Crystal Morphology and Crystal Symmetry

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1.1 Brief Historical Introduction

Crystals, with their plane faces, sharp angles, and color, have excited interest since the earliest times. Their color and decorative qualities are recorded in the Bible [1]: we need not start as far back as that, but will consider instead some of the highlights in the build-up of the science of Crystallography.

The Swiss naturalist Conrad Gessner [2] observed in 1564 that "one crystal differs from another in its angles, and consequently in its figure," and Pliny [3], Caesalpinus [4], and Buffon [5] also denied "the fixity of crystals." Niels Stensen, a Dane, also known as Nicolaus Steno [6], showed in 1669 that crystals of quartz, although of varying edge lengths, nevertheless preserved constant angles between corresponding faces, an observation that led, after further work, to the law of constant interfacial angles (q.v.), sometimes called Steno's law. Some examples of Steno's figures for quartz are shown in Fig. 1.1. Pliny referred to quartz as *krustallos* (Gk. $\kappa\rho\nu\sigma\tau\alpha\lambda\lambda o\sigma =$ ice), believing it to be ice permanently congealed by intense cold: "rain-water and pure snow are needed for its formation." In the same year, Bartholinus [7] published his work on the Iceland Spar modification of calcium carbonate: he measured the interfacial angles (q.v.) of crystal fragments and found that "the (cleavage) fragments have the same shape as the original crystal."

Johannes Kepler, best known for his research in astronomy, worked sometime for Emperor Rudolph II of Austria, who was somewhat negligent in paying salaries. Kepler, who was without money with which to purchase a Christmas present for a friend in 1611, wrote a booklet entitled *The Six-Cornered Snowflake* [8], Fig. 1.2. He had noticed that snow crystals of whatever shape always exhibited sixfold symmetry. He speculated on a relationship between the snow crystal and a hexagonal close packing of spheres: he recognized the genre of crystal symmetry, which was to be developed about two centuries years later. Jokingly, he passed off his "New Year's Gift" as a mere "nothing" (like his finances), making a play on the word *nix*, which means "snowflake" in Latin but "nothing" in Lower German, Kepler's language.

Over the period 1688–1705, many investigations by the Italian physicist Giovanni Guglielmini [9] confirmed and extended the work of Steno, and during 1772–1783, about a century after Steno, the Frenchman Jean-Baptiste Romé de l'Isle [10] carried out an extensive series of measurements that confirmed fully Steno's findings: he stated further, as a law, that "the interfacial angles of a crystal material are characteristic of it." In his work, he made much use of the contact goniometer, developed by Arnould Carangeot [11], for measuring interfacial angles on crystals.

His compatriot René Just (Abbé) Haüy [12] published a treatise on mineralogy in 1801 in which he envisaged crystals built up by stacking identical blocks of structural material in ways that led to the shapes of crystals, thus explaining Steno's law. He was led to this view by the observation that when

M. Ladd and R. Palmer, *Structure Determination by X-ray Crystallography: Analysis by X-rays and Neutrons*, DOI 10.1007/978-1-4614-3954-7_1,

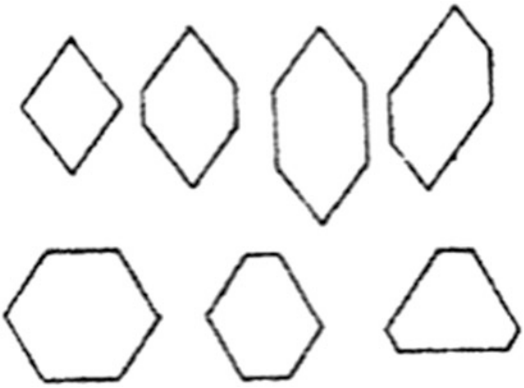
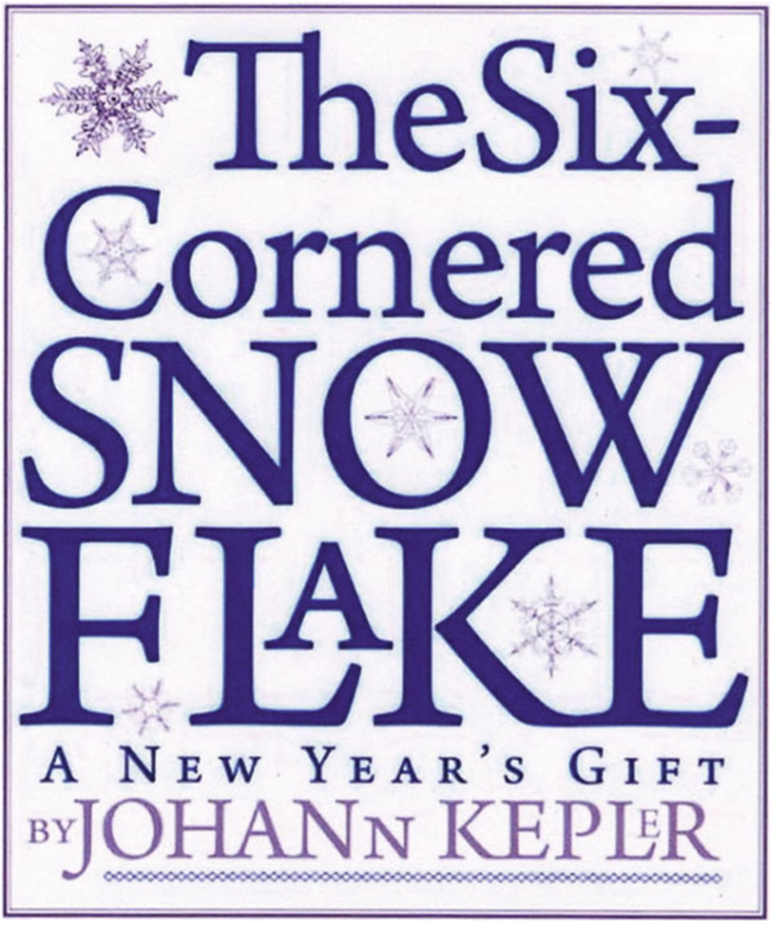


Fig. 1.1 Examples of Steno's drawings of transverse sections of different crystal specimens of quartz, SiO_2; the interfacial angles are 120° or (120/2)° in each case



The Six-
Cornered
SNOW
FLAKE
A NEW YEAR'S GIFT
BY JOHANN KEPLER

Fig. 1.2 The cover (in translation) of Kepler's booklet on *The Six-Cornered Snowflake*; some of Kepler's many drawings of snowflakes appear on the cover (reproduced by courtesy of Paul Dry Books)

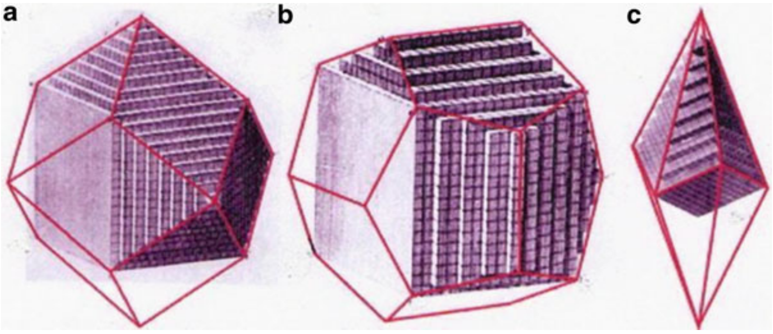


Fig. 1.3 Examples of Haüy's figures. (**a**) Rhombic dodecahedron formed from stacked cubes, as in garnet (idealized formula $Ca_3Al_2Si_3O_{12}$). (**b**) Pentagonal dodecahedron formed from stacked cubes, as in $K_2Mn_2(SO_4)_3$. (**c**) Scalenohedron formed from stacked rhombohedra, as in calcite, $CaCO_3$

crystals of calcite were broken, they always formed rhombohedral-shaped fragments whatever the shape of the original crystal, an observation similar to that made by Bartholinus. Other crystals cleaved into different shapes, such as cubes; Fig. 1.3 illustrates some of Haüy's figures. He laid the foundation for the law of rational intercepts (q.v.), which demonstrated, albeit implicitly, a shape for the unit cell (q.v.) of a crystal. He described also different crystal shapes, or *habits*, obtained by the packing of different shaped blocks.

In the period 1804–1815, the German scientists Christian Weiss [13] and Frederick Mohs [14], independently, identified the six "major" crystal systems (q.v.)—it seems that they did not distinguish between the two systems that we now recognize as trigonal and hexagonal. Another German scientist Johann Hessel [15] determined the 32 crystallographic point groups (q.v.) in 1835 and his compatriot Moritz Frankenheim [16] also described six crystal systems and, additionally, the 32 crystal classes in 1842. Crystal classes are names for the general forms (q.v.) of crystals, of which we shall have more to say later, Sect. 1.4.2; Fig. 1.4 illustrates two examples of crystal class.

A next landmark was that contained in the work of William Miller, 1839, who proposed an unambiguous notation for specifying the orientations of the faces of a crystal, leading to the *Miller Indices* [17] (q.v.), based on the scalar equation of a plane; the law of rational indices is clear from Miller's work—the descriptor "law of rational ratios of intercepts" is perhaps more apt.

The regular arrangements of points in space were addressed by August Bravais [18] in 1846, who derived the 14 Bravais lattices. Actually, Frankenheim had derived 15 such lattices in 1842, but Bravais showed that two of them were identical. For his infelicity, Frankenheim's name is frequently omitted from a discussion of lattices, albeit the nature of his 15th lattice was never completely clear.

Continuing the development of crystal symmetry, we have at the end of the nineteenth century, Yevgraf Fyodorov [19] (in Russia), Artur Schönflies [20] (in Germany), and William Barlow [21] (in Britain), all independently, describing the 230 ordered spatial patterns, or space groups (q.v.), that represented the possible ways of arranging infinite arrays of points (atoms) regularly in space, commensurate with the 14 Bravais lattices.

By that time, the work of mineralogists and mathematicians had led to a well-defined study of the external form (morphology) of crystals, as well as to predictions about their internal structure. The totality of mineralogical studies was collected in the extensive six-volume treatise *ChemischeKristallographie* of Paul von Groth, the first part of which was published in 1904. The time was right for a major breakthrough, and we arrive at the year 1912 and the inception of the study of crystals by X-ray diffraction methods: X-ray Crystallography was born.

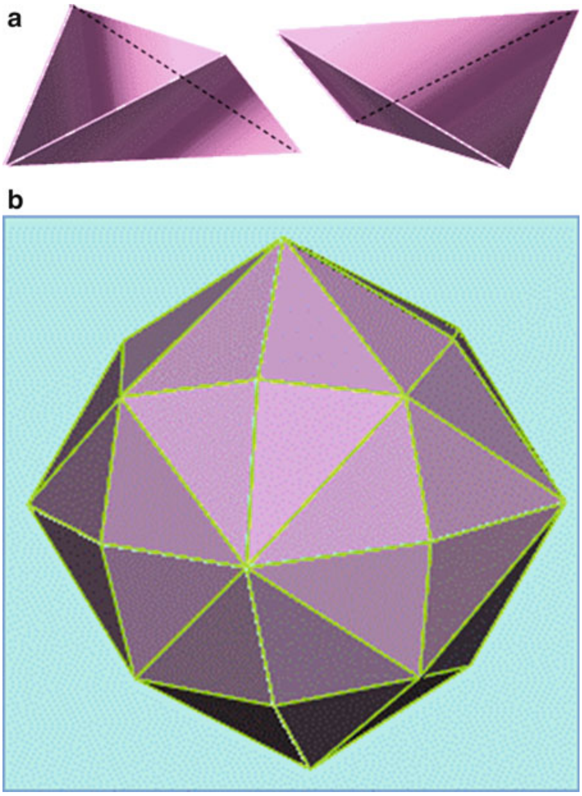


Fig. 1.4 Examples of crystal classes: (**a**) Rhombic disphenoid, showing left-hand and right-hand enantiomorphs (q.v.). (**b**) Hex(akis) octahedron

The classic experiment [22], suggested by Laue,[1] and performed by Paul Friedrich and Walter Knipping, demonstrated the diffraction of X-rays from a crystal of copper sulfate. This material was, perhaps, not the best choice because of its low (triclinic) symmetry. Nevertheless, the diffraction effects showed conclusively both that crystals were periodic in three dimensions and that X-rays possessed wave-like properties. Figure 1.5 shows X-ray diffraction patterns from early experiments on X-ray diffraction.

The results from this work may be said to be a landmark in the development of modern science. The diffraction technique that was initiated by Laue was improved quickly by W. L. Bragg, in his work on crystals of the alkali-metal halides and other crystals. Barlow, one of those who had derived the space groups earlier, had also developed structure models for some metallic elements, and simple binary compounds such as sodium chloride, cesium chloride, and zinc blende. None of his results was proved at that time: all were speculative, but remarkably accurate, as it turned out.

Bragg [23] investigated the X-ray diffraction patterns of sodium chloride and other alkali halides and zinc blende (ZnS). He found that the models suggested by Barlow were correct, and other models proposed by Barlow, such as cubic close-packed and hexagonal close-packed structures for metallic elements, were confirmed. The number of structure analyses grew very rapidly: Fig. 1.6 is a stereoview of the structure of sodium chloride, NaCl. Several stereoviews are used in this book in order to

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[1] In 1913, Laue's father was raised to the ranks of hereditary nobility; Laue then became von Laue.

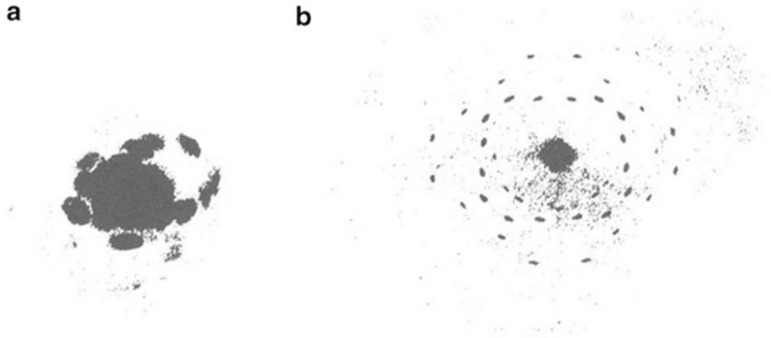

Fig. 1.5 The first X-ray diffraction photograph by Friedrich et al. [22]. (**a**) Copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, showing no symmetry. (**b**) Zinc blende (the first crystal structure to be fully determined), ZnS, showing fourfold symmetry (Bragg WH, Bragg WL (1949) The crystalline state, vol 1. G. Bell and Sons)

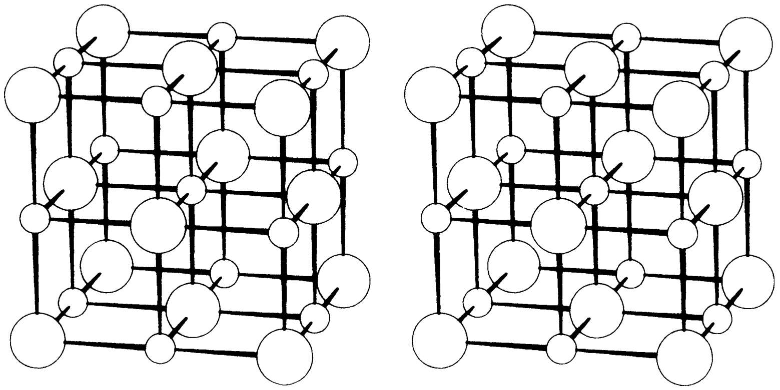

Fig. 1.6 Stereoview of the face-centered cubic unit cell and its environs for the crystal structure of sodium chloride: ◯ = Cl^{-}, ○ = Na^{+}

demonstrate clearly the three-dimensional nature of crystal structures, and Appendix A describes the process of stereoviewing, and the construction of a simple stereoviewer.

The early structure analyses were carried out with the aid of an X-ray ionization spectrometer, the forerunner of the modern single-crystal X-ray diffractometer, designed largely by W. H. Bragg [24]. Generally, the name Bragg refers to W. L. Bragg, but his father (W. H.) also played a highly significant role at the very beginning of the technique of crystal structure analysis by X-ray diffraction.

X-ray diffraction provides the most powerful technique for probing the internal structures of crystals and for determining with high precision the actual atomic arrangement in space. Figure 1.7 shows a three-dimensional contour map of the electron density in a medium-sized molecule, euphenyl iodoacetate [25], $C_{32}H_{53}O_2I$. The contour lines join points of equal electron density in the structure; hydrogen atoms are not revealed in this map because of their relatively small scattering power for X-rays.

If we assume that the centers of atoms are located at the maxima in the electron density map, we can deduce the molecular model in Fig. 1.8a; the chemical structural formula is shown for comparison in Fig. 1.8b. The iodine atom is represented by the large number of contours at the extreme left of Fig. 1.7. The carbon and oxygen atoms are depicted by approximately equal numbers of contours. The atoms in the side chain, shown on the extreme right of the figure, have contours that are spaced further apart. Thermal

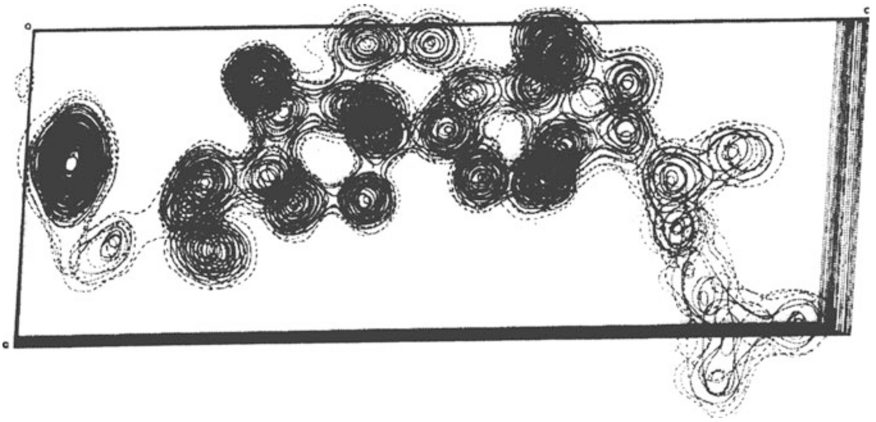

Fig. 1.7 Three-dimensional electron density contour map for euphenyl iodoacetate, as seen along the *b* direction of the unit cell; the contours connect points of equal electron density: the electron density contours have been drawn on a set of perspex sheets and stacked normal to *b*

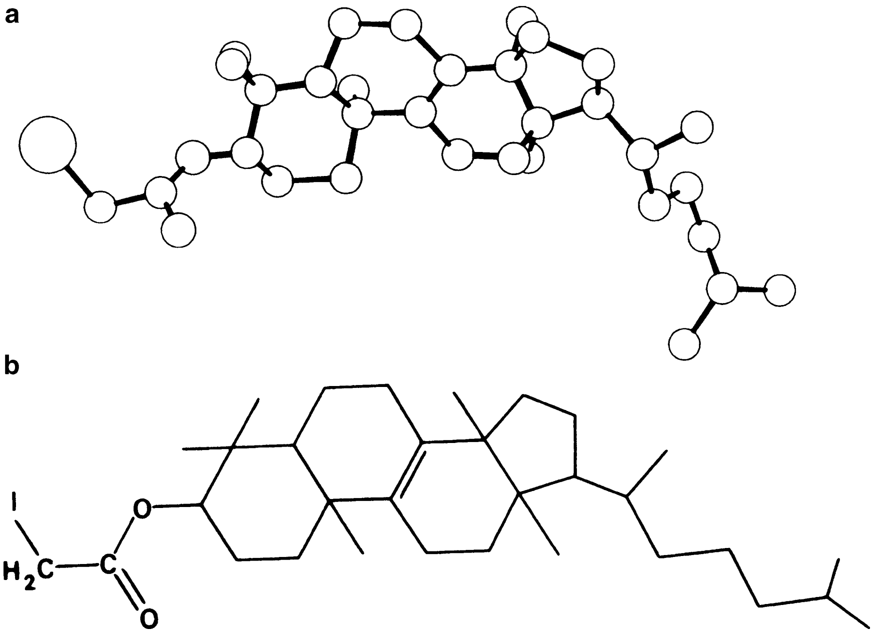

Fig. 1.8 Euphenyl iodoacetate, $C_{32}H_{53}O_2I$. (**a**) Molecular model, excluding hydrogen atoms. (**b**) Chemical structural formula: the orientations at carbon atoms 13, 14, and 17 are α, β, and α, respectively (standard numbering)

vibrations of the atoms are most severe in this portion of the molecule, and they have the effect of smearing out the electron density, so that its gradient, represented by the closeness of the contours, is less steep than in other parts of the molecule.

