Solid State Chemistry
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Lecture - 15
Review of Week 3, Practice Questions

Now we will go to the fifth and last lecture of week 3 of this course. In this lecture, I will review what we learnt in week 3 and do a practice questions. So, we will review week 3 and do practice questions.

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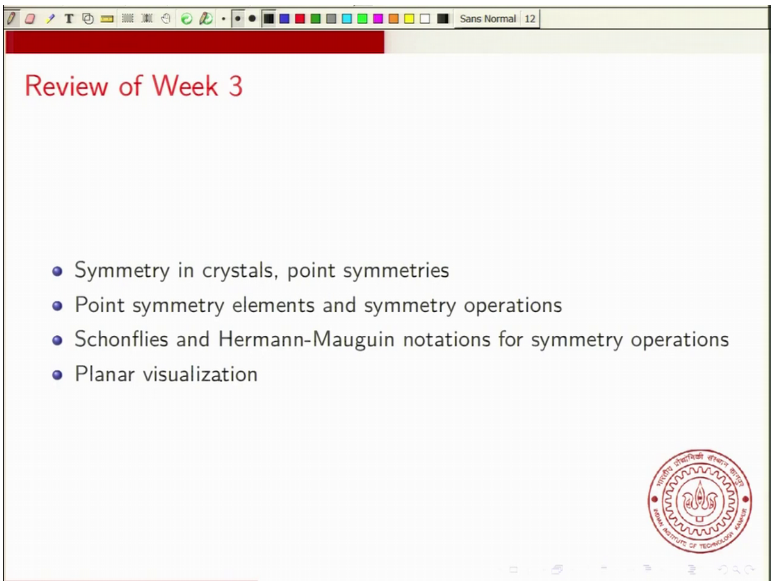

Now, in week 3; we learnt about symmetries in crystals and in particular we learnt about point symmetries ok. I will mention here that the translational symmetries will be discussed in week 4; then we discussed the different point symmetry elements and the symmetry operations.

We talked about 2 kinds of notations the Schonflies and the Hermann-Mauguin notations for symmetry operations. And then at the end we came back to fractional coordinates and talked about planar visualisation of crystals. Now to understand symmetries in crystals better; it is always good to look at examples and now today I am going to take an example of diamond lattice or the diamond crystals that we studied in the last lecture ok.

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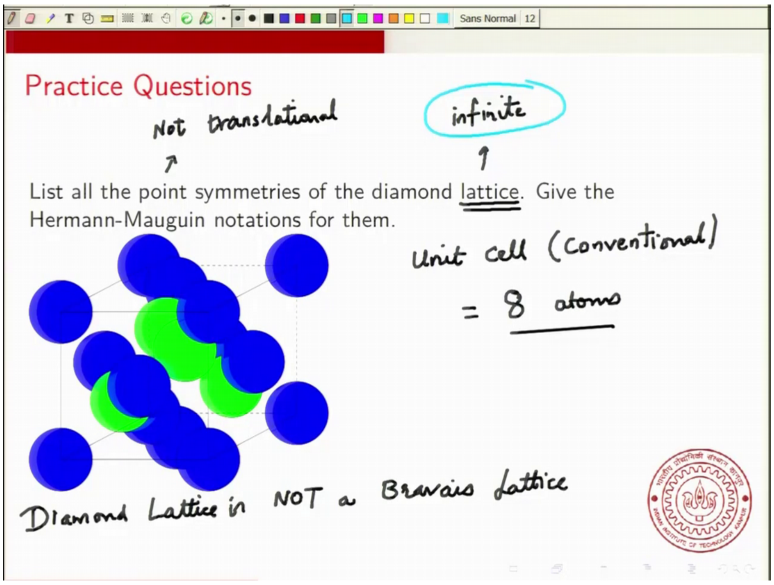

And what I am going to try to do is to your question is to list all the point symmetries of the diamond lattice and give the Hermann Mauguin notations for them ok.

And I will turn out that this; this exercises will turn out to be nontrivial what you should keep in mind is that a lattice is infinite ok. That means, its stretches in 2 infinity in all directions and we are listing only the points symmetries ok. Now again the word point in this context just refers to symmetries of the unit cell and point in this context refers to those symmetries which are not translational symmetries ok; so, its point in the sense of not translational.

