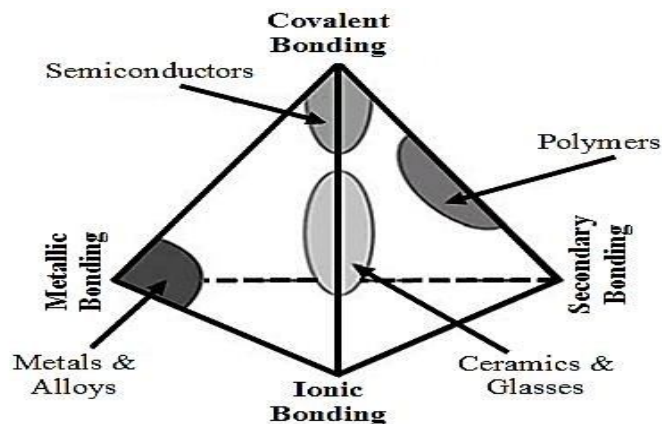




TUTORIAL & ASSIGNMENTS WORKBOOK
For
(ENGINEERING MATERIALS I)

ENG 207



- **SURNAME:** _____
- **OTHER NAMES:** _____
- **REG. NUMBER:** _____
- **DEPARTMENT:** _____
- **SCHOOL:** _____
- **MANUAL SERIAL NUMBER:** _____



UNIT ONE

INTRODUCTION

This is a workbook containing **tutorials** and **assignments on** Introduction to Engineering Materials I (ENG 207). It is intended to assist students to master the principles taught in the lectures as well as provide opportunity to do **assignments** and **exercises** that will enhance knowledge of the course in addition to attracting course marks.

The following topics are covered in this workbook:

- Introduction to Materials Science and Engineering (MSE) and Classification of Engineering Materials
- Review of Atomic Bonding in Materials
- Elements of Crystallography including Lattice Imperfections in Materials

Students are advised to get information on the remaining topics from lectures and reference textbooks:

- Phase Equilibrium and Alloy Theory, Hume-Rothery Rules, Phase Rule, Solid solutions, Lever Rule,
- Introduction to Extractive Metallurgy
- Introductory Heat Treatment of Steels

The author hereby acknowledges gleaned the information contained in this manual from several sources, particularly the under listed **references**:

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Department of Materials & Metallurgical Engineering

UNIT TWO INTRODUCTION AND CLASSIFICATION OF MATERIALS

2.1 WHAT ARE ENGINEERING MATERIALS?

Materials are everywhere around us. We encounter and utilize materials in transportation, housing, clothing, communication, recreation, and food production— virtually every segment of our everyday lives is influenced to one degree or another by materials. Our level of development and comfort depend on our level of materials usage. The development and advancement of societies have historically, been intimately tied to the citizens' ability to produce and manipulate materials to fill their needs. In fact, early civilizations have been designated by the level of their materials development (Stone Age, Bronze Age, Iron Age, etc.). Recently, we had the Silicon Age, which revolutionized electronics and led to the computer and information age. Currently, we are in the age of nanomaterials and smart materials.

Materials are solid substances or stuffs of which something (products, articles, goods, equipment, machines, etc.) is made. They are derived from the Earth (mineral resources) or from plants and animals (bio-resources). Materials science and engineering (MSE) disciplines involve investigating the relationships that exist between the structures and properties of materials and based on these structure–property correlations, designing the structure of a material to produce a predetermined set of properties for various applications. It involves the extraction, synthesis and refining or processing of substances into useful materials.

2.2 CLASSIFICATION OF MATERIALS

Engineering materials can be classified on the basis of structure, function and chemical bonding. The most common, convenient and in fact traditional way of classifying materials is based on chemical bonding.

Traditional Classification of Materials

❖ **Metallic Materials (Metals and Alloys)** are inorganic substances that are composed of one or more metallic elements and may contain some nonmetallic elements. Examples of metallic elements are iron, copper, aluminum, nickel, and titanium. Nonmetallic elements such as carbon, nitrogen, and oxygen may also be contained in metallic materials as impurities or alloying elements. Metals have a crystalline structure in which the atoms are arranged in an orderly manner. Metals in general are good thermal and electrical conductors. Many metals are relatively strong and ductile at room temperature, and many maintain good strength even at high temperatures. Metals and alloys are commonly divided into two classes: **ferrous metals and alloys** that contain a large percentage of iron such as the steels and cast irons and **nonferrous metals and alloys** that do not contain iron or contain only a relatively small amount of iron. Examples of nonferrous metals are aluminum, copper, zinc, titanium, and nickel. The

distinction between ferrous and nonferrous alloys is made because of the significantly higher usage and production of steels and cast irons when compared to other alloys.

- ❖ **Ceramic Materials** are compounds between metallic and nonmetallic elements; they are most frequently oxides, nitrides, and carbides. For example, common ceramic materials include aluminum oxide (or *alumina*, Al_2O_3), silicon dioxide (or *silica*, SiO_2), silicon carbide (SiC), silicon nitride (Si_3N_4), and, in addition, what some refer to as the *traditional ceramics*—those composed of clay minerals (i.e., porcelain), as well as cement and glass. In contrast to traditional ceramics the new family of oxides, nitrides, and carbides (e.g. Al_2O_3 , Cr_2O_3 , Si_3N_4 , SiC), with improved properties, are called *engineering ceramics*, *technical ceramics*, *structural ceramics*, or *advanced ceramics*. *They have* higher strength, better wear and corrosion resistance (even at higher temperatures), and enhanced thermal shock resistance.
- ❖ **Polymeric Materials** or **Polymers** include the familiar plastic, textile and rubber materials. Many of them are organic compounds that are chemically based on carbon, hydrogen, and other nonmetallic elements (i.e., O, N, and Si). Furthermore, they have very large molecular structures, often chainlike in nature, that often have a backbone of carbon atoms. Some of the common and familiar polymers are polyethylene (PE), nylon, poly(vinyl chloride) (PVC), polycarbonate (PC), polystyrene (PS), and silicone rubber. These materials typically have low densities, whereas their mechanical characteristics are generally dissimilar to the metallic and ceramic materials—they are not as stiff nor as strong as these other material types. Plastics, elastomers (rubber), fibres, adhesives, foams, and some films and coatings or paints are all polymers.
- ❖ **Composite Materials:** A composite may be defined as two or more materials (phases or constituents) integrated to form a new one. The constituents keep their properties and the overall composite will have properties different from each of them. Most composite materials consist of a selected filler or reinforcing material and a compatible resin binder to obtain the specific characteristics and properties desired. Usually, the components do not dissolve in each other (as in alloys or solid solutions), and they can be physically identified by an interface between them. The two (or more) individual materials, come from the categories previously discussed—metals, ceramics, and polymers. The design goal of a composite is to achieve a combination of properties that is not displayed by any single material, and also to incorporate the best characteristics of each of the component materials. A large number of composite types are represented by different combinations of metals, ceramics, and polymers. Furthermore, some naturally occurring materials are composites—for example, wood (consisting of **cellulose** fibre as reinforcement and **lignin** as binder) and bone (consisting of the ceramic **hydroxyapatite** and the protein/polymer **collagen**). However, most composites are synthetic (or human-made), e.g. concrete and fibreglass.