Molecules of much greater complexity than that in this example are now being investigated; the structures of proteins, enzymes, and nucleic acids—the "elements" of life itself—are being revealed by powerful X-ray diffraction techniques [25a].

1.2 The Crystalline State

A crystalline substance may be defined as a homogeneous solid having an ordered internal atomic arrangement[2] and a definite overall chemical composition, albeit non-stoichiometric in some examples. In addition to the more obvious manifestations of crystalline materials, like sugar and common salt, other substances, such as cellophane sheet and fibrous asbestos, which reveal different degrees of long-range order (extending over many atomic dimensions), may be described as crystalline.

With the unaided eye, fragments of glass and of quartz look similar to each other, yet quartz is crystalline and glass is non-crystalline, or *amorphous*. Glass has an atomic arrangement that displays only very short-range order (extending over a few atomic dimensions). Figure 1.9 illustrates the structures of quartz and silica glass; both of them are based on the same atomic group, the tetrahedral SiO_4 structural unit, but in quartz these groups are arranged regularly throughout three-dimensional space.

A crystal may be defined as a substance that is crystalline and periodic in three dimensions and bounded by plane faces. We have now made the useful distinction that crystalline substances exhibit long-range order in three dimensions or less, whereas crystals have both this three-dimensional regularity and plane bounding faces; see also Sect. 1.4.3.

1.2.1 Crystallographic Reference Axes

In describing the external features of crystals, we make use of relationships in coordinate geometry. It is important to set up a system of reference axes, and three such axes are needed in the description of a crystal, Fig. 1.10. By convention, the x, y, and z crystallographic reference axes are set parallel to important directions in the crystal. We shall see later that these directions (crystal edges, or possible crystal edges) are related closely to the symmetry of the crystal; in some cases, a choice of non-orthogonal axes then will arise naturally.

It is usual to work with right-handed axes. In Fig. 1.11, $+y$ and $+z$ are in the plane of the paper, as shown, and $+x$ is directed forward; the succession $+x \rightarrow +y \rightarrow +z$ simulates an anticlockwise screw motion, which is one way of describing right-handed axes. Notice the selection of the interaxial angles α, β, and γ and the mnemonic connection between their positions and the directions of the x, y, and z axes.

1.2.2 Equation of a Plane

The plane ABC shown in Fig. 1.12 intercepts the x, y, and z axes (which need not be orthogonal) at A, B, and C, respectively. ON is the perpendicular from the origin O to the plane; it has the length d, and its direction cosines (see Web Appendix WA1) are cos χ, cos Ψ, and cos ω with respect to OA, OB, and OC, respectively, which have the lengths a, b, and c, and P is any point X, Y, Z in the plane ABC. Let PK be parallel to OC and meet the plane AOB at K, and let KM be parallel to OB and meet OA at M. Then the lengths of OM, MK, and KP are X, Y, and Z, respectively. Since ON is the projection of OP on to ON, it is equal to the sum of the projections OM, MK, and KP all on to ON. Hence,

$$d = X\cos\chi + Y\cos\Psi + Z\cos\omega \tag{1.1}$$

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[2] See also Sect. 8.9.

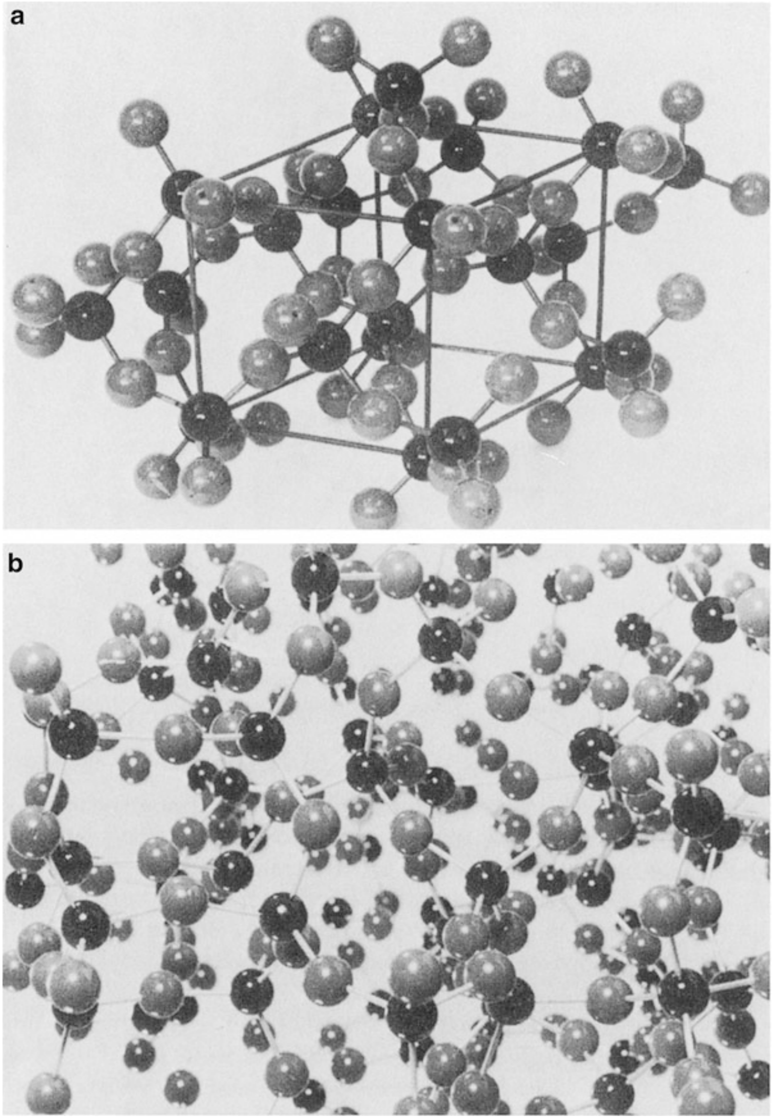

Fig. 1.9 Arrangements of SiO_4 structural units (the *darker spheres* represent Si). (**a**) α-Quartz. (**b**) Silica glass (reproduced by courtesy of NPL)

In ΔOAN, $d = OA \cos \chi = a \cos \chi$. Similarly, $d = b \cos \Psi = c \cos \omega$; dividing by d:

$$(X/a) + (Y/b) + (Z/c) = 1 \tag{1.2}$$

Equation (1.2) is the intercept form of the equation of the plane *ABC*.

1.2.3 Indices of Planes and the Law of Rational Intercepts

Miller Indices

The faces of a crystal are planes in three-dimensional space. Once the crystallographic axes are chosen, a parametral plane may be defined and any other plane described by reference to it in terms of three numbers *h*, *k*, and *l*. If the parametral plane is designated by integral values of *h*, *k*, and *l*,

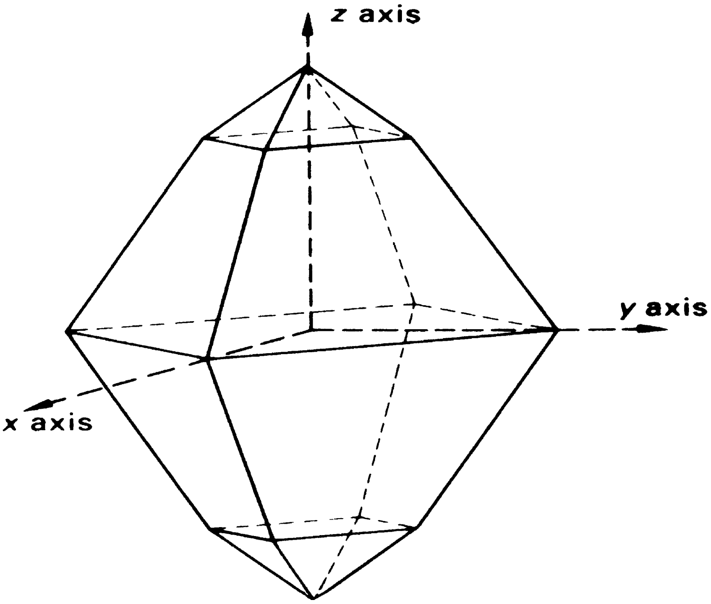

Fig. 1.10 Idealized tetragonal crystal with orthogonal (mutually perpendicular) axes x, y, and z drawn in

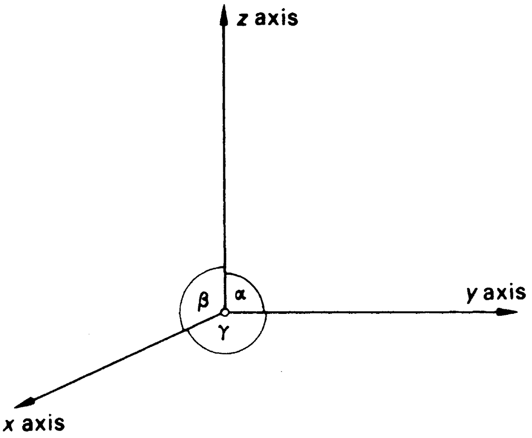

Fig. 1.11 Right-handed, general crystallographic axes x, y, and z, and the interaxial angles α, β, and γ

normally (111), then the indices of all other crystal faces are small integer values, rarely more than 5. This result is known as the *law of rational intercepts* (*indices*) (q.v.) and has a basis in lattice theory. A notation for describing the faces of a crystal was introduced first by William Whewell in 1825 and developed fully by Miller [17] in 1839, and h, k, and l are the Miller indices.

In Fig. 1.13, let the parametral plane (111) be ABC, making intercepts a, b, and c on the crystallographic axes x, y, and z, respectively. Another plane LMN makes corresponding intercepts of lengths a/h, b/k, and c/l. The Miller indices of plane LMN are expressed by the ratios of the intercepts of the parametral plane to those of the plane LMN. If in the figure, $a/h = a/4$, $b/k = b/3$, and $c/l = c/2$, then LMN is (432), see also Sect. 2.3. If fractions occur in formulating h, k, or l, they are

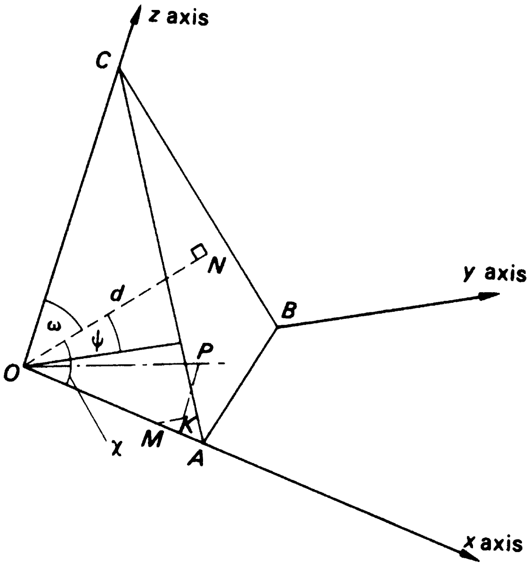

Fig. 1.12 Plane *ABC* in three-dimensional space; *ON*, of length *d*, is the normal to the plane from the origin *O*

cleared by multiplication throughout by the lowest common denominator. Conditions of parallelism to axes and intercepts on the negative sides of the axes lead respectively to zero or negative values for *h*, *k*, and *l*. Thus, *ABDE* is the plane (110), *BDFG* is (010), and *PBQ* is $(\bar{2}1\bar{3})$.[3] It may be noted that it has not been necessary to assign numerical values to either *a*, *b*, and *c* or α, β, and γ in order to describe the crystal faces by their Miller indices. In the next chapter, we shall identify *a*, *b*, and *c* with the edges of the crystal unit cell in a lattice, but this relationship is not needed at present.

The preferred choice of the parametral plane leads to small numerical values for the Miller indices of crystal faces. If *LMN* had been chosen as (111), then *ABC* would have been (346). Summarizing, we may say that the plane (*hkl*) makes intercepts a/h, b/k, and c/l along the crystallographic *x*, *y*, and *z* axes, respectively, where *a*, *b*, and *c* are the corresponding intercepts made by the parametral plane. The conventional choice of reference axes leads to special relationships between the intercepts *a*, *b*, *c*, and the (111) parametral plane, and between the interaxial angles α, β and γ, in all crystals other than triclinic (q.v.).

From (1.1) and (1.2), the intercept equation of the general plane (*hkl*) may be written as

$$(hX/a) + (kY/b) + (lZ/c) = 1 \tag{1.3}$$

The equation of the parallel plane passing through the origin is

$$(hX/a) + (kY/b) + (lZ/c) = 0 \tag{1.4}$$

it must satisfy the condition $X = Y = Z = 0$. It follows from (1.4) that the Miller indices of a crystal plane cannot be determined if the origin is chosen on that plane.

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[3] Read as "bar-two one bar-three," or "two-bar one three-bar" in the USA.

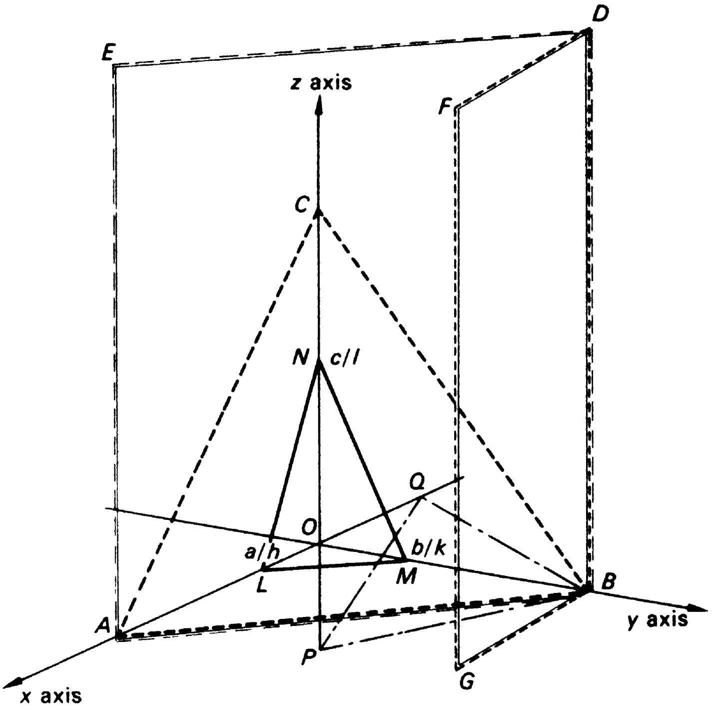


Fig. 1.13 Miller indices of planes: $OA = a, OB = b, OC = c$; ABC is the parametral plane (111), and LMN is the plane (hkl)

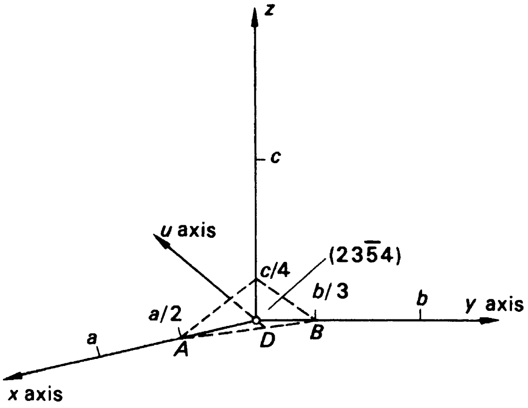


Fig. 1.14 Miller–Bravais indices ($hkil$). The crystallographic axes are labeled x, y, u, z, and the plane $(23\bar{5}4)$ is shown; the parametral plane is $(11\bar{2}1)$

Miller–Bravais Indices

In crystals that exhibit sixfold or threefold symmetry referred to hexagonal axes, see Table 1.3, four axes of reference may be used, an extension of the Miller indices due to Bravais [18]. The axes are designated x, y, u, and z; the x, y, and u axes lie in one plane, at 120° to one another, and the z axis is perpendicular to the x, y, u plane, Fig. 1.14; the sequence x, y, u, z is right-handed. Planes in these crystals are described by four numbers, the *Miller–Bravais* indices h, k, i, and l. The index i is not independent of h and k: thus, if the plane ABC in Fig. 1.14 intercepts the x and y axes at $a/2$ and $b/3$, for example, then the u axis is intercepted at $-u/5$. If also the z axis is intercepted at $c/4$, then the plane is designated $(23\bar{5}4)$. From Problem 1.14, we show that, in general, $i = -(h + k)$.

Law of Rational Intercepts

Planes that appear as external crystal faces are those most densely populated by the units of structure. Consider a P orthorhombic lattice, Fig. 2.4. The (010) planes are more densely populated in proportion to $1/ac$ than are the (110) planes at $1/(c\sqrt{a^2 + b^2})$ which, in turn, are more densely populated than, say, the (210) at $1/(c\sqrt{a^2 + 4b^2})$. The more densely populated planes are those of wider spacing in a given material: d is proportional to the reticular density or to 1/reticular area. The planes with the lower values of S^2, where $S^2 = h^2 + k^2 + l^2$, lead to the more stable (lower energy) crystal state. If we consider a cubic crystal, for example, then $d = a/(h^2 + k^2 + l^2)^{1/2} = a/S$, from Table 2.4, so that for the three cubic lattices, Fig. 2.4, we have:

P

hkl	100	110	111	210	211	221
S^2	1	2	3	5	6	9

Showing a preference for hexahedral {100} forms, as in caesium chloride or sodium chlorate.

I

hkl	110	200	211	310	420	442
S^2	2	4	6	10	20	36

Showing a preference for dodecahedral {110} forms, as in garnet structures.

F

hkl	111	200	220	310	420	422
S^2	3	4	8	10	20	246

Showing a preference for octahedral {111} forms, as in diamond and calcium fluoride. Thus, on grounds of stability, planes of larger d-values (smaller values of h, k, and l) are to be expected.

1.2.4 Axial Ratios

If both sides of (1.4) are multiplied by b, we obtain

$$\frac{hX}{a/b} + kY + \frac{lZ}{c/b} = 0 \tag{1.5}$$

The quantities a/b and c/b are termed *axial ratios*; they can be deduced from an analysis of the crystal morphology, but not the individual values of a, b, or c.

1.2.5 Zones

Most well formed crystals have their faces arranged in groups of two or more with respect to certain directions in the crystal. In other words, crystals exhibit symmetry; this feature is an external manifestation of the ordered arrangement of atoms in the crystal. Figure 1.15 illustrates zircon,

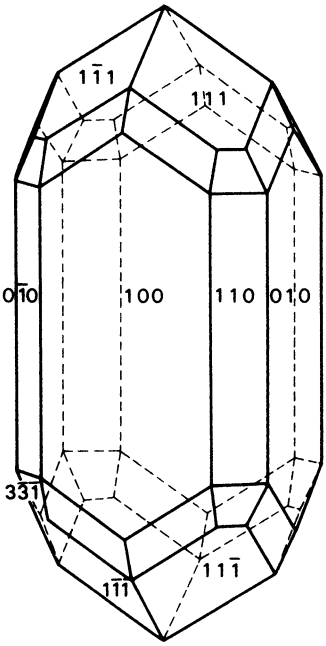


Fig. 1.15 A highly symmetric crystal (zircon, $ZrSiO_4$), showing the Miller indices of some of its faces. What are the Miller indices of the other faces on this crystal?

$ZrSiO_4$, an example of a highly symmetric crystal. It is evident that several faces have a given direction in common. Such faces are said to lie in a *zone*, and the common direction is called a *zone axis*. Any two faces, $(h_1k_1l_1)$ and $(h_2k_2l_2)$, define a zone. The zone axis is the line of intersection of the two planes and is given by the solution of the equations

$$\begin{aligned}(h_1X/a) + (k_1Y/b) + (l_1Z/c) &= 0\\(h_2X/a) + (k_2Y/b) + (l_2Z/c) &= 0\end{aligned} \tag{1.6}$$

for the two planes passing through the origin (since we are concerned here only with the directionality). The solution is given by the line

$$\frac{X}{a(k_1l_2 - k_2l_1)} = \frac{Y}{b(l_1h_2 - l_2h_1)} = \frac{Z}{c(h_1k_2 - h_2k_1)} \tag{1.7}$$

which must also pass through the origin. It may be written as

$$X/(aU) = Y/(bV) = Z/(cW) \tag{1.8}$$

where $[UVW]$ is called the *zone symbol*.

If any other face (hkl) lies in the same zone as that defined by $(h_1k_1l_1)$ and $(h_2k_2l_2)$, then it follows from immediately from (1.4) and (1.8), that

$$hU + kV + lW = 0 \tag{1.9}$$

which is an expression of the *Weiss zone law* [13]. For if planes $(h_1k_1l_1)$, $(h_2k_2l_2)$, and (hkl) lie in one and the same zone (*tautozonal*), then applying (1.6) to (hkl) and using (1.8) in the result leads to (1.9). We shall show this result in another way in Sect. 2.5.4.

