Crystal Structure

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Introduction

Among the condensed phases of a substance solid state is characterised by its hardness, rigidity, mechanical strength and definite shape. All these properties are due to closest proximity of atoms, molecules or ions by which the solid is constituted. In solid state due to closest proximity attractive force between the constituent units is maximum. The structural units (atoms, ions or molecules) do not have translational motion and this gives rise to rigidity and shape. Atoms can only oscillate about their mean position in solid crystal.

Solids are generally classified as crystalline solid and amorphous solid. Crystalline solids have definite geometrical shapes characteristic to the substance. In crystalline solid building units are repeatedly arranged following a definite pattern. X-ray diffraction study indicates regular arrangement of units within the crystal. The crystalline state is a state of long range ordered state and short range disordered state which is just opposite to the liquid state. In liquid state long range disordered state and short range ordered state is observed. Crystalline solid has sharp melting point.

An amorphous solid has no characteristic crystal shape. They melt over a range of temperature. They are supercooled liquids with high viscosity. A glass belongs to amorphous solid. It is obtained by cooling a liquid and is a supercooled highly viscous liquid. The substance becomes hard due to high viscosity at room temperature and behaves as a solid. X-ray diffraction shows a disorder structure. Polymer often forms amorphous solid. When a polymer is cooled the long polymer chains become twisted and tangled in a random, irregular manner giving rise to the three dimensional rigid structure which is an amorphous solid.

Crystallography

Crystallography is the study of geometrical forms and properties of the crystal. It deals with both internal and external structure. Crystals have planar surfaces arranged in a definite manner depending upon the internal arrangement of the builiding units. The surfaces are called the faces and the angle between two intersecting faces is called the interfacial angle. A crystal grows from melt or solution or from gaseous state due to deposition of atoms or ions on its faces during cooling. To grow a big crystal which is the replica of the small crystal special measures are to be taken. Otherwise during cooling a melt or saturated solution polycyrstalline substance is produced where each grain is a tiny crystal which has irregular haphazard form due to non-symmetric growth of the faces. If atoms or ions deposit preferentially on a certain face, that face will not extend rapidly in area compared to other faces and the faces with large area have a slower rate of deposition of atoms or ions. Very slow cooling of melt or supersatuarated solution allows to grow a monocrystal.

Three basic laws of crystallography regarding the structural symmetry of the crystal are derived from external form of crystal.

(i) Steno's law of constancy of interfacial angles; (ii) Haüy's law of rational intercepts; (iii) Law of constancy of symmetry.

Steno's Law

This law states that the interfacial angles between the corresponding faces of different crystals of the same substance are constant.

The crystal faces are unequally developed leading to various shapes of the crystal depending upon the condition of crystallisation. But in spite of that the interfacial angle between the two intersecting corresponding faces will remain constant. If X and Y are two different crystals of the same substance then the angle a between the two corresponding faces, a and b of the two crystals remain the same(fig.1). The different shape of the crystal is due to different rate of deposition of atoms or ions in different faces. Sodium chloride grows as cube when the crystallised from aqueous solution but as octahedron from aqueous solution containing urea.

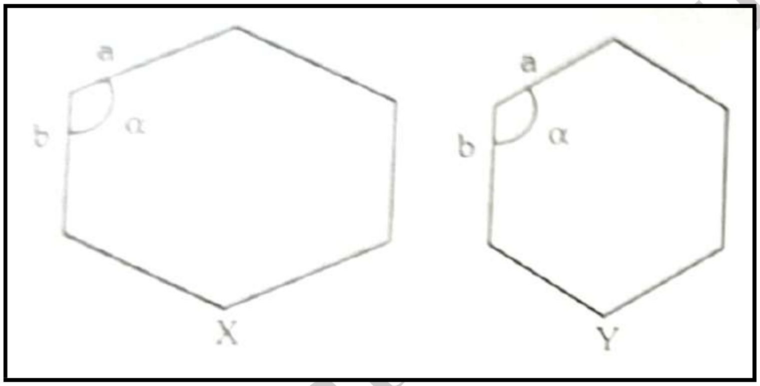

Figure1: Constancy of interfacial angles of two crystals

Haüy's Law: Haüy in 1784 proposed that the regular extremal form of a crystal is the reflection of regular internal arrangement of its building units. This proposition is the basis of crystallography and Haüy's proposition was verified a century later when X-diffraction study of crystals was done.

