Symmetry and Structure in the Solid State
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Lecture – 13
Point Group and Crystal Systems 2

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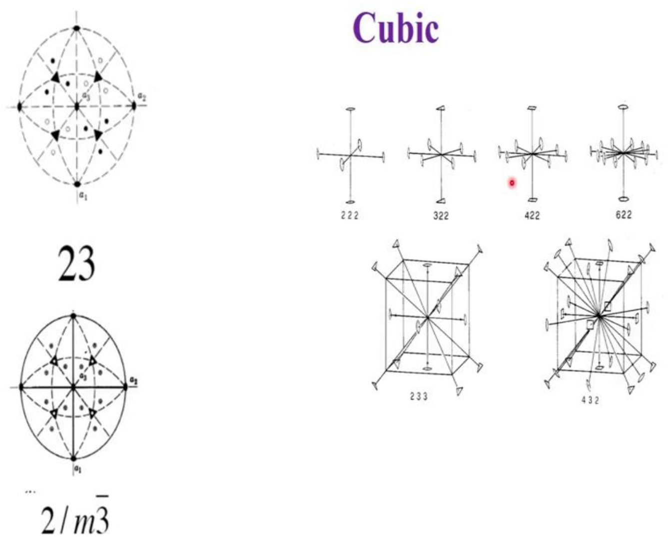

Because now the threefold symmetry is not along a given axis, but the threefold symmetry you see here is along the diagonal and this you must bear in mind because when you talk about the point group symmetries, you will have to worry about this. Now let us come back to the Trigonal symmetry which we were discussing.

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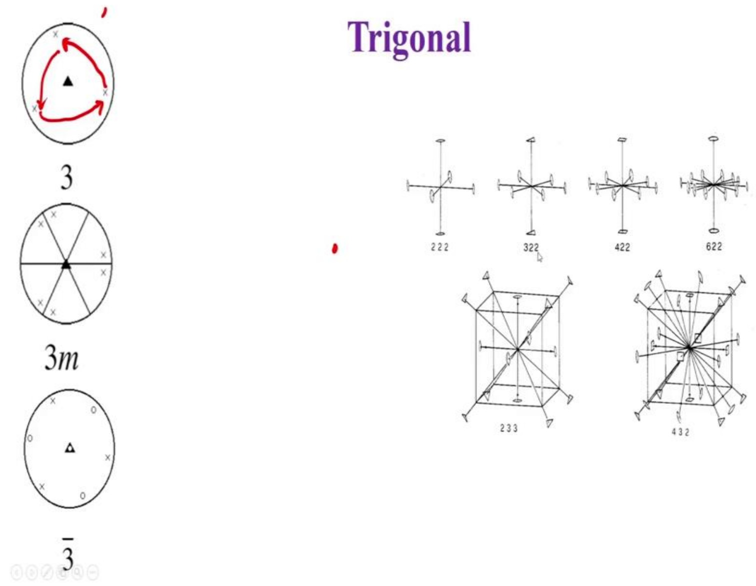

So, the Trigonal symmetry have therefore must have is represented with the z direction to have the threefold symmetry. So, the other two symmetries which can occur in this particular case are either along this given x direction or along the 120 degree angles because there is a threefold symmetry. The threefold symmetry can take this point to that point to that point and also, it can take this point to that point on that point. So, 120 degree rotations on either side with a twofold symmetry will be representing the 322 symmetry for example.

So, what we consider here is only the 3 symmetry. So, that means there is no symmetry associated with x and y directions. Now, how will you represent a trigonal system, in terms of the *a b c* ? The trigonal system is represented in terms of *a b c*, It is actually a similar representation to the hexagonal system and the values of *a b* and *c* and alpha beta gamma will be represented slightly differently and how differently it is represented, we will discuss later when we go to the discussion on the crystal system, the bravais latices and the assignment of the space group.

