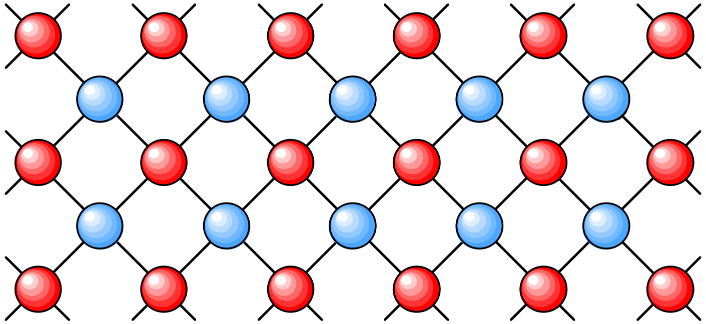
MRES216 Physical Techniques for the Study of Biological Systems

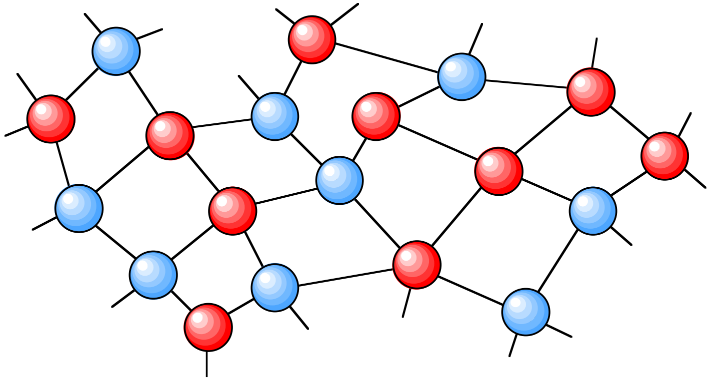
Lecture 1 The Crystal Structure of Solids

Solids can be divided into two categories – crystalline or amorphous.

A **crystal** has long range order

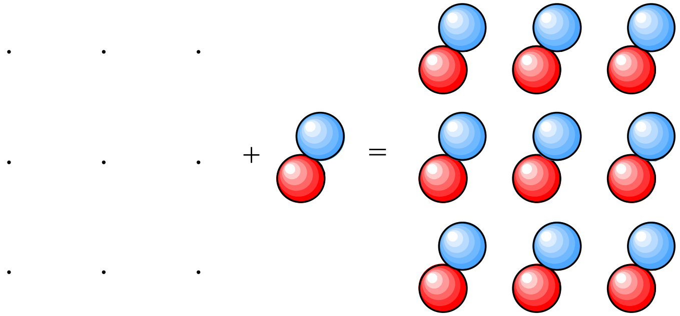


Amorphous materials have some short range order only



In this module we shall concentrate on crystalline materials, as the lack of order in amorphous materials makes them more difficult to study.

A crystal comprises a **space lattice** and a **basis**



space lattice + basis = crystal structure

Note that the space lattice is *not* an arrangement of atoms, but a lattice of points which form the framework onto which the atoms are “hung”. In order to describe a crystal structure completely, we must specify the underlying lattice and the basis of atoms associated with every point in the lattice – the number of atoms in the basis and their positions.

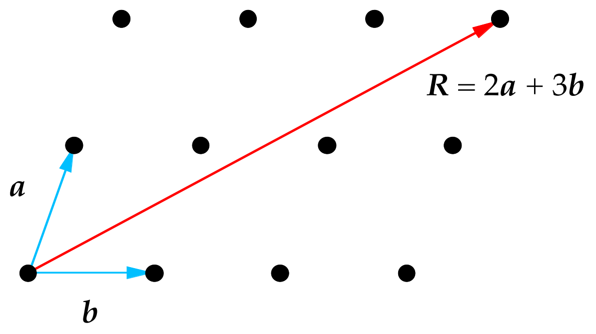
For simple elemental solids, such as Argon, the basis is a single atom and so the description of the basis is trivial. Other elements have a two-atom or four-atom basis, whereas compounds must have a basis of *at least* one molecule of the substance; complex organic compounds can have thousands of atoms in the basis.

