D; planes in 3D) *separates points closer to chosen point than neighbors*
- 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

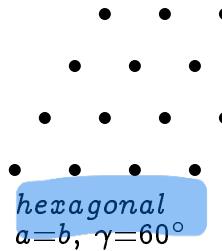
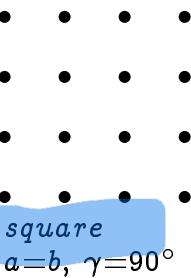
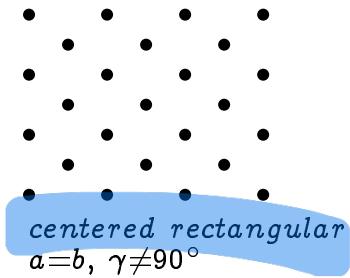
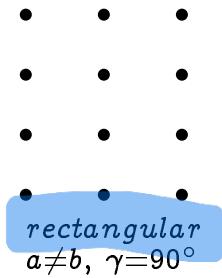
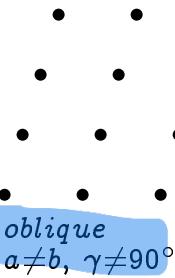
- ▶ Crystal structures are distinguished by their symmetries. These are operations that leave the crystal unchanged.
- ▶ These include
  - translations, by lattice vector  $\vec{R}$
  - inversion,  $\vec{r} \rightarrow -\vec{r}$
  - reflection in a mirror plane
  - $n$ -fold rotation, by  $360^\circ/n$  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

► CNT

# The 5 Bravais space lattices in 2D

The Bravais lattices are symmetrically distinct lattices

► Bravais

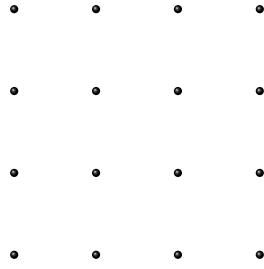


► Surface structure

# Symmetry classification

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

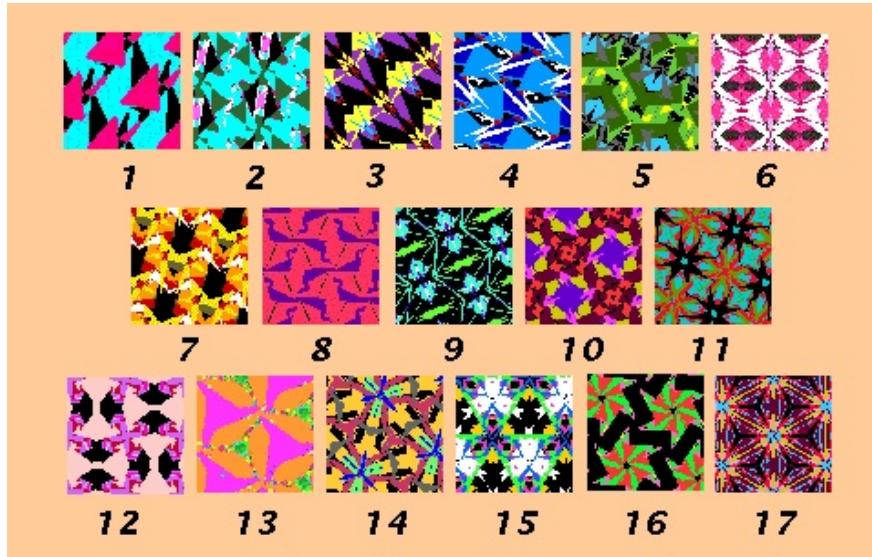
e.g. square lattice



— 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 online and confirm all wallpaper belongs to one of these groups!

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

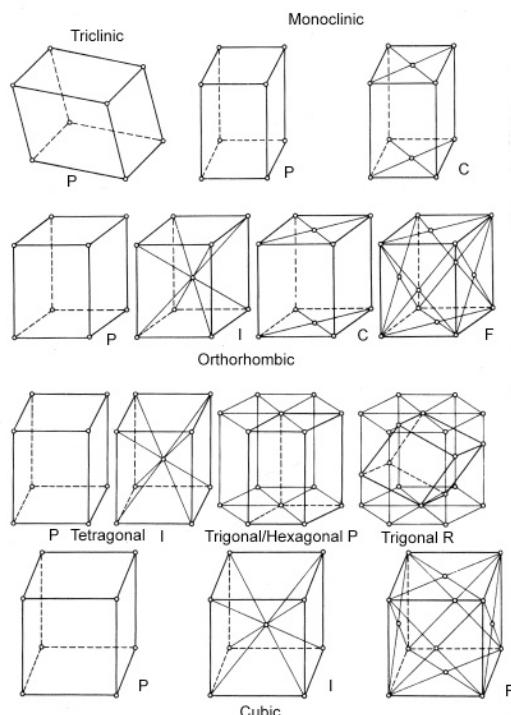
System	Conventional unit cell	Bravais lattice
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	P
Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$	P C
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P C I F
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P I
Trigonal	$a = b = c$ $120^\circ > \alpha = \beta = \gamma \neq 90^\circ$	R
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 60^\circ$	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  $\alpha, \beta, \gamma$  are those between the cell vectors,  
with  $\alpha$  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

Li Be

Na Mg

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

He

B C N O F Ne

Al Si P S Cl Ar

hcp fcc bcc diamond other

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

## simple cubic (sc)

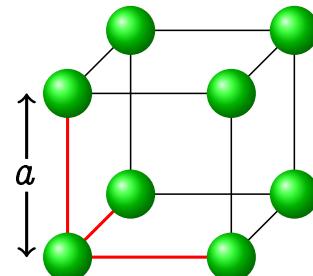
Primitive cell: cube, side  $a$  (the *lattice constant*)

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

<sup>†</sup>  $R_{nn}/2$  gives an estimate of the atomic radius

<sup>#</sup> Fraction of space filled by touching spheres.

