

1

Fundamentals

1.1

Ideal Crystals, Real Crystals

Up until a few years ago, crystals were still classified according to their morphological properties, in a similar manner to objects in biology. One often comes across the definition of a crystal as a homogenous space with directionally dependent properties (anisotropy). This is no longer satisfactory because distinctly noncrystalline materials such as glass and plastic may also possess anisotropic properties. Thus a useful definition arises out of the concept of an *ideal crystal* (Fig. 1.1):

An ideal crystal is understood as a space containing a rigid lattice arrangement of uniform atomic cells.

A definition of the lattice concept will be given later. Crystals existing in nature, the *real crystals*, which we will now generally refer to as crystals, very closely approach ideal crystals. They show, however, certain deviations from the rigid lattice arrangement and from the uniform atomic cell structure. The following types of imperfections, i.e., deviations from ideal crystals, may be mentioned:

Imperfections in the uniform structure of the cells. These are lattice vacancies, irregular occupation of lattice sites, errors in chemical composition, deviations from homogeneity by mixed isotopes of certain types

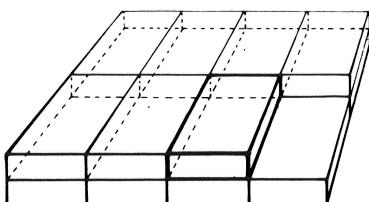


Figure 1.1 Lattice-like periodic arrangement of unit cells.

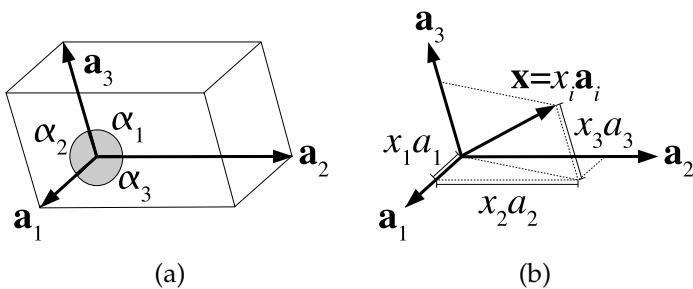


Figure 1.2 (a) Parallelepiped for the definition of a crystallographic reference system and (b) decomposition of a vector into components with respect to the reference system.

of atoms, different excitation states of the building particles (atoms), not only with respect to bonding but also with respect to the position of other building particles (misorientation of building particles).

Imperfections in the lattice structure. These refer to displacement, tilting and twisting of cells, nonperiodic repetition of cells, inhomogeneous distribution of mechanical deformations through thermal stress, sound waves, and external influences such as electric and magnetic fields. The simple fact that crystals have finite dimensions results in a departure from the ideal crystal concept because the edge cells experience a different environment than the inner ones.

At this point we mention that materials exist possessing a structure not corresponding to a rigid lattice-type arrangement of cells. Among these are the so-called quasicrystals and substances in which the periodic repetition of cells is impressed with a second noncommensurable periodicity.

To characterize a crystal we need to make some statements concerning structural defects.

One must keep in mind that not only the growth process but also the complete morphological and physical appearance of the crystal is crucially determined by the structure of the lattice, i.e., the form of the cells as well as the spatial arrangement of its constituents.

A unit cell in the sense used here is a parallelepiped, a space enclosed by three pairs of parallel surfaces (Fig. 1.2). The edges originating from one of the corner points determine, through their mutual positions and length, a *crystallographic reference system*. The edges define the *basis vectors* \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . The angle between the edges are $\alpha_1 = \angle(\mathbf{a}_2, \mathbf{a}_3)$, $\alpha_2 = \angle(\mathbf{a}_1, \mathbf{a}_3)$, $\alpha_3 = \angle(\mathbf{a}_1, \mathbf{a}_2)$. The six quantities $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \alpha_1, \alpha_2, \alpha_3\}$ form the *metric* of the relevant cell and thus the metric of the appropriate crystallographic reference system which is of special significance for the description and calculation of morphological properties. The position of the atoms in the cell, which characterizes the

structure of the corresponding crystal species, is also described in the crystallographic reference system. Directly comprehensible and useful for many questions is the representation of the cell structure by specifying the position of the center of gravity of the atoms in question using so-called parameter vectors. A more detailed description is given by the electron density distribution $\rho(\mathbf{x})$ in the cell determined by the methods of crystal structure analysis. The end of the vector \mathbf{x} runs through all points within the cell.

In an ideal crystal, the infinite space is filled by an unlimited regular repetition of atomistically identical cells in a gap-free arrangement. Vector methods are used to describe such lattices (see below).

1.2

The First Basic Law of Crystallography (Angular Constancy)

The surface of a freely grown crystal is mainly composed of a small number of practically flat surface elements, which, in the following, we will occasionally refer to as faces. These surface elements are characterized by their normals which are oriented perpendicular to the surface elements. The faces are more precisely described by the following:

1. mutual position (orientation),
2. size,
3. form,
4. micromorphological properties (such as cracks, steps, typical microhills, and microcavities).

The orientation of a certain surface element is given through the angles which its normal makes with the normals of the other surface elements. One finds that arbitrary angles do not occur in crystals. In contrast, the first basic law of crystallography applies:

Freely grown crystals belonging to the same ideal crystal, possess a characteristic set of normal angles (law of angular constancy).

The members belonging to the same ideal crystal form a crystal species. The orientation of the surface elements is thus characteristic, not, however, the size ratios of the surface elements.

The law of angular constancy can be interpreted from thermodynamic conditions during crystal growth. Crystals in equilibrium with their mother phase or, during growth only slightly apart from equilibrium, can only develop surface elements F_i possessing a relatively minimal specific surface energy σ_i . σ_i is the energy required to produce the i th surface element from 1 cm² of the boundary surface in the respective mother phase. Only then does

the free energy of the complete system (crystal and mother phase) take on a minimum. The condition for this is

$$\sum F_i \sigma_i = \text{Minimum(Gibbs' condition)},$$

where the numerical value for F_i refers to the size of the i th surface element. From this condition one can deduce Wulff's theorem, which says that the central distances R_i of the i th surface (measured from the origin of growth) are proportional to the surface energy σ_i . According to Gibbs' condition, those surfaces possessing the smallest, specific surface energy are the most stable and largest developed. From simple model calculations, one finds that the less prominent the surface energy becomes, the more densely the respective surface is occupied by building particles effecting strong mutual attraction. The ranking of faces is thus determined by the occupation density. In a lattice, very few surfaces of large occupation density exist exhibiting prominent orientations. This is in accord with the empirical law of angular constancy.

A crude morphological description follows from the concepts *tracht* and *habit*. Tracht is understood as the totality of the existent surface elements and habit as the coarse external appearance of a crystal (e.g., hair shaped, pin shaped, stem shaped, prismatic, columned, leafed, tabular, isometric, etc.).

1.3

Graphical Methods, Stereographic Projection

For the practical handling of morphological findings, it is useful to project the details, without loss of information, onto a plane. Imagine surface normals originating from the center of a sphere intersecting the surface of the sphere. The points of intersection P_i represent an image of the mutual orientation of the surface elements. The surface dimensions are uniquely determined by the central distances R_i of the i th surface from the center of the sphere (Fig. 1.3). One now projects the points of intersection on to a flat piece of

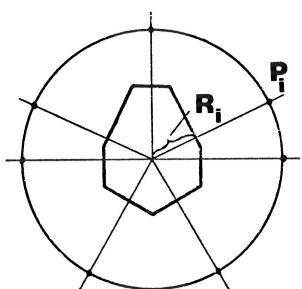


Figure 1.3 Normals and central distances.

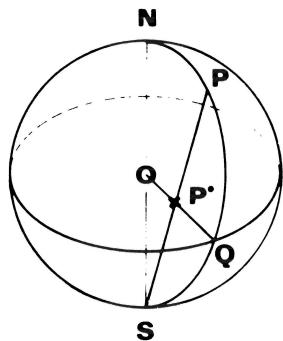


Figure 1.4 Stereographic projection P' of a point P .

paper, the plane of projection. Thus each point on the sphere is assigned a point on the plane of projection. In the study of crystallography, the following projections are favored:

1. the stereographic projection,
2. the gnomonic projection,
3. the orthogonal projection (parallel projection).

Here, we will only discuss the stereographic projection which turns out to be a useful tool in experimental work with crystals. On a sphere of radius R an arbitrary diameter is selected with intersection points N (north pole) and S (south pole). The plane normal to this diameter at the center of the sphere is called the equatorial plane. It is the projection plane and normally the drawing plane. The projection point P' belonging to the point P is the intersection point of the line PS through the equatorial plane (Fig. 1.4).

The relation between P and P' is described with the aid of a coordinate system. Consider three vectors a_1, a_2 , and a_3 originating from a fixed point, the origin of the coordinate system. These we have already met as the edges of the elementary cell. The three vectors shall not lie in a plane (not coplanar, Fig. 1.2b). The lengths of a_i ($i = 1, 2, 3$) and their mutual positions, fixed by the angles α_i , are otherwise arbitrary. One reaches the point P with coordinates (x_1, x_2, x_3) by starting at the origin O and going in the direction a_1 a distance $x_1 a_1$, then in the direction a_2 a distance $x_2 a_2$, and finally in the direction a_3 by the distance $x_3 a_3$. The same end point P is reached by taking any other order of paths.

Each point on the sphere is now fixed by its coordinates (x_1, x_2, x_3) . The same applies to the point P' with coordinates (x'_1, x'_2, x'_3) . For many crystallographic applications it is convenient to introduce a prominent coordinate system, the *Cartesian coordinate system*. Here, the primitive vectors have a length

of one unit in the respective system of measure and are perpendicular to each other ($\alpha_i = 90^\circ$). We denote these vectors by e_1, e_2, e_3 . The origin is placed in the center of the sphere and e_3 points in the direction ON . The vectors e_1 and e_2 accordingly lie in the equatorial plane. It follows always that $x_3 = 0$. If P is a point on the sphere, then its coordinates obey the spherical equation $x_1^2 + x_2^2 + x_3^2 = R^2$. For $R = 1$ one obtains the following expressions from the relationships in Fig. 1.5:

$$\dot{x_1} = \frac{x_1}{1+x_3}, \quad \dot{x_2} = \frac{x_2}{1+x_3}.$$

These transform to

$$x_1 = \frac{2\dot{x}_1}{1+\dot{x}_1^2+\dot{x}_2^2}, \quad x_2 = \frac{2\dot{x}_2}{1+\dot{x}_1^2+\dot{x}_2^2}, \quad x_3 = \frac{1-\dot{x}_1^2-\dot{x}_2^2}{1+\dot{x}_1^2+\dot{x}_2^2}.$$

In polar coordinates, we define a point by its geographical longitude η and latitude ($90^\circ - \xi$). Therefore, from Fig. 1.5 we have

$$x_3 = \cos \xi, \quad r = OP^* = \sin \xi, \quad x_1 = r \cos \eta = \sin \xi \cos \eta, \\ x_2 = r \sin \eta = \sin \xi \sin \eta.$$

Thus

$$\dot{x_1} = \frac{\sin \xi \cos \eta}{1+\cos \xi}, \quad \dot{x_2} = \frac{\sin \xi \sin \eta}{1+\cos \xi},$$

and

$$\tan \eta = \frac{x_2}{x_1} = \frac{\dot{x}_2}{\dot{x}_1} \quad \text{and} \quad \cos \xi = x_3 = \frac{1-\dot{x}_1^2-\dot{x}_2^2}{1+\dot{x}_1^2+\dot{x}_2^2}.$$

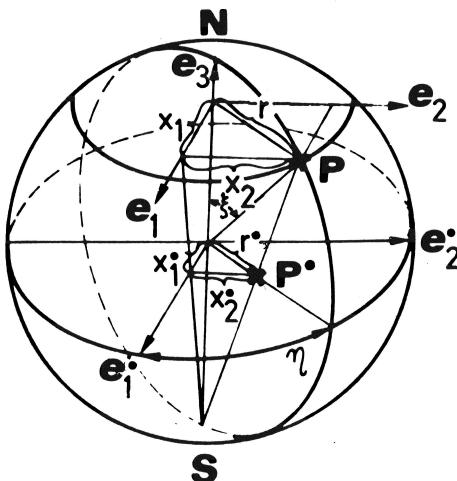


Figure 1.5 Stereographic projection.

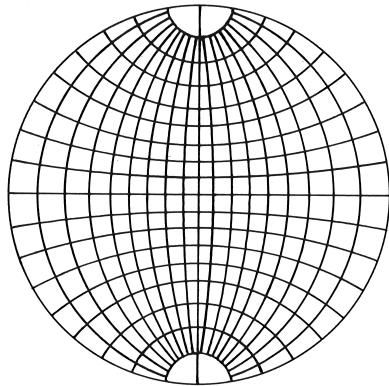


Figure 1.6 Wulff's net.

The stereographic projection is distinguished by two properties, namely the projections are circle true and angle true. All circles on the surface of the sphere project as circles in the plane of projection and the angle of intersection of two curves on the sphere is preserved in the plane of projection. This can be proved with the transformation equations above. In practice, one uses a Wulff net in the equatorial plane, which is a projection of one half of the terrestrial globe with lines of longitude and latitude (Fig. 1.6). Nearly all practical problems of the geometry of face normals can be solved to high precision using a compass and ruler. Frequently, however, it suffices only to work with the Wulff net. The first basic task requires drawing the projection point $P^* = (x_1^*, x_2^*)$ of the point $P = (x_1, x_2, x_3)$ (Fig. 1.7). Here, the circle on the sphere passing through the points P , N , and S plays a special role (great circle PSN). It appears rotated about e_3 with respect to the circle passing through the end point of e_1 and through N and S by an angle η , known from $\tan \eta = x_2/x_1$. The projection of this great circle, on which P^* also lies, is a line in the projection plane going through the center of the equatorial circle and point Q , the

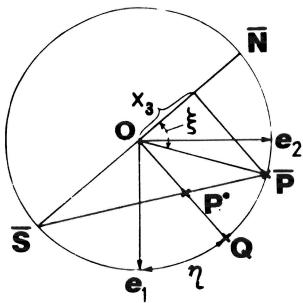


Figure 1.7 Construction of $P^*(x_1^*, x_2^*)$ from $P(x_1, x_2, x_3)$.

intersection point of the great circle with the equatorial circle. The point Q remains invariant in the stereographic projection. It has an angular distance of η from the end point of e_1 . If one now tilts the great circle PSN about the axis OQ into the equatorial plane by 90° one can then construct P' directly as the intersection point of the line OQ with the line $\bar{P}\bar{S}$. \bar{P} and \bar{S} are the points P and S after tilting. One proceeds as follows to obtain a complete stereographic projection of an object possing several faces: the normal of the first face F_1 is projected parallel to e_1 , so that its projection at the end point of e_1 lies on the equatorial circle. The normal of F_2 is also projected onto the equatorial circle at an angular distance of the measured angle between the normals of F_1 and F_2 . For each further face F_3 , etc. the angles which their normals make with two other normals, whose projections already exist, might be known. Denote the angles between the normals of F_i and F_j by ψ_{ij} . The intersection point P_3 of face F_3 then lies on the small circles having an angular distance ψ_{13} from P_1 and an angular distance ψ_{23} from P_2 . Their projections can be easily constructed. One of the two intersection points of these projections is then the sought after the projection point P'_3 . The reader is referred to standard books on crystal geometry to solve additional problems, especially the determination of angles between surface normals whose stereographic projections already exist.

