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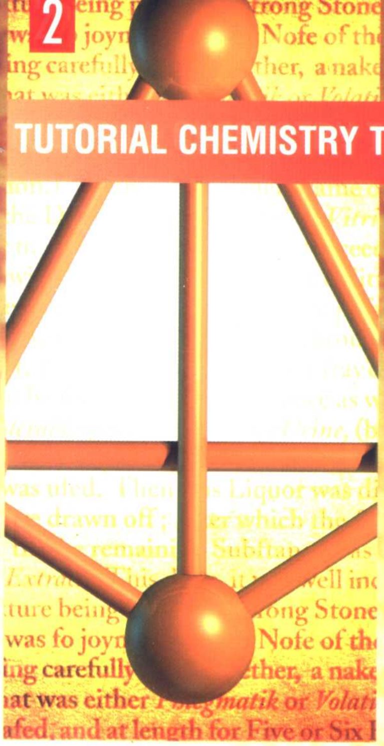

Reactions and *Characterization* of SOLIDS

by SANDRA E. DANN

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2

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ROYAL SOCIETY OF CHEMISTRY

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Preface

Materials is one area of research which brings together all the physical sciences: chemists to synthesize and characterize the solids, physicists to investigate their properties and engineers to fabricate them into useful devices.

Since the last decade, when I studied my degree, the materials subject has become an essential part of a chemistry degree, as the relationship between chemical structure and inherent physical properties has been recognized.

This book is designed as an introductory text to the synthesis and characterization of materials in the solid state, which are rather different to their solution-made, mononuclear counterparts. The text covers the salient information in a way which I would have found useful when I was studying for my degree. In addition, the last chapter introduces some recent discoveries, *e.g.* the superconducting oxides, which have been developed owing to the collaboration of chemists, physicists and engineers.

I have many people to thank in the conception and writing of this text. Firstly, Professor J. Derek Woollins for his invitation and, not least of all, Dr Mike Webster for his endless help and encouragement when I started teaching at Southampton. I would also like to thank Dr Paul Andrews, Deana McDonagh-Philp and Jennifer Armstrong for their proofreading and help, when I was less than gracious at the time, and a generation of Southampton and Loughborough University students, who were unknowing guinea-pigs for the questions in this book. Finally, I would like to thank my parents, for finding the money to send me to university, and the continual support of my family.

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1

Solid State Structure

Although the majority of this book will be concerned with crystalline inorganic materials, background knowledge of the different types of structures and bonds is essential for an understanding of the properties of *any* material.

Until recently, the structures of inorganic systems have been relatively mysterious, since the large number of possible coordination numbers and geometries, as well as possible combinations of elements, made these materials more difficult to characterize than their organic counterparts. This was particularly true of glassy and disordered materials, which could not be investigated using standard techniques such as X-ray diffraction.

Aims

This chapter deals with the fundamental concepts of crystal classification, symmetry and inorganic crystal chemistry. By the end of this chapter you should be able to

- Understand the differences between crystalline and amorphous materials
- Draw, as projections, the simple structures derived from close-packing and 'atom count' to show the number of formula units in each unit cell
- Use ionic radius ratios to predict likely structures

1.1 Types of Solid

Many industrially and technologically important materials are solids. In addition to the magnetic, optical or mechanical properties and anything else which makes them interesting, a chemist would also want to know about their **structure**: which atoms and/or ions are involved, where they are relative to each other and how they are bonded together.

All materials fall into two groups:

• Crystalline:	long-range order (>10^3 molecules)
• Non-crystalline (amorphous):	small particles with no long-range order (100 Å, where 1 Å = 10^{8} cm)

Nearly all materials can be prepared in the amorphous state. Interest in amorphous materials has grown with the development of techniques which can be used to characterize them. Glasses are a special type of amorphous material which melts at the **glass transition temperature**; here the rate of cooling and the viscosity of the liquid, when the material solidifies, are too great to allow the atoms to rearrange into an ordered crystalline state.

