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

Lecture - 17
Crystal Structures

Before considering the octahedral tetrahedral void in external close pack crystal, let me revise some of the concepts will learnt with regard to octahedral and tetrahedral voids in the cubic close pack crystal. So, we say that there are two kinds of voids of importance.

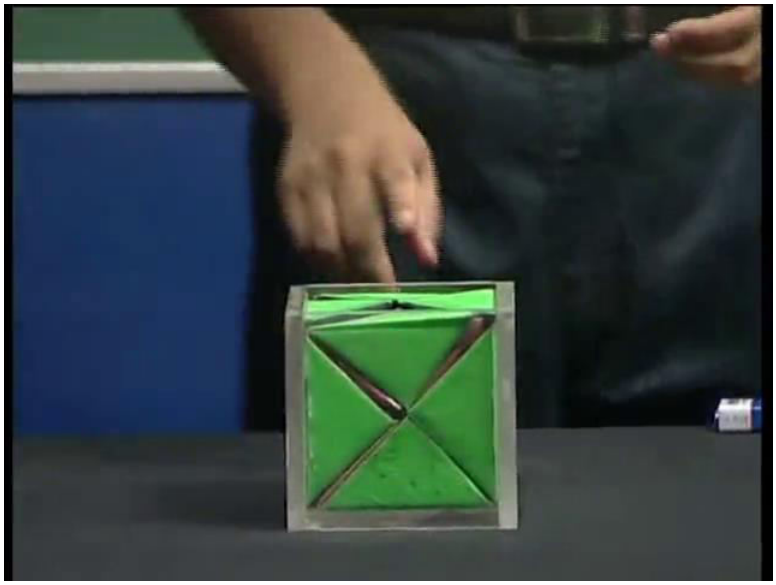
(Refer Slide Time: 00:41)

This is octahedral and regular tetrahedral. We also say that for instance this position of the tetrahedral void which in the common unit cell which is starting from one corner and we say that within a unit cell there eight of such tetrahedral. We say that the octahedral is located at the body center and also the edge centers as the body center is related to the edge center by the face centering translation which is half zero. Now, we also say that suppose I have two tetrahedral voids and the octahedral void in middle. This combination cannot like a primitive unit cell for the cubic close pack crystal and therefore, this the primitive unit cell.

So, it consist of one octahedral in center and two tetrahedral and they adjoin along the body diagonal of the cube. Now, let us try to look at in alternate model of these F C C voids. So, that we can understand that how some tetrahedral and octahedral pack within

the unit cell and the most important thing. So, that I mean I could uses this model which I have got here.

(Refer Slide Time: 01:48)



The most important thing we noted was that the octahedral void is shared between four unit cells. That means within unit cell you got only one portable octahedral void. So, the illustrate that I got the model in front of me here and here you can these are my octahedral voids and you can see that this is one fourth of an octahedral void. So, how do understand it is one fourth? I can put together four of these voids which are located here in front of me to make regular of the octahedral. So, I put together therefore of these and I get regular octahedral. So, in the unit cell I said there two positions, I would like to distinguish.

One octahedral void one is the body center which I will take out these tetrahedral voids and show that actually body center the seat of an octahedral void. So, these in octahedral voids which is located at the body center, these four positions are tetrahedral voids which are starting from these vertices of the cube is converge of the cube and therefore, I got four tetrahedral voids. These blue face you see or nothing but the phases of the octahedral void which are sitting on these vertical edges.

So, this edge this edge as I said all edge center or centers of octahedral voids positions and similarly, the bottom positions like you can see the bottom vertices also have octahedral voids at them at the center. This can equally be seen by the top edges here.

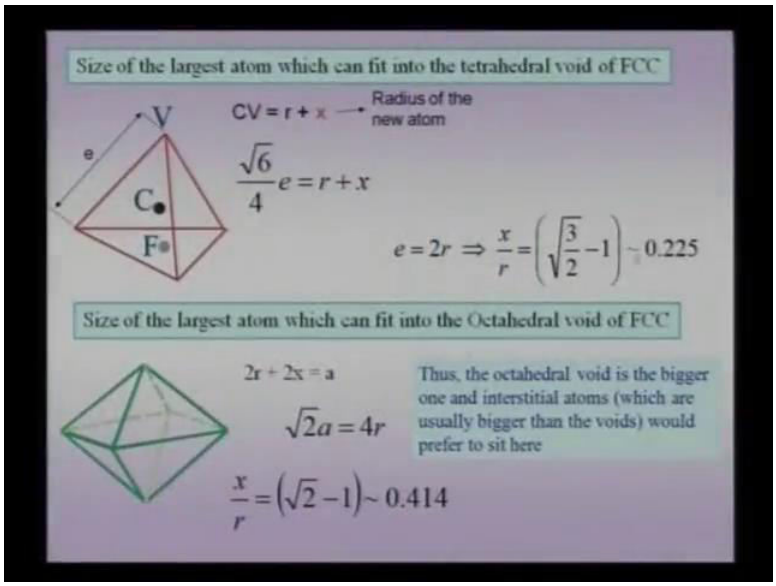
So, let me do the repacking to show you how these tetrahedral and octahedral voids fit together. So, I already have in position four quarters of octahedral voids at the four edges of which make the bottom phase, the 4 vertical edges there are 4 quarters of an octahedral void already sitting in place.

Then I placed one octahedral void in the body center. So, this is my octahedral void which case in the body center then next thing I do is put this tetrahedral voids in place. So, I got four of these tetrahedral voids here. Therefore, I got total of eight tetrahedral void four pink tetrahedral voids top, four pink at the bottom which we already saw when I remove these pieces and now these four quarters are octahedral voids which can see here the various the green phase are phases which I mean cut.

Therefore, when I join this green phase together I get my regular octahedral. So, I cut into four quarters and put one quarter each in one of the edges and this octahedral void is shared between four unit cells. So, particular suppose I take this octahedral void it is share putting this unit cell, the unit cell above it, the unit cell to the left of it and unit cell below that. It share be four unit cells and therefore contribution of this octahedral void to these unit cell is just one-fourth.

So, I have since twelve edges one-fourth integral three plus one at the body center therefore, there are four octahedral voids per cell which matches exactly with the number of atoms in the cubic close pack structure which is four. The four for every atom in the cubic close pack structure I have one octahedral void and you say the eight tetrahedral void which implies for every atom in the cubic close pack crystal I have two tetrahedral voids. Therefore, there are 8 tetrahedral voids. So, this void model is very illustrative and understanding that how voids themselves can be cut and associated with unit cells. So, this is an important model and unit you need to keep this picture in view and understand that what is the contribution of voids to a signal unit cell may do a counting.

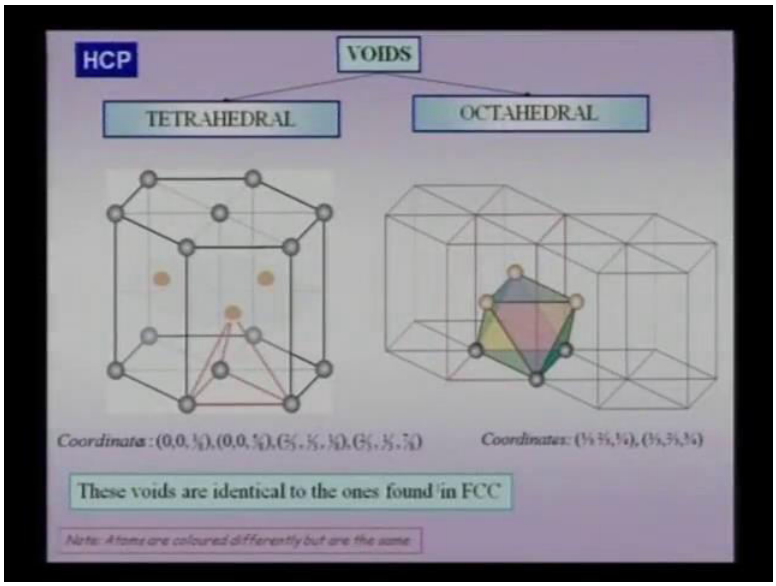
(Refer Slide Time: 05:33)



So, we had seen that the tetrahedral void in the cubic close pack crystal is a smaller void, but there are twice, so many tetrahedral voids as octahedral voids. If you look at the size ratio of the voids atom which can sit in void with respect to reduce the atom at the lattice point it is 0.225 for the tetrahedral void and 0.414 for the octahedral void. Later on, we will actually try to compare this we convert this radius ratio into actually dimension for certain like for instance ion crystal, and then try to compare with the carbon atom which actually goes tries to certain some of this voids.

So, in that case you will get a realistic feel of what these voids as I mean with respect to the atoms sitting in the lattice positions. Therefore, this also tells you another important point that I need to know not only the total volume available, but how it is partition between that is total volume available in the forms void. But also need how it is partition between various kind of voids I have numerical those void are. Now, let me take up the voids in the external close pack crystal.

