Chapter 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 homogeneous solids that possess a long-range three-dimensional array of ordered atoms. That is, the arrangement of the atoms in one small volume of a crystal is identical (excepting localised mistakes or defects that can arise during crystal growth or that are inserted deliberately) to that in any other similar but remote part of the crystal. Crystallography is the study of crystals and 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 of solids depend upon crystal structure, and knowledge of crystallography is essential if the properties of materials are to be understood and exploited.

1.1 CRYSTAL FAMILIES AND CRYSTAL SYSTEMS

Crystallography first developed as an observational science: an adjunct to the study of minerals. Minerals were (and still are) described by their morphology or **habit**, the shape that a mineral specimen may exhibit, which may vary from an amorphous mass to a well-formed gemstone. 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 of a well-formed crystal provides an obvious means of classification. For example, some crystals resemble cubes or octahedra, whilst others are brick-like or form prisms with a hexagonal cross-section (Figure 1.1).

The external shape of a well-formed crystal reflects the internal order of the solid,

Crystals and Crystal Structures, Second Edition. Richard J. D. Tilley.

(a) (b)

Figure 1.1 (a) Quartz (SiO_2) crystals, showing hexagonal morphology; (b) pyrite (FeS_2, fool's gold) crystals showing cubic and octahedral morphology.

especially the presence of internal symmetry. Symmetry will be developed later (especially in Chapters 3 and 4), but for the moment we can note that the most important symmetries displayed by crystals, and used in their classification, are the mirror plane, across which two parts of the crystal are related by reflection, and rotation axes. There are four different rotation axes: the diad or two-fold, in which successive rotations by (360/2)° leave the crystal unchanged; the triad or three-fold, in which successive rotations by (360/3)° leave the crystal unchanged; the tetrad or four-fold, in which successive rotations by (360/4)° leave the crystal unchanged; and the hexad or six-fold, in which successive rotations by (360/6)° leave the crystal unchanged. Careful measurement of mineral specimens using these symmetry criteria have allowed crystals to be classified in terms of six **crystal families** – anorthic, monoclinic, orthorhombic, tetragonal, hexagonal, and isometric or cubic – later expanded slightly by crystallographers into seven **crystal systems** (Table 1.1).

The crystal systems are sets of reference axes, which have a direction as well as a magnitude, and hence are vectors.[1] The allocation of a crystal to a particular system is made on the basis of the internal symmetries that are inferred from the crystal habit, which includes the apparent external symmetry. For instance, a crystal that resembled a hexagonal prism would be allocated to the hexagonal crystal system. It is common sense to allocate one reference axis to lie parallel to the hexagonal prism length and the other two axes to be normal to two chosen faces of the hexagonal prism. The axis lying along the prism length is really the defining axis for this designation because it is the unique hexad axis about which the crystal could be rotated by successive 60° turns to reproduce the same shape. Similarly, if a crystal has the form of a brick with a square cross-section, it is assigned to the tetragonal system, and the axes are positioned parallel to the three edges of the crystal. The defining axis this time is a tetrad perpendicular to the square cross-section, and this time the crystal can be rotated by

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

Table 1.1 The seven crystal systems

Crystal family	Crystal system	Required symmetry[a]	Axial relationships
Anorthic	Triclinic	None	$a \neq b \neq c$, $\alpha \neq 90°$, $\beta \neq 90°$, $\gamma \neq 90°$
Monoclinic	Monoclinic	1 diad or 1 mirror plane	$a \neq b \neq c$, $\alpha = 90°$, $\beta \neq 90°$, $\gamma = 90°$
Orthorhombic	Orthorhombic	3 diads or 1 diad + 2 mirror planes	$a \neq b \neq c$, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$
Tetragonal	Tetragonal	1 tetrad	$a = b \neq c$, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$
Hexagonal	Trigonal	1 triad	$a = b = c$, $\alpha = \beta = \gamma$ (rhombohedral axes); or $a' = b' \neq c$, $\alpha' = 90°$, $\beta' = 90°$, $\gamma' = 120°$ (hexagonal axes)
	Hexagonal	1 hexad	$a = b \neq c$, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$
Isometric	Cubic	3 tetrads	$a = b = c$, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$

[a]Symmetry nomenclature is expanded in Chapters 3 and 4.

successive 90° turns to regenerate the same shape. Thus the allocation of the reference axes and the placement of a crystal into a crystal family depends upon the external symmetry of the crystal.

