Material Science
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Lecture No 6
Crystal Structure Determination, X-ray Diffraction (Powder Method)

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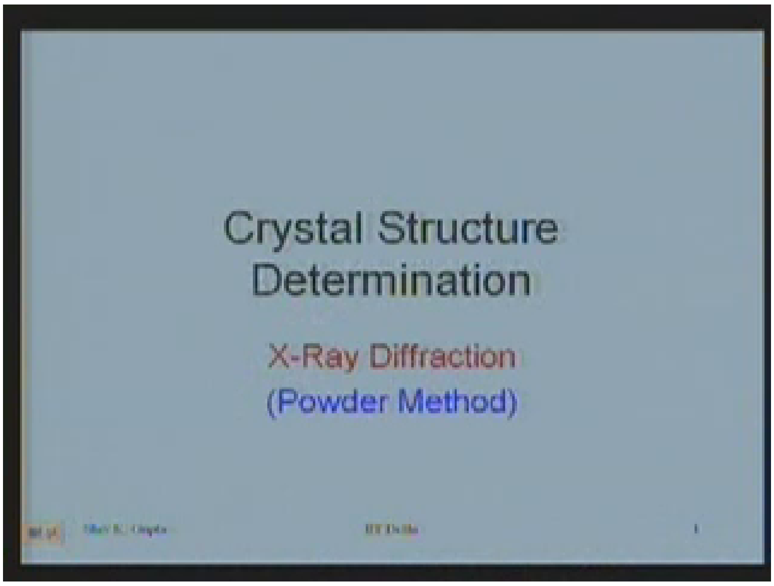
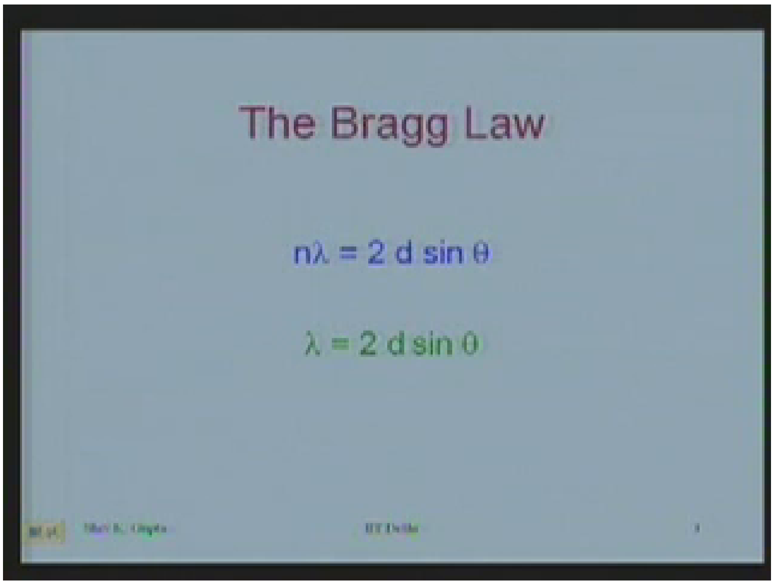


Crystal Structure Determination

X-Ray Diffraction

(Powder Method)



The Bragg Law

$n\lambda = 2\, d \sin\theta$

$\lambda = 2\, d \sin\theta$

Well in the last class we were discussing the determination of crystal structures in case of in case of simple crystals like from the cubic space lattices it is easy to do that and we said that for using that we normally can use x-rays, neutrons or electrons and x-rays what we use are the characteristic radiations of some of these targets which I told you yesterday. Then we also looked at Bragg Law which we exploit in trying to determine the Miller indices of the plane which are diffracting, x-rays which are incident on the crystal work it out n lambda is equal to

2 d sin theta where n we discussed is the order of diffraction we said that we will take it to be 1 because otherwise it is not possible to distinguished 1st order from one plane and the 2nd from the another plane which are superimposed.

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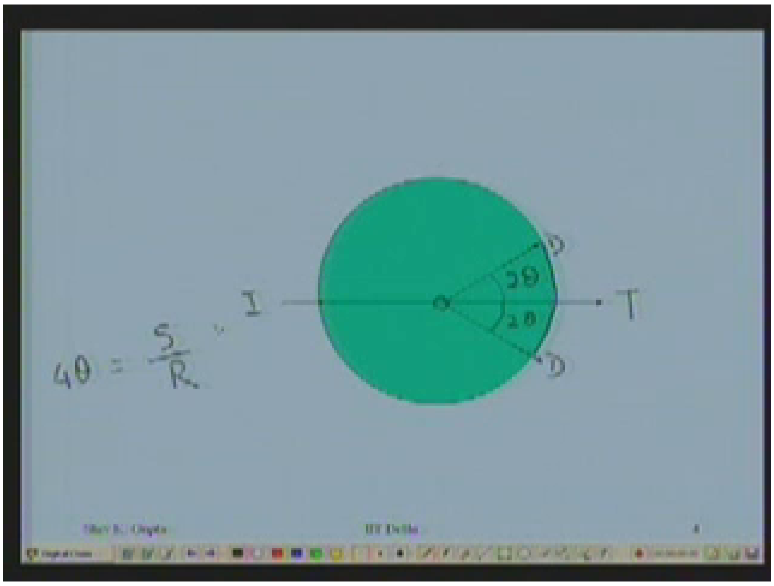

In the camera which we use for powder Method generally how we measure theta values I described that that this is the incident ray of x-rays, this is directly transmitted out from the camera these are the diffracted days which from a cone from the specimen which is somewhere here in the center of the camera, the angle which is form here between the incident ray and the diffracted ray is 2 theta similarly this angle is also 2 theta and if I am able to measure the distance between these 2 points of the length of the ark which is let us say is S divided by R becomes 4 theta that is the angle that is how it is possible for us to measure the angles of diffraction. Similarly if we are using a diffractometer the only the lower half of the geometry is required then I am directly measuring with the help of the Geiger counter, the 2 theta angle for diffraction and from there again I know the value of theta.

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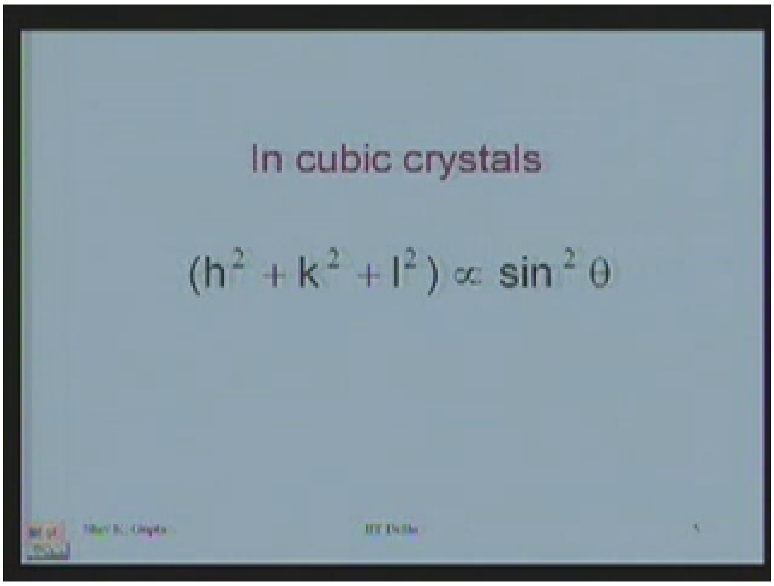

In cubic crystals

$$(h^2 + k^2 + l^2) \propto \sin^2\theta$$

Then in cubic crystals we also saw that sum of the squares of the Miller indices the planes which are diffracting h square plus k square plus l square is directly proportional to sin square theta and since we have measured theta values I know their ratios sin square theta ratio therefore I ratio of h square plus k square plus l square values which we observed.

