An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

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Lecture – 22
Ionic Solids (contd..)
Formation of Structures

So, in the previous lecture, we have discussed the guidelines which we follow to build structures of ionic solids. And those guidelines are basically based on that anion cation should touch each other; and anions cations do not touch, anion do not touch anions and cations do not touch cations. And they should be maximum possible coordination of anions and cations to minimize the electro static energy. So, now what we look at is some of the examples of solid which have various co-ordinations based on radius ratios. And we will start with the formation of solids in ionic solid category.

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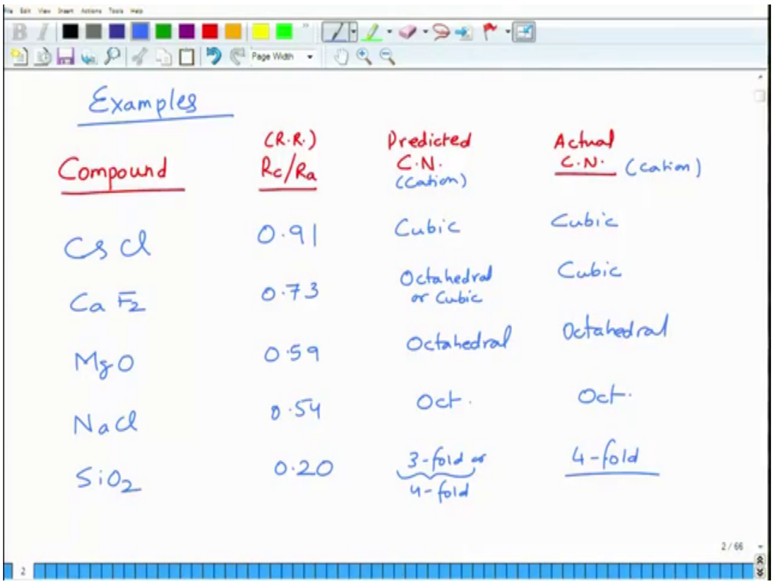

Examples

Compound	(R.R.) Rc/Ra	Predicted C.N. (Cation)	Actual C.N. (cation)
CsCl	0.91	Cubic	Cubic
CaF_2	0.73	Octahedral or Cubic	Cubic
MgO	0.59	Octahedral	Octahedral
NaCl	0.54	Oct.	Oct.
SiO_2	0.20	3-fold or 4-fold	4-fold

So, the first I will give you a few examples. And you will see in this these examples there are certain deviations its life is not always rosy as per the guidelines, there are certain deviation and those deviations are mainly because of bonding ok. So, so let us say we start with on left side we have compound and then we write R c by R a which is nothing, but R R. And then we write predicted coordination C N predicted and then actual coordination ok. So, let us see how do we go there.

So, if you look at for example, cesium chloride. So, we take example of cesium chloride the predicted one is 0.91, 0.91 is on the higher side. As a result, the predicted coordination is cubic coordination and actual is also cubic. Ca F 2 that we looked at radius ratio is 0.73, predicted is at the boundary it is at the boundary, it could be octahedral, it could be cubic, but it tends to have so basically this is octahedral or cubic. Because it is at the boundary, it tends to have cubic. And this is coordination number of cations ok.

So, here we when we talk about coordination number, we generally talk about coordination number of cation; anion is determined accordingly. Then we look at Mg O the predicted is 0.59. As a result you should have octahedral it is more than 0.414, but lesser than 0.732. And it has octahedral coordination.

Then we have example of Na Cl the most famous example it has 0.54 again it has octahedral, and it actually it has octahedral. Then we have example of silicon oxide, this has 0.20. 0.20, if you look at it if you look at the table that I showed you earlier 0.2 will go into 3-fold or four fold right. So, it will have 3-fold or actually it is in 3-fold right slower than 0.2 to 5. These are the boundary so you can say it could have 4-fold it has four-fold because of covalent bonding Si O 2 ok. So, because of strong covalent character, it tends to have a tetrahedral bonding as compared to 3-fold coordination. So, there are certain another deviation that we will see specially in case of covalently bonded solutions which occur.

