Introduction to Materials Science and Engineering
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Lecture - 21
Voids in close-packed structures

Hello, let us continue our discussion on the geometry of Close-Packed Structure. In this video we will look at the voids in the close-packed structure. We have already looked at the lattice and motif structure of various crystal structures which form by close packing in particular 2 of them AB, AB and ABC, ABC where AB, AB form hexagonal close packed and ABC, ABC form cubic close packed.

Now in these close packed layers between the atoms there are spaces available these spaces can be can accommodate other elements or other atoms. So, in the structure of alloys or solid solutions which we will come to soon these voids are very important. So, let us look at the geometry of these voids.

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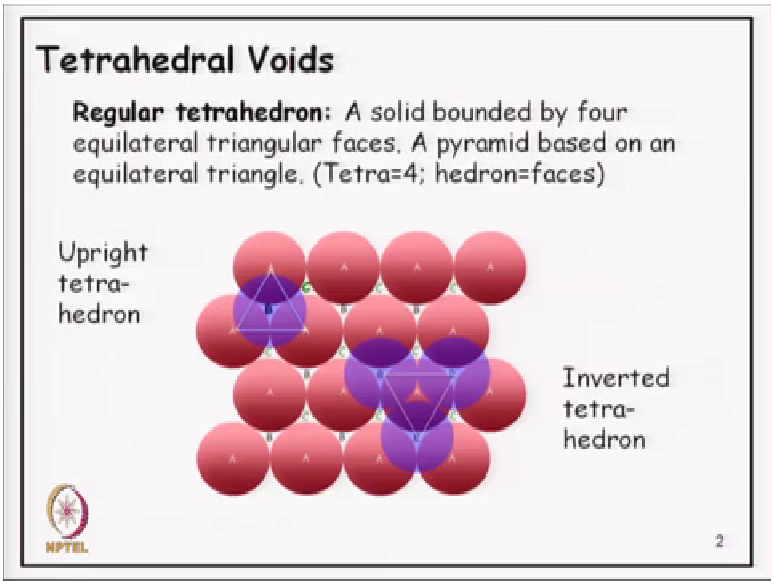

First let us look at what kind of voids and where they are located. So, one of the important kind of voids which is there is the Tetrahedral Void, Now tetrahedral the adjective tetrahedral comes from tetrahedron and A regular tetrahedron is A solid bounded by 4 equilateral triangular faces. A pyramid based on equilateral it is or can also be called A pyramid based on equilateral triangle tetra means 4 and hedron faces so 4 faces these 4 faces are equilateral triangles in A regular tetrahedron. So, where we do we form such equilateral triangle in our close packed structure? So, this is A layer familiar layer one layer of close package spears which we are calling A layer.

In this A layer, the location of B and C sides are also marked. The next layer if we consider the next layer to be the B layer, so the B atoms set on these sides above A atoms. Let us look at one of those atoms. So, on this triangle of 3 A atoms, we locate a B atom at its Centroid. So this B atom it is sitting on these 3 A atoms, it is touching each of these 3 A atoms, this forms as regular tetrahedron.

The centroids of these 4 spheres form a regular tetrahedron, similarly if we look 3 B centers here located above an A sphere. So, if we place these 3 B atoms and concentrate on these 3 B atoms then we find that the A atoms comes from below and closes the void between these 3 B atoms. So, again the 4 atoms these 3 B with a single A atoms from below also forms a tetrahedron. The centroids or the centers of these spheres form a regular tetrahedron the space left between these spheres is the void which is given the name tetrahedral void.

So, we can see that between 2 layers between 2 close pack layers A and B we have tetrahedral voids and there are 2 kinds of tetrahedral void. One is the upright tetrahedron with the base of 3 A atoms and B atom coming on top or with the base of 3 B atoms and A atom coming from below will give us an inverted tetrahedron. So, tetrahedral voids are there between 2 layers of close packed spheres and they are in 2 different orientations upright tetrahedron and inverted tetrahedron.

