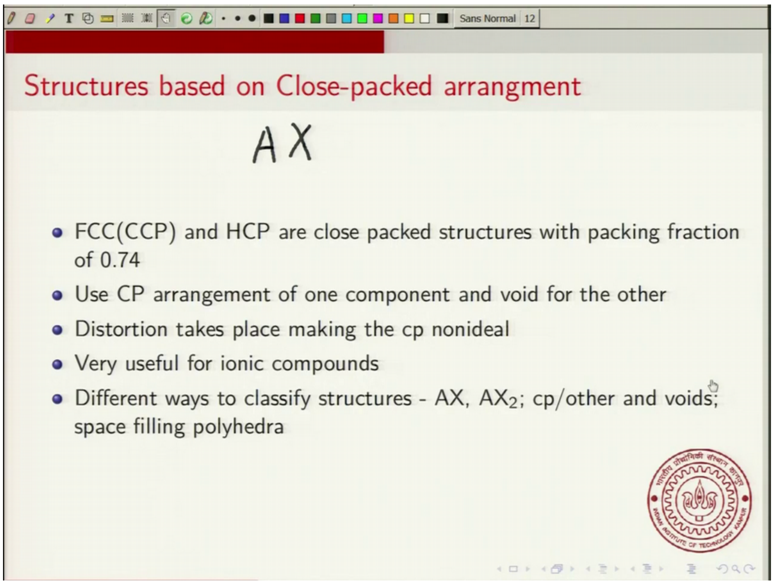
Solid State Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 47
Crystal Structures of Binary Compounds

Now, I will go to the second lecture of this 10th week of this course and in this lecture we will look at very common Crystal Structures of Binary Compounds ok. In the last lecture we looked at the close packed structures and we looked at the crystal structures of elements. In this lecture I will look at binary compounds and one of the ideas that I will emphasize is how we use the idea of close packing arrangement of one of the two constituents of the binary compounds in this description. So, week 10 lecture 2 will be crystal structures of binary compounds.

(Refer Slide Time: 00:58)



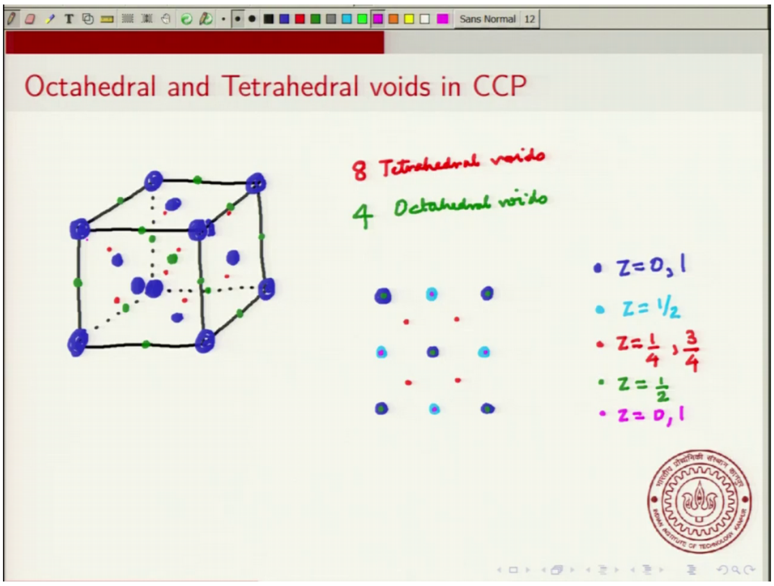
So, now we will be looking at lot of structures based on a close packed arrangement, we most of the structures that I will be talking about today are based on a close packed arrangement not all of them ok. Now as we have as we already know that the cubic close pack and the hexagonal close pack are close pack structures with packing fraction of 0.74 ok. And the idea is to use is that we have a binary compound, so we have a binary compound something like AX ok.

And what we are going to do is use a close packed arrangement of one component and use voids for the other component. So, maybe A will be in a close packed arrangement and X will be in the voids and we have already seen the voids in FCC and HCP ok. So, now one of the things that will happen is that when you put this X and the voids ok, then the there will be a distortion in the cell ok. So, the close packing will become non ideal.

So it would not be an ideal close packed arrangement and so the cell might expand when you put this atom X in the void. This description is very useful for ionic compounds and I am going to only talk about a few different compounds, but actually there are different ways to classify these crystal structures ok.

