
UNIT 3 THE CRYSTAL STRUCTURES OF SOLIDS

Structure

- 3.1 Introduction
 - Objectives
- 3.2 Ideal Structures
 - 3.2.1 Unit Cell and Bravais Lattices
 - 3.2.2 Cubic Structures and Packing Fractions
 - 3.2.3 Directions in a Cubic Crystal
 - 3.2.4 Planes in Cubic Crystals and Miller Indices
- 3.3 Crystal Structures of Metals
 - 3.3.1 Close-packed Structures
 - 3.3.2 Concept of Atomic Radius
 - 3.3.3 Solid Solutions
 - 3.3.4 Polymorphism or Allotropy
- 3.4 Ceramic Crystal Structures
 - 3.4.1 Sodium Chloride Crystal Structure
 - 3.4.2 Perovskite Crystal Structure
 - 3.4.3 Spinel Crystal Structure
- 3.5 Crystal Structure Determination
 - 3.5.1 Principle of X-ray Diffraction
 - 3.5.2 Determination of Cubic Structures
 - 3.5.3 Neutron and Electron Diffraction
 - 3.5.4 Other Methods
- 3.6 Summary
- 3.7 Key Words
- 3.8 Answers to SAQs

3.1 INTRODUCTION

In **Nature**, we see perfection in the form of some beautiful crystals. You must have seen natural quartz crystals **as** well **as** gem stones or their pictures. The striking aspect of these is the perfection of the surfaces. How does such perfection occur? We **know** that every solid contains **atoms** (or ions), and **these** are the building blocks. Their **arrangement**, in three dimensions, should lead to this perfection. We shall see, in this unit, that many properties of a material stem from its crystal structure and from the electron states within these structures. We shall also see that there is a strong correlation between structure **and** type of bonding in a solid.

In the unit on **Classification** of Materials, we had seen that it was possible to classify materials as crystalline and amorphous. We had seen that a perfect arrangement of **atoms** led to mechanical strength, while amorphous materials showed resistance to corrosion. **Though**, at first sight, we may feel that there are an **infinite** number of ways in which atoms can arrange themselves, in reality the diversity of the structures is rather small. The concepts of the ionic size and coordination number, **developed** in Unit 2, also determine the type of structure **that** the solid would **crystallise** in,

Objectives

It should be evident to you that the determination of crystal **structures** give a lot of information of the material. One can get the same properties in a material provided one uses methods of processing that yield the same crystal **structure**! In **this** unit we shall describe the various structures possible in an **ideal** case. We also discuss methods commonly employed to determine the crystal structure in solids.

At the end of the unit you should be able to :

- appreciate the difference between a **primitive cell** and a **unit cell**,
- distinguish between **Bravais** lattices and actual crystal structures,
- calculate the theoretical density of a solid by **knowing** its **lattice parameter**,
- determine the crystal structure by knowing the first few X-ray diffraction lines, and
- understand the **general theory** of diffraction and choose the appropriate method of structure determination in practice.

3.2 DEAL STRUCTURES

Whenever we consider a model of a solid, we find that it is very difficult to take into account a real situation. It is better that we idealise it as, in that way, we can work out a mathematical model, and account for the differences in reality as arising out of non-perfection or defects. The one advantage of considering a perfect **structure** is that we can consider the **neighbourhood** of any one atom and stipulate that the **environment** of every other atom is the same. In this way we can consider the forces acting **on** one atom **and** then generalise the situation. Of course, it is obvious that, in such a model, we do not consider what happens to atoms at the surface. We consider an **infinite**, mathematically perfect arrangement of **point** in space or a **lattice**. We then assign to each lattice point an atom to form the crystal structure.

On space being three-dimensional, three-dimensional arrangements are the ones that we should **try** and understand though they are difficult to represent on paper. The **important point** to remember is that we are talking about a structure **in** which a small unit repeats itself in a way that the structure is generated. Also the **unit** of repetition should not leave gaps in the structure. In nature, we do come across one dimensional structures (such as long chain polymeric materials) as well as two-dimensional structures such as mica and sheet silicate structures. Understanding them, however, is more complex as their properties show dependence on direction (*i.e.* **anisotropy**). Also the distances between atoms varies greatly along different directions. It is possible to actually simplify the consideration of atomic structures in three dimensions by remembering that the structure should be such that there is no empty space left in the **arrangement**.

In nature we see the **honeycomb** structure which is made up of hexagons packed together to fill up the total space. So also, you can imagine how cubes can be packed together to leave no gaps. In building houses, one uses **tetragonal** bricks to completely fill up space and that is another unit of **repetition** possible. The strength of the **wall** can be correlated to the strength of a brick by assuming **that** all the bricks are identical, Something similar is done in the study of crystal structures.

3.2.1 Unit Cell and Bravais Lattices

If we assume an atom to be a point, the regular arrangement of these points in space constitutes a lattice. To form a crystal structure, then, each lattice point must be associated with an atom (or a group of atoms). This association is called a **basis**. The crystal lattice plus a basis gives the crystal structure. It is convenient to emphasise that each atom occupying a lattice point is identical to that occupying any other lattice point in the structure. One may consider this idea as analogous to the indistinguishability of electrons in a solid. If every atom occupying a lattice point is the same, *i.e.* it has the same surroundings and so is indistinguishable from its **neighbour**, the crystal structures that are formed are called **Bravais Lattices**. In three dimensions, the number of Bravais lattices are limited to just 14. These are listed in Table 3.1. In the table are also given the most common basis vectors. These are not **the vectors** for a **unit cell** but are those that display the symmetry of the structure in Cartesian co-ordinates. a , b and c represent the cell dimensions and the angles α , β and γ are the inclinations of the vectors such that α is the angle between vectors b and c , β the angle between c and a and γ the angle between a and b .

Sl. No.	Crystal System	Cell Dimensions and Angles	Bravais Lattice
1	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred Face-centred
2	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred
3	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Body-centred Face-centred Base-centred
4	Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Simple
5	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Simple
6	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	Simple Base-centred
7	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	Simple

In engineering materials, we will come across the cubic systems very often, i.e. the simple cubic, the body-centred cubic and the face-centred cubic lattices and these are shown in Figure 3.1.

