Lecture - 19
Crystal Structures

The next example is of an ordered structure. We consider Fe 3 Al.

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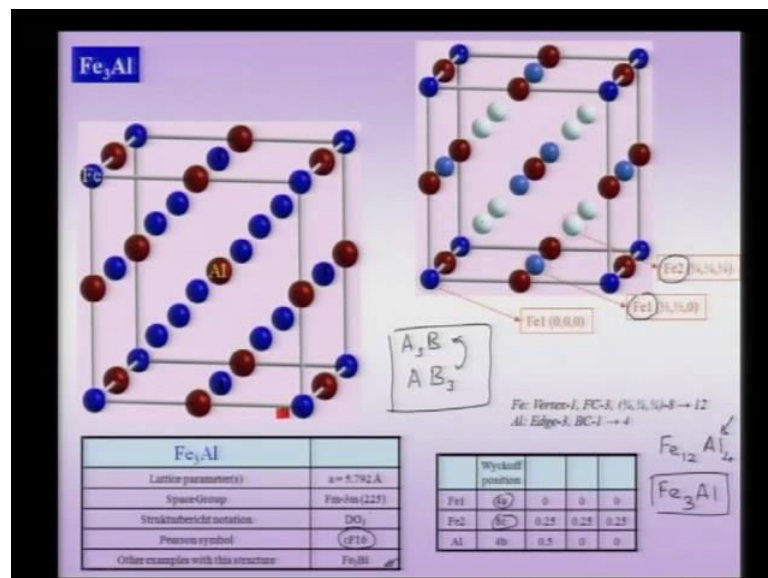
Now, as we are going from the simple ordered structure to more complex ordered structures, we will have to use certain techniques to understand them, certain techniques to visualize them. Also, we will come across certain concepts, which we have not considered before. So, these examples are not just examples of ordered structures. But they additionally serve to highlight certain aspects with regarding especially to, for instance the coordination of atoms etcetera, which we have not dealt with before in Fe 3 Al.

As you can see, it is a large unit cell, not very large but larger than some of the simple atoms. We have considered so simple elements we have considered so for. It has got a lattice parameter of about 5.8 angstroms. It has got the complete cubic symmetry, which is F 4 by m 3 bar 2 by m. There is this notation, which is known as a Struktur Bericht notation, which is given a name of D O 3.

Such rather popular structure is in the Pearson symbol. It is cubic face centered. There are 16 atoms in the unit cell. So, how do I count the 16 atoms in this unit cell? So, again, even though there are so many atoms, the lattice is still our face centered cubic lattice. That means whatever atom apart from the face centering position, so you can see there are atoms in the face centering position the blow atoms. Whatever other atoms are have to go part of the motif, so we have to calculate the 16 atoms in the unit cell.

How do we do that? So, we can see. First, we let us start do the calculation on the iron atoms. So, the iron atoms are the ones, which are occupying the corners and also the phase centers in an addition. I have also shown them by this light blue colors. So, the dark blue and the light blue colored atoms are iron. We shall see they are actually in some sense different kind of iron atoms. So, we will see that aspect in a coming slide. So, let us first make a calculation of number of atoms per unit cell. So, you can see that totally all the 8 atoms in the vertices 1, 2, 3, 4 all the 8 atoms together give us a contribution of one iron atom to this unit cell. So, vertex atom is 1.

There are 6 faces. There are iron atoms at these faces. In together they give a contribution of 3 iron atoms to this unit cell. Then, we have this other iron atom, which is located at quarter, quarter, and quarter position. So, this is the quarter, quarter, and quarter position. If there is one here according to the face centering this symmetry of this point group and this face group, we will see that there has to be an iron atom. Here, the 4 fold will take it here. There will be one more here. There will be one more here. So, this will be a position like quarter, quarter, and quarter. The second position will be a quarter, 3 quarter, and quarter.

So, therefore, you will have other positions. There you will have 8 atoms within the unit cell. Therefore, all the 8 which are contained within the unit cell will go as contributions to this unit cell. They will have 8 iron atoms located in this quarter, quarter, and quarter position and other equivalent positions. So, therefore, what is the total number of iron atoms in this unit cell? 8 from these, I call the iron 2 atoms. Why I call them the iron 2 atoms? I will explain in a moment.

Then, we have 3 from the face centering positions and 1 from the vertex; making it of total of 12. So, I have 12 iron atoms in the unit cell. So, let me count the number of aluminum atoms. The aluminum atoms are the ones, which are in brown color. You can

see they are all located at the 12 edges. So, 12 edges with one fourth contribution to this unit cell; from each edge. Therefore, I have 3 iron atoms, which come from the edges. There is one more iron atom located at the body centre, aluminum atom located at the body centre. Therefore, that gives a contribution of 1. Therefore, total of 4 aluminum atoms in this unit cell.

So, I can write the chemical formula of this unit cell as Fe 12 Al 4. I reduce it to the common factors. Make it Fe 3 Al. So, this is my reduced chemical formula. But, if I want to use the complete chemical formula for the unit cell, I will have to write it as Fe 12 Al 4. Now, as I told you, I will use the slightly more complicated example. So, this is obviously; these are more complicated atoms. There are more number of atoms in the unit cell. There are 16 atoms in the unit cell; unlike some of the simple structures we have seen before, wherein they are just 1 or 2 or 4 atoms in the unit cell.

Therefore, I need more and more techniques and more and more visualization so as to understand these structures in a simpler way as possible. Of course, later on in this course, we will see more complicated examples, wherein no simple visualization is possible to understand these structures. They will continue to remain rather complicated structures. But, wherever possible, we will try to understand them in some of the simple terms we have used so far. Ravi has a question.

Student: Sir, what are the factors that will determine that these atoms will sit on the FCC position? This question is that what will determine if these atoms sit in FCC positions or some other different positions. Now, this is actually a very profound question. In some aspects of this question, we will address later that. Even the very simple question, why does for instance, iron form an f c, face centered cubic crystal structure? Why does for instance chromium form a BCC crystal structure?

So, these are some more profound questions. There have been techniques and approximations to understand these crystal structures in terms of the energetic. But nevertheless, to understand larger and larger unit cells like this. The overall computation and the techniques get more sophisticated. It becomes rather profound question to answer in one line. Actually, we will have to solve the Schrodinger equation for the entire crystal, which is as you can see a very complicated task.

Is the position of iron and aluminum interchangeable in this? As in sodium chloride, we can put the sodium and chloride in the clearly not because you can see the stoichiometry is so different. If I did the interchanging then, my stoichiometry will completely change, at least for this example. But, there could be other examples, wherein for instance I am, let me use the same space as board. So, do not relate it to this crystal structure. But, this space is meant for general explanation. So, I can see that you could have a structure, wherein an A 3 B is stabilized. It could also be possible that the same phase diagram also shows an A B 3.

Of course, A 3 B and A B 3 need not have the same crystal structure. But, there could be special cases, wherein A 3 B and A B 3 exist. The crystal structure has obtained just by merely interchanging the position. So, there is this possibility existing, but, not in this particular example Fe 3 within the example. If I change it, then I am obviously changing the stoichiometry. Now, I mentioned that I am designating two different iron positions. That means, I am calling one as iron 1 here, another iron as iron 2. Now, I will, I need to understand this. To understand this, though we have not gone into the detail of this, what do you known as the Wyckoff position etcetera?

These have been designated for instance in y Wyckoff notation as 4 A and 4 C. So, we will not take up details of this. But we will understand it in our normal knowledge of coordination polyhedral. Later, so, the iron 1 is located in 0 0 0 and equivalent position. The iron 2 is located in quarter, quarter, quarter positions like these and equivalent positions. So, we try to understand. We will also notice that there are other examples of crystal structures, which go into this DO 3 kind of crystal structures. Since, DO 3 has basically no signs behind it, it is just a listing while C F 16, we have already seen the rationale behind using this kind of the Pearson symbol. So, let us try to understand this structure a little more.

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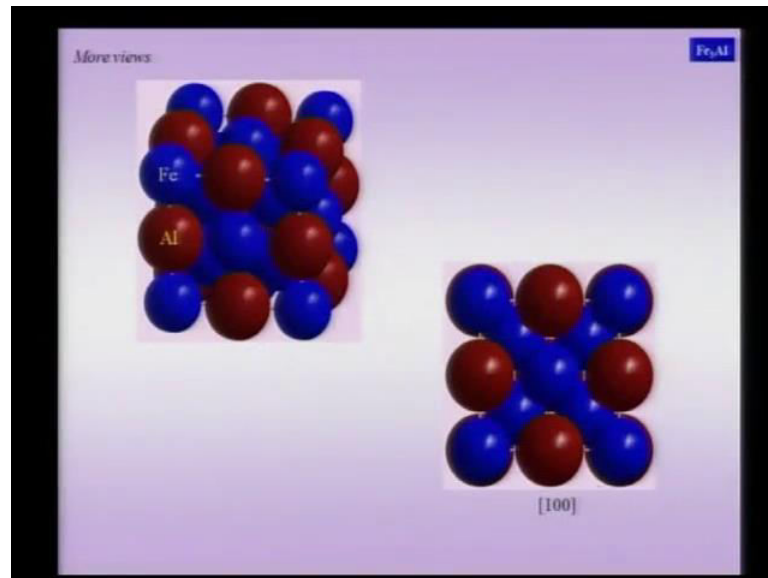
So, this is the space filling model of the same, wherein you can clearly see the aluminum and iron atoms touching each other. This is as 1 0 0; one view of the same. So, the only way to understand such complex crystal structures is to actually try to visualize them from many angles. Try to understand the various kinds of models we have dealt with. Before like, we told you, the space filling model, the ballistic model, the wire frame model etcetera. So, you can see clearly from this that the normal face centering positions are occupied from in this and this.

