Symmetry and Structure in the Solid State

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Lecture – 20
Space Groups 3

So, we have been looking at the Generation of Space Groups and the way in which the equivalent points arrange themselves in the unit cell. The simplest of the space groups is *P*-1; of course *P*1 being redundant as it has no symmetry operation.

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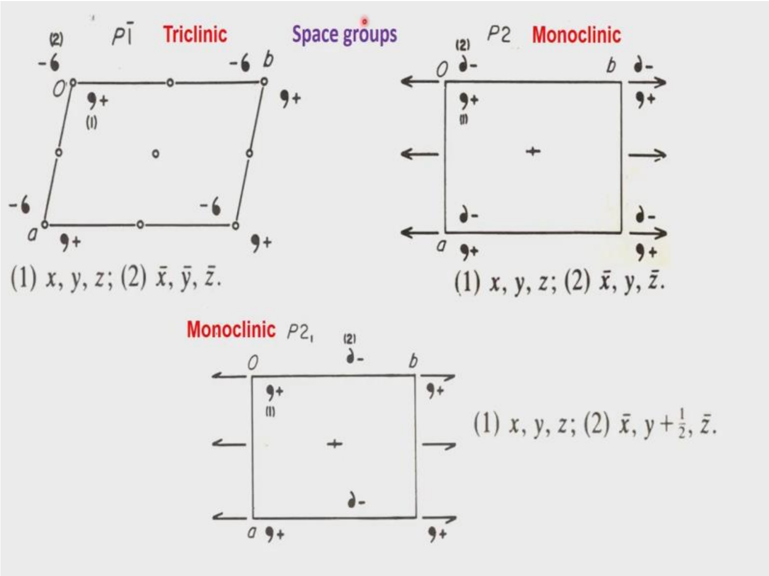

In a triclinic system *P*-1 is only allowed space group other than *P*1 and this space group has a center of symmetry. The presence of the inversion center is shown with respect to the equivalent points here. So, we have taken the object to be in the shape of a comma, it could be a molecule an atom ion or whatever. And the plus sign here indicates that it is in the forward direction and the minus sign indicates it is in the backward direction.

So, we did the generation of the equivalent points found out the presence of centers of symmetries at different positions other than the origin, one of course, due to translation along "*a*", another due to translation along "*b*" and halfway points getting the centers of symmetry. And as a consequence of that this symmetry operation which goes outside of the unit cell can be brought into the unit cell by 1 unit translation along "*a*", 1 unit translation along "*b*". So, it is actually representing two such units to such objects in the unit cell we call them the number of molecules or whatever number of units number of objects inside the unit cell in this case it is 2.

So, we extended this to the monoclinic system the point group symmetry is being 2 and 2/*m*. The point group symmetry 2 gives raise to in the primitive lattice 2 cells *P*2 and $P2_1$. So, the presence of the two fold axes and the presence of the 2_1 axes we discussed, and we see that these equivalent points get generated as are marked here.

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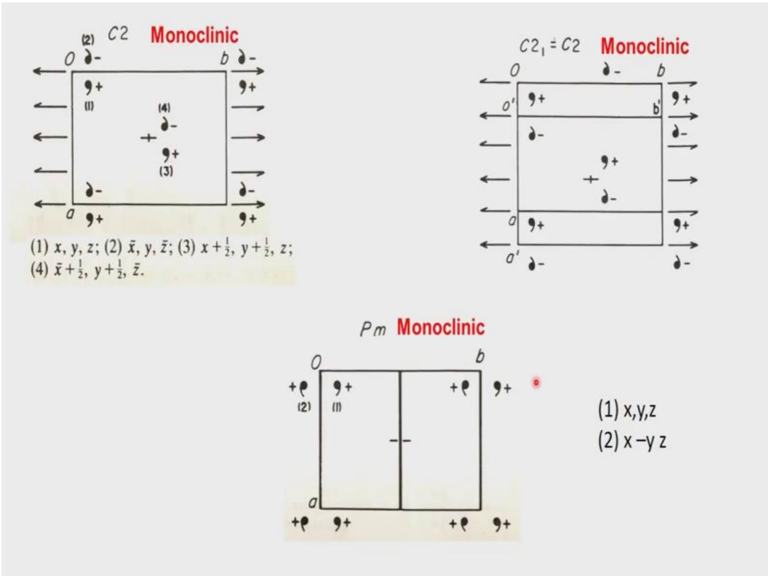

Then, we also looked at the possibility of the centering of the lattice in a monoclinic system and *C*2 and $C2_1$ get generated. We also indicated that $C2_1$ can be changed to *C*2. This is just a recollection of the previous class.

