Carbon Materials and Manufacturing

Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture - 07

Sp^3, sp^2 and sp Hybridization: Diamond, Graphite and Carbyne

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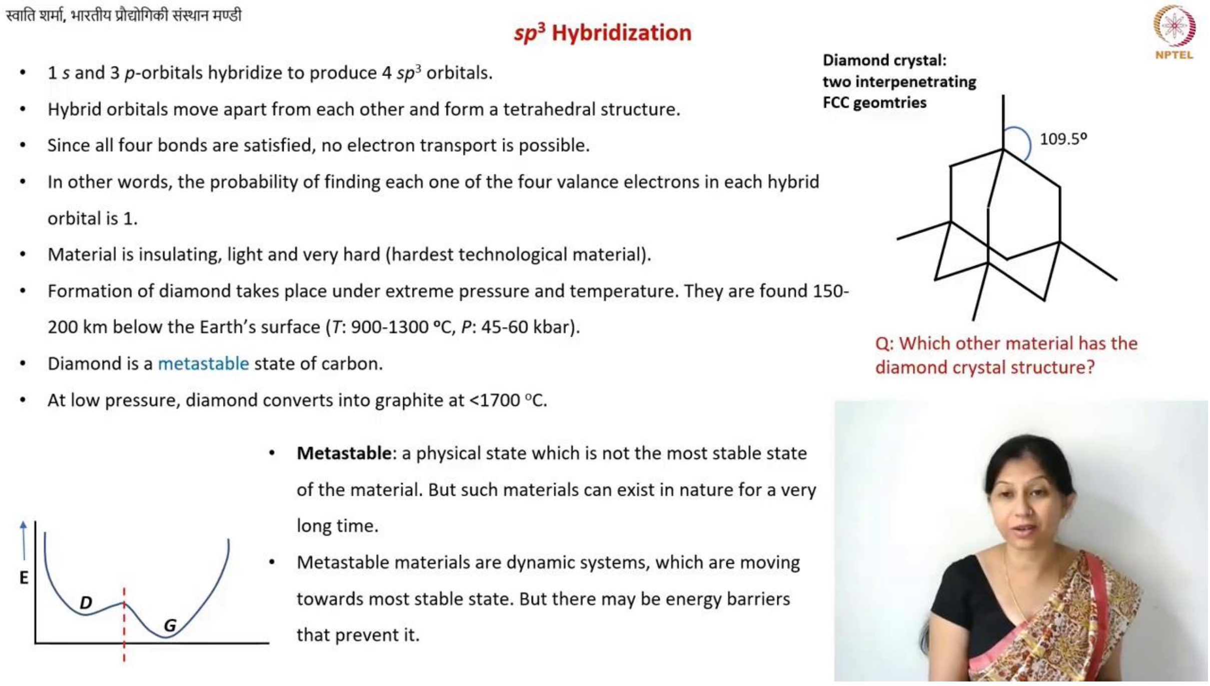

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sp^3 Hybridization

- 1 *s* and 3 *p*-orbitals hybridize to produce 4 sp^3 orbitals.
- Hybrid orbitals move apart from each other and form a tetrahedral structure.
- Since all four bonds are satisfied, no electron transport is possible.
- In other words, the probability of finding each one of the four valance electrons in each hybrid orbital is 1.
- Material is insulating, light and very hard (hardest technological material).
- Formation of diamond takes place under extreme pressure and temperature. They are found 150-200 km below the Earth's surface (*T*: 900-1300 °C, *P*: 45-60 kbar).
- Diamond is a metastable state of carbon.
- At low pressure, diamond converts into graphite at <1700 °C.

Diamond crystal: two interpenetrating FCC geomtries

Q: Which other material has the diamond crystal structure?

- **Metastable**: a physical state which is not the most stable state of the material. But such materials can exist in nature for a very long time.
- Metastable materials are dynamic systems, which are moving towards most stable state. But there may be energy barriers that prevent it.

Hello everyone! from this lecture onwards, we are going to talk about carbon materials. So, different carbon materials basically mean you have different crystal geometries. We are still talking about elemental carbon but we are talking about different crystal geometries that are formed because of the different hybridization states. You already know what the shape of sp^3 and sp^2 hybridized orbitals are. But we are going to talk about the materials that are formed because of these hybridization states.

