Solid State Chemistry
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Lecture – 11
Symmetry in Crystals, Point Symmetries

Now, we will start the 3rd week of this course. So, in this 3rd week, I will start talking about the concept of Symmetries in Crystals and the topic of symmetries in crystals will also be continued into the 4th week. So, we will start the topic of symmetries in crystals and in the first in the first part that is the 3rd week, I will be talking mainly about Point Symmetries. So, let us talk about symmetries in crystals.

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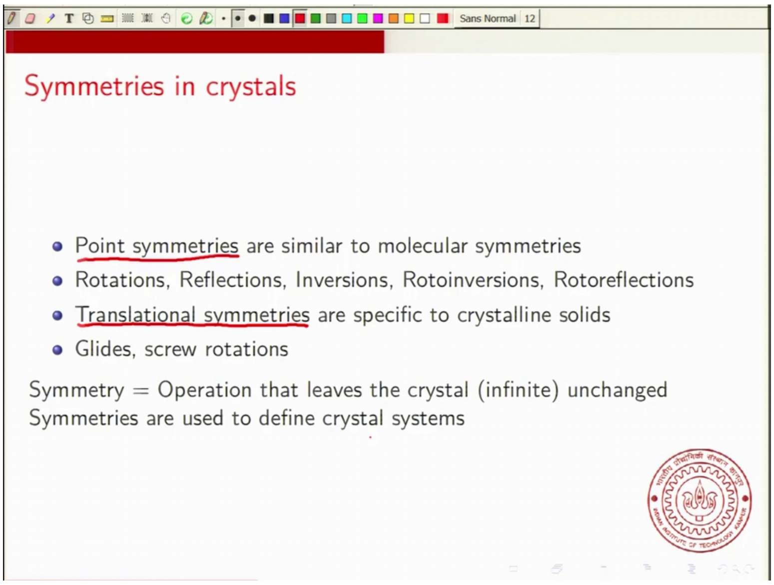

So, in crystals there are two kinds of symmetries. There are the Point symmetries and these are similar to molecular symmetries that you might have encountered in course on group theory. In crystals there are additional symmetries called translational symmetries which are very specific to crystalline solids and we will talk about both of these in more detail. So, the point symmetries as I already said they are similar to what you see in molecular symmetries ok. So, there are rotations, reflections, inversions and then, there are combinations like rotations and inversions. So, rotoinversions and then, there is rotoreflections.

Now, conventionally when we are talking about molecules, we do not usually talk about rotoinversions, we talk mainly about rotoreflections. Sometimes they are referred to as improper reflection. In crystals it turns out that rotoinversions have been used conventionally ok. The translational symmetries are specific to crystalline solids and they do not exist for molecules and there these include things like glides or glide plane and screw rotations and these are very specific and we will see this in more detail. Now what is a symmetry? A symmetry is an operation that leaves the crystal and you should keep in mind that is an infinite crystal and it leaves this crystal unchanged.

So, it is some operation so, for example, rotation is an operation. So, rotation about an axis ok, reflection about a plane, inversion about a point of inversion and so on. And what is important about symmetry it is these symmetries that are used to define the crystal systems. So, when you say a crystal system is cubic, you mean that it satisfies some specific symmetries ok.

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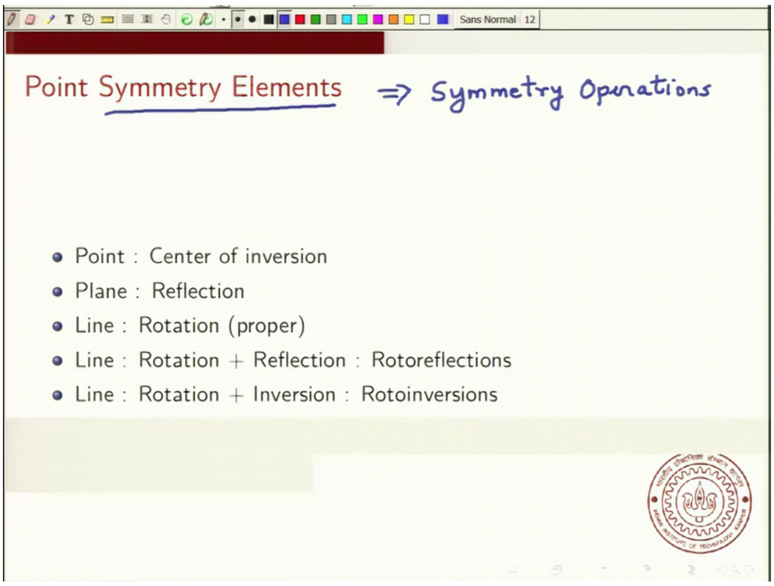

