

3.1 INTRODUCTION

The matter which surround us is found to exist in three states viz, solids, liquids and gases.

All these materials are composed of atoms and molecules. The constituent particles; atoms or molecules of matter are held together through forces of attraction. *The attractive forces which hold the constituent particles of a substance together are called bonds.*

We know that, some solids are brittle, some are ductile, some are malleable, some are strong, some are weak, some are good conductors of heat and electricity, some are bad conductors of heat and electricity, some are magnetic, some are non-magnetic and so on. The reason for these different properties of the solids are due to their structure. That is, the behaviour of the solid materials is closely related to the structure of the material.

3.2 CLASSIFICATION OF SOLIDS

If we examine the solid materials with which we daily come across, we shall find that most of them do not have any characteristic difference in their outward appearance. But, if we

examine them under a microscope we shall find these materials have different internal atomic structures.

Based on the internal atomic structure, the solids can be classified into two categories namely (i) Crystalline (ii) Non-crystalline or Amorphous solids.

3.2.1 Crystalline Solids (Crystals)

Crystalline solids or crystals are those, in which the constituent atoms or molecules are arranged in an orderly fashion throughout in a three dimensional pattern.

Each atom or molecule is fixed at a definite point in space at a definite distance from and in a definite angular orientation to all other atoms or molecules surrounding it. Therefore, crystalline solids have well defined geometrical form (pattern), i.e., they have well defined faces and angles between them.

[In a crystal, the atoms are arranged like soldiers on a parade ground in a well defined columns and rows].

Further when crystal breaks, the broken pieces are all having regular shape. *The crystalline solids have directional properties and therefore they are called anisotropic substances.*

A crystalline material may be either in the form of a single crystal, (where the solid contains only one crystal) or an aggregate of many small crystals or grains separated by well defined grain boundaries also known as *polycrystalline solid*.

Few examples for crystalline solids: Copper, silver, aluminium, iron etc.

Crystallography: *The study of the geometric form and other physical properties of crystalline solids by using X-rays, electron beams and neutron beams etc., is termed as the science of crystallography.*

Note:

- **Grains:** The crystals are also known grains.
- **Grain boundary:** The boundary separating the two adjacent grains is called grain boundary.
- **Whisker:** Whiskers are nothing but artificially produced crystals. They are produced under some special conditions so that, they do not have any structure defects.
- **Examples for single crystals:** Sugar, common salt (NaCl), diamond etc. These single crystals are produced artificially from their vapour or liquid state.

3.2.2 Amorphous Solids (Non-crystalline Solids)

"Amorphous" means "without form".

In amorphous solids, the constituent particles, atoms or molecules are not arranged in an orderly fashion, i.e., The same atomic groups are arranged more randomly.

These solids have no directional properties and therefore they are called isotropic substances. These amorphous solids do not have a sharp melting point.

Examples: Plastics, rubber and glass.

Note:

- Supercooled liquids

The materials like glass, which exhibit some of the properties of a solid like hardness, definite shape etc., but are not crystalline, are regarded as supercooled liquids.

3.2.3 Difference between Crystalline and Non-crystalline Material

S. No.	Crystalline material	Non-crystalline material
1.	They have a definite and regular geometrical shapes which extend throughout the crystal.	They do not have definite geometrical shape.
2.	They are anisotropic.	They are isotropic.
3.	They are most stable.	They are less stable.
4.	They have sharp melting point.	They do not have sharp melting point.
	Examples: Diamond, NaCl, KCl	Examples: Glasses, plastics, rubber

3.3 CRYSTAL STRUCTURE

The crystal structure gives the arrangement and disposition of atoms within a crystal. *Determination of crystal structure with the help of X-rays is known as X-ray crystallography.*

X-rays are most widely used to study the crystal structure because the wavelength of X-rays (10^{-12} to 10^{-10} m) are most comparable with the inter atomic distances.

3.3.1 Fundamental Crystallographic Terms (Definitions)

1. Lattice

Lattice is defined as an array of points such that every lattice point has got the same environment or every point is indistinguishable from the other lattice point.

It is an imaginary concept.

2. Space Lattice or Crystal Lattice

Definition 1: A three dimensional collection of points in space is called a space lattice or crystal lattice. The environment about any particular point is in every way the same.

Definition 2: A geometrical representation of the crystal structure in terms of lattice points is called space lattice. Provided, the environment about every point is identical to that of every other point.

That is, space lattice is an idealised geometrical (imaginary) concept by which crystal structures can be described.

Explanation

We know that, a metal consists of a number of crystals, and each crystal in turn, consists of a large number of atoms.

Consider the cross-section of a crystal, in which the atoms be arranged in a rectangular pattern as shown in Figure 3.1.

