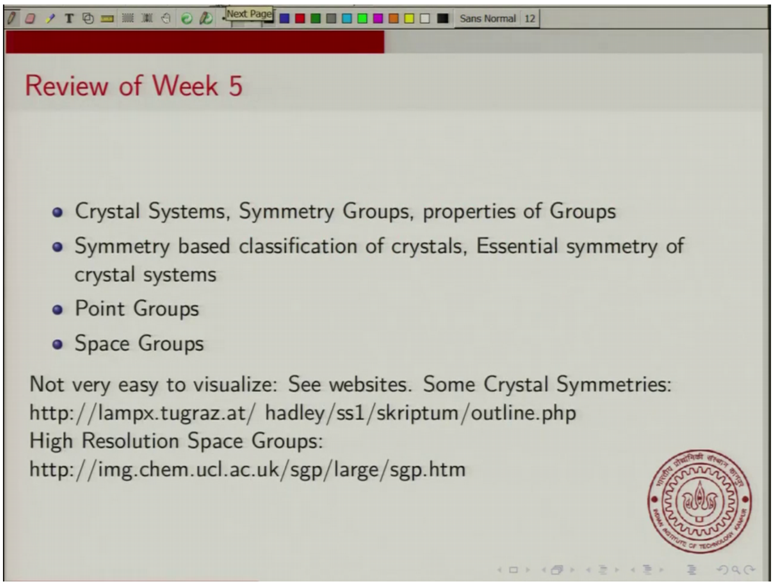
Solid State Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture – 25
Summary of Week 5, Practice Problems

Now, we will go to the 5th and last lecture of week 5 of this course. And in this lecture, I will summarize everything that you learnt in week 4, and do a couple of practice problems. So, week 5, lecture 5 will be summary of week 5 and practice problems.

(Refer Slide Time: 00:35)



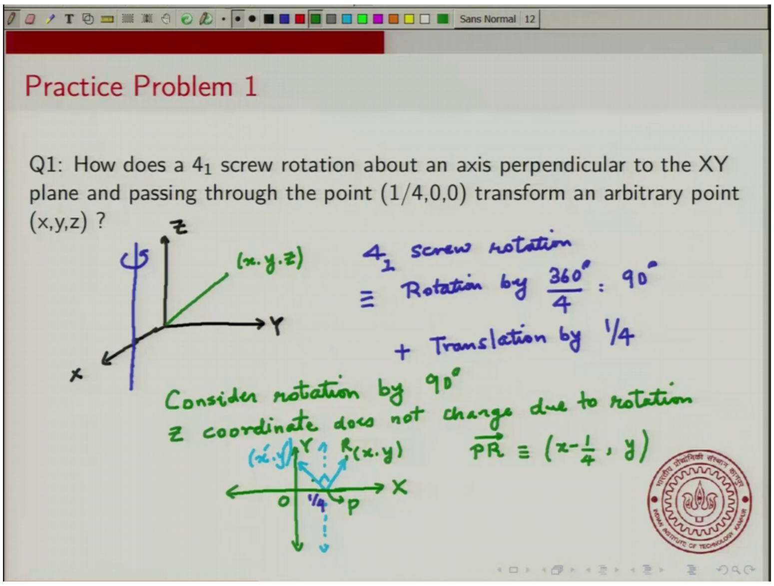
In this week, we learned about mainly about point groups and space groups, but first I look we looked at the crystal systems, and we and we said what are symmetry groups, and what are the properties of groups. So, we defined these things called groups ok, which have certain properties.

And then we talked about the symmetry based classification of crystals, and the essential symmetry of the crystal systems. So, what are the essentials symmetries that are required to put crystals in different crystal systems. Then we discussed in detailed about the point groups and about the space groups. And one of the things is that, some of these things you know identifying all the symmetry operations necessary to classify crystals into a point groups and space groups, it is not always very easy ok.

