X-Ray Crystallography
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Lecture - 1
Geometry of Crystals

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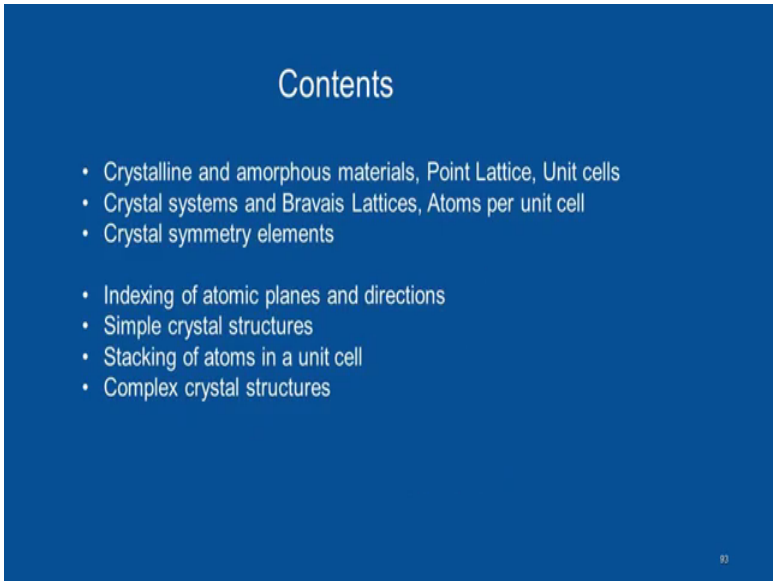

In this lecture I will talk about the geometry of crystals. A crystal is a three-dimensional material where all the atoms are arranged periodically in three-dimensions.

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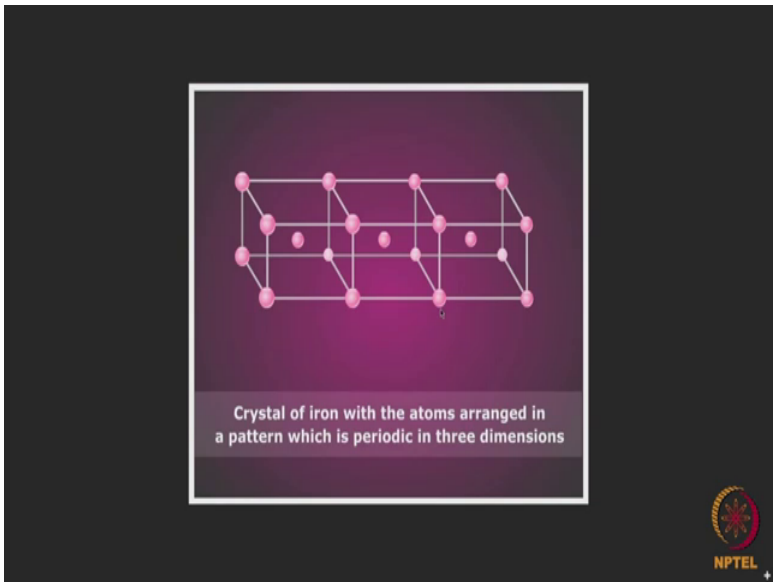

This is a crystal of iron and we can see all the iron atoms are arranged in a regular fashion within the material. Now as we all know matter can be crystalline as well as non crystalline, so there are materials in which the arrangement of atoms are not regular.

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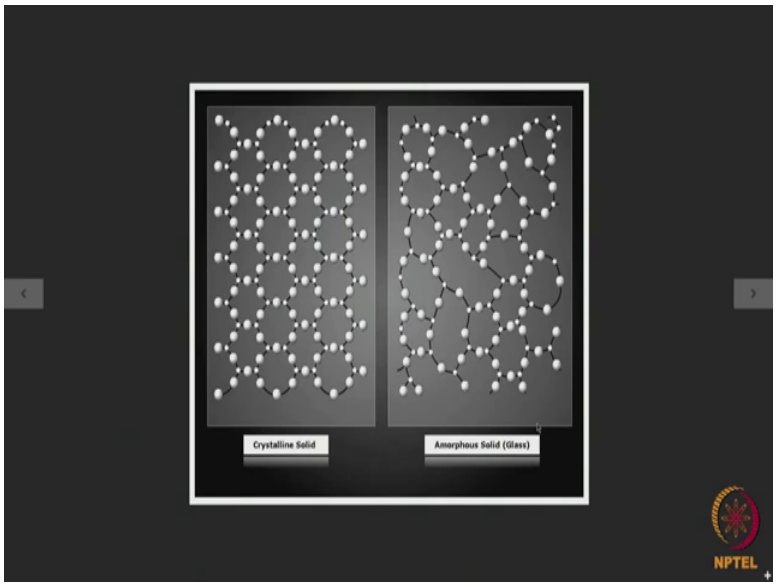

For example, this shows what a crystalline material looks like that we arrangement in a crystalline material and this is where an amorphous solid looks like say for example, glass.

Now, when we look at a crystal there are atoms at definite positions. Now if we consider the positions of the atoms and consider them as single points then a crystal looks like as an array of points only.

