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

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Lecture – 21

Ionic Solid

Stability

Rules of Formation of Ionic Solids

So, today we will start a fresh lecture on ionic solids continuing from what we started in last class. We will continue talking about the stability for little while, and then we will look at the rules of the formation of ionic solids ok. There are certain guidelines which need to be kept in mind while forming the ionic solid structures. So, what we were discussing in the last class is about the ionic bond right.

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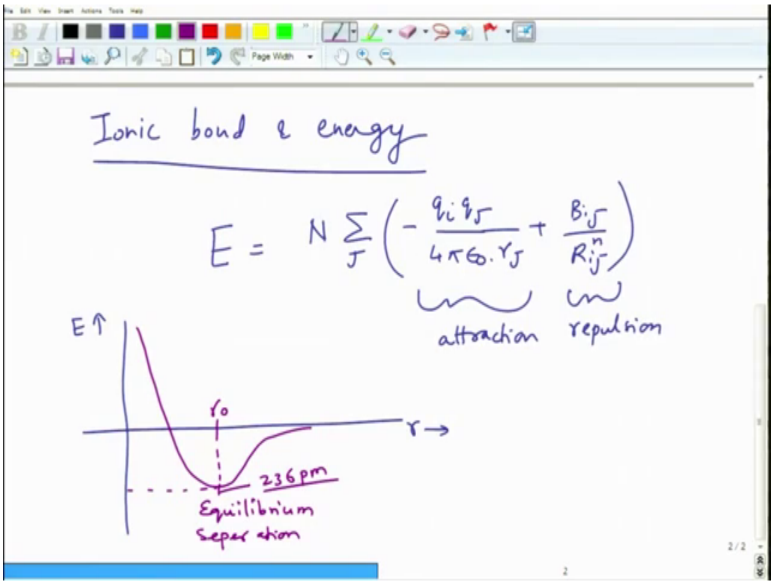

Ionic bond & energy

$$E = N \sum_{J} \Big(\underbrace{- \frac{q_i q_J}{4\pi\epsilon_0 . r_J}}_{\text{attraction}} + \underbrace{\frac{B_{iJ}}{R_{iJ}^{n}}}_{\text{repulsion}} \Big)$$

Ionic bond and its energy because eventually this is what determines whether you have to solid is going to be stable or not. So, energy was equal to N of epsilon J and you have sum of J plus B i J divided by R i J to the power n. And this is basically for some of your you have attractive term here this is attraction, and this is where you have repulsion; and balance of these two is going to determine how are they going to be ensembled.

So, there are two kinds of energies. So, basically when you need to form a bond you need to spend some energy and then you gain the energy by putting them together if they remain as a isolated molecules you do not gain that energy. So, it is a balance of these two energy which eventually determines whether they structural stabilize or related molecule is stable. And it turns out there is a net attraction when you form a solid.

So, you have overall energy landscape look something like that. So, if you plot the energy as a function of separation distance, the overall energy look something like this ok. And basically at sudden separation distance R naught, you have net attraction between the components, and basically this is what is this is where energy is equal to 0.

So, this defines your let us say the equilibrium separation distance, and this is for instance for ionic solids like Na Cl. Na Cl has a distance of 236 picometer between the ions. And that basically implies that your solid is stable as a ensemble of molecules is structurally stable rather than isolated molecules being stable. So, isolated molecules obviously in comparison to describe I am going to have higher energy as a result they are not stable.