The Space Lattice

A space lattice is a set of points such that a translation from any point *P* in the lattice by a vector

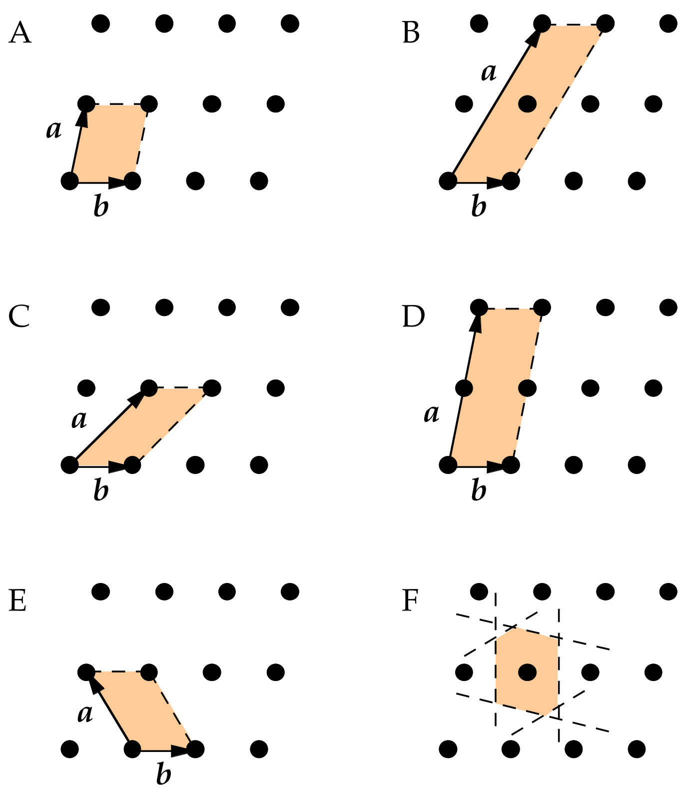
$$\boldsymbol{R}_{\mathrm{lmn}} = \mathrm{l}\boldsymbol{a} + \mathrm{m}\boldsymbol{b} + \mathrm{n}\boldsymbol{c} \qquad (\mathrm{l, m, n\ integers})$$

locates an exactly *equivalent* point, *i.e.* a point with the same environment as *P*. This is **translational symmetry**. The vectors ***a***, ***b***, ***c*** are known as **lattice vectors**.



The **unit cell** is defined as the parallelepiped (or parallelogram, in 2-d) whose edges are formed by these lattice vectors ***a*** , ***b*** , ***c***.

For each space lattice we can select **primitive lattice vectors** and an associated **primitive cell** containing just *one* lattice point (it doesn't matter where the lattice point is in the unit cell – it is conventionally placed at the corner). Note that a set of primitive vectors is not necessarily unique.



The unit cells labelled A, C, E and F are primitive as they only contain one lattice point. The cells labelled B and D contain two lattice points and so are non-primitive.

Cell F is a special case in which the cell has been formed by drawing the perpendicular bisectors (lines in 2-d, planes in 3-d) of lines joining a chosen lattice point to all of its neighbours. The smallest polygon (polyhedron in 3-d) thus formed is called the **Wigner–Seitz** primitive cell.

Lattice Symmetry

Translation transforms a lattice into itself, *i.e.* a lattice that has been translated by a combination of primitive vectors is indistinguishable from the original. In addition to translation, there are other symmetry operations which can do this

Reflection in a plane
Rotation about an axis
Inversion through a point
Glide (= reflection + translation)
Screw (= rotation + translation)

The latter two, requiring a combination of actions, are known as **compound operations**. Inversion can also be considered as a compound operation as it is equivalent to a rotation of π followed by reflection in a plane perpendicular to the axis of rotation. (A lattice has inversion symmetry if the environment of a point at **r** is identical to that of a point at –**r**.)

A lattice possesses n–fold **rotational symmetry** if rotation of the lattice through an angle of $2\pi/n$ transforms it into itself. What values of n are valid ? Some simple maths shows that n can take values of 1, 2, 3, 4 or 6.

Note that a lattice cannot have 5–fold rotational symmetry, but there are interesting materials, called **quasicrystals**, that can. (Ask Dr McGrath if you want to know more about quasicrystals.)