The three reference axes for each family, allocated with respect to the crystal symmetry, are labelled **a**, **b** and **c**, and the angles between the positive directions 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 1.2). The angles are chosen to be greater or equal to 90° except for the trigonal crystal system, as described below. In the 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 relative lengths are written *a*, *b* and *c*.

The most symmetric of the crystal systems is the cubic or isometric system, in which the three tetrad axes are arranged at 90° to each other

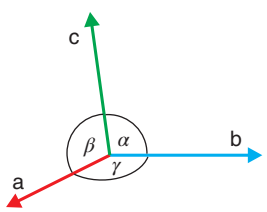

Figure 1.2 Reference axes used to characterise the seven crystal systems.

and the axial lengths are identical. These form the familiar Cartesian axes. The tetragonal system is similar, with mutually perpendicular axes, but two of these, usually designated **a** (= **b**), are of equal length, whilst the third, the tetrad axis, usually designated **c**, is longer or shorter than the other two. The orthorhombic system has three mutually perpendicular axes of different lengths parallel to the three diads. 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, whilst the third **c**, normally parallel to the diad axis or mirror normal, is perpendicular 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 the hexad axis. The trigonal system has three axes of equal length, each enclosing equal angles α (= β = γ), forming a rhombohedron. The axes are called rhombohedral axes and the triad axis is allocated to the body diagonal of the rhombohedron. 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 parallel to the triad axis (Figure 1.3). 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 A].) The arithmetical relationships between the axial lengths are given by:

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

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

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

1.2 UNIT CELLS AND MILLER INDICES

Observations of the cleavage of crystals, that is, the way in which they can be fractured along certain directions in such a manner that the two resultant fragments have perfect faces, suggested that all crystals might be built up by a stacking of infinitesimally small, geometrically regular elementary volumes, each unique to the crystal under consideration. These elementary

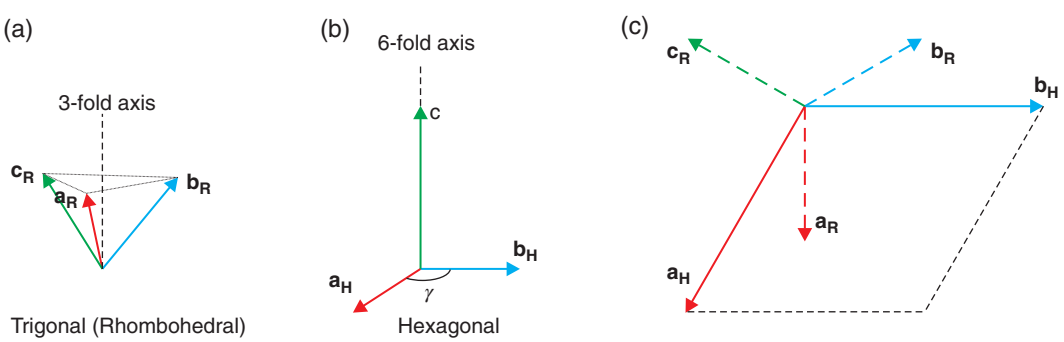

Figure 1.3 Rhombohedral (trigonal) and hexagonal axes: (a, b) axes in equivalent orientations with the trigonal three-fold axis parallel to the hexagonal six-fold axis (**c**-) axis; (c) superposition of both sets of axes, projected down the hexagonal **c**-axis (the rhombohedral three-fold axis).

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 unit cell type was then given the same name as the corresponding crystal system: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal or cubic. The absolute lengths of the axes, also written *a*, *b* and *c*, determined by diffraction techniques, yield the **structural unit cell** of the material. Unit cell parameters now refer only to these structural values, but the morphological names (triclinic, monoclinic, etc.) are still used. In these terms, the vectors that define the edges of the structural unit cell, **a**, **b**, **c**, are called the **basis vectors** of the direct lattice, whilst *a, b, c* are the lengths of the basis vectors or lengths of the structural unit cell edges, and are called the **lattice parameters**.

