X-Ray Crystallography

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Lecture – 05
Point Groups and Space Groups

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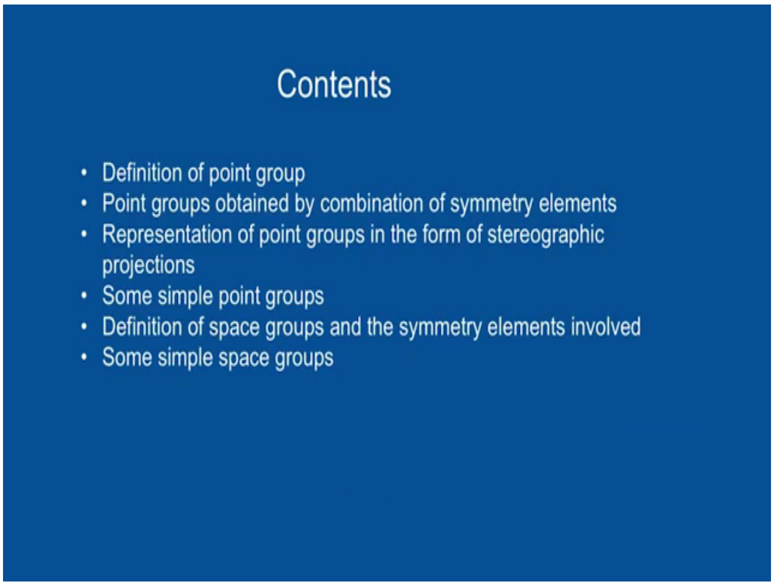

This lecture will give an idea of what point groups and space groups are in crystallography. These are two important concepts and these help us in finding out the precise locations of atoms at an around lattice points and also in the three dimensional extended crystal.

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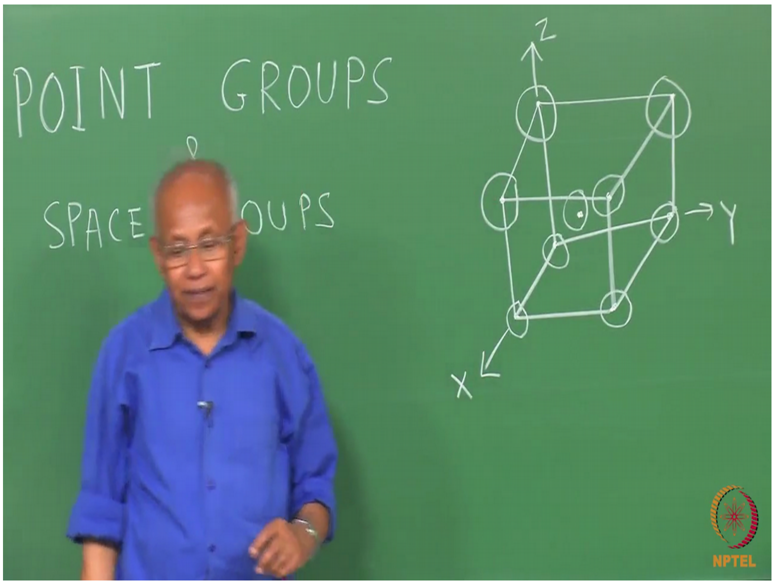

In simple metals, when we talk about a unit cell; the lattice points in the unit cell are occupied by one atom each. Say for example, if we have a crystal of pure iron then the lattice is body centered cubic, so in the unit cell there are 8 corner points and 1 body centered point, where we put the iron atoms at these lattice positions, then it becomes the unit cell of an iron crystal. In simple metals, one atom is associated with each lattice point, but there are complex systems where each lattice point may be associated with more than one atom.

Now when such a situation arises how to figure out the locations of the atoms around a lattice point, the fact is in such cases the atoms are not located in a random fashion or in a haphazard way, but there are some rules which dictate where the individual atoms surrounding a lattice point will be.

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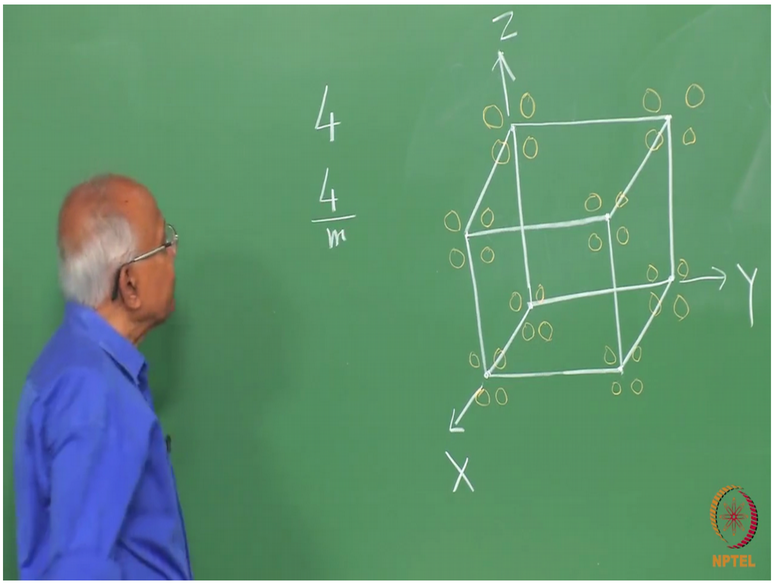

Let us take a very simple case, say again we have got a unit cell of a material say in the cubic system and say suppose that; this is a simple cubic unit cell with 8 points of the 8 corners. Now, if every lattice point here is associated with same 4 atoms, so here suppose there are 4 atoms associated with each of the lattice points as shown. Say, we have a material the unit cell of which has four number of atoms associated with which lattice point as shown on the board.

Say for example, these 4 atoms here they lie on the same plane say they are lying in a plane which is parallel to the top surface which is the 001 plane. Similarly, say at all these four locations, the atoms are lying on a plane parallel to the top plane. Similarly, let us suppose that in all the four cases here the 4 atoms around each lattice point; they all are lying on the plane which is the 00 bar 1 plane; that means, this particular the bottom plane.

So, we have a situation where we have a cubic unit cell of a material at the top four corners of the unit cell. There are 4 atoms per lattice point and they lie in the same plane the 001 plane and the bottom, again there are four lattice points and 4 atoms are surrounding each lattice point they are and atoms lie on the 00 bar 1 plane, so these are parallel planes.

Now, how can we rationalize the location of the different items around this a particular lattice point, say for example here; at this lattice point we have got four different; 4

atoms surrounding it in the same plane. So, if we assume for example, that there is a 4-fold rotor perpendicular to the top plane, then we can explain given the location of one of the atoms, where the other three atoms are going to be. So, if we assume that yes at each lattice point in this unit cell, there is a 4-fold rotor lying in this manner; then we can rationalize the locations of each and every atom around the lattice points.

Now, this is quite interesting say for example, if on the other hand we had instead of four, if we had 8 atoms per unit cell apart lattice point in this unit cell and if it. So, happened that at each lattice point on top of the lattice point there are 4 atoms as slightly below the lattice point that another 4 atoms. How can we rationalize the location of these 8 atoms at this particular lattice point?

If we assume that there is a 4-fold rotor; going in this direction Z direction; the Z direction and side by side if there is a mirror perpendicular to that then the combination of these two symmetry elements will help us to rationalize the locations of those 8 atoms at this particular unit cell. So, simply because there is a 4-fold rotor, so there will be from one position the atom we can find out the positions of the other three and if there is a mirror perpendicular to that so we will have another four which are reflected through the mirror, so there will be 8 atoms and their locations can be rationalized.

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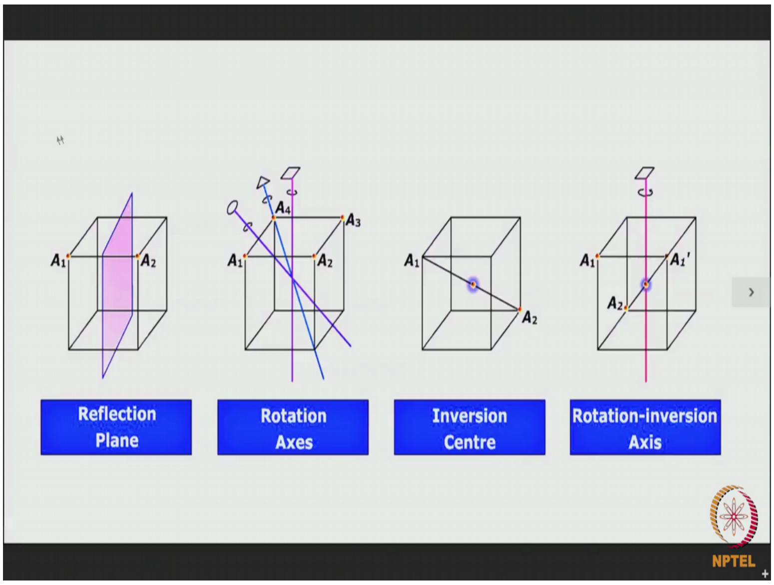

Now, we have already seen that several symmetry elements are available to us, for example, you can have a mirror or a reflection plane of reflection line of symmetry then rotation axis may be a 4-fold rotation axis, a 3-fold rotation, a 2-fold rotation axis and also a six fold rotation axis; then an inversion centre or in inverter and also a rotation inversion axis, so all these symmetry elements are available to us. Now, if we look at the innumerable number of crystals and look at the locations of the atoms around a lattice point, the unit cell unit cells of these crystals, then we find that the locations of the atoms around a lattice point can be easily rationalized by assuming a single such symmetry element or a combination of such symmetry elements.

