AN INTRODUCTION TO X-RAY CRYSTALLOGRAPHY MICHAEL M WOOLFSON

SECOND EDITION



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This is a textbook for the senior undergraduate or graduate student beginning a serious study of X-ray crystallography. It will be of interest both to those intending to become professional crystallographers and to those physicists, chemists, biologists, geologists, metallurgists and others who will use it as a tool in their research. All major aspects of crystallography are covered - the geometry of crystals and their symmetry, theoretical and practical aspects of diffracting X-rays by crystals and how the data may be analysed to find the symmetry of the crystal and its structure. Recent advances are fully covered, including the synchrotron as a source of X-rays, methods of solving structures from powder data and the full range of techniques for solving structures from single-crystal data. A suite of computer programs is provided for carrying out many operations of data-processing and solving crystal structures - including by direct methods. While these are limited to two dimensions they fully illustrate the characteristics of three-dimensional work. These programs are required for many of the problems given at the end of each chapter but may also be used to create new problems by which students can test themselves or each other.

An introduction to X-ray crystallography

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SECOND EDITION

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Contents

		Page
	Preface to the First Edition	x
	Preface to the Second Edition	X11
1	The geometry of the crystalline state	1
1.1	The general features of crystals	1
1.2	The external symmetry of crystals	1
1.3	The seven crystal systems	7
1.4	The thirty-two crystal classes	9
1.5	The unit cell	12
1.6	Miller indices	15
1.7	Space lattices	16
1.8	Symmetry elements	20
1.9	Space groups	23
1.10	Problems to Chapter 1	30
		51
2	The scattering of X-rays	32
2.1	A general description of the scattering process	32
2.2	Scattering from a pair of points	34
2.3	Scattering from a general distribution of point scatterers	36
2.4	Thomson scattering	37
2.5	Compton scattering	42
2.6	The scattering of X-rays by atoms	43
	Problems to Chapter 2	48
3	Diffraction from a crystal	50
3.1	Diffraction from a one-dimensional array of atoms	50
3.2	Diffraction from a two-dimensional array of atoms	56
3.3	Diffraction from a three-dimensional array of atoms	57
3.4	The reciprocal lattice	59
3.5	Diffraction from a crystal – the structure factor	64
3.6	Bragg's law	67
3.7	The structure factor in terms of indices of reflection	72
	Problems to Chapter 3	/4
4	The Fourier transform	76
4.1	The Fourier series	76
4.2	Numerical application of Fourier series	79

Con	tents
-----	-------

4.3	Fourier series in two and three dimensions	83
4.4	The Fourier transform	85
4.5	Diffraction and the Fourier transform	92
4.6	Convolution	94
4./	Diffraction by a periodic distribution	99
4.8	The electron-density equation	99
	Problems to Chapter 4	106
5	Experimental collection of diffraction data	108
5.1	The conditions for diffraction to occur	108
5.2	The powder camera	112
5.3	The oscillation camera	118
5.4	The Weissenberg camera	125
5.5	The precession camera	130
5.6	The photographic measurement of intensities	135
5.7	Diffractometers	140
5.8	X-ray sources	143
5.9	Image-plate systems	150
5.10	The modern Laue method	151
	Problems to Chapter 5	154
6	The factors affecting X-ray intensities	156
6.1	Diffraction from a rotating crystal	156
6.2	Absorption of X-rays	162
6.3	Primary extinction	169
6.4	Secondary extinction	173
6.5	The temperature factor	175
6.6	Anomalous scattering	179
	Problems to Chapter 6	188
7	The determination of space groups	190
7.1	Tests for the lack of a centre of symmetry	190
7.2	The optical properties of crystals	196
7.3	The symmetry of X-ray photographs	208
7.4	Information from systematic absences	210
7.5	Intensity statistics	215
7.6	Detection of mirror planes and diad axes	227
	Problems to Chapter 7	229
8	The determination of crystal structures	231
8.1	Trial-and-error methods	231
8.2	The Patterson function	233
8.3	The heavy-atom method	249
8.4	Isomorphous replacement	255
8.5	The application of anomalous scattering	267
8.6	Inequality relationships	274
8.7	Sign relationships	282

Contents

8.8	General phase relationships	290
8.9	A general survey of methods	297
	Problems to Chapter 8	298
9	Accuracy and refinement processes	301
9.1	The determination of unit-cell parameters	301
9.2	The scaling of observed data	307
9.3	Fourier refinement	309
9.4	Least-squares refinement	317
9.5	The parameter-shift method	320
	Problems to Chapter 9	322
	Physical constants and tables	325
	Appendices	327
	Program listings	
	I STRUCFAC	328
	II FOUR1	333
	III SIMP1	335
	IV FOUR2	336
	V FTOUE	339
	VI HEAVY	346
	VII ISOFILE	349
	VIII ISOCOEFF	350
	IX ANOFILE	352
	X PSCOEFF	353
	XI MINDIR	354
	XII CALOBS	366
	Solutions to Problems	367
	References	395
	Bibliography	397
	Index	399

ix

Preface to the First Edition

In 1912 von Laue proposed that X-rays could be diffracted by crystals and shortly afterwards the experiment which confirmed this brilliant prediction was carried out. At that time the full consequences of this discovery could not have been fully appreciated. From the solution of simple crystal structures, described in terms of two or three parameters, there has been steady progress to the point where now several complex biological structures have been solved and the solution of the structures of some crystalline viruses is a distinct possibility.

X-ray crystallography is sometimes regarded as a science in its own right and, indeed, there are many professional crystallographers who devote all their efforts to the development and practice of the subject. On the other hand, to many other scientists it is only a tool and, as such, it is a meeting point of many disciplines – mathematics, physics, chemistry, biology, medicine, geology, metallurgy, fibre technology and several others. However, for the crystallographer, the conventional boundaries between scientific subjects often seem rather nebulous.

