1

Crystals and crystal structures

- *What is a crystal system?*

- *What are unit cells?*

- *What information is needed to specify a crystal structure?*

Crystals are solids that possess long-range order. The arrangement of the atoms at one point in a crystal is identical, (excepting localised mistakes or defects that can arise during crystal growth), to that in any other remote part of the crystal. Crystallography describes the ways in which the component atoms are arranged in crystals and how the long-range order is achieved. Many chemical (including biochemical) and physical properties depend on crystal structure and knowledge of crystallography is essential if the properties of materials are to be understood and exploited.

Crystallography first developed as an observational science; an adjunct to the study of minerals. Minerals were, (and still are), described by their habit, the shape that a mineral specimen may exhibit, which may vary from an amorphous mass to a well-formed crystal. Indeed, the regular and beautiful shapes of naturally occurring crystals attracted attention from the earliest times, and the relationship between crystal shape and the disposition of crystal faces, the crystal morphology, was soon used in classification. At a later stage in the development of the subject, symmetry, treated mathematically, became important in the description of crystals. The actual determination of crystal structures, the positions of all of the atoms in the crystal, was a later level of refinement that was dependent upon the discovery and subsequent use of X-rays.

1.1 Crystal families and crystal systems

Careful measurement of mineral specimens allowed crystals to be classified in terms of six **crystal families**, called anorthic, monoclinic, orthorhombic, tetragonal, hexagonal and isometric. This classification has been expanded slightly by crystallographers into seven **crystal systems**. The crystal systems are sets of reference axes, which have a direction as well as a magnitude, and hence are vectors[1]. The crystal families and classes are given in Table 1.1.

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[1]Vectors are set in **bold** typeface throughout this book.

Table 1.1   The seven crystal systems

Crystal family	Crystal system	Axial relationships
Isometric	Cubic	$a = b = c$, $\quad \alpha = \beta = \gamma = 90°$;
Tetragonal	Tetragonal	$a = b \neq c$, $\quad \alpha = \beta = \gamma = 90°$;
Orthorhombic	Orthorhombic	$a \neq b \neq c$, $\quad \alpha = \beta = \gamma = 90°$;
Monoclinic	Monoclinic	$a \neq b \neq c$, $\quad \alpha = 90°$, $\beta \neq 90°$, $\gamma = 90°$;
Anorthic	Triclinic	$a \neq b \neq c$, $\quad \alpha \neq 90°$, $\beta \neq 90°$, $\gamma \neq 90°$;
Hexagonal	Hexagonal	$a = b \neq c$, $\quad \alpha = \beta = 90°$, $\;\gamma = 120°$;
	Trigonal or	$a = b = c$, $\;\; \alpha = \beta = \gamma$; or
	Rhombohedral	$a' = b' \neq c'$, $\alpha' = \beta' = 90°$, $\gamma' = 120°$;
		(hexagonal axes)

The three reference axes are labelled **a**, **b** and **c**, and the angles between the positive direction of the axes are α, β, and γ, where α lies between $+$**b** and $+$**c**, β lies between $+$**a** and $+$**c**, and γ lies between $+$**a** and $+$**b**, (Figure 1.1). The angles are chosen to be greater or equal to $90°$ except for the trigonal system, as described below. In figures, the **a**-axis is represented as projecting out of the plane of the page, towards the reader, the **b**-axis points to the right and the **c**-axis points towards the top of the page. This arrangement is a **right-handed coordinate system**.

Measurements on mineral specimens could give absolute values for the inter-axial angles, but only relative axial lengths could be derived. These lengths are written a, b and c.
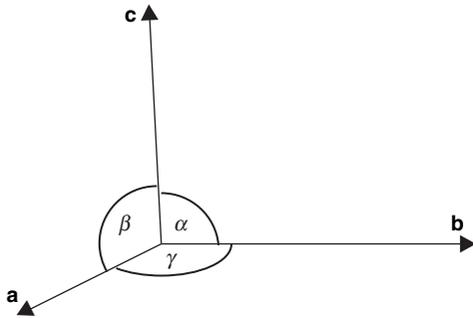
Figure 1.1   The reference axes used to characterise the seven crystal systems

The seven crystal systems are named according to the relationship between the axes and the inter-axial angles. The most symmetric of the crystal classes is the cubic or isometric system, in which the three axes are arranged at $90°$ to each other and the axial lengths are identical. These form the familiar Cartesian axes. The tetragonal system is similar, with mutually perpendicular axes. Two of these, usually designated **a** ($=$**b**), are of equal length, while the third, designated **c**, is longer or shorter than the other two. The orthorhombic system has three mutually perpendicular axes of different lengths. The monoclinic system is also defined by three unequal axes. Two of these, conventionally chosen as **a** and **c**, are at an oblique angle, β, while the third **c**, is normal to the plane containing **a** and **b**. The least symmetrical crystal system is the triclinic, which has three unequal axes at oblique angles. The hexagonal crystal system has two axes of equal length, designated **a** ($=$**b**), at an angle, γ, of $120°$. The **c**-axis lies perpendicular to the plane containing **a** and **b**, and lies parallel to a six-fold axis of rotation symmetry, (see Chapter 4).

