An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)

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Lecture - 19
Covalent Solids

So we will start with this new lecture today lecture 19.

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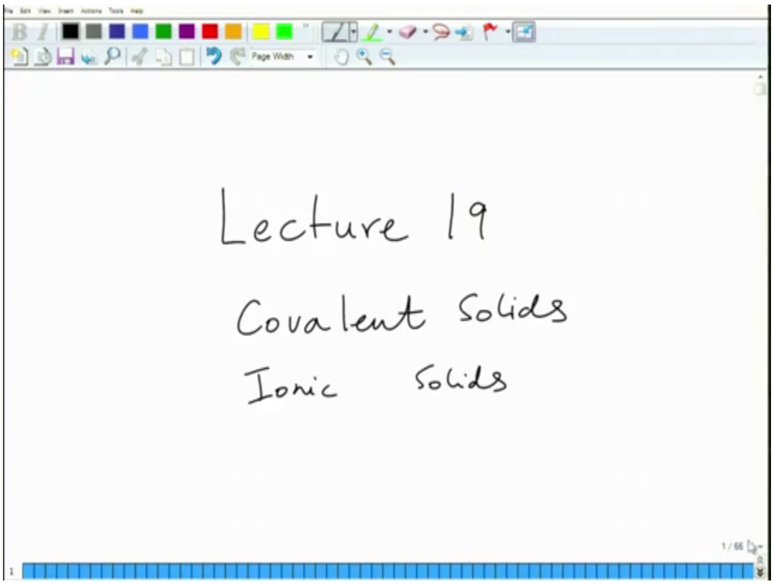

Lecture 19

Covalent Solids

Ionic Solids

In which we will talk about covalent solids and if we are able to finish that early we can start ionic solids, but it is unlikely. So, let me just recap what we have studied so far.

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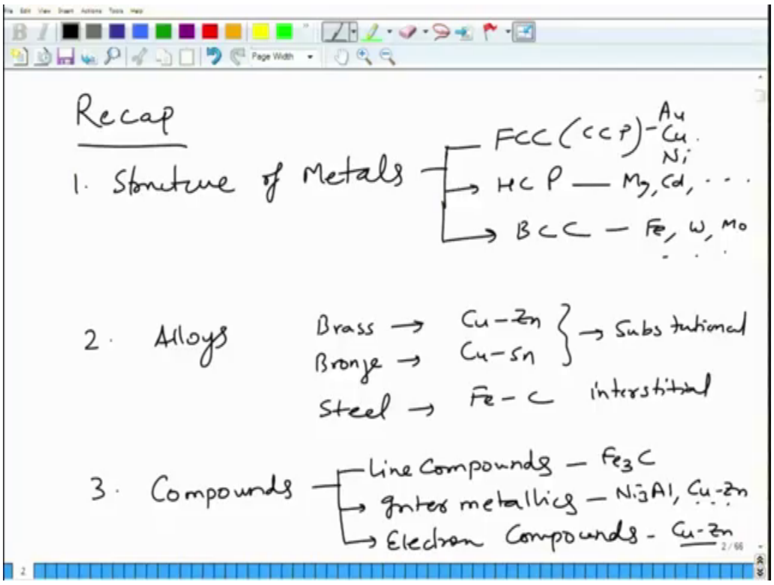

Recap

1. Structure of Metals
- FCC (CCP) – Au, Cu, Ni
- HCP — Mg, Cd, . . .
- BCC – Fe, W, Mo . . .

2. Alloys
- Brass → Cu – Zn
- Bronze → Cu – Sn
- } → Substitutional
- Steel → Fe – C interstitial

3. Compounds
- Line Compounds – Fe_3C
- Inter metallics – Ni_3Al, Cu-Zn
- Electron Compounds - Cu-Zn

We looked at the in the past few lecture the structure of metals ok. So, structure of metals typically is of 3 types most metals are FCC structured or you can say CCP structured, cubic close packed structured or hexagonal close packed and BCC structured. There is only one example of simple cubic metal which is polonium, but by (Refer Time: 01:05) most of the metals and alloys fall in this category.

Now so FCC based space structures materials were typically things like gold, copper etcetera nickel, HCP based materials are magnesium, cadmium etc and then BCC based materials are for example, titanium tungsten, molybdenum all of these are BCC structure materials. Now the alloys most metals do not exist in pure form and we also use then in a impure form for improving their properties; for example, iron is iron is used as a alloy of iron and carbon because, carbon is intentionally put to make iron stronger. So, the question arises is where does carbon go?

For example, similarly we also use brasses and bronzes which are solid solution of tin and zinc or zinc and so it is you can have brass which is Cu Zn you can have bronze which is Cu Sn and you have steel which is iron carbon. And there are many other examples there are 3 famous examples of materials, that we use in develop applications. So, where do these atoms go for example, where does zinc go, where does tin go, where this carbon go? So, it happens it is determined by the size of the atom, it is determined by the size difference between the host lattice and the impurity atom, it is determined by the valence difference the structural difference and so on and so for.

