Symmetry and Structure in the Solid State
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Lecture – 16
Additional Symmetry Elements

So, the presence of glides and screw axes in other crystal systems can occur. We have the trigonal axis; we have the tetragonal axis and then the hexagonal axis. So, these three axes correspondingly can have the screw translations symmetry.

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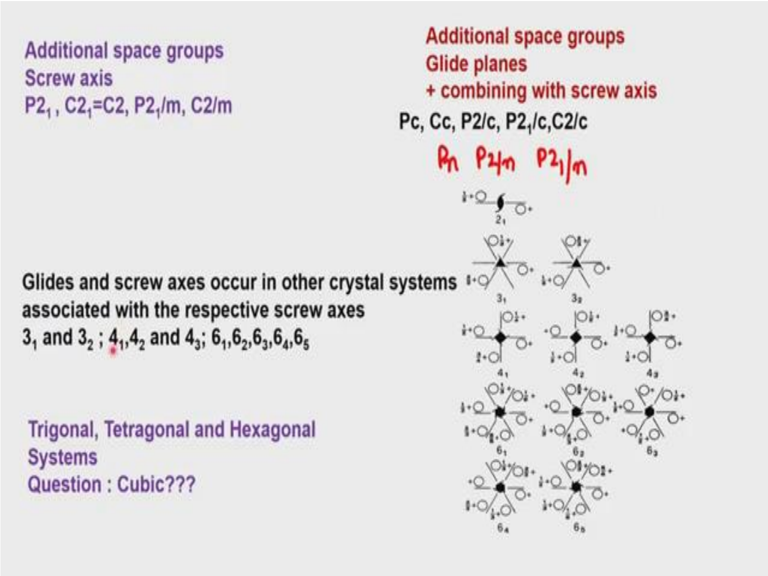

So, the screw translations can be one-third, two-third with respect to 3 fold axes, 1/4, 2/4 and 3/4 with respect to the 4 fold axes and so on. So, that means the trigonal tetragonal and hexagonal systems we will also have the presence of glide planes and screw axes that is shown here the screw axes are shown here. And the corresponding symmetry informations which we have discussed before as well are appearing here.

Now, as I said in the last part a few minutes ago we have to see what happens with the cubic system I already gave a hint that it could be along the 3 fold direction. So, we could have the cubic symmetry, but then I was discussing about the hierarchy of operations. The hierarchy of operations comes in such a way that we talk about the nature of the latice first and then we talk about the presence of the screw axes on the glide planes.

This will have a very important repercussion when we see the x-ray diffraction patterns, because the x-ray diffraction patterns we analyze with respect to the various values we see from the presence of these reflections. And the presence or absence of these reflections is governed by the way in which this space group develops. And therefore, some of these elements the presence of the C centering, the presence of the I centering we will introduce what are known as systematic absences.

And so, also the presence of the 2_1 screw axes on the mirror on the glide planes, but the screw axes on the glide planes we will affect only the so called projection reflections whereas, the general reflections are affected by the centering operation. And that is why the priority is given to the lattice type and then the 2 fold and the translation involved symmetries like 2_1 and *n* and so on, right.

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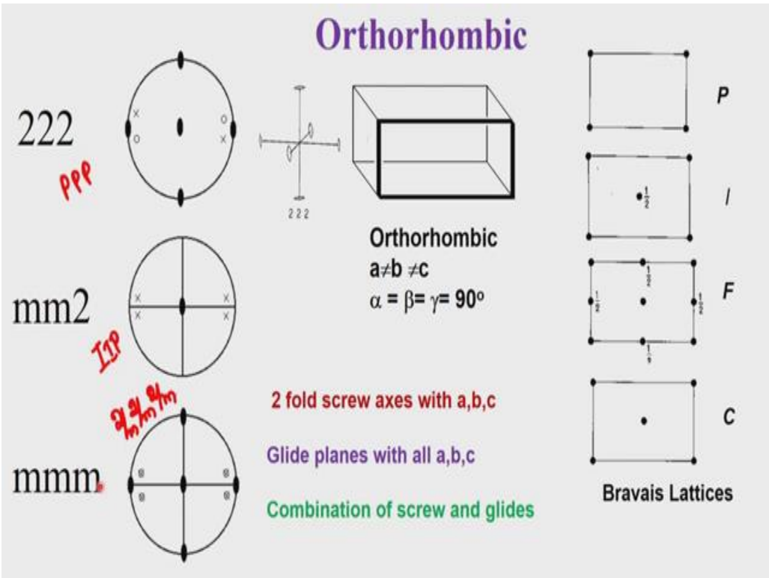

