Advanced Ceramics for Strategic Applications
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Lecture -3
Crystal Structure

Having made some introductory remarks about the ceramic materials in general and differentiating between traditional ceramics as well as advanced ceramics and also giving you some idea about the compounds, the particular chemical compounds, whether they are ionic in nature or coherent in nature; who are known to be ceramic materials, which are used extensively as ceramic materials. Our next course of discussion will be on the structure property relationship. In fact, throughout this course, we will be taking up the structure of different materials and these structures, how they give rise to different properties. That will be one of our major points of discussion.

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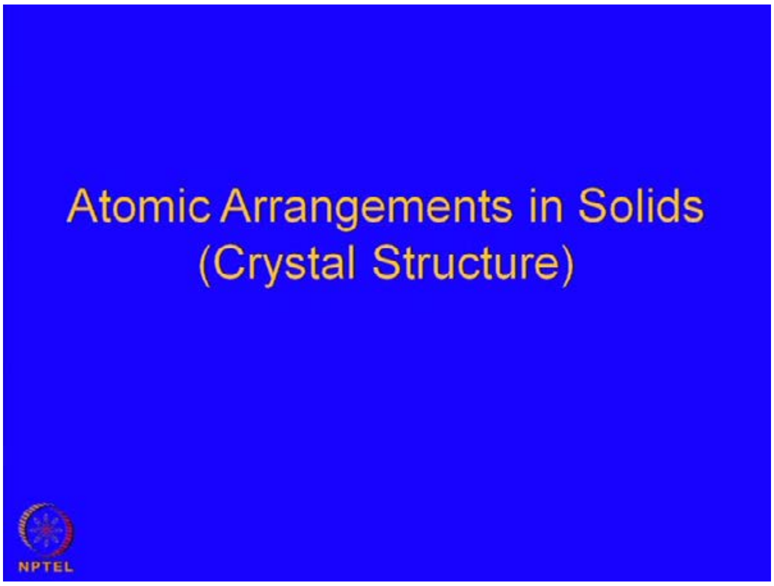

Atomic Arrangements in Solids
(Crystal Structure)

So, to start with, let us try to understand what do we mean by structures, particularly the crystal structures and what are the different structures in which many of these oxides or ceramic materials in general crystallizes. In fact, by structure, we are meaning at this point of time as the crystal structures or the atomic arrangement of the different elements present in the particular compound. So, we will be discussing about the crystal structure of different oxides as well as other compounds. Before that let us see what kind of atomic arrangement we can expect in different kinds of solids.

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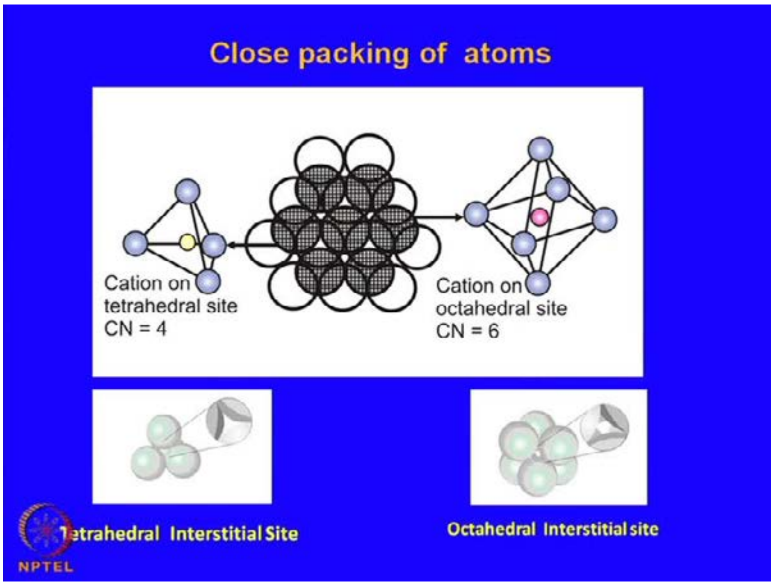

Close packing of atoms

Cation on tetrahedral site
CN = 4

Cation on octahedral site
CN = 6

Tetrahedral Interstitial Site

Octahedral Interstitial site

Here, we are discussing about the close packing of atoms. For our purpose, we will be always discussing or will be considering the atoms as solid spheres, so that you can understand their geometry and the kind of packing they can have under different conditions. In this case, you have two layers of atoms. One is the white layers; they are closely packed, in fact closest packing. They are brought together as close as possible without any further compression or any further closing by, so they touching each other. In fact, these are spheres. Of course, in two dimension, you are seeing only the circles. The circles are touching each other. So, around a particular atom or a circle, there are six such circles, so that they come close to each other.

In three dimension, we will have number of layers of such close packed layers or close packed arrangements. So, while the white ones may be the base one, base layer, on top of that, there is another layer, the black ones. So, the black ones have been placed over the white ones. But, they are not exactly on each other. So, the black ones are not exactly vertically over the white ones. They are actually placed about 120 degree, the rotation, so that on the (( )), prepared or made by the arrangement of the first layer, the top layer sets. As a result, you get different kind of interstitial spaces. So, you have the bottom layer as well as the top layer and in between, we have some interstitial spaces. Now, the interstitial spaces, around each interstitial space, the number of atoms are actually not equal. In some of them, we have what we call a tetrahedral. A tetrahedral is formed by making a close packing arrangement of the bottom layers. These 3 are in the bottom layers and this one is in the top layer. So, in between you have a space. You have a space which is not filled up by the atoms, whereas, there is another kind of space which is also created, interstitial site is also created by the same structure or the same arrangement of two layers, two close packed layers, in which you see a bi pyramid kind of thing.

In the middle layer you have 4 atoms. These four atoms in the middle layer touching each other. Of course, for clarity, we have not shown them as touching each other, but actually in this structure, they are touching each other. Whereas, even if they are touching each other at the surface, you will get some space in between and that is another kind of interstitial space and in this case, the number atoms surrounding this particular interstitial space is 6. Not 4 and this is called the octahedral site or the particular interstitial site as an octahedral code inertion. So, this is actually the code inertion number of this interstitial site is 6, whereas there is another set of interstitial site which has a coordination number of 4. In this case, it forms a tetrahedral and in this case, the atoms form an octahedral. So, coordination number in this case is 6 and the coordination number here, it is 4. This has been a exploded view of this tetrahedron is shown here and a exploded view or actual size or actual arrangement of the octahedron is shown here. So, this is the octahedron and this is the interstitial site, which is magnified in this part of diagram. Here, it is the tetrahedron, the tetrahedral site which has been magnified here. So, we have two different kind of interstitial sites created by bringing together two close packed layers. So, that is one of our primary considerations for understanding the structure of different materials and different oxides in general.