In writing this book the aim has been to provide an elementary text which will serve either the undergraduate student or the postgraduate student beginning seriously to study the subject for the first time. There has been no attempt to compete in depth with specialized textbooks, some of which are listed in the Bibliography. Indeed, it has also been found desirable to restrict the breadth of treatment, and closely associated topics which fall outside the scope of the title – for example diffraction from semi- and non-crystalline materials, electron- and neutron diffraction – have been excluded. For those who wish to go no further it is hoped that the book gives a rounded, broad treatment, complete in itself, which explains the principles involved and adequately describes the present state of the subject. For those who wish to go further it should be regarded as a foundation for further study.

It has now become clear that there is wide acceptance of the SI system of units and by-and-large they are used in this book. However the ångstrom unit has been retained as a unit of length for X-ray wavelengths and unit-cell dimensions etc., since a great deal of the basic literature uses this unit. A brief explanation of the SI system and some important constants and equations are included in the section *Physical constants and tables* on pp. 325–326.

I am deeply indebted to Dr M. Bown and Dr S.G. Fleet of the Department of Mineralogy, University of Cambridge and to my colleague, Dr P. Main, for reading the manuscript and for their helpful criticism which included suggestions for many improvements of treatment. Preface to the First Edition

My thanks are also due to Professor C. A. Taylor of the University of Cardiff for providing the material for figs. 8.9 and 8.10 and also to Mr W. Spellman and Mr B. Cooper of the University of York for help with some of the illustrations.

M.M.W.

Preface to the Second Edition

Since the first edition of this book was published in 1970 there have been tremendous advances in X-ray crystallography. Much of this has been due to technological developments – for example new and powerful synchrotron sources of X-rays, improved detectors and increase in the power of computers by many orders of magnitude. Alongside these developments, and sometimes prompted by them, there have also been theoretical advances, in particular in methods of solution of crystal structures. In this second edition these new aspects of the subject have been included and described at a level which is appropriate to the nature of the book, which is still an introductory text.

A new feature of this edition is that advantage has been taken of the ready availability of powerful table-top computers to illustrate the procedures of X-ray crystallography with FORTRAN[®] computer programs. These are listed in the appendices and available on the WorldWideWeb*. While they are restricted to two-dimensional applications they apply to all the two-dimensional space groups and fully illustrate the principles of the more complicated three-dimensional programs that are available. The Problems at the end of each chapter include some in which the reader can use these programs and go through simulations of structure solutions – simulations in that the known structure is used to generate what is equivalent to observed data. More realistic exercises can be produced if readers will work in pairs, one providing the other with a data file containing simulated observed data for a synthetic structure of his own invention, while the other has to find the solution. It can be great fun as well as being very educational!

I am particularly grateful to Professor J.R. Helliwell for providing material on the new Laue method and on image-plate methods.

M. M. Woolfson York 1996

1 The geometry of the crystalline state

1.1 The general features of crystals

Materials in the crystalline state are commonplace and they play an important part in everyday life. The household chemicals salt, sugar and washing soda; the industrial materials, corundum and germanium; and the precious stones, diamonds and emeralds, are all examples of such materials.

A superficial examination of crystals reveals many of their interesting characteristics. The most obvious feature is the presence of facets and well-formed crystals are found to be completely bounded by flat surfaces – flat to a degree of precision capable of giving high-quality plane-mirror images. Planarity of this perfection is not common in nature. It may be seen in the surface of a still liquid but we could scarcely envisage that gravitation is instrumental in moulding flat crystal faces simultaneously in a variety of directions.

It can easily be verified that the significance of planar surfaces is not confined to the exterior morphology but is also inherent in the interior structure of a crystal. Crystals frequently cleave along preferred directions and, even when a crystal is crudely fractured, it can be seen through a microscope that the apparently rough, broken region is actually a myriad of small plane surfaces.

Another feature which may be readily observed is that the crystals of a given material tend to be alike – all needles or all plates for example – which implies that the chemical nature of the material plays an important role in determining the crystal habit. This suggests strongly that the macroscopic form of a crystal depends on structural arrangements at the atomic or molecular level and that the underlying factor controlling crystal formation is the way in which atoms and molecules can pack together. The flatness of crystal surfaces can then be attributed to the presence of regular layers of atoms in the structure and cleavage would correspond to the breaking of weaker links between particular layers of atoms.

1.2 The external symmetry of crystals

Many crystals are very regular in shape and clearly exhibit a great deal of symmetry. In fig. 1.1(a) there is shown a well-formed crystal of alum which has the shape of a perfect octahedron; the quartz crystal illustrated in fig. 1.1(b) has a cross-section which is a regular hexagon. However with many other crystals such symmetry is not evident and it might be thought that crystals with symmetry were an exception rather than a rule.

Although the crystals of a particular chemical species usually appear to



have the same general habit a detailed examination reveals considerable variation in size and shape. In particular one may find a selection of platy crystals looking somewhat like those shown in fig. 1.2(a). The shapes of these seem to be quite unrelated but, if they are rearranged as in fig. 1.2(b), a rather striking relationship may be noted. Although the relative sizes of the sides of the crystal cross-sections are very different the normals to the sides (in the plane of the figure) form an identical set from crystal to crystal. Furthermore the set of normals is just that which would be obtained from a regular hexagonal cross-section although none of the crystals in fig. 1.2 displays the characteristics of a regular polygon. While this illustration is essentially two-dimensional the same general observations can be made in three dimensions. Although the crystals of a given species vary greatly in the shapes and sizes of corresponding faces, and may appear to lack symmetry altogether, the set of normals to the faces will be identical from crystal to crystal (although a crystal may occasionally lack a particular face completely) and will usually show symmetry that the crystals themselves lack. For example, fig. 1.3(a) shows the set of normals for an octahedron. These normals are drawn radiating from a single point and are of equal length. This set may well have been derived from a solid such as that shown in fig. 1.3(b) but the symmetry of the normals reveals that this solid has faces whose relative orientations have the same relationship as those of the octahedron.

