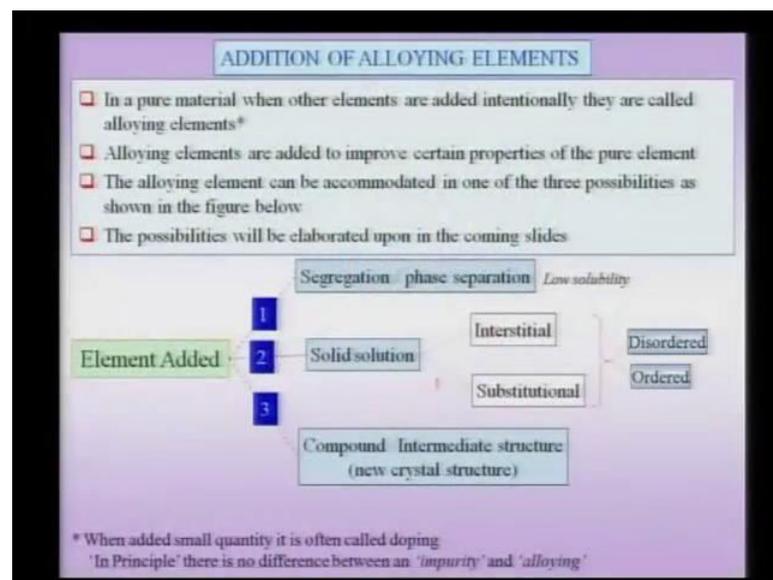


**Structure of Materials**  
**Prof. Anandh Subramaniam**  
**Department of Materials Science and Engineering**  
**Indian Institute of Technology, Kanpur**

**Lecture - 18**  
**Crystal Structures**

So far, we have considered in detail the structure of many metallic elements, and also especially the structure, the void structure that is where the voids are present. How they are distributed and how these voids are coordinated with the parent host atoms. Now, we will consider the addition of alloying elements to this pure element, and we will see some of the important structures if come about what happens this alloying element etcetera.

(Refer Slide Time: 00:58)



These alloying elements when in especially, in a pure metal, when you add other elements and especially when you do so intentionally they are called alloying elements. Though in principle, there is no difference between an alloying element and an impurity, but it is the intentionality which comes in to picture even if an impurity is present. It would give an type of impurity, it will occupy the perhaps the same positions as in international alloying elements will occupy and its role on the properties would be identical.

But only thing is that when I talking about an alloying element, it has been intentionally added to engineers, some important properties in the material or to study some important aspects phase evolution. So, this might be scientific or engineering oriented goals. When the alloying element is small in quantity, often it is called doping; so doping is the term used when you add a very small amount of an alloying element and this is typically done semiconductors, where in you want to produce a n type or a p type semi conductor, say for instance, silicon.

Now the alloying element when you add can be accommodated in one of the three possibilities as shown here. So, when you add an alloying element, it can either segregate that means it has no solubility or a very little solubility in the parent lattice and therefore, it gets segregate. Suppose, I am talking about single crystal, then obviously it can get segregated only to the surface. Suppose, we are talking about a poly crystal or a crystal with a lot of defects, then there are other possibilities where in this other alloying element can go.

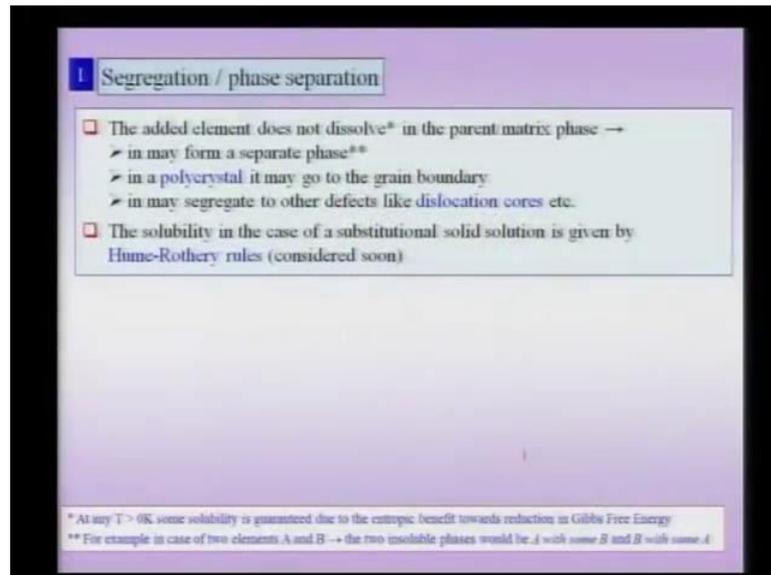
The second possibility when you add an alloying element is that it can form a solid solution now solid solutions are in some sense like liquid solutions, but they have certain very important difference when you contrast them with liquid solutions. When you talking about a solid solution there are two types the interstitial solid solution and the substitution of solid solution and further both these types of solid solutions can be ordered or disorder. Of course, we will take up each one of these cases in some more detail in the coming slides, but this is the overview of the possibilities.

The third possibility is the possibility that the alloying element can form a compound or an intermediate structure this intermediate structure would have a new crystal structure. That means it would not correspond to the any of the parent it do not correspond to the parent lattice, but would be a new a structure. We will see that these intermediate structures could be very different from the normal valence compounds, which we often deal with in chemistry. Therefore, to summarize this slide they are three possibilities when you add an alloying element raw material and this alloying element could be in a large quantity or a small quantity.

I am talking about small quantity, it could be even in parts per million in which case you would call it doping. This alloying element could occupy one of the three positions or

could go in to one of the three possibilities with respect to the host lattice either it could segregate or phase separate. That means that it has got very low solubility in the parent lattice the alloying element added could form a solid solution. These solid solutions could be interstitial type or substitutional type and as we shall see that this solid solution could be ordered or disordered.

(Refer Slide Time: 04:47)



Finally, it could form a compound or an intermediate structure, so let us take up the first case which is segregation or phase separation. When I am talking about segregation, I mean that the alloying element has low solubility and whenever I add more than the solubility element then the extra material added would obviously segregate. We should note that whenever I am talking about negligible solubility or zero solubility, what I exactly mean is that it has limited to very small amount zero solubility.

Theoretically, it is not possible because we know that there will be a reduction and give free energy due to entropic benefit and therefore, some small amount of the alloying element would always dissolve in a parent lattice. So, this is coming purely from the benefits in give free energy. If you are working at constant temperature and pressure and that is the benefit of the give free energy is coming from the multiple configurations which are possible when you add an alloying element.

Therefore, some little solubility is always guaranteed, but in this case, what we are talking about is a larger quantity of solubility means a larger amount of the alloying

element is trying to put in to the matrix. If that solubility is very limited, then it may segregate. Of course, this segregation can be called a separate phase and I mean a separate phase.

Suppose, I have two elements a and b then the two in soluble phases in each other would be that the phase a would have little amount of b and the phase b would have a little amount of a. Typically, when you talk in a language, you will call them the terminal solid solutions and you will call them by alphabets alpha and beta. So, there is some little solid solubility which is always guaranteed and you would call them the terminal solid solutions alpha and beta.

Student: Sir, what is the difference between solid solution and liquid solution actually, such as L C P this is a liquid solution and also it is called a crystal liquid crystal, but solid solution it is alloy or something different?

Okay, good question. When I am talking about a solid solution definitely, it is an alloyed, so especially I could give an example you could had copper to zinc or you could had manganese to aluminum. There are so many other possibilities, so these are all examples of alloys and we will take up some more examples in the coming slides. In a liquid solution as you can note that, there is no specific lattice of the host, there is no specific position in to which in solvent atom would go in to.

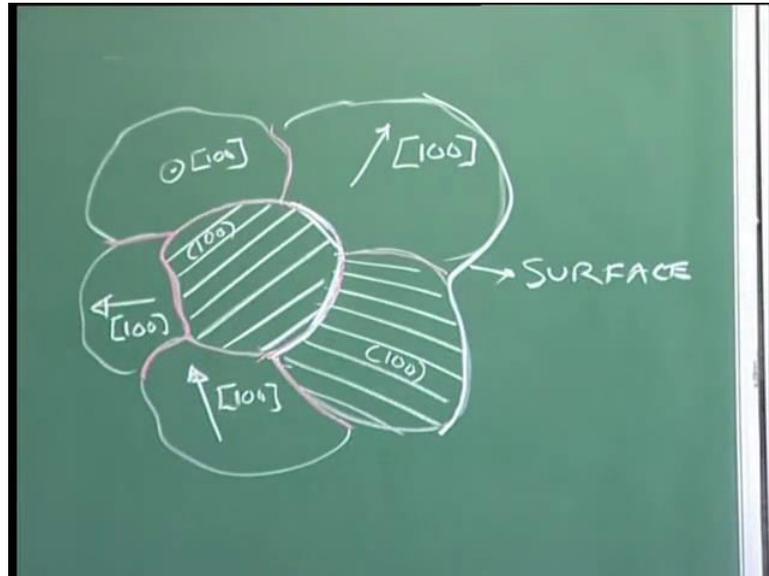
But in case of solid disordered solutions, we know that there is a parent lattice and therefore, with respect to that lattice by whole solubility or the solid solution has to be discussed. As I mention that you could have interstitial solid solutions, in which case the added atom would go in to the interstitials or it could be a replacing a parent atom. And there are specific cases where in an atom would go in to either the interstitials or the host positions there are those kind of possibilities also which already there.

