Introduction to Materials Science and Engineering

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Lecture – 31
Ionic solids

So, today we will discuss the structure of ionic solids. We have already discussed structure of metals. So, we have discussed metals.

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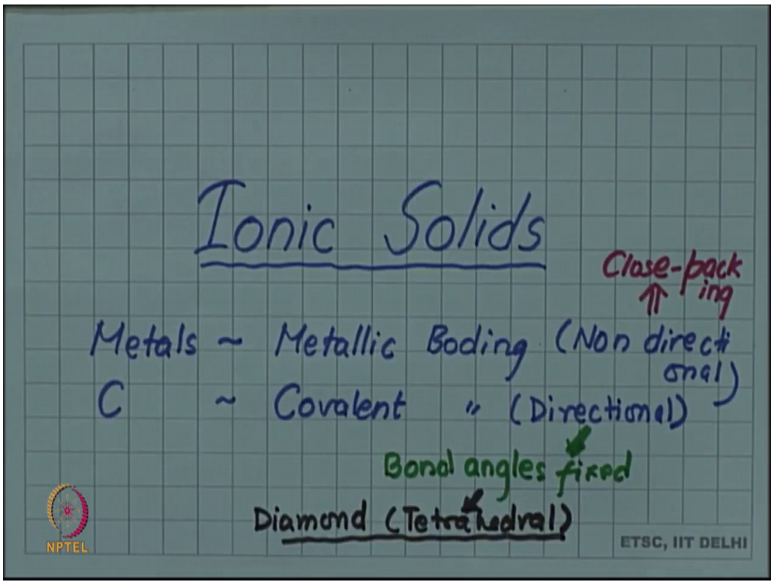

Ionic Solids

Close-packing
⇑

Metals ~ Metallic Boding (Non directional)
C ~ Covalent " (Directional)

Bond angles fixed

Diamond (Tetrahedral)

So, metals are metals have metallic bonding, if you look at it in terms of bonding. We have not talked about bonding in any detail just for reference. So, metals have metallic bonding. Then we discussed the structure of carbon in form of graphite, diamond, nanotube and fullerene. Carbon is a typical element to represent covalent bonding. We have not yet discussed anything which is ionically bonded. So, that will be the topic of this presentation. So, let us look at ionic solids.

So, the difference here you in the metallic bonding; metallic bonding was non directional this is what led to remember close-packing since it is non directional you can flap back as closely as possible. Whereas, in covalent bonding the carbon structures were not close packed because they are strongly directional; directional bonding and by directional bonding we mean if you remember that the bond angles are fixed. So, you cannot do closed-packing.

Because you have to keep bond angles fixed. For example, in diamond it was the tetrahedral bonding in the diamond tetrahedral bonding, which means around one carbon you can place only four other carbons where is a closed-packing would have allowed if you remember closed-packing would have allowed 12 atoms around a given atom, but diamond demands only 4 around itself because it will not accept anything other than the tetrahedral bonding.

So, now let us discuss ionic bonding in this slide ionic solids.

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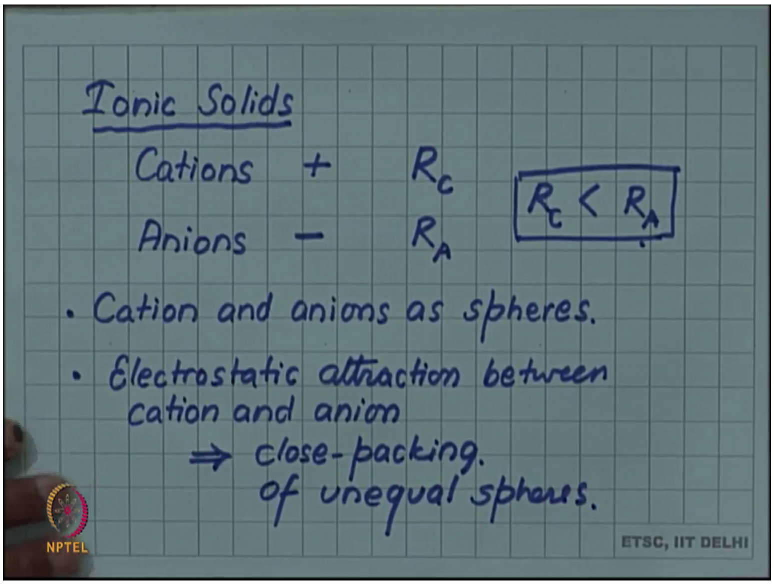

