An introduction to

X-ray crystallography

SECOND EDITION

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Contents

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

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

(*a*)   (*b*)
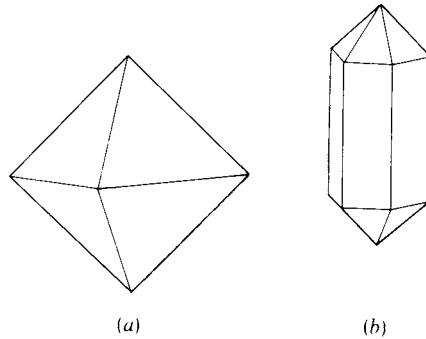
have the same general habit a detailed examination reveals considerable
variation in size and shape. In particular one may find a selection of platy
crystals looking somewhat like those shown in fig. 1.2(*a*). The shapes of
these seem to be quite unrelated but, if they are rearranged as in fig. 1.2(*b*), 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 crystallog-
rapher. 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*).

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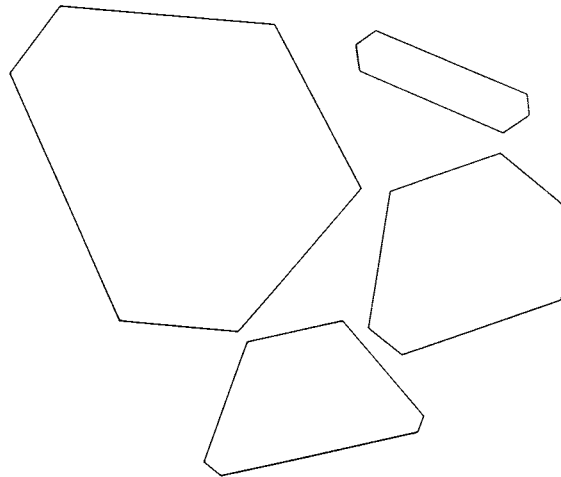
(*a*)
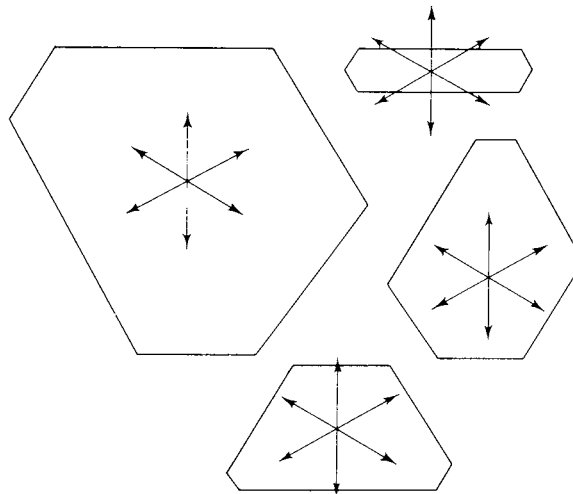
(*b*)

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.
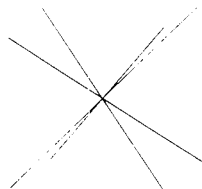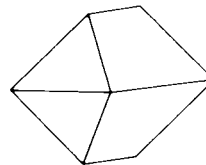
(*a*)   (*b*)

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.

(*a*)