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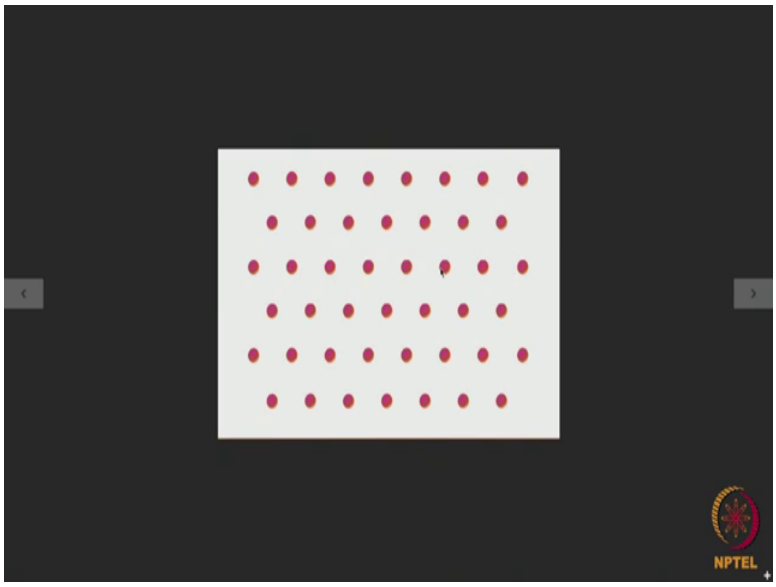

Say for example, here these are all the atoms that are present in a crystal. Now their locations if we look at only the locations, now and consider them as single points then this whole thing looks like an array or arrangement of points. But it is just not any arrangement of points there is some kind of an order in this arrangement. For example, if you look at any point in the array it has got about 6 other points surrounding it, now we go from one point to the other the pattern is the same; that means, here each point has got what we say identical surrounding. Now when we have got an array or arrangement of points in space where each point has identical surroundings we call that arrangement of points as a lattice.

Whenever we put atoms at each and every point of the lattice we build up a crystal. Now within a lattice or within a crystal we can figure out the smallest possible part which is a representative of the entire lattice or entire crystal.

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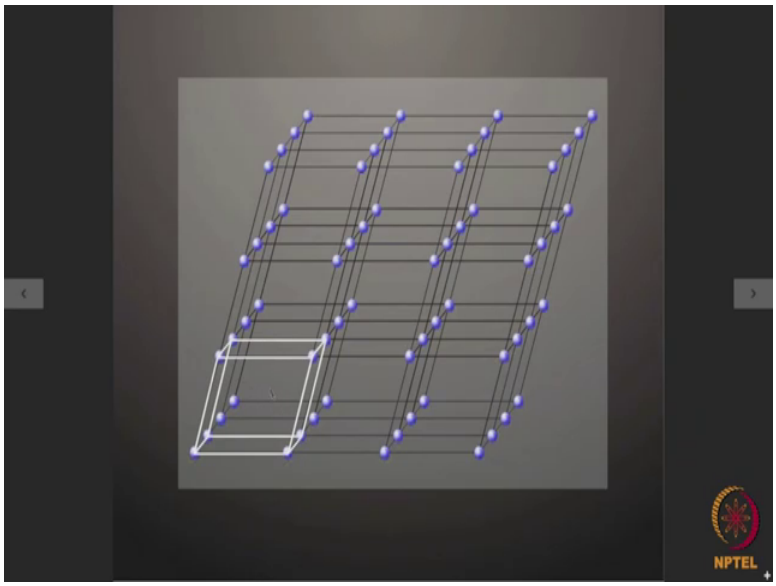

For example here we see this parallelepiped portion and the entire lattice on the entire crystal can be made up by translating this parallelepiped volume in every possible directions. Now this volume which is representative of a lattice or a crystal is known as the unit cell of the lattice or unit cell of the crystal. So, so far as this lecture goes I will use the word lattice and crystal in the same way. So, you know if I say the unit cell of a lattice it also means the unit cell of a crystal. Now the unit cell can be defined by some parameters.

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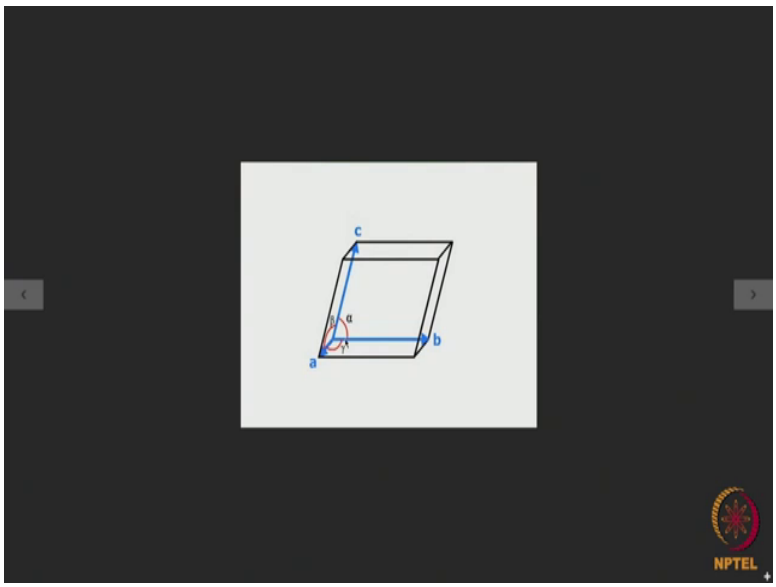

One way of defining a unit cell is by talking about these vectors a, b and c, we call them the lattice parameters. There is another way of saying the same thing if we find out the lengths of these vectors a b and c and if we at the same time specify the angles within those vectors for example, alpha which is the angle between the vectors b and c, beta the angle between the vectors a and c, and gamma the angle between the vectors a and b in that case the lengths a b c and the angles alpha beta and gamma define this volume completely. So, these are known as the lattice parameters of the crystal.

Now, all materials, all crystalline materials that we see under the sun depending on their unit cells these crystals can be divided in to 7 crystal systems so to say.

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And these are the cubic, the tetragonal, orthorhombic, rhombohedral, hexagonal monoclinic and triclinic. So, you see that there are 7 crystal systems. So, as I said already that a crystal system a particular crystal system is characterized by a particular shape of the unit cell. So, the unit cells of all crystalline materials in this world come in these 7 systems.

