

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

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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	$m\ \bar{3}5\ (\bar{5}3m)$	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.

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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 m	[010] None†	$[u0w]$ [010]
Monoclinic Unique axis c	2 m	[001] None†	$[uv0]$ [001]
Orthorhombic	222 $mm2$	None [001]	$[0vw]$; $[u0w]$; $[uv0]$ $[uv0]$
Tetragonal	4	[001]	$[uv0]$
	$\bar{4}$	None	[001]; $[uv0]$
	422	None	$[uv0]$; $[0vw]$ $[u0w]$; $[uuw]$ $[u\bar{u}w]$
	$4mm$	[001]	$[uv0]$
	$42m$ $4m2$	None None	$[uv0]$; $[0vw]$ $[u0w]$ $[uv0]$; $[uuw]$ $[u\bar{u}w]$
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 31m	[001] [001]	[100] [010] $[\bar{1}\bar{1}0]$ $[\bar{1}\bar{1}0]$ [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]	$[uv0]$
	$\bar{6}m2$ $\bar{6}2m$	$[\bar{1}\bar{1}0]$, [120], $[\bar{2}\bar{1}0]$ $[\bar{1}\bar{1}0]$, [010], $[\bar{1}\bar{1}0]$	$[uuw]$ $[\bar{u}0w]$ $[0\bar{v}w]$ $[u2uw]$ $[\bar{2}u\bar{u}w]$ $[u\bar{u}w]$
Cubic	23 } $\bar{4}3m$ }	Four threefold axes along $\langle 111 \rangle$	$[0vw]$ $[u0w]$ $[uv0]$ $[0vw]$ $[u0w]$ $[uv0]$
	432	None	$[0vw]$ $[u0w]$ $[uv0]$; $[uuw]$ $[uvv]$ $[uvu]$; $[u\bar{u}w]$ $[uv\bar{v}]$ $[\bar{u}vu]$

† 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

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morphological analysis is ambiguous, the crystallization of a small amount of the compound on a seed crystal, ground to a sphere, is useful. By this procedure, faces of additional forms (and often of the characteristic general form) appear as small facets on the sphere and their interfacial angles can be measured.

In favourable cases, even the space group can be derived from the morphology of a crystal: this is based on the so-called *Bravais–Donnay–Harker principle*. A textbook description is given by Phillips (1971, ch. 13).

Furthermore, measurements of the interfacial angles by means of the optical goniometer permit the determination of the relative dimensions of a ‘morphological unit cell’ with good accuracy. Thus, for instance, the interaxial angles α , β , γ and the axial ratio $a:b:c$ of a triclinic crystal may be derived. The ratio $a:b:c$, however, may contain an uncertainty by an integral factor with respect to the actual cell edges of the crystal. This means that any one unit length may have to be multiplied by an integer in order to obtain correspondence to the ‘structural’ unit cell.

3.2.2.3. Etch figures

Additional information on the point group of a crystal can be gained from the face symmetry, which is usually determined by observation of etch figures, striations and other face markings. Etch pits are produced by heating the crystal in vacuum (evaporation from the surface) or by attacking it with an appropriate reagent, which should not be optically active. The etch pits generally appear at the end points of dislocation lines on the face. They exhibit the symmetry of one of the ten two-dimensional point groups which, in general,²² corresponds to the symmetry of the crystal face under investigation.

The observation of etch figures is important when the morphological analysis is ambiguous (*cf.* Section 3.2.2.2). For instance, a tetragonal pyramid, which is compatible with point groups 4 and $4mm$, can be uniquely attributed to point group 4 if its face symmetry is found to be 1. For face symmetry m , group $4mm$ would result. The (oriented) face symmetries of the 47 crystal forms in the various point groups are listed in column 6 of Table 3.2.1.3 and in column 3 of Table 3.2.3.2.

In noncentrosymmetric crystals, the etch pits on parallel but opposite faces, even though they have the same symmetry, may be of different size or shape, thus proving the absence of a symmetry centre. Note that the orientation of etch pits with respect to the edges of the face is significant (*cf.* Buerger, 1956), as well as the mutual arrangement of etch pits on opposite faces. Thus, for a pinacoid with face symmetry 1, the possible point groups $\bar{1}$, 2 and m of the crystal can be distinguished by the mutual orientation of etch pits on the two faces. Moreover, twinning by merohedry and the true symmetry of the two (or more) twin partners (‘twin domains’) may be detected.

