Solid State Chemistry
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Lecture - 49
Space filling Polyhedra, Alloys

Now, I will go to the fourth lecture of week 10 of this course. And in this lecture, I will talk about a slightly different way to visualize crystal structures that is through Space filling Polyhedra and then I will talk about Alloys ok. I will talk about alloys what are the different kinds of alloys you can form and just show you how you can get many different kinds of alloys ok. So, week 10 lecture 4 will be space filling polyhedra and alloys.

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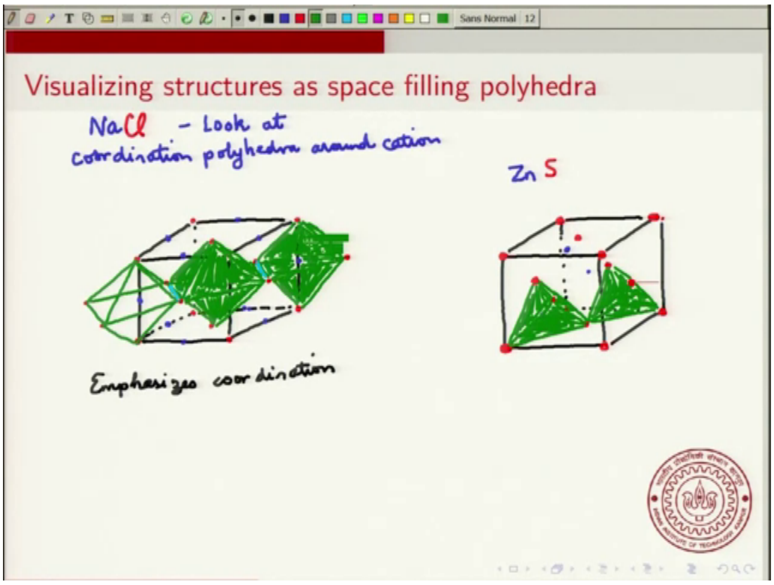
Visualizing structures as space filling polyhedra

NaCl - Look at coordination polyhedra around cation

ZnS

Emphasizes coordination

So, now let us visualize some structures as space filling polyhedral, I will just show this through an example ok. The example I will take is the sodium chloride structure ok. So, we will start with the sodium chloride structure ok. Here in a sodium chloride structure ok, you take the let me show the chloride ions as forming the close packed and the sodium ions as forming the as I as occupying the octahedral voids.

So, so if we take sodium chloride ok, I will show the chloride as forming a close packed and the sodium as occupying the octahedral voids ok. So, what you will have is I want to show so these are the chloride ions which are occupying the close packed structure which are forming a closed pack structure cubic close packed. So, just to show what the cubes look like, they look like this. Then there will be a few more chloride ions, they will be at the centers of each of the phases. So, this is a close packed structure formed by the chloride ions and now the sodium ions are going to occupy the octahedral voids.

Now let me show the one octahedral void in the center first ok. So, at the center of the crystal there is an octahedral void where the sodium ion is enclosed. I will start with this void and then I will go to the other voids, other sodium atoms. So, in the idea of space filling octahedral, you look at coordination polyhedra around cation ok.

So, the focus is on the cation and look at the coordination polyhedra around the cation. So, let us look at the cation right in the center, let me show the other cations, but now I will first focus on the cation in the center ok. So, now the cation right at the center, if you if I look at its the coordination polyhedra; that means, you look at the nearest the atoms that are closest to it or these 6 chloride ions. So, these are the ions that are closest to this ok.

So, these are this these 6 ions are closest to the center sodium ion and now you can make a polyhedron ok. So, we just see that this will form you can clearly see what this will form, this will form an octahedron. So, the coordination polyhedra is an octahedral ok. So, clearly it is an octahedron that is formed around this and let me erase these lines that are inside just for clarity and so this is what the coordination polyhedron, this is what this octahedron will look like and we will just shade it just to emphasize ok. So, this octahedron will contain only the sodium atom at the center and no other atom, no other atom will be inside this octahedron ok. So, this octahedron is a coordination polyhedron for this sodium atom.

