Symmetry and Structure in the Solid State
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Lecture – 17
Additional Symmetry Elements (Continued)

So, let us look at the tetragonal and how the tetragonal representation takes place. This is a bit of a change from the triclinic, monoclinic and the orthorhombic. In case of a triclinic of course, we do not have to worry about a b or c, because a is not equal to b, b not equal to c, so we can take any of those three crystallographic directions. And In fact, there is no question of any rotation axis associated with that, and therefore, as a consequence we need not have to worry about the direction in which we fix the axis, because there are no options in case of trigonal

In the case of the monoclinic system we have that choice and the choice is either a b or c depending upon what two angles, we would like to take as 90 degrees and technically, and from convention it is always the b axis which is taken as the unique axis.

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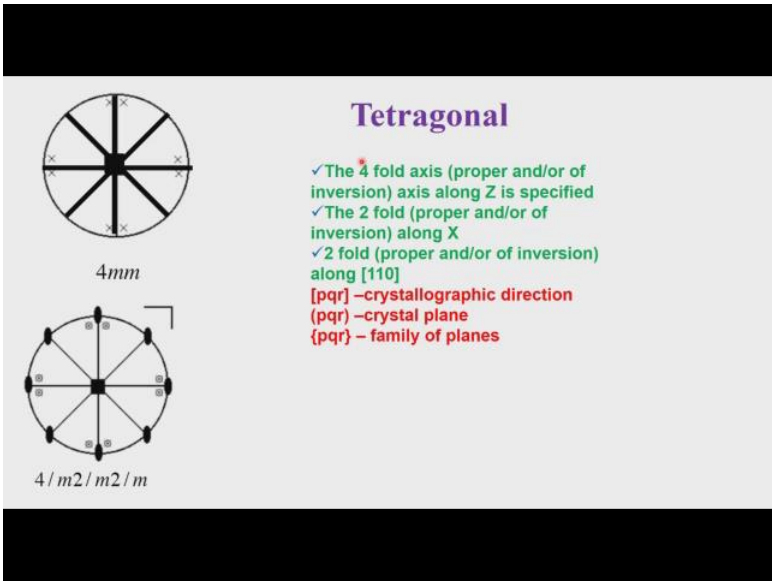

So, the Y direction is the direction in which the 2 fold axis exist in case of the monoclinic system, and therefore, we normally refer to this as the unique axis the b axis. It may be possible to have a different setting in a monoclinic system where we can also either a or c, in which case we have to mention the uniqueness associated with the 2 fold

axis. When we come to the orthorhombic system we have no choice, because a b and c all three are 2 fold axis and. So, the nomenclature is that first when we say a point group like 2 2 2, the direction is now along a, along b and along c, the three directions.

So, as far as up to the point of orthorhombicity is concerned, the order is a b and c. When we come to the tetragonal system the order changes and this is something which is not mentioned in any textbook and people forget about it, or with fact people are ignorant of it and that is where I thought I should mention that the 4 fold axis associated with the tetragonal system always comes in the middle beginning.

So, when you say a point group symmetry, when you see a point group symmetry starting with a 4 or any of the proper and improper inversion axis associated with the 4 fold axis, like $4/m$ or $\bar{4}$ or 4_1 4_2 4_3, then it means that we have a tetragonal system. So, tetragonal system is characterized in terms of the first number associated with the Z direction, we always have this along the Z direction.

The 2 fold is then in since we have 422 as a possible combination of 3 axis. See in tetragonal we can have only one 4 fold axis alone and that itself satisfies the condition required for a tetragonal symmetry; that means, a not equal to a equals b not equal to c, α β γ 90 degrees. So, that is a single axis operation.

We can also have the 3 axis operation as per the rules of the Euler's Theorem, then we have something like 422 which have already seen in the previous class, and in this case we have a proper improper, improper axis which is $4mm$. So, this combination is also allowed and then we the second 2 fold; therefore, or the mirror symmetry a represents a proper and or of inversion along the X direction. So, the 4 fold is along the Z direction, the next 2 fold or any associated 2 fold with mirror inversion and so on is along the X direction.

