

Atomic arrangement in solid

As compared to gaseous and liquid state, the atoms and molecules in solid state are more closely-packed and are held together by strong mutual forces of attraction. These interatomic forces are basically electrostatic in nature and are a direct consequence of the electronic structure of matter. When atoms come close and finally unite to form molecules, their electrons *rearrange themselves in such a way as to achieve a stable configuration*. This rearrangement of electrons gives rise to different types of bonds which hold the atoms together in a solid state. The principle types of bonds in solids are:

- (i) Ionic or electrovalent bonds
- (ii) Covalent or homopolar bonds
- (iii) Metallic bonds *and*
- (iv) Molecular bonds (Van der Waal's forces)

These bonds are electrostatic in origin and, in many cases, determine the characteristic physical properties of a solid. Depending on the type of bonding force, the different solids may be categorized as follows:

- (i) Ionic or electrovalent solids: NaCl, MgO, CaF₂.
- (ii) Covalent or homopolar solids: C, Si, Ge.
- (iii) Metallic solids: Na, Al, Cu, Ag.
- (iv) Molecular solids: Solid Ar, solid Kr and solid Xe.

Ionic bonds

Ionic bonding is the electrostatic force of attraction between positively and negatively charged ions (between non-metals and metals). These ions have been produced as a result of a transfer of electrons between two atoms with a large difference in electro negativities. The metallic elements have only up to the valence electrons in their outer shell will lose their electrons and become positive ions, whereas electronegative elements tend to acquire additional electrons to complete their octet and become negative ions. NaCl is a typical example of ionic bonding.

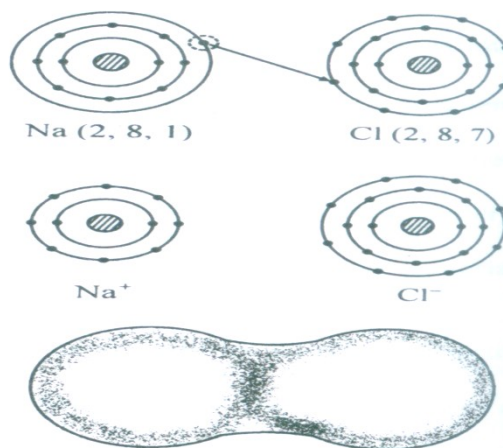


Fig. 1. Ionic bond

Consider the formation of ionic bond in NaCl. Notice that when sodium loses its one valence electron it gets smaller in size, while chlorine grows larger when it gains an additional valence electron. After the reaction takes place, the charged Na^+ and Cl^- ions are held together by electrostatic forces, thus forming an ionic bond. When the Na^+ and Cl^- ions approach each other closely enough so that the orbits of the electron in the ions begin to overlap each other, then the electron begins to repel each other by virtue of the repulsive electrostatic Coulomb force. Of course the closer together the ions are the greater the repulsive force. But the repulsive forces are of shorter range than the attractive one.

Covalent bonds

A covalent bond is formed when two similar or dissimilar atoms (*between non-metals and non-metals*) achieve stability by sharing valence electrons (*i.e., s and p electrons*) between themselves. By sharing electrons, the two atoms, acquire the noble gas electronic configuration. The compound so formed is known as *covalent* compound. Each electron in a shared pair is attracted to both nuclei involved in the bond.

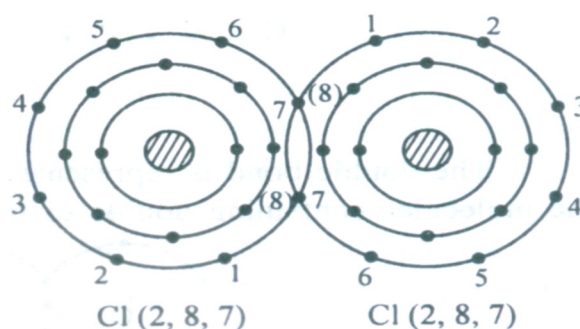


Fig. 2. Covalent bond

Consider the case of Cl atoms. As shown in fig. 2, each Cl atom has 7 valence electrons. Covalent bond is established between the two atoms because each contributes one electron and the electron *pair* is shared by the two atoms so that each has 8 electrons in its valence shell thereby achieving stability, *i.e.*, each chlorine atom achieves argon structure.