And so I mentioned that it is not very easy to visualize and I recommend see looking at some websites. So, there are some crystal symmetries on this website, this is the tugraz graz website ok. And also there are some there are the full detailed high resolution space groups which are available on this website ok. This, is actually in a lot of detail and we will probably you I mean it is it is good to know that these websites if this second website exists and probably you will use it more after week 6 of this course.

But definitely the crystal symmetries, there are some crystal symmetries that are there. This is actually a course on solid state on solid state, and in that there are some links to crystal structures. And actually the nice thing is that not only have they shown the crystal structures like FCC, diamond, zinc blend and so on, but they have also described all the symmetry operations both in the space group; so, all the symmetry operations of the space group are described here.

(Refer Slide Time: 02:50)



Now, let me do a couple of practice problems ok. See one of the things you learned in this week was how to transform an arbitrary point due to due to some symmetry operation ok. So, this question will test just your mathematical ability on how you can, how you can do this transformation due to a symmetry operation. So, the question is how does a 4 under subscript 1 screw rotation about an axis perpendicular to the XY plane and passing through the point one-fourth, 0, 0 transform an arbitrary point x, y, z ok.

So, just to set up the problem what you have is you have these axis ok. If you call this x, y and z-axis ok, and you have an axis perpendicular to the XY plane and passing through the point one-fourth 0, 0. So, one-fourth quarter, 0, 0 is some point somewhere here. And you imagine that you have an axis like this ok, and it goes below the below the XY plane. So, this axis and now you are doing a screw rotation about this axis.

So, what you are doing is a is a rotation. So, a 4 1 screw ok, so this means rotation by 360 degrees divided by 4 equal to 90 degrees plus translation by on one-fourth ok. So, what you have to do is you have to take a point rotated by 90 degrees ok. But the rotation is about this axis, about this axis that is shifted from the from the origin and then translation by one-fourth ok.

So, now let us look at an arbitrary point. So, if you have an arbitrary point that will have coordinates x, y, z. And let us look first at rotation by 90 degrees, first consider rotation by 90 degrees ok. Now, what is important is that this rotation is about this axis. So, so now suppose you had just the rotation about the z-axis by 90 degrees, then you know how to do the transformation ok. So, but now you have a rotation about a different axis ok.

So, now this axis is again parallel to the z-axis. So, first thing you note is that z coordinate does not change during rotation ok. So, only the xy coordinates change. And so you can look at this in terms in the XY plane, so if you just look at the rotation in the XY plane the so in the X and Y plane. And now this axis of rotation is located here at a distance of 1 by 4 ok. So, this axis is perpendicular to the XY plane in the is it along or a parallel to the z-axis in an arbitrary point ok.

If you look at an arbitrary point at let us say I will take an arbitrary point right here, its coordinate is x, y, we are not bothering about the z coordinate, because the z coordinate is not changing. So, we are just looking at its x and y coordinates. And now we are rotating about this point ok. So, now, with respect to this point ok, if you can imagine that you are just you can imagine just shifting this y-axis, so it comes here ok.

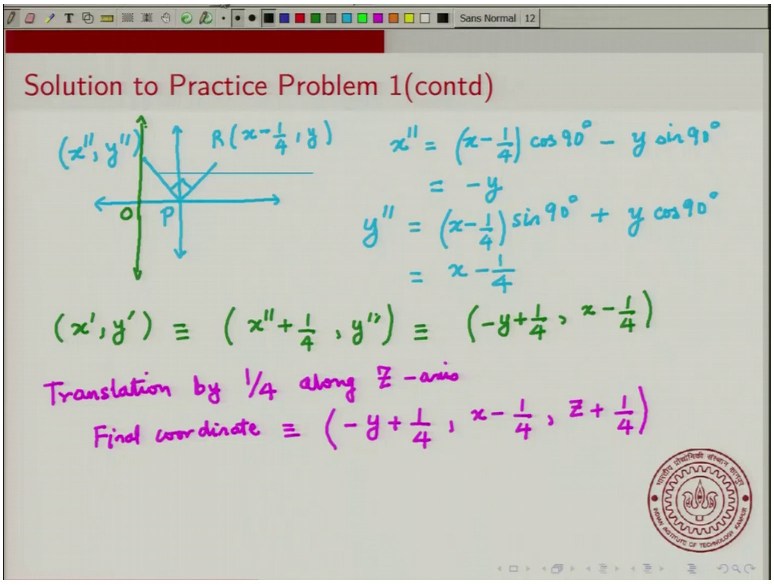
And if you imagine it, if you imagine shifting this y-axis here, and now and now you can you can think of this rotation about, you can think of rotation of this vector ok. And if you rotate it by 90 degrees, it will point you can see that it will point somewhere here ok. And you will have the new x and y coordinate. So, this will give you the new x prime y prime ok. And you have to identify, what this new x prime and y prime are in terms of x and y, and this is 90 degrees this rotation is by 90 degrees ok.

