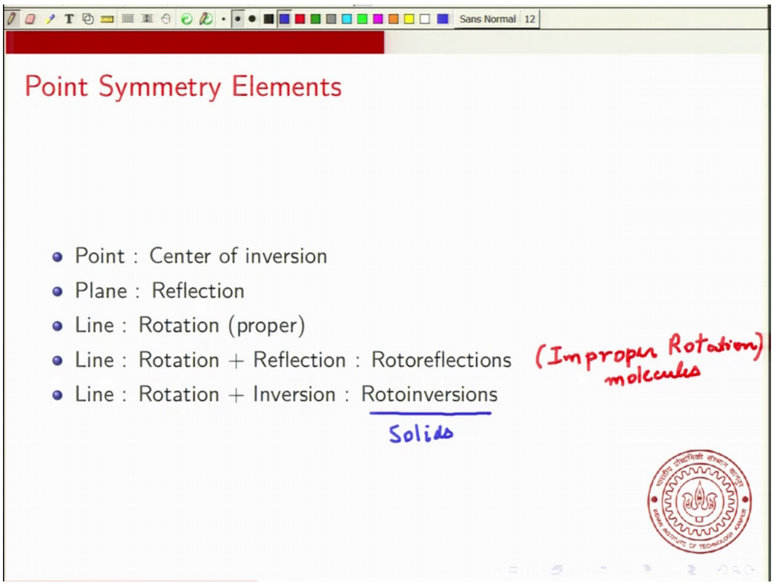
Solid State Chemistry

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

Lecture - 12
Reflections, Inversions and Rotoinversions

So, let us continue the discussion on symmetries in crystals. We were discussing point symmetries in the last lecture and now, we talked about Rotations. Today in this lecture, I will talk about the other symmetry elements, the other point symmetry elements; in particular I will talk about Reflections, Inversions and Rotoinversions. So, let us continue from where we left off last time. So, in this lecture, I will be talking about reflections, inversions and rotoinversions.

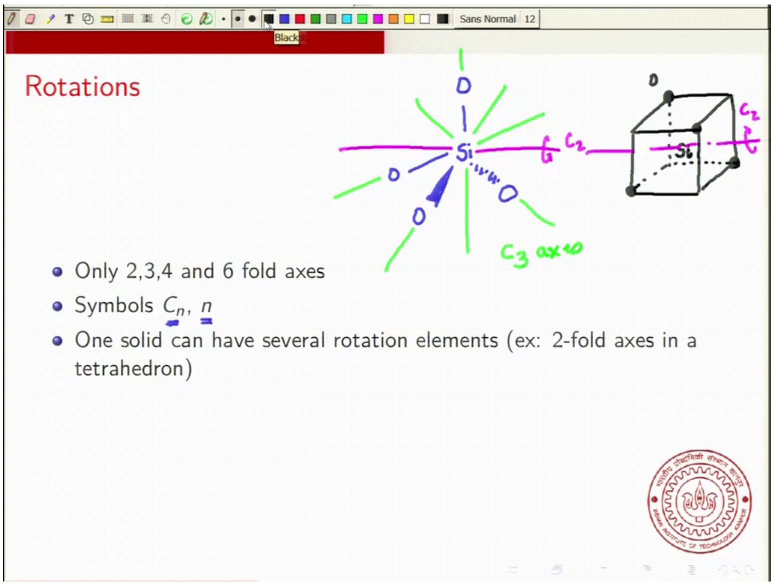
(Refer Slide Time: 00:59)



So, to remind you what we discussed in the last class, we said that there are point symmetry elements and these the each symmetry element generates an operation and we said that a point generates a centre of inversion; a plane generates a reflection; a line can generate either a rotation or a rotation and a reflection which is called a rotoreflection or a rotation and inversion which is called rotoinversion.

