Defects in Materials
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Lecture – 06
3 – D Lattice – c

Welcome you all to this class on Defects in Materials. In the last class we have discussed about how from a 2 D lattice a 3 dimensional lattice can be generated, what are the point of symmetries which are associated with that lattice, how to understand and read the international table of crystallography to construct a crystal structure. We mentioned a little bit about how a crystal structure can be constructed from the international table of crystallography, especially looking at the special and general position coordinate and the site symmetries which are given in the table. So, let us have a recap of that and go into little bit in detail.

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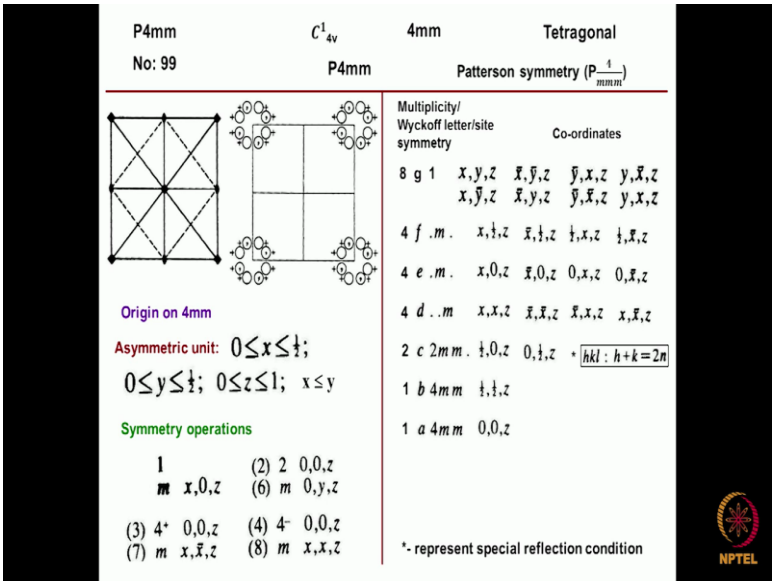

What I am considering in today is 1 typical example, which I had mentioned in the last class also, essentially a space group 4 having P4mm symmetry. So, when we consider P4mm symmetry is essentially a tetragonal structure and the positions of the atoms if you try to look at it. It has got four fold symmetry and the mirror symmetry associate the 4 mm symmetry at the lattice points and the center and at the edges if you look at the

middle we have 2 mm symmetry, and then there are 3 types of mirror symmetry. Planes are also associated with it right.

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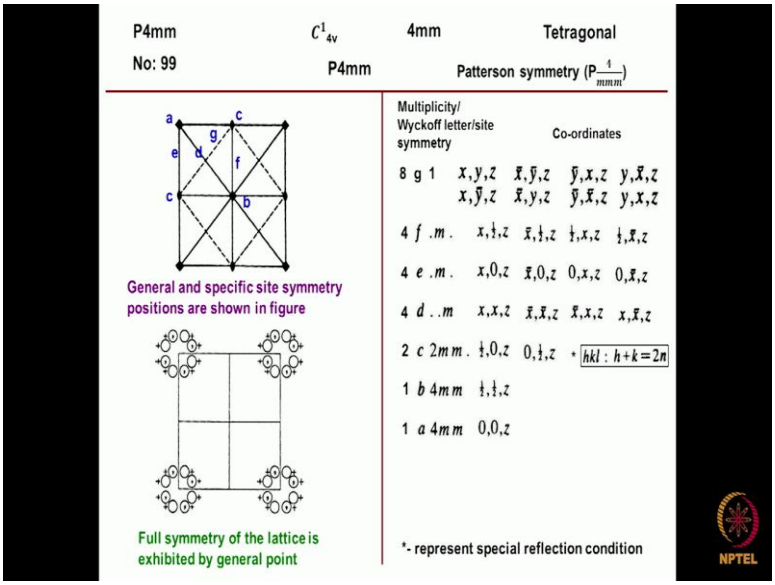

The atomic positions are also given these are all the positions we can fill their atom. So, generally if you look at that any of the space group table, what they mention are the graphical representation, when they show is only of the symmetry associated with the lattice in the graphical representation in the unit cell the how where the symmetry appears on the symmetries are shown. Another graphical representation is where only the position of a motif a symmetric motif, if we keep it at any general point how the equivalent positions are generated.

And why only this is being shown? If we look at is the reason for this is because, if you consider a general position when all the equivalent positions are generated the complete symmetry operation has been performed only in this case. In other cases if we consider where some symmetry elements that is a symmetric motif itself has got some symmetry associated with it, if it is sitting at a particular point that symmetry operation need not be carried out only the other symmetry operations will be carried out. So, the complete symmetry operation is can be represented graphically only if we put an asymmetric motif at a general point we will take up this with examples later in the class.

