Symmetry and Structure in the Solid State
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Lecture – 46
Systematic Absences 3

So, having got an idea of the Systematic Absences, it is now necessary to read it out of the international tables for crystallography. This as we have already discussed this equivalent point diagrams we have discussed the symmetry diagrams. So, we do not have to go into detail of that again.

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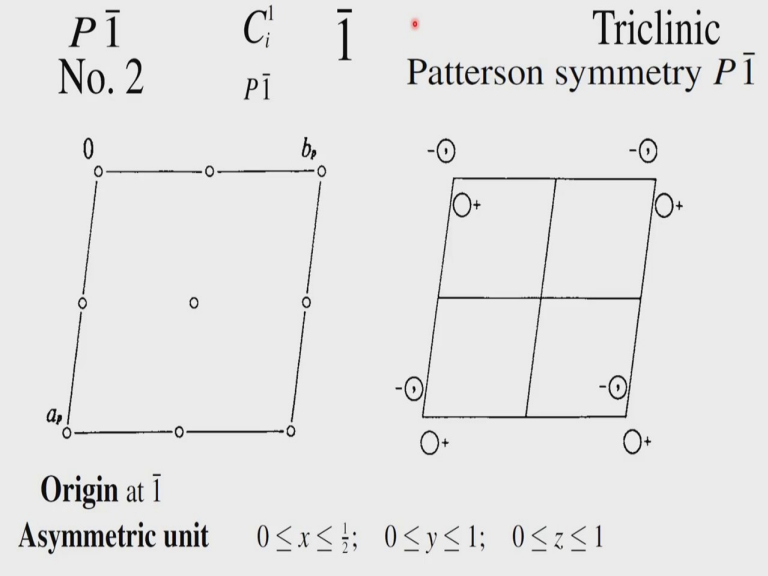

But, what I will do is to show you some of these space groups and see how the systematic absences appear and we will see how to associate systematic absences with respect to general and special positions.

So, the ***P***1 of course, is a redundant set. So, I am not going to take into account ***P***1 instead we will go to number 2, ***P***-1. I just recollect for you, this is a full symbol is -1 and this is triclinic and the point group symmetry is -1, it has a center of symmetry. So, what happens is that the center symmetry is developed as per the symmetry diagram here and the equivalent points developed as per the equivalent points here and this particular slide we have discussed before in full detail.

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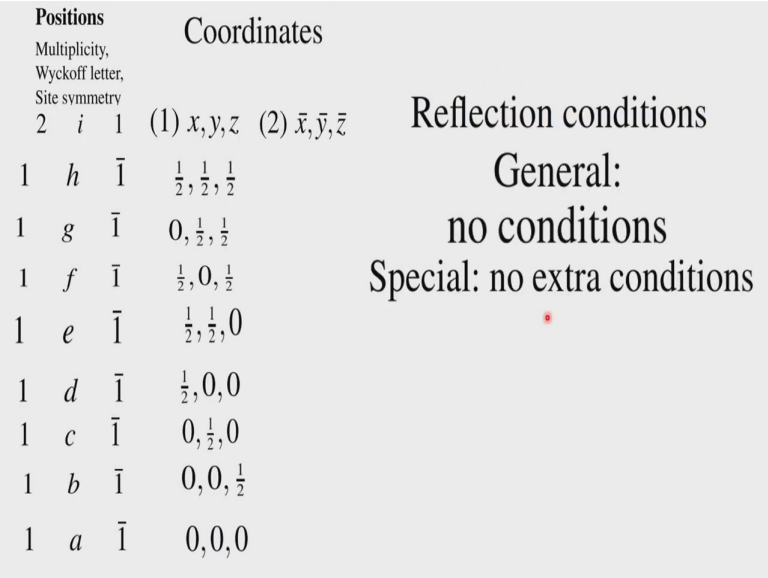

Now, comes the centri I said we will discuss this later on and this centri tells us the possibility of the multiplicity, Wyckoff letter and site symmetry associated with each one of the types of reflection that types of coordinates we can have.

