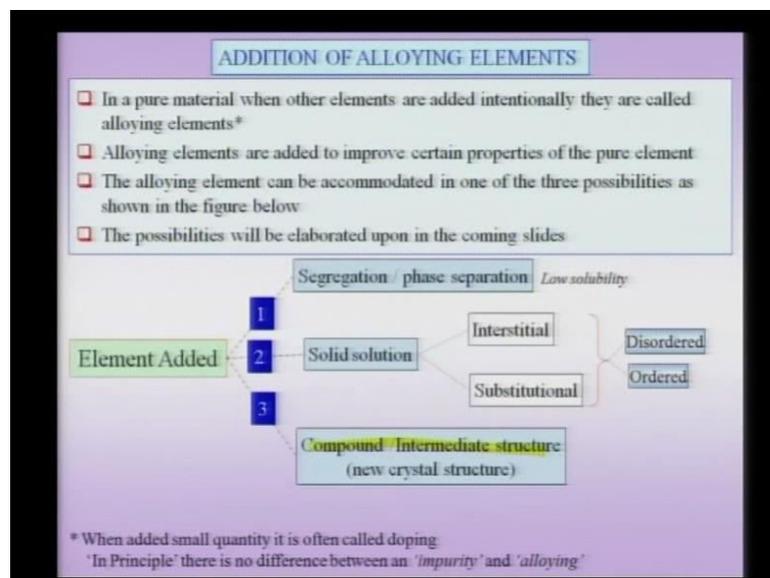


**Structure of Materials**  
**Prof. Anandh Subramaniam**  
**Department of Materials Science and Engineering**  
**Indian Institute of Technology, Kanpur**

**Lecture - 20**  
**Crystal Structures**

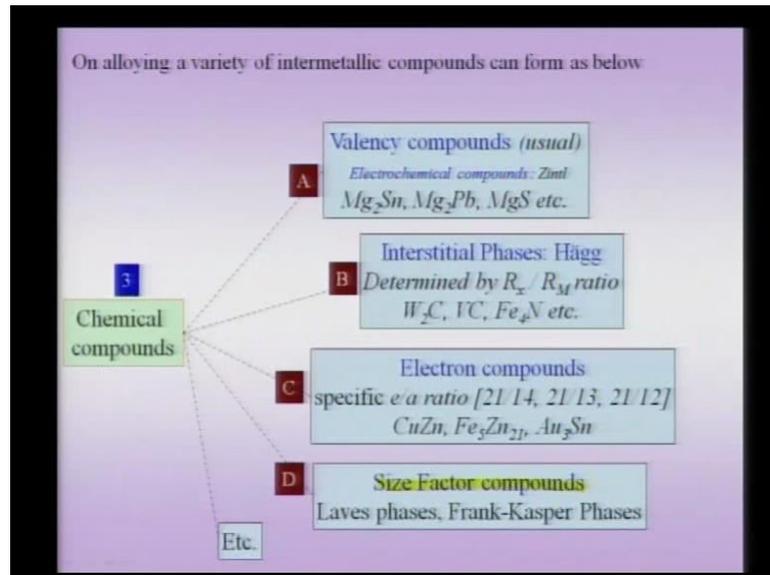
To revise what we have been doing so far, we have been discussing the affect of alloying elements.

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And specially of we have been discussing this compound structures which formed, so to revise element added can either go become segregated, you can form a solid solution which can be an interstitial or substitutional solid solution. It can be an ordered or in disordered form, and it can form an compound or an intermediate structure, then we went on to see the kind of intermediate structures which can form.

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And we were discussing that we could have various kind of intermediate compounds and we had specially discussed the differences between traditional compounds, and the compounds which form an inter metallic phases. And we were discussing valency compounds, interstitial phases electron compounds and we were taking of the size factor compounds. We are also said this is a small subset of all the possibilities, but nevertheless this is a very illustrative subset.

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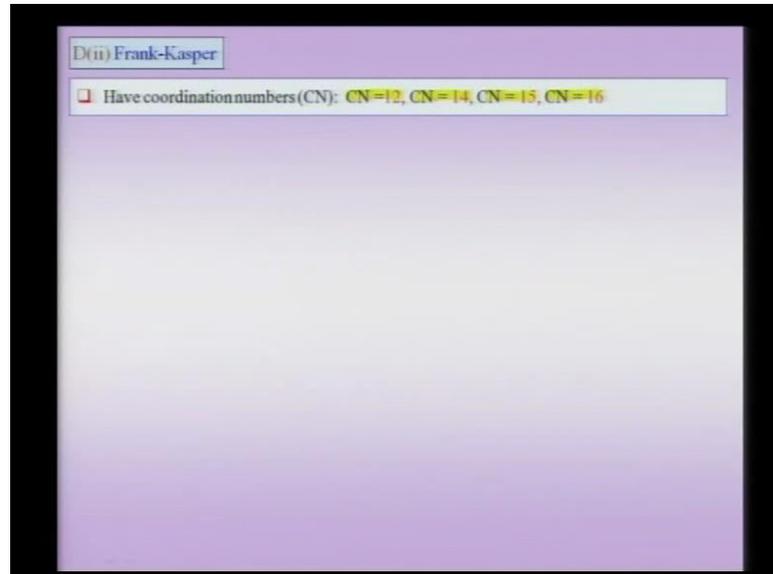
**D** Size Factor compounds: (i) Laves phases (ii) Frank-Kasper Phases

D(i) Laves Phases

- These phases have a formula:  $AB_2$
- Laves phases can be regarded as tetrahedrally close packed (TCP) structures with an ideal ratio of the radii  $(r_A/r_B) = (3/2)^{1/2} - 1.225$  [or usually  $r_A/r_B \in (1.1, 1.6)$ ]
- If  $r_A/r_B = 1.225$  then a high packing density is achieved with the chemical formula  $AB_2$  with a average coordination number of 13.3
- Crystal structures:
  - Hexagonal →  $MgZn_2$  (C15),  $MgNi_2$  (C36)
  - FCC →  $MgCu_2$  (C14)
- There are more than 1400 members belonging to the 'Laves family'
- Many ternary and multinary representatives of the Laves phases have been reported with excess of A or B elements. Some ternary Laves phases are known in systems with no corresponding binary Laves phases.
- The range of existence of the three phases (C15, C36, C14) in ternary Laves phases is influenced by the *e/a* ratio

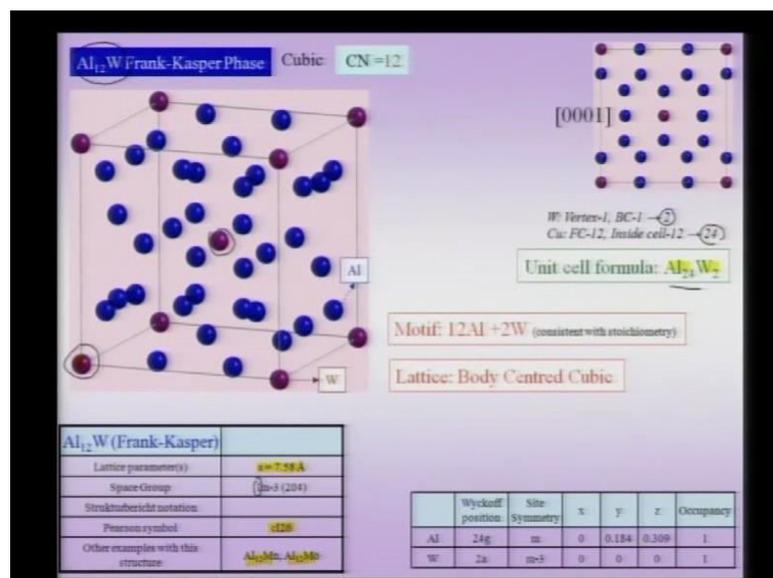
So, we had already taken up the size factor compounds and we had discussed the laves phases.

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So, let us now progress to the Frank-Kasper phases and Frank-Kasper phases typically have somewhat complicated structures, the coordination number in these phases can be 12, 14, 15 or 16.

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To illustrate what are these Frank-Kasper phases we will take up one example and specially we will take up the example of Al<sub>12</sub>W which is a coordination number 12.

That means, if you look at any tungsten atom, for instance the tungsten atoms are located in the corners here, so let me highlight the tungsten atoms. So, these are my tungsten atoms and as you can see, this is a body centered cubic lattice, therefore in my space group I have the first symbol as *i*, which tells me that it is a body centered cubic lattice.

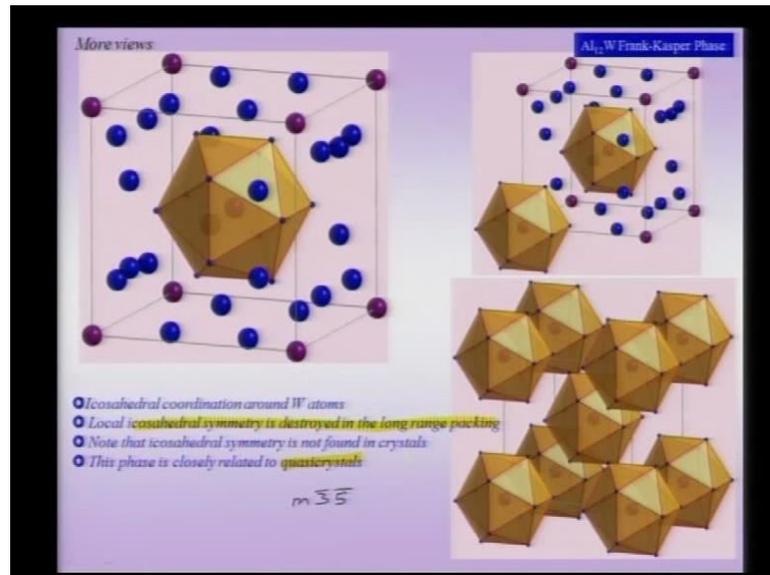
So, around each tungsten atom there are 12 aluminum atoms, and as we shall see they form an icosahedrons around the tungsten atom, this is actually a very interesting example, though a complex example, but very nevertheless a very interesting example. If I try to calculate the number of atoms in the unit cell, I see that tungsten is located at the vertices contributing 1. And there is one more tungsten atom at the body centre, therefore I have a total of 2 tungsten atoms in the unit cell.

If we want the copper atoms, at the phase centers there are 12 copper atoms and inside the cell there are 12 copper atoms, making a total of 24 copper atoms in the unit cell. So, if I write down the formula for the unit cell, it will become  $A_{12}W_2$  which are reduced to  $A_{12}W$ , so I have my formula  $A_{12}W$ , and if the total formula for the unit cell is  $A_{12}W_2$ . Now, what is the lattice we already seen the lattice is a BCC lattice, and the motif now is 12 aluminum atoms and 2 tungsten atoms, which is consistent with the stoichiometry of the unit cell or stoichiometry of the compound.