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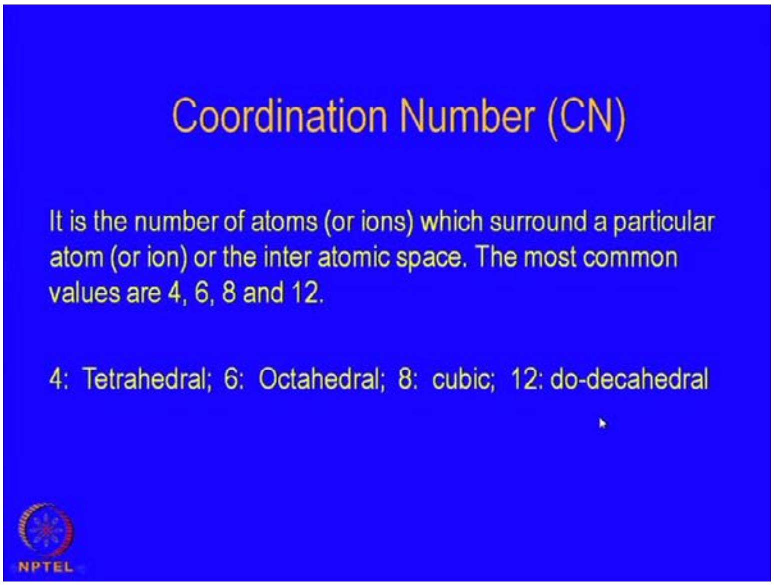

Coordination Number (CN)

It is the number of atoms (or ions) which surround a particular atom (or ion) or the inter atomic space. The most common values are 4, 6, 8 and 12.

4: Tetrahedral; 6: Octahedral; 8: cubic; 12: do-decahedral

So, the coordination number, the definition of coordination number is like this. This has been just discussed. It is the number of atoms or ions which surround a particular atom or ion or inter atomic space. So, it may be space or that particular space may be occupied by a second atom or second ion. So, the coordination number refers to the site or if the site is occupied by a particular atom or ion, the coordination number refers to that particular atom or ion. The most common values of coordination number are 4 as we have disused in case of tetrahedron. If it is octahedron, it is 6. Then there will be some arrangement where the coordination number, particularly a cubic arrangement, the coordination number is 8 and then there may be situation, where the coordination number may also 12. We will look into these possibilities later on, but these are different kind of coordination number and these are the polyhedron formed around that particular space, the tetrahedral, octahedral, and cubic or do-decahedral. So, this kind of coordination number, we will be disusing this coordination number time and again, when we discuss these structures.

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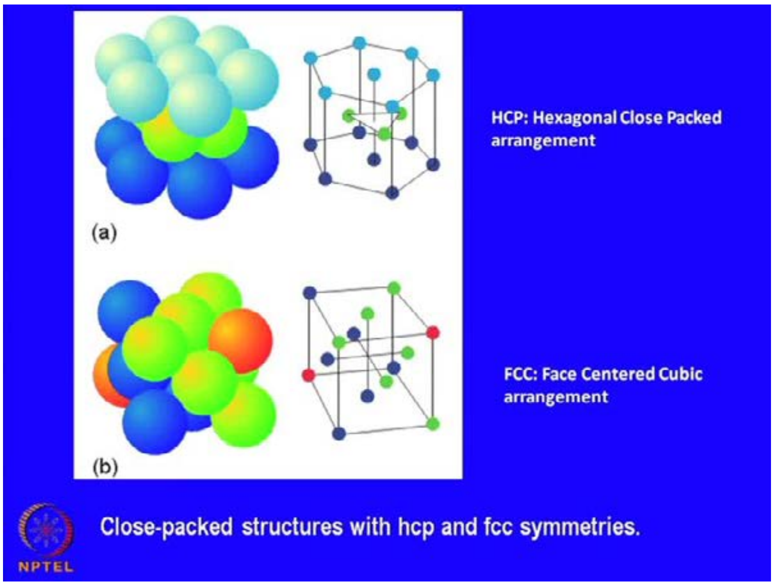

HCP: Hexagonal Close Packed arrangement

FCC: Face Centered Cubic arrangement

Close-packed structures with hcp and fcc symmetries.

These are another way of looking at the same layers. Here, instead of two layers, you have three layers. This is the bottom layer. This is a little bit of three dimensional view and this is the middle layer on top of that and there is another layer, the third layer on the top of the second one. So, they are all touching each other, either both in the vertical direction and in horizontal direction. So, that is what you call the closest packing possible. When you put the third layer, there are actually two possibilities. There is a half center, when you put the second layer over the first layer. The second layer is here; whereas the first layer is slightly half center and third layer, you can see here, it is exactly vertical above the first layer. In this particular structure, the third layer may be exactly vertically above the first layer.

So, if we call this layer that is A layer, middle layer is the B layer, the third layer, the top layer, you can call it A layer which is equivalent to the A layer. So, in a stacking arrangement, as if the whole structure, the whole space is being filled up with the atoms arranged in a particular manner and if you stack one up the other, one layer after other, then this is A layer, this is B layer and this is again A layer, which is equivalent to the bottom layer. So, this arrangement gives rise to a symmetry and you can draw this kind of a geometric, three dimensional geometric body or in short, we call it unit cell, which actually can repeat itself in all the three different directions to fill up the complete space. So, this particular geometry is a, what is called the hexagonal geometry or hexagonal close packed arrangement. The atoms are arranged in a hexagonal close packed arrangement. So, for clarity, this has been shown here as smaller atoms. They are not touching each other in this direction. But, in actual practice, in reality, they are touching each other. We are just trying to represent the same picture over there. So, you have a hexagon on the top, another hexagon on the bottom and the middle layer is actually not forming a hexagon, but it is a triangle.

So, they are in between the top hexagon and bottom hexagon. So, there are three layers, three atoms, of course within this particular volume of the solid and then these are in the form of a hexagon. So, that is the reason we call it hexagonal close packed arrangement. There is another arrangement. It is also very simple geometry. In this case, of course the layers are slightly inclined. Layers are not horizontal layers, but you can see, this is one layer, the green one is one layer; blue one is another layer and the orange is another layer. Orange has one layer, only one atom and other atoms are missing here. Has not been drawn. The green one is, there are 6 layers, 6 atoms and this also has 6 atoms, but it has been in a different orientation. Whereas, the bottom one, there will be another bottom one, which is equivalent to the orange one in the top. So, actually there are 4 layers in this compared to 3 layers in the top.