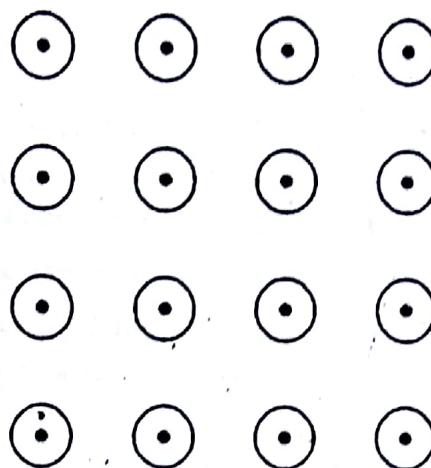


Figure 3.1: Arrangement of atoms [cross-section of a metal crystal]

From the Figure it may be noted that, each atom present in the crystal has its surroundings identical to that of every other atom. Now, if we replace all the atoms in this cross-section by points (corresponding to the centres of all atoms), then the resulting collection of points shown in Figure 3.2 is called a *lattice*. This is the case of a two dimensional lattice or *plane lattice*.

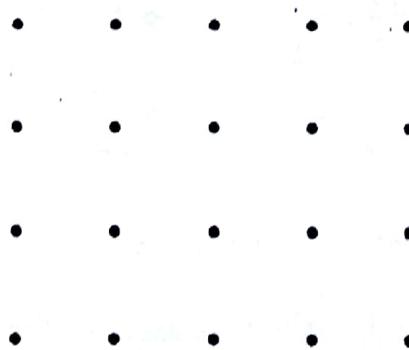


Figure 3.2: Plane lattice

Similarly, the group of lattice points in the three dimensional pattern is known as *crystal lattice* or *space lattice*.

It may be noted that, in a crystal lattice each point has its surrounding identical to that of every other point.

3. Lattice Points

Definition 1: Lattice points denote the position of atoms or molecules in the crystal.

Definition 2: The points in the space lattice are called lattice points.

4. Basis or Motif

A crystal structure is formed by associating with every lattice point a unit assembly of atoms or molecules (i.e., one or more atoms or molecules) identical in composition, arrangement and orientation. This unit assembly is called the basis or pattern or motif, Figure 3.3(b).

The logical relation is

$$\text{Space lattice} + \text{Basis} = \text{Crystal structure}$$

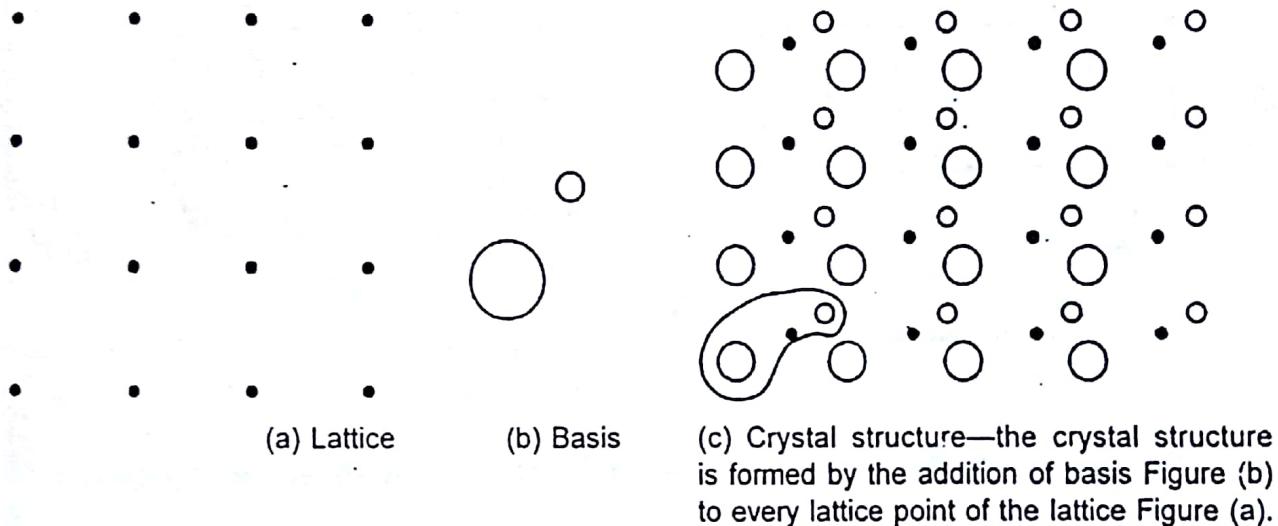


Figure 3.3: Formation of crystal structure

The number of atoms in the basis may be as low as one. Example, aluminium and barium. In NaCl and KCl the basis is two atoms and in CaF₂ the basis is three atoms. But, there are structures for which the basis exceeds 1000 atoms.

Note:

- A crystal lattice refers to the geometry of a set of points in space. Whereas, the crystal structure refers to the actual ordering or alignments of its constituent ions, atoms or molecules in the space.

5. Lattice Planes

A set of parallel and equally spaced planes in a space lattice which include all lattice points are called as lattice planes.

