Solid State Chemistry
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Lecture – 21
Crystal Systems

Now, we will start the 5th week of this course. During this week we will talk about Crystal Systems, point groups and space groups and in the first lecture I will talk about crystal systems, this will continue into the second lecture and I will try to show how we understand crystal systems from the perspective of symmetry. So, week 5 lecture 1 will be on crystal systems.

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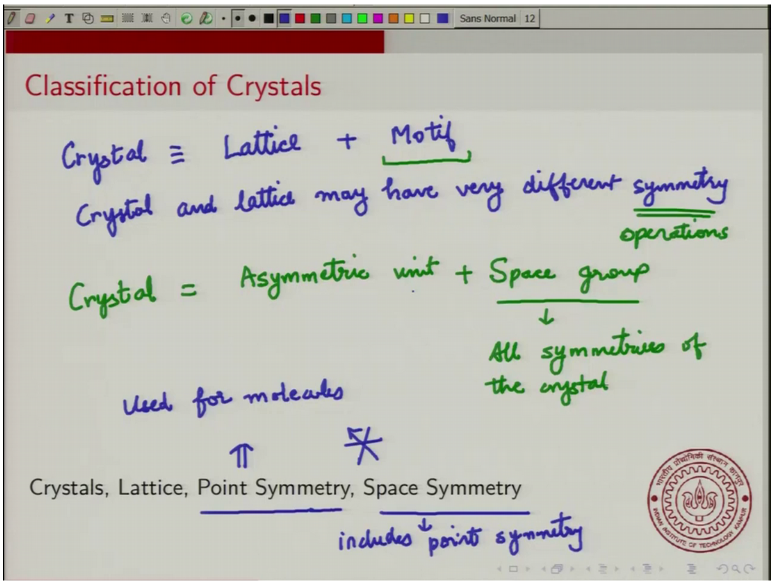

Now, let us talk about the classification of crystals ok. So, we often say that a crystal is can be thought of as a lattice plus a motif, what we mean is that you have a lattice which is an ordered set of points and in those points at each point you put a motif and the motif might be a single atom might be a few atoms might be a collection of atoms and so on ok. And now if you just look at the lattice then the lattice might have very different symmetry properties than the crystal itself ok.

So, what is important is that crystal and lattice may have very different symmetries and when we are talking about symmetry we are only we are really talking about symmetry operations in terms of operations, in terms of the symmetry operations like the rotations reflections and so on ok. And now and the motif will have its own symmetry associated with it.

So, each motif will have some sort of symmetry associated with it ok, now with this idea what we realize is that the way we classify symmetry depends on whether we are looking at the lattice the motif for the entire crystal ok. Now we can alternatively think of the crystal in a slightly different way, we can think of it as crystal consists of an asymmetric unit plus space group ok. Now the space group looks at all symmetries of a crystal, all symmetries ok.

So, it looks at all the symmetries of the crystal and so, if you know the asymmetric unit then by all these symmetry operations you can generate the entire crystal and remember it also includes translational symmetry. So, you can generate the entire set of symmetries of the crystal now we already saw that crystals have both a point symmetry and a space symmetry. The space symmetry refers to the operations that involved translation in addition to the operations of a point symmetry ok. So, what is important is that space symmetry includes point symmetry; includes point symmetry and additional translation operations ok.

So, if you just had point symmetry then typically you will have the elements of space symmetry. So, we will not have the translational symmetry elements. So, that also explains why point symmetry is used for is used for molecules, it is also used for clean crystals, but if you have isolated molecules then we use only point symmetry and no space symmetry ok. So, space symmetry is not used for molecules it is not used for molecules ok. So, you cannot use space symmetry for molecules. So, the point symmetry is the space symmetry minus those translational symmetry elements ok.

So, now we can think of crystals in two different ways, we can think of them as a lattice plus a motif or an asymmetric unit plus a space group ok. And the second characterization is based on the; based on the symmetries of the crystal ok.

