Structure of Materials
Prof. Anandh Subramaniam
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture -16
Crystal Structures

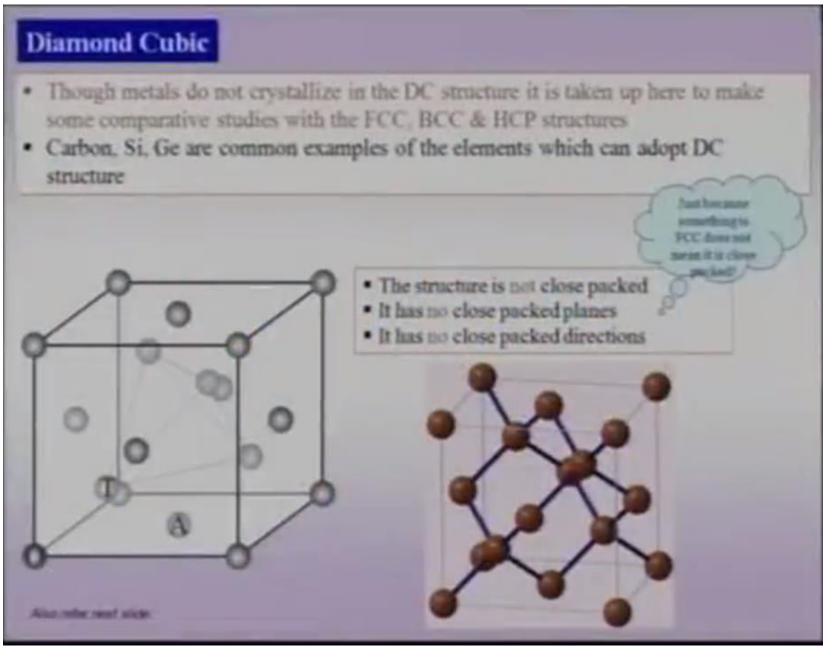
To understand the primitive unit cell of the b c c structure, I have a model here and as you can see it is somewhat difficult to visualize the primitive unit cell of a b c c crystal. To understand this, you will have to visualize that there are actually 1, 2, 3, 4, 4 unit cells in this conventional representation, which are put together to actually generate the parallelepiped which is outlined in green here.

The face is green faces, which is the primitive unit cell of the b c c crystal. This vertices, there are 8 vertices to this parallelepiped, and as you can see 4 of these vertices are the body centring atoms. There is 1 here from this top unit cell, 1 from the bottom unit cell,1 from the left unit cell and 1 from the unit cell in the front. So, you have 4 of those which belong to the b c c positions and there are 4 which are the original corner positions like the 1 here, the 1 here and, for instance, the 1 here and the 1 at the back.

So, you can see this is a rather oblique kind of a parallelepiped, but never the less we have already seen that all kinds of parallelepiped are space filling. So, this primitive unit cell will also be a space filling unit cell which will fill entire space and often as you would have noticed that we do not use this as a conventional unit cell. We use the 1 which is represented by these red out lines here. The volume of this parallelepiped is half the volume of the other conventional unit cell, as you can see because there is only 1 atom associated with each unit cell here. And there are 2 associated with the normal conventional unit cell.

To tell you once again that actually it is very, very difficult to visualize this unit cell even with a model in hand. Therefore, if you do not have a model in hand you should pay particular attention to understand that how actually this unit cell is constructed. So, let me rotate this model a little in for a few angle. So, that you can actually see how the unit cell looks from various angles. So, as you can see this is actually a double l kind of shape. So, there is one l like this and there is another l like this and this is has an extent in 4 unit cells.

(Refer Slide Time: 02:50)



Diamond Cubic

- Though metals do not crystallize in the DC structure it is taken up here to make some comparative studies with the FCC, BCC & HCP structures
- Carbon, Si, Ge are common examples of the elements which can adopt DC structure

Just because something is FCC does not mean it is close packed!

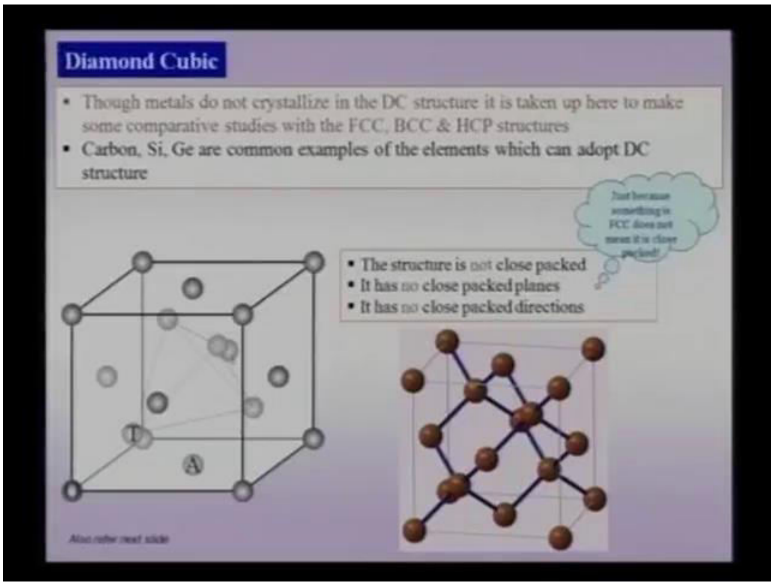
- The structure is not close packed
- It has no close packed planes
- It has no close packed directions

Also refer next slide

So, let us return to the main slides after having looked at this primitive unit cell of a b c c, and let us take up the diamond cubic structure. We have already dealt with this structure in at least somewhat detail, but we will take up some more aspects of this structure which we have not seen before and also revise some of the familiar concepts. We said that for instance, this the no metals crystallize in the diamond cubic structure, but still this is important for us from the point of view of understanding structures.

The common elements which are crystallized in this structure are carbon, silicon and germanium and as we shall see later on the chapter on when you talk about covalently bonded structures that carbon also has as other allotropic forms, but 1 of them is diamond, which as you known is the hardest material in nature. And we also noted this important point that the structure is not a close packed structure, it has no close packed planes and has no close packed directions. So, what I am emphasizing here is a fact that just because I call something and as an f crystal belonging to the f c c lattice it need not be a closed pack crystal. So, this is 1 example of that. This also as I told you is an important example to illustrate another point that actually this structure,

(Refer Slide Time: 03:58)



Diamond Cubic

- Though metals do not crystallize in the DC structure it is taken up here to make some comparative studies with the FCC, BCC & HCP structures
- Carbon, Si, Ge are common examples of the elements which can adopt DC structure

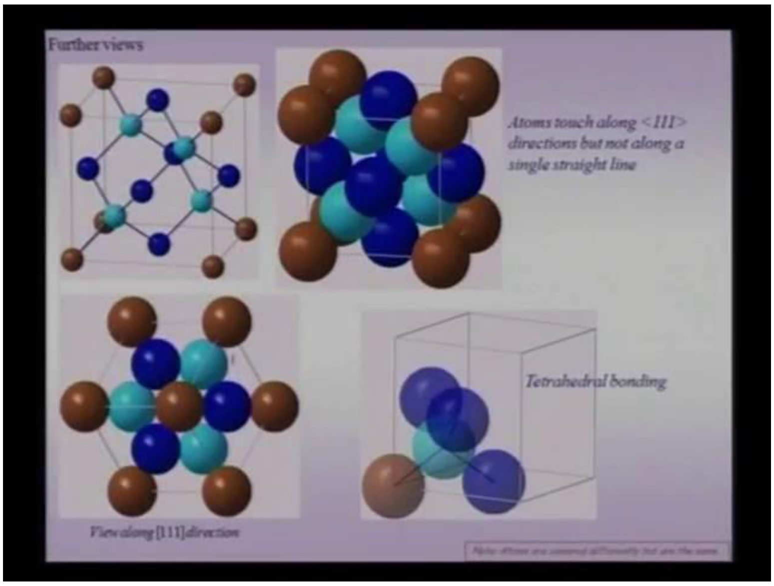
- The structure is not close packed
- It has no close packed planes
- It has no close packed directions

Just because something is FCC does not mean it is close packed!

Also refer next slide

Does not have a true fourfold axis and still it comes under the cubic class, which essentially implies that fourfold is not a true fourfold. That means, a pure rotational fourfold is not a requirement of cubic crystal. So, that another aspect which we have seen. We already seen a model of this diamond cubic structure.

(Refer Slide Time: 04:19)



Further views

Atoms touch along <111> directions but not along a single straight line

Tetrahedral bonding

View along [111] direction

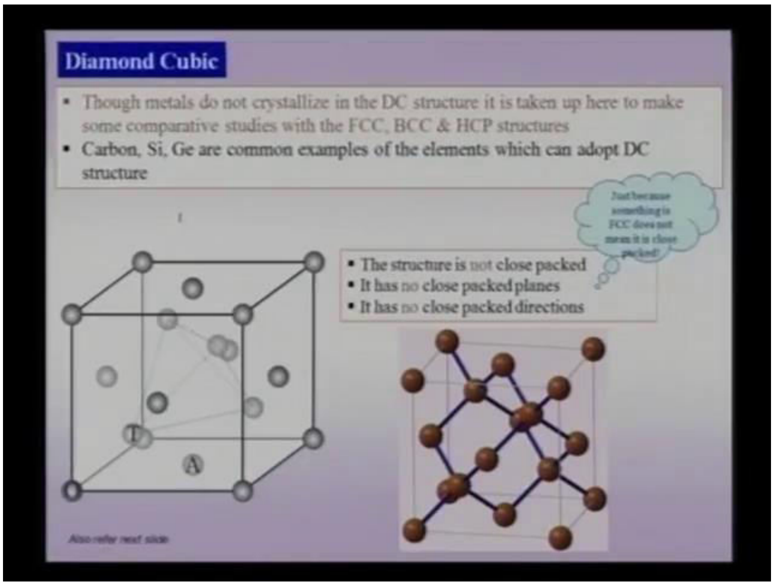
Note: Atoms are coloured differently but are the same

I will take that model again to shown some important aspects like how the atoms touch actually. So, what I have is here is the model which I shown before and the important point which we will emphasize again using the slides is a fact that every atom, all the atoms here, are carbon. Of course, or germanium if the structure is talking about the germanium or silicon, every atom is tetrahedrally bonded. That means, suppose, I have pick up an atom then there are 4 atoms which are at the vertices of a regular tetrahedron. So, for any. So, this kind of a tetrahedral order propagates in 3 dimension. Suppose, I start from the origin here then I would have an atom here which is tetrahedrally bonded then this atom would be bonded, this atom is tetrahedrally bonded.

So, if you see that how the atoms touch each other they actually touch along the 1 11 directions, but the touching does not propagate. So, it actually bends off into these tetrahedral angles and therefore, there is no single direction which is a closed pack direction. Now, this is the convention unit cell of the diamond cubic structure and as you know because this is based on the f c c lattice, it has got 4 lattice points per cell and each lattice point is occupied by 2 carbon atoms.