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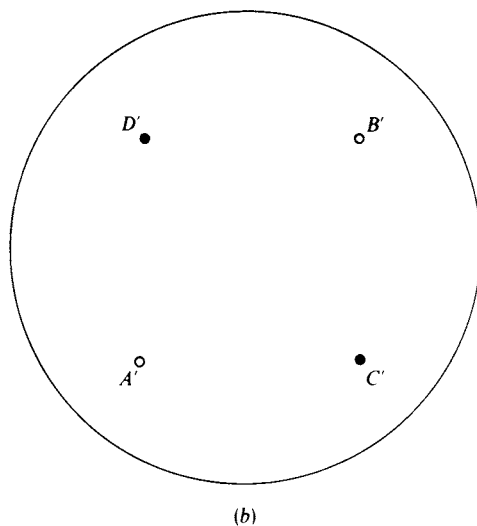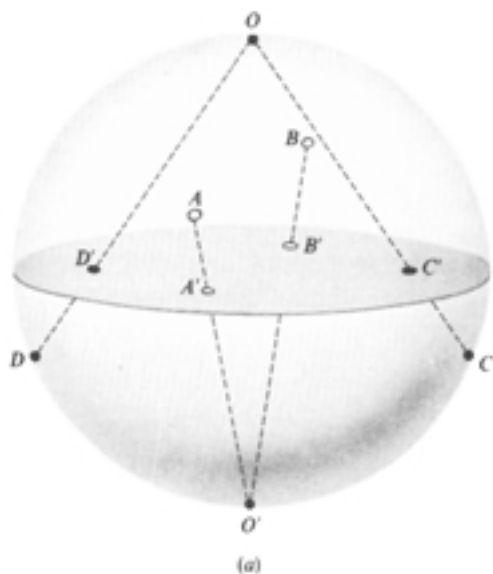
We now consider the symmetry elements which may be present in crystals – or are revealed as intrinsically present by the set of normals to the faces.

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

collinear pairs. The way in which this shows up on a stereographic pro-jection 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 opposite 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.

(*a*)

(*b*)
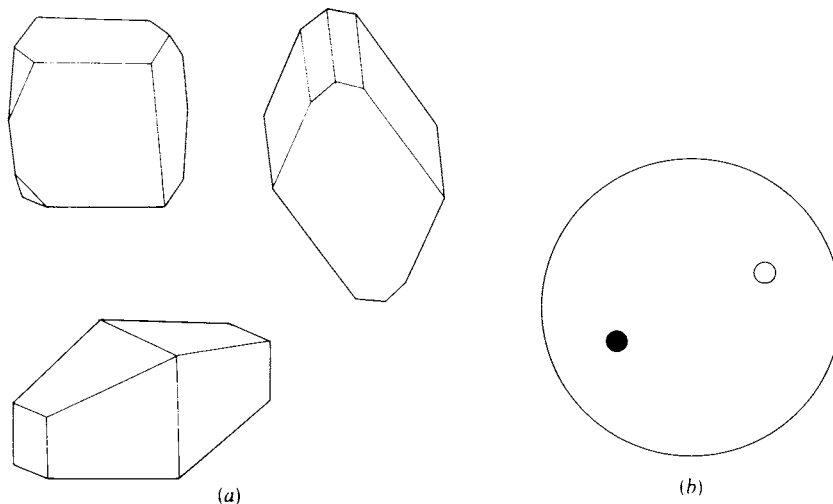
Fig. 1.6.
(*a*) Crystals with mirror planes.
(*b*) The stereographic projections of a pair of faces related by a mirror plane when the mirror plane is (i) in the plane of projection; (ii) perpendicular to the plane of projection.

(*a*)

(i)   (ii)

(*b*)
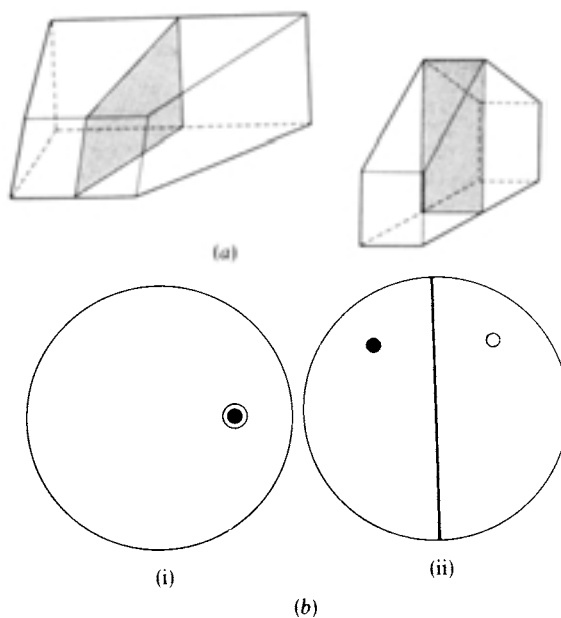
Rotation axes (written symbols 2, 3, 4, 6; graphical symbols
⬩, ▲, ◆, ⬢)

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 $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$; graphical symbols
o, *none,* ▲, ◈, ⬣)

The inversion axes relate crystal planes by a combination of rotation and inversion through a centre. The operation of a $\bar{4}$ 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 $\bar{1}$ is identical to a centre of symmetry and $\bar{1}$ is the accepted symbol for a centre of symmetry. Similarly $\bar{2}$ 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.