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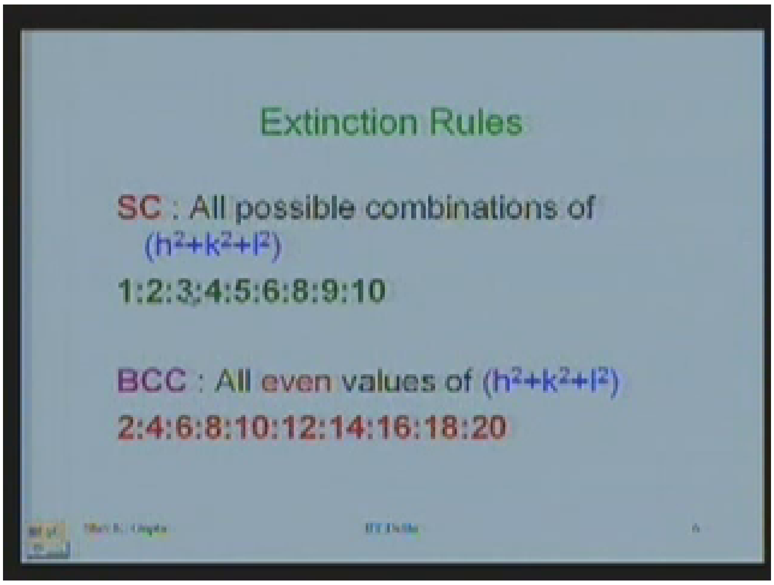

Extinction Rules

SC : All possible combinations of $(h^2+k^2+l^2)$

1:2:3:4:5:6:8:9:10

BCC : All even values of $(h^2+k^2+l^2)$

2:4:6:8:10:12:14:16:18:20

And the what is the first value will give me all the subsequent values that is given by the extinction rules, extinction rule say that in a particular crystal like simple cubic what values of h square plus k square plus l square are observed. In this case all of them are observed 1, 2, 3, 4, 5, 6 of course 7 is not there we know the reason there are no 3 integers the squares of which are summed up to give you 7 like that there is going to be 15 there are going to be 23 and so on and so forth, so when body centric cubic stills we have it is all even values of h square plus k square plus l square well as I have repeated yesterday again I repeat this at 2, 4, 6, 8 again becomes 1, 2, 3, 4 but the difference comes when you look at the 7th here it is 14 but there is no 7 here, okay.

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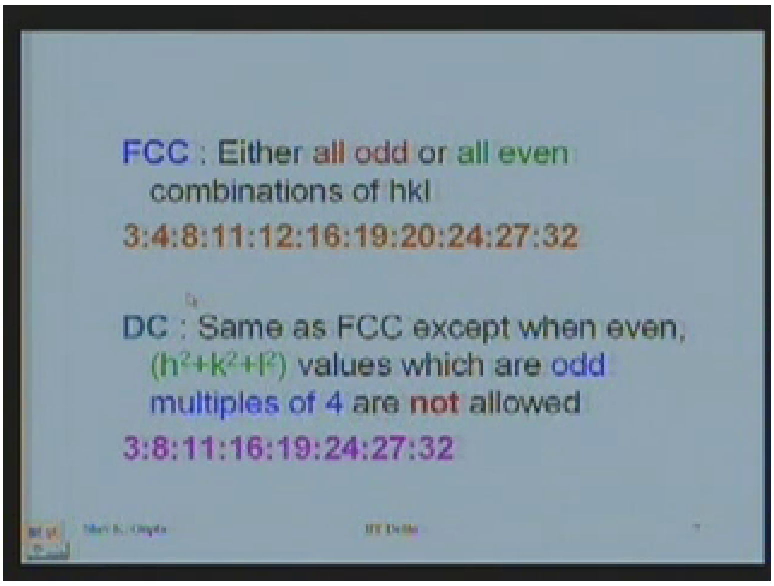
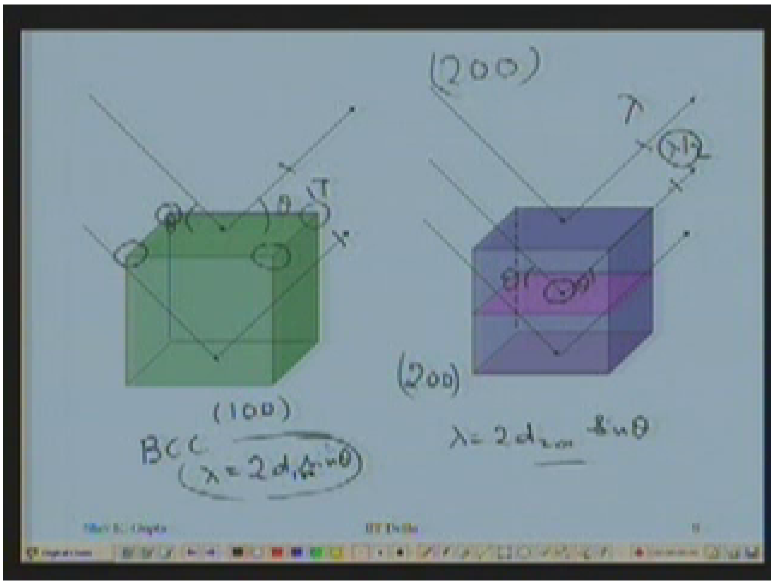


FCC : Either all odd or all even combinations of hkl

3:4:8:11:12:16:19:20:24:27:32

DC : Same as FCC except when even, $(h^2+k^2+l^2)$ values which are odd multiples of 4 are not allowed

3:8:11:16:19:24:27:32



Like that we discussed this extinction rules for FCC and diamond cubic I will just give you an example here why we do not see certain h square plus k square plus l square values, let us consider this to be a BCC unit cell and here I am looking at the diffraction from 1 0 0 which satisfies the condition lambda equal to 2 d sin theta and this is my angle theta here and that is another angle theta there at the same time in BCC I also have an intermittent living plane which is called 2 0 0, when this is satisfying Bragg law as the 1st order at means the path difference between this ray and this ray is one lambda that is the meaning of first-order, right.

These 2 consecutive 1 0 0 plane give the diffracted ray the path differences is one lambda. Now this 2 0 0 plane sitting in middle also forms the same angle theta and the diffracted ray here, here to there is path differences only lambda by 2 these are completely out of phase when this condition is satisfied, so when this is satisfied I should see the diffraction from 1 0 0 but because of the 2 0 0 sitting in between physically sitting there I cannot see that because that gives me completely outer phase it is total cancellation of intensity is, okay.

Student: (())(6:33 till 6:38)

Professor: Intensity will be exactly same as long as this is BCC and the atom sitting there and the atom sitting on the body center is exactly the same, number of atoms per unit area the scatting center is the same here is also one in this area this is also one in that area, so from the given plane the number of scatting centres are exactly identical number of electrons on the outer orbits of the nucleus is the same because it is the same atom however the atoms are different amplitudes may not be same because scatting centres are different there but here identical scatting centres with equal number setting per unit area therefore I get the same intensity, same amplitude only thing is it is out of phase

Student: So both cancel each other?

Prof: Both cancel each other completely, so that is why we call it extinguished it is not that the Bragg law is not satisfied, Bragg law is satisfied for the 1st order from 1 0 0 but it gets extinguished that is why I call it extinction rules.

Student: (())(7:46) 2 0 0 also gets extinguished?

Prof: No, when I say 1st order from 2 0 0 the path difference between these 2 consecutive rays instead of lambda by 2 is lambda. Once that happens is becomes 2nd order from 1 0 0 that is why we call it 2 0 0. See the meaning of first-order is the given plane hkl set the path difference of the diffracted rays coming from the 2 consecutive plane is one lambda that is the meaning of the order diffraction which I explain yesterday. This is what it is, is that clear? Right.

Student: (())(8:28 till 8:31)

Prof: It is not implying it is saying this is path difference is lambda by 2 it is out of phase.

Student: In the 2nd order.

Prof: It will become 2nd order when only the path difference is lambda then the theta would be different that condition would be different that would be this is d 1 0 0 that would be lambda is equal to 2 d 2 0 0 sin theta that would be satisfied again this would be the 1st order from 2 0 0 but when I rewrite this and it becomes 2nd order from 1 0 0, is that clear? Why we do not see 1 0 0 in the body centred cube? Right with this it is possible now therefore for us to determine the simple crystal structure with there is only one atom sitting on the lattice point and it is a cubic crystal.

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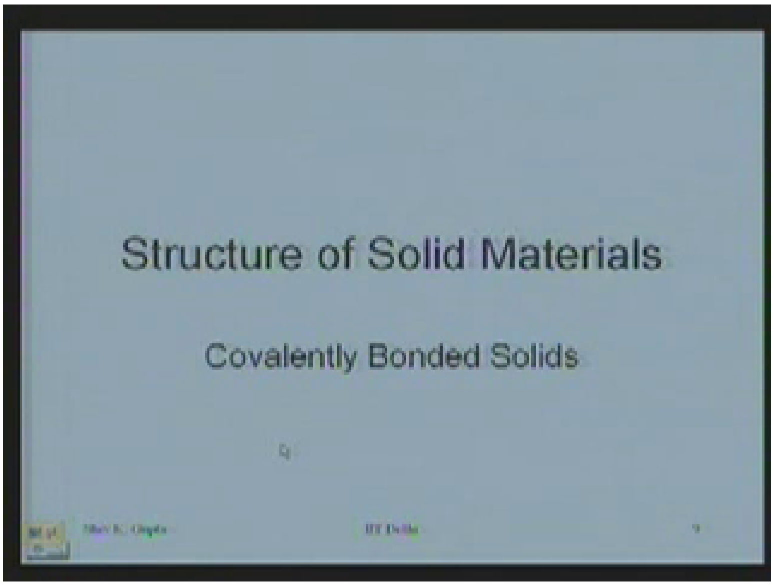

Structure of Solid Materials

Covalently Bonded Solids

Now we shall look at the structure of solid material and today we shall try to look at the covalently bonded solids. Solids could be having basically by enlarge covalently bonding or they could have metallic bonding or they could have ironic bonding, well you have studied this in chemistry but you have also seen that no system or no 2 bonds or no bond in particular is 100 percent covalent or 100 percent ironic or 100 percent metallic is for the simple reason electrons are not stationary they keep on orbiting around the nucleus and thereby if there is mostly time spend sharing their together in the same but it is covalent. If they spend most of the time only on one atom it is ironic, if they shared equally between all the atoms in the solid we metallic, so it depends how much time they are spending in which form, we named them as covalently bonded or ironically bonded or metallically bonded. Today we shall 1st as I said look at the covalently bonded solids.