And then we the, that leaves us with the third 2 fold axis which is again proper or inversion, and that proper or improper and or inversion and that goes into the direction which is 110 in the crystallography nomenclature. What we mean by this 110 is, whenever we have a nomenclature like this in square brackets, it means that it is a direction in the crystallographic point of view. Suppose we have a crystal structure with a b and c as the directions, X Y Z are the directions to which a b and c will now coincide

in which case we will say [110] means 1 unit along the X direction, 1 unit along the Y direction and 0 along this. So, this represents therefore, a crystallographic direction.

So, this is a vector which is pointing out in a direction which is [110], characterized by [110]. Just to complete discussion on the nomenclatures if you have open square brackets, it is a crystallographic direction and if you have them in normal brackets, it represents crystallographic plane or planes the family of planes in that particular orientation. We will be discussing this in more detail when we go over to this space group nomenclature and beyond.

And particularly when we discussed the scattering coming from X ray diffraction, I think that context we will postpone the discussion on the nomenclatures here, just to, you should remember, and when we discuss it we will recollect that [pqr] in brackets, square brackets represents crystallographic direction; (pqr) in brackets, normal brackets represents a crystal plane and if you have this flower bracket, it actually talks about family of planes. And In fact, it is it is coming very often in higher symmetry point groups and we will discuss this again with respect to the crystal and the X rays diffraction conditions which follow as a consequence of it.

So, just remember that these are the nomenclatures you will find in text books and one has to be very cautious in looking at these brackets carefully, and then the meaning associated with those brackets when someone reads a, writes a technical paper in the area.

So, the tetragonal system therefore, can be 4*mm* which is essentially a proper improper improper axis, and in this particular case down here, it is 4/*m* 2/*m* 2/*m*. In fact4/*m* 2/*m* 2/*m* can also be written as 4/*mmm* and that is the shorter form of, this is essentially it means that we have a combination of a proper and an improper axis associated at each direction.

So, for this 4/*m* 2/*m* 2/*m* means that there is a 4/*m* symmetry associated with the Z direction and then a 2/*m* symmetry associated with the x direction and a 2/*m* symmetry associated with the direction [110]. So, this is how a tetragonal point group representation comes out. Having seen this let us go further into the trigonal system.

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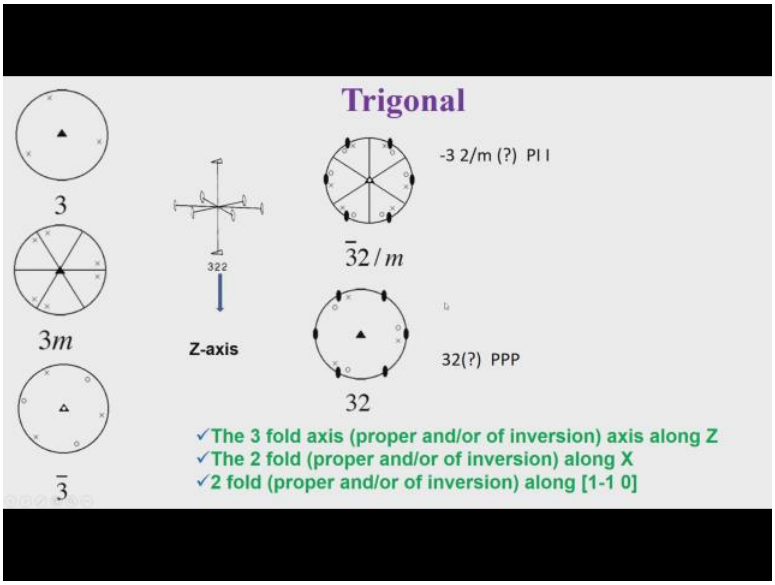

So, we see now that a similar nomenclature is utilized in the case of trigonal symmetry as well. So, the 3 fold axis proper inversion along the Z direction. So, now, the 3 fold takes the Z direction in that a representation, as we discussed in the case of a tetragonal symmetry the 3 fold will also be along the Z direction and it can stand alone, or it can be with a combination of two other symmetries like 322 for example.

