SECTION

1

INTRODUCTORY MATERIALS CONCEPTS

chapter 1

Structure and Properties

1.1 ATOMIC PACKING

Think of atoms in a solid as hard, round spheres that exert attractive forces in all directions. Given a number of these hard, spherical bodies, how can they be arranged to be as close-packed as possible, i.e., to occupy a minimum volume? It is easiest to consider the two-dimensional case first. When a given number of atoms are fitted together in a hexagonal pattern like the cells of a honeycomb, this criterion is achieved and they cover a minimum area.

Because they have relatively high densities, metals must consist of atoms that are packed very closely together as patterned in Fig. 1.1. It represents the closest possible packing of spheres on a flat sheet. To make a three-dimensional array of spheres occupying a minimum volume, it is necessary to place the centers of the atoms of the second sheet over the holes between the atoms of the first sheet. In Fig. 1.2, crosses show the locations of the centers of the atoms of the second sheet. Note that the atoms of the second sheet cover only half the holes in the first sheet. The other set of holes, the ones not marked by crosses, could have equally been used for the atom centers of the second sheet. The atomic structure of the two layers would look the same in either case.

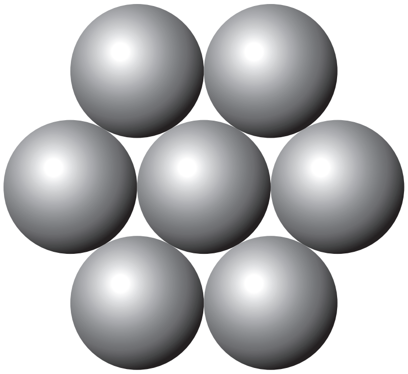

Figure 1.1 Packing of equal-sized spheres on a single plane to occupy a minimum area.

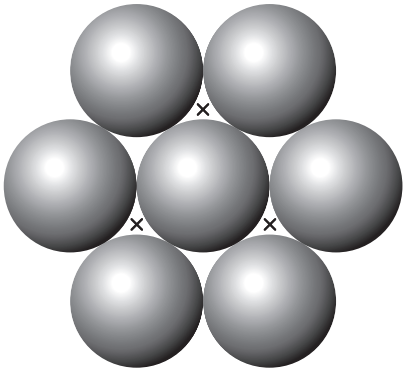

Figure 1.2 Location of the centers of the atoms in positions marked **x** of a second layer similar to Fig. 1.1.

The metal crystal that has been constructed by stacking up hard spheres is only two atomic layers thick. A third layer introduces a slight complication because there are two different ways in which it can be added. One way is to put the centers of the atoms of the third layer over the holes of the first layer that are not marked by crosses. In order to describe this structure, let the first layer be called *A*, the second layer, with its atom centers at the **x** positions, be called *B*, and the third layer, with its atom centers over the unmarked holes in *A*, be called *C*. The stacking sequence of close-packed layers is then *ABC* in this case. All the possible alternative positions for close-packed layers have been used up in this stack of three layers of atoms, but the fourth layer can be added in the *A* position again. In this way a sequence of layers *ABCABCA* can be built up to any desired thickness. The result is a three-dimensional array of spheres packed as closely as possible. Figure 1.3 shows a plane view of this structure.

There is a second way in which the close-packed layers of Fig. 1.1 can be stacked up to make a close-packed crystal. The first two layers are stacked as in Fig. 1.2, but the third layer is now added so that it is directly over the first. This structure is obviously close-packed, like the one derived above, but the stacking sequence is *ABABA*. Many metals are found to have either the *ABCABCA* or the *ABABA* type of close-packed structure. Some metals have more complicated structures; these will be described later.

For many purposes it is convenient to think of the close-packed structures as stacks of close-packed layers according to the description given above. Sometimes, however, it is convenient to single out a small group of atoms in the stack and then describe the atom arrangement in this group. The group of atoms chosen for this purpose is called a unit cell of the structure. One can choose a number of equally accurate ways of representing the unit cell, but experience has shown that, for each structure, there is one cell which is most easily visualized. This one best shows the symmetry of the atom arrangement.