And also we should keep in mind that; keep in mind that 2 things to keep in mind; you know diamond lattice is not Bravais lattice. And the other thing to keep in mind which you can see from here is that this unit cell or the conventional unit cell that is the diamond cell shown as a cube. This has a total of 8 atoms ok there are 4 due to the FCC and 4 due to this green atoms at the tetrahedral voids ok.

So, it has a total of 8 atoms in this conventional cell ok. So, clearly it is not a primitive cell and in fact, this cell does not even have all the symmetries of the diamond lattice ok. So, these are things to be kept in mind. So, you should always look at you should always look at lattice; it is an infinite as you know infinite set of points; that means, it extends in all directions. And you should also keep in mind that this is the convenient unit cell that is used to represent the diamond lattice ok. So, now let us go to the symmetry element.

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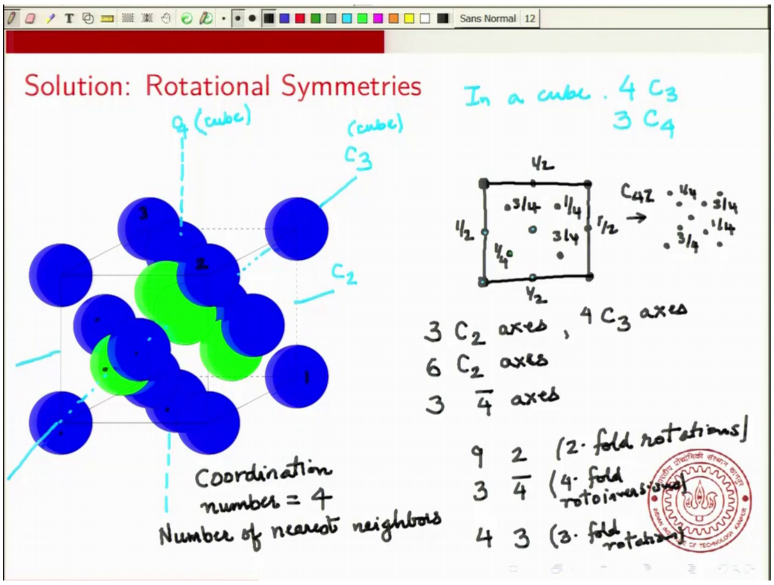

So, let us look at the rotational symmetry elements and this will turn out to be highly non trivial ok. Now we had seen that a cube you remember the cube had this 4; you know characterized by 4 C 3 axes and 3 C 4 axes ok. So, remember in a cube ok. So, in cube you had 4 C 3 axes and and 3 C 4 axes the 3 C 4 axis; where the one set were going through the centre of the phase like this and going all the way and coming out from the other side through this centre of this space ok.

So, I will just show this ok. So, this is an example of C 4 axes ok. So, this is C 4 axes of the cube ok. So, cube this is a C 4 axes for cube and this is the C 2 axes for the cube and there are 3 of these. So, there is one in the z direction, one in the x direction and one in the y direction. Now you can already see that some of this will not be the same axis anymore ok. So, and to see this it is convenient to go back to the fractional coordinates that we discussed in the last lecture.

So, let us show the fractional coordinates. So, this is at z equal to 0; then you have z equal to 1 by 4 you had these 2 points 1 by 4 ok. And at 3 by 4 you had these 2 points and you had all these 6 points at half ok. And the remaining point for at z equal the corner in the phase centre where at z equal to 0 ok; so this is the this is a planar representation.

And now you can see that if I let us look at this oh this should be C 4 sorry this is the mistake this should be C 4 for a cube I made of couple of mistakes this should be C 3 for a cube and this should be C 4 for a cube ok. So, the 4 C 3 this is C 3 for a cube this is a C 3 4 for a cube. Now what happens to this let us look at this 3 4 ok; now you can see you can see that the C 4 axes in if you look in a plane ok.

