1. Module I.

1.1 Historical Perspective

The material possessions of our earliest ancestors were probably their tools and weapons. In fact, the most popular way of naming the era of early human civilization is in terms of the materials from which these tools and weapons were made. The Stone Age has been traced as far back as 2.5 million years ago when human ancestors, or hominids, chipped stones to form weapons for hunting. The Bronze Age roughly spanned the period from 2000 B.C. to 1000 B.C. and represents the foundation of metallurgy, in which alloys of copper and tin were discovered to produce superior tools and weapons. (An alloy is a metal composed of more than one element.)

Contemporary archaeologists note that an earlier but less well known "Copper Age" existed between roughly 4000 B.C. to 3000 B.C. in Europe, in which relatively pure copper was used before tin became available. The limited utility of those copper products provided an early lesson in the importance of proper alloy additions. The Iron Age defines the period from 1000 B.C. to 1 B.C.

By 500 B.C., iron alloys had largely replaced bronze for tool and weapon making in Europe (Figure 1.1). Although archaeologists do not refer to a "pottery age," the presence of domestic vessels made from baked clay has provided some of the best descriptions of human cultures for thousands of years. Similarly, glass artifacts have been traced back to 4000 B.C. in Mesopotamia.
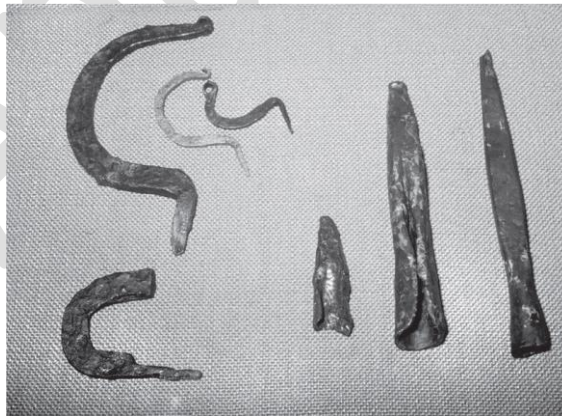

Fig. 1.1 Celtic Iron Age tools from 1st century B.C.

Modern culture in the second half of the 20th century is sometimes referred to as "plastic," a not entirely complimentary reference to the lightweight and economical polymeric materials from which so many products are made. Some observers have suggested instead that this same time frame should be labeled the "silicon age," given the pervasive impact of modern electronics largely based on silicon technology.

1.2 Importance of Materials

Why do we study materials? Many engineers, whether mechanical, computer, civil, chemical, or electrical, at one time or another are exposed to a design problem involving materials, such as a transmission gear, the superstructure for a building, an oil refinery component, or an integrated circuit chip. Of course, materials scientists and engineers are specialists who are totally involved in the investigation and design of materials.

Many times, a materials problem is one of selecting the right material from the thousands available. The final decision is normally based on several criteria. First, the in-service conditions must be characterized, for these dictate the properties required of the material. On only rare occasions does a material possess the maximum or ideal combination of properties. Thus, it may be necessary to trade one characteristic for another. The classic example involves strength and ductility; normally, a material having a high strength has only a limited ductility. In such cases, a reasonable compromise between two or more properties may be necessary.

A second selection consideration is any deterioration of material properties that may occur during service operation. For example, significant reductions in mechanical strength may result from exposure to elevated temperatures or corrosive environments. Finally, probably the overriding consideration is that of economics: What will the finished product cost? A material may be found that has the ideal set of properties but is prohibitively expensive. Here again, some compromise is inevitable. The cost of a finished piece also includes any expense incurred during fabrication to produce the desired shape.

The more familiar an engineer or scientist is with the various characteristics and structure–property relationships, as well as the processing techniques of materials, the more proficient and confident he or she will be in making judicious materials choices based on these criteria.
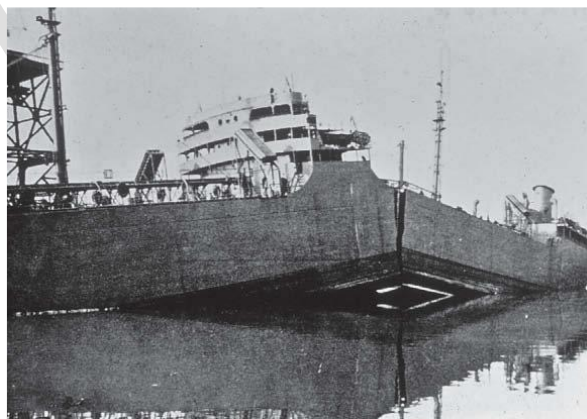

Fig. 1.2 Liberty ship S.S. Schenectady, which, in 1943, failed before leaving the shipyard.

1.3 Fundamentals of crystal structure

Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another. A crystalline material is one in which the atoms are situated in a repeating or periodic array over large atomic distances—that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest neighbor atoms. All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; these are called non-crystalline or amorphous materials.

Some of the properties of crystalline solids depend on the crystal structure of the material, the manner in which atoms, ions, or molecules are spatially arranged. There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials.

Crystal lattice

The crystal lattice is the symmetrical three-dimensional structural arrangements of atoms, ions or molecules (constituent particle) inside a crystalline solid as points. It can be defined as the geometrical arrangement of the atoms, ions or molecules of the crystalline solid as points in space.

Unit Cell

A unit cell is the smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire crystal. A crystal can be thought of as the same unit cell repeated over and over in three dimensions. The Figure below illustrates the relationship of a unit cell to the entire crystal lattice.
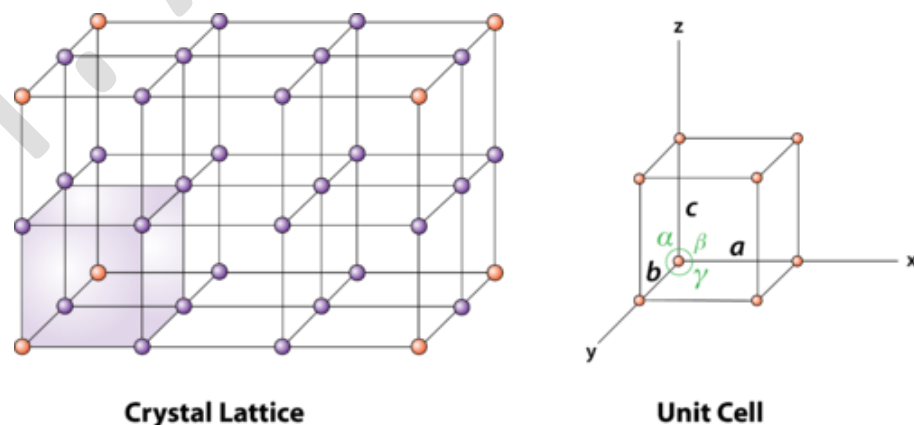