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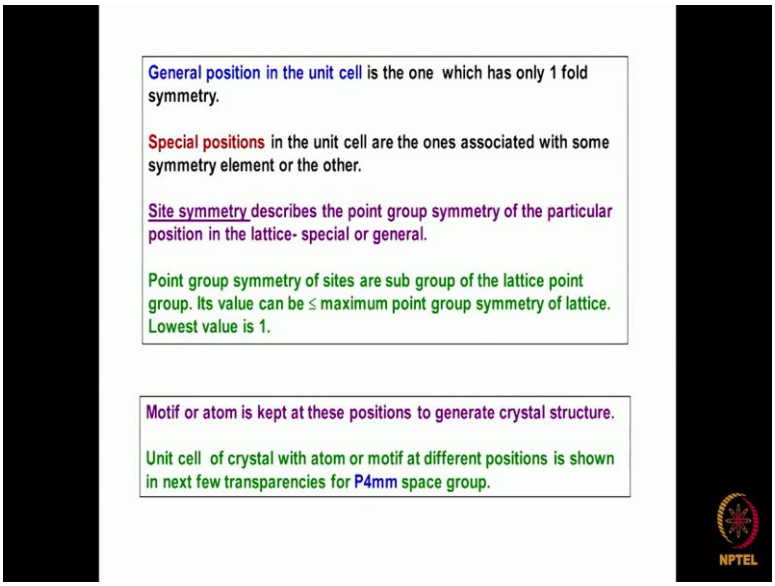

Let us have some idea about these special positions. What are special positions these are all the positions in the, once the unit the lattice has been created. Had different points if you try to consider it, different type of symmetries can exists. Some points there need not be any symmetry associated with it and some point in the lattice if we consider there could be some symmetries which are associated with it, the symmetries which are associated with these points are called as the site symmetry.

The term wise site symmetry is used at that particular point, what all symmetry elements which are crossing through that point it is something equivalent to point group symmetry. But if, but if we look with respect to that point, where that site symmetry is there. If we consider the nearest neighbors which are going to be there, they will exhibit the cluster will exhibit the symmetry which will be that of the site symmetry.

And, another factor also which we have to understand that: all the site symmetries which are being mentioned are subgroup of the maximum symmetry which the crystal exhibits. Now generally, another thing to do that to construct a crystal structure what do we do? We keep up motif either a are an atom at a general point are a special position. We will consider this in the case of a p 4mm symmetry, space group in this, if you take an atom.

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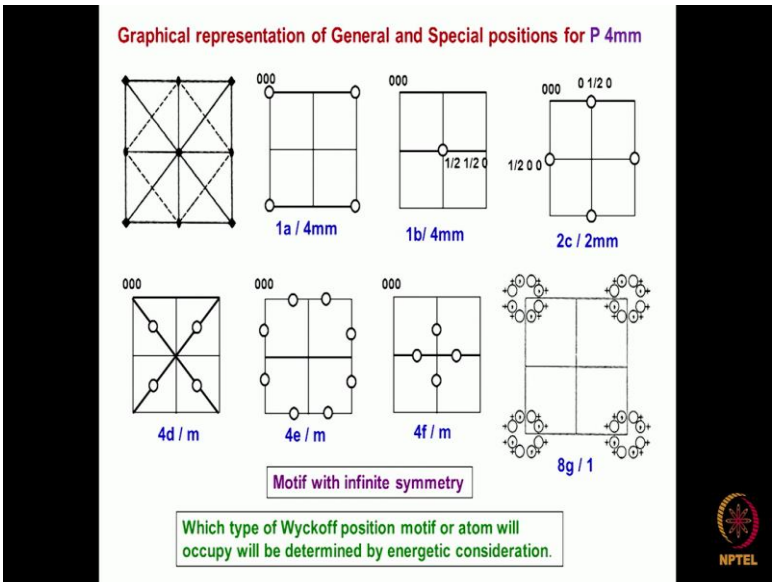

We assume the atom to be a spherical. So, it has got an infinite symmetry is associated with it. Since it has got an infinite symmetry if we keep it at any specific point, it will exhibit the symmetry of that point that at whatever be the lattice point we keep that atom.

Student: We special position or (Refer Time: 06:00).

Special position if we keep it, it will be all the symmetries of the special questions will also be coinciding with that of the atom. So, essentially we can keep it anywhere, but where we keep it at that point the lattice will have some symmetry. So, it always matches with that symmetry, it assumes that symmetry of that lattice point correct. Though it has their full symmetry I it has an infinite symmetry.

Suppose we keep it at the lattice point the lattice point has got a 4mm symmetry. So, we require now all the symmetry operations can be performed under same atom itself. It since it is present on the lattice point and as per the definition of point group symmetry that point remains unmoved. So, if you infinite symmetry only 1 atom point is required, 1 atom has to be placed at that particular position.

Suppose for example, if we are keeping an atom at a point which is far away from it that for example, if we keep their atom at this particular specific position, it is at a general point now by symmetry operation for the same atom now this item has got only 1 fold symmetry where we have kept it. So, though it is spherical and now it has to be by the

symmetry operation of the lattice, we have to generate all other equivalent position. It is equivalent to when is a if we move all these atoms from here gradually, maintaining that symmetry then at the lattice point all of them will much together and join into 1. So, only because of that we have to keep only 1 atom at that particular point right.

Student: That means if we put an atom on motif as been at any general position then we need more atoms.

