

STRUCTURE OF MATTER

The elements and their chemical compounds generally occur in three states of aggregation: the solid ~~set~~ state, the liquid state and the gaseous state. In solids and liquids the distance between neighboring atoms is of the order of a few Angstroms i.e. they contain $(10^{22} - 10^{23})$ atoms per cm^3 .

Crystalline solid: In crystalline solids atoms are stacked in a regular manner forming a three dimensional pattern which may be obtained by a three dimensional repetition of a certain pattern unit. Just like the soldiers do on a parade ground.

Non crystalline solid: The solids in which atom, molecules and group of ions do not follow fixed combination are called amorphous/ non crystalline solid.

Single crystal and polycrystal:

When the periodicity of the pattern extends throughout a certain piece of material, one speaks of a single crystal.

In polycrystalline materials the periodicity of structure is interrupted at so-called grain boundaries; the size of the grains in which the structure is periodic may vary from macroscopic dimensions to several Angstroms.

Unit cell:

Unit cell is the smallest block or geometric structure in which by repetition three dimensional crystal system are formed.

Now let us consider a plane lattice which is a part of two dimensional crystal. Atoms are arranged in a pattern as illustrated in fig-1. It is clearly

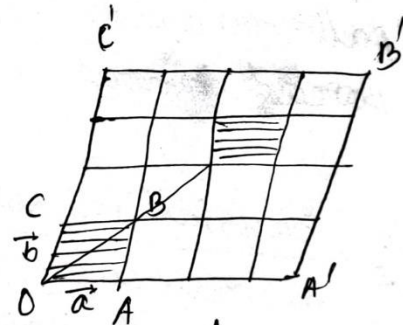


fig-1

observed that the crystal is formed by regular repetition of OABC parallelogram. Thus OABC is called a unit cell. The region surrounded OABC, will be unit cell in of two dimensional system.

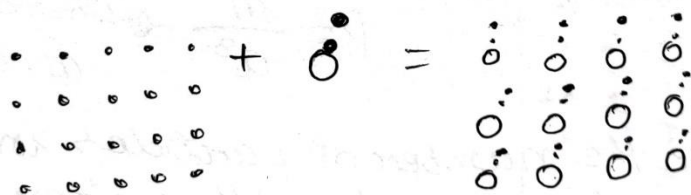
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2

If we denote a vector \vec{a} as $4\vec{a}$ and \vec{b} as $3\vec{b}$ then parallelogram $OACB$ will be transformed as $O'A'B'C'$. In three dimensions, a similar procedure may be followed by stacking parallelepipeds in a regular manner.

Lattice: A lattice is a regular periodic arrangement of points in space that looks a net like structure, it has the environment about any particular point which is in every way the same as that about any other point.

Basis: The basis consists of an atom or a group of atoms and in an ideal crystal it is identical in composition, arrangement and orientation. The distinction between the crystal and the lattice is illustrated in fig-2



Lattice + Basis = Crystal Structure

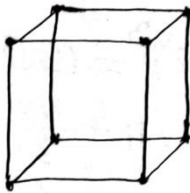
Types of lattice:

Two dimensional lattice:

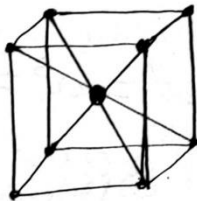
- (I) oblique (II) Rectangular
- (III) Square (IV) Hexagonal

Three dimensional:

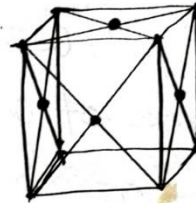
- (I) Cubic (II) Monoclinic (III) Triclinic
- (IV) Tetragonal (V) Orthorhombic (VI) Trigonal
- (VII) Hexagonal



Gen. Cubic



BCC

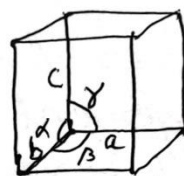


FCC

Crystal: So, crystal is that solid in which atoms are well organized and periodically stacked. This pattern must be three dimensional. So crystal is formed by connecting basis with lattice. Hence, lattice is mathematical conception and crystal structure is physical conception.

Lattice Crystal Constants:

The numbers a, b, c specifying the size of a unit cell are called its lattice constants.



For cubic lattices, evidently a single number a serves all the purpose.