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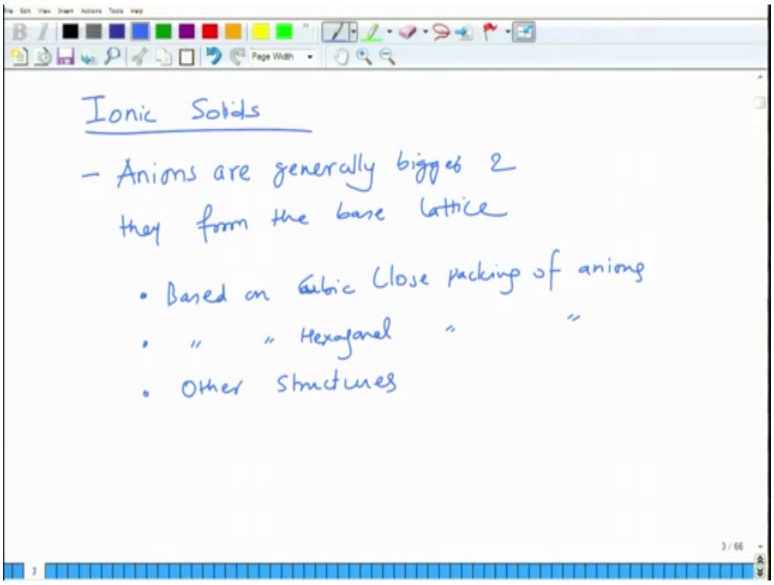

Ionic Solids

- Anions are generally bigger & they form the base lattice
  - Based on Cubic Close packing of anions
  - " " Hexagonal " "
  - Other Structures

But now what will do is that we will look at the some of the structure examples of the structures of ionic solids. See, in typically in ionic solids, anions are generally bigger, and they form the base lattice they form the base lattice. And these structures are based by enlarge and cubic close packing of anions.

So, since they form the base lattice, the structures are categorized as structures based on cubic closed packing of anions, structures based on hexagonal close packing of anions. And structures which are let us say we put them in one category as other structures, which could have you know primitive cubic structure something like that ok. So, we will first look at the structure which are based on cubic based packing of anion. The anions make a lattice which is cubic closed pack for FCC in nature and cations go and occupy the inter stresses in them.

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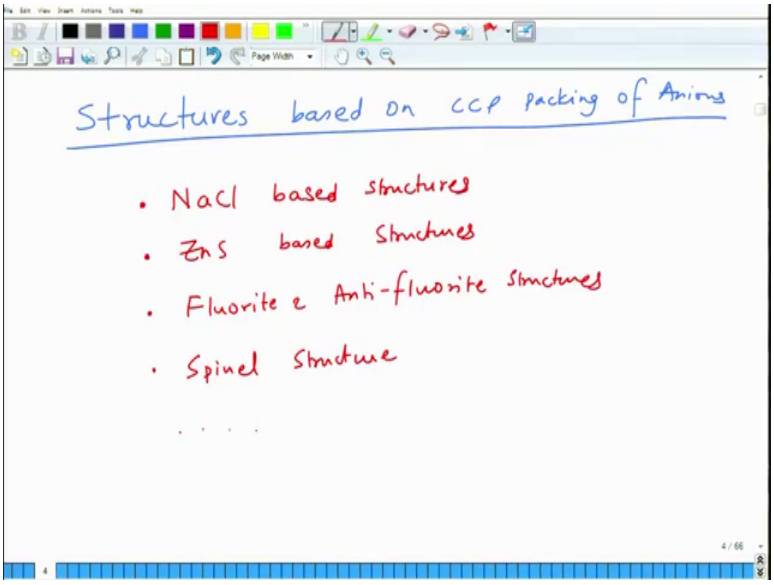

Structures based on CCP packing of Anions

- NaCl based structures
- ZnS based Structures
- Fluorite & Anti-fluorite Structures
- Spinel Structure

. . . .

So, these the first in this category is structures based on CCP packing of anions ok. So, in this there are certain kind of structures, there are structures which are called as Na Cl based structures. Then we have zinc sulfide based structures, then we have fluoride and anti fluoride structures. These are three important structures then we have spinel structure and a few more. So, we will first start our discussion with sodium chloride based structures.

