Symmetry and Structure in the Solid State
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Lecture - 22
Additional Information on Space Groups

So, from $P2_1/c$ now, we will go to the other space groups which are possible in the monoclinic symmetry.

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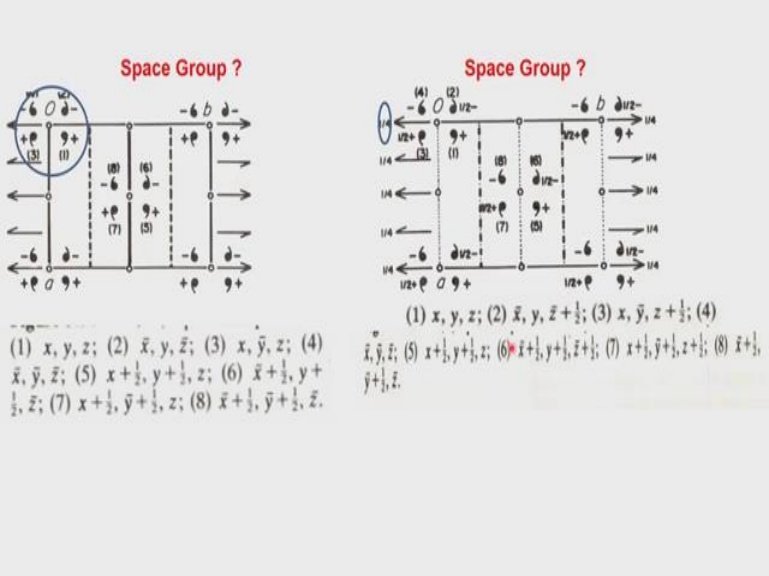

I have indicated 2 space groups here, I given the equivalent points diagram overlapping the symmetry points. So, I want you to examine this equivalent points and the location of the symmetry points and make a guess of what could be this space group. The equivalent points of course, are already given here. So, making a guess of the space group is not going to be very difficult if we follow all the rules which we lead out in the case of $P2_1/c$ for example.

So, here is a case where you have a twofold axis associated with the centre of symmetry and 1, 2, 3, 4 are marked here the four equivalent points are marked here and four other equivalent points are marked at this point. Now this refers to half along y and half along x. So, this therefore, now indicates the addition of 1/2+x 1/2+y tells us this is has to be a *C* centred system. So, it is monoclinic and *C* centred.

So, the four equivalent points are surrounding this particular point and there is a twofold axis coincident with this and a mirror plane which is coincident with the origin. What is very interesting is to see that apart from the presence of twofold and this we also develop a glide plane at one fourth that is because the if we work out the relationships between 1, 2, 3, 4 and 5, 6, 7, 8 we will see the presence of a one fourth glide plane operation. So, what is the space group?

We have an indication that the lattices *C* centred. There are no marks of shift of the axis with respect to this position, the twofold axis are coincident with the origin and there is a mirror plane which is perpendicular to that. What is very interesting is that you also develop a 2_1 screw axis between this point and this point which is halfway removed that was the centres of symmetries you have the 2_1 screw axis also located. So, the at the outset the diagram looks very complicated.

So, many symmetry elements are shown here, for example the 2_1 screw axis is shown, the glide plane is shown, the mirror plane is shown, the twofold axis is shown. So, how do we discern that the space group is whatever it is? One conclusion we immediately came by looking at these four and these four is that it is a c centred lattice so; that means, we should have any equivalent point corresponding to *x y z* which generates number point 5 which is *1/2+x 1/2+y z* so; that means, the c centring is clear. So, we have therefore, a c centred lattice.

The fact that we have a point which is *-x -y -z* tells us it has to be a centre of symmetric system. So, if it is has to be a centre of symmetric system and a c centred lattice the point group symmetry should be 2/*m* it cannot be 2 it, cannot me m alone and therefore, it is a *C*2/*m* kind of a symmetry operation.

In fact, these if you look at the first four equivalent points you will see a similarity between this and the *P*2/*m* space group which we saw a few slides before and therefore, this is 2/*m* and this is *C* centred lattice so, this space group must be *C*2/*m*. So, the diagram here and the set of equivalent points now we can verify that with respect to the occurrence of 2/*m*. So, since it is 2/*m* symmetry, there are no translations that are required and therefore, the mirror the twofold and the centre of symmetry the intersect at 0 0 0 and the *C* centring generates the 1 at half along x, half along y.

What is very interesting is in this particular space group because of the presence of

centre symmetry as well as the *C* centring we develop 2 additional symmetry elements; one is the symmetry element 2_1 screw axis which is one fourth at this point and the other is the glide plane which is removed by one fourth. So, I want you to take it as a home exercise where you find out in what way this glide plane generates the equivalences of these four onto these four in other words operate the c glide operation on 1 and see to which of the 5, 6, 7, 8 it corresponds to glide plane operation. Likewise you operate the 2_1 screw axis about this point and see which of the 5, 6, 7, 8 associates itself with the operation of the 2_1 screw axis.

