CHAPTER 1 CRYSTAL STRUCTURES AND INTERATOMIC FORCES

Good order is the foundation of all good things.

Edmund Burke

1.1 INTRODUCTION

To the naked eye, a solid appears as a *continuous* rigid body. Experiments have proved, however, 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. This statement will be amply illustrated in the following chapters.

In the first part of this chapter, we shall expand on the meaning of the crystalline structure, and introduce some of the basic mathematical definitions employed in describing it. We shall then enumerate the various structures possible, and introduce the concept of Miller indices. We shall also present a few examples.

The atoms in some solids appear to be randomly arranged, i.e., the crystalline structure is absent. Such noncrystalline—or *amorphous*—solids will also be described briefly.

The chapter closes with an account of the interatomic forces that cause bonding in crystals.

Chapter 2 will discuss the experimental determination of crystal structure by x-rays.

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 repetitivity) in both the x and y directions from $-\infty$ to ∞. 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.
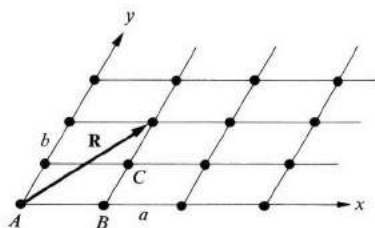

Fig. 1.1 A crystalline solid. All the atoms are arranged periodically.

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

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joining two atoms, say **R** in Fig. 1.1, the crystal appears exactly the same as it did before the translation. In other words, the crystal remains *invariant* under any such translation. The consequences of this translational symmetry or invariance are many, and a great portion of this book will be concerned with them.

Strictly speaking, one cannot prepare a perfect crystal. For example, even the surface of a crystal is a kind of *imperfection* because the periodicity is interrupted there. The atoms near the surface see an environment different from the environment seen by atoms deep within the crystal, and as a result behave differently. Another example concerns the thermal vibrations of the atoms around their equilibrium positions for any temperature $T > 0°K$. Because of these vibrations, the crystal is always distorted, to a lesser or greater degree, depending on T. As a third example, note that an actual crystal always contains some foreign atoms, i.e., impurities. Even with the best crystal-growing techniques, some impurities ($\simeq 10^{12}$ cm^{-3}) remain, which spoils the perfect crystal structure.

Notwithstanding these difficulties, one can prepare crystals such that the effects of imperfections on the phenomena being studied are extremely minor. For example, one can isolate a sodium crystal so large ($\simeq 1$ cm^3) that the ratio of surface atoms to all atoms is small, and the crystal is pure enough so that impurities are negligible. At temperatures that are low enough, lattice vibrations are weak, so weak that the effects of all these imperfections on, say, the optical properties of the sodium sample are negligible. It is in this spirit that we speak of a "perfect" crystal.

Imperfections themselves are often the main object of interest. Thus thermal vibrations of the atoms are the main source of electrical resistivity in metals. When this is the case, one does not abandon the crystal concept entirely, but treats the imperfection(s) of interest as a small perturbation in the crystalline structure.

Many of the most interesting phenomena in solids are associated with imperfections. That is why we shall discuss them at some length in various sections of this book.

1.3 BASIC DEFINITIONS

In order to talk precisely about crystal structures, we must introduce here a few of the basic definitions which serve as a kind of crystallographic language. These definitions are such that they apply to one-, two-, or three-dimensional crystals. Although most of our illustrative examples will be two-dimensional, the results will be restated later for the 3-D case.

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*, or simply the *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'. This is so whether the atoms A and A' are of the same kind (for example, two H atoms) or of different kinds (for example, H and Cl atoms). 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. Thus, in Fig. 1.2, the basis is the two atoms A and A', or any other equivalent set.
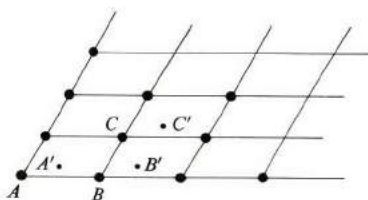

Fig. 1.2 A non-Bravais lattice.

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.

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

$$\mathbf{R}_n = n_1 \mathbf{a} + n_2 \mathbf{b}, \qquad (1.1)$$

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, $(n_1, n_2) = (1, 0)$, and for F, $(n_1, n_2) = (0, -1)$.

The two vectors $\mathbf{a}$ and $\mathbf{b}$ (which must be noncolinear) form a set of *basis vectors* for the lattice, in terms of which the positions of all lattice points can be conveniently expressed by the use of (1.1). The set of all vectors expressed by

this equation is called the *lattice vectors*. We may also say that the lattice is invariant under the group of all the translations expressed by (1.1). This is often rephrased by saying that the lattice has a *translational symmetry* under all displacements specified by the lattice vectors $\mathbf{R}_n$.
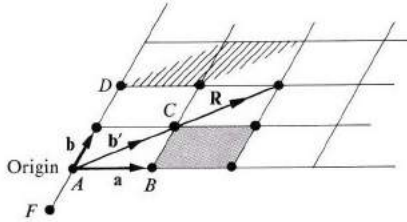

Fig. 1.3 Vectors **a** and **b** are basis vectors of the lattice. Vectors **a** and **b'** form another set of basis vectors. Shaded and hatched areas are unit cells corresponding to first and second set of basis vectors, respectively.

The choice of basis vectors is not unique. Thus one could equally well take the vectors **a** and **b'** ($= \mathbf{a} + \mathbf{b}$) as a basis (Fig. 1.3). Other possibilities are also evident. The choice is usually dictated by convenience, but for all the lattices we shall meet in this text, such a choice has already been made, and is now a matter of convention.

The unit cell

The area of the parallelogram whose sides are the basis vectors **a** and **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 of (1.1), 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, like a mosaic pattern.

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 **a** and **b'** in Fig. 1.3 is also an acceptable unit cell; once again the choice is dictated by convenience.

The following remarks may be helpful.

i) All unit cells have the same area. Thus the cell formed by **a**, **b** has the area $S = |\mathbf{a} \times \mathbf{b}|$, while that formed by **a**, **b'** has the area $S' = |\mathbf{a} \times \mathbf{b'}|$ $= |\mathbf{a} \times (\mathbf{a} + \mathbf{b})| = |\mathbf{a} \times \mathbf{b}| = S$, where we used the result $\mathbf{a} \times \mathbf{a} = 0$. 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.

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.
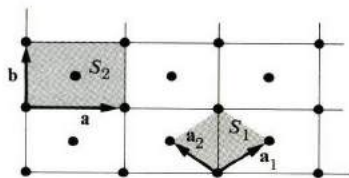

Fig. 1.4 Area S_1 is a primitive unit cell; area S_2 is a nonprimitive unit cell.

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 (and somewhat arbitrary) 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

$$\mathbf{R}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}, \tag{1.2}$$

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 $0, \pm 1, \pm 2$, 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.
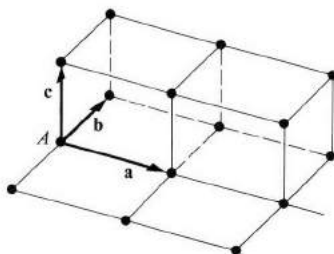

Fig. 1.5   A three-dimensional lattice.   Vectors **a, b, c** are basis vectors.

