

CRYSTALLOGRAPHY

Mineralogy

Descriptive

Physical

Optical

Crystallography

κρυσταλλος KRUSTALLOS = Clear ice; Quartz = Frozen ice

Introduction

Crystal: A homogeneous solid possessing long range, three-dimensional internal order.

May be defined as a polyhedral solid bounded by plane faces, which express an orderly internal arrangement of atoms or molecules.

Crystallography: The study of crystalline solids and the principles that govern their growth, external shape and internal structure.

Crystalline: (adjective) is applied to any material having a regular internal arrangement of its constituent atoms or ions; i.e. crystalline materials may or may not be bounded by crystal faces is called xlline solids.

Macro-xlline: Coarse-grained xlline that can be detected by naked eye.

Micro-xlline: fine grained xlline substance that can be determined only with the help of microscope.

Crypto-xlline: xls that can detected by x-ray diffraction techniques.

Amorphous: lack of ordered internal atomic arrangement.

Mineraloids: Naturally occurring amorphous substance. E.g. Glass (Volcanic) Opal $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ – not totally amorphous (4 to 9 wt%)

Well formed (developed) crystal faces = **Euhedral**

Imperfectly developed xl faces = **Subhedral**

Without any faces = **Anhedral**

Development of xllography:

Between 1815 and 1824, the 6 xl systems were distinguished: the isometric, tetragonal, orthorhombic, and hexagonal systems by C.S.Weiss (1780-1856); the monoclinic and triclinic systems independently by Friedrich Mohs (1773-1839) and K.F. Naumann (1797-1873).

In 1830, the German mineralogist J.F.C. Hessel (1796-1872) showed that 32 xl classes are possible.

In 1848, the French physicist Auguste Braivais (1817-1863) showed that 14 and only 14 kinds of regular patterns – space lattice – can result from arranging identical points in space such that any point is repeated at regular intervals along each row of the pattern.

Between 1885 and 1894, 230 space groups were derived independently by the Russian xllographer E S Federov (1853-1919), the German mathematician Arthur Schonflies (1853-1928) and the semi-retired English Businessman William Barlow (1845-1934).

Crystallization:

Crystals are formed from solutions, melts and vapors.
e.g. NaCl solution – water is allowed to evaporate – the solution contains more and more Na⁺ and Cl⁻ per unit volume.

- Xls also formed from solution by lowering the temperature or pressure. e.g. salt in hot water – lowering the temp, salt xllises. Higher the pressure, the more salt water can hold in solution. Thus lowering the pressure of saturated solution, super saturation will result and xls will form.
- May formed from a melt in much the same way as from a solution. Most familiar example – formation of ice crystals when water freezes (xllisation from fusion), formation of igneous rocks from molten magmas.
- Xllisation from a vapor is less common. As the vapor is cooled, the dissociated atoms or moles are brought closer together, eventually locking themselves into an xlline solid. Most familiar example – formation of snowflakes from air laden with water vapors.

Crystal Growth:

Natural xls may grow wherever:

1. Their constituent atoms or ions are free to come together in the correct proportions.
2. The existing conditions are such that 'growth' will take place at a reasonably slow and steady rate.
3. The external surface of the growing xl is not constrained (tight) physically.

Most well developed mineral xls occur lining the walls of open spaces in rocks, such as open fractures, solution cavities and vesicles.

Many such xls have been deposited from

- i) Hydrothermal solutions (hot aqueous solution)
- ii) By condensation from gaseous fluids,

- iii) As the result of late-stage crystallization of magma within cavities (kept open by accumulations of magmatic gases and vapors).

Excellent crystals can also be grown in the laboratory by various processes – i. Slow cooling or evaporating of a saturated solution of a salt.

ii. By constant temperature.

Growth: 1st stage – nucleation (nucleus or seed) – nucleus is the result of the coming together of various ions (in the solution or melt) to form the initial regular structural pattern of a crystal solid.

- A cubic crystal of NaCl, one cm along each edge, would contain approx. 10^{23} ions or atoms
- In halite the energy of attachment is greatest at corners, intermediate at edges and least in the middle faces.
- In some crystals, differ from NaCl – due to nonionic bonding, atoms accrete on the outer surface as clumps of atoms – outer surface develops.