In the example, just given by me if there are 4 atoms per lattice point in one plane, then the whole thing, the location of the atoms can be rationalized assuming a 4-fold rotor passing through the lattice point. If on the other hand you have got 8 atoms; at this particular lattice point, 4 of them above and 4 of them below, then their locations can be rationalized by assuming as if there is a 4-fold rotor and a mirror perpendicular to that rotor at each and every lattice point.

So, we have to figure out it can be seen that you know by X-Ray diffraction experiments, it is quite possible to figure out what kind of symmetry elements can be invoked in order to explain the locations of the different atoms around the lattice point. So, it is a question of finding out; which symmetry elements can be invoked? Whether it is a single symmetry element or a group of symmetry elements at a lattice point?

Now a point group is defined as a collection of symmetry elements at a lattice point, a point group is defined as a collection of symmetry elements at a lattice point which will allow us to explain the location of all the atoms around that lattice point. So, you see that here for example, when you have 4 atoms surrounding this particular lattice point and the atoms are lying in one plane, then the symmetry element involved was a 4-fold rotor and when we consider a situation where there are 8 atoms per lattice point. In that case four in one plane for in a plane parallel to that then their locations can be explained by assuming a 4-fold rotor which is perpendicular to a reflection plane, we can write it in this manner.

So, you see that assuming that such a element acts at each and every lattice point of the unit cell, we can explain the atom position in a particular unit cell; in another case by assuming that two symmetry elements a 4; 4 rotor mirror are present together at this point, we can explain the locations of the 8 items per lattice point in a unit cell. So, as I already mentioned, the point groups are nothing but a collection symmetry elements at a lattice point which will allow us to find out the location of all the atoms surrounding that particular lattice point.

Now, so it is a question of in how many different ways all the symmetry elements we know about can be combined so that each combination we will have a distinct arrangement of atoms, which is indistinguishable one from the other; I am sorry which is distinguishable one from the other. So, what we are looking at is how many such combinations of symmetry elements are possible at each such combination should yield a distinct pattern of atoms, which is completely different from those given by the other combinations.

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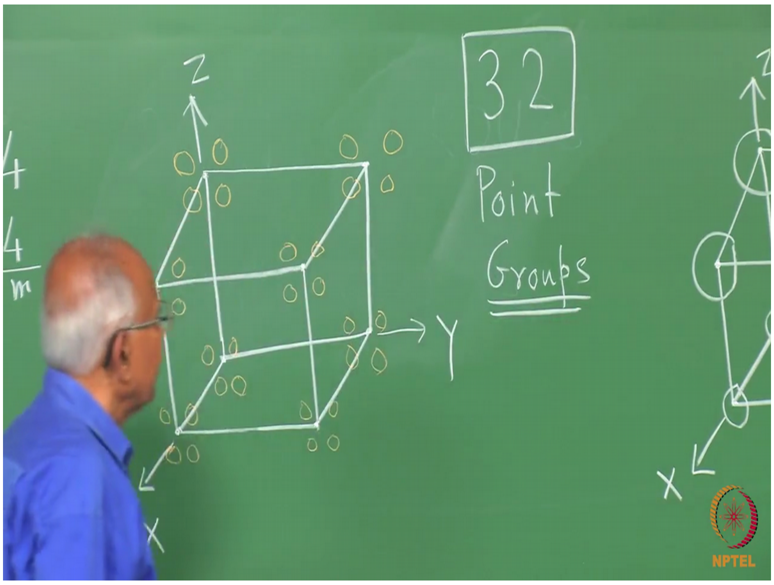

So, in this manner it has been found that a maximum of 32 such combinations are possible; a maximum of 32 such combinations are possible and hence we say that there are 32 point groups. So, there are 32 different combinations of the different symmetry elements we know about; each combination giving rise to a pattern of atoms which is totally different from the others

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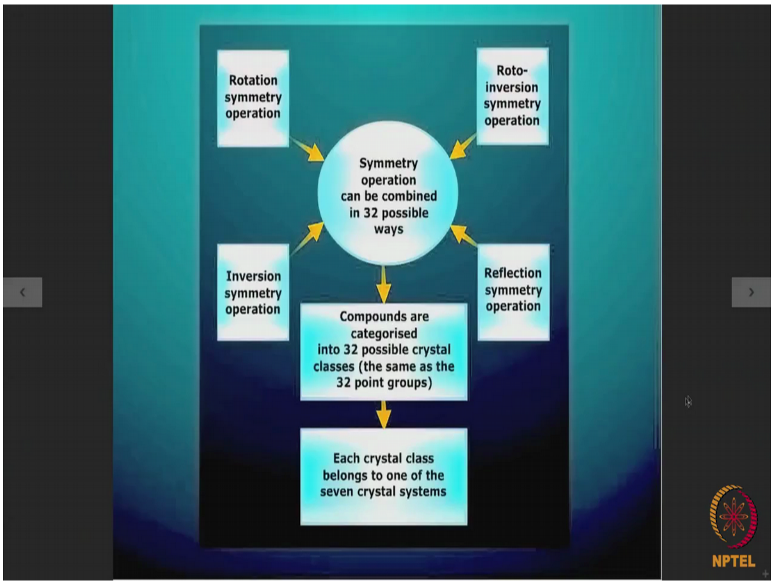

So, now we can see that the symmetry elements that we have they can be combined in 32 different ways and which symmetry elements are involved rotation symmetry like the axis of symmetry, then inversion symmetry, then reflection symmetry and roto-inversion symmetry. So, there are 32 different combinations of these symmetry elements which will lead us to 32 distinct arrangements of atoms around a lattice point.

So, all such compounds are categorized into 32 possible crystal classes, so there are 32 point groups or 32 possible crystal classes. Now, each crystal class of course belongs to one of the 7 crystal systems which we have already described.

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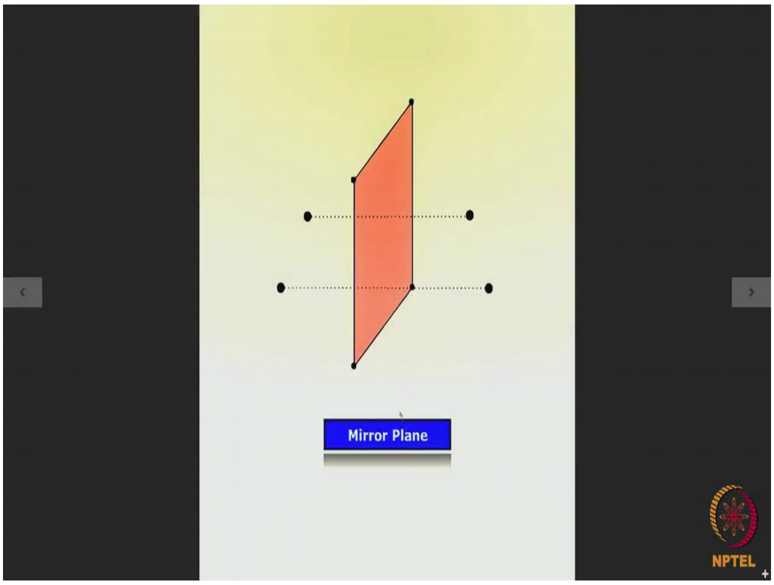

Now, so far as point groups are concerned the symmetry elements can be thought of as operators; what is meant by operator? Say for example, if we take a plane of symmetry or a mirror as shown here; if there is a point on the left hand side by reflection through the mirror, another point will be produced on the other side at equal distance from the mirror.

Again, if we have a point here by reflection through the mirror are exactly same distance on the opposite side another point is created. We can say that a plane of symmetry or a mirror acts as a operator, so What is this function? This function is to cause reflection and what happens due to reflection one point will generate one more point. So, a mirror plane or a plane of symmetry, it will generate one point from another from a given point; so there are two equivalent points for a mirror plane symmetry.

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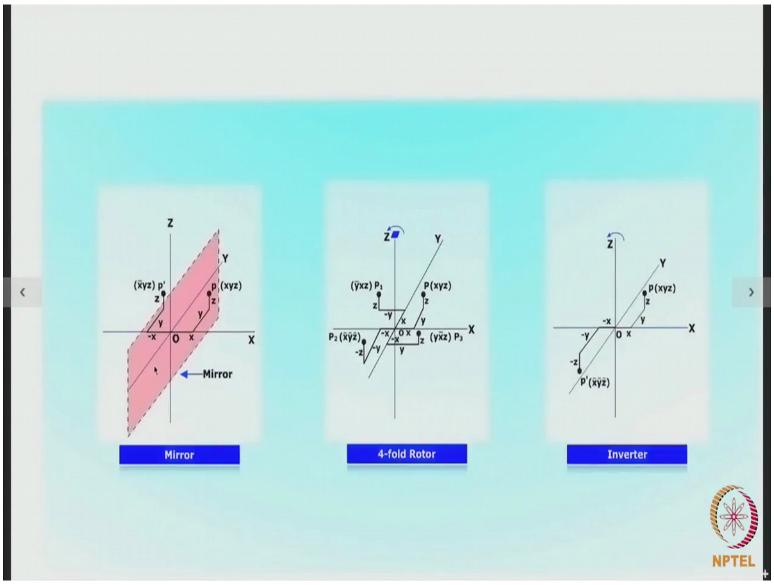

Now, here the operation of the mirror playing has been illustrated; say for example, if we have a plane in the y; z plane; if we have a plane in the y, z plane then what will happen; this is the mirror; if we have a mirror in the y, z plane if we take a point, here whose coordinates are x, y and z then after reflection through this mirror the point will come here. So, p the point p gets reflected through the mirror comes over there and what are the coordinates of that now its x coordinate is minus x, y coordinate does not change Z coordinate does not change. So, the point xyz becomes bar xyz by reflection through the mirror operator, we can say that the mirror operator produces two equivalent points the given points p and the one produced is p dash.

