

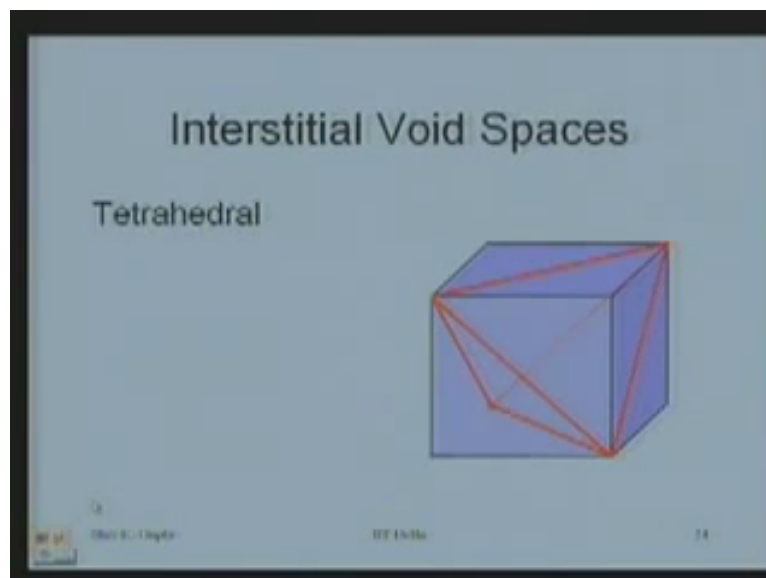
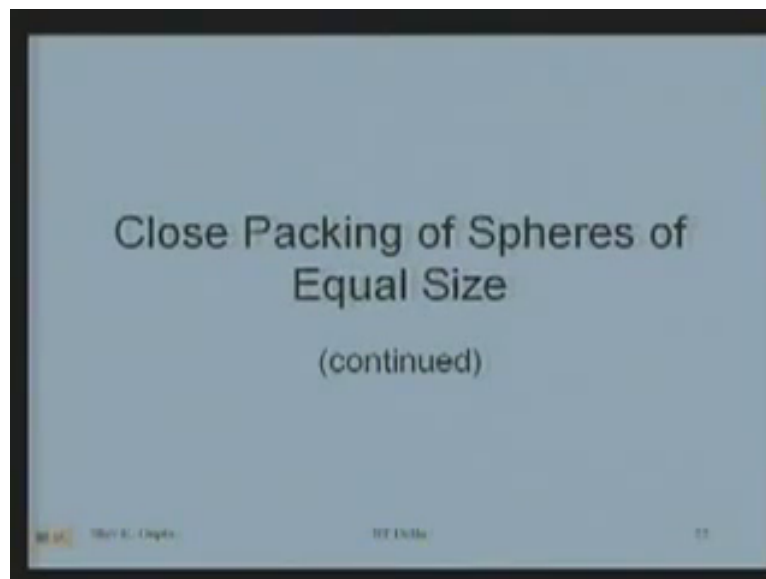
Material Science
Professor S. K. Gupta
Department of Applied Mechanics
Indian Institute of Technology Delhi
Lecture No 8
Close Packing of Spheres of Equal Size (Contd.)

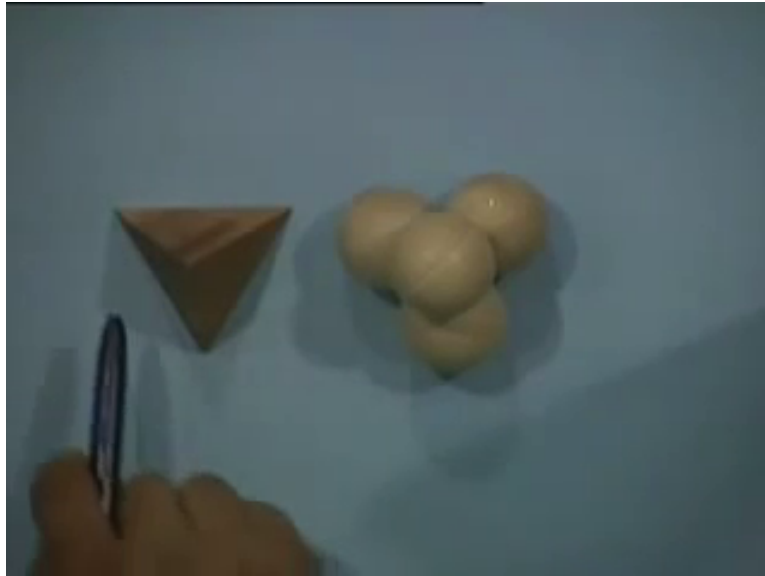
In the last class we were talking about the metallic crystal which have non-directional bonding, basically what we tried was to fill space with equal size spheres in as close packed manner as possible and we got 2 crystalline arrangements one is FCC where the stacking was of closed packed plane abc abc and another one hexagonal close packed structures where the stacking was ab ab ab. We had seen the packing efficiency of such closed packed structures is 74 percent probably the highest leaving some 26 percent space which we will see today.

Then while talking about that we also said there are some metals which do crystallise as body centred cubic crystals and either they are alkali metals or transition metals the reason could be in alkali metals the thermal entropy being very high tries to randomise the arrangement and if our contention is correct then at low temperatures they should be become closed packed structures we saw that they do, some of them but in transition metals there is partial covalent nature of the bond which tries to Orient the bonds rather than making the stacking close packed and tends to become body centred cubic.

If that is correct this can be seen in iron, iron starting from 0 Kelvin right up to 910 degree centigrade remains body centred cubic covalency or partial covalency is playing its role and 910 degree centigrade the thermal vibrations so much that covalent nature is overcome and becomes metallic becomes FCC face centred cubic. Once again thermal energy takes over randomisation thermal entropy increases at 1410 degree centigrade or so again it becomes body centred cubic, so we can see both these arguments working in iron.