Calculation for lattice constant (a):

Let us consider a unit cell of with a lattice constant a . If ρ be its density and m its mass, then

$$\rho = \frac{m}{a^3} \quad \text{--- (1) where, } a^3 = \text{Its volume}$$

Let, n be the number of particles in the cell. These particles may be either atoms or molecules (sometimes ion-pairs). Letting it consists of molecules, the mass of one molecule is M/N_A where M is the molecular weight of the

crystal and N_A the Avogadro number. Then

$$m = n \cdot \frac{M}{N_A}$$

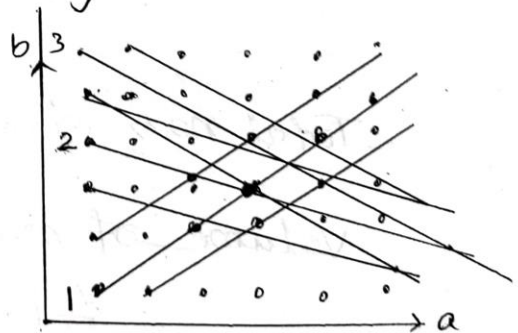
$$\therefore \text{From eqn (1) we get, } \rho = \frac{nM}{N_A a^3}$$

$$\text{or, } a^3 = \frac{nM}{N_A \rho}$$

$$\therefore a = \left(\frac{nM}{\rho N_A} \right)^{\frac{1}{3}}$$

This calculates the lattice constant of a lattice. For crystals consisting of atoms, the value of n , M and N_A must be in reference to atoms.

Crystal planes: The lattice points forming a space lattice may be thought of as occupying various sets of parallel planes, are called crystal planes.



Packing fraction:

The ratio of the volume occupied by the atoms to the total volume of the crystal is called packing fraction.

$$\therefore P.F = \frac{\text{The volume occupied by atoms}}{\text{Total volume of the crystal}}$$

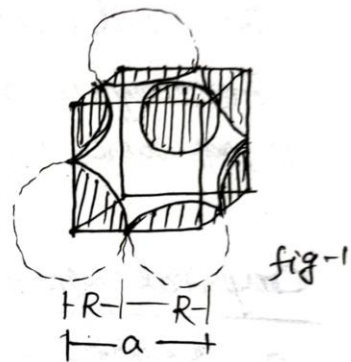
Determination of Packing Fraction:

(1) For simple cubic crystal:

Let us consider a unit cell ^{of length a .} Let the radius of an atom = R .

$$\therefore a = 2R$$

$$\begin{aligned}\therefore \text{Total volume}_{\text{of the crystal}} &= a^3 \\ &= (2R)^3 \\ &= 8R^3\end{aligned}$$



$$\text{Total no. of atom inside the cell} = \frac{1}{8} \times 8 = 1$$

$$\text{Volume of an atom} = \frac{4}{3} \pi R^3$$

$$\therefore P.F = \frac{\frac{4}{3} \pi R^3}{8R^3} = \frac{\pi}{6} = 0.53$$

প্রতি কোনাতে $\frac{1}{8}$ পরিমাণ Atom থাকে এবং ৪ টি কোনা হওয়ায় মোট ৪টি দিয়ে গুন করা হয়েছে।

$$\therefore \text{The P.F} = \frac{\frac{4}{3} \pi R^3}{\frac{64}{3\sqrt{3}} R^3} = \frac{\sqrt{3} \pi}{8} = 0.68$$

(III) For fcc lattice:

For fcc lattice,

$$AC = R + 2R + R = 4R$$

Again,

$$AC^2 = AB^2 + BC^2$$

$$\text{or, } (4R)^2 = a^2 + a^2 = 2a^2$$

$$\text{or, } a^2 = \frac{16R^2}{2} = 8R^2$$

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

$$\text{Volume of a unit cell} = a^3 = (2\sqrt{2}R)^3 = 16\sqrt{2}R^3$$

$$\text{No. of atoms inside a unit cell} = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

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

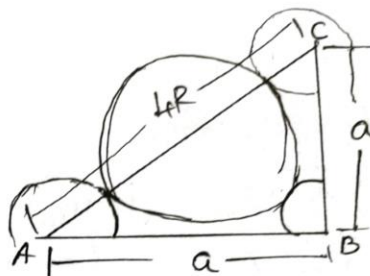
$$= 3 + 1$$

$$= 4$$

\therefore Total volume occupied

$$\text{by atoms} = 4 \times \frac{4}{3} \pi R^3 = \frac{16}{3} \pi R^3$$

$$\therefore \text{P.F} = \frac{\frac{16}{3} \pi R^3}{16\sqrt{2} R^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$



