Solid State Chemistry
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Lecture - 46
Close-packed structures and voids

Now, I will start the 10th week of this course. And in this week you will see the common crystal structures. So, it will be you will look at various crystal structures of elements of simple binary compounds and a few oxide compounds and these are the common crystal structures that you encounter in lot of materials. So, in a sense this will be fairly descriptive and it will be nice to see how some of the concepts that we have talked about so far in this course they actually apply in the calculation of in the actual structures of different materials.

So, it will be in some sense it will be rewarding because all this work we have done about structures and symmetry and packing and so on. We will actually be applied to see how to understand the structures of different crystals. And I will start this 1st lecture of the 10th week with discussion on closed packing and voids and as I had said earlier that a lot of crystal structure can be understood in terms of thinking of atoms as spheres which pack into a space ok. So, week 10 in the 1st lecture we look at Close-packed structures and voids.

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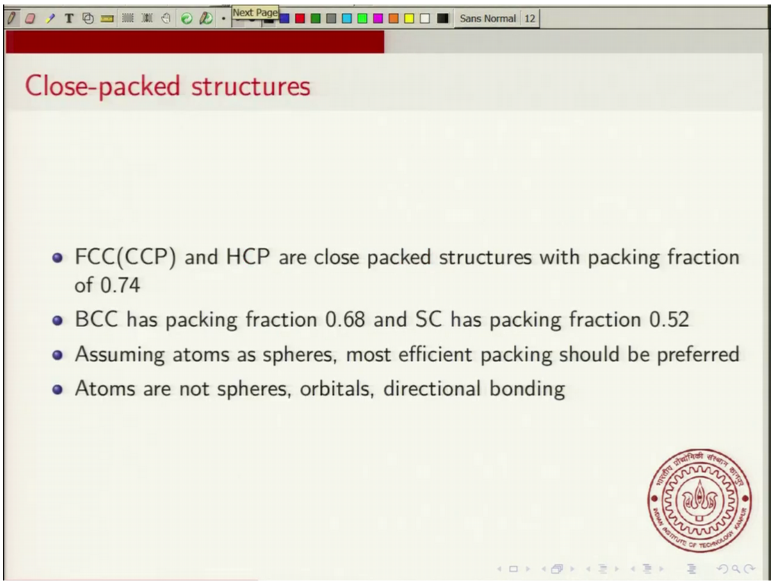

Close-packed structures

- FCC(CCP) and HCP are close packed structures with packing fraction of 0.74
- BCC has packing fraction 0.68 and SC has packing fraction 0.52
- Assuming atoms as spheres, most efficient packing should be preferred
- Atoms are not spheres, orbitals, directional bonding

What are close-packed structures? As we already learnt the FCC or the cubic closed-packed and the HCP that is a Hexagonal Closed-Packed or closed-packed structures and they have a packing fraction of 0.74 and that is the highest possible packing fraction if you have spheres ok. So, if your atoms are perfect spheres, then this is the highest packing fraction that you can get.

The body centered cubic has a packing fraction of 0.68 and the simple cubic has a flat packing fraction of 0.52. This is the monatomic BCC crystal and similarly this is a monatomic simple cubic crystal. And as I had already said that this idea of packing assumes that the atoms are spheres and intuitively we feel that the most efficient packing should be preferred because they would like to pack very closely to each other ok. So, you might expect that most of the structures you will see are FCC and HCP, but the fact is that atoms are not spheres and there are orbitals ok. So, the bonding between atoms goes through orbitals and there is a directionality in the bonding.

So, what we will see is that even though you would expect most of the atomic crystals to be FCC or HCP, we will find that significant number of them are BCC and other structures.