The presentation of a three-dimensional distribution of normals as done in fig. 1.3 makes difficulties both for the illustrator and also for the viewer. The normals have a common origin and are of equal length so that their termini lie on the surface of a sphere. It is possible to represent a spherical distribution of points by a perspective projection on to a plane and the stereographic projection is the one most commonly used by the crystallographer. The projection procedure can be followed in fig. 1.4(*a*). Points on the surface of the sphere are projected on to a diametral plane with projection point either O or O', where OO' is the diameter normal to the projection plane. Each point is projected from whichever of O or O' is on the opposite side of the plane and in this way all the projected points are contained within the diametral circle. The projected points may be conventionally represented as above or below the projection plane by full or open circles. Thus the points A, B, C and D project as A', B', C' and D' and, when viewed along OO', the projection plane appears as in fig. 1.4(*b*).

2

Fig. 1.1.(a) Alum crystal.(b) Quartz crystal.

Fig. 1.2. (a) Set of apparently irregular plate-like crystals. (b) Crystals rearranged to show parallelism of faces and underlying hexagonal symmetry.



(b)

Fig. 1.3. (*a*) Set of normals to the faces of an octahedron. (*b*) Solid whose faces have same set of normals as does an octahedron.





The geometry of the crystalline state

Fig. 1.4. (*a*) The stereographic projection of points from the surface of a sphere on to a diametral plane. (*b*) The final stereographic projection.



We now consider the symmetry elements which may be present in crystals – or are revealed as intrinsically present by the set of normals to the faces.

Centre of symmetry (for symbol see section below entitled 'Inversion axes')

A crystal has a centre of symmetry if, for a point within it, faces occur in parallel pairs of equal dimensions on opposite sides of the point and equidistant from it. A selection of centrosymmetric crystals is shown in fig. 1.5(a). However even when the crystal itself does not have a centre of symmetry the intrinsic presence of a centre is shown when normals occur in

4

collinear pairs. The way in which this shows up on a stereographic projection is illustrated in fig. 1.5(b).

Mirror plane (written symbol m; graphical symbol —)

This is a plane in the crystal such that the halves on opposide sides of the plane are mirror images of each other. Some crystal forms possessing mirror planes are shown in fig. 1.6(a). Mirror planes show up clearly in a stereographic projection when the projecting plane is either parallel to or perpendicular to the mirror plane. The stereographic projections for each of the cases is shown in fig. 1.6(b).



Fig. 1.5. (a) A selection of centrosymmetric crystals. (b) The stereographic projection of a pair of centrosymmetrically related faces.

Fig. 1.6.

planes.

Rotation axes (written symbols 2, 3, 4, 6; graphical symbols $(\bullet, \bullet, \bullet)$

An *n*-fold rotation axis is one for which rotation through $2\pi/n$ leaves the appearance of the crystal unchanged. The values of *n* which may occur (apart from the trivial case n = 1) are 2, 3, 4 and 6 and examples of twofold (diad), threefold (triad), fourfold (tetrad) and sixfold (hexad) axes are illustrated in fig. 1.7 together with the stereographic projections on planes perpendicular to the symmetry axes.

Inversion axes (written symbols $\overline{1}$, $\overline{2}$, $\overline{3}$, $\overline{4}$, $\overline{6}$; graphical symbols **o**, none, \triangle , \diamondsuit , \bigotimes)

The inversion axes relate crystal planes by a combination of rotation and inversion through a centre. The operation of a $\overline{4}$ axis may be followed in fig. 1.8(*a*). The face *A* is first rotated about the axis by $\pi/2$ to position *A'* and then inverted through *O* to *B*. Starting with *B*, a similar operation gives *C* which in its turn gives *D*. The stereographic projections showing the symmetry of inversion axes are given in fig. 1.8(*b*); it will be noted that $\overline{1}$ is identical to a centre of symmetry and $\overline{1}$ is the accepted symbol for a centre of symmetry. Similarly $\overline{2}$ is identical to *m* although in this case the symbol *m* is more commonly used.

These are all the symmetry elements which may occur in the external form of the crystal – or be observed in the arrangement of normals even when the crystal itself lacks obvious symmetry.

On the experimental side the determination of a set of normals involves the measurement of the various interfacial angles of the crystal. For this purpose optical goniometers have been designed which use the reflection of



Fig. 1.7. (*a*) Perspective views and views down the axis for crystals possessing diad, triad, tetrad and hexad axes. (*b*) The corresponding stereographic projections.

1.3 The seven crystal systems

Fig. 1.8.
(a) A perspective view of the operation of an inverse tetrad axis.
(b) Stereographic projections for 1, 2, 3, 4 and 6.



light from the mirror-like facets of the crystal to define their relative orientations.

1.3 The seven crystal systems

Even from a limited observation of crystals it would be reasonable to surmise that the symmetry of the crystal as a whole is somehow connected with the symmetry of some smaller subunit within it. If a crystal is fractured then the small plane surfaces exposed by the break, no matter in what part of the body of the crystal they originate, show the same angular relationships to the faces of the whole crystal and, indeed, are often parallel to the crystal faces.

The idea of a structural subunit was first advanced in 1784 by Haüy who

was led to his conclusions by observing the cleavage of calcite. This has a threefold axis of symmetry and by successive cleavage Haüy extracted from calcite crystals small rhomboids of calcite. He argued that the cleavage process, if repeated many times, would eventually lead to a small, indivisible, rhombohedral structural unit and that the triad axis of the crystal as a whole derives from the triad axis of the subunit (see fig. 1.10(b) for description of rhombohedron).

Haüy's ideas lead to the general consideration of how crystals may be built from small units in the form of parallelepipeds. It is found that, generally the character of the subunits may be inferred from the nature of the crystal symmetry. In fig. 1.9 is a cube built up of small cubic subunits; it is true that in this case the subunit could be a rectangular parallelepiped which quite accidentally gave a crystal in the shape of a cube. However if some other crystal forms which can be built from cubes are examined, for example the regular octahedron and also the tetrahedron in fig. 1.9, then it is found that the special angles between faces are those corresponding to a cubic subunit and to no other.

