Solid State Chemistry

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Lecture – 31
Coordination number, voids

Now, we will start week 7 of this course. And in the last 3 weeks we had a fairly intense discussion on the symmetries of crystals. And the discussion was quite intense and quite at times fairly mathematical, and as I had mentioned that sometimes these are not very easy to visualize. And you need to practice by looking at models and various solved examples ok.

So, but now in the next few weeks we will change the topics a little bit we would not talk about symmetries, but we will start talking about different aspects of crystals ok. So, today in this lecture and this week we are going to talk about coordination number and defects and packing in crystals ok.

So, week 7, lecture 1, I will talk about coordination number and voids. Now, you are somewhat familiar with these terms like coordination number and voids you might have seen them, in your earlier discussion of solids ok. So, some of this will seem like a reservation, but it is always good to think about these concepts again.

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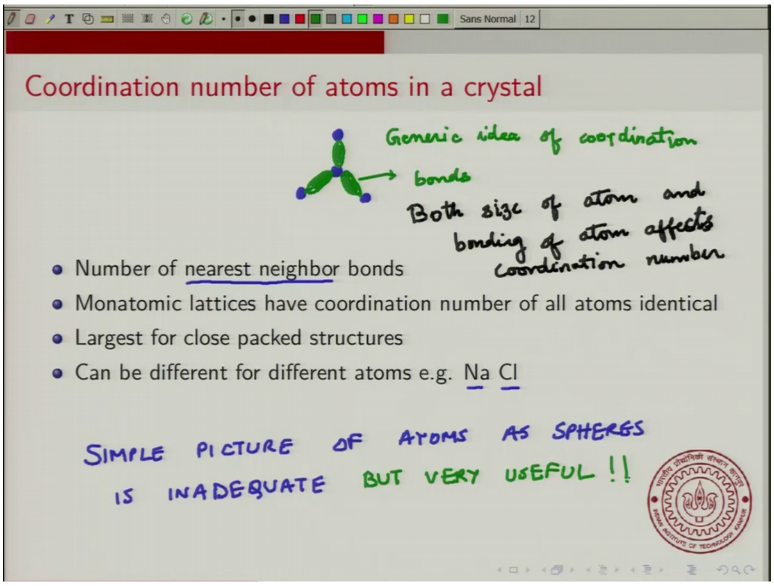

Coordination number of atoms in a crystal

Generic idea of coordination

bonds

Both size of atom and bonding of atom affects coordination number

- Number of nearest neighbor bonds
- Monatomic lattices have coordination number of all atoms identical
- Largest for close packed structures
- Can be different for different atoms e.g. Na Cl

SIMPLE PICTURE OF ATOMS AS SPHERES IS INADEQUATE BUT VERY USEFUL !!

So, let us ask, what is the coordination number? So, the coordination number first we will talk about coordination number of atoms in a crystals ok. So, if you have an atom in a crystal, then its coordination number is simply the number of nearest bonds, nearest neighbor bonds, that that atom has.

So, you just count how many other atoms it is closest to ok and that number will be the coordination number. The important point is that you have to look only at the nearest neighbors ok. Now, if you had a monatomic lattice like an FCC with a single atom basis ok, then the coordination number of all the atoms will be identical.

So, all the lattices monatomic lattices, because each lattice point is identical ok, the each lattice point will have the same coordination number. And if there is an atom at each lattice point, then that atom will have the same all the atoms will have the same coordination number ok. Now, the coordination number is of atoms is usually largest for close packed structures and we will see examples of that and you know each atom in the crystal can have a different coordination number ok. And you can look at individual atoms and crystals and look at their coordination number.

So, for example, you would have a coordination number for sodium and a coordination number for chlorine, in a sodium chloride rocks rock salt crystal, turns out that both of them have the same coordination number in this case, but you can imagine there are cases when the constituent atoms will have different coordination number ok.

