

AN INTRODUCTION TO THE METHOD

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By the end of this chapter you should be able to:

- Gain an appreciation of crystallography as a technique;
- Understand the concept of the unit cell, and of the asymmetric unit in a crystal lattice;
- Recognize and identify the 7 crystal systems and the 14 Bravais lattices.

Contrary to predictions made almost a century ago, X-ray crystallography as a technique has certainly not caused the premature death of chemical research; instead it has greatly influenced and contributed to our knowledge and understanding of the world around us, and will doubtless continue to do so.

Have you ever wondered how we know today that a humble crystal of table salt consists of sodium and chloride ions arranged in a cubic close-packed structure [2] or how is it known that graphite and diamonds [3] are both simply carbon atoms arranged differently? Or perhaps you might have questioned how Watson, Crick, and Wilkins determined that the basic building block of life, DNA (deoxyribonucleic acid), consists of a double helix structure.

The answers to these questions lie in X-ray crystallography, an analytical technique that uses X-rays to identify the arrangement of atoms, molecules, or ions within a crystalline solid.

1.1 X-RAY CRYSTALLOGRAPHY AS AN ANALYTICAL TOOL

Section learning outcomes

To be able to:

- Distinguish between spectroscopy and diffraction;
- Recognize the differences between small molecule and protein crystallography.

In the fields of chemistry and biology there lies an inherent need to identify, both qualitatively and quantitatively, the components (molecules, atoms, or ions) within any given *matter*. This identification serves not only to inform and educate, but also allows some form of further design or invention to take place once identification has been achieved.

Apart from X-ray crystallography, other analytical methods based on spectroscopy also provide an insight into the content and components of a sample under study.

1.1.1 Diffraction vs spectroscopy

The science of X-ray crystallography is based on the diffraction of X-rays by a crystalline material. It is the only analytical technique that can provide, with uncompromising certainty, the molecular structure of a given compound in the solid crystalline state.

Diffraction can be explained using an analogy to light being refracted by microscope lenses, when a sample is examined under a microscope.

If we refer to Fig. 1.1, (a) shows in outline how a microscope works while (b) is an outline of an X-ray diffraction experiment. A microscope is used when a sample is too small to be seen with the naked eye. When such a sample is examined under a microscope, as seen in Fig 1.1(a), light (from the light source) passes through the sample and is scattered. When the scattered light reaches the microscope lenses, the light is *refracted* and refocused by the lenses. The image of the sample can then be seen by eye through the lens (or eyepiece).

Just as a microscope sample is too small to be seen with the naked eye, the content of a crystal lattice is also too small to be viewed without instrumentation. A typical X-ray diffraction experiment requires only a small single crystal sample, usually of a few micrometres. The crystal sample physically interrupts the flow of X-rays from a source, causing the X-rays to scatter. This form of scattering is known as *diffraction*. The diffracted X-rays are detected

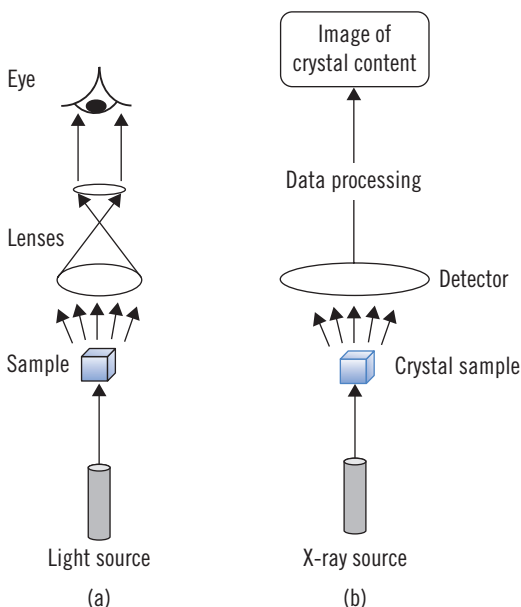


FIGURE 1.1 (a) Refraction of light from a microscope; (b) diffraction of X-rays in a crystallography experiment

by a detector. The way in which X-rays are diffracted by a particular crystal depends on the structure of the crystal, such that every crystal generates a unique diffraction pattern.

Although a detector is comparable to a microscope lens, while a microscope lens is able to refocus light in order to produce an image of the sample, a detector cannot. After the X-ray diffraction is collected by the detector, a range of corrections and computation takes place on a computer. This computer-based process is known as data processing. This process culminates with the generation of a visual image of the content (atoms, molecules, or ions) of the crystal lattice.

Data obtained from an X-ray diffraction experiment allow the direct inference of information. For example, the actual contents of the crystal sample, the types and arrangements of atoms, molecules, or ions within the crystal, and information on the bond lengths and angles can be obtained from an X-ray diffraction experiment. (Further details of the X-ray diffraction experiment are outlined in Section 8.5.)

In comparison, analytical methods based on spectroscopy that are used to identify molecular structures frequently exploit the inherent vibrations within a molecule. When a molecule is irradiated with a low-energy source, such as ultraviolet-visible or infrared radiation, the resulting absorptions or emissions of radiation can be measured and subsequently analysed. Spectroscopic methods, such as infrared spectroscopy, nuclear magnetic resonance (NMR), and Raman spectroscopy, are able to provide information about the energy levels within a molecular system, from which inferences about the molecular connectivity can then be made. These inferences sometimes can be extended to provide geometric information such as bond length and angles.

Examples of information obtained from spectroscopic methods include carbonyl (-C=O) and hydroxyl (-OH) stretches in infrared, which allow the presence of these groups to be determined, and the identification of different proton and carbon types from NMR.

While spectroscopy and X-ray diffraction are both very different techniques, in many ways they are complementary. The use of spectroscopy often provides very quick results, whereas an X-ray diffraction experiment can sometimes take days or weeks. The samples for a spectroscopic analysis are also not required to be a crystalline solid and spectroscopy can often be used as a bulk technique. This means that it is often safe to assume that the spectroscopic analysis of a small sample is representative of the bulk.