The trigonal system has three axes of equal length, each enclosing equal angles α ($=\beta = \gamma$), forming a rhombohedron. The axes are called rhombohedral axes, while the system name trigonal refers to the presence of a three-fold axis of

rotation symmetry in the crystal (see Chapter 4). Crystals described in terms of rhombohedral axes are often more conveniently described in terms of a hexagonal set of axes. In this case, the hexagonal **c**-axis is parallel to the rhombohedral body diagonal, which is a three-fold axis of symmetry (Figure 1.2). The relationship between the two sets of axes is given by the *vector* equations:

$$\mathbf{a}_R = \tfrac{2}{3}\,\mathbf{a}_H + \tfrac{1}{3}\,\mathbf{b}_H + \tfrac{1}{3}\,\mathbf{c}_H$$
$$\mathbf{b}_R = -\tfrac{1}{3}\,\mathbf{a}_H + \tfrac{1}{3}\,\mathbf{b}_H + \tfrac{1}{3}\,\mathbf{c}_H$$
$$\mathbf{c}_R = -\tfrac{1}{3}\,\mathbf{a}_H - \tfrac{2}{3}\,\mathbf{b}_H + \tfrac{1}{3}\,\mathbf{c}_H$$
$$\mathbf{a}_H = \mathbf{a}_R - \mathbf{b}_R$$
$$\mathbf{b}_H = \mathbf{b}_R - \mathbf{c}_R$$
$$\mathbf{c}_H = \mathbf{a}_R + \mathbf{b}_R + \mathbf{c}_R$$

where the subscripts R and H stand for rhombohedral and hexagonal respectively. [Note that in these equations the vectors **a**, **b** and **c** are added vectorially, not arithmetically, (see Appendix 1)]. The arithmetical relationships between the axial lengths is given by:

$$a_H = 2\,a_R \sin\frac{\alpha}{2} \qquad\qquad c_H = a_R\sqrt{3 + 6\cos\alpha}$$

$$a_R = \frac{1}{3}\sqrt{3a_H^2 + c_H^2} \qquad \sin\frac{\alpha}{2} = \frac{3a_H}{2\sqrt{3a_H^2 + c_H^2}}$$

where the subscripts R and H stand for rhombohedral and hexagonal respectively.

1.2 Morphology and crystal classes

Observations of the shapes of crystals, the crystal **morphology**, suggested that the regular external form of a crystal was an expression of internal order. Among other observations, the cleavage of crystals, that is, the way in which they could be fractured along certain directions in such a manner that the two resultant fragments had perfect faces, suggested that all crystals might be built up by a stacking of infinitesimally small regular 'brick-like' elementary volumes, each unique to the crystal under consideration. These elementary volumes, the edges of which could be considered to be parallel to the axial vectors **a**, **b** and **c**, of the seven crystal systems, eventually came to be termed **morphological unit cells**. The relative axial lengths, *a*, *b* and *c* were taken as equal to the relative lengths of the unit cell sides. The values *a*, *b*, *c*, α, β and γ are termed the **morphological unit cell parameters**. [The absolute lengths of the axes, also written *a*, *b* and *c* or a_0, b_0 and c_0, determined by diffraction techniques, described below, yield the **structural unit cell** of the material. Unit cell parameters now refer only to these structural values.]

Figure 1.2 Rhombohedral and hexagonal axes: (a, b), axes in equivalent orientations with the trigonal 3-fold axis parallel to the hexagonal **c**-axis; (c) superposition of both sets of axes, projected down the hexagonal **c**-axis (= the rhombohedral 3-fold axis)

A central concept in crystallography is that the whole of a crystal can be built up by stacking identical copies of the unit cell in exactly the same orientation. That is to say, a crystal is characterised by both **translational** and **orientational** long-range order. The unit cells are displaced repeatedly in three dimensions, (**translational** long-range order), without any rotation or reflection, (**orientational** long-range order). This restriction leads to severe restrictions upon the shape (strictly speaking the symmetry) of a unit cell; a statement which will be placed on a firm footing in later chapters. The fact that some unit cell shapes are not allowed is easily demonstrated in two dimensions, as it is apparent that regular pentagons, for example, cannot pack together without leaving gaps (Figure 1.3). [A regular pentagon is a plane figure with five equal sides and five equal internal angles.]

Not only could unit cells be stacked by translation alone to yield the internal structure of the crystal, but, depending on the rate at which the unit cells were stacked in different directions, (i.e. the rate at which the crystal grew in three dimensions), different facets of the crystal became emphasised, while others were suppressed, so producing a variety of external shapes, or **habits**, (Figure 1.4),
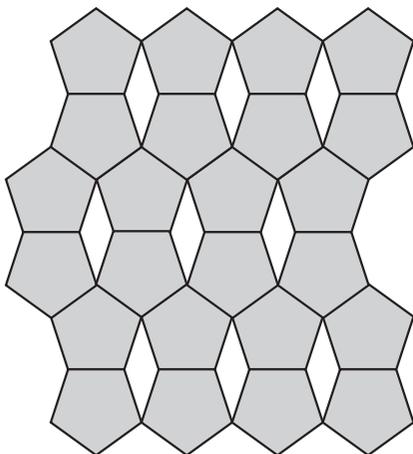
Figure 1.3   Irrespective of how they are arranged, regular pentagons cannot fill a plane completely; spaces always appear between some of the pentagons. Just one arrangement is drawn, others are possible
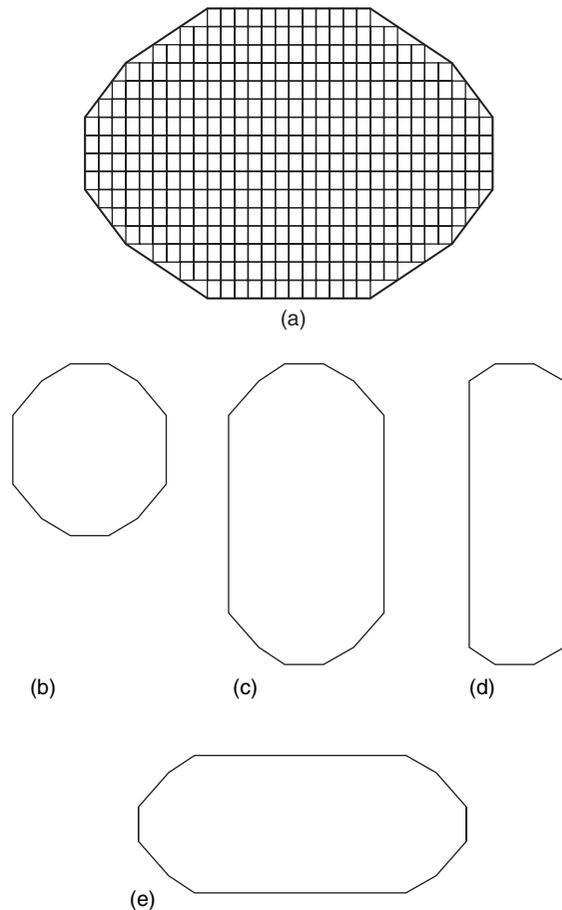
Figure 1.4   (a) schematic depiction of a crystal built of rectangular (orthorhombic) unit cells. The unit cells must be imagined to be much smaller than depicted, thus producing smooth facets. (b – e) different crystal habits derived by differing rates of crystal growth in various directions

thus explaining the observation that a single mineral could occur in differing crystal morphologies.