(5)

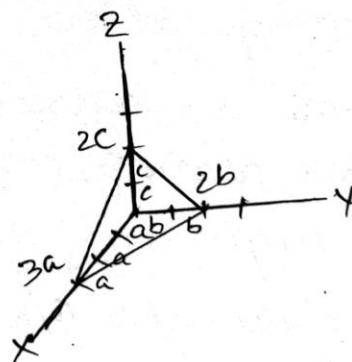
#Miller indices:

If the crystal position and orientation of a crystal plane are explained by a set of three numbers are called Miller indices. The Miller indices of the set of planes are then given by three numbers h, k, l . Miller indices are determined as follows —

- (i) Intercept points are determined towards crystallographic axis by lattice constants a, b, c . Axes may be primitive or non primitive.
- (ii) Inverse numbers of the intercepts are taken. Such as $(\frac{1}{a}, \frac{1}{b}, \frac{1}{c})$ or $\frac{1}{h}, \frac{1}{k}, \frac{1}{l}$

Example:

In the figure, the plane intersects x, y and z axis at a distance of $3a, 2b$ and $2c$. The inverse



values of those numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. Now multiplying them by their common integer

6 we get 2, 3, 3. So the miller indices of the plane are (2, 3, 3).

Determination of interplanar spacing and interms of miller indices:

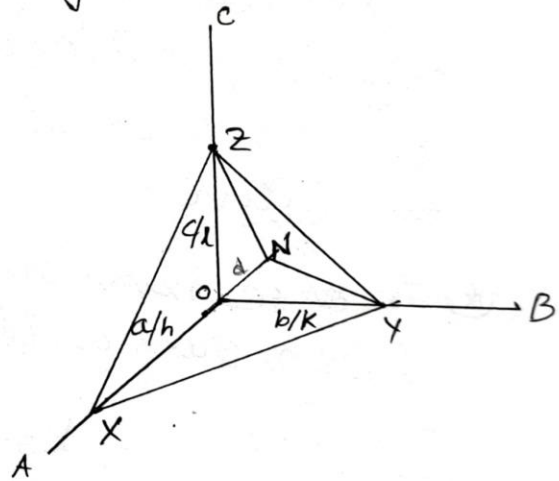
The normal distances among the periodic parallel planes of the atoms of a crystal are called interplanar spacing. This is also called interplanar gap.

In the figure, OA, OB and OC are orthogonal axes.

Now we consider two planes, one of them is going through origin and another XYZ plane ~~are~~ intersects a/h , b/k and c/l ~~resp~~ respectively.

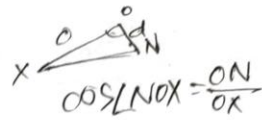
Now we draw a normal line ON on XYZ plane. We determine ON by a, b, c and h, k, l .

Hence $ON = d$.



We get from the fig.

$$\begin{aligned} ON = d &= \frac{a}{h} \cos \angle NOX \\ &= \frac{b}{k} \cos \angle NOY \\ &= \frac{c}{l} \cos \angle NOZ \end{aligned}$$



$$\begin{aligned} \cos \angle NOX &= \frac{ON}{OX} \\ ON &= OX \cos \angle NOX \\ &= \frac{a}{h} \cos \angle NOX \end{aligned}$$

$ON = d =$ interplanar spacing.

$$\therefore \cos \angle NOX = \frac{dh}{a}$$

$$\cos \angle NOY = \frac{dk}{b}$$

$$\text{and } \cos \angle NOZ = \frac{dl}{c}$$

According to the directional cosine rule, we get -

$$\cos^2 \angle NOX + \cos^2 \angle NOY + \cos^2 \angle NOZ = 1$$

$$\text{or, } \left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{b}\right)^2 + \left(\frac{dl}{c}\right)^2 = 1$$

$$\text{or, } d^2 \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) = 1$$

$$\text{or } d_{hkl}^2 = \frac{1}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)}$$

$$\therefore d_{hkl} = \frac{1}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2}}$$

for a cubic lattice $a = b = c$

$$d_{hkl} = \frac{1}{\left(\frac{h^2 + k^2 + l^2}{a^2}\right)^{1/2}} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

