Introduction to Solid state physics

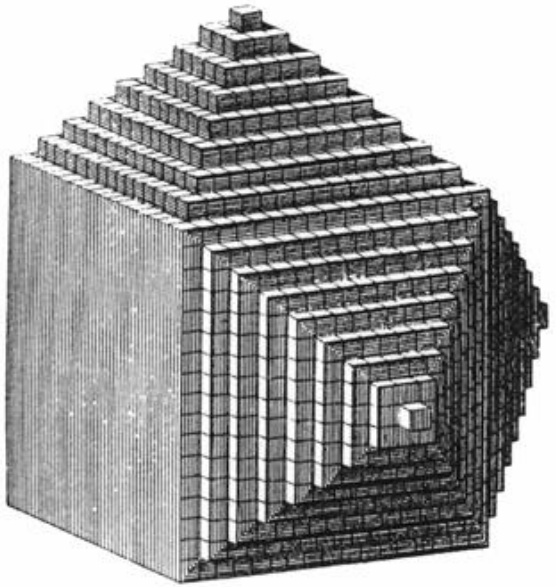
Chapter 1

Crystal Structures

Introduction

Solid state physics is largely concerned with crystals and electrons in crystals. The study of solid state physics began in the early years of this century following the discovery of x-ray diffraction by crystals.

When a crystal grows in a constant environment, the form develops as if identical building blocks were added continuoũsly (Fig. 1). The building blocks are atoms or groups of atoms, so that a crystal is a three-dimensional periodic array of atoms.



(a)

In 1912 Laue developed an elementary theory of the diffraction of x-rays by a periodic array. In the second part, Friedrich and Knipping reported the first experimental observations of x-ray diffraction by crystals.[2]

The work proved decisively that crystals are composed of a periodic array of atoms.

The studies have been extended to include amorphous or noncrystalline solids, glasses, and liquids. The wider field is known as condensed matter physics.

Periodic Arrays of Atoms

An ideal crystal is constructed by the infinite repetition of identical structural units in space. the structural unit is a single atom, comprise many atoms or molecules.

The structure of all crystals can be described in terms of a lattice, with a group of atoms attached to every lattice point. The group of atoms is called the basis.

The concepts of Lattice & Basis

Lattice Translation Vectors

The lattice is defined by three fundamental translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ such that the atomic arrangement looks the same in every respect when viewed from the point $\mathbf{r}$ as when viewed from the point

$$\mathbf{r}' = \mathbf{r} + u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 \ , \qquad (1)$$

where u_1, u_2, u_3 are arbitrary integers. The set of points $\mathbf{r}'$ defined by (1) for all u_1, u_2, u_3 defines a **lattice**.

A lattice is a regular periodic array of points in space. A lattice is a mathematical abstraction; the crystal structure is formed when a basis of atoms is attached identically to every lattice point. The logical relation is

$$\textbf{lattice} + \textbf{basis} = \textbf{crystal structure} \ . \qquad (2)$$

With this definition of the **primitive translation vectors**, there is no cell of smaller volume that can serve as a building block for the crystal structure.

The crystal axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ form three adjacent edges of a parallelepiped.
If there are lattice points only at the corners, then it is a primitive parallelepiped.

A lattice translation operation is defined as the displacement of a crystal by a crystal translation vector

$$\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 \ . \tag{3}$$

The symmetry operations of a crystal carry the crystal structure into itself. These include the lattice translation operations. Further, there are rotation and reflection operations, called **point operations**.

Finally, there may exist compound operations made up of combined translation and point operations.