So, at this moment we just consider the operation of a threefold symmetry on an object. The object now is representing threefold symmetry. So, that means the object is located here represented here. It rotates by 120 degrees. No I am on the wrong one. This object rotates by 120 degrees and again rotates by 120 and again rotates by 120 and comes back to the same position and therefore, this is a point group symmetry 3. There are no additional symmetry elements. So, there are 3 equivalent points here and in this particular situation, there is no special position either because we do not invoke any possibility of a special position. On the other hand if we have a 3 system as it is shown here where which will see that this point which is xyz now rotates by 120 degrees goes to that point and rotates again by 120 degrees and comes to this point.

The second symmetry that is operating is an improper symmetry. So, when the first is a proper symmetry, the second one is an improper symmetry. What should be the third one? The third one should be also either a proper or an improper rotation, so which is the one which is possible. So, if there is a proper rotation and then an improper rotation, the third one has to be improper. So, that means that is also a mirror symmetry in the 3rd direction. So, these 2 twofold axis which are shown here in 322 case now will become 3*mm*. In fact, it is 3*mm* we write it as 3*m* for simple purposes because we know that the other mirror will automatically appear. There is no possibility of any other symmetry to appear other than the mirror symmetry and that is why you see that each one of them is related by a mirror symmetry. So, we generate 6 equivalent points.

Now, what happens to if the object is sitting on a mirror in any of these positions? Then the object will mirror reflect onto itself and therefore, there is a possibility of special positions which can come in this particular point group symmetry. The next symmetry is the operation where we have a threefold symmetry followed by an inversion. So, there is an inversion which is associated with the threefold symmetry and both of them are along the same axis. That means, this is the axis which is 3. Now, it becomes $\bar{3}$ it carries the inversion operation along with it and there for it again generates 6 equivalent positions in the projection diagram, in the stereographic projection. The threefold symmetry will generate these 3 axis and then, the corresponding inversions occur and so, we generate these 3 open circles. So, if this is x y z will you get an $\bar{x}$ $\bar{y}$ z bar in a $\bar{3}$ symmetry, this could be taken as an assignment. In fact, probably it will appear in the assignment sheet.

So, what is 3 bar? 3 bar is different from 2 bar. See in case of a $\bar{2}$, we have a twofold rotation followed by an inversion and the two fold it is not even followed by an inversion the two fold itself inverts. The option for the two fold itself to inwards is given because it is 180 degree rotation. In a threefold symmetry, we have 120 degree rotation. So, the inversion about 120 degrees itself is not activated if you have a 3 followed by $\bar{1}$. $\bar{1}$ can take only x y z to $\bar{x}$ $\bar{y}$ $\bar{z}$. So, if this is at one-third position, then going to minus one-third and minus two-third is not going to put them on top of each other. So, $\bar{2}$ degenerates to mirror where as $\bar{3}$ will be actually an operation 3 followed by 1 bar. So, 3 followed by $\bar{1}$ is not going to generate any mirror symmetry and therefore, this becomes an independent point group and this particular point group has 6 equivalent points.

So, the trigonal system therefore is now described with respect to the possibility of having one single axis in these through 3 diagrams. In these two diagrams, 3 and $\bar{3}$, 3*m* is a situation where it can have a the presence of 2 twofold axis as is shown here or it could be two mirrors and what is shown here is the presence of 2 mirrors. So, it is a proper improper improper rotation which essentially generates again 6 equivalent points. You will see that the mirror planes are now 3 of them associated with each threefold rotation.

So, that means they are mutually perpendicular to each other, the mirror operations as we seen here. So, there is a mirror operation up here, the mirror operation there, mirror operation there instead of the twofold and therefore, you indicate all those 3 in these three dark lines, the dark lines representing the mirror operation.

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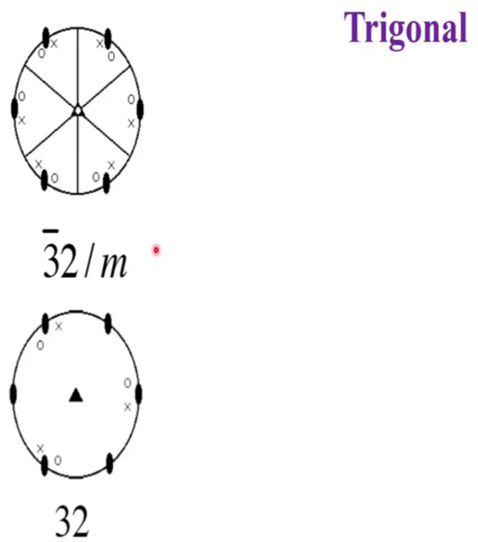