So, if we take this as A layer, this becomes B layer and this is not equivalent to the A layer. It is not vertically above the E layer. In fact, it is a third position. Third position, where it can go? So, it actually goes to the third orientation and it becomes A layer, B layer and C layer. So, it is A B C packing. So, this orange atom and the orange atom down are equivalent. So, although there are 4 layers you have arranged, but actually, 3 of them are distinctively different and one is equivalent another one. So, 4 layer forming a stacking of what you call A B C, A B C stacking. So, this A B C A B C will repeat itself. In this case, the earlier one, the hexagonal one, A B A B will be repeating, whereas in the bottom one or in the case of cubic arrangement, the symmetry here is not hexagonal. The symmetry here is cubic and it is face centered, so we call it face centered cubic. Why it is called face centered cubic? These are forming a cube and at each corner, you have atoms and also at the center of each face, if you draw two diagonals on each of the faces, at the center of each face, there will be another atom.

So, this is another way of representing same structure. It is not in the form of a stacking arrangement, but in the form of a unit cell, what we call the unit cell and this is a smallest unit of that volume, which can repeat itself in all the three different directions, A B C directions and fill up the complete space. So, in case of this arrangement, this hexagonal unit cell will repeat itself, whereas in case of this A B C A B C stacking, the cubic arrangement will repeat itself. So, from the same closed packed structures or close packed atoms, just by reorienting or rearranging themselves, you can have two different symmetries. One is hexagonal close packed and another one is face centered cubic.

The volume packs are occupied or the open space in both, the structures is same. If you can calculate what is the volume fraction of this space, which is empty because of this curved nature of the atomic surfaces, there will be some empty space and that empty space is exactly the same because both of them have the close packed arrangement. So, that also you have to, one have to remember, although the unit cells are different, the basic symmetry is different, but that is because of both of them have the close pack arrangement. All the atoms are touching each other in the closest possible manner. Therefore, the volume fraction occupied by the solid is same or in other words, the open space available is also same.

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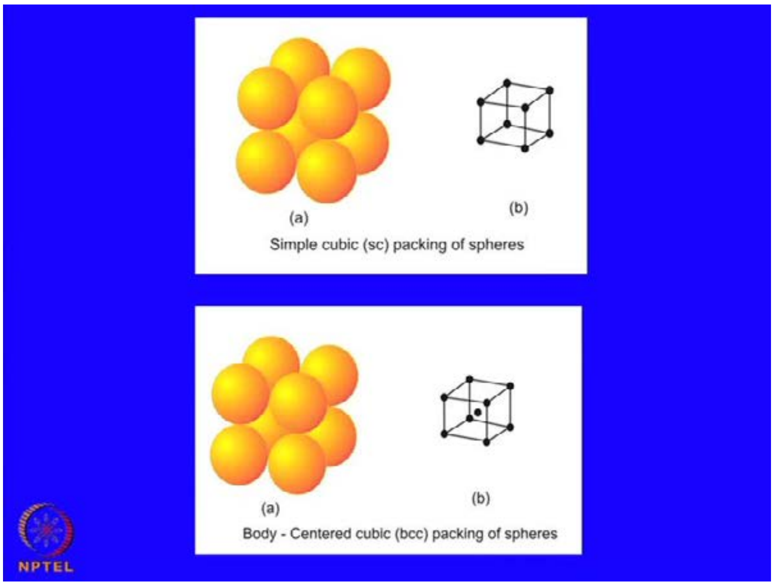

Simple cubic (sc) packing of spheres

Body - Centered cubic (bcc) packing of spheres

These are few other arrangements which may not be completely close packed. They may be touching on one particular direction, the atoms may be touching in one particular direction or more than one particular direction, but they may not be touching in all the directions. So, in some layer, they may be touching each other and in others, they may not be touching each other. So, they are relatively open structures, but they have also certain amount of symmetry and this is another kind of symmetry or the arrangement of atoms in which some compounds may be available. This is what we call a simple cubic.

Simple cubic is nothing but you have the cube. If you draw a cube, and at each corner of the cube, you place one atom and that will give you the simple cubic structure. If you can imagine, you will find that it is not fully close packed. It has relatively some open space. There are some more open space in the structure, in the arrangement than what we get in the close packed structure, which we had discussed earlier. There is another open structure, which is called body centered structure. Again, it is a cubic symmetry. You have 8 corners are occupied by the atoms. In addition, at the center of the cube or where the 3 body diagonal intersects, at that point also you have another atom. So, that is the reason this particular symmetry is called body center symmetric or B C C. So, H C P, F C C, then S C, simple cubic and then body centered cubic or B C C. These are 4 very important structures, in which the materials crystallize.

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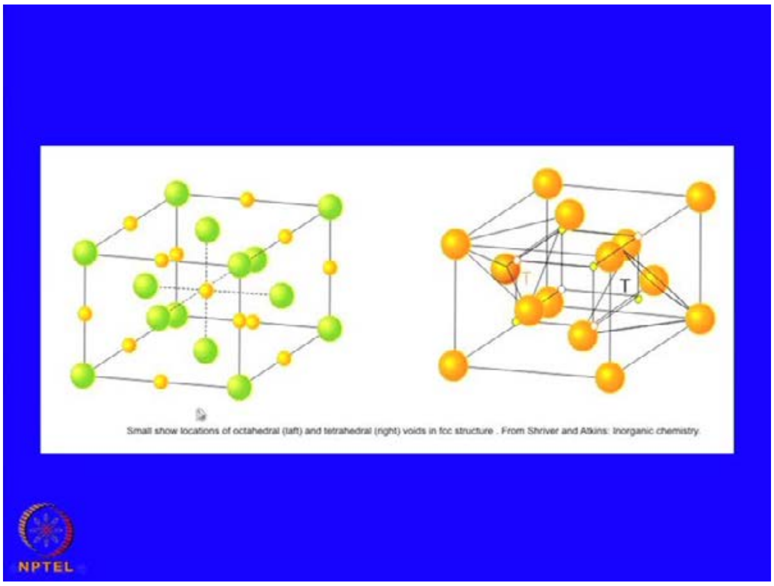

Small show locations of octahedral (left) and tetrahedral (right) voids in fcc structure . From Shriver and Atkins: Inorganic chemistry

Now, if you take a cubic symmetry, you have seen earlier, this is a cubic symmetry. The green ones are the cubic symmetry and in fact, it is not only cubic symmetry, it is actually face centered cubic symmetry, close packed face centered cubes. So, you will have 14 green atoms or green ions. In which case, there will be some interstitial spaces. As you have discussed, some of them will be 4 coordination or tetrahedral coordination and some of them will be octahedral coordination. So, any close packed structure will have basically two different kind of interstitial spaces. One is surrounded by 4 atoms and in another, it is surrounded by 6 atoms.

