# Crystal Structure : No of lectures 4

Unit Cell and crystal system, symmetry and a choice of unit cells, Bravais lattice, Lattice planes, Miller indices, Indices of direction, d-spacing formulae, Unit cell contents, and crystal densities, Point group space group and crystal structures.

As we have seen yesterday that While teaching solid state chemistry, one has to addressed four questions;

1. Structures of solids

2. Bonding in solids

3. Chemical and physical properties of solids

4. Defects in solids

Therefore, starting with the first topic. I.e. Structure or rather crystal structure of a solid.
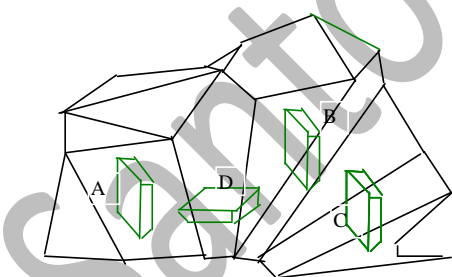
Crystal Classes:

 A microscopic obeservation of a crystal creates a first impression that it is a **homogeneous but has anisotropic structure.** If we took large crystal of quartz **,** cut plate out of it of some given dimensions, and examine its physical properties . We would find that the two geometrically identical i pieces cut from two different locations will have identical physical properties provided their positions in the crystal is parellel to each other.i.e. *they differs no more than rigid translation.* However, with translation if we include rotational component i.e. if we rotate the crystal while translation, their properties will be generally very different.

Now instead of small piece in the crystal which undergoing **translational operation,** we are free to chose whole crystal itself. If we translation the whole crystal from one point to another with involvement of rotation, again the properties of the crystal will not change.

We will introduce now one more translational operation on the whole crystal in which atleast there will a one point in the crystal whose coordinate remains undisturbe after carring out the operation. Obviously it is possible only and only when

- we rotate a crystal at partucular axis, then points on the roatational axies will remain undisturb after the operation.

- We take mirror image, in which after the operation, the coordinates of the points on the plane will remain undisturbe.

- Or combination of above two operation.

All three above operations are called **'point operations'.**

It is found that for the most of the crystals, there are some special point operations which do leave the properties of the crystal **invarient.** Thus for quartz crystal it is found that there exists a line or axies along which the crystal can be rotated by 120^0 without changing the propoerties. Further, there is one more axies about which if crystal rotates by 180° without changing the properties. **The list of all point opererations which leaves the macroscopic propoerties of a crystal invarient is called a crystal class.(macroscopic) point group of a crystal. There are total 32 different crystal classes.**
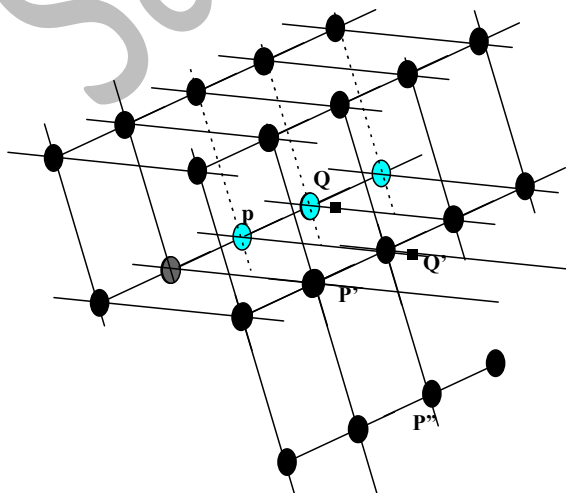
Bravais Lattice:

We have see the symmetry of the crystal in macroscopic point of view. If we able to see the crystal in the microscopic scale, obviously what we will see is the regular arrangement of atoms in the three dimentional space. The general

translation at any direction and distance will not reproduce the original structure. However, if we take the arbitrary point **P** in the crystal structure, we can easily identify a large number of points **P'** or **P"** which are equivalent to **P**. That is crystal looks exactly identical from all these points. **The translation vector** does reproduce the original structutre. Such translation vector is called **Lattice translation Vector.** The set of translation vector is indepent of choice of **P.** A vector equal to **PP'** but originating at point **Q** will terminate at **Q'** which is equivalent to **Q.** The set of these three dimentional points which are equivalent to each other forms a pattern called a **Bravais Lattice.**

It is theoretical symmetric array of structureless points. Strictly speaking, it is **mathematical concept** and not to be interchange with crystal structure.