Student: Why do call solutions? These are the solid alloyed.

Yeah, precisely they are called solutions because it is hangover of the terminology from liquid solutions, but essentially what you are telling is true that there are alloy. So, as I said if I am not talking about the single crystal where in this segregation can occur only at the surface. Then if I am talking about either a poly crystal or we are talking about a material with lot of defects we are not yet consider some of these defects. Therefore, we

will take these things up later during our course, but it just worth wide noted this point of time. Suppose, I dint have a single crystal but, the poly crystal and let me draw a crudes schematic of the poly crystal on the board for you to understand.

(Refer Slide Time: 07:57)



For instance, now as you know any real material has to be finite and therefore, it cannot be infinite extent in space, this is in by single crystal and suppose this is a particular plane in my single crystal picture for instance. If I consider an FCC crystal for ends in this could be the 1 0 0 planes. Now, if the single crystal, then this all the crystal I need to consider, but suppose I am talking about a poly crystal and any common metal. For instance, a copper wire or an a piece of aluminum, which is use in structure or all poly crystals.

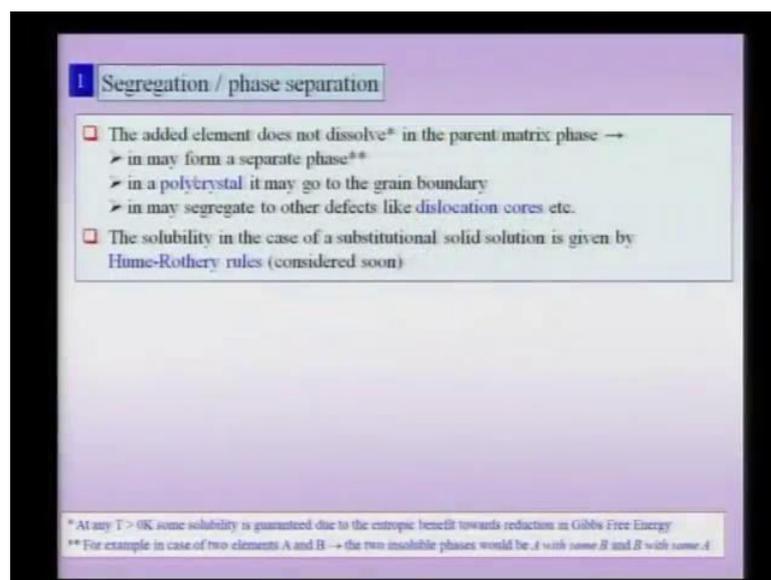
In fact single crystals are much rarer to find. Then you would notice that there will be other regions around a, other crystals once this is of course, crudes schematic which have different orientation of these 1 1 planes. So, this two-dimensional picture in three dimensions this would be could be the 1 0 0 planes and alternately I could even draw for instance 1 0 0 direction in some of these. I can show that saying on one of these other ones 1 0 0 plane could actually be coming out for the direction.

]We can some inclination in other words each one of these crystals is oriented differently with respect to its neighbors. Therefore, the alloying element I add if it is not soluble within the crystal can either go to the free surface saying this on my free surface. So, it

can go in to the free surface or it could get in to the grain boundary region, so it could actually get. Let me use a different chalk grain boundaries are typically regions of higher free volume. Therefore, it could get in to these grain boundary regions obviously the amount of grain boundary region per unit volume of the material would be a function of the grain size.

You go to the smaller grain sizes you would find that this grain size is being a size of this crystallite smaller the grains size, you go you will get larger amount of grain boundary area per unit volume. But we have to remember this is still a limited amount of volume available for a volume this sample. Therefore, the amount of material, which can go in to for instances are grain boundaries is very limited as compare to the total volume of material available.

(Refer Slide Time: 10:26)



So, even in this cases segregation to the grain boundary would mean a small amount of material as compare to the total volume of sample available, again further there could be even lower dimensional effects functions. The line defects known as dislocations and the material you added for instance I can give an example. For instance carbon in B C C ion can go to dislocations and sit there this location course, but again the amount of dislocation core available could be a function of the dislocation density.

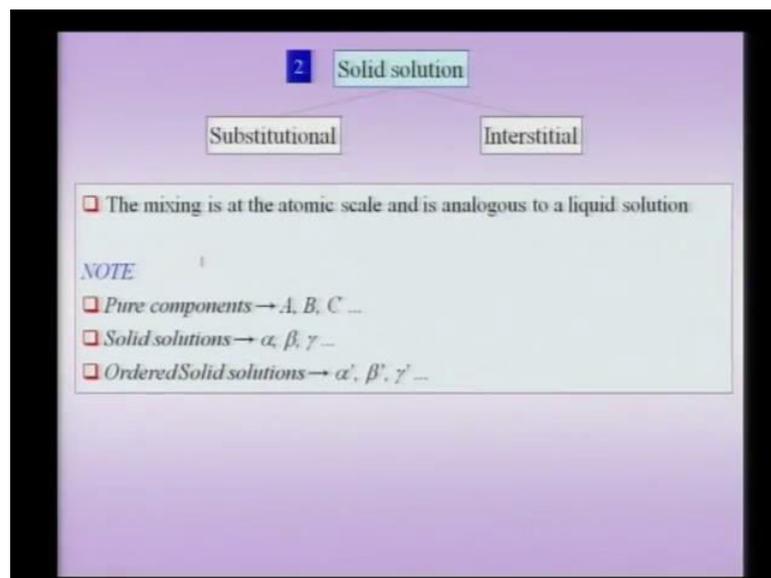
But again a small compare to the total volume of the material, but these are possibilities in other words when I add a alloying element and it is exceeded its saturation limit,

solubility limit then it will go and sit in one of these other places. This has profound consequences in terms of the properties of the material for instances when carbon it is in BCC iron, you will find an effect known as the yield drop when you do a stress strain by graph. When certain material functions go and sit in a grain boundary they can severely affect the properties of the material to give an extreme example.

For instance, when you add a gallium in aluminum it can actually go and sit on the grain boundary and often the gallium diffuses through the grain boundary very fast and actually can lead to severe weakening of the crystal. Often, this crystal would just separate under tension, so in other words when I am having adding an alloying element, the alloying element itself is going to give me some effect when it is in within the host crystal. But additionally when it tries to segregate to some of these other defects in the material, it could cause very different kind of effects in terms the material behavior.

Now, when I am talking about a solid solution and especially a solid substitutions solid solution then this solubility is govern by a set of rules. Of course, these are guidance rules and they are not what I might call is strict theorems, they are more like guidance rules and these are known by the name of the Hume Rothery rules, which we will take up next when we are talking about solid solubility.

(Refer Slide Time: 12:17)



The second possibility is which we have been of course, discussing already is the possibility of the formation of a solid solution. In this case, I am assuming that I am

within the solubility element and often this solubility element could be pretty large. The extreme case would be when I am talking about element a and b and any proportion of a is soluble in any proportion of b, in the liquid analog you can talk about for instance alcohol water mixture alcohol dissolves in water in a neat proportion.

Similarly, you could have a solid solution case and where you can add any amount of a in to b and this kind of possibility only exist in substations solid solutions. In the case of interstitial solid solutions typically, you do not find complete solid solubility. This we are already discuss when we are talking about the voids in some of the simple crystal structures. We had notice that when you add a parent or alloying element, which goes in to the void then it cause distortion to the lattice. Therefore, it cause energy to the system. Hence, you cannot add too much of this alloying element to interstitial positions.

We will also see that when we are talking about ordered system, you have interstitial solid solution which can get ordered. Now, to particular emphasis the point which, but I will made the mixing is that at the atomic scale and is analogous to a liquid solution. Now, in the context of the solid solutions, it is worthwhile to note that when you have pure components we typically denote them by alphabets like capital A B C when you have solid solutions.