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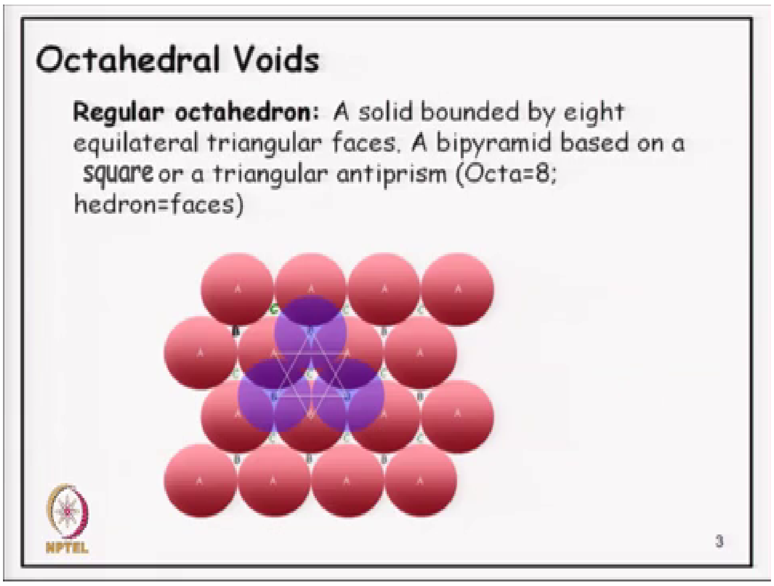

Let us now look at the other kind of void the other important kind of void is the octahedral voids this also forms between 2 close packed layers. Again we start with one close packed layer the A layer and we focus on the C side, around this C side there 3 A atoms in its own plane and above the C side in the next layer there are 3 B atoms and of course, between these 2 the C side is unoccupied between 2 close packed layers A and B there is an unoccupied C side.

So, between any 2 layers if we see the location of these unoccupied sides the C side we get an octahedral void, again octahedral void comes from the name regular octahedron which is A solid bounded by 8 equilateral triangles, Octa is 8. So, 8 equilateral triangles define a regular octahedron. This solid can be also considered as a bipyramid based on I am sorry it’s a bipyramid based on equilateral triangle let me fix this it is a bipyramid based on a square not equilateral triangle so it is a bipyramid based on a square or a triangular antiprism so this is a definition of regular octahedron and the location of that regular octahedron can be seen here as I was telling around AC side.

So, when we place the B atoms there are 3 B atoms around this C side and there are also 3 A atoms below, so 3 A atoms on 1 plane and 3 B atoms on another plane the centers of these 6 spheres are 6 corners of the octahedron so octahedron has 8 faces, but has only 6 corners. So, you require 6 spheres to define the octahedron and the space between them is the octahedral void so that is the triangle of the B atoms on top and another triangle of

A atoms an inverted triangle of A atoms below that is why they are 2 triangles and a solid bounded by a bottom triangle and top triangle and 6 triangular faces other 6 triangular faces making total 8 triangular faces.

So, a top triangle, a bottom triangle and other 6 triangles are inclined triangles so that is why it is called since the top and bottom triangles are not parallel if they were parallel we would have got a prism and the side faces would have been rectangles. But since the top and bottom faces are inverted triangles we get an anti prism with 8 equilateral triangles so this is the space between such a solid is an octahedral void and with this we now finished with the slides and let us come to the pen and paper where we will like to derive the size of these voids.