Yeah.

Student: (Refer Time: 08:06).

General position we require more atoms because equivalent position by symmetry has to be generated if when we put it at a.

Student: Lattice point.

Lattice point depending upon the symmetry dictates how many atoms have to be placed there correct. So, that is what essentially is being done. At this point the maximum symmetry of the lattice it exhibits. So, we have to put only 1 or the another equivalent point which exhibits 4mm symmetry is this particular point similarly if we put at these positions also since it has an infinite symmetry 1 is good enough, but now we know that an another equivalent position has to be generated. So, that, the symmetry of the lattice will be exhibited by the unit cell. So, when we put an atom at a particular position it should satisfy the side symmetry, but when it has been when we consider the unit cell, the unit cell as a whole should satisfy the symmetry of the lattice that is both the considerate both these conditions have to be met.

So, like as I mentioned earlier for if it is a mirror symmetry there are 3 options are there these are all the 3 possibilities which position the atom will occupy will be determined by what are the positions at which. If there is an another atom which is being present then that consideration will tell, suppose it is an comb ode which contains 2 elements then the internet the bonding between the atoms also will be safe if one atom has occupied 1 position where exactly the another atom will come.

So, if you look at this structure. Generally, if it is only one type of an atom which is there what is the most likely choice? Is the one which has got the maximum symmetry because, that love the lowest energy?

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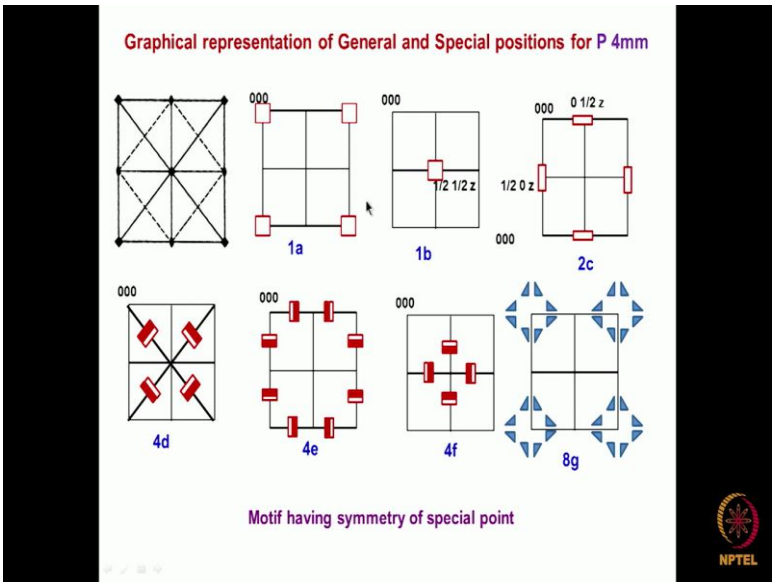

Suppose the motivators got a different type of a it is not an atom. We are putting a cluster of a molecule at that point, and then what will happen? Then if the molecule has got the full symmetry, if a 4mm symmetry it exhibits in this particular case, then we can put at this position 1 molecule each. So, that it satisfies the symmetry of the lattice or the other alternate position is at the center of the unit cell.

If we are putting a molecule, at this position which has got 2 mm symmetry then the molecule if only one molecule has to make up there then the molecule should satisfy. There have the 2 mm symmetry then only the only in that case the molecule occupy this position, then the energetically also if when we have to consider both of them. This is the most likely position where the molecule will occupied. So, if you put it at a mirror symmetric position then this should have the mirror symmetry should be exhibited by heat, it can have a symmetry higher than that of this it can be.

Student: Minimum symmetry.

Minimum symmetry which you should have is that of that site and when we place it there those symmetry elements also has to match with each other, that is very important,

I will come to that later. Here what we have done it is that in this particular case, if you put it at a general position it has a symmetry which is 1 4. So, you can put an as symmetric motif itself there to generate very the crystal having 4 mm symmetry correct.

Student: (Refer Time: 11:50).

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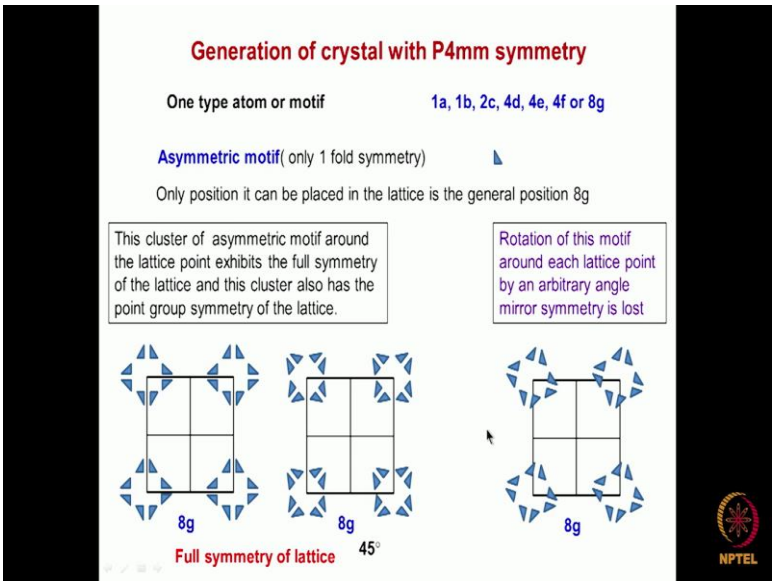

Now let us take the case, the options which are available, we have is that if you are putting an atom or an asymmetric motif it can be 1a, 1b, 2c these are all the various positions in which and I atom are the motif could be placed. So, if you to exhibit the full symmetry if we keep this motif at any particular point to maintain that full symmetry of the lattice are to satisfies the full symmetry of the lattice.