Now, you would say sp^2 and sp^3 hybridization or the diamond and graphite formation are very fundamental things, but it is important for us because if we want to manufacture our materials, let us say from polymers or whatever sources of carbon, in that case, the hybridization becomes very important. Sometimes you can induce certain parameters that will make your material more graphite-like or more diamond-like. Sometimes there is a certain process which even though give you diamonds, but it will give you maybe some diamond and some graphite. So, these processes are very much connected to each other, but let us start with the fundamental geometries and primary representative materials of each type. We will start with sp^3, you already know that there are three p and one s orbitals, form a molecular orbital which is of sp^3 type. And what is the geometry of this kind of molecular orbital? Then you have this tetrahedral kind of geometry. What does that mean? This is more like you have a tripod stand and then on top of that, there is one more orbital. So, it looks like a pyramid especially if you connect all 4 corners.

So, in terms of explanation, this is very easy, you have 4 electrons and you have 4 hybridized orbital's. So, all of them are at the same energy level and each one will have 1 electron.

So, this is kind of a very stable geometry and definitely, there is no free electron. There is no electron that is available for electrical conductivity. This is basically your diamond crystal. Now, if I have this pyramid-like geometry, that is the structural unit. I can have one more and one more and one more and that is how your large-scale diamond crystal would be formed. Here I have shown these orbitals with straight lines, but you know that these are the lobes of your sp^3 hybrid. But the angle between them is 109.5 degrees in all cases. So, this is your primary structure of diamond.

If you want to think of diamond-type crystal structure in terms of the traditional crystal lattice types, you have basically two interpenetrating FCC or Face Centered Cubic structures. So, if you take one FCC and then you insert another FCC inside that is how your diamond crystal looks like.

There are more very technologically important materials apart from carbon have the diamond type of crystal structure, this is in fact called the diamond cubic structure. Maybe you can do a little bit of assertion and you can find it out for yourself which another technologically important element has the diamond crystal structure.

As I said already that the electron transport is not possible in diamonds because all 4 bonds are satisfied. These electrons participate in bonding with other carbon other sp^3 hybridized carbons. They do not participate in bonding with any external chemical, they do participate in the bonding with each other. You only get the hybridization at the time of bonding, when bonding is between carbon and carbon.

We also know few things that, if you have 4 electrons and 4 carbon orbitals then in that case the probability of finding each electron in each orbital equals 1. So, this is also the reason for all the properties of diamond. One is of course, electrical property, but also the fact that it is one of the hardest known materials, also I am saying one of the hardest known materials because even the single sheets of graphite are known as harder than diamond. But in the case of technological materials diamond still remains the hardest material except maybe some very advanced compounds like ceramics and so on.

But in elemental materials and still among all the materials as such diamond is one of the hardest materials and that is extensively used in technological applications. For example, for making cutting tools, drilling tools and even surgical tools and so on.

So, the point is that it is very light and it is very hard. Why is some diamond light? Graphite is also light. So, being light in terms of weight is actually has little to do with the crystal structure. All the crystal structure does play a role in the density like how closely packed your atoms are. But other than that, one more important reason for all carbon materials to be lightweight is the fact that carbon as an element is very light. It has only 6 electrons. So, it is one of the lighter elements and also it forms very strong bonds.

Where are diamonds found? We have also talked about deep carbon. So, this is about the natural occurrence of diamond, this is found about 150 to 200 kilometers below the earth's crust, and it is known to be formed under very high temperature and pressure conditions.

There are various theories about the formation of diamond and these theories have been validated by some experimental data. One widely acceptable theory is that diamonds are formed when there is also some atomic hydrogen, not hydrogen molecules, present in the atmosphere.

So, if you have atomic hydrogen that basically means that the conditions must be extreme because a hydrogen molecules splits into hydrogen atoms only at around 2000 degree centigrade or under plasma or any other very you know extreme conditions.

But if you have this atomic hydrogen present, then in that case during the formation of diamond, the hydrogen sort of links attaches to this 4th orbital. So, three of them are already satisfied but 4th one attaches to hydrogen to provides temporary stability. And then this hydrogen is replaced by another carbon atom that is how you have this sp^3 type of geometry.

Otherwise given that graphite or sp^2 type geometry is more thermodynamically stable, you know this structure would flatten and you would get graphite. So, we will probably learn about it in one of the lectures when we talk about diamond-related materials.