If it is a carbon diamond I am speaking about 1 at 000, other is at quarter, quarter, quarter. Therefore, there are eight atoms in a single unit cell. Four of these atoms would be on the outer side of the unit cell and 4 of them are contained within the unit cell which themselves form a tetrahedron. So, let us see that tetrahedron which is the four carbons.

(Refer Slide Time: 05:50)



Diamond Cubic

- Though metals do not crystallize in the DC structure it is taken up here to make some comparative studies with the FCC, BCC & HCP structures
- Carbon, Si, Ge are common examples of the elements which can adopt DC structure

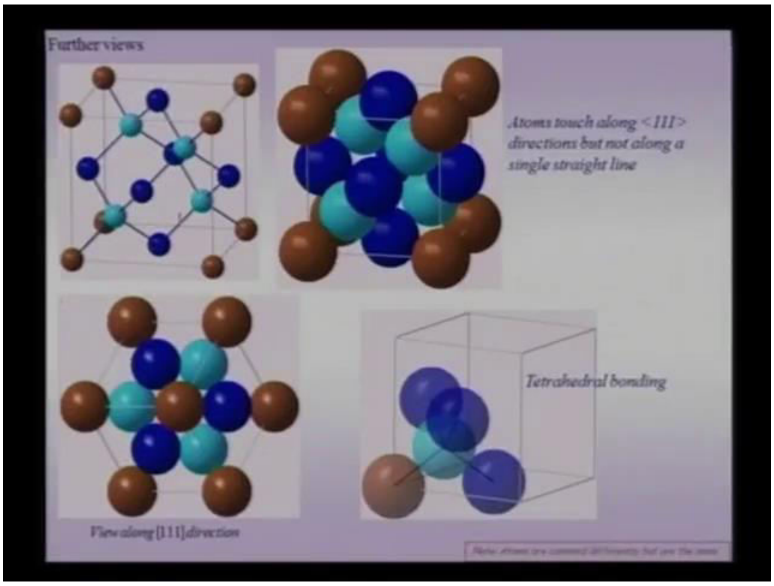
- The structure is not close packed
- It has no close packed planes
- It has no close packed directions

Just because something is FCC does not mean it is close packed!

Also refer next slide

Which sit inside the unit cell which are marked here as the outline of this tetrahedron. You can see here. So, this cell is a tetrahedron and as you know a tetrahedron when you look from upstairs has got only a two fold symmetry, or if you want to look in terms of a rotor inversion symmetry it has got a four bar kind of a symmetry.

(Refer Slide Time: 06:08)



Further views

Atoms touch along <111> directions but not along a single straight line

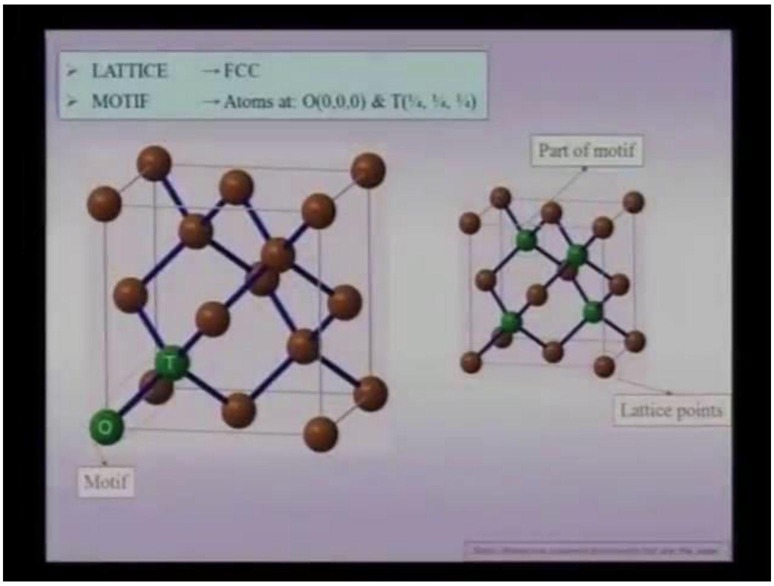
Tetrahedral bonding

View along [111] direction

Now, let us toward other views of this diamond cubic structure and for instance, this view bottom here shows along the 1 1 1 direction. So, you can and I have clearly mark the items in tetrahedral positions inside with this light blue colour, the 1 sitting in the phase centering position as dark blue colour and the remaining 1s are maroon or brown colour. So, please note all atoms are of the same kind. They have been coloured differently for better visualization. So, I have an atom here which is seen near the top in the 111 projection.

This atom is even below this atom. These 3 atoms are same as these 3 atoms and the 3 blue atoms are above those and finally, I have the hexagon formed by these other outer carbon atoms. And as I pointed out, any atom is touching 4 other atoms and is tetrahedrally bonded to the 4 by the s p 3 hybridized bond. So, this is how the diamond cubic structure is and we have to remember this is not aclosed back structure even though it is based on the f c c lattice. So, you have the lattice which is f c c.

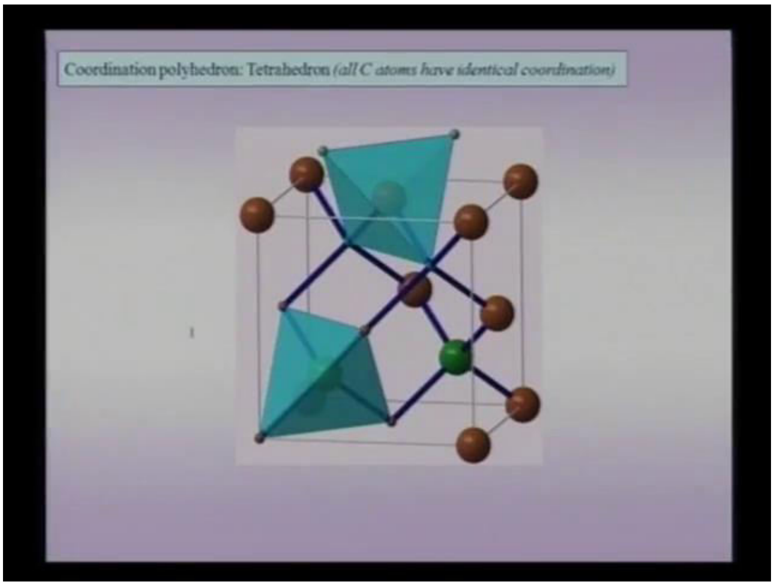
(Refer Slide Time: 07:06)



- LATTICE → FCC
- MOTIF → Atoms at: O(0,0,0) & T(¼, ¼, ¼)

And 2 atoms from the motif. The O and T atoms which are 000 and quarter, quarter, quarter and therefore, here the motif actually consists of 2 identical atoms. I could alternatively choose my origin instead of O and T and I will find the structure remains unaltered. So, that is another important point to be noticed. So, either the O and equivalent atoms form a lattice or the T and equivalent atom form a lattice and correspondingly O and T would be the motif.

(Refer Slide Time: 07:35)

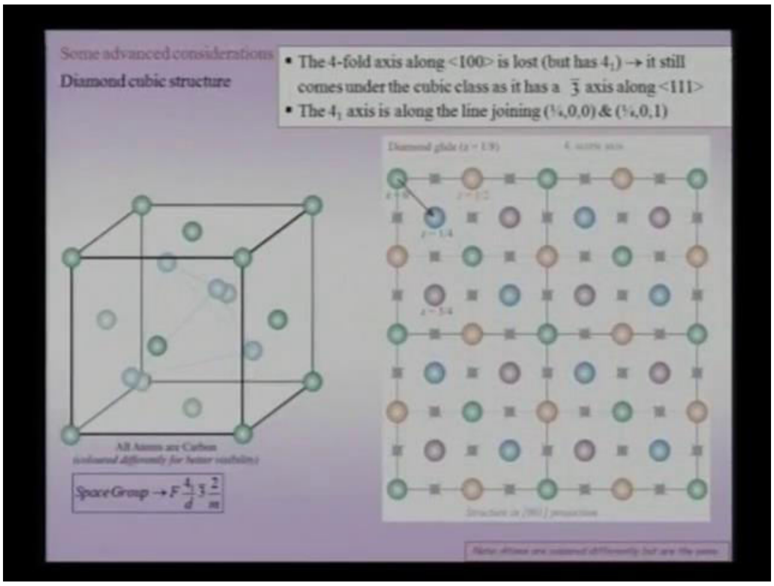


Coordination polyhedron: Tetrahedron *(all C atoms have identical coordination)*

As I mentioned, every atom irrespective of where it sits with respect to the unit cell, for instance, it could be atom sitting on the phase. It could be atom sitting on the corner or it could be atom sitting on the quarter, quarter, quarter position, all of them have tetrahedral coordination around them of identical type atoms. So, the atoms which are in around a central atom have been shown in small size for better visualization.

So, you can see that this is my central atom which is in the phase centering position and we can see that there is a tetrahedral of carbon atoms around the central atom. So, for this one. So, this is my coordination polyhedron which is a tetrahedron and this also reflects the bonding characteristic which I told you is a normal tetrahedral bonding. And again to emphasize the point irrespective of where the carbon atom sits, its environment is identical and tetrahedral. So, there is no difference between the atom which is sitting at O and the atom which is sitting at T and this aspect has to be clear because with respect to the unit cell they may look very different.

(Refer Slide Time: 08:36)



Some advanced considerations

Diamond cubic structure

- The 4-fold axis along <100> is lost (but has 4_1) → it still comes under the cubic class as it has a $\bar{3}$ axis along <111>
- The 4_1 axis is along the line joining (¼,0,0) & (¼,0,1)

All Atoms are Carbon
(coloured differently for better visibility)

Space Group → $F\frac{4_1}{d}3\frac{2}{m}$

But they are identical now these are some advanced considerations and few things out of this we need to focus upon, the remaining can be left for study for later study, it is the important thing I mention that this structure does not have a true fourfold axis. And still it is comes under the cubic class and the reason it is still comes under the cubic class is because it has got a 3 bar axis still. If somebody want to write down the formal space group of the structure, he will call even f 41 by d 3 bar 2 by m. Where the d actually is a special symbol which stands for the diamond glide.

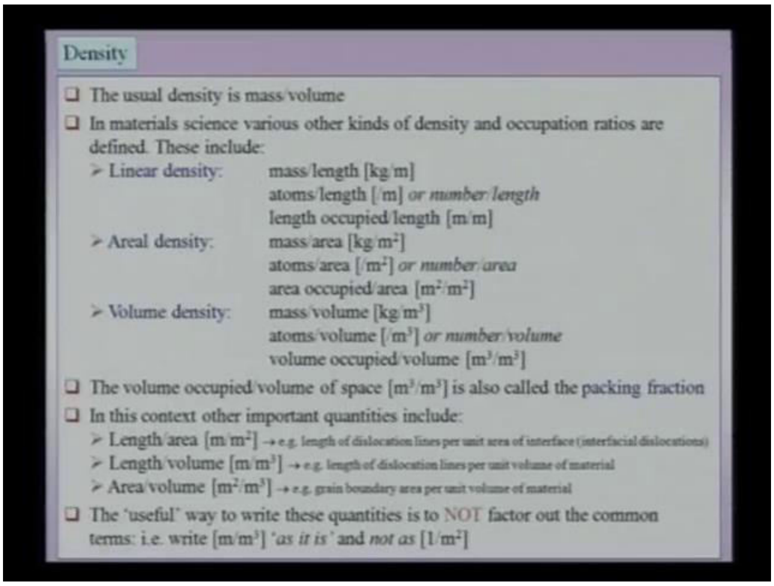
So, it is a glide of the type which is shown here in by the red arrow mark which translates by quarter quarter. Now, if I look at this structure, the important descript is symmetry is the 41 square axis and the 4 3 square axis. So, every one of these perhaps is a 41 and the every alternate set which is diagonally located is a 4 3 square axis and the 41 square axis is connected to the 43 square axis by a diamond glide. As we know, symmetry operators just do and act on atomic entities, but they also act on other symmetry operators present in the structure and therefore, you can see that they are connected by a diamond glide.

