

Chapter One

Crystal Structures

1.1 Introduction

Experiments have proved that all solids are composed of discrete basic units-atoms. These atoms are not distributed randomly, but are arranged in a highly ordered manner relative to each other. Such a group of ordered atoms is referred to as a crystal. There are several types of crystalline structure, depending on the geometry of the atomic arrangement; a knowledge of these is important in Solid State Physics because these structures usually influence the physical properties of solids.

The atoms in some solids appear to be randomly arranged, i.e., the crystalline structure is absent. Such non-crystalline structures are called amorphous solids.



1.2 The Crystalline State

A solid is said to be a crystal if the atoms are arranged in such a way that their positions are exactly periodic. Figure 1.1 illustrates the concept. The distance between any two nearest neighbors along the x direction is a , and along the y direction is b (the x and y axes are not necessarily orthogonal). A perfect crystal maintains this periodicity (or repetitiveness) in both the x and y directions from $-\infty$ to $+\infty$. It follows from the periodicity that the atoms A, B, C , etc., are equivalent. In other words, to an observer located at any of these atomic sites, the crystal appears exactly the same.

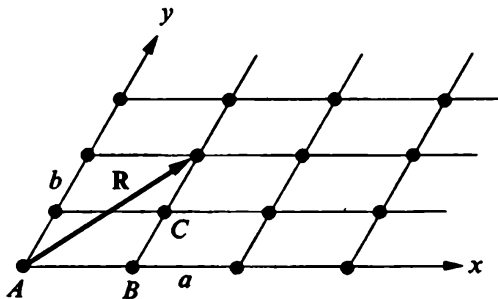


Fig. 1.1 A crystalline solid. All the atoms are arranged periodically.

The same idea is often expressed by saying that a crystal possesses a translational symmetry, meaning that if the crystal is translated by any vector joining two atoms, say R in Figure, the crystal appears exactly the same as it did before the translation. In other words, the crystal remains invariant under any such translation.



1.3 Basic Definitions

In order to talk precisely about crystal structures, we must introduce here a few of the basic definitions:

1. The crystal lattice

In crystallography, only the geometrical properties of the crystal are of interest, rather than those arising from the particular atoms constituting the crystal. Therefore, one replaces each atom by a geometrical point located at the equilibrium position of that atom. The result is a pattern of points having the same geometrical properties as the crystal, but which is devoid of any physical contents. This geometrical pattern is the crystal lattice; all the atomic sites have been replaced by lattice sites.

There are two classes of lattices; the **Bravais** and the **non-Bravais**. In a Bravais lattice, all lattice points are equivalent, and hence by necessity all atoms in the crystal are of the same kind. On the other hand, in a non-Bravais lattice, some of the lattice points are nonequivalent. Figure 1.2 shows this clearly. Here the lattice sites A, B, C are equivalent to each other, and so are the sites A', B', C' among themselves, but the two sites A and A' are not equivalent to each other, as can be seen by the fact that the lattice is not invariant under a translation by AA' . A non-Bravais lattice is sometimes referred to as a lattice with a basis, the basis referring to the set of atoms stationed near each site of a Bravais lattice.

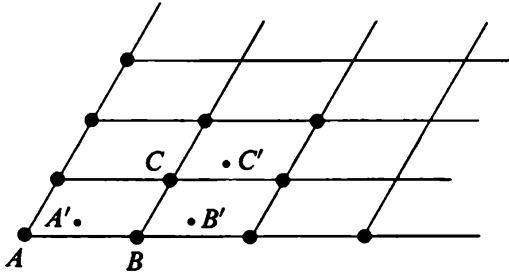


Fig. 1.2 non-Bravais lattice

The non-Bravais lattice may be regarded as a combination of two or more interpenetrating Bravais lattices with fixed orientations relative to each other. Thus the points A, B, C , etc., form one Bravais lattice, while the points A', B', C' , etc., form another.

2. Basis vectors

Consider the lattice shown in Fig. 1.3. Let us choose the origin of coordinates at a certain lattice point, say A . Now the position vector of any lattice point can be written as

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

where $\mathbf{a}, \mathbf{b}$ are the two vectors shown, and (n_1, n_2) is a pair of integers whose values depend on the lattice point. Thus for the point D , $(n_1, n_2) = (0, 2)$; for B , $(n_1, n_2) = (1, 0)$, for F , $(n_1, n_2) = (0, -1)$.

The set of all vectors expressed by previous equation is called the *lattice vectors*. We may also say that the lattice is invariant under the group of all the translations vectors. That is to say that the lattice has a translational symmetry under all displacements specified by the lattice vectors $\mathbf{R}_n$. The choice of basis vectors is not unique. Thus one could equally well take the vectors $\mathbf{a}$ and $\mathbf{b}'$ (or $\mathbf{a}$ and $\mathbf{b}$) as a basis.

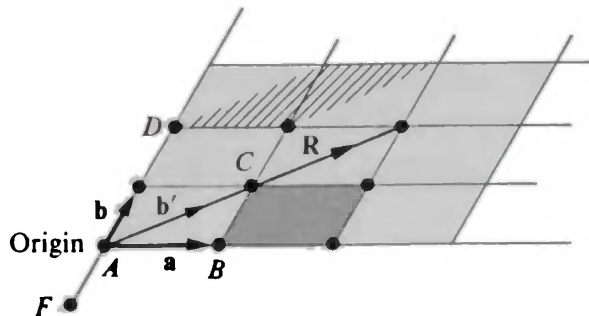


Fig. 1.3 Vectors $\mathbf{a}$ and $\mathbf{b}$ are basis vectors of the lattice. Vectors $\mathbf{a}$ and $\mathbf{b}'$ form another set of basis vectors. Shaded and hatched areas are unit cells corresponding to first and second set of basis vectors, respectively.

For a lattice to represent a crystal structure, we associated every lattice point with one or more atoms called the *basis* or the *pattern*. When the basis is repeated with the correct periodicity in all direction, it gives the actual crystal structure. The crystal structure is real, while the lattice is imaginary. Thus,

$$\text{Lattice} + \text{Basis} = \text{Crystal structure}$$

3. The unit cell

The area of the parallelogram whose sides are the basis vectors $\mathbf{a}$ and $\mathbf{b}$ is called a *unit cell* of the lattice (Fig. 1.3), in that, if such a cell is translated by all the lattice vectors, the area of the whole lattice is covered once and only once. The unit cell is usually the smallest area which produces this coverage. Therefore, the lattice may be viewed as composed of a large number of equivalent unit cells placed side by side. The choice of a unit cell for one and the same lattice is not unique, for the same reason that the choice of basis vectors is not unique. Thus the parallelogram formed by $\mathbf{a}$ and $\mathbf{b}'$ in Fig. 1.3 is also an acceptable unit cell.

The following remarks may be helpful:

- i) All unit cells have the same area. Thus the cell formed by $\mathbf{a}$, $\mathbf{b}$ has the area $S = |\mathbf{a} \times \mathbf{b}|$, while that formed by $\mathbf{a}$, $\mathbf{b}'$ has the area $S' = |\mathbf{a} \times \mathbf{b}'| = |\mathbf{a} \times (\mathbf{a} + \mathbf{b})| = |\mathbf{a} \times \mathbf{b}| = S$. Therefore, the area of the unit cell is unique, even though the particular shape is not.
- ii) If you are interested in how many lattice points belong to a unit cell, refer to Fig. 1.3. The unit cell formed by $\mathbf{a} \times \mathbf{b}$ has four points at its corners, but each of these points is shared by four adjacent cells. Hence each unit cell has only one lattice point.



4. Primitive versus nonprimitive cells

The unit cell discussed above is called a *primitive cell*. It is sometimes more convenient, however, to deal with a unit cell which is larger, and which exhibits the symmetry of the lattice more clearly. The idea is illustrated by the Bravais lattice in Fig. 1.4. Clearly, the vectors $\mathbf{a}_1$, $\mathbf{a}_2$ can be chosen as a basis set, in which case the unit cell is the parallelogram S_1 . However, the lattice may also be regarded as a set of adjacent rectangles, where we take the vectors $\mathbf{a}$ and $\mathbf{b}$ as basis vectors. The unit cell is then the area S_2 formed by these vectors. It has one lattice point at its center, in addition to the points at the corner. This cell is a *nonprimitive* unit cell.

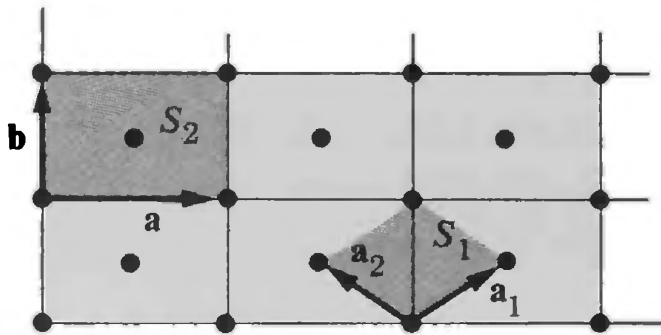


Fig. 1.4 Area S_1 , is a primitive unit cell; area S_2 is a nonprimitive unit cell.

The reason for the choice of the nonprimitive cell S_2 is that it shows the rectangular symmetry most clearly. Although this symmetry is also present in the primitive cell S_1 (as it must be, since both refer to the same lattice), the choice of the cell somehow obscures this fact.



Note the following points:

- i) The area of the nonprimitive cell is an integral multiple of the primitive cell. In Fig. 1.4, the multiplication factor is two.
- ii) No connection should be drawn between nonprimitive cells and non-Bravais lattices. The former refers to the particular choice of basis vectors in a Bravais lattice, while the latter refers to the physical fact of nonequivalent sites.

**Three dimensions**

All the previous statements can be extended to three dimensions in a straight-forward manner. When we do so, the lattice vectors become three-dimensional, and are expressed by:

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

where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are three noncoplanar vectors joining the lattice point at the origin to its near neighbors (Fig. 1.5); and n_1, n_2, n_3 are a triplet of integers $0, \pm 1, \pm 2, \text{etc.}$, whose values depend on the particular lattice point.

The vector triplet $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ is the *basis vector*, and the parallelepiped whose sides are these vectors is a *unit cell*. Here again the choice of primitive cell is not unique, although all primitive cells have equal volumes. Also, it is sometimes convenient to deal with nonprimitive cells, ones which have additional points either inside the cell or on its surface. Finally, non-Bravais lattices in three dimensions are possible, and are made up of two or more interpenetrating Bravais lattices.

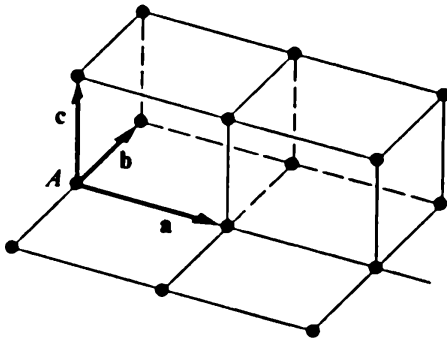


Fig. 1.5 A three-dimensional lattice. Vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are basis vectors.

The basis is the quantity of matter contained in the *unit cell* of volume:

$$V = |\mathbf{a} \times \mathbf{b} \cdot \mathbf{c}|$$

**1.4 Crystal systems**

It is common practice to divide all the crystal systems into seven groups or basic systems. These seven basic crystal systems are distinguished from one another by the angles between the three axes and the intercepts of the faces along them. In every case the cell is a parallelepiped whose sides are the bases $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. The opposite angles are called α , β , and γ , as shown in Fig. 1.6.

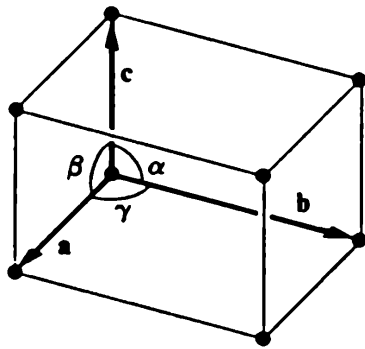


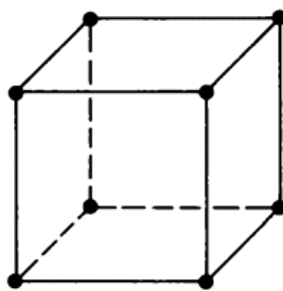
Fig. 1.6 Unit cell specified by the lengths of basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$; also by the angles between the vectors.

The seven basic crystal systems are:

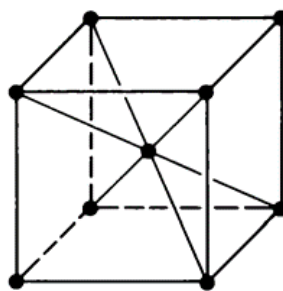
1. Cubic:

$$a = b = c \quad , \quad \alpha = \beta = \gamma = 90^\circ$$

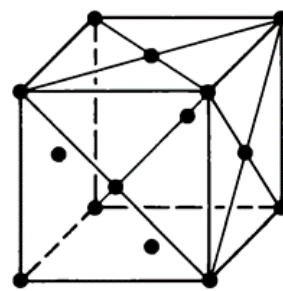
The crystal axes are perpendicular to one another, and the repetitive interval is the same along all the three axes. Cubic lattices may be simple, body-centred or face-centred.



