Defects in Crystalline Solids (Part-I)
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Lecture - 07
Interstitials in Iron

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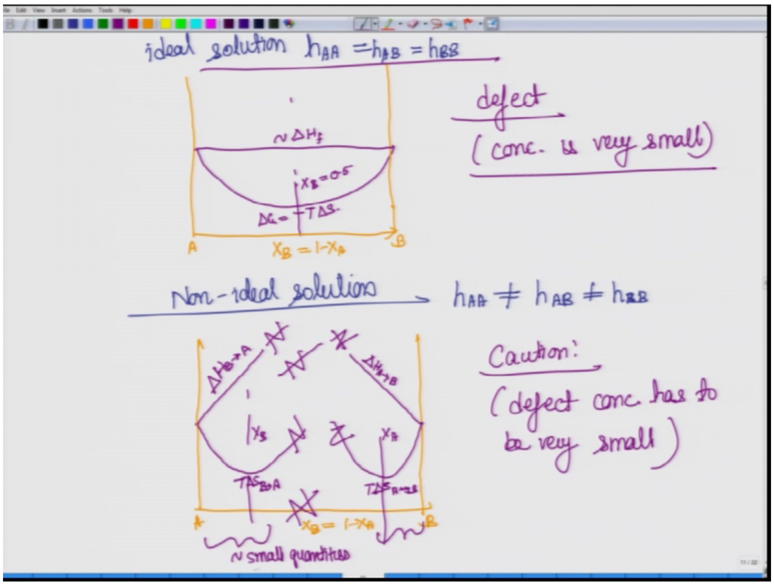

So, let us start from where we left in the last lecture. So, we were looking at substitutional kind of impurity. In substitutional impurity, as we said that one of the atom has been replaced. A has been replaced by impurity B. Therefore, we have different kind of bond. So, initially what should have been AA bonds, now has been replaced by AB bonds. And we said that this delta H f, the enthalpy of formation can now be approximated by difference in these bonding energies.

Now, let us we also considered the situation of ideal solution, where h A A that is a bond between A A is same as the bond between A B, and the bond between B B. And in that case, as you can see is the delta H f comes out to be approximately 0. So, we have a straight line here. And this is on the x axis, what we have is the fraction of B impurities or B particles. And as you keep going this side is the pure B. And then you go from here, it is like adding A impurity. So, this is delta H f, it comes out to 0. And this is the minus T delta S term, which is which becomes equal to delta G. So, delta G equal to minus T delta S forms like this. And this will be minimum at X B equals to zero 0.5.

Now, next thing that we said we will look consider is the non-ideal solution. So, here what we have is that h A A is not equal to h A B not equal to h B B. So, how would it look like? This is now ours simple the one the way we have been drawing so far which is so again we are taking the same axis A, pure A over here, pure B over here. And we keep increasing, and on the y-axis is the energy scale.

So, what will happen? So somewhere over here is the 0. So, when you have let us talk about the pure A, so you are adding B impurity. So, there will be delta H. So, delta H, when B is the inserted in as impurity in pure A, so this is delta H. And simultaneously, for this there will be at T delta S, which will something you go something like this. On this side again, we will have pure B and A is being put in as impurities, so this will let me draw it in a more straight line, this is supposed to be straight line. So, this is delta H, A going to B.

So, here A is acting like impurity, and B is the pure material. Here B is the impurity, and A is the pure material. So, here this will be something like this. So, this is the minus T delta S, and again to differentiate I will said B going in A, and here A going in B. And I should not put minus, because it is already in the negative scale. So, this is how it would look like. And corresponding to that, you will find X B, corresponding to for this your find X A.

And remember this is since this is non-ideal solution. We have to again limit ourselves to very small concentration. So, this region that we are talking about are very small quantities, whether we are talking about here or whether we are talking about here. And in between we do not know, we will will need to have a phase diagram to understand what is going on over here. So, I have given a break mark over here.

So, in between this you do not know what is going to happen, whether there is a intermetallic farming or something. So, there is gap of knowledge in here. Anyhow like I said last time, the cool have to maintain a caution that when we are dealing with this solution defective as a solution, you have to remember that defect concentration has to be very small.

