Solid State Chemistry

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Lecture – 23
Point Groups

Now, I will go to the third lecture of week 5 of this course and in this lecture we will look at Point Groups in more detail ok. We have already seen about point symmetry operations space symmetry operations and we have also said where the concept of a group comes from and now we look at point group which basically represents the set of all point symmetry operations in a in a crystal. So, in this lecture we will talk about point groups.

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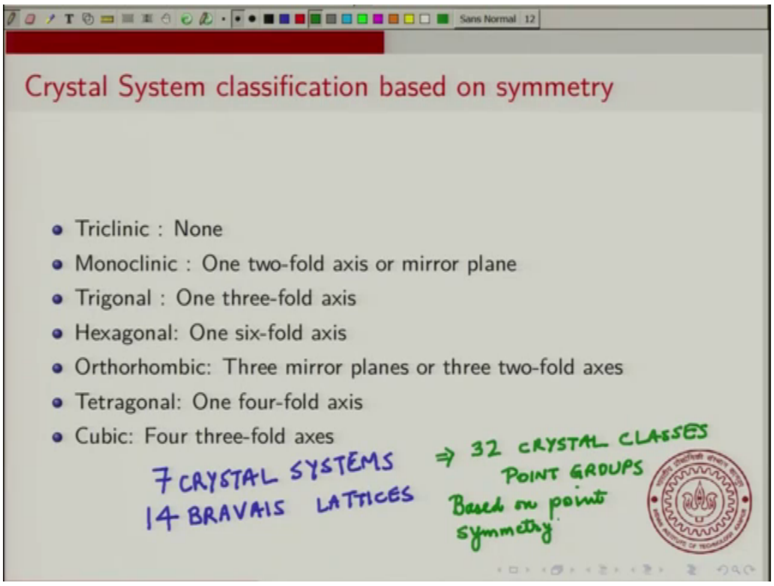

Now, we have already seen the crystal system classification based on symmetry and we had various essential symmetry requirements for the 7 crystal systems now. So, this gives us 7 Crystal Systems and further if you if you look at the lattices, if you look at the various lattices that are possible in each of these system they are classified into 14 Bravais Lattices ok. So, we can get those by looking at the looking at the unit cell for each of the crystal system and having it either centered or primitive.

So, that gives they had give us 14 Bravais lattices, now what we will see today is that is that this leads to 32 crystal classes or point groups or point groups I will not show all the

30 32 point groups ok. But I will just mention that if you look at the so these crystal classes or point groups ok. So, these are based on symmetries based on and in particular point symmetries point symmetries of the unit cell symmetry of one primitive cell.

Now, let us we will we will see we will see some of these 32 crystal classes in today's in today's in this lecture and then we will see in the next lecture how these 32 crystal classes or point groups are expanded to many more space groups.

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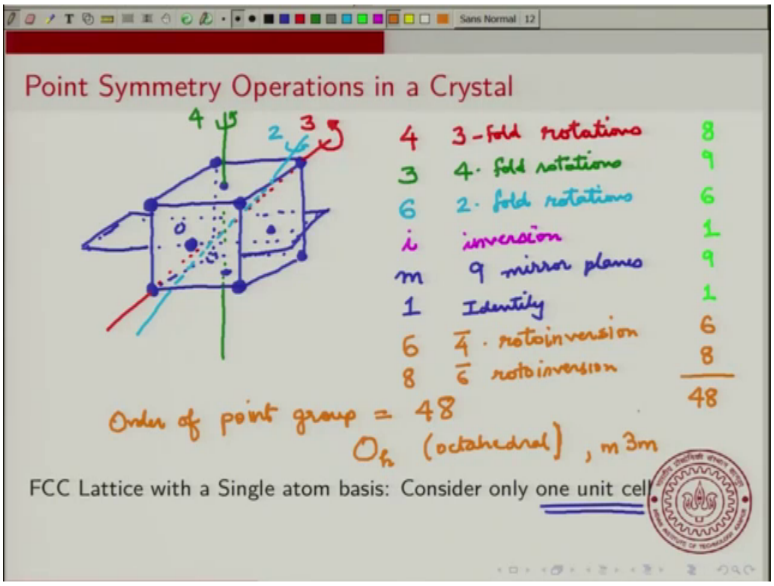

So, let us look at the point symmetry operations in a crystal and let me take the example of an FCC lattice with a single atom basis and let me emphasize that we are just considering 1 unit cell we are just considering a single unit cell which is cubic in shape ok, so for an FCC if you just take 1 cell you have it looks it is cubic in shape and we are just looking what are the symmetry operations that will take this cube this cube with atoms at the corners and atoms at the face centers what are the symmetry operations that we will leave this cube unchanged ok.