So, now let us now we will first talk about the point symmetry elements and as I had said these are similar to those seen molecular symmetry. In fact, they are identical to those seen in molecular symmetries and the point symmetries when you learn molecular group theory, you will learn that these symmetry elements all passed through one point in the molecule ok. So, that is why they are referred to as point symmetries and we will just use that same terminology ok. So, what are the different kinds of point symmetries ok? Now, whenever we are discussing symmetries, there is a concept of a symmetry element ok.

So, symmetry element and this symmetry element leads to a symmetry operation. So, we always talk about symmetries in terms of both symmetry elements and symmetry operations ok. Now, what are the symmetry elements and symmetry operations? So, a symmetry element a point is a symmetry element and what is the symmetry operation that is possible if you take a point as a symmetry element and the only symmetry operation that is possible is a centre of inversion. So, if that point is a centre of inversion, then the operation is actually inversion. And I am emphasizing the centre because you are inverting about the centre ok.

So, its inversion about the centre is the operation for that symmetry element. Then you could have plane; plane is a symmetry element and a plane, the operation that is carried out by the plane is a reflection about that plane. So, you reflect the entire system about that plane and you will get a new system and this is the symmetry operation that is carried out by the plane. Then, you could have a symmetry element that is a line and you could do a rotation, sometimes is called a proper rotation in especially in molecular group theory or so you could rotate about, you could rotate the entire system about that line ok.

And in that case, line will be called the axis of rotation. You rotate by some number of degree, you have to specify by what amount you do the rotation. Now, a line can also act as an axis for rotation followed by a reflection ok; followed by a very specific reflection and we will see this in more details.

These are referred to as rotoreflections or sometimes they are referred to as improper rotations in the molecular group theory. The line can also act as a rotation plus followed by an inversion that is called a rotoinversions. This is also another common operation especially in crystals, it is rotoinversions that are more commonly used. So, these are the common these are the point symmetry elements and these are the various symmetry operations that will be talking about. So, and usually the way to learn symmetry is through simple examples.

And we will illustrate this ok; we will illustrate this for we will now illustrate some simple example through simple examples; we will illustrate the symmetry operations relating to rotations and reflections, just proper rotations and reflections.

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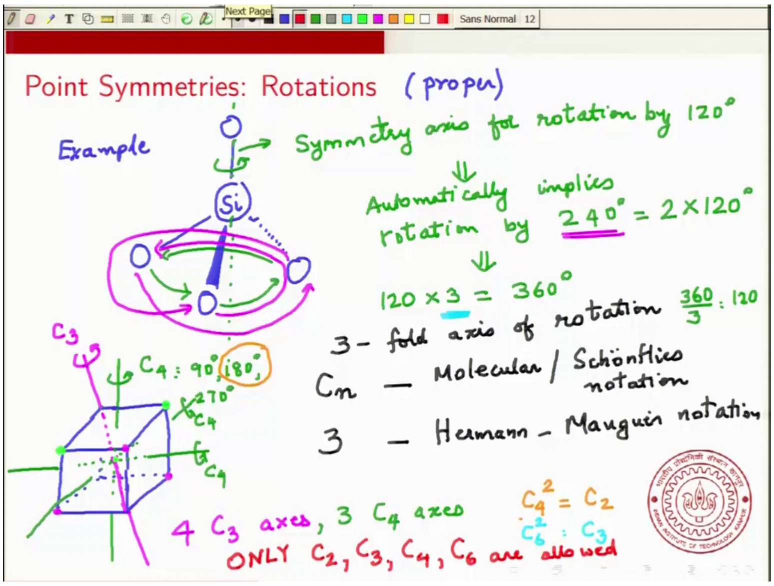

So, let us go to rotation ok, this is a point symmetry and we are specifically in this case, we are referring to proper rotations proper means rotation without any reflection or inversion ok. Now, let us take an example and let us take the typical tetrahedron like a like a silicate.