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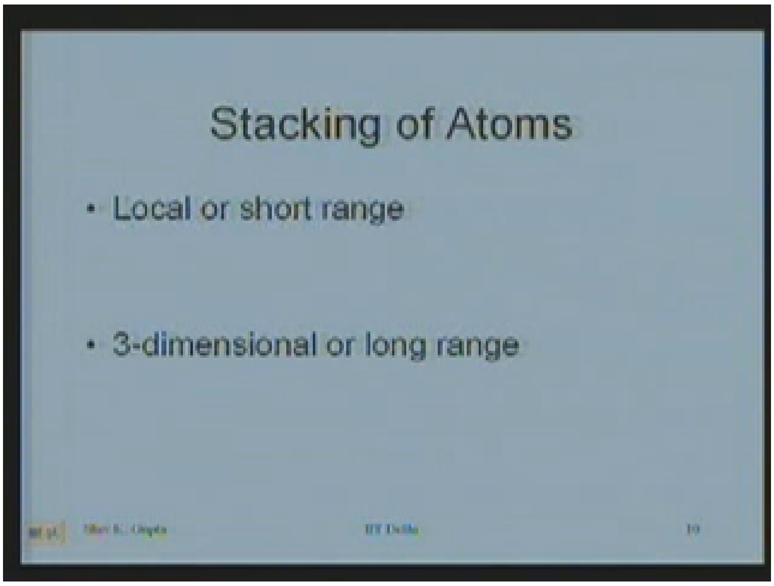

Stacking of Atoms

- Local or short range
- 3-dimensional or long range

Now before I look at that the stacking in the solid can be seen 2 ways one what is the local or short range arrangement around a central sphere or central atom. I am calling sometimes sphere sometimes atom because I have already said we will consider all atoms to be hard spheres around the central atom or central sphere how the neighbours (())(11:26) that is why I have to call the local arrangement this is by and large dictated by the nature of the bond between the 2 atoms, right then this local arrangements have to continue in three-dimensions whether it can continue in a repeating manner or it cannot I get a three-dimensional crystal which is crystalline or non-crystalline. If it repeats in a periodic manner this crystalline if it does not it is non-crystalline, alright so that is the three-dimensional or long-range arrangement is what shall dictate whether it is crystalline or not.

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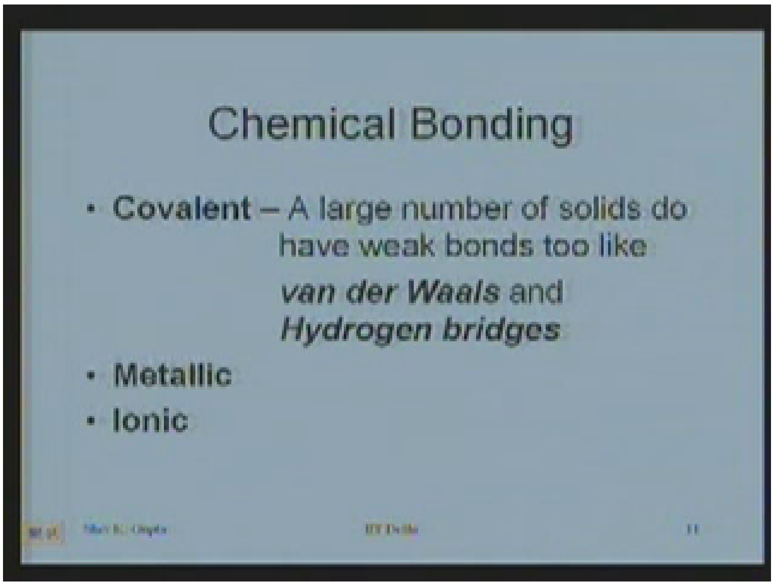

Chemical Bonding

- **Covalent** – A large number of solids do have weak bonds too like ***van der Waals*** and ***Hydrogen bridges***
- **Metallic**
- **Ionic**

Well as I just said the solids are covalently bonded, metallically bonded or ironically bonded. When they are covalently bonded sharing of electrons occurs and this are localised sharing we also find in such many of such solids their other kinds of bond present in the system which are weak bonds Van der Waals forces or hydrogen bridges. When there are 2 kinds of bonds one primary like a covalent bond or the other one which is a physical or a secondary bond like Van der Waals force or a hydrogen bridge properties of the material will be dictated by the weaker one, weaker one are the Van der Waals forces and the hydrogen bridges, right. We will see that there are many such solids there then we shall look at long-range arrangement which many a times we find in metallic and ionic crystals, there it is possible to see the long-range arrangement.

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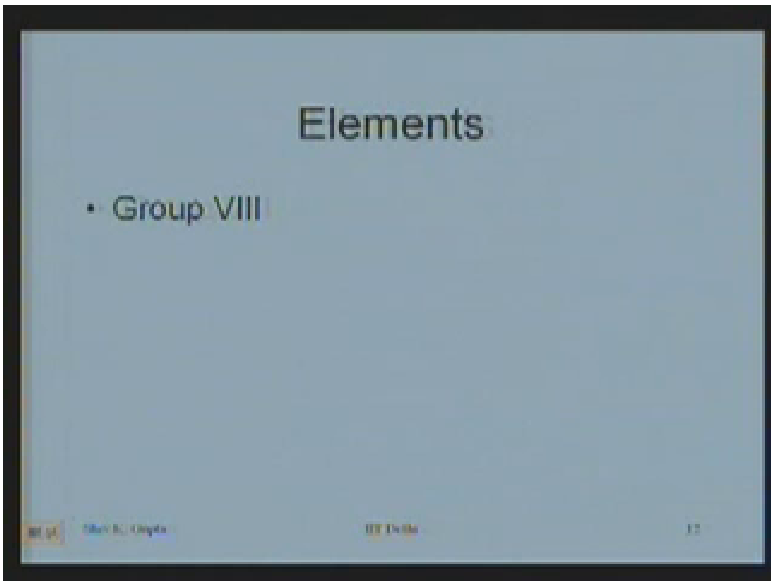

Elements

- Group VIII

1st of all we shall look at the periodic table we shall look at the elements and instead of going from group 1 I start from group 8, in group 8 around the nucleus each atom or sphere has 8 electrons in the outermost orbit its octet is complete it is satisfied that means what we call the octet rule. Octet is complete it has no tendency to form a bond with any neighbour thereby there are only Van der Waals forces between them which are non-directional in nature. When I have non-directional nature of the bond in 3 dimensions the atoms will come from all possible direction around a central sphere, how this central localise arrangement curse and how it goes on to the long-range? We shall see when we are talking about the metallically bonded crystals because their the bonds are also non-directional in nature and central sphere like to have the neighbours from all possible directions that we shall see with that.

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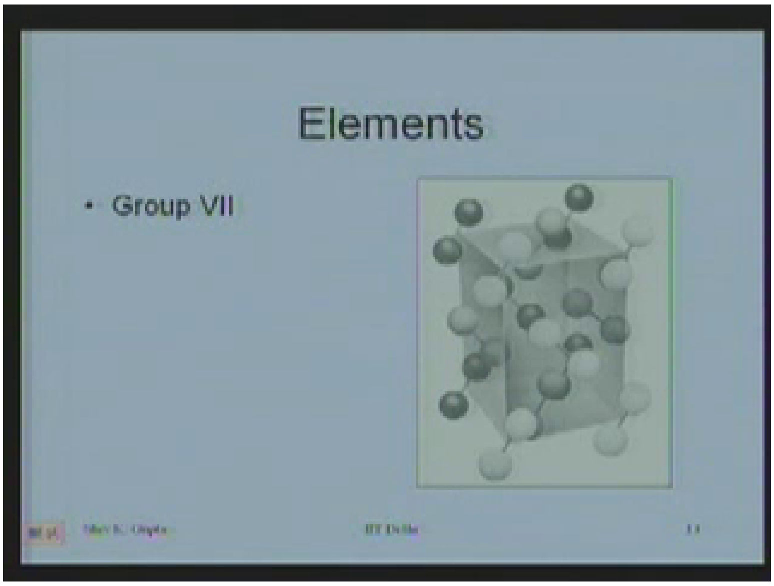

Elements

- Group VII

Coming to the group 7 where we have halogens, fluorine, chlorine, bromine, iodine there are 7 electrons in the outermost orbit one is shared with the neighbour and a molecule formed there is a very strong bond between fluorine fluorine, very strong bond between chlorine chlorine it is a covalent bond but between the 2 chlorine molecules there are Van der Waals forces again there is a non-directional nature of the bond and non-directional bond is weaker bonds are very longer as compared to the primary covalent bond and there are also non-directional.