So, it turns out that carbon and iron will make a interstitial solid solution, whereas zinc and tin will make a substitutional solid solution because, the size of zinc and tin is the larger than the size of interstities that occur in these solids. So, carbon prefers to go to interstitial size because is smaller atom. So, whether it is a gamma iron or alpha iron depending upon the temperature it goes in interstitial sites, where as zinc and tin below their; so solid solubility limit and they make a substitution solid solution and then we also saw some examples of compounds which are.

So, you can have line compounds which have fixed composition intermetallics, line compounds intermetallics can often be similar also and then we also looked at electron compounds. So, these were 3 compounds which form when you mix 2 metals with each other and they tend to have fixed composition and for example, electron electron compounds they have fixed electron to atom ratio; similarly intermetallics like.

So, Fe 3 C for example, is a line compound it is a fixed composition you have intermetallics like Ni 3 Al Cu Zn and so on and so forth, a electron compounds we looked at some Cu Zn type of compounds system which has electron specifically electron to atom ratios. So, these are all materials which are metallically bounded materials predominantly although intermetallics and line compounds may have some fraction of covalent ionic bonding, predominantly these are metallically boundary materials. So, now, we will look at the case of what we call as covalently bonded materials.

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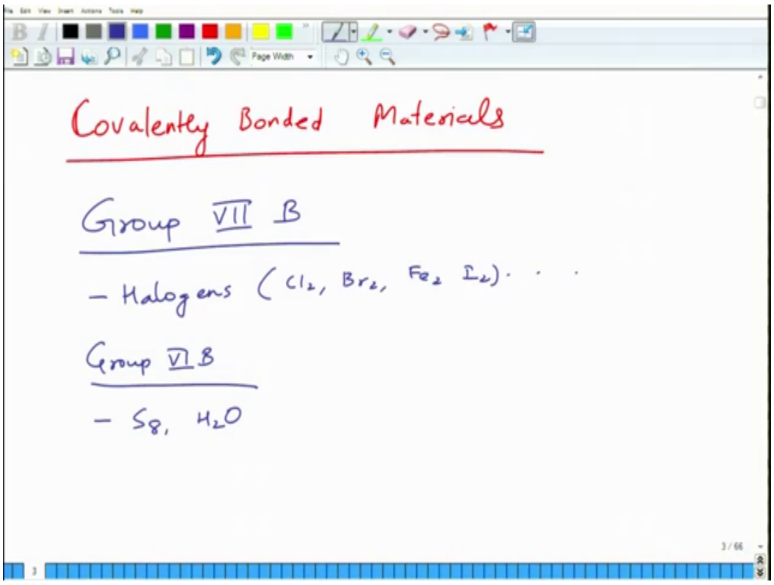

Covalently Bonded Materials

Group VII B

– Halogens (Cl_2, Br_2, Fe_2 I_2) . . .

Group VI B

– S_8, H_2O

And this is again a important class of materials because, there are lot of materials which occur which have covalent bonded for example, you take you take group 7 B. So, 7 B will mean basically halogens right. So, your Cl 2 your Br 2 Fe2 I2 in solid state, they have they are covalently bonded and they make a particular crystal structure which is based on covalent bonding.

Similarly, if you look at look at group 6B, 6 B will have molecules like S8 or even H 2 O. So, H 2 O will make for example, hexagonal ice crystal right. So, these are also covalently bonded materials this not something that we use in routine basis group 5 elements.

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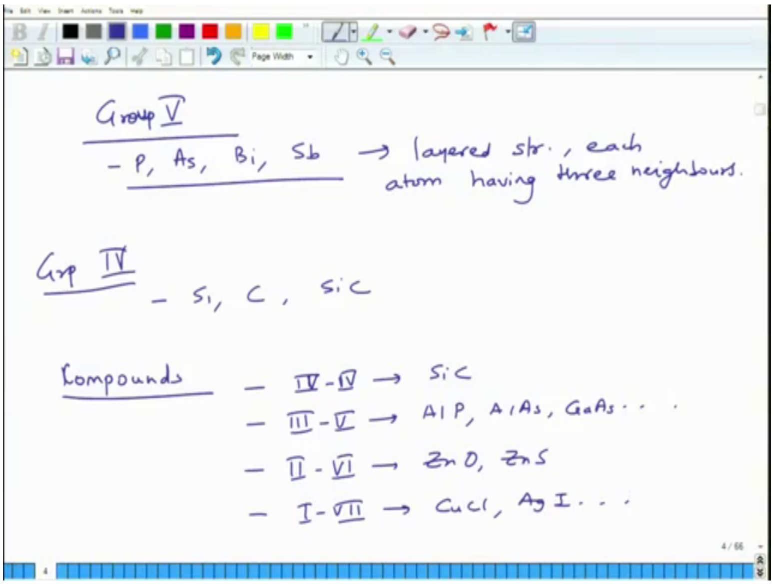

Group V

- P, As, Bi, Sb → layered str., each atom having three neighbours.