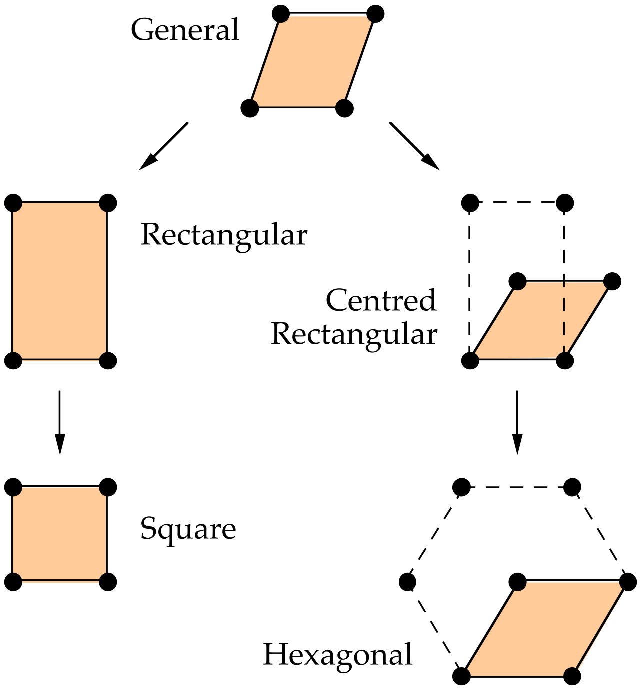
The Bravais Lattices

There are an infinite number of possible space lattices as there are no restrictions on the size nor direction of the primitive vectors $\boldsymbol{a}$, $\boldsymbol{b}$. A 2-d lattice with arbitrary vectors is known as an **oblique lattice** and has 1– and 2–fold rotational symmetry. By choosing the vectors with more care, we can construct lattices that possess 3–, 4– and 6–fold symmetry, and have different degrees of reflection symmetry.

To create such lattices we must impose restrictions on the primitive vectors $\boldsymbol{a}$, $\boldsymbol{b}$. Each distinct set of restrictions leads to a distinct type of lattice, called a **Bravais lattice**, which is characterised by the set of symmetry operations that transform the lattice into itself.

In 2-d there are four such sets of restrictions and so there are five Bravais lattices — one is the general oblique type and the four others correspond to the four sets of restrictions.

The Five Bravais Lattices in 2-d



The general **oblique** lattice has 1- and 2-fold rotational symmetry, and no mirror reflection symmetry.

By restricting the primitive vectors to be perpendicular, we create the **rectangular** lattice which has, in addition to the symmetries of the oblique lattice, mirror reflection symmetries.

3-d Bravais Lattices

In 3-d things are a little more complicated and so, as you would expect, there are more 3-d Bravais lattices than there are in 2-d; a total of 14 in all.

These 14 lattices are subdivided into seven classes, with one lattice in each class being “simple” and the others being variations. These variations involve either extra lattice points being added at the centre of cell faces (“face centred...”) or a single lattice point being added at the centre of the cell (“body centred...”).

It is not really necessary to go through the derivation of the 14 Bravais lattices, considering all the symmetries that they possess, nor to prove that they are all distinct and cover every possible arrangement of lattice points.

It is sufficient at this point to present the names and definitions of the lattices in terms of the relationships between the unit cell vectors $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ (these are for reference only — you will not need to remember them all).

The 14 Bravais Lattices in 3-d

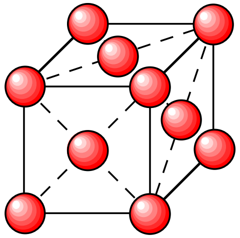
			lengths	angles
Cubic	(SC)	Simple	$a = b = c$	$\alpha = \beta = \gamma = \pi/2$
	* (BCC)	Body centred		
	* (FCC)	Face centred		
Tetragonal		Simple	$a = b \neq c$	$\alpha = \beta = \gamma = \pi/2$
		Body centred		
Orthorhombic		Simple	$a \neq b \neq c$	$\alpha = \beta = \gamma = \pi/2$
		Body centred		
		Face centred		
		Base centred		
Triclinic		Simple	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic		Simple	$a \neq b \neq c$	$\alpha = \gamma = \pi/2 \neq \beta$
		Base centred		
Rhombohedral (trigonal)		Simple	$a = b = c$	$\alpha = \beta = \gamma \neq \pi/2$
Hexagonal	*	Simple	$a = b \neq c$	$\alpha = \beta = \pi/2$ $\gamma = 2\pi/3$

($\alpha = \angle bc$, $\beta = \angle ca$, $\gamma = \angle ab$)

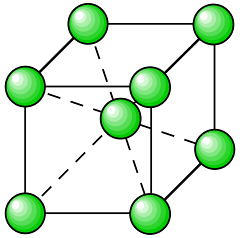
(* most common metallic crystal structures)

Non-primitive cells are sometimes easier to visualise and handle mathematically.

