

SOLID STATE PHYSICS

C M KACHHAVA

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Preface

There are a number of standard textbooks on solid state physics. They present a diversity as regards level and content. However, an observation of many teachers and students is that while the coverage in these books is wide, the treatment is not indepth. My attempt in this book is to present a comprehensive coverage with detailed treatment to meet the requirements of students of MSc (General) and BSc (Hons). It should also be useful for chemists, material scientists and electrical engineers. My aim has been to offer the students a unified presentation of the essentials of solid state physics with an emphasis on basic ideas to help them clearly understand the theoretical meaning of these essentials and recognize their experimental foundations. This will make it easier for them to study the more specialized periodical literature subsequently.

A short summary of the plan of the book is given here. Chapter One deals with the crystal structures and their determination. A knowledge of point and space groups is assumed while describing the structures. The concepts of reciprocal lattice and Brillouin zones are developed. Chapter Two is devoted to the definitions, determination and interrelationships of the three fundamental elastic constants of a cubic crystal. The subject of atomic motion is developed from the standpoint of the force constant model in Chapter Three, which also includes a quantum description of lattice vibrations through coupled oscillators. This would assume a knowledge of the definitions of particle operators as developed, for instance, in Merzbacher's *Quantum Mechanics*. It is only here that the student is exposed to second quantization; lattice specific heats, thermal expansion, equation of state and thermal conduction are grouped in Chapter Four. The free electron theory of metals is included in Chapter Five, which gives a coverage of the Boltzmann equation as well as the Hall effect. The various theories on energy bands in solids are dealt with in Chapter Six, which begins with a comprehensive discussion of the physical basis of the formation of bands. The most important concept in the field—Fermi surfaces—is projected as an abstract mathematical construction in Chapter Seven, along with its experimental studies. The exposition of crystal imperfections and associated physical phenomena are presented in Chapter Eight, which also includes a summary of various colour centres. Various theories of magnetism are detailed in Chapter Nine, which provides sufficient space for spin waves and magnon dispersion relation. Chapter Ten provides a vivid discussion of bizarre experimental properties of superconductors and their electromagnetic theories. The physical basis and properties of a Cooper pair are explained and form the basis of the BCS-theory and Josephson effect. The chapter finally

includes a brief description of the most fascinating discovery of high temperature superconductivity.

The physics of solids is a rather diverse subject and hence it is almost impossible to cover all areas which fall in this field. Some topics like semiconductor physics and dielectric properties have not been included in the book. I have deliberately refrained from making any direct reference in the text to the original literature. For such information, the student should consult the monographs and review articles listed at the end of each chapter. Finally, a book like this can lay little claim to originality. I owe a great debt to the standard texts on the subject, and several others mentioned in the Bibliography.

C M KACHHAVA

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ONE

Crystalline State

1.1 INTRODUCTION

Most solid substances are crystals, which may be defined on the macroscopic scale as homogeneous solids, in which some of the physical properties are function of direction. Microscopically, a crystal may be defined as a solid having an arrangement of atoms (or molecules) in which the atoms are arranged in some repetitive pattern in three dimensions. The arrangement of atoms is termed as the *crystal structure*. The internal regularity of placement atom in solids often leads to a symmetry of their external shapes. Rock salt crystals, for example, are rectangular parallelepipeds with faces which are identical when looked at from several different directions; these crystals have a high degree of symmetry. Crystalline quartz, on the other hand, has symmetry of a lower order.

This chapter is devoted to the study of the geometry of atomic arrangements and the symmetry it displays. Vector notations are summoned to describe some direct and reciprocal lattices. Finally, an experimental study for the determination of crystalline structure is presented.

1.2 TRANSLATIONAL SYMMETRY

A crystal is said to be translationally symmetric or periodic if there exist three linearly independent vectors (\mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3) such that a translation by

$$\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (1.1)$$

where n_1 , n_2 and n_3 are arbitrary integers, brings a point back to an equivalent point in the crystal. Two points are said to be equivalent if they have an identically same surrounding. Thus, the translational symmetry is defined by the three vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 (called the *basis* or *fundamental vectors*), which must not be coplanar. The end points of vectors defined by Eq. (1.1), form the *space lattice*. A property such as charge density is the same at all points $\mathbf{r} + \mathbf{R}_n$, as it is at \mathbf{r} , i.e., it is periodic in space.