(Refer Slide Time: 06:41)

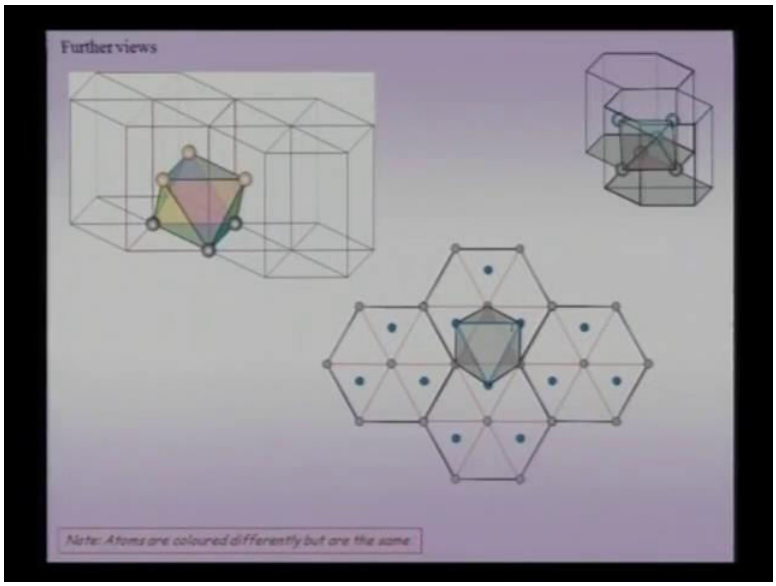


We already mention that external close pack crystal as identical voids as compared to the cubic pack close crystal in other it has got an regular octahedral and regular tetrahedral as its voids. What are the positions of these voids in the unit cell? So, you can see here in this external close pack crystal unit cell that the tetrahedral void is form between three atoms in the Bessel plane and the atom which is located in the mid plane. So, the position of the void would be for instance this actually in the centroid position.

It is one-fourth way above. So, it is actually in the void position are written here as one-third, two-third, one-fourth and one-third, two-third, three-fourth. This is for the octahedral void and the co-ordinates for the tetrahedral void are written here. So, this tetrahedral void for instance below located two-third, one-third, 1 x this is the positioned tetrahedral void. Now, we will actually take up model to understand where this tetrahedral and octahedral void are located and in this case, in the case of the external close pack crystal it is actually very difficult to visualize especially the octahedral void.

Now, the packing the direction we are packing upwards is the 0 0 0 1 direction of external closed pack crystal in other words to direction of the packing of the close pack planes. So, we are packing the close pack plane in a b a b passion in the direction which is the c direction. Now, the difficult unit visualizing the octahedral void comes from the following.

(Refer Slide Time: 08:15)



If you look at the octahedral void it is sitting not within a signal unit cell, but within multiple unit cells. So, for this suppose when I want to visualize this octahedral void it is sitting this may unit cell it is sitting been one unit cell the second unit cell in the third unit cell. So, it is shared between three unit cell and this makes visualization of this octahedral void more difficult. The tetrahedral void is easy to visualize it is for instance this is one position for tetrahedral void and there is equivalent position of the tetrahedral void. But now if you look at with respect to the orientation of the tetrahedral this tetrahedral is orientated upwards, but you look at the tetrahedral in this figure it is orientated downwards.

So, this tetrahedral is formed by the three atoms in the mid plane and suppose I am talk about say zinc crystal this is be three zinc atoms sitting in a mid plane and the atom which is share between three unit cells. Therefore, this tetrahedron is share between multiple unit cells and more importantly it is orientated the other way around as compare to the tetrahedron in this figure. As you will see that using model especially that the octahedral as got signal orientation in the external close pack crystal while the tetrahedral as got two orientations and to repeat the voids are identical to those found in the cubic close pack crystal.

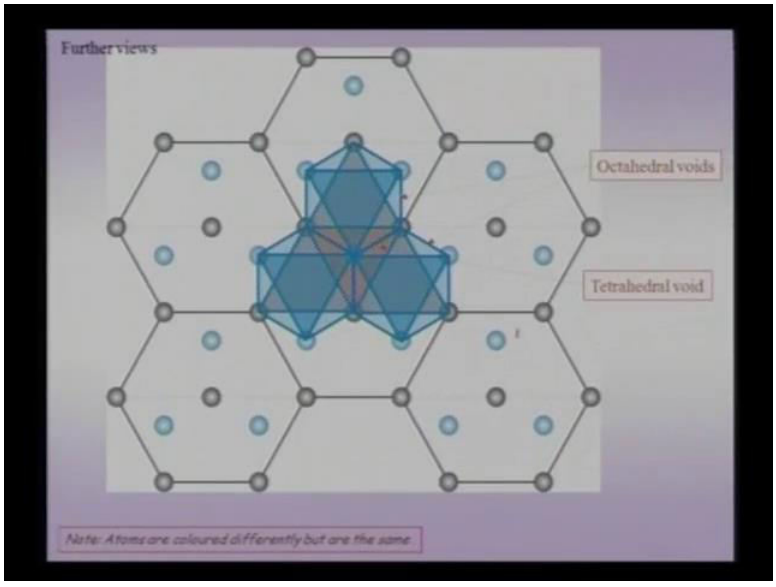
So, there is no difference between the voids and this will become obvious when I show you the models which are use to illustrate the point. Now, let me try to understand where

the octahedral void is in the external close pack crystal and how we can pack this octahedral voids and along with the tetrahedral voids to fill space? This exercise we are undertaking for the cubic close pack crystal and it was easy exercise because we could actually cut the octahedral voids into one-fourth take them put them along the edges. Then includes full tetrahedral void along with one fill octahedral void to fill a unit cell once the packing of a single unit cell has been achieved then I know the packing of the crystal can be achieved.

But as pointed out in the case of this octahedral void in the external close pack crystal this truncation is not illustrative in fact the truncation if you had to do will be down this plane. Therefore, you will be cutting the step octahedral along this plane which goes down this direction and it is difficult visualize. So, for instant this is my orientation octahedron with respect to two unit cells in the external close pack crystal.

This was an alternate view of that wherein I have included three atoms in the mid plane and three atoms in the Bessel plane. The all atoms as before identical they have been colored differently just for better visualization. So, looking down the 0 0 0 1 direction in other word c direction I see that this is the direction of my three fold in the cubic external close pack crystal, we can see that this three atoms come from c equal to half plane and these three atoms come from the bessel plane.

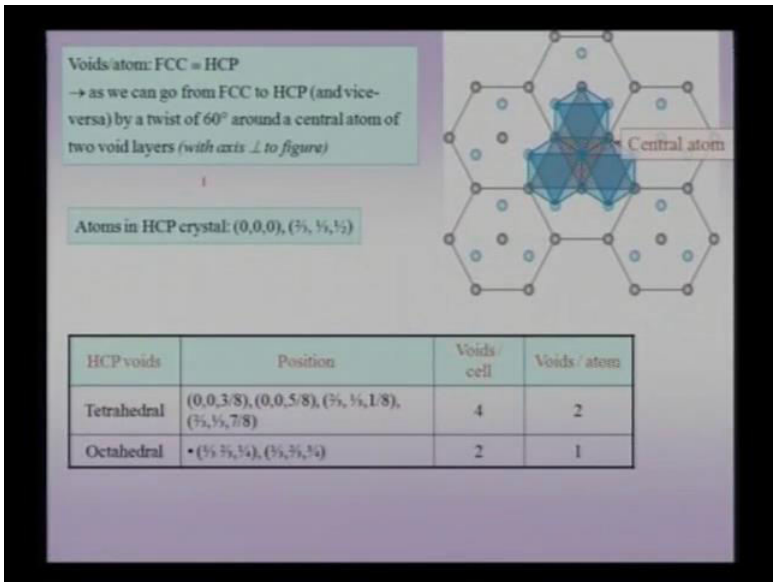
(Refer Slide Time: 11:12)



Now, the way I start my packing is actually putting three octahedral together the way of done here. So, this three octahedral are put together and the space left in between is what is colored orange is a tetrahedral which is pointing upwards. Therefore, I can put my octahedral together, and then put one tetrahedral in the middle of these three octahedron, which is pointing upwards. Therefore, an offer I can put another other octahedral around these and go on to fill entire space.

But now these are not filling of space with signal polyhedron, but with two that are solids the octahedron and the tetrahedron. So, these points will become clearer when you actually take up the real models would models which I have got here and as I told you these are seat of the void models. So, these are the picture I use which I called the void model picture.

(Refer Slide Time: 12:08)



Now, I would also like to know how many voids are present per cell and this calculation again can be performed either based on the diagram I am showing here or based on the void models I am using. So, number of void per atom in F C C and H C P we will see these that actually that I can go from when I making layer by layer construction of void models I can go from F C C to H C P crystal by a 60 degree rotation around the center atom. So, this I will show using the model and the center atom which I am using is been marked here. Just to revise these two voids what are this void model void model are

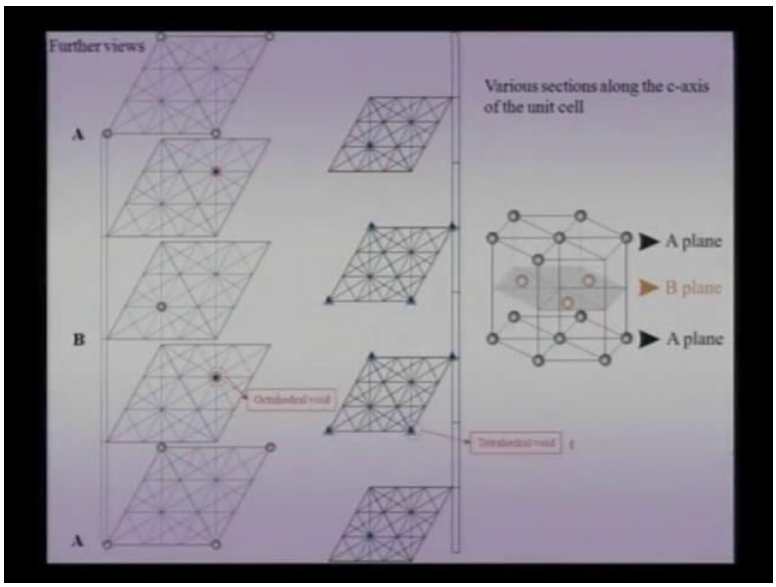
wherein atom has been shrunk to points. I use a polyhedral shape to denote the coordination around the central void atom sitting in the void.

