

3. PREPARATION AND EXAMINATION OF SPECIMENS

Table 3.1.2.1. Use of crystal properties for selection and preliminary study of crystals (cont.)

Crystal property	Relation with structure
Magnetic properties	
Paramagnetism; diamagnetism	In an isomorphous series of paramagnetic salts, the values of the average susceptibility and of magnetic anisotropy are dependent on the nature of the paramagnetic ion. The shape of the coordination polyhedron may be found from the crystal anisotropies In aliphatic non-conjugated organic crystals, the numerically largest diamagnetic susceptibility is along the direction in which lie the largest molecular directions In crystals containing aromatic compounds or molecules with coplanar conjugated bonds, the numerically largest molecular diamagnetic susceptibility is normal to the plane of the molecular orbitals, and may thus indicate the molecular orientations
Ferromagnetism; antiferromagnetism; ferrimagnetism	Neutron diffraction by magnetic compounds may give information about the directions of the resultant spin and orbital moments. X-ray diffraction effects are usually unimportant In magnetic materials, the interatomic distances, and, in antiferromagnetic oxides, the valency angles at the oxygen ions are related to the diameter of the electron shell
Nuclear magnetic resonance	The line width in NMR spectra is related to the distances between the nuclei with magnetic moments
Electrical properties	
Ferroelectricity; pyroelectricity	See <i>IT A</i> (2002), Section 10.2.5, p. 807. Ferroelectricity indicates (i) a structure of polar symmetry, and (ii) the probability of another high-symmetry structure of nearly equal energy, derivable from the ferroelectric by a displacive transition. Often there are several related structures, some ferroelectric and some antiferroelectric Pyroelectricity indicates noncentrosymmetry. Second-harmonic generation is ordinarily a more sensitive test
Piezoelectricity	Piezoelectricity gives information on symmetry; it occurs only in ten crystal classes. See <i>IT A</i> , Section 10.2.6
Thermodynamic properties	
Heat capacity ('specific heat')	Anomalies indicate polymorphic transitions, disorder, approach to melting point, and temperature variation gives Einstein and/or Debye characteristic temperatures
Melting point	Atoms in crystals with a low melting point often have large thermal movements; diffraction experiments should preferably be carried out at low temperatures Anomalies in the variation of melting point in a series of homologues indicate a change in packing or bond type
Density	For measurement, see Chapter 3.2. Necessary for determination of number of formula weights per cell. May indicate liquid of crystallization, isomorphous replacement, degree of approach to close packing, first-order transitions with change of temperature or pressure
Thermal expansion	Thermal expansion is usually greatest in directions normal to layers or chains. Abrupt variation with change of temperature or pressure indicates a second-order transition
Chemical properties	
Chemical analysis	Gives kinds of atoms in the structure and (in conjunction with the density) the number of each kind in the unit cell
Attack of surface	May be used to shape crystals Etch figures are sensitive indicators of point-group symmetry (see <i>IT A</i> , Section 10.2.3). Change of orientation of etch figures on a face may reveal twinning. Rows of etch pits may reveal grain or sub-grain boundaries
Oriented growth on parent crystal	Epitaxy often reveals similarity of lattice parameters and even of atomic arrangement in the interface Grain boundaries and twinning orientations may be marked by epitaxial growth, or by oriented growth of crystals or reaction products on the mother crystal ('topotaxy')

reflections, leading to poor data quality in certain regions of the diffraction pattern.

The ultimate test of the quality of a crystal and its suitability for a structure analysis is the quality of the diffraction pattern. Ideally, the reflections should appear in the case of monochromatic radiation as single spots without satellites, tails, or streaks between the spots. The diffraction pattern should be indexable in terms of a single lattice.