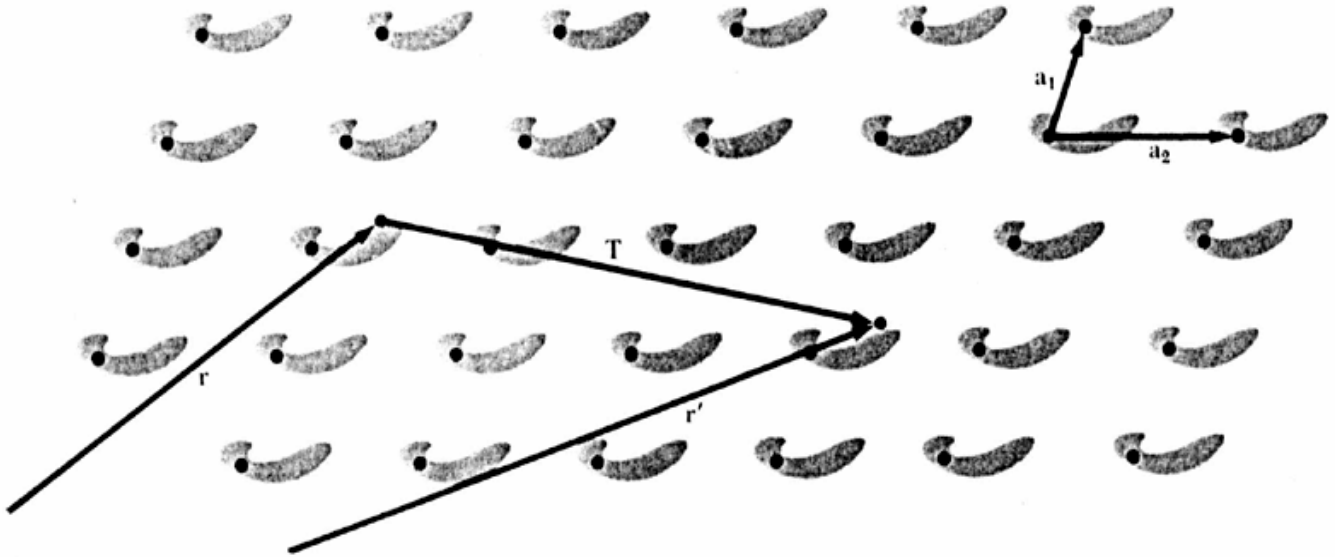


Figure 2 Portion of a crystal of an imaginary protein molecule, in a two-dimensional world. (We picked a protein molecule because it is not likely to have a special symmetry of its own.) The atomic arrangement in the crystal looks exactly the same to an observer at $\mathbf{r}'$ as to an observer at $\mathbf{r}$, provided that the vector $\mathbf{T}$ which connects $\mathbf{r}'$ and $\mathbf{r}$ may be expressed as an integral multiple of the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. In this illustration, $\mathbf{T} = -\mathbf{a}_1 + 3\mathbf{a}_2$. The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are primitive translation vectors of the two-dimensional lattice.

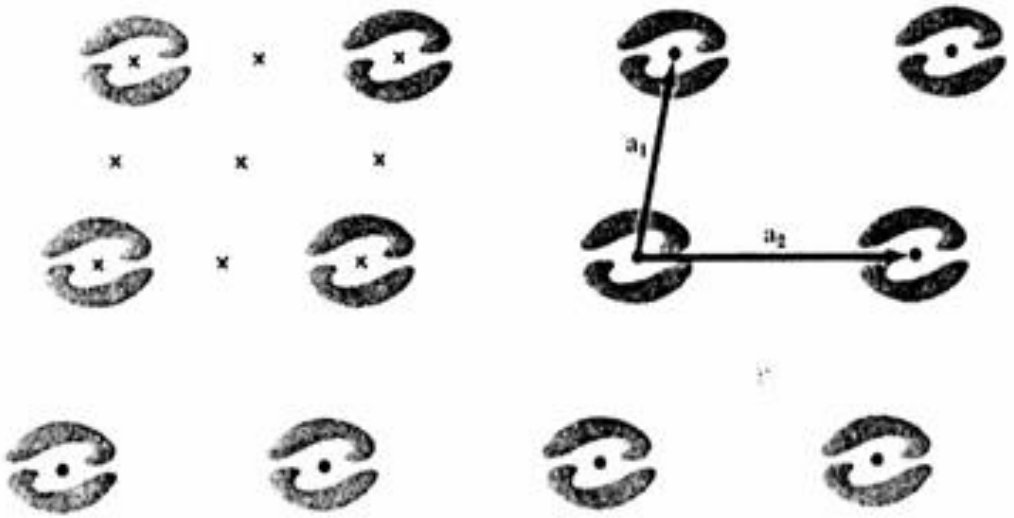


Figure 3 Similar to Fig. 2, but with protein molecules associated in pairs. The crystal translation vectors are $\mathbf{a}_1$ and $\mathbf{a}_2$. A rotation of π radians about any point marked × will carry the crystal into itself. This occurs also for equivalent points in other cells, but we have marked the points × only within one cell.

