Symmetry and Structure in the Solid State
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Lecture – 11
Stereographic Projections (Continued)

So far we have seen the classification of point groups.

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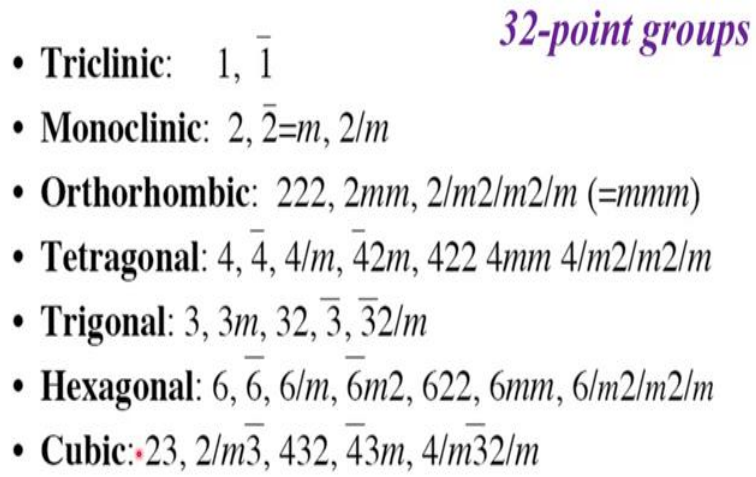

We have seen there are 32 point groups and they can be put into the 7 crystal systems which we have defined earlier. On the 7 crystal systems, they qualify themselves in terms of their dimensions in terms of the 6 parameters *a, b, c, α, β, γ* and in case of a triclinic system, it has 1 and $\bar{1}$ as the point groups. In case of a monoclinic system, we have 2, $\bar{2}$ which is mirror 2/*m* and so on.

If we read any text book, the textbook will tell you only about how we can represent these stereographic projections of each one of these point groups and then, straightaway classifies them into these crystal systems. What I would like to do and I would like you to understand is how this classification takes them into the individual crystal systems and in what way we can generate the objects inside the stereographic projection which will give us the relationship between the equivalent points, so that we can understand how many equivalent points get generated in this stereographic projection of the point group for a given crystal system.

So, each and every crystal system therefore has to be examined independently and individually with respect to their distributed point groups and that is what we will try to attempt.

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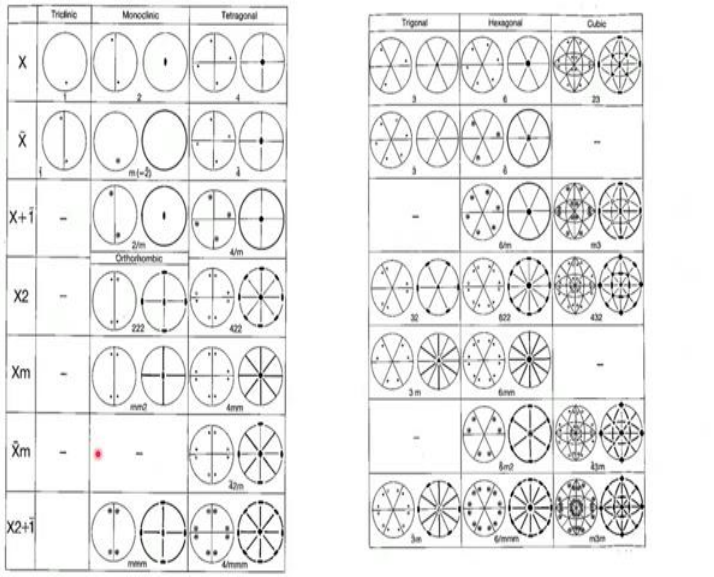

What I was trying to say is that you now if you look at this picture which will essentially we found in many of the textbooks, they will simply give the point group stereo graphic projection and show where the objects are and then, they say triclinic and x being the rotation axis, this is by far the best description you can find. This is taken from the textbook of, but then you see the understanding of these has to come only if we go individually and discuss each one of them and how the crystal systems go in to it and I thought that would be the job of a course which describe symmetry and structure in the solid state.