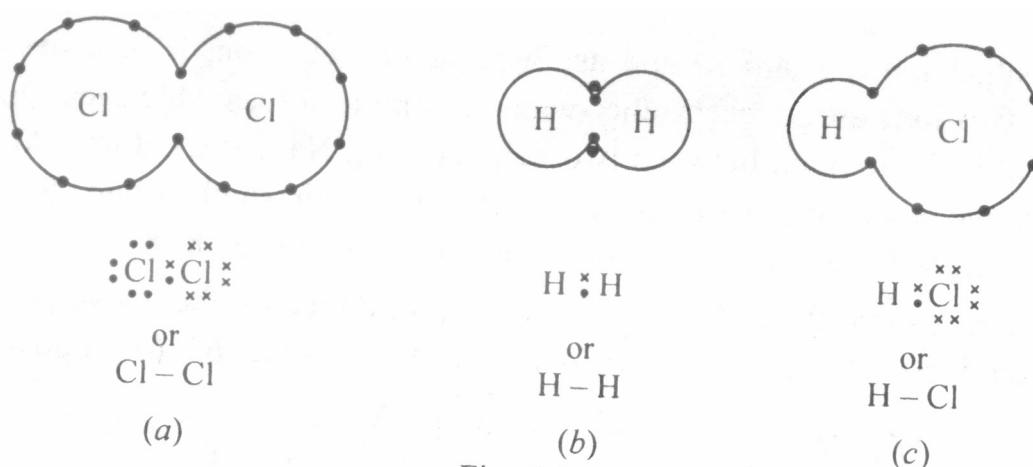


Fig. 3. Covalent bond

For clarity sake, the two electrons have been shown by dots and crosses in fig. 3(a). Similarly, covalent bond between hydrogen atoms is created due to their sharing their 1s electrons [fig. 3(b)]. The two hydrogen atoms acquire helium structure. Fig. 3(c) shows covalent bond between hydrogen and chlorine atoms. In this case, hydrogen achieves helium structure whereas chlorine achieves the argon structure.

Metallic bonds

Metallic bonding is the type of bonding found in metal elements. This is the electrostatic force of attraction between positively charged ions and delocalized outer electrons. A metallic bond results from the sharing of a *variable* number of electrons by a *variable* number of atoms. In metals, each atom loses all its valence electrons and becomes positively-charged ion. All valence electrons in a metal combine to form *cloud of electrons* that move freely between the atom cores. The positively charged cores are held together by these negatively charged electrons. The metallic bond is weaker than the ionic and the covalent bonds.

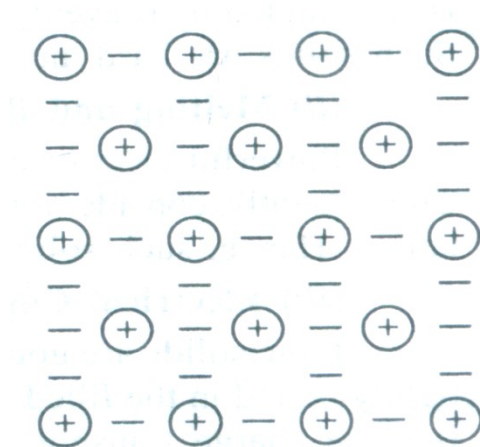


Fig. 4. Metallic bonds

Molecular bonds

It occurs for those elements or compounds whose electronic configuration is such that little electron transfer between their atoms. The explanation of these weak forces of attraction is that there are natural fluctuation in the electron density of all molecules and these cause small temporary dipoles within the molecules. It is these temporary dipoles that attract one molecule to another by a force called Vander Waals' forces.

Therefore atoms or molecules containing dipoles are attracted to each other by electrostatic forces. These forces are due to the electrostatic attraction between the nucleus of one atom and the electrons of the other. Van der Waals interaction occurs generally between atoms which have noble gas configuration.

Characteristics of Ionic solids

Ionic solids are found to possess the following properties:

Crystal structure: Ionic solids have crystalline structure. Their compounds are *ions* not molecules. For example, in NaCl crystal, each Na^+ ion is surrounded by 6 evenly-spaced negative Cl^- and every Cl^- ion is surrounded by 6 Na^+ ions. Such solids are hard and brittle.

Melting and boiling points: Powerful electrostatic forces exist between the ions in the crystal lattice of an ionic solid. Considerable energy is required to overcome these forces and break down the crystal lattice. Hence, Ionic solids have high melting and boiling points.