Functional Classification of Materials

Although engineering materials are best classified on the basis of predominant bonding type into (i) metals and alloys, (ii) ceramics, (iii) polymers, and (iv) composites; we can also classify materials based on whether the most important function [based on the most significant property] they perform is mechanical (structural), biological, electrical, magnetic, or optical. We can also refer to some materials as advanced materials because of their novel properties and sensitive applications. Examples of functional materials are semiconducting materials, electronic materials, photonic/optical materials, magnetic materials, structural (load-bearing) materials, biomedical materials, smart materials, aerospace materials, etc.

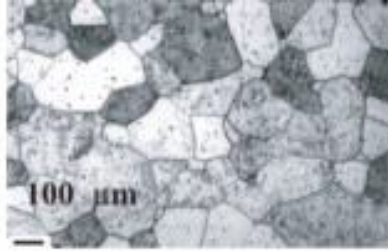


Figure 2.1: Micrograph of stainless steel

Classification of Materials Based on Structure

The term “**structure**” means the arrangement of the atoms of a material; the structure at a microscopic scale is known as “**microstructure**.” We can view these arrangements at different scales, ranging from a few angstrom units to a millimeter. Some materials may be **crystalline** (the atoms are arranged in a periodic or regular fashion) or they may be **amorphous** or **noncrystalline** (the arrangement of the atoms does not have long-range order). Some crystalline materials may be in the form of one crystal and are known as **single crystals**. Others consist of many crystals or **grains** and are known as **polycrystalline**. The characteristics of crystals or grains (size, shape, etc.) and that of the regions between them, known as the **grain boundaries**, also affect the properties of materials. A **micrograph** of stainless steel showing grains and grain boundaries is shown in Figure 2.1. One of the most fascinating aspects of materials science involves the investigation of a material’s structure. The structure of materials has a profound influence on many **properties** of materials, even if the overall **composition** does not change!

UNIT THREE REVIEW OF ATOMIC BONDING IN MATERIALS

3.1 PRIMARY OR CHEMICAL BONDS

An understanding of many of the properties of materials is predicated on knowledge of the interatomic forces that bind the atoms together. Three different types of **chemical bond** or **primary bond** are found in solid materials, namely: **ionic** or **electrovalent**, **covalent**, and **metallic**. Chemical bonding has become the most convenient basis for grouping or classifying

engineering materials. *Ionic bond* dominates and characterizes **ceramic materials**. In **polymers** and **semiconductors**, *covalent bond* dominates. **Metals** are characterized by *metallic bonding*. As **composite materials** involve the combination of two or more of these basic classes of materials, it can be understood that they have mixed bonding. For each type, the bonding necessarily involves the **valence electrons**. Furthermore, the nature of the bond depends on the **electron structure** of the constituent atoms. In general, each of these three types of bonding arises from the tendency of the atoms to assume stable electron structures, like those of the inert or noble gases, by completely filling the outermost electron shell.

a) IONIC BONDING

Ionic bonding is always found in materials that are composed of both metallic (electropositive) and nonmetallic (electronegative) elements that are situated at the horizontal extremities of the periodic table. The attractive bonding forces are **columbic**; that is, positive and negative ions [cations and anions], by virtue of their net electrical charge, attract one another. The predominant bonding in ceramic materials is ionic. Ceramic materials are most frequently oxides, nitrides, carbides and halides, and range from clay-based products, to cement, glasses and technical or engineered ceramics. Ionic materials are characteristically hard and brittle and furthermore, electrically and thermally insulative.

b) COVALENT BONDING

Two atoms that are covalently bonded will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms. For N valence electrons, an atom can covalently bond with at most $8 - N$ other atoms. Polymeric materials (plastics and rubber) typify this bond, the basic molecular structure being a long chain of carbon atoms [catenation] that are covalently bonded together. Also, this type of bonding is found in **elemental semiconductors** [the metalloids of Group IVA] such as carbon (diamond), silicon and germanium, and other solid compounds [especially **compound semiconductors**] composed of elements that are located close to Group IVA, such as gallium arsenide (GaAs), indium antimonide (InSb), and silicon carbide (SiC).

It is possible to have inter-atomic bonds that are partially ionic and partially covalent, and, in fact, very few compounds exhibit pure ionic or covalent bonding. For a compound [e.g. ceramics and compound semiconductors], the degree of either bond type depends on the relative positions of the constituent atoms in the periodic table or the difference in their electronegativities. The wider is the separation (both horizontally and vertically) from the lower left to the upper right-hand corner (i.e. the greater the difference in electronegativity), the more ionic the bond. Conversely, the closer the atoms are together (i.e. the smaller the

difference in electronegativity), the greater the degree of covalency. The **percentage ionic character** may be given by the expression:

$$\% \text{ Ionic Character} = [1 - e^{-0.25(X_A - X_B)^2}] \times 100 \quad [3.1]$$

Where, X_A and X_B are the electronegativities for elements A and B forming the bond respectively, A being the more electronegative. It follows that the **percentage covalent character** can be expressed as:

$$\% \text{ Covalent Character} = [e^{-0.25(X_A - X_B)^2}] \times 100 \quad [3.2]$$

c) METALLIC BONDING

Metallic bonding is found in metals and their alloys. Metallic materials have one, two, or at most, three valence electrons. These valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal. They may be thought of as belonging to the metal as a whole, or forming a “*sea of electrons*” or an “*electron cloud*”. The remaining nonvalence electrons and atomic nuclei form what are called **ion cores**, which possess a net positive charge equal in magnitude to the total valence electron charge per atom. The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces, which they would otherwise exert upon one another; consequently the metallic bond is nondirectional in character. In addition, these free electrons act as a “glue” to hold the ion cores together. Metals are good conductors of both heat and electricity because of their free electrons.

3.2 SECONDARY OR PHYSICAL BOND

Physical forces and energies or **secondary bonds** are also found in many solid materials; they are weaker than the primary ones, but nonetheless influence the properties of some materials. Secondary bonding arises from *dipole–dipole attraction* e.g. **van der Waals bonding** and **hydrogen bonding**. Figure 3.1 which was used as the cover image illustrates how different materials are grouped on the basis of the dominating bonding type.

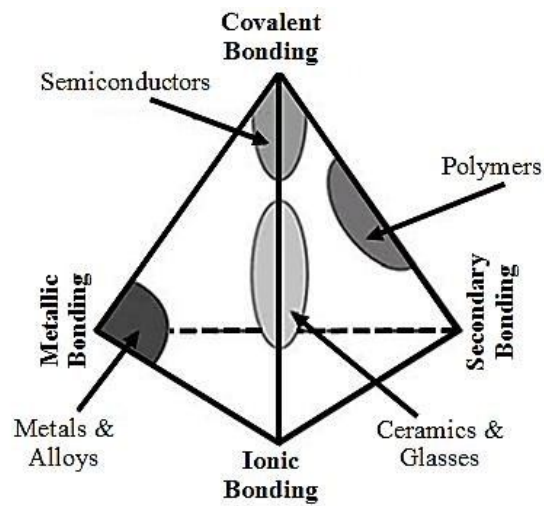


Figure 3.1: Bonding types present in different classes of engineering materials. [*Covalent, ionic, and metallic bonds are strong primary (or chemical) bonds while van der Waals attraction is a weak, albeit influential secondary bond present in polymers.*]

UNIT FOUR CRYSTALLOGRAPHY: ARRANGEMENT OF ATOMS IN MATERIALS

4.1 ATOMIC PACKING AND CRYSTAL STRUCTURES

The arrangement of atoms in a solid, whether regular in the long-range (i.e. crystalline structure) or irregular (i.e. glassy or noncrystalline) depends on the bonding type and the relative sizes of atoms involved. When trying to understand why atoms are arranged the way they are in solid, it

