

3.2. POINT GROUPS AND CRYSTAL CLASSES

- (i) For the face forms the cubic point groups 23 and $m\bar{3}$ (Table 3.2.3.2), and for the point forms the cubic space groups $P23$ (195) and $Pm\bar{3}$ (200) have to be considered. For each ‘initial’ triplet (hkl) , the set of Miller indices of the (general or special) crystal form with the same face symmetry in 23 (for group 235) or $m\bar{3}$ (for $m\bar{3}5$) is taken. For each ‘initial’ triplet x, y, z , the coordinate triplets of the (general or special) position with the same site symmetry in $P23$ or $Pm\bar{3}$ are taken.
- (ii) To obtain the complete set of icosahedral Miller indices and point coordinates, the ‘cubic’ (hkl) triplets (as rows) and x, y, z triplets (as columns) have to be multiplied with the identity matrix and with
 - (a) the matrices Y, Y^2, Y^3 and Y^4 for the Miller indices;
 - (b) the matrices Y^{-1}, Y^{-2}, Y^{-3} and Y^{-4} for the point coordinates.

This sequence of matrices ensures the same correspondence between the Miller indices and the point coordinates as for the crystallographic point groups in Table 3.2.3.2.

The matrices²⁰ are

$$Y = Y^{-4} = \begin{pmatrix} \frac{1}{2} & g & G \\ g & G & -\frac{1}{2} \\ -G & \frac{1}{2} & g \end{pmatrix}, \quad Y^2 = Y^{-3} = \begin{pmatrix} -g & G & \frac{1}{2} \\ G & \frac{1}{2} & -g \\ -\frac{1}{2} & g & -G \end{pmatrix},$$

$$Y^3 = Y^{-2} = \begin{pmatrix} -g & G & -\frac{1}{2} \\ G & \frac{1}{2} & g \\ \frac{1}{2} & -g & -G \end{pmatrix}, \quad Y^4 = Y^{-1} = \begin{pmatrix} \frac{1}{2} & g & -G \\ g & G & \frac{1}{2} \\ G & -\frac{1}{2} & g \end{pmatrix},$$

with²¹

$$G = \frac{\sqrt{5} + 1}{4} = \frac{\tau}{2} = \cos 36^\circ = 0.80902 \simeq \frac{72}{89}$$

$$g = \frac{\sqrt{5} - 1}{4} = \frac{\tau - 1}{2} = \cos 72^\circ = 0.30902 \simeq \frac{17}{55}.$$

These matrices correspond to counter-clockwise rotations of $72^\circ, 144^\circ, 216^\circ$ and 288° around a fivefold axis parallel to $[1\tau 0]$.

The resulting indices h, k, l and coordinates x, y, z are irrational but can be approximated closely by rational (or integral) numbers. This explains the occurrence of almost regular icosahedra or pentagon-dodecahedra as crystal forms (for instance pyrite) or atomic groups (for instance B_{12} icosahedron).

Further descriptions (including diagrams) of noncrystallographic groups are contained in papers by Nowacki (1933) and A. Niggli (1963) and in the textbooks by P. Niggli (1941, pp. 78–80, 96), Shubnikov & Koptsik (1974) and Vainshtein (1994). For the geometry of polyhedra, the well known books by H. S. M. Coxeter (especially Coxeter, 1973) are recommended.

3.2.1.4.3. Sub- and supergroups of the general point groups

In Figs. 3.2.1.4 to 3.2.1.6, the subgroup and supergroup relations between the two-dimensional and three-dimensional general point groups are illustrated. It should be remembered that the index of a group–subgroup relation between two groups of order infinity may be finite or infinite. For the two spherical

²⁰ Note that for orthogonal matrices $Y^{-1} = Y^t$ (t = transposed).
²¹ The number $\tau = 2G = 2g + 1 = (\sqrt{5} + 1)/2 = 1.618034$ (Fibonacci number) is the characteristic value of the golden section $(\tau + 1) : \tau = \tau : 1$, i.e. $\tau(\tau - 1) = 1$. Furthermore, τ is the distance between alternating vertices of a regular pentagon of unit edge length and the distance from centre to vertex of a regular decagon of unit edge length.

