Symmetry and Structure in the Solid State
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Lecture – 23
Additional Information on Space Groups

In the towards the end of the last discussion I realise that the diagrams which were being shown for the space groups they were not of reasonably high resolution. And in fact, they were too very tiny particularly if you are going to view it on your YouTube or whatever.

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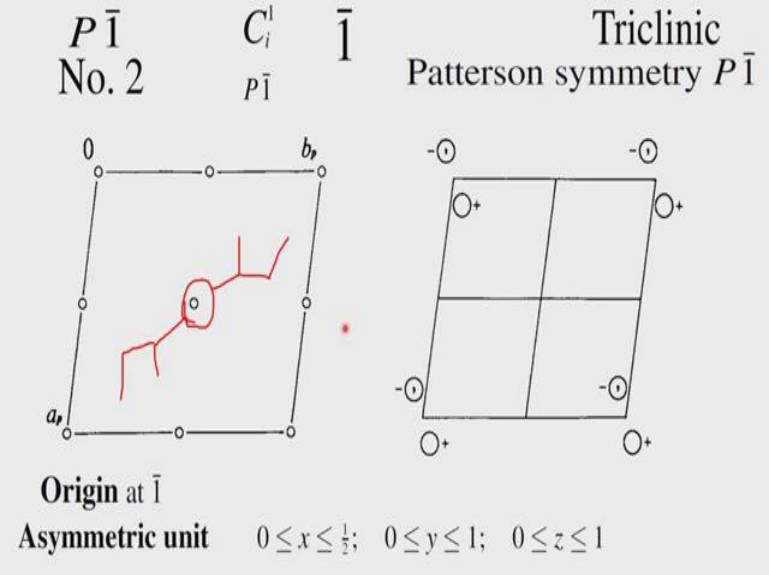

So, having the after discussing with our technical people and also the students I have my students have in fact, recast the whole thing. So, it is not the type of entry we will see in the international table they have split the entry into different possible PPT slides. So, that you see the entire thing in very comfortable viewing because that is very important particularly concerning the fact that some of these for example, the directions of a and b and all were not properly seen in the earlier part of the ending part of the previous presentation.

So, this will make it a little more visible and clearer for your understanding because this is more or less the what should we say the heart of understanding crystallography. What happens to molecules when they get into the crystal structure?

What happens to atoms when you they are getting into the crystal structure and even larger smaller whatever be the size of the species which gets into a crystal structure? It has to obey all these 230 space groups. The idea is not to present to you all the 230 space groups that is immaterial and irrelevant at this moment. But to give you the flavour of how it is helpful to study the international table content so that you will understand how to appreciate the formation of equivalent points and the identification of special positions and so on.

I have started I am starting from *P* $\bar{1}$ which is number 2 in the list of 230 space groups because *P* 1 is redundant it has no symmetry at all. So, there will be only one object in the unit cell. So, this symmetry the corresponding Schoenflies notation which I discussed before is C_i and the point group symmetry is $\bar{1}$. So, the moment a space group of this type *P* $\bar{1}$ is given to you, these two pictures should come into mind immediately.

And in fact, these two pictures are sufficient enough to find out what space group it belongs to. This is the particular representation. The first representation is a representation of the symmetry positions. And the second representation is that of the equivalent points. The first representation as you can see is the showing the presence of the centre of symmetry at the origin. And of course, it will be generated in various places as we have discussed in very many times before.

So, if we now look at the number of molecule in unit cell there are two in the unit cell this represents now the unit cell there are two in the unit cell. And this part represents the so called asymmetric unit whose dimensions are given below. So, this essentially tells you that unit of the molecule or atom or whatever the specimen or the species which is now put into this unit cell in such a way that its presence is felt in the unit cell, but not the symmetry operations.

So, if we show the symmetry operations along with then it will become the number of repetitions in the unit cell following x y z, $\bar{x}$ $\bar{y}$ $\bar{z}$ in case of *P* $\bar{1}$. So, this represents therefore, the asymmetric unit and this represents the full unit cell.