We go to the next slide where we in shift the system now to orthorhombic. Orthorhombic is more or less a expansion of a monoclinic discussion we had so far to three dimensions. This is very straight forward, because in case of the monoclinic system we have a single 2 fold axes whereas, in case of the orthorhombic symmetry. We have three 2 fold axes intersecting at a point, and these three 2 fold axes come at 90 degrees with respect to each other.

So, because of the fact that whenever there is a 2 fold axes two of the angles should be 90 degrees. If there is another 2 fold axes perpendicular to the given 2 fold axes, the other two angles will be 90 degrees the consequence of which is all 3 angles should be 90 degrees and that is what happens here α, β, γ are equal to 90 degrees. So, a ≠ b ≠ c, α, β, γ are 90 degrees defines the so called orthorhombic system.

The way in which these three 2 fold axes are disposed with respect to each other is illustrated here, as you can see this is the intersection point, so you have along the x direction, you have along the y direction, you also have it along the z direction. The minimum symmetry therefore, is 222 and that is the point group symmetry 222 which is described here. So, we have a 2 fold axes associated with direction coming towards us and as a consequence we have a 2 fold axes in plane and there are two 2 fold axes intersecting with each other in plane and therefore, this would be the illustration of that.

So, you also have this circle a little darker than necessary to show the 2 fold, 2 fold, 2 fold there are three 2 fold intersections. So, suppose there is an object here it sees the 2 fold up here and goes over to that. And after having gone to that position it sees the presence of the 2 fold, but then this 2 fold is in the back side of it which is at an angle of 90 degrees with respect to that and as a result it goes over to this position. And this now since the 2 fold here and comes back to this position and vice versa. So, it keeps therefore, 4 equivalent points and those 4 equivalent points now you are experts you can write them down yourselves the 4 equivalent points were 222.

You can also write the equivalent points for the next set of symmetry elements because we have been discussing this issue many times already, so maybe I should just write ones to remind you what we are talking about. So, here this now represents a PPP axis; here it represents a II sorry not primitive proper; proper; proper rotation axis improper; improper correction; it is not primitive proper, proper, proper rotation axis improper, improper, proper rotation axis and then the last one which is improper, improper, proper. A combination of three *mmm* will represent the 3.

Now, how does *mmm* come about? Mmm comes not about 3 improper rotations because we already showed by Euler’s theorem that 3 improper rotations will not go in conjugation. So, mmm therefore, is not *mmm*, but it is actually 2/*m* 2/*m* 2/*m* So, it is a combination of a proper and an improper rotation that is the point group which is which we have discussed before. So, instead of writing 2/*m* 2/*m* 2/*m* consistently we can just make it simplified to *mmm*. So, please note that *mmm* did not come from 3 improper rotations combining with each other than you would be violating the Euler's theorem. So, therefore, it is $2/m\ 2/m\ 2/m$.

So, whenever you see more than 3 mirror combinations coming, like for example, later you will see in the tetragonal system $4/mmm$, it actually means it is $4/m\ 2/m\ 2/m$. So, if you remember that carefully in fact, it is a part and parcel of your understanding this whole course then you will never make a mistake ok.

So, 3 proper rotations 222, now will take us to the point group symmetry 222 and now we have to see how many lattices which we have to consider combining 222 with. In the case of the orthorhombic system we have all possibilities, we have the primitive one, we have the body centered one where we have at the center of the body half position. So, please count the number of lattice points for every one of these systems. In case of the primitive system it is 1, in case of the body center it is 2. What happens in case of the F center? The in case of the F center we have 1 2 3 4 and then two half ones 5 and two half ones 6. So, totally how many are there? 1 corresponding to the edges and 2 more corresponding to the centering with respect center of these axis and 1 at the center. So, totally it will be 4.

