

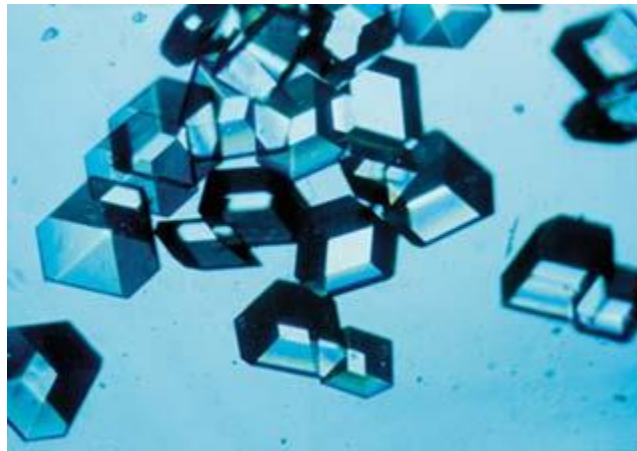
ANALYSIS OF MATERIALS

3. THE STRUCTURE OF CRYSTALS

3.1. Background Information

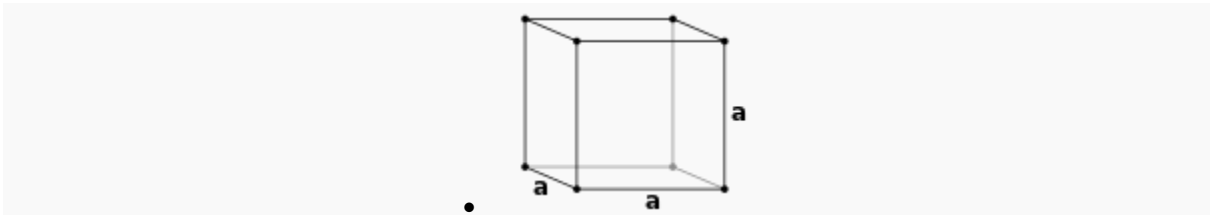
In mineralogy and crystallography, a crystal structure is a unique arrangement of atoms or molecules in a crystalline liquid or solid. A crystal structure describes a highly ordered structure, occurring due to the intrinsic nature of molecules to form symmetric patterns. A crystal structure can be thought of as an infinitely repeating array of 3D 'boxes', known as unit cells. The unit cell is calculated from the simplest possible representation of molecules, known as the asymmetric unit. The asymmetric unit is translated to the unit cell through symmetry operations, and the resultant crystal lattice is constructed through repetition of the unit cell infinitely in 3-dimensions. Patterns are located upon the points of a lattice, which is an array of points repeating periodically in three dimensions. The lengths of the edges of a unit cell and the angles between them are called the lattice parameters. The symmetry properties of the crystal are embodied in its space group.

A crystal's structure and symmetry play a role in determining many of its physical properties, such as cleavage, electronic band structure, and optical transparency.

