

3. ADVANCED TOPICS ON SPACE-GROUP SYMMETRY

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) $[010]^\dagger$	+ (8)	+	+ (4)
		m	+ (2) $[u0w]^\dagger$	+ (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) $[001]^\ddagger$	+ (6)	+	+ (2)
	$\bar{3}2/m$	32	–	+ (2)	+	+ (2)
		$3m$	+ (1) $[001]^\ddagger$	+ (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	$m\ \bar{\infty}\ (\infty\ \infty\ m)$	$2\infty\ (\infty\ \infty)$	–	–	+	+ (1)

† Unique axis b . ‡ Hexagonal axes.

Uniaxial stress parallel to $[111]$:

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

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 $\mathcal{R} = 2/m\ \bar{\infty}\ (\infty\ \infty\ m)$ (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 textbooks 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, roto-reflections) 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.

3.2. POINT GROUPS AND CRYSTAL CLASSES

Table 3.2.2.2

Polar axes and nonpolar directions in the 21 noncentrosymmetric crystal classes

All directions normal to an evenfold rotation axis and along rotoinversion axes are nonpolar. All directions other than those in the column 'Nonpolar directions' are polar. A symbol like $[u0w]$ refers to the set of directions obtained for all possible values of u and w , in this case to all directions normal to the b axis, *i.e.* parallel to the plane (010). Symmetry-equivalent sets of nonpolar directions are placed between semicolons; the sequence of these sets follows the sequence of the symmetry directions in Table 2.1.3.1.

System	Class	Polar (symmetry) axes	Nonpolar directions
Triclinic	1	None†	None
Monoclinic Unique axis b	2	[010]	$[u0w]$
	m	None†	[010]
Monoclinic Unique axis c	2	[001]	$[uv0]$
	m	None†	[001]
Orthorhombic	222	None	$[0vw]$; $[u0w]$; $[uv0]$
	$mm2$	[001]	$[uv0]$
Tetragonal	4	[001]	$[uv0]$
	$\bar{4}$	None	[001]; $[uv0]$
	422	None	$[uv0]$; $[0vw]$ $[u0w]$; $[uuw]$ $[u\bar{u}w]$
	$4mm$	[001]	$[uv0]$
	$42m$	None	$[uv0]$; $[0vw]$ $[u0w]$
	$4m2$	None	$[uv0]$; $[uuw]$ $[u\bar{u}w]$
Trigonal (Hexagonal axes)	3	[001]	None
	321	[100], [010], $[\bar{1}\bar{1}0]$	$[u2uw]$ $[\bar{2}u\bar{u}w]$ $[u\bar{u}w]$
	312	$[\bar{1}\bar{1}0]$, [120], $[\bar{2}\bar{1}0]$	$[uuw]$ $[\bar{u}0w]$ $[0\bar{v}w]$
	$3m1$	[001]	[100] [010] $[\bar{1}\bar{1}0]$
	$31m$	[001]	$[\bar{1}\bar{1}0]$ [120] $[\bar{2}\bar{1}0]$
Trigonal (Rhombohedral axes)	3	[111]	None
	32	$[\bar{1}\bar{1}0]$, $[01\bar{1}]$, $[\bar{1}01]$	$[uuw]$ $[uvv]$ $[uvu]$
	$3m$	[111]	$[\bar{1}\bar{1}0]$ $[01\bar{1}]$ $[\bar{1}01]$
Hexagonal	6	[001]	$[uv0]$
	$\bar{6}$	None	[001]
	622	None	$[u2uw]$ $[\bar{2}u\bar{u}w]$ $[u\bar{u}w]$ $[uuw]$ $[\bar{u}0w]$ $[0\bar{v}w]$
	$6mm$	[001]	$[uv0]$
	$\bar{6}m2$	$[\bar{1}\bar{1}0]$, [120], $[\bar{2}\bar{1}0]$	$[uuw]$ $[\bar{u}0w]$ $[0\bar{v}w]$
	$\bar{6}2m$	[100], [010], $[\bar{1}\bar{1}0]$	$[u2uw]$ $[\bar{2}u\bar{u}w]$ $[u\bar{u}w]$
Cubic	23 } $\bar{4}3m$ }	Four threefold axes along $\langle 111 \rangle$	$[0vw]$ $[u0w]$ $[uv0]$ $[0v\bar{w}]$ $[u0\bar{w}]$ $[uv\bar{0}]$
	432	None	$[0v\bar{w}]$ $[u0\bar{w}]$ $[uv\bar{0}]$; $[uuw]$ $[uvv]$ $[uvu]$; $[u\bar{u}w]$ $[uv\bar{v}]$ $[\bar{u}v\bar{u}]$