So, if you are looking at this C 4 you can see this plane and in this planar representation; you can see that C 4 will take will take any of these points located at one fourth and move it directly below the point that is located at 3 by 4 ok. So if you do a C 4 ok; if you a C 4 and in particular this is along the along the z direction, along the z direction then what you will get is then I will just show it the corners I will show it a little smaller do not do not be.

So, you have the corner atoms you have the phase centre and now this one fourth actually comes here. So, these are the 2 one fourth remember C 4 will not change the z co ordinate and these are the 2 -three fourth.

So, in the plane the location of the one fourth and C fourth are changed ok. So, clearly there is no C 4 axes in this in this diamond lattice; however, if you do C for twice then you can then you will get back to exactly something like this. Because the 2 the 2 points that are located at z equal to 3 4 will swapped the points that are located at z equal to one fourth will swapped. So, clearly you have you have 3 C 2 axes this is directly due to the cube ok.

Now, the 4 3 4 rotations ok; they are also symmetry operations for diamond lattice ok. So, you still have 4 C 3 axis; so these are the axis along the body diagonals ok. Now let us look at this 4 C 3 axes along the body diagonals once again. Now if you do C 3 operation along about the body diagonal now what we said is that that will that will actually if you are doing along if you consider this C 3 axes ok; then the corner atoms which are represented by 1 2; 1 2 and 3 will get exchanged with each other ok.

And now this will actually and this will cause and exchange of these 3 atoms. So, these 3 atoms which are tetrahedrally located with respect to with respect to this corner atom will get exchange. So, there are 4 C 3 axes in the diamond lattice ok. In fact, what is what is interesting about the diamond lattice is that the coordination number equal to 4 ok.

So, in a diamond lattice again we will see this in more detail, but the number of nearest neighbours for any atom is 4 ok; this is a property of the diamond lattice. And you can see this you can easily take any atom and show that it has 4 4 nearest neighbours ok. So, this is the number of nearest neighbours. So, it is a number of atoms that are closest to it. So, if you take for example, if you take if you take this atom; this atom in green ok. So, that has 4 neighbours this 1 2 3 and 4; so this 4 are nearest neighbours to the screen atom ok.

So, in other words if I the green atom was this atom ok. So, it has 4 nearest neighbours and those nearest neighbours I will show them in light blue here. So, they will be this, this, this and this this will be the 4 nearest neighbours of this atom ok. So, the coordination number is just 4 now. So, we have the 3 C 2 axes and the 4 C 3 axis; now in a cube there are other symmetries one there are there are actually 6 other C 2 axes, those 6 C 2 axes of a cube those go from ok. So, they go from they go from through the edges ok; through one edge and the diametrically opposite edge ok.

So, this axis that goes from the centre of one edge to the centre of the diametrically opposite edge ok; this in a cube this is the C 2 axes ok. So, this C 2 axes in the cube is also there in the in the; in the diamond lattice; so there are additional 6 C 2 axes ok. So, we end up with the total of 9 C 2 axes, you have 4 C 3 axes and the question is that all that are there with the rotations and the answer is no ok.

So, what was the C 4 axes in a cube that becomes an S 4 axes. So, the C 4 axes of the cube becomes an S 4 axes of a cube ok. So, there are 4 4 S 4 axes or rather let me let use 4 bar axis 4 4; bar means you rotate it and you invert about the center ok. So, if you do that you can see you can clearly seen that if you if you rotated by 90 degrees then this point will come somewhere here ok. Then you flip it about the centre and it will come on top of this point you invert it around the centre ok. So, this is inversion around this is rotation by 90 degrees followed by inversion about the centre ok.

So, there are total of 9 C 2 axes 4 C 3 axes and 4 and sorry it should not be 4 and it should be 3. So, there are 3 3 4 bar axis ok. So, the 4 fold 4 fold rotation axes are actually inversion axis. So, in the Hermann-Mauguin notation you have 9 2 rotations ok. So, you have 9 these 2s 2 this is 2 fold rotation; you have 3 of 4 bar, this is rotoinversions, this is 4 fold rotoinversions and finally, you have 4 3 axes; that is 3 fold rotation ok. So, these are the all the rotation axis that are present in the diamond lattice ok. Now, next let us go to the reflection symmetry.