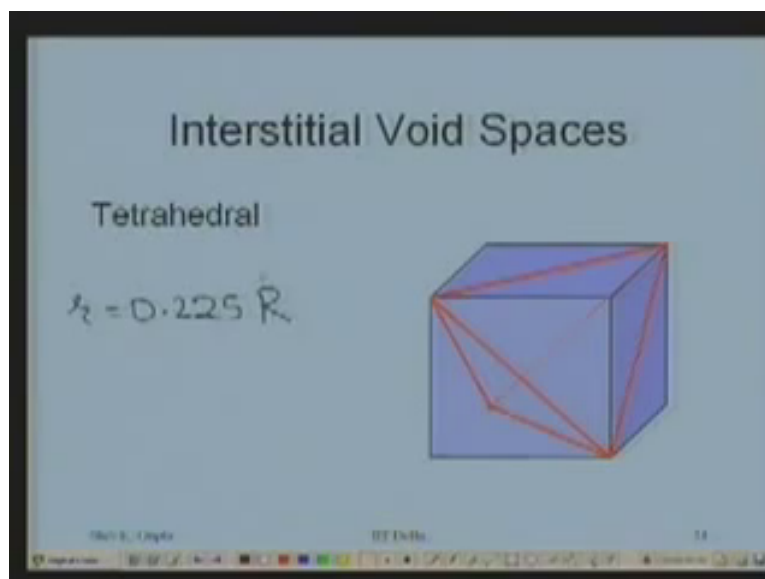
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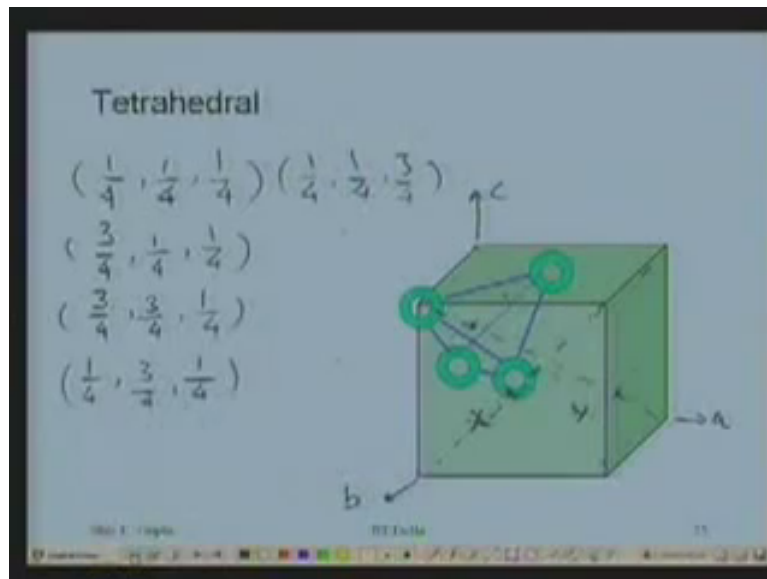




So today we shall try to look at the void spaces and then try to see if I have spheres of a different size not of the same size what happens? Yesterday we had begun to see this, this is tetrahedral void is formed like this, so the a atoms on the lower plane of 3 of them form a cavity and the forth the b plane comes and sits on top of these the space in between here is the tetrahedral void. Why we call it tetrahedral void is because of the shape formed when I joined the centres of this spheres these are the 3 spheres centres the a plane and this is the top and the b plane they form a regular tetrahedron like this and then the centre of this tetrahedral void is the centre of the cavity which we are looking for.

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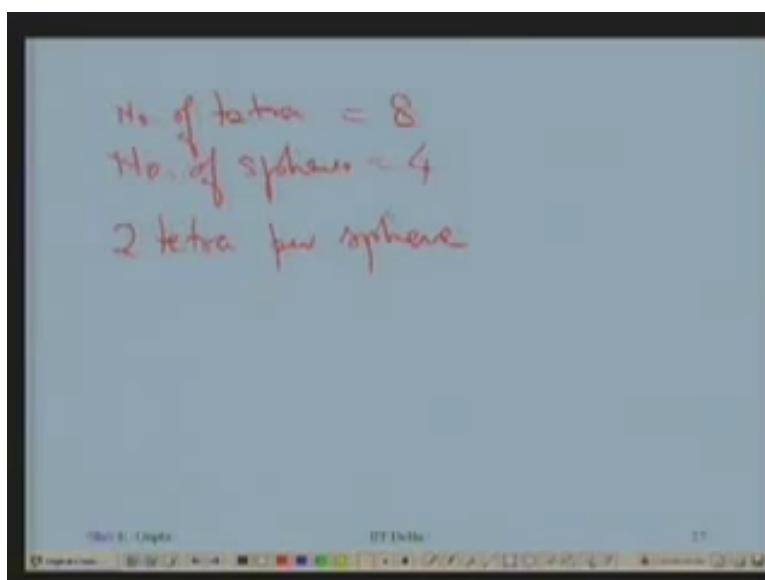
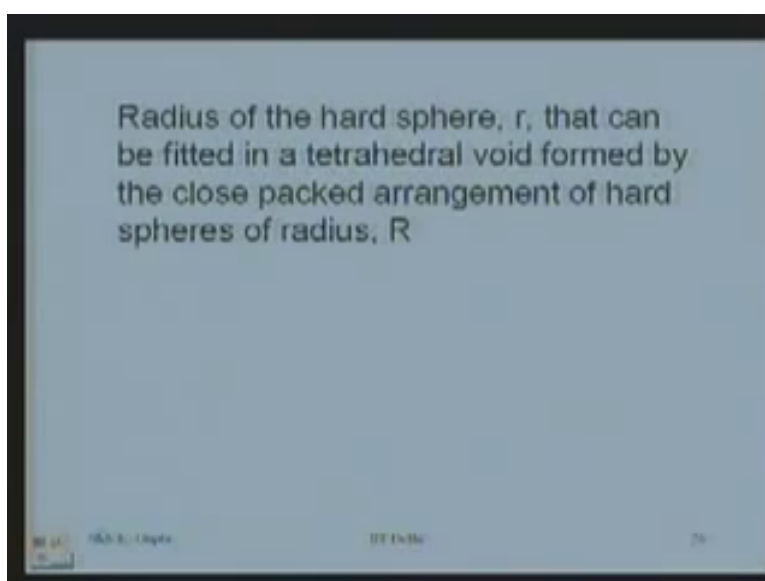




In the last class that is we saw the a tetrahedral void and we try to work out the size of the sphere that can small sphere that can be fitted in and we did work it out to a value of about 22.5 percent of the sphere that forms the tetrahedral, right. Now coming back to face centred cubic crystal I have shown one tetrahedral the more such tetrahedral in this unit cell where are these? This is the corner this is the face centre that is the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ face centre that is the face centre joining this I get one tetrahedral hole here which is actually on this body diagonal. Alright this you can find at each corner of the cube there will be a tetrahedral formed, right can we write down the coordinates of these how many such corners would be there, there are 8 corners like that and that shall be the another one is going to be here on this.

This corner the face centre here the face centre here and the face centre at the back they will form a tetrahedral, so each corner is forming a tetrahedral and if you start from one origin you will find that one of them is at 1 by 4, 1 by 4, 1 by 4 can start you can do that put this a axis call this as the b axis call this as the c axis that is the one at that corner near the origin that is on this body diagonal somewhere here. Then similarly you can find out this one which will be 3 by 4th on a, 1 by 4 on b and 1 by 4 on c, can find out the one on this body diagonal here that would be 3 by 4 on a, 3 by 4 on b and 1 by 4 on c and then the next one you can find out which is on this body diagonal here that shall be one by 4 on a 3 by 4 on b and 1 by 4 on c. It will be similar other 4 on top but the c height instead of becoming 1 by 4 there will be 3 by 4 is similar to that, okay. 1 by 4, 1 by 4 and 3 by 4 and so on and so forth you can add all the 8 coordinates but all these 8 volumes of the tetrahedral are well within the volume of the unit cell itself right.