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

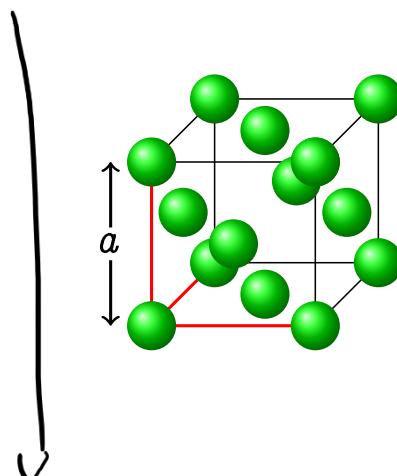


## face centered cubic (fcc)

Fill

Conventional view: simple cubic lattice + 4 atom basis

- ▶ The conventional unit cell is a cube, side  $a$
- ▶ 4 atom basis:
- ▶  $(u, v, w) =$
- ▶  $R_{nn} = a/\sqrt{2}$ ,  $PF =$
- ▶ 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)

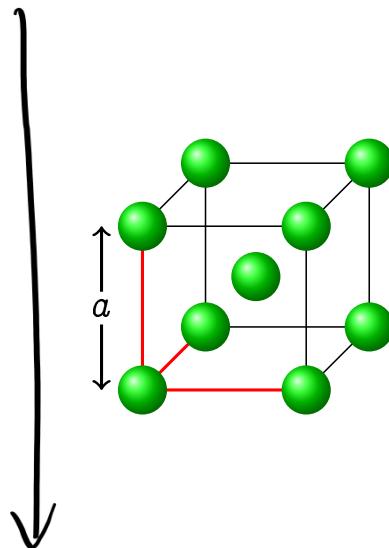
Conventional view: simple cubic lattice + 2 atom basis

- ▶ The conventional unit cell is a cube, side  $a$
- ▶ basis:
- ▶  $(u, v, w) =$
- ▶  $R_{nn} = \sqrt{3}a/2$ ,  $PF =$  ► packing
- ▶ e.g. alkali metals, Ba, V, Nb, Ta, W, Mo, Fe

Primitive cell contains 1 atom: primitive vectors

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

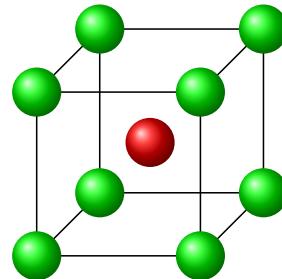
▶ volume  $V = |\vec{a} \cdot (\vec{b} \times \vec{c})| = a^3/2$  [check!]



## Cesium Chloride, CsCl

simple cubic lattice + 2 atom basis

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



[See lecture slides on Moodle for sodium chloride, NaCl.]

- missing sodium chloride   
(check ✓ have the updated  
lecture notes ver°)

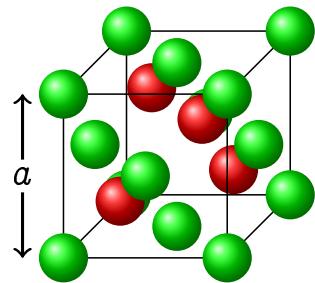
## zincblende, diamond

Simple cubic lattice + basis of atoms

- ▶ atoms at  $(u, v, w) =$



$R_{nn} = \sqrt{3}a/4$ ,  $PF =$   
e.g ZnS, GaAs. [Ashcroft & Mermin list 28]



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

# Specifying directions in crystals

[ ]

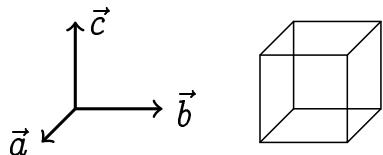
Directions are given in terms of the lattice vectors:  $\vec{r} = h\vec{a} + k\vec{b} + l\vec{c}$ .

The prefactors are scaled to integers with no common denominator.

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

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

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



**Notation:**

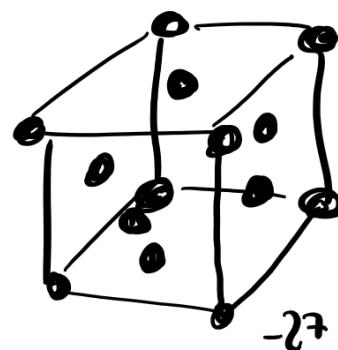
- Overbar is used for negative values
- Set of symmetrically equivalent directions is denoted  $\langle h k l \rangle$   
e.g. cubic structure:  $\langle 1 0 0 \rangle \equiv [1 0 0], [\bar{1} 0 0], [0 1 0]$  etc

(Ex) Calculate ° U should be able to do

Cu  
copper

$\downarrow$  mass density  
atomic weight 63.55  
fcc

size of Cu atom?



$$\text{mass density} = \frac{\text{mass}}{\text{vol}} = \frac{4 \times 63.55 \times 1.66 \times 10^{-27} \text{ kg}}{a^3} = 8.96 \times 10^{-3} \text{ kg} \frac{1}{10^{-24} \text{ Å}^3}$$

$$a = \sqrt[3]{\frac{422.3 \times 10^{-27} \text{ kg}}{8.96 \times 10^{-3} \text{ kg}}} = 47.13 \text{ Å}^3$$

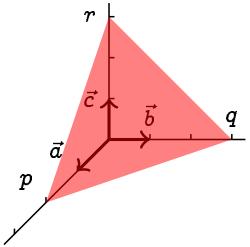
$$R_{nn} = \frac{a}{\sqrt{2}} = 2.56 \text{ Å}$$

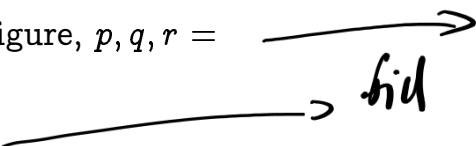
$$R = \frac{R_{nn}}{2} = 1.28 \text{ Å}$$

