**Symmetry and Structure in the Solid State**
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**Lecture – 26**
**Details of Space Groups 4**

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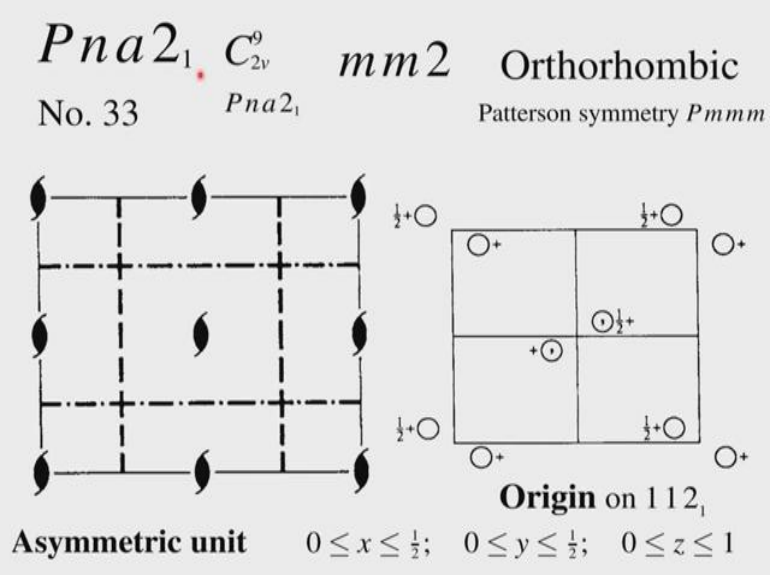


So, as we now continue with the $P\ n\ a\ 2_1$ , one other aspect which we should notice here is that the origin now, see everywhere here after the definition of the location of the origin is important. The one once we draw these two diagrams these two diagrams refer to some origin 0 0 0 and in case there is a centre of symmetry no problem. Because, the 0 0 0 will coincide with the centre of symmetry.

But in case we do not have a centre of symmetry, we have to specify where the origin is. So, in this particular case, it is at 1 1 $2_1$. So, the $2_1$ screw axis in the z direction is now coinciding with the origin. So that means, the value of z is put equal to 0 at that point. So, this is very crucial because we have to define the origin term very clearly.

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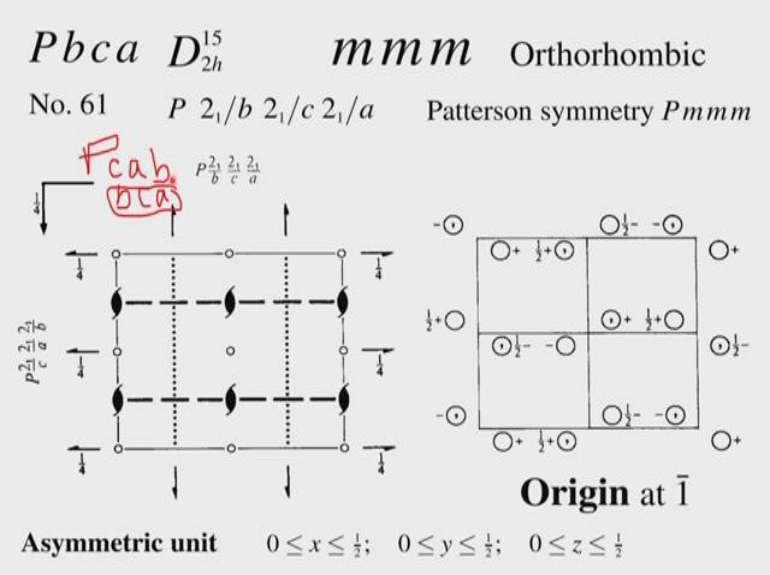


Now, we go to the next system when the orthorhombic symmetry which is all three mirrors. So, you see that the diagrams look start to look more and more complicated. But one once you have got the gist of it and you have understood what is it all about, it becomes fairly straightforward. Let us see how quickly and how comfortably we understand the space group *P b c a*. This is another space group which is fairly common among various organic and inorganic compounds, particularly when you have a flexible inorganic system or organic inorganic framework structure and so on; *P b c a* is a preferred space group.