So, we have to remember that this diamond cubic structure actually does not have a true fourfold axis, but it still has a 41 kind of a square axis and therefore, in international tables, for instance, you would find the point group written as 4 by m 3 bar 2 by m. So, this basically reflects the fact that it has got a 41 square axis even though it does not have a true fourfold axis. So, these are actually four unit cells which I have shown here, wherein I have superimposed some of the square axis in the structure and you can see this square axis is does not pass through any of the atomic positions. It passes between the atomic positions and the diamond glide actually connects an atom with z equal to 0 to the atom and z equal to 4.

So, actually the glide reflection plane is at z is equal to one-eighth. So, it is located at one-eighth the height and therefore, it will move an atom at z equal to 0 to z equal to one-four and that could this vector shows only the direction of the diamond glide and not the glide plane itself. Now, we switch somewhat gears and try to define a quantity known as density.

The reason we have to describe what is density here is because in usual normal terms density is mass per unit volume, but in material science we have other kind of densities. And we have to remember that often when we are talking about density, we are talking about some of these other numbers. Therefore, we should not be confused by the units they have. For instance, linear density could be mass per unit length.

(Refer Slide Time: 11:12)

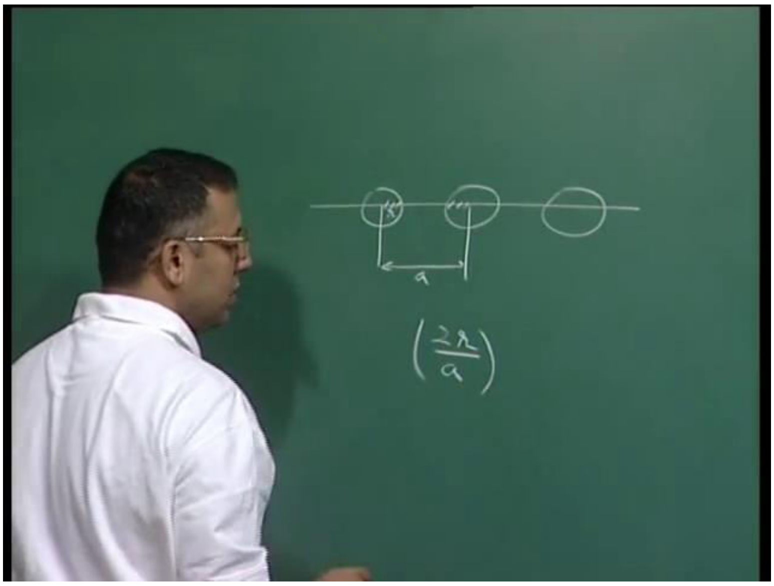


Density

- ☐ The usual density is mass/volume
- ☐ In materials science various other kinds of density and occupation ratios are defined. These include:
  - ➢ Linear density: mass/length $[\mathrm{kg/m}]$
    atoms/length $[/\mathrm{m}]$ *or number/length*
    length occupied/length $[\mathrm{m/m}]$
  - ➢ Areal density: mass/area $[\mathrm{kg/m^2}]$
    atoms/area $[/\mathrm{m^2}]$ *or number/area*
    area occupied/area $[\mathrm{m^2/m^2}]$
  - ➢ Volume density: mass/volume $[\mathrm{kg/m^3}]$
    atoms/volume $[/\mathrm{m^3}]$ *or number/volume*
    volume occupied/volume $[\mathrm{m^3/m^3}]$
- ☐ The volume occupied/volume of space $[\mathrm{m^3/m^3}]$ is also called the packing fraction
- ☐ In this context other important quantities include:
  - ➢ Length/area $[\mathrm{m/m^2}]$ → e.g. length of dislocation lines per unit area of interface (interfacial dislocations)
  - ➢ Length/volume $[\mathrm{m/m^3}]$ → e.g. length of dislocation lines per unit volume of material
  - ➢ Area/volume $[\mathrm{m^2/m^3}]$ → e.g. grain boundary area per unit volume of material
- ☐ The 'useful' way to write these quantities is to NOT factor out the common terms: i.e. write $[\mathrm{m/m^3}]$ '*as it is*' and *not as* $[1/\mathrm{m^2}]$

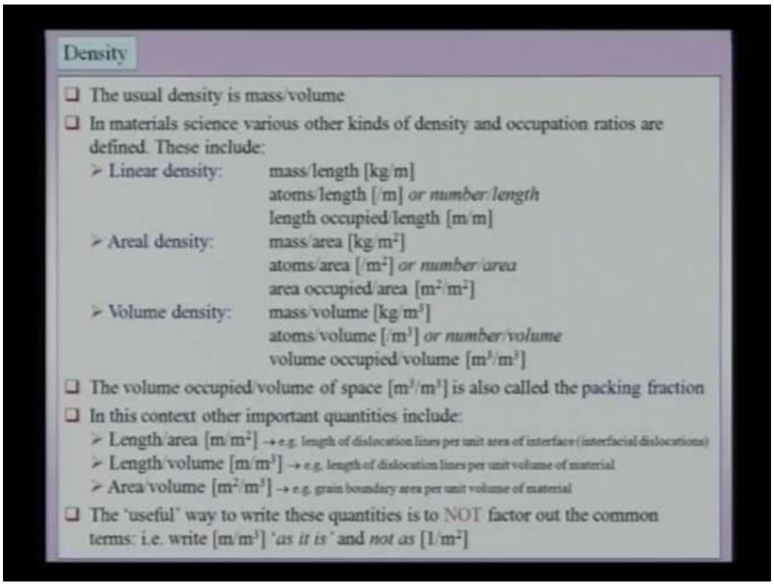
Which is k g per meter or it could actually be counting number of atoms in a unit length of is typically you would take a straight line of course. So, atoms per unit length. So, that will be a number per unit length. So, units will be per meter. You could have a length occupied per unit length of material. So, suppose there is an some lenient or suppose you talk about a one-dimensional crystal or a one-dimensional line on which you have an atom. So, certain part of the line will be occupied by atoms. So, I will count that fraction which is occupied by atoms and I can calculate a linear density. So, just show you a figure in the board. So, what I mean here.

(Refer Slide Time: 11:48)



Suppose, I draw a line through the crystal and I have an array of atoms here. So, I will find out suppose of course, this is my unit cell length, I know that this is going to be repeating in finite unit. So, part of the line which is occupied is this part of the line and the total suppose this is a and say this is r. So, my total will be 2 r by a. Since it is length by length it is a dimensionless quantity, but still remember this is a kind of density I am defining that means the it is an length fraction which has been occupied by atoms along this length this line.

(Refer Slide Time: 12:24)



Density

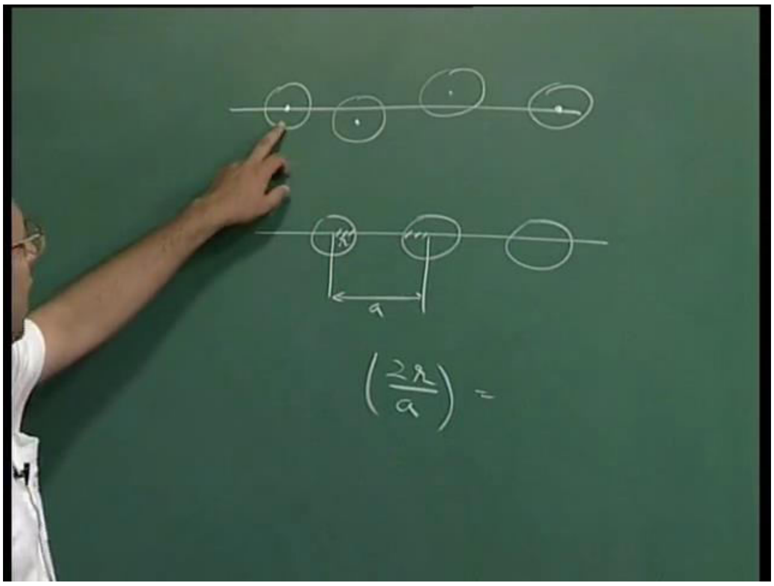
- The usual density is mass/volume
- In materials science various other kinds of density and occupation ratios are defined. These include:
  - Linear density: mass/length $[kg/m]$
    atoms/length $[/m]$ *or number/length*
    length occupied/length $[m/m]$
  - Areal density: mass/area $[kg/m^2]$
    atoms/area $[/m^2]$ *or number/area*
    area occupied/area $[m^2/m^2]$
  - Volume density: mass/volume $[kg/m^3]$
    atoms/volume $[/m^3]$ *or number/volume*
    volume occupied/volume $[m^3/m^3]$
- The volume occupied/volume of space $[m^3/m^3]$ is also called the packing fraction
- In this context other important quantities include:
  - Length/area $[m/m^2]$ → e.g. length of dislocation lines per unit area of interface (interfacial dislocations)
  - Length/volume $[m/m^3]$ → e.g. length of dislocation lines per unit volume of material
  - Area/volume $[m^2/m^3]$ → e.g. grain boundary area per unit volume of material
- The 'useful' way to write these quantities is to NOT factor out the common terms: i.e. write $[m/m^3]$ '*as it is*' and *not as* $[1/m^2]$

So, apart from linear density you could have areal density. So, we saw that even in linear density, for instance, you have various units like, for instance, you have k g per meter you could have number per unit length which means basically per meter you, could have meter per meter which is basically dimensionless. As I will emphasize once more later but, the useful way to write these quantities is not to factor out the common terms.

That means when I am writing meter per meter cube, write it as meter per meter cube and not as per meter square because meter per meter cube is better instructive of the kind of quantities, I am dealing with and is physically a better representation of the density I am talking about. So, when I am talking about areal density again I can go for mass per unit area which would mean k g per meter square and I am when including areal density.

I perhaps would include those atoms whose centre of mass lies on a particular plane like, for instance, when I am doing this calculation here I can do the linear density calculation in 2 ways. I have a line here and assume that there are some atoms which are which has centre of mass coinciding on the line. There could be other atoms which do not have centre of mass coinciding on the line. In such cases,

(Refer Slide Time: 13:38)



I have 2 options at my disposal either I include only these atoms whose centre of mass coincides with my centre, or I include all atoms whose centre even does not coincide that means I will include these lines. So, let me mark those lines. So, possibility number 1 is to include these lines. Possibility number 2 is to include those lines and additionally these lines. So, whenever I am doing the definition it has to be absolutely clear which of these 2 definitions I am using to actually calculate my linear density.