So, the interesting observation which we make here is, even though the space group is *C*2/*m*. There are no movement of the translation involved components we generate translation involved component as a consequence of the presence of the *C* centring. The *C* centring where which gives rise to 1/2+x 1/2+y will automatically generate additional symmetry elements.

Now this is the beauty of crystallography. So, when molecules crystallise in such a space group, they get confined to not only obey the requirements of *C*2/*m* as we have seen here it also should obey the requirements of the presence of a glide plane one fourth removed from the origin and a screw axis which is again one fourth removed along the a direction.

So, one once we have any axis at one fourth we will have automatically have the same axis at three fourths and that is what is marked here you have the one fourth and you also have the three fourths. Similarly, the 2_1 screw axis appears that one fourth and three fourths. So, therefore, the space group is *C*2/*m*. And the next space group which I have indicated here I want you to again examine it carefully and see what is your conclusion on this one.

The conclusion on this one is a little complicated, but its straightforward again if you look at 1, 2, 3, 4 and look at 5, 6, 7, 8 it tells you it is a *C* centred lattice. The only difference or a major difference which you see is that the twofold axis are now removed by one fourth. Since this twofold axis get removed by one fourth what is your guess? The guess is that there is a translation involved component in a direction perpendicular to this and the component which can be perpendicular to this is related to a mirror. And normally in a monoclinic system the component that is related by a mirror symmetry is the one which is now it is so happens that it is the one which associates itself with the *C*

centred lattice.

And the way with respect to the *C* centred lattice it is the one which is associated with the *c* glide plane. So, there must be a *c* glide plane now associated with this. So, the *c* glide coincides with the origin twofold symmetry moves by one fourth, this generates therefore, the space group *C*2/*c*.

So, as you see by just looking at the presence of the equivalent points and the locations of the presence of the symmetry elements and the location of the symmetry element you can determine this space group. And one once you have determined the space group you can write the equivalent points and these equivalent point diagram which is shown here along with the presence of the symmetry information will uniquely determine the space group and so we get the space group *C*2/*c*. And that way at this juncture we will now go and try to examine the space groups more thoroughly; to examine the space group more thoroughly there is no other method better than observing them through what we call as the international tables for crystallography.

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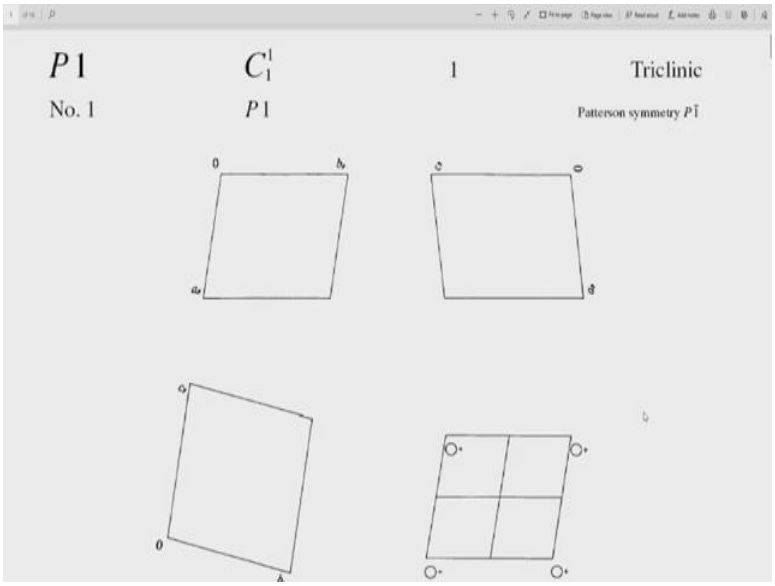

So, we now crossover to the international tables entry. A little story about the international tables because when more and more structures started getting accumulated and it was required that the practising crystallographers will have a direct axis to the existence of the 230 space groups, their corresponding space group diagrams, the diagrams associating them with the objects, the diagrams that are generally associated

with the equivalent points and so on.

A listing of the equivalent point is also necessary and as a consequence the international tables for crystallography was developed early 1950's. In fact, first issue was I think issued in 1951 and that was called Red Book because the colour of the international tables was read. It has undergone many changes in metamorphoses and at this particular time it is available online. So, one can download the international tables and then look at the details of the space groups.

So, whatever we have discussed so far in terms of the space groups, in terms of the equivalent points, in terms of the special positions, in terms of the Wyckoff notation which we are going to introduce now all these issues will be listed out under one entry in the international tables. So, this is more or less the bible for crystallographers in order to get all the details of the given space group.

So, suppose I crystallises in a given space group, most often the not nowadays the possible space groups are indicated by the automatic machines on which data collection is carried out and it is not required that you have need to be a crystallographer. If the space group is identified uniquely, but if this space group is not identified uniquely by the automatic machines then I think a little knowledge on crystallography becomes essential and this particular course is aimed at giving you that kind of knowledge as a background.

So, that you will be able to use the automatic machines within coats automatically; that means, you will now make use of these machines to the fullest extent possible. And in case the machine is not able to decide the space group by examining certain details of the machine data in principle you should be able to find out what is the space group.