Now, when we deal with a 4-fold rotation axis or a 4-fold rotor it acts as a operator. So, it acts as a rotor operator what is this function; say if we have a 4-fold rotor; if it is rotating the anticlockwise direction say this is the X axis, this is the Y axis and this is the Z axis. See, if we have a point with xyz this is x, this much is y, this much is z due to the rotation of the 4-fold rotor; the next position of this point will be P 1 and its coordinates will be bar yxz, the third position will be P 2 bar x bar, y bar, z and the fourth position will be here P 3 y bar xz.

So, you see that due to the presence of a 4-fold rotor along the Z direction, if we have a point p xyz; with xyz coordinates then three more points are produced due to the rotation operation and how many equivalent points we find here four, so a 4-fold rotor operator will have four equivalent points will give us 4 equivalent points.

Now, if we will look at the function of an inverter what happens say again this is the X axis this is the Y axis and this is a Z axis; if we have a point p with coordinate's xyz and if we have an you know inversion point at O, then what will happen? This point will produce a point p prime and the coordinates of p if it is xyz the co-ordinates of p prime will be the X bar Y bar and Z bar. So, you see that if we have any inversion operation then there are two equivalent points produced.

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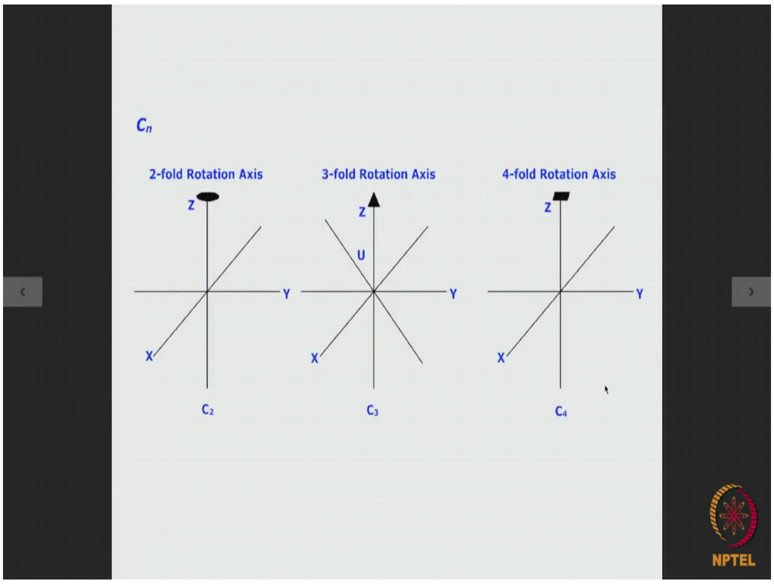

Now, so far as naming of the point groups are concerned; there are two different ways the older system is known as the Schoenflies system and the newer system is known as the Hermann-Mauguin system.

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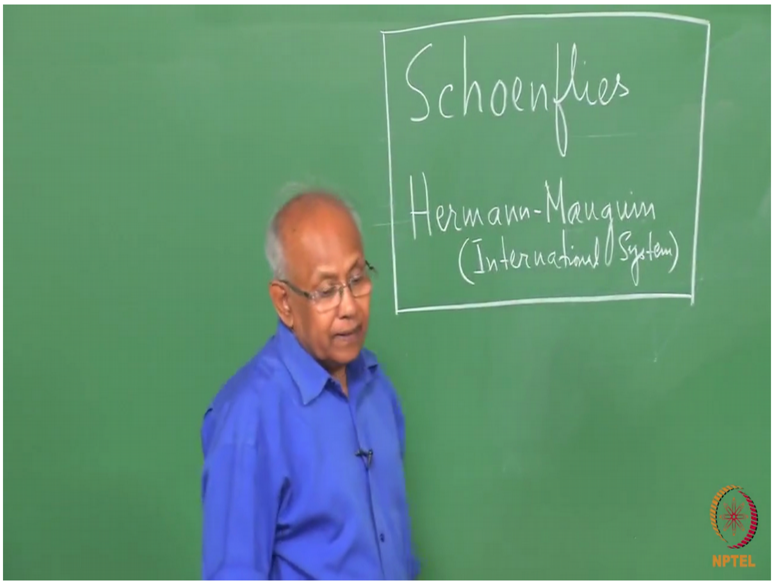

This second one is also known as the international system, so following these systems point groups have been given certain nomenclature. Say for example, in the Schoenflies system c with a subscript n refers to a point group which contains just one rotation axis nothing else. So, if it is C 2; it means that this refers to a point group where is lattice point is associated with simply a 2-fold rotor this is the way a 2-fold rotor is shown

Now, in case of a 3-fold rotation axis we can have a point group having just one 3-fold rotation axis, then in the Schoenflies system; it is written as C 3; just as in the 2-fold rotation axis in the Schoenflies system is it (Refer Time: 25:50) C 2. Similarly for a 4-fold rotation axis, the point group can be written as C 4. Now in case a point group is obtained by combining a rotor and a horizontal mirror as shown here.

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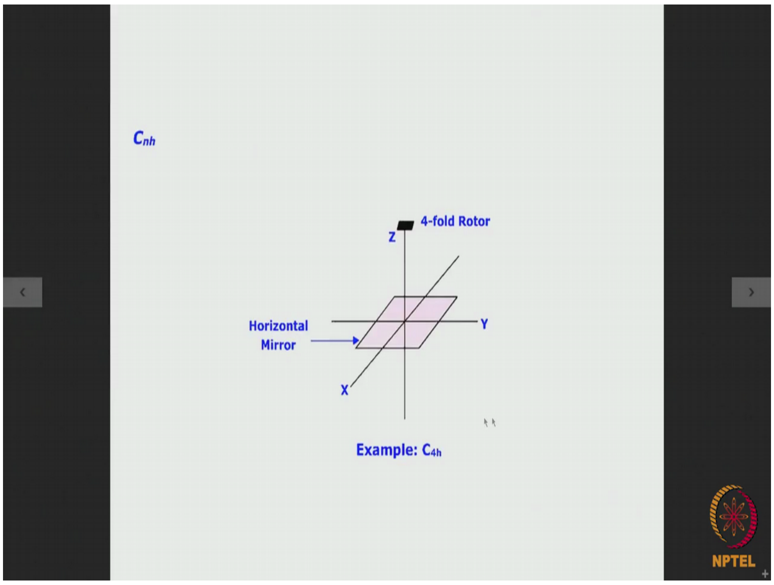

For example, they are written as C subscript n h in the Schoenflies system. So, here we have got a 4-fold rotor along the Z direction and a horizontal mirror in the X, Y plane, so according to the Schoenflies notation; it can be written as C subscript 4 h.

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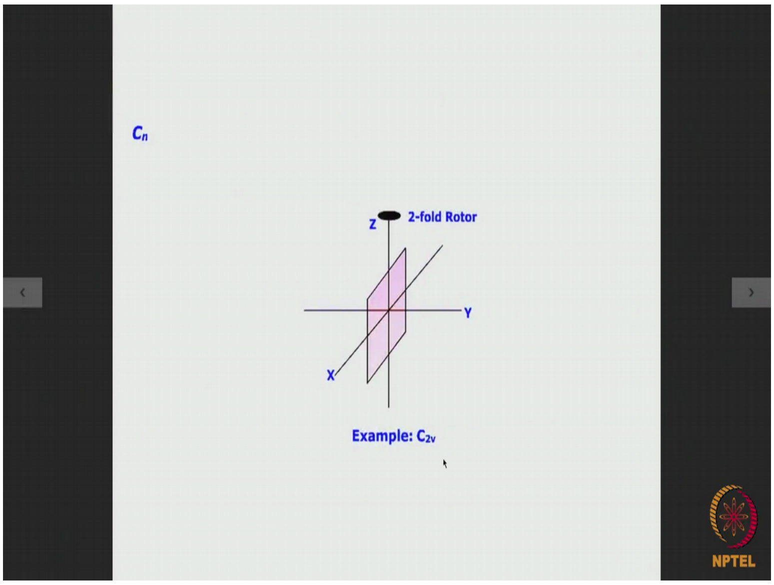

On the other hand, if the rotor is parallel to the mirror plane, so it is a vertical mirror then the Schoenflies system is written as C subscript n v here unfortunately the v is missing. So, it will be C n v. So, in this particular case since a 2-fold for rotor; it will be C 2 and since it is a vertical mirror; so it will be C 2 v.

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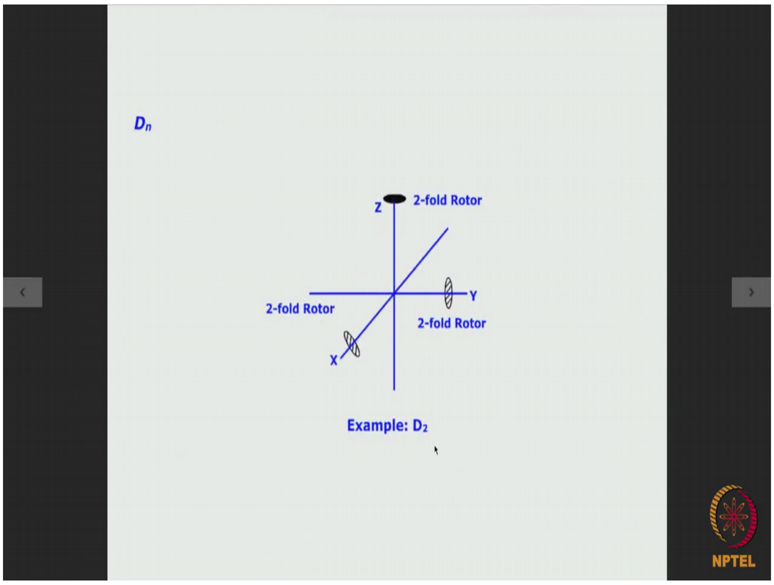

Now, in the Schoenflies system; a point group is denoted as d subscript n and what it means if in a system; if in a point group, you have got a 2-fold rotor with two other; 2-fold rotors which are mutually perpendicular and both of them are perpendicular to the first rotor, in that case such a point group is given the designation D 2. So, this is another type of point group another point group notation by the Schoenflies system.