Similarly, when I am talking about areal density I need to know, if I am actually including only those atoms whose centre of mass coincides with the plane or I am including those atoms. Also whose centre of mass does not coincide with the plane that means that there is only a part of the atom which lies on the plane. So, again I have areal density defined as mass per unit area, which would be k g per meter square or it can be atoms per unit area. Which it means is basically a number areal density, which means it will have units of per meter square or it could be an area occupied per unit area, which would mean that is meter square per meter square.

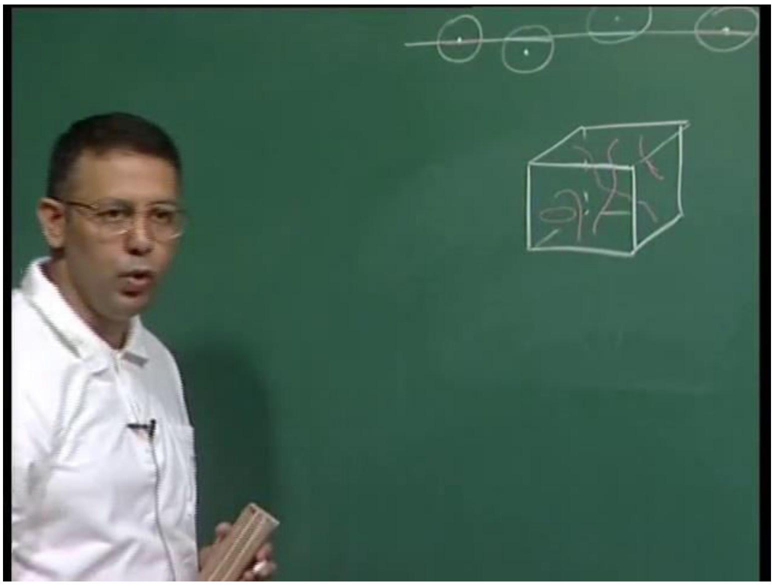
And when I am talking about number per unit area, typically I would exclude those atoms whose centre of mass does not lie on the plane, but then you could extend the definition and include those also depending on the kind of need you have. Finally, the volume density. Again you can define mass per unit volume the way you had defined mass per unit length and mass per unit area.

So, only thing is that here it will be k g per meter cube. You going to have count the number of atoms in a unit volume which will be a number per unit volume. And which will have the units of per meter cubed, or you can calculate volume occupied per unit volume. We have seen that this is the definition you will use and we have somewhat been mentioning this before is the concept to the packing fraction. So, here I would write the units as meter cube per meter cube just to emphasize the fact that it is volume per unit volume, I can of course, cancel out the units and say that it is dimensionless, but I would prefer not to do that just to emphasize this aspect.

The volume occupied per unit volume as I said is also called the packing fraction and we have been dealing with this number before though we have never formally defined it. Since, we are talking about these density, in this context certain other important quantities are like length per unit area. For instance you could define a length meter per meter cube and later on you will see this is an very important definition in the context of dislocations and for instance, we would like to define the length of a dislocation lines, for instance, per unit area of interface.

So, this is in the context of interfacial dislocations or even in the context of dislocations I may want to define length per unit volume. That means I would like to find out what is my length of dislocation line in a volume of material. So, again I will write it as meter per meter cube just to emphasise that it is length of a dislocation line in a volume of material. Of course, suppose I am talking about a length of a certain line I known do not have to have a continuous line in other words, I could have curved lines I could have broken lines etc.

(Refer Slide Time: 16:58)



Just to draw a schematic. Suppose, this is the volume of material I am considering a cubic volume. Of course, you could also consider a spherical volume and now I am talking about some entity which is the linear entity and in this context we are using dislocations. Of course, we have not formally defined dislocations in this course we will do that later but, for now, you need to consider them as lines. So, I have a line here and suppose I have a line going through and finishing here.

So, it is not only not a straight line it is a curved line and this is somewhere embedded somewhere in the volume of the material. There could be other lines which go like this and there could be other lines which go like this and finish here. Of course, these are continuous lines but, there are in pieces. So, add up all my lines like this which are in various parts in the crystal and there could be some lines which will end within the crystal, for instance, there could be loops within the crystal and I add up all those length of all those lines and divide it by the volume of the material. So, in other words. I have a length of, for instance, in this context a dislocation lined in a volume of material.

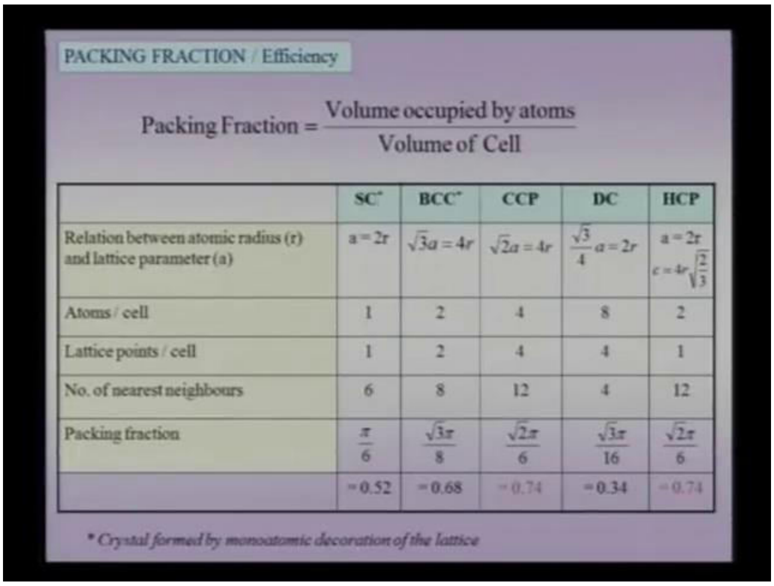
Well I could talk about an areal density, for instance, area per unit volume and this would be a very important quantity, for instance, the context of, for instance, grain boundary area or any 2 dimensional defect. So, we have not defined again what is a grain boundary. We will come to it during a later session, but here we I am talking about planar planes which exist within a volume of material. So, I calculate the total area of my plane. This could be straight planes, this could be curved planes, they could be planes closing on themselves.

For instance, they could be a spherical entity therefore, I have an interface which is a sphere, it could be polyhedral, it could be anything but, I am talking about that surface area of those entities per unit volume of the material. So, these are the some of the extended definitions which I need to keep in mind, though of immediate concern only will be this definition, which is the definition of packing fraction where I am talking of a volume per unit volume.

But, this is a worthwhile tabulation that in material science when I was we say density it is important to remember that what is the kind of density we are talking about. Is it length per unit volume? Is it area per unit volume or is it area per unit area? Also, for instance, suppose I have an plane and I have a certain set of spherical entities sitting here. I need to know what is the area occupied by those entities on this plane. So, there could be various kinds of density I am talking about.

Some of them are number densities, some of them are units like k g s, some of them could just be a volume density. I need to know that and second thing what are the details in the definition like I mention am I counting all those atoms who just intersect the. For instance, a particular plane or am I counting only those whose centre of mass lies on the plane. So, these aspects have to be kept in mind when I am defining density in a material science. Now, let us explore it a little more in packing fraction and especially the packing fraction of the important crystals we have been considering so far. So, the important crystals we have been talking about are a simple cubic,

(Refer Slide Time: 19:56)



PACKING FRACTION / Efficiency

$$\text{Packing Fraction} = \frac{\text{Volume occupied by atoms}}{\text{Volume of Cell}}$$

	SC*	BCC*	CCP	DC	HCP
Relation between atomic radius (r) and lattice parameter (a)	$a = 2r$	$\sqrt{3}a = 4r$	$\sqrt{2}a = 4r$	$\frac{\sqrt{3}}{4}a = 2r$	$a = 2r$ $c = 4r\sqrt{\frac{2}{\sqrt{3}}}$
Atoms / cell	1	2	4	8	2
Lattice points / cell	1	2	4	4	1
No. of nearest neighbours	6	8	12	4	12
Packing fraction	$\frac{\pi}{6}$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\sqrt{2}\pi}{6}$	$\frac{\sqrt{3}\pi}{16}$	$\frac{\sqrt{2}\pi}{6}$
	$= 0.52$	$= 0.68$	$= 0.74$	$= 0.34$	$= 0.74$

** Crystal formed by monoatomic decoration of the lattice*

body centred cubic then the cubic closed pack which is sometimes casually called the f c c crystal, the diamond cubic and the hexagonal close pack crystal. Now, obviously all these are the cubic symmetry and this is got hexagonal symmetry and as if you find packing fraction, it is a volume occupied the atoms per unit volume of the cell. So, this is what I need to remember. Now, first thing I do is write down the relation between the atomic radius and the lattice parameter. For simple cubic crystal, since the atom touch along the edges cell edges, a is equal to 2 r. So, there are 2.

For the body centred cubic, the atoms touch along we have seen already touch along the body diagonal and the length of body diagonal is root 3 a and there is a central atom which is 2 r contribution to this length and also there are 2 atoms sitting at the edges of the body diagonal which give a contribution of 2 r. So, there is 4 r is equal to root 3. In the cubic close pack crystal, the atoms touch along the phase diagonal.

As you know the miller indices of the phase diagonal is of the type 110 kind of direction and therefore, root 2 a is equal to 4 r. For the diamond cubic crystal, which we have seen before this is slightly more difficult to visualize. So, let me take up this crystal. So, this is my diamond cubic crystal and, for instance, I am talking about the atom located at 1 vertex and an atom located at quarter quarter, quarter along the body diagonal.

So, this distance is root 3 a by 4 because my body diagonal is root 3 a, a being the edge of the unit cell and this is root 3 a by 4 and this itself is equal to 2 r. That means it is twice the radius that means it is equal to 1 diameter. So, for the body diamond cubic structure root 3 a by 4 is equal to 2 r. For the hexagonal close pack crystal, the atoms touch along the, if we talking about the bessel plane, the atom touch along any other cell edges.

So, a is equal to 2 r and c is little more complicated its 4 r the root 2 by 3 a which we can derive from simple geometry. Of course I will leave it as an excise to the reader to actually do this derivations. So, that you convenience yourself that c is also related to the r. B c c as 2 and the simple cubic has 1 and c p has 2. Number of lattice points per cell again we have seen its 1 for a simple cubic,2 for body centred cubic,4 for a cubic close pack ,4 for d c and 1 for h c p.

The number of nearest neighbours is 6 for simple cubic,8 for b c c,12 for c c p and h c p and 4 for diamond cubic. We will do a sample calculation of the packing fraction for c c p later, but now it is important to note that packing fraction. Since, it is a volume per unit volume has the transcendal number pi in which definition therefore, whatever numbers there are coating often as 0.74 is just an approximate number. So, as you know transcendal numbers go on and on. There is only where truncated to 2 decimal places or rounded off to 2 decimal places.