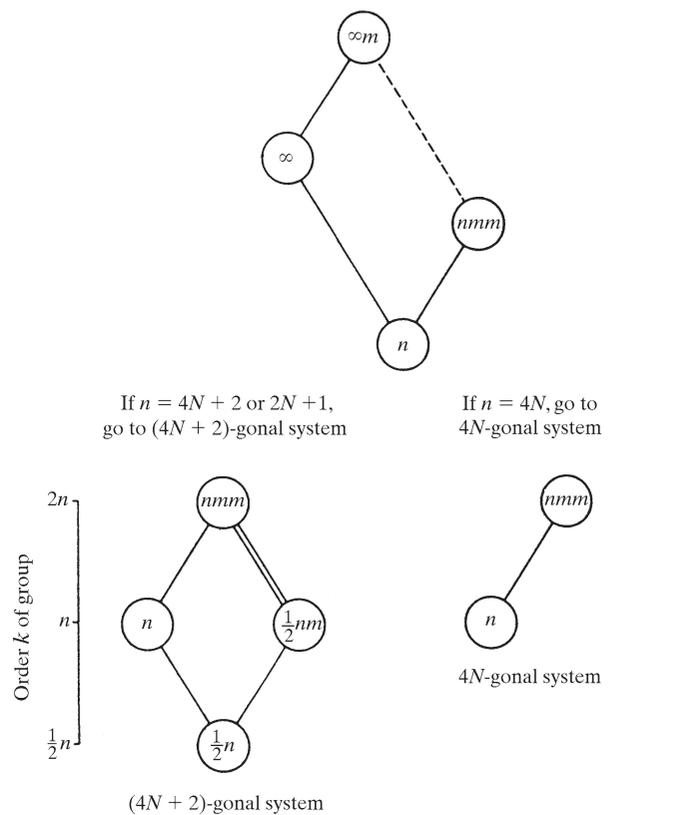


Figure 3.2.1.4 Subgroups and supergroups of the two-dimensional general point groups. Solid lines indicate maximal normal subgroups, double solid lines mean that there are two maximal normal subgroups with the same symbol. Dashed lines refer to sets of maximal conjugate subgroups. For the finite groups, the orders are given on the left. Note that the subgroups of the two circular groups are not maximal and the diagram applies only to a specified value of N (see text). For complete examples see Fig. 3.2.1.5.

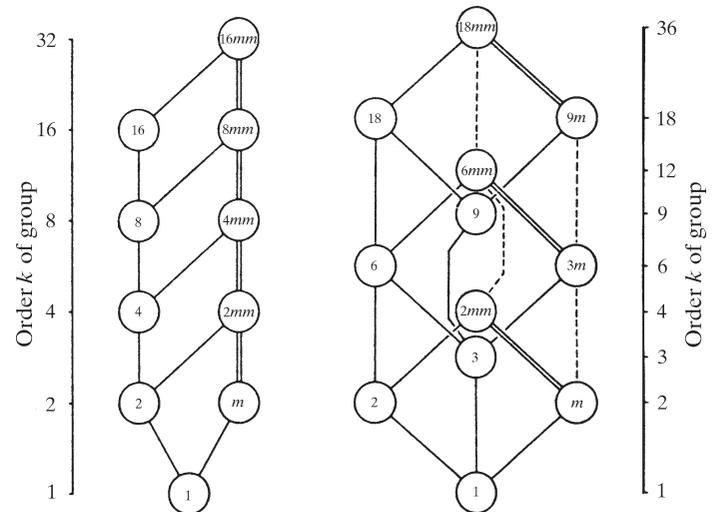


Figure 3.2.1.5 The subgroups of the two-dimensional general point groups $16mm$ ($4N$ -gonal system) and $18mm$ [$(2N + 1)$ -gonal system], including the $(2N + 1)$ -gonal groups]. Compare with Fig. 3.2.1.4 which applies only to one value of N .

groups, for instance, the index is $[2]$; the cylindrical groups, on the other hand, are subgroups of index $[\infty]$ of the spherical groups.