It has to be kept at some specific positions equivalent positions this is; what is the general position which you see it in the internal crystallography. The graphical representation also it is being shown what is the other position in which this could be kept satisfying the full symmetry. Because here if you look at it the mirror planes are both along the axis correct, there is another mirror plane which is there.

Student: (Refer Time: 12:59).

Which is along the diagonal? So, that position also could be chosen. So, these are all the 2 positions in which the molecule can arrange itself, around that specific lattice point current.

Student: (Refer Time: 13:17).

Now, if you rotate it by some arbitrary angle then in this position it will have fourfold symmetry, but it does not exhibit the mirror symmetry. So, this position is not possible correct.

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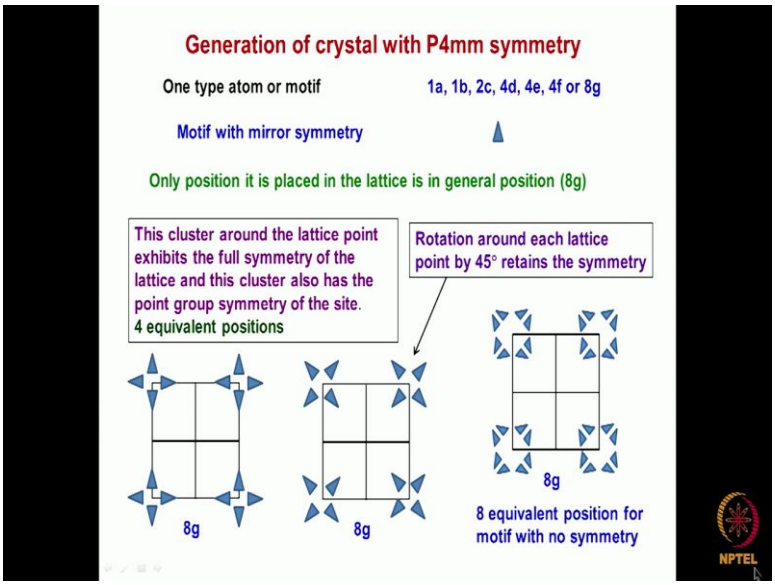

So, by an arbitrary angle rotation cannot be done and so most of the time when we put a motif at a lattice point the motif tries to arrange itself in such a way that symmetry elements of the motif and the symmetry elements around that lattice point are lying on top of each other.

Now, let us consider a case where the motif is not an symmetric motif. It has got the mirror symmetry associated with it, the other option which we have is there it can be the motif can be kept coinciding with the mirror symmetry which is existing on the diagonal element, then in that case also that is centrally rotating it by an angle of 45 degree correct. Then, if it is an symmetric motif we require 8, that is the way it is. Suppose this motif itself is the symmetry axis does not match, if I rotate it by an arbitrary angle from this position then we have to, then 8 motifs have to be kept or if we keep one motif at an opposition which has 1 fold symmetry then another 8 equivalent positions will be generated, where the same motif has to be kept. So, that the full symmetry of the lattice is satisfied. Only this way we can generate a crystal though the crystal motif has motif

are the atom has got a twofold symmetry or the molecule has got a twofold symmetry, if it is kept at an arbitrary position in this particular lattice.

At 8 more equivalent position it has to be kept. So, that the crystal exhibits the full symmetry of the lattice.

Student: For these mirror symmetry motif we need 4 equivalents (Refer Time: 15:38).

No, for mirror symmetry if the mirror symmetry coincides with that of the crystal, suppose I assume that I am keeping this motif this is at 45 degrees, at some angle 10 degrees from the mirror symmetry. Then I will have to keep are around another 7 equivalent positions more where the same, though the mirror motif has got twofold symmetry. The symmetry of axis of the motif and that of the lattice, if you see the point where we consider they do not match them symmetry which the motif in the lattice is going to exhibit is as if it has only 1 fold symmetry. So, 8 more positions it has to be kept

Student: So, then that 8g or 8g means.

8g means that g is the Wyckoff symbol.

Student: (Refer Time: 16:31).

8 means that how many equivalent and positions which are required and here it will become that in this particular case that number will be, since this has a symmetry which is to it will be only 4 motifs will be required.