Ionic Solids

Cations + R_C

Anions − R_A

$\boxed{R_C < R_A}$

- Cation and anions as spheres.
- Electrostatic attraction between cation and anion
  ⇒ close-packing of unequal spheres.

They are made up of cations and anions. Cations are attracted to cathode, so they are positively charged. The anions are attracted to anode, so they are negatively charged; because of the positive it to get the positive charge they lose electrons. So, usually their size let me call it R cation radius of the cation, R anion the radius of the anion and usually, cations will be smaller in size then anion because anion is gaining electrons. So, it may add extra orbital to gain those electrons to form anion. So, the size will increase whereas, cation if you have one or two electrons in the outer shell and it loses that so then lose one whole orbital.

So, the size will reduce. So, cations are usually smaller than anions this is an important fact when we want to contrast this with the metallic structure, because the metallic elements all atoms were of equal size, but here now we have to think about ions of different sizes. We can is again model cations and anions as spheres. Cations and anions as spheres also there will be electrostatic attraction between cation and anion.

So, they will like to come close together. So, they will like to come close together. So, this will also be we can model the structure as close-packing of the as spheres, so this also indicates close-packing; however, because of this inequality in the size this is close packing of unequally spheres. Also it cannot be a totally random packing; it cannot be a totally random packing because cations will like to be attracted to anions and anions to cations whereas, anion anion will ripple and cation cation will ripple.

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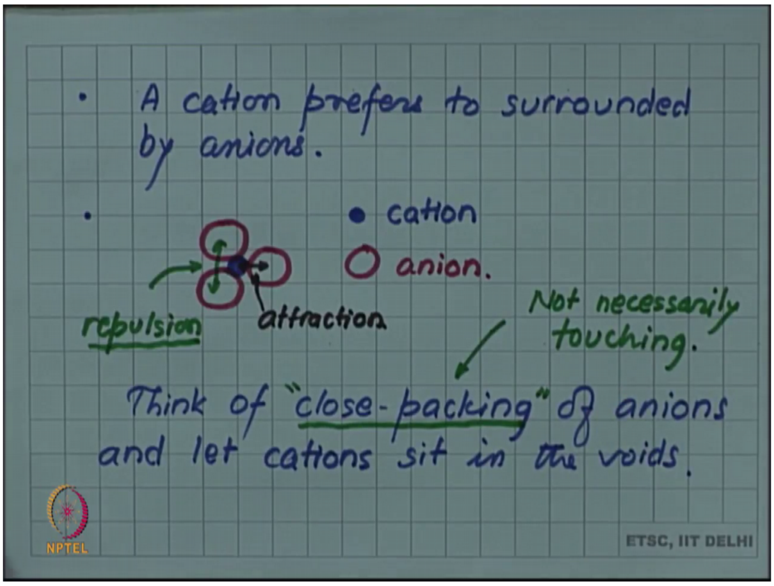

- A cation prefers to surrounded by anions.
- ● cation
  O anion.

repulsion

attraction

Not necessarily touching.

Think of "close-packing" of anions and let cations sit in the voids.

So, any given cation cation prefers to be surrounded by anions around that cation you have a cage of anion who means if I try to draw schematically if I have a cation, then it will attract anions around it this is small cation, large anion. Now anions also are repelling. So, they will like to maximize this distance; this is repulsion whereas; obviously, there is attraction between anion and cation. So, they are as close as possible.

So, the structure the way the structure is model is to think of a closed-packing of anions and let cations sit in the voids. Now it will not be exactly close-packing, because remember we are saying that there is a repulsion we are saying there is repulsion and we are also saying close packing which means they will be as close as possible.

