Symmetry and Structure in the Solid State
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Lecture - 21
Space Groups 4

So, the next one is to see how these now translates themselves to the presence of the newer space groups.

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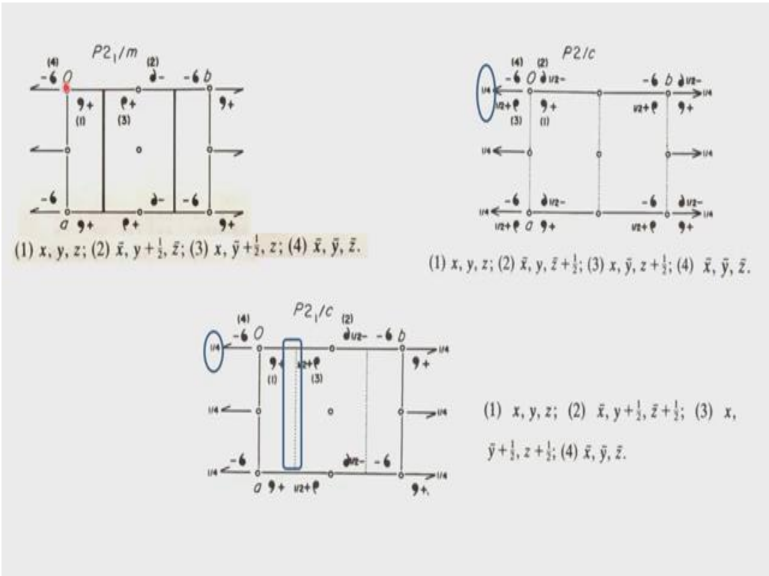

The next space group we discuss will be $P2_1$/m. So, what is the take home lesson in 2_1/m? In the case of 2_1/m, the mirror symmetry is the one we shift by one fourth. So, you see in this diagram the mirror symmetry if you look at only the symmetry diagram, the symmetry elements diagram we draw this unit cell and draw the centres of symmetry at the origin then we know that the twofold 2_1 screw axis will coincide with this. So, we write the 2_1 screw axis to coincide with the direction of the origin along the "b" direction because the unique axis is b and we have shown the "*ab*" projection as before as always.

So, we see that because of the presence of the 2_1 screw and the center of symmetry at this position, the same will repeat at half position and then of course, the full unit cell. In addition, the centres of symmetry will develop at the half positions along the "*b*" direction. Notice that since there is only one axis of rotation in a monoclinic system. We should remember that the symmetry operations are restricted to around the y axis which is the unique axis. So, we do not have any other symmetry elements which will come in a monoclinic system. So, there is only one unique axis about which the symmetry operation take place.

So, in other words if it is a twofold axis operation or a mirror alone or a combination of 2 and m, whether it is a $2_1/c$ operation all these symmetry operations are restricted to operate only along the y direction and that is why it is called a unique axis along "*b*" in a monoclinic system and that *b* axis therefore, is the one which shows the presence of the twofold along with it.

Just as we saw in the previous slide, that the mirror comes one fourth removed from the origin since there is a mirror that is generated here another mirror will generate at three folds. So, the equivalent point diagram now. So, these are the this is the symmetry diagram. In the symmetry diagram therefore, we have the centre of symmetry indicated at all the corners of the unit cell as well as at the half positions along *"a"* and "*b"* the presence of the 2_1 axis is illustrated along the "*b*" direction and also at the cell ledgers and also halfway distance along the "a" direction and the mirror symmetry is now moved away from the origin the intersection of the origin and the 2_1 screw axis by one fourth.

So, the mirror now appears at one fourth and three fourth and therefore, the symmetry operations now become slightly different. So, if you take the point number 1, operate now the presence of the 2_1 screw axis. The 2_1 screw axis will take this rotate by 180 degrees translate by this unit. The rotation of 180 degree is as usual $-x$ and $-z$ and the addition of half unit is $1/2+y$. So, you get to this point number 2, one unit translation of the point 2 will bring it inside the units. So, we have generated 1 and 2 inside the units cell.

