Symmetry and Structure in the Solid State
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Lecture – 24
Details of Space Groups 2

See we have been looking at the Space Group *C*2 unique axis b.

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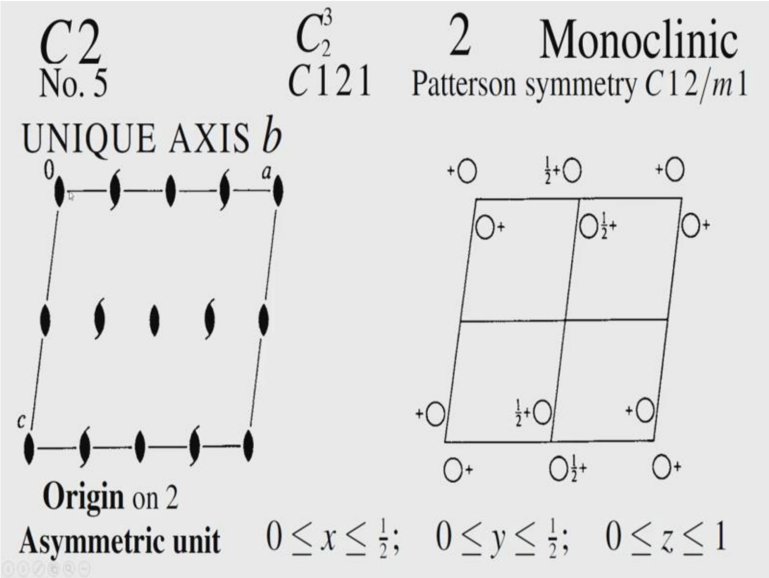

But what is one issue which we have to keep in mind is that the presence of the y axis is not unique the 0 of the y axis that means, the origin can be anywhere along this direction. So, suppose we move the origin to this 2_1 screw axis what happens? We have already discussed this issue suppose I take this origin and move to this particular point, now it becomes $C2_1$ the space group becomes $C2_1$. So, we already showed that $C2$ and $C2_1$ are one and the same.

So, it is necessary to specify the origin and you say here origin is on 2; that is why the international tables is very careful very cautious. So, they say the origin is on 2 if the origin is shifted to the 2_1 position, it will become $C2_1$, but these two are one and the same. So, the question of fixing the y value is crucial here and that y value is put at 0. So, this will be the 0 0 0 that is the presence of these and the 2-fold axis.

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Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates $(0,0,0)+ \quad (\frac{1}{2},\frac{1}{2},0)+$	
4	*c*	1	(1) x,y,z	(2) $\bar{x},y,\bar{z}$
2	*b*	2	$0,y,\frac{1}{2}$	
2	*a*	2	$0,y,0$	

If we look at the possibility of special positions here interestingly, special positions do develop that is why I define where the origin is and when once the origin is fixed then the special positions will come at any value of y. So, the value of y is dependent upon where you fix the origin. The origin is fixed at 2 fold axis then two special positions come up and those are a and b Wyckoff notations and these have 2 equivalent points because the total number of equivalent points here due to 0 0 0 and 2 fold is this, due to the presence of the *C* centring with this is that which we have already indicated in the diagram. So, we have come to a stage where we have finish the all the possible symmetries that can be associated with a 2-fold axis.

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Reflection conditions

General: Special: no extra conditions

hkl : $h+k=2n$
$h0l$: $h=2n$
$0kl$: $k=2n$
$hk0$: $h+k=2n$
$0k0$: $k=2n$
$h00$: $h=2n$

Now, the reflection conditions as I mentioned we will not worry about it now, we have already prepared the slides. So, let it be there, but we will look at the slide in more detail when we discuss the diffraction conditions.

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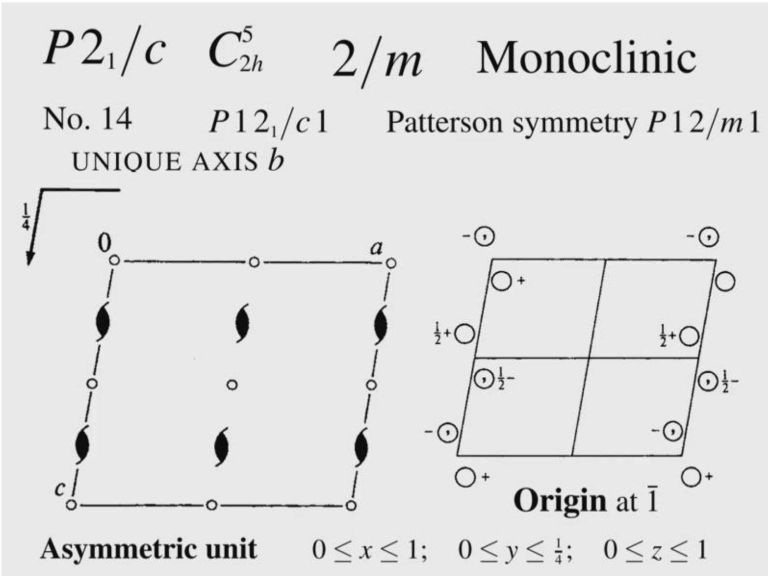

