**Symmetry and Structure in the Solid State**
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**Lecture – 18**
**Space Groups 1**

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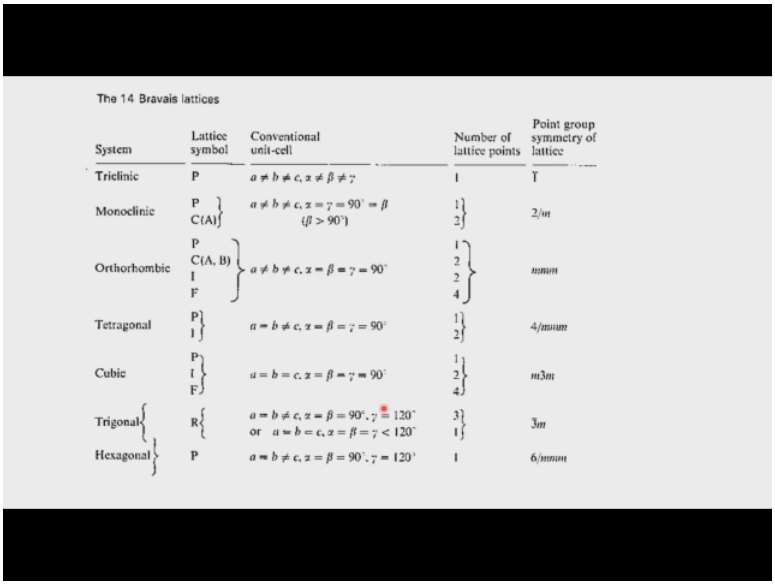


So, one other little point which in fact, was mentioned to me by one of my students while I was winding up the discussion on this table; is the fact that in trigonal, we represent it as *R* which is the rhombohedral lattice. And, then we write a equals b equals c alpha beta gamma are equal to each other. Of course, obviously, we cannot make it three-dimensional closure objective. Any of these angles are greater than 120 in such a situation, so, this has to be less than 120. The point that is also important is if alpha beta gamma are equal 90 degrees, then it will go to the cubic system. So, there is a very subtle difference just like between trigonal and hexagonal as we see from the notations here there is a subtle difference between this and the trigonal and the cubic system.

The trigonal system also has a three-dimensional rotation axis, the threefold rotation axis sorry. And the presence of the trigonal axis which is non 90 degree makes it a rhombohedral system. So, even if the angle instead of 90 degrees is 89.9 or something like that it will be pseudo cubic. So, most often than not trigonal symmetry is (Refer Time: 01:49) into the cubic symmetry and many of the materials which go into the

trigonal symmetry. Therefore, have a near cubic symmetry. So, for all practical purposes they are cubic symmetry, in the sense that the properties associated with those materials will be cubic. So, it is an issue which I thought I will mention before we go further.

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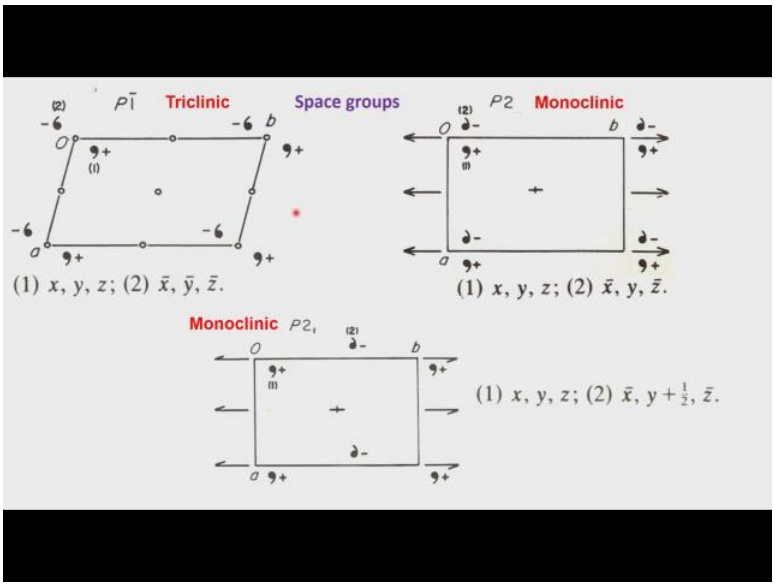


So, now let us get into the as to say, because these are the main issues of how we look into the so, called space groups. So, far we saw all the 32 point groups, how the axis developed with respect to individual point groups and so on. As the definition of the point group refers to it is with respect to a point, but what happens in a, when once we associate that with a Bravais lattice this is that they get into a crystal system. And now with point of discussion takes us to how the objects inside this particular unit cell get generated by the symmetry operations that are associated both with the Bravais lattice as well as with the point group symmetry which is associated with that lattice.