Basis and the Crystal Structure

A basis of atoms is attached to every lattice point, with every basis identical in composition, arrangement, and orientation.

The number of atoms in the basis may be one, or it may be more than one. The position of the center of an atom j of the basis relative to the associated lattice point is

$$\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3 . \qquad (4)$$

We may arrange the origin, which we have called the associated lattice point, so that $0 \leq x_j,\ y_j,\ z_j \leq 1$.

Primitive Lattice Cell

The parallelepiped defined by primitive axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ is called a **primitive cell** (Fig. 5b). A primitive cell is a type of cell or unit cell.

A primitive cell is a minimum-volume cell.

There are many ways of choosing the primitive axes and primitive cell for a given lattice. The number of atoms in a primitive cell or primitive basis is always the same for a given crystal structure.

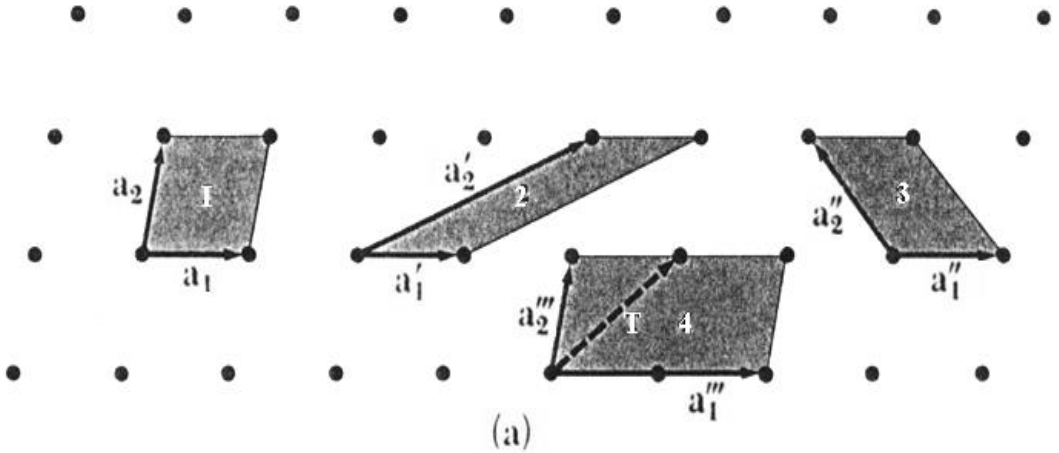


Figure 5a Lattice points of a space lattice in two dimensions. All pairs of vectors $\mathbf{a}_1$, $\mathbf{a}_2$ are translation vectors of the lattice. But $\mathbf{a}_1'''$, $\mathbf{a}_2'''$ are not primitive translation vectors because we cannot form the lattice translation $\mathbf{T}$ from integral combinations of $\mathbf{a}_1'''$ and $\mathbf{a}_2'''$. All other pairs shown of $\mathbf{a}_1$ and $\mathbf{a}_2$ may be taken as the primitive translation vectors of the lattice. The parallelograms 1, 2, 3 are equal in area and any of them could be taken as the primitive cell. The parallelogram 4 has twice the area of a primitive cell.

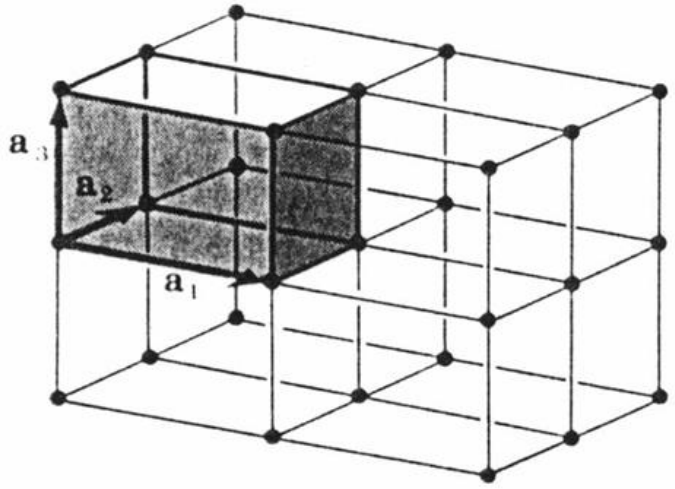


Figure 5b Primitive cell of a space lattice in three dimensions.