If a crystal is suitably divided on and on, we have gradually smaller and smaller crystals where each one is the replica of the original one. In this way of subdivision ultimately a smallest crystal generally called unit crystal can be obtained having same symmetry as that of the original one. Further breaking of the unit crystal causes its distribution into constituent atoms, ions or molecules.

Since macroscopic crystal is the result of regular arrangement of unit crystals, any unit crystal within a crystal can be defined by choosing suitable coordinate system. Three non-coplanar axes can be considered together as the coordinate system. The axes may be mutually at right angle to one another like cartesian coordinate or they may be at any suitable angle, arbitrarily chosen, to define the internal geometry. The axes of the coordinate system may coincide with the principal faces of the crystal or may be parallel to it. Any face of the unit crystal will cut one or more of the axes, the face being extended if necessary. Since the corresponding faces of unit crystal are at a regular separation, they will cut any given axes at regular interval. If along the three axes unit intercepts are represented by a,b,c and can be considered as primary intercepts, then the intercepts (x, y, z) on three axes by any plane can rationally be expressed in terms of a, b, c as ma, nb, pc where m, n and p are small integer, i.e, x : y: z = ma : nb : pc. Therefore, all faces a given axis at several distances from the origin which ratio to one another. This is the law of rational intercepts.

The law of rational intercepts makes it possible to define any plane of the crystal in terms of the coefficients of the primary intercepts a, b and c. Thus, the plane which makes intercepts x.y and on three crystallographic axes and x = ma,y=nb, z = pc can be defined by a set of indices (m, n, p) which are the co-efficients of a,b and This set of indices formed by the coeffients of a,b and c is called **Weiss indices**. In the figure the plane ABC makes intercepts OA, OB, OC on three axes where OA=3a, OB = 3b and OC = 2C (fig.2). Therefore, the plane ABC can be defined by the set of indices (332), Each plane has a separate Weiss index of its own. Even for a set of parallel planes, each plane will have a different set of Weiss indices.

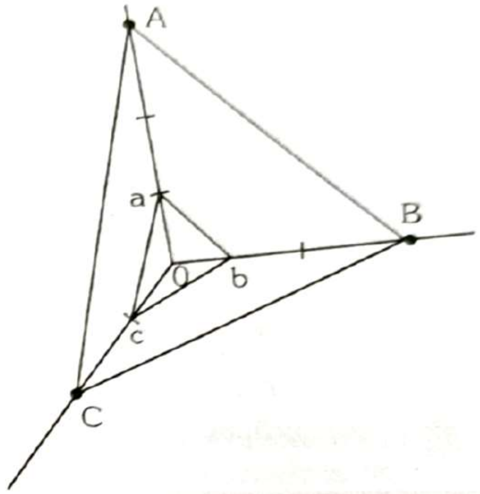

Fig2. Plane ABC makes intercept on crystallographic axes

If the plane cuts the x-axis at 2a but is parallel to y and z axes i.e, cuts y and z axis at infinity, then the intercepts on y and z axes are represented by ∞ band ∞a respectively. Hence the weiss indices of the plane will be (2∞ ∞)

Instead of using **Weiss indices** all the equivalent parallel planes in the same quadrant can be expressed Miller indices are obtained by taking the reciprocals by a single set of indices called **Miller indices** of the coefficients of a, b and c and if any fraction appears in taking the reciprocal, the ratio of the reciprocals of coefficients of a,b and c is converted to ratio of small intergers. For examples if the Weiss indices of a set of equivalent parallel planes are (1.2.1),(2,4,2), (3,6,3) then the reciprocals are (1, 1/2, 1),(1/ 2 , 1 /4 , 1/ 2),(1 /3 , 1/ 6 , 1/ 3). Converting the fraction into whole number we get (2,1,2), (2,1,2), (2.1.2). So (212) is the **Miller indices** of all the above parallel equivalent planes. If plane is parallel to any axis say z axis, then it cuts the z axis at infinity, i.e. the coefficient of c is ∞. In Miller indices the reciprocal of c will be zero. For the weiss indices (1/2, ∞, 1) the Miller indices will be (201). Miller indices in general is represented by (hkl) for any plane ABC which makes intercepts OA, OB and OC on the three crystallographic axes. Then h=a/ OA, k=b/ OB and l=c/ OC. If the plane cuts any axis in the negative direction then in Miller indices of using negative sign with the reciprocal, bar is used above the number. Thus the plane with Weiss indices (1, - 1, ∞) will have the Miller indices $(1\,\bar{1}\,0)$