Now, the next operation is the mirror operation. The mirror operation is not now associated with the y equals to 0, but we have to move it by one fourth. So, the mirror operation is moved by one fourth along the "*b*" axis and because of the fact that mirror is one fourth removed you will add for example 1 now goes to the point 3 which is now x, y, z going to x instead of x $-y$ z it acts on a half unit with that 1 and therefore, we get x $-y+1/2$ z as the third equivalent point. Why do we get this half? We get this half because the mirror has moved by one fourth and there is a mirror at three folds as well which is going to generate the further operations in the other unit cells.

So, you see now that we have point number 1, point number 3 and this point which was translated all three in the unit cell. So, there must be one more, that one more is automatically the centre of symmetry operation because if you now take point 1 operate the centre of symmetry you go to point 4. 4 now can be translated by 1 unit in the a direction and 1 unit in the b direction you will get this point. You notice now that the unit cell is up here and you have 1, 2, 3 and 4.

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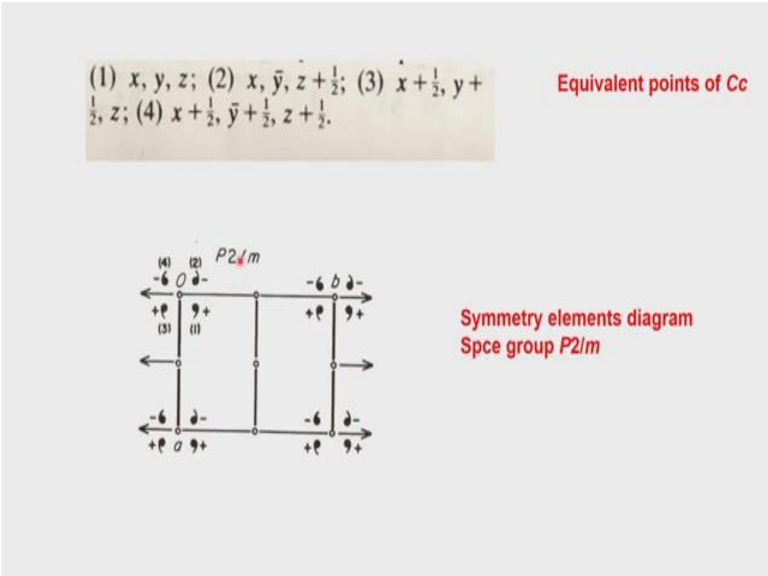

So, there are four equivalent points again in *P*2/*m* just like *P*2/*m* which you saw just now. *P*2/*m* has all the four around these centre here and because of the presence of 2_1 axis and the mirror now moving to one fourth position you will get the different space group identification with respect to equivalent points, now the equivalent points are the ones given below

Notice that you operate again $-x$ $-y$ $-z$, you operate the centre of symmetry again you will go here, operate the mirror symmetry you will go there and operate the twofold you will 2_1 screw axis you will go there. So, the symmetry is still maintained and therefore, the property of the group is still maintained that is the requirement. So, $P2_1/m$ therefore, is a space group we have where we have moved the mirror by one fourth and the moment of the mirror by one fourth is the one which kind of indicates the presence of the translation involved symmetry element. This is only happens; this only happens in crystal systems because we are now required that we have a unit cell and therefore, a lattice in order and the object should e confined within the crystal in order to have this symmetry. He said start. So, I started.

So, the space group is $P2/m$ and the equivalent points clearly indicate now the presence of the mirror symmetry which is removed by one fourth. So, this operation which is operation number 3, symmetry operation number 3 has a half translation associated with -y that is the one which invokes the presence of the mirror symmetry. So, these are the four equivalent points in case of $P2/m$.

We will now shift our attention to the space group $P2/c$. Now the moment we see these space group as $P2/c$, we know the lattice is primitive the presence of $2/c$ in fact the full symbol for this space group should be given as the symmetry along the a direction or the symmetry along the x axis, symmetry along the y axis and symmetry along the z axis. So, it should read $P1\ 2/c\ 1$, but it is normally the 1 symmetry is not indicated. So, when we say $P2/c$ it tells us two things, one is that whatever symmetry operations we are having the 2/m point group symmetry is along 1 single axis and this presence of the twofold indicates that it is monoclinic symmetry.