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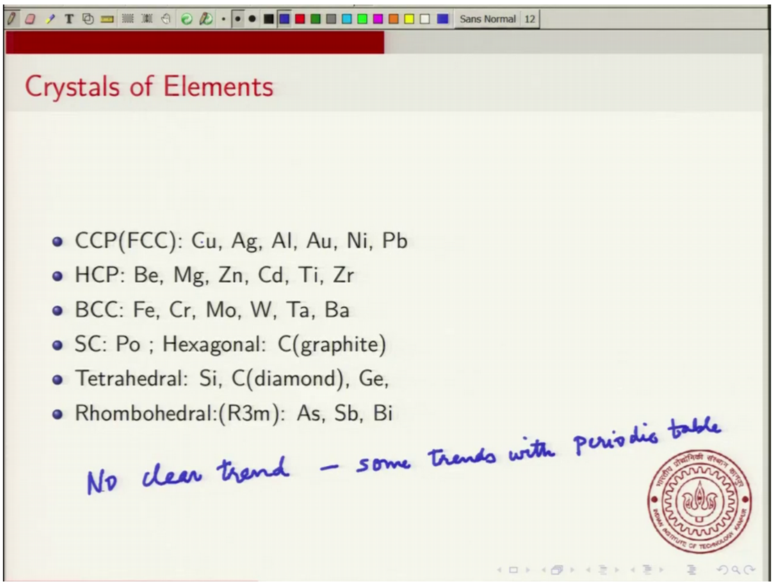

Crystals of Elements

- CCP(FCC): Cu, Ag, Al, Au, Ni, Pb
- HCP: Be, Mg, Zn, Cd, Ti, Zr
- BCC: Fe, Cr, Mo, W, Ta, Ba
- SC: Po ; Hexagonal: C(graphite)
- Tetrahedral: Si, C(diamond), Ge,
- Rhombohedral:(R3m): As, Sb, Bi

No clear trend – some trends with periodic table

So, let us look at the crystals of elements. So, I am just listing some elements and they are crystal structures. So, if you look at the cubic closed-packed or the FCC, you have copper, silver aluminum, gold, nickel, lead. These are some of the metals that form a cubic closed-packed the hexagonal closed-packed. You have barium, magnesium, zinc, cadmium, titanium, zirconium. These are just some of the examples.

For BCC Body Centered Cubic you have ion actually also forms an FCC, but at much higher temperatures at more than 1000 Kelvin. Chromium, molybdenum, tungsten, tantalum, barium, these all form body centered cubic structures. Simple cubic there is only one example of an element that crystallizes in simple cubic that is polonium .There is a hexagonal structure like for example graphite, carbon in the form of graphite crystallizes in a hexagonal structure, there are several tetrahedral materials. We have already seen the diamond structure of silicon or diamond carbon or germanium.

There are several others ok, then there are some elements that actually crystallize in a rhombohedral structure with a space group R3m. So, some of these examples are arsenic, antimony and bismuth. So, this is actually you know the trigonal crystal system can have either the trigonal or the hexagonal and you can have the hexagonal or the rhombohedral ok. So, this comes in the rhombohedral crystal system ok. Arsenic, antimony and bismuth are some examples of this ok. So, what you notice is that there is no clear trend; no clear trend ok, you cannot say that heavier elements for prefer certain structures or something of that. We notice that arsemenic arsenic antimony and bismuth are in the same period ok.

So, there is some similarity for example carbon, silicon, germanium, they are in the 4th row of the period the 4th period and they also have tetrahedral structure. Similarly the rhombohedral elements are in the 5th period. And so, there is some trends ok, some trends with periodic table some, but it is not overall there is no clear trend. And for example, there is no clear understanding of why iron is BCC whereas, copper is FCC and really these are just; these are just the crystal structures that are observed and it turns out that the electronic structure of these elements makes them prefer a BCC makes ion prefer a BCC whereas, it makes copper prefer of prefer an FCC ok. Now these are some of the crystals of elements.

Now one of the very useful concepts when you go to crystals of multi element compounds for example binary compounds. What we like to think is that we like to visualize these elements as forming some crystal structure and then the other element occupies some voids in that structure ok.