The different ways of drawing the lattice planes for the array of Figure 3.3(a) is shown in Figure 3.4.

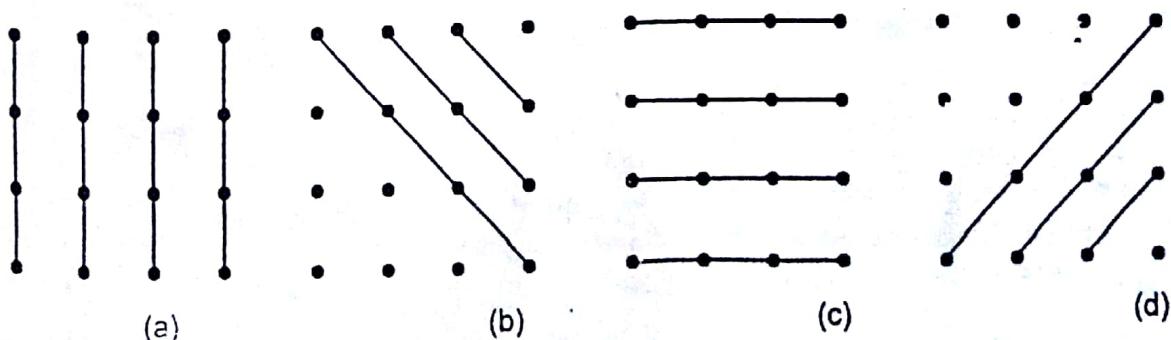
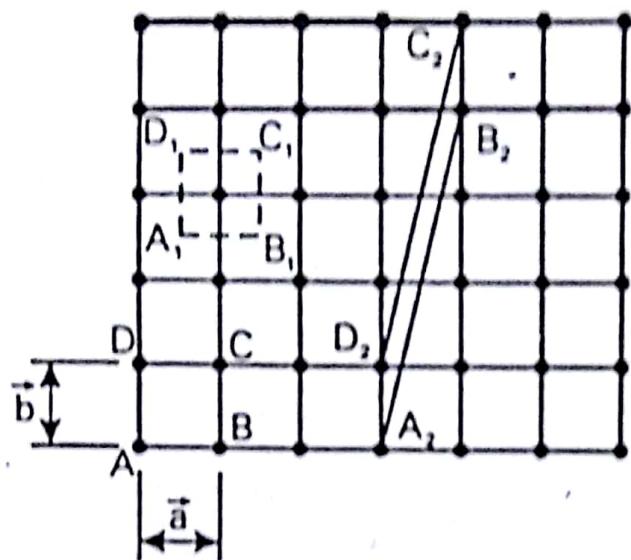


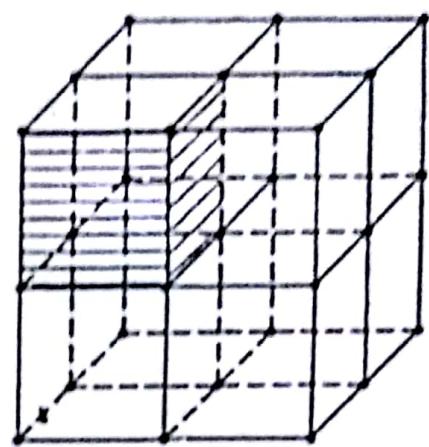
Figure 3.4: The different ways of drawing lattice planes

o. Unit Cell

The unit cell is the smallest block or geometric Figure from which the entire crystal is built up by repetitions in three dimensions.



(a) Two dimensional



(b) Three dimensional

Figure 3.5: Unit cell

Consider a two dimensional crystal lattice shown in Figure 3.5(a). When a parallelogram such as ABCD is rotated repeatedly by any integral multiple of vectors a , b then, corresponding to AB and AD whole pattern or array may be obtained. The whole crystal may thus be reproduced.

This region ABCD is called a unit cell and a , b the basis vectors.

7. Lattice Parameters

The Figure 3.6 shows a unit cell of a three dimensional crystal lattice.

The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes.

The intercepts a , b and c are nothing but the edges of the unit cell, (i.e., the distance between two lattice points) which defines the dimensions of an unit cell. *These intercepts are known as its primitives or characteristic intercepts along the axes.*

These three quantities a , b and c are also *called the fundamental translational vectors.* The angles between (a, b) , (b, c) and (c, a) are denoted by γ , α and β respectively. *The three angles (α , β and γ) are called interfacial angles.*

Both, the intercepts and interfacial angles constitute the lattice parameters of the unit cell.