We denote them by alpha beta and gamma typically for instance, alpha and beta are used for terminal solid solutions that means solid solutions which are close to the pure compositions a and b and you could have order solid solutions as we mention before. You use the prime this prime is use to designate that we are using talking about an order solid solution. So, suppose added disordered solid solution I will call it alpha and the ordered version of that would be call alpha prime just to summarize this slide.

Once more, when I had a parent to other parent lattice or to the parent crystal when I add an alloying element depending on the typical in a size of the alloying element either it can replace or go and sit in a lattice position. Of course, when I say lattice position I mean that any one of the lattice or motive positions any positions available part if where in the large size atom said or it could go into one of the interstitial positions. Further, these solid solutions can be disordered or order. Now I talked about Hume Rothery rules which govern the rules, which tell you that when would I get extensive solid solubility in the case of substitutions solid solution.

(Refer Slide Time: 15:11)

**Substitutional Solid Solution**

**HUME ROTHERY RULES**

*Empirical rules for the formation of substitutional solid solution*

- The solute and solvent atoms do not differ by more than 15% in diameter
- The electronegativity difference between the elements is small
- The valency and crystal structure of the elements is same

*Additional rule*

- Element with higher valency is dissolved more in an element of lower valency rather than vice-versa

These are empirical rules which govern in the formation of substitutional solid solutions these are simple rules to understand. They can be rationalized in terms of usual common sense materials, thinking the first one is that the solute and solvent atoms do not differ by a large amount. Its large size the difference in diameter is typically less than 15 percent smaller, the size difference larger. We expect the solubility to be this is obvious because when you put an atom in to a parent lattice, which is very large, very different in size as compare to the host atom. Then the distortion cause to the lattice would be large.

The second rule says the electronegativity difference between the elements is small. This again easy to understand, if there is an electronegative difference which is very large then there would get a tendency to form compounds and not form solid solutions again the valence and crystal structure of the element is same. So, the closer the valence in the crystal structure the closer would be the solid solubility. Now, this again easy to understand what these rules are in other words is saying is that like dissolves like.

So, if your elements are very similar in size and valence in crystal structure then the solid solubility would be extensive. Now, suppose let me take another extreme above the crystal structures are very different for instance one is an FCC other is an HCP, one is BCC and other is say a tetragonal crystal. Obviously, a complete solid solubility of a and b is not possible because one hand you have a say, a face centered cubic crystal other hand you have an hexagonal close packed crystal. Somewhere, you can notice that

the transition has to take place and that means that complete solid solubility of a and b or b in a is not possible.

In, that case there is additional rule, which is heighth along with Hume-Rothery rules which say that an element with higher valence is dissolve more in a element of lower valence rather than vice-versa. So, we will take up an example to actually illustrate this principle that how an element with higher valence is dissolve more in an element of lower valence then the other way about. So, we will take up an example to understand this, so let us look up the applicability of the Hume Rothery rules and also the exceptions with regard to some specific examples.

(Refer Slide Time: 17:26)

*Examples of pairs of elements satisfying Hume Rothery rules and forming complete solid solution in all proportions*

System		Crystal structure	Radius of atoms (Å)	Valency	Electronegativity
Ag-Au	Ag	FCC	1.44	1	1.9
	Au	FCC	1.44	1	2.4
Cu-Ni	Cu	FCC	1.28	1	1.9
	Ni	FCC	1.25	2	1.8
Ge-Si	Ge	DC	1.22	4	1.8
	Si	DC	1.18	4	1.8

A continuous series of solid solutions may not form even if the above conditions are satisfied *e.g. Cu-γ Fe*

The first example here is these three examples here in the table are examples where in you find complete solid solution in all proportions. That means I could take element A in 40 percent or 20 percent or 5 percent or 95 percent and add element B which is of course, the specific element here in this table and I would get complete solid solubility that means now we would obtain a solid solution. These examples are silver gold, copper nickel, germanium silicon and you can see that the first two relate to an F C C, F C C solid solution, germanium silicon are both diamond cubic crystal structures.

Now, if we let me take the first example: silver and gold both have the same crystal structure, both have the radius of the atom is very similar, to second decimal place they look very similar, the valency is very similar and the electronegative difference is also

not too large. So, I obtain complete solid solubility between silver and gold and you know that silver and gold are noble metals wherein you would expect complete solid solubility. Now, the second example is between copper and nickel.

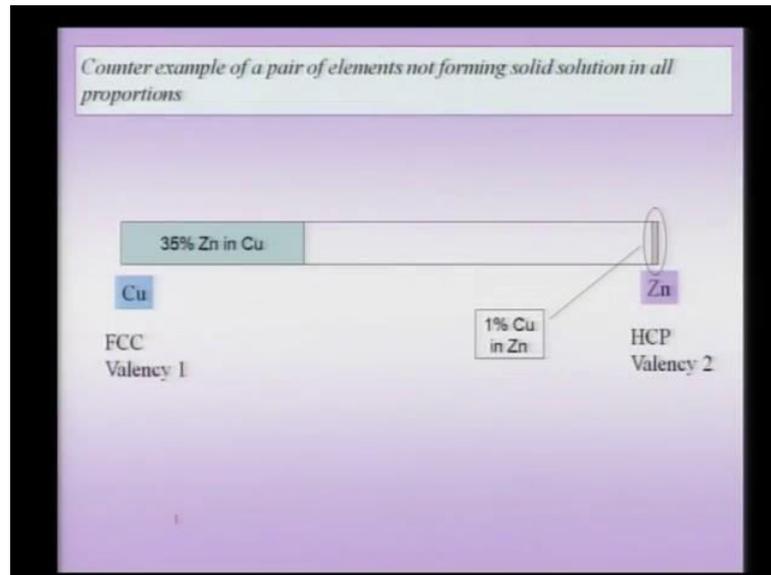
If I look at a crystal structures again the crystal structures are both fcc the size difference. The radius of the atoms is almost similar but, its only different in the second decimal place, this is 1.2 in angstroms, this is 1.25 angstroms, the valency is different, but again not too much and the electro negative difference is also not too much. So, this is a second example where in you find complete solid solubility between copper and nickel. The third example is of course an interesting example because it happens to be diamond cubic crystal and in the diamond cubic crystal structure.

Of course, you have atoms located at 0 0 0 on quarter, quarter, quarter. Suppose, I take a germanium crystal and start adding silicon, it would go and replace any one of the atoms in any of this position and would continue to be tetrahedral bonded to the other atoms in the crystal structure. If you look at the radius they are very similar, of course even this difference for instance would mean that there will be some strain, but the strain would be small, the valency is identical, the electro negative difference is also negligible.

Therefore, you can see that these are nice examples where in you get complete solid solubility, where in the elements obey our Hume Rothery rules. Now, the exception to this also exists, in other words when you find that some of these parameters are satisfied, even then you may not get complete solid solubility and the example usually sighted is the copper gamma. In example where in some of these criteria is satisfied and still you never find complete solid solubility.

So, as I again point out just emphasize the important thing, these are guiding principles Hume Rothery rules are guiding principles and it is not strict rule. In a sense that, if these rules are satisfied then you would get complete solid solubility and the example here to disprove that it is actually not a theorem is a fact that there is the example of the copper gamma where in you do not find complete solid solubility. Now, I had mentioned when I talked about the Hume Rothery rules that an element with higher valency dissolve more in an element of lower valency, then call them vice versa too.

(Refer Slide Time: 20:49)



Just to illustrate, this is an example, I have got an example here and this is the example of copper and zinc. So, you can straight away see that there is no region to expect complete solid solubility. In this case, because copper is FCC and zinc is HCP, so there is no possibility for us to obtain complete solid solubility. If you want to contrast with liquids then, this crystal structure aspect is obviously absent and therefore, some of the guiding principles would be very different.

Now, when I am talking about solubility, if you see that copper has a valency 1 here and zinc has a valency 2. So, the higher valency element is zinc and as the rule says the higher valency element dissolves more in the lower valency element and the solubility in this case happens to be 35 percent. That means I can dissolve 35 percent zinc in copper, while if you look at the other part of the diagram that how much of copper, can I dissolve in zinc. So, copper is a lower valency element and zinc is the higher valency element and therefore, we can see the solubility is very limited. It is only 1 percent.