1.4

The Second Basic Law of Crystallography (Law of Rational Indices)

Consider three arbitrary faces F_1 , F_2 , F_3 of a freely grown crystal with their associated normals h_1 , h_2 , h_3 . The normals shall not lie in a plane (nontautozonal). Two faces respectively form an intercept edge a_i (Fig. 1.8). The three edge directions define a crystallographic reference system.

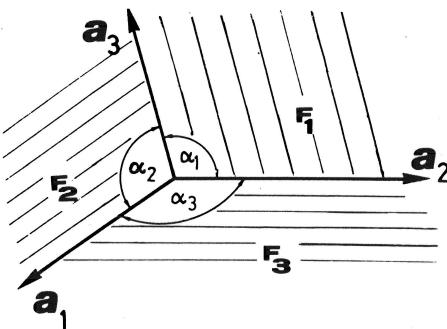


Figure 1.8 Fixing a crystallographic reference system from three non-tautozonal faces.

The system is

$$\begin{aligned}\mathbf{a}_1 &\parallel \text{edge}(F_2, F_3), \\ \mathbf{a}_2 &\parallel \text{edge}(F_3, F_1), \\ \mathbf{a}_3 &\parallel \text{edge}(F_1, F_2),\end{aligned}$$

in other words $\mathbf{a}_i \parallel \text{edge}(F_j, F_k)$. The indices i, j, k run through any triplets of the cyclic sequence 123123123

\mathbf{a}_i are perpendicular to the normals \mathbf{h}_j and \mathbf{h}_k since they belong to both surfaces F_j and F_k . On the other hand, \mathbf{a}_j and \mathbf{a}_k span the surfaces F_i with their normals \mathbf{h}_i . The system of \mathbf{a}_i follows from the system of \mathbf{h}_i and, conversely, the system of \mathbf{h}_i from that of \mathbf{a}_i by the operation of setting one of these vectors perpendicular to two vectors of the other respective system. Systems which reproduce after two operations are called *reciprocal systems*. The edges \mathbf{a}_i thus form a system reciprocal to the system of \mathbf{h}_i and vice versa.

The crystallographic reference system is first fixed by the three angles $\alpha_i =$ angle between \mathbf{a}_j and \mathbf{a}_k . Furthermore, we require the lengths $|\mathbf{a}_i| = a_i$ for a complete description of the system. This then corresponds to our definition of the metric which we introduced previously. We will return to the determination of the lengths and length ratios later. Moreover, the angles α_i can be easily read from a stereographic projection of the three faces F_i . In the same manner, the projections of the intercept points of the edges \mathbf{a}_i and thus their orientation can be easily determined.

We consider now an arbitrary face with the normal \mathbf{h} in the crystallographic basic system of vectors \mathbf{a}_i (Fig. 1.9). The angles between \mathbf{h} and \mathbf{a}_i are denoted by θ_i . We then have

$$\cos \theta_1 : \cos \theta_2 : \cos \theta_3 = \frac{1}{OA_1} : \frac{1}{OA_2} : \frac{1}{OA_3} = \frac{1}{m_1 a_1} : \frac{1}{m_2 a_2} : \frac{1}{m_3 a_3},$$

where we use the Weiss zone law to set $OA_i = m_i a_i$. The second basic law of crystallography (law of rational indices) now applies.

Two faces of a freely grown crystal with normals \mathbf{h}^I and \mathbf{h}^{II} , which enclose angles θ_i^I and θ_i^{II} with the crystallographic basic vectors \mathbf{a}_i , can be expressed as the ratios of cosine values to the ratios of integers

$$\frac{\cos \theta_1^I}{\cos \theta_1^{II}} : \frac{\cos \theta_2^I}{\cos \theta_2^{II}} : \frac{\cos \theta_3^I}{\cos \theta_3^{II}} = \frac{m_1^{II}}{m_1^I} : \frac{m_2^{II}}{m_2^I} : \frac{m_3^{II}}{m_3^I}.$$

m_i/m_j are thus rational numbers. The law of rational indices heightens the law of angular constancy to such an extent that, for each crystal species, the characteristic angles between the face normals are subject to an inner rule of conformity. This is a morphological manifestation of the lattice structure of crystals. A comprehensive confirmation of the law of rational indices on numerous natural and synthetic crystals was given by René Juste Hauy (1781).

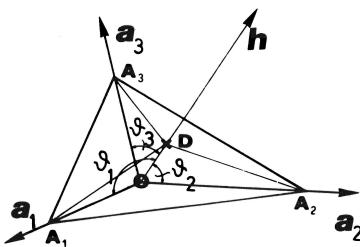


Figure 1.9 Axial intercepts and angles of a face having the normal \mathbf{h} .

It was found advantageous to introduce the *Miller Indices* (1839) $h_i = t/m_i$ instead of the Weiss indices m_i which fully characterize the position of a face. t is an arbitrary factor. The face in question is then symbolized by $\mathbf{h} = (h_1 h_2 h_3)$. The so-called axes' ratio $a_1 : a_2 : a_3$ now allows one to specify, by an arbitrary choice of indices, a further face F_4 defined by $\mathbf{h}^{(4)} = (h_1^{(4)} h_2^{(4)} h_3^{(4)})$. For each face then

$$\cos \theta_1 : \cos \theta_2 : \cos \theta_3 = \frac{h_1}{a_1} : \frac{h_2}{a_2} : \frac{h_3}{a_3}.$$

If the angles of the fourth face are known, one obtains the axes ratio

$$a_1 : a_2 : a_3 = \frac{h_1^{(4)}}{\cos \theta_1^{(4)}} : \frac{h_2^{(4)}}{\cos \theta_2^{(4)}} : \frac{h_3^{(4)}}{\cos \theta_3^{(4)}}.$$

Moreover, the faces F_1 , F_2 , and F_3 are specified by the Miller indices (100), (010), and (001), respectively.

Now the path is open to label further faces. One measures the angles θ_i and obtains

$$h_1 : h_2 : h_3 = a_1 \cos \theta_1 : a_2 \cos \theta_2 : a_3 \cos \theta_3.$$

As long as morphological questions are in the foreground, one is allowed to multiply through with any number t , so that for h_i the smallest integers, with no common factor, are obtained satisfying the ratio.

1.5 Vectors

1.5.1 Vector Addition

Vectors play an important and elegant role in crystallography. They ease the mathematical treatment of geometric and crystallographic questions. We de-

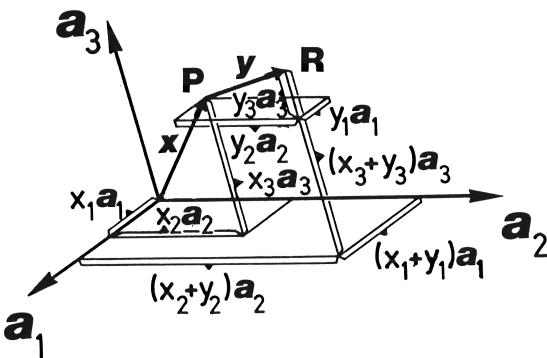


Figure 1.10 Addition of two vectors x and y .

fine a vector by the specifications used earlier for the construction of a point P with coordinates (x_1, x_2, x_3) and a second point Q with coordinates (y_1, y_2, y_3) . Now consider the point R with the coordinates $(x_1 + y_1, x_2 + y_2, x_3 + y_3)$ (Fig. 1.10). We reach R after making the construction (x_1, x_2, x_3) and finally attaching the distances y_1a_1 , y_2a_2 and y_3a_3 directly to P . One can describe this construction of R as the addition of distances OP and OQ . We now assign to the distance OP the vector x , to the distance OQ the vector y , and to the distance OR the vector z . We then have $x + y = z$. The coordinates are given by $x_i + y_i = z_i$. Quantities which can be added in this manner are called vectors. The order of attaching the vectors is irrelevant.

A vector is specified by its direction and length. Usually it is graphically represented by an arrow over the symbol. Here we write vectors in boldface italic letters. The length of the vector x is called the magnitude of x , denoted by the symbol $|x|$. Vectors can be multiplied with arbitrary numbers as is obvious from their component representation. Each component is multiplied with the corresponding factor. A vector of length one is called a unit vector. We obtain a unit vector e_x in the direction x by multiplication with $1/x$ according to $e_x = x/x$.

From the above definition we now formulate the following laws of addition:

1. commutative law: $z = x + y = y + x$ (Fig. 1.11),
2. associative law: $x + (y + z) = (x + y) + z$,
3. distributive law: $q(x + y) = qx + qy$.

The validity of these three laws shall be checked in all further discussions on vector combinations.

Since $-x$ can be taken as a vector antiparallel to x with the same length ($-x + x = 0$), we have the rule for vector subtraction $z = x - y$ (Fig. 1.11).

Examples for the application of vector addition are as follows.

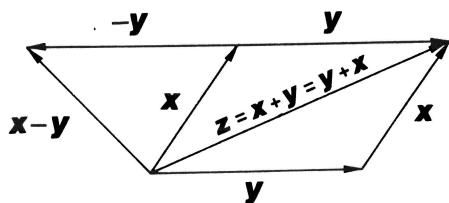


Figure 1.11 Commutative law of vector addition; vector subtraction.

1. *Representation of a point lattice* by $\mathbf{r} = r_1 \mathbf{a}_1 + r_2 \mathbf{a}_2 + r_3 \mathbf{a}_3$, where r_i run through the integer numbers. The end point of \mathbf{r} then sweeps through all lattice points. We use the symbol $[[r_1 r_2 r_3]]$ for a lattice point and for a lattice row, also represented by \mathbf{r} , the symbol $[r_1 r_2 r_3]$. As before, we denote any point with coordinates x_i by (x_1, x_2, x_3) .
2. *Decomposition of a vector into components* according to a given reference system. One places through the end points of \mathbf{x} planes running parallel to the planes spanned by the vectors \mathbf{a}_j and \mathbf{a}_k . These planes truncate, on the coordinate axes, the intercepts $x_i \mathbf{a}_i$ thus giving the coordinates (x_1, x_2, x_3) . This decomposition is unique. We thus construct the parallelepiped with edges parallel to the vectors \mathbf{a}_i and with space diagonals \mathbf{x} (Fig. 1.12).
3. *The equation of a line* through the end points of the two vectors \mathbf{x}_0 and \mathbf{x}_1 is given by $\mathbf{x} = \mathbf{x}_0 + \lambda(\mathbf{x}_1 - \mathbf{x}_0)$. λ is a free parameter.
4. *The equation of a plane* through the end points of \mathbf{x}_0 , \mathbf{x}_1 , and \mathbf{x}_2 is given by $\mathbf{x} = \mathbf{x}_0 + \lambda(\mathbf{x}_1 - \mathbf{x}_0) + \mu(\mathbf{x}_2 - \mathbf{x}_0)$. λ and μ are free parameters. In component representation, these three equations correspond to the equation of a plane in the form $u_0 + u_1 x_1 + u_2 x_2 + u_3 x_3 = 0$, which one obtains after eliminating λ and μ (Fig. 1.13). If the components of the three vectors

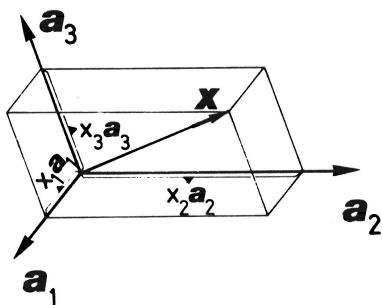


Figure 1.12 Decomposition of a vector into components of a given reference system.

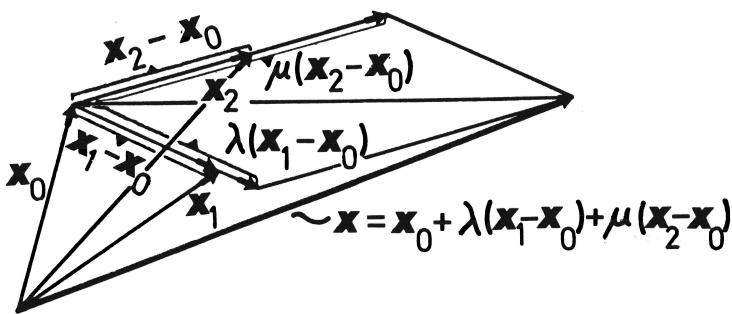


Figure 1.13 Equation of a plane through three points.

have integer values, i.e., we are dealing with a lattice plane, then u_i take on integer values.

1.5.2

Scalar Product

Linear vector functions hold a special place with regard to the different possibilities of vector combinations. They are, like all other combinations of vectors, invariant with respect to the coordinate system in which they are viewed. Linear vector functions are proportional to the lengths of the vectors involved. The simplest and especially useful vector function is represented by the scalar product (Fig. 1.14):

The scalar product $x \cdot y = |x||y| \cos(x, y)$ is equal to the projection of a vector on another vector, multiplied by the length of the other vector.

For simplification we use the symbol (x, y) for the angle between x and y . The commutative law $x \cdot y = y \cdot x$ is satisfied as well as the associative and distributive laws, the latter in the form $x \cdot (y + z) = x \cdot y + x \cdot z$.

The scalar product can now be determined with the aid of the distributive law when the respective vectors in component representation exist in a basic system of known metric. We have $x = \sum x_i a_i = x_i a_i$ (one sums over i , here

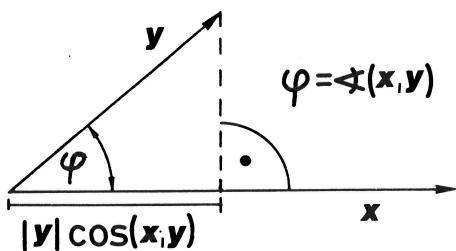


Figure 1.14 Definition of the scalar product of two vectors.

from $i = 1$ to 3 ; Einstein summation convention!) and $\mathbf{y} = y_j \mathbf{a}_j$. Then $\mathbf{x} \cdot \mathbf{y} = (x_i \mathbf{a}_i) \cdot (y_j \mathbf{a}_j) = x_i y_j (\mathbf{a}_i \cdot \mathbf{a}_j)$. The products $\mathbf{a}_i \cdot \mathbf{a}_j$ are, as assumed, known ($\mathbf{a}_i \cdot \mathbf{a}_j = a_i^2$ for $i = j$ and $\mathbf{a}_i \cdot \mathbf{a}_j = a_i a_j \cos \alpha_k$ for $i \neq j, k \neq i, j$).

Examples for the application of scalar products are as follows.