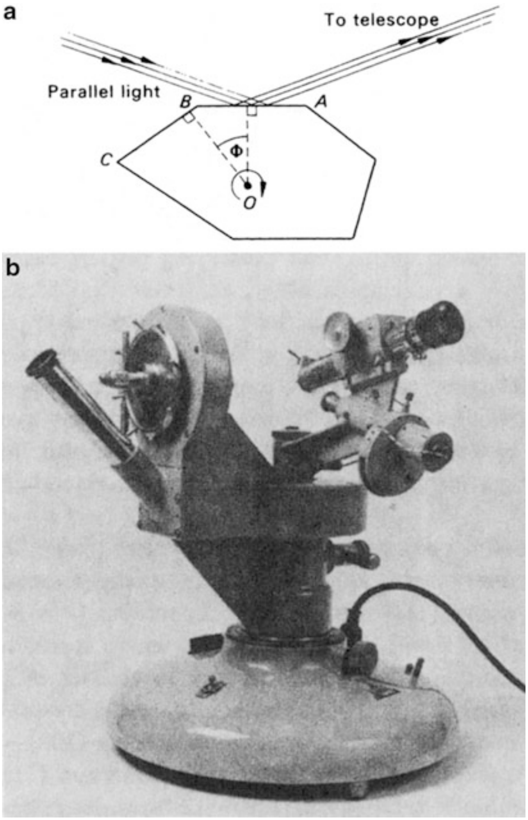


Fig. 1.16 Optical goniometry. (**a**) Principle of the reflecting goniometer; *AB* and *BC* represent two adjacent tautozonal faces on the crystal. (**b**) Two-circle optical goniometer; the crystal rotates about the vertical circle (the zone axis through *O*), and the telescope and collimator rotate about the horizontal circle

In the zircon crystal, the vertical (prism) faces lie in one zone. If the prism faces are indexed in the usual manner, as in Fig. 1.15, then, from (1.7) and (1.8), the corresponding zone symbol is [001]. The symbols [*UVW*] and $[\bar{U}\,\bar{V}\,\bar{W}]$ refer to lines that are collinear, but of opposite sense. From (1.9), we see that (110) and (100) are faces in the [001] zone, but (111) is not. Other relationships follow from (1.9) in a similar way. In the manipulation of these equations, it may be noted that a zone axis is described by [*UVW*], the simplest symbol; the axes that may be described as [*nU*, *nV*, *nW*] ($n = 0, \pm1, \pm2, \ldots$) are coincident with [*UVW*] in crystal morphology. From (1.6), a zone symbol cannot be determined from two faces (*hkl*) and $(\bar{h}\,\bar{k}\,\bar{l})$. Thus, although both the (110) and $(\bar{1}\bar{1}0)$ planes lie in the [001] zone, this zone symbol could not be determined from these two planes alone.

Angle Between Two Directions (Zone Axes)

The angle θ between two directions [*UVW*] and $[U'V'W']$ is given by

$$\theta = \frac{\mathbf{r}_{[UVW]} \cdot \mathbf{r}_{[U'V'W']}}{r_{[UVW]}\, r_{[U'V'W']}} \tag{1.10}$$

the evaluation of which follows from (2.16).

Constancy of Interfacial Angles

The *law of constant interfacial angles* states that in all crystals of the same substance, angles between corresponding faces have a constant value. Interfacial angles may be measured by a *goniometer*, the first of which was that developed by Carangeot [11], as we noted earlier.

The principle of the more precise reflecting goniometer is shown in Fig. 1.16a, which forms the basis of modern optical goniometry. A crystal is arranged to rotate about a zone axis *O*, which is set perpendicular to a plane containing the incident and crystal-reflected light beams. Parallel light reflected from the face *AB* is received by a telescope. If the crystal is rotated in a clockwise direction, a reflection from the face *BC* is received next when the crystal has been turned through the angle Φ; then, the interfacial angle is $180 - \Phi^\circ$. Accurate goniometry brought a quantitative significance to observable angular relationships in crystals. Figure 1.16b illustrates a simple two-circle optical goniometer.

1.3 Stereographic Projection: Brief Survey

A representation of the many faces of a crystal by means of a convenient two-dimensional illustration may be achieved by means of a *stereographic projection*, or *stereogram*. Figure 1.17 shows a cubic crystal set within a sphere of arbitrary radius, with the normals to the sets of crystal faces drawn to intersect the sphere. Lines are drawn from the intersections with the sphere to meet the horizontal plane, or *primitive*, which becomes the plane of projection. An intersection from the upper hemisphere on to the horizontal plane, a *pole*, is marked as ● and that from the lower hemisphere as ○; where the two coincide the notation used is the dot inside the circle. Thus, we obtain Fig. 1.18, which may be indexed for the given crystal as shown in Fig. 1.19. Later in this chapter, we shall introduce a modification for the notation of points on a stereogram, for reasons that will be there described.

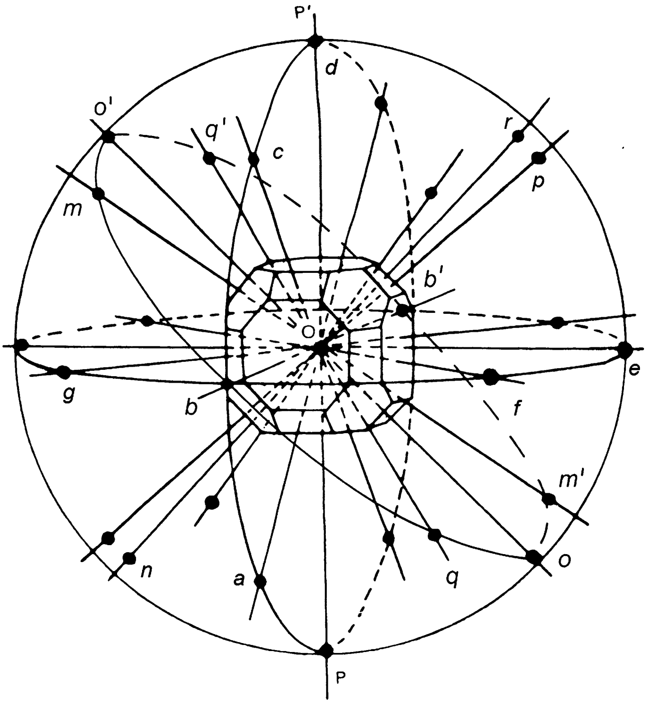


Fig. 1.17 Spherical projection of the cubic crystal showing three forms of planes: *cube*—faces *b*, *e*, *d*, and parallel faces; *octahedron*—faces *r*, *m*, *n*, *q*, and parallel faces; *rhombic dodecahedron*—faces *f*, *g*, *p*, *o*, *c*, *a*, and parallel faces. The *x*, *y*, and *z* axes are chosen parallel to important (symmetry) directions in the crystal; the radius of the sphere is arbitrary. The inclined great circle, *b*, *m*, *o*′, *q*′,. . ., projects as G_3G_3' in Fig. 1.18

Fig. 1.18 Stereogram of the crystal shown in Fig. 1.17; the zone circle (great circle) G_1G_1', symbol [101], passes through e, q, a, n, e', q', a', n'; the zone circle G_2G_2' symbol [1$\bar{1}$0], passes through f, r, d, q', f', r', d', q; the zone circle G_3G_3', symbol [011], passes through b, m, o', q', b', m', o, q

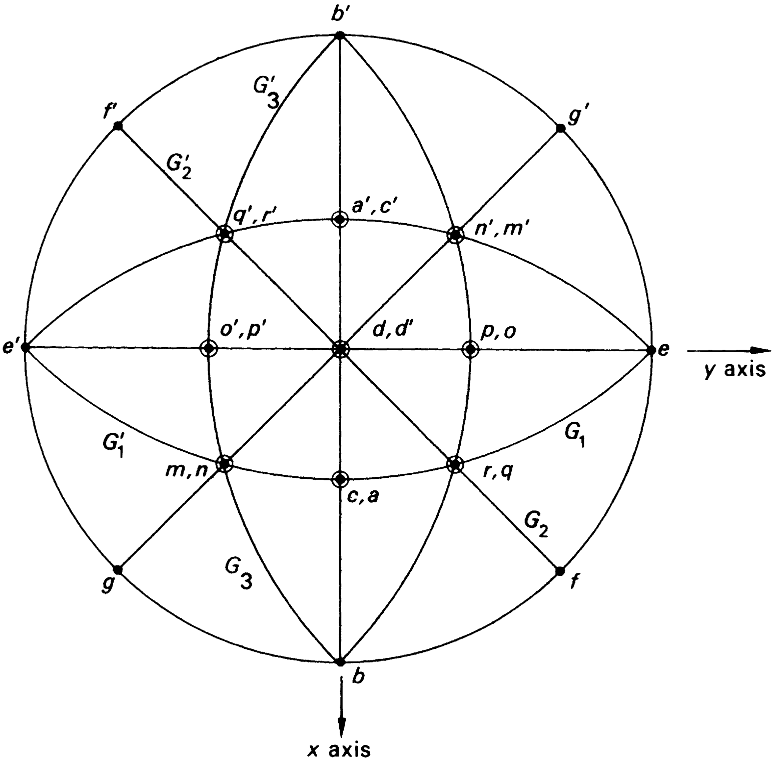
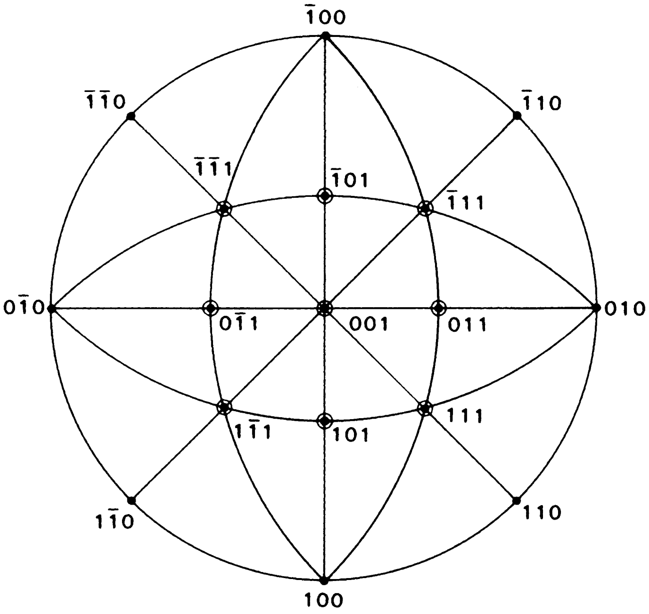


Fig. 1.19 Stereogram in Fig. 1.18 indexed, taking r as 111. The zone containing (100) and (111) is [0$\bar{1}$1], and that containing (010) and (001) is [100]. From (1.7), (1.8), and (1.9), it follows that the face p common to these two zones is (011)



The important feature of the stereogram for our purposes is that it preserves the interfacial angles of the crystal and, hence, displays faithfully the crystal symmetry. A more detailed description of the stereographic projection may be found in the Web Appendix WA2.

1.4 External Symmetry of Crystals

The existence of faces on a crystal in groups of two or more, in a similar orientation with respect to some line or plane in the crystal, is a manifestation of symmetry. The crystal drawing of zircon in Fig. 1.15 shows several sets of symmetrically arranged faces.

Few of us have difficulty in recognizing symmetry in two-dimensional pictures of objects such as a dumbbell, the three-legged emblem of the Isle of Man, a Maltese cross, the five-petal Tudor rose, the six-pointed Star of David; see Problem 1.10(c). But it is a rather different matter when we are dealing with three-dimensional objects.

The problem arises first from the fact that we can see all parts of a two-dimensional object simultaneously, and thus we take in the relation of the parts to the whole; but we cannot do that so easily with three-dimensional objects. Secondly, while some three-dimensional objects, such as flowers, pencils, and architectural columns, are simple enough for us to visualize and to rotate in our mind's eye, few of us have a natural gift for mentally perceiving and manipulating more complex three-dimensional objects. Nevertheless, the art of doing so can be developed with suitable aids and patience. If, initially, you have problems, take heart. You are not alone and, like many before you, you will be surprised at how swiftly the required facility can be acquired. Engineers, architects, and sculptors may be blessed with a natural three-dimensional visualization aptitude, but they have learned to develop it—particularly by making and handling models.

Standard practice in the past was to reduce three-dimensional objects to one or more two-dimensional drawings (projections and elevations): it was cheap, well suited to reproduction in books, and less cumbersome than handling three-dimensional models. In this book, we shall continue to use such two-dimensional representations where appropriate, but to rely on them exclusively only delays the acquisition of a three-dimensional visualization ability. Fortunately, we can now use stereoscopic image pairs, such as that shown in Fig. 1.6. These illustrations are a great help, but, because they provide a view from only one standpoint, they are not always quite the equal of models that can be examined by hand.

Symmetry

Symmetry may be defined as *that spatial property of a body* (*or pattern*) *by which the body* (*or pattern*) *can be brought from an initial state to another indistinguishable state by means of a certain operation—a symmetry operation*. For our purposes, the operation will be considered to take place in n-dimensional space ($n = 1, 2,$ or 3) and to represent an action with respect to a symmetry element.

Symmetry Elements and Symmetry Operations

A *symmetry element* is a geometrical entity (point, line, or plane) in a body or assemblage, with which is associated an appropriate symmetry operation. The symmetry element is strictly conceptual, but it is convenient to accord it a sense of reality. The symmetry element connects all parts of the body or assemblage as a number of symmetrically related parts. The term *assemblage* is often useful because it describes more obviously a bundle of radiating face normals, Fig. 1.17, or a number of bonds emanating from a central atom in the case of a molecule or ion, Fig. 1.34, to which these symmetry concepts equally apply.

The *symmetry operation* corresponding to a symmetry element, when applied to a body, converts it to a state that is indistinguishable from the initial state of that body, and thus the operation *reveals*

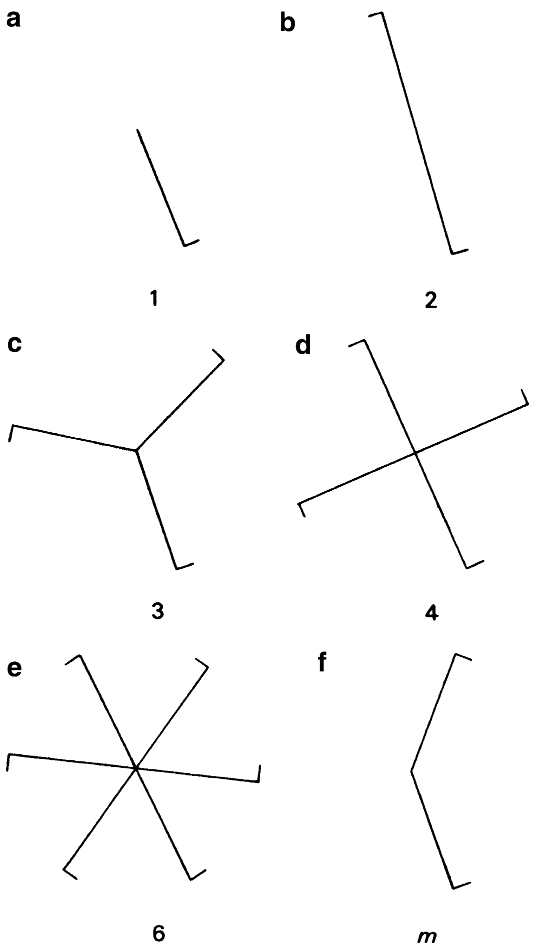


Fig. 1.20 Some two-dimensional objects and their point-group symbols. The motifs are built up from the asymmetric unit (**a**), by operating on it according to the point-group symmetry. Note that, except in (**a**), the symmetry element intersects the asymmetric unit and lies at the center of each figure

the symmetry inherent in the body. In many cases, different symmetry operations can reveal one and the same symmetry element. Thus, 3^1 (=3), 3^2, and 3^3 (=3) may be regarded as either multiple steps of 3, a threefold operation (q.v.), or single-step operations in their own, but all are contained within the same single symmetry element, 3. The latter idea is of particular importance in the study of group theory. Symmetry elements may occur singly in a body, as in Fig. 1.20, for example, or in certain combinations, as in the example of Fig. 1.22.

Point Groups

A set of interacting symmetry operations in a finite body, or just one such element, is referred to as a *point group*. A point group may be defined as *a set of symmetry operations the action of which leaves at least one point unmoved*: this point is taken as the origin of the reference axes for the body, through which all symmetry elements pass. The assembly of points defining a rotation axis or a mirror plane is effectively unmoved by their operations.

It can be contended that, in real objects, since they are imperfect, even if only on a microscopic scale, an indistinguishable second state can be obtained only by a rotation of 360° (or 0°); this operation is *identity*, or “doing nothing.” For practical purposes, however, the effects of most

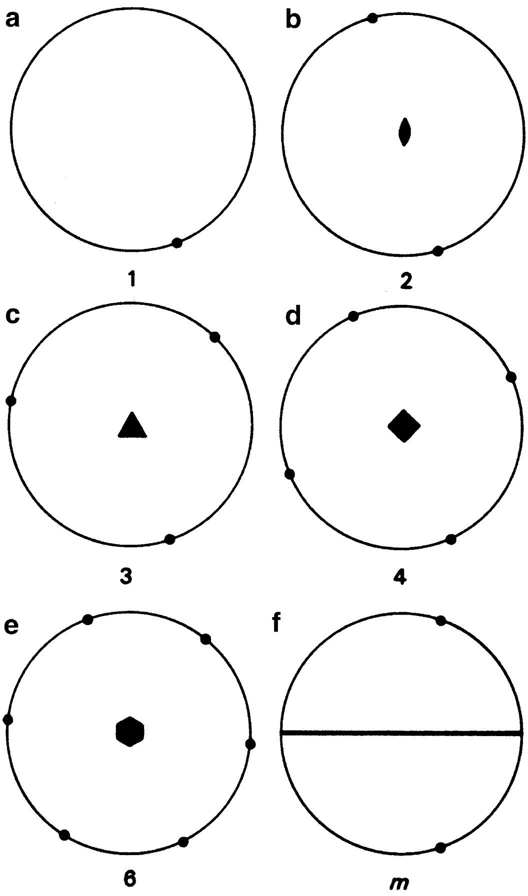


Fig. 1.21 Stereograms of the point groups of the objects in Fig. 1.20; the conventional graphic symbols for R ($R = 1$, 2, 3, 4, 6) and m are shown

imperfections are small, and although our discussion of symmetry will be set up in terms of ideal geometrical objects, the extension of the results to real situations is scientifically rewarding.

The observable symmetry may depend upon the nature of the examining probe, and different results for a given material may arise in terms of its optical, magnetic, and photoelastic properties, and from neutron diffraction, Sect. 11.1. Here, we shall be concerned with the symmetry shown by *directions in space*, such as the normals to the faces on crystals, or the bond directions in chemical species. Such angular relationships can be presented conveniently on stereograms, Sect. 1.3, and we shall draw fully on this method of representation in the ensuing discussion.

Several concepts in symmetry can be introduced conveniently with two-dimensional objects; subsequently, the third dimension can be introduced mainly as a geometrical extension of the two-dimensional ideas. There is a single one-dimensional point group; it is more difficult to grasp conceptually, and we shall not be particularly concerned with it in this book.