So, although we have exaggerated here, to draw the whole plot and even here, we are trying to show the both sides, but the ideally that is not that right thing. It is just to give you a better understanding not what it would been, it would mean when h A A is equal to h A B, and when h A A is not equal to h A B. But, otherwise we should not extend this information from beyond small quantities ok.

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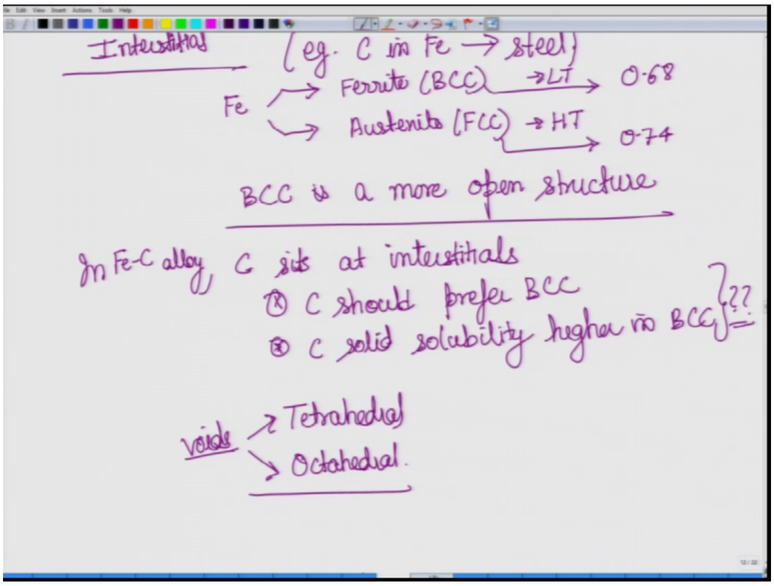

So, with that will move on to another kind of the interstitial sorry thus substitution sorry, we have already looked at substitutional. Now, we look at interstitial, so, impurity of different kind, which is interstitial. So, we saw some of the characteristics like, it is easy to find a site, because all the sites are available it easy to move, because there are all most all vacancies everywhere.

And the major problem here is thus availability sorry the size the size that is available here. And to understand this, we will look at carbon in iron, which is what which is what we call as steel ok. So, most of you would already know that iron exist in two states. One is the ferrite, what is the structure BCC. And the other is the austenite, which is the FCC - face centered cubic. And this is a body centered cubic. And this is at low temperature, and this is found at high temperature.

Now, what is the percentage of space occupied in BCC or what is called as packing fraction. We know that packing of BCC is equal to 0.68. And what is the packing fraction of FCC, it is equal to 0.74. So, what does this imply that BCC is a more opening structure right, because it has more empty space. Now, if I give you are we would already be knowing that carbon sets in interstitial the carbon in the Fe- C alloy in Fe-C alloy, which is steel primarily steel carbon sits at interstitials.

Then one would be inclined to say that since BCC is a more open structure. And if carbon sits can go in both FCC and BCC, you would been cline to say that carbon should prefer BCC. And solid solubility carbon solid solubility, it should be higher in BCC. This is something that you would expect given these information that in Fe-C alloy carbon sits in interstitial, BCC has a packing fraction of 0.68, and FCC has a packing fraction of 0.74. And assuming that the approximate lattice parameter are similar, not of not different very, very large magnitude. But, the question is, is it true.

So, we will see. To understand this, we need to understand that in this cubic structure, you have two different kinds of voids. Because, now we are talking about interstitial, so the atom with set are going go to a particular void. And there are two different kinds of voids in cubic system. One is called tetrahedral. And the other is called octahedral ok.