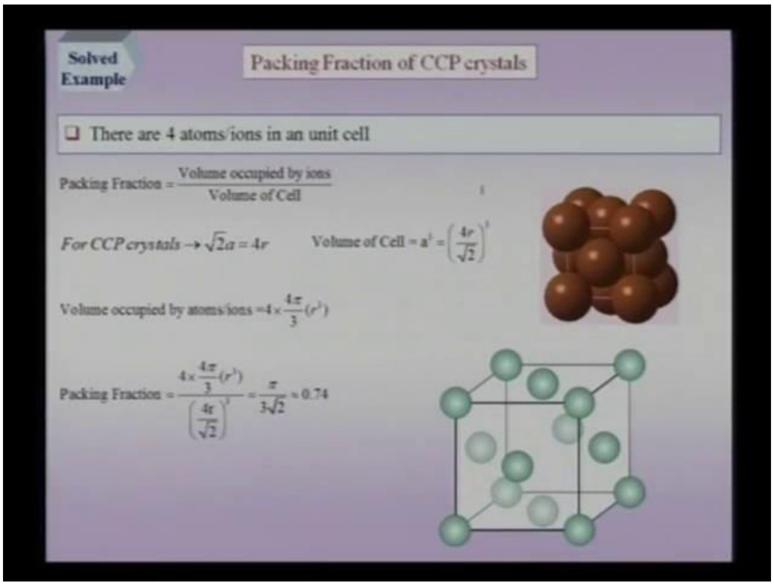
The packing fraction of simple cubic is 52 percent, b c c is 68 percent, c c p and h c p is 74 pecent and diamond cubic is 34 percent. So, again to emphasis the point that highest possible packing fraction from in nature. For sphere packing is only 74 percent that means you cannot obtain a packing more than 74 percent of equal sizes spheres. And some of the other structures have actually, a lower packing fraction and often you would find that if the element has more covalent characterizing bonding then it will not go for a maximum nearest neighbours. Maximum nearest neighbours is promoted by more metallic kind of bonding where there is no preferential bond angles.

And therefore, you would prefer to have the maximum packing. If you do not have a metallic kind of pure metallic character to the bond, then you consider the extreme example of diamond cubic for carbon where in the bonding is purely covalent. It is not a close pack crystal. In fact, it is very poor packing fraction about one-third. That means one-third of space is actually filled by atoms the remaining two-third space is actually vacant.

Now, for simple cubic structures it is about 50 percent and b c c is about 68 percent packing fraction, and that is why you might note that very few metals. Actually crystallize in the simple cubic form it is only polonium, which is got a simple cubic structure and b c c and c c p and h c p has a more common structures in which you would find metals. So, to summarize this slide once more packing fraction is described as volume occupied by atoms, total volume of space.

In other words, volume of the unit cell. Of course, I am doing the calculation you will include the only those atoms, which are present within a unit cell if you are restricting a calculation to the unit cell. We have the highest fraction possible which is 74 percent for c c p and h c p and the others. For instance, functions b c c and simple cubic have lower packing fractions that means more of the structure is actually open. But, then we will have to know that is because structure is more opened does not mean, that you will able to put material into those volumes and some of these aspects we will consider, later in the coming chapter.

(Refer Slide Time: 25:12)



Solved Example

Packing Fraction of CCP crystals

❑ There are 4 atoms/ions in an unit cell

$$\text{Packing Fraction} = \frac{\text{Volume occupied by ions}}{\text{Volume of Cell}}$$

$$\textit{For CCP crystals} \rightarrow \sqrt{2}a = 4r \qquad \text{Volume of Cell} = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3$$

$$\text{Volume occupied by atoms/ions} = 4 \times \frac{4\pi}{3}(r^3)$$

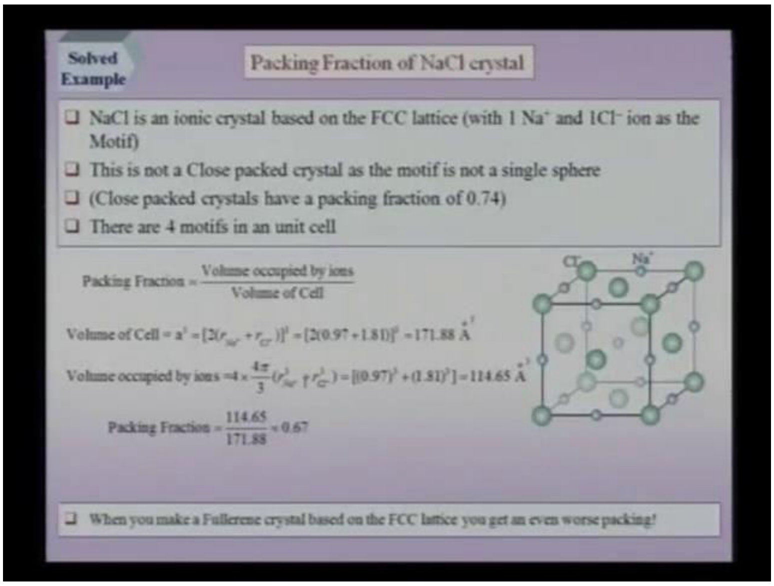
$$\text{Packing Fraction} = \frac{4 \times \frac{4\pi}{3}(r^3)}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

So, let us calculate the packing fraction for cubic close pack crystals. We already know the answer is approximately 74 percent. So, we know that there are 4 atoms or ions in the unit cell. So, we want to calculate the volume occupied by the ions by the volume occupy of the total cell. For cubic close pack of the crystals, we know root 2 a is equal to 4 r as atoms are touching along the 110 direction. So, this is my 110 kind of a direction and atoms are touching along. The volume of the cell is nothing but a cube which is 4 r by 2 the whole cube.

So, I am just taking it from here and doing the a cube. The volume occupied the atoms ions are each assuming. Now, I will approximate each atom to the spheres to the volume will be 4 by 3 pi r cube and there are 4 such atoms in a cell 4 into 4 pi by 3 r cube. So, my packing fraction will be 4 into 4 pi by 3 r cube into 4 r by root 2 the whole cube which is turns out to be pi by 3 root 2 which is 74 percent.

Now, there is 1small or big step missing in this whole this is a proof actually that cubic close packing or the hexagonal close packing is a highest possible and there is no higher packing possible. So, this proof happens to a very complicated mathematical proof. It was proved within the last 15 years some point of time and it is actually complicated proof and we will not take up the proof here. So, sometimes some of these things which have been known for a long time have been proved only late of pretty late times and the proof itself is very complicated and it was lot of deep mathematics. Now, we will assume that even though there is a proof, we will assume that this is highest packing fraction possible for equal size spheres.

(Refer Slide Time: 26:55)



Solved Example

Packing Fraction of NaCl crystal

- NaCl is an ionic crystal based on the FCC lattice (with 1 Na^+ and 1Cl^- ion as the Motif)
- This is not a Close packed crystal as the motif is not a single sphere
- (Close packed crystals have a packing fraction of 0.74)
- There are 4 motifs in an unit cell

$$\text{Packing Fraction} = \frac{\text{Volume occupied by ions}}{\text{Volume of Cell}}$$

$$\text{Volume of Cell} = a^3 = [2(r_{Na^+} + r_{Cl^-})]^3 = [2(0.97 + 1.81)]^3 = 171.88\ \text{Å}^3$$

$$\text{Volume occupied by ions} = 4 \times \frac{4\pi}{3}(r^3_{Na^+} + r^3_{Cl^-}) = [(0.97)^3 + (1.81)^3] = 114.65\ \text{Å}^3$$

$$\text{Packing Fraction} = \frac{114.65}{171.88} = 0.67$$

- When you make a Fullerene crystal based on the FCC lattice you get an even worse packing!

To contradict or to compare my packing fraction of the simple phase centred cubic, which I mean that each lattice bonds occupied by single sphere. Which are in other structure, which we were considered before, which is the sodium chloride structure, which is also based on the h c p lattice, but now each lattice point is occupied by 2 ions, one is a sodium ion, other one is a chlorine ion. So, this is my motif here which we have seen before.

So, the chlorine ions at 000 and a sodium ion is at half 00 and we construct this structure as 2 interpenetrating f c c lattices. That means, I can place no origin either at the sodium or at the chlorine and these 2 it is this structure super lattice it show sub lattices or in other words this crystal itself is a super crystal with 2 sub crystals, one sub crystal of chlorine ions, one sub crystal of sodium ions. And the important point I want show in this calculation is that this is not a close pack structure.

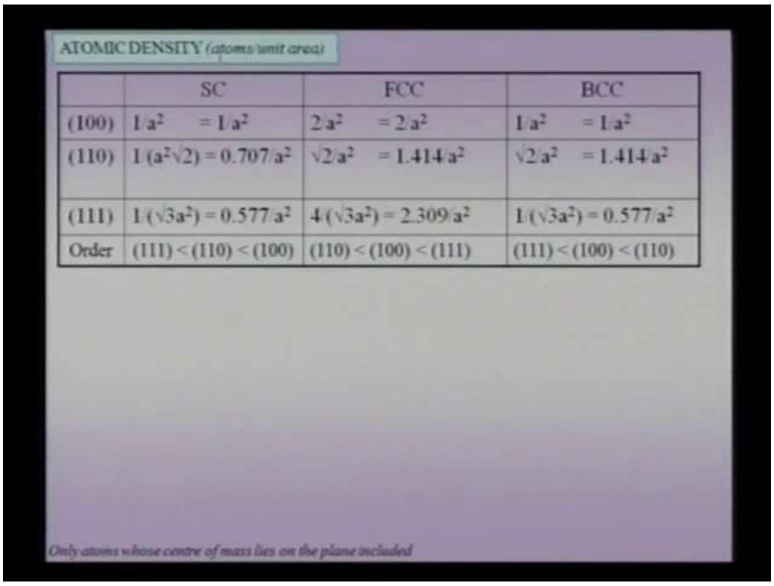
Even though it is based on only f c c lattice and diamond cubic, we show as even lower packing fraction, but there could be even worse than diamond cubic structures which are also based on the f c c lattice and we will take up one example later in the course, which is a case the fullerene. So, we have four motif in unit cell because it is an f c c lattice as before the definition of packing fraction is volume occupied ions by the volume of the unit cell and now, for we will assume these ions are spherical. Volume of this cell a cube which is nothing but you can see that a is nothing but twice radius of sodium ion plus twice radius of chlorine ion. The whole cube which turns out to be for the actual sodium chloride structure is 1.710.88 Angstrom cubed.

Volume occupied by ions is 4 times 4 pi by 3, radius of sodium ion cube plus radius of chlorine ion cubed which is nothing but, simple volume calculation for the spheres and I it transecting 114.65 Angstroms. Here, the packing fraction is a division of these 2 numbers which is about 67 percent and if you compared it with this table here it is somewhere along the b c c and not close to the c c p structures. So, it is got a lower packing fraction than the c c p structure or the h c p structure.

So, as I mentioned you can have structures like the fullerene crystals which are based on the f c c lattice, and fullerene happens to a beautiful example because it is not a metallic or covalent or ionic crystals actually it is a molecular crystal. There in you will get even worse packing fractions and there, I am talking about packing fraction in terms of the volume occupied by atoms or volume of the entire space. You could also alternately define the volume occupied by a molecule by volume occupied by space and that will be alternate definition of packing fraction, I am not taking the definition of packing fraction.