Simple cubic



Body-centered
cubic

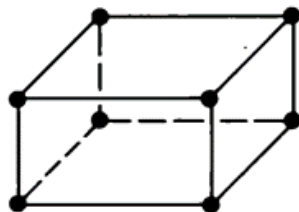


Face-centered
cubic

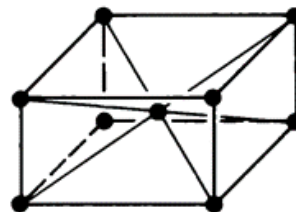
2. Tetragonal:

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

The crystal axes are perpendicular to one another. The repetitive intervals along two axes are the same, but the interval along the third axis is different. Tetragonal lattices may be simple or body-centred.



Simple
tetragonal

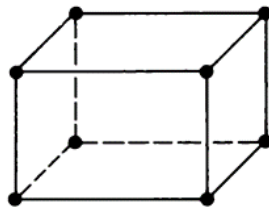


Body-centered
tetragonal

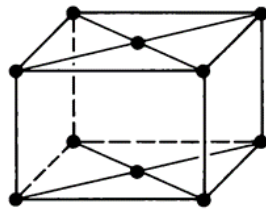
3. Orthorhombic:

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

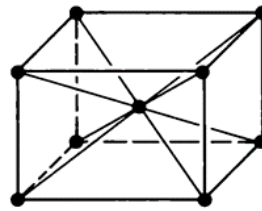
The crystal axes are perpendicular to one another, but the repetitive intervals are different along all the three axes. Orthorhombic lattices may be simple, base-centred, body-centred, or face-centred.



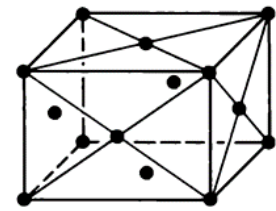
Simple
orthorhombic



Base-centered
orthorhombic



Body-centered
orthorhombic

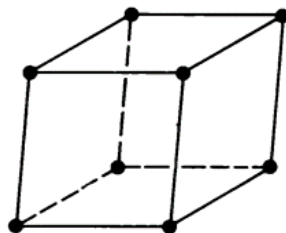


Face-centered
orthorhombic

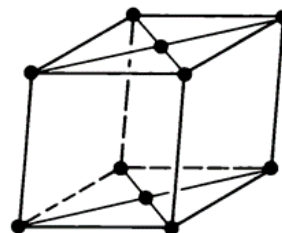
4. Monoclinic:

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

Two of the crystal axes are perpendicular to one another, but the third is obliquely inclined. The repetitive intervals are different along all the three axes. Monoclinic lattices may be simple or base-centred.



Simple monoclinic

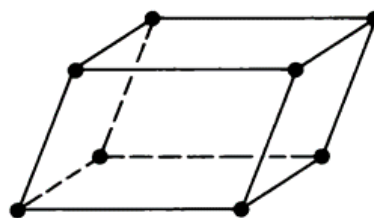


Base-centered
monoclinic

5. Triclinic:

$$a \neq b \neq c, \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$$

None of the crystal axes is perpendicular to any of the other, and the repetitive intervals are different along all the three axes. Triclinic lattices may be only simple.

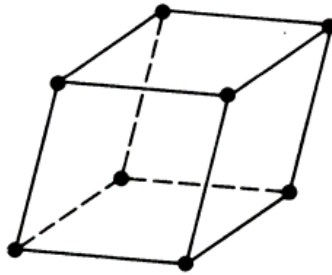


Triclinic

6. Trigonal (Rhombohedral):

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

The three axes are equal in length and are equally inclined to each other at an angle other than 90° . The repetitive intervals are different along all the three axes. Trigonal lattices may be only simple.



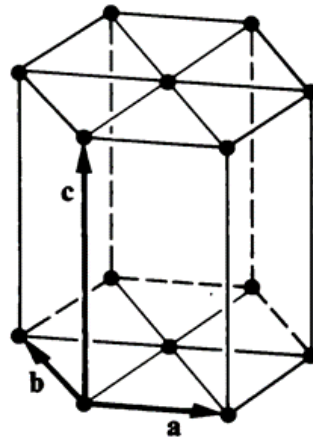
Trigonal



7. Hexagonal:

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

Two of the crystal axes are 60° apart while the third is perpendicular to both of them. The repetitive intervals are the same along the axes that are 60° apart, but the interval along the third axis is different.



Hexagonal



1.5 The Fourteen Bravais Lattices

In three dimensions, there are only **14** different Bravais lattices. The number of non-Bravais lattices is much larger (**230**), but it also is finite. Table 1.1 enumerates the systems, lattices, and the appropriate values for **a**, **b**, **c**, and α , β , and γ .

Table 1.1. The Seven Crystal Systems Divided into Fourteen Bravais Lattices.

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

Note that a *simple* lattice has points only at the corners, a *body-Centred* lattice has one additional point at the center of the cell, and a *face-Centred* lattice has six additional points, one on each face. Let us again point out that in all the *nonsimple* lattices the unit cells are nonprimitive.

The 14 lattices enumerated in Table 1.1 exhaust all possible Bravais lattices, although a complete mathematical proof of this statement is quite lengthy. It may be thought, for example, that a *base-Centred tetragonal* should also be included in the table, but it can readily be seen that such a lattice reduces to the *simple tetragonal* by a new choice of a unit cell (Fig. 1.7).

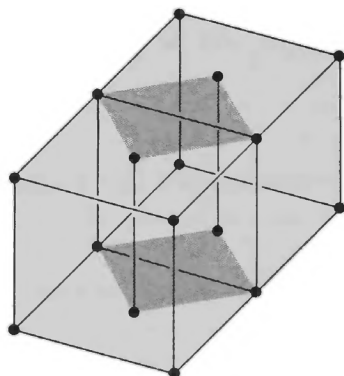


Fig. 1.7 A base-centred tetragonal is identical to a simple tetragonal of a different unit cell. Shaded areas are the basis of the simple tetragonal cell.

1.6 Crystal Symmetry (Elements of Symmetry)

The definite ordered arrangement of the faces and edges of a crystal is known as *crystal symmetry*. A sense of symmetry is a powerful tool for the study of the internal structure of crystals. Crystals possess different symmetries or symmetry elements. They are described by certain operations. A symmetry operation is one that leaves the crystal and its environment invariant.

Symmetry operations performed about a point or a line are called **point group symmetry operations** and symmetry operation performed by translations as well as rotation are called **space group symmetry operations**. Crystals exhibit both types of symmetries independently and in compatible combinations.

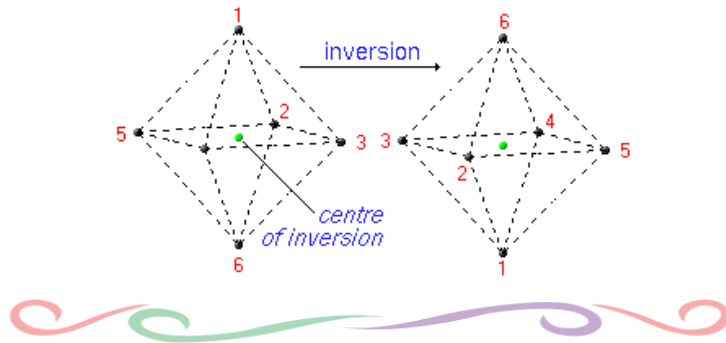
A symmetry operation is a transformation performed on the body which leaves it unchanged or invariant. That is after performing an operation on the body, if the body becomes indistinguishable from its initial configuration, the body is said to possess a symmetry elements corresponding to that particular operation.

Each of the unit cells of the 14 Bravais lattices has one or more types of symmetry properties, such as inversion, reflection, or rotation.



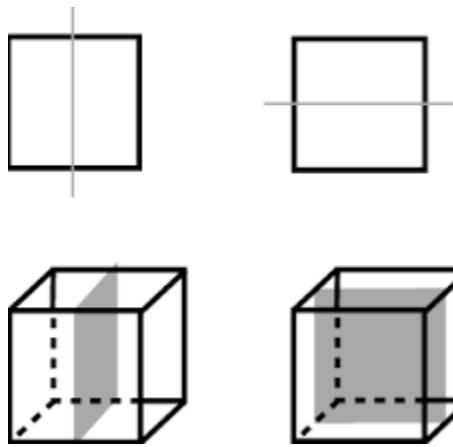
1. Centre of symmetry (Inversion centre):

A cell has an inversion center if there is a point at which the cell remains invariant when the mathematical transformation $r \rightarrow -r$ is performed on it. All Bravais lattices are inversion symmetric, a fact which can be seen by noting that, with every lattice vector $\mathbf{R}_n = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$, there is associated an inverse lattice vector $\mathbf{R}_n = -n_1\mathbf{a} - n_2\mathbf{b} - n_3\mathbf{c}$. A non-Bravais lattice may or may not have an inversion center, depending on the symmetry of the basis.



2. Reflection Symmetry:

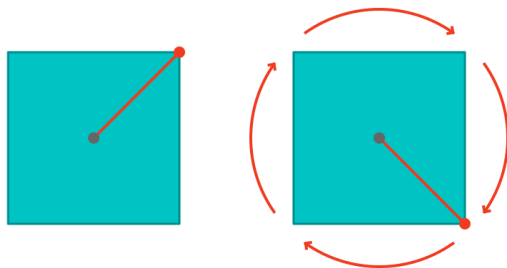
A plane in a cell such that, when a mirror reflection in this plane is performed, the cell remains invariant. The triclinic has no reflection plane, the monoclinic has one plane midway between and parallel to the bases, and so forth. The cubic cell has nine reflection planes: three parallel to the faces, and six others, each of which passes through two opposite edges.



Symmetry transformations of the square and the cube.

3. Rotation Symmetry:

This is an axis such that, if the cell is rotated around it through some angle, the cell remains invariant. The axis is called n -fold if the angle of rotation is $2\pi/n$. The triclinic has no axis of rotation (save the trivial 1-fold axis), and the monoclinic has a 2-fold axis ($\theta = 2\pi/2 = \pi$) normal to the base. The cubic unit cell has three 4-fold axes normal to the faces, and four 3-fold axes, each passing through two opposite corners.



Square has rotational symmetry of order 4.

1.7 Twenty-Three Symmetry Element in a Cubic Crystal

A cube possesses a centre of symmetry, i.e., the body centre of the cube is a centre of symmetry. This centre lies at equal distances from various symmetrical positions. Centre of symmetry is also known as inversion centre. Thus, inversion is a symmetry operation in a crystal equivalent to reflection through a point. This is shown in Fig. 1.8.

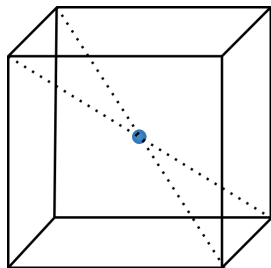


Fig. 1.8 Centre of inversion in a cubic crystal.

The second kind of symmetry element in a crystal is a reflection symmetry (plane of symmetry). A crystal is said to possess reflection symmetry about a plane if it is left unchanged in every way after being reflected by the plane. Highly regular crystals may be bilaterally symmetrical about several planes cutting them in different directions. The three straight planes of symmetry in a cube are shown in Fig. 1.9 and the six diagonal planes of symmetry in a cube are shown in Fig. 1.10.

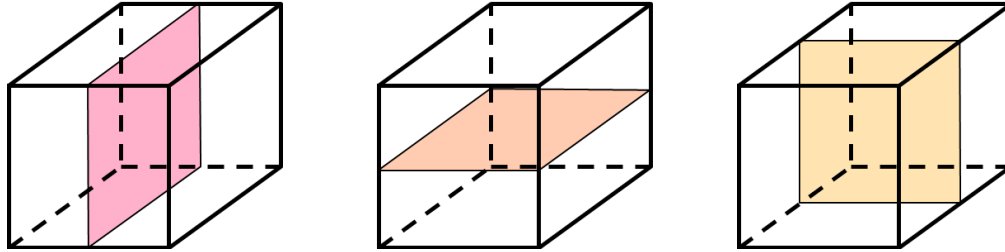


Fig. 1.9 The three planes of symmetry parallel to the faces of the cube.

