Symmetry and Structure in the Solid State

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Lecture - 14
Point groups and Space Groups

So, in the last few classes we have been looking at the Point Group Symmetries and also looking at how the point group symmetries can be combined with the 7 crystal systems. Because since we are going to deal with only crystals and crystalline lattices, we have introduced several grammar, grammar words. As we went along we introduced point group, we introduced space group and we discussed 7 various crystal systems. We also introduced equivalent points and then, we introduced the number of molecules in the unit cell and so on.

So, what I thought was in the last two classes even though you have I have got a reasonable gist of the whole thing I thought I will make a set of slides which will completely revise what all we have studied, so that this is something which you will never forget. And in that sense this class will be somewhat repetitive, but then it is constructive in the sense that we will now put all the knowledge which we have gained in order to understand how we take a crystal system. And in the crystal system we have a unit cell and in a unit cell repeats itself to form a three dimensional crystal structure overall and the points which repeat themselves in three dimensional space or refer to as the lattice and things like that.

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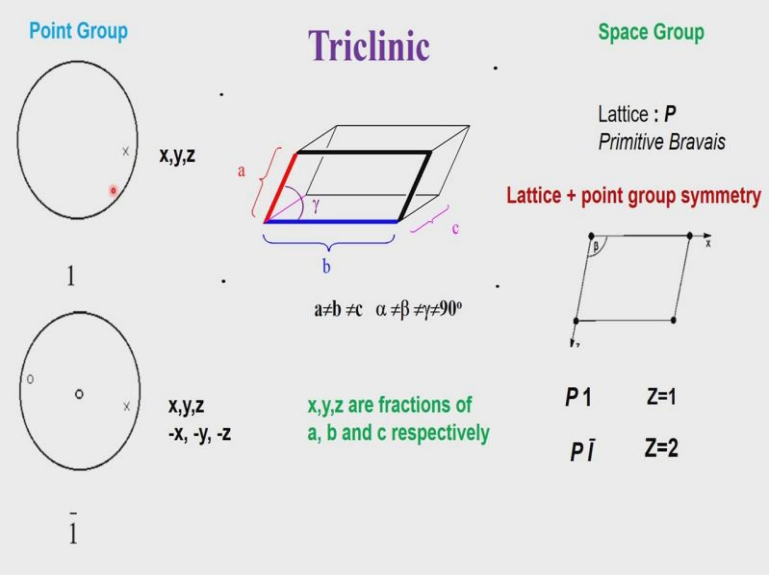

So, let us begin at the start with the least symmetric system which is the triclinic system. In a triclinic system, there are no axis of rotation and therefore, there are no planes across which reflections can take place. The only possibility that can happen in a case of a triclinic system is a point about which we can have the centre of inversion. So, the possibility of having a centre of inversion is the only issue which you have to consider in the case of a triclinic system.

So, the two point groups which fall into this category are shown on the left. The one is the space group the point group 1 with a equivalent point x y and z and the other is the point group $\bar{1}$ which now takes any point x y z in space to any other point -x -y -z.

So, even though we are shown only one point here, this can represent a collection of points and those points could be atom positions, it could be positions of ions, they could be positions of fragments of molecules. Whatever that is they will always be following this particular point group principle, that is in the case of the point group 1 there is only one set of such things and in the case of $\bar{1}$, we will have a the axis sorry the centre symmetry related equivalent point for every point. That means, the centre of inversion will be present on the set of objects which are represented by x and the set of objects represented by the open circle here will represent that we do have a centre of inversion.

So, therefore the there will be two objects here and that is why we say this system has two molecules or two units of repeat which are in the so-called asymmetric unit of the

unit cell. So, the unit cell of a triclinic system as we have been refined defining again and again is given by this rule *a* not equal to *b* not equal to *c* α, β, γ are not equal to each other. What we have to remember also which we revised several times yesterday is to remember that x y z or the fractions of *a b* and *c* and this is very important because the value of x y and z is always in fraction numbers.

So, suppose there is an atom here in a triclinic system sitting here, we will express it as fractions of *a*, fractions of *b* and fractions of *c*. So, if we say there is an atom at 0.1, 0.2, 0.3, it means 0.1 along a direction and 0.2 along b direction and 0.3 along z direction considering the full length as 1 1 1 each. That means, this 1 unit is taken as 1.0. So, the value of a will now appear at a distance of 1.0. Suppose there is an atom at the just about the end of *a*, then it is at 0.95.