It is instructive to look at the symmetry of the subunit and the symmetry of the whole crystal. The cube has a centre of symmetry, nine mirror planes, six diad axes, four triad axes and three tetrad axes. All these elements of symmetry are shown by the octahedron but the tetrahedron, having six mirror planes, three inverse tetrad axes and four triad axes, shows less symmetry than the cube. Some materials do crystallize as regular tetrahedra and this crystal form implies a cubic subunit. Thus, in some cases, the crystal as a whole may exhibit less symmetry than its subunit. The common characteristic shown by all crystals having a cubic subunit is the set of four



Fig. 1.9. Various crystal shapes which can be built from cubic subunits: (*left*) cube; (*centre*) octahedron; (*right*) tetrahedron. triad axes – and conversely all crystals having a set of four triad axes are cubic. Similar considerations lead to the conclusion that there are seven distinct types of subunit and we associate these with seven *crystal systems*. The subunits are all parallelepipeds whose shapes are completely defined by the lengths of the three sides a, b, c (or the ratios of these lengths) and the values of the three angles α , β , γ (fig. 1.10(a)). The main characteristics of the seven crystal systems and their subunits are given in table 1.1.

1.4 The thirty-two crystal classes

In table 1.1 there is given the essential symmetry for the seven crystal systems but, for each system, different symmetry arrangements are possible. A crystal in the triclinic system, for example, may or may not have a centre of symmetry and this leads us to refer to the two *crystal classes* \overline{I} and 1 within the triclinic system. As has been previously noted \overline{I} is the symbol for a centre of symmetry and the symbol 1, representing a onefold axis, corresponds to no symmetry at all. These two crystal classes may be shown conveniently in terms of stereographic projections as in fig. 1.11(*a*) and (*b*). The projections show the set of planes generated from a general crystal face by the complete group of symmetry elements.

The possible arrangements for the monoclinic system are now considered.





(c)

Fig. 1.10. (a) A general parallelepiped subunit. (b) A rhombohedron showing the triad axis. (c) The basic hexagonal subunits which are packed as shown to give hexagonal symmetry.

System	Subunit	Essential symmetry of crystal
Triclinic	No special relationships	None
Monoclinic	$a \neq b \neq c$ $\beta \neq \alpha = \gamma = 90^{\circ}$	Diad axis or mirror plane (inverse diad axis)
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$	Three orthogonal diad or inverse diad axes
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^{\circ}$	One tetrad or inverse tetrad axis
Trigonal	a = b = c $\alpha = \beta = \gamma \neq 90^{\circ}$ (see fig. 1.10(b)) or as hexagonal	One triad or inverse triad axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$ (see fig. 1.10(c))	One hexad or inverse hexad axis
Cubic	a = b = c $\alpha = \beta = \gamma = 90^{\circ}$	Four triad axes

 Table 1.1. The seven crystal systems

Fig. 1.11. Stereographic projections representing the crystal classes (a) 1 and (b) $\overline{1}$.



These, illustrated in fig. 1.12, have (a) a diad axis, (b) a mirror plane and (c) a diad axis and mirror plane together. The orthorhombic and trigonal systems give rise to the classes shown in fig. 1.13.

Some interesting points may be observed from a study of these diagrams. For example, the combination of symbols 3m implies that the mirror plane *contains* the triad axis and the trigonal symmetry demands therefore that a set of three mirror planes exists. On the other hand, for the crystal class 3/m, the mirror plane is perpendicular to the triad axis; this class is identical to the hexagonal class $\overline{\delta}$ and is usually referred to by the latter name.

It may also be noted that, for the orthorhombic class *mm*, the symmetry associated with the third axis need not be stated. This omission is permissible due to the fact that the two orthogonal mirror planes automatically generate a diad axis along the line of their intersection and a name such as 2*mm* therefore contains redundant information. An alternative name for *mm* is 2*m* and again the identity of the third symmetry element may be inferred.

For the seven systems together there are thirty-two crystal classes and all

1.4 The thirty-two crystal classes



crystals may be assigned to one or other of these classes. While the general nature of the basic subunit determines the crystal system, for each system there can be different elements of symmetry associated with the crystal. If a material, satisfying some minimization-of-potential-energy criterion, crystallizes with some element of symmetry, it strongly implies that there is some corresponding symmetry within the subunit itself. The collection of symmetry elements which characterizes the crystal class, and which must also be considered to be associated with the basic subunit, is called a *point group*. It will be seen later that the point group is a macroscopic

manifestation of the symmetry with which atoms arrange themselves within the subunits.

1.5 The unit cell

We shall now turn our attention to the composition of the structural subunits of crystals. The parallelepiped-shaped volume which, when reproduced by close packing in three dimensions, gives the whole crystal is called the *unit cell*. It is well to note that the unit cell may not be an entity which can be uniquely defined. In fig. 1.14 there is a two-dimensional pattern which can be thought of as a portion of the arrangement of atoms within a crystal. Several possible choices of shape and origin of unit cell are shown and they are all perfectly acceptable in that reproducing the unit cells in a close-packed two-dimensional array gives the correct atomic arrangement. However in this case there is one rectangular unit cell and this choice of unit cell conveys more readily the special rectangular repeat features of the overall pattern and also shows the mirror plane of symmetry. Similar arguments apply in three dimensions in that many different triclinic unit cells can be chosen to represent the structural





arrangement. One customarily chooses the unit cell which displays the highest possible symmetry, for this indicates far more clearly the symmetry of the underlying structure.

