Symmetry and Structure in the Solid State
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Lecture – 19
Space Groups 2

So, now we will go further to the next crystal system, which is the monoclinic system. Monoclinic system as we know is associated with three point groups. 2, *m* and 2/*m* these are the 3 translation free point groups.

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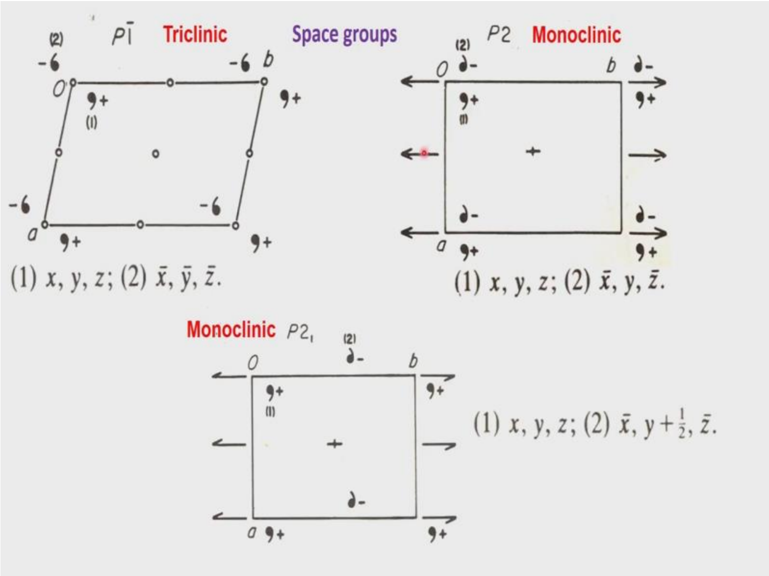

Because of the fact that we have 3 dimensional periodicity, we get into the introduction of two other additional symmetry elements which are the screw axes as well as the glide planes. So, we have to now consider the combination of the Bravais lattice with the presence of the twofold and 2_1 screw the mirror and also the associated glide planes. So, we will thereby generate several space groups.

So, the first space group among these is the twofold symmetry associated space group *P*2, and here what happens is that if you have an object which is x y z which is sitting at point 1, which it looks at and it undergoes a twofold rotation, it goes from x y z to $\bar{x}$ y $\bar{z}$. The location of the twofold is now could be anywhere along the b direction. So, the value of the y is arbitrary, whatever is the value of x and y it will change to -x -z, but once we fix the value of y, then the value of y will remain unchanged.

So, the location of the twofold axes could be anywhere along this direction. As a result we do not get any other positions associated in the b direction. Notice that this is a projection of *ab* looking down the c axis and therefore, the angle between a and b is 90 degrees. So, this is a nice rectangle. You also notice that when once we have this twofold axes associated with b direction, in the *ac* plane particularly with respect to the a value which we have shown here in the projection, there will be an additional development of a twofold axes at half position by definition.

Any periodic repetition as we have seen will repeat its symmetry at half the distance and therefore, we have this at half the distance. And this half the distance repetition will have allow for the possibility of this point being related by a twofold symmetry.

So, it not only generates that point why in the normal twofold operation the translation per 1 unit is generated here and these 2 objects are related by the twofold symmetry and these are the 2 objects we will see in this space group. And therefore, this is Z is equal to 2 and in this Z equals 2 we can always have an object associated and sitting on the twofold symmetry.

Suppose you have a twofold symmetry objects just like the pointer here the laser pointer here, it has a twofold symmetry it is a circular point. So, it has all kinds of symmetry. So, twofold is also incorporated in the laser pointer. So, the laser pointer therefore, has a twofold symmetry and suppose it sits anywhere along the length of this, you see that half the object on the top and half the object on the bottom are related by a twofold symmetry and as a consequence this will be the special position in *P*2.

