Symmetry and Structure in the Solid State
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Lecture –12
Point Group and Crystal Systems 1

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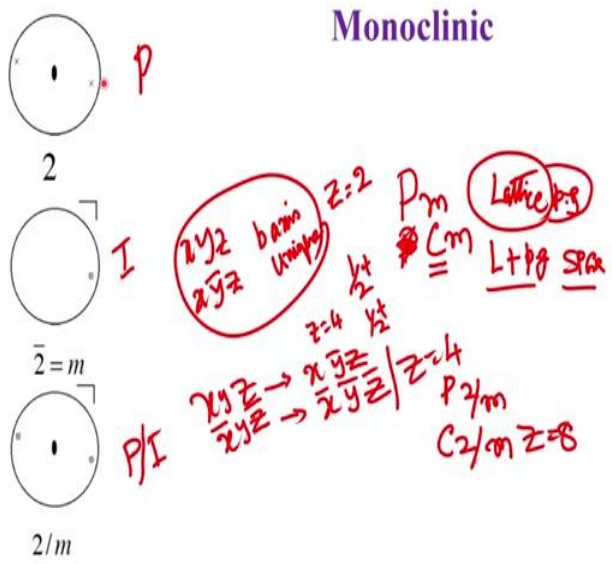

So, when we come to the case of use of a mirror symmetry, here we therefore have the operation 2 followed by inversion centre or immediately on acting on the two fold and therefore, we get a mirror. So, in a mirror symmetry we have equivalent points at x y z and x $\bar{y}$ z. So, the axis again is the unique axis again is the b axis. So, x y that goes to x $\bar{y}$ z and the b axis being unique, if the c axis is unique, the equivalent points will be x y z and x y $\bar{z}$ and if a axis is unique, it will be x y z and $\bar{x}$ y z.

So, again you see that there are two in the unit cell and therefore, one in their symmetric units. So, the value of z is equal to 2 and the value of z prime is equal to 1. The system to which it goes into again can be a primitive lattice which is now going to give us the space group *Pm* and it can also give the space group *P* sorry *Cm Cm*. So, we can therefore have two possible space groups; the primitive with a mirror as the, so this is in fact the way in which one represents the space group. We are going to do more seriously the space groups later on, but this is the way. So, one once we know the crystal system, we tell first the lattice symmetry. The first we tell what the type of the lattice we have

and when once we know the lattice type whether it is *P* or *C* centred or whatever as we go further in case of the triclinic there is only primitive, but in this case it is primitive and *C* centred lattice. The *C* centring can also change to a centring or *B* centring depending upon the nature of the unique axis. In case the b axis is unique, the standard convention is to have the correct centred lattice.

So, as I mentioned that one once the *C* centring comes up, you will have addition of half plus along x and half plus along y for these two equivalent points thereby generating 4 equivalent points in which case z is equal to 4. So, you will generate 4 equivalent points. So, whenever we represent there for a space group, the first we represent the lattice and then followed that with the indication of the point group symmetry. So, the point group symmetry with the lattice now will tell us this space group. So, a space group representation is a lattice plus the point group.

So, this will tell us in fact something very interesting that we are now dealing with three dimensional object a crystal is a three dimensional object. We have identified the crystal system into which it goes into with *a, b, c, α, β, γ* based on that we have decided the nature of the crystal lattice that crystal lattice can have the crystal system. The crystal system will have a different kinds of lattices depending upon the bravais lattice conditions you remember that in a primitive two dimensional rectangular system, we have a primitive lattice and c lattice, the little p and the little c.

So, similarly we will have a capital *P* and a capital *C* in case of the monoclinic symmetry. We have the lattice plus the point group now representing this so-called space group. So, the representation of any space group therefore will tell us the complete three dimensional information associated with the system. So, when once we have the space group information, we automatically know the nature of the lattice, the nature of the point group the equivalent points, the number of equivalent points in the unit cell and so on.

So, that way the entire representation of any crystallographic symmetry along with the presence of systematic, sorry along with the presence of symmetry operations are given in a monoclinic system and in this particular case. So, similarly monoclinic system with a two way have already discussed, monoclinic system with a mirror we have now discussed we can go to these system which is. Now a combination of a proper and an

improper axis. So, this corresponds to a proper axis, this corresponds to an improper axis operation and this is a proper plus improper.