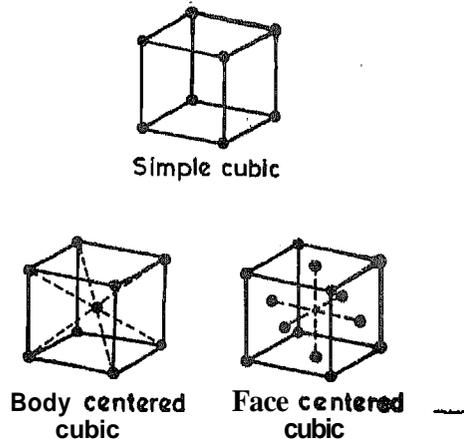


Figure 3.1 : The Three Cubic Lattices

We must emphasise the extremely small sizes that make up a unit cell. A typical side of a unit cell is 3 Å or 300 pm; this means that the number of unit cells lined side by side in 1 cm is more than 30,000,000. Let us discuss the main features of these cubic structures.

3.2.2 Cubic Structures and Packing Fractions

We have seen in Unit 2 that we can conveniently consider the ions in an ionic solid to behave as incompressible hard spheres, and assign an ionic radius to the ion, Let us extend that idea and say that in the crystal structure the atoms behave as incompressible spheres and occupy a definite volume and that these spheres touch each other so that the structure occupies the minimum volume in space. Remember that as the atoms are spheres, they will always leave gaps. These gaps are called Interstices and we shall see that the gaps have a definite role to play.

It is relevant to ask the question: what is the fraction of the volume actually occupied by the atoms in a given structure. This quantity, called the packing fraction determines the density of the solid. Larger the packing fraction, larger the density, It also means that if an

element has a larger density then it should exhibit a crystal structure with a larger **packing fraction**. Structures with large packing fractions are called close-packed structures. It follows **that** in metals we should see close-packed crystal structures. But let us calculate the **packing fraction** for a simple cubic structure. In Figure 3.2 we have shown the

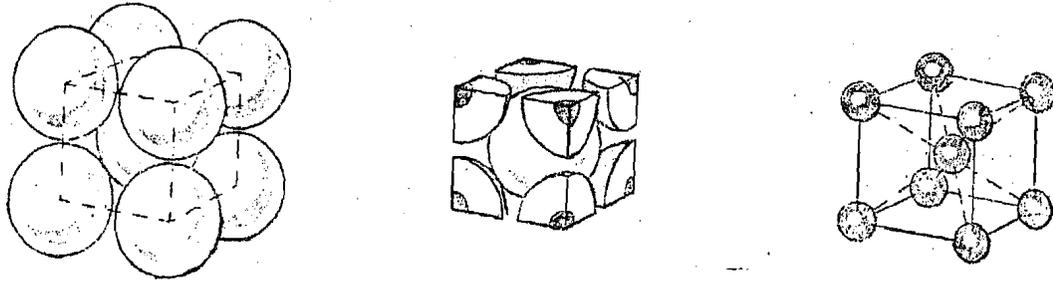


Figure 3.2 : Body-centered Cubic Structure

structure and the lattice parameter a . If the radius of the atom is R then we can see that:

$$a = 2R \quad \dots (3.1)$$

In the volume a^3 there is one atom as each atom on **the** cube corner is shared equally by eight **surrounding** cubes; and the 8 atoms on the corners contribute to one atom in the unit cell. Hence, the packing fraction, PF is :

$$PF = \frac{\text{volume occupied by atoms in a unit cell}}{\text{volume of the unit cell}} \quad \dots (3.2)$$

$$PF = \frac{4\pi}{3} \times \frac{R^3}{a^3} = \frac{\pi}{6} = 52\% \quad \dots (3.3)$$

The simple cubic crystal structure is a fairly **open** structure with nearly half the space **vacant**.

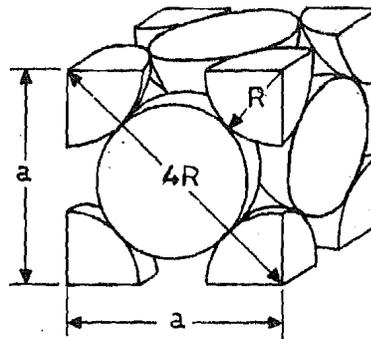


Figure 3.3 : Facecentered Cubic Structure ; Three-dimensional View

What about the face-centred cubic arrangement? In Figure 3.3, a plane of this structure is shown along with the unit cell. One can see that the atoms touch along **the** face diagonal and there are 4 **atoms** in a unit cell so :

$$4R = \sqrt{2} a \quad \dots (3.4)$$

$$PF = 4 \times \frac{4\pi}{3} \times \frac{R^3}{a^3} = \frac{\pi\sqrt{2}}{6} = 74\% \quad \dots (3.5)$$

In the face-centred cubic, or FCC structure, only about 1/4th of the space is unoccupied.

SAQ 1

Determine the packing fraction for a body-centred cubic (or BCC) structure.

The FCC structure is the most densely packed. Another structure, which is not a Bravais lattice, the hexagonal close-packed or HCP structure also has the same packing fraction as the FCC structure. You should be able to see that BCC metals would have a larger range for alloying than FCC metals. Also the interstices in BCC structures would be larger than that in FCC structures. Can we specify the positions in crystals which these additional atoms would occupy? In order to do this we would need to assign directions in crystals. This is done in the next sub-section.

3.2.3 Directions in a Cubic Crystal

For simplicity, consider the simple cubic structure as shown in Figure 3.4. It is convenient to assign the Cartesian co-ordinates to coincide with the a , b and c axes. But as

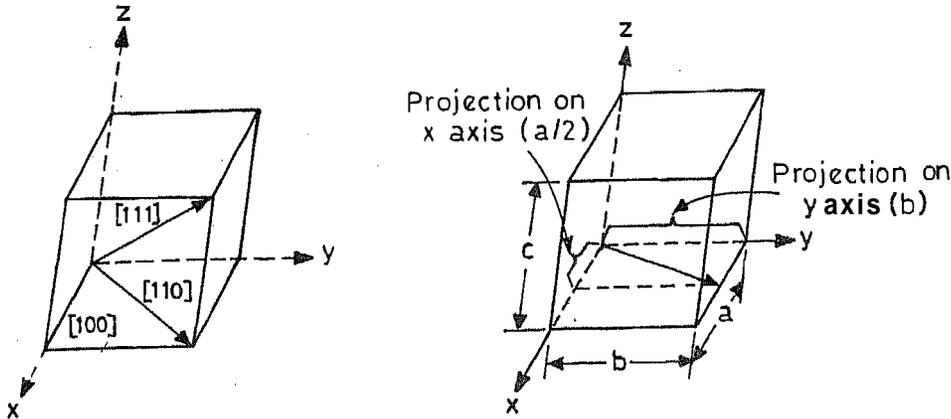


Figure 3.4: Crystallographic Indices of Lattice Directions

the three axes are the same, it does not matter which is which. This means that any property measured along a given axis would be the same along the other two axes. This, then, would be a principal direction in a cubic crystal. You should also be able to see that along this direction, if we rotate the crystal by 90° , we would get the same arrangement of the atoms. As rotation by 360° , is the same as no rotation at all, one can say that along the axes, a cubic crystal has a four-fold rotation axis. Are there any other rotation symmetries? Well, along the body diagonal, the cubic crystal has a three-fold rotation symmetry; this means that by rotating the crystal by 120° , about this axis, we get the same atomic arrangement. So also, about the face-diagonal, there is a two-fold rotation symmetry. These are the principal directions in a cubic lattice. You should be able to see easily that the same symmetry elements exist for the body-centred and face-centred cubic crystals also. Physical properties such as resistivity, optical absorption, magnetic induction etc. are normally measured along these directions as such measurements can be readily interpreted by theory. Measured quantities along random directions are difficult to understand on the basis of simple theories. We will now try and see whether we can talk of these directions with respect to the Cartesian co-ordinates.