In contrast, X-ray diffraction provides very detailed, accurate information on the particular single crystal under study. It is necessary for that sample to be a crystalline solid. The results from a single crystal diffraction experiment are often assumed to be representative of the bulk of the sample, but this is not necessarily always true and bulk analysis usually needs to be carried out and reconfirmed using a spectroscopic technique.

While the field of X-ray crystallography relies on the analysis of X-ray diffraction from crystalline samples of very small sizes, in practice, X-ray crystallography can be further subdivided into small-molecule crystallography and macromolecular crystallography.

1.1.2 Small-molecule crystallography

Small-molecule crystallography, in which molecular sizes range from a few atoms to several hundred, is also commonly known as chemical crystallography. This can include inorganic, organic, and organometallic molecules.

Refraction refers to a change in the direction of a source of light, when the light moves from one medium to another while *diffraction* is a phenomenon that is often described as 'waves bending around corners'. Diffraction occurs when waves encounter an obstacle.

Small-molecule crystallography is widely employed in the identification and structural confirmation of newly synthesized molecules in various fields ranging from catalysts and new materials to new drugs. Owing to the small size of the molecules under study in small-molecule crystallography, it is usually possible to identify accurately all of the atom types within the molecule.

Within the crystal lattice of a 'small molecule', it is possible to find a range of intramolecular and intermolecular interactions; hydrogen bonding and π -stacking are examples of solid-state interactions that can be identified within a crystalline solid. These are discussed in further detail in Section 7.4.

1.1.3 Macromolecular (protein) crystallography

In contrast to chemical crystallography, macromolecular crystallography, which is also known as protein crystallography, is used to elucidate the three-dimensional structure of large biological molecules. In general, biological macromolecules can be divided into two groups: nucleic acids and proteins.

Possibly the most famous of all macromolecular structures is that of a nucleic acid, DNA (deoxyribonucleic acid), the elucidation of which won Watson, Crick, and Wilkins the Nobel Prize in 1962. Biologically, nucleic acids store and transmit genetic information. However, only a small number of these nucleic acids can be crystallized for study by X-ray crystallography. These consist mainly of derivatives of DNA, RNA (ribonucleic acid), and various combinations of both DNA and RNA.

Proteins are long-chain polymers (polypeptides) built from a combination of the 20 naturally occurring amino acids. While proteins as a group can be further divided into two subcategories, globular and fibrous proteins, crystallographers are interested mainly in globular proteins as these can be crystallized as single crystals.

The 'globular' nature of these proteins allows a large number of both intramolecular and intermolecular interactions to operate, in particular hydrogen bonding. These interactions both stabilize the protein, and give it its characteristic three-dimensional shape, which contributes to its crystallinity. The medium or solution in which the protein is crystallized also contributes to the stabilization of the crystal structure as these (usually) smaller solvent molecules fill in the spaces of the protein, and are usually extensively hydrogen bonded.

While small-molecule crystallography focuses on the identification of each atom and the positions of these atoms in three-dimensional space, macromolecular crystallography is usually more concerned with identifying the secondary structures – the shapes and motifs of the overall structure – rather than each individual atom. The two main types of motif typically found in protein structures are helices and β -pleated sheets. These are shown schematically in Fig. 1.2. The identification of secondary structures subsequently leads to the determination of the tertiary or quaternary structure, from which usually emerges the overall three-dimensional structure of a protein. An example of a tertiary structure containing both helices and β -pleated sheets can be seen in Fig. 1.3.

While chemical and protein crystallography differ somewhat in the types of molecule under study, the fundamentals of both (outlined in this book) remain congruous and highly similar.

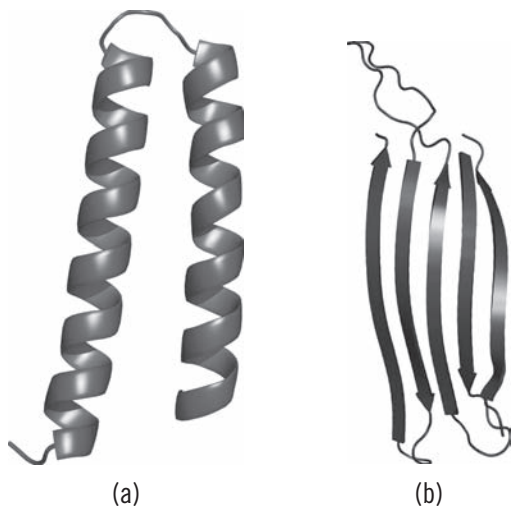


FIGURE 1.2 Secondary protein structures: (a) helices; (b) β -pleated sheets (images kindly provided by J. Crowe)



FIGURE 1.3 A tertiary protein structure (image kindly provided by J. Crowe)

SELF-TEST QUESTIONS

1. A newly synthesized chemical compound appears as an amorphous white solid and is soluble in most polar solvents. Which techniques could the chemist attempt in identifying this new compound?
2. Write brief notes comparing the identification processes of spectroscopy and diffraction.
3. What types of protein are suitable for X-ray diffraction and why?
4. Experiment with virtual diffraction online at <http://www.ngsir.netfirms.com/englishhtm/Diffraction.htm>

1.2 SOLIDS: CRYSTALLINE AND NON-CRYSTALLINE

Section learning outcomes

To be able to:

- Differentiate the different states of matter;
- Distinguish between crystalline and amorphous solids;
- Identify motifs and crystal packing in crystalline solids;
- Recognize two- and three-dimensional repeating patterns.

X-ray crystallography is a solid-state technique, in which samples have to be crystalline solids. X-rays can be diffracted from a crystal due to the periodic arrangement within a crystalline solid. The periodic nature of the crystalline solid is explained in further detail next, while X-ray diffraction is outlined in Section 2.3.

1.2.1 What are solids?

The three primary states of matter are the gaseous, liquid, and solid states. These states are most commonly identified by their physical form but they differ on an atomic or molecular scale too.