Monoclinic symmetry is the one which will have the twofold symmetry alone along the y axis along a given axis and that we take as the y axis. So, the symmetry operation $2/c$ indicates that we are dealing with a monoclinic system. So, if someone gives you the space group in principle you should be able to automatically find the crystal system. You not only find the crystal system of course, the moment you see the lattice identification you see the lattice also the Bravais lattice that is associated with it. The examination of the symmetry that is given here convert it to a point group symmetry.

Suppose you are giving $2/c$, the corresponding point group will be no translation involved that is $2/m$. So, it is a centre of symmetric space group and we conclude that it is a $2/m$ point group we have the primitive lattice and therefore, this is a monoclinic system.

So, we say now uniquely the looking at $P2/c$ we identify it is a monoclinic system, it is a primitive lattice and then we now can also say the operation of $2/c$ just like $2/m$ operation will give rise to 4 equivalent points. So, by just looking at this we can anticipate how many equivalent points come to this in general and in the unit cell and also we tell us about the way in which this operation takes place.

We have already seen that whenever there is a non translational component that is associated with the symmetry operation that particular symmetry which is not involving the translational symmetry that is the twofold will have to move by one fourth from the origin. n order to accommodate the requirement of 2/*m* symmetry which is the presence of the centre of symmetry.

Just to repeat this presence of the centre of symmetry we will necessitate the symmetry which is not having a translational component to be associated with a distance movement of one fourth along the direction perpendicular to the axis to the unique axis. And therefore, you see that if you look at this twofold symmetry the one fourth symmetry is indicated very clearly here; that means, the twofold is not with the origin 0, 0, 0, but the twofold symmetry is one fourth removed, that is why it is coming up by one fourth.

So, the twofold axis will pass somewhere there it one fourth if this is the *"c'* direction and of course, it can come at an angle beta. So, the symmetry operation therefore, now will be these are the equivalent points which are given you see that the equivalent points are very similar to *P*2/*m* if you go back and see the *P*2/*m* the symmetry points are all clustered around this origin.

Once again the clustered around the origin except that the point 2 and point 3 you notice here we will see the twofold axis one fourth from here and as a consequence they move by half unit. So, these 2 positions therefore, have a half translation in a direction which is perpendicular to this plane of operation and therefore, we it is not really perpendicular it is at along the c axis. So, we have to remember that in a monoclinic system the third axis is not at 90 degrees right

So, this is now, therefore, going along the c axis it is half translation along the c axis. Please remember the half translation along the c axis will not involve a 90 degree angle which is very important in monoclinic systems. So, it is moved by half the translation. So, what is important is the unit cell dimension. So, whenever there is a glide operation or a 2_1 screw operation what is important is the dimension of that particular axis not the orientation of that axis about which the operation takes place.

So, we therefore, have the mirror operation which is one fourth removed, and then we have the symmetry which is generating the c glide system on the equivalent points are given below. So, you see here that the 1 to 2 operation involves the twofold operation, but the twofold operation is now at one fourth distance along the c direction. So, it become -z+1/2. So, it is -x y -z+1/2. -x -z will tell us that it is a twofold rotation the presence of half will tell us that the twofold axis is located one fourth along the c direction.

Now, if you look at this point x y z and see how point 3 gets generated, the point 3 is now a mirror symmetry operation and it is not just a mirror symmetry we see that there is a translation of half involved in this and so, you see x, -y+1/2 z you see glide translation symmetry is added on here and so, you get this presence of the c glide. If you just look at these 2 then it represent straight away the c glide symmetry elements. And then of course, because of the fact that it is a 2/m point group symmetry $P2/c$ will also have x y z and -x -y -z the centres centre of symmetry.