3.2.4 Planes in Cubic Crystals and Miller Indices

Planes in a lattice are recognised by the intercepts they make on the Cartesian axes. The intercepts are converted into numbers called the Miller indices. These are three numbers derived by taking the reciprocals of the intercepts and converting the fractions to a common denominator. For example, a plane having intercepts a , $2a$, and $3a$ along the x , y and z axes will have reciprocals of the intercepts as $1/a$, $1/2a$ and $1/3a$, which have to be converted to a common denominator, i.e. $6/a$. The Miller indices are thus $6/a$, $3/a$ and $2/a$ and the plane is denoted as the $(6\ 3\ 2)$ plane. You can immediately see that all planes parallel to this plane would also be denoted by the same set of numbers and so would be the $(6\ 3\ 2)$ plane.

SAQ 2

What are the Miller indices for the planes parallel to the axes, parallel to the face diagonal and parallel to the body diagonal in a cubic crystal?

It is also possible to use the Cartesian axes to designate the positions of the atoms as well as the directions in crystals. Consider the origin to signify the position of an atom and designate this position as $(0,0,0)$. One near neighbour of this atom is at a distance a along the x -axis. The position of the neighbour can be denoted as $(a,0,0)$. The direction of the axis from the origin is then denoted by reducing the numbers a , 0 and 0 to a common denominator to give the direction indices for the cubic crystal, i.e., $[1\ 0\ 0]$. Similarly, the y -axis would be $[0\ 1\ 0]$ and z -axis $[0\ 0\ 1]$. To denote the negative x -axis direction we write the number with a bar on top, viz. $[\bar{1}\ 0\ 0]$. We remember that the x , y and z directions in a cubic crystal are identical. The length a is the repeat length in the structure and is called the **cell parameter**. This means that there are six identical $[1\ 0\ 0]$ directions.

The positions of the atoms in a simple cubic cell with cell constant of unity are: $(0,0,0)$, $(1,0,0)$, $(0,1,0)$, $(0,0,1)$, $(1,1,0)$, $(0,1,1)$, $(1,0,1)$ and $(1,1,1)$ (see Figure 3.4). Each of these eight atoms is shared with other unit cells in a way that each atom is shared by eight cells. The contribution of each atom to the unit cell is therefore $1/8$ and as there are eight atoms the number of atoms per unit cell is *one*.

SAQ 3

Write down the atom positions for a BCC and for a FCC structure. Also work out the number of atoms per unit cell in the two cases.

You should have worked out that the square brackets are used to denote the directions in a crystal and the normal brackets denote the planes. You should also be able to work out that the direction of the body diagonal in a simple cubic cell would be denoted by $[1\ 1\ 1]$ and that there would be eight such directions. This can be got as follows. The atom positions are $(0,0,0)$ and $(1,1,1)$. The vector components for this direction are: $x = 1 - 0 = 1$; also y and z are also 1. The direction is therefore written as $[1\ 1\ 1]$.

SAQ 4

Determine the indices of the cubic direction between the position coordinates of $(-3/4, 0, 1/4)$ and $(1/4, 1/2, 1/2)$.

An important relationship for the cubic system is that the indices of a direction perpendicular to a crystal plane are the same as the Miller indices of that plane. This means that the $[1\ 0\ 0]$ direction is perpendicular to the $(1\ 0\ 0)$ plane; the $[1\ 1\ 1]$ direction perpendicular to the $(1\ 1\ 1)$ plane. Of course one should remember that the indices have a significance only in terms of atom positions and we should speak of direction indices from one atom to another and so also of planes passing through definite atoms. In this way we can talk about the interplanar spacing between two nearest parallel planes. As the planes are parallel they have the same set of Miller indices, say h , k and l . Then the interplanar distance between neighbouring planes is given by:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \dots (3.6)$$

In this equation, a is the cubic cell parameter also called the **lattice constant**. We shall see, later in this unit how this equation helps us to determine the crystal structure using X-ray diffraction.

3.3 CRYSTAL STRUCTURES OF METALS'

As was seen in Unit 2, the bonding in metals is such that the metal atoms are stripped of their electrons and the solid is really an arrangement of metal ions bonded together by a sea of free electrons. We can write the equation for the potential energy of the metallic bond as a sum of an attractive and repulsive term in a manner similar to that worked out

earlier for the case of the ionic bond. The major difference in our picture would stem from the fact that as the electrons overlap there is a strong part of energy arising from this overlap and the metallic bond is also considered to be predominantly covalent. Unlike the covalent bond, however, the metallic bond is not directional and so each ion would like to have as many ion neighbours as possible. This leads to metals having crystal structures that represent a densely packed arrangement of ions. We will now discuss these close-packed structures.

3.3.1 Close-packed Structures

Metals are characterised by high densities and so prefer the densely packed crystal structures. Most metals crystallise upon solidification from the melt into the BCC, FCC and HCP structures. The HCP lattice is shown in Figure 3.5.

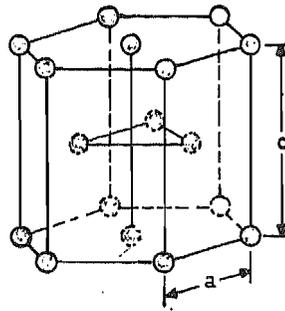


Figure 3.5 : Hexagonal Close-packed Structure

We have seen that these structures have large packing fractions. The BCC structure contains two atoms per cubic unit cell and these have positions $(0,0,0)$ and $(1/2, 1/2, 1/2)$. The FCC structure has four atoms per cubic unit cell and these positions are $(0,0,0)$, $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$. The HCP structure is really a variation of the FCC structure and has the same packing density.

SAQ 5

Given that the density of aluminium is 2.70 mg/m^3 , its atomic weight is 26.98 and its FCC lattice parameter is 405 pm, determine the number of atoms in a unit cell volume.