Now, so, really what at the center of this whole discussion is the idea that you have some atom in a crystal and you are looking around that atom. So, you look around that atom and you look in various directions and you look at the other atoms that are later around it ok. So, this is a very central idea that you imagine that you have an atom in a crystal. And you are looking at all the other atoms around it ok.

So, this is the generic idea of coordination number ok. And let me say; let me say that this is a very general idea and therefore, you can apply to several other objects other than just atoms ok, but the other point I want to make is that, as a chemist you know that this atom in a crystal ok, if there are 2 atoms in a crystal, they are going to form some sort of a bond ok. There will be some sort of a bond between these 2 atoms ok, I will just show it this way.

So, this so, they will be some sort of a bond between neighboring atoms. Especially, there if they are closest to the nearest neighbor ok. So, there will be some sort of bonds ok. So, you expect some sort of chemical bonds between atoms in a crystal ok. And so, the coordination number is really a combination of the chemical bonding that these two atoms have and some size ok. So, let me emphasize that this point it will become clear as we go along.

So, both size of atom and let us say I can say the nature or the bonding of atoms effects coordination number. And this is again a very we will come back to this a little later, you know we often in our picture of crystals, we like to visualize atoms as solid spheres ok.

So, atoms as solid spheres, but really the way they bond ok, its not obvious I mean you have to look at the; you have to look at the valence orbitals of the atom in your to see, what is the hybridization that it can have and only then you can decide what kind of bonds it forms ok. So, I will just leave this point here, that the simple picture of atoms as fears is not adequate. And we will see it very will inadequate we will see it very often, that you know just thinking of an atom as a sphere and all these spheres as packed together is actually fairly limited, but it is still a useful concept ok.

It is inadequate, but still very useful. So, this is a point that I want you to keep in your mind that, you know we will often treat atoms as though they are just fears and we will do various calculations ok. So, you might calculate things like packing fraction or the size of the void, where you treat where you explicitly treat atoms as spheres ok. And in principle this is not adequate and we will see soon why this is not adequate, but it is still a very useful and very powerful idea ok.

So, let us look at some examples. Let us look at the very simple lattice monatomic lattices. So, if you have FCC ok, then what is the coordination number of the atoms?

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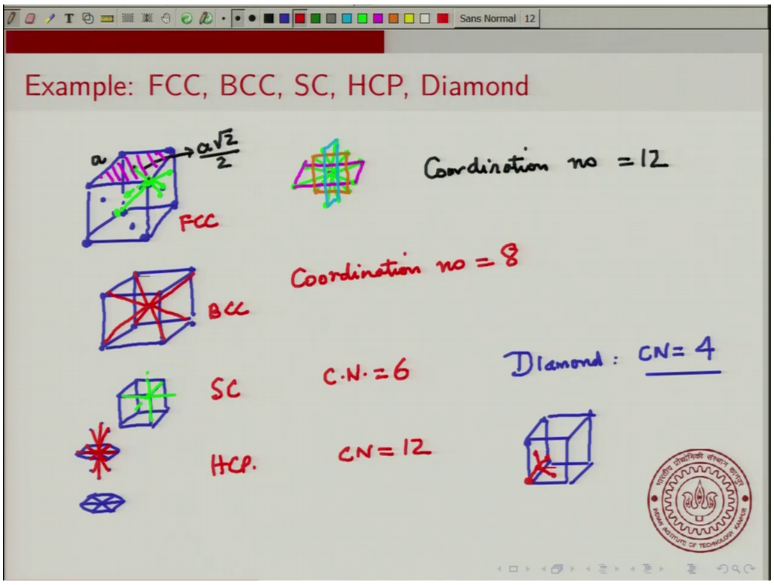

Example: FCC, BCC, SC, HCP, Diamond

So, here if you are here you can see that in an FCC, I will show one conventional unit cell of the FCC, the cubic unit cell with the atoms at the corners and the atoms at the phase centers ok. Now, what you can see from this and it is more clear if you extend the lattice is the following that let us take I will mean I will just take this atom that I am coloring in light green and I will look at the coordination around it ok.