1.4.1 Two-Dimensional Point Groups

"We proceeded straight from plane geometry to solid bodies in motion without considering solid bodies first on their own. The right thing is to proceed from second dimension to third, which brings us

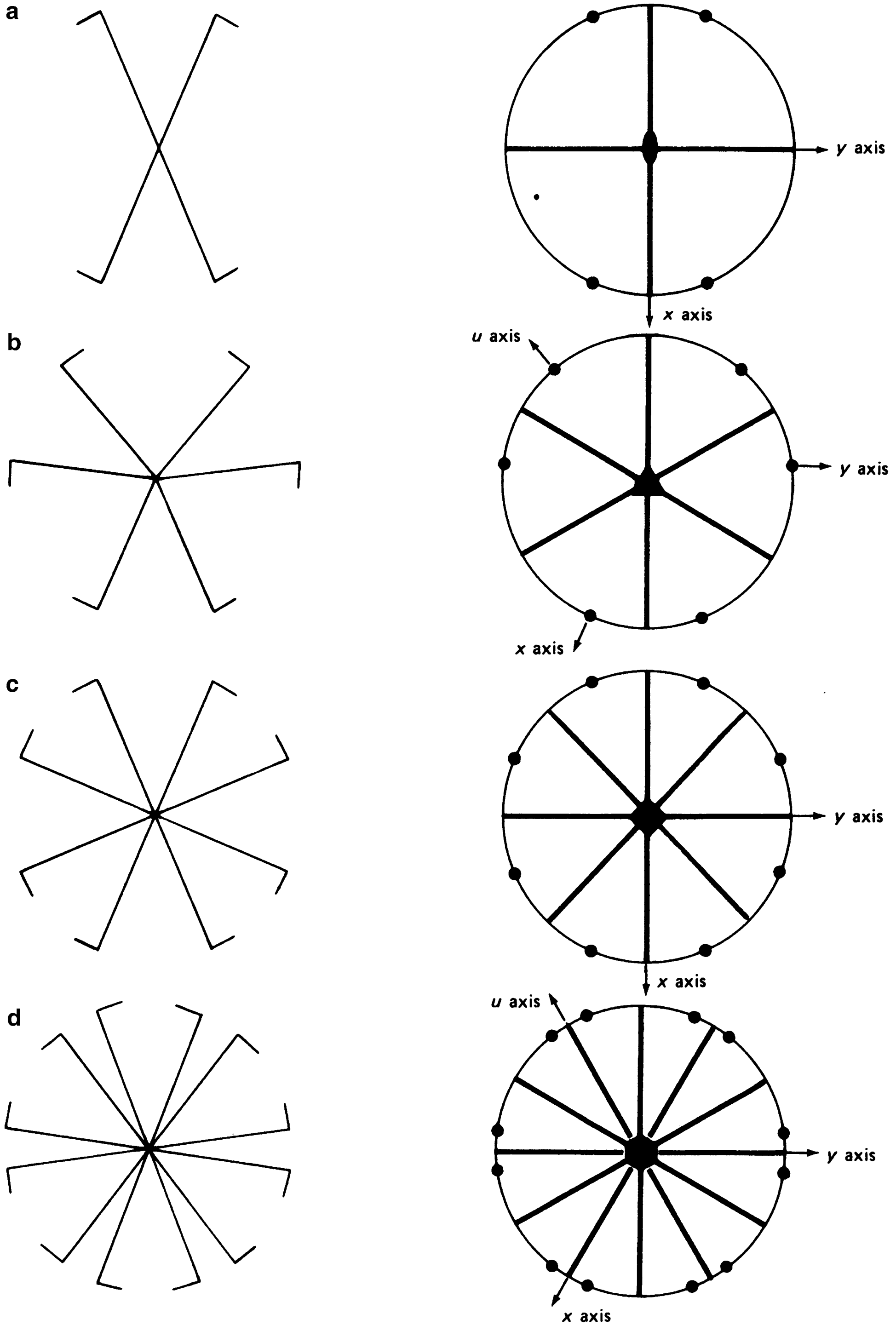


Fig. 1.22 Further two-dimensional objects with their stereograms and point groups. (**a**) 2*mm*. (**b**) 3*m*. (**c**) 4*mm*. (**d**) 6*mm*

Table 1.1 Two-dimensional point groups and notation

		Symbol meaning, appropriate to position occupied		
System	Point groups	First position	Second position	Third position
Oblique	1, 2	Rotation about a point	–	–
Rectangular	$1m$[a]	As above	$m \perp x$	–
	$2mm$	As above	$m \perp x$	$m \perp y$
Square		As above	–	–
	$4mm$	As above	$m \perp x, y$	m at 45° to x, y
Hexagonal	3	As above	–	–
	$3m$	As above	$m \perp x, y, u$	–
	6	As above	–	–
	$6mm$	As above	$m \perp x, y, u$	m at 30° to x, y, u

[a] Usually written as m, but the full symbol is given here in order to clarify the positions of the symmetry elements in the symbol

to cubes and other three-dimensional figures" [26]. If we examine the two-dimensional objects in Fig. 1.20, we can discover two types of symmetry elements that can bring an object from one state to another indistinguishable state: parts (a) to (e) of Fig. 1.20 depict rotational symmetry, whereas (f) shows reflection symmetry.

Rotation Symmetry

A two-dimensional object possesses rotational symmetry of degree R (or R-fold symmetry) about a *point* if it can be brought from one state to another indistinguishable state by each and every rotation of $(360/R)°$ about that symmetry point. Figure 1.20a–e illustrate the rotational symmetry elements R equal to 1, 2, 3, 4, and 6, respectively. The onefold element is the identity element and is crystallographically trivial; every object has onefold symmetry.

Reflection Symmetry

A two-dimensional object possesses reflection symmetry, symbol m, if it can be brought from one state to another indistinguishable state by reflection across the symmetry *line*. The operation is not one that we can perform physically with an object, unlike rotation, but we can appreciate from the object itself (and its stereogram) that m symmetry is present. The m line divides the figure into its *asymmetric unit*,  , and a mirror image or enantiomorph of this unit, , which situation (left-hand–right-hand relationship) is characteristic of reflection symmetry, Fig. 1.20f.

Each of the objects in Fig. 1.20 has a symmetry pattern that can be described by a two-dimensional point group, and it is convenient to illustrate these point groups by stereograms. Figure 1.21 shows stereograms for the two-dimensional point groups 1, 2, 3, 4, 6, and m. It should be noted that in using stereogram-like drawings to illustrate *two-dimensional* symmetry, the representative points (poles) must fall on the perimeter; such situations may represent special forms (q.v.) on the stereograms of three-dimensional objects.

Combinations of R and m lead to four more point groups; they are illustrated in Fig. 1.22. We have deliberately omitted point groups in which $R = 5$ and $R \geq 7$, for a reason that will be discussed in Chap. 2.

It is convenient to allocate the ten two- dimensional point groups to two-dimensional *systems* and to choose reference axes for the objects in close relation to the directions of their symmetry elements. Table 1.1 lists these systems, together with the meanings of the positions in the point-group symbols. It should be noted that combinations of m with R ($R > 2$) introduce additional reflection lines of a different crystallographic form. In the case of $3m$, however, these additional m lines are coincident with the first set; the symbol $3mm$ is not meaningful.

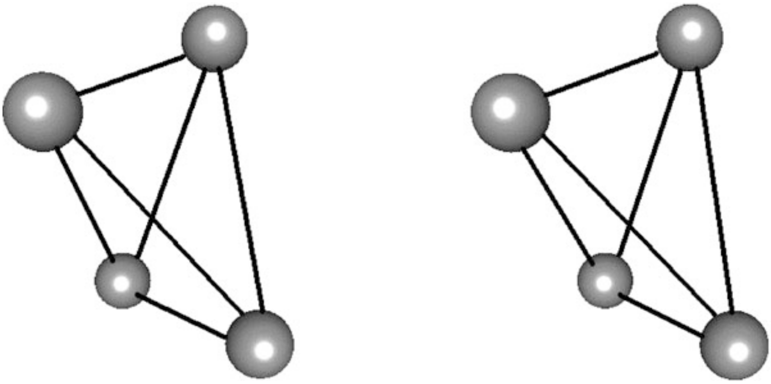


Fig. 1.23 Stereoview of a hypothetical C_4 molecule; the $\bar{4}$ axis is in the vertical direction

It is important to remember the relative orientations of the symmetry elements in the point groups and the variations in the meanings of the positions in the different systems. In the two-dimensional hexagonal system, three axes may be chosen in the x, y plane; this selection corresponds with the use of Miller–Bravais indices in three dimensions.

1.4.2 Three-Dimensional Point Groups

The symmetry elements encountered in three dimensions are rotation axes (R), inversion axes ($\overline{R}$), and a reflection (mirror) plane (m). A *center of symmetry* can be present also, although this symmetry element may be included in a point group that contains the element $\overline{R}$, as we shall see, and a check for this must be made.

The operations of rotation and reflection are similar to those in two dimensions, except that the geometric extensions of the operations are now increased to rotation about a *line* and reflection across a *plane*, respectively.

Inversion Axes

An object is said to possess an inversion (strictly, roto-inversion) axis[4] $\overline{R}$ if it can be brought from one state to another indistinguishable state by the combined actions of rotation by $(360/R)^\circ$ about the axis and inversion through a point on the axis that also serves as the origin point; the two actions comprise a *single* symmetry operation. Like mirror symmetry, Sect. 1.4.1, the inversion axis is a physically non-performable symmetry operation on a model, but it may be represented conveniently on a stereogram. It is a little more difficult to envisage this operation than those of rotation and reflection. Figure 1.23 illustrates a hypothetical molecule having a vertical $\bar{4}$ axis: the stereoscopic effect can be created by using a stereoviewer (see Appendix A for instructions for making a model with $\bar{4}$ symmetry). In crystals, R in $\overline{R}$, can take only the values 1, 2, 3, 4, and 6; this is sometimes referred to as the *crystallograpic restriction theorem*. A simple explanation for this restriction is that only figures that are based on these rotational symmetries can be stacked together to fill space completely in a periodic manner, as Fig. 1.27 shows; see also Sect. 1.4.3. A further discussion of these restrictions on R is given in Sect. 2.6.

In pictorial representations of the three-dimensional point groups, it is helpful to indicate the third dimension on their stereograms and, in addition, to illustrate the change-of-hand relationship that

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[4] Read as "bar-R", or "R-bar" in the United States.

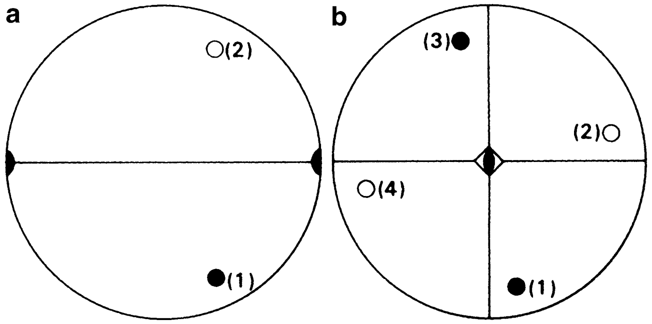

Fig. 1.24 Stereograms of general forms. (**a**) Point group 2 (axis horizontal and in the plane of the stereogram). (**b**) Point group $\bar{4}$ (axis normal to the plane of the stereogram). In (**a**), the point ● is rotated through 180° to O: (1) and (2). In (**b**), the point ● is rotated through 90° and then inverted through the origin to O; this combined operation generates, in all, four symmetry-equivalent points: (1) → (4) → (3) → (2)

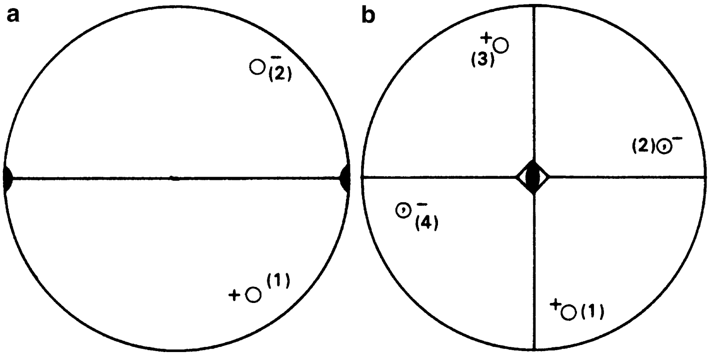

Fig. 1.25 (**a**) Stereograms from Fig. 1.24 in the revised notation: the different natures of points (2) in (**a**) and (2) and (4) in (**b**), all with respect to point (1), are now clear

occurs with $\overline{R}$ (including *m*) symmetry operations. For example, referring to Fig. 1.24, the element 2 lying in the plane of projection and the element $\bar{4}$ normal to the plane of projection, when acting on a point derived from the upper hemisphere (symbol ●), both move the point into the lower hemisphere region (symbol O). Both operations involve a reversal of the sign of the vertical coordinate, but only $\bar{4}$ involves also a change of hand, and this distinction is not clear from the conventional stereogram notation. Consequently, we shall adopt a symbolism, shown in Fig. 1.25, that is common to three-dimensional space groups, and which will affect the necessary distinction.

With the modified notation, a representative point in the upper, *l*-positive hemisphere will now be shown by O$^+$, signifying, for example, the face (hkl), or its pole. A change of hemisphere to $(hk\bar{l})$ will be indicated by O$^-$, and a change-of-hand on reflection or inversion by ⊙+ or ⊙− Fig. 1.25. This notation may appear to nullify partially the purpose of a stereogram. However, although the stereogram is a two-dimensional diagram, it is helpful here to convey a three-dimensional impression clearly, and this notation is used as an aid to this end.

Figure 1.26a shows a stereogram for point group *m*. The inverse diad ($\bar{2}$) is lying normal to the *m* plane. A consideration of the two operations in the given relative orientations shows that they produce equivalent actions. It is conventional to use the symbol *m* for this operation, although sometimes it is helpful to employ the symbol $\bar{2}$ instead; potassium tetrathionate, Fig. 1.26b, crystallizes in point group *m*.

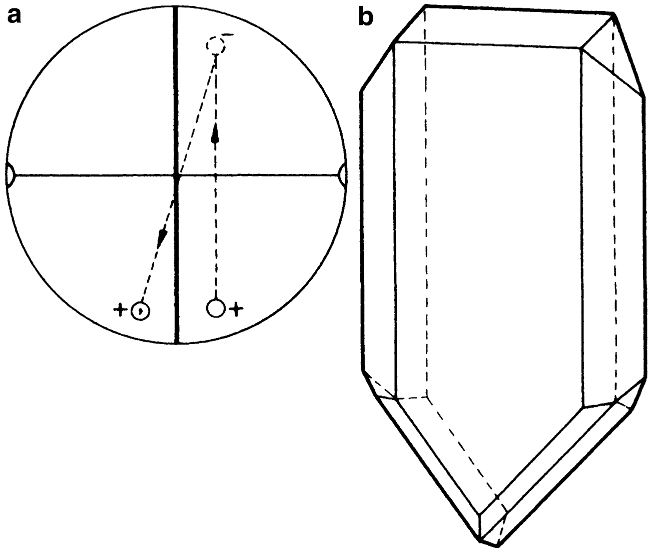

Fig. 1.26 Point group m. (**a**) Stereogram showing equivalence of m and $\bar{2}$ (the graphic symbol ◖ used here for $\bar{2}$ is useful, albeit not conventional). (**b**) Crystal of potassium tetrathionate ($K_2S_4O_6$), point group m

We shall not be concerned here to derive the crystallographic point groups—and there are several ways in which it can be done[5]—but to give, instead, a scheme which allows them to be worked through simply and adequately for present purposes. In addition, the program EULR, Sect. 13.2, shows how the combinations of symmetry operations based on R and $\overline{R}$ ($R = 1, 2, 3, 4$ and 6) lead *inter alia* to the 32 crystallographic point groups. The symbols for rotation and reflection symmetry in three dimensions are similar to those already discussed; certain additional symbols are now required, and Table 1.2 lists them all.

Crystal Classes

There are 32 crystal classes that describe the possible types of crystals that occur. Each class has a name that corresponds to the *general form* on the crystal, and each class is characterized by a point group. A crystal form is the set $\{hkl\}$ of faces (hkl) related by the point group of the crystal: if it is "general" then none of the (hkl) faces lies on symmetry elements; if it is a *special form*, then the faces of the set lie on symmetry elements.

Two crystal classes were illustrated in Fig. 1.4: the rhombic disphenoid class (a) belongs to the orthorhombic system (to be discussed next) and shows point group 222; it has four similar scalene triangle faces and can exist in enantiomorphic forms. An example is Mozartite, $CaMn(SiO_4)(OH)$, which was first noted in 1991, the 200th anniversary of the death of Mozart. Another, less exotic, example is Epsomite, $MgSO_4{\cdot}7H_2O$. The hexakisoctohedron (cl. Gk. *hexakis*—six times; aka hexoctahedron) of class (b) belongs to the cubic system with point group $m3m$ and is exhibited by some specimens of native silver; each face is a regular octahedron sub-divided into six equal triangular faces.

Crystal Systems and Point-Group Scheme

Crystals are grouped into seven *systems* according to the *characteristic* symmetry listed in Table 1.3. The characteristic symmetry refers to that minimum necessary for classification of a crystal in a given system; a crystal of a given system may contain more than its characteristic symmetry.

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[5] See Bibliography (Ladd 1989).

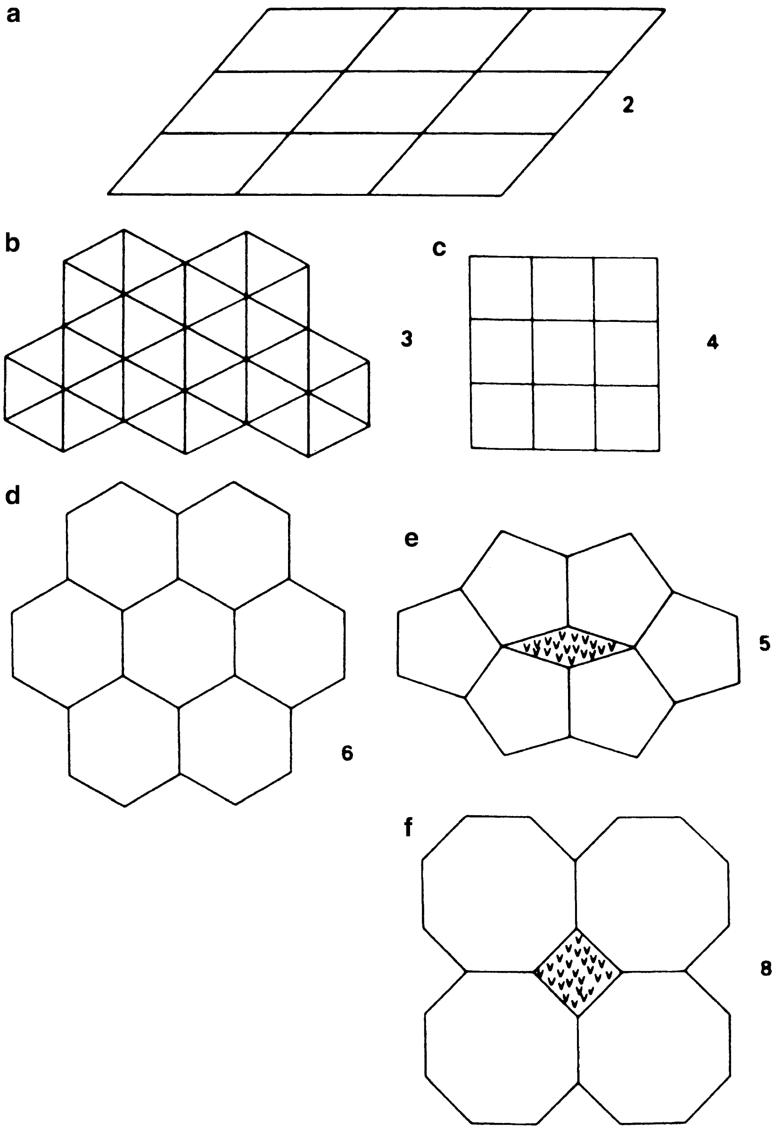

Fig. 1.27 Sections of three-dimensional figures and the rotational symmetries of their smallest structural units; (**a**–**d**) Space-filling patterns. In (**e**) and (**f**) the *v-marks* represent voids in the pattern (see also Problem 1.10a)

Table 1.2 Three-dimensional symmetry symbols

Symbol	Name	Action for indistinguishability	Graphic symbol
1	Monad	360° (0°) rotation; identity	None
2	Diad	180° rotation	⬮ ⊥ projection, ⬮ ∥ projection
3	Triad	120° rotation	▲ ⊥ or inclined to projection
4	Tetrad	90° rotation	◆ ⊥ projection, ▮ ∥ projection
6	Hexad	60° rotation	⬢ ⊥ projection
$\bar{1}$	Inverse monad	Inversion[a]	o
$\bar{3}$	Inverse triad	120° rotation + inversion	△ ⊥ or inclined to projection
$\bar{4}$	Inverse tetrad	90° rotation + inversion	◈ ⊥ projection, ▯ ∥ projection
$\bar{6}$	Inverse hexad	60° rotation + inversion	⬡ ⊥ projection
m	Mirror plane[b]	Reflection across plane	▬ ⊥ projection, (∥ projection

[a] $\bar{R}$ is equivalent to R plus $\bar{1}$ only where R is an odd number: $\bar{1}$ represents the center of symmetry, but $\bar{2}$, $\bar{4}$, and $\bar{6}$ are not centrosymmetric point groups. For R even, $R + \bar{1} \equiv R/m$

[b] The symmetry elements m and $\bar{2}$ produce an equivalent operation, with $\bar{2}$ oriented perpendicularly to the mirror plane

Table 1.3 Crystal systems and their characteristics

System	Characteristic symmetry axes, with their orientation	Parametral plane intercepts and interaxial angles, assuming the simplest indexing of faces[a,b]
Triclinic	None	$a \not\subset b \not\subset c$; $\alpha \not\subset \beta \not\subset \gamma \not\subset 90°, 120°$
Monoclinic	One 2 or $\bar{2}$ axis[c] along y	$a \not\subset b \not\subset c$; $\alpha = \gamma = 90°$; $\beta \not\subset 90°, 120°$
Orthorhombic	Three mutually perpendicular 2 or $\bar{2}$ axes along x, y, and z	$a \not\subset b \not\subset c$; $\alpha = \beta = \gamma = 90°$
Tetragonal	One 4 or $\bar{4}$ axis along z	$a = b \not\subset c$; $\alpha = \beta = \gamma = 90°$
Trigonal[d] Hexagonal	One 3 axis along z One 6 or $\bar{6}$ axis along z	$a = b \not\subset c$; $\alpha = \beta = 90°$; $\gamma = 120°$
Cubic	Four 3 axes inclined at 54.74° ($\cos^{-1} 1/\sqrt{3}$) to x, y, and z	$a = b = c$; $\alpha = \beta = \gamma = 90°$

[a] We shall see in Chap. 2 that the same relationships apply to conventional unit cells in lattices

[b] The special symbol $\not\subset$ should be read as "not constrained by symmetry to equal"

[c] It must be remembered that $\bar{2}$ is equivalent to an m plane normal to the $\bar{2}$ axis

[d] For convenience, the trigonal system is referred to hexagonal axes (but see also Table 1.5)

Table 1.4 Crystallographic point-group scheme[a]

Type	Triclinic	Monoclinic	Trigonal	Tetragonal	Hexagonal	Cubic[b]
R	1	2	3	4	6	23
$\bar{R}$	$\bar{1}$	m	$\bar{3}$	$\bar{4}$	$\bar{6}$	$m\bar{3}$
R + center	—	$2/m$	—	$4/m$	$6/m$	—
		Orthorhombic				
$R2$		222	32	422	622	432
Rm		$mm2$	$3m$	$4mm$	$6mm$	
$\bar{R}m$		—	$\bar{3}m$	$\bar{4}2m$	$\bar{6}m2$	$\bar{4}3m$
$R2$ + center		mmm	—	$\frac{4}{m}mm$	$\frac{6}{m}mm$	$m\bar{3}m$

[a] The reader should consider the implications of the spaces (marked —) in this table

[b] The cubic system is characterized by its four threefold axes; R refers here to the element 2, $\bar{2}$, 4 or $\bar{4}$, but 3 is always present along ⟨111⟩

A crystallographic point-group scheme is given in Table 1.4, under the seven crystal systems as headings. The main difficulty *in understanding point groups lies not so much in knowing the action of the individual symmetry elements, but in appreciating both the relative orientation of the different elements in a point-group symbol and the fact that this orientation changes among the crystal systems according to the principal symmetry axis, that is, the rotation axis R of highest degree*. These orientations need to be learned: they form the key to point-group and space-group studies.