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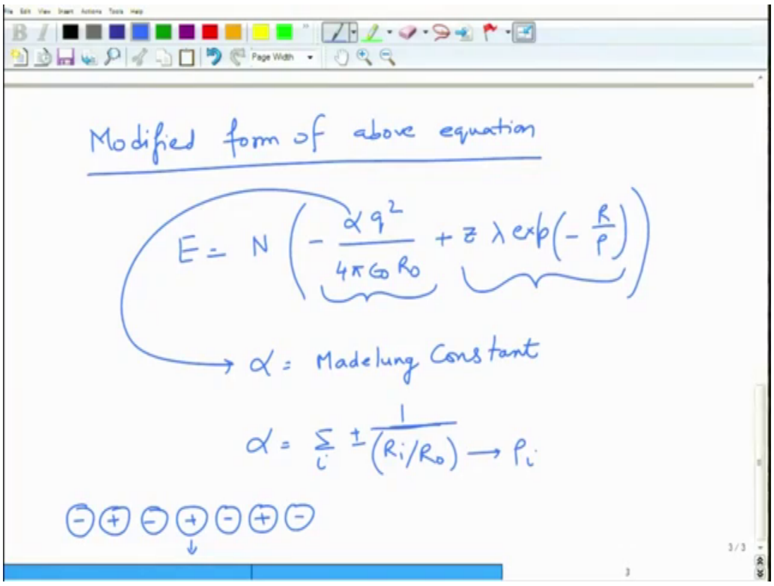

Modified form of above equation

$$E = N\left(\underbrace{-\frac{\alpha q^2}{4\pi\epsilon_0 R_0}} + \underbrace{z\lambda \exp\left(-\frac{R}{\rho}\right)}\right)$$

α : Madelung Constant

$$\alpha = \sum_i \pm \frac{1}{(R_i/R_0)} \rightarrow \rho_i$$

So, this equation gets modified to so the modified form of this equation is E is equal to N minus of alpha q square divided by 4 pi epsilon naught R naught plus z lambda exponential of minus R divided by rho. Where alpha is something which is called as. So, basically again this is a repulsion time you can see and it varies exponentially as a function of distance. And this is your attractive term, attraction term. And this Madelung constant is defined as a alpha is defined as epsilon i plus minus 1 over R i divided by R naught. And this is basically also called as rho i. So, basically alpha Madelung constant is a constant which depends upon the interaction between the ions.

So, for example, you can put these ions like, so if you do if this is a reference ion let us say a positive ion and you are going to put all these ion in this fashion, let us say. So, you can make a bun 1D case of this ensemble of ions, and calculate this value of alpha if you choose this as a reference for all the neighbors.

Then alpha value will so for so the first neighbor interaction second neighbor interaction third neighbor interaction and so on and so forth. So, calculate this alpha value for each iron i and the sign will determine on the sign on the on the sign on the charge of i iron itself. So, if it is if it is positive the value will be positive; it is if it is negative it is the value will be negative.

So, basically it will form a series for which if you take the first nearest neighbor, second nearest neighbor, third nearest neighbor, fourth nearest neighbor and so on and so forth, it will form a series and the series needs to be converged ok. So, you will see that you can form various configurations in 1D, then 2D, then 3D, and when you make these such series for 2D and 3D series will not is not going to converged for all the configuration this going to converge only for certain configuration which are mentally stable configurations..

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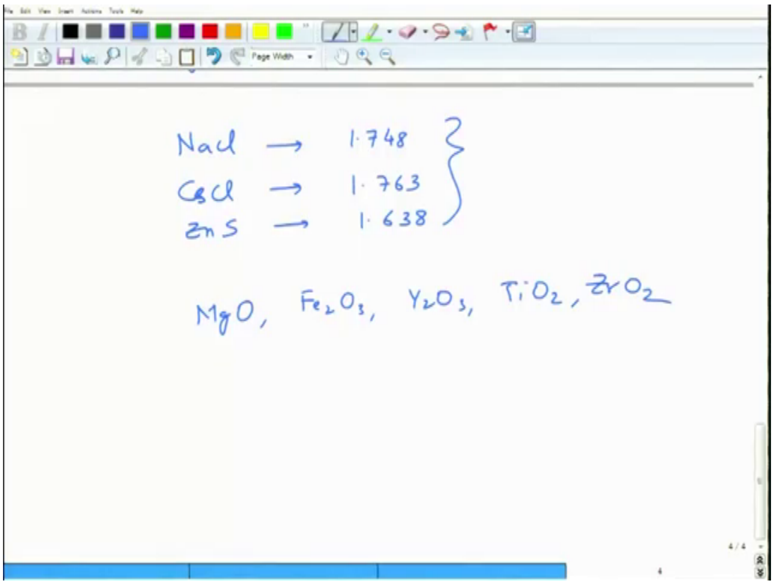