Fig. 1.3 Crystal Lattice and Unit Cell

1.3 Crystal Systems

The space lattice of a crystal is described by means of a 3-dimensional co-ordinate system in which the coordinate axes coincides with any three edges of the crystal intersecting at one point. To describe the basic crystal structure seven different coordinate system of reference axes are required as shown in Fig. 1.4.
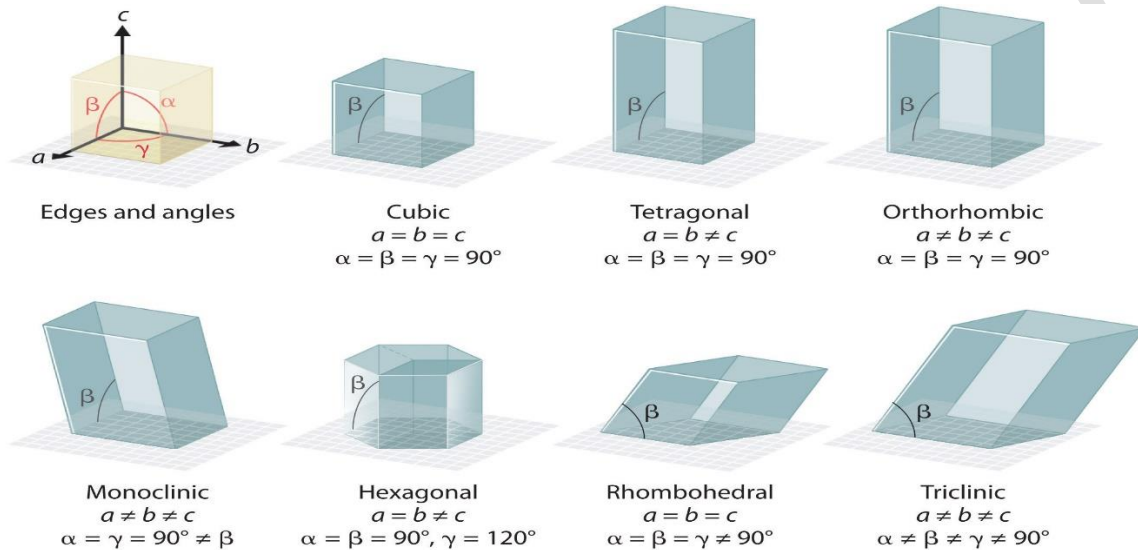

Fig. 1.4 Basic crystal systems

1.4 Simple Cubic Unit Cell

In the primitive cubic unit cell, the atoms are present only at the corners. Every atom at the corner is shared among 8 adjacent unit cells. There are 4 unit cells in the same layer and 4 in the upper (or lower) layer. Therefore, a particular unit cell has the only 1/8th of an atom. Each small sphere in the following figure represents the centre of a particle that occupies that particular position and not its size. This structure is known as an *open structure*.
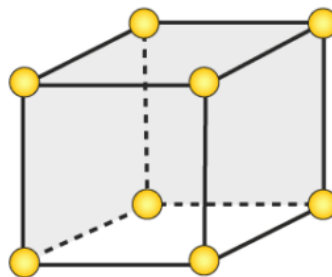

Fig. 1.5 Simple cubic or primitive unit cell

In each cubic unit cell, there are 8 atoms at the corners. Therefore, the total number of atoms in one unit cell is $8 \times 1/8 = $ **1 atom**.

1.5 Metallic crystal structures

Three relatively simple crystal structures are found for most of the common metals: face-centered cubic, body centered cubic, and hexagonal close-packed.

1. The Face-Centered Cubic Crystal Structure

The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces. It is aptly called the face-centered cubic (FCC) crystal structure. Some of the familiar metals having this crystal structure are copper, aluminum, silver, and gold. Figure 1.6 a shows a hard-sphere model for the FCC unit cell, whereas in Figure 1.6 b the atom centers are represented by small circles to provide a better perspective on atom positions. The aggregate of atoms in Figure 1.6 c represents a section of crystal consisting of many FCC unit cells.
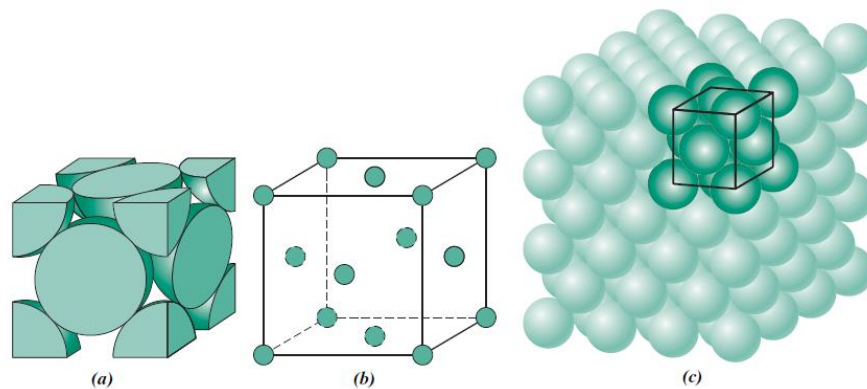

Fig. 1.6 The face-centered cubic crystal structure, (a) a hard-sphere unit cell representation, (b) a reduced sphere unit cell, and (c) an aggregate of many atoms.

Number of atoms in FCC unit cell

On occasion, we need to determine the number of atoms associated with each unit cell. Depending on an atom's location, it may be considered to be shared with adjacent unit cells—that is, only some fraction of the atom is assigned to a specific cell. For example, for cubic unit cells, an atom completely within the interior "belongs" to that unit cell, one at a cell face is shared with one other cell, and an atom residing at a corner is shared among eight. The number of atoms per unit cell, N, can be computed using the following formula:

$$N = N_i + \frac{N_f}{2} + \frac{N_C}{8} \quad 1.1$$

Where N_i are number of interior atoms, N_f are number of face atoms and N_c are number of corner atoms.