So, we will go further on the trigonal system. The next trigonal problem will come up because of the following. Let me erase this unnecessary stuff here. So, you see here two space groups which are now containing operations. What is bothering you at this moment I am sure is that where is the 3rd axis. Say you are saying there is a $\bar{3}$, you earlier said $\bar{3}$ is a threefold and a $\bar{1}$ operation and then, there is $2/m$. There must be one more operation.

Now, the $2/m$ operation is also a center of symmetric operation. $2/m$ by itself is a center of symmetric operation. Now, that centre of symmetry comes up there. So, you have a threefold along with that a center of symmetry. So, the presence of the three fold and the centre of symmetry takes this, this particular fellow well it rotates. Let us take this one it rotates by 120, again 270 and then, comes back that is the threefold and the corresponding inversion axis will take them to these open circles, they are also related to each other by an inversion. So, therefore, we have $\bar{3}$ and 2m generated automatically.

So, what would be you think would be the next direction? So, you have 3 directions in a hexagonal system. Let me go back to the previous slide. In this slide you see that we have a threefold rotation and then, you have two fold rotation axis which are at 120 degrees to each other and they are intersecting with each other at this center here. The threefold rotation is the one which has generated these axis and then, we can associate with these axis either we can associate a rotation axis or just leave it ourselves. If we leave it to our self such we get the threefold rotation or the $\bar{3}$ rotation.

If we do not leave it our self such we can have option of a twofold and a twofold which means we have two proper axis. Now, if you have two proper axis under three fold rotation, is it possible to have a space group? Sorry is it possible to have a point group ? That is possible here in the one which is shown below. So, this shows three fold along the z direction, two fold in a direction which is x and that is enough because the 3rd direction will automatically get defined and that 3rd direction will have to be a proper axis and in this particular case this has to be an improper axis. So, you will have effectively a mirror here and a twofold here. And in order to represent that in a simpler manner, the accepted representation of point group symmetries are 3 bar $2m$ and 32.

So, here in fact the full symmetry associated with this will be $\bar{3}$, $2/m$ and m and in this case it is 322. So, the moment you have a combination of a proper and improper axis, the 3rd axis will be automatically improper whereas, if you have two proper axis and one remaining improper is not possible and therefore, you will have proper axis. So, it will be 322 and $\bar{3}$, $2mm$. Those are the actual representation of full symmetry and that is not necessary to describe. So, we just say it is $\bar{3}2/m$ and in this case it is 32. So, these two trigonal systems therefore now we will define a set of equivalent points. In this particular case, you see 1 2 3 4 5 6 7 8 9 10.

So, there are 10 equivalent points and this is interesting because what will happen when it is put in three dimensional lattice? In other words what will happen to this point group symmetry when we describe it with respect to your lattice? This question you keep thinking about we will discuss it when we describe the space group associated with the trigonal symmetries. Trigonal symmetry therefore is always a very interesting system and not many molecules go into this trigonal symmetry and if they do go into the trigonal symmetry, there will be some very interesting properties which will develop. So, we will just keep that in mind and we go further to the Tetragonal system.

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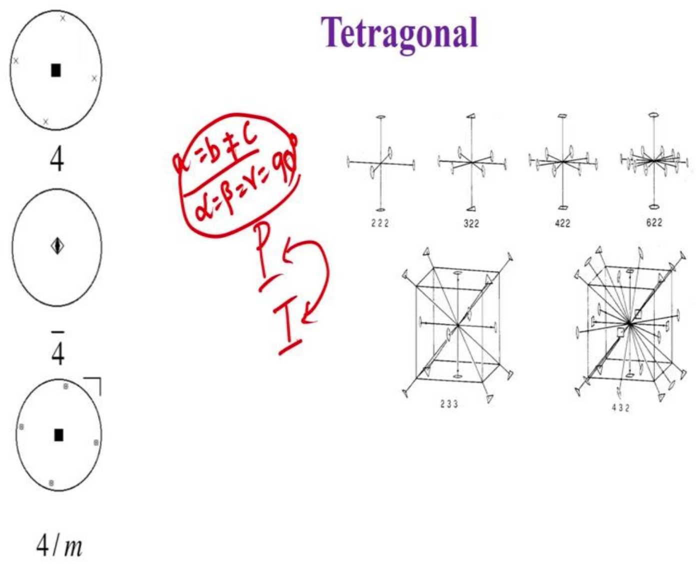

