An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

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Lecture - 23
Ionic Solids
Close Packing of Anions
FCC Packing
Cubic Packing

So, today we start this lecture 23, in which we will continue from the last lecture in which we started about description of ionic solid structure based on face centered cubic packing.

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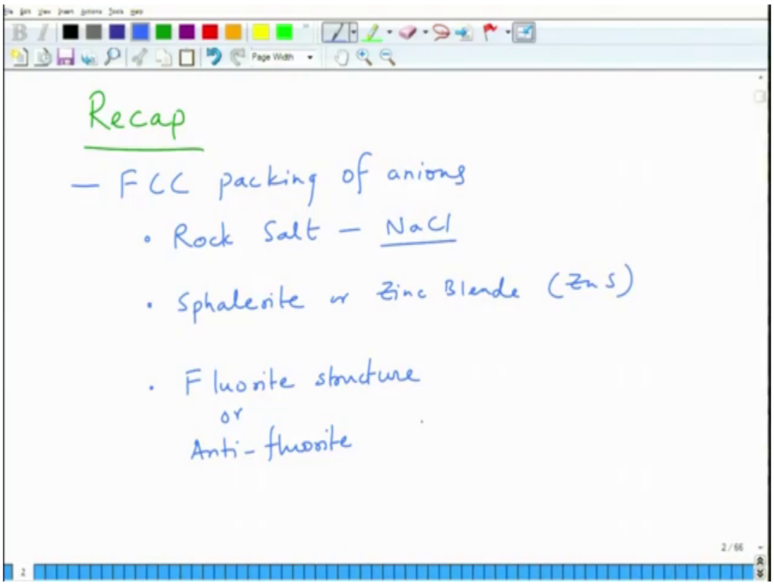

So, just to give you a recap we discussed the structures based on FCC packing off we started discussing structures based on HCP packing of anions. And there we first started with the rock salt structure which is basically based on NaCl based compounds which make a in which chlorine makes FCC lattice and sodium ions occupy the octahedral industries is all of them 100 percent occupancy of interstices and this is based on radius ratios.

So, the variety of oxides which follow this kind of structure like Fe O, Ni O, Mg o and; so on and so forth. Second structure that we looked at was sphalerite or zinc blende structure which is based on zinc sulphite. This structure is again sulphur makes a FCC lattice. And zinc occupies the tetrahedral sides. And you can see that since FCC lattice has 8 tetrahedral sides that is 2 per ion as a result only half of tetrahedral sides are filled. So, you can consider both NaCl and zinc sulfide as if there are two interpenetrating FCC lattices.

In case of NaCl the FCC lattice of sodium is shifted by a vector half zero zero whereas, with respect to chlorine lattice; whereas, in zinc sulfide the FCC lattice made by zinc is shifted by a vector 1 by 4, 1 by 4, 1 by 4 with respect to sulfur lattice. And then we started discussing about fluorite structure. And this also includes fluorides or anti-fluorite. So, this we will discuss while we discuss fluorite structure. So, we started discussing this.

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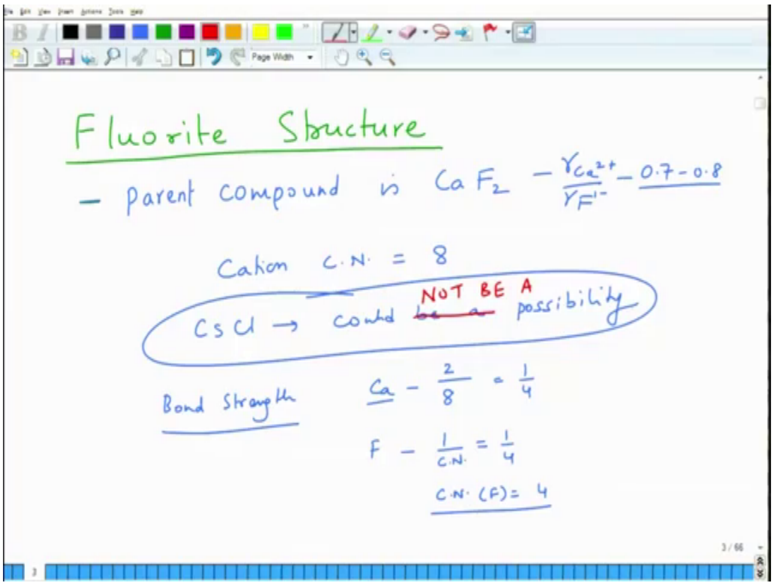