A lattice is completely characterised by six parameters: three distances a_1 , a_2 , a_3 and three angles α_1 , α_2 , α_3 as shown in Fig. 1.1.

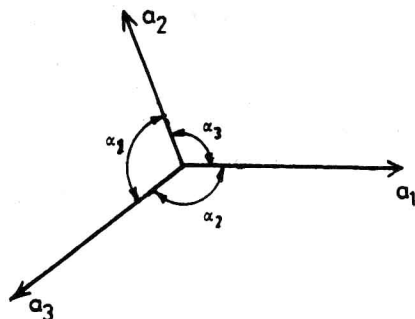


FIG. 1.1 Lattice parameters

1.3 UNIT CELL

An ideal crystal may be made up of a set of polyhedral blocks which fit exactly together. Each block is identical and may contain several nuclei, each with an associated cloud of electrons. It is called a *unit cell* and may be conveniently chosen in a number of different ways.

One obvious way to define a unit cell is as the parallelepiped bounded by the basis vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . Even then, the midpoint of the cell can be arbitrarily chosen although it is usual to centre it on one of the atomic positions. Figure 1.2 shows for a two-dimensional lattice, two forms of the unit cell as a parallelogram with different centres.

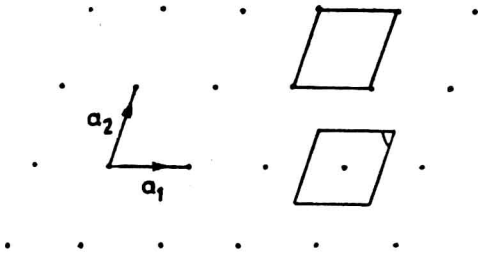


FIG. 1.2 General two-dimensional space lattice showing two forms of the unit cell as a parallelogram with different centres

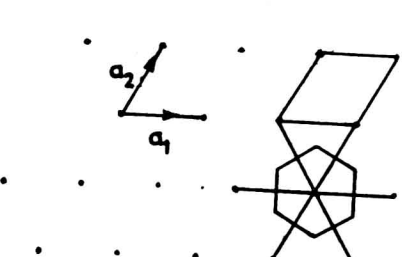


FIG. 1.3 Triangular plane lattice $|\mathbf{a}_1| = |\mathbf{a}_2|$ and angle between them is $\pi/3$

Another convenient way of choosing the unit cell is to take the volume bounded by the planes which right-bisect the nearest \mathbf{R}_n . Such a unit cell is often referred to as a *Wigner-Seitz cell*. Figure 1.3 shows two forms of the unit cell—one as a parallelogram and the other as a hexagon obtained by drawing perpendicular bisectors to each lattice vector from a central site.

The unit cell can contain one or more atoms. Naturally, if it contains only one atom, we put that on the lattice site, and say that we have a *Bravais lattice*. On the other hand, if there are several atoms per unit cell, then we have a *lattice with a basis*.

1.4 BASIS AND CRYSTAL STRUCTURE

In order to convert the geometrical array of points (the lattice) into a crystal structure, we must locate atoms or molecules on the lattice points. The repeating unit assembly—atom, molecule, ion or radical—that is located at each lattice point is called the *basis*. Every basis is identical in composition, arrangement and orientation. No basis contains fewer atoms than a primitive basis contains.

The crystal structure is thus given by two specifications:

1. the lattice, and
2. the assembly that repeats itself.

Hence, the logical relation is

$$\text{lattice} + \text{basis} = \text{crystal structure}$$

This relationship is depicted in Fig. 1.4.

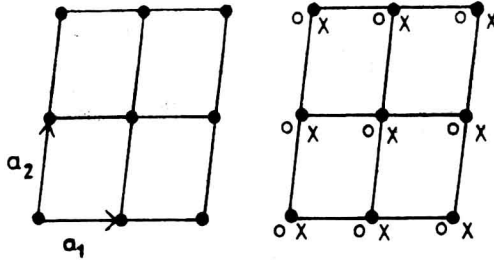


FIG 1.4 Two-dimensional lattice. (a) Bravais lattice;
(b) Lattice with a basis of three atoms;
●, O, X

1.5 CRYSTAL CLASSIFICATION

The most obvious feature of a crystal is its regularity or symmetry. Therefore, the basis of classification of crystals is the symmetry exhibited by them. In a well-defined crystal, the various symmetry elements (rotation, reflection, inversion etc.) intersect at a point. Each set of symmetry elements intersecting at a point (the centre of the unit cell) is called a *point-group*. Since there are 32 point-groups, there are equal number of *crystal classes*, which can be grouped together into seven groups known as *crystal systems*. In Table 1.1, we list description of various systems. Figure 1.5 shows how seven crystal systems can be obtained by successive distortion of a cube.