So, let us say if you have a silicate tetrahedron. So, you have a silicon atom at the centre and you have oxygen atom from your regular tetrahedron. So, you have 4 oxygen atoms from your regular tetrahedron and the this is coming outside the plane of the paper. So, I am showing it in dark this oxygen and this is going behind the plane of paper. So, I am showing it in dash line ok so, this is a silicate, this is tetrahedron ok. Now, if you imagine taking an axis that passes through the silicon and one of the oxygen atoms.

So, for example if I imagine taking an axis that passes through the silicon and this oxygen. So, it goes through this silicon oxygen one and it goes all the ways through so, just extend that axis all the way around ok. Now, you can see that this axis is a symmetry axis is a symmetry axis for a rotation and it is a rotation it is a symmetry axis for rotation by and its rotation by a specific number rotation by 120 degrees.

So, if I rotate and usually we follow the convention that the direction of rotation should be counter clockwise. So, if I rotate by 120 degrees ok; then, you can see that even I rotate my 120 degrees, this this oxygen will go it to this; this oxygen will come to this; this oxygen will come to this and essentially, you will get a structure that is identical. You will get a structure that looks identical to the original silicate structure ok. So, that is what happens when you do a rotation by 120 degrees and you can see that once you have rotation by 120 degrees, then you automatically have it automatically implies rotation by 240 degrees which is same as twice you do the rotation by 120 degrees.

So, you rotate by 120 degrees and rotate by 120 degrees again that would also be a symmetry operation and let me show this in a slightly different color. So, if I rotate by 240 degrees, then this atom will go all the way to this atom ok. Similarly, this atom will come all the way to this atom and this atom will rotate all the way to this atom.

So, that is what happens when you rotate by 240 degrees and if you do it 3 times, if you do it 3 times ok; 120 into 3 equal to 360 and so, what this says it that if you rotate it if you do this rotation operation 3 time then you get back the original structure and there is no change from the original structure ok. So, this axis is called the 3-fold axis of rotation and we will see later on that there are two notations; we either call this as a call this symmetry as C n ok. This is in the molecular notation, this is molecular or Schoenflies notation; Schoenflies notations.

This is very common in spectroscopy or we will just call it 3 in terms of in what is called the Hermann -Mauguin notation ok. So, usually crystals have several row axis of rotation and several symmetry axis. So, just an example if you take a cube; if you take a cube so, if I take a cube, then you can see that it has several rotational axis; several axis of rotation. So, if you take a cube, you can imagine that I can held draw a few axis of rotation. So, if you take an axis that goes this way; goes through the crystal comes out from the other side and comes here ok.

So, it goes through the centre of this crystal, you can see immediately that for a perfect cube this is a C 4 axis ok. So, if you if you C 4 means a C 4 axis means you rotate it by 90 degrees ok. So, the way to think if you have the 3 fold axis of rotation, then the rotation by 360 divided by 3. So, just keep in mind in that case we saw 360 by 3 is equal to 120. So, if you rotate by 120 degrees, you get the symmetry operation in this case. So, for a 3 - fold axis in this case you rotate by 90 degrees.

So, if you rotate by 90 degrees, then you can see that this point will go to this point and so on ok. So, the crystal will the cube will remain unchanged for rotation by 90 degrees. So, if you rotate by 90 degrees, you still retain the cube about this axis ok. And since you can rotate by 90 degrees, so 90 degrees rotation you can also rotate by 180 degrees where is twice 90 or you can rotate by 270 degrees that is 3 into 90 and if you rotate by 4 time 90 degrees you get 360 degrees which is back to the original structure.

