

3. ADVANCED TOPICS ON SPACE-GROUP SYMMETRY

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
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 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.