There is always one lattice point per primitive cell. If the primitive cell is a parallelepiped with lattice points at each of the eight corners, point is shared among eight cells, so that the total number of lattice points in the cell is one: $8 \times \frac{1}{8} = 1$.

The volume of a parallelepiped with axes $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ is

$$V_c = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| \ , \tag{5}$$

The basis associated with a primitive cell is called a primitive basis. No basis contains fewer atoms than a primitive basis contains.

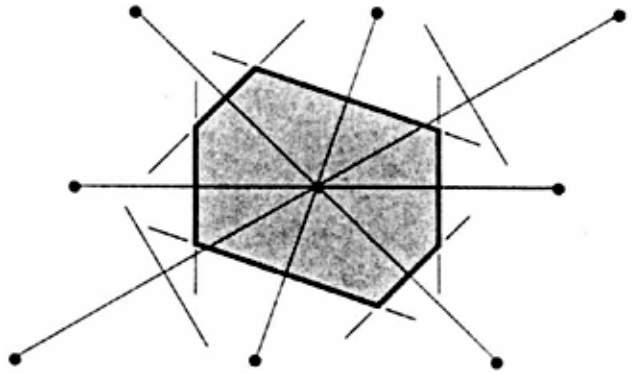


Figure 6 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells, just as by the cells of Fig. 5.

Another way of choosing a primitive cell is shown in Fig. 6. This is known to physicists as a **Wigner-Seitz cell**.

A typical symmetry operation is that of rotation about an axis that passes through a lattice point. Lattices can be found such that one-, two-, three-, four-, and sixfold rotation axes carry the lattice into itself, corresponding to rotations by 2π, $2\pi/2$, $2\pi/3$, $2\pi/4$, and $2\pi/6$ radians and by integral multiples of these rotations.

A single molecule properly designed can have any degree of rotational symmetry, but an infinite periodic lattice cannot. We can make a crystal from molecules that individually have a fivefold rotation axis, but we should not expect the lattice to have a fivefold rotation axis.

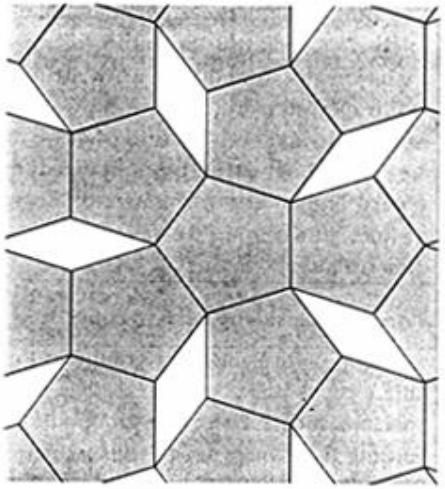


Figure 7 A fivefold axis of symmetry cannot exist in a periodic lattice because it is not possible to fill the area of a plane with a connected array of pentagons. We can, however, fill all the area of a plane with just two distinct designs of "tiles" or elementary polygons. A quasicrystal is a quasiperiodic nonrandom assembly of two types of figures. Quasicrystals are discussed at the end of Chapter 2.

We can have mirror reflections m about a plane through a lattice point. The inversion operation is composed of a rotation of π followed by reflection in a plane normal to the rotation axis; the total effect is to replace $\mathbf{r}$ by $-\mathbf{r}$.