So, these are the various symmetry operations that you get from this symmetry element, from this C 4 axis ok. Now, you can also have C 4 axis like this passing through this phase ok. So, this is another C 4 axis and you can have a third C 4 axis passing through this phase. So, you come this way (Refer Time: 15:38) through and it comes out from that side ok. So, you could have this three C 4 axis ok so, this is also a C 4 axis. So, it basically goes to the centre of one phase and its perpendicular to that phase so these of all C 4 axis.

Now, it turns out that a cube also has some C 3 axis and these are slightly harder to see, but not much more difficult to see and I will show them in this violet color ok. So, suppose I take an axis that starts from one corner goes through the body diagonal and comes out from the other corner ok. Again, it comes out from the opposite corner along the body diagonal. So, an axis that starts at one of the corners, one of the edges of the cube goes along the body diagonal and comes out of the other edge ok. So, this is what we are saying and this axis in properly better to show this in dots.

Let me show this way ok. So, it goes through the centre of the cube; it goes through the centre of the cube and comes out from the other side ok. So, this is an axis and you can see that this is actually a C 3 axis C 3 axis; that means it is a 3 - fold axis of rotation and again its I mean this is slightly harder to see, but not that much harder ok. You have to visualize this by actually taking a cube, but what you will find is that you will have these 3 points turn into one other during this rotation and these 3 points go to another ok.

So, again its not I am not going to demonstrate this, but essentially you can see that this will permute 3 points ok. So, I will just show you so, if you do this rotation, then these 3 points will go into each other. So, if you rotate by 120 degrees, this point to go here; this point to go here and this point to go here. If you do it again by and similarly these 3 points will also get permuted. The opposite 3 points, I will show this in a different color. Let me take a light green. So, if you do by 120 degrees this, the back corner and this point will get permuted into each other.

So now you can immediately see that there are 3 more C 3 axis. So, there are total so, a cube has 4, C 3 axis because you can start with any corner and goes to its opposite diagonal ok. So, there are 8 corners in a cube. So, there are 4, C 3 axis and we already saw we have 3, C 4 axis ok. So, this is what characterize as a cube ok. Now one of the things that you notice is that if you have a C 2 axis ok. So, we notice that C 4 also generates 180 degrees and so, we see that C 4 if you do it twice; if you do it twice. So, I write it as C 4 square so, you do the C 4 operation twice, you get a C 2 operation.

So, if you do 90 degrees and 90 degrees, you get 180 degrees; 180 degrees is 360 divided by 2 so, that is a C 2 operation. So, the symmetry operation C 4 square is same as C 2 and so, when you C 4 axis includes in itself in it C 2 axis, you could have additional axis that is the C 2 axis, but not a C 4 axis and that is also possible. The similarly, if you have the C 6 axis that would include C 3 axis; a C 6 axis would contain a net of C 3 axis would contain a net the C 3 axis. So, we will have some will have C 6 twice is nothing but C 3 ok. This is the general property and you can see this you can do this by just by looking at the rotations ok. Now the most interesting thing about crystals is that the crystals is it is required that crystals should fill space ok.

So, since crystals are required to fill the entire space, there are restrictions on the kinds of axis that you can have ok. So, and let me emphasize this so, I choose a red color just to emphasize this. So, and I will write this here so, only C 2, C 3, C 4 and C 6 are allowed. So, for crystals these are the only rotational symmetry axis that are allowed ok. So, you can have C 2, you can have a C 3, you can have a C 4 or you can have a C 6; you cannot have a C 5 and the reason you cannot have a C 5 it has to deal with the fact that if you have a C 5 axis, then you would have something like a pentagon like a regular pentagon and if you have a regular pentagon ok, you cannot fill space with regular pentagons ok.

So, this is the restriction again that has to do with the it goes back to the crystal systems that are allowed and the types of Bravais lattice that you have. So, since you have to since the crystal has to fill the entire space, it cannot have C 5 axis and this is the very interesting property that a perfect crystal cannot have a C 5 axis ok. So, that itself is a very interesting point.