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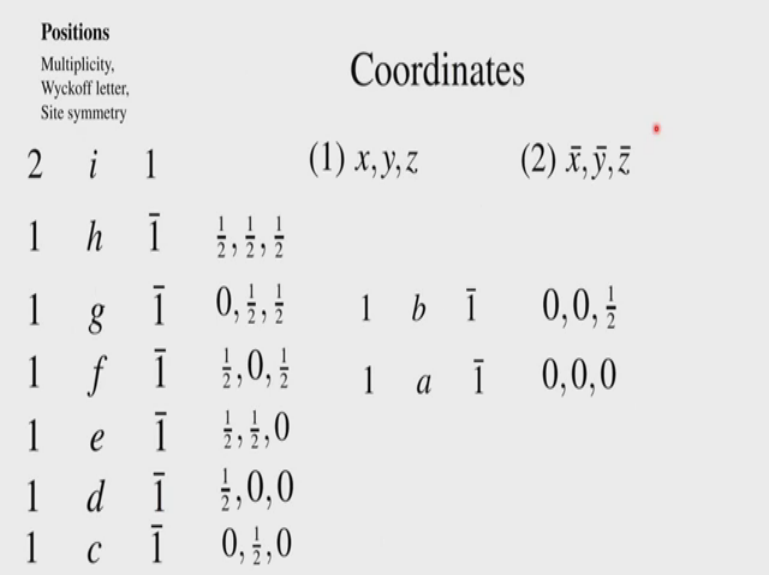

Now, the corresponding equivalent positions are shown here. What is important to notice here is there are three issues. One is called the multiplicity, the other is the Wyckoff letter and the third one is the site symmetry. So, these are the three issues we should we already discuss, but we will go into it in more detail with this clear diagrams which we have now got.

So, the first one is the multiplicity it tells you given a position x y z how many such positions gets generated by this space group. And that happens to be 2 because it is x y z, $\bar{x}\ \bar{y}\ \bar{z}$ in case of *P* $\bar{1}$. The way in which we arrange this Wyckoff letter is to look at the most symmetric possible position in the unit cell. The most symmetric possible position in this unit cell of *P* $\bar{1}$ is at 0 0 0 where there is a centre of symmetry located.

Now if we operate these two equivalent point operations it gives back the same 0 0 0. And therefore, the multiplicity associated with this site is 1 and the symmetry of course that is associated is $\bar{1}$. So, this gets an alphabet "*a*" which is the first letter of the English alphabet and this is what was designed by Wyckoff.

And this is now to give us a clear understanding of where the atoms are located in what way they generate equivalent points and so on. I will take an example in a minute. So, the as we go to other symmetry positions we see that we go from the z y and x we will

say b c and d and then we will go to the half positions along x and y, x and z, and y and z in that order.

So, these numbers therefore, represent different centres of symmetries that are present in this space group *P* $\bar{1}$, 2 *i* represents the general positions. So, there are totally one two three four five six seven eight equal the special positions and one is the *i* is there, one single general position. Now, what is the meaning of this special position? Let us interpret it with respect to the position which we show now by marking it.

So, let us say there is an atom which is located at this point. This atom now is associated with this centre of symmetry. According to the special position nomenclature it will have only one symmetry that is generated so that atom will not generate any other atom in the unit cell. So, the occupancy now we are I am defining a new word which is referred to as the occupancy.

The occupancy of that site therefore, is now half. So, we say this occupancy of this site is half because half the atom is associated with one part of the symmetry the centre of symmetry is the other half. Now if there is a molecule which is something like this which we actually discussed in the other class yesterday or day before.

Let us say it goes it has a substitution like that on one side and the substitution on like this on the other side. I am trying to make it as symmetric as possible which is not a bad diagram in my hand writing. So, you see that this is the possibility of a position of a metal. So, the metal sits here let us say and this is a ligand which is attached to the metal.

And you see that this part of the ligand is centrosymmetrically related to that part of the ligand. Now suppose you take this position and call it as x y z, this has generated the $\bar{x}$ $\bar{y}$ $\bar{z}$ over here. Let me show it on a using the laser pointer.

