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An Introduction to Crystal Structures

In the last decade of the twentieth century, research into solid state chemistry expanded very rapidly, fuelled partly by the dramatic discovery of ‘high temperature’ ceramic oxide superconductors in 1986, and by the search for new and better materials. We have seen immense strides in the development and understanding of nano-technology, micro- and meso-porous solids, fuel cells, and the giant magnetoresistance effect, to mention but a few areas. It would be impossible to cover all of the recent developments in detail in a text such as this, but we will endeavour to give you a flavour of the excitement that some of the research has engendered, and perhaps more importantly the background with which to understand these developments and those which are yet to come.

All substances, except helium, if cooled sufficiently form a solid phase; the vast majority form one or more **crystalline** phases, where the atoms, molecules, or ions pack together to form a regular repeating array. This book is concerned mostly with the structures of metals, ionic solids, and extended covalent structures; structures which do not contain discrete molecules as such, but which comprise extended arrays of atoms or ions. We look at the structure and bonding in these solids, how the properties of a solid depend on its structure, and how the properties can be modified by changes to the structure.

1.1 INTRODUCTION

To understand the solid state, we need to have some insight into the structure of simple crystals and the forces that hold them together, so it is here that we start this book. Crystal structures are usually determined by the technique of **X-ray crystallography**. This technique relies on the fact that the distances between atoms in crystals are of the same order of magnitude as the wavelength of X-rays (of the order of 1 Å or 100 pm): a crystal thus acts as a three-dimensional diffraction grating to a beam of X-rays. The resulting diffraction pattern can be interpreted to give the internal positions of the atoms in the crystal very precisely, thus defining interatomic distances and angles. (Some of the principles underlying this technique are discussed in Chapter 2, where we review the physical methods available for characterizing solids.) Most of the structures discussed in this book will have been determined in this way.

The structures of many inorganic crystal structures can be discussed in terms of the simple packing of spheres, so we will consider this first, before moving on to the more formal classification of crystals.

1.2 CLOSE-PACKING

Think for the moment of an atom as a small hard sphere. Figure 1.1 shows two possible arrangements for a layer of such identical atoms. On squeezing the square layer in Figure 1.1 (a), the spheres would move to the positions in Figure 1.1 (b) so that the layer takes up less space. The layer in Figure 1.1 (b) (layer A) is called **close-packed**. To build up a close-packed structure in three-dimensions we must now add a second layer (layer B). The spheres of the second layer sit in half of the hollows of the first layer: these have been marked with dots and crosses. The layer B in Figure 1.2 sits over the hollows marked with a cross (although it makes no difference which type we chose). When we add a third layer, there are two possible positions where it can go. First, it could go directly over layer A, in the unmarked hollows: if we then repeated this stacking sequence we would build up the layers ABABABA ...and so on. This is known as **hexagonal close-packing (*hcp*)** (Figure 1.3(a)). In this structure, the hollows marked with a dot are never occupied by spheres, leaving very small channels through the layers (Figure 1.3(b)).

Second, the third layer could be positioned over those hollows marked with a dot. This third layer, which we could label C, would not be directly over either A or B, and the stacking sequence when repeated would be ABC ABC AB...and so on. This is known as **cubic close-packing (*ccp*)** (Figure 1.4). (The names *hexagonal* and *cubic* for these structures arise from the resulting symmetry of the structure—this will be discussed more fully later on.)

Close-packing represents the most efficient use of space when packing identical spheres—the spheres occupy 74% of the volume: the **packing efficiency** is said to be 74%. Each sphere in the structure is surrounded by *twelve* equidistant neighbours—six in the same layer, three in the layer above and three in the layer below: the **coordination number** of an atom in a close-packed structure is thus 12.

Another important feature of close-packed structures is the shape and number of the small amounts of space trapped in between the spheres. Two different types of space are contained within a close-packed structure: the first we will consider is called an **octahedral hole**. Figure 1.5(a) shows two close-packed layers again but now with the octahedral holes shaded. Six spheres surround each of these holes: three in layer A and three in layer B. The centres of these spheres lay at the corners

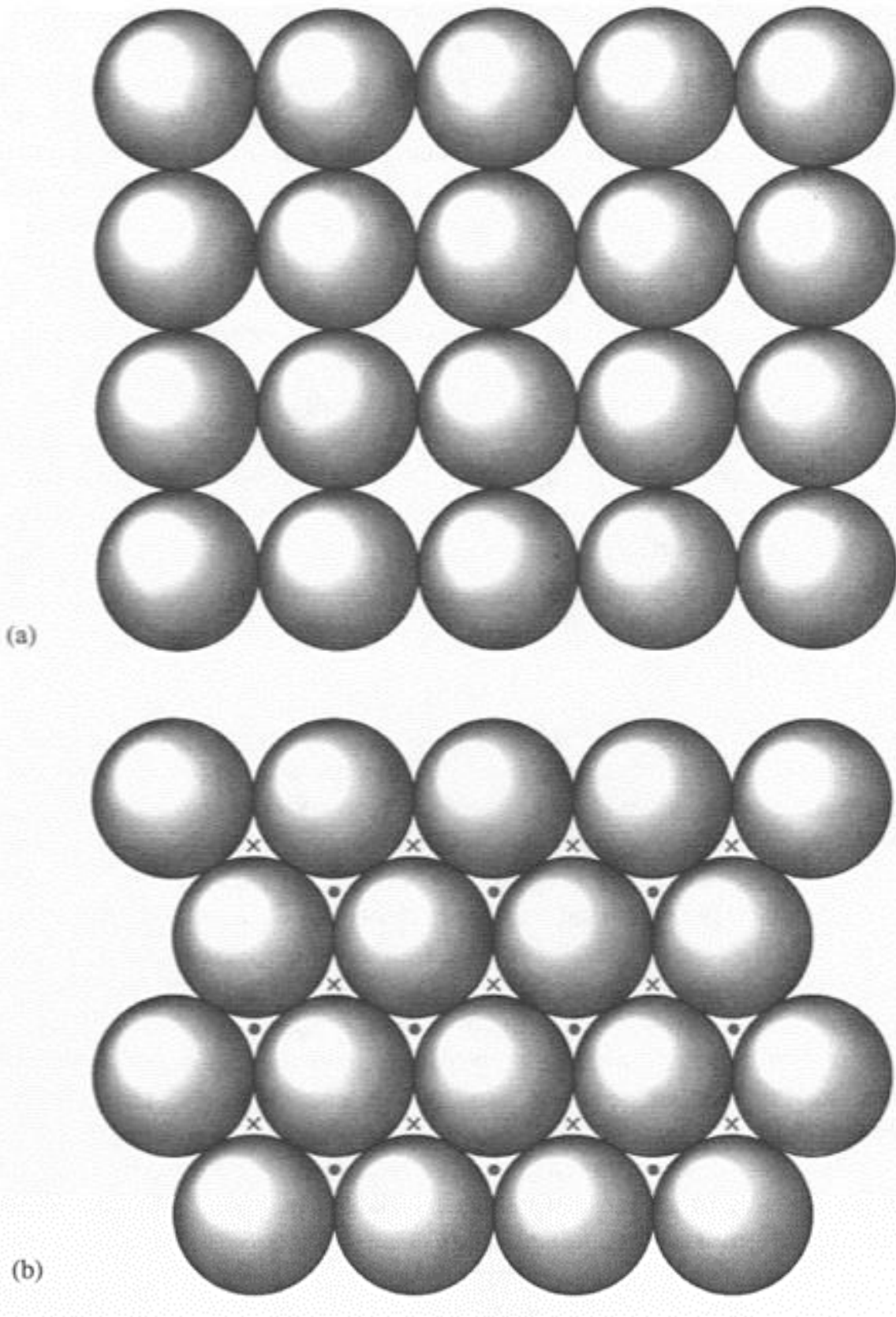


FIGURE 1.1 (a) A square array of spheres; (b) a close-packed layer of spheres.

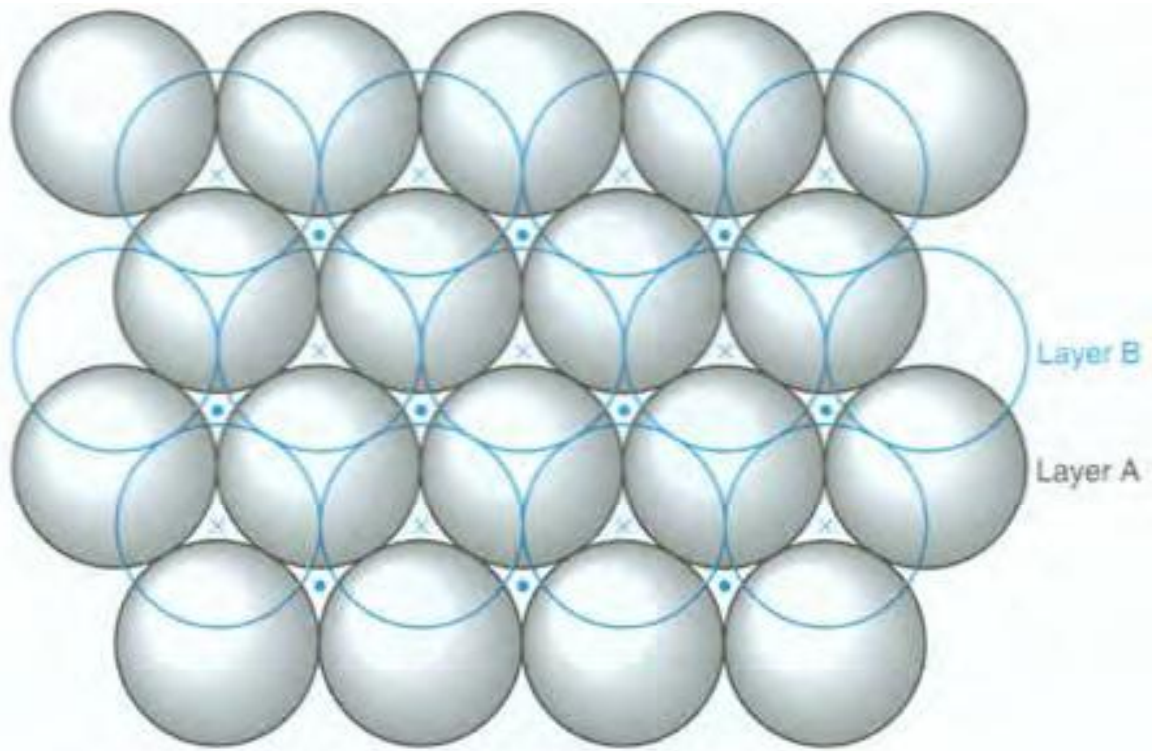


FIGURE 1.2 Two layers of close-packed spheres.

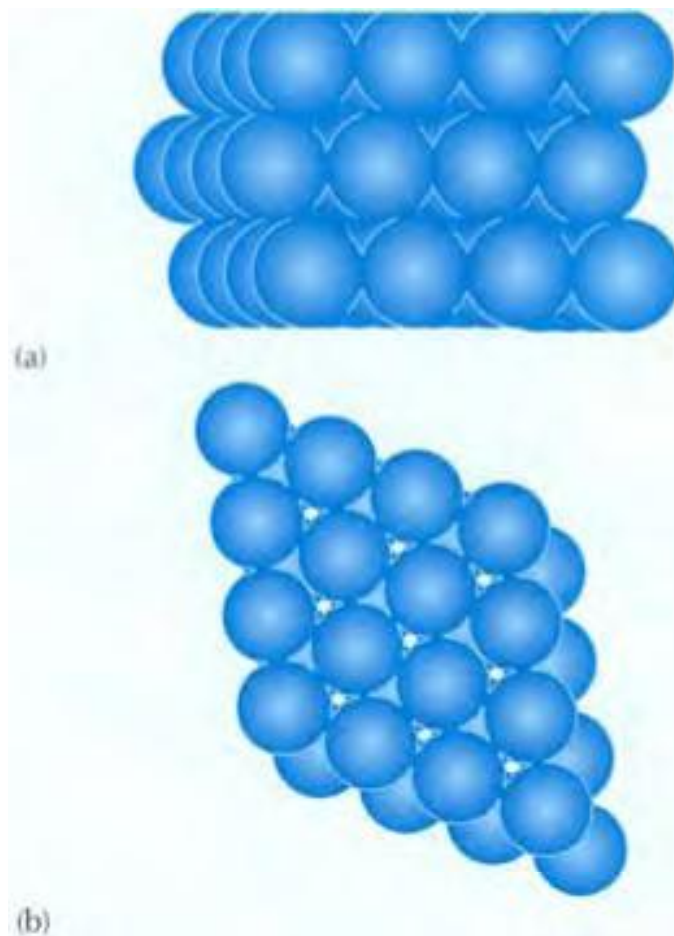


FIGURE 1.3 (a) Three *hcp* layers showing the ABAB...stacking sequence; (b) three *hcp* layers showing the narrow channels through the layers.

of an octahedron, hence the name (Figure 1.5(b)). If n spheres are in the array, then there are also n octahedral holes.