Referring to Fig. 1.4(a) we see that the atoms and molecules in solids are ordered and arranged with little movement except for vibrational energy around a central point.

The atoms and molecules within the liquid and gaseous states in Fig. 1.4(b) and (c), however, are less ordered and contain comparably greater amounts of energy. This energy enables the atoms to move. In solids, the movement of atoms is very restrained, akin to vibrations, while in a liquid, the atoms, having more energy, are able to move and take on the shape of the liquid's container. The atoms in gases, however, have the most energy and are able to move the most.

Solids, as we know them in the world around us, can broadly be divided into two distinct groups: *crystalline* and *non-crystalline* (also known as amorphous) solids. As X-ray crystallography relies on the principle of diffraction, it can only be used to analyse crystalline solids.

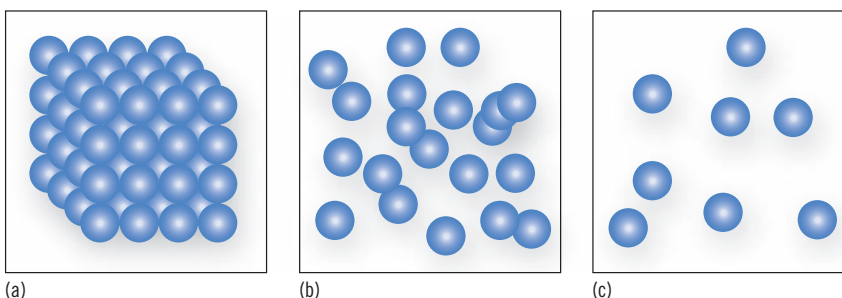


FIGURE 1.4 The atomic representations of the three states of matter: (a) solid; (b) liquid; and (c) gas

1.2.2 Crystalline and amorphous solids

The two main classes of solid, crystalline and amorphous solids (glasses, plastics, semiconductors, for example), are difficult to distinguish physically or visually, as differences lie at the atomic scale within the molecular make-up of each type of solid. While both contain *short-range order*, determined by the chemical bonds within the molecules, the lack of *long-range order* within the amorphous solids makes them unsuited to crystallographic analysis. The lack of long-range order, by definition, means that they cannot form crystal structures – and it is the structure of ordered crystals that is determined by X-ray crystallography.

Referring to the two-dimensional diagram in Fig. 1.5, both types of solid contain hexagonal molecules arranged in two distinctly different ways. In Fig. 1.5(a), we find that the molecules are ordered and arranged with specific distances between specific points or locations and this repetition is translated throughout the crystal. This is known as long-range order or translational periodicity.

Looking at Fig. 1.5(b), however, we notice that while all molecules also contain six atoms, the atoms are not regularly arranged to form uniform hexagonal shapes. While these atoms are not randomly distributed throughout space as in gases, they do lack the repetitive order that gives rise to translational periodicity or *long-range order* that we can find within crystals.

1.2.3 Motifs and packing within crystalline solids

As we now know, a crystalline solid consists of atoms and molecules arranged in a consistent fashion, giving rise to *long-range order*. The specific arrangement of these atoms and molecules within the crystal lattice also gives rise to identifiable motifs. The characteristic arrangement of atoms and molecules within the lattice is known as crystal packing. Figure 1.6(a–c) represents crystal packing in two dimensions, while Fig. 1.6 (d) represents packing in three dimensions. Each diagram consists of an ‘object’ that is repeated throughout the space, thereby ensuring that each is related to the next by translation.

On closer examination of the diagrams, you can identify the repetitive motifs and how the translations occur. Looking at Fig. 1.6(a), we can identify that each flower is an exact copy of the next; for Fig. 1.6(b), similarly, the four-point star objects are repetitions throughout. Although there are similarities between Fig. 1.6(b) and (c) the use of two colours in Fig. 1.6(c) now mean that the ‘object’ consists of two four-point stars (one dark and one light).

The *translation* of an object occurs when the object is moved up, down, or sideways without being reflected or rotated.

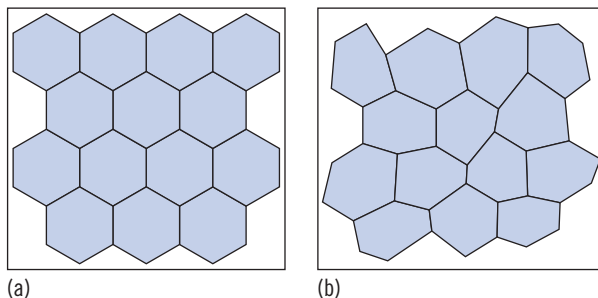


FIGURE 1.5 Molecular order within (a) a crystalline solid and (b) an amorphous solid