Of course, one can discuss the other space groups like *Pc*, *Pm* and so, on, but that is not the idea as I told you that it is not required here to learn all 230 space groups. So, instead we now go to the space group to $P2_1/c$. $P2_1/c$ have been mentioning again and again that this is a space group where we find most of the organic compounds go in to. And therefore, it is better we understand this space group a little more clearly. Again, this is the space group number in this case is 14. So, we have now jumped from the space group 5 to space group 14.

The arguments which go with the definition of the asymmetric unit, the special positions and so on, will be very similar in the other space groups from between 5 and 7. So, we do not have to go into the detail of it. So, we go to this space group number 14 very important space group the unique axis is taken as b and a full symbol is $P\ 1\ 2_1/c\ 1$. You see that $2_1/c$ will convert itself to a point group symmetry of $2/m$. So, the moment we see $2/m$ the system has to be centrosymmetric we have learnt it already. So, since this system has to be centrosymmetric the origin must be at the centre of symmetry that also we decided and in fact, we derived the equivalent points of $P\ 2_1/c$ in the previous class based on this.

So, here you see that the origin is centre of symmetry the presence of the 2_1 screw is at ¼ the distance and then you see the presence of the glide plane which is shown up here because, it is coming in a direction perpendicular to that and that is also at ¼ that is also at ¼. And therefore, we see that the 2-fold axis screw axis and the glide planes are shifted by ¼ and ¼. This is shifted ¼ perpendicular to that and this is the nomenclature which we learnt long long ago in the earlier classes and this is the 2_1 screw axis which is now appearing at ¼ position.

So, if this diagram is given again and nothing else is given, is it possible for us to guess the space group. It is fairly simple now very easy because we see the centre of symmetry. So, we know it is a centrosymmetric space group $2/m$ symmetry is centrosymmetric. So, we say that this system is centrosymmetric, and we see a 2_1 axis ¼ removed and a glide plane ¼ removed. We have understood that whenever there is a translational periodicity involved space group; the systems with the no translation symmetry they move by ¼. In this particular case both the systems 2_1 as well as c has the ¼ movement and therefore, both of them move by ¼; one moves with respect to the other by ¼ let us put it that way.

So, we therefore, have now this equivalent point diagram. Now looking at the equivalent point diagram is it possible for us to identify the symmetry element. So, if you look at this point to this point you get a centre of symmetry, you look at this point to this point you will get a 2_1 screw axis straight away ok. So, you therefore, have this and a 2_1 screw axis. Now the fact that there is a centre of symmetry here brings a centre of symmetry here as well and these two therefore, are related by the centre of symmetry. If they are these two are related by the centre of symmetry and these two are by the 2_1 screw axis, then there must be a possibility of a glide plane which is placed at ¼ the distance because these two points will not be generated otherwise.

And this is one of the points which is generated by the *c* glide system and therefore, you have 4 equivalent points these two equivalent points again are related by the presence of the centre of symmetry here, these two are related by the presence of the centre of symmetry there, these two are related by the 2_1 screw axis compared to this diagram you can we see that these two are related by a 2_1 screw axis, these two are also related by a 2_1 screw axis. The fact that we are adding ½ to the symmetry related one here and the half to symmetry related one here tells us that there is a possibility of glide plane at ¼.

So, this is therefore a uniquely determined space group. So, we have the ¼ translation along the direction which is down here which is the c direction the 2_1 screw axis developing and ¼ which is along the b axis which is the unique axis in case of $P\ 2_1/c$. So, the equivalent positions in fact, they are symmetric unit now is very interesting. The asymmetric unit is the y value which is the value perpendicular to this stops at ¼ and the other 2 are in the full unit; that means, that we again have 2 molecules in the unit cell now that is interesting because we should get only 1 molecule in the unit cell.