So, simultaneously operating at a point. So, at this particular point which is up here the symmetry operates in such a way that we have this point two fold is located. So, what happens now is x y z will go to $\bar{x}$ y $\bar{z}$ and then, each one of these points now we will see the mirror plane which is perpendicular to it, so that the proper and improper operations are operating simultaneously. So, the proper operation will take x y z to $\bar{x}$ y $\bar{z}$ which is the twofold rotation and each of these points now we will see the mirror plane and therefore, x y z will go to x $\bar{y}$ z and this one which is $\bar{x}$ y $\bar{z}$ will go to $\bar{x}$ $\bar{y}$ $\bar{z}$. Let me write it down, so that you are not confused.

So, if you have an x y z will go to x y z first will go to $\bar{x}$ y $\bar{z}$. This is the two fold operation. Now, we have generated therefore two equivalent points. Now, these two equivalent points will now see the mirror which is perpendicular to the two fold axis, the improper axis. So, x y that will carry over to x $\bar{y}$ z and this one which is $\bar{x}$ y z bar will carry over to its mirror reflection which is $\bar{x}$ $\bar{y}$ $\bar{z}$.

So, therefore the value of z now is equal to 4 and what are the types of space groups we can have here? We can have *P*2/*m* and *C*2/*m* and these will have now 4 equivalent points z equals 4 and *C*2/*m*. We will have z is equal to 8. So, there will be 8 equivalent points. Now, I want you to go home and work out what are all the possible special positions that can come in this situation. For example, we can locate the object on the twofold symmetry, we can locate the object with respect to the mirror. So, in what way these operations will come up is something which we will see as we go along, but at this particular point we have covered the monoclinic symmetry.

We have covered the monoclinic symmetry in such a way that we look at all the three possible point groups which belong to the system. We have looked at the crystal lattices which are now *P* and *C*, *P* and *m*, we have looked at the lattices which are possible *P* and *m*. Let me go through it with a lazer pointer. We have the three projection, the stereographic projections shown here. The first one corresponds to 2, the second one corresponds to mirror, the third one to 2/*m* and we see the symmetry operations generating the equivalent points just to keep the interest of the chemist, the pharmacists

and maybe even some of the faculty members and also those who are not so very inclined to mathematics biologists for example.

So, just to keep their interest going at this stage what I can say is that if there is a system, if there is a biological system or a chemical system which goes into a monoclinic symmetry. And it crystallizes in such a way that we have *P* monoclinic *P* lattice which will appear, we will not know at this moment how we can identify whether it is *P* lattice or C lattice that will come much later when we do the diffraction experiments. at this particular stage. We now identify whether it is a primitive or *C* centred lattice.

Then, let us say the representation of x here is now replaced by our biological molecule. It could be a small amino acid, it could be a peptide chain or it could be a protein in the long run, it could even be a virus or a collection of viruses particles proteins more than one protein and things like that protein crystallizing with a steroid molecule. So, you have that stored in this particular x and if the space group turns out to be *P*2, then what will happen is there will be such two units in the unit cell here. There is a small suggestion to the biologist that is if there is a biological molecule and that biological molecule has what they define a subunits in the biological molecule. Like for example myoglobin and haemoglobin, myoglobin as a single subunit whereas, haemoglobin has 4 subunits.

Now, the presence of these subunits need not utilize the symmetry. So, the asymmetric unit of myoglobin can still have 4 molecules of individual myoglobin units and then, it may go into a space group to which it belongs to. Let us say it goes to *P*2, then we will have 4 plus 4, 4 units of myoglobin accumulating as a haemoglobin molecule, but there will be 2 haemoglobin molecules in the unit cell and as a consequence we will effectively have the 2 big units of haemoglobin crystallizing in the unit cell.

So, it is not necessary that when we point out an x, it is one single point. It is a collection of all possible atom positions. So, what I write as x y z could be x_1 y_1 z_1, x_2 y_2 z_2, x_3 y_3 z_3 and x_n y_n and z_n, where n is the total number of atoms representing that particular molecule. So, the asymmetric unit if you now consider a symmetric unit will have this all the four units of myoglobin defining the haemoglobin molecule. The haemoglobin molecule has an internal symmetry is a molecular symmetry. So, that particular internal symmetry when it crystallizes may or may not be used in that situation.