Now, the Pearson symbol tells me that structure  $C_{i26}$  that means, that there are 26 atoms in the unit cell, and you have seen that these 26, 24 are aluminum and 2 are tungsten, and this is a body centered cubic lattice. Now, if you look at other structures which form other kind of compounds, which are the similar kind of structure you have  $A_{12}m_1$  and  $A_{12}m_o$ , which also have a similar kind of structure.

Looking at the lattice parameter it is clear that it is a large unit cell it is 7.58 angstroms, and this is therefore somewhat of a complicated structure. So, how do I go about understanding this structure, here you see this has to be a 001 view not the 0001, it is a 001 view you can see that, you can clearly see the kind of symmetry it is present which is a 2-fold symmetry along the 001 direction. Now, let us try to understand the coordination polyhedron in this structure.

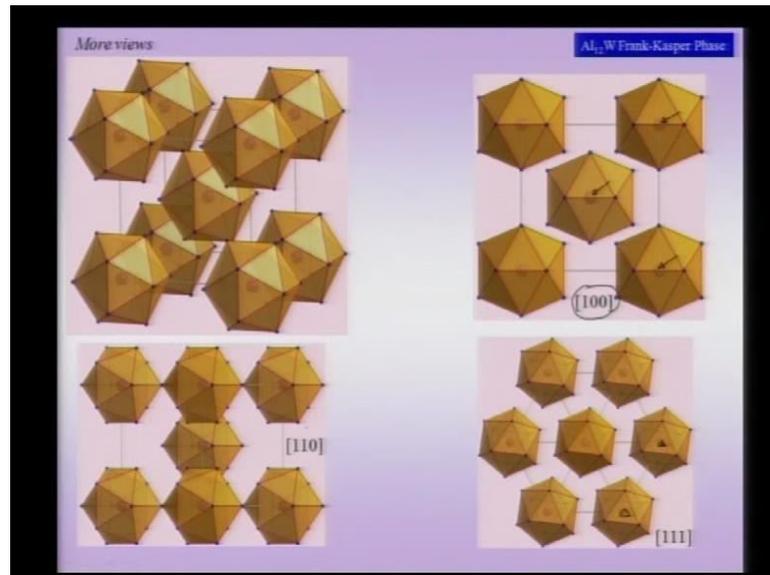
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So, I was telling you that, if I look at any tungsten atom for instance the one located at the body centered here, then I can see that there is an icosahedron of aluminum atoms around this central tungsten atom. Now, clearly icosahedral symmetry is not consistent with space filling that means, the local icosahedral symmetry is destroyed on long range packing. In the locally this structure has icosahedral symmetry, but in the long range since icosahedral symmetry is not consistent with crystalline packing, therefore I clearly see that local icosahedral symmetry is broken.

So, what is the icosahedral symmetry I am talking about, this is actually an  $m\bar{3}5$  symmetry which I write down here, so this icosahedral symmetry I am talking about this is an  $m\bar{3}5$  kind of symmetry. And this symmetry is broken in the long range ordering of the atoms in this alloy, an important point about this compound exact it is closely related to the quasi crystals. So, meaning of the quasi crystals actually have some sort of a local coordination which looks like this. But, this local icosahedral symmetry pervades in the long range in quasi crystals, which is absent in this particular crystal structure the Frank-Kasper phase. But, it is clear that this structure is closely related to the structure of quasi crystals, and often many of these structures are called rational approximates.

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So, you can see that each one of these tungsten atom, if you go on the right hand side you can see that, each one of the tungsten atom as an icosahedron around it, as you can see in this figure on the right hand side above. And the figure on the right hand side below shows that, all the icosahedra drawn around each one of the tungsten atoms. So, you can see that clearly that the 2-fold the icosahedron is facing the 001 direction of the cubic axes.

That means, along the basic directions all along it is a 2-fold direction and the 3-fold is placed along the 3-fold, so that the 3-fold direction is maintained and therefore, this is a cubic crystal. So, there are more views to understand this somewhat complicated structure, so this is my view along the 1 0 0 direction which shows my 2-fold direction of the icosahedron coinciding with this 1 0 0 direction, which is my figure on the right. So, this is my figure on the right you can see that, this is my 2-fold direction of the icosahedron which is now coinciding with my 0 0 1 direction of the cube or the 1 0 0 direction of the cube.

Now, I also mentioned that if I am looking along the 1 1 1 direction of the cube, that 1 1 1 direction actually coincides with the 3-fold direction or the 3 bar axis of the icosahedron, so that is what is clearly seen here. This is my now my 3-fold direction and it clearly coincides with the 3-fold direction of the cube and since the 3-fold axis is maintained is retained I call this a cubic crystal. Now, there is also a view which is along

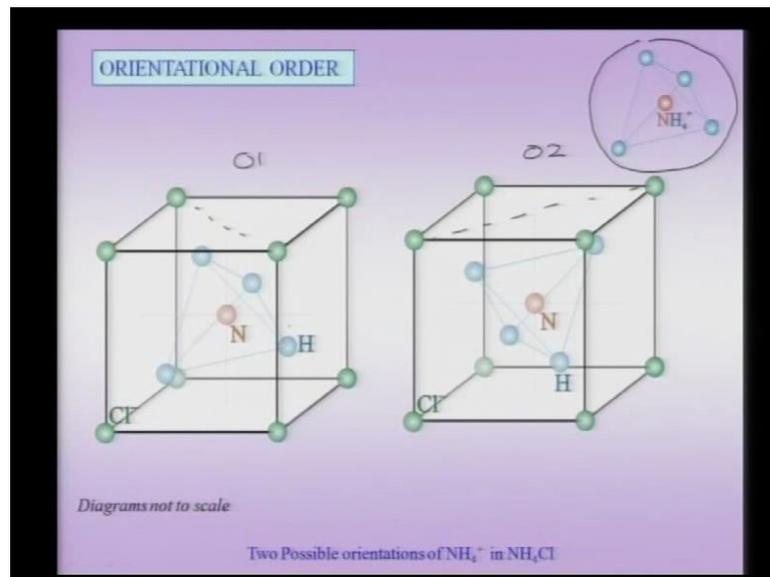
the 1 1 0 direction of the cube, and you can use all these views to understand the somewhat complicated structure.

So, if I look at the raw structure here, this might be very difficult to understand with 26 atoms in the unit cell, but once I identify my coordination polyhedra, I try to identify the symmetries of the coordination polyhedra. And try to see how the coordination Polyhedra are oriented with respect to the cubic axis and therefore, how some of the symmetries are broken, some of the symmetries are retained. Then the understanding of this crystal structure becomes somewhat accessible and somewhat easy, so and again as I pointed out even though this is a BCC lattice, it has got 26 atoms in the unit cell of two types aluminum and tungsten.

And this as I pointed out before, can also be understood from the Wyckoff positions they occupy, so the Wyckoff position is 24 g remaining there are 24 aluminum atoms, and this Wyckoff number is 2, which means there are 2 tungsten atoms in the unit cell. So, you have seen that there are variety of intermediate compounds, they can range in complexity as we seen very simple ordered structures, like the copper zinc to really complex structures.

And one of these was this A<sub>12</sub>W structure, but there can be even more complicated structures and often the number of atoms in unit cell, would go even up to 1000 or more. So, but when we want to understand these structures, often there are mechanisms or methods available to simplify these structures and to understand them. So, before we had considered the question of positional order and we had mentioned in that context that, often we defined crystals either with respect to complete order. That mean complete positional an orientational order or often we define a crystal based only on positional order or only on orientational order, so this is one example I am giving here to exemplify the point that, there could be orientational order and there could be orientational disorder also in crystals.

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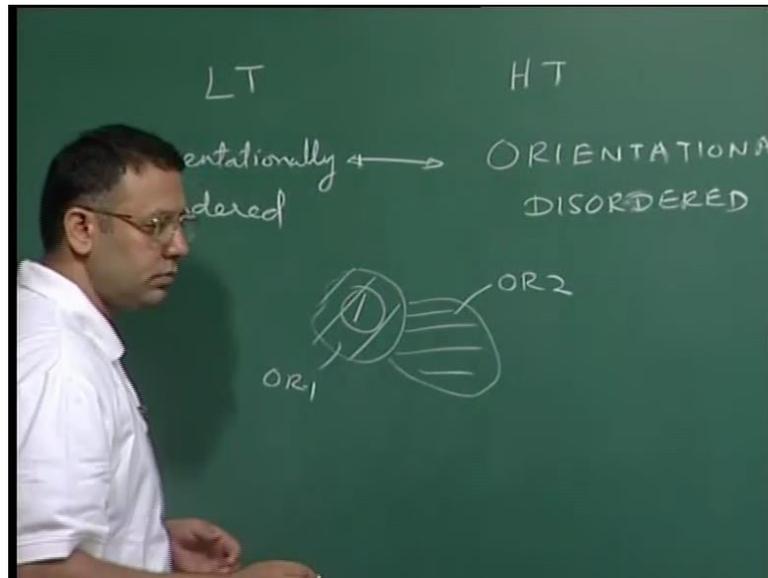
We will take up one more example later when we discuss fullerenes in the context of covalent crystals and covalent molecules, but here we take up this example. Wherein, you can clearly see that you got chlorine ions at the corners of the cube, and there is a nitrogen at the center of the cube, and there are hydrogen which form a tetrahedron around the nitrogen atom. Now, this tetrahedron has been shown on the right hand side for clarity of viewing, now this kind of a structure can show orientational order and orientational disorder.

So, how do I understand this orientational order and disorder, now in a single unit cell for instance the tetrahedral could be oriented such that, this is my preferred orientation. That means, the 3-fold of the tetrahedron that this atom is located along this side of the body tagging, it could also happen, now my this edge is not along this edge, but along the other edge that means, there are two available orientations for the NH<sub>4</sub> complex. It could so happen in a single structure that unit cell to unit cell, this NH<sub>4</sub> complex could be oriented randomly that means, in 1 unit cell it could be in this orientation 1.

Suppose I call this orientation 1, and I call this orientation 2, then it could be the orientation could change from unit cell to unit cell, in other words now this would be an orientationally disorder structure. The orientationally ordered version of the structure would be a structure, in which you would find that every unit cell has identical orientation that means, all the NH<sub>4</sub> ions are oriented identically from unit cell to unit

cell, that would be an orientationally ordered structure. So, you could have this phase transition, wherein I have typically for instance, so let me go to the board and write it down.