† In class 1 any direction is polar; in class m all directions except [010] (or [001]) are polar.

Enantiomorphic crystals can also be built up from achiral molecules or atom groups. In these cases, the achiral molecules or atom groups form chiral configurations in the structure. The best known examples are quartz and NaClO_3 . For details, reference should be made to Rogers (1975).

3.2.2.1.4. Polar directions, polar axes, polar point groups

A direction is called *polar* if its two directional senses are geometrically or physically different. A polar symmetry direction of a crystal is called a *polar axis*. Only proper rotation or screw axes can be polar. The polar and nonpolar directions in the 21 noncentrosymmetric point groups are listed in Table 3.2.2.2.

The terms *polar point group* or *polar crystal class* are used in two different meanings. In crystal physics, a crystal class is

considered as polar if it allows the existence of a permanent dipole moment, *i.e.* if it is capable of pyroelectricity (*cf.* Section 3.2.2.5). In crystallography, however, the term *polar crystal class* is frequently used synonymously with *noncentrosymmetric crystal class*. The synonymous use of polar and acentric, however, can be misleading, as is shown by the following example. Consider an optically active liquid. Its symmetry can be represented as a right-handed or a left-handed sphere (*cf.* Sections 3.2.1.4 and 3.2.2.4). The optical activity is isotropic, *i.e.* magnitude and rotation sense are the same in any direction and its counterdirection. Thus, no polar direction exists, although the liquid is noncentrosymmetric with respect to optical activity.

According to Neumann's principle, information about the point group of a crystal may be obtained by the observation of physical effects. Here, the term 'physical properties' includes crystal morphology and etch figures. The use of any of the techniques described below does not necessarily result in the complete determination of symmetry but, when used in conjunction with other methods, much information may be obtained. It is important to realize that the evidence from these methods is often negative, *i.e.* that symmetry conclusions drawn from such evidence must be considered as only provisional.

In the following sections, the physical properties suitable for the determination of symmetry are outlined briefly. For more details, reference should be made to the monographs by Bhagavantam (1966), Nye (1957) and Wooster (1973).

3.2.2.2. Morphology

If a crystal shows well developed faces, information on its symmetry may be derived from the external form of the crystal. By means of the optical goniometer, faces related by symmetry can be determined even for crystals far below 1 mm in diameter. By this procedure, however, only the eigensymmetry (*cf.* Section 3.2.1.2.2) of the crystal morphology (which may consist of a single form or a combination of forms) can be established. The determination of the point group is unique in all cases where the observed eigensymmetry group is compatible with only one generating group.

Column 6 in Table 3.2.1.3 lists all point groups for which a given crystal form (characterized by its name and eigensymmetry) can occur. In 19 cases, the point group can be uniquely determined because only one entry appears in column 6. These crystal forms are always characteristic general forms, for which eigensymmetry and generating point-group symmetry are identical. They belong to the 19 point groups with more than one symmetry direction.

If a crystal exhibits a combination of forms which by themselves do not permit unambiguous determination of the point group, those generating point groups are possible that are common to all crystal forms of the combination. The mutual orientation of the forms, if variable, has to be taken into account, too.

Example

Two tetragonal pyramids, each of eigensymmetry $4mm$, rotated with respect to each other by an angle $\neq 45^\circ$, determine the point group 4 uniquely because the eigensymmetry of the combination is only 4.

In practice, however, unequal or incomplete development of the faces of a form often simulates a symmetry that is lower than the actual crystal symmetry. In such cases, or when the