So you have shown the orthorhombic unit cell of bromine it could be chlorine, these are the spheres here the white ones are on the front plane, front face this is in the center face centre, these are in the corners in the bottom. Those like ones are the back face and these grey ones are in the middle faces, right and this is also the face centre you see the top face and the bottom face their arrangement looks similar oriented in this direction but the middle face they are oriented opposite means this is gone mirror image. Pardon.

Student: What is the motif in this…?

Prof: I will come to that just wait just wait if you want to talk about motif we will talk about that, so this what I am trying to say is between the molecules there is a long-distance and this is a Van der Waals forces between them at very low temperature they can condense like this. This is a very short distance and this is a covalent bond between chlorine chlorine or fluorine fluorine, right. These dimensions of the unit cell will be large as compared to this bond length very large, now my friend is asking what the space…if it is an orthorhombic what is going to be the space lattice. Then we shall look at the motive, what would be a space lattice where this is arranged in this orientation to the right tilted to the right and this is a mirror image tilted to the left on the middle faces. So if you take this 1 0 0 plane top and bottom is identical, the 2 0 0 plane orientation is different.

What should be the name of the space lattice for such a cell? How you will name it? Pardon somebody said something encentred orthorhombic is not face centred orthorhombic. Why is it not face centred? This arrangement is not identical to the corners that is not identical, so these one in the middle plane or not the lattice points those of the lattice points and those are the lattice points and you see now in all if you look at this there are 4 molecules in this volume but there are only 2 lattice points. Therefore there are 2 molecules on each lattice points, so basis would have 1 molecule here another molecule there that is going to form the basis and that you will find to be seen everywhere.

Similarly for this you will find there, for this one you find it here, alright. So and for the one which is your this is the one and this face centred there that will form the basis. So these are the problems you have to understand after you have understood what the space lattice is? Each lattice point is having identical surroundings and then after substituting that you see what is it left out on each lattice point that will become your motif, is that clear? Alright that is group 7 and these are most of the times we are using them as chlorine and fluorine are gases but bromine could be…could be liquid and iodine could be solid close to room temperature.

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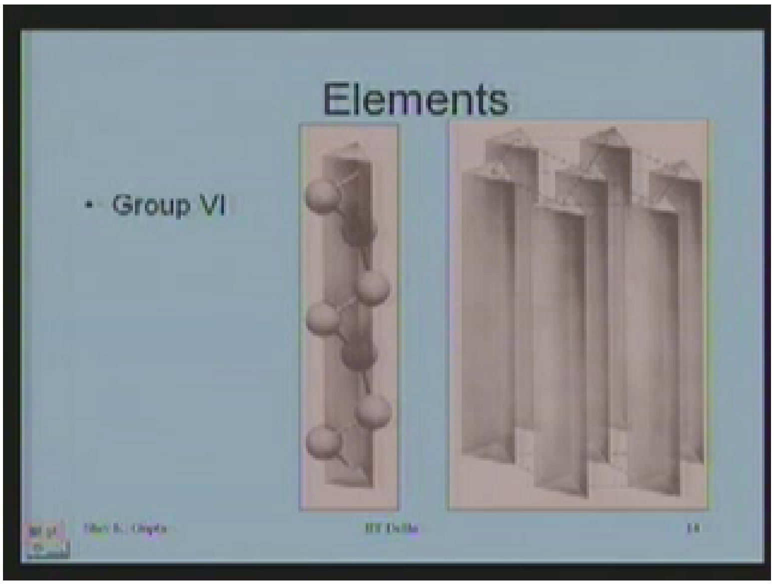

Elements

- Group VI

Now elements from group 6 there are 6 electrons in the outermost orbit to complete the octet they have to share 2 electrons there are 3 orbits px, py, pz and there are 6 electrons which you will px, py, pz have only 4 electrons to our gone into the s and therefore 2 of them share either px py share or py pz share means 2 of the p orbitals are shared and p orbitals normally are at 90 degrees and therefore we find that group 6 elements form the chain, a zigzag chain at 90 degrees like it is shown here one atom forming one bond with one neighbour, the 2nd bond this one bonds with the 2nd neighbour here and the bond angle between this is 90 degrees. Similarly this forms one bond here, another one here this angle is 90 degrees.

This one forms a bond there and a bond there this angle is 90 degrees and this zigzag chain has been araised around a triangular prism each atom is on the edge of the triangle prism and the angles are maintained at 90 degrees. When the crystalline arrangement takes place but between the chains there cannot be primary bonds like we have here. These primary bonds have satisfied the octet alright so these are arranged in a hexagonal manner here these triangle prism but between the prism the (())(21:34) between the chain there are only secondary bonds the Van der Waals forces. So distances between them are very large as compared to the dimensions of the triangle prism or the bond length here they are much larger distances here that is what you find sulphur selenium et cetera some other (())(21:51) crystallising in this manner, right again these are elements not very much used by as bulk material in engineering.

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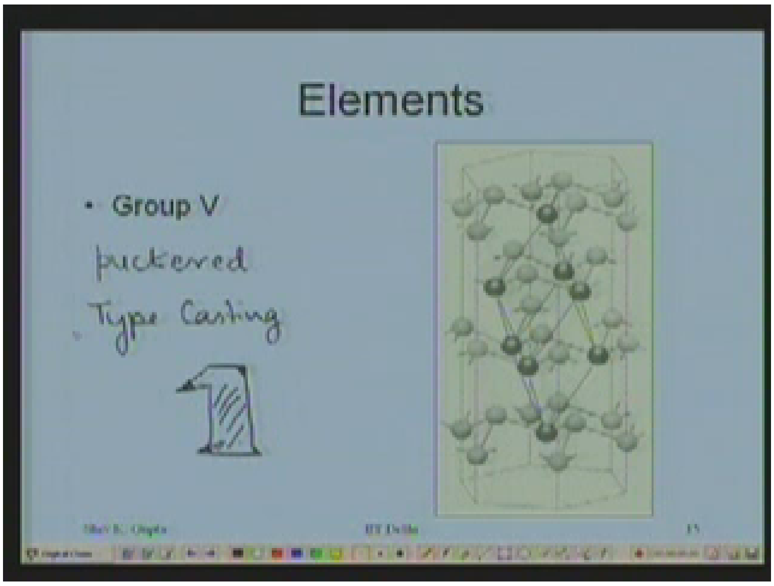

Elements

- Group V

puckered

Type Casting

We go to the group 5 elements now there are shortage of 3 electrons, so each px, py, pz can share and this is 90 degrees, when they share 90 degrees like that are sharing does not form a sheet, I mean it does from a sheet but that sheet is not a plane sheet like I show it here this atom here is a bonded to this one 2nd and the 3rd here and similarly this one is bonded one already there 2nd here and 3rd here all these angle are 90 degrees that is what you have to check then this is bonded to 31 here 2nd there and 3rd here, this one is bonded to 31 there 2nd here and 3rd here.

So this is forming a sheet but the sheet has a certain thickness some are projected out some are projected below the sheet thin sheet, okay so that is how this sheets are arranged then there is a 2nd sheet here then there is a 3rd sheet here then there is a 4th sheet there but between the sheets there is no sharing of electrons and therefore there are only Van der Waals forces between them again between the sheet there is a large distance and these sheets are not plane sheets these are called puckered sheet okay such elements antimony, bismuth et cetera which are there in group 5 we do use them as engineers and they are very helpful in type casting the reason for that is very simple, when melting of such a crystal occurs it is the Van der Waals forces which are going to give away because this is a weaker one.

Once that happens these sheets collapse and start translating one over the other the Van der Waals forces are gone so they start translating one over the other that is the liquid state as a result the volume in the liquid state is lower than the volume in the solid-state, so once these kind of solids crystallise or solidify from the melt the volume extends that is why they are useful in type casting, so for example I want to make a type like you have seen the typewriters or the computers of course these days we have all the laser printers I want to make a shape like this what is this? Digit 1 and the type right, this is a sharp corner here, these are the sharp corners there.

When I fill a cavity like this liquid metal because of the surface tension it does not fill the whole of it. Liquid gets filled in and but there is a space in which it does not go in like this alright rest of it, it can fill. So when it solidifies this liquid has to expand now in the solid-state, metal has to expand and this will fill the space to get the corners, very sharp corners possible to get that is why they are used in type casting, okay these elements are use in those alloys.