Now, let us look the number of void spiral cell void per atom in the tetrahedral octahedral voids. In H C P, there are four we can see the position of tetrahedral void there are four voids per cell and number of void per atom is two. For octahedral void again there are two position have as shown here there two void per cell and there is one void per atom. Ravi has a question.

Student: I want to know the difference between voids per cell and voids per atom.

As you know in F C C there are four atom in unit cell right there I have for instance number of tetrahedral void in an F C C are cubic close pack crystal is eight. But then you have four atoms in the unit cell. So, I divide them that eight by four and get two. So, that is what I am doing here, in the case of the H C P about two atoms per cell. So, that is clear. So, I divided the factor by two. Now, in order to better visualize the position of this voids have certain other diagrams here.

(Refer Slide Time: 13:58)



Wherein the hexagonal unit cell has been spit into various planes, so this is plane for instant located at 0, this a plane located at half, this is a plane located one-fourth, this is three-fourth and 1. Similarly, there is a diagram right hand side which is been you stood locate the position of the tetrahedral void. So, you can see that if you look make such a

diagram then there are two octahedral void position and this are on the centroid of the triangles. This is one in at in the plane and there is one in this plane similarly, when you look at the tetrahedral void, we can see that in the Bessel plane, there is one center of the tetrahedral void here.

Then it is not the Bessel plane this is a plane which located one four one eighth above. So, this is one two three four five six seven eight above and therefore, have one tetrahedral voids centered sitting there. Similarly, in the plane which is one-eighth, two-eighth, three-eighth, I can see that there center of four tetrahedral voids. Then this is four-eighth five-eighth. I can see again four tetrahedral voids and as you know this again would be repeated upward in the plane which is about. So, now I can locate and this diagram is useful, because it actually helps you and locates localizing it with respect to the triangle this triangle represents. So, this is more Bessel unit cell and half triangle I can located them with represent to centroid of the external unit cell.

Student: What is the difference between Bessel plane and single plane?

These are all Bessel plane what I mean these are all of course, starting of Bessel planes, but this is shifted to this in the c direction. This is one two three four. So, this is c one-fourth. So, there are two octahedral void one at c equal to one-fourth and there is one at c equal to three-fourth that is what I am showing there in the diagram. So, as I pointed out locating and associating these octahedral and tetrahedral voids and external close pack crystal is some more difficult and visualizing them with respect to especially the unit cell. In cubic close pack crystal there is different kind of problem where in your packing along the 1 1 1 direction typical the close pack layer.

But, you typically visualize the unit cell of the cubic pack crystal along the 1 0 0 direction which is the four fold direction. Now as you do the packing of the close pack layer long three fold direction of the six fold direction of individual planes that is 1 1 1 direction of the cubic. But you visualize as unit cell typical along the four fold direction why in external close pack crystal you draw and visualize planes along the original six fold of these individual layers, which later on we can see as we saw six three two axis are three fold, but even in this case because of the strange orientation of octahedron. Typically when we draw an octahedral we end up drawing an octahedral with the four fold up, but in this case I have to visualize an octahedral with three fold upwards.

So, let me show with respect to model for instance. Actually it is related to the fact that the way the octahedral we normally end up drawing octahedral this way. It would be equally for instructive for us to draw octahedral like this that means with three fold upward right. But if you rarely draw octahedral like this and therefore it becomes difficult for us to visualize how we can drawn octahedral like this and how this octahedron is shared between unit cells in the conventional representation of the external close pack crystal.

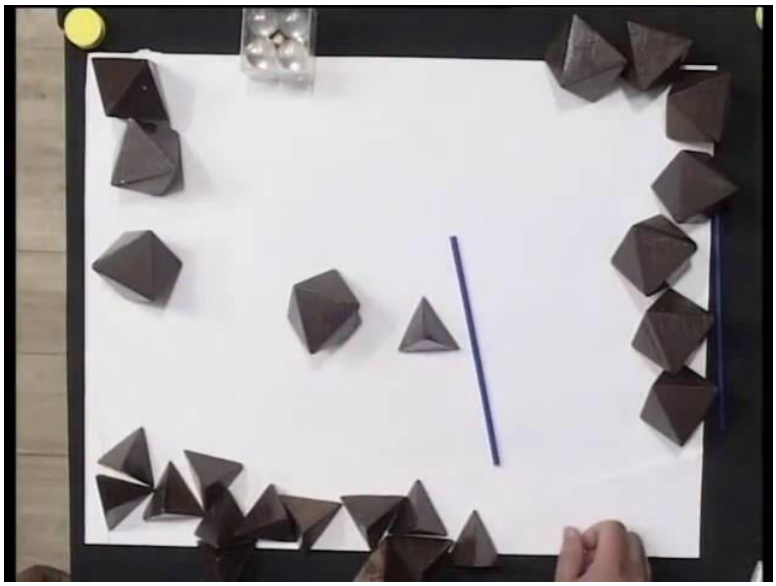
That is where the issue is and that is why we required as certain amount of time to be spent in understanding this void in the external close pack crystal. So, if once we start drawing octahedral like this and start visualize along the three fold of this octahedral then it becomes very easy for us to understand where the octahedral sits in the external force pack crystal.

Student: Basically octahedral void due to this we have only one orientation and tetrahedral we have two orientations. So, we can see in crystal how we can see the models.

Yeah very good question I will show you that you when I take up the wood models. So, I just do that for you next. So, the point I am trying to make here is that when you want to understand octahedral void in external close pack crystal you have multiply ways of understanding the same. You need to look at them using pictures like this wherein I am drawing plane by plane locating in the center of this void.

I am using actually voids to do a space filling. So, that many ways I can locate the same octahedron and tetrahedron. This is very important because otherwise it is very difficult to localize these octahedral and understand how they actually fill space to form the external close pack crystal. So, let us try to understand the position of the octahedral and tetrahedral voids which rise to the external close pack crystal.

(Refer Slide Time: 18:49)



Also, the cubic close pack crystal. So, here I have my regular octahedral and my regular tetrahedral which have been place along by direction of packing which is now the 0 0 0 one packing in external close pack crystal and the 1 1 1 direction of the cubic close pack crystal. Now, any such for instance, if I take a tetrahedron actually represents two layers of atoms. So, there is one atom which is be reduce point here and there are three atoms which are here. Similarly, this also represents two layers of atoms. So, there is one layer of atom at the bottom here and this is one more layer of atom at the top.

So, any such figure actually represents two layers of atoms wherein atoms have been shrunk to points as we do in standard void model. So, let me start with a tetrahedron and put three octahedrons around it. Now, as you can see the center tetrahedral is in upward orientation where all this three octahedrons are in the same orientation. Now, I could continue in the plane by putting more and more this octahedral which all will have happen to be in the same orientation.

Now, I got void here between this octahedral wherein I can put additional tetrahedral in the upward orientation like this. So, so far I got all my tetrahedral upward orientation and they set here, here, here, here and one tries to the center. Further, I can of course put tetrahedral right also and propagate this order throughout my plane, this two dimensional plane, which actually I see my model is two layers of atoms. Because if there is one plane which is a plane of the paper and there is additional plane here whether atoms.

Now, when I want to complete this two layers atoms and I have to put additional this tetrahedral second orientation which is orientated downwards. So, this is my second orientation of the tetrahedral and it is downwards. So, I have constructed two layers of atoms which now can extend to infinite. To make another layer above this I have two options. So, I have octahedral for instance and I can put. So, I call say this position of the octahedral as the a position then this would be a b position. Now, suppose position I put octahedron on top on octahedron then I would see that this is my position this is my b position. But, this position is exactly above the original position which is a position therefore, I getting a b a.

So, I am putting octahedron for instance a b a b kind of packet. In other words whenever I put octahedron on octahedron to make the second layer of voids which would actually constitute three layers of atoms then I would get in a b a b kind of packing which would give you the external close pack crystal. Now, instead of putting an octahedral on an octahedron, suppose I put a tetrahedron and octahedral like this then again a then b and this is new position which was not there in the two layer atoms below this.

Therefore, this would be c position and therefore, wherever I put in tetrahedral on an octahedral I have get in a, b, c and a, b, c kind of packing. In other word I would get cubic close pack crystal packing. So, I can start of by putting and take now octahedron trying making third layer atoms when I put an octahedron on top of octahedron existing octahedron, so this multiplication an octahedral on an octahedral.

Similarly, I can take octahedral put in existing octahedron and you take octahedron put it on this existing octahedron. Now, we can see these octahedrons are actually whole in center wherein tetrahedron can fit and they also leave holes here in this position wherein additional tetrahedral can fit. Now, an important point we noted at the stage is that, suppose I am looking at central atom and atom which is located here then using these void models, I can calculate the number of atoms which come together at this voids.