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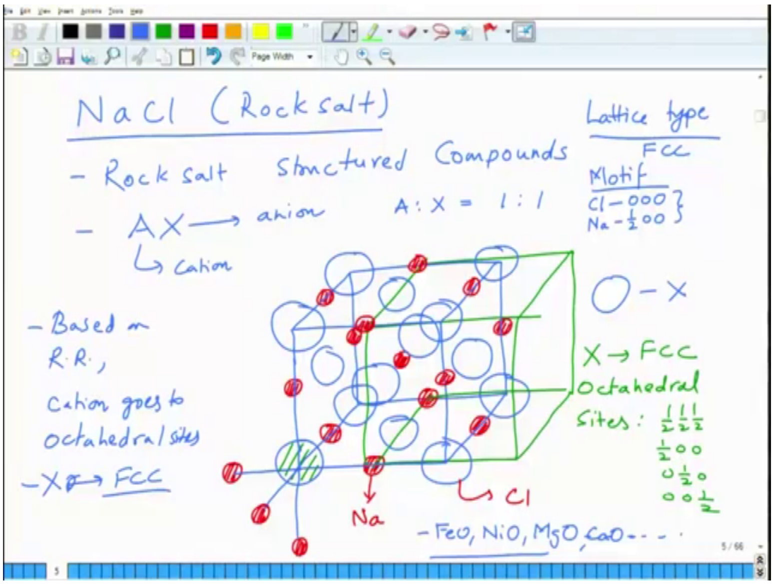

NaCl (Rock salt)

- Rock salt Structured Compounds
- AX → anion; ↳ cation
A : X = 1 : 1

Lattice type
FCC
Motif
Cl – 000
Na – ½ 0 0

- Based on R.R., cation goes to octahedral sites
- X → FCC

○ – X
X → FCC
Octahedral Sites : ½ ½ ½
½ 0 0
0 ½ 0
0 0 ½

- FeO, NiO, MgO, CaO - - - .

So, if you look at sodium chloride base structure, Na Cl, it is also called as rock salt ok. So, these compounds are called as rock salt structured compounds ok, rock salt structured compounds. They have A X kind of structure where A is cation and C is anion and A is to X is equal to 1 is to 1.

So, basically what happens here is you have a face centered cubic packing of cations here. So, you have structure like this ok, and this is your anion ok. So, this is a phase centered cubic packing of anions. So, this is X where can the cation go cation we are staying on the radius ratio, cation goes to based on R R cation goes to octahedral sites. And X makes a X makes a FCC lattice. It has made FCC lattice which are the cock octahedral sites now. This is a octahedral site in the center ; this is an octahedral site; this is an octahedral site; this is an octahedral site this is an octahedral sites. So, octahedral sites are basically.

So, X makes FCC lattice octahedral sites are at 1 1 half half half, and then half 0 0, 0 half 0, and 0 0 half, basically center of the edges. So, this is one atom, this is two atom three. So, all the atoms can be put at the center of these edges. So, you have now 12 of these sodium atoms rings at 12 edges and since each edge is shared by one neighbor. As a result each has shared by 4 neighbors; as a result you will have 3 effective atoms of sodium sitting at the octahedral sites plus 1 at the center. So, this will make a sodium chloride structure rock salt. So, this is chlorine this is sodium.

So, FCC this is basically the lattice type in this case. What is the lattice type?

Student: FCC

Lattice type is FCC, very good. Lattice type is FCC. How do you describe the motif? Now that there are two atoms, you need to describe the motif. So, you first to define the motif for the coordinates of chlorine chlorine is at. And if you define FCC lattice and chlorine at 000 it means all the FCC atoms have been taken care of, but you have sodium also. So, how do you describe the position of the sodium? Sodium is displaced with respect to chlorine by one by two. So, you can write it as half 0 0,. So, this is the motif, chlorine at 000, sodium at half 0 0,.

Now, let us look at the coordination number of sodium how many how many of let us look at the coordination number of chlorine how many of sodium atom surrounded. So, if I look at this for instance you have one neighbor on the right, one in this direction, one in that direction. And you are going to have one in this direction one in this direction one below. So, basically you going to have one here, one here, and one there. So, chlorine is also surrounded by 6 atoms ok.