So, now, what you can do is? You can do this for all the other atoms for example, you could do it for this sodium atom ok. Now and again you will see that you will have another octahedron in this case you have an atom here I have to extend the structure to this side and put an atom here, I have one that is in the sense and I will have one that is in the back plane, another one that is here, this is in the plane on the back and then.

So, these are the 6nearest neighbor chloride nearest neighbor sodium ions and you can again see that they will form this octahedron and again if I shade it, you can see this coordination octahedral, there is a little bit of smudging that happened here, but its that is just due to this program ok. Now you can do the same for all the sodium ions and you can make; you can make similarly you can make coordination polyhedra what I mean I will emphasize this point by looking at this sodium ion just to show a point ok.

Now if you look at; if you look at the coordination if you look at the nearest neighbors so, there is one on this face, one here and then one similar one will be located here, there is one on the back face and one here and one here ok. Now what you see what you see is that the coordination polyhedra will share this edge. So, these two coordination polyhedra will share the same edge ok. So, you can see that in this octahedron here I will not share it, but I will just emphasize that there is one edge which is shared between the two octahedrons similarly here also there will be one edge that is shared between the two octahedrons ok.

So, you can really look at this structure as a set of polyhedra as you can do this for all the sodium ions and so the whole structure will just look like a set of octahedra edge sharing octahedra ok. So, this is just a way to visualize the structure that emphasizes the coordination so this emphasizes coordination of ions. And additionally there are points that are that relate to how these octahedron touch how these octahedron are connected with each other. In this case, there is a side sharing octahedron you can do the same.

Let us take the case of zinc blende. Now in zinc blende ok, let me put the sulfide ions at the cubic close packed structure and now I will put the zinc ions as before I will show this and so these are the sulfide ions that are forming a close packed structure cubic close packed. And now the zinc ions will occupy the tetrahedral voids that will there will be one here, one that is along this diagonal so that will be somewhere here located here it is actually along this body diagonals and a fourth one will be located that will be located close to this along this body diagonals so that will be located one fourth way along this.

Now let us look at this particular zinc ion ok. Now this is closest; this is closest to 4 other it is closest to 4 other sulfide ions and those are and one in the front face I did not show this is in the it is closest to these 4. And now you can see that the coordination polyhedra will be a tetrahedron ok. So, it will look like this ok.

And now if you take; if you take this neighboring this other zinc ion now this the polyhedra for this so these are the 4 and this one in the back face, these are the 4 nearest neighbors and now you can see that you get another tetrahedron. Now in this case the two tetrahedrons only share one corner ok. So, this is an edge sharing tetrahedron ok.

So, now, the structure looks like a set of corners sharing tetrahedron and you can extend both these octahedron and tetrahedron to fill the entire space ok. So, this is how you visualize structures as in terms of space filling polyhedral.

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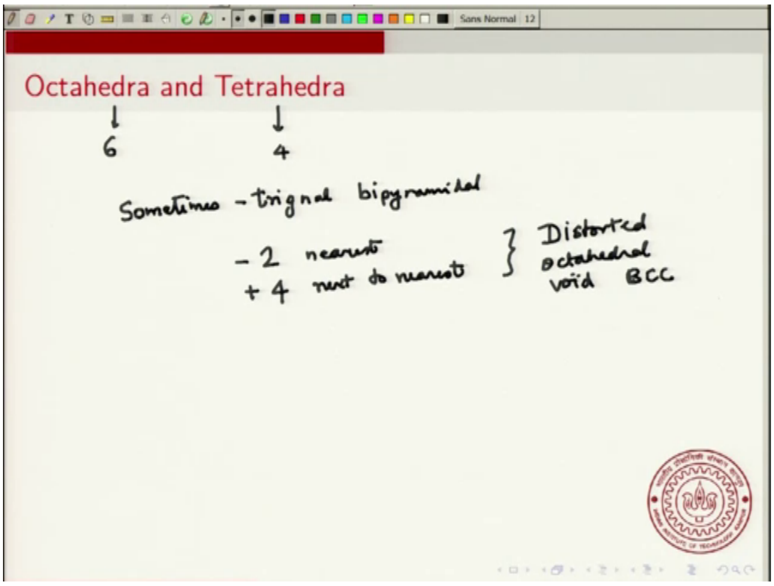