So, from that particular point of view I will now take you through the crystal systems and the corresponding point groups as we go along.

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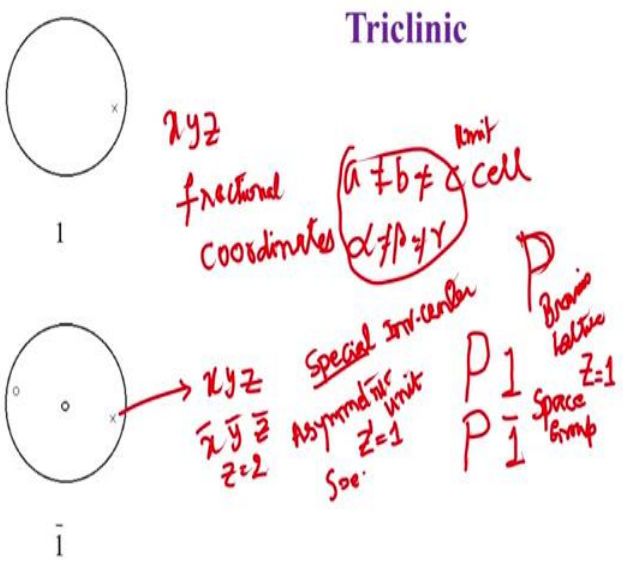

So, let us start with the simplest of the systems Triclinic and well in some sense it is not the simplest. It is probably the most complicated from the structure point of view because *a* is not equal to *b* not equal to *c*, alpha beta gamma are not equal. So, *a* not equal to *b* not equal to *c* alpha not equal to beta not equal to gamma and in fact, you can even say they are not equal. It could be 90; one of them could be 90. So, the way in which this particular unit cell is now described, there is no question of any directional preferences of the symmetry operations in this.

That means, we cannot invoke any rotational symmetry in a triclinic system or for that matter as the consequence of which is that we cannot any plane of symmetry in a triclinic system. So, when a crystal system, when the object goes into the triclinic symmetry, it can now only have a centre of symmetry or an inversion centre and therefore, when we do the two projection diagrams, we will have this as x y z. Let us say the cross mark (x) will identify a coordinate system and this coordinate system could be with respect to these *a b c* and $\alpha\ \beta\ \gamma$. So, the coordinate system will be x y and z.

Now, for all practical purposes in a all of crystallographic literature these x y and z represent what we call as fractional coordinates. So, x y z is a fraction of *a* fraction *b* and fraction of *c*. Remember in this particular case, it is not a system with 90 degree angles as well. So, these are referred to as fractional values of *a b* and *c*. So, normally the x value will appear as let us say 0.1 which means it is 0.1 of the distance a or the length a.

So, the fractional coordinates are representations of the 3-dimensional coordinate system in the given particular crystal system. So, if the system is triclinic, we have this particular way of representation that is to see that x y and z now represent fractions *a*, fractions of *b* and fractions of *c*. This is a very important point because when we talk about the coordinate system in a triclinic system, we should not assume that the x y and z are coming from a rectangular coordinate system.

That means, the 90 degree angle is not there in this system. So, if you want to really look at the and particularly people who do energy calculations and theory calculations based on these kind of information, they should convert the x y z to the proper set up of coordinates before they use their theoretical approaches because most of the theoretical approaches assume a the system to have 90 degree angles and *a b* and *c* will then correspond to x y and z axis.

So, that is why the nomenclature is to be carefully noticed here when we say little x, little y, little z. These represent the 3 directions x, y and z, but these x y and z now represent actually the cell dimensions *a b* and *c*. So, we should remember this issue and one once we have in a triclinic system, the presence of a inversions centre is a possibility because inversion centre is with respect to a single point. There is no question of involvement of any rotation axis or mirror plane or whatever with that and therefore, only these two now represent the point groups in the triclinic system.

Now, the way in which we generate the equivalent points in that situation are that if you call this x y z, then if you call this as x y z this point, then the corresponding point which is a open circle will be -x -y and -z which we pronounce as $\bar{x}$ $\bar{y}$ $\bar{z}$ that actually is the inversion of x y z about itself across the centre of inversion.