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 leads to severe restrictions upon the shape (strictly speaking the symmetry) of a unit cell. The fact that some unit cell shapes are not allowed is easily demonstrated in two dimensions, as it is apparent that regular pentagons (a plane figure with five equal sides and five equal internal angles), for example, cannot pack together without leaving gaps (Figure 1.4).

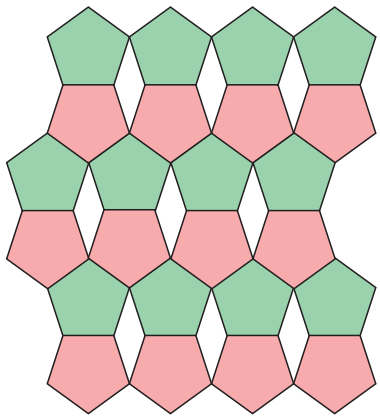

Figure 1.4 Irrespective of how they are arranged, regular pentagons cannot fill a plane completely; spaces always appear between some of the pentagons.

Not only can 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 are stacked in different directions (i.e. the rate at which the crystal grows in three dimensions), different facets of the crystal become emphasised, whilst others are suppressed, so producing a variety of external shapes or habits (Figure 1.5), thus explaining the observation that a single mineral can occur in differing crystal morphologies.

The faces of a crystal, irrespective of the overall shape of the crystal, can always be labelled with respect to the crystal axes. Each face is given a set of three integers, (*h k l*), called **Miller indices**. These are such that the crystal face in question makes intercepts on the three axes of *a*/*h*, *b*/*k*, and *c*/*l*. A crystal face that intersects the axes in exactly the axial ratios is given importance as the **parametral plane**, with indices (1 1 1). Miller indices are 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.

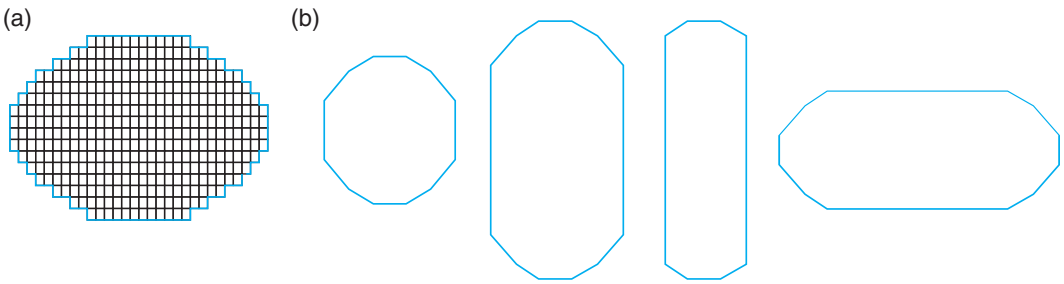

Figure 1.5 (a) schematic depiction of a crystal built of rectangular (orthorhombic) unit cells. The unit cells must be imagined to be much smaller than depicted, thus producing smooth facets. (b) Varying crystal habits derived by differing rates of directional crystal growth.

1.3 THE DETERMINATION OF CRYSTAL STRUCTURES

The descriptions of crystals above are mainly the result of the application of optical techniques. 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 twentieth 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 7.

1.4 THE DESCRIPTION OF CRYSTAL STRUCTURES

Any crystal structure is described in terms of its unit cell. Although unit cells are correctly defined in terms of the symmetries present, for the moment we will simply assume that the unit cell is an experimentally determined small volume of the crystal, which, if translated (repeated) in three dimensions without rotation or reflection, will build up the entire 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. The x, y and

z coordinates are plotted with respect to the unit cell axes, not to a Cartesian set of axes. 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 basis vectors (unit cell axes). To summarise:

a, b, c are the basis vectors of the direct lattice

a, b, c are the lengths of the basis vectors or lengths of the unit cell edges

x, y, z are the coordinates of a point as fractions of *a, b, c*.

In addition:

X, Y, Z refer to Cartesian axes when required.

In figures, the conventional origin is placed at the left rear corner of the unit cell. 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 (Figure 1.6). 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**-axis is drawn pointing down, (from top to bottom of the page), and the **b**-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.