But additionally, these are these other atoms which are located at quarter, quarter, and quarter. So, this is my quarter, quarter, and quarter kind of atoms. The ones here which you are seeing from the side view, which in the previous view, you can clearly see are these atoms. So, you can see those atoms form the side view. Additionally, you can see the space filling view of this entire ordered crystal structure.
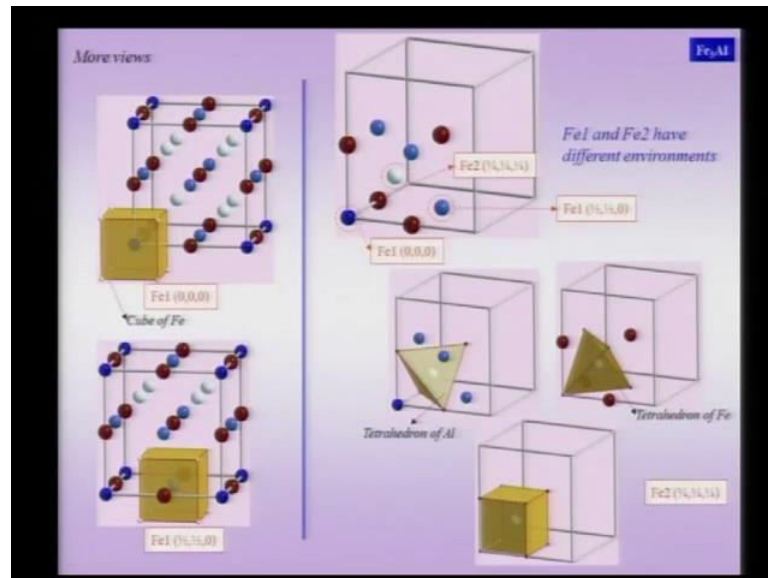
So, I was mentioning that I am using two designations for the iron atoms. Well, I am using only one designation or one position for the aluminum atom. The aluminum atom is located in the corner position and all the face centering positions. So, this it is very clear. So, this atom is related to this other atom of aluminum by the standard face centering translation. So, there is no problem. There is no other for instance no other atom located anywhere else, which I need to consider.

Now, let me look at the coordination polyhedron around an iron atom, which is located in the corner and also at the phase center. So, this is my iron atoms. So, let me go back to this original site. So, what I am considering here is my coordination around the aluminum atoms, coordination of the iron atoms which are located here and the coordination around the iron atoms, which are located in a different position. Now, if I look at the coordination around what I call the iron 1 position, which is 0 0 0 position. As I told you, because this is a face centered cubic kind of structure lattice is face central.

So, any other atom which is located here also has to be identical in terms of its environment because that is a lattice position. So, that is clearly verified. So, if you look at an iron atom here, you can clearly see you have a cube of iron around it. So, the coordination polyhedron around this is 8 iron atoms or ions around this central iron ion. Similarly, the cube would be identical, when I look around the iron, which is located at half zero. It is related to the face centering translation to the atom at 0 0 0. Clear? So,

there is no problem with respect to this. Therefore, but, now, I would like to contrast this kind of a coordination with the coordination of an iron atom or an ion. It is located at quarter, quarter, and quarter.

So, this is I am contrasting the coordination shell around the atom, which is located at 0 0 0 with the coordination shell around an atom, which is at quarter, quarter, and quarter. So, let me look at the coordination shell. So, first let me try to understand, identify atoms of the same type, which sit around this. So, if I try to observe that, I will see that there is a tetrahedron of aluminum around this central iron atom. So, this tetrahedron is formed as you can see the 4 iron atoms, which are located at centers and the body center. So, this is my tetrahedron of aluminum around my iron, which is located at quarter, quarter, and quarter.

Now, I alternately visualize a tetrahedron of iron located around the same iron atom. It is at the center, which is the iron 2 atom. This is my atom, which is right here at the middle here. You can see that this is a tetrahedron of iron. But the coordination polyhedron is not just this tetrahedron of aluminum or this tetrahedron of iron. But it is actually a combination of both of them. In other words, it is a cube. But now all the vertices the cube are not identically populated. As you can see this, whatever the subset, which is this tetrahedron is populated by aluminum atoms.

This tetrahedron is populated by iron atoms. So, I can draw this sub tetrahedron within this. If I draw any these atoms for instance so, I can complete this tetrahedron like I will find there are 2 tetrahedral like this and one. Therefore, what I have around the central iron atom is a cube half populated by aluminum atoms and half populated by iron atoms. So, clearly my coordination environment around the central ion atom, which is located at 0 0 0 is different from the iron atom. It is located at quarter, quarter, and quarter, which is clearly designated by looking at the Wyckoff positions here.

In other words, there are iron 1 is A 4 contributes 4 atoms to the unit cell. Therefore, there is this 4 A position and iron 2, there are 8 atoms. Therefore, 8 C, so clearly, their non-equivalent positions are with regard to the coordination polyhedron. The number of such equivalent points or equivalent atoms within the unit cell is also different. So, there are 8 belonging to this type. There are 4 belonging to this type. This calculation is easy to

make because we know there is one contribution from the corner atoms and 3 from the face centering atoms.

So, there are 4 of this type and there are 8 of this type. So, that much is very clear. So, this example is a beautiful example, wherein we have now not only understood more complicated versions of ordering. So, let me revise some other ordering. We already had seen the simpler versions of ordering like. So, we started off the very simple form of ordering, wherein a BCC crystal in the copper zinc system became a simple cubic crystal.

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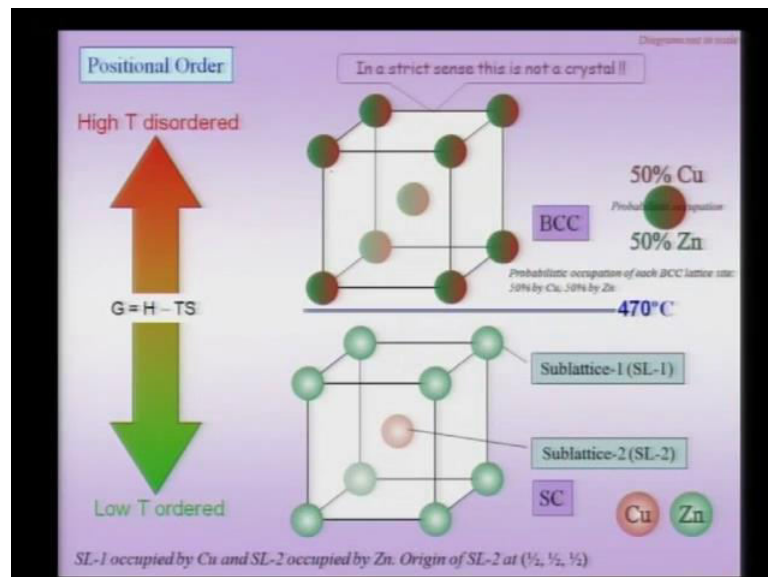
We had, we could describe this in of two sub lattices. Now, we considered a little more complicated example.
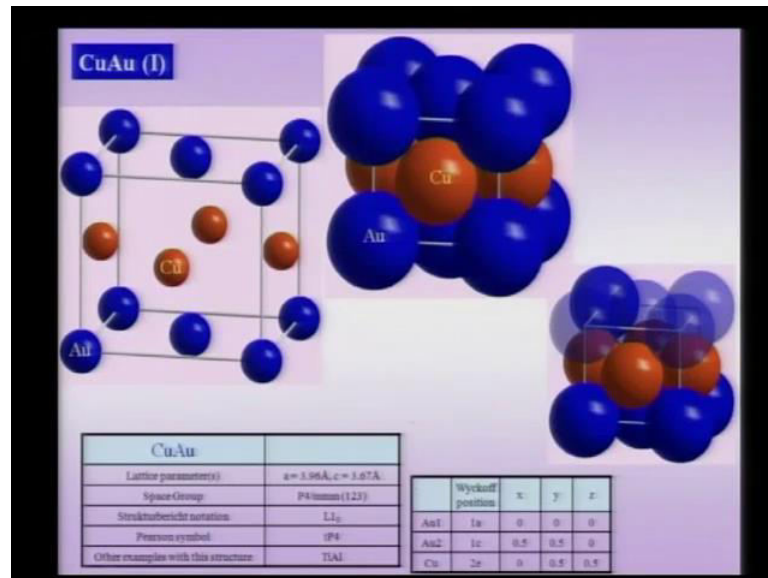
Now, I have a ordering. So, in other words, the face centered, the disordered structure would be a face centered cubic structure. The order structure would again be a simple cubic structure, which is now again indicated by the p. It means it is a primitive structure. So, I have a primitive structure, which is my ordered structure. Again, that means that whatever other atoms are located apart from the corners, which are lattice points have to be accounted for in the form of a motive.