(*b*)
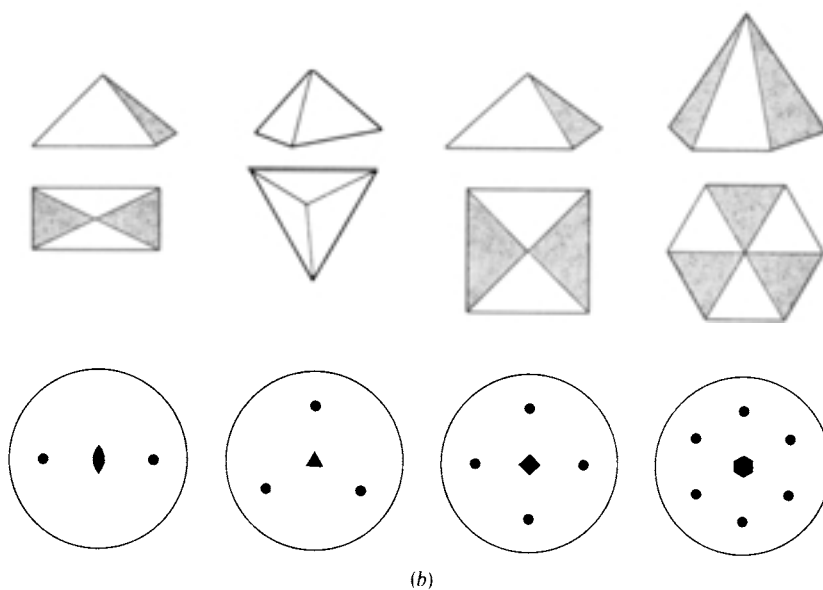
Fig. 1.8.
(*a*) A perspective view of the operation of an inverse tetrad axis.
(*b*) Stereographic projections for $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$.
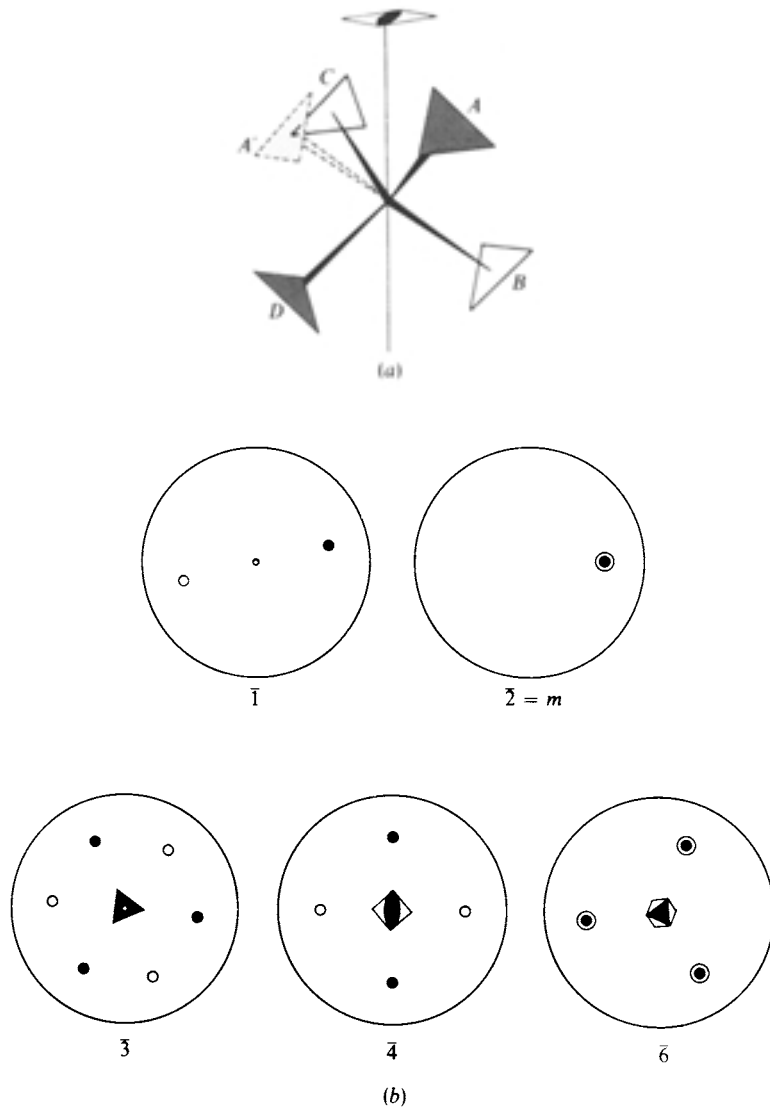
light from the mirror-like facets of the crystal to define their relative orientations.