Now do we get 2 or 1 we get. In fact, only 1 because x value is full. So, the x value which is up here is full and then the y value is only one fourth, and the z value is also full. So, we get therefore, this plus that as the unit cell identifiers, but then you see that these two are centrosymmetrically equivalent objects and then there is a half translation in a direction perpendicular to that. So, it goes again beyond the ¼ plane. So, this is only one let me explain again. The number of equivalent number of points in the asymmetric unit here in this case is only 1 it is because of the fact it is a primitive lattice. So, in a primitive lattice you should have only 1 in a C centred lattice you should have 2, in a F centred lattice you will have 4 and, in a body centred lattice you will have 2, the symmetry positions then give us the equivalent positions in the entire symmetry.

So, here you see that this if you consider the asymmetric unit as this one, since we are stopping at ¼ along the y direction this point will not come this point none of these points will come and therefore, will get only 1. So, when we get only 1 object it means that it is primitive. So, these are all fairly consistent with the mathematical theory of group groups and group theory is straightaway proves all these points.

But then when we are visualising the crystal structures, we cannot think of group theoretic theoretical principles instead we can think of where the molecules are, where the atoms are, and in what way the symmetry elements are related. So, this would be the best way to learn about the space groups in my opinion of course, you will you by now you also agree because you are going to recourse anyway. So, you will agree this is the best method anyhow.

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Positions Multiplicity, Wyckoff letter, Site symmetry			Coordinates	
4	*e*	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$
			(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$
2	*d*	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
2	*c*	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$
2	*b*	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$
2	*a*	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$

So, now these are the equivalent points we get 4 equivalent points written as 1 2 3 and 4 these 1 2 3 4 go to the references here. In fact, it is not marked here, but we can mark 1 2 3 4 given 1 2 3 4, I would suggest that you mark the 1 2 3 4 positions in the projection given here which is 1, which is 2, which is 3, which 4 for example, this is 1 and this is 4. So, the clue is already given you mark which is 2 which is 3. So, these are the 4 equivalent positions and there are special positions again in this space group these special positions come like this. We have a position which is and the when the object is associated with the origin. So, if you take the origin and put x y z to be 0 0 0, then you will get 0 ½ ½ as the second possibility this will again be 0 0 0 this will be 0 ½ ½ the translation along y the translation along z. So, the 0 ½ ½ will be the second equivalent point.

So, there will be 2 objects rather than 4 associated when they are sitting in this special position. So, you go to the other equivalent points the other Wyckoff letters we have 4 possibilities and these possibilities come at ½ 0 0, 0 0 ½, 0 ½ 0 what is the very important here to remember and notice is that, if there is a molecule associated with 0 0 0 it is a different situation because we have only molecules at 0 0 0, 0 ½ ½ . So, if there is something which is associated with ½ 0 0; that means, this particular centre of symmetry is different from this centre of symmetry that centre of symmetry is different from that centre of symmetry and so, on.

And that is why the Wyckoff notation change if all of them were similar than Wyckoff notation would have been a and all 8 would have been grouped under this, but that is not the case because the way in which these operate this 4 equivalent points operate decides what are all the special positions. And therefore, we get 4 special positions and these 4 special positions have a multiplicity of 2 and therefore, these are independent special positions; that means, if there is a molecule let us say we take a cluster of molecules there are 2 molecules 2 different molecules and they crystallize inside a $P2_1/c$ and there are not very well defined interactions between these two molecules. So, it is a purely vanderwall interactions.

Then the molecule one can sit here and a molecule can 2 can sit here and they can be in the 2 different special positions that is alone. And that way you know in when you make the co crystallization experiments when you make co crystals when you make salts when you make eutectics and things like that, it may so, happen that these are the positions in which these molecules can sit and they may have an interaction they may not have an interaction between them. And that interaction is a question of intermolecular feature which is independent of the location of the molecules.

So, that way we can have a molecule in this position and a molecule in that position, then you will have 4 of those molecules and 2 of these molecules which will give a different stoichiometric ratio. I am mentioning this because particularly from the pharmaceutical point of view and also from materials industry point of view, this become very very crucial. The way the molecules and them and sits themselves in the allowed positions of the Wyckoff nature will tell us what is the nature of the molecule eventually, which all what is the nature of the material which eventually a comes out of this whole arrangement of super molecular assembly. So, that way it is very important.

