Chemical Crystallography
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Theoretical Understanding of Crystal Packing And X-Ray Diffraction in Direct and Reciprocal Space
Lecture - 18
Cubic Structures and atomic packing factors

Welcome back to the course of Chemical Crystallography, in the previous lecture we learnt about the linear density repeat distance and then we tried to calculate the planar density of various crystallographic planes; in case of simple cubic body centered cubic lattices and I left it for you to work out for the face centered cubic lattices.

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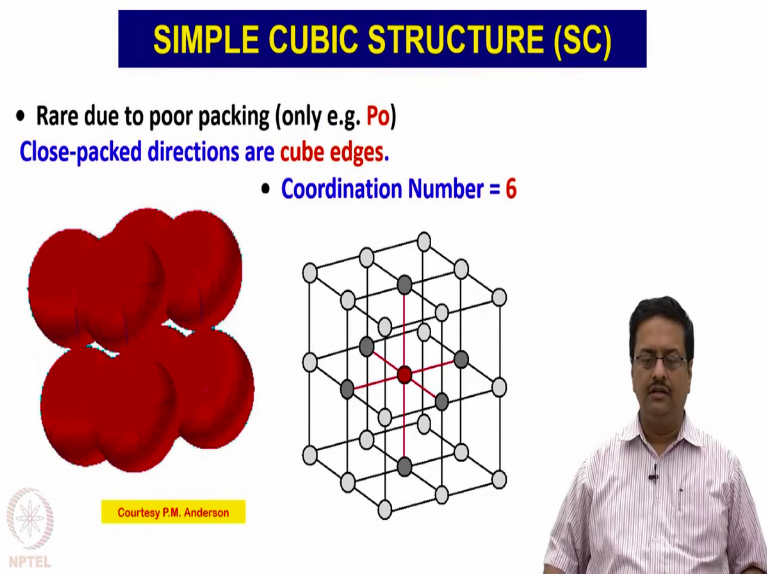

SIMPLE CUBIC STRUCTURE (SC)

- Rare due to poor packing (only e.g. Po)

Close-packed directions are cube edges.

- Coordination Number = 6

Courtesy P.M. Anderson

So, today we will try to understand these 3 basic systems simple cubic structure, first body centered cubic and face centered cubic structures and we will try to calculate their packing fractions and things like that. So, in case of simple cubic lattice as we have already indicated there are 8 atoms located at 8 corners of a cube and this is shown here in this particular slide. So, if you look at any atom that is marked here as red that particular atom has 6 nearest neighbors from 6 different Latin unit cells.

So, the left right back front top and bottom corresponds to a coordination number of 6 for every corner atom of this simple cubic structure, remember you have only corner atoms in case of single simple cubic structures.

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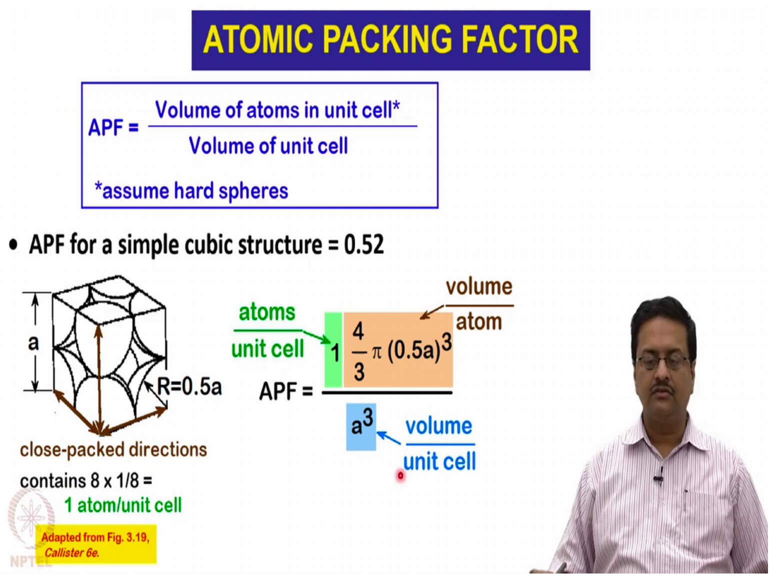

ATOMIC PACKING FACTOR

$$\text{APF} = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52

$$\text{APF} = \frac{\underset{\text{atoms/unit cell}}{1}\;\overset{\text{volume/atom}}{\frac{4}{3}\pi(0.5a)^3}}{\underset{\text{volume/unit cell}}{a^3}}$$

close-packed directions

contains 8 x 1/8 =
1 atom/unit cell

Adapted from Fig. 3.19, Callister 6e.

So, when we try to calculate the atomic packing fraction or atomic cracking factor we write APF equal to volume of the unit cell divided volume of the atoms in the unit cell divided by volume of the unit cell. So, now in case of simple cubic structure this is calculated to be 0.25 how in case of simple cubic if you note that the corner atoms touch each other along the face edge along the edge direction which is again. So, we can write a equal to twice R and from that you can calculate the volume of 1 such atom because, every atom sitting at corner contributes 1 by 8.

So, all together 8 corner atoms contributing 18 gives you 1. So, number of atoms per unit cell is 1 and the volume of that atom is 43 pi R cube R is half of a. So, 43 pi R cube is the volume occupied by those atoms and the volume occupied by the unit cell is a cube, so the result turns out to be just 0.52. Which means in case of simple cubic there are lots of wide space in the lattice.