Similarly, Figure 1.6(a) shows two close-packed layers, now with the second type of space, **tetrahedral holes**, shaded. Four spheres surround each of these holes with centres at the corners of a tetrahedron (Figure 1.6(b)). If n spheres are in the array, then there are $2n$ tetrahedral holes.

The octahedral holes in a close-packed structure are much bigger than the tetrahedral holes—they are surrounded by six atoms instead of four. It is a matter of simple geometry to calculate that the radius of a sphere that will just fit in an

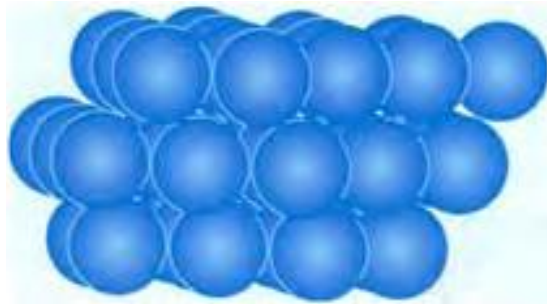


FIGURE 1.4 Three *ccp* layers.

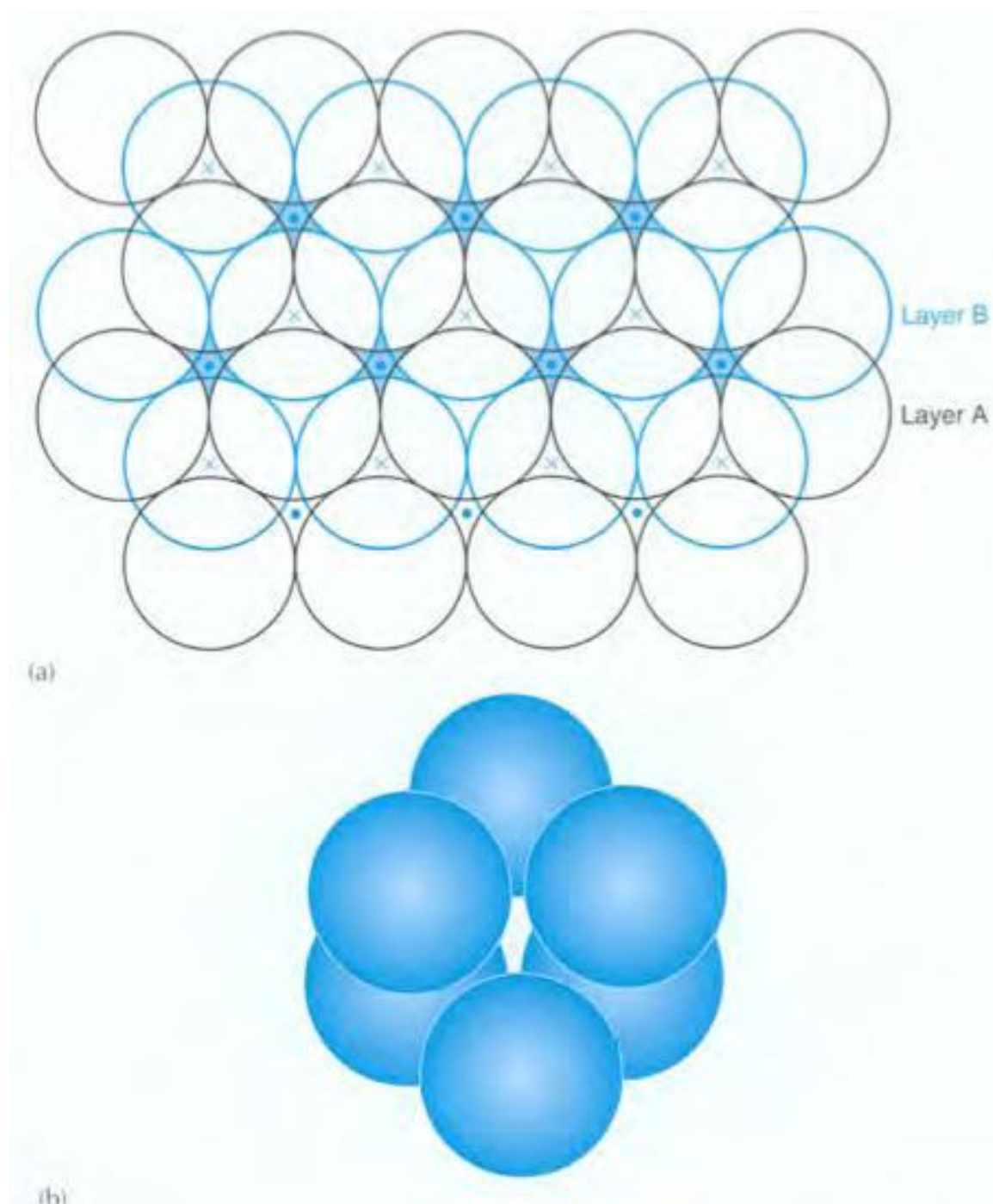


FIGURE 1.5 (a) Two layers of close-packed spheres with the enclosed octahedral holes shaded; (b) a computer representation of an octahedral hole.

octahedral hole in a close-packed array of spheres of radius r is $0.414r$. For a tetrahedral hole, the radius is $0.225r$ (Figure 1.7).

Of course, innumerable stacking sequences are possible when repeating close-packed layers; however, the hexagonal close-packed and cubic close-packed are those of

maximum simplicity and are most commonly encountered in the crystal structures of the noble gases and of the metallic elements. Only two other stacking sequences are found in perfect crystals of the elements: an ABAC repeat in La, Pr, Nd, and Am, and a nine-layer repeat ABACACBCB in Sm.

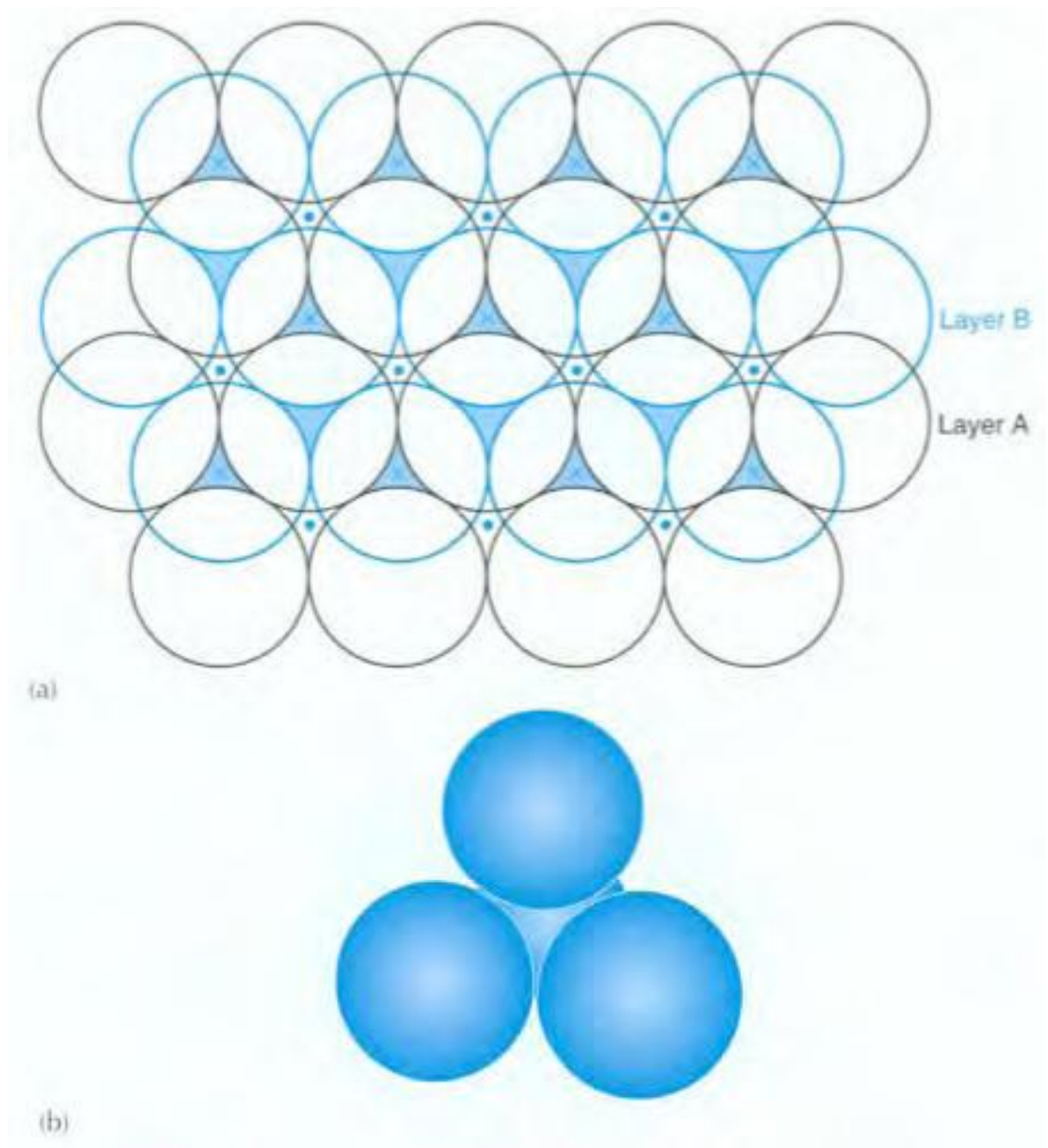


FIGURE 1.6 (a) Two layers of close-packed spheres with the tetrahedral holes shaded; (b) a computer representation of a tetrahedral hole.

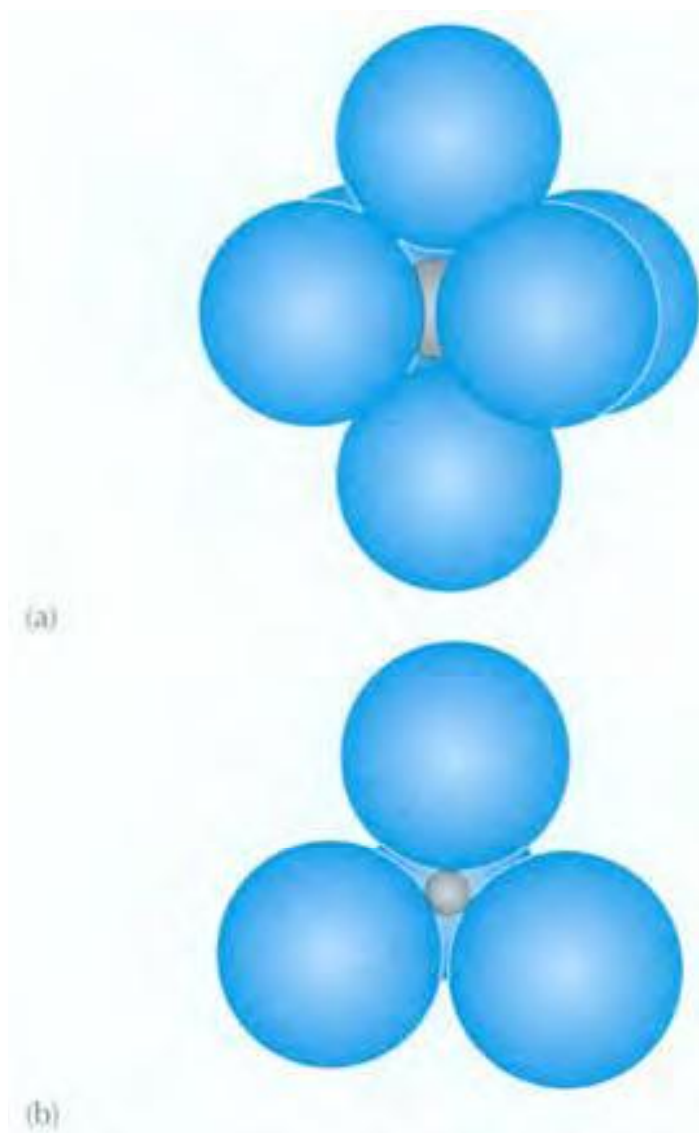


FIGURE 1.7 (a) A sphere of radius $0.414r$ fitting into an octahedral hole; (b) a sphere of radius $0.225r$ fitting into a tetrahedral hole.