Electrical conductivity: Ionic solids are good insulators. There is no electronic conduction because the electrons are tightly bound in the filled shell of the two types of ions involved. However, in ionic crystals, there is some charge transport by the *charged ions themselves*. In other words, ions are the charge carriers. Since ionic mobility increases with temperature, the electrical conductivity of the ionic solids also increases with temperature.

Solubility: Ionic solids are readily soluble in solvents like water (H_2O) and liquid ammonia (NH_3) because their molecules interact strongly with the crystal ions. Dissolution is also favored by the decrease of the electrostatic force between crystal ions because of the high permittivity of the solvents.

Ionic reactions: Ionic reactions are practically *instantaneous* (i.e. precipitation). For example, Cl^- ions present in NaCl and BaCl_2 give a white precipitate of AgCl as soon as Ag^+ ions in the form of AgNO_3 solution are mixed.

Relation between the lattice constant and the density of crystal material:

Let us consider a unit cell with volume V (cm^3), which can be calculated from the unit cell dimensions. Let ρ (gm/cm^3) be the density of the crystal. Then the weight of the matter in the unit cell will be $V \times \rho$.

If n is the number of atoms or molecules per unit cell and M being the atomic (molecular) weight of one atom or molecule. Then the weight of matter in the unit cell is given by $n \frac{M}{N}$.

$$\text{Thus } n \frac{M}{N} = V \times \rho$$

$$\therefore n = \frac{V \times \rho \times N}{M}$$

For a cubic crystal, $V = a^3$. Thus

$$n = \frac{a^3 \times \rho \times N}{M}$$

$$\therefore a^3 \rho = n \frac{M}{N}$$

Mathematical Problems

Problem-1: The atomic weight of silver is 108. It has lattice constant 4.077 \AA . Calculate the density of silver if it has the fcc structure.

Solution: We know

$$\rho = \frac{nM}{a^3 N}$$

$$\therefore \rho = \frac{4 \times 108}{(4.077 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

$$\therefore \rho = 10.58 \text{ gm}/\text{cm}^3 (\text{Ans})$$

Here,

$$n = 4$$

$$M = 108 \text{ gm}$$

$$N = 6.023 \times 10^{23}$$

$$a = 4.077 \times 10^{-8} \text{ cm}$$

$$\rho = ?$$

Problem-2: Calculate the number of atoms per unit cell for a face centered cubic (fcc) lattice of copper crystal. Given $a = 3.60 \text{ \AA}$, Atomic weight of copper = 63.6 and density of copper = 8.86.

Solution: We know

$$n = \frac{a^3 N \rho}{M}$$

$$\therefore n = \frac{(3.60 \times 10^{-8})^3 \times 6.023 \times 10^{23} \times 8.86}{63.6}$$

Here,

$$a = 3.60 \times 10^{-8} \text{ cm}$$

$$M = 63.6 \text{ gm}$$

$$\rho = 8.86 \text{ gm}/\text{cm}^3$$

$$N = 6.023 \times 10^{23}$$

$$n = ?$$

$$\therefore n = 3.96 \approx 4 \text{ (Ans)}$$

Problem-3: NaCl has fcc structure. The density of sodium chloride is 2180 kg/m^3 . Calculate the distance between two adjacent atoms. Given the atomic weight of sodium=23 and the Chlorine=35.5. Take $N = 6.02 \times 10^{23}$ per kg-mole.

Solution: We know

$$a^3 = \frac{nM}{\rho N}$$

$$\therefore a = \left(\frac{4 \times 58.5 \times 10^{-3}}{2180 \times 6.023 \times 10^{23}} \right)^{1/3}$$

$$\therefore a = 5.63 \times 10^{-10} \text{ cm}$$

Distance between the adjacent atoms

$$d = \frac{a}{2} = \frac{5.63 \times 10^{-10}}{2} = 2.815 \times 10^{-10} \text{ cm} = 2.815 \text{ \AA} \text{ (Ans)}$$

Here,

$$n = 4$$

$$\rho = 2180 \text{ kg/m}^3$$

$$M = (23 + 35.5) \text{ gm} = 58.5 \text{ gm}$$

$$= 58.5 \times 10^{-3} \text{ kg}$$

$$N = 6.023 \times 10^{23}$$

$$d = ?$$

Problem-4: Iron has bcc structure. Its density is 7.86 gm/cm^3 and. Atomic weight of Iron is 55.85. Calculate the dimension of the unit cell.

