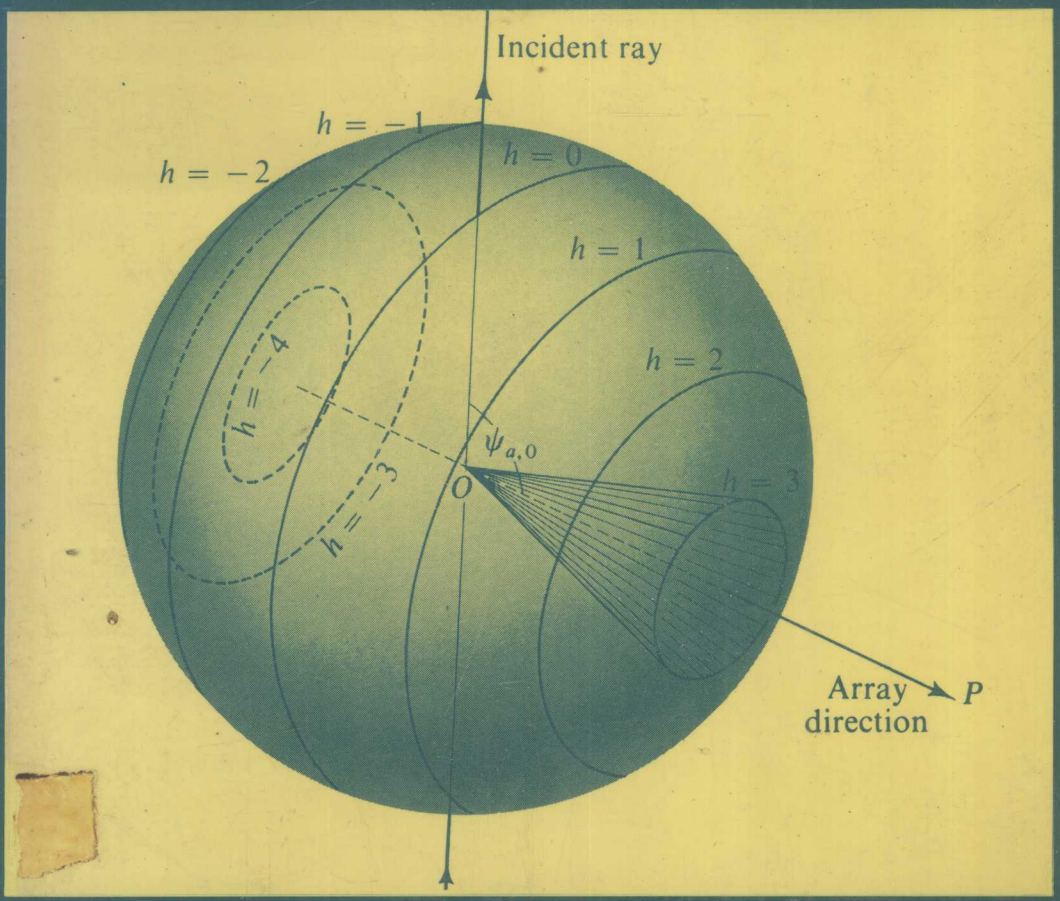
An Introduction to X-ray Crystallography

M. M. WOOLFSON



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AN INTRODUCTION TO

X-RAY CRYSTALLOGRAPHY

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PREFACE

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 Tables on page 356.

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.

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.

CONTENTS

CHAPTER 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.

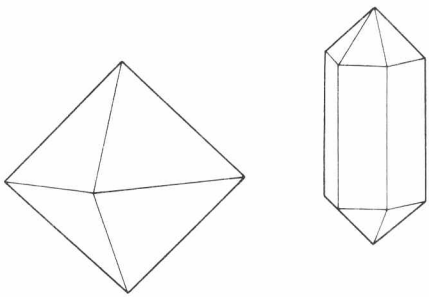
It can easily be verified that the significance of planar surfaces is not confined to the exterior morphology but is also inherent in the interior structure of a crystal. Crystals frequently cleave along preferred directions and, even when a crystal is crudely fractured, it can be seen through a microscope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



(*a*) (*b*)

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

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.