The method of etching can be applied not only to growth faces but also to cleavage faces or arbitrarily cut faces.

3.2.2.4. Optical properties

Optical studies provide good facilities with which to determine the symmetry of transparent crystals. The following optical properties may be used.

²² It should be noted, however, that asymmetric etch figures may occur that are due, for example, to an inclination of dislocation lines against the surface.

Table 3.2.2.3

Categories of crystal systems distinguished according to the different forms of the indicatrix

Crystal system	Shape of indicatrix	Optical character
Cubic	Sphere	Isotropic (not doubly refracting)
Tetragonal } Trigonal } Hexagonal }	Rotation ellipsoid	Uniaxial } Anisotropic (doubly refracting)
Orthorhombic } Monoclinic } Triclinic }	General ellipsoid	Biaxial }

3.2.2.4.1. Refraction

The dependence of the *refractive index* on the vibration direction of a plane-polarized light wave travelling through the crystal can be obtained from the optical indicatrix. This surface is an ellipsoid, which can degenerate into a rotation ellipsoid or even into a sphere. Thus, the lowest symmetry of the property ‘refraction’ is $2/m\ 2/m\ 2/m$, the point group of the general ellipsoid. According to the three different forms of the indicatrix, three categories of crystal systems have to be distinguished (Table 3.2.2.3).

The orientation of the indicatrix is related to the symmetry directions of the crystal. In tetragonal, trigonal and hexagonal crystals, the rotation axis of the indicatrix (which is the unique optic axis) is parallel to the main symmetry axis. For orthorhombic crystals, the three principal axes of the indicatrix are oriented parallel to the three symmetry directions of the crystal. In the monoclinic system, one of the axes of the indicatrix coincides with the monoclinic symmetry direction, whereas in the triclinic case, the indicatrix can, in principle, have any orientation relative to a chosen reference system. Thus, in triclinic and, with restrictions, in monoclinic crystals, the *orientation* of the indicatrix can change with wavelength λ and temperature T (orientation dispersion). In any system, the *size* of the indicatrix and, in all but the cubic system, its *shape* can also vary with λ and T .

When studying the symmetry of a crystal by optical means, note that strain can lower the apparent symmetry owing to the high sensitivity of optical properties to strain.

3.2.2.4.2. Optical activity

The symmetry information obtained from *optical activity* is quite different from that given by optical refraction. Optical activity is in principle confined to the 21 noncentrosymmetric classes but it can occur in only 15 of them (Table 3.2.2.1). In the 11 enantiomorphism classes, a single crystal is either right- or left-handed. In the four non-enantiomorphous classes m , $mm2$, $\bar{4}$ and $\bar{4}2m$, optical activity may also occur; here directions of both right- and left-handed rotations of the plane of polarization exist in the same crystal. In the other six noncentrosymmetric classes, $3m$, $4mm$, $\bar{6}$, $6mm$, $\bar{6}2m$, $\bar{4}3m$, optical activity is not possible.

In the two cubic enantiomorphous classes 23 and 432, the optical activity is isotropic and can be observed along any direction.²³ For the other optically active crystals, the rotation of the plane of polarization can, in practice, be detected only in directions parallel (or approximately parallel) to the optic axes. This is because of the dominating effect of double refraction. No optical activity, however, is present along an inversion axis or along a direction parallel or perpendicular to a

²³ This property can be represented by enantiomorphic spheres of point group 2∞ , *cf.* Table 3.2.1.6.

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mirror plane. Thus, no activity occurs along the optic axis in crystal classes $\bar{4}$ and $\bar{4}2m$. In classes m and $mm2$, no activity can be present along the two optic axes if these axes lie in m . If they are not parallel to m , they show optical rotation(s) of opposite sense.

3.2.2.4.3. Second-harmonic generation (SHG)

Light waves passing through a noncentrosymmetric crystal induce new waves of twice the incident frequency. This second-harmonic generation is due to the nonlinear optical susceptibility. The *second-harmonic coefficients* form a third-rank tensor, which is subject to the same symmetry constraints as the piezoelectric tensor (see Section 3.2.2.6). Thus, only 20 noncentrosymmetric crystals, except those of class 432, can show the second-harmonic effect; cf. Table 3.2.2.1.