Solution: Do yourself. (Ans: 2.87 \AA)

Unit face, Numerical Parameter & Axial units

In fig. 1, let OX , OY and OZ be taken as the reference axes. The faces $a_3 b_1 c_1$ and $a_2 b_3 c_6$ make certain intercepts or segments on these axes. The first face or plane intercepts segments of oa_3 , ob_1 and oc_1 and the second – oa_2 , ob_3 and oc_6 . These segments represent the respective *linear parameters* of the two faces.

It is seen that the first face intercepts one spacing along each axis whereas second face intercepts two, three and six spacing's along the respective axes. The first face is called the *unit face* which may be defined as *the face which makes one intercept on each axes*.

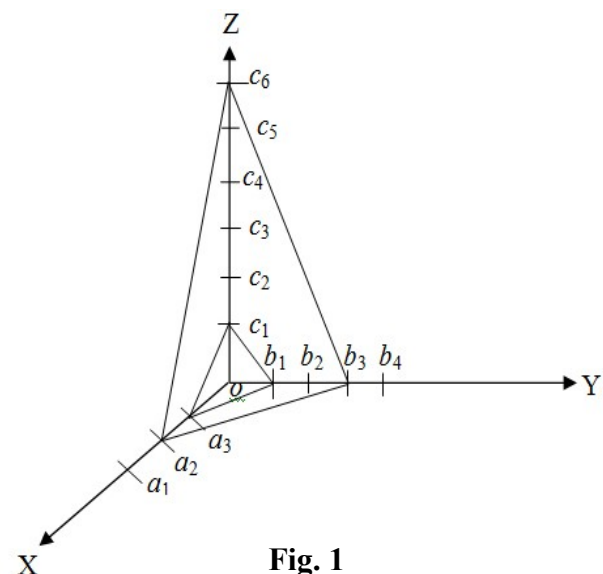


Fig. 1

Obviously, the unit face produces three values which are related to each other as $1 : 1 : 1$. The second face produces three values $2a$, $3b$, $6c$ which are related to each other as $2 : 3 : 6$. These figures of 1, 2, 3, and 6 represent the *numerical parameters* of the faces and must be whole numbers.

Linear parameters intercepted by the *unit face* are called the *axial units*. In the present case, these are a_1 , b_1 , and c_1 although they are represented generally by a , b , and c along X , Y , and Z axes respectively.

Miller indices

The position and orientation of a crystal plane is determined by three numbers (integers) is called Miller indices. It is denoted by $(h\ k\ l)$.

Determination of Miller Indices:

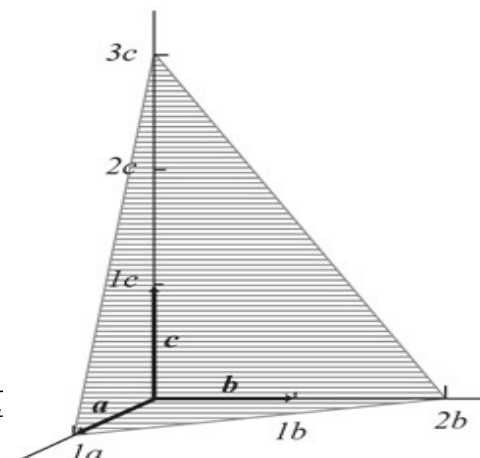
- (v) Taking any atom in the crystal as the origin and erect coordinate axes from this atom.
- (vi) Taking intercepts on the axis a , b , c in terms of the lattice constants.
- (vii) Taking the reciprocal of these intercepts.
- (viii) Taking the lowest common multiple of the denominator.
- (ix) Multiplying each reciprocal by the lowest common multiple of the denominator, thus obtained into smallest set of integers. These integers are denoted by h , k , l .
- (x) The result is conventionally enclosed in first parenthesis (hkl) which is Miller indices of the plane. The meaning of these indices is that a set of parallel planes (hkl) cuts the a -axis into h parts, the b -axis into k parts and the c -axis into l parts.