In other words, number of voids per atom I can make a calculation very easily. So, phase of the atom sitting here would be shared between one two three octahedral which for below this and there are one two three four tetrahedral when I make the next layer as use as you trying to do just now, then you will have three octahedral in the plane above and there be 4 tetrahedral. In other words 3 plus 3, 6 octahedral come together at a single

vertex in the external close pack crystal. As we shall see this number remains unaltered when you go from an external close pack crystal to as to be cubic close pack crystal.

So, one, two, three tetrahedral in this plane plus 3 above, 6 octahedral coming together at each atom, one two three in bottom orientation, one in top orientation, four tetrahedron of here and four tetrahedron above. So, 8 tetrahedron coming together at vertex in the planes which is an atom in the cubic close pack in the external close pack crystal. This could are equally well be visualized my alternate models which we have construct before for instance we have a model like this here an one atom here and I can for instance take this matter. I will use the camera above actually show you that for instance there are 8 we have see here three, one, two, 3 tetrahedral 4 here.

So, there will be 8 unit cells and 8 tetrahedral coming together as, so this is one tetrahedron here 8 of them similar octahedron there is one from here one from which is shared between this unit cell. Similarly, you can see that we can visualize using alternate models this calculate the number there is actually 6 tetrahedral or 6 octahedral coming together at the vertex. So, let us return to the void model once again. Now, let me make this second layer of atoms by putting an octahedral on third layer of atom the second layer of voids to make a void model or void space fill model.

So, I got my layer one of the atoms here, the layer two layer atoms here and the layer three of atoms about. So, I got three layers of atom and two layers of voids. Now, this structure in the propagate to actually get the external close pack crystal and this external close pack crystal because we started by putting an octahedral on top of an octahedral these is one of the we started. Now, let me do the other alternative which will lead to the cubic close pack crystal, which is by putting a tetrahedron on of on octahedron are equivalently I can put an octahedral on top these tetrahedral.

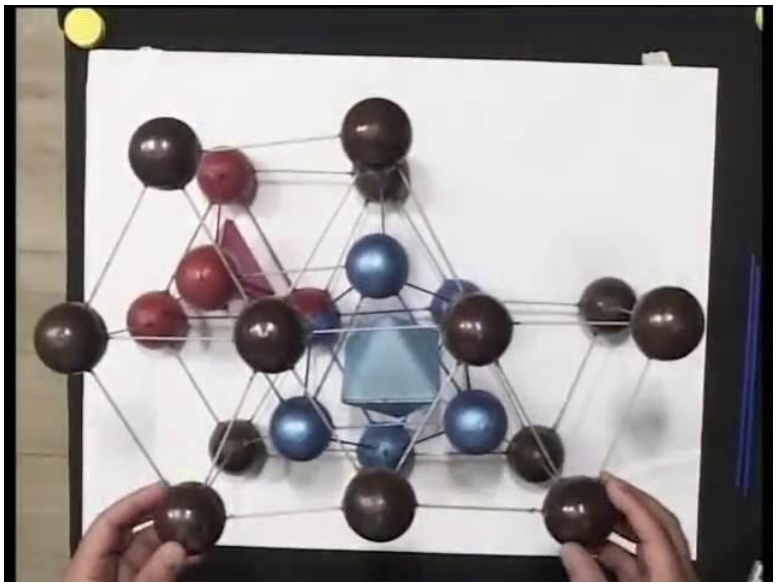
So, I put tetrahedral on top of these octahedron and octahedron top of this tetrahedron. So, this is a tetrahedron I put an octahedron there and this tetrahedron here. This is my another octahedron. This is my cubic closed pack structure and this is related to my external close pack structure by actually a twist about this central atom and twist will occur along this axis and how to do visualize the twist. If I try to twist all these atoms, all these voids will fall down. So, let me do the twist single pair of voids to go from at tetrahedron on top of an octahedron when octahedron on top of tetrahedron.

Of course, it could do a translation like this wherein for instance I can take an octahedron on top of tetrahedron. But, more precisely I can do this twist around this. Now, what happens is I get to tried on top of tetrahedron and octahedron on top of octahedron and into these rotation about this axis for instance equivalent off course I could do another operation. So, I can get an octahedron on the top of octahedron and tetrahedron on the top of tetrahedron. So, this can be done and you can see these two structures are closed related as well as the voids course.

In term of coordination polyhedron, we see that it is a cube octahedron in the case of cubic close pack crystals and in case of the external close pack crystal it was a twinned cube octahedron. We have coordination model which reflect this spinning operation. So, we have void module here. Let me summarize once again the salient furthers of this voids model that this model is very useful especially in making calculation as said number of voids per atom right. Suppose, now I have certain atoms since a carbon atom sitting octahedron void.

I would know that how many carbon atoms can sit around central atom for instance of ion in the cubic close pack crystal to those kind of calculation are easy to make with this kind of void models and additionally it helps to visualize the voids the way they can fill space. Also pointed out that, the same set of voids that regular octahedral regular tetrahedral can be use to fill make to fill to be close pack crystal as well as the external close pack crystal. So, there are these void models.

(Refer Slide Time: 28:18)



I have here a model of the external close pack crystal wherein I have three layer of atom. The Bessel layer, there is one layer of atom in the middle which is pointed out, goes part of motive and there is a third layer above. Here, I want to illustrate the presence of the octahedral and the tetrahedral voids. Let me start the easier of the two which is the tetrahedral void and as a point out the tetrahedral void is made by the atom in the Bessel plane and an atom which is sitting above.

So, let me lift this model up and show from different camera angle the same thing. So, here I got my tetrahedral void which I want to show from different direction this my tetrahedral void. So, there are three atoms in Bessel plane and one atom in the c equal to half plane which constitutive m tetrahedral void. Now, there is a unit of this crystal. So, I can construct my unit cell as this form the prism, this is my unit cell. Therefore, this tetrahedral void for instance lies completely within the unit cell.

But I can locate an alternate tetrahedral void whose orientations as we say as opposite to this tetrahedral void and that can be formed by this atom which is been painted red and blue the one on the Bessel layer, these three atoms which on this c equal to half plane. So, these are three atoms one red and two blue and one which is painted half red and half blue. Putting together these four, I would get a tetrahedral void, which is pointing downwards equivalently I could took another tetrahedral void which is pointing upwards by taking this atom and these three atoms.

That means I take this brown atom, this red atom this blue and this blue atoms. So, this will found the base triangle base and this will be fourth which will form the tetrahedral. As you known the tetrahedral is nothing but triangular pyramid. So, I have this tetrahedron right here. So, I can have two tetrahedrons which have centers along this vertical edge within these vertical edges no different from the other vertical edge like this. Therefore, they were also be seed of centers of tetrahedral voids. So, right here of the along this edges one tetrahedral pointing upward and one pointing downward.

Now, this model is illustrated to understand the position of the octahedral void. Now, let me taken an equivalent unit cell for instance this unit cell form by this four atom one two three four. Similarly, on the Bessel plane there is a one brown colored atom one blue colored atom here another blue colored atom here and an atom which is colored half blue half red. So, these four along with four corners here vertices here would form the rhombic prism which is the unit cell for the external close pack crystal with this atom at c equal to half contain within the unit cell.

Now, the octahedral void is as a pointed out shared between more than one unit cells in fact three unit cells. Now, this unit cell which contains one atom which belongs to octahedral void there is this unit cell with contains one more and there will be an equivalent cell here which contains one more atom. In other words this octahedral void which is shown here with these vertices colored blue. So, there are three triangular atom which form triangle which is sitting in the bessel, three in the mid plane which are the six vertices of octahedral.

Out of these three in the Bessel plane all set contain within of course, have at least some part of within this unit cell, but there are this three two which lay completely outside the unit cell. Therefore, this makes a little difficult to visualize the octahedral with respect to the standard conventional unit cell. So, let me go way this process again. So, I got my tetrahedral void which can be contained to them completely within a unit cell of course, I could also visualize of the tetrahedral void which like been between unit cells and this octahedral void which always shared between the conventional unit cells.

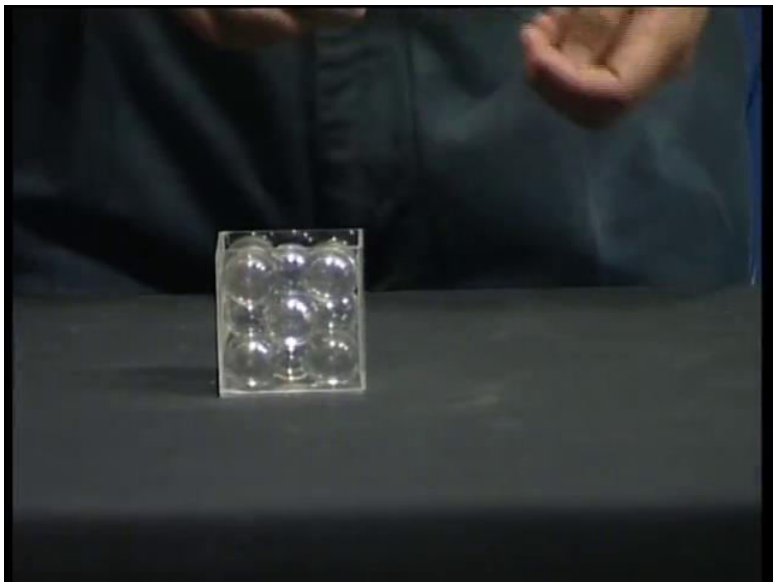
So, this is pointing this direction of course, as you known this is my seat of the six three two axis. In other words, this is the position, this is b position and c position is completely vacant which is the seat of the six threes two axis. Along the center, along

that axis lays my octahedral void and my octahedral void as you can see this atom has vertices. Since, this voids are actually solid model, voids are actually shrunk down versions of this actually polyhedron and this is been done just for visualization. You should know the actual void would be found by this phases which are right here this full complete face.

