

3.1. PREPARATION, SELECTION, AND INVESTIGATION OF SPECIMENS

Table 3.1.2.1. *Use of crystal properties for selection and preliminary study of crystals, adapted from MacGillavry & Henry (1962); morphological, optical, and mechanical properties*

Crystal property	Uses and comments	Relation with structure
Morphological properties		
Crystal habit	Setting crystal parallel to edge, or to symmetry axis, derived from goniometric measurement Habit can be influenced by solvent, crystallization conditions, trace impurities Well formed crystals can be accurately measured for analytical corrections for absorption	Morphological determination of crystal class may narrow down choice of space group Best-developed faces correspond to net planes with large density of lattice or pseudo-lattice nodes (Bravais' law, extended by Donnay & Harker) Prominent faces tend to be parallel to important bond systems Face development correlates inversely with surface free energy
Twinning	Twins may be hard to detect by morphological or diffraction methods. Investigate under the polarizing microscope: optical anomalies strongly indicate mimetic twinning, stacking faults, <i>etc.</i> Mechanical twinning may occur when a single crystal is cut or ground. In such cases, the crystal should be shaped by use of a solvent	May indicate hemimorphy or pseudo-hemimorphy of the cell or supercell; see Chapter 1.3 Pseudo-symmetrical stacking
Etch figures; epitaxy	See <i>IT A</i> (2002), Section 10.2.3 (pp. 805–806), and chemical properties below	
Optical properties		
Refractive index; birefringence (see <i>IT A</i> , Section 10.5.4, p. 790)	Checking quality of crystal: homogeneous extinction, interference figures Extinction direction is used for setting badly formed or ground crystals Magnitude of refractive index may be used for identification of crystal orientation	High refractive index may indicate close packing Shape and orientation of indicatrix may be useful for finding orientation of large atomic or ionic groups with strongly anisotropic polarizability (<i>e.g.</i> flat or rod-shaped groups)
Optical activity	Distinguishes between optical antipodes in studies of absolute configuration	Difficult to measure, or even detect, in optically biaxial crystals. No obvious relation with structure
Pleochroism	Identification of crystal orientation through dependence of colour on direction of light vibration	Extended conjugated-bond systems have strong absorption of light vibrating parallel to system; weak absorption perpendicular to system String-like arrangement of some atoms [<i>e.g.</i> iodine in poly(vinyl alcohol)] produces strong absorption parallel to string In inorganic compounds, absorption is greatest for light vibrating along directions in which ions are distorted
Reflection of light		Opaque substances contain loosely bound electrons
Raman effect		May give information on the orientation and symmetry of scattering groups
Mechanical properties		
Cleavage	Useful for obtaining good surfaces for crystal setting Useful for improving crystal shape	Correlates with bond-strength anisotropy
Hardness	Anisotropy of hardness may produce ellipsoids instead of spheres when an abrasion chamber is used	Hardness gives an indication of bond strength and bond density Hardness may be very sensitive to impurities, changes in texture through ageing or heat treatment, <i>etc.</i>
Plasticity	Single crystals: avoid cutting or grinding Polycrystalline material: plastic deformation is often strongly anisotropic, and may then be used to produce single or double orientation	Non-directive bonding between large strongly bonded units (long-chain paraffins, layer structures) Plastic flow may also be associated with mechanical twinning or lattice imperfections

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