Symmetry and Structure in the Solid State
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Lecture – 05
Point Group Generation

So, just to recapitulate what we did in the last class, we say now that the symmetry elements are associated with a point or axis and or planes.

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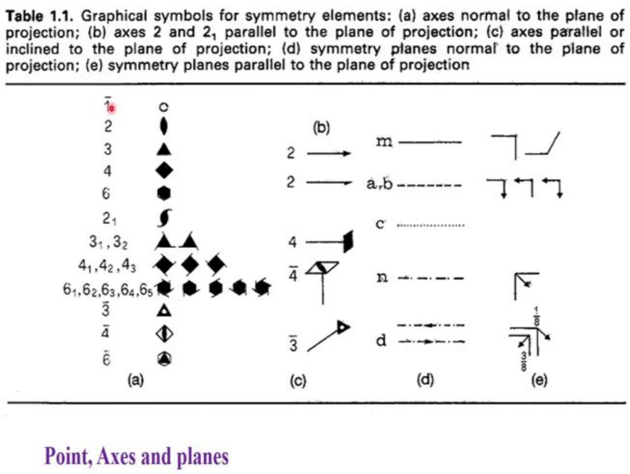

So, the ones which are associated with the axis we have shown they are limited to 1, 2, 3, 4 and 6 in case there is periodicity; that means, in case of crystalline materials we do have only these axes that are present. We of course, have a mirror plane which could be along different directions; mirror plane perpendicular to an axis, mirror plane along a given direction and so on.

We will bring in the issue of various orientations of the planes, but the operation is just that of a mirror plane. So, there is only one symmetry element that will come which is the mirror plane. As far as axis are concerned we get 2, 3, 4 and 6 and as for as the inversion centre is concerned we get this so called 1 bar symmetry.

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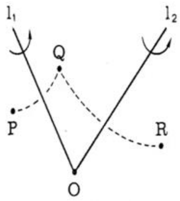
Proper axis	Improper axis	Proper and improper axis
1	$\bar{1}$	$(1/\bar{1} = \bar{1})$
2	$\bar{2} \equiv m$	$2/\bar{2} = 2/m$
3	$\bar{3} \equiv 3\bar{1}$	$(3/\bar{3} = \bar{3})$
4	$\bar{4}$	$4/\bar{4} = 4/m$
6	$\bar{6} \equiv 3/m$	$6/\bar{6} = 6/m$
5 +	5 +	3 = 13

In crystals, with or without Translations symmetry Operations may Coexist

POINT GROUPS

Combination of symmetry axes	α (deg)	β (deg)	γ (deg)
2 2 2	90 (2 2)	90 (2 2)	90 (2 2)
3 2 2	90 (2 3)	90 (2 3)	60 (2 2)
4 2 2	90 (2 4)	90 (2 4)	45 (2 2)
6 2 2	90 (2 6)	90 (2 6)	30 (2 2)
2 3 3	54 44′08″ (2 3)	54 44′08″ (2 3)	70 31′44″ (3 3)
4 3 2	35 15′52″ (2 3)	45 (2 4)	54 44′08″ (4 3)



Arrangement of equivalent objects around two intersecting symmetry axes.

$(x\,y\,z) \rightarrow \bar{x}\,y\,\bar{z} \rightarrow (x\,\bar{y}\,z)$

The next slide I am going to illustrate how these now become point groups and how many such point groups we can generate. So, the first set of axis we will consider or they are limited to the 1, 2, 3, 4 and 6 because it is a periodic lattice and these 1, 2, 3, 4, 6 are referred to as proper axis because they represent if you recollect again the previous classes they represent direct congruence objects.

So, whenever these operations are there 1, 2, 3, 4 and 6 they represent the direct congruence objects. So, objects of direct congruence only will be corresponding to these proper axis systems. So, we can have a 1, 2, 3, 4 and 6. So, a total number of 5 such proper axis alone point groups that we will generate in a given crystal system. So, in crystals with or without translational symmetry as we pointed out so far operations may coexist. See, if there is no translational symmetry like in the case of a 2_1 screw axis we have a translation symmetry.

So, if there is no translation symmetry that is present like in the case of a operation like the inversion centre, then we can combine the one with the inversion centre which will give us the so called 1 bar. What now happens is that the object which is at x y z goes to -x -y -z; that means, there is an inversion axis that is present. The moment we have an inversion axis we if you recollect the previous classes we have objects which are present with this improper axis being present these objects will be of opposite congruence. So, they will be of opposite congruence; that means, to say that we can have therefore, the value of this angle between the two directions which we define being negative.