Let us say what it means is it is just away from the full length of a. So, these fractional coordinates therefore represent the positions of atoms or molecules or units or whatever. Now, what we also define is what we call as a lattice. In this particular case, the lattice is made up of points which are at these edges, the cell edges and they will also repeat uniformly in all three directions keeping the definition of a unit cell. So, in this case of triclinic system, we can have only one type of lattice where only the edges are occupied and therefore, we call it a primitive lattice. So, if you count the number of lattice points in a primitive lattice suppose you sit at this point and then, count the number there are 1 2 3 4 5 6 7 and 8 points.

Now, each of these 8 points are occupied by one-eighth because the other unit cells around that surrounding that in three dimensions, they will also have this point as a common point and therefore, each and every point here corresponds to one-eighth. So, if we sum them up 8 colon points, one-eighth occupancy of each the total number comes out to be 1. Whenever the total number of lattice points is 1, we call such a lattice as a primitive lattice and this is the primitive Bravia lattice. We have already seen there are 14 Bravia lattices with 7 crystal systems

So, this is the first of the case where we have a triclinic system with a Bravia lattice P. So, if we now combine the lattice with the point group symmetry that defines what we call as a space group, so the space group now represents the three dimensionality associated with our crystal. It will also tell us about the three dimensionality of the object

that is inside this unit cell. So, whenever the objects are put inside the unit cell, there three dimensionality is the expressed in terms of various values of x y and z and at the same time the lattice combined with the point group symmetry will define the so-called space group.

So, this particular space group comes up because of the definition of a group. For example, if you take $\bar{1}$ symmetry and combine it with the primitive lattice, it becomes *P*1 bar. Now, by the rules of the group definition when we operate x y z, use the centre of symmetry and take it over to $\bar{x}\ \bar{y}\ \bar{z}$ we operate the centre of symmetry. The inversion centre takes x y z to $\bar{x}\ \bar{y}\ \bar{z}$. The rules of the group say that one once we have this coordinate system, if we operate on this coordinate system again the same operation the same symmetry operation, so $\bar{x}\ \bar{y}\ \bar{z}$ in this case the same symmetry operation we will come back to x y z. So, that way there is a closure property we do not go out of this. When we have x y z, we get $\bar{x}\ \bar{y}\ \bar{z}$ and when we have $\bar{x}\ \bar{y}\ \bar{z}$ we get back to x y z and we not do not go out of the system.

And therefore this is known as a group and so such property is seen both with respect to a point here and with respect to this space which is now made up of a lattice plus the point group symmetry combined and which is referred to as the space group. So, the two space groups we can realize in a triclinic system are *P*1 and $P\bar{1}$. So, *P*1 gives rise to one such unit in the unit cell and so, we call it the asymmetric unit as well and in this case Z is equal to 1. We identify the number of molecules or number of units which occur in the inside the unit cell let us say number of molecules.

When we consider a molecular structure, then the number of molecules is 1. If the number of molecules is 2, it generally goes to $P\bar{1}$ position because it prefers to have a inversion centre utility, but suppose we say that the number of molecules in the unit cell are 2 and it is *P*1, then it means that there are two different molecules, but not related by any symmetry. So, that means the presence of the so-called x y z in this particular case refers to what is known as a asymmetric unit.

So, in an asymmetric unit there is no invocation of symmetry whereas, one once we invocate invoke asymmetry it becomes now a equivalent point x y z becomes -x -y -z. These two are equivalent of each other from the symmetry operation. Whereas, x y z is by itself independent of it. So, therefore that represents the asymmetric unit that unit in

which there is no symmetry operation and then, the symmetry operation when we operate it becomes now the equivalent point in the space group $P\bar{1}$. So, this generally describes the overall view of any crystal system.

So, when we talk about a crystal system, we talk about the crystal system, we talk about the point group symmetry associated with the crystal system and the corresponding space group that gets generated by combining the nature of this lattice which is either primitive centred or body centred or face centred. In this particular case of a triclinic system, it is only primitive and therefore, we have the point group symmetry, the space group information the triclinic being the crystal system. So, whenever there is a material which crystallizes in this particular crystal system, all these issues which I have put on this slide should be identified and discussed. One once we discuss all these issues, then we say we have described the crystal structure.

Now, the x y z can be more than one as I mentioned it could be x_1 y_1 z_1 , x_2 y_2 z_2 each representing different atoms inside this unit cell. Now, if we find out the positions of x y z that is the next step, in this particular step which we have discussed. So far we are not able to find out where x y z is. If x y z is at x y z, then all these rules apply, but where the where is x y z? We do not know and that is what we want to eventually determine when we talk about the structure determination. We want to determine the structure of the molecule where the atoms are sitting inside the molecule.