Grp IV - Si, C, SiC

Compounds
- IV-IV → SiC
- III-V → AlP, AlAs, GaAs . . .
- II-VI → ZnO, ZnS
- I-VII → CuCl, AgI . . .

Such as phosphorus arsenic bismuth antimony they also have strong covalent character and they basically have these sheet like layered structure in which each atom has 3 neighbors. So, it is a layered structure each atom having 3 neighbors and then the most famous is group 4. Group 4 contains your silicon, carbon, silicon carbide, solid solution of silicon and compound made by silicon and carbon, these are all diamond structured materials and they are covalently bonded very strongly covalently bonded and then we have compounds.

So, compounds for example, you have 4-4 compound which is silicon of carbide, then, then we have 3-5 compounds things like aluminum phosphide, aluminum arsenide your gallium arsenide these are all famous semiconductors, they are 3-5 semiconductors they are strongly covalent in nature; then we have 2-6 compounds such as ZnO and ZnS these are also strongly covalent, then we have 1-7 compounds these are CuCl or Ag I and so on and so for.

The covalent bonding typically takes place by, so the theory which is about covalent bonding is called as valence bond theory.

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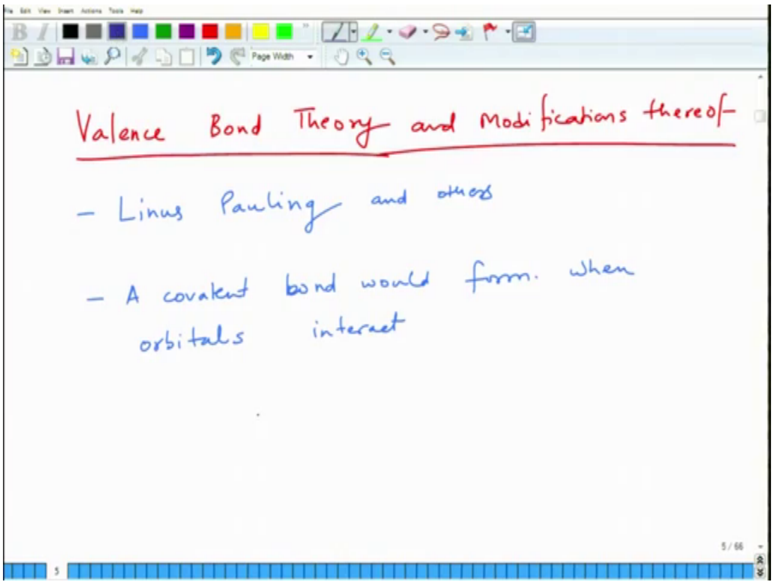

Valence Bond Theory and Modifications thereof

- Linus Pauling and others

- A covalent bond would form. when orbitals interact

Now this valence bond theory basically started with people like Linus Pauling, he was Linus Pauling he was a famous physicist or chemistry you can solid set quantum mechanics person. So, he said that the; a covalent they said basically Linus Pauling and let say others. So, a covalent bond would form when the orbital’s on the atoms would interact with each other ok.

So, for example, if you take and this orbital will depend upon how they align with each other ok. So, if I give you the example for example, in case of hydrogen, so when orbital’s interact now this valence bond theory has undergone several modifications, the reason for that is earlier atomic this orbital interaction was fine, but there was no concept of orbital hybridization.

So, it is it was reasonably straightforward for spherical orbital’s to interact or linear orbital’s to interact, but when it came to things like silicon when it came to things like methane, the question was why would something having 2 electron in the outer shell make 4 nearest neighbors and that would not be possible until you have SP3 kind of hybridization in the system, so hybridization concept came later. So, this modified uh, so I can write here valence bond theory and modifications they are off which was based on hybridization.

Basically, so it is not only just orbital interaction it is also orbital hybridization which leads to better orbital interaction I if we can say that so for example, if you take example Of hydrogen.