Tetragonal system is a little simpler system than the trigonal system from the point of view of understanding. So, we will make an attempt to understand the tetragonal system. What do we how do we define a tetragonal system? We define a tetragonal system the following way. We say that in a tetragonal system *a* is equal to *b* not equal to *c* alpha beta and gamma are at 90 degrees. So, a know *a* equals *b* not equal to *c*. So, it is the *c* direction again which is unique just like in the trigonal system the threefold symmetry was the unique axis, the fourfold symmetry is the unique axis for this system and therefore, you see that if you have just the presence of a fourfold symmetry and no other symmetry intersecting with each other, then you have a fourfold symmetry which will generate four equivalent points.

These equivalent points get generated at 90 degrees with respect to each other. What is important to notice here is that since *a* is equal to *b*, they are degenerate. So, you can call *a* as *b* or *b* as a, it does not matter because a equals *b* defines a square planar lattice and that square planar lattice will be associated with 90 degree angle at so happens that the c direction which is now coming perpendicular to this square lattice, the value of the *c* will now decide that it is going away from a cube because in the case of a cube *a* equals *b* equals *c*.

So, now this c lattice the presence of *c* which is different from *a* and *b* tells us that we take a cube and pull it out, it is a stretched cube in the direction of the z axis that is what is shown here. You see that the fourfold is stretching out away from their axis. So, this is the point of intersection.

So, at the point of intersection we can still invoke the presence of other axis, but the point group symmetry can exist as itself as 4 and therefore, we can invoke $\bar{4}$ which is associated with a center of symmetry. Now, what do you think are the equivalent points in $\bar{4}$? I have left this equivalent point positions unattended or unmarked. So, these equivalent points therefore will now bring in a separate concept altogether.

So, I want you to take it as a home as assignment and mark the equivalent points for $\bar{4}$. 4/*m* symmetry which is simultaneous existence of 4 along with a mirror will create a center of symmetry. These two are non-center symmetric. There is no centre of symmetry that is involved in this. These are non-center symmetry and therefore, you have now 1 2 3 4 and the corresponding fourfold rotation as well as the mirror symmetry.

In fact, this so you will have 8 equivalent points here. You have 4 equivalent points. Therefore, 4 equivalent points here and 8 equivalent points there, so what it means is that if we take the value of z the value of z now varies considerably. So, if you have a molecule which can be put into a tetragonal system, obviously the presence of the four-fold system will invoke the presence of more than one molecule and in fact, it will be more than one.

In fact, it is 4 or 8 or even higher. So, depending upon the nature of the crystal system, therefore the molecules which will now go into these higher symmetry systems this can be considered a higher symmetry crystal system. The number of molecules can increase, but what is interesting to remember and note it is just a note at this particular point is that when we are now dealing with the trigonal systems as I already mentioned most of the tetragonal systems are inorganic rather than organic and the reason is that the tetragonal system now can accommodate and invoke the presence of the presence of the possibility of 90 rotation.

So, the molecule therefore can go 90 degrees, another 90 degrees and further 90 degrees before it can come and overlap. So, the symmetry like the trigonal, the tetrahedral and octahedral geometries are most suited for molecules to go into the tetragonal system. So, if the system does not go into a cubic system, the inorganic systems prefer the tetragonal symmetry. So, if you look into literature you will see a very large number of tetragonal systems which take the octahedral tetrahedral molecules into them and that is something which we should note because tetragonal symmetry occurs very often in inorganic systems.