# Specifying atomic planes in crystals ( )

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

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



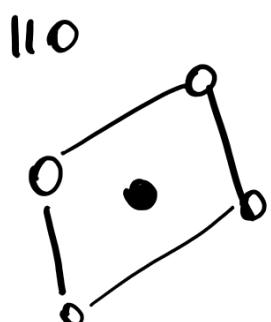
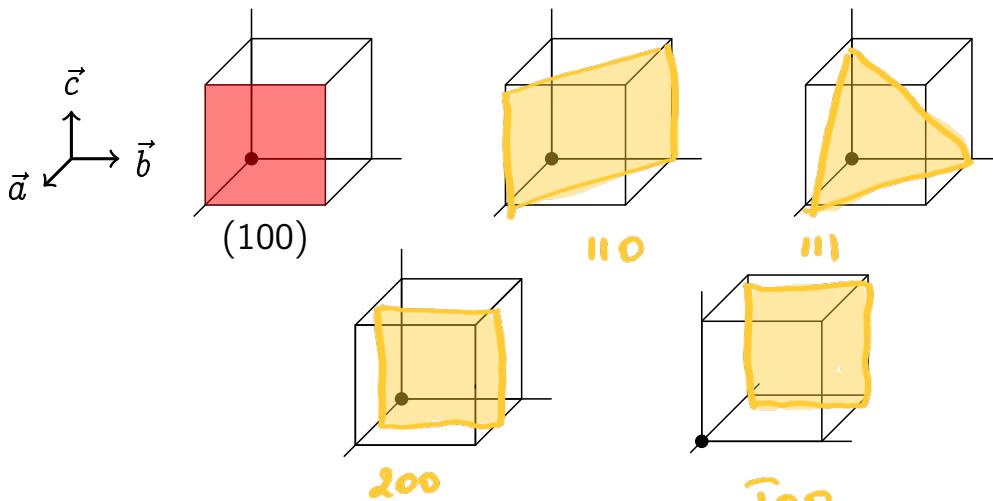
- ▶ Consider a plane crossing the axes at distances  $p, q, r$  (could be  $\infty$ ).
- ▶ Then  $h = \alpha a/p, k = \alpha b/q, l = \alpha c/r$  where  $\alpha$  (normally) chosen to give integers  $h, k, l$  with no common denominator.
- ▶ In the figure,  $p, q, r =$  

**Notation:** Set of symmetrically equivalent planes is denoted  $\{h \ k \ l\}$

e.g. cubic structure:  $\{1 \ 1 \ 1\} \equiv (1 \ 1 \ 1), (\bar{1} \ 1 \ 1), (\bar{1} \ 1 \ \bar{1})$  etc

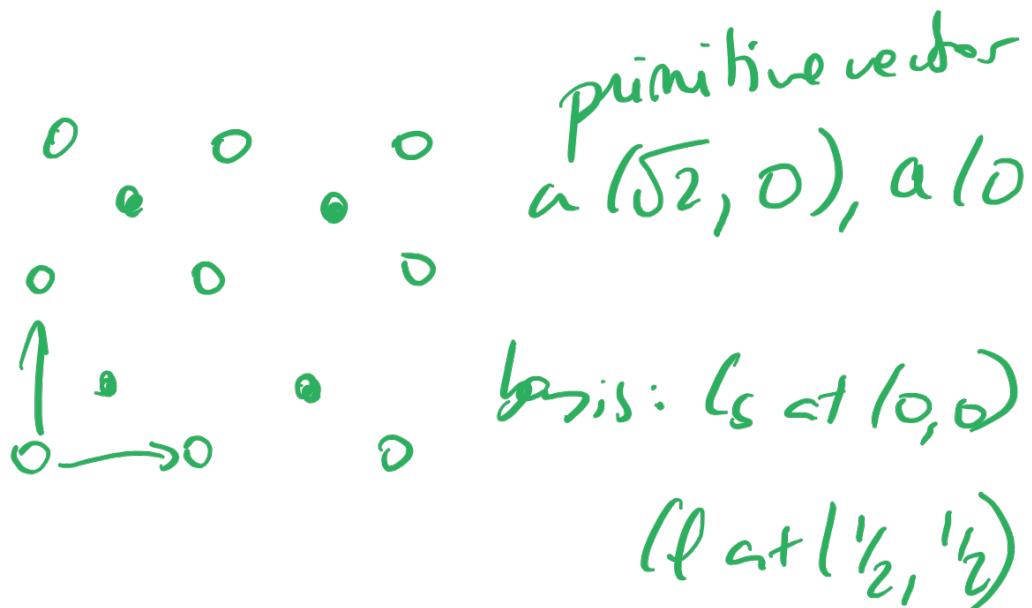
*not to memorise, will not be asked in the exam*

# The most important planes in cubic crystals



$\overline{1}00$   
bar = back plane

rectangular  
lattice



# Experimental determination of crystal structure

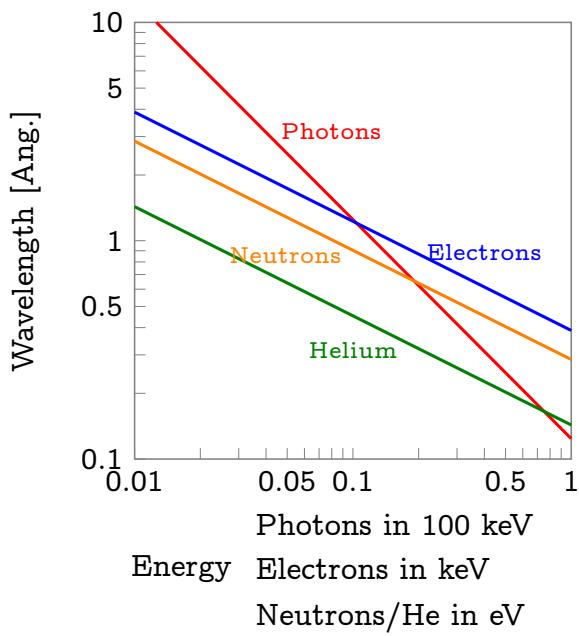
Basic idea:

- ▶ 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"

photon

de Broglie

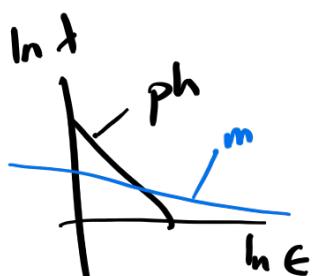
$$E = p \cdot \epsilon$$

$$p = h/\lambda$$

$$\lambda = \frac{hc}{\epsilon}$$

$$t = \frac{hc}{\lambda}$$

$$\ln \lambda = \ln hc - \ln \epsilon$$



massive particles  $\epsilon = \frac{p^2}{2m}$  (non-relativistic)

$$= \frac{h^2}{2m} \frac{1}{\lambda^2}$$

$$\lambda = \sqrt{\frac{h^2}{2m}} \frac{1}{\sqrt{\epsilon}}$$

$$\ln \lambda = \ln \sqrt{\frac{h^2}{2m}} - \frac{1}{2} \ln \epsilon$$

# Probes

low energy neutrons  
massive particles

Typical numbers:

	energy $E$	wavelength $\lambda$	scattered by	penetration depth
X-rays	$10^4$ eV	1.2 Å	electrons	$\sim$ cm
Scattered by electrons				
neutrons	$10^{-2}$ eV	2.8 Å	nuclei	$\sim$ cm