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So...well this is something we have worked out within the same unit cell we have 8 and how many atoms do I have in the unit cell? Yes please.

Student: 4.

Prof: I have 4 spheres, number of tetrahedral holes?

Student: 8.

Prof: 8 Number of spheres is equal to 4. So therefore every sphere there are 2 tetrahedral holes, is that clear? So if I have a crystal one mole let us say one mole of FCC copper, how many tetrahedral holes do I have this one mole of FCC copper? 2 moles as a meaning of it, there are 2 moles tetrahedral holes are there and if I have spheres of the right size of 0.225 are

I can fit in those 2 moles of those atoms, right. Usually you will find that when you are (()) (11:20) such small spheres are not there even hydrogen is bigger than that usually.

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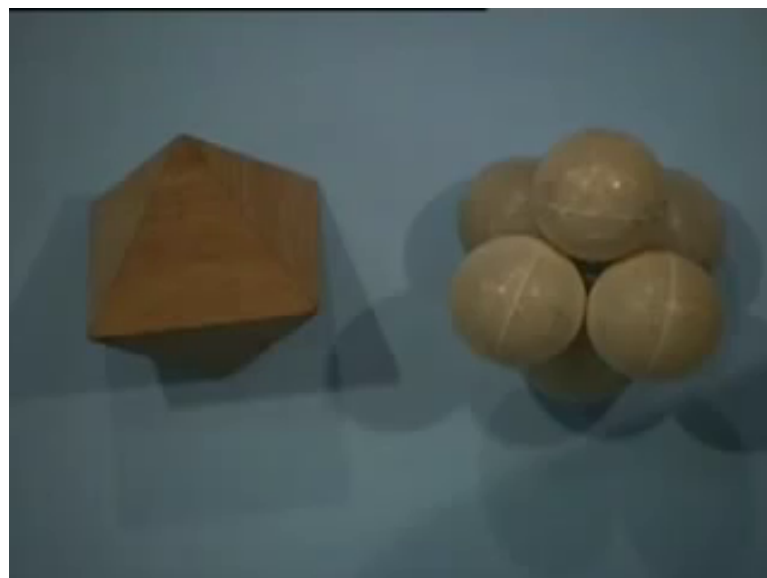
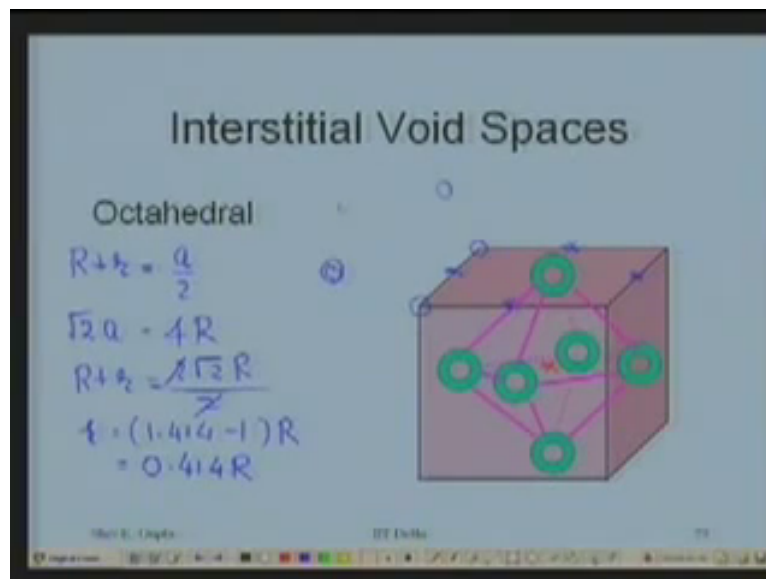
Alright now let us look at the octahedral holes which are formed, these are formed when a cavity in the middle is a c cavity in the a plane and the b cavity are in the adjacent ones and I put b plane on top, so that adjacent cavity are on the b atoms, so this is also gain a c cavity in the b plane this is also a c cavity in the a plane, right. If I slight tilt this I get a picture like this in the middle I have a square form by 4 spheres, one sphere on top once sphere in the bottom forms an octahedral whole like this where I have 8 faces as equilateral triangle.

I tilt this it becomes like the one which I show here once again the corners here are the centre of the spheres and the centre of this octahedral is the centre of the cavity here, so this is how a solid shape is formed and I do not have any 3rd kind of a void in a closed pack arrangement these are the only 2 kinds of voids which I have one when an b atoms comes and sits on the cavity of a, a tetrahedral hole is formed when adjacent b atoms are sitting on the b cavities, the middle cavity the c cavity neither occupied in the a plane nor occupied in the b plane it forms a octahedral whole. Since I do not have any other arrangement of these atoms in three-dimensional space I have only a, b and c arrangement I have no other cavity formed.

Student: And these are found in both ab ab and abc abc?

Prof: Exactly see what is called a and b and what is called b and c, it is you who are naming it nobody have named this spheres as a, b or c. b is a close spectrum like an a, c is a close plane like b it will be similar geometry between any 2 close packing the geometry will be identical. I am showing between 2 only similarly it will be between a and c or it will be between b and c right? it will not be it will not be different naming abc we have done it right so it is the same thing whether I talk about a and b or I talk about b and c or I talk about a and c it will be exactly the same no difference, is this clear? Right.

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Now I shall show you this octahedral hole in the FCC unit cell which you see here this is a face centred on the top this is the face centre at the bottom these are the 4 face centres in the middle front and back, left and right okay. This form a similar figure to this they form a figure like this right so therefore I get an octahedral hole which is the location of an octahedral whole?

Student: Body centre.

Prof: Body centre very good that is the location of the octahedral hole. What size sphere you can fit in there?

Student: (())(15:51)

Prof: Yes you can work it out the radius of this sphere which is forming an octahedral whole plus these small sphere which can fit inside is how the distance equal to the edge that is from the face centre to the body centre there is a by 2. What is the relationship between a and R? Under root 2 of a is equal to 4R, so we can eliminate a from here what we will get? 2 cancels with 2 and we are left with is small r is equal to 1.414 minus one of R, this r goes on to the right hand side that becomes 0.414 of R. Now what you can fit in is much bigger than what you can fit in the tetrahedral hole that was only 22.5 percent of the size but this one is 41.4 percent of the size right so much bigger cavity right where else such locations are there in the unit cell of FCC?