1.4 THE FOURTEEN BRAVAIS LATTICES AND THE SEVEN CRYSTAL SYSTEMS

There are only 14 different Bravais lattices. This reduction to what is a relatively small number is a consequence of the translational-symmetry condition demanded of a lattice. To appreciate how this comes about, consider the two-dimensional case, in which the reader can readily convince himself, for example, that it is not possible to construct a lattice whose unit cell is a regular pentagon. A regular pentagon can be drawn as an isolated figure, but one cannot place many such pentagons side by side so that they fit tightly and cover the whole area. In fact, it can be demonstrated that the requirement of translational symmetry in two dimensions restricts the number of possible lattices to only five (see the problem section at the end of this chapter).

In three dimensions, as we said before, the number of Bravais lattices is 14. The number of non-Bravais lattices is much larger (230), but it also is finite.
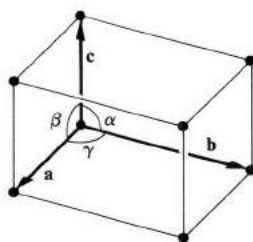
Fig. 1.6   Unit cell specified by the lengths of basis vectors **a, b,** and **c**; also by the angles between the vectors.

Triclinic

Simple monoclinic

Base-centered
monoclinic

Simple
orthorhombic

Base-centered
orthorhombic

Body-centered
orthorhombic

Face-centered
orthorhombic

Simple
tetragonal

Body-centered
tetragonal

Simple cubic

Body-centered
cubic

Face-centered
cubic

Trigonal

Hexagonal

Fig. 1.7 The 14 Bravais lattices grouped into the 7 crystal systems.

The 14 lattices (or crystal classes) are grouped into seven crystal systems, each specified by the shape and symmetry of the unit cell. These systems are the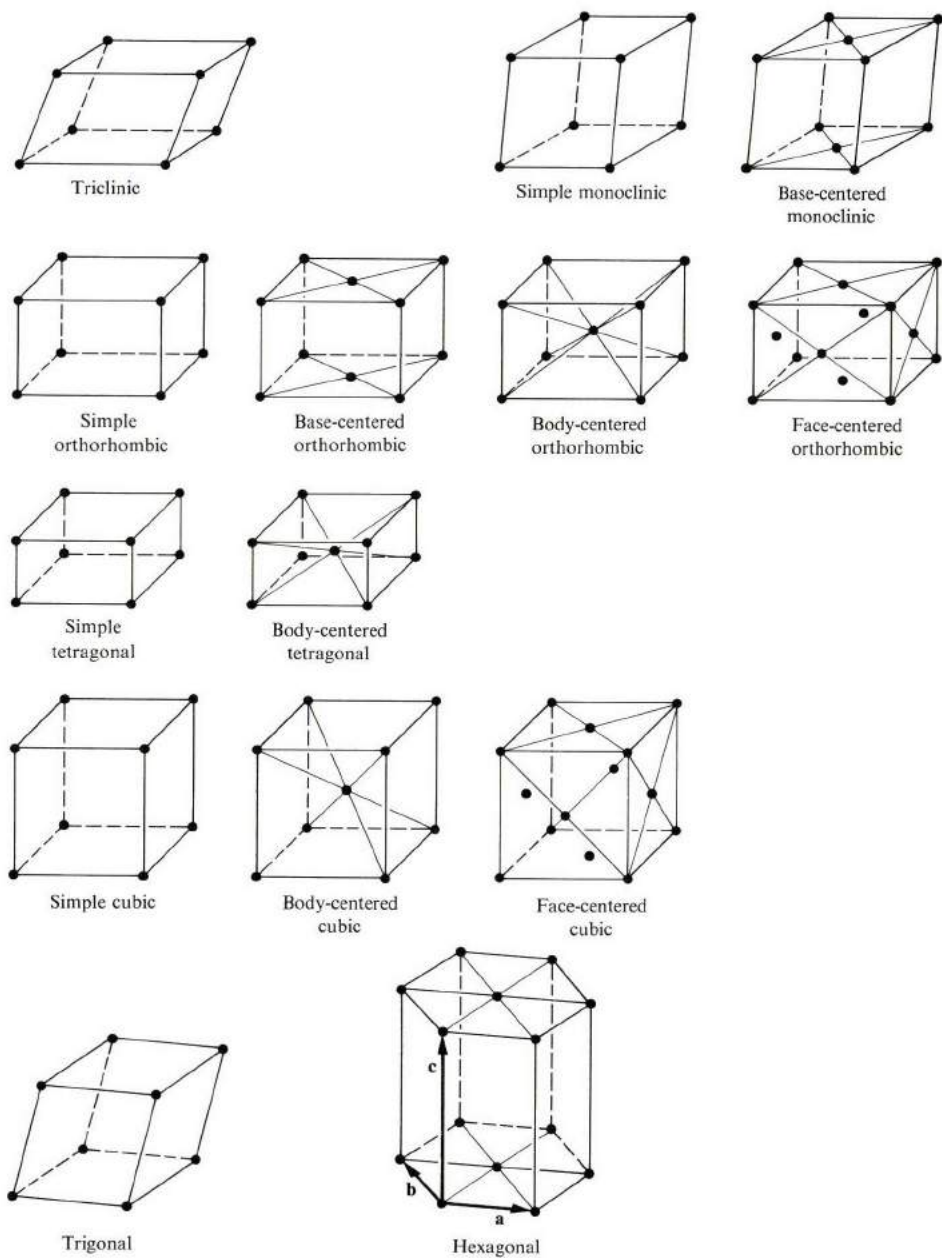 triclinic, monoclinic, orthorhombic, tetragonal, cubic, hexagonal, and the trigonal (or rhombohedral). In every case the cell is a parallelepiped whose sides are the bases $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. The opposite angles are called α, β, and γ, as shown in Fig. 1.6. Figure 1.7 shows the 14 lattices, and Table 1.1 enumerates the systems, lattices, and the appropriate values for $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, and α, β, and γ. Both Fig. 1.7 and Table 1.1 should be studied carefully, and their contents mastered. The column referring to symmetry elements in the table will be discussed shortly.

Table 1.1

The Seven Crystal Systems Divided into Fourteen Bravais Lattices

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

Note that a *simple* lattice has points only at the corners, a *body-centered* lattice has one additional point at the center of the cell, and a *face-centered* 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-centered 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. 1.8). Other cases can be treated similarly.
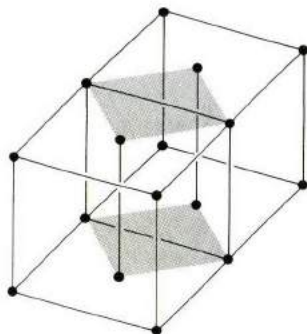

Fig. 1.8 A base-centered tetragonal is identical to a simple tetragonal of a different unit cell. Shaded areas are the basis of the simple tetragonal cell.