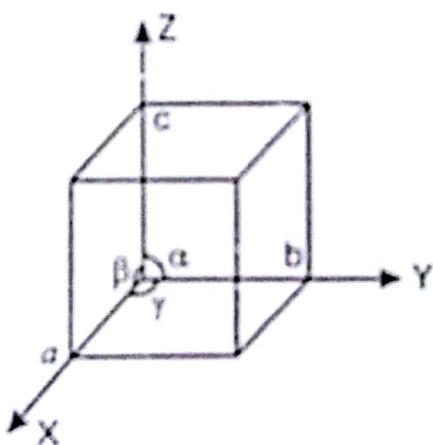


Figure 3.6: Lattice parameters

The form and actual size of the unit cell can be determined if the values of intercepts and interfacial angles are known.

Table 3.1: Seven crystal system and their Bravais Lattice

<i>System</i>		<i>Bravais Lattice</i>
Cubic	3	SC or P, BCC or I, FCC or F
Tetragonal	2	SC or P, BCC or I
Orthorhombic	4	SC or P, BCC or I, FCC or F & Base centered or C
Monoclinic	2	SC or P, Base centered or C
Triclinic	1	SC or P
Trigonal	1	SC or P
Hexagonal	1	SC or P
Total	14	-

Table 3.2: The 7 Crystals Systems and their 14 Bravais lattices

System	Bravais lattice	Unit cell Characteristics	Characteristic Symmetry elements	Example
Cubic	Simple (P)	$a = b = c$	Four 3-fold rotation axes	
	Body centered (I)	$\alpha = \beta = \gamma = 90^\circ$	(along cube diagonal)	
	Face centered (F)			
Tetragonal	Simple (P)	$a = b \neq c$	One 4-fold rotation axis	
	Body centered (I)	$\alpha = \beta = \gamma = 90^\circ$		
Orthorhombic	Simple (P)	$a \neq b \neq c$	Three mutually orthogonal	
	Base centered (C)	$\alpha = \beta = \gamma = 90^\circ$	2-fold rotation axes	
	Body centered (I)			
	Face centered (F)			
Monoclinic	Simple (P)	$a \neq b \neq c$	One 2-fold rotation axis	
	Base centered (C)	$\alpha = 90^\circ \neq \gamma$		
Triclinic	Simple (P)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	None	
Trigonal (Rhombohedral)	Simple (P)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	One 3-fold rotation axis	
Hexagonal	Simple (P)	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	One 3-fold rotation axis	

3.6 MILLER INDICES

Introduction

In a crystal, there exists direction and planes which contain a large concentration of atoms.

Therefore, it is necessary to locate these directions and planes for a crystal to analyse. The problem is that, how to identify the direction and to designate (to choose) a plane in a crystal.

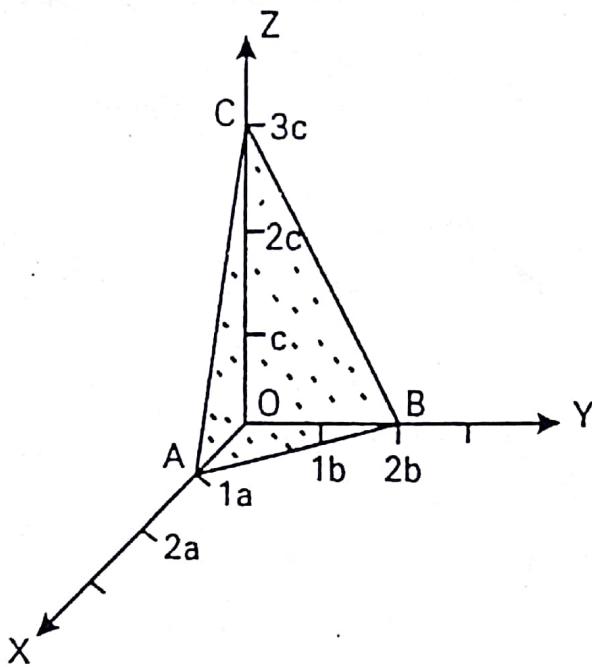


Figure 3.16: Crystal plane

Here, let us discuss briefly the method of designating a plane in crystal. This method was suggested by Miller.

Miller indices

Miller introduced a set of three numbers to designate a plane in a crystal. This set of three numbers is known as Miller indices of the concerned plane.

3.6.1 Procedure for Finding Miller Indices (Steps in the determination of Miller indices)

The steps in the determination of Miller indices of a plane are illustrated with the aid of Figure 3.16. Consider the plane ABC which cuts 1 unit along the X-axis, 2 units along the Y-axis and three units along the Z-axis.

Step 1:

Find the intercept of the plane ABC along the three axes X, Y, and Z. Let it be OA, OB and OC. Express the intercepts in terms of multiples of axial lengths, i.e., lattice parameters. Let them be $OA = pa$, $OB = qb$ and $OC = rc$ where p, q and r are the intercept numerical values along the three axis.

In this example shown:

$$p = 1, q = 2 \text{ and } r = 3$$

$$\begin{aligned} \text{Hence, } OA : OB : OC &= pa : qb : rc \\ &= 1a : 2b : 3c \end{aligned}$$

Therefore, the intercepts are 1a, 2b and 3c along the three axes.

