Theory of Crystal Structure

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Abstract:

During this paper we will focus on discussing crystals with a discrete translational symmetry, i.e. crystals which are formed by the combination of a Bravais lattice and a corresponding basis. Despite this restriction there are still many different lattices left satisfying the condition. However, there are some lattices types that occur particularly often in nature. Or some - actually distinct - lattices share certain properties. These aspects arise from the symmetry of the lattices.

Introduction

Solids are of two types: Amorphous and crystalline. In amorphous solids, there is no order in the arrangement of their constituent atoms (molecules). Hence no definite structure could be assigned to them. A substance is said to be crystalline when the arrangement of the units (atoms, molecules or ions) of matter inside it is regular and periodic.

Space lattice:

An array of points which describe the three dimensional arrangement of particles (atoms, molecules or ions) in a crystal structure is called space lattice. Here environment about each point should be identical.

Basis:

A crystal structure is formed by associating with every lattice point a unit assembly of atoms or molecules identical in composition. This unit assembly is called basis.
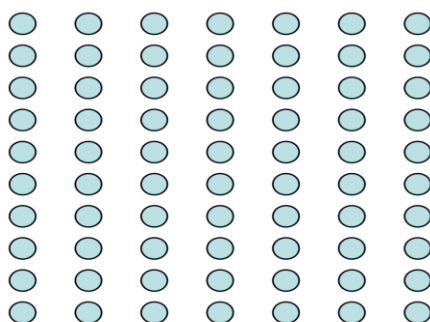
A crystal structure is formed by the addition of a basis to every lattice point.

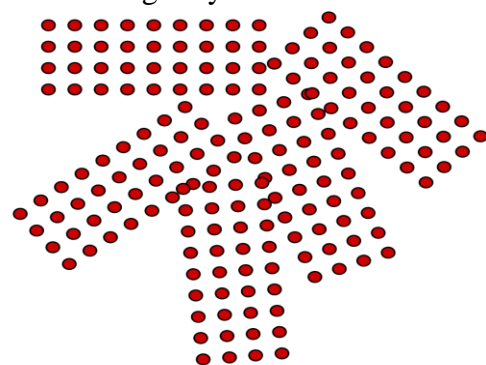i.e., **lattice + Basis = crystal structure**.

Thus the crystal structure is real and the crystal lattice is imaginary.
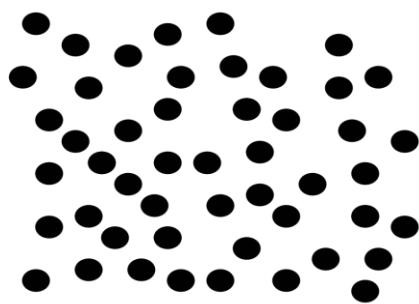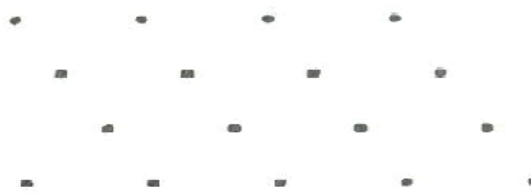

Amorphous   crystalline   polycrystalline

Bravais lattice:

For a crystal lattice, if each lattice point substitutes for an identical set of one or more atoms, then the lattice points become equivalent and the lattice is called Bravais lattice. On the other hand, if some of the lattice points are non-equivalent, then it is said to be a non-Bravais lattice.
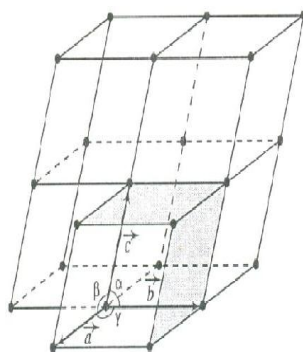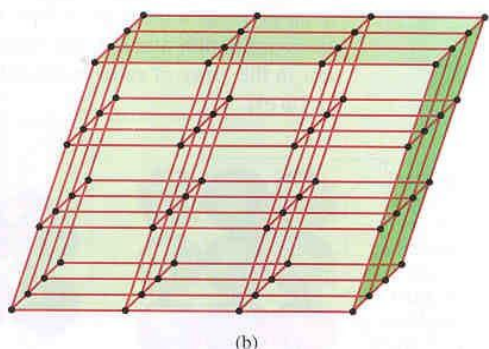
BRAVAIS LATTICE   NON-BRAVAIS LATTICE

Unit cell and lattice parameters:

The smallest portion of the crystal which can generate the complete crystal by repeating its own dimensions in various directions is called unit cell.

The position vector R for any lattice point in a space lattice can be written as

$$R= n_1a+n_2b+n_3c$$

.

(b)

Where **a, b** and **c** are the basis vector set and n_1, n_2, n_3 are a triplet of integers $0, \pm1, \pm2$, etc., whose value depends on the particular lattice point . The angles between the vectors **b** and **c**, **c** and **a**, **a** and **b** are denoted as α, β and γ and are called interfacial angles. The three basis vectors and the three interfacial angles, form a set of six parameters that define the unit cell, and are called lattice parameters

Primitive and Non primitive cells:

A primitive cell is a minimum volume unit cell. Consider a bravais lattice (in two dimensions) as shown below:
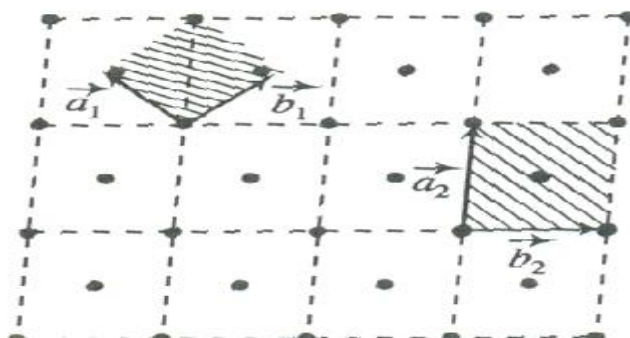
We can imagine two ways of identifying the unit cell in this structure. One is, with a_1 and b_1 as the basis vectors in which case, the unit cell will be a parallelogram. Here four lattice points are located at the vertices. This is a primitive cell. Other one is with the basis vectors a_2 and b_2 which would make a rectangle for the unit cell. Here in addition to the 4 points at the corners, one lattice point is at the centre. This is a nonprimitive cell. Thus the area of the non primitive cell is an integral multiple of the primitive cell.

Crystal Systems
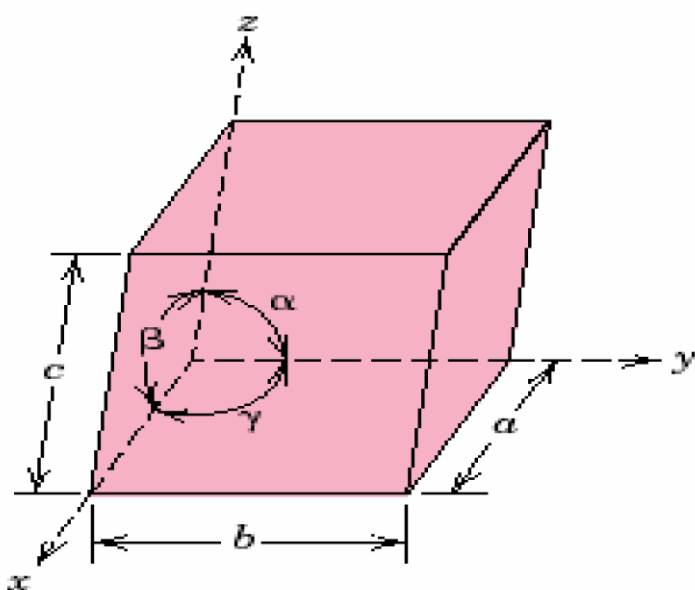
Crystallographers have shown that only seven different types of unit cells are necessary to create all point lattice

Cubic $a = b = c$; $\alpha = \beta = \gamma = 90$

Tetragonal $a = b \neq c$; $\alpha = \beta = \gamma = 90$

Rhombohedral $a = b = c$; $\alpha = \beta = \gamma \neq 90$

Hexagonal $a = b \neq c$; $\alpha = \beta = 90$, $\gamma = 120$

Orthorhombic $a \neq b \neq c$; $\alpha = \beta = \gamma = 90$

Monoclinic $a \neq b \neq c$; $\alpha = \gamma = 90 \neq \beta$

Triclinic $a \neq b \neq c$; $\alpha \neq \gamma \neq \beta \neq 90$

Bravais Lattices

Crystal systems:

Bravais demonstrated mathematically that in 3-dimensions, there are only 14 different types of arrangements possible. These 1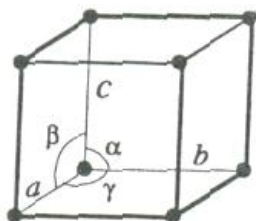4 Bravais lattices are classified into the seven crystal systems on the basis of relative lengths of basis vectors and interfacial angles.
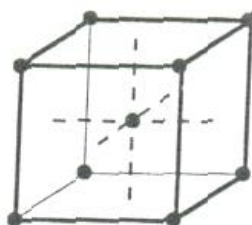
Seven crystal systems are:

1. Cubic   2. Tetragonal   3. Orthorhombic   4. Monoclinic   5. Triclinic   6. Trigonal (Rhombohedral)   7. Hexagonal

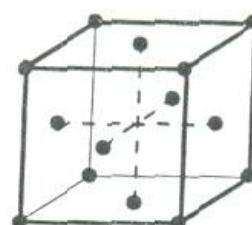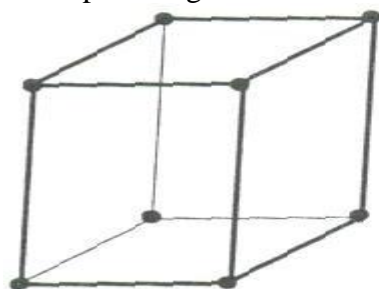**The 14 Bravais lattices are**

1. Simple cubic

2. Body centered cubic

3. Face centered cubic

$$a = b = c, \quad \alpha = \beta = \gamma = 90°$$
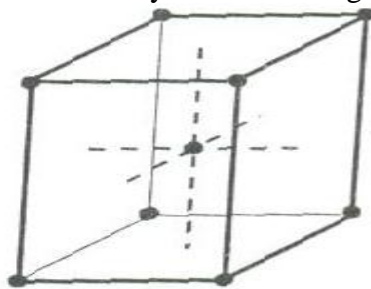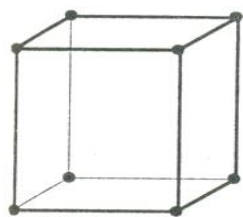
4. Simple tetragonal