But this adjust from down versions for better visualization of this centers of the voids, I have this unit cell having part of this void, this alternate unit cell having some part of void in this a third unit cell having some part void. So, this three units cell together form the complete have part put together those part I get the complete octahedral void which is located with this three-fold axis upwards. So, this module is very illustrating model and let me take little time out actually show this model from various prospective. So, this you can see this is more in this prospective we can go round this little bit actually visualize the voids. Little rotate around, so that I can visualize show you the c axis.

Using this opportunity let me show you an alternate model for you position of voids and kind of spheres which can set in voids. Let me show how and see model like that before for instance model.

(Refer Slide Time: 34:20)



Now, this is my set of c sphere transparent glass ball which have been used to fill the unit cell in a cubic close pack crystal. So, I got these void models here and let me take out center sphere and put a void I want show the related side of the atoms. So, we can see that the size of the atom which can sit in the void is considerable smaller then the size of the atom which goes into later you can see that the related sizes clearly. So, let me put that in the central void position as you know this my octahedral position and therefore, I put an atom which goes inside only octahedral void that my atom. To show an atom which actually see in the tetrahedral void, I got an alternate sphere here and you can see that this atom is even smaller than the atom which goes in the octahedral void.

So, let me show the relative sizes. So, this is my atom which goes into the octahedral void which is bigger void in the cubic close pack crystal this atom which goes into the tetrahedral void which is smaller. Of course, I have my sphere which is larger than both of those and known by seeing the tetrahedral void and let me carefully try to put it here. To put an atom into the tetrahedral void, this is a exactly difficult task because the atom tent to fall into the lower tetrahedral void are this sphere so does not matter try to get into. So, this is my tetrahedral void where matter can sit.

So, any how the point I want to make here is to actually for you to get the feel of the relative sizes of the atom. So, let me try to put it in the tetrahedral void which is slightly more successful if I can put on this atom. So, this is my position of the tetrahedral void. So, I mange that I can see that now I have atom sitting in the tetrahedral void which can be seen which is smaller and there is an additional atom write it the center which sitting in the octahedral void. So, this is my tetrahedral center of tetrahedral void this may center the octahedral void and you can clearly see that relatively sizes of these three figures I got my space filling solidly.

So, we have to remember this when I actually try to make interrelation analysis which we study later that since this sphere which can fit into this voids are rather small solubility sum of this are very limited. So, once again use this transparent sphere models to understand the relative sizes of the atom which can set in the octahedral, in the tetrahedral void in the B C C crystal. So, I have shown here two unit cell of the B C C crystal, where in a how atom like this sits in the body centering position and these atoms set on the vertices on the cube. Of course, I should go these crystals for that the putting

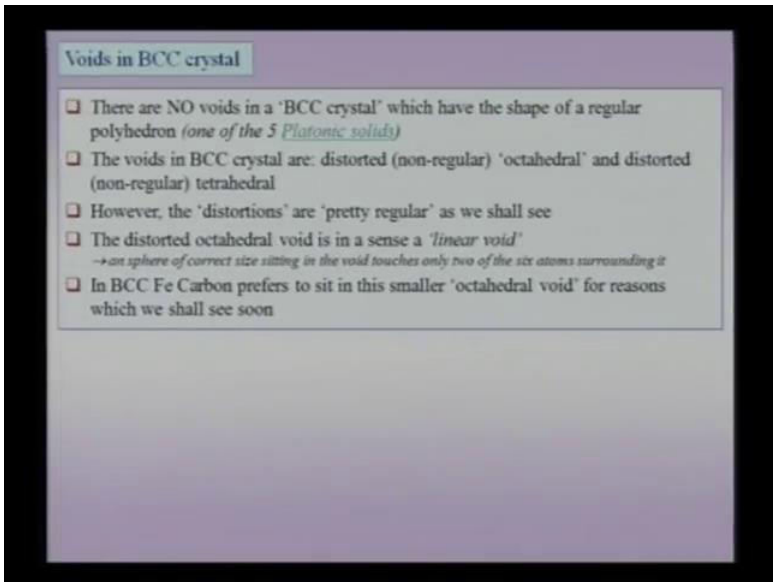
more of this spheres along the vertical direction. So, this would have been body centering positions.

Now, the two this side are the relative sides of two atom which can set in this vertices are shown here and I would not take there is putting them into spheres because they will tend to fall down into wrong places. So, this is my largest sphere which can set in octahedral void this is my largest sphere which can set in the tetrahedral void. So, let me place in down here for the relative sizing. So, I got my three sizes. So, you can see that the sizes of sphere which can fit into these octahedral voids are rather small. So, these are 0.15 0.29 and this is my full size sphere which is the lattice point.

Now, let me try to locate the relatives have position of these voids the octahedral void which is the smaller void. As we say that the atoms sitting in the octahedral void only touches the atoms which are above in below it center of the octahedral void is right between the this two body centering position right here are equivalently between these body centered atom, which I place above. So, write between these two kinds of atoms is my octahedral void position wherein this kind of sphere is.

Now, the tetrahedral void is as we say located between put a commitment like this as located. If you take half mid plane this is located at center of half mid plane. So, another words my tetrahedral which is formed, is form between one two three four this is my vertices of the tetrahedral. We see this is not a regulated this is a distorted are as non regulated tetrahedron. So, let me locate my octahedron. So, let me take say for instance this sphere. So, octahedron in this made of this central sphere one two three four five and this much sixth. So, this is my octahedral which is made by sixth atoms. The tetrahedral is made by one two, this body centering one and this body centering position and this three four. So, my tetrahedral void and relative sizes as we say before are this which can set in these relative positions.

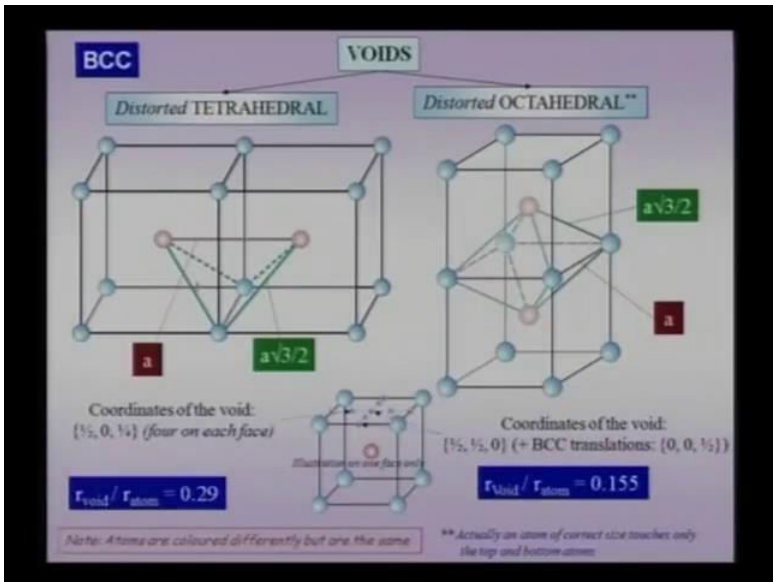
(Refer Slide Time: 39:29)



So, let us look at the void in a B C C crystal and as we pointed out there are more regular shape void. In other words, voids which are presented in the B C C crystal are not one of the five platonic solid. As we shall see you can call in the distorted for I would prefer what is non regular octahedral and non regulatory tetrahedral void which are representing in the B C C crystal. We shall see that I would draw use the word non regular are then irregular, because we shall see there is some symmetry to this non regular tetrahedral and octahedral.

As an important point, we noted and we will actually try to make some calculation based on this concept. It is the fact that the distorted are the non regular octahedral void is actually not even an octahedral void. In other words, an atom sitting in the right side in this octahedral void actually will be touching only two atoms and this is an important point to be noted. The surprising thing which is coming out of this is a fact that in the B C C ion carbon sets prefer set in the smaller octahedral void and we will try to understand the region of this for this based on the configuration along the voids.

(Refer Slide Time: 40:45)



So, where are the voids in the B C C crystal. So there are two kind of voids as we say one on right is the non regular octahedral and one of the left is non regular tetrahedral void. So, let us consider for the tetrahedral void. So, tetrahedral is made up of the edges which are two different kind of lengths the tetrahedral consider of this and this two lens which have length. This is nothing but a length of the unit cell auditioning in this got this four which are among them green and the length of this edge is root 3 a by 2. In other words, it is half the body diagonal of the cube.

So, even though it is non regular tetrahedral it is not fully distorted. As you can see, you can have two fold directions which is going along the center of these edges and the three fold direction have been lost because of the distortion. Now, various this center of this tetrahedral void with respect to the unit cell and let me locate it for instance using this cube, so the tetrahedral void. Suppose, I may face like this I take half my face, this is my half my face which is rectangle it is located in the centroid of that rectangle. So, I have model here to show you where the tetrahedral void is located. So, let me show you this model.

So, I have this two unit cell right here. So, I can divide this unit cell into two half along the mid plane like this. Now, if I take the central face which is shared between these two cubic unit cells, then I would note that it is at the center of that half rectangle which made of this face. Unless I pointed out this tetrahedron is made up of two lens one which

is red which is shown here which is a and this blue length is root 3 a by 2 and this is my two fold axis of these tetrahedral. So, how this tetrahedral would come at each phase as you known this cubic unit cell as a fourfold axis which goes along the 0 0 1 direction and that means this is one tetrahedral void tell, we four of them in each phase and how many unit cells will this tetrahedral be shared between.