So, basically so the fluoride structure basically is based on compound. So, parent compound is compound is Ca f 2, now this is based on your radius ratio. So, here basically r Ca to r F is such that you tend to follow. So, this is close to I think it is between 0.7 to 0.8 depending upon the radius, but I think it is about 0.8 closer to 0.8 nevertheless it falls in the boundary of octahedral two cubic coordination.

So, you can check up the radiuses online. It falls on the boundary of octahedral and cubic coordination; as a result, what happens is that the cation coordination number is 8.

So, we discussed that if the cation coordination number is 8, one possibility is to have a cesium chloride kind of structure. So, cesium chloride could be a possibility where you know cesium can be quoted where fluorine can 8 of fluorine atoms will surround 1 calcium atom. However, if you have that kind of structure the problem is calcium, the fluorine will also be surrounded by eight calcium atoms which is not possible because of constant check because we can see that if you do the bond bond strength then bond strength of cations and anions should be equal they should balance each other.

So, if you look at the web for calcium for example, the valence of calcium is 2, and the coordination is 8, this is 1 by 4. In case of fluorine, the valence is 1, coordination number must be equal to so this must be equal to 1 by 4. Coordination number of fluorine must be equal to 4. As a result the Cs Cl is not a possibility ok. So, we will see Cs Cl structure later on, but basically it is a it us a structure in which both cesium and chlorine are cubically coordinated so that is the way this is structure works out is in this fashion.

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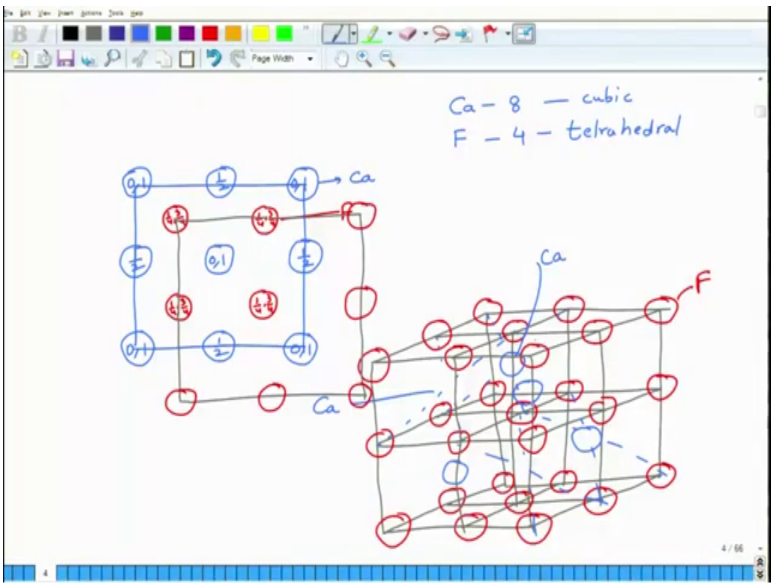

So, if you make a you make it FCC lattice off. So, I am just going to draw the top view here. So, if I draw the top view, so remember coordination numbers calcium is no, calcium coordination number is.

Student: 8.

8, and fluorine coordination number is 4. So, fluorine is tetrahedrally coordinated this is cubic. So, let us just draw these a top view of the lattice here. So, here what I am going are these are all.

Student: Top view.