So, the presence of the fourfold, the $\bar{4}$ symmetry and $4/m$ symmetry the point group symmetries are shown here, the equivalent points are generated and as I said the assignment will be for you to generate the equivalent points of $\bar{4}$. Apart from that since *a* is equal to *b* and not equal to *c*, the number of types of lattices as a consequence will reduce. It will be now only a primitive lattice and body centered lattice.

Only these two are possible in a tetragonal symmetry. We are going to prove this later on in when we discuss the possible bravia lattices that can be associated with crystal systems. Even though we have listed it out in the previous classes, the detailed analysis of why only P and I are possible will be done in the coming classes.

So, please notice that as far as the tetragonal system is concerned, there is no question of having F centered lattice or A B C centered lattice because of the fact that the geometry sort of forbids any other lattice that can exist other than primitive and I centered lattice. So, the number of space groups associated with the tetragonal as a consequence will reduce to that extent. However, the number of point groups that are associated with the fourfold system increase and so, we get a very large number of systems that are possible.

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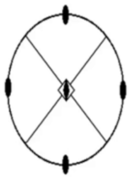
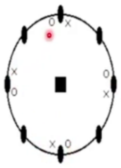
Tetragonal



$\bar{4}2m$



422

So, for example in this particular illustration you see that we have now the possibility of the fourfold rotation along with the possible perpendicular rotations associated with the fourfold rotation. That means, the fourfold rotation can go 90 degree, 90 degree and another 90 degree. So, the total number of possible symmetry elements are indicated here.

So, 4 can go with a twofold as well as a twofold. That means, 4 can go with a mirror and a mirror. So, we have to consider all combinations of proper improper and proper proper axis combinations and so, we get additional point group symmetries which is $\bar{4}2m$ and 422. Again in this particular case we have illustrated the equivalent point positions of the 422.

You see that this is the fourfold position and this fourfold position will generate 4 of these equivalent points and with the operation of the twofold which is now associated in a direction of 90 degrees with respect to each other. As you see that there is an axis which will go like that which is a twofold axis the perpendicular axis like this and then, two diagonal twofold axis which can go with the fourfold symmetry. Let me show it again clearly. You have an axis going like that and axis coming like that and both these are twofold axis. Perpendicular to that are the two axis which go along the diagonals, this is the twofold axis and that is the twofold axis.

So, because of that we will end up with the 8 equivalent points that are associated with 422. $\bar{4}2m$ now, we will have additional mirror symmetries which now go along the diagonal. We have the fourfold symmetry and then, we in addition we also have the twofold symmetry which will get embedded with respect to this.

So, the last *m* is actually 2/*m*. So, we will also have a twofold symmetry at the centre of it. So, tetragonal systems therefore are defined with respect to the presence of the fourfold axis on the various possible twofold symmetries that can be associated with the fourfold axis. The fourfold axis again in general is representing along considered along the z axis just like the trigonal axis where we consider the three fold along the z axis.

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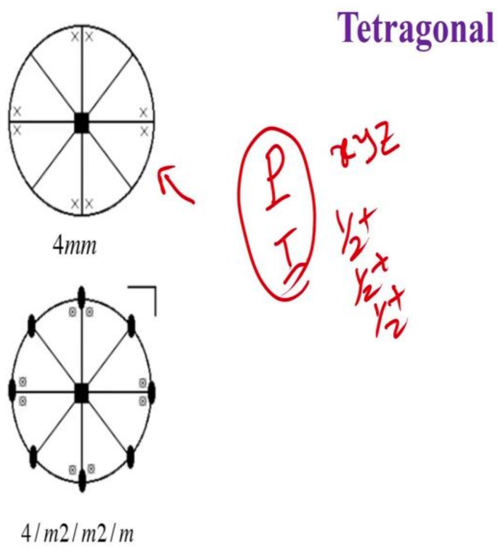

The same story goes with the hexagonal lattice as well which is 622, we will go to the hexagonal system now after showing the remaining part of the fourfold rotation.

So, we can have the 4, for this 4*mm* is there and we also have the 4/*m* 2/*m* 2/m. Both these systems point group systems will generate in one case it is 8 equivalent points, in the other case 16 equivalent points. Along with the possibility of these now going into more than one type of lattice that means, they can go both into the primitive lattice as well as let me write it down it can go into the primitive lattice as well as I centered lattice. So, the moment we have I centered lattice for every x y z every coordinates which we generate, of course every equivalent point which gets generated by the P lattice operation, you have to add half plus along x half plus along y and half plus along z.