So, because of this repulsion this close-packing will be not exactly close-packing, but something like close-packing. So, anions can come close, but they need not be necessarily touching. So, let us mark that close-packing, but not necessarily; not like metal not necessarily touching. So, let us look at a start with a very simple anion cage and that is a triangular cage.

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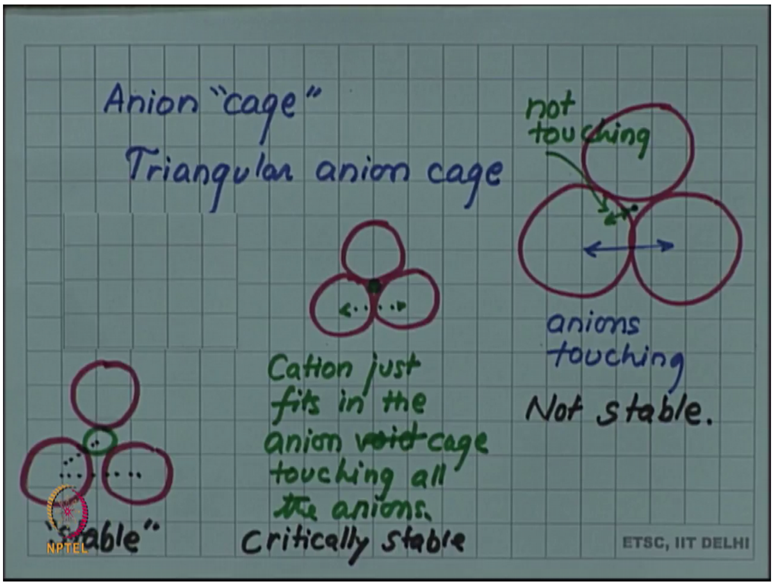

Call this anion cage. So, a triangular anion; by this I mean that I will take my anions sitting on the vertices of an equilateral triangle. And let me introduce a very small very small cation there. So, its not even. So, anions are touching you can see anions are touching anions touching whereas; cation and anion are not touching. So, which means this is exactly opposite of what we want; because anion anion there is a repulsion, but they are very close and whereas, cation anion have attraction, but they are not so close. So, this is not a favorable situation.

So, we label this as not a stable. Let me then consider the next case where it just fits in the void. Cation just fits in the anion void or anion cage I was calling it touching all the surrounding anions. So, cation, anion touching there is an attraction and they are touching. So, that’s good we have minimized the distance. So, at least we have achieved some more stability than what we had discussed here.

Because, now cation and anion are in contact whereas, still we have not achieved a separation between anion anion which is not good from electrostatic energy point of view. So, this we will call critically stable it its little better than not a stable, but actually it is a still not fully stable. And, now in the third case; let me try to make a really comparatively large cation which forces the anion out of contact it forces anion out of contact. This is a very good news this is a stable I will call this stable, because now the ions which are attracting are as close as possible because they are touching and ions which are repelling have also been separated out.

So, this will be the stable situation. So, which means I can think of a radius ratio I can think of a critical radius ratio.

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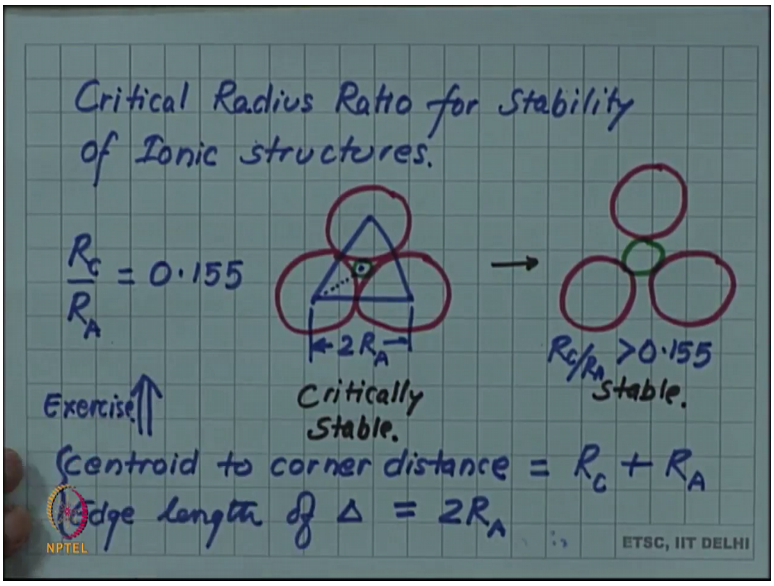

Critical Radius Ratio for Stability of Ionic structures.