$NaCl \rightarrow 1.748$

$CsCl \rightarrow 1.763$

$ZnS \rightarrow 1.638$

MgO, Fe_2O_3, Y_2O_3, TiO_2, ZrO_2

So, this Madelung constant will determine the so whether the solid is stable or not. So, for example, the values of alpha if you take for Na Cl and cesium chloride let us say, and for zinc sulfide. Na Cl the value is nearly 1.748, 1.763 and 638. So, these are typical values of alpha that you get by summing over all the neighbors. So, essentially you can see that if your alpha value is large, the attraction term is large, and if alpha values low then the attraction value term is lower.

You want this time to dominate as a result your for ionic solids which forms strong ionic bond, the sulfur term tends to be higher. Ionic balls also tends to become stronger when the you can see that the q square term here right, this q square term is basically the charge on each of the ion right. So, as a charge on each of the ion becomes more, this q square also becomes larger all right. So, if you have for example, e e it will make e square if you have 2 e 2 e, it will make 4 e square.

So, it increases quite substantially. So, if you look at solids like for example, Na Cl compare that that with Mg O or compare that with the Fe 2 O 3 for instance or compare that would with Y 2 O 2, and then Ti O 2, Zr O 2, you can see that the charges are increasing right. So, you go from plus 1 to minus 2 to plus 2 minus 2 2 and 3 and then 4. So, as a result they these this solid tend to have higher ionic bond strength and their melting points also tend to increase generally in general speaking ok.

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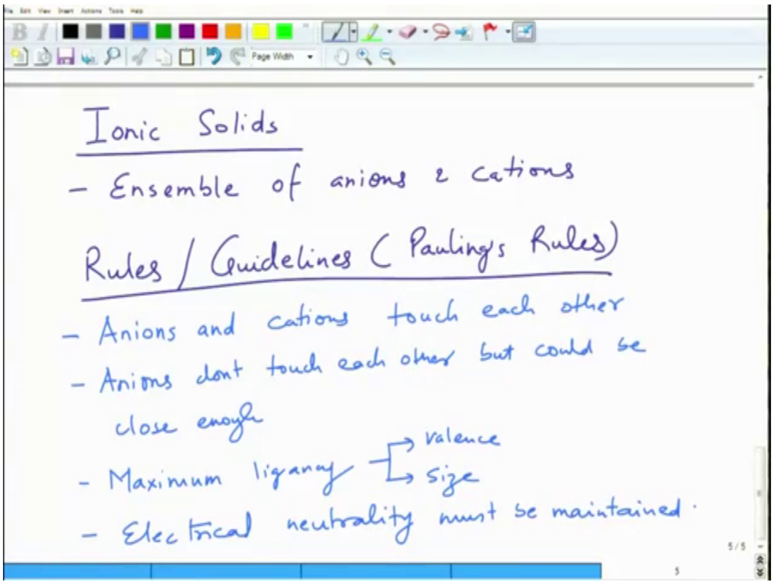

Ionic Solids

- Ensemble of anions & cations

Rules / Guidelines (Paulings Rules)

- Anions and cations touch each other
- Anions dont touch each other but could be close enough
- Maximum ligancy → valence → size
- Electrical neutrality must be maintained.

So, so basically when you look at ionic solids they are nothing, but ensemble of anions and cations. So, as a result electro statistics or electrical neutrality and balance of forces required to follow certain guidelines. And there are some obvious things like you cannot put two cations together because I they will be substantially repulsion, you cannot put similarity to anions together because it will be substantially repulsion. So, there are certain guidelines which must be followed to to build these structures.

What are these guidelines we call them rules slash guidelines and they are called as Pauling’s rules ok. So, the first thing is anions and cations touch each other. And here we assume that they are hard disc spears. And anions generally do not touch each other they do not touch each other, but they may be close enough. So, because the repulsive force typically tapers of exponentially. So, as a result little bit separation the repulsive forcibility tapered off. So, anions do not touch each other, but could be close enough, so that there is not very substantial.