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.
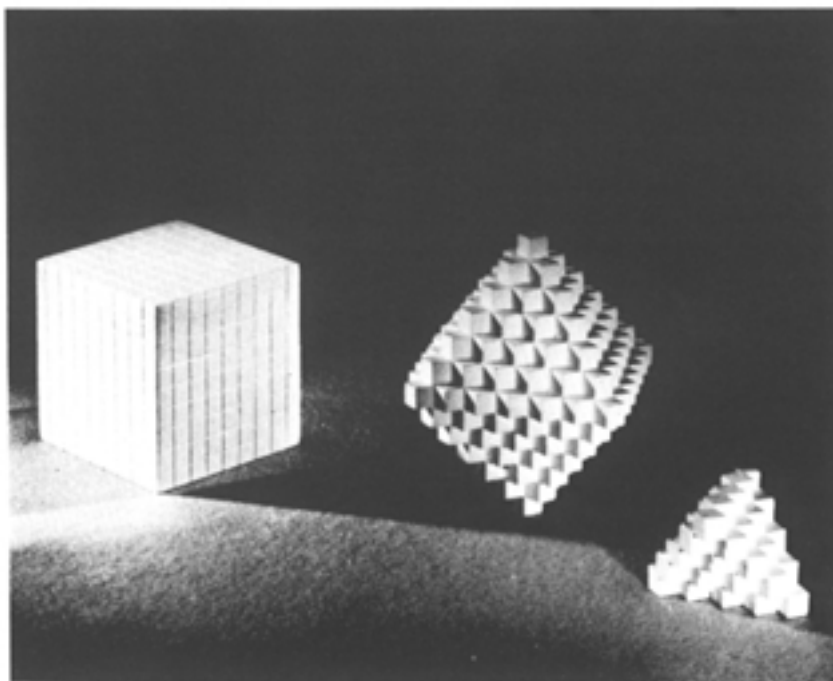
triad axes – and conversely all crystals having a set of four triad axes are cubic.

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 symmmetry 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* $\bar{1}$ and 1 within the triclinic system. As has been previously noted $\bar{1}$ 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.

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.
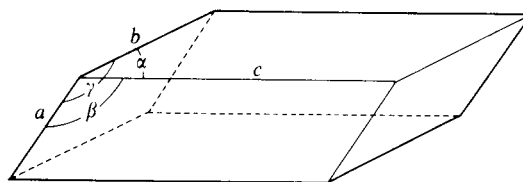
(*a*)

(*b*)

(*c*)