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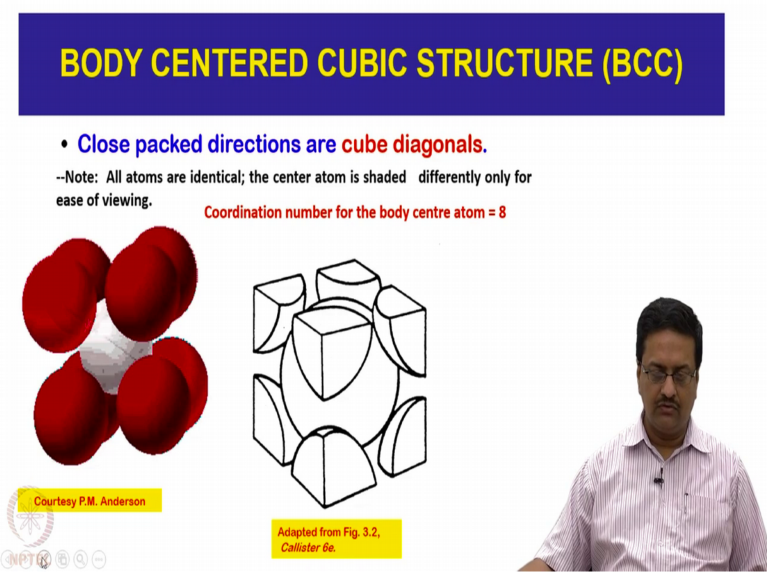

BODY CENTERED CUBIC STRUCTURE (BCC)

- Close packed directions are cube diagonals.

--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

Coordination number for the body centre atom = 8

Courtesy P.M. Anderson

Adapted from Fig. 3.2, *Callister 6e.*

So, when we go to the body centered cubic lattice or body centered cubic structure as we write it as BCC, in this case the close packed direction is the body diagonal. So, from one corner through the center atom to the other corner the atoms are touched touching one another considering them as hard spheres. So, in that case if you consider the atoms located at the center of the body center of the unit cell, then you have 8 such atoms which are touching to this particular central atom. So, that is why we write that the coordination number of a body centered lattice is 8 and the body centered atom has coordination number 8.

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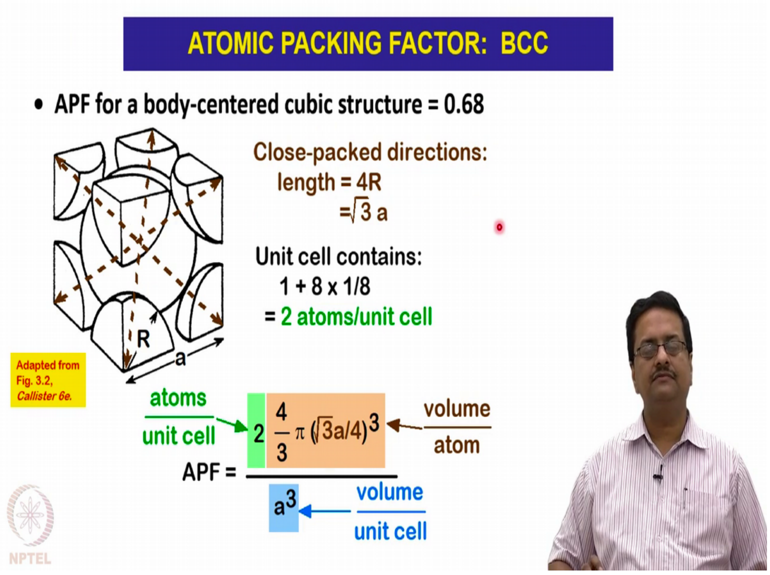

ATOMIC PACKING FACTOR: BCC

- APF for a body-centered cubic structure = 0.68

Close-packed directions:
length = 4R
$= \sqrt{3}\,a$

Unit cell contains:
1 + 8 x 1/8
= 2 atoms/unit cell

Adapted from Fig. 3.2, *Callister 6e.*

$$\text{APF} = \frac{\overset{\text{atoms/unit cell}}{2}\;\overset{\text{volume/atom}}{\frac{4}{3}\pi(\sqrt{3}a/4)^3}}{\underset{\text{volume/unit cell}}{a^3}}$$

So, in case of body centered lattice the atomic packing fraction turns out to be 0.68 how because, the body diagonal is capital R which is sorry body diagonal is root 3 a which is equivalent to 4 R, R is the radius of each atom and then every unit cell contains 18 contribution from the corner atoms. So, there are 8 such atoms at corner so contributing to 1 and then the body center atom which is totally inside the unit cell, so it contributes to 1.

So, you have total 2 atoms per unit cell, so now we try to calculate the atomic packing factor here. So, if this is equal to 2 times that is 2 atoms per unit cell the volume of the atom. So, now this R capital R is root 3 by 4 a, so the volume of 1 atom is 4 third pi root 3 by a for whole cube and the volume of the unit cell is a cube once again. So, if you do this calculation you will find that the result comes out to be 0.68, it means this is slightly more compact packing compared to the simple cubic lattice.