So, one way to classify them is like AX, AX 2 etcetera, the other way which we will be looking at is to look at one of the components as either a close packed or some other structure and the other atom as present in the voids. Alternatively we can also look at these in terms of space filling polyhedra which I will touch upon a little later.

(Refer Slide Time: 03:04)



So, now let us look at the cubic close pack, cubic close pack or FCC and let us remind ourselves where the octahedral and tetrahedral voids are. I will use a planer, I will show both the planer and the three dimensional representation. So, if we look at a cubic close packed, the cube will look like this and we have our first species let us say it forms a cubic close packed array.

I am not showing the spheres as touching each other I am just showing them small for ease of visualization this is in the back face there will be one here and the center of the front face, the centre of it ok. So, these are the this is the cubic like close packed arrangement and the voids ok, so the tetrahedral voids are located at one-fourth along the body diagonal. So, along each of the body diagonals, so there will be one here, one along this body diagonal; along this body diagonal.

So, these all will be at a these all will be at the same height and then there will be 4 more which are located at the center of these at these other voids, other 4 tetrahedral voids ok. So, these are the tetrahedral voids 8 tetrahedral voids, so there are 8 tetrahedral voids, in this conventional cell, so in this conventional cell there are 8 tetrahedral voids ok.

And then the octahedral voids will be there will be an octahedral void located right at the center and then it will be at each of the edge centers. Now there are 12 edge centers, but the void in an edge center belongs to multiple unit cells, the void at each edge center belongs to a 3 other unit cells. So, these 12 contribute only one-fourth to this unit cell and the when the void is the center correspond contributes 1 ok.

So, we have a total of 4 octahedral voids ok. So, in this close packed element there are 8 tetrahedral and 4 octahedral voids. Let me for completeness show the planar representation because this is much easier to draw ok. So, this is the z equal to 0 plane.

This is z equal to 0 or 1 and then you have let me show it in a different in a slightly different color. This is the z equal to half plane and these are the this is the structure of this is the cubic close packed structure ok. And now the voids; voids will be located at one-fourth and three-fourth. So, these are the tetrahedral voids will be located right here at z equal to one-fourth and three-fourth ok, so they will be voids located by this.

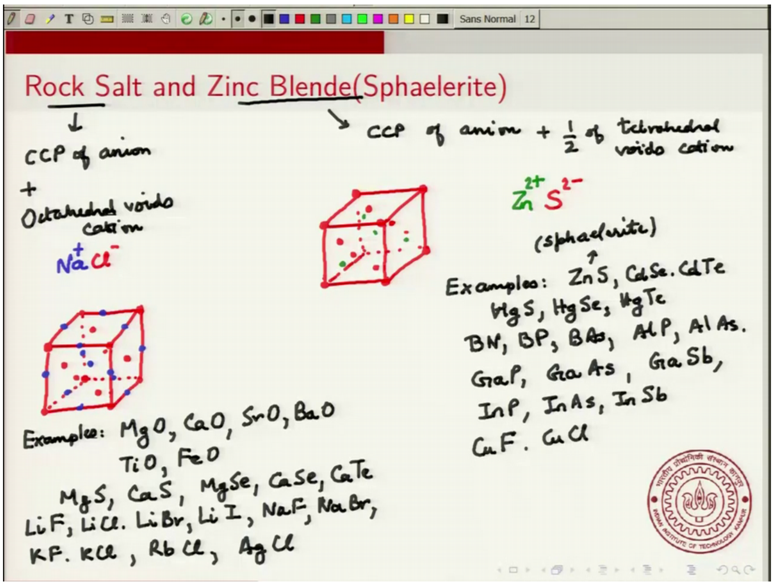
The octahedral void will be located. So, this I am showing 1 at z equal to half. So, z equal to half you will have you will also have these edge center voids ok, so z equal to half you will have exactly you will have exactly on top of these. So, these are at z equal to half and then you will also have you will also have at z equal to 0. So, at z equal to 0 you can see you can see in this figure, so there are octahedral voids located at these edge centers these are at z equal to 0 ok.

So, you have z equal to 0 z equal to half and z equal to 1, so you have octahedral void located at each of those coordinates and each of them I am showing, so this is at z equal to 0 sorry this is at z equal to half; this is at z equal to half and at z equal to 0. They will be located the octahedral voids at z equal to 0 will be located at edge centers that will be that will be directly below this ok. So, these are the octahedral voids located at is z equal to 0.