So, this is here is calcium atom ok. So, these are all calcium atom; this is at 0 1 this is at half; this is at 0 1; this is at half, half, half, 0 1, 0 1, 0 1 ok. So, calcium makes FCC lattice here and the zinc and the fluorine atom goes here, here, here, and here. And the coordinates which are going to be filled are 1 by 4 and 3 by 4. All the tetrahedral sides are filled here. Now, this we have drawn on the basis of cation forming a lattice and anion going to the tetrahedral interstices.

However, if you want to look at the structure in the perspective of how what will happen if cations form the lattice, then you need to consider a unit cell in a different manner. So, let us say I draw a unit cell which is something like that. Now, this is a bit complex unit cell. So, so I need to divide this unit cell into eight unit cells. So, what I do is that, this is the problem with a drawing should be done in such a manner, so that we are not able we should not get parallel lines ok.

And let us say I make these in it cells which are ; and we need to create a division in the middle as well. So, the middle division is going to be created in this fashion. And it is going to be a boundary here as well. So, you have eight of these unit cells ok. Now, you start filling in the fluorine. These are all fluorine atoms. And I needed to draw one line there and one line here, so that I have one atom at center also one here. So, is everything complete now, these are not complete here ok.

So, how many unit cells now you have, you have eight cubes formed by fluorine. These are all fluorine ones this is fluorine. So, this was fluorine here. Now, you need to put calcium in it. So, the problem is these are eight unit cells, you have eight fluorine atoms, you can only put for fluorine in there. So, the way four fluorines get in is like this. So, this is the first unit cell, the center of this unit cell is this is first fluorine atom, the second fluorine atom is this.

Student: Calcium atom.

Sorry.

Student: Calcium atom.

Sorry calcium atom yeah I am sorry here, thank you. This is calcium atom. And the other two calcium atoms go in these unit cells. So, center of this and so this is how you are going to make a calcium fluoride structure. So, this structure is basically you can see now what you can do is that if you if you take the plan view, now instead of keeping the lattice corner at calcium, you keep the lattice corner at this side. Let us say I keep the lattice corner at this side. I need to go here, I need to come here, I need to go there, then and the way you then.

So, this is another chlorine atom fluorine, this will be another fluorine, this will be another fluorine, and this will be another fluorine. So, and then you need to create. So, this is these are at 1 by 4 1 by 1 by 4 and 3 by 4. So, you have only three positions you need to create under position which is another 1 by 4. So, you need to stack two layers of fluorine in such a fashion, so that you have first one at 1 by 4 second one at 3 by 4 the next one is that again 1 by 4 and when you make 1 by 4 as zero the 3 by 4 becomes half right. So the position will be zero half zero or 0 half 1. So, all the atoms will be.

So, these will make eight cubes and then you can see that the position of these atoms this is at 0 1 this is at 0 1. So, this will become quarter right. So, when you make these distinctions here, so sorry there was there is a bit of a yeah. So, you can see that these two atoms go in this fashion, these two atoms will go in this fashion. So, if you take the top view, the top view will be the mistake I have made here I think look this atom will sorry let me just rub it out remove this blue blue atom here. So, you have one blue there.

So, one blue is at 0 1, second blue so this lets say if this is the blue here, the second blue will come here because 0 1 half. And now we are looking at the top view right. And the third blue will go it is at the half position. So, it will go here and the fourth one will come here on top right diagonally. So, two will go this way - will go that way they will make a. So, in the first unit cell here; I did not draw that very well. So, this is my first one, the second one will come directly oppose it here at the center of this unit cell. So, these two will go diagonally there you can see diagonal arrangement and these two will come diagonally here, just like you have in zinc sulfide lattice, so that was a modification we can make.

So, let me just reiterate what you have here is I just maybe redo it ok. So, if you if you look at this bigger unit cell which is now made by calcium. So, this calcium will be all of these all of these are at 1 by 4, 3 by 4, 1 by 4, 3 by 4, 1 by 4, 3 by 4, 1 by 4, 3 by 4 and then 1 by 4 3 by 4 these are at 0 1.