In §§ 1.3 and 1.4 the ideas were advanced that the symmetry of the crystal was linked with the symmetry of the unit cell and that the disposition of crystal faces depends on the shape of the unit cell. We shall now explore this idea in a little more detail and it helps, in the first instance, to restrict attention to a two-dimensional model. A crystal made of square unit cells is shown in fig. 1.15. The crystal is apparently irregular in shape but, when the set of normals to the faces is examined we have no doubt that the unit cell has a tetrad axis of symmetry. The reason why a square unit cell with a tetrad axis gives fourfold symmetry in the bulk crystal can also be seen. If the formation of the faces AB and BC is favoured because of the low potential energy associated with the atomic arrangement at these boundaries then CD, DE and the other faces related by tetrad symmetry are also favoured because they lead to the same condition at the crystal boundary.

For the two-dimensional crystal in fig. 1.16 the set of normals reveals a mirror line of symmetry and from this we know that the unit cell is rectangular. It is required to determine the ratio of the sides of the rectangle from measurements of the angles between the faces. The mirror line can be located (we take the normal to it as the *b* direction) and the angles made to this line by the faces can be found. In fig. 1.17 the face AB is formed by points which are separated by 2a in one direction and *b* in the other. The angle θ , which the normal AN makes with the *b* direction, is clearly given by

$$an\,\theta = b/2a.\tag{1.1}$$

Fig. 1.15. A two-dimensional crystal made up of unit cells with a tetrad axis of symmetry. t



Fig. 1.16. A two-dimensional crystal built of rectangular units.



Fig. 1.17. The relationship between the crystal face AB and the unit cell.





$$\tan\theta = \frac{mb}{na}$$

or

$$\frac{b}{a} = -\frac{n}{m} \tan \theta. \tag{1.2}$$

The angles θ for the crystal in fig. 1.16 are 32° 12′, 43° 24′ and 51° 33′ so that we have

$$\frac{b}{a} = 0.630 \frac{n_1}{m_1} = 0.946 \frac{n_2}{m_2} = 1.260 \frac{n_3}{m_3}.$$
(1.3)

14

We now look for the simplest sets of integers n and m which will satisfy equation (1.3) and these are found to give

$$\frac{b}{a} = 0.630 \times \frac{2}{1} = 0.946 \times \frac{4}{3} = 1.260 \times \frac{1}{1}.$$

From this we deduce the ratio b:a = 1.260:1.

This example is only illustrative and it is intended to demonstrate how measurements on the bulk crystal can give precise information about the substructure. For a real crystal, where one is dealing with a three-dimensional problem, the task of deducing axial ratios can be far more complicated.

Another type of two-dimensional crystal is one based on a general oblique cell as illustrated in fig. 1.18. The crystal symmetry shown here is a diad axis (although not essential for this system) and one must deduce from the interfacial angles not only the axial ratio but also the interaxial angle. Many choices of unit cell are possible for the oblique system.

The only unconsidered type of two-dimensional crystal is that based on a hexagonal cell where the interaxial angle and axial ratio are fixed.

All the above ideas can be carried over into three dimensions. Goniometric measurements enable one to determine the crystal systems, crystal class, axial ratios and interaxial angles.

1.6 Miller indices

In fig. 1.19 is shown the development of two faces AB and CD of a two-dimensional crystal. Face AB is generated by steps of 2a, b and CD by steps of 3a, 2b. Now it is possible to draw lines parallel to the faces such that their intercepts on the unit-cell edges are a/h, b/k where h and k are two integers.

The line A'B' parallel to AB, for example, has intercepts OA' and OB' of the form a/1 and b/2; similarly C'D' parallel to CD has intercepts a/2 and b/3. The integers h and k may be chosen in other ways – the line with

Fig. 1.18. A two-dimensional crystal based on an oblique unit cell.



Fig. 1.19. The lines A'B' and C'D'which are parallel to the crystal faces AB and CDhave intercepts on the unit-cell edges of the form a/h and b/k where h and k are integers.



intercepts a/2 and b/4 is also parallel to AB. However, we are here concerned with the smallest possible integers and these are referred to as the *Miller indices* of the face.

In three dimensions a plane may always be found, parallel to a crystal face, which makes intercepts a/h, b/k and c/l on the unit-cell edges. The crystal face in fig. 1.20 is based on the unit cell shown with OA = 3a, OB = 4b and OC = 2c. The plane A'B'C' is parallel to ABC and has intercepts OA', OB' and OC' given by a/4, b/3 and c/6 (note that the condition for parallel planes OA/OA' = OB/OB' = OC/OC' is satisfied). This face may be referred to by its Miller indices and ABC is the face (436).

The Miller indices are related to a particular unit cell and are therefore not uniquely defined for a given crystal face. Returning to our two-dimensional example, the unit cell in fig. 1.21 is an alternative to that shown in fig. 1.19. The face AB which was the (1, 2) face for the cell in fig. 1.19 is the (1, 1) face for the cell in fig. 1.21. However, no matter which unit cell is chosen, one can find a triplet of integers (generally small) to represent the Miller indices of the face.

1.7 Space lattices

In figs. 1.19 and 1.21 are shown alternative choices of unit cell for a two-dimensional repeated pattern. The two unit cells are quite different in appearance but when they are packed in two-dimensional arrays they each produce the same spatial distribution. If one point is chosen to represent the unit cell – the top left-hand corner, the centre or any other defined point – then the array of cells is represented by a lattice of points and the appearance of this lattice does not depend on the choice of unit cell. One property of this lattice is that if it is placed over the structural pattern then each point is in an exactly similar environment. This is illustrated in fig. 1.22 where the lattice corresponding to figs. 1.19 and 1.21 is placed over the two-dimensional pattern and it can be seen that, no matter how the lattice is displaced parallel to itself, each of the lattice points will have a similar environment.

If we have any repeated pattern in space, such as the distribution of atoms in a crystal, we can relate to it a *space lattice* of points which defines completely the repetition characteristics without reference to the details of the repeated motif. In three dimensions there are fourteen distinctive space

1.7 Space lattices

Fig. 1.20.

The plane A'B'C' is parallel to the crystal face ABC and makes intercepts on the cell edges of the form a/h, b/k and c/l where h, kand l are integers.



Fig. 1.21.