So, in the next structure of F C C or face centered cubic in this case, which are the positions, where these interstitial sites are available. It has been found or one can very usually visualize that, if this cubic structure is a close packed structure, that means these atoms are actually touching each other along the diagonal of the face. This is the, although for clarity, they have been drawn separated from each other, but in practice, actually they are touching along this line. They are also touching along this line, along the face diagonal, the other face diagonal.

In fact, similarly, in along all the face diagonals, these green atoms are actually touching each other. If so but they are not touching along this line, along the edges, what we call the edge of the cube. They are touching along the face, along the diagonal of the cube, face diagonal actually. There are two types of diagonal in these structures. One we call the face diagonal and other is the body diagonal. Body diagonal means, if this atom touches this atom or a line is drawn from this atom, this corner atom to the next or the opposite corner atom, then it passes through this center of the cube and that is what we called the body diagonal and a diagonal drawn on the face is called the face diagonal.

So, in this case, they are not touching each other along the body diagonal, but these green atoms are actually touching along the face diagonal. If so it is not touching along this edge. These two are not touching, because they are touching on this side. So, they cannot come closer than that. So, there will be some space or interstitial voids. We call it, this is interstitial voids. Similarly, on the middle of each edge of the cube, there will be interstitial voids, which are shown here by in a low servo are a low it is a sphere. So, this (( )) sphere are all actually voids. Voids in the interstitial sites give some space in between the actual atoms. So, this interstitial sites, which has been shown here by a yellow circles, they are actually the coordination number. Those interstitial sites are actually 6. That is not 4 coordination number. 4 coordination number not showing here. But, they are actually present. We will see where exactly the coordination number of 4 interstitial sites, with coordination number of 4 actually resides. So, as far as this structure is concerned, cubic structure, the edge centers, edge centers are the places where you have interstitial sites. In addition of course, another interstitial or the six fold coordination, octahedral structure is present also at the body center or the center of the body also has a octahedral side. In addition, there are 12 edged centers. So, in all, there are actually, if you calculate what is the number of atoms, what is the exact number of atoms in this particular cell, in this particular unit, you will find there are 4, effectively there are 4 atoms, 4 atoms, 4 green atoms per unit cell. Why?

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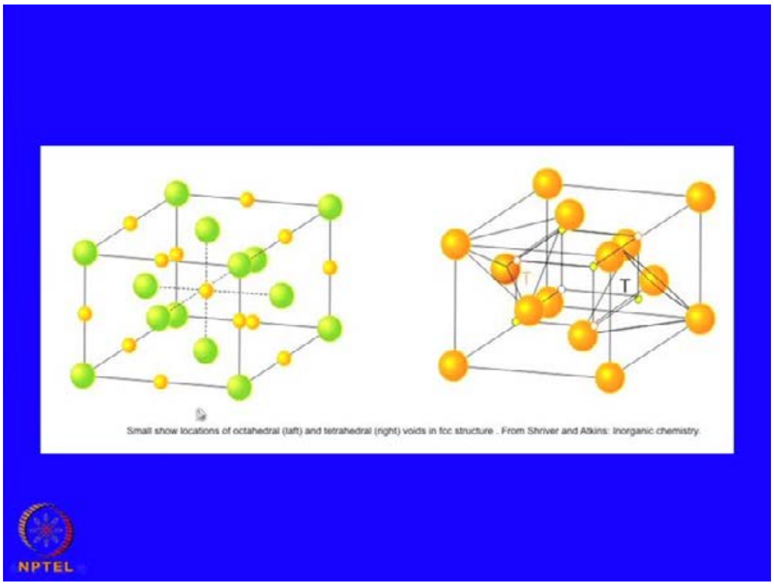

Small show locations of octahedral (laft) and tetrahedral (right) voids in fcc structure . From Shriver and Atkins: Inorganic chemistry

One can find out, this is actually at the corner of a cube and if you want to fill up the space, there will be 8 such cubes, which will join at this point. 4 on one layer and second and another 4 on the top layer. So, each of this corner atoms or corner ions are actually shared by 8 unit cell. So, 8 search unit cells are joining at this point. 4 on one layer and 4 on the just layer above. So therefore, the contribution of share of this particular atom to one unit cell, which is shown here, is actually one-eighth. So, one-eighth into 8, 8 corner atoms, so the total contribution or total share of this unit cell as far as the atoms are concerned, from the corner atoms is only 1, whereas, if you consider the face centered positions, these atoms, they are shared by two unit cells.

One, this one and there will be another on the top. So, that will be placed on the top and therefore, that half of it will go to that unit cell and half of it will be in the bottom unit cell. So, the contribution or share of this particular atom to this unit cell is only half and there are 6, on 6 different faces, we have 6 such atoms having a contribution of a share half. So, that makes 3 and this also, these 8 atoms contribute only 1. So, the total contribution or the total volume shared by this particular unit cell of the atoms is only 2.

So, there are 2 atoms per unit cell. We call it 2 atoms per unit cell. Although it had been shown large number of atoms, about 14 different atoms are seen here, but actual contribution to this particular unit cell is only 2 and rest of it is actually being shared by the neighboring unit cells.

You can make some similar calculations with these interstitial spaces. How many of the interstitial spaces are available in this unit cell? One can find out, there are also 2. How? See, these are on the edge, center of the edge. How many unit cells are sharing this particular atom? You will find there are 4 atoms, 4 unit cells are actually sharing this particular site. This is an interstitial site. So, all these 12 are shared by 4. So, each one is contributing actually one-fourth. One-fourth into 12 is 3. So, these sites are actually shared by 4. So, 12 sites are shared or the contribution to this particular unit cell is 3.

In addition, we also have seen that at the center of the cube, center of this particular cube, you have another site. This site is completely inside this unit cell. It is not being shared by any other neighboring cell, neighboring unit cells. So, this is 1. Its contribution is full. So, 1 plus 3, once again it is 4. So, there are 4 actual atoms occupying these sites and there are 4 interstitial sites, octahedral interstitial sites within that unit cell, within that structure. So, there are equal number of atoms and octahedral unit cells. So, that is another very important characteristics of the so called closed packed structure, whether it is hexagonal packed where we have two layers or it is a F C C or face centered closed cubic packed structure and there are equal number of atoms and interstitial sites. The octahedral interstitial sites, particularly.