The system we shall encounter most frequently in this text is the cubic one, particularly the *face-centered cubic* (fcc) and the *body-centered cubic* (bcc). The hexagonal system will also appear from time to time.

1.5 ELEMENTS OF SYMMETRY

Each of the unit cells of the 14 Bravais lattices has one or more types of symmetry properties, such as inversion, reflection, or rotation. Let us consider the meanings of these terms.

Inversion center. A cell has an inversion center if there is a point at which the cell remains invariant when the mathematical transformation $\mathbf{r} \to -\mathbf{r}$ is performed on it. All Bravais lattices are inversion symmetric, a fact which can be seen either by referring to Fig. 1.7 or 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 $\mathbf{R}_n \equiv -\mathbf{R}_n = -n_1\mathbf{a} - n_2\mathbf{b} - n_3\mathbf{c}$. A non-Bravais lattice may or may not have an inversion center, depending on the symmetry of the basis.

Reflection plane. A plane in a cell such that, when a mirror reflection in this plane is performed, the cell remains invariant. Referring to Fig. 1.7, we see that 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.

Rotation axis. 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 $2\pi/n$. When we look at Fig. 1.7 again, we see that 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.

We have discussed the simplest symmetry elements, the ones which we shall encounter most frequently. More complicated elements also exist, such as rotation–reflection axes, glide planes, etc., but we shall not pursue these at this stage, as they will not be needed in this text.

You may have noticed that the symmetry elements may not all be independent. As a simple example, one can show that an inversion center plus a reflection plane imply the existence of a 2-fold axis passing through the center and normal to the plane. Many similar interesting theorems can be proved, but we shall not do so here.

Point groups, space groups, and non-Bravais lattices

A non-Bravais lattice is one in which, with each lattice site, there is associated a cluster of atoms called the *basis*. Therefore one describes the symmetry of such a lattice by specifying the symmetry of the basis in addition to the symmetry of the Bravais lattice on which this basis is superimposed.

The symmetry of the basis, called *point-group symmetry*, refers to all possible rotations (including inversion and reflection) which leave the basis invariant, keeping in mind that in all these operations one point in the basis must remain fixed (which is the reason for referring to this as point-group symmetry). A close examination of the problem reveals that only 32 different point groups can exist which are consistent with the requirements of translational symmetry for the lattice as a whole. One can appreciate the limitation on the number of point groups by the following physical argument: The shape or structure of the basis cannot be arbitrarily complex, e.g., like the shape of a potato. This would be incompatible with the symmetry of the interatomic forces operating between the basis and other bases on nearby lattice sites. After all, it is these forces which determine the crystal structure in the first place. Thus the rotation symmetries possible for the basis must be essentially the same as the rotational symmetries of the unit cells of the 14 Bravais lattices which were enumerated in Section 1.4.

When we combine the rotation symmetries of the point groups with the translational symmetries, we obtain a *space-group symmetry*. In this manner one generates a large number of space groups, 72 to be exact. It appears that there

are also in addition some space groups which cannot be composed of simple point groups plus translation groups; such groups involve symmetry elements such as screw axes, glide planes, etc. When one adds these to the 72 space groups, one obtains 230 different space groups in all (Buerger, 1963). Figure 1.9 shows a tetragonal D_{2a} space group. However, further discussion of these groups lies outside the scope of this book.
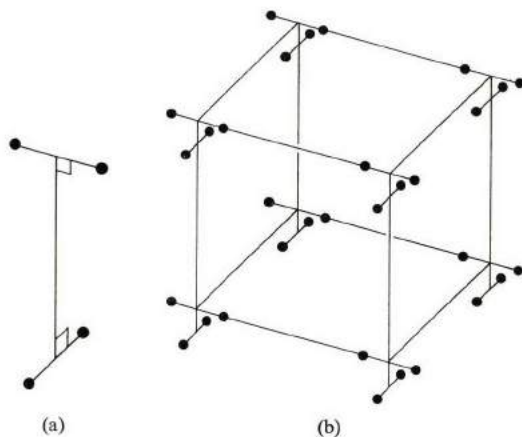

(a)   (b)

Fig. 1.9   (a) A basis which has a D_{2d} point group symmetry (two horizontal 2-fold axes plus two vertical reflection planes). (b) A simple tetragonal lattice with a basis having the D_{2d} point group.

1.6 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.

Crystal directions

Consider the straight line passing through the lattice points A, B, C, etc., in Fig. 1.10. 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

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

The direction is now specified by the integral triplet $[n_1n_2n_3]$. If the numbers n_1, n_2, n_3 have a common factor, this factor is removed, i.e., the triplet $[n_1n_2n_3]$ is the smallest integer of the same relative ratios. Thus in Fig. 1.10 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. 1.10) which are completely equivalent by virtue of the translational symmetry.
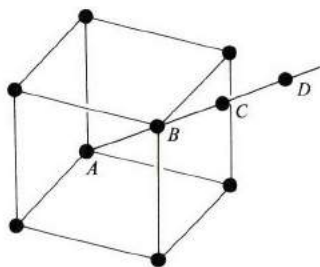

Fig. 1.10 The [111] direction in a cubic lattice.

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.

Note that a direction with large indices, e.g., [157], has fewer atoms per unit length than one with a smaller set of indices, such as [111].

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. 1.11(a), we find its intercepts with the axes along the basis vectors **a**, **b**, and **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

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

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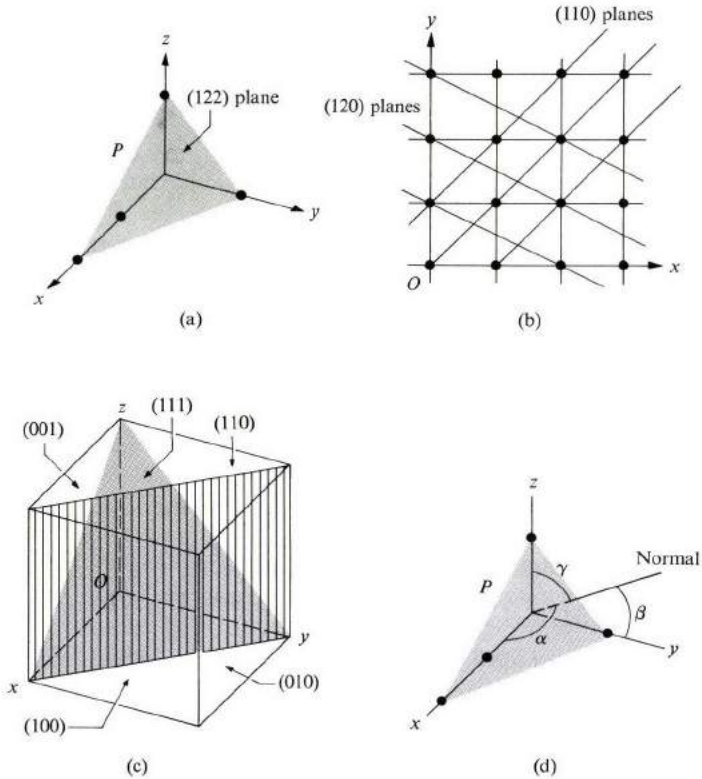

Fig. 1.11 (a) The (122) plane. (b) Some equivalent, parallel planes represented by the Miller indices. (c) Some of the planes in a cubic crystal. (d) Finding the interplanar spacing.

