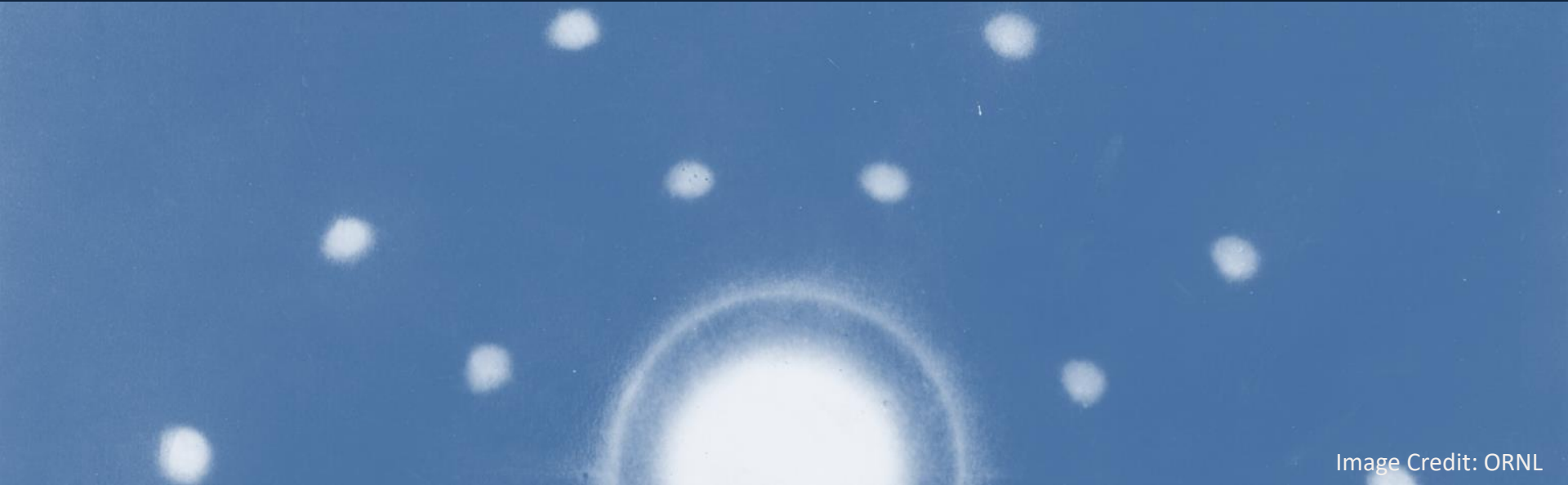


Diffraction from Crystalline Materials

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17th Oxford School on Neutron Scattering

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Lecture 1 Objectives

In Lecture 1 we will explore:

1. The building blocks of crystalline materials, including the **lattice**, **basis** and **unit cell**, and how to describe them using **fractional coordinates**,
2. Symmetry in crystals, including **lattice symmetry**, **point group symmetry** and **space group symmetry**,
3. How we can demonstrate the principles of diffraction in two-dimensions through **lattice planes** and **Bragg's law**,
4. How we can extend these concepts to consider diffraction in three-dimensions using the **reciprocal lattice** and **Ewald construction**,
5. What determines Bragg peak intensities, including the **structure factor** and **systematic absences**,
6. The **complementarity of neutron and X-ray diffraction**, including a case study of a novel Li-ion battery material.

The material covered in this lecture links to tutorial questions C1, C4 and C5.

Functional Solid-State Materials

In the solid state, most elements and inorganic compounds form crystalline phases

The properties and applications of such solids directly depend on their crystal structure

By characterising this structure, we aim to develop new materials with targeted functions

Diffraction is the process by which characterise the structure of crystalline materials



**Battery
technology**



**Global
health**



**Renewable
energy**



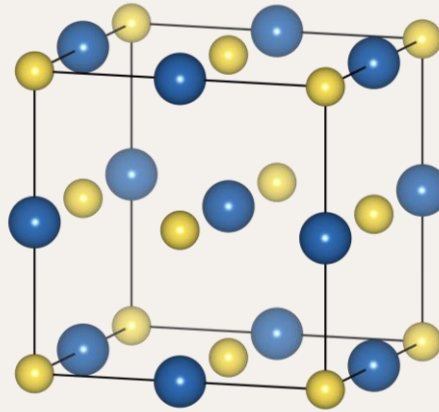
**Hydrogen
economy**

What is a Crystal?

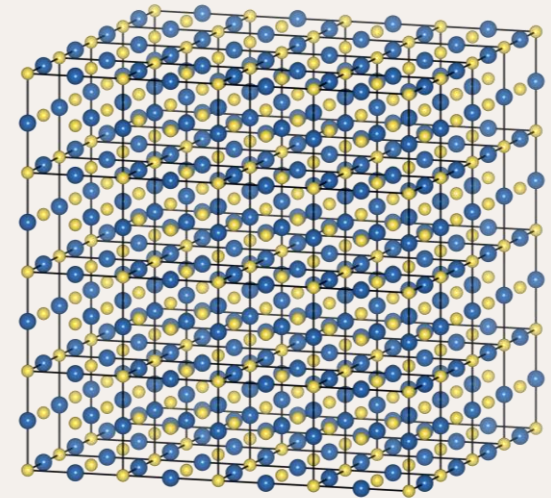
Crystals are a regular, **periodic arrangement** of atoms, ions or molecules



Crystal



Unit cell



Crystal structure

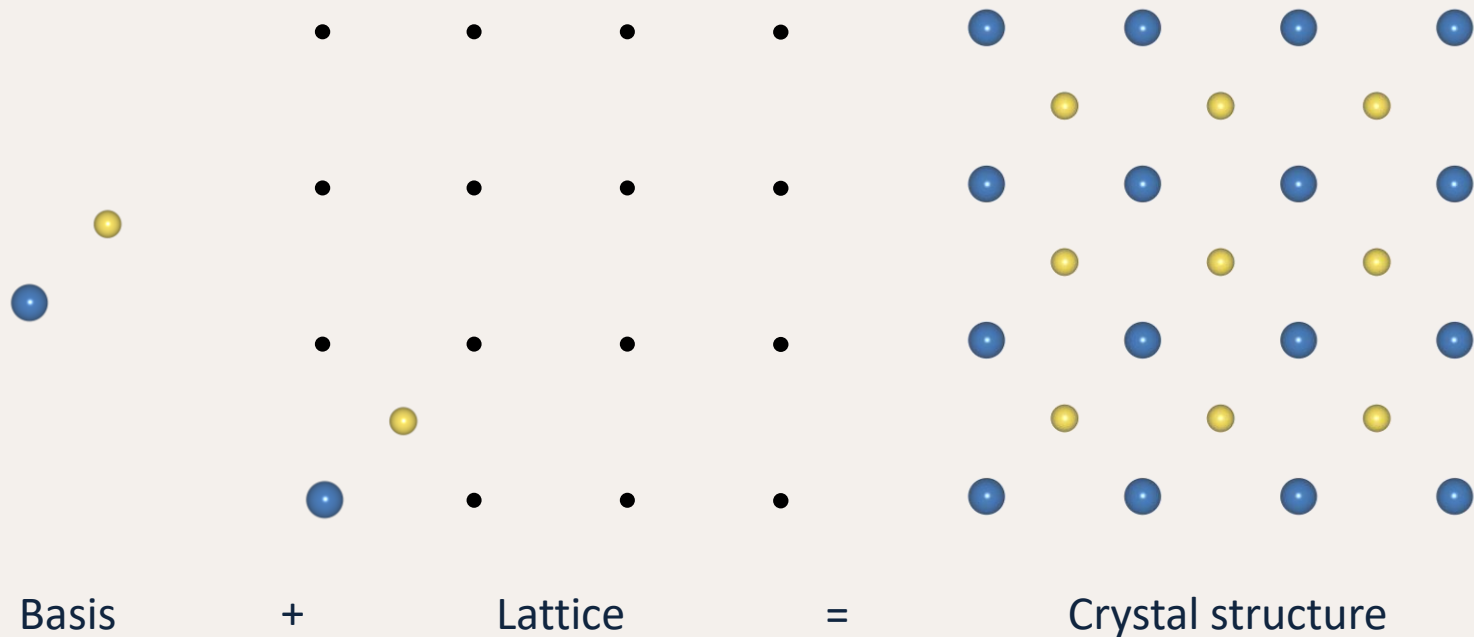
This is in contrast to non-crystalline or glassy materials, which lack long-range periodicity