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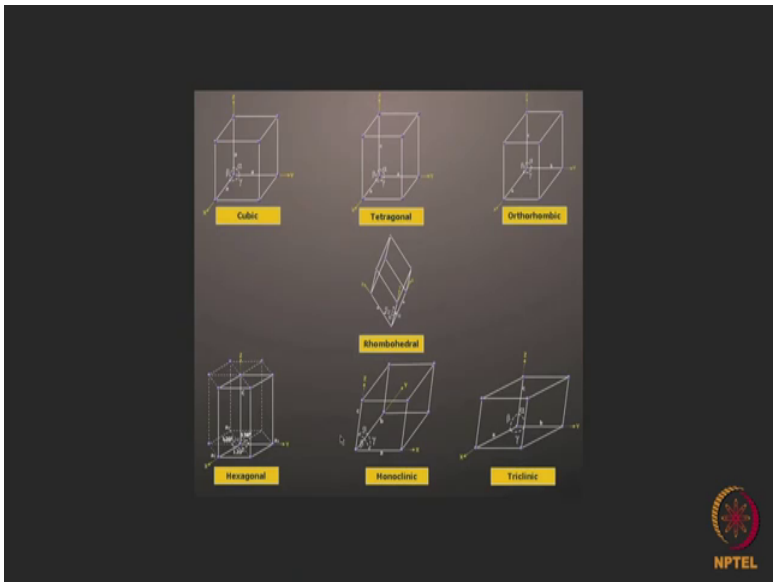

Now, if we look at the unit cells in the 7 crystal systems for example, this is the cubic we can say that the cubic system the unit cell is defined by the lengths a, a and a; that means, all these are equal along x y and z, and alpha beta and gamma these angles are all 90 degrees. When we talk about a tetragonal unit cell then we see that these two lengths are the same a and a along x and y the length c is different from the length a. So, it is a a c and the angles alpha, beta and gamma each one of them is again 90 degree. In case of orthorhombic unit cell the parameters along x y and z are all different. For example, a b and c they are not equal they are all different, but the angles alpha, beta and gamma in this case they are all each one of them is again 90 degrees.

Now in case of the rhombohedra system we see that the lengths again along x y z are a a and a which are same and the angles alpha, beta and gamma all are equal, but not equal to 90 degrees. When we talk about the unit cell of a hexagonal material a hexagonal material unit cell is defined by four axis along x y z and in another direction, say for example, along this direction the length is A 1, this direction the length is A 2, in this direction the length is a 3 all are equal and the length in the z direction is c which is different from the other three. And the angles between the lengths along x and y its 120 degrees the same for the others, same for the third one and these are this particular length along the z direction is perpendicular to this plane over here.

Now in case of the monoclinic unit cell we find that a b and c along x y and z 3 parameters are all unequal and amongst and no angles alpha, beta and gamma two are equal, are not equal to the third one, not equal to 90 degree in any case. In case of the triclinic unit cell we find that the parameters a b and c are all unequal and alpha, beta and gamma again all are unequal, non equal to 90 degrees. So, if we specify the values of the parameters a b c and alpha, beta and gamma we can easily find out what is the unit cell is like.

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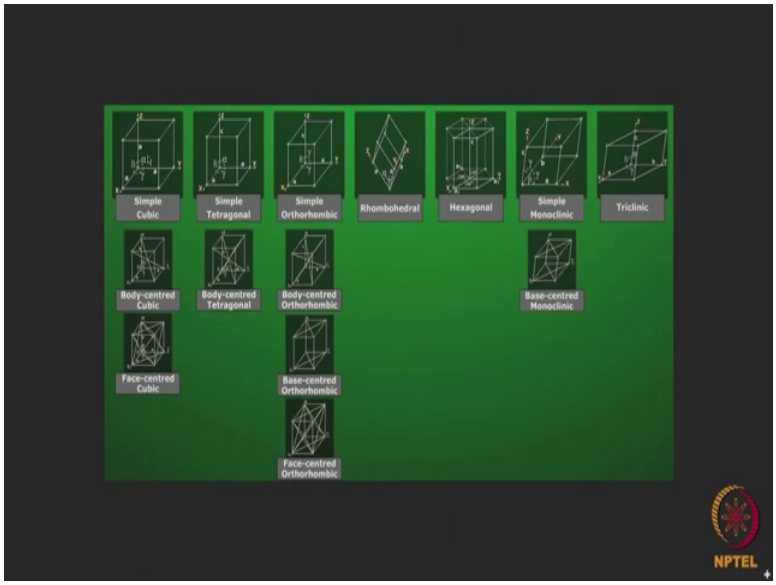

Now, there are 7 crystal systems as we have already found out cubic, tetragonal, orthorhombic, Rhombohedral, hexagonal, monoclinic and triclinic. Now if you look at the cubic system if we put a point right at the center of the body of the cube you know at the intersection of the three body diagonals then the lattice that is formed from that particular unit cell again satisfies the criterion of the lattice.

That means if we consider instead of a simple cube if we consider that we have a lattice where the unit cell is a cube with 8 corner points and there is a point right at the center and if it repeats in space the lattice that we get you know the array of points that you can get can also be called the lattice because each point will have identical surroundings. So, that is the reason why a unit cell with a body centered point at the center of the cube in the cubic system also satisfies the criterion of a lattice. Similarly if in the unit cell of the cubic system we put 6 other points at the centers of the 6 faces and then if this is an array

of points is built up by repetition of these unit cell then that array of points also satisfies the criterion of being called a lattice. So, out of the cubic system we find, we now have three different lattices - one can be called the simple cubic the other body centered cubic and the third the face centered cubic.

Similarly if we go to the tetragonal system there if we put a point right at the center of the unit cell of the tetragonal system and build up the lattice you know that will satisfy the criterion that each point will have identical surroundings. So, that is also a lattice a different lattice form the simple tetragonal. So, you see that in the tetragonal system, we can have a simple tetragonal unit cell we can also have a body centered tetragonal unit cell. In a similar manner from the orthorhombic we can find out a body centered orthorhombic base centered orthorhombic.