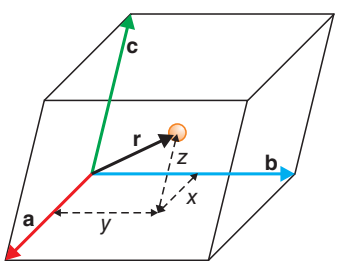

Figure 1.6 The position of an atom, *x*, *y* and *z*, in a unit cell.

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 1.7). 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.

A vast number of structures have been determined, and it is very convenient to group those with topologically identical structures

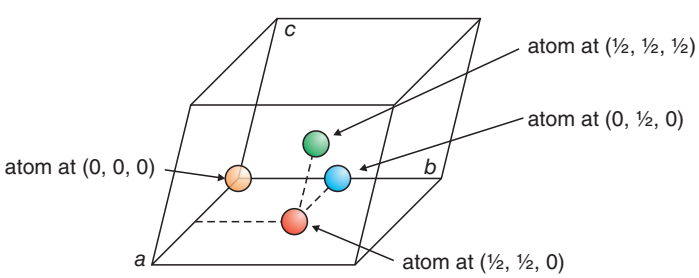

Figure 1.7 Atoms at positions 0, 0, 0; 0, ½ 0; ½, ½, 0; and ½, ½, ½ in a unit cell.

together. On going from one member of the group to another, the atoms in the unit cell differ, reflecting a change in chemical composition, and the atomic coordinates and unit cell dimensions change slightly, reflecting any differences 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 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 B. Some mineral names of common structures are found in Table 1.2 and Appendix B.

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 for the description of simple structures. Some *Strukturbericht* symbols are given in Table 1.2.

1.5 CRYSTAL STRUCTURES: METALS

In these simple structures, only one atom type is present, and all the atom positions are listed. (More complex crystal structures will contain many atoms in the unit cell, and those of proteins contain thousands. To make the list of atom positions manageable use is made of the

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, zincblende	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

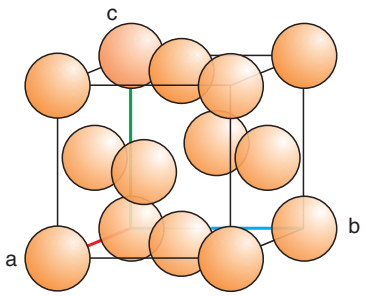

Figure 1.8 The cubic unit cell of the A1, copper, structure.

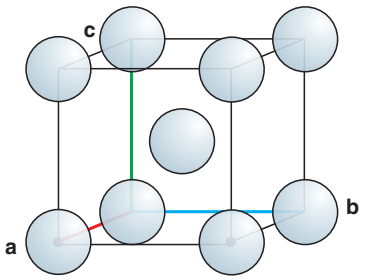

Figure 1.9 The cubic unit cell of the A2, tungsten, structure.

underlying symmetry elements present in the unit cell, which allows a minimum number of atoms to be specified such that application of the symmetry operators generates the whole cell contents, described in more detail in Chapter 7.)

1.5.1 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[2] for copper: a = 0.360 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 1.8). Besides a number of metals, the noble gases, Ne(s), Ar(s), Kr(s) and 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 0.7405. More information on this structure is given in Chapter 7.

1.5.2 The Body-Centred Cubic (A2) Structure of Tungsten

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

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 (Figure 1.9). 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 eight nearest neighbours and six next-nearest neighbours at only 15% greater distance. If the atoms are supposed to be hard

[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 to crystallographic practice.

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.

1.5.3 The Hexagonal (A3) Structure of Magnesium

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

(The atoms can also be placed at ⅔, ⅓, ¼; ⅓, ⅔, ¾, by changing the unit cell origin. This is preferred for some purposes.) There are two magnesium atoms in the unit cell. The structure is shown in perspective (Figure 1.10a) and projected down the **c**-axis (Figure 1.10b). 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:

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

More information on this structure, and the relationship between the A1 and A3 structures, is given in Chapter 8.