Then, we introduce the next symmetry element after the point group symmetry 2; we have the point group symmetry *m*. We looked at the monoclinic symmetry primitive and then we find further and looked at the monoclinic symmetry *Pc*, with *P* is the primitive and "*c*" is the glide plane. So, then we looked into the mirror symmetry operation with respect to the *C* centering and then we had arrived at this point where we had the *Cc*.

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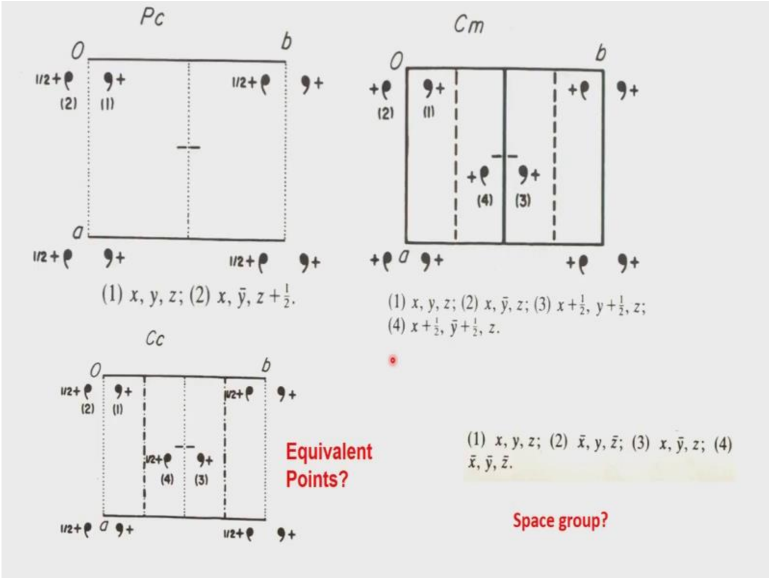

Now, so just keeping the logic of arguments going if one looks at this particular diagram, suppose you are given only this diagram and then the positions of the equivalent points. In this case of course, both the positions of the equivalent points and symmetry operations are given. But suppose you are given only these equivalent points in principle. One should be able to get to the equivalent points, one should also be able to get to the equivalent points when once we are given the symmetry diagram and that is what you will find when we go and discuss the international tables later on.

But at this particular moment in this case suppose you are asked to find out the equivalent points how would you go about it. Of course, I have already marked 1 2 3 4 for your convenience, so there are four equivalent points in *Cc*. So, the way they are the objective way in which we go is to take this point which is marked as 1 as *x y z*, corresponding to the coordinates *x y z* then because of first you operate the *C* centered lattice symmetry; that means, the lattice symmetry gets the predominance prominence.

So, when once you operate the *C* centering that means, there is a *1/2+x* and *1/2+y* added to the *x y z*. So, suppose we call 1 as *x y z*, then we have a point number 3 which is marked here which is due to the *C* symmetry operation which is half this is the a direction, so *1/2+x* and then there is a "*b*" direction *1/2+y*, so we get this point. So, these equivalent points one and three are generated by the *C* centered lattice.

The glide operation which is now coincident with the origin, so that is the glide is perpendicular to the origin and therefore, we get a glide operation which takes this mirror symmetry and in the direction coming towards you along the *C* direction it adds a half. So, the glide plane "*c"* now operates the mirror on one and then adds a half.

So, this is the point 2, so we therefore, get this as *x* and *y* this is the mirror symmetry, so we get *x -y 1/2+z.* So, therefore, we can actually arrive at the equivalent point the first equivalent point being *x y z*, this is *1/2+x 1/2+y z* and this is *x -y 1/2+z*.

Now, what about what happens to this? This particular point this particular point can be translated by 1 unit and if you translate by 1 more unit it goes out of the unit cell so, but in this case if you translate it by 1 unit, it comes to this point, half plus this object. Now, what a what you see here is that, there is a by definition we are never there is a symmetry operation at 0 and the symmetry operation 1 unit translation the same symmetry operation will develop at half position.

So, using this half position the *c*-glide we can generate its corresponding *c* operation c-glide operation, so that means, this now goes into a mirror symmetry and then it adds on half in the direction of *C* and therefore, we get to this point 4. So, one can therefore, in principle given this picture write down the equivalent points.