$\frac{R_c}{R_A} = 0.155$

Centroid to corner distance $= R_c + R_A$

Edge length of $\Delta = 2R_A$

Ratio for a stability of ionic structures and what is that critical we have already seen that; let me draw it again already seem that in a situation like this where the central cation just touches the outside anion this is the critical situation, critically stable and what we really want to make it stable make the cation is still larger. So, that anions are separated out of contact. So, this is what we called a stable. So, we can easily solve the geometry of this; this is an equilateral triangle and this is the distance of the centroid to the corner of the equilateral triangle.

So, centroid to corner distance should be R cation plus R anion whereas, the edge length of the triangle is equal to two times R anion, this is two R anion. And then if you use the geometry of equilateral triangle, you can find the ratio of R c to R a. I leave this as an exercise to you to do if you do that what you will find that R c by R a for this critically stable structure comes out to be 0.155 which means for a stable structure we will need R c by R a to be greater than 0.155 for a stable structure should be greater than 0.155. So, please do this as an exercise a simple geometry in geometrical exercise.

So, which means if we now consider this is what we call a triangular coordination triangular coordination of anions around a cation.

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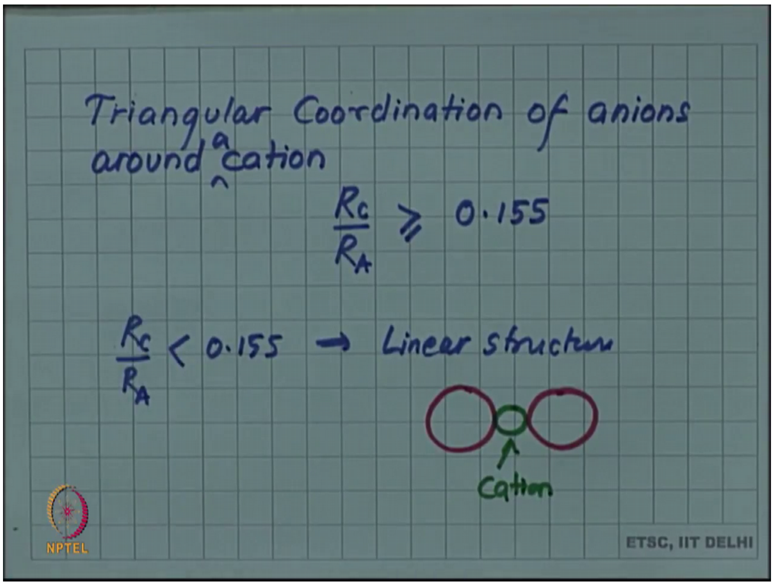

Triangular Coordination of anions around a cation

$$\frac{R_c}{R_A} \geqslant 0.155$$

$$\frac{R_c}{R_A} < 0.155 \rightarrow \text{Linear structure}$$

So, this was the triangular coordination and for triangular coordination we found that the stability requires R c by R a to be greater than 0.155 equal to 0.155 the critical situation. So, we include that also; what will happen if the radius ratio is less than this? So, then the triangular coordination is not a stable. So, maybe you will have a linear molecule. So, R c by R a less than 0.155 will imply linear structure that is the coordination number of 2 if the cation will prefer to have only 2 anions.

So, if you now think; if you then this was a planar case and it was a in 2D, but the structure will; obviously, be 3D. So, if you come to now three-dimensional structure to now come to three dimensional structure and think of the next higher coordination number. So, that is 4; 4-coordination or tetrahedral coordination of anions around a cations.