Table 1.1 Seven Crystal Systems

System	Crystallographic axes	Unit cell
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_1 \neq \alpha_2 \neq \alpha_3$	a parallelogram-based skew prism or parallelepiped
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_1 = \alpha_3 = 90^\circ \neq \alpha_2$	a parallelepiped-based right prism
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_1 = \alpha_2 = \alpha_3 = 90^\circ$	a rectangular-based right prism
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_1 = \alpha_2 = \alpha_3 = 90^\circ$	a square-based right prism
Cubic	$a_1 = a_2 = a_3$ $\alpha_1 = \alpha_2 = \alpha_3 = 90^\circ$	a cube
Trigonal (Rhombohedral)	$a_1 = a_2 = a_3$ $\alpha_1 = \alpha_2 = \alpha_3 \neq 90^\circ$	a rhombohedron
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_1 = \alpha_2 = 90^\circ, \alpha_3 = 120^\circ$	a rhombus-based right prism

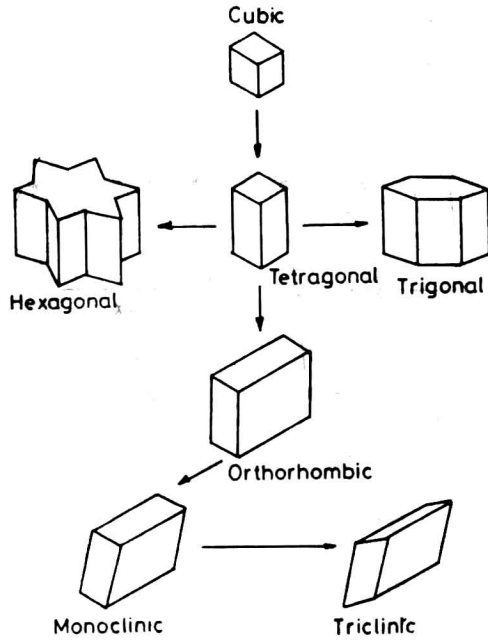


FIG. 1.5 Seven crystal systems in three dimensions

1.6 DIRECTION INDICES

To find the direction indices:

1. Find any vector in the desired direction.
2. Express this vector in terms of the basis (a_1, a_2, a_3) .
3. Divide the coefficients of (a_1, a_2, a_3) by their greatest common divisor. The resulting set of three integers u, v, w defines a direction. $\langle uvw \rangle$ means all vectors equivalent to $[uvw]$. Negative sign in any of the numbers are indicated by placing a bar over the number (thus, \bar{u}).

Let $a_1 = 2, a_2 = 3, a_3 = 4$ units and the vector be

$$\mathbf{r} = 6 \hat{\mathbf{i}} + 12 \hat{\mathbf{j}} + 10 \hat{\mathbf{k}}$$

Then

$$\mathbf{r} = 3(2) \hat{\mathbf{i}} + 4(3) \hat{\mathbf{j}} + 2.5(4) \hat{\mathbf{k}}$$

Thus, the coefficients of (a_1, a_2, a_3) are 3, 4, 2.5. The relevant greatest common divisor is 0.5. Thus, the three numbers 6, 8, 5 are found. Hence, for the example considered the indices of direction are $[685]$. In the cubic system, u, v, w are proportional to the direction cosines of the chosen vector.

Further, the cube edge \mathbf{a}_1 would be denoted by $[100]$, and that of direction \mathbf{a}_2 by $[010]$, and the negative direction of \mathbf{a}_1 would be $[\bar{1}00]$. The general set of all the cube edge directions would be the carets $\langle 100 \rangle$. The face-diagonals of the cube are $\langle 110 \rangle$ and the body diagonals are $\langle 111 \rangle$.