For instance, the conventional (non-primitive) cells of the face centred and body centred cubic lattices are



FCC



BCC

Note that in all of these diagrams of crystal structure, the atoms are drawn as widely separated small spheres for clarity (often refered to as a “ball and stick” model). In reality, the separation between atoms is such that the atomic “spheres” touch, *i.e.* the atoms fill as much space as the crystal structure allows.

Common Crystal Structures

Body Centred Cubic

The BCC structure is commonly found for the elements at the lighter end of all the rows of the periodic table, from the alkali metals (Li, Na, K, Rb, Cs) through to the start of the transition metals (V, Cr, Fe, Nb, Mo, Ba, Ta, W).

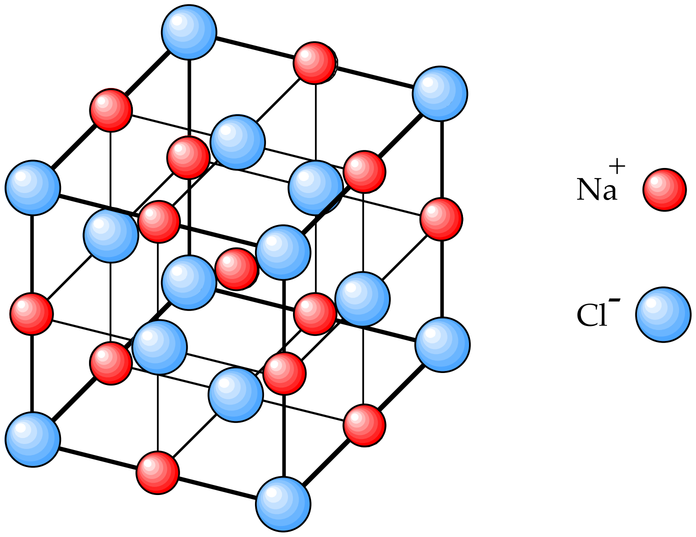
Face Centred Cubic

The FCC structure is adopted by a large number (~20) of metals, including the heavier end of the transition metals (Ni, Rh, Pd, Ir, Pt), the noble metals (Cu, Ag, Au), and some of the rare gases (Ne, Ar, Kr, Xe).

In addition, many compounds and alloys are based on the cubic structure. Two examples of general interest are NaCl and CsCl, and these compounds have given their names to these generic types of structure.

Sodium Chloride

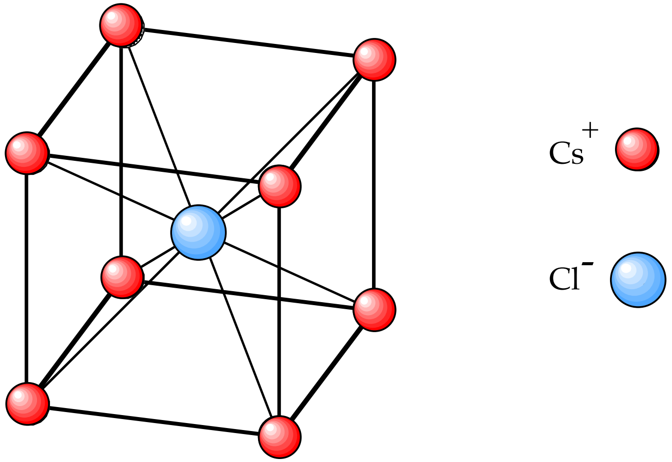
The Bravais lattice is FCC and the basis comprises one Na atom and one Cl atom separated by half the body diagonal of the unit cell cube.



Examples of this structure include KCl, PbS, MgO, MnO, KBr.