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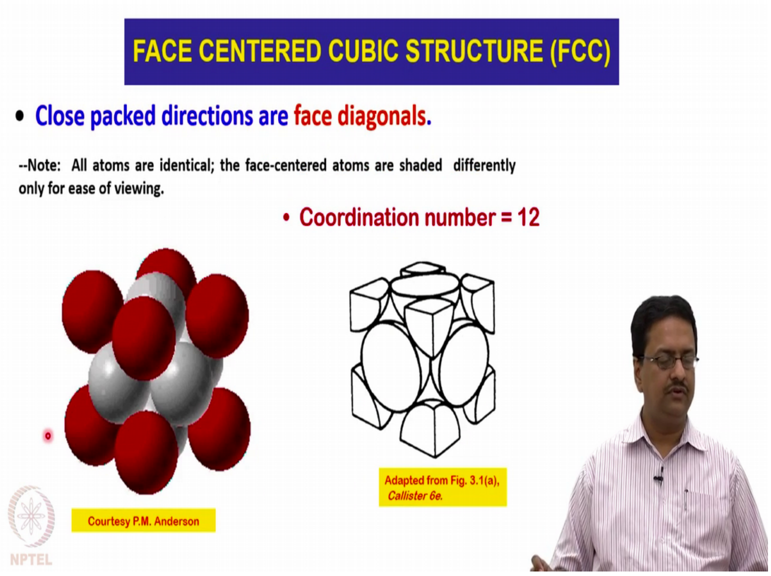

FACE CENTERED CUBIC STRUCTURE (FCC)

- Close packed directions are face diagonals.

--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

- Coordination number = 12

Courtesy P.M. Anderson

Adapted from Fig. 3.1(a), Callister 6e.

So, now if we try to see what happens when it is face centered cubic lattice, in case of a centered cubic lattice the closed pack direction is your face diagonal; which means along this face the atoms are connected to each other. So, in case of face centered lattice the coordination number is 12; that means, every atom has 12 nearest neighbors associated with it.

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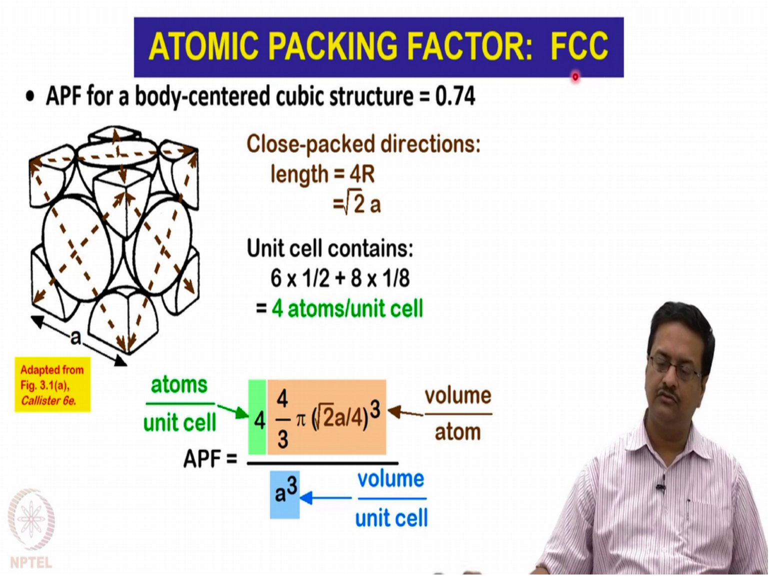

ATOMIC PACKING FACTOR: FCC

- APF for a body-centered cubic structure = 0.74

Close-packed directions:
length = 4R
$= \sqrt{2}\,a$

Unit cell contains:
6 x 1/2 + 8 x 1/8
= 4 atoms/unit cell

Adapted from Fig. 3.1(a), *Callister 6e.*

$$\text{APF} = \frac{4 \quad \frac{4}{3}\pi(\sqrt{2}a/4)^3}{a^3}$$

$\frac{\text{atoms}}{\text{unit cell}}$ → 4

$\frac{\text{volume}}{\text{atom}}$ → $\frac{4}{3}\pi(\sqrt{2}a/4)^3$

$\frac{\text{volume}}{\text{unit cell}}$ → a^3

So, in case of this face centered cubic the atomic packing factor for FCC turns out to be 0.74 highest among all the 3. So, how do you calculate that you see again the face diagonal which is root 2 a corresponds to R 2 R and R; which means the length of the what the face diagonal turns out to be 4 R which is equivalent to root 2 a and then the unit cell contains 4 atoms per unit cell. How see the face atoms contribute half and there are 6 such faces, so those 6 such faces contribute to 6 such faces contribute to 3 and 8 corner atoms contribute 18 th each. So, 8 into 18 th gives you 1.

So, 3 plus 1 equal to 4, so then we calculate atomic packing factor again in the same manner 4 into 4 third pi R cube here R equal to root 2 a by 4. So, then if you compute this turns out to be 0.74, so this is the maximum that 1 can have in case of these 3 different packings.