Although glasses and other amorphous materials are difficult to characterize, this does not make them useless. For example, amorphous silicon can be used to transform solar energy into electricity, and glasses obviously find applications in window panes, bottles, drinking glasses, *etc.*

In the crystalline state, regular atomic order persists over distances which are very large in comparison with interatomic distances. However, even in the most perfect of crystals there are some small and usually random departures from regularity. These imperfections result in minor changes to physical properties, such as resistance and conductivity, but are a feature of solid state materials in general. It is noteworthy that reactions of materials often involve the whole crystal lattice, imperfections and all, rather than just the atoms of the 'pure' substance.

Crystals can be formed in numerous ways, including cooling from molten salts and deposition from vapours. Whether the material is obtained as a single crystal or a polycrystalline mass depends on the conditions used. The polycrystalline mass often has random directional properties, so it is better to characterize physical properties using a single crystal rather than the mass. However, the external symmetry of even the smallest crystallite is characteristic of that particular substance, and is normally related to the arrangement of the atoms in the crystal. The macroscopic appearance of the crystal therefore gives information on the microscopic arrangement of its atoms.

1.2 Properties of Large Crystals

The word crystal is derived from the ancient Greek word for ice. The ancient Greeks believed that quartz (SiO_2) was water so deeply frozen it would never melt. Although quartz was found much later to contain silicon and oxygen rather than hydrogen and oxygen, the name 'crystal' is still used as a general term today.

1.2.1 Characteristics of Macroscopic Crystals

Some properties of large crystals found in museums or grown in the laboratory are given below:

- Flat faces (to a good approximation)
- Relative *sizes* of faces can vary from crystal to crystal of the same substance
- The *angle* between similar faces is found experimentally to be a constant
- Crystals break (cleave) parallel to certain well-defined faces

Although the angles between faces remain constant, the relative sizes of faces may vary from crystal to crystal. This behaviour is described as **crystal habit**, and the growth of the same substance from different solutions can result in different shapes. For example, sodium chloride crystals grown in water are cubic, but if urea is added to the water they become octahedral (a regular octahedron and a cube have the same overall symmetry).

Polymorphism occurs when different structures can occur for the same chemical formula. The atoms are the same but their atomic arrangement differs between the structures. Although ultimately thermodynamics (the minimum Gibbs free energy) dictates which of the probable structures is formed at a particular temperature and pressure, other factors such as electrostatic interaction mean that a variety of different structures is possible. Polymorphism applies not only to elements, *e.g.* black and red phosphorus, but also to compounds such as calcium carbonate, which can exist in a number of forms including calcite, aragonite and vaterite.

1.3 Crystal Lattices

A classification of crystals which is based on bonding is useful in understanding structure–property relations in solids. Five types of solid are readily defined by considering the bonding in them: ionic, covalent, metallic, molecularly bonded and hydrogen bonded. The last two are concerned with molecules rather than with lattices and will not be discussed here. They are discussed in detail in other texts (*e.g.* Rao and Gopalakrishnam[1]). Important properties of the particular lattices are summarized in Table 1.1.

1.3.1 Ionic Crystals

Ionic crystals are formed between highly electropositive and highly electronegative elements when electron transfer has occurred between the atoms, resulting in oppositely charged ions with closed shell (octet) electronic configurations. Ionic crystals such as potassium chloride

Table 1.1 Important properties of particular lattices

Type	*Particles*	*Characteristics*	*Examples*
Ionic	Ions	Brittle, insulating, high melting point	NaCl, CaF_2
Covalent	Atoms	Rigid, high melting point, non-conducting (pure)	Diamond SiC
Metallic	Positive ions in a 'sea' of electrons	High conductivity	Na, Au

consist of spherical ions, where charged ions are surrounded by ions of the opposite charge. This results in highly symmetrical structures in which like charges are as far apart as possible.

1.3.2 Covalent Crystals

When the elements in a crystalline material have similar electronegativities, bond formation occurs through the sharing of electrons, each atom contributing one electron to the bond. The force of attraction between two atoms of similar electronegativity arises from the overlap of atomic orbitals and the consequent net lowering of energy. This results in the formation of an electron pair, where the electrons are shared between neighbouring atoms. Typical examples of covalently bonded solids include those in Group 14, where sharing of the four s^2p^2 electrons achieves a closed shell electronic configuration, *e.g.* SiC. Hybridization of the atomic orbitals results in a tetrahedral arrangement of the four covalent bonds.

