Symmetry and Structure in the Solid State
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Lecture - 07
Arrangement of Symmetry Equivalent Objects

So, in the last class, we looked at the types of symmetry operations and the symbols that we give for the type of symmetry operations. For example, in this very first illustration here, you see the presence of an inversion centre. The presence of the inversion centre is indicated as $\bar{1}$ which actually tells us that if a point x y z is taken in 3-dimensional space, it goes to the $\bar{x}\ \bar{y}\ \bar{z}$; that means, -x -y -z.

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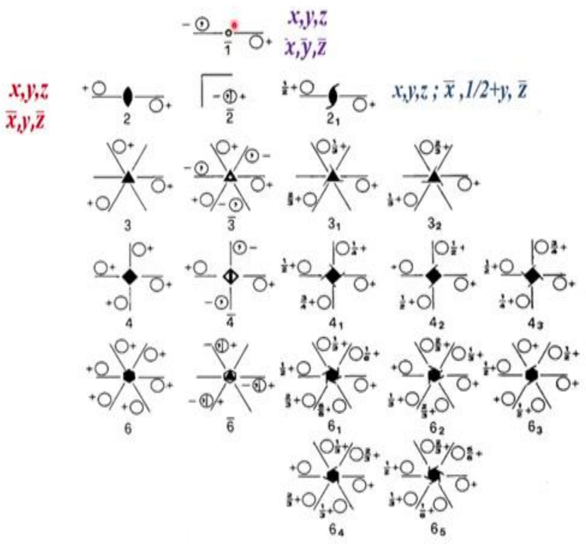

And now we operate the same one bar operation on this $\bar{x}\ \bar{y}\ \bar{z}$. It will come back to x, y, z. Now, as we defined in the last class such an operation is referred to as the point group. So, this now represents a point group symmetry and that is represented by a small open circle which represents $\bar{1}$. So, in literature, you may find just this return or in literature you may find only $\bar{1}$ written. And when you want to display the objects and their nature on which they are present in this using the $\bar{1}$ symmetry, it is normally represented this way.

So, the object is written as a bigger open circle and the sign positive tells that it is coming towards us, towards me in this example and then when we operate the $\bar{1}$

symmetry this x and suppose this is represented in the x y plane, then this goes to minus x minus y and then of course, z goes to -z that is illustrated by the presence of a 'comma' in the middle of the open circle. So, the operation $\bar{x}$ z $\bar{y}$ is indicated by a negative sign here which is taking the indicating that this object which is in front has gone to the backside of the plane of this representation.

So, essentially we therefore, generate two equivalent points with a symmetry operation which is the centre of inversion. And if the centre of inversion in the crystal context is also referred to as the centre of symmetry because the object here and the object there are related to each other by a centre of symmetry that is how we interpret. It also tells us that if by chance the object sits on the centre of symmetry; if it is located at the $\bar{1}$ position, then you see that it will be represented by let us say in this particular example x is 0, y is 0, z is 0 that defines the origin. And the centre of symmetry sits on the origin, then you see that 000 and -0 -0 -0 will represent the same point. And therefore, the number of objects that will get repeated in this point group operation will remain the same. In other words there will be only 1 symmetry operation and that is referred to therefore, as this special position.

So, in this special position, you will have the object both positive and negative indicated at that particular position. In fact, the if there is a nomenclature which has to be indicated here, you can remove the open circle and put the closed circle and put a representation which is something like this which is shown here; I just show you the example. This unit which is half plus and half minus with a negative can be taken up and put over there saying that half the objects of object will occupy this position.

So, the number of equivalent points in general is 2 and the number of special positions in this particular example is 1. So, there is special positions are a special situations with respect to the position x y z and if the x y z sits at a centre of symmetry which could which is shown in this diagram at this position and it could be anywhere in 3-dimensional space. Whenever there is a centre of symmetry that is present in the three dimensional space, it will occupy the so, called special position and therefore, we will have half the molecule or which if you consider this as a molecule; half the molecule will be present at that position.