 The crystal structure is obtained if some thing (atoms, ions or molecules, called basis) is repeated in the space in the pattern of Bravais lattice. The Bravais lattice is therefore, the recipies for locating the identical copies of basis in the space.

Crystal structure= Lattice + Basis (atoms, ions)
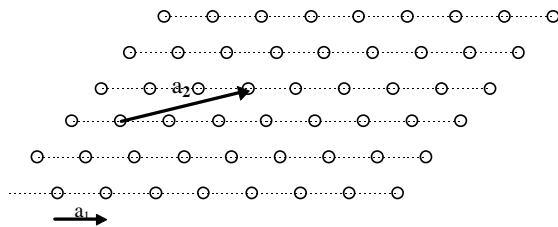
Primitive Translational Vectors:

Now suppose, consider the reverse case. The Bravais lattice is given to us and we have to find out three translational vectors a_1, a_2 and a_3. such that any lattice vectors can be written in the form **R**= $la_1 + ma_2 + na_3$. where l, m. and n are integers. The procedure of finding out a_1, a_2 and a_3 is as follows.

o   o   o   o   o   o   o   o   o

$\xrightarrow{a_1}$
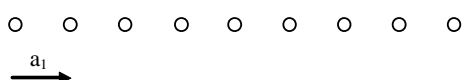
- Choose any lattice vector a_1. Only condition is it should be shortest one in its direction and if we obey this

condition then obviously there will be no lattice point lying onto the vector. Now *every* point in the whole lattice lies on the identical parellel lines with identical spacings.

- Find now two such lines such that common plane between them will have no lattice point. Choose a_2 as any lattice vector which now connects the two. Succesive application of a_2 generates plane of points from a single line. Further more every point of the lattice lies on the identical parellel "a_1-a_2" planes.
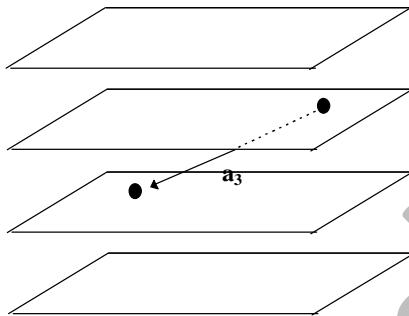
- Find now two such planes which has no lattice points lying between them. Choose a_3 any lattice vector which connect the two.

These three vectors, a_1, a_2, and a_3 are called *Primitive translation vectors.* Obviously these set of vectors are not unique there is a great freedom to choose them.

The parellelepiped defined by a_1, a_2, and a_3 whose volume is $a_1 a_2 x a_3$ contains no points except the corners . If we imagin the lattice made of such parellelepipedal *primitive cells* then we see that eight cells will meet at each lattice corner.

In the converse, if translation vectors are know then whole lattice can generated by applying the **translation symmetry operation** to the basis.

Suppose I have to generate one dimensional lattice. Then I have to apply translational symmetry operator `t' to the basis.

Similarly the two dimensional lattice can be generated by applying two primitive translational vectors t_1 and t_2. Suppose now we have two such vector of magnitude $|t1|$ and $|t2|$ respectively and 90° to each other. It will leads to two dimensional square lattice.

Suppose now angle between t1 and t2 is less than 90° then the lattice would be obliged.

The lattice concept may be now expanded to 3D by the linear combination of 3 conjugated vectors. Thus, the net translation vector can be defined   as

$T = ut_1 + vt_2 + wt_3$, where u,v and w are arbitrary chosen integers.

Reference:.

1. **Solid state Chemistry**, A.R. West

2. udc-530.41/wei/274343 **Solids: Elementry Theory for advanced students,** John Wily and Sons   G. Weinreich   1965

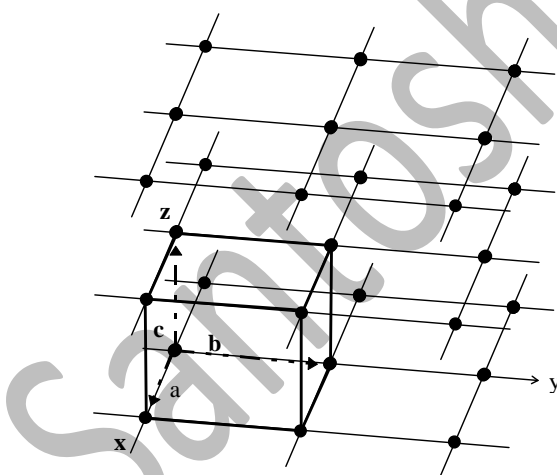# Lattice and Unit cell in the light of symmetry consideration[1]:

Lattice:

A lattice may be defined as a regular infinite arrangment of points in space for which any point has a same environment as every other point. Lattice may be 1, 2 or with three dimension but the above defination will hold for all three types of lattices.

