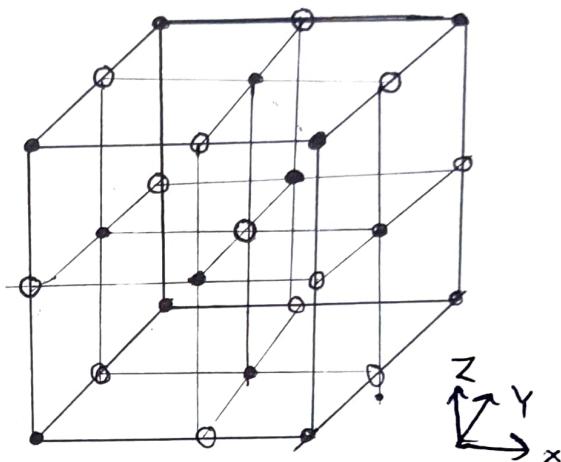


Lecture 7

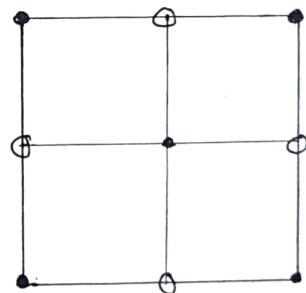
Examples of simple crystal structures

Sodium Chloride Structure

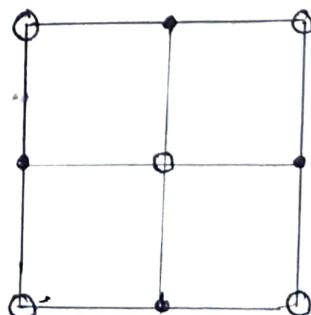
This structure is assumed by ordinary salt, NaCl. The structure is cubic, and is such that along the three principle axes, there is an alternation of Na^+ and Cl^- ions. The second figure shows this alternation in the XY plane for $Z=0$ and the third figure shows in the XY plane for $Z=\frac{a}{2}$. The unit cell is shown in the first figure. It should be evident from the figure that one can consider the structure as being made from two interpenetrating fcc Bravais lattices — one made by Na^+ , another by Cl^- ion.



$\text{Na}^+ \rightarrow \bullet$
 $\text{Cl}^- \rightarrow \circ$



$XY(Z=0)$ plane view



$XY(Z=\frac{1}{2}a)$ plane view

To clarify, consider just the unit cell shown in ~~figure~~ first figure, but without the chlorine ions. This results in an fcc lattice with Na^+ ions. If you now consider the cube ~~at~~ starting from $z = \frac{1}{2}$ to $z = \frac{3}{2}$, you see, excluding Na^+ ions in this cube gives you an fcc lattice with Cl^- ions. So, these two interpenetrating ~~two~~ fcc lattices are displaced relative to each other by $\frac{a}{2}$.

One can also construct an fcc Bravais lattice, where each point is associated with a basis. The basis consists of one Na^+ and one Cl^- ion. You can choose $(0,0,0)$ Na^+ and $(0,0,\frac{1}{2})$ Cl^- as your basis. Now, replace all lattice points by $\xrightarrow{\text{a}_0}$ this basis, and you get the NaCl structure. However, one can also choose ~~an axis~~ a basis without specific axis preference, like a basis made up of $(0,0,0)$ Na^+ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ Cl^- . Again, replacing each lattice points of an fcc Bravais lattice with this basis should give you the NaCl crystal structure.

Each Na^+ ion is surrounded by 6 nearest neighbouring Cl^- ion. Similarly each Cl^- is surrounded by 6 nearest neighbouring Na^+ ion. We say, the coordination number for Na^+ and Cl^- is 6.