So, for every x y z we have to add half plus, half plus, half plus in order to take it to the I center. So, if there are 8 equivalent points in this 4 mm and if we now take it to the I system where the I centering is introduced, you will have another 8 additional equivalent points and therefore, there will be 16 equivalent points. What it essentially means is that you as I mentioned already you can pack 16 molecules, but what is also interesting at the same time is that when we really crystallized the inorganic systems particularly because of the presence of the tetragonal symmetry and the octahedral symmetry, these symmetry elements can adjust themselves across the fourfold symmetry.

And because they adjust across the fourfold symmetry, the number of molecules will reduce considerably. In other words, the molecules are the molecules which go into these kind of systems generally utilize the fourfold special positions. The special positions which are offered in these crystal systems will be utilized and as a consequence the number of molecules in the unit cell will anyway reduce. So, as we go to higher crystal systems as I mentioned already, already the number of equivalent points will increase. In fact, when we go to the cubic system, there will be 192 equivalent points, but when you crystallize systems into these only highly symmetric systems crystallize.

And that is the reason why organics prefer only the triclinic, monoclinic and orthorhombic systems and here the inorganic systems tend to crystallize. And therefore, if you things of the recent organic, inorganic, hybrids for example. The hybrid structures can go into higher symmetry space groups because they maintain the inorganic symmetry, inorganic crystal symmetry intact and then incorporate the organic molecules, so that the organic molecules now are forced to obey these symmetries and therefore, the property of the organic crystal system therefore can be controlled and this is how the you know metal organic frameworks structures and the covalent organic framework structure is and so on the and all that are becoming more and more exciting.

Because they have a highly, they are put in a highly symmetric atmosphere and therefore, they are constrained in their conformational flexibility. As a consequence some special reactions can be carried out inside these moieties and that is how these compounds become extremely important.

This is just a side point I thought I will mention.

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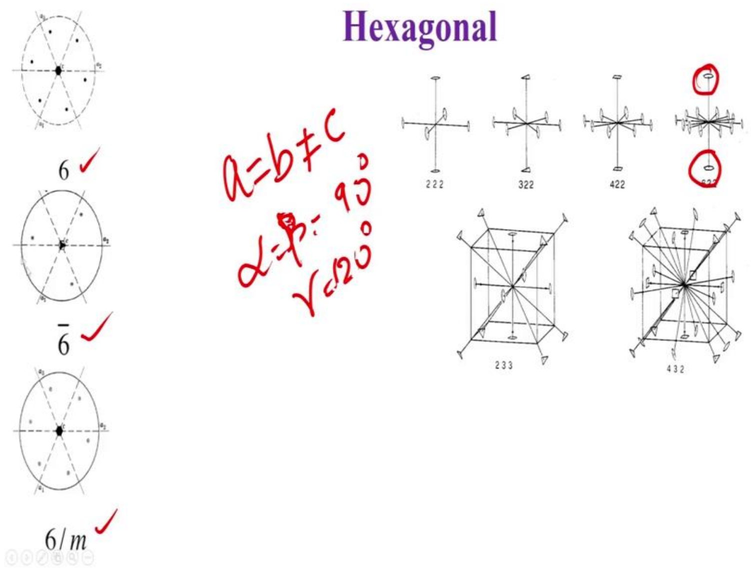

Now, we will go to the hexagonal system. Again in the hexagonal system you see that the sixfold symmetry is now perpendicular to that direction. In fact, this is a six fold symmetry, it looks like a twofold in this diagram, but it is a six fold symmetry and six fold by itself can exist just like the threefold and the fourfold. So, we get the $\bar{6}$ and 6/*m* and in this particular case the equivalent points appear at 60 degree rotations because it is a hexagonal symmetry and in fact, the value of *a b* and *c* will be a equals b not equal to *c* alpha equals bet,. and gamma is 120 degree. So, this kind of a relationship exists for a hexagonal system and we have there for 6 points which will be generated by a six fold symmetry. $\bar{6}$ bar generates you see also 6 points one above and one below each other because do you see here there is a six fold and then, a threefold incorporated into that.

