



Crystalline State

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KEY WORDS

array of points, lattice, unit cell, periodic lattice, crystal structure, rock salt crystals, degree of symmetry, periodic arrangements, space lattice, two dimensional space lattice, position vector, fundamental translation vectors, basis or pattern, lattice point, unit cell, crystal lattice, fundamental elementary pattern, translation repetition, identical blocks, Bravais lattices, centre of symmetry/centre of inversion, plane of symmetry, reflection symmetry, axis of symmetry, congruent position, degree of axis/fold of axis, point groups, rotation-inversion axis, self coincidence, translation symmetry elements, glide plane, screw axis, space groups, five-fold rotation axis, packing fraction/density of packing, simple cubic structure, lattice point, primitive cell, coordination number, nearest neighbour distance, loosely packed and closely packed structures, closest packing, fcc and hcp structures, c/a ratio, Avogadro's number, lattice parameter, atomic volume, diamond cubic structure, NaCl structure, lattice planes, interplanar spacings, cleavage planes, Miller indices, reciprocal lattice, x-ray diffraction and electron diffraction, square reciprocal lattice, Ewald, Bragg's condition of reflection, crystal defects, thermal vibrations, point defects, vacancies, Arrhenius plot, powder method, substitutional and interstitial atoms, Debye and Scherrer, Laue, powder method, Bragg diffraction equation, rotating crystal method, stereographic projection, Laue spots.

2.1 INTRODUCTION

By far the most important fact about materials in general and metals in particular is that they are *crystals*. All their mechanical and physical properties are closely related to this fact. We start by neglecting the nature of the ions of the crystal and simply consider a regular *array of points* in space. This array is the *lattice* and we are concerned with its geometric properties. Because it is a periodic structure, it can be described very simply by defining a *unit cell* as a volume containing one or more points, which may be repeated by unit translations so that a *periodic lattice* is generated. The solids of primary interest for us have an arrangement of atoms (or molecules) in which the atoms are arranged in some regular repetitions pattern in three dimensions. The arrangement of atoms is termed the *crystal structure*. The internal regularity of atoms - placement in solids often leads to a symmetry of their external shape. *Rock salt crystals*, for example, are rectangular parallelepiped with faces which are identical when viewed from many different directions; these crystals have a *high degree of symmetry*.

Prior to the discovery of x-rays, there was no tool to investigate the internal structure of a crystalline solid. However, after the discovery of x-rays in 1895, a systematic study of crystal structure was started—science of crystallography was born.

Q 2.1 Give a brief historical account of the basic terms frequently used in the study of the structure of crystals.

Answer: The study of the *regular and periodic arrangements* of atoms or molecules in space is called *crystal structure*. The crystal structure may be described in terms of an idealized geometrical concept called a *space lattice*. It may be defined as an array of points in space such that the environment about each point is the same. The *three dimensional space lattice* may be defined as an infinite array of points in three dimensions in which every point has an identical environment as any other point in the array.

Example

Let us now consider the case of *two dimensional array of points* as shown in Fig. Q 2.1.1. It is obvious from the figure that the environment about any two points is the same; hence it represents a space lattice. In a mathematical form, the space lattice may be defined as follows:

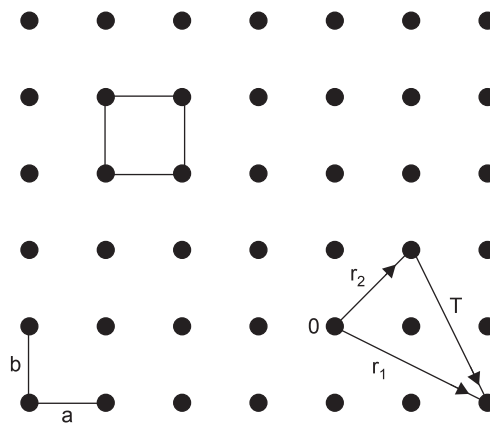


Fig. Q 2.1.1 Two dimensional array of points

We choose any arbitrary point 0 as origin and consider the *position vector* \vec{r}_1 and \vec{r}_2 of any two lattice points by joining them to 0. If the distance \vec{T} of the two vectors \vec{r}_1 and \vec{r}_2 satisfies the following relation,

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b}$$

where n_1 and n_2 are integers and \vec{a} and \vec{b} are *fundamental translation vectors* characteristic of the array, then the array of points is a *two dimensional lattice*. For *three dimensional lattice*,

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

Hence it should be remembered that a crystal lattice refers to the geometry of a set of points in space whereas the structure of the crystal refers to the actual ordering of its constituent ions, atoms and molecules in the space.

The Basis and Crystal Structure

For lattice to represent a crystal structure, we associate every lattice point with one or more atoms (i.e., a unit assembly of atoms or molecules identical in composition) called the *basis* or *pattern*. When the basis is repeated with correct periodicity in all directions, gives the actual crystal. The *crystal structure* is real, while the lattice is imaginary.

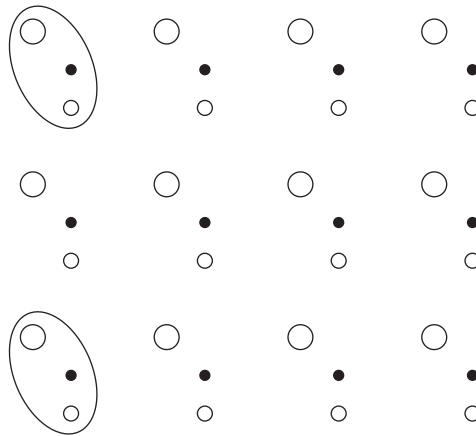


Fig. Q 2.1.2 Basis or Pattern

Thus

lattice + basis = crystal structure

Fig. Q 2.1.2 shows the *basis* or *pattern* representing each *lattice point*. It is observed from the figure that the basis consists of three different atoms. It can also be observed that basis is identical in composition, arrangement and orientation. In crystals like aluminium and sodium the basis is a single atom; in NaCl, KCl, etc. the basis is diatomic whereas in crystals like CaF_2 the basis is triatomic.

Unit Cell and Crystal Lattice

For discussing the unit cell, let us consider a two dimensional crystal in which the atoms are arranged as in Fig. Q 2.1.3. If we consider a parallelogram such as ABCD with sides $AB = a$ and $AD = b$, then by rotating the parallelogram by any integral multiple of vectors \vec{a} and \vec{b} , the whole crystal lattice may be obtained. In this way the fundamental unit ABCD is called a *unit cell*. Thus a unit cell is the smallest geometric figure, the repetition of which gives the actual crystal structure. The unit cell may also be defined as the *fundamental elementary pattern* of minimum number of atoms, molecules or group of molecules—which represent fully all the characteristics of the crystal. It should be noted that the choice of a unit cell is not unique but it can be constructed into a number of ways as EFGH or PQRS shown in Fig. Q 2.1.3. The unit cell should be chosen in such a way that it conveys the symmetry of crystal lattice and makes the mathematical calculations easier.

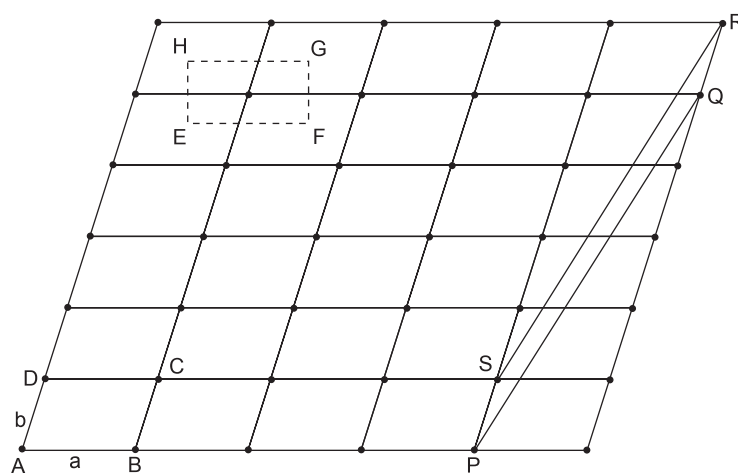


Fig. Q 2.1.3 Two dimensional arrangement of atoms

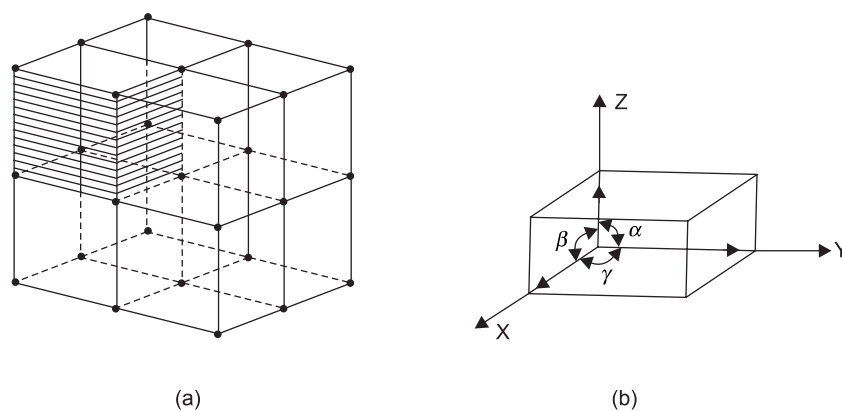


Fig. Q 2.1.4 Three dimensional unit cell

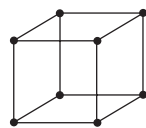
For a three dimensional case, the same procedure may be adopted. A three dimensional unit cell is shown in Fig. Q 2.1.4(a). The unit cell is a parallelepiped formed by the basis vectors \vec{a} , \vec{b} , \vec{c} as concurrent edges and including angles α , β , γ between \vec{b} and \vec{c} , \vec{c} and \vec{a} and \vec{a} and \vec{b} respectively as shown in Fig. Q 2.1.4(b). Thus in general, a unit cell may be defined as that volume of a solid from which the entire crystal may be constructed by *translational repetition* in three dimensions. The entire lattice structure of a crystal is found to consist of *identical blocks* or *unit cells*.

Q 2.2 Discuss the seven systems of crystals and the fourteen types of Bravais lattices with tables and figures.

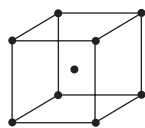
Answer: On the basis of lengths and directions of the axes of symmetry, crystals may be classified into the following systems.