1.3.3 Metallic Crystals

Metals are significantly different from non-metallic solids both in structure and physical properties. They usually crystallize with dense structures (see Section 1.5) with large coordination numbers (eight to twelve). Typically they consist of positively charged ions in a 'sea' of electrons, in which the outer electrons of the metal atoms are free to move, hence giving high electrical and thermal conductivity. The properties of metallic crystals cannot be accounted for in terms of localized bonds or electron clouds, and are best described by a 'delocalized electron' approach.

A simple explanation for the many characteristic features of the metallic state is given by '**free-electron**' theory. In metallic crystals the atoms are assumed to take part collectively in bonding, where each atom provides electrons from outer electron energy levels to the bond. The crystal

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is considered to be 'held together' by electrostatic interaction between the resulting cations and the free electrons. Within the boundaries of the crystal, the free electrons move under a constant potential, while at the boundaries there is a large potential difference which prevents escape of the electrons.

Polymorphism in metals is common, often occurring as the temperature of the metal changes, and the different forms are normally (though not exclusively) labelled α, β, γ . . . with increasing temperature. In some cases, metals can revert to a lower temperature form at high temperature. For example α-Fe is stable up to 906 °C and then alters to γ-Fe at 1401 °C before reverting to α-Fe at 1530 °C. In this case, β-Fe is not stable under normal conditions and is only found at high pressure.

1.4 Unit Cells and Symmetry Elements

The properties observed for large macroscopic crystals suggested to early observers that crystals were made up by the regular repetition in space of the *same* unit of structure. Each **unit cell** displays the full symmetry of the structure.

A three-dimensional unit cell is described as a small volume defined by six faces. Each face is a parallelogram and there are three identical pairs. The bulk material is made up by translation (displacement) along the unit cell axes by an integral number of lengths of the axes. For example, Figure 1.1 gives a picture of a two-dimensional repeating pattern. For a two-dimensional pattern the unit cell is a parallelogram with two pairs

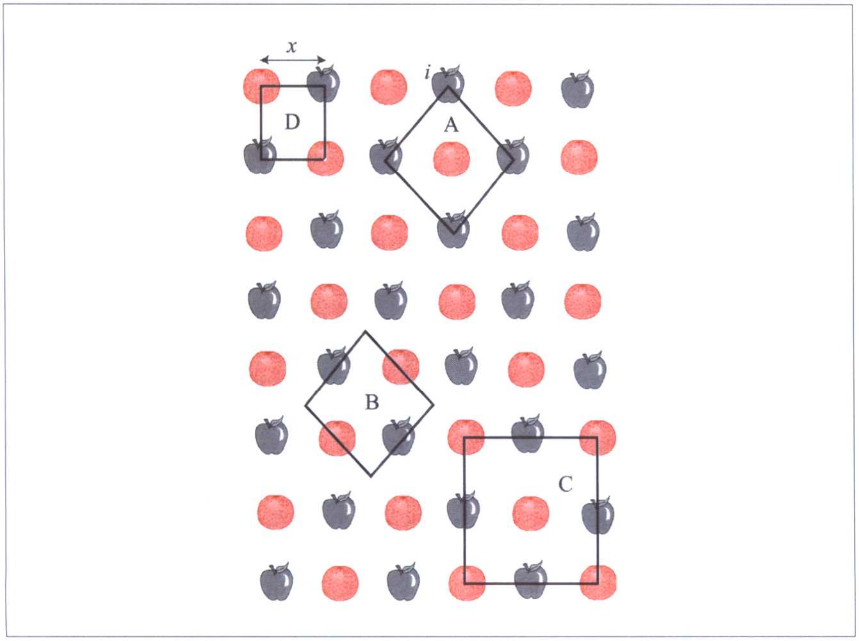

Figure 1.1 Two-dimensional repeating lattice

of identical sides which must show the full symmetry of the structure. Although any of the cells A, B or C could be chosen, the unit cell D is not a suitable choice as translation by the distance x translates an apple on to an orange. Movement of the other cells by a distance equal to their cell edges always maps apple on to apple or orange on to orange. The fact that the points chosen here are apples and oranges is irrelevant, as unit cells and symmetry apply to *any set of points* and do not necessarily relate directly to atoms. Any identical array of repeating points can be referred to as a lattice and hence can show symmetry and possess a unit cell.