For the close-packed structure of the *ABCABCA* type, the group of atoms forming the unit cell is shown in Fig. 1.4*b*. Note that the close-packed layers are in an

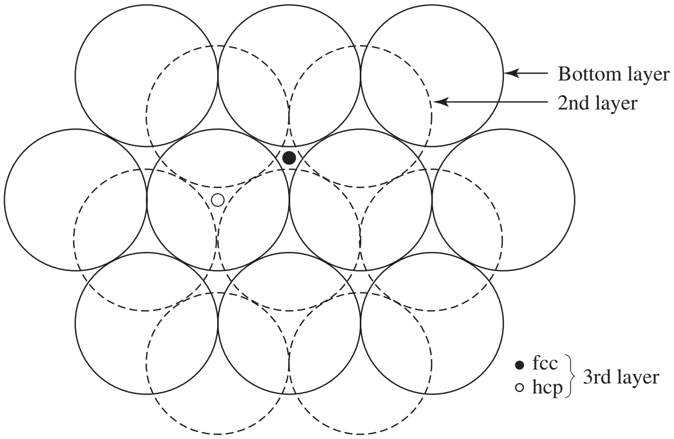

Figure 1.3 Solidly outlined circles represent a bottom plane of atoms, and dash-outlined circles represent a second plane nested on the first. In a close-packed structure, the third layer can be centered at the position of either the closed dot (*C* layer) or the open dot (another *A* layer).

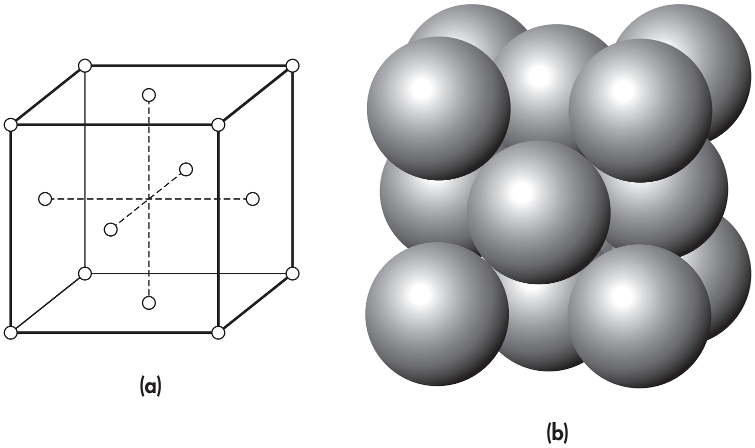

Figure 1.4 (*a*) The positions of the centers of the atoms in one unit cell of the fcc structure. (*b*) The packing of atoms in a unit cell of the fcc structure. Each atom on a face center touches each of the nearest corner atoms as well as the face-centered atoms in front and in back of it, making 12 nearest neighbors. There are four atoms in this unit cell (one-half of each face-centered atom plus one-eighth of each corner atom).

inclined orientation in this drawing. Figure 1.4*a* shows a schematic representation of the location of the atoms in this structure. In this representation, the cubic symmetry of the atomic arrangement is evident. Because of the arrangement of atoms in the unit cell, the *ABCABCA* type of close-packed structure is given the name face-centered cubic structure (usually abbreviated fcc). Typical fcc metals are copper, aluminum, and nickel.

The group of atoms forming the unit cell for the *ABABA* type of structure is shown in Fig. 1.5*b*. In this case the close-packed planes are horizontal and are easily recognized. The hexagonal symmetry of the atom arrangement can be seen from Fig. 1.5*a*. The structure is called hexagonal close-packed (hcp). Magnesium and zinc are examples of hcp metals.

If the hypothesis that the atoms of metals are hard, round spheres exerting attractive forces equally in all directions were true in all cases, then it would be expected that all metals would have either the fcc or the hcp structure. It is known from the study of chemistry, however, that many atoms do not attract other atoms equally in all directions but tend to form bonds preferentially in certain directions. Some metal atoms behave in this way, and the resulting crystal structures are not close-packed. One structure that deviates only slightly from being close-packed is the body-centered cubic (bcc) one shown in Fig. 1.6. Many of the important metals, including iron, chromium, and tungsten, have the bcc structure.