If you talk about the tetrahedral interstitial sites, is little difficult to imagine where exactly the tetrahedral interstitial sites, but you have accept my saying that these tetrahedral interstitial sites, all the tetrahedral interstitial sites are within this unit cell and not being shared with the neighboring unit cells. If you draw a body diagonal, then there will be 2 interstitial sites on that body diagonal. It is about one-fourth from each corner. So, if you draw a body diagonal from this atom to this atom, then there will be one somewhere here, one somewhere here, which is about one-fourth of the total length of the body diagonal and similarly, one-fourth from other side. So, there will be, there are 8 corners, 8 corner atoms and corresponding to 8 corner atoms, there will be one tetrahedral site, about one-fourth distance of the total body diagonal length. So, from this corner, there will be tetrahedral site here and from other side also, there will be another tetrahedral site somewhere here. So, corresponding to each corner atoms, there will be one tetrahedral site. So, 8 corner atoms and all of them, the tetrahedral sites are within the unit cell and therefore, there are not shared by the neighboring atoms, by the neighboring cells. Therefore, the contribution of all the 8 is to this particularly unit cell. Therefore, the total number of tetrahedral sites is actually 8. So, in a sense, what we are saying, in any close packed structure, the number of tetrahedral site is double the number of atoms present. So, there are equal number of atoms and the equal number of and the same number of octahedral sites and double is the number of tetrahedral sites. So, that is also another very important consideration when you are talking about the geometric pattern of different oxides or different other compounds.

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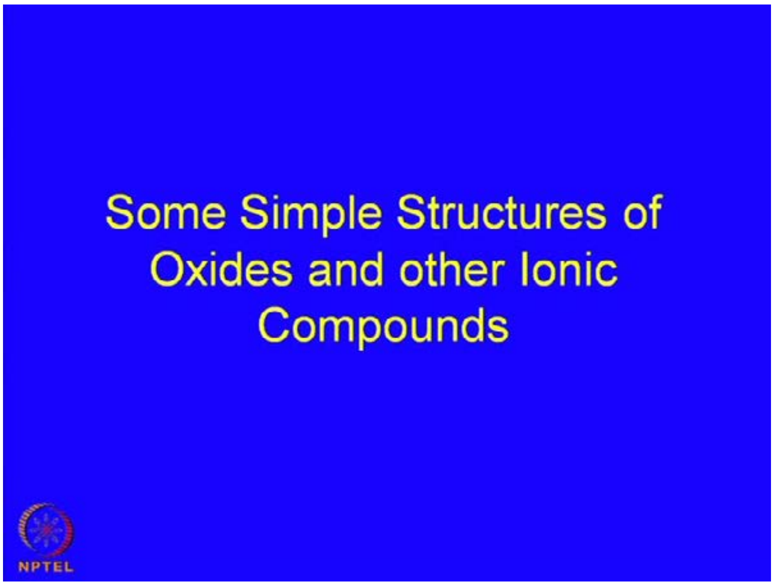

Some Simple Structures of
Oxides and other Ionic
Compounds

With this back ground, let us go to look at some of the actual example of oxides, some simple structures of oxides and few other compounds. How we can drive, how we can visualize some of these structures, the atomic arrangement in some of this oxides.

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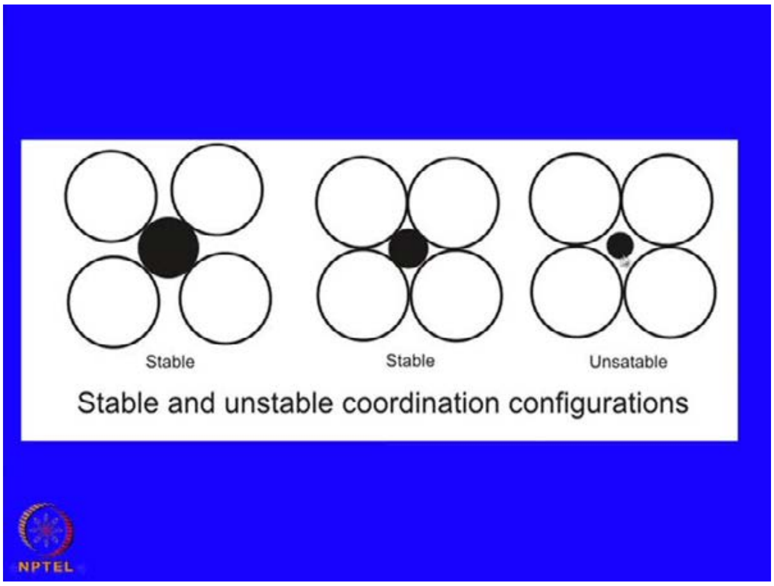

Stable and unstable coordination configurations

Now, the basic difference between an element like metal, iron, nickel, cobalt and these are only elements and they are present in the form of element. So, there is only one kind of atom. Either iron atom or in another case, cobalt atom or copper atom so on. So, in all metals, there are only one variety or one size of atoms. So, whatever we have discussed earlier, that very well applies, these structure very well apply to these metals because we can have only one variety of atoms and we have discussed so far only one variety of atoms. Others are of course, interstitial sites. They are not occupied. They are just the interstitial sites, the voids. In fact, iron, the metallic iron has few polymers. They have different structures and have different temperature ranges. So, mostly at room temperature, it has a B C C structure, body centered cubic structure, whereas, in slightly higher temperature, it has F C C structure, that is face centered cubic structure

So, copper, for example, has a hexagonal structure. Not a cubic structure. It has a hexagonal structure and so on. However, when we are discussing about oxides, we have to deal with two different ions. One is cation and another is anion. In an oxide, of course, the anion is always oxygen or oxygen ion, but there will be different kind of metals or metal ions present in different kind of oxides and you may very well imagine that their sizes are different. Cation is a smaller ion than the oxygen ion. The oxygen ion, the ionic radii is about 1.4 angstroms. Whereas, most of the metals has a ionic radii, which is less than 1 angstrom. So, there is a big difference between the ionic sizes of cation and the anion. So, that makes our life simple. In the sense that, cations actually resides in the interstitial sites created by a closed packing, either closed packing or a open space, created by the arrangement of anions or in this case, in case of oxides, is the oxygen ion.

So, oxygen form, oxygen ion forms a kind of a skeleton and this skeleton has, because of its particular spherical nature, it has inherently, it has some interstitial spaces and these interstitial spaces have been occupied by some of the cations and that is how an oxide structure is built up. So, we consider in this particular situation, these white circles are actually oxygen ions. They are larger ions and the black circle is a cation. It is a metal ion and it is a smaller ion. Normally, they will go and sit in the interstitial site created by the atomic arrangements of the oxygen ions.