If one wants to count the number of atoms in the conventional unit cell, this is done in the following way:

- (i) The corner points are shared by 8 such cells.
- (ii) The points at the midpoint of the edges are shared by 4 such cells.
- (iii) The center point is only shared by the unit cell.
- (iv) The face points are shared by 2 such cells.

$$\text{So, no. of } \text{Na}^+ \text{ ions} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{no. of } \text{Cl}^- \text{ ions} = 1 + 12 \times \frac{1}{4} = 4$$

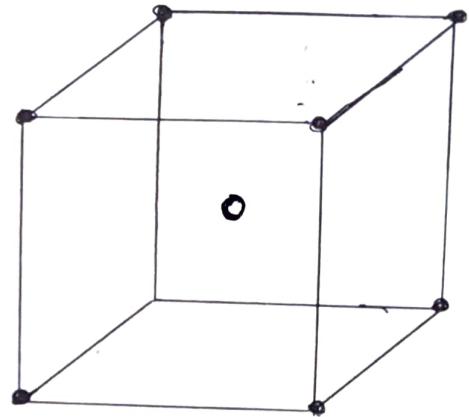
So, the conventional unit cell contains 4 Na^+ and 4 Cl^- ions. This crystal structure is also seen in LiH , MgO , MnO , LiCl , NaF , CsF , CaO etc.

Cesium Chloride Structure

The Cesium Chloride structure consists of equal number of cesium and chlorine ion, placed at the points of a bcc lattice, so that each ion has 8 nearest neighbours of the other kind. So, the coordination number is eight.

This structure can be thought of composed by two interpenetrating simple cubic lattice, one made up of Cesium ions, and another of Chlorine ions, displaced by half the body diagonal (think about the figure where we discussed the equivalence of all the Bravais lattice points of a bcc lattice). Of course, this is a non-Bravais lattice.

To consider this structure as a Bravais lattice, one can think it as a simple cubic Bravais lattice with the basis of $(0,0,0)$ Cs^+ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ Cl^- . There are few compounds that follow this structure such as CsCl , CsBr , CsF , AlNi_3 , BeCu etc.



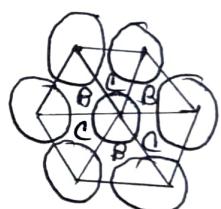
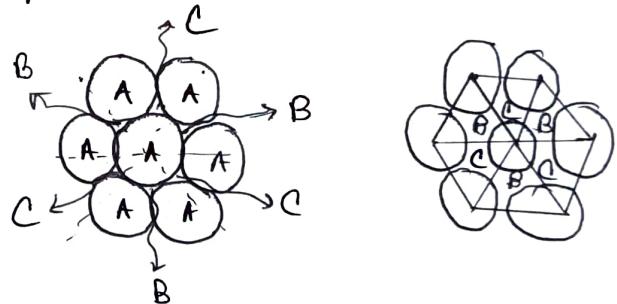
• Cs^+

○ Cl^-

Hexagonal closed pack (HCP) structure

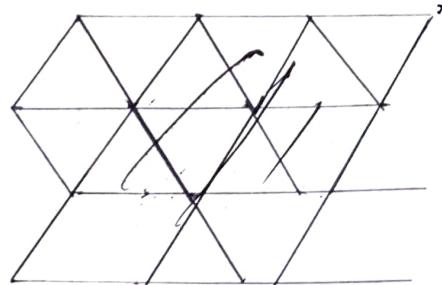
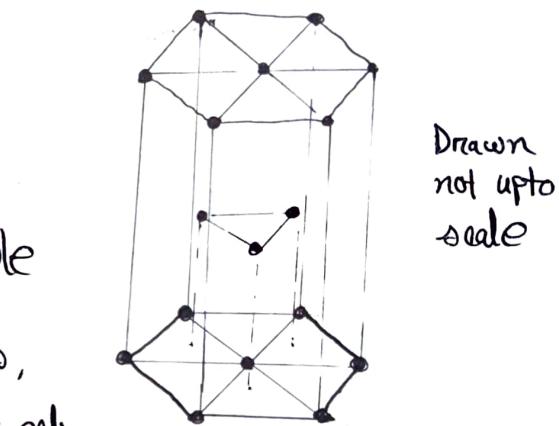
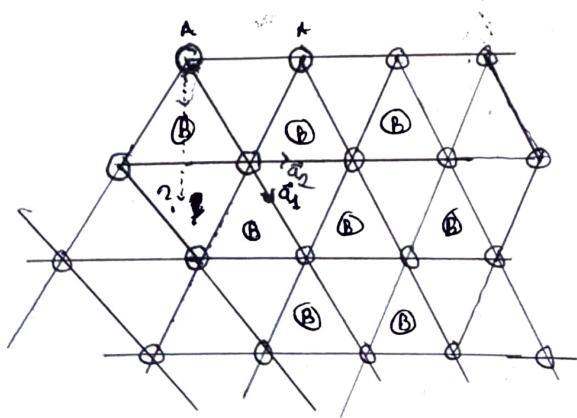
Although not a Bravais lattice, the HCP structure ranks importance with the body centered cubic and face centered cubic Bravais lattices; about 30 elements crystallize in the HCP form. The underlying structure of the HCP lattice is a simple hexagonal Bravais lattice, as we will see.