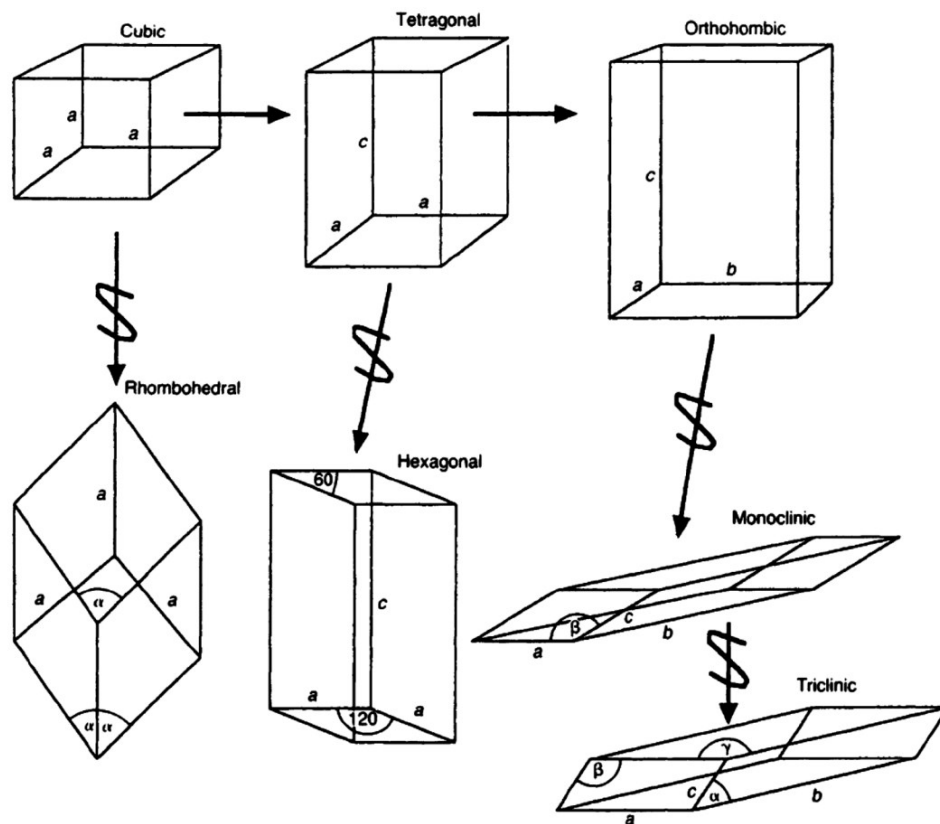
is necessary to divide inter-atomic bonds into two categories, **directional** and **non-directional**. Covalent and permanent dipole bonds are directional; metallic, ionic, and van der Waals bonds are ideally non-directional. Atoms bonded by directional bonds are packed in a way that satisfies the bond angles. Atoms bonded by non-directional bonds behave in general as tightly packed spheres and obey certain geometrical rules dictated by their difference in size. This gives rise to the various crystal systems of the **Bravais lattices** (Figure 4.1).

Solid materials are known to have definite shape and size, and they can be classified as either **crystalline** or **amorphous (non-crystalline)** in accordance with the regularity with which atoms or ions are arranged with respect to one another. In crystalline solids, the atoms are situated in a repeating or periodic array over large atomic distances. This **long-range order** (as it is called) ensures that upon solidification, the atoms of crystalline solids will position themselves in a repetitive three-dimensional pattern so that each atom is bonded to its nearest-neighbour atoms. All metals, many ceramics materials, and certain polymers form crystalline structures under normal solidification conditions.

On the other hand, non-crystalline or amorphous solids have random distribution of atoms or molecules, and long-range order of atoms is absent. Any order found in the arrangement of atoms is said to be **short-range order**. Apart from a slight change (decrease) in density, there is no practical structural change in the liquid as compared to the solid form of an amorphous material. They are therefore described as **super-cooled liquids**. Examples include glasses and plastics.

4.2 CRYSTAL, UNIT CELLS AND LATTICE POINTS

A **crystal** is an ordered pattern (arrangement) of atoms in 3Ds over a long range. Sometimes the term **lattice** is used in the context of crystal structures and it connotes a three-dimensional array of points coinciding with atom positions (or sphere centres). In describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells**. The crystal structures of metals derive from unit cells of cubic geometry (FCC and BCC) and hexagonal geometry (HCP) as shown in Figures 4.2 and 4.3. A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions (**lattice points**) in the crystal may be generated by translations of the unit cell integral distances (**lattice constant, a**) along each of its edges. Thus, the unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.



System	Axes	Axial angles
Cubic	$a_1 = a_2 = a_3$	All angles = 90°
Tetragonal	$a_1 = a_2 \neq c$	All angles = 90°
Orthorhombic	$a \neq b \neq c$	All angles = 90°
Monoclinic	$a \neq b \neq c$	Two angles = 90° ; 1 angle $\neq 90^\circ$
Triclinic	$a \neq b \neq c$	All angles different; none equal 90°
Hexagonal	$a_1 = a_2 \neq c$	Angles = 90° and 120°
Rhombohedral	$a_1 = a_2 = a_3$	All angles equal, but not 90°

Figure 4.1: The seven systems of crystal symmetry [S = skew operation]

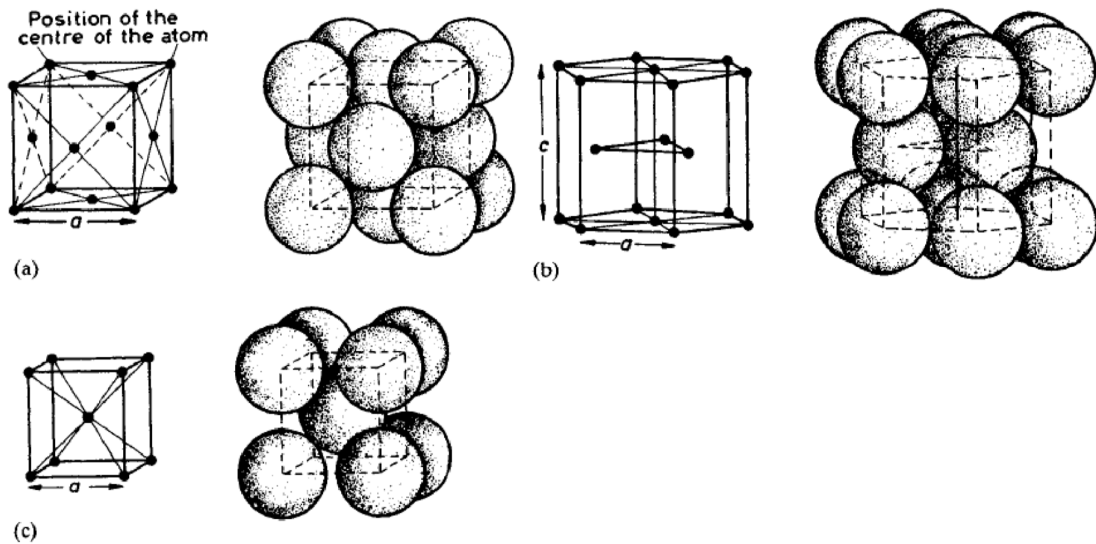


Figure 4.2: Arrangement of atoms in (a) FCC, (b) HCP and (c) BCC structures

Table 4.1: Unit cell structures for metals and the packing economy of atoms

Unit Cell	Examples	Total number of atoms	Relationship between a and r	Atomic Packing Factor (APF)
Simple Cubic (SC)	No Metal	$8 \times \frac{1}{8} = 1$	$a = 2r$	$\frac{\pi}{6} = 0.52$
Body Centred Cubic (BCC)	Cr, Mo, W, α -Fe	$8 \times \frac{1}{8} + 1 = 2$	$a = \frac{\sqrt{3}}{4}r$	$\frac{\pi\sqrt{3}}{8} = 0.68$
Face Centred Cubic (FCC)	Al, Pb, Ni, γ -Fe	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$	$a = 2r\sqrt{2}$	$\frac{\pi}{3\sqrt{2}} = 0.74$
Hexagonal Close Packed (HCP)	Zn, Cd, Co, α -Ti	$1 + 1 + 1 + 3 = 6$	$a = 2r$ $c = 1.633a$	$\frac{2(4/3)\pi r^3}{a(a \sin 60^\circ)c} = \frac{\pi\sqrt{2}}{6} = 0.74$