Now, in the case of molecules we usually use a rotation and reflection. So, this in the case of molecules is called an improper rotation and this is mainly used for molecule for describing molecules as supposed to solids where we use rotoinversions this is used for solids. So, for crystals will be mainly focusing on rotoinversions; we would not be talking about rotoreflections ok. So, let us continue. So, I have already talked about proper rotations ok.

(Refer Slide Time: 02:22)



Now, I will briefly summarise what we talked about rotations in the last lecture. We said that only 2 fold, 3 fold, 4 fold and 6 fold axes of rotations are possible and there are two types of symbols. You can call it as C n under what is called as Schoenflies notation or simply n under the Herman Morgan convention ok. We will be discussing these conventions in more detail later on, but just bear in mind that there are two kinds of symbols; there is the C n and there is the n. And what should be kept in mind is that one solid can have several rotation elements ok, it need not have only one rotation axes.

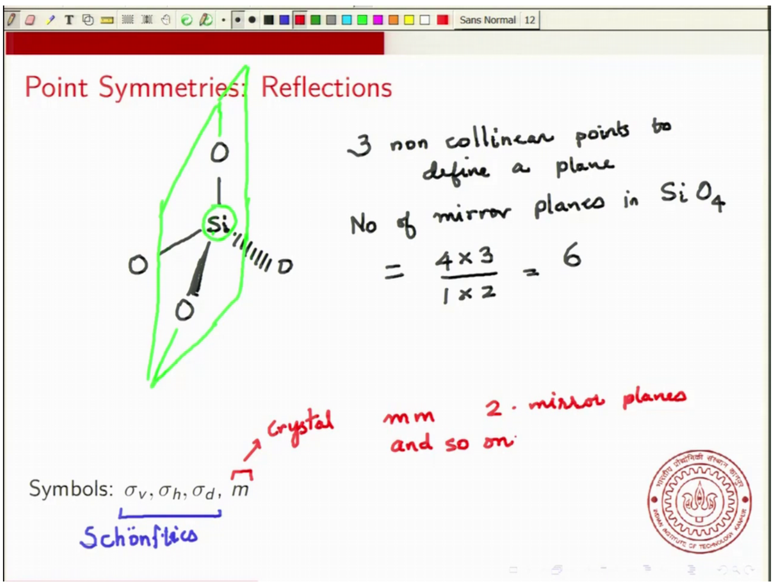
So, for example, we were talking about the tetrahedron. So, we talked in particular about the silicon with the 4 oxygen's forming a tetrahedron and we identified we said that the axes passing through anyone oxygen atom and the central silicon atom. So, it could be any of these so, these are all 3 fold axes of rotation. So, each of these are C 3 axes ok. But additionally, we will see that there are also some C 4 axes and I will just show you what the C 4 axes is and then, I will describe it in more detail. So, or a C 2 axes there are also C 2 axes so, there are 2 fold axes ok.

So, it goes like this and basically this is a C 2 axes. So, what is this C 2 axes and how do I understand it? So, the easiest way to understand it is to look at a tetrahedron in terms of a cube. So, a tetrahedron can be visualised as it as in the following way using a cube. So, you put the silicon atom at the centre of this cube and you put 4 oxygen's at so, this is the representation of an oxygen at up at alternate corners of the cube. So, you take a corner and then you skip one corner and go to the alternate corner skip one and go to the alternate and you do this and you will get what you will get here is a tetrahedral arrangement around this central Si Si atom.

So, this is exactly the same structure as what we shown here. So, if you visualize the tetrahedron in this way, then we can easily see it that this axes passing through the centre of the cube and going through the central silicon atom and coming out on this side of the cube ok. So, this axes coming out from this centre is clearly a 4 fold axes this or sorry it is a 2 fold axes so, this is your 2 fold axes, this is a C 2. You can see if I rotate by 180 degrees around this, the silicon atoms stays where it is this oxygen moves to this, moves to this oxygen and this oxygen moves to this oxygen. So, you get an identical configuration.

