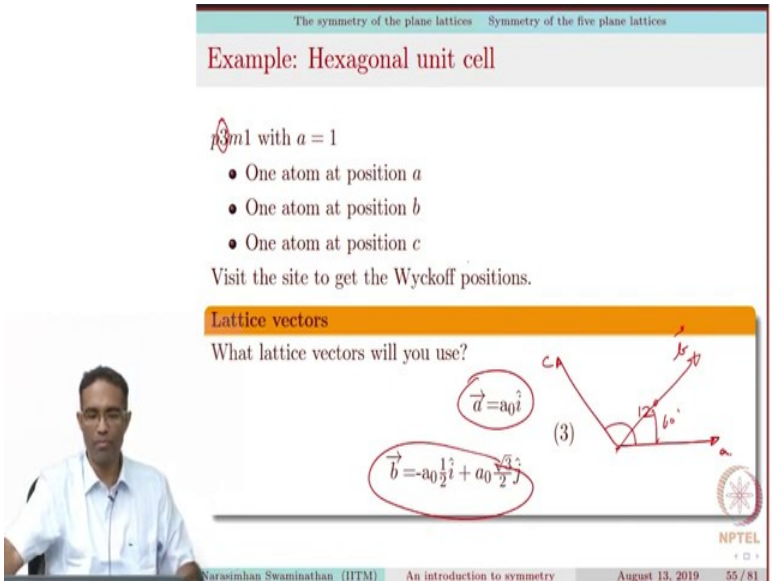
Foundations of Computational Materials Modeling
Professor Narasimhan Swaminathan
Department of Mechanical Engineering,
Indian Institute of Technology Madras
Symmetry of Space Groups

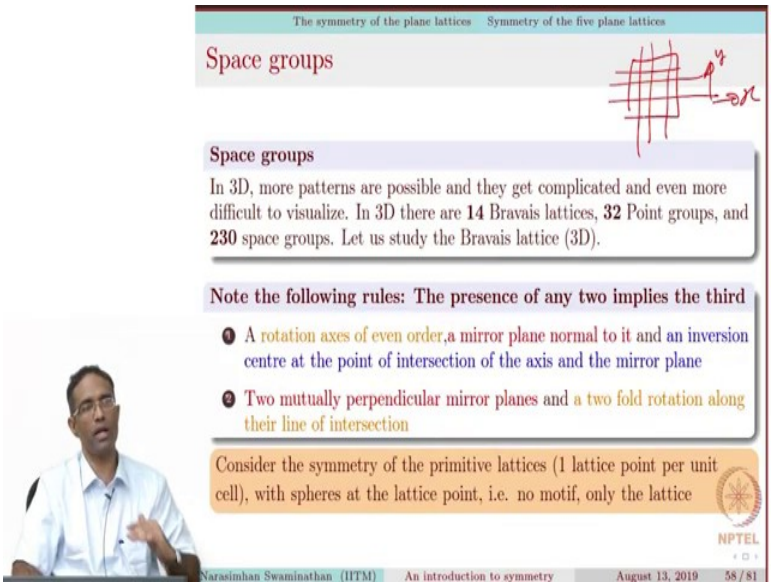
(Refer Slide Time: 00:31)



Computational materials modelling,~~,~~ ~~we~~We essentially were looking at plane groups where we talked about generating 2 dimensional crystals using simple MATLAB programs. The important thing for us to remember is a proper choi~~o~~sce of the bases vectors especially when it has the three fold~~urth~~ symmetry, it is a good idea to actually choose lattice vectors which have a 120 degree angle between them whether you have the 6 fold symmetry here or the 3 fold, it works well for both.

We saw the this the following program, problem in the in last class were we wanted to generate a plane group with p3m1 as its space group, we clearly saw that if you choose these set of lattice vectors you are able to generate the crystal or the 2 dimensional lattice in such a way that it has the 3 fold symmetry and we demonstrated that that would not be the case if you choose a lattice vector that had 60 degree between them. So, there is a this needs to be kept in mind, so whenever you are generating space lattices also a similar rule will apply, so you have to be careful in the lattice vectors that you actual choose in order to generate the space lattice or plane lattice.

(Refer Slide Time: 01:56)



So, with that being said it is important for us to now move on and start talking about space lattices. So, we talked about plane groups when we are talking about 2 dimensional stuaff, so when we talk about a point arranged in 3 dimensional space, we start talking about space lattices, space groups and point groups in 3 dimensions.

So, naturally once you are in the third dimension you have more possibilities for example you can have mirror in this can you had in the plane lattice you had probably mirror planes which were you know having either the y axis or the x axis normal. Now, once you are talking about 3 dimensions you can have mirror planes which are actually having normalize the zeasy axis also.

So, in this manner you can have rotations about one of the three axis instead of just the two axis and so on and so forth, then you can have glide planes on all the three with normal perpendicular with normal as either of 3 axis and we will have 1 more additional translational operator which we will see in a little bit, but the presence of these additional opportunities for you to create new symmetries within the structure gives rise to more number of point groups so there are 32 point groups, how many where there in plane lattice? How many point groups where there?

Student: 10 point.

Professor: 10 point groups. And if you look at space, space lattice.

Student: 17.

Professor: There where 17.

Now, when you talk about,… sorry, when you talk about the space 3 dimensional space the total number of point groups increases to 32, there are 32 different possibilities and there are 230 different space groups only, there are only 230 different ways you can basically arrange things in 3D so that you have lattice translation, so there it is a 3 dimensional crystal infinite crystal.

Just like how we looked at a plane lattices, it is a good idea to actually study first the symmetry associated with the Bravais lattice. So, what is a Bravais lattice? A Bravais lattice is only an arrangement of imaginary points in 3 dimensional space such that when you set on any point it looks exactly the same and there were 14 such possibilities when you talk about the space Bravais lattice and 5 such things where existing for the 2 dimensional.

So, these some of these rule needs to be remembered when you are actually looking at the symmetry associated with the plane, with the space lattice, the presence of rotation axis 2 of these things any 2 of the following symmetry elements will automatically imply the third, for example a rotation axis of even order, a mirror plane normal to it and inversions center at the point of intersection of the axis and the mirror plane.

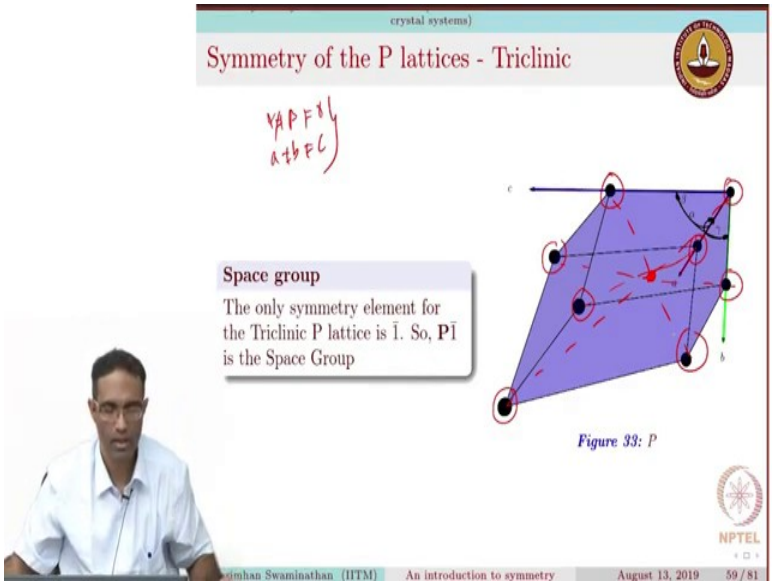
The presences of any 2 of these things will automatically mean the other one, so if there is a rotation axis of order 4 and a mirror plane is normal to it, it means there is going to be an inversion center at a point of intersection of the axis and the mirror plane. You can just thing about it we already saw this example when we were discussing the various symmetry elements.