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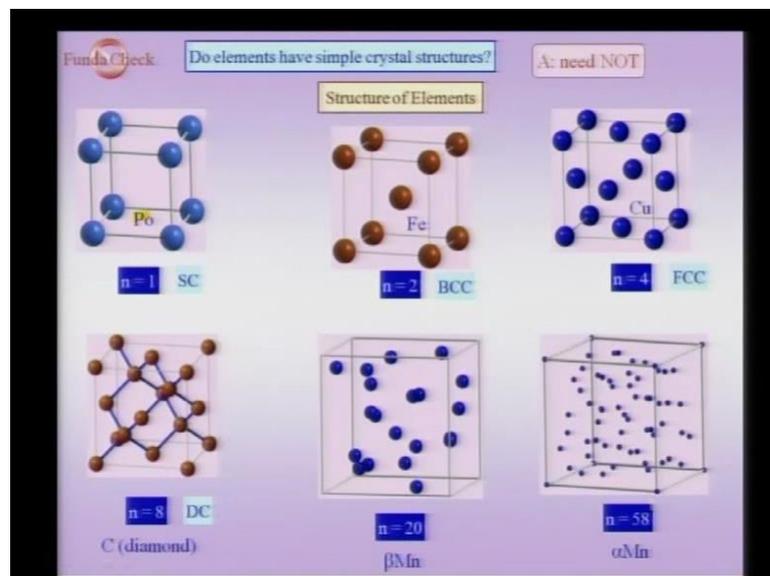


So, I have a high temperature structure and a low temperature structure, and could have low temperature structure which is. And the important point to be noted is that, in a single crystal for a or in a single material for instance you could have regions, wherein the orientational order is of type 1 in certain regions. So, this I call OR 1 and there could be a neighboring region, wherein you would have a domain wherein the orientational order could be different, so you could have OR 2 that means, orientational order 2 in a neighboring region.

Therefore, you have a boundary between these two regions, which are differently orientationally ordered, so this is clearly an example of an order disorder transformation, but this is not based on positional order, but is based on orientational order. So, this is an important point to be noted and as I said we will take up one more example later on, but for now this is the interesting and nice example, which is an example unlike the case where we the copper zinc system or the order ordered intermetallics. Wherein, we were discussing the order with respect to positional order, so this is clearly not that case, but this is a case of orientational order.

Of course, even in these systems there could be some amount of, in many of the system not particularly this example, but there could also be additionally issue of positional disorder also. But, since this motive in question does not have spherical symmetry, there is a possibility of orientating in more than one way and therefore, I have the issue of orientational order. So, this is just one example to illustrate the concept of orientational order and orientational disorder. So, now, let us go back and ask some of the fundamental questions, which we have of course, taken up in detail to answer, but nevertheless these are illustrative examples to check our fundamentals regarding crystal structures.

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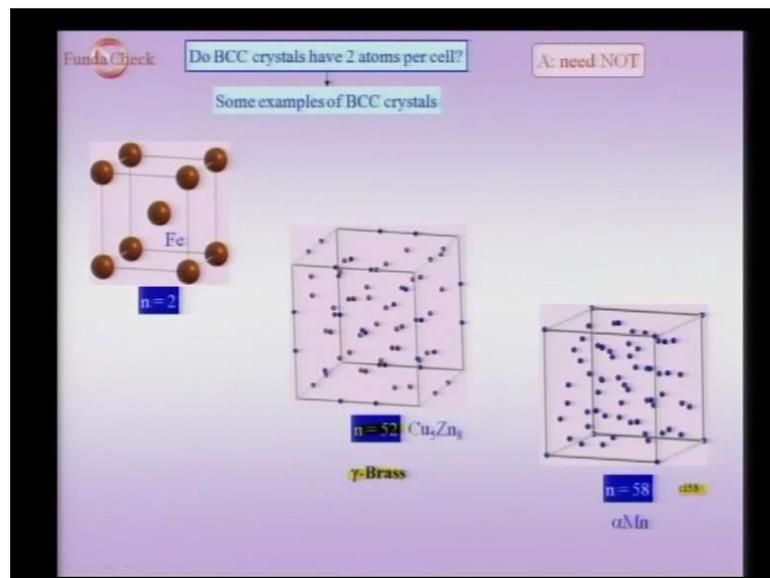
So, the first question we ask ourselves, do elements have simple crystal structures, the answer is they need not and we already considered many, many examples to illustrate the point, for instance you could have an element which is a simple cubic structure. That means, there is just 1 atom per unit cell, in the conventional representation polonium for instance, is the only element which crystallizes in simple cubic structure. And you can see that there is just 1 atom in the unit cell, you could have a BCC, for instance iron which has 2 atoms in the unit cell, you could have an example of copper FCC which has 4 atoms in the unit cell.

You could have a diamond cubic which has 8 atoms in the unit cell or you could have elements like beta manganese of course, beta representing the kind of phase it is, there

are 20 atoms in the unit cell. Or you could have the alpha manganese that means, the alpha manganese and beta manganese are two allotropic forms of manganese. So, this is also illustrating the concept of allotropy, wherein now and one common example of allotropy we have seen before is the existence of iron in both FCC and BCC forms, but here you see that, you could have alpha manganese with 58 atoms in the unit cell.

So, clearly just because you are talking about pure elements, it does not mean that the crystal structure they crystallize in need to be simple, they could get very complicated or they could of course, be simple, but it depends on the individual element, I am talking about. And there is no general rule regarding how simple or how complicated that particular element has to be. Let us try to understand, since we have mentioned that this alpha manganese has 58 atoms in the unit cell, may be later on you can take up this example.

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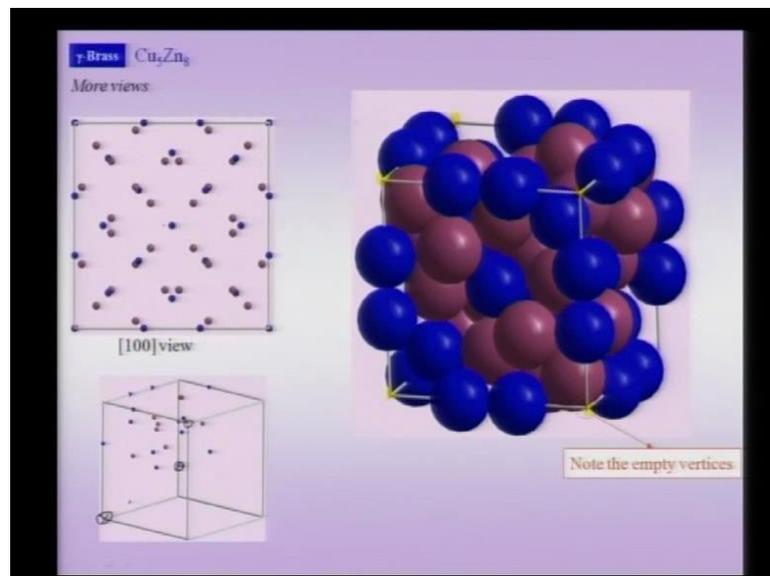


Now, the second question we are asking ourselves is that, do BCC crystals of course, you could ask the question with respect to FCC, you could ask the same question with respect to simple cubic, but here specifically you ask the question with respect to BCC crystals. 2 BCC crystals have only 2 atoms per unit cell, for instance previously we have seen the iron atom in this example had 2 atoms in the unit cell. So, the question we are asking do BCC crystals have 2 atoms per unit cell, again your answer is need not.

That means, if you have a simple example like ion, then you have 2 atoms in the unit cell, but BCC is a lattice and you could decorate this lattice with more and more complicated, more and more numerous kinds of atoms. And therefore, you could land up with larger unit cells or more complicated structures, so for instance there is a structure known as gamma brass, which is a copper zinc alloy and here you have 52 atoms in the unit cell. And we will try to understand the structure in the next line, but for now we will note that there could be 52 atoms in the unit cell.

And we already seen the example of alpha manganese which is also a body centered cubic structure, which has 58 atoms in the unit cell, and it is a body centered cubic lattice which is... So, therefore, just because a crystal is called simple cubic or a primitive cubic, it does not mean that, it has to have only one atom in the unit cell, from the clear cut examples in the case of BCC shown to in front, that there could be consists 2 or 52 or 58 or even more number of atoms in the unit cell. And in this case of course, these two are elements ion and alpha manganese, but the copper zinc is an alloy and this is an ordered alloy with specific crystal structure.

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So, let me try to understand this gamma brass, because this happens to be very interesting kind of crystal structure. And we have here this is just one slide to explain what is this gamma brass structure, often this gamma brass structure is visualized as a 3 by 3 by 3 unit cell starting with an simple BCC kind of a or a kind of a structure. But, the

structure is much more complicated than that, because after making this 3 by 3 by 3 unit cell, actually you take out all the atoms from the vertices. I mean all the 8 vertices are empty and since this is BCC that means, the vertex is connected to the body centered position by a body centering translation.

So, the body centering position should also be an empty position, so ((Refer Time: 17:36)) this is vacant, this corner is vacant, as you can see here the vertices all are vacant. So, clearly the body center also which I may be I have to draw here, the body center also has to be vacant, so all my vertices and body center are vacant, there are no atoms there. The structure of gamma brass has been understood in very many ways, and all I am giving here is a few views, for instance the 1 0 0 view shows that, all the atoms are arranged in this unit cell; and you can clearly see in the 4-fold symmetry.

And similarly you can see the space filling model of this structure, wherein this copper and zinc atoms are put together to form a rather complicated unit cell. So, clearly just because I mention term simple cubic or body centered cubic, I should not be confused by that it has to be a mono atomic decoration. In fact, it will be a multi atom decoration or it will be a decoration with more than one kind of atoms in many numbers so finally, we can land up with a rather complicated unit cell with a large number of atoms or ions in the unit cell. So, the next question on the other hand, the other extreme kind of question I can ask, the first question we had asked was with respect to an element, how can element form, what kind of a structures can an element form, so the other extreme of the question is that.

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Funda Check Does it imply that an alloy with many elements needs to have a complex crystal structure? A: need NOT

S.No	Alloy	Elements	At. %	Crystal structure	Lattice parameter (Å)	Crystal Structure of Alloy
1.	AlCoCrCu <sub>2</sub> NiFe	Al	18.18	FCC	4.049	Disordered BCC
		Co	18.18	FCC	3.537	
		Cr	18.18	BCC	2.910	
		Cu	9.09	FCC	3.610	
		Ni	18.18	FCC	3.524	
		Fe	18.18	BCC	2.866	
2.	Al <sub>2</sub> CoCrCuFeNi	Al	9.09	FCC	4.049	Disordered FCC
		Co	18.18	FCC	3.537	
		Cr	18.18	BCC	2.910	
		Cu	18.18	FCC	3.610	
		Fe	18.18	BCC	2.866	
		Ni	18.18	FCC	3.524	

Suppose, I have an alloy with many elements, so the question I am asking, does it imply that an alloy with many elements needs to have a complex crystal structure. So, this is the other extreme of the question and the answer again is need not, just because you have a pure element, single element, you cannot assume the crystal structure has to be simple. Similarly, if you have many many many elements, again you cannot assume the crystal structure has to be complex, yes it could be complex or it could turn out to be very simple.

And there are these examples which I am listing here couple of examples, the details of these examples are not important, but you can see that this alloy, for instance consists of many 1, 2, 3, 4, 5, 6 elements. And for instance this contains, aluminum, cobalt, chromium, copper, nickel and iron of course, this subscript which I had listed out are 1, and the copper is present in half that amount. And you can see that both these alloys actually form and of course, exact percentages are given here, the atomic percentages are listed here for these elements.