The Building Blocks of Crystalline Materials

The **lattice** imparts the characteristic periodicity of a crystal and its **translational symmetry**

A set of atoms, ions or molecules that may dress the points of a lattice is known as a **basis**

The combination of a lattice and a basis that generates a **crystal structure**



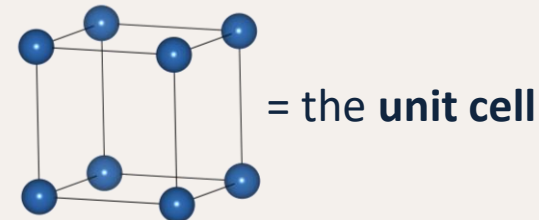
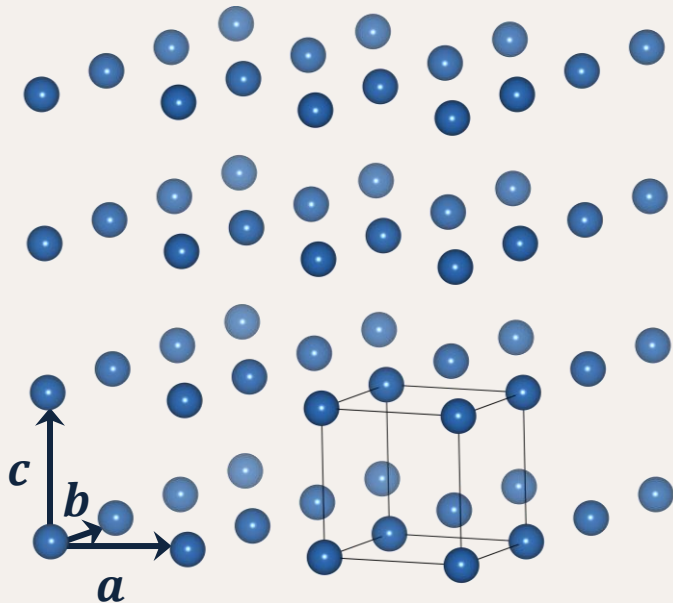
Primitive Lattices

The lattice is an infinite array of equivalent **lattice points**

The underlying periodicity defined by the lattice can be described mathematically by:

$$\mathbf{r}' = \mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

A lattice is **primitive** if any two points \mathbf{r}' and \mathbf{r} with the same environment within the lattice obey this relationship with integer values of n_1 , n_2 and n_3



The unit cell is a repeating unit that can generate the entire crystal by translation in 3-dimensions

Its size and shape are defined by the **unit cell parameters** a , b , c , α , β and γ

Primitive Lattices

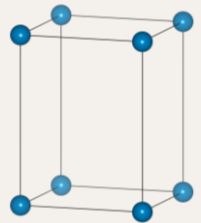
The number of independent unit cell parameters depends on the **lattice symmetry**

Lattice symmetry gives rise to seven **crystal systems**



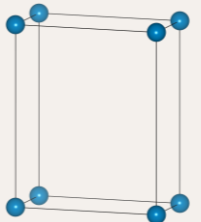
4 × 3-fold axes
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$

Cubic



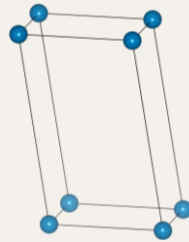
1 × 4-fold axis
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$

Tetragonal



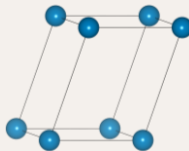
**3 × 2-fold axes or
3 × mirror planes**
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$

Orthorhombic



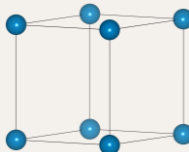
**1 × 2-fold axis or
1 × mirror plane**
 $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$

Monoclinic



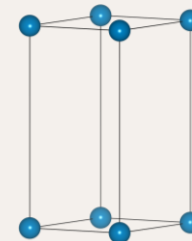
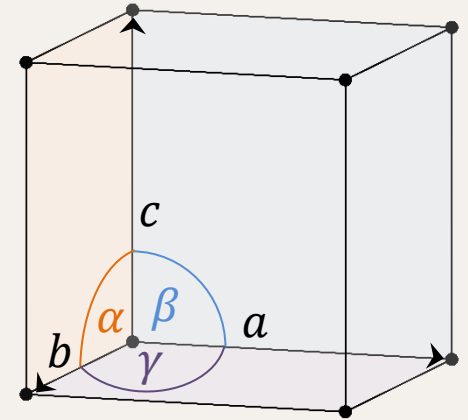
None
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$