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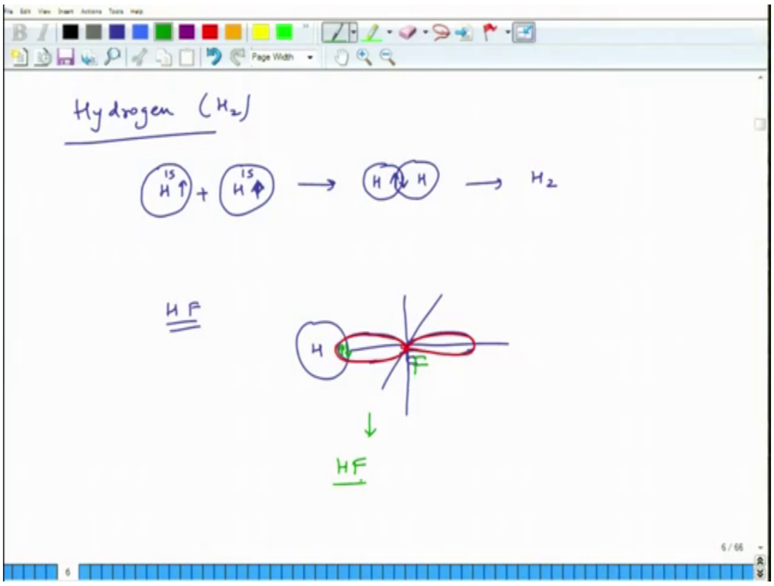

So, hydrogen you know we know H atom is 1 S and another H atom is again 1 S and if you put these 2 together they form, so there is this overlap of orbital’s and they will have the. So, I mean you can put it this way, but when they interact with each other 1 spin would be up another spin would be down. So, this would be H and they would form what we call as H2 molecule, which is covalently molecule and you can see that orbital’s can in interact with each other because, they are spherical orbital’s symmetric orbital’s and they just have to share one electron each.

For example, if you take case of hydrogen fluoride hydrogen fluoride has a H atom here, but the problem with F atom is F atom has P orbital’s, thro through which it has to interact why does interact with a P orbital’s, so it will interact with a P orbit or something like that. So, you have a this center F and this will be other orbital, so this would be F and then you have these axis x y and z axis here total of 6 orbital’s right. I am not drawing all the orbital’s but if I put them in different color, so this would be ok

So, you will have a spin, so if you just put on this spin there they will be 1 2 spin up another spin down and this would make. So, this is F molecule this would make HF this is again a covalently bonded molecule similar examples you can give for fluorine for example F 2 gas.

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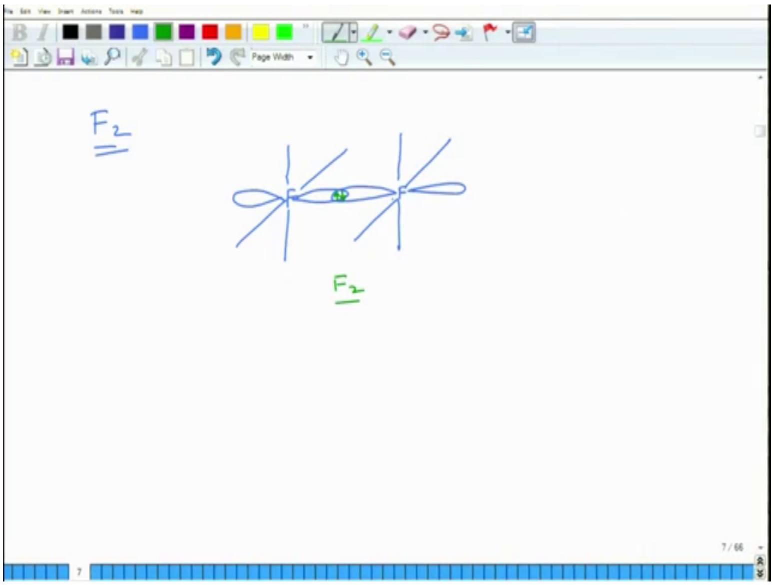

So, F 2 gas has again F it will have 1 orbital on this side, another orbital on this side and it will interact with the neighboring fluorine atom which will have P orbital like this and orbital like this of course, you will have other 2 axes as well and this will give you F 2 molecule ok. So, this is this is fine the but the problem arose with for example, things like silicon or let us say CH4 methane is a good example, so or in carbon compounds carbon compounds.

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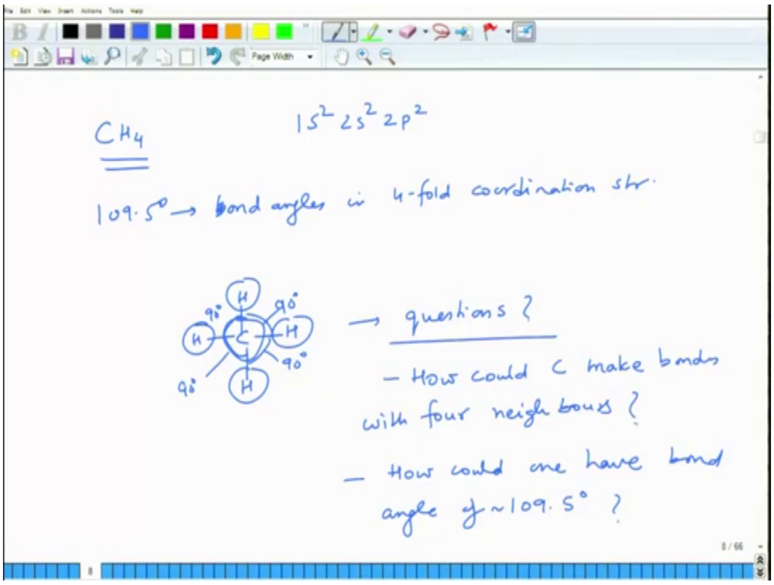