Table Q 2.2.1 The seven crystal systems

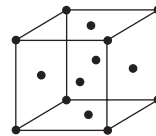
S. No	Name of the crystal system	Relation of length of axes of unit cell	Relation of angle between axes	Examples
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Cu, NaCl, CaF_2
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SnO_2 , NiSO_4
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO_3 , BaSO_4
4	Monoclinic	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	Na_2SO_4 , FeSO_4
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq 90^\circ \neq \gamma$	CuSO_4 , $\text{K}_2\text{Cr}_2\text{O}$
6	Trigonal (Rhombohedral)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaSO_4 , As
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$	Zn, Cd, SiO_2



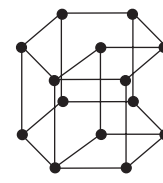
s c



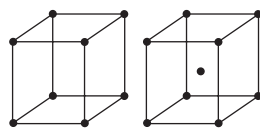
b c c



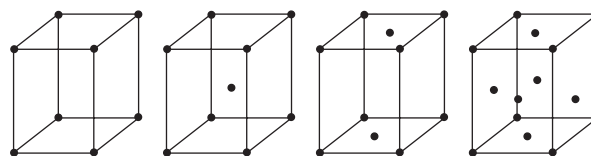
f c c



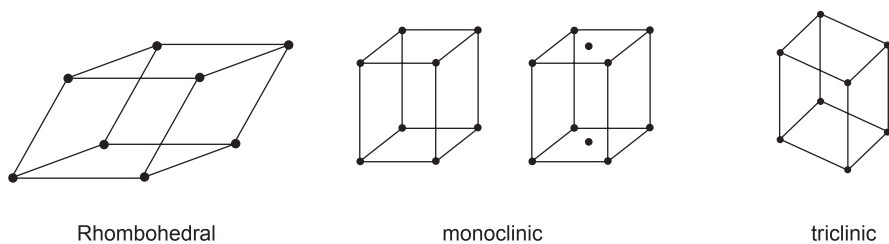
hexagonal



tetragonal



Orthorhombic



Bravais in 1848 theoretically proved that there are precisely 14 possible ways of arrangement of points in a regular three dimensional pattern. Therefore, 14 types of space lattices possible. These are called *Bravais lattices* after the name of their discoverer. Since the atoms in a crystal are also arranged in a regular and definite pattern as in a space lattice, therefore, there can be only 14 possible types of crystals. Any other type of crystal (or arrangement of atoms) except these 14 is just theoretically impossible.

Table Q 2.2.2 Fourteen Bravais lattices in three dimensions and conventional unit cells

S. No.	System	Number of lattices in the system	Space lattices or Bravais lattices	Lattice symbol	Nature of unit cell [Axial length and interaxial angles]
1	Cube	3	Simple Body centred Face centred	P I F	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
2	Tetragonal	2	Simple Body centred	P I	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
3	Orthogonal	4	Simple Base centred Body centred Face centred	P C I F	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
4	Monoclinic	2	Simple Base centred	P C	$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$
5	Triclinic	1	Simple	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$
6	Trigonal	1	Simple	P	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$
7	Hexagonal	1	Simple	P	$a = b \neq c$ $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$

Q 2.3 Explain the following symmetry elements with suitable diagrams for a cubic crystal.

(i) Centre of symmetry (ii) Plane of symmetry (iii) Axis of symmetry

Answer: (i) **Centre of symmetry**

This is a point in the cubic crystal such that any line passing through it meets the surfaces of the crystal at equal distances in both directions is known as *centre of symmetry* or *centre of inversion*. Fig. Q 2.3.1(a).

(ii) **Plane of symmetry**

A crystal is said to possess *reflection symmetry* about a plane if it is left unchanged in every respect after being reflected by the plane. Highly regular crystals may be bilaterally symmetrical about several planes cutting them in different directions. They may have several planes of symmetry. However a plane of symmetry is different from a plane of geometrical symmetry in that a plane of symmetry cuts the crystal into two halves such that one is the mirror image of the other (i.e., one is identical to the other in all respects). A cube has three straight planes of symmetry and six diagonal planes of symmetry. Ref. Fig. Q 2.3.1(a), Q 2.3.1(b) and Q 2.3.1(c).

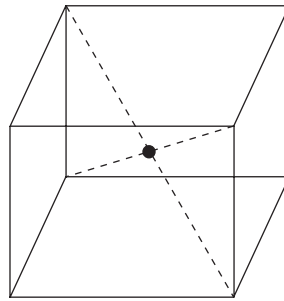


Fig. Q 2.3.1 (a)

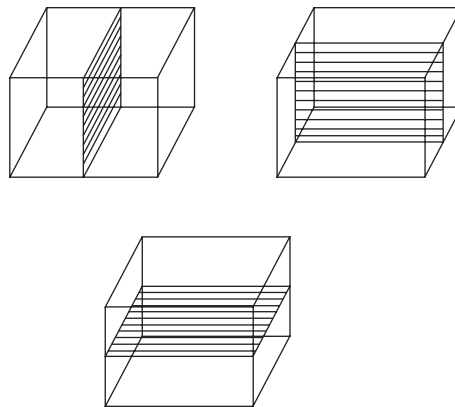


Fig. Q 2.3.1 (b)

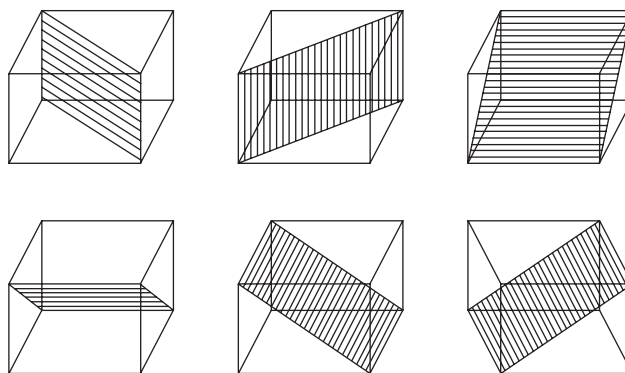


Fig. Q 2.3.1 (c)

(iii) *Axis of symmetry*

The third kind of symmetry element is the axis of symmetry. Let a cube be rotated anti-clock wise about a line passing through the top face centre, centre of symmetry and bottom face centre. For every rotation of 90° , the cube comes to a new position indistinguishable from the previous position. This means that rotation of a cube about this perpendicular axis through 90° brings it into self-coincidence or *congruent position*. The line is then called the *axis of symmetry*. See Fig. Q 2.3.2.

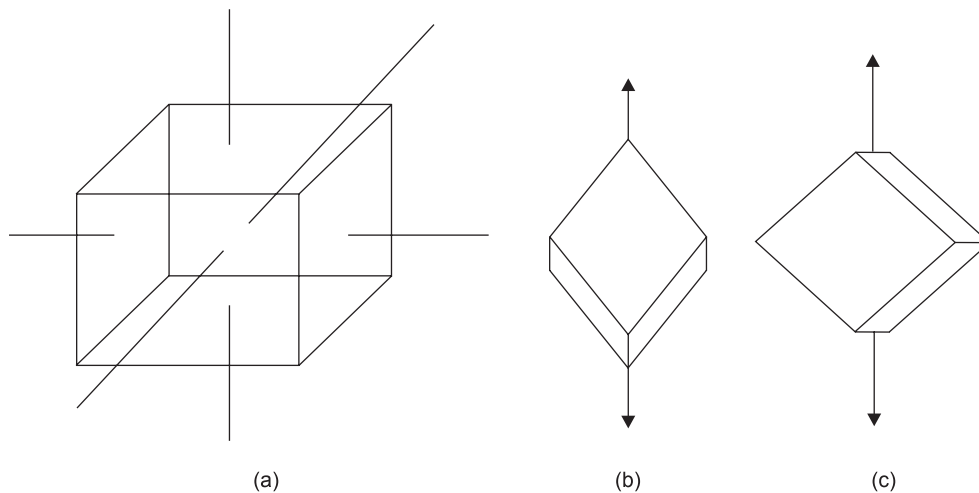


Fig. Q 2.3.2 *Axis of symmetry* (a) The three tetrad axes
(b) One of the triad axes (c) One of the diad axes

In general *axis of symmetry* is defined as a line such that the crystal comes to *congruent position* for every rotation of $\left[\frac{360}{n} \right]^\circ$. The value of n decides the degree or *fold of the axis*. A cube possesses 3 tetrad axis, 4 triad axis and 6 diad axis. The total number of crystallographic symmetry elements of the cubic system are:

– centre of symmetry	1	1 point of symmetry
– straight planes	3	} 9 planes of symmetry
– diagonal planes	6	
– tetrad axes	3	} 13 axes of symmetry
– triad axes	4	
– diad axes	6	
Total	23	symmetry elements

Q 2.4 Write a small note on the combinations of symmetry elements. Also show that 5 fold or any axis of symmetry for $n > 6$ is not permissible in a single crystal.

Answer: The different symmetry elements discussed above can be combined if they are *compatible*. The different combinations give rise to different symmetry points in the crystal. It must be noted that all the crystals do not possess all the symmetries enumerated above. The different crystal systems exhibit different symmetries. It is found that there are 32 compatible combinations of the above three point group-symmetry elements, called simply *point groups*. Crystals belonging to different crystal systems can be classified on the basis of point groups.

1. **Rotation-Inversion Axis**

A crystal structure is said to possess a rotation-inversion axis if it is brought into *self-coincidence* by rotation followed by an *inversion* about a *lattice point* through which the rotation axis passes.

2. **Translation Symmetry Elements**

Glide plane and screw axis are the two symmetry elements discussed here.

(i) *Glide plane*: When a mirror plane is combined with a simultaneous translation operation in a crystal, one gets a glide plane.

(ii) *Screw axis*: Just as it is possible to combine a proper rotation with an inversion to produce a hybrid rotation inversion axis, it is possible to combine a proper rotation with a translation parallel to the rotation axis, i.e., the rotation axis coupled with a translation parallel to the rotation axis will give rise to new symmetry element called the *screw axis*.

(iii) *Space groups*: In a crystal, point group symmetry operations can also be combined with translation symmetry elements, provided they are compatible. Such combinations are called

(iv) *space groups*. There are 230 space groups exhibited by crystals. The study of symmetry elements of the different crystals enables one to classify the crystals and their properties based on different symmetries.

Five-fold Rotation Axis is not Compatible with a Lattice

Let us explain this with reference to Fig. Q 2.4.1. Let us rotate the vectors PX and QY through an angle

$\phi_n = \left[\frac{360}{n} \right]^\circ$ in the clock-wise and anti clock-wise directions respectively. The tips of vectors P_1 and

Q_1 in the two positions must be lattice points if the lattice were to possess n -fold rotation axis of symmetry. As per the definition, rotation operation must leave the lattice *invariant*. Clearly P_1Q_1 must be parallel to PQ and must be equal to an integral multiple of the translation a ; $P_1Q_1 = ma$ where m is an integer.

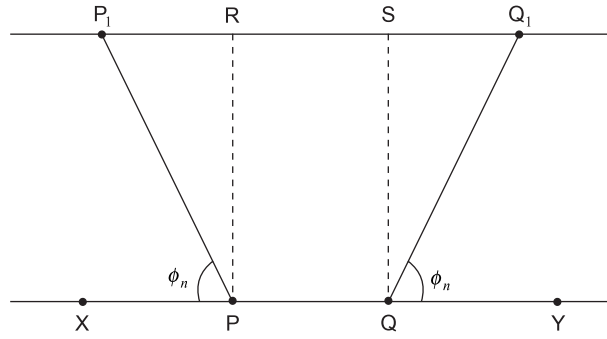


Fig. Q 2.4.1 The possible rotation axes in a single crystal

$$\cos \phi_n = \frac{P_1 R}{PP_1}$$

$$P_1 R = PP_1 \cos \phi_n = a \cos \phi_n$$

Similarly,

$$SQ_1 = a \cos \phi_n$$

Therefore,

$$P_1 Q_1 = P_1 R + SQ_1 + RS$$

$$P_1 Q_1 = 2a \cos \phi_n + a = ma$$

Thus

$$1 + 2 \cos \phi_n = m$$

$$2 \cos \phi_n = (m - 1) = N \text{ where } N \text{ is an integer}$$

$$\cos \phi_n = \left[\frac{m - 1}{2} \right] = \frac{N}{2}$$

Table 2.4.1 Absence of five-fold rotation axis

N	$\frac{N}{2}$	$\cos \phi_n$	ϕ_n	Possible fold of axis, $n = \left[\frac{360}{\phi_n} \right]$
-2	-1	-1	180°	2
-1	-½	-½	120°	3
0	0	0	90°	4
+1	+½	+½	60°	6
+2	+1	+1	360°	1

Q 2.5 What you understand by packing fraction? Compute the packing factor for simple cubic structure and body-centred cubic structure explaining the various terms used with suitable diagrams.