The structures of a number of metals deviate more markedly from close packing. Bismuth, antimony, and gallium have an atomic arrangement with the symmetry of a rhombohedron rather than that of a cube. These metals have so-called open structures, meaning that there is a substantial amount of empty space surrounding each atom, considered as a hard sphere. It is interesting in this connection that these

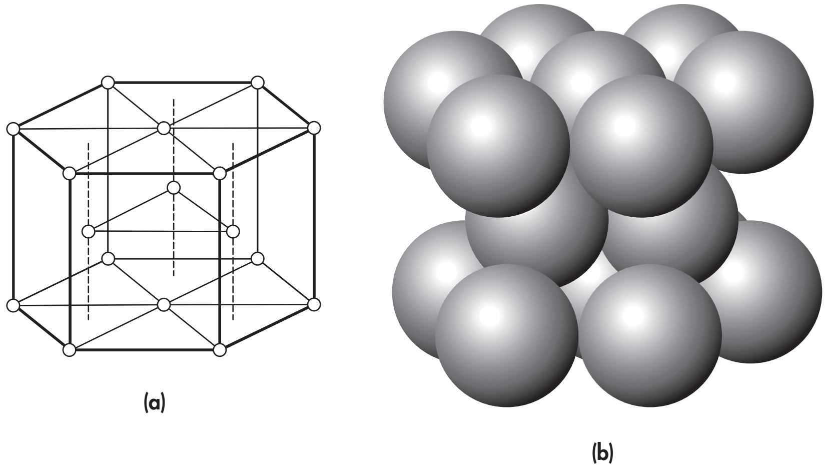

Figure 1.5 (*a*) The positions of the centers of the atoms in one unit of the hcp structure. (*b*) The packing of atoms in one unit cell of the hcp structure. As in the fcc structure, each atom has 12 nearest neighbors, with 6 on the same horizontal layer, 3 on the layer below, and 3 on the layer above.

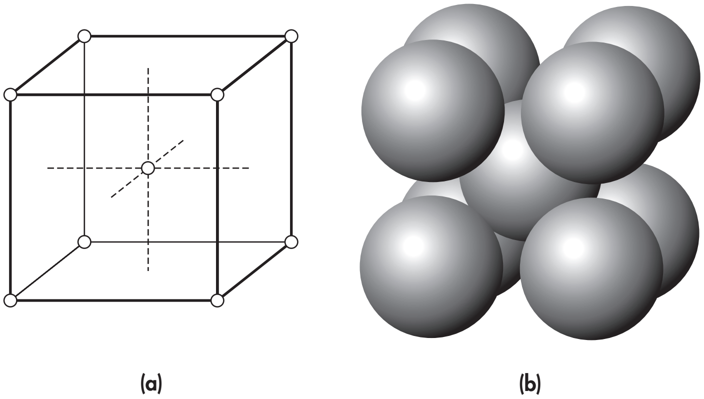

Figure 1.6 (*a*) The positions of the centers of the atoms in one unit cell of the bcc structure. (*b*) The center atom touches each corner atom, but these do not touch each other. There are two atoms per unit cell (one centered atom plus one-eighth of each corner atom), and each atom has eight nearest neighbors.

metals decrease in volume when they melt, whereas most metals have a greater specific volume in the liquid state than in the solid state.

Atomic Size

To the extent that the atoms of a metal can be considered to be hard spheres, they can be assigned a definite diameter. The atomic diameter can be calculated when the crystal structure and lattice parameters of a metal are known. The atoms of a crystal structure are in contact along certain directions in the unit cell known as the close-packed directions. Inspection of Fig. 1.4 shows, for example, that the close-packed directions in the fcc structure are along the diagonals of the cube faces. If a is the lattice parameter, the length of a face diagonal is $a\sqrt{2}$ and the atomic diameter must be $\frac{1}{2}a\sqrt{2}$.

The hard-sphere model of the atoms of a metal is only a first approximation. It is found, in fact, that the atoms of a given metal may not always appear to have the same diameter. For example, iron atoms behave as if they had one diameter when in pure iron metal, another slightly different one when in an iron-nickel alloy, and still another in ferric chloride crystals. Nevertheless the concept of atomic diameter has proved to be a useful one in metallurgy and plays an important role in understanding the formation of alloys.