So, if you look at this atom the atom that is nearest to it is actually this atom ok, that atom is a distance if this distance is a ok, then this distance is a root 2 by 2 ok. Because, the diagonal the phase diagonal is the total length of the phase diagonal is a root 2. And so, this is half of the phase diagonal. So, the distance between these 2 atoms is a root 2 by 2.

So, that is this distance ok. Now, this is the closest neighbor for an FCC ok. And now let us take this out and we will see; we will see where else, now you can immediately see that there will be one in this in the same plane ok, but in neighboring unit cells ok. Then, we also noticed that this atom is the same distance away, this atom here is also the same distance away, that is at the center of this face that is also a root 2 away ok. Similarly, this atom in the center of this face is also a root 2 away ok. And what you can see is that in one plane, if you take this if you take this central atom ok.

So, in the in one plane in the z in let us say in this in this plane that I will shade in a slightly different color ok, this plane and you imagine that this is extended to many structures ok. So, you have so, the central atom has 4 nearest neighbors, but then there would also be 4 nearest neighbors in a perpendicular plane like this, that is perpendicular to the screen of the paper. And then there would be a third plane also where there would be 4 atoms and that would be in the plane of the screen ok. And you can see now that basically there are 12 nearest neighbor atoms ok.

So, the coordination number will be 12 ok. Again, its you can draw the different plane. So, there would be one that is the plane of the screen and the third plane would be perpendicular to this ok. So, you can easily see that there are the central atom has 12 of these atoms as the nearest neighbor. So, coordination number equal to 12 and since FCC is a blob a lattice every atom is identical. So, the coordination number of every atom is 12.

What about BCC again? In the case of BCC again you can easily see that in fact, in fact it is BCC is you can see it very easily, because if we take the central atom the atom that is usually represented as the center of this cube. You can see clearly that it has 8 of these cube corners, which are the nearest neighbors. So, here you can see coordination number ok. So, FCC has higher coordination than BCC ok.

This is FCC; this is BCC ok. What about simple cubic? Simple cubic you can see that the coordination number will be 6, because in this case now each atom will have 1 2 3 and then it will have 11 4 5 6. So, each atom will have 6 nearest neighbors. So, in simple cubic I will write coordination number equal to 6 ok.

So, the coordination number increases as you go from simple cubic to body centered cubic to face centered cubic. What about the HCP? So, HCP you can see fairly easily I would not do this in detail, but you can see that HCP the coordination number is 12 ok. And to see this you just imagine that, you have this hexagon, hexagonal plane, that is perpendicular to the screen and you have another hexagonal plane that is perpendicular to the screen ok.

And, if you look if you imagine the center of this yeah so, if you imagine that now you look at this central atom ok. And keep in mind that you have you have 3 more atoms here in the halfway between ok. And you will have you will have 3 more atoms the top face above it ok. And you can see that this central atom in red is coordinated to 6 other atoms in the in the plane and then it is coordinated to 3 of them here in this direction and 3 of them in this direction. So, coordination number is 12 ok. And you can show that indeed 4 for each atom the coordination number will be 12 ok. What about the, what about our favorite diamond cubic structure?

So, for diamond ok, the coordination number is just 4. For a diamond cubic structure and you can see this because each atom is we will have only 4 nearest neighbor atoms. So, for example, if you take let us say this the typical diamond cubic structure ok. And now an atom in a diamond cubic structure, let us say; let us say you take this atom that is one fourth along the body diagonal ok. That will be coordinated to this corner atom, it will be coordinated to this face center, this face center and this face in the face that is directly in front ok.

So, there will be 3 of these face centered atoms and this corner atom. So, all you to all of them the distance will be one-fourth root 3 ok. So, these are fairly basic exercises and many of few already familiar with these exercises ok. So, now, let us go to the next topic that is the packing fraction and again, I will come back to the idea of bonding and crystals ok. And now you have probably seen how to calculate packing fraction on soft crystals ok.