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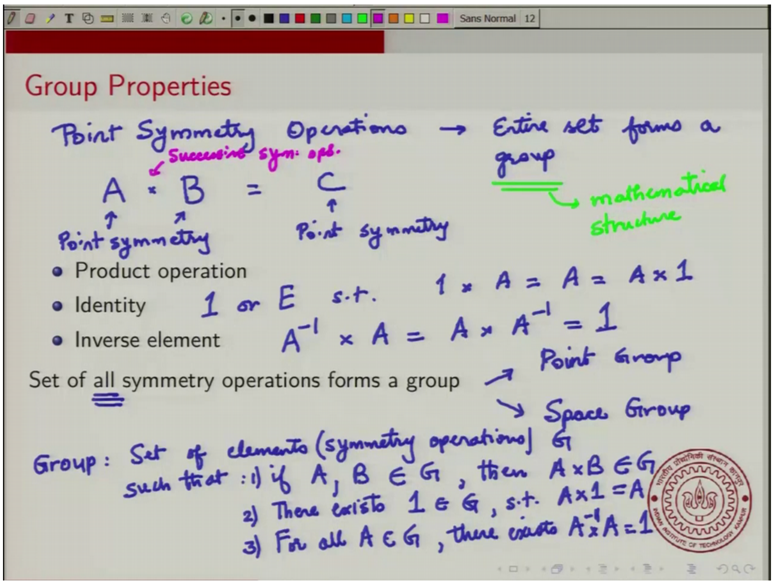

Now, one of the things is that both point symmetry operations. So, we have this operations this the entire set. So, the entire set of point symmetry operations forms a group ok. Now group is a mathematical object so, group is a mathematical object; mathematical we should say its really a mathematical structure ok. So, what do we mean by something forms a group ok?

So, what; that means, is that if you take a product of 2 point symmetries ok. So, suppose you have a point symmetry operation A ok. So, A is one point symmetry and then you take a product I will write a minus sign ok; that means and B; B is also a point symmetry ok. So, this will give you another object C which is also which will also be a point symmetry ok. So, if you have a set of objects such that you take a product of any of those two and you get another member of the object, then that is one of the properties for that set of objects to form a group ok.

So, what we will show is that the set of all and the word all is very important, all symmetry operations form a group whether you take point symmetry operations you get point group which is only we involves point symmetry operations and space group if we have point and space symmetry operations ok. So, there are certain other properties. So, we have already seen the product, the other property is that there is one element called the identity which is which we can denote as either 1 or E such that 1 times A equal to A for all the elements of the group ok.

So, you take 1 time say you get A and this is same as A times 1 ok; that means, you take your crystal, you operated by the identity of operation and then you operate it by A that is the same as operating it just by A ok. So, this 1 is called the identity element and 1 is part of the group ok. So, 1 is contained in there in your group and similarly there should be an inverse element. So, suppose you have A, then you should have A inverse such that A inverse into A is equal to A into A inverse equal to identity ok. So, so what is important is that you should have.

So, group consists of a set of elements and these elements are your symmetry operations ok, these are these are your symmetry operations such that if such that if A and B let me call this group G set of elements G, if A and B are a part of G, then A into B is also a part of G ok. So, this symbol epsilon means it is contained in G ok; that means, you multiply any two elements you will get another element. And so, this is the first condition, second one there is there exists there exists an identity element contained in G. So, identity element; so, the identity symmetry is also a symmetry operation where you do nothing and this has to be part of the symmetric group.

So, the symmetry group the set of all symmetry operations will include the identity operations such that A times 1 is equal to A ok, A times A times 1 is also equal to 1 times A, and the third one is that for all a that is contained in G. So, for any element of G; so, any or any operation you can have an inverse operation ok, there exists A inverse which is also a part of G such that A A inverse is equal to identity and A A inverse is also equal to A inverse A. So, A inverse into A is identity and lets remind ourselves again that the product of symmetry operations means successively you apply one symmetry followed by the other.

So, a multiplied by B means you first operate by B and then by A ok. So, keep that in mind ok. So, A times B means successive operations, symmetry operations that is to be kept in mind.

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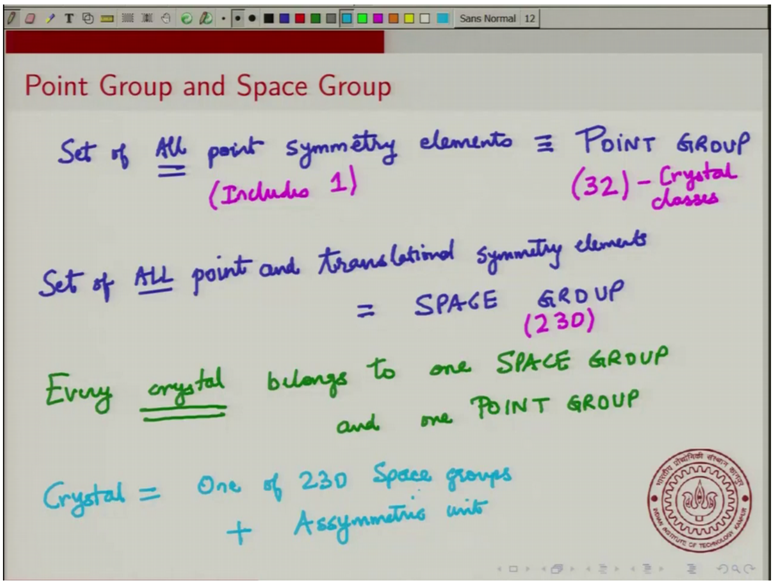

Now, now let us go to the point group and space group ok. So, what we said is that the set of all point the word all is important here, all point symmetry elements this is called this is the set of this called a point group. And remember identity is also a point symmetry operations ok. So, keep in mind that this includes identity ok.