Cesium Chloride

The structure of CsCl is similar to that of NaCl in that it has a basis of two different species of atom, separated by half of the body diagonal of the unit cell cube. The lattice, by comparison, is a *simple* cubic and so the resultant structure is more easily visualised.



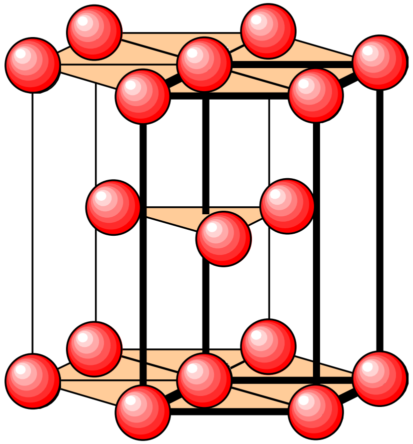
Examples of the CsCl structure include alloys such as CuPd, CuZn (b-brass), AgMg, BeCu.

Hexagonal Close-Packed

The HCP structure is based on the simple hexagonal lattice and has a two-atom basis. The second atom of the basis is positioned half way up the cell and so forms another hexagonal layer of close-packed atoms half-way between the top and bottom layers of the unit cell.

There is no way of choosing a primitive unit cell such that the basis contains only one atom.

The primitive cell usually drawn for the HCP crystal structure is shown in bold.

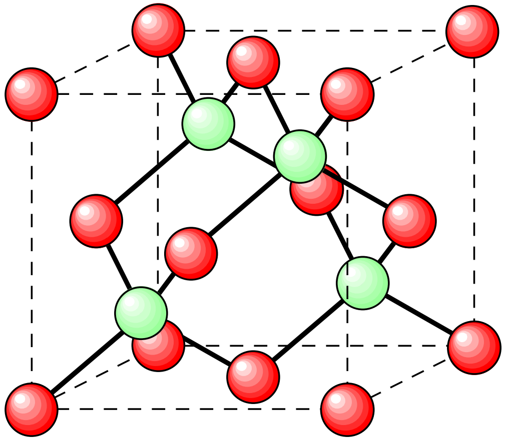


It is conventional to refer to the lattice constant (interatomic separation) in the plane of hexagons as *a* and that in the perpendicular, or axial, direction as *c* (where the latter is the height of the unit cell, and *not* the separation of adjacent layers of hexagonal planes).

Diamond

The diamond structure has an FCC space lattice and a basis comprising two identical atoms – as with the HCP structure there is no way of choosing a primitive unit cell such that the basis contains only one atom. Alternatively, the structure may be viewed as two interpenetrating FCC lattices, one displaced relative to the other along a body diagonal by a quarter of its length.

The atoms on each of the two FCC "sub-lattices" have been drawn in red and green (or dark and light grey) to clarify the diagram, but in fact are identical.

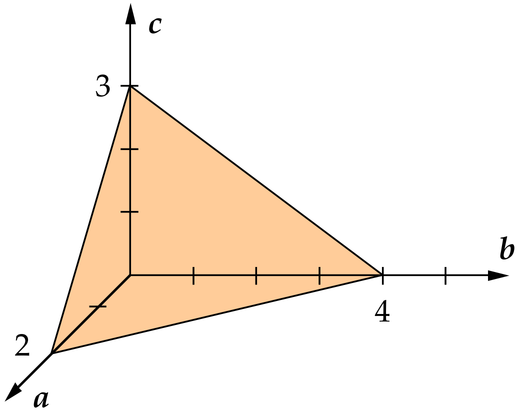


Relatively few elements exist in the diamond structure. Carbon is the most obvious example, but the importance of this structure in solid state physics is mainly due to the fact that this is the natural state of the semiconductors silicon and germanium.

Many two-element compounds form in a diamond-like structure in which the first element occupies one FCC sub-lattice and the second element the other. This structure is named after its prime example, ZnS.

Mathematical Notation of Crystal Planes

To define a particular plane of atoms in a crystal we use a mathematical notation known as **Miller indices**.