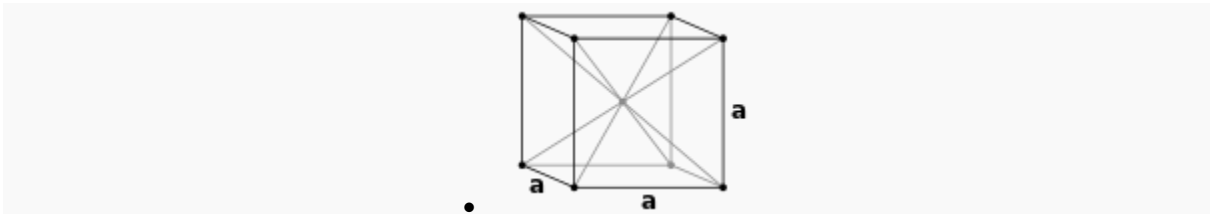


3.2. Unit Cell

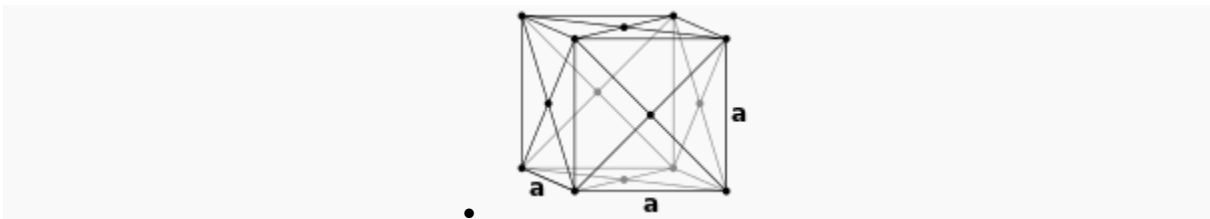
The crystal structure of a material (the arrangement of atoms within a given type of crystal) can be described in terms of its unit cell. The unit cell is a small box containing one or more atoms arranged in 3-dimensions. The unit cells stacked in three-dimensional space describe the bulk arrangement of atoms of the crystal. The unit cell is represented in terms of its lattice parameters, which are the lengths of the cell edges (a, b and c) and the angles between them (α, β and γ), while the positions of the atoms inside the unit cell are described by the set of atomic positions (x_i, y_i, z_i) measured from a lattice point. Commonly, atomic positions are represented in terms of fractional coordinates, relative to the unit cell lengths.



Simple cubic (P)



Body-centered cubic (I)

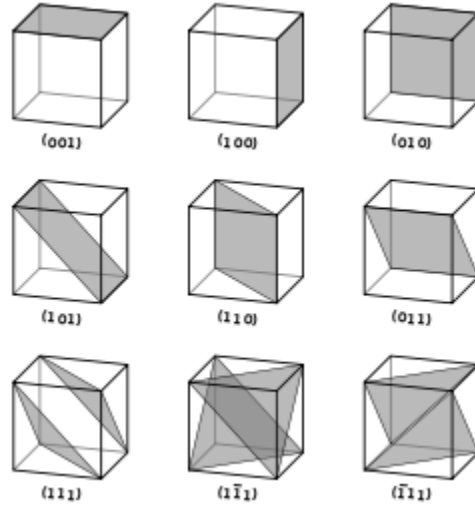


Face-centered cubic (F)

The atom positions within the unit cell can be calculated through application of symmetry operations to the asymmetric unit. The asymmetric unit refers to the smallest possible occupation of space within the unit cell. This does not, however imply that the entirety of the asymmetric unit must lie within the boundaries of the

unit cell. Symmetric transformations of atom positions are calculated from the space group of the crystal structure, and this is usually a black box operation performed by computer programs. However, manual calculation of the atomic positions within the unit cell can be performed from the asymmetric unit, through the application of the symmetry operators described within the 'International Tables for Crystallography: Volume A'

Miller Indices



Planes with different Miller indices in cubic crystals

Vectors and atomic planes in a crystal lattice can be described by a three-value Miller index notation (lmn). The l , m , and n directional indices are separated by 90° , and are thus orthogonal.

By definition, (lmn) denotes a plane that intercepts the three points a_1/l , a_2/m , and a_3/n , or some multiple thereof. That is, the Miller indices are proportional to the *inverses* of the intercepts of the plane with the unit cell (in the basis of the lattice vectors). If one or more of the indices is zero, it means that the planes do not intersect that axis (i.e., the intercept is "at infinity"). A plane containing a coordinate axis is translated so that it no longer contains that axis before its Miller indices are determined. The Miller indices for a plane are integers with no common factors. Negative indices are indicated with horizontal bars, as in (12 $\bar{3}$). In an orthogonal co-ordinate system for a cubic cell, the Miller indices of a plane are the Cartesian components of a vector normal to the plane.

