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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 [*u*0*w*] 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<br>Unique axis *b* | 2 | [010] | [*u*0*w*] |
| | *m* | None† | [010] |
| Monoclinic<br>Unique axis *c* | 2 | [001] | [*uv*0] |
| | *m* | None† | [001] |
| Orthorhombic | 222 | None | [0*vw*]; [*u*0*w*]; [*uv*0] |
| | *mm*2 | [001] | [*uv*0] |
| Tetragonal | 4 | [001] | [*uv*0] |
| | $\bar{4}$ | None | [001]; [*uv*0] |
| | 422 | None | [*uv*0]; [0*vw*] [*u*0*w*];<br>[*uuw*] $[u\bar{u}w]$ |
| | 4*mm* | [001] | [*uv*0] |
| | $\bar{4}2m$ | None | [*uv*0]; [0*vw*] [*u*0*w*] |
| | $\bar{4}m2$ | None | [*uv*0]; [*uuw*] $[u\bar{u}w]$ |
| Trigonal (Hexagonal axes) | 3 | [001] | None |
| | 321 | [100], [010], $[\bar{1}\bar{1}0]$ | [*u*2*uw*] $[\overline{2u}\bar{u}w]$ $[u\bar{u}w]$ |
| | 312 | $[1\bar{1}0]$, [120], $[\bar{2}\bar{1}0]$ | [*uuw*] $[\bar{u}0w]$ $[0\bar{v}w]$ |
| | 3*m*1 | [001] | [100] [010] $[\bar{1}\bar{1}0]$ |
| | 31*m* | [001] | $[1\bar{1}0]$ [120] $[\bar{2}\bar{1}0]$ |
| Trigonal (Rhombohedral axes) | 3 | [111] | None |
| | 32 | $[1\bar{1}0]$, $[01\bar{1}]$, $[\bar{1}01]$ | [*uuw*] [*uvv*] [*uvu*] |
| | 3*m* | [111] | $[1\bar{1}0]$ $[01\bar{1}]$ $[\bar{1}01]$ |
| Hexagonal | 6 | [001] | [*uv*0] |
| | $\bar{6}$ | None | [001] |
| | 622 | None | [*u*2*uw*] $[\overline{2u}\bar{u}w]$ $[u\bar{u}w]$<br>[*uuw*] $[\bar{u}0w]$ $[0\bar{v}w]$ |
| | 6*mm* | [001] | [*uv*0] |
| | $\bar{6}m2$ | $[1\bar{1}0]$, [120], $[\bar{2}\bar{1}0]$ | [*uuw*] $[\bar{u}0w]$ $[0\bar{v}w]$ |
| | $\bar{6}2m$ | [100], [010], $[\bar{1}\bar{1}0]$ | [*u*2*uw*] $[\overline{2u}\bar{u}w]$ $[u\bar{u}w]$ |
| Cubic | 23 | Four threefold axes along ⟨111⟩ | [0*vw*] [*u*0*w*] [*uv*0] |
| | $\bar{4}3m$ | Four threefold axes along ⟨111⟩ | [0*vw*] [*u*0*w*] [*uv*0] |
| | 432 | None | [0*vw*] [*u*0*w*] [*uv*0];<br>[*uuw*] [*uvv*] [*uvu*];<br>$[u\bar{u}w]$ $[uv\bar{v}]$ $[\bar{u}vu]$ |

† 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 4*mm*, rotated with respect to each other by an angle $\neq 45°$, 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 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 $\alpha$, $\beta$, $\gamma$ 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 4*mm*, can be uniquely attributed to point group 4 if its face symmetry is found to be 1. For face symmetry *m*, group 4*mm* 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 — Anisotropic (doubly refracting) |

#### 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 $\lambda$ 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 $\lambda$ 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*, *mm*2, $\bar{4}$ 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, 3*m*, 4*mm*, $\bar{6}$, 6*mm*, $\bar{6}2m$, $\bar{4}3m$, 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 $2\infty$, *cf.* Table 3.2.1.6.



references