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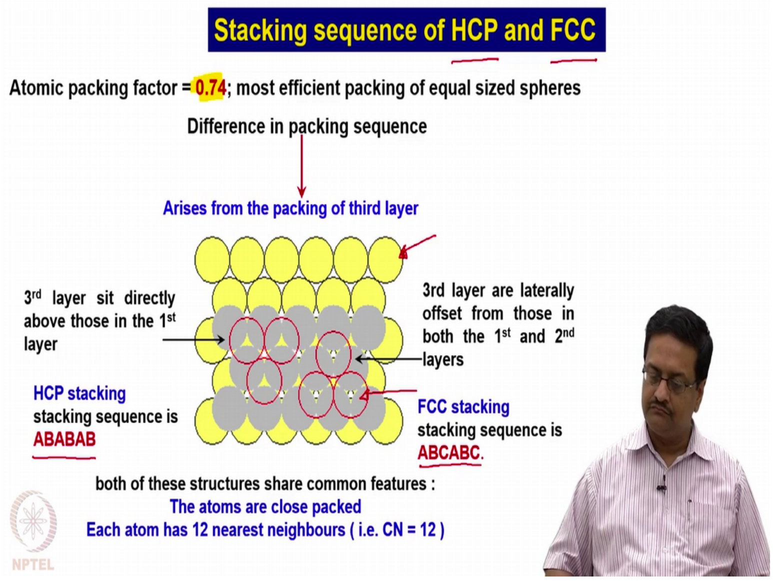

Stacking sequence of HCP and FCC

Atomic packing factor = 0.74; most efficient packing of equal sized spheres

Difference in packing sequence

Arises from the packing of third layer

3rd layer sit directly above those in the 1st layer

3rd layer are laterally offset from those in both the 1st and 2nd layers

HCP stacking
stacking sequence is
ABABAB

FCC stacking
stacking sequence is
ABCABC.

both of these structures share common features :

The atoms are close packed

Each atom has 12 nearest neighbours (i.e. CN = 12)

So, in case of face centered cubic and hexagonal closed packed structures this atomic packing factor is turned out to be 0.74 and this is the highest packing fraction that 1 can achieve. The most efficient packing for equal sized this spheres, but now we need to understand the stacking in HCP that is hexagonal close packed and stacking in FCC the face centered close pack if we assume that the first layer is placed like this, then there are 2 ways the second layer can be placed. So, when you place the second set of atoms like that in gray it is like ABABAB packing.

So, the third layer can be placed on exactly on the yellow or third layer can be placed like the red; so that means, there are 2 ways 1 can put the third layer and that third layer decides whether it is hexagonal close pack or a face centered close parking structure. So, in case of hexagonal close packing it is ABABAB type of packing and in case of FCC it is ABC ABC ABC type of packing. So, both of these structures here common features the atoms are closely packed each atom has 12 nearest neighbor, so that is the coordination number 12, to see this packing we can use a simple demonstration.

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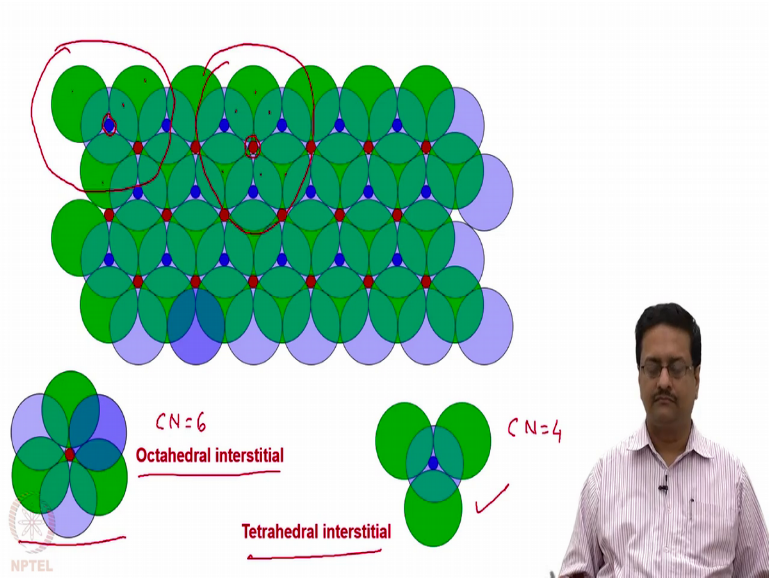

This green layer indicates the lowermost level in that we are designating some of these points with blue dots and we will see that they end up showing as tetrahedral interstitials. So, now I am placing 1 layer of red dots which are alternate with respect to the blue and the it will correspond to the octahedral interstitials. So, once we place the another layer of the spherical atoms which are now represented in blue, you see that when we look at this region here we have 3 greens 1 blue and then at the center we have 1 blue.

So, that central blue atom corresponds to the tetrahedral interstitial like this, if we concentrate at a different location where you can see this arrangement; for example, when we try t o see here the arrangement at this point. You have 3 green atoms at the lower end layer 3 blue atoms at the upper layer and in between these 6 atoms you have 1 central red atom located at the octahedral interstitial.

So, when you place 2 layers of atoms you generate two different types of sites one is called the tetrahedral site or tetrahedral interstitial the other point is octahedral site or octahedral interstitial. What is the difference the tetrahedral interstitial has coordination number equal to 4, while the octahedral interstitial has a coordination number 6.