The atoms adjacent to a given atom along the close-packed directions of a crystal are called the nearest neighbors of the given atom. Each atom in the fcc structure has 12 nearest neighbors, as can be seen from Fig. 1.4. So does each atom in the hcp structure. But in the bcc structure each atom has only 8 nearest neighbors. The number of nearest neighbors found in a given crystal structure is said to be the coordination number of the structure. Thus, bcc iron has a coordination number of 8 and copper has a coordination number of 12.

1.2 CRYSTAL STRUCTURE

Lattice Parameters

The term lattice is frequently used in the description of crystal structures. A lattice is an array of atoms repeated regularly throughout space. If a point is placed at the center of each of the atoms in the fcc crystal structure, the array of points so generated is the fcc lattice. Lattices for the bcc and hcp structures can be generated in the same way.

An important characteristic for understanding alloying behavior of metals and ceramics is the lattice parameters. These are the lengths of any side of a unit cell of a given crystal structure. In the metals having cubic symmetry, the size of the lattice is fixed when the length of the edge of the cubic unit cell is given. Cubic metals have, therefore, only one lattice parameter. The lattice parameter of a metal can be measured by observing the diffraction of an x-ray beam passed through the metal. The results of such measurements are usually reported in angstroms, where $1\ \text{Å} = 10^{-8}$ cm. Typical values of the lattice parameters of cubic metals are Al, 4.04 Å, and Mo, 3.14 Å.

When the unit cell does not have cubic symmetry, more than one lattice parameter has to be specified. In hexagonal crystals, these are, first, the distance a between neighboring lattice points in the close-packed planes (or basal planes, as they are often called) and, second, the distance from the top to the bottom of the unit cell. If a hexagonal metal is truly close-packed, i.e., is made up of spherical atoms stacked *ABABA*, then the distances a and c must bear a fixed relation to each other. In fact the ratio $c/a = (8/3)^{1/2} = 1.633$ represents perfect close packing. The forces between the atoms in most metals that crystallize in the hexagonal structure are such that there are usually slight deviations from ideal close packing. In zinc, this deviation is unusually large, and the axial ratio c/a is 1.85. This affects the strain-hardening rate, which will be discussed later in this chapter.

Crystal Planes and Axes

The points of a crystal lattice define an array of crystal planes. Some of these planes are easily visualized. For example, the planes that mark out the unit cells of the fcc and bcc lattices shown in Figs. 1.4 and 1.6 constitute a set of crystal planes known as the cube planes. Each of these planes is repeated indefinitely throughout the lattice as an array of parallel planes separated by a distance equal to the lattice parameter in the simple cubic structure and to half the lattice parameter in the fcc and bcc structures. Some other important planes are shown in Fig. 1.7. Note that each set of crystal planes has its own characteristic interplanar distance.

Because a given type of crystal plane is repeated throughout the lattice, the location of a specific plane is not of much interest in crystallography. The orientation of a plane or a set of planes relative to the edges of the unit cell is important, however, in understanding deformation modes of the crystal. In order to specify this orientation, it