The faces of a crystal, irrespective of the overall shape of the crystal, could always be labelled with respect to the crystal axes. Each face was given a set of three integers, $(h\ k\ l)$, called **Miller indices**. These are such that the crystal face in question made intercepts on the three axes of a/h, b/k and c/l. A crystal face that intersected the axes in exactly the axial ratios was given importance as the **parametral plane**, with indices (111). [Miller indices are now used to label any plane, internal or external, in a crystal, as described in Chapter 2, and the nomenclature is not just confined to the external faces of a crystal.]

The application of Miller indices allowed crystal faces to be labelled in a consistent fashion. This, together with accurate measurements of the angles between crystal faces, allowed the morphology of crystals to be described in a reproducible way, which, in itself, lead to an appreciation of the symmetry of crystals. Symmetry was broken down into a combination of symmetry elements. These were described as mirror planes, axes of rotation, and so on, that, when taken in combination, accounted for the external shape of the crystal. The crystals of a particular mineral, regardless of its precise morphology, were always found to possess the same symmetry elements.

Symmetry elements are operators. That is, each one describes an operation, such as reflection. When these operations are applied to the crystal, the external form is reproduced. It was found that all crystals fell into one or another of 32 different groups of symmetry operations. These were called **crystal classes**. Each crystal class could be allocated to one of the six crystal families. These symmetry elements and the resulting crystal classes are described in detail in Chapters 3 and 4.

1.3 The determination of crystal structures

The descriptions above were made using optical techniques, especially optical microscopy. However, the absolute arrangement of the atoms in a crystal cannot be determined in this way. This limitation was overcome in the early years of the 20th century, when it was discovered that X-rays were scattered, or **diffracted**, by crystals in a way that could be interpreted to yield the absolute arrangement of the atoms in a crystal, the **crystal structure**. X-ray diffraction remains the most widespread technique used for structure determination, but diffraction of electrons and neutrons is also of great importance, as these reveal features that are complementary to those observed with X-rays.

The physics of diffraction by crystals has been worked out in detail. It is found that the incident radiation is scattered in a characteristic way, called a **diffraction pattern**. The positions and intensities of the diffracted beams are a function of the arrangements of the atoms in space and some other atomic properties, such as the atomic number of the atoms. Thus, if the positions and the intensities of the diffracted beams are recorded, it is possible to deduce the arrangement of the atoms in the crystal and their chemical nature. The determination of crystal structures by use of the diffraction of radiation is outlined in Chapter 6.

1.4 The description of crystal structures

The minimum amount of information needed to specify a crystal structure is the unit cell type, i.e., cubic, tetragonal, etc, the unit cell parameters and the positions of all of the atoms in the unit cell. The atomic contents of the unit cell are a simple multiple, Z, of the composition of the material.
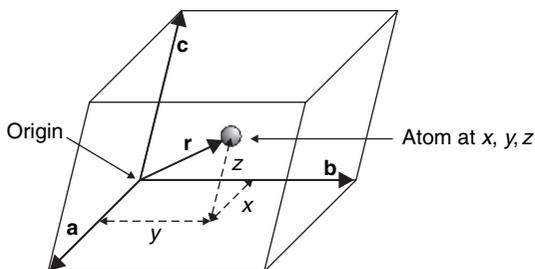
Figure 1.5 The position of an atom in a unit cell, *x*, *y* and *z*, is defined with respect to the directions of the unit cell edges. The numerical values of *x*, *y* and *z* are specified as fractions, (½, ¼, etc.) of the unit cell edges *a*, *b* and *c*

Figure 1.6 Atoms at positions 0, 0, 0; 0, ½, 0; ½, ½, 0; and ½, ½, ½ in a unit cell

The value of Z is equal to the number of **formula units** of the solid in the unit cell. Atom positions are expressed in terms of three coordinates, *x*, *y*, and *z*. These are taken as **fractions** of *a*, *b* and *c*, the unit cell sides, say ½, ½, ¼. The *x*, *y* and *z* coordinates are plotted with respect to the unit cell axes, not to a Cartesian set of axes, (Figure 1.5). The position of an atom can also be expressed as a vector, **r**:

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

where **a**, **b** and **c** are the unit cell axes, (Figure 1.5).

An atom at a cell corner is given the coordinates (0, 0, 0). An atom at the centre of the face of a unit cell is given the coordinates (½, ½, 0) if it lies between the **a**- and **b**-axes, (½, 0, ½) if between the **a**- and **c**-axes, and (0, ½, ½) if between the **b**- and **c**-axes. An atom at the centre of a unit cell would have a position specified as (½, ½, ½), irrespective of the type of unit cell. Atoms at the centres of the cell edges are specified at positions (½, 0, 0), (0, ½, 0) or (0, 0, ½), for atoms on the **a**-, **b**- and **c**-axis, (Figure 1.6). Stacking of the unit cells to build a structure will ensure that an atom at the unit cell origin will appear at every corner, and atoms on unit cell edges or faces will appear on all of the cell edges and faces.