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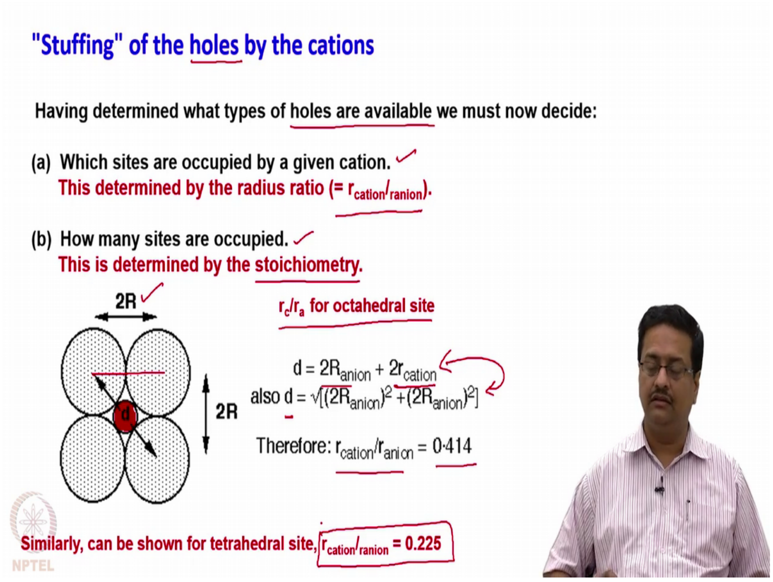

"Stuffing" of the holes by the cations

Having determined what types of holes are available we must now decide:

(a) Which sites are occupied by a given cation. ✓
This determined by the radius ratio (= r_{cation}/r_{anion}).

(b) How many sites are occupied. ✓
This is determined by the stoichiometry.

r_c/r_a for octahedral site

$d = 2R_{anion} + 2r_{cation}$

also $d = \sqrt{[(2R_{anion})^2 + (2R_{anion})^2]}$

Therefore: $r_{cation}/r_{anion} = 0{\cdot}414$

Similarly, can be shown for tetrahedral site, $\boxed{r_{cation}/r_{anion} = 0.225}$

So, these interstitials are also termed as holes or octahedral holes or tetrahedral holes and we can think of generating different ceramic structures where you have a cation and anion and in general the anions are larger in size cations are smaller in size and as a result the cations occupy these different interstitial sites.

So, when we have determined that there are different types of holes available, now we must decide which sites are occupied by a given atom and how many sites are occupied. The first point which sites are occupied by a given atom is decided by the radius ratio that is the ratio of the radii of cation to anion; whereas, the number of sites inside the lattice occupied by a number of atom is decided by the stoichiometry and charges on those cations and anions this we will see in future slides. So, let us see what is the ideal radius ratio for cation and anion for octahedral site. So, in case of octahedral site the central atom which is marked here which is marked here in red, the central atom is connected to 4 atoms on this plane.

So, the distance d from the center of 1 anion 2 the centre of other anion through the cation that distance d is equal to 2 R of cation plus 2 R of sorry 2 R of anion and 2 R of cation. So, once again this distance d can be calculated as this is the this the distance is 2 R as we indicated. So, the value d is 2 R and anion square plus 2 R anion square and square root of that. Therefore, we can equate these 2 equations and calculate the ideal value for cation to anion radius ratio for an octahedral site.

In the same manner it can be shown for tetrahedral site the value is 0.225, I would like to leave it to you to determine how can you calculate this value. So, now we apply this radius ratio rule.

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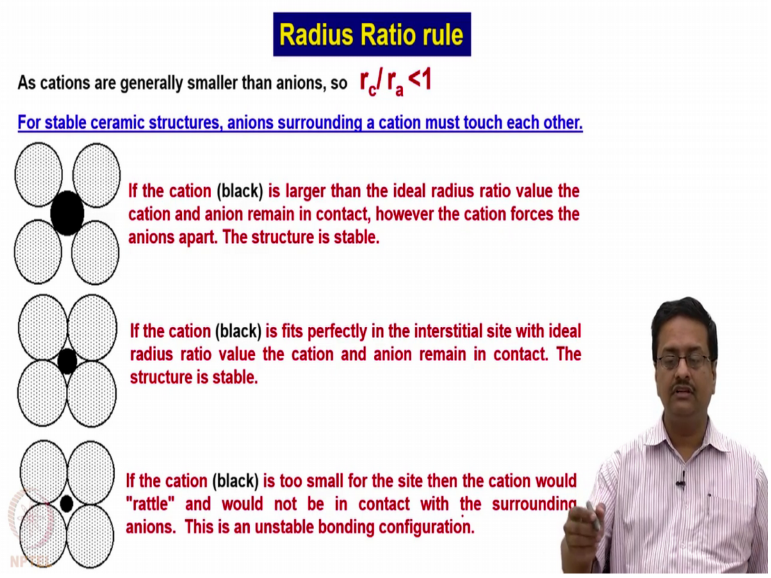

Radius Ratio rule

As cations are generally smaller than anions, so $r_c/r_a<1$

For stable ceramic structures, anions surrounding a cation must touch each other.

If the cation (black) is larger than the ideal radius ratio value the cation and anion remain in contact, however the cation forces the anions apart. The structure is stable.

If the cation (black) is fits perfectly in the interstitial site with ideal radius ratio value the cation and anion remain in contact. The structure is stable.

If the cation (black) is too small for the site then the cation would "rattle" and would not be in contact with the surrounding anions. This is an unstable bonding configuration.

As we know the cations are generally smaller than anions, so in general rc by ra is smaller than 1. So, now for as to have a stable ceramics structure and I am surrounding a cation must touch each other. So, now there can be 4 different situations in the situation 1 where the cation is touching all the 4 anions, but the cation is large enough to drive these anions away and generating a gap between the anions.