Table 1.5 lists the meanings of the three positions in the three-dimensional point-group symbols. Tables 1.4 and 1.5 should be studied carefully in conjunction with Fig. 1.32. For example, consider carefully point groups 222 and 422, and note how and why the orientations represented by the three positions in the symbol change their meanings. In 222, the three symmetry axes are along x, y, and z, respectively. In 422, 4 is taken along z, by convention; the first symbol 2 (second position in the symbol) represents both the x and y directions, because they are equivalent under fourfold symmetry. This combination of 4 and 2 introduces symmetry along [110] and [$1\bar{1}0$], so that the second symbol 2 represents this symmetry. Similar situations exist among other point groups where the principal symmetry axis is of degree greater than 2.

The reader should not be discouraged by the wealth of convention which surrounds this part of the subject. It arises for two main reasons. First, there are many different, equally correct ways of describing crystal geometry. For example, the unique axis in the monoclinic system could be chosen as x or z instead of y, or along some arbitrary direction. Secondly, a strict system of notation is

Table 1.5 Three-dimensional point groups and Hermann–Mauguin notation

		Symbol meaning for each position		
System	Point groups[a]	First position	Second position	Third position
Triclinic	1, $\bar{1}$	All directions in crystal	–	–
Monoclinic[b]	2, m, $\frac{2}{m}$	2 and/or $\bar{2}$ along y	–	–
Orthorhombic	222, $mm2$, mmm	2 and/or $\bar{2}$ along x	2 and/or $\bar{2}$ along y	2 and/or $\bar{2}$ along z
Tetragonal	4, $\bar{4}$, $\frac{4}{m}$	4 and/or $\bar{4}$ along z	–	–
	422, $4mm$, $\bar{4}2m$, $\frac{4}{m}mm$	4 and/or $\bar{4}$ along z	2 and/or $\bar{2}$ along x, y	2 and/or $\bar{2}$ at 45° to x, y and in xy plane, i.e., along $\langle 110 \rangle$
Cubic[c]	23, $m\bar{3}$	2 and/or $\bar{2}$ along x, y, z	3 and/or $\bar{3}$ at 54°44′[d] to x, y, z, i.e., along $\langle 111 \rangle$	–
	432, $\bar{4}3m$, $m\bar{3}m$	4 and/or $\bar{4}$ along x, y, z	3 and/or $\bar{3}$ at 54°44′[d] to x, y, z, i.e., along $\langle 111 \rangle$	2 and/or $\bar{2}$ at 45° to x, y, z, i.e., along $\langle 110 \rangle$
Hexagonal	6, $\bar{6}$, $\frac{6}{m}$	6 and/or $\bar{6}$ along z	–	–
	622, $6mm$, $\bar{6}m2$, $\frac{6}{m}mm$	6 and/or $\bar{6}$ along z	2 and/or $\bar{2}$ along x, y, u	2 and/or $\bar{2}$ perpendicular to x, y, u and in xy plane
Trigonal[e]	3, $\bar{3}$	3 and/or $\bar{3}$ along z	–	–
	32, $3m$, $\bar{3}m$	3 and/or $\bar{3}$ along z	2 and/or $\bar{2}$ along x, y, u	–

[a] R/m occupies a single position in a point-group symbol because only *one* direction is involved

[b] In the monoclinic system, the y axis is taken as the unique 2 or $\bar{2}$ axis. Since $\bar{2} \equiv m$, then if $\bar{2}$ is along y, the m plane represented by the same position in the point-group symbol is perpendicular to y. The latter comment applies *mutatis mutandis* in other crystal systems (it is best to specify the orientation of a plane by that of its normal)

[c] Earlier notation uses $m3$ and $m3m$ for $m\bar{3}$ and $m\bar{3}m$, respectively

[d] Actually $\cos^{-1}(1/\sqrt{3})$

[e] For convenience; the trigonal system is referred to hexagonal axes; on the axes of a rhombohedral unit cell (q.v.), the orientations of the first and second positions of the symbol are [111] and $\langle 1\bar{1}0 \rangle$, respectively

desirable for the purposes of concise and unambiguous communication of crystallographic material. With familiarity, the conventions cease to be a problem.

We now consider two point groups in a little more detail in order to elaborate some of the topics discussed so far.

Point Group mm2

Once we fix the orientations of two of the symmetry elements in this point group, the third is introduced in a unique orientation. Referring to Fig. 1.28, we start with mm ($m \perp x$ and $m \perp y$) as shown by the thick lines. Point (1), in a general position, is reflected across the m plane perpendicular to the x axis (m_x) to give point (2). This point is now reflected across the second m plane (m_y) to (3). Then either (3) across m_x or (1) across m_y produces (4). It is evident now that the points in each of the pairs (1), (3) and (2), (4) are related by the twofold rotation axis along z, which is, here, the line of intersection of the two m planes.

Point Group 4mm

If we start with the fourfold axis along z and m perpendicular to x, we see straightaway that another m plane (perpendicular to y) is required, Fig. 1.29a, b; the fourfold axis acts on all other symmetry elements in the

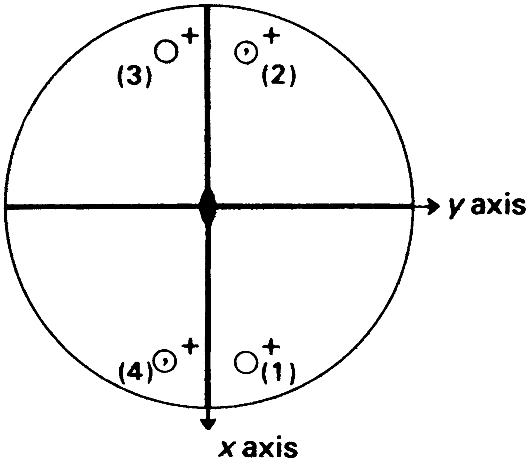

Fig. 1.28 Stereogram, symmetry elements, and general form for point group $mm2$

crystal as well as on crystal faces. A general point operated on by the symmetry $4m$ produces eight points in all, Fig. 1.29c. The stereogram shows that a second form of (vertical) m planes, lying at 45° to the first set is introduced, Fig. 1.29d. More concisely, we may say that the normals to the two forms of m planes lie at 45° to one another. No further points are introduced by the second set of m planes: a fourfold rotation (1) → (2), followed by reflection across the mirror plane normal to the x axis, (2) → (3), is equivalent to reflection of the original point across a mirror at 45° to x, (1) → (3). The reader should now refer again to Table 1.5 for the relationship between the positions of the symmetry elements and the point-group symbols, particularly for the tetragonal and orthorhombic systems, from which these detailed examples have been drawn.

In this discussion, we have used a general form $\{hkl\}$ to illustrate the point group, and each symmetry-equivalent point lies in a general position, point-group symmetry 1, on the stereogram of the group. The crystal planes that coincide with symmetry planes or symmetry axes are special forms, and their poles lie on symmetry elements: the forms $\{110\}$ and $\{010\}$ in $4mm$ are examples of special forms. The need for the general form in a correct description of a point group is illustrated by Fig. 1.30. The poles of the faces on each of the two stereograms shown are identical, although they may be derived from crystals in different classes, $\bar{4}2m$ and $4mm$ in this example (and also in $\dfrac{4}{m}mm$).

Figure 1.31 shows crystals of these two classes with the $\{110\}$ form, among others, developed. In Fig. 1.31b, the presence of *only* special forms led originally to an incorrect deduction of the point group of this crystal.

The stereograms for the 32 crystallographic point groups are shown in Fig. 1.32. The conventional crystallographic axes are drawn once for each system. Two comments on the notation are necessary at this stage.

The symbol – ⦶ + indicates two points, O^{+} and $\odot^{-}$, immediately below it and related by a mirror plane in the plane of projection. In the cubic crystal system, the four points related by a fourfold lying axis in the plane of the stereogram lie on a stereographic small circle, which is a circle on the surface of the sphere that does not pass through the center of the sphere, Fig. 1.33. In general, two of the points are projected from the upper hemisphere and the other two points from the lower hemisphere. We can distinguish them readily by remembering that 2 is a subgroup (q.v.) of both 4 and $\bar{4}$.

The use of the program SYMM for assisting with point-group recognition is described in Sect. 13.3, and the reader may wish to refer forward at this stage. Appendix B discusses the Schönflies symmetry

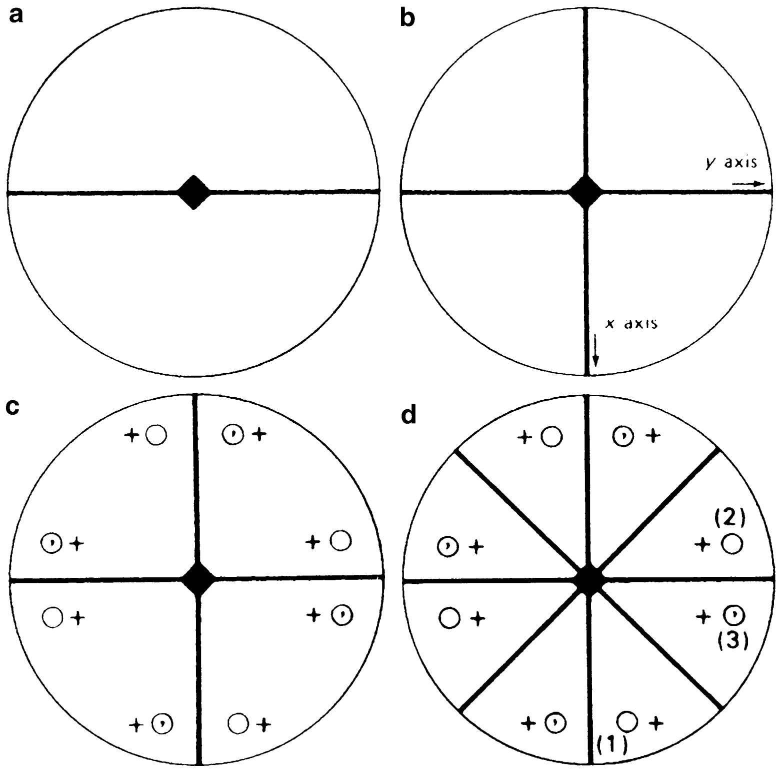

Fig. 1.29 Intersecting symmetry elements. (**a**) One *m* plane intersecting the fourfold axis is inconsistent. (**b**) Consistent group of symmetry elements. (**c**) General form of points generated by 4*m*. (**d**) Complete stereogram, point group 4*mm*

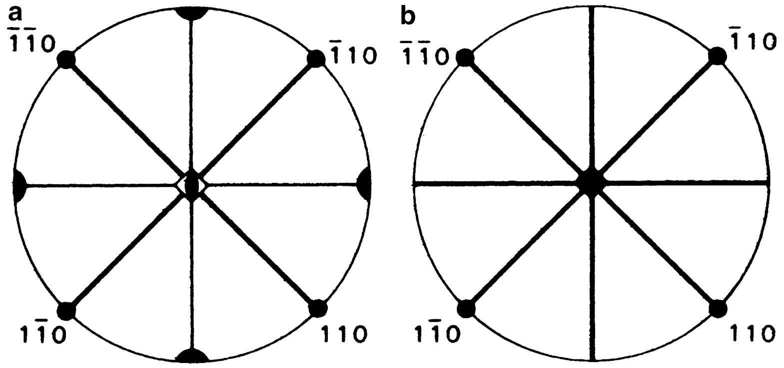

Fig. 1.30 The {110} form in tetragonal point groups. (**a**) Point group $\bar{4}2m$. (**b**) Point group 4*mm*

notation for point groups. Because this notation is also in use in certain contexts, we have written the equivalent Schönflies symbols in Fig. 1.32, in parentheses, after the Hermann–Mauguin symbols.

Subgroups, Laue Groups, Centrosymmetric Groups, and Projection Symmetry

Subgroups

A subgroup of a given point group is a point group of lower symmetry than the given group, contained within it and capable of separate existence as a point group. For example, 32 is a subgroup of $\bar{3}m$, 622, $\bar{6}m2$, $\frac{6}{m}mm$, 432 and $m3m$, whereas $\bar{4}$ is a subgroup of $\frac{4}{m}$, $\bar{4}2m$, $\frac{4}{m}mm$, $\bar{4}3m$, and $m3m$. The subgroup principle provides a rationale for some of the graphic symbols for symmetry elements. Thus, $\bar{4}$ is shown by a square (fourfold rotation), unshaded (to distinguish it from 4), and with a twofold rotation symbol inscribed (2 is a subgroup of $\bar{4}$).

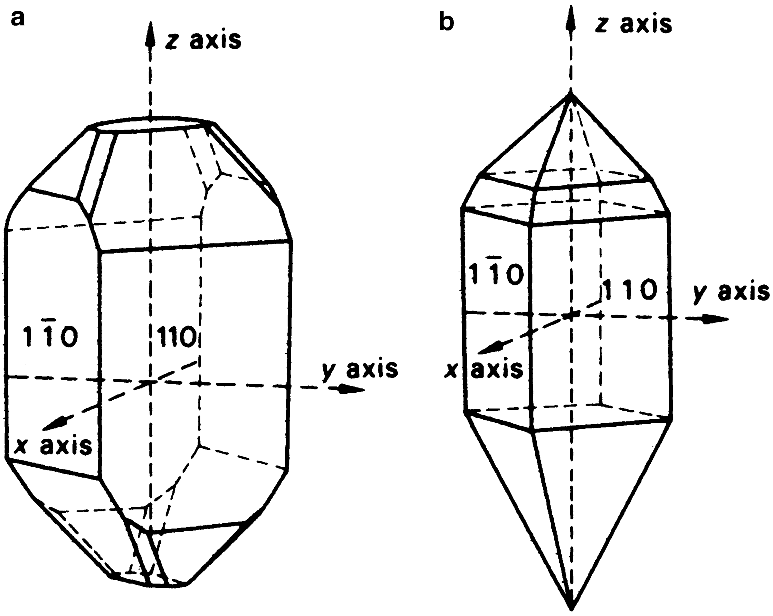

Fig. 1.31 Tetragonal crystals showing, among others, the {110} form. (**a**) Copper pyrites, point group $\bar{4}2m$. (**b**) Iodosuccinimide, apparent point group $4mm$; X-ray photographs revealed that the true point group is 4

Laue Groups

Point group $\bar{1}$ and point groups that have $\bar{1}$ as a subgroup are centrosymmetric. We shall see later that X-ray diffraction patterns are, in the absence of significant anomalous dispersion (q.v.), effectively centrosymmetric, so that the arrangement of spots on the X-ray diffraction photograph of a crystal can exhibit only the symmetry that would be found from a crystal having the corresponding centrosymmetric point group. In the case of a crystal belonging to a non-centrosymmetric point group, the corresponding centrosymmetric point group is simply the given group combined with a center of symmetry.

There are 11 such point groups; they are called *Laue groups*,[6] since symmetry is often investigated by the Laue X-ray method, Sect. 5.4.1ff. In Table 1.6, the point groups are classified according to their Laue group, and the symmetry of the Laue flat-plate film photograph is given for directions of the X-ray beam normal to the crystallographic forms listed.

Laue-Projection Symmetry

The Laue-projection symmetry corresponds to one of the ten two-dimensional points groups. What is the Laue-projection symmetry on {110} for a crystal of point group $4mm$? This question can be answered with the stereogram of the corresponding Laue group, $\frac{4}{m}mm$. Reference to the appropriate diagram in Fig. 1.32 shows that an X-ray beam traveling normal to {110} encounters $2mm$ symmetry. The entries in Table 1.6 can be deduced in this way. The reader should refer again to Table 1.5 and compare corresponding entries between Tables 1.5 and 1.6

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[6] Strictly, the term Laue group should be *Laue class*, but the former is in general use.

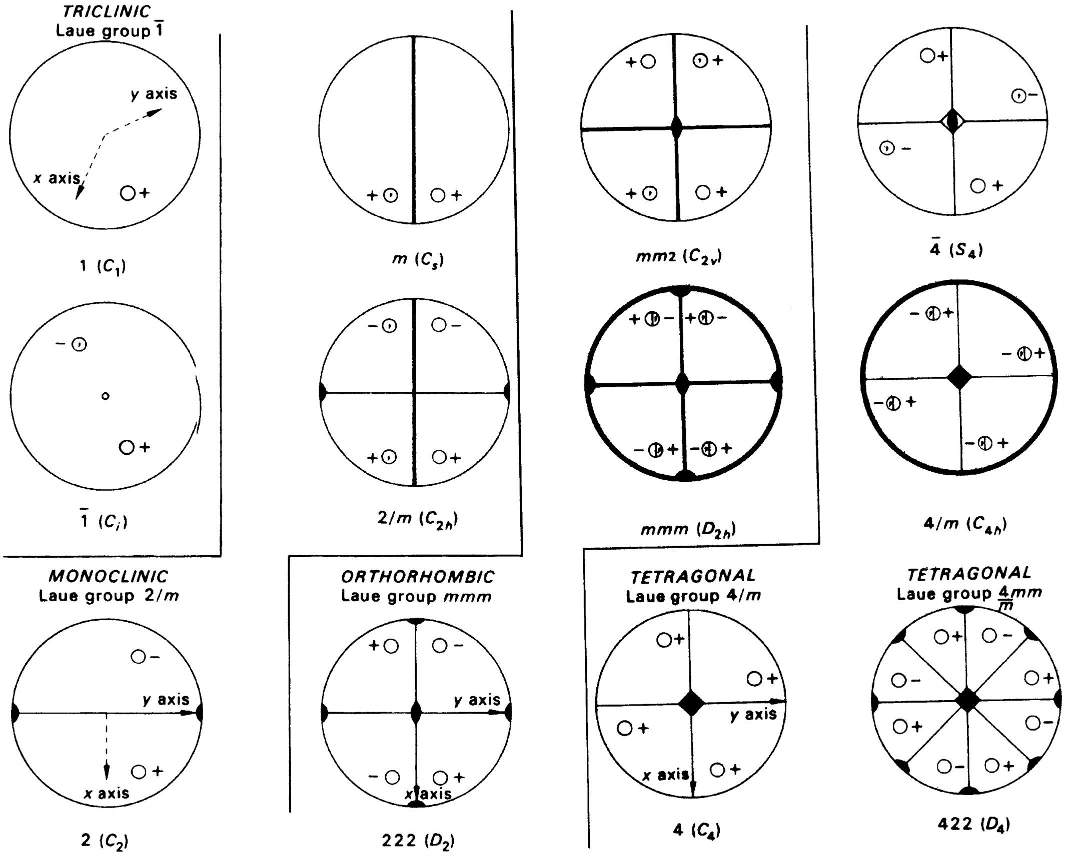

Fig. 1.32 Stereograms showing both the symmetry elements and the general form {*hkl*} in the 32 crystallographic point groups. The arrangement is by system and common Laue group. The crystallographic axes are named once for each system and the *z* axis is chosen normal to the stereogram. The Schönflies symbols are given in *parentheses*

Point-Group Projection Symmetry

Point-group projection symmetry is the symmetry of the projection of the general form of a point group on to a plane. Thus, the point-group projection symmetry of 4*mm* on {110} is *m*.