Although cells A, B and C all show the full symmetry of this lattice, C is twice the size of the other cells. This introduces the principle of *point counting* and sharing to calculate how many lattice points a cell contains. In order to count points, the number of cells each point is shared between must be considered. Point i in cell A is on a corner, and if cells were drawn in both directions it could be seen that i is shared between four cells. This means that i is only worth one quarter of a whole point to the cell A. If we repeat this procedure for the whole of A, this generates one whole orange and one whole apple inside A. Thus for apples: $4 \times \frac{1}{4} = 1$ apple; for oranges $= 1 \times 1 = 1$ orange

Worked Problem

Q Repeat this procedure for cell C.

A Repeating this procedure for C produces two apples and two oranges in a unit cell. A unit cell which contains only one lattice point of a particular type is known as **primitive**. So here A is a primitive unit cell and C is non-primitive as it contains two lattice points (two apples and two oranges).

For a three-dimensional unit cell, the lengths (**cell parameters**) and angles are conventionally given the symbols a, b, c, α, β and γ, and are defined as shown in Figure 1.2. In three-dimensional unit cells, atom sharing leads to the proportional quantities given in Table 1.2.

The unit cell shown in Figure 1.2 has no symmetry in that the cell parameters and angles may take any values. All the cell parameters (a, b, c) have different lengths and all the angles are not right angles (90°). Increasing the level of symmetry produces relationships between the various cell parameters. For example, if a, b and c are all the same length and all the angles are right angles, then the shape of the unit cell is **cubic**. Seven crystal classes are obtained by the different possible combinations of cell parameters and angles which are given in Table 1.3 and illustrated in Figure 1.3.

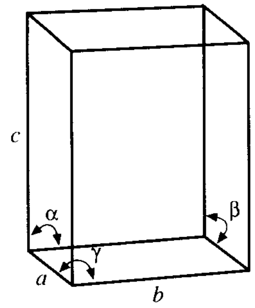

Figure 1.2 Three-dimensional unit cell with conventional lattice parameters

Table 1.2 Proportional quantities in three-dimensional unit cells

Position point	*Fraction of lattice*
Corner	1/8
Edge	1/4
Face	1/2
Inside Cell	1

Worked Problem

Q Take eight sugar cubes, place the first four in a two-by-two formation. Place the remaining four on top of the first four to form a larger cube. Imagine a sphere at the centre of the large cube, on a corner of each of the sugar cubes. One eighth of the sphere lies within each sugar cube.

(i) Repeat the process for a sphere which lies on the face of a sugar cube.
(ii) Locate the sphere on the edge of a sugar cube.
(iii) Place the sphere inside a sugar cube.

How much of the sphere lies within each sugar cube in the three tasks?

A (i) One half.
(ii) One quarter.
(iii) One.