5. Body centered tetragonal

$$a = b \neq c, \quad \alpha = \beta = \gamma = 90°$$

6. Simple orthorhombic   7. Base centered   8. Body centered   9. Face centered
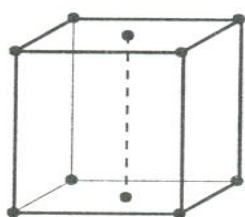
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$a \neq b \neq c$; and $\alpha = \beta = \gamma = 90°$

10. Simple monoclinic   11. Base centered monoclinic   12. Triclinic
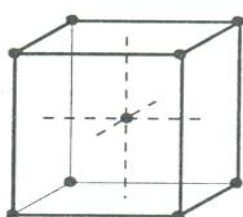
$a \neq b \neq c, \quad \alpha = \gamma = 90° \neq \beta$

$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

13. Trigonal(Rhombohedral)   14. Hexagonal

$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

$a = b \neq c$
$\alpha = \beta = 90°, \quad \gamma = 120°$

Direction and planes in a crystal:

CUBIC

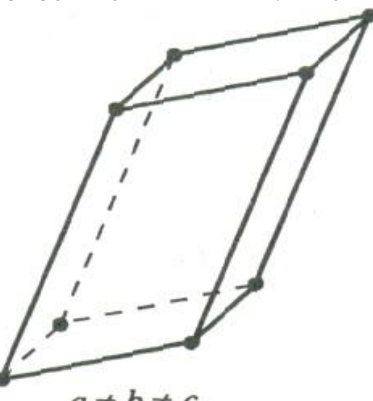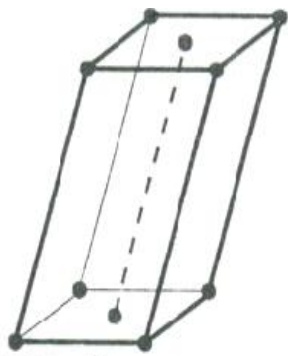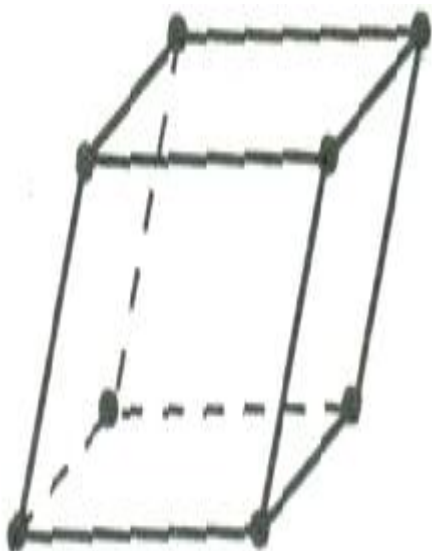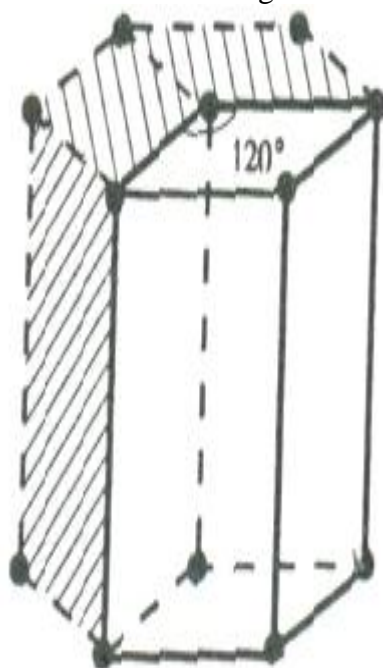$a = b = c$
$\alpha = \beta = \gamma = 90°$

P   **I**   **F**

TETRAGONAL

$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

P   **I**

ORTHORHOMBIC

$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

P   **I**   **F**   **C**

HEXAGONAL

$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

P

TRIGONAL

$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

P

MONOCLINIC

$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

P   **C**

TRICLINIC

$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

P
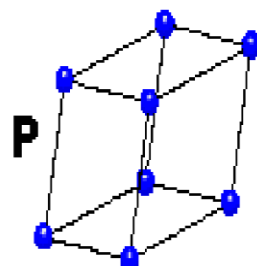
4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

Structures of Metallic Elements

Many physical properties of crystalline solids are dependent on the direction of measurement or the planes across which the properties are studied. In order to specify directions in a lattice, we make use of lattice basis vectors **a**, **b** and **c**.

In general, any directional vector can be expressed as

$$\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

where n_1, n_2 and n_3 are integers. The direction of the vector **R** is determined by these integers. If these numbers have common factors, they are removed and the direction of R is denoted as $[n_1\ n_2\ n_3]$. A similar set of three integers enclosed in a round bracket is used to designate planes in a crystal.

Lattice planes and Miller indices:

The crystal lattice may be regarded as made up of a set of parallel, equidistant planes passing through the lattice points. These planes are known as lattice planes and ma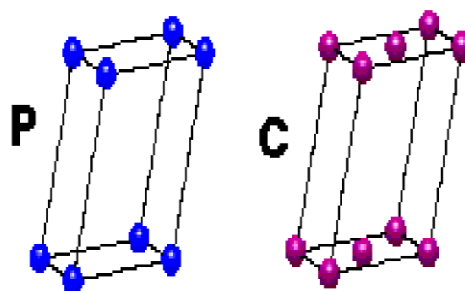y be represented by a set of three smallest possible integers. These numbers are called 'Miller indices' named after the crystallographer W.H.Miller.