So, the first one is 2, is a general position atom x, y, z it gives raise to -x, -y, -z. This is ***P***-1 and you see there are several centers of symmetry which will develop because of the nature of the center of symmetry itself and also the periodicity associated with the lattice. So, we have therefore, 1,2,3,4,5,6,7,8 Wyckoff positions and addition, the general position taking the value of i and the occupancies are the multiplicities that are associated with these are in these case it is 2 coordinates in all these cases is 1 coordinate.

So, this part also we have studied in detail and thoroughly. So, I will not repeat it. What we see is on the right hand side? Right hand side there is nothing much to discuss in ***P***-1 because the reflection condition. So, what are the conditions in which the reflections occur? This is general; that means, this reflections which are referred to as the general reflections the general reflections have no conditions and as a consequence this special reflections, special positions which are shown here also has no extra conditions. So, ***P***-1 is that way not very exciting to discuss any further, it has no systematic absences.

So, as I have already mentioned between ***P***1 and ***P***-1 therefore, there are no systematic absences. So, when you determine the by the based on the diffraction condition when

you determine the space group you say this space group at this moment is either ***P***1 or ***P***-1 and later we will decide how to distinguish between ***P***1 and ***P***-1 and then finally, determine the structure.

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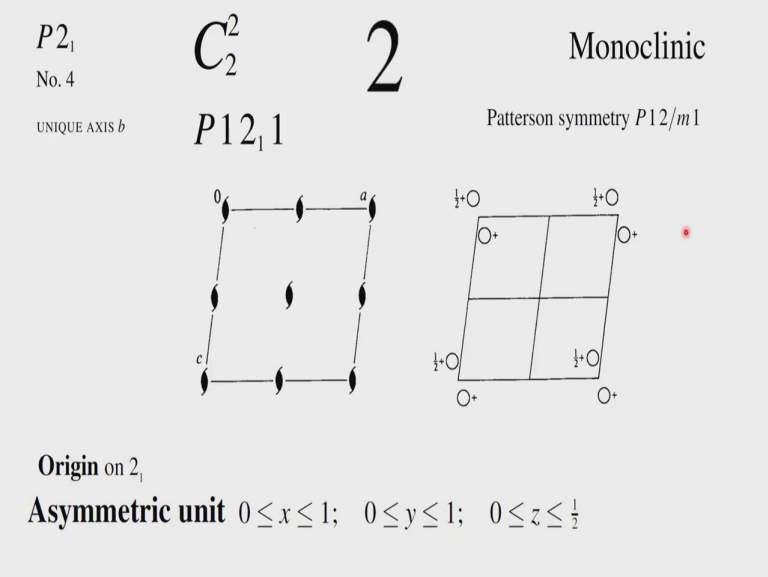

So, let us now go further to the space group number 4. Again, P 2 is not listed because it is not going to have any systematic absences.

P2_1: ***P***2_1 has a 2_1 screw axis, the full symbol is 1 2 1 1 and you know what the symmetry diagram as well as the equivalent point diagram. So, we will not go into the unnecessary discussion of that again.

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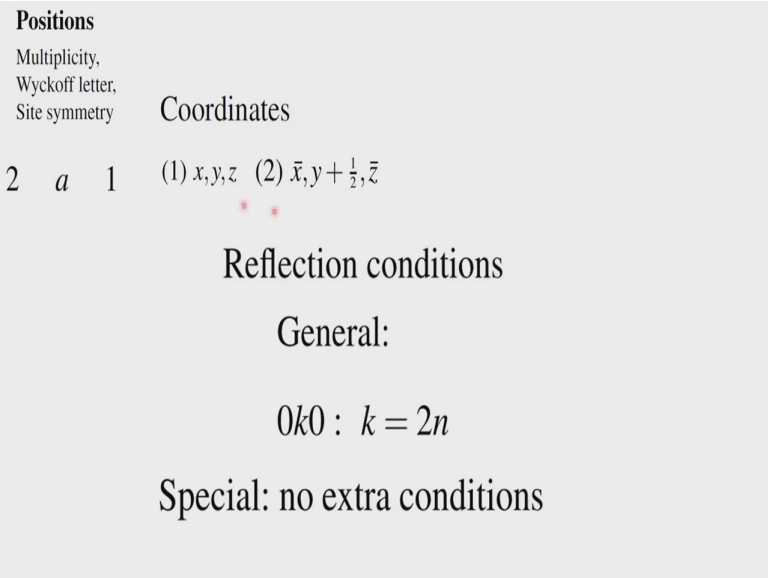