In the case of a realistic situation, haemoglobin does not use that centre of symmetry or the symmetry that is present in the 4 subunits. So, therefore that is referred to as a noncrystallographic symmetry. So, for biologists when they read their papers you should remember that is a non crystallographic symmetry. In fact, the presence of non crystallographic symmetry is utilized in structure determination of very large molecules. There are various ways in which people can use this information to the advantage of solving the phase problem and therefore, determine the crystal structure.

So, this I thought is a point which I should mention at this situation, so that there is no confusion when we discuss with respect to x y z and say the x y z goes to x $\bar{y}$ z in a mirror operation. It means that the entire set of atoms associated with the molecule will go to the other molecule. So, that way we have a situation where it is possible to now identify the molecular symmetry and that molecular symmetry need not be associated even though Kitaigorodsky said that molecular symmetry should be associated that is a symmetry which is associated with a single molecule. Here there is a subunits which are related by a symmetry. So, that is a non crystallographic symmetry.

So, there is a difference between a regular symmetry in the molecule, single molecule and the non crystallographic symmetry associated with individual components. So, this is something which I thought you should bear in mind and that is a crucial point which we should discuss when we do the structural determination protocols. So, we have now covered the point group descriptions of triclinic monoclinic.

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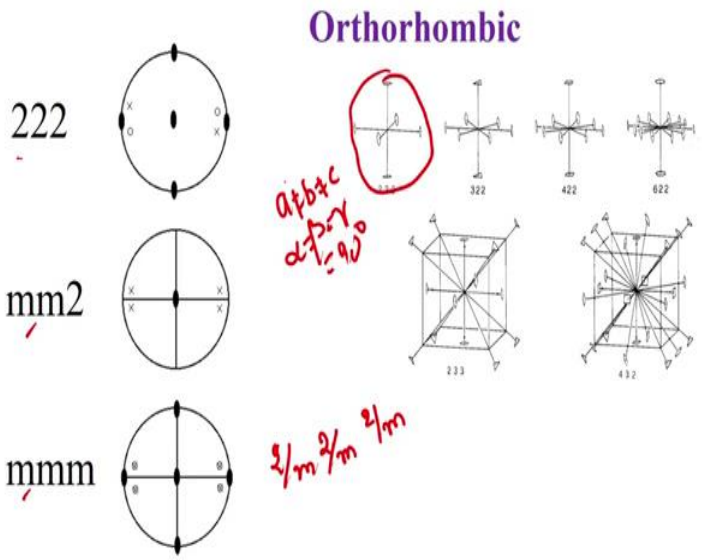

And we will now proceed to the orthorhombic symmetry and then go for the description of individual point groups. Here what I did here was to also overlay the diagram which you have already seen which tells you the orientation of the axis when we have a situation where there is more than one axis of rotation.

So, when we go to the orthorhombic system, we have three axis of rotation which will intersect at a point and Euler's theorem makes sure that if we have two of them, the third-one will automatically come. So, the way in which the orthodontic symmetry therefore comes is an intersection of 3 two-fold axis. So, when we represent the corresponding point group, we should be able to represent all 3 two-fold axis in this diagram and that is how 222 is a diagram where we have shown the two fold axis which comes here at the centre which is along the direction which is perpendicular to us.

There are two-fold axis of rotation also associated with the x axis direction and also the y axis direction. So, that way the two fold axis operation is quite interesting here. Suppose you take this point x, this point x now goes over to that point x. This is the first two operation which is let us say about the x or y or that it does not matter which one in a case of an orthorhombic system.

So, we will say x y z now goes to $\bar{x}$ y $\bar{z}$. That means, it is a two fold perpendicular to the y direction, then the two fold perpendicular to the x direction and the two fold perpendicular to the z direction will also simultaneously operate on that and as a result

you get the 4 equivalent points. So, the 4 equivalent points I want you to take it as a home assignment where you write what are all the 4 equivalent points which I have written here. It is very obvious by looking at the nomenclature how they should be defined, but then this is interesting to see how you will define it. For example, how would you write this to that if I give that example, then you will write all the four. So, I would not give the example except to say that you do see the relationship between these two turns out to be a relation which is the inversion, kind of because you have a open circle and x mark here, but what are the equivalent points of these, how do I get that point to this point notice.