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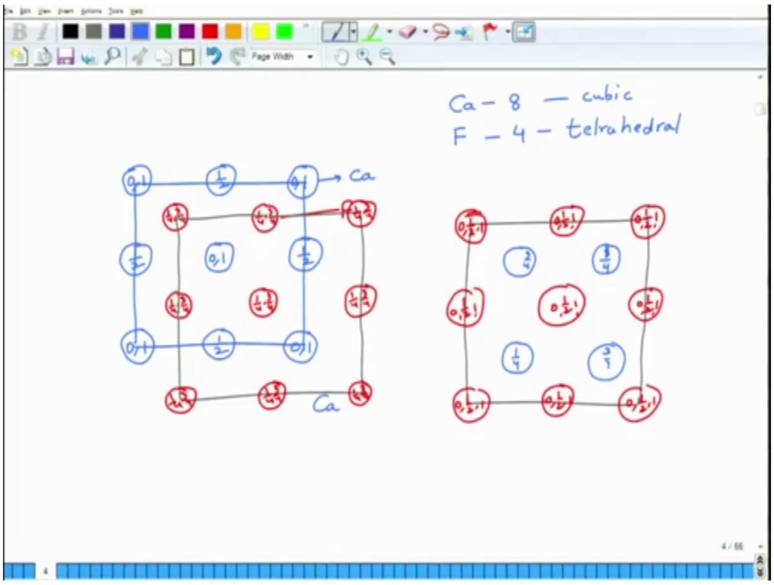

When you convert these two, so if I now take it away ok, if I now take it away make this unit cell like this, just the top view ok, just the top view and then now I put it put these here if I convert 1 by 4 to 0 then the central one will become at so 0, half and then 1. Here you will have again 0, half, 1; these will also be 0, half, 1; all of these will be all of these will be 0, half and 1; all of these right 0 half 1, 0 half 1, 0 half 1, 0 half 1, 0 comma half comma 1. So, these are at z positions ah.

So, when you convert the 1 by 4 into 0, the 0 which is there becomes minus 1 by 4 right minus 1 by 4 is equivalent to 3 by 4 and 1 will become, so 1 will become 3 by 4 also. So, this is. So, this is at atom which you put here which is the blue one. The blue ones are fluorine right. So, we have converted half quarter to 0, so which means we are subtracting by one quarter ok.

So, when we subtract by one quarter this will become minus 1 by 4, this will become 3 by 4. And this half one will become you had under so this is at half this half wall will become three quarter, no half minus 1 quarter, 1 quarter, this will become 1 by this will become minus 1 by 4 3. So, we can take only one of them we do not have to take both of them because one is below the unit cell and address above within the unit cell. So, this position will be so you can modify this as only 3 by 4, only 3 by 4. So, basically you have two atom sitting here at 3 by 4 and two atom sitting diagonally at 1 by 4.

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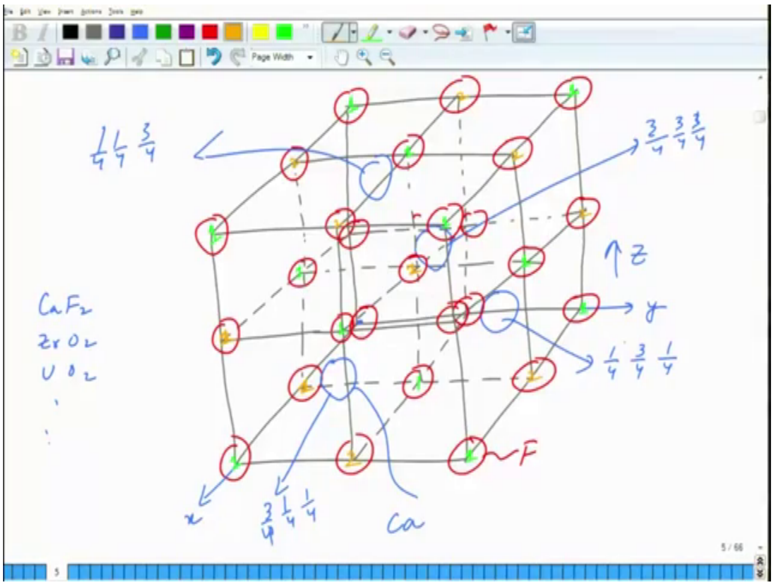