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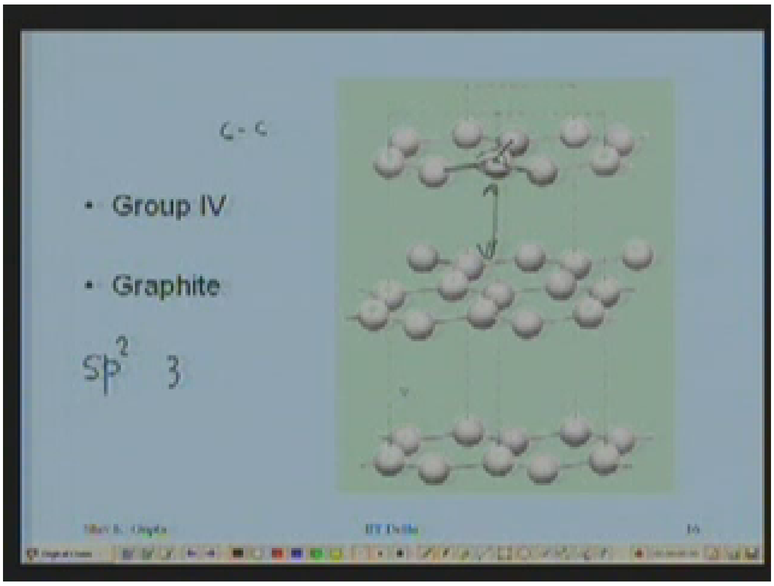

C - C

- Group IV
- Graphite

Sp^2 3

Now from group 5 we can move into the group 4, we shall talk about the carbon 1st, carbon has 2 allotropic forms one is diamond another is graphite. 1st of all we shall look at the graphite form there here now we have 4 electrons in the outermost orbit and to share it as need to share with 4 but out of orbits px, py, pz there are only 3 so therefore to share with 4, 2 S electrons and 2 P electrons hybridise to form Sp 3 that is the diamond but when they hybridise to give me only Sp 2 and the 4th electron remains free it gives me graphite. Sp 2 hybridisation means there are only 3 neighbours equally oriented in space, 3 neighbours equally oriented in space will find that to be in a plane at 120 degrees each other and that is what it is.

If you look at this one bonded to that neighbour at 120 degrees, bonded to this neighbour at 120 degrees bonded to that neighbour these 3 bonds at 120 degrees to each other alright this we form a plane sheets now these are not the as compared to group 5 they are different these are plane sheets but again between the sheets there are Van der Waals forces only because therefore the electrons does not take part in bonding at all, it remains free to move about in the sheet and as a result causes a Van der Waals forces between these sheets. The distance between them is much larger than the bond length or the carbon carbon bond length is much shorter than the distance between the sheets. Alternate sheets or rather consecutive sheets are displaced by the one bond length.

This is the bond length it is displaced by that bond length, okay like that backward it is gone, so therefore it is all displaced by one bond length and you can take any one of the 3 it is so symmetrical you can take the displacement around anyone of the 3 it will be the same situation or the same story, alright. So the alternate sheet therefore after 2 displacements it comes out to be exactly same, so it forms a hexagonal unit cell I have shown only half the hexagonal unit cell here other half is to be extended out and this forms a graphite crystal which is hexagonal in nature between the sheets being the secondary bond it gives very interesting characteristics to graphite.

A plane sheets with very weak bonds between them it is easy for them to slide like this. If it is a strong bond between them it is not so easy to slide but it is a weak bond it is easy to slide so this is a very soft material sheet slides one over the other easily and we use it in lubrication. In bearings we use it as dry lubricant, use it as bushes because the free electrons which is present in the sheet it can conduct electricity to use it as bushes in motors, right. This is also used as heating elements only thing is in the atmospheric oxygen can easily react to form carbon oxide and carbon dioxide so we have to keep it maintain this in an inert atmosphere or we have to maintain it in vacuum so that we can use this as a heating element.

Well if you look at the Sp 2 bond it is very strong as a result any direction on the sheet where it has only Sp 2 bonds is very strong, so if you try to stretch it with a force parallel to the sheet act as very strong but if you apply force in any direction which is perpendicular or not perpendicular to the sheet but not on the sheet it behaves in a very weak manner because the Van der Waals forces are very weak. It is possible for us to make fibres the axis of the fibre lies on the sheet, so whenever there is a fibre the force whatever force is coming it is coming in the axis of the fibre because the other 2 dimensions are very small in the fibre and therefore it acts very strong fibre.

Strength of this fibre is very high, so carbon fibres you must have heard of because of that because only Sp 2 bonds are there and this is the use of graphite as lubricant graphite as a conductor is very much used by engineers. Well the pencils you use are also having graphite though we call it lead but this is not lead, the lead of the pencil is nothing but graphite but this has different hardness value you know starts from 4b can go up to 4h. 4b may be very soft is almost pure graphite and then we mix clay in it as a binder and then it becomes 3b, 2b, b, hb, h, 2h more and more clay from more and more hard and then it will not be possible for these sheets to slip and it will not leave a mark on the paper when it is like 4h or 6h it will be very hard.

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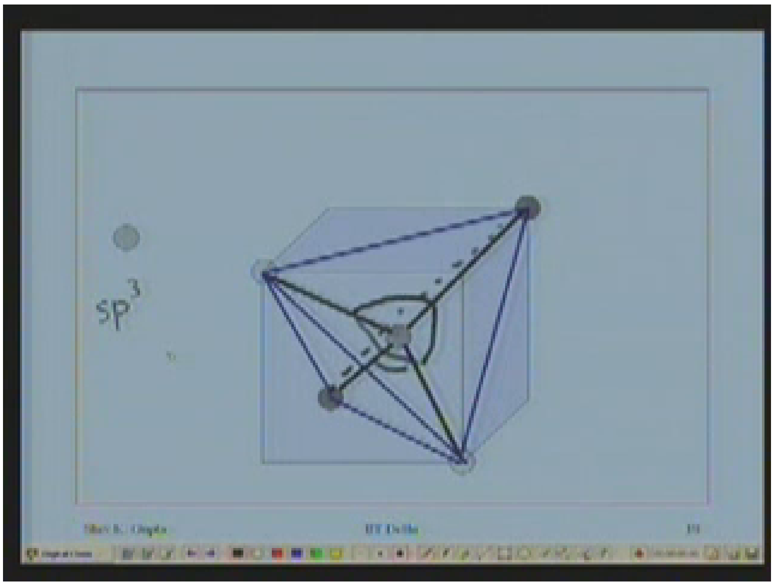

Now we come to the 2nd form of carbon which is diamond, here have shown the unit cell will come back to this unit cell again but before we come back to unit cell again but before we come back to unit cell we have to see what the local packing is and how do you get the long range arrangement. In diamond form there is Sp 3 bonding s and p all 3 orbits electrons and hybridise there is no distinction and they form 4 orbitals which are equally oriented in space again like in Sp 2 there were 3 orbitals equally oriented in space, now I have 4 and we know that we have seen this in chemistry this is also called tetrahedral bonds a form tetrahedral.

I show a tetrahedral here inscribe in a cube this is the front top corner this is the bottom right corner this is back left corner and this is the back top right corner. This is the center body center of the cube this one is equally oriented in space and with reference to this 4 corners which in a cube I have taken alternate one this one leave out that one next one leave out this one take that one leave out this one take that one again leave out that come back to this, so alternate corner I have taken body centre is equally oriented to the 8 corners of the cube I have taken alternate corners so it is also equally oriented to this 4 corners and I can inscribe a tetrahedral inside. Well the 4th of the a side of the tetrahedral probably it would be at the back that is the that is the back…

Student: (())(36:10).

Prof: This one, this one?

Student: Yes.

Prof: It is the body centre of the cube this is the body centre of the cube that is why it is bonded to this diagonal or this is the body diagonal half the body diagonal, this is also half the body diagonal that is also half the body diagonal this is also half the body diagonal. These are the tetrahedral angles this one, this one, this one these are all tetrahedral angles, well this one is also the tetrahedral angle 4 corners so 4 angles there, these are all tetrahedral angles which are formed and the angle you know this is 109.5 degrees this is the basic unit I have in Sp 3 bonding this its short-range arrangement. I have to see whether I can arrange these in the long-range to get a crystalline arrangement or it will not give me crystalline arrangement.