So, now, how do you go about doing this ok. So, if this were the origin, if this point if this point that we are looking at was the origin of your system ok, this point in particular was the origin of your system while call this point P ok. So, so the coordinate of the; this vector this vector given, so from P to this point R, which is x y ok. So, I am calling I am calling this O as the origin P as this point where the axis of rotation where the screw axis intersects the XY plane and R as the point x y.

So, now the vector from P to R, this vector ok, this corresponds to x minus 1 by 4, and y ok; y is the y coordinate ok. The y coordinate is the same as it were if it were with respect to the origin O ok, only the x coordinate is shifted by 1 by 4 ok. And now what you can imagine is you can imagine doing a rotation of this point ok. If you imagine rotating this point about so, so you can think of rotating this about the z-axis by 90 degrees.

So, if you do this rotation, then what you will get is you will get the coordinates of the new point ok. So, the coordinates of the new point will be given by rotation of x minus 1 by 4 by 90 degrees and y by 90 degree. Now, notice that this we can this P R is like the coordinate of x y with respect to P as the origin. And we are doing a rotation about the z-axis for a coordinate system, where P is the origin ok. So, let me let us redraw this in a slightly different way.

(Refer Slide Time: 11:46)



So, what we will say is that you have a you have a, so this is the modified coordinate system. And now you have your origin at P. And you have this coordinate, in this modified coordinate you have coordinate of R is x minus 1 by 4 and y. And what you are doing is doing a 90 degree rotation in this coordinate system. So, you will get some new coordinates that look like this. So, after 90 degrees, you will get some new coordinates ok.

And so in this coordinate system ok, let me call these coordinates x double prime y double prime ok. I will just call them x double prime, y double prime, they are in this coordinate system where the origin is at one-fourth at x equal to one-fourth, y equal to 0, z equal to 0. So, so you can immediately write that x double prime is equal to x minus 1 by 4 that is the original coordinate multiplied by cosine of theta, theta is 90 degrees. So, cosine of 90 degrees minus y, which is the y coordinate times sin of 90 degrees this equal to. So, cosine of 90 degrees is 0, so this will just give you; and sin of 90 degrees is 1, so this will just give you minus y.

Similarly, y double prime is equal to x minus 1 by 4 times sin of 90 degrees plus y cos of 90 degrees ok. And this is just equal to x minus 1 by 4. So, now, you have these coordinates ok, but these are coordinates where the origin is actually shifted ok. So, if you go back to your coordinate, if you go back to the earlier to the actual coordinate system where you had where you had this as the origin O as the origin ok. Now, if you go back to that coordinate system ok, then you know that the x coordinate, the x coordinate should be is actually shifted back by 1 by 4 ok.

So, what you will get is that in this in the in the coordinate system at O ok, so the x prime y prime which was the which was in the correct coordinate system ok. So, this is nothing but x double prime plus 1 by 4 y double prime ok. Now, the plus sign is because you shifted this with respect to P, this O is shifted back by 1 by 4. So, the x coordinate will be increased by 1 by 4.