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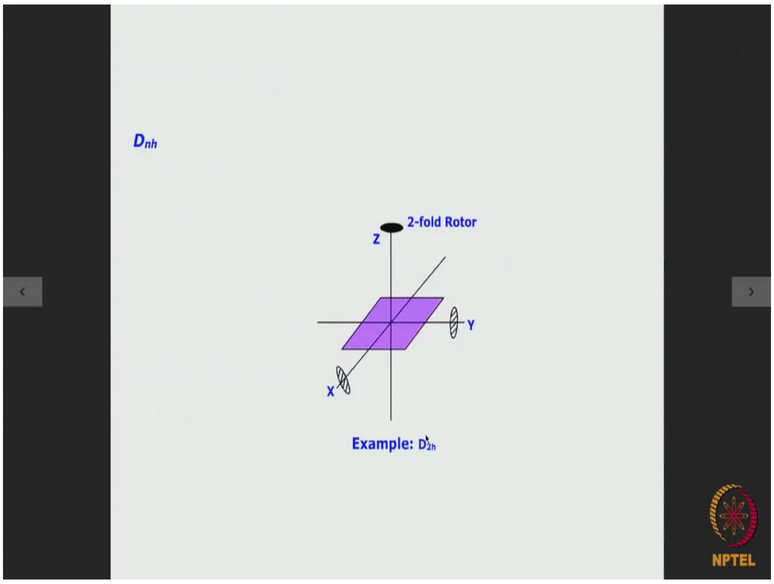

Now, D subscript n h stands for if you have a 2-fold rotor with another two perpendicular rotors lying perpendicular to the original rotor and if there is a horizontal plane perpendicular to the original 2-fold rotor.

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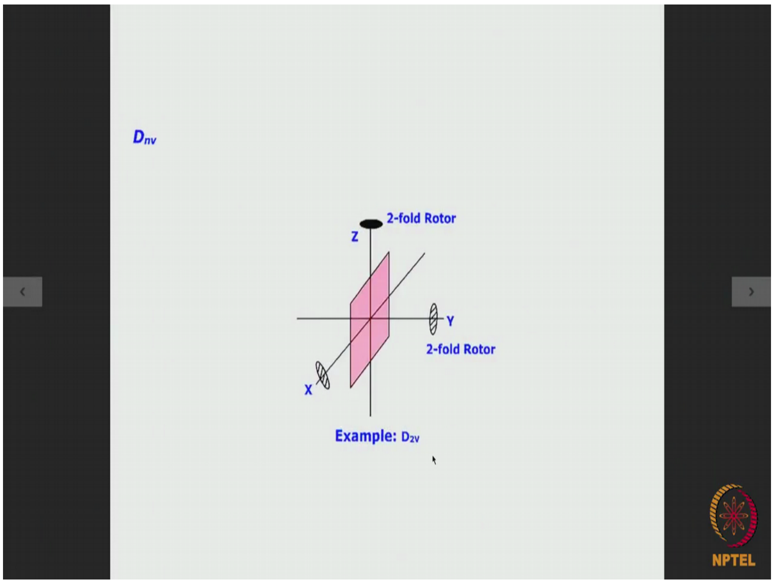

Then according to Schoenflies, it will be D 2 h; again D subscript n v stands for the case where the mirror is not a horizontal mirror, but a vertical mirror, so in this case it will be D 2 v.

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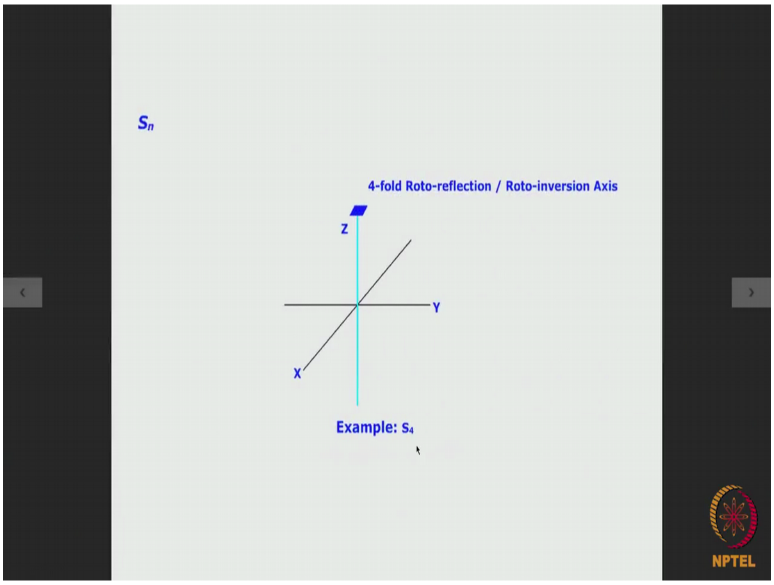

In this Schoenflies; notation there are point groups denoted by S subscript n and it means a Roto-reflection or Roto-inversion axis. So, if it is written as S subscript 4; it means a 4-fold Roto-reflection or Roto-inversion axis.

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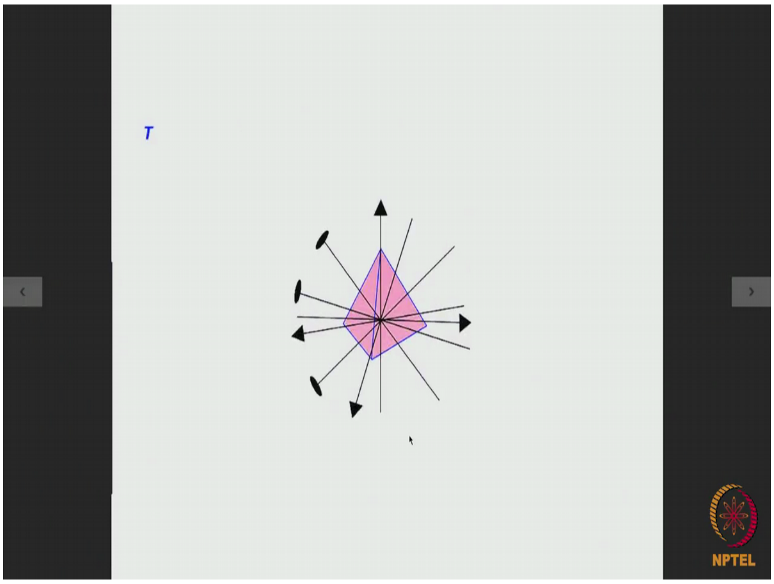

Another notation is capital T that refers to a combination of symmetry elements that are possible to have for a tetrahedral and what are those symmetry elements you can have in a tetrahedron. For example; 4; 3-fold rotation axis as well as 3; 2-fold rotation axis, so this is the kind of symmetry we can observe in a tetrahedral and this combination of symmetry elements is denoted by the letter capital T.

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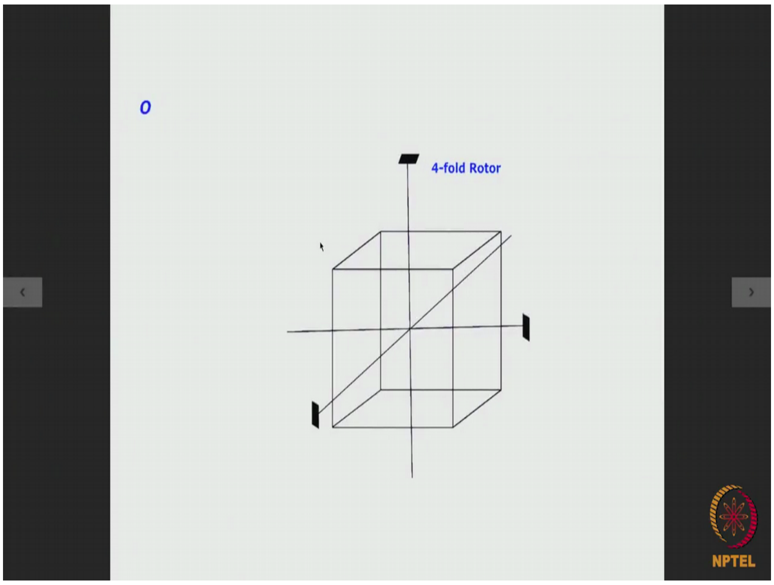

Then another combination of symmetry elements is designated as O; capital O in the Schoenflies system and in this there are three 4-fold rotors plus 4; 3-fold rotors plus 6; 2-fold rotors.