So, this therefore now tells us the importance of symmetry representation. It tells us the representation of equivalent points. It also tells us how the objects are oriented with respect to each other this representation. Notice that this representation also is effectively bringing a 3 dimensionality because we are talking about this object being in the front and that object being in the back thereby indicating the third axis which is perpendicular to the plane of the representation here.

We now go to the next example which is the so called the two-fold symmetry, and in this particular two-fold symmetry, this is the symbolic representation it is it is marked with a close figure instead of a open figure like that; it is a closed unit here.

And again you see that these symmetry operations now, are our for any given operation x y z. It is -x y -z or $\bar{x}$ y $\bar{z}$ which indicates that the object which is shown here undergoes a 180 degree rotation. So, x changes to -x, z changes to -z. This is about the operation is about the y axis. This also tells us that the y axis is now coming perpendicular to the plane of the representation which we have here and therefore, the y axis is now perpendicular and its coming towards me and going inside the inside this particular representation. So, if that is the case there is no change in y coordinate and so the object which is in front remains in front, object which can go to the back remains in the back.

So, if you have an object which is now a open circle with a negative sign it will now be an open circle with a negative sign. So, both possibilities occur in case of a two-fold symmetry; that means, to say that the two-fold symmetry, suppose let us say for the sake of argument, that there is the object which is present on two-fold itself. I want you to think about it and see how you write the equivalent points. In other words if x y z is 0 0 0, what would be the representation of $\bar{x}$ y $\bar{z}$? Will that be a special position or not? I think it is better you think about it as an audience and the participants of this particular workshop, rather than I explain.

It is also another issue which comes up here that since there is no origin definition here because if we have a object in front, this object is also in front; if there is an object in the behind, the object is also going to the behind part and therefore, the location of the two-fold axis could be anywhere along the y axis. This is a very important point. It is not necessary that the two-fold axis should coincide with 000; it can be anywhere along the y axis. Hence this kind of a representation is still valid that is both plus and both minus depending upon where the two-fold is located which means to say that whenever we have a two-fold axis about a direction that particular two-fold axis can be anywhere along that direction and there is no fixed origin for that.

This we will see more in detail when we look at the monoclinic symmetry and the way in which the space groups developed, we have not introduced the world space group as yet, but when once we introduce that we will see how it how it operates. I also want you to look at this particular representation and see that it is represented as $\bar{2}$. I also want you to look at this and make sure that $\bar{2}$ is equal to m where, m is the mirror symmetry.

So, the equivalent points there will be x y z and x $\bar{y}$ z and that is something I leave again for you to work out as a home exercise. So, if you look at this particular representation, in this representation the mirror plane is indicated in this fashion showing that the mirror is now coincident with the plane of the representation here. So, that is coincident with the plane of the board and the operation will take this part of the object to the other part of the object on the other side of the zero and it will be therefore, plus and minus and you have a 2 bar axis which is nothing, but a mirror.

So, we therefore, have covered it now one. two and three symmetry operations and these 3 symmetry operations are all point group operations because by definition they define the requirement of a group and therefore, these 3 point group operations that are now, considered among the 32 point groups which we will display later on.

The next operation is the screw axis and in this screw axis operation, what we will do is to see the operation is done in such a way that now we have to consider an axis which is coming perpendicular to the plane of the board and that particular axis has a certain dimensionality. Now if that axis has no dimensionality remember when we described the two-fold symmetry, we said two-fold can be located anywhere along the y axis. Now it is important to define the 0 of that two-fold axis because there is a translation component associated in that direction; that means, this operation will exist only in crystalline materials. So, the so called translation involved the symmetry operations like the 2_1 screw symmetry, we will exist only in crystalline operations, crystalline objects and crystalline materials.

Here again the object which is shown here will now undergo a 180 degree rotation and then there is a half unit translation along the direction of the axis of rotation. Let me repeat, the axis of rotation is associated with the y direction; the x and z values will now go from +x, +z to -x, -z. Now you might see the difference between this representation and the representation over here where the value of y is also changed and therefore, we have put a 'comma' inside the circle. Here we do not put a comma inside the structure because this has only undergone a rotation of 180 degrees.