1. *Calculating the length of a vector.* We have

$$\mathbf{x} \cdot \mathbf{x} = \mathbf{x}^2 = |\mathbf{x}|^2 = x_i x_j (\mathbf{a}_i \cdot \mathbf{a}_j).$$

2. *Calculating the angle between two vectors \mathbf{x} and \mathbf{y} .* From the definition of the scalar product it follows that $\cos(\mathbf{x}, \mathbf{y}) = (\mathbf{x} \cdot \mathbf{y}) / (|\mathbf{x}| |\mathbf{y}|)$.
3. *Determining whether two vectors are mutually perpendicular.* The condition for two vectors of nonzero lengths is $\mathbf{x} \cdot \mathbf{y} = 0$.
4. *Equation of a plane perpendicular to the vector \mathbf{h} and passing through the end point of \mathbf{x}_0 :* $(\mathbf{x} - \mathbf{x}_0) \cdot \mathbf{h} = 0$.
5. *Decomposing a vector \mathbf{x} into components of a coordinate system.* Assume that the angles δ_i (angles between \mathbf{x} and \mathbf{a}_i) are known. Then one also knows the scalar products $\mathbf{x} \cdot \mathbf{a}_i = |\mathbf{x}| a_i \cos \delta_i$. This gives the following system of equations:

$$\begin{aligned}\mathbf{x} &= x_i \mathbf{a}_i \\ \mathbf{x} \cdot \mathbf{a}_j &= x_i \mathbf{a}_i \cdot \mathbf{a}_j \quad \text{for } j = 1, 2, 3.\end{aligned}$$

The system for the sought after components x_i always has a solution when \mathbf{a}_i span a coordinate system.

1.5.3

Vector Product

Two nonparallel vectors \mathbf{x} and \mathbf{y} fix a third direction, namely that of the normals on the plane spanned by \mathbf{x} and \mathbf{y} . The vector product of \mathbf{x} and \mathbf{y} generates a vector in the direction of these normals.

The vector product of \mathbf{x} and \mathbf{y} , spoken “ \mathbf{x} cross \mathbf{y} ” and written as $\mathbf{x} \times \mathbf{y}$, is the vector perpendicular to \mathbf{x} and \mathbf{y} with a length equal to the area of the parallelogram spanned by \mathbf{x} and \mathbf{y} , thus $|\mathbf{x} \times \mathbf{y}| = |\mathbf{x}| |\mathbf{y}| \sin(\mathbf{x}, \mathbf{y})$. The three vectors \mathbf{x} , \mathbf{y} , and $\mathbf{x} \times \mathbf{y}$ form a right-handed system (Fig. 1.15). The vector $\mathbf{x} \times \mathbf{y}$ lies perpendicular to the plane containing \mathbf{x} and \mathbf{y} and in such a direction that a right-handed screw driven in the direction of $\mathbf{x} \times \mathbf{y}$ would carry \mathbf{x} into \mathbf{y} through a clockwise rotation around the smaller angle between \mathbf{x} and \mathbf{y} .

The vector product is not commutative. In contrast, we have $\mathbf{x} \times \mathbf{y} = -\mathbf{y} \times \mathbf{x}$. From the definition, one immediately recognizes the validity of the associative law. It is more difficult to prove the distributive law $\mathbf{x} \times (\mathbf{y} + \mathbf{z}) =$

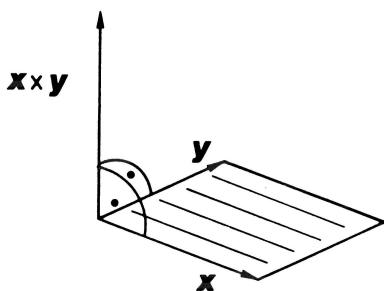


Figure 1.15 Vector product.

$x \times y + x \times z$. We refer the reader to standard textbooks like *Kristallgeometrie* for a demonstration.

For two vectors specified in the crystallographic reference system, i.e., $x = x_i a_i$ and $y = y_j a_j$, we find

$$\begin{aligned} x \times y &= (x_i a_i) \times (y_j a_j) = (x_2 y_3 - x_3 y_2) a_2 \times a_3 + (x_3 y_1 - x_1 y_3) a_3 \times a_1 \\ &\quad + (x_1 y_2 - x_2 y_1) a_1 \times a_2. \end{aligned} \quad (1.1)$$

Thus the vector products of the basis vectors appear. These we have met before. They are the normals on the three basic faces F_i . It is found useful to introduce these vectors as the base vectors of a new reference system, the so-called reciprocal system (see Section 1.3). For this purpose we need to normalize the length of the new vectors so that the reciprocal of the reciprocal system is in agreement with the basic system. This is accomplished with the following definition of the basic vectors a_i^* of the *reciprocal system*

$$a_i^* = \frac{1}{V(a_1, a_2, a_3)} a_j \times a_k,$$

where i, j, k should observe a cyclic sequence of 1, 2, 3, 1, 2, 3, ... $V(a_1, a_2, a_3)$ is the volume of the parallelepiped spanned by the basic vectors. a_i^* is spoken as "a-i-star."

Correspondingly, for the basic vectors we have $a_i = a_j^* \times a_k^* / V(a_1^*, a_2^*, a_3^*)$. The proof that $(a_i^*)^* = a_i$ is given below.

To calculate V we use the so-called *scalar triple product* of three vectors:

$$\begin{aligned} V &= \text{base surface times the height of the parallelepiped} \\ &= (y \times z) \cdot x = |y| |z| |\sin(y, z)| e \cdot x. \end{aligned}$$

Here e is the unit vector of $y \times z$. If one considers another basic face, then the same result is found, i.e.,

$$(y \times z) \cdot x = (x \times y) \cdot z = (z \times x) \cdot y = x \cdot (y \times z) \quad \text{and so on.}$$

The order of the factors may be cyclically interchanged as well as the operations of the scalar and the vectorial products. A change in the cyclic order results in a change of sign of the product. For $\mathbf{x} \cdot (\mathbf{y} \times \mathbf{z})$ we use the notation $[\mathbf{x}, \mathbf{y}, \mathbf{z}]$. Thus

$$V(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3].$$

The vector product can be calculated formally using the rules for the calculation of determinants. A third-order determinant $D(u_{ij})$ with the nine quantities u_{ij} has the solution

$$\begin{aligned} D(u_{ij}) &= \begin{vmatrix} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{vmatrix} \\ &= u_{11}(u_{22}u_{33} - u_{23}u_{32}) - u_{12}(u_{21}u_{33} - u_{23}u_{31}) \\ &\quad + u_{13}(u_{21}u_{32} - u_{22}u_{31}). \end{aligned}$$

Now using the vectors $\mathbf{x} = x_i \mathbf{a}_i$ and $\mathbf{y} = y_i \mathbf{a}_i$ we construct the corresponding scheme and obtain

$$\mathbf{x} \times \mathbf{y} = V(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) \begin{vmatrix} \mathbf{a}_1^* & \mathbf{a}_2^* & \mathbf{a}_3^* \\ x_1 & x_2 & y_3 \\ y_1 & y_2 & y_3 \end{vmatrix}.$$

V can be directly calculated from the scalar products of the basic vectors with the aid of Grams determinant. The solution is

$$V^2(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) = \begin{vmatrix} \mathbf{a}_1 \cdot \mathbf{a}_1 & \mathbf{a}_1 \cdot \mathbf{a}_2 & \mathbf{a}_1 \cdot \mathbf{a}_3 \\ \mathbf{a}_2 \cdot \mathbf{a}_1 & \mathbf{a}_2 \cdot \mathbf{a}_2 & \mathbf{a}_2 \cdot \mathbf{a}_3 \\ \mathbf{a}_3 \cdot \mathbf{a}_1 & \mathbf{a}_3 \cdot \mathbf{a}_2 & \mathbf{a}_3 \cdot \mathbf{a}_3 \end{vmatrix} = a_1^2 a_2^2 a_3^2 \begin{vmatrix} 1 & \cos \alpha_3 & \cos \alpha_2 \\ \cos \alpha_3 & 1 & \cos \alpha_1 \\ \cos \alpha_2 & \cos \alpha_1 & 1 \end{vmatrix}.$$

The vector product has three important applications:

1. Parallel vectors \mathbf{x} and \mathbf{y} form a vanishing vector product $\mathbf{x} \times \mathbf{y} = 0$.
2. The normals \mathbf{h} of the plane spanned by the vectors \mathbf{x} and \mathbf{y} are parallel to $\mathbf{x} \times \mathbf{y}$.
3. The intercept edge \mathbf{u} of two planes with the normals \mathbf{h} and \mathbf{g} is parallel to $\mathbf{h} \times \mathbf{g}$.

The fundamental importance of the reciprocal system for crystallographic work is made clear by the following statement:

A normal \mathbf{h} with the Miller indices $(h_1 h_2 h_3)$ has the component representation $\mathbf{h} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^*$.

As proof, we form the scalar product of this equation with \mathbf{a}_i and obtain $\mathbf{h} \cdot \mathbf{a}_i = h_i$, where h_i are rational numbers. From the definition of the scalar

product it follows that $\mathbf{h} \cdot \mathbf{a}_i = |\mathbf{h}| |\mathbf{a}_i| \cos \theta_i$ and thus $\cos \theta_1 : \cos \theta_2 : \cos \theta_3 = h_1/a_1 : h_2/a_2 : h_3/a_3$, i.e., the corresponding face obeys the law of rational indices and h_i correspond to the reciprocal axial intercepts.

Now we consider the length of \mathbf{h} . The length is related to the distance $OD = d_h$ of the plane from the origin (Fig. 1.9). We have $\cos \theta_i = OD/OA_i = d_h/(m_i a_i) = d_h h_i/a_i$ with $m_i = 1/h_i$. One does not sum over i ! On the other hand, from $\mathbf{h} \cdot \mathbf{a}_i = h_i = |\mathbf{h}| a_i \cos \theta_i$ we get the value $\cos \theta_i = h_i/|\mathbf{h}| a_i$. Thus the lattice plane distance is $OD = d_h = 1/|\mathbf{h}|$. It may be calculated from the so-called quadratic form $(1/d_h)^2 = |\mathbf{h}|^2 = (h_i \mathbf{a}_i^*) \cdot (h_j \mathbf{a}_j^*)$. Here we encounter other triple products which we will now turn to.

1.5.4

Vector Triple Product

The scalar triple product of three vectors $[\mathbf{x}, \mathbf{y}, \mathbf{z}]$ was our first acquaintance with triple products. A further expression is the vector product of a vector with a vector product given by the following theorem, which is called *Entwicklungsatz*:

$$\mathbf{x} \times (\mathbf{y} \times \mathbf{z}) = (\mathbf{x} \cdot \mathbf{z})\mathbf{y} - (\mathbf{x} \cdot \mathbf{y})\mathbf{z}.$$

Applications of the commutability of scalar and vector multiplication are as follows.

1. Scalar product of two vector products

$$(\mathbf{u} \times \mathbf{v}) \cdot (\mathbf{x} \times \mathbf{y}) = \mathbf{u} \cdot \{\mathbf{v} \times (\mathbf{x} \times \mathbf{y})\} = (\mathbf{u} \cdot \mathbf{x})(\mathbf{v} \cdot \mathbf{y}) - (\mathbf{u} \cdot \mathbf{y})(\mathbf{v} \cdot \mathbf{x}),$$

2. Vector product of two vector products

$$(\mathbf{u} \times \mathbf{v}) \times (\mathbf{x} \times \mathbf{y}) = \{(\mathbf{u} \times \mathbf{v}) \cdot \mathbf{y}\}\mathbf{x} - \{(\mathbf{u} \times \mathbf{v}) \cdot \mathbf{x}\}\mathbf{y} = [\mathbf{u}, \mathbf{v}, \mathbf{y}]\mathbf{x} - [\mathbf{u}, \mathbf{v}, \mathbf{x}]\mathbf{y}.$$

With the aid of these identities it is easy to prove that $V(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*) = 1/V(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$. For the metric of the reciprocal system we have

$$a_i^* = a_j a_k \sin \alpha_i / V(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$$

and

$$a_1^* : a_2^* : a_3^* = \sin \alpha_1/a_1 : \sin \alpha_2/a_2 : \sin \alpha_3/a_3$$

as well as

$$\cos \alpha_k^* = \frac{\cos \alpha_i \cos \alpha_j - \cos \alpha_k}{\sin \alpha_i \sin \alpha_j},$$

with $i \neq j \neq k \neq i$.

1.6

Transformations

Often it is practical to turn to another reference system that, e.g., is more adapted to the symmetry of the respective crystal or is easier to handle. Let us designate the basic vectors of the old system with \mathbf{a}_i and those of the new system with A_i . Correspondingly, we write all quantities in the new system with capital letters.

We are now confronted with the following questions:

1. How do we get to the new basic vectors from the old ones, i.e., what form do the functions $A_i(\mathbf{a}_j)$ have?
2. What do the old basic vectors look like in the new system, i.e., what form has the inverse transformation $\mathbf{a}_i(A_j)$?
3. How do position vectors transform in the basic system $\mathbf{x} = x_i \mathbf{a}_i = \mathbf{X} = X_i A_i$ and what form do the functions $X_i(x_j)$ have?
4. How does one get the inverse transformation $x_i(\mathbf{X}_j)$?
5. How do position vectors transform in the reciprocal system $\mathbf{h} = h_i \mathbf{a}_i^* = H_i A_i^*$ and what form do the functions $H_i(h_j)$ have?
6. What form does the inverse transformation $h_i(H_j)$ have?

To (1) imagine that the basic vectors of the new system are decomposed into components of the old system; thus $A_i = u_{ij} \mathbf{a}_j$. Decomposition is possible with the aid of the scalar products $\mathbf{a}_i \cdot A_j$. For that purpose, the length of the new basic vectors and the angle between \mathbf{a}_i and A_j must be known. We collect the resulting u_{ij} in the transformation matrix U ; thus

$$U = (u_{ij}) = \begin{pmatrix} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{pmatrix}.$$

To (2) the inverse transformation is given by $\mathbf{a}_i = U_{ij} A_j = U_{ij} u_{jk} \mathbf{a}_k$. This means $U_{ij} u_{jk} = 1$ for $i = k$ and $= 0$ for $i \neq k$. A similar expression is known from the expansion of a determinant $D(u_{ij}) = u_{jk} U'_{ij}$ with $U'_{ij} = (-1)^{i+j} A_{ji}$ for $i = k$ and $U'_{ij} = 0$ for $i \neq k$. Here, $D(u_{ij})$ is the determinant of the transformation matrix and A_{ji} is the subdeterminant (adjunct) after eliminating the j th row and i th column. Thus $U_{ij} = (-1)^{i+j} A_{ji} / D(u_{ij})$. We call $(U_{ij}) = U^{-1} = (u_{ij})^{-1}$ the inverse matrix of (u_{ij}) .

To (3) in the basic system we have $\mathbf{x} = x_i \mathbf{a}_i$ and with $\mathbf{a}_i = U_{ij} A_j$ we find $\mathbf{x} = x_i U_{ij} A_j = X_j A_j$, i.e., $X_i = U_{ji} x_j$ (after interchanging the indices). The

components of the position vector x are transformed with the transposed inverse matrix $(U_{ij})^T = (U_{ji})$.

To (4) we have $x = X_i A_i = X_i u_{ij} a_j = x_j a_j$ and thus $x_i = u_{ji} X_j$. The transposed transformation matrix is used for the inverse transformation.