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. We can prove this by following the above procedure for determining the indices. Therefore a set of Miller indices specifies not just one plane, but an infinite set of equivalent planes, as indicated in Fig. 1.11(b). There

is a good reason for using such notation, as we shall see when we study x-ray diffraction from crystal lattices. A diffracted beam is the result of scattering from large numbers of equivalent parallel planes, which act collectively to diffract the beam. Figure 1.11(c) shows several important planes in a cubic crystal.

[The reason for inverting the intercepts in defining the Miller indices is more subtle, and has to do with the fact that the most concise, and mathematically convenient, method of representing lattice planes is by using the so-called reciprocal lattice. We shall discuss this in Chapter 2, where we shall clarify the connection.]

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}$).

Spacing between planes of the same Miller indices

In connection with x-ray diffraction from a crystal (see Chapter 2), 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. We can calculate this by referring to Fig. 1.11(d), visualizing 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

$$d_{hkl} = x \cos \alpha \quad y \cos \beta = z \cos \gamma.$$

But there is a relation between the directional cosines $\cos \alpha$, $\cos \beta$, and $\cos \gamma$. That is, $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$. If we solve for $\cos \alpha$, $\cos \beta$, and $\cos \gamma$ from the previous equation, substitute into the one immediately above, and solve for d_{hkl} in terms of x, y, and z, we find that

$$d_{hkl} = \frac{1}{\left(\dfrac{1}{x^2} + \dfrac{1}{y^2} + \dfrac{1}{z^2} \right)^{1/2}}. \tag{1.3}$$

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

$$h = n \frac{a}{x}, \quad k = n \frac{b}{y}, \quad l = n \frac{c}{z}, \tag{1.4}$$

where n is the common factor used to reduce the indices to the smallest integers possible. Solving for x, y, and z from (1.4) and substituting into (1.3), one obtains

$$d_{hkl} = \frac{n}{\left[\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}\right]^{1/2}}, \tag{1.5}$$

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

1.7 EXAMPLES OF SIMPLE CRYSTAL STRUCTURES

In order to gain an appreciation of actual crystals, let us familiarize ourselves with a few of the better-known structures, and with the sizes of their unit cells. The cumulative knowledge obtained over the years on the structures of various crystals is truly enormous, but here we shall touch on only the few simple and better-known examples which we shall meet repeatedly in this book.

Face-centered and body-centered cubic

Many of the common metals crystallize in one or the other of these two lattices.

Thus the most familar metals—Ag, Al, Au, Cu, Co(β), Fe(γ), Ni(β), Pb, and Pt—all crystallize in the fcc structure (Fig. 1.12a). 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.
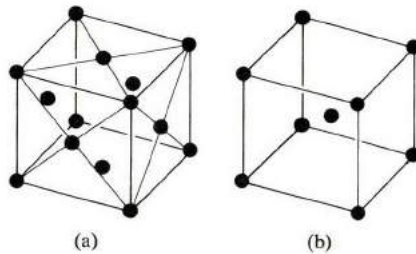

(a)   (b)

Fig. 1.12 (a) An fcc unit cell. (b) A bcc unit cell.

Some of the metals which crystallize in the bcc structure are: Fe(α), and the alkalis Li, Na, K, Rb, and Cs (Fig. 1.12b). 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.

The 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. 1.13(a). In three dimensions the unit cell appears as shown in Fig. 1.13(b). That is, the cell is a face-centered 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
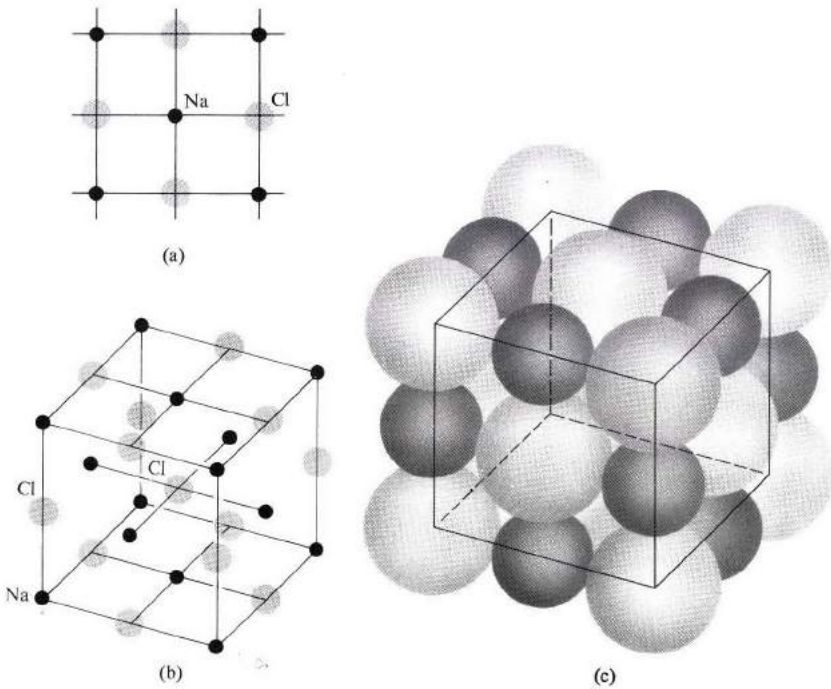
Fig. 1.13 (a) A two-dimensional view of the NaCl structure. (b) The NaCl structure in three dimensions. The Na atoms form an fcc structure which is interlocked with another fcc structure composed of the Cl atoms. (c) The NaCl structure drawn close to scale, with the ions nearly touching. The sodium atoms, small solid spheres, reside in the octahedral voids between the chlorine atoms.

the four Cl atoms are located at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $00\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$ (the numbers refer to coordinates given in fractions of the cubic edge).

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 $\frac{1}{2}\mathbf{a}$.

Many ionic crystals such as KCl and PbS also have this structure. For a more complete list, including the lattice constants, refer to Table 1.2.

The cesium chloride structure

This again 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. 1.14. There are, 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. For a list of certain ionic compounds crystallizing in this structure, see Table 1.2.
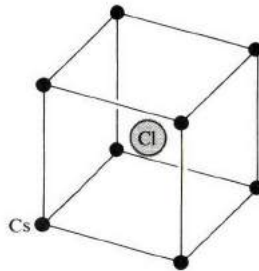
Fig. 1.14 Structure of cesium chloride. The Cs atoms form an sc lattice interlocked with another sc lattice formed by the Cl ions.