Student: edge centres.

Prof: edge centres very good all the edge centres are also identical because this face centre, this face centre here, right this corner, this corner and the face centre on the top and a face centre at the bottom they form a similar arrangement what is formed here.

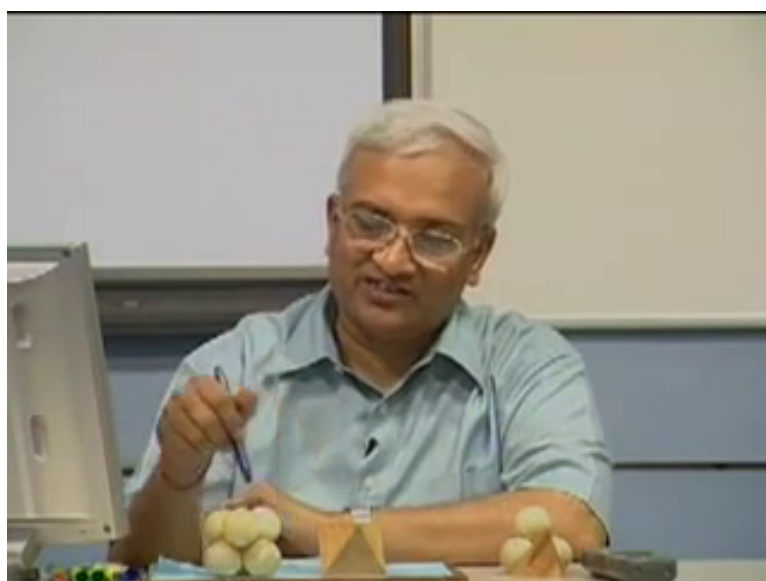
Student: Here we are (18:18) FCC type?

Prof: FCC only, FCC is also a closed pack arrangement abc abc.

Student: What about ab ab?

Prof: ab ab is also similar thing octagonal holes will be there right.

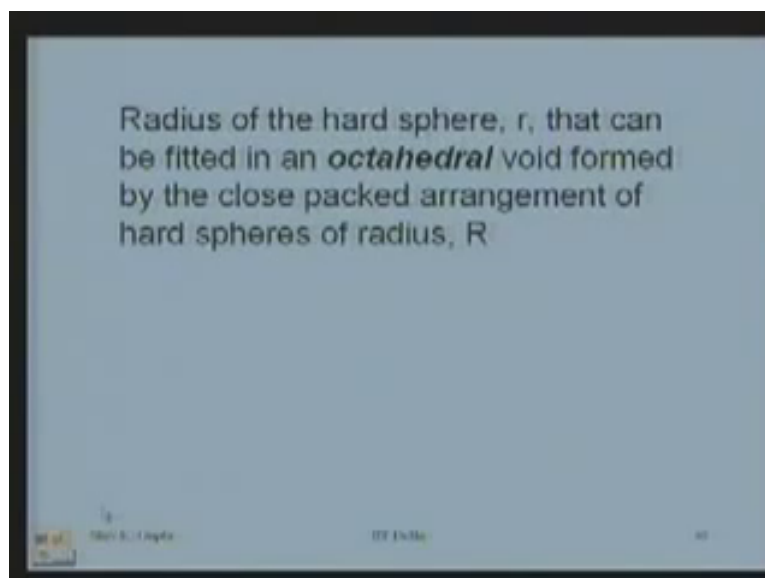
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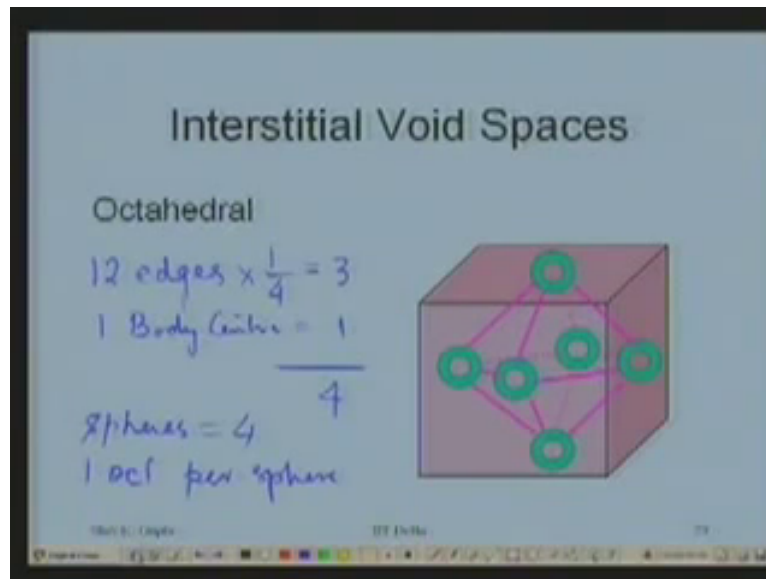




This is a this is b there is an octahedral hole this will be found in the unit cell right and then number will also be similar you will be able to see these things when you see the models in the laboratory to count the numbers both in FCC and HCP I am just counting in FCC now also this are the edge centres but you see that this edge centre is common between 4 cells while this or a centre one is within the volume of the cell right, so how many of these are there.

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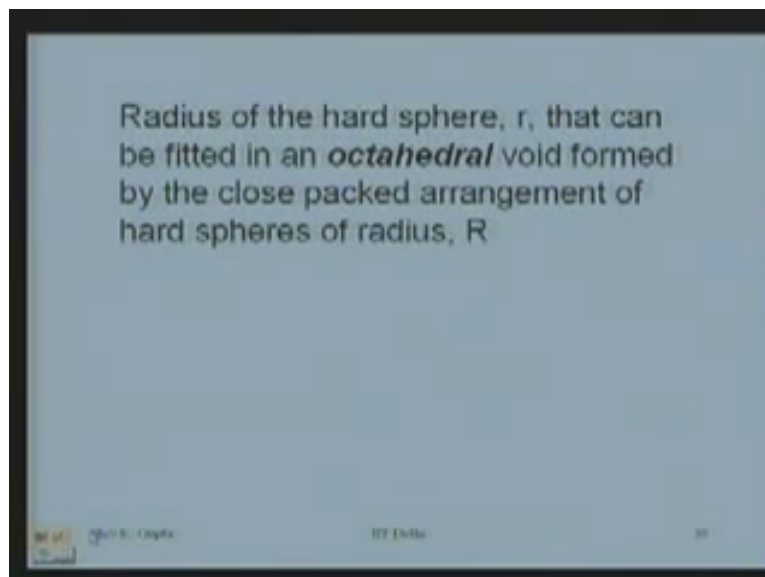
Well that's is what we have worked out right so this is this is I have to go back on to the previous slide, so this is there and the body centre and this is also there at the edge centres there are going to 12 edges and each edge is common between 4 cells that makes it 3 of such volumes of the hole plus 1 in the body centre that is well within the volume of the cell and total I have 4 and number of spheres I have is also 4 therefore there is one octahedral hole per sphere right, so this is the geometry in close pack arrangement of the void spaces and in these void spaces some small spheres which are available can go in sometimes they are slightly bigger than the small hole and they squeeze the neighbouring electron clouds of the parent matrix thereby increase the enthalpy of the crystal but by being there they can increase the entropy as well and therefore can lower the free energy of the crystal, so something can be there in these interstitial void spaces.