So, the improper axis therefore, now represent the combination of a proper axis with an improper axis which happens to be the inversion centre. So, if we now combine a twofold proper axis with an inversion centre we will get a mirror. So, we will work out how this happens, below here. Now, we will do the operation of a twofold which will give us x y z which goes over to -x y -z assuming that our twofold axis is along the y-direction. So, the value of x and z now became -x, -z this is the twofold operation and this is a proper axis operation. So, the symmetry that is defining now the point group symmetry is to we take x y z to -x y -z.

In case we have a 2 bar symmetry; that means, we operate a twofold and that twofold operation will now undergo a centre of symmetry inversion. So, there is an inversion centre which now, therefore, x y z is no longer staying at -x y -z, but it goes to its corresponding inversion centre operation; that means, x goes to x , -x goes to a value of x, y becomes -y and z becomes as such z. So, -z becomes z, -x becomes x.

Now, this operation therefore, is the operation of a $\bar{1}$ symmetry because we have taken this value of x y z which is now $\bar{x}$ y $\bar{z}$ and we have operated the centre of symmetry to go to x $\bar{y}$ z. So, the so called equivalent positions with this improper axis operation or x y z and x $\bar{y}$ z. Examine these two carefully; if you examine these two carefully it means to say that you have a mirror plane now and there is a reflection across the y-direction.

So, if the axis was coming perpendicular to the board, if the axis was coming perpendicular to the board the plane of symmetry is with the board and so, we have a point x y z which is above the board now we will go below the board x $\bar{y}$ z and therefore, this now is referred to as a mirror symmetry operation. So, what we therefore, see is that $\bar{2}$ now gets represented as equal to a mirror. So, we have 1 which is a proper axis, $\bar{1}$ is an improper axis, 2 is the proper axis, $\bar{2}$ which is a mirror is an improper axis.

Now, we have to consider the issue that we can at, since the operation is about a point you see this is referred to as the point groups. So, the operation is about a given point and this particular point is identified with respect to x y z. So, the point we have identified is x y z. The space in which this object, which is identified as x y z, is located is governed by this particular symmetry.

So, if the symmetry is 2 we will get xyz equals $\bar{x}\ \bar{y}\ \bar{z}$. If the symmetry is that of a mirror symmetry we get x y z is x -y -z and nothing else. It is a point group because of the fact that if we operate the mirror symmetry again, we will get back x y z. If we operate the twofold axis again we will get x y z and therefore, we now define these as point groups.

So, 1, 2, 3, 4 and 6 which were they which are the proper axis defined 5 point groups. There are total of 32 so, 5 of these are now accounted for. Similarly the improper axis combination with 1, 2, 3 and 4 will give rise to these combinations and these combinations will add another 5. So, totally it has now become 10. We should also realize that since the operations do not involve translational periodicity, both these operations the proper axis operation and the improper axis operation; proper axis is 1, 2, 3, 4, 6 and improper one is the 1 bar symmetry, the inversion centre.

These two operations do not involve any translational component, like we have in the case of a screw or a glide plane and therefore, these now can be combined with each other. So, when we combine for example, 1 and $\bar{1}$ we can show that it turns out to be equal to $\bar{1}$ only. So, there is nothing new which will get created. In other words the presence of the improper axis remains the same, whether you combine it with 1 and make it 1 and $\bar{1}$ simultaneously operating you will get one bar only. Similarly, 2 and $\bar{2}$ now will introduce a combination of the proper axis twofold followed by a mirror symmetry.

Now, what happens to the equivalent points? The equivalent points now will change I will show you in a minute how it will change, the equivalent points will change.

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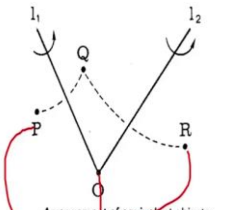

Arrangement of equivalent objects around two intersecting symmetry axes.

$xyz \rightarrow \bar{x}y\bar{z} \rightarrow x\bar{y}z \rightarrow \bar{x}\bar{y}\bar{z}$

So, what happens is now x y z, we are now considering the symmetry operation 2 by m ok. So, we are considering, this operation, 2 by m. So, there is a twofold symmetry and there is a mirror perpendicular to the two fold symmetry. So, this is a different operation than just a mirror or just a twofold axis. So, this is an additional symmetry additional point group symmetry which is illustrated.

