Carbon Materials and Manufacturing
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Lecture – 13
Graphite Crystal Structure

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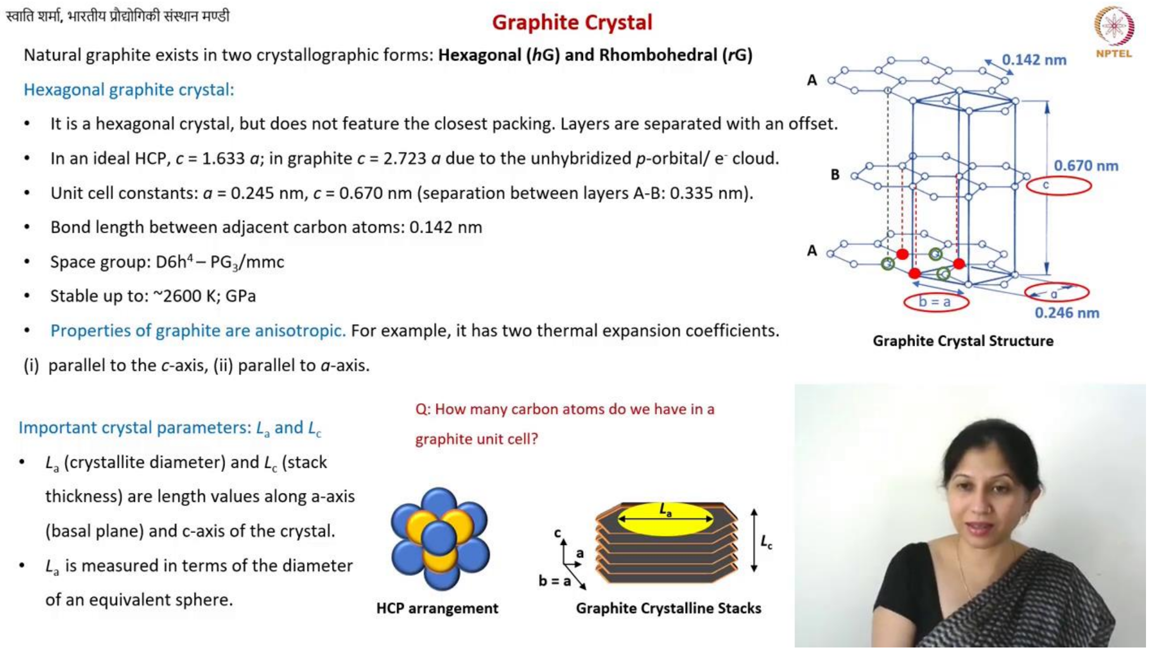
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Graphite Crystal

Natural graphite exists in two crystallographic forms: **Hexagonal (*h*G) and Rhombohedral (*r*G)**

Hexagonal graphite crystal:

- It is a hexagonal crystal, but does not feature the closest packing. Layers are separated with an offset.
- In an ideal HCP, c = 1.633 a; in graphite c = 2.723 a due to the unhybridized p-orbital/ e^- cloud.
- Unit cell constants: a = 0.245 nm, c = 0.670 nm (separation between layers A-B: 0.335 nm).
- Bond length between adjacent carbon atoms: 0.142 nm
- Space group: $D6h^4 – PG_3/mmc$
- Stable up to: ~2600 K; GPa
- Properties of graphite are anisotropic. For example, it has two thermal expansion coefficients.

(i) parallel to the c-axis, (ii) parallel to a-axis.

Graphite Crystal Structure

Important crystal parameters: L_a and L_c

- L_a (crystallite diameter) and L_c (stack thickness) are length values along a-axis (basal plane) and c-axis of the crystal.
- L_a is measured in terms of the diameter of an equivalent sphere.

Q: How many carbon atoms do we have in a graphite unit cell?

HCP arrangement

Graphite Crystalline Stacks

Let us talk about the crystal structure of graphite. Now the natural graphite that we were talking about, is available in two crystallographic forms. One of them is known as hexagonal graphite that is something that we mostly talk about this is the more common form of graphite and the other one is known as rhombohedral graphite. Now it is called rhombohedral because it has a crystal structure which is rhombohedral.

