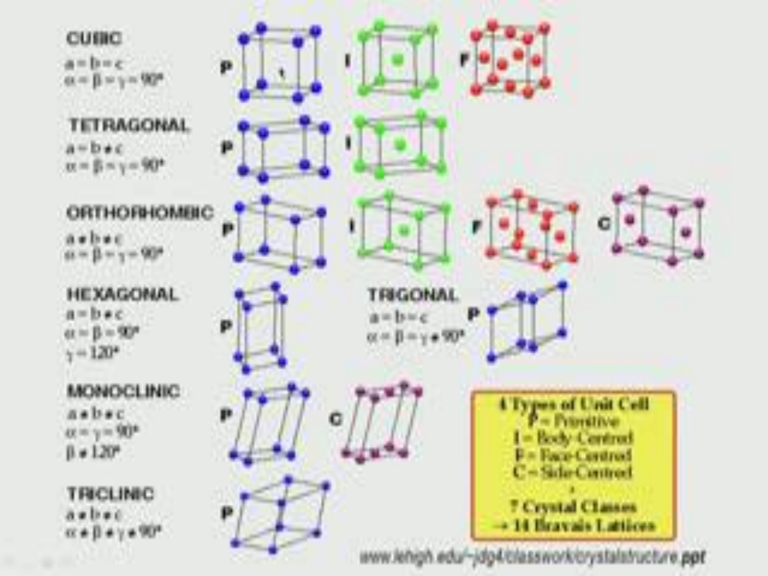
Medical Biomaterials
Prof. Mukesh doble
Department of Biotechnology
Indian Institute of Technology, Madras

Lecture – 26
Metallic biomaterials

Hello everyone welcome to the course on medical bio materials. We will continue on this topic of metals. In the previous class I was talking about crystal structure, different type classes of crystals and the bravais lattices, and before that I talked about miller index and how to calculate miller index of a plane.

(Refer Slide Time: 00:39)


CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$

TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

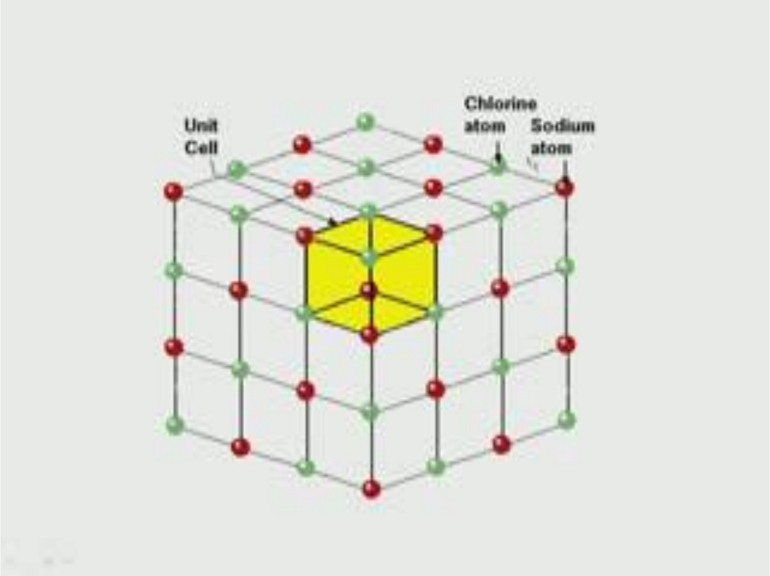
TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

www.lehigh.edu/~jdg4/classwork/crystalstructure.ppt

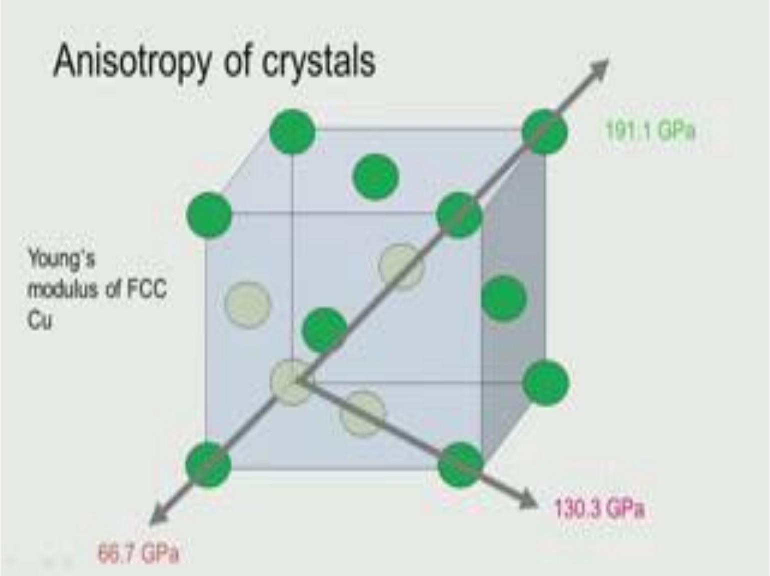
So, I did mention there are 7 classes cubic, tetragonal, orthorhombic, hexagonal, mono clinic, triclinic and trigonal, and each of the class you can have a primitive structure. You can have a body centred cubic, face centred, cubic or side centred. So, there are 14 bravais lattices all the metals even salts for example, fall will fall into this, if they have crystalline in nature. So, crystallinity determine some of their physical chemical properties, and if you are interested in preparing metal alloys, and what type of metal to add to existing metal to change its properties; if you know in which crystal class it will fall and what based on the dimension of the element, we can decide what type of new crystal class it will fall into. So, understanding the crystal structure is very important. We have powder x ray crystallography which can help us to find out the crystal structure of various materials, organic molecules, inorganic molecules and so on. So, trying to understand, this is very important, like I said that determines the physical chemical properties. This crystal structures can change as a function of time. It can change depending upon the presence of impurities and so on.

(Refer Slide Time: 02:20)



So, if you take for example, sodium chloride, sodium chloride forms an ice crystal. So, like I said this is their unit cell that is the repeating unit keeps on happening. So, we can have this like a chlorine atom, this is sodium atom. So, NACL. So, for every sodium there will be a chlorine. So, they are nicely beautifully packed like this, because their valency is also 1 1. So, they all nicely packed alternatingly alternatingly. So, if you take one unit cell. So, as you can see, there are some sodium is present, but not the whole as you can see this particular sodium is available for this unit cell, this unit cell, this unit cell, this unit cell, again 4 on top. So, basically this is only 1 2 3 4 8. So, only 1 8 is available for this particular unit cell, you understand.