We had previously defined the quantity known as atomic density which was atoms per unit area. So, we will see and this is an important example.

(Refer Slide Time: 30:07)



ATOMIC DENSITY *(atoms/unit area)*

	SC	FCC	BCC
(100)	$1/a^2 = 1/a^2$	$2/a^2 = 2/a^2$	$1/a^2 = 1/a^2$
(110)	$1/(a^2\sqrt{2}) = 0.707/a^2$	$\sqrt{2}/a^2 = 1.414/a^2$	$\sqrt{2}/a^2 = 1.414/a^2$
(111)	$1/(\sqrt{3}a^2) = 0.577/a^2$	$4/(\sqrt{3}a^2) = 2.309/a^2$	$1/(\sqrt{3}a^2) = 0.577/a^2$
Order	(111) < (110) < (100)	(110) < (100) < (111)	(111) < (100) < (110)

Only atoms whose centre of mass lies on the plane included

Important consideration because you will see that depending on the kind of plane we are considering and depending up on the crystal structure, the atomic density changes from plane to plane. Here I am using the definition that atomic density, I am considering only those atoms who centre of mass coincides with the plane ion plane in question. If the impotent point to note, which I will this is a conclusion, first I will jump to that and we will see the details.

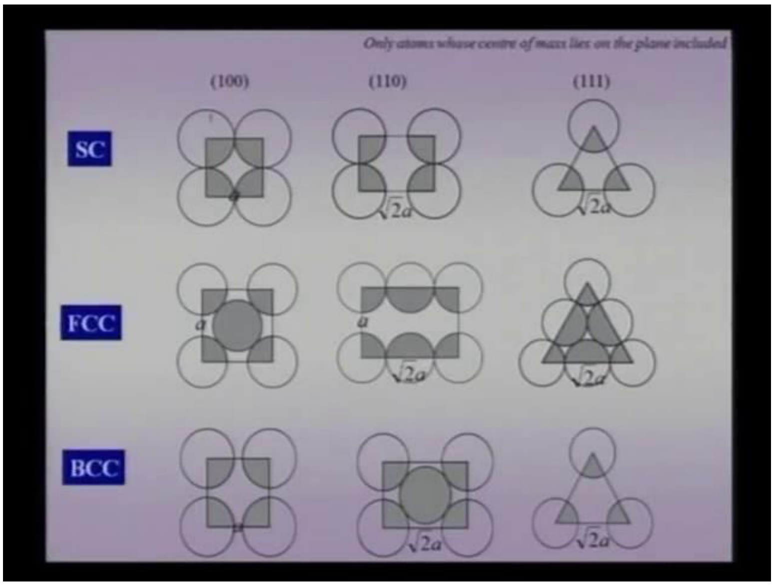
If we take a simple cubic structure then the 11 1 plane is a least close pack plane the 110 is higher density and finally, the 100has even higher density. On the other hand, suppose I look at an f c c crystal, it is suppose a cubic close pack crystal. The 111 plane has the highest density and the 100, 110 plane has the lowest density, with 1110 plane having an intermediate density.

And b c c crystals, the order is change again and here the 111 and plane with the lowest density like the simple cubic but, here unlike the simple cubic which has been 100 higher density at the 110 which has the highest density. Now, why is that we need to construct these planes with highest density. Of course, these planes, for instance, could be performing the role of a slip plane. For instance, in dislocation motion which is very,

very important in plasticity and so many other kind considerations we would like to know.

For instance, what is my atomic density like suppose I am talking about a crystal and what phase would develop during crystal growth or the equilibrium shape then the energy it cost for me to put a surface would depend on. Of course, on the atomic density because then they would have number of bonds, which are broken based on number of atoms which are there on the surface. Therefore, I would like to know my atomic density on each one of these planes. Now, to go through the table100 plane in simple cubic as an atomic density of 1 by a square. So, the area of the square.

(Refer Slide Time: 32:03)


Only atoms whose centre of mass lies on the plane included

So, let pick up this square. So, this is my simple cubic structure I am considering the 100 plane and if you look at plane you will see that this is my unit parallel unit cell, the phase at unit cell and volume the number of atoms is 1 which have 4 coordinates and the area is a square. So, it is 1 by a square. If you look at the 110 plane. So, this is my 110 plane in the simple cubic structure as you can see that the atoms are touching along 100 direction and not along the 110 directions which is this direction.

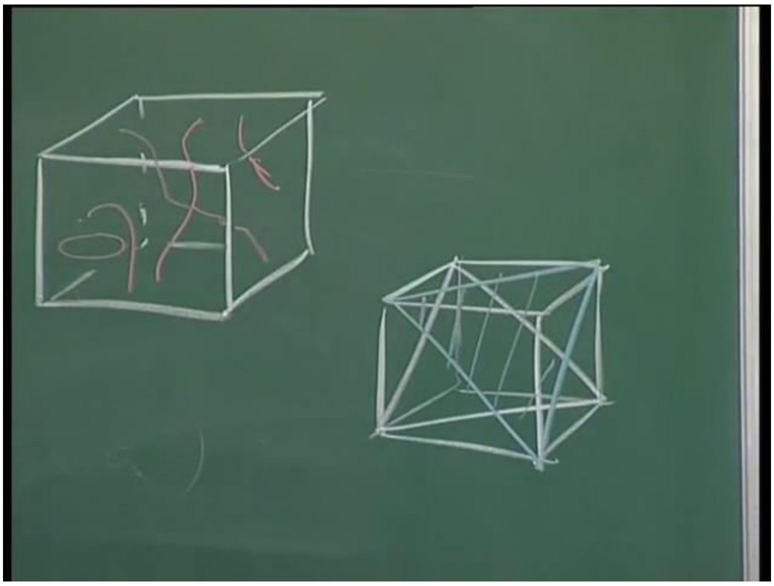
Now, my area, this is root 2 a and this is a. So, my area will be root 2 a into 1 and the number of atoms is again 1. So, the area will be 1 by a square root 2. It is here, it is 0.707 by a squared and suppose if you look at the 111 plane, the atom is do not touch along these directions. So, you can see along the 111 plane the atoms are well separated and this length is root 2 a and for I calculate the area of my triangle which is root 2 a into. So, this is my plane of density I am calculating here.

Therefore, this area occupied by the atoms in this case would be 1 by root 3 a square which is 0.577. It would be instructive to actually do some of these calculations yourselves by considering the triangle and the area occupied by this spheres. Of course, visualizing important thing, how these spheres intersect these planes and which part of that lies within the unit cell.

So, you could see here that these totally do not give an single atom and therefore, my packing fraction of the 11 plane is the least here. Similarly, I can do my calculation for the f c c again noting the fact that how atoms sit. So, this is my plane. The 110 plane in the f c c and you can see that it has the central atom plus four coordinative atoms. The110 plane has lot of space here you can see in a middle. Therefore, it is lower packing fraction and the 11 1 plane has got the highest packing fraction and it turns out to be. You can see it is closely packed along the plane. As we already seen, this is nothing.

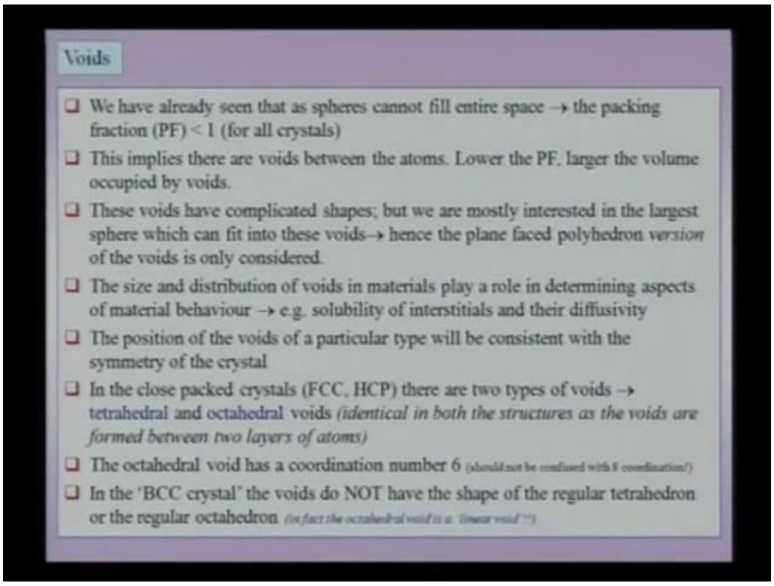
The 11 plane in f c c is nothing but the hexagonal layer which is the close pack layer. So, it is not surprising for us that 111 plane in f c c has the highest packing density. Similarly, we can do so in the b c c and you can see that in the 1 11 plane has the lowest density, which is also seen from this figure that most of the 11 1 plane is not occupied by atoms. And I made warning when we talked about miler indices that when I am taking a plane to do the calculation, I have to make sure that plane is a space filling plane. In other words part of the plane, which lies in unit cell if repeated should actually fill the entire two-dimensional plane. Like I told you that suppose I take a 11 1 plane and the two possibilities of taking the 1 11 plane. One plane which is a typical one let me draw that again in board for you.

(Refer Slide Time: 35:03)



So, this my 11 1. But, I cannot pick up plane which is hexagonal shape which lies between these two planes because that plane we saw was not a space filling plane. Therefore, if you make such a plane for calculation of this atomic density you will end up with of erroneous values. The next important topic we consider now is a topic of voids.

(Refer Slide Time: 35:36)



Voids

- We have already seen that as spheres cannot fill entire space → the packing fraction (PF) < 1 (for all crystals)
- This implies there are voids between the atoms. Lower the PF, larger the volume occupied by voids.
- These voids have complicated shapes; but we are mostly interested in the largest sphere which can fit into these voids → hence the plane faced polyhedron *version* of the voids is only considered.
- The size and distribution of voids in materials play a role in determining aspects of material behaviour → e.g. solubility of interstitials and their diffusivity
- The position of the voids of a particular type will be consistent with the symmetry of the crystal
- In the close packed crystals (FCC, HCP) there are two types of voids → tetrahedral and octahedral voids *(identical in both the structures as the voids are formed between two layers of atoms)*
- The octahedral void has a coordination number 6 (should not be confused with 8 coordination!)
- In the 'BCC crystal' the voids do NOT have the shape of the regular tetrahedron or the regular octahedron *(in fact the octahedral void is a 'linear void'!!)*

Now, we have already seen that the sphere, the atoms, themselves do not fill the entire space and this is reflected in the packing fraction being smaller than one. This implies that there are voids between atoms and lower the packing fraction larger is the volume occupied by these voids. As we shall see, these voids have complicated shapes but, we are mostly interested in the largest sphere, which can fit into these voids.

Typically, we will assume in that not only is the basic lattice of the basic crystal spheres, but we will assume for now, but actually the atom going into this intersection which will is what we have interested in are also spheres. Typically, we will consider only a plane faced polyhedron version of these voids and not actually, the complicated shape of the voids and what I mean by this I will show using models very soon. The size and distribution of the voids in materials play an important role in determining aspects and many of these aspects material behaviour. For instance, solubility of interstitials, the diffusivity and many other important behaviour. Wherein I need to construct these voids and the atoms with sitting these voids.