So, here is an example where we see that there is actually standalone 3 fold, standalone $\bar{3}$ and then we have here 3*m*. Essentially it means that it is a proper and an improper combination, so; obviously, the third one will be also an improper axis which is not represents generally, and $\bar{3}2m$ now represents the presence of $\bar{3}2$/m which is proper and improper simultaneously and then the last one which is 32. I am just writing a question mark here, it was then saying that it is a proper improper improper or proper proper by improper or improper by proper, whatever that is, I want you to find out what could be the symmetry in the third direction given this nomenclature.

Similarly, in the case of 32, it is probably easier, because I have already written proper proper proper. So, that will tell us the issue associated with 322. So, basically what we are now representing, or the 5 possible point group symmetries that can be associated with a trigonal system and the Zdirection, is the 3 fold axis. The 2 fold axis is again along the X direction and the 2 fold which is proper and of inversion or whatever it just noticed that there is a change between the tetragonal and the trigonal system.

In the trigonal system it is 1T0, in the tetragonal system, it is 110. Let me point it out with a laser, it is 1T0, in the case of the tetragonal system, it was 110.

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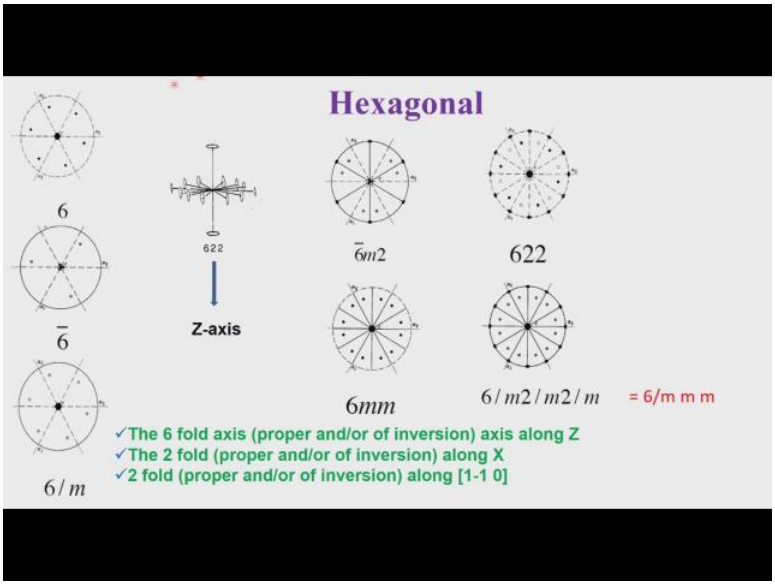

So, having seen the trigonal and a tetragonal which are represented in the corresponding 3 fold direction and the 4 fold, it is obvious that the hexagonal system will again have a Z axis, representation of the 6 folds symmetry. Remember when we did the point group symmetries which can exist just along 1 axis, we discussed the possibility of 2 3 4 and 6 and the 2 corresponds to a monoclinic system, 3 corresponds to a trigonal system, 4 corresponds to a tetragonal system and 6 corresponds to a hexagonal system. And therefore, we have 6 and $\bar{6}$ which are indicated here and along with that goes the 6 by m symmetry.

So, these are stand alone single rotation axis symmetries, but we can also have the combinations like 622 for example, which means that the 2 fold axis. Now again along X and the 2 fold proper are inversion again along 1T0. So, there is no much difference in their direction aspect, except that the symmetry is now controlled by the presence of the 6 fold axis compared to the trigonal system, where it was controlled by the 3 fold axis. In fact, there is not much of a difference between the trigonal and the hexagonal, we do not have enough time to go into the discussion of how the systems can be, for example, hexagonal can be also viewed as a rhombohedral system, may be now in one of the ta classes, this can be discussed the hexagonal to rhombohedral system.

And then how the rhombohedral system develops and both of them can be converted one to the other. This is something which maybe can, may can be done in one of these classes, but I generally feel that it is not immediately required for the continuation of this course. So, we will assume that hexagonal and rhombohedral are convertible to one to other.