3.3.2 Concept of Atomic Radius

The PFs were worked out assuming the atoms to be incompressible spheres. We can consider the atomic size as the radius which would occupy a spherical volume equal to that of the unit cell. For the BCC structure this can be easily worked out as $4R = \sqrt{3} a$; R is defined as the atomic radius for the metallic element. Some values for selected metals are given in Table 3.2.

Table 3.2 : Some Metals which Possess the BCC Crystal Structure at Room Temperature ; their Lattice Constant, Atomic Radius and Melting Point

Metal	Lattice Constant (a , pm)	Atomic Radius (R^* , pm)	Melting Point ($^{\circ}\text{C}$)
Chromium	289	126	1875
Iron	287	124	1525
Molybdenum	315	136	2610
Potassium	533	231	63.9
Sodium	429	186	97.8
Tantalum	330	143	2996
Tungsten	316	137	3410
Vanadium	304	132	1900

*The atomic radius R is calculated using equation $4R = \sqrt{3} a$.

A similar calculation can be done for metals which exhibit the FCC structure at room temperature. Some representative values are given in Table 3.3 for selected metal elements.

Table 3.3 : Selected Metals which Possess the FCC Structure at Room Temperature ; the Lattice Constant, Atomic Radius and Melting Point for the Elements

Metal	Lattice Constant (a , pm)	Atomic Radius (R^* , pm)	Melting Point (in $^{\circ}\text{C}$)
Aluminium	405	143	660
Copper	361	128	1083
Gold	408	144	1063
Iridium	384	135	2454
Lead	495	175	327
Nickel	352	125	1453
Platinum	392	139	1769
Silver	409	144	961

*The atomic radius R is calculated using equation $4R = \sqrt{3} a$.

We now ask ourselves the question whether we can alloy one metal with any other metal. Specifically we would like to know whether lead and nickel (that is two metals with widely varying atomic radii) would form a solid solution. Also whether a FCC metal would alloy with a BCC metal. Some of these questions are addressed in the next section.

3.3.3 Solid Solutions

An alloy, or more specifically a metal alloy is a mixture of two or more metals or of a metal and a non-metal. A common example of a metal alloy is brass which is typically 70% Cu mixed with 30% Zn. The magnetic alloy named Alnico V is 8% Al, 14% Ni, 24% Co, 3% Cu and 51% Fe. A solid solution is a simple type of alloy and consists of two or more elements atomically dispersed in a single phase structure. The major constituent is called the parent element and the minor constituent the solute. In general there are two types of solid solutions: substitutional and interstitial.

In a substitutional solid solution, a solute atom replaces or substitutes for a solvent atom of the parent element. The crystal structure of the parent element is unchanged. However, the lattice may be slightly distorted to accommodate the solute atom, particularly if there is a difference in the radius of the solute and solvent atoms. The solid solubility or the extent to which one atom can replace the other can range from a fraction of a percent to 100%. For extensive solid solubility the conditions that need to be satisfied are :

- 1) The radii of the atoms of the alloying elements must not differ by more than 15%.
- 2) The crystal structures of the two elements must be the same.
- 3) The electronegativities of the two elements should be nearly equal to prevent the formation of compounds.
- 4) The two elements should have the same valence.

Example 3.1

Cu and Ni show 100% solid solubility. This can be understood as follows. Both Cu and Ni have FCC structure. Their atomic radii differ by about 2%. Their electronegativities are the same. Hence all conditions favour extensive solid solubility.

Cu and Pb show little solid solubility (a maximum of 0.1%). Both are FCC. However their radii differ by 37%. Electronegativity difference is 0.2. Conditions do not favour solid solubility.

In an interstitial solid solution, the solute atom fits into the spaces between the parent atoms. These spaces are called interstices. Such solid solutions would be possible only when the solute atoms are much smaller than the solvent atoms. Solute atoms are commonly H, C, N and O. A common example of such a solid solution is carbon in the FCC phase of iron or γ -iron. The atomic radius of FCC iron is 129 pm and that for C is 75 pm. There is a radius difference of $(129 - 75)/125$ or 42%. However, in spite of this large difference about 2% of C can dissolve in FCC iron.

3.3.4 Polymorphism or Allotropy

In nature, many elements and compounds exist in different crystalline forms at different temperatures. This phenomenon is termed as **polymorphism** or **allotropy**. Many industrially significant metals show allotropic transformation at high temperatures. Some selected cases are listed in Table 3.4.

Table 3.4 : Allotropic Forms of Some Metals

Metal	Room Temp. Crystal Structure	Transformation
Ca	FCC	BCC(> 447°C)
Co	HCP	FCC(> 427°C)
Fe	BCC	FCC(> 912°C) BCC(>1394°C)
Li	BCC	HCP(<-193°C)
Na	BCC	HCP(<-233°C)
Ti	HCP	BCC(>883°C)
Y	HCP	BCC(>1481°C)
Zr	HCP	BCC(>872°C)

SAQ 6

Calculate the volume change accompanying a polymorphic transformation from FCC to BCC crystal structure, assuming that the atomic radius does not change.

3.4 CERAMIC CRYSTAL STRUCTURES

Let us now take a look at some ceramic materials and the crystal structures they possess. Amongst the simplest ceramic compounds are those that have one cation to one anion, such as MgO, BeO, ZnO etc. We have chosen oxide ceramics just because they are simple as well as because they tend to be preferred in applications as they are not very susceptible to environmental degradation. A convenient way to look at the crystal structure of these compounds is to consider the lattice formed by the anions (remember that they are the larger ions), and try to fit the cations in the available spaces in the structure. A most often encountered arrangement of the anions is the FCC structure. In this structure we can find sites which can be four-fold or six-fold co-ordinated. Let us first take the six-fold coordination of the cations as seen in the sodium chloride crystal structure.

3.4.1 Sodium Chloride Crystal Structure

As mentioned above, first let us consider the lattice formed by the chlorine ions. This is a FCC lattice. Consider one ion to be in the position (0, 0, 0), then the near neighbours are in positions (1/2, 1/2, 0). The next near neighbours are in (1, 0, 0). Now if the sodium ions are placed in the (1/2, 0, 0), then each chlorine ion would have six sodium neighbours and every sodium ion would also have six chlorine neighbours. This would make up the sodium chloride or rock salt crystal structure as shown in Figure 3.6.