Answer: *Packing fraction* or *density of packing* is defined as the volume occupied by massive atoms in unit volume. Or, it is the ratio of volume occupied by atoms in a unit cell to the total volume of the unit cell. If v and V are the volume occupied by atoms in a unit cell and the volume of the unit cell respectively, then

$$P.F = \frac{v}{V}$$

The packing fraction tells us how closely the atoms are stacked or packed together in the unit cell and hence the name assigned. A high value of $P.F$ tells that the atoms are very closely packed in the unit cell or crystal and there is little unoccupied space. A low value of $P.F$ is the reverse of the above statement. The very interesting part of it is that the properties of many metals and materials depending on the way in which the atoms are arranged in the unit cell or in the crystal as a whole.

1. Simple cubic structure (sc)

In this space lattice, the lattice points are situated only at the corners of the unit cells constituting the three dimensional structure. Each cell has eight corners, and eight cells meet at each corner. Thus only

one-eighth of the lattice point belongs to each cell. That is, there is only one *lattice point* $\left(\frac{1}{8} \times 8\right)$ or one atom per unit cell. A unit cell containing only one lattice is called a *primitive cell*. Since the simple cubic lattice is built of *primitive cells*, it is also known as cubic P lattice. The number of nearest neighbours around an atom (or lattice point) is called *coordination number*. In this structure each atom is coordinating 6 atoms one in the front, another at the back and then one at the left and the other at the right. Finally one set of atoms at the top and the other at the bottom. All the atoms touch each other along the edges. Thus the *nearest neighbour distance*, $2r = a$; and the *coordination number* is defined as the number of nearest neighbours around any lattice point (or atom) in the *crystalline lattice*. Let us now compute the packing factor of this structure.

1. the nearest neighbour distance, $2r = a$
2. the lattice parameter, $a = 2r$
3. number of atoms in the unit cell, 1
4. volume of all the atoms in a cell, $v = 1 \times \frac{4}{3} \pi r^3$
5. volume of the unit cell, $V = a^3 = (2r)^3$
6. coordination number, CN = 6

Thus the packing fraction or density of packing of this structure is,

$$P.F = \frac{v}{V} = \left[\frac{4\pi r^3}{3} \right] \left(\frac{1}{a^3} \right) = \frac{4\pi r^3}{3 \times 8 \times r^3} = \frac{\pi}{6} = 0.52$$

$P.F = 0.52 \text{ or } 52\%$

(Q 2.5.1)

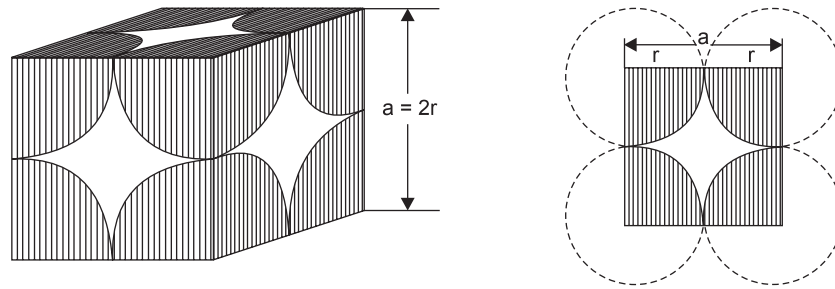


Fig. Q 2.5.1 Simple cubic structure

2. Body-centred cubic (bcc) lattice

Here the lattice points (or atoms) are situated at each corner of the unit cell. Also one more atom is located at the body centre (centre of symmetry) where the three body diagonals intersect along which the atoms touch each other. Thus the total number of lattice points in a unit cell is $\left(\frac{1}{8} \times 8 + 1\right) = 2$ and $(4r)^2 = 3a^2$. The atom at the body centre is in contact with the 8 corner atoms. Hence the coordination number of bcc structure is 8.

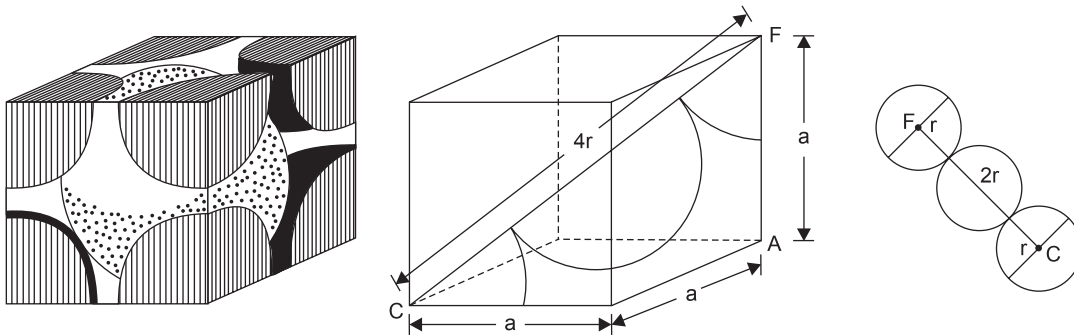


Fig. Q 2.5.2 Body centred cubic

The packing fraction of this lattice or structure is computed using the following data:

1. the nearest neighbour distance, $2r = \frac{a\sqrt{3}}{2}$
2. the lattice parameter, $a = \frac{4r}{\sqrt{3}}$
3. number of atoms in the unit cell, 2
4. volume of all the atoms in the unit cell, $v = 2 \times \frac{4}{3} \pi r^3$

5. volume of unit cell, $V = a^3 = \frac{64r^3}{3\sqrt{3}}$

6. coordination number, $CN = 8$

Thus packing fraction,

$$P.F = \frac{v}{V} = \frac{8 \times \pi r^3 \times 3\sqrt{3}}{3 \times 64r^3} = 0.68$$

$$P.F = 0.68 \text{ or } 68\%$$

(Q 2.5.2)

Sodium, iron, chromium and CsCl are some examples of bcc structure; sc and bcc structures are commonly known as loosely packed (respectively) structure and closely packed structure.

Q 2.6 Explain what is meant by closest packing in crystals? Describe face centred cubic lattice and hcp structure which are the two illustrations of closest packing structures.

Answer: 1. **Closest packing**

For crystals in which all the atoms are identical, there are two forms of closest packing: face centred cubic (fcc) space lattice and hexagonal close packed structure (hcp). It is a way of arranging equi-dimensional objects in space such that the available space is filled very efficiently. This is achieved only when each object is in contact with the maximum number of like objects as shown in Fig. Q 2.6.1.

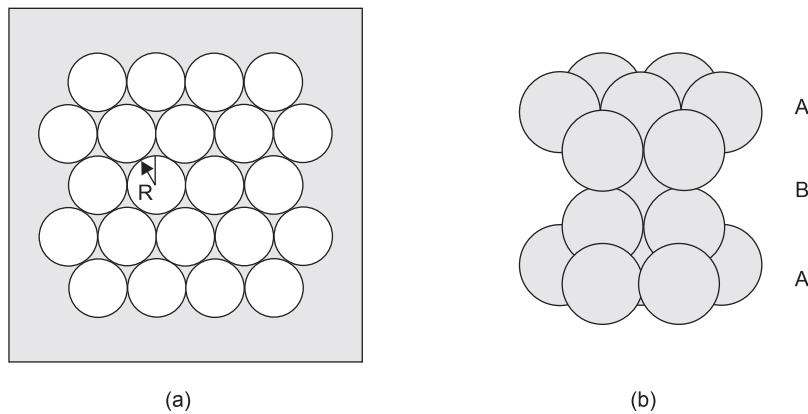


Fig. Q 2.6.1 Closest packing of spheres in two-dimension and in three-dimension

Let us now discuss the two well known closest structures, fcc and hcp.

2. Face centred cubic structure (fcc)

Here the lattice points (or atoms) are situated at all the eight corners as in the previous two cases, but also at the centres of the six faces. The face centre atom shares with two unit cells. Hence the number

of atoms in a unit cell is $\left(\frac{1}{8} \times 8 + 3\right) = 4$. This lattice is also known as cubic F lattice. The atoms touch along the face diagonals. The packing fraction is now calculated.

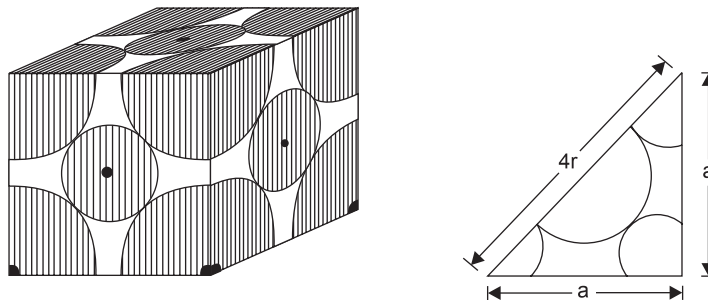


Fig. Q 2.6.2 Face centred cubic structure

- | | |
|--|---------------------------------|
| 1. the nearest neighbour distance, $2r$ | $= \frac{a\sqrt{2}}{2}$ |
| 2. the lattice parameter, a | $= \frac{4r}{\sqrt{2}}$ |
| 3. number of atoms in the unit cell, | $= 4$ |
| 4. volume of all the atoms in the unit cell, v | $= 4 \times \frac{4}{3}\pi r^3$ |
| 5. volume of unit cell, V | $= a^3$ |
| 6. coordination number, CN | $= 8$ |

Thus density of packing fraction,

$$P.F = \frac{v}{V} = \left[\frac{16\pi r^3}{3} \right] \left[\frac{2\sqrt{2}}{(4r)^3} \right] = \frac{32\pi\sqrt{2}}{3 \times 64} = 0.74$$

$$P.F = 0.74 \text{ or } 74\%$$

(Q 2.6.1)

3. Hexagonal close packed structure (hcp)

Hexagonal close packed structure is a closest packing one and its packing fraction is almost as that of fcc space lattice. The unit cell contains one atom at each corner, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell. Each atom touches three atoms in the layer below its plane, six atoms in its own plane, and three atoms in the layer above.

Hence the coordination number of this structure is 12. Further the atoms touch each other along the edge of the hexagon.

Thus $2r = a$.

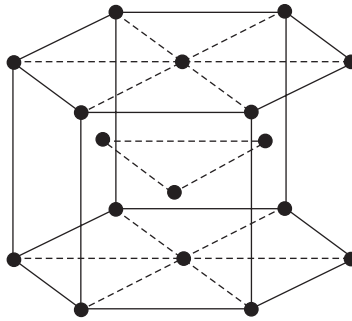


Fig. Q 2.6.3 *Ideal hexagonal close packed structure*

The top layer contains seven atoms. Each corner atom is shared by surrounding hexagon cells and the centre atom is shared by 2 surrounding cells. The three atoms within the body of the cell are fully contributing to the cell.