And similarly they will also be there it z equal to 0 and z equal to 1 ok. So, this is the representation of the tetrahedral and octahedral voids in a cubic close packed structure. And now we can go and try to imagine that structures will be formed where the where usually the larger ion if you have a binary compound ok, you have a cation and an anion then the larger ion will occupy the close packed structures.

And the smaller ion can occupy either the tetrahedral or the octahedral voids; it may be some of the tetrahedral voids maybe not all ok. So, we will just look at a few representative structures. I am not trying to describe all the structures ok, I am just going to represent I am just going to show a few representative structures ok.

(Refer Slide Time: 10:32)



So, the first two we will consider or rock salt and zinc blende ok. So, rock salt ok, so we can look at both of these as, so rock salt is basically CCP plus octahedral voids. So, CCP arrangement of anion and octahedral voids for cation and in this particular case you can exchange them, but we will just follow the we will just follow convention, where we will show the we will show the anion as the CCP.

Anion is typically the larger ion ok, anion is typically larger in size in the cation and so at least at least in most of the structures we will show the anion forming the close packed structure and you can easily see what it will look like ok. So, if I show if I use blue for the for, so an example of compound that forms this is Na Cl; Na and let me use red for the Cl this is this is an ionic compound. So, it is actually it is in the form sodium plus and chloride minus ok. So, and the chloride minus ions will form the will form the close packed structure. So, you will have a chloride which forms a close packed structure.

Again I am not showing the chloride ions as touching each other let us ok. And the sodium ions will occupy all the octahedral void, so there is one octahedral void right in the right in the middle of the cell that is an octahedral void and then and then there are octahedral voids at each of these edge centers. So, these will be occupied by sodium; sodium ions ok. So, this is the rock salt structure it is a very it is a very common structure I mean it is a very it is it is one of the first and the simplest binary structures that you that you will encounter ok.

Now, rock salt is actually quite common ok. So, in addition to a sodium chloride there are other examples of rock salts of compounds that crystallize and rock salt ok. There are several oxides for example you take Mg O, Ca O, Sr O, barium oxide ok. So, we can see all the all the group 2 the alkali earth metals ok.

So, they are oxides from this, there are also some transition metal oxides like titanium oxide Fe O etcetera which form this. In addition there are sulfides, so oxygen and sulfur are in the same group. So, in addition you can also have sulfides like Mg S, Ca S, you can have selenides again Mg Se, Ca Se or even tell you rights, even like calcium tell you right forms in this structure ok.

So, these are oxides and sulphides and these are sulfides selenides and tellurides. Additionally there are also like the alkali metal with a halide ok. So, alkali halides, so many alkali halides also crystallize in the structure for example, lithium fluoride, lithium chloride, lithium bromide, lithium iodide, again we already saw Na Cl, but also sodium fluoride, sodium bromide K F, KCl and I do not; I do not want to go there are several others there is rubidium chloride, silver chloride ok.

So, there are there are several others I am just showing a few examples just to say that you know this rock salt is not unique only two sodium chloride, the same rock salt structure is found in several binary compounds ok. Now the next structure that I am going to talk about is again something that you have already seen which is zinc blende or a sphalerite ok. So, here you have a CCP of anion and half of tetrahedral voids for the cation occupied by the cation and again we can we can show the we can show the structure easily.

So, if I again use the same representation ok. So, we have the anions forming a closed packs from your cubic close packed and we have one-fourth of the tetrahedral voids let me show it in green this time. So, if you take if you take this body diagonal, then you can put a tetrahedral void along one fourth of this direction.

Then you skip the next one and you go to the you go to the alternate corners ok, so that will give you the tetrahedral void right. Here then again you will you take this tetrahedral void and you take this tetrahedral void. So, 4 of these alternate tetrahedral voids you take ok. So, that they are not they are not adjacent to each other. So, these 4 tetrahedral voids are not adjacent to each other.