For the FCC crystal structure, there are eight corner atoms ($N_c = 8$), six face atoms ($N_f = 6$), and no interior atoms ($N_i = 0$). Thus, from Equation 1.1,

$$N = 0 + \frac{6}{2} + \frac{8}{8} = 4$$

or a total of four whole atoms may be assigned to a given unit cell. This is depicted in Figure 1.6a, where only sphere portions are represented within the confines of the cube. The cell is composed of the volume of the cube that is generated from the centers of the corner atoms, as shown in the figure.

Coordination Number

Coordination Number is defined as number of nearest-neighbor or touching atoms. For face-centered cubics, the coordination number is 12. This may be confirmed by examination of Figure 1.6a; the front face atom has four corner nearest-neighbor atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front (not shown).
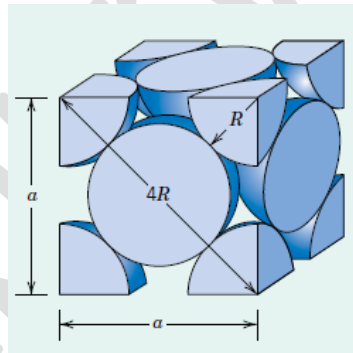
Determination of FCC atomic radius Unit Cell Volume

Fig. 1.7

In the FCC unit cell illustrated, the atoms touch one another across a face-diagonal, the length of which is 4R. Because the unit cell is a cube, its volume is a^3, where a is the cell edge length. From the right triangle on the face,

$$a^2 + a^2 = (4R)^2 \qquad\qquad 1.2$$

or, solving for a,

$$a = R\sqrt{2} \qquad\qquad 1.3$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \qquad 1.4$$

Atomic Packing Factor for FCC

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

$$Atomic\ Packing\ Factor = \frac{volume\ of\ atoms\ in\ a\ unit\ cell}{total\ unit\ cell\ volume} = \frac{V_S}{V_C} \qquad 1.5$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R. The volume for a sphere is $\frac{4}{3}\pi R^3$ and because there are four atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = (4)\frac{4}{3}\pi R^3 = \frac{16}{3}\pi R^3$$

Therefore, the atomic packing factor is

$$APF = \frac{V_S}{V_C} = \frac{\frac{16}{3}\pi R^3}{16R^3\sqrt{2}} = 0.74$$

2. The Body-Centered Cubic Crystal Structure

Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. This is called a body-centered cubic (BCC) crystal structure. A collection of spheres depicting this crystal structure is shown in Figure 1.8c, whereas Figures 1.8a and 1.8b are diagrams of BCC unit cells with the atoms represented by hard-sphere and reduced-sphere models, respectively.

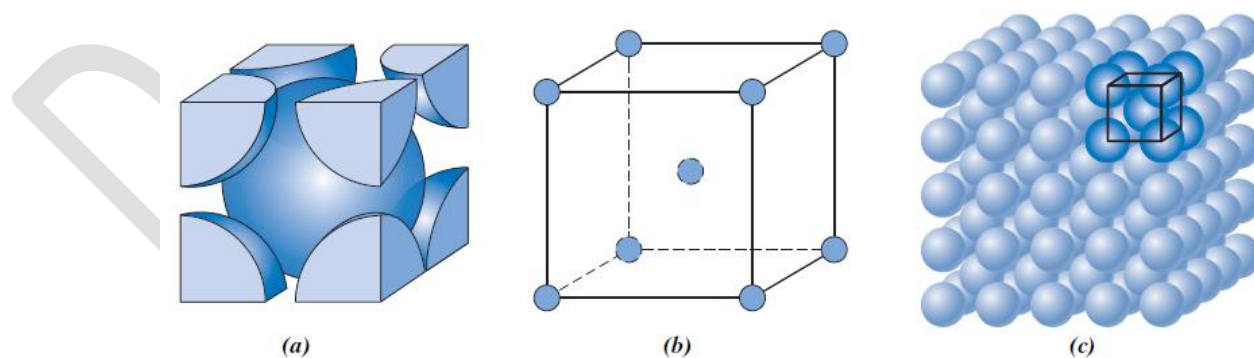
(a)   *(b)*   *(c)*

Fig. 1.8 The body-centered cubic crystal structure, (a) a hard-sphere unit cell representation, (b) a reduced sphere unit cell, and (c) an aggregate of many atoms.

Each BCC unit cell has eight corner atoms and a single center atom, which is wholly contained within its cell; therefore, from Equation 1.1, the number of atoms per BCC unit cell is

$$N = N_i + \frac{N_f}{2} + \frac{N_C}{8}$$

$$N = 1 + 0 + \frac{8}{8} = 2$$

The coordination number for the BCC crystal structure is 8; each center atom has as nearest neighbors its eight corner atoms.

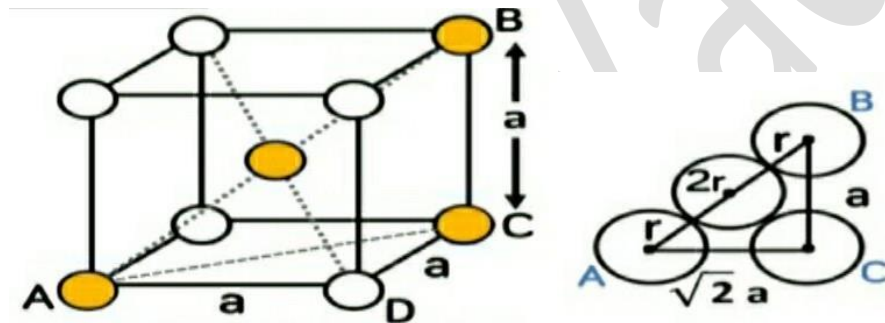**Determination of BCC atomic radius Unit Cell Volume**

Fig. 1.9

$$AB^2 = BC^2 + AC^2 \qquad 1.6$$

$$(4R)^2 = (a)^2 + (\sqrt{2}a)^2$$

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

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

$$4R = \sqrt{3a^2} = \sqrt{3}a$$

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

The BCC unit cell volume V_C may be computed from

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

Atomic Packing Factor for BCC

The number of atoms per BCC unit cell are 2, therefore, the atomic packing factor is

$$APF = \frac{V_S}{V_C} = \frac{(2)\frac{4}{3}\pi R^3}{\left(\frac{4}{\sqrt{3}}R\right)^3} = 0.68$$

3. The Hexagonal Close-Packed Crystal Structure

Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a unit cell that is hexagonal. Figure 1.10a shows a reduced sphere unit cell for this structure, which is termed hexagonal close-packed (HCP); an assemblage of several HCP unit cells is presented in Figure 1.10b. The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes.
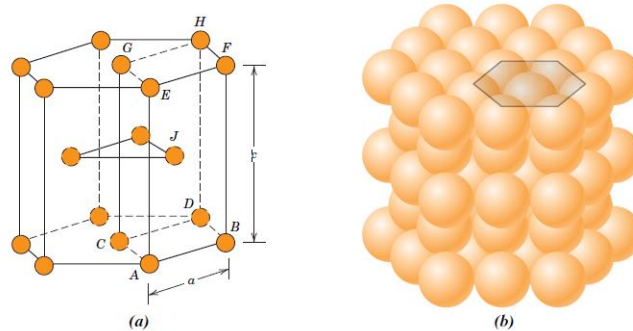

Fig. 1.10 the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell (a and c represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms.