(Refer Slide Time: 03:27)


Anisotropy of crystals

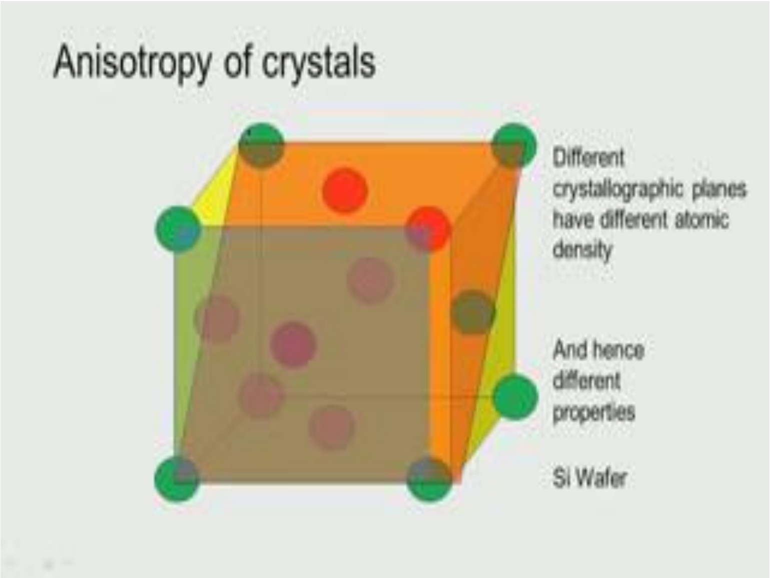
Young's modulus of FCC Cu

Similarly, same thing goes for your chlorine also. So, one interesting thing is the anisotropy of crystals. For example, let us take this particular crystal, what is this particular crystal. So, its got in the corners 1 2 3 4 5 6 7 8, and also its got 1 2 3 4 5 6 in their faces. So, that is called face centred cubic. Now depending upon the direction, the atoms, the number of atoms can change what does that mean. What does it mean .Young's modulus of this is a copper, it forms a face centred cubic suppose the direction is like this. So, these type of atoms are going to be; that means, direction of the force or load, is in this direction, these atoms or undergoing that particular force or tensile strength or tensile force, compressive force, then the Young's modulus is 66.7 Giga Pascal.

Now, if it is the force is in this direction, as you can see not only these two corner atoms, but also this particular atom is also a part of this pull. So, the Young's modulus increases to 130 Giga Pascal. See if it is in this direction it 66.7, if is in this direction its 130.3 that is a big difference; where as if it is in another direction like this, this goes to 191; that is the longer diagonal, its 191.1 Giga Pascal lot of difference. So, if it is along the side, or if it is a long the face or if it is a long the longer diagonal, so the Young's modulus can change dramatically.

So, if the direction of the force for the tension, and the way the crystal is oriented of copper for example, we may have to consider different types of numbers for the Young's modulus. So, if we think calculate everything based on this, where as if it is oriented in this, then we are in big trouble, because the young's modulus comes down by almost factor of 3 which is big change.

(Refer Slide Time: 06:13)



Anisotropy of crystals

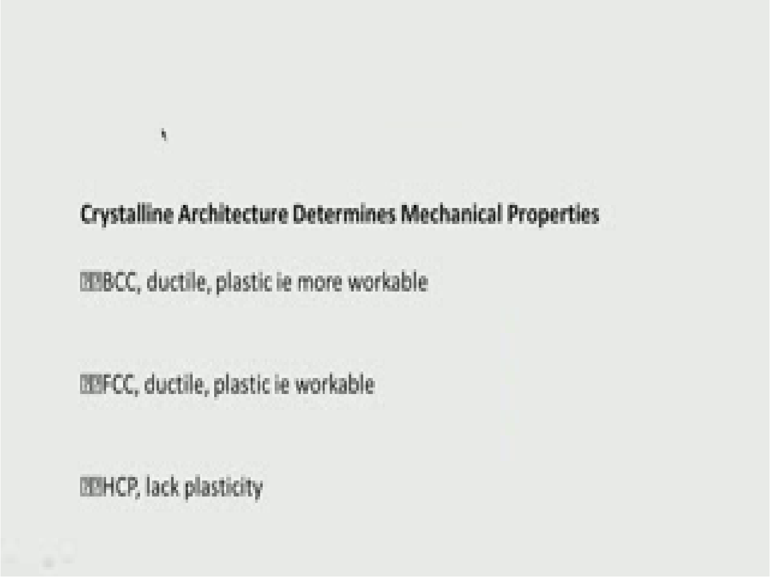
Different crystallographic planes have different atomic density

And hence different properties

Si Wafer

So, that is very important look at this. So, suppose if the plane is like this or if it is like this, the number of atoms of for the particular material or metal; that is in contact is changing dramatically, if it is like this only the corner atoms face the particular load. Whereas, if it is like this it is not only corner also the atoms on the face is also faced. So, there is going to be lot of difference in their yield strength or the young's modulus so, you need to keep that in mind. So, different crystallographic planes have different atomic density, or the number of atoms in that particular unit cell will be going to be different, so; obviously, and hence different properties. So, the properties can dramatically change. So, you need to keep that point in mind. Silicon for example, this is say example of a silicon before. So, when they undergo load, if it is along this plane, as against along the longer diagonal the young's modulus are going to be very different, and that is called the anisotropy of crystals.

(Refer Slide Time: 07:44)

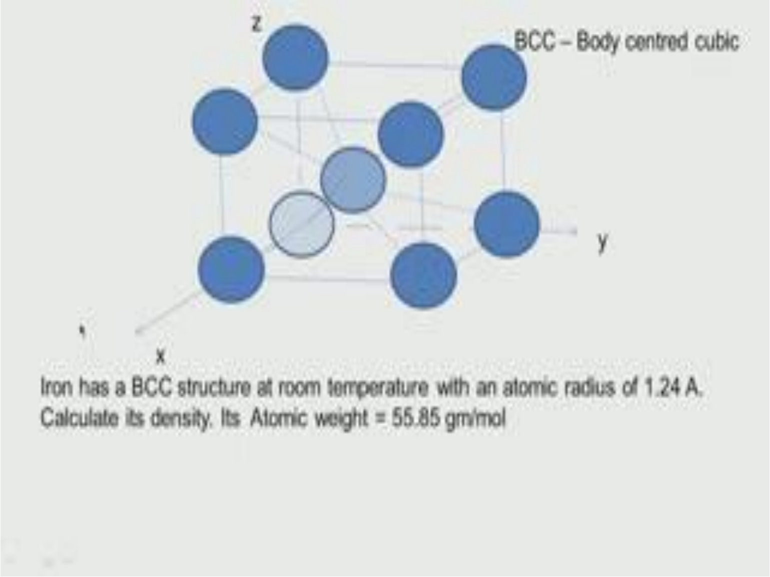


Crystalline Architecture Determines Mechanical Properties

- BCC, ductile, plastic ie more workable
- FCC, ductile, plastic ie workable
- HCP, lack plasticity

And that is another point. The other point is whether the crystal unit cell is a BCC or FCC or HCP or primitive that also determines its mechanical properties. For example, BCC is our ductile plastic, so it is more workable. FCC ductile plastic, but a little bit work, but if you take hexagonal it lacks plasticity. So, it is not possible for you to work on that. So, ideally a BCC its very ductile and plastic, so we can nicely work on it and get a nice shapes of different shapes whereas, FCC slightly more difficult, and HCP is practically impossible to work on it.