So, the number of lattice points for a F centered orthorhombic lattice will be 4 and of course, we can have A or B or C separately centered like in the a monatomic system and then we will have therefore, the C centering. So, C centering means also it could be a centered it could be B centered because it just depends upon how you define the values of a, b and c. You see in the case of an orthorhombic system you can always interchange a, b and c. So, when you interchange a, b and c the correspondingly the A centering, B centering, C centering will change. So, they are one and the same. So, therefore, we have 4 types of lattices with which we have to combine the 3 point groups. So, 4 lattices 3 point groups with no translational symmetry associated with them.

And therefore, you have generating system like $P222$, $Pmm2$, $Pmmm$. So, these are the 3 crystal systems which you can generate with P. With I again you can generate these three, with F again you can generate these three and with C centering also you can generate these three and you can keep on doing that. So, you see the number of space groups will increase considerably now. We had something like 17 space groups or so on till now it is adding up considerable number.

So, orthorhombic in fact, is one of those systems which has the highest number of possible space groups because it has the combinations of *P*, *I* centered lattices, *F* centered lattices as well as *A* or *B* or *C* centered lattices. So, the possibility of a molecule to crystallize in orthorhombic symmetry must be the maximum and so the possibility of the occurrence of orthorhombic symmetry in overall crystal systems if one analyzes the database organic orthorhombic systems are many more compared to the rest of the crystal systems. It does not mean that orthorhombic is the preferred crystal system. It so happens that it allows for several possible space groups. This is the point which you should remember.

So, point group symmetry as well as the lattice symmetry combinations therefore, give us the space group that you are very clear now. Now, we also have possibilities of 2 fold screw axes. The 2 fold screw axes now is the with respect to a with respect to b with respect to c and therefore, we have glide planes with respect to all of *a b c*. We can also have combinations of screw axes and glides. So, you see now that is the 3 proper axes can take for example, screw axes.

So that means, we can have a space group like $P2_122$, $P2_12_12$. We can also have a space group like $P2_12_12_1$, in fact, all 3 are possible and it depends upon how the molecule decides to pack itself inside the unit self. So, we can therefore, invoke the in insertion of the 2 fold screw axes by getting space groups $P2_122$, $P2_12_12$ and $P2_12_12_1$. $P2_12_12_1$ is the most favorite space group for organic molecules particularly if they carry an asymmetric carbon and that is because it allows for the maximum flexibility in the system.

When we study the space groups in detail we will derive those equivalent points. What are the equivalent points that can come for the $P2_12_12_1$ and see what I mean by that. You remember this class and then we will discuss $P2_12_12_1$ when we discuss this space group I will make clear why there is so much adjustment space available for rather flexible functional organic functional molecules organic molecules.

Glide planes; glide planes again you know we can have with the primitive lattice. We have three 2 fold axes perpendicular to each other. So, we can have all 3 glides *a, b* and *c.* So, we can have combinations of the 2 fold axes with the glides like *P*2*ab* and things like that. We can also have all glide combinations like *Pnab* or *Pbca* and so on. So, you see the number of possible space groups we can generate in a case of an orthorhombic system increases enormously.

And so, this is I am talking only with respect to the primitive lattice, we can go to the *I* centered lattice, we can go to the *F* centered lattice, we can go to the *C* centered lattice. For example, we can have a space group like *C*2*ab*. So, we may all these space groups now become possible and now you see the flexibility that is available in the solid state.

Until now we were talking about the restrictions available in the solids. We were talking about the fact that translational periodicity locks the molecules into their respective positions, but now the way in which the space groups can manifest themselves as we go further into the higher symmetry space groups starting from triclinic monoclinic and now in orthorhombic we see there is a now considerable amount of flexibility. So, the molecules are very happy now, because the molecules now can crystallize into their choice space groups.