Planar and Space Lattice:

Motif: The smallest representative unit of a structure. An atom or group of atoms that when repeated by translation, give rise to an infinite no. of identical regularly organized units.

Unit cells: The fundamental parallelepiped, that forms a crystal structure by regular repetition in space. Some unit cells consist of more than one such parallelepiped are termed multiple.

Structure: The ordered arrangement (i.e. the actual positions) of the atoms or groups of atoms within a crystal substance.

Lattice: An imaginary three dimensional framework that can be referenced to a network of regularly spaced points, each of which represents the position of a motif.

Planar Lattice:

One dimensional (a = vector)
eg in wallpaper, printed clothes (draperies).

Two dimensional – identical rows – parallel – equally spaced – (eg brick or tiled walls) same directional orientation.

Overall arrangement = net = plane lattice = clino net = oblique lattice.

Unequal length, angle 90°
= Ortho-net = Rectangular Lattice

= Rhombo – net = Centered Rectangular Lattice

Hexa- net = Hexagonal Lattice

Square – net = Square Lattice

Space Lattice:

When a number of identical nets are stacked, the resulting array (arrangement) of lattice points becomes a space lattice, if the following four conditions obtain:

- i. the nets are parallel to one another
- ii. they are equally spaced
- iii. they are identical
- iv. they have one point in each net falling on a straight row that extends through all of the nets.

Space lattice can be generated from a planar net by translation along a non-coplanar vector 'b'.

14 Braivais Lattices:

1. Isometric: $a=b=c$; $\alpha=\beta=\gamma=90^\circ$

Primitive (P)

Body centered (I) – which consists of two lattices interpenetrating in such a way that the points of the second lattice lie at the center of the unit cells of the first lattice.

Face centered (F) – in which 4 cubic lattices interpenetrates.

2. Tetragonal: $a=b\neq c$; $\alpha=\beta=\gamma=90^\circ$

Primitive (P)

Body centered (I)

3. Orthorhombic: $a\neq b\neq c$; $\alpha=\beta=\gamma=90^\circ$

Primitive (P)

End centered (C)

- (c face centered) C, B or A

Body centered (I)

Face centered (F)

4. Monoclinic: $a \neq b \neq c$; $\alpha = \gamma = 90^\circ \neq \beta$

Primitive (P)

End centered (c) \equiv 'C' (equivalent to 'c' face centered) or 'A' by a change in choice of alpha or beta.

5. Triclinic: $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$

Primitive (P)

6. Hexagonal: $a_1 = a_2 = a_3 \neq c$;
 $a_1 \wedge a_2 = a_2 \wedge a_3 = a_3 \wedge a_1 = 120^\circ$, $a \wedge c = 90^\circ$

Primitive (P) (3 of whose unit cells together form the hexagonal prism)

Rhombohedral (R)

Primitive = If the unit cell is considered to have lattice points only at its vertices.
(Vertices = a point that terminates a line, comprises the intersection of two or more lines).

Geometrical Nature of order of crystal:

Geometrical Operation

Translation:

Translation in one dimension alone generates a linear pattern at intervals equal to the translation distance t .

Rotation: alone, through an angle α , about an imaginary axis, generates a sequence of the motif along a circle.

Translation and Rotation: Together generates a regular pattern as long as the axis of rotation is parallel with the translation direction. This combination of two operations results in a 'screw motion'.

Symmetry Elements:

Plane of symmetry:

Through each motif and midway between each two adjacent motifs there is a plane perpendicular to the row, which may be called a mirror (or reflection) plane of symmetry, designated by m or P.

Axes of symmetry: (A)

Through each motif and midway between any two adjacent motifs there are axes perpendicular to the row, which may be called two fold rotation axes of symmetry, designated by 2.

Graphic symbol:-

The rotational symmetry, which occurs about an axis i.e. perpendicular to the originally described mirror planes, would be designated n/m with n indicating that the "—fold" of the rotational symmetry is indeterminate (not known, not fixed). In xls with 3-D lattices, n can only be 1,2,3,4 or 6. The two-fold symmetry perpendicular to mirror planes parallel to the length of row, the two fold rotation axes should be indicated as $2/m$ (International Space Notation by Herman Mauguin System). Similarly there are $3/m$ $4/m$ $6/m$ etc.