So, if you see here this atom, this atom now sees this centre of symmetry under goes the symmetry operations. So, if this I call it as x y z then the corresponding one here is the $\bar{x}$ $\bar{y}$ $\bar{z}$. So, there are two positions so this atom is now sitting in the general position.

The atom which is sitting at this special position is our metal atom let us say it could be zirconium or something. So, some heavy metal atom can sit there and the ligands that are attached to this are these positions. So, this molecule therefore, which is eventually

generated with this kind of a contact which is shown here has a centre of symmetry. So, this satisfies the Kitaigorodsky principle that if there is a centre of symmetry associated with the molecule then the molecule prefers to sit at the centre of symmetry.

If they if there is no centre of symmetry associated with the molecules suppose we put another substituent here let us say in which case this will move away and there will be two such molecules in the unit cell following the rules of the space group. So, that is how the positions of the atoms come up. We will discuss it with realistic example as we go along further.

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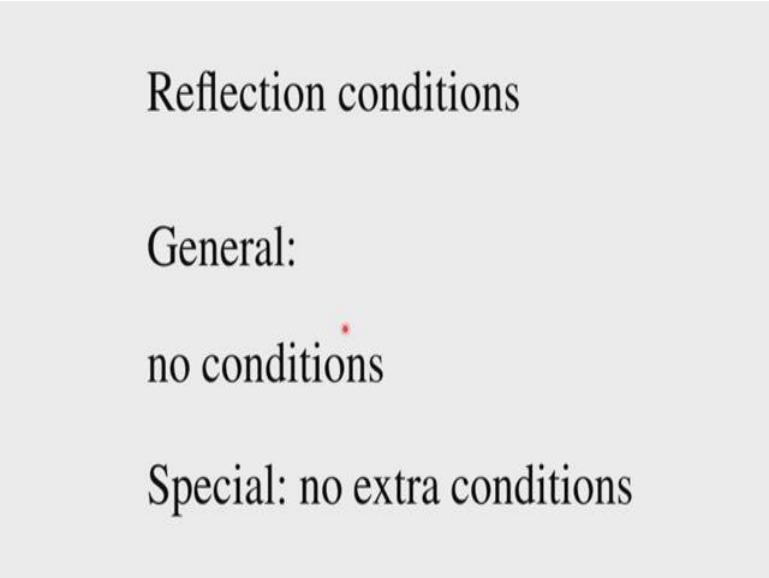

Now these are the right hand side entries in the international table, we will discuss these entries in more detail when we do this the scattering theory followed by the experiment the diffraction experiment. So, in a diffraction experiment what we record are the so called reflections. You are already probably familiar with this but have no idea how these come up these are the *hkl* reflections.

So, this so called *hkl* reflections which represent a plane. So, in diffraction experiment we send in x rays. They come off the *hkl* plane and we get the intensity of the reflection at a certain point. So, we identify where the *hkl* is and also identify the intensity. That is controlled the symmetry now controls that the way in which this diffraction positions come, the reflections come. And that is why this reflection conditions is put here and in this particular case of $P\bar{1}$ there are no such situation.

So, there is no extra conditions and no general conditions either. So, all the reflections that are possible in a diffraction experiment will appear with no changes coming up. We will see as we go along into the scattering theory what fills up in these position separately. We will not worry about it at this moment.

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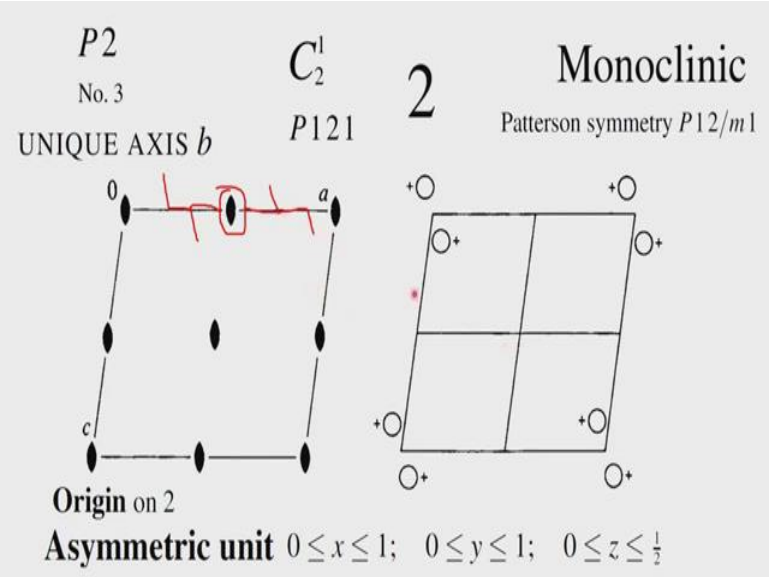