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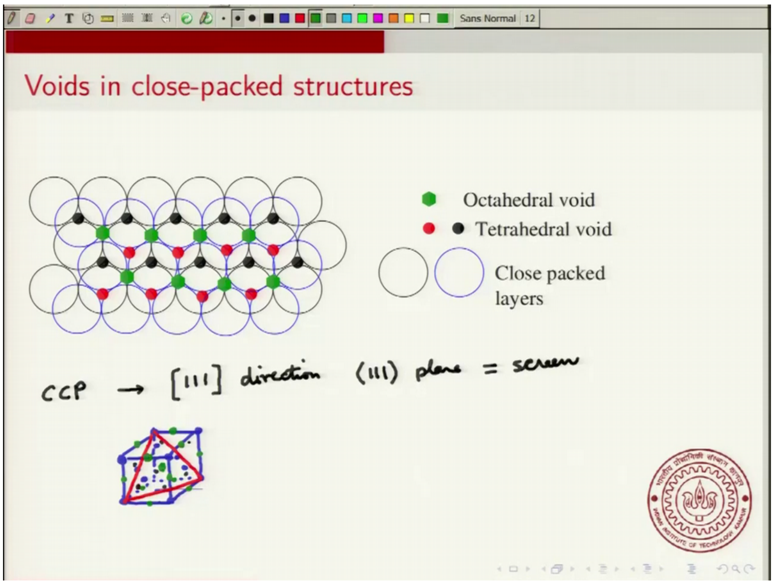

Voids in close-packed structures

⬢ Octahedral void

● ● Tetrahedral void

○ ○ Close packed layers

CCP → [111] direction (111) plane = screen

So, we will come to the concept of voids in the cubic closed-packed structure. And now here I am showing; I am showing 2 layers of a cubic closed-pack structure ok. So, the black circles this black circle represents the bottom layer and the next layer on top is represented by blue. So, these are atoms that form a cubic closed-packed array ok. I am just showing 2 layers.

Now, the difference between hexagonal and cubic closed-packed comes in the 3rd layer in the hexagonal closed-packed. The 3rd layer is on top of the 1st layer on top of this black layer whereas, in the cubic closed-packed its actually in the its directly on top of these green hexagons ok. So, that is where the 3rd layer would be, but we are just looking at these two layers and what these two layers if you just look at these two layers, you know we can immediately identify location of voids in cubic closed-packed structures ok.

So, what do we notice is that this black circle ok, this black circle it is now imagine that it is at the center; it is at the center of 1 2 3 and 4. The 3 black; the 3 black circles and this blue circle. So, it is right at the center of these four and clearly it is in a tetrahedral void. So, all these black; all these black filled circles they correspond to tetrahedral voids ok. Now there are other tetrahedral voids which are indicated by these red circles again very similar to the black circles.

The only difference is that in these red circles ok. So, there is one they are directly on top of this black atom and they are in the middle of these 3 blue atoms ok. So, in a sense the orientation of the tetrahedron around the red and black circles is inverted ok. So, with respect to the black filled circles ok, the orientation of the tetrahedron has 3 bonds going down and 1 bond coming up whereas, the red one has 1 bond coming, has 3 bonds coming up and 1 bond going down again. Please excuse the fact that I have I have not drawn these exactly ok. So, actually the location of some of these dots is not precise, but you can clearly make out where they should be ok.

So, we can immediately what this tells you is that these tetrahedral voids are going to be there in any cubic closed-packed structure whether it is HCP or FCC. And similarly the octahedral voids they will be located ok, they will be located right here at the center of these 3. So, if you look at this green hexagon ok, now that is equidistant from these 3 blue circles and these 3 black circles ok. So, clearly it is equidistant from these 6 circles and this is going to be a octahedral void ok. Again I should emphasize that this is actually below the blue atom ok. So, it is in between the blue layer and the black layer ok. So, the black layer black open circles are the bottom layer.

On top of that or the blue open circles and in between those two right at this center right here, there is a octahedral void, there is an octahedral void and the end due to periodicity it is there in all these locations. So, what this shows is that you can immediately identify the tetrahedral and octahedral voids in both and hexagonal closed-packed and a cubic closed-packed ok. As I said a cubic closed-packed the 3rd layer will be directly on top of these hexagons in a hexagonal closed-packed. The 3rd layer will be directly on top of these black circles ok, however let us I mean in. So, also we should keep in mind that for cubic closed-packed.