The point group symmetry is 2 and therefore, this has two positions no special positions for this. So, what is important is this now; the reflection conditions h, k, l since there are no systematic absences associated with primitive lattice, we have taken $\boldsymbol{P}2_1$ as the example, no systematic absences will be there. But, if we look at the systematic absences due to the symmetry element the symmetry element is 2_1 screw and therefore, you get, but the reflections which are now along the axis 0k0 they will be systematically absent. So, k is equal to so and so.

So these entries will be there in the international table. I have blown it up so that we discuss it more detail. Normally, this appears parallel in this direction to this in their in the international table sheet which you have already seen. So, I do not want to go into the detail of it. So, the equivalent points are 2 and the systematic absences 0k0, k equals even, unique even.

So, therefore, we can uniquely determine the space group $\boldsymbol{P}2_1$ provided as we discussed earlier on the b-axis has sufficiently large you know cell dimension. It so happens many organic compounds which show particularly photo reactions and they have the 2 plus 2 additions among ring systems and so on. They always have a normally in the sense that unite cell dimensions or less than 4 angstroms because it so happens in a photo reaction condition when two double bonds have to interact with each other then the distance

between the two double bonds should be closer than 4 angstrom this is the Smith rule. And, in fact, that is the beginning of crystal engineering, we will discuss that later.

So, the two double bonds when they come close to each other they should come within 4 angstrom and therefore, the unit cell dimension there is a consequence will be short and this short units cell, the confidence we can put in the observed systematic absence becomes less and therefore, we can we can generally see whether this crystal system is either ***P***2 or ***P***2_1 and in fact, in the systems the organic systems which undergo this deals order 2 plus 2 addition reactions you do see that they form a four membered ring and it is so happens that the crystal structure does not change much that is that is the aspect of crystal engineering which we will discuss in a later class.

But for all practical purposes if we have a ***P***2_1 symmetry for our current discussion 0k0, k odd will be absent. So, we identify the actually absence and determine the space group uniquely. So, it is ***P***2_1 system which can be uniquely determined.

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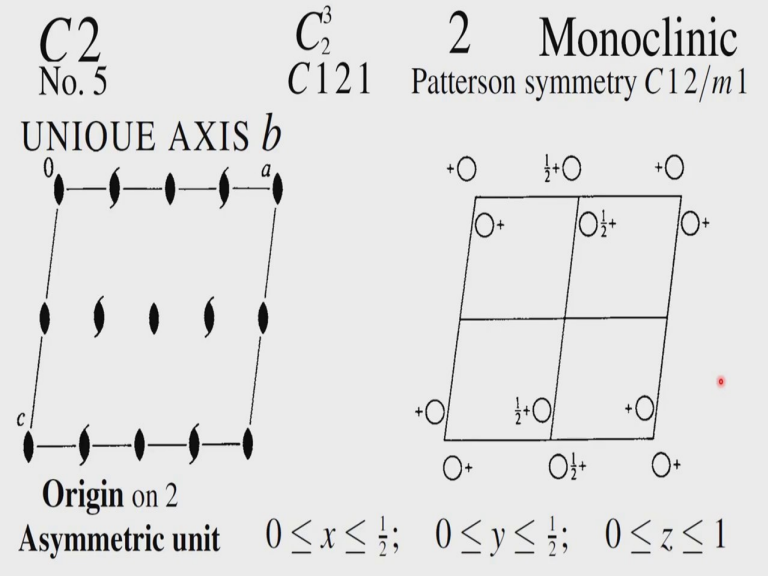

Next we go to the case where we have a centering I am going through the lower symmetry space groups essentially because I want you to get this point very clearly in your mind and how to also read it out of the international tables because when you do the structure determination and the machines are used automatically these days, systematic absences will be listed then. In fact, the programs will pick up the space group also for you.