Determination of Miller indices:

Consider a crystal plane intersecting the crystal axes as shown:
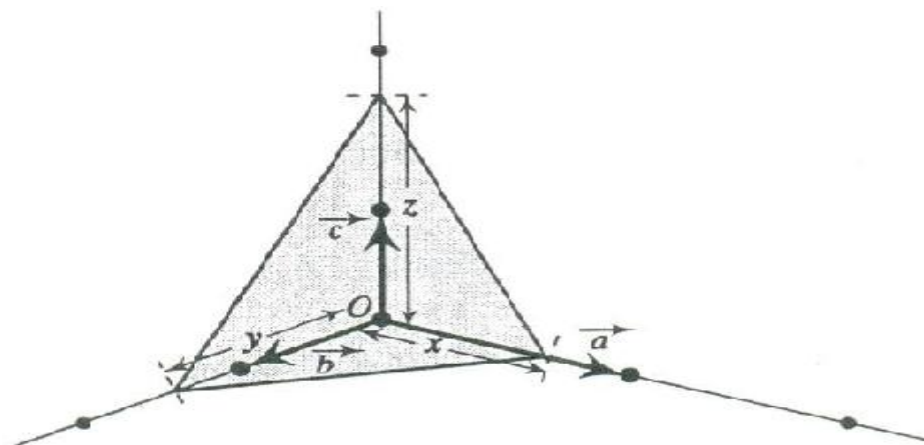
The procedure adopted to find the miller indices for the plane is as follows:

1. Find the intercepts of the plane with the crystal axes along the basis vectors **a**, **b** and **c**. Let the intercepts
   be x, y and z respectively.

2. Express x, y and z as fractional multiples of the respective basis vectors. Then we obtain the fractions,
   $\frac{x}{a}, \frac{y}{b}, \frac{z}{c}$.

3. Take the reciprocal of the three fractions to obtain $\frac{a}{x}, \frac{b}{y}, \frac{c}{z}$.

4. Find the least common multiple of the denominator, by which multiply the above three ratios. This
   operation reduces them to a set of 3 integers (h k l) called miller indices for the crystal plane.

For the plane given above,

1. $x = \frac{2a}{3}$ $y = \frac{3b}{2}$ $z = 2c$

2. $(\frac{x}{a} \ \frac{y}{b} \ \frac{z}{c}) = (\frac{2}{3} \ \frac{3}{2} \ 2)$

3. Taking reciprocal, $(\frac{3}{2} \ \frac{2}{3} \ \frac{1}{2})$

4. Multiplying throughout by the least common multiple 6 for the denominator, we have the miller indices,
   (9 4 3)

Expression for interplanar spacing:
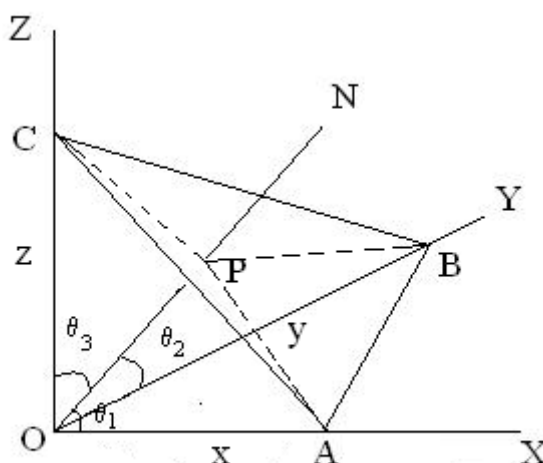
    Let ABC be one of the parallel planes represented by the miller indices (h k l). Its intercepts on the crystal axes are x, y and z. Another plane parallel to the plane ABC passes through the origin O. If OP is drawn perpendicular from O to the plane ABC, then OP is equal to the interplanar distance d_{hkl}. Let the angle made by OP with respect to the axes X, Y and Z be θ_1, θ_2 and θ_3 respectively.

$$\text{Now } \cos \theta_1 = \frac{d_{hkl}}{x}$$

Similarly we can write $\cos \theta_2 = \frac{d_{hkl}}{y}$ and $\cos \theta_3 = \frac{d_{hkl}}{z}$

But for orthogonal co-ordinates, $\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 = 1$

i.e., $\dfrac{d_{hkl}^2}{x^2} + \dfrac{d_{hkl}^2}{y^2} + \dfrac{d_{hkl}^2}{z^2} = 1$

But from the definition of miller indices, $x = \dfrac{a}{h}$ $y = \dfrac{b}{k}$ and $z = \dfrac{c}{l}$

∴ The interplanar spacing d_{hkl} is given by,

$$d_{hkl} = \dfrac{1}{\sqrt{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}}}$$

For a cubic lattice, $a = b = c$

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

Number of atoms per unit cell (n):

1. Simple cubic lattice

There are eight corner atoms. Each corner atom is shared by eight unit cells. Hence the share of each unit cell is equal to one eighth of an atom. Therefore the total number of atom in one unit cell = 8 x 1/8 = 1.

2. Body centered cubic lattice

There are eight atoms at the eight corners of the unit cell and one atom at the body centre. As each corner atom is shared by eight unit cells, the contribution to each cell is 8 x 1/8 = 1. Moreover, there is one body centre atom per unit cell. Therefore total number of atoms per unit cell = 1+1 = 2.

3. Face centered cubic lattice

There are eight atoms at the eight corners of the unit cell and six face centered atoms at the centre of six faces. As each corner atom is shared by eight unit cells, the contribution to each cell is 8 x 1/8 = 1. Each face centered atom is shared by two unit cells. Hence the contribution of six face centered atoms to each unit cell is 6 x ½ = 3. Therefore the total number of atoms per unit cell = 1 + 3 = 4.