Now, therefore we should know something about this space group you see the space group number is 61; you are graduating very fast towards 230. In fact, after this I do not think we will do any more. So, we can as well say we are now coming towards the end of understanding the space groups, by looking at two diagrams. And then comparing those two diagrams with the equivalent points which are appearing in the next part, next page in fact, in the international table and next slide in our presentation.

So, let us see what happens in case we have a *P b c a*; so, one of the things which is immediately obvious says that it is a primitive lattice. So, we will not have any any centering information coming in, any here face centered information coming in and things like that. So this therefore, is a situation where we have no problems primitive and there is therefore, the number of lattice points will be one. So, we have to worry about

only one lattice point. The moment we bring in a *C* centered lattice let us say it is *C m m a* or something or *C m n a* or something. In which case we ha_ve to now bring in two lattice points, one at x y z the other at ½ + x ½ + y z.

If it is the face centered lattice we have to bring in four lattice points. If it is a body centered lattice we bring in two lattice points and I am bringing that discussion here because orthorhombic symmetry allows for all kinds of lattices. It allows for the primitive lattice, it allows for *A* centering, *B* centering, *C* centering of course, A B C are interchangeable. So, we can always say it is *A* centered or *C* centered, one once we say that they are interchangeable with respect to each other because, the three angles are 90 degrees with respect to each other $a \neq b \neq c$.

So, but we can define *abc* as *bca* and *cab*. So, the symmetry is still maintained. The 360 degree rotation of the symmetry is still maintained and so, we can call them interchangeably. The interesting fact is that since all these possible lattice symmetries can come up in an orthorhombic system, it is very easy to interpret it at this stage. So, whenever you have a primitive lattice you have only one lattice point to worry about xyz and after that symmetry elements we generate is purely by symmetry operations. If you have a *F* centered lattice there are four center related operations the face centered related operations.

So, for an every x y z you will get a ½ + x ½ + y z, ½ + y ½ + z x and so on. So, four of them you will get and if it is a body centered system you will get for every x y z, ½ + x ½ + y ½ + z. So, whatever symmetry operations you are now going to perform on x y z the same in symmetry operations you have to perform on the next lattice also. So, what happens is, that the number of equivalent points will increase, but the number of symmetry related points will still remain the same.

So, in other words if this is instead of *P b c a* it becomes *I b c a*, what will happen is, that the number of number of equivalent points which occur here which is in fact, 8 will become 16. So, the same 8 will exist with the same symmetry, but now all of them are moved by ½ ½ ½ along the unit cell. So, additionals operations of symmetry appear, and the signature of the point group symmetry remains exactly the same.

So, whether it is *P b c a* or *I b c a* the point group symmetry is still *m m m.* And this is a point which should be noted and this is a point which is which is going to be important

when we actually try to solve the structures and fix the positions of the atoms and so on. So, the lattice points we will see all the symmetry operations associated with them independently. So, if the *C* centered lattice we will have two, *I* centered lattice two and *F* centered lattice four. I am, I am a bit repetitive basically to drive home the point that you have to worry about these issues when you derive the equivalent points and particularly when you try to discern the difference between these two diagrams which are shown here. So, this diagram shows you the symmetry points and this diagram now shows you the equivalent points.

So, the space group number is 61 and you see the full symbol the full symbol is $2_1/b$ $2_1/c$ and $2_1/a$. Obviously, because we cannot have a *m m m* combination, we have already proved long long ago in earlier classes that, a improper improper improper combination is not allowed. So, it has to be when we write *m m m* that is why we are happy to write *m m m*, because *m m m* actually represents 2/*m* 2/*m* 2/*m* and therefore, if you now see the independent derivation for each of these in the full symbol you will see it is *P* 2/*m* 2/*m* 2/*m*. In fact, that is what it is and we reduce it to *P b c a*.