We are going to also learn about that. Let us first talk about hexagonal graphite or the common graphite. And the crystal structure of this graphite looks like this. As we have previously learned that it has this ABABA type crystal structure. You see this box that I have shown there, that actually shows the unit cell of this graphite.

We are not taking the entire hexagon as a unit cell, we are rather connecting two atoms of one carbon hexagon and then one atom of the neighboring hexagon and that is how we are forming unit cell. This is also important to see that we are taking not two but three layers, and then we are forming the unit cell.

Now, there are different crystal parameters you see the value of *a*. This is my one hexagon, if the value of *a* is the separation between this atom and this atom and if you draw a line that is going to be your value of *a*. Now also the other values for example, the value of *c* is the distance between the two A layers. The unit cell contains two A layers and *c* connects these two A layers. Now the value of *c* is 0.67 nanometer, but if somebody asks you what is the separation of layers in a graphite crystal? Then that is not 0.67, the separation is half of 0.67 because we have one extra layer in between.

There is one interesting thing is that the graphite crystal is a hexagonal closed-packed structure. Do you know what is a hexagonal closed packing or the closest packed structure which takes a hexagonal shape? That actually has the closest packing by volume for any spherical objects. That is how it should be but that would be possible only when you have the closest packing which means that you have one layer exactly on top of that touching the atoms. Without any space in between the two layers, you have the layers stacked on top of each other. That would be the closest packing. So, here I have shown it with this arrangement. So, you have layer number 1, let us say this is your A layer, this is your B layer and then this is again your A layer(refer to slides). So, it's like a pyramid of balls. This is the hexagonal closed-packed structure. In the case of graphite, you have hexagonal crystal structures. But it is not the closest packed structure, the layers are slightly separated. They are not exactly on top of each other. Can you guess why does this happen? Everything in graphite is caused by this unhybridized p orbital and the electron that is in that unhybridized orbital. Because that electron forms a cloud, it is delocalized and it does all kinds of funny things. Because of that electron, you have the clouds of both of these layers. So, there is a little bit of a gap. It is not the closest packing and that is why you do not call graphite structure an HCP structure, you just call it hexagonal crystal. In the case of an ideal HCP type arrangement, if you do the geometric calculations, you will find that the value of c should ideally be 1.633 times that of *a*.

But in the case of graphite that is not the case. As I already mentioned you have it slightly higher because of our electron cloud and the unhybridized orbital. Now other lattice constants a equals 0.245 nanometers. In this image where do you see a here it is. This is between atom number 1 and 3 of any hexagon and that is 0.246 nanometer. You see *a*, you see *c* where is *b*? *b* is actually here, we just do not mention *b* because *b* equals *a*(refer to slides).

So, we are always talking about either *a* or talking about *c*. *b* is there but because it is equal to *a*, we do not specifically mention its value. Now the separation between two layers as I said will be 0.335 nanometer which is half of 0.67. Whenever you see these transmission electron microscope images and I have also shown you these crystallographic lines when you take the cross-section. There you see the separation in the case of perfect graphite the separation should be 0.335 nanometer.

Now if I talk about the two adjacent carbon atoms then the bond length is 0.142 nanometer. Remember that this is actually much shorter than what you have in the case of diamond even though diamond has you know it has sp^3 hybridization. The electronegativity of your bond is higher in the case of graphite which is caused by the fact that you have more s character in the hybridization and because of that you have a shorter bond length which means this is the stronger bond. A shorter bond length will always give you stronger molecules because the closer they are the more tightly bound they are.

So, a shorter bond length means stronger. That is why if you take a single layer of graphite i.e graphene, that in principle would be stronger than diamond because the bond length in the case of diamond is 1.54 Å but in the case of graphite, it is 1.42 Å. So, that is why this is the shorter bond length, we will also discuss it further when we talk about diamonds.

There is an atom that I have marked with a red color and there is a dashed line going up. What does it indicate? It indicates that this atom has its neighbor directly on top of it in the next layer. Let us see another red atom, it also has a neighbor on the top layer then the third one, it also has a neighbor in the top one.