So, this is therefore, one of the most important part of our course where we will see how the objects relate themselves to each other across the symmetry in the unit cell and the contents of the unit cell and how the equivalent points get generated. So, we will start from of course, *P*1 is obvious. So, I did not take *P*1, because in *P*1 you will have a system which is represented. Suppose, we look at this ab projection; that means, this particular angle between a b is $\gamma$ and this gamma value is non 90 degrees.

We will have no none of the symmetry elements associated with *P*1, because it is only a one fold symmetry; that means, 360 degree rotation. So, there will be an object

somewhere and that remains there in the unit itself no other relationships were possible. And so, there is no point in indicating the diagram for *P*1 even though the international tables and crystallography will also list the *P*1 as the first space group. When we go to the discussion on the international tables for crystallography, we will look at the possibility of *P*1 as well.

So, the next point group symmetry which we can have which we try to make system as this is indicated here is $P\bar{1}$. So, $\bar{1}$ is the symmetry operation and *P* represents the lattice, the moment we represent a lattice by *P*, we know that the number of lattice points in this particular unit cell is 1. So, there are effectively in projection, we are looking down the c axis. So, this unless, otherwise specified the convention is always like this, down this is a the down the origin, origin is taken as the left hand top corner. And with respect to the left hand top corner, you mark a downwards and b across, c is perpendicular to us.

So, unless otherwise specified in all the diagrams which we are going to see in the next few discussion half hours, we will see that the projection is always down c. If it is different, it will be mentioned; we will have some discussion on what happens if it is a different axis. So, in a triclinic system, we have a b c not equal to each other; alpha beta gamma also not equal to each other. And therefore, we have the object which is sitting here which I have marked as 1. Now, here after we will represent the object to show that we have an atom or a molecule or a collection of atoms or an ion or whatever in the form of a comma.

So, comma now represents our object. It could be a protein structure, it could be a virus structure, it could be a single atom and so on. So, comma(**,**) is the object on which we do the symmetry operations, the advantage of using this nomenclature comma also allows us to turn it around and show the different orientations that the object can check on the operation of the symmetry. And at the same time, we can also indicate whether it is in the direction towards +c or -c by indicating them with the plus and the minus as is shown here. For example, if you take this point 1 which is now represented as x y z the coordinates of which are x y z. So, there is an object, here the object is put inside the $P\bar{1}$ symmetry.

When you put the object in the $P\bar{1}$ symmetry, which sees the center of symmetry at the origin; remember that every point in this three dimensional box which is now shown as a

two dimensional projection for our understanding, every point will have the center of symmetry. So, it means that if the object is here or object is there, object is there they will all see the center of symmetry. The location of the center of symmetry is with respect to this projection is shown here, when once it is at 0 0 0 that is our definition of 0 0 0. So, when once we are defined the origin, the location of the symmetry is fixed. So, the location of the symmetry is fixed at 0 0 0, it will of course, repeat after one translation along a, because of the periodicity that is required in a crystal. It will also repeat one unit along b, because of the periodicity and one unit along c.

So, if you now consider this particular object and say it is coming towards as from the board then we have the x y z as the coordinate. So; that means, if you now take this as the x value and that has the y value, z will be the value which is coming out of the board then we have the position of this object located. And that is located at x y and z, we can have any number of objects which can be at different values of x y and z and what happens is that now it will see the center of symmetry at the origin. When it sees the center of symmetry of the origin, it undergoes the symmetry operation which we all now very thoroughly know. If x y z goes to -x -y -z which we pronounce as $\bar{x}\ \bar{y}\ \bar{z}$.

So, we have the second objected generated which is marked as 2. So, we have the object 1, we have the object 2, you see that the object now inverts and also goes down in the c direction. So, x changes to -x y changes to -y z changes to -z, the problem here is that we have generated a point outside of the unit cell, we want all the points generated within the unit cell. So, in order to do that what we do is we now apply a translational periodicity to this point 2 which will take it to that point; translation periodicity associated with the a direction. And then, if we now apply the translation periodicity associated with b direction, we will get to this point which is inside the unit cell.

Notice that this point and this point, this object and this object are related by a center of symmetry which is located at ½ ½ ½ half along x, half along y, half along z, it is also located at ½ ½ 0. So, there is a issue which one we will take. In this diagram which I have shown as a projection, we can take it as 1/2 1/2 0 at this position. So, we have therefore, a this as x y z, this will be $\bar{x}\ \bar{y}\ \bar{z}$. What all you have done is to now see that this particular origin has moved over to this position, we are not going to call this as 0 0 0.