So, when we say *P b c a* the two and the presence of $2_1$ with respect to each of the axis is already implied which is already there. So, the in the way in which we described this space group is not we have a primitive space group, there is a *b* glide perpendicular to *a*, a *c* glide perpendicular to *b* and *a* glide perpendicular to *c*. Suppose I have a space group which is *P c a b* is that possible is the question.

So, this is a question which we can answer right away, suppose instead of *P b c a* I have a space group, let me write it down for you so, that we discussed that, instead of *P b c a* we have a space group *P c a b* is it a possible space group? If *P c a b* is a possible space group is it different from *P b c a* or it is a new space group. We said there are only 230 space groups right and is it going to define a new space group? These questions come up.

So, a primitive lattice is a primitive lattice there is no change. What it represents here is there is a *b* glide perpendicular to the *a* direction. Here there is a *c* glide perpendicular to the *a* direction. And in this case there is a *c* glide perpendicular to the *b* direction, here if there is an *a* glide perpendicular to the *b* direction. And in the last there is an *a* glide perpendicular to the *c* direction there is a *b* glide perpendicular to the *c* direction. So, what is the answer? The answer is inherent in this definition the way in which we now

invoke the presence of the glide planes. So, *P b c a* is a commonly represented space group which refers to *a b* and *c* axis.

Now, what all you have done is you have taken the c axis to be *b* and the *a* axis to be *c* and of course, the *c* axis to be *a* ok. So, since you have change the axis directions, the glide plane directions have also changed. Remember in an orthorhombic system the three angles are 90 degrees with respect to each other. a ≠ b ≠ c. So, we can call any one of them as *a* any one of them as *b* and any one of them as *c*. So, we can have therefore, equivalences of space group. So, *P b c a* is same as *P c a b* except that your *a b c* positions are interchanged.

So, in this particular case the positions are *a b c* ok. And in this particular case the positions are this position with respect to this is *a* and this is *b* and this is *c*, am I right *c* perpendicular to *b, a* perpendicular to *c*. So, this is your crystal system now. It does not matter whether *b* is *c, c* is *a* or *a* is *b* because we can interchange them with respect to *a b c*. So, these two space groups *P b c a* and *P c a b* are one and the same. So, this is something which we should remember when we are dealing with the orthorhombic systems. In orthorhombic systems we can therefore, you it may so, happen that your molecules they do not know the definition which you want to give. They do not know which should be *a* which should be *b* which should be *c* your molecules will go on crystallize and when you go to the machine and determine the space group believe it or not this the computer says it is *P c a b*.

Then you will quickly go into your international tables *P c a b*, *P c a b* where is it where is it. You want to see where the equivalent positions are, and you will never find it. You will never find it because the standard for this is *P b c a*. The standard space group as we call it or the normally accepted space group is *P b c a*. So; that means, you have to change your axis directions, your *a b c* now has to follow the *P b c a* the space group. So, the *a b c* should be changed such that we get a *b* axis perpendicular to *a*, *c* axis perpendicular to *b* and then *a* axis perpendicular to *c*. So, when we do this particular change then it is one and the same.

So, this is something which you should remember and then whenever you have a situation like this where the molecule has gone into *P c a b* you can either change the symmetry elements and make them into *P b c a* or you solve the structure in *P c a b*, but

eventually report in *P b c a*. Yeah all are allowed. It depends upon what you would like to look in that molecule. Suppose that molecule has a very special behavior, suppose there is one direction which is very very large and that is the direction which is very crucial for the property that compound is showing, and that happens to tell us that the space group is *P c a b* and that large direction is *b*. Then we would rather keep it in this form then report as *P b c a*.