And in the next slide I have shown what are those equivalent points.

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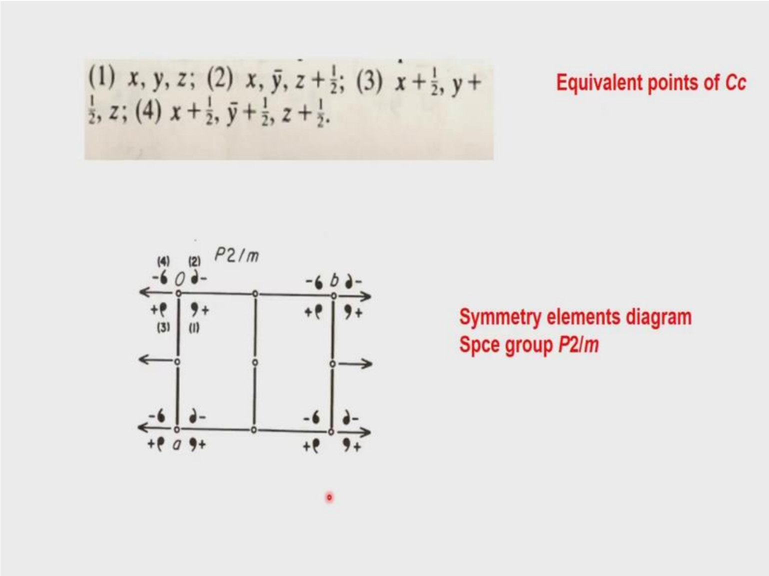

Those equivalent points are *x y z*, *x -y 1/2+z*, *x+1/2 y+1/2 z*. So, as you see that this is the c-glide operation and this third is the *C* centering operation and then the c-glide operation on this object which is due to the *C* centering we now operate the *C* sorry this is due to the c-glide we operate on the c-glide the C centering operation. So, now, this goes to x+1/2 -y+1/2 and z+1/2. So, these are the 4 equivalent points. So, the take home lesson here is that given this diagram in principle we should be able to write the equivalent points.

So, this the next example we can take up is given the equivalent points like here, given the equivalent points as is given here you will be asked to determine the space group. So, if one ask that question in this particular case it is a very simple example, in principle you should be able to identify the space group.

So, you see here point 1 and point 2 they are related by what? They are related by a twofold axes perpendicular to the y direction. So, you have a twofold symmetry. And you also do not have any *1/2+x 1/2+y* or *1/2+y 1/2+z* or for that matter *1/2+x 1/2+z*, so that means, that the centering is not seen.

Generally, since the monoclinic symmetry is *C* centered you should have equivalent points 1/2+x 1/2+y and that since that is not appearing this is a primitive lattice. So, the first conclusion is examine the equivalent points, find out if there are any half translations associated with *x* or *y* or in this particular example of a monitoring symmetry and then you see and conclude that it is a primitive lattice.

So, we have found that it is the primitive lattice. It has a twofold symmetry. Now, if you look at the point number 2, it is a mirror operation perpendicular to the "b" direction. So, we have a twofold symmetry along the "b" direction a mirror plane perpendicular to the "b" direction; that means, it has and that also has a center of symmetry equivalent point which is *x y z* going to *-x -y -z*.

So, we are now looking at a central symmetric space group. So, the way logical way to go about when equivalent points are given is to first see whether it is a the like type of lattice. So, suppose it is a primitive lattice like here, identify the primitive lattice. Then look for the existence of *x y z*, *-x -y -z* that will tell us that it is a center of symmetric system, and then you look for the operation of the twofold in the operation of the mirror symmetry as we see here. So, if this is very easy to conclude the space group is *P*2/*m*.

So, when once we conclude the space group is *P*2/*m* in principle we should be able to generate at equivalent point diagram, and also a diagram for the symmetry positions. This is something which you will have to practice taking some examples of other space groups, this I have taken an easy example for you to illustrate the whole thing and that is given here. So, you see that there is a twofold axes about along the b direction.

So, the twofold notation is here the twofold notation is here because this is along the "b" direction we are giving the *ab* projection. We are looking down "c", so this angle is 90 degrees it is a monoclinic system primitive lattice and then we have these four equivalent points around the centre of symmetry. So, 1, 2 which is generated by the twofold axes symmetry, then the mirror symmetry from here goes there and then the central symmetry operation takes it over there.