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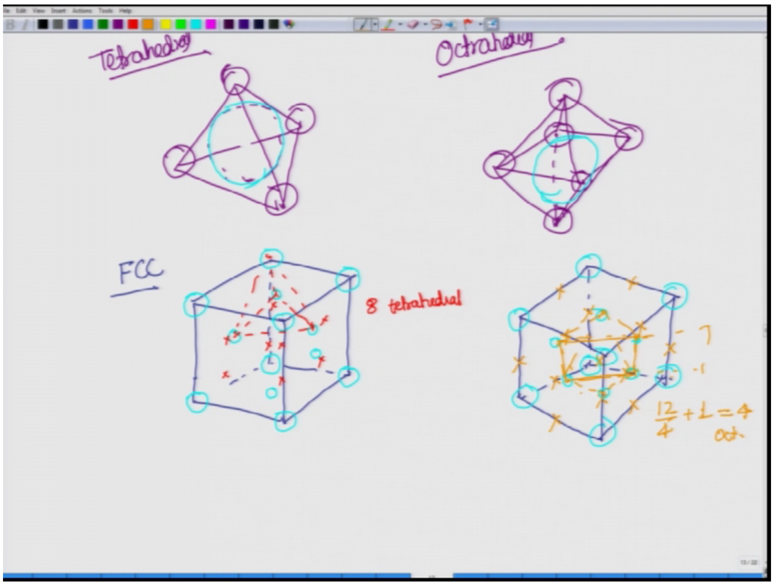

So, now let us look at how do the what do we mean by tetrahedral and octahedral? Tetrahedral means that, you have four faces. So, it is like a pyramid, which has but a little different from pyramid. So, here you have atom, here you atom, here you atom, here you atom. And inside this is face is there is sufficient space for one atom. Now, that will depend on the lattice parameter, and where exactly the tetrahedral site, we are talking about that we will see more detail in a moment. So, let me so this is the pyramid with four faces, four triangular faces. And we have some space in here, where you can make atom set.

What is the octahedral, in octahedral you can assume it that it has eight faces not assume, basically it has eight faces. So, it goes like, so here you have atom, here you have atom, here you have atom. Now, the way I am trying I am intentionally showing a much larger space than it is actually available, just to make you understand, where this void is, because if I really draw it in the scale of the atoms, you would see it would appear that there is no space here at all here, but to make you understand that there is a space here. I drawn the atoms to be very small. And so there is a space in over here, where your atom can set. So, this is the octahedral void.

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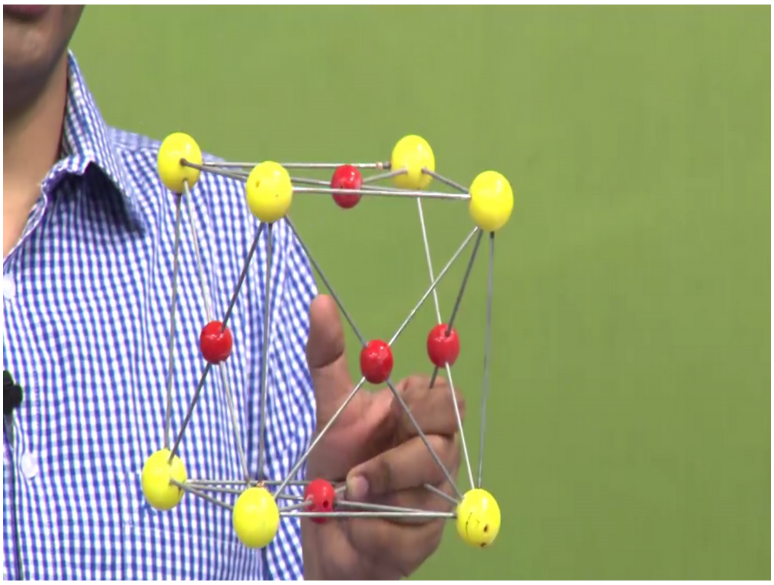

Now, we will look at the two different systems, which is one is the first let us look at FCC. So, now I have brought model over here. So, this is not really FCC. Why it is not FCC, because here the two atoms have been given different colors. It is showing that these are two different atom, but let us assume that these are same atoms ok, I did not have the model, where both of them of where of same color. So, for now you will assume that yellow and red are same atom. So, this is a FCC. Now, this is how the FCC would look like, now where is the tetrahedral void in this.

So, first look at let us look at the tetrahedral void. So, now where is a tetrahedral void, remember this is the same atom, this is same atom, all these are similar atom. So, now if you point, if you look at it carefully, this atom, this atom, this atom, and this atom, now what do you see, does it form a tetrahedral? These four together all of them remember are same atom, like I said for the time being forget the colors, assume that they are same atom; so, 1, 2, 3, 4. So, three face centre and one corner atom. Do you see, at a tetrahedral kind of structure? So, this is the tetrahedral void in FCC, so now you are able to see that.