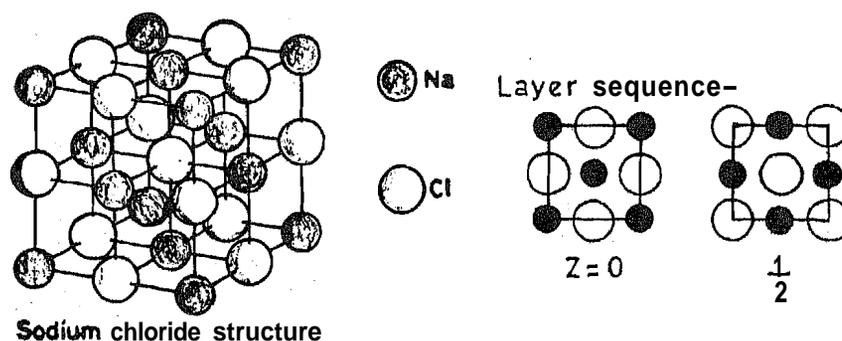


Figure 3.6 : Sodium Chloride or Rock Salt Structure

Examples of ceramics with the rock salt structure are: MgO, FeO, CaO, SrO, BaO, NiO etc. Recalling the rules about the radius ratios, this structure would be stable when (i) the cation to anion radius ratio lies between 0.732 and 0.414 and (ii) when the cation and anion have the same charge.

SAQ 7

Determine the radius ratios of the cations for CaO, MnO and CsCl. Hence predict the crystal structure possible.

The other possibility in the FCC arrangement of cations is when the cation is put in the interstitial position (1/4, 1/4, 1/4). This would make every cation have four anion neighbours and every anion have four cation neighbours, as shown in Figure 3.7.

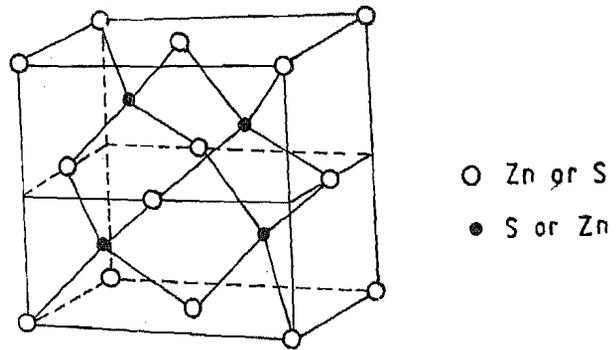


Figure 3.7 : Sphalerite or Zincblende (ZnS) Cubic Close-packed Structure, Lattice Constant $a = 540.93 \text{ pm}$ (5.4093 Å)

Such a structure is called the zinc blende structure and examples are ZnS, BeO, SiC etc. (Note: Not all the cation sites are occupied. In the rock salt structure all the cation sites are occupied but in the zinc blende structure only half the cation sites are occupied. If the cation and anion are the same then this gives us the diamond structure.) We shall see later that this structure has important contributions to the field of semiconductors.

3.4.2 Perovskite Crystal Structure

This is another important type of crystal structure and is named after the mineral perovskite, which has the chemical formula CaTiO_3 . In this structure, the Ca^{2+} and O^{2-} ions combine to form the FCC structure and the tetravalent titanium ions occupy the octahedral interstices. The structure is shown in Figure 3.8.

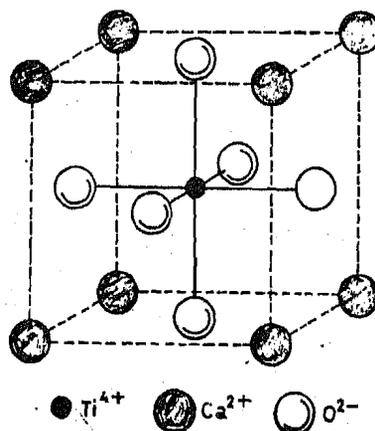


Figure 3.8 : Perovskite Structure

As can be seen, each oxygen is surrounded by four Ca^{2+} and eight O^{2-} ions, i.e. 12 near neighbours as in the FCC lattice. The Ti^{4+} ions occupy the centre of the FCC cell. Each unit cell would then contain one Ca^{2+} , one Ti^{4+} and three O^{2-} ions exactly as in one formula unit. The CN for Ti^{4+} is 6 while that for Ca^{2+} is 12. The most important compound in this class is barium titanate, BaTiO_3 . Other examples are PbZrO_3 , KNbO_3 , YAlO_3 etc.

SAQ 8

Refer to the ionic radii table in the previous Unit and determine the density of NaCl crystal.

SAQ 9

Assuming that the bonding in BaTiO_3 is completely ionic, and that the lattice parameter is determined by the $\text{O}-\text{Ti}-\text{O}$ distance, calculate the density of the ceramic. Compare the value obtained from the calculation with the experimental value of 6.0 mg/m^3 .

3.4.3 Spinel Crystal Structure

This crystal structure has gained in importance due to the development of magnetic insulators, the ferrites. The structure is named after the semi-precious stone spinel which has the chemical formula of MgAl_2O_4 . Here again the oxygen ions form a FCC lattice. The cations, however, occupy, partially, both the types of interstices discussed above, viz. the tetrahedral and octahedral interstices. The oxygen ions have a CN of 4, while the cations have CN of both 4 and 6. Note that for charge balance, the cations have different valence states. If the divalent ion occupies the tetrahedral site, the spinel structure is called normal. If the tetrahedral sites are filled up by trivalent ions and the remaining trivalent and the divalent ions occupy the octahedral site, the structure is called inverse. Many divalent ions have a tendency to occupy both the sites. Such spinels are called random spinels. Examples of spinels are: Magnesium ferrite and copper ferrite are random; nickel ferrite and ferrous ferrite are inverse; zinc ferrite and cadmium ferrites are normal. We will see in a later unit how these structures give a good explanation of the magnetic properties in ferrites.

The crystal structure is quite complex and a part of it is shown in Figure 3.9. It is convenient to consider the unit cell to be cubic; however each cubic unit cell contains eight

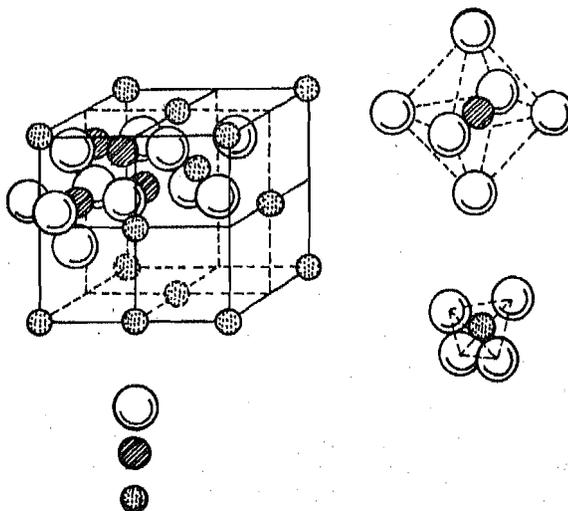


Figure 3.9 : Spinel Crystal Structure

formula units or 56 ions. In each cubic unit cell, 16 of the 32 octahedral sites (also called B sites) are occupied; and of the 64 tetrahedral sites (also called A sites) only eight are occupied. The ions that can occupy the sites can be worked out using the radius ratio rules. Trivalent Fe and Mn can easily replace Al in the structure and the iron containing spinels are normally called as ferrites, while the manganese spinels are called manganites. Divalent Zn, Mn, Fe, Cu etc., are often used to replace the divalent Mg. The divalent ion gives the compound its name. Thus NiFe_2O_4 is called nickel ferrite while CuMn_2O_4 is called copper manganite. The oldest magnetic material known to mankind, the lodestone is really Fe_3O_4 which is really the ferrous ferrite $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$.

