

# PHY2002: CRYSTALLOGRAPHY

## Additional Notes

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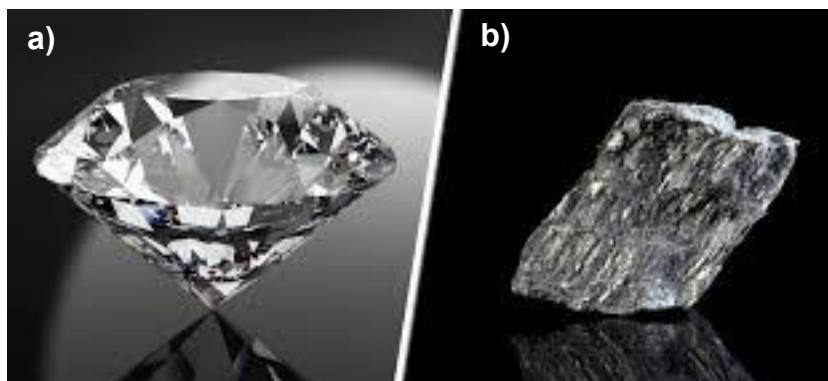
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## 1. Introduction

Crystals can be found everywhere in nature, from minerals (gemstones, graphite, etc) to snowflakes, ice and grains of salt. For centuries scholars have been fascinated by the study of crystals. The study of crystals (crystallography) underpins the development of practically all materials, from everyday products like computer memory cards to flat television screens, cars and aeroplane components. Although the interest in crystals is an old subject, it was not until 1912 that Max Laue reported the first observation of the diffraction of X-rays by a crystal, ZnS, initiating the study of crystal structure at the atomic level. Today, crystallography is a field in its own right that continues developing, with a full scientific community dedicated to it (the International Union of Crystallography). Crystals are made of matter, atoms, molecules and/or ions that fit together in repeating patterns, called *unit cells*, which like bricks stacked in three dimensions, form the whole crystal structure.

Crystallography is the study of the atomic arrangements in solids, concerned with structure at one level up from atomic bonding. Crystallography is a powerful technique that can be used to look inside materials and generate a three-dimensional picture of the arrangement of atoms and molecules inside a crystal. Importantly, it enables us to understand the link between atomic arrangement and material properties.

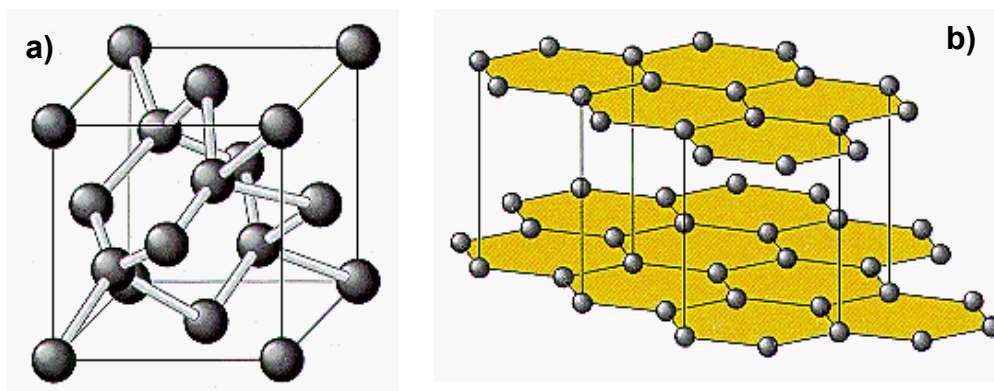
Consider carbon as an example. Carbon is found in nature in two different forms (allotropes), diamond and graphite (Fig. 1). These allotropes have same chemical composition but different crystal structure with very different properties. Diamond is a colourless, transparent material, while graphite is black and opaque. Moreover, diamond is an excellent insulator while, graphite is a good conductor of electricity (graphite electrodes are used in electrical cells); diamond is the hardest naturally occurring material, while graphite is soft and flakes easily.



**Figure 1.** Two different crystal forms of carbon: (a) polished diamond and (b) graphite.

The differences between the properties of these Carbon allotropes are due to the different arrangement of their atoms, their crystal structure. Diamond (Fig. 2a) has a tetrahedral coordination and strong covalent bonds. This means that the carbon atoms are all bonded to four different nearest neighbours in a three-dimensional lattice, determined by the angles of the  $sp^3$  hybridised bonding orbitals, where each C-atom is at the centre of a

tetrahedron, with another C-atom at each corner. Graphite, on the other hand, is a layered structure. Within the layers or sheets, the C-atoms are strongly bonded together by  $sp^2$  hybridised orbitals, so that each atom sits at the centre of a triangle, with another C-atom at each corner, creating flat sheets of hexagons. The sheets are weakly bound together by van-der-Waals forces. Thus, the materials' properties are a direct consequence of their crystal structure.



**Figure 2.** The crystal structure of (a) diamond and (b) graphite. Both materials are forms of pure carbon, but with different atomic arrangements, leading to very different materials properties.

### Why is Crystallography important?

1. Establishes a framework to understand much of solid state physics: thermal physics, phonons, electronic structure and semiconductors.
2. Furthers the understanding and prediction of properties: Any physical property displayed by a crystal adheres to the symmetry of that crystal (Neumann's Principle).
3. Scattering by a crystal can be used to determine the internal structure of complex molecules if formed into crystalline array: DNA, nucleic acids, etc.

**Note:** Crystallography can be challenging, as it requires to visualise structures and operations in 3D. Thus, useful links have been added throughout this material to help the student. Importantly, although these notes are meant to compliment the lecture notes, these are not full notes and reading the recommended resources is highly recommended.

### Learning Objectives:

- To understand how crystals are defined, the symmetry elements involved and how these are represented.
- To recognize the importance and relationship of *Crystallography* and *diffraction*.

## 2. Definitions

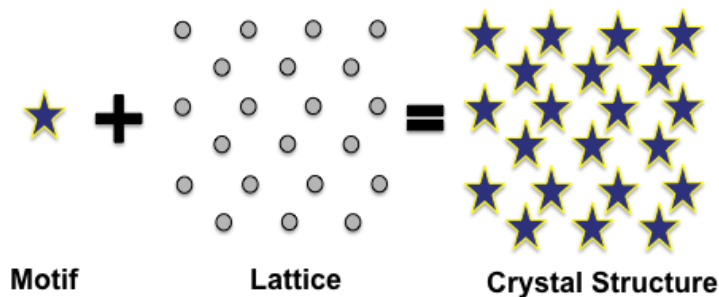
In condensed matter physics and materials science, materials can be divided into two types: **crystalline and amorphous**. The classification depends on the basis of the regularity of this atomic arrangement. Crystalline materials (or crystals for short) have long-range order, i.e., the atoms are arranged in a repeating (periodic) array over length-scales many times the atomic radius. Materials that do not show long-range order in their atomic arrangement are called non-crystalline or amorphous. Amorphous materials may still show short-range order, such as a set number of nearest-neighbours for each atom. However, on a longer length-scale the material is disordered with no periodicity.

Crystalline materials exhibit a wide variety of different crystal structures, which describe the spatial arrangement of the atoms or ions in the material, ranging from relatively simple structures, for most metals, to extremely complex ones for ceramic and polymeric materials. Crystalline materials can be **single crystals or polycrystalline**. Single crystals have perfect periodicity throughout the whole sample (or volume). If a single crystal is grown without external constraints it may take a form with flat faces where the shape indicates the crystal structure. Polycrystalline samples are made up of a collection of small grains, which themselves are single crystals. The grains are generally randomly oriented, so that the crystallographic directions vary between grains. Where grains meet, there is a mismatched region known as a grain boundary.

### 2.1. Crystal, Lattice and Unit Cell

A **crystal** is an arrangement of matter (atoms, ions or molecules) that repeats periodically in three dimensions. *It is said to be a convolution of a lattice with a motif: Lattice + Motif = Structure*

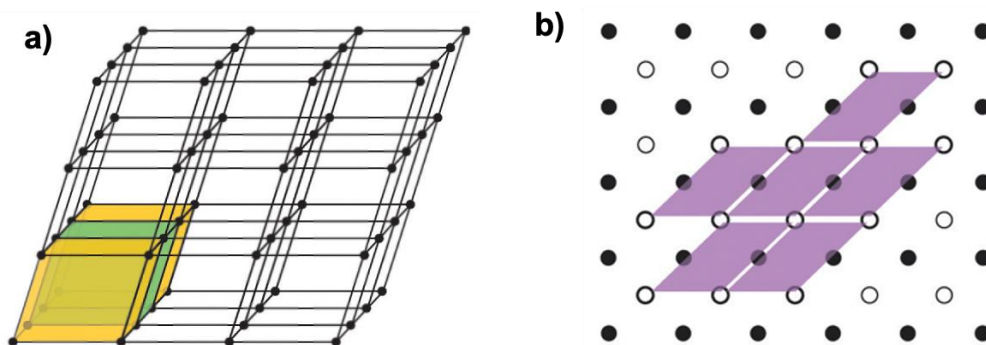
A **lattice** is defined as an infinite regular array of points (known as **lattice points**) repeated periodically throughout space. Hence, the environment of each lattice point is identical to and indistinguishable from all others. A lattice is a mathematical tool that acts as a template, defining the position of atoms and molecules in space. The **motif** is that element of the structure (i.e., atoms, ions or molecules) associated with each lattice point such that the complete crystal structure is produced by adding the motif to each lattice point. An example of this convolution can be seen in Fig. 3.



**Figure 3.** Two-dimensional schematic of the elements forming a crystal structure.

All crystal structures can be built up from a lattice by placing an atom or group of atoms at each lattice point. The crystal structure of a simple metal and that of a complex protein may both be described in terms of the same lattice, but whereas the number of atoms allocated to each lattice point is just one for a simple metallic crystal, it may easily be 1000 for a protein crystal. For example, the diamond structure (Fig. 2a) can be regarded as a cubic face centred structure and with two-point motif (carbon atoms) at (0,0,0) and ( $\frac{1}{4}$ ,  $\frac{1}{4}$ ,  $\frac{1}{4}$ ); both of which are assigned to the cubic lattice.

The structure of a perfect crystal can be seen as a repetition of identical units across all space. To study the crystal structure as a whole it is simpler to consider the basic unit that repeats itself: the unit cell. The **unit cell** is a region of space which when repeated by translational symmetry fills all space, with no gaps between them. Thus, a lattice can be thought of as a build-up of repeating unit cells. In 3D, unit cells are described by parallelepiped shapes, with lattice points at its vertices, and in 2D, the unit cell can be defined as a parallelogram whose vertices are lattice points (Fig. 4). The unit cell defines the crystal structure, it contains the maximum symmetry that uniquely defines the crystal structure and typically, it contains more than 1 atom or molecule.



**Figure 4.** Illustration of unit cells in a) three and b) two dimensions, respectively.

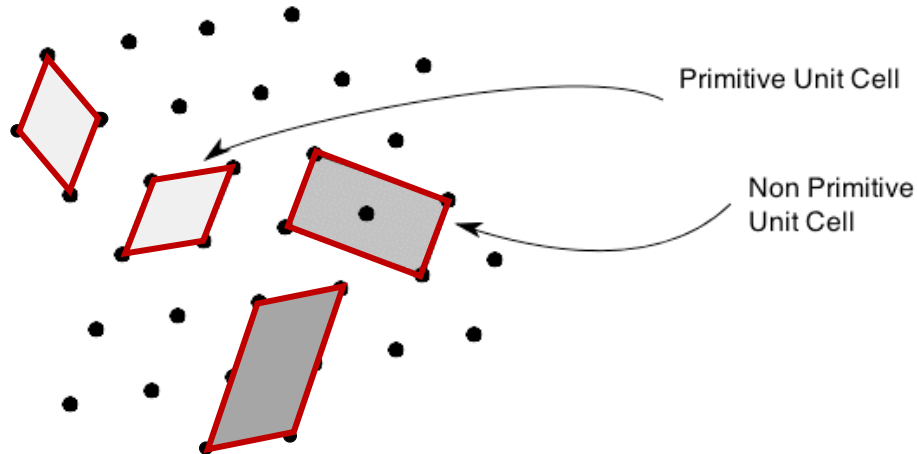
There are two types of unit cell, shown in Fig 5:

- **Primitive:** Contains only one lattice point per unit cell\*, and are labelled P.
- **Non-primitive:** Contains more than one lattice points per unit cell.

\*It should be noted that although the lattice points delimit the unit cell these are not contained within the unit cell in their totality. For example, in a square primitive unit cell only a quarter (the corner) of each lattice point is strictly within the unit cell. This is, the total contributing lattice point(s) in one square primitive unit cell is one lattice point:  $\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} = 1$ . As shown in the simple cubic structure (SC) in Fig. 9.

It is often the case that a primitive unit cell *will not reflect the symmetry* of the whole crystal structure, in that case a suitable non-primitive unit cell can be identified. Non-primitive unit cells can be further classified as:

- **Face centred (F):** Unit cells have a lattice point at each corner, plus one lattice point in the centre of each face.
- **Body centred (I):** Unit cells have lattice points at each corner, plus one lattice point in the centre of the body of the cell.
- **Side centred (A, B, or C):** Unit cells have lattice points at each corner, plus one lattice point each on a pair of opposite sides of the cell.



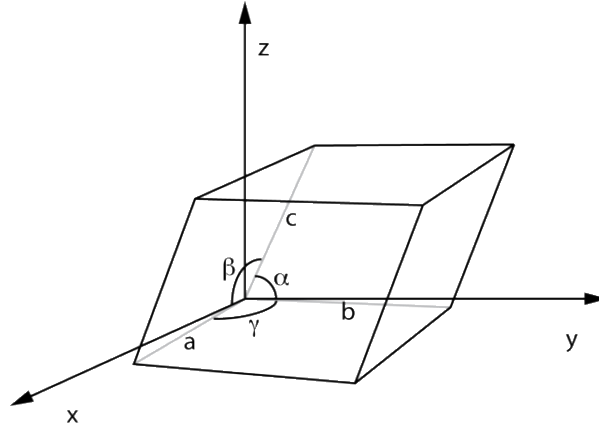
**Figure 5:** Possible primitive and non-primitive unit cells for the same 2D lattice.

★ [More on unit cells](#)

## 2.2. Lattice parameters, points and vectors.

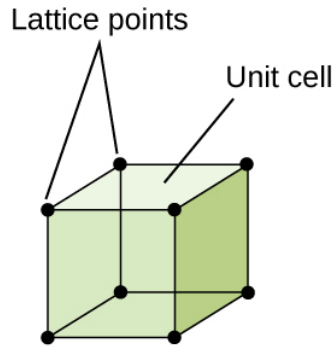
A unit cell can be defined by the lengths of the cell edges:  $a$ ,  $b$  and  $c$ , and the angles these edges make with each other:  $\alpha$ ,  $\beta$  and  $\gamma$ , as shown in Fig. 6. Since the lattice is built from repeating the unit cell, these six geometrical parameters describing the unit cell also describe the whole lattice and are known as **lattice or unit cell parameters**.

In crystallography, it is customary to define a right-handed coordinate system where the  $x$ ,  $y$  and  $z$  axes are parallel to the unit cell edges  $a$ ,  $b$  and  $c$ .



**Figure 6.** A generic unit cell illustrating the lattice parameters against an orthogonal xyz coordinate system.

As previously mentioned, the unit cell is the smallest representation of the lattice and the lattice points make up the unit cell, where each lattice point has exactly the same environment. **Lattice points** represent the location of the motif (atoms or ions, Fig. 7), such that each lattice point can be given a point coordinate  $\mathbf{P}(u, v, w)$  defined with respect to the origin of the lattice. By the definition of lattice, any lattice point can be chosen as the origin.



**Figure 7.** A generic unit cell illustrating the lattice points within a unit cell.

Lattice points can also be expressed in **fractional coordinates** of the unit cell. A fractional coordinate is given by  $\frac{x}{a}$ , where  $x$  is that coordinate in absolute measure (Å or nm) and  $a$  is the unit cell lattice parameter in the same direction as the lattice point. Thus, a position  $\mathbf{x}$  at 1.45 Å along the unit cell of edge length 12.34 Å corresponds to a fractional coordinate of 0.1175.