So, therefore, these are two and these three of them can be brought inside by translational symmetries as we discussed before that is point number 4, we will go undergo a translation along the a and translation along "*b*", we get this and so also this one translation will bring it here, this is one translation will bring it there. So, there are four equivalent points in the unit cell.

We also have marked the mirror symmetries as the dark lines here. They appear at the edge cell edges as well at the central point. And the axes is about the y direction, so no other thing happens except that one once the centre of symmetry develops here there will be a centre of symmetry up there.

Now, because of the presence of the centre of symmetry up there this will also see now a 2/*m* operation and therefore, we have these kind of equivalent points. I will leave it to you as a home exercise to find out the presence of special positions in this space group. Since, we have discussed the special positions in detail in the earlier classes it not be very difficult, but then it will need something here why or do or special positions allowed in this space group, if so how many of them are allowed. And when we actually go into the examination of the international tables entries you will see that, all these things are given in the entry and it is just a question of interpretation of the entries in the right context.

So, this therefore, now brings us to the understanding of two of the symmetry elements. In fact, we today we have seen the *Cc* the presence of the mirror point group symmetry, we have also seen the presence of the presence of two as well as a perpendicular mirror. So, this now this space group analysis now tells us about the fact that we are now looking into the center of inversion related space group. All the earlier space groups *Pc*, *Cm*, *Cc* belong to the non-center of symmetric space group.

So, what really happens is that when objects get into these kinds of space groups there is always a possibility that they will have a homo central non-central symmetric presence in this structure. Some of them for example, in the case of an organic molecule they may even have a asymmetric carbon.

But it is not necessary that a asymmetry carbon should be present in these three symmetry systems because we have a mirror. So, the presence of the mirror can always invert a central symmetric or an asymmetric carbon as well. So, what we have to look for is the fact that there is no *-x -y -z* coordinate system, in these three space groups and therefore, these three space groups belong to the non-centre of symmetric space groups.

Crystals have a tendency to prefer and crystallize in a given space group depending upon their symmetry as we already saw. The molecular symmetry decides what kind of a crystal symmetry it should occupy. So, having kept that in mind we will now go further and discuss the presence of the 2/*m* symmetry. We have already seen the one with the primitive system, now we have to see the combination of the twofold axes with the mirror.

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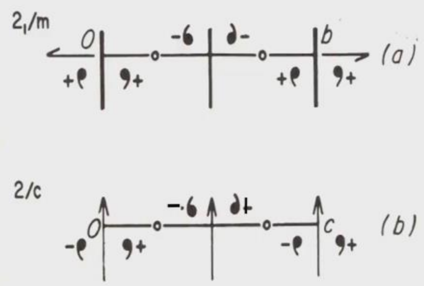

Figure 3.34. (*a*) $2_1/m$ with screw in *b* direction and mirrors at $b = 0, \frac{1}{2}$. (*b*) $2/c$ with *c*-glide perpendicular to *b* and axes at $c = 0, \frac{1}{2}$.

Now, when we are talking about the presence of the twofold axes with the mirror something very interesting develops here. So, now, you take for example, this is the "*b*" direction and your twofold axes is along the "*b*" direction as is indicated by the half arrow. And at the origin we have an intersection of the 2_1 axes and the mirror. So, this is the origin O at which position we have the intersection of the twofold axes on the mirror.

Now, the presence of the twofold axes on the mirror generates equivalent points and we have taken a one dimensional, 1 unit example along the "*b*" direction. You see that the operation of this the mirror operation on this particular point will take you over there. And the 2_1 screw operation will go up here twofold rotation and a half translation.

And then the twofold rotation and half translation will bring this object which is now 1 unit translated of that object, and these two are now you see that there is a centre of symmetry which develops at this point. The point at which the presence of the center of symmetry is found in the $2_1/m$ system is one-fourth removed because the mirror repeats itself at half position along the axes. So, the centre of symmetry repeats at one-fourth.

The convention in crystallographic nomenclature is not to have a center of symmetry if there is a center of symmetry in the system, it should coincide with the origin that is nomenclature and therefore, the it is a rule that the centre of symmetry becomes the origin. That means, we have to now shift this O to this position. When we shift this O to this position you see that we now develop a one-fourth position mirror.