The closed-packed direction is actually the 111 direction of the crystal. That means, this screen ok. Screen is the 111 plane ok. So, that is the closed-packed direction and you can easily take cubic closed-packed or an FCC structure and see this packing arrangement and what it says is that you know whether you have an FCC or an HCP, you can identify the location of the voids and for the and so, this is very useful and if you go back to the lectures where we discussed the location of voids and HCP.

You can go back and confirm that these were indeed the location of the voids. Now, what is interesting about these voids is that these voids are spaces where you could in principle fit an atoms ok, but if you wanted to fit an atom in a void, you need to know the size of the void. And again so, we are going to do some calculations from the with respect to the size of the voids. Now, let me emphasize one point which might not have been clear is the following that you know we usually show the FCC structure in the form of a cube.

So, we usually show it in the form of a cube and we show; and we show the location of the voids ok. So, the tetrahedral voids as you are familiar will be located along the body diagonals along each of the body diagonals. So, there are 8 tetrahedral voids located along each of the body diagonals. I am not focusing on the sign of these tetrahedral voids ok, but you know that there are 8 of these located along the body diagonals ok. These are what I want to emphasize that these are exactly the same as shown here ok. There is no difference between what is shown in this diagram and in this figure ok.

So, the tetrahedral voids exactly the same locations that are described here this is just a different way of looking at the structure. In fact, you are looking at it from the 111 direction which is which can be shown as let us see if we take this as the origin x y z. So, we can take this as the 111 direction has a 111 plane, for actually the screen it corresponds to this plane. And if you look; if you look in this plane, then you will get you will see exactly the structures that we are seeing here. And now if you go to the layer below this plane ok, then you will see the packing arrangement that is seen here and you can immediately identify the tetrahedral voids and you can show that what you see in this figure is the same as what you see here.

Similarly, for the octahedral voids octahedral voids you know are located at the edge centers and the body centers. So, there is one right at the body center that is an octahedral void I will use the green colour and located at each of the edge centers and again this is exactly the same that you see in the other figure and until you draw it and convince yourself ok, you will not be sure of this ok. So, these two are two different ways to look at the cubic closed-packed structure. Now let us calculate the radius of these voids.

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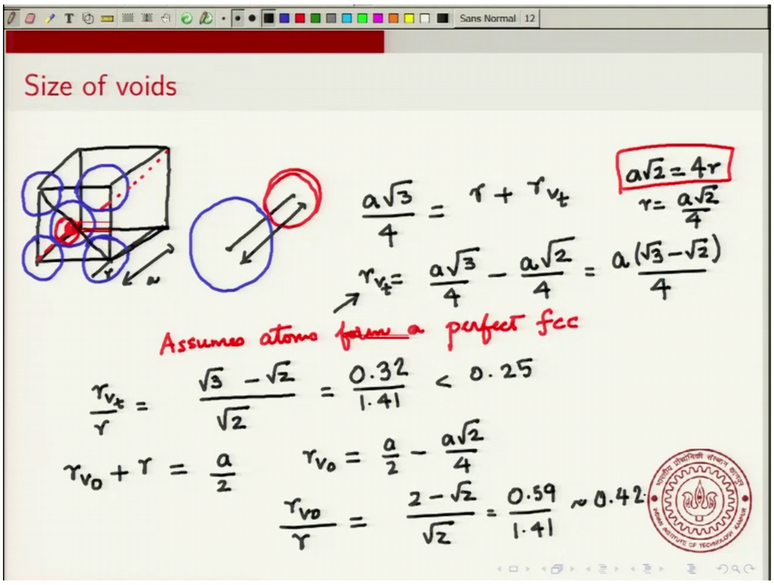

Size of voids

$\boxed{a\sqrt{2} = 4r}$

$r = \frac{a\sqrt{2}}{4}$

$\frac{a\sqrt{3}}{4} = r + r_{v_t}$

$r_{v_t} = \frac{a\sqrt{3}}{4} - \frac{a\sqrt{2}}{4} = \frac{a(\sqrt{3}-\sqrt{2})}{4}$