So, this one thing is clear that you need extreme conditions for the formation of diamond and that is also the reason you find more graphite in nature compared to diamond.

There have been also a lot of experiments where people have been able to synthetically prepare diamonds. There has been a lot of interest in this area and we have been able to make synthetic diamonds. In fact, they are commonly used in cutting tools and these are not nice natural diamonds.

But on the other hand, the conditions that are required for formation are still there because you require high temperature and pressure conditions. And the crystallites that we obtained using synthetic processes are relatively small. So, they are not like you know Kohinoor diamonds, they are not really large-scale diamond crystals, but rather relatively small and that is why we use it for making tools and so on. We also have films of diamonds that are used as coatings for a lot of tools.

You know that diamond is not the most thermodynamically stable state that is graphite forever. Diamond although is a metastable state, it can survive up to thousands of years.

You would think that metastable means the material should only be stable for like a couple of seconds or less than that, but the truth is that metastable materials or any materials that are not the most stable material can actually survive for thousands of years, like in the case of diamond.

So, despite the fact that it is not the most stable state it survives for long period. However, if you heat it let us say at 1700 degree centigrade in that case it would convert into graphite. Now, why does that happen? Because there is a certain activation energy that is required to convert diamond into graphite, that activation energy has to be artificially provided. That kind of energy is not really available in nature. When it is available in that case, diamond converts into graphite also in nature.

We are going to discuss all of this and all the calculations about activation energy in one of the lectures later. But briefly let me explain it to you.

This is the diagram where you see diamond and graphite. So, I have mentioned D for diamond and G for graphite and E is your energy of formation or enthalpy of formation. You can see here that diamond is at higher energy level than graphite. So, in principle, the overall structure has higher energy which basically makes your graphite a more stable state.

However, you also see that there is a certain energy barrier or this hump in the graph, that the diamond would have to cross to go into more stable state. This hump is basically activation energy that you need to provide to diamond to convert into graphite.

So, in general, metastable systems are are dynamic systems. You can say that every system tries to attain its lower energy state right like diamond is trying to attain its lower energy state, but because of the fact that you have this very high activation energy involved it doesn’t naturally take place. But we can definitely convert diamond into graphite although you might not want to do it. The other way around graphite to diamond is more interesting rather than diamond to graphite.

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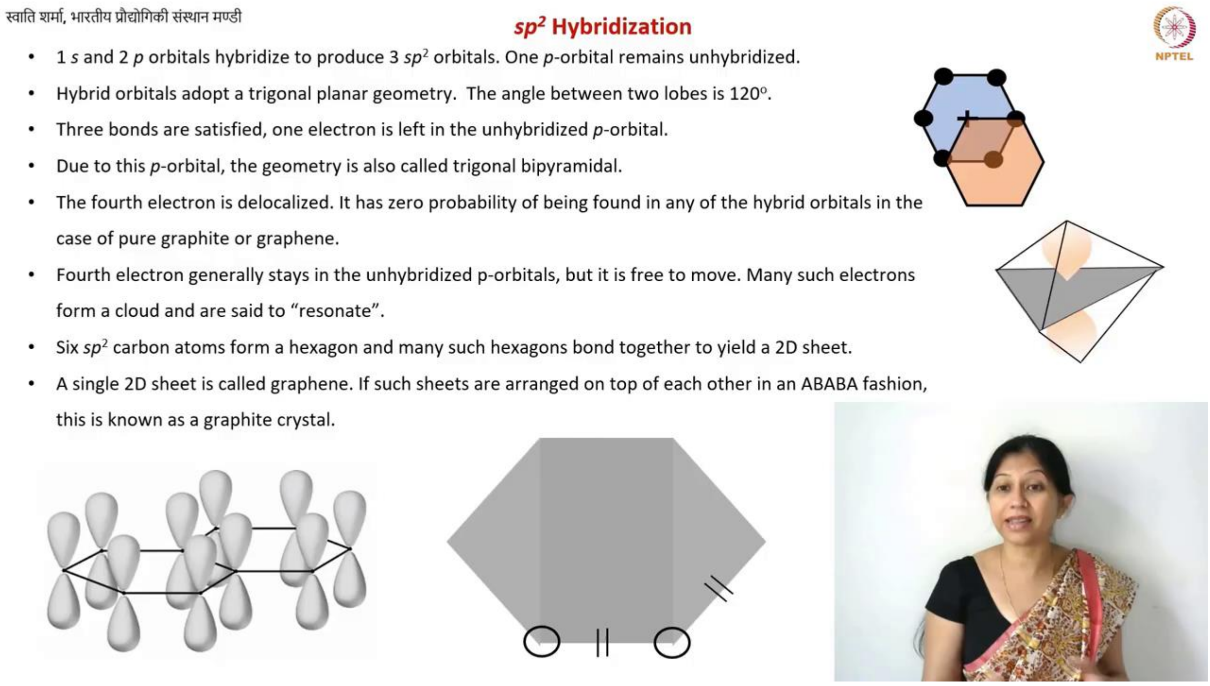