While finding Miller Indices of a plane, following points should be kept in mind:

- (xi) When the plane is parallel to one of the coordinate axes, it is said to meet that axis at infinity. Since $\frac{1}{\infty} = 0$, the miller index for that axis is zero.
- (xii) If a plane cuts on axis on the negative side of the origin, the corresponding index is negative and is indicated by a bar sign, above the index $(\bar{h}\ \bar{k}\ \bar{l})$.

Example: The figure shows a plane whose intercepts are $1a, 2b, 3c$. The Miller indices of the family to which this plane belongs are obtaining by taking the reciprocals of these numbers: $1, \frac{1}{2}, \frac{1}{3}$ and reducing these fractions to the smallest set of integers. This can be done by multiplying each of the fractions by the lowest common multiple of the denominator 6. In this case we get 6, 3, 2.

Thus the Miller indices of this plane are (632)



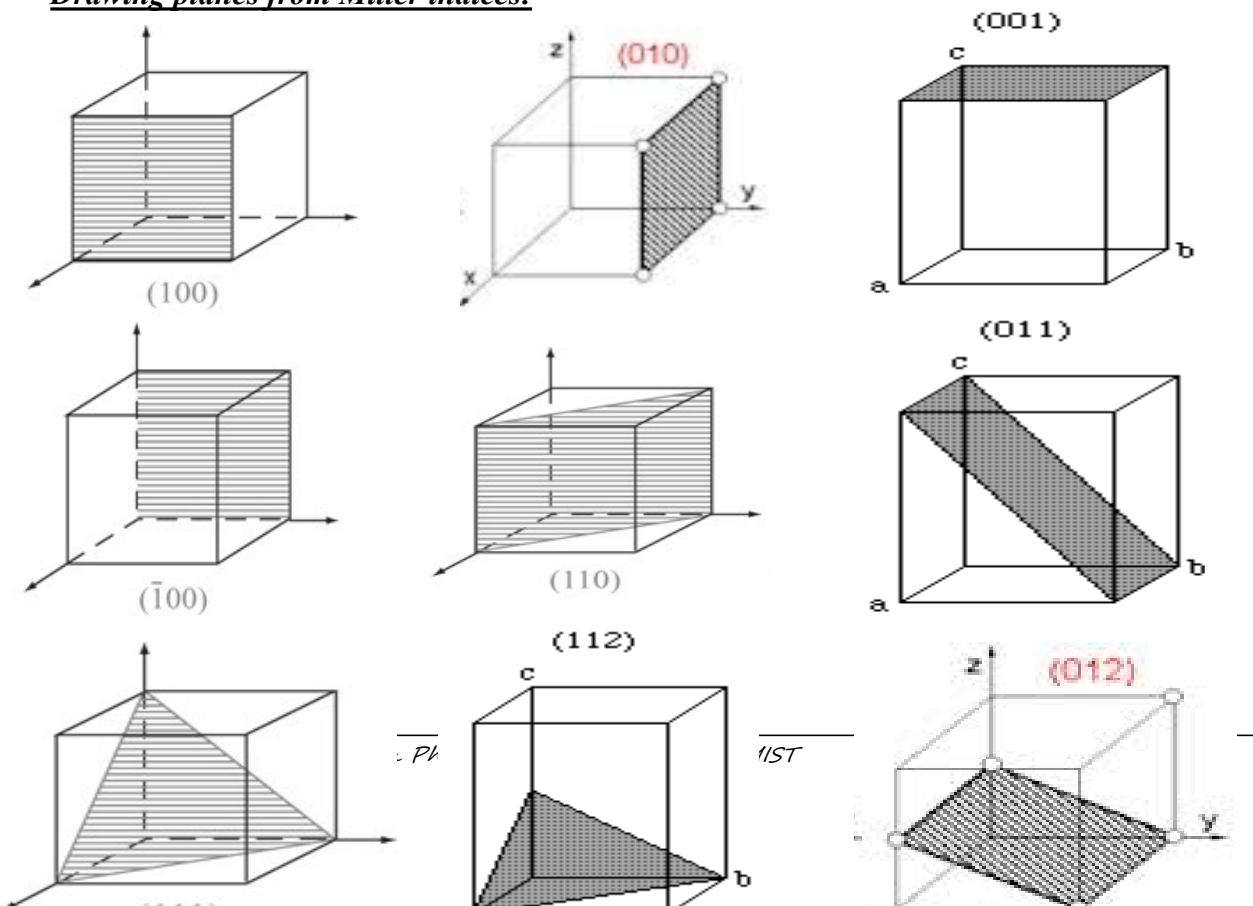
Miller indices for planes in each of the following sets of intercepts:

- (i) $a, 2b, \infty$ (ii) $a, \frac{b}{2}, c$ (iii) $3a, 3b, 3c$

Solution: (i) It indicates a plane whose intercepts are $a, 2b, \infty$. For c -axis the intercept is at ∞ . The Miller indices of the family to which this plane belongs are obtained by taking the reciprocals of these numbers: $1, \frac{1}{2}, \frac{1}{\infty}$. From this we can write: $1, \frac{1}{2}, 0$. For reducing these fractions to the smallest set of integers, multiply each of the fractions by the lowest common multiple of the denominator 2. In this case we get the Miller indices $(2, 1, 0)$.

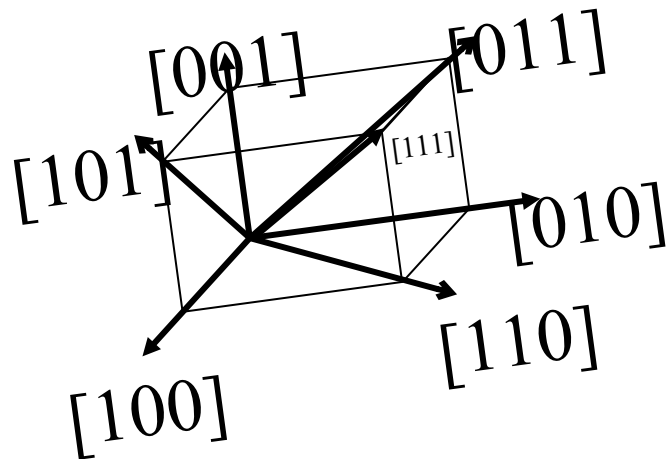
(ii) It indicates a plane whose intercepts are $a, \frac{b}{2}, c$. The Miller indices of the family to which this plane belongs are obtained by taking the reciprocals of these numbers: $1, 2, 1$ and reducing these fractions to the smallest set of integers. This can be done by multiplying each of the fractions by the lowest common multiple of the denominator 1. In this case we get the Miller indices $(1, 2, 1)$.

(iii) It indicates a plane whose intercepts are $3a, 3b, 3c$. The Miller indices of the family to which this plane belongs are obtained by taking the reciprocals of these numbers: $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ and reducing these fractions to the smallest set of integers. This can be done by multiplying each of the fractions by the lowest common multiple of the denominator 3. In this case we get the Miller indices $(1, 1, 1)$.

Drawing planes from Miller indices:

Direction of plane: Any vector drawn from the origin to a lattice point is defined as direction. It is denoted by $[hkl]$. For example, in a cubic unit cell, if the origin is at the one corner and axes are parallel to the edges, the body diagonal would be represented as $[111]$.

$[hkl]$: The direction specified by this symbol is obtained as follows: Move from the origin over a distance ha along the a -axis, kb along the b -axis and lc along the c -axis. The vector connecting the origin with the point so obtained is then the direction specified by the symbol $[hkl]$. Thus in a cubic crystal, the direction of the X-axis is indicated by $[100]$, the Y-axis by $[010]$ and the Z-axis by $[001]$. Similarly, the direction of the negative X-axis is indicated by $[\bar{1}00]$, the negative Y-axis by $[0\bar{1}0]$ and the negative Z-axis by $[00\bar{1}]$.



In cubic crystal $[hkl]$ direction is normal to the (hkl) plane:

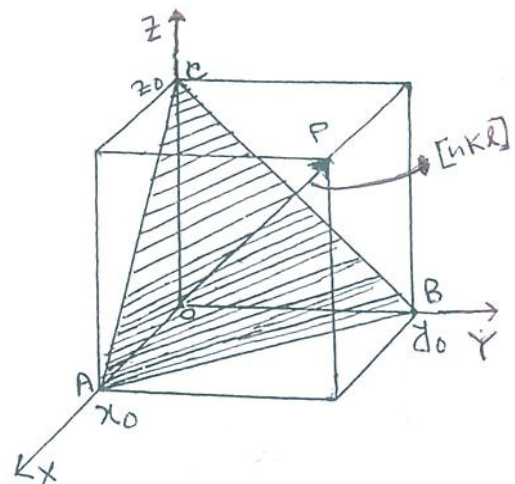
Let OP be the direction of $[hkl]$ and ABC be the (hkl) plane. Again, let x_0 , y_0 and z_0 are the intercepts of the plane (hkl) along X, Y and Z directions.