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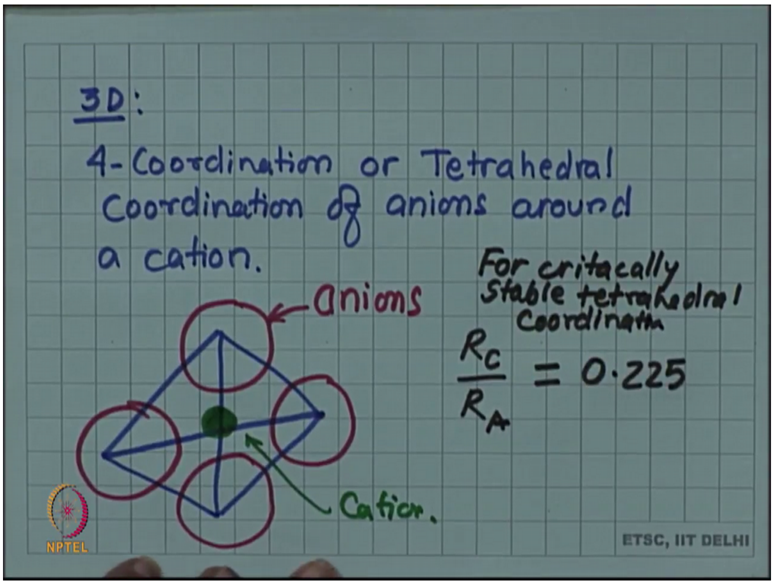
3D:

4-Coordination or Tetrahedral Coordination of anions around a cation.

For critically stable tetrahedral coordination

$$\frac{R_C}{R_A} = 0.225$$

This geometry we have already done. When we were discussing close-packed structure we came to tetrahedral voids, we said that 4 atoms can be sitting on the vertices of a tetrahedron, this case there will be anions and there will be a central cation. And if the anions are touching if anions are touching you have already found what the largest cation which can sitting is? So, in that ratio let me now write it as cation, anion ratio R c by R a is equal to you remember it was 0.225 that was the largest sphere which can fit into a tetrahedral void we derived this as a close-packed structure review that derivation you should be able to do this.

So, for critically stable; so for critically stable tetrahedral coordination, this will be the situation, the stable tetrahedral coordination again following our argument from the triangle because in the critically stable one anions also will be touching we have allowed anions to form a close packed structure.

So, anions also are touching, but we don’t want anion should touch; if you don’t want anions to touch R c should be larger than this critical value, because then it will open out the tetrahedron and will force anions to separate and forcing anions to separate because they are like charged is a good thing. So, actually is stable structure get for a tetrahedral coordination will require a value larger than this.

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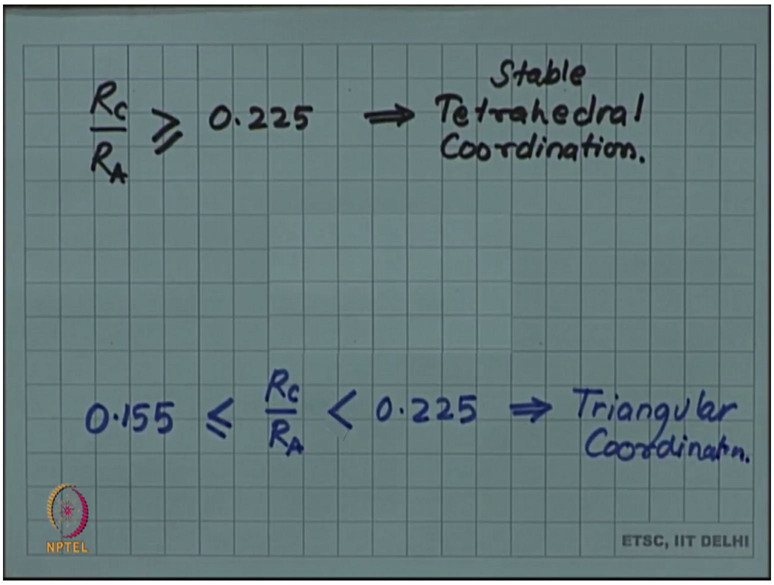

$\frac{R_c}{R_A} \geqslant 0.225 \Rightarrow$ Stable Tetrahedral Coordination.

