

Solid State

(Part 2)

(For B.Sc 1st year)

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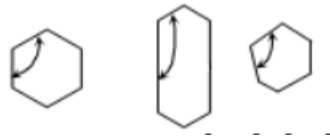
Crystallography

The branch of science that deals with the study of structure, geometry and properties of crystals is called crystallography.

Law of crystallography:

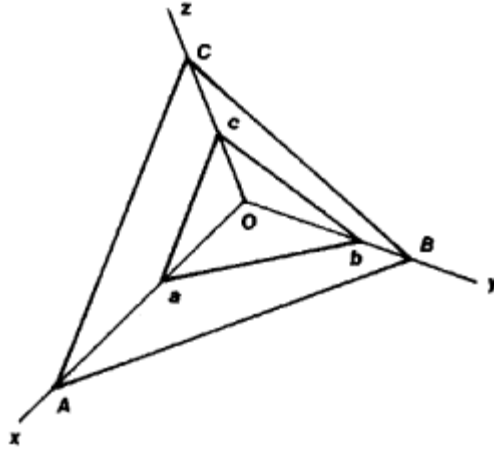
The geometric crystallography is based on the three fundamental laws

1. ***The Law of constancy of the interfacial angles:*** This law states that angle between the adjacent corresponding faces that is the interfacial angles of the crystal of the particular substance, is always constant in spite of having different shapes and sizes and mode of growth of crystal. (The interfacial angle is the angle between two faces of the crystal). The size and shape of the crystal depend upon the conditions of the crystallization. This law is also called as Steno's Law.



Constancy of interfacial angle

2. ***Hauy's law of rationality of indices:*** it is possible to choose along the three coordinate axes unit distance (a , b , c), not necessarily of the same length, such that the ratio of the three intercepts of any plane in the crystal is given by $(h a : k b : l c)$ where h , k , l are either:
 - (i) Same as those of the unit plane, or
 - (ii) Simple whole number multiples of those of the unit plane, or
 - (iii) One or two intercepts may be infinity, if the face is parallel to one or two axes, i.e. the face does not cut one or two axes.



In the figure the intercepts of the parametric plane with the crystallographic axes are all equal, and the intercepts are arbitrarily chosen to be a , b , c along with x , y and z axes respectively

$Oa = a$; $Ob = b$ and $Oc = c$ where a , b , c have any arbitrary value but their ratios are constant.

Let us consider different values for h , k and l as follows:

$h=1, k=1$ and $l=1$	Then $(a : b : c)$
$h=1, k=1$ and $l=\infty$	Then $(a : b : \infty c)$
$h=2, k=1$ and $l=\infty$	Then $(a : b : \infty c)$
$h=1/2, k=2$ and $l=3$	Then $(a/2 : 2b : 3c)$

Like this the planes of the crystals can be represented, here the coefficients a , b and c are known as **Weiss indices**.

3. The law of constancy of symmetry: according to this law, all crystals of the same substance possess the same elements of symmetry.

A crystal possesses following three types of symmetry,

- I. **Plane of symmetry:** It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions which are exactly the mirror images of each other.

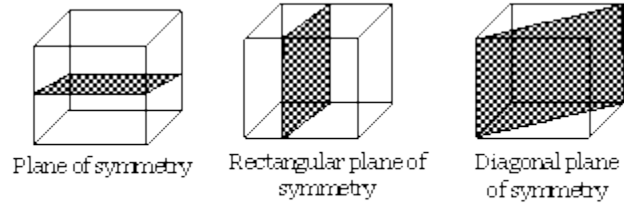
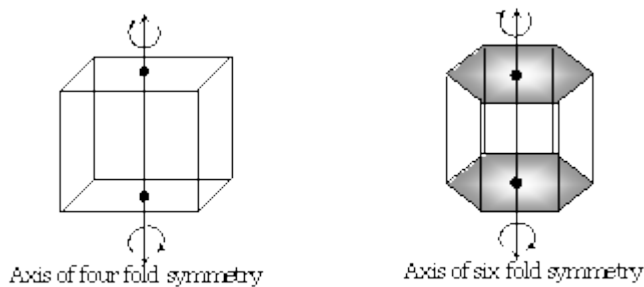
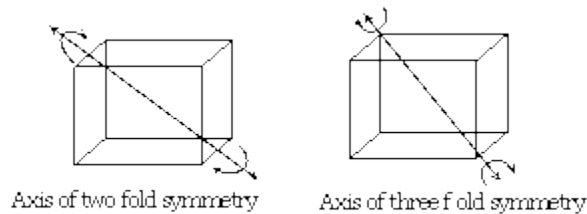