In Miller indices (h,k,l) the more near is the value of h towards zero, the plane will be more parallel x-axis. If h = 0 then the plane becomes parallel to x-axis. Similar is the case for k and l. When k = 0 the plane is parallel to y-axis and l = 0 represents the plane parallel to z-axis.

Since a crystal is an infinte array of atoms the origin of the crystallographic axes may be considered at the corner of a crystal or at any atom. Starting from the origin if translatory motion is considered until and unless repeatition of the same starting point is obtained along each crystallographic axes, the minimum distance between the two similar atoms or ions is called the primitive translation. Primitive translation along three axes are represented by the term standard

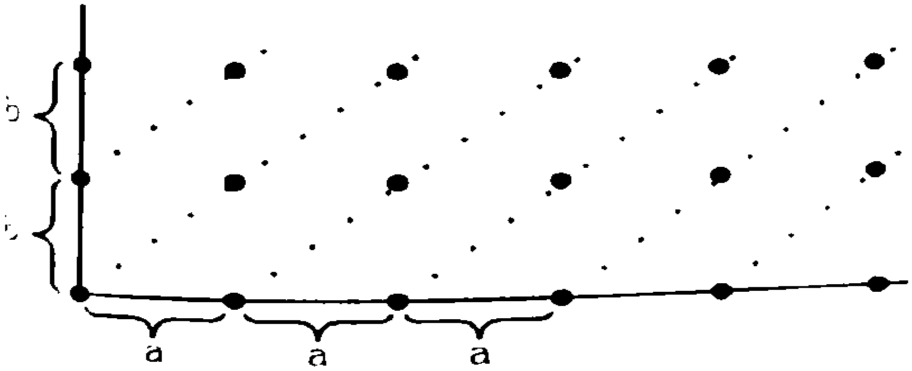

Fig. 3 Primitive translations (a, b) in two dimensional space lattice

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or primary intercepts and are indicated by a, b and e. Let us consider a two dimensional array of points as (fig. 3).

From this array of point in two dimension the following planes can be defined (fig. 4)

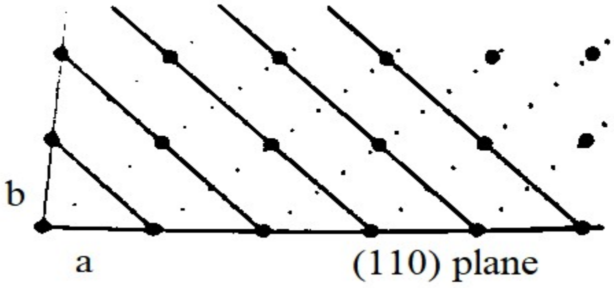

Fig.4:110 planes in two-dimensional space lattice

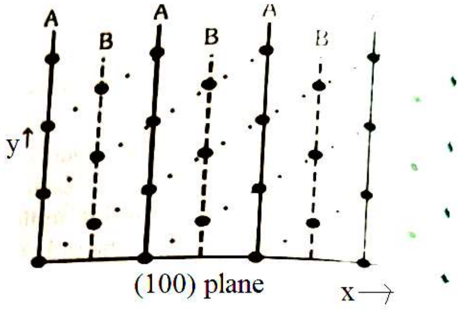

Fig.5: 100 ans 200 planes in two-dimensional space lattice

In Fig. 5, A planes are 100 plane. But if we consider A and B planes together where both planes are same and equivalent, planes make intercepts on x-axis at a / 2 interval and are parallel to y and z-axis. So all these planes are designated by Miller indices (200).