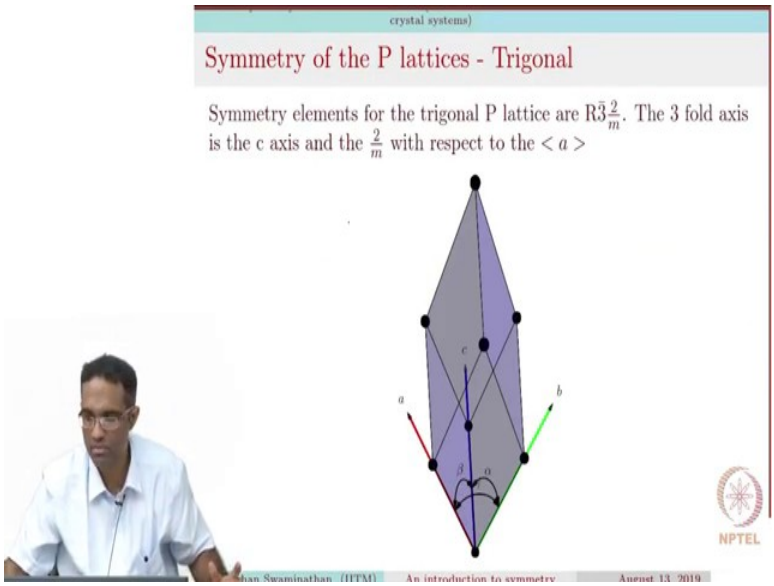
The second one is the presence of any two mutually perpendicular mirror planes automatically implies a presences of a 2 fold axis, if you have 2 mirror planes perpendicular to each other then it automatically means that there is a 2 fold rotation axis that is passing through the intersection of these 2 mirrors.

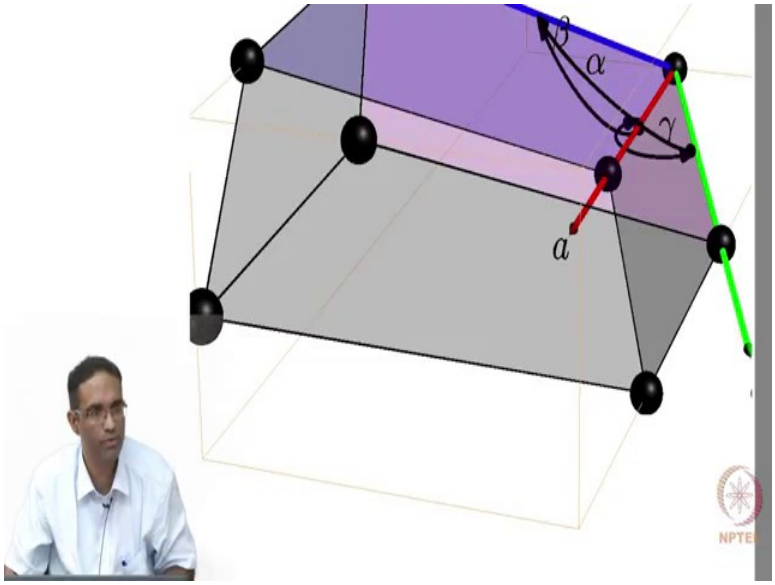
There is no need for us to specify all the 3 things if they exist, the presence of any 2 will automatically imply the third. So, sometimes you will find that one of the things is missing, what do you thing is obvious is missing in the Hermann Mauguin symbol, but that is mostly

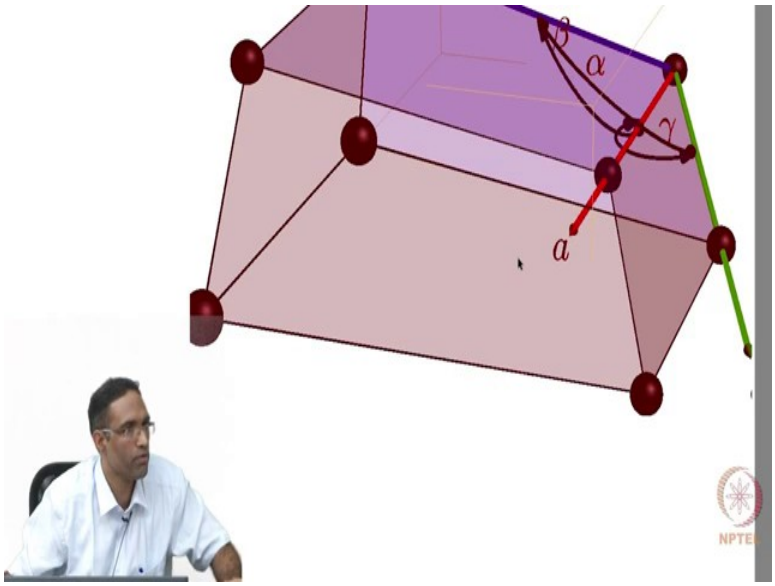
because there is something else in some other symmetry operator that is present which is implying whatever is not there.

(Refer Slide Time: 06:30)







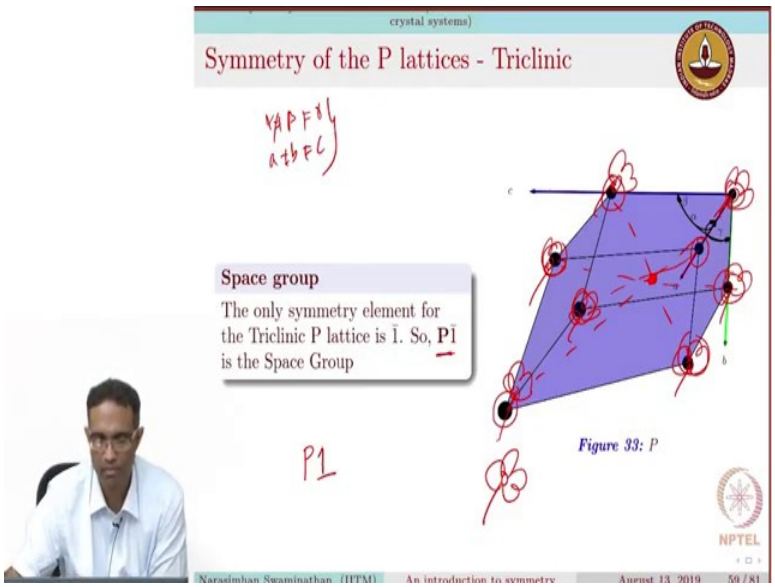


So, we will look at the symmetry of the Bravais Lattices the first Bravais lattice is basically the triclinic unit cell, so are the triclinic unit cell means alpha and beta and gamma are all not equal to each other and a is not equal to b is not equal to c are basically characterizing the triclinic unit cell.

So, if there is a 3 dimensional sphere at each of the 4 corners of the unit cell then the only symmetry element there is actually present here is the inversion center there is located right at the center of the unit cell. There is a inversion center right there, provided whatever is there in the corners is actually an atom with spherical symmetry, so it might be a good idea for us to take a look at this picture, so at this point at all these points you can only spheres at all the points you can see only spheres. The second I put some motif at that particular location

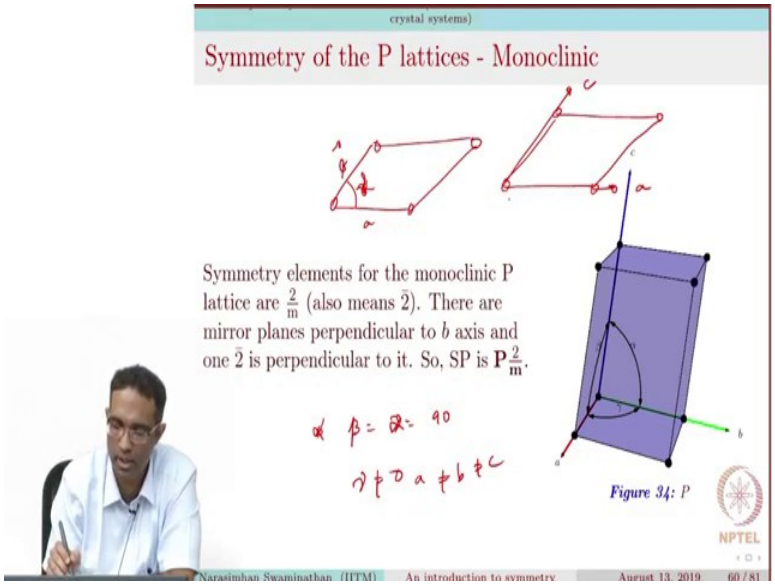
depending on what the symmetry of that particular motif is you may or may not have this one bar.