(Refer Slide Time: 08:33)

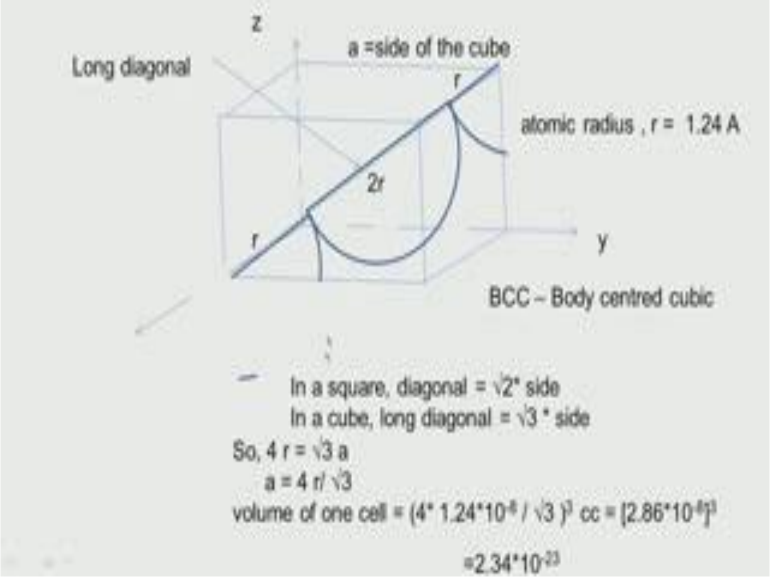


BCC – Body centred cubic

Iron has a BCC structure at room temperature with an atomic radius of 1.24 A.
Calculate its density. Its Atomic weight = 55.85 gm/mol

So, let us go back, take an iron its called a BCC structure. So, each of these corners and one in the middle here. So, it has a BCC structure at room temperature with an atomic radius of 1.24 Armstrong, calculate, its density its atomic weight is 55.85 gram per mole. So, we take one unit cell we need to know how many atoms are there. Can you tell how many atoms are there? So, this atom with inside the body centre is fully available for the unit cell. Whereas, this corner atoms are not available, because its shared by 8 unit cells. So; obviously, only, although there are 8 atoms each one is shared by 8, so its 8 divided 8, so there will be only one. So there will be two atoms available for one unit cell.

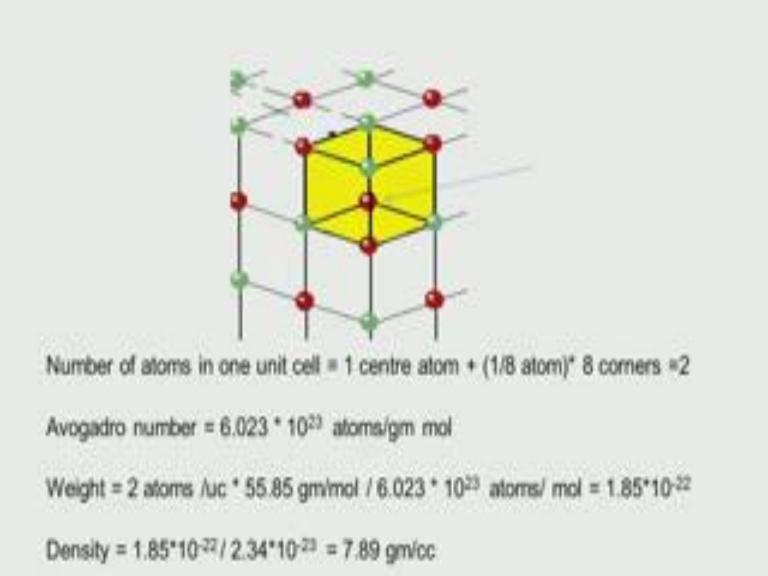
(Refer Slide Time: 09:36)



In a square, diagonal = $\sqrt{2}$* side
In a cube, long diagonal = $\sqrt{3}$ * side
So, 4 r = $\sqrt{3}$ a
a = 4 r/ $\sqrt{3}$
volume of one cell = $(4^* 1.24^*10^{-8} / \sqrt{3})^3$ cc = $[2.86^*10^{-8}]^3$
$=2.34^*10^{-23}$

Let us look at it more in detail. So, this is the central atom. So, its got a radius of 2 r, if you take the long diagonal, let us take the long diagonal, this is the central atom, and then these are the corner atom. So, we have r. So, the long diagonal will be equal to 4 r, and suppose a is the side of the cube, and the long diagonal is 4 r, where r is the radius of each of these atoms. And like you must have studied in your school, the long diagonal square root of 3 into side, just like an square the diagonal is square root of 2 into side for a cube long diagonal square root of 3 into side. So, you must have studied this right. So, side is a, so; obviously, 4 r is equal to square root of 3 a. So, there is a relation we can develop between r and a. So, 4 r is equal to, 4 r, r plus 2 r plus r that is 4 r is equal to square root of 3 a. So, a is equal to 4 r divided by square root of 3. Now, volume of one unit cell, volume of one unit cell is equal to 4 into r is 1.24 Armstrong. So, we convert it into centimetre 10 power minus 8 cube a into a into a is the volume; that is so many this is this, because r is given here 1.244 into 1.24 into 10 power minus 8 whole thing cube raise to the power 3. So, this is volume of one cell.

(Refer Slide Time: 11:26)



Number of atoms in one unit cell = 1 centre atom + (1/8 atom)* 8 corners =2

Avogadro number = $6.023 * 10^{23}$ atoms/gm mol

Weight = 2 atoms /uc * 55.85 gm/mol / $6.023 * 10^{23}$ atoms/ mol = $1.85*10^{-22}$

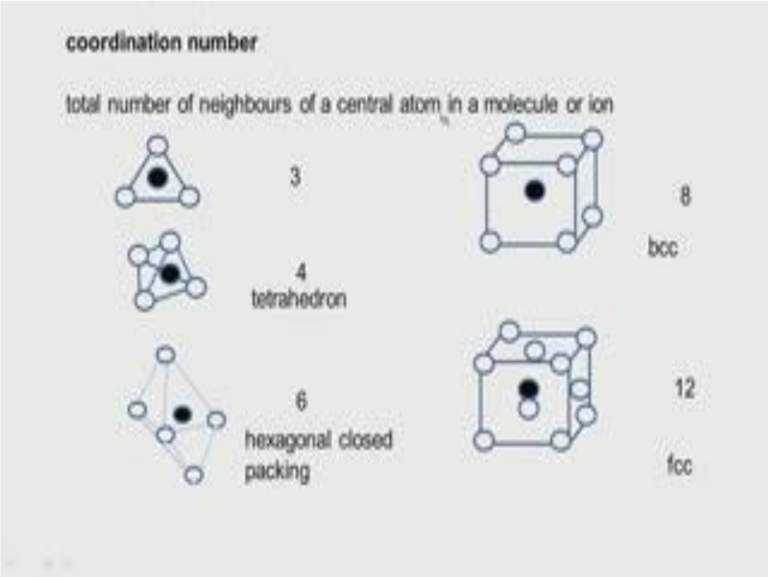
Density = $1.85*10^{-22} / 2.34*10^{-23}$ = 7.89 gm/cc

Now, we need to know the mass. Now number of atoms like I said one central atom plus 1 by 8 of 8 corners. So, two Avogadro number is 6.023 into 10 power 23 atoms per gram mole. So, two atoms you have, the atomic weight is given as 55.85 gram per mole. So, 55.85 gram per mole, then you have the 6.023, and atoms are there per gram mole. So, we need to divide that do we understand 2 atoms per unit cell multiplied by 55.85 gram, but in 1 gram mole there are 6.023 10 power 23. So, we need to divide that. So, the weight is 1.85 into 10 power minus 22.