In a base centered orthorhombic we put two points at the centers of two opposite phases and this unit cell if it is repeated in space in three-dimensions we build up an array of points which also satisfies the criterion of being a lattice; that means, each point will have identical surroundings. So, this itself will be another lattice. In a similar way the you know body centered orthorhombic and face centered orthorhombic these are also different lattices.

Finally, in the monoclinic system if we put two points at the centers of two opposite faces then we can build up another lattice which is called the base center monoclinic lattice. So, if we now count the number of lattices for crystals that we have, so it is 1 2 3 4 5 6 7 8 9 10 11 12 13 14. So, now, we have got 14 different lattices which a crystal may belong to. These 14 lattices are known as Bravais Lattices. So, now, we can say that all the crystals that will come across in this word they will belong to 7 crystal systems the cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic, but in total there can be 14 different lattices to which they may belong, the 14 Bravais Lattices.

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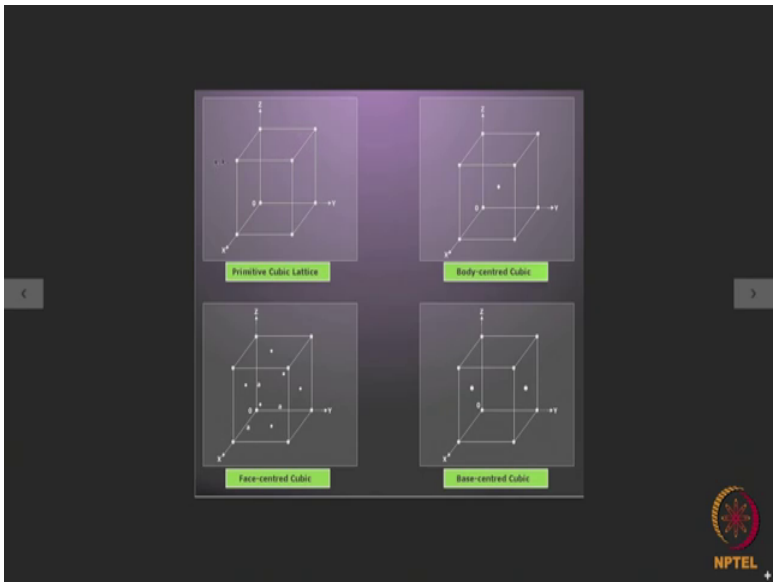

Now, if we look at a simple cubic unit cell in the simple cubic unit cell we have a point at each corner of the cube. Now in this case as we will see very soon when we talk about the entire cubic lattice each corner atom will be shared by 8 unit cells. So, as a result the contribution of one point at the corner to a particular unit cell will be 1 by 8. So, since there are 8 such points in the unit cell the total number of points belonging to this unit cell will be equal to 1 by 8 into 8 that is equal to 1.

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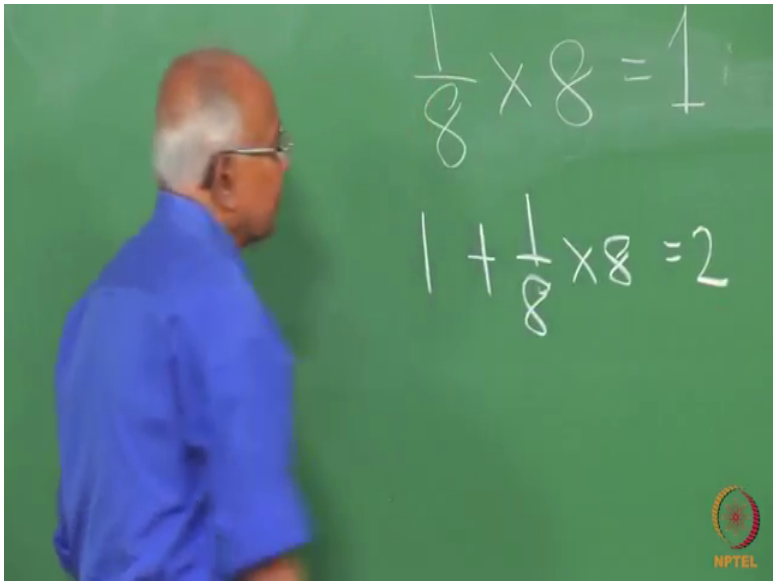

So, a unit cell which contains just one point is known as a primitive cell. So, this is a primitive cubic lattice or unit cell of a primitive cubic lattice or primitive cubic unit cell. Now when it comes to the body centered cubic lattice in addition to the 8 corner points we have a central point too, now this central point belongs only to this particular unit cell it is not shared by any other cell, but so far as the corner points are concerned each one is shared by 8 unit cells. So, what is the total number of points which belong to this particular unit cell the central point plus 1 by 8 into 8; that means, the total is 2. So, the number of points which belong to the unit cell of a body centered cubic lattice is simply 2.

Now when we talk about a face centered lattice the situation is different, now what happens is in addition to the points at the 8 corners we also have 6 points at the centers of the 6 faces. Now what happens to the face centered atoms you know this is a cubic unit cell we can put another cubic unit cell on top of it, so you see that this particular point can be shared by a maximum of two unit cells. So, so far as its contribution of this point to this particular unit cell is concerned it will be only half. So, we have got 6 such points and contribution of all these 6 points to this particular unit cell will be 6 in to half that is 3 and the corner points, 8 corner points will contribute as 1. So, we have 3 plus 1; that means, 4 points per face centered cubic unit cell.