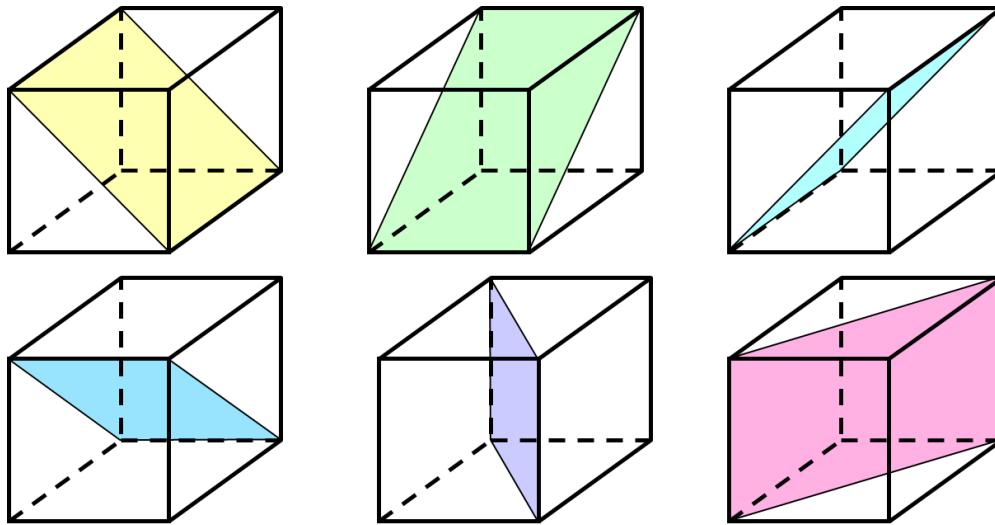


Fig. 1.10 The six diagonal planes of symmetry in a cube.

The next kind of symmetry element is the symmetry about a line, known as axis of symmetry or rotation axis.

If a cube is rotated about a line perpendicular to one of its faces at its midpoint, it will turn into a congruent position every 90° (indistinguishable from the position it occupied originally), four times during a complete revolution; the normal is thus an axis of four-fold symmetry. A cube possesses three such axes, one normal to each of the three pairs of parallel faces. The three tetrad axes of a cube are shown in Fig. 1.11-a.

Let the cube be now rotated about a solid diagonal (body diagonal) through 120° to get congruence, and such a line, of which there are four, is therefore a triad axis as shown in Fig. 1.11-b.

Finally, a line joining the mid points of a pair of opposite parallel edges proves to be a diad axis, and there are six such axes present in cube, as shown in Fig. 1.11-c.

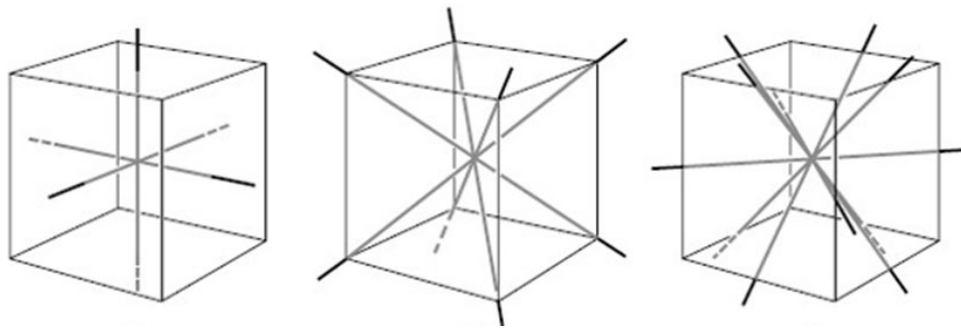


Fig. 1.11 (a) The three tetrad axes of a cube. (b) The four triad axes of cube. (c) The six diad axes of cube.

The total number of crystallographic symmetry elements of the cubic system are thus given by:

centre of symmetry	1	(1 centre)
straight planes	3	} (9 planes)
diagonal planes	6	
tetrad axes	3	} (13 axes)
triad axes	4	
diad axes	6	



1.8 The Wigner-Seitz cell

As we have mentioned, the procedure of choose of the elementary cell is not unique and sometimes an arbitrary cell does not reflect the symmetry of the lattice. There is a very convenient procedure to choose the cell which reflects the symmetry of the lattice. The procedure is as follows:

1. Choose a zero point of the lattice.
2. Draw lines connecting a given lattice point to all neighboring points.
3. Draw bisecting lines (or planes) to the previous lines at a right angle.
4. A subset of all your planes will form some closed body, and that is your Wigner Seitz cell.

The procedure is outlined in Fig. 1.12.

Notes:

1. A Wigner–Seitz cell is an example of a primitive cell, which is a unit cell containing exactly one lattice point.
2. The volume of a Wigner-Seitz cell is the same as a primitive cell.

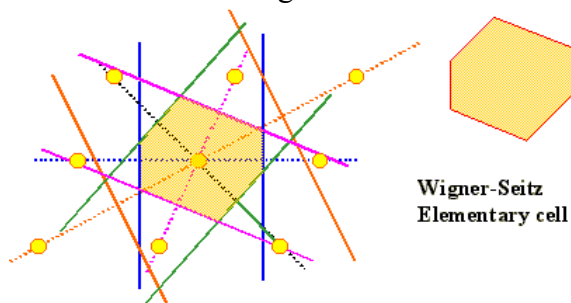


Fig. 1.12 (a) determination of Wigner-Seitz cell in two dimension.

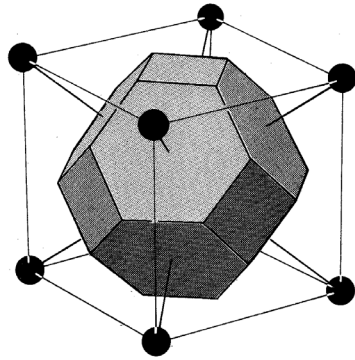


Fig. 1.12 (b) Wigner-Seitz cell for BCC structure.

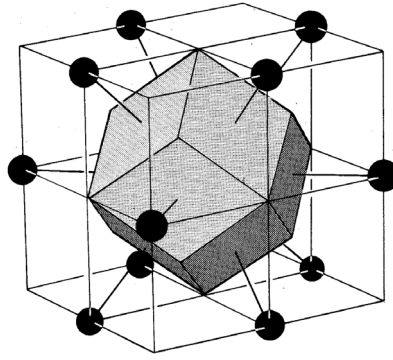


Fig. 1.12 (c) Wigner-Seitz cell for FCC structure.

1.9 Atomic Packing Factor

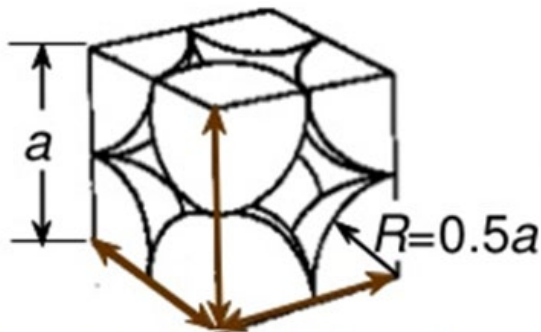
In crystallography, atomic packing factor (APF), packing efficiency or packing fraction is the fraction of volume in a crystal structure that is occupied by constituent particles. It is dimensionless and always less than unity. In atomic systems, by convention, the APF is determined by assuming that atoms are rigid spheres. The radius of the spheres is taken to be the maximal value such that the atoms do not overlap. For one-component crystals (those that contain only one type of particle), the packing fraction is represented mathematically by:

$$APF = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

$$APF = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}}$$

where N_{particle} is the number of particles in the unit cell, V_{particle} is the volume of each particle, and $V_{\text{unit cell}}$ is the volume occupied by the unit cell.

1. APF for Simple Cubic (SC) Structure



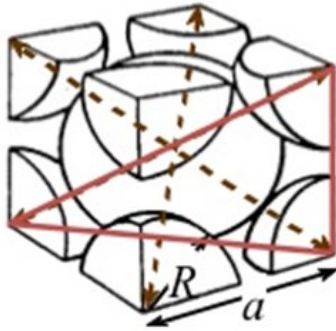
$$\text{Number of atoms/unit cell} = 8 \times \frac{1}{8} = 1$$

$$\text{Close packed direction: } a = 2R$$

$$R = 0.5a$$

$$APF = \frac{(1) \frac{4}{3} \pi R^3}{a^3} = \frac{(1) \frac{4}{3} \pi (0.5a)^3}{a^3} = \frac{1}{6} \pi = 0.524 \quad \text{or} \quad 52\%$$

2. APF for Body-Centred Cubic (BCC) Structure



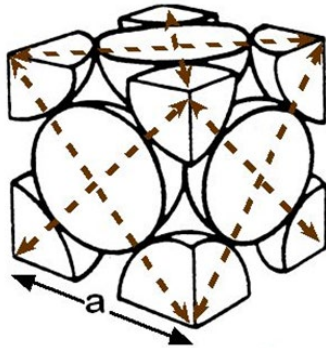
$$\text{Number of atoms/unit cell} = 1 + 8 \times \frac{1}{8} = 2$$

$$\text{Close packed direction: } \sqrt{3}a = 4R$$

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

$$APF = \frac{(2) \frac{4}{3} \pi R^3}{a^3} = \frac{(2) \frac{4}{3} \pi (\sqrt{3}a/4)^3}{a^3} = \frac{1}{8} \pi \sqrt{3} = 0.68 \quad \text{or} \quad 68\%$$

3. APF for Face-Centred Cubic (FCC) Structure



$$\text{Number of atoms/unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Close packed direction: } \sqrt{2}a = 4R$$

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

$$APF = \frac{(4) \frac{4}{3} \pi R^3}{a^3} = \frac{(4) \frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3} = \frac{1}{6} \pi \sqrt{2} = 0.740 \quad \text{or} \quad 74\%$$

1.10 Examples of Simple Crystal Structures

Face-Centred and Body-Centred Cubic

The most familiar metals all crystallize in the FCC structure (Fig. 1.13-a). The unit cell contains four atoms: one from the eight corner atoms which it shares with other cells, and three from the six surface atoms it shares with other cells. Some of the metals crystallize in the BCC structure (Fig. 1.13-b). Here the unit cell has two atoms. One is from the shared corner atoms and the other is the central atom, which is not shared.

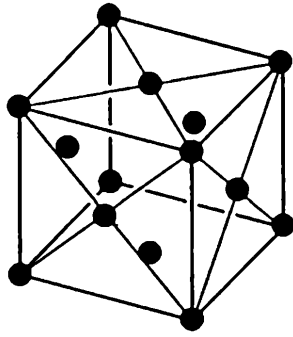


Fig. 1.13 (a) An FCC unit cell.

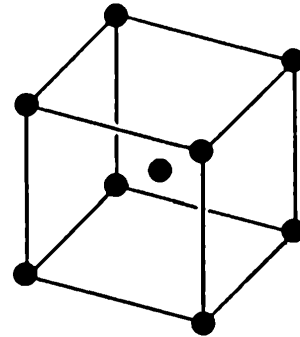


Fig. 1.13 (b) A BCC unit cell.

If we examine the face-Centred- cubic (FCC) lattice of Fig. 1.14-a we can see that the simplest *primitive* cell is rhombohedral, with three translational vectors each of length $(a/\sqrt{2})$, which make angles of 60° with respect to each other. The strong cubic symmetry is demonstrated if we display the lattice instead in terms of a non-primitive *unit cube*, with three mutually perpendicular translational vectors of length a . The unit cube has a volume a^3 , but the volume of the rhombohedral cell is only $a^3/4$. Thus matter associated with four primitive basis units must be associated with the volume of the unit cube.

Similarly, for the body-Centred-cubic (BCC) lattice of Fig. 1.14-b, the cubic symmetry is best demonstrated by choice of a nonprimitive unit cube of side L , rather than a primitive rhombohedral cell that can be constructed with primitive vectors of length $(a\sqrt{3}/2)$, make 109° angles with each other. The primitive cell has a volume of $a^3/2$, just one-half that of the cube shown with dashed lines.

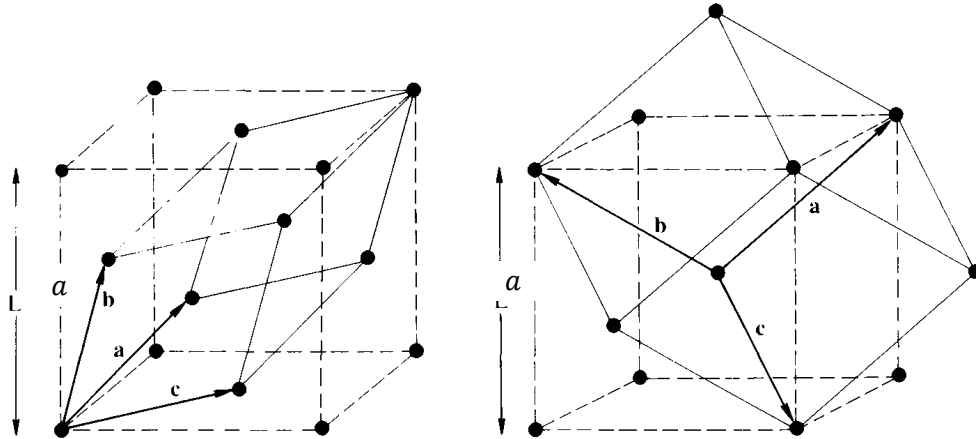


Fig. 1.14 (a) The face-centred-cubic lattice, and (b) the body-centred-cubic lattice. Each part of the figure shows the conventional unit cube as dashed lines, with one possible rhombohedral form for the primitive unit cell as solid lines.