But, very often in a situation like what I discussed before about the 2 plus 2 addition reaction compounds the machine may decide something which may be wrong and that is where you are required to know what is going on here; and that is the reason why we are discussing this in detail. And, if you if this space group is really $\boldsymbol{P}2_1$ and you want to solve this structure in $\boldsymbol{P}2$ you will never solve this structure and that is the beauty of crystallography.

So, the presence of the symmetry dictates everything and that is why we are studying symmetry and structure in detail in this particular course. So, this is the diagram of C2. There is no need to discuss this anymore. We have done it many times. So, it develops additional 2_1 screw axis and so on and then these are the equivalent point dispositions.

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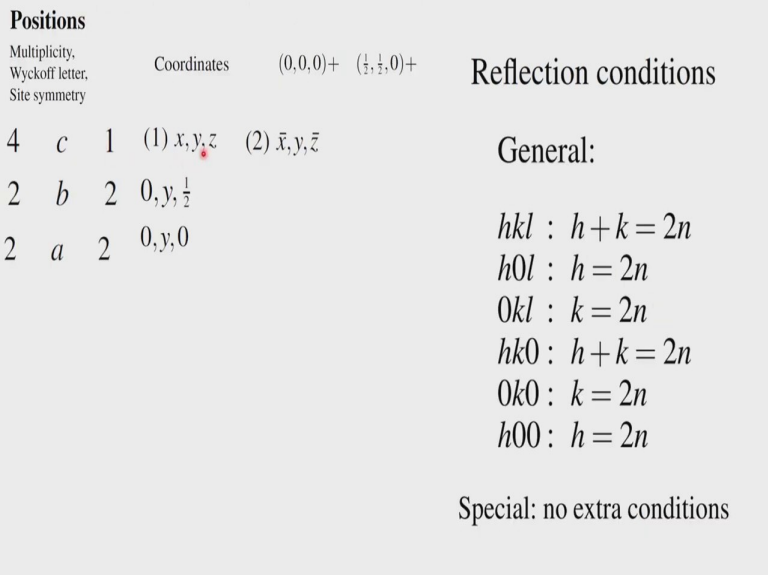

So, because it is a *C* centred lattice we have four equivalent points, two due to x y z; -x y -z that is the two-fold operation and then we have the additional 1/2 1/2 0 as a additional lattice point. So, we get 1/2+x 1/2+y z; 1/2-x 1/2+y -z and these will be the four equivalent points in general positions. And, in general positions we have the set of systematic absences which will allow us to see this space group to be $\boldsymbol{C}2$. We have to see this a little carefully and you will see you will enjoy this discussion in some sense because you see some of the reflections which are shown here corresponds to the systematic presences associated with glide planes.

Now, you see the diagram here there is no glide plane in this diagram, right. There is no glide plane in this diagram. It is only possibly presence of the new 2_1screw axis, but when you look at the systematic absences you will see absences due to glide plane. You may be wondering what is going on and this is very crucial to analyse this. So, we will go through this systematic absences in this space group C2 a little carefully. So, the four equivalent points and the centering causes the general reflection hkl to show systematic absences. So, h+k odd will be systematically absent. So, h+k = 2n is only present this is clear. So, we will have the general reflections, analyse them, you will get h+k = 2n.

In addition, you will get these many additional systematic absences. Now, these additional systematic absences are not going to complicate your space group because the crystal system is monoclinic you have already determine a, b, c, alpha, beta, gamma. You have determined also it is the *C* centered lattice. So, *C* centering gets the preference. So, it is always the centering of the lattice which gets the preference; that means, the Bravais lattice information gets the preference over and above the glide plane systematic absence and over and above comes the screw axis operations.