So, we will see something called as bond balance pool later on. The bond bond valance who will basically allows you to determine how many whether your valance is between whether that distribution of whether the number of neighbors for cations and anions are in such a manner so that solid is electrically neutral and you satisfy the conditions of valances or electrical neutrality condition. We will see that in the coming few slides. Let us do for some more examples of this case before we get into that.

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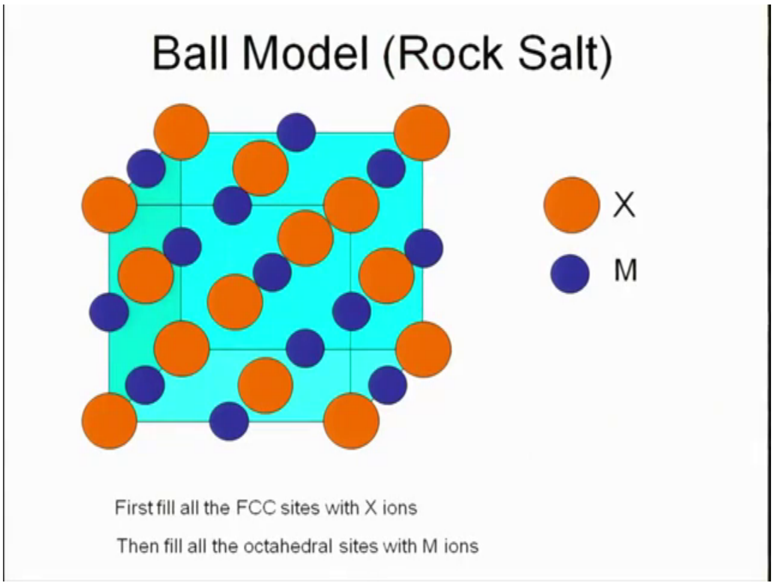

Ball Model (Rock Salt)

First fill all the FCC sites with X ions

Then fill all the octahedral sites with M ions

So, this is your rock salt structure compound in which let me show you how it looks like in terms of. So, this is what it looks like basically. So, this is the ball model you first fell all the FCC site for X ions and then fill all the octahedral sites with m ions. So, this is what makes a FCC structure of NaCl.

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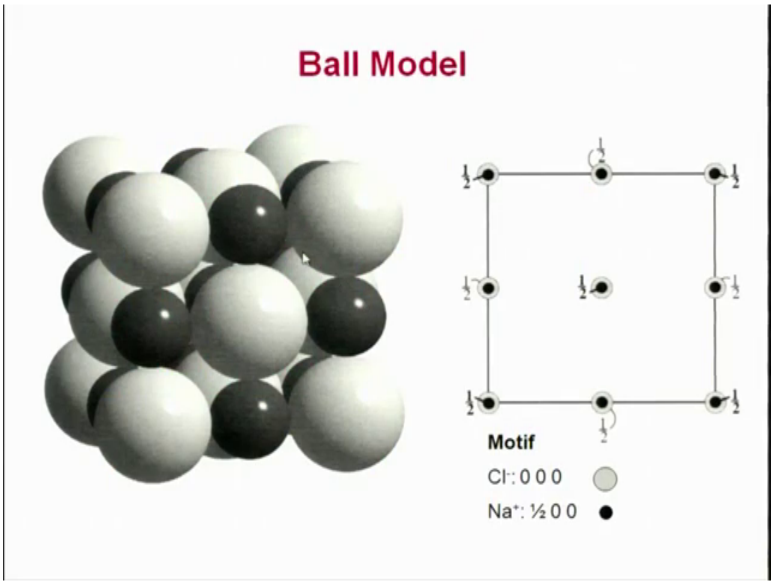

Ball Model

Motif

Cl^-: 0 0 0 ○

Na^+: ½ 0 0 ●

And this is what the touching model basically looks like you have these balls as the white ones are anions, the red ones are cations. And if you look at the top view, top view will look like that. So, this is top view X and Y positions are satisfy self explanatory only Z position is mentioned. So, you can see that the sodium ions are at half vocations at the edges as well as at the body center all right.