And to minimize electrostatic energy they should be maximum ligancy maximum ligancy means that each anion or cation should have maximum number of neighbors. The coordination number should be as high as possible, so that your electro static energy is minimum. And that make sense I mean if you if you surround the cations by anions by cations more number of neighbors the electrostatic energy is going to be minimum because they will attract each other.

However it is not that simple because this is valance which plays an important role and size which plays important role. So, this is determined typically by valence and size. And then you need to maintain electrical neutrality. This is very important. Solid cannot be electrically not neutral it has to be electrically neutral which means that total positive charge must be equal to total negative charge that is a (Refer Time: 11:03) condition. So, let us see how do we co about making this structure.

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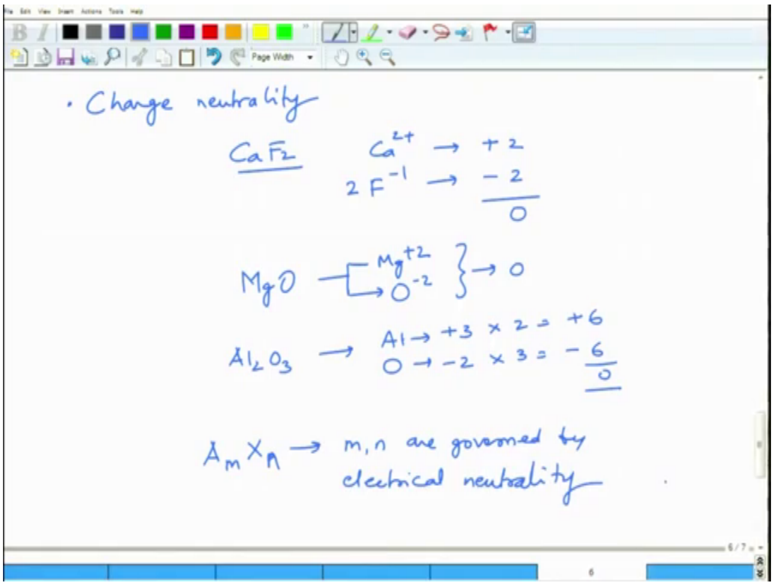

- Charge neutrality

CaF_2 $\quad Ca^{2+} \rightarrow +2$

$2F^{-1} \rightarrow -2$

$\underline{\qquad}$

0

$MgO \rightarrow \left.\begin{matrix} Mg^{+2} \\ O^{-2} \end{matrix}\right\} \rightarrow 0$

$Al_2O_3 \rightarrow$ $Al \rightarrow +3 \times 2 = +6$

$O \rightarrow -2 \times 3 = \underline{-6}$

$\underline{0}$

$A_mX_n \rightarrow$ m, n are governed by electrical neutrality

So, basically when you talk about charge neutrality, so for instance you have Ca F 2 Ca has it is Ca plus 2 cation it has pus 2 charge and fluorine as minus 1. You have 2 of minus 1 you have minus 2 net charges equal to 0. Same is to about Mg O Mg is plus 2 oxygen is minus 2 net charge is equal to 0. Another example Ti O 2, Al O 2, you have Al O 3 for example, Al O 3 where Al is plus 3, oxygen is minus 2.

So, plus 3 into 2 is plus 6, minus 3 minus 2 into 3 is minus 6, net is equal to 0. So, the electrical neutrality and the net charge in the structure should be equal to 0. Now, so general form you can write A m let us say A m X p or A m X n where m and n are governed by electrical neutrality right; so, depending upon the valance and electrical neutrality.