CH_4

$1s^2 2s^2 2p^2$

109.5° → bond angles in 4-fold coordination str.

→ questions?

- How could C make bonds with four neighbours?

- How could one have bond angle of ~109.5° ?

Carbon has a configuration of 1S2, 2S2 and 2p2 and we know that CH4 may in CH4 carbon will make 4 bonds, in carbon or silicon also diamond or silicon also it makes 4 bonds the question is why will it make 4 bonds? So, and how will the orbital's align with each other then and the measured angles bond angles are 109.5 degrees this these are bond angles.

In this fourfold coordination coordinated structure. So, for example, if you look at the top view this is carbon you do not have hydrogen sitting like that, they do not make if you if you look at the top view this angle would be 90 degrees, they do not make 90 degrees.

So, this is like 90 degree according to valence bond theory this should be 90 this should be 90 this should be 90 this should be 90, but then if it was 90 then how come it is making 4 bonds because, 4 bonds means carbon will have to share the 4 atom 4 electrons where do those 4 electrons come from. So, these were the questions which led to sort of modified theory and this led to. So, so this is what gave rose and gave rise to questions, the questions were how could carbon make bonds with 4 neighbors; how could 1 have bond angle of 109.5 I think it is nearly 5 degree.

So, these were the questions they led to the answers in what we call as now hybridization.

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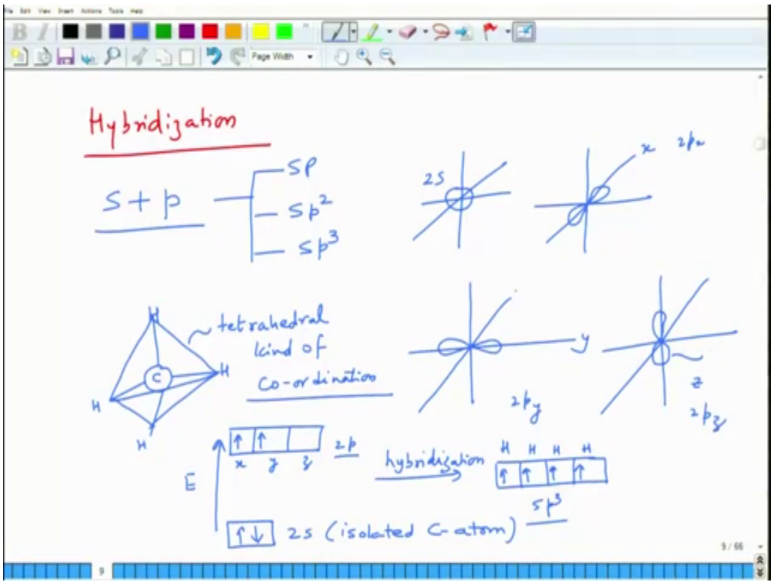

So there are various kind of hybridization which occur. So, for example so basically it is S and P type of hybridization. So, you can have SP hybridization you can have SP2 hybridization you can have SP3 hybridization, the hybridized S and P orbital's give you the enough number of electrons; so that you can have sufficient number of neighbors to make that particular structure, so that for example, the covalently bonded structure. So, in case of methane the structure looks something like this, so you have this carbon atom sitting here the hydrogen atom is here, 1 hydrogen atom is here next hydrogen atom is here another hydrogen atom is here.

So, this is hydrogen this is hydrogen this is basically what they make is a tetredral kind of structure, so basically this is a tetredral kind of coordination. So, essentially what happens is that you have 1 S orbital this is S ok, so this is 2 S orbital you can have 2 P orbital's as for example, you can have if I have if this is my x axis I can have 1 P here, this is along the x I can have another P along. So, let us say this is y ok, so this is y and then another P can be along z.

So, you can have this; these lobes of P orbital's along z. So, this is 2S this is 2px 2py and this is 2pz. So, hybridization basically gives you. So, if you look at the if you look at the energetic. So, this is for example, the energy scale, the isolated carbon atom has so this is 2 S of isolated carbon atom ok, this has spins like this is satisfied all right. So, whereas, in case of P we have 3 orbital's, this is up this is up and this is empty ok, so this is x this is y this is z and this is 2 P all of them are 2P 2px 2py 2pn.