And then we have to see how these molecules orients itself inside this unit cell making use of the available symmetry information in the point group symmetry and therefore, generate the molecular dimensions in the space in the three dimensional space which is allowed by the spacecraft. So, again to conclude this discussion on this slide I will repeat a crystal system triclinic if we had to describe this in full, we have to first describe the unit cell, the nature of the unit cell $a\ b\ c$ not being equal $\alpha\ \beta\ \gamma$ not being 90. And then, we had to describe the corresponding point group into which the system goes into and then, talk about the equivalent points which we can generate the presence of the symmetry element inside the unit cell.

And as you know once $\bar{1}$ is the point group symmetry, the entire three dimensional aspects associated with the unit cell every point in this unit cell will see the centre of symmetry. And the centres of symmetry location is at this possibility as we have drawn,

it could be at the possible edges of this three dimensional box. So, the centre of symmetry is here the moment there is a central symmetry here 1 unit translation along a will create another centre of symmetry, 1 unit translation along b will create another central symmetry 1 unit translation along c will create another centre of symmetry.

So, there will be 8 centres of symmetry that get created at all the edges. We have seen in the two-dimensional space group discussion the what we call as the plane groups. We have seen that whenever there is a symmetry element at the origin and one unit translated a same or a similar in many cases, one in this particular case the same symmetry develops halfway between the two.

So, we will therefore have centres of symmetries at these positions as well and that will tell us all the aspects that are associated with this space group, that point we will take up separately when we discuss the 230 space groups which form in the 7 crystal systems under 32 point groups. At this moment we consider only the space group and the corresponding point groups. So, we have 32 point groups, we consider only the crystal system and when we want to look at the space groups and look at the details of the space groups, we will discuss them separately in a later class. So, this is the information I wanted to give you in a nutshell about the triclinic system.

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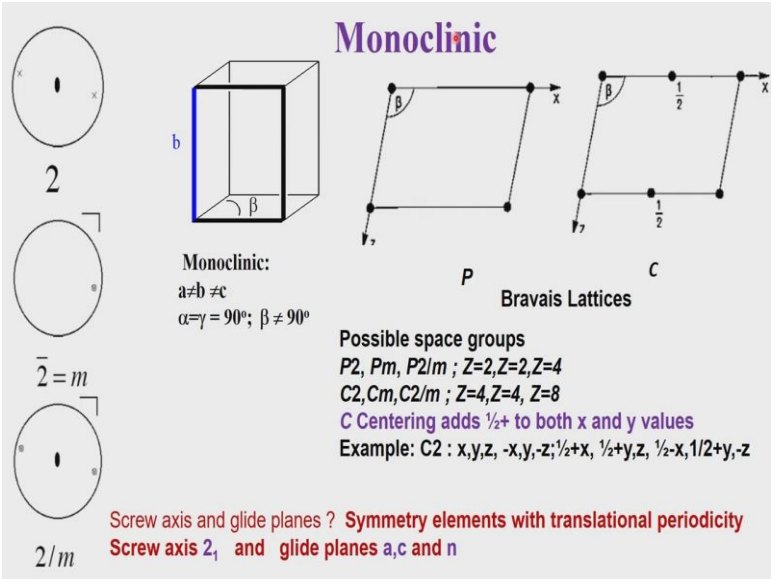

Let us see what happens when we go to the monoclinic system. When we go to the monoclinic system, if we look at the unit cell to start with the unit cell will have this

condition *a* not equal to *b* not equal to *c* alpha gamma are 90 degrees and beta is not 90. So, one of the angles is not 90 and it is if beta is not 90, then it means that the twofold axis which is a compulsory symmetry that has to be present to describe a monoclinic lattice monoclinic cell will have to be along the y direction.

So, the y axis is the one which is then referred to as the unique axis, it is not necessary that we should always have the y axis as the twofold rotation axis, but convention says that it is better to keep it as the unique axis. There are cases where there are certain special properties. See on crystalline systems along other directions and it so happens that it necessitates the definition of a twofold axis not being along y, but either x or z. In such a circumstance, the definition of the monoclinic cell will change instead of the beta non 90 we can have either the gamma not 90 and this one alpha being not 90 degrees.

So, one of the angles therefore is not 90 degrees, the other *a b c* are all independent of each other, there is no relationship between *a b* and *c* , *a* is not equal to *b* and not equal to *c*. This brings up 3 point group symmetries as we can see here the first one is the so-called twofold point group operation, the next one is the mirror operation that is so-called *m* operation and the third one is these 2/*m* operation. As we see here that there is only one axis of symmetry. So, we are now considering the case of one axis of symmetry being present and therefore, we have a twofold, $\bar{2}$ which is m and the operation of both two and mirror simultaneously there is a twofold and there is a perpendicular mirror to the twofold axis.