1.3 BODY-CENTRED AND PRIMITIVE STRUCTURES

Some metals do not adopt a close-packed structure but have a slightly less efficient packing method: this is the **body-centred cubic structure (*bcc*)**, shown in Figure 1.8. (Unlike the previous diagrams, the positions of the atoms are now represented here—and in subsequent diagrams—by small spheres which do not touch: this is merely a device to open up the structure and allow it to be seen more clearly—the whole question of atom and ion size is discussed in Section 1.6.4.) In this structure an atom in the middle of a cube is surrounded by *eight identical and equidistant* atoms at the corners of the cube—

the coordination number has dropped from twelve to eight and the packing efficiency is now 68%, compared with 74% for close-packing.

The simplest of the cubic structures is the **primitive cubic structure**. This is built by placing square layers like the one shown in Figure 1.1 (a), directly on top of one another. Figure 1.9(a) illustrates this, and you can see in Figure 1.9(b) that each atom sits at the corner of a cube. The coordination number of an atom in this structure is six. The majority of metals have one of the three basic structures: *hcp*, *ccp*, or *bcc*. Polonium alone adopts the primitive structure. The distribution of the packing types among the most stable forms of the metals at 298 K is shown in Figure 1.10. As we noted earlier, a very few metals have a mixed *hcp/ccp* structure of a more complex type. The structures of the actinides tend to be rather complex and are not included.

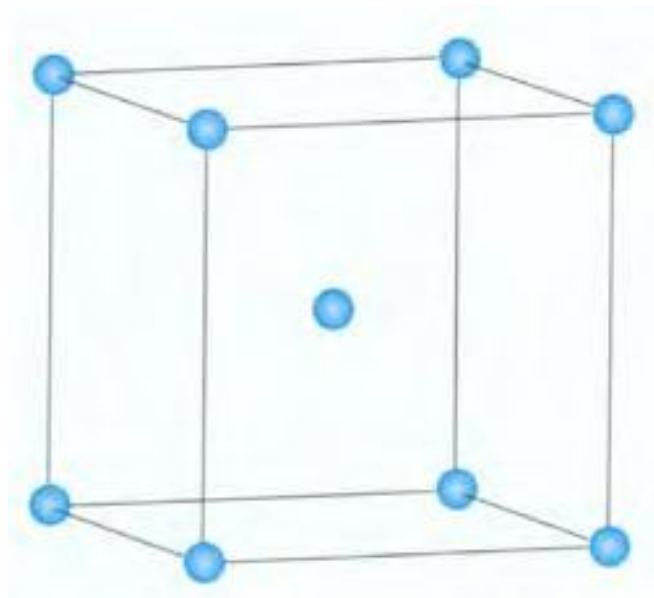


FIGURE 1.8 Body-centred cubic array.

1.4 SYMMETRY

Before we take the discussion of crystalline structures any further, we will look at the symmetry displayed by structures. The concept of symmetry is an extremely useful one when it comes to describing the shapes of both individual molecules and regular repeating structures, as it provides a way of describing similar features in different structures so that they become unifying features. The symmetry of objects in everyday life is something that we tend to take for granted and recognize easily without having to think about it. Take some simple examples illustrated in Figure 1.11. If you imagine a mirror dividing the spoon in half along the plane indicated, then you can see that

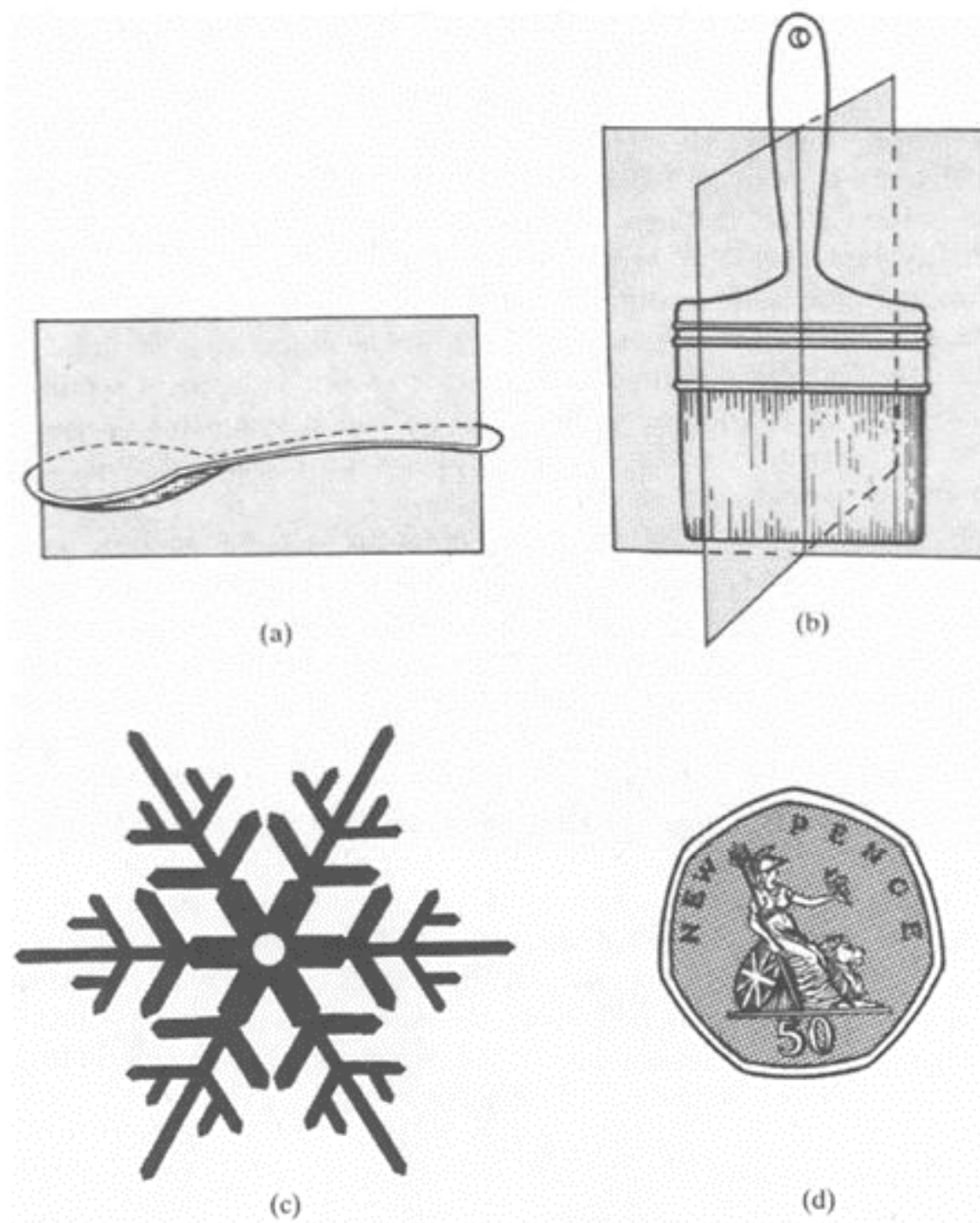


FIGURE 1.11 Common objects displaying symmetry: (a) a spoon, (b) a paintbrush, (c) a snowflake, and (d) a 50p coin.

one-half of the spoon is a mirror image or reflection of the other. Similarly, with the paintbrush, only now two mirror planes at right angles divide it.

Objects can also possess rotational symmetry. In Figure 1.11(c) imagine an axle passing through the centre of the snowflake; in the same way as a wheel rotates about an

axle, if the snowflake is rotated through $\frac{1}{6}$ of a revolution, then the new position is indistinguishable from the old. Similarly, in Figure 1.11(d), rotating the 50p coin by $\frac{1}{7}$ of a revolution brings us to the same position as we started (ignoring the pattern on the surface). The symmetry possessed by a single object that describes the repetition of identical parts of the object is known as its **point symmetry**.

Actions such as rotating a molecule are called **symmetry operations**, and the rotational axes and mirror planes possessed by objects are examples of **symmetry elements**.

Two forms of symmetry notation are commonly used. As chemists, you will come across both. The **Schoenflies** notation is useful for describing the point symmetry of individual molecules and is used by spectroscopists. The **Hermann-Mauguin** notation can be used to describe the point symmetry of individual molecules but in addition can also describe the relationship of different molecules to one another in space—their so-called **space-symmetry**—and so is the form most commonly met in crystallography and the solid state. We give here the Schoenflies notation in parentheses after the Hermann-Mauguin notation.

1.4.1 AXES OF SYMMETRY

As discussed previously for the snowflake and the 50p coin, molecules and crystals can also possess rotational symmetry. Figure 1.12 illustrates this for several molecules.

In Figure 1.12(a) the rotational axis is shown as a vertical line through the O atom in OF_2 ; rotation about this line by 180° in the direction of the arrow, produces an identical looking molecule. The line about which the molecule rotates is called an **axis of symmetry**, and in this case, it is a twofold axis because we have to perform the operation twice to return the molecule to its starting position.

Axes of symmetry are denoted by the symbol n (C_n), where n is the order of the axis. Therefore, the rotational axis of the OF_2 molecule is 2 (C_2).

The BF_3 molecule in Figure 1.12(b) possesses a threefold axis of symmetry, 3 (C_3), because each $\frac{1}{3}$ of a revolution leaves the molecule looking the same, and three turns brings the molecule back to its starting position. In the same way, the XeF_4 molecule in (c) has a fourfold axis, 4 (C_4), and four quarter turns are necessary to bring it back to the beginning. All linear molecules have an ∞ (C_∞) axis, which is illustrated for the BeF_2 molecule in (d); however small a fraction of a circle it is rotated through, it always looks identical. The smallest rotation possible is $1/\infty$, and so the axis is an infinite-order axis of symmetry.

1.4.2 PLANES OF SYMMETRY

Mirror planes occur in isolated molecules and in crystals, such that everything on one side of the plane is a mirror image of the other. In a structure, such a mirror