(Refer Slide Time: 21:59)

**Substitutional Solid Solution**

**HUME ROTHERY RULES**

*Empirical rules for the formation of substitutional solid solution*

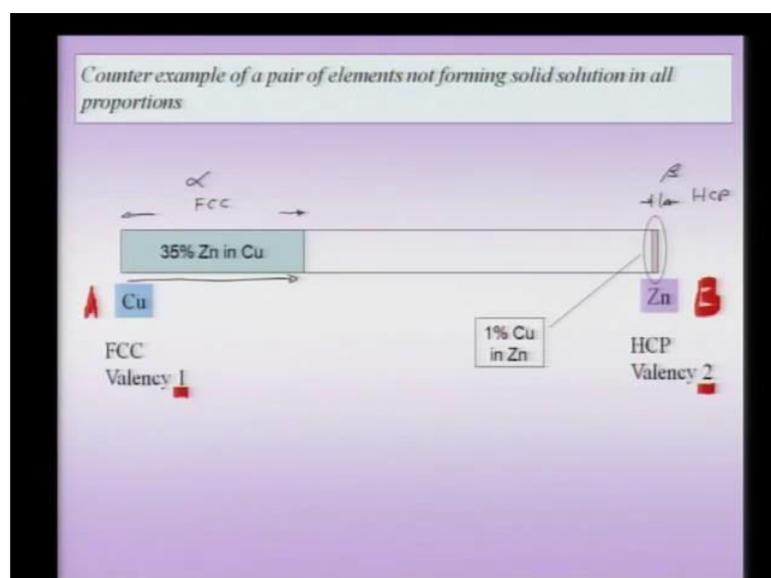
- ❑ The solute and solvent atoms do not differ by more than 15% in diameter
- ❑ The electronegativity difference between the elements is small
- ❑ The valency and crystal structure of the elements is same

*Additional rule*

- ❑ Element with higher valency is dissolved more in an element of lower valency rather than vice-versa

So, just to pre-iterate the principle and summarize this diagram so that you have a better understanding of this rule it says that, so let me since I have got this slide in front of me, let me revise the Hume Rothery rules for you. This empirical rules for the solid and solvent atoms do not differ in size for more than 15 percent, that means they should have as similar as size is possible. The electro negativity difference between the elements is small, the valency and crystal structure the elements is as similar as possible. An additional rule, which is what I was explaining now is that the elements of higher valencies dissolve more in an element of lower valency rather than vice versa.

(Refer Slide Time: 22:37)



The example I am sighting now is example of copper and zinc and as I pointed out because crystal structures are different, there is no region to expect complete solid solubility. But then when I am trying to track the asymmetry in the solubilities, that how much? Suppose, I call this a for instance and I call this b and then I am asking the question how much of b would go into a and how much of a would go in to b? I can clearly see that this asymmetry is pronounced, it is not just a slide asymmetry that means asymmetry with respect to the 55 percent composition the element with higher valency.

Zinc dissolves much, much more in copper and that is 35 percent and the element with lower valency, which is copper dissolves very little in zinc. Of course, these solid solutions if I am talking about a solid solutions which lie in this region we take up a different pointer. For instance, so I am talking about solid solutions in this region, then obviously all these solid solutions would have a FCC structure. That means I will have a parent host crystal made up of copper atoms wherein slowly as I increase my percentage of zinc, I will keep on replacing more and more of copper atoms with zinc atoms.

On the other hand these solids solutions, so for instance using my normal terminology I could call these solid solutions are alpha and these solid solutions is beta and when I am using alpha and beta, I mean they are disordered solid solutions. So, in this region for instance where in I am finding beta, obviously you will have an HCP crystal where in the zinc crystals structure I would slowly replace some of the atoms with copper. So, this is my copper zinc system, we will also later on discuss some other interesting structures from this very same copper zinc system. Now, I had mentioned that when I am talking about interstitial solid solution or a substitution solid solution I can have two possibilities the ordered and the disordered structures.

(Refer Slide Time: 25:41)

Order-Disorder Transformations

- ❑ On interesting class of alloys are those which show order-disorder transformations
- ❑ Typically the high temperature phase is dis-ordered while the low temperature phase is ordered (e.g. CuZn system → next slide)
- ❑ The order can be positional or orientational
- ❑ In case of positionally ordered structures:
  - The ordered structure can be considered as a superlattice
  - The 'superlattice' consists of two or more interpenetrating 'sub-lattices' → with each sublattice being occupied by a specific elements

*(further complications include: SL-1 being occupied by A-atoms and SL-2 being occupied by B & C atoms- with probabilistic occupation of B & C atoms in SL-2, which is disordered)*

When I am talking, already we have dealt with this concept in a previous lecture, that what is I disorder structure. What is an order structure and we had clearly seen disorder structures are describe by language of probabilistic occupation, that means that suppose I have 50 50 alloy, 50 percent a and 50 percent b, then I would say that any lattice point there is a possibility. Suppose, I am talking about a simple BCC crystal, then I have 50 percent chance that a occupies any lattice point or 50 percent chance that b occupies any lattice point.

On another hand, when we talked about order structures, we used al language of sub crystals and sub lattice. We use that language, so we need to understand that when I am talking about order structures I need to use a language of sub crystals and sub lattice and is important for us to understand disorder transformations and quickly pick up some examples of this orders structures. Now, it is typically found that the high temperature phase is the disorder phase while a low temperature phase is order where ever you are you do observe order disorder transformations.

You will see that the high temperature phase is the disordered one and the low temperature phase is the ordered one and we will rationalize it in terms of the given energy known. Of the coming slides, we already notice that when were we are talking about order I could be talking about two kinds of order orientational order and positional order. Most of the examples we will be taking up in this lectures could be related to positional order, but I will give you one example or perhaps more than one example of orientational order as well never the less again.

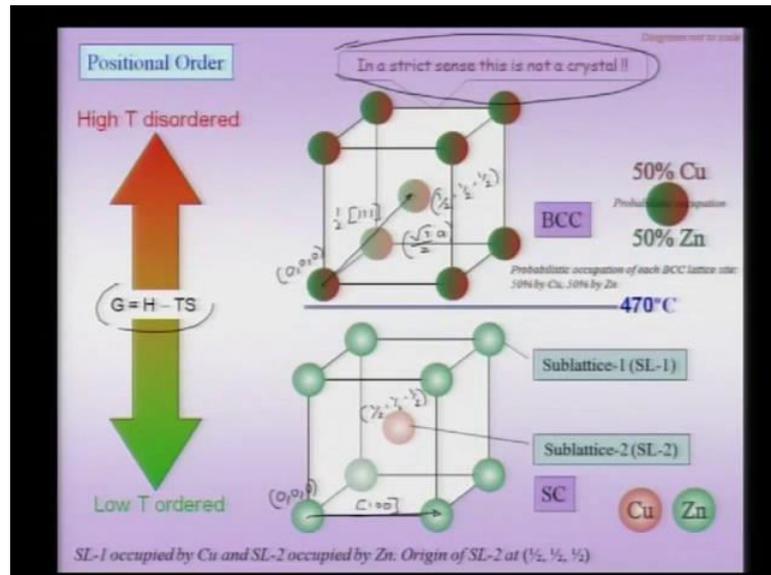
Whenever I am talking about the disorder phase orientational or positional, it will be the high temperature phase and the low temperature phase could be the ordered phase. In the case of positionally ordered structures I have already seen that the order structure can be called super lattices and the super lattices can consists of more than one penetrating interpenetrating sub lattices. Typically each one of this sub lattices occupied by a specific element, so we already seen that you could have one sub lattice, two sub lattice or more sub lattices.

We have also noticed when we did took up an example on the board that we could actually have two sub-lattices one completely ordered with respect to an element say a either sub-lattices, could be actually occupied by two different element b and c and there could be with that sub lattices could be disordered with respect to b and c. So, the only two sub lattices layers purely occupied by a second sub lattice, sub lattice two is now occupied by b or c and it is occupied by b or c in a random fashion.

Now, distortion symmetry will tell me that how much of each lattice point in the sub-lattice two is occupied by b or c and that would depend on the percentage of b and c in the alloy. So, these are the possibilities, so let me take up some examples also to understand this order disorder transformation. The simplest and the nicest example perhaps is a example of the copper zinc system where near 50 percent copper and 50 percent zinc and as I had mentioned the high temperature phase is the disordered one and the low temperature phase is the ordered one.

Now, we will of course, emphasize this later again, once more we have to note that the properties of the system change when we have an ordered disordered transformation, that means that the ordered phase and the disordered phase are not the same phases. In fact, they could be different, they have to be different crystal structures and all the properties would change and that is why we need to be careful whenever talking about. I cannot just work in terms of compositions, I have to work in terms of the exact crystal structure. In other words, I need to know am I working at the high temperature phase or I am talking about the low temperature phase even for a given composition.