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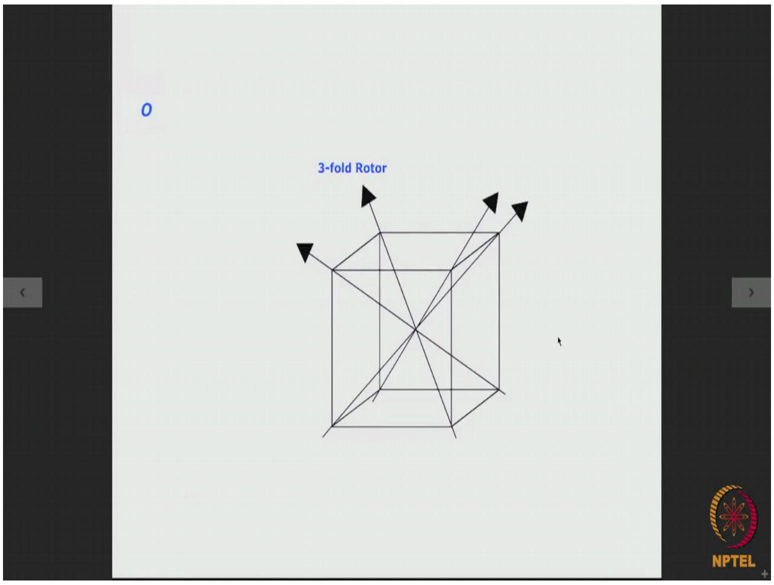

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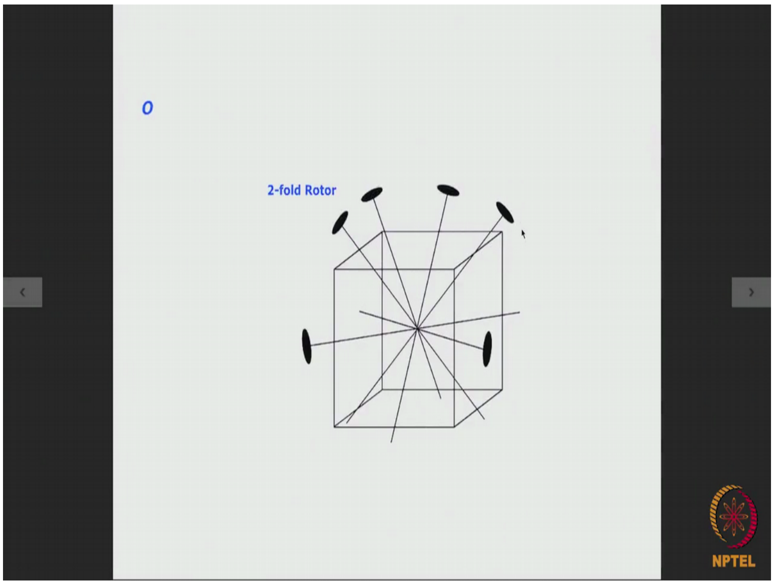

So, the O in Schoenflies system refers to a point group containing 3; 4-fold rotors, 4; 3-fold rotors and 6; 2-fold rotors

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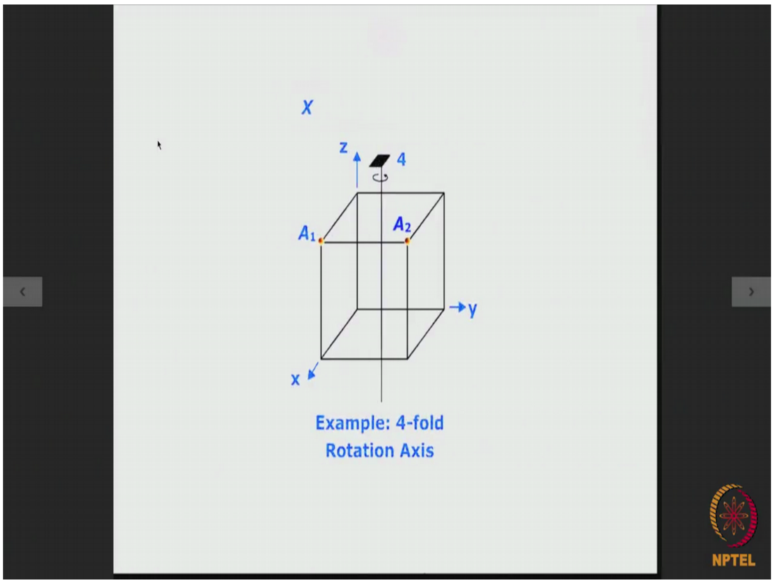

Now, when you come to the other system the modern one the Hermann-Mauguin system or the international system nomenclature is quite it is more easy; say for example, here a single a point group is a single rotation axis is denoted by a number say for example, if we have simply a point group which is simply a 4-fold rotation axis it is denoted by the number 4. So, for a 2-fold rotation axis; it is denoted by 2; if it is a 3-fold rotation axis is denoted by three etcetera etcetera.

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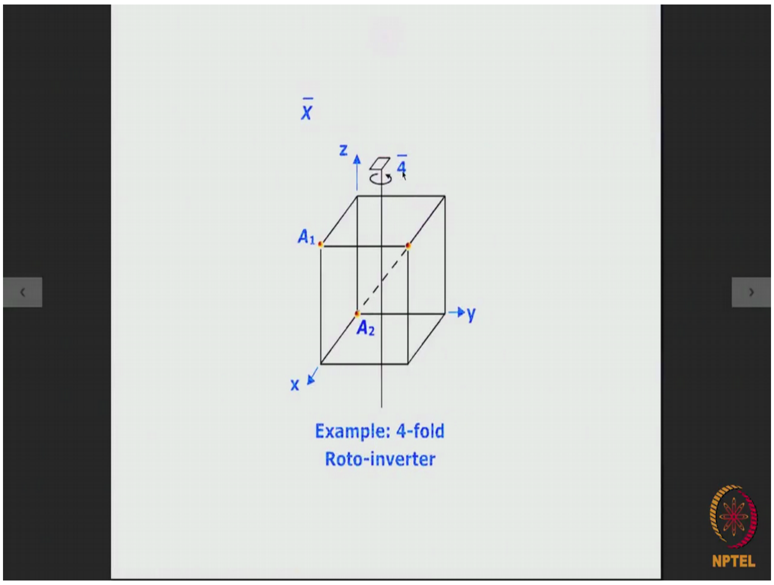

Now, if we have a number with a bar on top of it; as shown in this diagram that will mean a Roto-inverter: so a 4 with a bar means a 4-fold Roto-inverter. Similarly you can have a 2-fold inverter, 3-fold Roto-inverter etcetera etcetera.

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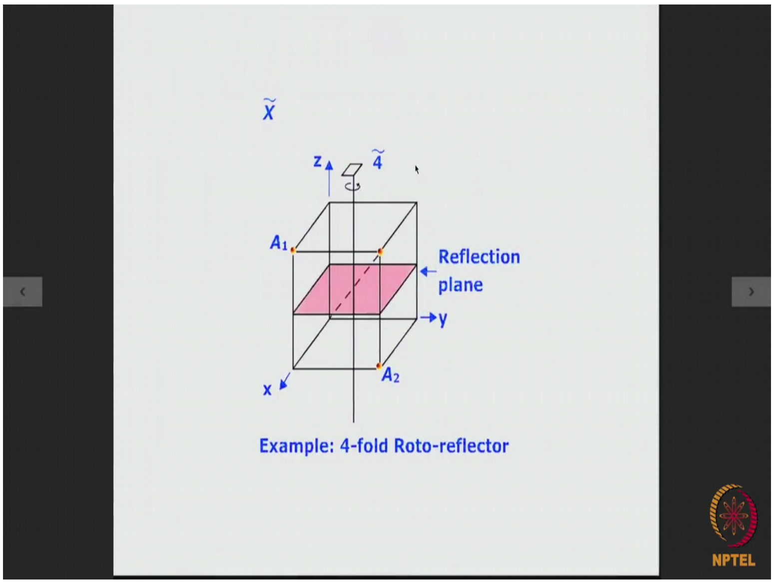

If you have a sign like this on the number that will indicate a Rot- reflector, so if we have a sign like this say for example, here we have a 4-fold Roto-reflector. So, because it is a rotor come reflector; what happens during its rotation first 90 degree rotation; point A 1 will come to this point here and then it will get reflected through a mirror plane and come to this, so this point will produce this point by its action.

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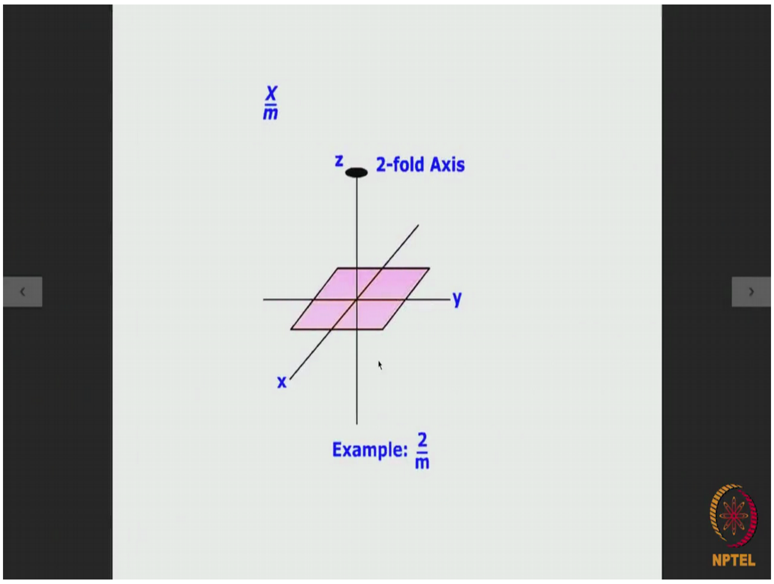

Now, when the number is put on top of the letter m as here it means a rotor with a horizontal mirror perpendicular to the rotor; so if we write it as 2 by m; it means a 2-fold rotor with a mirror perpendicular to it; that means, it is a horizontal mirror.