So, this now becomes a new point group where what happens is that x y z will now go over to, first there is a twofold operation which will take it to -x y -z, then on the x y z we will also operate a mirror symmetry. So, it becomes x $\bar{y}$ z. So, we call minus y as $\bar{y}$ and then we operate on this the inversion centre. So, we operated the twofold axis we operated the mirror. Now, we can operate the inversion centre. Inversion centre is also operated on the original x y z.

So, you will get -x -y -z. So, the number of equivalent points has double, in case of the twofold axis there were only x y z and $\bar{x}$ y $\bar{z}$. In case of the mirror plane it was x y z and x $\bar{y}$ z those were the two equivalent points. Now, the operation 2 by m that by m means that 2 is the twofold axis, so, let us say about the y axis about the y direction the mirror plane is perpendicular to the y direction. So, 2 by m therefore, defines a new point group because the number of equivalent points now become 4 instead of 2 and this represents a different kind of space altogether, the three-dimensional space.

So, in three-dimensional space therefore, or even in two dimensions for that matter, this becomes a new point group symmetry. So, remember whether we are now talking about two dimensions or three dimensions it does not matter, because the operation is about a point. This point is located in space. The space could be two dimensional, three dimensional or a multi dimensional. It does not matter because we now considering only the point on which the operation is being performed and we have three coordinates x y and z which identify that particular point and that particular point now goes through these operations of twofold followed by mirror and the combination of twofold and mirror giving rise to the centre of symmetry.

This x y z and $\bar{x}$ $\bar{y}$ $\bar{z}$ are equivalent points of a centre of symmetry or we can in fact, better define it as an inversion centre. This means that this particular point group has an inversion centre in addition to the presence of two fold and mirror. Please note this statement that in addition to the presence of two fold and mirror. It will also have a centre of inversion, in this particular case there was a centre of inversion only and that centre of inversion insisted that the twofold went into a mirror symmetry.

In the case of $\bar{3}$ where, however, it is different because the $\bar{3}$ is an operation which goes first the threefold operates and then followed by an inversion centre. I am not going to write down the equivalent points, but I suggest that you work out the equivalent points and find out how the 3 bar now is different because we first operate 3 and then $\bar{1}$ symmetry. Likewise the $\bar{4}$ is similar to $\bar{2}$, but we will have to find out in this particular case there is no separate operation like 3 and $\bar{1}$; in $\bar{6}$ there is a separate operation like 3 divided by m; that means, threefold symmetry for which there is a perpendicular mirror and that results in a $\bar{6}$ symmetry.

So, some of these things can be worked out by looking at various kinds of pictures or diagrams or looking at structures which go into these kind of point group symmetries. We shall do that in a later time when we actually look at molecules and relating the molecules to the space group and so on in which it crystallizes. It is a little premature to discuss those issues right, now. So, we will restrict ourselves to the combination of proper and improper axis. So, 3 and $\bar{3}$ is not going to give us you point group; however, 4 and $\bar{4}$, 6 and $\bar{6}$ will give rise to two different point groups 4 by m and 6 by m.

So, we cut off these two fellows; these two fellows are 1 and the same 3 $\bar{3}$ equals $\bar{3}$ and 1 $\bar{1}$ is $\bar{1}$. So, we generate three new additional point group symmetries and therefore, we have 5 plus 5 plus 3 total 13 point group symmetries which are single rotation axis operations. We have considered only 1, 2, 3, 4 and 6 and in three-dimensional space it is not necessary that we should have only one axis. We can have more than one axis and they can intersect at a point.

So, the point group symmetry is associated with the point. So, at that particular point which is not necessary that we should have a single axis of symmetry, we can have more than one axis of symmetry. One axis could be twofold, another axis could be threefold and so on. One axis could be twofold; another axis could be a mirror. Now, the mirror is not perpendicular to that axis, but the mirror is with respect to some oriented direction which is different from the original twofold rotation.

So, effectively what we can say is look at this particular diagram. This particular construction is referred to as the Euler's construction in mathematics. So, suppose you take a point P and then there is a point O about which we now consider the presence of combination of symmetry axis. So, right now we looked at the combination, no combinations we looked at independent individual rotation axis now we look at combination of symmetry axis.