Now, we go to the next space group *P2* which is number 3. The moment we say 2-fold, the moment we say there is a 2-fold symmetry in the as a point group symmetry associated with the object which is there in our crystal system. Then we realise that it has to be a monoclinic a single 2-fold representation. That means, the single axis operation 2-fold represents a monoclinic as we have studied many times earlier.

So, the presence of the 2-fold in fact, is indicated in a full symbol in this form it says *P* 1 2 1. The 1 represents the symmetry along the x direction assuming that this unique axis is b here, 2 represents the 2-fold axis associated with the b axis along the y direction. And then the z value the z axis is again has no symmetry or 1-fold symmetry. So, instead of writing the full symbolise *P* 1 2 1 we write this space group as *P* 2.

The equivalent points on the space group we will see in a little while from now. But what you see here are the two diagrams which are of immediate importance. So, the discussion now should be centred around. Suppose you are given only this particular symmetry positions for your material. So, you have a material it crystallizes and somebody tells you that this is where it crystallizes and gives you only the symmetry information.

Now from the symmetry information you can infer several things. One is of course, there is a 2-fold rotation axis coming away from the plane of a and c which is shown here the projection is down the b direction. So, this is the ac plane. Now if this is the ac plane and b is the unique axis this angle will be the non 90 angle in monoclinic symmetry the so called beta.

So, that angle a o c will be the so-called beta angle which is a non 90 angle. So, this now represents that there are 2-fold symmetries which are coming out from the surface of the projection here to achieve. And also going inside you inside the projection and these now represent the 2-fold symmetries.

And so the moment you see a picture like this you can conclude that this is a primitive system because there are no additional indications here of the appearance of additional symmetry elements. The symmetry elements correspond only to the 000 and therefore, there is no centring here associated with it. So, effectively you conclude that this is this space group *P*2.

It may so happened that in some example you may be given only this diagram. This diagram is an extremely useful diagram because we now already see the asymmetric unit which is now in fact, the dimensions of which is shown here. The asymmetric unit it has only one object. This object now undergoes the 2-fold rotation goes up there.

And then this translated once translated once these two now will be related by the 2-fold. So, if you are given this diagram alone still it is possible to identify this space group so the space group will *P*2. So, having seen that we will also see whether there are anything like special positions in this particular space group.

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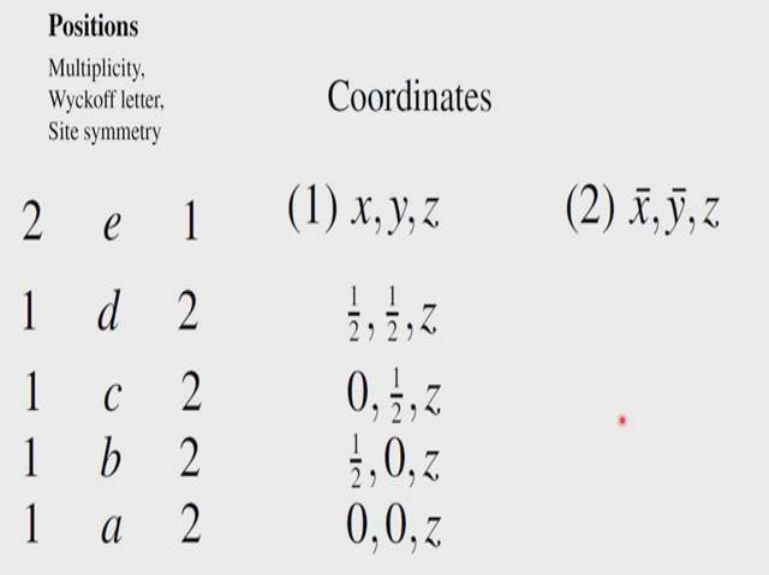