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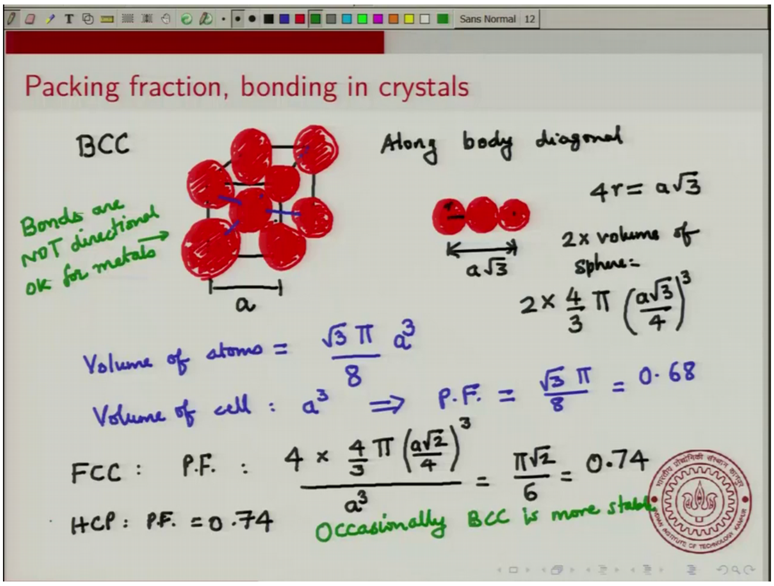

Packing fraction, bonding in crystals

BCC

Bonds are NOT directional → ok for metals

a

Along body diagonal

$a\sqrt{3}$

$4r = a\sqrt{3}$

2x volume of sphere:

$2 \times \frac{4}{3}\pi\left(\frac{a\sqrt{3}}{4}\right)^3$

Volume of atoms = $\frac{\sqrt{3}\pi}{8}a^3$

Volume of cell : a^3 $\Rightarrow$ P.F. = $\frac{\sqrt{3}\pi}{8} = 0.68$

FCC : P.F. : $\frac{4 \times \frac{4}{3}\pi\left(\frac{a\sqrt{2}}{4}\right)^3}{a^3} = \frac{\pi\sqrt{2}}{6} = 0.74$

HCP : P.F. = 0.74

Occasionally BCC is more stable

So, let us take the example of BCC ok. So, in BCC we say that if you look at the structure of BCC, you have a cube and you have an atom at the body center. Now, this atom at the body center ok, let us draw it as a spheroid I am deliberately drawing it a little big ok. Now, this atom it is coordinated to all these it is nearest neighbors with all these other 8 atoms all the other 8 atoms at the corners of the cube ok. So, therefore, since it is closest to all these we can now imagine that this is a sphere and its a sphere that is large enough.

So, that it touches it just touches all these fears of the same size that are located at the corners ok. So, let us another sphere at this corner, these are all supposed to be the same size ok, same size and they are supposed to be spheres ok. And similarly it will touch, it will be in contact with this fear at this in contact with the sphere here.

Similarly, it will touch this fear and it will also it will also touch this fear from it will be in contact with this and similarly it will also be in contact with this ok. So, really this is in contact with all these atoms, it is in it is also touching this atom all the way behind ok. Now, what is important is that, if you look along the body diagonal ok, if I just stretch out the body diagonal to a straight line ok.

So, the length of the body diagonal, if this side is if this lattice size is a then the body diagonal size is a root 3. So, if you take this distance a root 3, you have this corner atom, you have this one atom at the body center and you have this other corner atom. In this distance is a root 3 ok. And if the radius of this sphere is are ok, then you immediately conclude that 4 r equal to a root 3 you conclude that 4 r equal to a root 3.

And now what you say is that is that in this BCC in this cube there are 2 spheres. So, volume of sphere into so, 2 into volume of sphere is equal to 2 into 4 by 3 pie, now r cube; r cube I will write as a root 3 by 4 cube ok. So, the volume of atoms so we say that the volume of atoms is this is this number, this quantity and that is.