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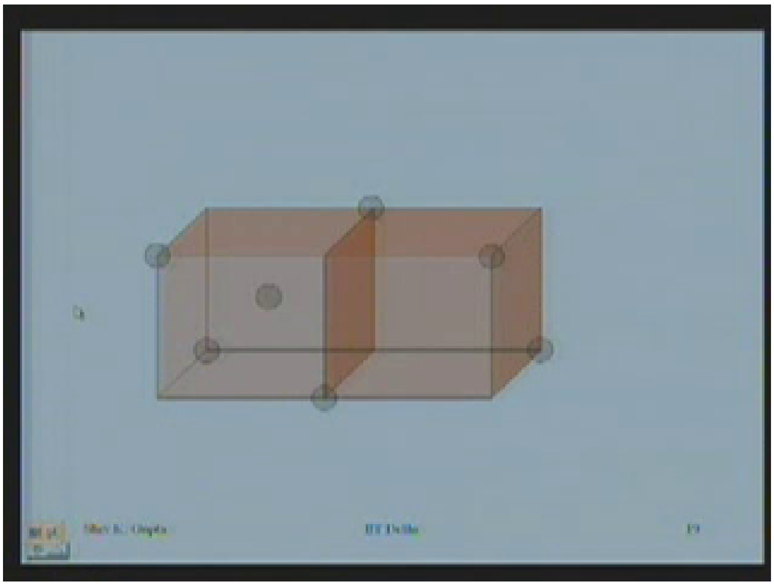

I have now removed that tetrahedral drawing this is the initial cube which I have these for alternate corners and this is the body centre, alright. Now I put next to it another cube which is identical in size, can I repeat whatever arrangement is here in this position, if I repeat this sphere goes there once I have that sphere here this is at the same distance from this body center, so this body center will have more than 4 neighbours or more than 4 bonds that is not possible, so it cannot go there so I have to leave it vacant, so this cube is left vacant then you make 3rd cube here, so this is translated from here to there.

Similarly this is translated from here to there this will be translated from here to the next here I just shown the 2 and therefore this will not be translated to this body center location it is translated to other body center location. So in other words I can say that I have a cube with a tetrahedral and body center inside, the neighbouring cube has a tetrahedral in this corner but does not have a body center, the moment I have that this will not have its 4 bounds it will have more than 4 bonds and I do not want any one of them to have more than 4 bonds because it is Sp 3 hybridisation in all three-dimension whether I look at this atom or I look at this atom all of them should have the same story to tell me therefore this has to be left vacant like that I can put 2 more let us see what happens when I do that?

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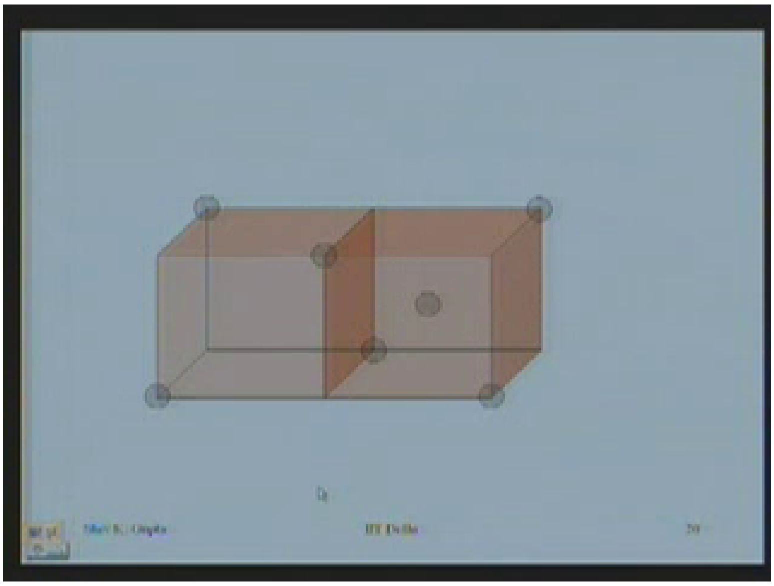

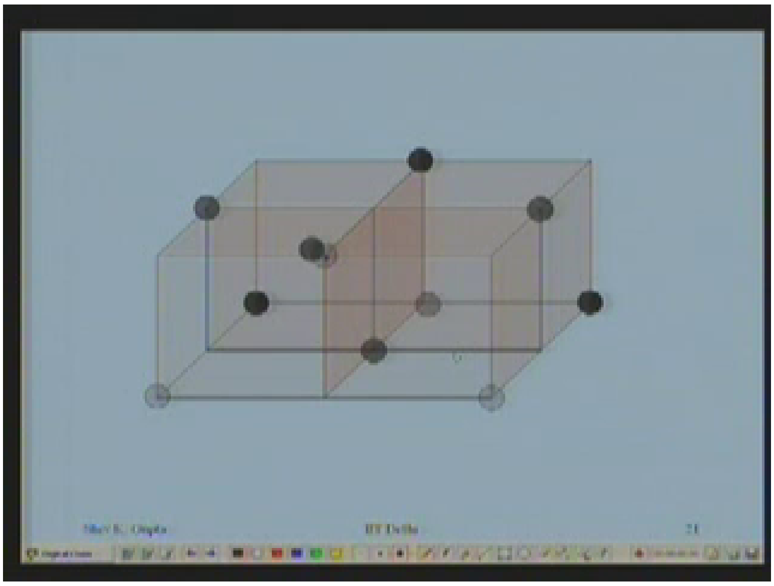

These 2 are made slightly differently a 1st one is the one which is empty and the 2nd one is the one which is going to have, so this 2nd one is actually my 1st one because I use that corner, this corner, this corner and this corner in other words you can say earlier I had extended it to the right, now I have extended to the left, to the left of this also will be empty and this pair and the previous pair which I showed that lets join them, the one the 1st one is the back the 2nd one is in the front, okay. The 1st one at the back has this as the body center, 1st one at the back has this as the body center and the 2nd one here in the front right has this one as the body center, looks as if I am putting in the corner, it is not I actually worked out the body center it is slightly displaced from there like it is slightly displaced from there.

So this is body center of the front cube which is here in the right, okay. So there this is a tetrahedral, that is a tetrahedral but this is empty and that one is also empty in the middle like this we can construct 4 on top of it but again you will have to displace, if there is a body center there the one on top will not have the body center but here there is no body center the top one this will have the body center, right. So like that you can build it again that shall be the one repeating unit because repeating distances is this.

Student: (())(41:29)

This is half the because I want to show the insights so it is half, other half will have to build on top of it like I have put 4 cubes here I have to put 4 more cubes like that each cube is only from one 8th of the total unit cell okay in volume, right.

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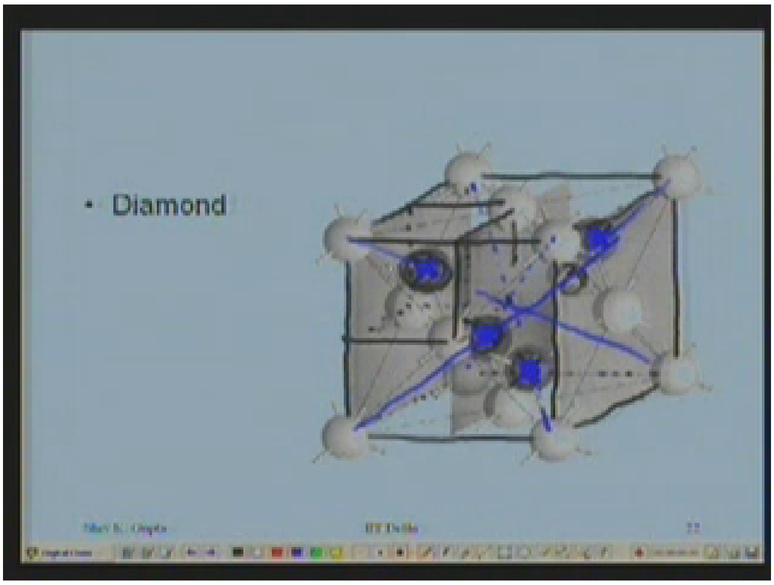

- Diamond

Let us see the next one come back to the 1st figure which I said see what have shown here is this is the unit cell that is the unit cell of course these are the…now you see the atoms have come at the 8 corners of the unit cell, atom have also come at the top face center, at the bottom face center, right face center, the left face center, the front face center and the back face center there. Then one has come here on the body center of the smaller cube here top in front of you see if I divided them this is the cube which I was trying to show you, you call that this is what I was trying to show you this one that one I showed you the 1st one this one and 2nd one, well this is actually that smaller cube is this and this is the body center of the bigger cube this one this corner there is nothing there and there is one here the next one is empty but then when you go at the back there is one in the body center there at the back one.

Similarly when I come below this this one in the body center here and when I go back of this front one here in the left is one and the body center there and this is how I have 8 corners 6 face centers and for within the cube this one, this one, this one and that one these are 4 within the cube these are within the cube. Look it carefully this one starts from here goes along the body diagonal which is here, this one starts from here goes along the body diagonal which went there I have not drawn the body diagonal very well and there is one here which is on this body diagonal that is the one and this 4th body diagonal starts here goes up to there and that is the one on that.

So these 4 which are inside they are on the 4 body diagonals of the cube they are within the volume of the unit cell this can be repeat in three-dimension and give me the diamond crystal long-range arrangement is possible now, it is a crystalline arrangement in diamond. Now there are no secondary bounds anywhere this is a part of a tetrahedral here which becomes a part of another tetrahedral there it becomes part of another tetrahedral here, this becomes part of this tetrahedral and becomes a part of tetrahedral elsewhere, so each one is in the body center of the tetrahedral and the same time it is also corner of the tetrahedral each one is bonded to 4 neighbours each one alright, so that goes on in three-dimensional as a result I have only Sp 3 bond in all the three-dimensions. I do not have any secondary bonds anywhere this is a hardest known material in the world there is no secondary bond anyway.