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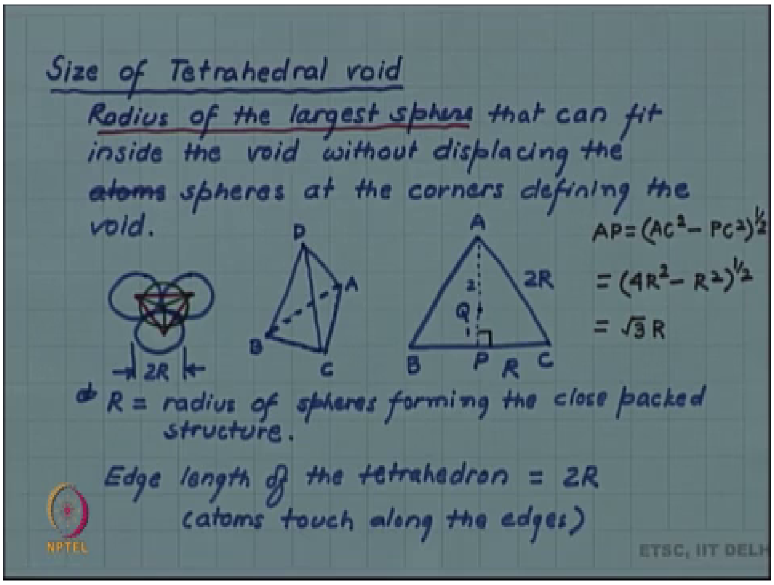

So, let us look at the Size of Tetrahedral Voids: By size we mean the radius of the largest sphere, sphere that can fit inside the void without displacing well atoms or spheres. Since I am using a sphere let us continue with that terminology without displacing these spheres at the corners defining the void this is how we define the size of a void.

So, let us look at a tetrahedral void we have seen that a tetrahedral void is defined by 4 spheres, 3 spheres on a base making an equilateral triangle, 3 spheres on a base making an equilateral triangle and one is sphere on the top making this a tetrahedron. So in perspective if I try to draw this tetrahedron so I have a base of an equilateral triangle so now I am representing that by let us say A, B and C and I have a sphere on the top sitting on this A, B and C. So now I am showing only the centers of the sphere so the center of the base spheres are A, B and C and center of the sphere sitting on the top is D, so if I join the; this is where I get one tetrahedron you can imagine a tetrahedron of the shape.

Now, if we if we want to find the radius of this largest sphere that is what is the size which will fit in this tetrahedral void. Let us try to work that out by first looking at the the base triangle A B C, so let me try to draw that base triangle A B C and let me drop a perpendicular from A to the other side AP, the centroid of the triangle will be on AP at some point Q which divides the height AP in a ratio 2 is to 1, this we know from geometry. So, let us locate this centroid in terms of our radius of atom so the diameter let us say that the diameter of the spheres making the close packed structure is 2R. So, R is a radius of spheres forming the close packed structure.

So, the edge length of the tetrahedron that is A B, B C, C A or A D any of these edge length of the tetrahedron is equal to 2 R, because atoms are in contact along these edges, atoms touch along the edges so AC for example AC becomes 2R and PC which is half of the edge becomes R. So this quickly gives us the height AP of the triangle these are the geometry of equilateral triangle. So AP in this triangle APC, in the triangle APC we have APC as 90 degree that is the right angle, so AC is the hypotenuse so AP will be by using Pythagoras theorem, AC square minus PC square which of course, becomes AC is 2 R, so 4 R square and P C's are 4 R square, square root of this so which means AP is nothing but root 3 R, AP is root 3 R. So, let us continue with this on the next page.

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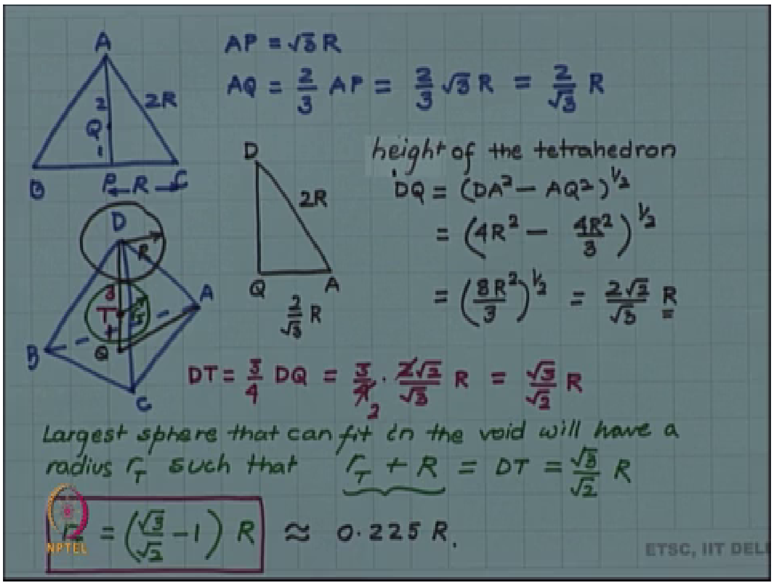