Center of symmetry: (or center of inversion) i

Each motif and each locus (center of activity or concentration) midway between two motifs acts as a center of symmetry, designated by the symbol C or i . (= $1+i$.)

Rotation about an axis, reflection by a mirror and inversion about a point are referred to as 'symmetry operations'.

Axis of rotary inversion (roto inversion) () is a composite element, which combines rotation about an axis with inversion about the center.

Glide reflection or Glide Plane:

A combination of a mirror and a translation produces a pattern with a glide reflection or glide plane.

Screw axis of symmetry: may be considered as rotation followed by translation i.e. parallel to the axis of rotation but along only a given fraction of length of the row period of that axis. There are 2,3,4 or 6 fold screw axes of symmetry.

Crystallographic axes: xl faces are conveniently referred to imaginary lines or directions, which may be used to describe the position of a face or group of faces in space. These lines or directions are called xllographic axes.

Systems according to axes:

Isometric system
Tetragonal system
Orthorhombic system
Monoclinic system
Triclinic system
Hexagonal system

Point Group and Space Group:

Point Group: A collection of symmetry operations (rotation about an axis, reflection by a mirror and inversion about a point) that operate around a point that represents an intersection of the elements of symmetry of its class.

There are 32 point groups – also called 32 crystal classes.

Space Group: If the 32 point groups are combined individually with the translation operations of each of the 14 Bravais Space Lattices, 73 different space groups can be defined. Thus a space group has operations that combine point group operations and translations.

Space groups, therefore, represent the various ways in which motifs (such as atoms in xl) can be arranged in space in a homogenous array.

If, in addition, glide planes and screw axis are added to the possible symmetry operations, the total no. of space groups is increased to the maximum of 230. In other words, each of the 230 space groups represents a unique combination of symmetry elements with one of the 14 Bravais space lattices functioning as its lattice of translation.

In short, the translation free symmetry combinations are point groups, whereas space groups define the symmetry and translations in space.

Characteristics of Space Groups:

1. They are based on one of the 14 Bravais Lattices, which is compatible with a specific point group.
2. They are isogonal (of equal angles) with one of the 32 point groups.

Symbols used in Space Lattices – P (primitive), A,B,C (face centered), F (all face centered), I (body centered), R (rhombohedral).

32 Point Groups (or Crystal Classes) and Their symmetry:

| <u>Crystal System</u> | <u>Crystal class</u> (Herman Mauguin Symbols) | <u>Class Name</u> | <u>Symmetry Elements</u> |
|-----------------------|---|-----------------------------|--------------------------|
| Triclinic | 1 | Pedial | None |
| | $\bar{1}$ | Pinacoidal (N) | C (i) |
| Monoclinic | 2 | Sphenoidal | 1A ₂ |
| | m | Domatic | 1P (m) |
| | 2/m | Prismatic (N) | C, 1A ₂ , 1P |
| Orthorhombic | 222 | Orthorhombic disphenoidal | 3A ₂ |
| | mm2 | Ortho. pyramidal | 1A ₂ , 2P |
| | 2/m2/m2/m | Ortho. dipyramidal (N) | C, 3A ₂ , 3P |
| | 4 | Tetragonal pyramidal | 1A ₄ |
| | 4 | Tetragonal Disphenoidal | 1 A ₄ |

