Phase Diagrams in Material Science Engineering
Prof. Krishanu Biswas
Department of Material Science and Engineering
Indian Institute of Technology, Kanpur

Lecture – 17
Phase Diagram of Binary Peritectic System with Intermediate Phases

So, today we are going to discuss on intermediate phases and many of these intermediate phases forms in the peritectic phase diagrams. This is the reason we need to discuss about this phases here itself. There are few intermediate phases, which forms by the (Refer Time: 00:32) reactions, but they are very less and not very useful. All the useful and industrially important materials are intermediate phases, normally comes from the peritectic reactions and that is the reason actually, I want to discuss it here.

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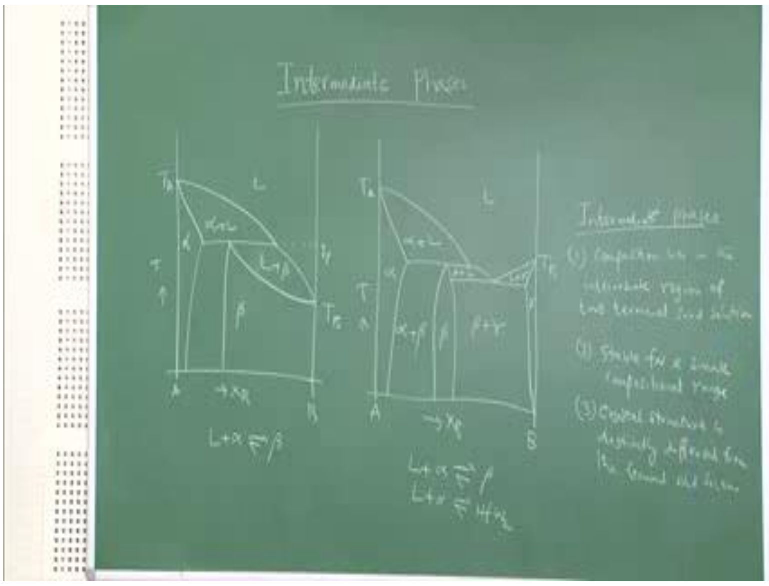

But let me just first draw the two peritectic phase diagram, the one, which I have already shown you and the new one also. So, first let me draw the one which I have shown you for the last one lecture. So, this is the classical peritectic phase diagram with, with the peritectic reaction. Say, this is the liquid, let me first draw the melting temperatures of A and B, liquid alpha, beta and this is alpha plus liquid, this is beta, liquid plus beta, right, correct. So, this has a peritectic reaction at the peri temperature T p, but I told you, that most of the peritectic reactions are followed by eutectic reaction. So, and this is where the intermediate phases forms.

So, let me again draw the modification of this diagram or little different from this. So, first is again remains same, then you have this and there is a separate. So, this is what I am trying to say, so the melting temperature of A, melting temperature of B, liquid alpha, this is beta, therefore, this is liquid plus alpha, alpha plus beta and there is a new phase, gamma, correct. So, this phase forms by eutectic reaction from the liquid. So, therefore, this will be beta plus liquid, this is liquid plus gamma.

Now, I am talking about this phase, which is formed here, beta, which is distinctly different from this. You can see your beta is, composition is only sitting at the center of the composition axis X-B almost, and it has a small span, it is not exactly a line, it is a small span of composition in which it is (Refer Time: 03:15) and this normally has a different crystal structure. So such a kind of phases are called intermediate phase.

The reason it is called intermediate phase is because of this. We know, that there are two solid solutions at the end, at the terminal positions of A and B respectively, one is alpha, which is a (Refer Time: 03:36) solid solution, other one is gamma, which is peric solid solution. Now, this phase comes in between of this composition or intermediate compositions of these two solid solutions. The beta comes intermediate compositions of alpha and gamma and that is why, this is called intermediate phase and because it is, does not have this fixed stoichiometric composition like sodium chloride, potassium chloride, any other phases, it is called intermediate phase.

So, intermediate phase means, its compositions lies intermediate of two solid solutions at the ends. So, first is the composition, composition lies in the intermediate region of two terminal solid solutions. That is the first thing you will see for this kind of phases and this is very common which I will show you in quick, after some time how this phases will appear in the phase diagram. So, this is the first condition to be satisfied for the intermediate phase.