So let us draw our triangle again, this is Q the centroid of the triangle, A B C is the equilateral triangle, AP is perpendicular from A on B C and we have PC is equal to R and we have AC is equal to 2R and we just found that AP is root 3 R. Now since AP is divided by the centroid Q, AP is divided in a ratio 2 is to 1, we have A Q two-thirds of AP which means two-thirds of root 3 R which gives us 2 by root 3 R AQ is 2 by root 3 R.

So, let us continue with this. Now let us look at the full tetrahedron so our full tetrahedron was something like this, this was our A B C this is the apex D, from D if we drop a perpendicular this meets the centroid Q, this align from the geometry of the tetrahedron and from if we now join A Q, so the next triangle which we will focus on is this triangle from the top corner D.

We have dropped a perpendicular on the base A B C which also is exactly at the centroid of the base A B C so that is D Q and we have A, we have already found A Q which is 2 by root 3 R , A D is again edge of the same tetrahedron and this is a regular tetrahedron all edges are equal along A D also atoms touch because this D is the top atom the B plane atom which is touching with the A plane atom so A D also is 2R.

So, we can easily solve now the height of the tetrahedron D Q is equal to D A square minus A Q square the square root of this quantity, D A square is 4 R square minus A Q which is 2 by root 3 R, so it is 4 R square by 3 this will be square root of 8 R square by 3 which gives us 2 root 2 by root 3 R. So, we have found the height of the tetrahedron in terms of the radius of the atom.

Now the centroid of the overall tetrahedron is located on this height in such a fashion that it divides the height into 3 is to 1. So let us call this centroid T, T is the centroid of the tetrahedron, D T will be three-fourths of the height of the tetrahedron D Q, three-fourth of 2 root 2 by root 3 R which is nothing, but we cancel here 2 so we can see that we can write this as root 3 by root 2R. So, D T is root 3 by root 2R.

Now, let us look at D there is a sphere of radius R sitting this sphere of radius R is already sitting, at T is where, the void atom can sit and the largest void atom will be one which just touches this outer sphere so this is the largest sphere R T. So, largest sphere that can fit in the void will have a radius R T, such that R T plus R is equal to D T root 3 by root 2R this is because along the line D T the 2 spheres should touch. So, the sum of their radii, the sphere which is fitting in the tetrahedral void R T and the sphere which is sitting at the corners of the void which is defining the void capital R. So, the sum of these 2 radii should be equal to the distance between corner and center which is what we have found D T which is root 3 by root 2R.

So, now it is a simple matter to calculate the distance RT, so rt becomes root 3 by root 2 minus 1 R. So, we have solved the radius of the tetrahedral void or radius of the largest atom which will fit in the tetrahedral void as root 3 by root 2 minus 1 R. If we solve this numerically we will find that this is nothing but this is approximately equal to 0.225 R. So, the radius which can fit the sphere which can fit into a tetrahedral void without disturbing the surrounding spheres will at the most will have 22.5 percent of the radius of outer spheres this sphere is defining the void. So, this is what we call or this is what we mean by the phrase size of the tetrahedral void.

Let us continue with our discussion to find the size of the octahedral void this is actually much simpler because the geometry of octahedral void is much simpler. So, now let us look at right the octahedral void size of the octahedral void.