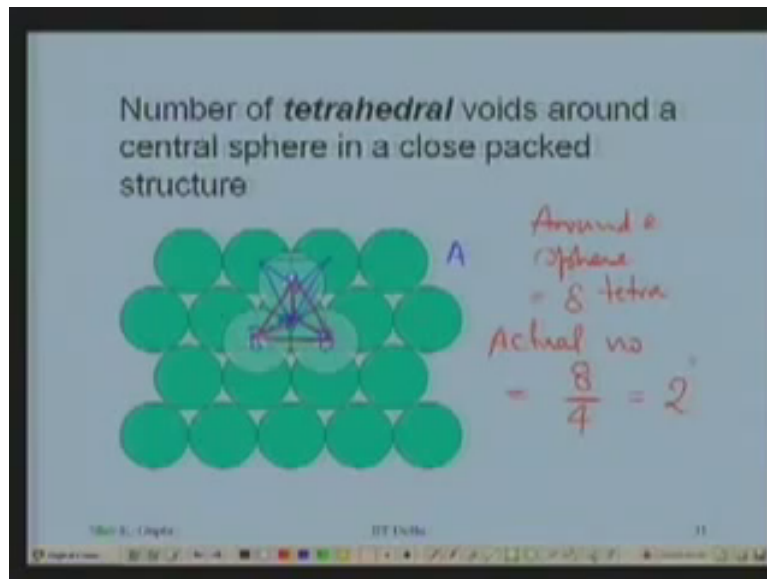
Such thing could not have been talked off inner diameter cubic crystal although a lot of space there it is only 34 percent packing efficiency but here this packing efficiency already 74 percent and we are still talking of this. Can you tell me one good reason why should we talk about that? Covalent bonding in diamond cube was sp^3 bonding each atom had to be bonded to 4 neighbours each carbon atom is bonded to the 4 neighbours at tetrahedral angles and the octet is complete there is no tendency to form bond with anything else when we have come to matters to the left of group 4 group 3, 2 or 1 octet is never complete even if it is shared that is why there is a delocalize sharing so whatever number of electrons are there are shared by all.

Sometimes or part of the time one can feel that I have all the 8 electrons but not 100 percent of the time therefore tendency to form bonds with as many neighbours as possible continues to be there because octet is never complete that is why if some other atom can come and sit in

the interstitial voids which is a smaller one but can share the electrons well it will be going towards more octet completing the octet in the outermost orbit that too towards having the 8 electrons in the outermost orbit which is a most stable configuration for any atom, right. Therefore there is a tendency for having more neighbours as many as possible in a metallic bond which is non-directional and octet it is never complete there alright.

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That is why we have talked about these void spaces and the holes in the crystalline arrangements of metals which are closed pack structures. Right in this slide we have this is already we have worked out (())(23:47) can write that. Here we can write that the small sphere that can fit in the octahedral hole is of the size 0.414 of R. Yeah this we have worked out with the help of FCC unit cell as one of my friends asked me what about the HCP where ab ab stacking is there, now I am showing between 2 close packed planes it could be ab it could be bc it could be ac it could be ba right this is one close packed plane. This is little darker one and these lighter ones another close packed plane on top and let us call this a let us call this as b this is b and this is b, b is sitting on top of a and I am forming tetrahedral holes tell me how many tetrahedral holes I have formed about this central sphere here? How we tetrahedral holes I have formed about this?

Student: (())(25:33).

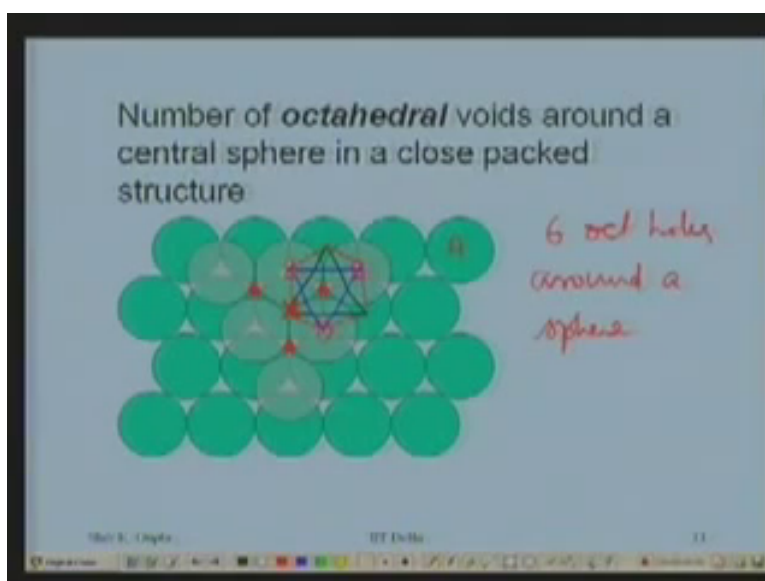
Prof: I have formed 4 somebody is right who says 4, one is this similarly one there, 3rd here and the 4th one is formed with this as the when the a plane the centre and these 4 or 3 on top like this, this is the 4th one you can put a different color for this maybe these are the d atoms on top and this is going towards a in the bottom so it is an inverted tetrahedral while the other 3 were upright tetrahedral this is an inverted tetrahedral and that central sphere is common to all 4 of them is between a layer and b layer. In a closed pack plane or closed packing of planes behind or below a I shall have either b or c, it will be a similar geometry there how many spheres will or how many tetrahedral hole will be there on the same central sphere there? Again 4, so 4 and 4 shall make it 8, so around a sphere we have 8 tetrahedral holes this will be true about this, this will be true about that, about this, about this, about this, about this,

about that, about this all of them it will be 8 geometries are going to be identical right but how many spheres form a tetrahedral hole? How many spheres form a tetrahedral hole?

Student: 4.