Now, there are three different situations here. You can see, let us start from there, on the right side. You will see 4 oxygen ions are touching with each other along the diagonal. If you form a square, so you form a square, so this, you add this and then it forms a square. So, you just join the center of all the four atoms, they will form a square. Now, if you have that, then you have some open space here. This is your interstitial site. In this case, this interstitial site basically has a fourfold coordination you can say. There are four atoms surrounding that particular site. Then we can introduce one cation here. Now, what kind of size you can have? This size may not be exactly fitting to this size of the interstitial fold. So, it may be little smaller or it may be larger. In this case, the cation is slightly smaller. So, before they can touch on this direction, these circles are touching along this line. So, there is a gap and this is called, according to this structure requirement, this is a unstable structure. This is not a very feasible structure. So, a cation cannot go inside and therefore, in an oxide, you may not have this kind of a situation. Any compound, you may not have this kind of situation. It is more unusual situation among stable situation.

You can have these kind of situations. One is the diameter of the cation is exactly matching with the highest diameter of the interstitial sites. So, the atoms are touching along this line, along this point, this point and this point, between them the oxides are touching each other and the cation and the anion is touching along this line. So, the exact size, or the size of the cation exactly matches with the size of the interstitial or the maximum size of the sphere, which you can introduce to that interstitial position. So, this is one situation, which is a very stable situation and they may be another situation, other situation and this is little bigger. The cation is bigger than the actual size here. If it goes on seats in the interstitial sites, then it will push back this oxygen ions. So, the oxygen ions, no longer touching along this line or along this line or this line, but it still remains symmetric. Symmetry is still cubic. It forms a cube. But, even if the symmetry is cube, but they are not touching. They are not fully close packed structure.

So, the atom or the size of the cation is such that it is larger than the critical size. We call the critical size of this particular structure. So, they oxygen ions, a few step out and a larger size of the cation goes and sits in the interstitial size. This is also stable. This is possible. In any structural, this is possible, but with a limitation. With a limitation, it can push to some extent. It cannot push too much. So, there are energetic considerations, based on which, one can find out how much it can be posted. Normally, the size may be is about 15 percent more than the critical size, 15 to 20 percent more than the critical size. Not more than that. So, this is not possible at all. It will go. It does not mean that this particular metal, this particular metal having a smaller size cannot form an oxide. It can still form an oxide, but its structure will be different. The structure will be different. It may not have a close packed structure like this or it may not form a compound with oxygen. It may form compound with something else. So, normally this kind of structure is not possible, but these two structures are possible. Keeping this thing in mind, one can go to a many different situations.

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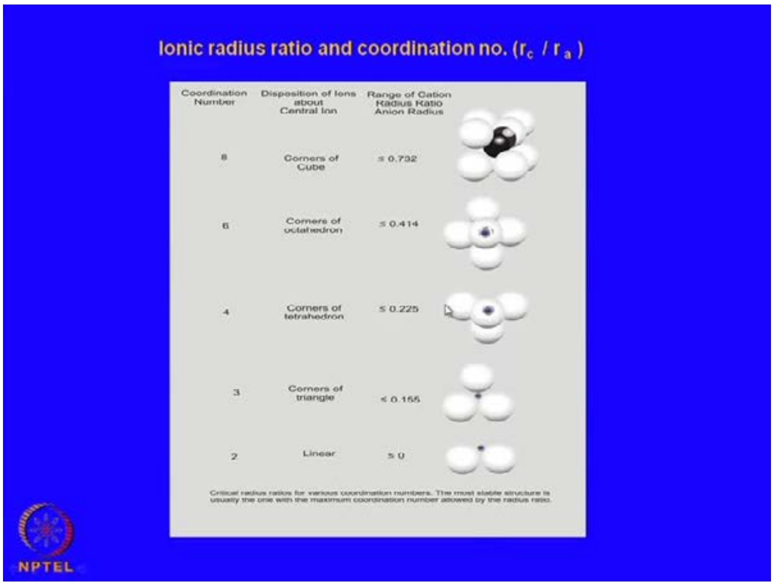

Ionic radius ratio and coordination no. (r_c / r_a)

Coordination Number	Disposition of Ions about Central Ion	Range of Cation Radius Ratio Anion Radius
8	Corners of Cube	≥ 0.732
6	Corners of octahedron	≥ 0.414
4	Corners of tetrahedron	≥ 0.225
3	Corners of triangle	≥ 0.155
2	Linear	≥ 0

Critical radius ratios for various coordination numbers. The most stable structure is usually the one with the maximum coordination number allowed by the radius ratio.

So, there are consideration of ionic radii, consideration of ionic radii which actually controls which particular kind of coordination, which particular kind of arrangement becomes stable in combinations of cation and an anion. That is very important. So, there may be, depending on the cation size and the anion size, different structures will be stable and the structures may change depending on the size of the cation and the anion. So, that is what we call a critical radius ratio for each of the coordination numbers. For each of the coordination number, we have a critical radius ratio. Below which, it is stable or above which, it is stable or below which, it is not stable. So, there is a least. One can find out from very simple geometry, solid geometry, for which kind of coordination, what ratio is the critical one. For example, we have several kinds of arrangements. This is a linear arrangement. You can say, there are 2 anions here and in between a cation. Well, that kind of arrangement can always be there. There is no restriction from the point of view of the geometric pattern. So, this is a, anything less than 0 is always have that, this kind of a coordination.

But, these coordination's are in general not possible and not feasible. So, we need not consider that. That is not very important. Triangular coordination, that means we have threefold coordination. This is a twofold coordination. This is threefold coordination. Once again, for triangular coordination, it is on a plane. It is not on different levels. It is on a particular plane. Three atoms are there on the same plane and also the anions and the cations on the same plane. So, three atoms are possible and once the three atoms are there, they would be also a critical radius ratio and that is given in the table. You can see, 0.155, that is the ratio of the r c by r a. r c by r a means, cation ratio by the anion ratio. The cation is smaller and anion is larger. So, if that ratio is 0.155, then that is the critical ratio for this triangular coordination or threefold coordination. Threefold coordination can exist, as I have mentioned earlier. Even if this ratio is slightly larger, the threefold coordination can still exist. But, it cannot be less than this value.