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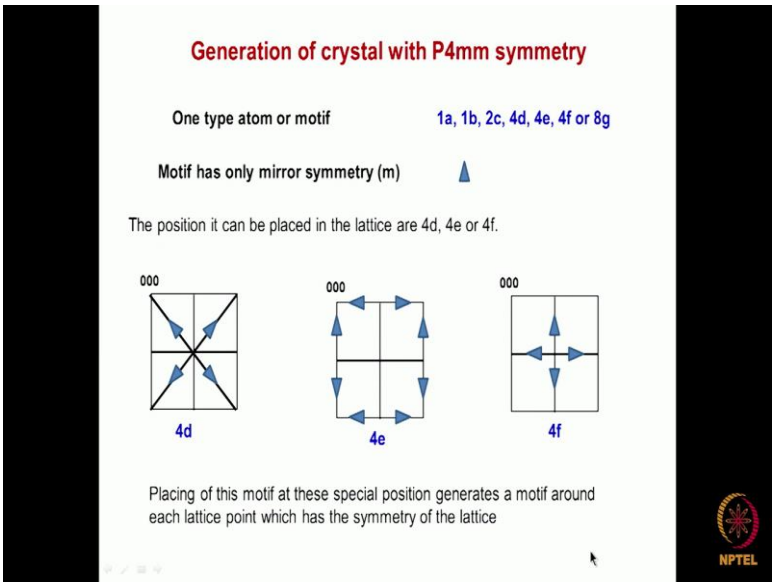

Suppose we keep the same motif there are on mirror symmetry position, what are position which we have to keep it? Like as I mentioned earlier they the motif will be kept with the mirror symmetry coinciding we can keep that one of the option is keeping it with mirror symmetry along that diagonal or it can be along the axis a and b axis r at the center also there is a mirror symmetric plane is there which is parallel to the axis. So, in these 3 options these are all the 3 ways in which it can be arranged.

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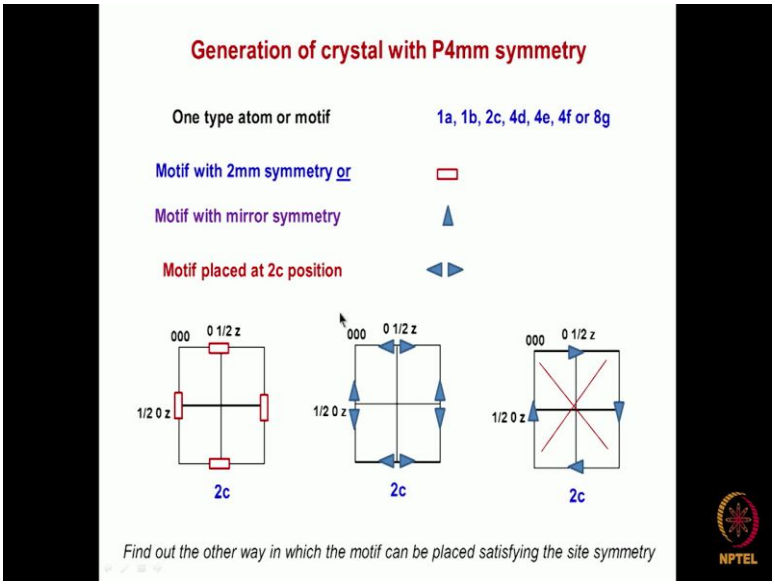

Here, I am considering another case, in which the motif has got the full symmetry of the lattice that is another case where the symmetry which the motif is exhibiting is only the mirror symmetry. Because, if we look at this particular position the symmetry of this position is 2 mm, this motif has also got a 2mm symmetry. So, only 1 motif has to be kept at this specific position. If I keep a motif with mirror symmetry this motif if I try to keep it there, there should be another equivalent position, the same motif should be kept. So, it is equivalent to generating, cluster like this which exhibits, this cluster exhibits the 2 mm symmetry.

Now, this can be kept at this lattice particular lattice point. So, this generates the full symmetry of the crystal. So, if we put this asymmetric motif at any particular position are at 2mm position now what we can make out is that the this structure does not exhibit that symmetry. This has got only a fourfold symmetry all the mirror symmetry has been lost correct. So, this is what it will happen. So, if only fourfold symmetry is there then the space group of the crystal is p 4, it is different from what the space group symmetry which we are considering now right.

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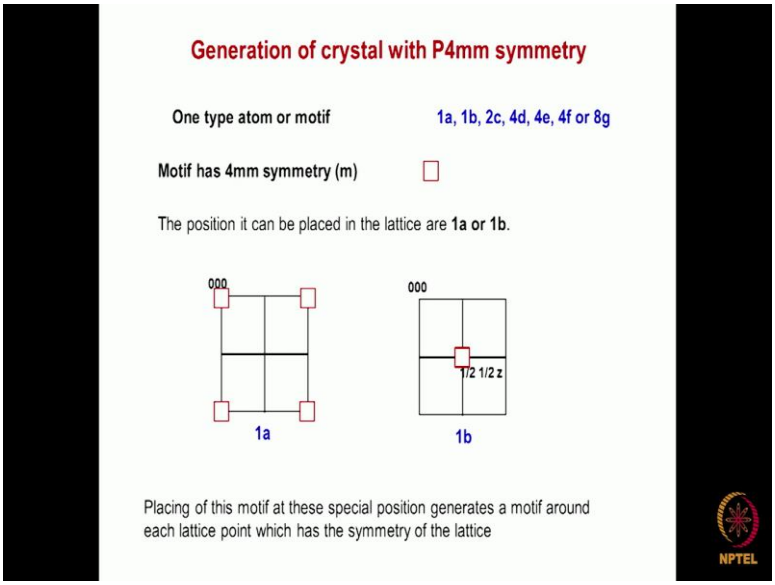