Triclinic



1 × 3-fold axis
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$

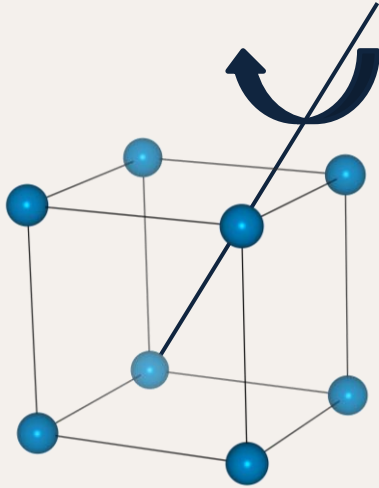
Rhombohedral



1 × 6-fold axis
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

Hexagonal

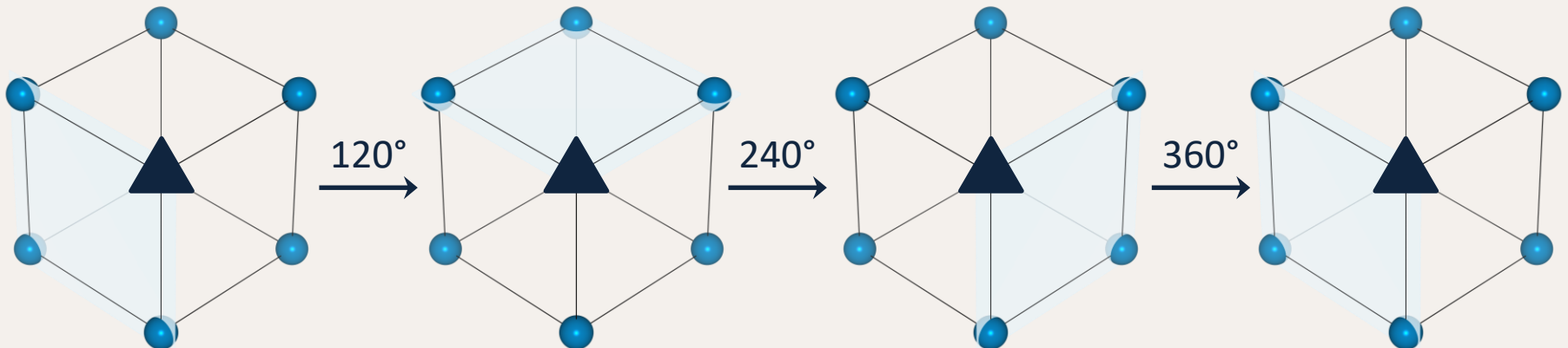
Lattice Symmetry



Cubic lattice symmetry is defined by its **4 × 3-fold rotation axes**

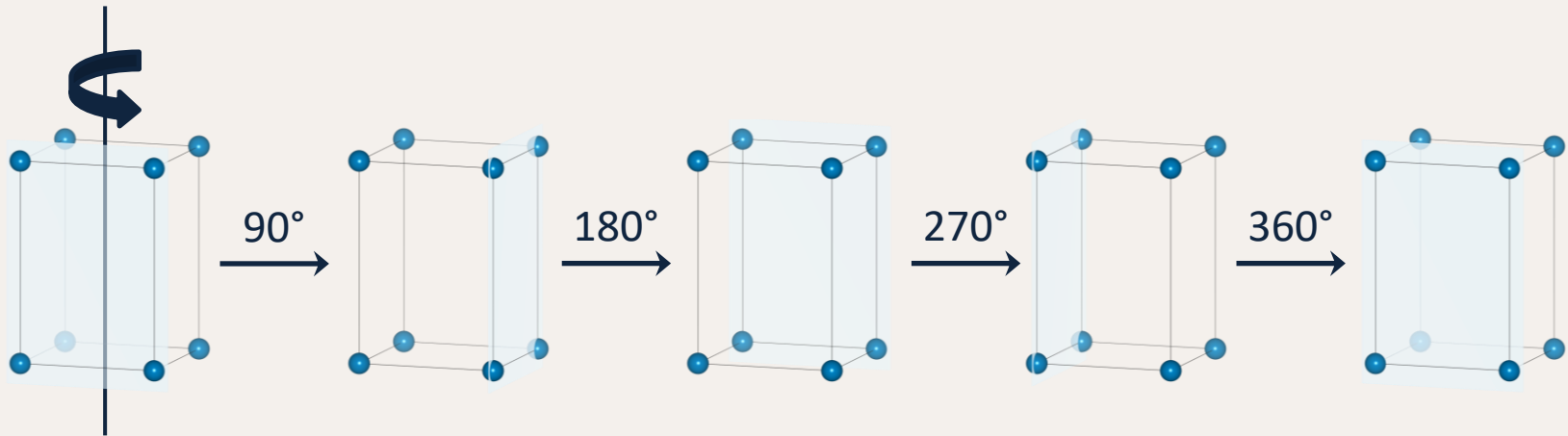
Each symmetry axis cuts through a body diagonal of the cube

Looking down this axis we can observe the 3-fold rotational symmetry operation

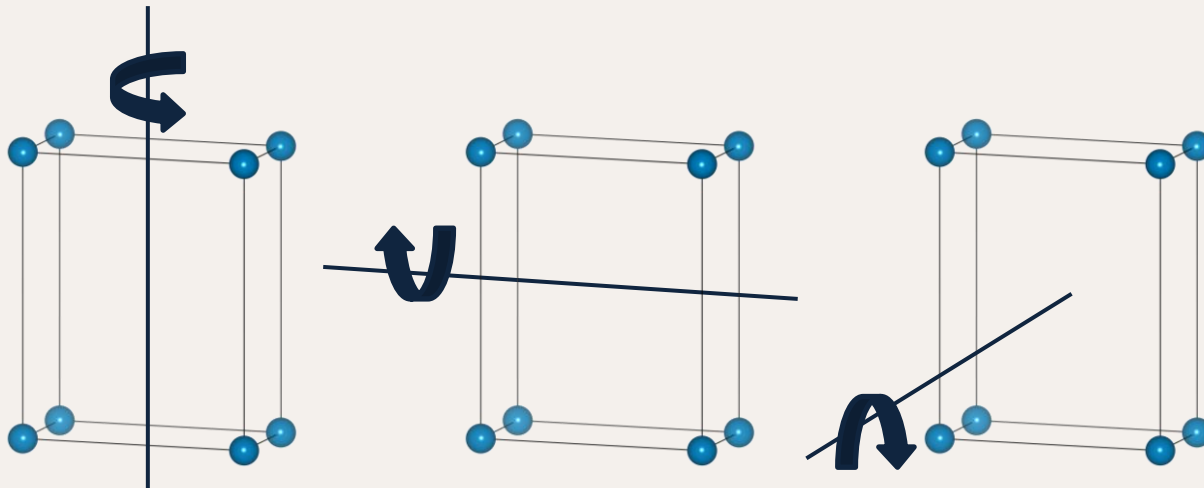


Lattice Symmetry

Tetragonal lattice symmetry is defined by a single **4-fold rotation axis**

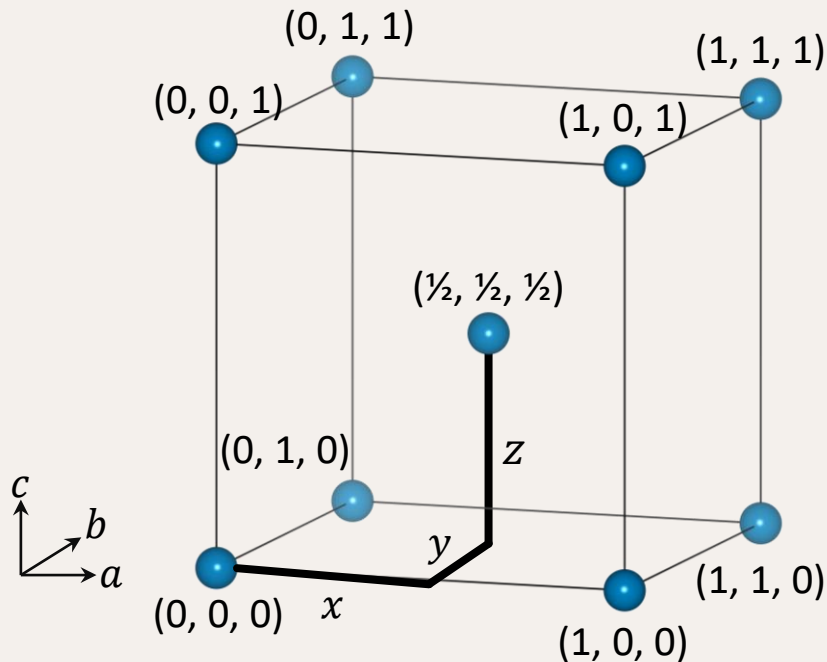


Orthorhombic lattice symmetry is defined 3 orthogonal **2-fold rotation axes**



Fractional Coordinates

The positions of atoms, ions or molecules within the a unit cell are described by **fractional coordinates** (x, y, z) , which are fractions of unit cell lengths a, b, c



When **counting the contents** of a unit cell, we have to remember the crystal is infinite:

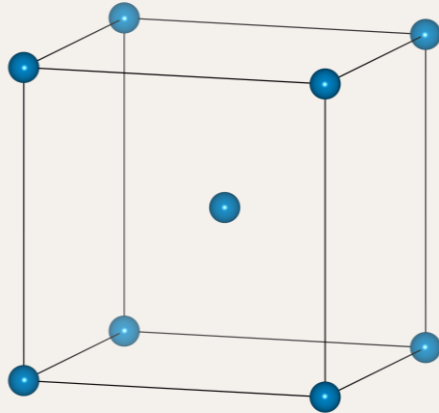
- Lattice points on cell corner shared by 8 cells
- Lattice points on cell edge shared by 4 cells
- Lattice points on cell face shared by 2 cells
- Lattice points fully within cell are not shared

Here, there are $(8 \times 1/8)$ lattice points on corners and (1×1) lattice points within the cell

Thus, there are two lattice points in total at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

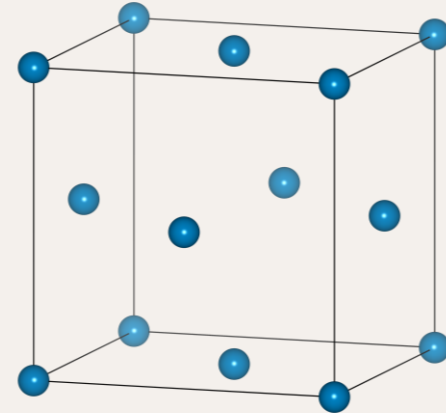
This is known as a **body-centred cell**