If a and c represent, respectively, the short and long unit cell dimensions of Figure 3.4a, the c/a ratio should be 1.633; however, for some HCP metals, this ratio deviates from the ideal value.

Number of atoms in HCP

In order to compute the number of atoms per unit cell for the HCP crystal structure, Equation 1.12 is modified to read as follows:

$$N = N_i + \frac{N_f}{2} + \frac{N_C}{6} \qquad 1.7$$

That is, one-sixth of each corner atom is assigned to a unit cell (instead of 8 as with the cubic structure). Because for HCP there are 6 corner atoms in each of the top and bottom faces (for a total of 12 corner atoms), 2 face center atoms (one from each of the top and bottom faces), and 3 midplane interior atoms, the value of N for HCP is found, using Equation 1.7, to be

$$N = 3 + \frac{2}{2} + \frac{12}{6} = 6$$

Thus, 6 atoms are assigned to each unit cell.

The hexagonal prism has 3 equivalent unit cells (yellow, green and blue). Each prism 6 atoms/3 = 2 atoms per unit cell

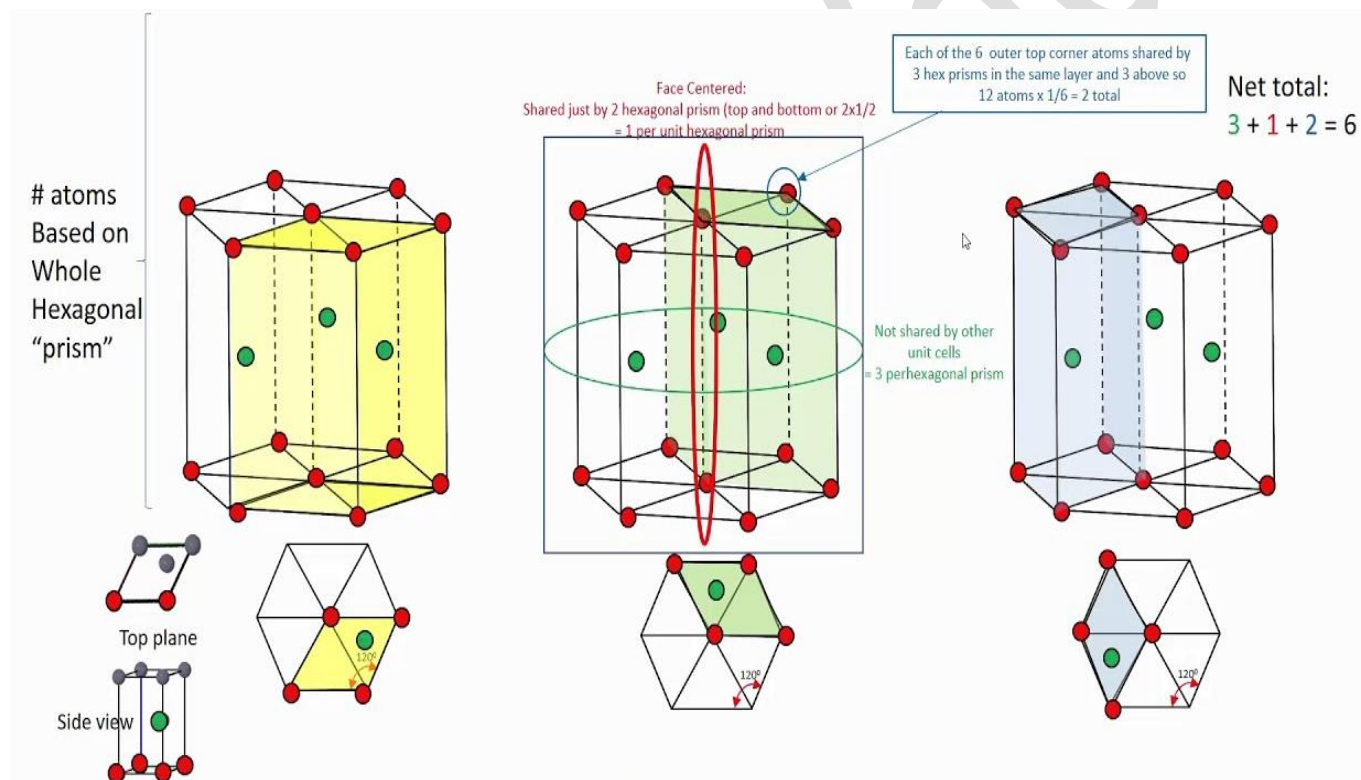Fig. 1.11 HCP as three unit cells

Volume of unit cell = Area of base × Height of the unit cell

The (HCP) is a hexagonal prism structure. The base of (HCP)is a hexagon. We know that the hexagon is made of the 6 equilateral triangles.

$$Area\ of\ equilateral\ traiangle = \frac{\sqrt{3}}{4}a^2$$

Therefore, the area of the base is given as,

$$Area\ of\ base = 6 \times \frac{\sqrt{3}}{4}a^2$$

Let's 'h' be the height of the hexagonal unit. Therefore we have,

$$\frac{h}{a} = \sqrt{\frac{8}{3}}$$

Now, substitute these values in the volume of (HCP) we have,

Volume of HCP = Area of base × height of the unit cell

$$Volume\ of\ HCP = 6 \times \frac{\sqrt{3}}{4}a^2 \times \sqrt{\frac{8}{3}}a$$

We know that the edge length 'a' is equal to twice the radius of the atom. That is,

$$a=2R$$

Substitute these values in the volume we get,

$$Volume\ of\ HCP = 6 \times \frac{\sqrt{3}}{4}a^2 \times \sqrt{\frac{8}{3}}a = 6 \times \frac{\sqrt{3}}{4}(2R)^2 \times \sqrt{\frac{8}{3}}(2R) = 24\sqrt{2}R^3$$

Therefore, the volume of the hexagonal close packing structure is

$$24\sqrt{2}R^3$$

Atomic Packing Factor for HCP

The number of atoms per HCP unit cell are 6, therefore, the atomic packing factor is

$$APF = \frac{V_S}{V_C} = \frac{(6)\frac{4}{3}\pi R^3}{24\sqrt{2}R^3} = \frac{1}{3} \times \frac{\pi}{\sqrt{2}} = 0.74$$

Density Computation

A knowledge of the crystal structure of a metallic solid permits computation of its theoretical density ρ through the relationship

$$\rho = \frac{nA}{V_C N_A}$$

Where

n = number of atoms associated with each unit cell

A = atomic weight

V_C = volume of the unit cell

N_A = Avogadro>s number ($6.022 * 10^{23}$ atoms/mol)

Q. Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density, and compare the answer with its measured density.