To (5) the position vector in the reciprocal system is $\mathbf{h} = h_j \mathbf{a}_j^* = H_i \mathbf{A}_i^*$. Scalar multiplication with A_i gives $A_i \cdot \mathbf{h} = H_i = u_{ij} \mathbf{a}_j \cdot (h_k \mathbf{a}_k^*) = u_{ij} h_j$. Because $\mathbf{a}_j \cdot \mathbf{a}_k^* = 0$ for $j \neq k$ and $= 1$ for $j = k$ it follows that $H_i = u_{ij} h_j$, i.e., the Miller indices transform like the basic vectors. This result deserves special attention.

To (6) $\mathbf{h} = H_j \mathbf{A}_j^* = h_i \mathbf{a}_i^*$. Scalar multiplication with a_i gives $a_i \cdot \mathbf{h} = h_i = U_{ij} A_j \cdot (H_k A_k^*) = U_{ij} H_j$ and thus $h_i = U_{ij} H_j$. The inverse transformation occurs naturally as with the corresponding inverse transformation of the basic vectors with the inverse matrix.

1.7 Symmetry Properties

1.7.1

Symmetry Operations

Symmetry properties are best suited for the systematic classification of crystals. Furthermore, the symmetry determines the directional dependence (anisotropy) of the physical properties in a decisive way. Many properties such as, e.g., the piezoelectric effect, the pyroelectric effect, and certain nonlinear optical effects, including the generation of optical harmonics, can only occur in the absence of certain symmetry properties.

We meet the concept of symmetry in diverse fields. The basic notion stems from geometry. Symmetry in the narrow sense is present when we recognize uniform objects in space, which can be transferred by a movement into each other (coincidence) or which behave like image and mirror image. Morphological features of plants and animals (flowers, starfishes, most animals) are examples of the latter. The concept of symmetry may be carried over to nongeometric objects. Accordingly, symmetry in a figurative sense means the repetition of uniform or similar things. This can occur in time and space as, e.g., in music. Also the repetition of a ratio, as in the case of a geometric series, the father-son relationship in a line of ancestors, or the generation of a number sequence from a recursion formula and the relationship of the members between themselves, belong to this concept.

Although it may be fascinating to search for and contemplate such symmetries, we must turn to a narrower concept of symmetry when considering crystallography. We are interested in symmetry as a repetition of similar or uniform objects in space and distinguish between two types of manifesta-

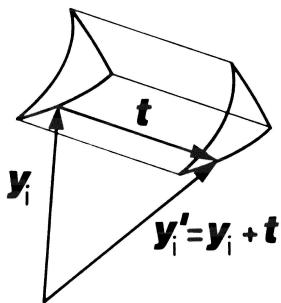


Figure 1.16 Translation.

tions, which, however, exhibit an internal association, namely the geometric symmetry in the narrow sense and the physical symmetry in space. The first case is concerned with the relationship between distances of points and angles between lines that repeat themselves. The second case refers to physical properties of bodies that repeat themselves in different directions. This symmetry arises in part from the structural symmetry of the crystals and in part from the intrinsic symmetry of the physical phenomena. We will come to these questions later. First, we will concern ourselves with geometric symmetry.

Two or more geometric figures or bodies shall be called geometrically uniform (or equivalent) when they differ only with respect to their position. Moreover, figures arising from reflection and centrosymmetry, such as, e.g., right and left hand or a right and left system of the same metric, shall be allowed to be equivalent. Each point specified by the end point of a vector y_i of the first figure shall be assigned a vector y'_i of the second or a further figure such that $|y_i - y_j| = |y'_i - y'_j|$ and $\angle(y_i - y_j, y_k - y_l) = \angle(y'_i - y'_j, y'_k - y'_l)$ (i, j, k, l specify four arbitrary points). The respective figures then exhibit correspondingly equal lengths and angles.

The geometric symmetries are now distinguished by the fact that one can describe the association of the equivalent figures with a few basic symmetry operations. Only those operations are permitted that allow an arbitrary repetition. In this sense, an arrangement of equivalent figures in an arbitrary position does not possess symmetry. There are three types of basic symmetry operations

1. *Translation:* We displace each point y_i (considered as the end point of a vector) of a given geometric form by a fixed vector t , the translation vector, and come to a second figure with the points $y'_i = y_i + t$ (Fig. 1.16). The required repetition leads to an infinite chain of equivalent figures. The symmetry operation is defined by the vector t .

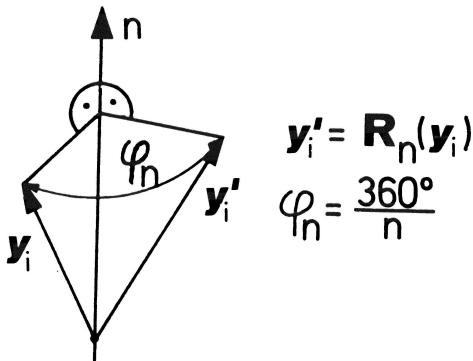


Figure 1.17 Rotation about an axis.

2. *Rotation about an axis:* A rotation through an angle φ about a given axis carries the points y_i of a given geometric figure or body over to the points y'_i of a symmetry-equivalent figure, where the corresponding points have the same distance from the axis of rotation and lie in a plane normal to the axis of rotation (Fig. 1.17). In this type of operation, the points coincide as with translation. Characteristic for the rotation is the position of the axis and the angle of rotation φ . We call $n = 2\pi/\varphi$, where φ is measured in radians, the *multiplicity* of the given axis. The axis of rotation has the symbol n . We write for the operation of rotation $y'_i = R_n(y_i)$. An axis of rotation is known as polar when the direction and reverse direction of the axis of rotation are not symmetry equivalent.
3. *Rotoinversion:* In this operation there exists an inseparable coupling between a rotation as in (2) and a so-called *inversion*. The operation of inversion moves a point y , through a point (inversion center) identical to the origin of coordinates, to get the point $y' = -y$ (Fig. 1.18). The order of both operations is unimportant. We specify the rotoinversion operation by the symbol \bar{n} (read “ n bar”). Thus $y'_i = -R_{\bar{n}}(y_i) = R_n(-y_i) = R_{\bar{n}}(y_i)$. Occasionally we will introduce a rotation–reflection axis instead of a rotation–inversion axis, i.e., a coupling of rotation and mirror symmetry, normal to the plane of the given axis of rotation. Both operations

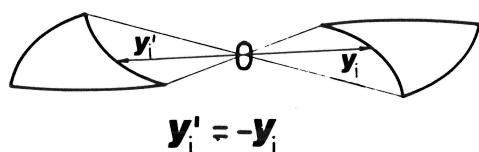


Figure 1.18 Inversion.

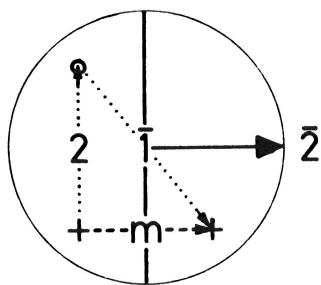


Figure 1.19 Identity of $\bar{2}$ and m (mirror plane).

lead to the same results; however, the multiplicity may be different for the given rotations.

Important special cases of rotoinversion are the inversion $\bar{1}$, in other words, the mirror image about a point, and the rotoinversion $\bar{2}$. The latter is found to be identical to the mirror image about a plane normal to the $\bar{2}$ -axis (mirror plane or symmetry plane; Fig. 1.19). The expressions *inversion center* or *center of symmetry* are also used for the inversion. The preferred notation of the mirror image about a plane is m (mirror) instead of $\bar{2}$.

How do these operations express themselves in the components of the vectors y and y' ? This will first be demonstrated for the case of a Cartesian reference system. The axis of rotation is parallel to e_3 . The rotation carries the basic system $\{e_i\}$ over to a symmetry-equivalent system $\{e'_i\}$ (Fig. 1.20).

$$\begin{aligned} e'_1 &= \cos \varphi e_1 + \sin \varphi e_2 \\ e'_2 &= -\sin \varphi e_1 + \cos \varphi e_2 \\ e'_3 &= e_3. \end{aligned}$$

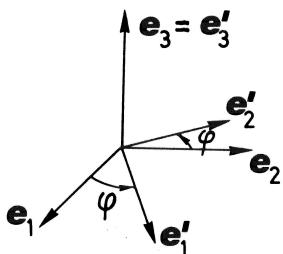


Figure 1.20 Rotation about an axis e_n of a Cartesian reference system.

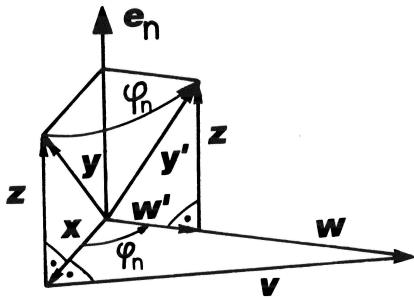


Figure 1.21 Vector relations for a rotation about an arbitrary axis e_n .

Thus the transformation matrix is

$$(u_{ij}) = \begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

What do the coordinates of a point, generated by the rotation, look like in the old system? As we saw in Section 1.6, the inverse transformation is described by the transposed matrix:

$$\begin{aligned} y'_1 &= \cos \varphi y_1 - \sin \varphi y_2 \\ y'_2 &= \sin \varphi y_1 + \cos \varphi y_2 \\ y'_3 &= y_3. \end{aligned}$$

We symbolize this by writing

$$R_{n||e_3} = \begin{pmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} = (v_{ij}) \quad \text{and} \quad y'_i = v_{ij} y_j.$$

The general case of an arbitrary position of the n -fold axis of rotation e_n may be understood with the aid of vector calculus (Fig. 1.21). Let φ_n be the angle of rotation. We agree upon the clockwise sense as the positive direction of rotation when looking in the direction $+e_n$. One finds

$$y' = [(y \cdot e_n)e_n](1 - \cos \varphi_n) + \cos \varphi_n y + (e_n \times y) \sin \varphi_n.$$

The individual steps are $y' = w' + z$; $z = y - x = (y \cdot e_n)e_n$; $w' = (w/|w|)|x| = w \cos \varphi_n$; $w = x + v$; $v = (e_n \times x) \tan \varphi_n = (e_n \times y) \tan \varphi_n$. If one decomposes the above equation for y' into components of an arbitrary coordinate system, whereby the unit vectors of the axis of rotation are $e_n = n_i a_i$ and $y = y_i a_i$, one gets the corresponding transformation matrix $R_n = (v_{ij})$.

For the case of a rotoinversion, we have $R_n = (-v_{ij})$, when the origin of the coordinates is taken as the center of symmetry.

To obtain all symmetry-equivalent points, arising from multiple repetitions of the symmetry operations on y , one must use the same R_n on y' according to $y'' = R_n(y') = R_n^2(y)$ and so on. In general, we have $y''' = R_n^m(y)$. These matrices are obtained through multiple matrix multiplication.

1.7.2

Point Symmetry Groups

We now turn to the question of which of the three types of symmetry operations discussed above are compatible with each other, i.e., what combinations are simultaneously possible. As a first step we consider only such combinations where at least one point of the given space possessing this symmetry property remains unchanged (invariant). We call these combinations of symmetry operations *point symmetry groups*. When dealing with crystals, the expression *crystal classes* is often used as a matter of tradition.

We should point out that a satisfactory treatment of symmetry theory and its applications to problems in crystal physics and also to problems in atomic and molecular physics is possible especially with the help of *group theory*. In what follows, we will give preference to group theoretical symbols (see also Section 8). Important methods of group theory for crystal physics are treated in Sections 8 and 9.

Textbooks on crystallography give a detailed analysis of the compatibility of different symmetry operations (e.g., Kristallgeometrie). Here we will only remark on the essential procedures and present the most significant results.

The whole complex reduces to the following questions:

- In which way are n or \bar{n} compatible with $\bar{1}$, 2, and $\bar{2} = m$?
- Under which conditions can n or \bar{n} simultaneously exist with p or \bar{p} when $n, p \geq 3$? p specifies a second rotation axis of p -fold symmetry.
- In (b) can $\bar{1}$, 2, and $\bar{2}$ also occur?
- How can operations n , \bar{n} and those combinations permitted under (a), (b), and (c) be combined with a translation?

We will defer case (d) because the invariance of all points is lifted by the translation. With respect to question (a), the following seven cases can be decided at once by direct inspection of stereographic projections:

- n or \bar{n} with $\bar{1}$,
- n or \bar{n} parallel to 2,

3. n or \bar{n} perpendicular to 2,
4. n or \bar{n} forms an arbitrary angle with 2.
5. n or \bar{n} parallel to $\bar{2}$ ($=m$),
6. n or \bar{n} perpendicular to $\bar{2}$ ($=m$),
7. n or \bar{n} forms an arbitrary angle with $\bar{2}$ ($=m$).

With a single principal axis n or \bar{n} , the following 7 permissible combinations result from the 14 possibilities above:

- n (only one n -fold axis),
- n/m (read “n over m,” symmetry plane perpendicular to an n -fold axis),
- nm (symmetry plane contains the n -fold axis),
- $n2$ (2-fold axis perpendicular to the n -fold axis),
- n/mm (symmetry plane perpendicular to the n -fold axis, a second symmetry plane contains the n -fold axis),
- \bar{n} (only one n -fold rotoinversion axis),
- $\bar{n}2$ (2-fold axis perpendicular to the n -fold rotoinversion axis).

All other combinations turn out to be coincidences to the seven just mentioned. One finds that apart from the “generating” symmetry operations, other symmetry operations are necessarily obtained which can also be used to generate the given combination. For example, $\bar{n}2 = \bar{n}m$ or $\bar{2}\bar{1} = 2/\bar{m}$. Normally we use the shorthand symbols with the respective generating symbols. The complete symbols, which comprise all compatible symmetry operations of a certain combination, play an important role in some areas of crystallography (structure determination, group theoretical methods). The *Hermann–Mauguin notation* used here is the international standard. The older notation of Schoenflies is still used by chemists and spectroscopists but will not be discussed in this book.

Before we turn our attention to case (b) let us consider which n -fold rotation axes or n -fold rotoinversion axes can occur in crystals, i.e., in lattices. From experience, one deduces the *third basic law of crystallography*:

In crystals one observes only 1-, 2-, 3-, 4-, and 6-fold symmetry axes.

The proof that no other n -fold symmetry is compatible with the lattice arrangement of uniform cells is as follows: We consider two parallel axes A_1 and A_2 of n - (or \bar{n}) fold symmetry which possess the smallest separation of such symmetry axes in the given lattice. We allow the symmetry operations to

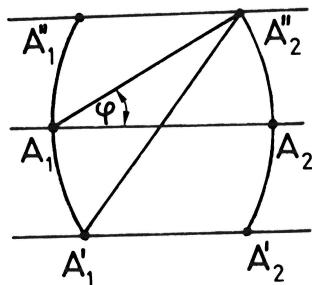


Figure 1.22 Compatibility of n -fold axes in lattices.