That means I am not only interested in the packing fraction but, I am also interested in the shape of these voids and the size of these voids. And I am talking about shape, as again emphasis, I am talking about the polyhedral version of the void and not only the real shape of the void. Now, the position of voids of a particular type will be consistent with the symmetry of the crystal. So, I will mention this by actually giving examples later when we consider the, for instance, the f c c and h c p crystals and also the b c c crystal.

In close pack crystals, the f c c and h c p, for instance, are what we call the c c p and h c p. There are two type of voids, the tetrahedral void and the octahedral void and we will take up these two kind of voids in detail in these two structure. An important point you note is that they are identical in both these two structures. That means as per a void picture of these structures close, I can have and we already seen that when we dealing with crystal structures we have especially four important types of models. We worked with, the wire frame model, the ball and stick model, the space filling model and in the last, but not least the void model.

And these voids themselves can actually be put together to make a entire structure which is a space filling structure. So, when I want to make a space filling structure for these close pack structures f c c and h c p, I would use the octahedral, the regular octahedron and the regular tetrahedron which I have seen before. For instance now, in these two structures, I have my regular octahedral and my regular tetrahedral and these two will put together from this space filling factor as we will see.

Now, one important point to note, whenever I mention the word octahedral, I should not be confused with the fact that the coordination number, even though I am saying octahedral actually the octahedron has eight phases, but the coordination number is only six. So, it is not confused octahedralvoid meaning actually coordination of eight. So, this aspect as to be kept in mind. The other important thing we will see is that the b c c crystal which we have seen already it is not a close pack crystal. This does not have a regular shaped void, it also has an octahedron and tetrahedron, but these two shapes are the octahedron and the tetrahedronare not the regular octahedron and the regular tetrahedron.

And we will see later that the octahedral void in fact can function like a linear void. So, what we mean by that also we will see. That means it could turn out that the coordination number is not six, but actually 2. So, before we go take up the voids in the close pack structure let me revise some of the points by actually taking an example. The first one I would like to mention is the examples of the polyhedron version. So, we take, for instance, a simple cubic crystal which I form here within this box with glass feeds.

So, you can see that there are eight spheres and now, these are glass spears which are put inside the unit cell to actually form a crystal. So, you can see here. Now, when I want to consider, for instance, the largest sized here which I can put into this void. I have already done so by putting a golden shape sphere. Let we show this by this point already. I have already put sphere and this is the largest sphere, which you put into this void without actually distorting this structure.

So, when I am talking about this central atom, it is coordinated to these eight atoms which are at the coordinates of the cube. If I were actually to consider the actual shape of this void which is a little more complicated shape, I have a model right here and I have done this by actually pouring wax into this model and taking out this spheres. So, you can see that actually the voids is considerable.

The amount of volume occupied void is considerable and it is in a very complicated shape. It has got curve phases, it has got straight phases. About the straight phases means basically that your truncating along the unit cell phases. So, but it is a complicated shape, but when I am talking about voids, I am not going to be considering this shape of the void. The true shape to the void, but what I might call the polyhedron version of this void.

So, what I mean by the polyhedron version is a version which we saw before a version like this. In other words, I only talk about the vertices of the atoms around the void which form a polyhedron and this polyhedron in this case happens to be the cube, which is around a central position where the impurity atom or an alloying element atom can sit. So, in future I have to remember even though these voids have very complicated shapes and complicated connectivity.

For instance, this kind of voids would should actually this kind of space for actually connect in 3 dimensions along the 3 directions and form a continuous network. But I am not considering a shape like this, but I am only considering a shape like this and I am talking about voids. So, this aspect has to be of set. And what I am worried about when I am actually talking about these voids the important question first question, I would like to ask is what is the largest size sphere, which I can put into this void without crossing distortion to this glass. As we shall see why I need to know this, suppose I am an alloying element which does not occupy the lattice position. Of course, I have two possibilities and I had an alloying element.

The alloying element can go and replace this atom at the lattice position like I could take an alloying element, for instance, we are in by sphere would be replaced by another. So, this is called a substitutional alloying elements as we shall see later but, we could have an alloying element it is not go and take up the subtitutional position, but actually takes the interstitial position which is what an atom has done in this case. So, golden colour in the atom in the centre.

So, let us see these three structures or these three representations of the void a little more carefully in projection before we take up the next topic. So, I have here my true shape of a void of course, a true shape which lies within a unit cell like this, the polyhedral version, when this case for the simple cubic happens to a cube and also the version wherein I have a sphere fitting at the right the void. Though I am interested only in sphere actually, which needs to sit in the void most of the time, but I will have a representation in terms polyhedron and rarely will I deal with at the actual shape of the void in my representations.

So, let me zoom in into this planer geometry to actually show you how this shape looks a little better. I am seeing the crystal along the 001 direction wherein have the eight glass spheres which are in atomic positions. Now, the central sphere which is the largest size sphere which can fit into this void. As you can clearly see in simple cubic, the void size very large and also we have already seen the packing fractions is small.

So, also we need this another important point, we will see when we are talking about crystals is not only the total amount of void which is available, but how they are splitting to these various void shapes and how we can actually put atoms in to that. That will actually go on to determine by solubility and therefore, it is not just the packing fraction which will determine my solubility. I need to know the shape of the voids and the largest sphere which can split into those voids. In the cubic close pack crystal, we have two kinds of voids, the octahedral void and the tetrahedral void.

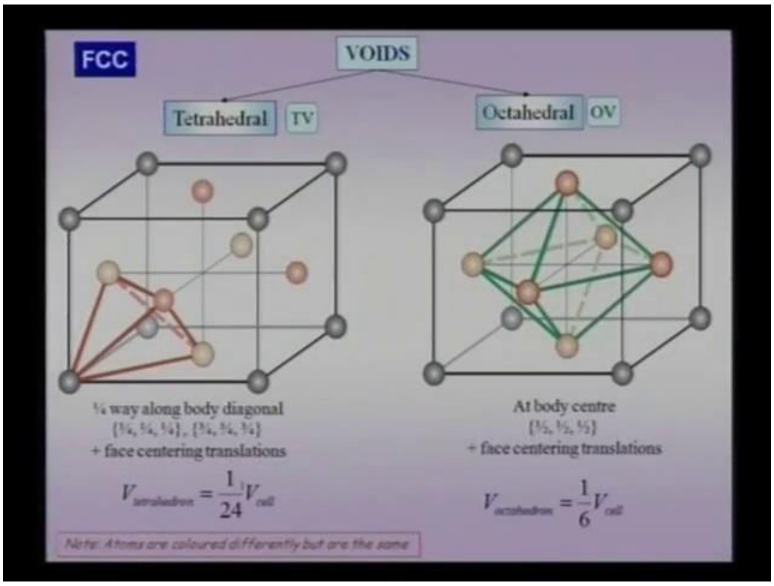
And we will consider these two voids in little detail. The tetrahedral void dislocated quarter way along the body diagonal and when I am saying that I mean the centre of the tetrahedral void is located a quarter way along the body diagonal. And now, when have a single tetrahedron located like this, then all the symmetry operations of the c c p crystal will operate on this tetrahedral void and give me the remaining tetrahedral voids. And, as we shall see there will be eight such tetrahedral voids.

Now, the volume occupied by the tetrahedral voids is 124 the volume of the unit cell. That is an important number because now that will tell you that how biggest sphere which can actually sit in this tetrahedral void. And when I am talking about symmetry operation, which I write the remaining tetrahedral voids, I would also use my phase centering translations to generate the remaining voids. So, let us see where this tetrahedral voids located with the unit cell in an actual model.

So, you can see here a model like this and ignoring these blue stars I have to take this blue tetrahedron which is sitting inside the unit cell. So, you can see the tetrahedral within the unit cell. And, I have to remember that, for instance, every vertex of my cube is identical therefore, if I have one tetrahedron sitting from pointed to this origin then there will be one tetrahedron here, one here, one here and one here.

So, the actually I will have eight tetrahedral within a single unit cell which is shown in this model here. So, I have eight tetrahedral, each one starting from a vertex. So, I have eight tetrahedron set in the unit cell. So, you can see this model. So, I will have eight tetrahedral voids in the unit cell and so the total volume of the unit cell which is occupied by the tetrahedral,

(Refer Slide Time: 46:06)



FCC

VOIDS

Tetrahedral TV

Octahedral OV

¼ way along body diagonal
{¼, ¼, ¼}, {¾, ¾, ¾}
+ face centering translations

$$V_{tetrahedron} = \frac{1}{24} V_{cell}$$

At body centre
{½, ½, ½}
+ face centering translations

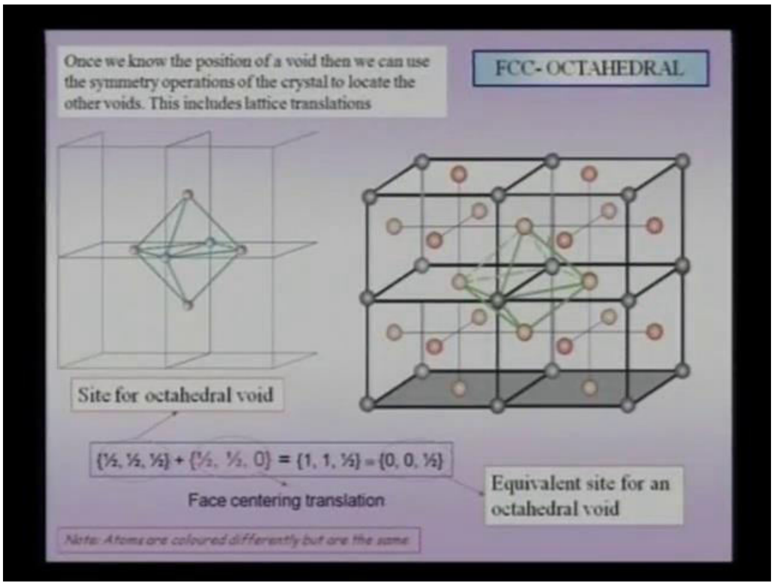
$$V_{octahedron} = \frac{1}{6} V_{cell}$$

Note: Atoms are coloured differently but are the same

voids will be eight times 24 which is about one-fourth. Now, the octahedral void and as I mention the octahedral void implies a coordination number 6 is one of these octahedral voids is located at the centre of the unit cell. That means, if I place a small sphere in the centre it will actually we touching all the six atoms at the vertices of the octahedral and therefore, this is my octahedral void.

But, if there is a octahedral at half, half, half then I can apply all my symmetries of the cube to obtain all the other octahedral voids in this c c p structure. The volume of the octahedral void is one-sixth the volume of the unit cell which clearly tells me it is a much bigger void than the tetrahedral void. So, the two voids I am going to talking about here again emphasis that these are the polyhedral versions of the voids I am talking. I have the tetrahedral void and the octahedral void. There are eight of these tetrahedral voids and you will soon see that we will make a calculation of number of octahedral voids percent.