Table 1.2

Structures and Cell Dimensions of Some Elements and Compounds

Element or compound	Structure	a, Å	c, Å
Al	fcc	4.04	
Be	hcp	2.27	3.59
Ca	fcc	5.56	
C	Diamond	3.56	
Cr	bcc	2.88	
Co	hcp	2.51	4.07
Cu	fcc	3.61	
Ge	Diamond	5.65	
Au	fcc	4.07	
Fe	bcc	2.86	
Pt	fcc	3.92	
Si	Diamond	5.43	
Ag	fcc	4.08	
Na	bcc	4.28	
Zn	hcp	2.66	4.94
LiH	Sodium chloride	4.08	
NaCl	Sodium chloride	5.63	
AgBr	Sodium chloride	5.77	
MnO	Sodium chloride	4.43	
CsCl	Cesium chloride	4.11	
TlBr	Cesium chloride	3.97	
CuZn (β-brass)	Cesium chloride	2.94	
CuF	Zincblende	4.26	
AgI	Zincblende	6.47	
ZnS	Zincblende	5.41	
CdS	Zincblende	5.82	

The 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. 1.15(a), and the whole cell in three dimensions is shown in Fig. 1.15(b). There are eight atoms per unit cell.
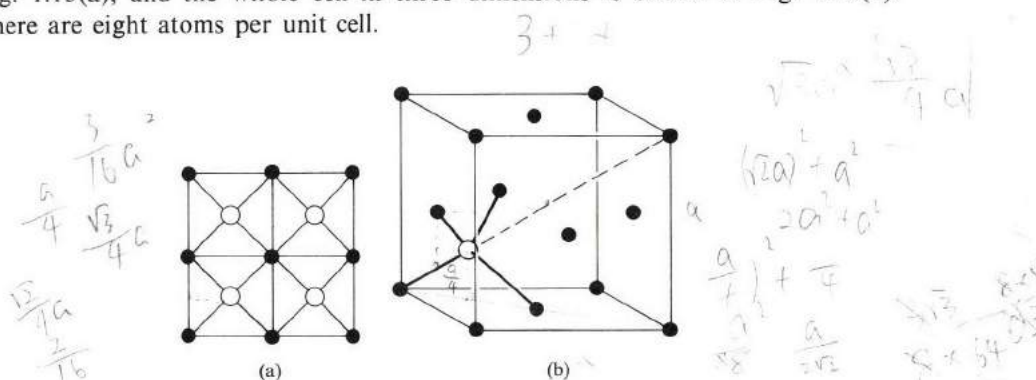

(a)   (b)

Fig. 1.15 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. (b) A simplified three-dimensional view. Only one of the 4 white spheres is shown, 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*. This structure occurs in many semiconductors, for example, Ge, Si, etc. Table 1.2 contains a few examples, with appropriate numerical values.

The zinc sulfide[†] (ZnS) structure

This structure, named after the compound ZnS, 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.

Many of the compound semiconductors—such as InSb, GaSb, GaAs, etc.—do crystallize in this structure (Table 1.2).

The hexagonal close-packed structure

This is another structure that is common, particularly in metals. Figure 1.16 demonstrates this structure. In addition to the two layers of atoms which form

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† Also known as the *zincblende* structure.

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. Examples of hcp crystals are Be, Mg, Ca, Zn, and Hg—all divalent metals.
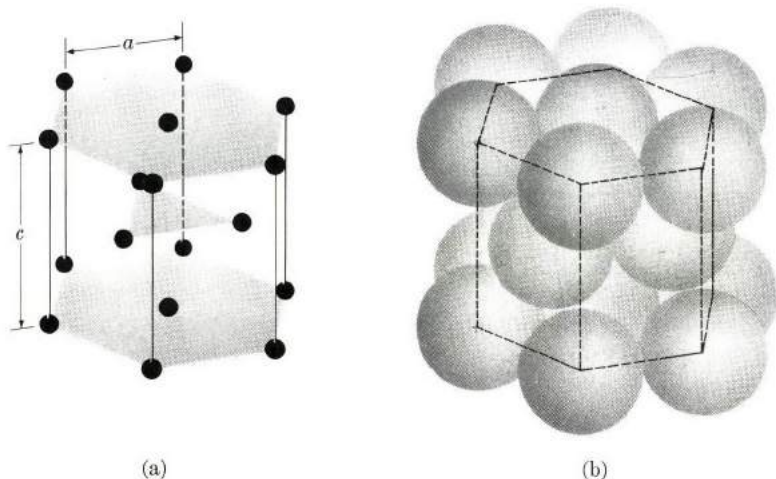

(a)   (b)

Fig. 1.16 (a) Hexagonal close-packed structure. (b) The hcp when the atoms are nearly touching, as in the actual situation.

1.8 AMORPHOUS SOLIDS AND LIQUIDS

Amorphous solids have received increasing attention in recent years, particularly as a result of the discovery of the electrical properties of amorphous semiconductors (Section 13.2). It behooves us, therefore, to glance at least briefly at the structure of these solids.

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.

Another familiar case of an amorphous structure is that of a liquid. Here again the system has no crystal structure, and the atoms appear to have a random distribution. As time passes, the atoms in the liquid drift from one region to another, but their random distribution persists.

This suggests a strong similarity between liquids and amorphous solids, even though the atoms in the latter are fixed in space and do not drift as they do in liquids. This is why amorphous solids, such as glass, are sometimes referred to as *supercooled* liquids. In fact, if one could take an instantaneous picture of

the atoms in a liquid, the result would be the same as, and indistinguishable from, that of an amorphous solid. The same mathematical formalism may therefore be employed to describe both types of substance.

Even a liquid does actually have a certain kind of "order" or structure, even though this structure is not crystalline. Consider the case of mercury, for instance. This metal crystallizes in the hcp structure. When the substance is in the solid state, below the melting point, all the atoms are in their regular positions, and each atom is surrounded by a certain number of nearest neighbors, next-nearest neighbors, etc., all of which are positioned at exactly defined distances from the central atom. When the metal is heated and melts, the atoms no longer hold to their regular positions, and the crystal structure as such is destroyed. Yet as we view the system from the vantage point of the original atom, we discover that insofar as the number of nearest and next-nearest neighbors and their distances is concerned, the situation in the liquid state remains substantially the same as it was in the solid state. Of course, when we speak of the "number of nearest neighbors" in the liquid state, we actually mean the average number, since the actual number is constantly changing as a result of the motion of the atoms.

It is apparent, therefore, that a liquid has a structure, and that this structure is quite evident from x-ray diffraction pictures of liquids. The important point, however, is that the order in a liquid is restricted only to the few shells of neighbors surrounding the central atom. As one goes to farther and farther atoms, their distribution relative to the central atom becomes entirely random. This is why we say that a liquid has only a *short-range order*. *Long-range order* is absent. Contrast this with the case of a crystal. In a crystal, the positions of all atoms, even the farthest ones, are exactly known once the position of the central atom is given. A crystal therefore has both short-range and long-range orders, i.e., perfect order.

It is not surprising that some order should exist, even in the liquid state. After all, the interatomic forces responsible for the crystallinity of a solid remain operative even after the solid melts and becomes a liquid. Furthermore, since the expansion of volume that is concomitant with melting is usually small, the average interatomic distances and hence the forces remain of the same magnitude as before. The new element now entering the problem is that the thermal kinetic energy of the atoms, resulting from heating, prevents them from holding to their regular positions, but the interatomic forces are still strong enough to impart a certain partial order to the liquid.