Assumes atoms ~~form~~ a perfect fcc

$\frac{r_{v_t}}{r} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = \frac{0.32}{1.41} < 0.25$

$r_{v_o} + r = \frac{a}{2}$ $\quad r_{v_o} = \frac{a}{2} - \frac{a\sqrt{2}}{4}$

$\frac{r_{v_o}}{r} = \frac{2-\sqrt{2}}{\sqrt{2}} = \frac{0.59}{1.41} \sim 0.42$

Now, to calculate the radius of the voids I will start with the; I will start with the cubic closed-packed, but is the same for the HCP. So, if you look at a cubic closed-packed now for the tetrahedral void; for the tetrahedral void, we know that so we have. So, now the tetrahedral void which along is located along the body diagonal and it is located at 1 by 4 at one-fourth of the way along the body diagonal ok. So, I will just show a tetrahedral void here and along the body diagonal ok. So, this is a corner and let us say this is a tetrahedral void. What you have is something like this. You have a your sphere which is the atom and you have the void and you know that this distance is a root 3 by 4.

And that is equal to r of the atom plus r of the void. And now r of the atom this again let me remind that r is the radius of the atom and a is the size of the cell ok. So, r of void is equal to a root 3 by 4 minus. Now r r of the atom r of the atom can be related to the lattice parameter because along the face diagonal you have a root 2 equal to 4 r ok. So, r is equal to a root 2 by 4 ok. So, then I can write this as root 2 by 4. So, you get the size of the tetrahedral void a times root 3 minus root 2 by 4 ok.

So, this is the radius of the tetrahedral void in terms of this in terms of the cell parameter a ok. Now this is the radius of a tetrahedral void in a perfect assumes atoms form a perfect FCC. So, in the sense we impose this condition which is only true if the blue atoms form a perfect FCC and then we use you use this condition to find the size of the tetrahedral void ok. Now, what I mean is that if you actually squeeze an atom ok, then the FCC might get distorted a bit ok, but still for in a perfect FCC this is the size of the void ok. Now, interestingly you can ask what is the ratio of the radius of the void to the radius of the atom. So, this is root 3 minus root 2 divided by root 2.

So, this is the ratio of radius of the void to the radius of the atom. So, all I did was take the radius of the void divided by the radius of the atom ok. So, this is for the tetrahedral void let me put a t in front next to the void ok. So, this for the tetrahedral void you can do for the octahedral void, now for the octahedral void ok. Again you can just go; you can just go along the edge and you can easily calculate that. So, for the octahedral void you have radius of octahedral void plus radius of atom this is equal to a by 2 ok. So, you can immediately see that the radius of octahedral void is equal to a by 2 minus a root 2 by 4 ok.

And further you can also do the same. You can divide by a root 2 by 4 to get the ratio of radius of octahedral void divided by radius of atom. This is 2 minus root 2 by root 2. So, we can work these things out and these are useful relations. You can do the same for hexagonal ok. You can if you want you can start with the HCP structure and you will get essentially the same result ok. So, the size of the voids ok. So, what this says is that you can fit another atom of this size ok, but now if you calculate these fractions ok, so this is of the order of ok.

So, this is only about this is only this is less than 25 percent ok. So, what this says is that the atom that you can fit in the tetrahedral void has to be extremely small ok. It has to be extremely small if it has to fit and if it has to fit in the tetrahedral void and keep the structure intact and clearly that seems very unreasonable. In fact, we will see structures like the zinc blende where the atoms fit in the tetrahedral void, but the size is a lot more ok, size is not the ratio of sizes is not this small ok.

So, that is what I meant by saying that you know this is in a perfect FCC, but there can be distortions. Similarly this is about and this is about this is much higher ok. So, this is nearly about 0.43 0.42 and yes I mean this is significantly larger ok, but still it is much smaller than what you would expect ok. So, this is about the size of the voids ok.