So, clearly this is a C 2 axes that essentially permutes these two oxygen's and these two oxygen's amongst each other ok. So, what is important is that your tetrahedron has these 4, C 3 axes and 2 C 2 axes and later, we will see that it is the presence of this symmetry elements that will actually define the type of solid that is used to classify solid.

(Refer Slide Time: 06:36)



So, now let us go to the next symmetry element that is the reflection and we will again consider the tetrahedron because the silicone and 4 oxygen's tetrahedron and let me show this in show this as a this form. So, now you can if you want to form a plane ok. Now you should notice that every the point symmetry elements will all contain the central silicon atom because there is only one silicon atom. So, then every symmetry element should go through that.

So, you can make a plane consisting of a silicon and 2 oxygen atoms ok. So, you can take this for example, I could take a plane formed by taking these three; so, this oxygen, this silicon and this oxygen ok. So, I would get a plane that looks something like this. This plane this contains the silicon and the 2 oxygen's and this would be this plane consisting of this oxygen, this silicon and this oxygen would be a reflection plane because if you reflect about this plane, then you can see that these 2 oxygen will get they will change their positions ok.

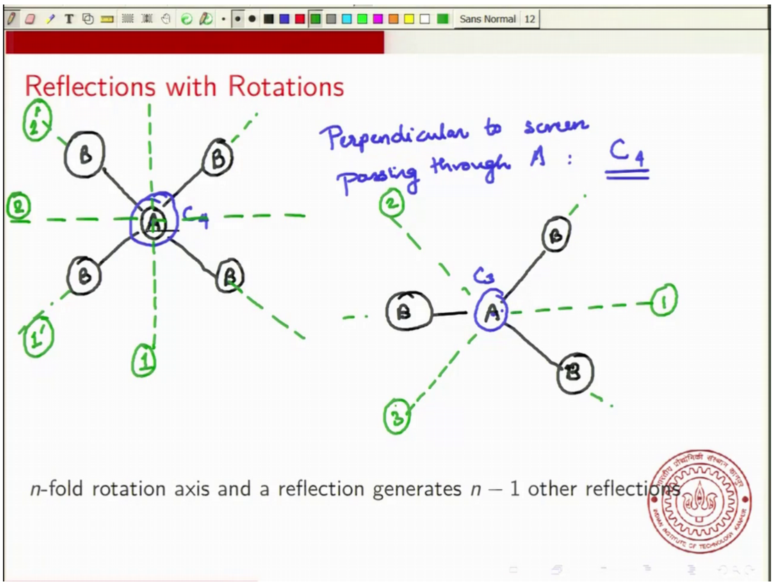
Remember that this plane is not perpendicular to the plane of this screen because this oxygen is actually outside it is coming outward ok. So, now you can clearly so basically what I want to mention is that you need 3 non collinear points to define a plane. So, if you have any if you have 3 points that are not all on a line ok, then you can define a plane so, you need 3 point. So, the silicon, the oxygen and this other oxygen; they together define a plane and this plane is turns out to be a plane of reflection. So, this turns out to be a reflection symmetry ok.

Similarly, you can also make a plane consisting any other 2 oxygen atom. So, you could take silicon and any 2 oxygen atoms ok. So, now the number of mirror planes ok. So, you have 4 oxygen's ok. Now, 4 oxygen and you have to choose two of them ok. So, again it is quite easy to see. So, you have to 4 the number of ways of choosing 2 out of 4 is 4 into 3 divided by 1 into 2 that is equal to 6.

So, there are 6 different planes mirror planes that you can construct using this tetrahedron in Si O4 ok. This is again an important concept that you can have several planes and each of these is a plane of reflection, is a plane of symmetry that that is it has a mirror reflection symmetry about this plane ok. Now, the symbols that are used for mirror planes in the molecular notation, we have you may have seen that there are terms like sigma v, sigma h and sigma d ok. So, these are in the Schoenflies or molecular symbols molecular group theory.