To turn now to the mathematical treatment: We take a typical atom and use it as a central atom in order to study the distribution of other atoms in the system relative to it. We draw a spherical shell of radius R and thickness ΔR around this atom. The number of atoms in this shell is given by

$$\Delta N(R) = n(R)4\pi R^2 \, \Delta R, \tag{1.6}$$

where $n(R)$ is the concentration of atoms in the system. Note that the quantity $4\pi R^2 \Delta R$ is the volume of the spherical shell, which, when we multiply it by the concentration, yields the number of particles. Note also that, since a liquid is isotropic, we need not be concerned with any angular variation of the concentration. Only the radial dependence is relevant here.

The structural properties of the liquid are now contained entirely in the concentration $n(R)$. Once this quantity and its variation with the radial distance R are determined, the structure of the liquid is completely known.

The concentration $n(R)$ versus R in liquid mercury as revealed by x-ray diffraction is shown in Fig. 1.17. The curve has a primary peak at $R \simeq 3\text{Å}$, beyond which it oscillates a few times before reaching a certain constant value. The concentration vanishes for $R \lesssim 2.2 \text{ Å}$.
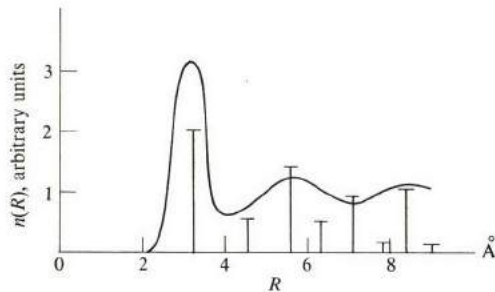

Fig. 1.17   The atomic concentration $n(R)$ in liquid mercury. Vertical lines indicate the atomic distribution in crystalline mercury.

These features can be made quite plausible on the basis of interatomic forces. The vanishing of $n(R)$ at small values of R is readily understandable; as other atoms approach the central one very closely, strong repulsive forces arise which push these atoms away (see the following two sections). These repulsive forces therefore prevent the other atoms from overlapping the central atom, which explains why $n(R) = 0$ at small R. One expects the value of R where $n(R) = 0$ to be nearly equal to the diameter of the atom.

The reason for the major peak (Fig. 1.17) is closely related to the attractive interatomic force. We shall explain below that, except at very short distances, atoms attract each other. This force therefore tends to pull other atoms toward the center, resulting in a particularly large density at a certain specific distance. The other oscillations in the curve arise from an interplay between the force of the central atom and the forces of the near neighbors acting on neighbors still farther away.

At large values of R, the concentration $n(R)$ approaches a constant value n_0, which is actually equal to the average concentration in the system. We expect this result because we have seen that a liquid does not have a long-range

order; thus at large R the distribution of the atoms is completely random, and independent of the position of the central atom, i.e., independent of R.

Instead of $n(R)$, it is customary to express the correlation between atoms by introducing the so-called *pair distribution function* $g(R)$. This is defined as

$$g(R) = \frac{n(R)}{n_0}. \tag{1.7}$$

Thus this function has the meaning of a relative density, or probability. Since n_0 is a constant, the shape of $g(R)$ is the same as that of $n(R)$, that is, the same as in Fig. 1.17. Note in particular that $g(R) \to 1$ as $R \to \infty$, which is the situation corresponding to the absence of correlation between atoms.

As alluded to above, the pair function $g(R)$ is determined by x-ray diffraction. We shall discuss this in Section 2.8.

1.9 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* (also the cohesive energy) of the crystal.
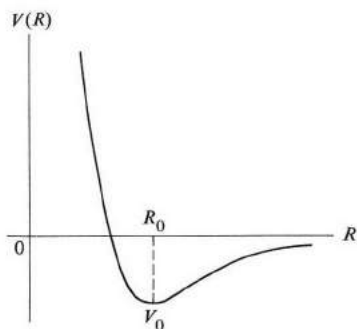

Fig. 1.18 Interatomic potential $V(R)$ versus interatomic distance.

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. 1.18, has a minimum at some distance R_0. For $R > R_0$,

the potential increases gradually, approaching 0 as $r \to \infty$, while for $R < R_0$ the potential increases very rapidly, approaching ∞ at small radius.

Because the system—the atom pair—tends to have the lowest possible energy, it is most stable at the minimum point A, which therefore represents the *equilibrium position*; the equilibrium interatomic distance is R_0, and the binding energy $-V_0$. Note that, since $V_0 < 0$, the system is stable, inasmuch as its energy is lower than that state in which two atoms are infinitely far apart (free atoms).

A typical value for the equilibrium radius R_0 is a few angstroms, so the forces under consideration are, in fact, rather short-range. The decay of the potential with distance is so rapid that once this exceeds a value of, say, 10 or 15Å, the force may be disregarded altogether, and the atoms may then be treated as free, noninteracting particles. This explains why the free-atom model holds so well in gases, in which the average interatomic distance is large.

The interatomic force $F(R)$ may be derived from the potential $V(R)$. It is well known from elementary physics that

$$F(R) = -\frac{\partial V(R)}{\partial R}. \tag{1.8}$$

That is, the force is the negative of the potential gradient. If we apply this to the curve of Fig. 1.18, we see that $F(R) < 0$ for $R_0 < R$. This means that in the range $R_0 < R$ the force is *attractive*, tending to pull the atoms together. On the other hand, the force $F(R) > 0$ for $R_0 > R$. That is, when $R < R_0$, the force is *repulsive*, and tends to push the atoms apart.

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.

We shall discuss the nature of the attractive and repulsive forces in the following section.

1.10 TYPES OF BONDING

The presence of attractive interatomic forces leads to the bonding of solids. In chemist's language, one may say that these 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 are: *ionic bonding*, *covalent bonding*, and *metallic bonding*. Let us now take these up one by one, and also consider secondary types of bonding which are important in certain special cases.

The 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, as pointed out in Section 7.

If we examine a pair of Na and Cl ions, it is clear that an attractive electrostatic coulomb force, $e^2/4\pi\epsilon_0 R^2$, exists between the pairs of oppositely charged ions. It is this force which is responsible for the bonding of NaCl and other ionic crystals.

It is more difficult, however, to understand the origin of the repulsive force at small distances. Suppose the ions in NaCl were brought together very closely by a (hypothetical) decrease of the lattice constant. Then a repulsive force would begin to operate at some point. Otherwise the ions would continue to attract each other, and the crystal would simply collapse—which is, of course, not in agreement with experiment. We cannot explain this repulsive force on the basis of coulomb attraction; therefore it must be due to a new type of interaction.

A qualitative picture of the origin of the repulsive force may be drawn as follows: When the Na^+ and Cl^- ions approach each other closely enough so that the orbits of the electrons in the ions begin to overlap each other, then the electrons begin to repel each other by virtue of the repulsive electrostatic coulomb force (recall that electrons are all negatively charged). Of course, the closer together the ions are, the greater the repulsive force, which is in qualitative agreement with Fig. 1.18 in the region $R < R_0$.