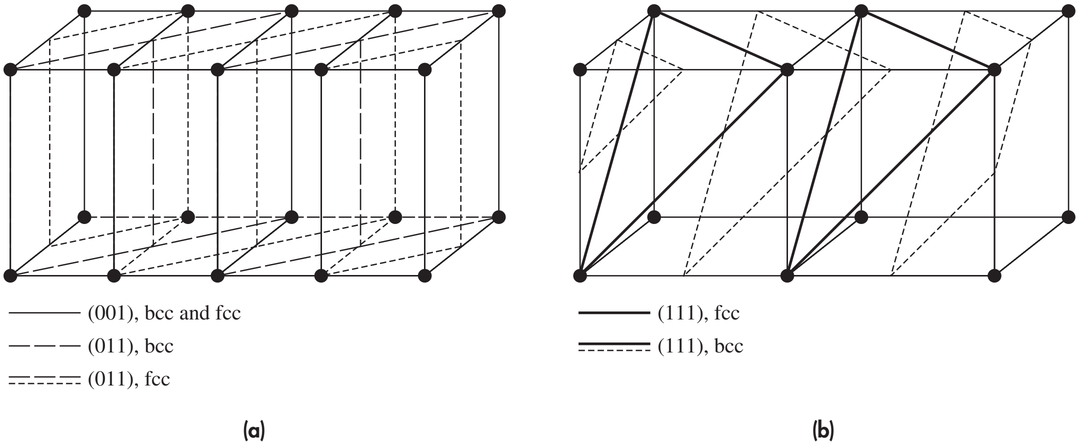

Figure 1.7 Two cells of a cubic lattice, showing only the corner atoms. (*a*) The cube-plane (001) spacing is the same for both the body-centered and face-centered structures. The dodecahedral-plane (011) spacing necessary to account for all atoms is twice as great for the body-centered as for the face-centered cube. (*b*) The reverse is true of the octahedral planes (111).

is convenient to establish, as a set of crystal axes, one set of the edges of one of the unit cells of the structure. For the fcc and bcc structures, then, the crystal axes are a set of rectangular cartesian coordinates. The intercepts of a crystal plane on these axes could be measured in units of centimeters or angstroms, but it proves to be more useful in crystallography to use the lattice parameters themselves as the units of measure on the crystallographic axes. Planes that are in the same orientation will then have the same intercepts in different crystals, even though the lattice parameters are different.

It has been found that six different kinds of crystal axes are needed to fit all the different possible kinds of crystal lattices. These six different sets of crystal axes are given in Table 1.1.

Table 1.1 The six crystal structures

	Axes		
Name	**Length of Unit Vectors**	**Axial Angles**	**Examples**
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Tin, indium
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Magnesium, zinc
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Gallium, sulfur
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	Phosphorus
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	Antimony, mercury

Allotropic Forms

Some metals exist in more than one crystalline form. Iron is bcc at temperatures ranging up to 910°C, but at this temperature it undergoes an allotropic transformation and becomes fcc. The fcc phase is stable to 1400°C, at which temperature it transforms back to the bcc structure, which it then retains up to the melting point. The different crystalline forms of a metal are said to be allotropic forms. Many metals such as aluminum and copper have only one crystal structure, but many others, particularly among the elements in the transition series of the periodic table, have two or more allotropic forms.

Allotropic transformations occur because in certain temperature ranges one structure is more stable than another is. It is found that the energy differences between the different structures of a metal that undergoes allotropic transformation are very small. Thus small changes in atomic forces can change the structure of a metal from one type of crystal to another. It is also found that in many cases allotropic transformations are due to magnetic interactions between the atoms, but in most cases theorists have not yet attained a full understanding of these forces.

Structure of Nonmetallic Solids

The crystal structures of the common metals, discussed above, are exceedingly simple in comparison with most of the structures found among the species of the mineral kingdom. The structures of some typical nonmetallic crystals are described below.

A number of different schemes can be used to classify substances when their structures are to be described. In mineralogy, for example, a classification based on chemical composition is generally used, and crystals are arranged according to whether they are elements, oxides, sulfides, silicates, etc. A classification based on the type of bonding forces acting between the atoms of the crystal will be used here. On this basis four main classes of crystals may be recognized. They are:

1. Metallic, already described above
2. Ionic, in which the interatomic forces are between electrically charged ions such as Na^+ and Cl^-
3. Covalent, in which the atoms are bound together with chemical covalent bonds
4. Molecular, which includes crystals made up of chemically saturated molecules held together by van der Waals forces

A few representative examples of the last three classes are given below.

Ionic Crystal Structures

One of the most common of the ionic crystal structures is that of sodium chloride (Fig. 1.8). This structure is based on the fcc lattice, but instead of having one atom

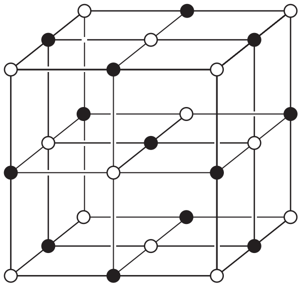

Figure 1.8 The crystal structure of rock salt, solid NaCl. Note that the close-packed directions here are cube edges rather than face diagonals.