If we take a crystal with a 4 if we take a motif with a 4mm symmetry and if you are trying to keep it at a point which has got the 4mm symmetry then we have to keep only 1 motif. So, here the motif which is used is a square that is a molecule which has got only

now 4 4mm symmetry, then we have to keep only 1 molecule either at the lattice point or at the center of the lattice.

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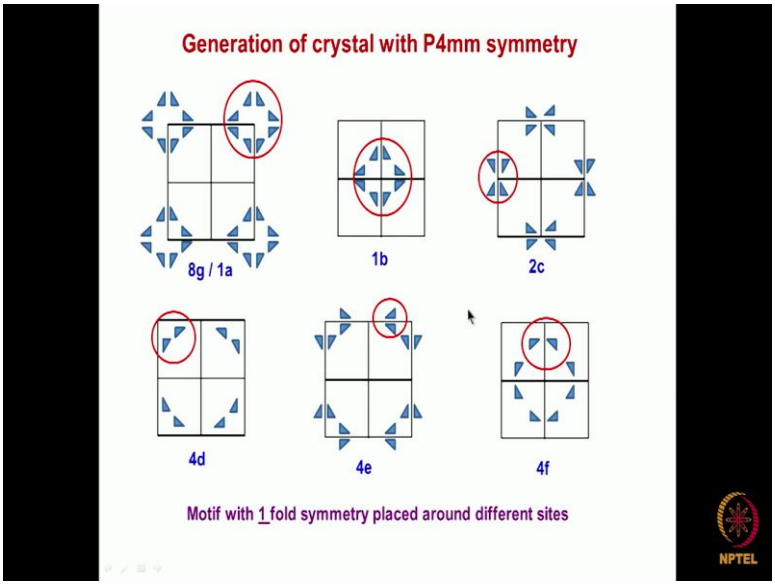

So, here what I have shown is there an asymmetric motif summing it up all together if you take an symmetric motif and if we wanted to put it, place it at different special or general points in the lattice what sort of a cluster we should be placed. So, that, that will satisfy the full symmetry of the crystal, which we wander to generate. So, this is the way it will happen, in this case this is what is going to be the cluster which has a 4mm symmetry.

If we wanted to keep it around the another position, it is the same cluster which can be kept at that center of the unit cell if it is around the, the special point which has got 2mm symmetry then ,this is the way it has to be kept. Satisfies the 2mm symmetry and in this case it has to be this is the way a cluster will have to be kept. So, that it is satisfies that symmetry element when the mirror symmetry is along a diagonal.

Student: (Refer Time: 21:03).

Face diagonal and this is the particular way in which has to be kept. When this is along that 1 of the axis and this is the sort of a cluster which has to be kept around this mirror symmetry axis. What we have done? We have taken only motif with one fold symmetry

which is placed. If you look at it here and this one it looks like almost the same type of a cluster, but only thing is that what we have considered this with respect to be the axis.

Student: (Refer Time: 21:44).

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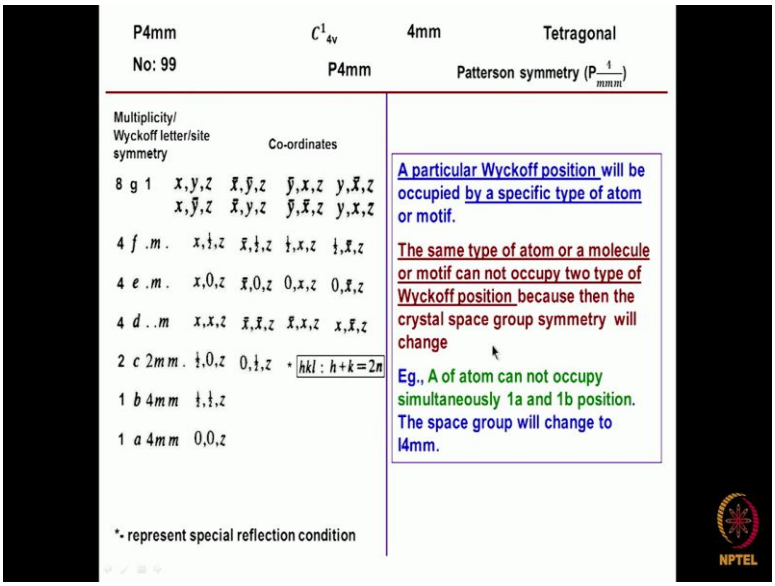

Correct. Another important aspect which we have to consider when we wanted to construct the crystal structure is that, the special positions and general positions are given in that international crystallography a table which gives the coordinates of the Wyckoff positions are given. Each of the special positions only one type of an atom can be kept at each position, suppose we try to keep at any particular point 1 type of an atom for example, if we consider the one a position a position if we keep one atom and in the same type of an atom if we keep it at the b position also it is just not possible, because if we keep the same type of an atom.