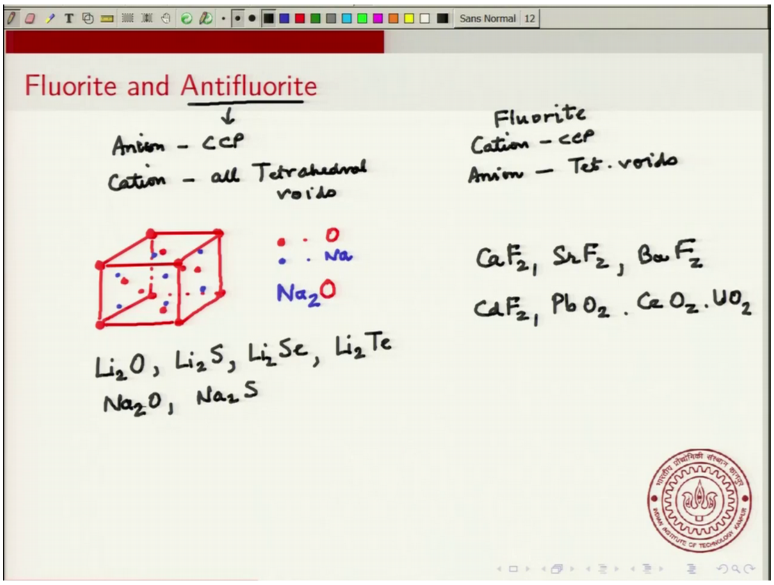
And; obviously, so this is sulfide and this is zinc 2 plus sulfide 2 minus and there might be some partial covalent character in these bonds ok, but we want discuss about that ok. So, this is the sphaelerite structure and sphaelerite or the zinc blende structure and again it is very common, there are several examples of compounds that form the sphaelerite structure.

So, examples of course, you have you have zinc blende then in the same group ok, so you; so you have Zn S ok, but you also have zinc cadmium. So, you have you have cadmium selenide, cadmium telluride ok. So, selenium is in the same group as sulfur selenium and tellurium and cadmium is in the same group as zinc. You have mercury compounds, sulphides, selenides tellurides of mercury ok. Then you have you also have you also have these 3 5 compounds, that is group 3 and group 5.

So, for example, you have boron nitride, boron phosphide, boron arsenide, aluminium phosphide ok, aluminum arsenide, gallium phosphide, gallium arsenide you also have you have gallium antimonide Sb, indium phosphide, indium arsenide, indium antimonide ok. So, these are these are some of the some of the some examples there are also some other examples like copper fluoride cuprous fluoride and cuprous chloride which also crystallized in this sphaelerite ok. So, the zinc blende or the sphaelerite structure is another common structure that can be seen as that can be understood in terms of CCP structure.

Now, we will come back to Zn S ok, so Zn S actually has 2 structures ok, this is the sphalerite form or them which is actually more stable, but Zn S also forms a wurtzite crystal and we will and we will come to that in a in a few slides ok.

(Refer Slide Time: 21:49)



Next we are going to look at these structures fluorite and anti fluorite ok. So, here the let us let us look at the anti fluorite ok. So, here the anion forms CCP and the cation occupies all tetrahedral voids ok. In the fluorite structure the only difference is that, the cation forms the CCP and the anion occupies tetrahedral voids ok.

So, so these two are you know related structures the anti fluorite is the is where the anions form the cubic close packed, but there is also a fluoride structure where the cations form the close packed structure ok. So, this is very similar to the sphaelerite only thing is instead of occupying only half the tetrahedral voids you occupy all the tetrahedral voids and I will; I will just I will just give some examples of these well ok, so let me let me show the fluoride structure. So, you have and you can immediately say that since there are 8 tetrahedral voids and there are only 4 cubic close packed atoms ok.

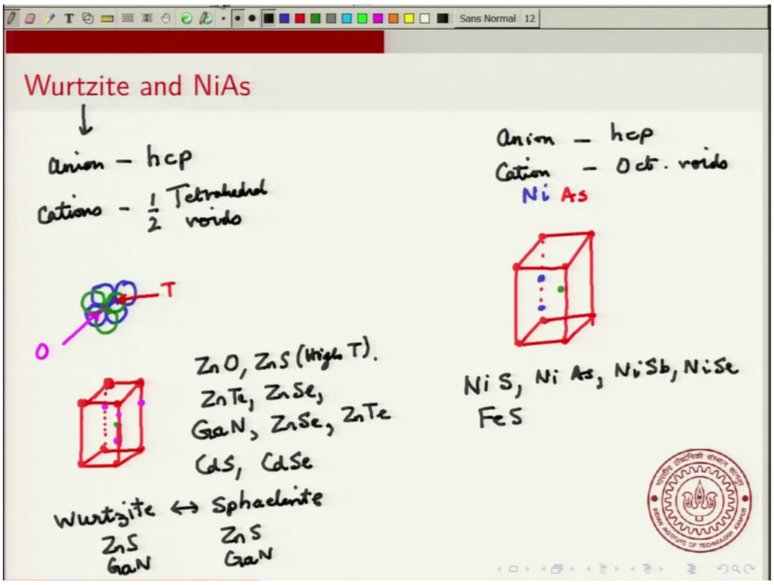
So, this will be AX 2 kind of kind of structure ok. So, the stoichiometry of these fluoride compounds will be AX 2, so all the tetrahedral voids are occupied. For example, this could be this could be the Na 2 O, so this could be oxygen and this blue could be sodium ok. So, this is Na 2 O the stoichiometry as I said there they have to be 2 cations to 1 anion in the.