And you can see that copper is present in half the amount as that as aluminum, the crystal structure this combination this alloys crystallizes is happens to be BCC or FCC, as which are very simple kind of crystal structures. Of course, it cannot be an ordered structure it has to be a disordered BCC or a disordered FCC, into which these many elements crystallizing to. Of course, this automatically implies that I am talking now

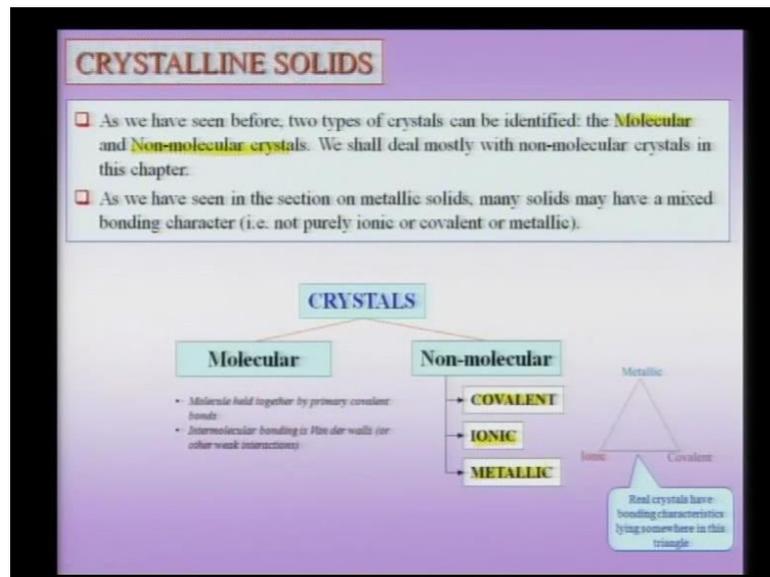
about a probabilistic kind of a definition of the crystal, but nevertheless the crystal structure is very very simple, in spite of the fact that I have added so many elements.

So, I have to be ((Refer Time: 20:30)) vary when I am using terminology like FCC BCC, I have to understand like we have already seen with many many examples that even I am just because using a term FCC crystal, I have to ask this question is in a mono atomic definition, decoration. Or suppose even in the case of the H C P as Ravi had asked before, if I am talking about an H C P crystals I have to ask, does it have an ideal C by a ratio before I can conclude that it is a closed pack crystal with 74 percent packing fraction.

If as you can see if the packing c by ratio is not ideal, then I am not going to have a 74 percent packing fraction, so I should not conclude any details before asking about the details of the crystal structure, and the elements which go on to form these crystal structures. So, with this we conclude the topic on metals and alloys, and we will take up the topic on ionic and covalent materials. So, with regard to the Frank-Kasper phase I have two corrections to I write at to point, which I need to point out to you, one is that the direction 0 0 1 which I pointed out.

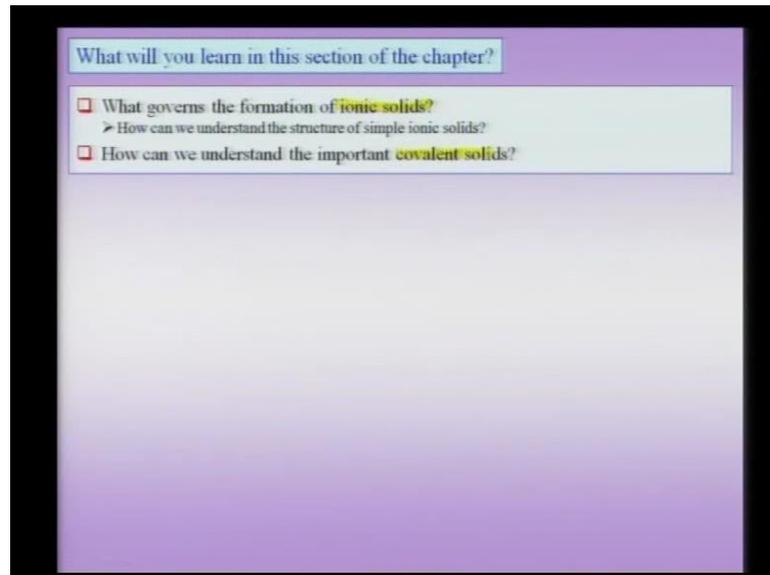
And also the motive is 12 aluminum and 1 tungsten not 2 tungsten's, so this has to be 1 tungsten, so kindly note these two errors in the slides. The next topic we take up is the topic of ionic and covalent solids and before that, let us revise the broad picture which we started off with, we already seen the crystalline solids we can identify a molecular and non molecular crystals.

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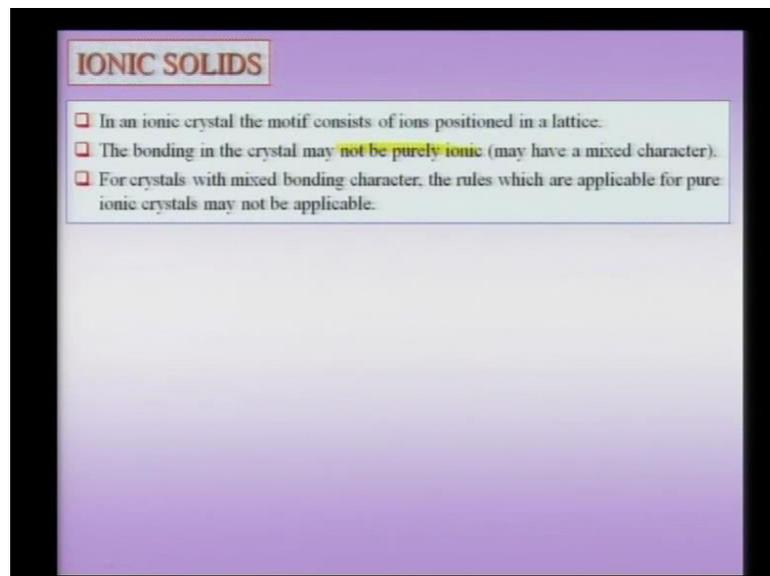
So, there are two type of crystals the molecular crystals and the non-molecular crystals, the most of the examples we are giving are actually non-molecular crystals. But, we will take up perhaps one example to illustrate the concept of molecular crystals later on in the set off lectures. Another thing which we had pointed out, though we often talk about molecular crystals of the type like, covalent crystals or ionic crystals or metallic crystals. We have to understand that more often than not the bonding character is exactly, it is not purely covalent or not purely ionic, and there is a mixed character to the bonding. And this mixed character obviously, influences the kind of structures which form and needless to say the kind of properties those structures have, so these are some of the points you need to keep in mind.

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Before, we try to understand what are the principles, which go on to form the ionic solids and how do we understand covalent solids.

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So, let us start with ionic solids, in ionic solids the motif consists of ions positioned in a lattice, so these are our usual lattices which we have been dealing with so far. And as before to reiterate the bonding may not be purely ionic that means, it can have a mixed character. The important thing about that the rules we will evolve for ionic crystals, may be violated when the bonding character is not purely ionic. That means, whatever the

rules or whatever concepts we evolved to understand the formation of certain ionic crystals, may be violated when the bonding character is not purely ionic.

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**Ionic bonds are:**

- ❑ The result of unequal sharing of electrons (electrons are with one of the atomic species participating the bond)
  - ▶ leading to negative (**anion**) and positive (**cation**) charges on the species
- ❑ **Non-directional**
- ❑ **Cation is usually smaller than the anion** (*Exception: In RbF  $\rightarrow$   $Rb^+ > F^-$* )
- ❑ The structure of ionic solids usually follow the principles elucidated by Linus Pauling (hence known as the **Pauling's rules**)

To understand the formation of an ionic crystal we 'worry' about the following (in the sequence):

**Local coordination  $\rightarrow$  Long range arrangement  $\rightarrow$  Crystal**

*The long range arrangement leads to the formation of the crystal*

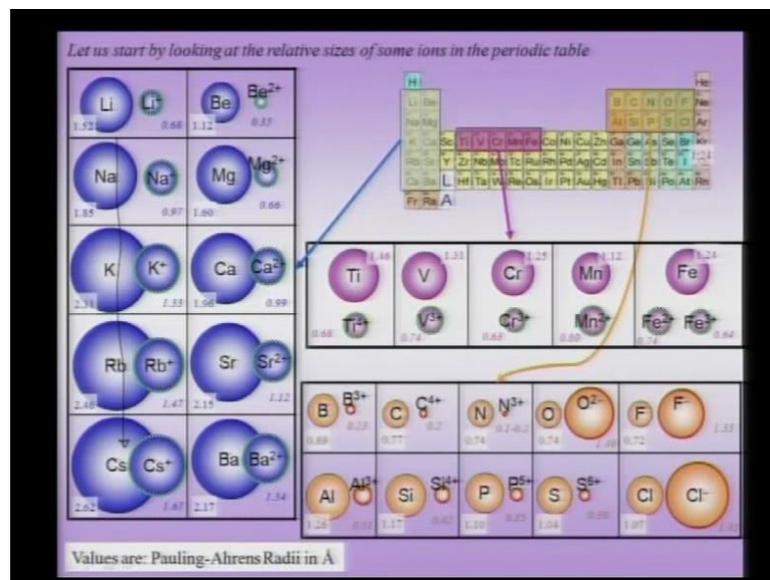
As we know already that, the ionic bonds are result of unequal sharing of electrons that means, to an leading to a negative charge on one of these species, which we call an anion and to a positive charge in another species which you call the cation. That means, anions are negatively charged species and cations are the positively charged species, and this is coming from unequal sharing of electrons. Suppose, I am talking about a covalent bond, then if there is unequal sharing in the covalent bond then we know that the it is called polar covalent bond and therefore, it is not purely a covalent bond.

We have note another thing which you might have noted is that, ionic bonds are non directional and in this sense they are similar to the metallic bond, which are also non directional. While covalent bonds has strong directionality, when you talking about the anion and cation, and both the relative size of the anion and the cation, typically the cation is smaller than the anion, so this is something which has to be noted. There are of course, exceptions like for instance in rubidium fluoride, the rubidium ion is larger than the fluorine ion, but the there are these are exceptions rather than the rule.

There are rules elucidated by professor Linus Pauling, the famous novel are it with regard to the formation of ionic solids, and you will try to understand the essence of these rules, we will not state these rules one by one, in the way they are usually stated.

But, we will try to derive the essence of these rules and try to understand some of the basic crystal structures which form, which are consistent with Pauling's rules. Now, whenever I need to understand an deformation of an ionic crystal, I first try to understand the local coordination, that how I can understand deformation of a local coordination, which involves an ion and certain ions around it. Then I worry about the long range arrangement of these ions which gives me the crystal. So, always start with the local arrangement and then I go on to the long range arrangement which would give me a crystal, so this is my sequence.