This is what I discussed when I actually initially talked about the 32 point groups symmetries I told you to find out the difference between the 6 bar symmetry and the $\bar{3}$ symmetry. The $\bar{3}$ symmetry has 6 possibilities. Here also there are 6 possibilities, but in the 6 bar symmetry because of the higher symmetry nature associated with a 60 degree rotation in the case of the 3 bar threefold rotation, it is a 120 degree rotation. You will generate 6 points there whereas; here you will generate the six 3 points up and 3 points down. Effectively again here the 6 points are generated, but their 1 on top and 1 on the bottom. The 6/*m* symmetry generates again a mirror symmetry which is now attached along with this and you now see apart because of the fact that there is a mirror symmetry which is perpendicular to the six fold symmetry, you will get now 6 equivalent points and 6 below.

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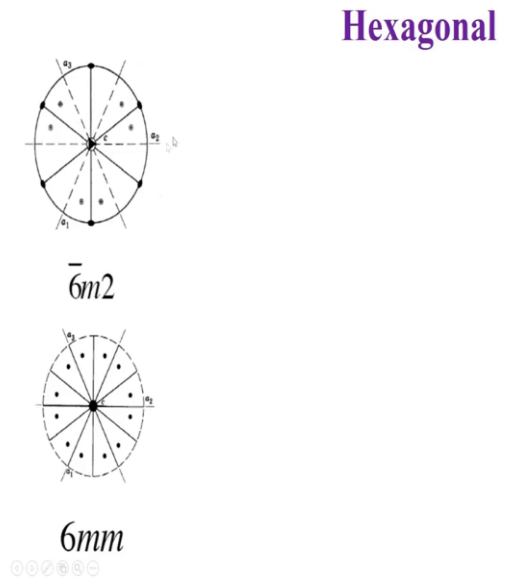

So, the hexagonal symmetry therefore is again representable in terms of the other intersecting axis. So, we have additional point group symmetries $\bar{6}m2$, $6mm$ and the equivalent points are marked here.

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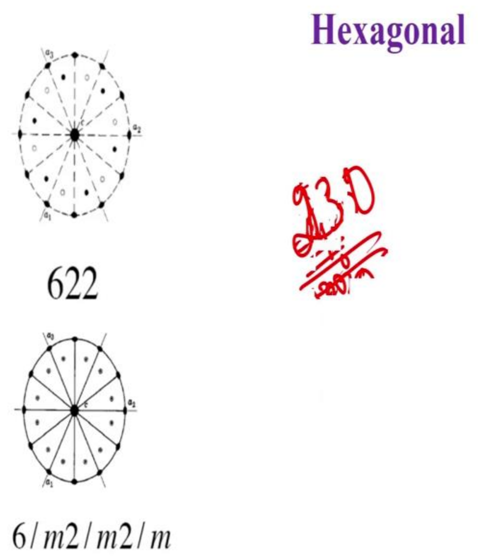

Then we are three additionally have 622, $6/m$ $2/m$ $2/m$. This is the highest symmetry that can be taken up by a hexagonal system. What happens to the hexagonal symmetry with respect to the lattice? It has only one type of lattice in fact, that is a primitive lattice. So, we only have a primitive lattice and the presence of the primitive lattice therefore is only invoked in a hexagonal system.

There is no other possibility and so, even though the number of point groups as we discussed in case of the tetragonal system are more, the number of lattices we can generate with hexagonal symmetry are less. And this now is coming is he going to help out to find out why only 230 space groups exists. So, we have only primitive lattice in the hexagonal system and as I was telling you that there are 230 space groups as a consequence. So, the number of space groups are limited to 230 and I do not know whether it develops some static or something.

So, the six fold symmetry is therefore get define the presence of the six fold symmetry. It now generates these many point group symmetry 6, $\bar{6}$, 6/*m*, $\bar{6}$*m*2 6*mm*, 622 and 6/*m* 2/*m* 2/*m*.