So, these are the 3 point group symmetries we will consider and the equivalent points you can write. In fact, we can see here the equivalent points are x y z and $\bar{x}$ y $\bar{z}$. So, you can write it down x y z and $\bar{x}$ y $\bar{z}$ as the two equivalent positions. Similarly, in this particular case you see that the mirror symmetry is notified like this we have seen this convention. That means, that the mirror is in the associated with the plane of our projection and therefore, you see both the points x as well as the other point which is generated by the mirror symmetry which is an open circle. They will fall on top of each other.

So, in this case considering b as the unique axis, it will be the equivalent points are x y z x $\bar{y}$ z, x y z and x $\bar{y}$ z. It also amounts to an operation of a twofold symmetry followed by an inversion centre that is exactly what we have done here. We have taken the twofold

symmetry and then, we have operated the centre of symmetry on that one. So, suppose you take an object here which is x, you operate the twofold, you will go over there and then, you inverted it, then you come back here and that is how we have a overlap of x and an open circle.

Let me repeat. If you have this point you operate the twofold, you go over there, but then you do not stop there you invert it. When you invert it, you will come back here with the open circle and that is what is shown here and that is how you have a mirror symmetry invoked at this situation. In the last diagram which we have here the 3rd point group symmetry which is the only other symmetry point group symmetry which can exist with monoclinic systems.

You see that we have 4 equivalent points two corresponding to the twofold operation and two corresponding to the corresponding mirrors because there is a mirror which is perpendicular now to the twofold axis. So, we get 4 equivalent points and you can write down as a as an exercise all the 4 equivalent points.

Now, we have the point group information on the left, we have the crystal system in the middle and now we have to see what kind of a lattice this can generate. As you can see that we have *a* not equal to *b* not equal to *c* so, we have therefore two such situations; one is a situation where we can have this beta angle. This is the projection diagram of this where we have projected the unit cell and in this particular case this is the x direction. So, this is the a cell dimension and this is the c direction which is the z direction. So, this is the ac projection and in the a c projection you can get a primitive cell which corresponds to occupancies of the lattice. These are the lattice points these are not atoms; these are lattice points. So, the lattice points now add up in this projection if you take it is a projection. So, it is 1/4 times 4 which is equal to 1. So, we will therefore have one total number of lattice points and therefore, it is a primitive lattice.

So, this is one possibility, the other possibility is because we have the in the perpendicular direction a rectangular cell, we remember you did the plain lattices and we found that there are two possible plane lattics, the primitive as well as the centred lattice which we called as the little c. Now, here also it is possible to have the lattice centre at this point. That means, you have now the lattice points at 000, this is 001 and this is the position at 100, 1 unit along x, 0 0 along y and z and this is the position where you have

a value of 1 for x and value of 1 for z. This is the z direction and this is the x direction. So, this will be 101.

So, if you consider these four now defining these four points which are exactly the same we will have the primitive lattice, but it is also possible to now have another set of two points as shown here; one in this line and one in associated with that line essentially there is only one. In fact, and that is removed by half along this direction. So, it is coming away from the like that it is coming away from the origin and at a distance of half we will have the presence of a lattice point. So, the lattice points therefore, add up one these four will give us one and this will be half and half each which will give us one more.

So, the number of lattice points therefore, is two in case of a C centred lattice. So, these are the two possible types of lattices we can have in a monitoring system a primitive lattice and a C centred lattice and this gives rise to several possible space groups and the possible space groups are also listed here for your convenience. So, these slides will be of immediate reference value as well if you look at the previous slide you have every information about triclinic systems you have every information we want about the monoclinic systems on this slide.

So, if you take for example, the space groups to be primitive the lattice to be primitive combine it with the point group symmetry to you get *P*2 and you will get a space group *Pm* and *P*2/*m* likewise. In all these cases the number of molecules in the unit cell in general is Z equals 2, Z equals 2 in the case of *Pm* as well and Z equals 4 as is illustrated here in the point group diagram. When we come to the case of a C centring we can again have a *C*2, *Cm* and *C*2/*m* it. So, happens that when we have to generate the C centring lattice what we have to do is to every x y z we add a half plus x and a half plus y considering that it is C centred that is a C direction is centred.

If the a direction is centred then you add half to y and also half to z, if C is the centred the if B cell direction is centred then you add half to x and half to z. Let me repeat you add half to x and half to z in case you have a C centred lattice and in case of A centred lattice you leave out the a that is corresponding to the value of x and add half to y and half to z and in case you have a B centred lattice add half to x and half to z leave out b.