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So, before I take up these Pauling's rules or the rules of formation of ionic solids, and also it is good idea to get a feel for the sizes of the various ions, typical ions which go on to form some of the common crystal structures. For instance one of the typical structures we will be dealing with, it will be sodium chloride and here on the right hand side I have my, right hand bottom corner I have the chlorine atom and the chlorine ion. And the sodium atom and the sodium ion are correspondingly given on the left hand side of the figure.

So, you can see that my sodium ion is much smaller, this is a sodium plus ion is much smaller than the sodium atom, but the chlorine ion is bigger than the chlorine atom. So, the once it acquires an electron, it grows in size and typically the size could be almost twice or even more like you can see, if you compare the C 4 plus ion which is much

smaller than the carbon atom. So, the size could be many factors or at least a factor of 2 or somewhere close to that, so this relative sizing is very very important for me, when I am forming an compound between an anion and a cation.

But, the cation is usually smaller, suppose I am talking about a sodium cation in comparison the chlorine anion, then you can see that the sodium cation is much smaller than the sodium anion. So, similarly you could talk about a lithium fluoride for instance, and you can see the lithium cation is of course, smaller than the lithium atom itself, the fluorine ion is bigger than the fluorine atom. And the lithium fluoride you can see that, the cation is much smaller than the anion, so this is something which is trend we would like to maintain, and some of these relative sizes and are important to keep in the mind, when we are talking about deformation of ionic solids.

And as you can see if you go down the period, the sizes of the atoms increase when we the go down a period, suppose I am going down the period here, I can see that the sizes of the atoms are increasing correspondingly size of the ions are also increasing, which is true for the first period or the second period where you can see, beryllium is smaller than magnesium, which is smaller than calcium, which is smaller than strontium, which is smaller than barium.

And similarly, you can see the corresponding ions also increase in size, again if I look at my periods you can see that on an average the ions on the right hand side are larger than the ions on this left hand side. So, this is of course, on an average and individually there could be slight differences, so summarize this slide I need to know individual ions, under relative sizes with respect to their atoms. The only thing I primarily worry about, when I am talking about two ions forming an ionic crystal is the relative sizes of the anion and the cation. And this will become clear when I try to elucidate the rules, which govern the formation of the ionic crystals.

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Local coordination → Long range arrangement → Crystal

**Rules for stable configuration (*local*)**

- ❑ An anion and cation are assumed to be hard spheres and touch each other
- ❑ Anions generally do not touch each other (*may get close*)
- ❑ As many anions as possible surround the cation for the maximum reduction of electrostatic energy

**Factors affecting the *long range* arrangement**

- ❑ Maintenance of overall electrical neutrality (*any net charge from the local configurations should be offset by long range order*)
- ❑ Close packing consistent\* with local arrangement should be realized
- ❑ For cations with large net charge (+3, +4) → cation - cation repulsion will be high ⇒ the LRO may maximize cation - cation distance; even if close packing is not possible

\*The ionic crystals are not close packed in the sense of CCP or HCP crystals

So, as I pointed out when I am talking about ionic crystals, I first worry about the local coordination and then I take up the long range arrangement which gives me a crystal. So, what are the rules for the local configuration or the local stable configuration in this of course, the starting assumption of as you can see any of the starting assumptions are often violated, but we will keep these assumptions in mind, when you are deriving these rules.

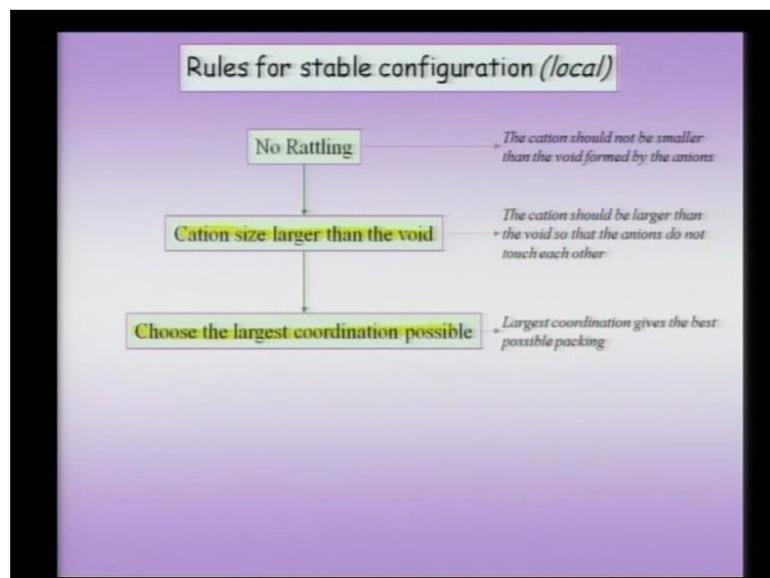
These are the anion and the cation are assumed to be hard spheres, and touch each other, this is in very similar their assumptions, we made when we talked about the metallic solids, especially the close packed structures. We have to note of course, that the anions generally do not touch each other, but may get close of course, why cannot ions of the same type touch each other obviously, they are of the same charge and therefore, there will be a repulsive force; and this will cost energy to my system, as many anions as possible surround the cation for maximum reduction in electrostatic energy.

That means, if I have a central cation, then I would like to put as many anions around it to shield the charge of the cation, which now the smaller species, the cation is a smallest species and this is the rule I will follow. Now, when I would use the term like, so let me go down to some of these rules which are for the factors governing for the long range arrangement. But, we have to remember that these rules we will take up later, but I have just listed them here for completeness, and there is just one point I would like to make

regarding, what I call the close packing in these crystals, I have to remember that ionic crystals are not close packed in senses of CCP or HCP crystals.

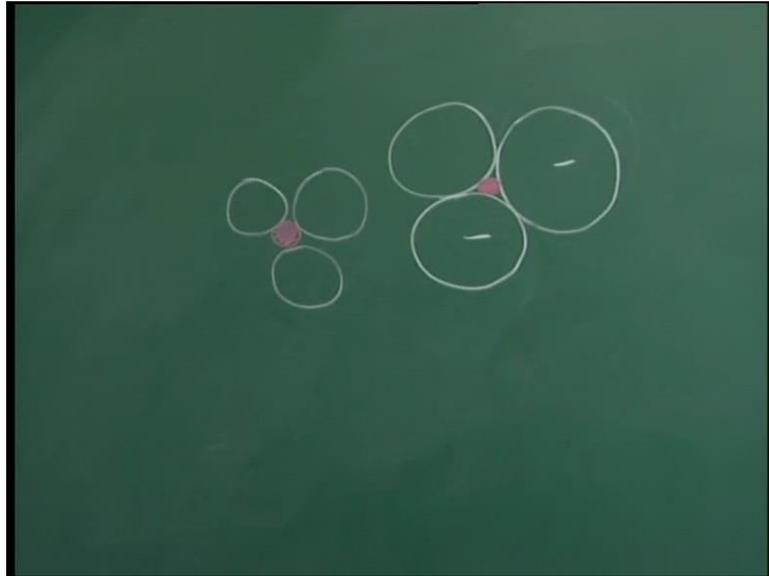
So, this point has been what we mean close packing, this is does not mean here the closest packing which would lead to a packing fraction of 0.74, this is not what I mean in this case, I just mean close packing consistent with these ionic solids. So, let me summarize the rules for stable configuration, local configuration we assumed that the anion and cation are hard spheres, the anions typically do not touch each other, but somewhat getting the close. And the cation would like to have a large coordination number around it of anions, this is what I have listed before.

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So, there is a way of listing the rules for local stable configuration, the first thing is that there should be no rattling. Suppose, I have a void form between my anions, then the cation should not be so small that it starts too rattling inside the void. So, let me draw a picture on the board to illustrate the point I am trying to say.

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Suppose, I am talking about triangular coordination of ions, these are not coming out to be the same size, but I will try to be draw them. So, I have 3 spheres here and suppose these are anions which are negatively charged, and I want to put a cation somewhere inside this void which is forming this. Now, the cation cannot be so small, that it is rattles inside the void, so that means, it cannot be like this, if it is so small then it will rattle and this is not a favorable situation.

The point number 2 I need to note is that the cation should be larger than the void, and this is obvious because suppose I have an cation of the correct size, so let me use the same figure to draw cation of the same size. So, now, if I have a cation of same size, so let me just go to the slide again, just show that people they show you the cation of the same size. So, the second point is that cation size should be larger than that of the void, so this point has to be noted and that is what I am illustrating on the board now.

Suppose, I have a cation of the correct size that means, just fix into the void this is also not a favorable situation, because if it is just of the correct size, then this anion would be touching another anion which is again not a electro statically effect to be caused, electrostatic energy and not a favorable situation. So, what I would like is that my central cation is larger than the void, so that my anion ions gets separated out, so my anions now are separated out, they do not touch each other.

So, this is the picture I want to have, now the rule that the cation should be larger than the void, sort of tells you the lower limit for the void size. Now, the consistent with this I also need to choose the largest coordination number possible that means, I have a maximum screening of the charge that means, my cation is now surrounded by as many anions as possible, which is consistent with this void rule.

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□ The ratio  $r_c/r_a$  (radius of cation : radius of anion) determines the coordination number / Ligacy for the cation → the local packing

Ligacy	$r_c/r_a$	Configuration	E.g.	
				$r_c/r_a$
2	0 – 0.155	Linear		
3	0.155 – 0.225	Triangular		
4	0.225 – 0.414	Tetrahedral		
6	0.414 – 0.732	Octahedral	NaCl	0.54
8	0.732 – 1.0	Cubic	CsCl	0.91
12	1.0	FCC or HCP		

- In the above only regular coordination polyhedra have been considered
- In some solids irregular coordination polyhedra may also be found (in which all anions are not equidistant from the cation):
  - these may be slight distortions of the regular polyhedra → with CN 2, 3, 4, 6, 8, 12.
  - in severely distorted polyhedra 5, 7, 9, 10 anions may be at different distances from the central cation (and there could be second and higher coordination shells are larger distances → these higher coordination shells have a decreasing interaction with the cation)

So, let us consider now, the radius ratios in other words, let me find out what are my void sizes and what kind of coordination numbers those void sizes give. So, obviously, the radius ratio of relevance is the radius of the anion to the radius of the cation, now this will determine my coordination number or legacy, and this will also determine my local packing. Now, I will first state all these things and I just take up one example to show the calculation, because some of these calculations we are performed before in the context of the void sizes in FCC crystals for instance.

Now, if my radius ratio happens to be in the range of 0 to 0.155, then the configuration will be a linear configuration and the legacy will be 2. Suppose, my radius ratios are in the range of 0.155 to 0.225, then I would have a triangular configuration, like the one I just showed on the board and the legacy would be 3 that means, around each cation there will be 3 anions. If my radius ratio on the other hand, happens to be between 0.225 and 0.414 and you would remember these two numbers, from our calculation of void sizes in FCC.