There is yet another equally important source which contributes to the repulsive force: the *Pauli exclusion principle*. As ions approach each other, the orbits of the electrons begin to overlap, i.e., some electrons attempt to occupy orbits already occupied by others. But this is forbidden by the exclusion principle, inasmuch as both the Na^+ and Cl^- ions have outermost shells that are completely full. To prevent a violation of the exclusion principle, the potential energy of the system increases very rapidly, again in agreement with Fig. 1.18, in the range $R < R_0$.

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. Experimentally, this strength is characterized by the high melting temperatures associated with ionic crystals. Thus the melting temperature for the ionic crystal NaCl is 801°C, while the melting temperatures for the Na and K metals are 97.8°C and 63°C, respectively.

Ionic bonding is most likely to exist when the elements involved are of widely differing electronegativities. Example: an electropositive alkali atom plus an electronegative halogen atom, as in NaCl.

The covalent bond

To introduce this bond, we consider a well-known covalent solid: diamond.

Recall from Section 7 that this crystal is formed from carbon atoms arranged in a certain type of fcc structure in which each atom is surrounded by four others, forming a regular tetrahedron. We cannot invoke the ionic bond to explain the bonding in diamond, because here each atom retains its own electrons, i.e., there is no transfer of electrons between the atoms, and in consequence no ions are formed. This is evident from the fact that all the atoms are identical. Hence no reason exists for an electron to transfer from one atom to another.

Instead, 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. 1.19). The bond here is composed of two electrons, one contributed by each of the two atoms. This double-electron bond is well known in chemistry and physics. It is referred to as a *covalent bond*. As an indication of the appropriateness of this bond in the case of diamond, 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 at hand (in this case the familiar p shell).
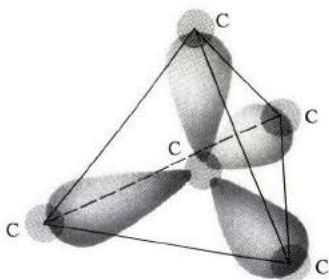

Fig. 1.19 The tetrahedral covalent bond in diamond. Each elongated region represents the charge distribution of the two electrons forming the corresponding bond.

This plausible account still does not explain just why a double-electron arrangement produces a bond, i.e., an attractive interatomic force. The explanation of the covalent bond can be given only through quantum mechanics. The simplest known example of the covalent bond occurs in the hydrogen molecule (H_2), in which the two atoms are held together by just this bond, i.e., they share their two electrons. We discuss the quantum explanation of bonding in H_2 in Section A.7, and its adaptation to the tetrahedral bond (as in diamond) in Section A.8. Refer to these sections for further details.

The covalent bond is also strong, as attested to by the unusual hardness of diamond, and its high melting point ($> 3000°C$). A typical value for covalent-bond binding energy is a few electron volts per bond.

The covalent bond is particularly important for those elements in column IV

of the periodic table. We have already mentioned diamond (C). Other elements are Si, Ge, and Sn, all of which crystallize in the diamond structure and are covalent crystals. The elements silicon (Si) and germanium (Ge) hold special interest, since both are among the best known semiconductors. We shall study them in considerable detail in Chapters 6 and 7, which concern the semiconducting properties of solids.

Covalent crystals tend to be hard and brittle, and incapable of appreciable bending. These facts are understandable in terms of the underlying atomic forces. Since the bonds have well-defined directions in space, attempts to alter them are strongly resisted by the crystal.

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.

The metallic bond

Most elements are metals. Metals are characterized by high electrical conductivity and mechanical strength, and also by the property of being highly ductile. We are particularly interested here in the bonding mechanism, but the model we shall invoke for this purpose is capable of accounting for the above-mentioned properties as well. (These properties will be the subject of ample discussions later; see Chapters 4, 5, and 11.)

To understand the metallic bond, let us consider a typical simple metal: sodium. How can an assembly of Na atoms, brought together to form a crystal, attract each other and form a stable solid? Quick reflection tells us that neither the ionic nor the covalent bond can account for the interatomic attraction in sodium (why not?). The correct explanation is this: 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. This picture of free valence electrons (in metals these are referred to as *valence* or *conduction* electrons) is drastically different from the valence electrons in ionic and covalent solids, in which the electrons are tightly bound to their atoms; it is, in fact, the primary feature distinguishing metals from these latter crystals.

The model we now have of sodium metal is an assemblage of positive Na^+ ions forming a bcc lattice, immersed in a gas of free electrons. The question confronting us now is: Why is the energy of such a system lower than that of free Na atoms? First, it is clear that the Na^+ ions would tend to repel each other as a result of the electrostatic coulomb force. But this force, which acts against

stability, is largely ineffective, because free electrons strongly screen ions from each other, resulting in essentially neutralized noninteracting ions, much as in the case of free atoms. But the great reduction in energy needed for the bonding can be explained only in quantum terms: It follows from quantum considerations that when a particle is restricted to move in a small volume, it must by necessity have a large kinetic energy. This energy is proportional to $V^{-2/3}$, where V is the volume of confinement (see Section A.3). The origin of this energy is entirely quantum in nature, and is intimately related to the *Heisenberg uncertainty principle*.

We now apply this interesting idea to the case of metals. When the Na atoms are in the gaseous state, their valence electrons have large kinetic energies because they are restricted to move in the very small atomic volumes. But, in the crystalline state, the electrons are free to wander throughout the volume of the crystal, which is very large. This results in a drastic decrease of their kinetic energies, and thus an appreciable diminution in the total energy of the system, which is the source of the metallic bonding. (Figuratively speaking, the free electrons, which are of course negative, act as a glue that holds the positive ions together.)

The metallic bond is somewhat weaker than the ionic and covalent bonds (for instance, the melting point of Na is only 97.8°C), but is still far from being small or negligible.

To account briefly for the other metallic properties listed earlier, we note that the high *electrical conductivity* is due to the ability of the valence electrons to move readily under the influence of an electric field, resulting in a net electrical current in the field direction. A similar explanation may be given for the high *thermal conductivity*. The high *density* is due to the fact that the metallic ions may be packed together tightly, even though the free electrons produce a strong and effective screening between them. The high *ductility* is a consequence of the fact that the metallic bond is nondirectional, so that if an external bending torque is applied and the ions change positions to accommodate this torque, the electrons, being very small and highly mobile, readily adapt themselves to the new deformed situation.

This metallic bonding model works well in the simple metals, particularly the alkalis. More complicated metals—especially the transition elements such as Fe, Ni, etc.—require more complex models, as one would expect. Thus in Fe and Ni the 3d electrons have well-localized properties, and hence they tend to form covalent bonds with their neighbors. This covalent bonding is in addition to the contribution of the 4s valence electrons, which produce a metallic bonding.