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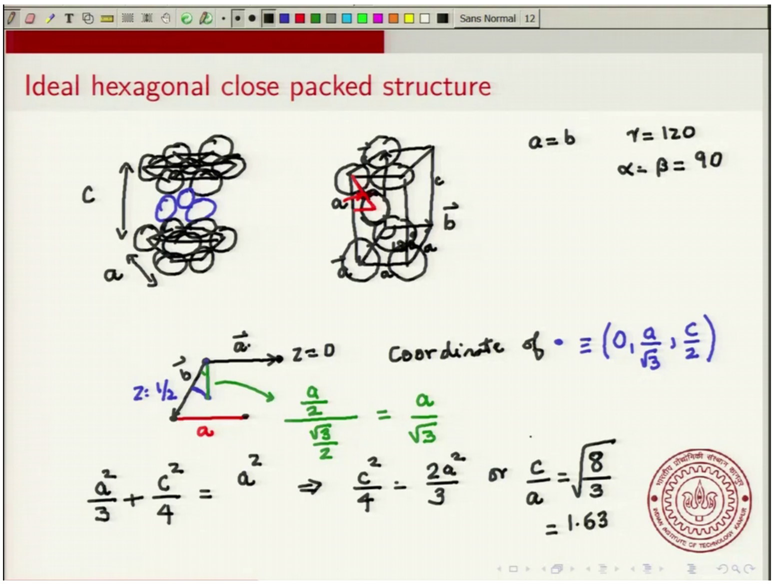

Ideal hexagonal close packed structure

$a = b$ $\gamma = 120$

$\alpha = \beta = 90$

Coordinate of $\bullet \equiv \left(0, \frac{a}{\sqrt{3}}, \frac{c}{2}\right)$

$\frac{\frac{a}{2}}{\frac{\sqrt{3}}{2}} = \frac{a}{\sqrt{3}}$

$\frac{a^2}{3} + \frac{c^2}{4} = a^2 \Rightarrow \frac{c^2}{4} = \frac{2a^2}{3}$ or $\frac{c}{a} = \sqrt{\frac{8}{3}}$

$= 1.63$

Let us look at something that we sort of skipped when we did the hexagonal closed-packed structure and this has to do with an ideal hexagonal closed-packed structure. Now what do I mean by an ideal hexagonal closed-packed structure? Now, let me draw the hexagonal closed-packed structure in the way that you are used to seeing ok.

So, this is where you show hexagonal say structure and what you have is you have these atoms here and you have the next layer which the layer below will have 3 atoms and then, you have another layer below where you have 6 atoms 6 or rather. And now the reason I am showing it this way is the following that this distance in a hexagonal in a high HCP, this is called c and this lattice parameter is called a.

Now, if you take a unit cell of this what you will see is the following that let me draw it in the following way. So, you have a b c, this angle is 120 degrees and now the question is if you have an ideal hex HCP then it turns out that there are some further constraints ok, c has to be related to a, c is not completely independent of a ok. So, this side is a and this side is c. So, there are 2 parameters ok. So, you have a equal to b and gamma equal to 120, alpha equal to beta equal to 90 and in an ideal HCP ok. Now there is going to be one other atom that is located right here inside this inside this cell ok.

It is not right at the center ok, it has to be it has to form a it is located in a it is located in this it is located at the center of these 3 atoms ok. So, what this tells you is the following that this distance in an ideal HCP should also be a ok. So, if it was perfectly closed-packed, then this distance this diagonal distance should also be a. This distance let me show it in red ok. So, this is from this corner to the center of this atom ok. So, that distance should also be a and it turns out that this. So, you immediately have a relation now you know that this is related to c in this way ok.

So, you will get a relation between c and a. Now, let us work out that relation now. So, you can let us see the location of this atom and for this let me use the planer representation. So, in the planer representation I have ok. So, I have these 4 atoms located here and then, I have this center atom is located at height c by 2 along this ok. So, let me these are all at z equal to 0; z equal to 0 and this is located at z equal to half and you know that this distance is a z is z equal to half or c by 2 more like c by 2 ok.

So, now let us look at the coordinate of this atom. So, the coordinate of this atom in blue this equal to, so let me make a choice of the origin. I will choose a this is my b ok. So, the coordinate of that is clearly the x coordinate is 0, it is located right here. So, the x coordinate is 0, the y coordinate now y in order to find the y coordinate you have to find this distance and this distance can be found out from this angle ok. So, this distance can be found out from this angle. So, it is a by 2 divided by cosine of this angle.