So, we will show the face centered atoms ok. So, these are the 6 face center atoms and the corner atoms ok. Now the question is you just take this single unit cell ok, so we are considering only one unit cell and we are asking what are the symmetry operations of this unit cell ok. What are the operations that will leave this unit cell unchanged ok?

Now, we can we can we can start with the 3 fold rotation. So, clearly there are 4 3 fold rotations ok, let me let me use a slightly different color to him to write this. So, I will just say 3 fold rotations and I will just show one of those I will show here. So, one of those is this one that is passing through the body diagonal and you have 4 of these. So, you have 4 3 fold rotations this is a 3 clearly there are 4 of these I am not going to show all the 4 ok.

But what else is there now you can have you can have 3 4 fold rotations. So, and the 3 4 fold rotations will I will just show one of them that comes out, so this is clearly 4 fold rotation. What else can you have well it turns out that there are other rotations that are possible ok, there is there are 6 2 fold rotations and these rotation axis actually go from is all right 6 and this go from the center of 1 edge to the center of the opposite edge.

So, that is a 2 fold rotation 2 fold axis of rotation and you can easily see that you rotate about 180 degrees about this you will get an equivalent configuration ok. There are 6 of these I am not showing all the 6 I am just showing one of each of them. Now other operations in addition to this and yes indeed there are lot of other operations and again I am not going to show all of them explicitly, but let me mention a few let me mention them. So, there is a inversion about this about this origin about this center.

Then there are mirror planes, so there are 9 mirror planes and you can you can easily see these 9 if you just take so and so you can you can you can see these quite easily is it. So, you will have diagonal mirror planes and you will have you will have along this midpoint ok. So, they will all be mirror planes there will be total 9 of them just to show some of these mirror planes let me I will just show 1 mirror plane that is perpendicular to the screen and it passes ok. So, you will have mean thesis I do not know if it is this is a mirror plane, it is actually perpendicular to the screen and it goes through the through the through the I mean it cuts the cube directly into 2 halves ok.

So, this is so that is and there will be there will be 2 others there will be 2 others and there will be 4 there will be 2 diagonals in each on each of the directions ok. So, there are total of 9 mirror planes and so now you can take each of these and then and then there is the identity operation I will just call it identity this is just one identity.

So, so now if you ask how many configurations you get of the how many how many different configuration or how many different configurations do you generate from all these operations. So, if you have a 3 fold rotation then the 3 fold rotation corresponds to rotation by 120 degrees, so you can have rotation by 120 degrees and rotation by 240 degrees.

Now 3 fold means you rotate it you do it 3 times you get back the identity. So, you get 2 distinct 2 new configurations for the due to this due to each 3 fold rotation. So, you can you can see that if you have 4 3 fold rotations you will generate 8 new configurations. If you have 3 4 fold rotations you will generate 9 new configurations ok. So, essentially the number of distinct symmetry operations are 8 9 here you would have 6 distinct, because here you will have you will have 1 distinct here you will have 9 distinct and here you just have the original one ok.

So, this is the total order of the symmetry operations or the number of distinct symmetry operations that you have ok, in addition to this you have some you have some more operations. So for example, each of these 2 fold so in addition to this you have some roto inversions ok, you have you have 4 bar roto inversion now this 4 bar roto inversion axes ok. So, actually the 6 2 fold rotations each of them is corresponds to a 4 bar roto inversion axes and similarly there is a 3 bar roto inversion axes ok.