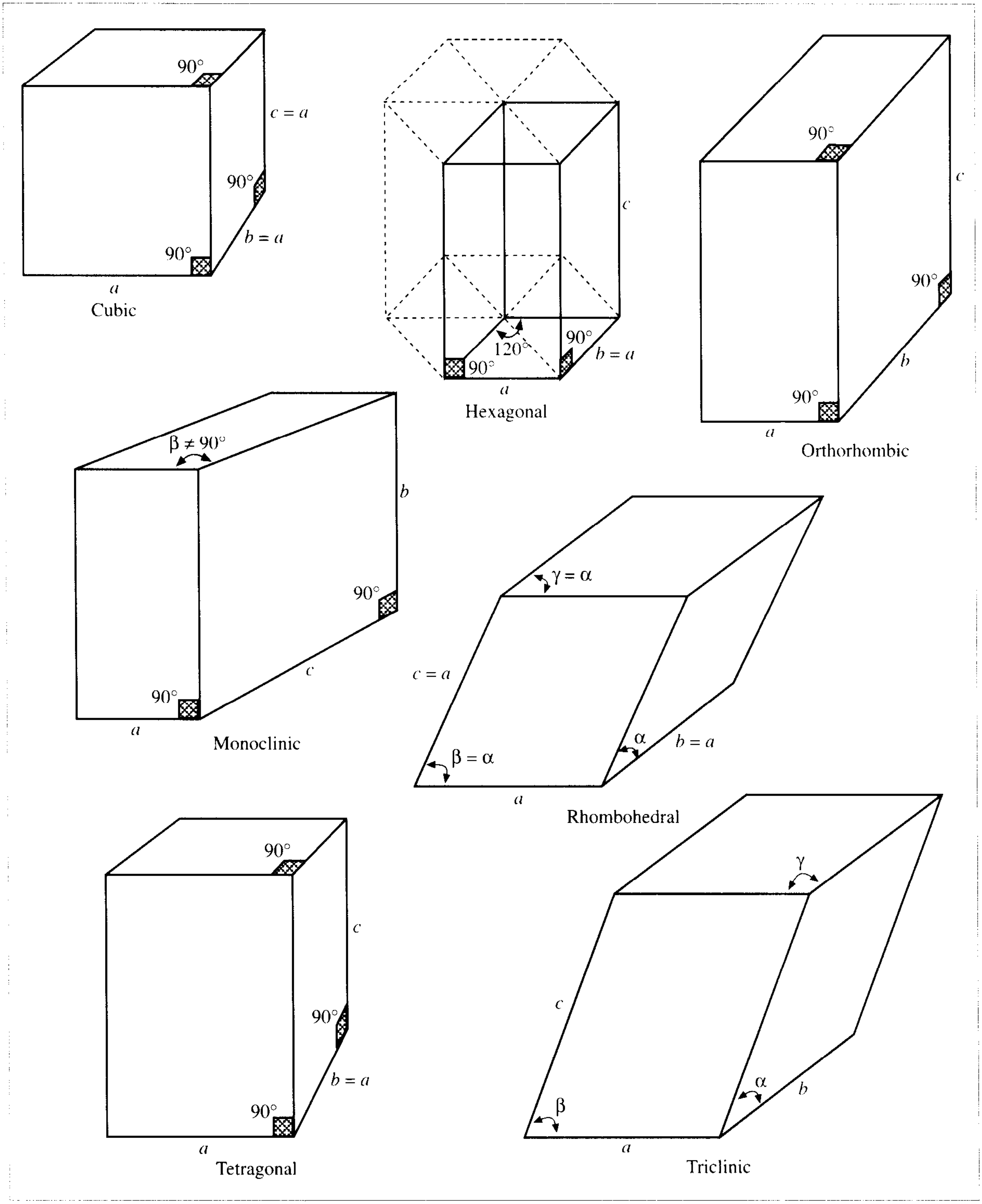
90°
c = a
90°
b = a
90°
a
Cubic
c
120°
90°
90°
b = a
a
Hexagonal
90°
c
90°
b
90°
a
Orthorhombic
β ≠ 90°
b
90°
c
90°
a
Monoclinic
γ = α
c = a
β = α
α
b = a
a
Rhombohedral
90°
c
90°
b = a
90°
a
Tetragonal
γ
c
β
α
b
a
Triclinic

Figure 1.3 The seven crystal systems

Table 1.3 Crystal classes

Cell parameter relationship		*Crystal class*
$a = b = c$	$\alpha = \beta = \gamma = 90°$	Cubic
$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Tetragonal
$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Orthorhombic
$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	Monoclinic
$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	Triclinic
$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Hexagonal
$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Trigonal (rhombohedral)

Three-dimensional figures such as these can be difficult to draw in an unambiguous way, so these diagrams are simplified by drawing a **projection**. In this, the structure is drawn by viewing it from a particular direction, normally along one of the unit cell axes. Viewing along an axis means that one of the faces of the unit cell is nearest to the viewer, and the distance of each atom from that face is written on the projection; the distance is measured as a fraction of the cell parameter along the axis of viewing. For example, Figure 1.4 shows a cube containing a lattice point at each corner and one at the centre of the cell and its two-dimensional projection. If we view the cube from the top face and consider first the atoms on the corners, for each corner there is one on the top face at 0 and one at the bottom at 1 (*i.e.* the whole unit cell away). The atom at the centre of the cube is half-way down the unit cell, so it is shown at a distance of $^1/_2$ on the projection.