So, if we if you write you can write this as root 3 pi by 8 8 and multiplied by a cube ok. And the volume of the volume of cell is equal to a cube ok. So, this implies the packing fraction is equal to root 3 pi by 8 ok, that is about 6 that is about 0.68 ok. So, the packing fraction of this cell is 0.68; that means, in this whole cube corresponding to a BCC to a monatomic BCC lattice ok.

The volume occupied by the atoms is about 68 percent ok. Now, what about FCC you for FCC in the now in the case of FCC the atoms along the face centers, along the face diagonal will be touching each other ok. So, the and then there are 4 atoms ok. So, if you put it all together you get a packing fraction, that is given by 4 atoms and the volume of the atoms of each atom is 4 by 3 pi. Now, a r cube r will be; r will be a root 2 by 4 instead of root 3 by 4 divided by a cube.

So, this becomes equal to pi root 2 by 6 and that is equal to about 0.74 ok. So, the packing fraction in FCC is more than that in BCC and we say that; we say that FCC is closely packed is a close packed structure and you know also HCP we have packing fraction of 0.74 ok.

And FCC and HCP they represent the closest packed structures for a single atom structures, for say fertile crystals made with a single atom, this is the best packing fraction that you can get or this is the highest packing fraction that can be obtained ok. Now, in this whole calculation, you notice that we have treated these atoms as spheres. In fact, we have treated them like hard spheres ok, that just touch each other and they like here you can see that they are just touching each other ok. But, they are not going into each other they are not distorting ok.

So, this picture inherently assumes that these atoms are spherical object ok. Now, as I said this is not this is not exactly correct I mean atoms do have electrons, which have orbitals and which can have shapes. And so it is not as it is not like spheres that are touching each other. Because, there is a there are orbitals and there is overlap between these between the orbitals of the atoms ok.

And this is a reason that you know though based on the packing fraction, you would expect that all most structures would be FCC and HCP and that is correct, but you do occasionally you find BCC structures to be more stable ok. So, the point is that occasionally BCCs is more stable is more stable and what I mean is that you see; that you see the element forming the BCC structure instead of the FCC or HCP structure. An extreme case where the bonding so, in this case we are we have assumed that bonds are not directional ok, which is largely true for metals ok.

So, in calculating this in this whole picture of how the atoms are packing into the crystals, we are somehow at the back of our mind our mind we have this picture that the bonds are not directional. And this is largely true for; largely true for metals ok so, this is for metals to some extent ok.

So, therefore, most of the metals crystallize in FCC or HCP ok, but not for nonmetals. So, definitely you know silicon crystallizes in a diamond cubic structure ok. And if you calculate the packing fraction of diamond cubic, it will be much lower. In fact, the coordination number is only 4. So, the packing fraction is actually only about 4 percent and that is also found ok. And that has to do the fact that the bonds in diamonds are really covalent bonds that have a very specific direction ok.

We will keep this in mind as we and then move ahead with the discussion ok. Next, we will talk about voids in crystals ok.

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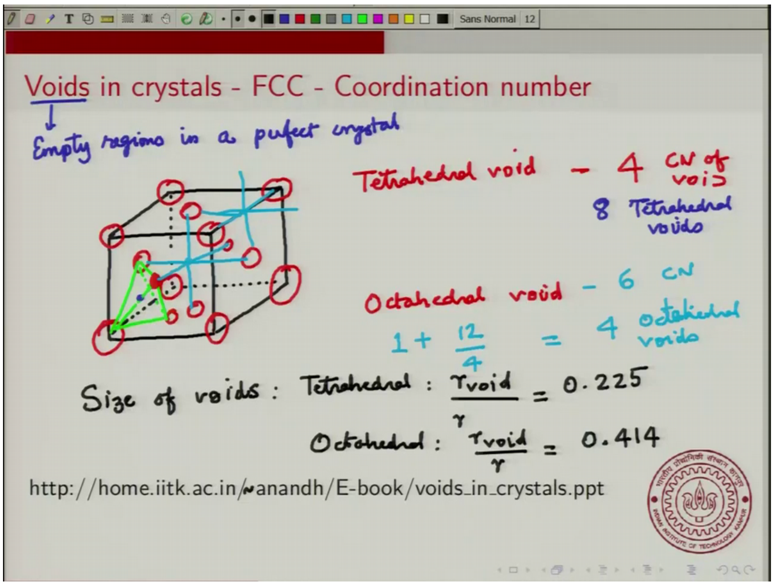