And then we also have the possibility of the same special position coming at the repeat distance along the a direction. So, other than that we have only the general positions x y z and $\bar{x}$ y $\bar{z}$ and this generates 2 equivalent points and the equivalent points on one translation take the objects outside of the unit cell and so, therefore, Z is always 2 in an operation *P*2. Suppose we now want to consider this projection such that it is we show the *ac* projection. If we show the *ac* projection you remember and you recollect that the two fold axes now will be represented by a set of symbols, which are now perpendicular to the 0 position and that you should keep in mind.

So, what is shown generally in all the projection diagrams including the international tables per crystallography, unless otherwise specified the projection is down x is a and down y is b and c is coming either in a perpendicular order going inside the board in a perpendicular direction. So, it is not necessary in a case of a monoclinic system, it should come in a perpendicular direction. So, this angle is β. So, the vector which comes out from the origin is at an angle of β. So, which is not necessarily the value, that it should be 90 degrees. So, that is a very important point, do not think that this is now coming in the direction at 90 degrees this comes at an angle of β.

And that therefore, qualifies this complete description of this space group *P*2. The addition of a half translation is invoked in the case of a 2_1 screw axes. So, instead of a twofold axis if we have a 2_1 screw axis, then you see the operations very clearly that x y z now will undergo a twofold operation and after the twofold operation we will see there is a half translation along the direction of b. So, in this particular case you have x y z, the rotation axes is y and therefore, the translation is along the y direction. So, x changes to -x z changes to -z; so, you generate this by twofold symmetry operation plus a translation along the direction about which the axes operated and so, we get to this position.

Now, this position on one translation will bring it down here, telling us that we do have a twofold symmetry operation at half position and these 2 now become the equivalent points in the unit cell corresponding to the coordinates x y z, $\bar{x}$ ½ + y and $\bar{z}$.

Notice that we can also have the twofold through axis symmetry at 0 as well as one the presence of the translation periodicity has brought as the additional 2_1 screw axis just like the logic we use for *P*2 and also to the triclinic system.

So, these are the 3 simplest of the space groups we can discuss with respect to the equivalent points, with respect to special positions and with respect to the a generation of the equivalent points and Z is equal to 2 and if there is a object which has a twofold symmetry then Z will be equal to 1.

If there is an object which is in $P2_1$, then there would not be any special position because the translation associated will destroy the possibility of having the special position; that means, the we cannot have these object because this particular object cannot have a twofold rotation followed by half translation within the rotation axis. That means, if it is here and it goes there, you still have the 2_1 operation possible, but then the chances of such objects being in the $P2_1$ symmetry are very little. So, twofold axes has a special position 2_1 axis can also have a special position I agree, but then we have to see it depends purely on the nature of the object. The object will not have its symmetry which is now including the translational part of the unit cell and therefore, the special position in $P2_1$ is not possible.

We go further now the possibility of now combining the presence of the second lattice which is available in a monoclinic symmetry and that is the *C* centered lattice. We saw the primitive lattice the *C* centered lattice now we are looking at the possibility of the twofold rotation being associated. So, we are going systematically, we are looking at the lattice symmetry first then the lattice symmetry changes from *P* to *C* then we look at individual point groups. So, far we have seen 2 and 2_1 in case of the primitive lattice now we see 2 and 2_1 in case of the centered lattice.