Second condition to be satisfied is that this phase is stable for a small compositional range. What I mean to say is, this is not a compound exactly. If it is a compound, then it will have a fixed composition, but it is not. It has a range of composition in which it is stable. It may be 2 percent, it may be 1 percent, it may be 3 percent, does not matter, but it has.

Third important criterion to be satisfied by these kinds of phases is that the crystal structure of this, crystal structure of this phase is distinctly different on the terminal solid solution, on the terminal solid solution and therefore, they are distinctly different phases. They are not same as either of these two terminal solutions, so they are distinctly different phases. So, you have already got an idea that such a kind of phases exist in the peritectic phase diagram.

As you see here, it forms a peritectic reaction. In fact, this phase diagram I have already shown you at the beginning, that is, for the iron-carbon phase, iron terminal phase diagram in which there is a phase called epsilon, which forms out of the peritectic reaction between alpha and liquid. So, in this case, beta is a solid solution, which has extend from this to this, but in this case beta is an intermediate phase, it is not a solid solution. That is a difference you must make out from this diagram. Here, beta forms by this reaction, here also beta forms by this reaction, same reaction, but things are different. One example of this is in the Hotmium constant phase diagram. There is a phase called HfW 2 forms as a, as a reaction, peritectic reaction. So, there are many hosts of phases.

Now, with this brief introduction I have given you, let me just show you few phase diagram where such a kind of phases exist and then, we will discuss further. So, let me just take you through the phase diagrams.

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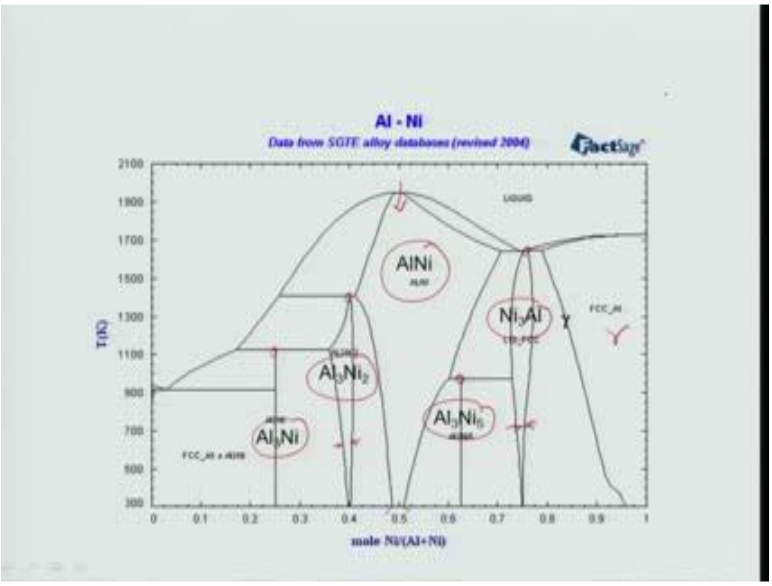

So, which will come alone and here it is. This is the 1st phase diagram; I am showing you aluminum-nickel. You can see here, I have written many phases like, Al 3 Ni, Al 3 Ni 2, Al 3 Ni 5 and Ni 3 Al, all of these phases form by peritectic reaction all. But you see, Al 3 Ni is a line, has a line like this, it is a line compound. Al 3 Ni 5 also is a line compound. On the other, Al 3 Ni 2 and Ni 3 Al has a stoichiometric has a compositional range in which it is stable, it is not only a line, but there is a domain range of composition is stable. So, therefore these phases are called intermediate phases because their composition lies in between the solid solutions of nickel and aluminum.

There is another phase called AlNi here with composition AlNi, which has a large compositional stability range. It is not forming by peritectic reaction, by a different one, it is called congruent solidification or congruent melting, melted compounds entirely formed from the liquid, but all of them form by peritectic reaction. Here, this is the peritectic reaction, there is a peritectic reaction, there is a peritectic reaction and there is a peritectic reaction there.

Now, this is a classic phase diagram, but you know all of these are useful material; most important one is Ni 3 Al, which is used in the real applications. All the, the turbine blades, which is used in the steam generators or even the jet engines, they are made of these alloy Ni 3 Al precipitates, gamma gamma 1 precipitate, you might have heard about it. So, gamma is this FCC solid solution of, aluminum, nickel and gamma prime is the Ni 3 Al precipitate. So, this is the first example (Refer Time: 09:46) by these phase diagrams, all are available online on the SGTE website or FactSage website. So, you do not need to look into the book, they are available free.