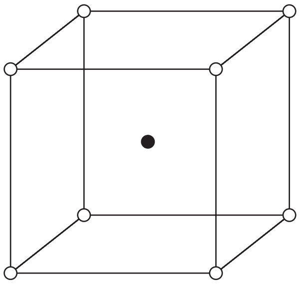

Figure 1.9 The crystal structure of cesium chloride, CsCl. The open circles are Cs ions and the closed circle is a Cl ion, or vice versa.

associated with each lattice point as in most metals, there are two atoms per lattice point, one centered on the point and another a distance ½*a* away along the edge of the fcc unit cell. The "atoms" in this case are actually ions, and of the pair associated with a lattice point, one will be Na^+ and the other Cl^-. Note that six negatively charged nearest neighbors surround each positive ion, and, conversely, each negative ion has six positive ions as nearest neighbors, as would be expected, since unlike charges attract.

Another simple ionic crystal structure is that of cesium chloride (Fig. 1.9). It may be derived from a simple cubic lattice by placing one ion on a lattice point and another, of opposite sign, halfway along the body diagonal of the unit cell. Thus an ion of one sign is surrounded by eight ions of the opposite sign.

In the NaCl and CsCl structures it is seen that there are no individual salt molecules present, that the entire crystal can be regarded as one gigantic molecule. In some ionic crystals there is more of a tendency to form molecules. In pyrite (Fig. 1.10) there are effectively FeS_2 molecules at each of the lattice points of an fcc lattice.

Covalent Crystal Structures

Diamond (Fig. 1.11) is a typical covalent (shared electrons) crystal that, as can be seen from the drawing, is based on an fcc lattice. The lines drawn between the atoms in the figure represent the covalent bonds, four for each carbon atom as in the molecule CH_4. In addition to diamond, the element silicon, germanium, and one

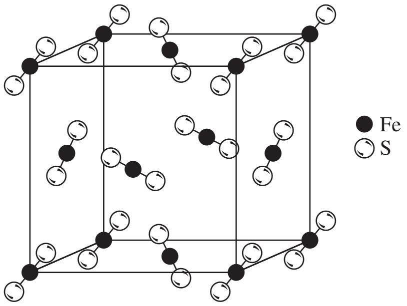

Figure 1.10 The structure of the mineral pyrite, FeS_2.

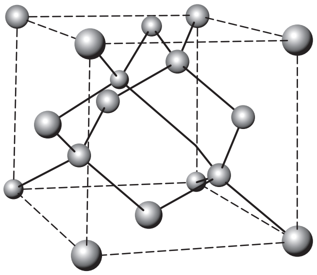

Figure 1.11 The crystal structure of diamonds, one of the allotropic forms of pure carbon.

allotropic form of tin have this diamond cubic structure. The network of covalent bonds extending throughout the structure is responsible for the great hardness of these elements.

The silicates represent a very important and very large class of covalent crystals. The basic unit from which these structures are built is the tetrahedral array of one Si and four O atoms shown in Fig. 1.12. Because these SiO_4^{4-} tetrahedra can be linked up in many different ways with each other and with various positive ions, a great variety of different silicate structures are possible. These are often rather complex, as is seen in Fig. 1.13. Silicate minerals constitute the great part of the lithosphere of the earth and so are of considerable interest to the geologist and mineralogist. They are also essential constituents of many of the refractories used in metallurgical furnaces.

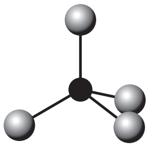

Figure 1.12 A tetrahedral array of four oxygen atoms and one silicon atom forms the group SiO_4^{4-}.

Amorphous and Polymer Structures

Substances such as glass and polymers are not crystalline. They have no regular, periodic arrangement of atoms. Most glasses consist primarily of silicate ions, SiO_2, to which an appreciable number of large-sized atoms such as Na and Ca have been added. The added atoms, since they do not fit into the silicate structure very well, make it more difficult for crystallization to occur when the melt is cooled. Glass is then a supercooled liquid having a very high viscosity. Glasses are discussed in more detail in Chap. 19.