As there are cations with two valence states, the spinel structure has led to the possibility of materials with very widely differing conductivity. This aspect, along with the fact that the structure also incorporates magnetic ions, has increased its technological importance.

SAQ 10

Distinguish between the normal and inverse spinel structure. Can a compound show either of these structures?

Many ionic substitutions have been tried out both in the perovskite and spinel ceramics. It is important to know the site occupancies of the ions and their valencies as then one can reasonably predict the properties. Of course, one assumes that in the substitutions, the overall symmetry of the structure is maintained. Let us see how we can determine the crystal structures of the materials.

3.5 CRYSTAL STRUCTURE DETERMINATION

To determine crystal structures we would need a probe which would be able to interact with the features in the crystal; that is it should "see" either the discreteness of mass or charge or magnetic moment. It should also have a wavelength which has the order of magnitude of or is lesser than the distance between atoms. A very common method of crystal structure determination is the method of X-ray diffraction. We now understand the principle behind this method.

3.5.1 Principle of X-ray Diffraction

Our present knowledge of crystal structures is an offshoot of the X-ray diffraction techniques in which we utilise rays having a wavelength approximately equal to the distance between the planes of atoms in a crystal. Such X-rays are produced when an accelerated beam of electrons strikes a metal target as shown in Figure 3.10.

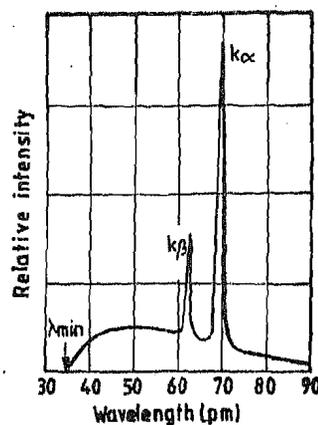


Figure 3.10 : The Distribution by Wavelength of the X-rays Produced when 35-keV Electrons Strike a Molybdenum Target. Note the Sharp Peaks Standing out above a Continuous Background. (1 pm = 10^{-12} m)

The X-rays emitted have a continuous range of wavelengths with sharp peaks corresponding to characteristic electron transitions in the inner shell of the metal atoms.

The white radiation and characteristic peaks are schematically shown in Figure 3.10. By using appropriate filters a monochromatic (i.e. single wavelength) beam of X-rays can be made to fall on a crystal. Common X-ray sources and their wavelengths are given in Table 3.5.

Table 3.5: Commonly Used X-ray Targets and their Wavelengths

Metal (target)	Transition	Wavelength (in pm)
Vanadium Copper Iron Molybdenum Tungsten	$K\alpha$ $K\alpha$	154.4

The principle of X-ray diffraction can be understood with the help of Figure 3.11.

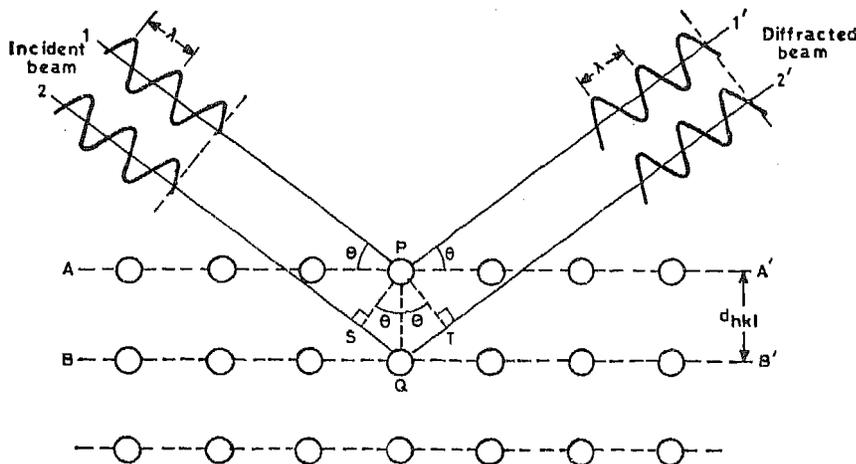


Figure 3.11 : X-ray Diffraction

Consider a monochromatic beam of X-rays to be incident on a crystal, whose lattice planes are spaced a distance d apart. Assume that the X-ray beam makes an angle θ with the lattice plane. For constructive interference to take place then the wave reflected from the first plane should have the same phase as that reflected from the second plane. This condition gives that the path difference between the two waves should be an integral multiple of the wavelength or:

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

This is the well-known Bragg law. The integer n is the order of diffraction and is usually taken as unity. By measuring θ , one can determine the value of d . Note that for the condition to be satisfied, λ should always be smaller than d .

3.5.2 Determination of Cubic Structures

The distance between (1 0 0) planes is different from that between say (1 1 1) planes. Hence d is a function of the Miller indices. For a cubic crystal whose lattice parameter is a , we have:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

as discussed above. As h, k or l can take only integral values, from a set of d values we can easily determine the value of a .

A convenient XRD technique is to employ powder samples to study diffraction. In the powder, as the crystallites are randomly oriented in space there would always be some particle for which the diffraction condition would be satisfied so that X-rays would be diffracted at that angle. By measuring the intensity of the diffracted beam as a function of

the angle of incidence, one can get a set of d values from which a is calculated. Each diffracted line is indexed according to the Miller indices. A representative XRD pattern is shown in Figure 3.12.