$0.155 \leq \frac{R_c}{R_A} < 0.225 \Rightarrow$ Triangular Coordinatn.

So, by the same argument if we now write R c by R a greater than 0.225 this will imply tetrahedral coordination and you can include equal as a critical stability stable stable tetrahedral coordination.

So, now what you have you got the ratio 0.155 for triangular you are getting a ratio 0.225 for tetrahedral. If you put these two together you will get both the upper and lower bounds for triangular coordination. So, if R c by R a is less than this value 0.225 then tetrahedral coordination will not be stable for anions will not be able to surround a cation. So, less than 4 is possible and we have less than 4 is 3 and for 3 we have already seen that it should be greater than equal to 0.155. So, for triangular coordination we have found both the upper and lower bounds by this analysis. So, you can carry on this analysis for other coordination so for octahedral coordination.

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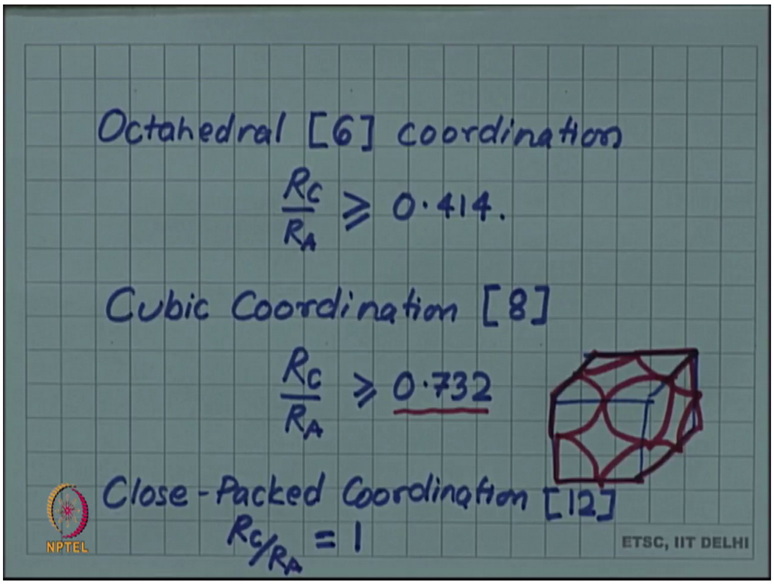

Octahedral [6] coordination

$$\frac{R_C}{R_A} \geqslant 0.414.$$

Cubic Coordination [8]

$$\frac{R_C}{R_A} \geqslant \underline{0.732}$$

Close-Packed Coordination [12]

$$R_C/R_A = 1$$

Remember the octahedral voids which have 6 vertices. So, 6 anions will be there

So, octahedral coordination will require an R c by R a; I am now writing it quickly without much discussion, because I am just reminding you of the octahedral void in cubic close-packed structure where we did this calculation. So, it comes out to be 0.414 for a stable octahedral coordination it will be 0.414 we never discussed a cubic void, but you can think of a cubic coordination, that is 8 anions around a cation and if you do a calculation you should be able to show that R c for R a for this will be 0.732.

We never discussed a simple cubic void, but you can imagine one that if you make if you make a cube and place atoms on all the corners of this cube something like this, then what will be the largest sphere? Which will be able to fit in the cubic void that is at the center of the cube and that number will come out to be 0.732?

So, for cubic coordination R c by R a again for R c by R a 0.732 anions will be touching and if you want not for them not to touch then you can increase the radius ratio if it is larger then the cation is larger and will force open this cube and anions will not be touching. So, for cubic coordination the number is 0.732.

And finally, trivially to just close this discussion we can write for close-packed coordination let us say; that is the maximum possible that you know largest number of a spheres which you can give around as given sphere is 12. So, in this case all are equally spheres so; that means, cation and anion ratio should be equal to 1, which will hardly be the case, but from geometrical point of view we can write yes.