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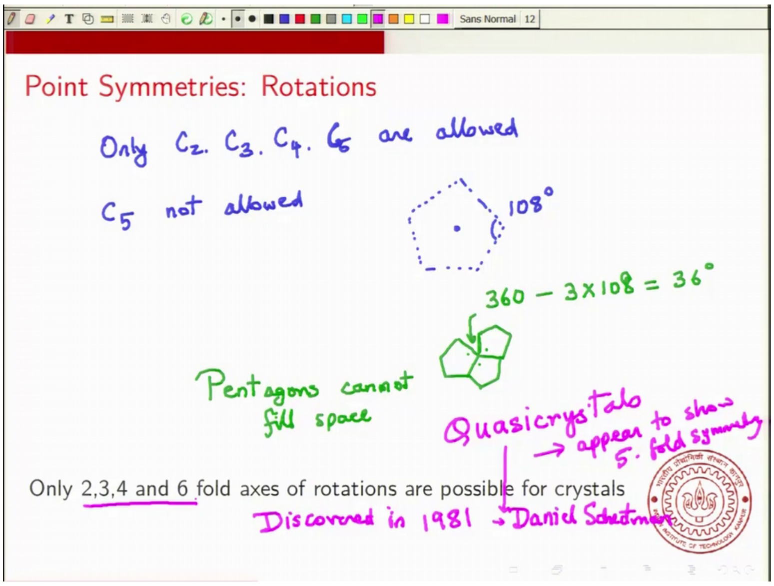

So, we said that only C 2, C 3, C 4 and C 6 are allowed. And the reason is that if you have C 5 not allowed and the reason for that is if you have a C 5 axis ok, then if you let us say I had a C 5 axis coming out of the out of the plane of the board ok. Then, around this C 5 axis there would be something like pentagonal symmetry. So, if you have a 5 - fold axis of rotation, then there should be some sort of pentagonal symmetry 5 - fold symmetries around this and so, your unit cell will have something like a pentagon and if you take pentagons ok so, pentagons cannot fill space.

So, suppose you take set of pentagons ok, again you can see this if you try to fill space ok, if you take perfect pentagon, these are all regular pentagons ok. So, the angle is 360 by 5 not ok so, they have the exact angle of the pentagon that is 108 degrees and if you take a regular pentagon ok. So, it is 108 degrees is the angle of a regular pentagon and if you just take regular pentagons and you try to fill space ok, then you will always get some voids.

So, if this is 108 degrees; this is 108 degrees. Now, if I put another 108 degree here, you can see that 108, 108, 108 and you can see that this angle is going to be 360 minus 3 into 108 is equal to 36 degrees ok. So, what that means and you cannot have a 36 degree angle in a pentagon. So, there would always be some empty space ok. So, pentagons cannot fill space fill space and in fact, this is why you never have 5 - fold axis in crystals ok. Now, it should be mentioned ok, I will just mention this that in around 1980 there was the discovery of this special crystals, they are not real crystals they are called Quasicrystals and these are not real crystals.

But these appeared to show 5 - fold symmetry ok. So, Quasicrystals they appear to show 5 - fold symmetry and the discovery of Quasicrystals ok. So, the Quasicrystals were discovered in 1981. So, they were discovered in 1981 by a scientist whose name is Daniel Shechtman and Daniel Shechtman was later on awarded the Nobel Prize in chemistry.

So, he was awarded the Nobel Prize in Chemistry in 2011 so, but essentially these are not perfect, these are not crystals in the usual sense they are referred to as Quasicrystals. And I mean you can read about them in the at in various sources we would not be discussing too much about Quasicrystals, but they essentially show this 5 - fold symmetry which is absent in regular crystals. As for as regular crystals go, the only axis of rotation that are possible are 2, 3, 4 and 6 fold axes.

So, in this lecture I have talked about symmetries of crystals and in particular I focused on the rotational symmetry. So, in the next lecture, I will look at the other symmetry elements of a crystal like reflections, inversions and then we look at rotoreflections, rotoinversions and see the standard notations for these operations.

Thank you.