Centred Cubic Lattices



A **body-centred cell (I)** has two lattice points

$$(x, y, z) \text{ and } (x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2})$$



A **face-centred cell (F)** has four lattice points

$$(x, y, z), (x+\frac{1}{2}, y+\frac{1}{2}, z), \\ (x+\frac{1}{2}, y, z+\frac{1}{2}) \text{ and } (x, y+\frac{1}{2}, z+\frac{1}{2})$$

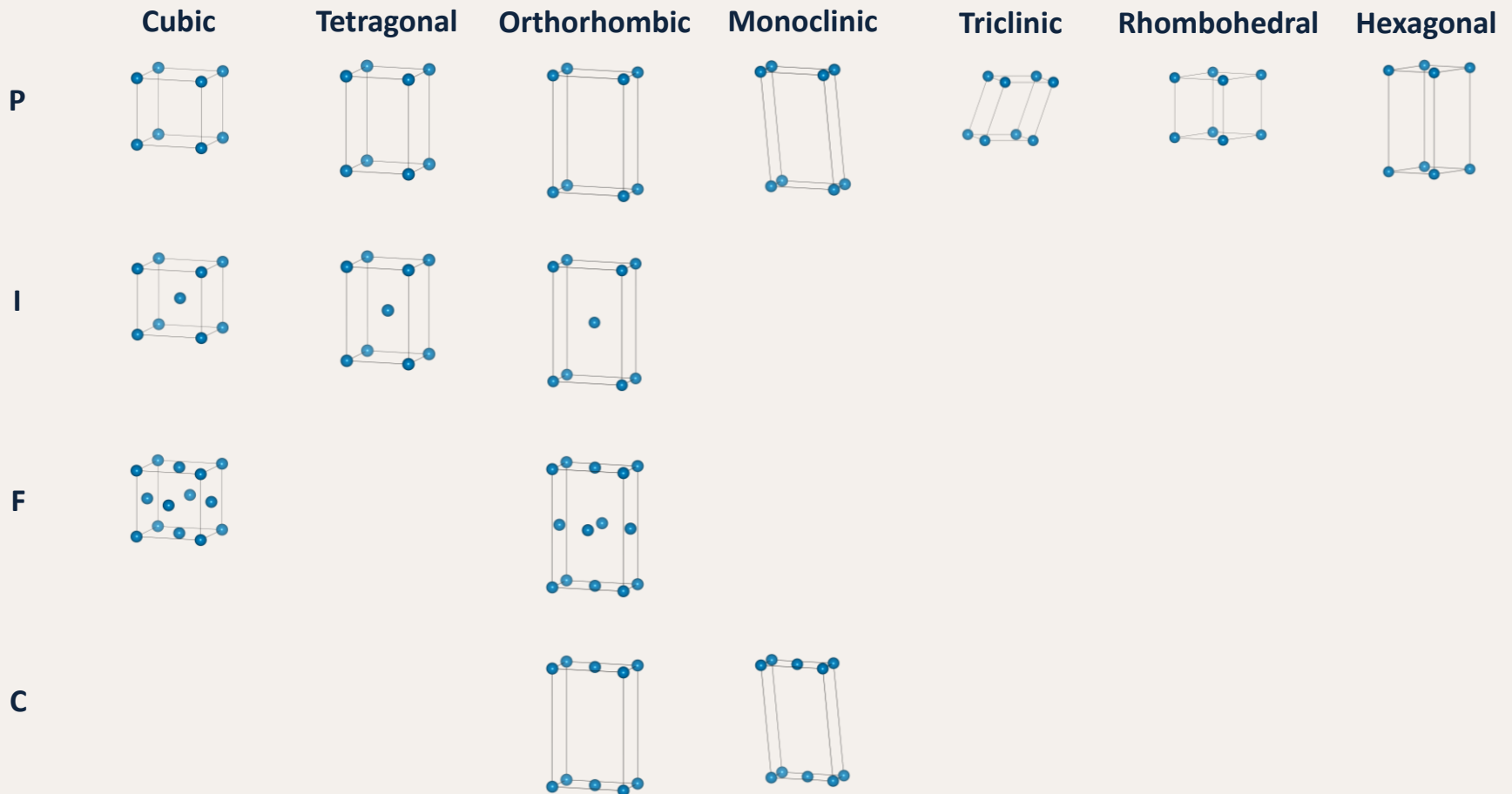
I and F lattices are not primitive (P), as the condition $\mathbf{r}' = \mathbf{r} + n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ with n_1, n_2 and n_3 being integer values no longer holds

Note that a P cell has one lattice point at (x, y, z)

Generally, we take (x, y, z) to be $(0, 0, 0)$

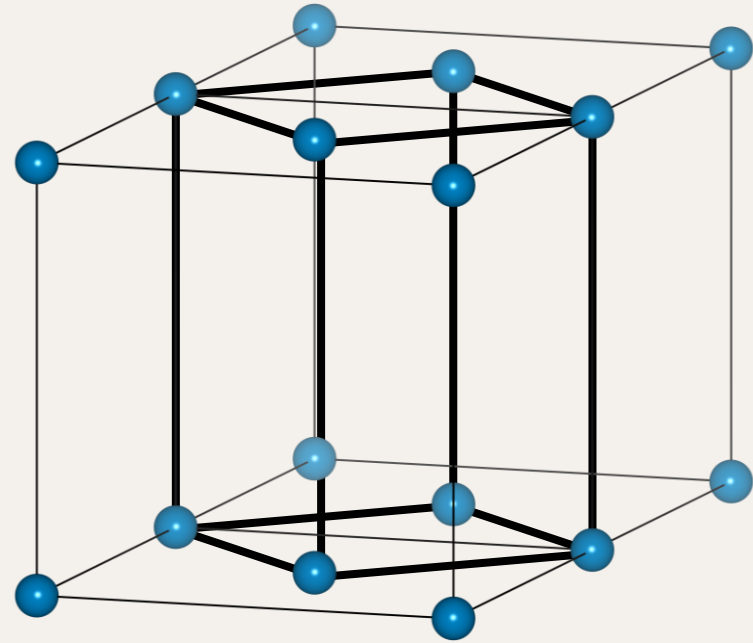
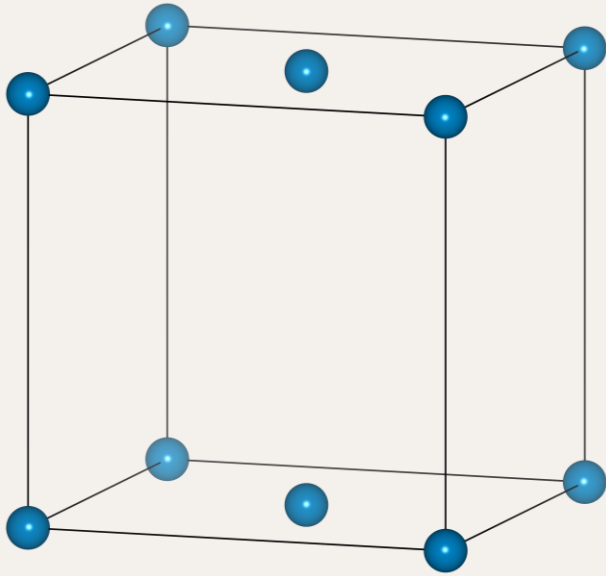
Bravais Lattices

Combining the symmetries of the seven crystal systems with lattice centring gives rise to fourteen unique **Bravais lattices**



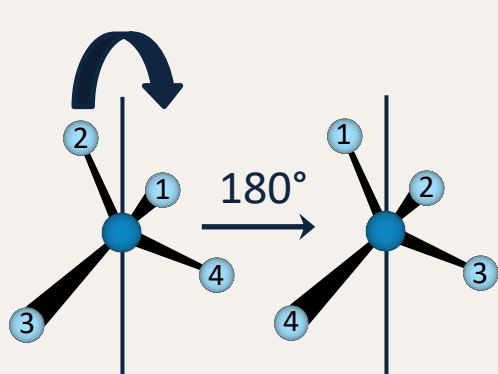
Bravais Lattices

Why is there no C-centred cubic lattice?