Co-ordination number:

Co-ordination number is the number of equidistant neighbours surrounding an atom in the given crystal structure. When the coordination number is larger, the structure is more closely packed.

1. Simple cubic lattice

Here any corner atom has four nearest neighbours in the same plane and two nearest neighbours in a vertical plane. Hence co-ordination number in this case is six.

2. Body centered cubic lattice

For any corner atom of the unit cell, the nearest atoms are the atoms which are at the centers of unit cells. A corner atom is surrounded by eight unit cells having eight body centered atoms. Hence co-ordination number is eight.

3. Face centered cubic lattice

For any corner atom, there will be four face centered atoms of the surrounding unit cells in its own plane as nearest neighbours and four face centered atoms each in two perpendicular planes. Hence co-ordination number is 4 + 4 + 4 = 12.

Relation between atomic radius and the lattice constant

Atoms touch each other at least in one direction in a unit cell. All atoms could be assumed to be spherical in shape.

1. Simple cubic lattice

The front view of one face of unit cell is shown:
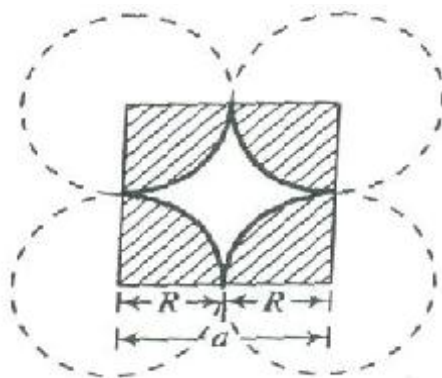
If 'a' is the lattice constant and 'R' the atomic radius, a = 2R.

2. Body centered cubic lattice

In this structure the corner atoms do not touch each other. But each corner atom touches the central atom. From the geometry of the cube,

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

But AB=4R, $BC^2=a^2+a^2$ and AC=a

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

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

$$a = (4/\sqrt{3})\ R \quad \text{where R is the atomic radius.}$$

3. Face centered cubic lattice
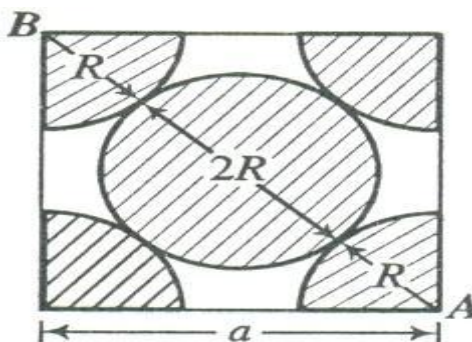
Corner atoms do not touch each other. But each corner atom touches the central atom in the corresponding face as shown:
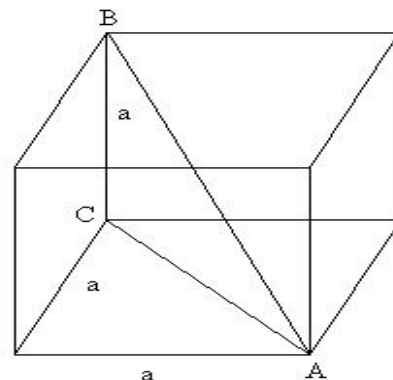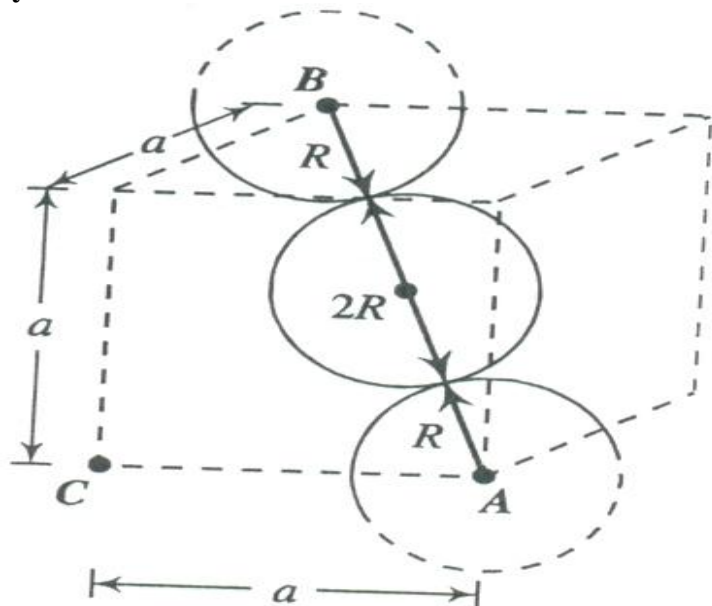
$$\text{From figure, } AB^2 = a^2+a^2$$

$$\text{But AB=4R}$$

$$\therefore (4R)^2 = 2a^2$$

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

$$\text{or} \quad a = \frac{4}{\sqrt{2}}\ R$$

$$a = 2\sqrt{2}\ R \quad \text{where R is the atomic radius.}$$

Packing factor (fraction):

Packing factor is the ratio of total volume of the atoms in the unit cell to the total available volume in the unit cell.

$$\text{Packing factor (p.f)} = \frac{n\left(\frac{4}{3}\pi R^3\right)}{a^3} \qquad \text{where 'R' is the atomic radius}$$

and 'a' is the lattice constant

1. Simple cubic lattice:

Here n = 1 and a = 2R $\qquad \therefore (p.f) = \dfrac{1 \times (\frac{4}{3}\pi R^3)}{(2R)^3} = \dfrac{\pi}{6} = 0.52$