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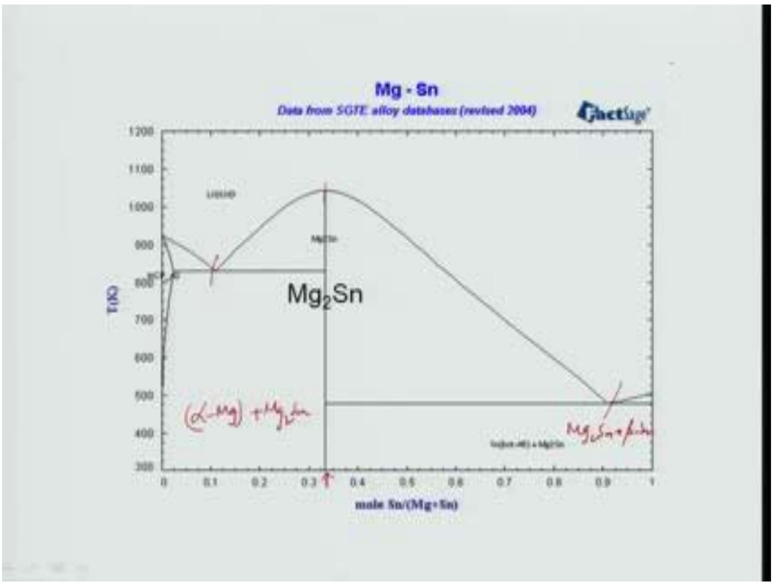

Now, let us know, what, there is another compound, here I am showing you for Mg-Tin system phase diagram. If you see here, there are two eutectic reactions in Mg-Tin system, eutectic I have already discussed and in between there is a compound Mg 2 Sn as a line, it is a fixed stoichiometric compositions. So, therefore, there are many intermediate phases where these stoichiometric compositions are maintained, but as I told you in the very beginning that it is not necessary the condition to be satisfied by the intermediate phases. They can have compositional domain ranges, but examples do exist where the composition is fixed and then, there is a line in the phase diagram.

So, whenever you see a line, that means, there is a fixed stoichiometric composition for the phase existing, so there Mg 2 Sn is, forms at a fixed compositions. It has a eutectic reaction between the solid solutions of pure Mg, pure Mg is alpha, Mg plus Mg 2 Sn. On the other hand, here you can see it is Mg 2 Sn plus the tin phase. So, Mg 2 Sn plus beta tin is a eutectic reaction, very simple phase diagrams, only difference is that there is an intermediate phase at the center, almost 33 percentage of tin.

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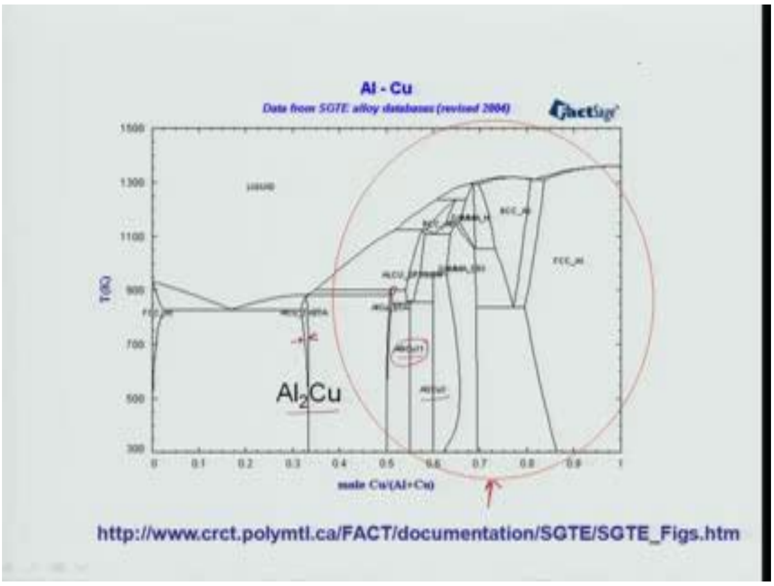

Now, for aluminum-copper there are many, many, many, many phases, I cannot discuss even that. So, region I marked like magenta colour circle, there are many, let us not discuss. Starting on is Al 2 Cu and it has, higher temperature it has a slightly larger compositional stability zone, but lower temperature it has fixed compositions. Then, you have Al 9 Cu 11, Al 2 Cu 3. There are many others phases, which exist with a, with a compositional range and some of them AlCu, AlCu, AlCu forms by peritectic reaction, even Al 9 Cu 11, it forms not by some other reactions, but on the other hand Al 2 Cu 3 is formed by peritectic reaction. So, most of the intermediate phases forms by peritectic reactions.