Now, let us go to the other void in this, which is the octahedral void. So, to understand octahedral void, let us look at so here is one missing atom over here. So, let us assume this tape of my finger is other atom. So, now look at 1 atom, 2 atom, 3 atom, 4 atom, 5 atom, and 6 atom. So, all the face centered atoms. So, this six atom together they make what do you see, what is the kind of structure it is making into the square on this plane, and that is two for two have one atom on the top, and one atom at the bottom, just around the centre of the axis.

And disputes look very similar to what we have drawn over here. So, this is octahedral. And this is first octahedral in the FCC. So, would now we have seen, how the octahedral void looks like, and how the tetrahedral void looks like. But, there is still one more thing, now I have shown you this void over here in the octahedral void for the FCC. Now, this is not the only octahedral void over here.

Assume that there is another atom, another cell over here. So, there will be a face centered over here, there will be face centered atom over here, there will be face centered atom over here. And this face centered atom over here. These four atoms again from a plane square, and along the centre axis you again see this atom, and this atom. So, this again this also forms of octahedral. So, in the FCC there is one octahedral at the very centre of the cell. And also at the edges of the at the centre of the edges centre of each of the edges.

So, will draw it again over here, but this is to make you understand this is where the octahedral voids like. So, they are two different place, where octahedral void lies in the FCC, so that is FCC. Now, let me just draw it over here, so that you can remember it. So, this is our cell. And I will draw the atoms light blue, so that it does not get to crowded. So, these are the corner atoms. And now I will draw the, I am drawing a little different size, so just again, so that it does not get to crowded.

So, now you can see the corner atoms, and the face centered atoms all of them being the same color. So where that I showed you the tetrahedral, so in the tetrahedral was like, if you assume that this, this, and this face centre, and this corner, so this is one tetrahedral in here. Now, you can imagine how many tetrahedral would be there, there should be eight. Around each corner is each corner is associated with one, and that particular tetrahedral site remains inside the cell. So, there is one over here, there is one over here, one over here and similarly on the bottom side. So, there are eight tetrahedral.

Now, let us go back to the octahedral. So, I will have to draw this again. So, let me draw the corner atoms. And by now you should be in a position to identify, where my the basic the first one. The first octahedron is, so where is the first octahedron, it is in the where it center. So, I will join this. So, this is the plane. And these are the two atoms ok I have drawn missing one atom in the bottom. So, I hope you are able to see, this is the plane. So, I will draw with solid line now. And these are the two atoms on top and bottom. So, inside this is the first octahedral void, and whereas did we say that there are octahedral voids there are octahedral voids on the edges.

So, if you can look at it then this face centre, this face centre, and then the face centre on the other atoms around it they will form a plane something like this and these are the two atoms octahedral void over here, octahedral void over here, here. So, similarly for all the edge centre, you would see one octahedral void. Now, if I were to calculate the number of octahedral void inside, this inside this particular cell, so these the once that are lying on the edges they are being shared by 4 atoms, which means there are 12 edges for 12 by 4 and plus 1 in the centre. So, it is equal to 4 in 1 unit cell. So, there are four octahedral voids ok.

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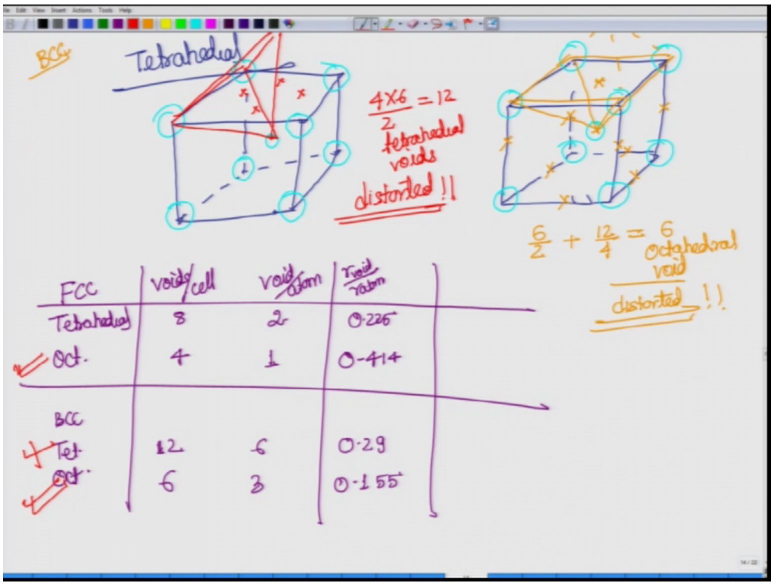