However, 000 is still associated with that one; if that is 000 and this is 100. We have already seen that the fact that there is a translation periodicity, the symmetry element will repeat itself half way through this. So, we get a symmetry element at that point, symmetry element at that point, symmetry element at this point and so, on. It will also happen at this 0 as well as ½ and also to full unit. So, the symmetry that is represented here is at ½ ½ 0. So, each one of these symmetry positions as you can see are independent of each other; that means, if you have this position you have over here, you see these two are operations now.

This is one unit translated along the x direction, this object translates one unit sorry, along the b direction you get this point. Now this point will see the center of symmetry, it will also generate that point which is outside of the unit. So, you see the consistency of the definition of the space group that is this point now translated by one unit will go there. Now, these two objects are related by a center symmetry, these two objects by translation, these two by center of symmetry, these two also by center of symmetry.

So, the translational periodicity which has come here, we now look at the 100 center of symmetry and go outside this point keeping the center of symmetry relationships intact. So, this is one center of symmetry that is the second center of symmetry and so, on. So, effectively we get two equivalent points one at x y z the other at -x -y -z. So, the system is triclinic the number of objects that are generated now will be 2 and this we have already seen is a nomenclature which we use as z is equal to 2 in the unit cell.

Now, let us look at a situation where this objects associates itself with the center of symmetry; obviously, if it associates itself with the center of symmetry, it cannot take the form of a comma. Even if it takes the comma, shape of a comma the comma has to be overlapping with each other; that means, this of this image and that image will overlap at that point. Half of the image of 1 and half of the image of 2 will overlap to generate the object. In other words, if there is a molecule we cannot change the molecule, we cannot say atoms are different now, because of the fact that it goes to the center of symmetry. So; obviously, the center of symmetry should have a center of symmetric object occupying that particular position.

So, the object by itself then is required to be center of symmetry. A non-center of symmetric object; that means, in terms of the molecule the molecular symmetry now

takes into take important role; if the molecular symmetry has a center of symmetry , it will coincide with the origin of the units. This is the point which you should know, because very often they are not these problems will come up when a molecular symmetry and the crystal symmetry are one and the same. If the molecular symmetry and the crystal symmetry are different then it will sit in the so, called general position.

So, these two positions are referred to as the general position. So, if x y z is 000 then the second position is also 000; that means, one half of this object and the other half of that object will jointly be present on this position; in such a way that the object shape is never changed, the objects shape remains the same. So, if the object has a center of symmetry, it cannot change its center of symmetry, I mean this is the point which will come as a very important issue when we discussed the, the various possibilities of what we call as special positions.

So, 000 is a special position. Now, if the object is associated with 000 and that is the special position then the other centers of symmetry which are in this diagram, they are all different centers of symmetry. So, each one of the center of symmetry has to get an identity. Now, this becomes an issue particularly when we go to higher symmetry space groups, because in higher symmetry space groups, this kind of degeneracy may be many more many more positions can come. So, effectively the center of symmetry position is a degenerate position. So, each one of these centers of symmetry therefore, are independent of each other. Now how do we identify these?

In order to identify their they are different from each other a convention defined by a person by name Wyckoff has been formulated, we will discuss the Wyckoff notation and Wyckoff formulation, when we looked at look at the entries in the international table, because most of you are non-practicing crystallographers from the crystallographic point of view, but you are practicing chemists who used crystallography, practicing physicist who used crystallography and so on. By biologist who use crystallography, so, for those people who use crystallography they a ready reference point for identifying. And then looking at the details of the space grouping is the international tables for crystallography.

So, we will look at the internal table of crystallography entries and at that time we will define what is known as a Wyckoff position. So, the Wyckoff positions; obviously, are referred to the special positions and also to the general positions. So, the way in which

Wyckoff designed this methodology was to look at the most symmetric position in the space group which according to him in this case the *P* $\bar{1}$ bar is 000, he calls it as a small symbol *a*. So, a small letter *a* is associated with this point, then ½ 0 0 is *b* and so, on. And the general position therefore, will be after all these eight positions identified.