So, you will see lot of literature particularly in inorganic compounds and also in materials oriented compounds the space groups which are not these normal space groups are acceptable. But what people do is when you read that literature in the brackets they will give the standard setting is *P b c a*. So, they will indicate that even though the structure is reported in this space group, the standard setting is *P b c a*. So, this is how the space groups are unique and therefore, there are not more than 230 space groups. Otherwise the numbers would have increased enormously. For any given *abc* we can define these interchangeably to the combinations.

So, the combinations will keep on increasing which we do not want to consider. So, *P b c a* is number 61, and if you crystallize the compound and it tells you the machine tells you and you do the analysis it is *P b c a*, you do not have to panic it is still the space group 61. Either you convert all these things to *P b c a*, which would be the most safe thing to do, but if you do not have to do it because you have something very special in your compound which is along the *b* direction and that wants to be along the *z* axis. Keep it along the *z* axis, suppose you have a crystal grown in that direction. And you want to measure some property associated with it. Of course, if you have a *P b c a* crystal it may not be very interesting. Because it is nicely beautifully, center symmetric.

But, if you have a system where the non centric behavior comes up; *P n a* the previous space group which we discussed for example, *P n a* $2_1$. So, what suppose you have an *n* glide perpendicular to *a* axis *a* glide perpendicular to *b* axis $2_1$ is along the *z* axis. You may have a equivalent space group *P* $2_1$ *n b*. So, this *P* $2_1$ *n b* is equivalent of *P n a* $2_1$; if for all practical purposes because we can change *a*, *b* and *c*. So, this particular table where we can have the standard representation given in the international table and all other possible variations which come up due to *a*, *b* and *c* being interchanged. A table of that is provided in the international tables towards the end.

So, we can go to the end of the international tables look for these tables. In case you get a space group which is not listed in the 230 space groups. The computer will give you the space group what whatever it finds with respect to the molecular system which is there in the in your crystal. Because it is going to base it on the diffraction conditions which it finds and one once it has happened then one has to go and look at the standard setting and so, in the when you report in literature, you have to report that the space group in which you determine the structure within bracket you should say standard setting is *P n a* $2_1$.

So, it may be very important that these $2_1$ axis which is found in *P n a* $2_1$ has a very special property like ferroelectricity or ferromagnetism shown in that particular direction, and you want that to be *z* axis because, your crystal is grown in that particular direction. It is very clearly seen in the morphology of the crystal. Then we would rather maintain that particular space group, rather than report the standard space group. So, this is something which you should bear in mind and never get into troubles when you discuss this.

So, when we go to *P b c a* therefore, these are the equivalent point positions. I want you to do an a little exercise again here. The exercise is to compare these and see which are these corresponding this of course, is very straightforward. Here you have a center of symmetry and this to this is now you are all experts. So, this to this is now the glide plane and also the $2_1$ screw. You see that the $2_1$ screw and the glide plane coincide because you have a system where this is *a* direction and in the *a* direction you have a *b* glide which is perpendicular to the *a* direction. You also have the $2_1$ axis in that direction.

So, the $2_1$ and the glide they move by one-fourth so, this is the glide direction. And similarly the *c* axis and the z axis there is *b* axis on the *c* axis are also having the glide planes with a $2_1$ screw which is now removed by one-fourth here. And in this case again it is in plane. So, you notice that the whenever you have a glide and they associated $2_1$ they are in the plane of the diagram. Whenever you have the center of symmetry and the $2_1$ the $2_1$ symmetry goes by one-fourth that defines the translational periodicity which is ½ unit along *a*, ½ unit along *b*, ½ unit along *c*. And therefore, you can now correlate this diagram with this diagram and at the same time also look at the equivalent points.