In figures, the conventional origin is placed at the left rear corner of the unit cell. The **a**- or *x*-axis is represented as projecting out of the plane of the page, towards the reader, the **b**- or *y*-axis points to the right and the **c**- or *z*-axis points towards the top of the page. In projections, the origin is set at the upper left corner of the unit cell projection. A frequently encountered projection is that perpendicular to the **c**-axis. In this case, the **a**- or *x*-axis is drawn pointing down, (from top to bottom of the page), and the **b**- or *y*-axis pointing to the right. In projections the *x* and *y* coordinates can be determined from the figure. The *z* position is usually given on the figure as a fraction.

A vast number of structures have been determined, and it is very convenient to group those with topologically identical structures together. On going from one member of the group to another, the atoms in the unit cell differ, reflecting a change in chemical compound, and the atomic coordinates and unit cell dimensions change slightly, reflecting the difference in atomic size, but relative atom positions are identical or very similar. Frequently, the group name is taken from the name of a mineral, as mineral crystals were the first solids used for structure determination. Thus, all crystals with a structure similar to that of sodium chloride, NaCl, (the mineral halite), are said to adopt the *halite* structure. These materials then all have a general

Table 1.2 Strukturbericht symbols and names for simple structure types

Symbol and name	Examples	Symbol and name	Examples
A1, cubic close-packed, copper	Cu, Ag, Au, Al	A2, body-centred cubic, iron	Fe, Mo, W, Na
A3, hexagonal close-packed, magnesium	Mg, Be, Zn, Cd	A4, diamond	C, Si, Ge, Sn
B1, halite, rock salt	NaCl, KCl, NiO, MgO	B2, caesium chloride	CsCl, CsBr, AgMg, BaCd
B3, zinc blende	ZnS, ZnSe, BeS, CdS	B4, wurtzite	ZnS, ZnO, BeO, CdS, GaN
C1, fluorite	CaF_2, BaF_2, UO_2, ThO_2	C4, rutile	TiO_2, SnO_2, MgF_2, FeF_2

formula *MX*, where *M* is a metal atom and *X* a non-metal atom, for example, MgO. Similarly, crystals with a structure similar to the rutile form of titanium dioxide, TiO_2, are grouped with the *rutile* structure. These all have a general formula MX_2, for example FeF_2. As a final example, compounds with a similar structure to the mineral fluorite, (sometimes called fluorspar), CaF_2, are said to adopt the *fluorite* structure. These also have a general formula MX_2, an example being UO_2. Examples of these three structures follow. Crystallographic details of a number of simple inorganic structures are given in Appendix 2. Some mineral names of common structures are found in Table 1.2 and Appendix 2.

A system of nomenclature that is useful for describing relatively simple structures is that originally set out in 1920, in Volume 1 of the German publication Strukturbericht. It assigned a letter code to each structure; A for materials with only one atom type, B for two different atoms, and so on. Each new structure was characterised further by the allocation of a numeral, so that the crystal structures of elements were given symbols A1, A2, A3 and so on. Simple binary compounds were given symbols B1, B2 and so on, and binary compounds with more complex structures C1, C2, D1, D2 and so on. As the number of crystal structures and the complexity displayed increased, the system became unworkable. Nevertheless, the terminology is still used, and is useful for the description of simple structures. Some Strukturbericht symbols are given in Table 1.2.

1.5 The cubic close-packed (A1) structure of copper

A number of elemental metals crystallise with the cubic A1 structure, also called the copper structure.

Unit cell: cubic

Lattice parameter for copper[2], $a = 0.3610$ nm.

Z = 4 Cu

Atom positions: 0, 0, 0; ½, ½, 0;
0, ½, ½; ½, 0, ½;

There are four copper atoms in the unit cell, (Figure 1.7). Besides some metals, the noble gases, Ne(s), Ar(s), Kr(s), Xe(s), also adopt this structure in the solid state. This structure is often called the face-centred cubic (*fcc*) structure or the cubic close-packed (*ccp*) structure, but the Strukturbericht symbol, A1 is the most compact notation. Each atom has 12 nearest neighbours, and if the atoms are supposed to be hard touching spheres, the fraction of the volume occupied is

[2]Lattice parameters and interatomic distances in crystal structures are usually reported in Ångström units, Å, in crystallographic literature. 1 Å is equal to 10^{-10} m, that is, 10 Å = 1 nm. In this book, the SI unit of length, nm, will be used most often, but Å will be used on occasion, to conform with crystallographic practice.
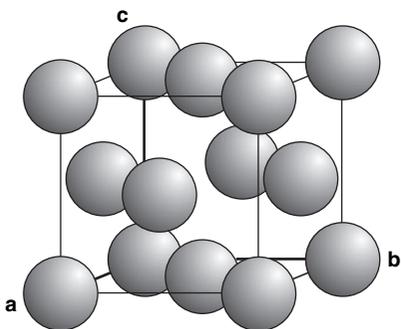
Figure 1.7   The cubic unit cell of the A1, copper, structure

Figure 1.8   The cubic unit cell of the A2, tungsten, structure

0.7405. More information on this structure is given in Chapter 7.

1.6   The body-centred cubic (A2) structure of tungsten

A second common structure adopted by metallic elements is that of the cubic structure of tungsten, W.

  Unit cell: cubic

    Lattice parameter for tungsten, $a = 0.316$ nm.

    Z = 2 W

  Atom positions: 0, 0, 0; ½, ½, ½;

There are two tungsten atoms in the body-centred unit cell, one at (0, 0, 0) and one at the cell centre, (½, ½, ½), (Figure 1.8). This structure is often called the body-centred cubic (*bcc*) structure, but the Strukturbericht symbol, A2, is a more compact designation. In this structure, each atom has 8 nearest neighbours and 6 next nearest neighbours at only 15% greater distance. If the atoms are supposed to be hard touching spheres, the fraction of the volume

occupied is 0.6802. This is less than either the A1 structure above or the A3 structure that follows, both of which have a volume fraction of occupied space of 0.7405. The A2 structure is often the high temperature structure of a metal that has an A1 close-packed structure at lower temperatures.

1.7   The hexagonal (A3) structure of magnesium

The third common structure adopted by elemental metals is the hexagonal magnesium, Mg, structure.