So, this new coordinate is nothing but minus y plus 1 by 4 and x minus 1 by 4 ok. So, this is the effect of the rotation part of this screw operation ok. So, if we go back what we wanted to do is we want to take an arbitrary point x, y, z, and we wanted to consider the effect of rotation ok. I will just mention that I call this x the actual coordinate of this new point is x, x, x prime, y prime ok.

But in this new coordinate system that is center at P, we call it x double prime y double prime ok. And we just use that tool just to get the final new coordinate. So, we started with a point x, y, and you end up with a point minus y plus 1 by 4, x minus 1 by 4 due to rotation by 90 degrees about this axis that is passing through P ok. So, this was the rotation part of the screw operation.

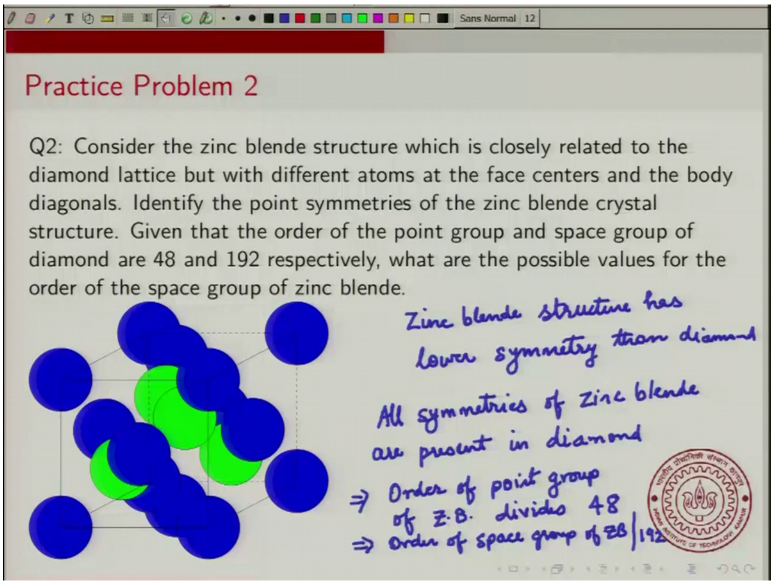
Now, the next thing is a translational by 1 by 4th along the z-axis. So, what we will get after the translation, so translation by 1 by 4th along z-axis ok. So, we had our initial point was x, y, z that had the z z coordinate of z. So, the new point, so it will give you the final coordinate ok. So, you have to take the coordinate after the screw operation ok, so the so after we did the screw operation, these were the coordinates, the this was the new x coordinate, this was a new y coordinate ok.

And now the z coordinate, we said that the rotation part did not really change the z coordinate. So, the z coordinate was what it was before. But, now after the translation, you will get a new z coordinate. So, so I will keep the x and y coordinate due to the rotation, but the new z coordinate will be shifted up due to translation. So, we are translating by 1 by 4th; so, this is the new z coordinate ok.

So, let us go back to our figure. So, we rotated about we took this point rotated about this axis by 90 degrees, and then you shifted it up by 1 by 4th ok. So, we so we took this point rotated about rotated about this axis by 90 degrees, and then translated it up by one-fourth, so and that new point will have these coordinates.

So, from x, y, z, you went to minus y plus 1 by 4 x minus 1 by 4 z plus 1 by 4. So, this just goes to show that you can take any axis and you can find out translation of an arbitrary point, and this is actually extremely useful to read lot of the crystallographic tables. So, some of the websites that I showed, they talk about translation of an arbitrary point ok, and then and then you can use this to follow that ok.

(Refer Slide Time: 19:17)



The next problem that I will briefly discuss now is the following, so consider the zinc blende structure which is closely related to the diamond lattice, but with different atoms at the face centers and the body diagonal. So, this is your diamond cubic structure. And if these blue and green atoms are the same, it is a diamond cubic structure. If it if they are different, if the green atoms are different from the blue atoms ok, then it is called the zinc blende structure. Given that the order of the point group and the space group of diamond are 48 and 192.

