3.2. POINT GROUPS AND CRYSTAL CLASSES

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 $\frac{1}{2}n\frac{2}{m}, \frac{1}{2}n2, \frac{1}{2}nm, \overline{\frac{1}{2}n}$ 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

By H. Klapper and Th. Hahn

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 $\mathcal{Q} = 2/m\,2/m\,2/m$, which is a proper supergroup of all triclinic, monoclinic and orthorhombic point groups with the only exception of the orthorhombic holohedry $\mathcal{P} = 2/m\,2/m\,2/m$, 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 $\mathcal{Q} = \infty/m\,2/m$ (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 $\mathcal{Q} = 2/m\overline{\infty}$ ($\infty\infty m$), 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 $4/m\,\overline{3}\,2/m$ (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}: $\mathcal{R} = \infty/m\,2/m$ (symmetry of a stationary centrosymmetric cylinder);

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

Shear stress σ_{ij}: $\mathcal{R} = 2/m\,2/m\,2/m$ (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 ($\mathcal{R} = \infty/m\,2/m$) along one of the (four) threefold rotoinversion axes $\overline{3}$ of cubic crystals with point groups $\mathcal{P} = 2/m\,\overline{3}$ and $\mathcal{P} = 4/m\,\overline{3}\,2/m$.

Electric field parallel to [111]:

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

Table 3.2.2.1
The 11 Laue classes, the 21 noncentrosymmetric crystallographic point groups (crystal classes) and the occurrence (+) of specific crystal properties

The number of non-zero independent tensor components is given in parentheses. For comparison, the icosahedral and the sphere groups (isotropy) are added. For first-rank tensors the direction [uvw] of the property vector is given. There are 10 pyroelectric, 20 piezoelectric, 11 enantiomorphic and 15 optically active crystal classes.

Crystal system	Laue class	Noncentrosymmetric point group	First-rank tensor (*e.g.* pyroelectricity, piezoelectricity under hydrostatic pressure)	Third-rank tensor (*e.g.* piezoelectricity, second-harmonic generation)	Enantiomorphism	Axial second-rank tensor (optical activity = optical gyration)
Triclinic	$\bar{1}$	1	+ (3) [uvw]	+ (18)	+	+ (6)
Monoclinic	$2/m$	2	+ (1) [010]†	+ (8)	+	+ (4)
		m	+ (2) [$u0w$]†	+ (10)	−	+ (2)
Orthorhombic	$2/m\,2/m\,2/m$	222	−	+ (3)	+	+ (3)
		$mm2$	+ (1) [001]	+ (5)	−	+ (1)
Tetragonal	$4/m$	4	+ (1) [001]	+ (4)	+	+ (2)
		$\bar{4}$	−	+ (4)	−	+ (2)
	$4/m\,2/m\,2/m$	422	−	+ (1)	+	+ (2)
		$4mm$	+ (1) [001]	+ (3)	−	−
		$\bar{4}2m$	−	+ (2)	−	+ (1)
Trigonal	$\bar{3}$	3	+ (1) [001]‡	+ (6)	+	+ (2)
	$\bar{3}2/m$	32	−	+ (2)	+	+ (2)
		$3m$	+ (1) [001]‡	+ (4)	−	−
Hexagonal	$6/m$	6	+ (1) [001]	+ (4)	+	+ (2)
		$\bar{6}$	−	+ (2)	−	−
	$6/m\,2/m\,2/m$	622	−	+ (1)	+	+ (2)
		$6mm$	+ (1) [001]	+ (3)	−	−
		$\bar{6}2m$	−	+ (1)	−	−
Cubic	$2/m\,\bar{3}$	23	−	+ (1)	+	+ (1)
	$4/m\,\bar{3}\,2/m$	432	−	−	+	+ (1)
		$\bar{4}3m$	−	+ (1)	−	−
Icosahedral	$m\bar{3}\bar{5}$ ($\bar{5}\bar{3}m$)	235 (532)	−	−	+	+ (1)
Spherical	$m\overline{\infty}$ ($\infty\infty m$)	2∞ ($\infty\infty$)	−	−	+	+ (1)

† Unique axis b.   ‡ Hexagonal axes.

Uniaxial stress parallel to [111]:

$$2/m\,\bar{3} \cap \infty/m\,2/m: \qquad \mathcal{P}_F = \bar{3} \qquad \text{along [111]}$$
$$4/m\,\bar{3}\,2/m \cap \infty/m\,2/m: \quad \mathcal{P}_F = \bar{3}\,2/m \quad \text{along [111]}.$$

Note that, in contrast to uniaxial stress, the electric field destroys centrosymmetry, leading to pyroelectricity and even optical gyration. The polarity and the gyration sense are reversed upon reversal of the electric field. If the electric field and the uniaxial stress were applied to an arbitrary (non-symmetry) direction of the above cubic crystals, point groups 1 and $\bar{1}$ would result in the two cases.

If a scalar influence $\mathcal{R} = 2/m\,\overline{\infty}$ ($\infty\infty m$) (centrosymmetric sphere group) is applied to a crystal, its symmetry $\mathcal{P}_F = \mathcal{P}$ is not changed, provided that no phase transition is induced.

For further reading on tensor properties of crystals the text-books in the references and *International Tables for Crystallography*, Volume D (2014) are recommended.

3.2.2.1.3. Enantiomorphism, enantiomerism, chirality, dissymmetry

All these terms refer to the same symmetry restriction, the absence of improper rotations (rotoinversions, rotoreflections) in a crystal or in a molecule. This implies in particular the absence of a centre of symmetry, $\bar{1}$, and of a mirror plane, $m = \bar{2}$, but also of a $\bar{4}$ axis. As a consequence, such *chiral* crystals or molecules can occur in two different forms, which are related as a right and a left hand; hence, they are called right-handed and left-handed forms. These two forms of a molecule or a crystal are mirror-related and not superimposable (not congruent). Thus, the only symmetry operations that are allowed for *chiral* objects are proper rotations. Such objects are also called *dissymmetric*, in contrast to *asymmetric* objects, which have no symmetry.

The terms *enantiomerism* and *chirality* are mainly used in chemistry and applied to molecules, whereas the term *enantiomorphism* is preferred in crystallography if reference is made to crystals.

Enantiomorphic crystals, as well as solutions or melts containing chiral molecules of one handedness, exhibit optical activity (*cf.* Section 3.2.2.4.2). Crystals and molecules of the other handedness show optical activity with the opposite sense of rotation. For this reason, two molecules of opposite chirality are also called *optical isomers*.

Chiral molecules form enantiomorphic crystals of the corresponding handedness. These crystals belong, therefore, to one of the 11 crystal classes allowing enantiomorphism (Table 3.2.2.1). Racemic mixtures (containing equal amounts of molecules of each chirality), however, may crystallize in non-enantiomorphic or even centrosymmetric crystal classes. Racemization (*i.e.* the switching of molecules from one chirality to the other) of an optically active melt or solution can occur in some cases during crystallization, leading to non-enantiomorphic crystals.

references