Considering only (ℓmn) planes intersecting one or more lattice points (the *lattice planes*), the perpendicular distance d between adjacent lattice planes is related to the (shortest) reciprocal lattice vector orthogonal to the planes by the formula:

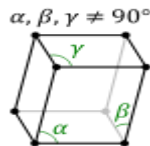
$$d = 2\pi / |\mathbf{g}_{\ell mn}|$$

3.3. Classification & Lattice Systems

The defining property of a crystal is its inherent symmetry, by which we mean that under certain operations the crystal remains unchanged. All crystals have translational symmetry in three directions, but some have other symmetry elements as well. For example, rotating the crystal 180° about a certain axis may result in an atomic configuration that is identical to the original configuration. The crystal is then said to have a twofold rotational symmetry about this axis. In addition to rotational symmetries like this, a crystal may have symmetries in the form of mirror planes and translational symmetries, and also the so-called compound symmetries, which are a combination of translation and rotation/mirror symmetries. A full classification of a crystal is achieved when all of these inherent symmetries of the crystal are identified. These lattice systems are a grouping of crystal structures according to the axial system used to describe their lattice. Each lattice system consists of a set of three axes in a particular geometric arrangement. There are seven lattice systems. They are similar to but not quite the same as the seven crystal systems and the six crystal families.

The 7 lattice systems (From least to most symmetric)

1. triclinic
(none)

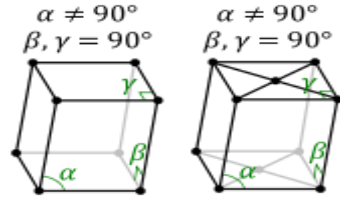


2. monoclinic

The 14 Bravais Lattices

simple base-centered

(1 diad)



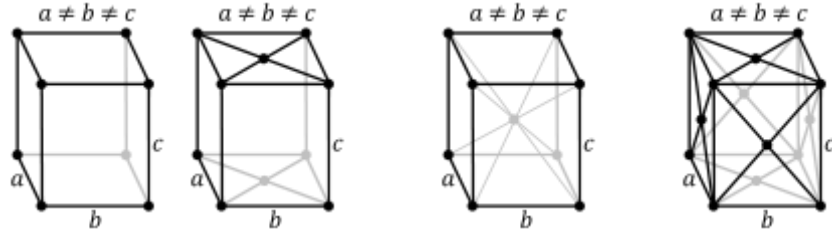
simple

base-centered

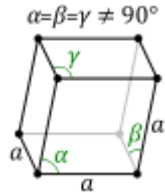
body-centered

face-centered

3. orthorhombic
(3 perpendicular diads)



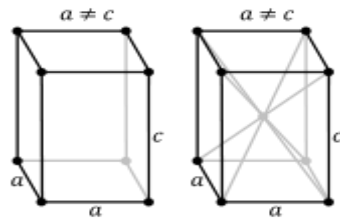
4. rhombohedral
(1 triad)



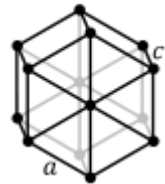
simple

body-centered

5. tetragonal
(1 tetrad)



6. hexagonal
(1 hexad)

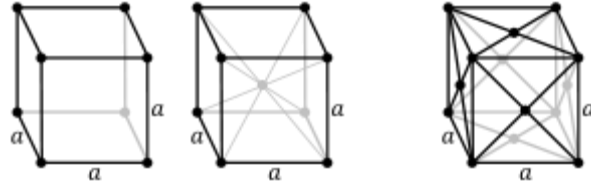


7. cubic
(4 triads)

simple
(SC)

body-centered
(bcc)

face-centered
(fcc)



The simplest and most symmetric, the cubic (or isometric) system, has the symmetry of a cube, that is, it exhibits four threefold rotational axes oriented at 109.5° (the tetrahedral angle) with respect to each other. These threefold axes lie along the body diagonals of the cube. The other six lattice systems, are hexagonal, tetragonal, rhombohedral (often confused with the trigonal crystal system), orthorhombic, monoclinic and triclinic.

Real crystals feature defects or irregularities in the ideal arrangements described above and it is these defects that critically determine many of the electrical and mechanical properties of real materials. When one atom substitutes for one of the principal atomic components within the crystal structure, alteration in the electrical and thermal properties of the material may ensue. Impurities may also manifest as spin impurities in certain materials. Research on magnetic impurities demonstrates that substantial alteration of certain properties such as specific heat may be affected by small concentrations of an impurity, as for example impurities in semiconducting ferromagnetic alloys may lead to different properties as first predicted in the late 1960s. Dislocations in the crystal lattice allow shear at lower stress than that needed for a perfect crystal structure.