So, that part is absolutely clear. So, it cannot be part of the lattice. So, these are all not lattice points; only lattice points are at the corners. So, even this was reasonably simple as compared to the last example. We considered and we could understand this in terms of a derivative of the FCC lattice. The Cu 3 Au was the next example.
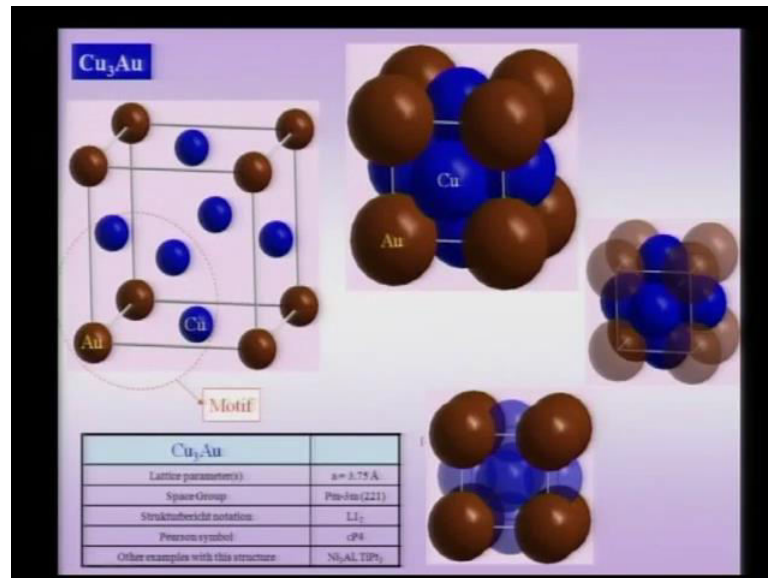
We considered and here again it was considered as a derivative of the face centered cubic lattice. Again, we saw that this stoichiometry is not a 50 50 stoichiometry. It is for every atom of gold. We had 3 atoms of copper or 3 ions of copper. If you want and this again can be it is thought of as a derivative of the face centered cubic lattice. But, the structure itself, the ordered structure is a primitive structure and not a face centered cubic structure again as before. Since, the primitive structure, the only lattice points are at the vertices of this cube and not any other point.

Therefore, every other atom in this has to go part of the motif. So, the motif now, will consists of for instance, one possible choice of motif is this gold atom at the corner vertex and these three face centering copper atoms, which again give my stoichiometry. This is Cu 3 Au. So, the motif itself should get my stoichiometry also. Now then, we have considered this example, wherein my ordering got little more complicated. There were nonequivalent positions of the same kind of atom and also the unit cell became rather large.

So, you can see here in this case also, the unit cell was about 3.7 5 angstroms. In dimension, it is also was tetragonal but, less than 4 angstroms. We saw that as we get to this more complicated example, my unit cell gets larger and larger. That means these are more longer, long range ordered structures. Just to summarize this slide, whenever, I want to understand these more complicated structures not only, I will look at the lattice

the motif, I also try to understand the coordination polyhedron around these individual atoms.

I try, if my understanding of face centered cubic for instance, lattice is obeyed. For instance, the coordination polyhedron around all the face centered atoms connected by the face centering translation. I have identical coordination polyhedra. And also, wherever possible, I will try to break up this even the coordination polyhedra into sub polyhedra. Then, assemble my larger polyhedra to understand the crystal structure. So, all these visualizations are very important, when I try to understand these more complicated versions of these structures.

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As you have told that, as we are going from easy to simple to complicated structure, the lattice parameter is increasing. Is there any rule of lattice distortion? Also, is there any rule of lattice distortion in the increasing lattice parameter? Let me try to understand the question you are asking that we are going from simple to more complicated structures. As we are considering more and more sophisticated forms of ordering, what is the role of lattice distortion?

There are 2 kinds of lattice distortions. We are talking about the regular ones, which lead to a change in symmetry of the structure. The irregular ones, which are typically found in solid solutions because in solid solution a local region, if I take up space atoms randomly occupy every lattice point's position. So, whenever I am talking about a lattice

parameter, I am talking about a average lattice parameter. So, locally, there are lots of distortions.

Suppose, I am considering a cubic shaped unit cell. There are lots of distortions to this unit cell local level. But, globally I have a sort of an average lattice parameter. So, that is the sort of what you been called irregular distortions at the local level. But, at the larger level, yes, there are distortions. We have already seen this example. So, this is the example of a regular distortion. Suppose, I had a disordered structure Cu Au 1. Then, what will happen that it will be a single lattice parameter structure though it will be a reflection in some sense of the kind of arrangement of the atoms.

But now, since it has got ordered, the symmetry has been lowered right. So, this is now become a tetragonal structure, which is reflected in this t here. So, it is a tetragonal structure. Therefore, when this ordering takes place, the c by a ratio will change. So, this is a more regular kind of a distortion. So, I would not call this a distortion. But what I meant call a dilatation or a contraction in the lattice parameters. So, because the word distortion would mean there is some irregularity to the whole process, which is taking place. Yes, therefore any ordering process will involve distortions. These distortions could be at the local level or at the global level.

So, both these are possible. Now, I have only considered, here for instance, Cu Au 1. It is a simple tetragonal structure. But there are larger periods Cu Au 2. Also for lattices, in the lattice, the periodicity along one the four fold direction increases to large value. So, that is another possibility of ordering in the very same Cu Au system. We are just considering these in a sequence. So, that it gives us a simpler understanding. So, we are going from a simple to complex not because they are any particular way they are ordered. But, simply because for a to increase our understanding, we are going step wise so that we can slowly trying to comprehend more complicated structures.

We have a path way to understanding certain inter metallics and other kind of structures, which have larger and larger unit cells. So far, we have been discussing substitutional solid solutions and their ordering. Similarly, we can also discuss interstitial solid solutions. When I mean a interstitial solid solution, I mean that the alloying element, which I am adding. As I said, there are some time equivalent terms like doping or impurity atoms, which now go and sit in the interstitials formed by the original parent

host lattice or the parent crystal. So, we already and detail, we have already seen the kind of voids which are present in these crystal systems.

Therefore, I have options at least in the simple crystal systems like simple cubic body centered cubic. I know where these atoms can sit. It is however worthwhile to repeat the sentence that there are of course, certain very special cases of atoms like boron, which can competed, which can sit either in the lattice position or sometime in later stages. But here, we will exclusively deal with those kinds of elements, which it sits in the interstitial void positions. We already have seen the kind of voids. For instance, we have seen octahedral and tetrahedral voids in cubic close packed external close packed and body centered cubic crystals.

Now, to for an atom to sit in the interstitial position, we have noticed that the atom has to be sufficiently small in size. So here, I have a comparison of some of the relative sizes of the various voids and also the relative size of the atoms. So, let me look at the smallest atom possible, which is the hydrogen atom. It has radius of approximately 0.46 angstroms. Now, if you go to larger and larger atoms for instance, oxygen is about 0.66 angstrom radius, nitrogen as .71 angstrom radius. So, this is my nitrogen. This is my oxygen. Carbon has a slightly larger radius of about 0.77 angstroms.

Carbon will be an important interstitial alloying element from our point of view because typically that is a very important alloying element in styrene. Boron has a larger radius.. As I pointed out, boron can form interstitial solid solution in some cases, substitutional solid solutions also. In very other cases can also set in both positions. Now, so the first role of something, if it has to form a interstitial solid solution, the atom which for an atom has to be a small in size. So, that is one thing you are seeing. So, let me try to compare these sizes, which I have written down here with a relative size of some of the voids, which we have already considered.

The largest void we saw in the regular structures were the octahedral void in the FCC or the cubic close packed crystal. The next bigger void was the tetrahedral void in the body centered cubic crystal. Then, was the size of the tetrahedral void in the cubic close packed crystal. Finally, the smallest void was the octahedral void in the BCC crystal. We had also noticed that actually the carbon atom sits in this void in the BCC crystal. So, we had noticed that aspect also. So, all these voids, atoms which go and sit in the interstitial

positions are small. There is a sort of general guidance, principle or general rule that if the diameter of the atom is less than about 0.6 times the size of the host atom.