  Unit cell: hexagonal

    Lattice parameters for magnesium, $a = 0.321$ nm, $c = 0.521$ nm

    Z = 2 Mg

  Atom positions: 0, 0, 0; ⅓, ⅔, ½;

There are two atoms in the unit cell, one at (0, 0, 0) and one at (⅓, ⅔, ½). [The atoms can also be placed at ⅔, ⅓, ¼; ⅓, ⅔, ¾, by changing the unit cell origin. This is preferred for some
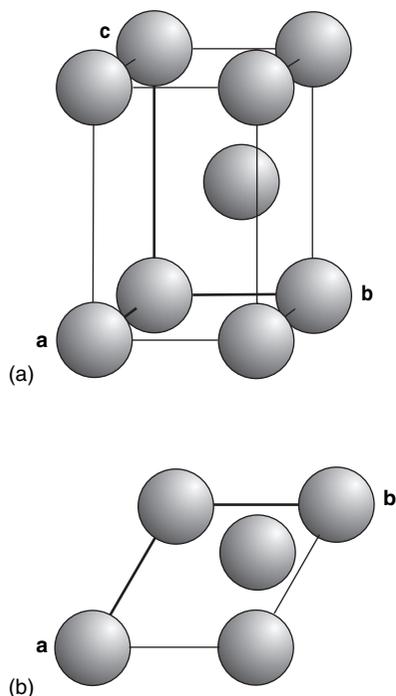
Figure 1.9 The hexagonal unit cell of the A3, magnesium, structure: (a) perspective view; (b) projection down the **c**-axis

purposes]. The structure is shown in perspective, (Figure 1.9a) and projected down the **c**-axis, (Figure 1.9b). This structure is often referred to as the hexagonal close-packed (*hcp*) structure. If the atoms are supposed to be hard touching spheres, the fraction of the volume occupied is 0.7405, equal to that in the A1 structure of copper, and the ratio of the lattice parameters, c/a, is equal to $\sqrt{8}/\sqrt{3}$, $= 1.633$. The ideal volume, V, of the unit cell, equal to the area of the base of the unit cell multiplied by the height of the unit cell, is:

$$V = \frac{\sqrt{3}}{2} a^2 c = 0.8660 \, a^2 c$$

More information on this structure, and the relationship between the A1 and A3 structures, is given in Chapter 7.

1.8 The *halite* structure

The general formula of crystals with the *halite* structure is *MX*. The mineral halite, which names the group, is sodium chloride, NaCl, also called rock salt.

Unit cell: cubic.

Lattice parameter for halite, $a = 0.5640$ nm.

$Z = 4$ {NaCl}

Atom positions: Na: ½, 0, 0; 0, 0, ½;
0, ½, 0; ½, ½, ½
Cl: 0, 0, 0; ½, ½, 0;
½, 0, ½; 0, ½, ½

There are four sodium and four chlorine atoms in the unit cell. For all materials with the *halite* structure, $Z = 4$. In this structure, each atom is surrounded by six atoms of the opposite type at the corners of a regular octahedron (see Chapter 7). A perspective view of the halite structure is shown in Figure 1.10a, and a projection, down the **c**-axis, in Figure 1.10b.

This structure is adopted by many oxides, sulphides, halides and nitrides with a formula *MX*.

1.9 The *rutile* structure

The general formula of crystals with the *rutile* structure is MX_2. The mineral rutile, which names the group, is one of the structures adopted by titanium dioxide, TiO_2. [The other common form

(a)

(b)

Na

Cl
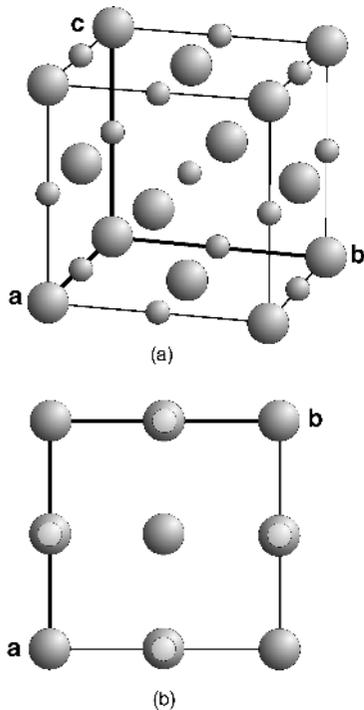
Figure 1.10   The cubic unit cell of the B1, *halite*, structure: (a) perspective view; (b) projection down the **c**-axis

of TiO_2 encountered is called anatase. Other structures for TiO_2 are also known.]

Unit cell: tetragonal.

Lattice parameters for rutile, $a = 0.4594$ nm, $c = 0.2959$ nm.

$Z = 2$ $\{TiO_2\}$

Atom positions: Ti: 0, 0, 0;   ½, ½, ½
O: $^3/_{10}$, $^3/_{10}$, 0; $^4/_5$, $^1/_5$, ½;
$^7/_{10}$, $^7/_{10}$, 0; $^1/_5$, $^4/_5$, ½

There are two molecules of TiO_2 in the unit cell, that is, for all materials that adopt the *rutile*

(a)

Ti

O

(b)
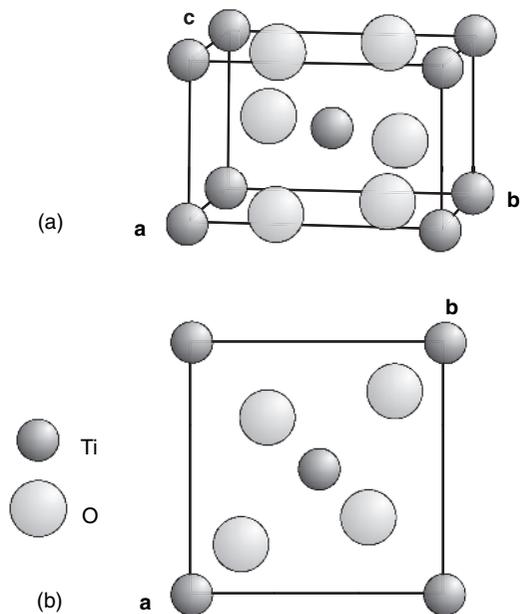
Figure 1.11   The tetragonal unit cell of the *rutile* structure: (a) perspective view; (b) projection down the **c**-axis

structure, $Z = 2$. In this structure, each titanium atom is surrounded by six oxygen atoms at the corners of an octahedron. A perspective view of the rutile structure is shown in Figure 1.11a, and a projection, down the **c**-axis, in Figure 1.11b.