So, it can increase, it can push back, the larger cations can push back the anions and the cation ratio will increase, till it reaches this value 0.225. So, 0.155 to 0.255. Once it reaches, as the cation size is increasing keeping the anion size same, so the total cation, the effective cation ratio is increasing from this label or this value to this, towards the end. So, in between 0.155 to 0.255, the triangular coordination or threefold coordination will be stable. Whereas, if it crosses the 0.255 value, this particular critical value, then the threefold coordination will no longer be stable. It will convert to fourfold coordination and that is, we have discussed has tetrahedral coordination.

So, this is fourfold coordination. So, it has a particular value. Fourfold coordination, if the site, in the interstitial site, fourfold coordination interstitial site has to be fully occupied or the cation has to be touched each of the four anions. Then the size of that cation must be 0.225 or more and less than that, it will convert itself to this particular conjometric configuration will be more stable than this configuration. So, this is a fourfold coordination in the form of a tetrahedron. Now, beyond that if the cation size still increases and anion size remaining same, because we are talking about primarily oxides, for oxygen ion or for oxygen cation or anion radius remain same and cation increases.

Then, you have next level is 0.414. All these things can be calculated in a simple way here by solid geometric consideration. So, from fourfold it will change over to six fold. There is no possibility of fivefold unfortunately. Fivefold symmetry is not normally possible. So, there are other considerations for which the fivefold is forbidden. It is a kind of forbidden symmetrical element and therefore, from four it will jump to six and the critical radius ratio is 0.414. So, if the radius ratio is between 0.225 and 0.414, then will have a stable octahedral, sorry, tetrahedral coordination, fourfold coordination till it reaches this value. The radius ratio still increases beyond 0.414, then the octahedral or six fold coordination will be stable, till it reaches another value 0.732. At 0.732, it will change from six fold to eightfold coordination and then it will, to the 0.732 will go to the eightfold coordination. Beyond that, the eightfold coordination will remain constant, until and unless we have r c by r a becomes 1. In 1, it will be a twelvefold coordination. That is, that means, radius of cation and radius of anion is exactly same. So, they are indistinguishable and they will form a complete close packed structure.

So, this is a very important consideration, what kind of coordination will have a particular cation in an oxide matrix or an oxide skeleton. So, depending on the size of the cation, it will go to different configuration and different interstitial sites and that will also change the symmetry in the unit cell and unit cell dimensions. So, this is another very important consideration, when you are considering, when you are talking about the geometry or the symmetric of the crystal structures.

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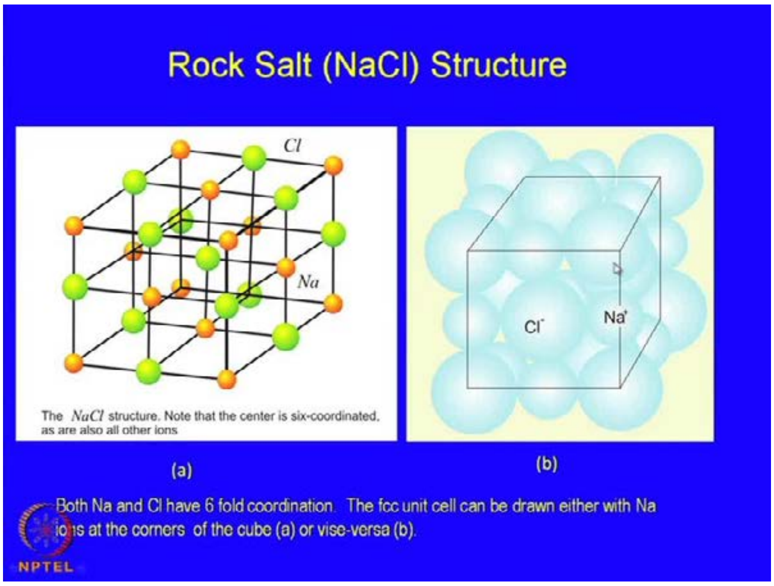

Rock Salt (NaCl) Structure

Both Na and Cl have 6 fold coordination. The fcc unit cell can be drawn either with Na ions at the corners of the cube (a) or vise-versa (b).

Well, with this background, let us try to look at some of the structure. It is very simple structures, which are possible and which are available in nature. The very first structure is what we call sodium chloride structure or the minological name of the sodium chloride is actually rock salt. So, this structure, in fact is a structure type we will see later on, that many different oxides have this particular structure. So, this is a very typical structure, in which very different oxides crystallize and what is the description of this crystal structure. There are obviously two ions; one is sodium ion and another is chlorine ion. Sodium is the cation, so it is smaller and chlorine is larger and it is an anion.

Of course, somehow sodium ions and the chlorine ions, they are anions, ionic sizes are not too different. They are much closer to charge ion, but there is a difference. So, this is on the right, the actual kind of geometric shapes and geometric pattern, in which the sodium and chlorine ion are placed. So, we can see these larger ions are actually chlorine ions. Of course, the color is more or less the same, but there is size difference. So, these smaller ions are sodium and these are chlorine ions. We have seen earlier that these are the centers, age centers, where octahedral site is possible; octahedral interstitial is available, right. You can see that the sodium ion is basically at the age centers. From here also it is seen that, these of course has been reversed. This has been reversed. The age centers are here and it is sodium ion and the corner of the, sorry, corners are the sodium ion and the middle position is of the chlorine ion and the arrangement is reversed. Whereas, let us talk about this kind of a structure or this geometry, where this is, in this cube, the chorine ion are initially placed at the corners and also at the face centers, for example here. This is in the face center, right. In fact, we have to extend this cube to that point; this one.

Although a smaller cube has been drawn, in fact, this may be something wrong. This cube has to extend up to there. This center and this center have to be joined. So, these are interstitial sites created by the arrangement of the oxygen ions. So sodium, since it is in the interstitial sites and if somebody calculates what is the radius ratio of sodium and chlorine, you will find that it satisfies the octahedral coordination. So, the sodium ion actually goes to the octahedral coordination and they are alternate sites actually. In this structure, you will find there are, in different directions, you will get one sodium, then chlorine and then sodium. In this also, in this direction also, this is chlorine and this is sodium. So, this unit cell has equal number, equal number of chlorine and sodium. Sodium and chlorine number ratio is 1 is to 1 and we have found earlier that, in a F C C structure, the face centered cubic structure or close packed cubic structure, the number of atoms and the interstitial sites, octahedral interstitial sites are same. So, in sodium chloride, if we just fill up all the octahedral sites by sodium atoms, all the octahedral sites created by the arrangement of the chlorine atoms, the octahedral sites created by them, if you fill by sodium atoms, they will maintain a ratio of 1 is to 1 because there are equal number of atoms and interstitial sites, octahedral interstitial sites of course.