Two-Dimensional Lattice Types

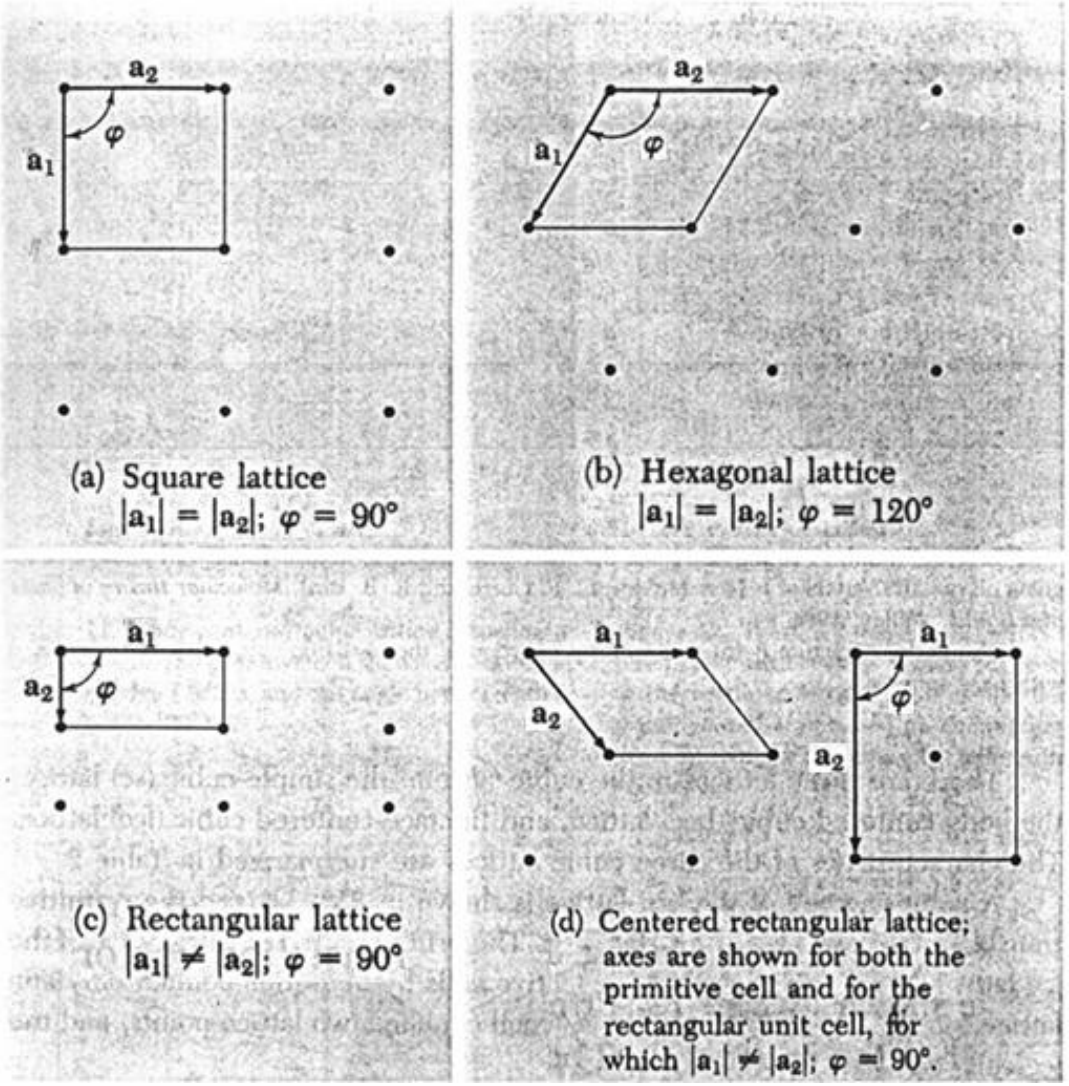
There is an unlimited number of possible lattices because there is no natural restriction on the lengths of the lattice translation vectors or on the angle φ between them. The lattice in Fig. 5a

general lattice such as this is known as an **oblique lattice** and is invariant only under rotation of π and 2π about any lattice point.

There are four distinct types of restriction, and each leads to what we may call a **special lattice type**. Thus there are five distinct lattice types in two dimensions, the oblique lattice and the four special lattices shown in Fig. 9. **Bravais lattice** is the common phrase for a distinct lattice type; we say that there are five Bravais lattices or nets in two dimensions.