"	$10^{-2}$ eV	2.8 Å	nuclei	$\sim$ cm
" nuclei				

electrons	{	10-100 eV	LEED	$\sim 1$ Å	electrons	$\sim$ nm
		$10^5$ eV	TEM	$\sim 0.04$ Å	& nuclei	$\sim \mu\text{m}$

- ▶ Strength of interaction with matter varies with probe

- can influence choice for specific crystal structure determination

charge - charge interact  
is very strong

Scattered by electrons  
" nuclei  
allows V to be measured  
different things

bulle of the probe (very high E energy)

surface structure: they do not penetrate deeply

# Bragg's Law

Basic analysis follows from Bragg's Law:

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

$n$  - (integer) diffraction order       $\lambda$  - wavelength of radiation  
 $d$  - spacing of lattice planes       $\vartheta$  - Bragg angle of diffraction.

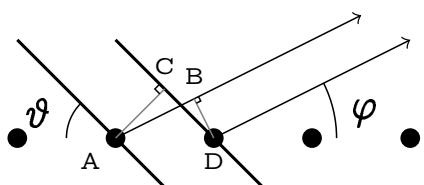
- ▶ This is a simple version of diffraction theory - see later.
- ▶ “The Bragg derivation is simple but it is convincing only because it reproduces the correct result.”

[Kittel, 5th ed. p39]

► The Braggs

## “Derivation” : constructive interference of waves

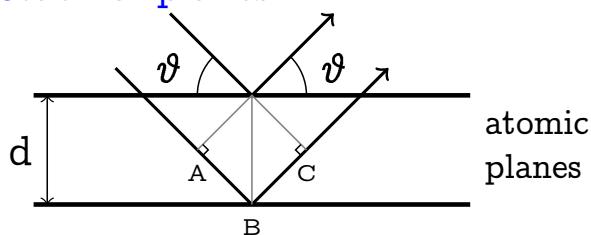
Single plane



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

$$AB = CD \Rightarrow \delta = \varphi \text{ i.e } \text{refl}^\circ$$

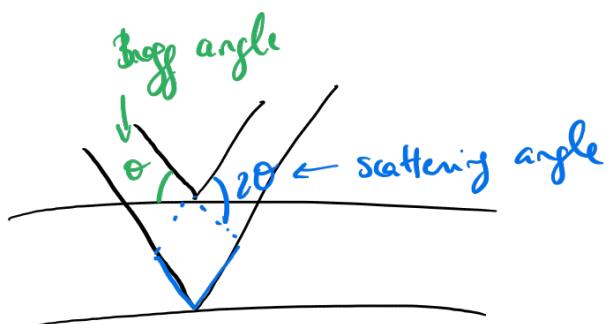
Stack of planes



To get waves scattered from adjacent planes in phase

$$ABC = 2d \sin \delta = n\lambda$$

$\approx$  Bragg's Law  
but...



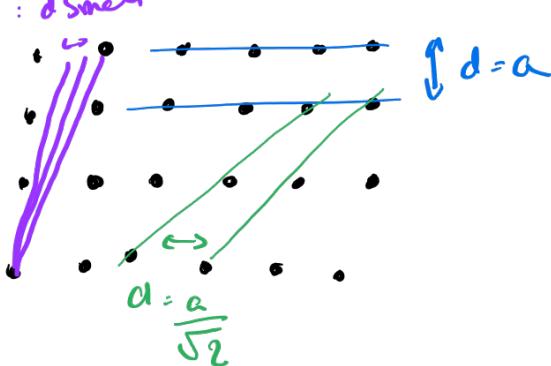
$$n\lambda = 2d \sin(\theta)$$

$$\sin(\theta) = \frac{n\lambda}{2d}$$

Square lattice:

$$d = \left\{ a, \frac{a}{\sqrt{2}}, \dots \right\} \leftarrow \text{ratio: } 1 : \frac{1}{\sqrt{2}} : \dots$$

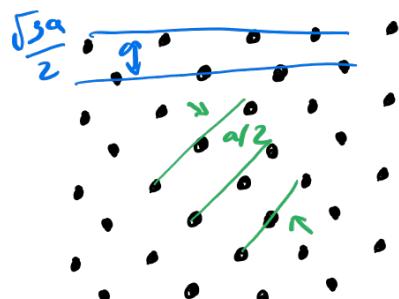
unlikely to give rise to diffraction



hexagonal lattice:

$$d = \left\{ \frac{\sqrt{3}a}{2}, \frac{a}{2}, \dots \right\}$$

$$\text{ratio: } \frac{\sqrt{3}}{2} : \frac{1}{2} : \dots$$



ratio provides info structure

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

~~A~~ satisfying the Bragg condition is not particularly likely

- ▶ Bragg's Law gives the scattering angle  $2\vartheta$  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  $\lambda$  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  $\vartheta$  and  $\lambda$  matching according to the Bragg formula.

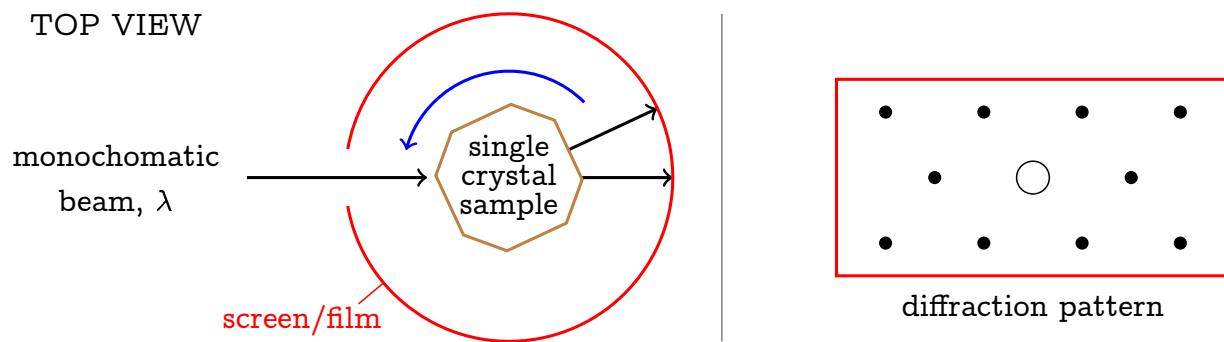
To ensure this happens, experiments scan either  $\vartheta$  or  $\lambda$ .

