

Structure of Crystalline Solids - Bravais Lattices

- Crystalline solids involve high degree of atomic or molecular organisation in a repeating pattern. The same regular arrangement of atoms and molecules continues in all three directions, indefinitely.
- There are actually 14 possible arrangements of molecules and atoms in crystalline solids.
- These arrangements are called the Bravais Lattices.
- All lattice structures involve repeated use of one “unit cell” to generate the three-dimensional structure.
- The unit cell is like a box and is characterized by the lengths of three sides and the angles these sides make with each other where they meet.

Figure 3-10 shows all 14 structures. Let us look at it through a transparency.

The resulting 7 primary arrangements are:

Cubic $\rightarrow a = b = c$, $\alpha = \beta = \gamma = 90^\circ$, this is the simplest arrangement possible.

Tetragonal $\rightarrow a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

Orthorhombic $\rightarrow a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

These three are relatively easy to visualise since the angles are all right angles. In this sense they are like the familiar shapes of cardboard boxes. The only thing different is that cubic has all three sides of same length, tetragonal has two sides of same length and orthorhombic has all three sides of different lengths. The other four involve at least one angle that is different than right angle.

Rhombohedral $\rightarrow a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$, it is like a cube that has been deformed in angles but the sides remain of equal length.

Monoclinic $\rightarrow a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$, All sides are of different length and one of the angles is different than right angle.

Triclinic $\rightarrow a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$, here all sides are of different length and no two angles are equal.

Hexagonal \rightarrow HCP $\rightarrow a \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$, this arrangement leads to the hexagonal close packing, which is one of the densest packing one can get with spheres of equal size.

Seven additional arrangements, which are called secondary arrangements, are obtained by locating additional points on the face, base or centre of the unit cell.

Face-centred cubic \rightarrow FCC

Body-centred cubic \rightarrow BCC

Base-centred monoclinic \rightarrow BCM

Body-centred tetragonal \rightarrow BCT

Base-centres orthorhombic \rightarrow BCO

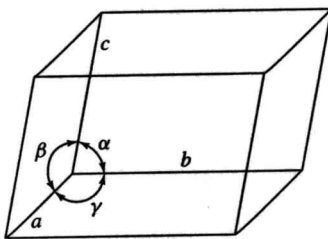
Body-centred orthorhombic \rightarrow BOCO

Face-centred orthorhombic \rightarrow FCO

These arrangements are shown in Figure 3-11.

Figure 3-12 shows the structure of NaCl crystals.

A unit cell is described by the lengths of the 3 sides and the three angles that the sides make with each other.



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3.8.3 Atomic Dimensions and Densities

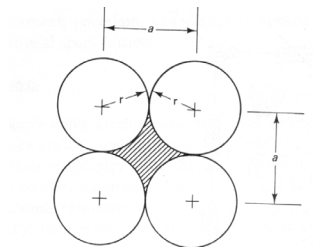
- We can create various possible crystal structures by arranging the atoms (or molecules) in different lattice structures.
- The bulk density of the solid crystal so created would depend on how many atoms are packed in a unit volume.
- Arrangements that pack more atoms per unit volume give denser solids.
- If you know the mass of each atom, and the number of atoms per unit volume, you can calculate the density of the solid.
- Conversely if you know density and the packing arrangement, that is the type of lattice involved and the lattice dimensions, you can calculate the atomic mass.
- If the known quantities are the atomic mass, the lattice structure and the density, you can calculate the lattice dimensions.
- These lattice dimensions provide a measure of the atomic dimensions, since it can be assumed that the atoms are touching one another.

Let us look at the simplest case of cubic lattice.

Simple Cubic Lattice

- A unit cell of cubic lattice has eight corners.
- In the repeating pattern, there is an atom at each corner, but this atom does not belong 100% to this unit cell. Each corner is shared by eight unit cells that meet there, four in one layer and four in the adjoining layer.
- Thus each corner atom is shared by eight unit cells, or you may say each cell has $1/8^{\text{th}}$ claim on the corner atom.
- Since there are eight corners, each containing $1/8^{\text{th}}$ atom, the total number of atoms in the unit cell is $8 \times 1/8 = 1$ atom.

Let us now see what the dimensions of the unit cell are. Each face looks like this picture



The length of each side is equal to $2r$, where r is the radius of the atom. Therefore the length of each side is equal to atomic diameter.