The host atom would for instance be an iron atom a molybdenum atom chromium atom or one of those even an aluminum atom or aluminum ion sitting in the lattice position. Then, we expect extensive solid solubility. When I use the word extensive, I do not mean complete solid solubility. But, extensive that means a large amount of solid solubility. Of course, since this is only a rule. Therefore, often we will find that in many systems, this rule is violated. It is noticed also that the solubility for interstitial atoms is more in transition elements. These transition elements already you know having complete inner shells.

The transition element showing good solubility for these interstitial atoms are iron, titanium, vanadium, zirconium, nickel, tungsten, uranium etcetera. Some of these as you know are very important commercially important elements. One point to be noted is that carbon is especially insoluble in most non transition elements. So, this is something, which is to be noted. Therefore since, it is so insoluble, we could actually use a crucible made of graphite to actually melt some of these non transition elements. This is because then, it will not actually dissolve any carbon.

Now, so to summarize this slide, here we are talking about the solubility of an interstitial element. In other words, a small sized atom in a parent lattice obviously. As you can see that the voids are available or smaller than most of these atoms, we are talking about except perhaps exception of hydrogen. So, most of these interstitial alloying elements are going to cause distortion to the lattice. Therefore, you expect that the solubility is not going to be 100 percent. That means if the number of available voids is going to be much larger, the number of atoms you will be able to put into these parent atoms..

As a general guidance principle, you can note that if the size of the atom is less than about 0.6 times the host atoms size then, large amount of solid solubility can be observed. It is the electronic structure plays a very important role in the solubility of these elements. For instance, carbon is insoluble in transition, practically insoluble in non transition elements. Many of these interstitial elements dissolve very well in the transition elements. So, this is something very important to note now before we leave this topic of interstitial solid solutions.

It is worthwhile to note that later on, we will be talking about interstitial compounds, wherein the portion of proportion of these interstitial elements will be pretty large. We again, we should not confuse interstitial solid solutions with interstitial compounds. So, they are different. In terms of their properties, in terms of their hardness, any one of those aspects. Therefore, they should not be confused with these interstitial solid solutions. The next big topic we are going to take up now is the compound or intermediate structure.

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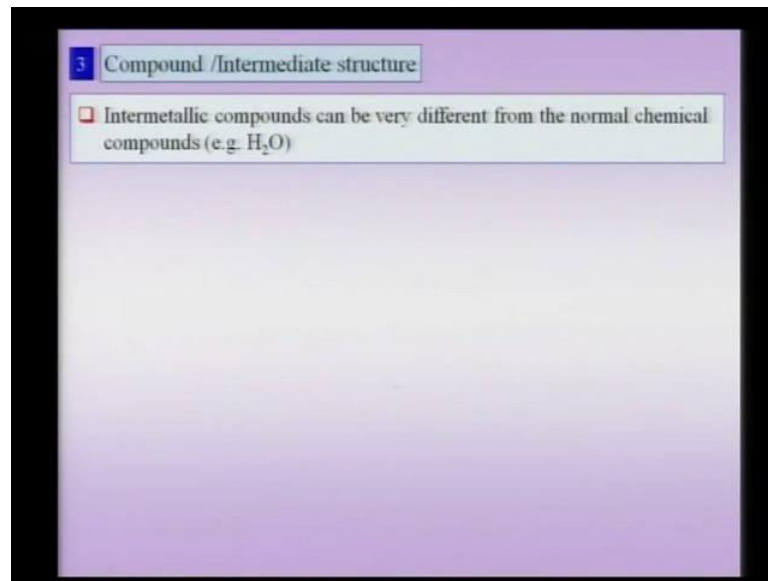
So, let me go back to the slide to revise what are the kinds of structures we are talking about. Why are we talking about these possibilities?
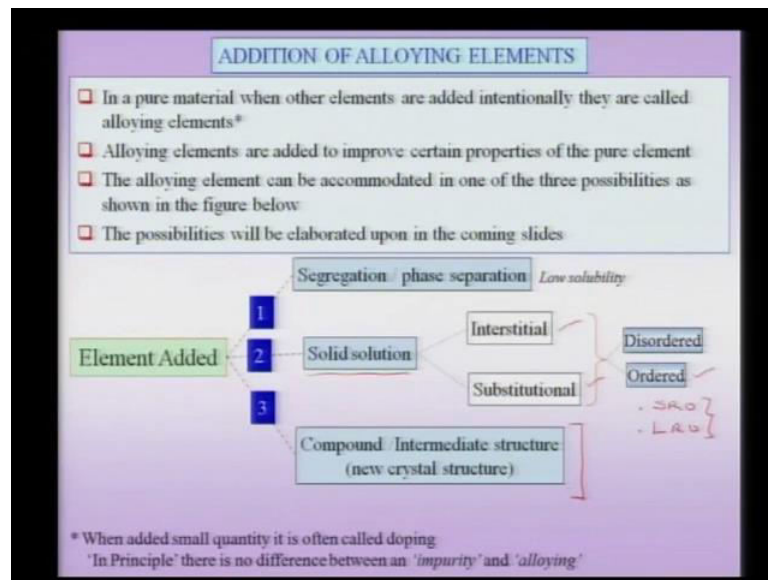
So, let me go back to the original slide where we started of here. We started off by saying, when I add as element to the post lattice; either it segregates. This is not a very interesting case for study too much because it means that it is not going to interact with the parent lattice. The second case, which we have been discussing extensively so far, is the case of the solid solution formation. We have discussed interstitial solid solutions, which is the last slide and also substitutional solid solution. We also have seen very many examples of ordered structures.

In this context of ordering, we have also seen the two important aspects, which is short range ordering versus long range ordering. So, these two are important concepts we came across when we dealt with this concept. Now, we are in a position to proceed to deal with the concept of compound or intermediate structures. Now, this is what you might call an ocean by itself. What we will be taking up here which are merely some examples to illustrate some of the important principles involved in the formation of intermediate compounds and structures.

A more important thing we will try to emphasize here is some of the intermediate compounds. They form inter metallic systems are very different in nature from some of these standard balancing compounds we have been dealing with in chemistry. Like, for instance, normal balancing compounds in chemistry have a very fixed composition. For instance, they, we have take about water. It is H_2O. There is no chance or no flexibility

with respect to the composition. These compounds in order to be dissociated required very high amount of energy.

So, we will see that some of the inter metallic compounds we are dealing with do not actually obey many of the valency rules. There is flexibility in the composition. Therefore, they form a complete class of compounds or intermediate structures all by themselves. They have to be contrasted with respect to the standard valency compounds we deal with in chemistry.

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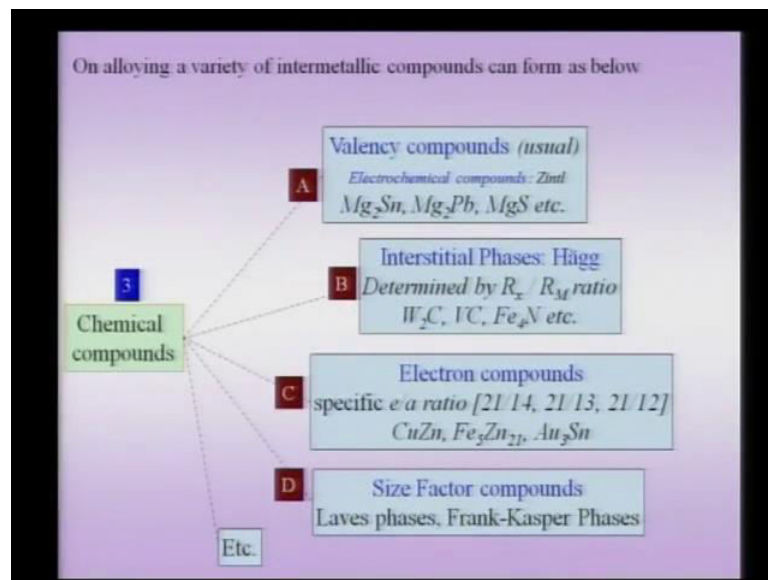
In this slide here, it is not an exhaustive collection of all the chemical compounds possible, all the inter metallic chemicals. When I am talking about inter metallic, I am also including metalloids and other kind of elements. For instance, like nitrogen and carbon, which go into interstitial positions. So, therefore, I am including a slightly larger class and pure metal- metal alloys. But, I am talking about a metal and non metal alloys also in this class. But, even then, this is not an exhaustive list of all the possibilities. The essential crux of the message of this whole slide is that what are the factors which govern deformation of some of these compounds?

As we shall see from these examples that it could be valency, that means the valance electrons play a very important role in the formation of these compounds. It could be size. So, there are lot of compounds, which were in size would play a very important role. So, first is valency. It could be size; many of the examples of why close packed

structures form etcetera; we have rationalized in terms of the size. They are all equal size spheres, which are packed equally. Then, if I were talking about interstitial elements then, obviously again, the different kind of aspect of size comes in which is the radius ratio.