(Refer Slide Time: 08:10)



For example if I put an arbitrary flower at that particular location something like, this always oriented in that manner, then this crystal is not having this as a symmetry there is no one bar, the one bar instantaneously disappears, the only symmetry now for this entire space will be one, there is no other symmetry operator that is present, what we are talking about is for the Bravais lattice which only has the atoms there, this distinction is kind of important it can be confusing at times.

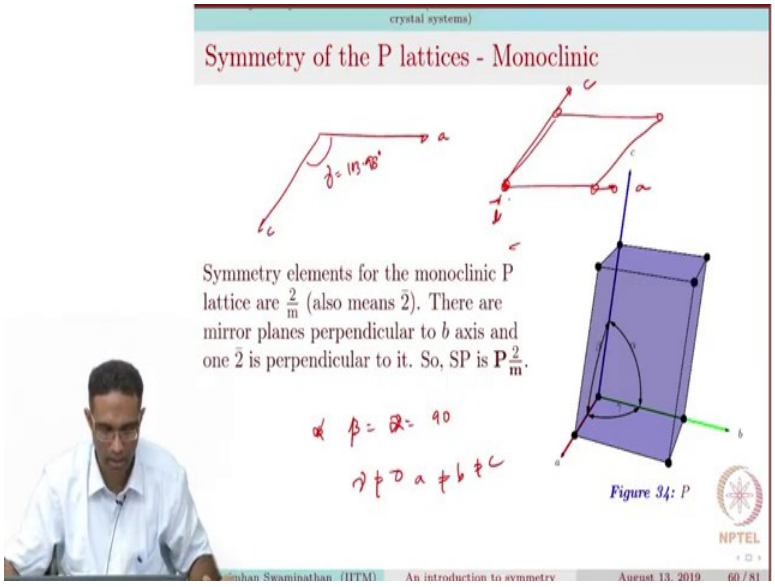
(Refer Slide Time: 08:53)



Next, we talk about monoclinic lattices. Monoclinic lattices was like our oblique plane lattices except that what is happing is you have a plane oblique lattice this is a and this probably b and this some angle alpha so this should be actually at your angel gamma and your stacking one more of this plane oblique lattice is right on top of it, so that will give you this unit cell and so you it is characterized by alpha sorry beta is equal to gamma is equal to alpha is equal to 90 degrees but gamma is not equal to 90 degrees.

And none of them are actually none of these sides are actually equal in this case. So, what are the various symmetry elements that is associated with this Bravais lattice? So, it should be obvious that it sorry... close this, what are the various symmetry elements that can think of? I will mark this as a and I will mark this as c, there is 2 fold symmetry is there.

(Refer Slide Time: 10:29)

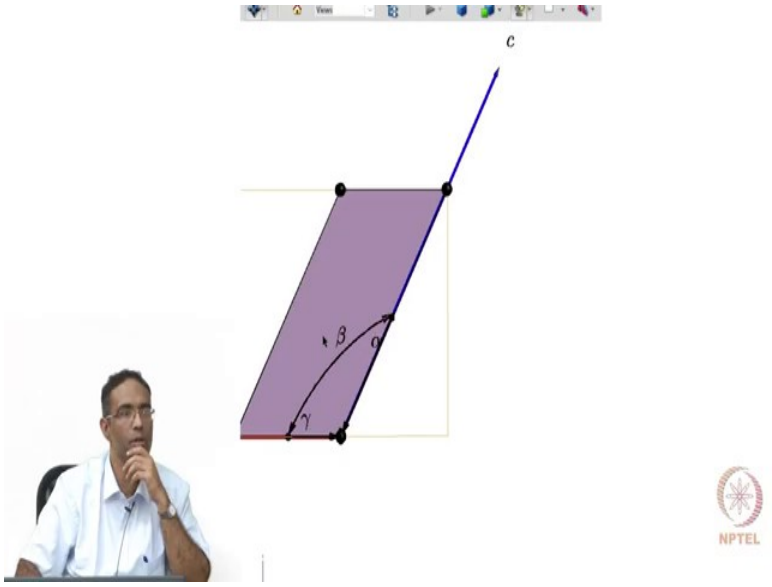


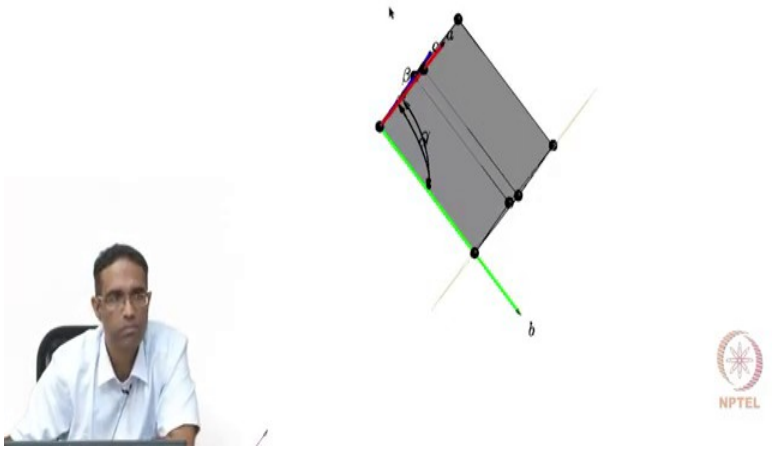
On top of this I have stacked another one there is only one 2 fold symmetry about this b axis, there is a to 2 fold symmetry about this b axis, I am intentionally writing down the vectors a c and b. Usually the b axis is chosen as the axis is called as unique axis which is going to have this 2 fold symmetry associated with it, that means you are going the b axis is basically the axis of the 2 fold symmetry. So, whenever you look at international tables of crystallography, whenever you are talking about space groups which have this 2 fold symmetry only associated with unlike monoclinic unit cells, they will usually mark a like that and a c like that.

The b is usually going to be pointing outside of the page the b is going to be pointing outside of the page and they will mention an included angle of gamma equal to whatever say 103.98

degrees or something like that, this will this sort of information will be present in what is refer to as the international tables of crystallography, we will show you some pages from that book hopefully in the next couple of lectures to see how exactly it looks. But the two fold axis is generally chosen as the unique axis or the axis which has the 2 fold symmetry. So, in addition to that do you have in addition to the 2 fold symmetry do you have any other symmetry elements for this Bravais lattice.

(Refer Slide Time: 12:04)

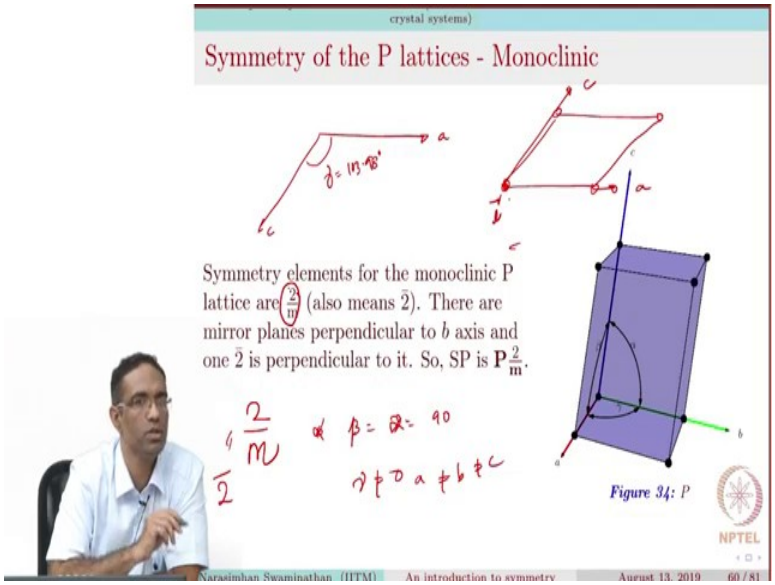




Imagine… ok, let me show you a three dimensional image so that it can be easy for you to imagine this, what can you say about if there is a mirror plane somewhere? Is there a mirror plane? Not here definitely not with c or a as a normal what about with b as a normal? What about where b as normal, do you think you have a mirror plane? You have a mirror plane,

that is what is going to distinguish between your triclinic and your monoclinic unit cell, because you have 2 oblique lattices stacked on right on top of each other this one is going to be your b axis, you have a 2 fold rotation and you are going to have a mirror plane that is perpendicular to that 2 fold rotation.