Table 1.1 Compatible multiplicities of n -fold axes in lattices.

n	φ	$ r'/r $	$ r'''/r $
1	360°	1	0
2	180°	3	2
3	120°	2	$\sqrt{3}$
4	90°	1	$\sqrt{2}$
5	72°	$\approx 0,38$	$\approx 1,18$
6	60°	0	1
$n > 6$	$< 60^\circ$	$0 < r'/r < 1$	$0 < r'''/r < 1$

work on each other and get further symmetry axes according to $A_1(A_2) \rightarrow A'_2$, $A_2(A_1) \rightarrow A''_1$ and A''_2 and A'_1 by a rotation in the opposite sense (Fig. 1.22). The new symmetry axes must either coincide or at least have the same separation as the axes A_1 and A_2 . Using the notation in Fig. 1.22 we have

$$r = A_1 A_2;$$

$$r' = A'_1 A'_2 = 2r \cos \varphi - r;$$

$$r'' = A'_1 A''_2 = \sqrt{r^2 + 4r^2 \sin^2 \varphi} = r \sqrt{5 - 4 \cos \varphi} \geq r;$$

$$r''' = A_2 A'_2 = \sqrt{(r - r \cos \varphi)^2 + r^2 \sin^2 \varphi} = r \sqrt{(2(1 - \cos \varphi)} = 2r \sin \varphi / 2.$$

Table 1.1 presents the values $|r'/r|$ and $|r'''/r|$ as a function of the multiplicity. They must be ≥ 1 or 0.

Similar considerations for rotoinversion axes lead to the same end result, namely, that crystals can only have 1-, 2-, 3-, 4-, and 6-fold symmetry axes. Other n -fold symmetries can, however, exist in noncrystalline forms. Even molecules can possess, e.g., 5-fold and higher symmetry axes not permitted in crystals. From the combinations in (a) and under the restrictions just mentioned, only 27 crystallographic point symmetry groups exist. These are listed in the annex.

Now to case (b): The combination of rotation axes n (or rotoinversion axes \bar{n}) with rotation axes p (or \bar{p}) for the case $n, p \geq 3$ leads to a mutual multiplicity

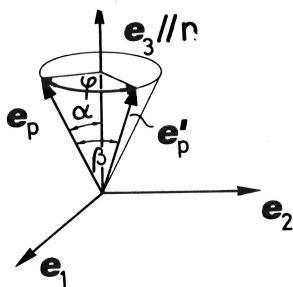


Figure 1.23 Compatibility of n -fold and p -fold axes.

of the axes, namely to at least n different p axes and p different n axes. In a Cartesian coordinate system let one axis n lie parallel to e_3 and a second axis p lie in the plane spanned by e_1 and e_3 perpendicular to e_2 (Fig. 1.23). Let the angle between these axes be α . Applying the operation n on the axis p gives us a second axis p' . Let the unit vectors along these axes be e_n , e_p , and e'_p . With $e_p = \sin \alpha e_1 + \cos \alpha e_3$ and

$$R_{n \parallel e_3} = \begin{pmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

one gets $e_{p'} = R_n(e_p) = \sin \alpha \cos \varphi e_1 + \sin \alpha \sin \varphi e_2 + \cos \alpha e_3$. We now calculate the angle β between p and p' . The result is $e_p \cdot e'_p = \cos \beta = \sin^2 \alpha \cos \varphi + \cos^2 \alpha = 1 + \sin^2 \alpha (\cos \varphi - 1)$. From this equation and with $(1 - \cos u) = 2 \sin^2 u / 2$ we derive the relationship $\sin \beta / 2 = \pm \sin \alpha \sin \varphi / 2$, where $\varphi = 2\pi/n$.

We first consider the simple case of the combination of a 3-fold axis with another axis $p \geq 2$, where for $p = 2$ the condition $\alpha = 0$ or 90° was already discussed. Thus several symmetry-equivalent 3-fold axes are created, which on a sphere, whose center is the common intercept point, fix an equal-sided spherical triangle, whose center also specifies the intercept point of a 3-fold axis. In this spherical triangle $\alpha = \beta$ (Fig. 1.24). For the case $n \geq 4$ let α be the smallest angular distance between two of the symmetry equivalent axes n . Then the angular distance α' between two axes resulting from the application of one on the other axis, respectively, must either vanish, i.e., both axes must coincide, or we have $\alpha' \geq \alpha$. However, the largest possible angular distance is 90° . As one can easily see from a stereographic projection (Fig. 1.25), the only possibility for $n \geq 4$ rotation axes is that both axes coincide since $\alpha' < \alpha$ in each case.

This means that in case (b) the intercept points of the symmetry-equivalent n -fold axes ($n \geq 3$) always form an equal-sided spherical triangle ($\alpha = \beta$). From the relationship derived above, we have for $\alpha = \beta$: $\cos \alpha / 2 =$

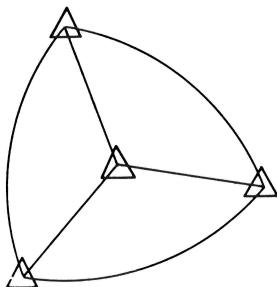


Figure 1.24 Combination of two 3-fold axes.

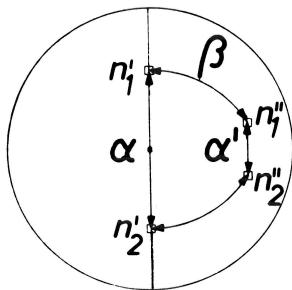


Figure 1.25 Combination of two n -fold axes with $n \geq 4$.

$\pm 1/(2 \sin \varphi/2)$. Table 1.2 lists the possible angles α as a function of the n -fold symmetry.

A combination of several symmetry-equivalent rotation axes with $n \geq 3$ is only allowed for $n = 1, 2, 3, 4, 5, 6$. The angles appearing are prescribed.

To case (c): The discussion of the combinations of n -fold axes ($n \geq 3$) requires a complement, since with the n -fold axes only the case $\alpha = \beta$ was settled. In the center of the equilateral spherical triangle, formed by the intercept points of the 3-fold axes on the sphere, there exists a further 3-fold axis, which with the other axes specifying the spherical triangle includes the angle α' with $\sin \alpha' = 2\sqrt{2}/3$, $\cos \alpha' = 1/3$. This is recognized by applying the formula

Table 1.2 Angles between possible n -fold axes. Concerning 2-fold axes see the results obtained in case a).

n	$\varphi = 2\pi/n$	$\cos \alpha/2$	$\alpha = \beta$
2	180°	$\pm 1/2$	$120^\circ; 240^\circ$
3	120°	$\pm 1/\sqrt{3}$	$109, 47^\circ; 250, 53^\circ$
4	90°	$\pm 1/\sqrt{2}$	$90^\circ; 270^\circ$
5	72°	$\pm 1/(2 \sin 36^\circ)$	$63, 43^\circ; 296, 57^\circ$
6	60°	± 1	$0^\circ; 360^\circ$
$n > 6$	$<60^\circ$	$ \cos \alpha/2 > 1$	—

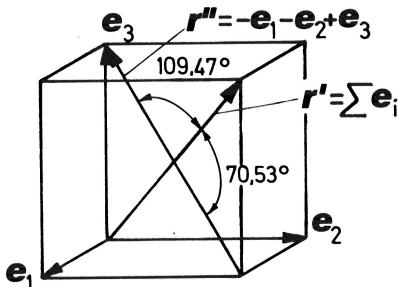


Figure 1.26 Symmetry of a cube.

derived above for the rotation about an n -fold axis according to Fig. 1.24. The result is $\alpha' \approx 70.53^\circ$. The question is now whether even with this small angular distance, 3-fold axes exist whose intercept points on a sphere also form an equilateral spherical triangle. With the same formula just used, one gets in this case, for a further 3-fold intercept axis in the center of the triangle, the angle $\alpha'' \approx 41.81^\circ$ from $\sin \alpha'' = 2/3$. This is in fact the smallest angle of two 3-fold axes occurring in the icosahedral groups through the combination of several 3-fold axes.

Just as with the case of the 3-fold axes, the equilateral spherical triangles of the intercept points of the symmetry-equivalent n -fold axes n'_1 , n'_2 , and n''_1 also possess a 3-fold axis in their centers (Fig. 1.25). Thus in all combinations of n -fold axes ($n > 3$), 3-fold axes are always present, which mutually include the angles just discussed. For further discussions of the combination possibilities of n -fold axes ($n > 3$) with other symmetry operations it is useful to consider the symmetry properties of a cube. Let e_i be the edge vectors of a unit cube (identical to the Cartesian basis vectors); then the directions of the space diagonals of the cube may be represented by $r = \pm e_1 \pm e_2 \pm e_3$ (Fig. 1.26). One obtains for the angle α between three different space diagonals $\cos \alpha = \pm 1/3$. The values $-1/3$ and $+1/3$ give for α approximately 109.47° and the complementary angle of 180° . In Table 1.2 we had $\cos \alpha/2 = \pm 1/\sqrt{3}$; therefore $\cos \alpha = -1/3$ (with $\cos u = -1 + 2 \cos^2 u/2$). Thus the space diagonals of the cube, themselves 3-fold rotation axes, intersect at angles identical to those for 3-fold axes given in Table 1.2.

The system of four space diagonals of the cube represents the simplest point symmetry group (abbreviated as PSG in what follows) of the combination of two polar 3-fold axes ("polar" means direction and inverse direction are not equivalent). As one can easily show with the aid of the transformation formulae or a stereographic projection, this arrangement also contains three 2-fold axes, which run parallel to the cube edges, that is, at half the angle of the larger angle between two 3-fold axes. This PSG is given the Hermann–Mauguin symbol 23 (Fig. 1.27).

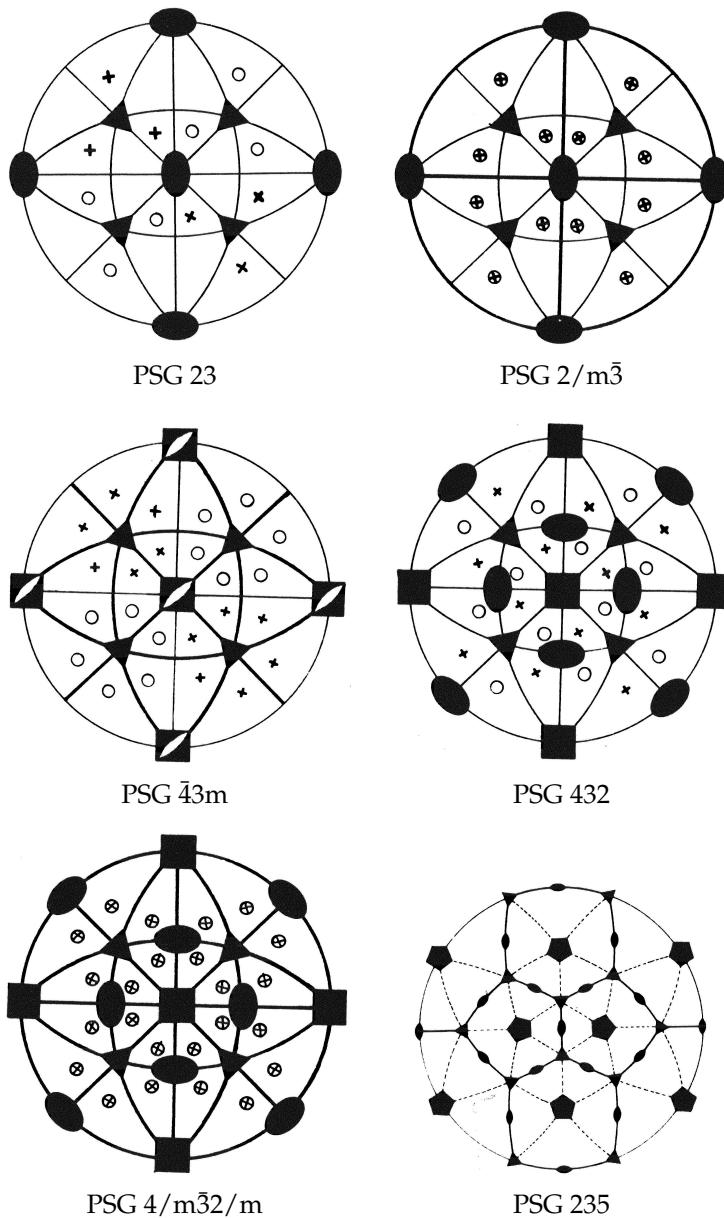


Figure 1.27 Stereographic projection of the symmetry operations in cubic point symmetry groups and in icosahedral PSG 235. The symmetry operations as well as the intercept points of the assembly of symmetry-equivalent normals are drawn. The intercept points on the northern hemisphere are indicated by a cross, those on the southern hemisphere with an empty circle.

The combination of 23 with symmetry planes perpendicular to the 2-fold axes or with $\bar{1}$ leads to PSG $2/m\bar{3}$ (Fig. 1.27). With symmetry planes, each containing two 3-fold axes, we get PSG $\bar{4}3m$, where the 2-fold axes of 23 turn into $\bar{4}$ -axes (Fig. 1.27). In $2/m\bar{3}$, short symbol $m\bar{3}$, the 3-fold axes are nonpolar; in $\bar{4}3m$, short symbol $\bar{4}3$, they are polar just as in 23. If we introduce 4-fold axes instead of 2-fold axes we get PSG 432 , short symbol 43 (Fig. 1.27). Here, additional 2-fold axes are generated at half of the smaller angles between two 3-fold axes. The 3-fold axes are nonpolar. Moreover, the 4-fold axes form an angle of 90° , as demanded in Table 1.2. Finally, symmetry planes perpendicular to the 4-fold axes can also be combined. This leads to PSG $4/m\bar{3}2/m$, short symbol $4/m\bar{3}$ or $m\bar{3}m$, the highest symmetry group in crystals (Fig. 1.27). We also obtain $4/m\bar{3}$ with the inclusion of $\bar{1}$ to 43 . The five point symmetry groups just discussed comprise the *cubic crystal system*.

For completion, let us discuss the noncrystallographic PSG of the combination of 5-fold axes. The basic framework here is also the arrangement of four space diagonals of the cube. In each field of the cube two further 3-fold axes are constructed so that the intercept points of neighboring axes mark spherical triangles on the sphere with the angular distance $\alpha' \approx 70.52^\circ$ ($\sin \alpha' = 2\sqrt{2}/3$) just discussed. This results in a smallest angular distance of $\alpha'' \approx 41.81^\circ$ ($\sin \alpha'' = 2/3$) between the inserted axes and the axes along the space diagonals. Thus arrangements of five 3-fold axes are formed whose intercept points on the sphere give the corners of regular pentagons (Fig. 1.27). The angle between two 5-fold axes may be easily calculated from the known angular distance of the 3-fold axes with the aid of the rotation formula. It is in agreement with the result of Table 1.2, namely $\cos \alpha/2 = \pm 1/(2 \sin 36^\circ)$. This symmetry group has the symbol 235 . It exhibits six 5-fold, ten 3-fold, and fifteen 2-fold axes. Introducing symmetry planes perpendicular to the 2-fold axes results in PSG $2/m35$. Both these so-called icosahedral groups play an important role in the structure of viruses, in certain molecular structures, such as, e.g., in the B_{12} -structures of boron and in certain quasicrystals.