So, in order to find out what is the space group we should know how this symmetry elements are disposed in a given space group and how each and every object repeats itself based on the symmetry that is present in a given space group. We have studied the triclinic and the monoclinic systems thoroughly and the study of the triclinic and the monoclinic systems. I have already enabled us to understand the logistics of how the objects find themselves with respect to a given space group. The thing which is missing from us at this moment is a complete knowledge of a given space group.

What are the things which we need of a given space group and can we make a list out of that and that is provided by the international tables for crystallography. At this time we also will start introducing a new set of symbols which are up here and these symbols are the ones which are referred to as the Schoenflies symbols are you able to see it. So, these are the Schoenflies symbols, spectroscopies they do not use the nomenclature which crystallographers use.

For example, in crystallography we use the point group information and also the lattice information and combine the lattice information with the point group information to derive the space group and this will be the space group nomenclature. This is refer to as the Hermann Mauguin notation and that is the notation we will follow throughout the course.

I will provide you with a chart probably in the next discussion where we can convert the Hermann Mauguin notation to what is called the Schoenflies notation and this Schoenflies notation is the one which the spectroscopies follow. So, since *P*1 is a space group where there is no symmetry at all. In case of spectroscopic symbols the no symmetry is indicated by C1, C1 represents a rotation 360 degrees and the one on top is the one which is now representing the space group.

So, if one wants to use the Schoenflies symbol and still use this nomenclature to represent the space group, then it is a C 1 1 we will see what representation *P*-1 will get when we go to the description of *P*-1. So, this has to be born in mind because spectroscopies and more often the not the practising mathematicians who use group theory they use this nomenclature more often than this nomenclature. This nomenclature is utilised essentially by crystallographers who look into the determination of structures, look into the details of structural motives. And then look at the structure of the molecule inside the crystal lattice and then the interaction of these molecules within the crystal lattice and so on.

So, the requirement is that we should stick to the Hermann Mauguin notation. So in the rest of the course we will stick to Hermann Mauguin notation, but for those spectroscopies and group theoreticians who would like to go into the detail of what is the corresponding symbol using the Schoenflies notation they can refer to the international table again or I will provide a diagram and probably a hand out also will be given by the

TAs which will show the conversion from the Hermann Mauguin to the Schoenflies notation. So, this is the first entry of the space group *P*1 in the International Tables.

So obviously, the first number is 1 out of the 230 space groups this is the first space group. *P*1 is the Hermann Mauguin notation as I mentioned and the point group symmetry which is mentioned here is 1. So, the point group symmetry is 1, the space group is *P*1 and this belongs to the triclinic system.

Now, something is written down here which we will discuss much later, but what it tells us these that there is something called the Patterson symmetry which will have the same space group converted to *P*-1. So, if you look at the Patterson symmetry associated with *P*1 we will get *P*-1.

Now, what is Patterson symmetry? We will be discussing this Patterson symmetry when we actually determine the structures of molecules inside crystal lattices in the later class. So, at this moment let us say we will take this off from this projection and look at only this, so, *P*-1 one fold symmetry triclinic.

The International Tables provides you 3 different projection diagrams depending upon the axis which we are choosing; which we have chosen and generally this is the preferred projection the first one, which is 0 a and 0 b, x axis down here an y axis that way. As I mentioned that the positions of any object inside this is mentioned as a fraction of the b value and a fraction of a value and those are referred to as the x and y coordinates in this particular projection. It does not mean that this particular angle has to be 90 degrees.

So, what you see as coordinates given in crystallographic analysis you see the coordinates of the atom positions and so on when you read literature, in the research papers and the review articles and all that which you read the coordinates that are given are those of fractional coordinates. Fractions of a and fractions of b now represent x and y similarly the fraction of c represents z.

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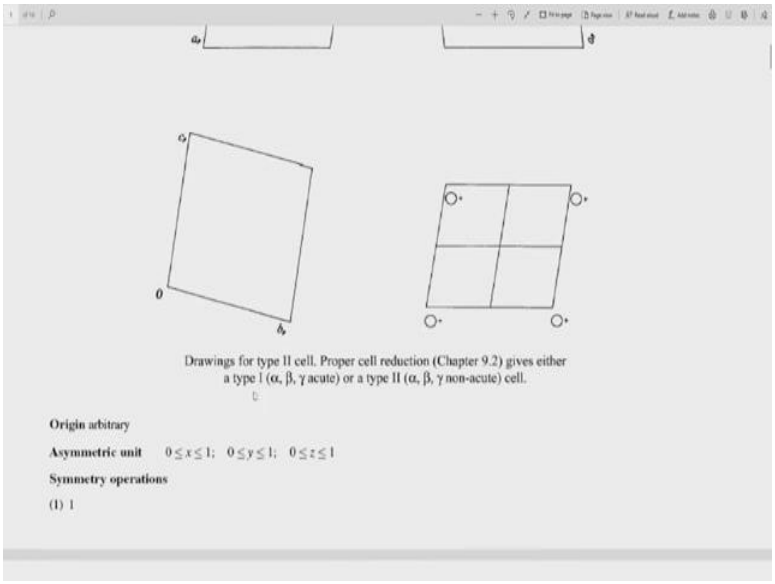

So, when we say *x y z* as a position which is indicated here in the diagram below here this tells us that there is a position which is for one particular object. In this particular stage just like the previous discussions we had instead of a gamma here circle is used and there is a plus which indicates that the object is coming away from the board or away from this projection.