Thus the total number of atoms in a unit cell is $\frac{3}{2} + \frac{3}{2} + 3 = 6$

$\frac{c}{a}$ ratio for an ideal hexagonal packed structure:

Let c and a be respectively the height and edge of the unit cell. The 3 atoms at the bottom and top face in a horizontal plane at $\frac{c}{2}$ from the orthocentres of alternate equilateral triangles at the top or base of the hexagonal cell. These 3 atoms just rest on the three atoms at the corners of the triangles.

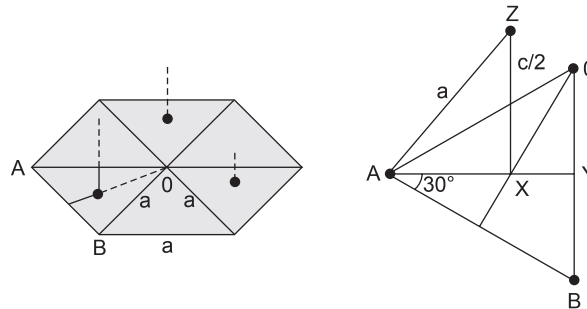


Fig. 2.6.3 (a) *Sketch of the bottom layer*

In the triangle ABY

$$\left\{ \begin{array}{l} \cos 30^\circ = \frac{AY}{AB}; AY = \frac{a\sqrt{3}}{2} \\ \text{and } (AZ)^2 = (AX)^2 + (ZX)^2 \end{array} \right\} \quad (\text{Q 2.6.2})$$

In the triangle AXZ,

$$AX = \frac{2}{3} AY = \frac{2a\sqrt{3}}{6} = \frac{a}{\sqrt{3}}$$

Substituting this value in Eqn. (Q 2.6.2), we get

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4}; \frac{c^2}{4} = a^2 - \frac{a^2}{3} = \frac{2}{3}a^2$$

or

$$\frac{c^2}{a^2} = \frac{8}{3}; \frac{c}{a} = \sqrt{\frac{8}{3}}$$

i.e.,

$$\boxed{\left\{ \frac{c}{a} = \sqrt{\frac{8}{3}} \right\}} \quad (\text{Q 2.6.3})$$

Volume of the unit cell

$$\text{Area of the triangle, AOB} = \frac{1}{2} (\text{BO}) (\text{AY})$$

$$= \frac{1}{2} a \left\{ a \frac{\sqrt{3}}{2} \right\}$$

$$\text{Hence area of the base, } \frac{6 \times a^2 \sqrt{3}}{4} = \frac{3}{2} \sqrt{3} (a^2)$$

$$\text{Volume of the unit cell, } V = \frac{3}{2} \sqrt{3} (a^2 \times c)$$

$$\boxed{\left\{ V = \frac{3 \times \sqrt{3} a^2 c}{2} \right\}} \quad (\text{Q 2.6.4})$$

Packing fraction calculation

- | | |
|--|--|
| 1. the nearest neighbour distance, $2r$ | $= a$ |
| 2. the lattice parameter, a | $= 2r$ |
| 3. number of atoms in the unit cell, | $= 6$ |
| 4. volume of all the atoms in the unit cell, v | $= 6 \times \frac{4}{3} \pi r^3 = \frac{24\pi r^3}{3} = \pi a^3$ |
| 5. volume of unit cell, V | $= \frac{3\sqrt{3} a^2 c}{2}$ |
| 6. coordination number, CN | $= 12$ |

$$7. \frac{c}{a} = \sqrt{\frac{8}{3}}$$

Thus density of packing fraction,

$$\text{P.F} = \frac{v}{V} = \frac{\pi a^3 \times 2}{3\sqrt{3} a^2 c} = \left[\frac{2\pi}{3\sqrt{3}} \right] \left[\frac{a}{c} \right] = \left[\frac{2\pi}{3\sqrt{3}} \right] \left[\frac{3}{8} \right]^{\frac{1}{2}}$$

$$\text{Thus P.F} = \left\{ \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\% \right\} \quad (\text{Q 2.6.5})$$

Q 2.7 Copper belongs to fcc space lattice. If M_A and ρ are respectively its atomic weight and density, find an equation connecting the lattice parameter and the said physical quantities. Also briefly discuss diamond cubic structure and the structure of sodium chloride crystal.

Answer: Let N_A be the Avogadro's number and $n = 4$ is the number of atoms in a unit cell and a be the lattice parameter.

Now M_A/ρ is the atomic volume which will contain N_A copper atoms. Hence a^3 (volume of the unit cell) will contain $\frac{\rho a^3 N_A}{M_A}$ atoms. This must be equal to n ($= 4$ in this case).

$$\text{i.e.,} \quad \frac{a^3 \rho N_A}{M_A} = n$$

$$\text{or} \quad a^3 = \frac{n M_A}{\rho N_A}$$

$$a = \left[\frac{n M_A}{\rho N_A} \right]^{\frac{1}{3}} \quad (\text{Q 2.7.1})$$

Diamond Cubic Structure

The space lattice of diamond is face-centred cubic (fcc) with a basis of two carbon atoms associated with each lattice point. The figures show the position of atoms in the cubic cell of the diamond structure projected on a cubic face. The fractions denote height above the base in units of a cube edge. The points at 0 and $\frac{1}{2}$ are on the face lattice, those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a similar lattice displaced along the body diagonal by one-fourth of its length. Thus the diamond lattice is composed of two interleaved fcc sublattices, one of which is shifted relative to the other by one-fourth of a body diagonal. In a diamond crystal the carbon atoms are linked by directional covalent bonds. Each carbon atom forms covalent bonds with four other carbon atoms that occupy four corners of a cube in a tetrahedral structure. The length of each bond is 0.154 nm and the angle between the bonds is 109.5° . Gray tin, silicon and germanium crystallize in the dc structure. In this structure each atom has four neighbours. The number of atoms per unit cell is 8.

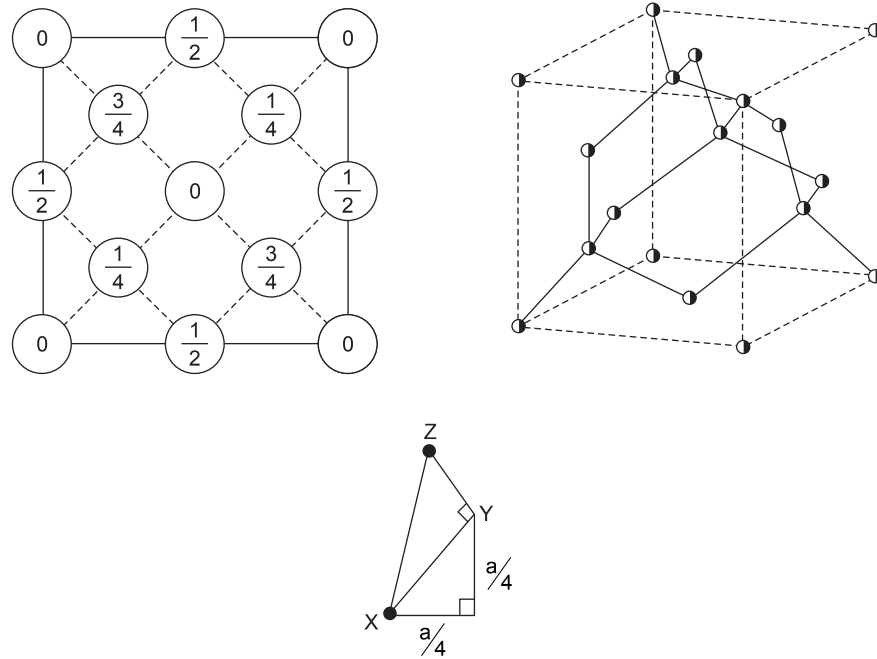


Fig. Q 2.7.1 Diamond structure

Computation of Packing Fraction

$$(XY)^2 = \frac{a^2}{16} + \frac{a^2}{16} = \frac{a^2}{8}$$

$$(XZ)^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{16} + \frac{a^2}{8} = \frac{3a^2}{16}$$

i.e.,

$$(2r)^2 = \frac{3a^2}{16}; \text{ or } 2r = a \left[\frac{\sqrt{3}}{4} \right]$$

- | | |
|--|----------------------------------|
| 1. the nearest neighbour distance, $2r$ | $= \frac{a\sqrt{3}}{4}$ |
| 2. the lattice parameter, a | $= \frac{8r}{\sqrt{3}}$ |
| 3. number of atoms in the unit cell, | $= 8$ |
| 4. volume of all the atoms in the unit cell, v | $= 8 \times \frac{4}{3} \pi r^3$ |
| 5. volume of unit cell, V | $= a^3$ |
| 6. coordination number, CN | $= 4$ |

Thus the packing fraction is,

$$\begin{aligned} \text{P.F} &= \frac{v}{V} = \frac{32\pi r^3 \times 3\sqrt{3}}{3 \times (8r)^3} \\ &= \frac{32 \times \pi r^3 \times 3\sqrt{3}}{3 \times 8 \times r^3} = \frac{\pi\sqrt{3}}{2 \times 8} = 0.34 \end{aligned}$$

$$\text{P.F} = 0.34 \text{ or } 34\%$$

(Q 2.7.2)

Sodium Chloride Structure

NaCl and KCl crystallize in this structure. Fig. Q 2.7.2 shows NaCl structure.

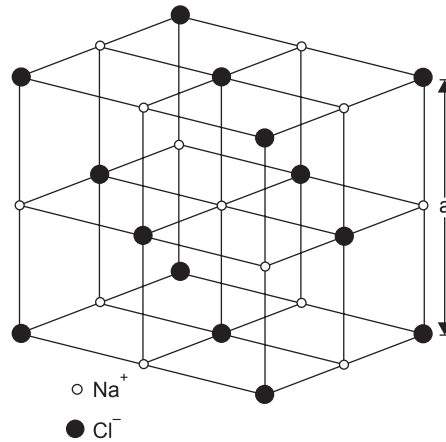


Fig. Q 2.7.2 Sodium chloride structure

Here the Na and Cl atoms (strictly ions) occupy alternately the corners of an elementary cube. Let d be the distance between adjacent atoms and hence $a = 2d$ is the lattice parameter or edge of the unit cell. Thus the number of ions in unit volume is $\frac{1}{d^3}$ and number of NaCl molecules in unit volume is

$\frac{1}{2a^3}$; where d is interionic distance.

Q 2.8 What are Miller indices? How are they obtained? Sketch the (0 1 0), (1 1 0) and (1 1 1) planes in a cubic crystal.

Answer: A crystal lattice may be considered as an aggregate of a set of parallel, equally spaced planes passing through the lattice points. The planes are called *lattice planes*, and the perpendicular distance between adjacent planes is called *interplanar spacing*. A given space lattice may have an infinite sets of lattice planes, each having its characteristic *interplanar spacing*. Out of these, only those, which have high density of lattice points are significant and show diffraction of x-rays. They are known as *Bragg planes* or *Cleavage planes*. When a crystal is struck, it breaks most easily across its cleavage planes. Hence it is essential to evolve a method to designate these planes in a crystal. Miller evolved a method to designate a set of parallel planes in a crystal by three numbers ($h k l$) known as *Miller indices*.

The steps in the determination of Miller indices of a set of parallel planes are illustrated with the aid of Fig. Q 2.8.1.