So, density is weight by volume. So, 1.85 into 10 power minus 22, and volume is 2.34 10 power minus 23 divide. So, you will end up with 7.89 grams per c c, and it sort of matches with the literature value also. So, what do you do? We know how many atoms will be there in one unit cell two and then multiplied by the weight of each one of them at that is atomic weight 55. We need to divide by Avogadro number, because it tell you how many atoms per gram mole. Now if you want to go look at the volume use geometry here if you take the long diagonal there is one central atom, and then two atoms placed on the corners.

So, that central diagonal will be 2 r plus r plus r 4 r. And in our school we must have studied for a cube the long diagonally is square root of 3 into side; that is a. So, 4 r is equal to square root of 3 a. So, the volume of one cell is a into a into a, which is 4 r divided by square root of 3 raised the power 3, and then of course, we need to convert Armstrong into centimetre. So, that is why we have this this 10 power minus 8. So, we end up with 7.89 grams per c c, quite straight forward.

(Refer Slide Time: 13:38)



coordination number

total number of neighbours of a central atom in a molecule or ion

3

4
tetrahedron

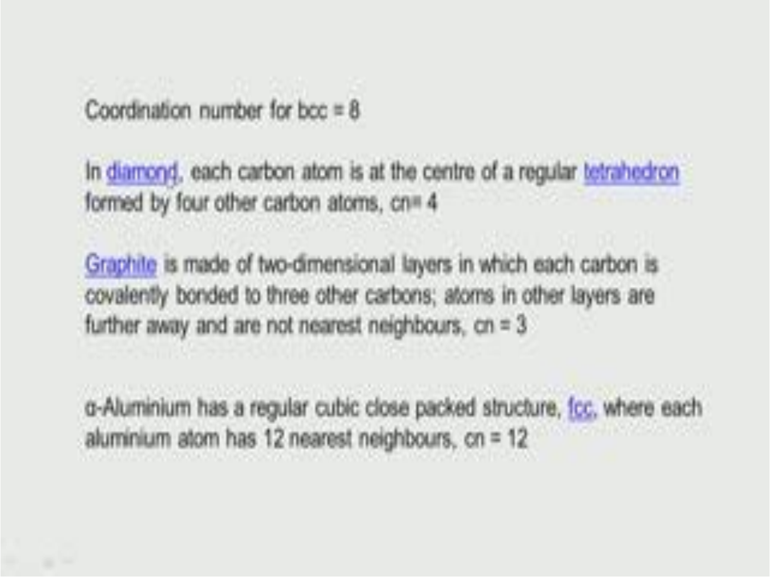
6
hexagonal closed
packing

8
bcc

12
fcc

Now, there is some other term which is called coordination number; that is the total number of neighbours of a central atom in a molecule or a ion. So; obviously, suppose we take this chap, there are 3 atoms; in a triangular coordination number is 3. Suppose this is a tetragon. So, there is one like a s p 3 type you know; 1 2 3 4 in the centre. So, we have 4 tetragon. So, if you have like this hexagonal; that is 6, 1 2 3 4 5 6. If we take a cube 1 2 3 4 5 6 7 8 BCC this is 8. If you take a FCC so apart from there are 12, 8. So, there are twelve for this, that is called the coordination number; that is number of atoms which are neighbours to this central atom, this is the black one.

(Refer Slide Time: 14:40)



Coordination number for bcc = 8

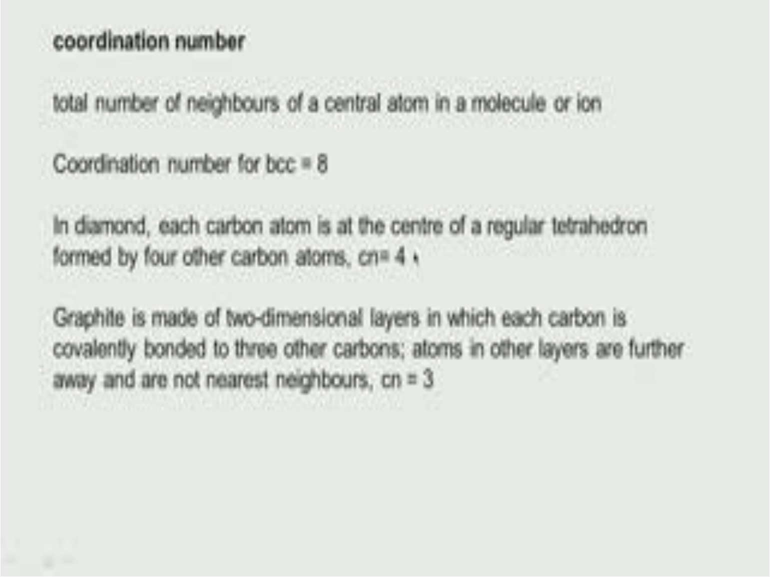
In diamond, each carbon atom is at the centre of a regular tetrahedron formed by four other carbon atoms, cn= 4

Graphite is made of two-dimensional layers in which each carbon is covalently bonded to three other carbons; atoms in other layers are further away and are not nearest neighbours, cn = 3

α-Aluminium has a regular cubic close packed structure, fcc, where each aluminium atom has 12 nearest neighbours, cn = 12

So, coordination number for BCC is 8, like I showed you here. In diamond for example, each carbon atom is at the centre of a regular tetrahedron. So, coordination number 4. So, we have diamond like here, diamond like structure here, so 4. Graphite is a two dimensional structure. So, graphite. So, the coordination number will be 3.; so we will be having layers and layers of graphite, and whereas diamond will be 3 dimensional like this a tetrahedron. So, coordination number is 4, and graphite. So, same carbons, but you can see that the coordination number changes depending upon their structural. And graphite is made up of two dimension, diamond is made up of 3 dimensional regular tetrahedron. So, coordination number for graphite is 3, coordination number diamond for 4. Alpha aluminium has a regular cubic close packed structure FCC sorry alpha FCC.