So, this gives us the symmetry operations which come inside the triclinic cell in the case of the point group symmetry. We can also put in another information on this slide and that is the information about the bravais lattice we have already seen the 14 bravais lattices in earlier class. So, this particular situation in case of triclinic systems because of the fact that there are no rotation axis and no plane of symmetry and so on, no other possibilities there except a primitive system.

So, we have a capital P. In fact, conventionally it is written in a way which is like this a italic *P*. This is the international union of crystallography representation an italics *P*,

capital *P* represents a primitive lattice. So, when we write a capital *P* and say it is a triclinic system, it can have only two of the symmetry elements which can be associated with this lattice. So, the first one will be there for *P*1 and the second one will be $P\bar{1}$. So, there are two possibilities therefore to combine the lattice symmetry with the symmetry that is associated with the crystal system.

So, the triclinic system therefore will have the triclinic system. Therefore, we will have two possible space groups. These are refer to as the space groups *P*1 and $P\bar{1}$. So, here we introduce the notation, the next point in the grammar that is the definition of a space group.

So, we have now in a triclinic system a full description that is available on this slide. Any triclinic system is characterized by *a* not equal to *b* not equal to *c*, α not equal to β not equal to γ. So, this gives us the crystalline nature or the three dimensional nature of the triclinic system and in that the coordinate fractional coordinate is presented as x y z.

If it is a symmetry associated with 1, it gives you only one position. That means, the number of points or number of what we call as equivalent points in this particular case is 1 and that is normally refer to with a symbol z. So, z is equal to 1 that means, there is one molecule. If there is a molecule sitting inside this triclinic cell that is 1 molecule in the unit cell because this is the unit cell.

So, very interestingly whatever we have learnt so far is more or less caught up in one slide. We have a triclinic system, we have the *a, b, c,* alpha, beta, gamma defining the dimensions of the unit cell and then, this in this particular unit cell if there is only a symmetry 1, then there will be one equivalent point which is identified as x. This could be anywhere in this space. This is a stereographic projection.

The corresponding stereographic projection of the $\bar{1}$ is shown here where x is x y z and this point which is the symmetry related across by the presence of the inversion centre is -x -y -z and therefore, there are two in this particular case. So, the value of z in this particular case will be 2 and the value of z will be 2. So, there are two units. So, suppose there is a molecule or an atom or an ion ionic species which is in the position x y z and equivalent atom or an ion or a molecule will be generated at this point.

So, therefore this particular unit cell with the dimension of *a, b, c,* alpha, beta, gamma in the triclinic system will carry two molecules in the unit cell. Therefore, the unit which appears independently of the unit cell, the so-called asymmetric unit is in this particular case is 1 and also in the other case of *P*1 is also 1. This is referred to as the asymmetric unit.

So, the asymmetric unit therefore in is 1 in both these cases and that is referred to as a quantity called that z' and that is equal to 1. So, in a literature if you see is z equals 1 and triclinic system, then it is automatically seen that it can have *P*1 that is not the correct statement because if z is equal to 1 and it is a triclinic system, it can also be *P*1 bar in which case the molecule atom or the ionic species will be associated with the inversion centre what we then refer to as the special position special position.

So, the special position in this particular case is the inversion centre is the invention centre. So, this inversion centre will hold now 1 unit whether it is an atom or a molecule or for that matter an ionic species. So, let me go through this again just for the convenience because and also for the fact that as we go along to the next set of crystal systems and symmetries, all these issues will not be explained again, but I will just tell you what is the z value, what is the number of equivalent points under parabolity way in which the symmetry develops and so on.

So, if we now are given a triclinic system, these are the parameters which we go automatically along with it. The first one is the unit cell which is characterized by *a* not equal to *b* not equal to *c* alpha beta gamma are not equal to each other which defines the unit cell. In the unit cell we have a representation of an object which could be identified with respect to a coordinate x y z which is fractional coordinate.