However, if I take the other three atoms(marked green in slides) of this hexagon, they do not have any adjacent atom in the layer right above them. They have to go all the way to the next A layer to find their neighbor. What I am trying to say here is all 6 atoms of the hexagon are not identical in the case of a graphite crystal and in fact that is the reason that we did not take all 6 atoms in our unit cell because unit cell basically should be the smallest repeating unit. All atoms have to be identical and that is why alternating 3 atoms of this hexagon are different from the other 3 because of the fact that you do not have their neighbors in the adjacent layers.

Now, we will discuss space groups and point groups later on. The space group of graphite, you can see over here, we will discuss that. This basically tells you about symmetry elements and that I will cover separately.

I have just written 2600 K but you know that graphite is stable up to very high temperature. Several GPa actually, I did not mention the value of GPa. You can see that in the phase diagram.

Now another property of graphite in general is anisotropic. Anisotropic means you have different values in one direction compared to the other direction. You can see that there is so much difference in the crystal structure when it comes to the in-plane graphite structure and the perpendicular to the plane graphite structure. So, it is very obvious that we are going to have different sets of properties whether it comes to electrical conductivity, whether it comes to thermal properties, whether it comes to any other magnetic properties.

You will always have a difference when it comes to what you have in parallel to the c-axis and parallel to the a-axis of the crystal. So, this is just an example that the thermal expansion coefficient is very much different in both of these directions. In general, this is a very interesting thing about graphite that you have very high anisotropy which means you have very different properties in parallel and perpendicular to the basal planes.

There are two important parameters that you need to learn, they are known as La and Lc. What are La and Lc? L actually is length, length in a direction and length in the c direction.

Now, what do we mean by length? Length of not a single crystal but length of a crystallite. We talked about what is crystallinity when we measure how many portions of a certain

solid are crystalline and then how do we measure it? We need to somehow measure the size of these crystallites.

Also when you are doing the mining and in the ore processing, you want to know what is the largest crystal you have? If you take a crystallite then how do you measure it? Again the anisotropy of graphite sometimes you will have very high stacks.

So, several layers of graphite stacked on top of each other. However, the diameter or the actual size if you look at it from the top view that might not be so, much that might be very small on the other hand sometimes you can have very sort of horizontal crystals. Sometimes the layers are not so many but at the same time, the spread in the horizontal direction is a lot. So, these two parameters have been defined. These are the standard parameters based on this you will say it is a good crystal or bad crystal. In a lot of crystallographic and diffraction studies, these are the two parameters that you use.

I have shown here, let us say this grey color, this is a stack of graphite crystals. They do not need to be hexagonal by the way, it is just I have shown that let us say all the sheets are hexagonal.

Now, Lc is this what is known as the stack thickness, and if you consider that this entire crystallite was a sphere then what would be the diameter of that sphere that is known as La. So, it is not just a single layer it is not a 2D structure, but if you consider an equivalent sphere for every crystallite because every crystallite has a slightly different shape then the diameter of that would be your La or the crystallite diameter and the Lc you already know as the stack thickness. Now how many carbon atoms do you have in one unit cell? So, you see the unit cell in this picture and now you just need to count how many total atoms you have in this unit cell.