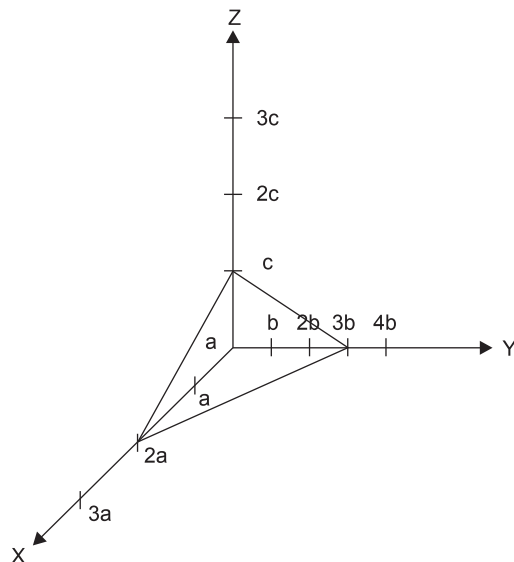


Fig. Q 2.8.1 *Miller indices of an important plane*

- i. Determine the coordinates of the intercepts made by the plane along the three crystallographic axes (x, y, z).

$$\begin{array}{ccc} x & y & z \\ 2a & 3b & c \\ pa & qb & rc \quad (p = 2, q = 3, r = 1) \end{array}$$

- ii. Express the intercepts as multiples of the unit cell dimensions, or lattice parameters along the axes, i.e.,

$$\begin{array}{ccc} \frac{2a}{a} & \frac{3b}{b} & \frac{c}{c} \\ 2 & 3 & 1 \end{array}$$

- iii. Get the reciprocals of these numbers.

$$\begin{array}{ccc} \frac{1}{2} & \frac{1}{3} & \frac{1}{1} \end{array}$$

- iv. Reduce these reciprocals to the smallest set of integral numbers and enclose them in brackets:

$$\begin{array}{ccc} 6 \times \frac{1}{2} & 6 \times \frac{1}{3} & 6 \times \frac{1}{1} \\ 3 & 2 & 6 \\ (3 \ 2 \ 6) \end{array}$$

Thus *Miller indices* may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers.

Conclusions

- i. All the parallel equidistant planes have the same *Miller indices*. Thus the *Miller indices* define a set of parallel planes.
- ii. A plane parallel to one of the coordinate axes has been intercept of infinity.
- iii. If the *Miller indices* of two planes have the same ratio; i.e., (8 4 4) and (4 2 2) or (2 1 1), then the planes are parallel to each other.
- iv. If (*h k l*) are the *Miller indices* of a plane, then the plane cuts the axes into *h*, *k* and *l* equal segments respectively.

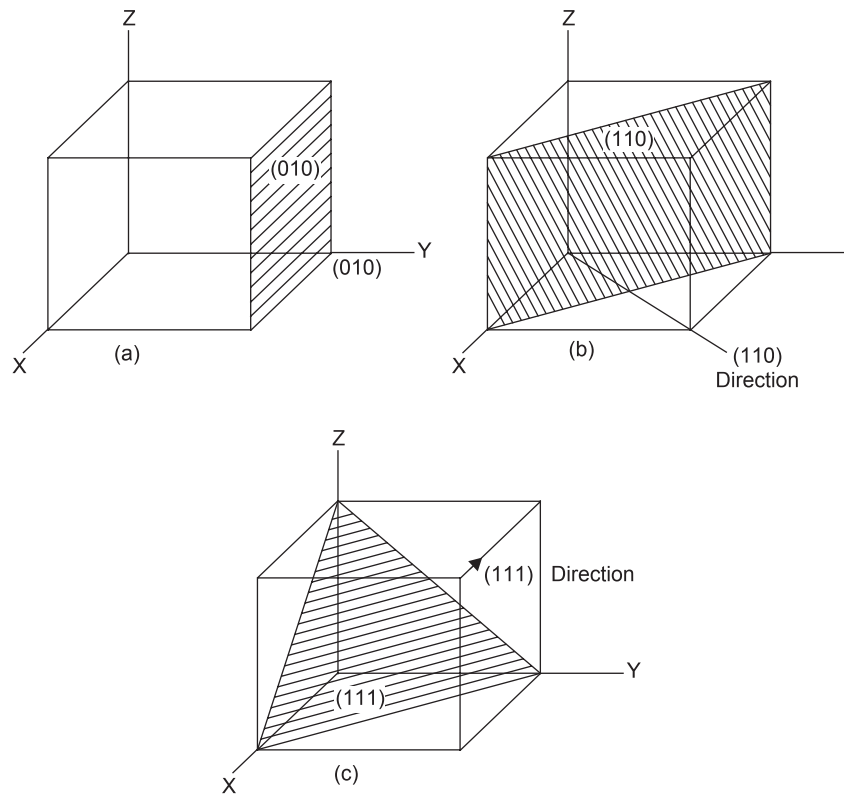


Fig. Q 2.8.2 Sketch of important planes in a cube

Q 2.9 Show that in a cubic crystal the spacing between consecutive parallel planes of Miller indices (*h k l*) is given by:

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

Answer: $(h\ k\ l)$ represents the *Miller indices* of the plane A B C. This plane belongs to a family of planes whose Miller indices are $(h\ k\ l)$ because Miller indices represent a set of planes. See Fig. Q 2.9.1.

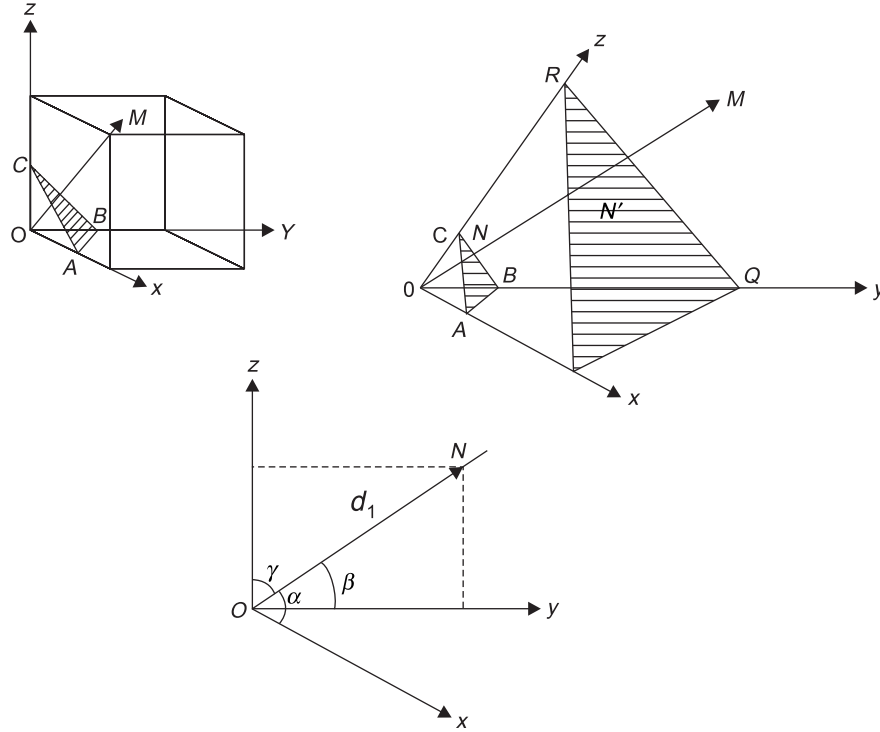


Fig. Q 2.9.1 Interplanar Spacing

Let α' , β' and γ' (different from the interfacial angles α , β and γ) be the angles between coordinates axes X Y Z respectively and ON.

$$OA = \frac{a}{h}, OB = \frac{a}{k} \text{ and } OC = \frac{a}{l}$$

From Fig. Q 2.9.1 (a),

$$\cos \alpha' = \frac{d_1}{OA}, \cos \beta' = \frac{d_1}{OB} \text{ and } \cos \gamma' = \frac{d_1}{OC} \quad (\text{Q 2.9.1})$$

From Fig. Q 2.9.1(b),

$$(ON)^2 = x^2 + y^2 + z^2 \text{ with } ON = d_1$$

i.e.,

$$d_1^2 = \left\{ d_1^2 (\cos^2 \alpha') + d_1^2 (\cos^2 \beta') + d_1^2 (\cos^2 \gamma') \right\}$$

or

$$d_1 = d_1 [\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma']^{1/2}$$

In the cartesian system of coordinates the sum of the squares of the direction cosines is equal to 1. So

$$\boxed{\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1} \quad (\text{Q 2.9.2})$$

Substituting this in equation (Q 2.9.1), we get

$$\left[\frac{d_1}{OA} \right]^2 + \left[\frac{d_1}{OB} \right]^2 + \left[\frac{d_1}{OC} \right]^2 = 1$$

i.e.,

$$\left[\frac{d_1 h}{a} \right]^2 + \left[\frac{d_1 k}{b} \right]^2 + \left[\frac{d_1 l}{c} \right]^2 = 1$$

$$\frac{d_1^2}{a^2} (h^2 + k^2 + l^2) = 1 \text{ for cubic system}$$

$$d_1^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

$$\boxed{d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}} \quad (\text{Q 2.9.3})$$

Let $OM = d_2$ be the perpendicular of the next plane P Q R parallel to the plane A B C. The intercepts of this plane on the three crystallographic axes are:

$$OA' = \frac{2a}{h}, OB' = \frac{2a}{k} \text{ and } OC' = \frac{2a}{l}$$

and

$$\boxed{\cos \alpha' = \frac{d_2}{OA'}, \cos \beta' = \frac{d_2}{OB'}, \text{ and } \cos \gamma' = \frac{d_2}{OC'}} \quad (\text{Q 2.9.4})$$

$$(OM)^2 = d_2^2 \cos^2 \alpha' + d_2^2 \cos^2 \beta' + d_2^2 \cos^2 \gamma' \text{ with } OH = d_2$$

i.e.,

$$\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$$

Substituting this in equation (Q 2.9.4), and simplifying one gets

$$\left[\frac{d_2 h}{2a} \right]^2 + \left[\frac{d_2 k}{2b} \right]^2 + \left[\frac{d_2 l}{2c} \right]^2 = 1$$

$$\frac{d_2^2}{4a^2} (h^2 + k^2 + l^2) = 1$$

i.e.,

$$d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}} \quad (\text{Q 2.9.5})$$

Thus the interplanar spacing between two adjacent parallel planes of Miller indices $(h \ k \ l)$ in a cubic lattice is given by:

$$d = d_2 - d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (\text{Q 2.9.6})$$

Q 2.10 Explain how crystal lattice is conveniently represented by *reciprocal lattice*

Answer: The crystal lattice is conveniently represented by what is known as *reciprocal lattice*. The concept of reciprocal lattice is useful in the study of *x-ray diffraction* and *electron diffraction* produced by a crystal. The reciprocal lattice of a real crystal is constructed as follows:

1. choose a point as origin.
2. draw normals to every set of planes from this origin.
3. make the length of the normal equal to the reciprocal of the inter planer spacing of that set of planes.
4. place a point at the end of the normal.