Whereas, the Herman Morgan or the Crystal convention is just to write it as an m. So, if you have a plane, you just write an m. If you have multiple planes, then you write it as m m so, that is 2 mirror planes and so on ok. Now, so you can have this mirror planes in any crystal.

(Refer Slide Time: 11:45)



And now let us look at what let us look a little bit more detail about mirror plane. Now, there is a special case when you have this is a combination of reflections and rotations. Particular case, I will take one example where let us take a simple 2D example. So, if you have something like a let us say A, an atom A at the centre and you have 4 B atoms forming some forming a square that is square symmetry ok.

Now, what you see is that if you take if you look so perpendicular to screen passing through A, there is a C 4 axes. So, we have a C 4 axes and let me show it in this notation, I will put a dot and I will put a circular around this ok so, this is your C 4 axes. You should remember that it is actually perpendicular to the screen of the paper of the perpendicular to the screen and it passes through the point A. So, this is a C 4 axes and we also notice that there are various mirror planes. So, I will just show it in a dash line ok so, this again everything is perpendicular to the screen ok.

Now perpendicular to the screen passing through these to these you have a mirror plane ok. Now, what similarly you can also have a mirror plane in this way; you can also have a mirror plane perpendicular to this A ok. So, now what we see in this is the following that and you can also have mirror planes along this and you can have mirror plane along this and what we see is that these mirror planes are related by a C 4 rotation.

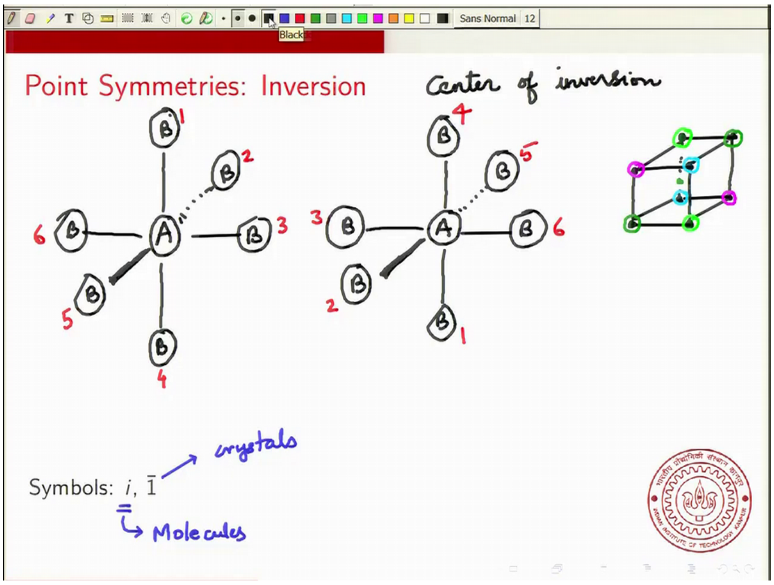
So, for example, if you take this mirror plane, I will call it 1 and rotated perform a C 4 operation ok, then you will get mirror plane 2 ok. So, and similarly when you take this mirror plane, I will call it 1 prime and perform a C 4 operation on it, you will get mirror plane 2 prime and so, this is a general rule that when you have an n fold rotation axis and the reflection you will generate other n minus 1 reflections ok.

So, just the existence of this one plane along with the C 4 axis ensures that you generate this other plane. Now it turns out that you could generate, you could do the C 4 again, but then you get back to the original mirror you could do the C 4 again you get back to this mirror. So, in general it generates 4 other reflections. In this case two of them are the same as the other two. So, let us take another example. Let us take a case where let us say I take A and I take A B 3 so, I take A B 3 ok.

Now, this is a now you see that if you had you have a C 3 axis going through A. So, you have a C 3 axis going through A and the C 3 and you have this mirror plane ok. Now, if I apply C 3 on this mirror plane ok, then I will end up with this axis and if I apply it again I will end up ok. So, essentially if you apply this C 3 twice ok.