So, if we look at combination of symmetry axis suppose let us say there is a point P, now it sees this rotation axis. This rotation axis now is centred at O and that rotation axis let us say is a two-fold axis; that means, the if P represents x y z, Q will represent assuming that this is the y direction. It could be any direction for that matter, but assuming it is y direction we will have $\bar{x}$ y $\bar{z}$ as the position Q.

Now, the position Q may look at another possible rotation axis and that particular rotation axis is represented by l_2; l_1 and l_2 are the two rotation axis. So, then Q will go to R by that particular symmetry operation. It could be any of these, it could be a two-fold, it could be a three-fold, it could be a four-fold, six-fold and such combinations we will see how many such combinations are there as a matter of fact in a minute from now.

So, when we do this operation then Euler's theorem states that if you have one operation which is taking the rotation from P to Q and another operation Q to R operating both at the same point O, then with respect to this point O there will be a third axis which will take R to back onto P into in order to define a point group. Remember the point group definition is that we have to get back to the original. If we have a x y z we have an x $\bar{y}$ z then operation of the mirror symmetry will bring the x $\bar{y}$ z onto xyz. So, that definition is very crucial.

So, keeping the same idea in mind if we have a point in space about which there is intersection of more than one symmetry axis, invariably the third symmetry axis is invoked automatically, and therefore, we should have three symmetry axes. Now, because of the fact that we have 2, 3, 4 and 6 we have to consider all combinations of these and when we consider the combinations of these it will end up giving us the angle between these two axis and that is what is given in this particular table.

So, this particular table tells us that if there is a intersection of three twofold axis 2 2 2 for example, one twofold axis going along the direction l_1, another two fold axis of going along l_2, then invariably I should be drawing it I will draw and show you in a second. It should be an axis which will go here such that now R gets related to P by another two-fold axis, ok. So, R and P now get related to each other by another twofold axis and that is the point which we have to think of and we should remember.

So, whenever there are two rotation axis intersecting at a point the third rotation axis is automatically generated because of the fact that we can have proper axis, improper axis and proper-improper combined for a given direction of axis. So, this particular axis may be a proper axis, it may be an improper axis, it may be a combination of proper and improper. So, all these we have to consider.

So, considering these we now look at only the proper axis combinations in this particular table below. When we have only proper axis for example, a proper axis rotation and a second proper of axis rotation will never give the third one as an improper axis rotation. This is the extension of the Euler theorem. See, Euler theorem originally stated that if you have a rotation axis P goes to Q and Q goes to R in another rotation axis the third rotation axis gets created, that is the first part of the Euler's theorem. The second theorem is that when we have this as a proper axis the l_1 is proper, l_2 is proper, then l_3 has to be proper. It cannot be an improper axis, if there is an improper axis we will see what are the combinations that are going to come as we go further in our discussion.

So, at this particular moment what we have therefore, is the 2 2 2 where we have a two-fold axis, a two-fold axis and a two-fold axis. In case of 3-dimensional space if these three two-fold axis are present simultaneously intersecting at a point the requirement is that these three now define three directions and these directions now are with respect to each other at 90 degrees with respect to each other. They have to be with respect to each other.

So, that means, to say that there is some amount of restriction on the nature of the lattice which you are going to generate based on this. There is an angle of 90 degrees between 2 and 2, 90 degrees between 2 and 2, 90 degrees between 2 and 2. The combinations of which the other rotation axis 3, 4 and 6 with 2 2 2 with 2 2 2 is possible. So, there are 4 possible rotation combinations which we can think of and they will give rise to the 90 degree angle between 2 and 3 in case of 3 2 2, 90 degree angle between 2 and 3 and 60 degree angle between 2 and 2.

Now, I want you to digress your mind and go back to the in your notes, go back to the Escher's diagrams and in those Escher's diagrams you will see the relevance of 60 degrees if you are looking at threefold axis. You will see the relevance of 45 degrees, if you are looking at 4 at four-fold axis combining two other twofold axes. In fact, in the diagram which we showed which related the lizards together we had the indication of both the four-fold rotation as well as the two-fold rotation. So, you have to just go back digress your go back a few classes and see how those diagrams are so relevant for the understanding of the combination of symmetry axis which we have just now discussed.