I just want to take give you a take home lesson at this point. Find out the conditions of the rhombohedral system; that means, what are the relationships between a b c and alpha beta gamma and then you see that there could be a relation between the rhombohedral and the hexagonal system.

So, these seven point groups now belong to the 6 fold hexagonal symmetry, and these point groups; therefore, represent the stand alone symmetry axis and then the combination of 6 and 2 and 2 and the arrangement of the axis are shown here. So, depending upon the 6 fold symmetry we will develop 6 2 fold orientations on either side of the 6 fold symmetry direction which is the Z axis.

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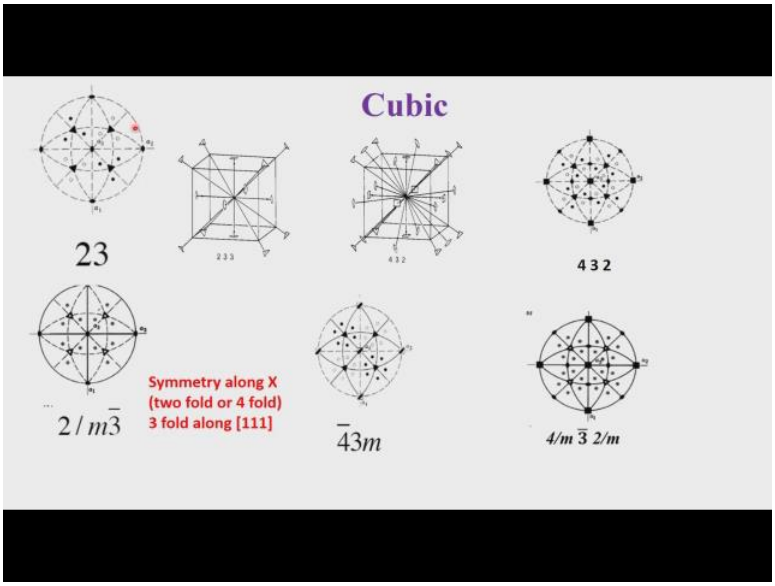

So, having seen this system, we now go to the system which is the most simple system, but most complicated to understand and that happens to be cubic system. The reason why it becomes a little more complicated to understand is, because that of the fact that the association of the rotation axis is not in principle with an origin and then the X direction, Y direction, Z direction. As you can see here in this particular case, you have a 233

represented in this particular diagram, which essentially outline say tetrahedral type of an arrangement and the cubic which is 432, it actually represents an octahedral type of an arrangement. So, here what we do is, we refer t; the center of the cube rather than one of the cube edges.

So, the symmetry information, the symmetry axis information will go with respect to the center here and as a result we have a 3 fold rotation, along the diagonals. And these 3 diagonals are shown here with a 3 fold rotation marked the on them, and then we will also have the 2 fold axis or the 4 fold axis in this particular case, which is along the direction, along the 2 fold or 4 fold; that is the symmetry along the X direction and then there is a 3 fold along the [111] direction.

So, what you see here is that the representation of the space group; therefore, which is now shown in the stereographic projection. So, the stereographic projection therefore, is with respect to the center of the cube and effectively you take this cube and put it inside this sphere, and mark these up and down points as per the definition of the stereographic projection as open and closed circles.

Then you will get the entire symmetry that is possible to be marked out on the stereographic projection and that is why the stereographic projection looks a little not so very easy to understand than the previous case. But if you look and compare this diagram with this diagram you will start saying the intersection points which are appearing here as different kinds of rotation axis.

So, in a in a typical cubic system we can have a 2 fold along the X direction or a 4 fold along the X direction. We will also have a compulsory 3 fold along the diagonal, the diagonal now is [111]. The presence of the compulsory 3 fold makes it unique associated with as a unique symmetry that is associated with a cubic system.

So, when we describe these possible 1 2 3 4 5 point groups with the cubic system, we have to consider the fact that we have the center now is associated with the center of the cube. So, the representation here is 23; of course, obviously, the third axis is also 3 fold axis which is not necessarily written here.