Solution

Because the crystal structure is FCC, n, the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_C for FCC was determined as $16R^3\sqrt{2}$, where R, the atomic radius, is 0.128 nm.

Substitution for the various parameters into density equation yields

$$\rho = \frac{nA_{Cu}}{V_C N_A} = \frac{nA_{Cu}}{(16R^3\sqrt{2})N_A}$$

$$= \frac{(4\ atoms\ /\ unit\ cell)(63.5\ g/mol)}{[16\sqrt{2}(1.28\ x\ 10^{-8}\ cm)^3](6.022\ x\ 10^{-23}\ atoms\ /mol}$$

$$= 8.89 g/cm^3$$

The literature value for the density of copper is 8.94 g/cm^3, which is in very close agreement with the foregoing result.

1.6 Types of material crystal structures

1. **Single or Mono Crystalline Materials**

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a single crystal. All unit cells interlock in the same way and have the same orientation. Single crystals exist in nature, but they can also be produced artificially. They are ordinarily difficult to grow because the environment must be carefully controlled.

2. **Multi or Poly Crystalline Materials**

Most crystalline solids are composed of a collection of many small crystals or grains; such materials are termed polycrystalline. The crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a grain boundary.
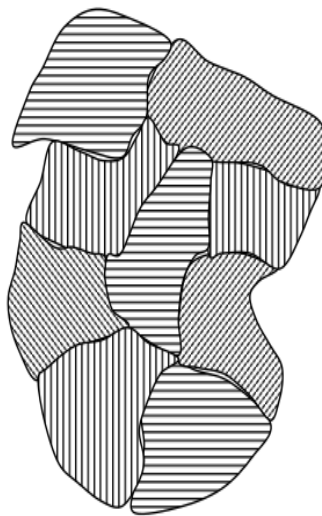
3. **Non Crystalline or Amorphous Materials**

Non-crystalline solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called amorphous (meaning literally "without form"), or supercooled liquids, in as much as their atomic structure resembles that of a liquid.
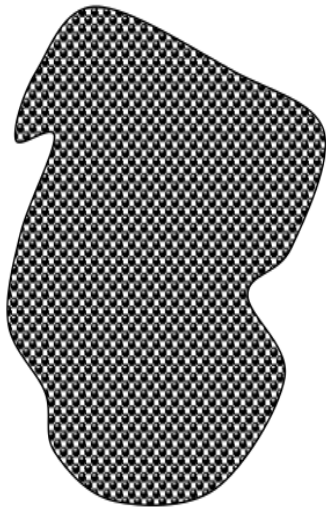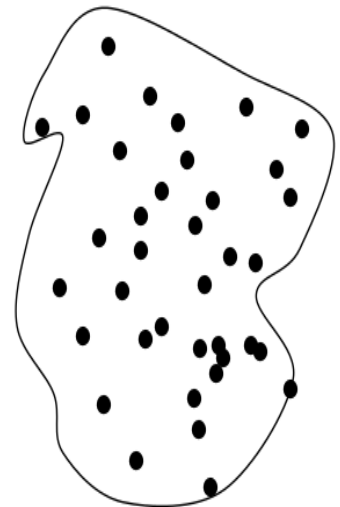

Fig. 1. 12 Types of crystalline structure

1.7 Miller Indices

The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the Miller Indices (*hkl*), which are a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

The following treatment of the procedure used to assign the Miller Indices is a simplified one (it may be best if you simply regard it as a "recipe") and only a **cubic** crystal system (one having a cubic unit cell with dimensions *a* x *a* x *a*) will be considered.
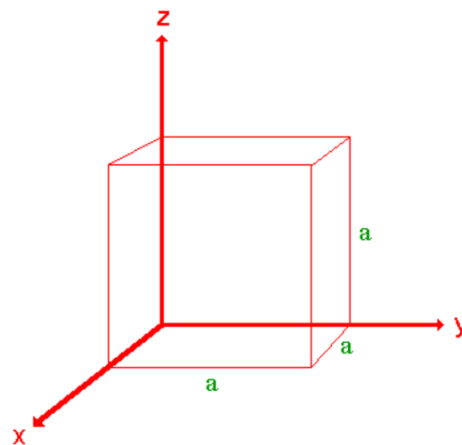

Fig. 1.13 A cubic crystal system

The procedure is most easily illustrated using an example so we will first consider the following surface/plane:
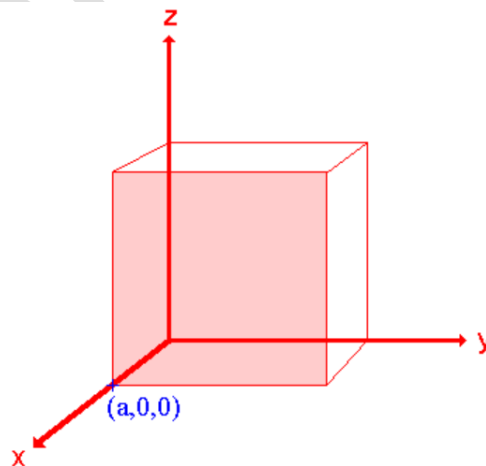

Fig. 1.14 A plane parallel to y-z axes

Step 1: *Identify the intercepts on the x-, y- and z- axes.*

In this case the intercept on the x-axis is at $x = a$ (at the point $(a,0,0)$), but the surface is parallel to the *y*- and *z*-axes - strictly therefore there is no intercept on these two axes but we shall consider the intercept to be at infinity (∞) for the special case where the plane is parallel to an axis. The intercepts on the *x*-, *y*- and *z*-axes are thus