Actually you will get from the 3 fro from the 4 3 fold rotations you will get you will get you will get 8 roto inversions ok. Now this 8 it should be 6 bar roto inversion ok. So, this each 3 fold rotation corresponds to a roto inversion axes by half that amount ok. So, this generates an additional 6 operations and this generates an additional 8 operations. So, the total number of operations if you if you add this had had all of these the total number of operations we will come out to 48. So, the order of the point group is 48 and this point group is given the notation in point group terminology this is called as oh or octahedral, octahedral point group in the this is a third terminology that is borrowed from molecules. In the we will come to the description in the in Herman McGraw convention a little later I mean the this is called m 3 m in the Herman McGraw notation ok, we will we will we will explain this in more detail in the in the next lecture ok. But the point is that you have 48 different symmetry operations they correspond to the octahedral group ok.

Now a few things to be kept in mind the you should you should keep in mind that you know this 4 bar roto inversion ok, if you apply twice you will get a c 2 you will get a you will get a 2 fold rotation. So, 4 four bar roto inversion corresponds to rotation by

90degrees and inversion. So, if you do it 2 times you will get rotation by 180 degrees and 2 inversions will cancel each other. So, that will just be a rotation by 180 degrees which is just a 2 fold rotation ok. So, actually the number of distinct operations that are generated by this is only 1 and again this is this is just a property of this of this of this crystal ok.

So, so these are the these are the distinct operations that are there in the crystal and the and the point group of FCC is octahedral ok. Now next we can ask the question see now keep in mind that we only we just looked at one unit cell and whatever operations we did we never we never mapped it all these atoms were mapped onto each other so the cube remained as it was ok. You never consider an operation where this atom was where 1 atom from 1 unit cell was mapped to a neighboring unit cell through an atom from a neighboring unit cell ok.

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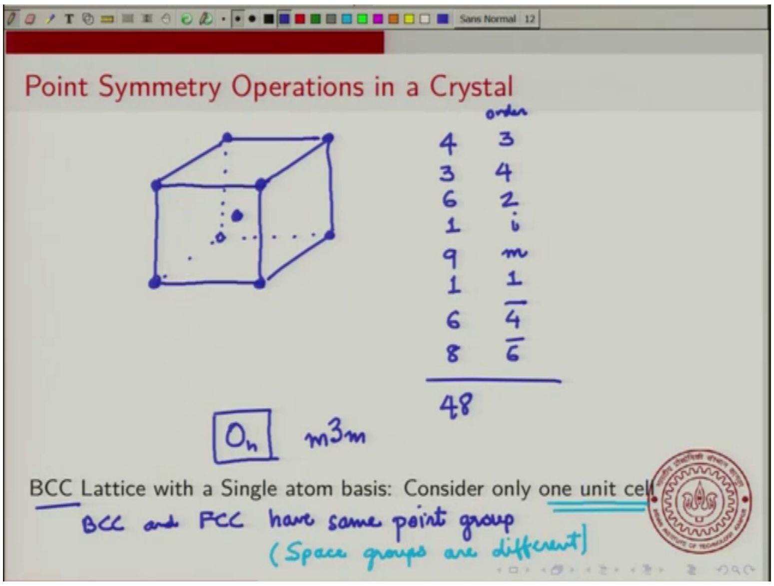

Now, what about a BCC lattice with a single atom basis now again you will consider only one unit cell and we will consider a BCC unit cell. So, you have all the atoms at the corners of a cube and one at the body center.

Now again you can see you can see without too much difficulty that you still have the you still have the 4 3 axis of rotation, you have the 3 4 fold axis of rotations you have the 6 2 fold axis of rotation and this is the order of rotation ok. So, the order of the rotation axis sox you have you have 3 you have the this is the number of number of different axis.

So, you have 4 3 three axis 3 4 axis 6 2 axis just like earlier, you have the inversion center again just like just like in the previous case and you still have the 9 mirrors right, 1 inversion center you have one identity I will call it oh one which is always there identity is always there and you can again convince yourself that you still have those you still have the 6 4 bar and 8 6 bar ok, so you still have all those ok.

So, again you have 48 operations and again the point group is octahedral ok. So, BCC and FCC and simple cubic also have same point group or they belong to the same point group, so the point group of BCC and FCC is the same there is no difference between the in the point groups of FCC and BCC ok.

However, keep in mind that space groups are different space groups will show that they are quite different ok. In fact, in fact you know since we considered only one unit cell ok, so we are just we are just looking at one of these cubes now essentially the whatever the symmetries are there in the cube there will be there in BCC or FCC ok, changing it from BCC to FCC is not going to change the symmetries of a cube right.