Figure 1.6 shows some important directions in the crystals. Note that

1. All parallel rows of atoms have the same $[uvw]$.
2. The angle θ between two crystallographic direction $[u_1v_1w_1]$ and $[u_2v_2w_2]$ in a cubic system is given by

$$\cos \theta = \frac{u_1u_2 + v_1v_2 + w_1w_2}{(u_1^2 + v_1^2 + w_1^2)^{1/2}(u_2^2 + v_2^2 + w_2^2)^{1/2}} \quad (1.2)$$

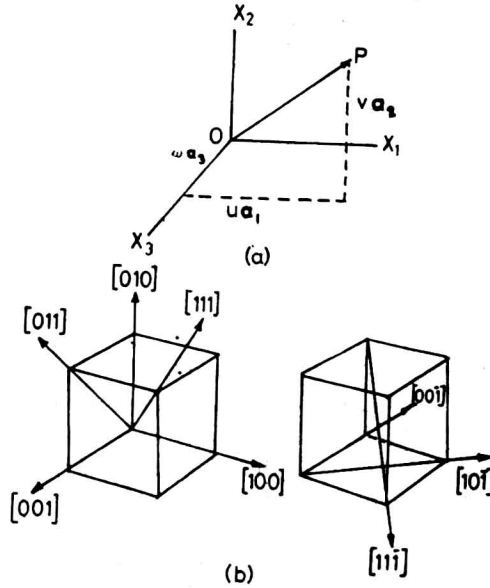


FIG 1.6 Notations for directions in crystals. (a) OP is the direction $[uvw]$, if u , v and w are smallest integers; (b) some important directions in the crystal

1.7 MILLER INDICES

To describe a plane ABC (Fig. 1.7) in a lattice:

1. Find the intercepts of the plane on the three axes defined by the basis vectors (\mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3) to get the three numbers n_1 , n_2 , n_3 .
2. Take the reciprocals of n_1 , n_2 , n_3 .
3. Divide the reciprocals by their greatest common divisor. The resulting set of three numbers (hkl) is called the Miller indices for the plane. $\{hkl\}$ means all planes equivalent (by symmetry) to (hkl) .

Thus, a plane satisfying the equation

$$h : k : l = n_1^{-1} : n_2^{-1} : n_3^{-1} \quad (1.3)$$

is said to have the *Miller indices* of (hkl) .

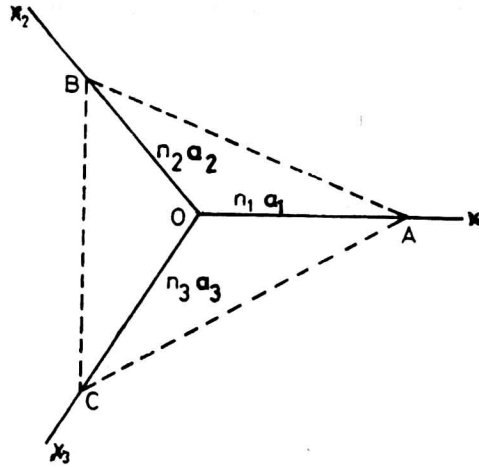


FIG. 1.7 Construction for description of a plane ABC

Note that:

1. A zero Miller index indicates that the plane is parallel to the corresponding crystal axis, e.g., (230) means, the plane is parallel to the a_3 -axis. (100) plane is parallel to both x_2 and x_3 -axes (Fig. 1.8).
2. A negative Miller index shows that the plane ($\bar{h}kl$) cuts the x_1 -axis on the negative side of the origin, e.g., ($\bar{1}00$) in Fig. 1.8.

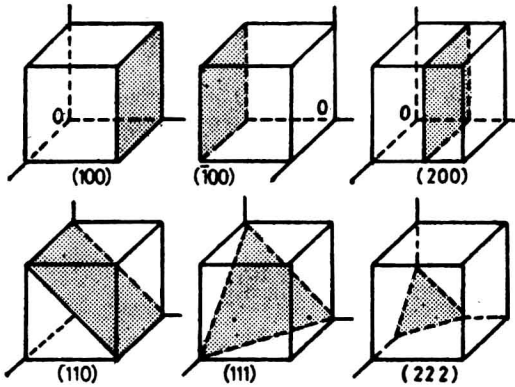


FIG. 1.8 Some of prominent planes for cubic lattices, with their Miller notations

3. The Miller indices, in fact, represent not a single plane but a family of parallel planes. For example, Fig. 1.8 shows a plane marked (200); the use of an integer other than unity for the first numeral indicates that the plane cuts the a_1 -axis at $a_1/2$ from the origin. Obviously, (200) and (100) are parallel planes. Of course, both would be represented by (100). The same comment applies to (222) and (111) planes.