Once the unit cell axes and origin have been chosen, all lattice points can be reached by a primitive translation lattice vector:

$$\mathbf{t}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad \text{Eq. (1)}$$

Where  $n_1$ ,  $n_2$  and  $n_3$  are *integers*.

Any unit cell will have a certain number of lattice points. However, the importance of defining a unit cell is that once this is identified then the lattice of the whole crystal will be automatically created by allowing the translation of the primitive translation lattice vector. This means that to describe a crystal, or a unit cell, it is not necessary to write down all the coordinates of the lattice points (or atoms) in the crystal. For example, the simple cubic structure of Fig. 7 has eight lattice points but the whole crystal structure can be identified with the point coordinate or motif (also known as basis): (0,0,0). This can be justified by considering that the origin is arbitrary and all of those eight lattice points are equivalent and can be considered the origin of another unit cell.

Additionally, a direction in a crystal is given by:

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c} \quad \text{Eq. (2)}$$

where  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are the **basis vector**; and  $u$ ,  $v$  and  $w$  are positive or negative integers (or zero) and (u,v,w) represent the positions of the atoms or ions in the unit cell. Negative directions are denoted with a bar on top of the number. For example:  $\bar{1}$ .

Under the premise of the translation required by the unit cell to create the lattice, it can be seen that **lattice vectors** connect two lattice points. **Primitive lattice vectors** are the shortest vectors possible, with a magnitude equivalent to the lattice parameter (unit cell edge length). For example, in a cubic unit cell, the three basis vectors can be labelled as  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$ . These vectors are parallel to the cubic unit cell edges and have the same length as  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ . When the lattice points are translated (or repeated) by the primitive lattice vectors it results in the whole lattice. For example, consider the diamond structure in Fig. 2, the primitive lattice vectors are:  $\vec{a}_1 = \frac{a}{2}\mathbf{x} + \frac{a}{2}\mathbf{y}$ ,  $\vec{a}_2 = \frac{a}{2}\mathbf{x} + \frac{a}{2}\mathbf{z}$  and  $\vec{a}_3 = \frac{a}{2}\mathbf{y} + \frac{a}{2}\mathbf{z}$ ; and, there are two atoms as basis (or motif) which in fractional coordinates of the conventional unit cell, the positions of these carbon atoms are (0,0,0) and (0.25, 0.25, 0.25).

### 2.3 Miller Indices

It is often necessary to characterize or identify planes and directions within a crystal. By convention, directions and planes can be described by the following notation, known as **Miller Indices**:

- **Direction [uvw]**. The indices [uvw] of a direction are given by the differences in the xyz coordinates between two points, see Fig. 8a.

The following steps can be used in determining [uvw]:

- i. Any vector may be translated throughout the crystal lattice without alteration, if parallelism is maintained.



- ii. The length of the vector projection on each of the three axes is determined; measured in terms of the unit cell parameters  $a$ ,  $b$  and  $c$ .
- iii. The three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
- iv. The three indices are enclosed in square brackets, without commas. Thus, the integers  $[uvw]$  correspond to the reduced projections along  $x$ ,  $y$  and  $z$  axes.

Moreover, directions are vectors that connect any two lattice points (or from the origin). For example, the direction connecting the lattice points  $(0,0,0)$  and  $(1,0,0)$  in a cubic unit cell can be found in the following way:  $(1,0,0) - (0,0,0) = [100]$ . In this particular case, the  $[100]$  direction is a lattice vector, parallel to the lattice parameter  $a$ .

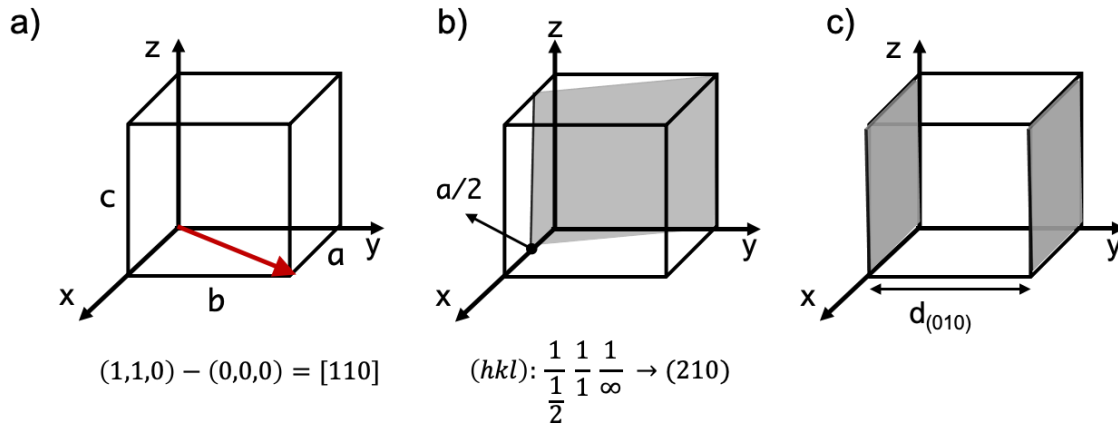
A set of directions related by symmetry, making them equivalent, is known as a family of directions and is denoted by the notation  $\langle uvw \rangle$ , using angle brackets. In most cubic materials the directions  $[001]$ ,  $[010]$ ,  $[100]$  and their negative counterparts are equivalent vectors, all related by symmetry. These vectors may then be written as  $\langle 100 \rangle$ , a family of directions.

- **Planes (hkl)**. The orientation of planes for a crystal are represented in a similar manner: the unit cell is the basis, with the three-axis coordinate system. In all but the hexagonal crystal system, crystallographic planes are specified by three Miller indices:  $(hkl)$ . Any two planes parallel to each other are equivalent and have identical indices. The procedure to determine the  $(hkl)$  indices is as follows:

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.
2. Identifying the point at which the plane intercepts (or parallels) the three axes. Planes intersect the lattice vectors at:  $a/h$ ,  $b/k$  and  $c/l$ . The length of the planar intercept for each axis is determined in terms of the lattice parameters  $a$ ,  $b$  and  $c$ . A plane that parallels an axis must be considered to have an infinite intercept.
3. The reciprocals of point ii) are taken.
4. If necessary, these three numbers are changed to the set of smallest integers by multiplication or division by a common factor.
5. The integer indices are enclosed in parentheses without commas:  $(hkl)$ .

For example, consider a plane in a cubic unit cell that which intercepts the axes in the following manner:  $x = 1$ ,  $y = \infty$  and  $z = \infty$ . Thus, the  $(hkl)$  Miller indices for this plane are the reciprocal of these interceptions such that:  $h = 1/1 = 1$ ,  $k = 1/\infty = 0$ ,  $l = 1/\infty = 0$ ; producing the miller indices  $(100)$ . An additional example is shown in Fig. 8b.

Similar to the notation for directions, a family of equivalent planes (related by symmetry) is written as  $\{hkl\}$ . For simplicity, fractions in both planes and directions are eliminated by multiplying all components by their common denominator.



**Figure 8.** Illustration of a) a vector  $[uvw]$ , b) a plane  $(hkl)$  and c) interplanar distance in a cubic unit cell ( $d_{hkl}$ ).

In most cubic materials the planes (001), (010), (100) and their negative counterparts, are equivalent planes, all related by symmetry. These planes can then be written as  $\{100\}$ , a family of planes. The number of different planes contained within a group is called its multiplicity. For example, the multiplicity of  $\{100\}$  in most cubic systems is 6, and 8 for  $\{111\}$ . In this way, every family of planes will 'cover' the whole crystal or unit cell.

Moreover, any set of parallel planes can also be characterized by a vector perpendicular to one of the planes, see Fig. 8c. This vector is the distance of the plane to the origin known as the **interplanar spacing** (distance between parallel planes):  $d_{hkl}$ . The interplanar spacing can be directly calculated from the Miller indices  $(hkl)$  and the values of the lattice parameters. The relationship between the planes indices  $(hkl)$  and the interplanar spacing depends on the crystal system. Table 1 shows the relationship for the different crystal systems.

Miller indices are useful in understanding many phenomena in materials science, such as explaining the shapes of single crystals, the form of the microstructure of some materials, the interpretation of diffraction patterns and the movement of structural defects such as dislocations. All of these can significantly determine the macroscopic properties of a material.

Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$
Triclinic	$\frac{1}{d^2} = \frac{1}{V^2} [h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma + 2hkabc^2 (\cos \alpha \cos \beta - \cos \gamma) + 2kla^2 bc (\cos \beta \cos \gamma - \cos \alpha) + 2hlab^2 c (\cos \alpha \cos \gamma - \cos \beta)]$

**Table 1.** The interplanar distance,  $d_{hkl}$ , as a function of lattice parameters for various crystal systems.

#### 2.4. The Weiss Zone Law

When any two non-parallel planes within a crystal can intersect in a line that lies in both planes. This line, is said to be the zone axis of the zone in which the two planes are situated. Frequently, a number of important crystal planes all lie in the same zone, i.e., intersect one another in parallel lines. Thus, if a lattice vector  $[uvw]$  is contained in the plane  $(hkl)$ , there is a relationship that links the lattice vector to the lattice planes:

$$hu + kv + lw = 0 \quad \text{Eq. (3)}$$

This is known as the **Weiss zone law** and it is the condition that the normal to  $(hkl)$  be itself normal to the direction  $[uvw]$ . This means that each set of planes  $(h_1 k_1 l_1)$  will intersect each member of a nonparallel set of planes  $(h_2 k_2 l_2)$  along parallel lines with direction  $[uvw]$ . This is, the direction  $[uvw]$  of the intersection of the two planes is given by:

$$\begin{aligned} u &= k_1 l_2 - l_1 k_2 \\ v &= l_1 h_2 - h_1 l_2 \\ w &= h_1 k_2 - k_1 h_2 \end{aligned} \quad \text{Eq. (4)}$$

$[uvw]$  is known as the "zone axis" of these two sets of planes. The planes of a zone axis  $[uvw]$  must satisfy the Weiss Zone Law. This law expresses the mathematical condition for a vector  $[uvw]$  to lie in a plane  $(hkl)$ . This condition can be determined through elementary vector considerations. In a cubic system, this is exactly analogous to taking the scalar product of the vector and the plane normal, so that if they are perpendicular,

the angle between them,  $\theta$ , is  $90^\circ$ , then  $\cos\theta = 0$ , and the direction lies in the plane. In cubic systems this can be expressed as the scalar (dot) product of  $[uvw]$  and the plane normal  $(hkl)$ . Importantly, the Weiss zone law applies to all crystal systems, including those that are not orthogonal.

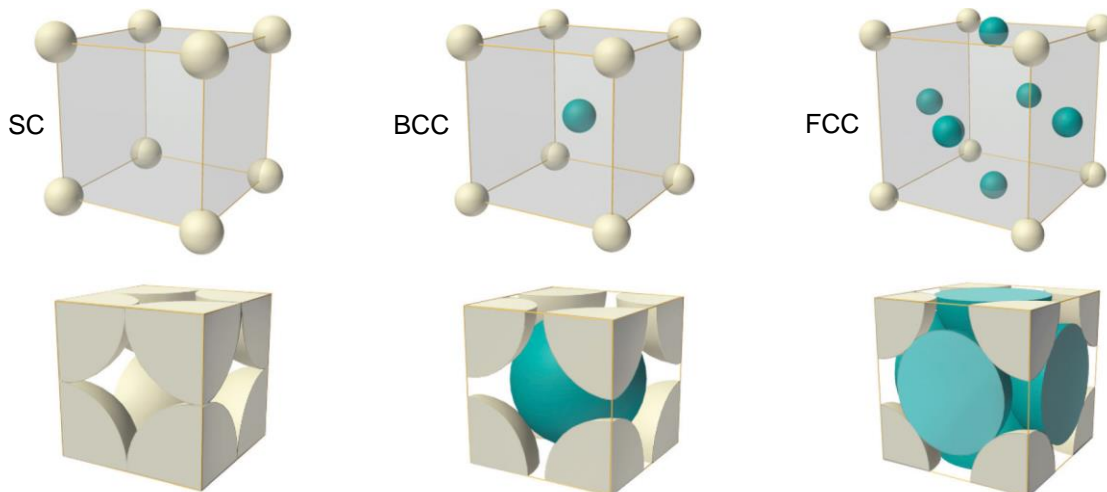
#### ★ Examples of [Miller Indices and Weiss Zone Law](#)

### 3. Close packing and packing efficiency

The atoms in a crystal structure are often considered as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is equal to one diameter of the hard sphere, in other words two times the radii. Crystals form due to the attraction between the atoms, forming bonds, often very close together – is energetically favourable to have many neighbours. Thus, the **coordination number (CN)**, or number of adjacent atoms, as well as the **packing efficiency** of the unit cell become important aspects in the crystal structure and these are linked to the material's properties.

In many cases the atoms of a crystal pack together as tightly as possible, forming a close-packed structure. This is the case for most metallic structures where, the atomic bonding is non-directional in nature and consequently, there are minimal restrictions as to the number and positions of nearest neighbour atoms. This leads to relatively large numbers of nearest neighbours and dense atomic packing.

However, it is not possible to pack spheres together without leaving some void spaces between the spheres and the way atoms are packed together produces different types of unit cells, shown in Fig. 9: simple cubic (SC), body-centred cubic (BCC) and face-centred (FCC).



**Figure 9.** Schematic models for simple cubic (SC), body-centred cubic (BCC) and face-centred (FCC) cubic unit cells, assuming only one atom per lattice point.

A simple cubic crystal has 8 lattice points and atoms, one in each corner. However, the unit cell contains only the parts of these atoms that are within it. Thus, the total of atoms within a **SC** unit cell is: 8 lattice points  $\times$  1/8 atom = 1 atom. This is, a SC unit cell contains 1 atom. Similarly, a **BCC** unit cell contains 2 atoms per unit cell and the **FCC** structure contains 4 atoms per unit cell.

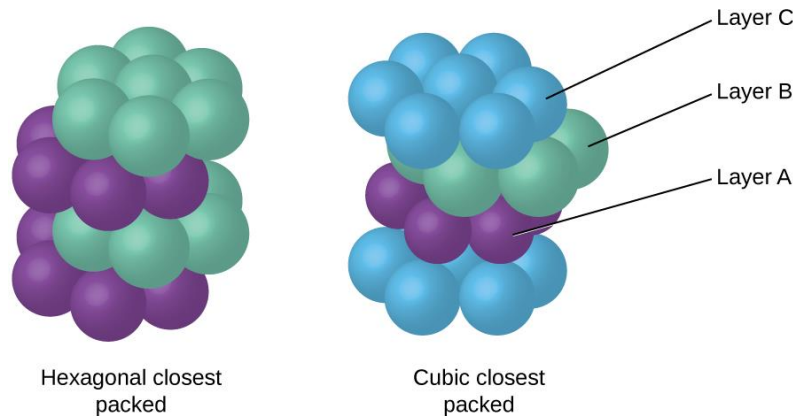
As seen in Fig. 9, there are voids in each of the atomic packings and it is useful to know the packing efficiency. **Packing efficiency (PE)** is the fraction of volume in a crystal that is actually occupied by atoms:

$$\begin{aligned} \text{PE} &= \frac{\text{Volume occupied by all atoms in the unit cell}}{\text{Volume of Unit cell}} \\ &= \frac{\frac{4}{3}\pi r^3 * \text{number of atoms}}{a^3} \times 100\% \end{aligned} \quad \text{Eq. (5)}$$

Where  $a$  is the unit cell edge length and  $r$  is the radius of each atom. Similar to equation (3), the packing efficiency in 2D can also be calculated by considering only the area of the atoms (as circles) in the unit cell and the area of the unit cell. This can also be used to calculate the planar density for a specific plane.

Close packed structures are often energetically favoured, and many crystals are based on this structure. The FCC unit cell is one of the most densely packed crystal structures, with atoms occupying 74% of the volume. For this reason, FCC is also called **cubic closest packing (CCP)**. The closed-packed atomic arrangement maximizes the overall attractions between atoms and minimizes the total intermolecular energy, most metals are packed in this manner.