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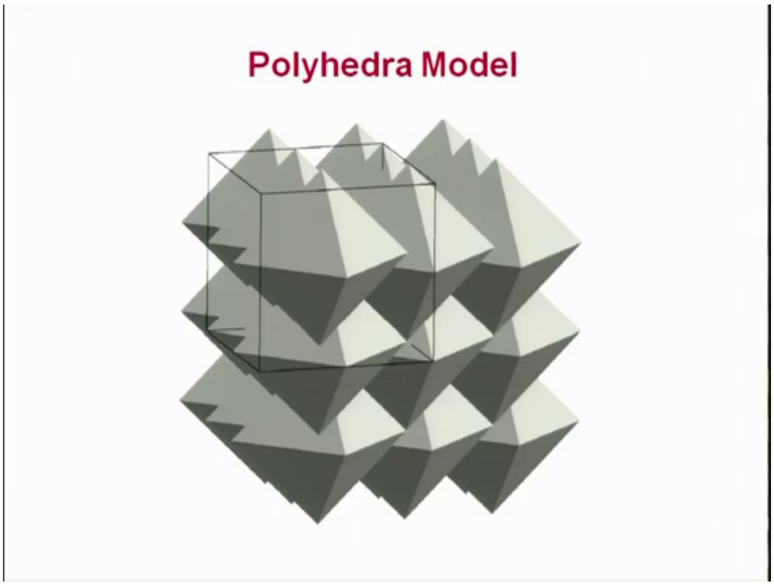

Polyhedra Model

This is the polyhedral model. In the polyhedral model, what happens is that the polyhedrons, you do not have to show any atom just show how the polyhedrons arranged. So, you can see that since these all polyhedras you know this is surrounded by a polyhedral which is octahedral, this is a octahedra, this is octahedral, it is like. So, if you draw the octahedras only all the octahedras are arranged vertically in such a fashion. So, this is a these are horizontally stacked octahedras these are all vertically stacked octahedras. So, this is a poly polyhedral model in which you show not the atoms, but just the polyhedras stacked in certain fashion depending upon how the atoms are coordinated with respect to each other ok. So, this is called as a rock salt structure.

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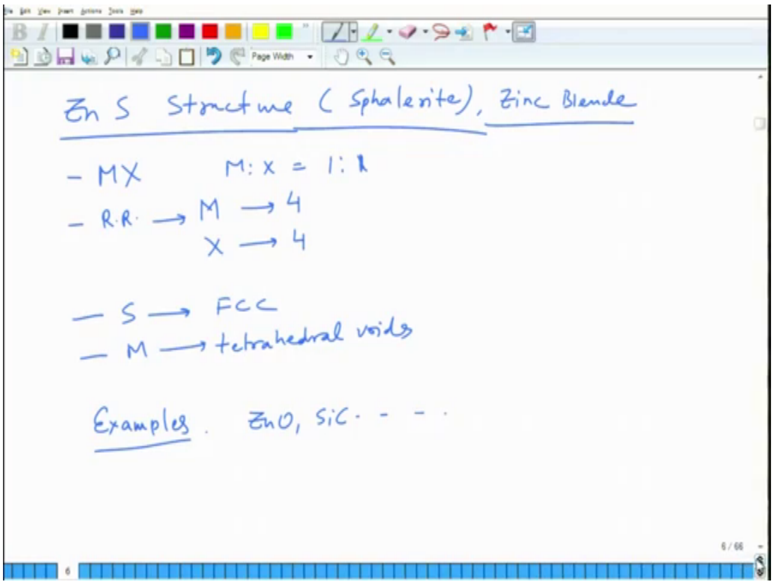

Zn S Structure (Sphalerite), Zinc Blende

- MX $M : X = 1 : 1$
- R.R. $\rightarrow$ M $\rightarrow$ 4
  X $\rightarrow$ 4
- S $\rightarrow$ FCC
- M $\rightarrow$ tetrahedral voids

Examples. ZnO, SiC . . . .

Now, let us look at the second structure that is called as zinc sulfide structure. And this is called as sphalerite a sphalerite is a mineral name of zinc sulphite.