So, let us summarize what we have said till now in terms of radius ratio and coordination number. So, let us have a column of radius ratio.

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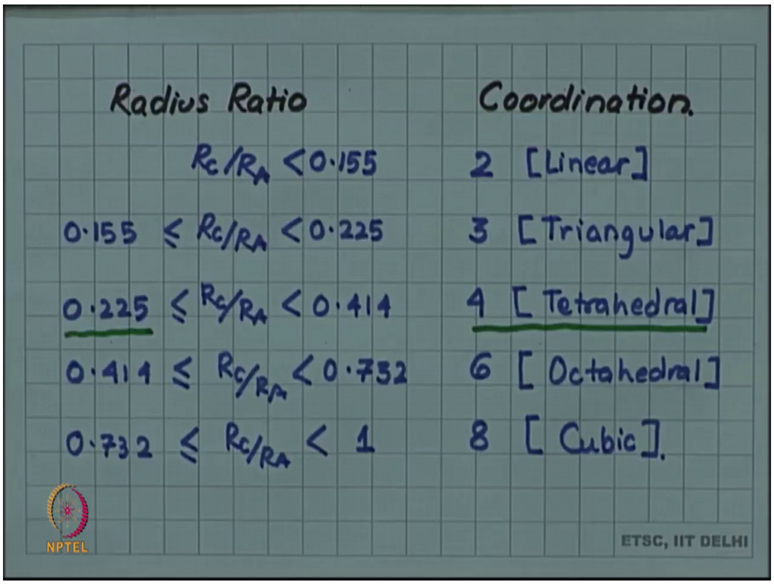

Radius Ratio	Coordination
$R_c/R_A < 0.155$	2 [Linear]
$0.155 \leq R_c/R_A < 0.225$	3 [Triangular]
$0.225 \leq R_c/R_A < 0.414$	4 [Tetrahedral]
$0.414 \leq R_c/R_A < 0.732$	6 [Octahedral]
$0.732 \leq R_c/R_A < 1$	8 [Cubic].

And let us have a column of coordination and now to what we have seen that if you have radius ratio R c by R a less than 0.155 then you have a coordination of 2 or what we call a linear coordination. The next critical value of R c by R a 0.225 greater than equal to 0.155 this gives you 3 triangular coordination. We are just summarizing what we discussed in the previous slides. So, we are just rewriting everything in a single table. So, if you have greater than equal to 0.225, but less than 0.414 then you have a coordination of 4 and that is tetrahedral. And then when you have 0.414 to 0.732 you will have a coordination of 6 which is octahedral; from 0.732 to 1 you will have a coordination of 8 which is cubic.

So, this table summarizes what we have discussed about the structure and it tries to predict essentially what it is try trying to do this table is to predict the kind of coordination which you expect simply on the basis of radius ratio. So, this will not always be you don't take this as some sort of fundamental law or which has to be always true, but its a kind of rough prediction based only on the geometrical size of the cation and anion. You know that the crystal structure or the bonding is a much more complex and many more phenomena happens, but this is a simple geometrical formulation which helps us in predicting the coordination number according to just the size ratio of cation anion; one thing which sometimes causes confusion to students.

So, let us look at the tetrahedral coordination. We find that 0.225 is the minimum radius ratio at which the tetrahedral coordination becomes stable, but the same number we derived when we were studying the cubic close-packed structure the same number we derive as the maximum size of a sphere which will fit in the tetrahedral void the two facts are not consistent, because that was our argument for deriving the radius ratio for tetrahedral void.

But sometimes it creates confusion that whether this is a minimum or maximum for tetrahedral coordination. So, 0.225 is the maximum sized sphere which will fit in a tetrahedral void in cubic or hexagonal close-packed structure, but it is the minimum radius ratio at which the tetrahedral low coordination becomes stable same argument goes for 0.414 it is the largest sphere which will fit in a tetrahedral void in close-packed structure, but it is the minimum ratio at which the octahedral void becomes stable.

So, with this we finish this session we will have another session on ionic solids where we will look at the application of these radius ratio to some real structures.