There are two types of closed-packed structures: CCP (or FCC) and **hexagonal closest packing (HCP)**, shown in Fig. 10. In a closer look, a closed-packed structure is made up of up to three repeating layers of hexagonally arranged atoms: ABCABC... So that each atom in the second layer B is in contact with three atoms in the first layer A. However, the order of the third layer can have two options: 1) directly above the atoms in the first layer, making the third layer also A, resulting in an ABABA stacking or 2) a different position, neither on top of the A or B layer, creating a third layer C and an ABCABC stacking. Option 1 is known as HCP and option two as CCP (or FCC).



**Figure 10.** Schematic models for simple close-packed structures: HCP and FCC.

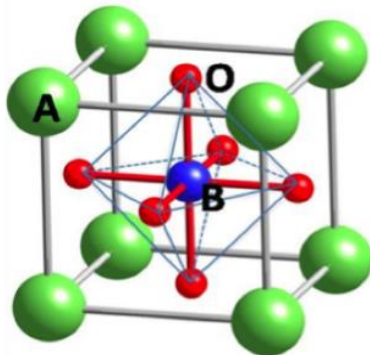
#### 4. Visualizing crystal structures in 2D

One convenient way to represent crystal structures on two-dimensions, is by a **structure plan or plan view**. These 2D representations are usually viewed down a particular crystallographic direction or onto a crystallographic plane. Structure plans help to visualise the crystal structure and the symmetry attached to it. To create a *structure plan* the following information is needed:

- lattice type
- fractional coordinates of the atoms, which constitute the motif of the crystal
- the viewing direction or plane of projection

Remember that the fractional coordinates of the atoms in a crystal are simply the vector positions in the terms of  $a$ ,  $b$  and  $c$ . If the fractional coordinates of the motif are specified then this motif must be represented at every lattice point.

An example of this representation is the group of materials known as *perovskites*, with the general formula  $ABO_3$ . Examples include  $BaTiO_3$ ,  $SrTiO_3$ , and  $CaTiO_3$ . A typical 3D perovskite unit cell of the form  $ABO_3$  is shown in Fig. 11 (which is not the same as the structure plan in Fig. 12).

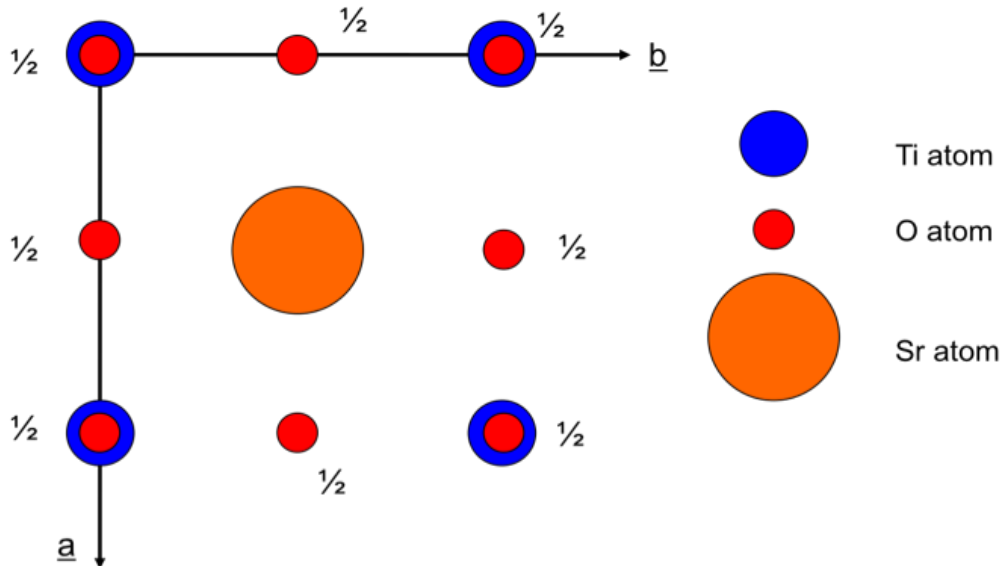


**Figure 11.** Typical representation of a perovskite unit cell, with the oxygens (O) marking the polyhedra. Figure from reference 2.

For a structure plan of this perovskite structure, consider the crystal structure of  $\text{SrTiO}_3$  viewed down  $[001]$ :

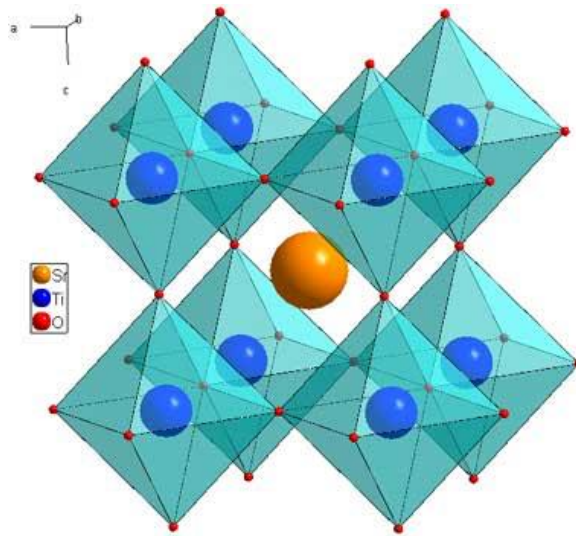
- Lattice type: Cubic P
- Motif:  $\text{Sr } (\frac{1}{2}, \frac{1}{2}, 0)$ ;  $\text{Ti } (0, 0, \frac{1}{2})$ ;  $\text{O } (\frac{1}{2}, 0, \frac{1}{2}), (0, 0, 0) \text{ and } (0, \frac{1}{2}, \frac{1}{2})$ .

The first step is to draw the axes, in this case  $a$  and  $b$  (as the view is down  $[001]$ ), and determine the array size: one unit cell in this case and locate the positions of the lattice points for a cubic P-type crystal structure. These lattice points are located at the corners of the cube. Then take each motif and locate it from every lattice point. Here we choose to start with the Sr atom at one of the lattice points. If we start with the lattice point in the top left corner and from there move  $\frac{1}{2}$  in  $a$  and  $\frac{1}{2}$  in  $b$ ; this makes the Sr atom sit in the middle of the drawing. Repeat these actions for the Ti and the three oxygen atoms; any atom that occurs at the origin of the plan view is also repeated at the other three corners. This results in the structure plan shown in Fig. 12, where the  $\frac{1}{2}$  label represents the position with respect to the 'c' axis.



**Figure 12.**  $[001]$  Structure plan for  $\text{SrTiO}_3$ .

Structure plans are easy to draw and relatively accurate but give a poor feeling for the 3D structure and sometimes it is therefore better to find another way to represent a crystal structure. For example, it is often useful to think of the coordination geometry. This is, distinct bonded units such as polyhedra, and of the full crystal structure as a series of linked polyhedra, sharing corners, edges or faces, as seen in Fig. 11, and emphasised in Fig. 13. If the  $\text{TiO}_6$  units in  $\text{SrTiO}_3$  are represented by octahedra then the structure may be easily visualised as corner-sharing  $\text{TiO}_6$  polyhedra, with the O atoms forming cages with Ti atoms at their centre. The Sr atom is then located between these oxygen octahedra.



**Figure 13.** Octahedral representation for  $\text{SrTiO}_3$ . Figure from reference 3.

★ [‘How to draw a structure plan of a ZnS crystal’](#)

Another way of referring to the crystal structure is using the **coordination number**. This is the number of nearest neighbours of a given atom in the crystal lattice. It determines the nature of the bonding in a crystal. The most common coordination numbers are 4, 6, 8, and 12. For example, a simple cubic (SC) crystal structure will have a  $\text{CN} = 6$ .

## 5. Symmetry

The idea that certain objects possess symmetry is common. However, specifically for crystallography, Glazer and Burns [4] define symmetry as:

*‘that property possessed by an object that, when transformed in some way (e.g., by rotation, inversion, etc.), looks the same after as before the transformation. In other words, symmetry is a demonstration of the invariance of an object to some sort of transformation’.*

The essence of crystallography lies in the study and understanding of crystal structure. However, the crystal structure alone is not sufficient to describe the full nature of a crystal and symmetry plays a key role. As Neumann’s principle states:

*“the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal”.*[1]

Therefore, understanding the symmetry of the crystal structure of a material will give us vital information about the possible symmetries of other physical properties of the material.



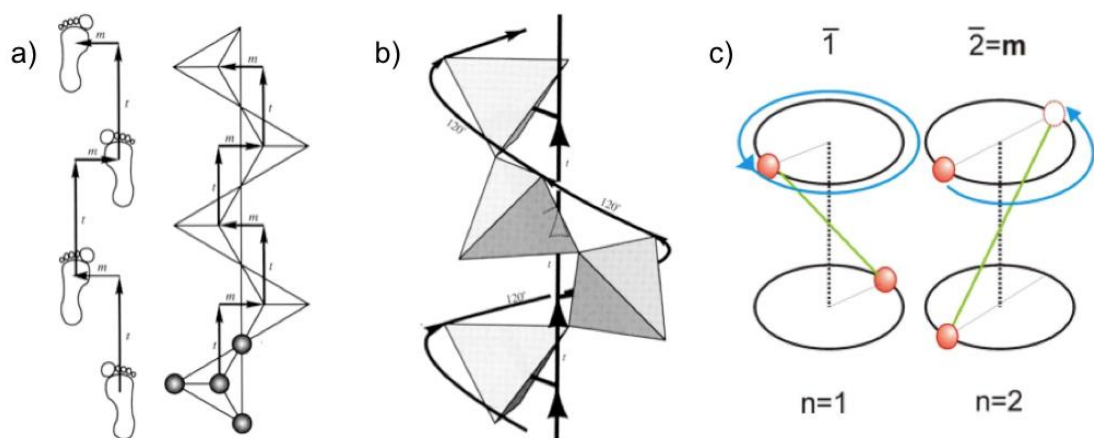
It should be noted that crystal symmetry is a product of energy minimization in the atomic arrangement.

This section introduces the basic symmetry concepts, and discuss the notation used to describe the symmetry operations and how these define the different crystal structures.

There are five basic symmetry operations:

- **Translation (*t*).** The lattice itself generates translational symmetry (the motif is repeated on every lattice point) – the unmoved crystal is indistinguishable from that moved by any lattice vector. In other words,
- **Rotation (*n*).** Rotational symmetry causes an object to come into coincidence with itself after rotation of  $360^\circ/n$ , where *n* is an integer and *n* = 1, 2, 3, 4 and 6. For example a two-fold rotation (or diad) is written as 2, and it indicates a rotation of  $180^\circ$ . Note that there's no 5-fold rotation as this would leave either voids or an overlap of the pentagons. The symbol for the rotation depends on the type of rotation (see Fig. 15). For example, a two-fold rotation ( $180^\circ$  rotation) is a diad -represented by an oval, and a three-fold is a triangle. Note that, the symbol for the rotation *n*=1 is not represented here, since this is the identity and no actual operation takes place. This means that the object is unchanged or is rotated by  $360^\circ$ . This particular case is called *Identity* (E or 1).
- **Mirror (*m*).** An object has mirror symmetry if reflection of the object in a plane brings it into coincidence with itself. The symbol for the mirror is a solid line.
- **Inversion (*i*).** This type of symmetry exists when for any point on the object *x, y, z*, an exactly similar point is found at *-x, -y, -z*. The origin is called a centre of symmetry, and the object is said to be centrosymmetric. This can be understood as the intersection of a mirror and a two-fold axis.
- **Mixed.** When two elemental symmetry operations are combined, this can be (see Fig. 14):
  - *Glide plane*: A mirror plane combined with a translation parallel to the plane of the mirror.
  - *Screw axes*: The rotation axis combined with a translation along the symmetry axes, in a defined crystallographic direction by a defined step (for example, half a unit cell). These are like spiral staircases.
  - *Rotoinversion* ( $\bar{1}$ ): A rotation axis combined with a centre of symmetry (inversion). For a rotation of  $360^\circ/X$ , the rotation axis is given by *X*, and the corresponding rotoinversion axis is given by  $\bar{X}$ .

✪ More about 5-fold rotation in Appendix A, “An Introduction to Mineral Sciences” by A. Putnis














**Figure 14.** Examples of mixed symmetry. a) Simple representation of a glide plane (feet) and glide planes in single chain of silicates – pyroxenes. b) Screw axes in a 3D network of silicates – quartz. c) Two rotoinversion symmetry operations. Figures from references 5 and 6.

In 2D, the symmetry operations are: mirror, identity, rotation and glide. In three dimensions, the symmetry operations are: inversion centers and screw axes. In addition, the mirror can become a mirror plane and the glide operation can become a glide plane.

Some symmetry operations are compatible with translations, some are not. For example, mirror, glide, diads, triads, four and six-fold rotations are compatible.

The symmetry elements can be represented by graphic symbols, with the symmetry they are representing; some of the most common elements and their symbols are shown in Fig. 15. Note that the symbol for the rotation  $n=1$  is not represented, since this is the identity and no actual operation takes place. Moreover, the subscripts denote the translation along the axis of rotation associated with each operation of the symmetry. A more comprehensive list of symmetry symbols can be found in [Appendix 6](#) of reference [4].

Symbol:				
Name:	Diad	Triad	Tetrad	Hexad
Notation:	2	3	4	6
Symbol:				
Name:	Screw Diad	Screw Triad	Screw Tetrad	
Notation:	$2_1$	$3_1$	$4_1$	
Symbol:				
Name:		Screw Hexad		
Notation:		$6_1$		
Name:	Mirror Plane			
Glide Plane (with translation in plane of paper)				
Glide Plane (with translation perp. to paper)				

**Figure 15.** Graphic representation of symmetry elements. From reference 7.

Another way to represent symmetry elements is by the Schoenflies and **Herman-Mauguin (H-M) symbols**, shown in Table 2. Both sets of these symbols, help identifying symmetries in geometrical objects and crystal structures.

The Schoenflies notation is not used for 2D representations and is more often applied to physical chemistry and spectroscopy, while **the H-M notation** is preferred in crystallography; it is the one used in the **International tables**.<sup>[7]</sup>

In summary, the H-M notation consists of some combination of numerals (1, 2, 3, 4 and 6) that denote an axis of rotational symmetry, numerals with a bar-over ( $\bar{1}$ ,  $\bar{3}$ ,  $\bar{4}$  and  $\bar{6}$ ;  $\bar{2} = m$ ) which describe an axis of inversion, the letter *m* that refers to a mirror plane and a slash (/) that means 'perpendicular to'. Thus,  $2/m$  means a 2-fold axis of rotation perpendicular to a mirror plane.

It should be noted that two symbols in succession means 'parallel to'. For example,  $3m$  denotes a 3-fold axis parallel to three mirror planes.

✪ Practice (and visualise) the symmetry operations at "[Symmetry Challenge](#)". This is chemistry based; and uses the Schoenflies notation.

Symmetry Operation	Description	Symbol	
		Schoenflies	Hermann-Mauguin
Identity	unchanged or rotation by 360°	E or C <sub>1</sub>	1
n-fold Rotation (n = 2, 3, 4, (5), 6)	Rotation by 360°/n about a rotation axis	C <sub>n</sub>	n
Mirror Plane	Reflection	σ <sub>v</sub> , σ <sub>h</sub> or σ <sub>d</sub>	m
Inversion	Point reflection through a centre of symmetry	i	$\bar{1}$
Improper Inversion (Sch.)	Rotation by 360°/n followed by a reflection in a plane perpendicular to the n-fold axis	S <sub>n</sub>	-
Rotoinversion (H.-M.)	Rotation by 360°/n followed by an inversion	-	$\bar{n}$

**Table 2.** Symmetry notations.

\* σ<sub>v</sub> - vertical mirror plane, σ<sub>h</sub> –horizontal mirror plane or σ<sub>d</sub> – diagonal mirror plane.

\* Improper rotation and rotoinversion actually describe the same.