Fig. 3.2.1.4 for two dimensions shows that the two circular groups ∞m and ∞ have subgroups of types nmm and n ,

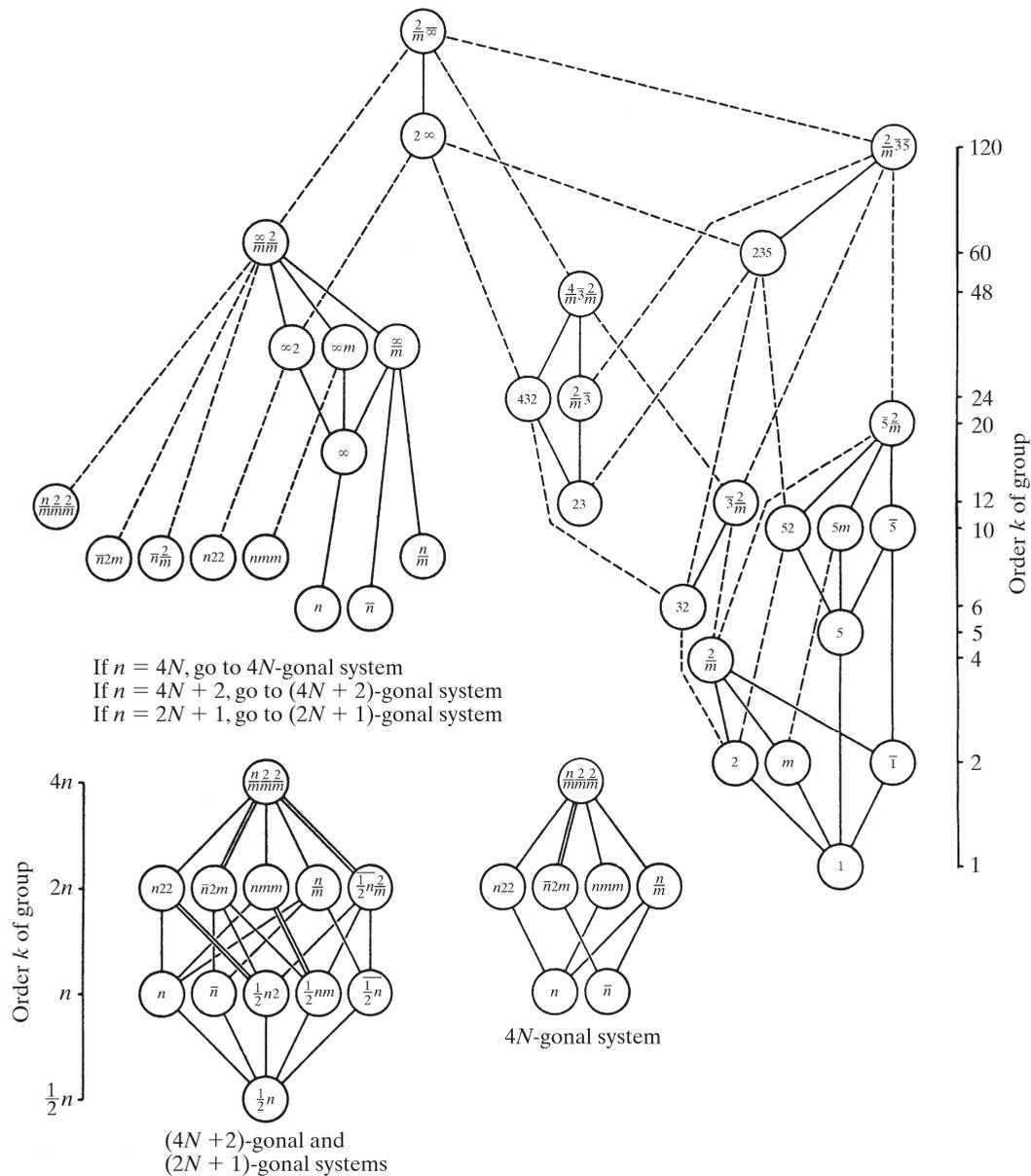


Figure 3.2.1.6

Subgroups and supergroups of the three-dimensional general point groups. Solid lines indicate maximal normal subgroups, double solid lines mean that there are two maximal normal subgroups with the same symbol. Dashed lines refer to sets of maximal conjugate subgroups. For the finite groups, the orders are given on the left and on the right. Note that the subgroups of the five cylindrical groups are not maximal and that the diagram applies only to a specified value of N (see text). Only those crystallographic point groups are included that are maximal subgroups of noncrystallographic point groups, cf. Fig. 3.2.1.3. Full Hermann–Mauguin symbols are used.

respectively, each of index $[\infty]$. The order of the rotation point may be $n = 4N$, $n = 4N + 2$ or $n = 2N + 1$. In the first case, the subgroups belong to the $4N$ -gonal system, in the latter two cases, they belong to the $(4N + 2)$ -gonal system. [In the diagram of the $(4N + 2)$ -gonal system, the $(2N + 1)$ -gonal groups appear with the symbols $\frac{1}{2}nm$ and $\frac{1}{2}n$.] The subgroups of the circular groups are not maximal because for any given value of N there exists a group with $N' = 2N$ which is both a subgroup of the circular group and a supergroup of the initial group.