An alternative unit cell to that shown in fig. 1.19. The faces *AB* and *CD* now have different Miller indices.





lattices known as *Bravais lattices*. The unit of each lattice is illustrated in fig. 1.23; lines connect the points to clarify the relationships between them. Firstly there are seven simple lattices based on the unit-cell shapes appropriate to the seven crystal systems. Six of these are indicated by the symbol P which means 'primitive', i.e. there is one point associated with each unit cell of the structure; the primitive rhombohedral lattice is usually denoted by R. But other space lattices can also occur. Consider the space lattice corresponding to the two-dimensional pattern given in fig. 1.24. This could be considered a primitive lattice corresponding to the unit cell shown dashed in outline but such a choice would obscure the rectangular repeat relationship in the pattern. It is appropriate in this case to take the unit cell as the full line rectangle and to say that the cell is *centred* so that points separated by $\frac{1}{2}a, \frac{1}{2}b$ are similar. Such a lattice is non-primitive. The three possible types of non-primitive lattice are:



(1st Part)

Fig. 1.23. The fourteen Bravais lattices. The accompanying diagrams show the environment of each of the lattice points. Fig. 1.23. (cont.)



Fig. 1.23. (2nd Part)

Fig. 1.24. Two-dimensionl pattern showing two choices of unit cell – general oblique (dashed outline) and centred rectangular (full outline).



- C-face centring in which there is a translation vector $\frac{1}{2}a, \frac{1}{2}b$ in the C faces of the basic unit of the space lattice. A and B-face centring may also occur;
- *F*-face centring equivalent to simultaneous *A*, *B* and *C*-face centring; and *I*-centring where there is a translation vector $\frac{1}{2}a, \frac{1}{2}b, \frac{1}{2}c$ giving a point at the intersection of the body diagonals of the basic unit of the space lattice.

The seven non-primitive space lattices are displayed in fig. 1.23. Any space lattice corresponds to one or other of the fourteen shown and no other distinct space lattices can occur. For each of the lattices, primitive and non-primitive, the constituent points have similar environments. A few minutes' study of the figures will confirm the truth of the last statement.

1.8 Symmetry elements

We have noted that there are seven crystal systems each related to the type of unit cell of the underlying structure. In addition there are thirty-two crystal classes so that there are differing degrees of symmetry of crystals all belonging to the same system. This is associated with elements of symmetry within the unit cell itself and we shall now consider the possibilities for these symmetry elements.

The symmetry elements which were previously considered were those which may be displayed by a crystal (§ 1.2) and it was stated that there are thirty-two possible arrangements of symmetry elements or point groups. A crystal is a single unrepeated object and an arrangement of symmetry elements all associated with one point can represent the relationships of a crystal face to all symmetry-related faces.

The situation is different when we consider the symmetry within the unit cell, for the periodic repeat pattern of the atomic arrangement gives new possibilities for symmetry elements. A list of symmetry elements which can be associated with the atomic arrangement in a unit cell is now given.

Centre of symmetry (\overline{I})

This is a point in the unit cell such that if there is an atom at vector position r there is an equivalent atom located at -r. The unit cell in fig. 1.25(*a*) has centres of symmetry at its corners. Since all the corners are equivalent points the pairs of atoms A and A' related by the centre of symmetry at O are repeated at each of the other corners. This gives rise to other centres of symmetry which bisect the edges of the cell and lie also at the face and body



(f)

Fig. 1.25. (a) A centrosymmetric unit cell showing the complete family of eight distinct centres of symmetry. (b) A unit cell showing mirror planes. (c) A unit cell showing glide planes. (d) A view down a tetrad axis of symmetry showing the other symmetry axes which arise. (e) The operation of a 2_1 axis.

(f) The operation of 3_1 and 3_2 axes.

centres. While these extra points are also centres of symmetry they are not equivalent to those at the corners since they have different environments.

Mirror plane (m)

In fig. 1.25(b) there is shown a unit cell with mirror planes across two opposite (equivalent) faces. The plane passing through O generates the points A_2 and B_2 from A_1 and B_1 . The repeat distance perpendicular to the mirror plane gives equivalent points A'_1 , B'_1 , A'_2 and B'_2 and it can be seen that there arises another mirror plane displaced by $\frac{1}{2}a$ from the one through O.

Glide planes (a, b, c, n, d)

The centre of symmetry and the mirror plane are symmetry elements which are observed in the morphology of crystals. Now we are going to consider a symmetry element for which the periodic nature of the pattern plays a fundamental role. The glide-plane symmetry element operates by a combination of mirror reflection and a translation.

The description of this symmetry element is simplified by reference to the vectors **a**, **b** and **c** which define the edges of the unit cell. For an *a*-glide plane perpendicular to the *b* direction (fig. 1.25(c)) the point A_1 is first reflected through the glide plane to A_m and then displaced by $\frac{1}{2}$ **a** to the point A_2 . It must be emphasized that A_m is merely a construction point and the net result of the operation is to generate A_2 from A_1 . The repeat of the pattern gives a point A'_2 displaced by $-\mathbf{b}$ from A_2 and we can see that A'_2 and A_1 are related by another glide plane parallel to the one through O and displaced by $\frac{1}{2}\mathbf{b}$ from it. One may similarly have an *a*-glide plane perpendicular to *c* and also *b*- and *c*-glide planes perpendicular to *c*, gives a displacement component $\frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b}$.