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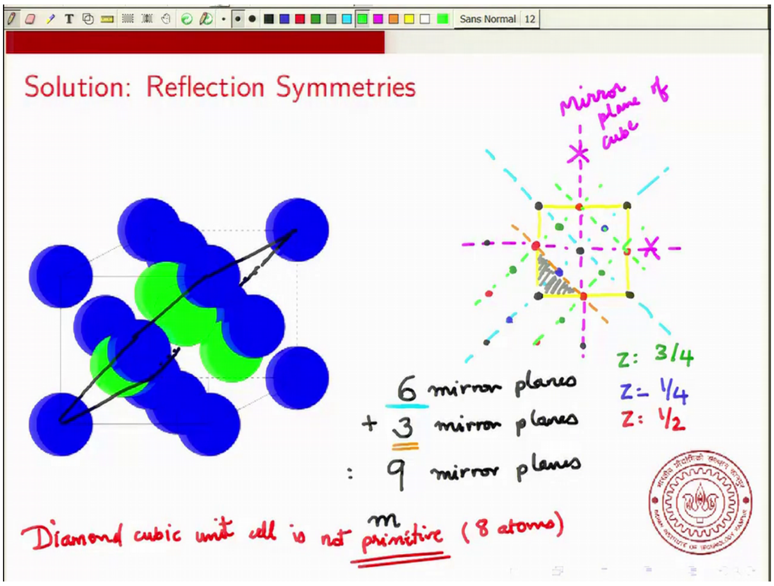

So, the reflection symmetries are shown in this figure ok. So, if we look at this 2 D planar representation that is seen here on the right ok; we can immediately see that there are 2 mirrors along these diagonals.

So, these are shown in light blue colour ok. Now recall that in the case of a cube you had 2 additional mirrors which I will which I will show in this purple colour; which are not there in the case of the diamond lattice. So, this was a mirror in the case of a cube and the corresponding perpendicular one. So, these were mirrors in the case of a cube. So, this is not a mirror for diamond lattice this is mirror plane of cube, but not diamond ok. So, this is not a mirror plane for diamond this is not a mirror plane of diamond ok. So, these 2 mirror planes of the cube or not mirror planes in diamond; however, these 2 other planes shown in light blue these are mirror planes ok.

So, now this planar representation is in the xy plane and it is in the xy plane and so you will have similar representations in the xz sand yz plane ok. So, clearly you will get you will get a total of 2 into 3 6 mirror planes from which are which correspond to these diagonals ok. So, there are 6 mirror planes corresponding to this diagonals shown in light blue ok. So, 2 in the xy 2 in the xz and 2 in the yz. So, here I have on the cube I have shown one of these planes what it looks like ok. So, this is he this is one of these diagonal planes ok.

Now, what are the other planes ok? There are it turns out that there are 3 more planes 3 more unique planes in the case of in the case of diamond lattice and these 3 planes I will just show. So, there will be one in the xy plane; you will see one another mirror plane I will show this an orange ok. Now you can see that this is a mirror plane of reflection whatever shown in this colour is a mirror plane of reflection and to see this you have to extend the crystal ok; so you will extend the crystal.

So, let us put another red point here another red point here and we will put a blue point here ok. Notice that you are you are translating the same crystal here and you will have a black point here ok. I am just showing this top right corner of the crystal and you can already see that this is the mirror plane. So, the point is this will be a plane of this will be a mirror plane just. So, I just repeated this entire unit cell just to just to emphasize that now you can clearly see that this is the plane of symmetry. So, what are shown in orange is a plane of symmetry ok.

And let me just show the original unit cell in yellow ok; just to emphasize that we had to extend the unit cell to see this symmetry operation. So, because and the way we are extended it first we just translated it ok. So, because of the translational symmetry of the cube you could just extend it and you could see the same cell ok.

Now, what is also important to note here is the following; there is a little subtlety. So, if you take this mirror plane which are shown in orange ok, now this in the xy plane ok. So, there should be one in the y z and one in the xz plane. So, you will get 3 more mirror planes ok. So, that gives a total of 9 mirror planes and in fact, in fact the diamond lattice has 9 mirror plane.