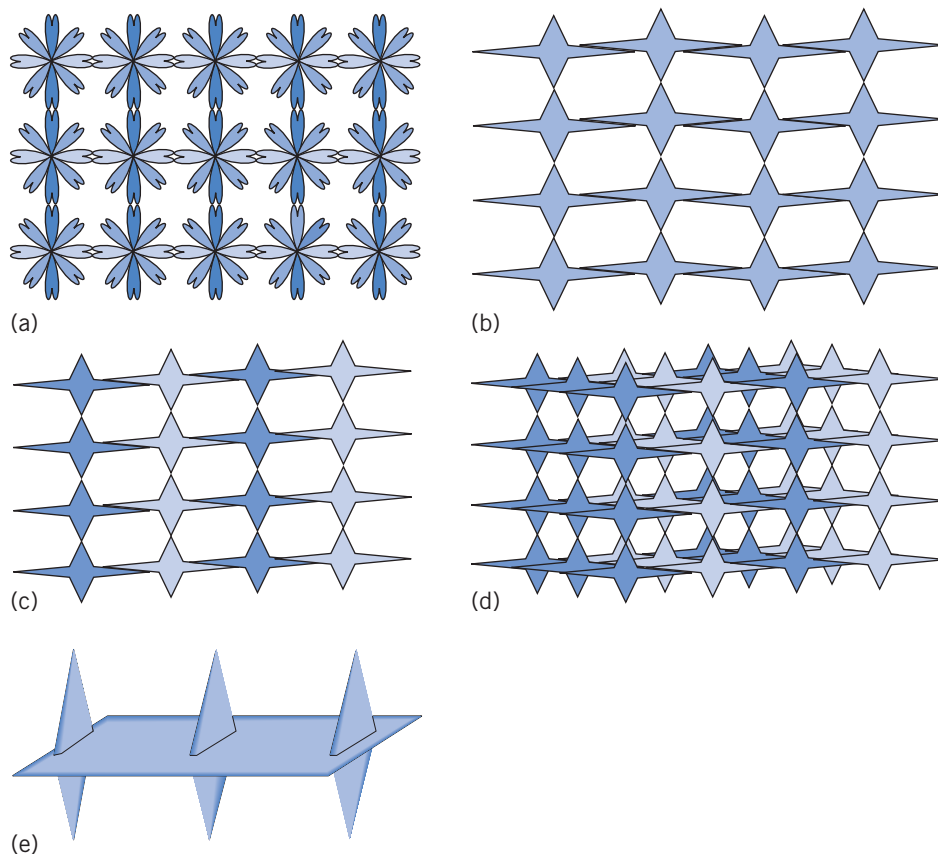


FIGURE 1.6 Examples of two- and three-dimensional packing

The two-dimensional array in Fig. 1.6(c) is repeated in ‘depth’ in Fig. 1.6(d), giving rise to an example of a three-dimensional packing system. On closer inspection, you will notice that, in three-dimensions, the packing system appears to consist of planes of alternating lines (dark blue and light blue) with peaks and ridges arising at precise intervals. A side-on view (from the left) is shown in Fig. 1.6(e).

A molecular example is given in Fig. 1.7 for coenzyme Q_0 (2,3-dimethoxy-5-methylbenzene-1,4-diol) where Fig. 1.7(a) and (b) represent a single molecule and Fig. 1.7(c) shows a view of part of the three-dimensional crystal lattice.

SELF-TEST QUESTIONS

1. Solids can broadly be divided into two classes. What are they?
2. With the help of diagrams, briefly describe the differences between the two classes of solid.
3. Give an example of *short-range* order and explain how it differs from *long-range* order.

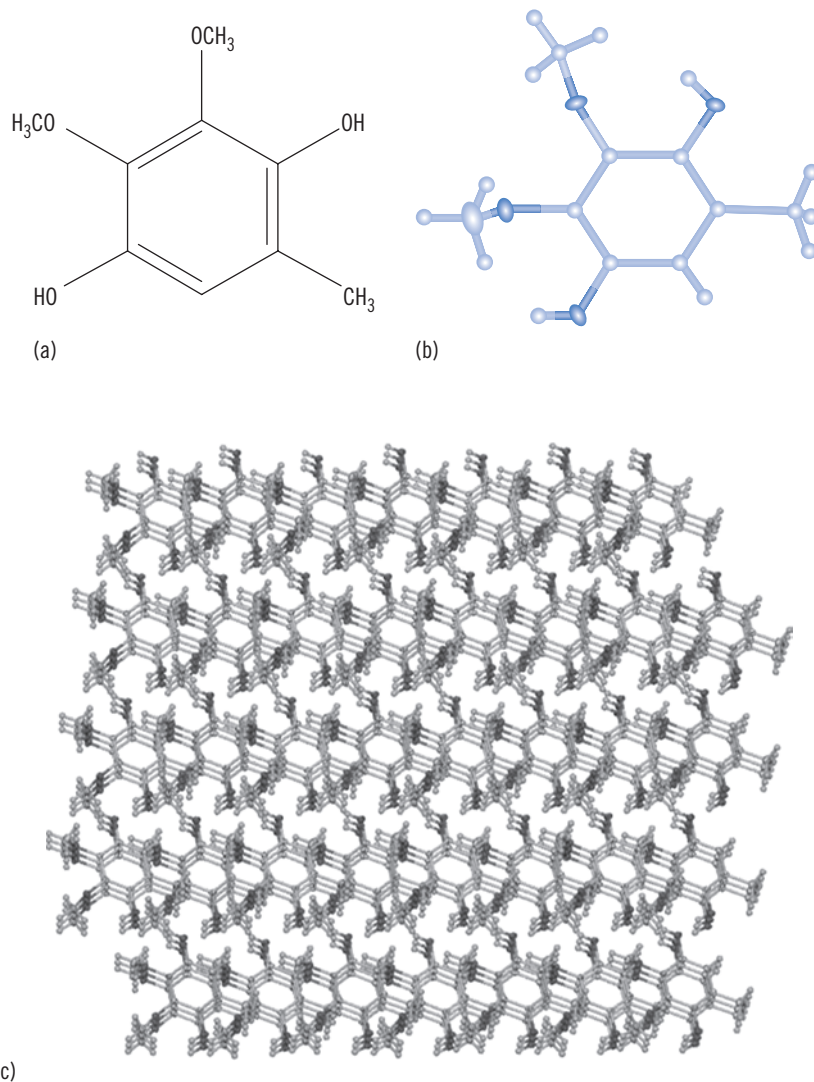


FIGURE 1.7 Coenzyme Q_0 : (a) and (b) the molecular structure; (c) the packing diagram

1.3 THE CRYSTAL LATTICE

Section learning outcomes

To be able to:

- Define and identify lattice points, lattice planes, and unit cells;
- Understand and apply the rules for selecting lattice points.