Non-crystallographic Point Groups

There are species that exhibit symmetries other than those of the crystallographic point groups. Indeed, *R* could, in principle, take any integer value between one and infinity. The statement $R = \infty$ implies cylindrical symmetry; the molecule of carbon monoxide has an ∞ axis along the C–O bond, if we assume spherical atoms.

A fivefold symmetry axis is present in uranium heptafluoride, Fig. 1.34, and the point-group symbol may be written as $\overline{10}m2$, or $\frac{5}{m}m$. The stereogram of this point group is shown in Fig. 1.35; the graphic symbol used here for $\frac{5}{m}$ is not standard.

Other examples of non-crystallographic point groups will be encountered among chemical molecules, and a stereogram can always be used to represent the point-group symmetry. In every such example, however, the substance crystallizing in one of the seven crystal systems will normally belong to one of the 32 crystal classes.

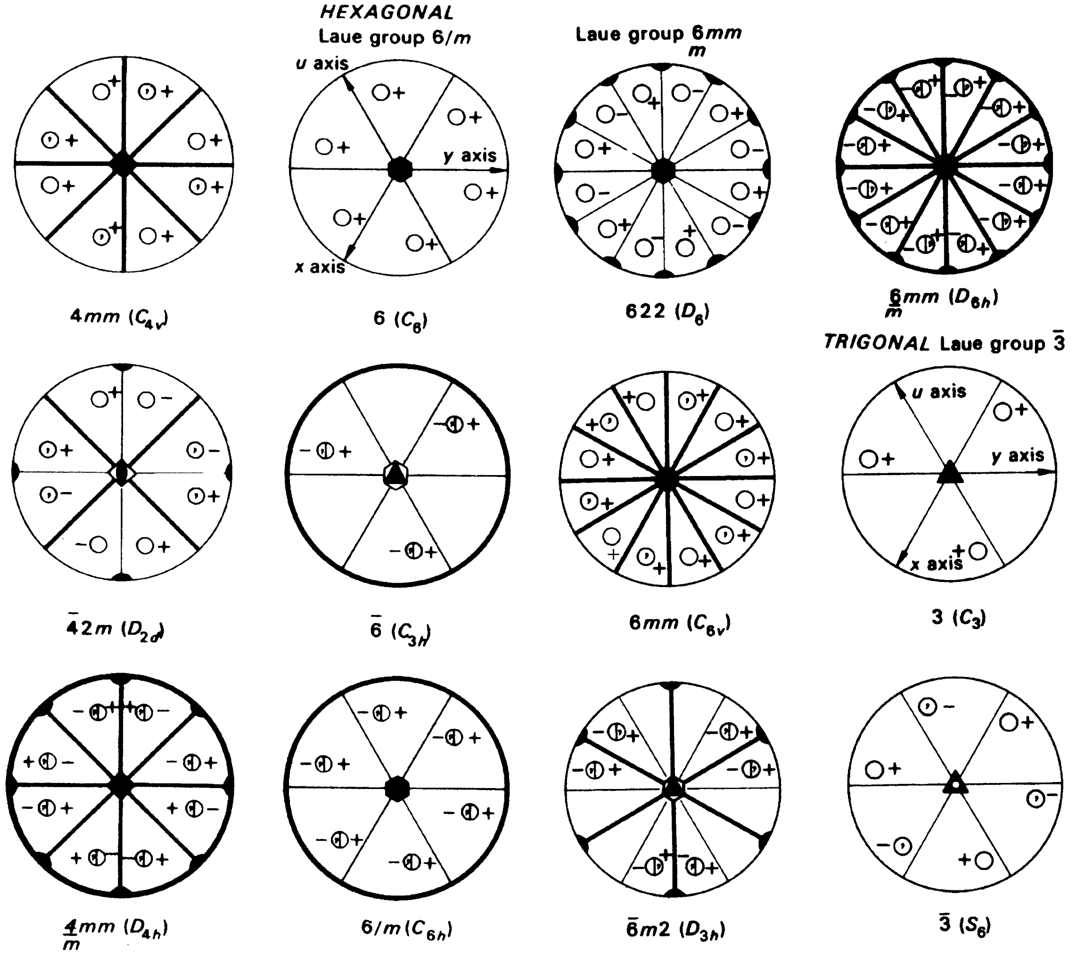

Fig. 1.32 (continued)

1.4.3 Quasicrystals, Buckyballs, and Icosahedral Symmetry

Quasicrystals

Our main task in this chapter has been the description of classical crystallography, in which a crystal is defined as an ideally infinite three-dimensional periodic arrangement of atoms, the periodicities being denoted by the directions of three crystallographic reference axes. Thus, we obtain a crystal structure, with building blocks of atoms (unit cells, q.v.) aligned so as to fill space. Most crystal structures can be described in terms of one of the 230 space groups (q.v.), which show the different types of symmetry elements present in the structures.

Until the year 1982, no scientist anywhere would believe in crystals with rotational symmetry degrees other than 1, 2, 3, 4, and 6, as we have discussed earlier: crystals had only these symmetries and were periodic in three dimensions. In that year, however, Professor Daniel Shechtman[7] was

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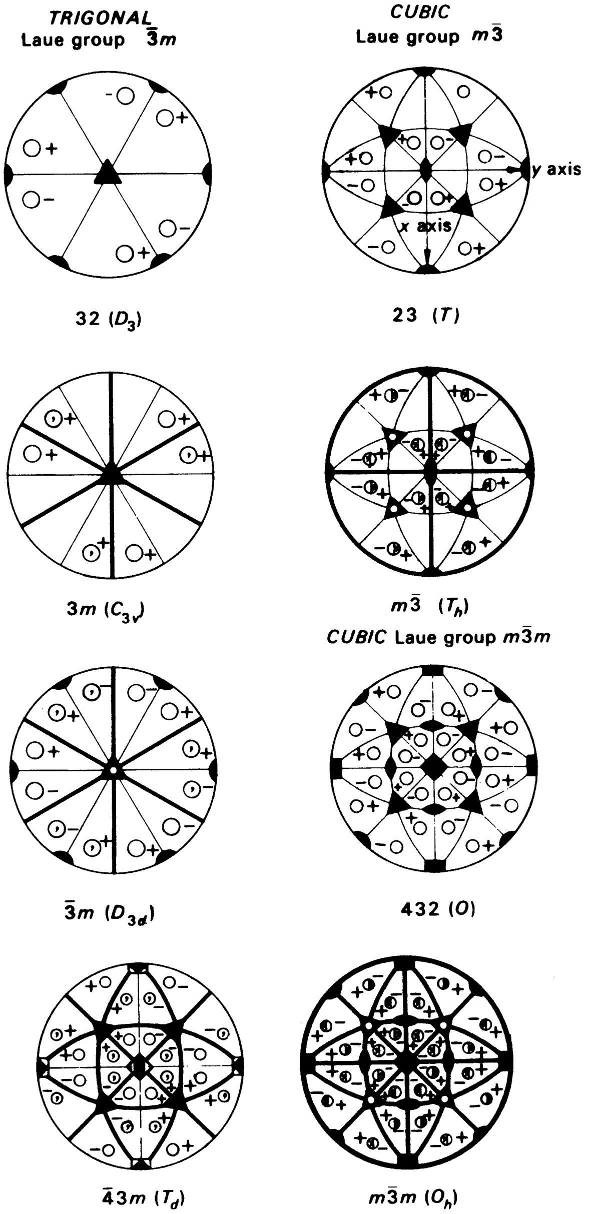
[7] Nobel Laureate in Chemistry, 2011.



TRIGONAL
Laue group $\bar{3}m$

CUBIC
Laue group $m\bar{3}$

$32\ (D_3)$

$23\ (T)$

$3m\ (C_{3v})$

$m\bar{3}\ (T_h)$

CUBIC Laue group $m\bar{3}m$

$\bar{3}m\ (D_{3d})$

$432\ (O)$

$\bar{4}3m\ (T_d)$

$m\bar{3}m\ (O_h)$

Fig. 1.32 (continued)

experimenting with an alloy containing aluminum and manganese, Al_6Mn; he was concerned about the appearance of certain areas of the metal surface, Fig. 1.36a, and took a transmission electron microscopy (TEM) photograph of that region of the surface. He observed diffraction spots in patterns of ten extending over the area of reciprocal space (q.v.) recorded, Fig. 1.36b, and he spent the next 2 years investigating an effect that he found hard to believe. Attempts to explain the results by a process of crystal twinning were unsuccessful, and after more experimentation he was forced to the conclusion of having discovered *fivefold symmetry* in a crystalline material. The crystal structure is *aperiodic*: it

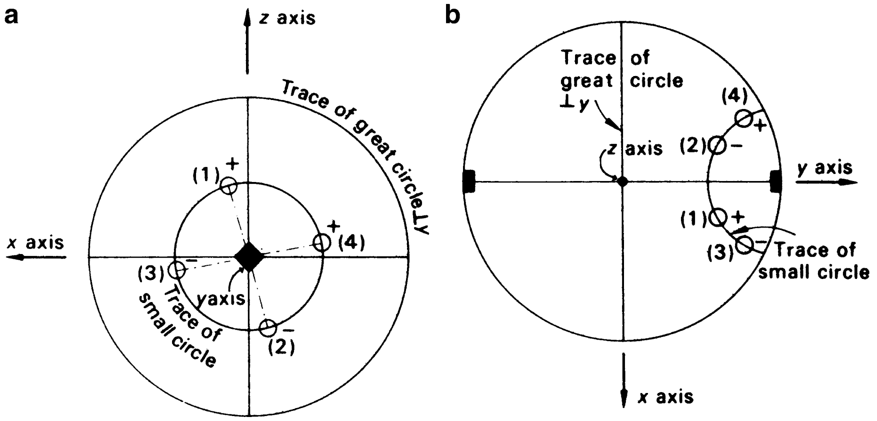


Fig. 1.33 Stereogram notation for points related by a fourfold axis (y) lying in the plane of a stereogram. The ± signs refer to the z direction. (**a**) Vertical section normal to the y axis. (**b**) Corresponding stereogram; the pairs of points (1)–(2) and (3)–(4) are related by twofold symmetry (subgroup of 4)

Table 1.6 Laue groups and Laue-projection symmetry

System	Point groups	Laue group	Laue-projection symmetry normal to the given form		
			{100}	{010}	{010}
Triclinic	1, $\bar{1}$	$\bar{1}$	1	1	1
Monoclinic	2, m, $2/m$	$2/m$	m	2	m
Orthorhombic	222, $mm2$, mmm	mmm	$2mm$	$2mm$	$2mm$
			{001}	{100}	{110}
Tetragonal	$4, \bar{4}$ and $4/m$	$4/m$	4	m	m
	$422, 4mm, \bar{4}2m, \frac{4}{m}mm$	$\frac{4}{m}mm$	$4mm$	$2mm$	$2mm$
			{0001}	$\{10\bar{1}0\}$	$\{11\bar{2}0\}$
Trigonal[a]	3, $\bar{3}$	$\bar{3}$	3	1	1
	32, $3m$, $\bar{3}m$	$\bar{3}m$	$3m$	m	2
Hexagonal	$6, \bar{6}, 6/m$	$6/m$	6	m	m
	$622, 6mm, \bar{6}m2, \frac{6}{m}mm$	$\frac{6}{m}mm$	$6mm$	$2mm$	$2mm$
			{100}	{111}	{110}
Cubic	23, $m3$	$m3$	$2mm$	3	m
	432, $\bar{4}3m$, $m3m$	$m3m$	$4mm$	$3m$	$2mm$

[a] Referred to hexagonal axes

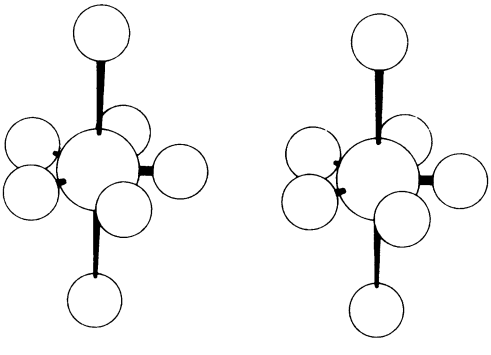


Fig. 1.34 Stereoview of the molecule of uranium heptafluoride, UF_7

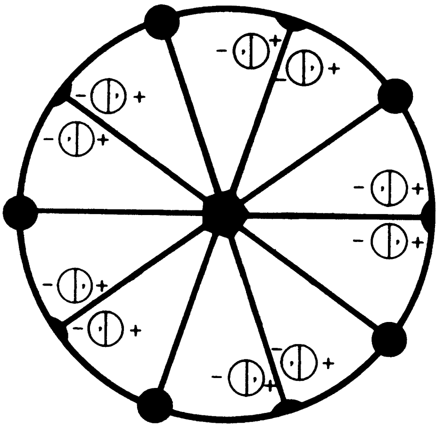


Fig. 1.35 Stereogram of the non-crystallographic point group $\overline{10}m2$ (D_{5h}) showing the general form (20 poles), and a special form of 5 poles lying on the *m* planes that can be used to represent the five F atoms in one plane in UF_7. The poles for the remaining two F atoms lie at these center of the stereogram, on the $\overline{10}$ axis

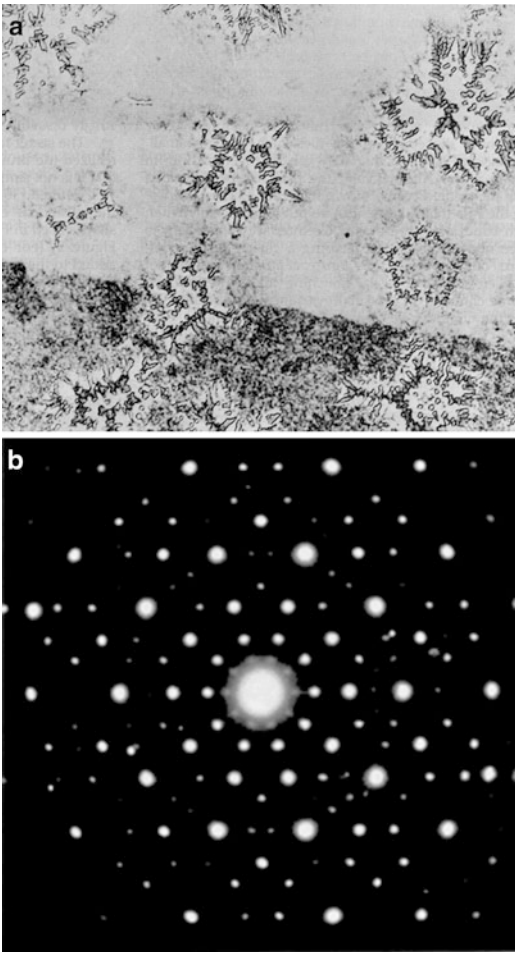


Fig. 1.36 Transmission electron microscopy (TEM) on an Al_6Mn alloy. (**a**) Surface of the Al_6Mn alloy, with irregularities inviting further examination. (**b**) Copy of Original TEM photograph of the alloy surface taken by Professor Shechtman, showing a tenfold spot pattern indicative of a crystalline nature, but without the periodicity of classical crystals (reproduced by courtesy of Professor Shechtman)

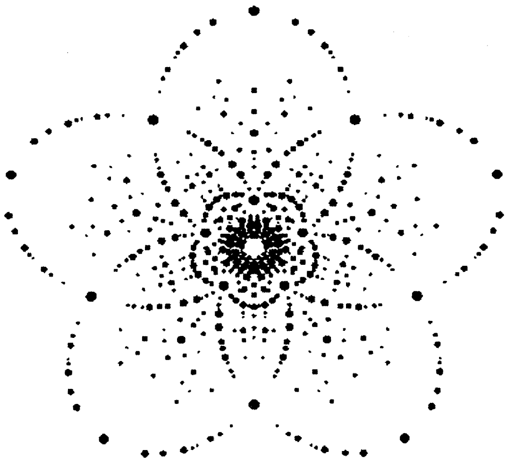


Fig. 1.37 Simulated Laue photograph of an icosahedral quasicrystal with the X-ray beam along a fivefold axis (reproduced by courtesy of Dr. Steffen Weber)

is space-filling, but with none of the three-dimensional periodicity that characterizes normal crystals. His first paper on these findings was rejected, but a detailed account was published in 1984 [27].

This alloy structure is denoted a *quasicrystal*: it has icosahedral symmetry, point group 532; Fig. 1.37 is a simulated Laue pattern for X-ray diffraction from an icosahedral crystal, with the X-ray beam along a fivefold axis.

Subsequently, many stable and metastable quasicrystals have been discovered, frequently as binary or ternary intermetallic compounds containing aluminum as one of the constituents. Icosahedral quasicrystals form one group of quasicrystals and polygonal quasicrystals, two-dimensional quasicrystals with 8-fold (Mn–Fe–Al), 10-fold (Al–Cu–Ni), or 12-fold (Al–Mn–Si) symmetry yet another. The former group is manifested in the occurrence of sharp diffraction spots and the latter by the presence of a non-crystallographic rotational symmetry. Figure 1.38 is an example of a simulated zero-layer X-ray precession photograph (q.v.) from a polygonal crystal showing 12-fold symmetry (decagonal symmetry) [28]. Two-dimensional quasicrystals symmetry have been reported for rapidly cooled samples corresponding to the compositions V_3Ni_2 and $V_{15}Ni_{10}Si$: TEM studies showed that they exhibit 12-fold rotational symmetry but no long-range periodicity [29].

Two-dimensional quasiperiodical structures have been said to occur in medieval mosques and other decorative tilings. Penrose [30] demonstrated the covering of plane space in a non-periodic manner by using two differently shaped units, or *tiles*, and Fig. 1.39 is an example of a Penrose tiling which shows two superimposed layers of fivefold symmetry. This tiling was extended to three dimensions and, subsequently, a similarity was discovered between Penrose three-dimensional tiling and icosahedral quasicrystals. Mackay has shown experimentally [31] that the diffraction pattern from a Penrose plane tiling has a two-dimensional Fourier transform consisting of sharp δ-peaks arranged in a fivefold symmetry pattern.

In 2009, naturally occurring quasicrystals were found in Russia [32]; in composition they were Cu–Al–Zn minerals with varying amounts of iron, including an $Al_{63}Cu_{24}Fe_{13}$ phase; the quasicrystal grains were stated to be of high crystalline quality [33].

Mathematically, the structures of quasicrystals are derivable by a general method that treats them as projections of lattices of higher dimensions. The icosahedral quasicrystals found by Shechtman were shown to be projections from a six-dimensional hypercubic lattice [34]. Whereas three integer

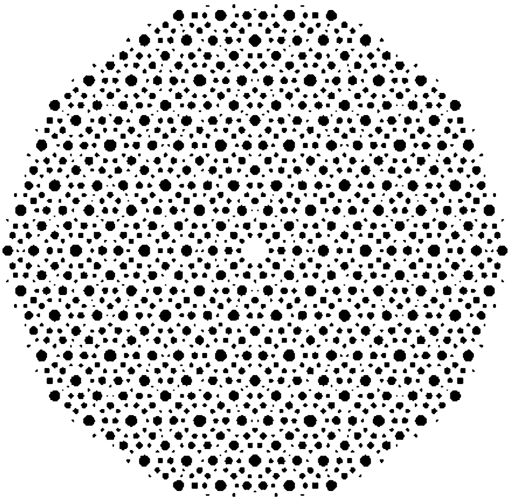


Fig. 1.38 Simulated zero-layer X-ray precession photograph of a polygonal crystal showing tenfold (decagonal) symmetry (reproduced by courtesy of Dr. Steffen Weber)

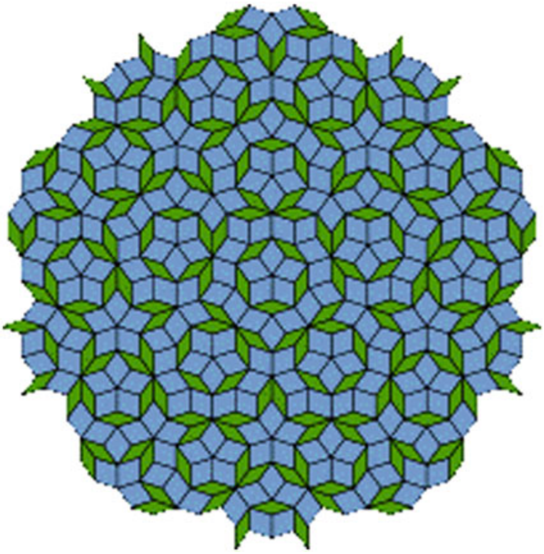


Fig. 1.39 Example of a Penrose tiling [30] that uses just two shapes of tile (reproduced by courtesy of Jeff Preshing)

values, the Miller indices, are sufficient to label reflections in normal crystals, five linearly independent vectors are needed for polygonal quasicrystals and six for icosahedral quasicrystals.