So, we are noted that the octahedral void is a larger void, wherein the radius ratio of the atom sitting in the void to the radius ratio of the parent atom itself was 0.414, and the tetrahedral void had as a radius ratio of 0.225. Now, if the radius ratio happens to be of course, for this range of anion sizes you will get tetrahedral coordination, or tetrahedral configuration and the legacy would be 4. That means, there will tetrahedron around the central cation, if the radius ratios are in the range of 0.414 to 0.732.

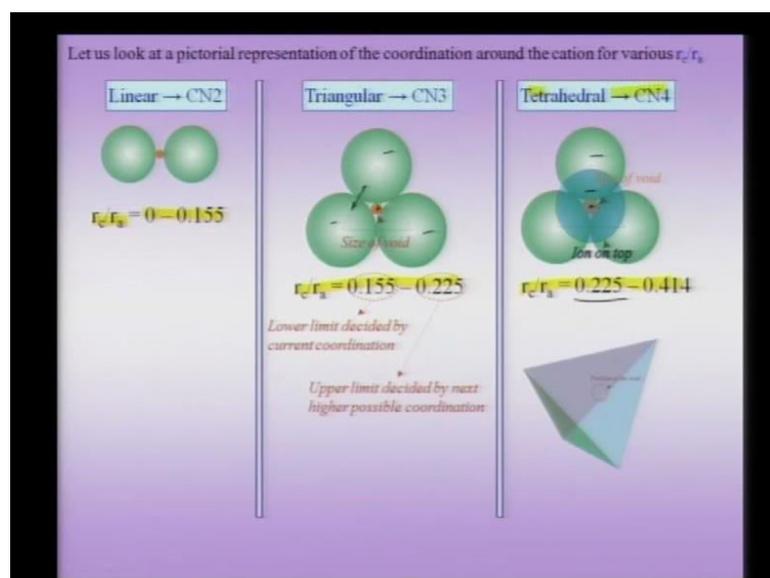
Then you would get an octahedral configuration, which means there will be 6 atoms or 6 ions of anions around the central cation. Again please remember, we had mentioned even this term this aspect before, just because the word octa appears, it is known as 8 coordination, but it is actually a 6 coordination. If the radius ratio happens to be 0.732 to 1, then the configuration of the cubic and the coordination number would be 8, and for instance we will take up an example of cesium chloride, wherein this is formed.

Now, we just got a specific  $r_c$  by  $r_a$ , cation by  $r_a$  is 0.91, now if  $r_c$  by  $r_a$  is equal to 1 that means, the cation is as large as the anion then you would find out familiar FCC or HCP kind of configuration which is a coordination number of 12. Now, there of course, these are simplified versions of the whole picture, wherein there could be many ionic crystals, wherein the picture is little more complicated. So, let us of course, keep the picture simple in this elementary course, but we need to note a few points. In the above only regular coordination polyhedra have been considered that means, you are not considered irregular coordination polyhedra.

And in some solids regular coordination polyhedra are also formed, so this is something to be noted, and if you find a irregular coordination polyhedra, as we saw in the case of the distorted octahedral and distorted tetrahedral void in BCC structure. That all there is a possibility, that there all the anions around a central cation may not be at equal distance, this is something which we need to note.

So, in other words all anions are not equidistance from the cation, if you have an irregular coordination polyhedra, so when I have a irregular coordination polyhedron. Then some of the ions may be closer, some of the anions may be closure to the central cation as compared to some of the other anions which are further away. And therefore, their interactions could have different strengths, so this is something which is possible, but we will not take up this aspect in detail during this course.

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So, let us look at this coordination polyhedra and try to understand how they form and how they look, so the linear coordination of course, simplest to understand, then this would be stabilized for a  $r_c/r_a$ , which is between 0 and 1 0.155. The triangular coordination which is what we considered on the board, would be stabilized for an  $r_c/r_a$  ratio in the range of 0.155 to 0.225. Now, wherever I have show a range, the lower limit is decided by the current coordination that means, what about the coordination sphere you are showing, the upper limited is decided by the next possible coordination.

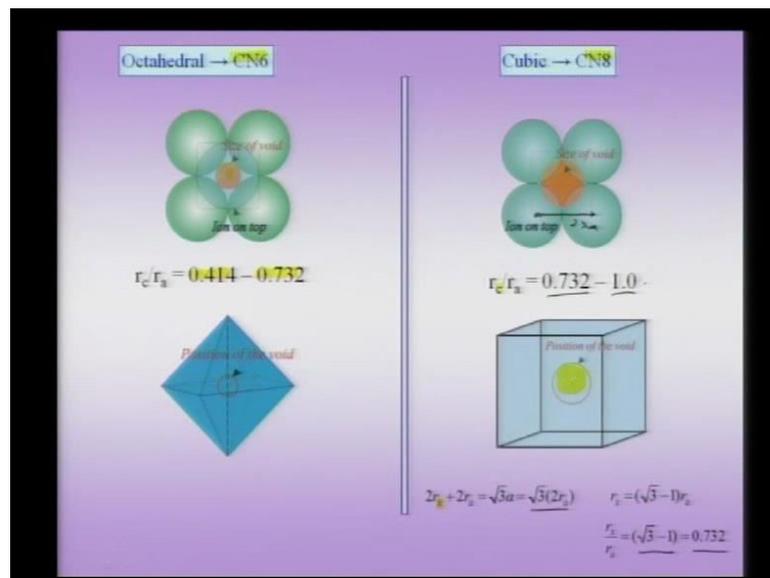
That means, the number 0.225 is not derived from the geometry which is the triangular geometry, but is derived from the next higher coordination which is tetrahedral coordination, which is a 4 coordination. So, you have the 2 coordination, the 3 coordination, the 4 coordination and the minimum possible size is 0.155 for triangular coordination and the maximum possible is 0.225. In other words, if I have a larger radius ratio of between the cation and the anion then it will prefer to have a tetrahedral coordination of, the central cation would like to have a tetrahedral coordination of anions around it rather than a triangular coordination.

And therefore, when I want to derive the number 0.155, I would look at my triangular coordination, and I want to dial the number 0.225 I would look at my tetrahedral coordination, and which actually we have done before in the case of void sizes, in the

cubic close pack crystal and the hexagonal close pack crystal. For the tetrahedral coordination which is CN 4, the radius ratios have to be in the range of 0.225 to 0.414, and I am talking about a central cation which is sitting in the central position, as you can see in this figure.

So, this is my central cation, the center here and this cation has 4 anions sitting around it in the shape of a tetrahedron. Again as before this is the least possible size and this least possible size is not a very stable size, because in that case the anions would all be touching each other. Suppose, if I have a cation of the size 0.155 times size of the anion, then my anions will be touching each other which is not a favorable situation. So, these are my negatively charged species and this is my positively charged species, similarly if I have a radius ratio of 0.225 again, my anions would be touching each other, so this is not a favorable situation.

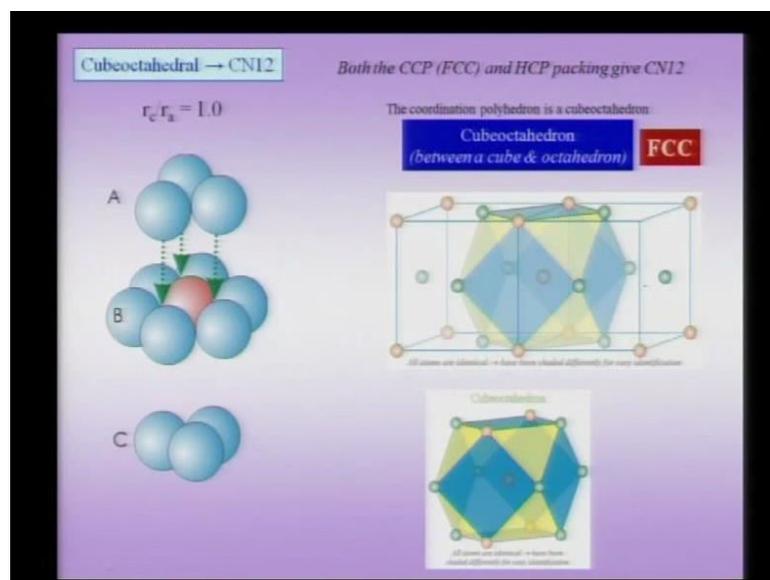
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Now, the next higher coordination number possible is CN 6, wherein you find that your 6 coordination number, wherein the central cation which is here shaded in orange has 6 anions around it, and this shape which it forms is the regular octahedron as shown below. So, for size of 0.414 which is determined by this geometry and the size 0.732 will be determined by the CN 8, geometry as shown by the calculation below, so for the CN 8 geometry, for instance suppose I have a void located at the centre.

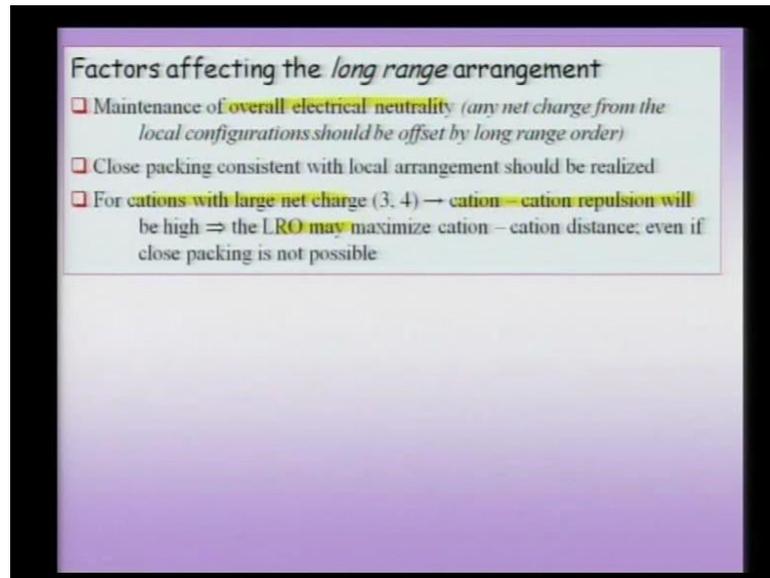
Then suppose,  $x$  is the size of the cation of course, here which is  $r_c$ , then  $2r_x$  plus  $2r_a$  is equal to the body diagonal which is  $\sqrt{3}a$ , which is  $\sqrt{3}$  into  $2r_a$ , because now my atoms are touching along this direction, so this is my distance to  $r_a$ . And therefore, it becomes  $\sqrt{3}$  into  $2r_a$  that means,  $r_x$  is  $\sqrt{3}$  minus  $1$   $r_a$ , where  $r_x$  by  $r_a$  becomes  $\sqrt{3}$  minus  $1$  which is  $0.732$ . In other words, the lower number is decided by the current configuration and the higher is stated by the higher coordination number. In this case the lower number happens to be  $0.732$  which is decided by the cubic configuration and that means, 8 anion sitting around the central cation.

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And the higher number is 1, which would be decided by the radius ratio  $r_c$  by  $r_a$  equal to 1 which is nothing but, our cases which we have already considered. And this happens to be the case of cube octahedral coordination and the twinned cube octahedral coordination. So, these two examples we already seen and therefore, we just this is just a revision for us.