So, you start with 1, then you will end up with 2 and then you will end up with 3 ok. So, you can see this C 3 and this 1, they ensure that you have two more mirror planes. So, this is a property that mirror planes are generally found, you can find you find multiple planes mirror planes whenever you have a C n axis that contain that mirror reflection.

(Refer Slide Time: 17:17)



Next, I will talk about inversion and this refers to the centre of inversion also its referred to as centre of inversion. So, some molecules some crystals have a centre of inversion and again we can look at the molecular description for this symmetry. Suppose I have an octahedron ok; suppose I have an octahedron so, let us say I put A at the centre and I have B, this is actually coming out of the paper and they have maybe I will just show this using dots, just to show that is going inside the paper and that this is coming outside.

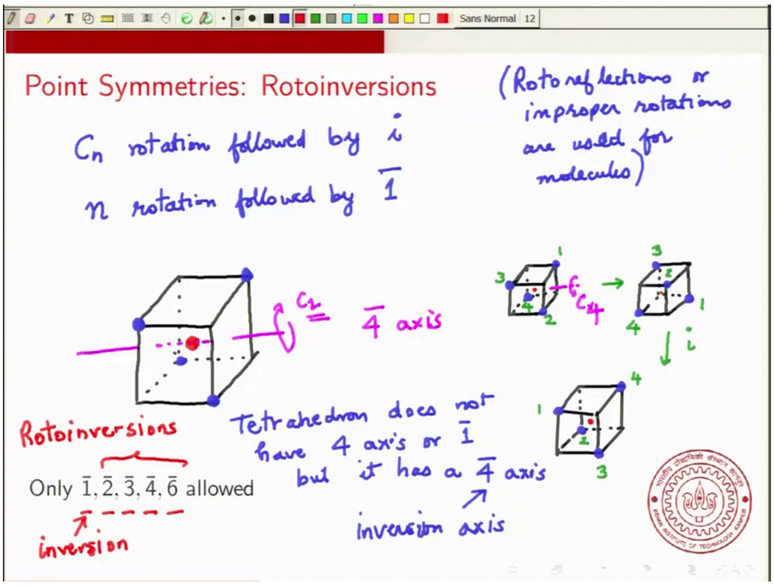
So, this B is coming out of the screen of the paper in 6 in so now, you see that this A, if you invert about this A ok. So, if I call it if I label this B atoms as 1, 2, 3, 4, 5, 6; then, what you see is that after inversion you end up with something that looks like A and now the B that is here is a different B ok.

So, now the B that is here after you invert, then this 4 comes here. So, you have 4 here and you have a 1 here, you have a 5 here and a 2 here, you have a 6 here and you have a 3 here ok. So, this is the effect of inversion and the centre of inversion. So, A is referred to as a centre of inversion. So, there are some crystals like which have you know local octahedral coordination will show a centre of inversion.

Now similarly, a cube will also show a centre of inversion. So, if I take a cube so, there is a point at the centre of the cube which is a centre of which is an inversion centre. So, the centre of the cube is an inversion centre ok. So, if I invert about the centre, then this point will go to this point; this point will go to this point; this point will go to this point and finally, this point will go to this point ok. So, the cube will get inverted along about its centre ok.

And so and the symbol for inversion so again there are two symbols; one is in molecular for molecules, we use which is the Schoenflies symbol is i and this is for Crystals we use 1 bar. So, 1 bar is the inversion about the centre as just as i is the inversion about the centre for a molecules ok. So, a crystals that have a there are crystals that have centres of inversion and there are crystal that do not have centres of inversion and in each of the case you will get different properties ok. We are usually look at crystals structures that do posses a centre of inversion, but there are often we look at those that do not have a centre of a inversion.