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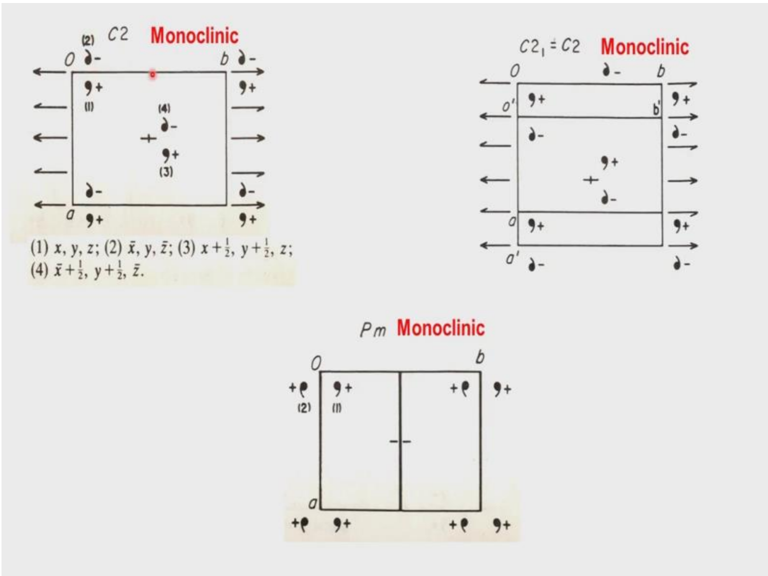

So, if you see the *C*2 symmetry that can be present in a monoclinic system; then what happens is that you now have the twofold operation associated with the b direction which will take the object 1 to object 2. Then object 1 will also have the *C* centered lattice. The moment we have the *C* centered lattice we generate this object at ½ + x and ½ + y, because it is C centered. The moment we say C centered the x and y will get the will be adding half and half, if you say a centered we will be adding y and z half and half.

So, in this particular case of C centering we add half and half to x and y and therefore, you have this equivalent point which is x y z. The x+1/2 y+ ½ z is an equivalent point that is generated by the lattice symmetry, this is not an equivalent point which is generated by the symmetry operation. So, the additional symmetry which we have got from the centering should also see the symmetry operation, in order to be consistent with the definition of the space group we have to have the closure property. And therefore, this point number 3 will also see the twofold axis, which is now generated automatically at half position. Because we have a twofold at 0 we have a twofold at *a*, but half position we will generate another twofold.

So, this twofold will take the object 3 on to object 4. Now what is the relationship between object 1 and object 4? Object 1 and object 4 will have to now go in a very interesting way, I want you to find out what is the relationship between 1 and 4. And see and satisfy for yourself that a combined centering operation along with the twofold operation will generate these 4 equivalent points.

Now, having generated these 4 equivalent points of course, this can be now translated by 1 unit. So, effectively these are the 4 equivalent points. So, 2 translated by 1 unit sees this particular twofold axes goes out of the unit cell, again this goes out of the unit cell and so on so. Inside the unit cell if you count the number of objects you will have 4 of them qualifying itself to be the $C2$ axis.

Now, comes the possibility of $C2_1$, what happens when we get to a space group curve $C2_1$? In the number of 230 space group placed $C2_1$ will not find its position that is because we can always convert $C2_1$ to $C2$, and that is the operation which is shown here. So, first of all let us look at how the $C2_1$ operation comes up, the $C2_1$ operation comes up from this point you take this as x y z, you rotate it by about the this is a 2_1 screw operation at the origin. If this 2_1 screw operation is at the origin it is something similar to $P2_1$. So, you do the symmetry operation $P2_1$ and you get this half translated at element that when translated down by 1 unit you will get this element.

So, these two now are related by 2_1 screw symmetry. Other than that we also have an additional point which will get generated due to *C* centering and that comes up here with ½ + x ½ + y z. Now these 2 objects are not directly related, but they are related through the operation of the twofold symmetry at 2_1 symmetry again. See what is important here is to look at where the 2_1 symmetry positions are located. Suppose we take this as the origin, the 2_1symmetry is located with respect to the 0 position here and therefore, this now defines the unit cell *Oa*, O*a* is the unit cell and O*b* is the unit cell that is associated with the $C2_1$ space group.

Now, if we now consider the presence of the 2_1 screw axis, the 2_1 screw axis will appear again at half position and so, this particular point which you see here now looks at the 2_1 screw axis here and because of that presence of this 2_1 screw axis this should undergo a 2_1 screw operation, which will take it to this point. So, as far as $C2_1$ is concerned, 4 equivalent points get generated inside this outer unit cell, the outer unit cell I mean the *ObOa* cell the cell which I have marked by shown by the pointer. That is the unit cell that is corresponding to the presence of this *C* followed by 2_1 axis.