We will look at:

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

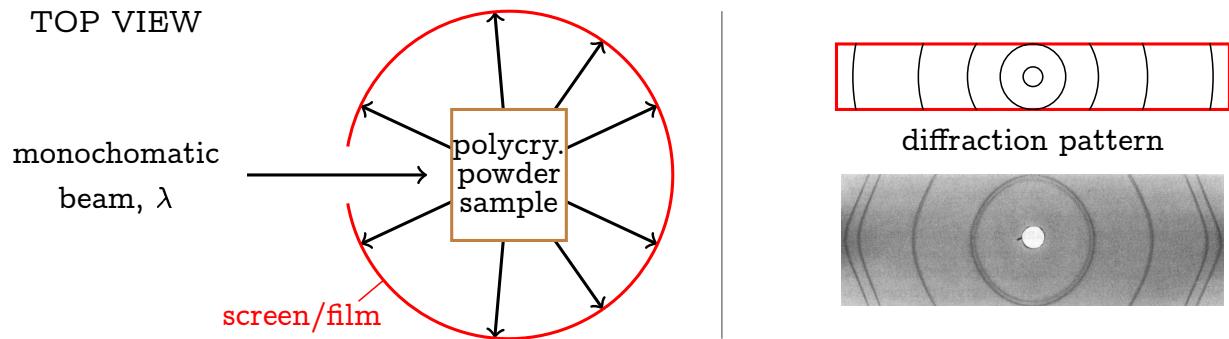
# Rotating crystal method

Fixed  $\lambda$ , vary  $\vartheta$  by rotating crystal



# Powder method (Debye-Scherrer)

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

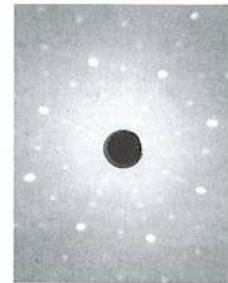
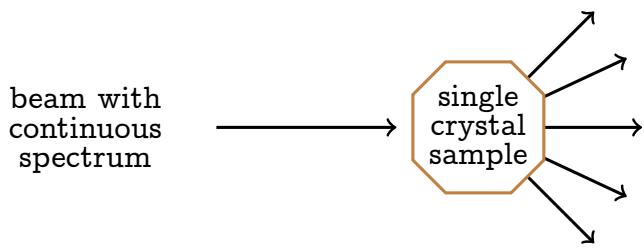


# Laue Method

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

Image taken by Laue, 1912

TOP VIEW



▶ von Laue

The  $\lambda$  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  $1.5\text{\AA}$  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  $47.56^\circ$ .

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]

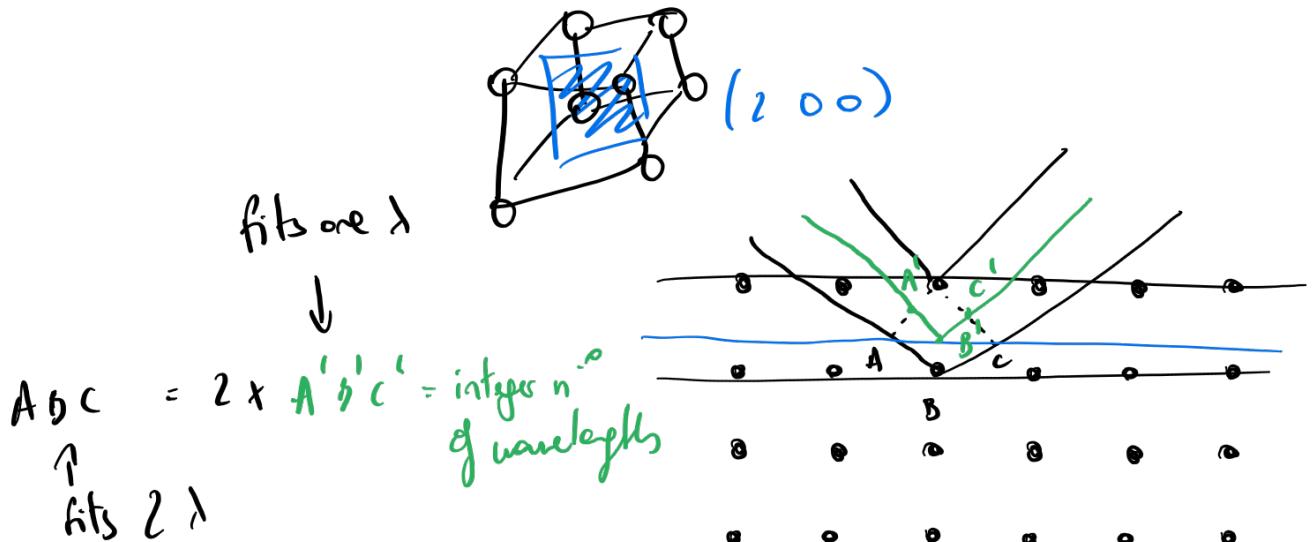
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
 where  $\left\{ \begin{array}{ll} \text{sc} & \text{all } h, k, l \text{ allowed} \\ \text{bcc} & \text{only } h+k+l \text{ even allowed} \\ \text{fcc} & h, k, l \text{ all odd or all even} \end{array} \right.$ 

*allowed*  
*symmetry specific*

*spacing miller planes*

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:  $\sin^2 \theta = \frac{\lambda^2}{4a^2} \times (h^2 + k^2 + l^2)$

$\lambda/a$  constant: the ratio of  $\sin^2 \theta$  values is the ratio of  $h^2 + k^2 + l^2$  values.