This structure is relatively common and adopted by a number of oxides and fluorides with a formula MX_2.

1.10   The *fluorite* structure

The general formula of crystals with the *fluorite* structure is MX_2. The mineral fluorite, calcium fluoride, CaF_2, which names the group, is sometimes also called fluorspar.

Unit cell: cubic.

Lattice parameter for fluorite, $a = 0.5463$ nm.

$Z = 4 \{CaF_2\}$

Atom positions:

Ca: 0, 0, 0; ½, ½, 0; 0, ½, ½; ½, 0, ½
F: ¼, ¾, ¼; ¼, ¾, ¾; ¼, ¼, ¼; ¼, ¼, ¾;
   ¾, ¼, ¼; ¾, ¼, ¾; ¾, ¾, ¼; ¾, ¾, ¾

There are four calcium and eight fluorine atoms in the unit cell. The number of molecules of CaF_2 in the unit cell is four, so that, for all *fluorite* structure compounds, $Z = 4$. In this structure, each calcium atom is surrounded by eight fluorine atoms at the corners of a cube. Each fluorine atom is surrounded by four calcium atoms at the vertices of a tetrahedron (see also Chapter 7). A perspective view of the structure is shown in Figure 1.12a, and a projection of the structure down the **c**-axis in Figure 1.12b.

(a)

(b)

○ Ca
○ F
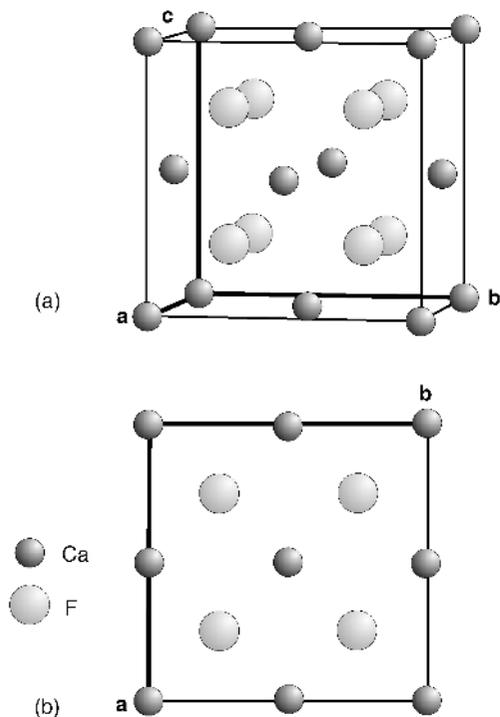
Figure 1.12 The cubic unit cell of the *fluorite* structure: (a) perspective view; (b) projection down the **c**-axis

This structure is adopted by a number of oxides and halides of large divalent cations of formula MX_2.

1.11 The structure of urea

The structures of molecular crystals tend to have a different significance to those of inorganic and mineral structures. Frequently, the information of most importance is the molecular geometry, and how the molecules are arranged in the crystallographic unit cell is often of less interest. To introduce the changed emphasis when dealing with molecular materials, the crystal structure of the organic compound urea is described. Urea is a very simple molecule, with a formula CH_4N_2O. The unit cell is small and of high symmetry. It was one of the earliest organic structures to be investigated using the methods of X-ray crystallography, and in these initial investigations the data was not precise enough to locate the hydrogen atoms. [The location of hydrogen atoms in a structure remains a problem to present times, see also Chapters 6 and 7.] The crystallographic data for urea is[3]

Unit cell: tetragonal.

Lattice parameters for urea,
$a = 0.5589$ nm, $c = 0.46947$ nm.

$Z = 2 \{CH_4N_2O\}$

Atom positions:
C1:	0, 0.5000, 0.3283
C2:	0.5000, 0, 0.6717
O1:	0.5000, 0, 0.4037
N1:	0.1447, 0.6447, 0.1784
N2:	0.8553, 0.3553, 0.1784
N3:	0.6447, 0.8553, 0.8216
N4:	0.3553, 0.1447, 0.8216

[3]Data adapted from: V. Zavodnik, A. Stash, V. Tsirelson, R. de Vries and D. Feil, Acta Crystallogr., B**55**, 45 (1999).

H1:   0.2552, 0.7552, 0.2845
H2:   0.1428, 0.6428, 0.9661
H3:   0.8448, 0.2448, 0.2845
H4:   0.8572, 0.3572, 0.9661
H5:   0.7552, 0.7448, 0.7155
H6:   0.2448, 0.2552, 0.7155
H7:   0.6429, 0.8571, 0.0339
H8:   0.3571, 0.1428, 0.0339
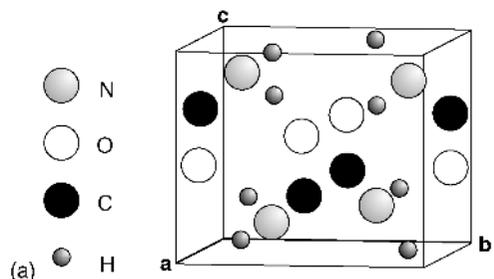
Notice that atoms of the same chemical type are numbered sequentially. The number of molecules of urea in the unit cell is two, so that $Z = 2$. The atoms in a unit cell, (including hydrogen), are shown in Figure 1.13a. This turns out to be not very helpful, and an organic chemist would have difficulty in recognising it as urea. This is because the molecules lie along the unit cell sides, so that a whole molecule is not displayed in the unit cell, only molecular fragments. [The unit cell is chosen in this way because of symmetry constraints, described in the following chapters.] The chemical structural formula for urea is drawn in Figure 1.13b, and this is compared to a molecule of urea viewed front on (Figure 1.13c), and edge on (Figure 1.13d) extracted from the crystallographic data. The crystal structure is redrawn in Figures 1.13e, f with the atoms linked to form molecules. This latter depiction now agrees with chemical intuition, and shows how the molecules are arranged in space.