Now this structure will exhibit their symmetry which is not p 4mm it becomes 4, 4mm right. So, it becomes a body centered tetragonal. So, the symmetry changes, so each of these points each of this special position or the general position when a specific type of atom only can be kept correct.

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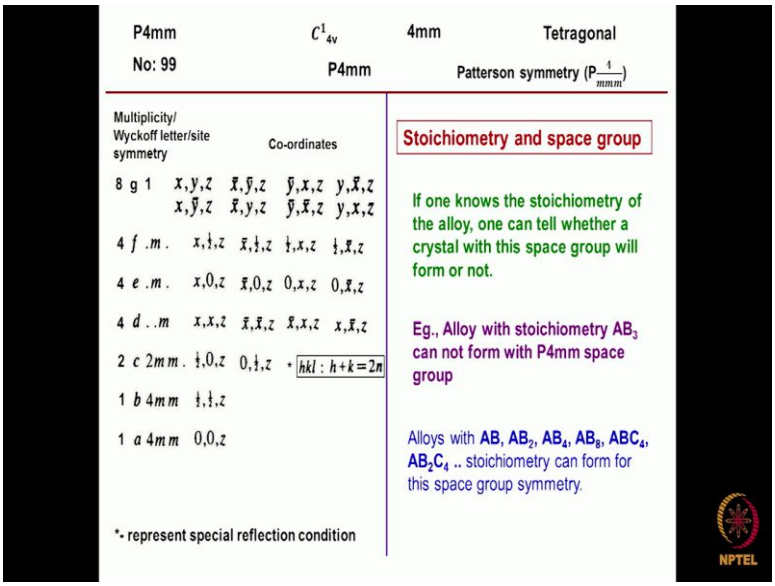

Another, information is that; now we know that at each of the position that same type of an atom cannot be kept. Suppose we assume the case where we are keeping a different type of an atom that is consider a material which contains 2 elements A and B. Then the question comes is that we can have with AB having different composition. So, if you have a different composition the stoichiometry will be different. So, we can be create a crystal with any stoichiometry, if that is can we create a crystal having P4mm symmetry with any stoichiometry or not that is the question which has to be answered or is there any restriction on the stoichiometry which we can have for a specific type of space group symmetry under consideration. This if we look at it for example, suppose we take an alloy with a composition AB 3.

If you assume that the a atom can occupy either 1a or 1b position, what all positions which the b atom can occupy either to c position are with the Wyckoff position 4d 4e are 4f are 8. So, if we take the ratio between the, because that number represents the number of atoms are the molecule which will be there in the unit cell from this we can determine the stoichiometry. From this, if we look at it if a atom occupies 1a and b atom occupies 2c then it will AB 2 if it is between a or b and between d position e or f it will be AB 4 or between 1 and general position it has to be AB 8. So, or suppose we have a 3 elements which are present a atom occupies 1a r 1b b atom occupies 2c position and c atom occupies anyone of this for d e or f position. Then it can have a b 2c 4 this is the stoichiometry. So, these are all the stoichiometry which the material can have.

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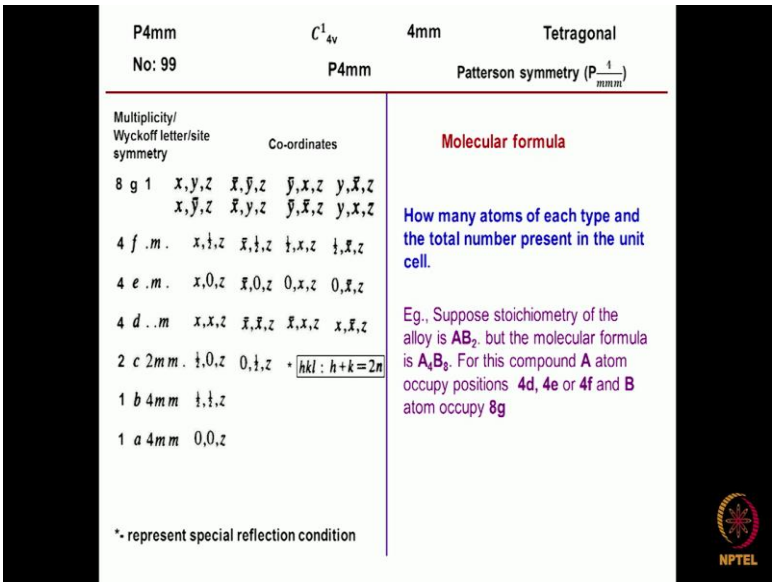

In addition to this stoichiometry, what we have to consider in this specific case is that, when we wander to construct a crystal the number of atoms which are going to be there in the unit cell is also important, that information is also available in this Wyckoff position table which is given in the international union of crystallography. That can be used to find out what positions with the same stoichiometry, but with different molecular formula when we talk of the molecular formula, we talk about not just the stoichiometry between the elements what is the total number of elements which are being present; that means, that an a b to structure when we consults the stoichiometry it could be 2 atoms of a and 4 atoms of b. That also have the same stoichiometry correct because of that.