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Reflection conditions

General:

$h0l : l = 2n$

$0k0 : k = 2n$

$00l : l = 2n$

Special:

$hkl : k + l = 2n$

$hkl : k + l = 2n$

$hkl : k + l = 2n$

$hkl : k + l = 2n$

The next thing we do is to we will skip the reflection conditions because this will come only after we do scattering.

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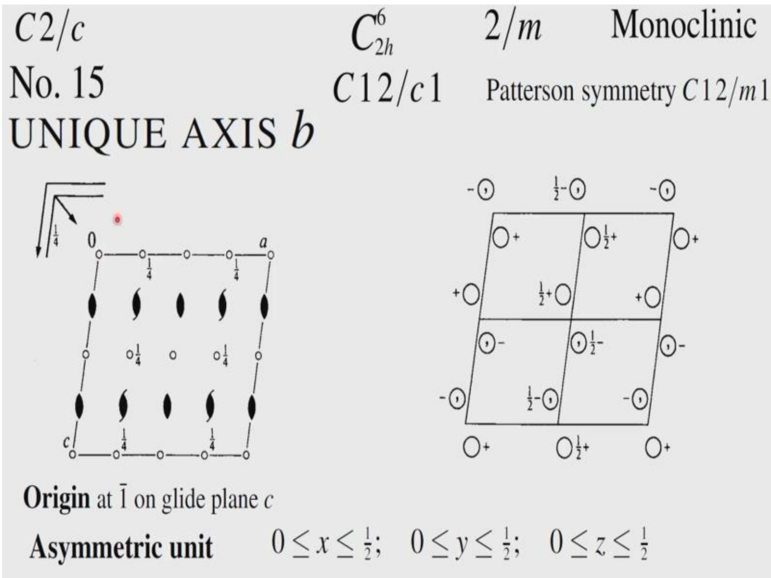

So, we go to the next space group which is the *C* centred space group and *C*2/*c*. So, we know that $C2_1/c$ is same as *C*2/*c* we already know that. Now, by looking at this diagram also you can verify if you want to make a $C2_1/c$ you move the origin to this fellow then you will make it $C2_1/c$ that anyway it is not important. What is important here is that this space group again the unique axis is b, the full symbol is *C* 1 2/*c* 1. So, if you now convert this symmetry in to point group symmetry it will be 2/*m* and its a monoclinic system.

So, the equivalent point diagram is shown here and the you see now the asymmetric unit is halved in all 3 directions. So, it is half here half there and half there. So, the moment that it is half this fellow will not come up and therefore, there are 2 of them present one here and one there or for that matter we are taking half the unit. So, this is half the unit and that is half the unit. So, there are 2 refer additional point due to the presence of the *C* centred lattice. So, since it is *C* centred lattice the asymmetric unit will contest consists of 2 independent molecules, they are not dependent on each other anymore and therefore, there will be 2 of those.

Also, we notice here that the origin is located at $\bar{1}$, and the glide plane *c* glide plane *c* is coincident with $\bar{1}$. What happens in that situation is that this particular notation tells us that there is a new symmetry that develops and that symmetry which develops is the so, called *n* glide. We talked about the *n* glide and this *n* glide will develop in the case we have a *C*2/*c* symmetry and *n* glide as you remember will add not just half to one of the directions where we are now considering.

For example, if you consider the glide plane associated with this origin is c and that is a. So, the translation symmetry that will be associated with *n* glide will be half along c and half along a. So, the equivalent points will be x ½ plus y ½ plus z kind of a thing and therefore, we now have a invoking a new symmetry element into the system, which is now the *n* glide and this *n* glide is now coming away from the origin and in a direction which is along the diagonal of a and c. So, there is a diagonal relationship like that. So, you see here that these two if you consider they are related by an *n* glide because it is half distance moved here and half distance up there. So, that is how you get the diagonal glide invoked

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Positions

Multiplicity	Wyckoff letter	Site symmetry	Coordinates $(0,0,0)+ \quad (\frac{1}{2},\frac{1}{2},0)+$			
8	*f*	1	(1) x,y,z	(2) $\bar{x},y,\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y},z+\frac{1}{2}$
4	*e*	2	$0,y,\frac{1}{4}$	$0,\bar{y},\frac{3}{4}$		
4	*d*	$\bar{1}$	$\frac{1}{4},\frac{1}{4},\frac{1}{2}$	$\frac{3}{4},\frac{1}{4},0$		
4	*c*	$\bar{1}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{1}{4},\frac{1}{2}$		
4	*b*	$\bar{1}$	$0,\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$		
4	*a*	$\bar{1}$	$0,0,0$	$0,0,\frac{1}{2}$		

Now, the equivalent points the equivalent points. Now, therefore, obviously, will double. So, will have a eight of those. And then we have a several sets of special positions in this. You notice that all these special positions to generate 4 equivalent points even though there are 2 types of special positions which come up. You see in the so, far in the previous examples up to this point where we discuss $P2_1/c$, this special position had the same symmetry in this case it was $\bar{1}$, but if you come to $C2/c$, you see that this special position are of 2 kinds.