Student: (Refer Time: 15:28)

So, (Refer Time: 15:29) zinc blende sphalerite. So, you can say zinc blende also. Sphalerite is a name of the mineral. Now, in this kind of structure the again it is a m X type of compound the stoichiometry of m is to X is one is to one. But the radius ratio requires that four coordination of M X is 4, and the valances are also required that the coordination number of anion is also 4. So, again in this case sulfur atoms makes FCC lattice. So, FCC lattice and M occupy the tetrahedral voids. So, let us see.

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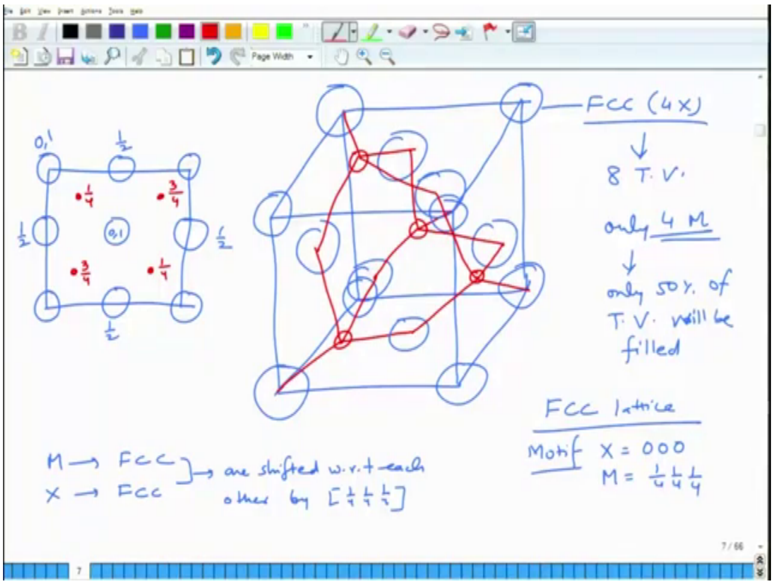

FCC (4X)
↓
8 T.V.
only 4 M
↓
only 50% of T.V. will be filled

FCC lattice
Motif X = 000
M = 1/4 1/4 1/4

M → FCC
X → FCC } → are shifted w.r.t each other by [1/4 1/4 1/4]

So, first you fill X this is X atom excuse me these are all X atoms. Now, you have to draw the M atom. Tetrahedral voids are located at positions 1 by 4, 1 by 4, 1 by 4 type of positions basically they are near the corners. Now, this atom has FCC structure with four X. How tetrahedral voids you have you have eight tetrahedral voids. So, you have 8 tetrahedral voids, but we have only 4 M atoms based on a stoichiometry. Stoichiometry allows that M is to X should be 1; that means, we have only 4 M which means only 50 percent of tetrahedral voids will be filled.

The question is which once and the electro statics are allows and the system symmetry allows the filling of only for example, in this case the one here, the one here, and the one here and the one there. So, which means this is coordinated by this, that, that and this. This is coordinated by this, this, this and that ok. This is coordinated by this, this atom, this atom and the one at the center of the phase that is here. And this will be coordinated by this atom, this atom, the one here and the one there. This is how the coordination going to look. It is a diamond cubic lattice basically diamond cubic lattice is just that that the atom sitting in the tetrahedral void is different.

So, basically this lattices again you can say it is a FCC lattice. The motif can be written as X at 0 0 0; and M at so you can say that it is a its basically two interpenetrating FCC lattices right two interpenetrating FCC lattices one of M, another of X which are separated by 1 by 4, 1 by 4, 1 by 4. So,. So, basically M makes FCC lattice, X makes

FCC lattice, but they are shifted with respect to each other by a vector 1 by 4, 1 by 4 1 by 4.

Similarly, in the previous case you can say you have two FCC lattices; one is made by M, second is made by X and they are shifted by a vector half 0 0. So, you have one cube of M which is shifted with respect to X by just horizontally shift just a horizontal shift. So, basically the cube edge can be made here I can make a cube edge here. So, this could be another representation of unit cell right all right. I can put the edge as far as representation is concerned this is also valid unit cell right. So, they are just shifted by half 0 0, vector.