Step 2:

Find the reciprocal of the numerical intercept values.

$$\text{i.e., } \frac{1}{p} \frac{1}{q} \frac{1}{r}$$

For the example shown the reciprocal of the numerical intercept values are

$$\frac{1}{1} \frac{1}{2} \frac{1}{3}$$

Step 3:

Convert these reciprocals into whole numbers by multiplying each with their least common multiple (LCM). In this example the LCM is 6. Therefore,

$$6 \times \frac{1}{1} \quad 6 \times \frac{1}{2} \quad 6 \times \frac{1}{3}$$

1 3 2

Step 4:

Enclose these numbers in bracket. This represents the indices of the given plane, and is called the Miller indices of the plane. For the example shown, the Miller indices are (6 3 2).

It is generally denoted by (hkl). It can also be noticed that

$$h : k : l = \frac{1}{p} : \frac{1}{q} : \frac{1}{r}$$

Definition - 1: Thus, Miller indices may be defined as the reciprocal of the intercepts made by the plane along the three crystallographic axes which are reduced to smallest numbers.

Definition - 2: Miller indices are the three smallest possible integers, which have the same ratio as the reciprocals of the intercepts of the plane concerned along the three axes.

Note:

- The indices of a plane is represented by a small bracket (hkl). Sometimes, the notations <> and [] or { } are also used.
- Negative indices are represented by putting a bar over the digit.

Example: $(\bar{1}\bar{1}0), (\bar{1}0\bar{1})$

3.6.2 Important Features of Miller Indices of Crystal Plane

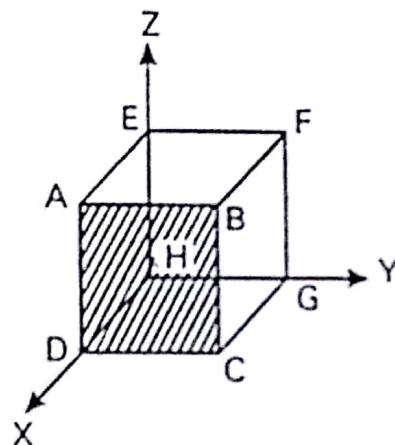
For the cubic crystal especially, the important features of Miller indices are:

- For an intercept at infinity, the corresponding index is zero, that is, if a plane is parallel to any one of the coordinate axis, then its intercept is at infinity. Hence, the Miller index for that axis is zero.
- All equally spaced parallel planes have the same Miller indices ($h k l$) or vice versa, that is, if the Miller indices of two planes have the same ratio like (8 4 4), (4 2 2) and (2 1 1) then the planes are parallel to each other.
- The indices ($h k l$) do not define a particular plane, but a set of parallel planes.

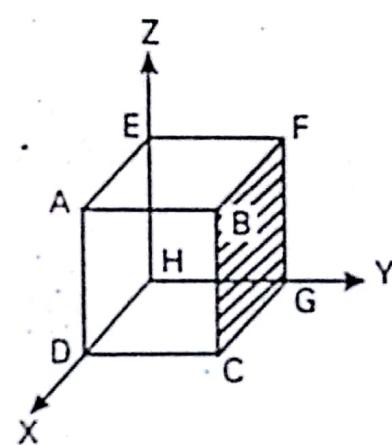
- It is only the ratio of the indices which is important in this notation.
- If a plane cuts the axis on the negative side of the origin, corresponding index is negative.

Examples

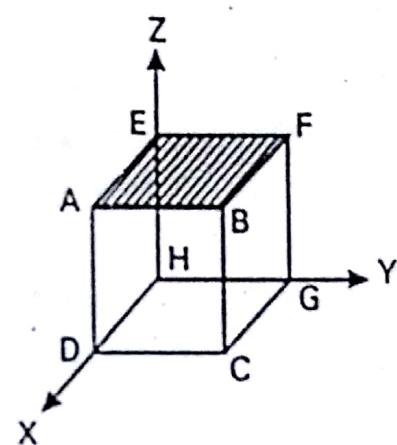
- For the Figures 3.17 a, b and c shown, the Miller indices of the plane ABCD, BFGC and AEFB are $(1\ 0\ 0)$, $(0\ 1\ 0)$ and $(0\ 0\ 1)$ respectively.