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sp^2 Hybridization

- 1 *s* and 2 *p* orbitals hybridize to produce 3 *sp*^{2} orbitals. One *p*-orbital remains unhybridized.
- Hybrid orbitals adopt a trigonal planar geometry. The angle between two lobes is 120°.
- Three bonds are satisfied, one electron is left in the unhybridized *p*-orbital.
- Due to this *p*-orbital, the geometry is also called trigonal bipyramidal.
- The fourth electron is delocalized. It has zero probability of being found in any of the hybrid orbitals in the case of pure graphite or graphene.
- Fourth electron generally stays in the unhybridized p-orbitals, but it is free to move. Many such electrons form a cloud and are said to “resonate”.
- Six *sp*^{2} carbon atoms form a hexagon and many such hexagons bond together to yield a 2D sheet.
- A single 2D sheet is called graphene. If such sheets are arranged on top of each other in an ABABA fashion, this is known as a graphite crystal.

Let us talk about graphite, this is our sp^2 hybridized carbon material and this is the main carbon material of this type of hybridization. If you have 100 percent sp^2 hybridization in that case you are going to get this kind of material. You already know about graphite properties and so on, but graphite is very important for us in this entire course. Because most of the engineering carbon materials that we are going to talk about; if they are not graphite they are trying to become like graphite. This is mostly our goal when we often perform any manufacturing process for carbon materials, we want them to become more and more graphite-like or we want the carbon atoms in that material to attain more and more sp^2 type hybridization.

Why do we do that? Because this is the material has a higher electrical conductivity. The perfect sp^2 type material like graphite is going to be our sort of the gold standard and we are always trying to reach there, that is the case with most of the disordered carbon materials.

I am saying graphite and not graphene here. Graphene as you know, it’s a single layer of graphite. But graphite is the one that has ABAB type 3D crystal arrangement. We are going to discuss in detail in this particular course. This is more stable geometry because you also have not just 2D, but 3D crystal arrangement. So, a perfect graphite crystal is actually the most stable arrangement for carbon atoms.

We know you have one s and two p orbitals that come together to form the sp^2 type molecular orbitals. Now, if you have these three sp^2 orbitals and I place three electrons in these sp^2 orbitals. These three electrons again will try to go as far, they will try to move apart from each other as much as possible.

So, what is the most stable geometry for any three atoms when they want to move as far from each other as possible? Well that is a trigonal planar geometry, which means, you have a triangle.

All of the sides of the triangle are equal basically this is just a triangle you can make when you connect these three atoms sitting there, but actually, these are just lobes of your sp^2 hybridized orbital's. So, you have an angle of 120 degrees between these three orbitals. And of course, the three bonding electrons will go and sit in each one of them. So, they bond with other similar sp^2 hybridized carbon in carbon entities.

But you have one unhybridized p orbital, let us call it p_z and you have the 2 lobes. The remaining 1 electron could be in any one of these two lobes. So, this unhybridized p orbital and this electron is practically responsible for all the interesting properties of graphite and graphite-like materials. Because of this unhybridized p orbital, you can also make a pyramid-like structure as I have shown in this picture. In that case what you would also hear this term trigonal as bipyramidal geometry of graphite structure.

This is basically the primary structural unit of any graphite-like carbon. Now what happens to the 4th electron? So, 4th electron will go into this unhybridized orbital, but will it have a 100 percent probability of staying there? Well, if you have this entire molecule alone in space, in that case, the electron will also sit in the unhybridized orbital. But as soon as there is a possibility for this electron to move it will start moving and that is why we call it the free electron. This is the electron that is responsible for the electrical conductivity of graphite and also maybe some other many other interesting properties actually.