| | | | |
|------------|------------------------|------------------------------|---|
| Tetragonal | 4/m | Tetragonal Dipyramidal | C, 1A ₄ , 1P |
| | 422 | Tetragonal Trapezohedral | 1A ₄ , 4A ₂ |
| | 4mm | Ditetragonal pyramidal | 1A ₄ , 4m |
| | $\overline{4}2/m$ | Tetragonal scalenohedral | 1 \overline{A}_4 , 2A ₂ , 2m |
| | 4/m2/m2/m | Ditetragonal dipyramidal (N) | C, 1A ₄ , 4A ₂ , 5P(m) |
| Hexagonal | 3 | Trigonal pyramidal | 1A ₃ |
| | $\overline{3}$ | Rhombohedral | 1 \overline{A}_3 (=C+1A ₃) |
| | 32 | Trigonal trapezohedral | 1A ₃ , 3A ₂ |
| | 3m | Ditrigonal pyramidal | 1A ₃ , 3P |
| | $\overline{3}2m$ | Trigonal scalenohedral (N) | C, 1A ₃ , 3A ₂ , 3P |
| | 6 | Hexagonal pyramidal | 1A ₆ |
| | $\overline{6}$ | Trigonal dipyramidal | 1 \overline{A}_6 (=1A ₃ +m) |
| | 6/m | Hexagonal dipyramidal | C, 1A ₆ , 1P |
| | 622 | Hexagonal trapezohedral | 1A ₆ , 6A ₂ |
| | 6mm | Dihexagonal pyramidal | 1A ₆ , 6m |
| | $\overline{6}m2$ | Ditrigonal dipyramidal | 1 \overline{A}_6 , 3A ₂ , 3m |
| | 6/m2/m2/m | Dihexagonal dipyramidal (N) | C, 1A ₆ , 6A ₂ , 7P |
| Isometric | 23 | Tetartoidal | 3A ₂ , 4A ₃ |
| | 2/m $\overline{3}$ | Diploidal | 3A ₂ , 4 \overline{A}_3 , 3m |
| | 432 | Gyroidal | 3A ₄ , 4A ₃ , 6A ₂ |
| | $\overline{4}3/m$ | Hextetrahedral | 3 \overline{A}_4 , 4A ₃ , 6m |
| | 4/m $\overline{3}$ 2/m | Hexoctahedral (N) | C, 3A ₄ , 4A ₃ , 6A ₂ , 9P |

Morphology of Crystals:

Crystal Faces: As xls are formed by the repetition in three dimensions of a unit of structure, the limiting surfaces, which are known as the faces of a crystal, depend in part in the shape of the unit. They also depend on the conditions in which the xl grows.

The conditions = external influences such as temperature, pressure, nature of solution, direction of movement of the solution, and availability of open space for free growth.

Two kinds: like faces and unlike faces.

The faces that have the same properties = like faces

The faces that have different properties = unlike faces.

Crystal Edge: An edge is formed by the intersection of any two adjacent faces.

Solid angle: A solid angle is formed by the intersection of three or more faces.

Interfacial angle: The angle between any two faces of a xl is termed the interfacial angle.

Measurement done by 'goniometer'.

Two types of goniometer: a) contact goniometer, b) reflecting goniometer.

Steno's Law:

Law of constancy of interfacial angles: "The angles between corresponding faces on different xls of a substance are constant".

Parameters: The parameters of a xl face are the ratios of the distances from the origin at which the face cuts the xlographic axes, i.e. the parameters are the ratios of the intercepts.

Parameters of the face ABC are given by the ratio of OA, OB & OC. In the case of the face DEF, OD=OA, OE is twice OB and OF is half of OC.

Therefore 1/1, 2/1, 1/2 are the parameters of DEF with reference to the standard face ABC.

Axial Ratios: The relative (not the absolute) length of the unit cell edges that correspond to the xlographic axes. E.g. Sulphur – a:b:c = 0.8131:1:1.9034 from morphological measurements and calculation in 1869.

From unit cell measurement by x-ray techniques in 1960 a:b:c = 0.8135:1:1.9029.

Indices: The reciprocals of the parameters are called the indices. Methods of notation to express the intercepts of xl faces upon the xl axes.

Crystallographic Notation: It is a concise method of writing down the relation of any xl face to the xlographic axes.

The most widely used systems depend upon either parameters or indices.

Mainly two – parameter system of Weiss and
Index system of Miller (modified by Braivais).

Parameter System of Weiss:

Unequal axes – a, b, c

Two equal axes – a, a, c

All equal axes – a, a, a

Intercept on a axis = a

Intercept on b axis = b

Intercept on c axis = c

Intercepts are measured in terms of the intercepts made by the unit form on the corresponding xlographic axes.