Table 4.1 shows examples of the unit cells or crystal structures found in metals. Details of derivation are given in lectures (class). Note that **a** is the lattice parameter (length of a side of the unit cell) and **r** is atomic radius (radius of spheres occupying the lattice points). The atomic packing factor is defined as:

$$APF = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_a}{V_c} = \frac{\text{No. of atoms per cell} \times \frac{4}{3}\pi r^3}{a^3} \quad [4.1]$$

As shown in the case of iron (Fe), some metals as well as nonmetals may exhibit **polymorphism** (more than one crystal structure). When found in elemental solids, the phenomenon is often called **allotropy** and the prevailing crystal structure is usually a function of both the temperature and the external pressure. Pure iron has a BCC structure at room temperature (i.e. α -Fe or **ferrite**), which changes to FCC iron or γ -Fe (**austenite**) at 912°C. As may be expected, changes in density and other physical properties accompany polymorphic/allotropic transformations. For example, alpha-iron is magnetic while gamma-iron is nonmagnetic.

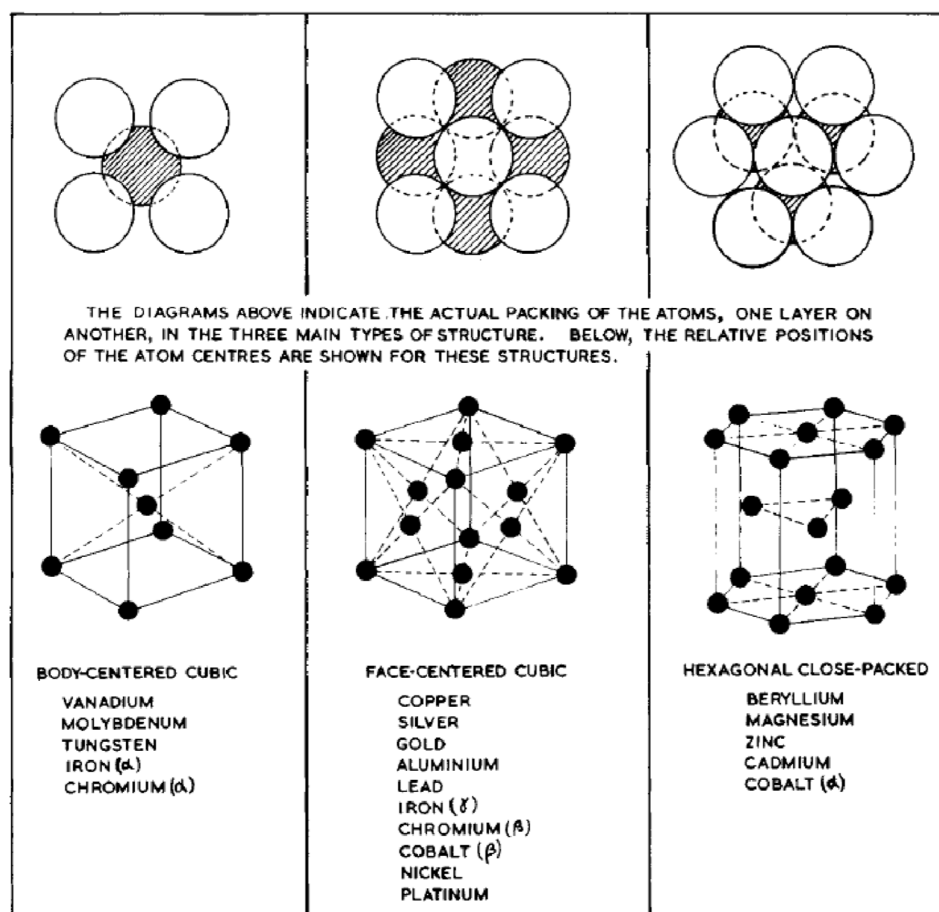


Figure 4.3: The three principal types of structure in which metallic elements crystallize

4.3 DIRECTIONS AND PLANES IN CRYSTALS

A crystallographic direction is defined as a line between two points, i.e. a vector. From the knowledge of vector mechanics in PHY 101, we know that the vector $\mathbf{A} = 3\mathbf{i} + 2\mathbf{j} + \mathbf{k}$ originates from the point whose coordinates are (000) [i.e. the origin] and heads to the point (321). In other words, the vector has components (projections) of 3 units, 2 units and 1 unit in the x-, y- and z-axis respectively. In crystallography and in the cubic system in particular, the x-, y- and z-axes are the directions [100], [010] and [001] respectively (Figure 4.4). One of the body diagonals has the direction indices [111] as shown.

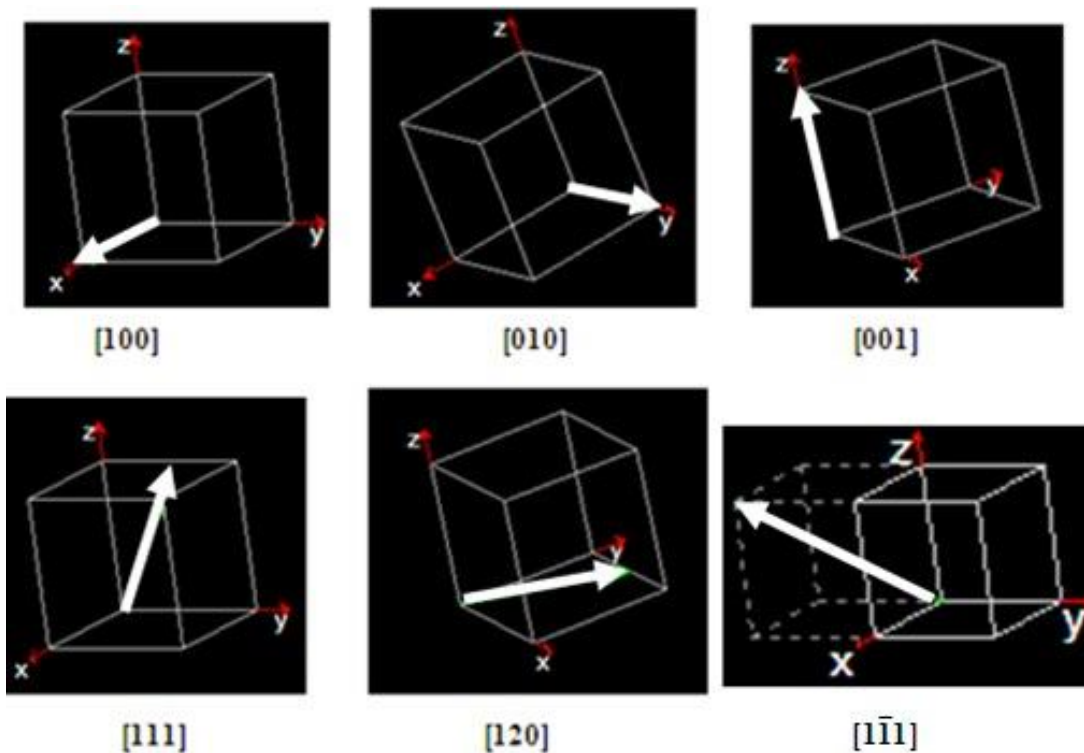


Figure 4.4: Some crystal directions in the cubic system

The determination of the three directional indices $[uvw]$ involves the following steps:

- A vector of convenient length is positioned such that it passes through the origin of the coordinate system.
- The length of the vector projection (its component) on each of the three axes is determined, e.g. $\frac{1}{2}$, 1, 0 along the x-, y- and z-axis respectively.
- The three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values; e.g. 1, 2, 0.
- The three indices, not separated by commas, are enclosed in square brackets thus $[120]$.