If $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors along three mutually perpendicular axes, then the FCC primitive cell is generated by the vectors:

$$\mathbf{a} = \frac{1}{2}a(\hat{y} + \hat{z}), \quad \mathbf{b} = \frac{1}{2}a(\hat{x} + \hat{z}), \quad \mathbf{c} = \frac{1}{2}a(\hat{x} + \hat{y})$$

For the BCC primitive cell, the generating vectors are:

$$\mathbf{a} = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}), \quad \mathbf{b} = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}), \quad \mathbf{c} = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

The characteristics of the three cubic lattice are summarized in the following Table:

	Simple	Body-Centred	Face-Centred
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$\sqrt{3}a/2 = 0.866 a$	$a/\sqrt{2} = 0.707 a$
Number of second neighbors	12	6	6
Second-neighbor distance	$\sqrt{2}a$	a	a
Packing fraction	$\frac{1}{6}\pi = 0.524$	$\frac{1}{8}\pi\sqrt{3} = 0.680$	$\frac{1}{6}\pi\sqrt{2} = 0.740$

Sodium Chloride Structure

This is the structure assumed by ordinary table salt, NaCl. The structure is cubic, and is such that, along the three principal directions (axes), there is an alternation of Na and Cl atoms, as shown in Fig. 1.15(a). In three dimensions the unit cell appears as shown in Fig. 1.15(b). That is, the cell is a face-Centred cubic one. The positions of the four Na atoms are $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$, while those of the four Cl atoms are located at $\frac{1}{2}\frac{1}{2}\frac{1}{2}, 00\frac{1}{2}, 0\frac{1}{2}0, \frac{1}{2}00$ (the numbers refer to coordinates given in fractions of the cubic edge).

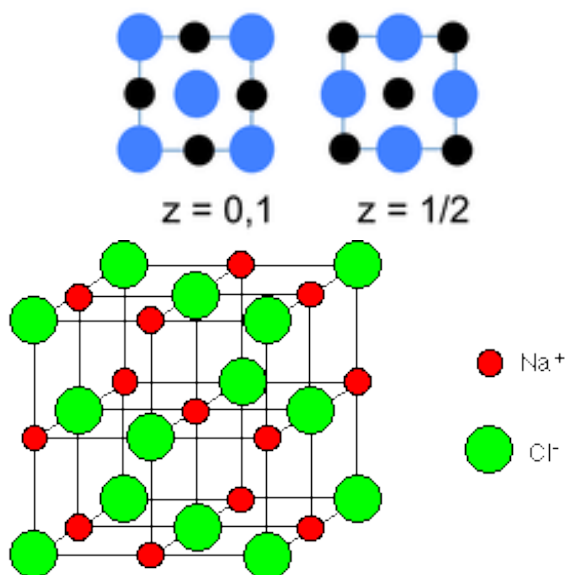


Fig. 1.15 (a) A two-dimensional view of the NaCl structure.

Fig. 1.15 (b) The NaCl structure in three dimensions. The Na atoms form an FCC structure which is interlocked with another FCC structure composed of the Cl atoms.

We summarize this by saying that NaCl is a non-Bravais structure composed of two interpenetrating FCC sublattices; one made up of Na atoms and the other of Cl atoms, and the two sublattices are displaced relative to each other by $\frac{1}{2}a$.

Representative crystals having NaCl structure are KCl, KBr, MgO, AgBr, etc.

Cesium Chloride (CsCl) Structure

This is a cubic crystal, but here the cesium and chlorine atoms alternate on lines directed along the four diagonals of the cube. Thus the unit cell is a BCC one, as shown in Fig. 1.16. There are 2 atoms per unit cell, one Cs atom located at the point 000 and one Cl atom located at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Therefore, this is a non-Bravais lattice composed of two SC (simple cubic) lattices which are displaced relative to each other along the diagonal by an amount equal to one-half the diagonal. CsCl, RbCl and LiHg are some materials crystallizing in this structure.

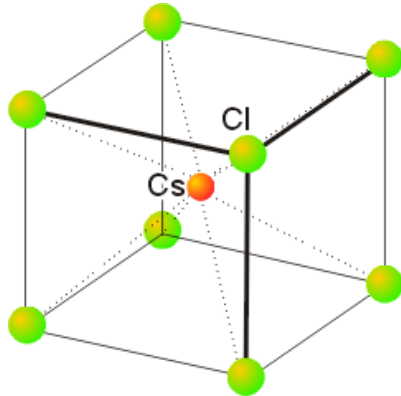


Fig. 1.16 Structure of cesium chloride. The Cs atoms form an SC lattice interlocked with another SC lattice formed by the Cl ions.

Diamond structure

The unit cell for this structure is an FCC cell with a basis, where the basis is made up of two carbon atoms associated with each lattice site. The positions of the two basis atoms are 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. A two-dimensional view of the cell is shown in Fig. 1.17(a), and the whole cell in three dimensions is shown in Fig. 1.17(b). There are eight atoms per unit cell.

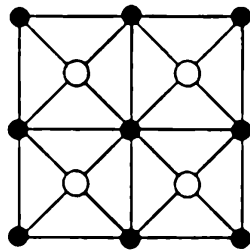


Fig. 1.17 (a) The diamond structure, (a) Projection of the atoms on the base of the cube. One dark circle plus an adjacent white circle form a basis for the structure.

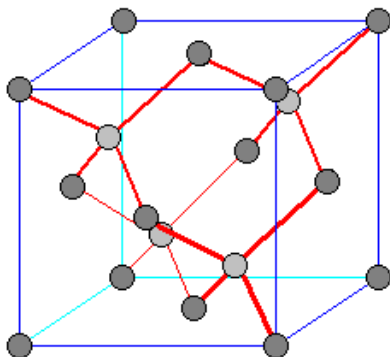


Fig. 1.17 (b) A simplified three-dimensional view of diamond structure.

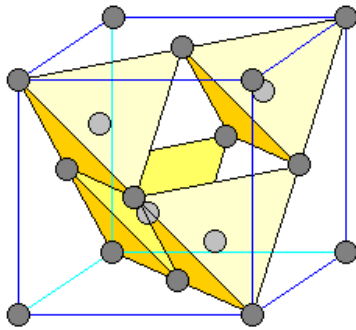


Fig. 1.17 (c) A simplified three-dimensional view of diamond structure, together with the tetrahedral coordination.

Note that the present structure is such that each atom finds itself surrounded by four nearest atoms, which form a regular tetrahedron whose center is the atom in question. Such a configuration is common in semiconductors, and is referred to as a tetrahedral bond.

Carbon, silicon and germanium crystallise in this structure.



Zinc sulphide (ZnS) structure

This structure, named after the compound ZnS, also known as the **Zinc Blende** structure, is closely related to the diamond structure discussed above, the only difference being that the two atoms forming the basis are of different kinds, e.g., Zn and S atoms. Here each unit cell contains four ZnS molecules, and each Zn (or S) atom finds itself at the center of a tetrahedron formed by atoms of the opposite kind. The compounds which have cubic zinc sulphide structure are CuCl, ZnS, InSb and CdS.

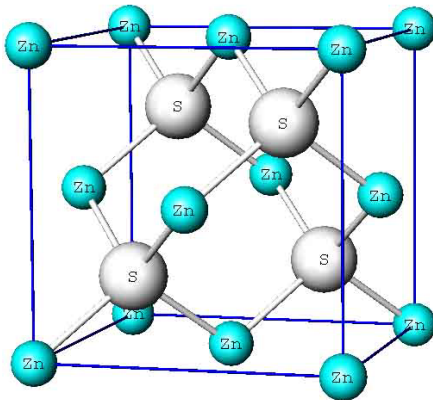


Fig. 1.18 Zinc sulfide (ZnS) or zincblende structure.



Hexagonal close-packed structure

This is another structure that is common, particularly in metals. Figure 1.19 demonstrates this structure. In addition to the two layers of atoms which form the base and upper face of the hexagon, there is also an intervening layer of atoms arranged such that each of these atoms rests over a depression between three atoms in the base. The atoms in a hexagonal close-packed (hcp) structure are thus packed tightly together, which explains why this structure is so common in metals, where the atoms tend to assemble very close to each other.

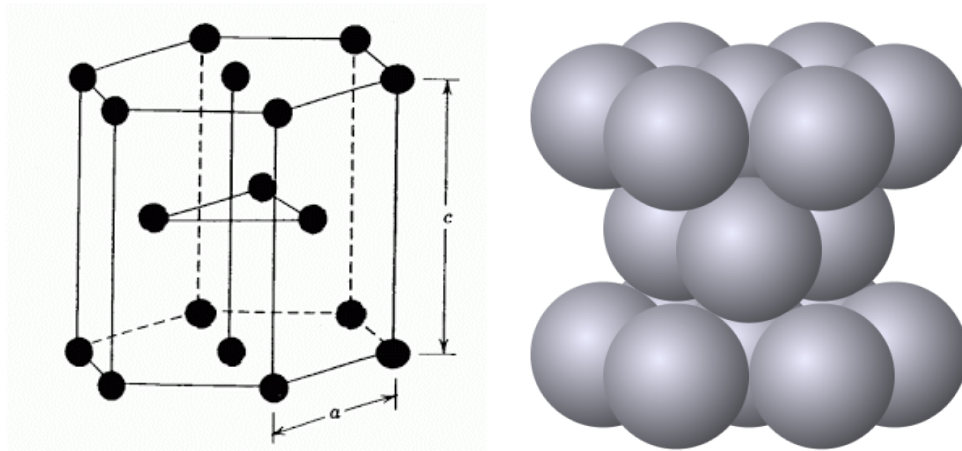


Fig. 1.19 Hexagonal close-packed structure (hcp), the atoms are nearly touching, as in the actual situation.

Underlying the hcp structure is a simple hexagonal Bravais lattice, given by stacking two-dimensional triangular nets directly above each other. The direction of stacking is known as the c-axis. Three primitive vectors are:

$$\mathbf{a} = \frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y} \quad ; \quad \mathbf{b} = \frac{a}{2}\hat{x} - \frac{\sqrt{3}a}{2}\hat{y} \quad ; \quad \mathbf{c} = c\hat{z}$$

The first two generate a triangular lattice in the x-y plane, and the third stacks the planes distance c above one another.

In hcp arrangements, each atom has 12 nearest neighbors: six in its own plane, three in the plane above, and three in the plane below.

The unit cell of the hcp structure with the atoms shrunk in order to display the geometric arrangement. The space lattice of the hcp structure is simple hexagonal with a basis of two atoms, one at (000) and the other at $(\frac{2}{3}\frac{1}{3}\frac{1}{2})$. Elementary geometry tells us that the ratio of the height of the cell to the nearest neighbor spacing should be:

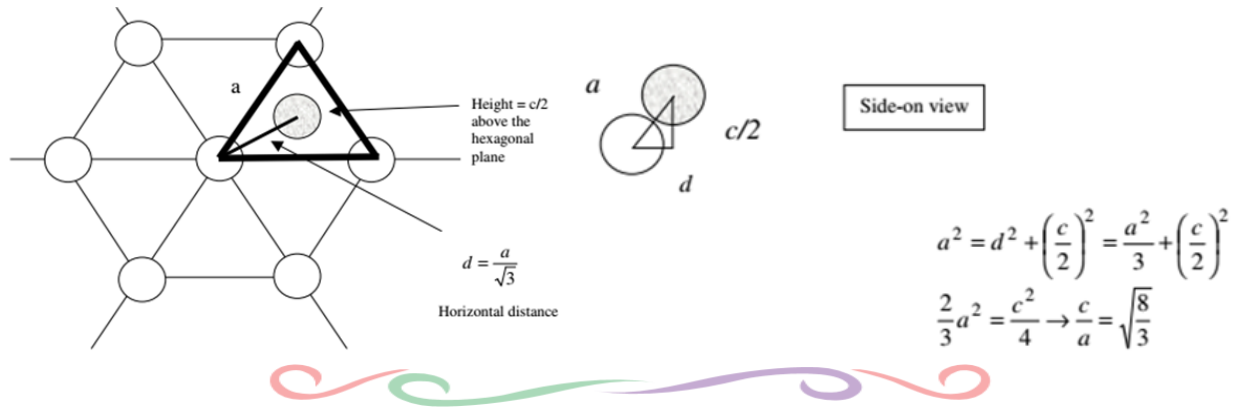
$$\frac{c}{a} = \left(\frac{8}{3}\right)^{1/2} = 1.633$$

Example 1.1:

Show that in an ideal hexagonal close-packed (hcp) structure, where the atomic spheres touch each other, the ratio c/a is given by:

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

Solution:

**Example 1.2:**

Calculate the APF for Hexagonal Close Packed (hcp) Structure.

Solution:

The unit cell of hcp 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, $a = 2R$.

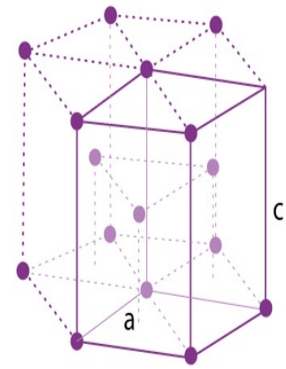
The top layer contains seven atoms. Each corner atom is shared by 6 surrounding hexagon cells and the centre atom is shared by 2 surrounding cells. The three atoms within the body of the cell are fully contributing to the cell.