Second-harmonic generation is a powerful method of testing crystalline materials for the absence of a symmetry centre. With an appropriate experimental device, very small amounts (less than 10 mg) of powder are sufficient to detect the second-harmonic signals, even for crystals with small deviations from centrosymmetry (Dougherty & Kurtz, 1976).

3.2.2.5. Pyroelectricity and ferroelectricity

In principle, *pyroelectricity* can only exist in crystals with a permanent electric dipole moment. This moment is changed by heating and cooling, thus giving rise to electric charges on certain crystal faces, which can be detected by simple experimental procedures.

An electric dipole moment can be present only along a polar direction that has no symmetry-equivalent directions.²⁴ Such polar directions occur in the following ten classes: $6mm$, $4mm$, and their subgroups 6, 4, $3m$, 3, $mm2$, 2, m , 1 (cf. Table 3.2.2.1). In point groups with a rotation axis, the electric moment is along this axis. In class m , the electric moment is parallel to any direction in the mirror plane (direction $[u0w]$). In class 1, any direction $[uvw]$ is possible. In point groups 1 and m , besides a change in magnitude, a directional variation of the electric moment can also occur during heating or cooling.

In practice, it is difficult to prevent strains from developing throughout the crystal as a result of temperature gradients in the sample. This gives rise to piezoelectrically induced charges superposed on the true pyroelectric effect. Consequently, when the development of electric charges by a change in temperature is observed, the only safe deduction is that the specimen must lack a centre of symmetry. Failure to detect pyroelectricity may be due to extreme weakness of the effect, although modern methods are very sensitive.

A crystal is *ferroelectric* if the direction of the permanent electric dipole moment can be changed by an electric field. Thus, ferroelectricity can only occur in the ten pyroelectric crystal classes, mentioned above.

3.2.2.6. Piezoelectricity

In piezoelectric crystals, an electric dipole moment can be induced by compressional and torsional stress. For a uniaxial compression, the induced moment may be parallel, normal or inclined to the compression axis. These cases are called longitudinal, transverse or mixed compressional piezoeffect, respectively. Correspondingly, for torsional stress, the electric moment may be parallel, normal or inclined to the torsion axis.

The *piezoelectricity* is described by a third-rank tensor, the moduli of which vanish for all centrosymmetric point groups. Additionally, in class 432, all piezoelectric moduli are zero owing to the high symmetry. Thus, piezoelectricity can only occur in 20 noncentrosymmetric crystal classes (Table 3.2.2.1).

The piezoelectric point groups 422 and 622 show the following peculiarity: there is no direction for which a longitudinal component of the electric moment is induced under uniaxial compression. Thus, no longitudinal or mixed compressional effects occur. The moment is always normal to the compression axis (pure transverse compressional effect). This means that, with the compression pistons as electrodes, no electric charges can be found, since only transverse compressional or torsional piezoeffects occur. In all other piezoelectric classes, there exist directions in which both longitudinal and transverse components of the electric dipole moment are induced under uniaxial compression.

An electric moment can also develop under hydrostatic pressure. This kind of piezoelectricity, like pyroelectricity, can be represented by a first-rank tensor (vector), whereby the hydrostatic pressure is regarded as a scalar. Thus, piezoelectricity under hydrostatic pressure is subject to the same symmetry constraints as pyroelectricity.

Like 'second-harmonic generation' (Section 3.2.2.4.3), the piezoelectric effect is very useful for testing crystals for the absence of a symmetry centre. There exist powerful methods for testing powder samples or even small single crystals. In the old technique of Giebe & Scheibe (cf. Wooster & Brenton, 1970), the absorption and emission of radio-frequency energy by electromechanical oscillations of piezoelectric particles are detected. In the more modern method of observing 'polarization echoes', radio-frequency pulses are applied to powder samples. By this procedure, electromechanical vibration pulses are induced in piezoelectric particles, the echoes of which can be detected (cf. Melcher & Shiren, 1976).

²⁴ In the literature, the requirement for pyroelectricity is frequently expressed as 'a unique (or singular) polar axis'. This term, however, is misleading for point groups 1 and m .