Prof: 4, so when you begin to count the same tetrahedral hole will get counted about 4 of this spheres because 4 of them are forming it. I counted these 4 here about this sphere but when I begin to count about this sphere this hole will again be counted. When I begin to count about this sphere this hole will again be counted right. Like similarly when I start counting about this b atom again this will be counted, so same hole is getting counted 4 times so actual count is one fourth of this okay, so that will be actual number will be 8 divided by 4 because each one is getting counted 4 times so that is what we get an FCC unit cell that is what we see in between any 2 closed pack plane ab bc ca or ba whatever you want to take it is the same thing, is it clear? Alright.

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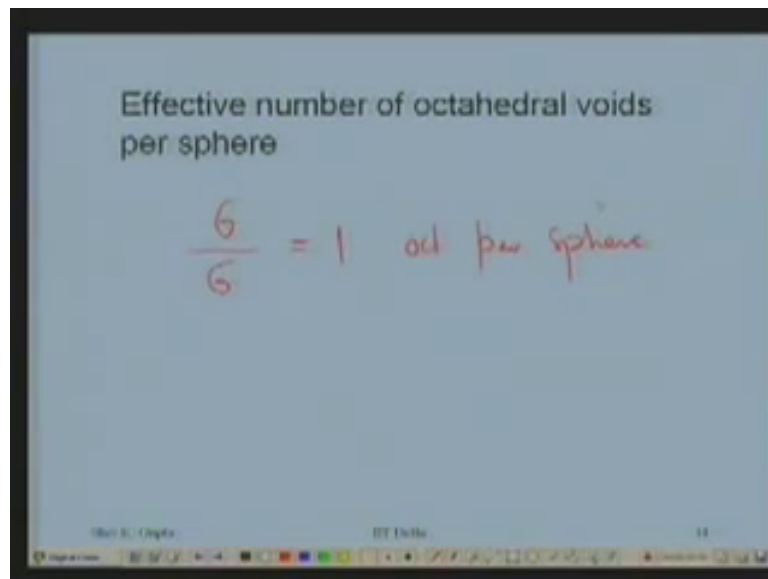


So that is what we have worked out effective number of tetrahedral voids per sphere is only 2 now let us look at the octahedral void in the same manner again 2 layers a and b. Alright this ones are a and these ones are b. Now the octahedral voids formed is now here, 3 spheres of a and 3 spheres of b if I joined them they form an octahedral hole like this and octahedral hole is formed in this manner. Now let us take one central sphere which is this one here let us say this central sphere let me cross it like this.

About this I have counted 1 octahedral or seen 1 octahedral hole here about this there is another octahedral hole here, about this another octahedral hole is here, so I have 3 octahedral

holes in the a layer and the b layer but if I continue in the three-dimensions behind the a layer or below the a layer there will be either b or c the similar geometry I shall have 3 more tetrahedral holes there so around this central sphere I have 3 in this layer above and 3 in the layer below I have 6 octahedral holes. Are you able to see this? alright. Then one hole is formed by how many spheres? 1 2 3 of a 1 2 3 of b so when I start counting about 1 sphere 6 holes like this same hole gets counted 6 times right.

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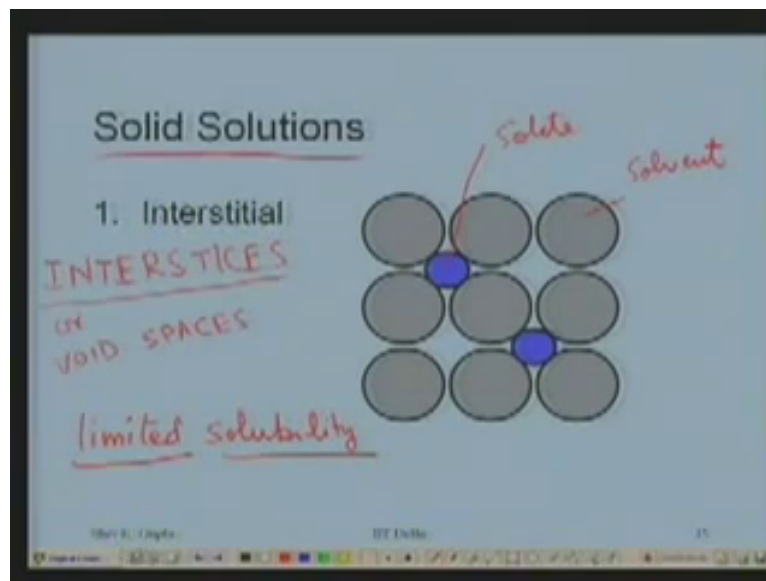


Effective number of octahedral voids per sphere

$$\frac{6}{6} = 1 \text{ oct per sphere}$$

So effective number of octahedral voids per sphere would be we have counted 6 around 1, we have counted 6 around 1 and 1 is 1 by 6 so that makes it one, so 1 octahedral void per sphere. So if you have one mole of FCC copper you have one mole of octahedral voids and it can have one mole of some atoms which are smaller in size of the order of 0.414 R can go in there.

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Right now since we started talking about something going in of a different size in the interstitial void spaces this tetrahedral voids and octahedral voids also called the interstitial void spaces as the word interstitial ti ti comes twice and this is also the void spaces are also called Interstices, void spaces are also called Interstices right or you call them whatever void spaces we talked about tetrahedral and octahedral in close packed structures, if it is not a closed packed structures (())(34:33) not be tetrahedral and octahedral okay right. Here I show may be a simple cubic arrangement in which these are the void spaces in which smallest spheres are sitting these are different atom different aliment and they have gone in there and dissolved in the crystalline arrangement it is called a solid solution like you have liquid solutions we have solid solutions as well. What is a difference between a solution and a mixture?

Student: In mixture there is no fix proportion.

Prof: When I mix sand and stone we call it a mixture go to the market to buy some grains you mix wheat with rice, it is a mixture. When you dissolve sugar in water you call it a solution or when you dissolve salt in water you call it a solution can you tell me the difference?

Student: Chemical bond...

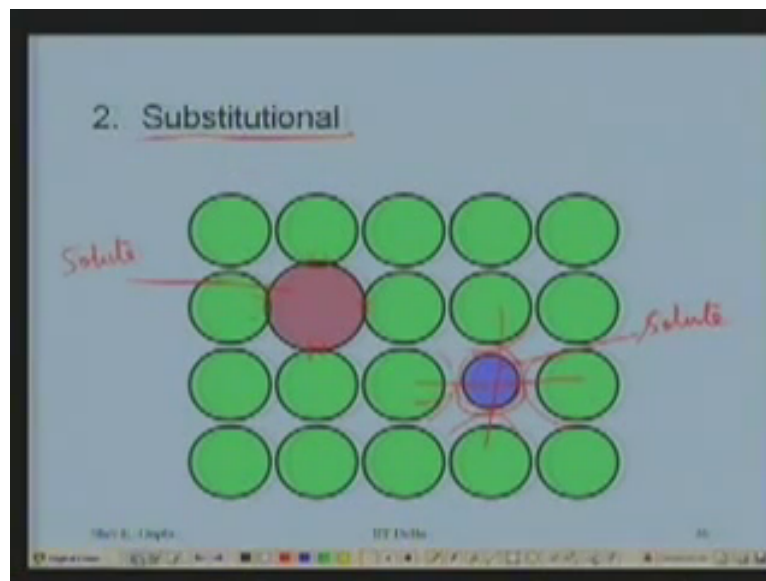
Prof: When it is a solution mixing occurs at the atomic or the molecular level, when it is a solution mixing occurs at the atomic or the molecule level, is it clear? That is since it is now it is happening at the atomic level interstices are between the atoms, spaces between the atoms I call it a solid solution, right. An interstitial solid solution is the one where the solute

goes and sits in the interstices, the void spaces okay. This is a solute and these are the solvents.