The external morphologies or shapes of crystals can range from cubic or tabular to hexagonal shapes; some examples are shown in Fig. 1.8. However, internally, as we have seen above,

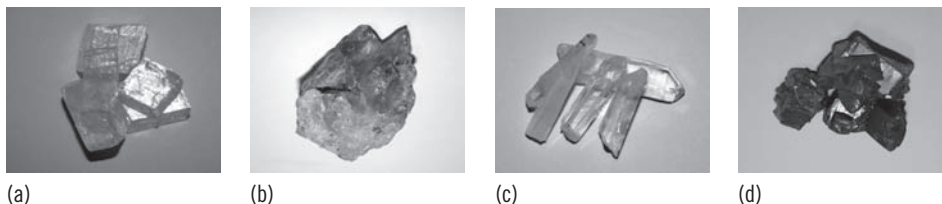


FIGURE 1.8 Different mineral crystals and their crystal morphologies ((a) calcite, (b) amethyst, (c) quartz, (d) pyrite)

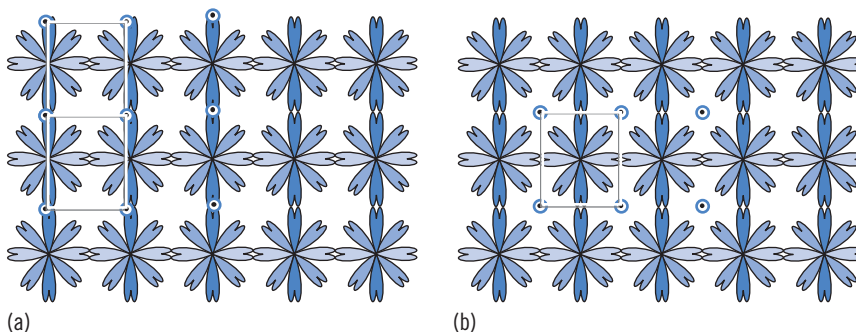


FIGURE 1.9 Examples of different possible lattice points

the atoms and molecules in a crystal form distinctive, organized three-dimensional arrays. We call these organized arrays **crystal lattices**. Specifically, a crystal lattice is defined as an ordered three-dimensional arrangement of ions, atoms or molecules within a solid.

The highly repetitive order within the crystal lattice makes it possible to identify positions within the lattice that are identical. These positions can then be marked with an imaginary point, referred to as a *lattice point*.

1.3.1 Rules for selecting lattice points

The key to selecting a lattice point is that the environment surrounding each point has to be the same. That is, the view from each lattice point is the same as that from every other point. In two dimensions, for example in Fig. 1.9(a), lattice points are selected at the tips of the dark petals and the surrounding environment of each lattice point consists primarily of the dark petals and the space between the 'flowers'. In Fig. 1.9(b) however, the lattice points are defined in the middle of the space between the 'flowers' and the immediate surrounding environment of each lattice point is mainly the white space and the blue petals.

It is important to point out that lattice points do not represent atoms or molecules, although sometimes they may be located on a particular atom within the crystal lattice. To understand this better, use the learning tip on visualization. (Refer also to Section 4.4).

Learning tip (visualization) If you were to imagine yourself standing on a lattice point and looking around, then the view all around should be exactly the same as that from any other lattice point.

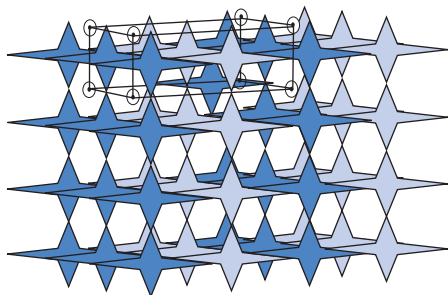


FIGURE 1.10 Identifying a unit cell

1.3.2 Lattice points and lattice planes

In two dimensions, we can then join four adjoining or adjacent lattice points to form a *lattice plane*. In Fig. 1.9(a) for example, it is possible to place a lattice point at the tip of the dark petals of each ‘flower’ and subsequently join the four lattice points to form a lattice plane that consists of two adjacent halves of the ‘flower’. In Fig. 1.9(b), however, the lattice points are connected to form a lattice plane that contains a whole ‘flower’.

When considering objects in three dimensions, the adjoining lattice points that are selected can be connected to form a ‘box’ or a container as illustrated in Fig. 1.10. The box is known as a *unit cell*. The unit cell can then be translated along (up or down, or sideways) through the lattice and its contents remain the same.

SELF-TEST QUESTIONS

1. Identify the possible lattice points in each of the diagrams in Fig. 1.6(a)–(c).
2. Using some samples of wrapping paper, identify some possible lattice points in each sample.
3. (a) Identify the lattice points in some of the symmetry-based pictures by M. C. Escher. These can be found online at <http://www.mcescher.com> under Picture Gallery and Symmetry.
(b) Discuss how the use of colour may influence the selection of the lattice points.

1.4 THE UNIT CELL AND ASYMMETRIC UNIT

Section learning outcomes

To be able to:

- Understand the association of crystal lattice with unit cell and asymmetric unit;
- Describe and recall the parameters used to define the unit cell.

Once selected, the unit cell forms the basic building block of the crystal lattice akin to the stacking of bricks in the building of a wall. The unit cell can then be reduced further to identify asymmetric units, as explained further in Section 1.4.2.

1.4.1 Definition of unit cell

A unit cell forms the basic building block of a crystal lattice. Each ‘box’ or container that defines the unit cell is related to the next unit cell by translation and the contents within each unit cell are exactly the same.

For example, if we refer to Fig. 1.11(a), the lattice points are selected so that each unit cell (or box shape) contains one dark blue and one light blue object. The unit cell and its contents are shown in Fig. 1.11(b).

In comparing Fig. 1.12(a) and Fig. 1.12(b), we notice that there are a number of possible choices in selecting the lattice points that make up a unit cell. How then do we decide which is the ‘right’ unit cell?

If we consider a two-dimensional plane of spots, as shown in Fig. 1.13, there are again several possible ways to select a ‘unit cell’; two examples are shown. If we are to compare the two, both are derived from adjacent lattice points.