1.6 CRYSTAL STRUCTURES: BINARY COMPOUNDS

1.6.1 The *Halite* (Rock Salt, NaCl) Structure

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

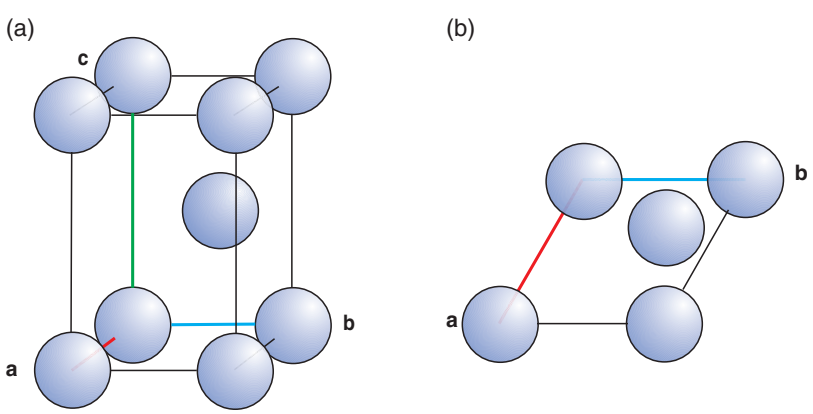

Figure 1.10 The hexagonal unit cell of the A3, magnesium, structure: (a) perspective view; (b) projection down the **c**-axis.

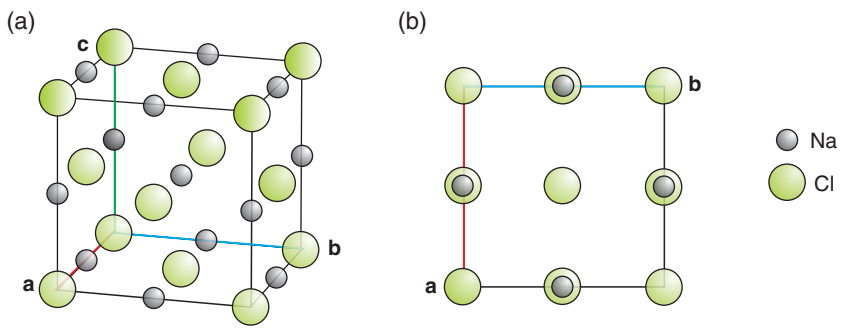

Figure 1.11 The cubic unit cell of the B1 (halite) structure of NaCl: (a) perspective view; (b) projection down the **c**-axis.

Unit cell: cubic
Lattice parameter for halite:
a (= b = c) = 0.5500 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. Each atom is surrounded by six atoms of the opposite type at the corners of a regular octahedron. A perspective view of the structure is shown in Figure 1.11a, and a projection, down the **c**-axis, in Figure 1.11b.

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

1.6.2 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 commonly encountered form of TiO_2 is called anatase. Other structures for TiO_2 are also known.)

Unit cell: tetragonal
Lattice parameters for rutile: a (= b) = 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 titanium and four oxygen atoms in the unit cell. In this structure, each titanium atom is surrounded by six oxygen atoms at the corners of a regular octahedron. A perspective view of the rutile structure is shown in Figure 1.12a, and a projection down the **c**-axis in Figure 1.12b.

This structure is relatively common and adopted by a number of oxides and fluorides of medium-sized cations.

1.6.3 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(s) for fluorite:
a (= b = c) = 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

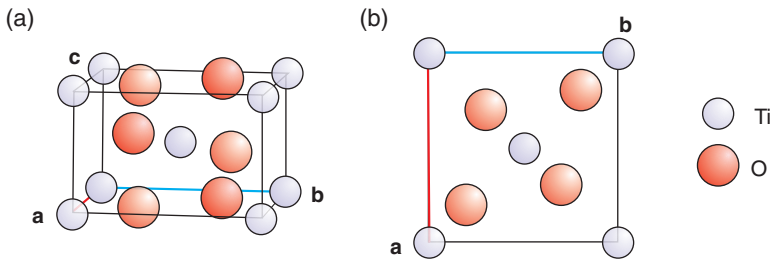

Figure 1.12 The tetragonal unit cell of the rutile structure TiO_2: (a) perspective view; (b) projection down the **c**-axis.