Voids in crystals - FCC - Coordination number

Empty regions in a perfect crystal

Tetrahedral void – 4 CN of void

8 Tetrahedral voids

Octahedral void – 6 CN

$1 + \frac{12}{4} = 4$ octahedral voids

Size of voids : Tetrahedral : $\frac{r_{void}}{r} = 0.225$

Octahedral : $\frac{r_{void}}{r} = 0.414$

http://home.iitk.ac.in/~anandh/E-book/voids_in_crystals.ppt

The voids are actually these are these refer to empty regions in a perfect crystal ok. And if you take the example of FCC ok, we will first take the example of FCC and then we will introduce the idea of coordination number of a void ok. So, we will show that even the void ok, which is not an atom ok, you can also talk about coordination number of the void ok. We will start with FCC and then we will do the other, we look at some other structures.

And, at this point let me point you out to this website ok. This is my colleague and Professor Anand Subramanyam from the Material Science and Engineering Department at Indian Institrute of Technology, Kanpur. He has an E-book and in that, he has an E-book on introduction to material science. And engineering and in that there is a very nice presentation, that is put up on voids and crystals ok.

And this is this really explains these ideas of voids extremely well and I encourage each of you to go and look at this; look at this link and you will understand the idea of voids very well ok.

So, let us get back to the FCC ok, now you might have learnt in your undergraduate or and or perhaps even in high school, that the FCC crystal a perfect FCC crystal ok, it has some regions in it ok, which we refer to as voids ok. And these have a very some very specific regions, which we call as voids ok. And let me just show the atoms, I would not; I would not show the atoms are touching each other, but really you should imagine that these are large spheres that are touching each other, one right in the center of this face ok.

Now, there are these regions ok. Now, the two kinds of whites I will show one of them in this light green color. So, if we take the center of this region ok. Now, the center of this had them at the center of this you have something called a tetrahedral void ok. So, this is located in the center of this of this region ok. And now this point in blue is equidistant from this face center, this corner, this face center and this face center.

So, this last one in red is actually located in the face directly on the in the plane of the screen. This point in blue is equidistant from each of these 4 points ok. And this is referred to as a tetrahedral void ok. And this coordination number is actually 4, coordination number of the void ok. So, this 4 is the coordination number of the void ok. And you can have tetrahedral voids, so, this is closest to this corner atom ok.

And since there are 8 corner atoms you can have a total of 8 tetrahedral voids ok. So, in this conventional unit cell you can have 8 tetrahedral voids ok. Now, there is another kind of void which is called the octahedral void ok. And I will show you one of them one of them is located right in the center of this cube ok. And that is coordinated to it is equidistant from each of these 6 face center atoms ok.

So, the octahedral void 6 is the coordination number. And now if it is located at the face center if it is located you can locate it at the center of the cube, you can also locate octahedral voids at these edge centers ok. So, this would also be on an octahedral void, because it would be connected to it would be coordinated to 6 atoms.

So, now, there is one at the; one at the center of the cube ok. And there will be there are a total of 12 edge centers ok. And each one, where each one contributes one-fourth to this to the cube, that we are looking at so, total of 4 octahedral voids; octahedral voids. So, in this one; in this one conventional cube that we consider so, with respect to this cube there are 4 octahedral voids and 8 octahedral voids and you should keep in mind that this cube has 4 atoms ok. So, now what is interesting is that, you can ask a question; you can ask the question about the size of these voids ok.