So, in this case its two interpenetrating FCC lattices shifted by vector half 0 0, in this case two interpenetrating FCC lattices shifted by vector 1 by 4, 1 by 4 1 by 4. And again if you want to draw the top view you can draw the top view top view makes it look better its very symmetric distribution of atoms. So, if these are M atoms, so M is at 0 1, this is at 0, 1, this is at half these are to. So, here also this is at half, this is at half, this is at half corner once are at 0 1, this is also at 0 1 ok. Where is the other atom going to go, so what is going to go here, another is going to go here, one is going to go here another is going to go here. This is at 1 by 4 this is at 1 by 4 this is at this is at 3 by 4 very similar to the diamond cubic lattice that we have all right. So, this the second cubic close packed structure which is called as zinc sulfide based structure.

Third category of compound is. So, in this case by the way I just give you the example in case of Na Cl. The examples are plenty examples in Na Cl oxide such as Fe O, Ni O, Mg O all of them followed Na Cl based structure, Ca O, Ca O and so on and so forth. All of these follow Na Cl based structure based on their radius ratio. And in this case zinc sulfide based structures examples are zinc oxide and your silicon carbide these follow zinc sulfide based structure.

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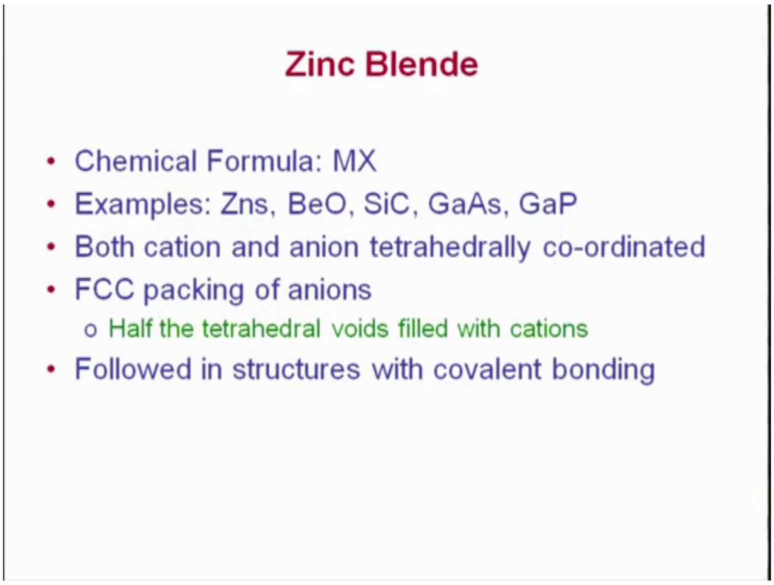

Zinc Blende

- Chemical Formula: MX
- Examples: Zns, BeO, SiC, GaAs, GaP
- Both cation and anion tetrahedrally co-ordinated
- FCC packing of anions
  - Half the tetrahedral voids filled with cations
- Followed in structures with covalent bonding

So, again I can show you the model zinc blende. So, this is the chemical formula M X the examples of zinc sulfide beryllium oxide is also there cilinica carbine, gallium arsenide, gallium phosphide that is also one example. So, both are tetrahedrally coordinated half of the tetrahedral voids are filled. And typically it is common to have this structure to be seen in in covalently bonded solids. So, there are some deviations from the radius ratio not all of them will followed radius ratio rule and that is why covalent bonding dominates because it require four-fold coordination

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Zinc Blende

So, this is the structure you have sulfur atoms, and these are tetrahedral coordinated zinc atoms. And this is the polyhedral model in which you can see that these are all tetrahedras, but you see in the previous case the octahedras aligned along vertical axis which is 1 0 0, 0 1 0, 1 0 0 axis here at tetrahedral stacked along 1 1 1 axis of the unit cell along the body diagonal.