2. Body centered cubic lattice:

Here n = 2 and a = $(\frac{4}{\sqrt{3}})R$ $\qquad \therefore (p.f) = \dfrac{2 \times \frac{4}{3}\pi R^3}{((\frac{4}{\sqrt{3}})R)^3} = \dfrac{\sqrt{3}\,\pi}{8} = 0.68$

3. Face centered cubic lattice:

Here n = 4 and a = $2\sqrt{2}\ R$ $\qquad \therefore (p.f) = \dfrac{4 \times \frac{4}{3}\pi R^3}{(2\sqrt{2}R)^3} = \dfrac{\pi}{3\sqrt{2}} = 0.74$

Lattice parameter and density:

Density of a cubic crystalline material can be written as

Density $\rho = \dfrac{\text{(Total mass of molecules in the unit cell)}}{\text{(volume of the unit cell)}}$

$\qquad = \dfrac{\text{(Number of molecules in the unit cell x Mass of each molecule)}}{\text{(volume of the unit cell)}}$
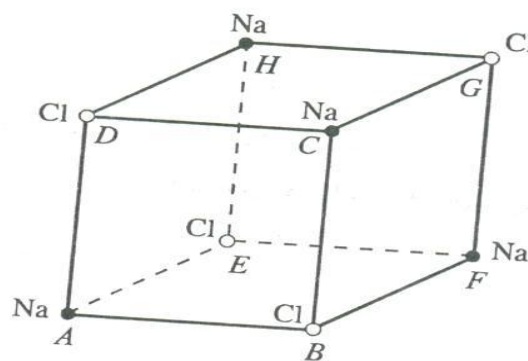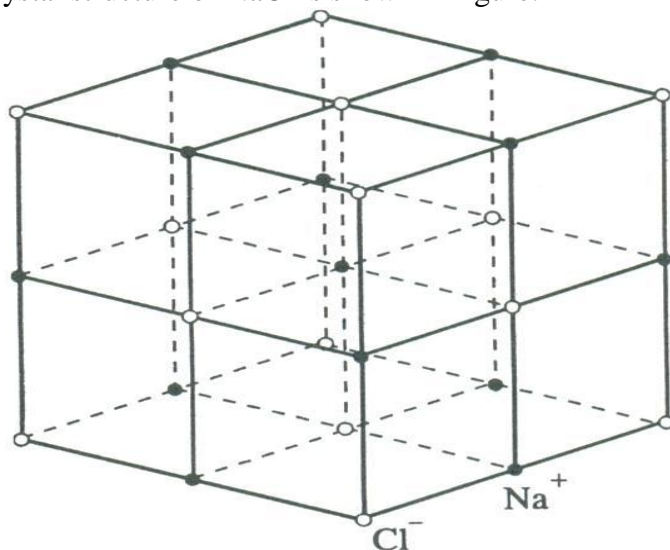
$\qquad = \dfrac{(n\frac{M}{N_A})}{a^3}$

Where 'M' is the molecular weight, 'N_A' the Avogadro number and 'a' the lattice parameter.

$\therefore a^3 = \dfrac{nM}{\rho N_A}$

or, $\mathbf{a = (\dfrac{nM}{\rho N_A})^{\frac{1}{3}}}$

Crystal structure of NaCl:

The crystal structure of NaCl is shown in figure:

CRYSTAL STRUCTURE OF NaCl
(FACE CENTERED CUBIC)

NaCl is an example of face centered cubic lattice. NaCl is an ionic compound and Na^+ and Cl^- ions occupy alternate positions in the lattice. Thus there are four Na^+ and Cl^- ion pairs (molecules) per unit cell. If a corner Na^+ ion is taken as origin, the position co-ordinates of Na^+ and Cl^- ions are as follows:

Na^+	0 0 0	½ ½ 0	½ 0 ½	0 ½ ½
Cl^-	½ ½ ½	0 0 ½	0 ½ 0	½ 0 0

Lattice constant is related to the atomic radius R through the relation $a = \dfrac{8}{\sqrt{3}}R$

The number of molecules per unit cell is 4 and the coordination number is 6.

Interatomic distance is 2.813 Å.

KCl, PbS, MnO and AgBr possess crystal structure identical to NaCl.

Crystal structure Diamond:

The diamond lattice is composed of two interpenetrating face centered cubic sub lattices, one of which shifted relative to the other by one fourth of a body diagonal as shown:

The position co-ordinates of carbon atoms are

0 0 0

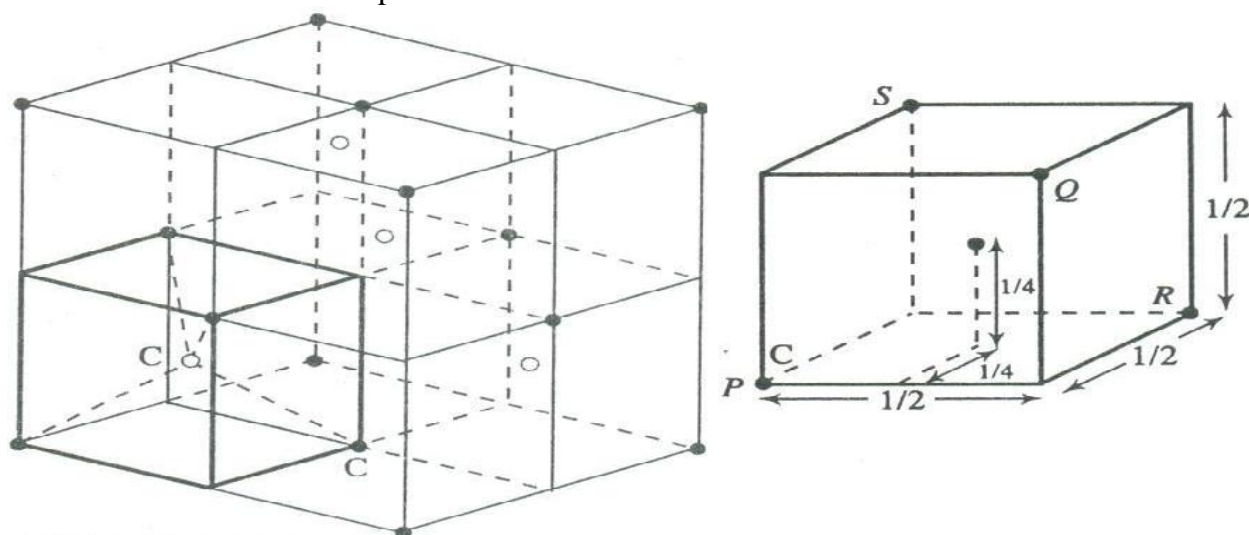½ ½ 0   ½ 0 ½   0 ½ ½   ¼ ¼ ¼
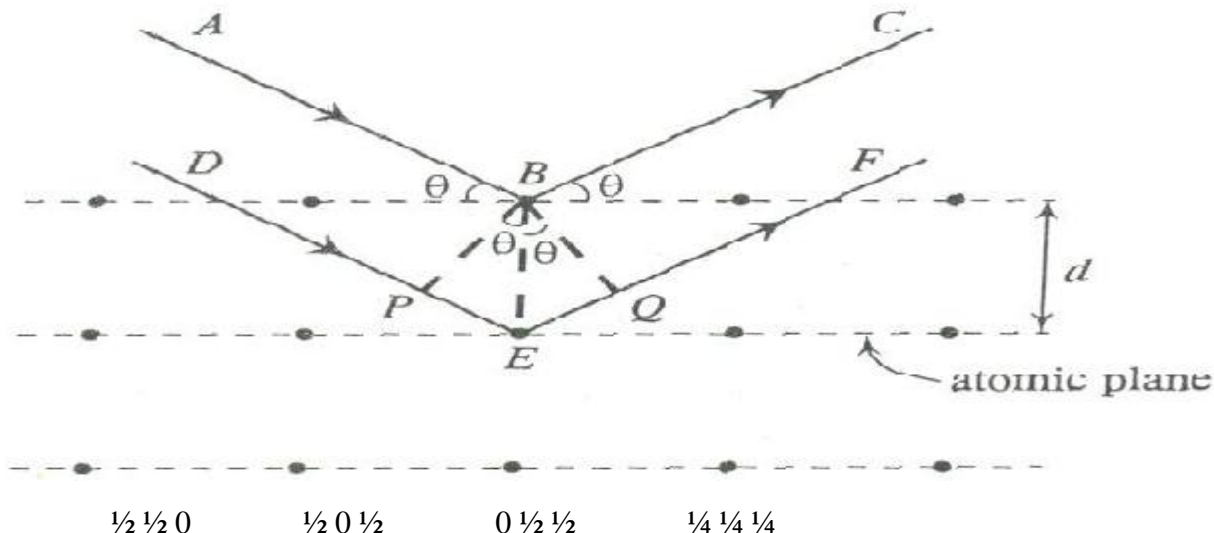
Lattice constant is related to the atomic radius R through the relation $a = \frac{8}{\sqrt{3}}R$

The number of atoms per unit cell is 8 and the coordination number is 4.

Packing fraction is $\frac{\sqrt{3}\ \pi}{16}$

Ge and Si possess diamond structure.

○ Hollow circles represent carbon atoms from the other penetrating sub-lattice

Bragg's law:

X-rays of wavelength 'λ' be incident upon the crystal at an angle 'θ'. The crystal acts as a series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between the two reflected waves from two different planes is nλ. Lattice planes are separated by a distance 'd'.