The circle which is going around here is also specially marked. It is there is a darkening of that circle. So, you have there for a two fold axis perpendicular to that a two fold axis along the x direction, a two fold axis along the y, so mimicking this representation. The same representation is carried over down here and you see a difference in the equivalent point position.

For example, in this particular case the two fold axis which is along the z direction is shown here. So, obviously this is telling us that x y z when operated by this two fold rotation will go to -x -y and z. So, here the rotation for x y z going to -x -y z can be written, then you end up with two mirror symmetries; one of the mirror symmetries will generate a mirror symmetry which is perpendicular to this direction which is the x direction and the mirror symmetry perpendicular, let us say this is the x direction conventionally and this is the y direction.

So, both x and y directions represent the mirror. Now, the question comes in the case of the mirror symmetry. You had earlier an x y z and the mirror goes, it goes to x $\bar{y}$ z. Now, here again if you see the x coordinate, here the x y z if you take this as the x y z how will you generate that point. you will generate that point using the two fold rotation using this particular two fold rotation and then, inverting it.

So, because of the fact that you do the inversion operation twice because of the presence of two mirrors here, you will get the same object repeated here. So, you write down the equivalent points of *mm*2 that will be the next home assignment for you. When you write the equivalent points of *mm*2, compare the equivalent points of *mm*2 with that of 222. So, these two space groups are very rare in occurrence, but when they do occur they will

show some certain special properties and those special properties give rise to systems which may show some non-linear effects and so on.

So, these space groups are very crucial for such situations. The next point group is the *mmm* symmetry where we have the three two fold axis now becoming simultaneously mirrors. So, this is in fact equivalent of representing the corresponding full symmetry as I can call it is 2/*m* 2/*m* 2/*m*.

So, there is the simultaneous operation of two fold as well as the mirror which we saw in the monoclinic case earlier on. So, a similar operation occurs here and you now see that the number of equivalent points in case of 222 is 4. Number of equivalent points in *mm*2 is 4, number of equivalent points in *mmm* is 8. That is because we have the two fold operation perpendicular to the mirror will take it onto itself and therefore, you will have 8 equivalent points. All these 3 symmetry operations correspond to this 222.

So, this now orthorhombic symmetry is identified with a minimum symmetry of 222, the point group symmetries therefore become 222 mm2 and *mmm*. The 2 by m 2 by m 2 by m is the highest possible symmetry that can be associated with an orthorhombic system. The number of equivalent points here is 4, the number of equivalent points again in mm2 is 4 whereas, the number of equivalent points in *mmm* happens to be 8. The restriction of course which we have not written, but which you know by now very clearly is the fact thatwe have an *a* not equals to *b* not equal to c. None of these are equal whereas, the angle between them alpha beta and gamma are equal to 90 degrees.

So, the three angles are 90 degrees to each other. They are mutually perpendicular to each other and we have this system which now represents the orthorhombic system. So, just like the monoclinic system was able to generate the 2, the mirror and the 2/*m* orthorhombic generates the 2, mirror and 2/*m* in all three directions because we have the three mutually perpendicular directions. So, therefore orthorhombic symmetry represents an additional set of symmetry elements which can go along with it mainly because of the fact that the angles alpha beta gamma are 90 degrees with respect to each other.

So, even though the geometry associated with the orthorhombic symmetry is simpler, the corresponding geometry which results in the accumulation of all the molecular symmetry inside the unit cell is more complicated. Let me make this sentence a little more clear say if you take a triclinic system. In the case of a triclinic system, you get only two

equivalent points. If it is $P\bar{1}$ bar if it is $P1$, you get only 1 equivalent point. So, the complexity associated with the molecule is less in the unit cell. So, in the unit cell either there is one molecule or two molecules, the relation between these two being only a centre of symmetry. If you go to the monoclinic system again it is not so very complicated because again you will get two equivalent points in two fold equivalent points in mirror and four equivalent points in $2/m$.