There exist a total of 32 different crystallographic PSGs. These are divided into seven crystal systems depending on the existence of a certain minimum symmetry (Table 1.3). These systems are associated with the seven distinguishable symmetry classes of the crystallographic reference systems. These systems are specified by prominent directions, the so-called *viewing directions*, along which possibly existing symmetry axes or normals on symmetry planes are running. It turns out that each system has at most three different viewing directions.

Table 1.3 The seven crystal systems.

System	Minimal symmetry	Conditions for lattice parameters of symmetry-adapted reference system (viewing directions)	PSG
Triclinic	1	a_i, α_i not fixed (1. arbitrary, 2. arbitrary, 3. arbitrary)	$1, \bar{1}$
Monoclinic	2 or $m = \bar{2}$	$\alpha_1 = \alpha_3 = 90^\circ$ (1. $a_2 \parallel 2$ or $\bar{2}$, 2. arbitrary, 3. arbitrary)	$2, m, 2/m$
Orthorhombic	22 or $mm = \bar{2}\bar{2}$	$\alpha_i = 90^\circ$ (1. $a_1 \parallel 2$ or $\bar{2}$, 2. $a_2 \parallel 2$ or $\bar{2}$, 3. $a_3 \parallel 2$ or $\bar{2}$)	$22, mm, 2/mm$
Trigonal (rhombohedral)	3 or $\bar{3}$	$a_i = a, \alpha_i = \alpha$ (1. $a_1 + a_2 + a_3 \parallel 3$ or $\bar{3}$, 2. $a_1 - a_2 \perp 3$, and $a_3, 3. 2a_3 - a_1 - a_2 \perp 3$ and $a_1 - a_2$)	$3, 3m, 32,$ $\bar{3},$ $\bar{3}m = \bar{3}2$
Tetragonal	4 or $\bar{4}$	$a_1 = a_2, \alpha_i = 90^\circ$ (1. $a_3 \parallel 4$ or $\bar{4}$, 2. $a_1,$ 3. $a_1 + a_2$)	$4, 4/m, 4m,$ $42, 4/mm,$ $\bar{4}, \bar{4}m = \bar{4}2$
Hexagonal	6 or $\bar{6}$	$a_1 = a_2, \alpha_1 = \alpha_2 = 90^\circ, \alpha_3 = 120^\circ$ (1. $a_3 \parallel 6$ or $\bar{6}$, 2. $a_1,$ 3. $2a_1 + a_2 \perp a_2$)	$6, 6/m, 6m,$ $62, 6/mm,$ $\bar{6}, \bar{6}m = \bar{6}2$
Cubic	23	$a_i = a, \alpha_i = 90^\circ$ (1. $a_1 \parallel$ edge of cube, 2. $a_1 + a_2 + a_3 \parallel 3$, 3. $a_1 + a_2$)	$23, \bar{4}3,$ $43, m3,$ $4/m3 = m3m$

1.7.3

Theory of Forms

We will now turn to the discussion of morphological properties. The complete set of symmetry-equivalent faces to a face ($h_1h_2h_3$) in a point symmetry group is designated as a form with the symbol $\{h_1h_2h_3\}$. The entirety of the symmetry-equivalent vectors to a lattice vector $[u_1u_2u_3]$ is symbolized as $\langle u_1u_2u_3 \rangle$; correspondingly, $\langle |u_1u_2u_3| \rangle$ means the entirety of the symmetry-equivalent points to the point $||u_1u_2u_3||$.

To calculate the symmetry-equivalent faces, lattice edges, or points we use the transformations already discussed with a transition from the basic system to a symmetry-equivalent system (Section 1.6).

In a symmetry-equivalent system the cotransformed face normals and vectors, respectively, possess the same coordinates as in the basic system. Thus one gets the symmetry-equivalent faces and vectors respectively or points by enquiring about the indices or coordinates of the transformed quantities in the old system. These result from the inverse transformation, thus in the case of the Miller indices, with the inverse transformation matrix U^{-1} and in the case of the vectors or points, with the transposed matrix U^T . We will call the number of symmetry-equivalent objects generated by a symmetry operation the order h of the given operation. Repeated application gives us all symmetry-

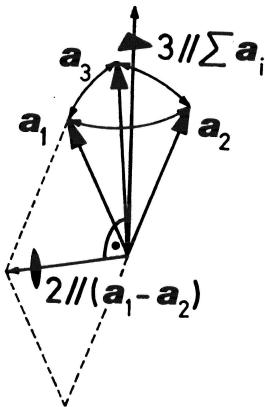


Figure 1.28 Symmetry operations of PSG 3m in a trigonal–hexagonal reference system.

equivalent quantities; thus $\{h_1h_2h_3\} = \{(U^{-1})^m(h_1h_2h_3)\} = \{U^{-m}(h_1h_2h_3)\}$ and correspondingly $\langle u_1u_2u_3 \rangle = \langle (U^T)^m[u_1u_2u_3] \rangle$ with $m = 1, 2, \dots, h$.

If several symmetry-generating operations exist, then the calculation of all symmetry-equivalent quantities requires that the additional symmetry operations be applied to the quantities already generated by the other operations. This is demonstrated by the example LiNbO₃, PSG 3m (Fig. 1.28). In a trigonal–hexagonal reference system, with a metric defined by $a_1 = a_2$, $\alpha_1 = \alpha_2 = 90^\circ$, $\alpha_3 = 120^\circ$, we have

$$U(3||a_3) = \begin{pmatrix} 0 & 1 & 0 \\ \bar{1} & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad U(3)^{-1} = \begin{pmatrix} \bar{1} & \bar{1} & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$U(3)^T = \begin{pmatrix} 0 & \bar{1} & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad U(\bar{2}||a_1) = \begin{pmatrix} \bar{1} & 0 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = U(\bar{2}||a_1)^{-1}.$$

With $U(3)^{-1}$ one finds for $\{h_1h_2h_3\}$ the faces $(h_1h_2h_3)$, $(\bar{h}_1 + \bar{h}_2.h_1h_3)$, $(h_2.\bar{h}_1 + \bar{h}_2.h_3)$ and with $U(\bar{2}||a_1)^{-1}$ the additional faces $(\bar{h}_1.h_1 + h_2.h_3)$, $(h_1 + h_2.\bar{h}_2h_3)$, $(\bar{h}_2\bar{h}_1h_3)$. These six faces together form, in the general case, a ditrigonal pyramid (Fig. 1.28). A two-digit or combined Miller index is separated by a dot from the other indices.

If one selects a trigonal–rhombohedral reference system with $a_1 = a_2 = a_3$ and $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$, which is permitted for trigonal crystals, then the symmetry operations of the PSG 3m have the following form:

$$U_{3||(a_1+a_2+a_3)} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{and} \quad U_{\bar{2}||(a_1-a_2)} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Table 1.4 The meroedries of the seven crystal systems.

System	tri-clinic	mono-clinic	ortho-rhombic	tri-gonal	tetra-gonal	hexa-gonal	cubic
Holoedrie	$\bar{1}$	$2/m$	$2/mm$	$\bar{3}m$	$4/mm$	$6/mm$	$4/m3$
Hemimorphie	–	–	$2m$	$3m$	$4m$	$6m$	–
Paramorphie	–	–	–	$\bar{3}$	$4/m$	$6/m$	$m3$
Enantiomorphie	1	2	22	32	42	62	43
Hemiedrie II	–	m	–	–	$\bar{4}2$	$\bar{6}2$	$\bar{4}3$
Tetartoedrie	–	–	–	3	4	6	23
Tetartoedrie II	–	–	–	–	$\bar{4}$	$\bar{6}$	–

For $\{h_1h_2h_3\}$ one finds, with the inverse operations, the faces $(h_1h_2h_3)$, $(h_2h_3h_1)$, $(h_3h_1h_2)$, $(h_2h_1h_3)$, $(h_3h_2h_1)$ and $(h_1h_3h_2)$. The difference clearly indicates that one must also specify the reference system used when characterizing faces of trigonal crystals.

Let us now consider the different forms in the different PSGs of a system. For this purpose, we will first investigate the relationships between the PSG of highest symmetry and the PSGs of lower symmetry in the same system. These PSGs, the holohedries, are $\bar{1}$, $2/m$, $2/mm$, $\bar{3}m$, $4/mm$, $6/mm$, $4/m3$. If one removes single minor symmetry elements from the holohedries, one gets the PSGs of lower symmetry of the same system. If 2-fold axes are missing or symmetry planes (only one in each case), the resulting forms are hemihedries, that is PSGs, in which only half the number of surfaces occur as in the holohedries. If one removes two minor symmetry elements, one gets the tetartohedries, PSGs with a quarter of the number of faces as in the holohedries. These are known as merohedral PSG depending on the type of symmetry elements removed or remaining. Each system has a maximum of seven PSGs including the holohedries. These are classified in Table 1.4.

The following holds true: In each holohedry there exists a spherical triangle whose repetition by the generating symmetry elements covers the whole sphere just once. In the merohedries, the symmetry elements cover only one part, namely, half the sphere in the hemihedries and a quarter of the sphere in the tetartohedries. The triangles are referred to as elementary triangles and represented in Fig. 1.29 . The arrangement of these triangles is characteristic for each point symmetry group. Their number corresponds to the order of the point symmetry group. Each face normal is associated with one of the following seven distinguishable positions in the spherical triangle of the holohedries (Fig. 1.30):

1. Corner 1,
2. Corner 2,
3. Corner 3,

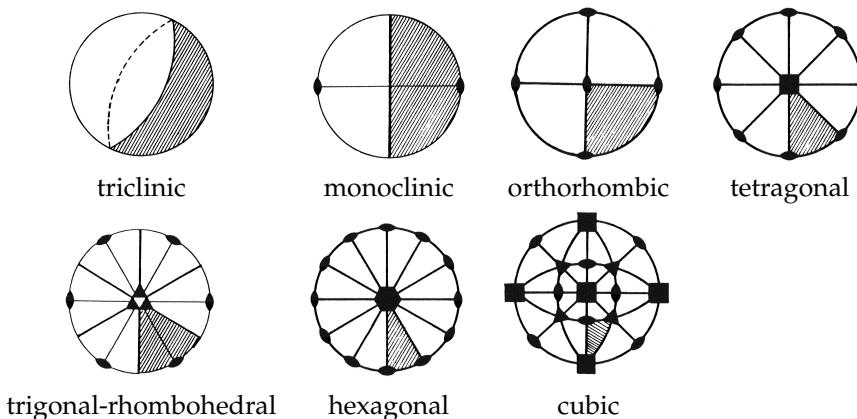


Figure 1.29 Elementary triangles in the seven crystal systems.

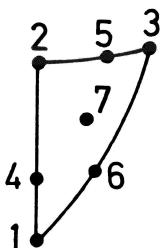


Figure 1.30 The seven positions in an elementary triangle.

4. On the side between 1 and 2,
5. On the side between 2 and 3,
6. On the side between 3 and 1,
7. Inside the triangle.

In each system, except triclinic and monoclinic, positions 1, 2, and 3 are associated with a fixed direction, i.e., the given faces have distinct Miller indices. The side positions 4, 5, and 6 possess one degree of freedom. Only the third position is not bound to any restrictions (two degrees of freedom). Special forms evolve from the first six positions. Position 7 generates general forms, characteristic for the given PSG and also for the distribution of the elementary triangles. Tables 1.5 and 1.6 present the seven forms for the orthorhombic and cubic systems. The forms have the following nomenclature (according to Groth):

Table 1.5 The seven forms of the orthorhombic PSG.

Pos.		22	2m	2/m
1	{100}	pinacoid	pinacoid	pinacoid
2	{010}	pinacoid	pinacoid	pinacoid
3	{001}	base pinacoid	base pedion	base pinacoid
4	{ h_10h_3 }	prisma II. position	doma II. position	prisma II. position
5	{ h_1h_20 }	prisma III. position	prisma III. position	prisma III. position
6	{ $0h_2h_3$ }	prisma I. position	doma I. position	prisma I. position
7	{ $h_1h_2h_3$ }	disphenoid	pyramide	dipyramide

Pedion: Single face, not possessing another symmetry-equivalent face.

Pinacoid: Face with a symmetry-equivalent counter face, generated by $\bar{1}$, 2, or m.

Dome: Pair of faces generated by a mirror plane.

Prism: Tautozonal entirety of symmetry-equivalent faces (all faces intercept in parallel edges, which define the direction of the zone axis).

Pyramid: Entirety of symmetry-equivalent faces, whose normals, with a prominent direction, the pyramid axis, enclose the same angle.

Dipyramid: Double pyramid, generated by a mirror plane perpendicular to the pyramid axis.

Sphenoid: A pair of nonparallel faces generated by a 2-fold axis.

Disphenoid: Two sphenoids evolving separately from a further 2-fold axis.

Scalenohedron: Two pyramids evolving from $\bar{n}2$ with $n \neq 4q - 2$ (n, q integers). Dipyramids are generated for the case $n = 4q - 2$ ($n > 2$).

Streptohedron: Two pyramids, mutually rotated by half the angle of the rotation axes (n odd number). This form is called rhombohedron in den PSGs $\bar{3}$, $\bar{3}m$, and 32.

The special nomenclature of the forms of the cubic system is mentioned in Table 1.6. Parallel projections of these forms are presented in Fig. 1.31. Table 1.7 gives an overview of the 32 crystallographic point symmetry groups.

Table 1.6 The forms of the cubic and icosahedral PSG. The Miller indices are only valid for cubic crystals.