But there is a little subtlety here and that is a following the subtlety has to do with the fact that we considered only one of these planes ok. Now you could consider other planes for example, let me show this you could consider a plane like this; this is also a mirror plane. Similarly, you could consider a plane like this should also be a mirror plane ok. So, this planes in green that are shown in green would also be mirror plane ok.

However, when we count the number of mirror planes; we only count the plane and plane and brown; hey we do not consider the planes in green and the reason for this is is slightly subtle. So, the first point to note that these are the green ones are also subtle planes; however, in the usual way of counting the number of mirror planes for a diamond lattice, we do not count this green ones ok.

So, reason and the reason these are not counted is actually quite subtle ok. So, keep in mind that that the diamond lattice is not a primitive lattice ok. So, diamond in fact, it is not even Bravais lattice, but essentially this diamond cubic unit cell is not primitive ok. So, this is it is not primitive and so it is not primitive in the sense it contains 8 contents 8 content 8 atoms.

And so what we want to say is at this small unit that is shown here that are shaded this unit ok; this is one eighth of the cell this is 1 in 8 of the cell ok. And it turns out that that you only need to consider the mirror operation on this one eighth of the cell. And this is because your unit cell is not primitive and so and so this is the asymmetric unit of this cell ok.

This might be a little complicated and in fact, these are the unique mirror plane ok; these 3 these 3 mirror plane these additional 3 mirror planes are the unique mirror plane ok. So, it might see may little complicated, but, but this is something to keep in mind it is something to keep in mind that your diamond is not this unit cell is not primitive it has 8 atoms ok. So, if you have just 1 atom ok; so we take one eighth of this cell then by symmetry operations you should be able to generate the entire cell.

So, what it means is at is, at you only consider this one eighth for all the operations ok. So, we will; so this is something to be kept in mind that it not always to always easy to count the number of unique symmetry elements ok. But nevertheless irrespective of that it is true; that these lines in green on this unit cell are also symmetry operations ok; so they are also mirror plane ok. So, we have all these mirror plane, but the number of unique mirror planes is just 3 ok.

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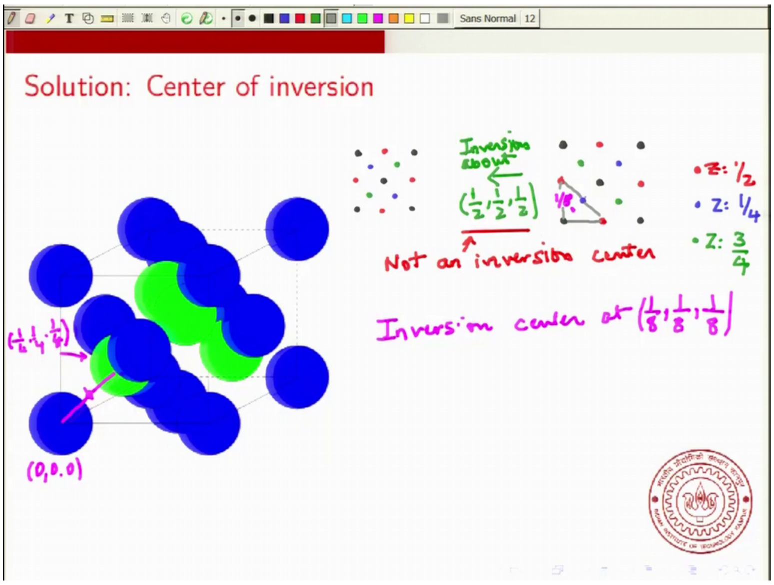

So, next we go to the centre of inversion ok. So, the diamond diamond lattice has a centre of inversion. Now it if you take the centre point of this diamond lattice ok.

So, that is the central atom actually there is no atom at the center of this cube, but if you take the centre of this cube if you take the centre of the cube and you invert about that point ok. Then what will happen is then atom at height 3 by 4 will become an atom at height 1 by 4 ok. And if you go through the whole exercise, you will see that inversion about this centre point the centre has coordinates half, half, half ok. So, the coordinates of the center point are fractional coordinates are half, half.