Have a look at Fig. Q 2.10.1. Consider a plane represented by the line $(3 \ 2)$. It is clear that $\frac{OB}{OA} = \frac{OC}{AC}$ (by similarity of triangles).

$$\frac{d}{b/h} = \frac{a/k}{\sqrt{(a^2/k^2 + b^2/h^2)}} \quad (\text{Q 2.10.1})$$

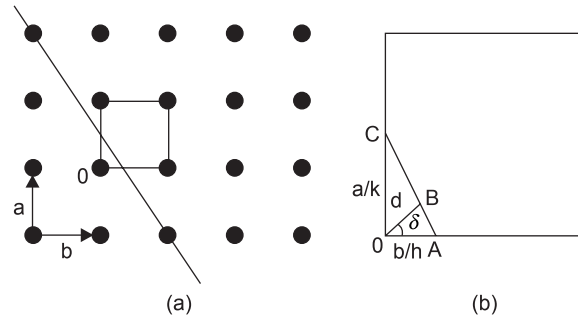


Fig. Q 2.10.1 (a) A square lattice showing the unit cell and a (h, k) plane; (b) the imagined unit cell

If $\sigma = \frac{1}{d}$, this will give,

$$\sigma = \frac{\sqrt{h^2 a^2 + k^2 b^2}}{ab} \quad (\text{Q 2.10.2})$$

The direction of σ is

$$\tan \delta = \frac{b/h}{a/k} \quad (\text{Q 2.10.3})$$

The point representing the (3 2) plane in the reciprocal lattice is shown in Fig. Q 2.10.2. The planes of a *square lattice* are represented by a *square reciprocal lattice* and so on. It can be shown that the diffraction of x-rays or of an electron beam by a real crystal lattice will give an array of points identical with its *reciprocal lattice*.

The Ewald Construction

Let us take a *two dimensional square reciprocal lattice* (Fig. Q 2.10.3). Let an x-ray beam of wavelength λ strike the surface. The radiation represented by a wave vector k whose length is $1/\lambda$ and its direction is the direction of the beam. Take a point O in the reciprocal lattice as the origin. Let one end of the wave vector be at O and draw circle of radius $1/\lambda$ with the centre at the other end A of the vector.

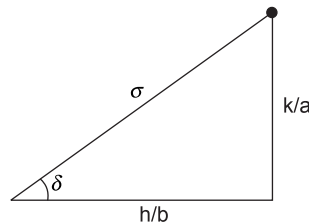


Fig. Q 2.10.2 The reciprocal lattice point

Let the circle pass through another point B in the reciprocal lattice. Construct a triangle AOB. Since OB joins origin O to a reciprocal lattice point, it is perpendicular to a set of planes in the real lattice whose interplanar distance $d = \frac{1}{OB}$. Since AC is perpendicular to OB, it is a lattice plane. The angle θ is the angle of incidence of the beam on the lattice plane since it is the angle between AC that is a lattice plane and AO (directions of the beam).

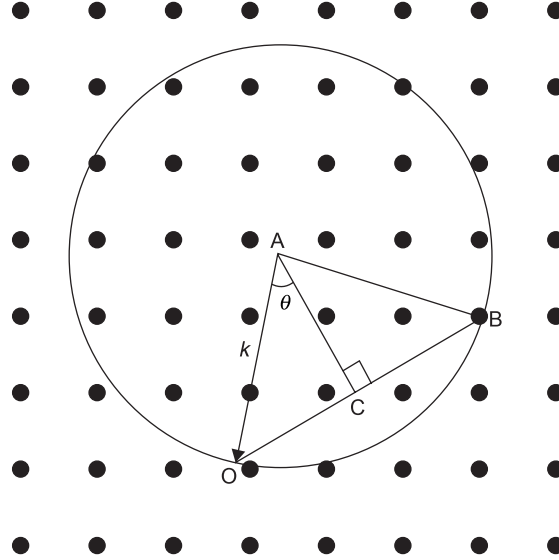


Fig. Q 2.10.3 The reciprocal lattice point

For the triangle AOC

$$\sin \theta = \frac{OC}{k} = \frac{OB}{2k}; \text{ but } k = \frac{1}{\lambda} \text{ and } OB = \frac{1}{d}$$

Hence

$$\sin \theta = \frac{\lambda}{2d}; \text{ i.e., } 2d \sin \theta = \lambda \quad (\text{Q 2.10.4})$$

This is same as the *Bragg's condition of reflection*. So, the reciprocal lattice is the diffraction pattern of the real lattice. This understanding makes it possible to construct the real lattice based on its diffraction pattern.

Q 2.11 Write a note on crystal defects.

Answer: One hundred percent of ideal crystals do not—cannot exist.

1. Thermal vibrations

The temperature of a solid is a measure of the amplitude of the random vibration of its atoms and these vibrations cause the displacement of the atoms from their ideal positions. This displacement is an important cause of electrical resistance in metals: without it pure metals would have very much less

resistance than they do have. At room temperature, for example, copper has about a hundred times the resistivity it has at liquid helium temperature (4.2 K), where thermal vibrations have almost ceased. Other crystal defects may be classified by their dimensionality.

2. Zero-dimensional (point) defects

There are three kinds of point defects in crystalline solids

- (i) Vacancies, the sites where atoms are missing
 - (ii) Substitutional impurities, which are foreign atoms that replace host atoms.
 - (iii) Interstitial atoms, or interstitialcies, are atoms located in the holes between atoms of the host lattice. They may be foreign atoms or host atoms that have become misplaced.
- (a) **Vacancies:** When a crystal forms, usually at high temperatures, many vacancies are present. As the crystal cools, the equilibrium number of vacancies falls too, by diffusion process. Eventually the rate of diffusion becomes so slow that the vacancies are frozen into the structure. Thus at room temperature, the vacancies in a solid are at equilibrium, but are in concentrations characteristic of some higher temperatures. Vacancies are important because they are responsible for diffusion and void reduction in solids. They play a minor role in the electrical resistivity of pure metals.

Suppose the energy required to form a vacancy is E_v . Then the equilibrium number of vacancies, n , at an absolute temperature, T , is given by the Boltzmann distribution

$$n = N \exp(-E_v/k_B T) \quad (\text{Q 2.11.5})$$

where N is a constant and k_B is Boltzmann's constant. A plot of $\ln(n)$ against $1/T$ will give a straight line of slope $(-E_v/k_B)$, sometimes known as *Arrhenius plot*. Now n can be measured by indirect means fairly simply: For example, by measuring the thermal expansion $(\delta l/l)$ of a sample as the temperature rises and comparing it with the change in lattice parameter found by x-rays $(\delta a/a)$. The x-rays do not take any notice of the odd vacant site, so the change in volume that they record is smaller than the actual change in volume. Alternately, the sample can be quenched (cooled rapidly) from high temperature to freeze in the vacancies, and the density at room temperature of the quenched sample can be compared to that of the slowly cooled sample. For aluminium,

$$\frac{E_v}{k_B} = 9700; E_v = 9700 \times 1.38 \times 10^{-23} \text{ J}$$

or $E_v = 0.84 \text{ eV}$ for convenience, energies in atoms are given in eV.

(b) Substitutional and interstitial atoms

When an impurity atom is dissolved in a solid it can take up a normal lattice by displacing a host atom, or it can squeeze into the spaces between host atoms: which it does depend largely on the relative sizes of host and impurity atoms. In the case of ionic solids the position is complicated by the requirement for charge neutrality. If CaCl_2 is dissolved in KCl , for example, the Ca^{2+} ions replace the K^+ ions, but because there must be charge neutrality in the solid, a vacant K^+ site must be formed at the same time. In Cu_2O , there is small fraction of Cu^{2+} ions each requiring a Cu^+ ion vacancy to maintain charge neutrality. The extra positive charge on the cations is mobile and is responsible for p -type conductivity in the material: Cu_2O is termed a defect semiconductor.

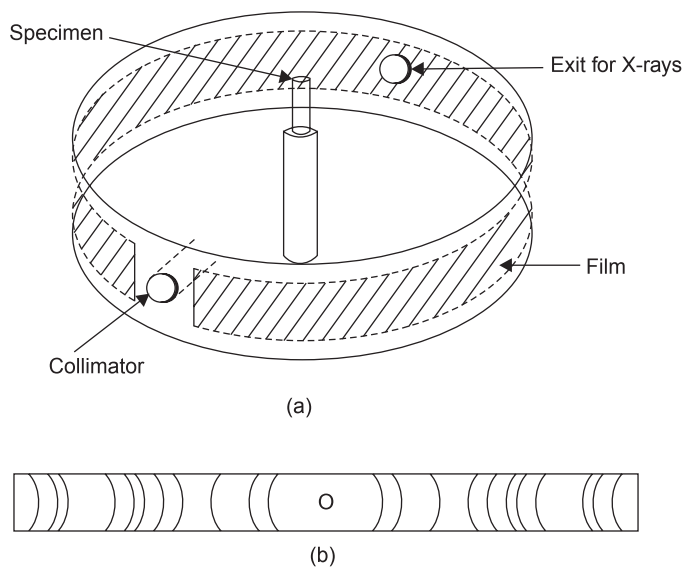
Q 2.12 Describe powder method of crystal structure study using x-rays.

Answer: Bragg's method of crystal analysis can be carried out only if large crystals are available. Hence it is not always possible to adopt this method. Debye and Scherrer adopted a method by means of which analysis can be done using a small amount of powdered crystal. The particles of the powder contain a large number of micro crystals. If a monochromatic x-ray beam falls on a single crystal, then for a Bragg diffraction, it is necessary to provide a range of values of either θ or λ . The various experimental ways to provide such arrangements is the basis of the different x-ray diffraction methods. In the powder method and the rotation crystal method, θ is variable while the powdered crystal and a single crystal is placed in a beam of monochromatic x-rays respectively. In the Laue method, λ is variable as the x-rays of many wavelengths are being used of a single angle of incidence.

In the powder method, the monochromatic x-rays are falling on a finely powdered or a finely grained polycrystalline specimen as shown in Fig. Q 2.12.1(a).

If we consider the diffracted beam from a large number of crystallites which are randomly oriented, then any crystallite giving the reflection will produce a diffracted beam making an angle 2θ with the incident beam and, therefore, the locus of all such diffracted beams is a cone of semiangle 2θ with apex at the specimen. When the film is made flat, the powder diffraction pattern looks like as shown in Fig. Q 2.12.1(b), the cones making a series of concentric rings around the central spot. If S is the maximum diameter of a ring and if R is the radial distance from specimen to the film, then the Bragg angle θ in

radian will be $\frac{S}{4R}$, as can be seen from Fig. Q 2.12.1(b). From the Bragg angle θ , the *interplaner distance* d can be determined with the use of *Bragg diffraction equation*. These distances are related to the *lattice parameters* and the *Miller indices* for any crystal. The observed interplaner spacings are compared with the spacings that would exist in unit cells of various dimensions and angles. In the less symmetrical crystal systems, this trial procedure is quite complicated. However, in highly symmetrical crystal system like cubic, the procedure is quite simple. Therefore, the structure of the simpler crystals can be completely determined by the powder method alone.