Fig. 5.1

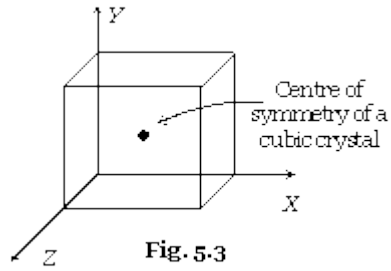
- II. **Axis of symmetry** : An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution i.e., in a rotation through 360° .

Suppose, the same appearance of crystal is repeated, on rotating it through an angle of $360^\circ/n$, around an imaginary axis, is called an n-fold axis where, n is known as the order of axis. By order is meant the value of n in $2\pi/n$ so that rotation through $2\pi/n$, gives an equivalent configuration.



E.g. the cubic crystal of NaCl has 13 axes of symmetry out of which 4 are threefold, 3 are fourfold and 6 are twofold.

- III. **Centre of symmetry**: It is an imaginary point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side.



Only simple cubic systems have one centre of symmetry. Other system do not have centre of symmetry. The total number of planes, axes and centre of symmetries possessed by a crystal is termed as elements of symmetry.

A cubic crystal possesses total 23 elements of symmetry.

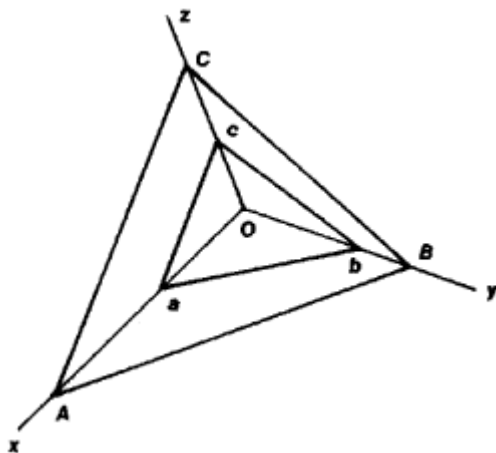
Plane of symmetry $(3 + 6) = 9$

Axes of symmetry $(3 + 4 + 6) = 13$

Centre of symmetry $(1) = 1$

Total symmetry = 23

Weiss indices and Miller's indices



If face ABC makes intercepts p , q and r on the three axes and the intercepts made by the unit plane abc are a , b and c then we have,

$$p = na, q = n'b \text{ and } r = n''c$$

where n , n' , n'' are simple whole numbers or infinity. Then the face ABC may be presented by (n, n', n'') .

The numbers used to represent a face are called **Weiss indices**.

Miller Indices may be defined as the reciprocal of the coefficients of the intercepts, expressed as integers. Thus the intercept made by plane ABC can be expressed as,

$$OA = a/h \quad OB = b/k \quad OC = c/l$$

Then the miller indices of the plane are (h, k, l). Obviously, the miller indices of a face are inversely proportional to the intercept of that face on the crystallographic axes.

Examples of miller indices:

1. If the intercepts made by plane ABC are 2a, 2b, 3c. The reciprocals of the coefficients of a, b, c are 1/2, 1/2, 1/3 and LCM of 2, 2, 3 = 6.
Multiplying the reciprocals by 6 we have 3, 3 and 2. Therefore the miller indices for the plane ABC are (3, 3, 2).
2. If the intercepts made by plane ABC are a, b, c. The reciprocals of the coefficients of a, b, c are 1/1, 1/1, 1/1 and LCM of 1, 1, 1 = 1.
Therefore the miller indices for the plane ABC are (1, 1, 1).
3. If the intercepts made by plane ABC are 2a, 3b, ∞c. The reciprocals of the coefficients of a, b, c are 1/2, 1/3, 1/∞ and LCM of 2 and 3 = 6.
Multiplying the reciprocals by 6 we have 3, 2 and 0. Therefore the miller indices for the plane ABC are (3, 2, 0).
4. If the intercepts made by plane is negative i.e. the face is cut by the axis when extended in the opposite direction, it is represented by putting a bar over it. e.g.
($\bar{1}$, 0, 0)

Bragg's Law

Bragg's law is a special case of Laue diffraction which determines the angles of coherent and incoherent scattering from a crystal lattice. When X-rays are incident on a particular atom, they make an electronic cloud move just like an electromagnetic wave. The movement of these charges radiates waves again with similar frequency, slightly blurred due to different effects and this phenomenon is known as Rayleigh scattering.