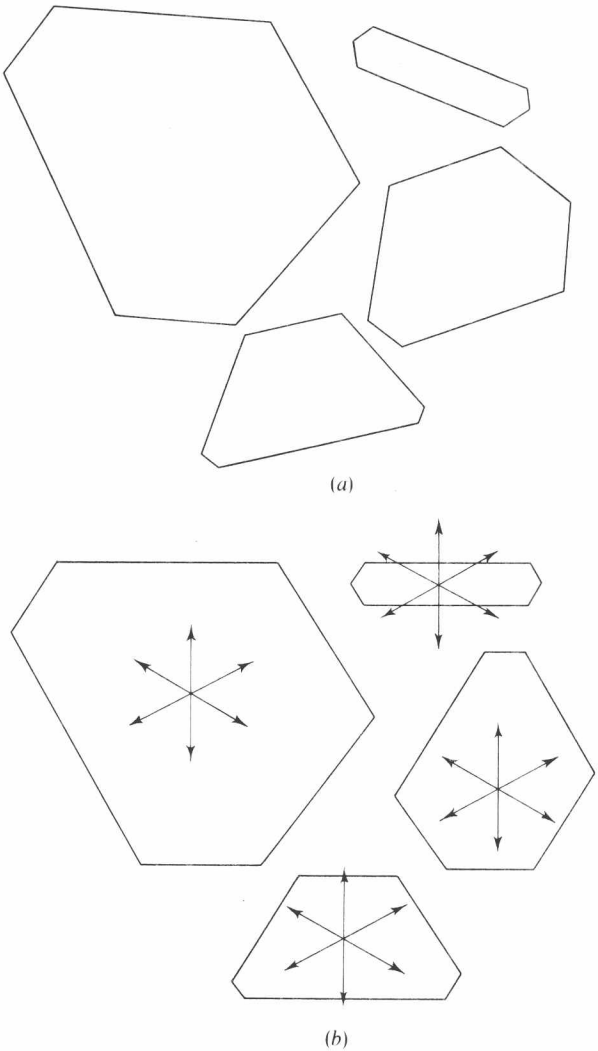
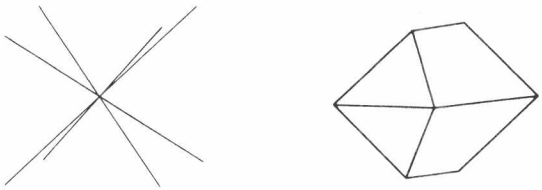


Fig. 1.2. (*a*) Set of apparently-irregular plate-like crystals. (*b*) Crystals rearranged to show parallelism of faces and underlying hexagonal symmetry.

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



(*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.

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*).

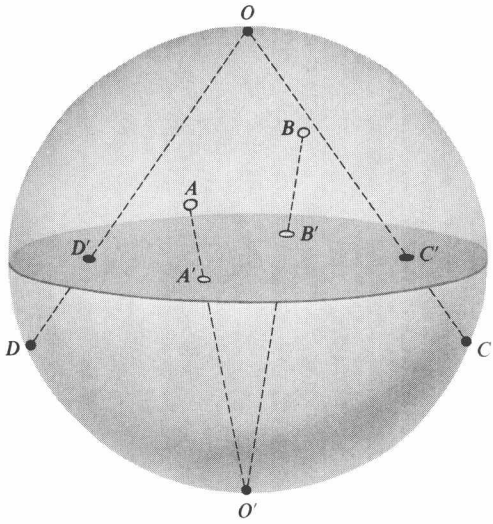
We now consider the symmetry elements which may be present in crystals—or are revealed as intrinsically present by the set of normals to the faces.