As a result of the findings on polygonal crystals and quasicrystals, the International Union of Crystallography revised the definition of "crystal" as given in Sect. 1.2 to *a material capable of producing a clear-cut diffraction pattern, with ordering that is either periodic or aperiodic*. The concept of an *aperiodic crystal* was introduced by Schrödinger [35]. He sought to explain how hereditary information is stored: molecules were deemed too small, amorphous solids were plainly chaotic, so it had to be a kind of crystal; and as a periodic structure could not encode information, it

Fig. 1.40 Example of a geodesic dome (reproduced by courtesy of Lotus Domes UK)

had to be aperiodic. Later, DNA was discovered and, although not crystalline, it possesses properties predicted by Schrödinger—a regular but aperiodic molecule [36]. In this book, however, the word 'crystal' is used in its traditional sense unless otherwise noted.

Buckyballs and Icosahedral Symmetry

The discovery of a new form of a chemical element is a very rare event, but this occurred with the finding of a new allotropic form of carbon. Mass spectrometric examination of the products of a high-energy laser interaction with graphite in a helium atmosphere contained fragments with varying numbers of carbon atoms, their distribution depending upon the pressure of helium [37]. A very stable carbon atom cluster was found to be C_{60}. Stability arises because a sheet of carbon atoms formed a ball, thereby satisfying fully the valence requirements of carbon.

This situation was met by a structural formation similar to that of a geodesic dome, Fig. 1.40, but with interlocking pentagons and hexagons, and completed to a full sphere, Fig. 1.41. The C_{60} structure was named buckminsterfullerene [37], after Richard Buckminster Fuller, an American engineer, who described the geodesic dome in detail. The geodesic dome was actually invented in 1922 by Walther Bauersfeld of the Zeiss optical company: it is a spherical or near-spherical lattice-type surface formed by a network of great circles, or geodesics, on a sphere. The geodesics intersect to form a rigid, stress-free triangular structure. Buckminster Fuller developed the mathematics of the dome and popularized it.

For simplicity, near-spherical fullerenes are termed *buckyballs*, the simplest stable structure being buckminsterfullerene [37], C_{60}. This buckyball structure has 32 faces: 20 hexagons and 12 pentagons, Fig. 1.41. Molecules that consist entirely of carbon atoms in the form of hollow spheres, ellipsoids, and tubes are known as fullerenes. Buckyballs and buckytubes are topics of intense research both in pure chemistry, in which fullerenes are manipulated to form compounds, and in technological applications, such as carbon nanotubes.

The C_{60} fullerene exhibits icosahedral symmetry. As icosahedral symmetry is not compatible with translational symmetry, there are no associated crystallographic space groups. Nevertheless, icosahedral symmetry can be classified conveniently under the Schönflies point group system: full icosahedral symmetry I_h comprises the following symmetry elements: E (identity), C_5, C_3, C_2, i (center of symmetry), S_{10}, S_6, σ. Thus, the *order* of the group, the total number of its symmetry elements, is 120. Figure 1.42 illustrates icosahedral symmetry; the similarity to C_{60} is clear in (b).

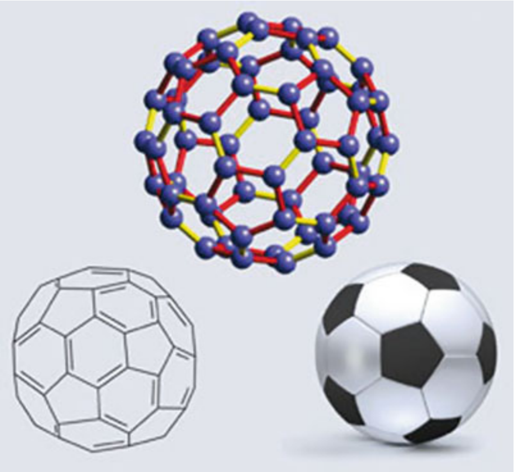


Fig. 1.41 Molecular structure of buckminsterfullerene, a C_{60} buckyball. There are two different bond lengths: 1.458 Å for the bonds fusing 5- and 6-membered rings and 1.401 Å for bonds fusing the 6-membered rings [38] (Harrison P, McCaw C (2011) Educ Chem 48:113. Reproduced by permission of The Royal Society of Chemistry)

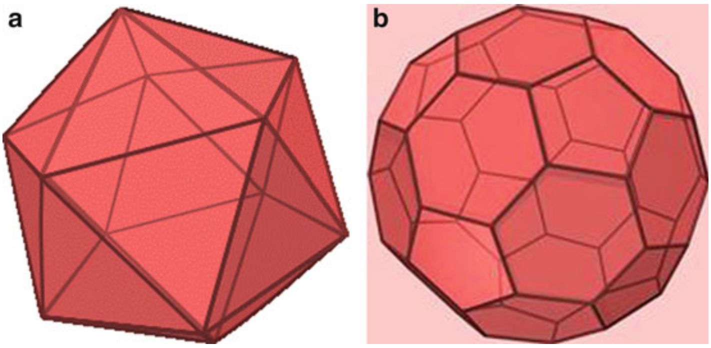


Fig. 1.42 Icosahedra. (**a**) Regular icosahedron of vertex figure 3.3.3.3.3: the vertex figure means that five triangles meet at a vertex. (**b**) Truncated icosahedron of vertex figure 5.6.6: one pentagon and two hexagons meet at a vertex. The symmetry is I_h in each case

The icosahedral group of lower symmetry I has the elements E, C_5, C_3, and C_2; it is of interest in some biological fields as it can represent a chiral structure.

1.5 Problems

1.1. The line AC, Fig. P1.1, may be indexed as (12) with respect to the rectangular two-dimensional axes x and y. What are the indices of the same line with respect to the axes x' and y, where the angle $x' Oy = 120°$? PQ is the parametral line for both sets of axes, and $OB/OA = 2$.

1.2. Write the Miller indices for planes that make the intercepts given below:
   (a) $a/2, -b/2, \|c$.
   (b) $2a, b/3, c/2$.
   (c) $\|a, \|b, -c$.

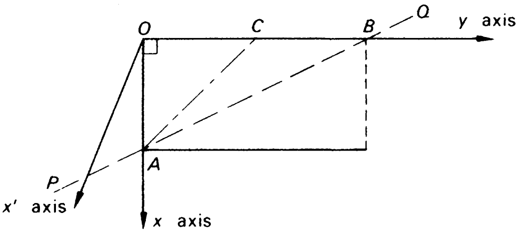


Fig. P1.1 *Line* referred to rectangular and oblique axes

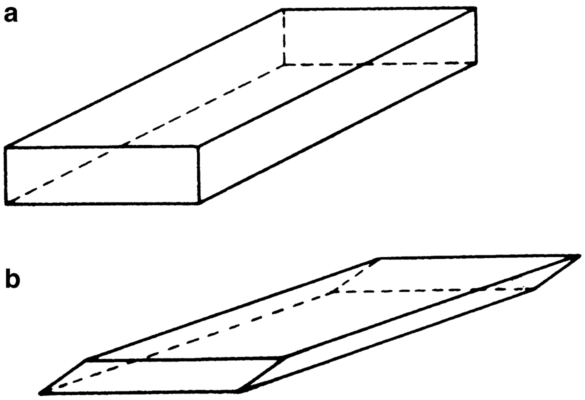


Fig. P1.2 Matchbox: (**a**) normal; (**b**) squashed

(d) a, $-b$, $3c/4$.
(e) $\|a$, $-b/4$, $c/3$.
(f) $-a/4$, $b/2$, $-c/3$.

1.3. Evaluate zone symbols for the pairs of planes given below:
 (a) (123), $(0\bar{1}1)$.
 (b) $(20\bar{3})$, (111).
 (c) $(41\bar{5})$, $(1\bar{1}0)$.
 (d) $(\bar{1}1\bar{2})$, (001).

1.4. What are the Miller indices of the plane that lies in both of the zones $[123]$ and $[\bar{1}1\bar{1}]$? Why are there, apparently, two answers to this problem and to each part of Problem 1.3?

1.5. How many different, unique point groups can be obtained from the symbol 422 by replacing one or more of the rotation axes by roto-inversion axes of the same degree. Write the standard symbols for the unique point groups so derived.

1.6. Take the cover of a matchbox, Fig. P1.2a.
 (a) Ignore the label, and write down its point group.
 (b) Squash it diagonally, Fig. P1.2b. What is the point group now?
 (c) In each case, what is the point group if the label is not ignored?

1.7. Draw stereograms to show the general form in each of the point groups deduced in Problems 1.6a and b. Satisfy yourself that in 1.6a three, and in 1.6b two, symmetry operations carried out in sequence produce a resultant action that is equivalent to another operation in the group.

1.8. How many planes are there in the forms $\{010\}$, $\{\bar{1}10\}$, and $\{11\bar{3}\}$ in each of the point groups $2/m$, $\bar{4}2m$, and $m3$?

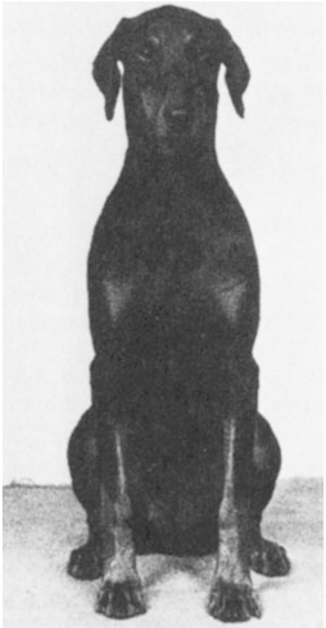


Fig. P1.3 Vijentor seal of approval at Valmara, JW

1.9. What symmetry would be revealed by the Laue flat-film photographs where the X-ray beam is normal to a plane in the form given in each of the examples below?

	Point group	Orientation
(a)	$\bar{1}$	{100}
(b)	$mm2$	{011}
(c)	m	{010}
(d)	422	{120}
(e)	3	$\{10\bar{1}0\}$
(f)	$3m$	$\{11\bar{2}0\}$
(g)	$\bar{6}$	{0001}
(h)	$\bar{6}m2$	{0001}
(i)	23	{111}
(j)	432	{110}

In some examples, it may help to draw stereograms.

1.10. (a) What is the non-trivial symmetry of the figure obtained by packing a number of equivalent but irregular quadrilaterals in one plane?

(b) What is the symmetry of the Dobermann in Fig. P1.3? This example illustrates how one can study symmetry by means of everyday objects.

(c) What is the point group of each of the objects in Fig. P1.4a–e, assuming that they all have depth, normal to the plane of the diagram?

1.11. Write the point-group symbol for the species (a) to (v) of molecule or ion in Fig. P1.5, in both the Hermann–Mauguin and Schönflies notations. Use the program SYMM* with this question for species (a) to (j) and allocate model numbers as follow:
(a) 90 (b) 49 (c) 3 (d) 18 (e) 42 (f) 91 (g) 30 (h) 16 (i) 65 (j) 71.

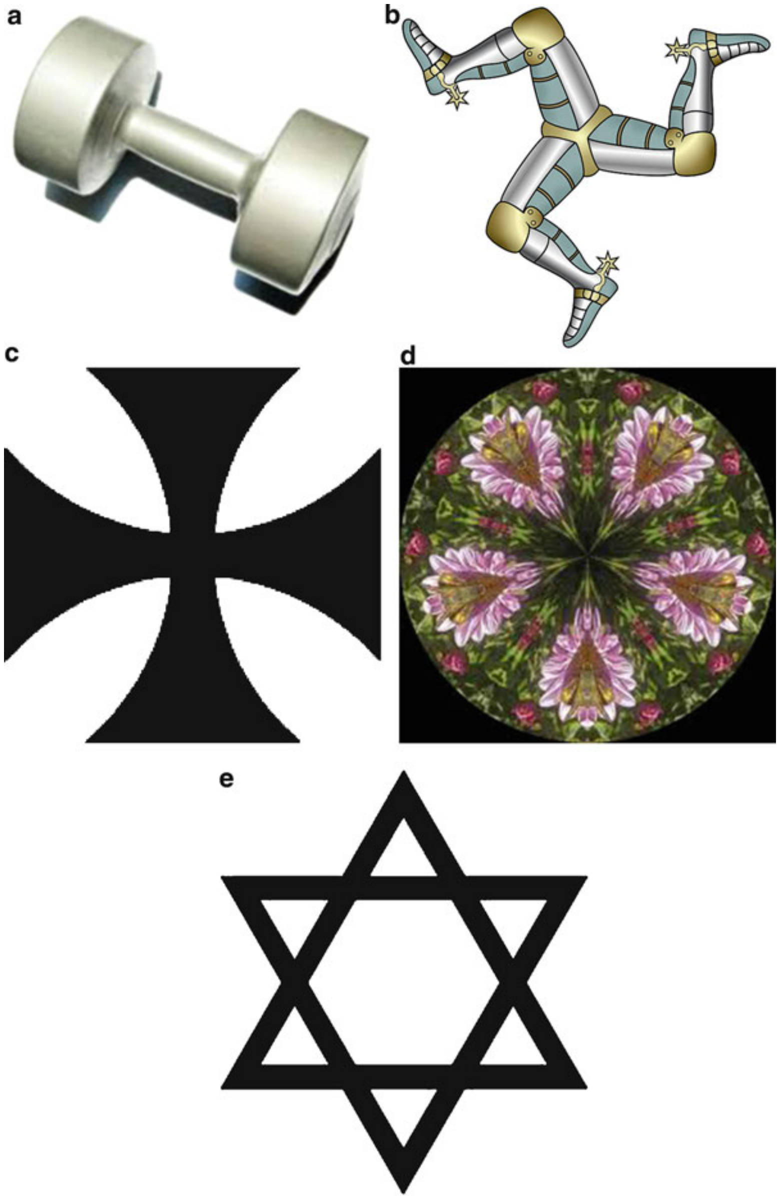


Fig. P1.4 Six symmetrical objects. (**a**) Dumbbell. (**b**) Isle of Man style emblem (reproduced by courtesy of Mapsof-World.com). (**c**) Maltese cross. (**d**) Flower pattern (reproduced by courtesy of Emeritus Professor John Huffman). (**e**) Star of David

1.12. What is the point-group projection symmetry for each of the examples in Problem 1.9?

1.13. What are the two-dimensional “Miller Indices” (hk) of the lines that form the perimeter of a rectangle? Are they the same for a parallelogram? (Choose appropriate x and y axes with the origin at the center of the figure.)

1.14. Show from Fig. P1.6 that with Miller–Bravais axes $i = -(h + k)$.

1.15. Twelve 1 Ω resistors are linked to form the edges of a cube, Fig. P1.7. Use the cubic symmetry to determine the effective resistance of the assembly of resistors to a current that is developed by connecting a battery across the ends of a threefold axis.

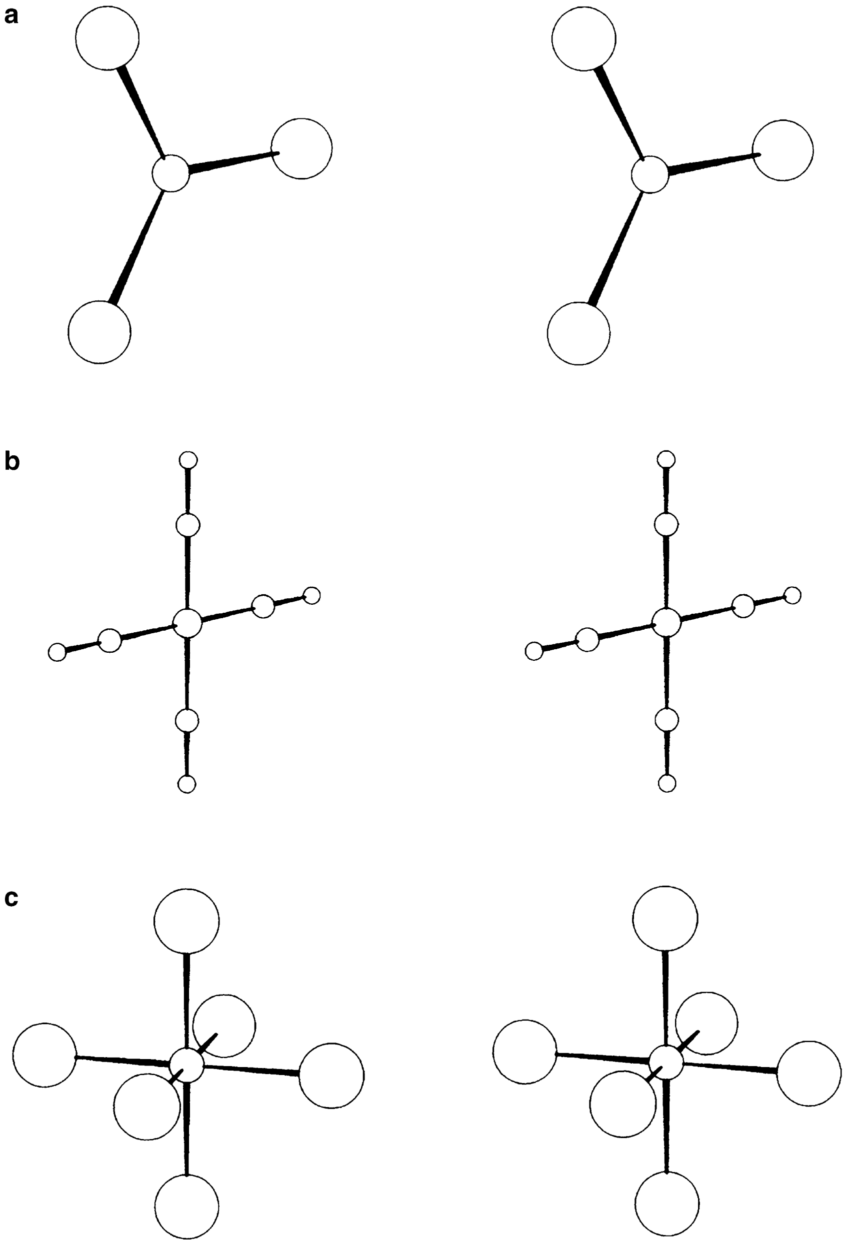


Fig. P1.5 (**a**) Carbonate ion; planar. (**b**) Tetrabromogold(III) ion; planar. (**c**) Hexachloroplatinum(IV) ion; all Cl–Pt–Cl angles are 90°. (**d**) Methane all H–C–H angles are 109.47°. (**e**) Trichloromethane; pyramidal. (**f**) Bromochlorofluoromethane. (**g**) Benzene; planar. (**h**) Monochlorobenzene; planar. (**i**) 1,4-Dichlorobenzene; planar. (**j**) 1,2-Bromochlorobenzene; planar. (**k**) Hydrogen peroxide. (**l**) Orhophosphoric acid. (**m**) Dibenzyl. (**n**) Hexanitronickelate(II) ion. (**o**) Dihydrogen phosphate ion; the hydrogen atoms are arranged statistically on the four positions shown. (**p**) 1,2,4,-Trichlorobenzene; planar. (**q**) 2,4,6-Triazidotriazine; planar. (**r**) *trans*-1,2-Dichloroethane; planar. (**s**) Cycloocta-1,5-diene. (**t**) Tetranitrodiamminocobaltate(III) ion. (**u**) Pentafluoroantimonate(III) ion. (**v**) Thorium tetrabromide