Spheres are first arranged in a single closest-packed layer A by placing each sphere in contact with six others, as shown in the figure here. We identify two types of gaps - type B and type C. If you just place the same layer of A just a distance c above, the centers of the spheres just form a simple hexagonal lattice. Say, we put the next layer either at B or C. We choose to put three spheres at a distance of $\frac{c}{2}$ from the centers of the base A layer. Then we again put the A layer at a distance



of 1 from the base layer. The structure formed by such packing is called the hexagonal closed pack structure. The stacking is then ABAB... A typical unit cell of the HCP structure (showing the spheres as points) is shown in the following figure. The HCP structure can actually be composed of two interpenetrating simple hexagonal lattice. To see this, consider the following 2D projection

of the HCP structure, where we reduce the sizes of the corresponding spheres for better clarity.

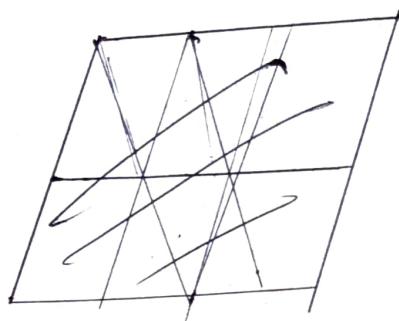
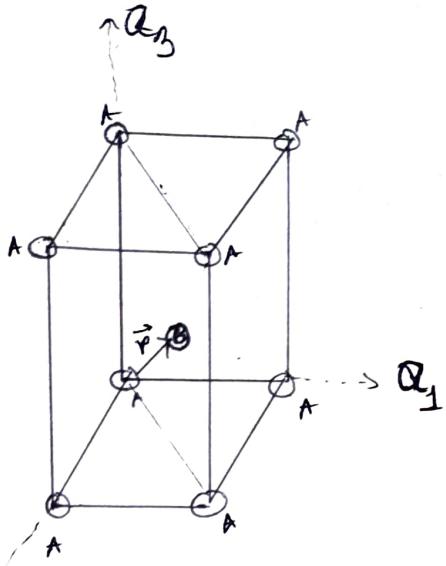


Here (A) are at the base plane, where (B) are at some height from the base plane. By stacking this pattern up, one can create the HCP structure. It should be evident from the figure that, while

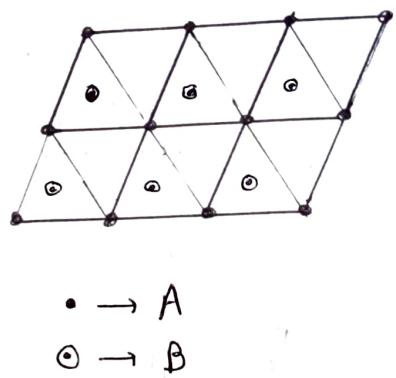
only considering \textcircled{A} spheres one gets a simple hexagonal structure, if one excludes \textcircled{A} and only consider \textcircled{B} spheres, s/he also gets a simple hexagonal structure, just displaced by some amount.