For example, the multiplicity Wyckoff letter site symmetry which is listed here shows that there are four special positions. Remember in *P* $\bar{1}$ there were 8 special positions, here there are 4 special positions and what is interesting is that these special positions have a value of z. This is in a different orientation this is probably seen down the z axis. So, this is something which should be seen down the y axis. So, I will correct it. This should be ½ y ½ and 0 y ½ then ½ y 0 and then 0 y 0.

So, this 0 y 0 essentially represents this 2-fold. So, why that confusion came I will explain. It came because of the fact that in this representation from which we copied this equivalent position which is not along the unique axis b, it is along the unique axis c. It is so happens that while taking this various diagrams it has come along the unique axis c. It does not matter, in a fact it is a education value to see this next one. In the next one you see that the 2-fold is not now associated with the b axis, the 2-fold is associated with the c axis.

So, this is a non unique axis setting. I am happy that this was this mistake we made because I can now tell about both the b axis as well as the c axis. So, the unique axis here as you see is c. So, suppose you are given only this part of the entry in the international table then you will be able to see that you see that in this particular case it is the c axis setting which is a non standard setting in a monoclinic system.

But again even if it is a non standard setting one once we have the 2-fold symmetry before special positions develop. And these special positions developed along now the unique axis only this particular case the unique axis is c. So, what would be the corresponding unique axis in the diagram we have shown before. In the special positions here will therefore be 0 y 0 which is corresponding to the 0 0 z here.

And ½ y 0, 0 ½ y and ½ y ½; that means, it corresponds to these directions in which the 2-fold is located. So, there three of them here which come directly and therefore, we see that this therefore, represents the overall representation of the space group *P*2. So, we have four special positions and one general position.

So, you see Wyckoff now let us now say a b c d and e. So, what is significant about this Wyckoff notation is; the fact that particularly as we go to higher and higher space groups. The possibility of materials crystallizing in higher space groups is restricted to only inorganic materials and materials with larger atoms. Organic compounds do not generally go in into higher systems, but even if organic compounds go into this kind of a system.

Suppose there is a situation where we have a molecule which is now going to sit here let me do that operation to make you feel comfortable. Suppose there is a same compound which we took earlier but now the heavy atom sits here and now the connectivity will go like that. Now tell me whether it will go up or it will go down? In this case it will go down and in that case it will go up. So, these are the 2-fold operations.

So, this atom and this atom suppose we consider these atoms, suppose we consider this atom and that atom; these two are not associated with the 2-fold symmetry, but they will go now such that the overall symmetry of 2 is maintained. So, these two atoms individually will again be 2, but at the heavy atom that is present here will be 1.

And this is something which also tells us the way in which the molecules arrange themselves inside the unit cell. Particularly when they have a symmetry that is associated with the molecule which also is the symmetry that is present in the crystal system. So, when we go to higher crystal systems the molecular symmetry may still be either lower or higher.

But the space group may have both higher and it may have all higher symmetries. So, the higher symmetry position can be occupied by a lower symmetry molecular system also. And that is how you can generate many possibilities in higher symmetry space group. So, if there is a very highly symmetric cubic system for example, where a=b=c, $\alpha=\beta=\gamma=$ 90 degrees the special positions are the ones which will which are preferably occupied by molecules.

And that is the reason the reason being that it will give us give the flexibility associated with the molecule. Otherwise you know you will end up with a large number of possible positions in the space group; which is not really the case the molecules are looking for. In other words the overall conceptual plan here is that a crystal, this is the definition; the crystal is a super supramolecular par excellence.

You cannot have the molecular arrangement any better than in a crystal. The crystal gives you the best possible arrangement. So, when you talk about the assembly of molecules; you have several molecules assembling together, the most preferred and the most energetically favoured one is the one in the crystal. So, the molecule now finds a very comfortable environment to go into a crystalline environment. And that is how we are studying the symmetry and structure in the solid state.