(Refer Slide Time: 28:33)



So, some of these concepts we already covered in detail, so it is not difficult for us to understand them. So, the high temperature phase for instance in a 50 percent copper 50 percent zinc alloy is a BCC crystal structure. In other words, it is a BCC lattice, wherein the motive is a 50 percent probability of copper or 50 percent of the zinc occupation at each lattice point. Now, this is the BCC phase, that means at the fundamental lattice translation vector, now is the one which connects atom its 0 0 0 to the atom. So, this are identical because now this are identical not in reality, because in reality this if you take any region of space. This could end the being copper and this going to be zinc and this going to be copper this is the random occupation.

But, this is now probabilistic sense of definition, so that we already noted because in the very stricter sense, this structure cannot even be called a crystal. We already seen this is the only crystal in the probabilistic sense that we already noted and given that important point, we already noted that this is actually a BCC crystal with the fundamental lattice translation vector. The shortest lattice translation vector being half, half, half whose length is  $\sqrt{3} \text{ by } 2 a$ . See all this aspect, that we have already seen, now what about the low temperature ordered phase?

The low temperature ordered phase can be now described as to interpenetrating simple cubic lattices or simple cubic crystals origin of one lattices z 0 0 0. The origin of the other is at half, half, half and the important point is now to know this is not a BCC

crystal. We already know this is a simple cubic crystal and this simple cubic crystal has a motive which is one copper atom here one zinc atom here, because I could always place the origin at half, half, half in which case the motive would just strip flip its positions. But nevertheless this is the simple cubic structure.

So, when I go from a B C C high temperature phase to a low temperature simple cubic phase which is now an ordered structure, the property is the whole material will change along with it. Now, for instance now the shortest lattice translational vector would be this which joins  $(0, 0, 0)$  to  $(1, 0, 0)$ , it is no longer the vector form. For instance, in case shortest translation vectors  $(1, 1, 1)$  vector and this case it will be  $(1, 0, 0)$  vector. Therefore, this ordering transition is also a complete by change in properties, for instance of above amount to describe the flip systems in this two crystals.

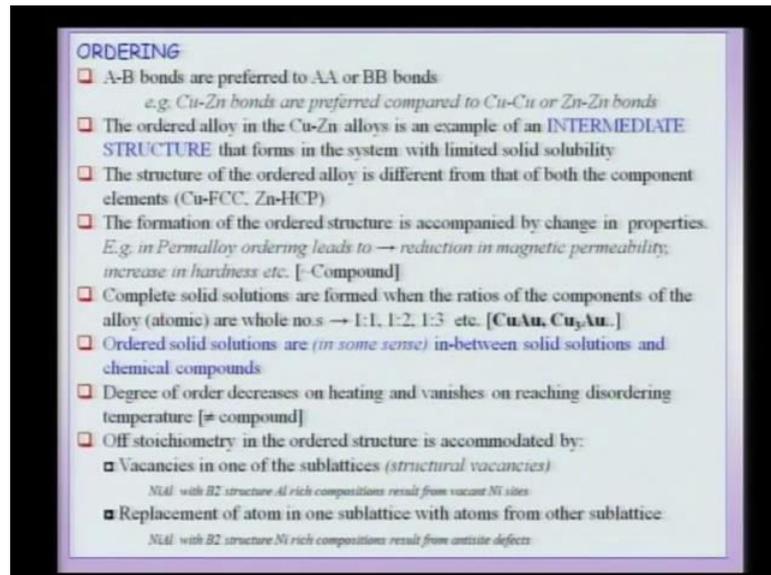
They will be different and the pulse stress for is in the fundamental stress I need to apply to dry a plastic deformation. In this materials that would change and therefore, many other properties would change along with this change in crystal structure. Now, the question we are asking is that why is the high temperature phase, disorder phase at the low temperature phase, the ordered one, the answer is, it gives free energy. So, we notice that the temperature is the weighing factor for entropy that means at the higher temperatures, this structure with higher entropy is stabilized and lower temperature, the structure with lower end entropies stabilize.

Now, suppose I had two sub lattices of course, assuming that is a completely ordered system, then one sub-lattice would be occupied by one element the other sub-lattice the other element copper and zinc in this case. Therefore, the number of configurations available to be is, there is just one possible configuration, but suppose I am talking about a disordered phase, then I have many configurations which can finally, give me a 50 50 probability at lattice point. Therefore, the system becomes configuration 1.

According to Boltzmann equations equal to  $k \tan \omega$ , I would notice that disordered structure, it is preferred high temperature. So, this is purely coming from gives free energy arguments, so just to summarize this slide and also the concept of positional order that I can describe my disorder crystal at high temperatures using a probabilistic occupation model. The low temperature phase typically which is the ordered phase which for instance I told you, suppose I call this by symbol  $\gamma$ .

Then I will call this gamma prime, because now this is an ordered phase. In the lower temperature phase then, there is a substantial change in properties. Now, assume this transformation in this particular system occurs at 470 degrees for a composition of 50 percent copper and 50 percent zinc and I can understand this order, disorder transformation in terms of the given free energy driven transformation.

(Refer Slide Time: 33:22)



Now, I will study here some of the salient features about ordering and this is an extensive list and I will go through this slowly one by one, so that we can understand some of the important aspects of disordering phenomena. Ordering take place because of the a b bonds are preferred compared to the a a or b b bonds, in other words when I have a structure like this, you can clearly see the environment of the copper atoms is completely zinc. So, there is it has got an eight fold coordination of zinc around the copper atoms.

In this case of course, the environment is random, there is no specific coordination. Therefore, whenever an atom of a different atom prefers different kinds of different types of neighbors that means the a b bonds that means the copper zinc bonds of its more energetically favorable as compare to the a a or b b bonds. Then, you find the phenomena of ordering the important point to notice the d ordered alloy. The previous example, I would call the copper zinc alloy is an example of something known as the intermediate structure and this would form in the case limited solid solubility also.

System solves the structure of the ordered alloy is different from both the component elements functions in the previous example copper of FCC is equal HCP, but the ordered alloy was a simple cubic had a primitive cubic crystal structure. So, we have to note this that the ordered alloy is different from both the parents and this is an important point to be noted. Arun has some questions.

Student: First question is, but vectors govern segregation.

So we already yeah what is the second question?

Student: second question is, can we say that substitutional solid solution is always called prime vacancy or because this is as in you say that the alloying element will sit on the vacancy or some vacancy, if they are some vacancy it will say we are or is it followed by vacancy or some.

Perhaps two good questions, let me answer the first one first. When I say, so let me consider substitutional solid solution, if I am talking about an element, if a soluble that means I am following Hume Rothery rules. Of course, we already seen that Hume-Rothery, have their own limitations assuming that Hume Rothery are cardinal for my explanation of solid solution. Whenever I do not have those criteria being met, then the second element cannot dissolve in this parental lattice, same in wherever the lattice it has to replace in atom, that is point therefore, it will segregate

Now, the question we are asking of course, he said very rude segregate of course, we have only it is a single crystal the only place it can segregate is to the surface in a polycrystal I mean a defected material there. Other possibilities where such a second where the alloying element or the dopant or the impurity whichever the way you want to call that added element can segregate. So, these are the other possibilities, we are noted and I said that little detail matters a lot to me regarding a material properties. As I said, if gallium segregates the grain boundary because it cannot dissolve in parent aluminum host atom, it cannot be replace such host atom, aluminum.

Then the material becomes extremely weak and the other phenomena which are similarly, found in steel where in the alloying element not only segregate to the grain boundary region, but also could form a compound. Now, the second question is related to the vacancies now, let us be very clear the vacancies again of course, we will see that

vacancies can be more than one type. So, you raise an important question or what is a vacancy first of all we will answer this, what is a vacancy what kind of vacancy is existent crystals in an upcoming lecture. Just for since you ask me this question a vacancy for the sake of audience is for instance if you take an F C C aluminum. Then is an atom missing from the lattice point so suppose I do not have an aluminum atom and ion.

It is not present in the lattice point I call that in vacancy now my solid solubility is in principle of course, in a simplest sense is not depend on the vacancy concentration. Because what I am saying is that when I am adding for instance in this case I am adding copper to zinc then the copper is replacing zinc in its lattice position. So, it is not that of course, then that means replacing means I do not take away the zinc, I mean that I am filling larger volume I am adding more units cells where I can in selectively in some of the unit cells I will put copper instead of the zinc originally present so there no vacancies here. Of course, if I am asking more specific questions what will happen to the diffusion of these alloying elements which we will perhaps consider later then vacancies play an important role? Yes, if they are pre-existing vacancy for instance in the zinc crystal then copper can obviously go and occupy those vacancies as well that is the possibility.