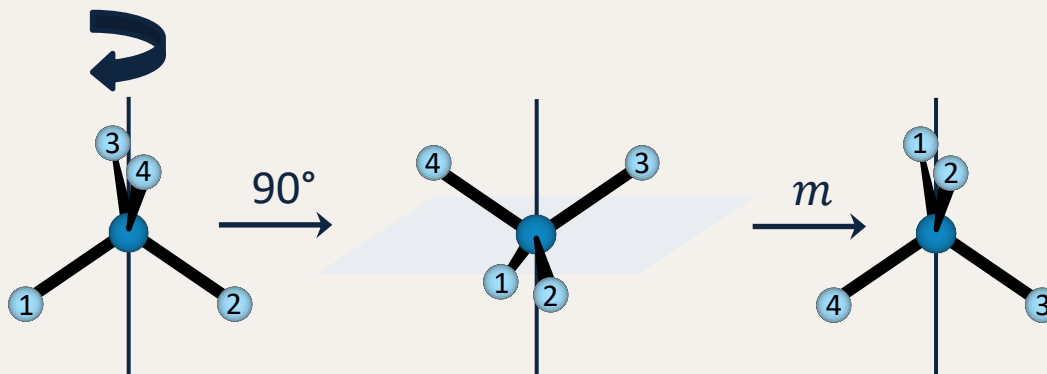


Point Groups

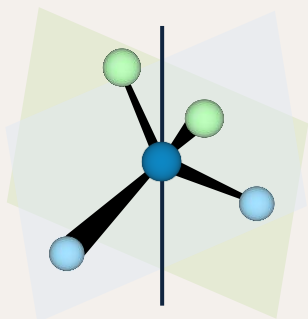
How do we consider the non-translational symmetry elements of a crystal, *i.e.* reflection, proper or improper rotations about a fixed point?



CH₄ 2-fold proper rotation (2)



CH₄ 4-fold improper rotation ($\bar{4}$)



$mm2$

The set of all symmetry operations of a finite object, *e.g.* a molecule, is known as a **point group**

CH₂Cl₂ has two mirror planes (m) and a proper 2-fold axis (2)

In **international** (Hermann–Mauguin) notation the point group of CH₂Cl₂ is $mm2$

Crystallographic Point Groups

Because crystals have periodic lattices, their rotational symmetry is restricted to 1-, 2-, 3-, 4- and 6-fold proper and improper rotation axes

This allows for 32 possible combinations of proper and improper rotational axes, which are known as the 32 **crystallographic point groups**

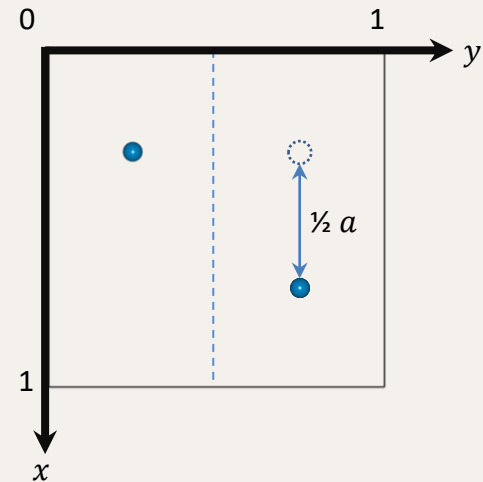
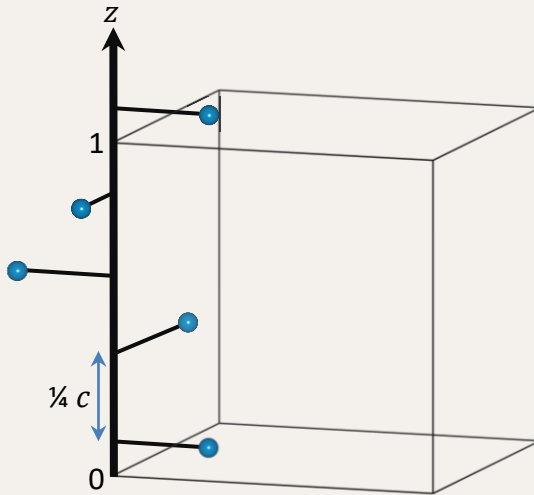
A crystallographic point group is denoted in international notation by up to three symbols that describe the symmetry along different directions of the crystal system

Crystal System	Crystallographic Point Groups	Notes
Triclinic	$1, \bar{1}$	Describes the presence ($\bar{1}$) or absence (1) of an inversion centre.
Monoclinic	$2, m, 2/m$	Describes the symmetry along the y -axis direction.
Orthorhombic	$222, mm2, mmm$	Describes the symmetry along the x -, y - and z -axis directions, respectively.
Tetragonal	$4, \bar{4}, 4/m,$ $422, \bar{4}2m, 4mm, 4/m\ mm$	The first place describes the symmetry of the z -axis. If in the xy -plane there are also any symmetrical directions, they are described in the second and third place.
Rhombohedral	$3, \bar{3}, 32, 3m, \bar{3}m$	Point group conventions are as in tetragonal system.
Hexagonal	$6, \bar{6}, 6/m,$ $622, \bar{6}2m, 6mm, 6/m\ mm$	Point group conventions are as in tetragonal system. Note, an axis with a perpendicular mirror plane is denoted as a fraction, <i>e.g.</i> $6/m$.
Cubic	$23, m\bar{3}, 432, \bar{4}3m, m\bar{3}m$	Cubic point groups are distinguished by a 3, which denote the symmetry of the body-diagonals of a cube. The first place describes symmetry of equivalent x -, y - and z -axis, and the third describes any symmetry between these axial directions.

Space Groups

The translational symmetry of a crystal combined with crystallographic point group symmetry results in additional symmetry operations with translational components

These are known as **screw axes** and **glide planes**



Screw axis (N_n) = rotation (N) + translation (n/N)
e.g. $N = 4$, $n = 1$, 4_1 screw axis

Glide plane = reflection + translation
e.g. a glide plane \parallel x -axis

The rotational, reflectional and translational symmetry of crystals allow for 230 possible combinations of symmetry operations known as **space groups**

How to Read and Understand the International Tables of Crystallography

Each of the 230 space groups describes the symmetry of a crystal belonging to that group

A full description of each is given in **Vol. A of the International Tables of Crystallography**

The diagram illustrates the space group $P4_32_12$ (No. 96) in a tetragonal crystal system. It includes the following components:

- Space group symbol (international notation):** $P4_32_12$
- Space group number (1 – 230):** No. 96
- Crystal system:** Tetragonal
- Point group:** D_4^8 (Schönflies notation) and 422 (Hermann-Mauguin notation)
- Space group symbol (Schönflies notation):** D_4^8
- Diagram of symmetry operations:** A 3D representation of the unit cell showing screw axes and rotational axes.
- Diagram of equivalent positions:** A 2D projection of the unit cell showing the positions of atoms.
- Projections along z:** Two diagrams showing the projection of the unit cell onto the xy-plane.
- Position of unit cell origin:** Origin on $2[110]$ at $2, 1(1,2)$
- Asymmetric unit:** $0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq \frac{1}{2}$
- Symmetry operations:**

(1) 1	(2) $2(0, 0, \frac{1}{2})$ $0, 0, z$	(3) $4^+(0, 0, \frac{1}{2})$ $0, \frac{1}{2}, z$	(4) $4(0, 0, \frac{1}{2})$ $\frac{1}{2}, 0, z$
(5) $2(0, \frac{1}{2}, 0)$ $\frac{1}{4}, y, \frac{3}{8}$	(6) $2(\frac{1}{2}, 0, 0)$ $x, \frac{1}{4}, \frac{1}{8}$	(7) 2 $x, x, 0$	(8) 2 $x, \bar{x}, \frac{1}{2}$