(Refer Slide Time: 15:48)



coordination number

total number of neighbours of a central atom in a molecule or ion

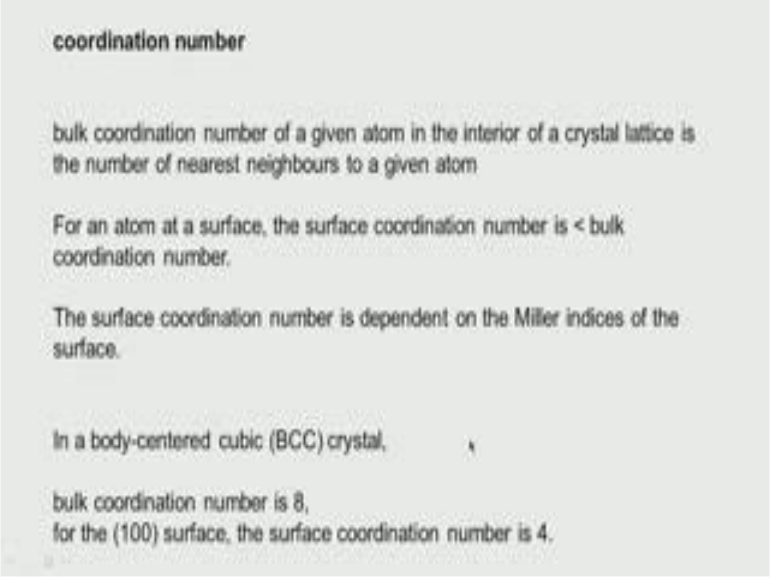
Coordination number for bcc = 8

In diamond, each carbon atom is at the centre of a regular tetrahedron formed by four other carbon atoms, cn= 4

Graphite is made of two-dimensional layers in which each carbon is covalently bonded to three other carbons; atoms in other layers are further away and are not nearest neighbours, cn = 3

So, the coordination number is twelve. So, coordination number for BCC is 8, coordination number diamond like I said I set it regular tetrahedron. So, its 4 graphite is got layer by layer two dimensional layer. So, see coordination number is 3.

(Refer Slide Time: 16:05)



coordination number

bulk coordination number of a given atom in the interior of a crystal lattice is the number of nearest neighbours to a given atom

For an atom at a surface, the surface coordination number is < bulk coordination number.

The surface coordination number is dependent on the Miller indices of the surface.

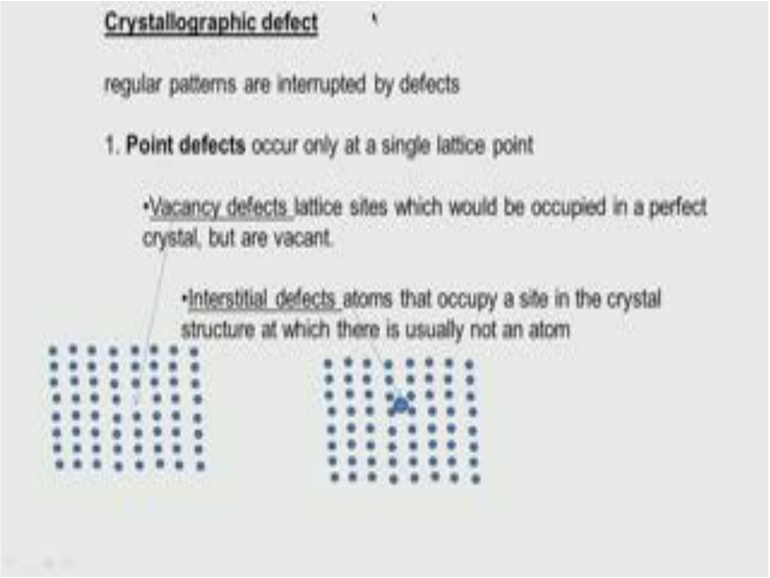
In a body-centered cubic (BCC) crystal,

bulk coordination number is 8,
for the (100) surface, the surface coordination number is 4.

Now, there is a slight difference in coordination number, depending upon whether its bulk coordination number of a given atom; that is the total or it is a surface coordination number; that is surface means on the surface like of a say cube. Generally surface coordination number will be less than the bulk coordination number. So, when we say surface we look at the surface atoms and see for a central atom what are the nearest neighbours. Whereas when we say bulk coordination number we look at the central atom in a bulk three dimension, and see what are the atoms that are surrounding it.

So, if you take BCC bulk coordination number is 8. Whereas, if you take this surface coordination of that, for the 1 0 0 plane that will be 4, because look at this there are 4 atoms. This one which is in the middle does not come in to the picture. So, for a BCC the bulk coordination number is 8, surface coordination for the 1 0 0 surface is 4. So, understand 1 0 0; that means, in the y and z axis it is not cutting only the x is cutting. So, its cutting x, but it is parallel to y and z axis. So if you have x y is that. So, it is parallel to the y and the z. So, this particular plane could be 1 0 0. Its cutting the x axis, but it is not cutting the y and z axis.

(Refer Slide Time: 17:41)



Crystallographic defect

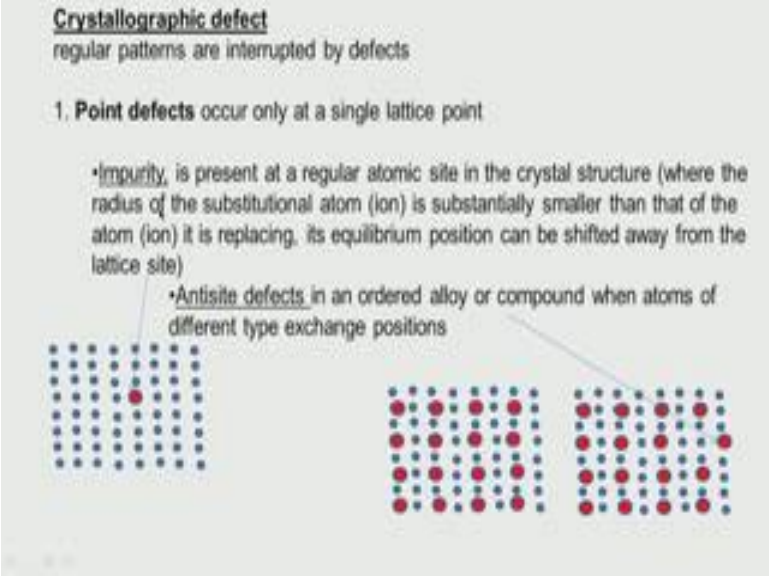
regular patterns are interrupted by defects

1. **Point defects** occur only at a single lattice point

- Vacancy defects lattice sites which would be occupied in a perfect crystal, but are vacant.
- Interstitial defects atoms that occupy a site in the crystal structure at which there is usually not an atom

Crystallographic defects, crystals as we said was formed, when it is formed, but there are always chances of defects, because of the crystals keeps forming and forming, mixing takes place, and the atoms come closer to each other, and this crystal starts growing. So, that could be defects. There are something called point defect, plane defect and so on actually. So, what is this point defect; that is it happens at one single lattice point. So, these are called vacancy defect, instead of having one atom there, there is no atom, there is a gap. So, that is called vacancy defect. Of course, when you have like this the structural strength goes down. Interstitial defect; that means, atoms are occupying instead of being regular in their place where they have to be, they are in some odd place where it should not be there; that is called the interstitial defect.