Octahedra and Tetrahedra

↓ 6

↓ 4

Sometimes - trignal bipyramidal

- 2 nearest
+ 4 next to nearest

} Distorted octahedral void BCC

Now I said that there are 2 common coordinations ok. So, octahedra is 6 coordinated and tetrahedron is 4 coordinated ok. So, if your cation is coordinated to 4 other anions then usually there is tetrahedron and there is octahedron if it is coordinated to 6 ok. Now you can now sometimes the coordination so sometimes the you can have things like trigonal bi-pyramidal sometimes the coordination number is just 2 nearest and plus 4 next to nearest this is in the case of the distorted octahedral void which we saw in the case of BCC so that is also possible ok. So, there are other possibilities, but the most common ones are the tetrahedral and octahedral and it is in these cases that we usually show the structure in terms of coordination polyhedra.

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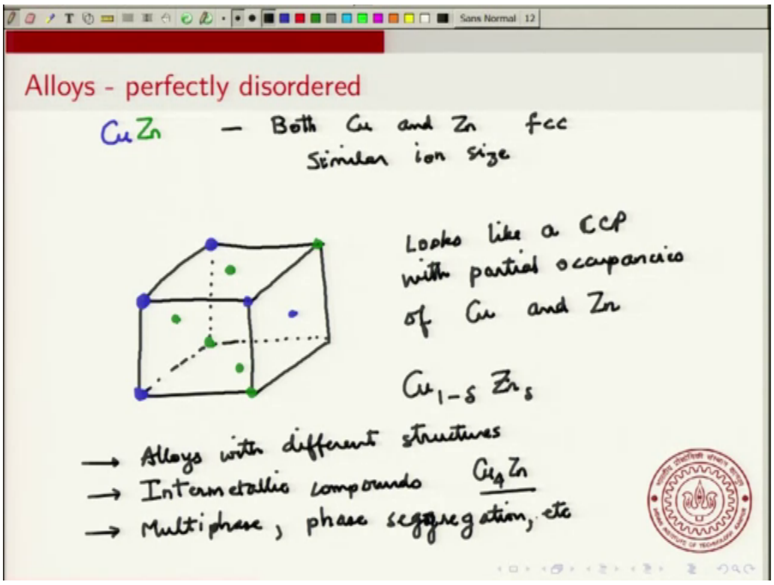

Alloys - perfectly disordered

$CuZn$ — Both Cu and Zn fcc
Similar ion size

Looks like a CCP with partial occupancies of Cu and Zn

$Cu_{1-\delta}Zn_{\delta}$

→ Alloys with different structures
→ Intermetallic compounds Cu_4Zn
→ Multiphase, phase seggregation, etc

Now that is about what I want to say about coordination polyhedra and now let me get to the topic of alloys and let us take, let us start with the example of copper zinc alloy. So, let us take copper zinc, alloy and now the point is that now both copper and zinc they are fcc and now you can sort of see what will happen if you have; if you have combination of copper and zinc. And they have very similar sizes ionic size zinc is 2 plus and copper is 1 plus ok, but I mean copper can be either plus 1 or plus 2, but basically they have very similar size of ions and now so, what can happen let us take one example of perfectly disordered alloy ok.

So, here y you can have cubic close packed structure. I have a cubic closed pack structure, but each and every side here is actually partially occupied either by copper or zinc ok. So, each site and have either a copper or a zinc and there is no it is perfectly disordered that means, you know you can have some copper some zinc and there is no you cannot really tell which is which and ok.

So, here you have a case of a completely disorder disordered alloy. So, alloys are and this is typically the case for alloys ok. So, they are perfectly disordered and it looks like it looks like CCP Cubic Close Packed with partial occupancies of copper and zinc ok. So, this is very typical of alloys and if the size of the 2, if the size of the 2 species is very similar ok, then yes you will get similar you may get something like this.

Now, is this the only possibility; is the only possibility. Now let us say you have large amount of copper ok, you have copper which is 1 minus delta and zinc, you do not have 1 is to 1 you have much more of copper and much less of zincs delta is very small delta is much less than 1. Then what are the possibilities that can take place ok?

So, you can get; you can get alloys with different structure, but also you can get intermetallic compounds. So, what is meant by intermetallic compounds is basically some sort of for example, if you get one example you might get Cu 4 Zn and you might get some sort of repeating unit of this unit showing up in your structure ok.