(Refer Slide Time: 47:13)



Once we know the position of a void then we can use the symmetry operations of the crystal to locate the other voids. This includes lattice translations

FCC- OCTAHEDRAL

Site for octahedral void

$\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\} + \{\frac{1}{2}, \frac{1}{2}, 0\} = \{1, 1, \frac{1}{2}\} = \{0, 0, \frac{1}{2}\}$

Face centering translation

Equivalent site for an octahedral void

Note: Atoms are coloured differently but are the same

Now, if as I mention, I have can apply all the symmetry elements to generate the remaining voids and let me try to do that for the octahedral void. Now, and these includes the lattice translations. So, let me repeat, once you know the position of void then we can use a symmetry operations or crystal to locate the other voids. This includes lattice translations and this is important because often by the way we draw some of the voids in the unit cell they may look different.

But we have to remember since it is just origin of the unit cell we are chosen differently which makes some look different but, actually they are identical. So, for instance, suppose I have octahedral void at half, half, half and I know my first centering translation, which is a fundamental lattice translation vector of the f c c lattice which is half, half, 0 I add to that, I get 11 half which is nothing but 00 half. Then, clearly I know that if half, half, half is the seat of an centre of an octahedral void then 00 half, which is nothing but edge centre is also an equivalent seat.

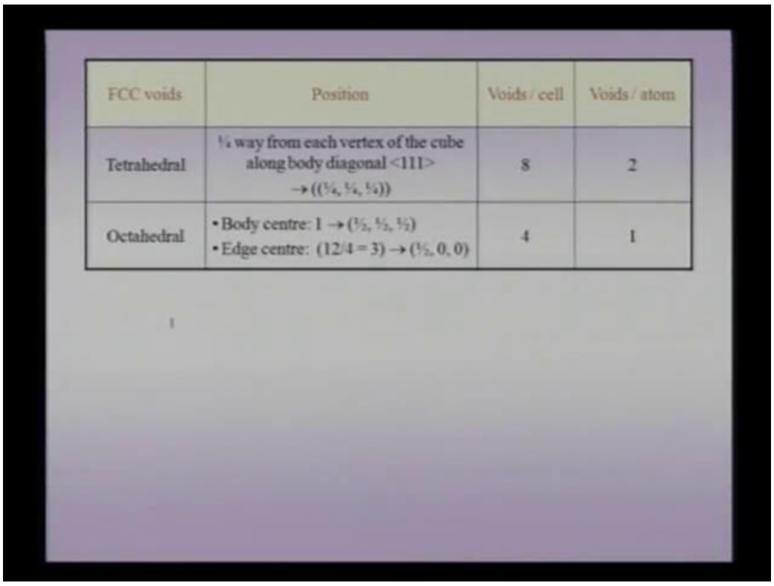
Therefore, will also be a seat of the centre of the another octahedral void. So, this, for instance, shown here in this picture. So, I have these four cubic unit cells, f c c unit cells and this centre which is located at a position like, for instance, 00 half and draw this is a actually seat of the octahedral void, this position. So, all edges since no edges different from any other edge would be a seat of the octahedral voids in this edge. So in this edge, this edge and so forth.

So, there are twelve edges to the cube and all the edge centres are also positions of the octahedral void, and I can understand that purely by using the phase centering translation knowing that the body centre is seat of the octahedral void. The central octahedral void has a complete contribution to the unit cell. In other words, it is completely contained within the unit cell and as we saw here. Therefore, an atom sitting in its central will contribute totally to the current unit cell, when I may trying to make calculations of number of octahedral voids or number of atoms within the octahedral void per cell.

But these octahedral voids sitting in the edges have only one-fourth content within the unit cell and of course, we have models to show you how we can visualizes this one-fourth content. Therefore, their contribution to the unit cell will be one-fourth, I have twelve edges with one-fourth we have contribution of 3 from those in the edges, one from the centre. Therefore, a four octahedral voids per unit cell in an f c c structure, cubic close pack structure.

And, as you know that there are four atoms in a unit cell in an f c c crystal structure, there are four octahedral voids. That means for every atom I have an octahedral void in an cubic close pack structure. On the other hand, we have seen that purely based on symmetry arguments, if this is my centre of a tetrahedral void, the quarter, quarter, quarter position then I should have eight of these tetrahedral in the unit cell. Since, I have only four atoms in this unit cell. That means, per atom I have twice the number of tetrahedral voids. That means, there are eight tetrahedral voids per cell. This is something which is important to note.

(Refer Slide Time: 50:24)



FCC voids	Position	Voids / cell	Voids / atom
Tetrahedral	¼ way from each vertex of the cube along body diagonal <111> → ((¼, ¼, ¼))	8	2
Octahedral	• Body centre: 1 → (½, ½, ½) • Edge centre: (12/4 = 3) → (½, 0, 0)	4	1

So, let me tabulate these values before I show you some models to better visualize these octahedral voids. The tetrahedral void is located one-fourth way from each vertex along the body diagonals. There are eight voids per cell and since there are four atoms per cell there are twice voids per atom. So, there are two tetrahedral voids per atom. The octahedral void is located at half, half, half which is nothing but the body centering position.

It is also located at the edge centre which is half 00 and equivalent positions. So, there are four voids per cell and as we saw that the ones at the edges only contribute one-fourth to the unit cell, and the number of voids per atom it is 41octahedral void per atom. So, let me try to visualize these things using models, before I take up the calculations based on the largest sphere which can fit into these models.

So, I got models here and I will show them from both the angular perspective and also and from the other perspective. So, let me show this model, for instance, I got a model here which sphere, this what I called the space filling model and you can see these four red coloured balls actually try to locate my tetrahedral void. That means, the centre of these tetrahedral atoms is my seat of the tetrahedral void. We have to remember all the spheres represent, the same kind of atoms and these four have been coloured differently just to locate my position of the tetrahedral void.

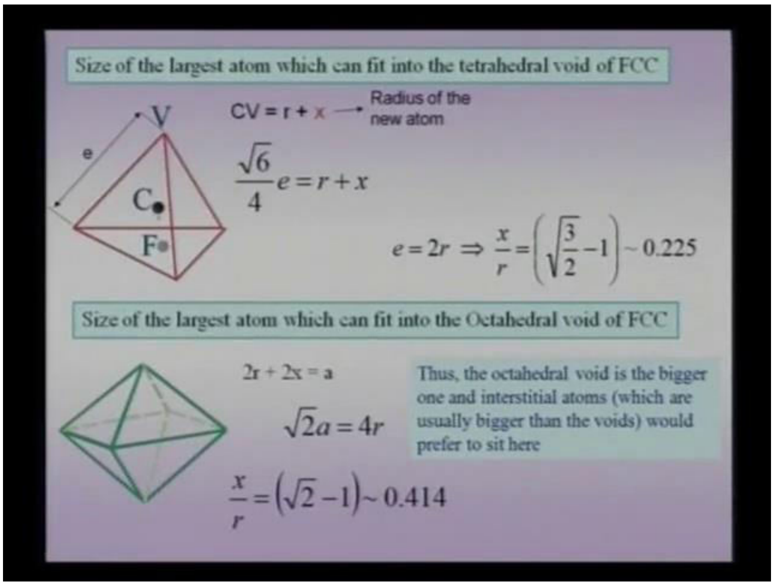
And, if I have one here, then obviously each one of these each vertex will also be a starting point of the tetrahedral void. So, I will have eight of them as it is seen from this other model wire frame model. So, I want tetrahedral void centre here. So, let me use a stick to point. So, there will be one here, one here which will be related by fourfold along this direction, there will be one here again the four fold rotation and there will be one here.

Similarly, there will be one here, one here, one here and one here. Since, the cubic close pack crystal has fourfold rotation, they are all equivalent positions and I have eight of these tetrahedral voids. So, let me take the same model to actually generate the structure wherein I have an octahedral void. So, let me take these spheres and make an octahedral void. So, I hope some of these this is visible from the camera angle from there. So, we can see this or able to see this.

So, I am trying to make an octahedral void in this structure. So, this is my octahedral which is setting is in the unit cell. So, this is my space filling model wherein I have used different colours of ball for the atom sitting in the space centering position to show you the position or the shape of the octahedral. That means, the atoms sitting of the centre of the octahedral void and if at the right size will actually be touching the atoms in the red colour or the orange colour. This colour balls will touching and we clearly see it is a six coordination.

Now, as I mentioned, one of the important questions we are trying to ask ourselves when we are dealing with voids is with respect a alloy element is with respect to the largest sphere which can fit into these voids. So, in this calculation, let me try to find largest sphere which can fit into the tetrahedral void and the largest sphere which can fit into the octahedral void in the cubic close pack crystal. Now, let me consider the tetrahedral as shown here.

(Refer Slide Time: 54:23)



Size of the largest atom which can fit into the tetrahedral void of FCC

$CV = r + x \longrightarrow$ Radius of the new atom

$$\frac{\sqrt{6}}{4} e = r + x$$

$$e = 2r \Rightarrow \frac{x}{r} = \left(\sqrt{\frac{3}{2}} - 1\right) \sim 0.225$$

Size of the largest atom which can fit into the Octahedral void of FCC

$$2r + 2x = a$$

$$\sqrt{2} a = 4r$$

$$\frac{x}{r} = \left(\sqrt{2} - 1\right) \sim 0.414$$

Thus, the octahedral void is the bigger one and interstitial atoms (which are usually bigger than the voids) would prefer to sit here

And, the distance C V is nothing but, the radius of the parent atom which is occupying the lattice positions and the radius of the new atom which is going to sit in the centre. So, this is my atom going to sitting in a tetrahedral centre. So, this centre of this point here to the vertex is r plus x, where x is the radius of the foreign atom. Now, this distance V is equal to root 6 by 4 e from geometry and therefore, again that is equal to r plus x.

Now, I know e is equal to 2 r because atoms are touching along the tetrahedral voids and this implies, x by r is root 3 by 2 minus 1 which is equal to 0.225. So, x by r is a ratio of the largest sphere which sits in the interracial tetrahedral position to the largest or to this sphere which is sitting in the lattice position. So, ratio of these two radii is 0.225. So, it is approximately this number and that means, if I put a sphere larger than the size then it is going to push my atoms around the lattice position and cause distortion. If I put an atom smaller than the size then it will tend to rattle around within that void. Assume that it is a hot sphere model. So, both this situations are not favourable.

In other words, if I have smaller size sphere then it will not be bonded properly to the four atoms around the state or tetrahedral position, these four atoms. And if I put a largest sized atom this is going to cause strain in the lattice. Therefore, the correct size sphere, which can fit into this void is a sphere whose radius which is above 22.5 percent of that the radius of the atom at the lattice positions. Now, the size of the largest atom which can split into the octahedral void in this cubic close pack crystal, again I can make a calculation at the centre to the vertex distance.

So, this may centre of the void to the vertex distance is 2 r plus 2 x and which is equal to a and we already know for the f c c crystal it is root 2 a is equal to 4 r. So, I can calculate my x by r as root 2 minus 1 which is 0.414 approximately. In other words, the octahedral void in cubic close pack crystal is the almost double size of the tetrahedral void. The tetrahedral void is very small and the octahedral void is a much larger void in the cubic close pack crystal. This is an important point to note and later on we will try to compare these sizes like the 0.225 and 0.141 with some of the other void sizes in the b c c crystal. Now, in the case of the hexagonal close pack crystal.