So, we are considering a case where there are 2 types of that is 1 molecule or 1 crystal where the stoichiometry of the alloy and the number of elements which are going to be there is only just that in this particular case AB 2 if you conducts only 3 atoms are going to be there in that unit cell. There is an another case which we can consider, where with the same stoichiometry, but the number of atoms which are going to be there is 12. If that is the case then we can make out that in this case when it is going to be total 3 atoms the only possibility which the atoms can occupy, possibility where the positions in the unit cell the atom can occupy is that b can occupy 2c position, because that is at c position 2atoms will be there the unit cell.

Another is a atom can occupy either a or b position, Wyckoff position correct and suppose the as I mentioned the molecular formula ac 4B 8 then what can happen. In this particular case essentially the position which asked to occupy is that a has to be 4 atoms. So, one of these 3 positions only it can occupy option and the b has got the 8 atoms. So, that has to occupy only these positions.

Student: That is why A3 B C it is not possible.

So that is why A 3B C is not possible, correct.

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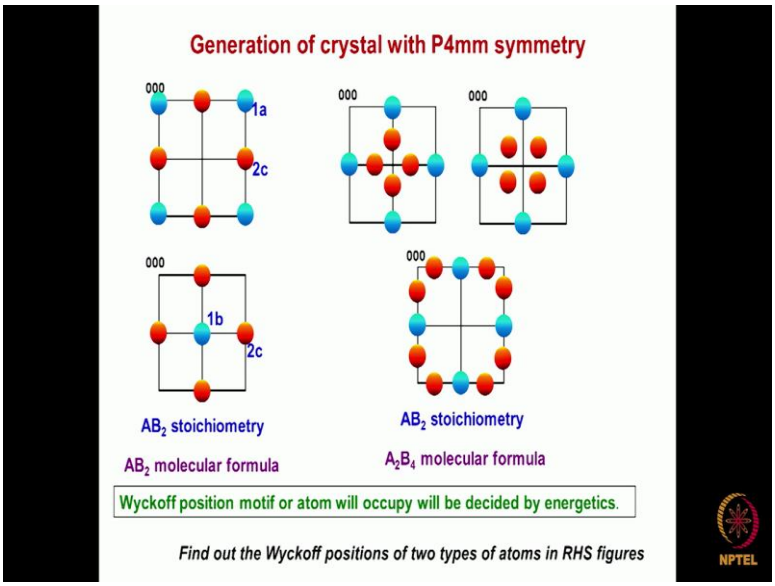

Now, I had just shown in this transparency. These possibilities which we have discussed here if we consider we have an A atom which is occupying the corner and the B atom is occupying the C position that is this is one position. In this particular case A atom is occupying the b position and c position is occupied by their b atom. So, these are all the 2 configurations because, sometime back or then the previous slide I showed it just with respect to a coordinate positions.

Now it is a graphical representation of it, now we can make out that these are all the 2 options which are available. So, which type of an option which is going to exercise will be determined by what is going to be the energetics? In this specific case if you try to look at it both these options are going to be the same. Because if I move the coordinate

from here to this position now I will be essentially generating this particular one there is no difference, here what I am considering it is not a 4.

Student: (Refer Time: 30:02).

B 8 it is a to b 4. So, if this is the molecular formula a to b 4 then a atom will have 2 equivalent positions, b atom will have 4 positions. In that case the a atom can occupy only the 2 c c position correct, the b atom can occupy 4 choices are there for you to occupy these positions correct. Which of the one which it will be actually in the particular crystal which option will be exercised or which type of a crystal structure will generate will be determined by the energetics. You have to look at the energetics of the all the 3 configurations for the particular atoms under consideration and which lowers the total energy of the unit cell that is the configuration which it will choose.

Student: It is not possible to occur a position and b position simultaneously for a b 2 structure.

A position and b position.

Student: This AB 2 [FL].

Yeah.

Student: First will put a (Refer Time: 31:29).

No, the first 1 has got in the unit cell 1 a atom that is a molecular formula only 3 atoms in the unit cell, that is 1 consideration another is you consider another set of a type of an atom 2 types of an atom were in the unit cell the number of atoms in the unit cell is 6, then what our positions which are possible in these 2 cases.

Student: No, write that a to b 4 [FL].

Yeah.

Student: A to b 2 means a should be 2 in 2 atoms in unit cell.

Yeah.

Student: So, for 2 means they therefore, these a has to be.

See.

Student: Put in a 2 c position you cannot put in a position and b site of position.

Because, as I mentioned if you the first rule which we have to follow in these is that no only 1 type of an atom can be put at one position. If you put it in another position then the symmetry of the lattice has changed now the space group symmetry is not the similar is not possible, that is why this is the only option which is available. The next class what we will discuss is how to construct a crystal with some examples. We will take it up we have just mentioned that using a crystallography how we can do it, it is essentially different types of crystal are which we know how using this table how various types of crystals could be generated.

We will stop here now.