So, when it goes into this system it cannot be any better. At the same time it may go into a system which is what is generally referred to as metastable systems; this happens very often in pharmaceutical sciences. This metastable system is not the one which is energetically favoured to go into that crystal system. And probably it will now revert itself to another crystal system and this is the issue of polymorphism. So, it will revert in a given time; this may take about 1 day, it may take about 100 years, it may take a millions of years.

Like for example, I give you a simple example of carbon. You all know that carbon crystallizes in the as diamond, it also can crystallize as graphite. And of course, we the C60, C70 and all that recently discovered; these are all different allotropic forms of carbon. If there is an atom and it goes into different forms we refer to them as allotropes. If there is a molecule and it goes it goes into different crystal forms then we call them as polymorphs.

So, that is the basic difference; so this is particularly useful for people from pharmaceutical industry. Because they will always be wondering what is this polymorphism about in types of crystalline material; so, this is polymorphism. Polymorphism is not restricted only to crystalline materials; polymorphism can exist in very many circumstances. It can be in liquids, it can be in gases, it can be in a single biological molecule, you can have different polymorphic forms emanating from the system.

It can be polymorphs in gene sequencing and things like that. Polymorph is a very common phenomena but in crystal when it happens it happens in this particular way. And therefore, it is of importance to know that crystal gives us the best possible environment for assembling a molecular species. So, when large number of molecules come together and crystallized, they prefer to go into the best possible form energetically favourable form.

The energy that is associated with that will be very minimum and the energy that is associated this with that if it is not the minimum then it can take the other forms. So, that is how the prediction of crystal structures becomes difficult. Otherwise we can just you know look at a crystal oh the molecule is here it is not that way. And so crystallography and the study of whatever we are doing in this course is still alive and it is important.

Because of late cryo-crystallography has cryo-EM crystallography; electron microscopy based crystallography has been established as a technique where we can see very very large molecules. In fact the latest one is a protein isolated from sea urchin whose size is millions and millions of Daltons. And have been able to look at the microscope and they get a microscopic image of the molecules, so that is the latest. Anyhow we will not going to the detail of it. We will go now and see the presence of the special positions. So, there are five, four special positions and one general position in the space group *P* 2. And this is not required now we will discuss it later on.

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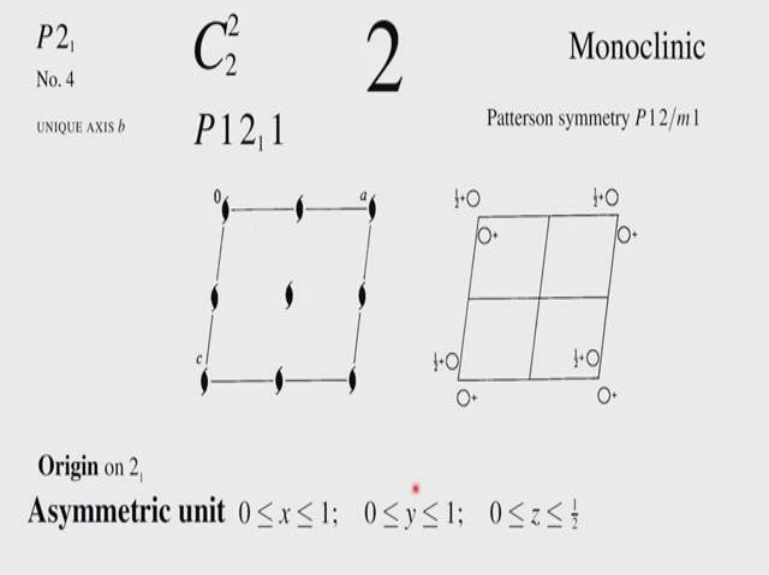

Now, we go to the space group $P2_1$. $P2_1$ is where we have now introduced a screw axis. So, the diagram if it is given like this; now you are experts you can easily say that just give me this diagram I will tell it is space group is $P2_1$. So, none of these are given except this diagram we will now say it is $P2_1$.