(Refer Slide Time: 13:18)



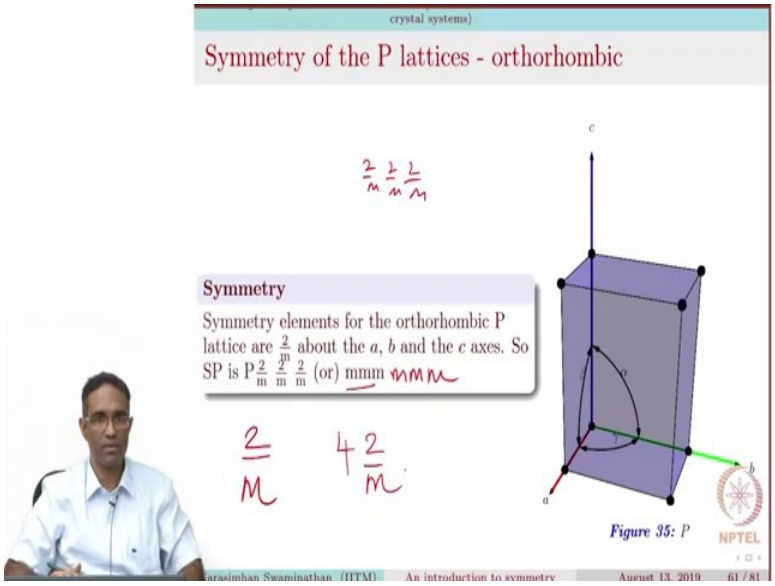
So, the space group for this thing is 2 bar m, 2 fold rotation and mirror, 2 fold rotation and ~~(())(13:29)~~perpendi… if you put 2 bar 2 over m means there is a 2 fold rotation and perpendicular that there is a mirror. Remember one of the rules that we just studied it means there are mirror planes perpendicular b axis and 1 2 bar is perpendicular to it. So, there is a inversion center also right in the center.

And we also looked at what happens when you have 2 bar,~~(())(13:51)~~ 2 bar, 2 bar is 2 fold rotation and an inversion center, that is also being present here, 2 bar is also present here, but we do not have to specify that because if I say 2 fold rotation and there is a mirror perpendicular it all it automatically means the other one. Generally, in Hermann Mauguin symbol we use this 2 over m is what is used in the Hermann Mauguin symbol to talk about the symmetry.

Student: Why are not writing 2 followed by m?

Professor: 2 followed by, 2 fold rotation is associated with the b axis the mirror is also perpendicular to the same axis, if you put it in a next slot it is associated with a different axis, it is not associated with the same axis.

(Refer Slide Time: 14: 49)



Now, while this might seem a little bit confusing you will see that the very quickly you will start understanding or recognizing the kind of unit cells the second you see the Hermann Mauguin symbol just like we did for the plane unit cells. Now, what happens in orthorhombic? What is orthorhombic? Orthorhombic is a rectangle on top of that another rectangle and everything in a side is also rectangle and we are talking about Bravais lattices.

So, there is 2 over m perpendicular to b axis, 2 over m for the a, 2 over m for the c axis, so for the 3 nonequivalent a b and c axis you have 2 over m which is same as 'mmm' you will because now the presences of 2 mirror plane implies a 2 fold rotation, so you can also write this as m m m, there are mirrors perpendicular to all the 3 axis, or there are mirrors for which the normal are the 3 axis a b and c axis.

So, this is basically the orthorhombic units the space group for the orthorhombic condition is P 2 over m, 2 over m, 2 over m, what is a point group? What can you tell about the what how will you tell me what the point group is? Just remove this P, 2 over m, 2 over m, 2 over m becomes a point group, OK?- Now, what is the next Bravais lattice we can think of? Orthorhombic, then?

Student: Tetragonal.

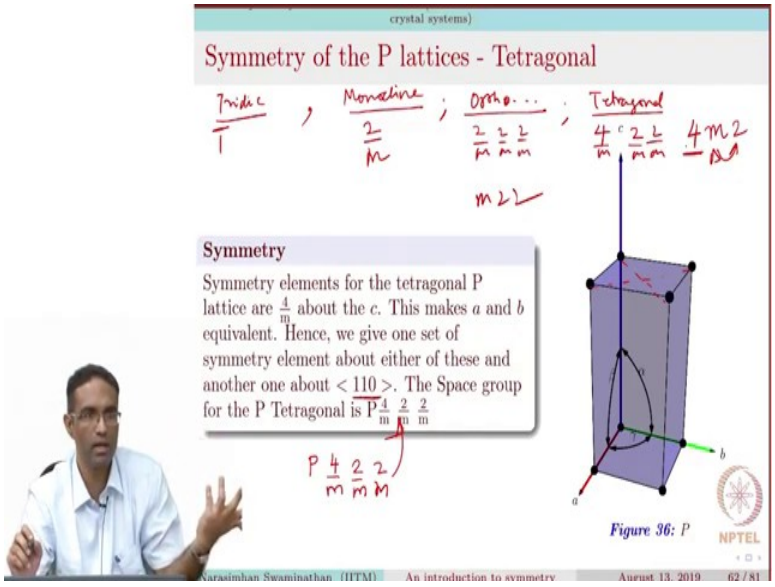
Professor: Tetragonal, what is tetragonal now?

Student; a is equal to b.

Professor: a is equal to b. So, basically you have a base is going to be a square and on the sides you are going to have the corresponding rectangles. So, in a way at least 2 directions are similar to orthorhombic and 1 direction is going to be similar to cubic, so you should be now able to write down the Hermann Mauguin symbol pretty easily. So, there is going to be a 4 fold rotation, the second there is a 4 fold rotation, the second there is a 4 fold rotation it makes a and the b axis equal, it makes a and the b axis equal and there is no difference.

So, the next nonequivalent axis that you can choose is what? ~~C~~c, so is that a mirror perpendicular to it, is there a 2 fold rotation about c? So, there is so 2 over m and what is the next possible nonequivalent axis? What about the diagonals of the square? Just like how we saw for the square lattice.

(Refer Slide Time: 17:42)



So, there is going to be this is the square the base is a square, so basically this gamma is 90 degrees here that makes a and b equal so there is a 4 fold rotation about the c axis and then the next one is basically the 2 over m which is about the b axis or equivalently the c axis and then you also have these mirrors and a 2 fold rotation about that, about the 110 direction. Right?

So, the space group for the tetragonal lattice is 4 over m, 2 over m, 2 over m as written down over here. So, now it should be very easy for us to now start writing down whatever we have studied, so first thing was triclinic, for triclinic what did we see? We saw 1 or what would we see we saw 1 bar, then we saw monoclinic, what happen there?

Student: 2 fold rotation and a mirror

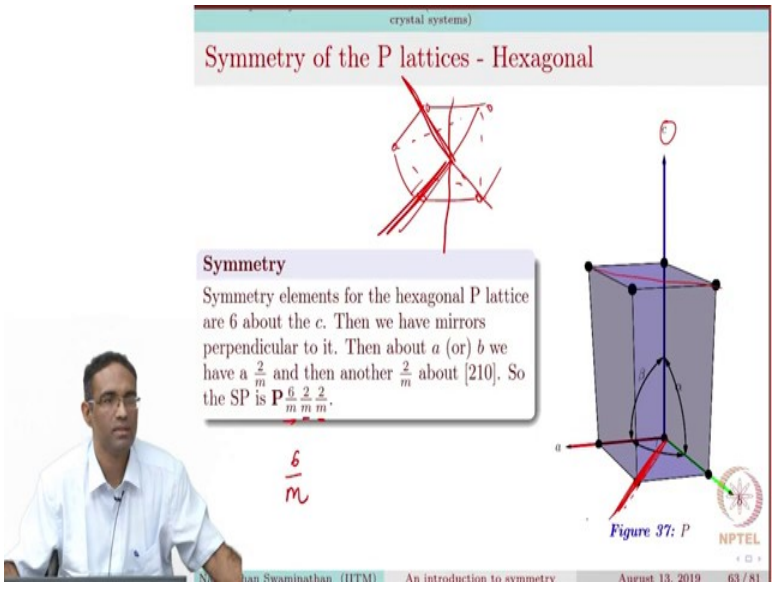
~~(())(19:00)~~

Professor: 2 fold rotation perpendicular to it mirror.