4. Miller indices are proportional to the direction cosines of the normal to the corresponding plane.

5. The normal to the plane with index numbers (hkl) is the direction $[hkl]$.

6. The purpose of taking reciprocals in the present scheme is to bring all the planes inside a single unit cell, so that we can discuss all crystal planes in terms of the planes passing through a single unit cell.

7. The distance d between neighbouring planes of the family (hkl) is given in terms of the cube edge a as

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \quad (1.4)$$

8. Most planes which are important in determining the physical and chemical properties of solids are those with low index numbers.

1.8 SIMPLE LATTICES

The most highly symmetrical lattices which occur naturally are cubic. These are, therefore, of some practical interest and also provide useful simple examples which help in visualising the more general case. The *simple cubic lattice* has basis vectors

$$\mathbf{a}_1 = a\hat{\mathbf{i}} \quad \mathbf{a}_2 = a\hat{\mathbf{j}} \quad \mathbf{a}_3 = a\hat{\mathbf{k}} \quad (1.5)$$

and the unit cell is a simple cube. The simplest crystal based on this lattice has single atoms at the lattice points, as shown in Fig. 1.9. Each atom has six identical nearest neighbours.

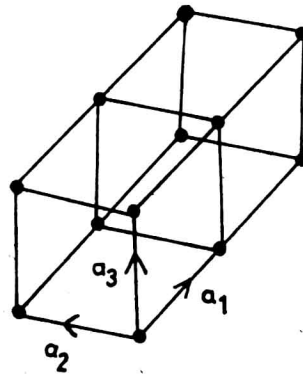


FIG. 1.9 Simple cubic lattice

The *body centered cubic* (bcc) lattice may be regarded as two interpenetrating simple cubic lattices with atoms at the centre of each cube as well as at the corners. However, such a description does not show up all the symmetry of the crystal very clearly. The space lattice may be taken with the basis vectors

$$\begin{aligned} \mathbf{a}_1 &= \frac{a}{2}(-\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}) & \mathbf{a}_2 &= \frac{a}{2}(\hat{\mathbf{i}} - \hat{\mathbf{j}} + \hat{\mathbf{k}}) \\ \mathbf{a}_3 &= \frac{a}{2}(\hat{\mathbf{i}} + \hat{\mathbf{j}} - \hat{\mathbf{k}}) \end{aligned} \quad (1.6)$$

and a better choice for the unit cell may be the parallelepiped defined by these vectors as edges or the truncated octahedron constructed by right bisecting the smallest \mathbf{R}_n , as shown in Fig. 1.10. For the simplest crystal, which has a single atom at each lattice point, each of these unit cells contains only one atom. If we had continued to regard this crystal as two interpenetrating simple cubic lattices, the space lattice would have contained only

half the number of translation vectors and the cubic unit cell would have contained two atoms. Thus that description, while sometimes convenient, does not show the full symmetry of the lattice.