Apart from these 4 combinations only other two combinations permitted under the Euler's scheme; that means, the Euler's rule has to be followed; that means, the P has to come back again itself. So, if we go and operate some rotation axis and go to Q, Q to R then R to P must be repeated. So, if you put that condition no other combinations are allowed except two other combinations which gives rise to 2 3 3 and 4 3 2. There are other combinations like n if there is an n-fold axis, but remember we are restricted to 1, 2, 3, 4 and 6 only because of the translational periodicity.

So, because in the crystalline state only 1, 2, 3, 4 and 6 are allowed, crystals cannot have any other combinations other than these 6 which are represented here and therefore, the 2 3 3 combination and 4 3 2 combination give rise to these kind of angles. You notice that these kind of angles look very scary to you in the beginning, but then once we get a hang of it you will see that these two represent the octahedral and tetrahedral arrangement in cubic systems and we will we will get a better look at this as we go along.

But, at this particular moment, please note that Euler's theorem has to be validated and we in this particular example which we have shown as combination of symmetry axes, we have considered only the proper axis and there are 6 possible combinations of these proper axis and those are illustrated with respect to the angles between them. So, the angles between them also get restricted; that means, the nature of the three-dimensional lattice you are going to get or the three-dimensional unit cell you are going to get will be the same. It cannot be more than these types remember that as we will go further to the next slide.

In fact, this slide is almost immediately relevant, will we have illustrated here the 2 2 2 how the three 90 degree angles come with respect to each other. So, if you look at 2 2 2 here the angles are 90 degrees with respect to each other.

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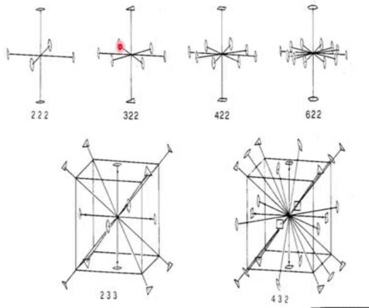

How about combinations

PPP, PII, IPI, IIP

PPP	PII	IPI	IIP	
2 2 2	2 m m			
3 2 2	3 m m	$\bar{3}$ 2 m		
4 2 2	4 m m	$\bar{4}$ 2 m		
6 2 2	6 m m	$\bar{6}\ 2\ \bar{2} \rightarrow \bar{6} 2 m$		
2 3 3	$2\ \bar{3}\ \bar{3} \rightarrow \frac{2}{m}\bar{3}\ \bar{3}$			
4 3 2	$4\ \bar{3}\ \bar{2} \rightarrow \bar{4}\frac{3}{\bar{1}}\frac{1}{m} \rightarrow \frac{4}{m}\bar{3}\frac{2}{m} \rightarrow m\ \bar{3}\ m$	$\bar{4}$ 3 m	$\left(\bar{4}\ \bar{3}\ 2 \rightarrow \frac{\bar{4}}{m}\frac{3}{\bar{1}}\frac{2}{m} \rightarrow \frac{4}{m}\bar{3}\frac{2}{m}\right)$	
6	+6	+4	+0	= 16

The next slide is shown here they 2 2 2 orientation. You see that the three are oriented at 90 degrees to each other. You see the relevance of the presence of the threefold axis in terms of the 60 degree angles because you now get 1 2 3 4 5 6 a hexagonal arrangement of the points on which the point group operation occurs; similarly, the 4 2 2 and the 6 2 2. As I mentioned the relevance of the axis with respect to 54 degrees and some minutes and some seconds and all that issue will tell us about the arrangement of the symmetry axis which is shown here. At this moment we are not going into the detail of this discussion, except to tell that it is not necessary in a crystal lattice if you have a b c directions, it is not necessary that the symmetry should be restricted to those directions. The symmetry axis can be anywhere.

So, these for example, in this case the symmetry axis is not along any given in this case there is it is along the given axis, this axis the twofold axis. But you see that the threefold axis is along the diagonal and in fact, threefold axis along the diagonal is a condition that is required to have cubic symmetry. And, therefore, the symmetry decides now how these proper axis should be oriented, how the improper axis will be oriented in case there is improper axis.

So, we have to therefore, consider not just the PPP, but we have to consider the possibility of improper axis also as combinations in the Eulerian case. So, for example, if there is a proper axis and an improper axis; the first one is a proper axis, the second one is an improper axis, the third one must be improper, it cannot be another proper axis.