Now, in a triclinic system there are two possible point groups 1 and $\bar{1}$. The point group 1 represents just one position and therefore, the number of objects in this unit cell is equal to 1. In the case of the $P\bar{1}$, the number of objects in unit cell will be 2 defined by x y z and $\bar{x}\ \bar{y}\ \bar{z}$ if it so happens that the object sits at the centre of inversion, then the number of the objects is z' which is equal to 1. So, the one in which we do not represent are the unit which does not contain information about the point group symmetry is they called so-called asymmetric unit. So, in both these cases the asymmetric unit that is the value of z is equal to 1.

So, this in a nutshell describes the entire features which we have developed so far including the feature that was associated with the bravais lattice that is the primitive lattice. So, triclinic system is only primitive and nothing else. So, all the information you want to know about a triclinic system appears here in this one single slide. We shall now go to the next slide which is now going to take us to the Monoclinic system.

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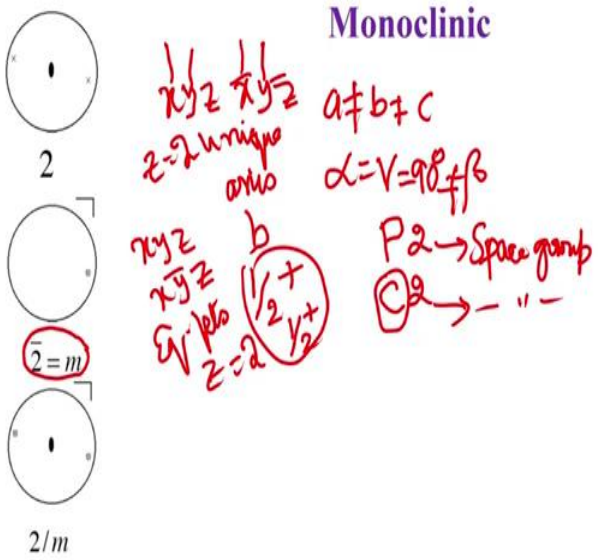

In a monoclinic system we will have definition of the unit cell, the definition of the number of possible point group symmetries the nature in which of the equivalent points which will develop and so on which is shown on the left. So, a monoclinic system therefore has the following features just like the triclinic system. We will write down now the features associated with the monoclinic system.

The first is that *a* not equal to *b* not equal to *c* and alpha and gamma, the two angles are 90 degrees with respect to each other which will essentially hold a twofold symmetry and then, not equal to beta as you can see since *a b* and *c* are not equal to each other. It is the angles which decide the direction of the two fold axis. So, in this particular case since alpha and gamma are 90 degrees and beta is non 90, the value of *b* the cell dimension *b* is the one which will now have the two fold symmetry. That means, the two fold axis which is shown up here, I will show you in a second the two fold axis which is shown here is now along the b direction and this is known as the unique axis in a monoclinic system. So, this is referred to as the unique access.

So, in fact as you can see that this is a definition which can be a variable definition. That means, if the two fold axis is along the x direction, the two fold axis along the a axis or it could be along the c axis. So, those are referred to as non-standard settings. A standard setting is the one in which the unique axis is b as far as monoclinic systems are concerned. So, generally the monoclinic system is defined with respect to b axis being unique the equivalent points are x y z and I want you to figure out what is that equivalent point given the two fold operation.

Obviously, two fold operation will now keep the identity of the object same. That means, there is no inversion here. So, what will happen is the value of x will go to -x, the value of z will go to -z because these are the b axis being unique there is no change of the y value. So, you will therefore get equivalent points corresponding to the two fold operation as follows and that will be x y z and $\bar{x}$ y $\bar{z}$.

So obviously the number of the objects which can come in this particular crystal system monoclinic with two-fold point group symmetry will be z equals 2 in the units cell. So, there are two molecules in the unit cell and these two molecules are related to each other by x y z and $\bar{x}$ y $\bar{z}$. Needless to say that there is not necessary it is not necessary that we have to have one cluster like what we show here. We can have more than 1 plus. I will just explain that in a second.