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So, we can go from coordination number 2, 3, 4 then we have 6, 8 and 8 is in the range of  $r_c$  by  $r_a$  equal to 0.7321 and finally, we have when the size of anion is equal to the size of the cation, which is we have the coordination number 12, which means that, the coordination sphere has a shape or the coordination polyhedron has a shape of a cube octahedron, or a twinned cube octahedron. Now, these are the rules so far we have considered are the rules for local coordination, so let us go back and revise the rules for local coordination.

We said that first number 1, then there should be no rattling in other words, the cation cannot be smaller than that of the size of the void which it forms, the cations size should be larger than the size of the void. And this is something very important to note, because later on we now I have to replace the terminology, often we use the terminology that the especially in the case of a interstitial alloys, use a terminology that the interstitial atom is sitting inside the void, that is the terminology.

Clearly in the case of ionic solids the cation does not sit inside the void, so that is a not an acceptable terminology, the centre of the cation coincides with the void center. So, that is a more appropriate description of the system or in a more liberal sense, the cation sits in the position of the void not inside the void, so this has to be clear. Because, in the position of course, I mean that sits in the position of the centroid of the void then we also said that the system would like to increase, it is coordination number to have a maximum

coordination of anions around the cations. So, these are the three rules we sort of listed and then we try to check out the radius ratios, wherein certain kind of coordinations are stable.

And we saw that coordination number 2, 3, 4, 6, 8 and 12 can be stable based on the radius ratios, next we need to worry about the long range coordination or the long range arrangement which can now give me a crystal. And it is obvious that since, we are talking about ionic solids and each of these species is charged, having net a crystal with net charge in it would not be a stable configuration. That means, I need to maintain overall electrical neutrality, so this is the first principle which is not very difficult to understand.

In other words, if I have a local configuration, wherein I land up with a charge for instance suppose, I have a charge of minus 1 on my anion and charge of plus 1 on my cation, then this configuration will give me a net charge of minus 2. And similarly, if I have a charge of minus 1 on my anion and plus 2 on the cation then I would still land up with a net charge of minus 2. So, this minus 2 has to be offset by an overall arrangement of anions and cations which will give me a an electrically neutral system.

Now, the close packing consistent with local arrangement should be realized that means, even though I am going for close packing, whatever the local configuration I had arrived at, looking at the radius ratios that has to be maintained. If wherever there is a possibility that the net charge in the cation is very large it is not a small charge like 1 or 2, but it is more like 3 or 4, the cation, cation repulsion will be very high.

And then the long range arrangement, long arrange order naturally try to maximize the cation cation distance even if close packing is not possible. So, this is something which is sometime observed, and again to reiterate this close packing word in this context does not mean, the closest packing which we typically deal with when we are talking about cubic close pack or hexagonal close pack crystals.

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$r_c/r_a = 0.414 - 0.732 \Rightarrow$  Octahedral coordination

► Crystal structure  $\rightarrow$  FCC / HCP packing of anions  
Cations occupying all or part of the octahedral voids in the structure

⊕ E.g. NaCl (rock salt)  $\rightarrow r_{Na^+}/r_{Cl^-} = (0.97 \text{ \AA}) / (1.81 \text{ \AA}) = 0.54$   
Structure  $\rightarrow$  FCC (Cl<sup>-</sup>)  
Octahedral void positions occupied  $\rightarrow$  All (Na<sup>+</sup>)  
 $=$  Two interpenetrating FCC lattices (origin of SL-1 at (0,0,0) with Cl<sup>-</sup>; origin of SL-2 at (1/2,0,0) with Na<sup>+</sup>)

NaCl  
 $a = 5.56 \text{ \AA}$

► Note: FCC positions and the position of octahedral voids are interchangeable.  
FCC  $\rightarrow$  (0,0,0) & (1/2, 1/2, 0) shift origin to a octahedral void  $\rightarrow$  (0, 0, 1/2)  
New  $\rightarrow$  (0, 0, 1/2) & (1/2, 1/2, 1/2)  $\rightarrow$  atoms are now in place of Octahedral voids

So, let us try to take up some examples to understand the formation of these ionic crystals, now we had noted that, when the  $r_c/r_a$  ratio is in the range of 0.414 to 0.732. Then you would have an octahedral coordination, and the crystal structure will be an FCC or HCP packing of anions. Now, let us take the example of sodium chloride, now in sodium chloride the radius of the sodium ion to the radius of the chlorine ion is 0.97 angstroms to 1.81 angstroms, which is 0.54. Clearly 0.54 lies in the range of 0.414 to 0.732 which is in the correct range for octahedral coordination.

Now, in this case of course, in this particular example all the octahedral void positions are occupied, but in general you could note that some of the octahedral void positions only may be occupied in some different structures. But, here in this particular case all octahedral void positions are occupied, in other words in all the void positions formed by these anions, the chlorine anions, you would find sodium cations sitting. Now, we already seen this structure and analyzed it in detail, in terms of its lattice, its motif, so we do not have to understand it.

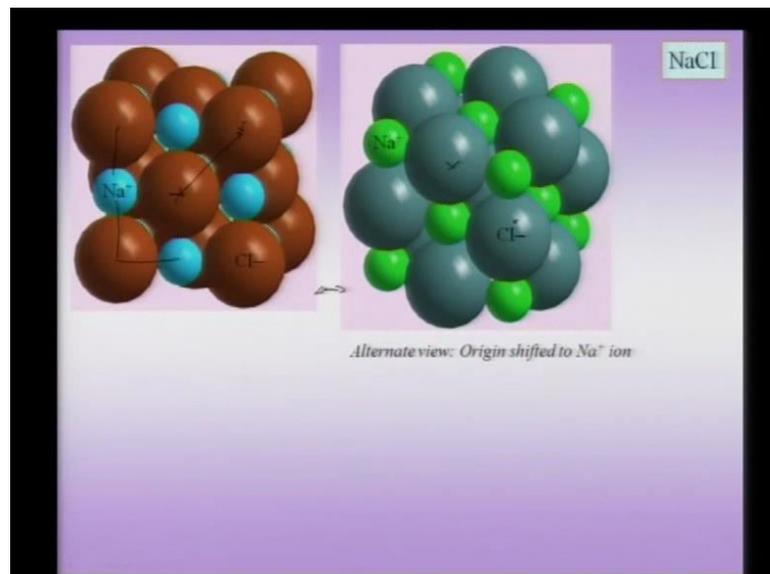
The only thing we need to understand it now, in terms of the packing of the anions and cations and the charge neutrality, so since this unit cell already we know has 4 sodium ions and 4 chlorine ions. Therefore, the charge neutrality is maintained, because the charge on sodium is 1, the charge on chlorine is 1 that means, there is 4 minus 4 plus in

the unit cell, which means the crystal the unit cell which also means that the crystal is electrically neutral, so this part is taken care of that.

Now, how do I understand the octahedral coordination in this looking at the crystal structure, that is obvious which we have already done before, but just to revise the concept. That if I take any anion, now this is my cation at the center, then this cation is surrounded by this anion here ((Refer Time: 48:21)), this anion here, this anion here, this anion here, this anion here this anion here. So, it has an coordination number 6, which is what I call octahedral coordination of anions, I can similarly pick up any cation for instance even if I pick up this, we find one is above and one is below.

And one is to the left, one is to the right and I will find that totally there are 6 anions around any cation, giving me the coordination number 6. Now, in this case of course, the lattice is FCC and the motif is as we had seen before is 1 anion plus 1 cation which is now my motif. We had also seen how to understand this structure in terms of two interpenetrating FCC sub crystals, or FCC sub lattices which are occupied selectively or two sub crystals, one sub crystal having sodium ions and one sub crystal having chlorine ions.

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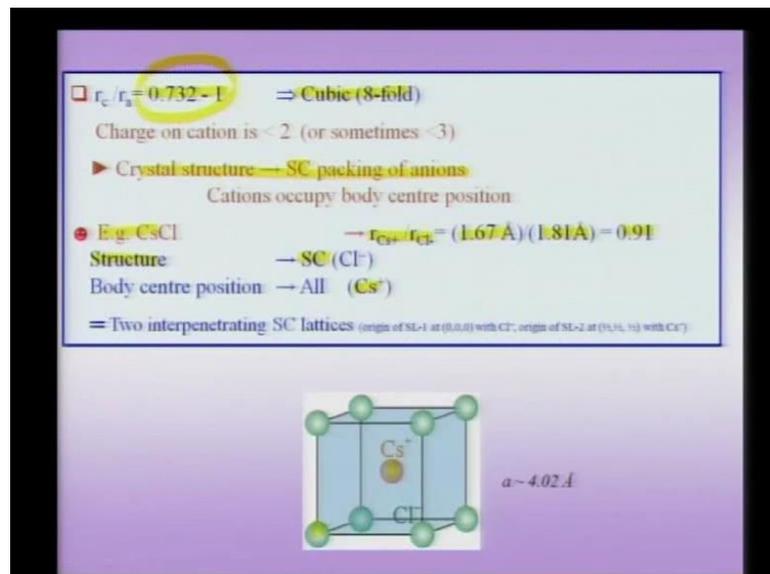
So, let us have a view of the same crystal, in terms of space filling, so this is a space filling model of the same and you can clearly see from this space filling model. Now, that the sodium ion is obviously, much bigger than the void size that means, that now my

chlorine anions are not touching each other, there is no physical touching between the chlorine anions. Or having this picture for this in this my chlorine anion and this is not touching my other chlorine anions, there is no physical touching.

So, my sodium ion is actually much bigger than the void, does not sit within the void and this is a necessary condition for me to have a lower energy. And this crystal as we have noted before can equivalently we describe, either by putting the chlorine ion at the origin or the sodium ion at the origin and these are, therefore two equivalent pictures of the sodium chloride crystal. Now, in the sodium chloride crystal it is not a very relevant question to ask, is there is a something known as a sodium chloride molecule, because in ionic solids this is just an array of sodium and chlorine ions.

So, there is the concept of a molecule does not arise in these systems, in other words the sodium ion is equi space between that means, this sodium chlorine bond or this sodium chlorine distance is exactly same as this sodium chlorine distance. Since, it is located in between the two or for instance this sodium chlorine distance is also exactly the same. So, there is no molecule of sodium chloride it is just an, r a of ions placed in a regular lattice and therefore, this is my sodium chloride distance.

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Now, let us take another example and this is an example of cesium chloride and we had noted before that suppose, I have my radius ratio in the region of 0.7321. Then I would have an eight fold or cubic coordination, in this case we are it is observed that the crystal

structure will be simple cubic with cations occupying the body centered position. So, to take up this specific example of cesium chloride,  $CsCl$  the radius of the cesium ion to the radius of the chlorine ion is 1.67 angstrom by 1.81 angstrom, which is 0.91.