So, a large part of the structure might just be repeating units of some structures such as Cu 4 Zn or something and it might not be it might not be a simple fcc in that case. You could get; you could get multiphase behavior more than one phase, you could get phase segregation; that means, in some region you only have copper and some region you only have zinc; essentially the number of possibilities become very large ok. So, you can get; you can get many different structures. Now let us look at the copper zinc system and let us look at some of the other possibilities that you can have.

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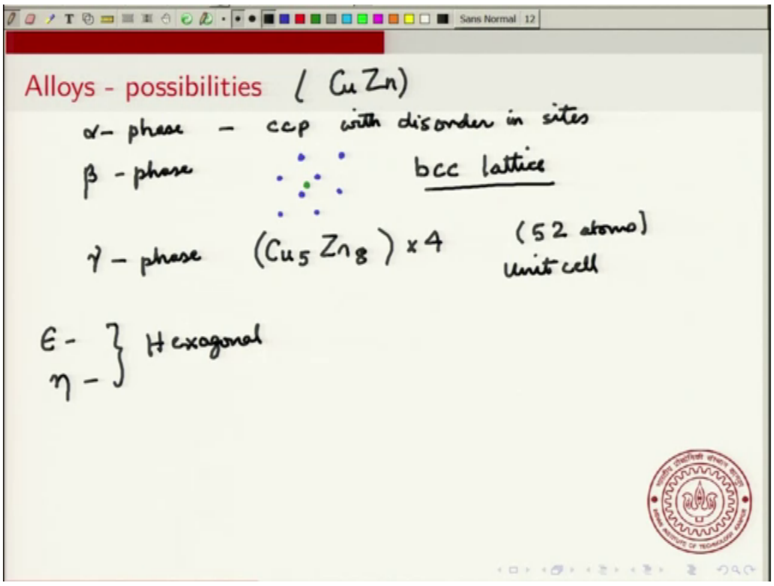

Alloys - possibilities (CuZn)

α- phase – ccp with disorder in sites

β - phase bcc lattice

γ - phase $(Cu_5 Zn_8) \times 4$ (52 atoms) unit cell

ϵ - } Hexagonal
η - }

So, this I will just list some of them. So, alpha phase is what we had earlier so CCP with disorder. So, this is for the copper zinc system and of course, this is also seen for several other alloys disorder; that means, the you do not know there is no ordering the positions of copper and zinc I mean they are all in the CCP, but each site disorder in sites. So, each site can be either copper or zinc. So, that is the face that we talked about, but now there are there have also been people have also observed something called a beta phase where essentially you have one of the ions forming cube simple cube and the other at the body center ok. So, you can have something like this.

So, this is a body centered. So, it is like it is like a bcc lattice this and you can have; you can have one or the other so, instead of having an fcc lattice, you have a bcc lattice with each site being either copper or zinc. Then but is this all no there is a very interesting phase in this system called a gamma phase which is actually. So, in this case there is a new in this gamma phase there is a stoichiometry of Cu 5 Zn 8; Cu 5 Zn 8 ok.

So, that is 13 atoms and 4 of these units; 4 of these units so that is total 52 atoms they form a big unit cell ok. So, the stoichiometry here is Cu 5 Zn 8 and 4 of these Cu 5 Zn 8 units together form a rather complicated looking unit cell which is called the gamma phase ok. There are other phases that are also possible there are hexagonal phases.

So, epsilon and eta these are hexagonal phases ok. So, you can see and all these are found as you vary the composition and as you vary the other external conditions you find all these several phases. And I do not want to get into too many details of this, but I just want to say that you know when you form alloys there are a lot of possibilities and that is what makes alloy is rather interesting and the hope is that by changing the composition you can get more you can get the properties of interest.