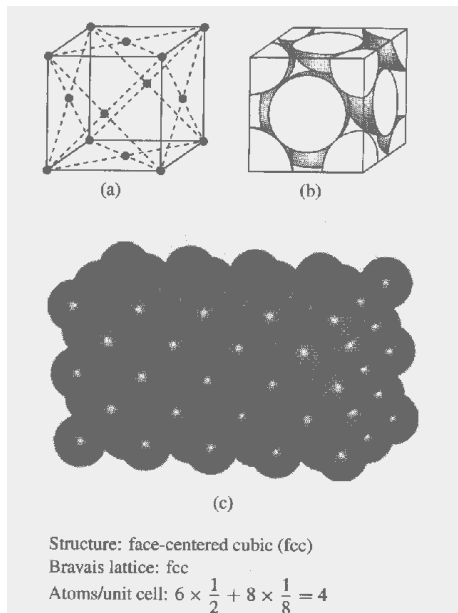
The volume of the unit cell is therefore equal to d^3 .

Mass of the unit cell, since it contains only one atom is equal to the mass of that atom. This is given by the mass of one mole of the substance divided by the Avagadro's number.

$$m = \text{atomic mass}/N_A, \text{ kg}$$

$$\text{bulk density} = m/d^3.$$

Let us now look at the face-centred cubic lattice. Its face will look like the following picture.



First the number of atoms in each unit cell. We know that the corner situation is same as in the case of the simple cubic cell. Each corner contains $1/8^{\text{th}}$ atom. The atom at centre of the face is shared by only two cells that share the face, hence $1/2$ belongs to each unit cell. Since there are six faces, the unit cell contains $6 \times 1/2 = 3$ face centred atoms. Combined with the one corner atom, this makes **four atoms per unit cell**.

Mass of unit cell = $4m$

Now let us look at the dimensions of a unit cell. We focus on the diagonal of a face of the unit cell. It has one atom in the middle and one at each end. The diameter of the middle atom is fully contained in the diagonal but the end atoms only contribute half a diameter each. Hence the length of the diagonal is equal to 2 times the diameter of the atom. When the diagonal is equal to $2d$, the side is given by $\sqrt{2} d$

$$\text{Volume of unit cell} = (\sqrt{2}d)^3 = 2\sqrt{2}d^3$$

$$\text{Bulk density of FCC materials} = \frac{4m}{2\sqrt{2}d^3} = 1.414 \frac{m}{d^3}$$

Which is 41.4 % higher than the simple cubic lattice.

Body-centred Cubic Lattice

The body centred cubic lattice contains one atom at the centre of the cube and $1/8^{\text{th}}$ at each corner. Hence, the total number of atoms is equal to 2.

$$\text{Bulk density of BCC materials} = 1.299 \frac{m}{d^3}$$

Which is lower than FCC but higher than the simple cubic. These relationships between the density and the atomic dimensions are very useful for calculating the atomic dimensions from measure values of density and a knowledge of the crystal structure.

Hexagonal Close Packing

We have seen that the densest packing in the cubic system is obtained in FCC arrangement. The HCP arrangement also provides equally dense-packing. The two systems are similar in some ways but there are also a few subtle but significant differences.

Density of HCP = Density of FCC system

Coordination number

- The number of nearest neighbours is called coordination number.
- Coordination number of FCC and HCP is 12.
- Coordination number of BCC is eight.
- The simple cubic arrangement has a coordination number of six.

Some Other Crystal Structures for Pure Elements/substances

Two examples are given in the text for sulphur and carbon. Let us look at the case of carbon.

The atomic structure of carbon is such that it contains 6 electrons, 6 protons and six neutrons, giving the atomic mass of 12.

Of the 6 electrons, 2 are in the inner K-shell and 4 are in the L-shell, which are the valence electrons. In a stable configuration the L-shell can have zero or eight electrons. Carbon atoms achieve this stable configuration by sharing the valence electrons with other neighbouring carbon atoms.

There are two well-known crystalline structures of carbon:

- Graphite
- Diamond

Graphite Structure

- Six atoms of carbon join together to form a hexagonal-ring-structure with alternating single and double bonds.
- Each atom shares its 4 valence electrons with 3 neighbours, all in the same plane.
- Such planes are held together by weaker van der Waals forces.
- The location of double bonds is not fixed; hence we get a resonating structure.
- This resonating structure results in free movement of electrons, hence high electrical and thermal conductivity
- The bonds on a layer are quite strong, but bonds between the layers are very weak.

Diamond Structure

- The arrangement of C atoms in diamond is quite different.
- 4 C atoms are located on the four corners of a regular tetrahedron.
- Several such tetrahedrons are combined into a lattice structure that is FCC but with four additional atoms located within the cubic structure.
- Thus, the diamond structure involves Carbon atoms that are well meshed-in, and all bonds are equally strong.

Polymorphism

The tendency of a substance to show more than one crystalline structure is called polymorphism.