So, this plus remains the same therefore, 0+ and to that we add a unit of half which is a consequence of the presence of the axis in a crystal. So, this particular symmetry operation, they will occur only in crystal systems; that means, to say that this 2_1 is not a part and parcel of the point group symmetry. This is a very special symmetry which exists only in crystalline materials. So, please note that point.

So, we will not now cover all the 2_1, 3_2, 4_1, 4_2 etc because these are all operations which will come as a consequence of the rotation axis having a translation component elongate direction in a crystal and we do not want to consider crystalline materials, at this moment we want to consider only operations about a point. And when we talk about operations about a point translation symmetry is not the component which we have to invoke and therefore, we will consider only this part of the diagram.

So, we now go to the three-fold symmetry. In a three-fold symmetry suppose this is our main object, this undergoes rotation of 120 degrees goes to that particular point and then another 120 degrees will bring it to this point. So, this is a three-fold symmetry operation indicated pictorially. I have not purposely written the equivalent points because that will come as a part of your assignments later on.

So, this equivalent points there will be now 3 of them and these three will be generated. So, these assignment will be for you people as well who are in the audience here. So, this now operates the three-fold symmetry and this three-fold symmetry now gives 120 degree. So, there are 3 objects now generated. Now we take any object in this among the 3, then you operate the three-fold symmetry; it will come back to the same object. So, the point group for definition is intact even in this particular case.

As we go further down we have the four-fold symmetry and the six-fold symmetry which will follow likewise. In the case of the four-fold symmetry we will get 4 objects and in the case of the six-fold symmetry, we will get 6 objects and this therefore, $\bar{1}$ 2 3, 4 and 6.

Now, define the point group symmetry, the $\bar{2}$ operation which is also the mirror symmetry operation is also indicative of the a point group symmetry. It also tells us the fact that if we have a point group operation, the operation which is now taking that on to itself across the centre of symmetry or the inversion centre will still be a part of the point group because this has no translational component. Please note, that if we now consider a two-fold axis and then operators inversion centre about the two-fold axis, these 2 will now contribute to a point group symmetry that is because there is no translation component involved in any direction.

This is just the change of the axis coordinate that is x to $\bar{x}$ in this particular case y to $\bar{y}$. So, there is no change in, no additional component coming like it came in this example where we had x y z and $\bar{x}$ 1/2+ y and $\bar{z}$. So, whenever this additional half comes, it is not a point group symmetry. So, you should note that, but; however, this operation is valid in crystalline materials and that will become an additional points group symmetry which can operate, even though it is not classified under the point group symmetry.

So, if you consider now $\bar{3}$, this now takes the positive to the negative, positive to the negative, positive to the negative. We generate 6 equivalent points. These 6 equivalent points will become 6 equivalent points in case of $\bar{6}$ which is demonstrated in this way. Once again this could form a part of your assignment, I want you to see why $\bar{3}$ which generates now 6 of these and $\bar{6}$ which also generates 6 of these equivalent points are different from each other.

The symbols inside are already indicating why they are different from each other. Here is a three-fold with a centre of inversion at the middle and here is a six fold rotation with a three-fold symmetry in the middle and this makes the difference. And the similarly we have of course, the $\bar{4}$ symmetry which can appear which along with the 4 symmetry. There is no additional concept associated it to our additional feature associated with it.

It is of interest to note the difference between $\bar{3}$ and $\bar{6}$ and to see how $\bar{3}$ and $\bar{6}$ are different from each other. So, these therefore, are some of the point groups and the representations in terms of equivalent points, in terms of position of the objects inside this operational unit and at the same time were indicating how many objects are generated inside this one unit operation. So, these are therefore, representatives of the point group symmetry whereas, these on this side are representatives of the symmetry whenever we have a crystalline system.