(Refer Slide Time: 18:37)



Crystallographic defect

regular patterns are interrupted by defects

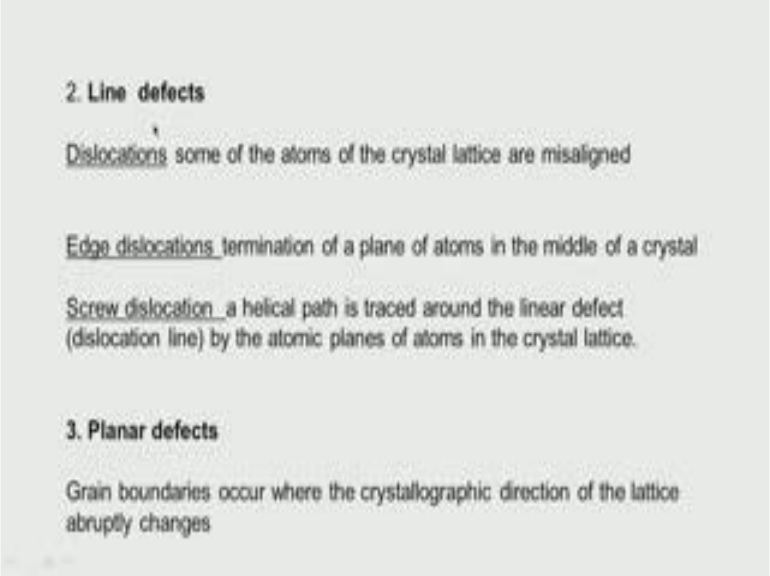
1. **Point defects** occur only at a single lattice point

- Impurity, is present at a regular atomic site in the crystal structure (where the radius of the substitutional atom (ion) is substantially smaller than that of the atom (ion) it is replacing, its equilibrium position can be shifted away from the lattice site)
  - Antisite defects in an ordered alloy or compound when atoms of different type exchange positions

So, point defect you can also have impurities there. There is an impurity atom, because crystals although they are supposed to be extremely pure with the 100 percent purity. Sometimes an impurity like carbon can go and sit there. So, the radius could be substantially smaller of that impurity or almost same, then there is something called anti side defect.

Suppose you have a ordered alloy of two different atoms. So, they are placed like this one after another, one after another like this, but there is a rearrangement look at this, look at this. So, instead of this being there and this being there; that is atom 1, atom 2 they get inter changed. This is called anti side defect.

(Refer Slide Time: 19:30)



2. Line defects

Dislocations some of the atoms of the crystal lattice are misaligned

Edge dislocations termination of a plane of atoms in the middle of a crystal

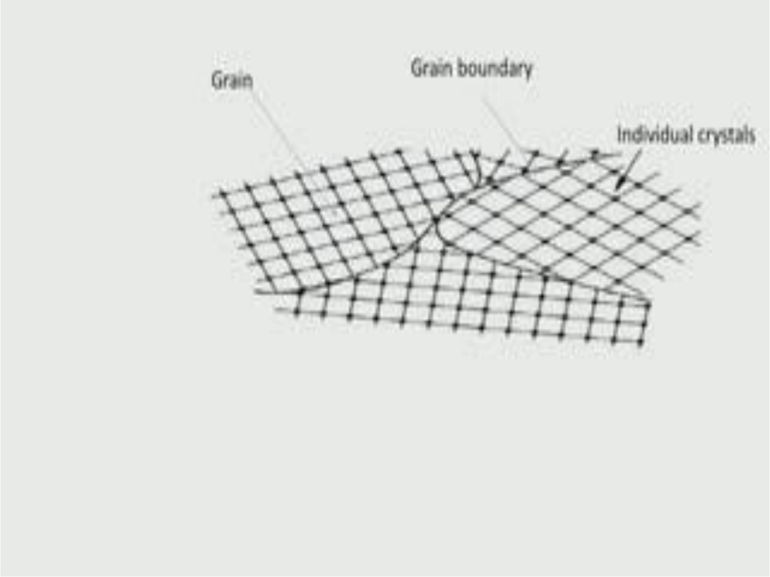
Screw dislocation a helical path is traced around the linear defect (dislocation line) by the atomic planes of atoms in the crystal lattice.

3. Planar defects

Grain boundaries occur where the crystallographic direction of the lattice abruptly changes

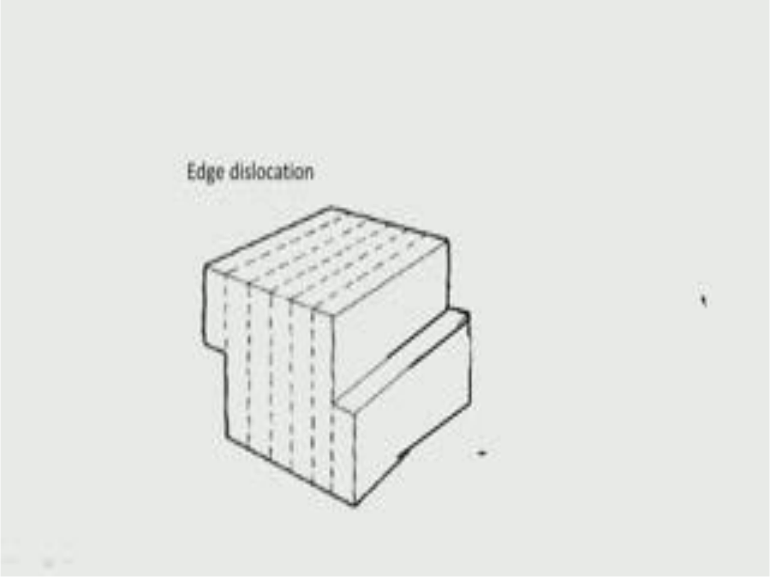
Line defects they are called dislocations; that means, some of the atoms or miss aligned. Instead of, suppose they are to be uniformly in a straight line, they are misaligned. So, they called misalignment can be in a linear fashion, or there could be a it could be in a curved fashion. Linear fashion we call it edge dislocation; that is termination of a plane of atoms in the middle of the crystal, or screw dislocation; that means, helical path is traced around the linear defects. So, instead of being a line it could be a twisted. So, we call it screw defect, screw dislocation; that is called line defect. Planar defect grain boundaries occur where the crystallographic direction of the lattice abruptly changes; that is called the planar defect. Instead of line the entire plane is defective.

(Refer Slide Time: 20:24)

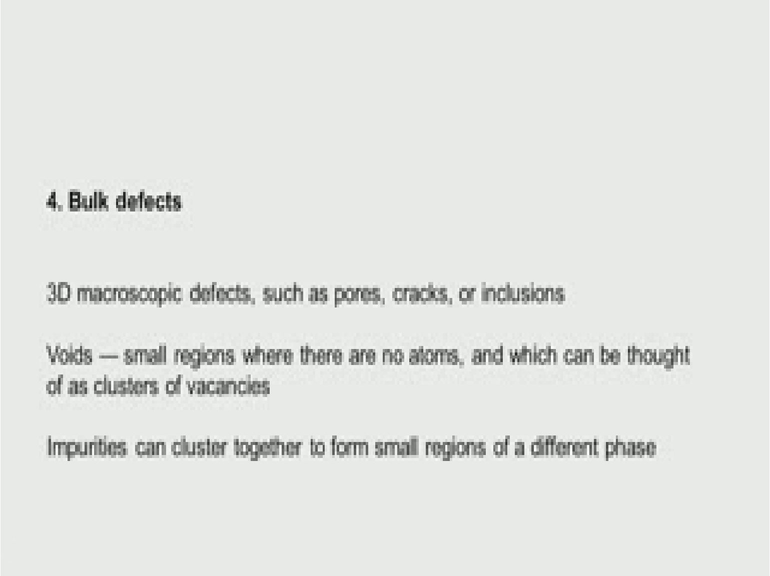


Now, look at this. So, in metals you can have individual, crystal like this. So, they are all forming farming forming, but then there could be another crystal all forming forming, and each crystal is growing growing, and then finally, they end up like this. These are called grain boundaries. So, this particular crystal is grown, this particular crystal has grown, they all grow from different directions, in they all hit, and this is called the grain boundary. So, these grain boundaries or little bit weak, and it is lot of a mechanical engineering studies talked about. So, we will not going into this, but if you take a crystal and look under very high resolution microscope, we can see these grain boundaries where defects, where the strength could be much lesser, there could be movement and so on actually, because as the crystal starts growing from different directions, and the inside the crystal they may be uniform, but as they hit another growing crystal, another going crystal, another going crystal they form this type of grain boundaries. These are individual crystals the whole thing is a grain, and each grain hits each other during their growth and they form the grain boundary.