In the triangle that I have shown, you know all 3 sides are equal here it's not visible in this diagram. You have this one triangle with three sp2 hybridized lobes and then you have another one. They come close to each other than what happens at a certain distance, now the corner atoms will also form bonds with each other and you will get a hexagon geometry.

This hybridization only takes place when a lot of carbon electrons are close to each other and when there is a possibility of bonding. So, these two electrons then also form a bond and the bond length you know of these sides of the hexagon will be equal.

Basically, all sides of the hexagon will be equal. In fact, the bond length in this case, is even smaller than that of the diamond. So, this is a very highly stable geometry for carbon.

Now, if I take two such hexagons as I have shown here. So, the hexagons will also then connect with each other, they will share the edges. So, if you see two such hexagons then all of them have these additional unhybridized orbitals and each one of them also contains that extra the 4th electron.

So, what actually happens these fourth electrons now become delocalized. Delocalized means it does not really sit on one carbon atom. We do not know what is the probability of finding this 4th electron in that unhybridized p orbital, because if I talk about one ring, 6 such atoms form this sort of a cloud of electrons. So, the electron can be found in that cloud, but we cannot say that electron will be on this one single carbon atom. So, this is what is known as delocalization. Now, this is also the case with a lot of chemical compounds not just elemental carbon, but also in the case of a lot of aromatic compounds. You will often hear this delocalized electron cloud of these carbon rings. This also is a very interesting phenomenon and is responsible for a lot of chemical properties of carbons. This electron basically resonates. Basically, we do not know what is the probability of finding it. We just know the probability of finding this electron in any of the hybrid orbitals is 0, because it does not go there.

So, if you have many such hexagons, I have shown two of them connected here, but if you had many more such hexagons then you will form one sheet-like structure. And these sheet and chain-like structures make carbon very interesting. We also going to learn about chain-like structures in a while.

You will often hear the term self-polymerization, although we can call these structures polymers, remembering that there is no monomer unit as such it is the carbon atom. Or you can consider one hexagon as a monomer in that case. Yes, you have multiple hexagons like 1000’s and millions of them connected together to form these extensively large sheets of carbon. The sheet-like molecules are formed when it comes to sp2 type hybridization, not in sp3.

If I take one hexagon and I place another one on top of it such that the corner atom of the second hexagon is at the center of the first hexagon of the first layer. In that case, we call it graphite and this crystal arrangement is known as ABA type crystal arrangement because this is you know one sheet is A the second one is B and the third one A will again be at the same position where your first layer was.

So, this kind of crystal structure is known as ABABA type crystal arrangement and that is what we have in the case of graphite. However, if you do not have a second layer if you just take one single layer of such hexagons, in that case you call it graphene.

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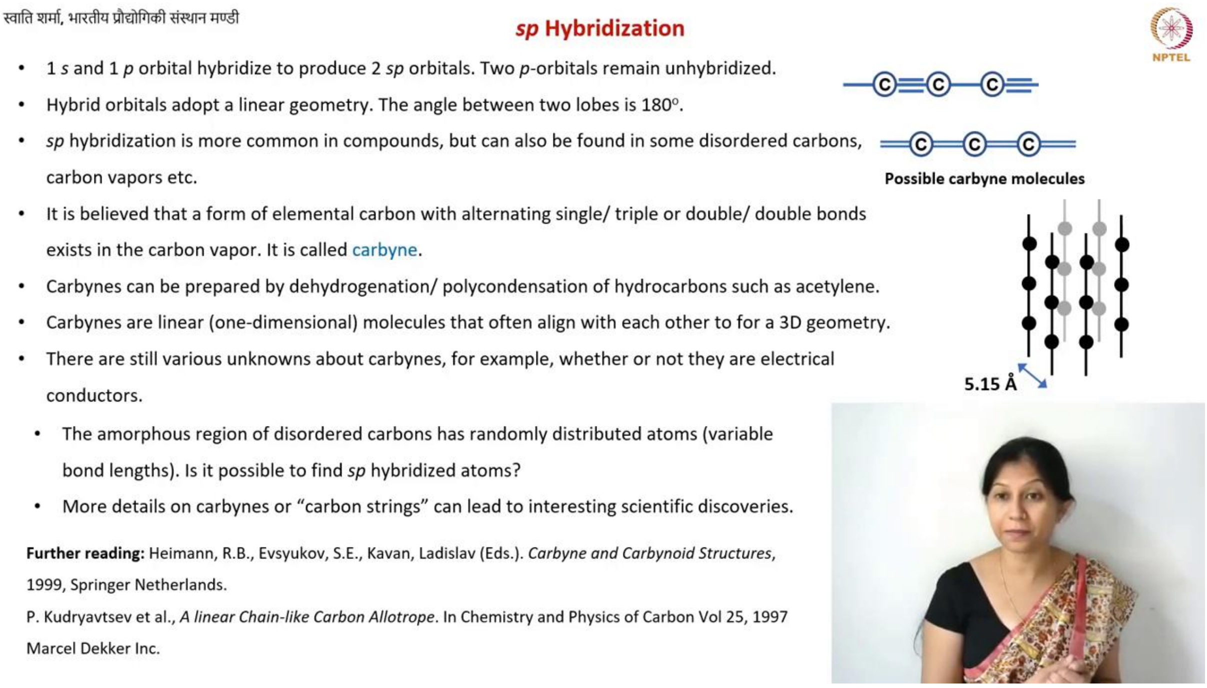