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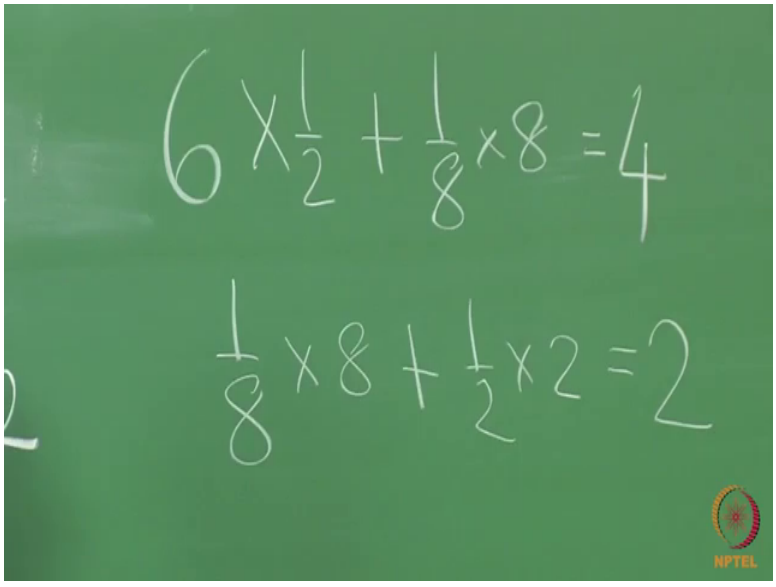

So, a face centered cubic unit cell will have 4 points per unit cell. When it comes to the base centered cubic unit cell what you find is each point on this face as well as on this face will be shared by two adjacent unit cells. So, the contribution of this point so far as this unit cell is concerned is half whereas, the contribution of this is also half. So, these two will constitute one point for this particular unit cell and then add up the contribution from the 8 corner points. So, that will make it 1 by 8 in to 8 that is 1 plus half into 2 one; that means 2 points per unit cell.

So, we now see that a primitive cubic unit cell contains one point per unit cell, a body centered cubic unit cell contains two points per unit cell, a face centered cubic unit cell contains four points per unit cell and the base centered cubic unit cell contains two points per unit cell. Now I already told you that each corner atom each corner point rather of a cubic unit cell will be shared by 8, a total of 8 unit cells.

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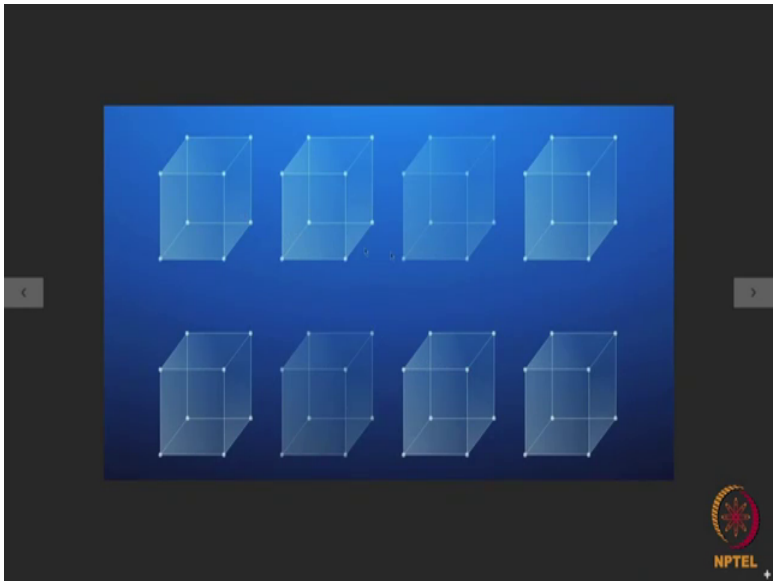

So, here I have got the 8 unit cells separately and then I combine them like this.

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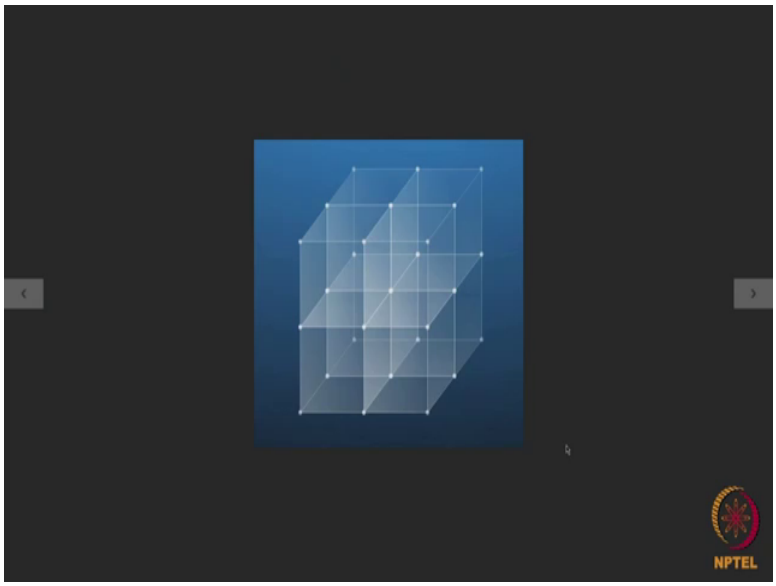

So, you can immediately see that each point each corner point will be actually shared by four unit cells at the bottom and four unit cells at the top; that means, each corner atom will be shared by a total of 8 unit cells which means that the contribution of each point to a particular unit cell will be only 1 by 8. A primitive unit cell that means, unit cell containing just one point is denoted as P it is written as P.

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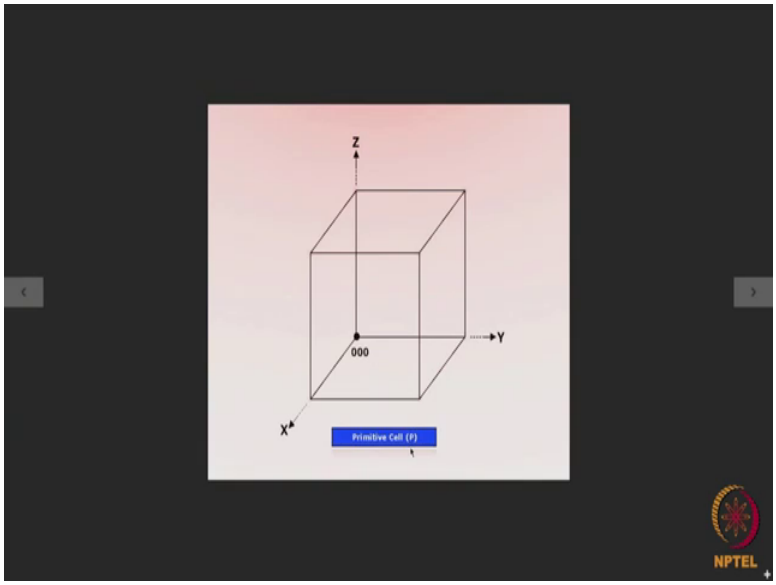