Not only the size of the atom but, also, there is size the atom with respect to the host atom. In the context of electronic contribution, there is a different one other parameter, which is very important. It is the e by a ratio. So, we have the very many type of compounds. The galaxy is very large. But, we were taking a small sampling here to understand some of the concepts. So, the sampling here includes for instance, a valency compounds B interstitial faces. They are sometime called the Hagg phases, C electron compounds, D size factor compounds.

The list is very large. When I am trying to rationalize the formation of many of these compounds, I identify some of the important contributions to the formation of these compounds. This could include some very well known principles like the usual principles of valency or valency coming in or the electron contribution coming in a different from, which is electron per atom ratio. It could be a size factor or it could be a radius ratio explicitly stated or even in size factor compounds. Obviously, if there is a radius ratio involved but, in the case of the interstitial faces, the radius ratio is perhaps the most important determining factor in terms of the compound formation.

So, we will try to go through some of these cases one by one and try to understand some take up some of the examples. Of course, some of the examples are given here; for instance Mg 2 Sn, Mg 2 Pb etcetera. We have seen many more examples here. Try to understand how we rationalize the formation of these compounds. Now, the first thing when you are talking about compounds is that we need to distinguish them from the solid solutions. So, either these could be compounds, wherein the atom size is very large. Therefore, they would themselves form a sub lattice. They could be sub lattice in the sense in the right of the same size; size being comparable to the parent atom. They could be very small and go into the interstitial..

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So, there are compounds of both types available. The important thing is that they, both these type of compound should be differentiated from the solid solutions because the properties of the solid solutions are very different from the compound. Typically, they have different crystals lattice. So, the different, they have a different crystal lattice as compared to these components. Many of these crystal structures or many other chemical compounds have a very complex crystal structures. So, we have seen some examples. But, things could get even more complicated. Each component obviously has a specific location or a sub lattice of its own..

So, this is something which we have already seen. The composition typically can be sort of characterized by a simple formula like A B n where A m and n are small whole number integers. Now, as we shall see in this respect, these intermediate compounds are somewhat different. This m and ns have some sort of variability within them in many other compounds. It is not like every compound would have lot of variability. But, there is some possibility of variation. I have already emphasized the aspect that the properties of the product, which is the compound is very different from that of the component.

So, this is something, which we have already seen. In the sense of this, these compounds having a constant melting point and dissociation temperature, they are very similar to the normal compounds. They are also accompanied by the substantial thermal effect, which is similar to the normal compounds. Typically, they are formed with elements with very

different electronic and crystal structures. In other words, what favors the solid solution formation are in some sense some sort of the rules are sort of opposite.

We cannot take it. Of course, this I just not, this has some sort of a guidance understanding rule kind of thing. You can think of it that if the electronic structure and crystal structure are very similar, you would have a tendency to form solid solutions. If they are very different then, you would have a chance of forming these kinds of chemical compounds, which are of course, I am talking about cell the valency compounds. So, what I mean by this chemical compounds here is the valency compounds. The bonding in inter metallic compound is usually metallic. But, the bonding can change quite a bit on formation of the compound if there is also a possibility that the bonding between a metal and a non metal could also be metallic.

In other words, even though one of the second component in the inter metallic compound is a nonmetal but, still, the properties of the compound which has formed could be metallic. A large number of inter metallic compounds do not obey valency rules or have constant composition. This is something which distinguishes them from the standard chemical compounds we deal with in chemistry. This is has to be kept in mind whenever we are dealing with inter metallic compounds.

So, this is perhaps a very important distinguishing feature, which we always have to keep in mind. So, just to summarize this slide, we always have to remember that the properties and the crystal structure of these intermediate compounds are different from the parent elements from which they are formed. You could of course, have binary ternary or even quaternary compounds though as you go to higher and higher, number of elements, which form compounds the number of examples become rarer.

Other is a number of tabulated examples. The second example I take up here is interstitial phases or which I have sometime called the Hagg phases. Here again, I need to distinguish these interstitial phases or interstitial compounds from the interstitial solid solutions in interstitial solid solutions. Typically, the concentration of say for carbon anion is usually small. But in the case of interstitial phases, the amount of carbon for instance, like for instance one example of an interstitial compound could be Fe 3 C, wherein the amount of carbon is large. Now, transition elements typically form these compounds with the element with small atomic size.

We have seen the example of such kind of elements, which have very small atomic size. About four of them listed here. The formulae for such compounds typically can be like of the form M X where X is the interstitial element. So, it could be M X, M 2 X, M 4 X etcetera. Some of the examples are given here. In each one of these cases, you can see that the smaller sized element is this one. There is a larger sized element, which is this one. So, you have tungsten carbide, vanadium carbide, titanium carbide, niobium carbide. Some of these interstitial phases are extremely hard. As we shall see in the M 2 X class, we have examples like W 2 C. It is a different form of tungsten carbide Mo 2 C, Fe 2 N. In M 4 X class, we have Fe 4 N, Mn 4 N as examples. Clearly, the radius ratio plays a very important role in the formation of these compounds.

So, when I am talking about the radius ratio, I am talking about the radius of the smaller atom R X. So, this is my X here. So, these are all my X atoms with respect to the radius of the metal atom. It is originally occupying my lattice positions. If the as I pointed out before, if R X by R M is less than 0.59, so this is some sort of a number we remembered from before. Then, we typically form. So, there are 2 possibilities if R X by R M is less than 0.59 and R X by R M is larger than 0.59. If R X by R M is less than 0.59 typically, will form simple crystal lattices like this could be the simple kind of cubic or hexagonal.

The non metal occupies specific interstitial size in the cubic or hexagonal crystal in this aspect. Some of these aspects, we have seen before that why they shock by specific interstitial positions. On the other hand, if my R X by R M is very greater than 0.59 that means that if this parent, if this interstitial atom is going to sit in the parent lattice then, it is going to cause large distortion to these lattices. Then, typically you end of forming complex crystal structures. One of the common complex crystal structures is Fe 3 C, which is otherwise called cementite. It is a very important phase, which forms in the iron carbon phase diagram.

So, even though, we are often talking only about the size ratio, we have to note that the valency of the interstitial atom also plays an important role in the formation of these compounds. So, this is an important point to be noted. These two aspects, the electronic structure and the size aspect, which is of course, in some sense coming out from the electronic interactions are simplified versions of our understanding. Overall reason why certain compounds form or certain existence of certain solid solutions and one of these could be playing a dominant role.

Therefore, we often can ignore the other, the role played by the other. But, whenever the influences of both of them are considerable or the effect they play in the contribution towards the formation of a structure. Then, both of them need to be consider in the analysis. So, even though when I am talking about interstitial phases, the dominant factor seems to be this radius ratio. Another is the radius for an atom, which is sitting in the interstices to the ratios of the host atom. But, the role of the valency or the electron, electronic contribution cannot be ignored.

Typically, interstitial phases are variable composition, which is similar to some of the other substitutional or the large atom analogs of this. The chemical formula indicates the

maximum amount of non metal in the structure. So, this is something, which is typically to be noted. Even though for instance, I may indicate one of these chemical formula structures like Mo 2 C here. This is here, my Mo 2 C. Now, the thing to be noted is that that this amount of carbon in this formula in for instance, is the largest maximum amount of carbon, which can be present. You could have a lower amount of carbon in the structure.

So, this aspect is again very characteristic or some of the inter metallic compounds or metal metalloid compounds. It is very different from some of the normal valency compounds we deal with in chemistry. The properties as I mentioned changes drastically with the formation of these compounds. Some of these important properties or some of these compounds, which I listed is that they have a high electrical conductivity. This electrical conductivity is similar to that of a metal. That means that the negative coefficient, that means the conductivity decreases with the increasing temperature as thermal scattering increases.

It has got metallic luster like you would expect for a normal metal. Many of these interstitial phases are very hard. Some of for instance, tungsten carbide as found very important industrial applications in cutting tools. Vanadium carbide is another example of a very hard phase. This vanadium carbide is an important structure from other points of view, which we shall see later. For instance, this comes in the context of what is known as vacancy ordered phases. These carbides have a very high melting point, which goes of course, very well with the hardness we are talking about. There is some covalent character to the bonding in some of these phases.

So, even though we are talking about a metallic luster and a electrical conductivity, which is characteristic of a metal. Then, there could be in some cases as certain covalent character to the bonding. This covalent character would influence many of the properties. So, let me summarize this slide of interstitial phases. These interstitial phases as I said have to be very clearly contrasted with the interstitial solid solutions. You can see from these very many examples that these interstitial phases have a large portion, large proportion of the interstitial element. For instance, in titanium nitride, we have about 50 percent possibility having nitrogen.