So, this is 1 of the stable conditions where the structure is stabilized, here is slightly the cation is slightly larger than ideal radius ratio value of that particular crystal packing. If the cation is perfectly fitting inside the interstitial site; that means, the cation and anions are touching in along the diagonal anions are also touching each other in all the 4 edges.

So, this is the ideal situation of ideal ratio of cation to anion and this is the most stable structure. But once the cation is too small it is not touching any of the anions and the anions can only touch each other, in that situation the cation can rattle; that means, the cation can vibrate inside the lattice as a result the structure becomes unstable and we do not have a large number of structures having this type of arrangements.

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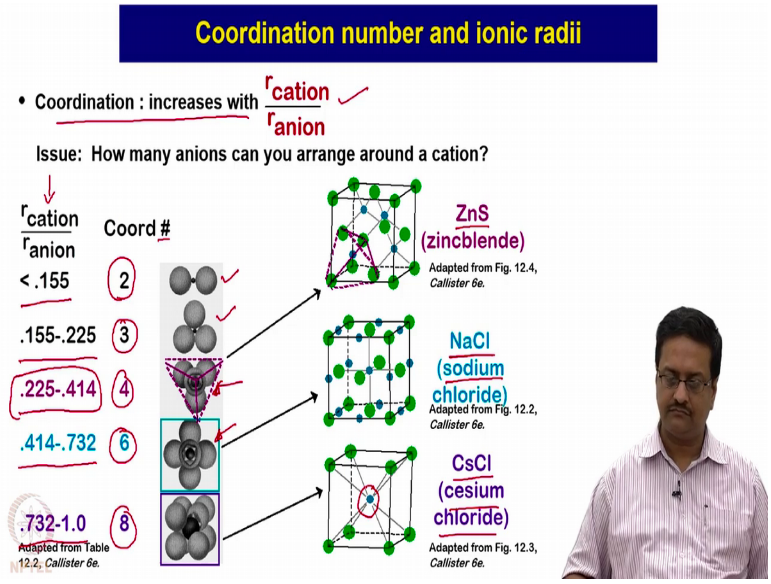

Coordination number and ionic radii

- Coordination : increases with $\frac{r_{cation}}{r_{anion}}$

Issue: How many anions can you arrange around a cation?

$\frac{r_{cation}}{r_{anion}}$	Coord #
< .155	2
.155-.225	3
.225-.414	4
.414-.732	6
.732-1.0	8

Adapted from Table 12.2, *Callister 6e.*

ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 6e.*

NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister 6e.*

CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 6e.*

So, now we need to learn: what is the coordination number and what is this relationship with ionic radius. So, coordination number increases with r c by r a that is the radius of cation by radius of anion. So, here we have a small table, on the first column we are giving the value for r cation versus r anion the ratio the corresponding coordination number and a probable structure representing that.

So, when it is this cation to anion ratio is 0.15; that means, cation is extremely small compared to the anion then the coordination number is 2 and you see a situation like this. When this coordination number falls between 0.15 and 0.225 the coordination number is found to be 3 and the situation arises like that.

The next higher ratio is between 0.25 to 0.14 0.41 this corresponds to the coordination number 4. So, when you have 4 coordinated system coordination number 4 this gives rise to a tetrahedral interstitial and that is seeing in case of zinc blende structure Zns structure. We will discuss the structure in detail in future slides, but what we can and see here is that you have sulfide atoms occupying the face centered positions the 8 corners and face centered positions and zinc atom occupying the alternate interstitial sites those are tetrahedral interstitial sites.

So, now when the radius ratio increases to about 0.41 to 0.73 the coordination number 6 is achieved and it represents the octahedral arrangement and that is seen in the most common crystal structure of sodium chloride; sodium chloride structure as you know is interpenetrating face centered lattice we will see it through an animation as well in future slides.

When the radius ratio is close to 1 then the coordination number increases to 8, which means you get a structure like cesium chloride structure where you have a simple cubic lattice of cesium sorry simple cubic lattice of chloride and a cesium atom sitting in the middle. So, this is another example of the important simple cubic lattice which is actually interpenetrating simple cubic lattice.

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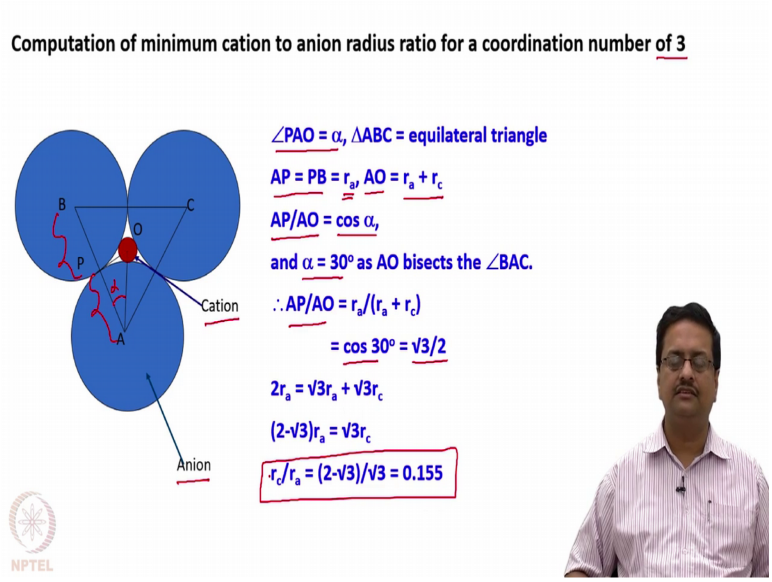

Computation of minimum cation to anion radius ratio for a coordination number of 3

$\angle PAO = \alpha$, ΔABC = equilateral triangle

$AP = PB = r_a$, $AO = r_a + r_c$

$AP/AO = \cos\alpha$,

and $\alpha = 30^\circ$ as AO bisects the $\angle BAC$.