So, a full description of the $P2/c$ is given here, but what is normally required is that we have to give this symmetry information separately, the symmetry operation information separately, equivalent point positions separately and that is how it will appear when we examine the international table a very soon. The international tables for crystallography is the handbook that is required to identify all the symmetry elements that we can generate in a space group taking into account the requirement of translational periodicity requirements of moving the axis or the aeroplanes by one fourth distance in this particular set of examples.

As we go to higher systems where we have three fold symmetry, we have four fold symmetry, we have six fold symmetry the amount of translations can be lower than that. In other words it start exactly half it could be lower than that. In fact, we will see one such case in a monoclinic system very soon and that will tell us that the movement of the axis need not always be half it can be even one fourth and that is the symmetry which you will see in the case of $C2/c$ we will go there in a few minutes from now.

So, what we see here is therefore, the case of the involvement of the translation involved components and the way in which the symmetry operations occur by shifting the non translation involved component in these cases by one fourth as we have seen here. Now we come to the case of $P2_1/c$ is by for the most important space group from the point of view of particularly small organic molecules. Most of the small organic molecules which do not have a symmetry they tend to go in to $P2_1$/c, because $P2_1$/c appears to be the most comfortable space group to lie down in that sense.

Suppose you are given a choice of this chair on which I am sitting and a stool on the across it is across the lecture hall and then a sofa across at the back of the hall you obviously, prefer the sofa. So, the organic molecules they want to relax keeping, their flexibility intact they want to relax and when they want to relax the flexibility is still allowed with a relaxation.

So, when you are sitting in a sofa or when you are sitting on the chair it does not matter you will still be moving around right, but the movement around this sofa is much more comfortable than the movement in this chair because you are restricted here in a sofa you can spread your wings. So, effectively organic molecules spread their wings with the flexibility that is allowed to them and that is why $P2_1/c$ is the most favourite space group for most of the organic molecules particularly when there is no asymmetric common in them.

It is not necessary that organic molecules must crystallise in $P2_1/c$, but that is a preferred space group. Any other crystallisation effort can take it away from $P2_1/c$ will give rise to systems which will have a higher energy located with them. So, it could be disorder for example, if you take it to a higher system like a tetragonal order, cubic system the organic molecule tends to be disorder and that is an issue we will discuss when we actually look at the details of structures and how intra and intermolecular interactions are important to study at that time we will look at the energy tips that are involved. So, $P2_1/c$ therefore, is a space group we will study in enormous detail

So, what are the operations here? The operations here are 2_1 screw and the c glide simultaneously at a intersection point. So, you quickly realise that 2_1 and c will have to move from each other. They cannot be associated and at intersect with each other because the point group symmetry happens to be $2/m$. Because the point group symmetry is $2/m$ you need to have a centre of symmetry and the presence of the centre symmetry and the requirements of the definition of a group will invoke for every given x y z across the centre of symmetry located 0, 0, 0 you will have to have -x -y -z.

So, one of the advantages is that, in this case we already have the 2 equivalent points already identified in $P2_1/c$. One of the questions which I would like to pose while to you of course, you have already shown it here there only 4 equivalent points even in the case of $P2_1/c$ and these four equivalent points can be derived based upon the diagram which is given here.

One could have spent some time on checking out what happens if 2_1 and c intersection point can be taken as an origin. This could be probably an assignment in your course work which will be given by TAs. What will be the equivalent points if 2_1 and a; 2_1 and c intersect at the origin, generate the equivalent points and see for yourself and convince for yourself that the presence of centre of symmetry gets invoked just like what we have seen in these 2 examples and see that the presence of the centre of symmetry is not then at the origin, but somewhere else.

In fact, that somewhere else is very interesting I want you to work it out and find out where is that somewhere else and that will be very interesting to find, that somewhere else will be not at half, half it will be at one fourth, one fourth and this is something which I thought I will derive, but I was thinking that we can as well derive it when we take a little more complex space group like $P2_1\ 2_1\ 2_1$ where there are 2 twofold axis and 2_1 screw axis do they really intersect with each other that would be a more exciting discussion than the discussion with $P2_1/c$.

But with $P2_1/c$ I thought a good assignment would be to see what happens when the 2_1 and c are coincident with the origin. So, that would that could be given as a home assignment or a assignment in the course to carry marks as well this is this something very important. So, it can carry remarks as well.