The diamond glide-plane d is the most complicated symmetry element and merits a detailed description. For the operation of a d-glide plane perpendicular to **b** there are required two planes, P_1 and P_2 , which are placed at the levels $y = \frac{1}{8}$ and $y = \frac{3}{8}$, respectively. For each initial point there are two separate operations generating two new points. The first operation is reflection in P_1 followed by a displacement $\frac{1}{4}\mathbf{c} + \frac{1}{4}\mathbf{a}$, and the second a reflection in P_2 followed by a displacement $\frac{1}{4}\mathbf{c} + \frac{1}{4}\mathbf{a}$. If we begin with a point (x, y, z) then the first operation generates a point an equal distance from the plane $y = \frac{1}{8}$ on the opposite side with x and z coordinates increased by $\frac{1}{4}$, i.e. the point $(x + \frac{1}{4}, \frac{3}{4} - y, z + \frac{1}{4})$. The second operation, involving the plane P_2 , similarly generates a point $(x - \frac{1}{4}, \frac{3}{4} - y, z + \frac{1}{4})$. These points, and all subsequent new points, may be subjected to the same operations and it will be left as an exercise for the reader to confirm that the following set of eight points is generated:

x	У	Ζ	$\frac{3}{4} + x$	$\frac{3}{4} - y$	$\frac{1}{4} + z$
$\frac{1}{4} + x$	$\frac{1}{4} - y$	$\frac{1}{4} + z$	x	$\frac{1}{2} + y$	$\frac{1}{2} + z$
$\frac{1}{2} + x$	y	$\frac{1}{2} + z$	$\frac{1}{4} + x$	$\frac{\bar{3}}{4} - y$	$\frac{\bar{3}}{4} + z$
$\frac{3}{4} + x$	$\frac{1}{4} - y$	$\frac{3}{4} + z$	$\frac{1}{2} + x$	$\frac{1}{2} + y$	Ζ.

These coordinates show that there are two other glide planes at $y = \frac{5}{8}$ and $y = \frac{7}{8}$ associated with displacements $\frac{1}{4}c + \frac{1}{4}a$ and $\frac{1}{4}c - \frac{1}{4}a$, respectively.

Rotation axes (2, 3, 4, 6)

The modes of operation of rotation axes are shown in fig. 1.7; the new feature which arises for a repeated pattern is the generation of subsidiary axes of symmetry other than those put in initially. This may be seen in fig. 1.25(d) which shows a projected view of a tetragonal unit cell down the tetrad axis. The point A_1 is operated on by the tetrad axis through O to give A_2 , A_3 and A_4 and this pattern is repeated about every equivalent tetrad axis. It is clear that A_1 , A'_2 , A''_3 and A''_4 are related by a tetrad axis, non-equivalent to the one through O, through the centre of the cell. A system of diad axes also occurs and is indicated in the figure.

Screw axes $(2_1; 3_1, 3_2; 4_1, 4_2, 4_3; 6_1, 6_2, 6_3, 6_4, 6_5)$

These symmetry elements, like glide planes, play no part in the macroscopic structure of crystals since they depend on the existence of a repeat distance. The behaviour of a 2_1 axis parallel to *a* is shown in fig. 1.25(*e*). The point A_1 is first rotated by an angle π round the axis and then displaced by $\frac{1}{2}a$ to give A_2 . The same operation repeated on A_2 gives A'_1 which is the equivalent point to A_1 in the next cell. Thus the operation of the symmetry element 2_1 is entirely consistent with the repeat nature of the structural pattern.

The actions of the symmetry elements 3_1 and 3_2 are illustrated in fig. 1.25(f). The point A_1 is rotated by $2\pi/3$ about the axis and then displaced by $\frac{1}{3}a$ to give A_2 . Two further operations give A_3 and A'_1 , the latter point being displaced by **a** from A_1 . The difference between 3_1 and 3_2 can either be considered as due to different directions of rotation or, alternatively, as due to having the same rotation sense but displacements of $\frac{1}{3}a$ and $\frac{2}{3}a$, respectively. The two arrangements produced by these symmetry elements are enantiomorphic (i.e. in mirror-image relationship).

In general, the symmetry element R_D along the *a* direction involves a rotation $2\pi/R$ followed by a displacement (D/R)a.

Inversion axes $(\overline{3}, \overline{4}, \overline{6})$

The action of the inversion axis \overline{R} is to rotate the point about the axis by an angle $2\pi/R$ and then invert through a point contained in the axis. Since $\overline{1}$ and $\overline{2}$ are equivalent to a centre of symmetry and mirror plane, respectively, they are not included here as inversion axes.

There is given in table 1.2 a list of symmetry elements and the graphical symbols used to represent them.

1.9 Space groups

Symmetry elements can be combined in groups and it can be shown that 230 distinctive arrangements are possible. Each of these arrangements is called a *space group* and they are all listed and described in volume A of the *International Tables for Crystallography*. Before describing a few of the 230

Type of symmetry element	Written symbol	Graphical symbol	
Centre of symmetry	1	0	
		Perpendicular In plane of to paper paper	
Mirror plane	m		
Glide planes	abc		
		glide in plane arrow shows of paper glide direction	
		glide out of plane of paper	
	n	7	
Rotation axes	2	•,	
	3		
	4	•	
	6	•	
Screw axes	21	(
	3 ₁ , 3 ₂	Á Á	
	4 ₁ , 4 ₂ , 4 ₃	***	
	6 ₁ , 6 ₂ , 6 ₃ , 6 ₄ , 6 ₅	****	
Inversion axes	3	Δ	
	4	•	
	6	A state of the	

Table 1.2.

space groups we shall look at two-dimensional space groups (sometimes called *plane groups*) which are the possible arrangements of symmetry elements in two dimensions. There are only 17 of these, reflecting the smaller number of possible systems, lattices and symmetry elements. Thus there are:

four crystal systems – oblique	e, rectangular, square and	hexagonal;
two types of lattice - primitiv	e (p) and centred (c); and	
symmetry elements –		
rotation axes	2, 3, 4 and 6	

rotation axes	2, 3, 4 and
mirror line	m
glide line	g.

Fig. 1.26.

We shall now look at four two-dimensional space groups which illustrate all possible features.

Oblique p2

This is illustrated in fig. 1.26 in the form given in the International Tables. The twofold axis is at the origin of the cell and it will reproduce one of the structural units, represented by an open circle, in the way shown. The right-hand diagram shows the symmetry elements; the twofold axis manifests itself in two dimensions as a centre of symmetry. It will be seen that three other centres of symmetry are generated – at the points $(x, y) = (\frac{1}{2}, 0)$, $(0,\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2})$. The four centres of symmetry are all different in that the structural arrangement is different as seen from each of them.