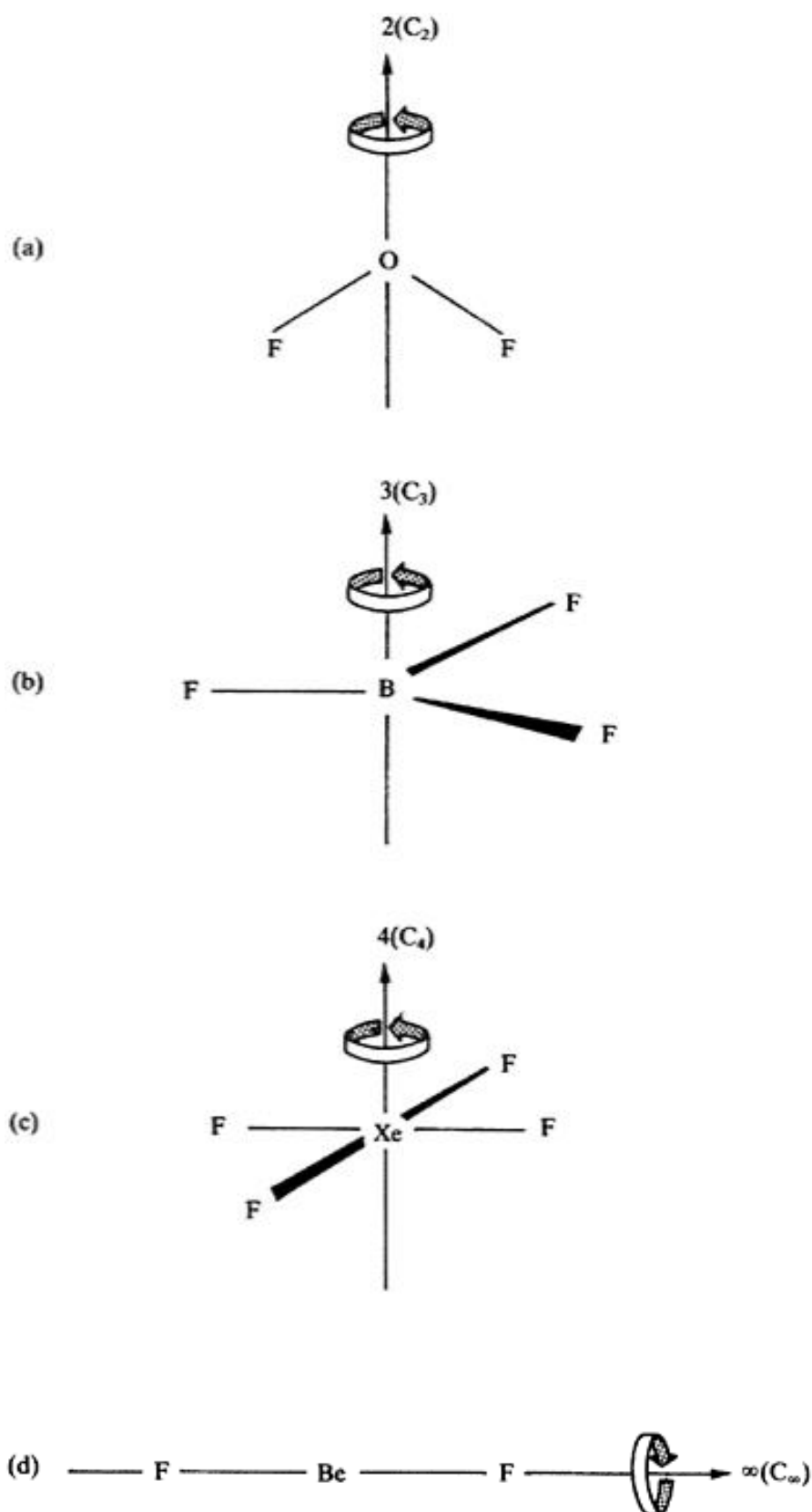


FIGURE 1.12 Axes of symmetry in molecules: (a) twofold axis in OF_2 , (b)

threefold axis in BF_3 , (c) fourfold axis in XeF_4 , and (d) ∞ -fold axis in BeF_2 .

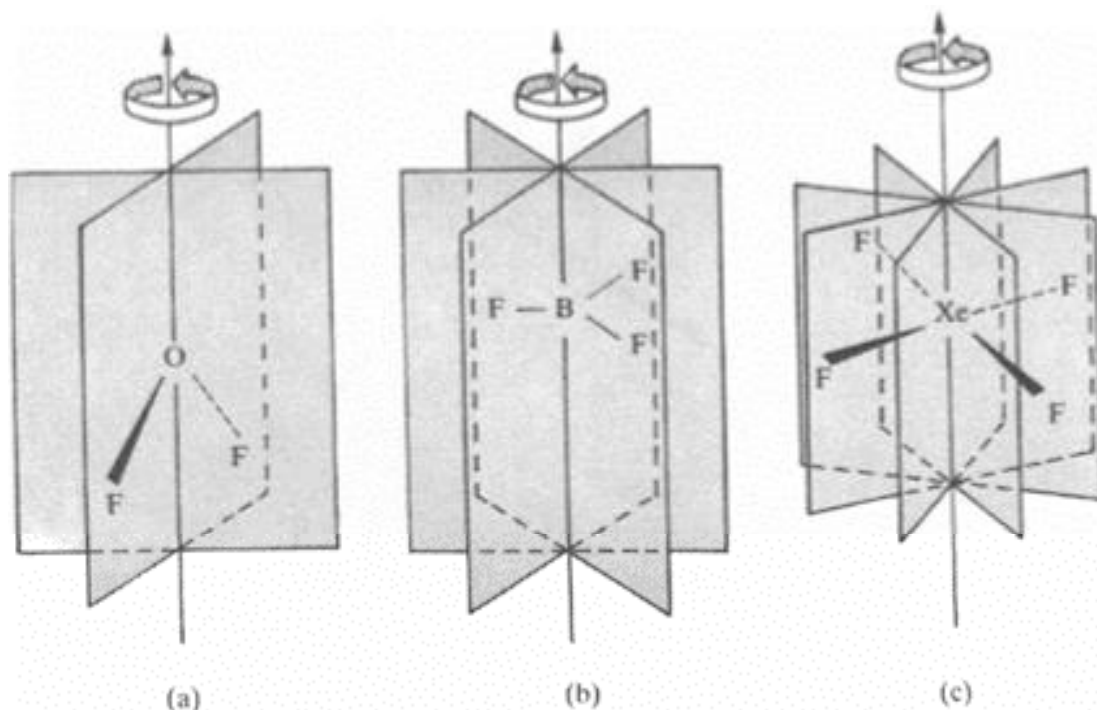


FIGURE 1.13 Planes of symmetry in molecules: (a) planes of symmetry in OF_2 , (b) planes of symmetry in BF_3 , and (c) planes of symmetry in XeF_4 .

plane is known as a **plane of symmetry** and is given the symbol \mathbf{m} (σ). Molecules may possess one or more planes of symmetry, and the diagrams in Figure 1.13 illustrate some examples. The planar OF_2 molecule has two planes of symmetry (Figure 1.13(a)), one is the plane of the molecule, and the other is at right angles to this. For all planar molecules, the plane of the molecule is a plane of symmetry. The diagrams for BF_3 and XeF_4 (also planar molecules) only show the planes of symmetry which are perpendicular to the plane of the molecule.

1.4.3 INVERSION

The third symmetry operation that we show in this section is called **inversion** through a centre of symmetry and is given the symbol $\bar{\mathbf{1}}$ (i). In this operation you have to imagine a line drawn from any atom in the molecule, through the centre of symmetry and then continued for the same distance the other side; if for every atom, this meets with an identical atom on the other side, then the molecule has a centre of symmetry. Of the molecules in Figure 1.12, XeF_4 and BeF_2 both have a centre of symmetry, and BF_3 and OF_2 do not.

1.4.4 INVERSION AXES AND IMPROPER SYMMETRY AXES

The final symmetry element is described differently by the two systems, although both descriptions use a combination of the symmetry elements described previously. The Hermann-Mauguin **inversion axis** is a combination of rotation and inversion and is given the symbol \bar{n} . The symmetry element consists of a rotation by $1/n$ of a revolution about the axis, followed by inversion through the centre of symmetry. An example of an $\bar{4}$ inversion axis is shown in Figure 1.14 for a tetrahedral molecule such as CF_4 . The molecule is shown inside a cube as this makes it easier to see the

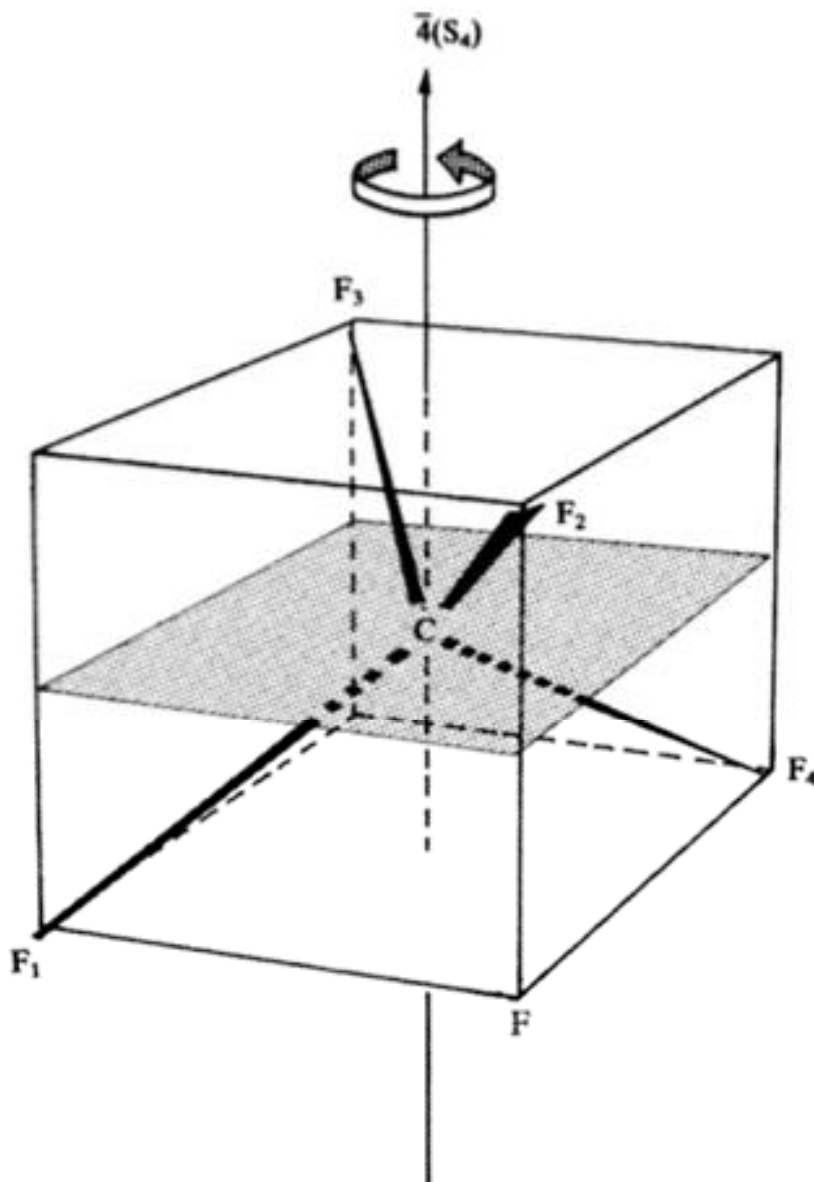


FIGURE 1.14 The $\bar{4}(S_4)$ inversion (improper) axis of symmetry in the tetrahedral CF_4 molecule.

symmetry elements. Rotation about the axis through 90° takes F_1 to the position shown as a dotted F ; inversion through the centre then takes this atom to the F_3 position.

The equivalent symmetry element in the Schoenflies notation is the **improper axis of symmetry, S_n** , which is a combination of rotation and reflection. The symmetry element consists of a rotation by $1/n$ of a revolution about the axis, followed by reflection through a plane at right angles to the axis. Figure 1.14 thus presents an S_4 axis, where the F_1 rotates to the dotted position and then reflects to F_2 . The equivalent inversion axes and improper symmetry axes for the two systems are shown in Table 1.1.

1.4.5 SYMMETRY IN CRYSTALS

The discussion so far has only shown the symmetry elements that belong to individual molecules. However, in the solid state, we are interested in regular arrays of

TABLE 1.1 Equivalent symmetry elements in the Schoenflies and Hermann-Mauguin Systems

Schoenflies	Hermann-Mauguin
$S_1 \equiv m$	$\bar{2} \equiv m$
$S_2 \equiv i$	$\bar{1} \equiv i$
S_3	$\bar{6}$
S_4	$\bar{4}$
S_6	$\bar{3}$

atoms, ions, and molecules, and they too are related by these same symmetry elements. Figure 1.15 gives examples (not real) of how molecules could be arranged in a crystal. In (a), two OF_2 molecules are related to one another by a plane of symmetry; in (b), three OF_2 molecules are related to one another by a threefold axis of symmetry; in (c), two OF_2 molecules are related by a centre of inversion. Notice that in both (b) and (c), the molecules are related in space by a symmetry element that they themselves do not possess, this is said to be their **site symmetry**.