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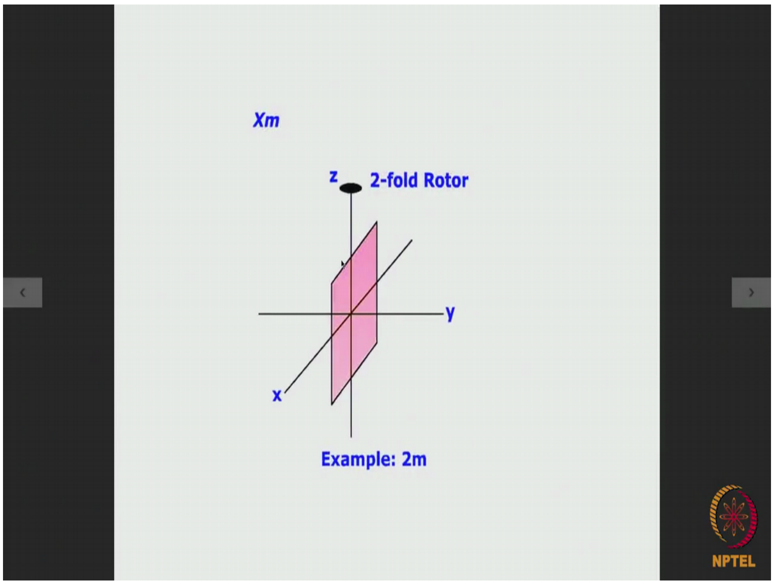

Now, X m in this system you known if you have say a 2-fold rotor and a vertical mirror, so it will be written as 2 m, so if it is a 3-fold rotor with a vertical mirror it will be 3 m etcetera etcetera.

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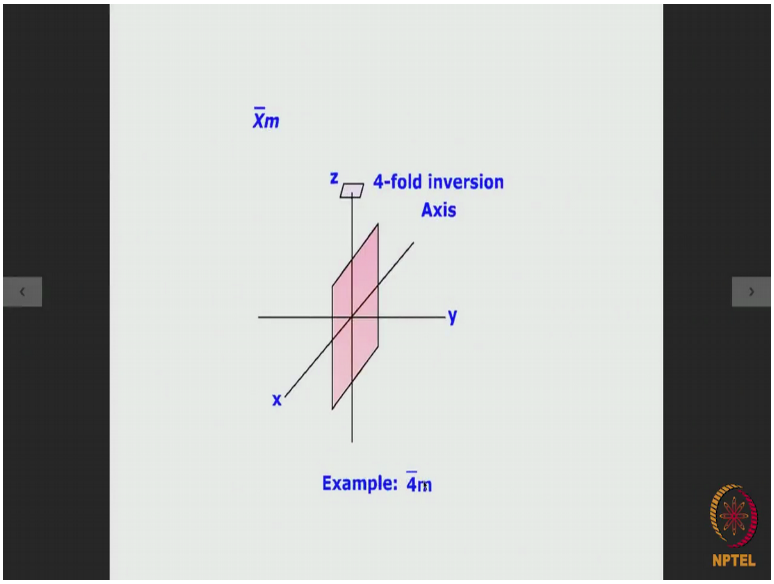

Now, when it is written as X bar m it means it is a combination of an inversion axis with a mirror as shown over here. Say for example, here we have a 4-fold inversion axis and there is a vertical mirror, so you can write this point group as bar 4 m.

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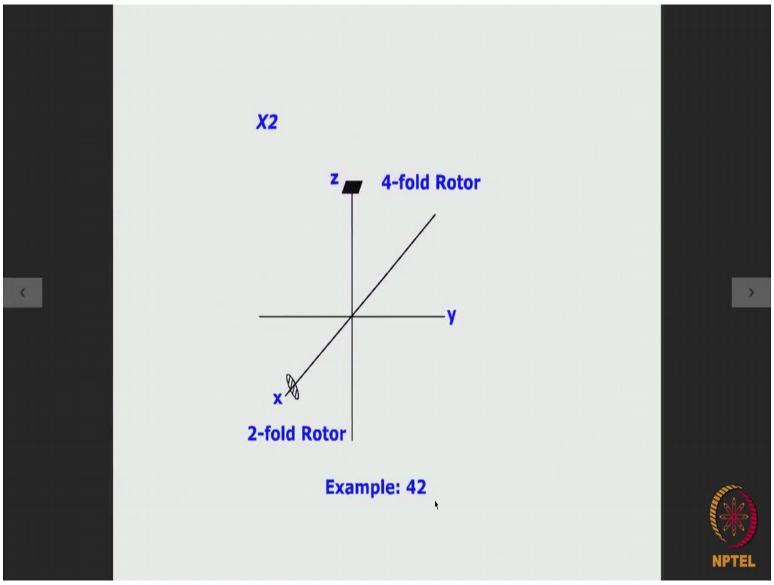

Sometimes you have got point group which are written as X 2; X stands for a number; say for example, if we have a 4-fold rotor and there is a combined with a 2-fold rotor perpendicular to it.

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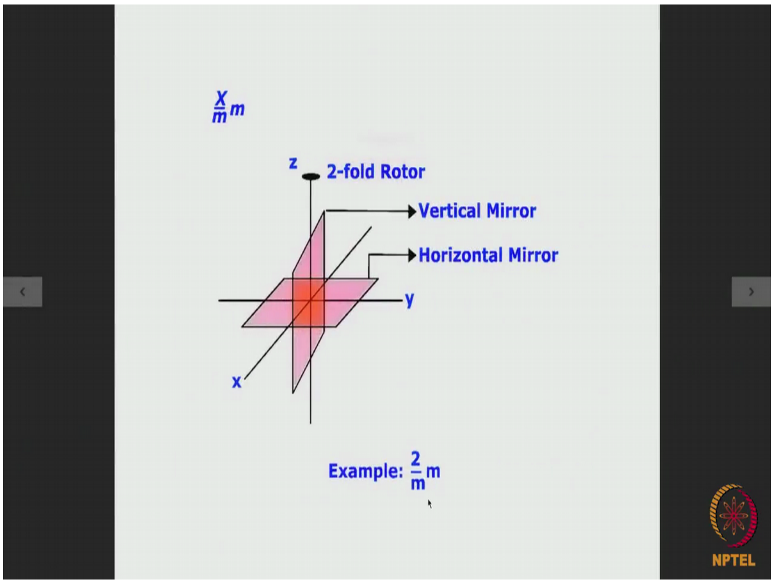

Then this point group can be written as 4; 2 there are cases of a point group where we combine a rotor with 2 mirrors; one vertical one horizontal as in this particular case. So, here we have a 2-fold rotor along the Z direction and then there is a vertical mirror containing the 2-fold rotor and a horizontal mirror perpendicular to the 2-fold rotor. So, how this combination of symmetry elements can be written is written as 2 by m; m.

Now, the point groups can also be represented in the form of a stereographic projection.

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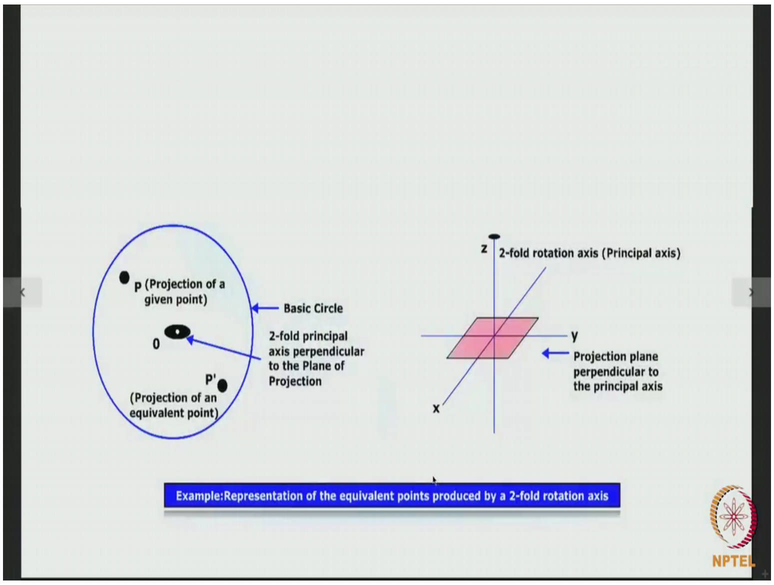

Say for example, here we have a point group as you can easily seen there is a combination of two symmetry elements here; there is a 2-fold rotation axis in the Z direction the principal axis and there is a; you know I am sorry; it is a simple it is a simple 2-fold rotation axis. So, here we are dealing with a k is a point group which just has one 2-fold rotation axis; a 2-fold rotor acting in the Z direction, then what we to do we take a projection plane perpendicular to the 2-fold rotor.

So, we have a 2-fold rotor in the Z direction we take a projection plane perpendicular to that and if we do that and if we draw the stereographic projection here; now what will find, we find that the 2-fold rotor will appear at the center of the projection plane. So, it will be over here, now if we have a point you know in this quadrant due to the operation of the 2-fold rotor, it will generate another point in this quadrant. So, if it so happens what will find at 180 degrees away, so this is the given projection or a equivalent point and this is projection of a given point. So, if we have a given point and if we have a projection point you know due to the 2-fold axis it will produce the second point.

Now, since the rotor is in the Z direction, so what will happen when you take a point and use the rotor you know to act use the 2-fold rotation axis to act as a router; this given point will produce another point and since the rotor is the Z direction; the X, Y coordinates of the given point and the point is which is produced they are the same; that means, the point and the equivalent point produced out of it; they are at the same level.

So, that is the reason why if this is the projection of a given point; this is a projection of an equivalent point, you see if the point the point that is produced by the action of the rotors is at a different levels then instead of a closed circle, we represented by an open circle as will be clear very soon.