### 5.1. Point Symmetry Operations

Symmetry operations can also be described mathematically, using matrices. Any point (r) in 3D can be represented using coordinates (x,y,z). This position can be an atom in the crystal structure. If a symmetry operator (R) acts on the point (carrying out a point-symmetry operation), the new position (r') can be described as:

$$r' = Rr \quad \text{Eq. (6)}$$

or by the matrix transformation:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad \text{Eq. (7)}$$

Thus, the multiplication of any coordinate position  $r \equiv (x, y, z)$  by the matrix, R, will give the new symmetry related coordinate. For example, the matrix that describes the symmetry element *identity* (E or 1) is called the unit or identity matrix, because it is the most basic symmetry operation which leaves all coordinates unaffected:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{Eq. (8)}$$

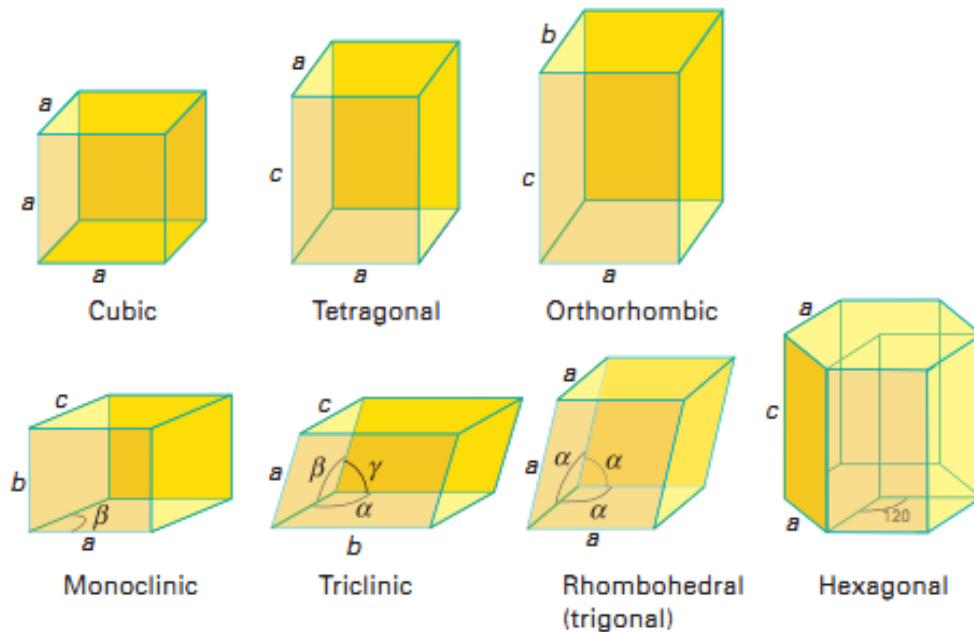
For a mirror on the xy-plane (analogous to a horizontal plane), the z coordinates will change sign, such as:

$$\begin{bmatrix} x \\ y \\ -z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad \text{Eq. (9)}$$

## 6. Bravais lattices

The unit cell is the smallest representation of the entire crystal structure and only by means of translation it creates the full lattice (as discussed in section 2). The number of lattices that can fill two- or three-dimensional space with periodically repeating units without leaving gaps or create overlaps is limited.

Thus, when a group of symmetry elements operates on the unit cell of a crystal, it restricts various aspects of the unit cell geometry, e.g., when a tetrad (4-fold rotation symmetry) operates along one of the crystallographic directions, the cell vectors perpendicular to the tetrad must be equal in magnitude and at 90° to each other. Such constraints lead to the existence of the 7 distinct unit cell geometries, or crystal systems, shown in Fig. 16. The limit in the number of crystal systems arises because only 1, 2, 3, 4 and 6-fold operations are possible in a conventional 3D lattice, discussed in section 5. Another way to see this is to try to stack together 5-fold and 7-fold polygons, they will always leave spaces.



**Figure 16.** The 7 basic crystal systems. Figure from reference 8.

As shown in Table 3, each crystal system has a defining symmetry, unique to it. For example, the most symmetric system is the cubic crystal system and the triclinic system is the least symmetric one: its only defining symmetry operation is translation and there are no restrictions on the values of the cell parameters. In the other crystal systems, symmetry reduces the number of unique lattice parameters.

System	Defining Symmetry	Unit Cell Geometry
Triclinic	Only translational	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$
Monoclinic	Diad parallel to b or/and one mirror plane perp. to b.	$a \neq b \neq c; \alpha = \gamma = 90^\circ; \beta \geq 90^\circ$
Orthorhombic	Diads parallel to a,b,c, and/or perpendicular mirror planes	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$
Trigonal (Rhombohedral)	One triad parallel to c. (One triad parallel to [111])	$a = b \neq c; \alpha = \beta = 90^\circ; \gamma = 120^\circ$ $a = b = c; \alpha = \beta = \gamma = 60^\circ$
Hexagonal	One hexad parallel to c.	$a = b \neq c; \alpha = \beta = 90^\circ; \gamma = 120^\circ$
Tetragonal	One tetrad parallel to c.	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$
Cubic	Four triads parallel to $\langle 111 \rangle$	$a = b = c; \alpha = \beta = \gamma = 90^\circ$

**Table 3.** The 7 crystal systems and their defining symmetry. The inequality sign means that the lattice parameters are not required to be equal by symmetry. However, they may be coincidentally equal.

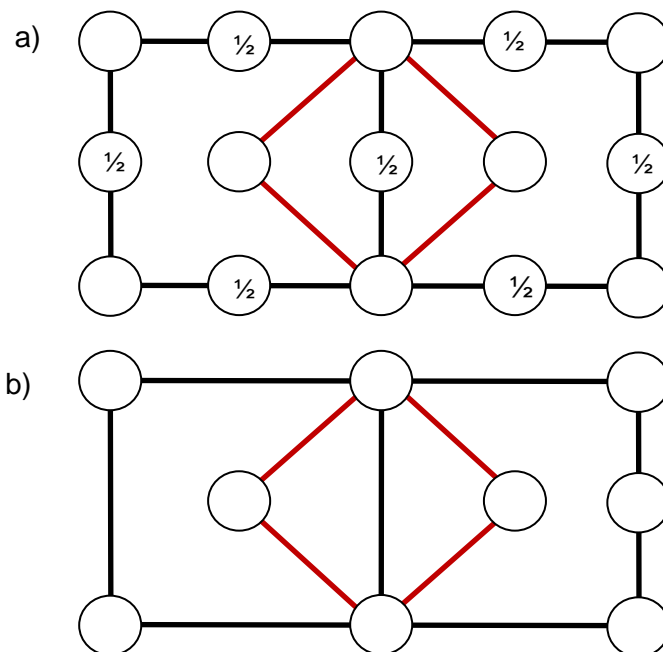
As discussed in section 2, lattices (and unit cells) may be of the type primitive (P), face centred (F), body centred (I) or side centred (C); and for each crystal system these four types of lattice exist. Therefore, the combination of the four lattice types (P, F, I or C) and the **7 crystal systems** leads to **14 distinct lattices** (and not 28, discussed below) known as **Bravais lattices** (Table 4). This is, *Bravais lattices* are lattices which fill space without gaps.

Lattice System	Primitive	Base-Centered	Body-Centered	Face-Centered
Triclinic				
Monoclinic				
Orthorhombic				
Tetragonal				
Rhombohedral				
Hexagonal				
Cubic				

**Table 4.** The 14 Bravais Lattices.

It is interesting to point out that although there are 7 crystal systems and 4 types of lattices, there are not  $7 \times 4 = 28$  Bravais Lattices. To explain the reason for this, consider two examples for the tetragonal system, shown in Fig. 17: The tetragonal-F crystal, shown by the black lines, may be represented by a simpler tetragonal-I cell, shown by the red lines. In the same way a tetragonal crystal of C-type (black lines in Fig. 17b) can be represented by a basic tetragonal-P cell (marked with red lines in Fig. 157b). Therefore, these are not

distinct Bravais lattices since  $F = I$  and  $C = P$ . Thus, the tetragonal crystal system has only two different Bravais lattices, I and P.



**Figure 17.** a) Plan view of tetragonal-F cell, also represented by a tetragonal-I cell, b) Plan view of tetragonal-C, also represented by a tetragonal-P cell.

## 7. Point groups.

In 1830, Johann Hessel proved mathematically that, since crystals exhibited only 2-, 3-, 4-, and 6-fold symmetry and as a result of Rene Hauy's Law of Rational Intercepts, there are only 32 possible combinations of symmetry elements, and thus only **32 possible classes of crystals**. The **Hermann-Mauguin (H-M) Notation** System is the International System of Notation used to convey in a concise manner the symmetry present in the 32 crystal classes, known as the **32 point groups**. A point group is the collection of symmetry operators found in a crystal; enabling us to describe the full symmetry of an object in a short manner. The word 'point' means that all the symmetry operations must act about one point of origin in common, *i.e.*, that translation is not considered. There are only 32 distinct ways that symmetry elements can act through a single point in space in a self-consistent manner. Importantly, *point groups tend to describe macroscopic symmetry and behaviour*. See Table 5.

Remember that the H-M notation consists of a combination of numerals (1, 2, 3, 4 and 6) that denote an axis of rotational symmetry, numerals with a bar-over ( $\bar{1}$ ,  $\bar{3}$ ,  $\bar{4}$  and  $\bar{6}$ ;  $\bar{2} = m$ ) which describe an axis of inversion, the letter  $m$  that refers to a mirror plane and a slash (/) that means 'perpendicular to'. For example, the symbol  $2/m$  indicates that a diad axis is normal to a mirror plane. While, two symbols in succession means 'parallel to'.



To determine a point group of an object, all the symmetry elements of the object should be listed and ordered following certain rules. The order (and combination) in which the symmetry operators are written in the H-M notation is governed by the rules described in Table 5. Consider that a point group symbol has the general form  $ijk$ . This represents the symmetry elements in primary (i), secondary (j) and tertiary (k) *directions*. A short hand is sometimes adopted, where j or k (or both) is skipped, for example if the symmetry is 1 in the secondary or tertiary direction. The rules are:

- The primary position (i) is given to the most important or defining symmetry element, which is often a symmetry rotation axis.
- The secondary position (j) is usually for secondary axes of rotation and/or mirror planes.
- The third position (k) is for the remaining symmetry.
- Symmetry axes are taken as parallel to the direction described.
- Mirror planes are taken to run normal to the direction described.
- If a symmetry axis and the normal to a symmetry plane are parallel, the two symmetry characters are separated by a slash (/).

Crystal System	Primary	Secondary	Tertiary	H-M symbols
Triclinic	-	-	-	1 and $\bar{1}$
Monoclinic	[010]	-	-	2, m and 2/m
Orthorhombic	[100]	[010]	[001]	222, 2mm and 2/m 2/m 2/m
Tetragonal	[001]	[100], [010]	$[1\bar{1}0]$ , [110]	4, $\bar{4}$ , 4/m, 422, 4mm, $\bar{4}2m$ and 4/m 2/m 2/m
Trigonal Rhombohedral	$[111]$	[111]	$[1\bar{1}0]$ , $[01\bar{1}]$ , $[\bar{1}01]$	3, $\bar{3}$ , 32, 3m and $\bar{3}m$
Hexagonal	[001]	[100], [010], $[\bar{1}\bar{1}0]$	$[1\bar{1}0]$ , [120], $[\bar{2}\bar{1}0]$	$\bar{6}$ (3/m), 6, 6/m, $\bar{6}m2$ (3/m), 6mm, 622 and 6/m 2/m 2/m
Cubic	[100], [010], [001]	$[111]$ , $[1\bar{1}\bar{1}]$ , $[\bar{1}\bar{1}1]$ , $[\bar{1}11]$	$[1\bar{1}0]$ , [110], $[01\bar{1}]$ , [011], $[\bar{1}01]$ , [101]	23, 2/m $\bar{3}$ (m $\bar{3}$ ), 432, $\bar{4}3m$ , and 4/m $\bar{3}$ 2/m (m $\bar{3}m$ )

**Table 5.** The order and symbols of point groups using of the H-M notation.

It can be seen that the triclinic system has no constraints, three unequal axes intersecting at oblique angles and hence has no defining symmetry element. On the other hand, the cubic crystal system is a little more difficult to treat than other systems because there is no single principal axis. The crystal system is defined by four 3-fold axes all making equal angles with one another for the cubic system. Thus, the point group is defined as follows: The first symbol refers to all three main axes  $\langle 100 \rangle$ , the second symbol to the four diagonal directions of the 3-fold symmetry (the  $\langle 111 \rangle$  directions pointing to the corners of the cube) and the third symbol refers to all the six directions at the edges of the cube

$\langle 110 \rangle$ . The point here is to identify which symmetry operators can be added and still remain within the cubic crystal system, leaving an equivalent position.

It should be noted that i) the symmetry operators in the point group should be unique and ii) the combination of symmetry elements must of course be *self-consistent*. This also means that when a symmetry element,  $A$ , is properly combined with another,  $B$ , then a third symmetry element,  $C$ , is automatically generated.

For all purposes, crystallographic point groups are described by:

- The Hermann-Mauguin (or Schoenflies) notation
- Stereographic projections
- Matrices of their symmetry operations

When combined with the 14 Bravais lattices, the 32 point groups result in 230 unique three-dimensional space groups. Every crystalline material belongs to one of these 230 structures. All **230 space groups** are listed in the “**International Tables** from the International Union of Crystallography”.<sup>[7]</sup> The main difference between point groups and space groups, is that initial letter of a space group symbol represents the lattice type which may primitive ( $P$ ), single-face centred ( $A$ ,  $B$ , or  $C$ ), all-face centred ( $F$ ), body-centred ( $I$ ), or rhombohedrally centred ( $R$ ). The cubic crystal system has 35 space groups, and the symbols of the symbols refer to the Bravais lattice type ( $P$ ,  $F$ , or  $I$ ) followed by the point group. For example, the  $m\bar{3}m$  point group can be form the following space groups:  $Pm\bar{3}m$ ,  $Fm\bar{3}m$  and  $Im\bar{3}m$ .

## 8. X-ray Diffraction

### 8.1. Introduction

X-ray diffraction is an area that has seen many Nobel Prizes. It all started with William Conrad Röntgen, who discovered x-rays in 1895 and was awarded the first Nobel Prize in Physics in 1901. Years later, Max von Laue and his co-workers, discovered that x-rays travelling through a crystal interacted with it and, as a result, were diffracted in particular directions, depending on the nature of the crystal. This discovery earned von Laue the Nobel Prize in Physics in 1914. Although Laue's work proved that x-rays could be diffracted by solid matter, which further proved the wave-like nature of x-rays, it was the Braggs (father and son) in 1913 that found that x-rays could be used to determine the actual crystal structure accurately. Bragg's equation has largely contributed to the modern development of all the natural sciences because the atomic structure governs the chemical and biological properties of matter. The Bragg duo were awarded the Nobel Prize in Physics in 1915, giving birth to the field of x-ray crystallography (also known as x-ray diffraction). Between 1920 and the 1960s, x-ray crystallography contributed greatly to the area of biology and chemistry, with important ramifications for health care. Dorothy Hodgkin, Nobel Prize in Chemistry in 1964, solved the structure of a number of biological molecules, including cholesterol, penicillin, vitamin B<sub>12</sub> and insulin. Sir John Kendrew and Max Perutz were the first to work out the crystal structure of a protein, earning them the Nobel Prize in Chemistry in 1962. Since that breakthrough, the structure of many biological molecules has been determined using x-ray crystallography.

One of the biggest milestones of the 20th century was the discovery of the DNA's structure by Rosalind Franklin. This discovery paved the way to macromolecule and protein crystallography, which are essential tools of today's biological and medical sciences.