Pos.		23	m3	$\bar{4}3$	43	$4/m3$	235 and m35
1	{100}	cube	cube	cube	cube	cube	regular pentagon-dodecahedron
2	{110}	rhombic dodecahedron	rhombic dodecahedron	rhombic dodecahedron	rhombic dodecahedron	rhombic dodecahedron	regular icosahedron
3	{111}	tetrahedron	octahedron	tetrahedron	octahedron	octahedron	rhombentri-contahedron
4	{ h_10h_3 }	pentagon-dodecahedron	pentagon-dodecahedron	tetrakis-hexahedron	tetrakis-hexahedron	tetrakis-hexahedron	pentakis-dodekahedron
5	{ $h_1h_2h_2$ } $h_1 > h_2$	tris-tetrahedron	deltoidikositetrahedron	tris-tetrahedron	deltoidikositetrahedron	deltoidikositetrahedron	tris-icosahedron
6	{ $h_1h_2h_2$ } $h_1 < h_2$	deltoid-dodecahedron	tris-octahedron	deltoid-dodecahedron	tris-octahedron	deltoidhexa-contahedron	tris-octahedron
7	{ $h_1h_2h_3$ }	tetrahedral pentagon-dodecahedron	dissododecahedron	hexakis-tetrahedron	pentagon-ikositetrahedron	hexakis-octahedron	235: pentagonal hexacontahedron m35: hekatonikosahedron

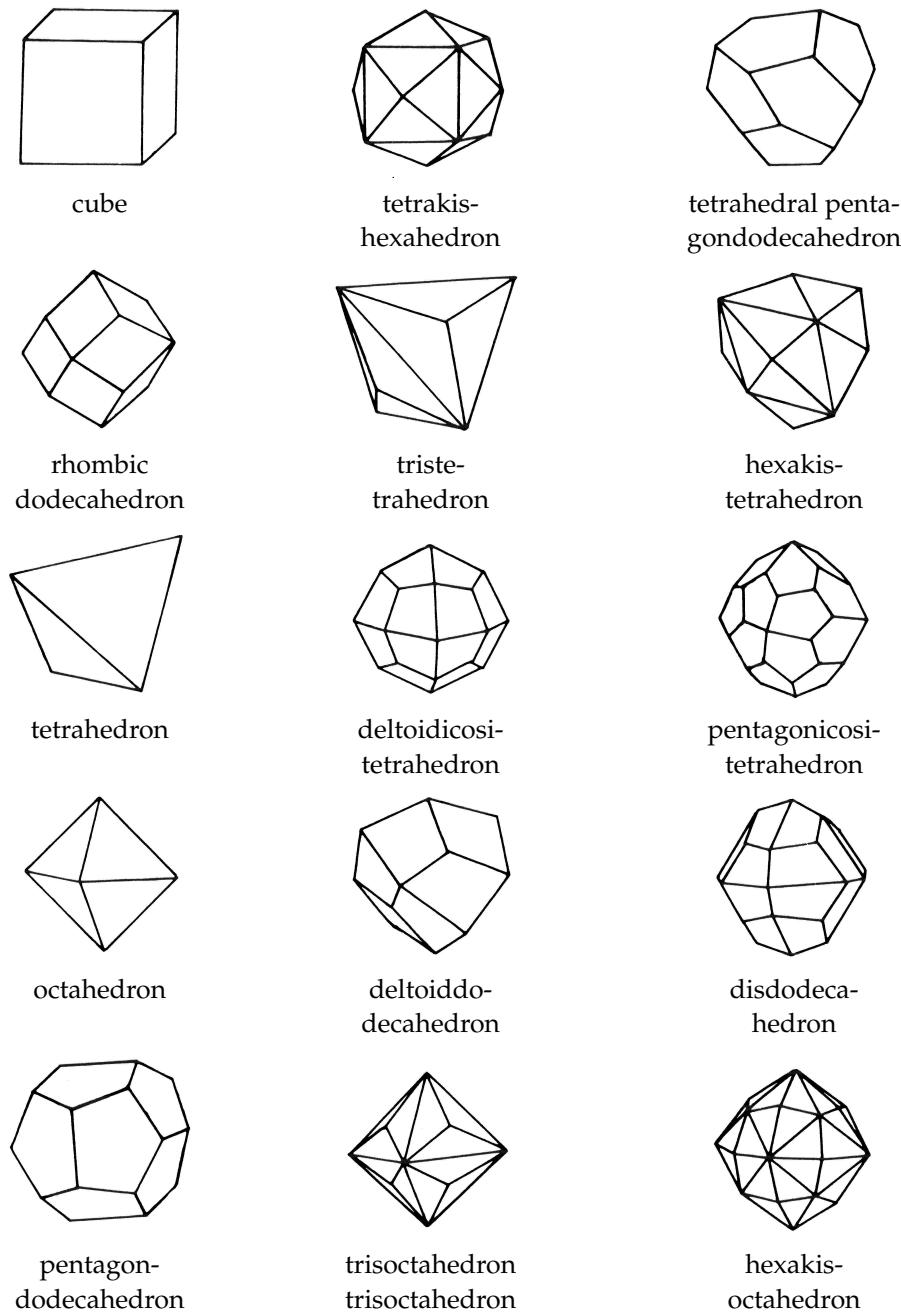


Figure 1.31 The 15 different forms of the cubic system.

Table 1.7 The 32 crystallographic point symmetry groups (crystal classes) with examples (symbols in parentheses give Schoenflies symbol).

Symmetry symbol (shorthand notation)	Groth designation	Examples Minerals	Synthetic crystals
1 (C ₁)	triclinic pedial	Wegscheiderite: Na ₂ CO ₃ · 3NaHCO ₃ Parahilgardite: Ca ₂ ClB ₅ O ₈ (OH) ₂	CaS ₂ O ₃ · 6H ₂ O LiHC ₂ O ₄ · H ₂ O CuSO ₄ · 5H ₂ O Ba(OH) ₃
ī (C ₁)	triclinic pinacoidal	Mikrokline: KAISi ₃ O ₈ Wollastonite: Ca ₃ Si ₃ O ₉	Li ₂ SO ₄ · H ₂ O tartaric acid (C ₄ H ₆ O ₆)
2 (C ₂)	monoclinic sphenoidal	Harmotome: BaAl ₂ Si ₆ O ₁₆ · 6H ₂ O Brushite: CaHPO ₄ · 2H ₂ O	K ₂ S ₄ O ₆
m (C _s)	monoclinic domatic	Hilgardite: Ca ₂ ClB ₅ O ₈ (OH) ₂ Klinodrite: Ca ₂ Zn ₂ (OH) ₂ Si ₂ O ₇ · H ₂ O	LiH ₃ (SeO ₃) ₂ KHCO ₃
2/m (C _{2h})	monoclinic prismatic	gypsum: CaSO ₄ · 2H ₂ O Diopside: CaMgSi ₂ O ₆	SnF ₂
22 (D ₂)	orthorhombic disphenoidal	Epsomite: MgSO ₄ · 7H ₂ O Descoizite: Pb(Zn,Cu)(OH)V ₂ O ₄	Seignette salt (NaKC ₄ H ₄ O ₆ · 4H ₂ O)
mm (C _{2v})	orthorhombic pyramidal	Dyskrasite: Ag ₃ Sb Shortite: Na ₂ Ca ₂ (CO ₃) ₃	Sr(HCOO) ₂ LiHCOOH ₂ O
2/m/m (D _{2h})	orthorhombic dipyramidal trigonal	baryte: BaSO ₄ olivine: (Mg,Fe) ₂ SiO ₄ Parisite: CaCe ₂ F ₂ (CO ₃) ₃	MgBaF ₄ K ₂ SO ₄ Ca(HCOO) ₂ NaJO ₄ · 3H ₂ O LiBO ₂ · 8H ₂ O benzil
3 (C ₃)	pyramidal	Roentgenite: Ca ₂ Ce ₃ F ₃ (CO ₃) ₅	Rb ₂ S ₂ O ₆
32 (D ₃)	trigonal	α-Quartz: SiO ₂	LiNbO ₃
3m (C _{3v})	trapezohedral ditrigonal pyramidal	cinnabarite: HgS tourmaline	KBrO ₃
		Proustite: Ag ₃ AsS ₃	

Table 1.7 (continued)

Symmetry symbol (shorthand notation)	Groth designation	Examples Minerals	Synthetic crystals
$\bar{3}$ (C_{3i})	trigonal rhombohedral	dolomite: $\text{CaMg}(\text{CO}_3)_2$ Diopside: $\text{Ca}_6\text{Si}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ calcite: CaCO_3 corundum: Al_{12}O_3 –	$\text{NiSnCl}_6\cdot 6\text{H}_2\text{O}$ Li_2MoO_4 NaNO_3 NH_4SnF_3 $\text{CS}_2 \text{BisO}_{28}$ iodosuccinimide ($\text{CH}_2\text{CO})_2\text{NJ}$ $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ TeO_2 $\text{Ba}_6\text{Ti}_2\text{Nb}_8\text{O}_{30}$ NbP
$\bar{3}\text{m}$ (D_{3d})	trigonal scaloedric	–	
4 (C_4)	tetragonal pyramidal	Mellite: $\text{Al}_{12}\text{C}_{12}\text{O}_{12}\cdot 18\text{H}_2\text{O}$ phosgenite: $\text{Pb}_2\text{Cl}_2\text{CO}_3$ Diaboleite: $2\text{PbC}_1\text{OH Cu(OH)}_2$ Fresnoite: $\text{Ba}_2\text{TiSi}_2\text{O}_8$ Scheelite: CaWO_4 Fergusonite: YNbO_4 rutile: TiO_2 zirkon: ZrSiO_4 Cahnite: $\text{Ca}_2(\text{AsO}_4)(\text{B}(\text{OH})_4)$ –	NaIO_4 AgC_1O_3 MnF_2 HgI_2 LiNH_2 pentaerythritol C($\text{CH}_2\text{OH})_2$ KH_2PO_4 urea $\text{CO}(\text{NH}_2)_2$
4m (C_{4v})	trapezohedral ditetragonal pyramidal		
$4/m$ (C_{4h})	tetragonal dipyramidal		
$4/\text{mm}$ (D_{4h})	ditetragonal dipyramidal tetragonal disphenoidal		
$\bar{4}$ (S_4)	tetragonal disphenoidal		
42 (D_{2d})	tetragonal scalenoedral hexagonal pyramidal	chalkopyrite: CuFeS_2 Stannine: $\text{Cu}_2\text{FeSnS}_4$ Mixite	
6 (C_6)	hexagonal pyramidal	Nepheline: $\text{KNa}_3(\text{AlSiO}_4)_4$ β -Quartz: SiO_2	LjIO_3 $\text{A}_1(\text{JO}_3)_3\cdot 2\text{H}_2\text{O}\cdot 6\text{H}_2\text{O}$ TaSi_2 LaPO_4
62 (D_6)	hexagonal trapezohedral	Kaliophilit: KAlSiO_4	ZnO
6m (C_{6v})	dihexagonal pyramidal	Wurtzite: ZnS Greenockite: CdS	$\text{LiCKV}_3\text{H}_2\text{O}$

Table 1.7 (continued)

Symmetry symbol (shorthand notation)	Groth designation	Examples Minerals	Synthetic crystals
6/m (C_{6h})	hexagonal dipyramidal bihexagonal dipyramidal trigonal dipyramidal ditrigonal dipyramidal cubic tetrahedral pentagonal dodecahedral cubic bisdodecahedral cubic hextetrahedral cubic pentagonal icositetrahedral cubic hexakis- oktaedral	Apatite: $\text{Ca}_5(\text{PO}_4)_3\text{F}$ Jeremejewite: AlBO_3 beryl: $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$ Covellite: CuS -	PrBr_3 $\text{Ce}_2(\text{SO}_4)_3\text{H}_2\text{O}$ Mg graphite Li_2O_2 NaLuF_4 K_2ThF_6 LiNaCO_3 NaC_1O_3 $\text{Na}_3\text{SbS}_4\text{-H}_2\text{O}$ alum $\text{Pb}(\text{NO}_3)_2$ urotopine GaAs NH_4Cl (?)
6/m (D_{6h})		Benitoite: $\text{BaTiSi}_3\text{O}_9$	
$\bar{6}$ (C_{3h})		Bastnäsite: CeFCO_3	
$\bar{6}2$ (D_{3h})		Ullmannite: NiSbS	
23 (T)		Langbeinite: $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$	
m3 (T_h)		pyrite: FeS_2	
$\bar{4}3$ (T_d)		Cobalttin: CoAsS zinc blonde: ZnS	
43 (O)		Eulytine: Bi_4SiO_4	
4/m3 (O_h)		Petzite: Ag_3AuTe_2 spinel: MgAl_2O_4 garnet	NaCl CaF_2

1.7.4

Morphological Symmetry, Determining the Point Symmetry Group

Sometimes the morphological symmetry of the freely grown crystals is lower than the associated point symmetry group. This case is called hypomorphy. It can occur when the mother phase, from which the crystals grow, possesses asymmetric molecules (e.g., from an aqueous solution of potassium sulfate with orthorhombic disphenoids, which simulate the PSG 22; but the true symmetry is mmm). If the crystals show a morphologically higher symmetry than the corresponding point symmetry group, then we have a hypermorphy, such as, e.g., with the α -alums. The hypermorphy is much more prevalent than the hypomorphy.

The PSG of a crystal can be determined as follows:

1. *Morphological diagnosis* with the aid of general forms or certain combinations of special forms. If the result is not unequivocal, one can try to obtain general forms by means of spherical growth experiments. This is done by preparing probes with spherically shaped regions from the crystal to be analyzed, and placing them in a slightly supersaturated solution of the given substance for further growth. One gets small plane surface elements (spherical caps) with normals belonging to faces with relatively minimal surface energy. The PSG can often, but not always, be derived from the distribution of these spherical caps.
2. *Investigating the surface symmetry* of different forms (growth assessories, etch figures, epitaxial growth figures, impact and pressure figures, directional dependence of the mechanical, chemical or physical erosion).
3. *Investigating the physical properties*. The suitable measures are discussed in Section 12.3.

1.7.5

Symmetry of Space Lattices (Space Groups)**1.7.5.1 Bravais Types**

We return now to point (d) of Section 1.7.2. The discussion concerned the combination of rotation axes and rotoinversion axes with translations. Since the operation of translation can be repeated an arbitrary number of times, bodies with translational symmetry always possess unlimited extension in the rigorous sense. If only one translation vector t_1 exists, then we are dealing with a one-dimensional lattice (lattice chain), whose symmetry-equivalent objects may take three-dimensional forms. Two different translations t_1 and t_2 result in a two-dimensional lattice (net). The general three-dimensional translation lattice exhibits three noncoplanar translations t_1 , t_2 , and t_3 , which, repeated

any number of times, always reproduce the lattices. For the description of the symmetry relationships and the consideration of the properties of the lattice, and thus that of the ideal crystal, it suffices to investigate a single cell of the lattice, the elementary cell.

We represent the entirety of the lattice with the end points of the vectors $\mathbf{r} = r_1\mathbf{a}_1 + r_2\mathbf{a}_2 + r_3\mathbf{a}_3 = r_i\mathbf{a}_i$, where r_1, r_2, r_3 are arbitrary integers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ form a basic system of three nonplanar vectors. An elementary cell of this lattice is the parallelepiped spanned by $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. This translation is called simple primitive because one cell contains just one lattice point. How do these translation lattices differ with respect to their symmetry properties? As we have already seen in our discussion of crystal systems, there exist, due to symmetry properties, only seven distinguishable metric types, and thus only seven distinguishable systems of primitive cells. These seven systems are called *primitive Bravais types* after the French mathematician Auguste Bravais. Each possesses the holohedral symmetry of the given crystal system (Fig. 1.32).

The question now remains to be answered, whether for primitive lattices with specific metric values, further distinguishable types exist. One can also pose this question in another light. Do certain axes ratios $a_1:a_2:a_3$ and angles α_i of the primitive Bravais types exist such that in the given lattice one finds larger cells with higher symmetry than the primitive cells? These larger cells, however, can only possess the holohedral symmetry of the crystal system. They contain more than one lattice point per cell and are thus designated as *multiple-primitive Bravais types*. How many different types of these exist? We imagine that a multiple-primitive cell is constructed from a simple-primitive cell by the addition of further lattice points. This new lattice must also be a translation lattice. Let $\mathbf{r} = r_i\mathbf{a}_i$ be a first primitive lattice. If one joins at the end point of \mathbf{p} , itself not a lattice vector, a further lattice of the same type, then one constructs a lattice consisting of points \mathbf{r} and $\mathbf{r}' = \mathbf{r} + \mathbf{p}$. A repetition of the translation \mathbf{p} must again lead to a lattice point, if the constructed lattice is to represent a translation lattice. Thus $\mathbf{r}' + \mathbf{p} = \mathbf{r} + 2\mathbf{p} = \mathbf{r}''$ and therefore $2\mathbf{p} = \mathbf{r}'' - \mathbf{r} = \mathbf{r}'''$ is a lattice vector of the first translation lattice, i.e., \mathbf{p} must be equal to half a lattice vector of the first lattice. One now selects \mathbf{p} so that it lies within the unit cell of the first lattice. This is not a restriction, since each other cell can be considered as an elementary cell. For \mathbf{p} , we then have the following possibilities:

- $\mathbf{p} =$ half basic vector, thus $\mathbf{p} = \mathbf{a}_i/2$ with $i = 1, 2, 3$.
- $\mathbf{p} =$ half diagonal vector of a basic face of the unit cell, thus $\mathbf{p} = (\pm \mathbf{a}_i \pm \mathbf{a}_j)/2$ with $i \neq j$.
- $\mathbf{p} =$ half space-diagonal vector of the elementary cell, thus $\mathbf{p} = (\pm \mathbf{a}_1 \pm \mathbf{a}_2 \pm \mathbf{a}_3)/2$.