The subgroup relations, for a specified value of N , within the $4N$ -gonal and the $(4N + 2)$ -gonal system, are shown in the lower part of the figure. They correspond to those of the crystallographic groups. A finite number of further maximal subgroups is obtained for lower values of N , until the crystallographic groups (Fig. 3.2.1.2) are reached. This is illustrated for both systems in Fig. 3.2.1.5.

Fig. 3.2.1.6 for *three dimensions* illustrates that the two spherical groups $2/m\infty$ and 2∞ each have one infinite set of

cylindrical maximal conjugate subgroups, as well as one infinite set of cubic and one infinite set of icosahedral maximal finite conjugate subgroups, all of index $[\infty]$.

Each of the two icosahedral groups 235 and $2/m\bar{3}\bar{5}$ has one set of five cubic, one set of six pentagonal and one set of ten trigonal maximal conjugate subgroups of indices $[5]$, $[6]$ and $[10]$, respectively (cf. Section 3.2.1.4.2, *The two icosahedral groups*); they are listed on the right of Fig. 3.2.1.6. For the crystallographic groups, Fig. 3.2.1.3 applies. The subgroup types of the five cylindrical point groups are shown on the upper left part of Fig. 3.2.1.6. As explained above for two dimensions, these subgroups are *not maximal* and of index $[\infty]$. Depending upon whether the main symmetry axis has the multiplicity $4N$, $4N + 2$ or $2N + 1$, the subgroups belong to the $4N$ -gonal, $(4N + 2)$ -gonal or $(2N + 1)$ -gonal system.

The subgroup and supergroup relations within these three systems are displayed in the lower left part of Fig. 3.2.1.6. They are analogous to the crystallographic groups. To facilitate the

use of the diagrams, the $(4N + 2)$ -gonal and the $(2N + 1)$ -gonal systems are combined, with the consequence that the five classes of the $(2N + 1)$ -gonal system now appear with the symbols $\frac{1}{2}n\frac{2}{m}$, $\frac{1}{2}n2$, $\frac{1}{2}nm$, $\frac{1}{2}n$ and $\frac{1}{2}n$. Again, the diagrams apply to a specified value of N . A finite number of further maximal subgroups is obtained for lower values of N , until the crystallographic groups (Fig. 3.2.1.3) are reached (*cf.* the two-dimensional examples in Fig. 3.2.1.5).

3.2.2. Point-group symmetry and physical properties of crystals

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In the previous section (Section 3.2.1), the crystallographic and noncrystallographic point groups are treated under geometrical aspects only. In the present section the point-group symmetries of the physical properties are considered. Among the physical properties, those represented by tensors are accessible to a mathematical treatment of their symmetries, which are apparent by the invariance of tensor components under symmetry operations. For more details the reader is referred to Nye (1957, 1985), Paufler (1986), Schwarzenbach & Chapuis (2006) and Shuvalov (1988). A similar comprehensive treatment of non-tensorial properties, such as cleavage, plasticity, hardness or crystal growth does not exist, but these properties are, of course, also governed by the crystallographic point-group symmetry.

3.2.2.1. General restrictions on physical properties imposed by symmetry

3.2.2.1.1. Neumann's principle

Neumann's principle (Neumann, 1885) describes the relation between the symmetry \mathcal{Q} of a physical property and the crystallographic point group \mathcal{P} of a crystal. It states that the symmetry of any physical property of a crystal is higher than, or at least equal to, its crystallographic point-group symmetry, or in the language of groups, the symmetry \mathcal{Q} of any physical property of a crystal is a proper or improper supergroup of its crystallographic symmetry \mathcal{P} : $\mathcal{Q} \subseteq \mathcal{P}$. This is easily illustrated for polar second-rank tensors, which are represented by ellipsoids and hyperboloids. The representation surfaces of triclinic, monoclinic and orthorhombic crystals are general ellipsoids or hyperboloids of symmetry $\mathcal{Q} = 2/m2/m2/m$, which is a proper supergroup of all triclinic, monoclinic and orthorhombic point groups with the only exception of the orthorhombic holohedry $\mathcal{P} = 2/m2/m2/m$, for which the two symmetries are the same. For the uniaxial crystals of the trigonal, tetragonal and hexagonal systems the representation ellipsoids and hyperboloids have rotation symmetries with the cylindrical point group $\mathcal{Q} = \infty/m2/m$ (see Table 3.2.1.6), which is a proper supergroup of all uniaxial crystallographic point groups. For cubic crystals, second-rank tensors are isotropic and represented by a sphere with point-group symmetry $\mathcal{Q} = 2/m\bar{3} (\infty\infty m)$, a proper supergroup of all cubic crystallographic point groups. For more details the reader is referred to Paufler (1986) and Authier (2014). A short resume is given by Klapper & Hahn (2005).