Centre of symmetry (*for symbol see inversion axis*)

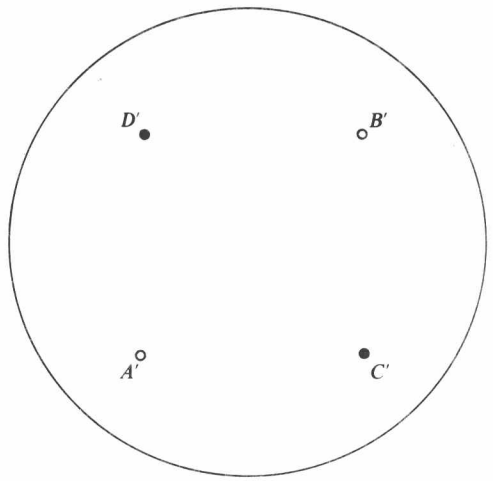
A crystal has a centre of symmetry if, for a point within it, faces occur in parallel pairs of equal dimensions on opposite sides of the point and equidistant from it. A selection of centrosymmetric crystals is shown in fig. 1.5(*a*). However even when the crystal itself does not have a centre of symmetry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



(*a*)

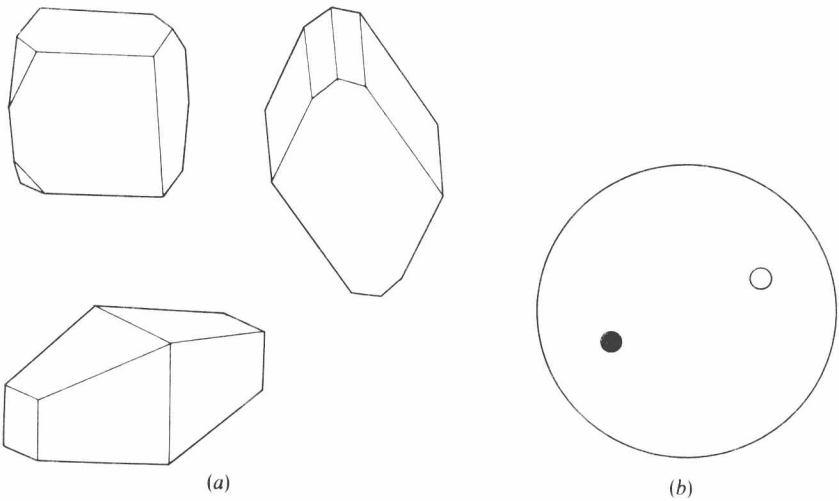


(*b*)

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.

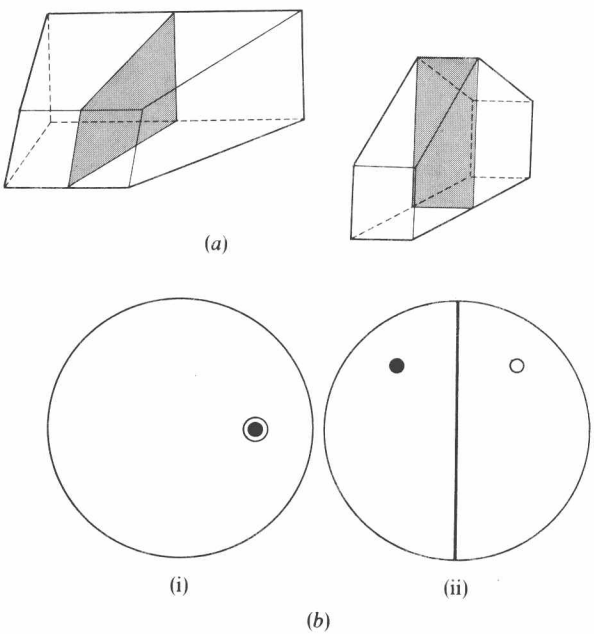
Rotation axes (*written symbols* 2, 3, 4, 6; *graphical symbols* ⬮, ▲, ◆, ⬢)

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



(*a*) (*b*)