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

structure	$h^2 + k^2 + l^2$ sequence							ratios
sc	1 <sub>100</sub>	2 <sub>110</sub>	3 <sub>111</sub>	4 <sub>200</sub>	5 <sub>210</sub>	6 <sub>211</sub>	·	8 <sub>220</sub>
bcc	·	2	·	4	·	6	·	8
fcc	·	·	3	4	·	·	·	8

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

ratio = 1.000 : 1.334 : 2.668 : 3.668 : 4.001

Comparing with the table, we identify the sequence as fcc

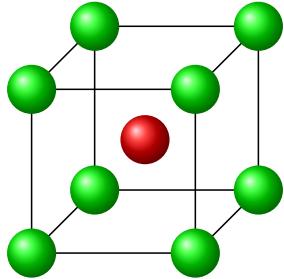
We can now associate  $h, k, l$  values to each diffraction angle, and so can find the lattice parameter.

e.g. first angle:  $\sin^2 21.65^\circ = 1.5^2/(4a^2) \times 3 \Rightarrow a = 3.82 \text{ \AA}$

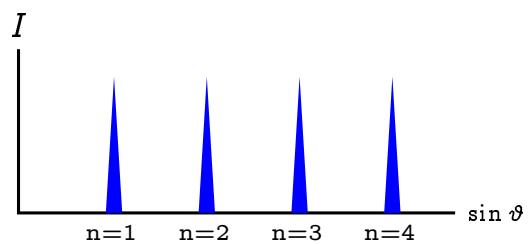
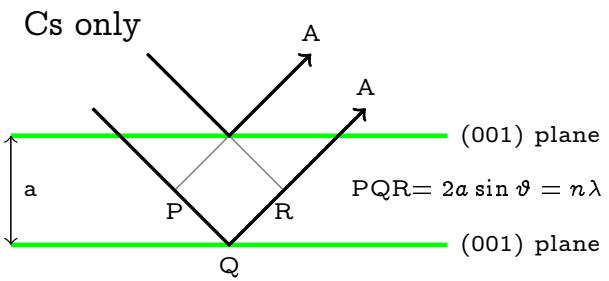
## Diffracted intensities – determining the basis structure

- ▶ Different atoms scatter radiation with different amplitudes (see later).
- ▶ This means

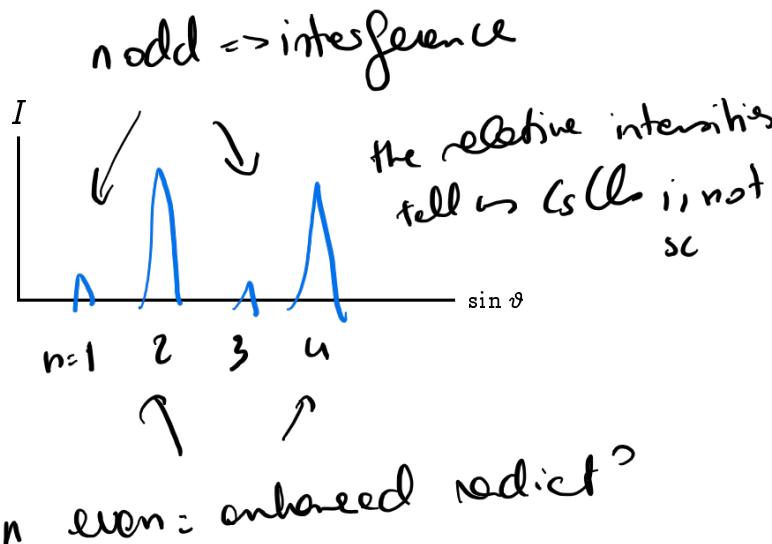
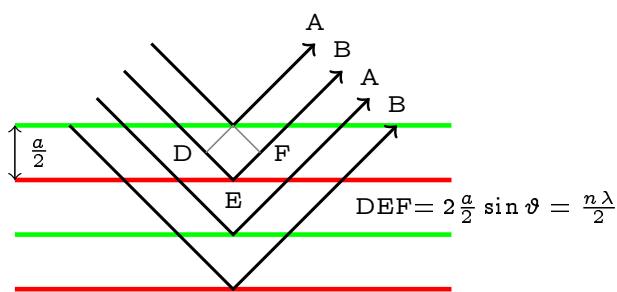
To see how, consider: CsCl



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



Include Cl



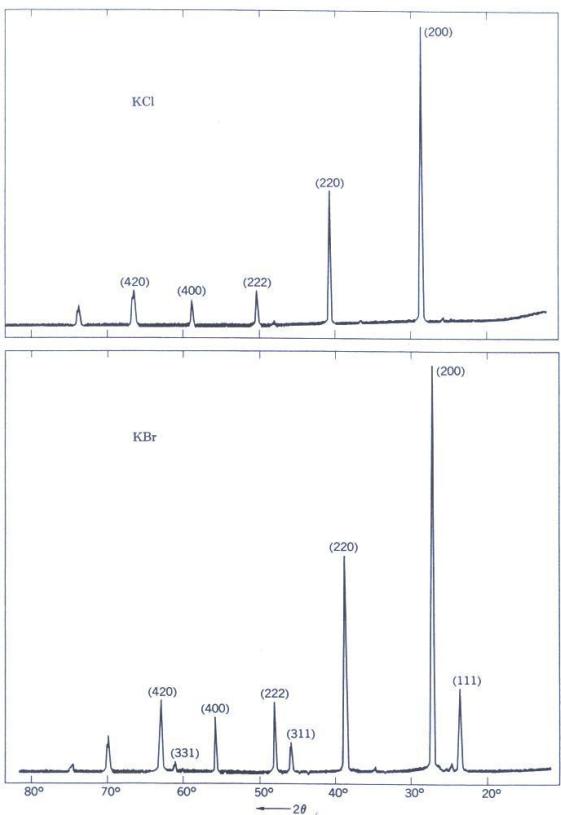
# Scattering amplitudes / form factors

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.



*white book*

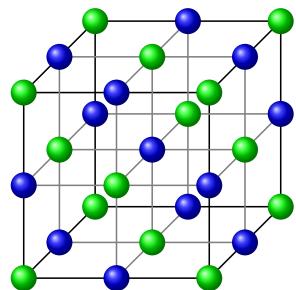


Figure 25 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of  $K^+$  and  $Cl^-$  ions are equal. The scattering amplitudes  $f(K^+)$  and  $f(Cl^-)$  are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice 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