So, suppose you come across a space group which is 32 and then there is a come across the point group which is 32 and a corresponding point group 23, it is now easily

designable. So, if the axis number starts with 3 in the beginning; that means, it is a 3 fold axis which is along the Z direction. So, it belongs to the trigonal system in this particular case, the 2 fold is with respect to the X axis.

So, the first one is again in the cubic system, the first representation is along the X axis or the or the a direction, because a b and c are same in a cubic system we can call it as a rectangular system, because alpha beta gamma are also 90 degrees, so we can use X and a interchangeable here.

So, the 2 fold symmetry or the 4 fold symmetry in this particular case, the different point group symmetry in both these cases we use that as the symmetry, identify along the X direction. Now the fact that we get a 2 fold and a 4 fold along the X direction does not just stop that, because we have them. The curve following 3 fold symmetry here and a 3 fold symmetry here, once again you see there is a 3 fold symmetry and a 2 fold symmetry which comes along the [111] direction.

And this is the way in which we now identify the cubic point, point group, because if you have a compulsory 3 fold along in the second position throughout all the point group symmetry, the presence of the 3 fold are of course, the related inversion center or the related mirror symmetry. As in this particular case this is a $\bar{3}$, 3 and $\bar{3}$ bar are both associated with a single direction axis.

So, we have therefore, the presence of the 3 fold as a very common and unique representation and that will come always in the second position in the point of symmetry. And we will see that when we look at the associated space groups which will be a very large number in the case of a cubic system, because cubic system can support different kinds of lattices.

A cubic system will support a primitive lattice, it will re support a phase centered lattice, it will also support an eye centered lattice and as a consequence he get a large number of possible, lattice symmetries that can be associated with these point groups.

So, to cut the long story short, cubic is the most symmetric system one can think of. The distribution of the symmetry elements in the cubic system looks too very complicated, but it is fairly straight forward in the sense that it is either a 2 fold or a 4 fold axis along the X direction. The 3 fold compulsorily is along the [111] direction and then the third

direction could have either a 2 fold or a 4 fold. As we can see here it could also be; of course, a combination of a proper and an improper axis depending upon the rules which have been laid out by the Euler's Theorem.

So, it has to be PII or PP/I IP/I or whatever, so those combinations therefore, or allowed combinations to represent the cubic point with symmetry. So, this essentially now covers what we would like to have covered for the point group symmetries. The 32 point groups now are distributed to the seven crystal systems, and the seven crystal system characterization we have already analyzed with respect to their shell dimensions a b c alpha beta gamma. They are identified with respect to the crystal system.

There corresponding lattice symmetries have also been identified. For example, there is always a primitive lattice that will be associated with triclinic and nothing else. With a monoclinic symmetry we can have a primitive as well as the possibility of a C centered lattice, c could be either A or B depending upon the definition of the unique axis. If our unique axis is b, then it is always refer to the C centering of the lattice as the possible Bravais Lattice.

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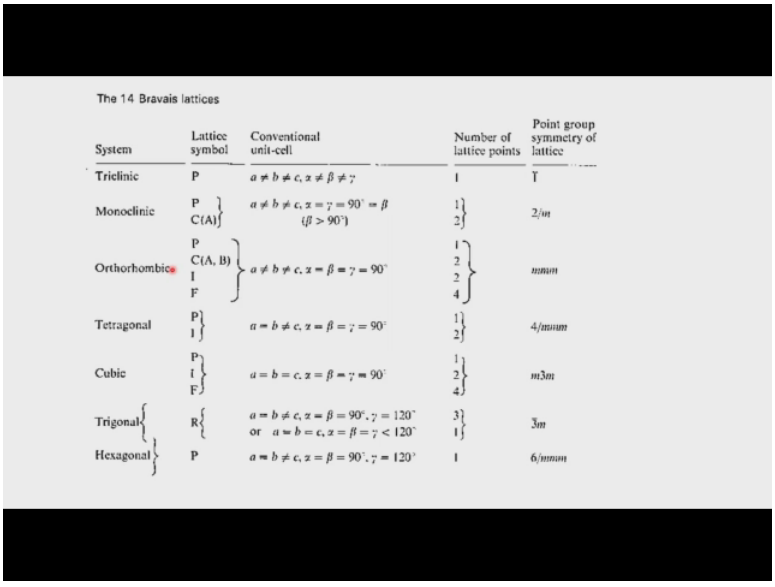