So the fluorine fluorine bond is very strong but between a fluorine molecules their secondary bond Van der Waals forces very soft its gas as a matter of fact at room temperature this is a solid crystalline material and the hardest known material because there are no secondary bonds. Group 7 also has secondary bonds, group 6 has secondary bonds, proof I has secondary bonds, group 8 anyway are only secondary bonds, so this is the 1st one and all covalent bonds in 3 dimensions because of this very hard nature of this material it is used by engineers for…alright we will, alright we will come to that I think there is a slide for that.

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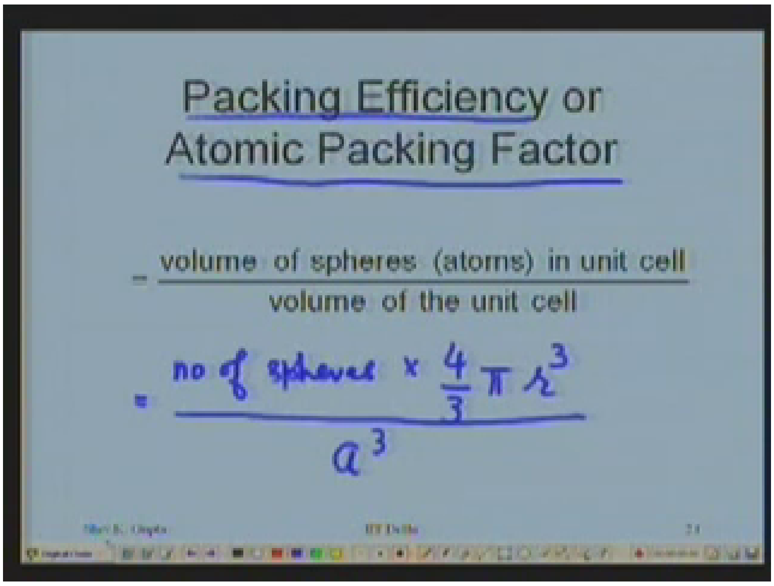

Packing Efficiency or Atomic Packing Factor

$$= \frac{\text{volume of spheres (atoms) in unit cell}}{\text{volume of the unit cell}}$$

$$= \frac{\text{no of spheres} \times \frac{4}{3}\pi r^3}{a^3}$$

The applications and properties which are look into because this is very hard material. Before we proceed further this is a crystalline arrangement where I have all covalent bonds in 3 dimensions we have seen that when I stack one cube after the next one, the next one each alternate one is not having a body center and the alternate one is having a body center that means there is space for that atom to come and sit there I mean there is lot of space there or more atoms to set but they are not sitting because they have to maintain Sp 3 bonding that means there the atoms space which is available to me is not been utilised in a very efficient manner that we refer to as packing efficiency or atomic packing factor.

Either sometimes we call it packing efficiency of the crystal we call it atomic packing factor that should be very small for this because there is lot of open space available and it is defined as volume of the sphere because I have consider atoms to be hard spheres so or volume of atoms of spheres in units cells divided by volume of the unit cell. This volume of the spheres will depend upon number of spheres into sphere is sphere 4 upon 3 pi r cube divided by volume of the side of the cube is a it is a cube. Now 1st of all we shall look at the number of spheres then we shall look the relationship if there is between r in a to simplified this.

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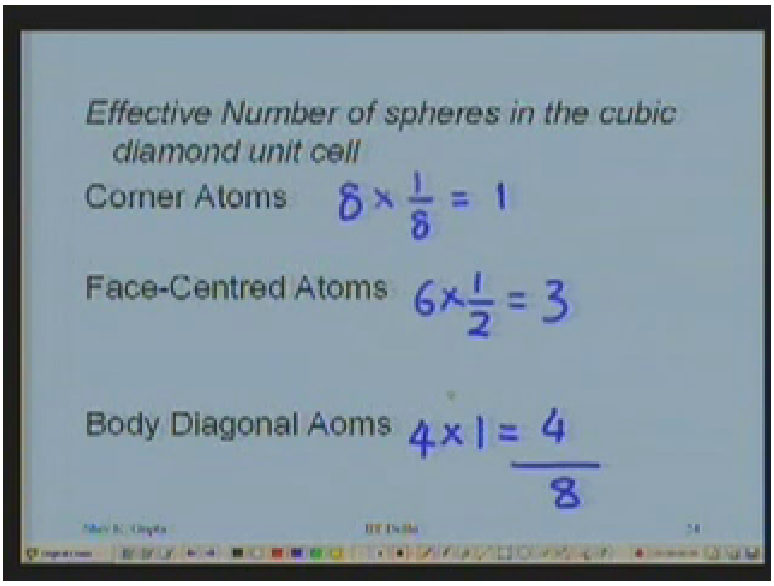

Effective Number of spheres in the cubic diamond unit cell

Corner Atoms $8 \times \frac{1}{8} = 1$

Face-Centred Atoms $6 \times \frac{1}{2} = 3$

Body Diagonal Aoms $4 \times 1 = \frac{4}{8}$

In the unit cell of a diamond cube we have seen they are corner atoms, how many of them are there? 8 each one is shared 8 unit cells so I have one, how many face centred items do I have? 6 very good and faces or common between 2 units cells, so it is only 3 in the volume of the unit cell. How many body diagonal and sphere in them? Each one has only one, okay I have 4 body diagonals and each one has only one that makes it 4 total numbers is how much? 8. In the unit cell total number of spheres we have is 8.

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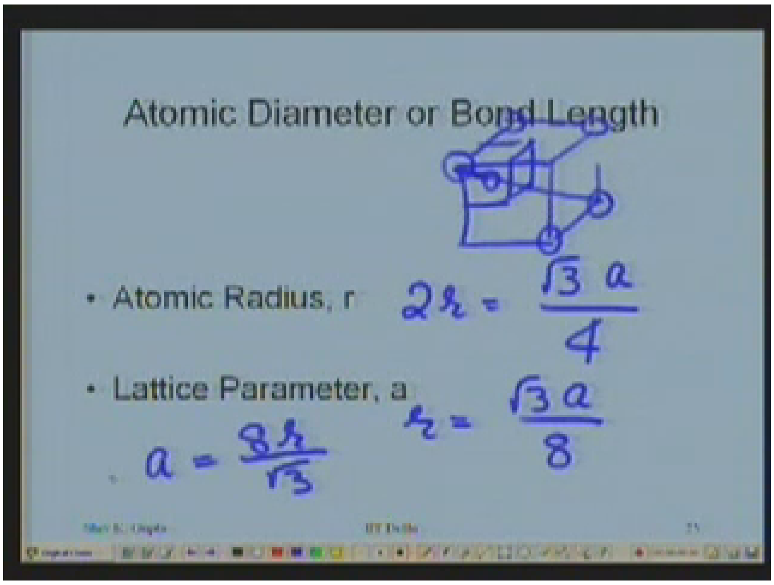

Atomic Diameter or Bond Length

- Atomic Radius, r $2r = \frac{\sqrt{3}a}{4}$
- Lattice Parameter, a $r = \frac{\sqrt{3}a}{8}$

$a = \frac{8r}{\sqrt{3}}$

Now let us look we have defined the diameter of the sphere as the closes distance of approach or the bond length, what is a bond length here? One atom sitting at the corner, others sitting at the body center or the center of the tetrahedral… root 3 a by… not to it is root 3 a by 4. On this diagonal I have one here which is a part of or body center of this cube only this is the body center there is no atom there, so it is this distance which is equal to 2 r. Here 2 r is equal to root 3 a by 4, very good. So in other words r is root 3 a by 8 or you can also rewrite this as a is equal to 8 r by under root 3, alright.