Table 1.1. *The seven crystal systems*

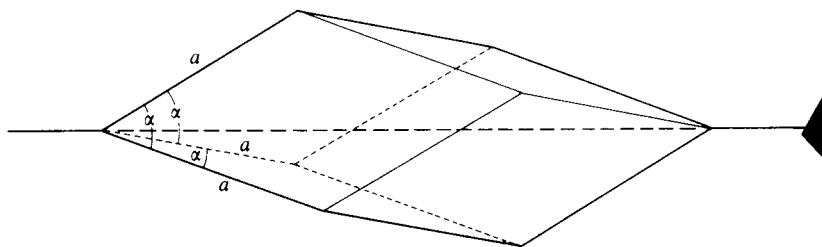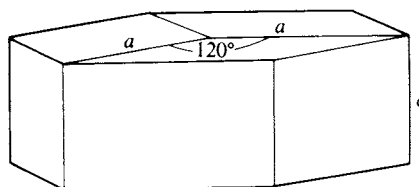| System	Subunit	Essential symmetry of crystal
Triclinic	No special relationships	None
Monoclinic	$a \neq b \neq c$ $\beta \neq \alpha = \gamma = 90°$	Diad axis or mirror plane (inverse diad axis)
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Three orthogonal diad or inverse diad axes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

Fig. 1.11. Stereographic projections representing the crystal classes (*a*) 1 and (*b*) $\bar{1}$.
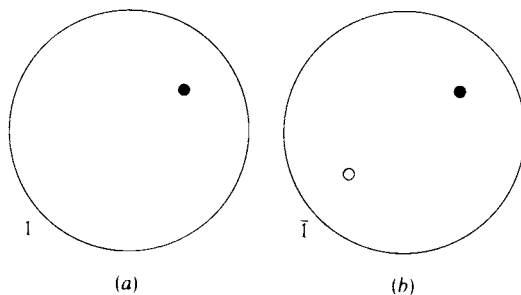
These, illustrated in fig. 1.12, have (*a*) a diad axis, (*b*) a mirror plane and (*c*) a diad axis and mirror plane together. The orthorhombic and trigonal systems give rise to the classes shown in fig. 1.13.

Some interesting points may be observed from a study of these diagrams. For example, the combination of symbols 3*m* 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 $\bar{6}$ 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

Fig. 1.12.
Stereographic projections representing the three crystal classes in the monoclinic system (a) 2, (b) m and (c) 2/m.
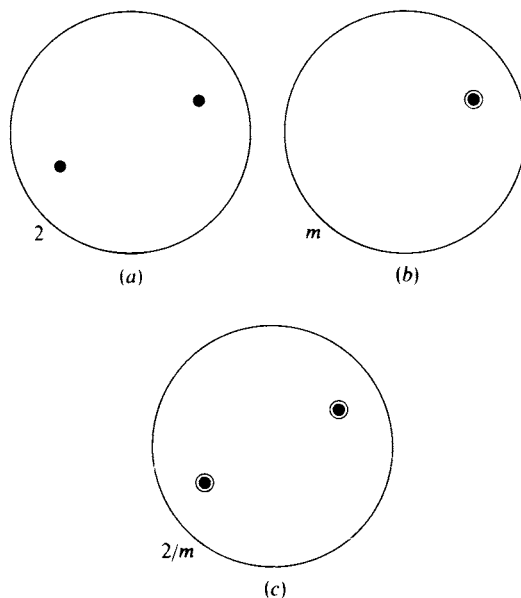
Fig. 1.13.
Stereographic projections representing the three crystal classes in the orthorhombic system and the six classes in the trigonal system.

Trigonal   Orthorhombic
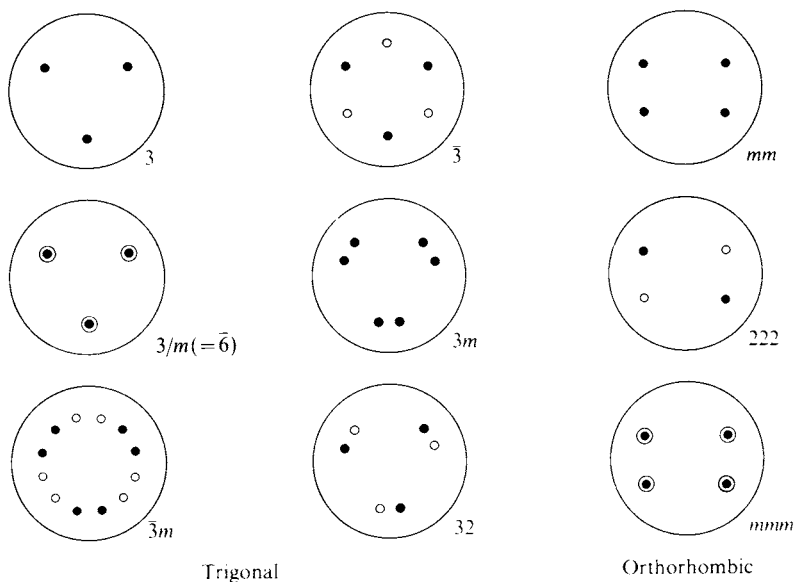
crystals may be assigned to one or other of these classes. While the general nature of the basic subunit determines the crystal system, for each system there can be different elements of symmetry associated with the crystal. If a material, satisfying some minimization-of-potential-energy criterion, crystallizes 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