So, you go by the alphabetical order *a b c i e f g h* and so, on. So, this kind of a nomenclature is referred to as the Wyckoff notation and many many publications who particularly in the field of inorganic chemistry complex materials and so on, people use the Wyckoff symbol to identify the position of the atom. So, they will just say that atom the Br atom or the or for that matter the Zr atom is sitting in a Wyckoff position *a* in this particular space group. So, if they say it is sitting in Wyckoff position a in *P* $\bar{1}$ then we know it is at 000. So, the position of the heavy atom is identified like that any atom for that matter which sits in a special position is identified with respect to its Wyckoff position

So, in a large molecule for example, it so, happens that some of the atoms might sit at special positions. Their occupancies is the new word, I am introducing their occupancies will not will be a, a fraction of the general occupancy. Let me define now the occupancy if there are two general positions, in this particular case of *P* $\bar{1}$ there is x y z and $\bar{x}$ $\bar{y}$ $\bar{z}$. Then there are two molecules or two objects in this unit cell the object which is left alone and as one here is referred to as the object in the asymmetric unit. So, we say that the asymmetric unit has one object, but due to the symmetry operation, we generate two objects which are symmetry related to each other.

So, these two positions are referred to as the equivalent positions. Now, if there is this object occupying each of these equivalent positions then we say that the number of equivalent position, we need two the occupancy is full associated with x y z and $\bar{x}$ $\bar{y}$ $\bar{z}$. So, we say occupancy is 1. The moment we put this into a special position, the let us say x y z is 0 0 0 then x y z and $\bar{x}$ $\bar{y}$ $\bar{z}$. will be one on the same and the occupancy now becomes half of the total occupancy. So, the total occupancy here is 1 with respect to a general position object, with respect to a special position object, it becomes half. So, the occupancy of half therefore, is a issue which we will have to discuss further when we get into this special position discussion.

So, just to put all the words we have introduced with respect to description of the space group. These are the words one is of course, the crystal system then the point group symmetry, then the space group information like $P\bar{1}$ , then the positions of the symmetry elements like the center of symmetry in this case and then the position of the object. So finally, it is the object we are interested in, we want to determine the structure of this object whatever it is that is the final goal. But, this object now is put into this unit cell with this information about the space group which will tell us how the object is now symmetry related and arranged itself inside the unit cell and also in the translational periodicity situation.

As a consequence the overall structure therefore, that can be determined for this is represented in terms of two objects related by this center of symmetry. So, this particular value of x y z now generates an $\bar{x}\ \bar{y}\ \bar{z}$. So, we have introduced the other word which is called the occupancy that is association with the position. So, if there are all these general positions in the unit cell are occupied then we say the occupancy is 1. The special positions have an occupancy in this particular space group of 0.5. The special positions can have lower and lower occupancies, depending on the symmetry that is associated with that point. Suppose, we have let us say a three fold axis, a six fold axis and things like that the occupancies will be correspondingly reduced from 1.

Because we, if we have an object sitting at a six fold symmetry, there will be six objects that is generated around it. Now if all these 6 become only 1, then the occupancy of that may be 1/6 of that position. So, the occupancy of this here is they are the number of equivalent points is 2, occupancy becomes 1/2. If number of equivalent points is 4 occupancy becomes one fourth and so, on. And therefore, the definition of the occupancy is given as a additional word which we have introduced in our grammar. The one more thing which we have introduced in our grammar is the Wyckoff notation. So, this Wyckoff notation is the highest symmetry position is given a little *a* the symbol alphabet *a*. And as we go to lower and lower symmetry positions associated with this position, we call them as b c d and so, on. Finally, the general position will gets its alphabet.

So, in case of *P*1 for example, what would be the Wyckoff notation think about it and that will tell you what would be the Wyckoff notation for *P*1, will there be any more alphabet than *a* ? think about it, right. So, we have now seen the if this triclinic system 2, space groups P 1 and P 1 bar the equivalent points, how we generate equivalent points

where are the symmetry positions. And, then we have always now looked at with respect to how the object gets placed inside the unit cell.

So we have now a complete picture of what to expect in a crystal structure with respect to an object which was crystallized in that particular crystal structure; obviously, triclinic is one of the simplest of space groups which we can understand. So, if you understand this all the 230 space groups could be understood in terms of the same logic. So, the logic is that we find the number of equivalent points, the number of symmetric positions that are present, the translational periodicity, the nature of the lattice, the lattice centering information and the point group symmetry that is associated in that.

If we know all these, then we know the crystal structure followed by the molecular structure. So, this our overall ambition in this is to find out where the atoms are sitting in the crystal so; that means, we want to determine the molecular structure, because we also see that the atoms join together with bonding features and so, on. And they are the definition of the object we have here. So, if the object is now a molecule there will be several atoms, but all these atoms now will be identified with respect to positions $x_1y_1z_1$ $x_2y_2z_2$ and so on. All of them will see the second equivalent point. In this case of space group $P\bar{1}$ bar and so, we will be generating the objects 1 and the object 2 and we will identify the symmetry.