So let me just give examples of these, so examples of anti fluorite structure are lithium oxide, lithium sulfide, lithium selenide, lithium telluride, sodium oxide which we have already seen and sodium sulfide ok. So these are some of the example, so you can see that you know the first group of the periodic table and oxides typically these because these will be the smaller cations and so; and so these form the anti fluorite structure.

The fluorite structure ok, so there are the examples of fluoride fluorite or calcium fluoride Sr f 2, barium fluoride, calcium strontium barium, then cadmium fluoride, led oxide, cerium oxide uranium oxide ok. So, these are these are some of the fluorite structures that are found ok.

And again the nice thing is you can understand both fluorite and anti fluorite just in the same way and you can see that our understanding of voids and close packing is actually very useful because you can easily categorize crystal structures ok. So, far we looked at we looked at the cubic close packed and we looked at voids and cubic close packed, but you can also have hexagonal close packed and you can have voids you can have you can have other elements occupying the voids of the hexagonal close packed ok.

(Refer Slide Time: 26:38)



And I will just take 2 examples one is called wurtzite; wurtzite and wurtzite is where in the where you have the anion forming a hexagonal close packed and the cations occupying half of the tetrahedral voids ok. And now; now in the case of in the case of hexagonal close packed we have seen the location of the tetrahedral and the octahedral voids and if you if you recall in the in the hcp you have you have this arrangement of close packed arrangement of atoms in a layer.

So, you have the close packed arrangement of atoms in a layer and the next layer, the next layer is right here, the next layer is sitting here and right at this right bit just below this below this green; green atom in or in between this green atom and the and the atoms forming the blue plane there is a tetrahedral void. So, the tetrahedral void is located right here. So, this tetrahedral void is located here and we also saw where the octahedral void will be located octahedral void will be located in this case; in this case since the you will have a cubic close packed you will have a close packed arrangement of these green atoms.

So, the green atoms will form another close packed array and there will be an octahedral void located right here ok. So, this is the octahedral void and this is the tetrahedral void ok. So now, so now, what does wurtzite look like? Let me I will draw it in a slightly different way ok, so let us again put the anion. So, we will take the hcp in this kind of representation. So, if you take the unit cell for hexagonal ok, now we want half of the tetrahedral voids to be occupied and if I should say that in this unit cell there is also an atom located an anion that is located right here ok.

Right this is the this is the green layer let me show it in green ok, this is this layer that I would I would shown in green there is also an anion ok. So, the green layer is also an anion we have to occupy half of the tetrahedral void. So, let us take a tetrahedral void that is directly below these we can we can take one that is at the center of these three and that will come somewhere here and you can see that this is equidistant from each of these atoms.

So, this is this is one of the. So, here what we will do is the tetrahedral void which show the green atom again I will just this to this again show the green atom right here ok. So, the so the green atom is also an anion which is shown in this intermediate in this in between these 2 hexagonal; hexagonal layers ok. So, now; now the tetrahedral voids ok, so there will be 1 that is just above the green atom ok.

So, in this in this you know right in between these 3; these 3 atoms and when above the green atom, so it will be will be located right here ok. So, that will be that will be one tetrahedral void. Additionally there will also be tetrahedral voids which are yeah. So, there will be a tetrahedral void located also directly below this green atom and so usually what if you want to occupy only half of the tetrahedral voids, then you can either occupy the one that is above that is directly above the green atom or the one that is below the green atom ok.

So, it is directly below the green atom as is shown in this in this figure here ok. So, what I will show is tetrahedral voids that are directly below the green atom. So, I will leave this blue I will remove this blue atom and I will and I will just show the tetrahedral void located directly below the green atom ok. And now there will be similar tetrahedral voids you can you can work this out ok, there will be similar tetrahedral voids located right here; here and here.