So, when you construct that bigger unit cell the bigger unit cell will now you understand the bigger unit cell. You have let say I start from here ok, ok, all right. Now, we draw this in 3D. So, my fluorine was the red one, these are fluorines, these are again fluorines, and these are fluorine again all right. So, there are two atoms at. So, if you look at the previous position to add 1 by 4 to add 3 by 4. You can say one in the back unit cell will be this is at 3 by 4; and one in the front will be at 3 by 4. And then one in this will be at 1 by 4 and one in that will be at 1 by 4, 1 by 4. These two add at 1 by 4 is that is equal to 1 by. So, this is z ok.

So, this is z is equal to 1 by 4, this is z is equal to 1 by 4, this is this is 3 by 4, xy coordinates are different in this case the xy will be. So, if you take half of it, and half of it, if you take this as an origin for example, coordinate of so and this is let us say x this is y. Coordinate of this will be 1 by 4, 3 by 4 and 1 by 4. Coordinate of this will be 3 by 4, 1 by 4 and 1 by 4. And accordingly you can take the coordinate of that this one will be 3 by 4, 3 by 4, 3 by 4. The coordinate of this will be 1 by 4, 1 by 4, 3 by 4. So, this will be the bigger unit cell which is constructed by fluorine atoms. So, this is fluorine, this is calcium ok.

So, this is how the coordination. And now you can see that each fluorine is coordinated by 8 of calcium, and each sorry 4 of calcium; and each calcium is coordinated by 8 of fluorine. So, this is how the coordination will go. And you can see that only half of the tetrahedral voids are or cubic whites are occupied there you can see only since there are eight cubes only half of the cubes are filled. So, only half of the cubic sides are filled all right. So, now this calcium fluorite structure is followed by a variety of materials there are a lot of fluorides which follow this structure. So, Ca F 2, but you also have Zr O 2, U O 2 and various other oxides follow this structure ok. So, these are all ionically bonded solids.

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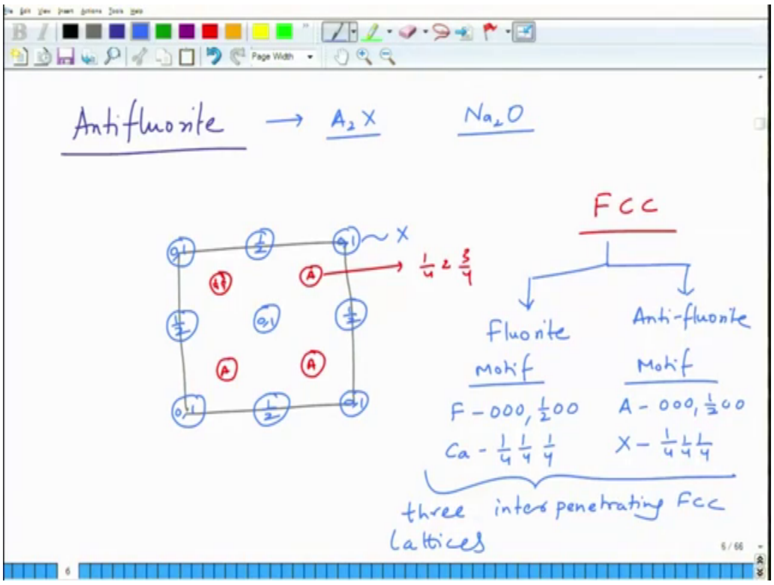

Now another compound in this series is called as anti fluorite. So, I am just going to draw a top view there I am not going to draw the anti fluorite is basically. So, if Ca F 2 was A x 2, this becomes A 2 x things like Na 2 O ok. So, these follow this structure which is opposite to what we see we saw there. So, if you have a should it shall I am just going to draw top view right 3D, you can work out yourself which we have drawn in case of the previous. So, in this case now this will be the this is an ion x.