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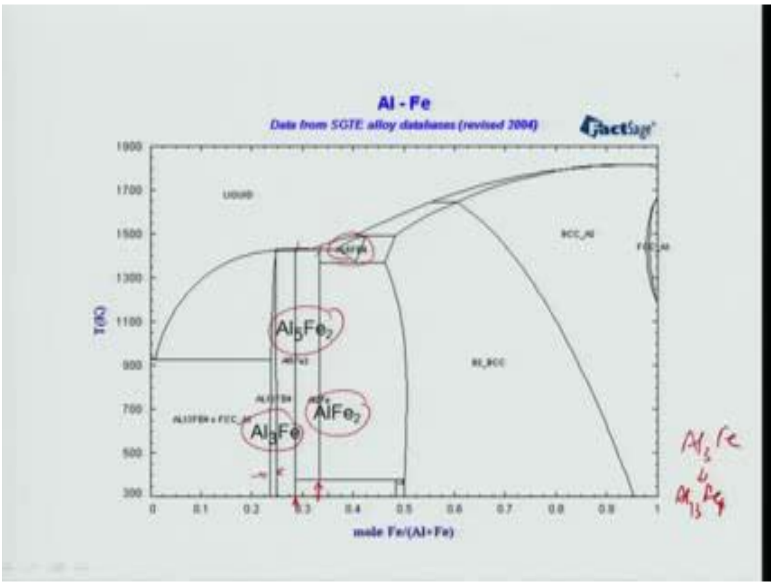

Now, another important phase diagram where this intermediate compounds exist in large or in several ones existing, aluminum-iron, this is what i am saying. You can see, there is Al 3 Fe, Al 5 Fe 2, AlFe 2, present and there is another one Al 5 Fe 4 at the top, correct. So, all of these are actually intermediate phase and this one, this one also, this one, all of these three or even this one, all of them, it should, here are forming by peritectic reactions. So, you have to simply look into their phase diagram database or data to see what is the, which phase it reacts with liquid and form this peritectic reaction. Sometime Al 3, Al 3 Fe is written as Al 13 Fe 4 because of compositional deviations, but you can see Al 3 Fe has a compositional range. On the other hand, the other two has no compositional range, usually it is stable, but it is stable only for a fixed composition, that is, Al 3 Fe.

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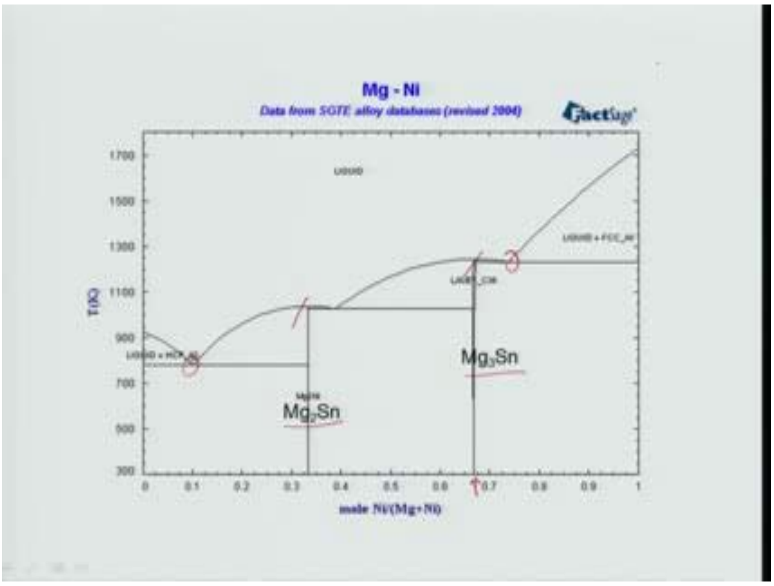

Now, let us look at, this is another very classic phase diagrams, Mg-Ni. Mg-Ni has two intermediate phases, Mg 2 Sn for a steam composition of 33 percent and Mg 3 Sn, tin concentrations of about 66 percentage, 66.66 percentage of tin here and these are called Laves phases, which we will discuss later, what is Laves and who discovered and how, what are the characteristics of that. But you know, both of these three phases has eutectic on the two ends, correct, but these also forms by peritectic reaction, this also forms by peritectic reaction. Now, this also forms, this forms congruently from, directly from the liquid, but this forms from peritectic reaction Mg 2 Sn.