So, this way you generate double the equivalent points. So, when we have a primitive cell it doubles in the case of a C centred lattice. So, you therefore, have 4, 4 and 8 respectively given the example of *C*2 the equivalent points in *C*2 are x y z, -x y -z because its a twofold operation. Now these are the two operations which are generated by the point group symmetry the lattice symmetry now generates two other points. So, this gives us 1/2+x 1/2+y z and 1/2-x 1/2+y -z.

So, you will have 4 equivalent points in case of the C centred lattice. What you have noticed also as we have discussed this issue of equivalent points is the fact that you are keeping the positions of x y z and the other equivalent points within the unit cell the way we have written here for example, if you take x y z you take x y z let us say at this point. Then if you operate a twofold symmetry on this one it will take you to -x which is the other side of x right outside of the unit cell, now you will be wondering how you have four equivalent points in the units.

Let me demonstrate one example here that is you have now the twofold let us say this is the position of x y z you operate the twofold symmetry the value takes it to minus of x and minus of z them. So, the twofold operation which is shown here this will now correspond to x y z and this will now correspond to -x y -z. So, you take this point kept keep it inside the unit cell let us say we take the primitive cell to start with we have this point and then it point the other point goes out of the unit cell.

Now, here comes the information which we already have on the translational periodicity this is the advantage in crystalline materials and that is why we study crystalline materials. The advantage is the fact that you from here if you add one translation along the z direction you will come there and add one more translation along the x direction you will come there. So, you see that the equivalent points now are up here and up there and they are related by a twofold symmetry. Now, therefore, there is a central centre of symmetry twofold symmetry created at the centre.

So, that is how you get additional symmetry elements inside the lattice. So, even though the lattice is primitive; lattice is primitive the symmetry elements will insist on generating additional twofold positions the lattice is still z equals 1, but you generate these positions if you have a twofold symmetry operation. In the case of the presence of the C centring lattice you will have additional points the same logic can be used by using

translational periodicity associated with x and z and y we can bring all the four points inside the unit cell.

So, if you have the this point which is x y z you will have the corresponding $\bar{x}$ y $\bar{z}$ up to here. So, there will be a position which is now here which is also a twofold symmetry. Now because of the presence of the C centred lattice we have to have if there is an x y z we will have 1/2+x 1/2+y.

So, the presence of 1/2+ x 1/2+ y and z will create a position up there corresponding to the value of z notice that minus x y -z will take it there whereas, the 1/2+x then 1/2+z will take it to the position which is different. So, we will have therefore, 4 equivalent points after we do unit translations

So, in order to see all the equivalent points inside the unit cell you may have to perform translation periodicity included operations. So, remember that do not get the way fetched with the fact that one once you operate the symmetry it goes outside the unit cell, you can always bring the point inside the unit cell by translational operations which are allowed only in crystalline materials and that is why we study structures in crystals. Because we now have the arrested these molecules inside the unit cell which must obey the conditions we put on based on the space group and the crystal system right.

The other aspect associated with this of course, which we have not discussed fully is the fact that we have these three space groups, which of the space groups are centre symmetric and which are non central symmetric needs to be analysed. And that is something which we will look again carefully because *P*2 and *Pm* will generate equivalent points which are not involving -x -y -z and therefore, they are non central symmetric systems. And the x y z and $\bar{x}$ $\bar{y}$ $\bar{z}$ a coordinates whenever we get, that represents the central symmetric system.

So, the threes point groups we have considered or 2, m and 2/*m* and we have now discussed the possible space group. So, this has generated 6 space groups triclinic at 2. So, we therefore, have covered 6 plus 2 total 8 space groups out of the 230 possible space groups considering all the seven crystal systems all the types of lattices and so on. It does not mean that as we go along we derive all the 230 space groups that will take another 300 hours that is not the idea.

The idea is to give you an information on how these can be generated and probably we go through each of the crystal systems and one once we reach a stage where we have understood the aspects associated with one or two crystal systems the same logic will apply.

So, whatever logics which have logistics which we have to change from one crystal system to the other is the one we have to keep in mind. In monoclinic systems we have another possibility that possibility sorry that possibility is to use additional symmetry information. The additional symmetry information we have can come from screw axis and glide planes we already mentioned about screw axis and glide planes these are symmetry elements with translational periodicity. The screw axis is represented as 2_1 and the glide plane is represented as *a c* or *n*, we will discuss this independently and individually in the next coming slides.