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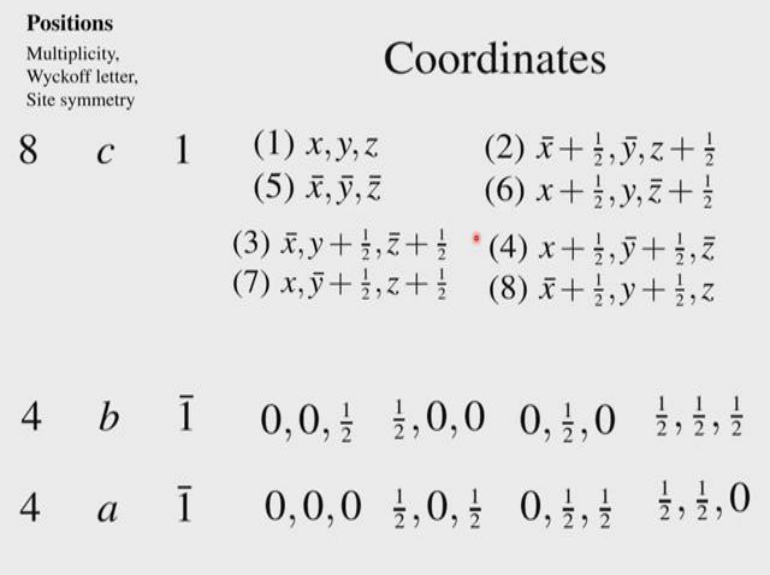


And here there are 6 equivalent points. Here is something which you have to see 1 and 5 are shown as x y z , . I want you to do a little exercise here. So 1, 5, 2, 6 you take these four to start with and then generate these four and one 1 is x y z. So, we go back to the previous slide you see this is one and then 5 is this one because 5 is the . So, like that you I want you to mark 1, 2, 3, 4, 5, 6, 7, 8 the 8 equivalent points in this diagram. And in this diagram we already know there are eight equivalent points because z is equal to 8.

So, I want you to isolate and identify the equivalent points which we have in the next slide with respect to 1, 2, 3, 4, 5, 6, 7, and 8. Whichever is there inside the unit cell I want to also tell you that it is still only one in the asymmetric unit and I want you to verify doubly why it is still only one object inside the asymmetric unit, you notice that the asymmetric unit have shrunk now. It is x= ½ y= ½ z= ½ and you see all other generations which you are making is either "½ + or ½-".

So, that does not go with the existing one. So, you will have therefore, only one. So, the primitive lattice is dominating in this particular structure and that is how it is a primitive lattice. If it is centered you will have 2 and *F* centered 4 and so on. Right so, the other thing which you have to notice here is that this also has special positions and these special positions both of them are center symmetry. Now this is something which I want to discuss a little bit here, before we end this particular session that discussion is the following.

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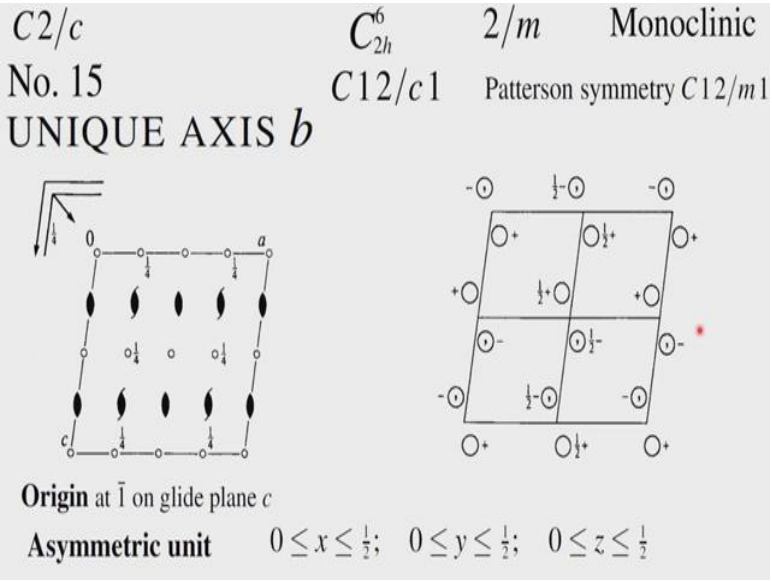


Say when we look at you see this is the *C* 2/*c* system, right? *C* centered lattice a 2/*c* is the point group which gives rise to 2/*m*. In fact, and you have these diagrams and you have related these two diagrams beforehand. Now, what you do is you look at the special positions. Here there is a special position associated with $\bar{1}$ as well as the 2 fold. The space group has the 2 fold and the $\bar{1}$. The space group has also got the *c* glide, but there is no possible association with *c* glide because it has a translation component agreed. Now, whenever you have a translation component symmetry element with a space group that particular component will not have special positions with respect to that.