So, now let us go to the BCC structure. So, I will take the other atom over here. Now, first let us look at where is the tetrahedral void. So, the first thing that I want to identify is the tetrahedral void. Now, let us look at 1 atom, 2 atom, 3 atom. And then imagine the base BCC draw the body centered atom on top of it.

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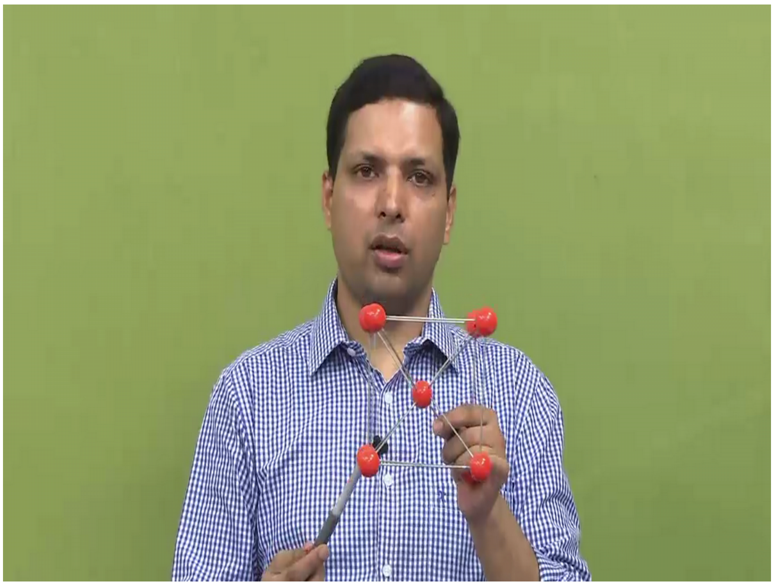

Now, this is the straight simple for a simple BCC. Here the two atoms are not shown different. It is simple as it is as it should be all the atoms are same color. This is the real

BCC. So, this one body centered atom in the two corners, and one over here. These four would form the corners of a tetrahedral void. So, we can see 1, 2, 3, and 4.

Now, so what do you see here, where will be the octahedral void. So, by symmetry you can say this is body centered, this is another centre. These two are in the plane. So, this should lie somewhere on this surface. So, there will be one on this on this side then another one would lie at here. So, each surface will have four atoms, 1, 2, 3, 4 atoms. Now, how many edges surfaces are there? There are six surfaces. So, each of the surfaces have four. So, we have 6 for the 24.

So, let me know to before we forget. So, let me draw this to be able to, so let us draw the atoms. These are the corner atoms. And then there is one in the centre. Now, let us join this, and like I said there will be one on the top. So, somewhere over here, not able to show it as properly and because of this now tetrahedral void would lie over here, over here. Now, there are four on a surface that.

I hopefully, we have to convinced that there are four voids on the surface. Similarly, there will be four voids on the surface four voids on this surface. Now, each of these voids are being shared by one more cell over here. So, this belongs to only half of it belongs to this. So, 4 into 6 is a total number, but each of them are being shared by 2. So, for a by 2, therefore there 12 tetrahedral voids.

Now, let us go back to our octahedral void. So, these are the tetrahedral void, now let us look at octahedral. So, for that again lets come back to our BCC model. So, this is the BCC unit cell. Now, we will concentrate on this body centered atom, these four atoms on the corners. So, this four atoms on the corner as you can see, they form a plane. And these two corner atoms sorry the body centered atom they form the atom, which are there along the centre axis. So, this is one atom, this is another atom. And one of your octahedral void would lie on this surface. So, this is the total this is the octahedral void, we are talking about.