In fact, the molecules can have more than one choice space group and that is where the issue of polymorphism comes. And this is an issue which is a big issue for pharma industries; we will discuss that towards the last few classes. Now, the combination of the screw and glide also is very critical, which screw can combine with which glide plane. Of course, we have to keep our Euler theorem in in mind because we cannot have different kinds of combinations which we will give rise to the IIP for example is a possibility, but anything beyond that is not a possibility and therefore, we have to therefore, have something like *Pmm*2, *Pmca* for example and things like that which will now correspond to the *mmm* point group symmetry.

Pmca is *mmm* point group symmetry which means it corresponds to 2/*m* 2/*m* 2/*m* and when we say *Pmca* a it will be 2/*m* 2/*c* 2/*a* ok. So, the glide planes will always invoke the presence of 222, so that is why the minimum symmetry you should have in an orthorhombic system is 222. Unless you have three 2 fold axes intersecting with each other in general you will not be able to generate orthorhombic systems. And so those are the restrictions all, right, but the flexibility is immense, so using the immense number of flexibilities the solid systems or in such systems in solid state can arrange themselves.

But there is always systematics which is associated with these arrangements and that is where we have an advantage to identify and locate the positions of the atoms in any given crystal system and in any given space group.

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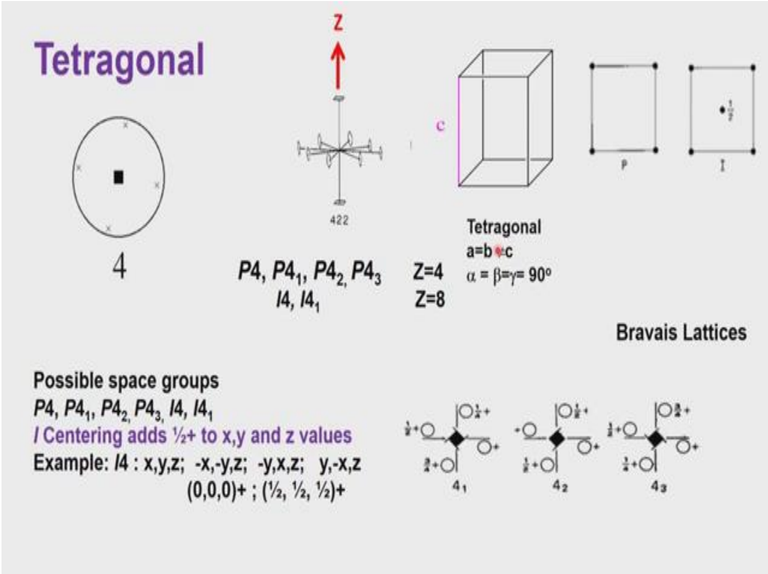

Now, comes the next set of crystal systems, we go to the tetragonal system. In the tetragonal system of course, there are several possibilities, one of them is illustrated here this you will so called 4 fold symmetry. That is also illustrated here. Remember that in a tetragonal system we have a equals b not equal to c alpha beta gamma are 90 degrees with respect to each other. The moment we have these three angles at 90 degrees to it each other we invoke automatically two intersecting 2 fold axes, in addition to the presence of the 4 fold axes.

The presence of the 4 fold axes generated will make the axes unique with respect and we fix that as the c direction. So, we fix the c direction to be the unique dire axis direction and that is why it is written here Z. So, we take this to be along the 4 fold axes and then the innumerable number of 2 fold axes can be present here. But the simplest point group we can consider is the 4 fold just the 4 fold which takes the objects into 4 different positions as a as illustrated here along with the 4 fold notation which we have in here. So, this generates 4 equivalent points.

Having generated 4 equivalent points we can also generate 4 equivalent points, if we take the combination of the 4 fold symmetry which the presence of 4_1, 4_2, 4_3. So, if you take for example, 4_1 the from this point to that point we will have a one-fourth translation added, from this to this we will have a two-fourth translation added, from this to this point we will have a three-fourth translation added.