The coefficients of a, b, c of the planes AB in fig.6 are 1/3 ,1/2. So Miller indices of the plane AB are (230). In the figure 6, the planes having higher Miller indices contain lesser number of point per unit area. For example, planes EF, GC, DH contains respectively 2,3,2,2 points in the given length as represent in Fig.6. It is clear from the figure that the higher is the values of h,k and l in Miller indices, the lower will be the point density of atoms on that plan During X-ray diffraction the lower be the intensity of diffracted beam from such planes having higher Miller indies. An (hkl) planes divide a into h equal parts and h parallel planes can be drown from them. Similarly the planes divide b into k parts and c into l parts.

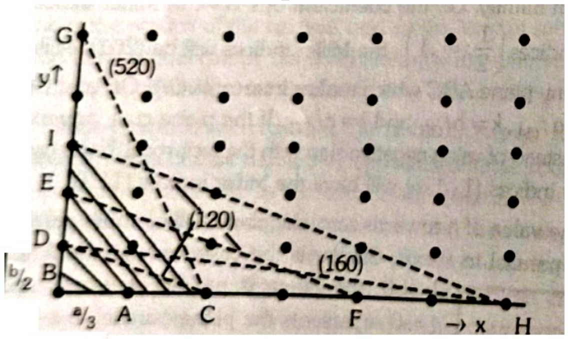

Fig. 6 Planes with different Miller indices in two dimensional parts space lattice

Therefore, the nearest plane to the origin has the intercept (a/h, b/k, c/l) or the Weiss indices is (1/h , 1/k , 1/l). This plane when represented in the figure may not exhibit at all presence of any atom. However, when this plane is extended, we will find atoms at large separations. If the crystal is a cube, the planes parallel to xy plane cut z axis at interval of c but x and y axis at infinity. So weiss indices are (∞, ∞, 1) and the Miller indices is (001). Similarly planes parallel to yz plane are (100) and planes parallel to xz plane are (010) plane fig. (7) In Fig.8 the plane ACGE is parallel to z-axis but cut the x- and y-axis having intercepts a and b. So the coefficients of intercepts are (1,1,∞) and the Miller indices is (110).

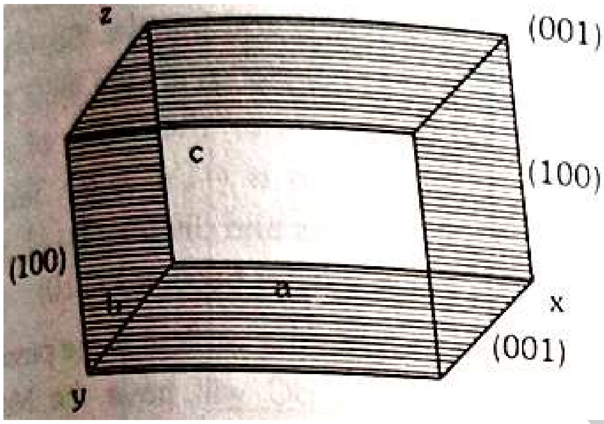

Figure 7: (100), (001) planes of a cube

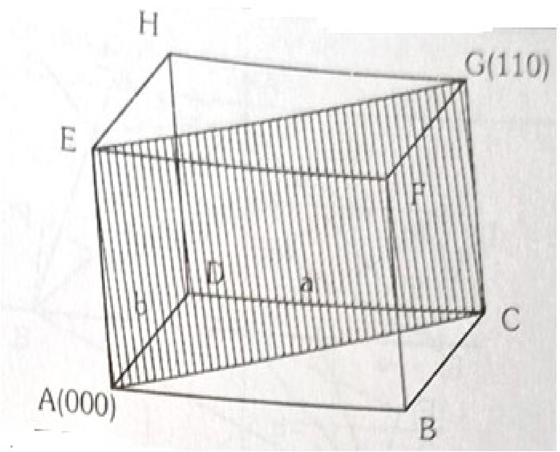

Figure 8: (110) plane

The plane (EDB) in the figure 9 cuts intercepts a, b, c from three axes and the coefficients of intercepts are (1,1,1). So the Miller indices of the plane is (111) with A as the origin. If the origin is shifted to B, the Miller indices of the plane EDB becomes $(\bar{1}\,1\,1)$. If the origin is shifted to D, the Miller indices of the plane becomes $(1\,\bar{1}\,1)$.

