Introduction to Materials Science and Engineering

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Lecture - 27
Structure of graphite

So, today we will discuss the structure of Graphite, in the last video as we have seen various polymorphs of Carbon or Allotropes of Carbon as a revision. I show you the slide again.

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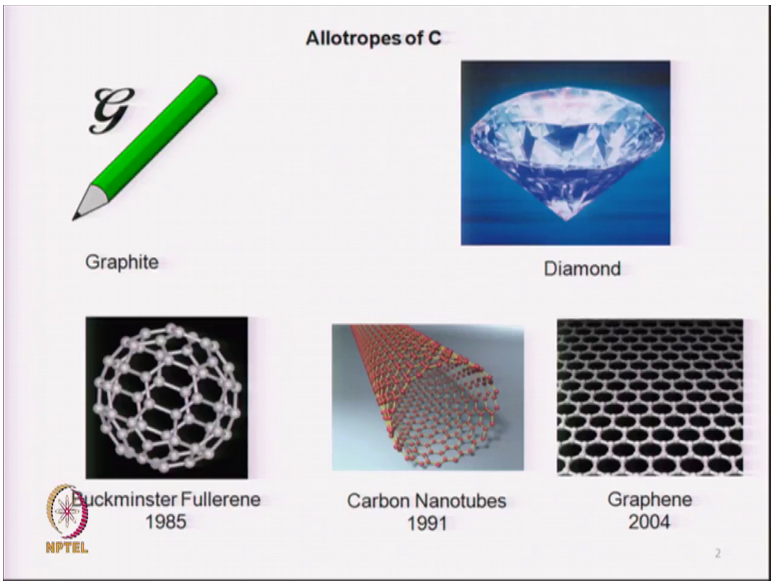

Allotropes of C

Graphite

Diamond

Buckminster Fullerene
1985

Carbon Nanotubes
1991

Graphene
2004

So, Carbon comes in variety of forms, some of them are listed here. The most important ones and the last 3 which you can see from the years shown here, they have been discovered very, very recently in the last 20 years or. So, in particular Graphene is the latest one and we started our discussion with Graphene, because it is a 2-dimensional simple structure and we saw the structure of Graphene in the last video.

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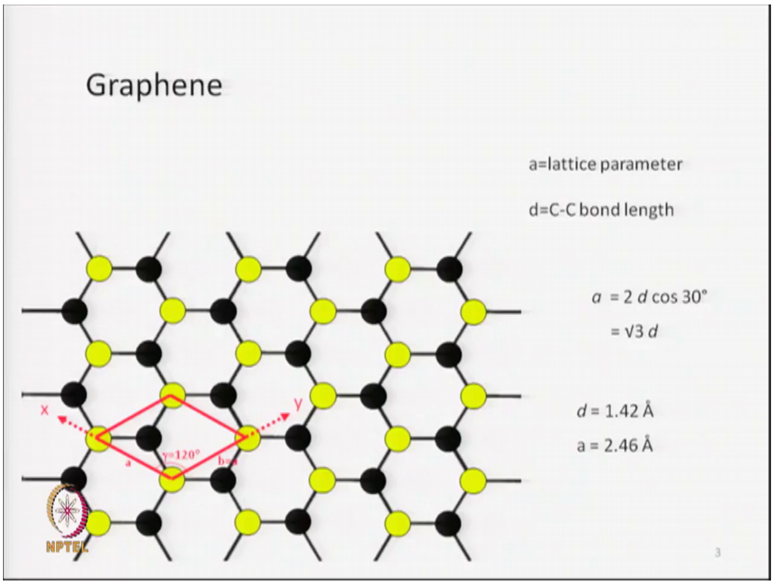

Graphene

a=lattice parameter

d=C-C bond length

$a = 2d\cos 30^\circ$

$= \sqrt{3}\,d$

$d = 1.42$ Å

a = 2.46 Å

Graphite is quite related to Graphene. So, we will take up the structure of Graphite in this video. So, let us recall the structure of Graphene and we saw that the structure of Graphene is based on tiling of hexagons. So, if you look at this hexagonal tiling, and we put a carbon atom at each of the vertices, what we get is the structure of Graphene. We also saw that, all carbon atoms in this Graphene structure are not equivalent in the lattice sense. So, the nearest neighbors are not equivalent, it is the next nearest neighbors which form the lattice. So, I am trying to distinguish the 2 kind of carbon atoms by giving them this color yellow and black which is what we did in the last video also. So, it is the same slide.