So, if you do an inversion about the centre point then you will get crystal that looks different from what you started with in the sense in the following sense. So, you have the blue points which red equal to 1 fold; along the body diagonal going in this direction. Now you have the green points at height 3 by 4 along this body diagonal ok. So, clearly half, half, half is not an inversion center ok.

However, again you can see this by extending the cell you can see that there is an inversion centre located at this point which is shown in this violet colour ok; this point shown in violet colour is an inversion centre. So, there is an innovation center at 1 8, 1 8 and 1 8. So, the coordinates of this point this point on this cell you can see it lies right here ok. So, since this green atom was at coordinates of 1 4, 1 by 4, 1 by 4; this is a midway point between 0 0 0 and 1 by 4, 1 by 4, 1 by 4. So, this is 0 0 0; this green atom is 1 by 4, 1 by 4, 1 by 4 ok.

And this point midway between these will have coordinates of 1 by 8, 1 by 8, 1 by 8. And you can again look at the entire crystal and show that this point is actually an inversion center ok. Again so when you invert about this point clearly the point at 0 0 0 and 1 4, 1 4, 1 4 will swap each other and you can show that you will generate the entire crystal in this way ok. Again inversion is not a very easy or easy operation to visualise however, you can you can easily extend the unit cell and see this ok.

Now, again there are several other inversion centres ok; if this is an inversion center you could have inversion centres at various at mid points of all these atom ok. So, there are several other inversion centres which are not; which are again not shown because of the reasons we mentioned the last time that you only need to consider the asymmetric unit to show to show the inversion centre. So, once again you keep in mind that will only show the invoice in centre in this small unit ok.

Againit is a fact that there are several other inversion centres ok. And you know we I want I want mention in fact each of these points in between in between theses dots will be an inversion centre ok. So, if you take any point by effecting any nearest neighbour any pair of nearest neighbour atoms that will be an inversion centre ok.

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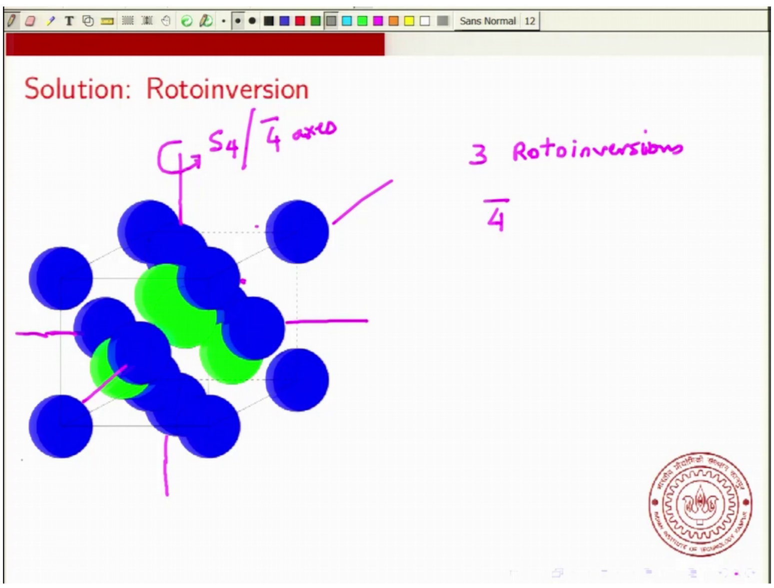

So, finally, we will come back to the rotoinversion; now we already talked about the rotoinversions we said that we said that each of these C 2 axes was is actually an S 4 axes ok. So, it is a or a folder axes; so there are 3 rotoinversions in the diamond lattice ok. So, no one will be in this direction one will be in this direction ok. So, these 2 are in the plane of the paper and then one is perpendicular to the plane of the paper that is this direction ok.

So, with that we have completed the identification of all the all the point symmetry elements and all the point symmetry operations of the diamond lattice ok. And this concludes our discussion on point's symmetry elements and it concludes week 3 of this course. Next week we will look at the translational symmetry elements.

Thank you.