Now, again going along with this composition aspect, we have to note that the chemical formula is indicative of the maximum amount of the non metal. Not necessarily, that all the amount of non metal, which is indicated by the formula need to be fulfilled. The common examples of these kind for instance, intra interstitial phases are they have these M X kind of formula, M 2 X kind of formula and many times M 4 X kind of formula. There is also this possibility we have seen here Fe 3 C, which for instance M 3 X kind of formula. The important thing as I mentioned is the size factor ratio. Two possibilities exist.

You get very simple crystal structures like cubic and hexagonal, when the radius ratio is less than 0.5 or less than 0.6. When the radius ratio gets larger than 0.6 then, you can get very complex crystal structures. As I said, even though we are now only constraining mainly the size factor, valency also plays an important role in the formation and in the properties of these compounds. The next possibility as we, let me go back to the table, where we considering this. So, we already considered these valency compounds here. So, this part we have considered.

Now, we also considered interstitial phases. Now, let us take up these electron compounds. Now, in electron compounds, as the name suggests, it is not the size factor which is the dominant factor in the formation of these compounds. It requires a special attention for us to understand why these compounds form and what are the e by a ratios at which they form.

These compounds typically form in mono vital metals, transition metals like iron, cobalt and manganese and some other metals also with other kind of valencies. So, you can see some prominent examples here; for instance, in this table here like for instance, copper zinc is a very prominent example. It forms more than one kind of an electron compound. Now, the more frequent ones, which from electron compounds are alloying elements; are the elements, we have present are copper silver and gold. Now, the important characteristic of these electron compounds is the e by a ratio in these compounds. That means all the compounds, which form is stabilized by a certain e by a ratio. Of course, the chemical formula itself will only tell you the number of atoms and the electrons have to be counted from the valency of these atoms.

So, what I find out that if there are certain elements, certain compounds, which are being stabilized here like these, very simple ratio ones like Cu 3 Al, Ni Al, Cu 5 Cd or Co 5 is there in 21. Of course, little more complicated in chemical formula than some other simpler ones. Now, all these compounds have been stabilized for a specific value of electron to atom ratio. Now, what are these electron to atom ratios? These electron to atom ratio; there are three possibilities. One is 21 by 14. The other one is 21 by 13. The other one is 21 by 12. Of course, I could reduce these numbers to smaller fractions like 21 by 14 is 3 by 2, which is 1.5. 21 by 13 is of course, cannot be reduced further. But, it is approximately equal to 1.62. 21 by 12 is 1.75 or which is 7 by 4.

So, it so happens that in these electron compounds, when the e by a ratio is the specific ratio then, you find that certain compounds are stabilized. Now, why do I divide this into three different types based on these e by a ratios? The reason is that when I have a 21 to 14 ratio, which is 3 by 2 ratio, then you typically find that the crystal structure forms is BCC complex cubic or hexagonal. Typically, these compounds are called beta compounds. Now, how do I calculate the e by a ratio in these cases? Now, let me take the example of copper zinc. Now, zinc gives as a valency of 2. Copper has a valency of 1. Therefore, there are total number of electrons in the system. So, now I am considering the example of copper zinc.

So, zinc as a valency of 2. So, this is my valency. Copper has a valency of 1. So, total number of electrons as you can see from the chemical formula, total number of atoms is 1 plus 1; 2. Therefore, my e by a ratio is the number of electrons divided by the number of atoms, which is 3 by 2, which is what is the number is stabilizing my 21 by 14 or 3 by 2. These kind of structures are typically BCC complex cubic or hexagonal. All these are called beta compounds. Now, when I have a 21 by 13 ratio, which is 1.62. Then, the crystal structure is typically more complex. These compounds are called gamma compounds.

So, these are my gamma compounds. Similarly, whenever Ii have a ratio of 7 by 4 or 1.75 then, these structures, which form are called epsilon phases. The crystal structure is hexagonal. There are these examples to these. Now, let me try to make a calculation for instance, this Cu 5 Zn 8. So, I have the next formula, which is I have Cu 5 Zn 8. So, number of atoms is 8 plus 5, which is 13 for this compound, a number of electrons because this is valency 2.

There is 16 plus 5; 21 electrons in this compound. So, I have my ratio as 21 by 13. So, this is my second case. So, after this first case, I have my second case, where in I have 21 by 13 electron by atom ratio. That stabilizes, that means Cu 5 is typically has a very complex crystal structure. Now, of course, I could make a calculation for some of these other cases. For instance, in this case Cu 3 Al; aluminum would give 3 electrons. Copper would give 3. There are 6 electrons and there are 4 atoms, which again gives me my 6 by 4, which is 3 by 2.

So, suppose I am talking about Cu Zn 3. So, the number of atoms in this unit cell is 4. The number of electrons is 3 into 2, 6 plus 1; 7. So, I have my e by a ratio as 7 by 4. Since, this e by a ratio is 7 by 4, I know that this will be having recursive structure, which is hexagonal. It comes from this specific e by a ratio. Again, as before many of these compounds can form over larger composition ranges that means that these are even though these are called compounds. They are not linear compounds. There is variability in the composition. These compounds, some of them can actually get disordered on heating, which means that they are actually showing an order disorder transformation as well.

So, just to summarize this slide which is highlighting a very important class of compounds, which are the electron compounds. In some context, wherein wherever e by a ratio is the mechanism responsible for stabilization of the crystal structure then, I sometimes refer these are referred to also as Hume Rothery compounds. All now, there are three important classes of these electron compounds; those which are stabilized with e by a ratio as 21 by 14, those which is stabilized by e by a ratio of 21by 13 and 21 by 12..

The crystal structure is correspondingly for these three types are BCC complex, cubic or hexagonal. In the typical 21 by 12, you have a very complex crystal structure. In external crystals, are the ones which form with 21 by 12. As before as we noted, some of the other compound before their composition can be variable. This can also show ordered, disordered transformations.

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Now, in this class, when you go back to the slide we were describing, in this class of chemical compounds, we are talking about. We now take up the fourth class, which is the size factor compound. There are of course, many possibilities. Here, we will take up two important classes, which are the laves phases and the Frank Kasper phases. These laves phases and as we shall see, they are an important class of compounds. There are more than 1400 members, which are known in this class. So, it is a large class of compounds, which come on to the laves class. They are all size factor compounds having a formula of A B 2.

So, here, we are describing actually a very large class of compounds. These compounds are called tetrahedrally close packed compound structures. We will take up some example to understand these tetrahedrally close packed structures. For an ideal, e by a ratio, they have an ideal C by ratio of the atoms. Suppose, I am talking about an A B 2 kind of compound. Then, you have an r A by r B, which is root of 3 by 2. This is approximately 1.225, even when the r A by r B ratio is sometimes not around, is the exactly, not this ideal value or around this ideal value.

Then, you would still form a tetrahedrally close packed structure, which has this kind of a formula, which is A B 2. Now, the important crystal structures which form under this laves class are typically designated according to the strukturbericht notation as the A C 15. Let we start with C 14, C 15 and C 36. So, there are three important classes of laves

phases. The C 14 class over the strukturbericht notation, the C 15 class according to the strukturbericht notation and the C 36 class. There are typical members, which are called what you might call the representative members. They are for the C 14 class. It is a Mg Cu 2 structure, which is a called FCC lattice.

For the C 15 class, it is Mg Zn 2 which is hexagonal. There is a more complicated having more number of atoms. This is Mg Ni 2, which is also form the hexagonal class. So, the important thing to be noted is that there are many ternary and multinary representatives laves phases with excess of A and B elements. Also, some ternary laves phases are known in system with no corresponding binary laves phases. So, when I am talking about ternary laves phase, I mean that some of these elements A and B are being replaced in the structure with some third element C.

Another important thing again, as we have seen before, even though we start off by saying that the important influencing factor is usually either an electron to atom ratio or a size ratio or a size factor. Then, obviously, we cannot ignore the other aspect, which is the electronic structure of the material. So, it is also seen in many cases especially, in this ternary laves phases that the e by a ratio plays an important role in the formation of these compound and stabilization of these compounds. So, let me summarize this slide before we take up the examples, which of course, we will see a few that these laves phases represent a large class of structures.

Typically, they have a formula A B 2; though we could have ternary variants of these also. When I am talking about ternary variants of these, we should understand that in many of these cases, the electron by atom ratio is also playing an important role in the stabilization of those ternary variants. The ideals r A by r b ratio around which these compounds form is about 1.2 to 5. These are called the tetrahedral close packed structures, which is some sense a variant of the close packed structures. We have been considering, wherein we have had one element, which was there and even when the single element case. We have already seen that if you talk about the low polyhedra, which form between two layers, it is the tetrahedron. The 3 important representative members of this class, two of them belonging to the hexagonal class and one belonging to the cubic class are Mg Cu 2, Mg Zn 2 and Mg Ni 2. It is a common factor between all these representatives, being Mg.