$\therefore AP/AO = r_a/(r_a + r_c)$

$= \cos 30^\circ = \sqrt{3}/2$

$2r_a = \sqrt{3}r_a + \sqrt{3}r_c$

$(2-\sqrt{3})r_a = \sqrt{3}r_c$

$\boxed{r_c/r_a = (2-\sqrt{3})/\sqrt{3} = 0.155}$

So, now let us see how 1 can calculate the radius ratio cation to anion ratio for a coordination number 3. So, here we have 3 3 anions the blue ones are the anions and we have a red cation at the center. So, now if we construct a triangle ABC which is equilateral triangle, in that we have the angle PAO as alpha what is that we have dropped a perpendicular from O to AB and maybe it OP. So, as a result AP equal to PB AP equal to PB equal to the radius of the anion and AO is nothing but radius of the anion plus radius of the cation.

So, now if we do AP by AO which is cos alpha and alpha is 30 degree because this is an equilateral triangle and the line AO bisects this BAC angle. So, it is the angle of 60 degree is bisected that means it is 30 degree. So, what we can do is AP by AO equal to AP is ra AO is ra plus rc which is again equal to cos 30 degree which means roots 3 by 2.

So, then if we simplify this we can then calculate the ideal radius ratio for a coordination number 3, this concept can be utilized when you try to calculate the a ideal radius ratio for the tetrahedral interstitial; when you have a tetrahedral interstitial filled with a cation and you have 4 anions forming a tetrahedral. You would need to utilize this type of simple geometrical method to find out the corresponding radius ratio for the for the cation and anion in case of tetrahedral structures.

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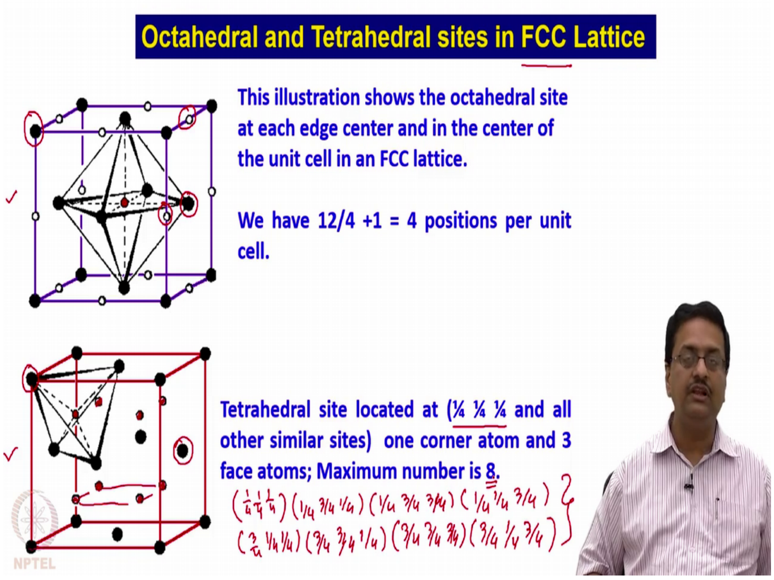

Octahedral and Tetrahedral sites in FCC Lattice

This illustration shows the octahedral site at each edge center and in the center of the unit cell in an FCC lattice.

We have 12/4 +1 = 4 positions per unit cell.

Tetrahedral site located at (¼ ¼ ¼ and all other similar sites) one corner atom and 3 face atoms; Maximum number is 8.

$(\frac{1}{4}\frac{1}{4}\frac{1}{4})(1/4\ 3/4\ 1/4)(1/4\ 3/4\ 3/4)(1/4\ 1/4\ 3/4)$
$(\frac{3}{4}\ 1/4\ 1/4)(3/4\ 3/4\ 1/4)(3/4\ 3/4\ 3/4)(3/4\ 1/4\ 3/4)$

So, now when we try to understand the tetrahedral and octahedral sites for face centered cubic lattice, here in this figure the figure above has a face centered lattice where you have black dots at 8 corners and 6 faces representing the face centered cubic lattice. So, in that in the middle we have identified 1 we have identified 1 point which is the octahedral hole or octahedral site, the octahedral site indicates that this atom has coordination number 6 and there are 12 such octahedral sites present in these lattice.

So, because you have 1 2 3 4 all the edge centers all the edge centers and all the edge centers, so total 12 octahedral sites along the edge centers plus the 1 which is at the center of the lattice.

So that means, you have 13 lattice sites 13 octahedral lattice voids. Now this corn edge center sites are shared by 4 unit cells as you can understand this 1 is shared by this unit cell the 1 which is on the next then on the top this side and then on the top on the right hand side.