On the other hand, if you have $P4_3$, from this point to that point we will have a three-fourth addition added this to this it will be two-fourth addition added and then in this to this will be one-fourth. So, the handedness associated with this we will change, in one case it is going this way this screw axes in the other case it goes rather way. So, this screw axes operations $P4_1$ and $P4_3$ are opposite of each other. If you consider $P4_2$ it is equivalent of if equivalent of a 2_1 screw axes effectively. So, it is just a single operation it is dichotomy in that particular case whereas, in case of 4_1 and 4_3 they go on opposite directions the screw operation.

If you look at the possible Bravais lattices associated with the tetragonal system, one can show *P* and *I* only exist which probably we will do in the form of an assignment later. But if you consider the two lattices that are allowed only *P* and *I* our load. Any other lattice like *F* for example or A B C center, because of the fact that we have a equals b as an additional condition which makes the basal plane square, the moment there is a square we cannot have it centered effectively and therefore, the centering of the phases is out.

So, whenever you have a square base you go back to your previous classes where we discussed the 5 plane symmetries, in that we had a squares symmetry the that is the little p, the primitive lattice in the in the 4 fold symmetry. There we cannot have a center because if we have a center you can generate another 4 fold there and so it is degenerate.

So, whenever you have a is equal to b you cannot have that phase centered. So, because this phase cannot be centered, that phase cannot be centered, likewise these are at 90 degrees with respect to each other. So, the 90 degree angles can also be space centered. Unless you have these 4 centered we cannot have the other two phases centered and therefore, *F* is ruled out. This is the logic which I am trying to give you. We can one can work out work it out mathematically, but I thought that logic is good enough to for our current discussion. So, we have the primitive lattice and the body centered lattice where you will have a additional lattice point at half. So, the z=1, sorry the lattice number; number of lattice points is 1 here, number of lattice points is 2 there.

Because of the fact that a is equal to b we will also not allow one single phase to be centered. So, A B and C separately being centered is also ruled out and therefore, we have only two possible lattices in the tetragonal system. So, the job now is to combine these lattices with the possible point groups the first point group is with 4, so all the possible combinations are shown here. The number of equivalent points initially is in this cases of primitive lattice is 4 whereas, in case of the body centered lattice it will be double that, so we will have z equals 8. So, as you all know that we had a half along x, half along y, half along z.

So, having seen the possible space groups here and the *I* centering is adding this we see if by an example of *I*4 is given here. Now, the type of rotation axis which we just now discussed can be described here 4_1, 4_2, 4_3, you see that exactly what I talked about 4_1 if you start, 4_3 if you start from this point that point will be three-fourth added and this point will be one-fourth added. So, rotate if you now look at the 4_3, rotation it is this way the left handed rotation and in this particular case it is the other way around this is a anticlockwise and this is the clockwise rotation.

So, 4_1 is anticlockwise, 4_3 is clockwise rotation and that is also illustrated by this combination here. 4_2 automatically generates only the half point, so there is no distinction between one direction and the other. This will be more interesting to discuss when we go to the trigonal system, but the trigonal system is an issue which we will see later if time permits we will go into it, because we have to cover a lot of other things in this course. So, we may not specially discuss that. Except that I would like when we go to the trigonal system, I will mention it of course. So, let us see what other possible point grooves that can occur with the tetragonal system, that is the next slide.

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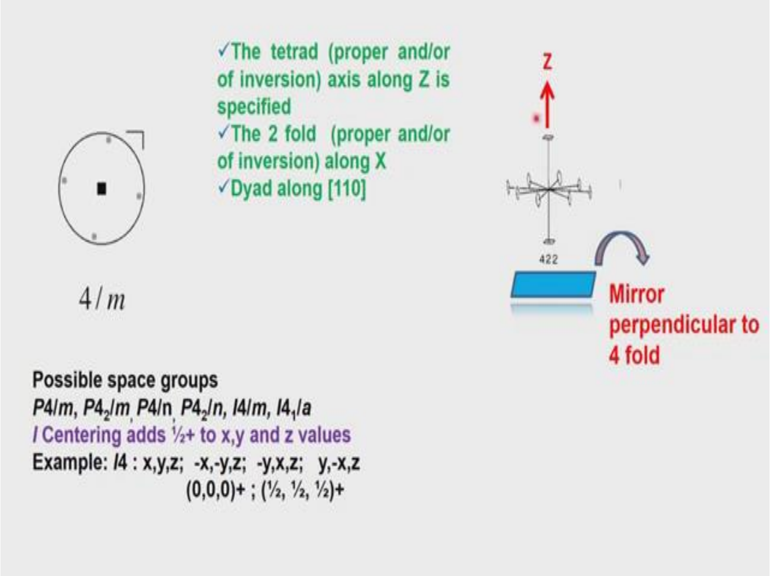