Now, the fact that we have these 4 equivalent points inside this box, does not qualify $C2_1$ to be a standalone space group because what is happening is the presence of the 2_1 screw at this point and the 2_1 screw half way and of course, the full way here they are going to generate a perfect twofold symmetry, but one fourth. The reason why a perfect symmetry at one fourth gets created is because of the centering.

Because we centered at half and half and then the corresponding 2_1 operation has taken place such that we also get the -1/2 -1/2 kind of a situation, where these 2 points are generated. The consequence of that is to generate there is a for example, if you look at these 2 points you automatically see a twofold axes between this and that.

This is the x y z you will see the corresponding -x y z and therefore, this defines a twofold axes. Now, this twofold axes we are now taking this as the origin *O'* therefore, we have to add one-fourth unit to this one, the 1 unit translation will now be defining the *a'*. The distance *O'a'* is same as distance *Oa*. So, there is no change in the a axis similarly the *O'b'* is the same distance.

The only thing that is changing here is the origin is shifting by one-fourth, once it shifts by 1/4 you see that the 2_1 axis is no longer in practice, but with respect to this o prime we have the twofold axes. This therefore, will generate another twofold axes at one unit translation, it will also generate a twofold axes at half point which now relates these two. So, if you now consider this unit cell the *O'a' O'b'* unit cell let me mark that with the laser pointer this unit cell then you see there are again 1 2 3 4; 4 equivalent points in that unit cell.

So, I want you to write down the possible equivalent points for $C2_1$ and also the equivalent points of $C2$ and verify yourself that this can be now considered as $C2$ because its just a question of shifting the position of the origin by one fourth the unit. And it so, happens that when once it shift by one fourth the unit cell, the 2 1 screw is replaced by a twofold axes. So, $C2$ and $C2_1$ are one and the same. So, the equivalent points will be exactly the same with respect to the $C2$. So, we do not have a space group $C2_1$ anymore.

So, any combination of a C centered lattice with a 2_1 is ruled out; that means, when we go to the other space groups like $C2_1/m$ and possibly $C2_1$ upon C which is the $2/m$ operation those 2 space groups will not be allowed. Will not be allowed in the sense they are one and the same. So, $C2$ and $C2_1$ are one and the same space groups, now we go further the twofold operations are completed. So, we have the twofold symmetry we have the $P2$ symmetry described, we have $P2_1$ described we have $C2$ described and we have shown $C2$ is equal to $C2_1$ and therefore, the number of space groups are in monoclinic system so, far are $P2$, $P2_1$and $C2$ as far as the twofold operations are concerned now we go to the mirror operation.

The mirror operation as we can see here from this diagram here it is defining the space group *Pm*. We can work out of course, the corresponding equivalent points, I want you to write it down I thought of writing it down, but I think now you are experts enough to write down the equivalent points. So, you have the origin here and then you have *a* here and the *b* here, where is the mirror located the mirror is perpendicular to the *b* direction and therefore, you see that these lines are darker are higher width description of the black line.

So, effectively the mirrors are perpendicular to the axis direction. The twofold axes is still along the *b* direction to define the minimum symmetry associated with the monoclinic system and therefore, we have a mirror plane, where this now undergoes a mirror operation. So, we have x y z and x $\bar{y}$ z. Now when once we have this generated this can be translated inside the unit cell by one unit and you see that automatically a mirror gets generated at half position, just like the twofold axes and the 2_1 axis which we saw. And therefore, we have mirror symmetries at these 3 positions and this now generates 2 equivalent points, x y z and x $\bar{y}$ z and I want you to see that even though I have not written it, it can be considered as the equivalent points.

The question is suppose there is an object with a mirror, the object has a mirror in itself would it generate a special position. This is something I want you to find out yourself. Having heard the argument so, far you have to find out whether the object can have a special position if it has a mirror symmetry, can the object with the mirror symmetry represent on the mirror, in which case what would be the number of equivalent points? So, this you can figure out yourself its not a very difficult proposition and if the object lies on the mirror what would be its coordinates?