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***sp* Hybridization**

- 1 *s* and 1 *p* orbital hybridize to produce 2 *sp* orbitals. Two *p*-orbitals remain unhybridized.
- Hybrid orbitals adopt a linear geometry. The angle between two lobes is 180°.
- *sp* hybridization is more common in compounds, but can also be found in some disordered carbons, carbon vapors etc.
- It is believed that a form of elemental carbon with alternating single/ triple or double/ double bonds exists in the carbon vapor. It is called carbyne.
- Carbynes can be prepared by dehydrogenation/ polycondensation of hydrocarbons such as acetylene.
- Carbynes are linear (one-dimensional) molecules that often align with each other to for a 3D geometry.
- There are still various unknowns about carbynes, for example, whether or not they are electrical conductors.
  - The amorphous region of disordered carbons has randomly distributed atoms (variable bond lengths). Is it possible to find *sp* hybridized atoms?
  - More details on carbynes or “carbon strings” can lead to interesting scientific discoveries.

Further reading: Heimann, R.B., Evsyukov, S.E., Kavan, Ladislav (Eds.). *Carbyne and Carbynoid Structures*, 1999, Springer Netherlands.

P. Kudryavtsev et al., *A linear Chain-like Carbon Allotrope*. In Chemistry and Physics of Carbon Vol 25, 1997 Marcel Dekker Inc.

Now, let us talk about the 3rd type of hybridization i.e sp hybridization. It is also possible to find some carbon materials which have this sp hybridization. So, what do we know about this type of hybridization? We have one s and one p orbital coming together and forming the molecular orbitals that have linear geometry. And the angle between 2 orbitals will be 180 degrees between two lobes.

We know that we will have a linear type of geometry of whatever is formed. It is known that you have a lot of hydrocarbons based on sp type hybridization in carbon atoms. But can you also have elemental carbon which has this kind of hybridization?

This is actually an interesting question and given the fact that we still do not know a lot about carbon materials despite the fact that we already have a lot of carbon materials. There are so many of carbon materials and it is difficult to fit all of them in one course and yet we still do not know a lot about carbon materials. We have little information about sp hybridized carbon materials although there exists elemental carbon structure that possesses this sp type of hybridization.

Again this is more common in hydrocarbons compared to in elemental carbon, but you can have is these linear chain-like structures that have alternating single double or triple single bonds. This will become more clear from this illustration. So, you can see these are the two possible structures of this type of linear chain-like carbon molecule which is called carbyne.

Now, the existence of carbyne to date is debated. However, there have been a lot of experimental studies that have suggested that sp type carbon exists and it has been reported that people have been able to produce carbynes on a large scale. But then there are some other studies also which suggest that carbon may exist, but it’s highly unstable.

This is one of those carbon materials which we are still trying to understand. But this is the proposed structure of carbon, and maybe the bonds are always resonating, they are changing their positions and you will call them carbon strings or carbon sutra that is basically what is carbyne.