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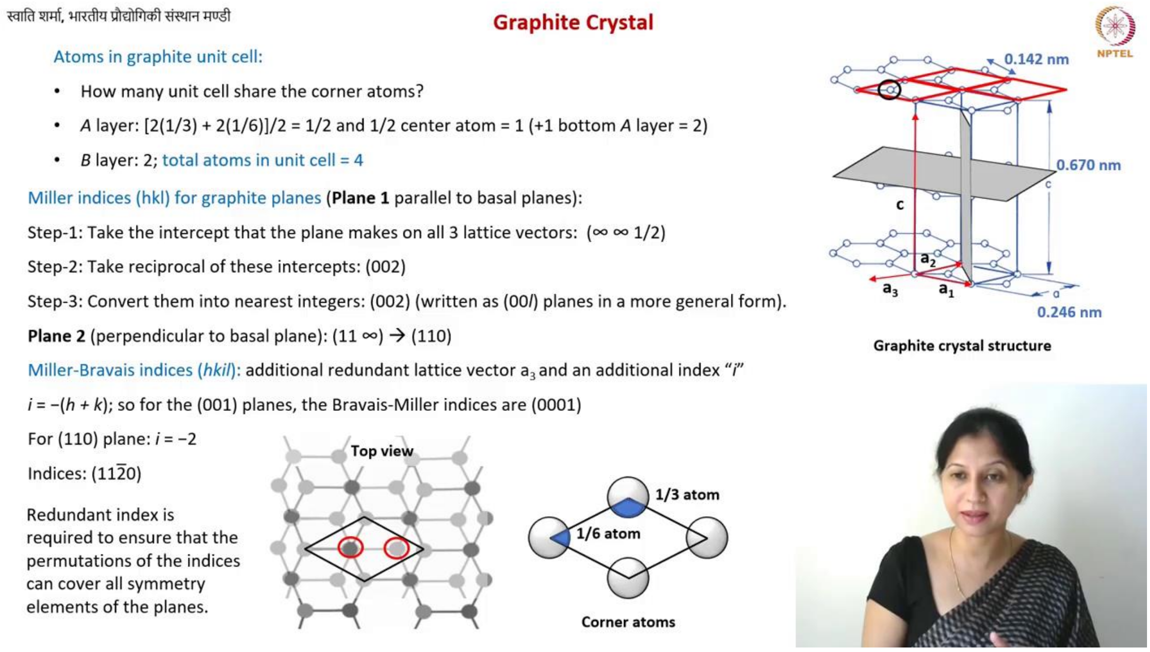

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Graphite Crystal

Atoms in graphite unit cell:

- How many unit cell share the corner atoms?
- *A* layer: [2(1/3) + 2(1/6)]/2 = 1/2 and 1/2 center atom = 1 (+1 bottom *A* layer = 2)
- *B* layer: 2; total atoms in unit cell = 4

Miller indices (hkl) for graphite planes (**Plane 1** parallel to basal planes):

Step-1: Take the intercept that the plane makes on all 3 lattice vectors: (∞ ∞ 1/2)

Step-2: Take reciprocal of these intercepts: (002)

Step-3: Convert them into nearest integers: (002) (written as (00*l*) planes in a more general form).

Plane 2 (perpendicular to basal plane): (11 ∞) → (110)

Miller-Bravais indices (*hkil*): additional redundant lattice vector a_3 and an additional index "*i*"

i = −(*h* + *k*); so for the (001) planes, the Bravais-Miller indices are (0001)

For (110) plane: *i* = −2

Indices: $(11\bar{2}0)$

Redundant index is required to ensure that the permutations of the indices can cover all symmetry elements of the planes.

Graphite crystal structure

There can be different ways of calculating it but there is one way which I personally found more convenient and this is probably similar to what you traditionally do to count the corner atoms. You see how many unit cells share these corner atoms and then if we have anything in addition to that.

Now, here we have to calculate this for three layers, A and then B and then A layers but let us see how we can do this. So, you see the unit cell, it will also have other unit cells surrounding it and it will also have the same number of unit cells on top of it. This is shown with the red color. I have drawn one neighboring unit cell, now you are going to have not just one, but more neighboring cells. So, if you think of it, how many unit cells would share the corner atoms?

If you take the corner of one of these cells, they are not squares or rectangles but this geometry(refer to slides). Now if you take one of the corner atoms, how many unit cells are actually sharing it? From here you see that one atom is shared with 4 unit cells and then you also have 4 on top of it. So, each corner atom is shared with 8 unit cells. However, if you have a cubic structure or if you have an FCC structure then 1/8th atom is shared at each corner of each cube. And each of these four atoms contributes equally to your unit cell. But because of the hexagonal geometry of crystal, let us have a look at the corner atoms alone of our unit cell. For now I forget there is anything in the center or in the middle of it or any other atoms.

We have these 4 corner atoms and now the unit cell looks something like this. Now you need to calculate what are the angles and how many fractions of a single atom is being considered for your calculation for the total number of atoms. If you will draw the connecting hexagons then you will figure out based on the angles you will find some 120 degree angles and some 60 degree angles.