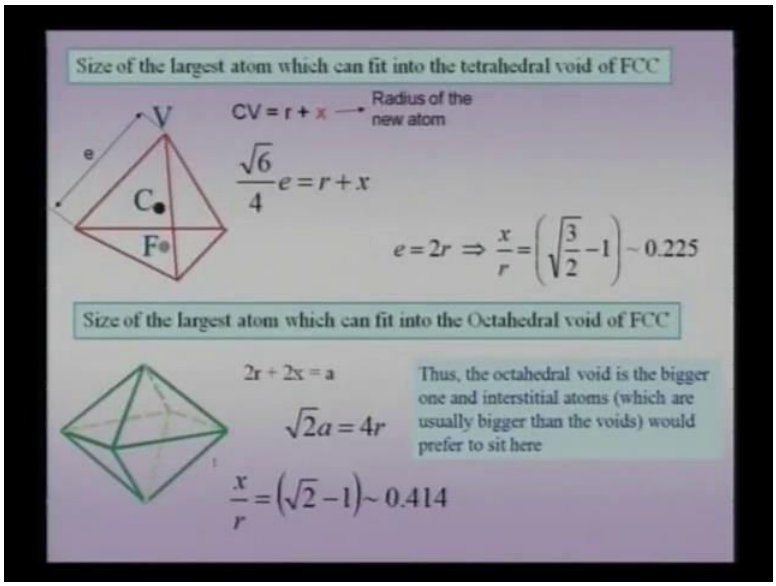
It will be two unit cells, because half of that could lie within this unit cell half of that would be like in the unit cell above as it is been shown in this figure, that each of this tetrahedral void is shared between two unit cells. So, each of these phases again would have similar kind of configuration of four tetrahedral void which have share between two unit cells. Now, I need to locate the octahedral void and as point out before this is non regular octahedral void and even though as pointed before these void are called octahedral they actually have only 6 atoms at their vertices.

So, the octahedral void is located at the phase centers. So, when I talk two unit cells and this is my octahedral void, the center of the octahedral void is at the face center. Now, again these octahedron is made of two edges lens the length which is mount brown is a and length which is mount in green is root 3 a by 2 and this exactly the two kind of length which are involved in the tetrahedral void.

Now, if I try to put an atom at the center then this length from the center of the void to the atom which is been colored orange noting again that the orange color in this two distinguish the position and all atoms are identically in this B C C crystal. Now, this distance is a by 2 while on the other hand this distance is from here from this vertex to the center is root 2 a by 2, this is a by 2 and that is root a by 2.

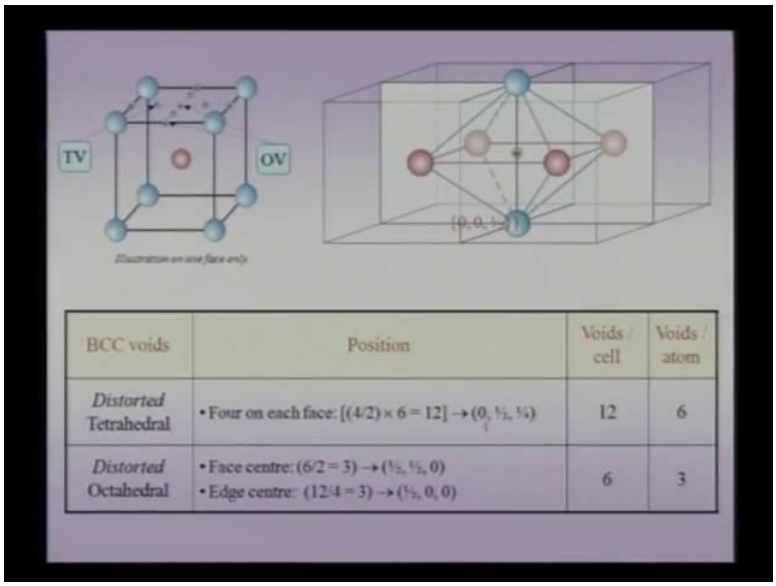
Another if I put an atom of correct side fitting within this octahedron, and then it will be only touching the atom which is upper above and below this void. In other words, it will not be touching the four in the mid plane and this octahedral void actually turns out to be a linear void. If the atom we are putting in is of exactly that size, which can fit into this void without causing distortion. Now, what is the relative size of these voids with respect to the host atom sitting in the lattice position for the tetrahedral void. The ratio of the void size to the atom radius size is 0.29 for the octahedral void it is approximately half that which is r void by r atom is 0.155.

(Refer Slide Time: 45:32)



As you can see these numbers are smaller than the void size numbers which we had noted for the cubic close pack crystal. So, what are numbers we had noted for the cubic close pack crystal, we saw that the tetrahedral void was 0.225 and the octahedral void is 0.414. So, we can see that especially this octahedral void is considerably smaller than any of the previous voids we have encountered. If this position is a seat of the octahedral void, then I can add any of the body centering translations to land up with other equivalent positions for the octahedral void. For instance, I could add for instance to half of 0 to this position which is 0 0 half and I would land up with all B C C translations to land up with equivalent identical points or this is to be half which is a body centering translation.

(Refer Slide Time: 46:27)



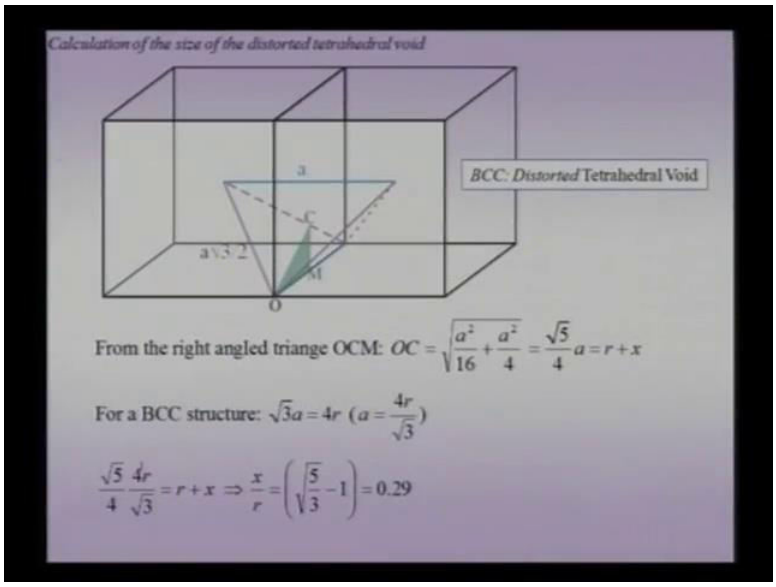
So, in other words I will land up with an octahedral void position which is at the center of edge which is zero zero half. So, that means if I have an octahedral void located at half half zero, then the center of the edge which is related by a body centering translation to this position is also a center of an non regular octahedral void. So, I have octahedral voids in one, which looks at the center of the unit cell or which look at the edges. So, with the important point to note this octahedral void is actually shared between two unit cells as you can see above and below while this octahedral void is shared between four unit cells this one, the one above, one to the left and one below that.

So, I have shown only the octahedral and tetrahedral voids located within on a single phase of the unit cell. But, we have to remember they are all the other symmetry translations, symmetry operations of the cube or the 4 by m 3 bar 2 by m symmetry operations will give me all the equivalent positions of the octahedral and tetrahedral voids. So, we have the distorted tetrahedral void we got 4 by 2 which is the one which is one located within. We saw here this kind of a thing and there are six of these phases.

So, I have twelve of these tetrahedral voids per cell as far as I am talking about the octahedral voids they are located in the face center and they have a contribution of half. So, there are six faces, half contribution they are three and there is one at the edge center which is located here and each contribution to the unit cell is four I have twelve edges, so 12 by 4 is 3. So, I have 3 plus 3 totally 6 voids per cell.

So, 6 octahedral voids per unit cell in a B C C crystal, I have twelve tetrahedral voids per cell in the B C C crystal. As there are two atoms in every unit cell of the B C C crystal, I can divided this 12 by 2 to get 6 voids per atom in the B C C crystal and 6 that is 6 tetrahedral voids per atom. There are 3 octahedral voids per atom in the B C C crystal. Now, having seen the relatively sizes of these voids the smaller being the octahedral and the larger being the tetrahedral void.