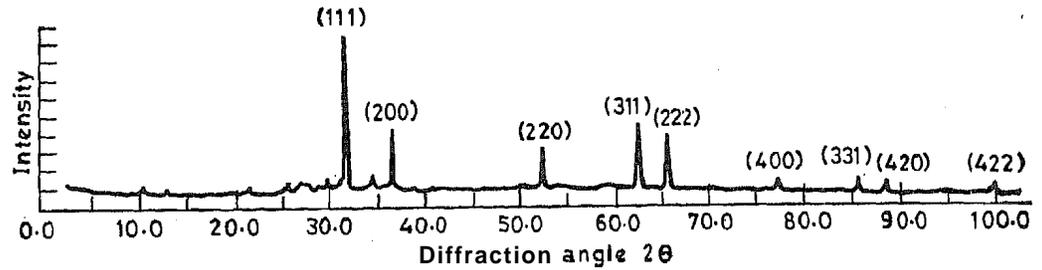


Figure 3.12: XRD Pattern

For cubic crystals, in addition to the value of the lattice parameter, the diffraction pattern contains more information. There are separate rules for the values that h, k, l can take for a simple cubic, BCC or FCC lattice. These are given in the Table 3.6.

Table 3.6: Rules for XRD Lines in Cubic Crystals

Bravais Lattice	Reflections Present	Reflections Absent
Simple Cubic	All values of h, k, l	nil
BCC	$(h + k + l) = \text{even}$	$(h + k + l) = \text{odd}$
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

The first three diffraction lines for a simple cubic lattice would be $(1, 0, 0)$, $(1, 1, 0)$ and $(1, 1, 1)$; for BCC they would be $(1, 1, 0)$, $(2, 0, 0)$ and $(2, 1, 1)$ while that for the FCC lattice would be $(1, 1, 1)$, $(2, 0, 0)$ and $(2, 2, 0)$.

SAQ 11

Determine the ratios of the $\sin^2 \theta$ values for the first two lines in a BCC lattice. What would this ratio be for a FCC lattice?

We have seen that by using the X-ray powder diffraction method, we can map the positions of the ions and determine the unit cell, or the repeating structure in the lattice. This has been possible by determining the d values for the diffracting planes. If we have a sufficiently large number of d values, we can also identify the element or the compound under investigation. Presence of another phase in the material is easily shown up as d values that do not conform to the structure. Hence, it is possible for us to determine whether or not complete reaction has taken place in a solid state reaction. For example, it is customary to add one mole of nickel oxide to one mole of ferric oxide when one is planning to make nickel ferrite. The mixture is thoroughly mixed, on a near atomic scale and the mixture heat-treated at temperatures about 1400 to 1600 K when, by a solid state reaction, called sintering, the ferrite gets formed. One can study the rate of formation by taking the X-ray diffraction pattern of the heat-treated powder after definite time intervals. One would see the gradual disappearance of a peak corresponding to Fe_2O_3 . Once this peak disappears, one can assume that the full reaction has taken place.

Powder XRD is a powerful technique which is used most frequently whenever new materials are to be made. Standard powder diffraction data is available in files and forms a useful data for comparison. Many a times one determines the extent of solid solution formation by studying the systematic variation in the lattice parameter as obtained from XRD. According to Vegard's Law, the lattice parameter of two completely miscible solids (or compounds), varies in proportion to the amounts of the solute added.

Though the XRD technique is versatile, there are a few difficulties. One is that the concentration of a phase that is detectable by XRD should be at least 5%. For lighter elements, the concentration should be larger, for heavier elements it can be smaller. Also, the valence state of the ion cannot be determined using XRD. Therefore, differences in magnetic properties of the ions cannot be studied. XRD is also not very sensitive to coordination number and so it is difficult to determine the cation distribution. Some recent studies have opened this possibility in some definite structures by studying the intensity of the lines but the information is not unique. Hence one needs some other method to study solids in terms of these aspects. Let us see some other methods of crystal structure determination.

3.5.3 Neutron and Electron Diffraction

Bragg's law gave us the condition for diffraction of waves by a crystal. Planes in the crystal reflect the waves and these are constructively reinforced if the wavelength and planar spacing satisfy the Bragg law. We know that, according to the de Broglie relation, a particle with momentum p will have a wavelength $\lambda = h/p$. We can therefore use any particle which has the correct wavelength. If we use neutrons with energy E the associated wavelength can be easily worked out as:

$$\lambda = \frac{h}{(2mE)^{1/2}}$$

For neutrons $m = 1.675 \times 10^{-27}$ kg. This would give λ (in pm) = $28.6/(E)^{1/2}$, with E expressed in eV. To get $\lambda = 200$ pm, we would need neutrons of energy 0.02 eV. This is of the order of energy that a particle would have at thermal equilibrium at room temperature. (Note: At 300 K the thermal energy of a particle is $k_B T$, which is 0.259 eV.) Higher the energy, lower the wavelength. In a nuclear reactor, neutrons of this energy are called thermal neutrons and are the ones used for diffraction studies.

Neutron diffraction, though similar in some ways to XRD, has some major differences.

First, the energies involved are different; X-rays having wavelength of 100 pm have an energy of 10^4 eV, neutrons on the other hand have energy of 10^{-1} eV.

Second, the scattering of X-rays becomes more predominant as the atomic number increases; the scattering of neutrons depends on the nuclear structure and not on the atomic number. Neutrons are therefore preferred for studying crystals of lighter elements.

Third, X-rays cannot see the difference in isotopes (atoms with same atomic number but different mass number) or in the valence state; neutrons distinguish easily between isotopes and between ions with different magnetic moments (and therefore different valence states).

In the case of electrons, as the mass is much smaller than that in neutrons, the wavelength calculation gives λ (in pm) = $122.7/E^{1/2}$, where E is expressed in keV (Note: 1 keV = 1000 eV). To get electrons of $\lambda = 100$ pm, they would need an energy of 1.5 keV. These energies are obtained by accelerating electrons in an electric field as is done in electron microscopes.

One should remember that for diffraction one uses a monochromatic beam. To get single wavelength beams of neutrons or electrons is not easy. Neutrons are often reflected by a crystal and a narrow scattered beam at the appropriate angle is taken to the diffraction chamber. Electrons with the same wavelength can be obtained by using appropriate magnetic fields. The other point to remember is that the diffracted beam intensity has to be measured, this is done by counting the particles (neutrons or electrons) using particle counters.

3.5.4 Other Methods

We have seen how crystal structural features are obtained using diffraction techniques. The powder technique relied on the fact that there would always be some plane in the crystal which would satisfy the Bragg law for any angle. Now if the material under study was a single crystal, Bragg law would be satisfied only for certain angles. Special techniques are needed to study single crystals. First the crystal has to be properly oriented and that is not easy. The crystal is mounted on a goniometer, a device by which the crystal can be rotated in any direction by minute amounts. The monochromatic beam is made to be incident and the diffracted beam observed usually as a photographic record. The

diffracted pattern consists of spots called Laue spots and from the position of the spots the crystal structure is worked out. Sometimes the crystal is rocked about a small angle. The spots then get smeared as lines. The line spacing is used to determine the lattice parameter.