So, let us go now straight away to the space group we have been discussing because, that is where a very important point comes up. If you see here the *P b c a* space group what is your take home? You have $2_1$ you have *b* you have $2_1$ you have *c* you have $2_1$ you have *a* so, what would be the special positions? The special positions cannot be associated with any of these symmetry elements individually. So, there cannot be anything associated with $2_1$ there cannot be anything associated with *b*, it cannot be anything associated with *c* and *a*. So, what is it where is the special position coming in a space group like this. If one examines that carefully you have a solution to the problem, in this particular case you know that this is a centre of symmetric space group.

Centre of symmetry is not associated with any axis or any translational periodicity. The periodicity that comes up from a centre of symmetry is only one unit along x y or z. And then of course, this it appears also at the half position as a consequence of symmetry. In other words this $2_1$ position can be this centre of symmetry position can be also this centre of symmetry position or this centre of symmetry position. That means, this framework is the lattice and this lattice we can slide down in all three directions and the again it have the position of the centre of symmetry fixed and since the centre of symmetry is a fixed position we will have special positions then the atom or molecule or the system which we are discussing sits at the centre of symmetric position ok.

It is very clear very simple and therefore, you will see now the special positions will be associated only with $\bar{1}$. You have all the other symmetries, but only $\bar{1}$ is allowed. So, if you look at all these special positions which you come across in the 230 space groups. All those special positions will occur only with symmetry elements which are not having translation components. So, it will be $\bar{1}$ it will be 2 it will be mirror and things like that it will not be associated with any of those so, $\bar{1}$, 2 and m these are all these special positions you will have. Of course, you can have combinations of those for example; in 4 fold symmetry you may have a 4/*m* symmetry.

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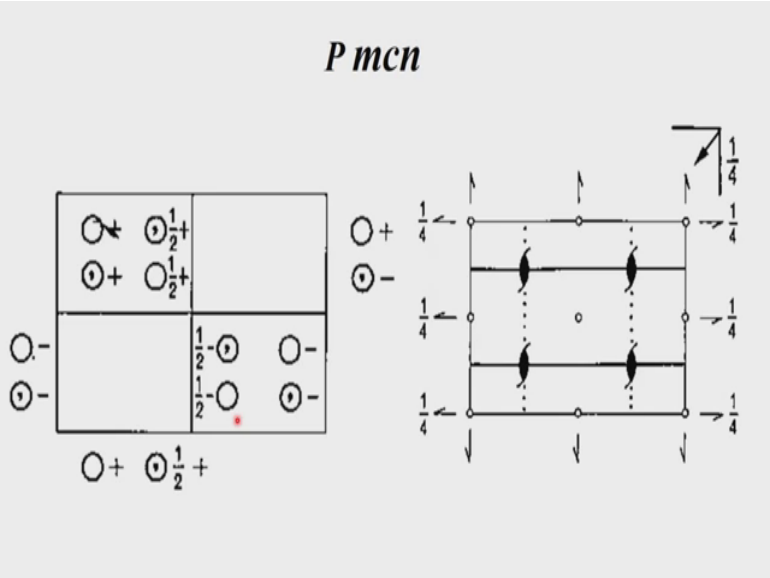

The 4/*m* symmetry in principle is centre of symmetric. Even though you have a 4 fold rotation 90 degree rotation coming up it is in principle so, it could be offering a special position. So, one studies the international tables fully which we are not going to hereafter we are going now a little forward and go eventually to the structure determination protocols and so on. At this particular position what we have to therefore, do is to to consists consolidate what we have learnt in space groups. And to consolidate what we have learnt in space groups. The best example would be to take something which is a realistic structure. Look at a realistic structure and see how the realistic structure distributes itself in a given space group.