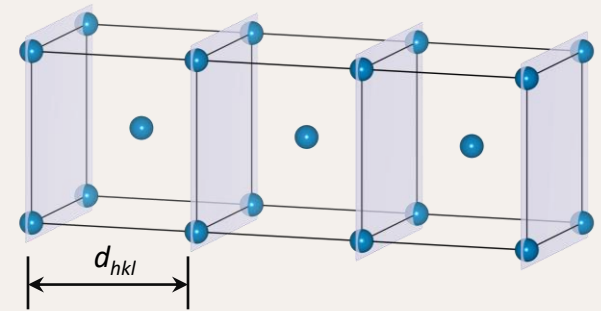
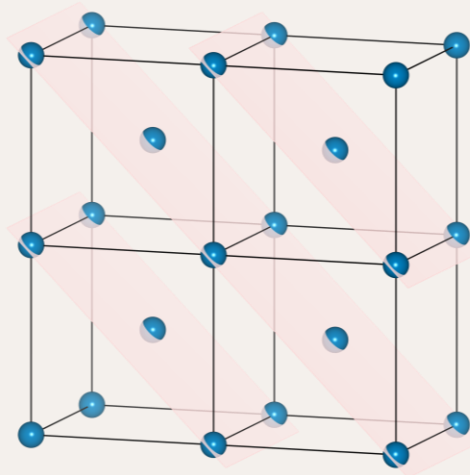
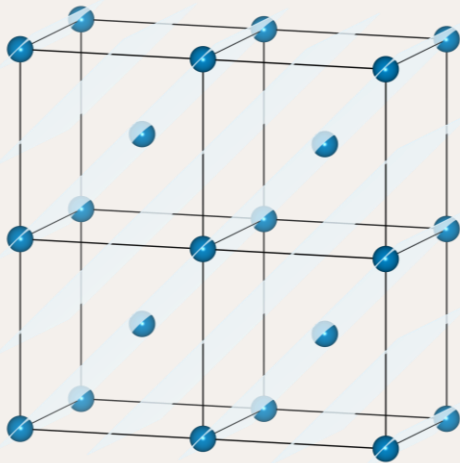
For further details, please see *How to Read (and Understand) Vol. A of the International Tables of Crystallography* by Dauter & Jaskolski, *J. Appl. Cryst.* **43**, 1150 – 1171 (2010)

Lattice Planes and Miller Indices

The three-dimensional array of lattice points within a crystal may be connected by a **lattice plane**, with each lattice point lying on one or more of these planes

Each lattice plane is representative of a set of equally-spaced parallel planes, separated by a distance known as the ***d*-spacing**, d_{hkl}

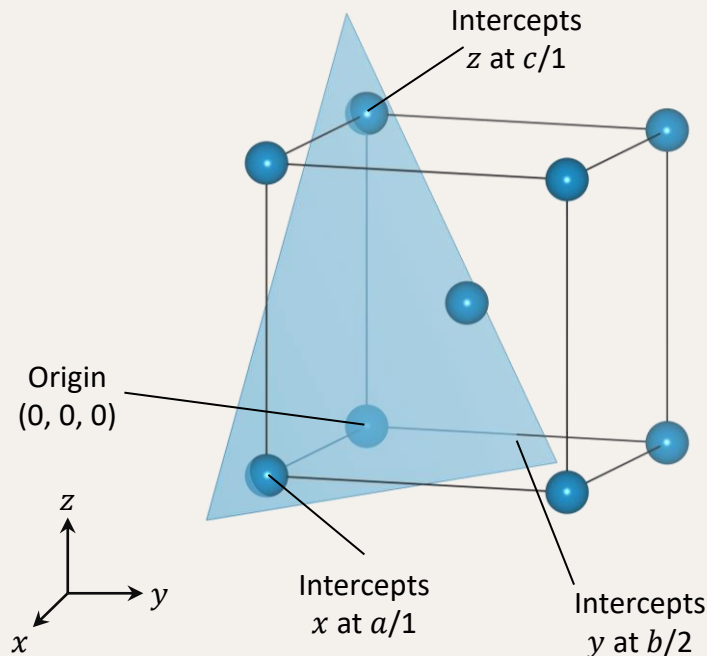
Each family of planes is labelled by a set of **Miller indices** written as (h, k, l)



Lattice Planes and Miller Indices

To determine the Miller indices of a set of lattice planes we must:

1. Define the unit cell origin
2. Find where the plane intercepts each unit cell axis
3. Express these intercepts as fractions of unit cell lengths a/h , b/k , c/l
4. Take the reciprocals of this fraction to find the (h, k, l) of the plane



Intercepts $a/h, b/k, c/l = a/1, b/2, c/1$

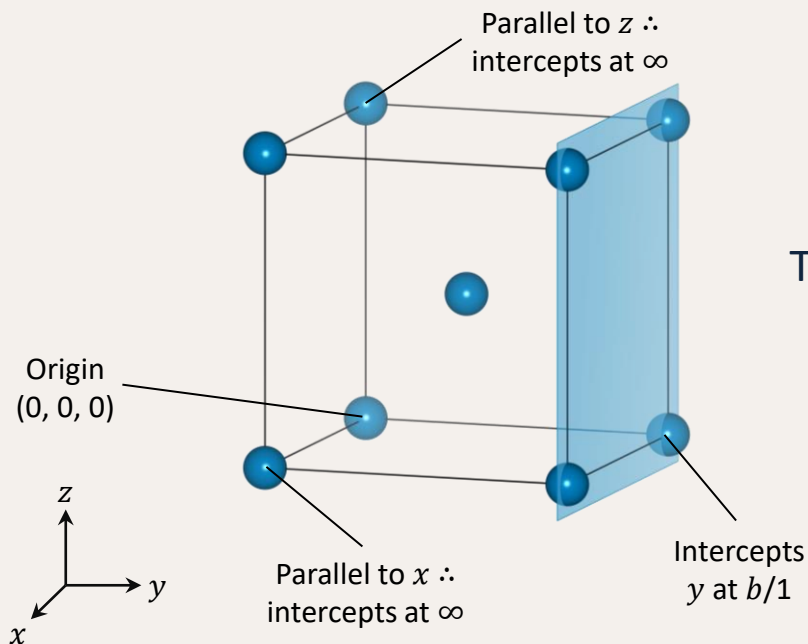
Taking reciprocals to find $(h, k, l) = (1, 2, 1)$

$(1, 2, 1)$ is the Miller index of this plane

Lattice Planes and Miller Indices

To determine the Miller indices of a set of lattice planes we must:

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2. Find where the plane intercepts each unit cell axis
3. Express these intercepts as fractions of unit cell lengths a/h , b/k , c/l
4. Take the reciprocals of this fraction to find the (h, k, l) of the plane