Note that the list of atoms in the unit cell is becoming lengthy, albeit that this is an extremely simple structure. The ways used by crystallographers to reduce these lists to manageable proportions, by using the symmetry of the crystal, is explained in later chapters.

1.12   The density of a crystal

The theoretical density of a crystal can be found by calculating the mass of all the atoms in the unit
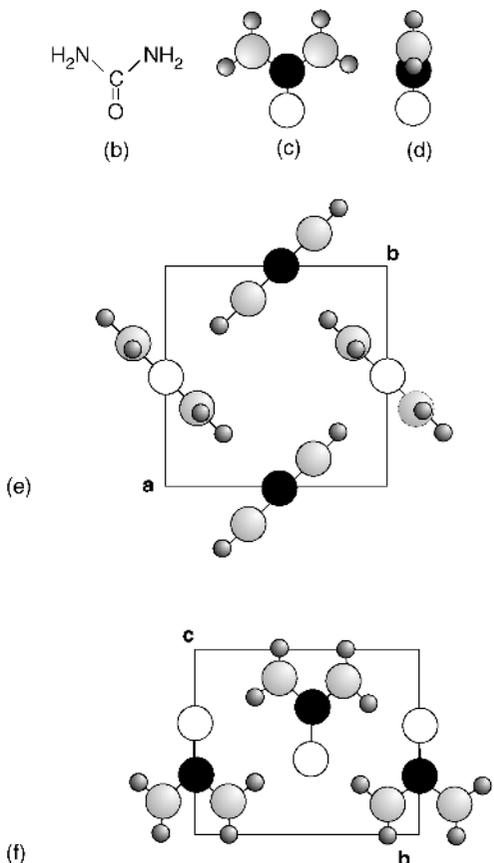
Figure 1.13   The structure of urea: (a) perspective view of the tetragonal unit cell of urea; (b) structural formula of urea; (c) a 'ball and stick' representation of urea 'face on', as in (b); (d) a 'ball and stick' representation of urea 'sideways on'; (e) projection of the structure along the **c**-axis; (f) projection of the structure down the **a**-axis

cell. The mass of an atom, m_A, is its molar mass (grams mol^{-1}) divided by the Avogadro constant, N_A, $(6.02214 \times 10^{23} \, mol^{-1})$

$$m_A = molar \; mass/N_A \quad (grams)$$
$$= molar \; mass/(1000 \times N_A) \; (kilograms)$$

The total mass of all of the atoms in the unit cell is then

$$n_1 \, m_1 + n_2 \, m_2 + n_3 \, m_3 \ldots /(1000 \times N_A)$$

where n_1 is the number of atoms of type 1, with a molar mass of m_1, and so on. This is written in a more compact form as

$$\sum_{i=1}^{q} n_i m_i /(1000 \times N_A)$$

where there are q different atom types in the unit cell. The density, ρ, is simply the total mass is divided by the unit cell volume, V:

$$\rho = \left\{ \sum_{i=1}^{q} n_i m_i /(1000 \times N_A) \right\}/V$$

For example, the theoretical density of halite is calculated in the following way. First count the number of different atom types in the unit cell. To count the number of atoms in a unit cell, use the information:

an atom within the cell counts as 1

an atom in a face counts as ½

an atom on an edge counts as ¼

an atom on a corner counts as ⅛

A quick method to count the number of atoms in a unit cell is to displace the unit cell outline to remove all atoms from corners, edges and faces. The atoms remaining, which represent the unit cell contents, are all within the boundary of the unit cell and count as 1.

The unit cell of the halite structure contains 4 sodium (Na) and 4 chlorine (Cl) atoms. The mass of the unit cell, m, is then given by:

$$m = [(4 \times 22.99) + (4 \times 35.453)]/1000 \times N_A$$
$$= 3.882 \times 10^{-25} \; kg$$

Where 22.99 g mol^{-1} is the molar mass of sodium, 35.453 g mol^{-1} is the molar mass of chlorine, and N_A is the Avogadro constant, $6.02214 \times 10^{23} \, mol^{-1}$.

The volume, V, of the cubic unit cell is given by a^3, thus:

$$V = (0.5640 \times 10^{-9})^3 \; m^3$$
$$= 1.79406 \times 10^{-28} \; m^3.$$

The density, ρ, is given by the mass m divided by the volume, V:

$$\rho = 3.882 \times 10^{-25} \, kg/1.79406 \times 10^{-28} \; m^3$$
$$= 2164 \, kg \, m^{-3}$$

The measured density is 2165 kg m^{-3}. The theoretical density is almost always slightly greater than the measured density because real crystals contain defects that act so as to reduce the total mass per unit volume.

Answers to introductory questions

What is a crystal system?

A crystal system is a set of reference axes, used to define the geometry of crystals and crystal

structures. There are seven crystal systems, cubic, tetragonal, orthorhombic, monoclinic, triclinic, hexagonal and trigonal. As the crystal systems are sets of reference axes, they have a direction as well as a magnitude, and hence are vectors. They must be specified by length and interaxial angles.

The three reference axes are labelled **a**, **b** and **c**, and the angles between the positive direction of the axes as α, β, and γ, where α lies between $+\mathbf{b}$ and $+\mathbf{c}$, β lies between $+\mathbf{a}$ and $+\mathbf{c}$, and γ lies between $+\mathbf{a}$ and $+\mathbf{b}$. The angles are chosen to be greater or equal to 90° except for the trigonal system. In figures, the **a**-axis is represented as projecting out of the plane of the page, towards the reader, the **b**-axis points to the right and the **c**-axis points towards the top of the page.