Suppose it lies at x equals 0 and then; obviously, it is perpendicular to the *b* direction and so, it can lie anywhere in the plane of *a c* and any point in the plane of *a c*, if it lies would it be a special position. This is something which you figure out as we go to the next crystal system.

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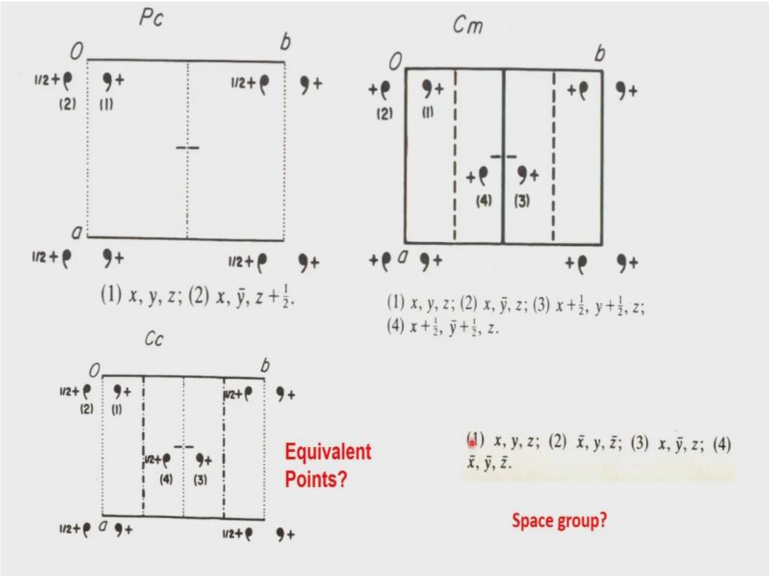

The next is crystal system is a *c* glide that can be associated with the primitive lattice as we discussed earlier, this is a consequence of the translational periodicity. So, again the diagram is fairly obvious here even though I will go through the description for the completion is sake. You have the position x y z and now what you do is you now operate the mirror symmetry. The mirror symmetry will take it to the other side and then it will not keep quite there it will either move along the which direction it will move? The direction in which it will move is given by half here; that means, it is moving half the distance along the *c* direction. So, in the space group is *Pc*. Suppose if space group is *Pa* then it will move half the distance along the *a* direction. And I want you to generate in your mind that diagram that equivalent point diagram where the space group is p a which is also a possibility. The *Pc* space group has the equivalent point where you generate the mirror and a half translation along the direction perpendicular to the mirror. In this particular case it is perpendicular to the *b* direction.

We can also move the plane of *a* and *c* and if you move it in the plane of *a* and *c* along the diagonal then it will become *Pn* an *n* glide operation. So, I want you to put some thought into this, because there is no point in me telling all these space groups and all the way in which the equivalent points developed, but I want you to think about how *Pn* can be generated. And if it this particular diagram I want you to generate for a P*m* may be it will be given as an assignment later by our teaching assistants.

So, find out what are the equivalent points if the space group is *Pm*. In this particular case the space group now generates an equivalent point which is x $\bar{y}$ ½ +z. So, it is the translation is along the z direction and that is why it is a *c* glide. If the translation is along the a direction you will have ½ + x. So, this now generates again 2 equivalent points and I want you to figure out whether this has any special positions *Pc*.

Next we go to the mirror symmetry, but now we will change the lattice type and we will change the lattice type to *C*. So, now, it is a *C* centered lattice in a monoclinic system; that means, for every point x y z you have a point at ½ + x ½ + y z. So, if your object is up here you have a corresponding point which will correspond to ½ + x ½ + y z. which is shown as number 3 here.