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

Close packed direction: $a = 2R \Rightarrow R = a/2$

We have: $c = \sqrt{8/3}a$

Volume of the cell: $= 3(\sqrt{3}/2)a^2c$



$$APF = \frac{(6) \frac{4}{3} \pi R^3}{3 \left(\frac{\sqrt{3}}{2} \right) a^2 c} = \frac{(6) \frac{4}{3} \pi \left(\frac{a}{2} \right)^3}{3 \left(\frac{\sqrt{3}}{2} \right) a^2 c}$$

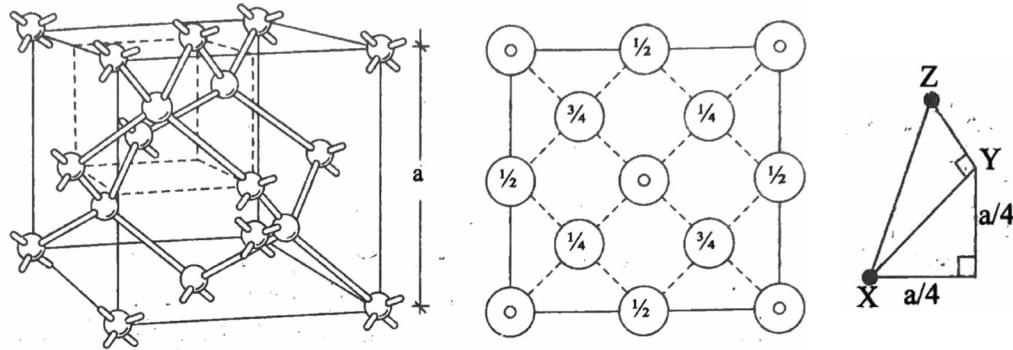
$$= \frac{(6) \frac{4}{3} \pi (a/2)^3}{3 \left(\frac{\sqrt{3}}{2} \right) a^2 (\sqrt{8/3}a)} = \frac{\pi a^3}{3\sqrt{2}a^3} = \frac{\pi}{3\sqrt{2}} = 0.740 \quad \text{or} \quad 74\%$$

Example 1.3:

Calculate the APF for Diamond cubic structure.

Solution:

The basic diamond lattice and the atomic positions in the cubic cell of diamond projected on a cube face are shown in following Figure. The fractions denote height about the base in units of cube edge. The point at 0 and 1/2 are on the FCC lattice, those at 1/4 and 3/4 are on a similar lattice displaced among the body diagonals by 1/4 of the cube edge.



The total number of atoms in a unit cell = $4 + 4 = 8$

$$(XY)^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 = \frac{a^2}{8}$$

$$(XZ)^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{8} + \left(\frac{a}{4}\right)^2 = \frac{3a^2}{16}$$

But,

$$XZ = 2R$$

Therefore,

$$(2R)^2 = \frac{3a^2}{16} \Rightarrow R = \frac{\sqrt{3}a}{8}$$

$$APF = \frac{(8) \frac{4}{3} \pi R^3}{a^3} = \frac{(8) \frac{4}{3} \pi \left(\frac{\sqrt{3}a}{8}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{16} = 0.34 \quad \text{or} \quad 34\%$$

Thus the diamond is a loosely packed structure.



1.11 Nomenclature of Crystal

Directions and Crystal Planes; Miller Indices

In describing physical phenomena in crystals, we must often specify certain directions or crystal planes, because a crystal is usually anisotropic. Certain standard rules have evolved which are used in these specifications.

1. Crystal directions

Consider the straight line passing through the lattice points A, B, C, etc., in Fig. 1.20. To specify its direction, we proceed as follows: We choose one lattice point on the line as an origin, say the point A. Then we choose the lattice vector joining A to any point on the line, say point B. This vector can be written as

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

The direction is now specified by the integral triplet $[n_1 n_2 n_3]$. If the numbers n_1, n_2, n_3 have a common factor, this factor is removed, i.e., the triplet $[n_1 n_2 n_3]$ is the smallest integer of the same relative ratios. Thus in Fig. 1.20 the direction shown is the $[111]$ direction.

Note that, when we speak of a direction, we do not mean one particular straight line, but a whole set of parallel straight lines (Fig. 1.20) which are completely equivalent by virtue of the translational symmetry.

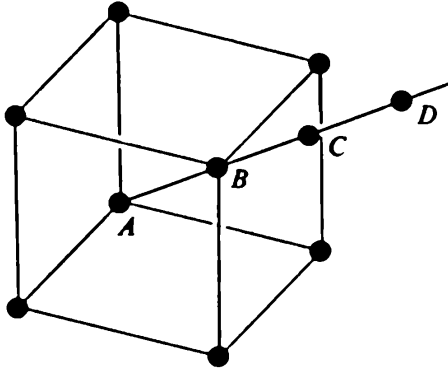


Fig. 1.20 The $[111]$ direction in a cubic lattice.

When the unit cell has some rotational symmetry, then there may exist several nonparallel directions which are equivalent by virtue of this symmetry. Thus in a cubic crystal the directions $[100]$, $[010]$, and $[001]$ are equivalent. When this is the case, one may indicate collectively all the directions equivalent to the $[n_1 n_2 n_3]$ direction by $\langle n_1 n_2 n_3 \rangle$, using angular brackets.

Thus in a cubic system the symbol $\langle 100 \rangle$ indicates all six directions: $[100]$, $[010]$, $[001]$, $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$. The negative sign over a number indicates a negative value. Similarly the symbol $\langle 111 \rangle$ refers to all the body diagonals of the cube. Of course the directions $\langle 100 \rangle$ and $\langle 111 \rangle$ are not equivalent.



Example 1.4:

In a cubic crystal with lattice constant a :

- A) Draw the crystallographic directions $[123]$ and $[1\bar{2}1]$ on a sketch of the cubic unit cell. Show an arrow for each direction starting at the origin and passing through the indicated lattice point.
- B) For each direction, write the corresponding Cartesian vector in units of a , calculate its length, and determine the associated unit vector.
- C) Compute the angle between the two directions.

Solution:

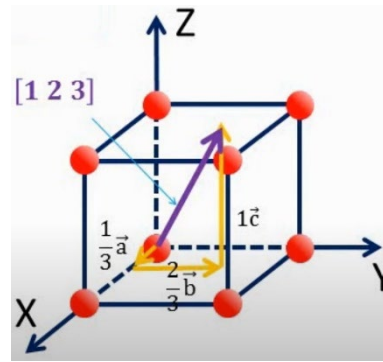
A)

To draw $[123]$:

We have $1\vec{a} + 2\vec{b} + 3\vec{c}$

To draw the direction in a Unit cell, these values should be divided by maximum absolute index:

$$\frac{1}{3}\vec{a} + \frac{2}{3}\vec{b} + 1\vec{c}$$

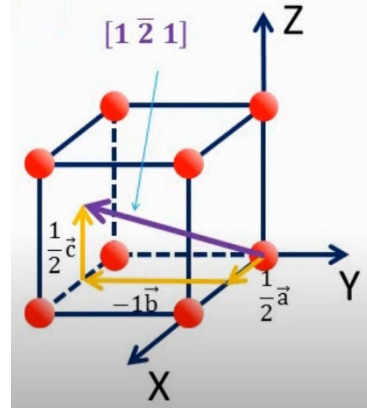


To draw $[1\bar{2}1]$:

We have $1\vec{a} - 2\vec{b} + 1\vec{c}$

To draw the direction in a Unit cell, these values should be divided by maximum absolute index:

$$\frac{1}{2}\vec{a} - 1\vec{b} + \frac{1}{2}\vec{c}$$



B)

Take lattice constant a . Represent vectors in Cartesian coordinates (units of a).

For $[123]$: $\vec{v}_{[123]} = (1, 2, 3)\vec{a}$

Length: $|\vec{v}_{[123]}| = a\sqrt{1^2 + 2^2 + 3^2} = \sqrt{14}a$

Unit vector:

$$\hat{v}_{[123]} = \frac{\vec{v}_{[123]}}{|\vec{v}_{[123]}|} = \left(\frac{1}{\sqrt{14}}, \frac{2}{\sqrt{14}}, \frac{3}{\sqrt{14}} \right) \quad \text{if } a = 1$$

For $[1\bar{2}1]$: $\vec{v}_{[1\bar{2}1]} = (1, -2, 1)\vec{a}$

Length: $|\vec{v}_{[1\bar{2}1]}| = a\sqrt{1^2 + (-2)^2 + 1^2} = \sqrt{6}a$

Unit vector:

$$\hat{v}_{[1\bar{2}1]} = \frac{\vec{v}_{[1\bar{2}1]}}{|\vec{v}_{[1\bar{2}1]}|} = \left(\frac{1}{\sqrt{6}}, \frac{-2}{\sqrt{6}}, \frac{1}{\sqrt{6}} \right) \quad \text{if } a = 1$$

C)

Use the dot product:

$$\cos \theta = \frac{\vec{v}_{[123]} \cdot \vec{v}_{[1\bar{2}1]}}{|\vec{v}_{[123]}||\vec{v}_{[1\bar{2}1]}|} = \frac{1 - 4 + 3}{(\sqrt{14})(\sqrt{6})} = 0$$

$$\theta = \cos^{-1} 0 = 90^\circ$$

So the two directions make a right angle.



2. Crystal planes and Miller indices

The orientation of a plane in a lattice is specified by giving its Miller indices, which are defined as follows: To determine the indices for the plane P in Fig. 1.21(a), we find its intercepts with the axes along the basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$. Let these intercepts be x , y and z . Usually x is a fractional multiple of a , y a fractional multiple of b , and so forth. We form the fractional triplet

$$\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right)$$

invert it to obtain the triplet

$$\left(\frac{a}{x}, \frac{b}{y}, \frac{c}{z}\right)$$

and then reduce this set to a similar one having the smallest integers by multiplying by a common factor. This last set is called the *Miller indices* of the plane and is indicated by (hkl) . Let us take an example: Suppose that the intercepts are $x = 2a$, $y = \frac{3}{2}b$, and $z = 1c$. We first form the set

$$\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right) = \left(2, \frac{3}{2}, 1\right)$$

then invert it $\left(\frac{1}{2}, \frac{2}{3}, 1\right)$, and finally multiply by the common denominator, which is 6, to obtain the Miller indices (346) (pronounced as “three four six”).

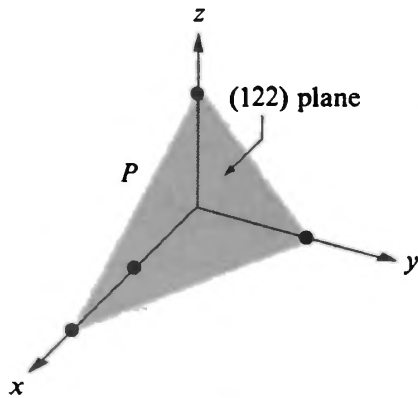


Fig. 1.21 (a) The (122) plane.

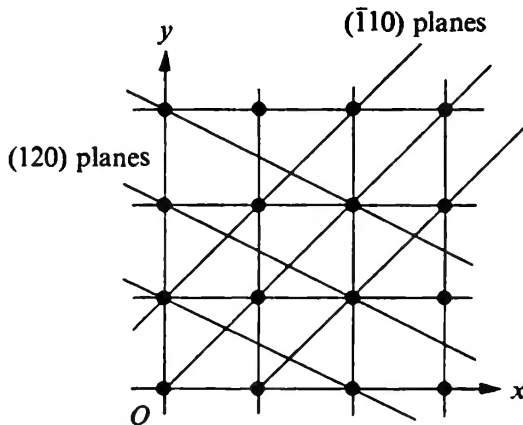


Fig. 1.21 (b) Some equivalent, parallel planes represented by the Miller indices.

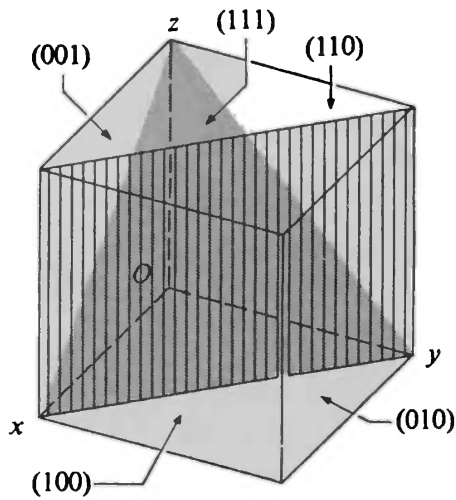


Fig. 1.21 (c) Some of the planes in a cubic crystal.

We note that the Miller indices are so defined that all equivalent, parallel planes are represented by the same set of indices. Thus the planes whose intercepts are x, y, z ; $2x, 2y, 2z$; $-3x, -3y, -3z$, etc., are all represented by the same set of Miller indices. Therefore, a set of Miller indices specifies not just one plane, but an infinite set of equivalent planes.

Sometimes, when the unit cell has rotational symmetry, several nonparallel planes may be equivalent by virtue of this symmetry, in which case it is convenient to lump all these planes in the same Miller indices, but with curly brackets. Thus the indices $\{hkl\}$ represent all the planes equivalent to the plane (hkl) through rotational symmetry. As an example, in the cubic system the indices $\{100\}$ refer to the six planes (100) , (010) , (001) , $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$.