What are unit cells?

All crystals can be built by the regular stacking of a small volume of material called the unit cell. The edges of the unit cell are generally taken to be parallel to the axial vectors **a**, **b** and **c**, of the seven crystal systems. The lengths of the unit cell sides are written a, b and c, and the angles between the unit cell edges are written, α, β and γ. The collected values a, b, c, α, β and γ for a crystal structure are termed the unit cell or lattice parameters.

What information is needed to specify a crystal structure?

The minimum amount of information needed to specify a crystal structure is the unit cell type, i.e., cubic, tetragonal, etc, the unit cell parameters and the positions of all of the atoms in the unit cell. The atomic contents of the unit cell are a simple multiple, Z, of the composition of the material. The value of Z is equal to the number of formula units of the solid in the unit cell. Atom positions are expressed in terms of three coordinates, x, y, and z. These are taken as fractions of a, b and c, the unit cell sides, for example, ½, ½, ¼.

Problems and exercises

Quick quiz

1 The number of crystal systems is:
  (a) 5
  (b) 6
  (c) 7

2 The angle between the **a**- and **c**-axes in a unit cell is labelled:
  (a) α
  (b) β
  (c) γ

3 A tetragonal unit cell is defined by:
  (a) $a = b = c$, $\alpha = \beta = \gamma = 90°$
  (b) $a = b \neq c$, $\alpha = \beta = \gamma = 90°$
  (c) $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$

4 A crystal is built by the stacking of unit cells with:
  (a) Orientational and translational long-range order
  (b) Orientational long-range order
  (c) Translational long-range order

5 Miller indices are used to label
  (a) Crystal shapes

(b) Crystal faces

(c) Crystal sizes

6 Crystal structures are often determined by the scattering of:

(a) Light

(b) Microwaves

(c) X-rays

7 In crystallography the letter Z specifies:

(a) The number of atoms in a unit cell

(b) The number of formula units in a unit cell

(c) The number of molecules in a unit cell

8 The position of an atom at the corner of a monoclinic unit cell is specified as:

(a) 1, 0, 0

(b) 1, 1, 1

(c) 0, 0, 0

9 The number of atoms in the unit cell of the halite structure is:

(a) 2

(b) 4

(c) 8

10 When determining the number of atoms in a unit cell, an atom in a face counts as:

(a) $\frac{1}{2}$

(b) $\frac{1}{4}$

(c) $\frac{1}{8}$

Calculations and Questions

1.1 The rhombohedral unit cell of arsenic, As, has unit cell parameters $a_R = 0.412$ nm, $\alpha = 54.17°$. Use graphical vector addition (Appendix 1) to determine the equivalent hexagonal lattice parameter a_H. Check your answer arithmetically, and calculate a value for the hexagonal lattice parameter c_H.

1.2 Cassiterite, tin dioxide, SnO_2, adopts the *rutile* structure, with a tetragonal unit cell, lattice parameters, $a = 0.4738$ nm, $c = 0.3187$ nm, with Sn atoms at: 0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; and O atoms at: $\frac{3}{10}$, $\frac{3}{10}$, 0; $\frac{4}{5}$, $\frac{1}{5}$, $\frac{1}{2}$; $\frac{7}{10}$, $\frac{7}{10}$, 0; $\frac{1}{5}$, $\frac{4}{5}$, $\frac{1}{2}$. Taking one corner of the unit cell as origin, determine the atom positions in nm and calculate the unit cell volume in nm^3. Draw a projection of the structure down the **c**-axis, with a scale of 1 cm = 0.1 nm.

1.3 The structure of $SrTiO_3$, is cubic, with a lattice parameter $a = 0.3905$ nm. The atoms are at the positions: Sr: $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; Ti: 0, 0, 0; O: $\frac{1}{2}$, 0, 0; 0, $\frac{1}{2}$, 0; 0, 0, $\frac{1}{2}$. Sketch the unit cell. What is the number of formula units in the unit cell? [This structure type is an important one, and belongs to the *perovskite* family.]

1.4 (a) Ferrous fluoride, FeF_2, adopts the tetragonal *rutile* structure, with lattice parameters $a = 0.4697$ nm, $c = 0.3309$ nm. The molar masses are Fe, 55.847 g mol^{-1}, F, 18.998 g mol^{-1}. Calculate the density of this compound. (b) Barium fluoride, BaF_2, adopts the cubic *fluorite* structure, with lattice parameter $a = 0.6200$ nm. The molar masses are Ba, 137.327 g mol^{-1}, F, 18.998 g mol^{-1}. Calculate the density of this compound.

1.5 Strontium chloride, $SrCl_2$, adopts the *fluorite* structure, and has a density of 3052 kg m^{-3}. The molar masses of the atoms are Sr, 87.62 g mol^{-1}, Cl, 35.45 g mol^{-1}. Estimate the lattice parameter, a, of this compound.

1.6 Molybdenum, Mo, adopts the A2 (tungsten) structure. The density of the metal is

10222 kg mol^{-1} and the cubic lattice parameter is $a = 0.3147$ nm. Estimate the molar mass of molybdenum.

1.7 A metal difluoride, MF_2, adopts the tetragonal *rutile* structure, with lattice parameters $a = 0.4621$ nm, $c = 0.3052$ nm and density 3148 kg m^{-3}. The molar mass of fluorine, F, is 18.998 g mol^{-1}. Estimate the molar mass of the metal and hence attempt to identify it.

1.8 The density of anthracene, $C_{14}H_{10}$, is 1250 kg m^{-3} and the unit cell volume is 475.35×10^{-30} m^3. Determine the number of anthracene molecules, Z, which occur in a unit cell. The molar masses are: C, 12.011 g mol^{-1}, H, 1.008 g mol^{-1}.