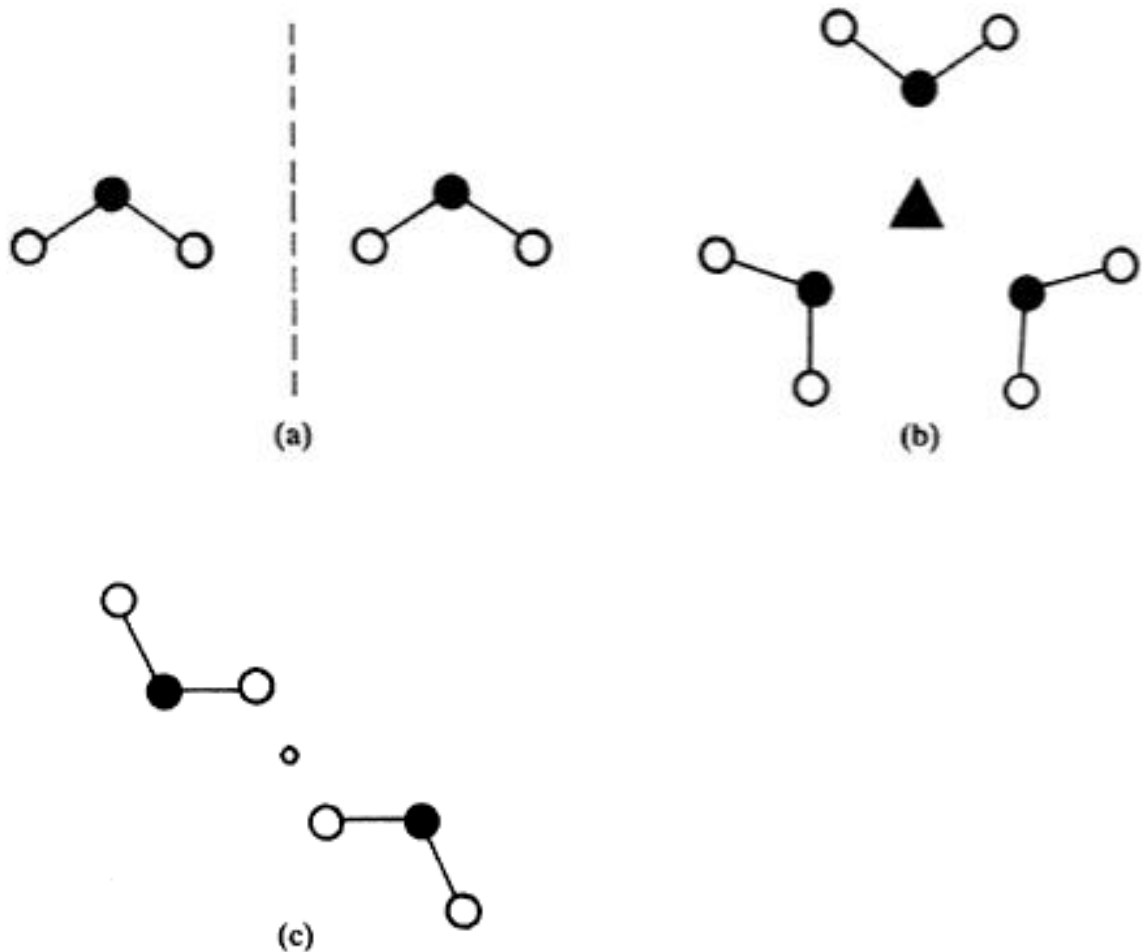


FIGURE 1.15 Symmetry in solids: (a) two OF₂ molecules related by a plane of symmetry, (b) three OF₂ molecules related by a threefold axis of symmetry, and (c) two OF₂ molecules related by a centre of inversion.

1.5 LATTICES AND UNIT CELLS

Crystals are regular shaped solid particles with flat shiny faces. It was first noted by Robert Hooke in 1664 that the regularity of their external appearance is a reflection of a high degree of internal order. Crystals of the same substance, however, vary in shape considerably. Steno observed in 1671 that this is not because their internal structure varies but because some faces develop more than others do. The angle between similar faces on different crystals of the same substance is always identical. The constancy of the interfacial angles reflects the internal order within the crystals. Each crystal is derived from a basic 'building block' that continuously repeats, in all directions, in a perfectly regular way. This building block is known as the **unit cell**.

To talk about and compare the many thousands of crystal structures that are known, there has to be a way of defining and categorizing the structures. This is achieved by defining the shape and symmetry of each unit cell as well as its size and the positions of the atoms within it.

1.5.1 LATTICES

The simplest regular array is a line of evenly spaced objects, such as those depicted by the commas in Figure 1.16(a). There is a dot at the same place in each object: if we now remove the objects leaving the dots, we have a line of equally spaced dots, spacing a , (Figure 1.16(b)). The line of dots is called the **lattice**, and each **lattice point** (dot) must have *identical surroundings*. This is the only example of a one-dimensional lattice and it can vary only in the spacing a . Five two-dimensional lattices are possible, and examples of these can be seen every day in wallpapers and tiling.

1.5.2 ONE- AND TWO-DIMENSIONAL UNIT CELLS

The unit cell for the one-dimensional lattice in Figure 1.16(a) lies between the two vertical lines. If we took this unit cell and repeated it over again, we would reproduce the original array. Notice that it does not matter where in the structure we place the

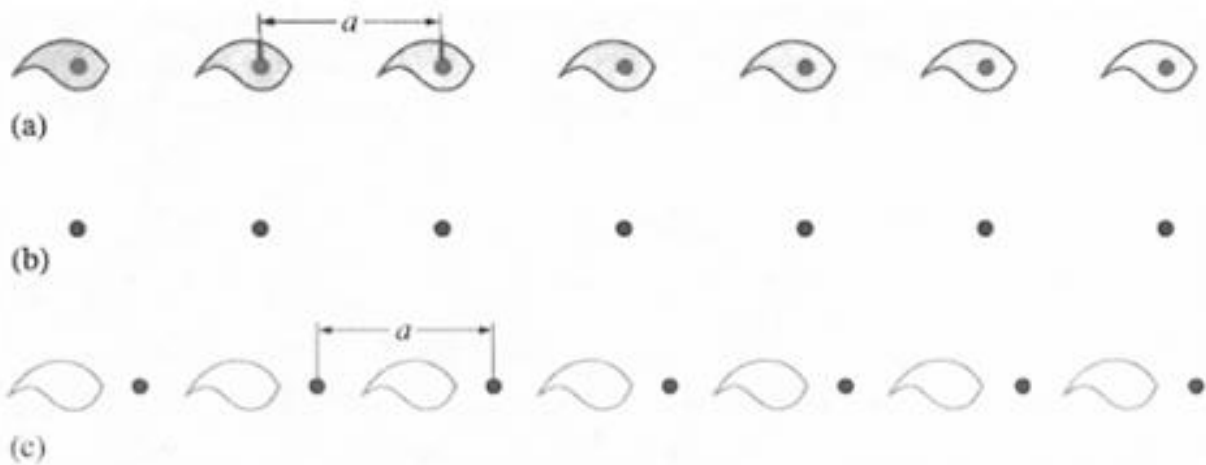


FIGURE 1.16 A one-dimensional lattice (a,b) and the choice of unit cells (c).

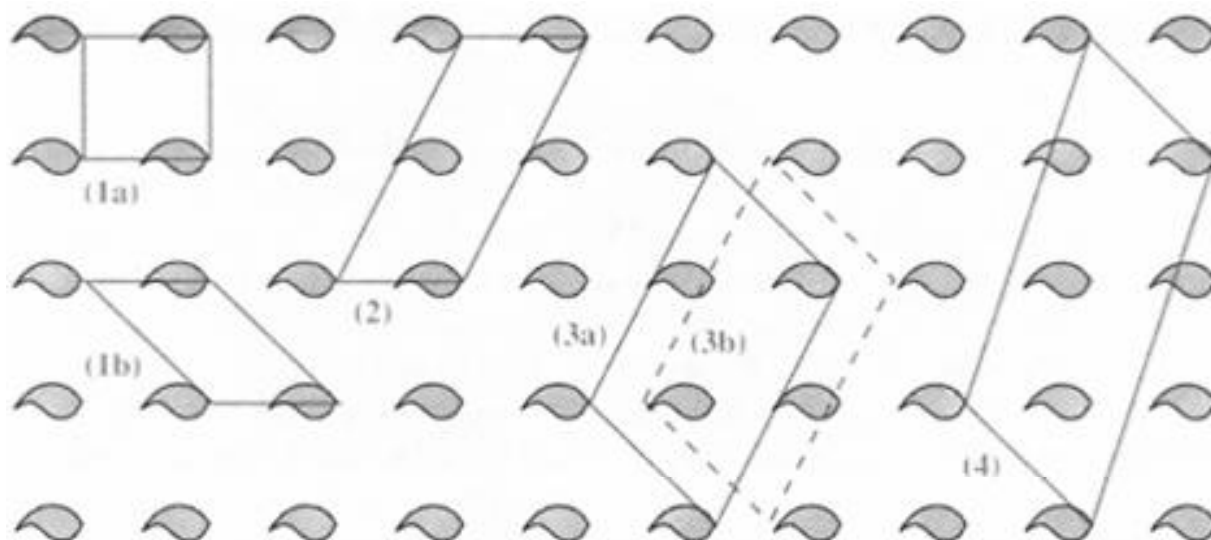


FIGURE 1.17 Choice of unit cell in a square two-dimensional lattice.

lattice points as long as they each have identical surroundings. In Figure 1.16(c), we have moved the lattice points and the unit cell, but repeating this unit cell will still give the same array—we have simply moved the origin of the unit cell. There is never one unique unit cell that is ‘correct.’ Many can always be chosen, and the choice depends both on convenience and convention. This is equally true in two and three dimensions.

The unit cells for the two-dimensional lattices are parallelograms with their corners at equivalent positions in the array (i.e., the corners of a unit cell are lattice points). In Figure 1.17, we show a square array with several different unit cells depicted. All of these, if repeated, would reproduce the array: it is conventional to choose the smallest cell that fully represents the symmetry of the structure. Both unit cells (1a) and (1b) are the same size but clearly (1a) shows that it is a square array, and this would be the conventional choice. Figure 1.18 demonstrates the same principles but for a centred rectangular array, where (a) would be the conventional choice because it includes information on the centring; the smaller unit cell (b) loses this information. It is always possible to define a non-centred oblique unit cell, but doing so may lose information about the symmetry of the lattice.

Unit cells, such as (1a) and (1b) in Figure 1.17 and (b) in Figure 1.18, have a lattice point at each corner. However, they each contain one lattice point because four adjacent unit cells share each lattice point. They are known as **primitive unit cells** and are given the symbol **P**. The unit cell marked (a) in Figure 1.18 contains



FIGURE 1.18 Choice of unit cell in a centred-rectangular lattice.

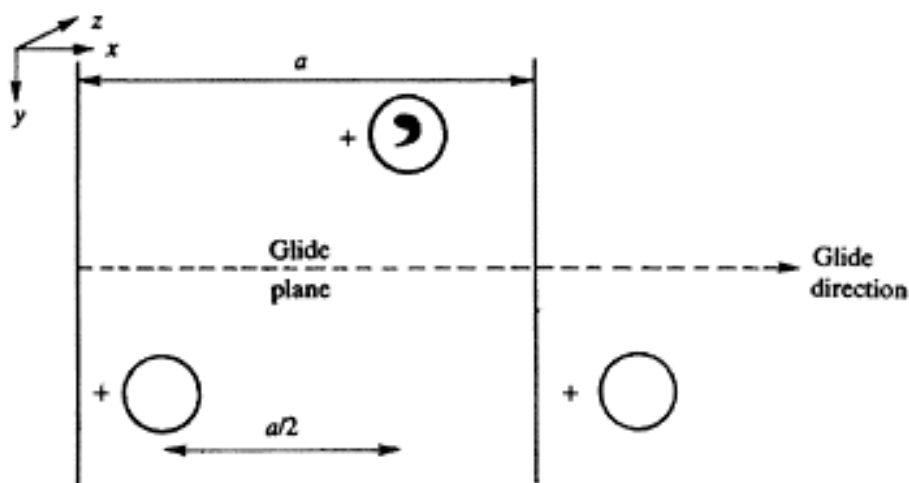


FIGURE 1.19 An a glide perpendicular to b .

two lattice points—one from the shared four corners and one totally enclosed within the cell. This cell is said to be **centred** and is given the symbol **C**.

1.5.3 TRANSLATIONS SYMMETRY ELEMENTS

Section 1.4 introduced the idea of symmetry, both in individual molecules and for extended arrays of molecules, such as are found in crystals. Before going on to discuss three-dimensional lattices and unit cells, it is important to introduce two more symmetry elements; these elements involve translation and are only found in the solid state.