The same process takes place upon scattering neutron waves via nuclei or by a coherent spin interaction with an isolated electron. These wave fields which are re-emitted interfere among each other either destructively or constructively creating a diffraction pattern on a film or detector. The basis of diffraction analysis is the resulting wave interference and this analysis is known as Bragg diffraction.

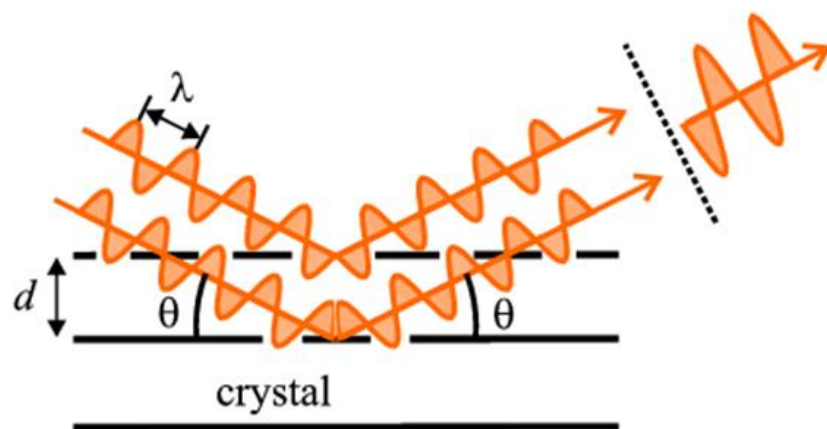
Bragg Equation

According to Bragg Equation:

$$n\lambda = 2d \sin\theta$$

Therefore, according to the derivation of Bragg's Law:

- The equation explains why the faces of crystals reflect X-ray beams at particular angles of incidence (θ , λ).
- The variable d indicates the distance between the atomic layers and the variable λ specifies the wavelength of the incident X-ray beam.
- n as an integer.



This observation illustrates X-ray wave interface which is called as X-ray diffraction (XRD) and proof for the atomic structure of crystals.

Braggs was also awarded with Nobel Prize in Physics in identifying crystal structures starting with NaCl, ZnS and diamond. Diffraction has been developed to understand the structure of every state of matter by any beam e.g. ions, protons, electrons, neutrons with a wavelength similar to the length between the molecular structures.

Applications of Bragg's Law

There numerous Bragg's law applications in the field of science. Some common applications are given in the points below.

- In the case of XRF (X-ray fluorescence spectroscopy) or WDS (wavelength dispersive spectrometry), crystals of known d-spacings are used as analyzing crystals in the spectrometer.
- In XRD (X-ray diffraction) the interplanar spacing or d-spacing of a crystal is used for characterization and identification purposes.

Bragg's diffraction

Bragg's diffraction was first proposed by William Henry Bragg and William Lawrence Bragg, in 1913. Bragg's diffraction occurs when subatomic particle or electromagnetic radiation, waves have wavelengths that are comparable to atomic spacing in a crystal lattice.

Bragg's law Conclusion

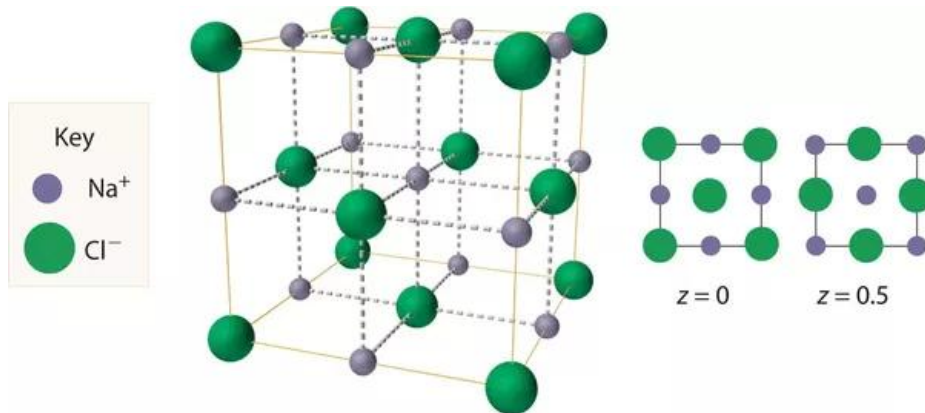
The concluding ideas from Bragg's law are:

- The diffraction has three parameters i.e, the wavelength of X rays, λ
- The crystal orientation defined by the angle θ
- The spacing of the crystal planes, d.