Fig. 1.14.
A two-dimensional
pattern and some
possible choices of unit
cell.
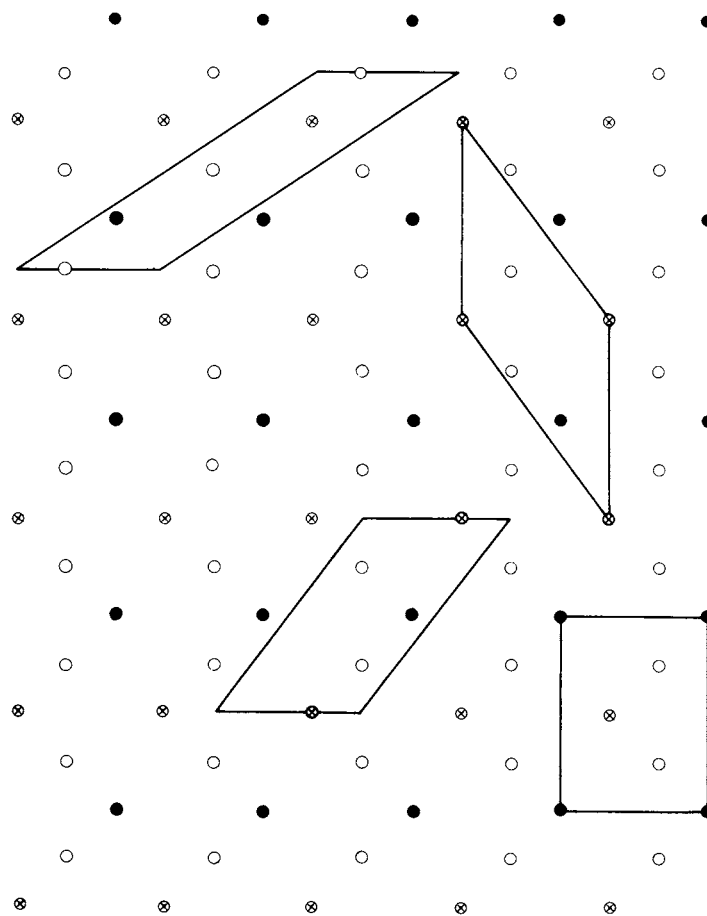
arrangement. One customarily chooses the unit cell which displays the highest possible symmetry, for this indicates far more clearly the symmetry of the underlying structure.

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 2*a* in one direction and *b* in the other. The angle θ, which the normal *AN* makes with the *b* direction, is clearly given by