★ ["How X-ray crystallography revealed the structure of everything"](#)

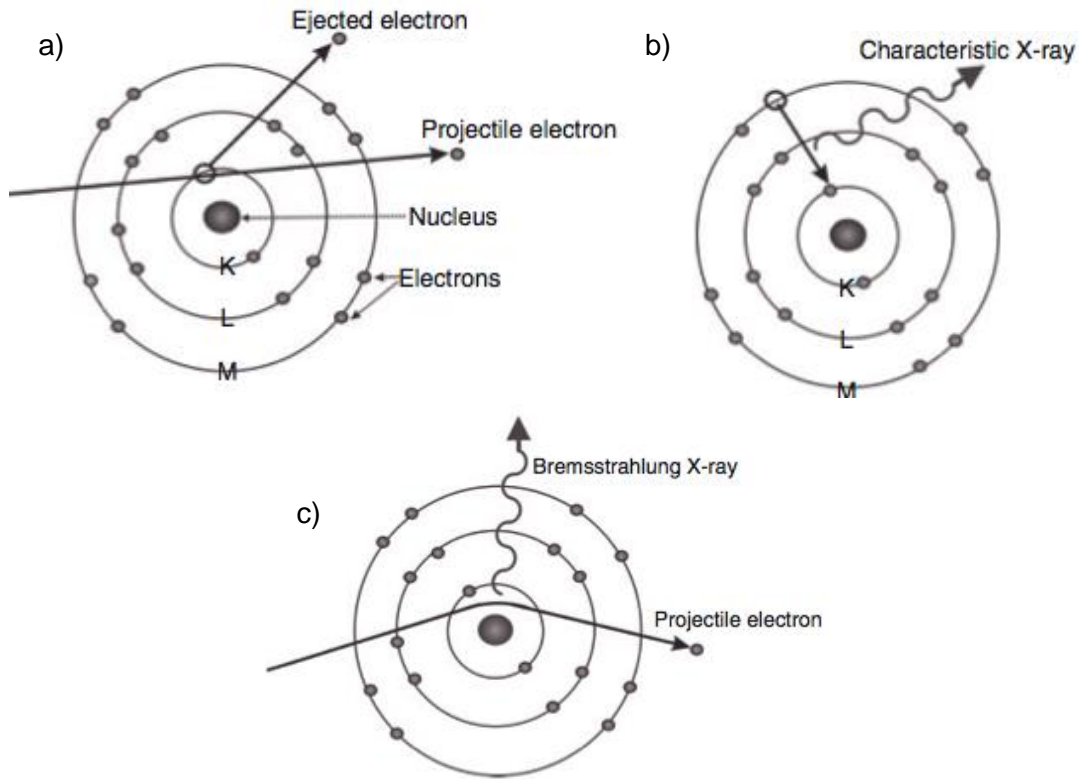
### 8.2. X-ray generation.

X-rays are photons, a form of electromagnetic radiation with wavelength ( $\lambda$ ) ranging from 0.01 to 10 nm. This range coincides with the range of inter-atomic distances in materials ( $\lambda \leq d_{hkl}$ ). Therefore, x-rays are ideal to be used for crystal diffraction. X-rays were discovered in 1895 by German physicist Roentgen. Before von Laue and Bragg discovered that x-rays could be scattered by the internal structure of solid objects, x-rays were used only to image the internal arrangement of bodies and objects.

In general, x-rays are produced when matter is irradiated by a beam of high-energy charged particles such as electrons. There are two types of x-rays:

- **Characteristic x-rays** are produced by electron transitions between the electron shells and therefore have discrete energies reflecting the electronic configuration of the parent atom, produced after ionization of an inner electron shell and subsequent relaxation of the excited atom.

- **Bremsstrahlung x-rays**, or braking radiation, are x-rays produced by slowing down and bending of the projectile electrons by the electric field around atomic nuclei in the sample. The energy used to slow the electron, has been absorbed by the atom and is excessive to the atom. Therefore, this excess energy will be radiated as x-radiation of equal energy and can take any energy value. Figure 18 shows the production of characteristic and Bremsstrahlung x-rays.



**Figure 18.** a) and b) illustrate the production of characteristic x-rays, and c) illustrates the production of Bremsstrahlung x-rays.

✦ The generation of [characteristic](#) and [Bremsstrahlung](#) x-rays.

### 8.3. Revisiting Young's experiment.

The most common technique for determining the crystal structure of a real sample is some form of diffraction; methods include x-ray, electron, and neutron diffraction. Diffraction involves the analysis of the interference patterns generated when waves are scattered by periodic structures. The strong periodicity associated with crystals means that a great deal of information can be obtained about crystalline materials by analysis of these diffraction patterns. The patterns resulting from crystal diffraction are more easily represented and analysed using the concept of the reciprocal lattice. However, the understanding of crystal diffraction starts by revisiting Young's double slit experiment. Consider a source emitting light with a certain  $\lambda$  and this light goes through the two slits ( $s_1$  and  $s_2$ ) and falls on the

screen at a point  $P$ , a distance  $y$  from the point  $O$ , that lies on the screen a perpendicular distance  $L$  from the double-slit system, see Fig. 19. A distance  $d$  separates the two slits ( $s_1$  and  $s_2$ ). Therefore, the light from  $s_2$  will travel an extra distance to  $P$  than the light from  $s_1$  of:

$$\delta = r_2 - r_1 \quad \text{Eq. (10)}$$

Using the law of cosines on the geometry in Fig. 2, we can write:

$$r_1^2 = r^2 + \left(\frac{d}{2}\right)^2 - dr \cos\left(\frac{\pi}{2} - \theta\right) = r^2 + \left(\frac{d}{2}\right)^2 - dr \sin \theta \quad \text{Eq.(11)}$$

$$r_2^2 = r^2 + \left(\frac{d}{2}\right)^2 - dr \cos\left(\frac{\pi}{2} + \theta\right) = r^2 + \left(\frac{d}{2}\right)^2 + dr \sin \theta \quad \text{Eq.(12)}$$

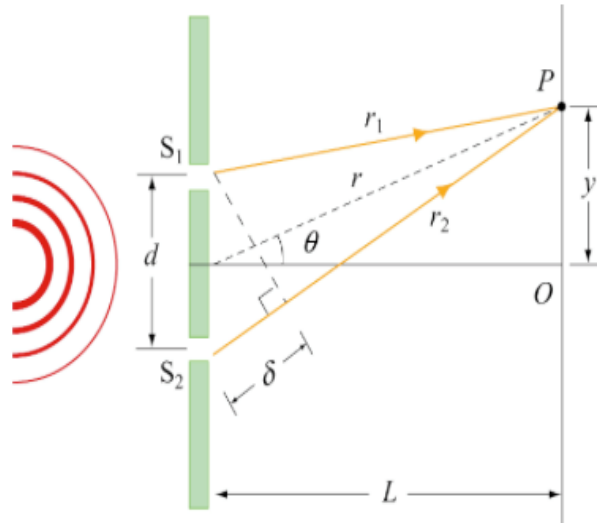
Subtracting Eq.) from Eq.) yields:

$$r_2^2 - r_1^2 = (r_2 + r_1)(r_2 - r_1) = 2dr \sin \theta \quad \text{Eq.(13)}$$

When  $L \gg d$ , i.e. when the slit separation is much smaller than the distance to the screen,  $r_2 + r_1 \approx 2r$  and the path difference, Eq. (10), becomes

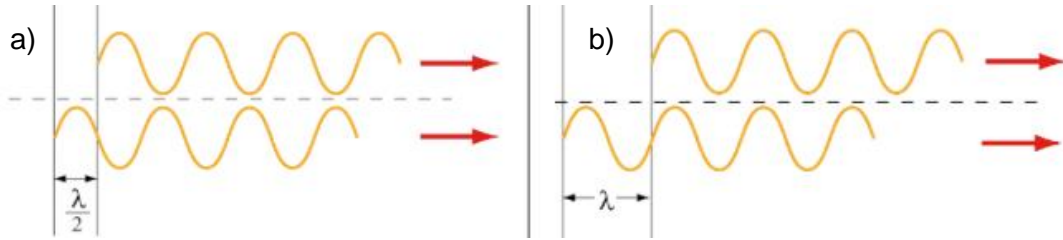
$$\delta = r_2 - r_1 \approx d \sin \theta \quad \text{Eq.(14)}$$

The two rays are being treated as parallel in this limit.



**Figure 19.** Double-slit experiment. Figure from reference 13.

The path difference  $\delta$  determines if the two waves are in phase or out-of-phase. These two cases are illustrated in Fig. 20. A path difference of  $\delta = \lambda/2$  ( $m=0$ ) results in destructive interference and  $\delta = \lambda$  ( $m=1$ ) leads to constructive interference.



**Figure 20.** a) Destructive interference for a path difference of half a wavelength. b) Constructive interference for a path difference of a whole wavelength. Figure from reference 13.

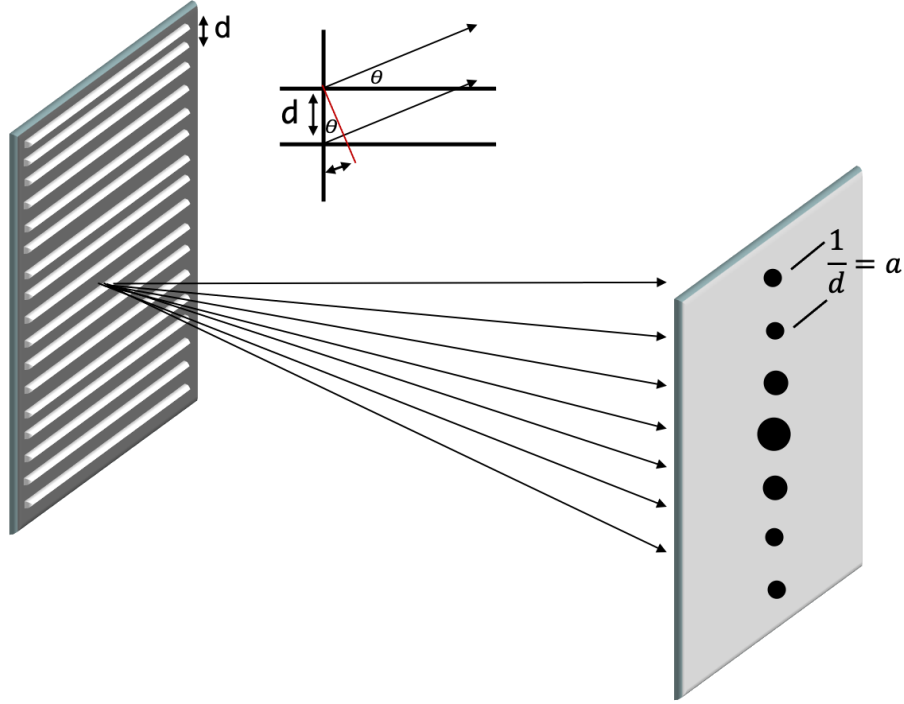
The equations for these two extreme cases are:

$$\delta_m = d \sin \theta_m = m\lambda, \quad m = 0, \pm 1, \pm 2, \pm 3, \dots \quad \text{Eq.(15)}$$

$$\delta_m = d \sin \theta_m = \left(m + \frac{1}{2}\right) m\lambda, \quad m = 0, \pm 1, \pm 2, \pm 3, \dots \quad \text{Eq.(16)}$$

where  $m$  is called the order number; Eq. (15) describes constructive interference, while Eq. (16) describes destructive interference. The zero<sup>th</sup>-order ( $m=0$ ) maximum corresponds to the central bright fringe at  $\theta=0$ , and the first order maxima ( $m=\pm 1$ ) are the bright fringes on either side of the central fringe. When  $\delta$  is equal to an odd integer multiple of  $\lambda/2$ , the waves will be  $180^\circ$  out of phase at  $P$ , resulting in destructive interference with a dark fringe on the screen.

Thus, diffraction can be considered a physical process where the incident beam interacts with the object, and the scattering process transfers spatial information about the object to the beam. Considering a one-dimensional grating illuminated by a laser, Fig. 21, in which (similar to Young's experiment) each slit acts as a source of secondary wavelets that overlap to produce an interference pattern. The diffraction (interference) pattern is produced because there are only certain directions for which constructive interference take place, which is when the beams from each slit are in phase. As indicated in equation (15), the path difference between the beams from each slit must be equal to an integral number of wavelengths ( $d \sin \theta_m = m\lambda$ ). Only under this condition, a diffraction pattern will then appear as an array of spots on a screen placed at a distance ( $L$ ) from the object.



**Figure 21.** Schematic of the formation of an optical diffraction from a 1D grating illuminated by a laser beam;  $d$  is the distance between the two slits and  $a$  is the fringe separation.

From trigonometry, the following relationship can be drawn:

$$a = L \tan \theta = L \frac{d \cos \theta}{d \sin \theta} \quad \text{Eq.(17)}$$

Where  $d$  is the spacing between slits,  $a$  is the spacing between the spots in the diffraction pattern and  $\theta$  is the angle through which the incident beam is diffracted. Remembering the relationships from the double slit experiment, Eqs. (14) and (15), where the path difference is:  $d \sin \theta = \lambda$  for 1<sup>st</sup> order of diffraction ( $m=1$ ); we have that:

$$a = \frac{L\lambda}{d \cos \theta} \quad \text{Eq.(18)}$$

From this analysis, the following conclusions can be drawn:

- a)** Because  $d \sin \theta = m\lambda$ ,  $d$  cannot be smaller than  $\lambda$  since that would lead to  $\sin \theta > 1$ , which is a mathematical impossibility. Hence, for diffraction to occur, the wavelength of the radiation must be similar or smaller in magnitude than the separation between diffracting units.
- b)** The spacing of diffraction spots on the screen ( $a$ ) is reciprocally related to the separation between diffracting units in the object:  $a \propto \frac{1}{d}$ .
- c)** The direction of the row of spots in the diffraction pattern is perpendicular to the lines of the grating in the object.

- d) The diffraction pattern can be thought of as *diffraction space*, so it can be considered that **diffraction space is the reciprocal space**.

The 1D grating treatment, can be extended to a 2D grating, this would generate a diffraction pattern with a 2D array of spots and this would be the scenario for crystal diffraction. For crystals, the diffracting units (similar to slits) are the crystallographic planes. Thus, the separation between parallel planes (the interplanar spacing,  $d_{hkl}$ ) is the periodicity that gives rise to diffraction spots. Following the same conclusions drawn from the optical diffraction experiment in Fig. 26, it can be then concluded that:

- a) For diffraction to occur, the wavelength of *the radiation must be smaller than the interplanar spacing*:  $\lambda \leq d_{hkl}$ . For example, X-rays and electrons (nm range) are used to examine periodicity in crystals because they can have wavelengths shorter than the distance between crystallographic planes.
- b) Each diffraction spot relates to a particular periodicity in the object. Parallel planes result in a single maxima point located a distance  $1/d_{hkl}$  from the lattice origin. Similarly, a vector from the origin to each spot is *perpendicular* to the plane producing diffraction (at that spot), and the magnitude vector is *reciprocally* related to the inter-planar spacing of those (hkl) planes.

In other words, diffraction space is the same as reciprocal space. Similarly, the reciprocal construction (space) can be thought of in terms of a diffraction pattern with an array of spots.

Crystal diffraction involves the analysis of the interference patterns generated when waves are scattered by periodic structures (the atomic planes). The strong periodicity associated with crystals means that a great deal of information can be obtained about crystalline materials by analysis of these diffraction patterns.

★ Watch the video [Crystallography and the reciprocal space](#).

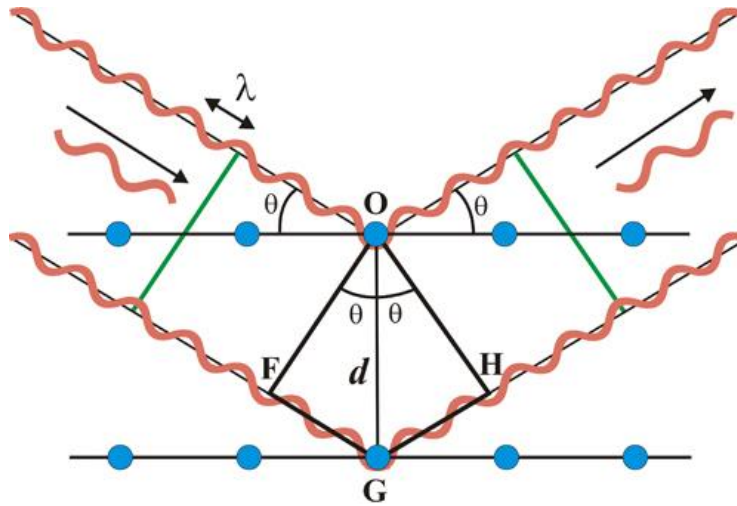
#### 8.4. Braggs Law

Bragg's law is a special case of Laue diffraction which considers a beam of radiation directed at a sample, a crystal. Bragg envisaged diffraction in terms of reflections from crystal planes giving rise to the simple relationship that we know today as Bragg's Law. In this relationship, the beam of radiation is partially reflected by the planes, with the rest of the beam continuing in the incident direction; when it hits the next plane, part of it is again reflected, and part of it transmitted, and so on through the crystal. So that, the rays (in this case x-rays) are scattered from successive parallel planes in the crystal and will travel distances differing by exactly one wavelength. Thus, Bragg's law describes the conditions for coherent and incoherent scattering (constructive and destructive interference), from a crystal lattice. It should be noted that in reality, x-rays are scattered by the electrons in the atoms contained in the planes, but for simplicity, we refer to the planes as the diffracting units.