So, 1 and 3 are related due to the presence of the C centering and now of course, the mirror operates. The mirror operation will take this point onto 2 a simple mirror operation and this now point also will add half and half. So, you will get this point and you see that there is a mirror which is automatically generated in the middle. So, if there is a mirror the mirror operation associated with 0 we will have mirror at half we will have mirror at full length.

Now, where is the *c* glide located? *C* centering located? The C centering is located at this point ½ + x ½ + y z.. As a consequence if you now examine the equivalent points 1 and 4 you find a relationship between them. The relationship tells you that there is a glide plane which is present at one-fourth the position. It is not in the space group the glide plane is a consequence of the centering, because the we have the centering the x y z is becoming ½ + x ½ + y z. that presence of the ½ + x ½ + y z. and the corresponding mirror operation relates 1 and 4 by a *c* glide operation.

So, if you examine 1 and 4 you see that it is a *c* glide and this particular glide operation is it a *c* glide or an *a* glide? You look at this equivalent points and see whether it is a *c* glide or an *a* glide? It is an *a* glide because the glide operation is adding half to the value of x and this is coming as a consequence of the presence of the mirror symmetry, which now takes the *C* centered object operates the mirror and therefore, you will get a *A* centered lattice associated with this. Of course, the presence of the mirror is half distance and you see that half distance mirror is shown by a dark line here and therefore, you have the mirror, when once you have the mirror at 0 you have the mirror at half, you have the mirror full length and you double up a glide which is an a glide here.

In the case of the *C* centered lattice with a mirror symmetry, you invoke the presence of an automatically available *a* glide. Even though it is a part and parcel it is not a part and parcel of the description of the space group, because the description of the space group the dominance is given to the *C* centering lattice. So, the lattice gets the highest priority and then it generates the equivalent points corresponding to the lattice, and then the symmetry operation takes over.

So, the presence of the *C* centering therefore, has given rise to a possibility of a glide plane which is at one-fourth this distance. So, at one-fourth disposition you will get an equivalent point. So, this brings us to the fact that, given the positions of the symmetry elements given the positions this positions of the objects, we can derive the symmetry points symmetry equivalence; that means, if this is the point x y z, we can derive the position of the symmetry position here by looking at the symmetry operations that are possible.

One is now we took this point 1 took it onto the point 3 operated the mirror plane. So, we got this. So, if that is how we can generate x y z and ½ + x ½ + $\bar{y}$ z. now we see that these 2 are related by a *c* glide sorry *a* glide.

So, what it essentially tells us is that, given the diagram like this it should be possible to find out the equivalent points. The other issue is given the equivalent points like this it should be possible for us to find the space group. And if you find the space group we should be able to generate the symmetry operation diagram. This is known as the symmetry operation diagram along with the objects which are shown here, but you can replace the objects and in international tables what is given is the objects are separately given in one side and the symmetry operations alone are given on the other side. We will get a look at it after we finish this discussion so, that we understand the operations of the symmetry elements and also the presence of the centering of the lattice and later when we go to the space groups, you will see that the international tables for crystallography which is an enormous effort put by early day crystallographers.

And eventually now it is undergoing recent changes, it is available online and one can actually look at 2 possible diagrams. One diagram corresponding only to the symmetry positions the other diagram related the objects. So, that this complexity that is associated if you think there is a complexity associated with this, I do not think there is any complexity anymore associated with this. Because you have just now understood the entire diagram, we have not only adjusted understood where the objects are coming and how they are coming, you also have understood how the symmetry elements are located with respect to displacement.

Having seen that I have given you the *Cc* diagram. So, the *Cc* diagram now its a *C* centered lattice with a *c* glide. Now it can also be *Ca* because *a* and *c* are interchangeable in a monoclinic system because a is not equal to b not equal to c and the two angles which are at 90 degrees which is essentially considering b as the unique axis will allow us to have either a or c. So, we can have a *Ca* or a *Cc* both space groups are possible and here the diagram of *Cc* is given.