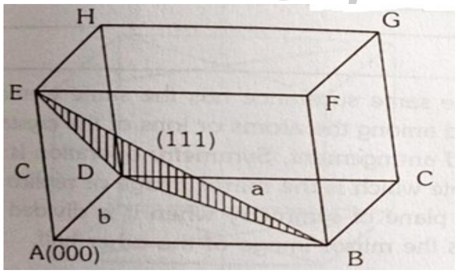

Figure 9: (111) plane

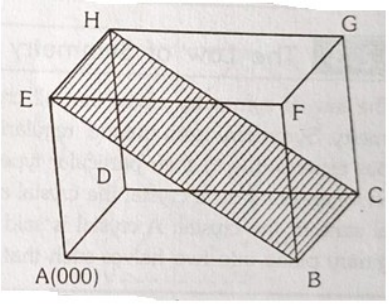

Figure 10: $(\bar{1}\,1\,1)$ plane

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In fig.10 plane EHCB cuts x and z axes with intercepts a and c and y axis at infinity. So, the Miller indices of the plane EHCB, is (101). If origin is shifted to B, the Miller indices of the plane becomes $(\bar{1}\,0\,1)$.

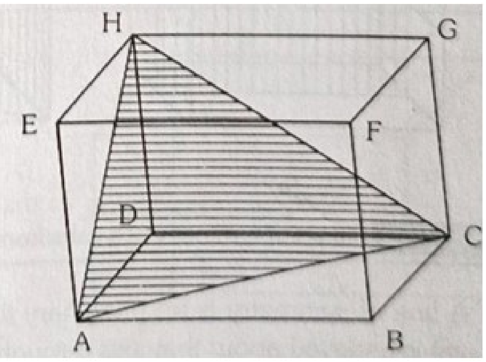

Figure 11: Change of Miller indices of the plane AHC with change of choice of origin

In fig.11 if origin is at A(000) then the coefficients of intercepts of the plane AHC are (1,1,1). The Miller indices of the plane are (111). If the origin is taken at B then Miller indices becomes $(\bar{1}\,0\,1)$. If the origin is at Die. shifted along y-axis, then Miller indices becomes $(\bar{1}\,0\,1)$. If the origin is shifted to H. then the Miller indices becomes $(1\,\bar{1}\,\bar{1})$.

In fiq.12 plane ABC, the Miller indices is (111); plane ABD, the Miller indices is $(1\,\bar{1}\,1)$: Plane AEC the Miller indices is $(\bar{1}\,1\,1)$. Plane ECB'D' is parallel to

z-axis and has the Miller indices is $(\bar{1}\,0\,1)$. Plane DBF'E' is parallel to z-axis and has the Miller indicies $(1\,\bar{1}\,0)$. Again both the planes equivalent and parallel. So $(\bar{1}\,1\,0)$ and $(1\,\bar{1}\,0)$ planes are the same. For, $(\bar{1}\,1\,0)$ plane, the ratio of coefficients is (-1: 1:∞). Taking reciprocals and dividing by -1the Miller indices becomes $(1\,\bar{1}\,0)$.

Again the vertical plane pasting through BC will have the Miller indices(110) and the vertical plane passing through ED will have the Miller indices $(\bar{1}\,\bar{1}\,0)$. These planes are parallel and equivalent. Hence (110) plane and $(\bar{1}\,\bar{1}\,0)$ planes are same.

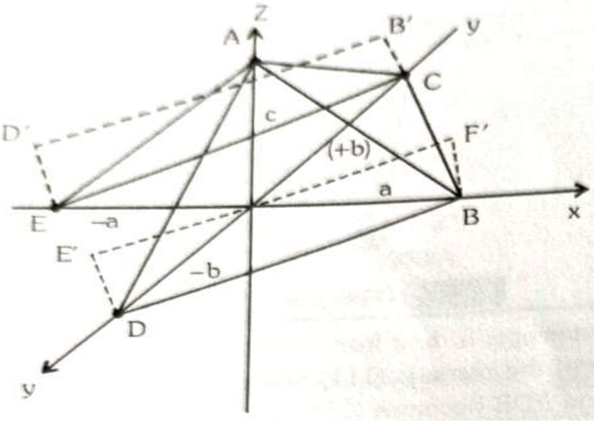

Fig 12: Equivalent planes with different Miller indices