Like we have seen while trying to mix water and alcohol you can mix them in all proportions you can start with 100 percent water keep on adding alcohol keep on removing maybe water ultimately you can have all alcohol it will still be the all solution always but if you try to do that with sugar you cannot can dissolve sugar up to the limit then you call it, it becomes saturated solution and then if you add any more sugar it does not dissolve, so in one case I have a limited solubility other case I have extensive solubility. In solid solutions sometimes even 20 percent solubility we can say extensive alright but in this case of kind of a solid solution can you have extensive solubility? Firstly I cannot have spheres which are of so small size that they can go in interstices without disforming the neighbouring atoms, without distorting the neighbouring spheres (())(38:09) they are going to be in overlap of electron clouds, when that happens the energy the enthalpy of the system goes up.

Only if it is compensated by the entropy it is stable free energy is lower otherwise it will not, it will not go into solution secondly I can put in as many spheres as many interstices are there. Let us talk about an octahedral hole which is a bigger one I can probably let us say find out a sphere which is of the size of $0.414 R$ let us say so and that goes in there, so I can put maximum as many solute atoms as many solvent atoms are there because there is one is to one ratio. I have 1 octahedral void per sphere so I can put 50-50 I cannot make solute to more than 50 percent right, so extensive solubility or going in all proportion is just not possible in interstitial solid solution we always invariably get only limited solubility right.

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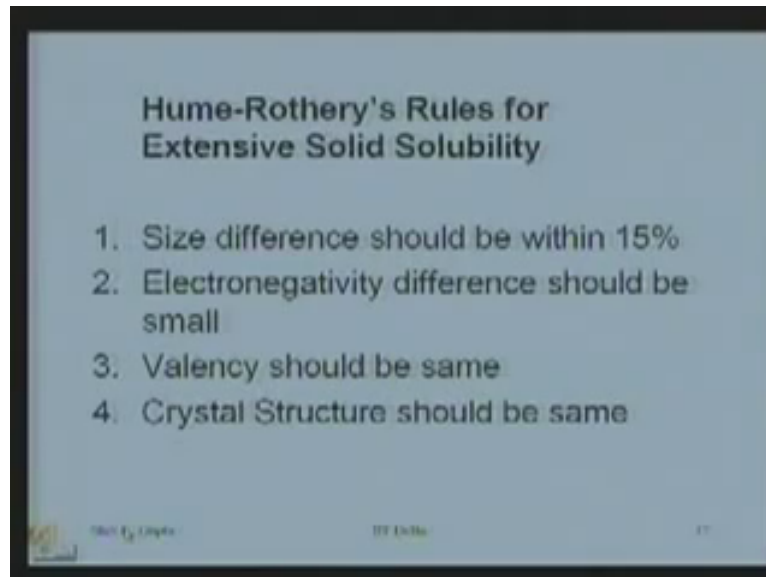


Then I have another kind of solid solutions where in the solute goes and substitutes for the parent atom say for example this solute of this solute, what is the difference between these 2 solutes? This one is bigger than the apparent atoms thereby you can see that it is compressing the electrons clouds, here there electron clouds have to extend to form the bond with it, it will depend upon which electron clouds are more flexible, rather electron clouds or the solute are more flexible or the electron clouds or solvent or more flexible the bonds have to be extended bond length is gone up, electron clouds have to extend right that means there is going to be an increase in enthalpy here there is going to be an increase in enthalpy here right and this is compensated by the increase in entropy, configuration entropy therefore it is there such solid solutions do form and we call them substitutions solid solutions because solute is substituting of the parent atom or the solvent.

Solvent is removed and solute is placed in place of that. Say for example I have copper and I add to it nickel, I can replace one atom of copper put one atom of nickel place another atom of copper put another atom of nickel I can go on doing this, I started with FCC crystal of copper if I do that I end up with FCC crystal of nickel. If nickel does not exist as FCC that is not a stable configuration it will not be possible but if nickel stays as FCC stable it will be possible right so I can get a very large extensive or rather solubilities in substitutions solid solutions could be from 0 percent to 100 percent like the example of alcohol and water they can mix in each other in all proportion gold and copper can do so, copper and nickel can do so they can mix in each other in all proportions that is possible because one is substituting for

the other. To get the extensive solubility certain empirical rules formed by Hume-Rothery for the substitution of solid solutions we shall look at those.

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Let us try to understand them one by one these are empirical rules and therefore please understand they are not so regulars I will give you the examples also after this we will discuss them, firstly the extensive solubilities are possible on substitution solid solutions only not in interstitial solid solutions. Size difference it says should be within 15 percent I am talking about the linear size, the diameter or the radius not the volume that should be within 15 percent, since these are empirical rules please do not ask 15 percent of the solute or 15 percent of the solvent okay so that marginal adjustment you have to keep in mind so 15 percent if the size is within that let us say size differences 5 percent, extensive solubility is possible because strains in the electron clouds to form the bond will be very small alright and that will be compensated by the entropy increase that is important very important empirical rule of the... 2nd one says the electronegativity difference should be small, what happens to let me ask the question, if the electronegativity difference is large?

Student: (())(44:28)

Prof: Yes let us say one element from group 1 other one from group 7 like sodium and chlorine, chlorine is more electronegative it will take the electron out from sodium which is more electropositive and 1 becomes positively charge other becomes negatively charged there is a different kind of bond formed now which is called an ionic bond this is no more a

metallic bond okay and there for electronegativity difference could be small otherwise it will tend to form a compound I am looking for solid solutions only.

Then I talk about the valency, valency please understand is not the chemistry valency you have studied in school chemistry or the first-year chemistry here this valency by that I mean as number of electrons in the outermost orbit, number of electrons in the outermost orbit right should be same and there can be still possibility with the difference of 1 or so that you can get extensive solubility, if it is same there are more chances that we shall get the extensive solid solubilities. Then it says crystal structure should be same example I have already given if any gold which in FCC I replace gold atom by copper atoms it becomes FCC copper and it is possible to get become FCC copper if copper also exist as FCC which it does in this case otherwise it will not be possible alright.