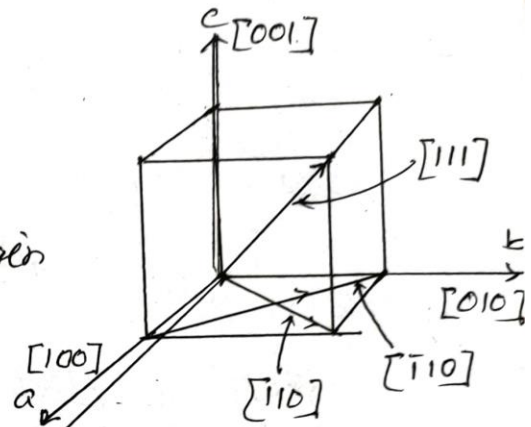
This is the interplanar spacing by Miller indices.

Lattice directions and planes:

Indices of a lattice are the three vector components divided ~~in~~ towards three axes.

Example:

If we consider a unit cell at the corner of origin then the axes will be parallel to the corner edges. Now, body diagonals can be written as $[111]$ (fig).



Square bracket or third bracket is used to indicate these numbers.

Indices towards a axis $[100]$

" " $-a$ " $[\bar{1}00]$

" " b " $[010]$

" " $-b$ " $[0\bar{1}0]$

Index of diagonal on ab plane is $[110]$

" " " " ac " " $[101]$

Difference between (hkl) , $\{hkl\}$ and $[hkl]$

Sign (hkl) is that Miller indices which indicate the position and orientation of a crystal plane.

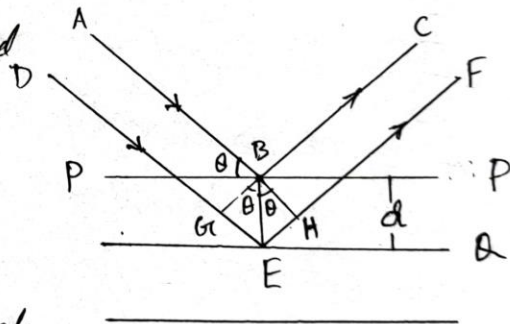
Sign $\{hkl\}$ indicates the combination of many planes

Sign $[hkl]$ indicates the direction of a lattice point in a cell.

The Bragg's law in X-ray diffraction:

W.L Bragg investigated the conditions for X-ray diffraction by means of a model which gives the correct mathematical results in

a very simple way. He found that "the directions of diffracted beams can be accounted for by making the assumption that the X-rays are specularly (i.e mirror-like) reflected from



parallel atomic planes in the crystal and the multiple reflections interfere constructively in those directions." It is common practice, therefore to interchange the words diffraction and reflection of X-rays.

Now, let us consider two parallel planes of atoms which are situated at a distance d . Again, we consider two parallel beams of X-ray of wave length λ incident on the points B and E on the lattice plane P and Q with the angle θ . Then they are reflected towards BC and EF. BG and BH are normal lines on DE and EF respectively. Now the path difference between incident and reflected wave front is $GE + EH$. According to the fig. both GE and EH will be equal to $d \sin \theta$.

So, the total path difference between two reflected beams -

$$\begin{aligned} GE + EH &= d \sin \theta + d \sin \theta \\ &= 2d \sin \theta \end{aligned}$$

$$\begin{aligned} \sin \theta &= \frac{GE}{BE} = \frac{GE}{d} \\ \therefore GE &= d \sin \theta \end{aligned}$$

This will produce constructive interference when the path difference ~~will~~ is equal to an integral number n of wavelength λ . Thus, the Bragg's condition for diffraction is -

$$2d \sin \theta = n\lambda \quad \text{--- (1)}$$

This equation (1) is called Bragg's law.

Introduction to Band Theory:

From the Bohr theory of atomic structure we know that, electrons inside an atom can move around the nucleus staying at certain permitted orbits. The radii of these orbits are fixed.

If some additional energy is supplied in an electron in the form of heat or light then the electron is transferred into next higher orbit. This state of an atom is called excited state. This state can not

last long because the electron comes back to its original orbit, losing the energy by radiation.

Energy band:

" There is a small variation of energies of the electrons of the same orbit in an atom of a solid. The range between the electrons of maximum energy and the minimum energy at the same orbit is called the energy band."

* Conduction Band (C.B)

* Valance Band (V.B)

* Forbidden energy gap (eg)

→ N/A → conductor
→ (6-13) eV → Insulator
→ ($E_g < 1\text{ eV}$) → Semiconductor