Consider the sketch in Fig. 22, where parallel planes in a crystal are being bombarded with two incident x-rays with a specific wavelength,  $\lambda$ . The beams make an angle  $\theta$  with the planes. To obtain a 'reflection', constructive interference should occur. This means that both the incident and diffracted beams should be in phase. For constructive interference, the path difference between the two rays has to be an integer multiple of the wavelength,  $n\lambda$ . From trigonometry, the path difference between the incident and diffracted rays should then be  $FG+GH = n\lambda$ . However, since  $FG = GH$  and  $\sin\theta = FG/d$ . The interplanar distance is  $d$ . Equating these two values for the path difference, yields Bragg's law:

$$2d_{hkl} \sin \theta = n\lambda \quad \text{Eq. (19)}$$



**Figure 22.** Constructive interference. Figure from reference 14.

Bragg's Law represents the (inverse) relationship between the angle of diffraction and the distance between repeating lattice points in real space. In other words, it defines the conditions where a crystal is oriented for coherent scattering.

Looking carefully at Eq. (19), it can be seen that:

- a)** The lattice planes behave like mirrors reflecting the rays only in certain positions given by:  $\theta = \sin^{-1} (n\lambda / 2d_{hkl})$
- b)** For given experimental conditions (specific  $\lambda$  and  $d_{hkl}$ ) only discrete values of the diffraction angles ( $\theta$ ) are obtained, which correspond to the different values of the integer  $n$ .
- c)** There are only a finite number of diffraction orders (as  $\sin \theta \leq 1$ ) and the maximum number of them depends on the given experimental conditions (crystal and wavelength):  $n_{\max} = 2d / \lambda$ . In crystallography, the different orders of diffraction are taken into account by changing the values of  $(hkl)$  to  $(nh \ nk \ nl)$ . For example, the first order

reflection from (111) planes occurs at an angle given by:  $\sin \theta$  (1<sup>st</sup> order 111) =  $\lambda/d_{111}$  and the second order reflection from the same set of planes then occurs at an angle  $\sin \theta$  (2<sup>nd</sup> order 111) =  $2\lambda/d_{111}$ . However, this is always referred to as the first order reflection from (222) planes i.e.,  $\sin \theta$  (1<sup>st</sup> order 222) =  $\lambda/2d_{222}$ . Note that as  $d_{222}$  is equivalent to  $d_{111}$ , hence the equations are formulated identical.

- d) The geometry of diffraction (i.e., the diffraction angle  $\theta$ ) depends only on the lattice geometry.

Within a crystal there are an infinite number of sets of parallel planes, and Bragg's law applies to all these. Thus, if a crystal (irradiated by a beam) is rotated, each set of planes will diffract when the value of  $\sin \theta$  becomes appropriate. This is the principle by which diffraction data is collected for the whole of the crystal.

Diffraction then, involves using crystallographic planes as gratings and it involves the analysis of the interference patterns that are generated when waves of smaller (or similar) magnitude to the interplanar spacing (separation between planes) are scattered by the periodic structure of crystals. The spacing of diffraction spots on the screen is *reciprocally* related to the separation between diffraction units (planes).

★ [‘Bragg's Law’ derivation and introduction to Bragg's Law and Crystal Structure](#)

## 8.5. Reciprocal Space

The concept of reciprocal space is over 100 years old, and has been particularly used by crystallographers because it provides a geometrical basis for understanding the geometry of x-ray and electron diffraction patterns from a crystal. In solid state physics, the reciprocal space is used to explain various properties by describing the behaviour of electrons in crystals (formation and motion of waves), such as thermal and electrical phenomena. For this reason, the reciprocal space is also called *Fourier space* or *wave-vector k-space*, in contrast to the real space.

The reciprocal space can be thought of as an imaginary or abstract space that displays an alternative view of the crystal structure. If we consider that the lattice itself is a mathematical concept, then the reciprocal space is also a mathematical space built on the real space. The relationship between the real and reciprocal space is such that if something is ‘big’ in real space, this will be ‘small’ in reciprocal space, and vice versa. Hence, the name reciprocal space.

To understand what reciprocal lattice is, how to construct it and how to make use of it, it is essential to first understand the real or direct space (Section 2). A lattice in real space is defined by the unit cell axes (basis vectors) and angles:  $\mathbf{a}^*$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ . Similarly, a reciprocal lattice is defined by the same parameters, adding an asterisk:

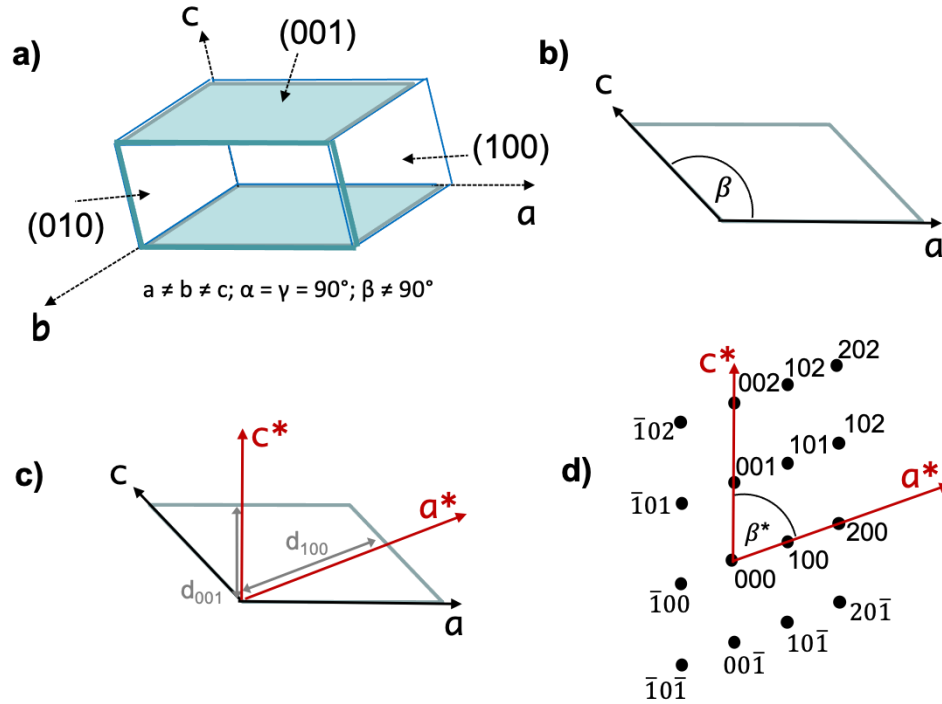
$\mathbf{a}^*$ ,  $\mathbf{b}^*$ ,  $\mathbf{c}^*$ ,  $\alpha^*$ ,  $\beta^*$ ,  $\gamma^*$ .

The basic relationship between real and reciprocal space can be rationalised from the conclusions drawn in sections 8.3 and 8.4. This is, crystal diffraction arises from the crystallographic planes acting as diffracting units, and the use of a suitable wavelength:  $\lambda \leq d_{hkl}$ . Thus, the separation between parallel planes (interplanar spacing) is that periodicity that gives rise to *diffraction spots*, and the space where those spots are localized is thought as *diffraction space*). This makes reciprocal and diffraction space to be equivalent. Such that, the reciprocal space deals with the crystals as seen through their diffraction images (or patterns); representing the scattering possibilities that results from a given crystal, where *planes can be represented by just one (diffraction) point*.

The reciprocal lattice can be constructed from the real crystal lattice graphically. The first thing needed is to identify the lattice planes. Consider a family of planes in a crystal, like those in Fig. 8c. Geometrically, the planes can be described by two quantities: 1) their orientation in the crystal (given by the Miller indices) and 2) their d-spacings. Where, any plane can also be characterised by a vector perpendicular to it.

It can then be said that a family of planes can be represented simply by their normal, which are then specified as (reciprocal lattice) vectors and which can then be used to define a pattern of points (reciprocal lattice), each point represent a family of planes. Thus, there is a key connection between families of planes in the crystal, Bragg law and the direction of the diffracted (or reflected) beams.

Consider the planes (hkl) that describe the faces of the monoclinic lattice in Fig. 23. The real space unit cell has a rhombus-shaped unit cell, with the b axis normal to the a and c axes. The main planes (or end faces) can be identified in Fig. 23a. From here, one can see that the family of planes {001} can be represented by one vector normal to these planes, and this one vector will have a length of  $d_{001}$ . In this way, the normal to the main faces of a unit cell can be found and from these relationships  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  can be established and the reciprocal unit cell can be constructed, as it will be explained below. In order to carry out this construction we need an origin that, for the sake of simplicity it can be the same as that of the real space lattice. The construction of a 3D reciprocal lattice is similar to that for a plane lattice. However, a 2D construction of the reciprocal lattice is usually simpler than a 3D construction. For example, to construct the  $\mathbf{a}^*$ - $\mathbf{c}^*$  section of the reciprocal lattice, draw the unit cell in real space projected down b, and draw normal to the end faces of the unit cell (Fig. 23c). These give the directions of the reciprocal lattice  $\mathbf{a}^*$  and  $\mathbf{c}^*$  axes. The reciprocals of the perpendicular distances from the origin to the faces of the unit cell give the axial lengths. These allow the reciprocal lattice plane to be drawn. The relationship between the real and reciprocal lattice is such that the b-axis is normal to a and c, so the  $\mathbf{b}^*$  axis is parallel to b and normal to the  $\mathbf{a}^*$  -  $\mathbf{c}^*$  section; and the length of  $\mathbf{b}^* = 1/b$ . In the  $\mathbf{a}^*$  -  $\mathbf{c}^*$  section the reciprocal lattice points are spaced  $\mathbf{a}^* = 1/d_{010}$  and  $\mathbf{c}^* = 1/d_{100}$  and  $\beta^* = 180 - \beta$ . Finally, from the origin, the reciprocal lattice points can be assigned and labelled accordingly in any direction.



**Figure 23.** Construction of a reciprocal lattice of a a) monoclinic crystal: b) a-c section in real space, c) reciprocal lattice axes lie perpendicular to the end faces (planes) of the unit cell in real space, d)  $a^*$ - $c^*$  section of the reciprocal lattice with its reciprocal lattice points.

✪ More on [constructing the reciprocal lattice](#)

Thus, the defining geometric relationship between the real and reciprocal vectors can be given by simply vector algebra:

$$a^* = \frac{b \times c}{V} = \frac{b \times c}{a \cdot [b \times c]} \quad \text{Eq. (20)}$$

$$b^* = \frac{c \times a}{V} = \frac{c \times a}{b \cdot [c \times a]} \quad \text{Eq. (21)}$$

$$c^* = \frac{a \times b}{V} = \frac{a \times b}{c \cdot [a \times b]} \quad \text{Eq. (22)}$$

Equations (20) – (22) define the reciprocal lattice vectors, where  $V$  is the unit cell volume, and from this definition, it is apparent that:

- i) the three vectors  $a^*$ ,  $b^*$  and  $c^*$  are normal to a set of lattice planes of the real lattice and their moduli are respectively equal to the inverse of the spacings of these three sets of atomic planes; and

ii) the dimensions of the moduli of the reciprocal lattice vectors are those of the inverse of a length. For example,  $\mathbf{a}^*$  is normal to the plane containing  $\mathbf{b}$  and  $\mathbf{c}$ , and its magnitude is equal to the reciprocal of the spacing of the (100) planes in the real lattice. And,  $\mathbf{c}^*$  is given by the cross product of  $\mathbf{a}$  and  $\mathbf{b}$ , i.e.,  $\mathbf{c}^*$  is perpendicular to the plane consisting of  $\mathbf{a}$  and  $\mathbf{b}$ , and similarly for  $\mathbf{a}^*$  and  $\mathbf{b}^*$ .

Therefore, the set of basic vectors satisfy the following relationships:

$$\mathbf{c}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{a} = 0 \quad \text{Eq. (23)}$$

$$\mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 1 \quad \text{Eq. (24)}$$

Equations (23) and (24) are equivalent. Equations (20) to (22) are sometimes used as the equations that define the reciprocal lattice. These relationships are symmetrical and show that if we apply the same operations, and take the reciprocal of the reciprocal lattice, we end up back where we started: with the real lattice.

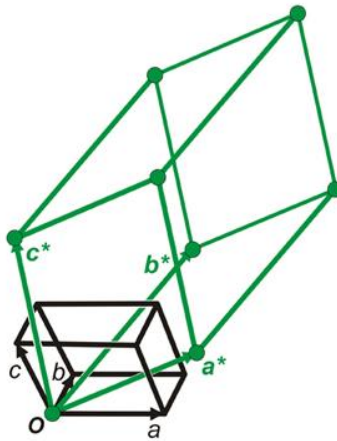
For *orthogonal lattices* (orthorhombic, tetragonal and cubic) the following relationships can be drawn:

$$\mathbf{a}^* \parallel \mathbf{a}, \quad \mathbf{b}^* \parallel \mathbf{b} \quad \text{and} \quad \mathbf{c}^* \parallel \mathbf{c} \quad \text{Eq. (25)}$$

$$\mathbf{a}^* = \frac{1}{a} = \frac{1}{d_{100}}, \quad \mathbf{b}^* = \frac{1}{b} = \frac{1}{d_{010}}, \quad \text{and} \quad \mathbf{c}^* = \frac{1}{c} = \frac{1}{d_{001}} \quad \text{Eq. (26)}$$

$$\alpha^* = \beta^* = \gamma^* = \frac{\pi}{2} \quad \text{Eq. (27)}$$

Thus, the size of a reciprocal lattice unit cell is inversely proportional to the size of the real space unit cell. For example, the relationship between a real and a reciprocal lattice in 3D is shown in Fig. 24.



**Figure 24.** Relationships between the real (black) and the reciprocal (green) unit cells in 3D. From Ref. 15.

From the diffraction point of view, the reciprocal lattice can be thought of as the set of points generated from reciprocal lattice vectors ( $r^*$ ) in which the basis vectors ( $a^*$ ,  $b^*$ ,  $c^*$ ) are multiplied by integers ( $hkl$ ):

$$r^* = ha^* + kb^* + lc^* \quad \text{Eq. (28)}$$

This means that the vector  $r^*$  is normal to the planes of Miller indices ( $hkl$ ) in the real lattice. Thus, if ( $hkl$ ) are given small integral values, the reciprocal lattice vector  $r^*$  represents the normals to the low index planes. It is important to note that the reciprocal lattice vectors are reciprocal to the real space translation vector (section 2.2). The magnitude of  $r^*$  is equal to the reciprocal of the spacing of the planes of the real lattice of Miller indices ( $hkl$ ):

$$d_{hkl}^* = 1/d_{hkl} \quad \text{Eq. (29)}$$

where  $h$ ,  $k$  and  $l$  are the Miller indices of the crystal plane ( $hkl$ ) and  $a^*$ ,  $b^*$  and  $c^*$  define the reciprocal space vectors - similar to the real space crystal with lattice vectors  $a$ ,  $b$ ,  $c$ .

In summary, the best approach is to think of any crystal as having two lattices. One describes the arrangement of the unit cells of atoms in the crystal, a second one is an array of points which is uniquely defined for any given crystal but does not correspond to arrays of atoms; instead, each point is associated with a particular set of planes in the crystal. This reciprocal lattice gives a physical picture of what happens when a crystal diffracts, an essential concept in crystallography that paves the way for the diffraction techniques. In this picture, the reciprocal vector *is always perpendicular to the plane ( $hkl$ ) in the real lattice*. In other words, the reciprocal vector from the origin to each spot is perpendicular to the atomic plane ( $hkl$ ) producing diffraction to that spot, and the magnitude vector is reciprocally related to the inter-planar spacing ( $d_{hkl}$ ) of those atomic planes.

✪ Visualise the relationship between the real and the [reciprocal lattice](#).