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		Equivalent positions	
Axis	Parallel to		
2	a	x, y, z	$x, \bar{y}, \bar{z}$
2	b	x, y, z	$\bar{x}, y, \bar{z}$
2	c	x, y, z	$\bar{x}, \bar{y}, z$
2_1	a	x, y, z	$x+1/2, \bar{y}, \bar{z}$
2_1	b	x, y, z	$\bar{x}, y+1/2, \bar{z}$
2_1	c	x, y, z	$\bar{x}, \bar{y}, z+1/2$
Plane	Perpendicular to		
m	a	x, y, z	$\bar{x}, y, z$
m	b	x, y, z	$x, \bar{y}, z$
m	c	x, y, z	$x, y, \bar{z}$
a	b	x, y, z	$x+1/2, \bar{y}, z$
a	c	x, y, z	$x+1/2, y, \bar{z}$
b	a	x, y, z	$\bar{x}, y+1/2, z$
b	c	x, y, z	$x, y+1/2, \bar{z}$
c	a	x, y, z	$\bar{x}, y, z+1/2$
c	b	x, y, z	$x, \bar{y}, z+1/2$
n	a	x, y, z	$\bar{x}, y+1/2, z+1/2$
n	b	x, y, z	$x+1/2, \bar{y}, z+1/2$
n	c	x, y, z	$x+1/2, y+1/2, \bar{z}$
d	a	x, y, z	$\bar{x}, y+1/4, z+1/4$
d	b	x, y, z	$x+1/4, \bar{y}, z+1/4$
d	c	x, y, z	$x+1/4, y+1/4, \bar{z}$

And now we will go to the next slide where I have indicated the equivalent point operations. In case the operations are about in a crystal and there about various directions, but this particular slide we will refer to later on. At this moment we will just notice that the two-fold axis we will generate x y z if it is along the a, direction $x\ \bar{y}\ z$ and if it is along the b direction, it will generate $\bar{x}\ y\ \bar{z}$. This will be $x\ \bar{y}\ \bar{z}$ sorry this is $\bar{z}$ and if it is x y z; the c and the two-fold axis is parallel to c, we get x y z and $\bar{x}\ \bar{y}\ z$. I am not introducing the concept of a b c at this moment because we are yet to define the concept of a unit cell and that is something which we will take up next and then we will be referring back to this particular slide again and then we will see how these operations develop.

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Lattices and Crystal System

a b c α β γ

Proper axis	Improper axis	Proper and improper axis	Crystal System
1	$\bar{1}$	$(1/\bar{1} = \bar{1})$	Triclinic
2	$\bar{2} = m$	$2/\bar{2} = 2/m$	Monoclinic
3	$\bar{3} = 3\bar{1}$	$(3/\bar{3} = \bar{3})$	Trigonal
4	$\bar{4}$	$4/\bar{4} = 4/m$	Tetragonal
6	$\bar{6} = 3/m$	$6/\bar{6} = 6/m$	Hexagonal
5 +	5 +	3	= 13

Orthorhombic and Cubic crystal systems have more than one axes intersecting at a point

*Trigonal, Tetragonal and Hexagonal also can have more than one axes in addition

So, this brings us to the issue of defining lattices and crystal system. What are lattices and what are crystal systems? As we just now saw from the symmetry operations and the point group symmetry operations that the operations involving 1 2 3 4 and 6 which represent the proper axis operations are point groups.

So, there are 5 point group symmetries which come up from this context and another 5 point group symmetries which come from $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$. So, totally we have therefore, 10 point group operations which can come from here and 3 additional ones proper and improper axis which comes from this. This we have already seen in the previous class.

So, you see that in the case where we have a no symmetry or a $\bar{1}$ symmetry which is also the proper and improper axis generating the same $\bar{1}$ symmetry. It is now required that we have to define a crystal system associated with this symmetry operation. It is also required to define a lattice symmetry associated with this operation. Now what is a lattice and what is a crystal system? A crystal system is one which represents essentially the dimensions of the unit cell. Now we saw in the very first couple of classes that we saw the Escher's diagrams and there we defined a unit cell.