So, this is what is called the point group and the set of all, now we have point and space or you could think of and I will say translational symmetry elements this is called a space group ok. So, if you take the set of all point ends and translational symmetry elements then you get something called the space group ok.

Now what is important is that every crystal; so, each and every crystal belongs to a belongs to one space group and one point group so. That means, for each crystal you can identify what is the point group and what is the space group and the other point I want to make is that the total number of point groups, total number of point groups in crystals is 32 point groups total number of space groups is 230 ok.

So, obviously, you can have a space group and you can have one or more translational, a space group consist of the point group plus translational symmetry elements ok. So, you can have many more space groups and the other terminology that is often used is that these 32 point groups are called as crystal classes. They just call crystal classes this is just a notation ok.

So, you can think of every crystal will belong to 1 of 32 crystal classes and 1 of 230 space groups ok. Now you can see that if you want to if you want to identify a crystal you give the asymmetric unit.

So, remember we said a crystal is equal to 1 of 230 space groups plus asymmetric units; that means, based. So, the 230 space groups 1 of the 230 space groups will tell you what are the symmetries and then you tell what is the asymmetric unit, then you can you can exactly identify the crystal ok. So, this is a different way of looking at the crystal as supposed to a lattice in a basis and this clearly tells what are the symmetries of it of the crystal ok.

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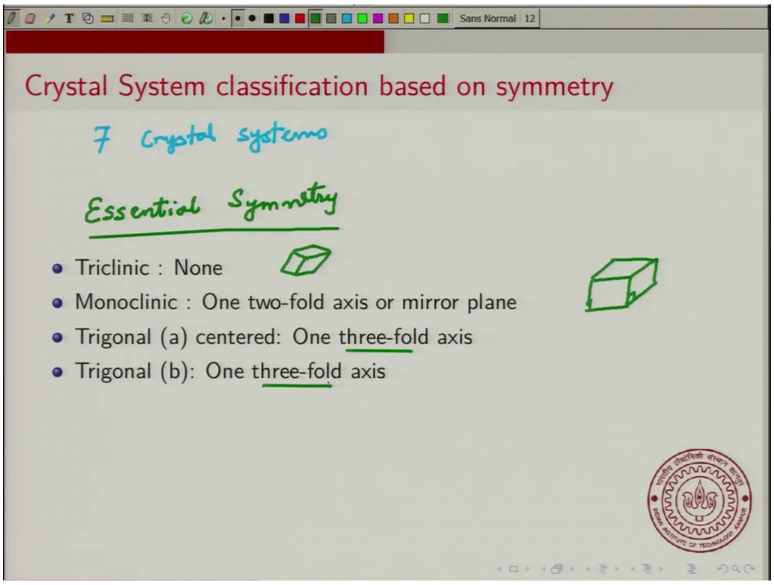

Now, one of the things is we have learnt that there are seven crystal systems and we said that we can we think of them in terms of the shapes of the unit cells and the restrictions on the shapes ok. But there is an alternate way to think of the seven crystal systems in terms of symmetries ok.

So, I list the first 4 here. So, suppose you take a triclinic system ok. So, what we are looking at is the essential symmetry ok. So, we are asking the question what is the essential symmetry a crystal needs to satisfy in order to be called a triclinic ok? And the answer is none, it need not satisfy any symmetry ok. What is the essential symmetry a crystal needs to satisfy in order to be called the monoclinic crystal it should have one two-fold axes or a mirror plane ok.

Now you might you might remember this that the triclinic we have you know all these angles were different and all these we had this unit cell shape where the lengths and angles were all different and this was our triclinic system where all the lengths and angles were different all this a b c alpha beta gamma were all different from each other.

So, that was a general triclinic system and there is no symmetry that it has to satisfy ok. No essential symmetry that it has to satisfy of course, since it is a crystal you know it should have a unit cell, it should have the translational symmetry of a crystal. But other than that there is no essential symmetry that has to be satisfied to call a crystal a triclinic, to say that a crystal is part of a triclinic system ok.

What about monoclinic? Monoclinic we said that it should have one two-fold axes or a mirror plane and if you remember the monoclinic crystal ok, it had the restriction that two of the angles were 90 degrees even though the sides could be arbitrarily different ok. So, what we had was at no.