So, we therefore, have the next slide shows us the possibilities of what kind of lattices which we can associate with each one of the seven crystal systems. So, we have for example, here triclinic. Triclinic is associated with the lattice symbol P which is an

accepted symbol and then we have a b c not equal alpha beta gamma, not equal that is the definition of the unit cell. And then the number of lattice points.

We have one lattice point in the case of a primitive and the point group symmetry. See this is very interesting, we can have two associated trigonal symmetries with the point group; that means, two point group symmetries 1 and $\bar{1}$ are possible, but notice that the symmetry that is associated with the lattice is always $\bar{1}$. So, if you just look at a triclinic lattice and you are given the information only about the tricliniclattice by some experimental procedure which is always a $\bar{1}$ symmetry; that means, the lattice associated with the triclinic system is $\bar{1}$.

On the other hand the point group symmetries are 1 and $\bar{1}$, so this happens throughout, in these cases the highest symmetry associated with. You see here it is *mmm* is 2/*m*2/*m*2/*m* and as we go down, these highest point group symmetry is the symmetry of that lattice.

So, the lattice symmetry always keeps the highest possible point group symmetry associated with the seven crystal systems. So, individually we can have more than one point group symmetry associated with each crystal system.

On the other hand, we can also have the types of lattices differ. So, here for example, in the case of a monoclinic system, it could be a primitive lattice or a C centered lattice. So, this is the definition for the unique axis being b. So, β is always different than 90 degrees. The convention says that β angle is preferably greater than 90 degrees, modern day crystallographers, particularly people who just solved structures without thinking about what is going on.

They even report β angles less than 90, but crystallographic convention demands β to be greater than 90. There are lots and lots of publications in literature, particularly by chemist practice in crystallographic or somebody who takes crystallographic for granted or the mistake of the manufacturers and also the software people who have developed these packages, beta is all some many times reported less than 90.

But as a quality crystallography expert one should always have β greater than 90. In a monoclinic representation, this is a must and people should take care of it. So, those pay structures even which β is less than 90. Well there are certain things which they will be

missing particularly in terms of data completion and so on. This is something which we will discuss when we come to the experimental methods of structure determination.

So, the number of lattice points associated with a primitive moniclinic is 1 and a number that is associated with a C centered lattice is 2 and a point group symmetry, as we saw is the highest symmetry that can be associated with the monoclinic system which is 2/*m*.

Then we go to the orthorhombic system. In case of the orthorhombic system we have four possible lattices; the primitive lattice, the *C* centered lattice which could also be represented as *A* and *B*, *A* centered, as well as *B* centered the because a is equal to b is equal to c. Then we have the *I* centered lattice which is the body centered lattice and then the phase centered lattice.

Notice that the lattices are independent of the point group symmetries. So, the point group symmetry of the lattice is very high. Whereas, the lattice symbols will generate different types of lattices; that is number of lattice points. The number of lattice points associated will decide on the nature of the Bravais Lattice, but the point group symmetry of the lattice is the highest point group symmetry associated with the crystal system.

So, just by looking at the point group symmetry of the lattice, one should not conclude the point group symmetry associated with that particular crystal system, the crystal system still has 1 and $\bar{1}$. For example, in case of the triclinic lattice these are issues which one has to thoroughly remember and understand. In fact, understand it when once you understand it, you will; obviously, remember it, it is not given in any textbooks, so this is something which has to be learnt by practice and at this time you are learning from this course.