So, the unit cell which you will select the 2 dimensional unit cell, which you will select will be a red unit cell like this, in which I have shown this as the lattice parameter a, this as the lattice parameter b along y axis, and the angle between them 120 degree and of course, this is a rhombus so a and b are equal, and by simple geometry which we showed in the last video, also you can relate the lattice parameter a to the carbon-carbon bond length which is we are calling d. So, the relationship between a and d can be easily found, which is a the lattice parameter is root 3 times the carbon-carbon bond length, you can see this is longer and you can easily solve this triangle to get this relationship.

So, the lattice parameter a is root 3 times the carbon-carbon bond length, and in the actual Graphite or Graphene this is spacing is approximately and the carbon-carbon bond length is 1.42 angstrom, which makes the lattice parameter 2.46 angstroms. So, this is Graphene and we looked at it in a little bit detail last time. So, in this unit cell of

Graphene you have 2 kinds of atom, one sitting at the corner which are the lattice points and another which is not sitting at the corner, but is sitting in the face on the basal plane in the plane of the Graphene not exactly at the centre. So, we cannot call it face center, but lying on the face it is at the center of this equilateral triangle which is half of this rhombus.

So, the rhombus unit cell can be divided into 2 equilateral triangles and at the centre of one of those equilateral triangle, you have the other kind of atom. Other kind in the sense of lattice, both of them are carbon atom. So, chemically they are the same, but in terms of lattice one is at the lattice point, another is not at the lattice point. So, you have 2 atom Motif one at the lattice point and one away from the lattice point. So, that is in the Graphene layer, now in Graphite is nothing but a stacking of these Graphene layers one above the other, parallel Graphene layers if they are stacked together in 3 dimension one above the other, we have what is called graphite.

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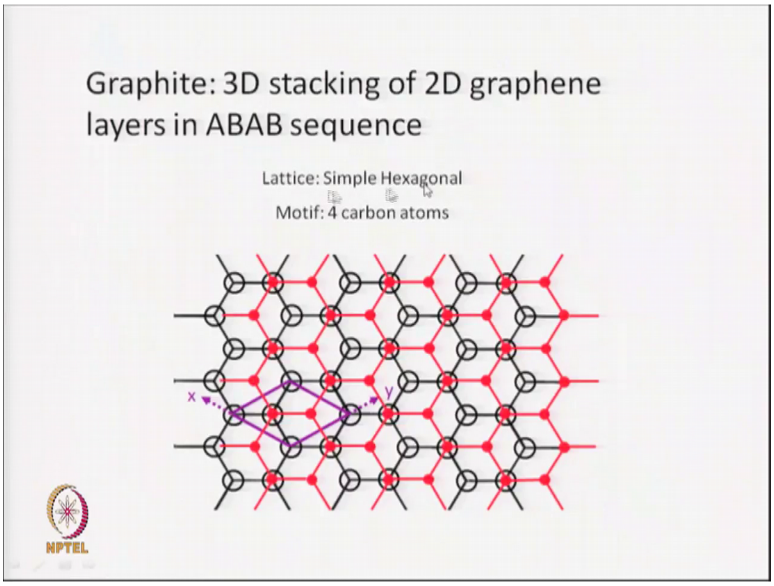

Graphite: 3D stacking of 2D graphene layers in ABAB sequence

Lattice: Simple Hexagonal

Motif: 4 carbon atoms

So, let us look at the structure of graphite. So, first of all note that, I am saying that the stacking sequence is AB AB, this is important to keep in mind, because many times incorrectly, it is assumed that the graphite layers are one above the other. So, the second layer is not exactly above the bottom layer, but it is shifted in it is plane. How it is done I will show you and now. So, let us introduce next layer and we are viewing in projection. So, these red atoms what I am showing the red atoms and red lines is another hexagonal network, which currently is projected in the plane of the original hexagonal layer, which is shown by the open circles.

So, open black circle is my basal plane, the red atoms are indicating the next layer, which is above the bottom layer and in current representation the top layer is exactly above the bottom layer, because in the projection they are coinciding, but this is not exactly what is there in graphite, in the graphite the next layer is shifted with respect to the bottom layer and how is this shifted. So, the shift is along one of the carbon-carbon bond length, you can take a carbon-carbon bond length, let me take the horizontal one which is the simplest to visualize.

So, if I look at the horizontal carbon-carbon bond length, and if I shift this red layer of atoms by along this direction by the carbon-carbon bond length; so the next layer note that the shift is along the carbon-carbon bond length, by an amount equal to the carbon-carbon bond length. So, let me do that. So, I have tried this animation to shift this plane by the horizontal carbon-carbon bond length in the horizontal direction so this is the shift. So, in this animation you can see now, Now these red atoms are in the correct position and you can quickly see now, that now you have 2 kinds of carbon atoms in this 3-dimensional structure of 2 layers itself, now of course the entire 3-dimensional structure once you have the 2 layers the third layer will be exactly above these black atoms and the 4th layer will be exactly above the red atoms and so on.