Dimension	Number or types possible	called as
1	1	Row
2	5	Net
3	14	Bravais lattice.

Since we are concerned with the solid state , we will be interested in Bravais lattice or space lattice only. Each Bravais lattice is specified by three noncoplanner vectors **a, b, c** . parellel to the reference axes *x, y and z* respectively. The axes forms right hand set and the angles α, β and γ refers to $b^\wedge c, c^\wedge a, a^\wedge b$ respectively.

From any point as an origin, any point in the lattice has a vector distance $R_{lmn} = l\mathbf{a} + m\mathbf{b} + n\mathbf{c}$. Where lm,n are the coordinate of the lattice point from the chosen origin. Since l,m and n could be negative positive or zero, it implises that all lattices are centrosymmetric. The lattice showed in the figure is a most general type of lattice in which, $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90 \text{ or } 120$ The neumerical values 90 or 120 imply that lattice has C_4 (4), or C_2 (2) or C_3 (3) or C_6(6) rotational symmetry axes. The numbers in the brackets indicate the symmtery groups of the type Hermann and Mauguin (international) symbols. The sign $\neq$ should be red as **"not constrain by symmetry to equal"** and not just "**not equal to**".

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[1] The Language of lattice and Unit cells, J. Chem. Ed., **74(4),** (1997) 461.

From the figure it is cleared that aligning rows of spacing **a** at another given spacing **b** guilds up the *net* and the *stackings* of nets **a,b** on one over other with spacing **c** leads to *Bravais lattice.* **Note that the framework shown in the figure is not a part of the lattice;** the lattice is just the set of mathematical points, the line being drawn is just for the sake of guiding and appreciating the lattice geometry.

System	Symbols of conventional Unit cell	Axial relationships with conventional unit cells	Symmetry of each lattice points
Triclinic	P	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90 or\ 120$	$\bar{1}$ (*i*)
monoclinic	P,C	$a \neq b \neq c$, $\alpha = \gamma = 90^o$ and $\beta \neq 90$ or 120	2/m, (C_{2h})
Orthorhombic	P,C,I,F	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$	*mmm* , (D_{2h})
Tetragonal	P,I	$a = b \neq c$, $\alpha = \beta = \gamma = 90^o$	$\frac{4}{m}mm$ (D_{4h})
Cubic	P,I.F	a=b=c, $\alpha = \beta = \gamma = 90^o$	*m3m* (O_h)
Hexagonal	P	$a = b \neq c$, $\alpha = \beta = 90^o$,$\gamma = 120$	$\frac{6}{m}mm$,(D_{6h})
Trigoanal	R	a=b=c, $\alpha = \beta = \gamma \neq 90, <120$	$\bar{3}$ *m* (D_{3d})

Points groups of the lattice:

The symmetry at each point of the lattice shown in the figure is $\bar{1}$ ($\boldsymbol{i}$, *point of*

inversion) . When lattice possesses symmetry higher than $\bar{1}$ at each point, then

vectors **a,b and c** has to be selected in specific manner. eg. if two fold axis

symmetry is passing through each point, then symmetry at each point is then *2/m*

$(C_{2h})^2$: the symmetry **2** at each points combined with $\bar{1}$ leads to *2/m.* For satisfing

this symmetry consideration, the vectors, **a,b and c** may be selected as $a \neq b \neq c$ and

$\alpha = \gamma = 90^o$ and $\beta \neq 90$ or 120 (choosing β is just a convention). More importantly

symmetry of the lattice will *not* change with the choice of unit cell.