Next slide we will take us to 4/*m*. So, here it is written tetrad that essentially means a 4 fold rotation. This is from a text book where they use tetrad and dyad for a 2 fold and so this has been taken from the textbook. But we will say this is the 4 fold. The 4 fold can be proper and are of inversion that means, proper or improper axis along the z direction and that we specify it first. So, the 4 fold is rotation is along the z direction all the time, and the mirror is now going to be perpendicular to that operation. So, if you see here the mirror is indicated perpendicular to the 4 fold.

So, the presence of the 2 fold axes is immaterial its 422. So, in this particular case the system can be just 4 by m the other 2 fold axes will be automatically implied when we derive the so called equivalent points. For example, here *I*4 is shown to have x y z, $\bar{x}$ y z, $\bar{y}$ x z and y $\bar{x}$ z that will be the 4 fold operation and along with the 4 fold operation if we add half plus half plus half plus to each of x y and z we will generate 4 more points. So, there will be 8 equivalent points for *I*4.

The possible space groups with 4/*m* combination however, are $P4/m$, $P4_2/m$, $P4/n$, $P4_2/n$, $I4/m$, $I4_1/a$ and there are additional ones which you can add depending upon the nature of the rotation axis remember we can have both 4_1 4_2 and 4_3. So, what you see here is only the 4_2 ones given 4_1 and 4_3 are also possibilities. Now, when 4_1 and 4_2 are considered possibilities there is probably not a possibility of an *n* glide. So, we have to work out why only these are given and that is something which is which could probably be taken as a home work by you guys so that you can have a look at it and then see how it all depends upon.

So, there is a 2 fold axes proper or improper along the x that also see. When we describe the tetragonal system since a is equal to b, the two directions are degenerated so that means, a can be b, b can be a. And because of this degeneracy issue we is represent only one of the axis to be associated let us say with the a direction.

So, on once we associate that with the a direction the second 2 fold axes will be in a direction which is perpendicular to 110 which is along 110. See, the directions and crystal systems are normally given by 110, in fact we are going to discuss that in the coming classes or in an assignment later on. So, 110 if we show it in square brackets it represents a crystallographic direction. So, 110 is a direction which is along at one unit along a and one unit along b, so 110 therefore, is the direction about which the 2 fold axes gets a represented in this case. So, we can have $4/m$ and the possible space groups are written here and this is an illustration which shows how the mirror plane can be perpendicular to the 4 fold axes.

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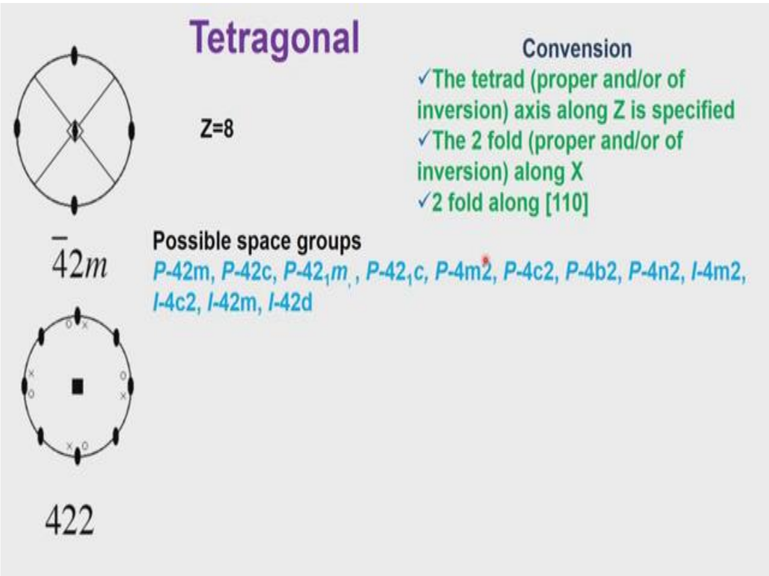

Having seen this, I think we can go to the further discussion on the $P4$ have space groups possible space groups are listed here you see many number will develop because of the presence of the 4 fold axes proper and or inversion because we can have 4 we can have $\bar{4}$ we can have 4_1 4_3 and so on 4_2 4_3.