Miller indices are $\frac{1}{x_0}, \frac{1}{y_0}, \frac{1}{z_0}$.

and the reduced indices becomes $\frac{g}{x_0}, \frac{g}{y_0}, \frac{g}{z_0}$

Where g is an integer.

For cubic lattice $h=k=l=1$.



$$\hat{i} x_0 = y_0 = z_0 = \alpha.$$

And the direction $\vec{OP} = \left(\hat{i} \frac{g}{\alpha} + \hat{j} \frac{g}{\alpha} + \hat{k} \frac{g}{\alpha} \right)$

But $\vec{AB} = \vec{OB} - \vec{OA} = \hat{j} \frac{g}{\alpha} - \hat{i} \frac{g}{\alpha}$

Now $\vec{OP} \cdot \vec{AB} = \left(\hat{i} \frac{g}{\alpha} + \hat{j} \frac{g}{\alpha} + \hat{k} \frac{g}{\alpha} \right) \cdot \left(\hat{j} \frac{g}{\alpha} - \hat{i} \frac{g}{\alpha} \right) = \frac{-g^2}{\alpha^2} + \frac{g^2}{\alpha^2} = 0$

Similarly we can write $\vec{OP} \cdot \vec{BC} = 0, \vec{OP} \cdot \vec{CA} = 0.$

Hence the dot product of \vec{OP} with \vec{AB}, \vec{BC} and \vec{CA} is zero. So, \vec{OP} is normal to \vec{AB}, \vec{BC} or \vec{CA} .

Hence $[hkl]$ direction is normal to the (hkl) plane.

What is meant by $\{100\}$?

A family of planes of a particular type is represented by enclosing the Miller Indices of any one of that family into curly brackets (braces). Thus $\{100\}$ represents the family of planes which has the planes $(100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$ as its members. The six planes represent the faces of the cube.

Plasticity and Elasticity

Plasticity is a property of a material or a system that allows it to deform irreversibly. Elasticity is a property of a material or a system that allows it to deform reversibly. Both plasticity and elasticity play major roles in fields such as material science, engineering, and any other field involving designing and developing mechanical objects.

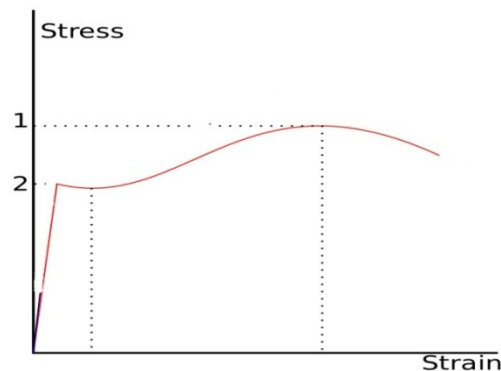


Fig. A stress-strain curve. 1. Ultimate Strength 2. Yield Strength

Elasticity: When an external stress is applied to a solid body, the body tends to pull itself apart. This causes the distance between atoms in the lattice to increase. Each atom tries to pull its neighbor as close as possible. This causes a force trying to resist the deformation. This force is known as strain. If a graph of stress versus strain is plotted, the plot will be a linear one for some lower values of strain. This linear area is the zone which the object is deformed elastically. The elastic deformation of a solid is a reversible process, when the applied stress is removed the solid returns to its original state.

Plasticity: When the plot of stress versus strain is linear, the system is said to be in the elastic state. However, when the stress is high the plot passes a small jump on the axes. This limit is when it becomes a plastic deformation. This limit is known as the *yield strength* of the material. The plastic deformation is sometimes known as the irreversible deformation. After the yield strength jump, the stress versus strain plot becomes a smooth curve with a peak. The peak of this curve is known as the *ultimate strength*. Plastic deformation is used in metal hardening to pack the atoms thoroughly.

What is the difference between Plasticity and Elasticity?

- Plasticity is the property that causes irreversible deformations on an object or a system. Such deformations can be caused by forces and impact.
- Elasticity is a property of objects or systems that allows them to deform reversibly. Elastic deformations can be caused by forces and impacts.
- An object must pass the elastic deformation stage in order to enter the plastic deformation stage.