So, in this particular case h0l for h = 2n is listed. In fact, we should put in principle all these in brackets to show this is a consequence of this absence, see because hkl. h+ k even is absent is a present, sorry, even is present, odd is absent. So, we will discuss systematic absences even though this systematic presences, we will discuss systematic absences. So, hkl: h + k = 2n, h0l: h = 2n that is because you put k = 0 here you get h0l: h = even. Same thing with 0kl: k = even. So, these two are a consequence of the main systematic absence. So, this has no meaning what is. These two will not carry any meaning you have to ignore this even though you will see this.

So, when you examine the systematic absences you will see absences due to glide planes, but these are not absences due to glide planes, ok. So, projection reflections are absent mainly as a consequence h plus k being even that is because you put the value of k equals 0, h equals even value of h equals 0 you get k equals even.

The then of course, hk0 you see it is shows h + k even; that is also a consequence of that because l is 0 here and it is a special case of l. See there are no systematic absences associated with l. So, l will be also showing h + k = even. All l values will show h + k

even and therefore, l equals 0 will also show that. Same logic 0k0 now shows as though there is a 2_1 screw axis h00 shows h equals 2n as though it is a screw axis.

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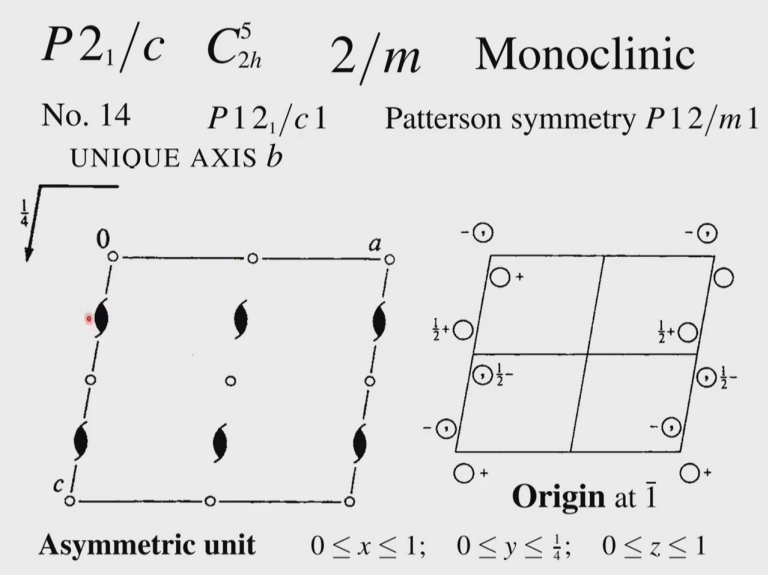

So, what is very important is if you look at this particular diagram there are screw axis one fourth removed from the origin and it is not a consequence of these screw axis which come as a special case because of the presence of the centering. Sorry, I went to the wrong one because of the presence of the *C* centering. So, this is the 2_1 screw axis which will develop at one fourth distance as a consequence of C centered. This has nothing to do with this systematic absences which you see here.

So, let me repeat it very quickly. So, that if there is no confusion we have a space group ***C***2. C is centering will ensure that we have hkl, h + k even only present.

So, the fact that this happens it gives raise to certain special additional conditions is not special additional conditions. The additional conditions are h0l: h even, 0kl: k even, hk0: h + k even, 0k0: k = even, h00: h = even. So, these are consequences of the fact that hkl is h + k even. The possibility of a special positions do exists in this particular space group. You see two possibilities, one is a presence of a symmetry element two-fold which is associated with 0, y, half another is a two-fold which is associated with 0, y, 0. But, it is not going to give us any special or no extra conditions that is because this is a two-fold axis. This does not carry any translational component, alright.

So, having noticed this we will go to the next system which is the most common system we come across when we are dealing with organics structure. So, $\boldsymbol{P}2_1/c$. $\boldsymbol{P}2_1/c$ the full symbol is P 1 $2_1/c$ 1 and it has the symmetry positions like this. We have the center of symmetry. We have the two-fold axis and we of course, have the one fourth at one fourth represents of the *c* glide above the plane and then these are the equivalent point diagram. This shows where the equivalent points are z is equal to 4.