So, when they hybridize when they go to hybridized, when the hybridization happens in case of hybridization what happens is that you make SP3 kind of hybridized orbital like this. So, this is we say as SP3 orbital and this what you form is basically for SP3 orbital's.

So, you have 4 electrons here each of them remains unpaired and these ones this is what is orbital hybridization. So, essentially what you will have is now you will have 1 hydrogen will come and attach to it, so this is another hydrogen will come in attached to you this hydrogen will come very attached to this, this is how you will make a methane molecule. So, methane will now interact in such a fashion, so that you will have 1 central atom here.

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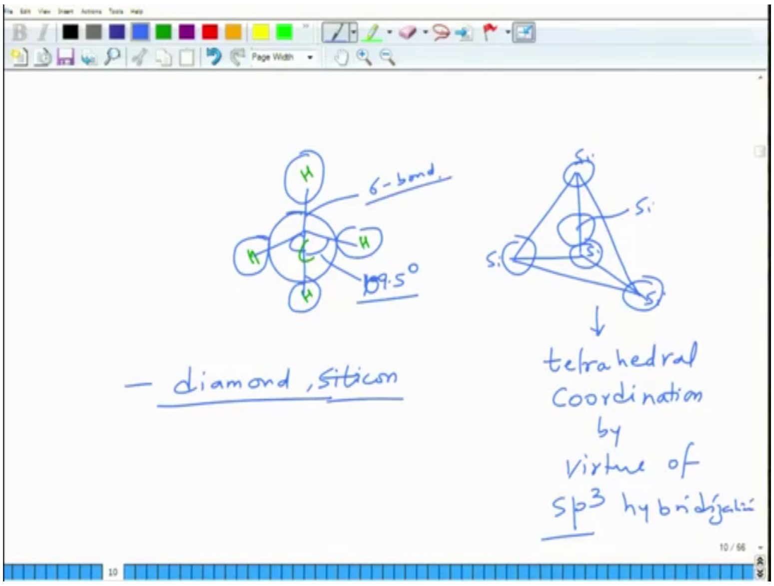

Methane carbon and this will have bond with 1 here 1 here 1 here, I mean I am showing the top view another would be somewhere here and they will make an angle such a fashion. So, that the angle between each of them will be 109.5 degrees, so these are all tetredral bonds. So this is basically you can say it is a SP3 hybridization in CH4 molecules this is what same happens in diamond, which makes a or silicon.

So, in case of diamond in silicon also, so in case of methane this would be carbon this would be hydrogen this would be hydrogen this would be hydrogen, in case of si silicon you will have if I just make a tetredron ok. So, this is tetredral that we can have, this is 1 silicon this is another silicon this is another silicon this is another silicon and 1 silicon will be sitting somewhere in the centre. So, this is again a silicon, again they make a tetredral coordination by virtue of SP3 hybridization which would not be possible just by orbital overlap ok.

Can we understood this hybridization in terms of energetic? There is a energetic of course, it leads lowering of energy, but I am not covering in this course because it is too extensive. But any basic book on for example, if you go if you do any basic book on chemistry the BSC first year level chemistry that will give you insights into that. So, for example, book I think book by Atkins should be suff, if I am a I cannot remember the names right.

Now, but there are there are a few books which can which deal with this any chemistry undergraduate books will give you introduction and there are a lot of theories, it is not just one theory you have valence bond theory which is modified then you have molecular or orbital theory there are lot of theories and covalent bonding.

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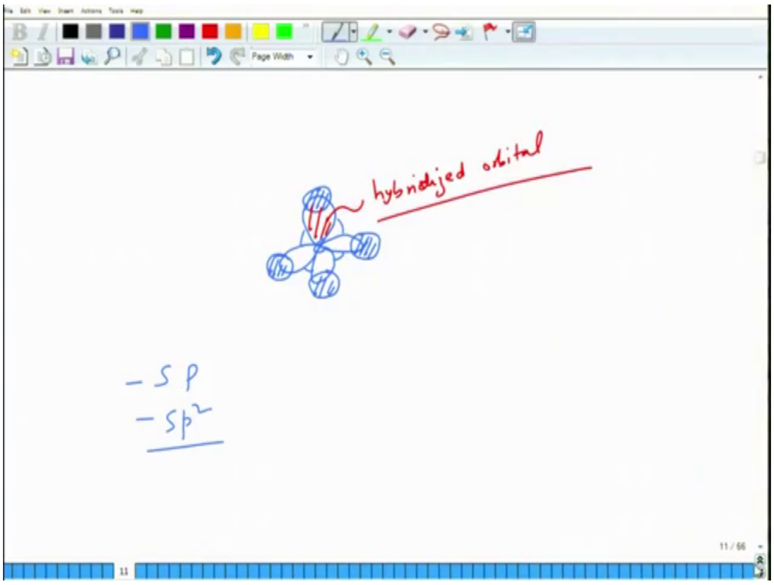

it looks like this you have a you have 1 lobe like that another lobe like that another lobe like that and another lobe like that. So, this is the vertical one which will interact with 1 hydrogen, this is another 1 which will lobe interact another hydrogen and at the center you will have C and all of the these will have angles 109.5 degrees. So, these are all hybridized SP3 orbital's they are not exactly P orbital these are all hybridized orbital's.