Then we saw orthorhombic, what did we see there? 2 by m, 2 by m, 2 by m. Then we saw this one tetragonal and that is 4 over m and then we saw 2 over m and 2 over m. So, in any space group by looking at the combination and the first by looking at the first rotation and see what is there adjacent to it you will be able to figure out what the space group or what crystal system you actually need to use in order to generate that structure.

So, if you see only 1 or 1 bar, then there is nothing else but triclinic. If you see 2 over m or 2 and nothing else after it, then it is monoclinic. If you see 3 mirrors 1 2 and 2 mirrors, 1 mirror and to 2 ~~(())(20:01)~~ four… if you see all these combinations it essentially means it is a orthorhombic lattices. Now, if you see the first one is 4 but after that if it is a combination of mirror and 2, either these then you will understand that because of the presences of 4 fold rotation you will understand that it is the tetragonal unit cell that you need to use to generate this crystal structure.

(Refer Slide Time: 20:27)

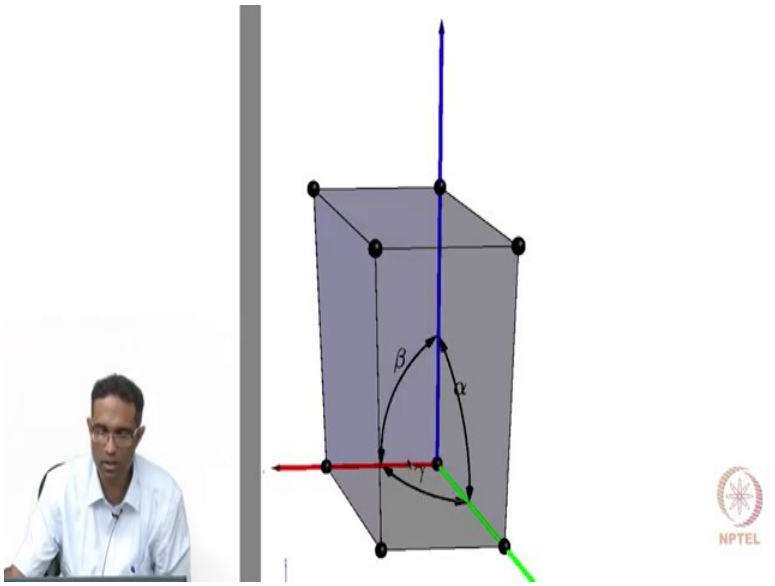


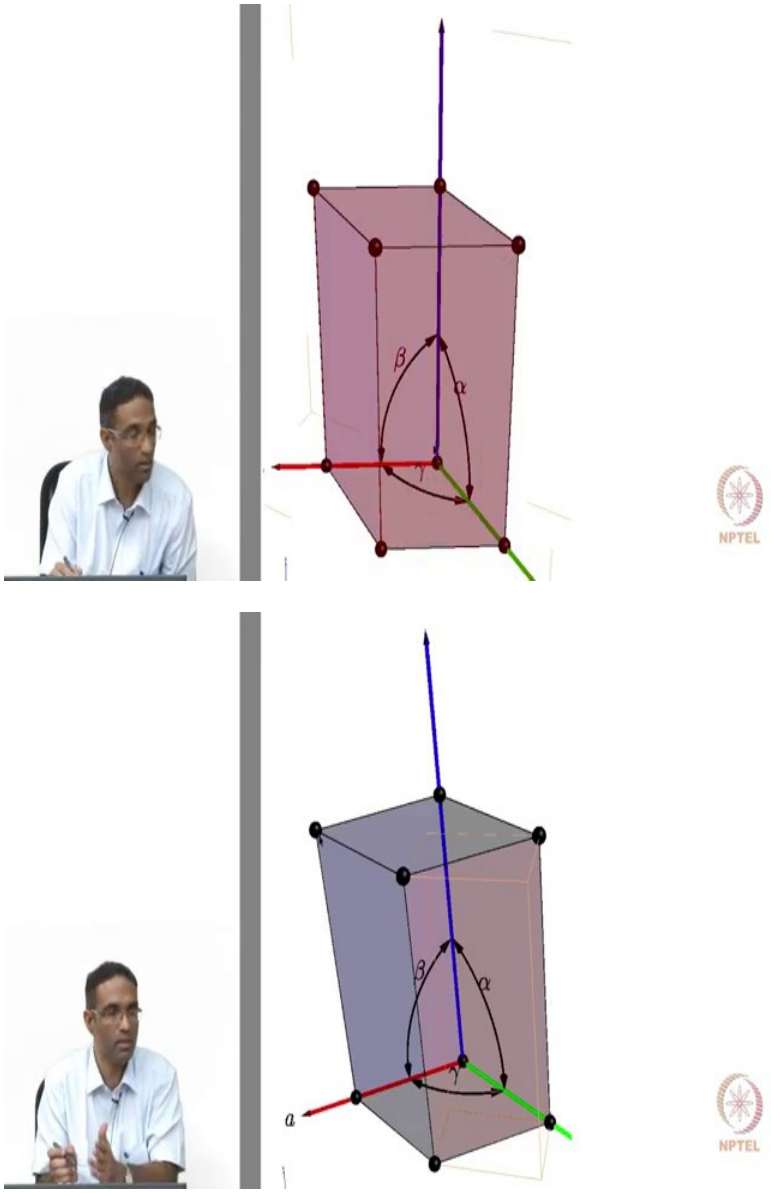
Now, we go to the next complicated one which is hexagonal, hexagonal everything is pretty much same like what we did in the plane lattice so obviously we are going to choose this as the unique axis c as the unique axis because it has the 6 fold rotation, there is a 6 fold rotation

which is about the c axis and there is a mirror perpendicular to it, so you have 6 over m. Now, the other 2 axis what where they in our…… remember we were talking about these unit cells, what where the 2 axis or the mirrors that we dealt with when we talked about the hexagonal plane lattices? We talked about mirrors which had this as the normal those darkly shaded things they were the mirrors, they were the enormous to the mirrors.

So, basically these were the mirrors. In addition to that we had mirrors which had the bisectors of these you know of these axis as a normal. So, these were the mirrors themselves the axis were mirrors themselves. For the space lattice these 2 are exactly the same directions except that now instead of having just mirrors you also have a 2 fold rotation above that axis, you can rotated them for example you can rotate the crystal about this axis and you essentially get back the same crystal structure and of course there is mirror that is perpendicular to this, this direction because it is getting reflected on the other side is that, can you see that? So, you want we can take a quick look at it.

(Refer Slide Time: 22:36)

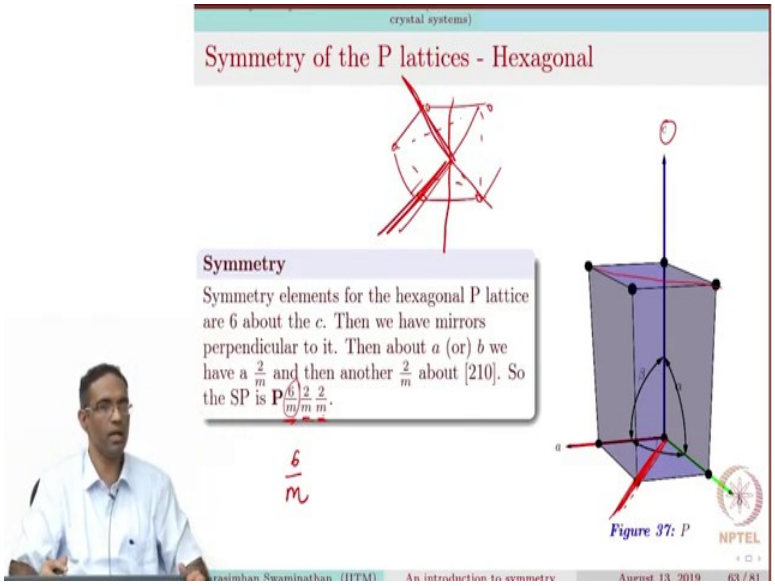




So, these are the this is the include angle of 120 degree the gamma is actually the included angle which has which is 120 degrees, so I said that if you rotate this you can rotate it about this line, are you able to see that cursor moving that so you get able to rotate it about that line. And when you rotate it about that about by 180 degrees you get back exactly the same crystal. And there is a mirror also that is perpendicular to it, so these atoms when you join them you will get a mirror.