Intercepts: ***a*, ∞, ∞**

Step 2: Specify the intercepts in fractional co-ordinates

Co-ordinates are converted to fractional co-ordinates by dividing by the respective cell-dimension - for example, a point (x,y,z) in a unit cell of dimensions a x b x c has fractional co-ordinates of (x/a, y/b, z/c). In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant, a . This gives

Fractional Intercepts: ***a/a*, ∞/*a*, ∞/*a*** i.e. **1, ∞, ∞**

Step 3: Take the reciprocals of the fractional intercepts

This final manipulation generates the Miller Indices which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indices are also enclosed within standard brackets (….) when one is specifying a unique surface such as that being considered here.
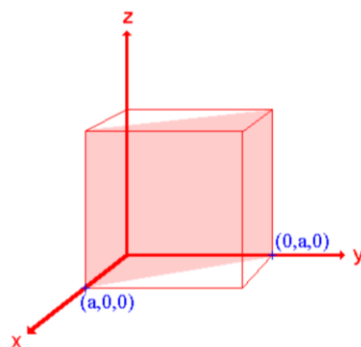
The reciprocals of 1 and ∞ are 1 and 0 respectively, thus yielding

Miller Indices: **(100)**

So the surface/plane illustrated is the (100) plane of the cubic crystal.
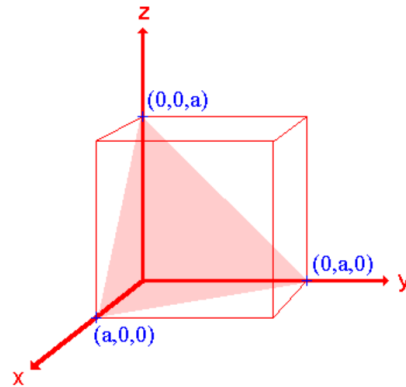
Other Examples

The (110) surface

Assignment

Intercepts: *a, a*, ∞

Fractional intercepts: 1, 1, ∞

Miller Indices: **(110)**
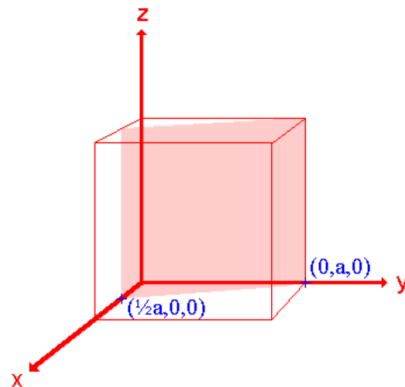
The (111) surface

Assignment

Intercepts: *a*, *a*, *a*

Fractional intercepts: 1, 1, 1

Miller Indices: **(111)**

The (210) surface

Assignment

Intercepts: ½ *a*, *a*, ∞

Fractional intercepts: ½, 1, ∞

Miller Indices: **(210)**

*Try this: https://www.doitpoms.ac.uk/tlplib/miller_indices/lattice_draw.php

The distances between parallel planes in a crystal are designated as d_{hkl}. For different cubic lattices these interplanar spacings are given by the general formula

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

Where a is the length of the cube side while h, k and l are the Miller indices of the plane.

1.8 X-ray crystallography

X-ray Crystallography is a scientific method used to determine the arrangement of atoms of a crystalline solid in three dimensional space. This technique takes advantage of the interatomic spacing of most crystalline solids by employing them as a diffraction gradient for x-ray light, which has wavelengths on the order of 1 angstrom (10^{-8} cm).

The structures of crystals and molecules are often being identified using x-ray diffraction studies, which are explained by Bragg's Law. The law explains the relationship between an x-ray light shooting into and its reflection off from crystal surface.

Bragg's Law

Bragg's Law was introduced by Sir W.H. Bragg and his son Sir W.L. Bragg. The law states that when the x-ray is incident onto a **crystal** surface, its angle of incidence, θ, will reflect back with a same angle of scattering, θ. And, when the path difference, d is equal to a whole number, n, of wavelength, a constructive interference will occur.

Consider a single crystal with aligned planes of lattice points separated by a distance *d*. Monochromatic X-rays A, B, and C are incident upon the crystal at an angle *θ*. They reflect off atoms X, Y, or Z.
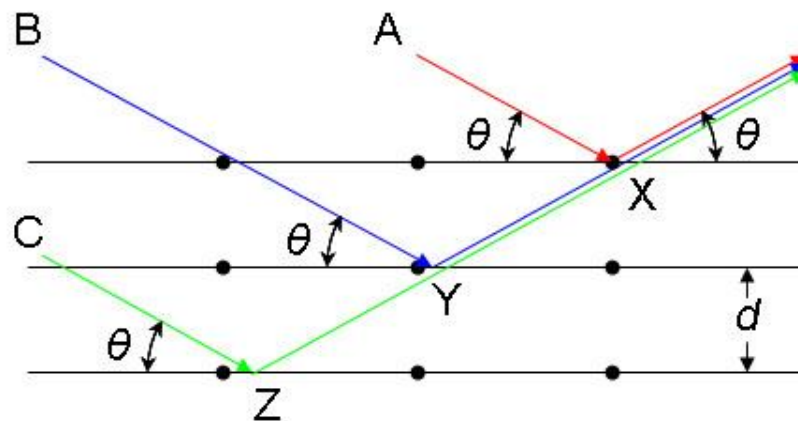

Fig. 1.15 Light incidence on a crystal

The path difference between the ray reflected at atom X and the ray reflected at atom Y can be seen to be 2YX. From the Law of Sines we can express this distance YX in terms of the lattice distance and the X-ray incident angle:

$$2YX = 2dsin\theta$$

If the path difference is equal to an integer multiple of the wavelength, then X-rays A and B (and by extension C) will arrive at atom X in the same phase. In other words, given the following conditions:

$$2YX = n\lambda$$

then the scattered radiation will undergo constructive interference and thus the crystal will appear to have reflected the X-radiation. If, however, this condition is not satisfied, then destructive interference will occur.

On combining these equations, mathematically Bragg's Law will be

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

where:

λ is the wavelength of the x-ray,

d is the spacing of the crystal layers (path difference),

θ is the incident angle (the angle between incident ray and the scatter plane), and

n is an integer

The principle of Bragg's law is applied in the construction of instruments such as Bragg spectrometer.