So, 0.91 lies in the radius ratio regime of 0.732 to 1, it means I will have a cubic coordination and the crystal structure will be simple cubic. So, the crystal structure is simple cubic and my chlorine ions would occupy all the corners, and my cesium ion would occupy the body centre. Again in this case you note that we already approaching radius ratio which is very close to one, therefore my cesium ion it is almost as big as my chlorine ion. We already know how to understand this crystal structure, in terms of two interpenetrating simple cubic lattices of simple cubic crystals.

That means, that I can have my origin of the one of the sub lattice at 0 0 0 and the origin of the other sub lattice at half half half, one sub lattice is preferentially occupied by chlorine ions, the other sub lattice is occupied by cesium ions. So, to revise this slide I have my radius ratios of cesium ion to chlorine anion as 0.91, which means that I in the correct radius ratio for an 8 fold coordination. And 8 fold coordination would imply that in the long range, I am going to get a cubic arrangement which happens to be a simple cubic crystal.

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Other examples

- Now we consider cases where the bonding is not purely ionic
- Si-O bond in Silica is 50% ionic and 50% covalent
  - $r_c/r_a = 0.29 \Rightarrow$  Tetrahedral coordination (assuming Pauling's rules)
  - $sp^3$  bonds  $\Rightarrow$  Tetrahedral coordination
  - Observed  $\Rightarrow$  Tetrahedral coordination

As I pointed out in the beginning of these set of lectures that, the bonding may or may not be purely ionic, and if the bonding is not purely ionic, then the possibility increase

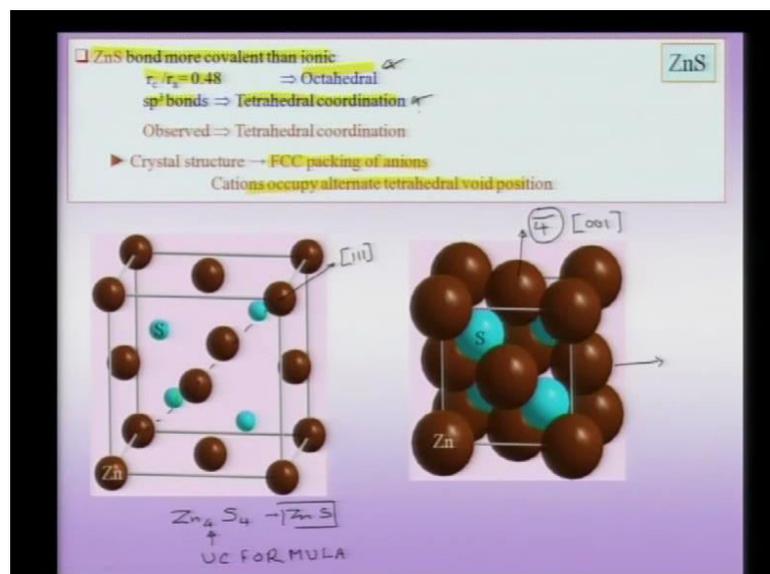
and let us consider two possibilities which will illustrate what I am saying now. So, let us take the example of silica  $\text{SiO}_2$ , wherein the bonding is 50 percent ionic and 50 percent covalent. In this case, if I talk about the radius ratio  $r_c/r_a$  turns out to be 0.29, which is in the correct region for tetrahedral coordination.

So, let us look at this is 0.29 in the table which we had considered before, so 0.29 is in the correct region for tetrahedral coordination, so this is my tetrahedral coordination, this is what it should have. Now, it so happens that in silica, the bonding as I said is not purely ionic, it has got some covalence to it and there is some  $sp^3$  kind of hybridization, an  $sp^3$  hybridization tells me that it needs to have a tetrahedral coordination again.

Since, the rules of the covalent character and the rules of ionic character are both coincident, which both tell me that there has to be tetrahedral coordination, the actual observed coordination is tetrahedral. And therefore, there is no problem, because the additional aspect that the bond is somewhat covalent, so this is actually very interesting example. Because, now even though I have my covalent character to the bond, but still this structure happens to be ionic.

I mean the what are the rules I get the ionic character, whatever the rules they dictate they happen to be consistent with my rules coming from the covalent character. And therefore, there is no change I need to make with respect to my understanding of the rules of the ionic bonding.

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Now, this is a different kind of an example, which is the example of zinc sulfide, zinc sulfide the two common forms is the zinc blend and ((Refer Time: 54:48)) side structures this is the cubic form, which is the zinc blend form. And here the bond is more covalent than ionic, if you look at the  $r_c$  by  $r_a$  ratio which is 0.48, so let me go back to my table to see where is 0.48? ((Refer Time: 55:04)) So, 0.48 lies in the region of 0.414 to 0.732 which means that, I need to have octahedral coordination or a coordination number 6.

So, have what my rules of ionic packing tell me is that the coordination number 6 is preferred, but here again we have got certain covalent character to the bond, and kind of hybridization which is observed as  $sp^3$  hybridization, which tells me that I need to have a tetrahedral coordination. This is something like what I would deal have in the case of diamond in diamond, you have  $sp^3$  hybridization and you would have a tetrahedral coordination. But, here the dominant factor happens to because now, what my ionic rule tells me is inconsistent with what my covalent rule tells me, there is sort of in mismatch in the kind of rules.

And therefore, the winner in this case happens to be the covalent character, in other words what is actually observed is a tetrahedral coordination and not the octahedral coordination, which what are purely understood from the rules of ionic packing. Therefore, what I actually observe is tetrahedral coordination, and the structure is shown here below, wherein I have an FCC packing of anions and the cations occupy alternate tetrahedral void positions. In other words, although again to say they do not sit in the void and they do not occupy all the void tetrahedral void positions, but only the alternate tetrahedral void positions.

So, my lattice now is FCC and my motif now would be one zinc and one sulfur ion of course, the zinc is sitting at 0 0 0 and the sulfur is sitting at quarter quarter quarter, but there are only four sulfur ions within the unit cell, which gives me, which they themselves form a tetrahedral. The stoichiometry for this structure is obviously, maintained, because zincs in the face centering positions and corner position together give me a perturbation of 4. So, there are 4 zincs, so the unit cell formula will become  $Z_n$  and there will be sulfur also 4 and therefore, it is the  $Z_n S_n$  it is my, so this is my unit cell formula.

So, on the right hand side you see a space filling model of the same, wherein you clearly see that out of the 8 available tetrahedral void positions, only the alternate set is occupied. Therefore, this structure obviously, does not have a 4-fold axis, it has only one a 2-fold axis or equivalently looking it has got a 4 bar axis along the 001 direction. So, this is my 0 0 1 direction or equivalently anyone of the other directions, I would have a 4 bar axis and not a 4-fold axis, nevertheless this is a cubic crystal, because it has got a 3-fold axis along the body diagonal.

So, my 3-fold axis and you get pure rotational axis, now this is my 1 1 1 direction, which is now has to be a 3-fold axis and since it has got a 3-fold axis, this is a cubic crystal. So, to revise what we have done so far, if we have pure ionic bonding and in the most simplest cases, all I need to worry about is the first coordination shell of anions around the central cation. I have rules for local packing, and I have rules for global packing which are consistent with whatever I have all for the local packing.

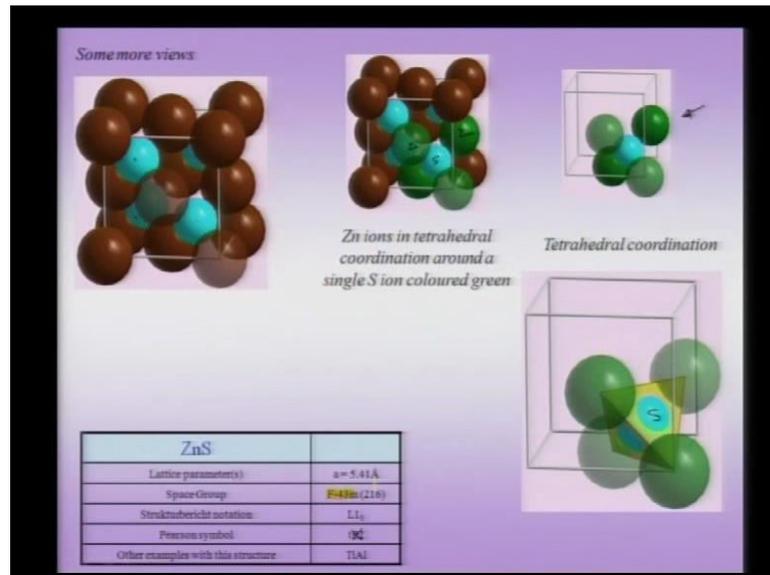
The local packing is simple that I need should not have no rattling, I should have an cation which is typically larger than the void, and I would like to maximize my coordination. The fact that I have to maximize my coordination, sets the upper limit for the number the coordination shell I need to consider that means, if suppose in the case for instance, let me take up in the table. Suppose, I have an cation to anion ratio, which is larger than 0.414 that means, that now the cation instead of having a tetrahedral coordination would actually put up an octahedral coordination around it.

So, it since you can have an higher coordination number it would rather not have a tetrahedral coordination this sets my upper limit, the lower limit is derived as we saw from the current configuration which is my tetrahedral configuration. So, this we already saw now the longer range packing has to be consistent with the short range packing and we have already seen that the important points was charge neutrality or electrical neutrality. And in some cases wherever there is a large charge in the cation you would sacrifice this close packing arrangements, but rather go for maximizing the cation distance.

Some of the simple compounds which are as close to ionic as possible or purely ionic as possible are sodium chloride for instance or cesium chloride which obey my rules for ionic packing, but then there are systems where in you have certain covalent character to

the bonding in other words in those systems. I find that the other rule or the other character to the bond for instance the covalent bond could be the dominant factor. In other words even though my in the zinc sulfide case my rules of ionic packing told me that I need to have an octahedral coordination, but actually I will land up with this actually a tetrahedral coordination for the sulfur atoms.

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So, actually you can draw tetrahedra of sulfur around the octahedra and this is some more views of the same zinc sulfide structure wherein you can see some of the atoms are shown transparent for you to have a better visualization. For instance you can see that the four sulfur ions clearly in this view and there are more ions here.

Four green ions have been shown around a sulfur ion. So, this is my sulfur and you can clearly see the four zinc ions are marked in green to show the tetrahedral coordination in the picture on the right hand side which I am marking here. I have removed all the other ions from view just to deal with the tetrahedral coordination around the central sulfur ion. So, this is something you can clearly see and in this last picture here this is my sulfur ion at the bottom and you can see clearly a tetrahedral coordination of zinc ions around the central sulfur ion.

Now, as I pointed out this is not this is a structure which is face centered cubic it is. So, this is wrong here. So, let me cross this off this is not a this is something which is wrong. So, I will this is not to. So, this is got a  $4\bar{3}m$  symmetry and it has not; that means, it

does not have the usual 4-fold axis which many of the proper FCC crystals have. So, this is of lower symmetry or than the higher symmetry possible for cubic crystals. So, with this we will take up covalent crystals.