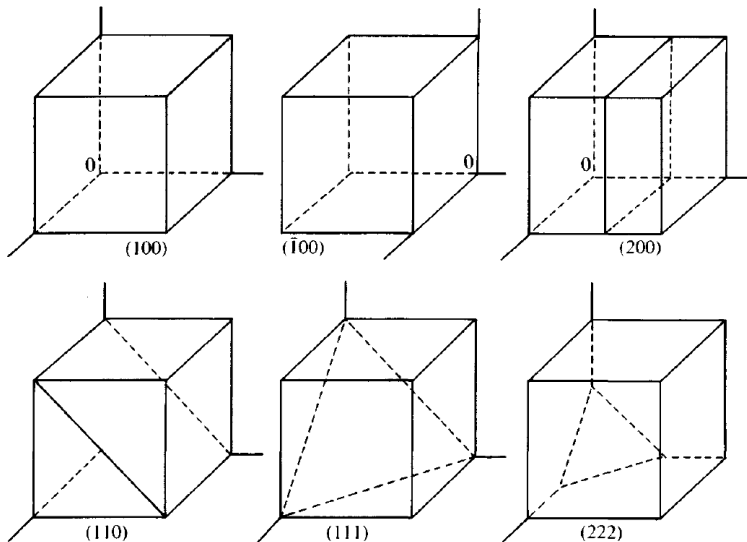


Fig. 1.22 Some of the more prominent planes for cubic lattices, with their Miller notations.

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.

Important features of Miller indices of crystal planes:

(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 an 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 (hkl) are the Miller indices of a plane, then the plane cuts the axes into h , k and l equal segments respectively.



1.12 Spacing between planes of the same Miller indices

In connection with X-ray diffraction from a crystal, one needs to know the interplanar distance between planes labeled by the same Miller indices, say (hkl) . Let us call this distance d_{hkl} . The actual formula depends on the crystal structure, and we confine ourselves to the case in which the axes are orthogonal. Referring to Fig. 1.23, let us visualize another plane parallel to the one shown and passing through the origin. The distance between these planes, d_{hkl} is simply the length of the normal line drawn from the origin to the plane shown. Suppose that the angles which the normal line makes with the axes are α , β , and γ , and that the intercepts of the plane (hkl) with the axes are x , y , and z . Then it is evident from the figure that

$$d_{(hkl)} = x \cos \alpha = y \cos \beta = z \cos \gamma$$

We have $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$. If we solve for $\cos \alpha$, $\cos \beta$, and $\cos \gamma$ from the previous equation, we find that:

$$d_{(hkl)} = \frac{1}{\left(\frac{1}{x^2} + \frac{1}{y^2} + \frac{1}{z^2}\right)^{1/2}}$$

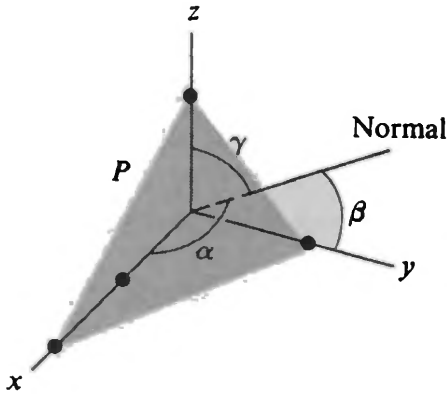


Fig. 1.23 Finding the interplanar spacing.

Now x , y , and z are related to the Miller indices h , k , and l . If one reviews the process of defining these indices, one readily obtains the relations:

$$h = n \frac{a}{x} \quad k = n \frac{b}{y} \quad l = n \frac{c}{z}$$

where n is the common factor used to reduce the indices to the smallest integers possible. Solving for x , y , and z , one obtains

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

which is the required formula.

For simple cubic crystal were $a = b = c$; The interplanar spacing between two adjacent parallel planes of Miller indices (hkl) in a cubic lattice is given by:

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

Thus the interplanar distance of the (111) planes in a simple cubic crystal is $d = a/\sqrt{3}$, where a is the cubic edge.

d-spacing in different crystal system:

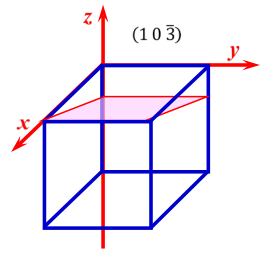
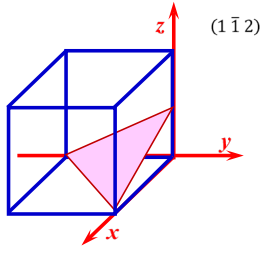
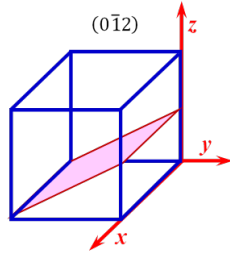
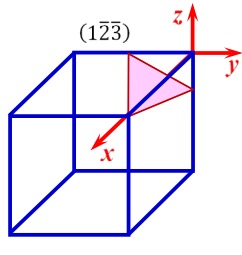
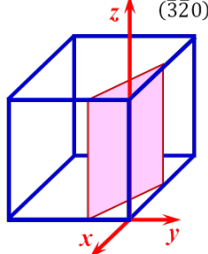
Cubic:	$\frac{1}{d_{(hkl)}^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d_{(hkl)}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d_{(hkl)}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d_{(hkl)}^2} = \frac{1}{\sin^2 \gamma} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2 \sin^2 \gamma}{c^2} - \frac{2hk \cos \gamma}{ab} \right]$
Trigonal (Rhombohedral)	$\frac{1}{d_{(hkl)}^2} = \frac{(1 + \cos \alpha)(h^2 + k^2 + l^2) - 2 \cos \alpha (hk + hl + kl)}{a^2(\cos \alpha - \cos 2\alpha)}$
Triclinic	$\frac{1}{d_{(hkl)}^2} = \frac{1}{V^2} [h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma$ $+ 2hkabc^2(\cos \alpha \cos \beta - \cos \gamma)$ $+ 2hlab^2c(\cos \alpha \cos \gamma - \cos \beta)$ $+ 2kla^2bc(\cos \beta \cos \gamma - \cos \alpha)]$ where $V = abc[1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma]^{\frac{1}{2}}$

Example 1.5:

Graph the plane and determine the axis intersects of a surface with the Miller indices $(10\bar{3})$, $(1\bar{1}2)$, $(0\bar{1}2)$, $(1\bar{2}\bar{3})$ and $(\bar{3}20)$.

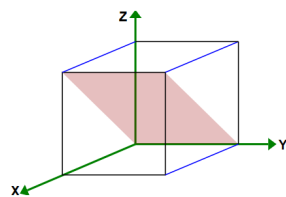
Solution:

for $a = 1$

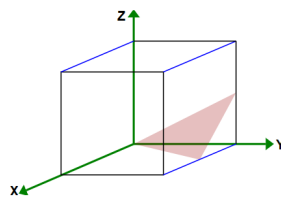
(10$\bar{3}$) $h = 1, k = 0, l = -3$ $x - \text{intercept} = a/h = 1/1 = 1$ $y - \text{intercept} = a/k = 1/0 = \infty$ $z - \text{intercept} = a/l = 1/\bar{3} = -1/3$	
(1$\bar{1}$2) $h = 1, k = -1, l = 2$ $x - \text{intercept} = a/h = 1/1 = 1$ $y - \text{intercept} = a/k = 1/\bar{1} = -1$ $z - \text{intercept} = a/l = 1/2 = 1/2$	
(0$\bar{1}$2) $h = 0, k = -1, l = 2$ $x - \text{intercept} = a/h = 1/0 = \infty$ $y - \text{intercept} = a/k = 1/\bar{1} = -1$ $z - \text{intercept} = a/l = 1/2 = 1/2$	
(1$\bar{2}$$\bar{3}$) $h = 1, k = -2, l = -3$ $x - \text{intercept} = a/h = 1/1 = 1$ $y - \text{intercept} = a/k = 1/\bar{2} = -1/2$ $z - \text{intercept} = a/l = 1/\bar{3} = -1/3$	
($\bar{3}$$\bar{2}$0) $h = -3, k = -2, l = 0$ $x - \text{intercept} = a/h = 1/\bar{3} = -1/3$ $y - \text{intercept} = a/k = 1/\bar{2} = -1/2$ $z - \text{intercept} = a/l = 1/0 = \infty$	

Example 1.6:

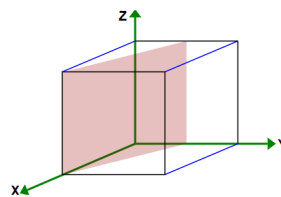
Identify the planes:



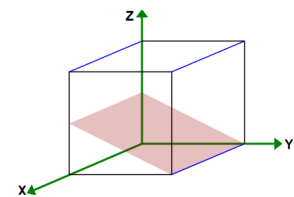
(a)



(b)



(c)



(d)

Solution:

(a)	$x - \text{intercept} = -1 \Rightarrow 1/x = -1$ $y - \text{intercept} = \infty \Rightarrow 1/y = 0$ $z - \text{intercept} = 1 \Rightarrow 1/z = 1$ $(\bar{1}01)$	
(b)	$x - \text{intercept} = 1/2 \Rightarrow 1/x = 2$ $y - \text{intercept} = -1 \Rightarrow 1/y = -1$ $z - \text{intercept} = 1/2 \Rightarrow 1/z = 2$ $(2\bar{1}2)$	
(c)	$x - \text{intercept} = 1 \Rightarrow 1/x = 1$ $y - \text{intercept} = 1/2 \Rightarrow 1/y = 2$ $z - \text{intercept} = \infty \Rightarrow 1/z = 0$ (120)	
(d)	$x - \text{intercept} = \infty \Rightarrow 1/x = 0$ $y - \text{intercept} = 1 \Rightarrow 1/y = 1$ $z - \text{intercept} = 1/2 \Rightarrow 1/z = 2$ (012)	

Example 1.7:

Aluminium is a face-centered cubic. Its atomic radius is 1.58 Å. Calculate:

- (a) the interplanar spacing for (111) and (210).
 (b) the distance of first and second nearest neighbors.

Solution:**(a)**

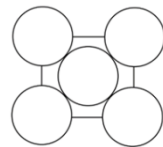
For FCC structure:

$$4r = a\sqrt{2} \quad \therefore \quad a = \frac{4r}{\sqrt{2}} = 4.47 \text{ Å}$$

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

$$d_{(111)} = \frac{4.47}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{4.47}{\sqrt{3}} = 2.580 \text{ Å}$$

$$d_{(210)} = \frac{4.47}{\sqrt{2^2 + 1^2 + 0^2}} = \frac{4.47}{\sqrt{5}} = 1.999 \text{ Å}$$

**(b)**First-neighbor distance: $a/\sqrt{2} = 3.160 \text{ Å}$ Second-neighbor distance: $a = 4.47 \text{ Å}$

Example 1.8:

What is the family of planes $\{hkl\}$ with an interplanar spacing of $d = 1.246 \text{ \AA}$ in nickel (Ni) with $a = 3.524 \text{ \AA}$?

Solution:

We know:

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

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{(hkl)}} = \frac{3.524}{1.246} = 2.828$$

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

The family of planes is $\{220\}$

**1.13 Amorphous Solids**

Amorphous solids have received increasing attention in recent years, particularly as a result of the discovery of the electrical properties of amorphous semiconductors. The most familiar example of an amorphous solid is ordinary window glass. Chemically the substance is a silicon oxide. Structurally it has no crystal structure at all; the silicon and oxygen are simply distributed in what appears to be a random fashion.

Even amorphous solid does actually have a certain kind of “order” or structure, even though this structure is not crystalline. This is why we say that amorphous solid has only a short-range order. Long-range order is absent.

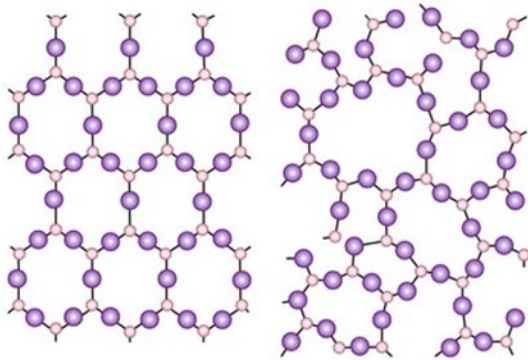


Fig. 1.24 Difference between crystalline and amorphous structures.

**1.14 Interatomic Forces**

Solids are stable structures, e.g., a crystal of NaCl is more stable than a collection of free Na and Cl atoms. Similarly, a Ge crystal is more stable than a collection of free Ge atoms. This implies that the Ge atoms attract each other when they get close to each other, i.e., an attractive interatomic force exists which holds the atoms together. This is the force responsible for crystal formation. This also means that the energy of the crystal is lower than that of the free atoms by an amount equal to the energy required to pull the crystal apart into a set of free atoms. This is called the binding energy of the crystal.