So, this is at 0 1, this is at half, 0 1, half, half, half, 0 1, sorry 0 1, 0 1, 0 1 and half. So, these are x atoms. The A atoms go to these positions ok. So, A atoms will be now at 1 by 4, 3 by 4. So, this is A, this is A, and this is A, all of them are at 1 by 4 and 3 by 4 that is the opposite of Ca F 2 structure.

So, you can see that now what does this structure. So, lattice type and both of these structure is FCC it is a FCC lattice if you look at the previous structure it is like. So, we have seen that calcium makes a FCC lattice right. Calcium surely makes FCC lattice, but for fluorine you are seeing as if there are 8 cubes, it is like two FCC lattices of fluorine put into each other. So, one lattice of fluorine is if I mark the atoms 1, 1, 1, 1, 1, 1 and though that faces one so 1, 2, 3, 4 and 1. This is the first lattice of fluorine.

Where is the second lattice of fluorine, second lattice of fluorine is this which is second shifted by what one quarter half 0, 0 vector right. This is this was the corner gone at. So, you can you can figure out yourself right this is one. So, all the atoms which are at edges and the body center will be at sorry number two. So, this is 2, 2, 2, 2. So, this is the second lattice off. So, basically you have first lattice or fluorine; second lattice is shifted by half 0, 0 vector they make eight cubes together. They give you eight cubes. And within those cubes you have these cubical arrangement of calcium atoms.

Similarly, here so it would be again FCC lattice or instead of instead of calcium instead of fluorine making two FCC lattices now the sodium will make two FCC lattices and anion will make only one FCC lattice. So, lattice type is FCC ok. In case of fluoride, motif will be will be at fluorine at 000, and half 0 0, and calcium will be at and then it will also make. So, all three will make FCC lattices you have three atoms. In this case, motif will be A at 000 and half 0 0, and x will go to.

So, basically it is a network of three inter penetrating FCC lattices. In the first case two of anion, one of cation; in the second case two of cation one off anion all right. So, this is how you make anti fluorite structure which is again FCC based again based on FCC packing of anions ok.

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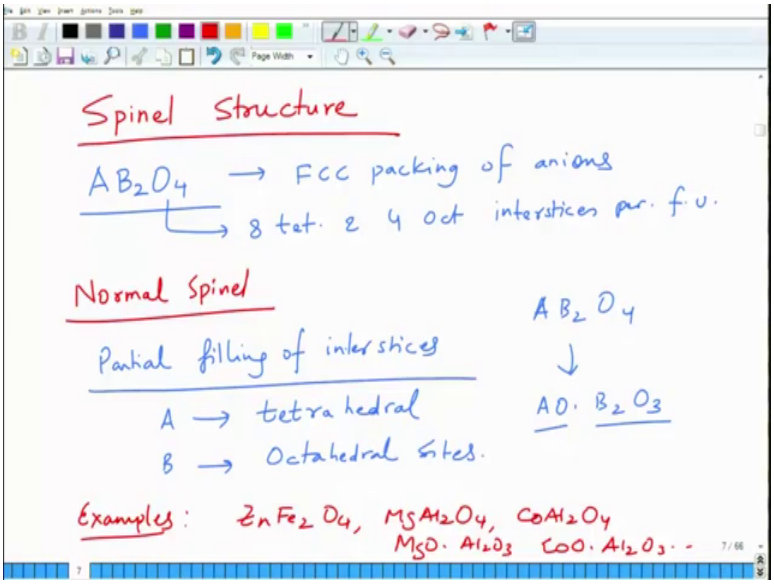

Now, what we will do is that we will look at another structure which is called as spinel structure. Spinel is a compound which is has a formula A B 2 O 4 ok. It is again based on FCC packing of anions. And if it is based on FCC packing of anions, you can see that for 4 oxygen, you will have 8 tetrahedral and 4 octahedral interstices per formula unit right per formula unit.