So, if you take a diamond cubic structure, not a zinc blende structure. If we take a diamond cubic structure, the order of the point group is 48 and the order of the space group is 192. And now I am asking the question, what are the possible values for order of space group of zinc blende ok. So, what can you infer from this about the about the order of the space group of zinc blende ok.

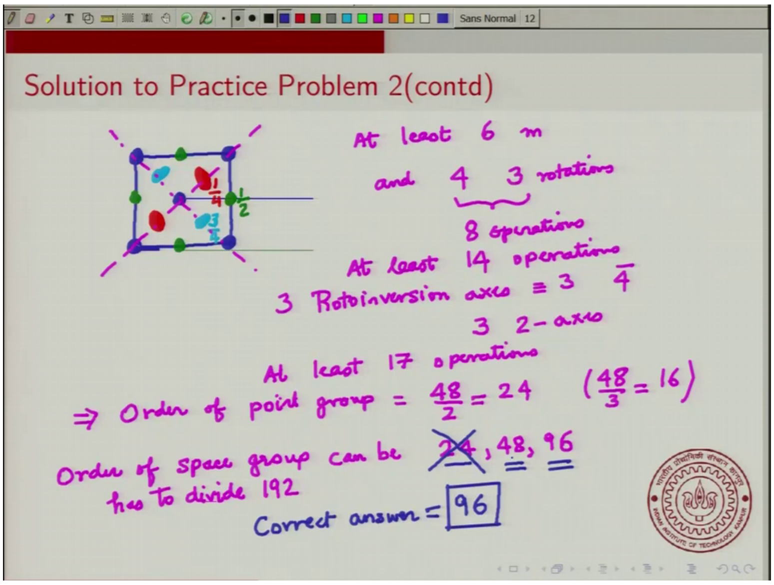
Now, the first point now this is more an exercise in reasoning. So, the first point you note is that zinc blende structure, the zinc blende structure has lower symmetry than diamond ok. So, first thing is first lower symmetry than diamond; in the sense that you know, because these atoms were different ok. All the symmetries of diamond that involved exchanging of these atoms are will be absent in zinc blende.

So, diamond is more symmetric, because in diamond will have all the symmetries of zinc blende, and some additional symmetries which are because this atom the green, and blue atoms are the same. So, the next point is that all symmetries of zinc blende are present in diamond ok. So, all the symmetries of zinc blende are actually present in diamond ok. So, diamond has all the symmetries that zinc blende has. So, diamond contains all the symmetries of zinc blende, of course zinc blende does not contain all the symmetries of z of diamond.

So, therefore you can immediately say that the order of point group of zinc blende Z B Z B for zinc blende it divides 48. So, the symmetry elements of zinc blende will form a subgroup of the of the point group of diamond ok. So, the order of the point group of zinc blende divides 48, and you can say order of space group of zinc blende, this will divide 192 ok. So, so since it is a subgroup of the diamond structure ok, so it is orders will divide the both the point group and space group orders we will divide 48 and 192 ok.

Now, you can see that there are some symmetries in the zinc blende structure. So, for example the zinc blende structure has the has the three-fold axis, that goes that passes through the body diagonals. So, it has the four three-fold axis four three-fold axis of diamond ok. So, these are present in the zinc blende structure ok. So, you can clearly see that there are quite a few symmetries that are present, similarly this rotoinversion axis four-fold rotoinversion axis will also be present in zinc blende, it will also be a roto inversion axis for zinc blende ok. And let us let us draw the planar representation of zinc blende ok.

(Refer Slide Time: 24:25)



So, the planar representation of zinc blende, we will look like this. So, this is at z equal to 0, and then you have at z equal to one-fourth, you will have I will show it in a slightly different shape in size. Just to emphasize that it is a sulfur, then at z equal to half you have so this is at 1 by 4 at z equal to half, you will have the atoms at the phase centers that are located here.