Now, the presence of the $\bar{4}$ system is interesting because we already saw in the previous days $4/m$. We also saw 4, but we have not seen the $\bar{4}$ operation. So, the $\bar{4}$ operation will also introduced will have the possibility of proper and this is an inversion axis on the 4 fold symmetry. So that means, in the z direction we can have not just the 4 fold rotation alone we can also have the inversion associated with the 4 fold rotation. So, that generates the equivalent points accordingly.

I do not think there is enough time for us or space for the us to discuss that in this particular course how to get the equivalent points and so on. So, what we will therefore, do is we will just illustrate as a particular space group like 422 let us say. Now, this space group 422 has additional 2 fold symmetries. So, you just compare this diagram with the diagram we have here this has only one 4 fold symmetry and that is an allowed point group symmetry in a tetragonal system.

That means, there is no symmetry which is imposed in the direction perpendicular to the z-axis. So that means, the x and y even though there is the 2 fold axes is implied in them there it is not specifically mentioned because in this particular case when the mention is made of 422 you see the number of equivalent points we will increase from 4 it will go to 8 because there are additional 2 fold symmetries which occur due to the 4 fold operation.

So, this 4 fold operation we will take 4 of these 2 fold screws and the between these two screws we develop additional 2 fold screw operations. So, the number of available symmetry operations we will start increasing in fact, they will multiply. So, as a consequence you will end up with several possible space groups written like this and therefore, tetragonal has also a very large number of a space the space groups that can gen be generated.

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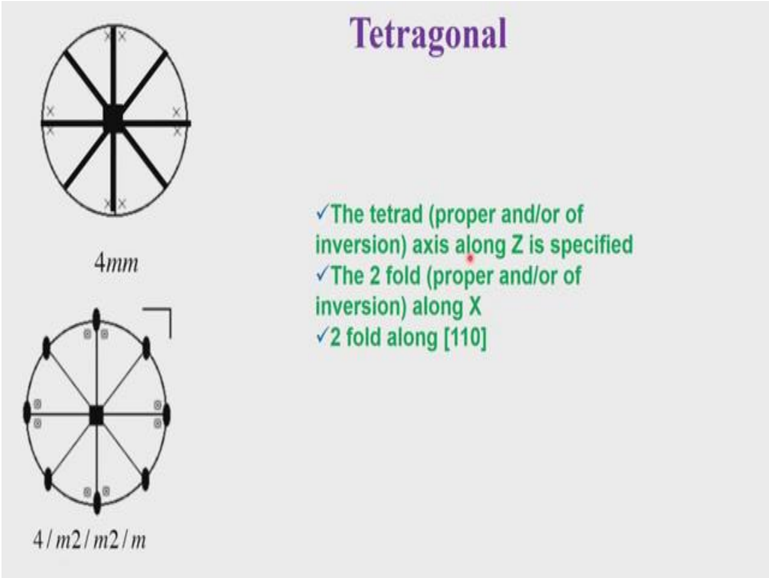

Trigonal still, tetragonal still continuous to have different kinds of symmetry combinations because we have not discussed the proper improper, improper axis associated with it. So, this is the one which I mentioned earlier 4/*m* 2/*m* 2/*m* which is it can also be written as 4/*mmm* and that is the maximum symmetry we can have in a tetragonal system.