Unit cell is the one which now repeats itself in all 3 directions a, b and c to generate the entire crystal, but whatever is present inside one unit cell is exactly the same as in the second unit cell as far as crystalline materials are concerned. There are cases which differ from each other, but essentially we are restricting ourselves in this course to crystalline material which display unit cell symmetry and this therefore, is referred to as the unit cell. The dimensions of the unit cell define the so called crystal system. The dimensions of the unit cell are defined with respect to the 3 axis a b and c. The 3 axis a, b and c and the inter axial angles alpha, beta gamma.

So, these 6 parameters define the nature of the unit cell and therefore, this now refers to the way in which a, b, c, α, β, γ come up refers to the unit cell and therefore, it refers to the crystal system. The lattice repeats these unit cells in all 3 directions. So, the essentially when we talk about the lattice, it is like you know a framework.

The framework is built up of a, b, c, alpha, beta, gamma which is the unit cell and now we can move the unit cell along the lattice points. So, the edges of the unit cell if we are considering them as lattice points, the edges of the unit cells now we will define the lattice points which now can be put across with translations along a, translations along b and translation along c directions. And therefore, we will generate these unit cells in such a way that we have the a, b, c directions repeating the translational periodicity.

The fact that we have translational periodicity in crystalline lattices and crystal systems produces the lattices. So, the lattice sometimes is described in textbooks as an imaginary concept, because the lattice can be present anywhere whereas, the unit cell one once we define the origin, will be associated with the origin of that unit cell. And therefore, the value of a, b and c alpha, beta, gamma define the unit cell. So, the crystal system therefore, which now defines in term these define in terms of the unit cell and with respect to an origin is unique with respect to the arrangement of molecules or atoms inside that particular moiety.

Once whatever is there in the unit cell gets repeated in the following unit cells that is controlled by last lattice translations. These lattice translations are again a, b and c in three mutually perpendicular directions, but; however, this lattice can be infinite. So, the points which we consider now need not be the ones which are associated with the origin which we have defined, it can be anywhere in the 3 dimensional space, but the repeat unit will still be the same and that is why the term lattice. It is something like you know, we have a window and we have made a frame for the window, the same frame can fit all the windows which have been put in that room because they have symmetry and so, we can take the framework from one point to put the framework on the other point.

So, the movement of the framework is independent of how and why these lattices are made, this can be considered a lattice. So, that is why in some textbooks lattices are defined as imaginary concepts. There is nothing imaginary about it; it is just a framework which can be slides along they already well defined unit cell concept which has the translational periodicity.

So, the presence of the translational periodicity makes it a realistic definition. So, we very often refer to in crystallography to unit cells and determine the unit cell. And one once we have the unit cell determined on the crystal system identified, we will say that we have already got the information above the lattice. The nature of the lattice is evident in terms of determining the position of the location and directions of a, b, c, alpha, beta, gamma and therefore, the definition of the units. I think that we will become clear as we go along when we define it in terms of pictures, but what I see here is, what I show here in colour is the crystal systems which develop by single proper axis or improper axis or proper improper axis being present in the system.

Suppose there is a crystal system into which an object goes into and that particular crystal system has only 1 axis of rotation of course, 1 is 360 degrees. The $\bar{1}$ operation is the presence of the inversion centre and therefore, that is if we now want to define a unit cell unit cell being of course, in two-dimensions, I will represent the unit cell like this. We will see the plane lattices in a minute.