This procedure is rather limited as it can only really be useful for unit cells with at least one 90° angle. A more universal approach involves the use of **fractional coordinates**. With these, each atom in the unit cell is given an x, y and z coordinate, where the atom is positioned at $(x/a, y/b, z/c)$ with respect to the origin of the unit cell. For example, in Figure 1.4 the atom at the centre of the unit cell would have a fractional coordinate of $(^1/_2, {}^1/_2, {}^1/_2)$ corresponding to a translation of half way along x, half way along y and half way along z with respect to the unit cell origin.

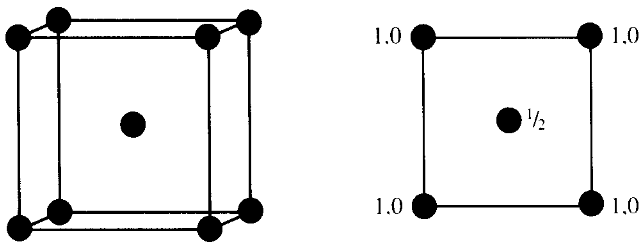

Figure 1.4 Orthographic projection of a body-centred cubic unit cell

In addition to different types of crystal system there are also different types of lattice within those crystal systems, which correspond to specific arrangements of the atoms/ions within them. As discussed earlier, the two-dimensional system with the simplest sort of lattice which contains only one lattice point, is termed **primitive**. Similarly, for each three-dimensional crystal system there is always a primitive unit cell which consists of atoms located at the corners of the particular parallelepiped (*i.e.* a solid figure with faces which are parallelograms). For example, Figure 1.5 shows primitive lattices (symbol **P**) for both tetragonal and hexagonal systems.

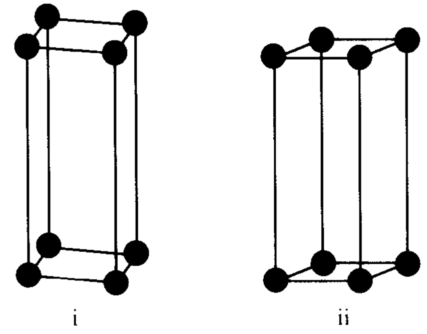

Figure 1.5 (i) Primitive tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$) and (ii) primitive hexagonal ($a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$) unit cells

For the remaining lattice types, as well as the translational symmetry from these corner points there is additional symmetry within the unit cell. The simplest of these is the **body-centred** example seen in Figure 1.4, where there is also an atom at the centre of the unit cell (with fractional coordinates ($^1/_2$, $^1/_2$, $^1/_2$). For a lattice to be body-centred therefore, if an atom or ion is placed on x, y, z there must be an identical one placed at $x+^1/_2$, $y+^1/_2$, $z+^1/_2$. A body centred lattice is given the symbol **I**.

In additional to body-centred, there are also two possible types of **face-centred** unit cells. A lattice where all the faces have a centrally placed atom is given the symbol **F**. If only one pair of faces is centred, then the lattice is termed **A**, **B** or **C** depending on which face the centring occurs. For example, if the atom or ion lies on the face created by the *a* and *b* axes, the lattice is referred to as C-centred. Examples of face-centred lattices are given in Figure 1.6.

Not all types of lattice are allowable within each crystal system, because the symmetrical relationships between cell parameters mean a smaller cell could be drawn in another crystal system. For example a C-centred cubic unit cell can be redrawn as a body-centred tetragonal cell. The fourteen allowable combinations for the lattices are given in Table 1.4. These lattices are called the **Bravais** lattices.

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