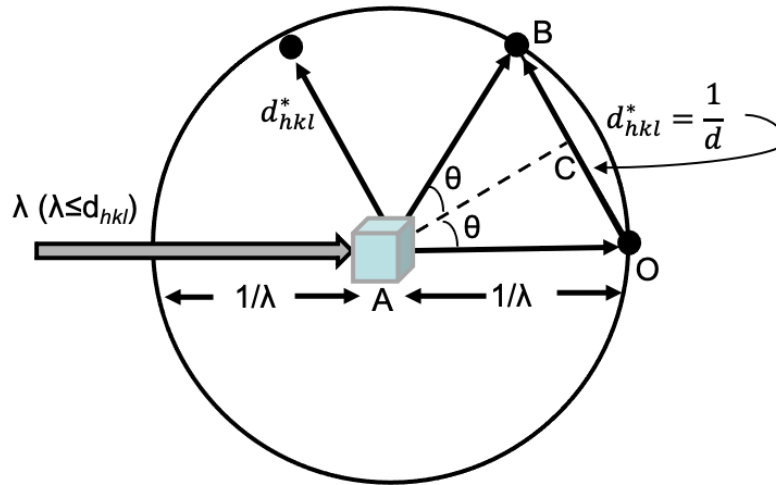
## 8.6. Ewald Sphere

The Ewald sphere provides a geometrical description of a crystal undergoing diffraction, in other words a geometrical formulation of Bragg's law which involves the reciprocal lattice and a 'sphere of reflection'. It is a useful tool to examine the corresponding diffraction pattern and to visualize which Bragg planes are in the correct orientation to diffract.

Consider a beam of radiation  $\lambda$  directed to a crystal. Now, construct a sphere of radius  $r = 1/\lambda$ , such that it is centred with the crystal, as shown in Fig. 25. This is the so-called Ewald sphere (or sphere of reflection). The first thing to note is that not all the rays in the beam will be diffracted, meaning that part of the direct beam travels through the crystal without being deflected and this will intersect the sphere at a point O. This point can then be assigned as the origin of the reciprocal lattice, with the vector  $OA = r$ . Since a crystal has many planes, it is then likely that the beam will be reflected (diffracted) by the parallel

planes (hkl) inside the crystal, and these will create a diffraction spot or a reciprocal lattice point (B). Thus, the vector AB marks the line from the centre of the sphere (crystal) to the point where the reciprocal lattice point intersects Ewald sphere. And,  $|OB| = d_{hkl}^*$  which is the diffraction or reciprocal lattice vector, known as  $g_{hkl}$ .

We know that i) constructive interference occurs when a set of parallel crystal lattice planes (separated by a spacing of  $d_{hkl}$ ) are oriented to an angle ( $\theta$ ) with respect to the incident beam (as shown in Fig. 27) and, ii) the reciprocal lattice vector is perpendicular to the crystal lattice planes and has a length inversely related to the spacing between the planes ( $d^* = 1/d$ ).



**Figure 25.** Graphical representation of Bragg's condition, showing the Ewald sphere.

Thus, we can construct a right-angled triangle (AOC) where:

$$|OC| = \frac{1}{\lambda} \sin \theta = \frac{1}{2} d_{hkl}^* \quad \text{Eq. (30)}$$

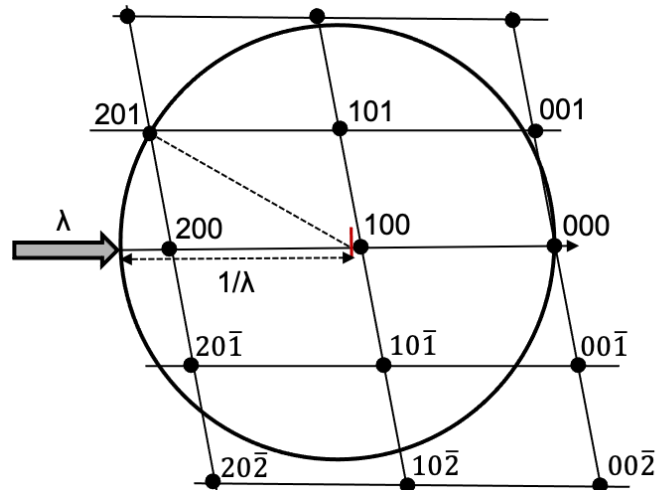
Substituting Eq. 29, we have:

$$\lambda = 2d_{hkl} \sin \theta \quad \text{Eq. (31)}$$

This is nothing else but Bragg's Law and exemplifies that, if a reciprocal lattice point lies on the surface of the Ewald sphere then Bragg's Law is obeyed, and there will be a diffracted beam from the crystal at an angle  $2\theta$  in the direction parallel to the line from O to the reciprocal lattice point. Conversely, if the reciprocal lattice point does not intersect the sphere's circumference then Bragg's law is not satisfied and that particular set of planes will not be in the correct orientation for diffraction to occur.

Figure 25 shows the construction of one reflecting set of planes, generating one reciprocal lattice point (B). It is then a matter to simply extend this to all the reciprocal lattice points in a crystal. Note again that in the Ewald construction, a sphere with diameter  $1/\lambda$  is drawn centred at the crystal. Thus, the origin of the reciprocal lattice cannot be at the centre of

the sphere but it is at the point where the direct beam exits or intersects the sphere (on the opposite side of the incident beam). The reciprocal lattice is then drawn on the same scale as the sphere. For example, Fig. 26 shows a section of the reciprocal lattice of a monoclinic crystal perpendicular to the  $\mathbf{b}^*$  reciprocal lattice vector. Thus, all the reciprocal lattice points in this section have indices of the form  $(h0l)$ . An incident x-ray beam is directed along the  $\mathbf{a}^*$  reciprocal lattice vector (along a direction in the crystal perpendicular to the  $y$  and  $z$  axes). In this section the Ewald sphere intersects the  $(201)$  reciprocal lattice point, which means that only the plane  $(201)$  satisfies Bragg's law, and its direction is indicated.



**Figure 26.** Ewald sphere and  $\mathbf{a}^* - \mathbf{c}^*$  section for a monoclinic crystal with the incident x-ray parallel to  $\mathbf{a}^*$ . The  $(201)$  reciprocal lattice point intersects the Ewald sphere, and its direction is indicated.

Now, when the crystal is rotated so that a reciprocal lattice point intersects the Ewald sphere, that reciprocal lattice point is in position to be measured as a point in the diffraction pattern. The orientation of the reciprocal lattice is coupled to the orientation of the crystal, and the rotation of the crystal about the centre of the Ewald sphere results in an equivalent rotation of the reciprocal lattice about the reciprocal lattice origin. Similarly, when the wavelength of the incident radiation changes, so does the radius of the Ewald sphere.

An important point to note, is that although in theory the reciprocal space describes all possible diffraction maxima, these only occur in an experiment when Bragg's law is satisfied; which is not always the case. Additionally, translational symmetry in real space can result in systematic absence of certain diffraction spots or reflections in the reciprocal lattice, originated from destructive interference.

✪ More on the [Ewald sphere](#) and how it [changes with wavelength](#).

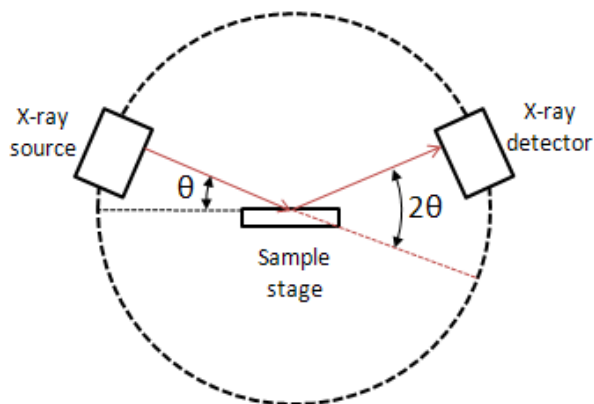


### 8.7. X-ray diffraction: The technique.

X-ray diffraction (XRD) is a rapid analytical technique primarily used for the identification of crystal structure of crystalline materials; it provides information about crystal structure and lattice parameters. This technique is based on the constructive interference of monochromatic x-rays and a crystalline sample. Therefore, the points covered in previous sections are important in order to understand how the technique works and in order to analyse and interpret the data. As shown in Fig. 27, x-ray diffractometers consist of three basic elements: an x-ray tube, a sample holder, and an x-ray detector.

In general, there are two main techniques of x-ray diffraction. The **Laue technique**, is unique in that it utilises white (polychromatic) x-ray radiation and all other x-ray diffraction utilise monochromatic (or near-monochromatic,  $K_{\alpha}$ ) x-ray radiation. The main difference between these techniques is that the Laue technique uses a thin stationary crystal, while the more common x-ray diffraction systems must move both the crystal and the detector (sphere) relative to one another; whenever a reciprocal lattice point touches the sphere then a diffracted beam is obtained. There are different ways in which the movement can be achieved. The geometry of these x-ray diffraction methods may appear to be complicated, but the basis of them all is the same.

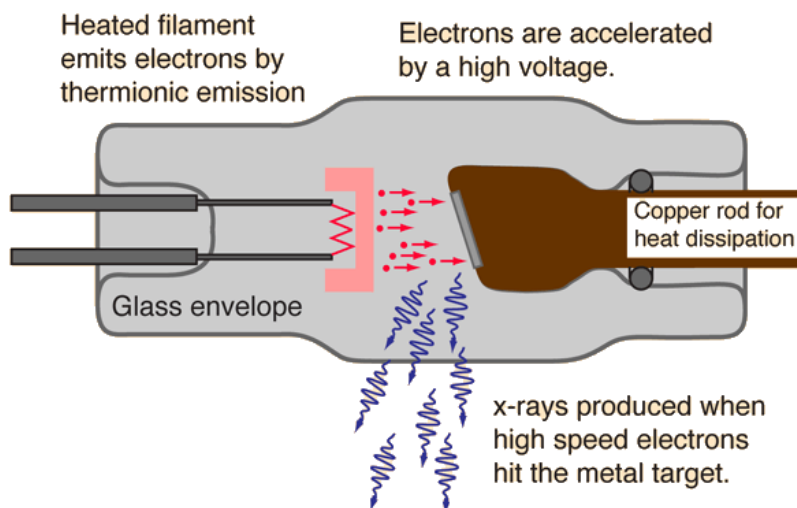
Most of the diffractometers use a **Bragg-Brentano** geometry. This geometry refers to a reflection geometry where the incident angle (between the x-ray source and sample) is always half of the diffraction angle (between the detector and the incident beam, Thus, the diffraction angle is always  $2\theta$ , Fig. 27. There are two main operational modes: 1) The X-ray tube is fixed, and the sample rotates at  $\theta/\text{min}$  and the detector always at  $2\theta/\text{min}$ ; and 2) the sample is fixed and the tube rotates at the same rate as the detector at  $\theta/\text{min}$  (known as a  $\theta:2\theta$  scan).



**Figure 27.** Schematic of an x-ray diffractometer. Figure from reference 16.

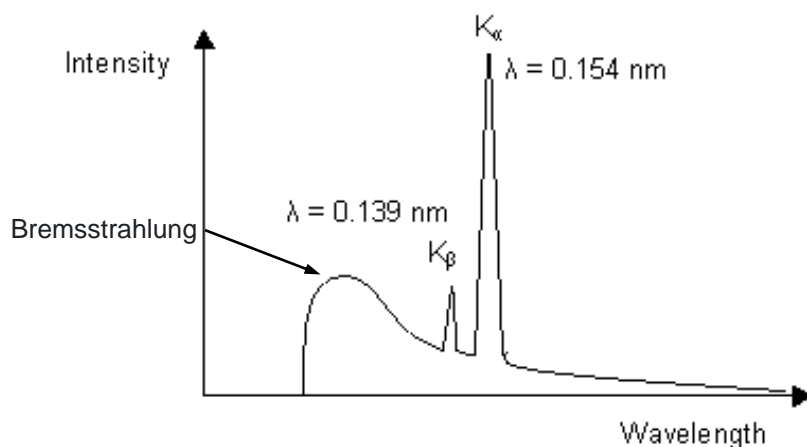
In XRD (and for medical diagnostics), the x-rays are produced in an x-ray tube, see Fig. 28. The process involves heating a filament to produce electrons and accelerating the

electrons towards a metal target (such as Cu) by applying a voltage. The bombarding electrons eject electrons from the inner shells of the atoms of the metal target, creating holes and x-rays will be emitted as previously described. Of course, the characteristic x-rays produced have specific wavelengths that depend on the target material (Cu, Fe, Mo, Cr). Copper is the most common target material for single-crystal diffraction, with the Cu- $K_{\alpha}$  x-rays having a wavelength  $\lambda = 1.54 \text{ \AA}$ .



**Figure 28.** Schematic of an x-ray tube. Figure from reference 17.

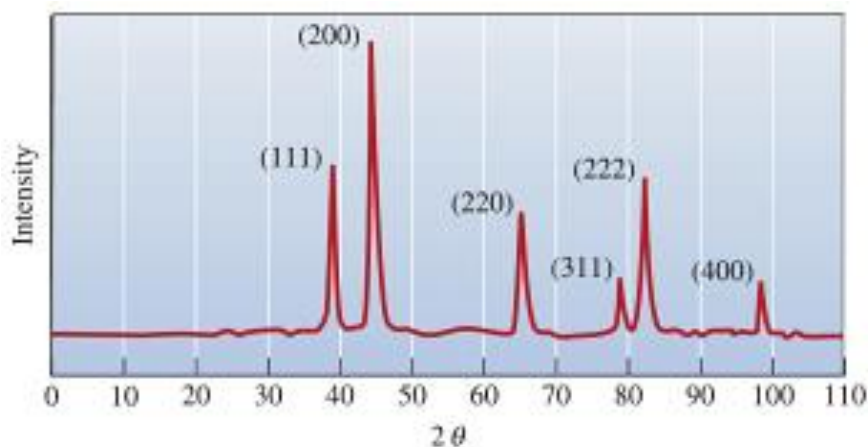
Figure 29 shows the characteristic x-ray spectrum from a Cu target. This further exemplifies that any x-ray spectrum will show both characteristic x-rays and Bremsstrahlung x-rays. The characteristic x-rays are the peaks labelled as  $K_{\alpha}$  and  $K_{\beta}$ , which originate from electronic transitions; the Bremsstrahlung x-rays exist as a continuum spectrum, usually referred to as background.



**Figure 29.** Cu x-ray spectrum. Figure from reference 18.

The x-rays produced by the x-ray tube are collimated (*i.e.*, made into a parallel beam) and directed onto the sample. As the sample and detector rotate, the intensity of the reflected x-rays is recorded. When the geometry of the incident x-rays bombarding the sample satisfies Bragg's law, constructive interference occurs and a peak in intensity will appear. The detector records this x-ray signal, processes it and converts the signal into a count rate, which is then output to a computer monitor, producing what is known as a XRD pattern or diffractogram (intensity vs scanning angle  $2\theta$ ), see Fig. 30.

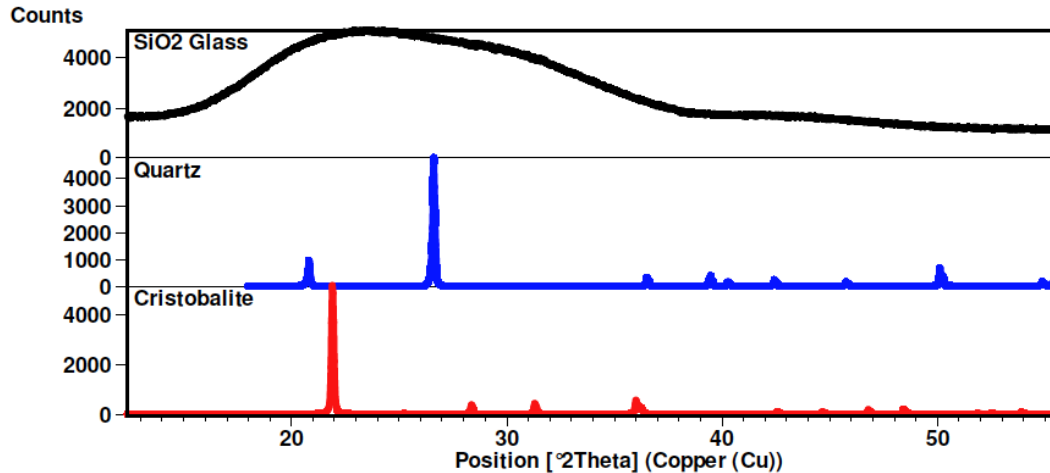
The geometry of standard x-ray diffractometers is such that the sample rotates in the path of the collimated x-ray beam at an angle  $\theta$  while the detector is mounted on an arm to collect the diffracted x-rays and rotates at an angle of  $2\theta$ . The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical diffraction experiments, data is collected at  $2\theta$  from  $\sim 5^\circ$  to  $70^\circ$ .