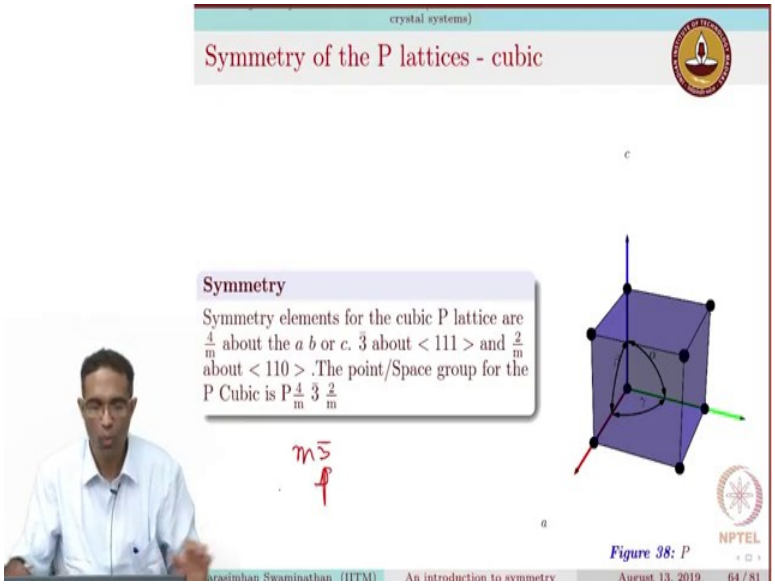
Like this there are mirrors abovecut all the planes for this similar to what had seen for the plane oblique lattice about the same directions with the same directions as a normal except there in addition to the mirror there is also a 2 fold rotation because there is a this is space lattice that we are talking about.

(Refer Slide Time: 23:32)



So, once you see, once you see a 6 fold rotation followed by 2 and 2 or m and m or some combination like that you will understand that it is basically a hexagonal unit cell that you have use, as soon as you see the space group. So, the key thing is when you see the space group you should be able to identify what unit cell you can used to actually generate it on the computer. So, these are some of the hints that you will get from the space group symbol to actually be able to generate that.

(Refer Slide Time: 24:03)

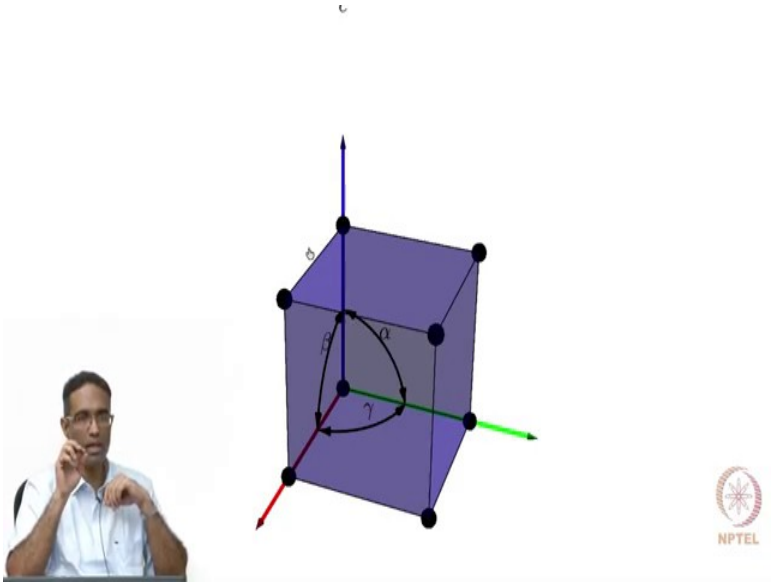


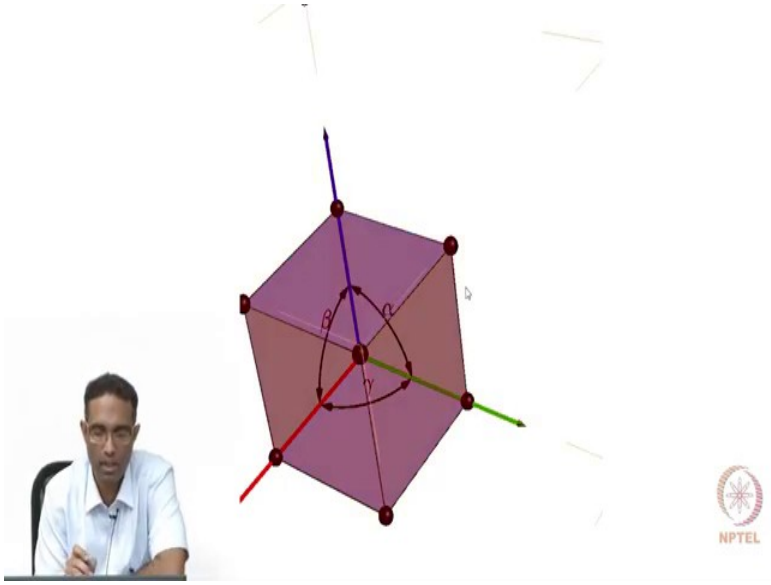
The next one is cubic, cubic becomes a little bit tricky because there is all the 4 axis, all the 3 axis a b and c are become are 4 fold have 4 fold symmetry associated with that, the second

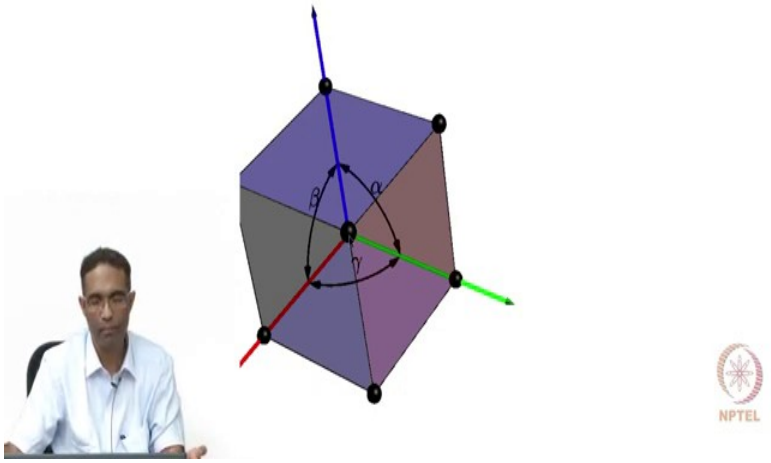
you see 4 it could either be what and what it either be tetragonal or it could be a cubic. So, now you have to try to understand how you can differentiate between space groups which start off with a 4. If it is tetragonal you will either see a 2 fold rotation mentioned or a mirror mentioned, for the cubic you will mostly see a 3 3 bar that is going to be present in the second group.

In fact this can also m 3 bar, if you see 3 bar in the second position 3 bar in the second position it generally means it means cubic it means that the symmetry is cubic. Now, what does these 3 bar mean and what direction that it refer to? The presence of the 4 fold rotation is making a, b and c equal, so the next is slot and Hermann Mauguin symbol cannot be referring to either a or b or c, it is got to refer to something, none of this something nonequivalent a b or c.