So, now let us examine the situation where we have taken care of this with the fact that the definition of $2_1/m$ and $2/c$ convinced us that whenever we have the centre of symmetry the centre symmetry should go to the origin. So, we decided to put this at the origin. So, if you put this at the origin then we have the point number 1 now goes to point number 2 which is the 2_1 screw operation, now the 2_1 screw operation is coincident here with respect to the presence of the twofold 2_1 screw, but you see that it is now removed by one fourth.

What is that in this particular case also it was removed by one fourth and we argued that it is due to the presence of translation associated with c; c glide here also we have a c glide and therefore, we move the 2_1 screw axis one fourth away from the origin. So, when we move this one fourth away from the origin then you see the 2_1 screw axis will develop at one half this position again one fourth removed and so on.

So, the symmetry operation 1 therefore, we will take this position 1 to a mirror position and then half translation. So, this half translation will generate this point 2 which is half minus ok; that means, it is below. So, what would be the equivalent point? If there was only a 2_1 screw axis, the equivalent points would have been -*x* 1/2+y -z.

Now, along the *c* direction we have to move by the axis moves by one fourth and therefore, the position of the equivalent point moves by half because the next operation on this particular symmetry element should take it to the next unit cell and it should overlap with 1 that is the requirement of a definition of a group and therefore, we see that the equivalent point now is -x -z ; -z also gets a half added to it along with the 1/2+y.

So, it is fairly straight forward to understand $P2_1/c$, the presence of 2_1 as well as *c* will move both the axis by one fourth, one fourth along the direction which is perpendicular to the *ab* plane in case of the 2_1 screw axis and in plane with respect to the *c* glide.

So, the *c* glide now as you have marked here we will move by one fourth. So, *c* glide moved by one fourth the 2_1 screw moved by one fourth. So, what happens if you move the *c* glide by one fourth. So, the point 1 now has to generate point 3; the point 1 generating the point 3 now will have a mirror half translation. So, it should have been if that was to be origin it would have been what? It would have been 1/2+x -y and z.

Now, you notice that we have moved it by one fourth along this direction and therefore, you have to add another one fourth to the z value. So, you have therefore, you have to add half to the -y value and 1/2+z is the *c* glide operation. So, x and 1/2+z is the *c* glide operation, -y operation now gets added on a half. So, therefore, we have x -y+1/2 and 1/2+z . The fourth equivalent point; obviously, gets generated because of the presence of the centre of symmetry which is shown up here.

Once again we see that the translational periodicity will bring this into this position the translational periodicity here the. So, point 1 and point 3 are already located here the twofold operate the 2_1 screw operation has gone outside of the unit cell we add one translation. So, it comes inside and there is a development of the one fourth *c* glide along with that there is a development of the *c* glide. So, the c glide at one fourth and three fourth will invoke the formation of four equivalent points inside $P2_1/c$.

So, anything further about $P2_1/c$ we will see in a few minutes. What we will notice here in this case of $P2_1/c$ is that if you have a object which is located at this particular point, you have the unit cell that is available to that particular object let us say it is a molecule, now you see that there is a half translation to generate point 3 and there is also a half translation to generate this point, because you are adding one fourth along the direction perpendicular to this and therefore, the molecules are as I mentioned well spread out inside this unit cell of course, you the unit cell dimensions now will adjust themselves so, that the flexibility associated with the molecule can also be created in.

If you look at the literature and if you analyse the Cambridge structural database and look at how many $P2_1/c$ structures are there in a recent evaluation it is found that something like 38 percent of the total more than that in fact, the 38-42 percent I think of the all organic compounds all so, far go in to this space group the reason being that many of the organic compounds have an asymmetric carbon.