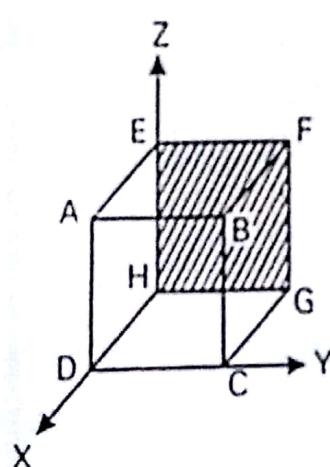
(a) plane $(1\ 0\ 0)$



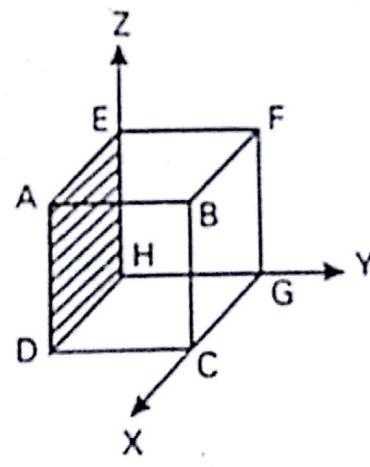
(b) plane $(0\ 1\ 0)$



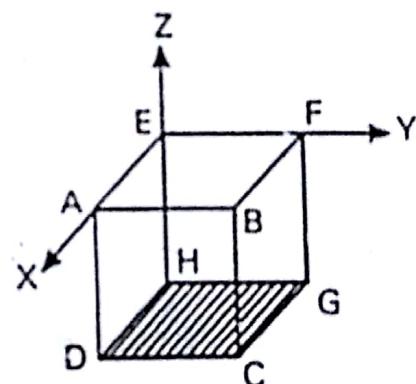
(c) plane $(0\ 0\ 1)$



(d) plane $(\bar{1}\ 0\ 0)$



(e) plane $(0\ \bar{1}\ 0)$



(f) plane $(0\ 0\ \bar{1})$

Figure 3.17: Crystal planes

- For an intercept along the negative axis, the indices of the plane are represented by taking the reciprocals of the intercept and placing a bar ($\bar{-}$) over the integer (intercept value).

For the Figures 3.17(d, e and f) shown, the Miller indices are $(1\ 0\ 0)$, $(0\ 1\ 0)$ and $(0\ 0\ 1)$ respectively.

To draw these planes the points D, G and E are taken as the origin.

3.6.3 Procedure for Sketching the Plane from the given Miller Indices

The following procedure is adopted for sketching any plane when, its Miller indices are given.

As a first step, take the reciprocals of the given Miller indices.

These reciprocals represent the intercepts in terms of the axial units along the X, Y and Z axes respectively.

For example, let the Miller indices be (221). Therefore, its reciprocals of intercepts will be $\frac{1}{2}, \frac{1}{2}$ and $\frac{1}{1}$ or 0.5, 0.5 and 1 respectively.

Now sketch the plane with intercepts of 0.5, 0.5 and 1 along the X, Y and Z axes respectively as shown in Figure 3.18.

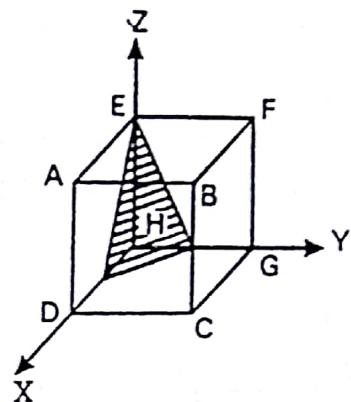


Figure 3.18: (221) Plane

3.6.4 Common Planes in a Simple Cubic Structure

Even though, there are a number of planes that can be drawn, the most common planes in a simple cubic structure are (1 0 0), (1 1 0) and (1 1 1).

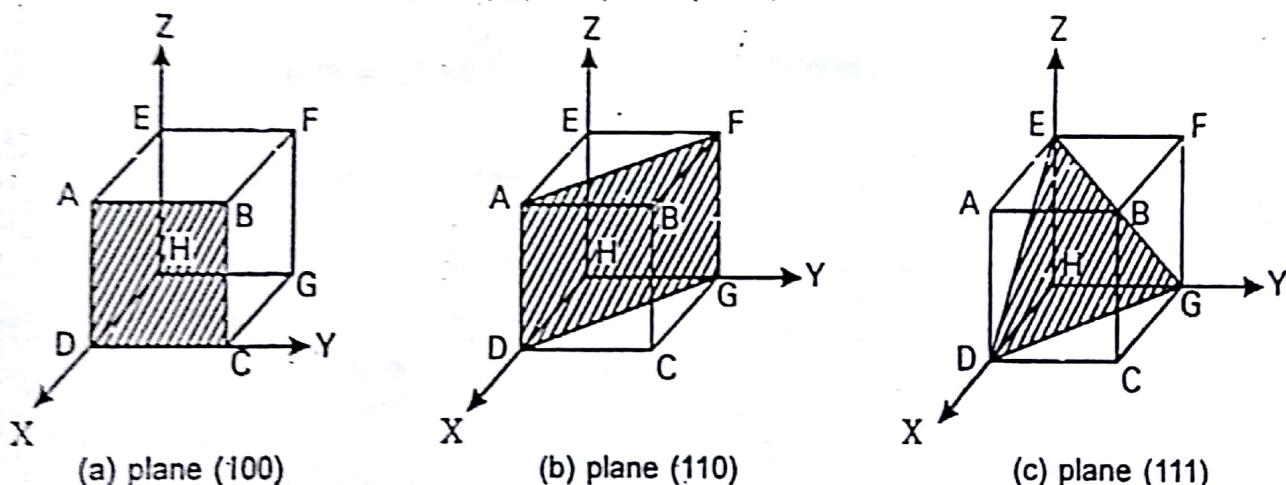


Figure 3.19: Common planes in a SC

The three most important planes in a simple cubic structure are shown in Figure 3.19 and the way of drawing all the above planes are explained one by one.