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

Fig. 1.15.
A two-dimensional crystal made up of unit cells with a tetrad axis of symmetry.
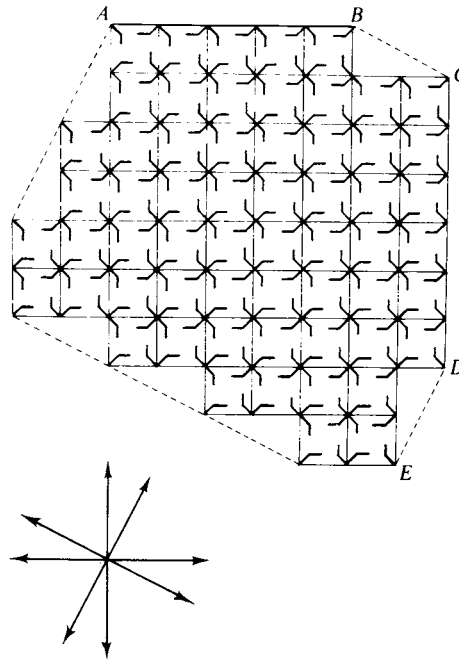
Fig. 1.16.
A two-dimensional
crystal built of
rectangular units.
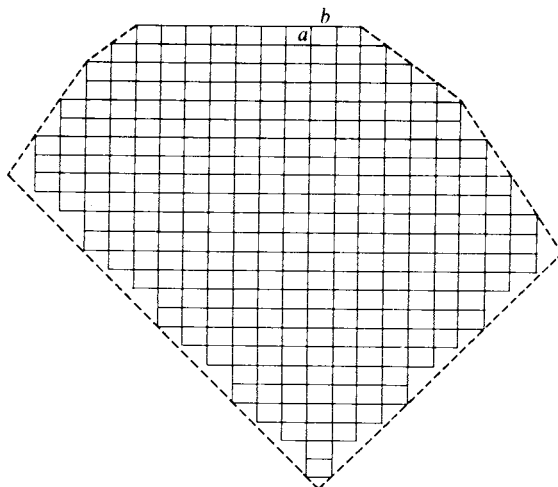
Fig. 1.17.
The relationship between
the crystal face AB and
the unit cell.
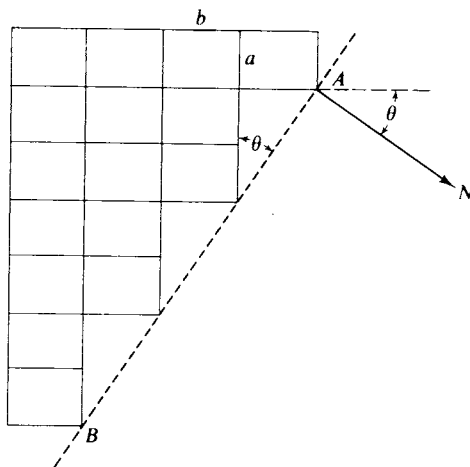
If the neighbouring points of the face were separated by na and mb then one would have

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

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

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

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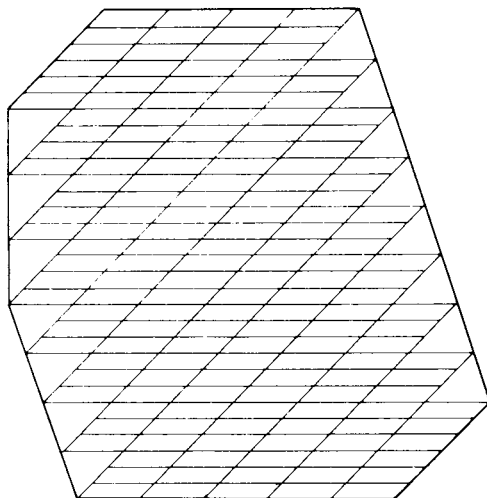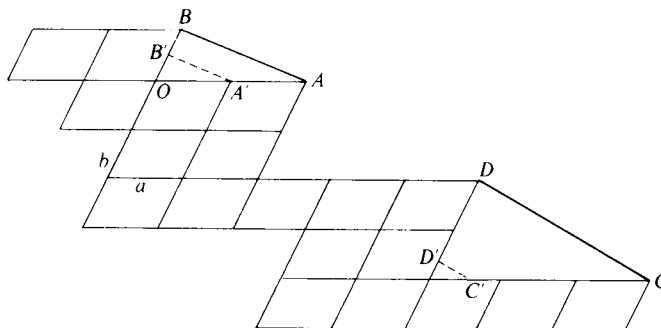A two-dimensional crystal based on an oblique unit cell.

Fig. 1.19.
The lines $A'B'$ and $C'D'$
which are parallel to the
crystal faces AB and CD
have 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