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Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		Reflection conditions
					General:
4	*e*	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	$h0l : l=2n$
			(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$0k0 : k=2n$
					$00l : l=2n$
2	*d*	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	Special:
2	*c*	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$	$hkl : k+l=2n$
2	*b*	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$hkl : k+l=2n$
2	*a*	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$	$hkl : k+l=2n$
					$hkl : k+l=2n$

And, therefore, the general positions are 4. The four general equivalent positions are listed here and then there are some special positions which are present in this particular space group and those special positions are now associated with a -1 symmetry. Remember that, this is again has no translation component, but it has a -1 symmetry; that means, it introduces and additional symmetry element these has two equivalent points rather than four equivalent points.

So, let us see what is the effect of this on the general reflection and special reflections. So, here the general reflections show the presence of $2_1/c$ uniquely. So, you can determine the space group without any false because this will have h0l: l odd absent and 0k0: k odd absent. So, the h0l: l = 2n will also additional introduce a condition 00l: l even because you put h = 0 there, l = even will be the reflection that will be present. So, it shows a systematic absence associated with axis in two directions, but there only one

direction that is the 0k0; k equals unique is unique with respect to the 2_1 axis. So, this is due to the *c* glide and this is due to the axis 2_1 and this is a consequence of the *c* glide.

So, you have to therefore, see when you get the systematic absences or presences indicated in the international table. Like this you have to make sure that which is the one ,which is a consequence of the earlier listed systematic absence. So, the preference goes from hkl. No general reflections are no conditions on them and when you go to h0l the projection reflection there is a condition and this projection reflections can put additional conditions as though there are coming on the actual reflections which is a special case of this. And, then 0k0: k odd will be re systematic absence that is due to the presence of the screw axis.

Now, there is something interesting that is happening here. Apart from the fact that we have the $2_1/c$ absence we get additional systematic absences with respect to each one of these. Now, what happened to the logic we defined here? The logic we defined was that if there is no translational component, no systematic absence, then how did this fellow come up? This fellow again came up because of the *C* centering. See, because what happens here is if you want to have the -1 to be evoked you see that the value of l here or z here has to be 1/2 or 0. So, the value of z is always either 1/2 or 0.

So, the value of z being half or 0 will decide where these systematic absences should come from. So, here everywhere it is k + l odd which has four equivalent points. It has special positions and these special positions are associated with the center sub symmetry. But, what happens when these are associated with the center of symmetry is that the value of z also becomes special in the sense there it is now either 1/2 or 0 and then 1/2 or 0, 0 or 1/2, 0 or 1/2.

Now, since these are now the positions of the covalent points. You see that the presence of the symmetry which is -1 will generate only two equivalent points associated with the particular space group and therefore, we end up with conditions which are special on the all these conditions now or with respect to the general reflections. So, along with the presence of the systematic absences which are written up here the general reflections will also show k + l = even, k + l = odd, k + l = even, h + l = even. All these are even when it has to be present. And, therefore, k + l even will make it make the hkl. This is now you

notice that with respect to the hkl. The systematic absences are with respect to the general reflections.

So, all the general reflections will show the presence of the -1 symmetry that is associated with $\boldsymbol{P}2_1/c$. So, if there is a molecule with a special symmetry which is occupying this particular space group you will have these additional special condition symmetry absences. It looks as though you know that general reflections have an absence; that means, it has to be centered it is not necessarily that it has to be centered this indicates the a centering, but it is not really *A* centering it is a consequence of the atoms sitting in special positions. So, the fact that when we are analyzing is crystal systems like $\boldsymbol{P}2_1/c$ we first look at these absences even though if the atoms are molecules are associated with this special symmetry then we will get additional special absences.

So, in general $\boldsymbol{P}2_1/c$ can be uniquely determined by just looking at these systematic absences.