As a consequence of the invariance of tensor components under a symmetry operation (or alternatively: under a transformation of the coordinate system to a symmetry-equivalent one),

some of the tensor components are equal or even zero. The number of independent components decreases when the symmetry of the crystal increases. Thus, an increase of the point-group symmetry from 1 (triclinic) to $4/m\bar{3}2/m$ (cubic) or to the sphere group $\infty\infty m$ (*i.e.* isotropy) reduces the number of tensor components for symmetrical second-rank tensors from 6 to 1. Even more drastic is this reduction for all tensors of odd rank (such as pyroelectricity and piezoelectricity) or axial tensors of second rank (*e.g.* optical activity): all components are zero if an inversion centre is present, *i.e.* properties described by these tensors do not exist in centrosymmetric crystals (see the textbooks of tensor physics mentioned above). These properties, which exist only in noncentrosymmetric crystals are, as a rule, the most important ones, not only for physical applications but also for structure determination, because they allow a proof of the absence of a symmetry centre.

For the description of noncentrosymmetric crystals and their specific properties, certain notions are of importance and these are explained in the following two sections.

3.2.2.1.2. Curie's principle

Curie's principle (Curie, 1894) describes the crystallographic symmetry \mathcal{P}_F of a macroscopic crystal which is subject to an external influence F , for example to an electric field \mathbf{E} , to uniaxial stress σ_{ii} , to a temperature change ΔT *etc.* For this treatment, the point-group symmetries \mathcal{R} of the external influences (Curie groups) are defined as follows (see Authier, 2014, p. 11; Paufler, 1986, p. 29):

Homogeneous electric field \mathbf{E} : $\mathcal{R} = \infty m$ (polar continuous rotation axis with 'parallel' mirror planes, *i.e.* symmetry of a stationary cone) [Note that a rotating cone (left- or right-handed) represents geometrically the polar enantiomorphous group ∞ ; a stationary cone represents the polar group ∞m with 'vertical' mirror planes, *cf.* Section 3.2.1.4.1.];

Homogeneous magnetic field \mathbf{H} : $\mathcal{R} = \infty/m$ (symmetry of a rotating cylinder);

Uniaxial stress σ_{ii} : $\mathcal{R} = \infty/m2/m$ (symmetry of a stationary centrosymmetric cylinder);

Temperature change ΔT or hydrostatic pressure p (scalars): $\mathcal{R} = 2/m\bar{3} (\infty\infty m)$ (symmetry of a stationary centrosymmetric sphere);

Shear stress σ_{ij} : $\mathcal{R} = 2/m2/m2/m$ (orthorhombic).

According to Curie's principle, the point-group symmetry \mathcal{P}_F of the crystal under the external field F is the intersection symmetry of the two point groups: \mathcal{P} of the crystal without field and \mathcal{R} of the field without crystal: $\mathcal{P}_F = \mathcal{R} \cap \mathcal{P}$; *i.e.* \mathcal{P}_F is a (proper or improper) subgroup of both groups \mathcal{R} and \mathcal{P} .

As examples we consider the effect of an electric field ($\mathcal{R} = \infty m$) and of a uniaxial stress ($\mathcal{R} = \infty/m2/m$) along one of the (four) threefold rotoinversion axes $\bar{3}$ of cubic crystals with point groups $\mathcal{P} = 2/m\bar{3}$ and $\mathcal{P} = 4/m\bar{3}2/m$.

Electric field parallel to [111]:

$2/m\bar{3} \cap \infty m$:	$\mathcal{P}_F = 3$	along [111] (polar, pyroelectric, optically active; <i>cf.</i> Sections 3.2.2.5 and 3.2.2.4.2)
$4/m\bar{3}2/m \cap \infty m$:	$\mathcal{P}_F = 3m$	along [111] (polar, pyroelectric, not optically active)