Because the 2_1 axis is at the origin, is 1 unit 1 unit away that is translation and they all appearing at half positions; so it is a 2_1 screw axis. If instead of this diagram this diagram is given; again you are experts enough now to say that this is the $P2_1$ system. Because you have this to 180 degree rotation and half translation the direction perpendicular to that, you have two equivalent points in the unit cell. One in the asymmetric unit which is the same asymmetric as before and full symbol is $P\ 1\ 2_1\ 1$.

This is the Schoenflies notation which is used by group theoretical specialists, and also by a most of the mostly mathematicians use that nomenclature along with spectroscopists. The reason why we prefer to use the Hermann Mauguin notation as we have here; is because of the fact that we can definitely straightaway delineate the lattice from the symmetry exhibited by the point group, and that is a very big advantage. Because we can identify the lattice here and the point group symmetry there, and the point group symmetry if it has a translation; obviously, the translation component has to go.

And therefore, the point group symmetry here is 2. So, the understanding of this space group therefore, in terms of the Hermann Mauguin notation is more straight forward when we consider crystallography. Crystallography has a lattice, crystallography has a unit cell, and these are not present in spectroscopy. And mathematicians do consider these as special cases of the normal cases, where they look at only the point group symmetries and that is all these notations are changing. So, the crystallographers prefer to have this notation.

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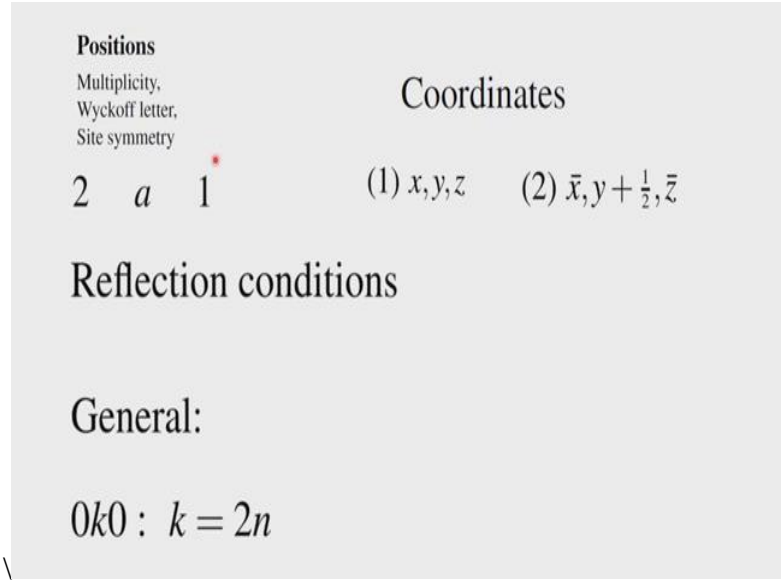

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Now, are there special positions in this space groups. Now the problem here is that if you want to have a special position in this space group one can think of a special position associated with this axis. But then there are there are issues associated with the translational symmetry periodicity.

So, we are going to translate it by half the unit. So, when we translate it by half the unit you do not have please note; you do not have the 2_1 screw axis and above half distance in that particular direction. You have only in this direction, because it is a single axis operation as you see it is operating only along the y direction; you do not have it in this direction. So, because the symmetry elements are not present you won't get special.

So, in the 2-fold case they are present again here they are not present. The half translation destroys the presence of the symmetry. And therefore, we end up getting into the situation ok. So, there is no there are no special positions in this. So, this 2a and x y z

$\bar{x}$ y+½ $\bar{z}$. There is something which is entered here again we will discuss that in the after we study the x ray diffraction techniques.