Secondary bonds

In addition to the three primary bonds discussed above (ionic, covalent, and metallic), there are other, weaker bonds which often play important roles in explaining some of the "fine-scale" bonding properties. 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 (Fig. 1.20a); the electron sharing makes it possible for the oxygen atom to have 8 valence electrons, i.e., a stable shell structure.   Thus the atoms in an H_2O molecule are stongly bonded.
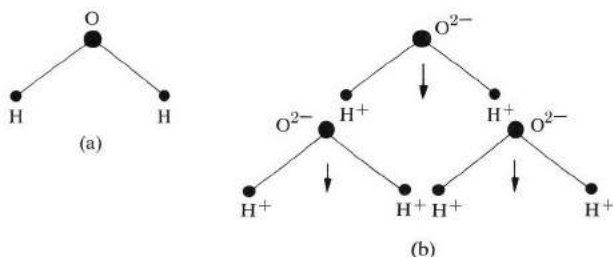

Fig. 1.20   (a) Water molecule. (b) Arrangement of ice molecule as a result of hydrogen bond. Arrows represent electric dipole moments of the molecules.

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 ice is only 0°C. The explanation of this is that, although each H_2O molecule is, on the whole, electrically neutral, the distribution of internal charge is such as to produce an interaction between the molecules. Thus in describing the electron sharing in the H-O bond, we should also mention the fact that the 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 (Fig. 1.20b). This produces a so-called *electric dipole* in the water molecule, as indicated by the vector in the figure. Now electric dipoles attract each other.   Thus water molecules are attracted to each other, forming a crystal (Fig. 1.20b).   (We can also appreciate the dipole attraction on a more elementary level by noting that the negative oxygen atom in one water molecule is attracted toward that corner in another water molecule which contains a positive hydrogen atom.)

The bond described here is referred to as the *hydrogen bond*—sometimes also known as the hydrogen bridge—because of the important role played by the small hydrogen nucleus (which is a proton).

Another bond which plays an especially important role in inert-gas solids is the *van der Waals bond*. You undoubtedly recall from basic chemistry that the inert-gas elements—i.e., those that occur in column VIII of the periodic table (He, Ne, Ar, etc.)—display extremely small attraction toward each other, or other elements. So these elements do not usually participate in chemical reactions (hence the name inert), and they form *monatomic* gases rather than *diatomic* ones such as H_2, O_2, or other polyatomic gases. The weakness of the interatomic forces in the inert-gas solids is also illustrated by their low melting points: -272.2, -248.7

and $-189.2°C$ for He, Ne, and Ar, respectively. In other words, He remains in the liquid state down to a temperature of only about one degree from absolute zero!†

If one uses the principles of quantum theory, it is not difficult to explain the weakness of interatomic forces in the inert gases. 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. This rules out any ionic and covalent forces, and likewise rules out any metallic-bonding forces in inert-gas crystals.

Yet even the inert-gas atoms exhibit interatomic forces, albeit very weak ones. The fact that Ne, for instance, solidifies at $-248.7°C$ indicates clearly that some interatomic forces are present, which are responsible for the freezing; by contrast, a system of truly noninteracting atoms would remain gaseous down to the lowest temperature. So our problem is not so much to explain the weakness of the forces, but rather to account for their presence in the first place.

Without becoming embroiled in physical and mathematical complexities, we may 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, then the effect would be to screen the nucleus completely from an adjacent atom, and the two atoms would not interact. This supposition is not quite correct, however. Although the distribution of the electrons is essentially symmetric, and is certainly so on the average, as time passes 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 (as mentioned in connection with the hydrogen bond), and this is the source of the van der Waals force. The resulting potential is found to decrease with distance as $1/R^6$, far more rapidly than the ionic potential, which decreases only as $1/R$.

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. Following the various steps in detail, however, one arrives at a net attractive force.

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† Actually He solidifies only if an external pressure of at least 26 atms is applied to it.

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QUESTIONS

1. What is the reason for the fact that the tetrahedral bond is the dominant bond in carbon compounds?
2. Estimate the strength of the hydrogen bond in water (in electron volts per bond).
3. Show that two parallel electric dipoles attract each other.
4. Estimate the strength of the van der Waals bond for neon.

PROBLEMS

1. Given that the primitive basis vectors of a lattice are $\mathbf{a} = (a/2)(\mathbf{i} + \mathbf{j})$, $\mathbf{b} = (a/2)(\mathbf{j} + \mathbf{k})$, and $\mathbf{c} = (a/2)(\mathbf{k} + \mathbf{i})$, where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the usual three unit vectors along cartesian coordinates, what is the Bravais lattice?
2. Using Table 1.2 and the data below, calculate the densities of the following solids: Al, Fe, Zn, and Si, whose atomic weights are respectively 26.98, 55.85, 65.37, and 28.09.
3. Show that in an ideal hexagonal-close-packed (hcp) structure, where the atomic spheres touch each other, the ratio c/a is given by

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

(The hcp structure is discussed in Section 7.)

4. The *packing ratio* is defined as the fraction of the total volume of the cell that is filled by atoms. Determine the maximum values of this ratio for equal spheres located at the points of simple-cubic, body-centered-cubic, and face-centered-cubic crystals.

5. Repeat Problem 4 for simple hexagonal, and rhombohedral lattices.
6. Repeat Problem 4 for an hcp structure.
7. Consider a face-centered-cubic cell. Construct a primitive cell within this larger cell, and compare the two. How many atoms are in the primitive cell, and how does this compare with the number in the original cell?
8. a) Show that a two-dimensional lattice may not possess a 5-fold symmetry.
   b) Establish the fact that the number of two-dimensional Bravais lattices is five: Oblique, square, hexagonal, simple rectangular, and body-centered rectangular. (The proof is given in Kittel, 1970.)
9. Demonstrate the fact that if an object has two reflection planes intersecting at $\pi/4$, it also possesses a 4-fold axis lying at their intersection.
10. Sketch the following planes and directions in a cubic unit cell: (122), $[122]$, $(1\bar{1}2)$, $[1\bar{1}2]$.
11. a) Determine which planes in an fcc structure have the highest density of atoms.
    b) Evaluate this density in atoms/cm^2 for Cu.
12. Repeat Problem 11 for Fe, which has a bcc structure.
13. Show that the maximum packing ratio in the diamond structure is $\pi\sqrt{3}/16$. [Hint: The structure may be viewed as two interpenetrating fcc lattices, arranged such that each atom is surrounded by four other atoms, forming a regular tetrahedron.]
14. A quantitative theory of bonding in ionic crystals was developed by Born and Meyer along the following lines: The total potential energy of the system is taken to be

$$E = N\frac{A}{R^n} - N\frac{\alpha e^2}{4\pi\epsilon_0 R},$$

where N is the number of positive–negative ion pairs. The first term on the right represents the repulsive potential, where A and n are constants determined from experiments. The second term represents the attractive coulomb potential, where α, known as the *Madelung constant*, depends only on the crystal structure of the solid.

a) Show that the equilibrium interatomic distance is given by the expression

$$R_0^{n-1} = \frac{4\pi\epsilon_0 A}{\alpha e^2}n.$$

b) Establish that the bonding energy at equilibrium is

$$E_0 = -\frac{\alpha N e^2}{4\pi\epsilon_0 R_0}\left(1 - \frac{1}{n}\right).$$

c) Calculate the constant n for NaCl, using the data in Table 1.2 and the fact that the measured binding energy for this crystal is 1.83 kcal/mole (or 7.95 eV/molecule). The constant α for NaCl is 1.75.