So, let us draw this part. So, again I will have to draw. So, these are these atoms are also connected with the atom on the body centered of the unit cell on the top. So, there is one over here. So, there is one tetrahedral sorry the octahedral void over here. Now, try to identify if there are any more octahedral voids over here, so can you identify? If you again either you can look over in the diagram or let us again come back to this BCC model, so now what you would see is we were talking about two atoms one over the other and a plane of atoms.

Now, if you look over here, similar kind of structure, you have over here. So, this is as well as good as a body centered atom for some other cell. If we had the cell orientation shifted by half x, half y, half z, then this would have become the body centered. So, this itself will become the centerline and this body centered plus this body centre plus this body centre they will from one plane and which means that at the edges of these also lies one octahedral void. So, we have octahedral void also at the edges.

So, how many do we have over here, we have 6 faces which means 6 octahedral void because of that, but this is being shared by 2 cells. So, this is 6 by 2 for this unit cell. And we have 12 edges; and on each edges, we have 1 octahedral void, but this one is being shared by 4. So, this is 6 by 2 plus 12 by 4. So, this is equal to 3 plus 3 - 6. So, we have 6 octahedral void. So, now, we have seen the different kinds of voids in FCC and BCC; however, there is still something that I have not informed you yet.

And what you need to see over here is again I will bring this back to show you first let us look at the octahedral void. So, how was octahedral void over here as is expected this is the plane of the atom this is the all the top two atoms. Now, look at the length of the edges, each of the length from here to here or from here to here or so each of the neighboring atoms they have same length.

But now let us look at the octahedral void in this one. The length from this and this atom to this atom this is how much equal is this is equal to root 3 by 2, and this one is equal to 1. So, the length of these the length here between the different neighbors are different and therefore, this octahedral void is in fact distorted. So, the void that is see over here in the BCC you must remember are distorted. So, this is a very important aspect that will help us understand the solubility of carbon in two different phases octahedral void here are distorted.

Now, similarly let us look at the tetrahedral void. For FCC you remember this and this plus this, these four atoms on the tetrahedral void. Now, you look at the length here to here, here to here, and here to here, all of them are exactly same in magnitude. But now let us come back to the magnitude of length for the different atoms in the tetrahedral void of BCC. So, here to here, here to here, here to here there are same. But now what is the length of this one to this one, this is equal to 1, and this one is equal to root 3 by 2. So, this is a different. So, again octahedral so tetrahedral voids are also distorted.

So, remember that in BCC both the voids are distorted. Now, this is a very important concept. So, before going let me just summarize what we have looked at. So, we have seen for FCC let us see tetrahedral, octahedral. Now, for BCC let us look at tetrahedral and octahedral. So, how many voids per cell we have? We will set with that in FCC 8 tetrahedral void per unit cell and 4 octahedral void per cell. In BCC, we saw that we have 12 tetrahedral and 6 octahedral void. How many now we also need to look at void per atom.

How many atom do we have in FCC? In FCC, per unit cell has 3 atoms. So, sorry the 4 atom, so that means that for each if we divide by if you want to get void per atom then will have to divide void per cell divided by 4. So, 8 by 4, it becomes 2; 4 by 4, it becomes 1. Now, for BCC there are two atoms in one unit cell. So, this becomes 12 by 2;6, this becomes 6 by 2;3. So, this has 3 tetrahedral void per atom; 6 tetrahedral void per atom, and 3 octahedral void for atom.

Now, the other important factor is that if you do a little bit of geometry not little bit, but a little bit involved geometry you would be able to show that r void by r atom ratio are something like this 0.225. So, it is just 22.5 percent of the in the radius for what is the radius of the atom. For octahedral it is 0.414. On over here, if you look tetrahedral voids a larger, so these are 0.29 and octahedral void are just 0.155 ok.

Now, I will leave you with just one thought; which one do you think would carbon atom prefer in FCC and which one it would prefer in BCC? So, here what you see is that octahedral voids are larger. So, this means it will be much more easier, less strength, and therefore you would say octahedral voids would preferred. In BCC would say that here the tetrahedral voids are preferred should be preferred because the sizes are larger, and therefore, it will be easier or less amount of strain in the lattice. So, you would say this, but then I would say it is not true, what they prefer is still is this one ok. So, we will extend this understanding in the next lecture, which will help us to understand more about this interstitial kind of impurity.

Thanks.