The direction $[120]$ is also shown in Figure 4.4.

In general, every direction can be determined once we know the coordinates of two points on the direction, usually tail point and head point. The vector projections will then be determined from:

(coordinates of head point) – (coordinates of tail point). For example: $\left(\frac{1}{2}, 1, 0\right) - (0, 0, 0) = \frac{1}{2}, 1, 0$.

For each of the three axes, there will exist both positive and negative coordinates. Negative indices are represented by a bar over the appropriate index. For example, $[1\bar{1}1]$ direction would have a component in the $-y$ direction as shown in Figure 4.6.

Crystallographic planes are specified by three **Miller indices** as (hkl) in all crystal systems except in the hexagonal system. The indices of three faces of the cubic unit cell are shown in Figure 4.5.

Any two planes parallel to each other are equivalent and have identical indices. The procedures for determining the h, k and l index numbers is as follows:

- i. The intercepts of the plane for each axis is determined. [NB: if the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell or a new origin must be established at the corner of another unit cell].
- ii. The reciprocals of the numbers (integers) are taken. For example, if the intercepts are 1, $\frac{1}{2}$, and ∞ , the reciprocals will be 1, 2 and 0. [Note: a plane that parallels an axis may be considered to have an infinite intercept and, therefore, a zero index].
- iii. Where necessary, these reciprocals are reduced or changed to the set of smallest integers by multiplication or division by a common factor. In the case of 1, 2 and 0 obtained above; there is no need for reduction.
- iv. Finally, the integer indices, not separated by commas, are enclosed within parenthesis thus, (120). The (120) plane and some other planes are shown in Figure 4.6.

An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index, e.g. plane ($\bar{2}$ 11) is also shown in Figure 4.6. One interesting and unique characteristic of cubic crystals is that planes and directions having the same indices are perpendicular to one another. Verify this by comparing Figures 4.4, 4.5 and 4.6.

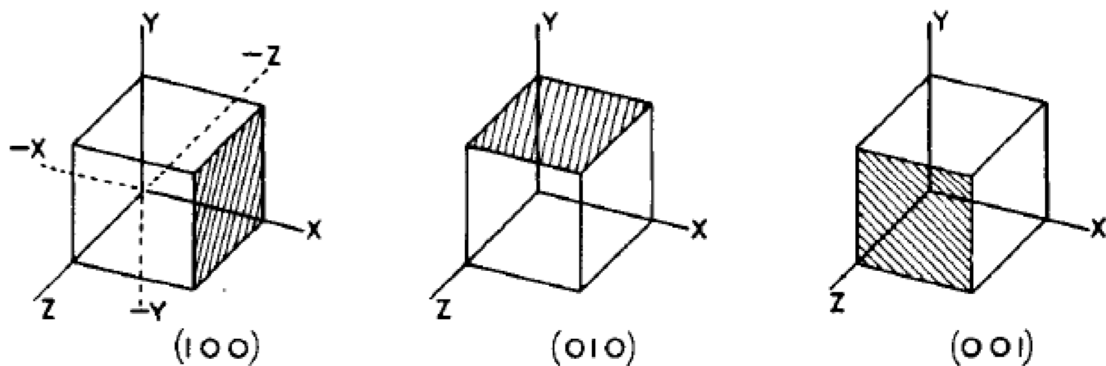


Figure 4.5: Miller indices of three faces in the cubic system

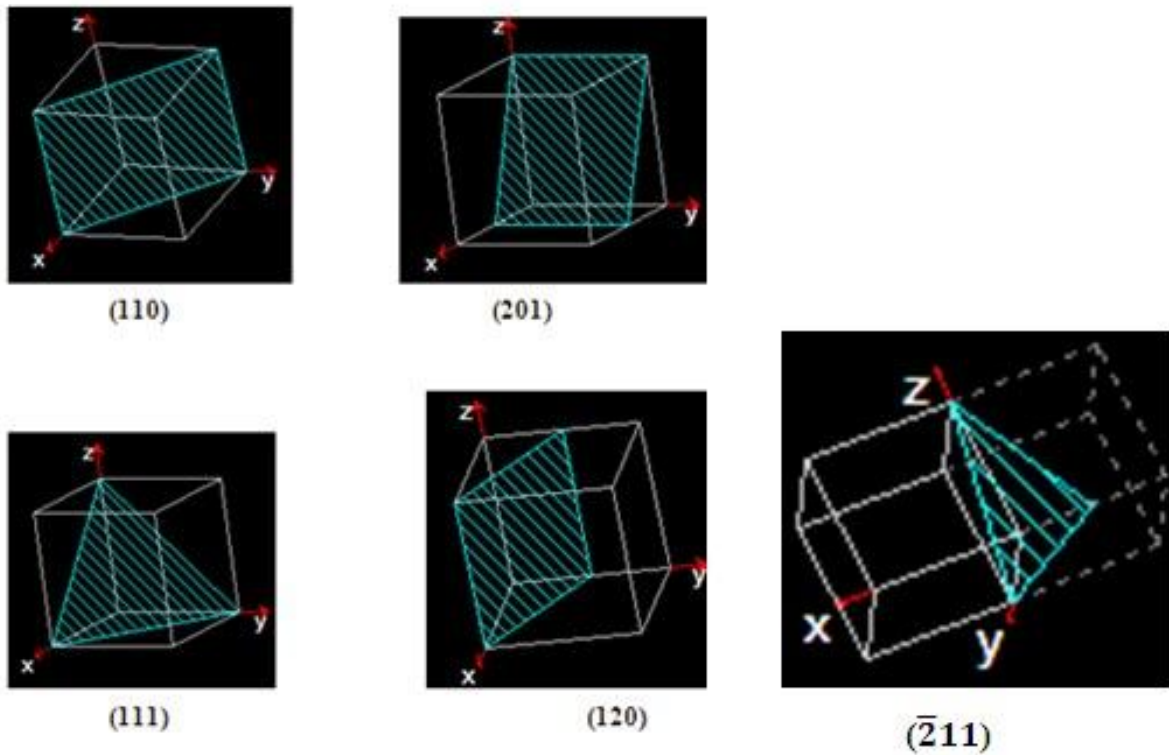


Figure 4.6: Some crystallographic planes in the cubic system

4.3.1 LINEAR AND PLANAR DENSITIES

The linear density for a unit cell is defined as:

$$LD = \frac{\text{number of atoms whose centers lie on a direction vector}}{\text{length of the direction vector}} \quad [4.2]$$

For example, the linear density of the direction $[110]$ in the FCC is:

$$LD_{110} = \frac{2 \text{ atoms}}{r + r + 2r} = \frac{2}{4r} = \frac{1}{2r},$$

expressed in atoms per nm.