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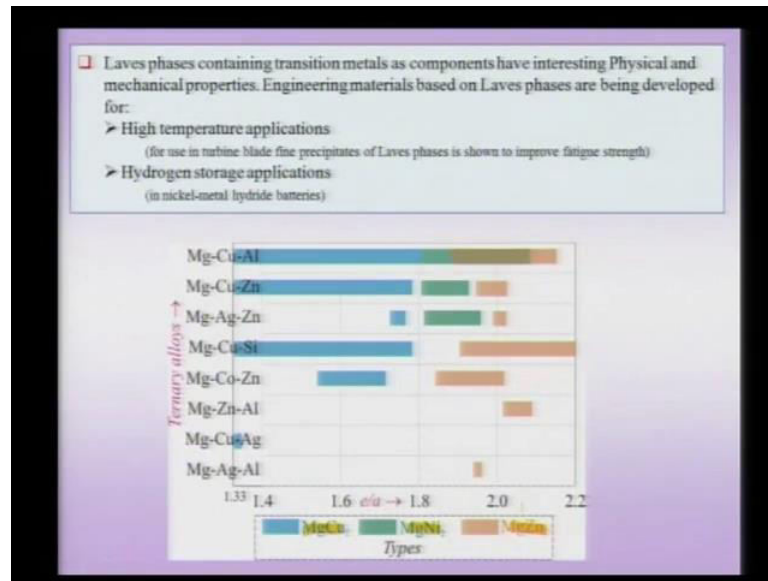
The laves phases containing transition elements as components have a interesting physical and mechanical properties. Slowly, a lot of engineering applications for these laves phases are being developed. Some of these applications are for high temperature applications like for instance, in turbine blade, fine precipitates of laves phases have been shown to improve fatigue strength. In hydrogen storage applications also like in nickel metal hydride batteries, laves phases are slowly finding applications. The diagram below shows the electron to atom ratio effect in the formation of some of these 3 type typical structures.

So, we already have seen the 3 important structures, the Mg Cu 2, the Mg Ni 2 and the Mg Zn 2 structures. It is seen here depending on the e by a ratio in some of the systems. For instance, let me take an example the magnesium copper aluminum system even. Let me take the simpler example, the magnesium copper zinc system, and the magnesium copper zinc system. For an e by a value up to about 1.8, it is seen that you form an Mg Cu 2 structure. Between a value 1.8 and 1.9, approximately from the Mg Ni 2 structure.

A value around centered around 2, you would try to you form the Mg Zn 2 structure. In other words, in this ternary laves phases, the electron to atom ratio has an important role to play in the formation and stabilization of these structures. So, let me take up examples of the C 15 structure and the C 14 structure to understand the laves phases and how these structures look.
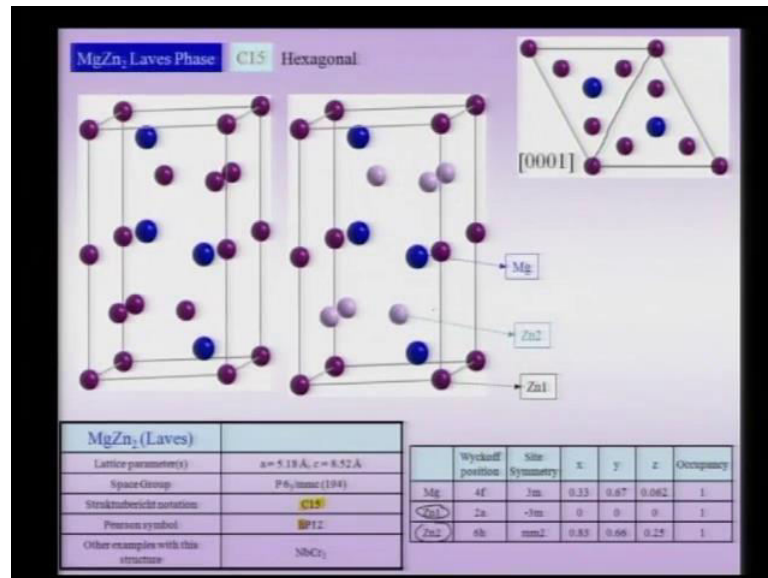
As we are considering these structures, we will also, as I said our goal is to fold here not only to understand what the criteria these compounds form but, also to slow introduce our self to more complex structures and more examples of these. What you might call hexagonal and cubic and other kind of phases which form? So, this is here M g Zn 2 laves phase, which is as a Struktur Bericht notation, which is C 15 as a structure like this in the Pearson symbol. It has got a symbol H P 12. That means it is hexagonal. It is primitive. As we know, there is only one lattice in hexagonal, which is primitive. There are 12 atoms in the unit cell even though it is hexagonal. Now, it has got the same symmetry as that of the normal hexagonal close packed crystal, which is P 63 by MMC.

It is still a unit cell with a larger lattice parameter. It is having more number of atoms. It has got 12 atoms unlike the normal hexagonal close packed crystal. It has only 2 atoms in the unit cell. So, this is an higher order or a more complicated version of an hexagonal crystal as compared to the hexagonal close packed crystal. Now, the ones, the magnesium atom is the one which is in blue. The zinc atoms are in the violet color, the dark violet and the light violet color or both here are in a dark violet color. So, you can see that this is the unit cell. If you look at the 0 0 0 1 projection, this is my 0 0 0 1 projection of the unit cell.

So, you can see in the projection that these blue atoms are located at the centroids of the. So, if you draw a triangle, the half triangle. So, these zinc or magnesium atoms are

located at the centroid at various positions; of course, not at the base but, some other various positions. You look at the zinc atom of course. One is located at the 0 0 0 position. But, you can also see that they are located at a C position from the 0.062 magnesium atom. Now, so, this is slightly above the Bessel plane. Now, the best way to understand these structures is looking at why I call them the tetrahedrally close packed structure.

How I can understand them by some of the usual rules of packing which we have seen before. Even though these unit cells are pretty instructive, you can see that even from these unit cells that there is this triangle of atoms within which I can visualize this. Now, my blue magnesium atom here but, the more interest instructive way look at these; is by looking at these kinds of diagrams.

But, before I go to that again, you should notice that if you look at the Wyckoff symbols. There are two kinds of zinc atoms. Here, at the bottom here, there is zinc 1 and there is zinc 2. So, zinc 1 is the one, which is located at the vertices here. The zinc 2 is the one, which is located at C equal to 0.25. That means it is one fourth the distance in C direction. So, this plane is one fourth pair.

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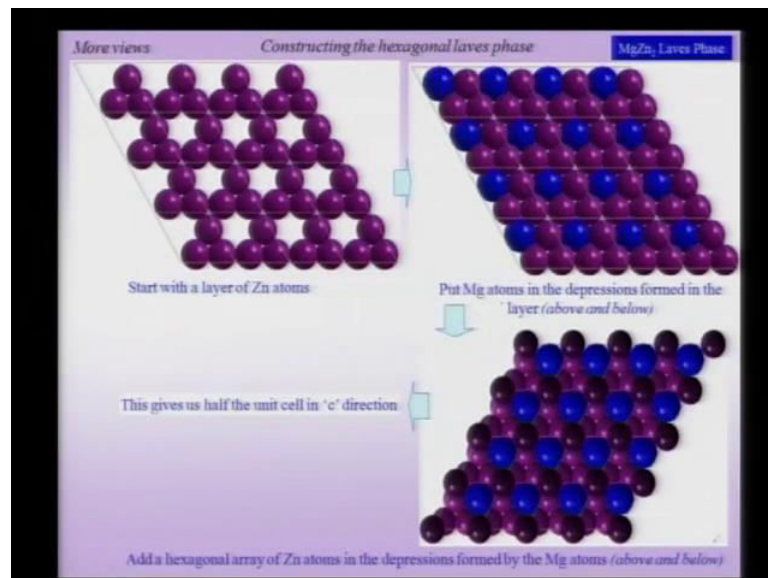
So, how do I understand the formation of these tetrahedrally close packed structures? I can start with a hexagonal array of zinc atoms. As you can see in this hexagonal array, I have not drawn taken my central zinc atom. That is not there. But I can get a hexagonal

net of atoms as shown here. So, this is somewhat related to the cargo maniac, which many people must have heard. So, you can see that there is a hexagon here. There is a triangle here. So, this is my hexagonal array with these triangular networks in between.

Now, what I do, I starting with this kind of a net of zinc atoms. I put my magnesium atoms and where do I put the magnesium atoms? The obvious choice is these places zinc being the smaller atom; I form the net first of the zinc atoms. Magnesium is larger atom, which I place this depression formed by these array of zinc atoms. Of course, I have two positions, in which I put these magnesium atoms. I put them on both those positions, that is one above this layer and one below the layer. So, we go to the diagram above. You can see that if you have a positions of the zinc atom for instance here, then, I can put magnesium atoms one above. I can put one below also, which is what I do. I form, put them in the depressions.