So, there is no PIP possible that is because one once we have a proper and an improper axis combination, let us go back to the previous slide. One once we have a proper and improper axis combination and we generated an improper axis in there as a consequence. So, suppose we have a 3, 4 and a 4 bar the third axis should be improper. So, the combinations therefore, get restrain to PII, IPI and IIP. So, these are the things which essentially restrict to four.

So, four possibilities are there P PPP, PII, IPI and IIP and these combinations therefore, are illustrated below and this now define the remaining part of our point groups. See remember we had 13 point groups proper improper and proper improper combine that gave to 13. And we have to now reach 32 which is the 32 point groups that are allowed in crystalline materials and therefore, we have to can have these combinations.

So, if you have all proper combinations as we saw just now with respect to the angles which are these, the 6 of these. So, we will give rise to six of those. Now, the requirement that it has to be a PII combination, will generate these 6. It so happens that all these six are not independent of each other and in fact, for that matter the 2 $\bar{3}$ will generate system which is 2 by m$\bar{3}$ $\bar{3}$. So, here you see that all these six are again degenerate. There are different kinds of point groups. These 6 are a set of point groups, these 6 are a new set of point groups; that means, 6 plus 6 now 12 point groups additionally to the 13 we have already seen.

Now, these are independently generated point groups and therefore, these combinations will have to find a place in the crystalline systems which we are going to have. So, this is the reason, this is the basis of why there are different crystal systems. If there was no differences in the crystal systems we would not have had these combinations. Now, these combinations therefore, decide how our lattice should develop into different crystalline motifs. The so called seven crystal systems which you have studied in starting almost from your standard 12 is a consequence of this.

So, you would have never asked this question in school that when the teacher said there are 7 crystal systems you believed it like well, god is there, right and then we never asked any questions. Now, the 7 crystal systems come as a consequence of the presence of the point groups and the combination of these point groups in three-dimensional space, which obeys periodicity. So, very interesting, crystalline state therefore, is the most interesting way in which we can study the objects because now the objects are kind of restricted. It is like you know in a class the students are all sitting in their respective places and we get them arrested in those places so that attention comes to you.

So, the attention if we want to get of the students one once the class is over is almost impossible. So, when they are restricted to those positions, these positions which we are restricted will generate the so called point groups and the presence of the satisfaction of the periodicity is a fundamental requirement and that induces the possibility of seven crystal systems. So, the 7 crystal systems and thirty two point groups now are very easily understandable in terms of the requirements of symmetry which govern the periodicity in the given system.

So, this is the state at which we see that we do now start getting the information on all possible point groups. Again to define the point group you should remember that the point group has this condition that if you have a point on which you operate this symmetry, the repeated operation of the symmetry should bring back the same point and unless that happens you cannot call it a point group. Putting that condition and also the condition that there is periodicity in the lattice that is a repeats along the a direction x direction b repeats along the y direction and c repeats along the z direction we have these restrictions of having 1, 2, 3, 4 and 6.

So, 1, 2, 3, 4 and 6 will give rise to the possible crystal systems, and then the combinations of these with respect to PPP, PII, IPI and IIP will give rise to the other crystal systems. So, these direct crystal systems which we can get or the orthorhombic, the trigonal, the tetragonal and the hexagonal systems and then these two now give rise to the cubic system. If none of these symmetries are there and there is simply a 1 symmetry or a $\bar{1}$ symmetry that defines the monoclinic system. And, in this therefore, the case where there is twofold symmetry or mirror sorry, it defines the triclinic system correction. And, in case we have the mirror plane or the twofold symmetry it defines the monoclinic system.

So, therefore, we have seven crystal systems, the triclinic system representing 1 and 1 bar the monitoring system representing twofold, mirror and 2 by m and therefore, these things which we say now 1 and 1 bar belong to triclinic, 2 mirror and 2 by m belong to monoclinic and then 2 2 2 to a 2mm belong to the orthorhombic and so on.

So, therefore, we have the orthorhombicity, the triclinic, the trigonal nature, the tetragonal nature, the hexagonal nature defined in these cases and then the cubic symmetry which is what also referred to as the isometric system because this system does not have any restrictions along given a, b, c directions. Now, since there are no restrictions and on given a, b, c directions we will see what kind of restraints we can put to define these seven crystal system as we go to the next class.

So, at this moment we will stop at this particular point and go over to the next class.