Is HCP a Bravais lattice? The answer is no since all the points are not equivalent. If you look at the last figure, you can go from a site \textcircled{A} to site \textcircled{B} (shown by the dashed line) which is in the upper layer. The position vector can be denoted by some $\Delta \vec{r}$. However, if you perform a similar translation from \textcircled{B} by \vec{r} , you see that there is no lattice point there, which is shown by the $\textcircled{?}$ on the figure. This means, not all the points are equivalent here, and hence the underlying lattice is not a Bravais lattice.

If you want to consider the primitive unit cell in the hexagonal lattice to show here, then it will now contain an inside atom of kind \textcircled{B} . The primitive cell and the projection is shown in the next page.



The primitive cell is just like the one in simple hexagonal lattice, except the \oplus atom. The position of the \oplus atom should be clear from the projection on the base plane as shown here.

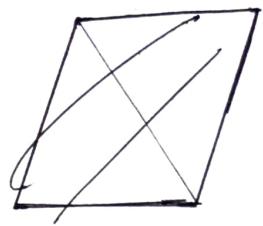
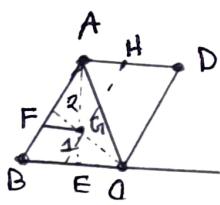


The projection of \oplus is at the centroid of the equilateral triangle, and actually is at a height of $\frac{c}{2}$ from the base surface. One can also define the HCP structure as simple hexagonal lattice with the basis of AB. If you place AB basis at the lattice points of HCP structure, you get the HCP structure. If you consider the coordinate system primitive vectors with origin as shown in the figure, then the basis AB will include the coordinates:

$$A = (0, 0, 0) \quad \text{and} \quad B = \left(\frac{1}{3}\alpha_1, \frac{2}{3}\alpha_2, \frac{1}{2}\alpha_3\right)$$

$$B = \left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$$

To see this, consider the figure shown here.



In the triangle ABE, the median line AE is divided into two parts, AG and GE by 2:1 proportion by the centroid G. Now, if FG is a parallel line to BC, then,

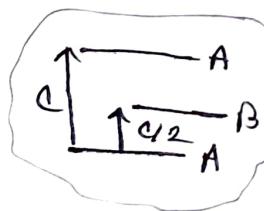
$$\frac{AG}{GE} = \frac{AF}{FB} = \frac{2}{1}$$

$$\therefore AF = 2FB$$

$$\therefore AF = \frac{AB}{3}$$

So, if $AB = b$ (the lattice parameter in \vec{a}_1 direction), then the position of B is $\frac{2b}{3}$ in \vec{a}_1 direction. Similarly you can show that $AH = \frac{1}{3}AD$ and so if $AD = a$ is lattice parameter in \vec{a}_2 direction, the position of B is $\frac{1}{3}a$ in \vec{a}_2 direction. Finally, B is at a position of $\frac{c}{2}$ in the \vec{a}_3 direction which is perpendicular to the base plane.

$$\therefore \vec{r}_B = \frac{1}{3}a \hat{a}_1 + \frac{2}{3}b \hat{a}_2 + \frac{1}{2}c \hat{a}_3$$



Other close packing probabilities

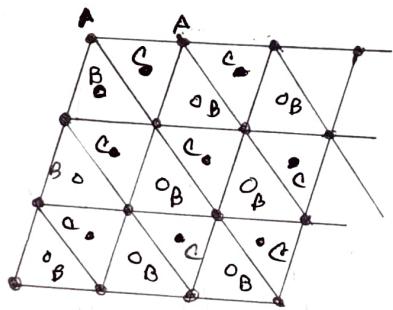
What would happen if we placed the layers in a different way? Say, the first two AB layers are the same as before. However, the third layer is now different. We put the third layer of atoms ~~at~~ the left out centroids of the A plane. We define this plane as the C-plane. The next layer will be the same as A, and so on so forth.