**Figure 30.** Typical diffractogram: Intensity vs  $2\theta$ . Figure from reference 19.

#### 8.7.1. XRD: The diffractogram

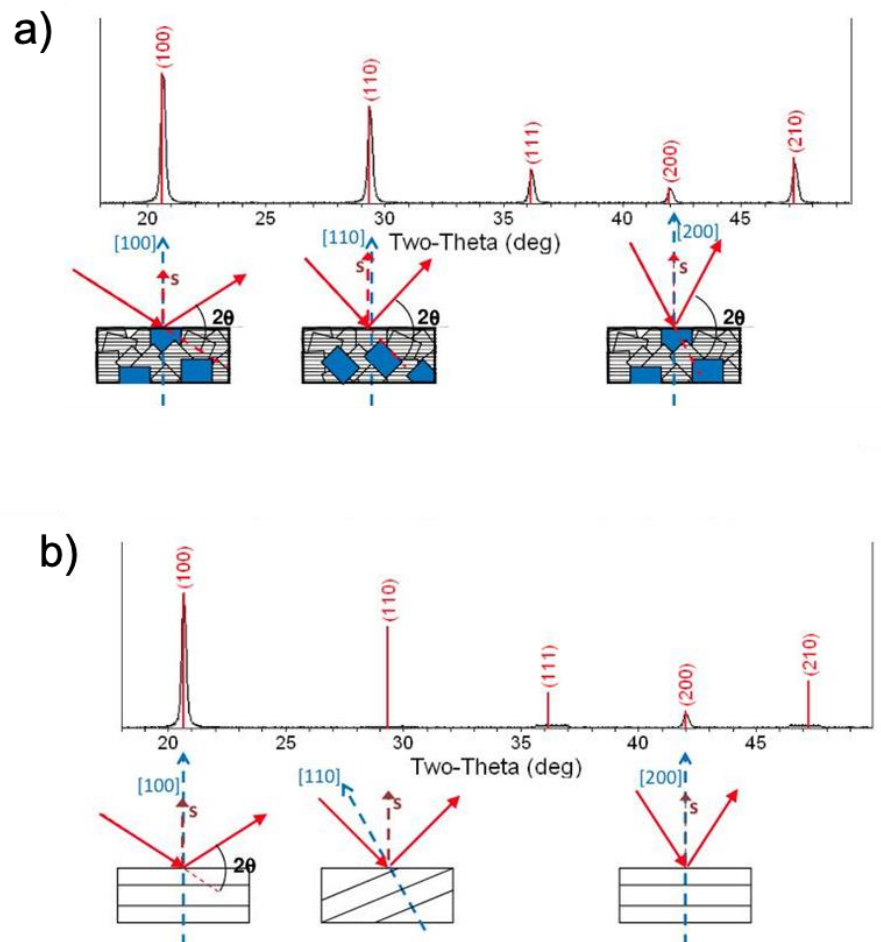
It was already mentioned that a diffractogram is the data resulting from XRD. Understanding that this diffractogram comes from Bragg's law, it could be said then that a XRD pattern is a spectrum that represents d-spacings in the crystal. Therefore, each diffraction peak represents a different (hkl) plane. The most obvious use of this technique is for identifying different crystal structures of the same material. For example, Fig. 31 shows three phases of  $\text{SiO}_2$  that are chemically identical but with different crystal structure; glass is amorphous while quartz and cristobalite have two different crystal structures. In these, the Si and O atoms are arranged differently. For materials without long range order such as amorphous systems (glass), no peaks are observed. While, the diffraction data for quartz and cristobalite present distinctive peaks.



**Figure 31.** Diffractograms for three different forms of SiO<sub>2</sub>. Figure from reference 20.

The XRD pattern will also be different depending on the nature of the sample. If the sample is polycrystalline, formed by 'little' crystals oriented in random directions, then different crystals will diffract in different directions. In theory, for this case all possible diffraction peaks should be included. On the other hand, a single crystal sample should only show a few peaks (planes) in the diffraction pattern, as shown in Fig. 32.

Every x-ray reflection (or peak) is characteristic of a unique plane  $d_{hkl}$ , as shown in Table 6. However, sometimes the order of diffraction should be taken into account. Thus, the diffraction data can be reduced to a list of peak positions and intensities. Furthermore, the intensity of the peaks depends on the atomic structure of the material, e.g., the position of atoms in the unit cell.



**Figure 32.** XRD patterns from a) a polycrystalline sample and b) a single crystal. Figure from reference 20.

Observed $^{\circ}2\theta$	Intensity ( $I/I_0$ )	Calculated $d$ -spacing	$h$	$k$	$l$
28.27	100	3.1571	1	1	1
32.75	36.19	2.7341	2	0	0
47.00	44.24	1.9333	2	2	0
55.76	38.97	1.6487	3	1	1
58.47	8.52	1.5785	2	2	2
68.66	5.84	1.3671	4	0	0
75.84	13.47	1.2545	3	3	1
78.17	9.77	1.2227	4	2	0
87.37	10.59	1.1162	4	2	2

**Table 6.** Example data obtained from a XRD pattern.

The analysis of the XRD data is known as *indexing*, and involves identifying the planes that are diffracting. This consists of assigning the correct Miller indices (hkl) to each peak in the diffraction pattern. To index an XRD pattern, some prior information about the data is needed and often references to standards and simulations are required. The most common and easiest way to analyse the XRD pattern is to speculate the values of (hkl) and then to compare the calculated (experimental)  $d_{hkl}$  values to the  $d_{hkl}$  known (expected) values. For this there are several crystallography databases that can be freely accessed and are listed at the end of these notes. The expected  $d_{hkl}$  values for any crystal can be calculated from knowledge of the lattice parameters (Table 1). Additionally, from Bragg's equation (where  $\lambda$  is known) and an analysis of the Ewald sphere and reciprocal lattice, experimental values  $d_{hkl}$ , can be calculated. These calculations will result in a list of  $d_{hkl}$  values for a crystal and the given experimental conditions. It is then possible to put these data together to determine the size of the unit cell of the material producing the diffraction pattern. For example, the interplanar spacing for any set of (hkl) planes in a cubic structure can be calculated using:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{Eq. (32)}$$

By combining Eq. 32 and the square of Bragg's law, the following relationship is found in terms of  $d$ :

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{4 \sin^2 \theta}{\lambda^2} \quad \text{Eq. (33)}$$

Rearranging in terms of  $\theta$ ,

$$\sin^2 \theta = \left( \frac{\lambda^2}{4a^2} \right) (h^2 + k^2 + l^2) \quad \text{Eq. (34)}$$

From Eq. 34, it is easy to see that  $\sin^2 \theta$  is proportional to  $(h^2 + k^2 + l^2)$ . This means that as  $\theta$  increases, planes with higher Miller indices (hkl) will diffract more.

For a full analysis of an XRD pattern we should remember that the presence of translational symmetry elements and centring in the real lattice causes some series of reflections to be absent, called systematic absences. Systematic absences occur if a set of lattice planes occupies a position such that the produced x-rays are completely out-of-phase with another set of lattice planes. In this case, no reflection will be observed, i.e., although the Bragg condition is satisfied for the sets of planes in question, the destructive interference "extinguishes" the reflection. These systematic absences (or *systematic extinctions*) indicate the presence of specific symmetry elements in the lattice and thus provide valuable information about the space group (crystal system and symmetry) of the crystal. The rules for some systematic absences and allowed reflections can be found in the International Tables for Crystallography. Moreover, a full indexing requires a more mathematical treatment by considering not only an initial speculation of the (hkl) planes but also taking into account the normalisation of the (hkl) or  $d$  values and the ratio of the (hkl) planes.

In summary, in an ideal XRD pattern there are two types of information that can be obtained: qualitative and quantitative. Qualitative analysis involves peaks identification and phase identification. The different peaks positions can shed light on the following:

- Crystal system
- Space group symmetry
- Translational symmetry
- Unit cell dimensions
- Qualitative phase information (peak intensity)

The peak intensity can be related to quantitative phase fractions. In a more detailed study, the peak shapes and widths can give information on crystallite (grain) size, microstrain and extended defects (stacking faults, antiphase boundaries etc).

A quantitative analysis leads to the determination of the lattice parameters and can also identify the fraction of each phase in a sample. The exact lattice parameters of each crystalline component are refined from the peak positions. The profile shape can be used to extract micro-structural information on the phases present such as crystallite size and strain for each phase.

Like all other analytical methods, XRD has both strengths and limitations. Therefore, it is generally a good idea to combine a number of characterisation techniques in order to check for data consistency and fully characterise a material.

★ More on [X-ray Diffraction Techniques](#) and [x-ray diffraction](#)

## 9. Crystallography web-sources

- <http://www.iucr.org/iucr>
- <http://www.crystallography.net>
- [The Materials Project](#)

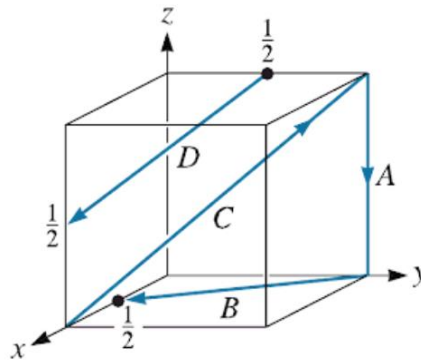
## 10. Exercises

- 1) In the 2D lattice shown in Fig. E1, identify possible primitive and non-primitive unit cells. Which one is more appropriate and why?



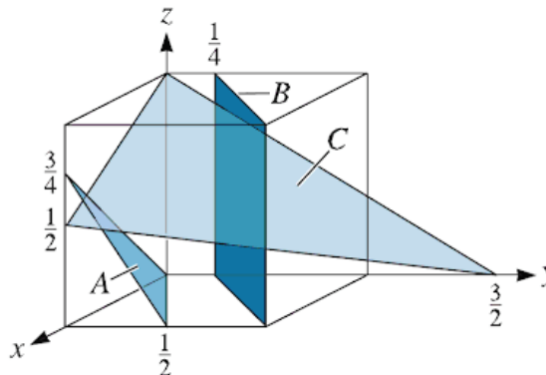
**Fig. E1.** 2D lattice.

- 2) Determine the directions in the cubic unit cell shown in Fig. E2.



**Fig. E2.** Standard cubic unit cell.

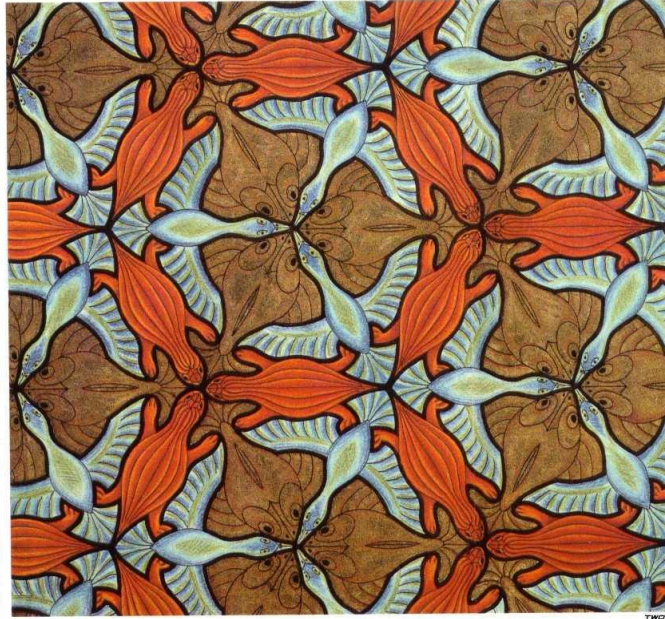
- 3) Determine the Miller indices for the planes in the cubic unit cell shown in Fig. E3.



**Fig. E3.** Standard cubic unit cell.

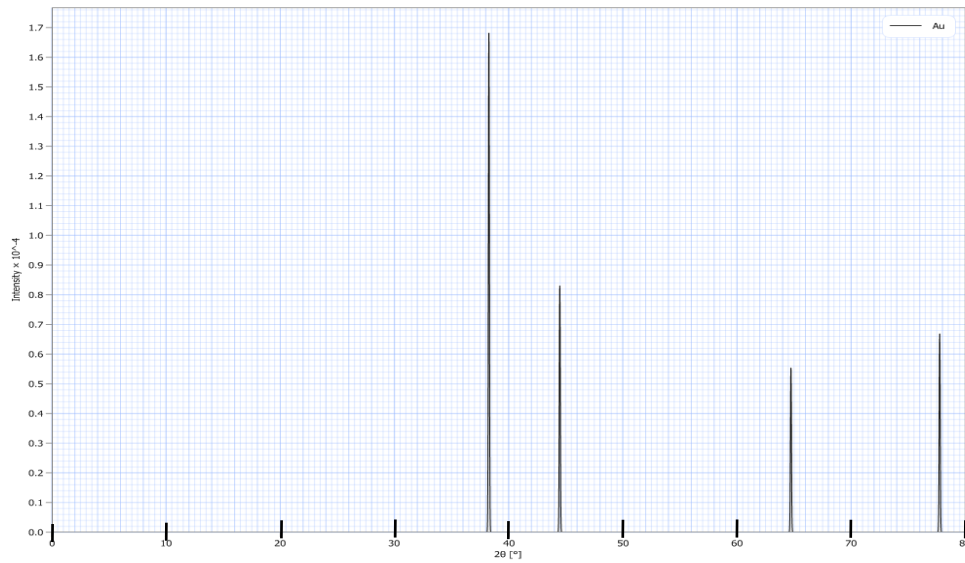


- 4) Identify the symmetry elements present in Fig. E4.



**Fig. E4.** Symmetry pattern

- 5)  $\text{Rb}_2\text{ZrO}_3$  has an orthorhombic crystal system, space group  $\text{Cmc}21$  and the following lattice parameters:  $a = 10.94 \text{ \AA}$ ,  $b = 7.46 \text{ \AA}$  and  $c = 5.97 \text{ \AA}$ . Draw the corresponding 3D reciprocal lattice and calculate the magnitude of the  $a^*$ ,  $b^*$  and  $c^*$  lattice vectors.
- 6) X-rays from a Mo x-ray tube ( $\lambda = 0.709 \text{ \AA}$ ) are diffracted at an angle of  $7.11^\circ$  from a sample of metallic Fe. Assuming that  $n=1$ , what is the distance between the planes that gives rise to this reflection?
- 7) Calculate the angle of diffraction when x-rays from a Cu tube ( $\lambda = 1.54 \text{ \AA}$ ) are diffracted by planes of atoms parallel to the faces of the cubic unit cell for Mg (260 pm), Zn (247 pm), and Ni (216 pm). The length on one edge of the unit cell is given in parentheses; assume first-order diffraction ( $n = 1$ ).
- 8) Gold crystallizes in the space group  $Fm\bar{3}m$ . A simulation of its XRD ( $\text{Cu-K}\alpha = 1.54 \text{ \AA}$ ) pattern is shown in Fig. E5.
- What does the  $F$  represent?
  - Calculate the d-spacing for the 4 peaks.
  - Calculate the lattice parameter  $a$ .
  - If the first 4 peaks are (111), (002), (022) and (113). Why is (001) not present in the diffractogram?



**Fig. E5.** Simulated Diffractogram for single crystal Au using Cu-K $_{\alpha}$  = 1.54 Å

- 9) A single crystal of Langisite ( $a = 3.53$  Å,  $c = 5.12$  Å, hexagonal crystal) is placed in a diffractometer such that CuK $_{\alpha}$  X-ray radiation (wavelength = 1.54 Å.) is incident along the  $a^*$  axis.
- Sketch the  $a^*$ - $c^*$  section of the reciprocal lattice and the circular trace of the Ewald Sphere associated with this incident X-ray beam.
  - The crystal is rotated with respect to the incident X-ray beam about an axis perpendicular to the  $a^*$ - $c^*$  reciprocal lattice. At what rotation angle could the 002 reflection in Langisite be observed?

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