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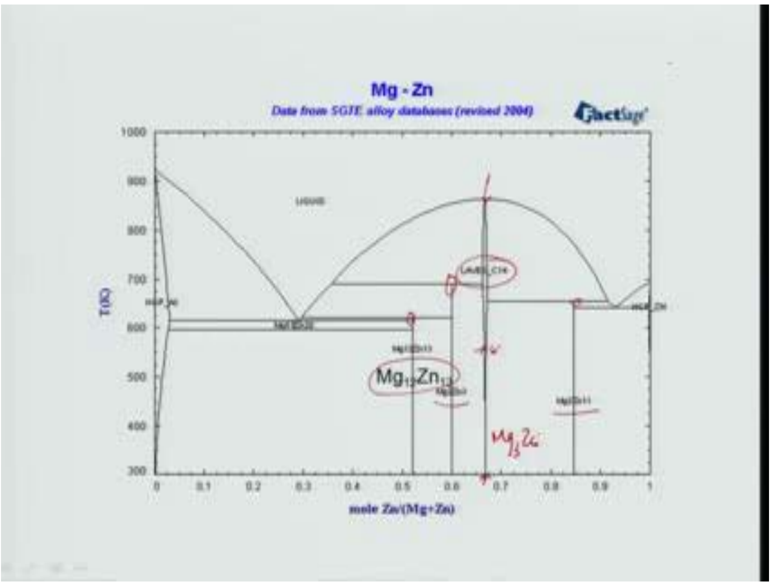

In this diagram, again complex phase diagram, but one can see, there are several phases Mg 12 Zn 3, Mg 2 Zn 3, Mg 2 Zn 11, this definitely form by peritectic reaction, this definitely forms by peritectic reaction, this one also, all of them. And there is another phase at the center, which does not form by peritectic reaction, but by congruent melting or congruent solidification is this is laves (Refer Time: 14:33) phase, which has a composition of about 66 percent zinc and rest of tin. So, it will be Mg 3, Mg 3, what, Mg 3, Mg 3 Zn, this composition, it will have Laves phase.

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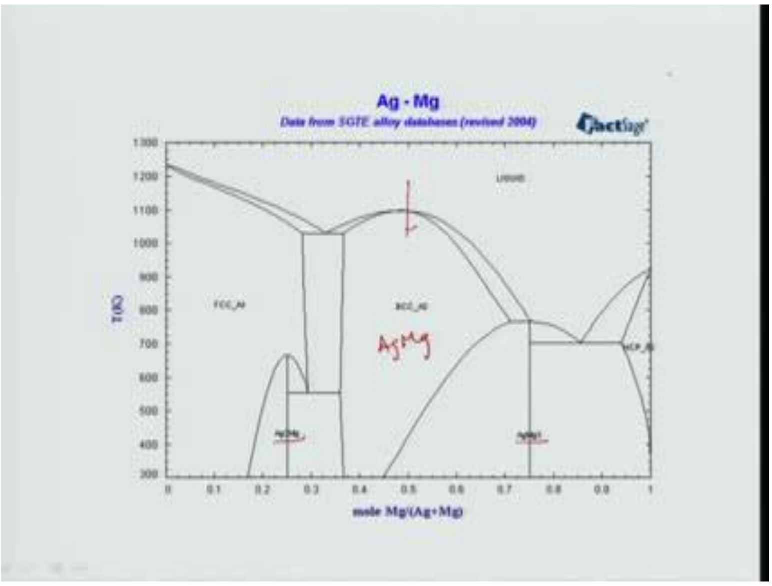

So, you can clearly, then there is, yeah there are others, like silver-magnesium, most of them are actually magnesium, Ag 3 Mg, AgMg 3, there are 2 and AgMg at the center, but these two Ag 3 Mg and AgMg 3, they are, I know, almost like a line, but AgMg has a large composition domain, but AgMg does not form by peritectic reaction, it comes by some other thing like (Refer Time: 15:16) solidification, which we will discuss later.

Silver-copper I have shown you now. So, therefore all these phase diagrams I showed you, I will again show you one more time just to, flashing you, to make you believe, that these are actually real phase diagram and these phases exist in the real phase diagram database. So, thus, it is important for us to understand them.