The glide plane combines translation with reflection. Figure 1.19 is an example of this symmetry element. The diagram shows part of a repeating three-dimensional structure projected on to the plane of the page; the circle represents a molecule or ion in the structure and there is distance a between identical positions in the structure. The + sign next to the circle indicates that the molecule lies above the plane of the page in the z direction. The plane of symmetry is in the xz plane perpendicular to the paper, and is indicated by the dashed line. The symmetry element consists of reflection through this plane of symmetry, followed by translation. In this case, the translation can be either in the x or in the z direction (or along a diagonal), and the translation distance is half of the

repeat distance in that direction. In the example illustrated, the translation takes place in the x direction. The repeat distance between identical molecules is a , and so the translation is by $a/2$, and the symmetry element is called an a glide. You will notice two things about the molecule generated by this symmetry element: first, it still has a + sign against it, because the reflection in the plane leaves the z coordinate the same and second, it now has a comma on it. Some molecules when they are reflected through a plane of symmetry are enantiomorphous, which means that they are not superimposable on their mirror image: the presence of the comma indicates that this molecule could be an enantiomorph.

The **screw axis** combines translation with rotation. Screw axes have the general symbol n_i where n is the rotational order of the axis (i.e., twofold, threefold, etc.), and the translation distance is given by the ratio i/n . Figure 1.20 illustrates a 2_1 screw axis. In this example, the screw axis lies along z and so the translation must be in

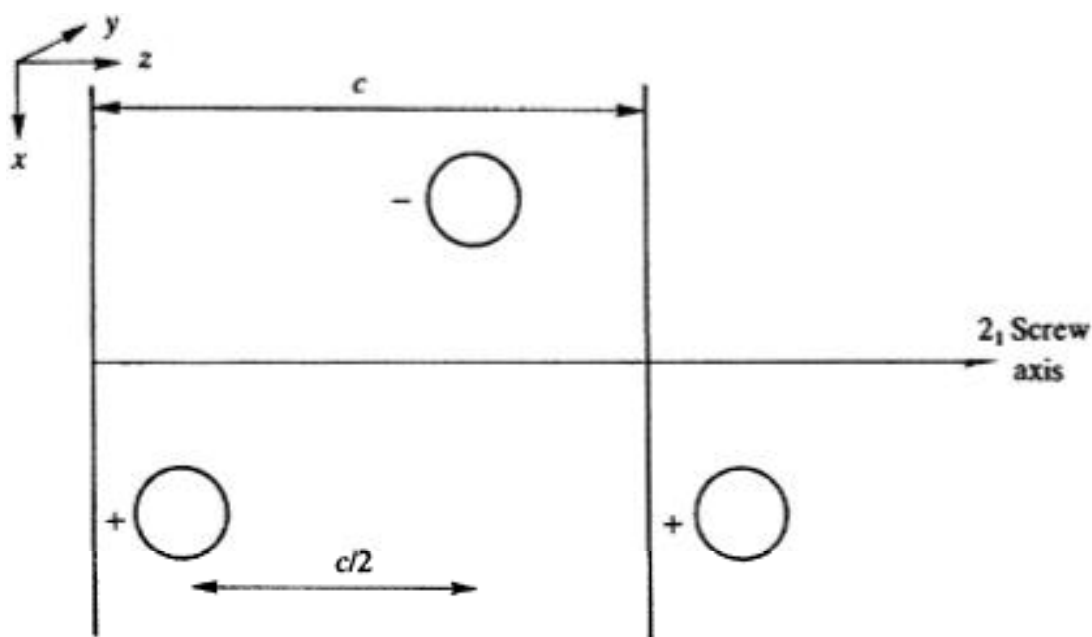


FIGURE 1.20 A 2_1 screw axis along z .

the z direction, by $c/2$, where c is the repeat distance in the z direction. Notice that in this case the molecule starts above the plane of the paper (indicated by the + sign) but the effect of a twofold rotation is to take it below the plane of the paper (- sign). Figure 1.21 probably illustrates this more clearly, and shows the different effects that rotational and screw axes of the same order have on a repeating structure. Rotational and screw axes produce objects that are superimposable on the original. All other symmetry elements—glide plane, mirror plane, inversion centre, and inversion axis—produce a mirror image of the original.

1.5.4 THREE-DIMENSIONAL UNIT CELLS

The unit cell of a three-dimensional lattice is a parallelepiped defined by three distances a , b , and c , and three angles α , β , and γ , as shown in Figure 1.22. Because the unit cells

are the basic building blocks of the crystals, they must be space-filling (i.e., they must pack together to fill all space). All the possible unit cell shapes that can fulfill this criterion are illustrated in Figure 1.23 and their specifications are listed in Table 1.2. These are known as the **seven crystal systems** or **classes**. These unit cell shapes are determined by minimum symmetry requirements which are also detailed in Table 1.2.

The three-dimensional unit cell includes *four* different types (see Figure 1.24):

1. The **primitive** unit cell—symbol **P**—has a lattice point at each corner.
2. The **body-centred** unit cell—symbol **I**—has a lattice point at each corner and one at the centre of the cell.
3. The **face-centred** unit cell—symbol **F**—has a lattice point at each corner and one in the centre of each face.
4. The **face-centred** unit cell—symbol **A**, **B**, or **C**—has a lattice point at each corner, and one in the centres of one pair of opposite faces (e.g., an A-centred cell has lattice points in the centres of the *bc* faces).

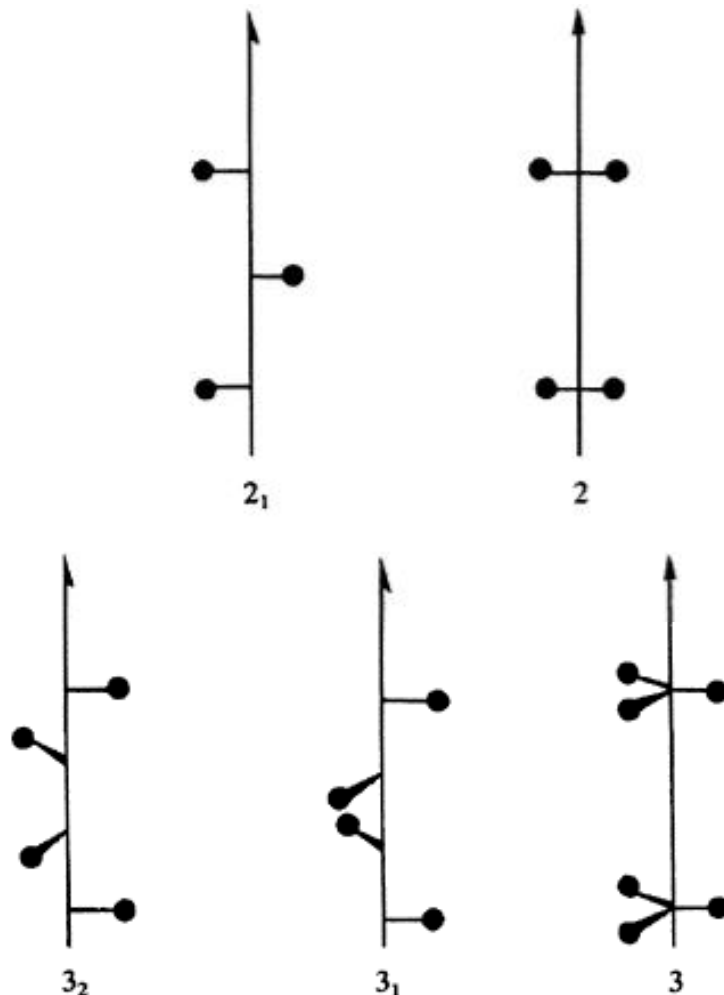


FIGURE 1.21 Comparison of the effects of twofold and threefold rotation axes and screw axes.

When these four types of lattice are combined with the 7 possible unit cell shapes, 14 permissible **Bravais lattices** (Table 1.3) are produced. (It is not possible to combine some of the shapes and lattice types and retain the symmetry requirements listed in Table 1.2. For instance, it is not possible to have an A-centred, cubic, unit cell; if only two of the six faces are centred, the unit cell necessarily loses its cubic symmetry.)

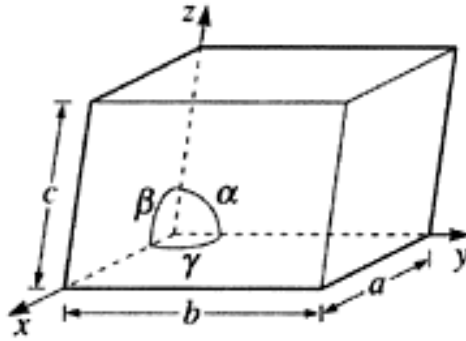


FIGURE 1.22 Definition of axes, unit cell dimensions, and angles for a general unit cell.

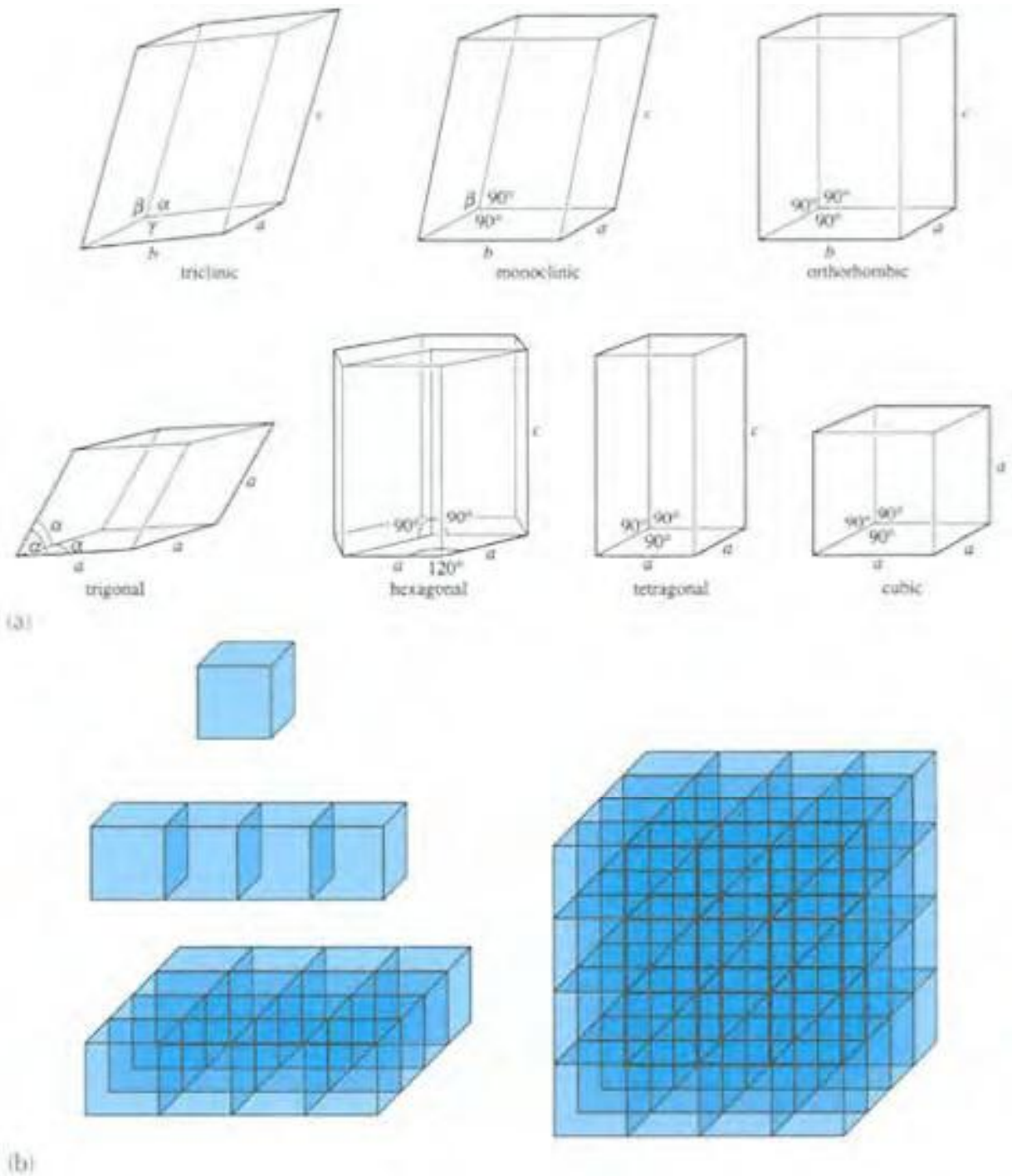


FIGURE 1.23 (a) The unit cells of the seven crystal systems, (b) Assemblies of cubic unit cells in one, two, and three dimensions.

