

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)	+
		$3m$	+ (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	–	–	+
		$\bar{4}3m$	–	+ (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.