I have purposely taken a space group which is not a standard space group. The corresponding standard space group will be what in this case *P m c n* find out. A mirror perpendicular to *a*, a *c* glide perpendicular to *b* and *n* glide perpendicular to *c*; so, we will have to find out what is the corresponding standard space group. So, we have to go to the international tables and go to the (Refer Time: 24:00) end of the international tables look at what is appear what is appearing as *P m c n* what is the translational change we have to do because it is an orthorhombic system.

So, *a b* and *c* have to be interchanged. What interchange will give us the standard crystal system. That is first thing we will do in the next class. So, to wind up this particular class we will see that we have the space groups now identified up to orthorhombic symmetry. We have seen the triclinic system, we have seen the monoclinic system, we have seen orthorhombic systems. In orthorhombic systems we have seen all possible point group symmetries we have seen 2 2 2, we have seen *m m* 2 and *m m m*.

Now, in that we have considered all possible variations we have considered the possibility of introducing $2_1$ axis and we have introduced the 3 non intersecting $2_1$ axis we have also introduce the positions 2 mirror positions and the $2_1$ axis the 2 mirrors now having glide planes. Like *P n a* $2_1$, which we have seen. And we have also seen *P b c a* which will involve the $2_1/m$, $2_1/m$, $2_1/m$ centre of symmetric operation. We have examined all in all cases wherever a special position is possible and in what way the symmetry elements rearranged themselves in those special positions starting from the triclinic system. We started from P $\bar{1}$ and ended up with this particular thing.

So, in essence we have covered now all aspects that are required to be known in space groups. We have not gone to the higher space groups because of the fact that which is not required for this course because now here onwards we have to find out the methodologies by means of which we find given a crystal. How do we find the space groups and how we assign the space group to a given material? And then how the material arranges itself in three dimensional space. So, we have come to that level and therefore, what I will do is I will take this system *P m c m*. And in this take an example of a known compound and we are going to look at the known compound being calcium carbonate.

So, in the next discussion we will look at calcium carbonate and see how calcium carbonate the calcium the carbon and the oxygen atoms arrange themselves in this space group *P m c n*. Keeping all the symmetry information intact, how calcium carbon and oxygen decide to go into this unit cell. Now how will they go into the unit cell is a very open question. So, we will have to therefore, in principle find out how many such calcium carbonate units can go into this unit cell. So, how will we do that? We do it by determining the unit cell dimension.

So, we know the *a b c* values. If we know the *a b c* values we can calculate the volume of the unit cell. Having calculated the volume of the unit cell since calcium carbonate we know the molecular weight we can now calculate given the volume and the molecular weight the density of the crystal. Assuming that this particular space group has; so, many equivalent points. So, *P m c n* we examine with respect to equivalent points, and these equivalent points how can we distribute the density which we can have in this particular case for calcium carbonate. It is also suggested and in fact, in our school days I mean when we were studying for our PhD not school days.

Whenever we looked at a crystal structure and whenever we grew a crystal we were asked to determine the density of the crystal. In fact, papers were not getting accepted without the acceptance of the density of the crystal. And therefore, determination of the density of the crystal is very important how are we going to determine the density of the crystal. So, we will start the next class from understanding how we determine the density of a crystal which is very crucial. And then we see one once we have the density we have the molecular weight we have the volume from *a b c* values we can then calculate how to distribute individual atoms inside this keeping the symmetry in mind.

Now, I am saying as though we have all solutions for all crystal structures, obviously not because we are taking a very simple compound calcium carbonate. Suppose we have a very large molecule suppose we have a protein I cannot use this approach which I am going to describe to find out where these atoms are. This is a very simple structure and it is going into a space group where it has to obey certain symmetries. And therefore, whatever symmetry it is going to obey we will try to reconstruct the structure in this particular space group.