(Refer Slide Time: 21:53)



Now, the last symmetry operation, I am going to talk about is rotoinversions ok. Now, notice that I mentioned that we would not talk about rotoreflections ok. So, rotoreflections or improper rotations, these are used for molecules; used for molecules ok, but for solids we use rotoinversions ok. So, what is a rotoinversion? A rotoinversion is essentially a C n rotation followed by inversion ok. So, or if you are using the; if you using the crystallographic notation, you will see an n rotation followed by 1 bar is the inversion operation ok.

Now, what is now how does this work ok? So, let us take an example of this tetrahedron again ok. So, I will look at the tetrahedron and for convenience I will look at using a cube and I would not I will just show the silicon atom at red in the centre. So, the red is the silicon atom and the 4 blues are the oxygen atoms. They are at alternate corners; I can choose any 4 alternate corners and I will get my cube.

So, this is my silicate tetrahedron that we already saw and we already saw that there is a twofold axis of rotation that looks like this; it looks like this. So, it passes through the centre one phase comes out through the centre of the opposite phase. So, this is a C 2 axis ok. Now, we can also see that this C 2 axis is also a 4 bar axis. So, it is a 4 fold inversion axis in the following sense. So, suppose I take this suppose I rotate by 90 degrees about the C 2 axis ok.

So, we will see it right here so, let me draw the cube, I will draw the cube; I will draw a little small just. So, we start with this and this should be in the rare corner ok I am not showing the I can show it. Now, if I perform this axis if I performer a C 2 ok, then what it will or C 4 rather if I perform a C 4 ok; then, let me label these atoms. So, let me label them as 1, 2, 3, 4.

So, if a perform a C 2, then what I will end up with this something that looks like this or C 4 rather if I perform a C 4, then this 1 will come down here, 1 will come end up here; the 2 will end up at this side ok. Now, the 3 will end up over here and the 4 will end up over here ok. That is what will happen if you perform a C 4 ok. So, C 4 will take it to this and then, now if you do and inversion if you invert about the centre, then what you will get is again the silicon atom is at the centre and you can see this 4 will get will come to this corner.

The 3 will come to the opposite corner that is here. The 1 will go to its opposite corner which is here and 2 will go to its opposite corner which is here which is essentially identical to what we started with; which is essentially the same as the starting configuration.

So, you can see that the C 4 axis that is a 4 bar axis that is a C 4 followed by an inversion that is actually a symmetry operation ok. So, though this tetrahedron does not have C 4 axis ok, it does not have C 4 axis; it does not have an inversion. However, it has an it has a 4 bar or C 4 i or a C 4 followed by i ok. So, important is again that tetrahedron does not have a 4 axis four fold rotation that is 4 axis or a 1 bar which is an inversion ok. It does not have a 4 axis or a 1 bar, but it has a 4 bar axis ok. So, this is referred to as a inversion axis ok. It is referred to as a inversion axis. So, this axis this same the C 2 axis is a 4 bar inversion axis. So, it has a so the tetrahedron has a C 2 axis and a 4 bar axis or it has a 2 axis and a 4 bar axis. It does not have a 4 axis that is important to realise.

Now, just as we saw in the case of rotations that only two fold, three fold, four fold and six fold rotations were allowed for crystals. Similarly, the only inversion axis that are allowed are the following. So, you are only allowed 1 bar, 2 bar, 3 bar, 4 bar and 6 bar ok; you do not have a 5 bar because we said pentagons do not fill space and 1 bar is nothing but inversion, 1 bar is just an inversion without any rotations ok; 1 bar is an inversion without any rotations. So, the only rotoinversion axis are 2 bar, 3 bar, 4 bar and 6 bar ok. So, these are the 4 rotoinversions that are allowed.

So, with this we complete the whole set of point symmetries that are possible for a crystal. So, and this will be the end of this lecture. So, in the following lecture, I will start discussing about the different conventions. We have already been talking about them in formally ok, but I will make it a little more formal and describe the convention that I used to that are initially we will show how they are used to describe the symmetry operations and then later on we will show how they can be used to specify the different crystal systems.

Thank you.