So, this will be directly below the red; red below this red anion and so and so and so these are half of the tetrahedral voids that are occupied in this in this in this unit cell ok. So, this is the wurtzite structure and wurtzite is actually quite common there are several like Zn O forms of wurtzite structure, zinc sulfide at high temperatures forms a forms a wurtzite structure ok. Then there is Zn Te, Zn Se, there is gallium nitride; gallium nitride, zinc selenide, zinc telluride, cadmium sulphide, cadmium selenide ok.

And we will find and we will see that you know several compounds ok, but that form the wurtzite structure also form the sphaelerite of the zinc blende structure and usually one of them is more stable than the other ok. So, there is always there is often wurtzite and sphaelerite ok. So, the same compound for example, like zinc Zn S can be either wurtzite or sphaelerite and usually there is an equilibrium and one of them is favored at some temperature.

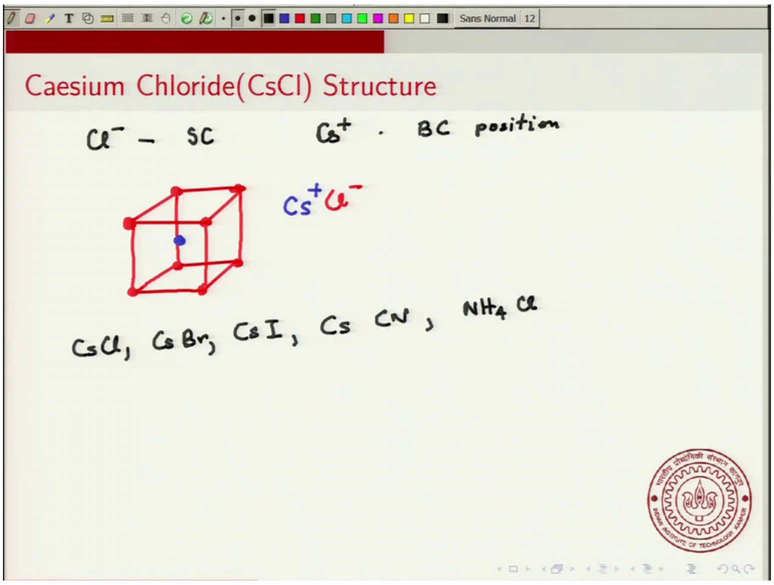
Similarly gallium nitride can also form either a sphaelerite or a or a wurtzite and usually in the case of gallium nitride the wurtzite is a more stable, in the case of zinc sulfide the sphaelerite is the most stable sphaelerite or zinc blende. The other structure that I am going to talk about is nickel arsenide, in nickel arsenide you have anion forming an hexagonal close packed structure and the cation occupying the octahedral voids.

And I will just I will just quickly show this the nickel arsenide. So, this is this is nickel arsenide and again if you go back if you go back to the previous nodes to find out where exactly the octahedral voids are located ok, then you will see that they will be located right in the in the I mean right in between in bit directly below these 3; these 3 atoms ok.

You can take you can actually alternate the octahedral and tetrahedral voids that is there is there is a choice there ok, but so it will be located right here and we should show this and the other octahedral void will be located symmetrically right, symmetrically below exactly here ok. So, these are the octahedral voids.

So, this would be the nickel arsenide structure and again there are several examples, so there is there is nickel sulfide, nickel arsenide, nick nickel antimonide, nickel selenide, ion sulfide etcetera ok. So, these are some of the structures that come from close packed that can be understood in terms of close packed structures ok.

(Refer Slide Time: 38:31)



Now, I will just mentioned one other structure that is very common and this is the caesium chloride structure. So, in cesium chloride the chlorine chloride anions form a form a simple cubic structure and the caesium ions will a occupy the body center position. So, the structure looks like this, so you have the chloride ions forming a and the CCM ions occupying the body center, so you have CS plus CL minus. This is another this is another fairly common structure and there are other compounds that form the caesium chloride structure. So, you have caesium chloride, caesium bromide, caesium iodide, caesium cyanide, ammonium chloride ok. So, these are these are examples of the cesium chloride structure.

So, with this I will conclude this lecture ok. So, in this lecture we saw the crystal structures of several binary compounds and we saw how we can understand them in terms of either a cubic close packed or a simple cubic arrangement of the anions with the cations occupying the voids ok. Now in the in the next lecture I will look at some more crystal structures and look at things like perovskites and spinels and then and then we look at we will also look at alloys ok. So, but I will conclude this lecture here.

Thank you.