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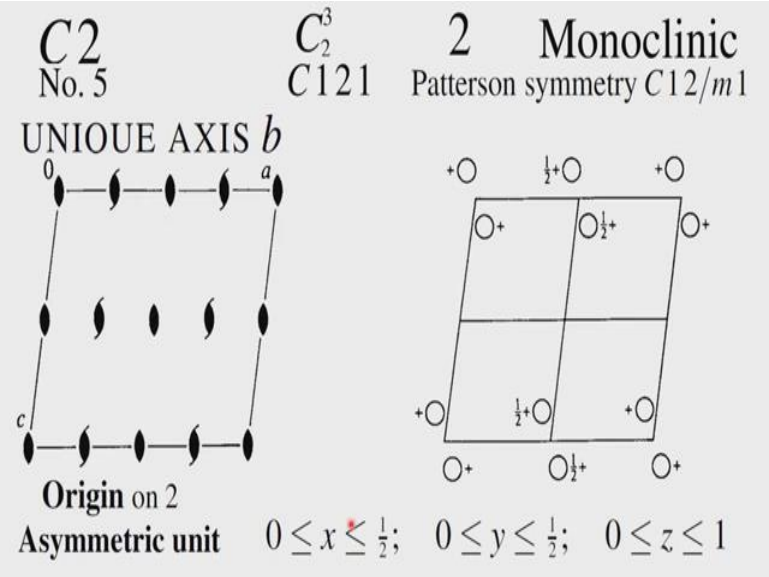

The next space group again we are still in the point group 2. So, as you all know that monoclinic symmetry gives a 2, m and 2/m. So, the 2, m and 2/m will represent one single axis operation that is the; twofold axis a mirror perpendicular to it. Or the presence of a 2-fold axis and a perpendicular all three are represented.

And therefore, the possibility of now considering the centred lattice which is associated with monoclinic systems becomes handy. So, the space group now is *C*2 and this goes takes us to the next space group which is space group number 5. So, in this particular space group we again have the diagram given here. Now this diagram will tell us that for every position here you have these so the twofold positions will define the presence of the 2-fold symmetry.

Apart from that you get indications of the presence of screw axis associated with this half one fourth positions. Now how does that come apart? It comes about by examining this diagram. So, we are going to now spend some time in examining this diagram and relating this diagram to that diagram. We did that already in the previous classes, but not with respect to the space group diagram and equivalent point diagram the symmetry diagram and the equivalent diagram given in the international table.

So, if we now understand this and correlate with what all we have already understood in the previous classes. Then our understanding in this whole concept becomes clear. So, you know when once a compound crystallizes in a *C*2 system, where are all the symmetry elements? In this particular diagram which we see that all the symmetry elements are shown here.

The moment additional symmetry elements come at one fourth position. Either along this direction or any other direction in this particular case since the unique axis is along b it will come only in this particular direction. So, the if there is a one fourth appearance of any symmetry element in this case is a 2_1 screw axis. The presence of the 2_1 screw axis tells us that is a *C* centred lattice.

So, we automatically know what how this *C* centred lattice is coming. And this is something we will discuss a little more in detail when we take up this diagram. If we take up this diagram we have the position of the x y z here then we have a 2-fold operation which is across here so this twofold now we will bring back this here so, we got two of the two equivalent points here.

Now, because of the *C* centring that is present in this particular space group you see that additional for this the additional one comes here at this point which is ½ + x in this case the projection is "*ac*" this diagram "*ac*" projection as you see here this is a and this is c. So, this will be ½ + x, ½ + y that is indicated by the ½ + up here because y is direction in which it is going perpendicular and then the z value remains the same.

And therefore, we get the first position here, second position there, third equivalent point where this second equal and point comes within the unit cell. And then there is a twofold axis which is present at this position which takes this over to here. So, we get this half plus object at this position. So, we have therefore, 1 2 3 4 equivalent positions; so therefore 4 units in the unit cell. And this is something which tells us the way in which we have to now choose the so called asymmetric unit.

So, you see the asymmetric unit dimensions are given below here. And this asymmetric unit therefore, gives $0 < x \leq ½$. So, x which is this one we take only half this distance and along the y direction we take only half the distance so this fellow will not come, and then along the z direction we take the full distance. So, what does the asymmetric unit consists the real asymmetric unit consists of two objects.

Now the two objects are *C* centred lattice related there is no symmetry so, the definition of asymmetric unit is still remaining. When we say asymmetric unit; there is no symmetry, the presence of the *C* centred lattice is a consequence of the nature of lattice. So, the lattices develop these two equivalent points so this asymmetric unit therefore, has two equivalent points in the asymmetric units; so there will be two objects in the asymmetric units. The moment there are two objects we know that it has to be a *C* centred monoclinic system.