The symmetry of a crystal is a point group taken from a point at the centre of a perfect crystal. Only certain point groups are possible because of the constraint made by the fact that unit cells must be able to stack exactly with no spaces—so only one-, two-, three-,

four-, and sixfold axes are possible. Combining this with planes of symmetry and centres of symmetry, we find 32 point groups that can describe the shapes of perfect crystals.

If we combine the 32 crystal point groups with the 14 Bravais lattices we find 230 three-dimensional **space groups** that crystal structures can adopt (i.e., 230

TABLE 1.2 The seven crystal systems

System	Unit cell	Minimum symmetry requirements
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$ $a \neq b \neq c$	None
Monoclinic	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$ $a \neq b \neq c$	One twofold axis or one symmetry plane
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$ $a \neq b \neq c$	Any combination of three mutually perpendicular twofold axes or planes of symmetry
Trigonal/rhombohedral	$\alpha = \beta = \gamma \neq 90^\circ$ $a = b = c$	One threefold axis
Hexagonal	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ $a = b \neq c$	One sixfold axis or one sixfold improper axis
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$ $a = b \neq c$	One fourfold axis or one fourfold improper axis
Cubic	$\alpha = \beta = \gamma = 90^\circ$ $a = b = c$	Four threefold axes at $109^\circ 28'$ to each other

different space-filling patterns)! These are all documented in the International Tables for Crystallography (see Bibliography at end of the book).

It is important not to lose sight of the fact that the lattice points represent equivalent positions in a crystal structure and not atoms. In a real crystal, an atom, a complex ion, a molecule, or even a group of molecules could occupy a lattice point. The lattice points are used to simplify the repeating patterns within a structure, but they tell us nothing of the chemistry or bonding within the crystal—for that we have to include the atomic positions: this we will do later in the chapter when we look at some real structures.

It is instructive to note how much of a structure these various types of unit cell represent. We noted a difference between the centred and primitive two-dimensional unit cell where the centred cell contains two lattice points whereas the primitive cell contains only one. We can work out similar occupancies for the three-dimensional case. The number of unit cells sharing a particular molecule depends on its site. A corner site is shared by eight unit cells, an edge site by four, a face site by two and a molecule at the body-centre is not shared by any other unit cell (Figure 1.25). Using these figures, we can work out the number of molecules in each of the four types of cell in Figure 1.24, assuming that one molecule is occupying each lattice point. The results are listed in Table 1.4.

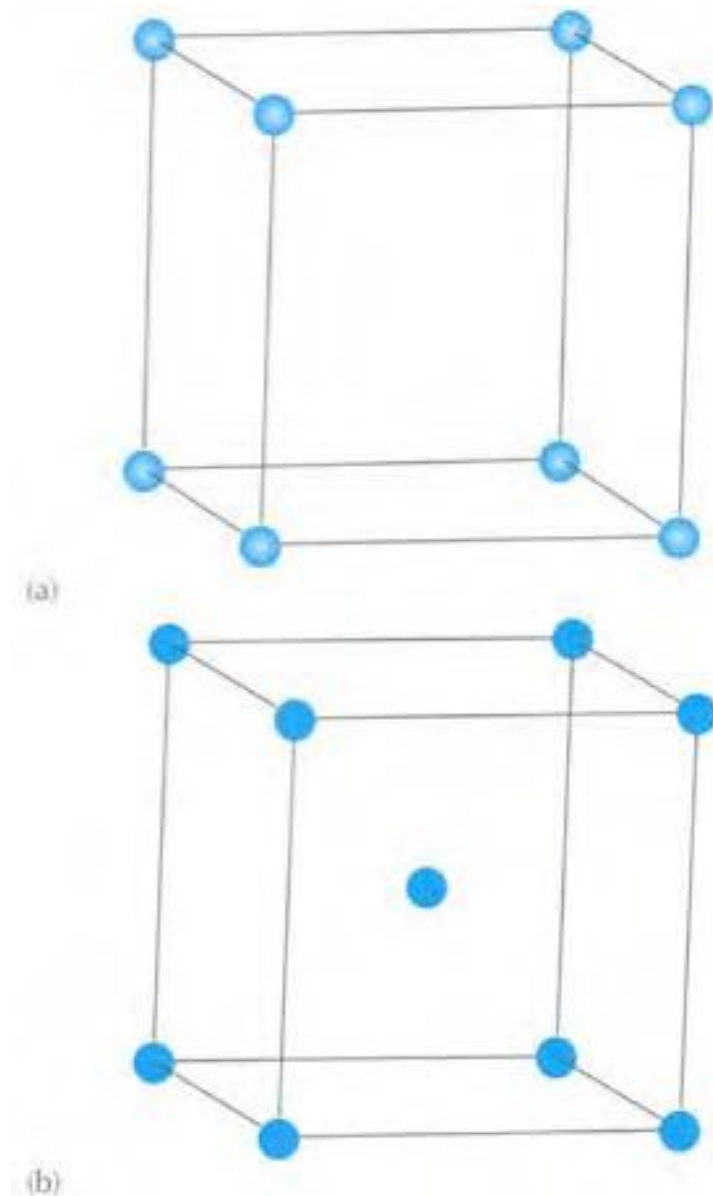


FIGURE 1.24 Primitive (a), body-centred (b), face-centred (c), and face-centred (A, B, or C) (d), unit cells,

1.5.5 MILLER INDICES

The faces of crystals, both when they grow and when they are formed by cleavage, tend to be parallel either to the sides of the unit cell or to planes in the crystal that contain a high density of atoms. It is useful to be able to refer to both crystal faces and to the planes in the crystal in some way—to give them a name—and this is usually done by using **Miller indices**.

First, we will describe how Miller indices are derived for lines in two-dimensional nets, and then move on to look at planes in three-dimensional lattices. Figure 1.26 is a rectangular net with several sets of lines, and a unit cell is marked on each set with the origin of each in the bottom left-hand corner corresponding to the directions of the x and

y axes. A set of parallel lines is defined by two indices, h and k , where h and k are the number of parts into which a and b , the unit cell edges, are divided by the lines. Thus the

indices of a line hk are defined so that the line intercepts a at $\frac{a}{h}$ and b at $\frac{b}{k}$. Start by finding a line next to the one passing through the origin, In the set of lines marked A, the line next to the one passing through the origin

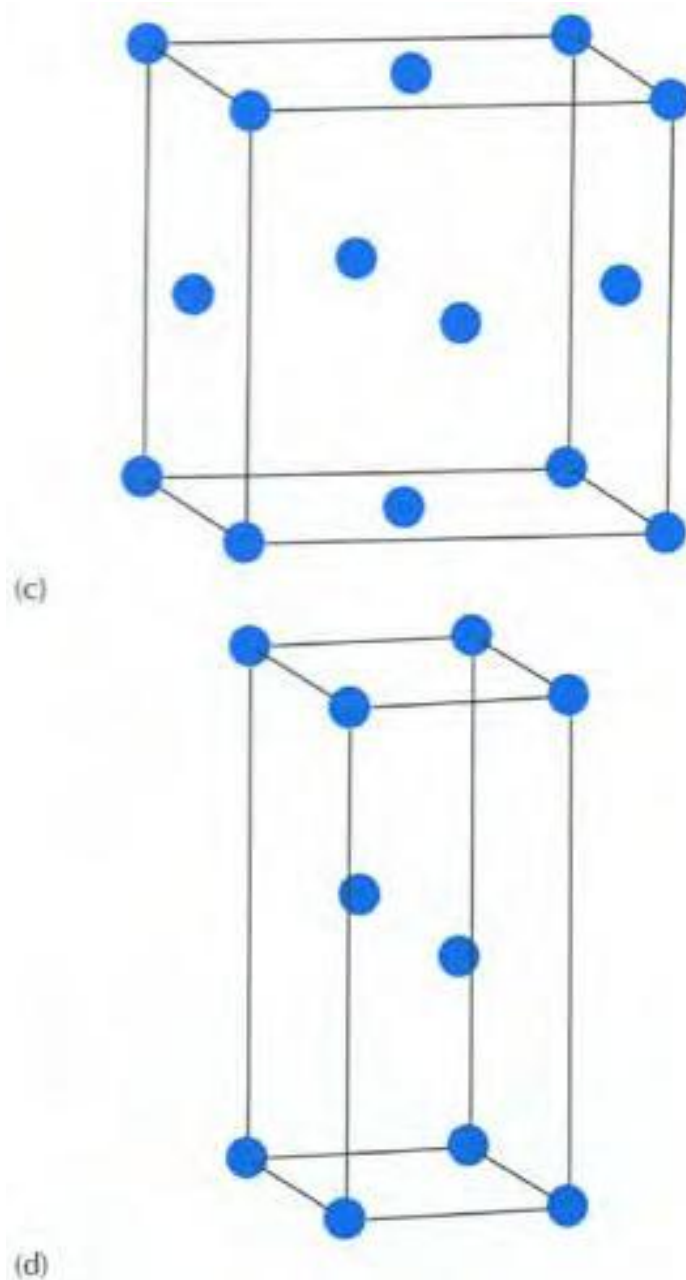


TABLE 1.3 Bravais lattices

Crystal system	Lattice types
Cubic	P, I, F
Tetragonal	P, I

Orthorhombic	P, C, I, F
Hexagonal	P
Trigonal (Rhombohedral)	P/R ^a
Monoclinic	P, C
Triclinic	P

^aThe primitive description of the rhombohedral lattice is normally given the symbol R.

TABLE 1.4 Number of molecules in four types of cells

Name	Symbol	Number of molecules in unit cell
Primitive	P	1
Body-centred	I	2
Face-centred	A or B or C	2
All face-centred	F	4

leaves a undivided but divides b into two; both intercepts lie on the positive side of the origin, therefore, in this case, the indices of the set of lines hk are 12 (referred to as the 'one-two' set). If the set of lines lies parallel to one of the axes then there is no intercept and the index becomes zero. If the intercepted cell edge lies on the negative side of the origin, then the index is written with a bar on the top (e.g., $\bar{2}$), known as 'bar-two'. Notice that if we had selected the line on the other side of the origin in A we would have indexed the lines as the $\bar{1} \bar{2}$; no difference exists between the two pairs of indices and always the hk and the $\bar{h} \bar{k}$ lines are the same set of lines. Try Question 5 for more examples. Notice also, in Figure 1.26, that the lines with the lower indices are more widely spaced.

The Miller indices for planes in three-dimensional lattices are given by hkl , where l is now the index for the z -axis. The principles are the same. Thus a plane is indexed hkl

when it makes intercepts $\frac{a}{h}$, $\frac{b}{k}$, and $\frac{c}{l}$ with the unit cell edges a , b , and c . Figure 1.27 depicts some cubic lattices with various planes shaded. The positive directions of the axes are marked, and these are orientated to conform to

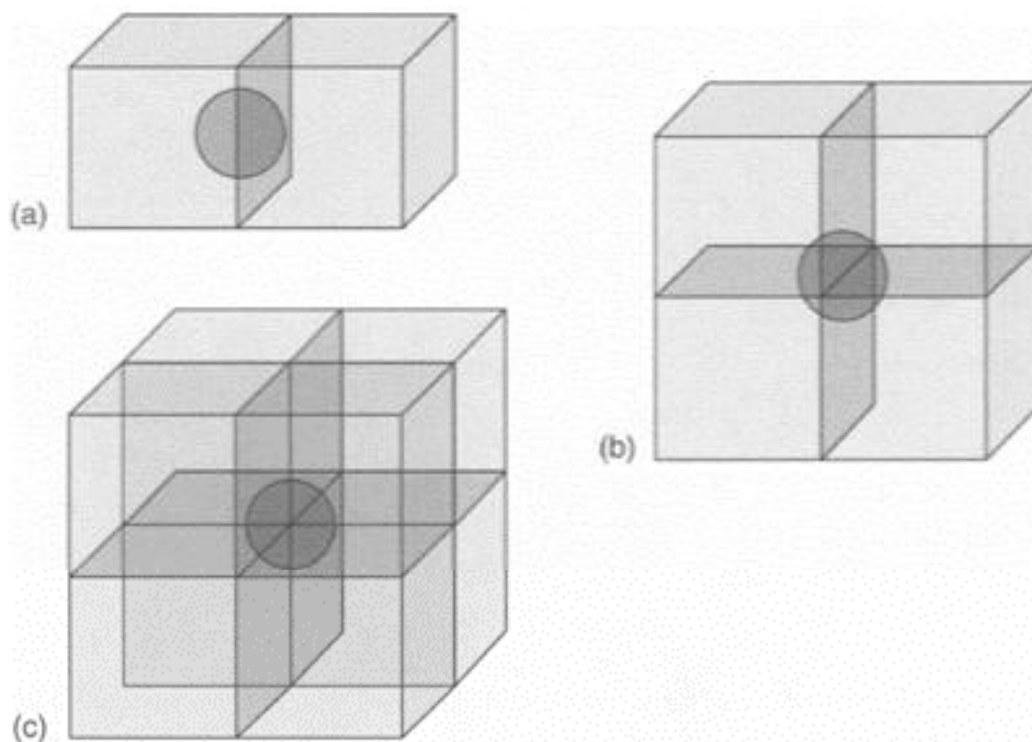


FIGURE 1.25 Unit cells showing a molecule on (a) a face, (b) an edge, and (c) a corner.