So, if the object goes inside this we indicate it by a negative sign. We will see what happens if we invert the object in a next projection where we discussed *P*-1 bar. So, in *P*1 therefore, if you see the unit cell this is the unit cell it is divided into half and half here and you see that the unit cell has only 1 object. So, that is the object which is a 360 degree operation brings a turn to itself as we say as defined earlier the requirement of a space group is that the object has to come on to itself after the symmetry operation.

So, in this particular case it comes onto itself and so the origin can be arbitrary we can choose the origin wherever we want in case of a triclinic system and then we define what is known as an asymmetric unit. Now the asymmetric unit in this particular case is the unit cell because there is no other object as we discussed then z is equal to 1 in this particular case and there are no special positions, no symmetry positions in *P*1 and therefore, the asymmetric unit is the unit cell. So, it is described as 0 less than or equal to x less than or equal to 1. Remember these are the fraction coordinates we talked about. So, this is now a, b and c the full value of a, b and c is taken. So, the value of x rangers

between 0 and 1 the value of y ranges between 0 and 1 and that of z also ranges between 0 and 1.

The symmetry operation that is present in *P*1 is only 1. So, this is the redundant set and you see therefore, this entry as the first entry for number 1 in the periodic table.

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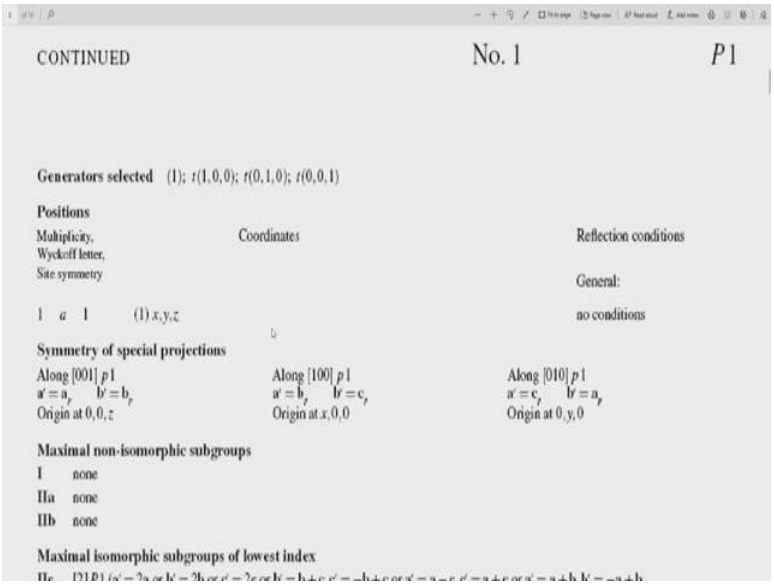
CONTINUED No. 1 *P*1

Generators selected (1); *t*(1,0,0); *t*(0,1,0); *t*(0,0,1)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
		General:
1 *a* 1	(1) *x*,*y*,*z*	no conditions

Symmetry of special projections

Along [001] *p* 1	Along [100] *p* 1	Along [010] *p* 1
$a' = a_r$ $b' = b_r$	$a' = b_r$ $b' = c_r$	$a' = c_r$ $b' = a_r$
Origin at 0,0,*z*	Origin at *x*,0,0	Origin at 0,*y*,0

Maximal non-isomorphic subgroups

I none
IIa none
IIb none

Maximal isomorphic subgroups of lowest index

Now, apart from that the types of translational periodicity is indicated here these are the generator selected the translational along a, translational along b and translational along the *c* direction or these are the ways in which we can represent the translational periodicity in the unit cell.

Now, the additional details which come here are the ones which we have to learn carefully. The additional information which comes here which is written here can you see it in the that these details clearly multiplicity, Wyckoff letter and site symmetry. So, these are the 3 issues which we will be discussing in more detail as we go to the higher space groups.

But in this particular case, the space group tells us about the multiplicity value, the Wyckoff letter and the site symmetry. We will define these 3 when we go to *P*-1 at this moment there is no entry associated with except this one which tells us that the multiplicity associated with this object is 1 which refers to *x y z* the Wyckoff letter is a that is the highest symmetry which is present in the system and then the site symmetry,

the symmetry associated with any position in the unit cell is 1. So, there is no symmetry its 360 degree rotation.

So, the equivalent points are written here that is x y and z. So, there is only one equivalent point and therefore, the required other issues associated with coordinates are not given. So, the coordinates are only 1 type which is x y and z. So, *P*1 is the number one space group which has no symmetry other than the 360 rotation symmetry and all the specifications which are given here fully qualifies this space group *P*1 or the diagram here the symmetry diagram here.