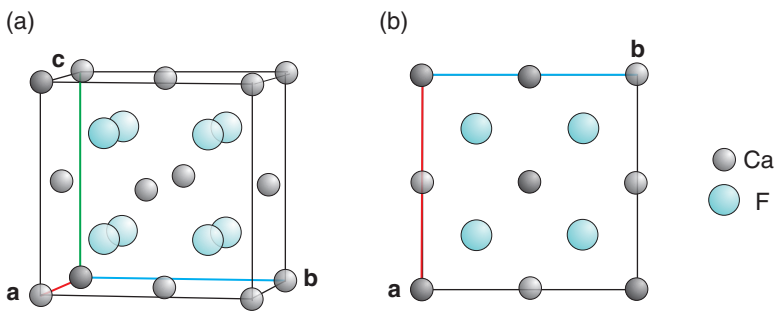

Figure 1.13 The cubic unit cell of the fluorite structure CaF_2: (a) perspective view; (b) projection down the **c**-axis.

There are four calcium and eight fluorine atoms in the unit cell. 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 1.13a, and a projection of the structure down the **c**-axis in Figure 1.13b.

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

1.7 THE CUBIC *PEROVSKITE* STRUCTURE

The general formula of crystals with the *perovskite* structure is ABX_3, and all are structurally related to the mineral perovskite, $CaTiO_3$. The simplest (ideal) structure is that adopted by strontium titanate, $SrTiO_3$.

Unit cell: cubic
Lattice parameter(s) for strontium titanate: a (= b = c) = 0.3905 nm
Z = 1 {$SrTiO_3$}
Atom positions: Sr: 0, 0, 0
Ti: ½, ½, ½
O: ½, ½, 0; ½, 0, ½; 0, ½, ½

There is one Ti atom at the cell centre and one Sr atom at the cell corners. The O atoms lie at the centres of the cell faces. Each Ti is surrounded by six O atoms arranged to give a regular octahedral coordination polyhedron, often stressed when describing perovskites in general (Figure 1.14).

The perovskite ABX_3 structure or slightly distorted variants of it are adopted by many compounds containing a large (A) and a

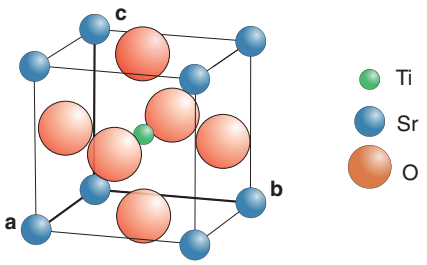

Figure 1.14 The cubic unit cell of the perovskite structure $SrTiO_3$.

medium-sized (B) cation when combined with anions (X) including oxygen, halogens and nitrogen.

1.8 THE STRUCTURE OF UREA

The structures of molecular crystals tend to have a different significance to those of the inorganic and mineral structures described above. Frequently, the information of most importance is the molecular geometry, and how the molecules are arranged in the crystallographic unit cell is often of secondary 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 the 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 7 and 8.) The crystallographic data for urea are as follows:[3]

[3] Data adapted from: Zavodnik, V., Stash, A., Tsirelson, V., et al. (1999). *Acta Crystallographica* **B55**: p45.

Unit cell: tetragonal
Lattice parameters: a (= b) = 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, 0.5000, 0.5963
O2: 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
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. This is because each different atom occupies a site with a different symmetry to the others (see Chapter 6). The atoms in a unit cell (including hydrogen) are shown in Figure 1.15a. 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, but 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 1.15b, and this is compared with a molecule of urea viewed front on (Figure 1.15c), and edge on (Figure 1.15d) extracted from the crystallographic data. The crystal structure is redrawn in Figure 1.15e and f with the atoms linked to form molecules. This latter depiction now agrees with chemical intuition, and