So, AB AB AB sequence will continue to give you 3-dimensional periodic structure of graphite. Now you can see that, the carbon atoms have been divided now into 2 kinds of groups. 2 groups are there of carbon atom one kind of carbon atom like this, one where I am putting my in arrow now, this carbon atom if I go vertically up I do not find a red atom. So, in the b layer there is no atom above this carbon atom. So, if I move along the c axis I will find the next carbon atom above this carbon atom only at a distance equal to c in the third plane, in the next a plane whereas, if I start with this carbon atom in the a layer there is exactly a carbon atom above that in the b plane.

So, the distance along the c axis of carbon-carbon atoms, along if I go vertically above this atom, then I will find carbon atoms at a distance c by 2 whereas, if I go vertically up above this carbon atom, I will find carbon atoms only at distance c. So, c by 2 c by 2 c by 2 here and c c c here. So, 2 kinds of carbon atoms can be distinguished in graphite. Now, how do we describe this structure in terms of lattice and motif. So, I have given you the hint here. So, lattice turns out to be simple hexagonal and motif will turn out to be 4 carbon atoms remember in Graphene itself we saw that they were the motif of 2 carbon atoms.

So, in a given plane there are 2 nonequivalent atoms. So, you get 2 carbon atoms per lattice point and now, since the red layer is not equivalent to the black layer that will also contribute 2 carbon atoms to each lattice point so you will get 4 atoms per lattice point. I have again shown you the unit cell here. So, you can see that this is the base of the unit cell and now you can imagine the 3-dimensional unit cell. I am going to show you soon, but first let us see it in the projection. So, the 3-dimensional unit cell will be prism based on this rhombus base.

So, we will start at the a layer, then there will be 2 atoms from the b layer and then the prism will be completed by the top a layer at a distance c. So, that is the hexagonal prism which will be the 3-dimensional unit cell and in this unit cell. So, the corners of the prism are atoms. So, you get one atom from the corner, then there is one at the base itself as in the Graphene layer that is the black open circle. So, you have 2 atoms on the base and then, these 2 atoms on the b layer also are part of the motif. So, one from the corner, one from the center of the bottom face and 2 from inside the unit cell these 4 atoms form the motif of this structure.

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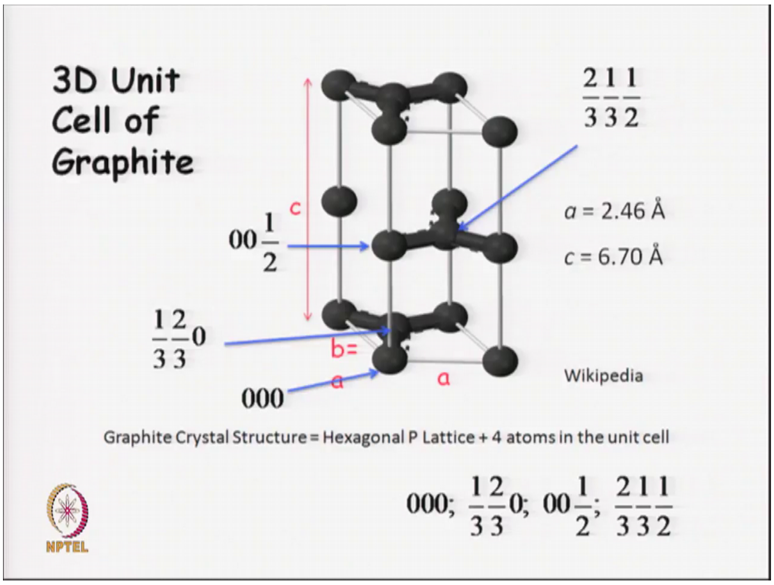

3D Unit Cell of Graphite

Graphite Crystal Structure = Hexagonal P Lattice + 4 atoms in the unit cell

$000;\ \frac{1}{3}\frac{2}{3}0;\ 00\frac{1}{2};\ \frac{2}{3}\frac{1}{3}\frac{1}{2}$

So, let us look at the 3-dimensional unit cell now. So, you can see I have drawn the 3-dimensional unit cell here, this is the a layer you can consider this to be the a layer, the middle layer is the b layer and finally, the top layer is the c layer. I told you that there are 2 kinds of carbon atoms, you know if I go from this carbon atom up, I find another atom at c by 2. So, this row is a c by 2 c by 2 row, but if I go from here, from the another atom in the base, if I go there is no atom on the top layer here, I have to go all the way to the top of the unit cell to find another carbon atom in that direction.