On closer examination, we will notice that the square has a higher internal symmetry than the diamond shape. We are able to divide the square into a greater number of smaller equivalent sections than the diamond. Hence, the square is a *better* ‘unit cell’.

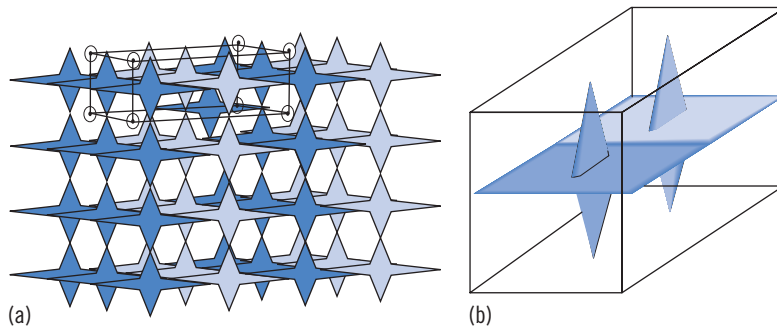


FIGURE 1.11 (a) The unit cell identified in and (b) A side-on perspective of the same unit cell

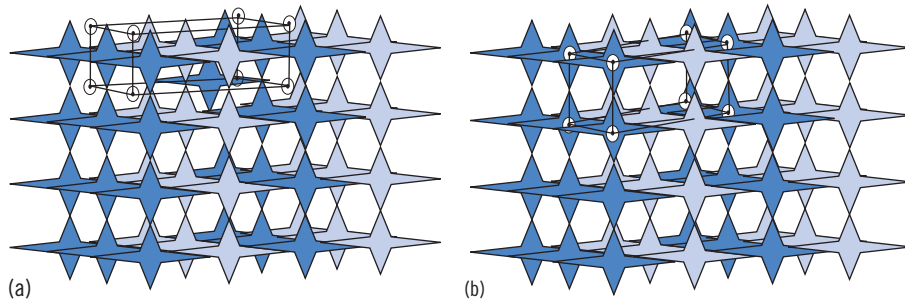


FIGURE 1.12 (a) The unit cell as selected in Figure 1.11; (b) an alternative unit cell

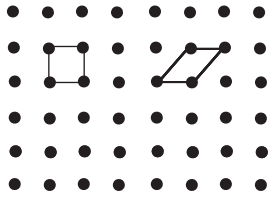


FIGURE 1.13 Two possible 'unit cells'

The same approach is used in three dimensions to select the 'best' unit cell. In summary, the rule for selecting the 'best' unit cell is to select the *smallest unit* that displays the *maximum symmetry* of the structure.

1.4.2 Definition of asymmetric unit

While a unit cell forms the basic building block of crystal, the contents within a unit cell can usually be reduced further to two or more asymmetric units that are related by symmetry. An asymmetric unit can be defined as the *smallest repeat unit* from which the crystal can be constructed. Each asymmetric unit is related by a symmetry element, for example rotation, reflection, or inversion, as detailed in Chapter 3.

Each asymmetric unit can be related to the next by a symmetry element.

Figure 1.14(b) to (d) shows how the asymmetric unit can be derived from the selected unit cell in Fig. 1.14(a). If we are to consider the symmetry in the unit cell in Fig. 1.14(b), we find that there are two planes along which the unit cell is symmetrical; we will label them x and z . If we then divide the unit cell along the vertical plane of z , as shown in (c) and along the horizontal plane x , as shown in (d), we find that the asymmetric unit is a quarter of the unit cell. We can also say that the unit cell consists of four asymmetric units.

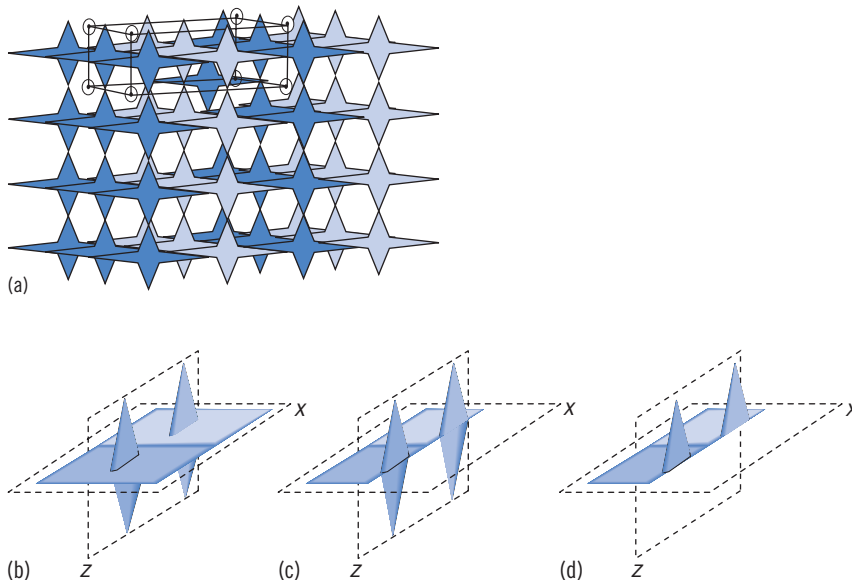


FIGURE 1.14 Deconstructing a unit cell to asymmetric units

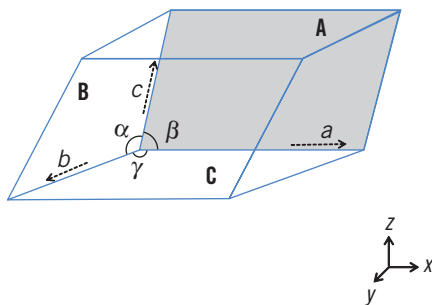


FIGURE 1.15 The parameters of a unit cell

A unit cell usually contains two or more asymmetric units, with only one exception (the exception of the triclinic space group P1 in which the asymmetric unit is the same as the unit cell – refer to Chapter 5). Each asymmetric unit is related to the next by a form of symmetry, which is detailed in Chapter 3.