Student: How we define solubility because normally we say that the at high temperature solubility is more at low temperature solubility is less? So, for segregation we said that we should have low solubility, very low solubility, so is there any temperature boundation on that? Because in case of solid solutions we are seeing that high temperature disorder low temperature ordered case or is there any possibility that high temperature because the solubility is more it forms some solid solution or low temperature is to segregation.

Now, the question I asked is slightly more difficult to answer at the stage because you were not really considered the concept of phase diagrams, the concept of solubility the concept of solubility with competing phases. Let, me give an example even though this is slightly advanced for this stage. That is suppose I am talking about solubility of carbon which is an interstitial solid solution and we will be taking that up in this lecture carbon in B C C. Now, obviously this carbon goes and sits in the interstitial position and we already seen its actually in the octahedral void position. Now, the solubility of carbon in

alpha n it is the iron B C C form of iron with carbon in it keeps on increasing to a certain temperature which we called you tetroy temperature, but after that actually decrease.

Because now, the alpha phase originally is in coexistence with the f e 3 c, which is cement, but later on after tetroy temperature actually, it is in coexistence of the gamma phase. So, actually solubility decreases with temperature, so it is not a general rule that solubility always has to increase in the alpha end with temperature that is point number one. But as a general rule yes, because you have this gives free energy benefit. Therefore, with increasing temperature you would find a largest availability, so that possibility exists, so what is the specific question.

Student: Because in solute substitution solid solutions, we are saying that high temperature disordered a and low temperature ordered a, but can be there at can there be any possibility that high temperature solid solution forms because of high because of high solubility and low temperature it results in segregation.

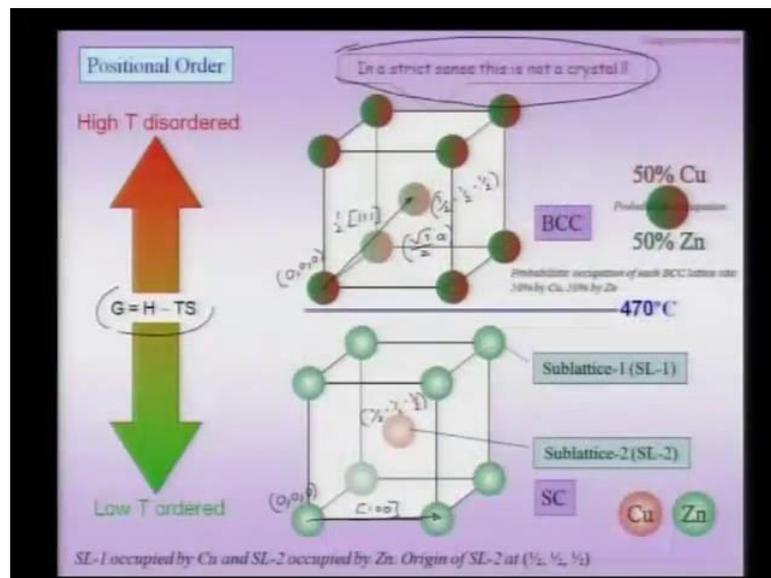
Absolutely, that possibility always exist in fact this in fact segregation is opposite of ordering segregation is where a type of atoms want to have a type of atoms around it ordering is a type of an atom. Sometimes b type of an around it, so segregation is opposite of the ordering in otherwise in some sense segregation is clustering and either the system is ordering or they show clustering. So, both this possibilities exist though not the same system in the same composition that you have to know some systems if you are ordering some systems might show segregation, so that we have to note this that absolutely a possibility.

So, getting back to list on ordering now we are noted the structure of the ordered alloy is different from both the component elements, that is an important to be noted. Deformation of the order structure is accompanied by changing the properties, this point I had already mention and the example would be for instance in term alloy ordering grids to the reduction in magnetic permeability. Increase in hardness etcetera either words the ordered structure the disordered structure can be thought of an solid solution while the ordered structure is something similar to a compound it is something similar to an intermediate phase.

Therefore, this intermediate phase, which has a different crystal structure has different properties; this point has to be clearly understood. When you consider more examples all

the more it will become clear that's why the properties would change because crystal structure is changing. I am talking about ordered solid solutions of course, I mean completely here completely ordered solid solutions are form when the ratios of components or ratios of whole numbers like 1 is to 1 is to 2 1 is to 3 etcetera. It in the example here for instance copper to gold ratios 1 is to 1 c u 3 u the ratios 3 is to 1. When you find these whole number ratios then the possibility are forming ordered solid solution is completely ordered solution is there.

(Refer Slide Time: 42:19)



It will become clear from the for instance even from the previous example it will be clear. Now suppose, I have a ratio of copper to zinc here 1 is to 1, then complete ordering is possible. If I have more than 50 percent copper, say for instance I have 51 percent copper. Then this system can never get totally ordered, because 1 percent of the copper has to either go and sit in the zinc positions. I will have to leave some of the zinc positions vacant, so as to maintain my stoichiometry.

In other words, in a positive stoichiometric, for instance I take copper and zinc of stoichiometry. Just an example, I would say more general example would be a b, if I considered a positive stoichiometric composition, then such as thing can never be obviously completely ordered with respect to that structure. I just emphasized the ordered solid solutions are in some sense between solid solutions and chemical compounds. When I mean chemical compounds, I am referring to what we normally call

the valency compounds of the standard chemical compounds we deal with in chemistry like  $H_2O$  or one of those compounds.

So, this is important to be kept in mind that these ordered solids solution are neither in full sense chemical compounds in which case of course, my stoichiometry will be completely fixed. I cannot change my stoichiometry, they are also not random solid solutions, and they are something in between and this is an important thing to be noted. The degree of order decreases on heating and vanishes on reaching disordering temperature and this sense it is not like a compound in other words. I will tell a little more about what I mean by order and degree of order, how we define degree of order and what I mean by this order.

I will tell little more, but the important point to note is that this disordering does not take place at a single temperature usually. There are special cases and this degree of order slowly decreases and in this sense most of the ordered disordered transformations or second order transformations and it vanishes, that order completely vanishes with an increasing temperature. Therefore, this behavior of it is not like a normal compound and this is what I was mentioning before, just to emphasize this point once more off stoichiometry in order structure can be accommodated in more than one way.

For instance, this is something very important note and the very fact that I have an off stoichiometry in an order structure tells me that that structure will never get completely order. We can see if I am talking about a simple example would have been nickel aluminum were 50 percent nickel and 50 percent aluminum. This my composition and this forms with b2 structure and when I say b2 structure I mean this kind of structure, this order structure which is a simple cubic structure. Now, the aluminum rich compositions; that means that if I have nickel less than 50 percent aluminum more than 50 percent, since I could talk about Ni 49 Al 51, then the aluminum bridge composition result from vacant nickel sites.

So, if I am ruining nickel from nickel sub lattice or the sub crystal automatically, it becomes aluminum bridge, but they the important thing to be noted here is the asymmetry between going to aluminum bridge site and going to the nickel bridge site. When I go to nickel rich compositions on the head that means for instance I could take nickel 51 aluminum 49, then this result from anti side defects, in other words no. Since I

have more nickel, this nickel starts sitting in a aluminum sub lattice, that means aluminum sub lattice cannot get fully ordered. What the fully ordered aluminum sub lattice were in all the aluminum sub lattice fully occupied aluminum.

Now, because of the composition variation and this composition variation tells me that this is not like an standard chemical compound where in you cannot tolerate such kind of  $H_2O$  means precisely two hydrogen molecules for every or two hydrogen atoms for every oxygen atom. But here, I can tolerate this off stoichiometry and nickel bridge composition forms when aluminum, nickel starts sitting in aluminum sub lattice. So, you can clearly see first number 1 is the fact that there is a pronounced asymmetry in the way my off stoichiometry is accommodated and this for instance is one nice example.

When nickel aluminum system, where in the aluminum bridge compositions are occupied or accommodated by putting that means removing with nickel atoms from the nickel sub lattice. So, already we have seen lot of important things we relate to ordering the fact that it is, you can call an order structure is intermediate structure. It forms when the a b bonds are prefer that means bonds of a different kind are preferred. Compared to the one of the same kind and to which was nicely answering some other questions raised by Arun wherein, we saw that if atoms bonds is the same type of preferred you would have clustering or segregation.