What happens if the material under study has no crystalline order and is amorphous? Well, in this case there would be no well defined peaks in the diffractogram. Generally, however, an amorphous material may not have a periodicity in the strict sense, but it does have an average distance between atoms which varies from a minimum to a maximum. Around this average lattice parameter, there would then be a broad maximum in the XRD pattern. The absence of sharp peaks shows the amorphous nature of this alloy when it is rapidly cooled from the melt. In highly crystalline materials the XRD peaks are very sharp. As the material ordering changes from single crystalline to polycrystalline, the sharpness of the peaks does not change as long as the grain size of the material is sufficiently large. However, as the grain size becomes finer, usually less than a micrometer, some broadening of the XRD lines can be seen. It is possible to estimate the grain size in fine-grained materials or nano-crystalline materials by determining the broadening of the XRD lines. A broad background maximum is an indication of the presence of an amorphous phase. In complex materials, there is a superposition of a broad peak and some sharp characteristic lines. By determining the area under the peaks, one may estimate the amount of amorphous to crystalline phase. But this has to be done with some care.

3.6 SUMMARY

In this unit we have seen that atoms are arranged in crystalline solids in a manner that can be described by a network of lines called a space lattice. Each space lattice can be described by specifying the position of atoms in a repeating unit called the unit cell. There are 14 Bravais Lattices in which a unit cell can be described which contains only one atom per unit cell.

In metals the most common crystal structures are the body-centred-cubic, face-centred-cubic and the hexagonal-close-packed structures. The HCP structure is not a Bravais lattice. These structures give a natural explanation for the high density seen in metals. They are also a reflection of the nature of the metallic bond which is non-directional and so the solid would like to have atoms in as high a coordination number as possible. This is because each bond reduces the lattice energy and the more the number of bonds the stronger the solid.

Crystal directions in solids are represented as $[u\ v\ w]$ and the numbers u , v and w are vector components along each component axis but reduced to the smallest integers. Families of directions are enclosed by pointed brackets such as $\langle w \rangle$. Crystal planes are indexed by the reciprocals of the axial intercepts of the plane, followed by the elimination of fractions. In cubic systems these are given as (hkl) and cubic crystal planes belonging to the same family are shown as $\{hkl\}$.

Using the hard sphere approximation for a solid, we calculated the packing fractions for some cubic structures. Some metals showed different structures at different temperatures, a phenomenon called polymorphism.

We also discussed some common ceramic structures such as the spinel and perovskite structures. In each case the unit cell was fairly complicated and contained many atoms per unit cell.

Lastly we saw that crystal structures could be determined by powder diffraction techniques. Though X-rays were the incident radiation that was most frequently used we also saw that electron and neutron diffraction could be used advantageously in some situations,

3.7 KEY WORDS

Atomic Packing Fraction	:	The fraction of actual space occupied by the atoms assuming them to be hard spheres.
Crystal	:	A solid composed of atoms or ions arranged in a pattern that is repeated in three dimensions.

- Crystal Structure : A **regular** pattern of atoms or ions in space. This pattern embodies symmetry elements such as rotation axis and **mirror** plane and a repeating **distance** (translational symmetry) in three dimensions.
- Lattice Point : One point in the array of points (lattice) representing the position of an atom. Every lattice point in the array is identical to every other, i.e. it has the same surroundings.
- Miller** Indices : Integers which specify **planes** in a crystal. They are derived by taking the reciprocals of the axial intercepts and clearing the fractions if **any**.
- Polymorphism : In metals it is **the** ability of a metal to exist in **two** or more crystal structures at a different **temperatures**.
- Space Lattice : Three-dimensional array of points such that each point has identical surroundings.
- Unit Cell : A convenient repeating unit of a space lattice. A lattice may be represented by more than one such cell. A unit cell containing only one atom is called a primitive unit cell.

3.8 ANSWERS TO SAQs

SAQ 1

The APF is defined as the fraction of solid sphere volume in a unit cell or

$$\text{APF} = \frac{\text{total sphere volume}}{\text{total unit cell volume}} = \frac{V_s}{V_c}$$

Both the total sphere and unit cell volumes may be calculated in **terms** of the atomic radius R . The volume of a sphere is $\frac{4}{3}\pi R^3$ and since there are **two** atoms per BCC unit cell, the total BCC sphere volume is

$$V_s = 2 \times \frac{4}{3}\pi R^3 = \frac{8}{3}\pi R^3$$

If the radius of the atom is R , then we can see that for BCC

$$(4R)^2 = a^2 + a^2 + a^2 = 3a^2$$

or, $R = \frac{\sqrt{3} a}{4}$

Total unit cell volume is

$$V_c = \left(\frac{4R}{\sqrt{3}}\right)^3$$

Therefore, the **atomic** packing factor is

$$\text{AFP} = \frac{V_s}{V_c} = \frac{\frac{8}{3}\pi R^3}{\left(\frac{4R}{\sqrt{3}}\right)^3} = 0.68 \text{ or } 68\%$$

SAQ 2

Check answers with respective preceding text.

SAQ 3**Body-centered Cubic Crystal**

The atom at the centre of the unit cell of BCC completely belongs to that unit cell. Therefore, effective number of atoms per unit cell of body-centered cubic crystal

$$= 8 \times \frac{1}{8} + 1 = 1 + 1 = 2 \text{ atoms}$$

Face-centered Cubic Crystal

The atom at the centre of the face of a cell can be shared by only two unit cells. Therefore, effective number of atoms per unit cell of face-centered cubic crystal

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4 \text{ atoms}$$

SAQ 4

Check answers with respective preceding text.

SAQ 5

In 26.98 kg there are 6.02×10^{26} atoms; 2700 kg occupy 1 m^3 . Therefore, in 1 m^3 there are 6×10^{28} atoms. In a volume of $(4.05 \times 10^{-10})^3$ there would be $6 \times (4.05)^3 \times 10^{-2}$ atoms; or 4 atoms.

SAQ 6

The volume per atom in the FCC structure is $V_{\text{FCC}} = a^{3/4} = 5.66 R^3$. Similarly, the volume per atom in the BCC structure is $V_{\text{BCC}} = a^{3/2} = 6.16 R^3$. The percentage change in volume is then:

$$\frac{6.16 R^3 - 5.66 R^3}{5.66 R^3} = 0.088 \text{ or } +8.8\%$$

The plus sign signifying an increase in the volume.

SAQ 7 to 11

Check answers with respective preceding text.