(Refer Slide Time: 25:34)





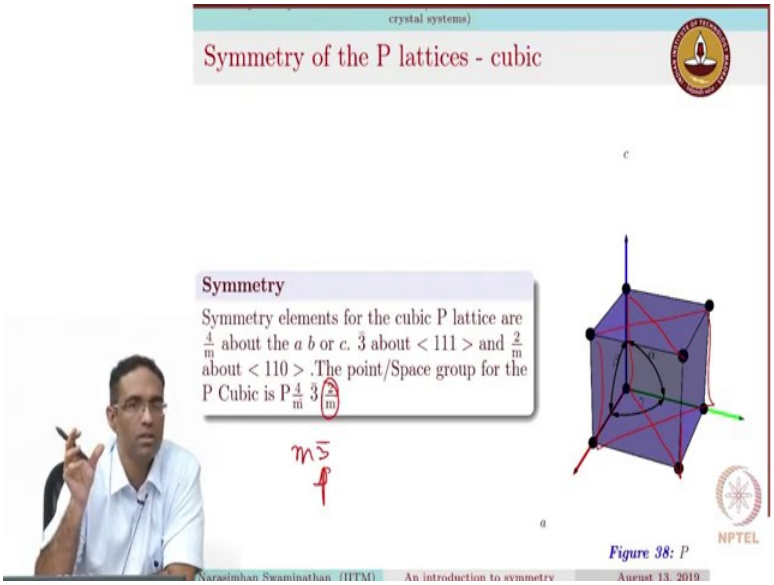


So, in cubic systems what we will happen is you have, in simple cube if you look about through the 111 axis about the 11 axis you will see that there is a 3 bar symmetry associated with that, see… is there a 3 bar?, for example consider this so I am looking through the 111 the 111 direction,… the 111 direction,… so consider the front 3 atoms this 3 atoms right here, so if you rotate it by 120 degrees and invert it through the center this atom rotated through 120 degrees and inverted through the center will take you to this particular atom right here and you keep doing that you will be able to understand that there is a symmetry 3 bar that is passing through the 111 direction.

And there are 4 equivalent 111 directions in the simple cubic… in the cubic crystal structure. So, where you looking through 111 or 1 bar 11 all of them are essentially equivalent, so the

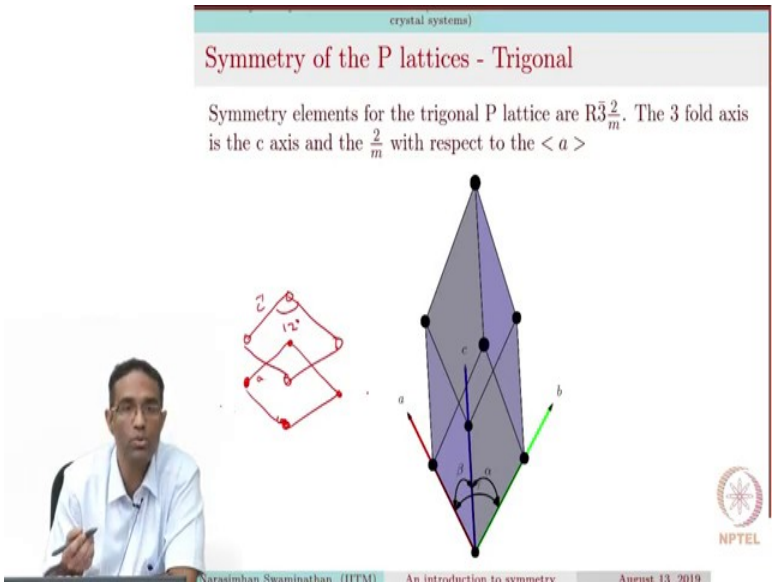
second you see a 4 fold rotation or a mirror and in the second slot you see a 3 bar, it will mean that the crystal structure has a cubic symmetry.

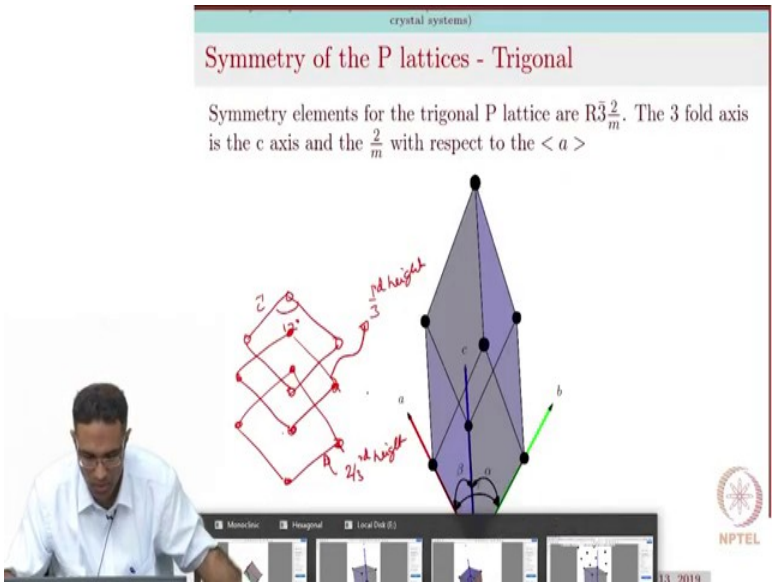
(Refer Slide Time: 27:50)



The next one the next symmetry element that is present in the cubic system is a 2 over m which is about 110 directions, that means a 2 fold rotation axis is the 110 direction and perpendicular to there is a mirror, so that is basically these, these are the mirrors, those are the mirrors, there are mirrors there, can you see it? So, the secret is, to look for the kind of rotation that is present and what sort of symbols are present following that and you should be able to distinguish or find out what crystals systems you can actually use to generate that crystal. And this is what you will apply for the entire 230 space group to generate the crystal structures.

(Refer Slide Time: 28:40)





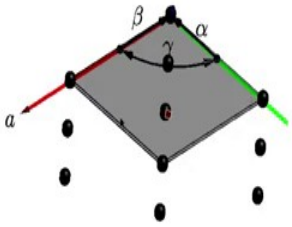
We~~You~~ still have not gone through one more it is called as the trigonal lattice or the rom and another words it is also generate something called as the rhombohedral lattice, this lattice is a little bit peculiar, so we will go over it and in a little bit of detail, this has a 3 fold symmetry and but otherwise it actually can use the hexagonal unit cell to be, to generate this crystal structure you can use the hexagonal unit cell.

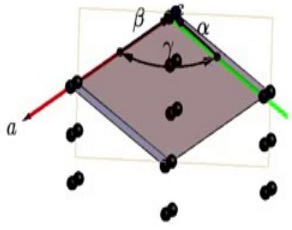
So, we will see what is the different between the hexagonal unit cell and this one, in… what happens in the, so in this unit cell in the rhombohedral unit cell what happens as the following? You have an~~d~~ included angle of 120 degrees, so this may be a this may be sayee~~e~~ c and this may be b whatever it is. If it was just the hexagonal unit cell you would just have this

repeat with you know with looking like a hexagonal like that, sorry I did not write well so this one, that is what would be there if you and then you would stack this up one on top of each other to basically realize your hexagonal unit cell.

Now, in the rhombohedral unit cell you have if you look at it from the top you will have one more plane of atoms this coming on top at one third the height and one more at two thirds the height. So, there will be.

(Refer Slide Time: 31:18)



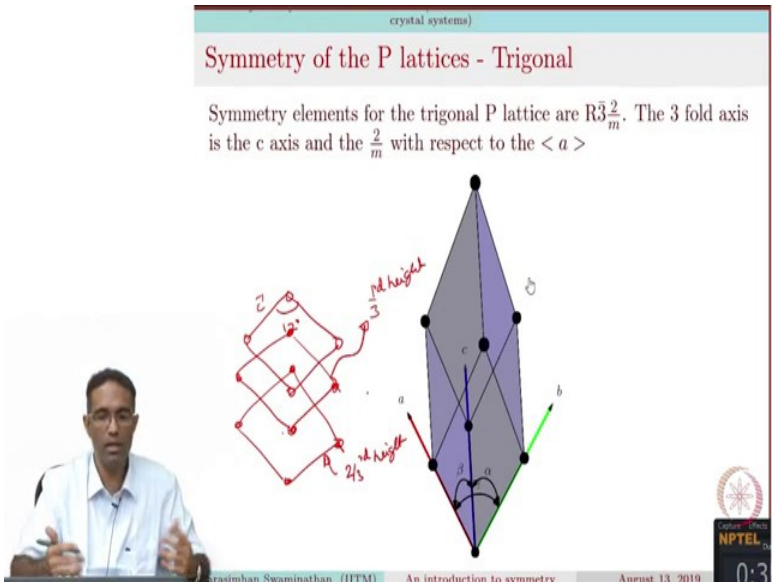


So, it will look if you if you have imagine this then you can actually look at.. looking at it from top view, you have the rhombus and then you have the first atom here that is actually present inside the unit cell but present at a height of 1 by 3 from the base. And this is the

corresponding rhombus that will be found this one right here, the second one is this atom this atom which is~~a~~ two by thirds the height from the base, so consequently this unit cell that you are seeing is basically like the hexagonal unit cell with an included angle of 120 degrees except that there are 2 additional atoms there are going to be present at heights 1 by 3 and 2 by 3.