Since just as we look we can look along we can take a line from this corner atom to the void atom any and if you imagine that there is a little sphere or there ok. Then, we can find; we can find out the size of that sphere that will fit into this void ok. And if you do that ok, its again very simple geometry to find out the size of the void size of voids ok.

So, for tetrahedral ok, you can easily show that the radius of the void divided by radius of this atom ok, it radius of this atom ok, this is equal to 0.225 for octahedral void. You can easily show again that the radius of the void divided by the radius of the atom ok, this is about 0.4 414 actually it is root 2 minus 1, so, it is 0.414 ok.

So, therefore, what you conclude is that the size of the tetrahedral void is smaller than that of the octahedral void. So, the tetrahedral void is smaller than the octahedral void ok. So, you would expect that only smaller atoms would go into the tetrahedral voids and the larger atoms would go to the octahedral voids ok. And again this picture is assuming that the atoms are spherical objects which they are not.

And in fact, we will show that, you do have atoms going into a tetrahedral and octahedral voids, which do not satisfy this ratio ok, what about voids in BCC and HCP ok. Again, I would not go into this in too much detail you can look at; you can look at the website that I pointed out to pointed about to ok.

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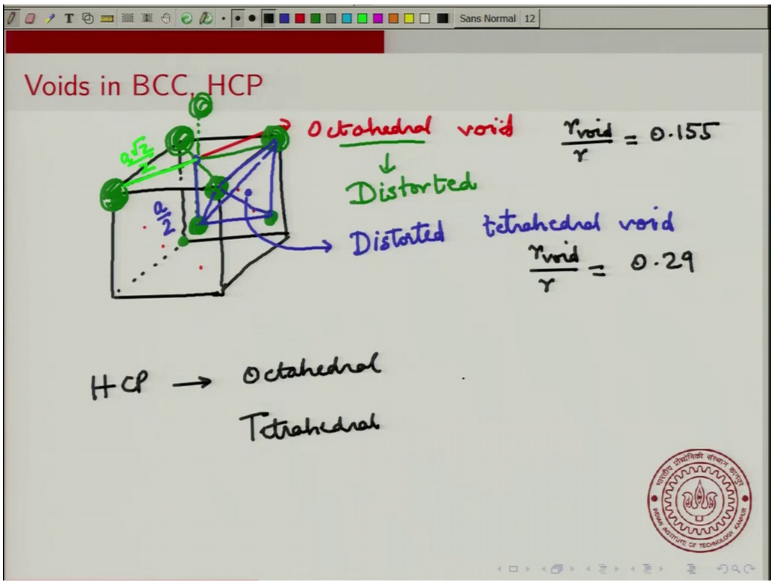

Voids in BCC, HCP

Octahedral void $\frac{r_{void}}{r} = 0.155$

↓

Distorted

→ Distorted tetrahedral void $\frac{r_{void}}{r} = 0.29$

HCP → Octahedral

Tetrahedral

But, you can show that in the BCC, if we take a conventional cube of the BCC with an atom at the body center ok, then you can show that these points will be octahedral voids ok. So, each of these each of the phase center the points of the phase centers would be would be an octahedral void ok. It would be; it would be coordinated to the central atom ok, but there is a little bit of a catch ok. And this is a catch that you get with BCC, let me explicitly show the atoms that are around this void and there would be one on one above it ok.

So, this is what we mean by an octahedral void here ok. Now, it is actually this is slightly distorted ok. The reason we say it is distorted is because this length ok. So, this side ok, let me show it in a different color this side in size in blue ok. So, the distance of this void to this atom is a by 2 whereas, the distance to this atom to any of these atoms is a root 2 by 2 ok, that is half of the phase diagonal ok. So, if a is the side of this BCC cube ok, then this distance is a by 2.