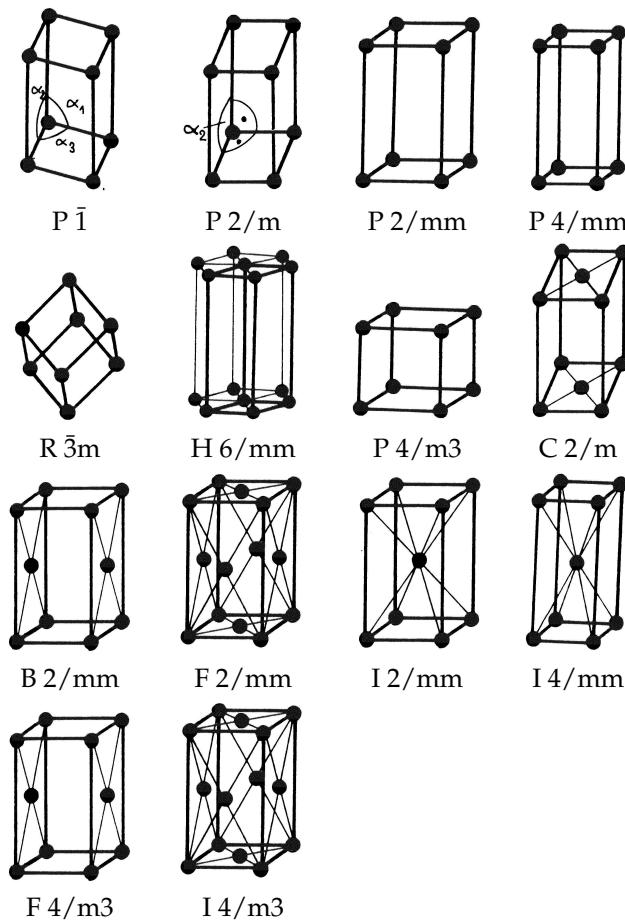


Figure 1.32 The 14 Bravais types, 7 primitive, and 7 multiple primitive.

This operation of construction is called *centering*. One can distinguish a total of seven multiple-primitive lattices, also presented in Fig. 1.32.

The following symbols are used to specify Bravais types:

P: primitive lattice

A, B, C: one-sided face-centered lattice, depending on the orientation of the face parallel to (100), (010), or (001),

R: instead of P in a lattice with trigonal-rhombohedral unit cell,

H: instead of P in a hexagonal lattice with trigonal-hexagonal unit cell,

F: face-centered lattice,

I: body-centered lattice.

These symbols are provided with the Hermann–Mauguin symbols for the holohedral symmetry of the given cell (Fig. 1.32).

1.7.5.2 Screw Axes and Glide Mirror Planes

Consider an arbitrary translation lattice with the properties of an *ideal crystal*. In primitive translation lattices the space is empty except for the lattice points. We now imagine that the cells of a general translation lattice are occupied with an arrangement (motif) which is described by further discrete points inside the primitive cells. These are represented by the parameter vectors p_i associated with a property A_i . For example, occupation by the center of gravity of certain types of atoms or by a continuous function $A(x)$ is dependent on the position vector such as, e.g., a time-averaged electron density. Which symmetry properties can now appear in such general lattices? Apart from the symmetry operations already discussed for the point symmetry groups, one must now consider the possible combinations resulting from translations with rotations and rotoinversions.

First we consider the combination of rotation axes n with a translation t applied to the end point of an arbitrary vector y in a general translation lattice. The transformation is thus $y' = R_n(y) + t$. We call this a *screw operation* (Fig. 1.33a). It turns out that only the component $t_{\parallel n}$ (parallel to the screw axis) brings anything new. After an n -fold screw operation, any point along the screw axis is displaced by nt . Arbitrary repetition creates a chain of equidistant points. The distance between points must be equal to the length a of a lattice vector in the direction of the screw axis or a multiple thereof; thus $nt = pa$, where $p = 0, 1, 2, 3, \dots, n - 1$. We obtain the condition $t = pa/n$. We introduce the symbol n_p for such a screw operation (screw axis). A total of 15 rotation and screw axes exist: 2, 2₁, 3, 3₁, 3₂, 4, 4₁, 4₂, 4₃, 6, 6₁, 6₂, 6₃, 6₄,

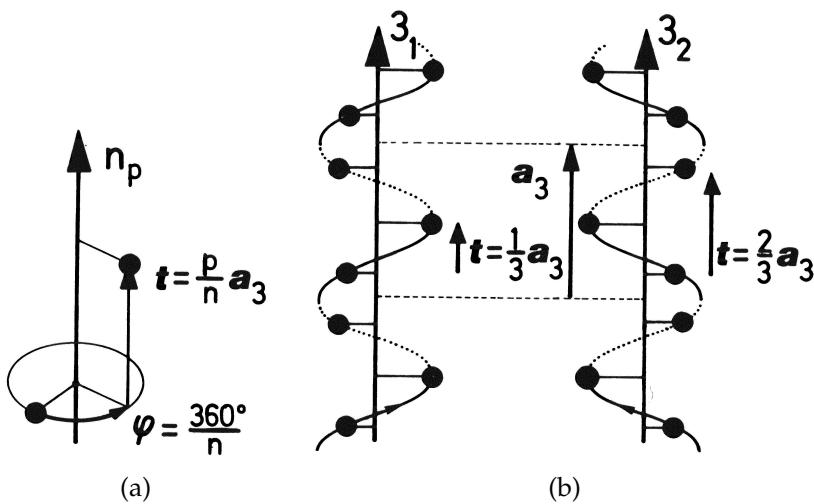


Figure 1.33 (a) Screw axis n_p with screw component $\parallel a_3$; (b) screw operation 3_1 and 3_2 (right and left screw).

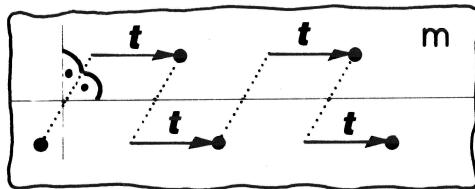


Figure 1.34 Glide plane.

65. The screw axes n_p and $n_{(n-p)}$ are distinguished only by the sense of screw rotation (right and left screws). Examples are presented in Fig. 1.33b.

The combination of translation and rotoinversion only leads, in the case of $\bar{2} = m$ (mirror plane), to new operations with the component $t_{\parallel m}$ (perpendicular to $\bar{2}$, i.e., lying in the mirror plane). A repetition of the operation $y' = R_m(y)$ results in a zigzag chain of points with a separation of $2t$. These chains must have the period a of a lattice vector, i.e., $t = a/2$. These operations are called *glide planes* (Fig. 1.34). Here, it also suffices to restrict oneself to lattice vectors lying within the elementary cell.

1.7.5.3 The 230 Space Groups

We now ask which distinguishable combinations of all the operations discussed so far exist in general translation lattices (with arbitrary motif of the elementary cells). One must also examine the compatibility of the different operations in a similar manner as with the derivation of the point symmetry groups. This work was completed independently by Fedorow (1890) and Schoenflies (1891). The result was 230 distinguishable combinations, the space groups. The symbols used today follow the Hermann–Mauguin symbols for the point symmetry groups. The first symbol represents the Bravais type of the lattice, hence P, R, H, A, B, C, F, I. These are followed by the symbols for the symmetry operations, ordered according to the three prominent viewing directions. Here also, it suffices in most cases only to give the symbol for the generating operation. To avoid alternative interpretations one should correctly note the absence of symmetry operations in a certain viewing direction with the symbol 1. Detailed explanations on the arrangement of the symmetry elements in the space groups and the selection of the origin as well as an overview on equivalent settings and further properties are found in the *International Tables for X-ray Crystallography*.

The important question of how one derives from a space group the appropriate point symmetry group, which describes the macroscopic symmetry of a finite space lattice, is quite simple to answer. In the macroscopic world, screw axes appear as ordinary rotation axes and glide mirror planes as ordinary symmetry planes. Rotoinversion axes are also directly expressed in the symmetry

of the point groups. In the macroscopic world an eventual centering of the unit cells seems to remain hidden. However, the Bravais-type as well as the screw axes and glide mirror planes often manifest themselves quite clearly in morphological and other macroscopic properties.

For the determination of the space group of a crystal, knowledge of the point symmetry group, the morphological metric and morphological details, especially the existence or absence of an inversion center, is an advantage. However, modern methods of structure analysis, especially with the aid of X-ray and neutron diffraction techniques, supported by computers and simulations, practically always allow us to disclose the symmetry of the space groups.

1.8

Supplements to Crystal Geometry

Many aspects of crystal geometry could not be taken up in the previous section. It may, however, be useful to point out some special features for the material scientist working in the field of crystal physics.

- *Bravais indices.* According to a suggestion from Bravais one can introduce in the trigonal-hexagonal coordinate system a fourth basic vector $a'_1 = -a_1 - a_2$ apart from the three base vectors a_1 , a_2 , and a_3 , produced by a rotation of a_2 about a_3 by an angle of 120° . The direction of a'_1 is symmetry equivalent to a_1 and a_2 . One can thus obtain, e.g., the symbols of symmetry-equivalent faces by the permutation of the first three Miller indices. Since the Miller indices transform as the basic vectors, we have $h'_1 = -h_1 - h_2$. From the normal triple indices $(h_1 h_2 h_3)$ we get the Bravais indices $(h_1 h_2 h'_1 h_3)$. In order to avoid confusion, one should always specify the reference system with triple indices used for trigonal or hexagonal crystals.
- *Twin formation.* The regular growth of several individuals of a crystal species orientated with respect to one another according to distinct rules is called twinning. Twin formation can be recognized using optic polarization microscopy and X-ray methods, and often macroscopically by re-entrant angles. A careful analysis of the mutual orientations of the parts leads to the corresponding twinning rule that the metric of the first part connects with the metric of the second part. A detailed presentation of twin and domain formation is given in Volume D, *International Tables for Crystallography* (2003).
- *Plane groups, line groups.* If one limits the translation symmetry to two vectors or one vector, one gets 17 or 2 different combination possibilities,

respectively, the so-called plane groups and line groups. They play a special role in the projection of space groups onto a plane.

- *Black–white groups, color groups.* The purely geometrical notion of symmetry may be broadened by connecting the geometric symmetry operations with the change of a certain property. The simplest type occurs when one generates a geometric symmetry-equivalent arrangement and simultaneously reverses the sign of a property. Thus one generates from +1 the sign –1 and vice versa. Instead of +1 and –1, other arbitrary two-valued properties, such as, e.g., black–white, on–off, up–down (spin orientation), can occur. Further broadening of the notion of symmetry leads to the color groups, in which the geometric symmetry operation is connected with a change in color or other multivalent properties, which repeats itself with the order of symmetry of the given operation. A clear representation of the color groups is made possible, e.g., when one attaches a fourth coordinate q to the geometric operation which delivers the value q^{m+1} with the m -fold application of the operation, where, e.g., in the case of the n -fold rotation axis $q^{n+1} = q$ and thus we must have $q^n = 1$. Here, the possible color values are specified by the unit roots $e^{2\pi im/n}$ ($1 \leq m \leq n$). The associated transformation matrix is then

$$R_n^F = \begin{pmatrix} v_{11} & v_{12} & v_{13} & 0 \\ v_{21} & v_{22} & v_{23} & 0 \\ v_{31} & v_{23} & v_{33} & 0 \\ 0 & 0 & 0 & e^{i\alpha} \end{pmatrix}$$

with $e^{i\alpha} = \cos \alpha + i \sin \alpha$, $i = \sqrt{-1}$ and $\alpha = 2\pi/n$.

There exist a total of 58 real black–white symmetry groups apart from the ordinary 32 PSGs, as well 32 further groups, the so-called gray point symmetry groups, created from the ordinary PSGs by the simultaneous inclusion of a negative property to a positive property. Thus we have a total of 122 distinguishable PSGs. The space groups have 1651 distinguishable cases, the Heesch–Shubnikov groups.

1.9

The Determination of Orientation with Diffraction Methods

The orientation of a macroscopic crystal, with a well-developed natural morphology, can very often be found with the help of the angles measured between neighboring faces or face normals. Additional information is obtained by studying thin slices under the polarization microscope. Finally, other properties, such as the propagation velocity of elastic waves in a certain direction

can contribute to the determination of orientation when the given elastic properties of the crystal are already known. Further details will be discussed in the following sections. More precise statements and with fundamentally higher certainty are obtained with the aid of X-ray methods. These, however, must be directly applicable to large crystals, or one must try to produce very small crystals of dimensions less than 1 mm as used in X-ray structure analysis, with a fixed relation to the object under study. This measure, however, requires special care. Thus, we will only outline the two most important methods for large crystals. These are the *Laue method* and the *Bragg method*.

In the Laue method, discussed at length in many textbooks, a beam of non-monochromatic X-rays (essentially the spectrum of the Bremsstrahlung) is incident on a probe and one observes the scattered reflections in different directions, each of which can be assigned to a certain assembly of lattice planes. This occurs with the aid of photographic films or sensitive detector systems, which also allow automatic evaluation. The respective gnomonic or stereographic projections of the normals of the lattice planes derived from the analysis allow us to determine the orientation of the crystallographic reference system of the object. The preferred method is to conduct the investigation in the transmission technique because, in general, it delivers more and sharper diffraction reflections than in the reflexion technique.

In the Bragg method one observes the diffraction in reflection with monochromatic radiation. The crystal is rotated in small steps about different axes, at a fixed direction of the primary X-ray beam, until the first reflection occurs with sufficient intensity. From the Bragg condition $2d(\mathbf{h}) \sin \theta = \lambda$, where λ is the wavelength of the radiation and 2θ is the diffraction angle (angle between the incident beam and the reflected beam), one gets, because of $d(\mathbf{h}) = 1/|\mathbf{h}|$, not only the orientation of the given lattice plane, but also the associated lattice plane spacing. If one succeeds in obtaining further reflections after directed rotation or tilting, then the orientation of the crystallographic reference system can be fixed. If the crystal possesses well-developed faces, one can measure the d -value at these without further manipulation, thus considerably simplifying the work. Nowadays, automatic equipment is available for this task.