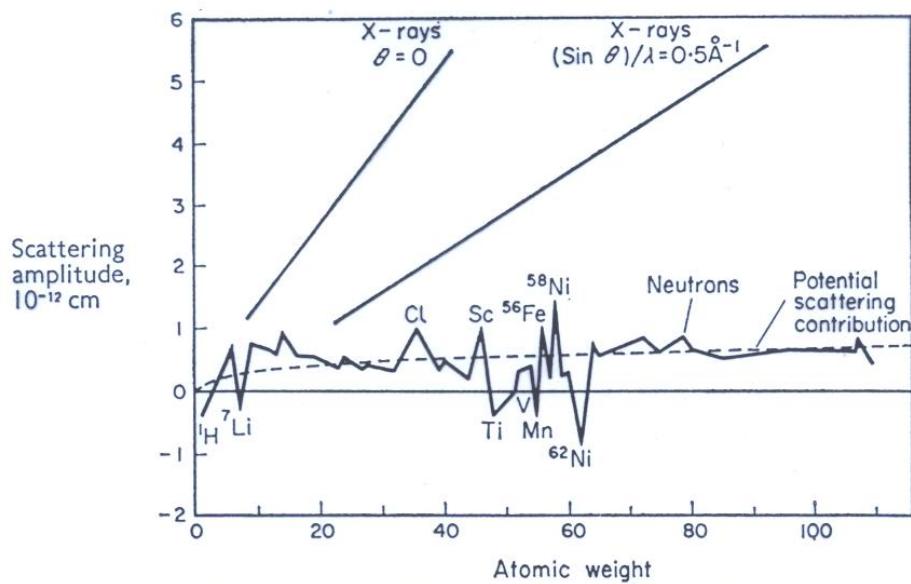


FIG. NI The variation of the scattering amplitude of atoms for neutrons, as a function of their atomic weight. The irregular variation is contrasted with the linear relation for X-rays (from *Research*, 1954, 7, 297).

# Neutrons as structure probe

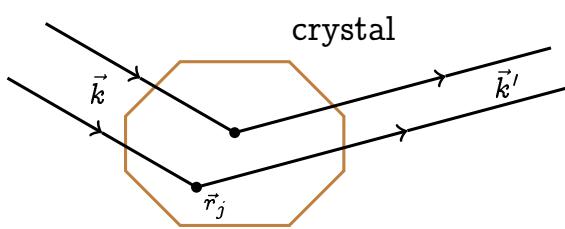
Neutrons are scattered by nucleons.

- ▶  $f$  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

	Probe
Elemental solid	X-ray
Uranium oxide	X-rays
Sucrose	Neutrons (H atom locat's undetectable by X-rays)
$\beta$ -brass	Neutrons
Platinum	Electrons ← surface segregation

# Diffraction from a crystal from an atomic perspective



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

Film/screen at  $\vec{R}$

$|\vec{R}| \gg$  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,  $|\vec{k}'| = |\vec{k}|$ .

— cont notes

# Amplitude at detector due to single atom

- Three-step process

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

ampl. of incident  
rad. at atom  $j$       atomic scattering  
amplitude      ampl. at detector of  
wave emitted by atom

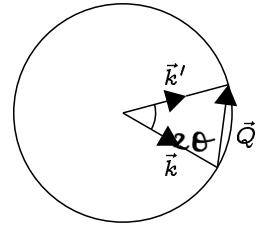
- If the detector is a long way from a small crystal, this can be approximated as

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

## Total amplitude

- Amplitude of radiation scattered from all atoms is

$$A_{TOT} = C \sum_j f_j e^{-i\vec{Q} \cdot \vec{r}_j} \quad \vec{Q} = \vec{k}' - \vec{k} \quad |\vec{Q}| = 24 \text{ nm}^{-1}$$



$\theta$ : 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  $\vartheta = 2\pi \times$  integer, when  $e^{-in\vartheta} = 1$ , or  $S = 0$ . (destructive)

So

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

some terms  $\Re > 0$

$< 0$

$\Im > 0$

$< 0$

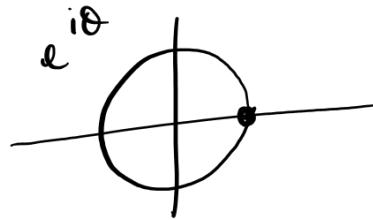
to lots of  
cancelat<sup>g</sup>

Or, physically:

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

But  $\vartheta = 2\pi \times$  integers

every term in form is = 1  
n terms in  $\sum$



## Laue conditions

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

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

**Laue conditions** - must be satisfied for diffraction to occur

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

$$\vec{Q} \cdot \vec{a} = 2\pi h \quad \text{etc}$$

$$\text{sc} \quad \vec{a} = a_i \quad \vec{b} = a_j \quad \vec{c} = a_k$$

$$\text{Let } \vec{Q} = Q_x \hat{i} + Q_y \hat{j} + Q_z \hat{u}$$

$$\vec{Q} \cdot \vec{a} = 2\pi h \Rightarrow Q_x a = 2\pi h$$

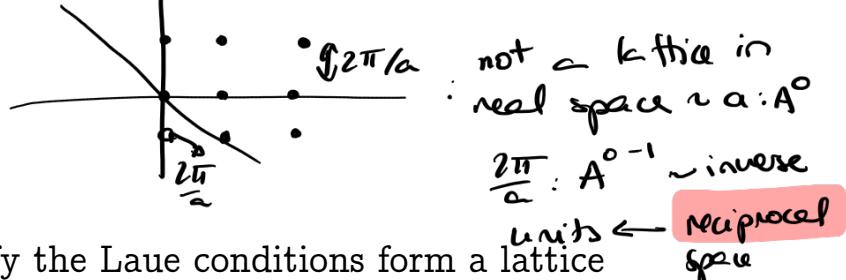
$$Q_y a = 2\pi k$$

$$Q_z a = 2\pi l$$

$$\vec{Q} = \frac{2\pi}{a} (h, k, l)$$

$\Rightarrow \vec{Q}$  sits at an sc lattice with lattice const  $\frac{2\pi}{a}$

## 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**  $\vec{A}, \vec{B}, \vec{C}$ :

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

- 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 [length]<sup>-1</sup>



## Real and reciprocal space

We conclude that

- every crystal has 1 lattice : "real"
- & reciprocal
- the reciprocal lattice is  $\propto$  lattice in reciprocal space - also called momentum or wave vector space
- diffraction experiments measure the reciprocal 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 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*

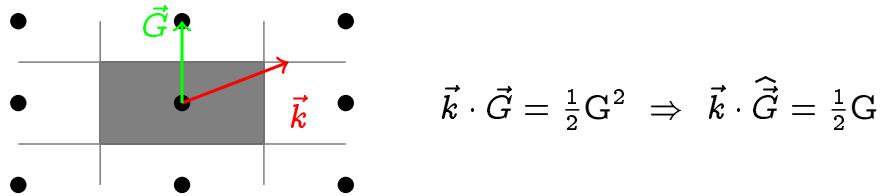
$$\begin{aligned} \vec{k}' \cdot \vec{k}' &= (\vec{k} + \vec{G}) \cdot (\vec{k} + \vec{G}) \\ &= \vec{k} \cdot \vec{k} + 2\vec{k} \cdot \vec{G} + \vec{G} \cdot \vec{G} \end{aligned}$$

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  $\mathbf{G}/2$ . This means  $\vec{k}$  lies on the bisector of the line to  $\vec{G}$ .