So, the mirror now suppose, this is our origin the mirror now comes at one-fourth removed from the centre of symmetry and then we will also have another mirror which comes at three folds as a consequence of the centre symmetry being present at the half position.

So, let me repeat. If you have the 2_1 fold and the mirror intersecting with each other the presence of the mirror symmetry and then 2_1 screw axes perpendicular to that you are shown here in the direction of the "*b*" axes. The first operation is the 2_1 screw axes, so you take this rotate by 180 degrees and translate by half the unit along the "*b*" direction and you will get this object. You see that the object now is going down and this object is on the top.

And this object now again sees the centre of symmetry, sees the mirror symmetry here and there is a mirror reflected operation. There is a mirror reflected operation here, there is a mirror reflected operation there at the half position and also there is a full position mirror reflected objects. So, you have 1 unit translation along this direction which takes this object this object sorry, this object onto that one and the mirror symmetry operation brings it back in. So, these are the four operations which we get, four symmetry positions we get inside the unit cell along the "*b*" axis.

The fact that this happens brings in the presence of a center of symmetry invokes the presence of a center of symmetry at one-fourth removed from the origin. The origin being the position where the 2_1 axes and the mirror plane intersect.

The crystallographic nomenclature and the crystallographic follow up of rules tells us that whenever there is a centre of symmetry the centre of symmetry should be at the origin 0 0 0. So, what we therefore, do is, we take this position O and move it to this origin.

So, now O is in this particular position. If O is in this particular position there is no other change 2_1 screw axes is going through this centre of symmetry at 0 0 0, so the presence of the 2_1 screw is not altered because it is going through the centre of symmetry at 0 0 0. What is altered is the position of the mirror plane the mirror plane now moves by one-fourth.

So, if you have an operation which has a translation involved component, along with that a component which is no translation involved component the no translation involved component moves away by one-fourth from the origin. The origin now is identified with respect to the presence of a center of inversion.

So, the center of inversion or the center of symmetry in the crystal system is now at 0 0 0, mirror comes at one-fourth and then you have the 2_1 screw are coinciding with the center of symmetry. So, this therefore, gives us the $2_1/m$ symmetry and this is where we have to be cautious in deciding the equivalent points, because the equivalent points now will change their faces in the sense that if we have the $2_1\backslash m$ operation here the mirror operation will take using this as the origin. It will take $x\ y\ z$ to $x\ {-y}\ z$.

On the other hand, the mirror operation which is now here if this is the 0 position, then this particular mirror operation the coordinates will change. The coordinates will change in such a way that the presence of the one, the mirror at one-fourth away from the center of symmetry needs to be recognized. So, this is as far as the $2_1/m$ symmetry is concerned.

Now, we will go and discuss the possibility of 2/*c*. Again, you remember that c has a half component, half translation component. So, if *c* has a half translation component then what is the way in which you infer where are the axes that will be located. For example, the twofold axes where do you think they will be located. The twofold axes now will be coincident with the origin.

Let us examine this carefully. Notice, that now instead of showing the "*b*' direction and showing the '*c*" direction, this is very important. So, this shows now the '*c*" axes not the "*b*" axes. See for all descriptions of the monoclinic systems we have taken the "*b*" axes. Here we are showing the "*c*" axes keeping in mind that the unique axes is still "*b*". The unique axes is still "*b*" in this example as well.

So, if you now look at the way in which the symmetry operations get disposed you will see that is a twofold axes, which will coincide with the origin and the presence of these twofold axes will generate these two points. Now, this point 1 unit translation will go there and this point 1 unit translation will come here. This will tell us that there is a twofold axes at the half position as well

Now, the fact that there is a there is a twofold axes here at 0, and the twofold axes at half, under twofold axes again at this particular position will generate the *c*-glide operation which is now remember this is the c axes. So, the half translation is along the *c* axes. So, you mirror reflect it and translate by half unit, and this point gets generated.

You notice that there is a relationship between this point and this point, and that is the presence of the inversion center. So, the presence of the inversion center is automatically invoked. And as we discussed in the previous example the presence of the centre of symmetry now should become the origin. So, we shift the origin to 0 0 0, to the presence of to the centre of symmetry. So, the O is now moved over here.

So, what therefore, happens is the, non-translation involved symmetry element. What is the non-translation symmetry element that is involved here? It is the twofold axes. So, the twofold axes now moves by one-fourth. So, this moves by one-fourth away from the centre of symmetry that will also generate the symmetry at threefolds.