(a) Plane (100)

In this case $h = 1$, $k = 0$ and $l = 0$. The reciprocals of h , k and l are

$$\frac{1}{1} \frac{1}{0} \frac{1}{0} = 1 \infty \infty$$

Now, sketch the plane with intercepts $(1, \infty, \infty)$ along the X, Y and Z axes respectively, see Figure 3.19(a).

(b) Plane (110)

In this case $h = 1$, $k = 1$ and $l = 0$. The reciprocals of h , k and l are

$$\frac{1}{1} \frac{1}{1} \frac{1}{0} = 1 1 \infty$$

Now, sketch the plane with intercepts $(1, 1, \infty)$ along the X, Y and Z axes respectively, see Figure 3.19(b).

(c) Plane (111)

In this case $h = 1$, $k = 1$ and $l = 1$. The reciprocals of h , k and l are

$$\frac{1}{1} \frac{1}{1} \frac{1}{1} = 111$$

Now, sketch the plane with intercepts $(1, 1, 1)$ along the X, Y and Z axes respectively, see Figure 3.19(c).

$$\left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \right] = \{1\ 0\ 0\}$$

The collective notation for a family of planes is $\{h\ k\ l\}$.

Each plane is identical except for the consequences of our arbitrary choice of axis labels and directions.

Similarly $\{1\ 1\ 1\}$ family includes eight planes and the $\{1\ 1\ 0\}$ family includes 12 planes.

Example 3.1

Figure 3.15 shows the three crystal planes. Compute the Miller indices of the given planes.

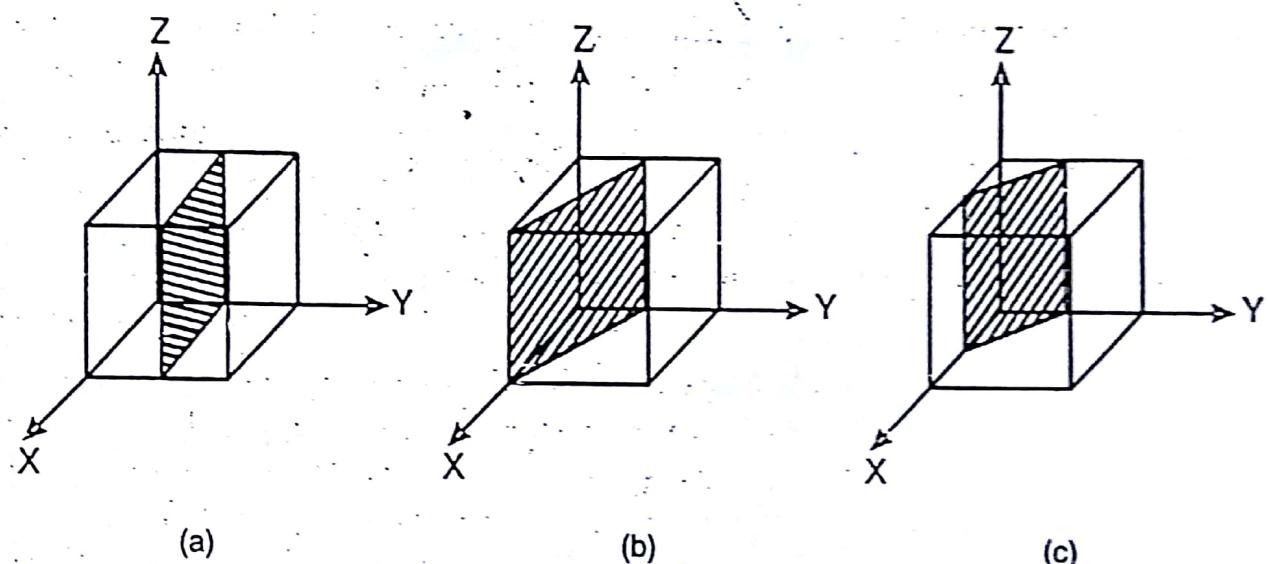


Figure 3.21:

Solution:

In Figure 3.21(a) the given plane is parallel to X and Z axes. Thus, its numerical intercepts on these two axes are infinity.

The numerical intercept on Y axis is $1/2$ or 0.5 . Thus, the numerical intercepts of the plane is $(\infty, 1/2, \infty)$.

Therefore, the Miller indices of the plane is $(0\ 2\ 0)$.