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



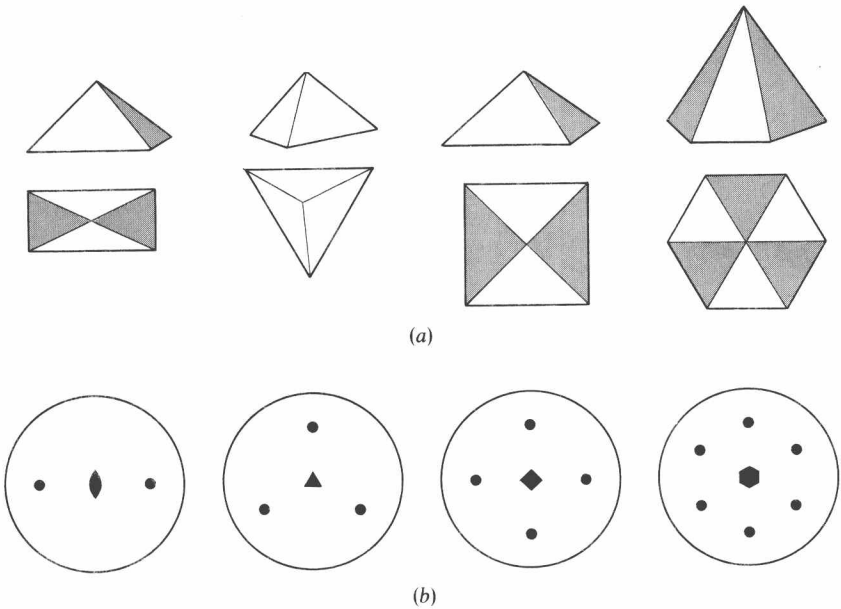
(*a*)

(i) (ii)

(*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.

(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.



(*a*)

(*b*)

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.

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

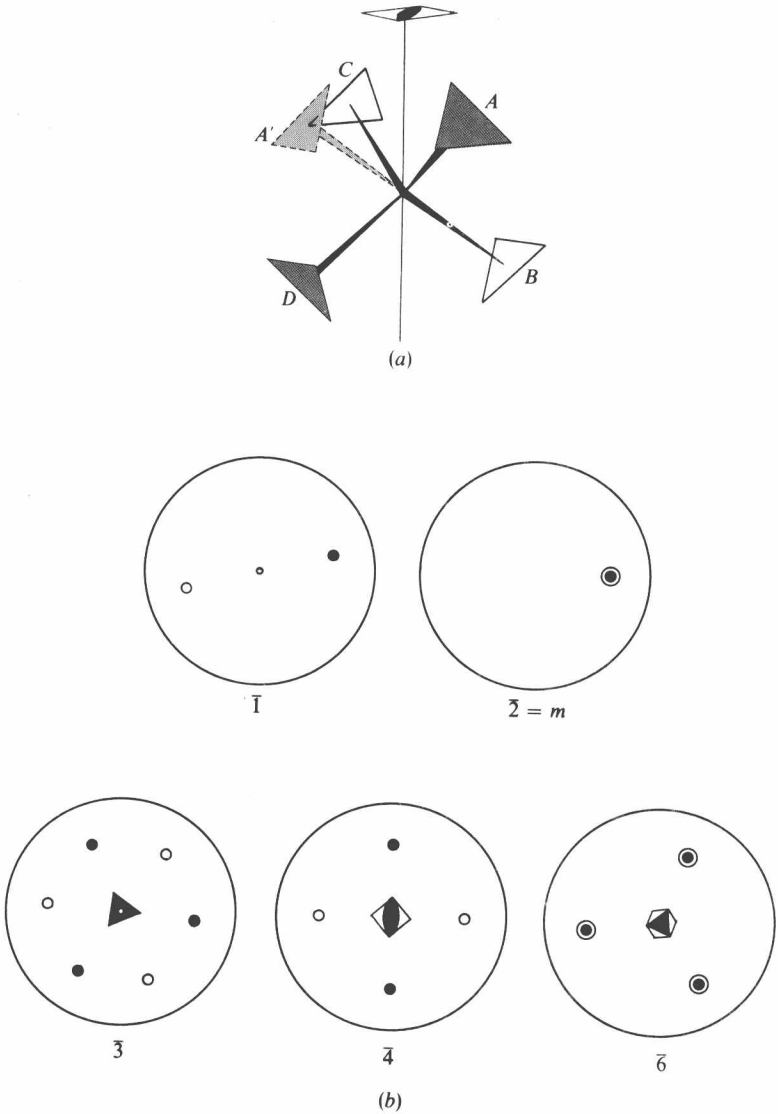


Fig. 1.8. (*a*) A perspective view of the operation of an inverse tetrad axis. (*b*) Stereographic projections for $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$.

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 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.