Figure 9

2 dimensional lattices (1 + 4)



Three-Dimensional Lattice Types

The point symmetry groups in three dimensions require the 14 different lattice types listed in Table 1. The general lattice is triclinic, and there are 13 special lattices. These are grouped for convenience into systems classified according to seven types of cells,

Table 1 The 14 lattice types in three dimensions

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90° \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120°, \neq 90°$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90°$ $\gamma = 120°$

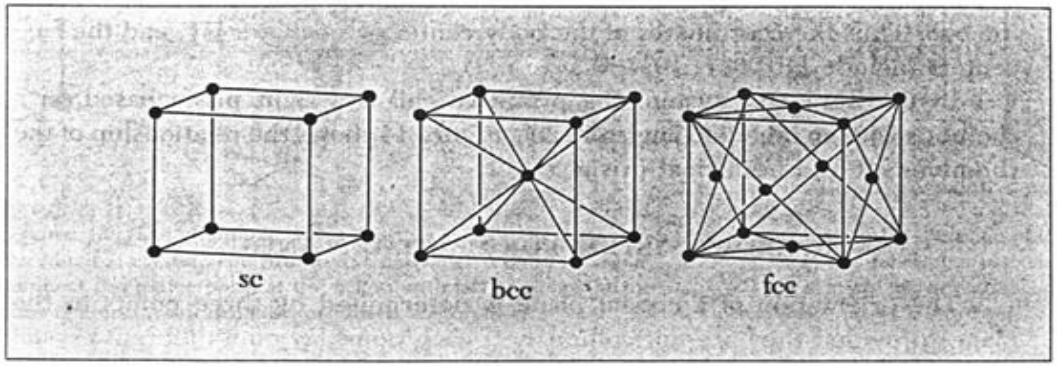


Figure 10 The cubic space lattices. The cells shown are the conventional cells.

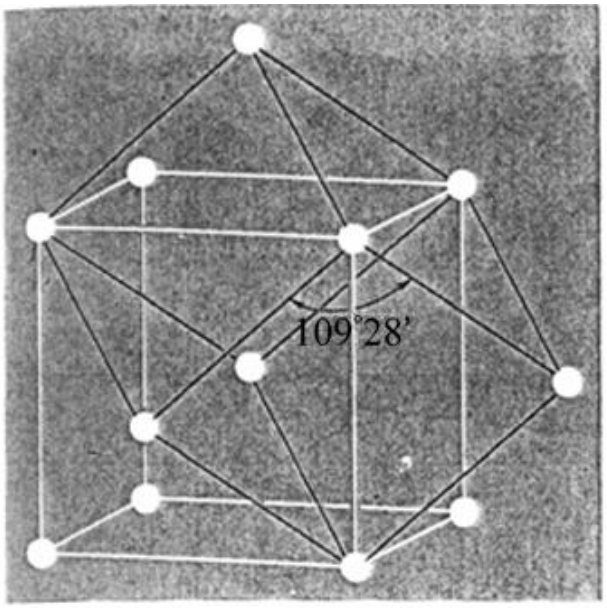
The cells in Fig. 10 are conventional cells;

Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
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[a]	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[b]	$\frac{1}{6}\pi$ $= 0.524$	$\frac{1}{8}\pi\sqrt{3}$ $= 0.680$	$\frac{1}{6}\pi\sqrt{2}$ $= 0.740$

There are three lattices in the cubic system: the simple cubic (sc) lattice, the body-centered cubic (bcc) lattice, and the face-centered cubic (fcc) lattice.

A primitive cell of the bcc lattice is shown in Fig. 11, and the primitive translation vectors are shown in Fig. 12. The primitive translation vectors of the