The most general expression for a xl face in the Weiss notation is na, mb and pc. Where n, m, and p are the lengths cut off by the face on the a, b, and c axis.

It is usual to reduce either n or m to unity

a, 2b, ∞c

a, ∞b, ∞c

Index System of Miller (Miller Indices):

a, 2b, ∞c : The reciprocals are 1, 1/2, 0; clearing the fraction and omitting the axial letters the Miller symbol is obtained as 2 1 0

a, ∞b, ∞c = 1 0 0

General symbol is h k l; for Hexagonal system – h k i l.

Law of rationality of indices: "The intercepts that any xl face makes on the xlographic axes are either infinite or small rational multiples of the intercepts made by the unit form". This law follows from the regularity of the space lattice representing the atomic structure of xls.

Forty-eight Forms:

Form: Form consists of a group of xl faces, all of which have the same relation to the elements of symmetry and display the same chemical and physical properties because all are underlain by like atoms in the same geometrical arrangement. Proposed by Groth (1895) and modified by A.F. Rogers (in 1935) – 48 forms- as distinguished by the angular relations of xl faces.

32 – general forms found in the 32 xl classes

10- special, closed forms of the isometric system

6 – special open forms (prisms) of hexagonal and tetragonal

---- systems

48

A xl made up entirely of like faces is termed a simple form

33 Non-isometric xl forms:

| S. No. | Name according to Groth-Rogers | No. of faces | Internationally recommended name (after Fedorov Inst.) |
|--------|--------------------------------|--------------|---|
| 1. | Pedion | 1 | Monohedron |
| 2. | Pinacoid | 2 | Parallelohedron |
| 3. | Dome | 2 | Dihedron |
| 4. | Sphenoid | 2 | -do- |
| 5. | Rhombic prism | 4 | Rhombic prism |
| 6. | Trigonal prism | 3 | Trigonal prism |
| 7. | Ditrigonal prism | 6 | Ditrigonal prism |
| 8. | Tetragonal prism | 4 | Tetragonal prism |
| 9. | Ditetragonal prism | 8 | Ditetragonal prism |
| 10. | Hexagonal prism | 6 | Hexagonal prism |
| 11. | Dihexagonal prism | 12 | Dihexagonal prism |
| 12. | Rhombic pyramid | 4 | Rhombic pyramid |
| 13. | Trigonal pyramid | 3 | Trigonal pyramid |
| 14. | Ditrigonal pyramid | 6 | Ditrigonal pyramid |

| | | | |
|-----|--------------------------|----|--------------------------|
| 15. | Tetragonal pyramid | 4 | Tetragonal pyramid |
| 16. | Ditetragonal pyramid | 8 | Ditetragonal pyramid |
| 17. | Hexagonal pyramid | 6 | Hexagonal pyramid |
| 18. | Dihexagonal pyramid | 12 | Dihexagonal pyramid |
| 19. | Rhombic dipyramid | 8 | Rhombic dipyramid |
| 20. | Trigonal dipyramid | 6 | Trigonal dipyramid |
| 21. | Ditrigonal dipyramid | 12 | Ditrigonal dipyramid |
| 22. | Tetragonal dipyramid | 8 | Tetragonal dipyramid |
| 23. | Ditetragonal dipyramid | 16 | Ditetragonal dipyramid |
| 24. | Hexagonal dipyramid | 12 | Hexagonal dipyramid |
| 25. | Dihexagonal dipyramid | 24 | Dihexagonal dipyramid |
| 26. | Trigonal trapezohedron | 6 | Trigonal trapezohedron |
| 27. | Tetragonal trapezohedron | 8 | Tetragonal trapezohedron |
| 28. | Hexagonal trapezohedron | 12 | Hexagonal trapezohedron |
| 29. | Tetragonal scalenohedron | 8 | Rhombic scalenohedron |
| 30. | Hexagonal scalenohedron | 12 | Ditrigonal scalenohedron |
| 31. | Rhombohedron | 6 | Rhombohedron |
| 32. | Rhombic disphenoid | 4 | Rhombic tetrahedron |
| 33. | Tetragonal disphenoid | 4 | Tetragonal tetrahedron |