In Figure 3.21(b) the given plane is parallel to Z axis. Thus, its numerical intercept on the Z axis is infinity.

The numerical intercept on X axis is 1 and Y axis is $1/2$. Thus, the numerical intercepts of the plane is $(1, 1/2, \infty)$

Therefore, the Miller indices of the plane is $(1\ 2\ 0)$.

In Figure 3.21(c) the given plane is parallel to Z axis. Thus, its numerical intercept on this Z axis is infinity.

The numerical intercept on X and Y axis is $1/2$ and $1/2$ respectively. Thus, the numerical intercepts of the plane is $(1/2, 1/2, \infty)$.

Therefore, the Miller indices of the plane is $(2\ 2\ 0)$.

Example 3.2

Draw the planes in a cubic structure for the given Miller indices, $(1\ 1\ 2)$, $(0\ 0\ 1)$, $(1\ 0\ 1)$, $(2\ 0\ 0)$ and $(\bar{1}\ 0\ 0)$.

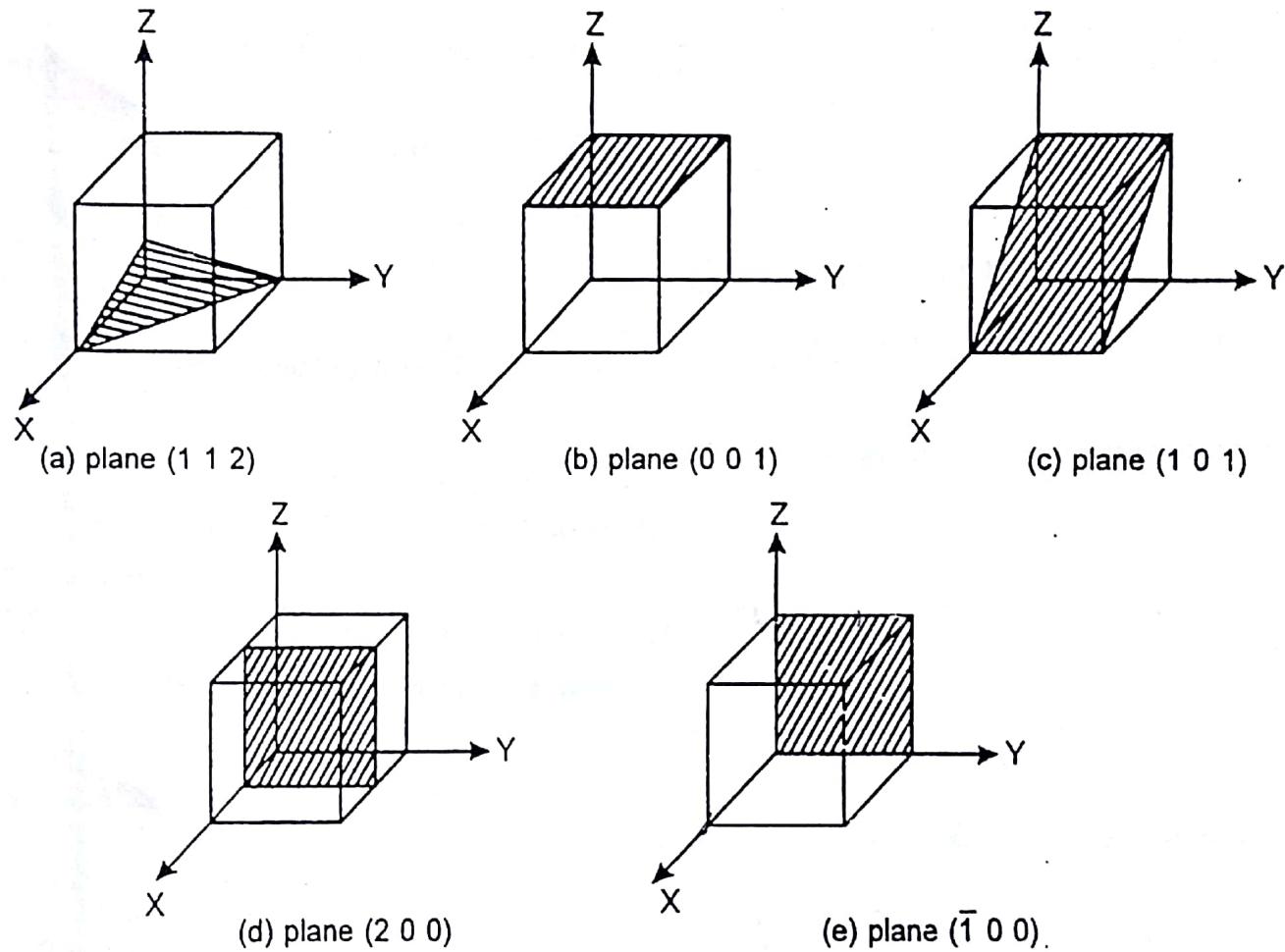


Figure 3.22