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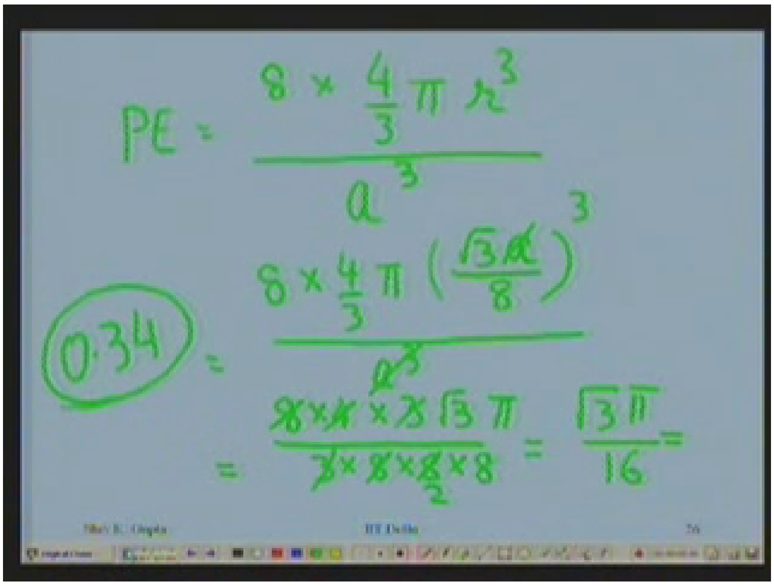

$$PE = \frac{8 \times \frac{4}{3}\pi r^3}{a^3}$$

$$\boxed{0.34} = \frac{8 \times \frac{4}{3}\pi \left(\frac{\sqrt{3}\cancel{a}}{8}\right)^3}{\cancel{a^3}}$$

$$= \frac{\cancel{8} \times \cancel{4} \times \cancel{3}\sqrt{3}\pi}{\cancel{3} \times \cancel{8} \times \underset{2}{\cancel{8}} \times 8} = \frac{\sqrt{3}\pi}{16} =$$

Let us go back to what we wrote in packing efficiency, I wrote packing efficiency as number of spheres which is 8 times the volume of these spheres divided by a cube now let us substitute one in terms of the other, yes what did we say? Root 3 a by 8 whole cube divided by a cube, now it is possible for me to cancel a cube with this a cube here because there is a cube there and if I simplify this what I get his 8 times 4 under root 3 cube is 3 under root 3 and the denominator I have 3 and cube of 8, 8 into 8 into 8, 8 cancels with this 8, 4 simplifies it to 2, 3 cancels with this 3 and there is also a pi there, so it becomes under root 3 pi by 16. Under root 3 is 1.73, pi is about 3.1 this is product becomes how much? Roughly 5.4 something divided by 16, how much it is going to be? It will be approximately alright let us write it here 0.34. That means 34 percent of the volume is occupied by this spheres and 66 percent is not occupied we call it vacant space but this vacant space is what? Is it vacuum, is it air, is it oxygen, what is it…this vacant space?

Student: Orbital.

Prof: You are right when you talk about orbitals there are electrons but probability of finding electrons in those spaces is very small. Probably of finding those electrons in those spaces is very small, alright. Therefore this is therefore it is simply a vacant space is not there is no air there, right and you do not refer to as vacuum either only electron clouds which as I say probability of finding this is very small.

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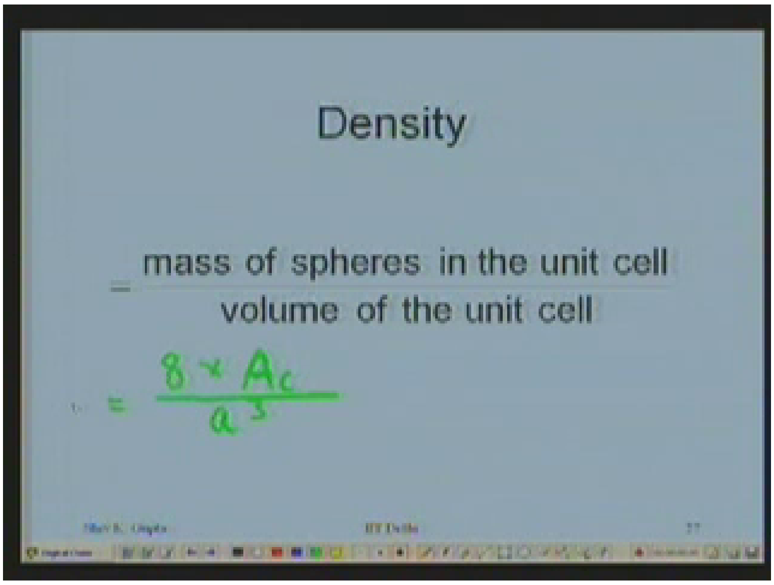

Density

$$= \frac{\text{mass of spheres in the unit cell}}{\text{volume of the unit cell}}$$

$$= \frac{8 \times A_c}{a^3}$$

Similarly you can define the density in healthy you need the mass of spheres so what will you do? You will write the number again which is 8 write the atomic mass of carbon and then whatever the unit cell. It is possible for us to relate the density to the packing efficiency, okay.

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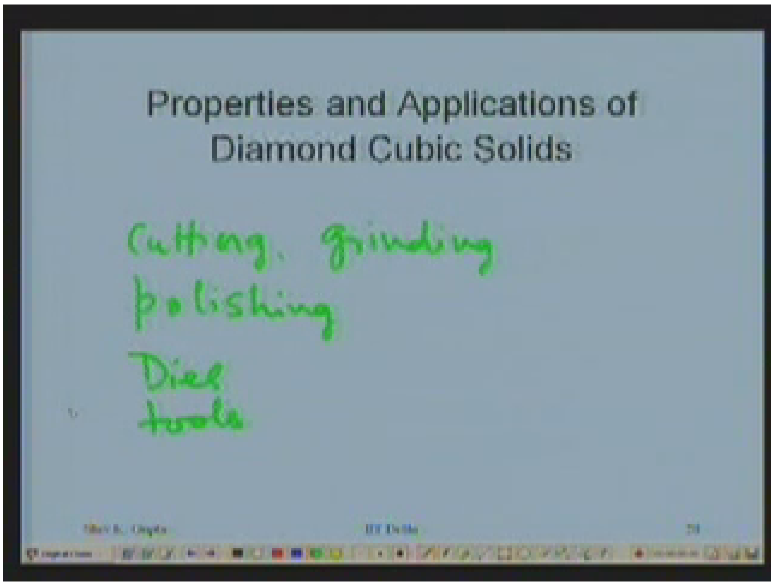

Properties and Applications of Diamond Cubic Solids

Cutting, grinding
polishing
Dies
tools

Now coming to the properties and applications of diamond cubic solids as I said already it is a very hard material, so engineers exploit them in such applications where we need very hard material like cutting, machining so you have cutting, abrasion, polishing, grinding. You can make the dye, tools, et cetera (())(57:18) common man has in jewellery application for diamond besides the diamond there are crystals which also form in a similar kind of arrangement with the Sp 3 bonding but they do not have only one kind of atom they may have 2 kinds of atoms and those are called the 50-50 compounds.

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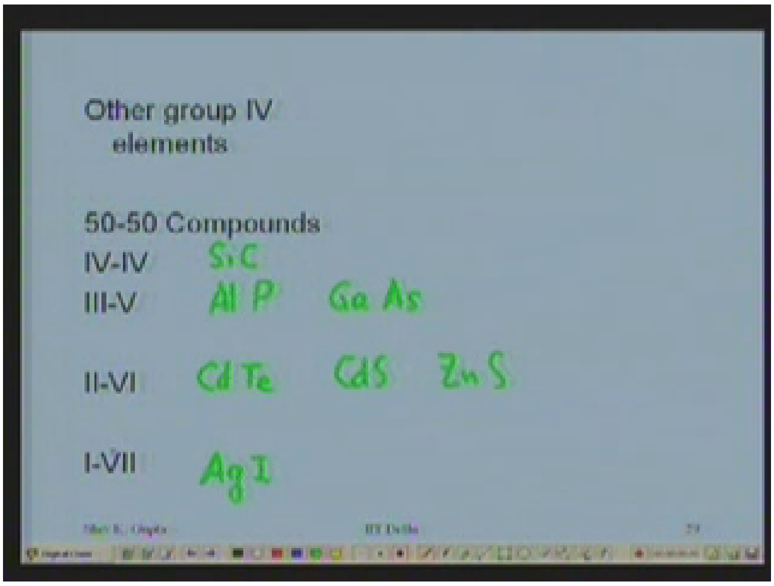

Other group IV elements

50-50 Compounds

IV-IV SiC

III-V AlP GaAs

II-VI CdTe CdS ZnS

I-VII AgI

Say for example 4-4 is silicon, carbon silicon Carbide. Silicon Carbide acts as a semiconducting material till up to about 700 (())(58:10) degree centigrade beyond that it becomes something like metallic, so we use exploit it as a heating element. Group 3-5 compounds like group 3 is let us say aluminium, group 5 let us say phosphorus or take gallium, arsenic these are semiconducting materials and important semiconducting materials then 2-6 similarly are also semiconducting materials, cadmium Telluride, cadmium sulphide, zinc sulphide, et cetera and similarly 1 and 7 are silver halide like silver iodide.

In here what is happening is the face centred cubic locations which are the corners and the face centres are occupied by one atom whether it is aluminium or phosphorus, the body diagonal position where 4 within the unit cell those are occupied by the other kind of atom, so the ratio is 50-50 we have seen that body corners gave me one face centres give me 3, so makes it 4 the one which have 4 on the body diagonal they make 4, so 4 and 4 becomes 50-50, right. So that is how the structures look like and when these elements are diffracted and axial diffraction is seen though I talked about yesterday diamond cube extinguishes some more lines diffraction lines from the FCC they will show all FCC because skating centres are not identical though they are out of phase but there is no total cancellation of intensities, those intensities will turn out to be weaker here but they will be there, is that clear? That also answers the question which you are trying to ask in the morning. I thank you we shall start from here in the next class.