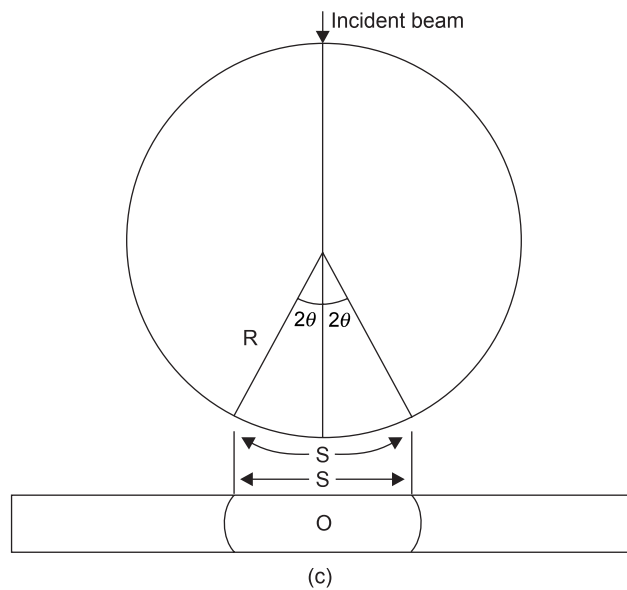


Fig. Q 2.12.1 (a) X-ray powder diffraction arrangement (b) Typical powder diffraction pattern (c) Conversion of linear distance on the film into Bragg angle

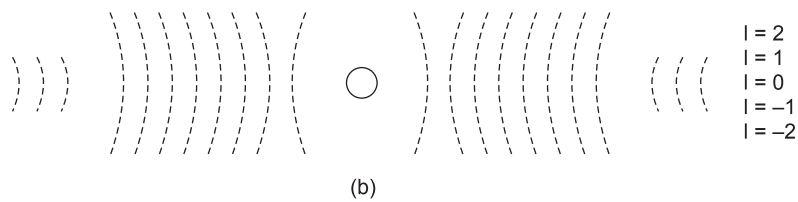
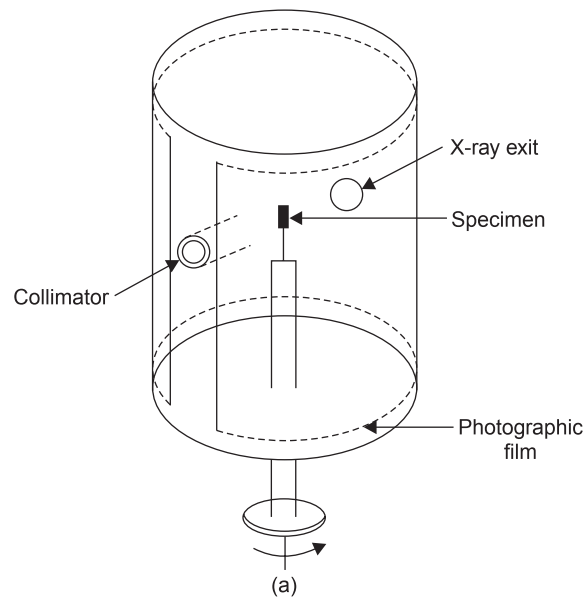


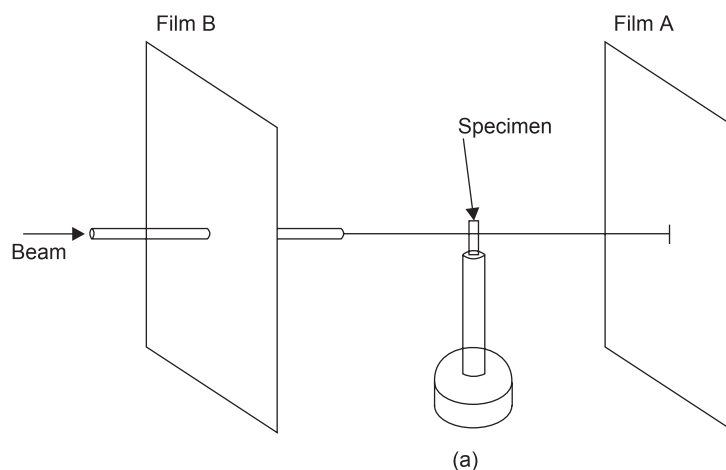
Fig. Q 2.12.2 (a) X-ray rotating crystal camera (b) Typical rotating crystal diffraction pattern indicating various layer lines

In order to overcome the difficulties faced in the powder method, the *rotating crystal method* is used whenever single crystals are available. In this method, the single crystal is rotated continuously about an axis that is perpendicular to the x-ray beam as shown in Fig. Q 2.12.2(a). The diffracted beams emerge out when the angle of incidence on a certain plane is according to Bragg equation for the monochromatic x-ray radiation. A cylindrical film from such method will give a pattern in Fig. Q 2.12.2(b). The characteristic feature of a rotation photograph is the occurrence of diffraction spots along a set of parallel straight lines, known as layer lines. The spots on the central layer line are reflections from planes whose normals are in a horizontal plane whereas the spots on any other layer line are from planes that have the same intercept on the axis of rotation. From the distance between these straight lines, one can find the dimension of the unit cell along the axis of the mounting of the crystal.

The separation of diffraction data into layer line in case of rotating crystal method is somewhat better than the powder diffraction pattern but still there is always some overlap of diffraction spots. Therefore, rotation photographs are rarely used for collection of intensity data. They are more often used for preliminary determination of unit cell dimensions and crystal system. In modern techniques, the photographic film is also replaced with a sensitive counter and a trace is taken of the count rate recorded while the crystal rotates slowly and the computer programmes are used to simplify the problem of crystal structure determination.

In *Laue method*, a narrow beam of non-monochromatic x-rays falls on a single crystal as shown in Fig. Q 2.12.3(a). There are two photographic films in this method, film A to record the diffraction pattern and film B to record the back-reflected pattern from the surface of the crystal specimen. On the photographic film A, one obtains a large number of diffraction spots as in Fig. Q 2.13.3(b). Laue pattern exhibits the symmetry of a crystal; when the x-ray beam is directed parallel to a six-fold axis of symmetry, the pattern will have the six-fold symmetry about the central point and a 60° turn will bring coincidence of all the spots. Therefore, the *Laue pattern* has been widely used in determining symmetry axes if the non-monochromatic x-ray beam is incident along or very close to the symmetry axis.

The diffraction pattern on a photographic plate is a two-dimensional representation of the reflection from the three-dimensional crystal planes. Therefore, *stereographic* projection has to be used to determine the relation between *Laue spots* and the actual distribution of lattice points in real space. It will be interesting to mention at this stage that Laue spots correspond to points of a *reciprocal lattice*.



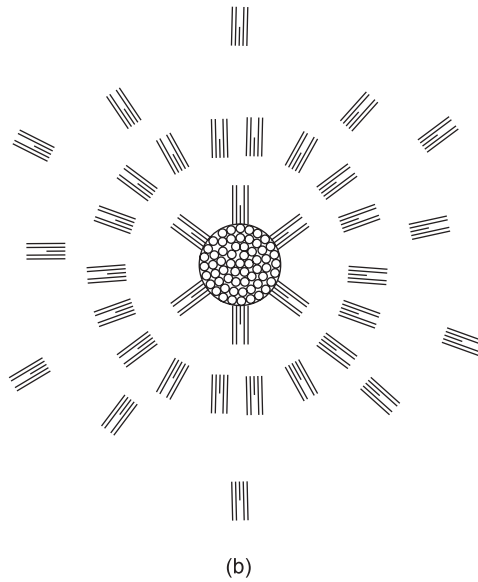


Fig. Q 2.12.3 (a) Laue camera (b) Laue pattern

Table 2. A Comparison of cell properties of some crystal lattices

S. No.	Properties	Diamond cube (dc)	Simple cube (sc)	Body centred cube (bcc)	Face centred cube (fcc)	Hexagonal close packed structure (hcp)
1	Volume of unit cell	a^3	a^3	a^3	a^3	$\frac{3}{2}\sqrt{3}(a^2 c)$
2	Number of atoms per cell	8	1	2	4	6
3	Number of atoms per unit volume	$\frac{8}{a^3}$	$\frac{1}{a^3}$	$\frac{2}{a^3}$	$\frac{4}{a^3}$	$\frac{4}{\sqrt{3}(a^2 c)}$
4	Number of nearest neighbours	4	6	8	12	12
5	Nearest neighbour distance ($2r$)	$\frac{a\sqrt{3}}{4}$	a	$\frac{a\sqrt{3}}{2}$	$\frac{a\sqrt{2}}{2}$	a
6	Atomic radius	$\frac{a\sqrt{3}}{8}$	$\frac{a}{2}$	$\frac{a\sqrt{3}}{4}$	$\frac{a\sqrt{2}}{4}$	$\frac{a}{2}$

Contd.

S. No.	Properties	Diamond cube (dc)	Simple cube (sc)	Body centred cube (bcc)	Face centred cube (fcc)	Hexagonal close packed structure (hcp)
7	Atomic packing factor	$\frac{\pi\sqrt{3}}{16} = 0.34$	$\frac{\pi\sqrt{3}}{6} = 0.52$	$\frac{\pi\sqrt{3}}{8} = 0.68$	$\frac{\pi\sqrt{2}}{6} = 0.74$	$\frac{\pi\sqrt{2}}{6} = 0.74$
8	Examples	Germanium, Silicon and Diamond	Polonium	Sodium, Iron, Chromium	Aluminium, Copper, Lead	Magnesium, Zinc and Cadmium

Table 2. B Crystal structure and selected properties of representative elements

Element	Symbol	Atomic weight	Density in 10^3 (kg/m^3)	Crystal structure	Lattice constant (20°C) (nm)	Approximate atomic radius	Melting point $^\circ\text{C}$
Aluminium	Al	26.97	2.7	fcc	0.4049	0.1428	660.2
Cadmium	Cd	112.41	8.65	hcp	$a = 0.2979$ $c = 0.5617$	0.1489	320.9
Carbon	C	12.01	2.22	dc	0.3564	0.0770	3700
Chromium	Cr	52.01	7.19	bcc	0.2885	0.1249	1890
Copper	Cu	63.54	8.96	fcc	0.3615	0.1278	1083
Germanium	Ge	72.59	5.36	dc	0.5658	0.1224	937
Iron (α)	Fe	55.85	7.87	bcc	0.2866	0.1238	1539
Lead	Pb	207.21	11.34	fcc	0.4949	0.1750	327
Magnesium	Mg	24.32	1.74	hcp	$a = 0.3209$ $c = 0.5210$	0.1594	650
Potassium	K	39.10	0.86	bcc	0.5339	0.2312	63.7
Silicon	Si	28.09	2.34	dc	0.5428	0.1176	1430
Silver	Ag	107.88	10.49	fcc	0.4086	0.1444	960.5
Sodium	Na	22.99	0.97	bcc	0.4281	0.1857	97.8
Zinc	Zn	65.38	7.13	hcp	$a = 0.2664$ $c = 0.4945$	0.1332	419.5

Table 2.C *Enthalpy of formation of vacancies in some crystals*

<i>Crystal</i>	<i>E_v (kJ/kmol) in 10³</i>	<i>E_v in eV/vacancy</i>
Zn	49.0	0.51
Al	68.0	0.70
Mg	56.0	0.58
Kr	7.7	0.08
Cd	38.0	0.39
Pb	48.0	0.50
Ag	106.0	1.10
Cu	120.0	1.24
Ni	168.0	1.74

Table 2. D *Equilibrium vacancies in a metal*

<i>Temperature °C</i>	<i>Approximate fraction of vacant lattice sites</i>
500	1×10^{-10}
1000	1×10^{-5}
1500	1×10^{-4}
2000	1×10^{-3}