(Refer Slide Time: 48:40)

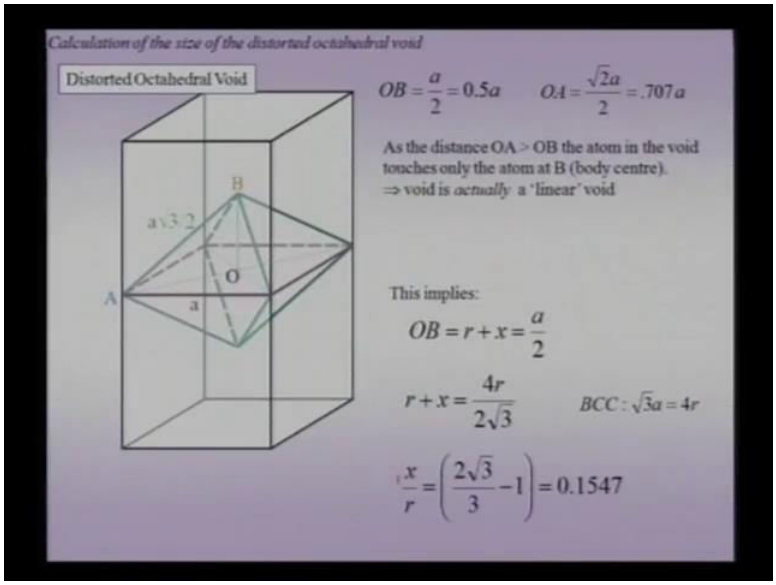


I would like to again just conform this by a calculation that actually this is the size of the tetrahedral void. So, let me do a calculation that where is my tetrahedral void located it is located at the centroid of the rectangle which is made by half this common phase. So, if I look at the tetrahedron here and I look at the centering central of the tetrahedron position c, then I can draw a right angled triangle c m o or o c m the o length o c can be got by Pythagoras theorem to be root 5 5 4 a which is nothing but the o c is where the atom sitting in the tetrahedral void.

We are touching the atom sitting in the lattice position. So, that will be equal to r plus x for the B C C structure I know that the atoms touch along the body diagonal. Therefore, root 3 a is equal to 4 r. In other words, a is equal to 4 r by root 3 I can substitute this value for r. So, r plus x becomes root 5 by 4 4 r by root 3 which is r plus x from this equation. Therefore, x by r is root of 5 by 3 minus 1 which is 0.29. So, using simple

geometry I can actually calculate the size of the atom with respect to the size of the atom sitting in the parent lattice which can fit into this tetrahedral void.

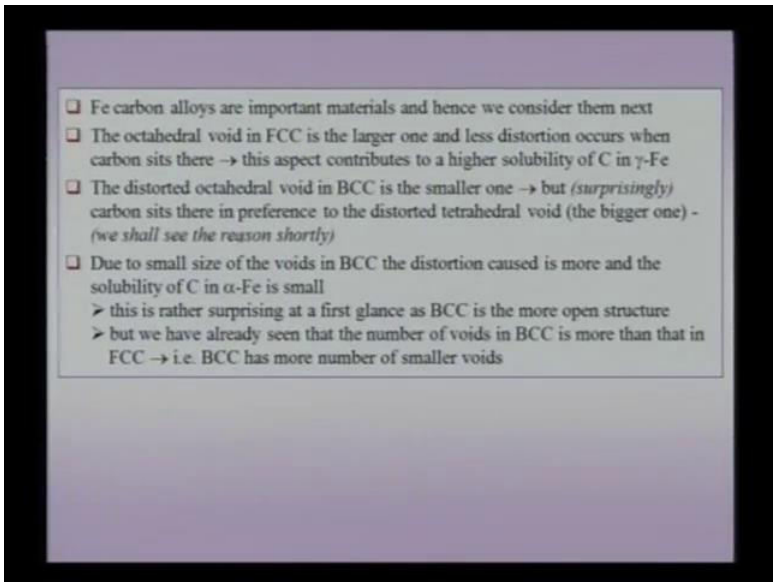
(Refer Slide Time: 49:58)



Similarly, I can make of course, the calculation for the octahedral void and noting in this case that my atom is now be touching along the O B direction. So, my atom along the O B direction which is a by 2 which is nothing but 0.5 a and that is equal to O B is equal to r plus x. Now, the x atom which is my for an atom or the atom sitting in the interstitial position would be touching the atom sitting in the parent lattice and that is equal to a by 2. Therefore, r plus x equal to 4 r into 2 root 3, now this is O A for instance this O A is my root 2 a b by 2 and I have known for B C C crystal root 3 a equal to 4 r.

Therefore, I can calculate my x by r to be 2 root 3 by 3 minus 1 which is 0.1547. Now, again this is of course, very simple kind of geometry which I am applying here to understand my kind of species which can sit in the tetrahedral and octahedral voids. A student has quested to go through these calculations once again to convince himself that, these calculations are right and also to understand the relative configuration of the atoms when they sit in the octahedral and tetrahedral voids.

(Refer Slide Time: 51:16)



Now, as I pointed out we will consider the special example of carbon in ion to and the relative size of the atoms. Especially, when you talking of a carbon sitting in B C C ion with respect to a carbon sitting in F C C ion to understand how the solubility would be affected by this relative size of the voids and which void the carbon atom preferentially sits in. So, in the case of the F C C it is very clear that the larger void is the octahedral void and when I add carbon to gamma n which is the F C C ion the carbon could sit there. There is no confusion regarding that, but in the case of the carbon and B C C ion as I said it surprisingly carbon sits in the smaller octahedral void which I pointed out in some sense is actually a linear void.

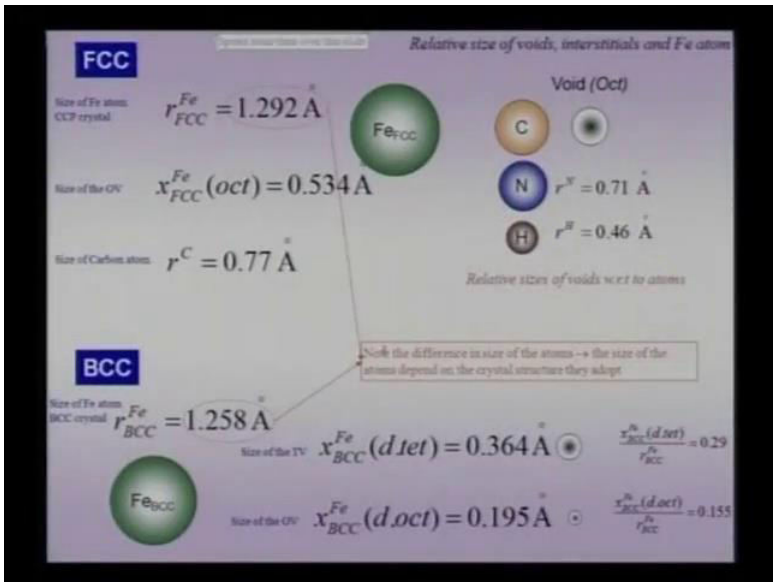
We will try to understand why this is. So, now however we notice that with respect to both the voids which are present in B C C even the largest of the voids. The voids are smaller in B C C, this is somewhat surprising because we know that the B C C is a open structured. But we already saw the number of voids in B C C is more than that in F C C. In other word, B C C has more number of smaller voids even though there is larger amount of space available in B C C crystal; it is divided up into smaller sized voids. That is why my carbon actually finds it difficult to sit in any one these voids which are actually small and this would affect its solubility.

We know that carbon is actually the solubility at room temperature and alpha n is extremely small. It is of the order of 0.001 percent or something very small. The gamma

n which is founded higher temperature actually some much as solubility for carbon. So, to repeat this important point we know that B C C is an open structure. So, at first glance we would assume that actually we will have a higher solubility of carbon in a B C C ion. But, when carbon tries to sit in the B C C voids the distortion caused is more and the solubility of carbon in ion is smaller.

This is because the number voids in B C C are the total space available in voids is actually split up into smaller number of smaller size, larger number of voids and this is a void in my solubility of carbon in B C C ion is smaller. Of course, this is one of the reason there are other region which would come out from various other aspect which we need to consider in detail. But, this is sort of a first level understanding of the solubility of carbon in ion.

(Refer Slide Time: 53:51)



So, let us look at the relative sizes of the voids and especially with respect to the size of the ion atom. Before this thing, I would point out in this tensor is the size of the ion atom itself. For instance, beside the ion atom in the cubic close pack crystal is 1.292, this is of course, an approximately value which is different from the size of an ion in the B C C crystal. So, this is something to be noted that means that the size you calculate also depend on the crystal structure. Now, what is the size of atom, how do we calculate is a subject by itself.

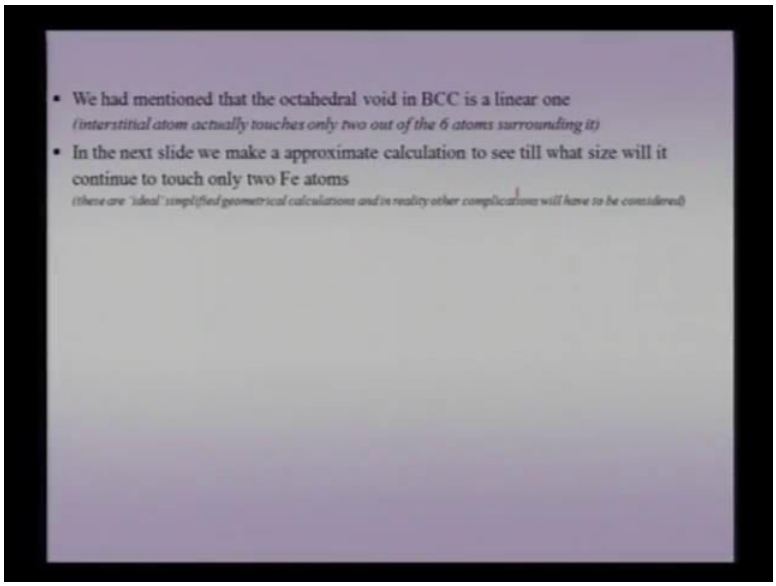
Typically I would assume in spherical distribution of electron probability and use some valuable truncate to get some value the radius of the atom. But, I need to note this important point that the radius is not equal in these two crystals structures. I have drawn a figure here to indicate the size of the ion sphere which is in the F C C crystal and also that which is in the B C C crystal of course, which are approximately similar. Now, let me look at the size of the carbon atom and the size of the carbon atom happens to be 0.77 Angstroms, which is drawn here to relative scale with respect to the green ion shown atom.