And based on simple triangle in hexagons then you will figure out the region with the blue color has 1/6th of an atom and the other one has 1/3rd of an atom. Now, we have two atoms contributing 1/6th each and two 1/3rd each. We have this for the top layer and we also have this for the bottom layer. So, altogether how many atoms do we have then?

So in the A layer if you want to count the number of atoms you have these 1/3rd and 1/6th in two each layer. So, I multiplied them by 2 and added them. However, now I have divided the entire thing by half because you also have something on the top. So, if you divide it by 2 then all together these 4 atoms to each individual unit cells in one layer would contribute half an atom.

Now half an atom will also come from the center atom which is circled with the black color that is not exactly at the center but that is not shared at the corners. The contribution is half because half atom goes to the top layer. So, 1/2+ 1/2 would make it 1 atom in each A layer and because we have two A layers then we have 2 atoms coming from the A layer.

Now, what about the B layer? For understanding the atoms and the geometry in the B layer it is better to look at the top view of this crystal structure. So, here is the top view we have one layer and on top of that, we have another layer.

Now, let us draw our unit cell. It looks like this(refer to slides), here easily you can see how many atoms do you have. You have these two atoms that are marked in the red in B layer. You have to complete B layer atoms contribution since they are not shared by the unit cell on top or bottom. So, we do not need to worry about that. We have 2 atoms now coming from the B layer all together we have 4 atoms in the graphite unit cell.

Now, coming to another aspect of crystal structure Miller indices. So, I expect that you have learned something about Miller indices in your basic material science courses, now we know that you know how to calculate Miller indices probably you know if not then I will briefly let you know for the planes we are calculating the Miller indices. So, let us say we start with a certain plane now we have this a1 a2 and a3 these are the different lattice vectors.

Now, we start with this basal plane. Why do we call it basal plane? Because that is the base of the hexagon. So, all these planes which are parallel to the base are called basal planes of graphite. We take one plane, from here now you need to calculate what are the intercepts. The first step of calculating the Miller indices for the planes is that you take the intercepts that plane would make on all three lattice vectors.

To find intercept of the basal plane at B layer of the unit cell, It will be infinite in the direction a1 and a2 lattice vectors because the plane is parallel to them it will never intercept them. This plane intercept at c/2 because your entire unit cell has two A layers. So, this is c/2 or 1/2 on the c axis ok. Now the second step of the calculation is that you take the reciprocal of these intercepts.

So, for infinity, you will have 0. And for half, you will have 2. If these values are not integers then you will typically multiply it any integer to in order to make sure that these are the smallest integers, but in this particular case, we anyway have 002. So, these are the Miller indices for our planes for the basal planes ok.

In general, these planes are also written as 00l planes. So, that is the more general form. This is very important in the case of graphite when we learn the characterization technique not just for graphite for any carbon material because in all carbon materials ultimately we are trying to find out the graphitic regions and what is the crystallinity.

So, whenever we characterize these things there should be some signature pattern of graphite and that signature pattern actually comes from this arrangement of layers which even differentiates between multi-layer graphene and graphite because in the case of graphite the layer separation is smaller than what you have in multi-layer graphene.

So, this 002 plane separation or 00l plane separation is very important parameter when you understand the crystal structure and when you characterize the carbon materials. Now also we can take another vertical plane (grey color plane in slides) you can do the calculations by yourself, but I have already shown that this would be your 110 plane.

Now, these were the Miller indices in the case of hexagonal crystals. You also have another parameter that defines your crystal which is known as the Miller-Bravais indices. Now Miller indices have h k and l but in the case of Miller-Bravais you will have h k i and l. So, there is a fourth additional index, this is actually a redundant lattice vector a3 which is added and now you also have this additional index which is known as i.

Why we call it redundant because you can actually obtain it by adding and then having a minus sign.

$i = - (h + k)$

For example, for the 001 planes you will have the Bravais Miller indices as 0001 because you -(0+0) is 0. Now if I take another plane the 110 plane that we were talking about, here your the value of i will be -2. Because by using the formula -(1+1) = 2 which is written as $\bar{2}$. This is just the common practice in the case of crystal structure. So, here you will have your MB or Miller-Bravais indices as $11\bar{2}0$.