So, the molecules or the atoms or whatever they makeup this structure, they can prefer the centrosymmetric positions for their special positions and get 4 of those or they can prefer the 2-fold location which is with respect to 0 y ¼ and they can get again 4 positions. So, the presence of the 2-fold or the $\bar{1}$ symmetry in other words the molecule now can either process a centre of symmetry or the molecule can process also a 2-fold symmetry. If the molecule possesses the 2-fold symmetry it will go and sit with respect to the 2-fold axis which is now a special position.

So, you notice that the Wyckoff notation the highest symmetry is always with respect to 0 0 0. So, it is going up there and we see that 4e is a position where you can have a 2-fold symmetry. So, objects which are which have 2-fold symmetry preferably sit there rather than in any one of these positions because these positions insist on having the centre of symmetry. So, if the molecule has a centre of symmetry it prefers to go into these 4 positions and if the molecules has a 2-fold symmetry it prefers to go to that particular system.

So, this analysis of the equivalent points you can do it very easily now because you have the 8 equivalent points listed up there take any one of these. For example, you take 0 y ¼ substitute that into these eight positions, you will end up with 4 positions. And those are the 4 positions corresponding to the Wyckoff notation 4 e and that is how we get the *C*2 by *C* space group

So, the discussion so, far has been now with respect to the monoclinic symmetry. We have discussed the triclinic symmetry, we have discussed the monoclinic symmetry, we have discussed the equivalent points, we have discussed the equivalent point diagrams we have discuss the symmetry diagrams. So, much of knowledge now pumped in the last maybe 3 or 4 classes, but what is very clear about this whole thing is that the symmetry is the driving force. So, the moment we have understood the symmetry over the previous classes, this now becomes a straight forward understanding.

So, looking at an international table it does not look anymore like you know Greek and Latin it will look like something which is very grammatically correct. Since you have understood all the grammar associated with the equivalent points with the space groups with the point groups and so, on it becomes a very facile thing to read the international tables. In fact, international tables I should have brought it here it is a big thick book it is like looks like a telephone directory and initially if you look at it looks very ugly because all these pictures are there, and you will think it is like as insipid as a telephone directory. But then one once you have got all the grammar understood, now you can read from one end to the other of the international tables which I do not suggest you do, because it will take half a lifetime.

But what is interesting to observe is that all these were worked out before any experimental method of determining structures were found out. So, people looked at crystal sitting in 1 place like I am just sitting for your class always here. So, the on the in the more or less same position there is no change in the position I am stuck here. So, like this people use to be stuck and the fellow who was stuck in was in fact, sitting at minus thirty degrees in Siberia. So, that poor fellow sat there and looked at the crystals and then arrived at all the possible space groups identify the crystal systems looking at crystals the shapes of the crystals doing stereographic projections.

He created the 32-point groups and this was way back in the 17th 18th century seventeen thirty and this is remarkable, but then if you happen to visit Siberia you will know why it is he did he could only do that. Because the temperatures there are on average very very low and it is always iced up you cannot go out and have enjoyment unless of course, you go skiing around and that is also very dangerous. And therefore, you sit in one place and do it and what is remarkable is all these were derived and shown x ray diffraction experiments when they came they showed some of them are wrong not all are wrong, but some of them are wrong and therefore, it is a very very important that you now learnt the grammar. So, you can now start reading the text.

What is the best way to read a text you know the you do not feel like reading your text books regularly instead if you are given a harry potter book or a lord of the rings book or some novel, some interesting spy novel or something you will prefer to read it. Of course, nowadays reading itself is avoided you read again on this stupid thing I am also now teaching it on this one, even though I personally prefer teaching with a board and a chalk which is what I do even now in my other class when I teach here IISc.

But then while we are all victims of modernization and computers have taken over and now eventually with artificial intelligence coming up in full swing with computers will probably rule us computers will tell you do not know how to teach, I will come and teach such a day will come very soon. So, it is completely automatized and automated understanding of everything will be clear. So, then I do not think we need the grammar or anything that is associated with we can always go ahead and then determine this.