The diffraction can be conspired to occur for a given wavelength and set of planes. For instance, changing the orientation continuously i.e, changing theta until Bragg's Law is satisfied.

Structure of Sodium Chloride

Sodium chloride, also known as **salt** or **halite** is an ionic compound with the chemical formula **NaCl**, representing a 1:1 ratio of sodium and chloride ions. With molar masses of 22.99 and 35.45 g/mol respectively, 100 g of NaCl contain 39.34 g Na and 60.66 g Cl.



Salient features of its structure are:

- Chloride ions are **ccp** type of arrangement, *i.e.*, it contains chloride ions at the corners and at the center of each face of the cube.
- Sodium ions are so located that there are six chloride ions around it. This equivalent to saying that sodium ions occupy all the octahedral sites.
- As there is only one octahedral site for every chloride ion, the stoichiometry is 1: 1.
- It is obvious from the diagram that each chloride ion is surrounded by **six** sodium ions which are disposed towards the corners of a regular octahedron. We may say that cations and anions are present in equivalent positions and the structure has 6:6 coordination.
- The structure of sodium chloride consists of eight ions a unit cell, four are Na⁺ ions and the other four are Cl⁻ ions.

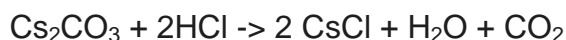
In this structure, each **corner ion** is shared between **eight** unit cells, each ion a face of the cell by **two** cells, each ion on a **edge** by **four** cells and the ion inside the cell belongs entirely to that unit cell

Structure of Caesium chloride

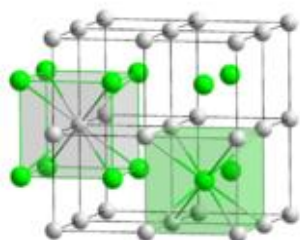
Caesium Chloride is a type of unit cell that is commonly mistaken as Body-Centered Cubic. This misconception is easy to make, since there is a center atom in the unit cell, but CsCl is really a Non-closed packed structure type.

CsCl has a boiling point of 1303 degrees Celsius, a melting point of 646 degrees Celsius, and is very soluble in water. For the most part this molecule is stable, but is not compatible with strong oxidizing agents and strong acids.

CsCl is an ionic compound that can be prepared by the reaction:



Salient features of its structure are:



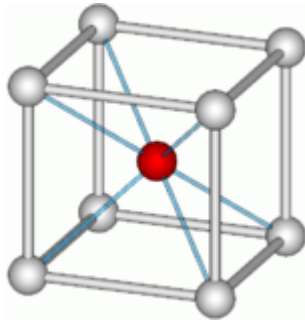
CsCl Coordination Cubes

- CsCl crystallize in a primitive cubic lattice which means the cubic unit cell has nodes only at its corners. The structure of CsCl can be seen as two interpenetrating cubes, one of Cs^+ and one of Cl^- . The ions are not touching one another. Touching would cause repulsion between the anion and cation.
- Some may mistake the structure type of CsCl with NaCl, but really the two are different. CsCl can be thought of as two interpenetrating simple cubic arrays where the corner of one cell sits at the body center of the other.
- As with NaCl, the 1:1 stoichiometry means that the cell will look the same regardless of whether we start with anions or cations on the corner. Note that each ion is 8-coordinate rather than 6-coordinate as in NaCl. CsCl is more stable than NaCl, it produces a more stable crystal and more energy is released.

Anions and cations have similar sizes. Each Cs^+ is surrounded by 8 Cl^- at the corners of its cube and each Cl^- is also surrounded by 8 Cs^+ at the corners of its cube. The cations

are located at the center of the anions cube and the anions are located at the center of the cations cube. There is one atom in CsCl. To determine this, the following equation is given:

8 Corners of a given atom \times $1/8$ of the given atom's unit cell = 1 atom



unit cell of CsCl