1.4.3 Unit cell nomenclature and parameters

Once a unit cell has been selected, parameters are used to identify the unit cell's axes and angles. These parameters provide a standard labelling scheme for unit cells.

Referring to Fig. 1.15:

The axes: if the a -axis is assumed to be the horizontal axis and the c -axis the vertical axis, then the b -axis is the axis that is perpendicular to both. If you assume the bottom edge of this book to be equivalent to the a -axis and the spine of the book to be the equivalent of the c -axis, then the b -axis is coming directly out of the book towards you.

The angles: the α angle lies between the b and c axes while the β angle lies between a and c . The γ angle lies between the a and b axes.

The faces: the A faces lie perpendicular to the a -axis (the front and the back of the unit cell) and the B faces are perpendicular to the b -axis (the left and the right side faces of the unit cell) while the C faces are perpendicular to the c -axis (the top and the bottom faces of the unit cell).

1.5 LATTICE TYPES

Section learning outcomes

To be able to:

- Recognize and identify the 7 crystal systems and the 14 Bravais lattices;
- Explain lattice reduction with the aid of diagrams.

Although it may seem that there is an infinite array of possibilities in selecting a unit cell, in reality there are only seven possible 'box' shapes that can be stacked together within a crystal lattice. These are known as the crystal systems. These seven crystal systems are cubic, tetragonal, orthorhombic, hexagonal, trigonal, monoclinic, and triclinic.

In some crystal lattices, it is also possible to identify lattice points other than those defining the unit cell.

The *primitive* (P) lattice is a lattice type in which the lattice points lie only at the corners of the unit cell. This type of lattice is denoted by a P and is found in all the crystal systems.

The *body-centred* (I) lattice is a lattice type in which the lattice points lie at the corners of the unit cell and one lattice point lies in the middle of the unit cell. This type of lattice is denoted by an I and is found in the cubic, tetragonal, orthorhombic, and monoclinic crystal systems.

The *face-centred* (F) lattice is a lattice type in which the lattice points lie at the corners of the unit cell and one lattice point lies in the middle of every face of the unit cell. This type of lattice is denoted by an F and is found in the cubic and orthorhombic crystal systems.

The other *single-face-centred* (*base-centred*) lattice types are those in which the lattice points lie at the corners of the unit cell and a lattice point lies at each of the two relevant faces. For example, the C-face centred lattice consists of lattice points at the corners of the unit cell and in the middle of both C faces of the unit cell. It is also possible for lattice points to be denoted on the A or B face, although these are considered to be equivalent and are not usually considered separately.

All three types of face centring can be found in the orthorhombic crystal systems while only the C-centred lattice can also be found in the monoclinic crystal system.

These additional lattice points, in conjunction with the seven crystal systems, form the 14 Bravais lattices.

1.5.1 The 7 crystal systems and 14 Bravais lattices

The seven possible unit cell shapes (see Table 1.1) and also known as crystal systems, are identified by their unit cell parameters. The unit cell shapes range from a cubic cell, with the highest possible symmetry, to a triclinic unit cell, with the lowest possible symmetry.

Cubic

In a *cubic* unit cell, all axes are of equal length and all angles are 90° . In essence, this cube shape, with no other lattice points, is the primitive lattice type (P). It is also possible within this unit cell type to identify other lattice points: the body-centred lattice point (I); and the face-centred lattice points (F; on all faces). These give rise to the different Bravais lattices for the cubic unit cell.

$$a = b = c,$$

$$\alpha = \beta = \gamma = 90^\circ.$$

Tetragonal


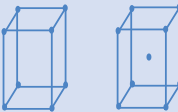
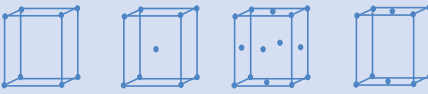



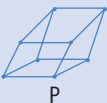
In a *tetragonal* unit cell, only the *a* and *b* axes are of equal length, with all angles at 90° . This cell type is similar to a rectangular-shaped box. The only two types of Bravais lattice that occur for this cell type are the primitive-type lattice (P), and the body-centred lattice (I).

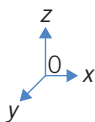
$$a = b \neq c,$$

$$\alpha = \beta = \gamma = 90^\circ.$$

The German physicist, **Moritz Ludwig Frankenheim** (1801–1869) was the first to categorize correctly the crystallographic lattices; however he had noted 15 lattice types. In 1850, **Auguste Bravais** (1811–1863), a French physicist, corrected Frankenheim's list of lattices, which contained an error of a repetition and subsequently the 14 types of crystallographic lattices today bear his name: Bravais lattices. (It is not certain which lattice was repeated in Frankenheim's list.)

TABLE 1.1 The 7 crystal systems and 14 Bravais lattices

Crystal system	Cell parameters	Lattice types
Cubic	$a = b = c,$ $\alpha = \beta = \gamma = 90^\circ$	 P I F
Tetragonal	$a = b \neq c,$ $\alpha = \beta = \gamma = 90^\circ$	 P I
Orthorhombic	$a \neq b \neq c,$ $\alpha = \beta = \gamma = 90^\circ$	 P I F A, B, or C
Hexagonal	$a = b \neq c,$ $\alpha = \beta = 90^\circ;$ $\gamma = 120^\circ$	 P
Trigonal	$a = b \neq c,$ $\alpha = \beta = 90^\circ;$ $\gamma = 120^\circ$	 P
Monoclinic	$a \neq b \neq c,$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	 P C
Triclinic	$a \neq b \neq c,$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	 P



Orthorhombic

In an *orthorhombic* unit cell, all the axes are different, although all angles are 90° . This again mimics a rectangular box. The types of Bravais lattice that occur for the orthorhombic cell are the primitive-type lattice (P), the body-centred lattice (I), and face-centred lattice points (F), on all faces and centring on a single face, the A, B, or C faces.