Interplanar Spacing and Diffraction Angle Computations

For BCC iron, compute (a) the interplanar spacing and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Solution

Here, a = 0.2866 nm, and h = 2, k = 2, and l = 0 because we are considering the (220) planes. Therefore,

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

$$d_{hkl} = \frac{0.2866\ nm}{\sqrt{(2)^2+(2)^2+(0)^2}} = 0.1013\ nm$$

(b) The value of θ may now be computed using Bragg's Law, with n = 1 because this is a first order reflection:

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790\ nm)}{(2)(0.1013\ nm)} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13°$$

The diffraction angle is 2θ, or

$$2\theta = (2)62.13° = 124.26°$$

1.9 Imperfection and defects

Thus far it has been tacitly assumed that perfect order exists throughout crystalline materials on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various defects or imperfections. Any irregularity in the pattern of crystal arrangement in a solid lattice is called imperfection in solids. The occurrence of defects takes place when crystallization (the process of formation of crystals) occurs at a very fast or at an intermediate rate. This is because particles don't get enough time to arrange themselves in a regular pattern.

Basically, defects fall out in two forms, point defect and line defect

1.9.1 Point Defect

Point Defect occurs when an atom is missing or is irregularly arranged in a crystal lattice. In other words, the deviations and irregularities observed around an atom or a point are known as a **Point Defect**.

Types of Point Defects

Point Defects are classified into two defects, namely: Stoichiometric Defects and Nonstoichiometric Defects

Stoichiometric Defects

The defects due to which the stoichiometry of solids remains undisturbed are called stoichiometric Defects. After stoichiometric defect, the ratio of cation and anions remain same in a solid. They are also known as intrinsic or thermodynamic defects.

Stoichiometric Defects are further classified into four defects:

1. Vacancy Defect

2. Interstitial Defect

3. Schottky Defect

4. Frenkel Defect

Vacancy Defect

Formation of vacancy defects take place due to vacant lattice sites. This defect generally occurs when we heat a solid. Vacancy defect also decreases the density of solid.
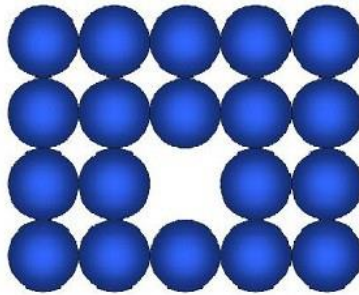

Fig.1.16 Vacancy defect

Interstitial Defect

When some extra constituent particles (atoms, molecules or ions) are acquainted in the interstitial sites, the solid lattice is said to have an interstitial defect. Interstitial Defects are responsible for increasing density of the substance.
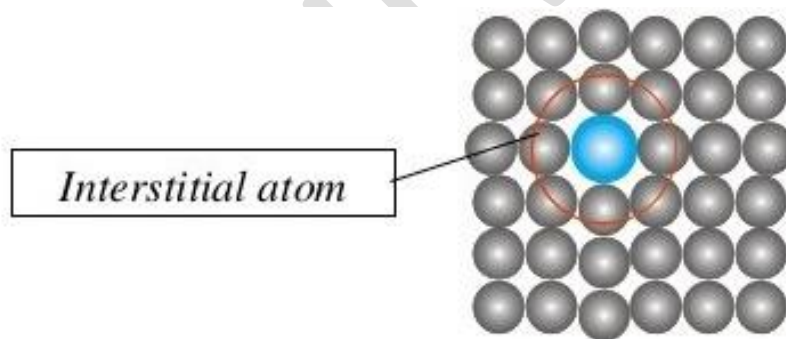

Fig. 1.17 Interstitial defect

Both vacancy and interstitial defects are depicted by non-ionic solids

Schottky Defect

If in an ionic lattice equal number of cations and anions are missing from the lattice site, the lattice is said to have Schottky defect. In Schottky Defect the electrical neutrality is maintained and it generally takes place in ionic solids. The compounds in which the size of cation and anion are nearly equal tend to show this type of defect.
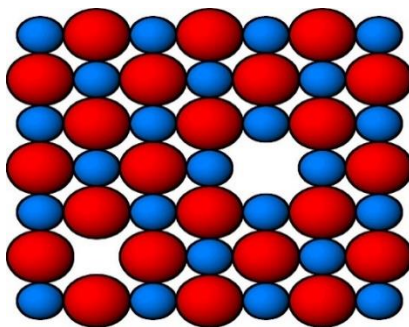
Fig. 1.18 Schottky defect

Some common examples of compounds depicting Schottky Defect are Sodium Chloride (NaCl), Potassium Chloride (KCl), Cesium Chloride (CsCl) and Silver Bromide (AgBr) Schottky Defect also decreases the density of the crystal lattice.

Frenkel Defect

Just like Schottky defect, Frenkel defect is also observed in ionic solids. When a smaller ion (generally cation) is moved from its normal position to a new interstitial site, Frenkel Defect occurs. This dislocation of ion creates vacancy defect at its original site and interstitial defect at its new position. The density of the crystal lattice remains same in Frenkel Defect. Ionic solids in which there are vast size differences between cation and ion tend to depict Frenkel Defect.
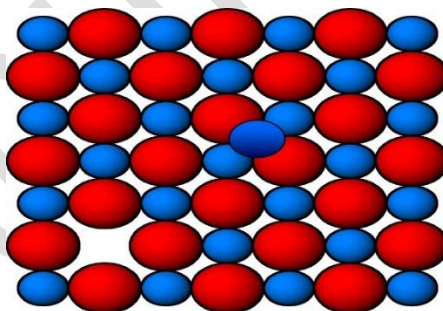

Fig. 1.18 Schottky defect

Some common examples of compounds depicting Frenkel Defect are as Zinc Sulphide (ZnS), Silver Chloride (AgCl), Silver Bromide (AgBr) and Silver Iodide (AgI)

Stoichiometric defects in ionic solids occur in form of Schottky and Frenkel Defect.

Remember electrical neutrality is of utmost importance for the existence of ionic solids.

Non-Stoichiometric Defect

The defect in which the ratio of cation and anion in an ionic lattice is variable is known as a non-stoichiometric defect. They are of two types, namely: Metal Excess Defect and Metal Deficiency Defect.

Metal Excess Defect

Metal Excess Defect occurs in two ways:

1. Due to anionic vacancies

   - Metal Excess Defect can be seen in alkali halides like NaCl and KCl. In this type of defect, the anionic vacancies are missing and are filled by an electron to ensure electrical neutrality. For Example, when a NaCl crystal is heated in presence of sodium vapor, the sodium atoms are deposited on the surface of the metal. The Cl- ions diffuse out from the crystal surface and combines with Na atom to give NaCl. To make this happen sodium loses electrons to become Na+ and the released electrons occupy the anionic vacancies. As a result, crystal gets excess sodium.
   - The anionic sites or vacancies which are filled by unpaired electrons are called F-centers and are responsible for imparting a yellow color to the flame of NaCl. Similarly in KCl excess of potassium is responsible for making KCl crystal flame violet.