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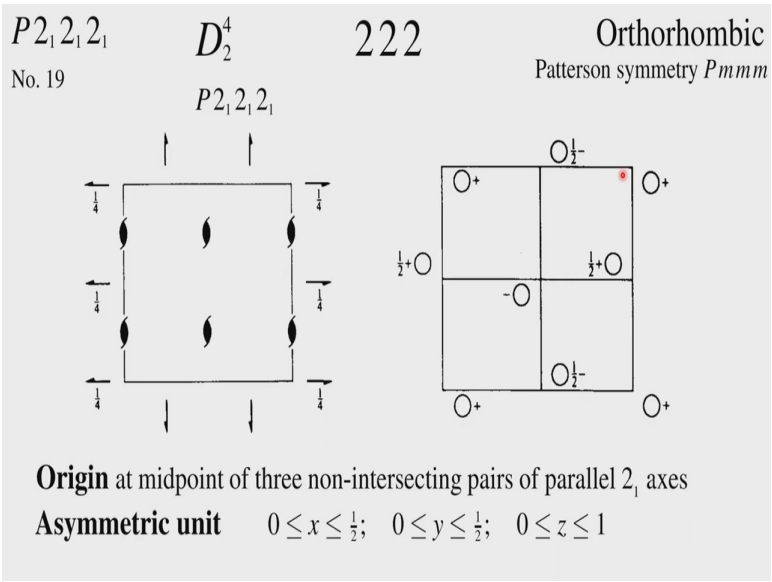

So, having done $\boldsymbol{P}2_1/c$ we will now go to an orthorhombic system where we have more than one axis intersecting with each other or not intersecting with each other as is this particular case the crystal system $\boldsymbol{P}2_12_12_1$. We have studied this in detail and we find that this has three non-intersecting screw axis removed from each other from a defined origin by one fourth in each direction. Therefore, this symmetry elements are indicated here and

equivalent points are indicated here there we have studied it in details. So, I would not go into the further discussion.

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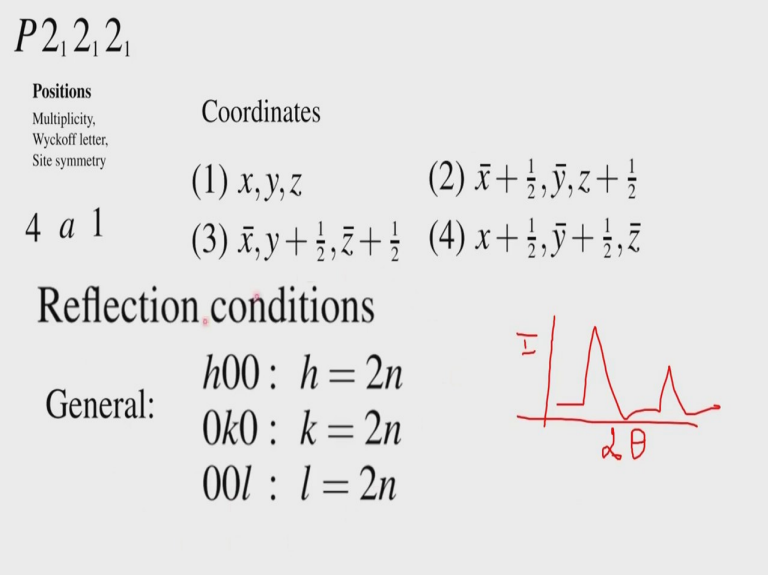

The equivalent points therefore, are 4 and there are no special positions in this crystal system obviously, because even these regular symmetries that are present are not intersecting with each other. So, therefore, you have four equivalent points and the conditions which come are independently for each 2_1 axis. So, we have h00: h even only present, 0k0: k even only present, 00l: l even only present. So, you can determine the space group $2_12_12_1$ again uniquely.

So, this is an advantage because these kind of systems the symmetry elements do not intersect with each other and this is a non centro symmetric system and in the non centro symmetric system there is no question of having a center of symmetry and also its association with the origin. So, the origin as no special significance in this space group except that it has to have the three to four axis perpendicular to each other removed by one fourth from this origin each in each direction. So, that will generate this systematic absences. So, $2_12_12_1$again is a crystal system we can uniquely determine.