Now, this is a primitive unit cell in the cubic system. So, as we all know this is contained only one atom. Now, so far as or only one point you see I am talking about points and

atoms in the same way because ultimately when you have a lattice containing points and when you put the atoms at any point of the lattice it becomes a crystal. So, it is the same thing. Now in a primitive unit cell as we all know we have got one atom or one point per unit cell.

Now we know that in the primitive unit cell we have a total of 8 points at the 8 corners, but although there are 8 atoms of 8 corners we have seen that each corner to be shared by 8 different unit cells. So, the total contribution of those 8 is only 1. So, which one to choose for this particular unit cell, now people have decided this will refers are decided that the point or atom at the origin will be considered to be the point or the atom belonging to this unit cell. So, this point over here will belong to some other unit cell this point over there we belong to another unit cell etcetera etcetera.

Now when we look at the origin, origin what are the coordinates of the origin? 000. So, we say that in the primitive unit cell there is only one point or one atom per unit cell and the coordinates of that of the position of that point or atom is 000. Now when it comes to a non primitive unit cell that means unit cells which contain more than one point or one atom say in this particular case it is the face centered cubic unit cell written as F.

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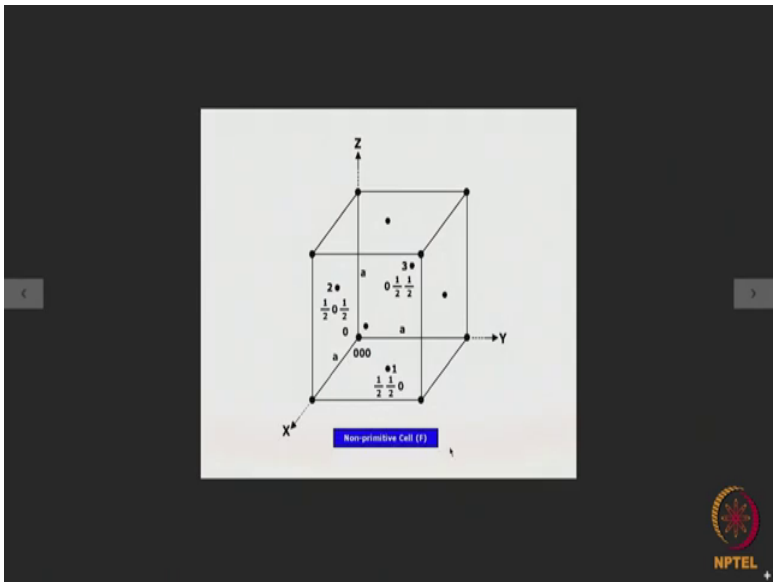

Again here there are 8 atoms or points of the 8 corners and as we have already seen that the total contribution of this 8 is only 1 to this particular unit cell, so we consider that that one atom is our point lies right at the origin with the coordinates 0 0 and 0.

What about the other 6 points or atoms at the centers of the 6 faces? We know that the total contribution of those 6 atoms or points is only 3. So, far as this particular unit cell is concerned. So, we have to assign three face centered atoms to this particular unit cell. So, what we do? We assign the point or atom at this point one, another one at this point two, another one at this point three to this particular unit cell and what are their coordinates? Now if you want to reach this point one from the origin you have to move half the lattice parameter along a, then half the lattice parameter along you know I am sorry you have to move half the lattice parameter along x then half the lattice parameters along y and then do not move at all. So, the fractional coordinates of the point one are half, half, 0.

In a similar way when you look at the atom on the points at the position two what are the fractional coordinates? We move half the parameter along x, do not move along y at all and then move half the lattice parameter along the vertical axis. So, the fractional coordinates of point two or atom two is half 0 half. In a similar way the point of the atom at three it has got the fractional coordinates 0 half half. So, if we have an FCC unit cell it will have four points or four atoms located at 000, half half 0, half 0 half and 0 half half. Then we come to another non primitive cubic unit cell this so called body centered cubic in itself written as capital I.

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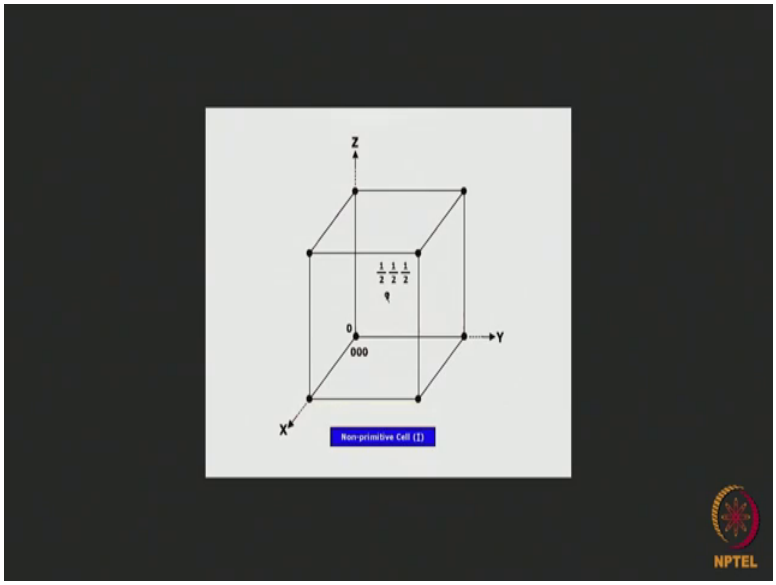

Now, in this case there are two points on atoms per unit cell. So, this one at the origin it represents the contribution from all the 8 corner points and there is another one which belongs solely to this unit cell the one at the body center.