And then of course, the equivalent point positions indicating the number of equivalent points in the unit cell which happens to be 1, the symmetry operation is also 1 asymmetric unit is defined by the unit cell here and then we have the definition 1 a 1 x, y, z telling us that there is no further symmetry operations that are possible in this case.

The special projections which are indicated here tell you very clearly that along 0 0 1 what is the axis, along 1 0 0 what is the symmetry, along 0 1 0 what is the symmetry. This symmetry you notice is indicated with a little p and 1, the little p tells us that we are now talking about two-dimensional projection or in other words two-dimensional lattice. This particular two-dimensional lattice which is in three dimensions triclinic has a symmetry 1.

Remember when we discuss the two-dimensional lattices, there was no third axis and there the symmetry was *P*2 there was always a twofold axis associated with lattice point. So, here the moment we introduce the c axis direction and say this is a three-dimensional object, the corresponding projections projection diagrams will have only 1 object and therefore, it is *P*1 all in all the 3 cases and the origin is taken at 0 0 z, z is arbitrary. So, we can say z is equal to 0 then this represents the diagram that is required. So, this diagram therefore, has the origin at this point by definition we have given z is equal to 0 it is arbitrary then this is the a value the cell dimension and that is the b value the cell dimension along this direction.

So, we are referring to this particular projection and in this projection we have these object which is represented as x, y and z the value of z is now coming up from the board or from the projection.

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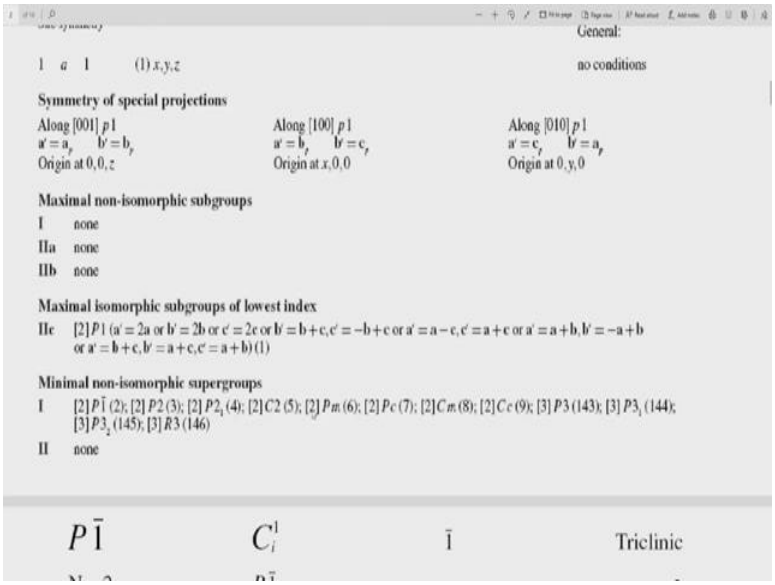

So, this now describes more or less the whole thing that is associated at this moment for us to note there are other entries in the International Table with at this moment we will not worry about because, we have to now fully understand all the 230 space groups in order to appreciate what are these entries. So, we will not worry about these entries at this moment; however, we are also not going to see all the 230 space groups in this way.

We will take a few representative examples. So, that we will now learn how to read the International Tables, you see for example, when you are try taught the grammar of a language like in English, the grammar is start with respect to the nature of the words, the way you can combine the words, the types of words, you can have is the noun is talked about, the adjective is talked about adverb is talked about. So, similarly we will tell all the language that is required in order to understand the grammar of the crystallography in 230 space groups.

The actual textbook which we write about each and every molecule will be different, but each and every molecule will have to follow these grammar book which we have prescribed. So, we cannot go away from the grammar book which we prescribe and therefore, all the elements of the grammar the a way in which we make sentences, the way we make the combinations of sentences, the phrases becoming sentences, they all become very important and once we study the space groups. Afterwards every novel can be different, every crystal structure can its own beauty, every crystal structure eventually

with the molecular species inside can have its own story it can have its own property and so on.

So, you can write a numerable number of stories and that is how the data accumulates in the understanding of a given molecular species. So, then we can classify these molecules into various kinds of organic inorganic organometallic and so on the categories we will go into those details later. But at this moment we are looking actually into the grammar book, the grammar book which tells us how we make this combinations and how these combinations will give rise to sentences which are meaningful.