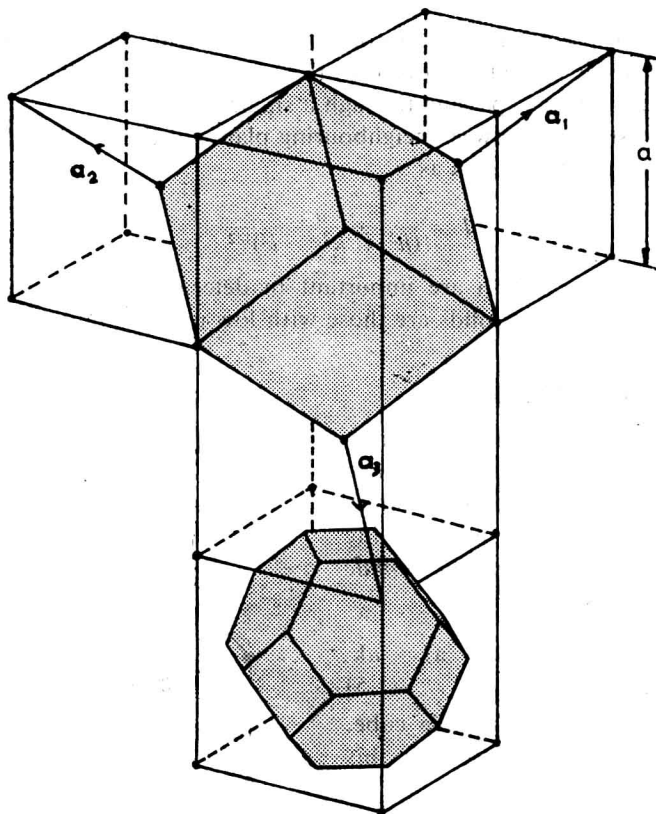


FIG. 1.10 *Body-centred cubic lattice showing two forms of the unit cell, a parallelepiped with basis vectors as edges and a truncated octahedron*

The *face centred cubic* (fcc) lattice can be considered as four interpenetrating simple cubic lattices giving a cubic unit cell with extra lattice points at the centres of the faces of the fundamental cube. Each point has 12 nearest neighbours. The full translational symmetry has basis vectors

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{j}} + \hat{\mathbf{k}}) \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{k}} + \hat{\mathbf{i}}) \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{i}} + \hat{\mathbf{j}}) \quad (1.7)$$

The primitive unit cell is again a parallelepiped bounded by these vectors or alternatively the rhombohedron shown in Fig. 1.11. The parallelepiped has edges parallel to the basis vectors and the faces of the regular rhombic dodecahedron are planes perpendicularly bisecting the smallest \mathbf{R}_n .

In the *hexagonal close packed* (hcp) structure shown in Fig. 1.12, the unit cell is a rhombic prism and the basis vectors are

$$\mathbf{a}_1 = a\hat{\mathbf{i}} \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{i}} + \sqrt{3}\hat{\mathbf{j}}) \quad \mathbf{a}_3 = c\hat{\mathbf{k}} \quad (1.8)$$

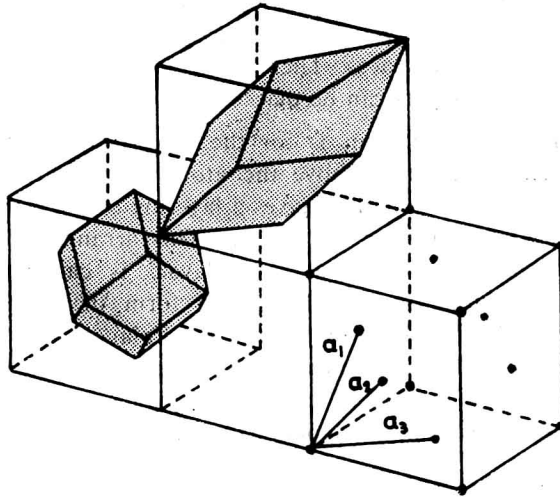


FIG. 1.11 Face-centred cubic lattice, showing two forms of the unit cell, a parallelepiped, with edges parallel to the basis vectors and a regular rhombic dodecahedron

In this structure, there are two atoms per unit cell separated by the vector

$$\mathbf{R} = \frac{1}{2} \left(a \hat{\mathbf{i}} + \frac{a}{\sqrt{3}} \hat{\mathbf{j}} + c \hat{\mathbf{k}} \right) \quad (1.9)$$

Here, as in the fcc structure, each atom has twelve neighbours, but the arrangement is slightly different.

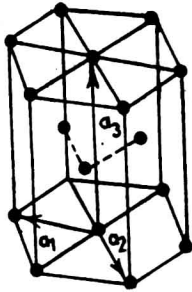


FIG. 1.12 Hexagonal close-packed structure

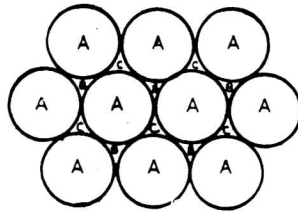


FIG. 1.13 Close-packed array of spheres. Note the three different possible positions, A, B and C for the successive layers

1.9 CLOSE-PACKED STRUCTURES

If the atoms are considered as hard spheres, then the most efficient packing in one plane is the close-packed arrangement shown in Fig. 1.13. There are two simple ways in which such planes can be layered on top of one another to form a three-dimensional structure. In the illustrated layer, the atoms are