So, the total number of points or atoms belonging to the body centered cubic unit cell is therefore, one at the location 000 and the other at the location of half half half, you say this point or atom has got the fractional coordinates half half half why, because in order to reach this point from the origin. You move half the lattice parameter along X another half the lattice parameter along Y and again another half the lattice parameter along Z. So, this makes this point half half half. So, the two points belonging to this BCC or body centered cubic unit cell are located at 000 and half half half.

Now whenever we talk about a crystal or whenever I talk about the unit cell of the crystal we find that it has got some symmetry elements associated with it. For example, a human body we can consider a plane of symmetry passing through the human body, so if we consider a plane cutting through my body here the right hand side and the left hand side these are mirror images of each other. So, I can consider that there is a plane of symmetry passing through my body, so this is a symmetry element. Similarly there can be access of symmetry center of symmetry etcetera etcetera. Now so far as the symmetry elements are concerned these are one a plane of symmetry and the function of a plane of symmetry is to cause reflection.

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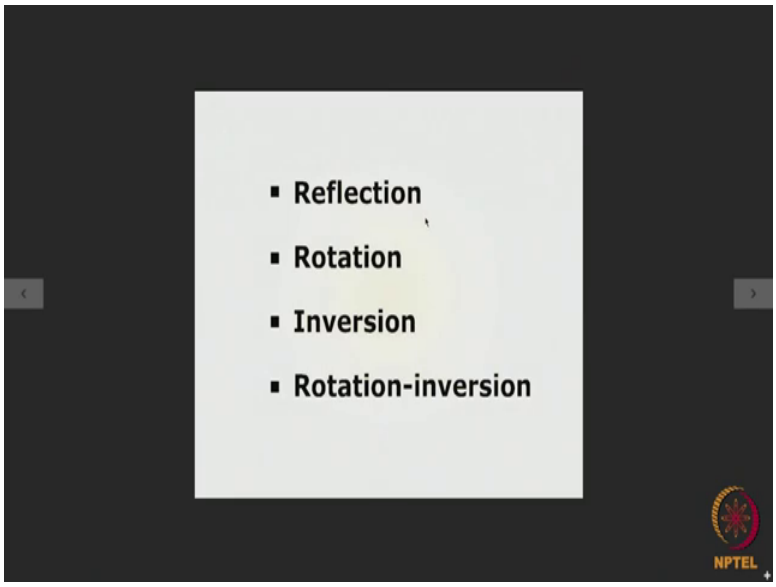

Then we can consider another kind of symmetry element which is an axis of symmetry and which causes a rotation to take place and then there is a part symmetry element which is known as center of symmetry or which causes inversion and there can be another axis of symmetry which is known as rotation inversion symmetry axis which causes rotation and inversion both. Now I will explain all those with the help of diagrams.

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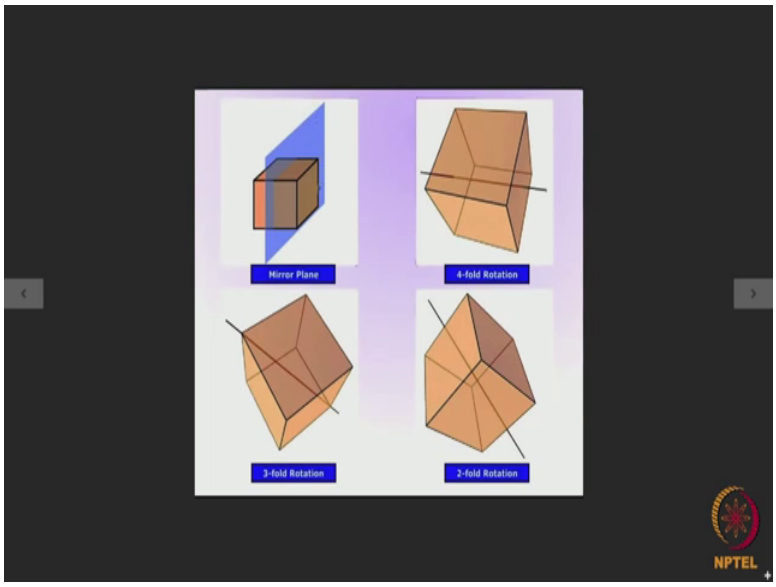

So far as the plane of symmetry is concerned a plane of symmetry will divide the unit cell of the crystal into halves one be the mirror image of the other that is why is also called a mirror plane. Then this is what is known as a fourfold rotation axis. So, if you have a cube and if you have an axis passing to the centers of two opposite faces then if we rotate the cube by 360 degrees around this axis the unit cell will occupy the same position in space four times, that is why we say that this axis is a 4-fold rotation axis.

Again if we can consider an axis passing through the opposite corners of the cubic unit cell and if we rotate the unit cell around this axis by 360 degrees then the unit cell occupies the same position in space three times. So, this axis is known as a 3-fold rotation axis.

Similarly, if we can consider an axis passing through the centers of the two opposite edges of a cubic unit cell then if we rotate this unit cell around this axis by 360 degrees

will find that the unit cell will occupy the same position in space two times. So, it is called a 2-fold rotation axis.