Electrical forces are responsible in binding the atoms and molecules giving different solid structures. Magnetic forces have only a weak effect in cohesion, and gravitational forces are negligible.

The forces between atoms can be of two kinds: attractive forces that keep the atoms together, and repulsive forces that come into play when the solid is compressed.

This may be illustrated by considering the following model: Suppose two atoms A and B exert attractive and repulsive forces on each other such that the bonding force F , between the atoms may be represented as:

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N} \quad \text{with } N > M$$

where r is the centre to centre spacing between the atoms and A , B , M and N are constants characteristic of the molecule. The first term represents the attractive force and the second term the repulsive force. Near the equilibrium position the second term must increase more rapidly for diminishing values of r than does the first and N is necessarily greater than M . Since the attractive forces in interatomic bonds are largely electrostatic, M is usually 2 as per Coulomb's law and the value of N is usually 7 to 10).

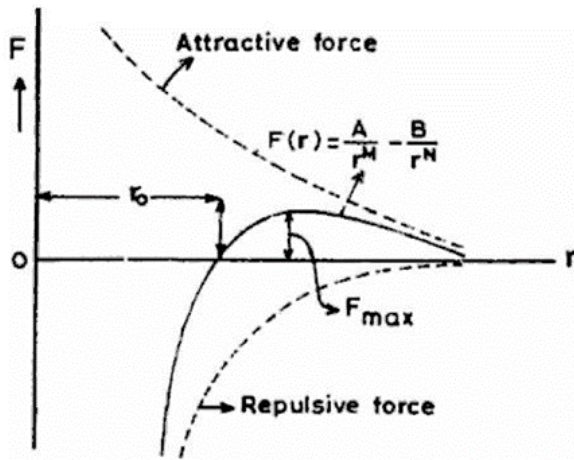


Fig. 1.25 Variation of interatomic force with interatomic spacing.

The equilibrium spacing, r_0 of the given system is obtained as follows:

$$F(r) = \frac{A}{r^M} - \frac{B}{r^N}$$

At the equilibrium spacing

$$F(r) = 0 \quad \text{when } r = r_0$$

Thus

$$0 = \frac{A}{r_0^M} - \frac{B}{r_0^N}$$

$$(r_0)^{N-M} = \frac{B}{A} \Rightarrow r_0 = \left(\frac{B}{A}\right)^{\frac{1}{N-M}}$$

The potential energy representing the interaction between the two atoms varies greatly with the interatomic spacing and is obtained by integrating $F(r)$ equation, Thus

$$U(r) = \int F(r) dr = \int \left[\frac{A}{r^M} - \frac{B}{r^N} \right] dr$$

$$= \int (Ar^{-M} - Br^{-N})dr = -\left(\frac{A}{M-1}\right)\left(\frac{1}{r^{M-1}}\right) + \left(\frac{B}{N-1}\right)\left(\frac{1}{r^{N-1}}\right) + C$$

$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} + C$$

where

$$a = \left(\frac{A}{M-1}\right), \quad b = \left(\frac{B}{N-1}\right), \quad m = M-1 \quad \text{and} \quad n = N-1$$

Setting $U = 0$ when $r = \infty$, we find $C = 0$ and

$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n}$$

The potential energy representing the interaction between two atoms varies greatly with the distance between the atoms. A typical curve of this pair potential, shown in Fig. 1.26, has a minimum at some distance r_0 . For $r > r_0$, the potential increases gradually, approaching 0 as $r \rightarrow \infty$, while for $r < r_0$ the potential increases very rapidly, approaching ∞ at small radius.

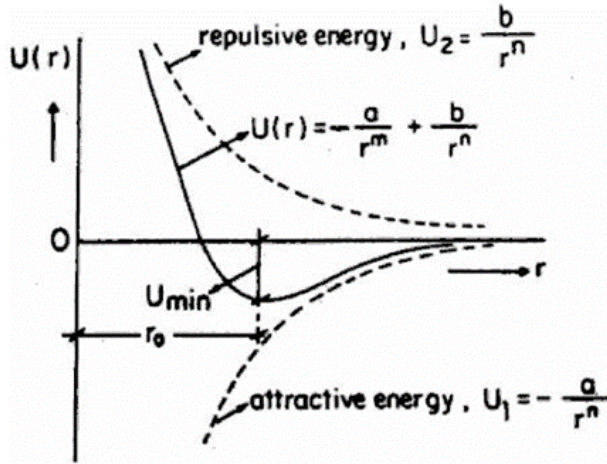


Fig. 1.26 Variation of potential energy $U(r)$ with spacing.

Because the system tends to have the lowest possible energy, it is most stable at the minimum point, which therefore represents the equilibrium position; the equilibrium interatomic distance is r_0 , and the binding energy exhibits a minimum for $r = r_0$.

Hence

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 = \frac{am}{r_0^{m+1}} - \frac{bn}{r_0^{n+1}}$$

Thus

$$\frac{am}{r_0^{m+1}} = \frac{bn}{r_0^{n+1}} \Rightarrow r_0 = \left[\left(\frac{b}{a}\right)\left(\frac{n}{m}\right)\right]^{\frac{1}{n-m}}$$

It follows from this discussion that the interatomic force is composed of two parts: an attractive force, which is the dominant one at large distances, and a repulsive one, which dominates at small distances. These forces cancel each other exactly at the point r_0 , which is the point of equilibrium.



Example 1.9:

Show that the potential energy of two particles in the stable configuration is equal to $-\frac{4}{5}\left[\frac{a}{r_o^2}\right]$ for $m = 2$ and $n = 10$.

Solution:

$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} = -\frac{a}{r^2} + \frac{b}{r^{10}}$$

$$\left[\frac{dU}{dr}\right]_{r=r_o} = 0 = \frac{2a}{r_o^3} - \frac{10b}{r_o^{11}}$$

Thus

$$\frac{a}{r_o^3} = \frac{5b}{r_o^{11}} \Rightarrow r_o^8 = \frac{5b}{a} \Rightarrow r_o^2 = \left[\frac{5b}{a}\right]^{1/4} \Rightarrow r_o^{10} = \left[\frac{5b}{a}\right]^{5/4}$$

Now the potential energy in the stable configuration is given by:

$$[U(r)]_{r=r_o} = -\frac{a}{r_o^2} + \frac{b}{r_o^{10}}$$

Substituting for r_o^2 and r_o^{10} , we get the equation for minimum energy as,

$$\begin{aligned} [U(r)]_{r=r_o} &= -a \left[\frac{a}{5b}\right]^{1/4} + b \left[\frac{a}{5b}\right]^{5/4} \\ &= a \left[\frac{a}{5b}\right]^{1/4} \left(-1 + \frac{b}{a} \left[\frac{a}{5b}\right]\right) \\ &= a \left[\frac{a}{5b}\right]^{1/4} \left(-1 + \frac{1}{5}\right) \\ &= a \left[\frac{a}{5b}\right]^{1/4} \left(-\frac{4}{5}\right) \\ &= -\frac{4}{5} \left[\frac{a}{r_o^2}\right] \end{aligned}$$

**Example 1.10:**

The interaction energy of two particles in the field of each other is given by $U(r) = -\frac{a}{r} + \frac{b}{r^9}$ where a and b are constants.

- Show that the particles form a stable compound for $r = r_o = [9b/a]^{1/8}$.
- Show that in the stable configuration the energy of attraction is 9 times the energy of repulsion.
- Show that the potential energy of the two particles in the stable configuration is $-(8/9)[a/r_o]$.

Solution:

Given

$$U(r) = -\frac{a}{r} + \frac{b}{r^9}$$

(a) For an equilibrium set:

$$\left[\frac{dU}{dr}\right]_{r=r_o} = 0 = \frac{a}{r^2} - 9\frac{b}{r^{10}}$$

Thus,

$$\frac{a}{r_o^2} - 9 \frac{b}{r_o^{10}} = 0 \quad \Rightarrow \quad ar_o^8 = 9b \quad \Rightarrow \quad r_o = \left(\frac{9b}{a}\right)^{1/8}$$

(b) The attractive contribution (magnitude) is a/r_o . The repulsive contribution is b/r_o^9 .

From the equilibrium condition

$$\frac{a}{r_o^2} - 9 \frac{b}{r_o^{10}} = 0 \quad \Rightarrow \quad \frac{a}{r_o^2} = 9 \frac{b}{r_o^{10}}$$

multiply both sides by r_o to obtain

$$\frac{a}{r_o} = 9 \frac{b}{r_o^9}$$

Thus the energy of attraction equals 9 times the energy of repulsion.

(c) the potential energy of the two particles in the stable configuration:

$$U(r_o) = -\frac{a}{r_o} + \frac{b}{r_o^9}$$

Using the relation from (b), replace

$$\frac{b}{r_o^9} = \frac{1}{9} \frac{a}{r_o}$$

$$U(r_o) = -\frac{a}{r_o} + \frac{1}{9} \frac{a}{r_o} = -\frac{8}{9} \frac{a}{r_o}$$



Example 1.11:

Assume that the energy of two particles in the field of each other is given by the following function:

$$U(r) = -\frac{a}{r} + \frac{b}{r^8}$$

where a and b are constants and r is the distance between the centres of the particles.

(a) Show that if the particles are pulled apart, the molecule will break as soon as

$$r = \left[\frac{36b}{a}\right]^{1/7} = r_o(4.5)^{1/7}$$

(b) Prove that in the stable configuration, the energy of attraction is 8 times the energy of repulsion

(c) Also show that the minimum force required to break the molecule is equal to:

$$\frac{a^{9/7}}{(36b)^{2/7}} \left[1 - \frac{8}{36}\right]$$

Solution:

(a)

$$U(r) = -\frac{a}{r} + \frac{b}{r^8} = \int F(r) dr$$

$$\frac{dU}{dr} = F(r) = \frac{a}{r^2} - \frac{8b}{r^9}$$

This will be zero, at $r = r_o$

$$0 = \frac{a}{r_o^2} - \frac{8b}{r_o^9}$$

$$r_o = \left[\frac{8b}{a} \right]^{1/7}$$

But, $\frac{dU}{dr} = F(r)$ will be minimum or maximum, when $\frac{dF}{dr} = 0$

$$\frac{dF}{dr} = \frac{d^2U}{dr^2} = -\frac{2a}{r^3} + \frac{72b}{r^{10}} = 0$$

$$\frac{2a}{r^3} = \frac{72b}{r^{10}}$$

$$r = \left[\frac{36b}{a} \right]^{1/7} = \left[\frac{4.5 \times 8b}{a} \right]^{1/7} = r_o(4.5)^{1/7}$$

(b)

The attraction energy in the stable configuration is:

$$\frac{a}{r_o} = \varphi_a$$

The repulsive energy is:

$$\frac{b}{r_o^8} = \varphi_r$$

Thus,

$$\frac{\varphi_a}{\varphi_r} = \frac{a}{r_o} \times \frac{r_o^8}{b} = \frac{a}{b} r_o^7$$

Substituting the value of r_o , we get:

$$\frac{\varphi_a}{\varphi_r} = \frac{a}{b} \left(\left[\frac{8b}{a} \right]^{1/7} \right)^7 = 8 \quad \Rightarrow \quad \varphi_a = 8\varphi_r$$

(c)

$F(r)$ will be minimum when d^2F/dr^2 is positive;

$$\frac{d^2F}{dr^2} = \frac{6a}{r^4} - \frac{720b}{r^{11}} = \text{positive}$$

The minimum force required to break the molecule is given by:

$$F_{min} = \frac{a}{r^2} - \frac{8b}{r^9}$$

Substituting $r = \left[\frac{36b}{a} \right]^{1/7}$

$$F_{min} = a \left[\frac{a}{36b} \right]^{2/7} - 8b \left[\frac{a}{36b} \right]^{9/7}$$

$$F_{min} = \frac{a^{9/7}}{(36b)^{2/7}} \left[1 - \frac{8}{36} \right]$$



1.15 Types of Bonding

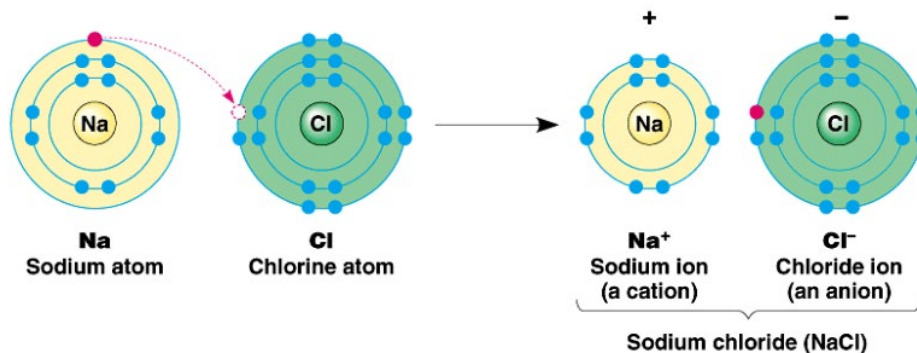
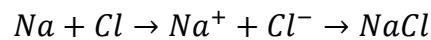
The attractive interatomic forces form bonds between atoms in solids, and it is these bonds which are responsible for the stability of the crystal. There are several types of bonding, depending on the physical origin and nature of the bonding force involved. The three main types of primary bonds: *ionic bonding*, *covalent bonding*, and *metallic bonding*. We also consider secondary types of bonding which are important in certain special cases.