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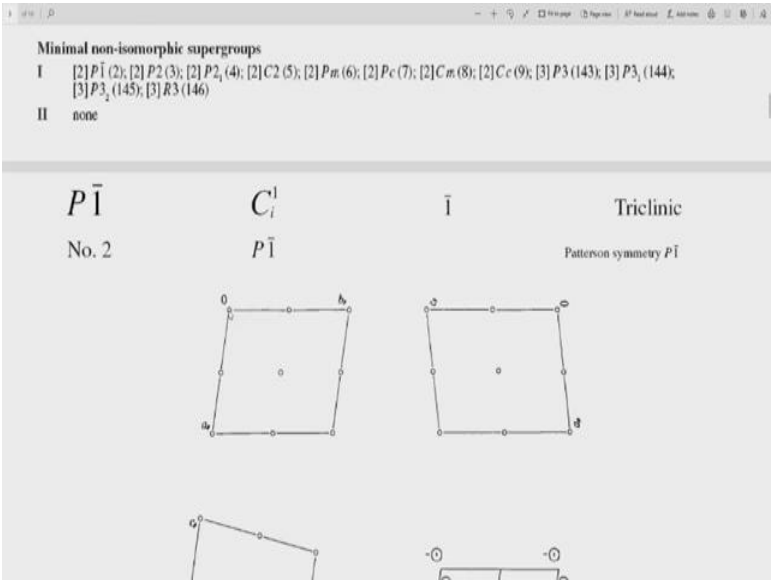

So, the next step would be to go to the next space group which is number 2 which is *P*-1. *P*-1 you see the symbol now is C of I, the moment we use a small i in spectroscopic symbol or in group theory it tells you the inversion centre; i refers to the inversion centre. So, therefore, we have the -1 which is indicated by the Hermann Mauguin notation, in this spectroscopic notation is C of i. So, group theory and the Hermann Mauguin notation followers in spectroscopic nomenclature they use C of i and both of them now belong to the first crystal system so it is 1. So, this is C i of 1 and the point group symmetry is -1as we already know and this belongs to the triclinic system.

Now, how does the projection diagram look like and where are the symmetry elements. So, that is given in these projections again we will concentrate only on this projection diagram. Now this particular projection diagram tells us the presence of a which is now

down the this direction and the presence of *b* which is now in the horizontal. So, the vertical down is the a direction remember this is not 90 degrees this is whatever is the angle between a and b which happens to be gamma for a triclinic system *a* not equal to *b* and *b* not equal to c, α not equal to β and β not equal to γ and therefore, we have the situation where we have now representing the projection diagram like this.

The centre of symmetry as we discussed all along until the last class, the centre of symmetry if it is present in a crystal in a space group it should be at 0 0 0. So, we therefore, move the centre of symmetry to the origin. One once we have the centre of symmetry at the origin there is a centre of symmetry at cell edges and therefore, all these cell edges develop the centre of symmetry and we have seen by the equivalent point distribution which is shown here.

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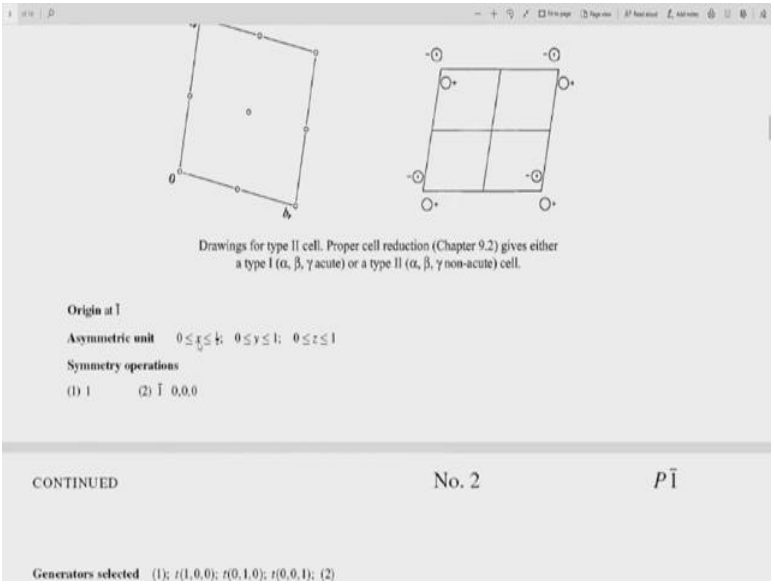

The equivalent point distribution which tells us this is *x y z* and this is *-x -y -z*. So, this is the centre of symmetry which is up here. So, you see that in earlier diagrams where we studied we put them together, putting them together was easy for our understanding and that is why we did that. But now we want to understand the symmetry positions differently from the positions of the objects and that is why 2 different diagrams are given. So, these 2 diagrams therefore, are of crucial importance this as well as this which will tell us the symmetry position symmetry that position diagram here and the equivalent point diagram here.

So, you see that this is now centre symmetrically going over there. So, the negative value associated with this open circle is indicated by the presence of a gamma inside. So, this is now a gamma inside the round representation and a minus indicates that it is going down the plane, plus is up the plane, minus is the on the plane and apart from that the other values of x and y in this case because this is the value of x that is the value of y. So, this represents *x y z* the value of x and y changes to -x -y and that is why it is shown with a gamma.

So, whenever there is an inversion the inversion is shown with a closed circle with a gamma inside. So, this now will also tell us how the translation symmetry takes them up into these objects and invokes the presence of the central symmetry at this 1/2+x 1/2+y which is up here and you see that these two this comes by translation along this direction and translation along that direction and so these two are related by a centre of symmetry.