3.1.2.3. Optical examination [see *IT A* (2002), Section 10.2.4]

Optical examination of a crystal under a polarizing microscope should be a prerequisite before mounting the specimen for a diffraction experiment. The presence of satellite crystals, inclusions, and other crystal imperfections will degrade the data quality, indicating the selection of a better specimen. The external morphology can often give a strong indication regarding

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the nature of the crystal system. A preliminary examination under crossed polars will often show whether the crystal is isotropic, uniaxial or biaxial (see, for example, Hartshorne & Stuart, 1960; Bunn, 1961; Ladd & Palmer, 1985). Crystals that comprise two or more fragments will often be revealed by displaying both dark and light regions simultaneously. For uniaxial crystals, a birefringent orientation is always presented to the incident light beam if the unique axis is perpendicular to the microscope axis, and extinction will occur whenever the unique axis is parallel to the crosswires (assuming that the crosswires are parallel to the planes of polarization of the polarizer and analyser). If the unique axis is parallel to the microscope axis, a uniaxial crystal presents an isotropic cross section and will remain extinguished for all rotations of the crystal. Biaxial crystals have three principal refractive indices associated with light vibrating parallel to the three mutually perpendicular directions in the crystal. The two optic axes and their correspondingly isotropic cross sections that derive from this property are not directly related to the crystallographic axes. In the orthorhombic system, the three vibration directions are parallel to the crystallographic axes, often enabling identification of this crystal system. A monoclinic crystal lying with its unique axis parallel to the crosswires will always show straight extinction. If the crystal is oriented so that the unique axis lies along the microscope axis then, in general, the extinction directions will be oblique. In the triclinic case, the three mutually perpendicular vibration directions are arbitrarily related to the crystal axes. Even if it is not possible to discover the nature of the crystal system unequivocally, the extinction directions should at least enable the principal symmetry directions to be identified and therefore suggest how the crystals should be mounted for optimum data collection (see Chapter 3.4).

3.1.2.4. *Twinning* (see Chapter 1.3)

If at all possible, twinned crystals should *not* be used for structure analysis studies, but the recognition of twinning is critical, since unnoticed or misinterpreted twinning can prevent structure determination or lead to errors in the final structure solution. A distinction should be made between multiple crystal growth, whereby single crystals grow on or from the faces of a

given single crystal, or from a common nucleation point, in non-specific orientations, and crystallographic twinning (see, for example, Phillips, 1971; Bishop, 1972). In the latter case, the relationship between the lattices of twinned crystals is normally that of rotation of 180° about a central lattice line, or reflection across a lattice plane. If the lattice is not geometrically symmetrical about the line or plane, two lattices with differing orientations will be produced, and the corresponding reciprocal lattices will be visible in the diffraction patterns. In ideal circumstances, the two patterns can be deconvoluted. If the lattice is geometrically symmetrical about the twin axis or plane, then the two reciprocal lattices will coincide and there may be no obvious signs of twinning in the diffraction pattern (merohedry). If the twins are present in almost equal amounts, the result will be an apparent mirror plane and perpendicular twofold axis in the Laue symmetry. It is therefore very important to examine carefully the Laue symmetry, preferably from a number of different crystals, if twinning is suspected. In some of these crystals, one twin component may be predominant, causing a breakdown in the pseudosymmetry.

Morphological evidence (a concave shape indicating an intersection between the two twin components) and optical examination under a polarizing microscope should also be employed to test for twinning. For lattices that are twinned in a geometrically nonsymmetrical manner, the different twin components will show extinction at different orientations. However, perfect optical extinction is not positive evidence of lack of twinning, since the geometrical symmetry plane (or axis) on which twinning takes place may be parallel to a symmetry plane (or axis) in the optical properties of the crystal.

Intensity statistics can also be used to detect twinning, particularly in the case of crystals twinned by merohedry (*e.g.* Britton, 1972; Fisher & Sweet, 1980). If crystallization conditions cannot be found that eliminate twinning, it is still possible, although difficult, to undertake structure analysis. Recent examples include $\text{Sr}_3\text{CuPtO}_6$ (Hodeau *et al.*, 1992), RbLiCrO_4 (Makarova, Verin & Aleksandrov, 1993), a serine protease from rat mast cells (Reynolds *et al.*, 1985) and plastocyanin from the green alga *Chlamydomonas reinhardtii* (Redinbo & Yeates, 1993).