Now, size of the octahedral void in F C C crystal is also shown here for relative size and as you can see the carbon atom is bigger than the octahedral void size. Now, this is my octahedral void size which happens to be 0.534 Angstroms while the carbon atom is 0.77 Angstroms. Therefore, the void is smaller than the size of the carbon atom. So, even though as I pointed out the solubility of carbon in ion, gamma ion is more which is F C C from or the cubic close pack of ion. Even then we note that the void is not even enough to fit a carbon atom the void just happens to be to fit for instance of hydrogen atom which is a diameter of about 0.46 Angstrom.

So, that can fit into an octahedral void, but if you take any other atom like nitrogen which itself a small atom or our carbon which is of technological importance this would not comparability fit. Then other I will try put carbon into F C C ion there will be solubility, but then this solubility is limited by the kind of distortion it causes to the lattice of course. Initially, we considered only dilute concentrations of carbon in gamma m we will take up the B C C crystal. Then we see that the void sizes are considerably smaller. This is my octahedral void which is smaller and the tetrahedral void which is bigger is also smaller than the octahedral void or any of the atoms.

So, my void of my tetrahedral void in B C C is about 0.364 which means that even a hydrogen atom cannot fit into this void. So, it will cause distortions when it tries to fit into this void or definitely the octahedral void is even smaller and it is a diameter a 0.195 Angstroms which radius is this therefore, the four its radius is which 0.15 Angstroms. Therefore, it is smaller than the tetrahedral void and consider it to be this smaller than the carbon atom.

(Refer Slide Time: 57:07)

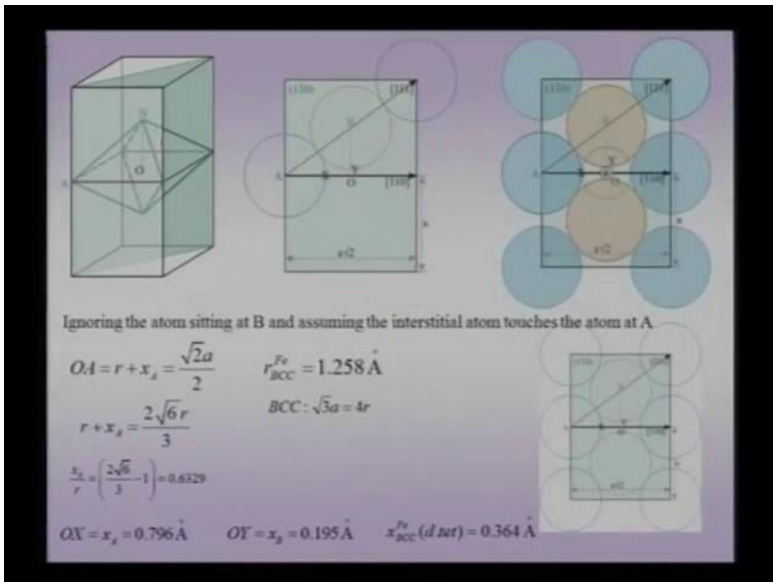


Now, let us try to answer this question which he had raised that why is that the carbon goes and sits in the octahedral void. The answers turns out that when I try to put a sphere which is now my carbon atom into this let us assume two options. Now, the tetrahedral void which is a larger one or the octahedral void which is a smaller one. So, it can choose one of the two and I pointed out that it actually goes and sits in the smaller of the two. The reason is that, when it sits in the octahedral void and it is definitely bigger than the octahedral void.

But still it needs to only push two atoms out of place when it sits in the octahedral void. While if it sits in the tetrahedral void, it is actually touching all the four atoms and as the carbon atom is bigger than the other void it will be actually pushing four atoms out word. So, the distortion it cause to the lattice that means the energy it cause to the system is large if the carbon atoms tries to sit in the tetrahedral void.

While, if it is in the octahedral void it can only push out two atoms and try to make space for itself. So, I will try to make an ideal calculation to see till what size it will end up only pushing two atoms. So, it is the question of ideal geometrical calculation which is highly simplified when try to push two atoms out ward that will lead to a chain of other distraction which will end by actually squeeze this also octahedral void shape at time. Ignoring all just you show that there is a considerable shape available if you are willing to tolerate pushing only two atoms.

(Refer Slide Time: 58:40)



So, before I considered now my octahedral void in the B C C structure and I choose my 1 1 0 plane to illustrate the point I want to make the 1 1 0 plane. I have chosen because among the 1 1 0 plane which is shaded green here. I can draw my 1 1 1 direction. This starts from this point and possess opposite body diagonal here and the atoms in the B C C crystal touch along those direction.

So, my atom which is sitting in the vertex here and the atom, which is sitting in the body centering position and the atom, which is sitting in the opposite vertex. So, again I over laid again all the atoms here on this 1 1 1 plane and this being my 1 1 0, 1 1 1 direction. This direction now is my 1 1 0 direction, which is nothing the 1 1 0 direction of the connecting a vector the opposite vertex here. Therefore, I have my 1 1 0 kind of plane here with 1 1 the actually plane would be 1 1 1 bar zero I have my 1 1 0 vector lying in this plane.

So, if an atom which is now compared to the side would be 0.15 the atomic size of action would be here, then it would be touching only these two atoms will not be touching the remaining four which is 1 2 are shown in these plane. The remaining two would be on this vertex in that vertex and they have not been shown in this diagram. So, they will be touching only the two atoms which are colored orange shade.

Now, assuming the ideality it can expand till it reaches a diameter which is shown in dotted line without having to push these two atoms. So, this is an ideal geometric

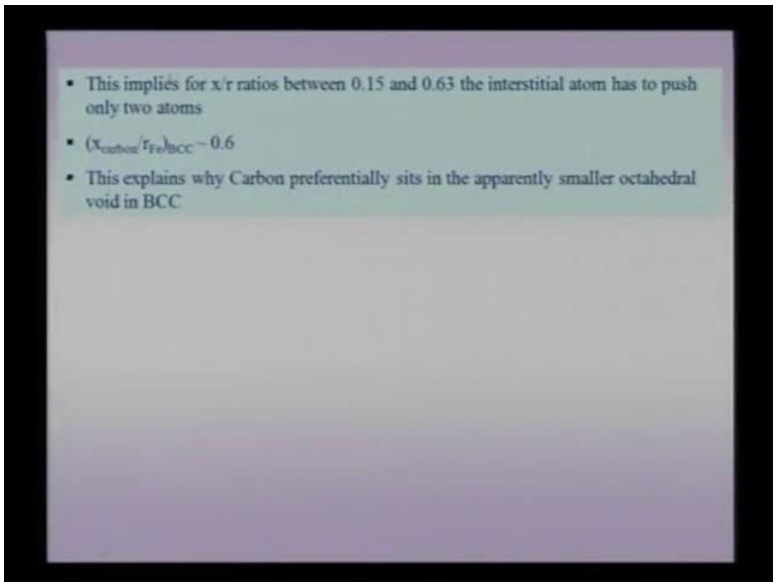
calculation. Once again I need to emphasize that it can continue to put larger and larger sphere into this small hole here which is shown here in the middle without actually having to push these two blue atoms. So, this is what I was trying to say.

This is the region that the carbon actually wants to sit in this smaller octahedral void. But again I need to point out that these are simplified first level understanding in a deeper understanding would come from a more detail calculation wherein you actually try to fit atoms of this and make a calculation of how that will affect the energy of the system. Now, let me try to calculate what is the size from O to X and ignoring. Of course, for that I will ignore the atoms sitting at B and assuming the interstitial atoms touches till the atom touches at T.

To this what I will try to make a calculations, now my O A is r plus x i. So, this is my atom at X which is now the expanded atom is equal to root 2 a by 2 and r plus x i is equal to root 6 by 3 r, now in terms writing in terms of r which for the B C C crystal. So, I can calculate x i by r to be 0.6329. Now, trying to translate this into real dimension my O X will be for the B C C ion crystal is 0.796 Angstroms while I know my carbon atom.

So, this is 0.796 atom. So, let me compare with the size of the carbon atom which is the size of 0.77 atom Angstroms. So, this O X is larger than the size of my carbon atom and if you compare this with O Y which is smaller number is 0.195. So, I can see that if larger size sphere is put into the B C C crystal, it would rather go and sit in the octahedral void and push out two atoms, which would cause my system lower energy. It will continue to put to do. So, till it start touching this atom which are sitting a kind of which have been shaded blue. This explains two things of course, why carbon atom goes and sits in the octahedral void. But, additionally it also points out why the solubility of carbon is extremely small in B C C ion.

(Refer Slide Time: 1:02:40)



To summarize, this x by r ratios between 0.15 and 0.63 and again pointing out this are some so on. So, the simplified calculation the interstitial atom has only push two atoms and therefore, it would go and sit in any octahedral void. So, with we have made a sort of an overview of all the void which are present in the cubic close pack crystal the body centered cubic crystal and the external force pack crystal.

We saw this for the C C P and H C P crystal, the voids are identical and they are able at right hand the regular octahedral the B C C crystal has larger space of void. But it is divided into smaller voids which are large in number and this is an important point to be noted and this aspect also would later on determined some of the other aspects like diffusivity, etcetera.