Unit cell:

In the crystallography, the term *unit cell* is refer to parellelepiped, based on three

nocoplanner vectors **a,b and c;** The face to face **stacking-sharing** of these

parellelepipeds builds up entire lattice. The table indicates the 14 Bravais lattices

express in terms of conventional unit cells in *seven* different crystal systems. The

use of conventional unit cells is each unit cell displays all symmetry elements of its

lattice, which is more convinient to treat. eg. three cubic lattices are represented by

unit cells (P,I and F), which has the same symmtery at each lattice point, *m3m* (O_h).

The conventional unit cells are actually a parellelepipeds of smallest volume in which

a, b and c are aligned with the highest symmetry directions of the lattice.

The volume V of the unit cell **(a,b,c)** is given by $V = a \cdot b \times c$ which can be written

as $V = abc(1 - cos^2\,\alpha - cos^2\,\beta - cos^2\,\gamma + 2\,cos\,\alpha\,cos\,\beta\,cos\,\gamma\,)^{\frac{1}{2}}$

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[2] That means it has C_2 axis and a horizontal mirror plane (a plane perpendicular to C_2 axis but not vertical plane like H_2O molecule)

Unit cell in the crystal system:

The choice of the unit cell: The external symmetry of the crystals immediately implies that there must be a regular arrangement of   constituents i.e. atoms ions or molecules inside the crystals. The whole arrangement can be represented by smallest possible repeated unit called unit cell. **The Unit cell may be defined as the smallest repeated unit which show full symmetry of the crystal structure.** We will more appreciate this fact through examples.

Figure 1: Two dimentional projection of NaCl crystal

● ○ ● ○ ●

○ ● ○ ● ○

● ○ ● ○ ●

○ ● ○ ● ○

● ○ ● ○ ●
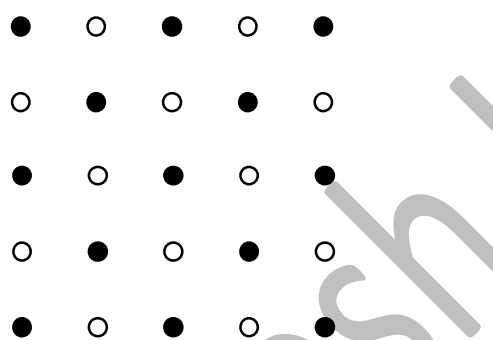
Let us see the slice section through NaCl crystal. We are considering the two dimensional projection of the NaCl crystal. As we know that each Na^+ is surrounded by 4 Cl^- ions and vice versa. We can now draw the various repeated unit in the 2D structure.

Figure 2
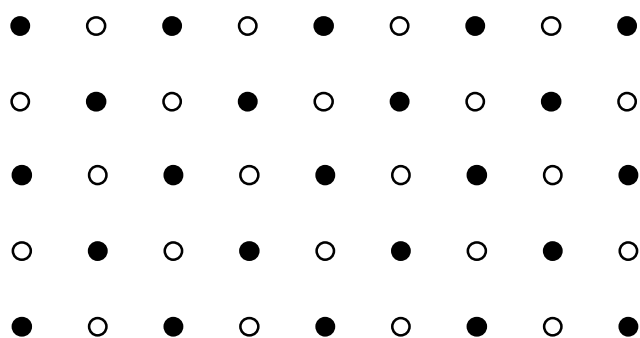
Now the question would be which unit cell among them is correct one ?

In principle, all the structures will act as repeated units. In the last structure, on translating the unit cell, the Cl^- and Na^+ will get interchange. This is the important guide line while choosing the unit cell. Another guide line is by convention, the unit cell is chosen such that the constituents are occupying the corner positions.

Another important guideline is the unit cell must have same symmetry elements to that of actual structure.

Another guide line is, it should be as small as possible. In this light, (e) preferred over (b) and (c). This is story for in two dimension. However, In three dimension, structure (b) and (c) is chosen over (e) as it shows cubic symmetry structure.

Q: suppose we have crystal structure of the type,
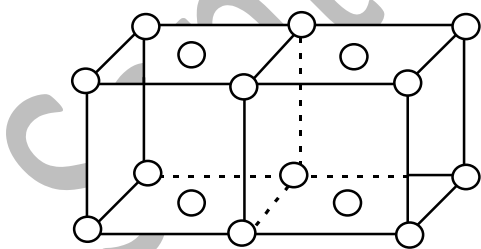
What would be the unit cell in that structure?