Now, what change has happened here? If you consider the primitive vectors as before,

$$\vec{r}_B = \frac{1}{3}a\hat{a}_1 + \frac{2}{3}b\hat{a}_2 + \frac{1}{2}c\hat{a}_3$$

We previously say that, if we do a similar translation from B by the vector \vec{r}_B , we do not find any atom, and we concluded that CCP structure is not a Bravais lattice. However, here, now if you do the same thing, you find ~~an~~ a 'C' atom, and you can go from C to another atom by performing a similar translation. So, all the points here are equivalent to each other, and so this structure forms a Bravais lattice.

The question is, what is this Bravais lattice?



It turns out that, such stacking sequence actually is in a face centered cubic lattice, where the body diagonal is perpendicular to the triangular planes.

The figure shows two planes of atoms,

viewed as a B and a C layer in the fcc lattice. If you consider a similar plane through A, you

basically create the ABC ~~ABAB~~ layers,

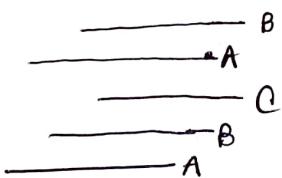
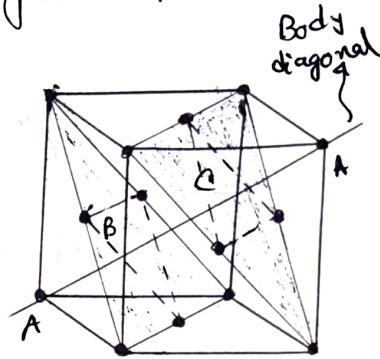
after stacking each other one gets the lattice that we

are talking about. This crystal is

called cubic closed packed (ccp)

crystal, while the underlying Bravais

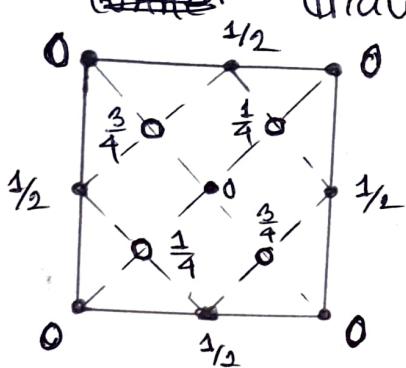
lattice is fcc with one atom basis.



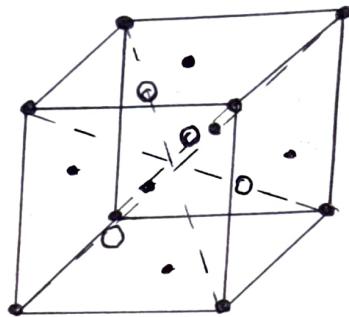
The diamond structure

The diamond crystal structure contains four additional atom than a simple fcc structure. They are at a distance of $\frac{1}{4}$ or $\frac{3}{4}$ th distance along the four body diagonals. If one atom is placed at a distance of $\frac{1}{4}$ th of the body diagonal from one atom, the other atom will be placed at a distance of $\frac{3}{4}$ th the body

diagonal ~~one~~ drawn from an adjacent atom.



2D projection



Diamond structure

The left figure shows the 2D projection of the structure on the base plane. The numbers beside the atoms are the z-coordinates of them. Each atom has four nearest neighbors. The tetrahedral bond arrangement can be found in Kittel (page 19).

The o atom is connected to the ~~two~~ three face atom and one corner atom. The length of the bond between each pair of these four atoms is the same - $\frac{\sqrt{3}}{4}a$, as you can verify.



You can also construct the structure by two interpenetrating fcc Bravais lattices, ~~separate~~ displaced along the body diagonal by one-fourth the length of the body diagonal (think about it). Also, you can construct an underlying fcc Bravais lattice using a basis of two points one at $(0,0,0)$ and another at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

Zincblende structure

This is the same as diamond structure, except that the four inside atom ~~s~~ are of a different kind than the ones in the fcc lattice. So, each atom here has four nearest neighbours of opposite kind.