OBJECTIVE QUESTIONS

- Which of the following has the least packing fraction
 (a) diamond cubic structure (b) face centred cubic structure
 (c) body centred cubic structure (d) simple cubic structure
- The number of triad axes of symmetry elements in a cubic system
 (a) 2 (b) 3 (c) 6 (d) 4
- The volume of the primitive unit cell of a fcc structure with lattice constant a is
 (a) $\frac{a^3}{8}$ (b) $\frac{a^3}{4}$ (c) a^3 (d) $\frac{a^3}{2}$
- The nearest neighbour distance in the case of bcc structure is
 (a) $\frac{\sqrt{3}}{2}a$ (b) $2a$ (c) $\frac{2}{\sqrt{3}}a$ (d) $\sqrt{3}a$
 where a is the lattice parameter
- The number of atoms present in the unit cell of hcp structure is
 (a) 2 (b) 4 (c) 6 (d) 7

6. The packing factor of diamond cubic structure is
 (a) 60% (b) 56% (c) 74% (d) none of these
7. Which of the following metals crystallizes in fcc structure?
 (a) zinc (b) sodium (c) aluminium (d) CsCl
8. The ideal c/a ratio for the hexagonal structure is
 (a) 1 (b) $\frac{\pi}{2}$ (c) $\frac{\sqrt{3}}{2}$ (d) $\sqrt{\frac{8}{3}}$
9. Magnesium crystallizes in hcp structure. If the lattice constant is 0.32 nm, the nearest neighbour distance in magnesium is
 (a) 0.32 nm (b) 0.16 nm (c) 0.64 nm (d) none of these
10. If n is the number of atoms in the unit cell of the cubic system, N_A and M_A are the Avogadro's number and atomic weight respectively and ρ is the density of the element, then the lattice constant a is given by
 (a) $\left[\frac{M_A \rho}{n N_A} \right]^{\frac{1}{3}}$ (b) $\left[\frac{n N_A}{M_A \rho} \right]^{\frac{1}{3}}$ (c) $\left[\frac{N_A M_A}{n} \right]^{\frac{1}{4}}$ (d) $\left[\frac{n M_A}{\rho N_A} \right]^{\frac{1}{3}}$
11. The number of ions in the unit cell of NaCl crystal is
 (a) 8 (b) 6 (c) 2 (d) 4
12. The Miller indices of the plane parallel to the x and y axes are
 (a) (0 1 0) (b) (0 0 1) (c) (1 1 1) (d) (1 0 0)
13. If (3 2 6) are the Miller indices of a plane, the intercepts made by the plane on the three crystallographic axes are
 (a) (2a 3b c) (b) (a b c) (c) (a 2b 3c) (d) none of these
14. In a simple cubic lattice $d_{100} : d_{110} : d_{111}$ is
 (a) 6 : 3 : 2 (b) 6 : 3 : $\sqrt{2}$ (c) $\sqrt{6} : \sqrt{3} : \sqrt{2}$ (d) $\sqrt{6} : \sqrt{3} : \sqrt{4}$
15. A plane parallel to one of the co-ordinate axes has an intercept of infinity
 (a) yes (b) no
16. A plane intercepts at a , $b/2$, $3c$ in a simple cubic unit cell. The Miller indices of the plane are
 (a) (2 6 1) (b) (1 3 2) (c) (1 2 3) (d) (3 6 1)
17. If ($h k l$) are the Miller indices of a plane, then the plane cuts the axes into h , k and l equal segments
 (a) yes (b) no

PROBLEMS AND SOLUTIONS

2.1 Silicon crystallizes in the diamond cubic structure. The radius of silicon atom is 0.1176 nm. The atomic weight and density of silicon are 28.09 and $2.3 \times 10^3 \text{ kg/m}^3$. Give me the number of atoms present in a unit cell.

Solution:

$$2r = \frac{a\sqrt{3}}{4}$$

$$a = \frac{8r}{1.732} = \frac{8 \times 0.1176}{1.732}$$

$$a = 0.5432 \text{ nm}$$

$\frac{M_A}{\rho}$ will contain N_A silicon atoms

$$a^3 \text{ m will contain } \frac{\rho N_A a^3}{M_A} = n$$

i.e.,

$$n = \frac{2.3 \times 10^3 \times 6.02 \times 10^{26} \times (0.5432 \times 10^{-9})^3}{28.9}$$

$$= \frac{2.3 \times 6.02 \times 0.5432^3 \times 10^2}{28.9} = 8$$

$n = 8$

Answer

2.2 Lead is a face centred cubic with an atomic radius of 0.1746 nm. Find the spacing (i) (2 0 0) planes and (ii) (2 2 0) planes

Solution:

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

For fcc structure,

$$a = \frac{4r}{\sqrt{2}} = \frac{4 \times 0.1746}{1.414} = 0.493 \text{ nm}$$

For 2 0 0 plane

$$d_{200} = \frac{0.493}{4} = 0.2465 \text{ nm and for the other plane}$$

$$d_{220} = \frac{0.493}{8} = 0.174 \text{ nm}$$

$d_{200} = 0.2465 \text{ nm}$ $d_{220} = 0.174 \text{ nm}$

Answer

2.3 The Bragg angle corresponding to the first order reflection from (1 1 1) plane in a crystal is 30° when x-rays of wave length 0.175 nm are used. Calculate the interatomic spacing.

Solution:

We know that

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

$$d_{111} = \frac{a}{\sqrt{3}}$$

and

$$2d \sin \theta = n\lambda$$

$$2 \times \frac{a}{1.732} \sin 30 = 1 \times 0.175 \times 10^{-9}$$

$$\frac{2a}{2} = 1.732 \times 0.175 \times 10^{-9} = a$$

$$\boxed{a = 0.3031 \text{ nm}} \text{ Answer}$$

2.4 A certain orthorhombic crystal has a ratio of a : b : c of 0.429 : 1 : 0.377. Find the Miller indices of the faces whose intercepts are:

$$0.214 : 1 : 0.183$$

$$0.858 : 1 : 0.754$$

$$0.429 : \infty : 0.126$$

Solution:

The intercepts in terms of the unit axial dimensions are as below:

$$\frac{0.214}{0.429} : \frac{1}{1} : \frac{0.183}{0.377}$$

$$\frac{0.858}{0.429} : \frac{1}{1} : \frac{0.754}{0.377}$$

$$\frac{0.429}{0.429} : \frac{\infty}{1} : \frac{0.126}{0.377}$$

$$\frac{1}{2} : 1 : \frac{1}{2}$$

$$2 : 1 : 2$$

$$1 : \infty : \frac{1}{3}$$

Taking the reciprocals of these numbers and reducing them to the smallest whole numbers, the Miller indices come out as follows:

$$\begin{array}{c} (2 \ 1 \ 2) \\ (1 \ 2 \ 1) \\ (1 \ 0 \ 3) \end{array} \quad \text{Answer}$$

2.5 Find the Miller indices of a set of parallel planes which makes intercepts in the ratio (3a : 4b) on the x-axis and y-axis and parallel to the z-axis; a, b, c being primitive vectors of the lattice.

Solution:

$$pa : qb : rc = 3a : 4b : \infty c$$

$$p : q : r = 3 : 4 : \infty$$

$$\frac{1}{p} : \frac{1}{q} : \frac{1}{r} = \frac{1}{3} : \frac{1}{4} : \frac{1}{\infty} = 4 : 3 : 0$$

The Miller indices of the given set of planes are (4 3 0)

$$(4 \ 3 \ 0) \quad \text{Answer}$$

2.6 Calculate the ratio of the number of vacancies in equilibrium at 300 K in aluminium to that produced by rapid quenching at 800 K. Enthalpy of formation of vacancies in aluminium is 68 kJ/mol.

Solution:

The general expression for the number of vacancies is given by,

$$n_1 = N \exp(-E_v/R_u T_1) \text{ and } n_2 = N \exp(-E_v/R_u T_2)$$

$$n_1 = N [\exp(-68 \times 10^3/8.314 \times 300)] = N \exp(-27.3)$$

$$n_2 = N [\exp(-68 \times 10^3/8.314 \times 800)] = N \exp(-10.2)$$

$$\frac{n_1}{n_2} = \frac{\exp(-27.3)}{\exp(-10.2)} = 3.75 \times 10^{-8}$$

$$\frac{n_1}{n_2} = 3.75 \times 10^{-8} \quad \text{Answer}$$

2.7 A diffraction pattern of a cubic crystal of lattice parameter $a = 0.316$ nm is obtained with a monochromatic x-ray beam of wavelength 0.154 nm. The first four lines on this pattern were observed to have the following values:

Line:	1	2	3	4
θ° :	20.3	29.2	36.7	43.6

Determine the interplanar spacings and Miller indices of reflecting planes.

Solution: $d = \frac{\lambda}{\sin \theta}$, or $\sin \theta = \frac{\lambda}{d}$

Line	θ	$\sin \theta$	d (nm)	$\frac{a^2}{d^2} = h^2 + k^2 + l^2$
1	20.3	0.3460	0.2240	2
2	29.2	0.4886	0.1570	4
3	36.7	0.5980	0.1290	6
4	43.0	0.6990	0.1150	8

For determination of h, k, l one has to resort to trial and error method

$$h^2 + k^2 + l^2 = 2 = 1^2 + 1^2 + 0; h \ k \ l = (1 \ 1 \ 0)$$

$$h^2 + k^2 + l^2 = 4 = 2^2 + 0 + 0; h \ k \ l = (2 \ 0 \ 0)$$

$$h^2 + k^2 + l^2 = 6 = 2^2 + 1^2 + 1^2; h \ k \ l = (2 \ 1 \ 1)$$

$$h^2 + k^2 + l^2 = 8 = 2^2 + 2^2 + 0; h \ k \ l = (2 \ 2 \ 0)$$

EXERCISE

2.1 Metallic iron changes from bcc to fcc form at 910°C. At this temperature, the atomic radii of the iron atom in the two structures are 0.1258 nm and 0.1292 nm respectively. Calculate the volume change in percentage during this structural change. Also calculate the percentage change in density.

(Ans: 0.493%, 0.4968%)

2.2 Compare the densities of lattice points in (1 1 1) and (1 1 0) planes in a simple cubic lattice.

(Ans: $\rho_{111} : \rho_{110} = \sqrt{2} : \sqrt{3}$)

2.3 Cadmium crystallizes in hcp structure. The radius of cadmium atom is 0.1489. What is the height of the unit cell?

(Ans: 0.4862 nm).

2.4 X-ray powder photograph of a cubic material with a wavelength of 0.1542 nm is taken. In the photograph, lines are observed at angles 19.25°, 22.38°, 32.58°, 39.15°, 41.26°, 49.59°, 56.08° and 58.36°. Determine the lattice constant and the nature of the cubic material.

(Ans: fcc, 0.405 nm)

2.5 The unit cell of aluminium is face centred with lattice constant, $a = 0.405$ nm (a) How many unit cells are there in an aluminium foil 0.005 cm thick and side 25 cm square? (b) It weighs 0.0085 kilogram. How many atoms are present? (c) How many atoms are in each unit cell?

(Ans: 4.7×10^{22} , 1.9×10^{23} , 4)

2.6 The fraction of vacancy sites in a metal is 1×10^{-10} at 500°C. What will be the fraction of vacancy

sites at 1000°C?

(Ans: $\frac{n}{N} = 8.8452 \times 10^{-7}$).