$$a \neq b \neq c,$$

$$\alpha = \beta = \gamma = 90^\circ.$$

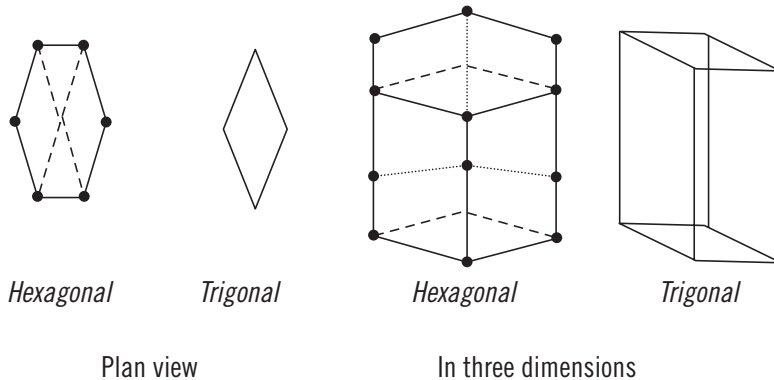


FIGURE 1.16 The trigonal and hexagonal unit cells

Hexagonal

In a *hexagonal* unit cell, both the top and bottom faces are hexagonal with the a and b axes of equal lengths and joined by a c -axis of a different length. The angles where the faces meet, α and β , are 90° , while the angles on the hexagonal face are 120° . Only the primitive-type (P) of Bravais lattice is found in the hexagonal unit cell.

$$a = b \neq c,$$

$$\alpha = \beta = 90^\circ; \gamma = 120^\circ.$$

Trigonal

The *trigonal* unit cell can be derived from the hexagonal cell. As shown in Fig. 1.16, the hexagonal cell can be subdivided into three trigonal cells (two whole cells and two half cells). Like the hexagonal cell, the axes a and b are of equal lengths and joined by the c -axis of a different length. The angles where the faces meet, α and β are 90° , while the γ angle on the trigonal face is 120° . Again, only the primitive-type (P) of Bravais lattice is found in the trigonal unit cell.

$$a = b \neq c,$$

$$\alpha = \beta = 90^\circ; \gamma = 120^\circ.$$

Monoclinic

The *monoclinic* unit cell has all its axes of different lengths with only the angles of α and γ equal to 90° . The primitive (P) and the single-face-centred (C) type of Bravais lattice can be found for the unit cell type. Both the body-centred (I) and the face-centred (F) Bravais lattice types can also occur in the *monoclinic* crystal system; however, as they can also be represented as C-type Bravais lattices, they are usually not considered separately.

$$a \neq b \neq c,$$

$$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$$

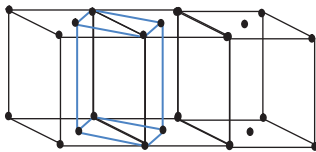


FIGURE 1.17 The face-centred cubic lattice (C) is reduced to the primitive-type tetragonal lattice

Triclinic

Of all the crystal systems, the triclinic unit cell has the least symmetry. The axes are all different and no angle is equivalent to 90° . Only the primitive-type (P) Bravais lattice occurs in the triclinic crystal system.

$$a \neq b \neq c,$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

1.5.2 Lattice reduction

We have now seen that there are four different types of Bravais lattice, P, I, F, and C. Given that there are seven different crystal systems, we might expect there to be 28 (4×7) different Bravais lattices. In practice, however, not all of the known Bravais lattices occur in all the crystal systems. The reason that there are only 14 Bravais lattices is that lattices can be reduced to a more effective lattice type.

For example, the C-type Bravais lattice does not occur for the cubic unit cell, as shown in Fig. 1.17. If we refer to Fig 1.17, the unit cells drawn in black denote a C-centred cubic lattice. However, this unit cell can be reduced further to a smaller unit cell with higher symmetry and this is shown with the lines in blue. The lines in blue are drawn to join the face-centred lattice points to the corners of the lattices. In doing so, a new lattice type can be found; the primitive-type (P) tetragonal lattice is obtained. This satisfies the rules for selecting the 'best' unit cell.

SELF-TEST QUESTIONS

1. Which crystal system consists of equivalent angles but has axes of different lengths?
2. List the unit cell parameters for a monoclinic crystal system.
3. Examine Fig. 1.12: which unit cell would you select as the 'best' unit cell? Explain the reasons for your choice.
4. Briefly explain how the trigonal and hexagonal unit cells are related.
5. Explain, with the aid of diagrams, why the face-centred (F) lattice type does not occur for the tetragonal crystal system.

CHAPTER SUMMARY

1. X-ray crystallography is a solid-state analytical technique based on diffraction of crystalline solids.
2. Chemical or small-molecule crystallography identifies the detailed atomic contents of a molecule within a crystal lattice
3. Macromolecular or protein crystallography mainly examines globular proteins where the recognition of ‘motifs’ such as helices and β -sheets are important.
4. Lattice points within a crystal are determined by the environment surrounding that point. All lattice points have the same surrounding environment.
5. A unit cell is a box shape obtained by joining up lattice points in three dimensions.
6. A unit cell, the building block of a crystal lattice, is defined as the smallest unit that displays the maximum symmetry of the structure.
7. The asymmetric unit is the smallest repeat unit within a crystal lattice. The asymmetric units in a unit cell are related by symmetry.
8. A unit cell is defined by its axes, a , b , and c , and its angles, α , β , and γ .
9. There are 7 crystal systems (triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic) and 14 Bravais lattices.

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LINKS

Online learning tools:

A Java applet to demonstrate diffraction: <http://www.ngsir.netfirms.com/englishhtm/Diffraction.htm>

A Java applet to demonstrate crystal structure and the 14 Bravais lattices:
<http://jas.eng.buffalo.edu/education/solid/genUnitCell/index.html>.

Here's a bit of fun: **A musical introduction to protein structure:**
http://whozoo.org/mac/Music/Primer/Primer_index.htm