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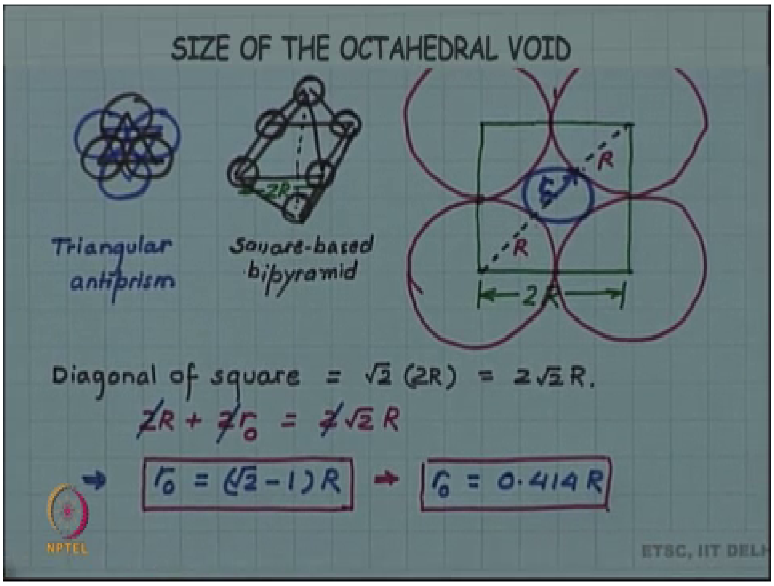

Now octahedron as we saw when we made the octahedral void we had 3 atoms below like this, and we also had 3 atoms above like this, this is how an octahedron will sit on a table it will sit on its triangular face.

However for calculation purpose it is more easy to do the calculation. If we stand the octahedron on one of its diagonal, if we make one of the diagonals vertical then we find that it can be considered as a square of 4 atoms or 4 spheres with one sphere sitting on the top and one sphere sitting on the bottom. So, essentially this becomes a square based dipyramid, this is the 2 faces which I had used in the slide either you can consider it as triangular antiprism or you can consider it as a square based dipyramid so there is a pyramid on top and there is a pyramid at the bottom.

Since it is a square we are looking at it from the square based dipyramid approach makes the calculation much simpler because geometry of the square is much simpler than geometry of triangles. So, we have let us say we have this squares and on the corners of these square these 4 atoms are sitting which are exactly toughing along the edges I am trying to draw these are the 4 spheres which are sitting on the corner of that square I have shown them actually touching here I had not shown them and touching for clarity, but actually they are touching. So, you can see that the side length of this is square now just like the edge length of the tetrahedron was 2 R, the edge lengths of octahedron also is 2 R, so the side of this square also is 2R.

The largest sphere that can fit into this void now will be sitting somewhere here and this will have radius RO for octahedral. So, if we see now if we connect this diagonal we can see that the full length of the diagonal of the square is root 2 times the edge length 2 root 2R. However, we can see that along that diagonal my radius sphere contributes a radius R from this corner and a radius R from this corner whereas, the central sphere the one in the void is contributing to RO. So, if I write that expression now that the diagonal of the square can also be written as 2R plus 2R octahedral and this will give me 2 root 2R.

Once we realize this it is easy to come up with a final result of course we can cancel 2, so R naught is nothing but root 2 minus 1 R or if you do it numerically you can show that R naught is equal to approximately is equal to 0.414 R.

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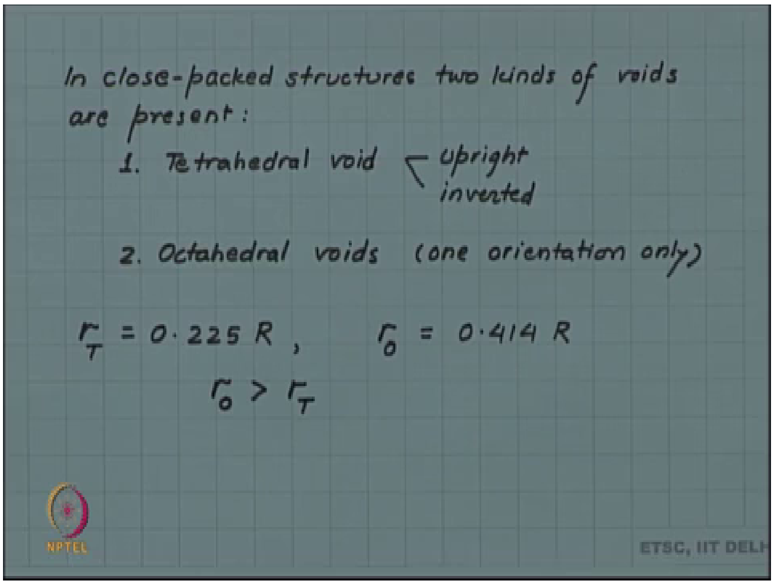