Example consists of ZnS , CuF , CuI etc.

Packing fraction

The measure of how dense a crystal structure is often given by the coordination numbers (number of first nearest neighbours). For fcc, bcc, sc and diamond lattice the number is 12, 8, 6 and 4 respectively. Another measure is called the packing fraction.

Suppose identical solid spheres are distributed through space in such a way that their centers lie on the points of each of the structures, and spheres on neighbouring points just touch, without overlapping. Such an arrangement of spheres is called a close packing arrangement. Packing ratio/density is the fraction of total volume of the cell that is filled by such spheres.

For simple cubic

Edge length = a

Volume of the cell = a^3

Radius of a sphere = r

Along one edge, $2r = a$

$$\therefore r = \frac{a}{2}$$

One sphere is shared by 8 cells. So, total spheres

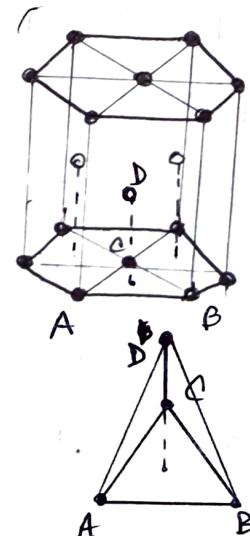
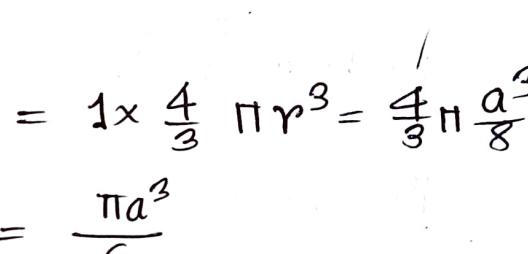
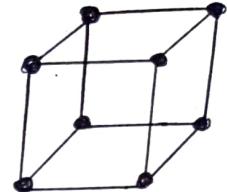
$$= 8 \times \frac{1}{8} = 1$$

$$\begin{aligned} \text{Volume of occupied sphere} &= 1 \times \frac{4}{3} \pi r^3 = \frac{4}{3} \pi \frac{a^3}{8} \\ &= \frac{\pi a^3}{6} \end{aligned}$$

$$\therefore \text{Packing fraction} = \frac{\frac{\pi a^3}{6}}{a^3} = \frac{\pi}{6} = 0.52$$

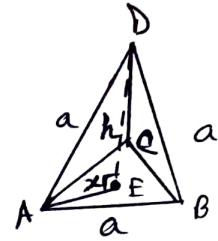
$\%/\alpha$ ratio of hcp structure

The ABCD points on the hcp structure forms a tetrahedron, which is shown in the figure below. We will use this tetrahedron to find the $\%/\alpha$ ratio.



We draw a perpendicular from the D point on the ABC plane, DE. Say, $DF = h$ and $AE = x$. Then,

$$h^2 + x^2 = a^2 \quad \text{--- (1)}$$



If we recall, then * E is the centroid of the ABC triangle. Then,

$$\cos 30^\circ = \frac{\sqrt{2}}{x} \quad \therefore x = \frac{\sqrt{2}}{\sqrt{3}/2} = \frac{a}{\sqrt{3}}$$



And again, h is nothing but $\frac{a\sqrt{3}}{2}$.

$$\text{So, } (1) \Rightarrow \left(\frac{a}{2}\right)^2 + \left(\frac{a\sqrt{3}}{2}\right)^2 = a^2$$

$$\Rightarrow \frac{a^2}{4} = a^2 - \frac{a^2}{3}$$

$$\Rightarrow \frac{a^2}{4} = \frac{2a^2}{3}$$

$$\therefore 1 = \sqrt{\frac{8}{3}} a$$

$$\therefore \frac{1}{a} = \sqrt{\frac{8}{3}}$$