From figure,

Path difference = PE + EQ = BE sinθ + BE sinθ = d sinθ + d sinθ = 2d sinθ

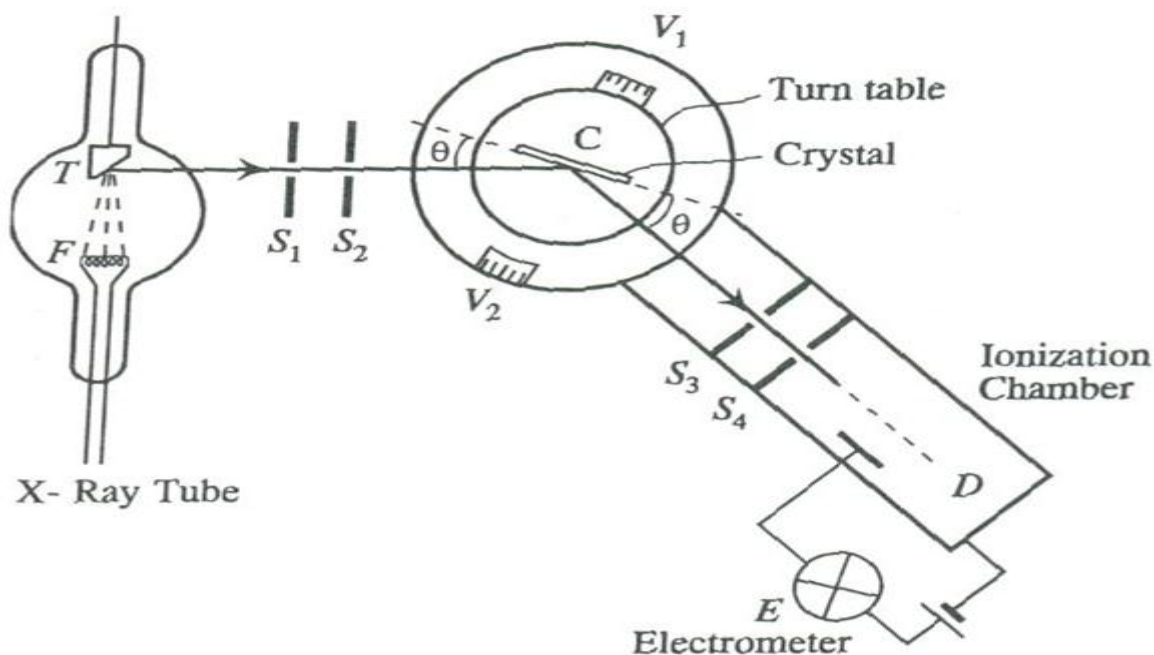Intensity of the reflected light will be maximum when path difference is nλ.

i.e., **2d sinθ = nλ**

This result is known as **Bragg's law**.

Where 'θ' is called Bragg angle or glancing angle and 'n' is the order of diffraction.

Bragg's X-ray spectrometer:

Bragg's X-ray spectrometer consists of three parts:
1. A source of X-rays (X-ray tube)
2. A crystal held on a circular turn table provided with vernier
3. A detector (ionization chamber)

X-rays from an X-ray tube collimated by two narrow slits S_1 and S_2 are allowed to fall upon the crystal C. The crystal is mounted on the turn table, which can rotate about a vertical axis and its position can be determined by vernier V_1. The table is provided with a radial arm which carries ionization chamber. This arm can also be rotated about the same vertical axis as the crystal. The position of this arm can be determined by the vernier V_2. The ionization chamber is connected to an electrometer E to measure the ionization current. The slits S_3 and S_4 limit the width of the diffracted beam.

The crystal table and ionization chamber are connected in such a way that the chamber turns through 2θ, when the crystal turns through θ.
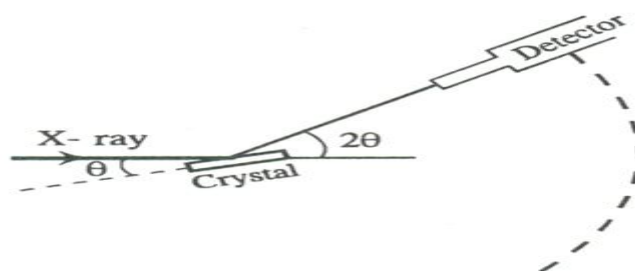
To begin with, the glancing angle θ is kept very small and corresponding ionization current is noted. The glancing angle is increased in equal steps and in each case, ionization current is noted down. The ionization current is plotted against the glancing angle.
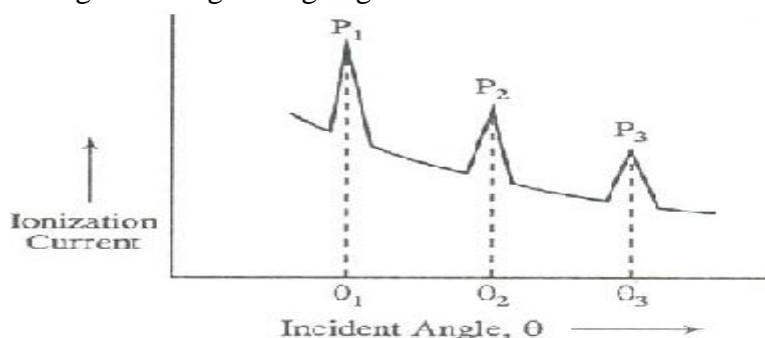
This graph is called X-ray spectrum. The peaks in the graph occur whenever Bragg's law is satisfied. One can measure the interplanar spacing 'd' through Bragg's relation $2d \sin\theta = n\lambda$, by

using the measured value of 'θ', the order 'n' and x-ray wavelength 'λ'.

sc, fcc and bcc   structures.

Conclusion:

Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research. The rapid advances in microelectronics, communication technologies, medical instrumentation, energy and space technology are possible only after the remarkable progress in fabrication of large perfect crystals. . Further progress in crystal growth technology is required for significant contributions to the energy crisis. Besides, the dream of laser fusion energy and other novel technologies can only be realized after appropriate progress in the technology of crystal. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. The rapid development of optical communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel systems of considerable potential and high performance and the improvements in the properties of the known crystals is a never ending 187 process. Therefore, special consideration is given not only to the possibility of changing significant functional characteristics of the crystal, but also to the creation of properties which is new to the pure crystal by adding different impurities. Potassium dihydrogen phosphate (KDP) is a model system for nonlinear optical device application, it continues to be an interesting material both academically and industrially and is extensively studied from various aspects. Its excellent qualities such as high nonlinear conversion efficiency, wide optical transmission range with low cutoff wavelength and high laser damage threshold has drawn the attention of several crystal growers. Many research works have been resulted in the modification of KDP properties and growth rates by varying the growth conditions and by adding suitable impurities

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