So, we can see that in close packed structure we will use the next page. Let us summarize in close packed structure 2 kinds of voids are present. One is the tetrahedral void which comes in 2 orientations upright and inverted. And octahedral voids which come only in one orientation and we computed the sizes of these voids also by showing that the radius of the atom largest atom which can fit in a tetrahedral void R T was approximately 0.225 R in the radius of the octahedral void was 0.414 R. So obviously, the octahedral void size is larger than the tetrahedral void size.

Let us continue the discussion on the voids by seeing where these voids are located in the unit cell of CCP and H C P.

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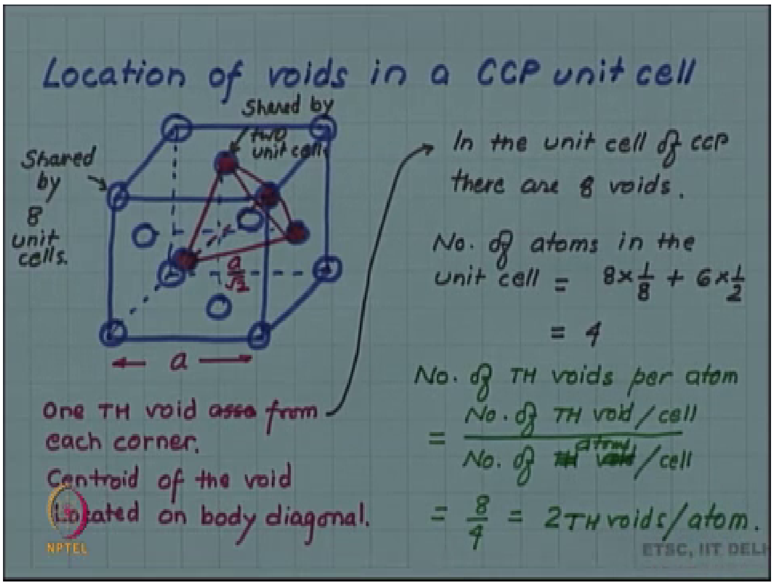

So, location of voids inside in a CCP unit cell, so let us draw we will draw a schematic CCP unit cell, now let me not draw the atoms in full size because that of course will make it too complicated. So, I draw a smaller atoms the corner atom as well as since it is C CP root face centered atoms.

Now if we look at let us locate the tetrahedral void. So, let us look at one corner and at every corner 3 faces meet so in this corner the top face, the right face, and the front face faces are meeting. So, let us look at those face centers which are meeting at our selected corner, the top face center, the front face center and the right face center. These 4 atoms let me claim that these 4 atoms form a tetrahedron each of these edge length you can easily compute each of these edge lengths in terms of the lattice parameter a, this is each of them is equal to half face diagonal so they are a by root 2, each face is our equilateral triangle and that is where you have a tetrahedral void.

This tetrahedral void is totally inside the unit cell you can see that the bounding edges are all either on the face of the cube or inside. So, one tetrahedral void from each corner center of this void will be located on the body diagonal. So since one tetrahedral void from each corner is there in the entire unit cell from this in the unit cell of CCP there are 8 voids.

But if you look at the number of atoms in the unit cell so there are 8 corner atoms, but effectively only one-eighth of the corner atom belongs to the cell because each corner atom is shared by 8 unit cells so corner atoms shared by 8 unit cells and there are 6 face centered atoms and they are shared by 2 unit cells.