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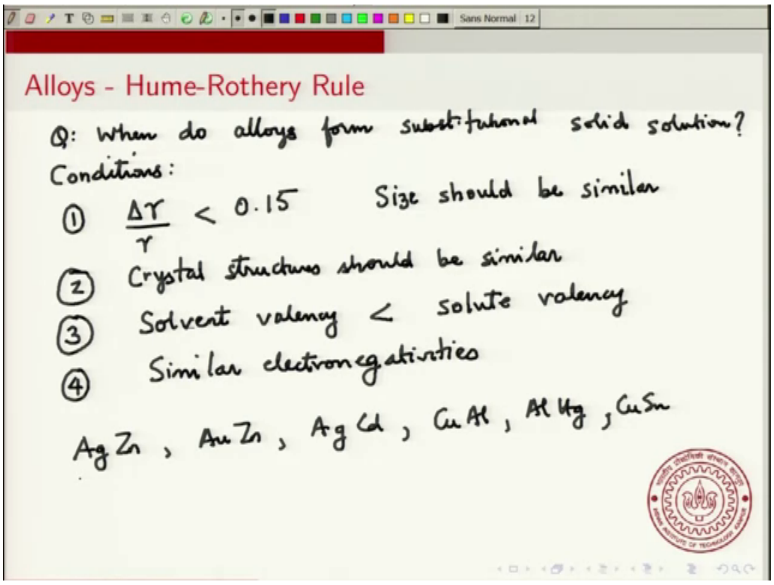

Alloys - Hume-Rothery Rule

Q: When do alloys form substitutional solid solution?

Conditions:

① $\frac{\Delta r}{r} < 0.15$ Size should be similar

② Crystal structures should be similar

③ Solvent valency < solute valency

④ Similar electronegativities

AgZn, AuZn, AgCd, CuAl, AlMg, CuSn

Now, I will just conclude this discussion with us with a rule which is very popular in alloys it is called the Hume Rothery rule and the question is when do alloys form a good substitutional solid solution ok? Solid solution is another word for alloy when I say substitutional solid solution what I mean is that is something like the like what we saw in the case of fcc where you have a close packed array, but some of the copper is substituted by zinc.

There are certain conditions the so the conditions according to the Hume Rothery rule of the following; these are rules of thumb to that help you predict which systems will form good alloys ok. So, the first condition is that the difference delta r by the radius of the larger species should be less than 0.15 ok. So, the percentage difference in size so size should be similar ok. So, if 2 atoms have similar size, then they are more likely to form an alloy ok, the second condition is that their crystal structure should be similar ok.

So, if they both have a cubic close packed so that is very good or if they both have hexagonal close packed that is very good, out of they both have body centered cubic that is also very good. Of course, their sizes will be different because they are 2 different atoms, but you could also imagine that cubic close packed and a hexagonal close packed could in principle form a solid solution because there is because as we have seen cubic close packed and hexagonal close packed are actually quite similar.

Then the solvent which is the larger of the one that is present in greater amount. So, solvent valency should be less than solute valency. So, in the case of copper zinc ok, if copper is a solvent and copper is usually taken as plus 1 and zinc is taken as plus 2 ok. So, copper valency is less than the solute valency which is the zinc valency and the fourth one is they should have similar electronegativities ok.

So, so systems that satisfy these usually form good solid solutions and there are several examples of good solid solutions. So, you can have silver zinc, you can have gold zinc, you can have silver cadmium, copper aluminum ok, aluminum mercury there are several others copper tin very famous system you could also have things like ion well. So, I will just stop here there are several others, but these are the ones that obey the Hume Rothery rule and they form good alloys.

So, with this I will conclude this lecture and with this we are almost at the end of this week. So, in the last lecture I will just summarize what we did and do some practice questions. But the point I want to make about this particular the contents of this week is that we have, I have tried to show you a lot of structures, I have tried to show you different ways of looking at crystals in terms of coordination polyhedra and closed packed with voids and the idea is of this week is to actually familiarize you with the language that is used in solid state chemistry ok.

So, when you read books on solid state chemistry or you read journal articles, you will often find lot of these terms. And so I at least wanted you to be familiar with some of these terms so that it will help you in reading ok, but as far as the actual may I mean I do not expect you to remember all the structures I expect you to remember maybe a few structures like zinc blende, wurtzite and so on just a few structures, but I do not expect you to know at the back of your you know immediately which material forms which structure. So, just if you just focus on the few structures that we have looked at you will be fine all right ok.

So, I will conclude this lecture here and in the next lecture I will summarize this week and do some practice problems.

Thank you.