The important thing, which we finally saw is that that how this off stoichiometry is accommodated in ordered structures. Now, just to emphasize some the point, which we have been talking about that the high temperature structure is disordered because the entropic aspect which comes in to play and the low temperature structure is the ordered structure

(Refer Slide Time: 47:28)

□ Solid solutions which have a negative enthalpy of mixing ( $\Delta H_{\text{mix}} < 0$ ) prefer unlike nearest neighbours  $\rightarrow$  show tendency for ordering

$\Delta G = \Delta H - T\Delta S$

- $\uparrow T \Rightarrow$  Disordered
- $\downarrow T \Rightarrow$  Ordered

$L = \frac{r_A - X_A}{1 - X_A}$

- $r_A \rightarrow$  probability that A sublattice is occupied with the right atom
- $X_A \rightarrow$  mole fraction of A in the alloy
- $L \rightarrow$  Long Range Order

As Arun pointed out, there are other possibilities wherein you may not have been ordering, but actually we get segregation. So, in this case there is a negative enthalpy of mixing I was talking about. This order and one of the important things is to actually quantify this order because I told that this is not a 100% situation. This means it is not like above a certain temperature is completely disordered and below a certain temperature it is completely ordered or below it is completely ordered.

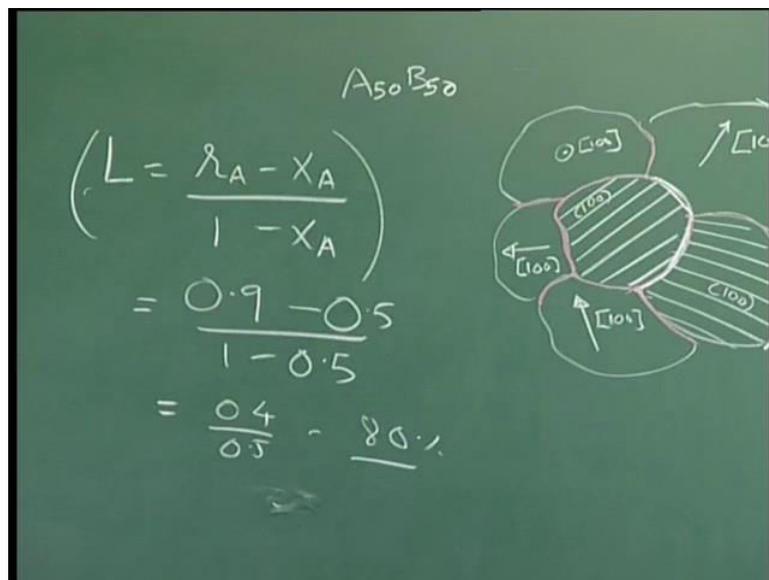
Above completely disordered, this happens over a range of temperatures, in other words in a specific alloy I could have especially as you have seen in the case of off stoichiometry alloys. I could have a certain amount of disorder built into the system. Now, how do I quantify this order. Typically this is quantified something is called  $L$ , this  $L$  is called long range order that which also gives me a clue that there is something else which I cannot call short range order. We had considered this aspect when we talked about crystals that crystals some cases can have long range order.

They have short range order and you could have situations where in you have short range order missing. There is long range order and the converse is also possible when there is short range order present, but there is no long range order. So, this  $L$  is the long range order parameter and it is defined as  $r_A - X_A$  divided by  $1 - X_A$  wherein  $r_A$  is the probability that the a of lattice occupied by the right atom where  $X_i$  is the mole

fraction of a in the alloy. So, this long range order is define with respect to a and equivalently you can describe it with respect to B.

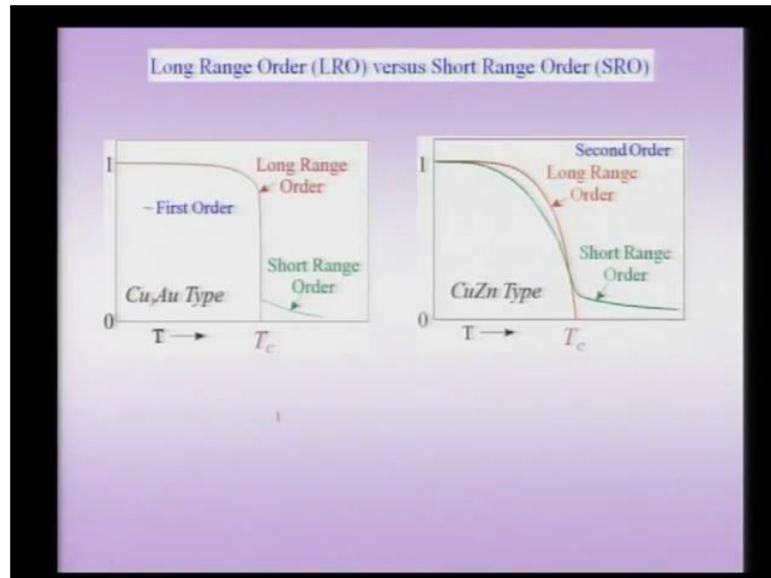
So, let me take an example for instance suppose I have an alloy where in r i is the probability that a sub lattice occupied with A atom. So, its 90 percent of A atoms are actually rightly sitting in the s sub lattice. This means that instant person are sitting the wrong sub lattice, so by mole fraction is 50 50; that means I am talking about A B alloy A 50 B 50 alloy.

(Refer Slide Time: 49:42)



So, I can write this equation as so I have ninety percent of my a atom is sitting in the right sub lattice of my r a s point mine my composition is A 50, B 50. So, L is r A minus x A 1 minus X A and my composition is A 50, B 50, that means X A is 0.5 and 1 minus 0.5, so this is 0.4 by 0.5 which is 80 percent, so or 8 percent that is better. So, this means that all are long range order parameter is 8 percent or 0.8 and as I said disordering is complete will find that each atom is the randomly present. This means that R i will approach 0.5 X A will be 0.5, so 0.5 minus 0.5 will be zero that means the order 1 will become 0.

(Refer Slide Time: 50:49)



This is my long range order parameter and as I pointed out that there is another way of looking at order, which is at looking at the short range order and this is important for us. Let me take two examples here though we are not considering crystal structure of these two, one is  $Cu_3Au$  another is  $CuZn$  of course,  $CuZn$  is this one we have already considered. This  $CuZn$  is an example which is nothing but,  $AB_2$  structure which is a simple cubic structure, but we are not considering  $Cu_3Au$  which will take up in the upcoming slide.

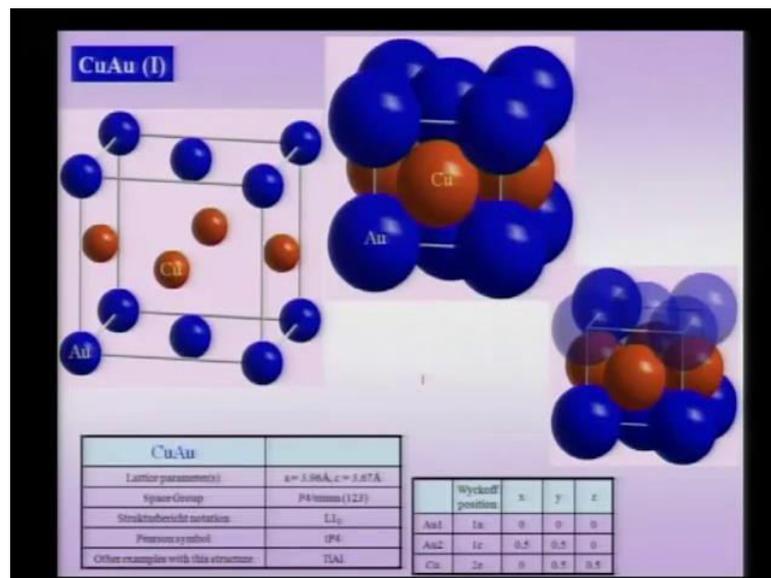
What I am focusing here, is the change in order with temperature and now, I am not only talking about the long range order, but I am also talking about the short range order. Now, suppose I have perfect ordering that means at all my  $r_i$  atoms are sitting in the right place, which means that this is  $1 - 0.5 = 0.5$ ,  $1 - 0.5 = 0.5$  That is  $l$  is equal to 1, so perfect order would be given by long range order parameter. One complete disorder would be that means a complete random occupation of A and B in both the sub lattices, that means there is no sub lattices would be characterized by a long range order parameter 0.

Therefore, the other parameter changes from 1 to 0, this is the extent of my long range order parameter  $l$ . So, I can plot my  $l$  with respect to temperature, I can see first. Let me interact, the long range order parameter which is shown in red the short range order parameter is shown in that means. The exits in the short range order you shown in green.

Now, you can see that the order slowly decreases and after certain temperature now, this beyond by  $T_c$ . There is no order, but the important point to note is at even though when I am talking about no long range order, still some short range order might persists. This is an this the important message.