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Element	Cryst. Str.	At. Rad. A	Valency	Electron negativity
Ag	FCC	1.44	1	1.9
Au	FCC	1.44	1	2.4
Cu	FCC	1.28	1	1.9
Ni	FCC	1.25	2	1.8
Zn	HCP	1.31	2	1.5
Ge	DC	1.22	4	1.8
Si	DC	1.18	4	1.8

Now with the help of example we will talk about these, these 4 parameters crystal structure, the atomic radius, the valency, the number of electrons in the outermost orbit and the electronegativity okay let us take the example of gold and copper just now I said size difference you can see is within 15 percent right valency, number of electrons in the outermost orbit is the same, electronegativity difference is not large and they dissolve in each other in all proportion that is why all the Goldsmith are able to give you impurities they can add copper easily without much problem right all these carat different carat of gold, 22 carat, 16 carat, 18 carat less the number of more of copper is going to be there okay.

So alright so that is the we get complete solubility between copper and nickel you see size difference is still smaller but valency is differed by 1 electronegative difference is still smaller than that they also dissolve in all proportion. Let us look at germanium and silicon diamond cubic both of them size difference is very small valency is the same electronegativity is the same they dissolve in each other in all proportions but I give you an exception silver and copper I can dissolve 5 to 7 percent only not more that too add about 725 degree centigrade at low temperatures the solubility is less at higher temperature the solubility is still less, maximum solubility around 725 degrees centigrade though substructure is same size differences within 15 percent valency is the same and electronegativity difference is 0 this is an exception that is why I said Hume-Rothery rules are only empirical rules right.

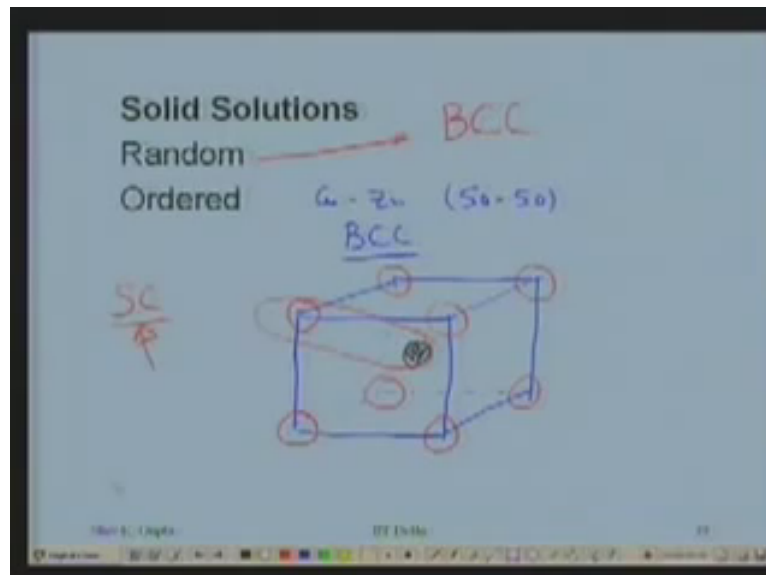
Now let us talk about an example of copper and zinc it is an interesting example to talk about copper and zinc one is FCC another is with HCP certainly I cannot have 0 percent to 100 percent solubility right size differences is not very large similar kind of size difference as in the copper and nickel, valency difference is same like what we have been copper and nickel and electronegativity difference is also not large and what we find is that is possible for us to dissolve almost 40 percent of zinc in copper or I cannot dissolve more than a few percent of copper in zinc.

Almost 40 percent zinc in (())(49:44) copper you have 70 – 30 brass you have 60 - 40 brass, 40 percent zinc is there, 30 percent zinc is there it goes in solution but I cannot dissolve copper and zinc the reason here is slightly different and we can try to understand that it is a possible explanation copper has only one atom in the outermost orbit when we add zing to it which has 2 atoms in the outermost orbit number of electrons in the outermost orbit goes beyond 1 going tending to go towards to 8 but never goes to 8 going towards 2, 40 percent of zinc can go in but when I add copper to zinc it is already 2 but when I add copper which has one electron in the outermost orbit it is going down for atom it is not tending towards 8 right that is why you cannot dissolve too much of copper and zinc well almost 40 percent zinc can go in copper.

So there are exceptions to the empirical rules as well as in the case with silver and copper. In solid solution which we have seen substitutions solid solutions these could be random or these could be ordered, say for example what I talk about random solid solutions let us say nickel going in copper, nickel replaces the copper atoms randomly I have added let us say 30 percent nickel in copper, it dissolves in all proportion so 30 percent dissolves but randomly

replaces it in FCC this is a random solid solution. In other words if you look at any atom in the FCC unit cell 30 percent of the time it is nickel 70 percent of the time it is copper effectively that atom is behaving as if it is 70 percent copper and 30 percent nickel such is a random solid solution.

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Ordered solid solutions the solute has a fixed location in the unit cell and the solvent has a fixed location, say for example I talk of brass which is a copper zinc alloy both are 50-50 and they form a BCC solid solution. In this BCC solid solutions let us say of the body centre is the zinc atom and the body corners are copper atoms and every unit cell is like that this becomes an ordered solid solution okay but this happens in this alloy which I am talked about copper zinc alloy 50-50 below about 450 degrees centigrade but above 450 degrees centigrade thermal energy or the oscillations are so vigorous then it becomes random that means this is 50 percent of the time copper and 50 percent of the time zinc this is also 50 percent of the time zinc and 50 percent of the time copper then at that time it is random solid solutions but once it is like this it is an ordered solid solution. Now what is the difference as far as if you take a deflection pattern from an ordered solid solution and a random solid solution what will be the difference in the reflection pattern? In other words what will you specify the space lattice or define the crystal structure as?

Student: In random we cannot strictly define it because we will be getting different vacuum pattern from different () (54:55).

Prof: In random solid solution it shall remain BCC each atom is behaving as 50 percent copper and 50 percent zinc because it is 50 percent time here it is zinc 50 percent time it is copper.

Student: It is in ordered.

Prof: In ordered solid solution this is no more BCC is simple cubic space lattice and my motif was going to become this, so crystal structure diffraction pattern I shall get that of a simple cube not of BCC because it is not changing its location it is there that is why I am calling it ordered, is that clear? Alright, so this is about the solid solutions and we have already introduced in terms of solid solutions routing in atoms of different sizes and that shall we shall continue with that in the next class then we have spheres of different sizes and we go to ironically bonded crystals 2 irons will be of spheres of different sizes that we shall see in the next class.