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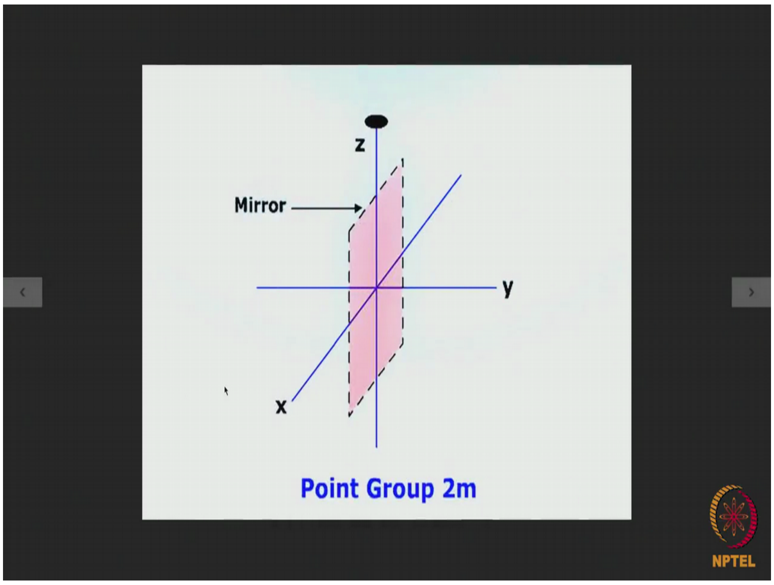

Say for example, we talked about the point group 2m, so if we have a point 2m it means we have a 2-fold rotor along the Z axis and a mirror which contains the vertical mirror which contains the 2-fold rotor. Now, how we can represent this in the form of a stereographic projection, normally the projection plane is the X Y plane; that means, the projection plane is perpendicular to the Z axis along which the rotor lies. So, naturally the position of the rotor would be shown by point right at the centre of projection because the projection plane is taken along X Y plane.

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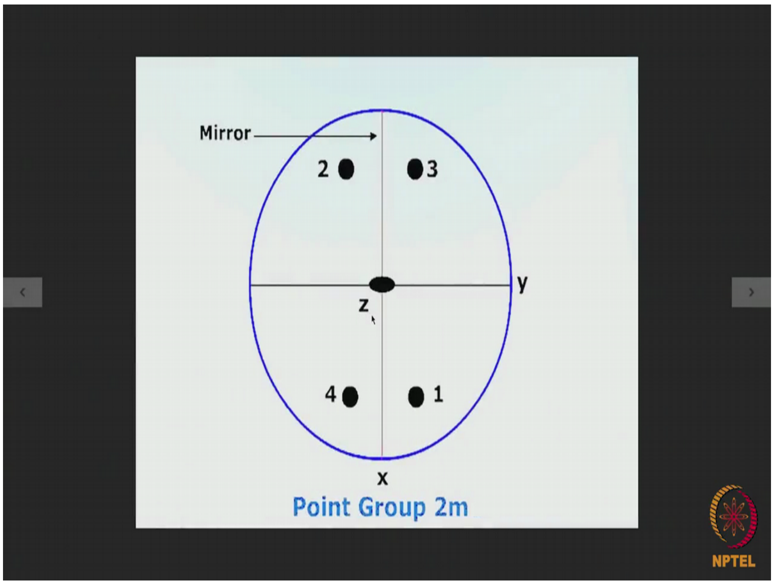

So, we will have a projection and the two fold rotor will lying right at the centre of the projection. Now, so if we have the points here what will happen that point will produce an equivalent point at 180 degree because it is a 2-fold rotor, but you know the two points; the equivalent the two points will be at the same level because the rotor is along the Z direction.

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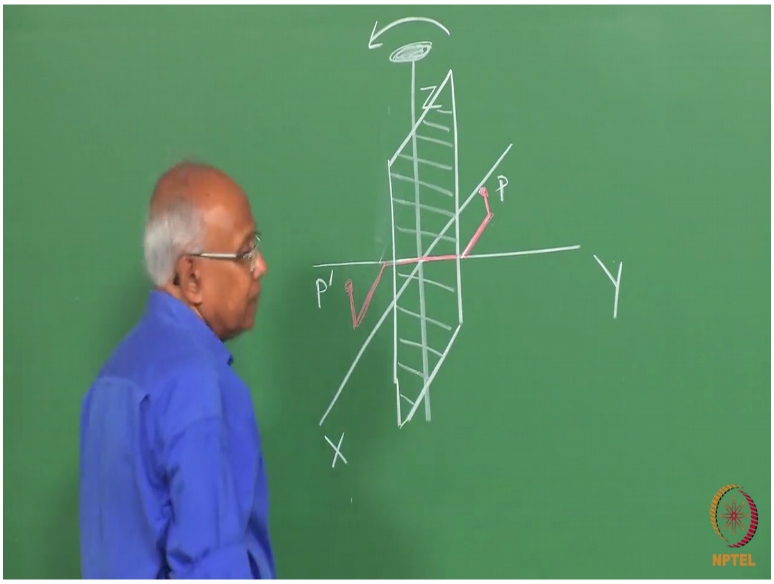

Say for example, so if we have it 2-fold rotor along the Z direction and then if we have a point P over here, then due to the rotation. Suppose, if this rotor goes on anticlockwise direction rotates in anticlockwise direction, so it will rotate and come to this point at 180 degrees. So, they are as you can see that the Z coordinate does not change; that means, they are at the same level.

Now, if we have a vertical mirror like this, then what will happen the mirror will reflect the given point and its equivalent, so P will be reflected through the mirror P prime will be reflected from the mirror. So, the whole thing can be shown in the form of a stereographic projection.

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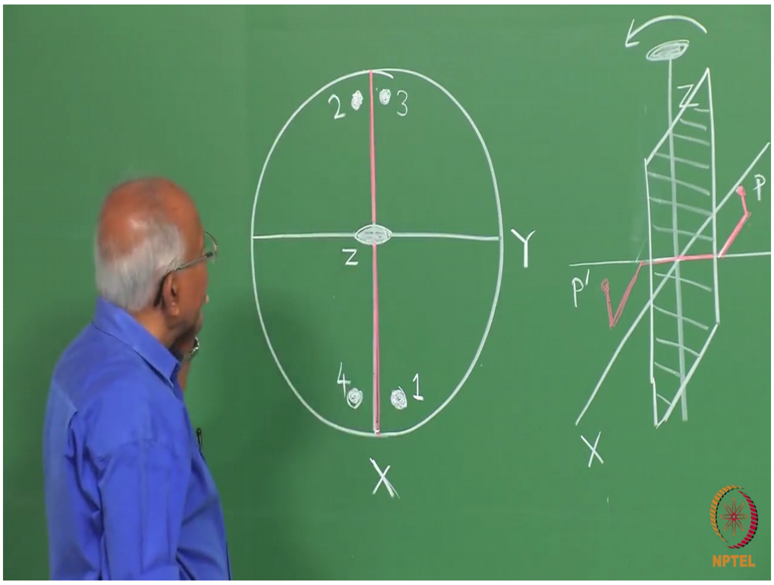

Say for example, if we take a stereographic projection parallel to the X Y plane then where will this; so this is my projection plane. So, this 2-fold rotor will come right at centre of the stereographic projection, so I got my 2-fold rotor here this is my projection plane.

So, where will be the mirror this is the vertical mirror lying in the X Z plane, so now we have got; this is the Y, this is the X and this is the Z, so we have a mirror in the X Y plane. So, our mirror will be over here, so our mirror in the stereographic projection will lie in this fashion; the mirror will be lying in this fashion. So, if we have a projection plane like this; right at the center of the projection there will be the 2-fold rotor X axis will be over here, Y will be projected over here and then the vertical mirror this vertical mirror will come as a line like this.

So, if we have a point given point P over here or given point 1; say we have a given point 1; due to the 2-fold rotor the next by rotation the next position of the point will be over here, so it will be like this; so 1 will produce the point 2. Now, because there is a mirror here this point will be reflected through the mirror and come over here. Again because of this mirror this point to be reflected through the mirror and come over here; say this is point number 3, this is number 4.

So, we can see that due to the operation of a 2-fold rotor with the vertical mirror have shown here from one point we produce three other points. So, there are four equivalent points due to the operation of this kind of a point group. So, that is what is shown that the point group 2m will produce you know point from point 1, it will produce point 2; 2 will produce 3 by reflection to the mirror and 1 will produce 4 by reflection through the mirror and we will have four equivalent points produced due to the operation of the point group 2m.

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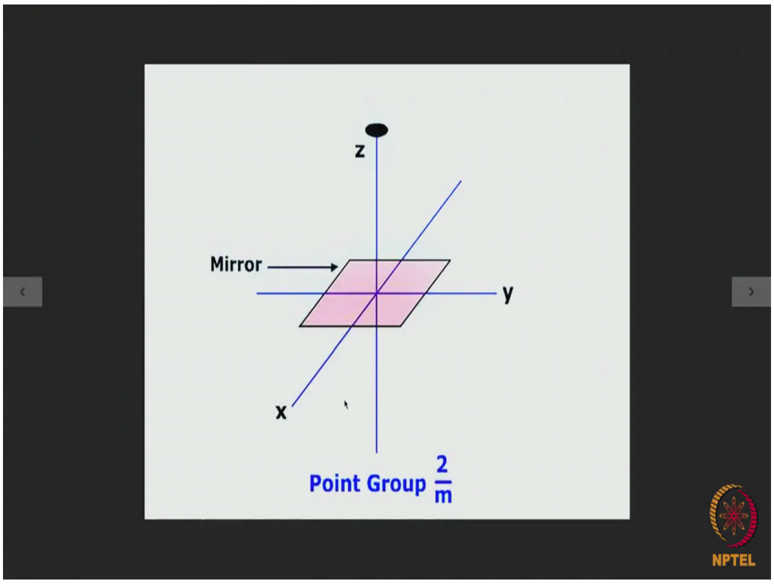

So, what will be situation like when we represent a point group 2 by m in the form of a stereographic projection, so here the mirror is not vertical but it is horizontal?