So, now, with giving this examples of intermediate phases let me just tell you, that we can classify them because you are (Refer Time: 15:49) many phases and compositions we can classify them as three types and that is what I am going to write you on the board, and this is very important lesson you should remember, you should not forget. This is very important because these are the data not available in many books which I am going to give you from this particular sheet, which I have taken down from the textbook.

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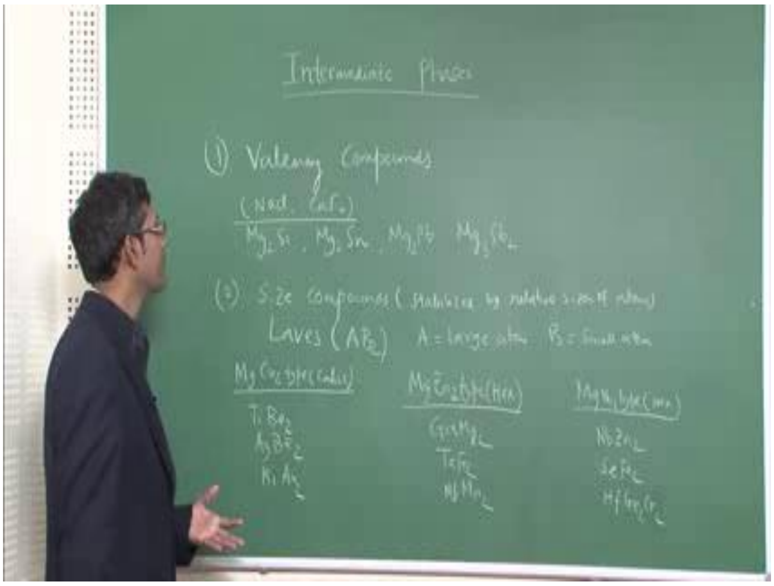

So, there are three types of intermediate phases classically, the first one is known as valency type. First one is known as valency type or valency compound they are called because they follow typical valencery. What is that? If you consider sodium and chloride, sodium loses one electron and becomes octet at the outer cell and chlroine takes up one octet and becomes octet in the outer cell that is why sodium becomes become plus ion, positive ion and chlorine becomes negative charged and then there is a, you know, natural attraction and it forms a compound. So, that is actually called a valence compound because valency is electron transfer takes place at the valence band.

So, there are many such compounds which obey this rule and they can be of these two compositions, NaCl or CaF 2, sodium chloride or calcium floride compositions. Both are ionic compounds, both, both are actually valency compounds. I will give you examples in inter-metallic phases, these are Mg 2 Si, magnesium 2, Mg 2 Sn I have shown you, say Mg 2 Sn is a valence compound, which exists in magnesium-tin diagram and Mg 2 Pb, another one and last one is Mg 2 Sb 2, magnesium-antimonides. These are very important, you know, antimonides are actually thermoelectric material, very useful. These are first type of compounds, they are called valency.

Second one is known as size factor compound. Why they are called size factor compound because they are stabilized by size factors or difference of sizes of the atoms, different sizes of atoms. Just like we know, that different irons are established by the size factors, similarly these are also stabilized by size factor and these are actually called Laves phases because scientist called Laves first time discovered this phases, that is why, it is called Laves phases. So, they are stabilized by, stabilized by size difference, size difference, relative sizes of the atoms, correct. There are two types of Laves phases and they, all of them will have a composition AB 2 type, all of them. There is another classic important aspect of Laves phases, all of them will have compositional AB 2 type where A is the large atom and B is the small atom, very simple to remember, AB 2.

Now, what are, these are, these are very, there are many examples, first we will be given the examples and then I will talk about structures MgCu 2 type, they are cubic and then MgZn 2 type, MgZn 2 type, these are hexagonal and last one is MgNi 2 type. This is also hexagonal, double unit cell which will sooner or later or maybe today itself is possible this is lecture. So, this is cubic, all of them have composition AB 2, MgCu 2, MgZn 2, MgNi 2, all of them. So, all of them, all, can be, all the cubic phases which are of these type size factor can be classified under Mg Zx C 2, they are titanium, this beryllium 2, silver-beryllium 2 and bismuth-gold 2, all cubic and all of them similar structures. Here, this is gallium-manganese, sorry, magnesium 2, tantalum-Fe 2 and niobium-manganese 2. Some of them are super conductors by the way and some of them are very interesting materials. The last category is NbZn 2, selenium-iron 2 and hoffium-gallium 2 Cr 2.