The asymmetric carbon involved a components will always go into a space group $P2_1\ 2_1\ 2_1$. So, that is why I mentioned the space group now itself when I say $P2_1\ 2_1\ 2_1$ what is the take home lesson? The take home lesson that now we have 3 intersecting twofold axis; one along x, one along y, one along z; that means, that it has to be 3 directions which are at 90 degrees with respect to each other alpha, beta, gamma are 90 degrees with respect to each other; obviously, there is no restriction and you have a twofold axis on any axis and therefore, a is not equal to b not equal to c. So, a not equal to b not equal to c alpha beta gamma 90 degrees will define an orthorhombic system and therefore, the space group $P2_1\ 2_1\ 2_1$ is in the orthorhombic system and because of the fact that it is in the orthorhombic system we will have three 2_1 intersecting axis.

Now, the question comes up if you use the same logic as we have used in case of $P2_1/c$ where we have shifted the axis by one fourth and one fourth axis as well as the plane, if there are 3 intersecting as axis what we do. Because the Eulers theorem tells us that if there are 2 points which are intersecting at a point, the third symmetry operation will automatically get generated, but that is third symmetry operation with respect to the point group will have to become a twofold.

So, if you have a let us say two 2_1 axis intersecting we will discuss that when we actually derive the equivalent points of 2_1 2_1 2_1 at a later date, but what really happens is if you have a 2_1 screw axis and another 2_1 screw axis intersects with that based on Eulers theorem the third invariably has to be a twofold axis. So, in which case we will have a space group $P2_1$ 2_1 2 or not 2_1 2_1 2_1 then how can we generate the space group 2_1 2_1 2_1 which forms the another 38 percent of the total number of organic molecules in literature which have in a asymmetry carbon they go in to 2_1 2_1 2_1 preferably.

So, how does the chart 2_1 come in violation of the Euler's theorem? It is not violating the Euler's theorem, the Euler's theorem has to be modified in fact, there is a corollary on Euler's theorem which tells that if there are such situations where the two intersections are generating a translation free component the if there is a translation component involved then we will have to separate them from each other.

So, the origin now has to be arbitrarily fixed, but it has to be fixed in such a way that effectively the three axis intersect if to generate a 2 2 2 symmetry from the point group point of view. So, translational periodicity that is involved in crystals is something which we will invoke in order to have 2_1 2_1 2_1; that means, only in crystals you can have the space group $P2_1$ 2_1 2_1 but what is very beautiful is that the organic molecules prefer to go in the space group 2_1 2_1 2_1. Organic component go into the space group $P2_1/c$ otherwise and $P2_1/c$ again as we have seen here is a fairly straightforward set of the equivalent points here in this case of course, it is only one single axis and so, there is no question of invoking the Euler's theorem because the full symbol of this space group is $P2_1/c$. So, that way we have a situation where we have the three systems $P2/m$, $P2/c$ and $P2_1/c$ having translational involved components. How many translational involved components come up is discussed here.

So, in a nutshell what we will see now is that we have discussed the primitive lattices associated with the $2/m$ symmetry. We now have to worry about the presence of the *C* centred lattices. So, if we now think of a c centred lattice we should have a space group $C2_1/m$, we should have a space group $C2_1/c$ and we should have a space group $C2_1/c$ and also $C2/c$.

We have already seen in the earlier class that $C2$ and $C2_1$are the same it is just a question of shifting the origin by one fourth and therefore, we will not have all those systems which I mentioned as we will see in the next few slides that the systems which we can have are limited. So, the wherever there is a *c* operation coming up one once it is the *C* centred lattice the 2_1 disappears and we will have only $C2$ and therefore, we have $C2/c$ and then $C2/m$ we will not have $C2_1/m$ and that is something which we will have to discuss as we go further.

So, so, far what we have done is to see the way in which the space groups formulate starting from the triclinic system to the monoclinic system and in the monoclinic system we have examined the occurrences of non translation involved components the screw axis as well as the glide planes.

Screw axis and the glide planes come only in the monoclinic system and definitely not in the triclinic system because triclinic system has no axis of rotation that is something we should remember and so, the triclinic systems have only 2 space groups whereas, there are several space groups which developed in the case of the monoclinic system.

Further, we have also seen that the presence of the translation involved components will involved translations of the individual components depending upon the nature of the non translation environment participation in the space group.