Now, cosine of this angle is root 3 by 2 ok. This is a 30 degree angle. So, the cosine of that is root 3 by 2. So, this is equal to a divided by root 3 ok. So, the y coordinate is a by root 3 and the z coordinate is c by 2 ok. So, now if you take a distance from the origin of this point and the origin is located at one of these origin is located right here ok. So, now if we take a distance from origin ok, then you can immediately find the you can say that a square by 3 plus c square by 4 that is the distance of this blue point from the origin ok. This should be equal to a by 2 square; a by 2 is square is sorry it should be a square.

And this immediately implies that c square by 4 is equal to 2 a square by 3 or c by a is equal to square root of 8 by 3 and this works out about 1.63 ok. So, this is the ideal ratio for a hexagonal closed-packed. So, if the atoms were really closed-packed, then the c by a ratio would be exactly 1.63 in a hexagonal closed-packed structure.

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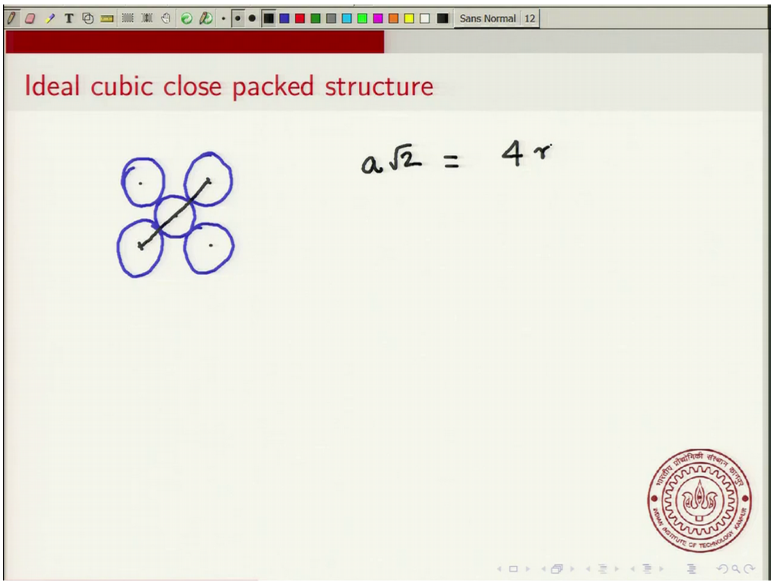
Ideal cubic close packed structure

$a\sqrt{2} = 4r$

Now, let us look at an ideal cubic closed-packed structure. As I had already said in an ideal cubic closed-packed structure, the face centers should be touching each other. So, let me again draw this. So, we just take the planar representation ok.

Now, it should be such , so in an ideal cubic closed-packed structure you should have now you have only; you have only one parameter a, so, a root 2 ok. So, this distance which is a root 2 should be equal to 4 times the radius of your atom ok. So, this is an ideal cubic closed-packed structure in the sense the atoms in blue are forming a perfect closed-packed structure ok.

So, interestingly so unlike the hexagonal closed-packed structure were we had a parameter c in this case there is no additional parameter and again this is just a convenience of notation. I mean if we had directly imposed the condition for ideal hexagonal closed-packed structure in that case also we would not have any independent parameter c; c would be equal to a into root 8 by 3 ok.

So, with this I will conclude this lecture, I will conclude this 1st lecture. So, here we have seen the idea how the idea of closed-packing can be used to understand the sizes of voids and also we saw the structures of simple elements. Now, in the next lecture I will look at and look at binary compounds and see how these can be understood in terms of closed-packed structures and atoms in voids.

And we have already seen this in several examples like the most common example that we see of the rock salt and the cesium chloride or the zinc blende structures ok. So, these are all these all can be understood in terms of one of the elements forming a closed-packed structure and the other elemental in a void. So, we look at this in more detail in the next lecture.

Thank you.