If you look at this situation here, you can have x, you can have a y, you can have a z on this side and the corresponding y z will appear after the twofold symmetry operation, with this operation x y z, $\bar{x}$ y $\bar{z}$ and they will appear on either side of x. So, you may have a y, up there y will come down here, z up here down here that will come as I said up there.

So, this could be clusters of molecules or different molecules or their molecules which can be related through hydrogen bonding in a co crystal whatever in such situations also the two fold axis is the prominent axis that is present in the monoclinic system and if the crystal system turns out to be a monoclinic one with a twofold axis, then x y z, $\bar{x}$ y $\bar{z}$ would be the relationship between various aspects, various sizes and different objects which may be present in this.

The objects may be connected to each other and may not be connected to each other. Also, they could be just in van der Waals interactions between these units. So, the overall

volume of the unit cell now we have not defined that yet. So, the volume of the unit cell will be defined now. The volume of the unit cell the unit cell of course is now there are two possibilities for the unit cell. So, let us first define the unit cell possibilities. The unit cells can be a primitive lattice as well as *C* centre lattice. So, this space group can be *P*2 as well as *C*2.

So, there are two possible space groups which can be associated with the two fold axis shown here, the two fold point group symmetry shown here. So, the primitive nature of the bravais lattice and the *C* centred of the bravais lattice both of them represent the monoclinic system as we saw in the previous class will essentially tell us the possible number of equivalent points.

Now, here is a situation where we will introduce how the equivalent points get generated when you have *C* centred lattice and I think it is better that is described in terms of understanding the bravais lattices rather than just write down the values here. So, at this particular point I will say that the presence of the C fold axis, this is all we have to note at this moment, but we will clearly derive it with respect to the understanding of the lattices and the and the types of lattices we can have in a given crystal system. So, at this particular time what we will say is that we will add a half along x and a half along y. So, we represent the so called *C* centred lattice.

So, what it means that in the case of the space group this is now the space group. So, in case of the space group *P*2 we have two equivalent points. In case of the space group *C*2, we will have 4 equivalent points. Each one of these half plus half plus will add on to each one of these coordinates. So, we will in effect have 4 equivalent points.

So, the presence of the 4 equivalent points in *C*2 tells us that these equivalent points can be generated either by the operation of the point group or by the presence of the translational periodicity which comes as a consequence of this centering associated with the lattice. We are going to examine this in more detail when we discuss the lattices and types of bravais lattices which occur in each one of the crystal systems.

So, at this moment *C*2 is also a space group which will have now 4 equivalent points. The definition of special positions might come up or they may not come up in a situation like this. For example, in *P*2 system if the object has a twofold symmetry, then the object can sit on the twofold symmetry and as a consequence in that situation the number of

equivalent points will turn out to be equal to 1. So, that will be a definition of a special position in C centred lattice as well there will be special positions. This special position can occur both due to the point group operation and also due to this centring operation and therefore, that needs to be examined more thoroughly which we will do in the coming classes.

The next system which we will take up is the point group symmetry which is corresponding to the mirror plane. So, in this particular case as you will see here there are different kinds of notations. So, if you write the mirror symmetry like that, that means that the mirror symmetry is now with the stereographic projection equatorial plane so which means that the mirror is in the plane of our presentation and you see here that the x y z and the generated mirror component which is x $\bar{y}$ z, they are on top of each other.

So, the mirror symmetry now can be either represented like that or we can make this in some text books they make this a darker circle to indicate that the mirror symmetry is resident in the plane. So, you have to be careful when you see the text books and see whether they have darken the image of the equatorial plane.

So, in this particular case the equivalent points will be x y z and x $\bar{y}$ z. That is why this operation which is shown here is also shown as two bar. So, we operated twofold rotation followed by an inversion. So, the operation of the two fold rotation with x y z to $\bar{x}$ y $\bar{z}$ and then, we invert that we go to x $\bar{y}$ z. So, x y z and x $\bar{y}$ z therefore or the equivalent points. So, again z is equal to 2 here and this also z equals to. So, we have therefore included now in the monoclinic system two possible space groups *P*2 and *C*2.