So, you see that the exercise we were doing before into understand the presence of symmetry elements and the way in which equivalent points develop and so on practically becomes redundant because if you do an X-ray diffraction experiment and record the pattern, the recorded pattern will tell us clearly what is the space group if we look at the

systematic absences. So, the appearance of the diffraction parts now which follow the rules of symmetry and therefore, the fact that direct space lattice and reciprocal space lattices are related to each other we are looking at the reciprocal lattice points hkl and the systematic absences associated with this hkl reflections will tell us this space group.

So, we do not have to go to the question of finding where the equivalent points develop with respect to the symmetry operation. So, the previous exercise which we have done is to get an understanding of how symmetry gets generated in this crystal systems and space groups and what effect it has on the diffraction is shown here in terms of the systematic absences. So, this is a very crucial issue in deciding the crystal system. If someone goes wrong in identifying the space group, if the machine goes wrong in identifying this space group which is quite possible then your structure will never be determined or whatever structure you determine will have all kinds of short contacts within atoms and so on and you will wonder what is going on.

So, for a practicing crystallographer who does not want to study crystallography or who does not want to look into this systematic absences and so on sorry, the symmetry positions and equivalent points the observation of systematic absences understanding of it is crucial because if you have to determine this space group uniquely before you proceed to determine this structure because this is therefore, the basement on which you are construction has to be developed. So, determining the space group is a very important factor.

So, you have three things here to remember one is the geometry of diffraction which is of course, decided by the Braggs law conditions. So, if you imagine a powder diffraction diagram you have the intensity versus sine theta, you have a powered diffraction which intensity this is the intensity I here it is the 2 theta, this is the powdered diffraction we record. So, your powdered profile will goes something like this. So, this will now the x-axis will tell you where the 2 theta value should be for the given peak this peak of course, assuming that it is all unique then we can determine where this peak positions come and this gives us the information on the d value and therefore, the cell dimensions.

So, we can determine the a, b, c, alpha, beta, gamma using that information. The intensity information now tells us the value of the intensity associated with this diffraction which is coming up for that particular plane hkl. So, we determine therefore, I

of I_{hkl}. So, then after determining the densities we now examine the systematic absences. When we examine the systematic absences we find that the you can determine this space group some of them get it determined uniquely.

So, we determine the space group and that is the issue. Space group determination therefore, involves both the x and y coordinates in its own way. Even though we do not still have the structure information, we have the intensity distribution available to us. The way intensity is distributed is decided by the nature of centering of the lattice or for that matter the presence of symmetry elements in a given direction and therefore, we see that the utility of all the information in an x-ray diffraction experiment goes into determine the space group. And, therefore, the determination of the space group by examining equivalent points is a very important step.

And, if there is some mistake done by the by the data collection protocol introduced into your machine; in fact, many often you will see that when you are doing the data collection in a practical sense you have crystal grown put it on the diffractometer, you measure the intensities coming out and then you press the button determine space group. More often then not it will say not possible to determine, no success it will say. Then you have a serious problem and that is why this is this part of the course is very important you should know what are the systematic absences you should look for in what way you have to do this diagnosis.

The diagnosis follows by looking at the general reflections and then followed by projection reflections, then of course, later the actual reflection. Based on that you identify the symmetry elements which might come for example, in this particular case a $2_12_12_1$you examine three axial reflection systematic absences. And, if they do appear like that then we have a situation where we have uniquely determine the space group. And, therefore, the information that we get from the hkl reflections enormously important; both the intensity as well as their appearance with respect to the geometry.

So, the full data associated with x-ray diffraction is incorporated into the determination of the space group and therefore, is a very important step. People generally ignore, particularly those practicing chemists and pharmaceutical people and also many of the people who are just physical chemists and the organic chemists and so on, they ignore this and if the space group is long they structure can never be determined. So,

determination of the structure therefore, solely depends upon uniqueness with which you are determine the space group and this is a point it should bear in mind.