(Refer Slide Time: 21:54)



(Refer Slide Time: 22:03)


4. Bulk defects

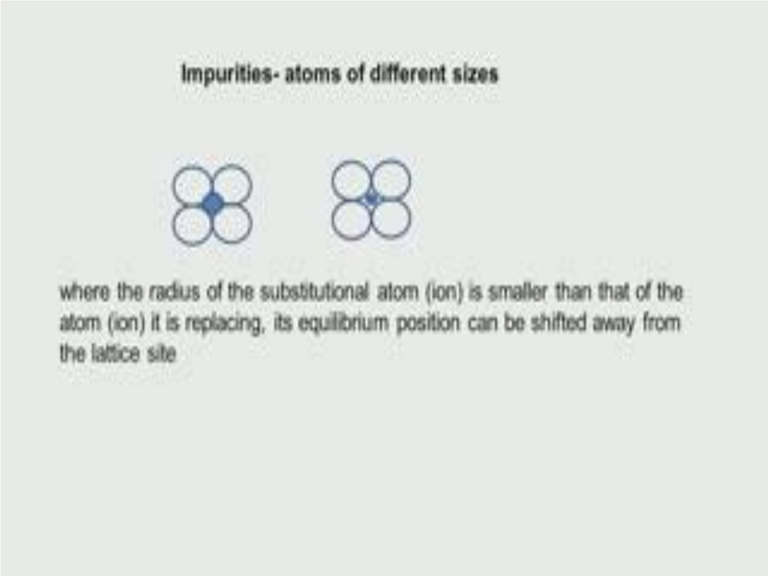
3D macroscopic defects, such as pores, cracks, or inclusions

Voids — small regions where there are no atoms, and which can be thought of as clusters of vacancies

Impurities can cluster together to form small regions of a different phase

Now, this is called the edge dislocation. Whereas you can see here there is a shift in their edges. Then you have the bulk defects these are all three dimensional microscopic defects such as pores, there could be small holes, there could be cracks, there could be some inclusion in bodies voids, where there are no atoms, cluster of vacancies, impurities can cluster together. There can be some impurities they may all come together. So, there could be patches of impurities. So, all these are also possible in a crystalline system.

(Refer Slide Time: 22:30)

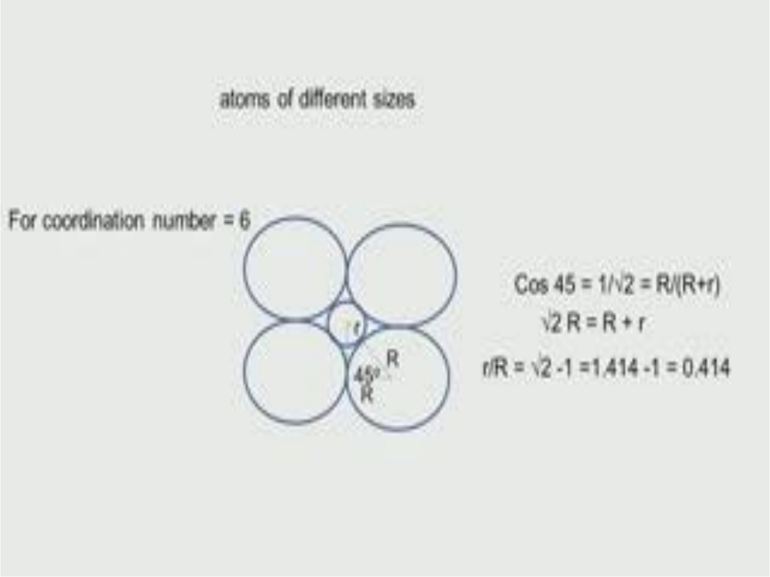


Impurities- atoms of different sizes

where the radius of the substitutional atom (ion) is smaller than that of the atom (ion) it is replacing, its equilibrium position can be shifted away from the lattice site

So, impurities you can have they can be filling up these voids, and if they are smaller or just equal, then they are, but if they are very big, they may completely dislocate, the equilibrium position can be shifted away from their lattices side. So, the impurities can be small like this, or just equal touching each other, touching all the other atoms. Whereas, when it became very big they are going to completely disrupt the crystal structure.

(Refer Slide Time: 23:03)



atoms of different sizes

For coordination number = 6

$\text{Cos } 45 = 1/\sqrt{2} = R/(R+r)$

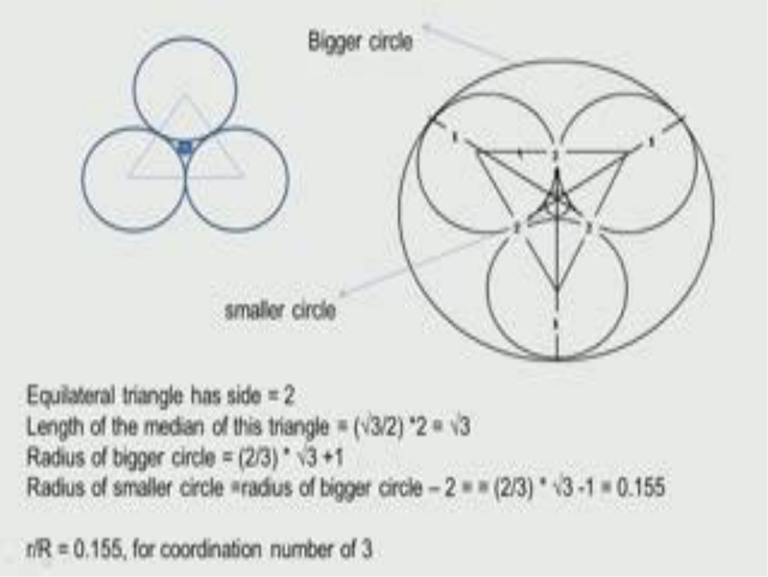
$\sqrt{2}\,R = R + r$

$r/R = \sqrt{2} - 1 = 1.414 - 1 = 0.414$

So, if h, let us look at this. Suppose we have a small atom for a coordination number 4, sorry 6. So, we have 4 atoms here of radius R, and 2; one on the top one on the bottom. So, we have this small r, which touches all of these 4 as well as one at the top and one at the bottom. We can get some relationship between this small r and the R. These are all from geometry. So, if I draw this radius that is r plus r, and if I draw a perpendicular line to the R, this angle is 45 degrees. So, cos 45 as all us know is 1 by square root of 2 which is equal to this small r divided by r plus r. this is from geometry, we must have studied in our tenth standard. So, cos 45 which is 1 by square root of 2 r divided by r plus r.