So, the tetragonal system all therefore, has a combination of point groups which are 1 2 here, 3, 4, 5 and 6. So, there are 6 possible tetragonal combinations 4, 4/*m*, $\bar{4}2m$, 422, 4mm and 4/*m* 2/*m* 2/*m*. So, all these points groups combinations can be now combined with the possible Bravais lattices which are two *P* and *I* centered. So, therefore, we get a plethora of possible space groups which we can generate in a tetragonal system.

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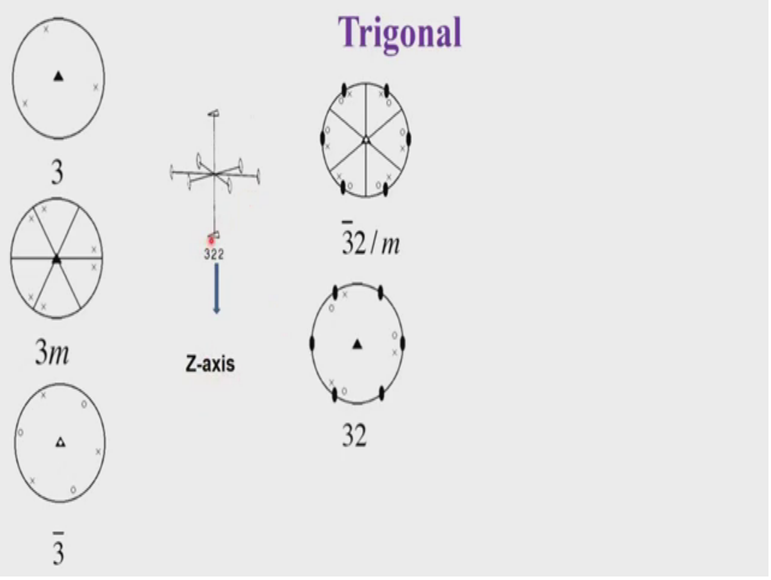

Now, we go to the issue of a trigonal system. We will discuss a little bit on the trigonal system at this point. The trigonal system is just like we have a Z-axis representation of the 4 fold we have a now a Z-axis representation of the 3 fold. So, the 3 fold now is associated with the Z-axis.

I purposely wrote this “ulta” arrow (opposite) to show that we can either have it in this direction or in that direction it is immaterial. So, it so happens that people generally write that and people think it is only along that direction we should have the 3 fold. So, I thought I will write it opposite you show that the 3 fold rotation axis can also be in the opposite direction.

So, we can therefore, have only these point two combinations we can have 3 fold which is just generating these three and then 3*m* which generates 6 of these because it is 3 followed by a mirror. Notice here it is not a $\bar{3}$m, it is 3 followed by a mirror operation. So, first we operate the 3 fold and then mirror invert it. And $\bar{3}$ operation which is again an operation which takes the 3 fold object on to an inverted 3 fold object. So, you see that there is a symmetry between the 3 open circles and a symmetry between the 3 closed circles.

So, consequently the 3 fold operations generate different kinds of equivalent points compared to the so far discussed in terms of tetragonal and orthorhombic. But what is the most important point is to consider the direction of rotation axis, so the direction of rotation axis when we refer to the point group symmetry and eventually in the space group is taken to be the z-axis. So, the z-axis representation of the presence of the 3 fold is a consequence of the presence of the lattice. So, when we say the 3 fold is along the z-axis we are already implying that there is a lattice corresponding to that. And how many lattices are possible in the trigonal symmetry? We will take it up in our next discussion.

So, at this point we can sort of conclude that the 3 fold, the 4 fold or along the z direction in case of the tetragonal and the trigonal symmetry and the tetragonal symmetry has *P* and *I* and with the *I* we will get an additional set of points added with half plus along x, half plus along y, half plug along z to every relationship which we generate in terms of equivalent points associated with the primitive lattice.

So, the other thing is we have seen in the case of the orthorhombic system is that there are three 2 fold axes perpendicular to each other. So, whatever property we associated with one axis and the monoclinic system can be associated with the other two, and there and also the possible existences of 4 types of lattices we will generate a large number of space groups. So, now if we can add up all these space groups we are going very quickly towards the 230 possible space group. We are not going to count them now, but eventually we will reach a stage where we will finish up all the 230 space groups.