So, the number of molecules you can put into the unit cell therefore will be either 2 or 4 or it sometimes depending on the special positions, it could be even 1 or 2. So, the distribute the way in which the molecule now looks at it is to see that it wants to arrange itself in a comfortable way. And as the molecule wants to arrange itself in a comfortable way in the unit cell, the triclinic and the monoclinic ones are preferred. Then, you have very flexible molecules and that is the reason why many of the organic systems with their flexibility and functionality is attached to the organic moieties and so on.

They want to go into the crystal systems which are triclinic, monoclinic, orthorhombic. Very rarely they go to higher crystal systems and in when they do go to higher crystal systems, they will have some exotic properties to display otherwise generally most of the organic systems crystallize either in a monoclinic or in an orthorhombic system because of the fact that the functionalities have lot of freedom associated with them.

On the other hand, if you look at the inorganic materials these inorganic materials are basically built up upon tetrahedral and octahedral units. It is only an association of tetrahedral and octahedral units with linkers which are again not so very flexible and as a consequence most of the inorganic materials they go to higher crystal systems, higher that is crystal systems with higher symmetry. So, tetragonal and beyond tetragonal, hexagonal cubic these are the preferred space groups in inorganic systems.

So, it is very interesting to note this point that the geometry associated with the surroundings of an atom effectively decides what crystal system it should take and therefore, the question of whether the molecule decides the crystal symmetry or crystal symmetry decides the molecule is still unanswered in the sence that the nature is eventually trying to minimize the energy.

So, the minimum energy configuration is what will occur in a crystal. So, in fact if you look at a crystal therefore the way in which the molecules assemble what we eventually

referred to as supramolecular assembly in a crystal molecule is the best way in which molecules can arrange in a supramolecular assembly and this is referred to very often as supramolecule molecular assembly par excellence, the crystal represents supramolecular assembly par excellence.

I mentioned it in between the discussions of our point group just not to keep the continuity going, but also to give you advance information of what we are going to do when once we understand the methods of structure determination. So, this is very crucial. So, now we have finished one of these multi-axis situations we can go to the further multi-axis situations.

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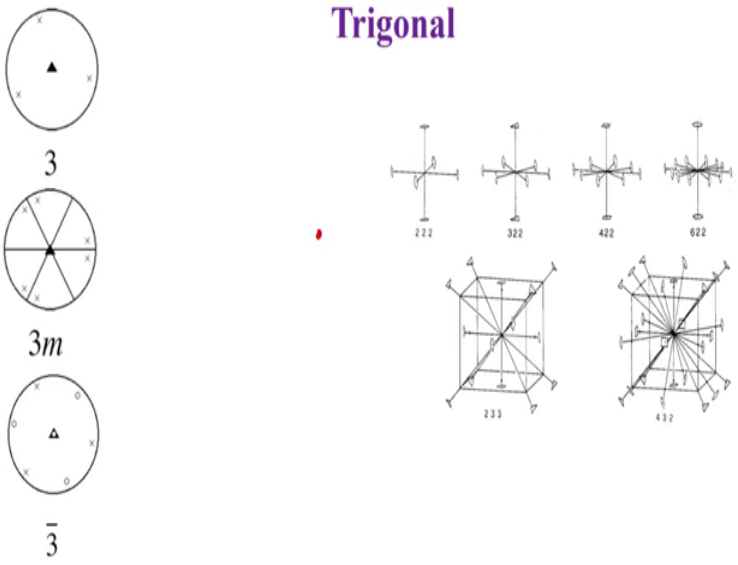

So, we will go to the next slide which is now the trigonal system three fold system. Interestingly when we come to the three fold system, it is it is always decided you know the three fold system can exist by itself which is what is shown here the three fold the 3 with a mirror and $\bar{3}$ system. Notice the difference between this point group 3*m* and the previous point group which we discussed with a monoclinic system, it is 2/*m*. The 2 slash m represents a two fold symmetry and a mirror perpendicular to that whereas, in this particular case the 3 and the mirror symmetry are operational together. That means, there is a second axis that can be associated with the three fold symmetry.

So, three fold symmetry therefore can exist by itself or a three fold symmetry can exist along with another. In other words, we can have a improper rotation or a proper rotation

associated with it and that will generate different space groups, sorry point groups. Obviously, it is different space groups depending upon the type of lattice we associate with the trigonal system. What we will do here after is bringing the space group information associated with this much later when we discuss the Bravais lattice along with the combination of Bravia lattice and the point group symmetry.