These are the so this is half at z equal to 3 by 4, you will have some more atoms here, which will again be the same as these atoms that are at 1 by 4 these are a 3 by 4 ok. Now, you can immediately see that the diagonal mirrors are also there, this immediately tells you that that the diagonal mirrors this will still be a mirror plane, the diagonal mirrors of the diamond structure are still mirrors in the zinc blende structure ok.

So, clearly it has the four three-fold axis and it has the diagonal mirrors ok. And you can immediately see that there are at least 6 mirrors ok, if not more, so and the 4 and the 4 three-fold axis, we will generate another 8 operations ok. So, you already have 6 plus 8, 14 operations that you have already generated from this just looking at mirrors. So, we clearly see that there are at least 6 mirrors and 4 three-fold rotations ok. And the 4 three-fold rotations this 4 3-fold rotations, we will give you we will give you so each three-fold rotation, we will generate two operations ok. There will be rotation by 120 degrees and rotation by 240 degrees ok. So, you have 8 operations, so at least 14 operations ok.

Now, you can also see that there are rotoinversion axis 14 operations, and then and then you have rotoinversion axes, this will be passing through passing through the center of this, it will be perpendicular to the plane, and passing through this center that is a four-fold rotoinversion axes. And you have you have at least 3 rotoinversion axes perpendicular one, perpendicular two x, y plane, one perpendicular to y, z, and one perpendicular to x, z plane ok. So, this each rotoinversion each four-fold so 3 4 bars ok.

Now, a four-fold rotoinversion axes, will generate we will generate another 9 operations. So, we fourfold rotoinversion axes will generate 3 and you have 3 of them. So, you have another 9 operations some of these will be redundant ok. So, but in any case, you will definitely generate 3 C 2s 3 C 2 axis due to this or 3 2 2-axis ok.

The point is that you will get at least 17 operations and probably a lot more ok. And now you can go back to this number ok, so we said the order of the point group of zinc blende has to divide 48 ok. And you can see that this implies that order of point group ok, if it has to divide 48. Now, 48 divide by 2 equal to 24 ok, 48 divide by 3 is equal to 16, and we already saw that we have more than 16 operations ok. So, this is not possible ok. So, 48 divide by 3, 16 is not possible. Since, we already had we counted at least 17 operations. So, the order of the point group is actually 24 ok. And it has to be 24, because it cannot be 48 and it has to divide 48, so it has to be 2 n it is at least 17, so it has to be 24 ok.

So, now what about the order of the space group ok. So, now the order of the space group has to be a divisor of 192, it has to be a multiple of 24 has to be a multiple of 24, and has to be a divisor of 192 ok. So, it can be 24, 48 or 92 ok, because these are the only three quantities which are multiples of 24 and devices of sorry 96 ok. So, these have to divide it has to divide 192 ok.

Now, again you can easily see that there are lot of screw axis that are there in zinc blende ok. So, we can directly rule out 24 so 24 can be ruled out, because there are additional operations. So, so 24 can be ruled out, because there are additional operations beyond the point group ok. So, 24 is ruled out ok, because there are because 24 is the order of the point group, and the space group has more than 24 operations definitely, because it has screw up screw operations. And then and then you can also get, you can also get symmetries by extending the cell ok.

Now, is it so it can be either 48 or 96 ok. And at this point unless you work it out, you cannot tell whether it is 48 or 96 ok. So, but the correct answer is 192. So, unless you work out, you cannot tell whether it is 48 or 96 ok, but the correct answer is 96 ok. This cannot be cannot be unless you need to work out ok.

So, this needs to be worked out ok, but again there are ways to see, why it should be why it has to be greater than 48 just as we showed that the order of the point group has to be greater than 17 ok. We can show that the order of the space group will be greater than 48, and the correct answer is 96 ok. So, with this I will conclude this problem, and I will conclude the lectures of week 5 of this course ok. And the next lecture, we will start week 6 of this course.

Thank you.