Now, what I do further is that to make the next layer that means I have already, I have constructed three layers. One layer of zinc atoms is in the net here on the left hand side picture. Then, I put 1 magnesium above the net. Of course, only one of those positions, I have seen for instance and 1 array of magnesium atoms below the layer. So, I got totally A 3 layers. But, one of those magnesium position layers only has shown here. Then, to construct the next layer, I can put my second layer of zinc atoms. So, there is only already one layer of zinc atoms.

The second layer of zinc atoms at a depression form by these original, these two layers. Let us suppose, I am looking at the layer from the top. That means, I am inverting, in which highlighted so, looking at this diagram. Suppose, I am having these magnesium atoms here; I invert my layer that means, I look from the other size. Then, I can see this magnesium atom, sitting like this here. What I do is that now, I have a depression form by these magnesium atoms. The previous layer of zinc atoms and I put zinc atoms in these new positions. So, these are for instance, let me choose a different color for showing these atoms.

So, I can see that these are my layers of zinc atoms. So, I am completing this procedure by putting of course, starting with one layer of zinc atoms. Then, I put the two layers of magnesium atoms. Then, I can put of course, as I did here, another layer of zinc atoms. Of course, now, correspondingly at other side also of the layers, I can put other layer of

zinc atoms. I would get half the unit cell along the C direction. So, half the unit cell, they consist of the zinc layer, the magnesium layer and the other zinc layer. Of course, I can proceed in both directions to complete the structure.

So, thus, I can see. I am following some of the principles, which I used when I have formed the single element close packed construction. That means, I started the array of atoms, a layer of atoms. I locate my depressions in that layer and start putting the next layer. This is what I am doing here. Only thing, the starting configuration is somewhat different from the starting configuration, which you normally see in many of the other. In the normal close packed crystals, so, these are called the tetrahedrally close packed crystals. Some other principles are as before. We can understand these structures by starting with layers of atoms.

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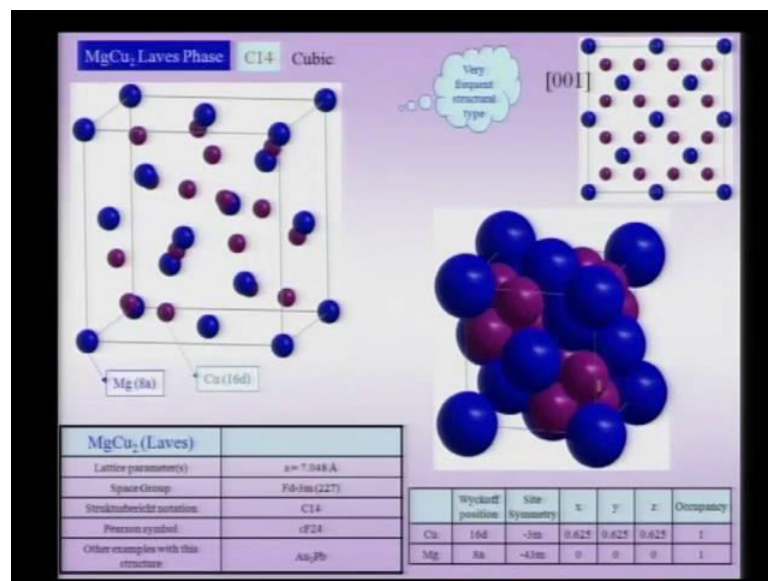
Now, the next structure we consider is the Cu C14 laves phase, which is tablified by the formula Mg Cu 2. This is again a very frequent structural type laves phase themselves are splendorous in number. This is another frequent crystal structure type, this structure unlike the Mg Zn 2, which is got hexagonal symmetry. Here, you can see, this is a hexagonal kind of symmetry. These crystals have cubic symmetry. Let us try to understand this crystal structure, which is not very difficult to understand. So, they have this phase group F d 3 bar m.

This d here tells me that this is a diamond cubic structure. The Pearson's symbol tells me it is cubic phase centered. There are 24 atoms in their unit cell. Of course, I can make a counting of these 24 atoms. One way to do it is looking at the Wyckoff position. There are 16 of those are copper and 8 of them are magnesium. So, the 8 magnesium atoms of course, I can count very easily because a there are all the in the face centering position, who contribute 4 in addition.

There are these 4, which are located within the unit cell. It gives me, which are a tetrahedron themselves because that is why they are as you know in diamond cubic structures. You have this kind of symmetry. Therefore, there are 4 of them, making a total of 8 atoms of magnesium within the unit cell. There are 16 copper atoms, which also I can go about counting. I will get 16 copper atoms in the unit cell. Now, how do I understand the structure?

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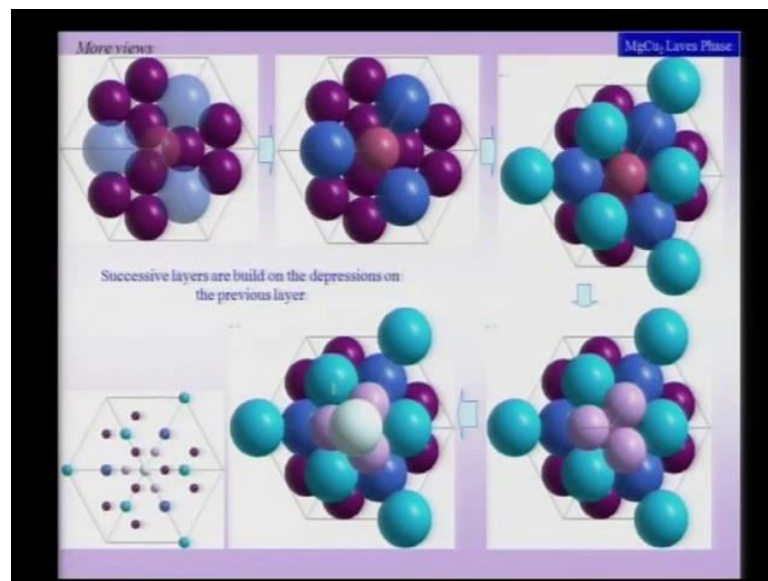
So, let me get to some of my, as I said, some these are all tetrahedrally closed packed structures. So, what I do as before? I start with the net of these atoms. In this case, of course, this is my, the blue is my magnesium atom. The other violet color is my copper atom. So, I start with the copper atoms, which are located in the form of this original net. Of course, I have shown only a part of the net in this diagram. Now, I am looking along the 1, 1, 1 direction of the cube. So, I have to note that this is my one direction of the

cubic crystal structure. This is not obviously a simple cubic structure. But this is a phase centered cubic and the precise kind of structure it is a diamond cubic structure.

So now, I have this layer and within this interstitials as before, I put my magnesium atom. So, this is, let me go back here. So, these are my magnesium atoms. I put my magnesium atoms in the voids from or the depressions formed by this layer of copper atoms. Then, additionally, I put another copper atom here in the void form by these magnesium atoms and the void of the previous copper atoms. So, I get a second layer, which is like this.

Then, I can make higher layers by putting these. This light blue and dark blue both refer to the magnesium atoms, which are in the unit cell here. The one which is the larger atom so, the magnesium atom is the larger atom, the smaller atom is the violet copper atom. So, I put more of these magnesium atoms. Again, so, I have a for instance the magnesium atom here. I have a depression here. So, I can put it in this depression. So, I form the third layer. This third layer now consists, if you look at this, if this layer consists of these blue, then you would note that they them self are a hexagonal array, but of course, not touching each other. Then further, I can make another layer above that by putting these copper atoms, which are the smaller atoms. Three of them in the gap formed between these three. So, I take this gap formed by these three. I put 3 copper atoms there.

And so forth I can proceed in that gap formed between these 3 copper atoms. I can put a magnesium atom; so all these blues there dark blue. This is somewhat fluorescent blue and the very light blue. All of them are magnesium atoms, which are the larger atoms, the copper atoms. Again, I have shown in light violet or dark violet. There are two colors we have used. We can put more of these. Finally, I can put a magnesium layer. So, I can go on making these kinds of close packed structures, which are tetrahedrally closed packed.

As you can see now, you can identify these tetrahedral very easily, for instance these 4 atoms. Let me mark them with crosses. This one at the top, these four form a tetrahedron. Right. Clearly, they form a tetrahedron. So, at each layer, you can identify this tetrahedral and who these structures propagate into filling complete space. The important thing of course, we note here is, that even though we are starting with layers, which are

hexagonal. We are and the unit with cubic symmetry in this case. So, we look and projection. So, if I note that in my color coding, it means I have an understanding of the color coding that the lower most layers are the violet colors. The next higher layers are light violet etcetera.

Then, I can note them in projection like this. So, just to summarize these two laves phases, we have seen so, for three important classes of laves phases. Mg Zn 2, Mg Ni 2 and Mg Cu 2, we have taken two examples to understand the structures that how they are tertahedrally closed packed; the Mg Zn 2, which is hexagonal and the Mg Cu 2, which is cubic. We have tried to understand these structures by starting with layers, putting more and more atoms and above and below layers to form the entire structure. So, these are two important laves structures and the next topic, we take up are Frank Kasper phases.