Planar density is defined as:

$$PD = \frac{\text{number of atoms whose centers lie on a plane}}{\text{area of plane}} \quad [4.3]$$

In the FCC,

$$PD_{100} = \frac{\left(\frac{1}{4} \times 4\right) + 1}{2r\sqrt{2} \times 2r\sqrt{2}} = \frac{2}{8r^2} = \frac{1}{4r^2},$$

expressed in atoms per square nm.

4.3.2 CALCULATION OF THEORETICAL DENSITY

Density is expressed as mass per unit volume, i.e.

$$\rho = \frac{\text{mass of a material}}{\text{volume occupied by the material}} \quad [4.4a]$$

$$\text{The mass of one atom} = \frac{\text{molar mass of the element}}{\text{Avogadro's number}} = \frac{M}{N_A} \quad [4.4b]$$

For a unit cell, this will be multiplied by n, the total number of atoms occupying the cell. The density of an element based on the knowledge of unit cell structure is therefore total mass of the atoms in the unit cell divided by the volume of the unit cell. That is:

$$\rho = \frac{n M/N_A}{V_c} = \frac{nM}{V_c N_A} \quad [4.4c]$$

In the case of a metal whose crystal structure is FCC, the cell volume V_c , the atomic packing factor APF and density ρ can be determined as follows:

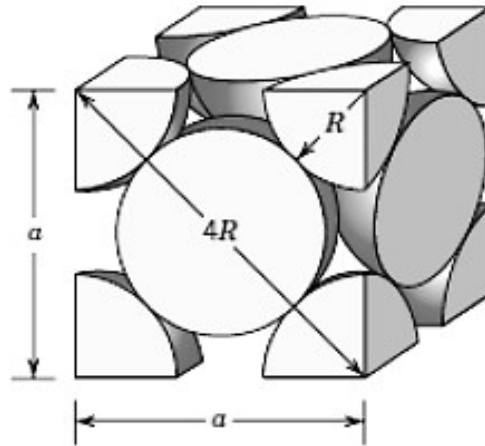


Figure 4.7: Geometrical relationship in the FCC

In the FCC unit cell shown above, the atoms touch one another across a face-diagonal the length of which is $4R$. Since 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, application of the Pythagorean principle results to:

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

So that,

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

The unit cell volume is therefore,

$$V_c = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2}$$

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

$$APF = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_a}{V_c} = \frac{\text{No. of atoms per cell} \times \frac{4}{3}\pi R^3}{a^3}$$

Since there are four atoms per FCC unit cell [explanation given in class], the total FCC atom (or sphere) volume is:

$$V_a = 4 \times \frac{4}{3}\pi R^3 = \frac{16}{3}\pi R^3$$

Therefore;

$$APF = \frac{V_a}{V_c} = \frac{\frac{16}{3}\pi R^3}{16R^3\sqrt{2}} = \frac{\pi}{3\sqrt{2}} = 0.74$$

The theoretical density is computed using:

$$\rho = \frac{nM/N_A}{V_c} = \frac{nM}{V_c N_A}$$

For example, copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic mass of 63.5 g/mol. its theoretical density can be determined as follows:

Since the crystal structure is FCC, n , the number of atoms per unit cell, is 4. Furthermore, the atomic mass is given as 63.5 g/mol. The unit cell volume for FCC was determined above as

$16R^3\sqrt{2}$ as where R , the atomic radius, is 0.128 nm.

Substitution for the various parameters into the density equation yields:

$$\begin{aligned} \rho_{Cu} &= \frac{nM_{Cu}}{V_c N_A} = \frac{4 \times 63.5}{16R^3\sqrt{2} \times (6.023 \times 10^{23} \text{ atoms/mol})} \\ &= \frac{4 \text{ atoms} \times 63.5 \text{ g/mol}}{16 \times (1.28 \times 10^{-8} \text{ cm})^3 \sqrt{2} \times (6.023 \times 10^{23} \text{ atoms/mol})} = \mathbf{8.89 \text{ g/cm}^3} \end{aligned}$$

NB: The literature (handbook) value for the density of copper is 8.94 g/cm³, which is in very close agreement with the above result.

Figures 4.8 to 4.10 show the geometrical arrangements in the FCC, BCC and HCP which can be used as aid in computing APF, LD, PD and theoretical density. Note that for the HCP (Figure 4.10a,c); the total number of atoms is: number in upper hexagonal plane [$6 \times \frac{1}{6} = 1$] + number in lower hexagonal plane [$6 \times \frac{1}{6} = 1$] + number in the centres of the hexagonal planes [$2 \times \frac{1}{2} = 1$] + number of interstitial atoms [3] = 1+1+1+3 = 6 atoms per HCP unit cell.