Whereas, this is a root 2 by 2 ok. So, it is slightly distorted it is not exactly octahedral it is slightly distorted ok. So, this is an octahedral void ok. Now, you can also have a; you can have a so you have a distorted octahedral void, you can also have a distorted tetrahedral void in a BCC structure. So, and that is easy to see you take the you take the atom from this cube, you take the atom at the body center of the neighboring cube ok. So, this is in the neighboring cube and then you take these 2 atoms ok.

And, you will get a tetrahedral you will get you will get a parameter structure and at the center of this of this polyhedron is a tetrahedral void ok. So, this is a distorted tetrahedral void ok. Now, the now the I will just; I will just mention that the octahedral void the radius. So, for this r void of this relative to the r of the atom is about 0.155 whereas, for the tetrahedral void the same ratio point 0.29 ok. Now, I will leave it as an exercise to you to show where the voids in HCP are, but you can have a; you can have a both HCP also has a octahedral and tetrahedral voids, it will voids and this is left as an exercise ok.

So, I am not going to work it out explicitly here so, the point that we have been talking about is that, if you look at the space available in a void.

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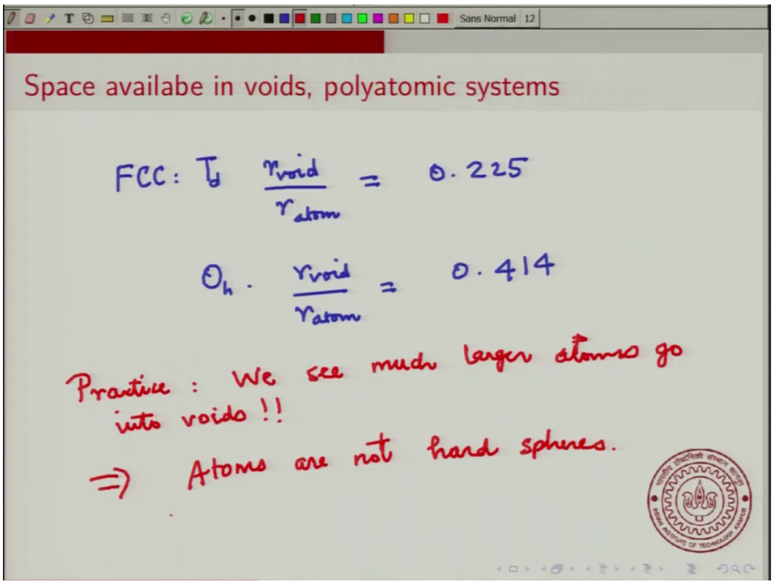

Space availabe in voids, polyatomic systems

FCC: T_d $\frac{r_{void}}{r_{atom}} = 0.225$

O_h. $\frac{r_{void}}{r_{atom}} = 0.414$

Practice : We see much larger atoms go into voids !!

⇒ Atoms are not hard spheres.

So, for FCC we saw that r void this is for the tetrahedral void. So, r void divided by r atom, this is equal to 0.225 for octahedral void ok, we said r void divided by r atom this was actually 0.414 ok.

So, what it seems to suggest, it seems to suggest, that if you had a; if you had a different atom, if you had an FCC lattice and you had a different atom ok. That was much smaller that letter whose size was 0.2 to 5 that of the of the FCC atom ok, then it would fit into the tetrahedral void. Similarly, if it was 0.414 times the size of the FCC I see atom it would fit into the octahedral void ok.

However, in practice or in practice we see much larger atoms go into voids ok. And this really again goes back to the idea that atoms are not spheres are not hard spheres ok, they distort they can actually stretch out the they can push the so, you can put a bigger atom into the tetrahedral void and FCC by pushing out the atoms of the FCC ok.

So, I will conclude this lecture here for now ok. This is a slightly long lecture where we have talked a lot about the about you know coordination number and voids ok. Now, in the next few lectures I want to start talking about the different kind of defect that you can have in crystals.

Thank you.