So, you can construct the rhombohedral structure with the hexagonal unit cell by making sure that you add these additional one by third and two by third atoms as the bases to create the rhombohedral unit cell, to create the rhombohedral structure.

(Refer Slide Time: 32:25)

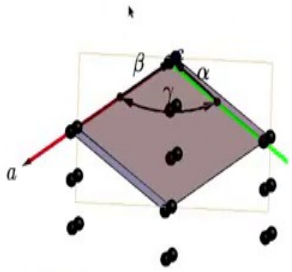


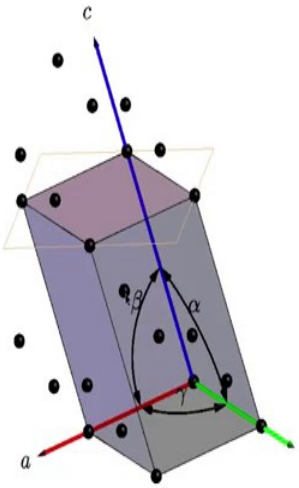
Otherwise, you can also use this one that you have a equal to b equal to c and alpha naught equal to beta naught equal to gamma also to actually generate the trigonal unit cell, ~~convention~~ Convention is to use the hexagonal units because there is simplest we understand it best. So, the presence of this atoms at 1 by 3 and 2 by 3 abov~~e~~ut the c axis if you take a look at it, it destroys a 6 fold symmetry that would have been present if those 2 atoms where actually not there or those 2 lattices point where not there.

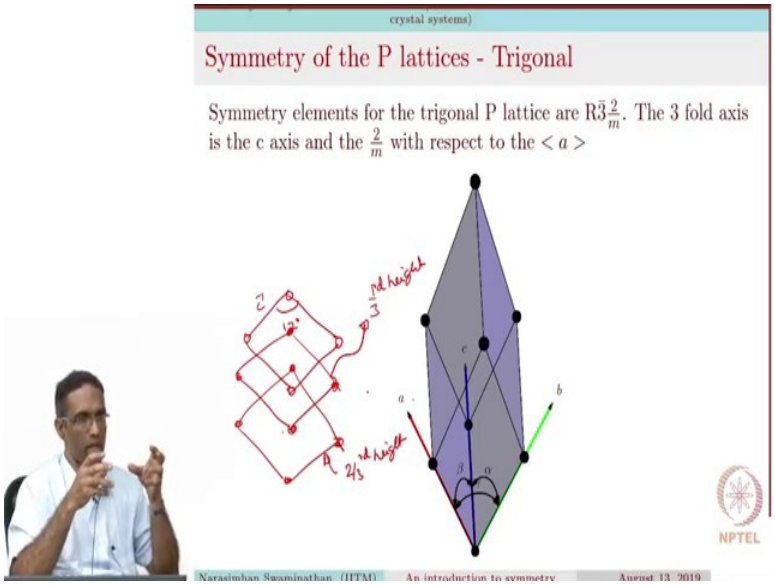
Therefore you have only a 3 4 symmetry followed by 2 by m in the other direction in any one of the other directions to actually generate your trigonal units.

Student: Please go to some slide ~~(())(33:13)~~

(Refer Slide Time: 33:24)







Professor: which one, previous slide, this one, this is not responding very fast see if you look it carefully the internal atoms the internal 1 by 3 and 2 by 3 atoms are actually going along the body diagonal of this hexagonal structure, this atom is present at height 1 by 3 and this one is present at height 2 by 3.

Student: ~~(())(33:45)~~They are the part of the unit cell ?

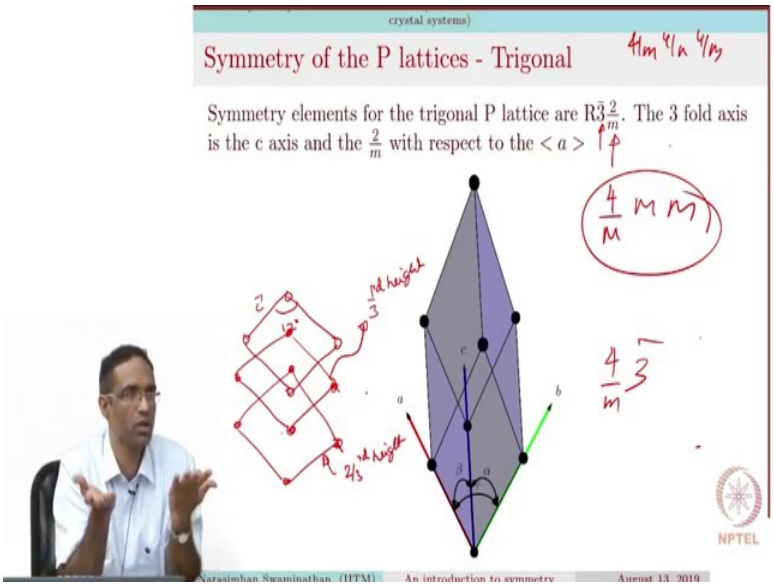
Professor: They are part of the unit cell, see what are trying, I think we have to clarify a few things, we are trying to find out the unit cell for the trigonal system. ~~in~~ In general the trigonal system is associated with alpha equal to beta equal to gamma and but none of them need to be equal to 90 degrees and then you have a equal to b equal to c, so it form some sort of a oblique system that looks like this. ~~this~~ This is how it should look like here alpha equal to beta equal to gamma and a equal to b equal to c.

But when you are trying to generate this crystal structure the convention is to not use a equal to b equal to c and you know arbitrary angles, it is convenient to use the hexagonal unit cell but by placing those atoms at one by third and two by third the portions. ~~both~~ Both this one and the other one will form the same lattice will have the same symmetry associated with that, I do not have the good picture made to show that this one is in fact a part of that lattice but next class I can actually bring that and show that to you to convenience that this is actually lying inside the hexagonal unit cell with the one by third atom on and two by third atom on.

I think you must have studied this previously at some point of time. So, this is actually the 3 bar the presence of the 3 bar and the 2 by m should indicate you that this is associated with the trigonal or the rhombohedral structure for which you will appropriately use the unit cells.

Student: In case of the cubic, It is 4 by m, 4 by m and 4 by m~~(())(35:22)~~

(Refer Slide Time: 35:41)



Professor: It is not 4 by m 4 by m 4 by m, no. There are other symmetry elements that you need to be showing. So, if it is 4 by m there is a little bit of group theory that we man need to understand so if you say the space group is 4 over m, 4 over m, 4 over m there are several symmetry elements are actually present in this, in this particular space group, which I need to introduce you to before we actually talk about it in length. I will give you a simple example may be at the end of the class.

Now, this group 4 by m, 4 by m, 4 by m consist of probably symmetry elements 4 over m, mm, now what would this mean? It would mean a crystal w~~id~~th with tetragonal unit cell. So, we are trying to represent the symmetry of so we know the crystal structure we you it is symmetry and we are trying to represented it represented using the Hermann Mauguin symbol and then read that symbol to construct it on the computer that is our goal, our goal is not to given an arbitrary crystal, classify its ~~state~~ space group that is not our goal, that goal is a little bit more complicated.

This is a simpler goal we have given the Hermann-Mauguin symbol how can we construct it on a computer? So, the second you see 4 over m and some 3 bar the second that immediately should strike to you that it is associated with the cubic unit cell, you can use a cubic unit cell to actually construct it.

Student: ~~(())(37:07)~~ Previously you have said that 4 by m means the cubic … Unless you will not give 3 bar after 4 by m ….

Professor: Yes, absolutely that is why I said we are not classifying a crystal after it is given to you, I am not giving you a crystal and asking you to classify it, I am asking you see what is appearing you and after that 4 by m to recognize that it is a cubic material otherwise given just a crystal and asking you to in index it is probably a not very easy thing to do or at least I do not know how to do it but this sort of understanding is useful when you want to generate this crystal structure for performing simulations on the computer that is the objective.