1. Ionic bond

The most easily understood type of bond is the ionic bond. Take the case of NaCl as a typical example. In the crystalline state, each Na atom loses its single valence electron to a neighboring Cl atom, resulting in an ionic crystal containing both positive and negative ions. Thus, each Na^+ ion is surrounded by six Cl^- ions, and vice versa.

The ionic bond is strong when compared with other bonds, a typical value for the binding energy of a pair of atoms being about 5 eV. This strength is attributed to the strength of the coulomb force responsible for the bonding. Ionic bonding is most likely to exist when the elements involved are of widely differing electronegativities.



2. Covalent bond

The covalent bond is formed by sharing of pairs of valence electrons between like atoms rather than by electron transfer. To introduce this bond, we consider covalent solid: diamond. This crystal is formed from carbon atoms arranged in a certain type each atom is surrounded by four others, forming a regular tetrahedron. The bonding in diamond takes place in the following manner: Each atom has four valence electrons, and it forms four bonds with its four nearest neighbors (Fig. 1.27). The bond here is composed of two electrons, one contributed by each of the two atoms. We note that as a result of electron sharing, each C atom now has 8 electrons surrounding it, resulting in a complete—and hence stable—shell structure for the valence shell.

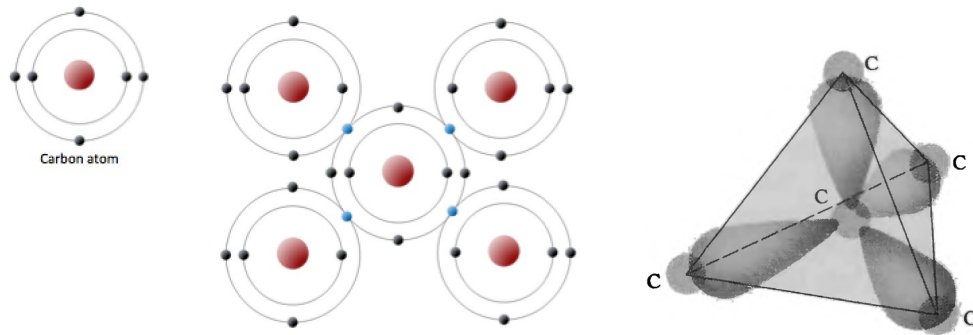


Fig. 1.27 The tetrahedral covalent bond in diamond. Each elongated region represents the charge distribution of the two electrons forming the corresponding bond.

The covalent bond is also strong, as attested to by the unusual hardness of diamond, and its high melting point ($> 3000^{\circ}\text{C}$). The covalent bond is particularly important for those elements in column IV of the periodic table (C, Si, Ge, and Sn), all of which crystallize in the diamond structure and are covalent crystals.

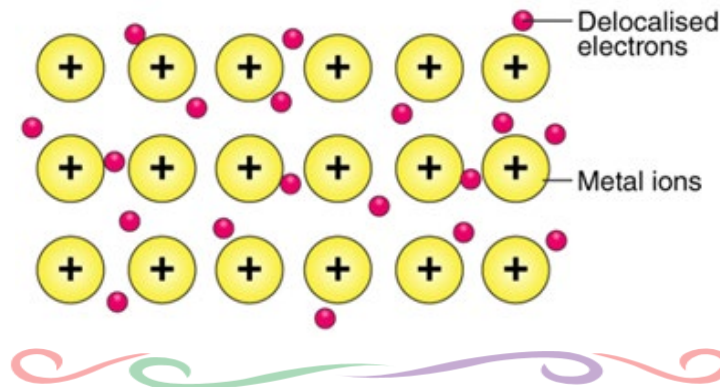
In our discussion of bonding, we have considered only pure ionic or pure covalent bonds. There are, however, many crystals in which the bond is not pure, but a mixture of ionic and covalent. A good example is the case of the semiconductor GaAs. Here a charge transfer does take place, but the transfer is not complete; only about 0.46 of an electron is transferred on the average from the Ga to the As atom. This transfer accounts for part of the binding force in GaAs, but the major part is due to a covalent—or electron-sharing—bond between the Ga and neighboring As atoms.



3. Metallic bond

To understand the metallic bond, let us consider a typical simple metal: sodium. Each free Na atom has a single valence electron which is only loosely bound to the atom. When a crystal is formed, the valence electron detaches from its own atom and becomes an essentially free electron, capable of moving throughout the crystal. Thus, the sodium metal is an assemblage of positive Na^+ ions forming a BCC lattice, immersed in a gas of free electrons. Metals are opaque to light since the light energy is absorbed by free electrons.

The metallic bond is somewhat weaker than the ionic and covalent bonds.



4. Secondary bonds

In addition to the three primary bonds discussed above (ionic, covalent, and metallic), there are other, weaker bonds. For example, the ice crystal (H_2O). First, consider the bonding in a single water molecule. A covalent bond is formed between the oxygen atom and each of the two hydrogen atoms. Thus, the atoms in an H_2O molecule are strongly bonded.

But when we consider the bonding between the water molecules themselves to form ice, we find that the bonding strength is much weaker, e.g., the melting point of water is only 0°C . The explanation of this is that, the shared electrons are actually pulled more strongly toward the oxygen atom, resulting in a net negative charge on the oxygen atom and a corresponding positive charge on the hydrogen atom. This produces a so-called electric dipole in the water molecule, as indicated by the vector in the Fig. 1.28. Now electric dipoles attract each other. Thus water molecules are attracted to each other, forming a crystal. The bond described here is referred to as the **hydrogen bond**, because of the important role played by the small hydrogen nucleus.

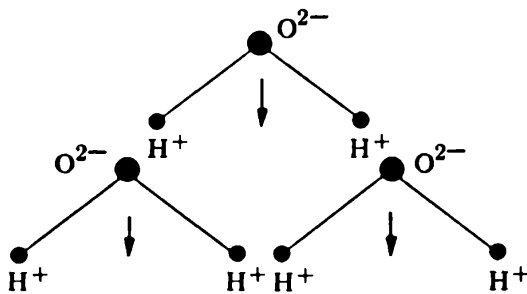


Fig. 1.28 Arrangement of water molecule as a result of hydrogen bond. Arrows represent electric dipole moments of the molecules.

Another bond which plays an especially important role in inert-gas solids is the **Van der Waals bond**. The inert-gas elements (He, Ne, Ar, etc.) display extremely small attraction toward each other, or other elements. The weakness of the interatomic forces in the inert-gas solids is illustrated by their low melting points: -272.2 , -248.7 , and -189.2°C for He, Ne, and Ar, respectively.

In each of these gases, the atom has an outer shell that is completely full. Consequently, an atom has very little predilection to exchange or share electrons with other atoms. Yet even the inert-gas atoms exhibit interatomic forces, albeit very weak ones.

We present the following model for the attraction in inert-gas elements. Consider two such atoms. Each contains a number of orbital electrons, which are in a continuous state of rotation around the nucleus. If their motion were such that their charge was always symmetric around the nucleus, the two atoms would not interact. Although the distribution of the electrons is essentially symmetric, there are small fluctuations, whose effect is to produce a fluctuating electric dipole on each of the atoms. The dipoles tend to attract each other, and this is the source of the van der Waals force.

Two reasons may be given to account for the smallness of the Van der Waals force (also known as the *London force*): (a) The fluctuating atomic dipoles are small, and (b) the dipoles on the different atoms are not synchronized with each other, a fact which tends to cancel their attractive effects.

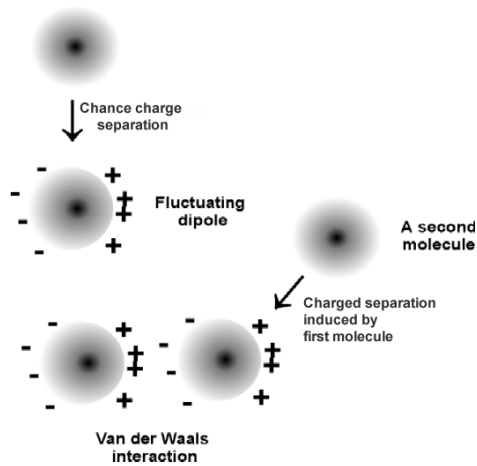


Fig. 1.29 Formation of Van der Waals bond.

1.16 Madelung constant

The Madelung constant is used in determining the electrostatic potential of a single ion in a crystal by approximating the ions by point charges. It is named after Erwin Madelung, a German physicist.

Returning to NaCl as a typical example of an ionically bound solid, we note that a sodium cation has

6	Cl^-	First	Neighbours at a distance of:	r_o
12	Na^+	Second	Neighbours at a distance of:	$\sqrt{2}r_o$
8	Cl^-	Third	Neighbours at a distance of:	$\sqrt{3}r_o$
6	Na^+	Fourth	Neighbours at a distance of:	$2r_o$

and so on. The total Coulomb attractive energy *per ion pair* is thus the sum of an infinite series:

$$U = - \left(\frac{1}{4\pi\epsilon_o} \frac{e^2}{r_o} \right) \left\{ 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots \right\}$$

$$U = -\alpha \left(\frac{1}{4\pi\epsilon_o} \frac{e^2}{r_o} \right)$$

$$\alpha = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots$$

The number α is the *Madelung constant* for the particular lattice, and a has a value controlled by the geometry of the lattice. The series in previous Equation which must be summed to obtain the Madelung constant has terms of alternating sign, and clearly converges rather weakly.

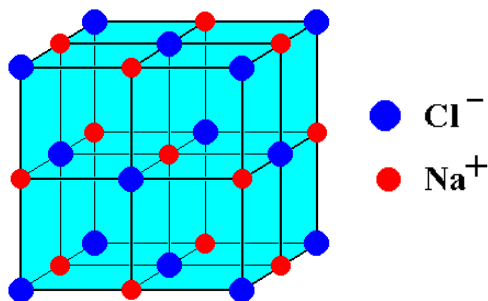
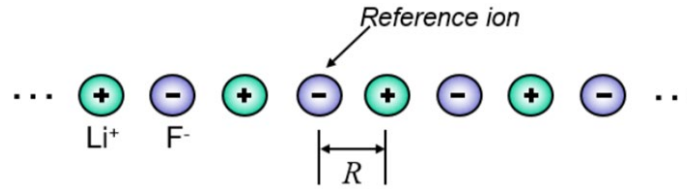


Fig. 1.30 The conventional picture, showing the arrangement of NaCl crystallographic planes.

Example 1.12:

Evaluate the Madelung constant for a 1-dimensional line of alternating positive and negative ions of separation R .

Solution:

$$U = \left(\frac{e^2}{4\pi\epsilon_0} \right) \left[-\frac{2}{R} + \frac{2}{2R} - \frac{2}{3R} + \frac{2}{4R} - \frac{2}{5R} + \dots \right]$$

$$U = \frac{-2e^2}{4\pi\epsilon_0 R} \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \frac{1}{6} + \dots \right]$$

$$\therefore \alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \frac{1}{6} + \dots \right] = 2 \ln 2 = 1.386$$

Example 1.13:

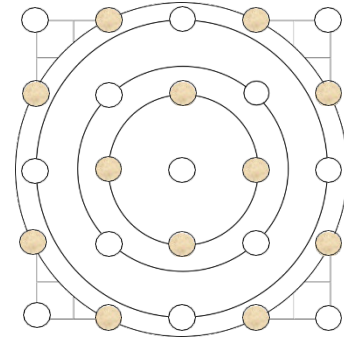
Evaluate the Madelung constant for a 2-dimensional square lattice of alternating positive and negative ions of nearest-neighbour separation r , considering only the first 4 terms in the expansion [$\alpha = 2.749$]

Solution:

Take the shaded circles to be $+$ ions and the unshaded to be $-$ ions. The central $-$ ion has 4 $+$ ions as first-neighbours, 4 $-$ ions as second-neighbours, 4 $-$ ions as third-neighbours and 8 $+$ ions as fourth-neighbours, and so on. Consider the first 4 terms in the expansion.

If the size of the square lattice edge is R , the first-neighbours are a distance R from the central ion, the second-neighbours are at $R\sqrt{2}$, the third-neighbours at $2R$ and the fourth-neighbours at $R\sqrt{5}$ etc.

Thus, the electrostatic potential at the central ion is:



$$U = - \left(\frac{e^2}{4\pi\epsilon_0} \right) \left[\frac{4}{R} - \frac{4}{\sqrt{2}R} - \frac{4}{2R} + \frac{8}{\sqrt{5}R} - \dots \right]$$

$$U = \frac{-e^2}{4\pi\epsilon_0 R} \left[4 - \frac{4}{\sqrt{2}} - 2 + \frac{8}{\sqrt{5}} - \dots \right]$$

Therefore:

$$\therefore \alpha = \left(4 - \frac{4}{\sqrt{2}} - 2 + \frac{8}{\sqrt{5}} - \dots \right)$$