So, this carbon atom is a c c c carbon row, you will have a row of atoms, where the carbon-carbon atoms are separated by c another row of carbon atoms, where they are separated by c by 2. So, this is the 3D unit cell lattice parameters are given here, a we had already seen was 2.46 angstrom, c happens to be 6.7 angstrom. Now, I leave this exercise to you, to work out the we have done some similar exercise for hcp structure, but now I leave this is an exercise for you to work out the motif coordinates for this one, but I supply you with the answer hopefully, if they are correct.

So, ooo will be the corner one. So, then we have another one 1 third 2 third o. Since, the third coordinate is o with this is still in the basal plane. So, this is the another unit atom in the motif, which is in the basal plane, then oo half will be this one and then 2 thirds 1 third half will be the another one in the middle plane. So, if I specify that this is ooo, this is one third 2 third o, oo half and 2 third 1 third half. I am showing you the results the working out is not that difficult by using the geometry of triangles you can work out these coordinates.

So, this is the 3D unit cell of graphite hexagonal primitive lattice with 4 atoms in the unit cell. So, this is something which till now, if we think about we the most complicated structure in terms of motif we have looked at although graphite structure is very simple, but describing it in terms of lattice and motif, requires a motif of 4 atoms and in that sense, it is a little bit more complicated than the simple hexagonal structure, which we saw hexagonal close packed structure, where we had 2 atom motif.

So, it is different from it is hexagonal, but it is different from simple hexagonal, which will have only one atom per lattice point it is different from hexagonal close packed, which will have 2 atom per lattice point this hexagonal structure has 4 atom per lattice point.

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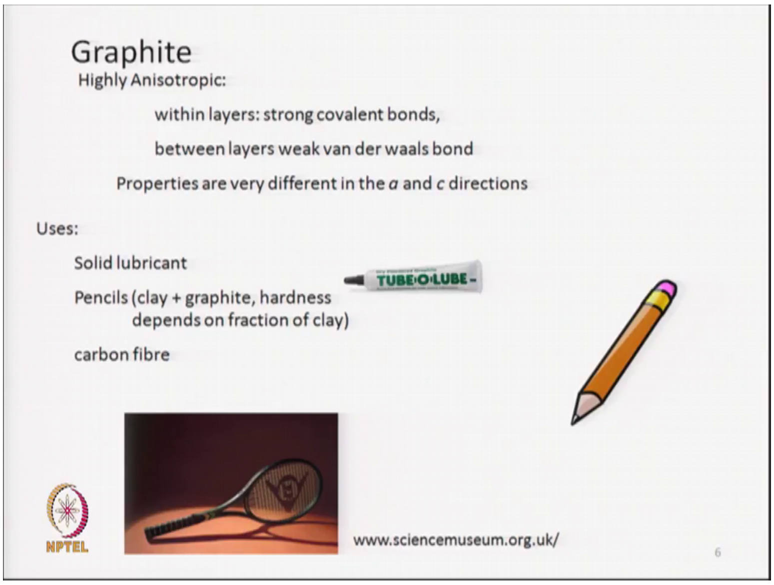

Graphite

Highly Anisotropic:

within layers: strong covalent bonds,

between layers weak van der waals bond

Properties are very different in the *a* and *c* directions

Uses:

Solid lubricant

Pencils (clay + graphite, hardness depends on fraction of clay)

carbon fibre

www.sciencemuseum.org.uk/

I end this video with a little bit of discussion on the uses and applications of graphite, one thing which should be now clear to you that within the layer graphite layer the carbon-carbon bonds are the strong covalent bond, but perpendicular to the layer that is in between the layer from one layer to another layer, you have only weak van der waals bond. So, this makes graphite highly anisotropic the properties perpendicular to the layers is very different from property within the layer. So, properties are very different in the a and c directions.

So, this makes graphite layers to easily slide over each other, because a layer to layer bond is the weak van der waal bonds that makes it induces like a solid lubricant and in pencils, which can easily shear and leave mark. Another important application in technology of graphite is that of carbon fiber, when you talk about a carbon tennis racket, that is not really just carbon racket it is a graphite racket. So, it is a and it is not really graphite it is a composite of plastic reinforced with graphite fibers carbon fibers.

So, commonly it is called a carbon graphic, but it is a carbon fiber or graphite fiber reinforced composite. We will have opportunity to discuss composite a little bit more in some later time, but just look at this an isotropic thing the carbon fiber or the graphite fiber will be strong, if the fiber axis is within the plane. So, if you take the carbon fiber the c axis is not aligned to the carbon fiber, because that is the weak direction. So, c axis will be should be perpendicular to the carbon fiber and it is the layer planes, which should be parallel to the fiber axis that is what will give you a strong graphite fiber.

So, with this we end this video in the next video we will look at other form of carbon, which is diamond and Carbon Nanotubes and also Fullerene. So, one by one we will look at these other forms.