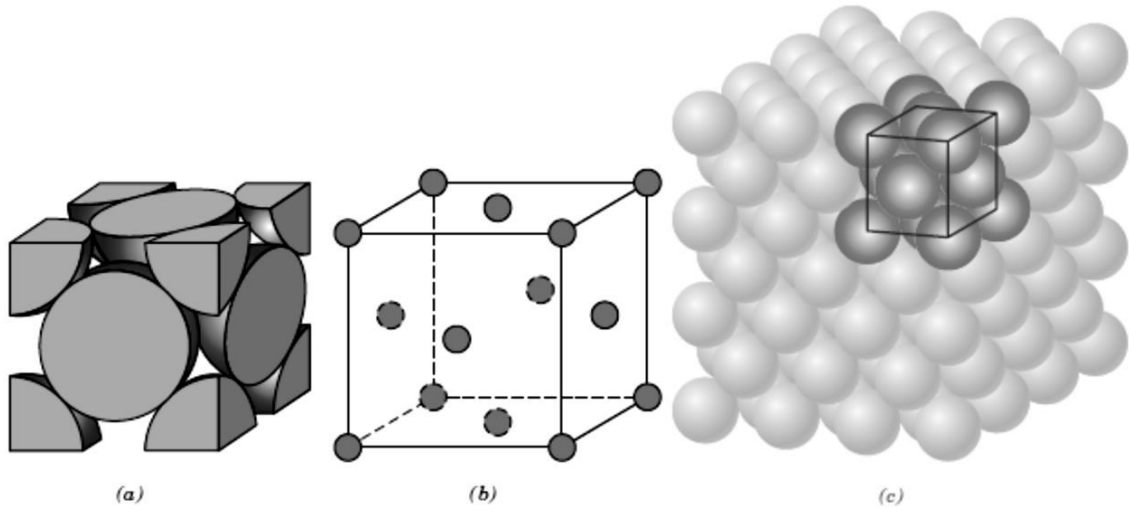


Figure 4.8: Geometrical arrangement in the FCC

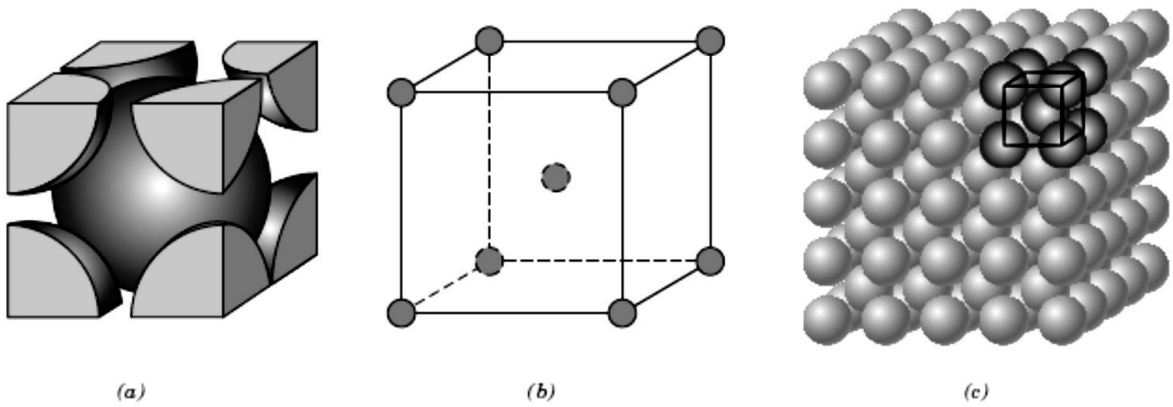


Figure 4.9: Geometrical arrangement in the BCC

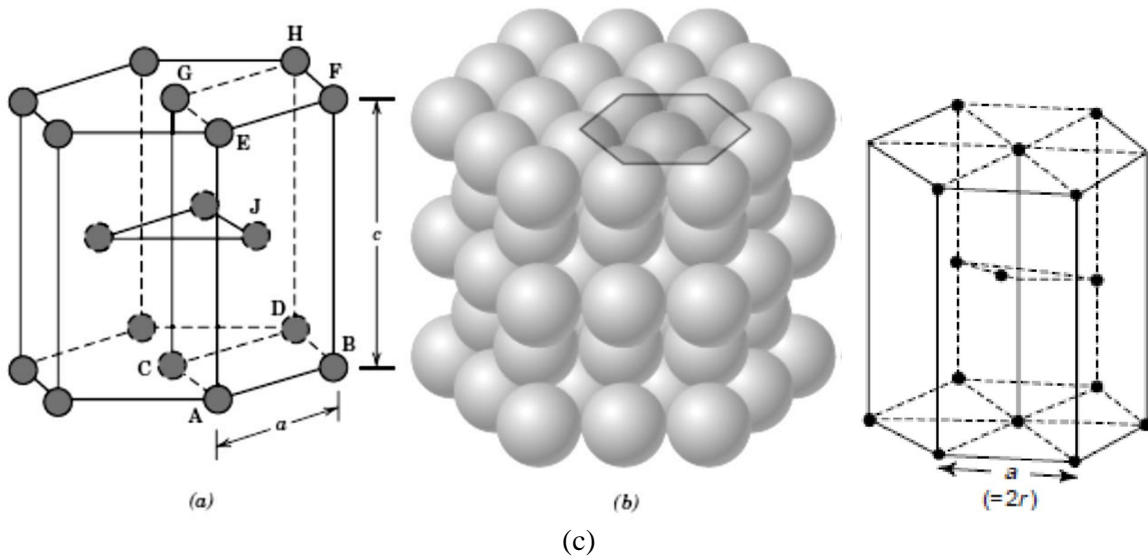


Figure 4.10: Geometrical arrangement in the HCP

Table 4.2 also gives data on the crystal structures and atomic radii of some metals.

Table 4.2: Atomic Radii and Crystal Structures for 16 Metals

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

^a FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

^b A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

4.4 DEFECTS OR IMPERFECTIONS IN CRYSTALS

So far, we have described perfectly regular crystal structures, called *ideal* crystals. In ideal crystals atoms were arranged in a regular way. However, the structure of real crystals differs from that of ideal ones. Real crystals always have certain defects or imperfections, and therefore, the arrangement of atoms in the volume of a crystal is far from being perfectly regular. Natural crystals always contain defects, often in abundance, due to the uncontrolled conditions under which they were formed. The presence of defects which affect the colour can make these crystals valuable as gems, as in **ruby** (chromium replacing a small fraction of the aluminium in aluminium oxide: Al_2O_3). So, the highly priced gem stone called **ruby** is actually alumina or corundum (Al_2O_3) doped with chromium oxide (Cr_2O_3)

Crystal prepared in laboratory will also always contain defects, although considerable control may be exercised over their type, concentration, and distribution. The importance of defects depends upon the material, type of defect, and properties which are being considered. Some properties, such as density and elastic constants, are proportional to the concentration of defects, and so a small defect concentration will have a very small effect on these. Other properties e.g. the colour of an insulating crystal or the conductivity of a semiconductor crystal, may be much more sensitive to the presence of small number of defects. Indeed, while the term defect carries with it the connotation of undesirable qualities, defects are responsible for many of the important properties of materials and much of material science involves the study and engineering of defects so that solids will have desired properties. A defect free, i.e. ideal silicon crystal would be of little use in modern electronics; the use of silicon in electronic devices is dependent upon small concentrations of chemical impurities such as phosphorus and arsenic which give it desired properties. That is,

silicon as an **intrinsic semiconductor** has little electronic application unless it is made **extrinsic** by being doped with the right concentrations of **dopants**.

Again, pure metals do not exhibit good mechanical properties of strength and hardness until they are alloyed. Alloying is intentional introduction of impurities or desirable imperfections in the crystal of the metal. Defects include:

- ❖ **Point defects** such as vacant atomic sites (or simply **vacancies**) and interstitial atoms (or simply **interstitials**), where an atom sits in an interstice rather than a normal lattice site; and **substitutions**.
- ❖ **Line defects** such as **dislocations** – edge and screw dislocations.
- ❖ **Surface or Planar defects** and **Grain boundary defects** such as stacking faults and twin boundaries
- ❖ **Volume defects** such as **voids**, gas bubbles and cavities

Figure 4.11 shows some examples of defects in crystals.

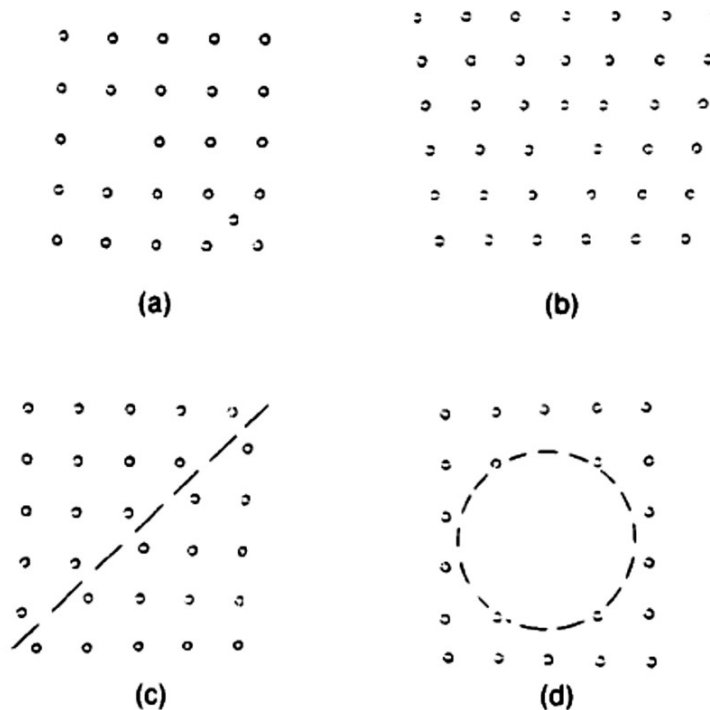


Figure 4.11: Some examples of defects or imperfections in crystals [(a) vacancy – interstitial, (b) dislocation, (c) stacking fault, and (d) void]

One can compute the number of point defects at equilibrium concentration at a certain temperature using the Arrhenius equation thus

$$N_{pd} = N_{sites} \exp\left[-\frac{Q_{pd}}{kT}\right] \quad [4.5]$$

Where N_{pd} is number of imperfections or point defects, N_{sites} is number of atomic sites or lattice sites per mole, k is Boltzmann's constant, Q_{pd} is free energy required to form the defect and T is absolute temperature. The free energy Q_{pd} is typically of order 1 eV [1 electron volt = 1.6×10^{-19} J]. In terms of eV, $k = 8.62 \times 10^{-5}$ eV/K. The above equation shows that the equilibrium number of vacancies for a given quantity of material depends on and increases with temperature. The number of point defects in a material may be reduced by slowly cooling the sample.