None of the tetrahedral interstitial sites in this case are occupied. So, tetrahedral interstitial sites are empty, whereas all the octahedral interstitial sites are completely filled and they have equal ratio of chlorine and sodium. So, sodium occupies an octahedral site and you will find here, from this structure, you will find that both chlorine and sodium, chlorine is surrounded by 6 sodium atoms and sodium is also surrounded by 6 chlorine atoms. So, octahedral of the coordination number for both these atoms, both these ions are same. Sodium ion has this six fold coordination and chlorine also has a six fold coordination. So, that is the typical situation in sodium chlorine structure and although we are discussing here the chloride structure, which is not an oxide, chloride is not a ceramics as such, but we are discussing it for the very basic purpose that this particular structure type is available in many of the oxides. Many of the oxides, particularly divalent metal oxides, all of them do crystallize in the sodium chloride structure. So, that is the description of sodium chloride structure.

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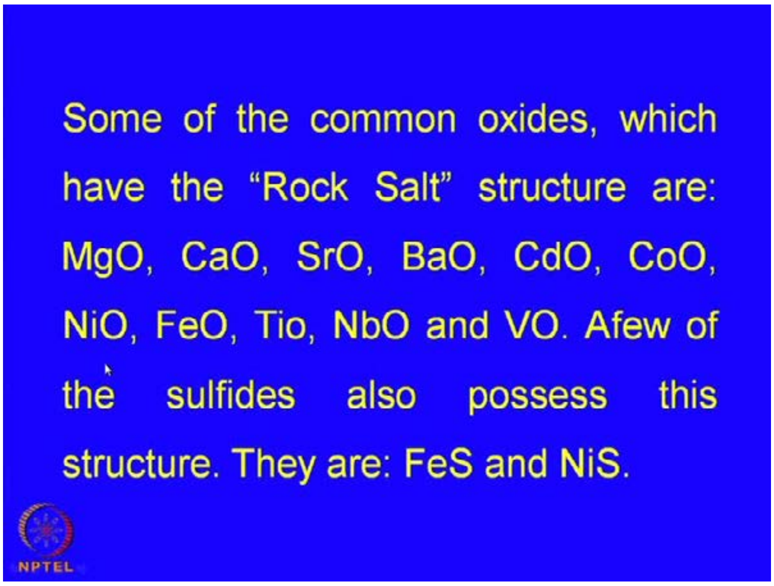

Some of the common oxides, which have the “Rock Salt” structure are: MgO, CaO, SrO, BaO, CdO, CoO, NiO, FeO, Tio, NbO and VO. Afew of the sulfides also possess this structure. They are: FeS and NiS.

Let us see what are the different oxides, which actually crystallizes in this particular structure. So, all divalent metal ions, like starting from m g o, calcium oxide, strontium oxide, all of them are actually ceramic oxides. They have some high temperature and high melting point and they are used for different purposes. We will discuss them at a later stage. So, whether barium oxide, strontium oxide, cadmium oxide, cobalt oxide, nickel oxide, all of them are divalent. F e o, of course is available in two different covalence stage, two plus and three plus. T i o 2, normal valence state of titanium is four plus but t i o is also available. This is another stable state. N b o and V o and few of the sulfides also possess this structure. They are F e s and N i s. Of course, sulfur we will not be discussing too much about it.

But, while discussing about the structure, there are different compounds having the same structure. The description is same. Oxygen forms, in all these cases oxygen forms a close packed cubic structure. F C C structure, face centered cubic structure, close packed cubic and face centered are equivalent. So, magnesium of the metal ion goes to the octahedral interstitial and the ratio, atomic ratio or the ionic ratio remains 1 is to 1 and that also satisfy that all the octahedral sites and the number of atoms are actually 1 is to 1 in this particular structure.

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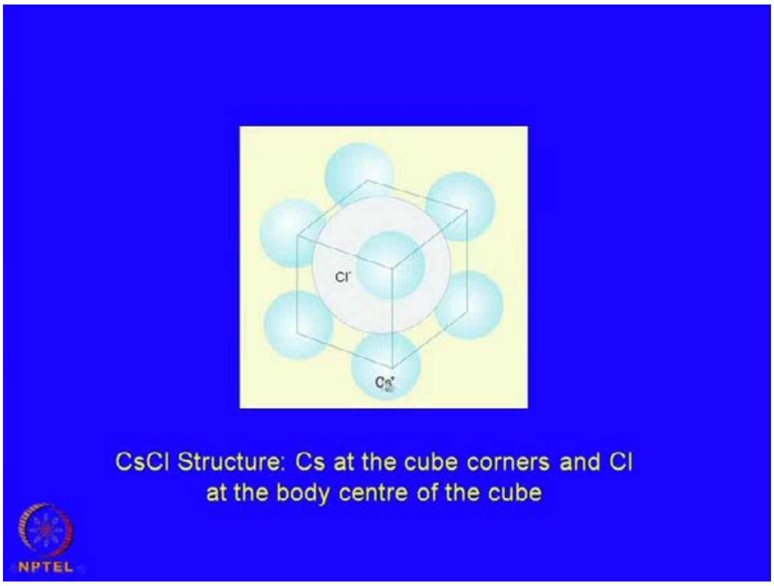

CsCl Structure: Cs at the cube corners and Cl at the body centre of the cube

So, this is the description of sodium chloride structure and it is a very very important structure as far as the oxides are concerned. Next, there is a structure which is called cesium chloride. Just like sodium chlorides, this is another alkali halide. So, this has a cesium chloride structure, but it is more of a open structure. You can see, cesium ion is much smaller than sodium ion. So, it does not form the sodium chloride structure. Although they are, chemically there are equivalent, chemically they are more or less the same. Both of them are basically an alkali halide. But, just because the ionic radii is different, the structure is different. Here, the chlorine ion is much bigger and it sits in the center of the cube, whereas, the cesium ions are in the corner of cubes. So, both together actually forms a kind of body centered cubic structure. So, at the center is a chlorine ion and at the corner of the cube is cesium ions. So, it is different from the sodium chloride structure. Chemically there are same, but structurally they are different. Primarily because the ionic radius ratio is much different.

So, with this we stop here. We have discussed some of the basic features of atomic arrangement. How the symmetry comes, and what kind of interstitial positions are created by a close packed structure. We have two different kinds of close interstitial. One is basically tetrahedron or fourfold coordination. The other is six fold coordination and then with oxides, because they have two different ions. One is the cation and another is anions. Anion is the much larger than the cation. So, normally you describe the oxide structure by filling up the interstitial sites by the appropriated size of the cation. So, that is how we have described. We will describe more and more oxides in the next class.

Thank you.