So, carbynes have several experimental validations. So, often when people are synthesizing carbynes, they are getting them back from the hydrocarbons. They perform the dehydrogenation of hydrocarbons such as acetylene and which is known as polycondensation.

Dehydrogenation means removing the hydrogen, that is actually what we do for a lot of carbon materials. It is not just for carbynes but you will see in the rest of this course that when we make any type of disordered carbon material, we often heat treat the polymers to get these kinds of materials.

Now, these are linear and these are the truly one-dimensional carbon structures. This is also interesting, what do we call one-dimensional? Let us say if I have fiber, if I can neglect its diameter compared to its length, in that case, I can call it one dimension.

However, maybe if we start talking about nanoscale, if we actually look at that fiber maybe its diameter is not negligible. Maybe it’s 100 nanometers we can very well measure it and we can even reduce it further.

When compared to the length, the diameter is very small, we can consider the structure one dimensional. But, for carbynes whether they actually exist or whether they can form industrial carbon materials, whether they are stable; these are different questions.

But if you think about this geometry this is a truly one-dimensional geometry similar to graphene which is a truly 2D structure because it is one atom thick. Similarly, a single strand of carbyne would be a truly one-dimensional structure because that would also be 1 atom thick.

So, these carbon strings are very important, however, you can imagine that for such one-dimensional strings to exist on their own is difficult. They are very high-energy structures. There are various proposed models on crystal structure or the arrangement of carbynes. How do they come together? I will not call it agglomeration, but an arrangement of some sort.

Here in this image, I have shown one suggested arrangement where you see that these linear strings come together in such a way that they end up forming a hexagon-like structure. So, I have only shown half of the hexagon. So, you actually do not have just one hexagon-like structure. If you see from the top, but you also have some more strings, not just the hexagons some more strings are placed inside this hexagon. This arrangement has this 5.15-angstrom distance between two chain-like structures. So, this has been found in some of the experiments, but there are also many other models of the crystal structure or the arrangement of these carbyne chains.

Again, I would say that there is a lot of work being done. It is debated whether they exist. However, one thing is clear that we do not know too much about their properties. Although you can prepare them by dehydrogenation of hydrocarbons and also exist in the vapor phase carbon.

So, what is vapor phase carbon? If I really provide a lot of energy to solid carbon graphite then it would convert into a vapor phase. But that takes place only at very high temperatures and pressures. Or if you are trying to do it at room temperature then it is going to be approximately above 3500-degree centigrade temperatures. And then in that case graphite without converting into the liquid phase, completely sublimates.

So, this is something we are going to discuss when we talk about the phase diagram of carbon. The point is that carbyne has been observed in those carbon vapors. The meteorites also carry some carbon, they are carbonaceous chondrites and when these meteorites hit the earth, then this is a very high impact process. So, you end up getting very interesting forms of carbon, like there has been found something called a white carbon or silver-white color carbon material and that material is also said to contain carbynes.

So, the point is that we do not know too much about the properties of these materials yet. It is believed or at least initial studies suggested that carbynes are semiconducting, but there are some studies that suggest that they are metallic and they are electrical conductors. These studies are still going on.

Now in our disordered carbon materials, we have both amorphous and crystalline regions. So, amorphous regions basically are regions where there is no well-defined hybridization, that is the definition of amorphous right. You have various bond lengths which basically means no proper or well-defined hybridization. You can have carbon atoms in other hybridization states like between sp2 and sp3 or the states between sp2 and sp1, is it possible? Or can we also have ground state atoms, or can we have sp hybridized atoms in these amorphous regions. And if yes, can we also find carbyne-like geometries in these regions? The answer I think is yes, but you can also think of it for yourself you know whether it is possible. And if it is possible one thing is for sure it’s going to be very difficult to characterize it and to find out that these are carbynes in my amorphous region.

Yeah, we can potentially find carbynes in various forms of carbon. And it is very clear if we know more about these carbynes then that will definitely help us in understanding various carbon materials, the discovery of more carbon materials and for development of new industry and carbon materials.

So, here are some references that I have provided, these are specific to carbynes, not for diamond and graphite. The first one is a book and the second one is the book chapter. You can find more details about all proposed models of the crystal structure of carbyne and you can also find out more details about the proposed mechanisms of the formation of carbyne and also other chemical pathways that can lead to carbyne formation.