BCC

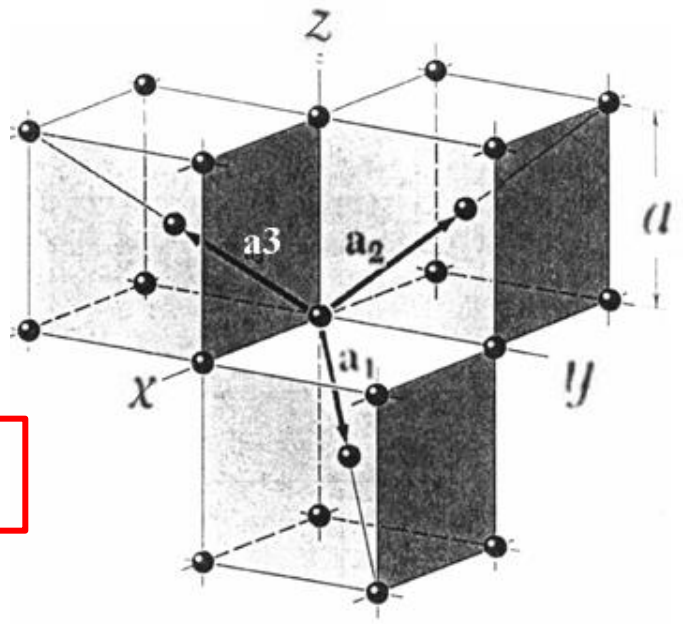


Figure 11 Body-centered cubic lattice, showing a primitive cell. The primitive cell shown is a rhombohedron of edge $\frac{1}{2}\sqrt{3}\,a$, and the angle between adjacent edges is 109°28′

Figure 12 Primitive translation vectors of the body-centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron. In terms of the cube edge a the primitive translation vectors are

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}) \; ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ;$$

$$\mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}) \; .$$

fcc lattice are shown in Fig. 13. Primitive cells by definition contain only one lattice point, but the conventional bcc cell contains two lattice points, and the fcc cell contains four lattice points.

In the hexagonal system the primitive cell is a right prism based on a rhombus with an included angle of 120°.

FCC

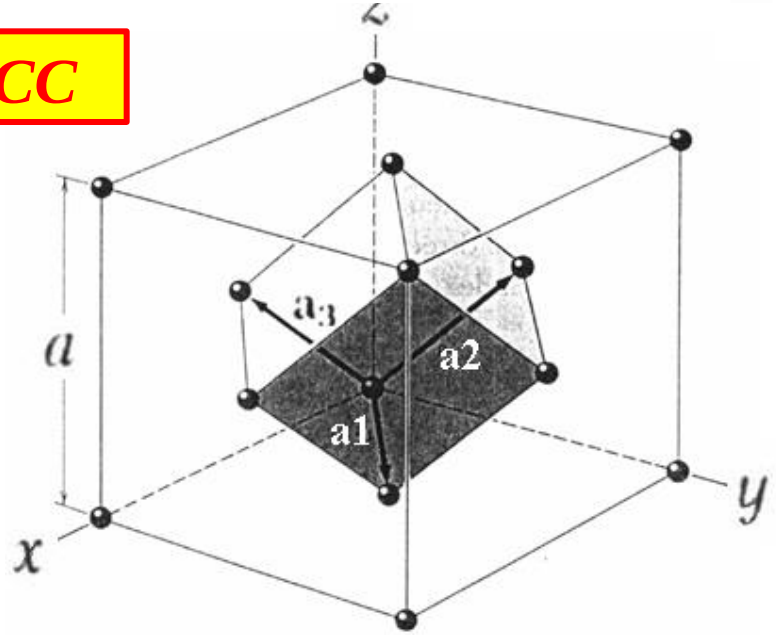


Figure 13 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

$$\mathbf{a}_1 = \tfrac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \; ; \qquad \mathbf{a}_2 = \tfrac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \; ; \qquad \mathbf{a}_3 = \tfrac{1}{2}a(\hat{\mathbf{z}} + \hat{\mathbf{x}}) \; .$$

The angles between the axes are 60°. Here $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ are the Cartesian unit vectors.