So, as is written here $2_1/m$ with screw in "*b*" direction and mirrors at b is equal to 0 and half. The mirrors are now at 0 and half as is shown in the diagram, but we now know we have to shift it to the centers of symmetry. So, the centre of symmetry up here now has a mirror at one-forth and three folds. And so also the presence of the c-glide invokes the moving of the twofold axes by one-fourth from the centre of symmetry. So, the non-translational symmetry two is moved by one-fourth.

Now, what is the consequence of this when we generate the space group diagrams? And in what way this influences the presence and description of the equivalent points. There are two ways in which we can argue with result. See the one of the things is that we have this condition of the definition of a space group. When we say the points belong to a space group then when we keep operating the symmetries we should get back to the original point.

Now, if you take this for as the origin the intersection of the mirror and the 2_1 you are *x y z* will see both 2_1 and mirror and apart from that operation, we do not have any further operation at that particular point with respect to 0. The fact that the center of symmetry develops at one-fourth position is not going to give us back the *x y z*, in other words if you take this point as *x y z* you operate the 2_1 symmetry on this one, you will go to that point which is which is what *-x -y -z*. So, you get the *-x -y -z* you get the *x y z* and the fact that this has happened is because of the operation of the 2_1 screw.

Then we have *x y z* and this point which is the mirror symmetry where which will take us to *x -y z*. So, the presence of the symmetry at *x -y z* and the at the origin and the presence of the symmetry 2_1, if we keep operating again one of them or operate them together, we will not get back to *-x -y -z* ; -x -y -z will not get invoked and therefore, the space group points will not complete the definition of a group.

So, mathematically in order to complete the definition of a group, it is required that we move the centre of symmetry to the origin. When once we move the center of symmetry to the origin, we already know the *x y z* and *-x -y -z* are two equivalent positions with respect to the centre of symmetry, and the rest of the equivalent positions can be generated as we can see when we go to the next discussion.

So, since this part is a little tricky and this is not explained in any detail in any textbooks except for this one which is the textbook of Stout and Jensen. I thought that. In fact, in Stout and Jensen there is a mistake on one of these equivalent points as well which we I think we have corrected and therefore, it one has to be careful in looking at some of these you think the correction is up here, in this particular position.

So, what we will do therefore is to see that whenever we have a translation involved symmetry that is associated with the space crew along with another symmetry operation which is a non-translational symmetry operation or for that matter if it is a symmetry operation. Suppose, we go to $2_1/c$ we will see that in a little while, that $2_1/c$ will invoke translations of both the symmetry elements.

So, the take home from this particular slide is whenever you have a non-translation involved symmetry element that particular non-center the non-translation involved symmetry element for the fact that it is a center symmetric space group because 2_1/m will translate itself to a *P*2/*m* point group. Since the point group is 2/*m*, it will represent a center of symmetry.

So, the presence of the centre of symmetry invokes the requirement that we should have a center of symmetry in the system. The fact that we have a center of symmetry in the system we have to associate that with 0 0 0. So, when once we do that operation what is, what we have to remember is whenever there is a non-translation involved component that is the one which moves by one-fourth and the translation component will stay along with this center of symmetry.

The same is true in the case of 2/*c* you see that the twofold axes which is going perpendicular to that stays along with the center of symmetry whereas, the sorry the glide plane stays along with the center of symmetry, the non-translational symmetry element the twofold is moved by one-fourth.

Now, this two observations have to be incorporated when we now discuss the space groups which involve non-translational periodicity associated with them. Space group like *P*2/*m*, space group like *P*2/*c*, space group *C*2/*m* which is also $C2_1/m$ as we have seen $C2_1$ and *C*2 are one and the same, then of course, *C*2/*c*. We will also have the combinations of both these having translational symmetry because a point group 2/*m* can generate a centre of symmetric space group $2_1/c$. So, we can have two additional space groups $P2_1/c$ and also $C2/c$.

So, we will have to now examine these and that will in fact, complete all the requirements of a monoclinic space groups. So, as you see from a single center of symmetry when we go to the presence of a minimum symmetry of a twofold and a maximum symmetry of $2/m$ in a monoclinic system, three point groups now will generate several space groups.

So, the number of space groups are now increased enormously compared to the two that is associated with the triclinic symmetry. Therefore, we have the condition here that the $2_1/m$ operation will now shift the mirror plane by one-fourth and the $2/c$ operation will shift the twofold symmetry by one-fourth.