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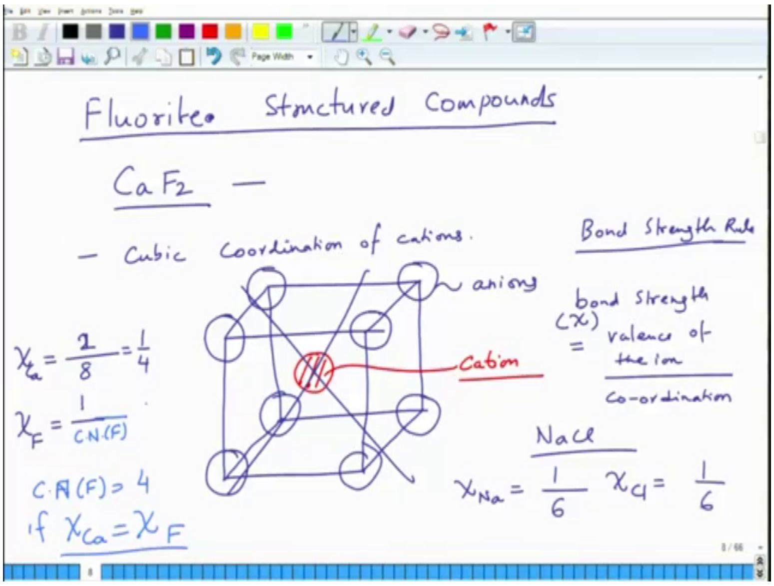

Fluorite Structured Compounds

CaF_2 —

– Cubic Coordination of cations.

$\chi_{Ca} = \frac{2}{8} = \frac{1}{4}$

$\chi_F = \frac{1}{C.N.(F)}$

$C.N.(F) = 4$

if $\chi_{Ca} = \chi_F$

Bond Strength Rule

bond Strength (χ) = $\frac{\text{valence of the ion}}{\text{Co-ordination}}$

NaCl

$\chi_{Na} = \frac{1}{6}$ $\chi_{Cl} = \frac{1}{6}$

Let us say the lets see the third example here now which is the third example is fluoride structured. So, third structure that we are going to look at is called as fluorite structured compound. And this fluorite structured compound basically what happens is you have this is a based on compound called as Ca F 2.

So, calcium fluorite is the parent compound and for this radius ratio as we have seen is falls in the category of nearly cubic coordination. So, Ca F 2 typically if you go to previous like one of the slides, it has a radius ratio of nearly 0.73 or so. And as we said it tends to follow cubic coordination of cations. And so based on this cubic coordination of cations can form like this one possibility is this that you make a cubic coordination means eight-fold coordination right which means there should be 8 anions cations surrounding an there should be 8 anions surrounding the cation.

Now, under what conditions is that possible its possible for example, in this condition. These are 8 anions. And the cations, cation can go somewhere in between this is let us say cation. But there is a problem, the problem is the valance because if you look at this structure, and if this follows in 3D, what is the number of neighbors of cation, 8. And if this follows in 3D, what will be the number of at neighbors for anions. So, how many neighbors will this be now surrounded by if you if you consider this as the reference atom let us say this as a reference atom, you have one here, you will have 7 on the other sites. So, this will also have 8 neighbors, what is the valance that you have. Valence is the stoichiometry is one is to two.

So, stoichiometry says that for each calcium I have to fluorines, but the coordination number based on the structure is saying that that it is one is to one because both of them have same number of neighbors. So, there is something called as what we look at that is bond valance ok, where we calculate a parameter called as bond strength which is equal to valence of the iron divided by coordination ok. Sorry, this is bond strength not bond valance what is strength rule.

This says bond strength is let us say chi ok. This says that for a charge neutral solid for a charge neutral solid if you have a let us say for a let us let us take for example, of calcium chloride for a charge neutral solid the bond strength of cat ions and anions must be equal to each other. So, now, calculate that for Na Cl first Na Cl. So, let us say chi and Na; chi, Na the valence of the iron was one coordination number was six.

If you look at chi c l this was also 1 over 6 same is true for Zns what about Ca F 2, chi, Ca I am saying the valence of the iron is one sorry two and the bond coordination is 8, this is. If this is structure was true then it would be one divided by 8, they are not equal to each other so which means this is not right.

For this to be equal let us say the coordination number is now let us say the coordination number is unknown. So, if these were equal the coordination number for florin now will be equal to will be equal to 4, if chi Ca is equal to chi F all right. So, now, we need to look at this is structure in a different manner. I think we need to do that in the next class because the time is running out. So, we will do that in the next lecture, but I hope that is clear the point was that the valances are different you need to look at in a different manner ok.