Mainly to avoid confusion because the number of space groups will now increase more or less exponentially because up to orthorhombic, we have a large number of systems. In fact, orthorhombic itself can have a primitive lattice, a body centred lattice *A B C* centred lattice and also a face centred lattice.

So, since orthorhombic symmetry can generate so many lattics, the corresponding space groups which can generate are quite large. So, instead of going into the discussion of the space groups with the orthorhombic system right now, we will finish up the assignment of the point groups with the rest of the crystal systems and then, come back to the discussion of associating lattice symmetry and the point group symmetry with individual crystal systems. That will also revise whatever we have done now for you once more and as a result, it will never be forgotten.

The whole idea is that this concept I do not want anyone of you to forget whether you are a mathematician, whether you are a physicist, biologists, chemists. The way in which the symmetry operations happen in these crystal systems because of the geometrical restrictions which get put due to the presence of the symmetry, we should be able to appreciate it the moment we see it.

So, we do not have to study this again once we embedded this in our mind, then we can describe any crystal structure and the description of crystal structure by someone else than in a let us say a paper or a review we can easily comprehend when the reviewer for example in his paper says you know the molecule is generated due to the presence of the twofold symmetry. We now know how these are generated and to that extent the understanding of the point group symmetry is crucial. So, we will go and understand all the point group symmetries before we go further.

So, in a trigonal system the threefold axis can exist by itself that is just the threefold axis as is shown in this place and this diagram here. So, this will now take this x y z and then, take it to this position which is 120 degree rotated and another 120 degree rotation brings

it to the 270 position and the 270 position comes back here and since it is a simple threefold rotation by nomenclature, we write this triangle and a darkened triangle that represents the three fold symmetry. And also, the fact that in the three fold symmetry we also take into account whenever we now associate the three fold symmetry with respect to the unit cell, trigonal unit cell we always associate that with respect to the z axis.

So, the three fold is referred to the z axis. This is a very crucial point because when you now see the location of the threefold symmetry in a trigonal system and the location of the three fold symmetry which you must have that minimum symmetry, the information that should be present in a cube. For example when you go to a cubic system, you will not find the three fold symmetry in the first position of the description. In other words, the first position of the description will now represent the threefold symmetry along the z axis in a trigonal.

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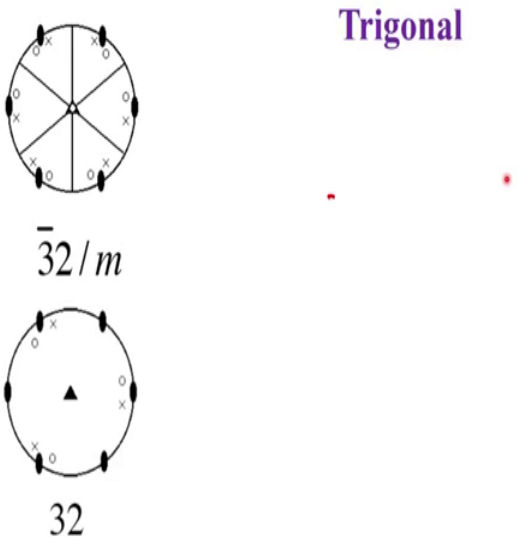

So, there is a space group like for example I will there is a point group like for example here 32 and there is also a point group 23.

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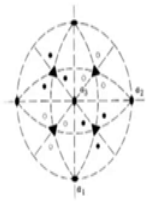

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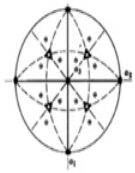
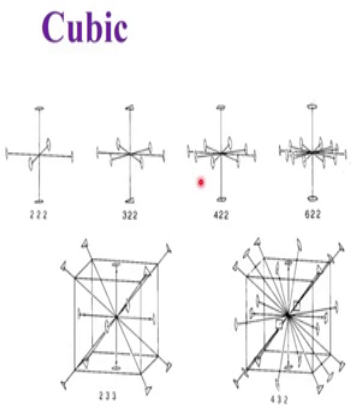


$2/m\bar{3}$



So, the point group 32 represents a trigonal system whereas, you will see here, a point 23 represents a cubic system.