So, do not get confused if you see these four indices. Basically, the fourth indices is the redundant one which is added in order to include all the symmetry elements to make sure that we can completely explain the crystal. Because you see the hexagonal crystals have more or different symmetry elements compared to the cubic crystals. So, in order to justify that we add this fourth index.

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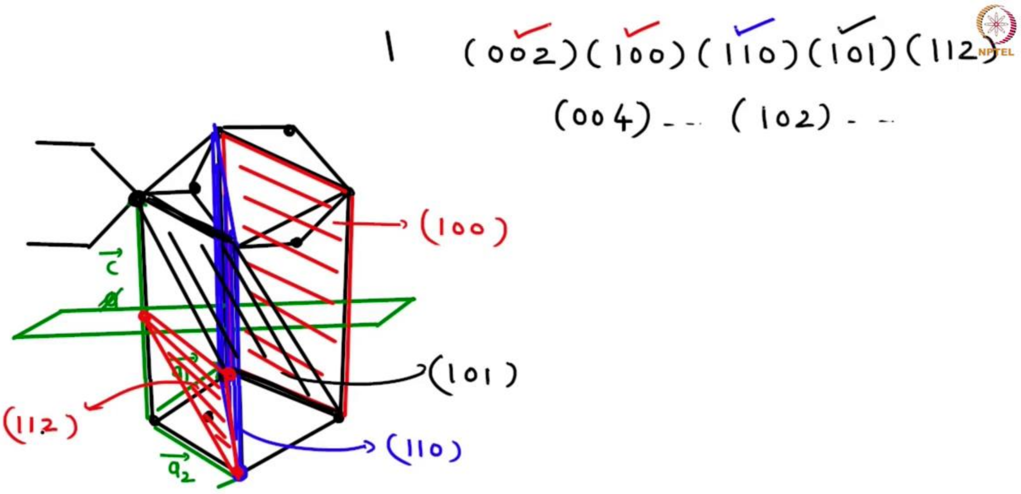

\ (002)(100)(110)(101)(112)

(004)- - - (102)- -

Now we are going to draw some of the planes in a graphite unit cell. So, first let us draw the graphite crystal, let us see how quickly we can draw this.

First, we draw the unit cell itself and then we are going to complete the hexagon at top of unit cell because that will give us a better idea of where do our planes lie. First of all, where are the atoms number 1, 2, 3 and 4 and there is one atom that lies here similarly for the bottom B layer you can draw these atoms.

So, you should remember that the corner atoms are not completely within the unit cell. They do not have 100 percent contribution but the one in the middle that is completely there in your unit cell of course it is shared with the top and bottom layers.

So, if we had the entire hexagon here, then it would look something like this(refer to slides). This is not a part of the unit cell remember, I am just showing it to you because I would like you to relate to the entire hexagonal geometry when we talk about or when we draw certain planes.

This is your graphite unit cell now what are we going to do here? We are going to draw some of these planes. First 002 plane which we already have seen multiple times then 100 plane. Let us also draw 110 plane, 101 plane and 112 plane also we can draw.

So, these are actually some of the planes that you will see when you characterize graphite for example, using X-ray diffraction studies. So, we will talk about X-ray diffraction later, but it is important for you to understand where do these planes lie in your graphite unit cell. So, these are some of the planes, in addition you will also sometimes see what is known as second-order peak like 004, 006 and you will also see 102, 104 up to 1006 planes.

But the five primary planes that we are going to draw here. Before we draw the planes, we should also mention where are our lattice vectors. So, you already know that we have lattice vector c and we have a1 and a2. Now, I am not drawing a3 here because you can always calculate it as a linear combination of a1 and a2 anyway.

Now let us start with the first plane 002 plane. So, 002 you already know it lies somewhere here(green plane in slides). We will not go into the details, you already know that 002 planes are here right in the middle of your c lattice vector. Now let us get started with other interesting planes. So, how about plane number two i.e 100 plane. So, now, you know already that when I say 100 that basically means the Miller indices.