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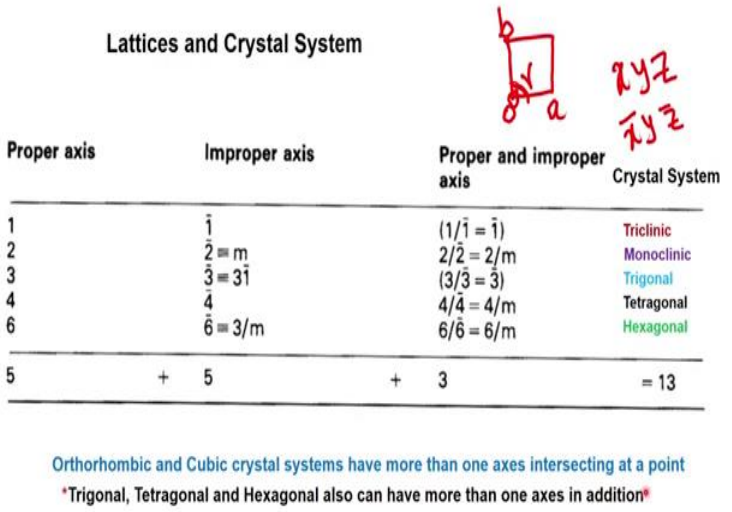

Suppose I say that I have a unit cell, this is the origin. Suppose I say this is a, that is b then you see the value of a, the value of b and value of c depend upon what where is the axis located and in what way the objects operating objects move around that particular axis. So, since there is no axis with respect to 1 is a 360 degree rotation, and the only possibility is the presence of a centre of symmetry. Let us say, it is located at this particular point O, we do not have any restrictions on the value of a and b and we also do not have any restrictions on the value of γ, the angle between a and b in this particular plane.

So, by convention the angle between a and b is γ, the angle between a and c is β and the angle between b and c is α. So, that is the convention. So, the a, b, c, α, β, γ have no significance when we have only a single operation which is now\ 360 rotation. So, if the axis of rotation 1 fold, then there is no restriction on the values of a, b, c, α, β, γ and that defines what is known as a triclinic system. When we go further and go to the presence of a two-fold axis, the two-fold axis now has the restriction of x, y, z should be going to x, y, z; should be going to -x y - z assuming y is the direction of the two-fold axis about which the two-fold is located.

So, x y z and $\bar{x}$ y $\bar{z}$ or the 2 equivalent points; if this restriction is put because of the presence of the two-fold and because of the presence of the two-fold width, an inversion centre which makes it a mirror symmetry or because of the combination of two-fold and a mirror which is perpendicular to the twofold, then the values of a, b, c, α, β, γ will change and later on we will see this then becomes what is known as a monoclinic system.

Now, in a monoclinic system therefore, we have no restriction on a b c values, but α and γ have to become 90 degrees if we consider y axis as what we call as the unique axis. We will see them in terms of pictures as we go later on to make it very clear. So, what I want to show here in this particular part of the talk is to say that there are independent single axis operations and along with these single point operations if we make them also improper axis and consider the combination of proper and improper axis which effectively makes it the consideration of 13 point groups.

Among these 13 point groups, we can have 1, 2, 3, 4, 5 crystal systems. And in fact, the triclinic system the monitoring system are more or less unique with respect to these allotments whereas, the trigonal tetragonal hexagonal systems as I have indicated here, the trigonal tetragonal and hexagonal can also have more than one axis in addition.

We have already seen this one axis operation, more than one axis operation and if it is more than 1 axis, the Euler's theorem takes over and based on the Euler theorem, we must have a third axis coming in. All these details we have already seen in the earlier classes and therefore, trigonal, tetragonal and hexagonal can have more than 1 axis. So, the presence of the proper axis and improper axis single pole single axis operation uniquely generates triclinic and monoclinic systems.

Trigonal, tetragonal, hexagonal have these along with that we can also have more than 1 axes that may be present and orthorhombic and cubic systems on the other hand have more than 1 axis intersecting at a point and that is why the 2 systems have some special properties. What special properties get introduced onto these crystal systems starting from trigonal, triclinic to the cubic system, we will examine when we examine the seven crystal systems in the next coming two classes.

However, we take home lesson from this last half an hour discussion is essentially the following. We now looked at we have looked at the operations of the point group symmetries, we have seen how the point group symmetries take the object to different object and again bring it back to the same position, obeying the definitions of a group. We have also seen the operations like the ones which involve a translational part of the periodicity; in case of b symmetry it is half and so on. And we also have seen how they generate these lattices and crystal systems in these generating seven crystal systems. So, we will stop at this point.