15 Isometric Forms:

| | | | |
|-----|----------------------|----|-------------------------|
| 34. | Cube | 6 | Hexahedron |
| 35. | Octahedron | 8 | Octahedron |
| 36. | Dodecahedron | 12 | Rhomb-dodecahedron |
| 37. | Tetrahexahedron | 24 | Tetrahexahedron |
| 38. | Trapezohedron | 24 | Tetragon trioctahedron |
| 39. | Trisoctahedron | 24 | Trigon trioctahedron |
| 40. | Hexoctahedron | 48 | Hexoctahedron |
| 41. | Tetrahedron | 4 | Tetrahedron |
| 42. | Tristetrahedron | 12 | Trigon-tritetrahedron |
| 43. | Deltoid dodecahedron | 12 | Tetragon-tritetrahedron |
| 44. | Hextetrahedron | 24 | Hextetrahedron |
| 45. | Gyroid | 24 | Pentagon-trioctahedron |
| 46. | Pyritohedron | 12 | Dihexahedron |
| 47. | Diploid | 24 | Didodecahedron |
| 48. | Tetartoid | 12 | Pentagon-tritetrahedron |

Typical xls showing combination of forms:

A xl that consists of two or more simple forms is called a combination.

Twinning in Crystals:

Twin: A twin is a symmetrical intergrowth of two (or more) xls of the same substance. Such crystallographically controlled intergrowths are also called twinned xls.

The two or more individual of the twinned aggregates are related by a symmetry element that is absent in a single (untwined) xl.

The plane dividing the twin so that one half is a reflection of the other half is called the twin-plane.

The axis about which rotation is necessary to restore the twin to its untwined state is called the twin-axis.

The plane along which the two halves of a twin are joined is called the composition-plane. Composition planes may or may not be twin planes.

Different types of xl twins:

1. Simple Twin: Consisting two halves symmetrical with respect to the twin-plane. It is also called a contact-twin.
2. Penetration Twins: Two halves of the twin has grown so mixed together that the twin cannot be divided into two separate halves.
3. Repeated Twins: Produced by the repetition of twinning according to the same law. A xl composed of 3 parts related to one another by the same twin law is called a trilling, of 4 parts fourling, of 5 parts fivelings, of 8 parts eightling. If the twin plane in all parts of a repeated twin remains parallel, it is called 'Polysynthetic', 'Cyclic' when not parallel.
4. Compound or complex: A twin in which twinning has taken place on two or more laws.

Twin Laws:

1. Cubic system: Twin plane is the octahedral face and twin axis is right angles to this.
Flour spar – inter penetrated twins on this law
Pyrite – inter penetrated twins on this law known as iron cross.
2. Tetragonal system: Rutile Law – Twin plane and composition plane are a face of the pyramid of the 2nd order.
3. Orthorhombic system: Aragonite – forms cyclic twins by repeated twinning.
4. Monoclinic system:
Gypsum – 'Swallow – tails' twins, with the 'a' pinacoid as the twin-plane.
Orthoclase – twins on three common laws:-
 - i) Carlsbad twin – twin axis is the vertical xlographic axis and the composition plane is the 'b' pinacoid.
 - ii) Bareno twin – the twin plane and composition plane are the (021) 1st order prisms.
 - iii) Manebach twin – twins are the basal pinacoid.
5. Triclinic system: Albite law – twin plane is (010) –'b' pinacoid – usually repeated twinning and polysynthetic.

This repeated twinning produces a striation in the basal planes of the xl, and is also excellently seen in thin sections of plagioclase examined under the microscope.

Cause of twinning:

Occurrence of twinning in a xl depends on the dimensional properties of the lattice.

Vectorial Properties of mineral:

Due to different atomic arrangement along different xl planes or directions.

Because magnitude of the property dependent on direction, differs with changing xlographic direction.

Continuous vectorial properties:

- Hardness
- Electric and heat conductivity
- Thermal expansion
- The speed of light

Discontinuous vectorial properties: (pertain only to certain definite planes or directions within the xl)

- Rate of growth – different forms of the xls
- Rate of solution – etch or pits
- Cleavage – weakest bonding.