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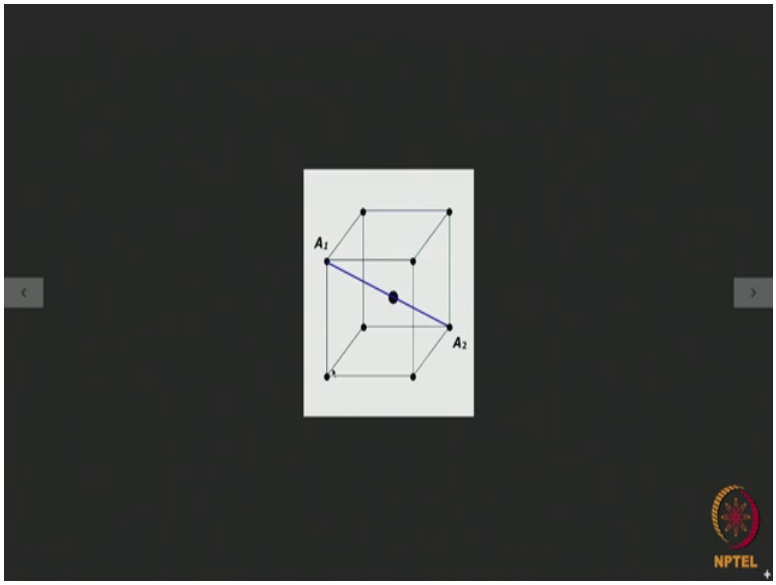

Now, if we consider a primitive cubic unit cell like this say we have, we consider the point a one over there we know that there will be a point A 2 on the other side. So, in this particular case we say that there is a center of symmetry in this unit cell. So, because of the center of symmetry you know if you have a point over here you will have another point on the opposite side.

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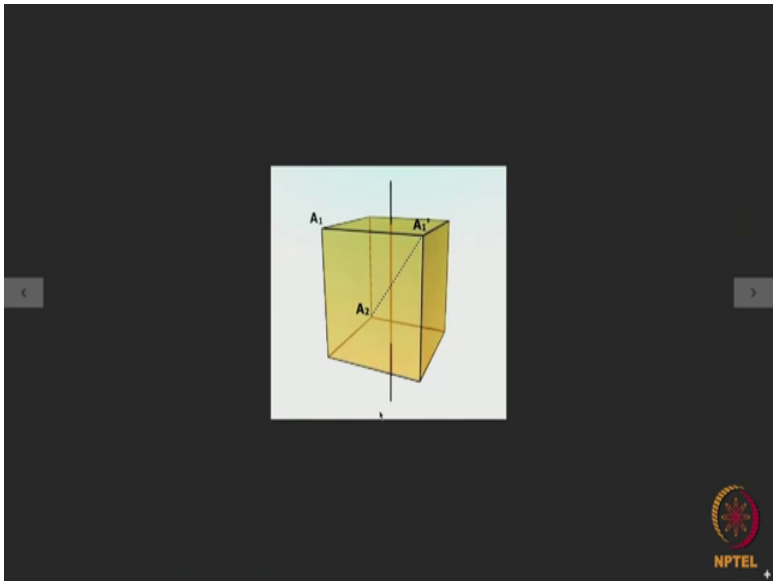

Now, this is what is known as a rotation inversion axis. So, as I told you earlier a rotation inversion axis does two things- it rotates and at the same time inverse. So, if the cubic unit cell say if we look at a point in this corner then if this axis passing through the centers of this opposite faces if it is a rotation axis a 4-fold rotation axis then due to rotation the point A 1 after 90 degree rotation should come to this position A 1 prime and if right after that this also gets inverted through the center of symmetry the point becomes A 2 after being inverted from A 1 prime to A 2. So, you see that because of the function of this kind of rotation axis from point A 1 will get the point A 2.

Now, there are a minimum number of symmetry elements which will catalyze a particular crystal system and these are all tabulated here.

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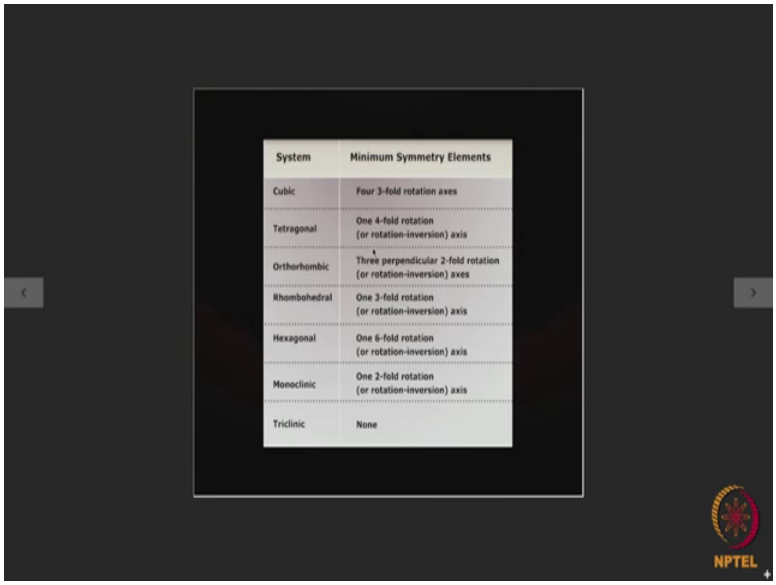

For example a cubic system is one in which there should be a minimum of four 3-fold rotation axis and the tetragonal one should have one 4-fold rotation or rotation inversion axis, an orthorhombic one must have three perpendicular 2-fold rotation or rotation inversion axis these are the minimum symmetry elements that is the system must have. A rhombohedral system must have at least one 3-fold rotation or rotation inversion axis, hexagonal system must have at least one 6-fold rotation or rotation inversion axis, a monoclinic system must have at least one 2-fold rotation or rotation inversion axis whereas, a triclinic system has none of the symmetry elements present.

I will now come to the question of naming an atomic plane. You see when we look at a three-dimensional crystal say a cubic crystal there are 6 different faces in the cubic unit cell. So, we can consider that 6 different crystal planes. Now they are all identical. So far as the crystal is concerned you know it does not recognize any difference between the 6 faces, but so far as we are concerned when we are dealing with crystals and crystalline materials it is needed to find out you know which plane is which; that means, we have designed a method by which we can name a particular phase. So, the cubic unit cell it has got 6 different phases and we have to name all those 6 different phases so that we can identify one from the other. So, I will now discuss how this is done.