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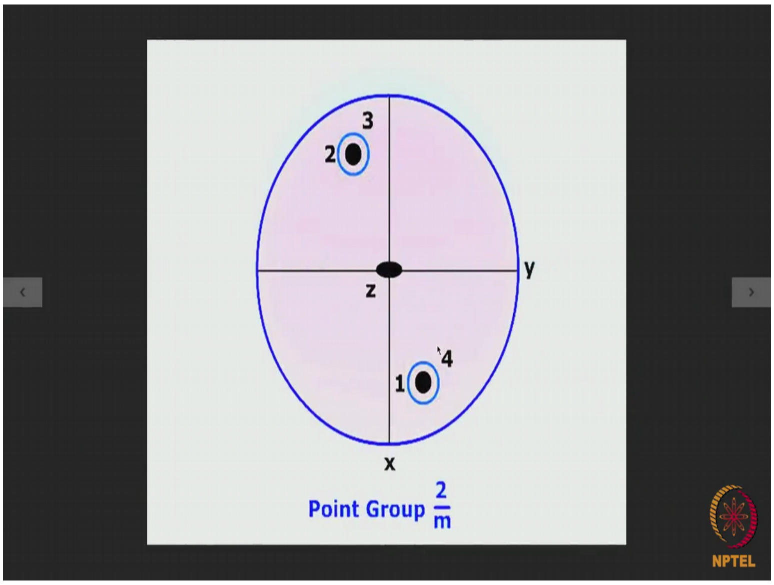

So, in the projection the mirror will be this along the periphery of the stereographic projection. So, the mirror position is like this, so from the point 1; the closed circle due to the operation of the 2-fold mirror; point 2 will be produced and then they will reflect through the mirror. So, now, the position of the points you know there will be at a different levels not at the same level as 1 and 2 because the mirror is lying parallel to the surface parallel to the plane here.

So, the point two produce the point 3 by reflection through this horizontal mirror and point 1 will produce point 4 by reflection through horizontal mirror. So, here also there are four equal points, but two are at the same level 1 and 2, whereas 3 and 4 are at a different level that is why 1 and 2 are shown as closed circles and 3 and 4 are shown as open circles.

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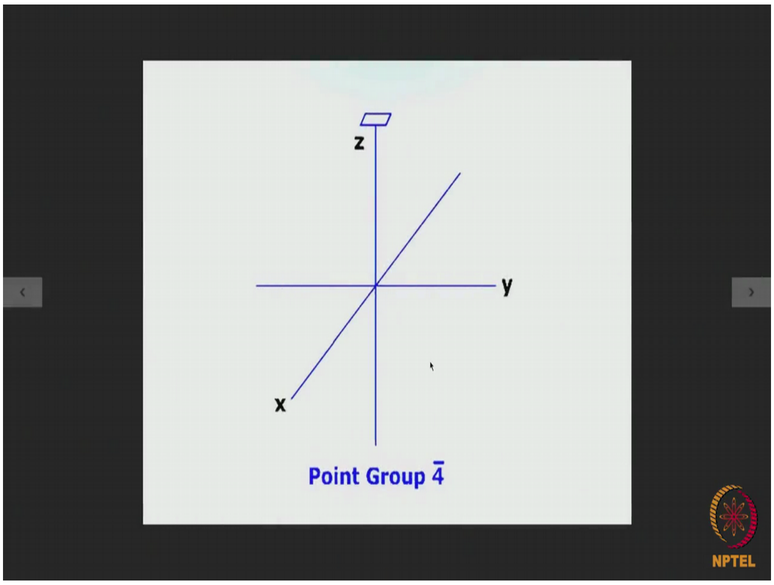

Now, if we look at say the point group given by bar 4; that means; a Roto-inverter then what will happen? So, as shown earlier; if we take a projection plane parallel to the X Y plane, then what will happen at the centre of the projection, we will have the 4-fold rotor you know it will projected over here and if we have a point here.

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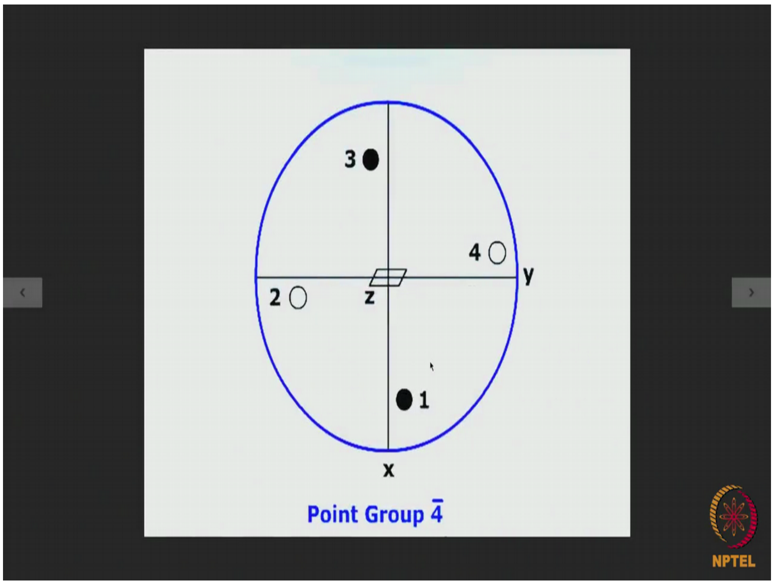

Then what will happen because this point group is 4 bar 4 means; it does two things simultaneously; that means, it rotates followed by immediately by inversion, so it rotates and then inverse. So, let us see if we had a point 1 here and if it were a simple 4-fold rotor, then 1 would have produced; 2 would have produced; 3 would have produced 4; all at the same level, but because it is a 4-fold rotor inverter, it rotates on the inverse.

So, one should have gone there as a solid circle, as a closed cycle but then it gets inverted at a different level it becomes an open circle and then next is another rotation it should come over here as an open circle, but then gets inverted, so become goes another level by represented by the close circle and since the next rotation because you know four rotations are necessary for a 4-fold rotor, it should have gone here as an closed circle then gets inverted through this and becomes an open circle. So, you see that here also there are four equivalent points; two are at one level and two are at a different level.

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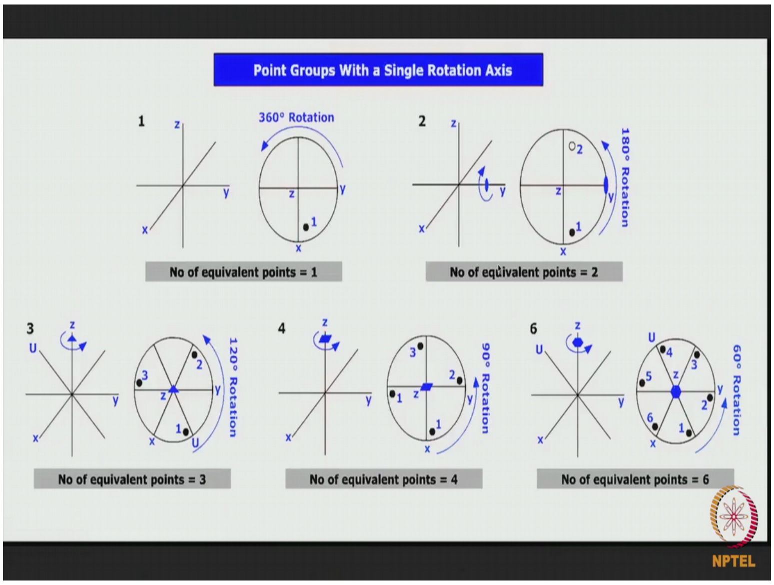

Now, when we talk about all these point groups; each point group consists of a single rotation axis only, then we can see; we can represent them as simple stereographic projections as shown here. So, for the rotation axis 1; point 1 does not produce any other point because you know it is a 360 rotation and (Refer Time: 49:44) same point, then comes rotation axis 2 say here we take the rotation axis in the Y direction. So, if we take a projection then the 2-fold rotor will come over here and if we have a point 1; it will produce a point 2 over here, but you see here the Z; the level of the 2 point, it is totally different that is why 1 is represented by a closed circle and the other one is represented by an open circle. So, if there is a 3-fold rotor and if the rotor is now in the Z direction, then if you take a projection; then in the projection plane the rotors position will be at the center. So, if there is a point 2 due to the rotation; 1 will produce 2; 2 will produce 3 etcetera etcetera.

Please remember a 3-fold rotor can exist in the hexagonal system and that is why here we have got four axis x, y, U and z. So, this is the situation the 3-fold rotor and as we have already seen, if there is a 4-fold rotor again at the along the Z direction 1 will produce 2; 2 will produce 3; 3 will produce 4; I am sorry this is misspell as 1; this will be number 4. So, four equivalent points are produced.

And again if we have 6-fold rotor a point group which consists only of a 6-fold rotor; such rotors are possible only in hexagonal system and if the rotor is along the Z direction, then we find 1 will produce 2; 2 will produce 3; 3 will produce 4; 4 will produce 5; 5 will produce 6. So, you see that from one point we get extra 5 points, so there are 6 equivalent points in the point group denoted by 6.