The only message I want to give from this graph because this involves some concepts which are not covered so far. Therefore, I will not go in the details like what is what I am talking about as a first order or second order phase transformation, but what I want to point out here easy fact that whenever even though the long range order has vanish the short range order persist. This is an important thing we noted from this and this can be seen for both the  $Cu_3Au$  type and  $CuAu$  type ordered structures which has i different order structure. You can see even here after the long range order is vanish the short range order persist, so this is something important to note.

(Refer Slide Time: 53:16)



So, let me consider these two alloys for instance now, I have talked about this  $u$  is in I have see you three  $Au$  and for instance, this is described here these two what are the crystal structures, how is this ordering different from the ordering we saw in the copper? Instead of the copper zinc system, so this is also brings us to some more interesting class of alloys, some in other inter metallic alloys, which I ordered and we already consider the SCC crystal in detail before right, which is the structure of copper aluminum etcetera.

You see in this that there is a FCC lattice which is now occupied by the single element, but now these are more complicated structures and the two elements. Therefore, this an alloy and therefore we have now gone to the next level in terms of the understanding a crystal structures. So, let me understand the crystal structure of the Cu Au, which is now an ordered inter metallic alloy. So, when I am saying order inter metallic alloy, I mean that there are specific sub lattices, for instance the gold and the copper in this case. Now, this structure clearly is not a cubic structure as you can see because it does not have 3, 4 threefold axes.

In fact, it has just one fourfold axis which is the axis going upward, so this is my tetragonal structure and yes you can see that this structure can be understood by replacing all my phase centering positions in the mid plane by copper atoms. So, I have copper atoms are ion sitting in the mid plane, while these planes are occupied by completely gold ions or atoms. So, this structure can be instead of alternate planes of copper and gold which pervades the structure and now the symmetry of the structure has to be lowered.

So, this structure is not a cubic structure, but it is actually a tetragonal structure and there is a notation known as the Strukturbericht notation, wherein certain alloys are name by certain alphabets and numbers and this is called an L1<sub>0</sub> structure. In the Strukturbericht notation, there are analogous structures like criteria aluminum, which also have the same kind of structure which is also on ordered alloy. So, you can see that this structure can be, I will just give the structure in more than 1. So, that I can understand this is my standard ball and stick model, this is my space filling model where I can clearly see that the gold occupies these phase centric positions.

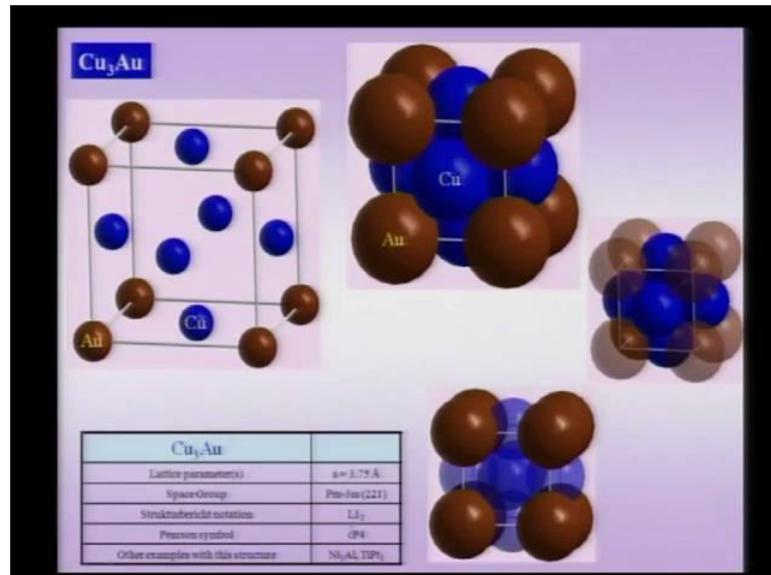
In these layers and the middle layer all the phase centering positions occupied by copper as lattice parameter of copper and gold cannot be identical. Therefore, this alloy would also have a lattice parameter c which is different from A, so this is my c axis and this is my A for instance and therefore, I can see that my a lattice parameters 3.67 times 6 and my c is 3.6. So, I would use this kind of a tetragonal units cell to describe this kind of a structure. Now, let me count the number of atoms of A and B to see that the stoichiometry is actually maintained. So, these eight gold atoms contribute one eight to this unit cell, that can make it 1 plus these two halves give me one.

So, there are 2 gold atoms in this structure, these four copper atoms are shared between two units cells. This means that gives me two so there are two gold atoms and two copper atoms in this unit cells that means actually the unit cell formula is  $Cu_2Au_2$ , which can be written in least with flow of the common factors  $CuAu$ . So, I can see that the stoichiometry is maintain when I am drawing my structure like this and since there are 4 atoms in this units cell two of copper two of gold. I know, I can describe the symptoms of a notation known as the pear sense symbol thought little advance for this stage, but still it is not very difficult to understand that is this is a tetragonal structure which shows this t.

The p here tells me it is a primitive structure that means it is no longer of a center cubic structure it is very clear and there are 4 atoms in the unit cell also. So, this a tetragonal primitive structure which is just four atoms in the unit cell, now let me consider the another kind of an ordered alloy which is also based on my original F C C kind of lattice now we of course, have to notice in this structure. This is a lattice point, but these are not lattice points. This is for instance not a lattice point, this is not a lattice point, this is a primitive structure, this is not a phase center keeps this is a primitive tetragonal structure and not the phase center cubic structure.

This has to be absolutely clear exactly the same way like we saw that this is simple cubic and not body center cubic. So, similarly this is not a phase centered cubic structure, but actually is a primitive tetragonal crystal. Now, similarly the way to understand this would be very nice if I can start at a F C C kind of lattice and then try to locate in terms of F C C lattice where my copper and gold are located.

(Refer Slide Time: 58:26)



Similarly, I will do the same thing and this again to emphasize this is a primitive structure. Now the formula is  $\text{Cu}_3\text{Au}$ , and let me write of locate the atoms within the unit cell. The gold atoms are all located within the corners are the corners of the unit cell, the copper is located at all the phase centers. So, again this is alloy, if this alloy is point this is not a lattice point; and this is obvious look at the environment of the atoms. Hence, in this, as for instance one another gold atom, at its right at a distance now, if I look at this point there is and has a gold atom to its right day.

So, obviously the environment here is different from the environment here and as I said, we have defined that lattice is such that an array of points if that all points of identical and environments. So, that environment criteria is not met therefore, it is a lattice point this cannot be a lattice point; so the other atoms will have to go part of the motive. Now the second thing after putting starting with in original FCC lattice in creating this primitive crystal, I have to note is the stoichiometry.

So, I have eight gold atoms making a total of one contribution to this unit cell in terms of gold. Now if I look at the blue copper atoms, which I being color blue for better visibility. Now, I can see that there are six phases and each one of them is shared half between two unit cells. Therefore,  $6 \times \frac{1}{2}$  is 3. Therefore, I have three copper atoms which tells me my stoichiometry, for the unit cell is  $\text{Cu}_3\text{Au}$ . So, this the space telling model of the same and in this space filling model I can I have shown these gold atoms

transparent, so that you can see that these inner copper atoms actually form a regular octahedron. So, they are formed in a form of a regular octahedron, so these blue atoms form an octahedron in the unit cell.

Now, what is the crystal structure, this crystal structure is cubic and not it is not lost any of its three fold axes in these body diagonals all of them has a threefold axis and in fact it is got highest symmetry for a cubic which is it is a primitive. It is called  $Fm\bar{3}m$  kind of symmetry and in the Strukturbericht notation, this is called an  $A1$  symbol. It has been given this order structural code  $A1$  symbol and since it is a cubic crystal.

All I need is a single lattice parameter to describe the crystal structure and lattice parameter for  $CaF_2$ , 3 points on 5 angstroms the  $Fm\bar{3}m$  symbol as I told you are something easy to understand this  $F$  stands for cubic because this is a cubic crystal. This is primitive crystal and not a phase index I have put a  $P$  and there are 4 atoms or ions in this unit cell. The 4, 3 of them being copper and 1 being gold, there are analogous structures to this  $CaF_2$ , they happen to be  $NaCl$ , which is also a technologically important compound and  $FePt$ .

So, my second structure  $CaF_2$ , which I understand in terms of the original FCC lattice, so that two nice structure which I can understand starting from a original FCC lattice of course, modifying it appropriately to fit in different kind of atoms. Accompanied with the kind of atoms I put, there will be distortion to unit cell obviously and that is what is being taken care of here.