So, there are, so you can clearly see there actually, that these are the three different types of size factor compounds, which are stabilized by the relative size of the items MgCu 2 type, which is cubic; other two, MgZn 2 and MgNi 2 are hexagonal type, and these are the examples.

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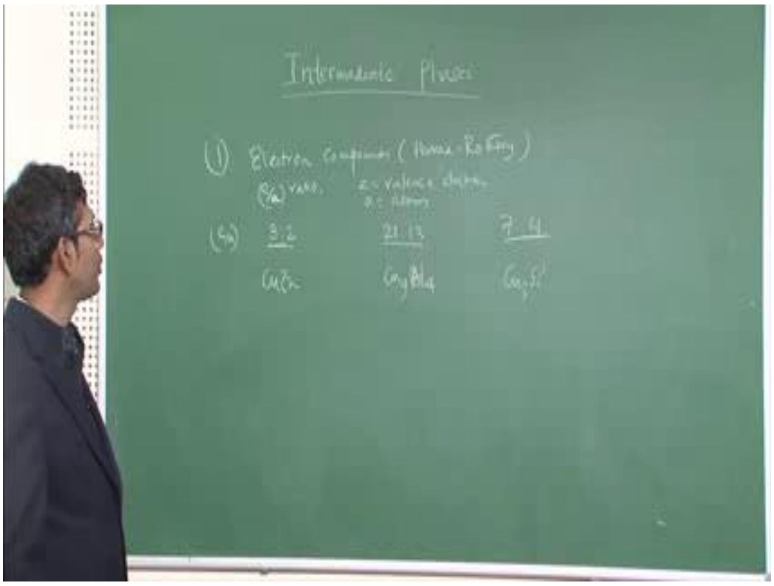

So, last one is called valency or it is called electron compounds because they are stabilized by electron to atom ratio, electron compounds, or it is known as Hume-Rothery compounds. Hume-Rothery is the person who discovered it, Hume-Rothery compounds, and they are stabilized by e by a ratio.

What is e by a ratio? e is the valence electron, number of valence electron and a is the number of atoms in the molecule, that is what is the factor stabilizes. It is not easy to explain this. This specifically depends on (Refer Time: 22:24) and the, the interaction between (Refer Time: 22:30) and the outer electron surface, many things, but I am not going in detail of that, but this is mostly stabilized by e by a ratio.

And there are three e by a ratio only at which this compound is stabilized. These three e by a ratios are: 3 is to 2, so there are three e by a ratio, 3 is to 2, 21 is to 13, 21 is to 13 and last one is, 3 is to 2, 21 is to 13, last one is something else, we will see and what is that? I think 2 by 3, yeah, correct. So, there are three ratios, sorry, not 2 by 3, 7 by, 7 is to 4, yeah. Sometime I also forget, 7 is to 4. So, there are three where this compound is stable.

So, let us see some of the examples, which will be clear to you, correct. So, 1st example of this actually is, 1rst example of this is, I will give you copper-zinc. How it is 3 by 2? There are 2 atoms copper has, 1 electron in outer shell, zinc has 2 electrons in outer shell. So, 2 plus 3 is 3 and there are 2 atoms. So, it becomes 3 by 2. So, and then, this is another phase of copper-zinc. Let me tell you, Cu 9, Zn 8, Zn 8, and Zn, what is the number? Cu 9, sorry, Cu 9, Al 4. How it is? So, 9 plus 4 is 13 atoms in a unit, a is 13 and 21 is how much? 9 Cu has 1 electron out of this electrons, so 9 into 1 and 4 into 3, 12. So, 12 plus 9 is 21 divided by 9 plus 4 is 13. So, it is 21 is to 13, that is what is stabilizing it.

And let us see the 7 by 2. 7 by 2 is Cu 3 Si. So, how it is 7 by is to 4? 4 is again 3 plus 1, this is 4, 3 atoms of copper and one atoms of silicon and the 7 is 3 plus, silicon has 4 electrons in outer shell, 7 plus 3 plus 4 is 7, 7 electrons in outer shell divided by 4 atoms, correct. So, this is what is the three ratios in which this compound are stable.

And in the next class, I am going to show you the structure as well as I am going to show you some more examples how to calculate and look into it.