The Wigner Seitz cell is enclosed by such bisectors.

*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:  $j = (J, \mu)$   $J \subseteq \text{will run through thousands of } n^o$   
 $J \subseteq 1, \dots, N$  labels unit cells  
 $\mu = 1, \dots, n$  labels basis  $\xrightarrow{\text{origin unit}}$   
 $\vec{r}_j = \vec{R}_J + \vec{r}_\mu$   $\xrightarrow{\text{cell}}$   
 $\xrightarrow{\text{where atom is}}$   
 $\xrightarrow{\text{within unit cell}}$

Runs over  $n^o$  atoms in the basis

$$H \sum a e^{b \vec{r}_c} = H \sum e^b \times \sum a e^c$$

$$A(\vec{Q}) = C \sum_{J\mu} f_\mu e^{-i\vec{Q} \cdot (\vec{R}_J + \vec{r}_\mu)} = C \sum_J e^{-i\vec{Q} \cdot \vec{R}_J} \times \sum_\mu f_\mu e^{-i\vec{Q} \cdot \vec{r}_\mu}$$

$$= \begin{cases} CN_{\text{cells}} + S(\vec{Q}) & : \text{Lau condit's satisfied} \\ 0 & : \text{Lau condit's not satisfied} \end{cases}$$

Structure factor if  $Q$  is in reciprocal lattice  $\xrightarrow{\text{not outside}}$

$$S(\vec{Q}) = \sum_\mu f_\mu e^{-i\vec{Q} \cdot \vec{r}_\mu}$$

Influences the relative intensities of different spots / lines

## Structure factor

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

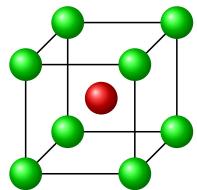
**Notation:** We denote  $S(\vec{Q} = \vec{G}_{hkl})$  as  $S_{hkl}$ .

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

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

The  $u, v, w$  values in the exponent are those for atom  $\mu$ .

## Structure factor example: CsCl



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

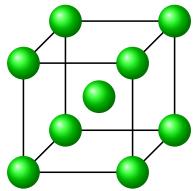
Cs at  $(0, 0, 0)$ , Cl at  $a(1/2, 1/2, 1/2)$

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

$$= f_{Cs} + f_{Cl} e^{-i(h+u+\ell)\pi} = \begin{cases} f_{Cs} + f_{Cl} & h+u+\ell \text{ even} \\ f_{Cs} - f_{Cl} & h+u+\ell \text{ odd} \end{cases}$$

For diffraction from (100) planes:  $S_{100} = f_{Cs} - f_{Cl}$   
 (Recall example from last topic, 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 <sub>100</sub> 2 <sub>110</sub> 3 <sub>111</sub> 4 <sub>200</sub> 5 <sub>210</sub> 6 <sub>211</sub> · 8 <sub>220</sub>
	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

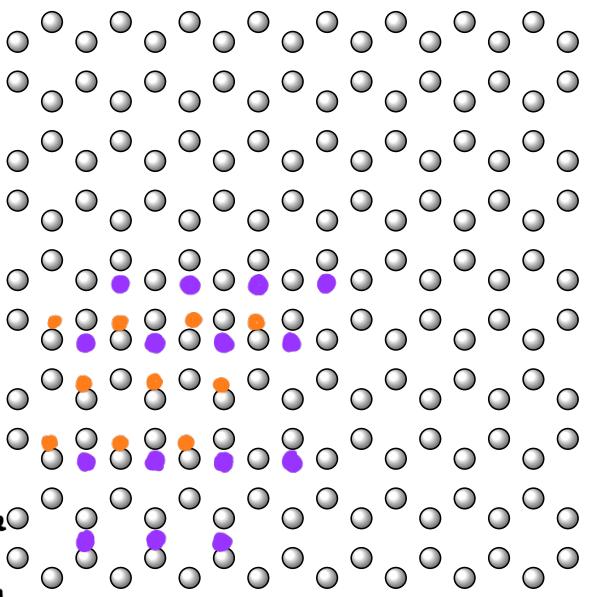
For alternative descriptions and explanations, often at a different level, plus further problems, see

## Crystal Structures

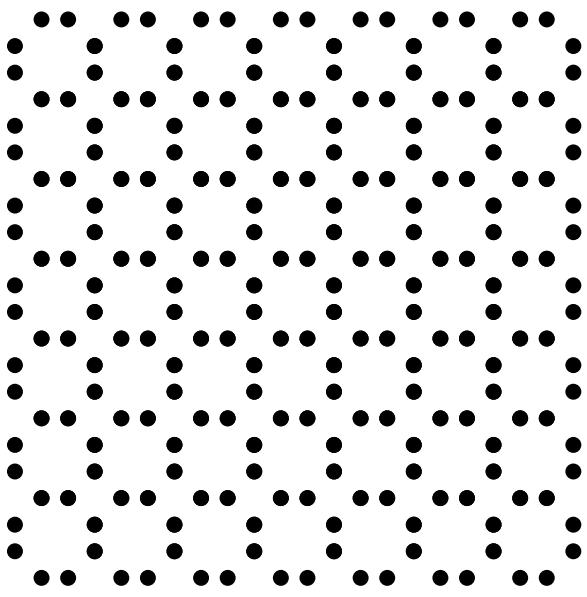
Hook and Hall	p1–19
Myers	p27–44
Kittel (5th ed.)	p3–34
Ibach & Lüth	p15–26
Ashcroft & Mermin	p64–83, p89–93, p112–129

## Diffraction

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



**lattice**  
also a  
lattice  
does not have  
to be the  
heat° of an atom



identity set of symmetrically  
quiv points in space  $\rightarrow$  lattice  $\sqcup$