So, what you see here this 1 this is a hybridized orbital ok. So, you can have other cases as well you can have for example SP hybridization also, you can have SP2 hybridization also; I will leave you to leave it to study for example, graphite will not have SP3 hybridization and graphite has only SP2 hybridization and there are some other materials which will have SP3 hybridization.

So, I will probably and the bond which forms between these is called as sigma bond and sigma bond is a very strong bond there is another kind of bond which forms in molecules which is called as covalent bond especially in polymeric materials. So, you can have if you look at, so you can have these P type of lobes ok.

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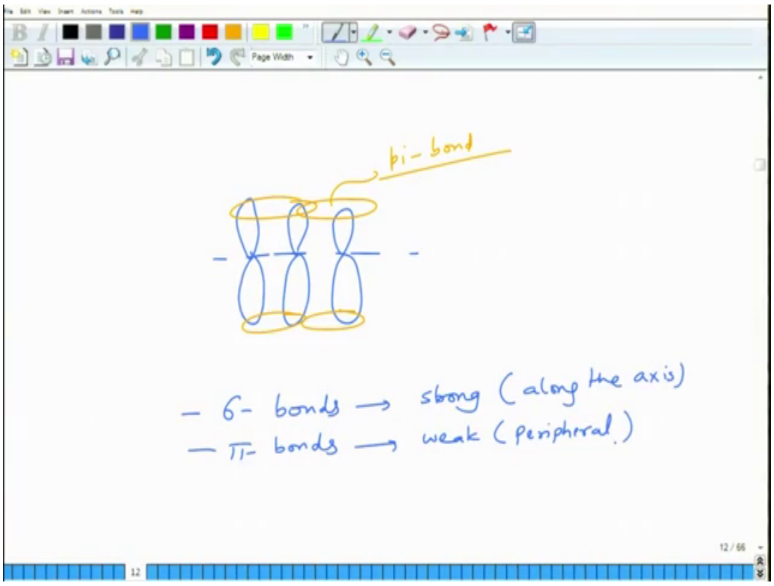

- σ- bonds → strong (along the axis)
- π- bonds → weak (peripheral)

So, suppose you have these P type of lobes along the chains of a poly bar like this, the bond which forms between these and the neighboring ones is called as pi bond; pi bond is a weak bond and sigma bond is a strong bond. So, there are these are the 2 terms that you will come across pi bonds sigma bonds and pi bond, strong basically along the axis and these are weak you can say these are basically at the periphery alright.

So, typically you will see if you have SP hybridization then, the configuration will be linear.

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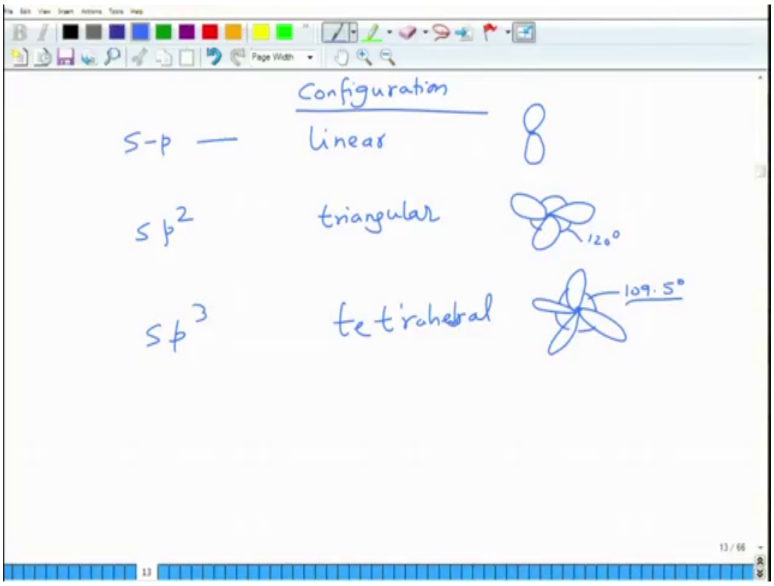

	Configuration
S-p —	linear
sp^2	triangular
sp^3	tetrahedral

So, if I write the configuration SP will lead to linear configuration. So, it would be something like that this would be the linear configuration, if you have SP2 you will have tri angular. So, I think like this and these angles will be 120 degrees ok. So, for example, in graphite you have and if you have tetredral then it is SP3. So, that I showed you have 1 lobe here another lobe here another lobe, here another loop here and these angles would be 109.55 degrees, close to 109.5 degrees and there are some other.