So, is there a way in which this can be investigated? Suppose you are given a crystal and you are asked to find out the position of the atom, is there a way ? it is something which we will be discussing through the course; obviously, there is a way we of course, are we do not have the power to look inside the crystal and see where the atoms are, because the size of the atom is not visible to the naked eye. Obviously we can use probes; the probes which we use can be of the wave length which will probably correspond to the size of the atom. The wave length which we use in normal light when we use this light and look at the objects we will, we will be allowed to see for example, this particular screen which is in front of me or the key board which is in front of me using this particular wave length, but and in fact, the wave length is also now at that resolution, where I can also read the alphabets which are written on the key board. Otherwise I will not be able to type these things. So, to that extent there is the resolution.

But suppose I want to see the way in which the springs are is connected inside this keyboard. And how this connection now goes to this that is not possible by a naked eye. So, what is, is needed is a probe. Most of the probes are essentially driven by the fact that we need the resolution that is associated with observing those. So, if the size of an atom is about $10^{-8}$ cm or $10^{-10}$ mm, In fact, it is one order of magnitude lower than the nanometer. If you are able to see these objects through a microscope then in principle we should be able to see the positions of the atoms, but that is not what is going to be. What is going to be is to find a probe by means of which we can probe the distances corresponding to the distance between atoms and the size of the atom.

And it so, happens that in electromagnetic radiation, we do have such a range and that particular range where we can see this are the X rays. So, therefore, we up we use X rays, one might ask a question can we use other matter ways? Certainly like matter waves which will make from let us say neutrons or matter waves which come from electrons. So, we can also use neutron diffraction and electron diffraction, but X ray diffraction is the one which is the most preferred. And the most conveniently usable wave, because electron ma diffraction and the neutron diffraction need very specialized equipment, very specialized conditions under which we can use those equipment. Whereas, it so, happens that X rays diffraction which was discovered soon after the X rays were discovered in 1900, the it was discovered in the year 1912.

And, the fact that if there is a regular arrangement of atoms inside the unit cell, then there should be some regularity in the diffraction pattern which comes out from this experiment. And if we reconstruct the image of the diffraction pattern, you should be able to see the positions of the atoms and that was the idea which triggered Max Von Laue. And later Bragg and Bragg to look at the possibility of structure determination. Then came a plethora of activity in X ray diffraction measurements. Particularly with respect to small molecules initially and eventually the stage was reached such that we can now conveniently look at structures or viruses and so on due to the technology advancements.

Technology advancements high speed computing for example, and also high reliable probed through which we can look into the crystal. And, also the reliability with which we can measure the diffraction pattern which comes out; all these add up to the advantage of looking at the atom positions. So, when we say that we are looking at a

crystal, we actually now do not look at what are the dimensions of the structure. So, the way in which we take the stereographic projection was actually by observation. We took the crystal, took the center of the crystal, drew normals to the crystal planes and then collected all these points into a stereographic projection that was one way of looking at it. But, that way of looking at it will give information only on the external morphology associated with the crystal and its corresponding point group symmetry.

Beyond that if you want to look at where the atoms are and so on, we need probes and such a probe is available in X rays. And therefore, with the future course classes, we will look at how we do this experimental protocol. And, this is the experimental protocol which is in fact, a requirement for many of the industries, many of the teaching faculty and many of the students who are taking this particular course. But, remember we the take home lesson is if we do not understand this part fully, then we are nobody to understand the rest of the program which we have in the course. And that is why I am spending an enormous amount of time in trying to describe the way in which objects arrange themselves in a given space group associated with a point group in a given system.

So, the equivalent points are important, the location of the symmetry positions is important, the way in which we describe the unit cell is important. And so the so, what we do therefore, in a structure determination is to determine the geometry of the object. The geometry with respect to the unit cell, what are the dimensions of the unit cell and that is the starting point. Once we have that particular starting point, the rest of the protocol can be developed such that we now get the information about all these points which we discussed here. And that is the one which will give us the information of where the atoms are, how they are located and how to identify them.

Now, how to identify them is a protocol which is developed through X ray diffraction techniques which we will go into at a much later time. So, at this moment, we have seen one space group, we have talked so, much but we now know one space group. So, today's job further job in the next few classes is to look at the few more space groups. Get a hands on training on identifying the symmetry positions, identifying the equivalent points, special positions and so on.

And then we cannot do all the 230 that is not the idea of this course. We will get sample points from triclinic, monoclinic systems then we go to a later situation where we just straight way look at the international tables for crystallography.