So, if we rearrange this square root of 2 r is equal to r plus r then I divide by R. I will end up with or by r is equal to square root of 2 minus 1, square root of 2 is 1.414 minus 1 is 0.414. So, ratio of the radius, this small r by R is 0.414; that means, I can fit exactly a smaller circle or a smaller, which will have a radius, equal to 0.414 of the bigger radius. If I have smaller then of course, the smaller circle will not touch all of them. If I have a bigger, is going to dislocate or shift all of these things. So, we have to keep that in mind.

(Refer Slide Time: 25:04)



Equilateral triangle has side = 2

Length of the median of this triangle = $(\sqrt{3}/2) * 2 = \sqrt{3}$

Radius of bigger circle = $(2/3) * \sqrt{3} + 1$

Radius of smaller circle = radius of bigger circle – 2 = = $(2/3) * \sqrt{3} - 1 = 0.155$

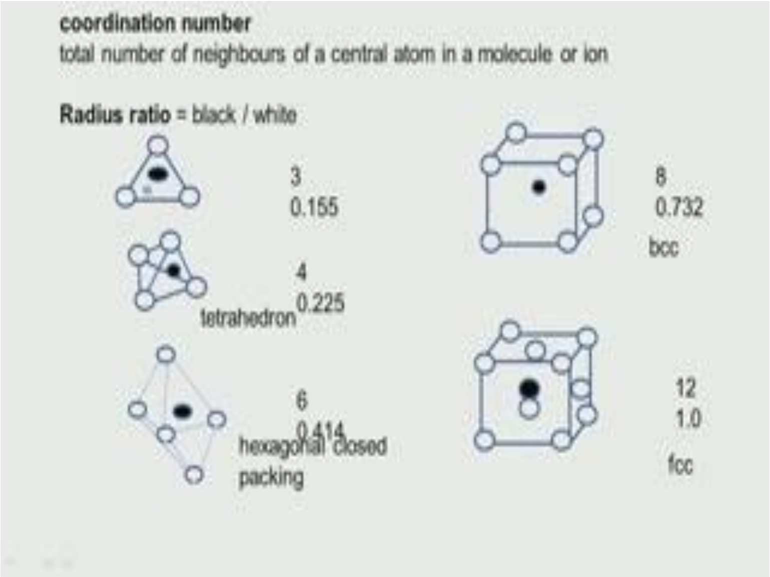
$r/R = 0.155$, for coordination number of 3

Similarly, if we want to look at 3, where this is touching 3 of them, again it goes through your geometry. So, how we go do that. First we draw a big circle, which will ah cover all this two three small circle. So, we have a big circle, which will cover, and then what will be the length of this particular perpendicular. Again it comes from your geometry, because this is an equilateral triangle; this radius r, this radius is R, or R R R R. So, the length, this is called the median. The length of median of this triangle. Suppose this equilateral triangle is r plus r that is 2 length of the median of the triangle is square root of 3 divided by 2 into a. Again you have studied in your school square median of an equilateral triangle square root of 3 by 2 into the side, side is 2, because this is one, this is one. So, that will give the square root of 3 that is this median.

The radius of this bigger circle is equal to, this length plus this length, this length is one. Now what is this length, 66 percent or two thirds of this median. Two thirds of square root of 3 plus this one do you understand. So, what is the radius of this bigger circle. It is made up of this length plus this radius this radius/ we will call it one now this radius that is the two third of the median of this triangle median square root of 3. So, 2 by 3 into square of 3; now once I know the radius of bigger circle. Radius of the smaller circle is Radius of bigger circle. Radius of bigger circle minus this that will give you the radius of this, so radius bigger circle minus this is 1 plus 1 2; that is the diameter of the this circle.

So, radius of bigger circle is given by 2 by 3 into square root of 3 minus one. So, because this plus 1 and this minus 2 goes to minus 1 so, it is 0.155. So, the radius of the small circle, which is touching all these divided by the radius of this bigger circle, will have ratio of 0.155. So, this this is obtained of course, from geometry. So, it is not very difficult. So, I can have a small circle, it can be placed inside which touches all this bigger circle, and that size of that circle will be related with the size of the bigger circle by r by r is equal to 0.55. Whereas, in this particular situation we saw r by r is equal to 0.414 and so on. So, we can do lot of this type of calculations.

(Refer Slide Time: 28:15)



coordination number

total number of neighbours of a central atom in a molecule or ion

Radius ratio = black / white

3
0.155

4
0.225
tetrahedron

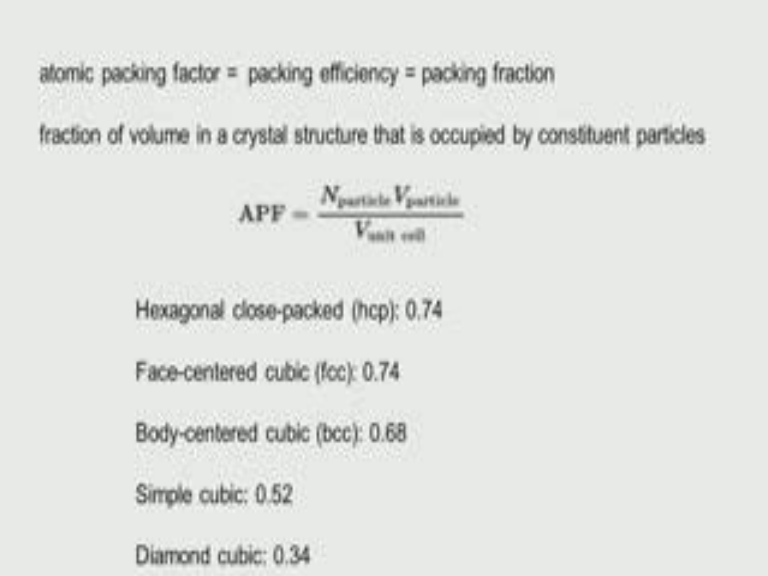
6
0.414
hexagonal closed packing

8
0.732
bcc

12
1.0
fcc

So, for coordination number 3; r by r that is radius of black to white 0.155. Coordination number 4, it is the tetrahedron radius of r by r 0.225, coordination number 6, 0.414 that is h c p coordination number 8 r by r is 0.732, coordination number twelve r by r is one. So, this tells you the central atom radius as against the bigger atom radius, this is the number it should be. If it is bigger it is going to disrupt the lattice that is. So, based on these numbers 1 can even think about what type of impurities to add to the existing metal.

(Refer Slide Time: 29:17)



atomic packing factor = packing efficiency = packing fraction

fraction of volume in a crystal structure that is occupied by constituent particles

$$\mathbf{APF} = \frac{N_{\text{particle}} V_{\text{particle}}}{V_{\text{unit cell}}}$$

Hexagonal close-packed (hcp): 0.74

Face-centered cubic (fcc): 0.74

Body-centered cubic (bcc): 0.68

Simple cubic: 0.52

Diamond cubic: 0.34

There is something also called the atomic packing factor. So, we will talk about this atomic packing factor in the next class.

Thank you very much for your time.