HCP

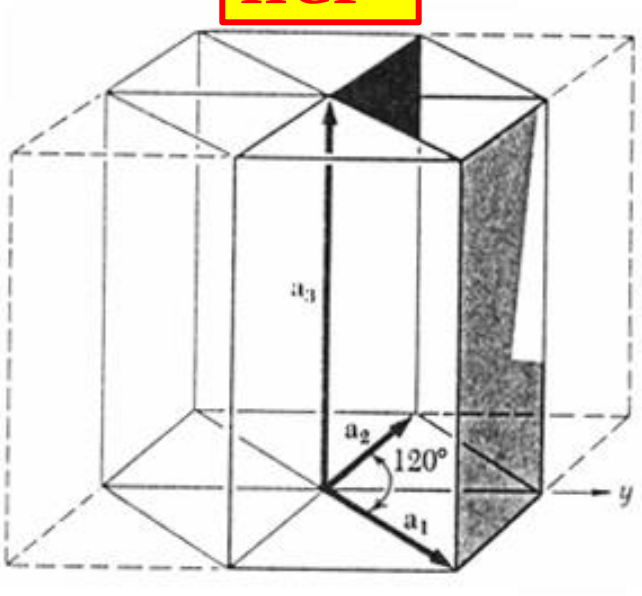
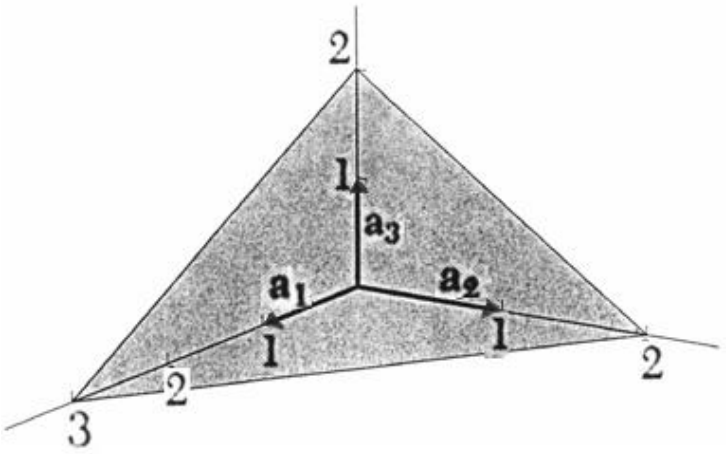


Figure 14 Relation of the primitive cell in the hexagonal system (heavy lines) to a prism of hexagonal symmetry. Here $a_1 = a_2 \neq a_3$.

INDEX SYSTEM FOR CRYSTAL PLANES

to specify the orientation of a plane by the indices determined by the following rules

- Find the intercepts on the axes in terms of the lattice constants a_1, a_2, a_3. The axes may be those of a primitive or nonprimitive cell.
- Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. The result, enclosed in parentheses (hkl), is called the index of the plane.



The indices of some important planes in a cubic crystal are illustrated by Fig. 16.

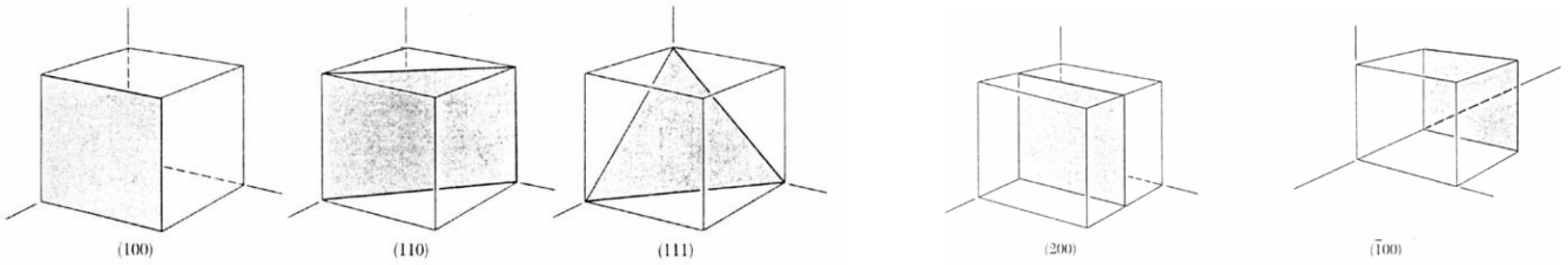


Figure 16 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to $(\bar{1}00)$.

the set of cube faces is {100}.

The indices (*hkl*) may denote a single plane or a set of parallel planes.

The indices [*uvw*] of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction, referred to the axes.

$[0\bar{1}0]$ direction. In cubic crystals the direction [*hkl*] is perpendicular to a plane (*hkl*) having the same indices, but this is not generally true in other crystal systems.