So, you had something like this was 90 degrees and you had some other angle which was not 90 degrees ok. So, basically two of the 3 angles were 90 degrees and one of them was not 90 degrees and this shape of the unit cell again and again there was no restriction on a b c ok. And the essential symmetry is that it should have one two-fold axes or a mirror plane then there were two trigonal systems ok. Trigonal systems are characterized by a three-fold axes and we look at the, we look at the exact conditions on the on the three-fold on the on the trigonal systems ok, but just to bring.

I mean I mean the so, the two trigonal systems one was one was the case where you had a say you had a centered one and you had one that was not centered ok and each of them have one three-fold axes ok.

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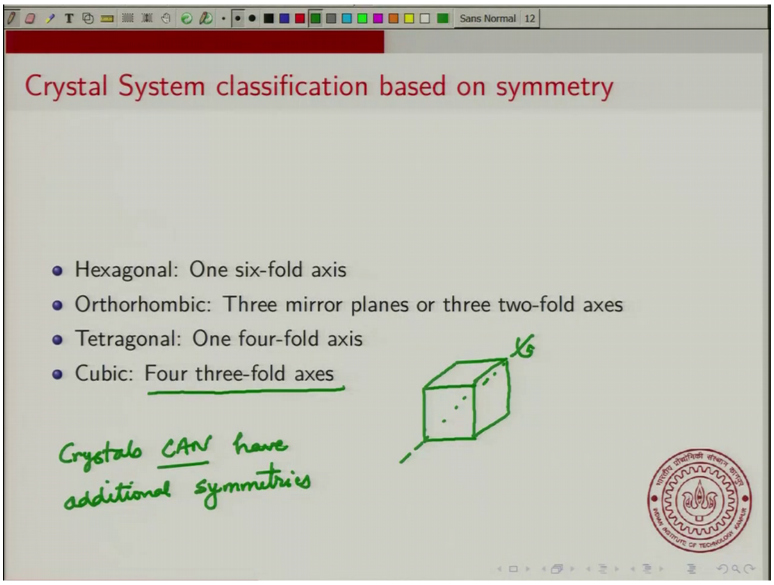

The next one was the hexagonal system this had one six--fold axes again I will not to I will not go into this in detail, but we have seen the hexagonal system many times ok, this is similarly the orthorhombic is characterized by three mirror planes or 3 two-fold axes ok. So, the orthorhombic system, the essential symmetry is that it should contain 3 mirror planes or 3 two-fold axes the tetragonal system the essential symmetry is 1 four-fold axes.

Similarly, the cubic system has 4 three-fold axes and remember this when we when we think of our cubic system we think that there are a lot more access, there are 4 three-fold axes there are 3 two-fold axes and so on ok.

But the essential symmetry for to call something a cube is the existence of 4 of these three--fold axes. So, there are four of these three axes and that is what defines the system as cubic, similarly the essential system for tetragonal system is that it should have 1 four-fold axes, it should have x only 1four--fold axes. It should have it should have 1 four-fold axes a any system that has a four-fold axes falls under is it can be a tetragonal system.

So, what you see is that is that as you go cubic is the highest symmetry it has 4 three-fold axes then you keep lowering the symmetry ok and I mean hexagonal has a six--fold axes which is slightly different from the others ok, but you find that you could tetragonal if it has one four-fold axes in addition it could have 4 three-fold axes.

So, a cube a cube can also be a tetragonal system ok. So, the existence of four three-fold axes is the highest symmetry and that is a cube ok. Now you could have one four-fold axes and that is it, that is sufficient to be called a tetragonal system alright. Now its we will see that this sort of way of looking at crystal systems is actually quite efficient and this helps us identify the space groups. Let me let me emphasize once again that the essential symmetry 4 is basically what is essential and if you.

So, for triclinic nothing is essential then; that means, it could have it could have a two-fold axes it could have some other symmetries, but it is not essential to call it a triclinic system ok. Similarly for monoclinic one two-fold axes or mirror plane is essentially it could have several other symmetries ok. So, what is important is that these are essential symmetries and you know crystals can have additional symmetries ok. So, and what you also see is I mean this way of defining a cubic system it makes it very compact.

So, the definition is very compact, any crystal system that has four three-fold axes is a cubic system if you have a crystal system that has a fourth cubic axes its a three-fold our three-fold axes then it is a cubic system. So, really it is a very very terse and very short description of the various systems and this is what will be used to identify crystals.

So, I will conclude this discussion on crystal systems, in the in the next lecture I will we will look at this in a little more detail we look at both the crystal system and the shapes of the unit cells. And we will try to correlate both these ideas.

Thank you.