2. Due to presence of extra cations at interstitial sites

   - In this type of defect, extra positive ions and electrons occupy interstitial sites and maintain electrical neutrality. In other words, this defect is losing non-metal atoms leaving their electrons behind and excess metal occupies interstitial positions. For Example, in white zinc oxide on heating, it leaves oxygen and becomes yellow.
   - $ZnO \rightarrow Zn^{2+} + O_2 + 2e^-$
   - Now due to excess of zinc in the crystal, the formula of ZnO becomes $Zn^{1}+xO$.

Metal Deficiency Defect

This defect occurs in metals containing less number of cations than anions. It is mostly seen in compounds depicting variable oxidation states. Due to unequal number of cations and anions the metals obtained are non-stoichiometric. Some common examples falling under this category of defect are $Fe_{0.95}O$, $Fe_{0.93}O$ etc.
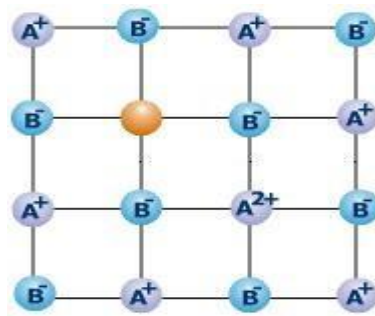

Fig. 1.19 Metal Deficiency Defect

1.9.2 Line Defect or dislocations

In materials science, dislocations are line defects that exist in metals. A dislocation is a crystallographic defect or irregularity within a crystal structure. The presence of dislocations strongly influences many properties of materials. Dislocations are generated and move when a stress is applied. There are two types of dislocations: edge and screw.

1. Edge Dislocation

Edge dislocation is a type of line defect in crystal lattices in which the defect occurs either due to the presence of an extra plane of atoms or due to the loss of a half of a plane of atoms in the middle of the lattice. This defect causes the nearby planes of atoms to bend towards the dislocation. Therefore, the adjacent planes of atoms are not straight. The region in which the defect occurs is the dislocation core or area.
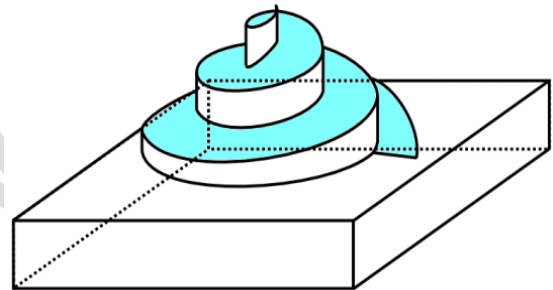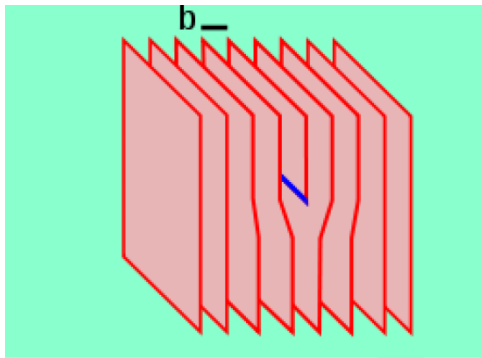

Fig. 1.20 (a) Edge dislocation and (b) Screw dislocation

When we apply stress on a crystal having this defect, the dislocation area moves parallel to the direction of stress. However, the movement at the region where a half of a plane of atoms is very small when compared with the region where the other half of that plane of atoms is absent. Edge dislocations can glide in any plane.

2. Screw Dislocation

Screw dislocation is another type of line defect in which the defect occurs when the planes of atoms in the crystal lattice trace a helical path around the dislocation line. Visualizing this type of defects in crystals is difficult. Unlike in edge dislocation, when we apply stress on a crystal having this defect, the dislocation area moves perpendicular to the direction of stress. However, the stress caused by screw dislocation is comparatively less complex than edge dislocation. Screw dislocations can glide in any plane

3. Slip

Slip is the large displacement of one part of a crystal relative to another part along the crystallographic planes and directions. A slip can occur by the passage of dislocations on close-packed planes. These are the planes containing the greatest number of atoms per area and in close-packed directions. Generally, we call the close-packed planes as slip or **glide planes**.
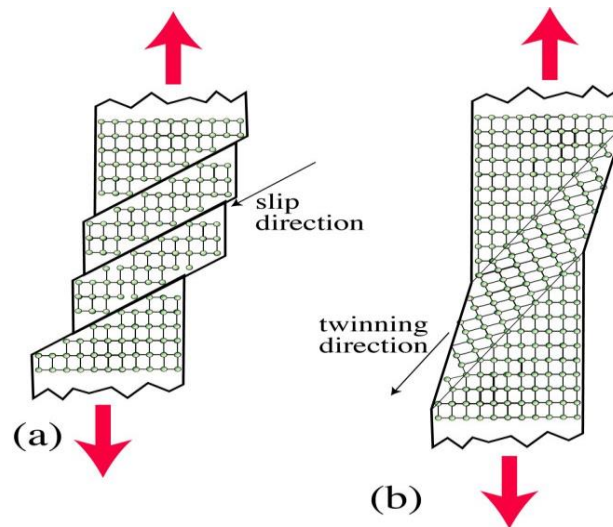

Fig. 1.21 (a) Slip and (b) twinning

Typically, an external force that is applied to a crystal lattice can cause the parts of the crystal lattice to glide along with each other, which can change the geometry of that material. We need a critical resolved shear stress in order to initiate a slip.

We can identify different slip systems, including the face-centred cubic system where the slip occurs along the close-packed plane, body centred cubic crystals where slip occurs along the plane of shortest Burgers Vector, hexagonal close-packed systems where the slip occurs along the densely packed plane, etc.

4. Twinning

Crystal twinning is the event where two different crystals share some of the same crystal lattices that are pointing in a symmetric manner. The result of the twinning in a crystal lattice is an intergrowth of two separate crystals in a variety of specific configurations. In this phenomenon, the surface along which the crystal lattice points are shared in a twinned crystal is known as "composition surface or twin plane". Twinning is often a problem in X-ray crystallography because the twinned crystals do not produce a simple diffraction pattern.