So, every corner the every edge center lattice site is shared by 4 unit cells. So, each of them contribute 14; that means, you have 12 such sites everyone contributing 14 is equal to 3 plus 1 equal to 4 positions per unit cell. Now, if we look at the lower representation of the same face centered lattice where; you have atoms at 8 corners and the atoms at 6 faces. So, now the positions which are marked here in red or this 1 this 1 this 1 and so on and all these points correspond to the tetrahedral sites. What are the coordinates of those sites I have written 1 here actually these sites are one forth one forth 14.

Suppose this 1 then you have 1 more which is one forth 34 14 then 14 34 3 fourth and 14 14 34 these are those 4 lattice point in the lower region and the upper regions are 34 14 14 34 34 14 34 34 34 and 34 14 34. So, inside this lattice there are 8 such locations which are tetrahedral sites and each 1 of those is inside the unit cell they are not shared by other unit cells unit cells like the face like the edge center atoms in case of the octahedral sites. So, they correspond to the 8 number of cations that can be placed inside the lattice.

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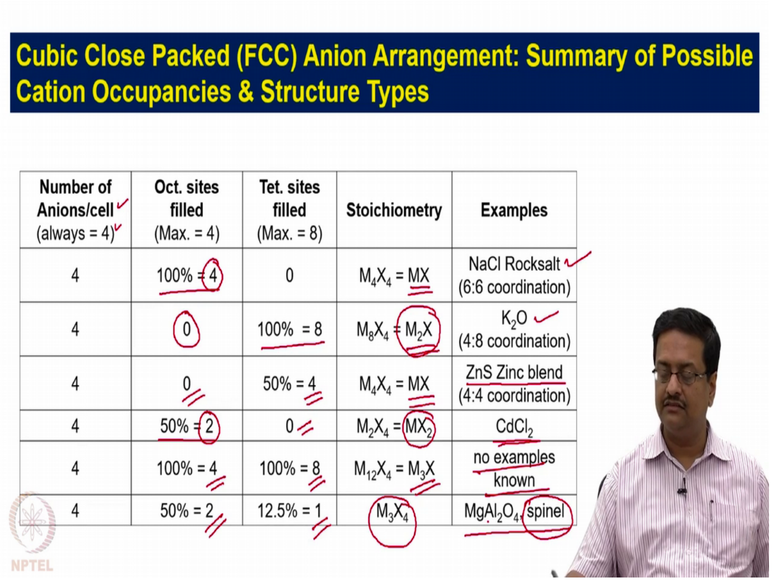

Cubic Close Packed (FCC) Anion Arrangement: Summary of Possible Cation Occupancies & Structure Types

Number of Anions/cell (always = 4)	Oct. sites filled (Max. = 4)	Tet. sites filled (Max. = 8)	Stoichiometry	Examples
4	100% = 4	0	M_4X_4 = MX	NaCl Rocksalt (6:6 coordination)
4	0	100% = 8	M_8X_4 = M_2X	K_2O (4:8 coordination)
4	0	50% = 4	M_4X_4 = MX	ZnS Zinc blend (4:4 coordination)
4	50% = 2	0	M_2X_4 = MX_2	$CdCl_2$
4	100% = 4	100% = 8	$M_{12}X_4$ = M_3X	no examples known
4	50% = 2	12.5% = 1	M_3X_4	$MgAl_2O_4$ (spinel

So, in case of cubic close packed structures the FCC structures anion arrangements and the summary of possible cation there is listed here. So, number of anions per unit cell is always 4 as you can see and then if we start filling the octahedral sites if we feel all the octahedral sites; that means, 100 percent of octahedral sites are filled you have 4 cations as well.

Then the stoichiometry turns out to be MX and the example is a sodium chloride structure the other extreme point is when there are no octahedral site occupied. But all the tetrahedral sites occupied we get a formula of M2X and we see a K2 or structure of which is like this a face centered cubic lattice with a different arrangement of cation and anions giving rise to different molecular formula or stoichiometric and it is one of the example is for K2O. In case of third set where there is no octahedral site occupied and only 50 percent of the tetrahedral sites occupied, once again we end up getting MX type of stoichiometry 1 is to 1, but here the interstitials are tetrahedral interstitials which are filled and 50 percent of those are filled.

So, the cation anion pair is an example of that is kind of structure is zinc sulfide or Zns. When the corresponding reverse happens that is 50 percent of the octahedral sites are occupied and not a single tetrahedral site is occupied. So, you have 2 cations and 4 anions that means; you have MX 2 type of structure so this is an example of cadmium chloride structure. The other theoretical possibility is both tetrahedral octahedral and tetrahedral sites are 100 percent occupied. So, one should have this type of formula m 3 x, but till now there are no such known structures having these 2 type of coordination geometry.

The last type that 1 can think of is 50 percent occupied in case of octahedral site and 12.5 percent occupied in the tetrahedral sites, the formula turns out to be m 3 x 4 and there is one type of example a structural type called spinels; which we will discuss in the next class this MgAl2O4 corresponds to a spinel structure where a part of the octahedral sites are filled and a very very small portion of the tetrahedral sites are filled.

So, in today's lecture we have learnt about the atomic pack packing factors for simple cubic body centered cubic face centered cubic, we have learned how to calculate the radius ratios for different types of coordination's for cation and anion and then we understood: what are the different types of interstitials tetrahedral and octahedral interstitials. So, from here we will continue in the next lecture.