Now, it means that we have a *C* centered lattice with a *c* glide associated with a *c* glide. I want you to think whether *Cb* is possible cb; that means, the b glide which is along the *b* axis. There is no possibility of a *b* glide along the b axis because in a monoclinic system b is given always to the twofold unique axis. Since the b is given to the twofold unique axes it is not possible to have *Cb*. So, *Cc* and *Ca* are both possibilities and in the case of *Ca* what we see here is that the object 1 now since the c glide perpendicular to the *b* axis. So, the *c* glide perpendicular to the *b* axis is indicated here and so, we generate these 2 equivalent points.

So, 1 and 2 will be generated by the operation of the *c* glide. Now we also have the *C* centered lattice the C centered lattice will generate point 1 and point 3 same logic as we used in the case of *Cm* using the same logic as we used here we generate 1 and 3 by *C* centered lattice 2 and 4 are the operations due to the *c* glide, now c glide being at 0 we will automatically generate one at half position because of translational periodicity and we have this as well.

So, we can now bring all 4 points inside the unit cell, I want you to write down. The equivalent points this is a home exercise, I want you to write down what is the value of 1 what is the value of 2 in terms of x y z and this kind of equivalences, which we have shown in case of *Cm*, modify the *Cm* equivalences to generate *Cc*. Its not a fairly difficult job its a very straight forward job so, you should be able to do that. When once you do that you will see something, very interesting just like what happened here. In case of mirror symmetry we developed a *c* glide at one fourth remember *a* glide sorry *a* glide at one fourth this position.

Now, what will happen is because of the operation of the *C* centered as well as the *c* glide you will generate an *n* glide at one fourth. I want you to find out how this *n* glide operation has come and write down those equivalent points as well which will be the same as the equivalent points that is allowed by *Cc*.

So, at this time we will just consolidate the diagram here we did in fact, we started from the twofold symmetry and then we went to the presence of the mirror symmetry, the second symmetry operation in a monoclinic system and we then looked at the possibility of having the *c* glide associated with the primitive lattice, then we brought in the *C* centering which is essentially is operating on the mirror symmetry. We find an appearance of an additional symmetry element which is not a part and parcel of this *Cm*, but indeed it in some sense it is a part and parcel of this because of the fact that we C centering takes x y z onto ½ + x ½ + y z equivalence and they as a consequence of that we develop the *a* glide which is at one fourth preposition.

And if we look at this situation where we have a *C* centered lattice with a *c* glide then we generate equivalent points which will result in the presence of an n glide which is at one fourth and three fourths. So, the additional symmetry elements start cropping up depending upon how we combine now the lattice symmetry with the point group symmetry. So, the flexibility that is allowed now for the objects which go into these sports groups kind of restricted, because we it has to satisfy the other symmetry elements which are also developing. For example, in the case of the *Cm* symmetry you had the mirror you wanted a you get a *a* glide. So, the equivalent points which we generate will have to also satisfy the *a* glide condition and therefore, the object is now arrested.

It is like you know putting all of you into a class room and making you sit in your respective chairs. So, it is essentially restricted by the additional symmetries. So, *Cc* will also generate additional symmetry the *n* glide and therefore, there are more restrictions on *Cc*. Now you can think of the situation when molecules crystallize in these kind of space groups. The molecules when they crystallize in these kinds of space groups will have to satisfy all the symmetries which are also coming in addition to the existing symmetry in the point group and the lattice type combination and thereby they are restricted to those places.

And these restrictions will therefore, tell us which compound can go into which space group. This leads us to the possibility whether they can a priory predict a crystal structure. A priory prediction of the crystal structure is also a possibility. It is also a possibility, but whether we can unconventionally or unequivocally determine the space group is an issue this is something we will discuss when we talk about crystal structure prediction.

It is not a straight forward way in which we can predict a crystal structure otherwise you know we would not be taking this course when doing x ray diffraction experiments to find out where the atoms are. Because the moment we see the object if we can predict which space group it goes into the job is all done. So, the solid will be described fully.