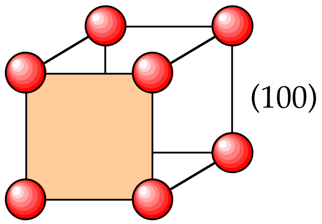
(*i*) Find the intercepts of the plane with the 3 crystal directions or axes in terms of primitive vectors ***a*** , ***b*** , ***c***
(*ii*) Take the reciprocals
(*iii*) Multiply the resulting 3 numbers by the smallest number that makes the result equal to 3 integers h, k, l

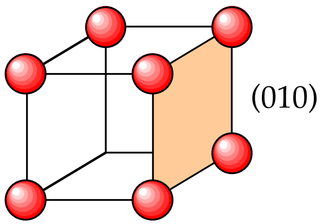
The plane is then defined by the notation $(h\,k\,l)$.

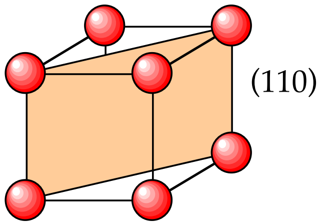
Thus, in the above example : intercepts $= 2\,,4\,,3$
reciprocals $= {}^1/_2\,,{}^1/_4\,,{}^1/_3$
x 12 $= 6\,,3\,,4$

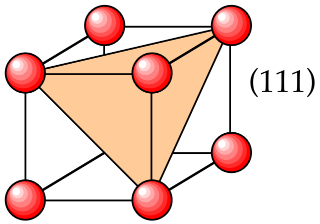
and so the plane is $(6\,3\,4)$.

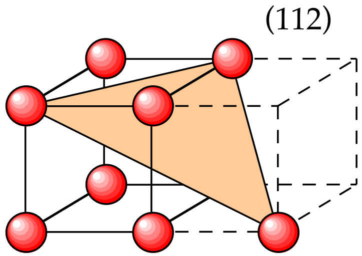
(Note that negative index is written as $\bar{h}$)

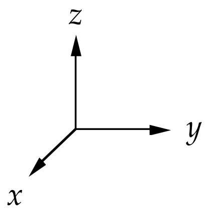


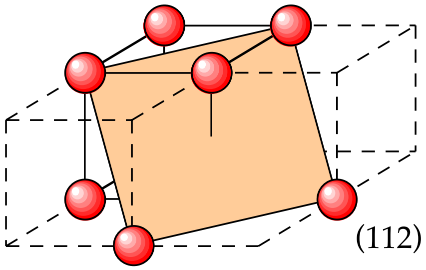












In a crystal with true cubic symmetry the choice of which of the three axes to label the "*x*-axis", and which the "*y*" and the "*z*", is entirely arbitrary. Thus the (100) plane is physically *equivalent* to the mathematically distinct (010) and (001) planes.

This leads to the grouping of various numbers of planes into sets, or families

(001) (010) (100) $(\bar{1}00)$ $(0\bar{1}0)$ $(\bar{1}00)$	3 x 2 = 6
(110) (011)	3 x 2 x 2 = 12
(111)	2 x 2 x 2 = 8
(210)	6 x 2 x 2 = 24
(321)	6 x 2 x 2 x 2 = 48

The sets of planes are denoted {h k l}.

For directions in a crystal, take components (or projections) on axes ***a***, ***b*** and ***c***. For example, the direction whose components are 2*a*, 3*b*, 2*c* is denoted [2 3 2]. Directions also occur in sets, and are denoted <h k l>.

For a **cubic** lattice, the direction [h k l] is perpendicular to the plane (h k l). In non-cubic systems, this is not necessarily true, so beware!

The Miller indices for **hexagonal** crystals are a special case (not considered here).

Summary of Crystal Structure of Solids

⊗ Crystal = Space lattice + Basis

⊗ Space lattice defined by lattice vectors ***a*** , ***b*** , ***c***

⊗ Unit cell has sides formed by these vectors

⊗ Primitive unit cell contains one lattice point

⊗ Conventional unit cell is not necessarily primitive

⊗ Lattice can have 1, 2, 3, 4, or 6-fold rotational symmetry

⊗ In 2-d there are 5 Bravais lattices
3-d 14 Bravais lattices

⊗ Most common 3-d lattices	Body centred cubic	(BCC)
	Face centred cubic	(FCC)
	Hexagonal	(HCP)

⊗ Crystal planes and directions defined by Miller indices

direction = [hkl]   set of directions = <hkl>
plane = (hkl)   set of planes = {hkl}

⊗ For hexagonal crystal structures, use four-index notation (hklm)