Each formula has 4 oxygen atoms, this will give you 8 tetrahedral and 4 octahedral; Number of cations that you have are only three. So, all the interstices are not going to be filled you will have partial filling of interstices because it is not possible you have total of 12 interstices and you have only of three cations. So, how do you fill them?

Well in the normal variant of. So, there is a variant of spinel which is called as normal spinel. In case of normal spinel structure, what you have is A you have basically you can say partial filling of interstices all the A atoms goes to the tetrahedral sites, and all the B atoms go to octahedral sites ok.

Student: If this is the convention form of.

Yeah, it is a convention I mean the because A and B have different sizes because a and b are not same cations, they are different cations they have different sizes. So, they prefer to go to different sides. So, as a result you can write this oxide in a different manner A B 2 O 4 can be written as if it is a mixture of A O dot B 2 O 3. So, there is a sub lattice of A

O there is a sub lattice of B 2, they are mixed into each other to give you what is A B 2 O 4. So, it turns out that all the oxygen atom will make FCC lattices and A will go to tetrahedral sides and B will go to octahedral sides.

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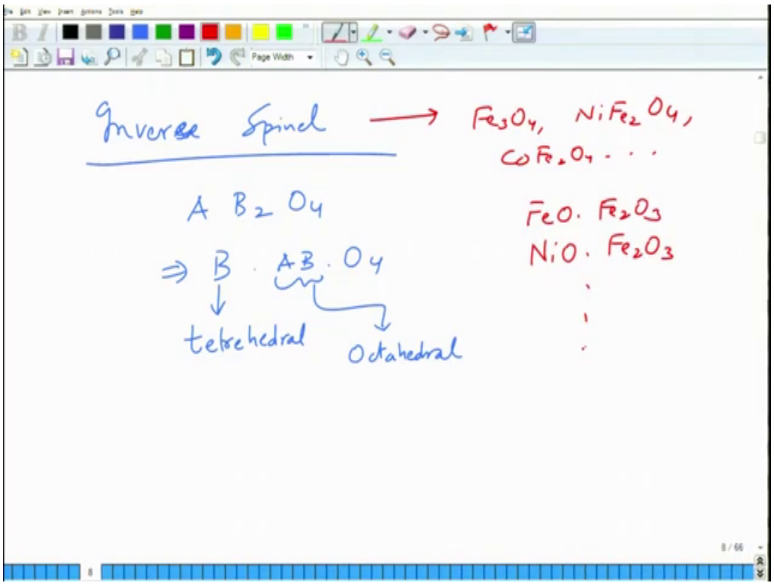

And there is another variant of this is called an inverse spinel. In inverse is spinel it is other way round it is different. So, A B 2 O 4 can be written as B A B O 4. The B 1 of the B atom goes to tetrahedral sides and A and B atoms go to octahedral sides.

So, these are two variants of spinels normal and inverse examples of normal spinels are are things like Zn Fe 2 O 4, Mg Al 2 O 4, Co Al 2 O 4 cobalt aluminate, magnesium aluminate and so on and so forth. And the example of these are inverse spinel are Fe 3 O 4, Ni Fe 2 O 4 Co Fe 2 O 4 most of the ferrets make this kind of structure inverse spinel.

So, you can see that you can write this Fe 2 O, Fe 3 O 4, as Fe o dot Fe 2 O 3, Ni Fe 2 O 4 can be written as Ni O dot Fe 2 O 3 and so on and so forth. Similarly, here you can write this as Mg o dot Al 2 O 3. Co O dot Al 2 O 3 and so on and so forth. So, we will stop here and then we will get back to the structure of spinel in the next lecture.