So, we will see the further details the asymmetric unit now is what? The asymmetric unit now is half along the x; that means, they asymmetric unit is only that much. The asymmetric unit is only that much because you have a centre of symmetry here; you have a centre of symmetry here; you have a centre of symmetry here. Effectively you can consider this as a unit cell which is a sub cell of this unit cell and in that sub cell there is only 1 object and that is why we call it as the asymmetric unit.

So, here the z value with number of equivalent points inside the unit cell is 2, *x y z* goes over to *-x -y -z* bar and each of these blocks therefore, now that is why these 2 lines are drawn each of these 2 blocks therefore, now represent the asymmetric unit. So, the asymmetric unit is 0 less than or equal to x less than or equal to half y is full and z is full you can also interchange them you can have this moving over to y and this moving over to z and you can have other types of asymmetric units both in the y direction as well as in the z direction.

But this is the definition of the asymmetric unit with respect to this diagram and with respect to the projection 0 a b that is *ab* projection, ok. Now you see that the symmetry operations become 2 there is a symmetry operation 1 and there is a symmetry operation -1 and this -1 symmetry operation is about the origin 0 0 0 and so the again the generator selected as before along the x direction along the y direction along the z direction.

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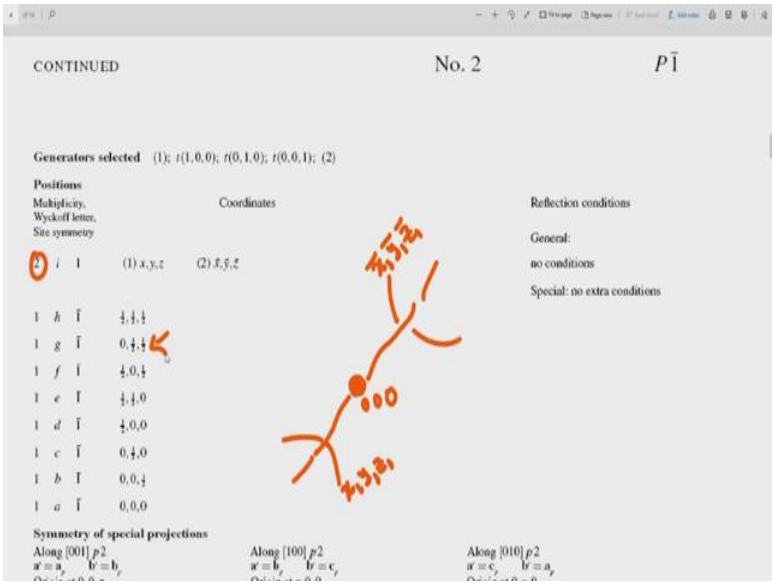

Now, the space group is number 2 as we have seen now what happens; this is a very crucial stage where we have to fully understand the concept of multiplicity, the concept of Wyckoff letter and the site symmetry. So, let us go through it a little carefully now there is something on the right hand side for which we will return much later, this is with respect to the experimental conditions which get generated due to the presence of the -1 symmetry right now we will not worry about it. So, forget about it at this moment.

What you have to remember is the fact that if there are there is a general position which is now associated with 1 symmetry 1 then there are 2 objects *x y z* goes over to *-x -y -z*, and that those are the 2 equivalent position. So, z is equal to 2 z prime which is now the asymmetric unit is equal to 1 and the asymmetric unit we have already defined as the half the value along x or y or z we can choose any one of them in this particular space group. So, having given that choice we will now look at the so called multiplicity.

Now, what is multiplicity, what is the number of the multiplicity that comes on the *x y z* suppose you take the coordinate as *x y z* how many of equivalent points we generate in other words the number of equivalent points the value of z, the value of z is represented here which is equal to 2. So, multiplicity is how many such objects are there in the unit cell? We have an object located at *x y z* corresponding to *x y z* how many such objects are located with respect to *-x -y -z*. So, there are 2 of them, so, therefore, it is 2.

The site symmetry still 1 wherever it is sitting it is 1 only because it is a triclinic system.

So, the site symmetry is 1, but the multiplicity associated with the site is 2 so that means, if you have an atom at *x y z* it has to have an atom at *-x -y -z* it depends upon where you define the origin. So, you go back to the figure here you can define the origin wherever you want in this projection diagram correspondingly all these centres of symmetry is will move the 0 will coincide with wherever we represent that and the *x y z* value will be read based on the value of the origin which is 0 0 0.

So, suppose I move this to this origin with the representation is different and therefore, the value of *x y z* will be different ah. With respect to the *x y z* here therefore, we have invoke now several centres of symmetry. So, this particular *x y z* position which is right here the position with respect to that can be expressed 8 different ways, the 8 different ways are 1, 2, 3, 4, half removed 5 and then 6, 7 and then 8 so totally 8 possible ways in which we can represent them and those are listed here a, b, c, d, e, f, g, h and the positions of these centres of symmetry are indicated.