As well for example you can have SP3 d and SP3 d 2 which I am not going to get into they are more complicated to draw. So, these are some examples of a this is, so this is basically the basis of covalent bonding, you based on the theoretical background.

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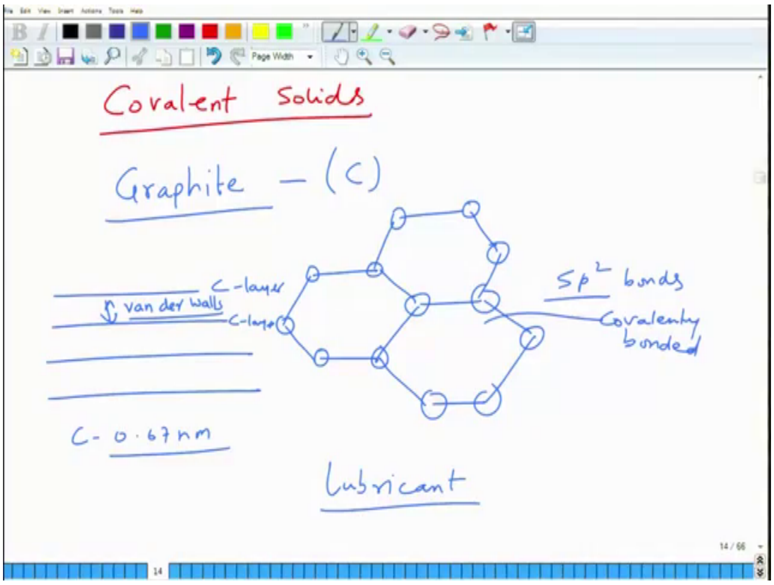

So, there are the covalent the solids now when we come to materials, the covalent solids that we come across we start with. For example graphite, graphite is a form of carbon it has these hexagonal sheets. So, you have these hexagonal sheets of graphite, so you can see that each having how many neighbors.

So, if you look at this it has 3 neighbors it makes an angle of it. So, this is SP2 hybridized structure and each of these layers, so when you put these layers, so if you if you now look at the cross section, so these are the layers. So, this is 1 carbon layer this is another carbon layer, so within the plane they are covalently bonded and between the plane they are under walls bonded.

So, that is why graphite has this. So, graphite makes a unit cell whose C axis is about C length is 0.67 and nanometer but graphite is. So, within the plane you have SP2 bonds with between the layers you have a Van Der Waals bond, as a result graphite has this very nice tendency to make slippery compounds. So, that is why graphite is used as a lubricant because, graphite can be shared easily because the Van Der Waals bonding. So, with within the sheet is strong it makes strong covalent bonds, but sheets themselves are not bonded strongly with respect to each other. So, we are a fight tends to shear very easily and that is why it is used as a lubricant.

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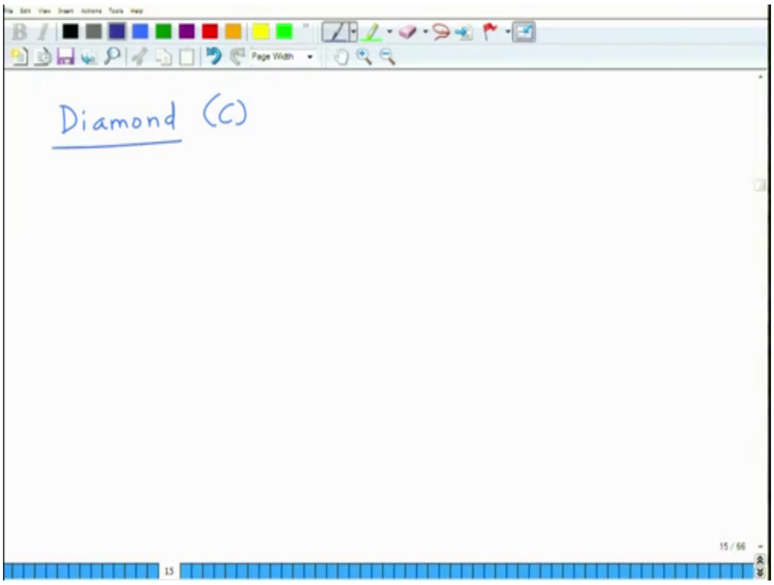

Now, in the next lecture there we will discuss about another form of carbon which is again a covalently bonded solids and that is diamond, which is SP3 hybridized material and perhaps we will also look at some other structures of carbon if possible ok.

Thank you.