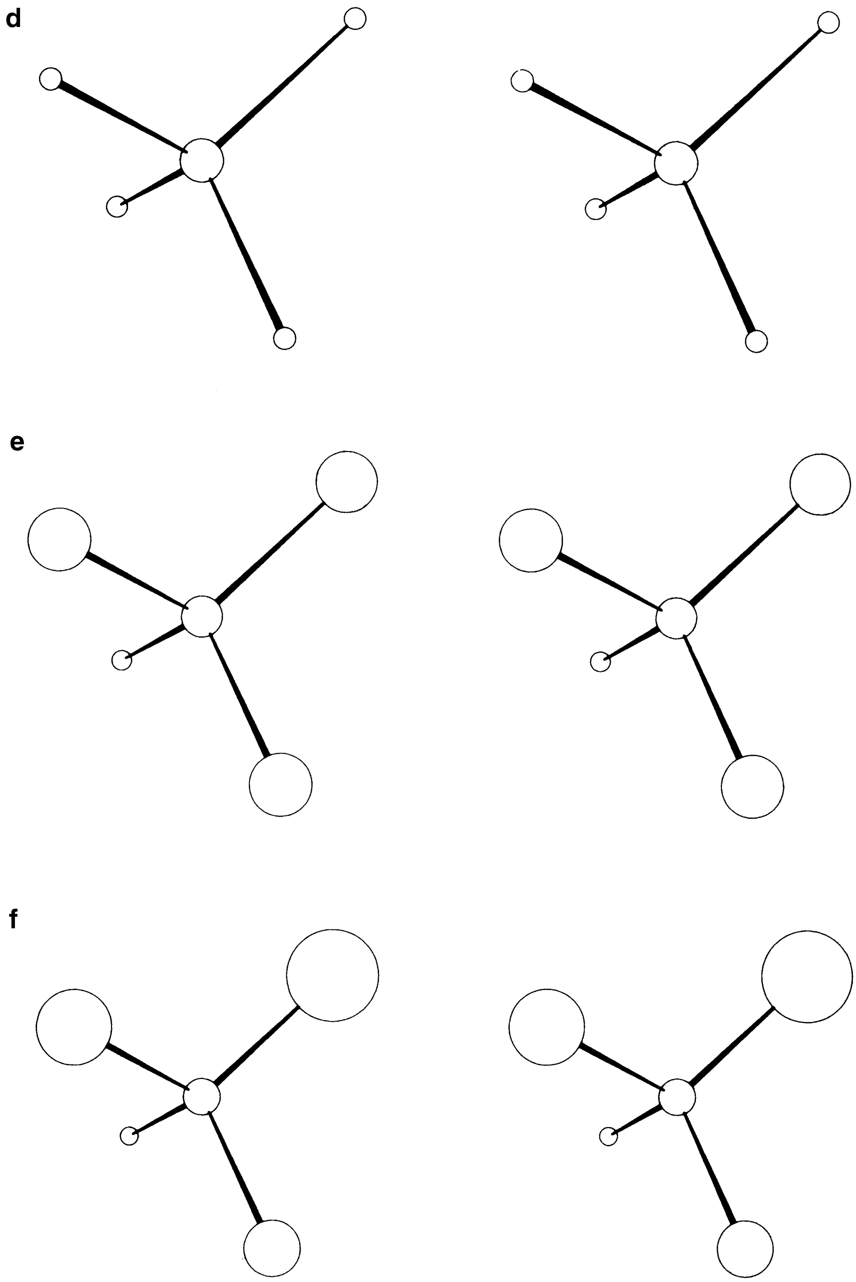


Fig. P1.5 (continued)

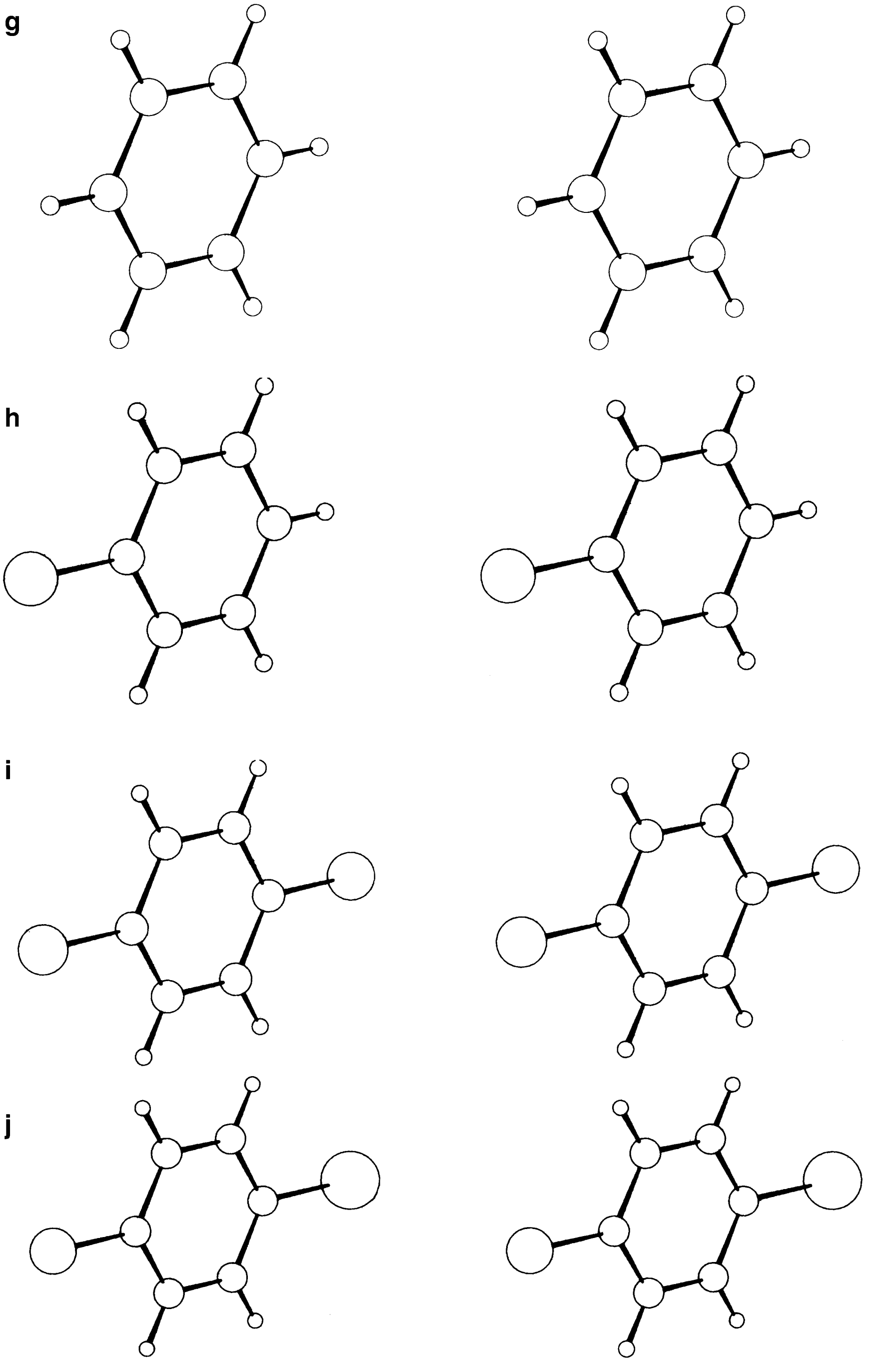


Fig. P1.5 (continued)

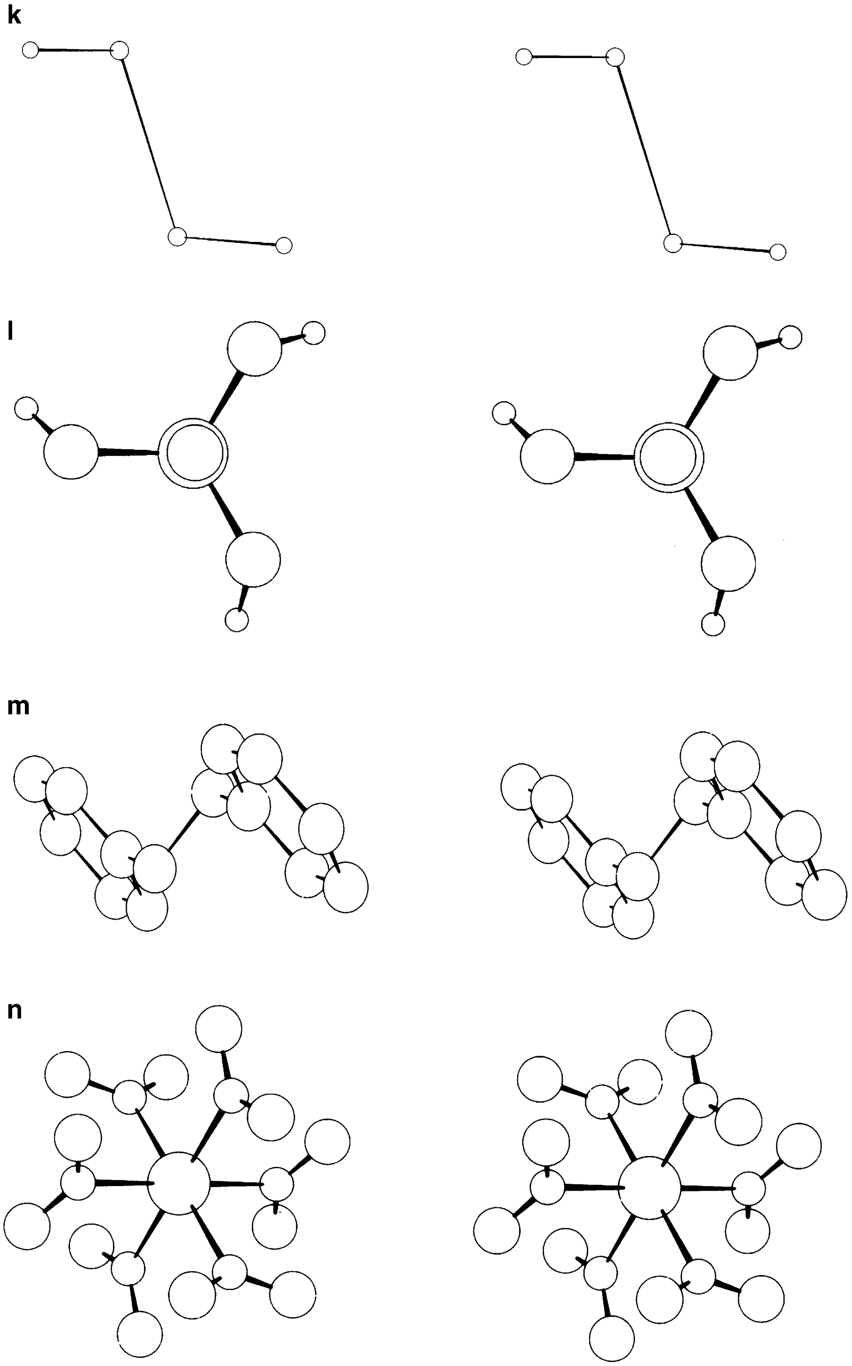


Fig. P1.5 (continued)

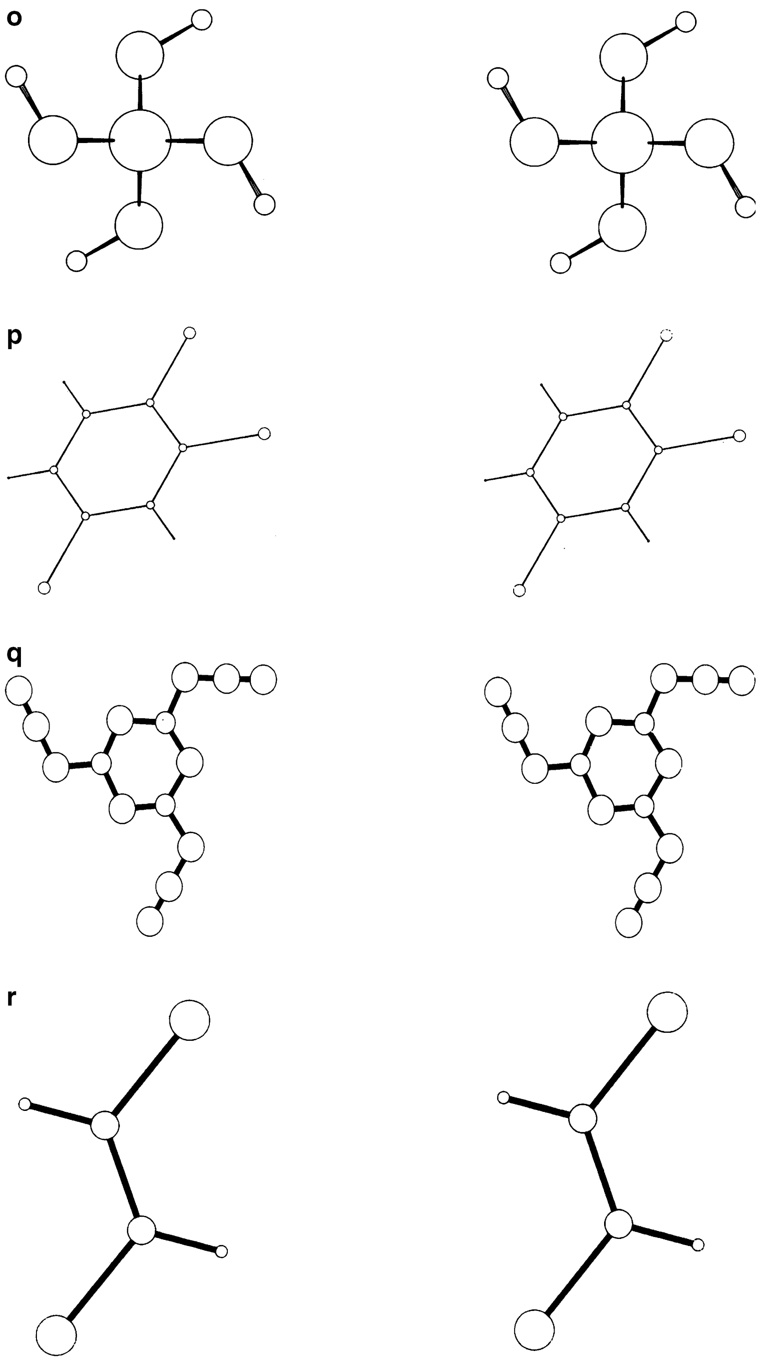


Fig. P1.5 (continued)

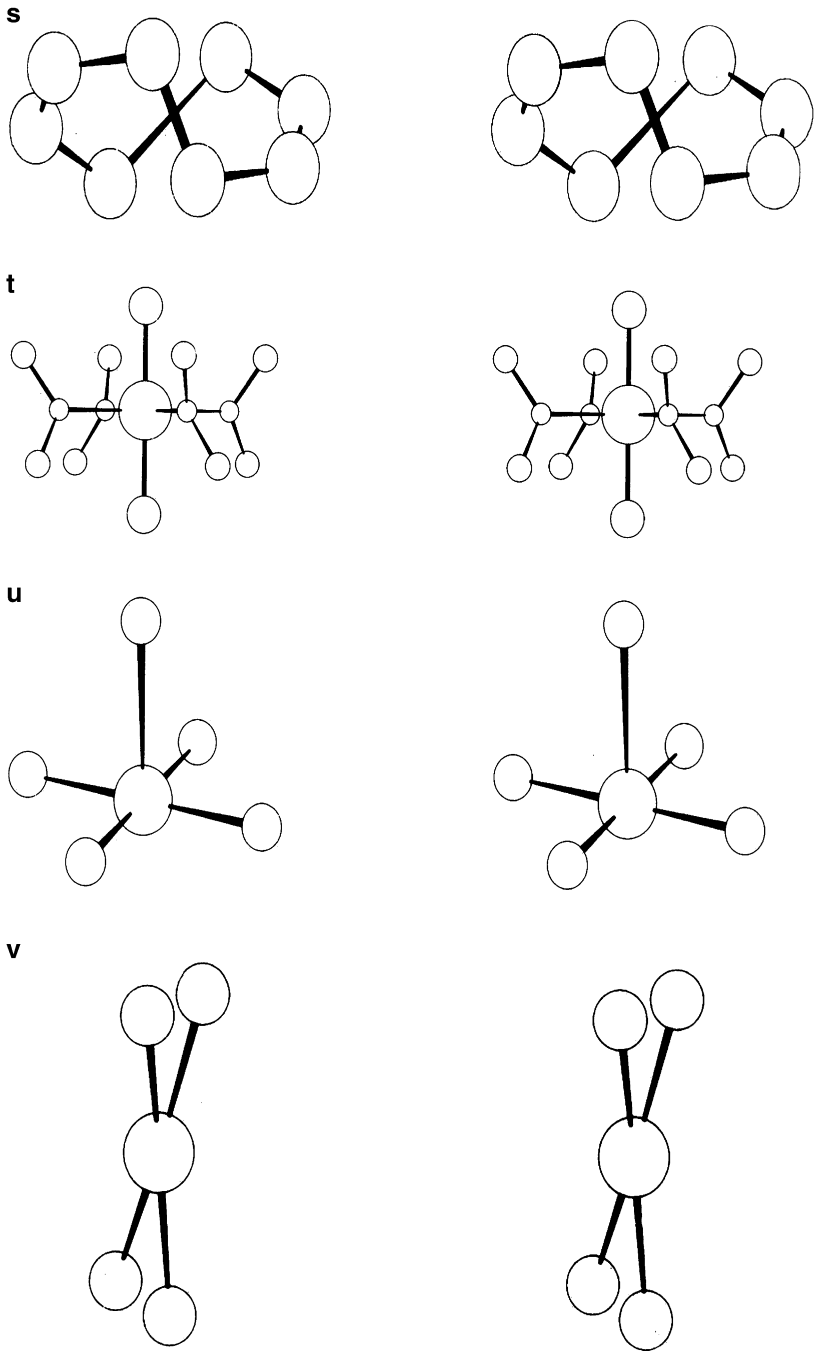


Fig. P1.5 (continued)

Fig. P1.6 Equivalence of i and $-(h + k)$ with Miller–Bravais axes

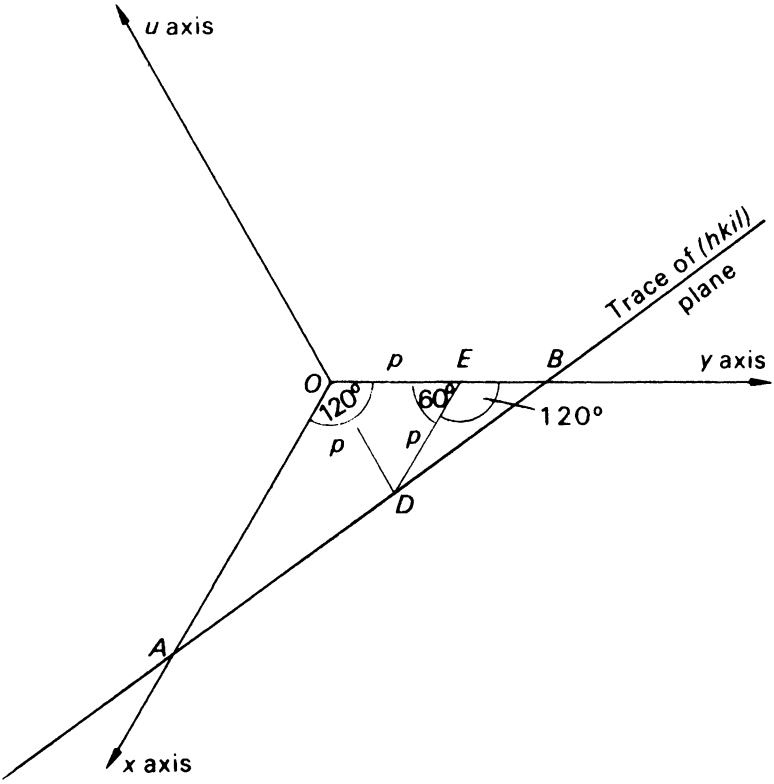
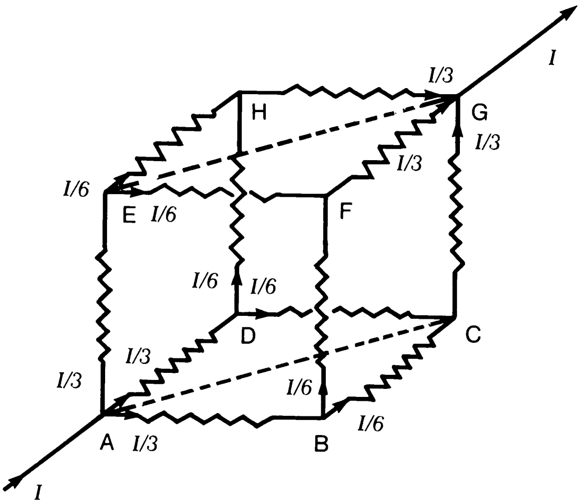


Fig. P1.7 The cube shown consists of twelve 1 Ω resistors; the current I follows a path from A to G



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