So, effectively half of that belongs to each unit cell so we get 4 atoms per cell. So, this gives us a calculation of the number of voids per atom, number of tetrahedral voids per atom, number of tetrahedral void per cell divided by number of sorry number of atoms per cell this is 8, this is 4 you get a nice number 2. There are 2 tetrahedral voids per atom.

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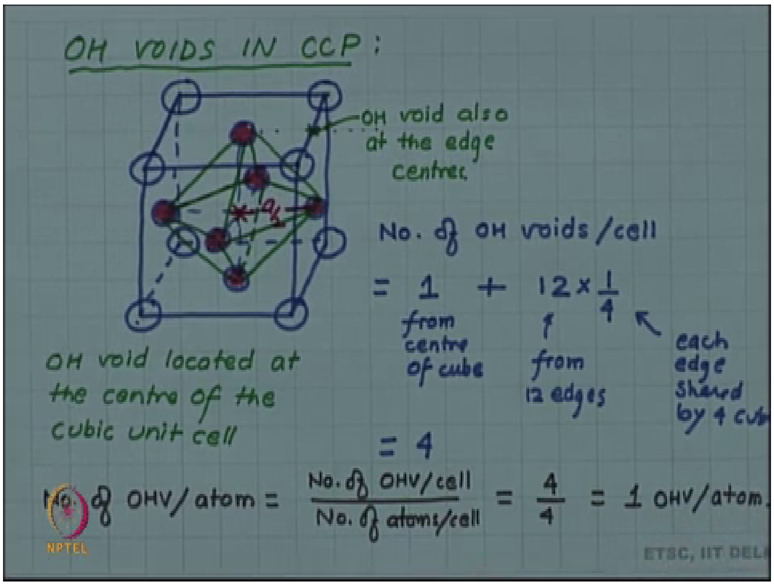

Similarly, we can try to locate the octahedral void in the cell. So, we start with our Q, it is open a center left and right face center and the front and the back face center. So, if you look at this the octahedral void is located at right in the center of the cube, because the 6 face centered atom.

If you look at these 6 face centered atoms they are 6 corners of an octahedron, these 6 atoms define nicely 6 bonds. So, if we join the 4 centers of the 4 horizontal faces you get a nice square and then the top and bottom then give you the 2 pyramids to complete our octahedral void, OH void located at the center of the cubic unit cell not we are trying to work out octahedral void in CCP so OH void is located in the center of the cubic unit cell.

But interestingly, if you now look at the geometry of this centroid, the center of the octahedral void it is center of 6 atoms and the location of those 6 atoms are one forward, one backward, one on the left, one on the right and one top and one bottom and each of them are at a distance a by 2, so a by 2 right, a by 2 left, a by 2 up, a by 2 down, a by 2 front, a by 2 back.

With this in view if you now examine the center of the edges of the cube you find that the center of the edge is also an location of an octahedral void also at the edge centers. Because you can see if I go from here a by 2 front I have an atom, a by 2 back I have an atom, a by 2 left I have an atom, a by 2 right I will have an atom when I consider the next unit cell. The unit cell on the right will provide an atom exactly at a by 2 to the right of this center, similarly I have a by 2 bottom, but a by 2 top from come from the next unit cell if you imagine that way it is easy to see that octahedral void is also at the edge centers of the unit cell.

So, the numbers here can now be calculated so number of octahedral voids per cell this center void is totally included in the cell. So, I have one from center of Q plus, I have 12 voids, there are 12 edges of the cube so I have 12 voids located at the edges. But since one edge if you look carefully in the 3 D structure, one edge each edge is shared by 4 cubes so effectively only one-fourth of the void belongs to each cube so 12 form twelve edges, and one-fourth because each edge shared by 4 cubes so this number then comes out to be 4.

So, the number of voids per atom here becomes simple number of octahedral voids per atom is equal to number of octahedral voids per cell divided by number of atoms per cell both of them are 4 so we get a nice number one so there is one octahedral void per atom in a cubic cell 1 OHV per atom.

So, with this all this geometrical study or geometrical study of the voids in the structure we now complete this topic and we will next look at the role of the voids in forming different kinds of solid solution so that we will do in a future videos.