4.5 ALLOYS AND SOLUBILITY

Metals of commerce are rarely pure metals. Industrial metals contain impurities which may be regarded as alloying elements if they produce desirable effects or if they are added intentionally. An **alloy** or **solid solution** results if the atoms of one element known as the **solute** dissolve in [i.e. are completely accommodated within] the crystal structure of the other element known as the **solvent**. The term "*solvent*" denotes the element that is present in the greatest amount; sometimes they are called *host atoms*. In alloys solvent atoms are always metallic elements. On the other hand, "*solute*" denotes the element present in a minor concentration; it could be a metallic element or a non-metal. Examples of solid solutions or alloys are: **steel** [where iron is the solvent and carbon is the solute; other solutes can also be added], **brass** [copper is the solvent while zinc is the solute], **solder** [having lead and tin as solvent and solute respectively], etc.

Impurity point defects are found in solid solutions either as **substitutional** impurities or **interstitial** impurities. In the first case, the solute or impurity atoms replace or substitute for the host atoms in accordance with a number of rules which have come to be known as the **Hume**

Ruthery's Rules, namely:

- i. **Atomic size factor**: - This rule specifies that a substitutional solid solution will form between elements A and B only when the difference in atomic radii between the two atom types is less than about $\pm 15\%$.
- ii. **Crystal structure factor**: - This stipulates that for appreciable solid solubility to occur between A and B, the crystal structure [e.g. BCC, FCC, and HCP] for metals of both atom types must be the same.
- iii. **Electronegativity factor**: - This rule states that an **intermetallic compound** will form instead of a substitutional solid solution if the difference in electronegativities of A and B is wide. That is, one element should not be electropositive and the other electronegative.
- iv. **Valency factor**: - Other factors being equal, the solvent metal will tend to dissolve atoms of the solute if the solute is a metal of higher or same valency. That is, the solute must not have a valency less than that of the solvent.

A classic example of substitutional solid solution is found for alloys of copper and nickel, two of which are completely soluble in one another at all proportions. They are said to exhibit *unlimited or complete solid solubility*.

In the case of interstitial solid solutions, impurity atoms [which must be smaller in size compared to the solvent atoms] fill the voids or interstices among the host atoms. There is therefore a *limitation of solubility* to the extent to which interstices or voids are available in the lattice of the host metal and the extent impurity atoms can fit into these voids. In steels and cast irons for example, carbon atoms are found in the *interstitial sites* between iron atoms.

Instruction: Answer all the questions SERIALY as they appear. Use the space(s) provided below each question for your calculations and sketches. For questions that have numerical answers, you MUST enclose your answers in a box thus,

Ionic Character = 45%

1. Sketch the (100) and (123) planes and the [101] and [011] directions in a simple cubic unit cell.

DO YOUR SKETCHES AND CALCULATIONS ON THIS PAGE



2. In the cubic system, a plane has the intercepts $\frac{2}{3}$, ∞ and $\frac{1}{3}$ on the x-, y- and z-axes respectively. (i) Determine the indices of the plane. (ii) What are the indices of a direction that is normal to the plane?

3. According to the Allred and Rochow table, the Pauling electronegativity values of Mg, O, and Fe are 1.2, 3.5 and 1.8 respectively. (a) Compute the percent ionic character of the

inter-atomic bond for MgO and FeO. (b) What are the corresponding percent covalent characters?

4. Calculate the percent ionic and covalent characters for (a) CaF_2 , (c) SiO_2 , and (d) Si_3N_4 given that the electronegativity difference between the elements in each case are respectively: (a) 3.0, (c) 1.7, and (d) 1.2.

5. Using appropriated diagrams (sketches), determine the number of atoms per unit cell in FCC and BCC systems.

6. Given that the radius of iron atom is 0.1258nm in the BCC structure and 0.1292nm in the FCC structure, and $M = 55.85\text{g/mol}$, determine:
- i. The lattice constant a of the unit cell in each case;
 - ii. The unit cell volume V_c in each case;
 - iii. The total number of atoms per unit cell in each case; iv. The volume occupied by atoms, V_a , in both cases;
 - v. The theoretical density of iron for both allotropes.

7. Using appropriate sketches determine (a) the linear density along the [111] direction and; (b) the planar density of the (111) plane of the BCC unit cell.



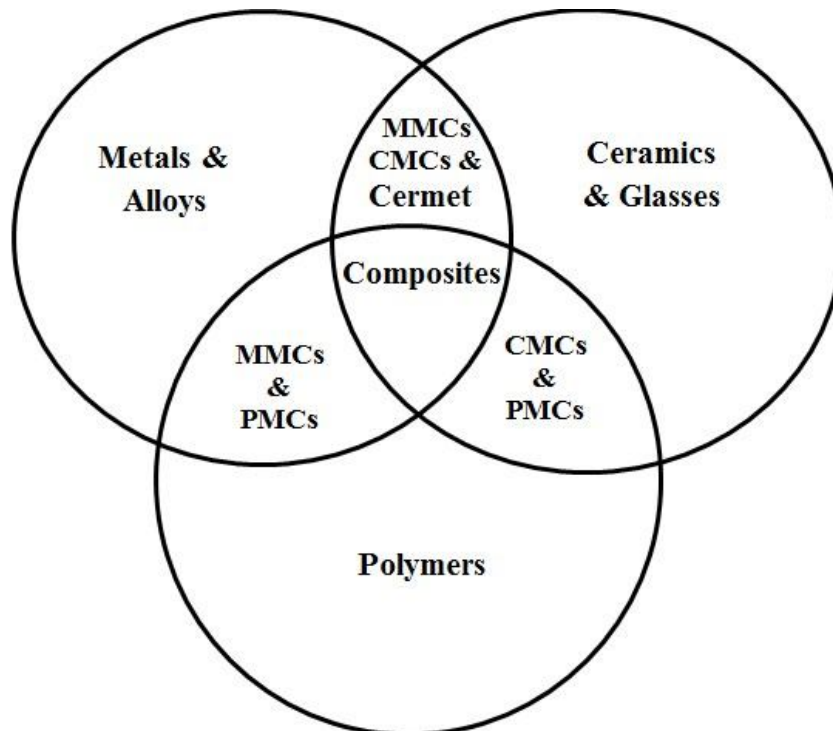
8. The theoretical density of copper was found to be 8.89 g/cm^3 while the handbook value is 8.94 g/cm^3 . Give reasons why the handbook (experimentally determined) value for the density of copper is slightly higher than theoretically calculated value.





TUTORIAL & ASSIGNMENTS WORKBOOK
For
(ENGINEERING MATERIALS I)

ENG 207





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