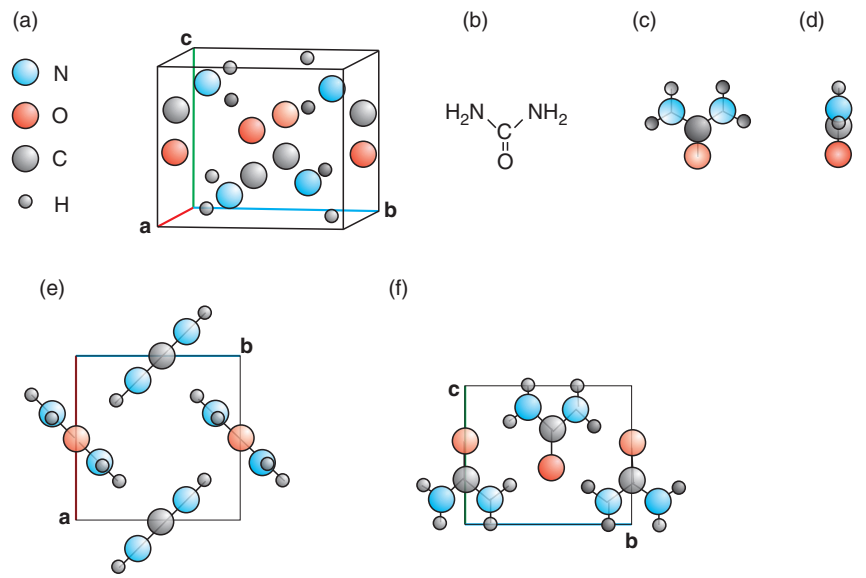

Figure 1.15 The crystal structure of urea: (a) perspective view of the tetragonal unit cell of urea; (b) structural formula of urea; (c) a 'ball and stick' representation of urea 'face on', as in (b); (d) 'sideways on'; (e) projection of the structure cell down the **c**-axis; (f) projection of the structure down the **a**-axis.

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 means used by crystallographers to reduce these lists to manageable proportions, by using the symmetry of the crystal, are explained in Chapter 6.

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

$$m_A = \text{molar mass}/N_A \text{ (grams)}$$

$$= \text{molar mass}/(1000 \times N_A) \text{ (kilograms)}$$

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

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

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:

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

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 1/2
an atom on an edge counts as 1/4
an atom on a corner counts as 1/8

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:

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

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, 6.02214×10^{23} mol^{-1}.

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

$$V = \left(0.5500 \times 10^{-9}\right)^3\ \text{m}^3$$
$$= 1.66375 \times 10^{-28}\text{m}^3$$

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

$$\rho = 3.882 \times 10^{-25}\text{kg}/1.66375 \times 10^{-28}\text{m}^3$$
$$= 2333\ \text{kg m}^{-3}$$

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, that were originally derived using the apparent external symmetry of mineral crystals. 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 +**b** and +**c**, β lies between +**a** and +**c**, and γ lies between +**a** and +**b**. The angles are chosen to be greater or equal to 90° except for the trigonal system. The axes are chosen by reference to the symmetry of the crystal under consideration, and some or all of the axes are chosen to be parallel to conspicuous symmetry elements displayed by the crystal. 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. 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). 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 parameters. Note that there is no unique unit cell for any crystal structure, and alternatives can usually be specified if this is helpful.

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 (lattice) 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. $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$
   b. $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$
   c. $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$
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. ½
    b. ¼
    c. ⅛

Calculations and Questions

1.1. The rhombohedral unit cell of arsenic, As, has unit cell parameters $a_R = 0.412$ nm, $\alpha = 54.17^\circ$. Use graphical vector addition (Appendix A) 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 = 0.3188 nm, with Sn atoms at: 0, 0, 0; ½, ½, ½; and O atoms at: $^3/_{10}$, $^3/_{10}$, 0; $^4/_5$, $^1/_5$, ½; $^7/_{10}$, $^7/_{10}$, 0; $^1/_5$, $^4/_5$, ½. 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, ½, ½, ½; Ti, 0, 0, 0; 0, ½, 0. Calculate the bond lengths (interatomic distances) from Ti to the surrounding O atoms. What is the shape of the O coordination polyhedron around the Ti?

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 10 222 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}.

1.9. Assuming CaF_2, fluorite, is ionic, and the F^- ions just touch, calculate the ionic radius of F^-. The lattice parameter of (cubic) CaF_2 is 0.5463 nm.

1.10 Estimate the C=O bond length in urea. The structure is tetragonal with lattice parameters a = 0.5589 nm, c = 0.46947 nm.