Rectangular cm

This rectangular space group is based on a centred cell and has a mirror line perpendicular to the y axis. In fig. 1.27 the centring of the cell is seen in that for each structural unit with coordinate (x, y) there is another at $(\frac{1}{2} + x, \frac{1}{2} + y)$. In addition, the mirror line is shown relating empty open circles to those with commas within them. The significance of the comma is that it indicates a structural unit which is an enantiomorph of the one without a comma.

The right-hand diagram in fig. 1.27 shows the symmetry elements in the unit cell and mirror lines are indicated at y = 0 and $y = \frac{1}{2}$. What is also



The two-dimensional space group cm as it appears in International Tables for X-ray Crystallography.

Fig. 1.27.



apparent, although it was not a part of the description of the two-dimensional space group, is the existence of a set of glide lines interleaving the mirror lines. The operation of a glide line involves reflection in a line followed by a translation $\frac{1}{2}a$. Because of the reflection part of the operation, the related structural units are enantiomorphs.

Square p4g

This two-dimensional space group is illustrated in fig. 1.28 and shows the fourfold axes, two sets of glide lines at an angle $\pi/4$ to each other and a set of mirror lines at $\pi/4$ to the edges of the cell. Starting with a single structural unit there are generated seven others; the resultant eight structural units are the contents of the square cell. Wherever a pair of structural units are related by either a mirror line or a glide line the enantiomorphic relationship is shown by the presence of a comma in one of them.



Hexagonal p6

As the name of this two-dimensional space group suggests it is based on a hexagonal cell, which is a rhombus with an angle $2\pi/3$ between the axes. As can be seen in fig. 1.29 the sixfold axis generates six structural units about each origin of the cell. A pair of threefold axes within the cell is also



Origin at 6

The two-dimensional space group p4g as it appears in International Tables for X-ray Crystallography.

generated. The complete arrangement of symmetry elements is shown in the right-hand diagram of fig. 1.29.

Having established some general characteristics of space groups by the study of some relatively simple two-dimensional examples we shall now look at five three-dimensional space groups where the third dimension introduces complications not found in two dimensions.

Triclinic $P\overline{I}$

This space group is based on a triclinic primitive cell which has a centre of symmetry. The representation of this space group, as given in the *International Tables*, is reproduced in fig. 1.30. The cell is shown in projection and the third coordinate (out of the plane of the paper), with respect to an origin at a centre of symmetry, is indicated by the signs associated with the open-circle symbols. This convention is interpreted as meaning that if one coordinate is +t then the other is -t. The comma within the open-circle symbol indicates that if the symmetry operation is carried out on a group of objects and not just on a point, then the groups represented by \bigcirc and \odot are enantiomorphically related. The diagram on the right-hand side shows the distribution of symmetry elements.

The information which heads figs. 1.30-1.35 is taken from the *International Tables* and, reading across the page, is (i) the crystal system, (ii) the point group, (iii) symmetry associated with *a*, *b* and *c* axes (where appropriate), (iv) an assigned space-group number and (v) the space-group name according to the Hermann-Mauguin notation with, underneath, the older and somewhat outmoded Schoenflies notation.

Fig. 1.30. The operation of the space group PI as shown in the International Tables for X-ray Crystallography.



Monoclinic Cm

This space group is based on a monoclinic C-face centred cell with the mirror plane perpendicular to the unique axis. The unique axis for monoclinic space groups is the one perpendicular to the other two and, by convention, this is taken as the b axis. The letters shown in fig. 1.31 do not appear in the *International Tables* but they assist in a description of the generation of the complete pattern starting with a single unit.

We start with the structural unit A_1 and generate A_2 from it by the operation of the C-face centring. The mirror plane gives A_3 from A_2 and the

Fig. 1.31. The operation of the space group Cm as shown in the International Tables for X-ray Crystallography. The letters have been added.



Origin on plane m; unique axis b

centring gives A_4 from A_3 . This constitutes the entire pattern. The + signs against each symbol tell us that the units are all at the same level and the commas within the open circles indicate the enantiomorphic relationships.

It may be seen that this combination of C-face centring and mirror planes produces a set of *a*-glide planes.

Monoclinic $P2_1/c$

This space group is based on a primitive, monoclinic unit cell with a 2_1 axis along b and a c-glide plane perpendicular to it. In fig. 1.32(a) these basic symmetry elements are shown together with the general structural pattern produced by them. It can be found by inspection that other symmetry elements arise; A_1 is related to A_4 and A_2 to A'_3 by glide planes which interleave the original set. The pairs of units A_4 , A_2 and A_1 , A_3 are related by a centre of symmetry at a distance $\frac{1}{4}c$ out of the plane of the paper and a whole set of centres of symmetry may be found which are related as those shown in fig. 1.25(a).

The International Tables gives this space group with the unit-cell origin at a centre of symmetry and the structure pattern and complete set of symmetry elements appears in fig. 1.32(b). If a space group is developed from first principles, as has been done here, then the emergence of new symmetry elements, particularly centres of symmetry, often suggests an alternative and preferable choice of origin.

Orthorhombic $P2_12_12_1$

This space group is based on a primitive orthorhombic cell and has screw axes along the three cell-edge directions. The name does not appear to define completely the disposition of the symmetry elements as it seems that there may be a number of ways of arranging the screw axes with respect to each other.

As was noted in §1.4 in some point groups certain symmetry elements appear automatically due to the combination of two others. If this occurs in the point group it must also be so for any space group based on the point group. If we start with two sets of intersecting screws axes and generate the structural pattern from first principles we end up with the arrangement shown in fig. 1.33(a) which corresponds to the space group $P2_12_12_2$. The other possible arrangement, where the original two sets of screw axes do not intersect, is found to give a third set not intersecting the original sets and