So, it is expected that BCC and FCC will have the same point group and you can you can call it octahedral or m 3 m will the I will I will explain this m 3 m again, so this is in the Hermann McGraw in rotation ok. But essentially there is only BCC and FCC belong to the same point group.

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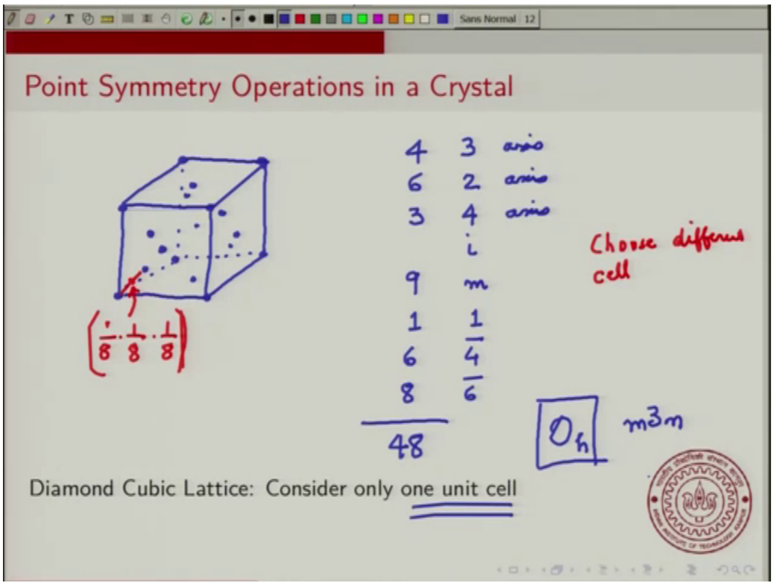

What about diamond now again if you just consider one unit cell and you take your additional points that you that we like to put that we always put 4 diamond along the body diagonals, along this one, one-fourth of the body diagonals along this one and along this one. So now, again it should not take you too much convincing that this still has the 4 3 axis, it still has the 6 2 axis it still has the 3 4 axis and it will still have the.

Now, diamond if you just consider one unit cell, then clearly diamond does not have a center of inversion ok. If you if you just look at a single unit cell then it would appear that diamond does not possess a center of inversion ok. However, we already saw earlier that the there is an inversion center and that is that is located between the between the corner atom and the center of and one of the one of the atoms on the body diagonal so there is an inversion center ok. Now here you have to if you want to see this inversion center in a single cell ok, then you have to you have to take a slightly different cell ok.

So, choose different cell and it is not very hard to do that ok. So, you just take your cube and if you choose it if you choose it in a slightly different direction ok, so that so that this is the this point that goes halfway here is now the center ok.

So, so if you if you if you choose a unit cell that is centered here ok, then again you can you can easily construct a unit cell that is centered here and again with just one cube that is instead of centering the cube at 0 you center it at you know instead of centering it at half you center it at 1 8 1 8 1 8 and you will get you will you will see a cell where the inversion axis is in the inversion center is very clear and similarly when you when you do that you will also see that all the remaining symmetry elements ok.

Which are which are part of this like you have the 9 mirrors you have the one identity you have the you have the 6 4 bar and you have the 8 6 bar all these are there, so you get 48 and this is also octahedral m 3 m ok. So, again this is something that you should work out you should not take these as given to you these are these are slightly involved to work out, but you can show that if you choose one unit cell if you center your unit cell appropriately then you will see all these symmetries of a Diamond Cubic Lattice.