So, the four types of lattices that we can associate with an orthorhombic system the *P C I* and *F*, we will carry the number of lattice points like this. 1 for primitive, 2 for *C A* or *B* and 2 for the body centered which is X corresponding to X Y Z and half along X, half along Y, half along Z to be added to. So, that means, ½ ½ ½ is an additional lattice point along with the 0 0 0 which will generate one-eighth of the points around in the lattice. The *F* centered lattice will have 4; 1 corresponding to all the corners and 1 each for each of the phases *A B* and *C* which is centered.

So, we then go to the tetragonal system, in the case of the tetragonal system because a is equal to b it is a square lattice. We cannot have any independent centering associated with it, because of the fact that a equals b and not equal to c. We cannot have a *F* centered lattice, because the face centering will automatically move the *A B C*, because we you know the translational periodicity is operational here and therefore, we get only a *P* and an *I* centered lattice in case of the tetragonal system, we do not get any other type of lattices.

And this therefore, gives us the number of lattice points 1 and 2, and the maximum symmetry that is associated with the tetragonal symmetry is 4/*m* 2/*m* 2/*m* which is simplified and written as 4/*mmm*.

Obviously, you know we cannot have a combination of this kind, it has to be 4/m 2/m 2/m which will have both primitive and inversion associated with it. Then we have the cubic system, we have the case of the cubic system as *P I* and *F* and 1 2 and 4 and you see the symmetry is *m*3*m*; that is the highest symmetry one can have, 2/*m* 3 or 3/*m* associated with it and then (Refer Time: 27:16) symmetry. So, m 3 m is the highest cubic symmetry we can have. So, 3 and $\bar{3}$ are possibilities, but *m*3*m* is the symmetry; that is associated with the lattice.

Then we have the trigonal and the hexagonal system, as I mentioned that the relationship between these two is very subtle and it can be converted. For example, if you see the rhombohedral, there are two settings; one setting is actually the setting associated with the hexagonal system a equals b not equal to c ,alpha beta of 90 degrees and gamma is 120 degrees.

On the other hand the hexagonal system is a primitive lattice which is a equals b not equal to c alpha beta 90 degrees, gamma is 120 degrees. You see in the rhombohedral setting we have a equals b equals c alpha beta gamma are all equal and this should be generally less than 120 degrees and the highest point group symmetry; that is associated with this is $\bar{3}m$, and in this case it is 6/*m* 2/*m* 2/*m*. So, this generally tells us how we now distribute the crystal systems, the Bravais Lattices, the type of the lattice we define that is the unit cell convention or unit cells, the number of lattice points and the highest point group symmetry which is associated with a lattice.

Of course we can have one more column up here which will tell us the all the point group symmetries which we can associate, but I think we have already seen the separate table for that, which is always good to have within a separate table, which we have already seen several times.

And therefore, this now generally tells us that in a crystal system when compounds crystallize they have a 3 dimensional crystal; the property of the 3 dimensional crystal we have seen so far is the periodicity; that is associated with the crystal. The translational periodicity which therefore, invokes the presence of a unit cell and there are several possible unit cells associated with each one of these crystal systems which we have seen and with them are associated the Bravais Lattices.

So, in order to actually represent an object inside this unit cell we need to have all these satisfied. That means, let us say a molecule goes into a one of these crystal systems. The molecule will now face the possibility of having any of these Bravais Lattices, depending on any of these Bravais Lattices, the number of lattice points will change.

So; that means, that the lattice; that means, associated with, let us say the *C* centered lattice will have to have the same object, also appearing with respect to the *C* centering here. Again in the case of the *F* centered orthorhombic lattice, there must be four of those and, this is the way in which we have to associate the objects and these objects when once associated with the lattice points. Now we will go the corresponding point group identification, they will be already symmetry associated with the lattice.

So, now the possibilities of the other independent space groups will come up and depending on that the compound reorganizes itself. So, when a compound crystallizes in a 3 dimensional lattice of this particular kind, it faces all these restrictions. And because it faces all these restrictions it is now possible to find out the position of the atom or the molecule or the association the molecular assembly. Whether it is a small atom or a big atom or a big molecule or a small molecule, it does not matter, when once we are in a crystal system these are the rules which have to be followed without fail.