Intercepts $a/h, b/k, c/l = \infty, b/1, \infty$

Taking reciprocals to find $(h, k, l) = (0, 1, 0)$

$(0, 1, 0)$ is the Miller index of this plane

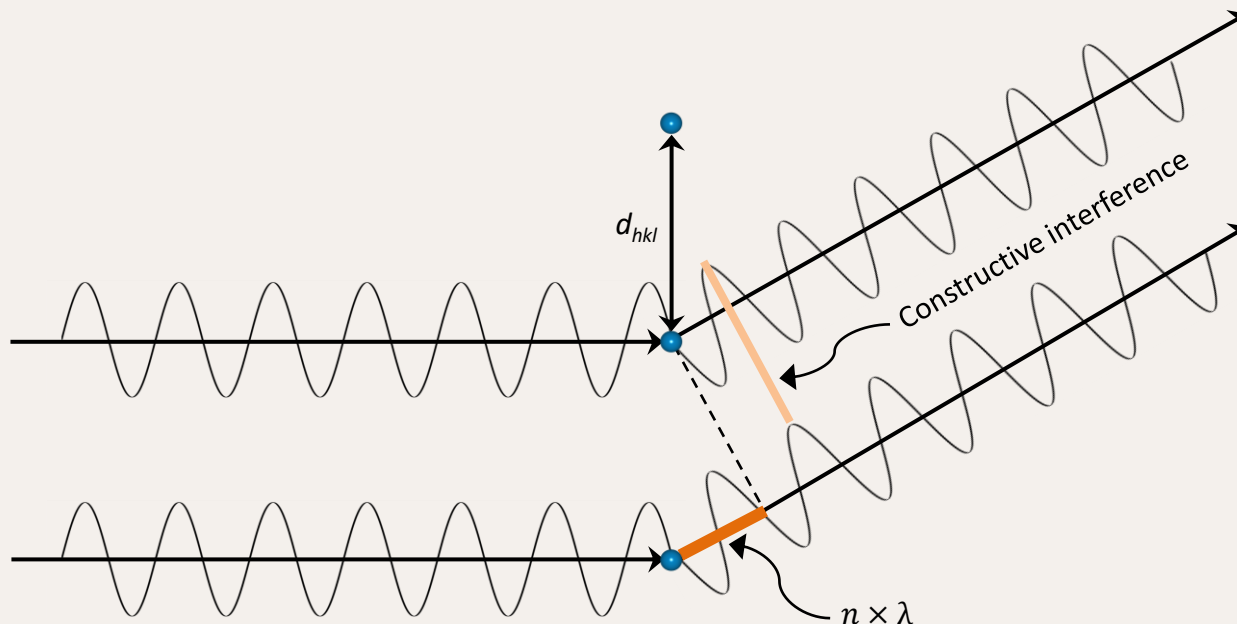
Lattice Planes and Bragg's Law

The typical d -spacing between the lattice planes of a crystal is $d_{hkl} \approx 10^{-10}$ m

Lattice planes act as a diffraction grating for waves (*e.g.* neutrons or X-rays) with $\lambda \approx 10^{-10}$ m

Waves are diffracted by the lattice planes of a crystal at certain angles of incidence, at which the conditions for constructive wave interference are met

Bragg's law relates the d -spacing of lattice planes with the angles where diffraction is observed



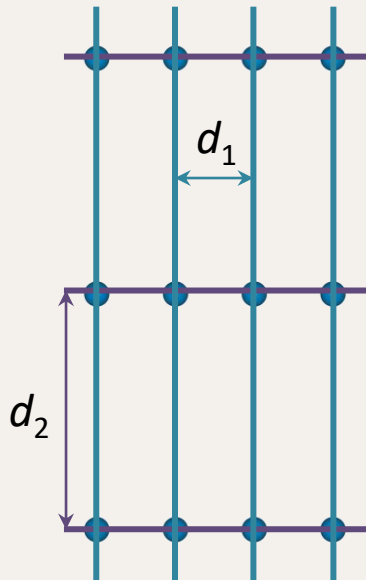
Bragg's law

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

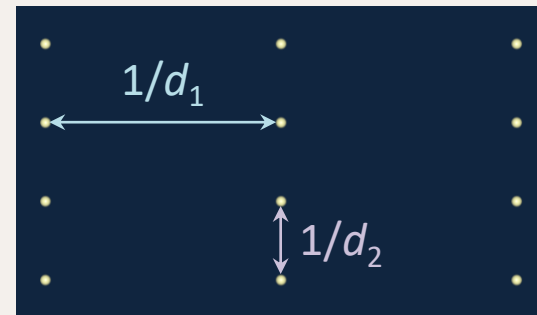
The Reciprocal Lattice

The periodicity of crystals gives rise to diffraction patterns with very sharp and well-defined maxima of scattering intensity, known as Bragg peaks

Thus, the diffraction pattern generated when waves are scattered by a periodic array of lattice planes can also be represented by a lattice, the **reciprocal lattice**



Real lattice
(crystal lattice)

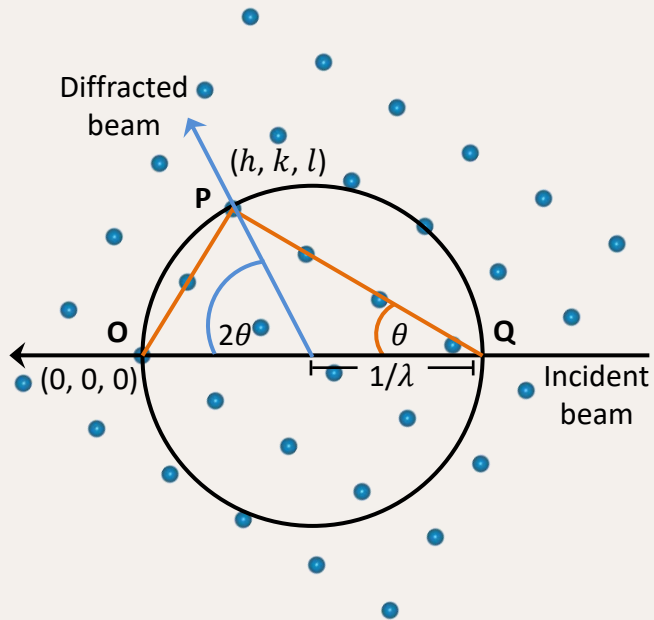


Reciprocal lattice
(diffraction pattern)

Ewald Sphere

Bragg's law is a useful demonstration of the principle of diffraction from crystals in two-dimensions but in reality, diffraction from a crystal is three-dimensional

Another model that helps us think about diffraction in three dimensions is the **Ewald sphere**



Constructing an Ewald sphere:

1. A 3-D crystal generates a 3-D reciprocal lattice, with each reciprocal lattice point representing constructive interference from a set of (h, k, l) planes.
2. Radiation with wavelength λ passing through the reciprocal lattice creates a sphere of radius $1/\lambda$ in reciprocal space, known as the reflecting sphere or Ewald sphere. Any reciprocal lattice points of the crystal within the Ewald sphere can be seen by the incoming radiation.
3. Reciprocal lattice points on the surface of the Ewald sphere satisfy Bragg's law, and hence give rise to constructive interference.
4. Rotating the crystal within the beam brings different lattice points into the Ewald sphere, meaning different (h, k, l) reflections can be observed.
5. Decreasing λ increases $1/\lambda$, allowing access to more reflections.

$$\mathbf{OP} = d_{hkl}^* = 1/d_{hkl} \text{ and } \mathbf{OQ} = 2 \times 1/\lambda = 2/\lambda$$

$$\sin \theta = \mathbf{OP}/\mathbf{OQ} = (1/d_{hkl})/(2/\lambda) = \lambda/2d_{hkl}$$

$$2d_{hkl} \sin \theta = \lambda \Rightarrow \text{Bragg's law!}$$

Watch [here](#) for more!



Structure Factor and Systematic Absences

Bragg's law gives us the condition required for diffraction from a crystal, but what determines the **intensity** of a Bragg peak from a given lattice plane?

The intensity of a Bragg peak I_{hkl} is given by $I_{hkl} \propto |F_{hkl}|^2$, where F_{hkl} the **structure factor**

The proportionality above includes parameters such as Debye-Waller factors, multiplicity of (h, k, l) planes, sample volume, beam intensity and measuring time

The structure factor defines the relationship between the position and nature of scattering matter within the crystal unit cell and the intensity of the Bragg peaks

$$\begin{aligned} F_{hkl} &= \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \\ &= \sum_j f_j [\cos 2\pi(hx_j + ky_j + lz_j) + i \sin 2\pi(hx_j + ky_j + lz_j)] \end{aligned}$$

f_j is the scattering factor for atom j at fractional coordinates (x_j, y_j, z_j) in unit cell

Sum is over all atoms j in the unit cell

For centrosymmetric crystals, *i.e.*, for crystals in which for every (x, y, z) there is an identical $(-x, -y, -z)$, the sine term cancels to zero

Structure Factor and Systematic Absences

Is scattering intensity from all (h, k, l) planes present in a diffraction pattern?