What it tell is also the fact that if there is an object which sits at any one of these positions the object is independent of the other positions. So, if you have 8 equivalent 8 positions here these 8 positions which are generated due to the presence of the -1 symmetry, they have already built in them the -1 symmetry; that means, every *x y z* will go to *-x -y -z* is built on to them. That means, if you take for example, 0 0 0 operate this in symmetry operation *-x -y -z* you will get 0 0 0 only. So, the -1 symmetry therefore, is already inherent at that point. It is true with everyone of these 8 points -1 symmetry is inherent at that point it recites at that point.

Since the -1 symmetry recites at those points these are referred to as are special positions. So, we have 1, 2, 3, 4, 5, 6, 7, 8 special positions and one general position. So, the special positions importance goes as we have arranged here we start from a then we take the z axis half as the b, the y axis half as the c and the x axis half as the d, this is the nomenclature which is now a, b, c, d now is referred to as the Wyckoff letter. Wyckoff used this symbol to identify the differences of atoms which can sit in these positions.

For example we can have an atom with 1 and some other atom sitting in let us say 0.5 0 0 these two atoms are not 1 and the same there different atoms. So, structurally they are different. So, indicate the differences in structure a and d are getting invoked. So, we say that suppose there is an atom 1 at "a" and atom 2 at "d" we say that this structure is

generated with the atom 1 at "a" and atom 1 at "d"; that means, the 2 atoms are different from each other.

In fact, if a same atoms sits in these two positions also their properties are different that is because if you sit at 0 0 0 operate the centre of symmetry you get 0 0 0 again, if you sit at 0.5 0 0 operate the centre of symmetry you get 0.5 0 0 you do not get 0 0 0 or any of these 8 and that way they are very special. So, these positions therefore, are refer to as special positions.

Wyckoff decided to follow a certain protocol and that protocol is generally followed for example, in this case we start from z, y and x and when we have two of these value is equal to half we start xy, xz and yz in that order. And this order depends also upon the other symmetry elements which are present in the space group if we go to higher space groups this order need not be followed. We will see that as an when we examine their space groups, but in a triclinic system we have 8 general special positions, 2 general equivalent positions, 8 special positions and they are indicated with the Wyckoff symbols a, b, c, d, e, f, g, h for the 8 special positions and i which is a general position.

So, the number value of z is 2 in case the atoms are or the molecules or whatever is sitting in general positions. So, in general positions the symmetry is 1 and therefore, it will generate its *-x -y -z*, so, we will have 2 objects generated. So any objects sitting in any of these special positions will generate only one object; that means, the object much itself possess the centre of symmetry. So, half of the object the other half of the object they should be related by a centre of symmetry then and only then the atoms can sit at those positions in this example.

So, *P*-1 therefore, already is looking very complex in the sense of understanding, but it also tells us that it is now given special occupancy positions for special issues. So, for example, let us say you have an organometallic component and you have a metal which is sitting at one of these Wyckoff positions the rest of the atoms need not sit at that position, but they should sit in such a way that the overall symmetry associated with the molecule is centre of symmetry otherwise this heavy element the metal cannot sit at any of these special positions.

So, imagine a situation where the metal atom is sitting else elsewhere the moment the metal atoms sits elsewhere there even though there is a centre of symmetry which might

be associated with the molecule which is a very rare chance the metal now will generate another unit which is going to give us z equal to and therefore, there will be two objects. So, let me repeat if you have a metal organometallic compound so there is a metal and then organic surroundings, the organic the metal will sit let us say at a special position because it atom by itself has a centre of symmetry, it is not just the atom we should consider we should also consider the bonding associated with it. The nature of the bonding and the way in which it is bonded to other atoms the environment should also be centre of symmetry.

So, the molecule may find itself in a centre of symmetric environment, but it is not necessary that all these atoms have to sit in this special position. So, they will have they will be sitting in their general positions. When we look at the realistic structures later on we will see how this really happens, even though it is this very interesting to notice that this can happen with respect to the way in which these things appear. Suppose, there is an atom which is sitting here and let us say this occupies anyone of these centres of symmetries, if that is a spherical atom let me make it perfect sphere if possible now its nearly spherical ok.

So, let us say this is our organometallic element then, whatever is the surrounding organic let us say there is some branch coming out like that ok. Now this branch should be identical to the coming out branch. So, these two should be centre of symmetrically related to each other, but you notice that if the coordinate of this is let us say 0 0 0 and the coordinate of this is x_1 y_1 z_1 then the coordinate of this will be $-x_1$ $-y_1$ $-z_1$ bar. So, these two are now related by a centre of symmetry; that means, there are 2 objects they are sitting in general position and the x y z is equal to is and $-x$ $-y$ $-z$ is getting generated this is a possibility then the metal can sit in the special position.

Suppose there is a structure in which there is a perfect centre of symmetry they can sit in any one of these positions, you notice that if this is not at 0 0 0 or some 0 1/2 1/2 then the coordinates will accordingly change with respect to 0 1/2 1/2. So, this molecule now will be only present with respect to 0 0 0 and that molecule will be present only with respect to 0 1/2 1/2 which where the metal is going to sit. I think this is a place where is a good place where we can stop today and then we will continue tomorrow.