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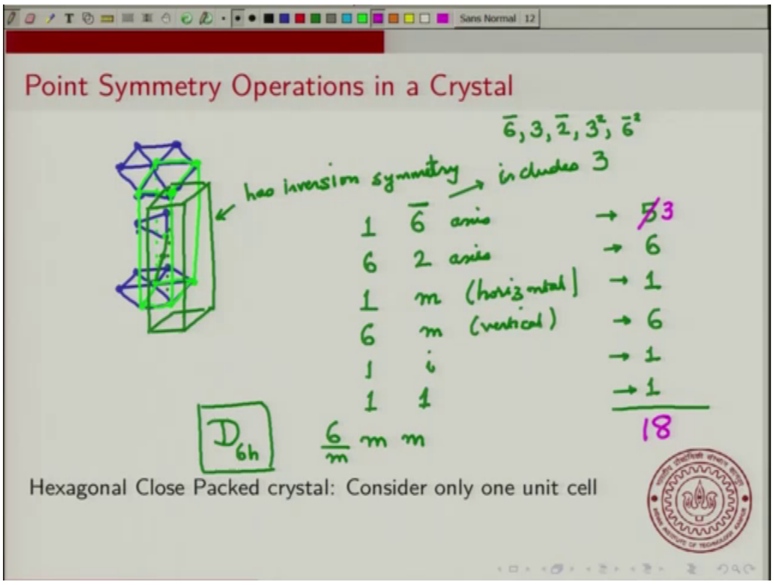

Now finally, let us take the example of a hexagonal close packed cell and now and now again we are going to consider only one cell, but again as we had shown earlier that it is possible to you can you can choose your cell, so that so that it shows a center of inversion. So, while usually we take we take the HCP in this in this form ok. Now usually we often take or unit cell having an atom at the corner ok, so if we take it this form and if you take it in this form then only one of these will be in the in the in the middle of the cell and so and so and it won't be exactly at the center it will be slightly off the center ok.

However, what we said is that it is possible to choose a slightly different shifted unit cell ok, where the where the midpoint is located the midpoint of the cell is located directly in the in the middle of this line right here ok. So, if you choose a new cell where the midpoint is located here and I will just show it schematically ok. Now in if you choose such a cell so this has an inversion has inversion symmetry actually. So, it has inversion symmetry with respect to these to the atoms that are there in the cell and now you can look at the various symmetry elements ok. So, the symmetry elements in an in an HCP crystal are the following, so there is 1 6 axis and. In fact, in fact this is a 6 bar axis it is not a 6 axis it is a 6 bar axis ok

There are 6 2 axis there is there is 1 mirror this is in the horizontal direction and there are 6 mirrors in the vertical directions and in addition in addition there is an inversion center inversion center and there is a one identity operation and now so the so the 6 th power axis we will generate a total of 5 symmetry operations including.

So, if you do 6 bar twice you will get a c 3. So, including that you get 5 symmetry operations you will get. So, 6 bar includes c 3 ok. So, 6 bar operated twice will give you us will give you a into it includes a 3 a 3 fold rotation. So, 6 correspond to rotation by 60 degrees, so if you do 60 degrees and inversion again you do 60 degrees and inversion. So, totally you have done one120 degrees and you have cancelled the inversion.

So, that is a that is a 3 fold axis of rotation then there are 6 2 axis of rotation there is one 1 operation due to a mirror there are 6 other mirrors there is one inversion and one more and this falls in the group this symmetry group is called D6 h in molecular symmetry language and in crystallographic symmetry it is called 6 by 6 by m. Now let us let us look at the 6 axis a little more closely ok, so let us look at 6 axis a little more closely so you have 6 bar 6 bar square is same as 3, then you have 6 bar cube 6 into 3 is nothing but the but 2 ok.

So, this is nothing but 2 bar and since and then you have you have 6 into 4 is just 3 square and 6 into 5 is 6 bar into 5 ok, so that will that will give you write it as 6 bar square and then you have the identity ok.

Now 2 bar 2 bar is actually nothing, but a mirror ok, so there will be some reduction in the in the number of number of symmetries due to due to this 6 bar axis ok, so it won't actually be 5 ok. So, the number of number of distinct symmetry operations due to this due to this 6 fold axis will be here, so this will be only 3 distinct operations ok. So, you have total 18 operations and d 6 h is a group of order 18 ok. So, with this I will conclude this discussion on point groups and I encourage you to actually look at various crystals of different kinds of crystals you could look at things like sodium chloride, you could look at zinc blende you could look at various crystal structures and try to identify the point groups ok.

Now, these point groups you can also find in the international tables of crystallography ok, there are several places where you can actually find the point groups and all the symmetry elements, but it helps to actually work out some of these point groups and you will realize when you when you actually work them out you will realize some of the subtleties that are there in the definition of the point group ok. So, I will conclude this lecture here in the next lecture I will talk about space groups.

Thank you.