The symmetry of a crystal can lead to destructive interference from certain (h, k, l) planes, resulting in their reflections being **systematically absent** from a diffraction pattern

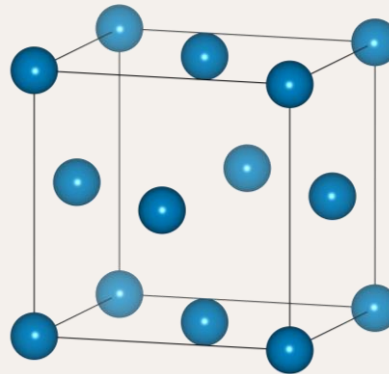
A good illustration of systematic absences stems from lattice centring

For example, consider the scattering from the $(1, 0, 0)$ lattice plane of elemental calcium, which adopts a face-centred cubic structure

$$(h, k, l) = (1, 0, 0)$$

$$(x, y, z) = (0, 0, 0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$$

$$\begin{aligned} F_{100} &= \sum_j f_j [\cos 2\pi(hx_j + ky_j + lz_j)] \\ &= f_j \cos 2\pi(1 \times 0 + 0 \times 0 + 0 \times 0) \\ &\quad + f_j \cos 2\pi(1 \times \frac{1}{2} + 0 \times \frac{1}{2} + 0 \times 0) \\ &\quad + f_j \cos 2\pi(1 \times \frac{1}{2} + 0 \times 0 + 0 \times \frac{1}{2}) \\ &\quad + f_j \cos 2\pi(1 \times 0 + 0 \times \frac{1}{2} + 0 \times \frac{1}{2}) \\ &= f_j [\cos 0 + \cos \pi + \cos 0 + \cos \pi] \\ &= f_j [1 + (-1) + 1 + (-1)] = 0 \end{aligned}$$



$$F_{100} = 0 \Rightarrow I_{100} = 0$$

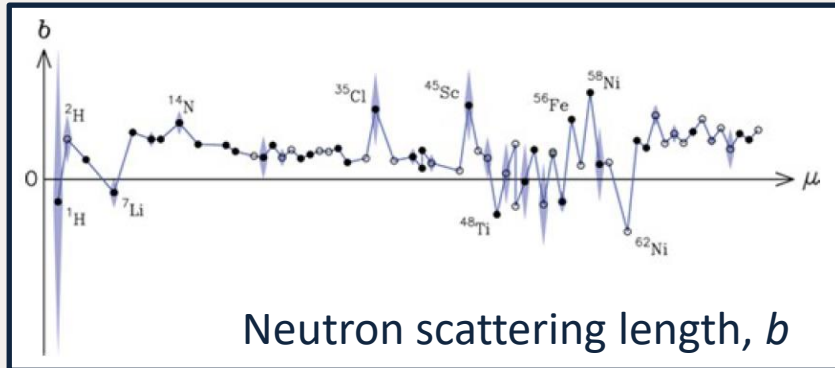
$(1, 0, 0)$ is absent

Lattice Centring	Systematic Absences
P	None
F	To observe a peak, h, k, l must be all even or all odd
I	To observe a peak, $h + k + l = 2n$

Neutron vs. X-ray Diffraction

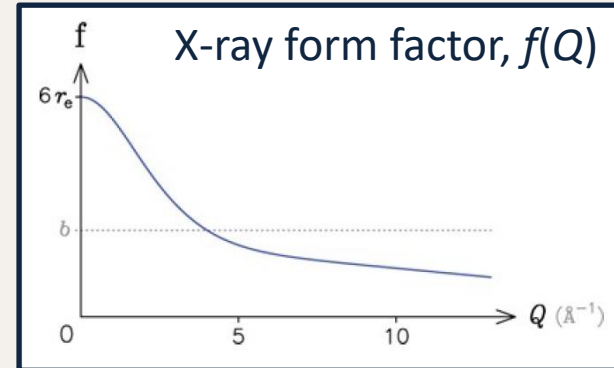
A key difference between the diffraction of X-rays and neutrons from crystals stems from their distinct interactions with matter, resulting in different f_j in F_{hkl}

Neutrons



- Short-range nuclear interaction
- No angular dependence
- Isotopic specific
- No simple variation with atomic number

X-rays



- Long-range electromagnetic interaction
- Decreases monotonically with scattering angle, θ
- Proportional to atomic number

These differences lead to the **complementarity of neutron and X-ray diffraction**, with the study of complex phenomena in functional crystalline materials often requiring combined insight

A Case Study

Materials grand challenge:

A high-performance all-solid-state
Li-ion battery

Research aim:

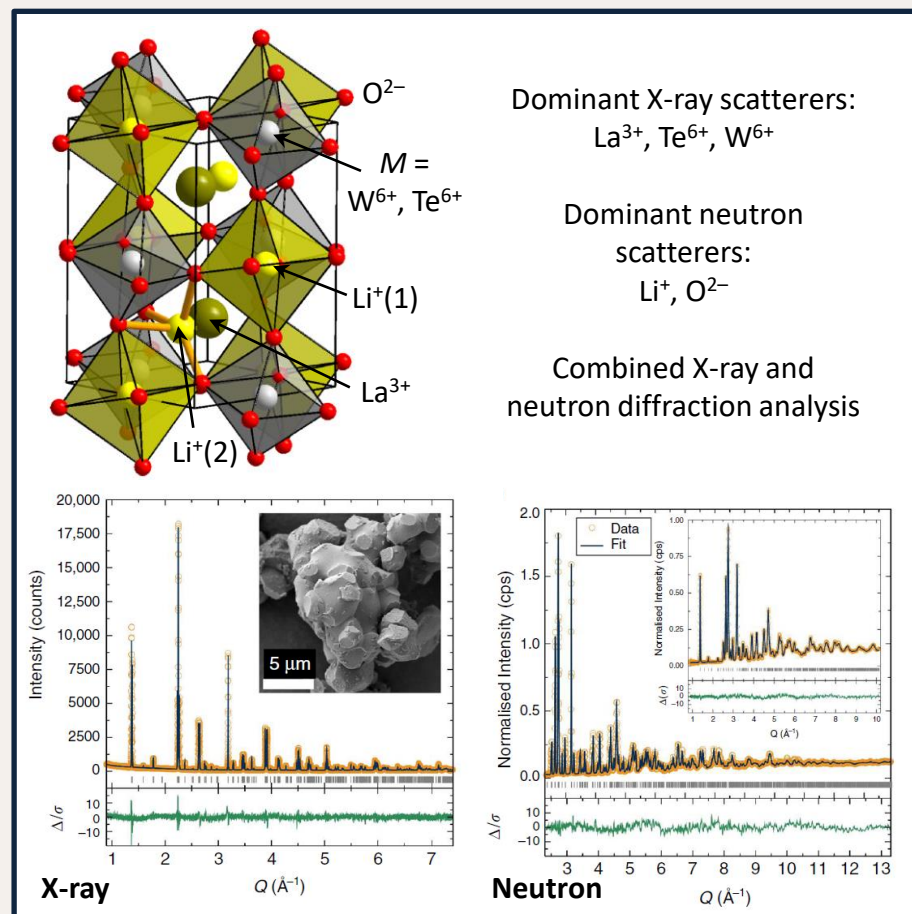
Exploit versatile structure-property
relationships in the perovskites, ABX_3 ,
to maximise performance at solid
electrolyte-electrode boundary

Research hypothesis:

Li^+ must occupy both *A* and *B* sites
in novel perovskite $(\text{La}_{1.5}\text{Li}_{0.5})(\text{Li}M)\text{O}_6$
to yield observed Li-ion mobility

Research outcome:

New material tuned from solid electrolyte
($M = \text{Te}^{6+}$) to electrode ($M = \text{W}^{6+}$), paving
the way for new battery technology



M. Amores *et al.*, *Nat. Commun.* **11**, 6392 (2020)