100 basically means that the intercept along a1 is 1 and 0 basically means that there is no intercept, the plane is parallel to a2 as well as it is parallel to c axis. This is not very difficult, first of all let us draw a line parallel to a2 and also draw a line parallel to c. This is our plane right, this is an easy one. So this is basically your 100 plane(red plane in slide). So, let me also mention here this is 100 plane.

So, now let us try to draw 110 plane. 110 what does that mean? It means, along a1 and a2 you have intercept 1 but the plane is parallel to the c axis which basically means this is the diagonal plane I hope you can see this along. So, it is parallel to the c axis which means it will look like this(the blue plane in slide), and this diagonal plane is basically going to be your plane of interest ok.

Now moving on to 101 plane. So, how will you draw 101 plane? Again this is over here the intercept is one a1 and c vector and it is parallel to a2. Basically this is the plane over here I hope you can see in the same diagram this plane(black plane in slide).

Let me write down this is your 101 plane. Now, what else do we have here? We just have one more plane left which is 112. So, 112 is actually rather easy, whenever we have 2 that means the intercept is half. So, this is an easy plane to draw. This particular plane is your 112 plane. So, now, we are done with most of our plane in the graphite crystal.

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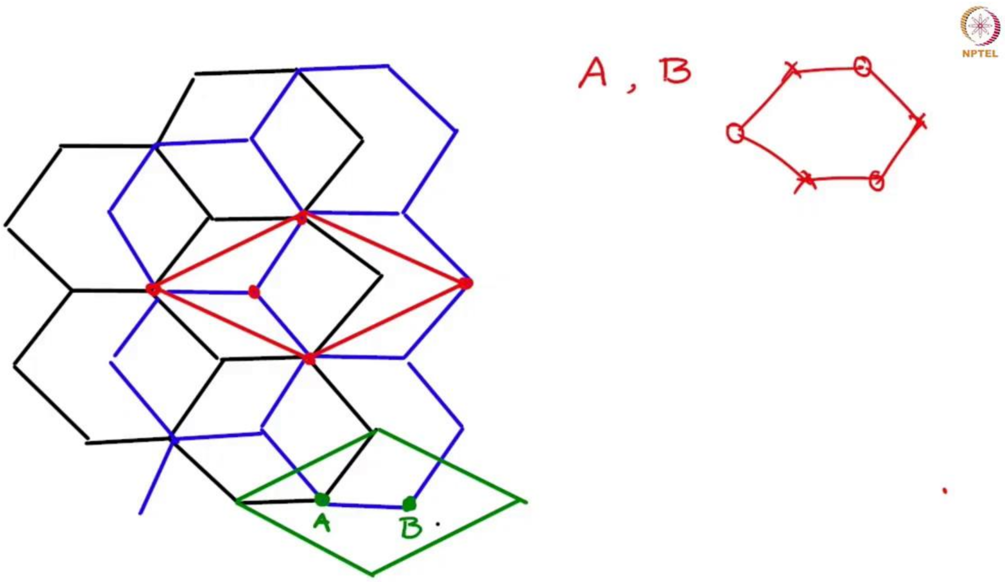

Another related quick exercise, you see that I have drawn one sheet of hexagons in black color and now I am trying to draw another one on top of it in blue color. So, this is how your 3D graphite looks like. This is how your graphite hexagonal graphite crystal looks like. This is how we select our unit cell (the red color geometry in slide).

We go from this point and we select our unit cell like this. We have atoms 1, 2, 3 and 4 at the corner of the unit cell and we have one atom sitting at the center of A layer. This is our first type of unit cell right. Why did we do that? Because you remember that we have two types of atoms right one. 3 atoms of the hexagon are different, they are not chemically different by the way. So, they are just not equivalent in terms of crystal geometry. So, A and B type of atoms we have. Now can we also have A and B type of atom of the same hexagon in 1 unit cell. So, if you see the blue hexagon then you have the A and B type atoms of the same hexagon. My question to you is that can we select our unit cell somehow such that we can accommodate these two atoms? So these two atoms fall in the center. So, again we have an A-type atom and B-type atom. So, the question is that can we have this kind of unit cell for 3-dimensional graphite and this is the top view that you are looking at.