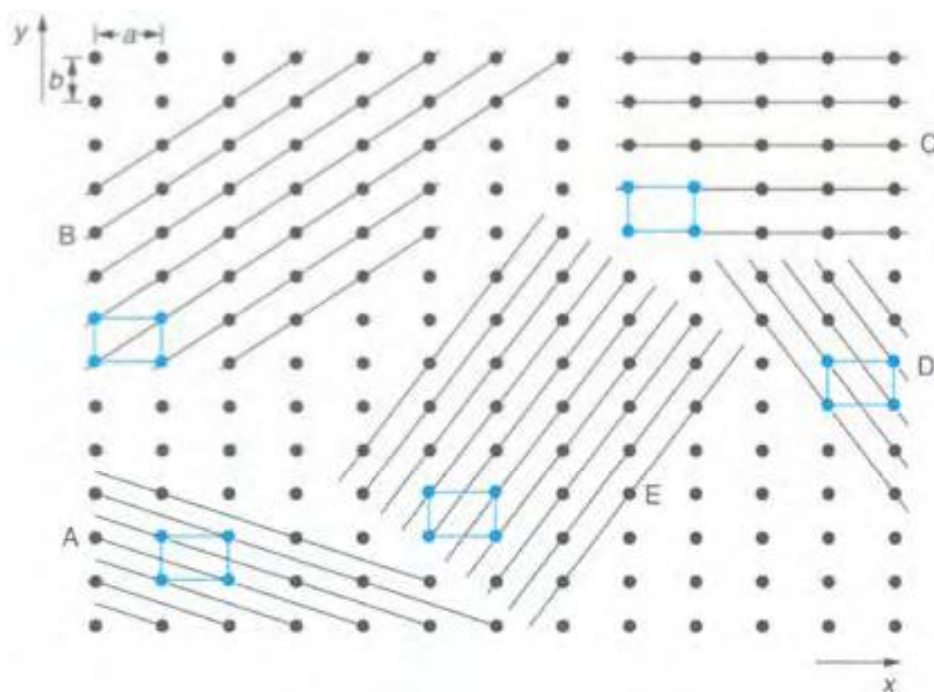


FIGURE 1.26 A rectangular net showing five sets of lines, A–E, with unit cells marked.

the conventional right-hand rule as illustrated in Figure 1.28. In Figure 1.27(a), the shaded planes lie parallel to y and z , but leave the unit cell edge a undivided; the Miller indices of these planes are thus 100 . Again, take note that the hkl and $\bar{h}\bar{k}\bar{l}$ planes are the same.

1.5.6 INTERPLANAR SPACINGS

It is sometimes useful to be able to calculate the perpendicular distance d_{hkl} between parallel planes (Miller indices hkl). When the axes are at right angles to one another (orthogonal) the geometry is simple and for an orthorhombic system where $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$, this gives:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Other relationships are summarized in Table 1.5.

1.5.7 PACKING DIAGRAMS

Drawing structures in three-dimensions is not easy and so crystal structures are often represented by two-dimensional plans or projections of the unit cell contents—in much the same way as an architect makes building plans. These projections are called **packing diagrams** because they are particularly useful in molecular structures

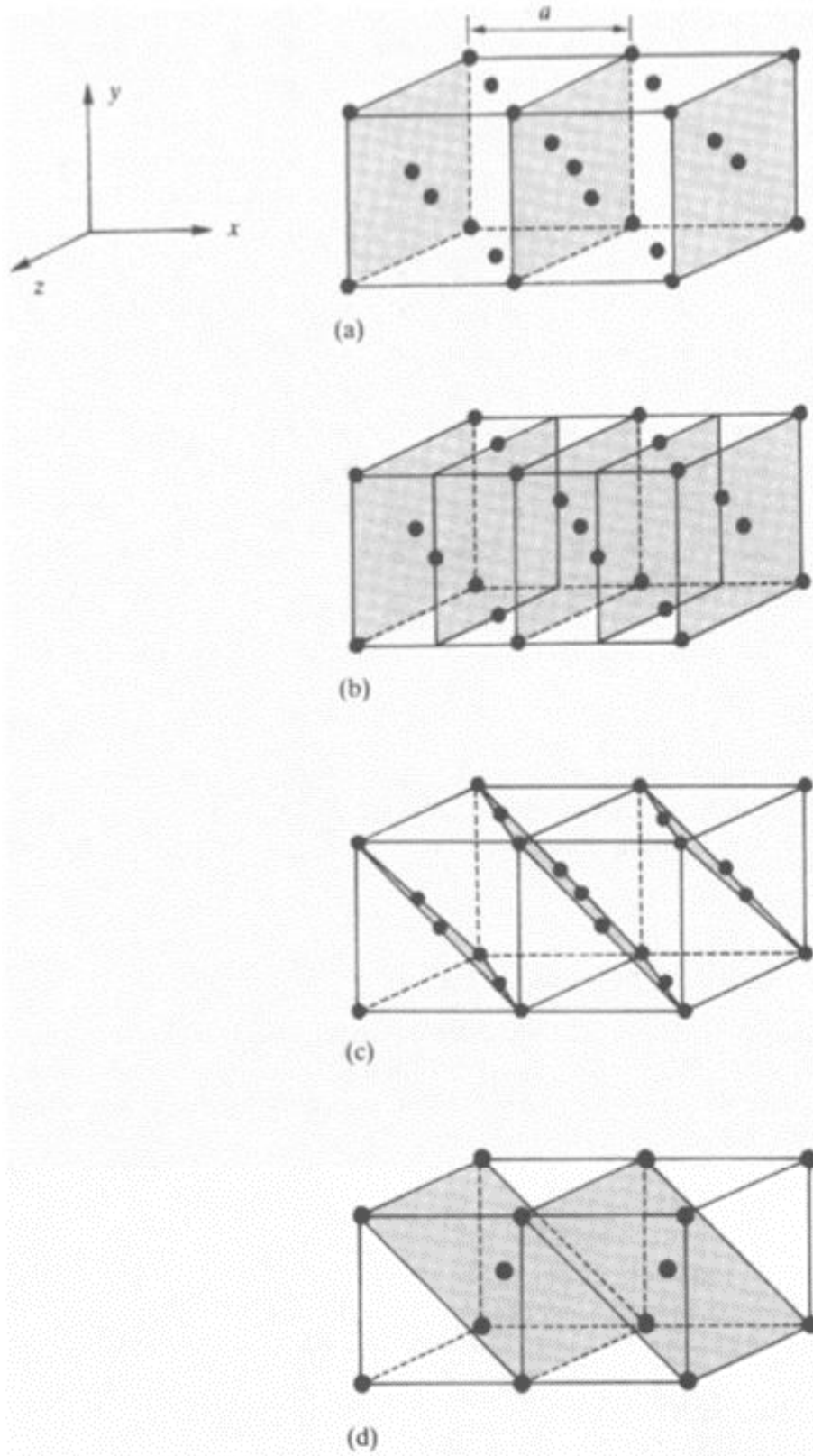


FIGURE 1.27 (a)–(c) Planes in a face-centred cubic lattice, (d) Planes in a body-centred cubic lattice (two unit cells are shown).

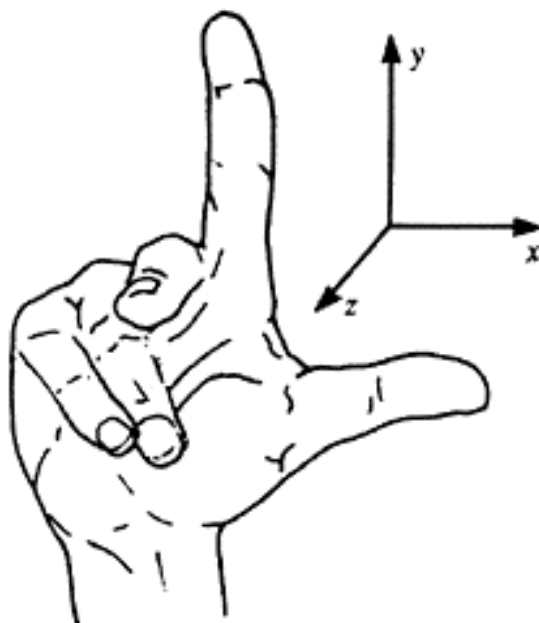


FIGURE 1.28 The right-handed rule for labelling axes.

for showing how the molecules pack together in the crystal, and thus the intermolecular interactions.

The position of an atom or ion in a unit cell is described by its **fractional coordinates**; these are simply the coordinates based on the unit cell axes (known as the **crystallographic axes**), but expressed as *fractions of the unit cell lengths*. It has the simplicity of a universal system which enables unit cell positions to be compared from structure to structure regardless of variation in unit cell size.

TABLE 1.5 d-spacings in different crystal systems

Crystal system	d_{hkl} , as a function of Miller indices and lattice parameters
Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$

Monoclinic

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac} \right)$$

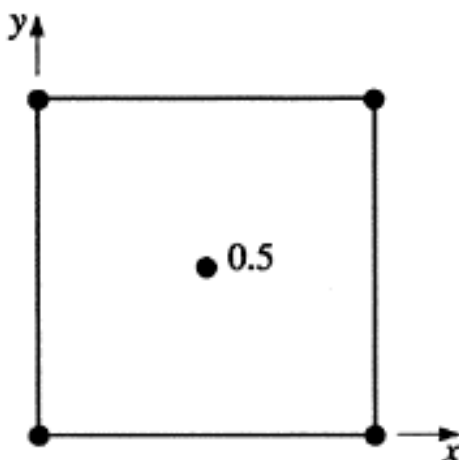


FIGURE 1.29 Packing diagram for a body-centred unit cell.

To take a simple example, in a cubic unit cell with $a=1000$ pm, an atom with an x coordinate of 500 pm has a fractional coordinate in the x direction of $\frac{x}{a} = \frac{500}{1000} = 0.5$. Similarly, in the y and z directions, the fractional coordinates are given by $\frac{y}{b}$ and $\frac{z}{c}$, respectively.

A packing diagram is shown in Figure 1.29 for the body-centred unit cell of Figure 1.8. The projection is shown on the yx plane (i.e., we are looking at the unit cell straight down the z -axis). The z -fractional coordinate of any atoms/ions lying in the top or bottom face of the unit cell will be 0 or 1 (depending on where you take the origin) and it is conventional for this not to be marked on the diagram. Any z -coordinate that is not 0 or 1 is marked on the diagram in a convenient place. There is an opportunity to practice constructing these types of diagram in the questions at the end of the chapter.

1.6 CRYSTALLINE SOLIDS

We start this section by looking at the structures of some simple **ionic solids**. Ions tend to be formed by the elements in the Groups at the far left and far right of the Periodic Table. Thus, we expect the metals in Groups I and II to form cations and the nonmetals of Groups VI(16) and VII(17) and nitrogen to form anions, because by doing so they are able to achieve a stable noble gas configuration. Cations can also be formed by some of the Group III(13) elements, such as aluminium, Al^{3+} , by some of the low oxidation state transition metals and even occasionally by the high atomic number elements in Group IV(14), such as tin and lead, giving Sn^{4+} and Pb^{4+} . Each successive ionization becomes