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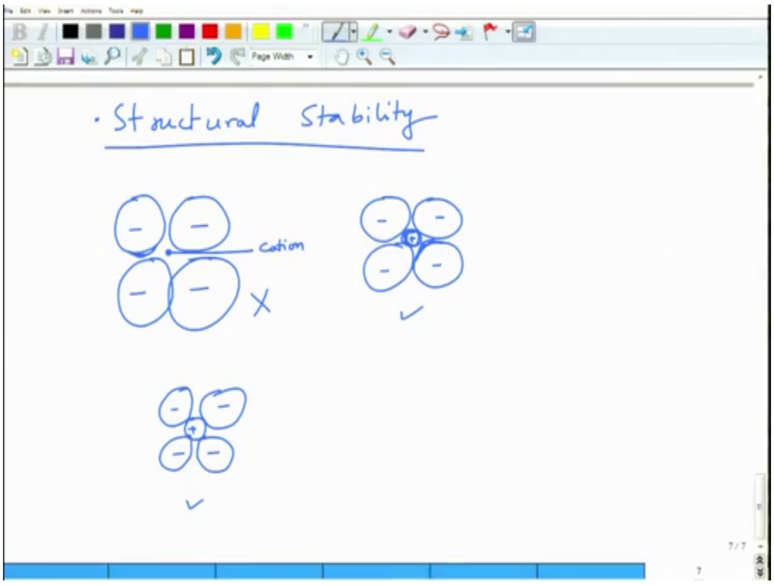

And then stability of structure; so, when you have for example, there are few configurations. So, let us say you have these big ions ok. These are cations, anions sorry. So, you have these anions, and you have very tinny cations getting somewhere here. Now, if you have such a tinny cations somewhere here, so this is plus this is sorry generally anions are bigger.

So, this will minus, minus, minus, minus, minus, minus, and this is let us say cat ion. Another configuration is you have anion which is cation which is nearly which is touching the anions like this. So, in this case, your anion is very cat ion is very small as compared to anions i is not touching the anions. And then you have another structure in which you have this is a cation. One of your anion is like, this one of your anion is like this, (Refer Time: 14:07) like this.

So, this is could form a stable structure given that there is little bit of difference between the cations and the anions and anions and cations are touching anions. So, this could be stable structure, this could be stable structure, but this is not a stable structure. Because here the cation is very small and it allows so the there is a violation of the guideline that cations and anions must teach touch each other, so that is the size plays an important role.

What kind of size, size will determine how many neighbors will you have, so that you have the structural stability so that you have cation and anion touching each other and anions are further away from each other by tiny distance. So, that there is no net and ionic repulsion. So, as a result that is something called as guidelines regarding coordination ratio.

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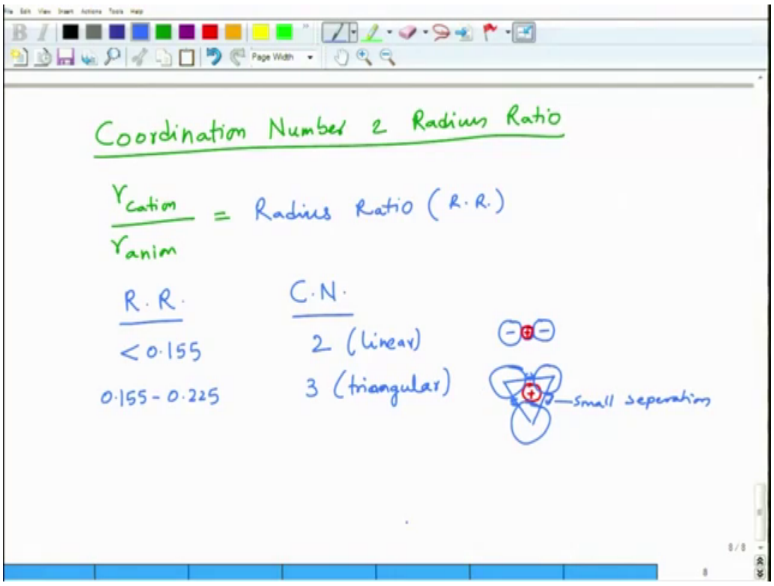

Coordination Number & Radius Ratio

$\frac{r_{cation}}{r_{anion}}$ = Radius Ratio (R.R.)

R.R.	C.N.
< 0.155	2 (linear)
0.155 - 0.225	3 (triangular)

So, coordination number sorry coordination number and radius ratio. To make stable structures with the following the behalf of guidelines where cations and anions must each touch each other, and they should be maximum possible and neighbors that are possible. So, basically you need to calculate what is R cation to R anions, this is called as radius ratio. And this radius ratio will determine how many nearest neighbors will you have by which will make a stable structure.

So, for example, there are various there are various kind of ratios which are possible. If I take let us say this as R R. So, R R when it is less than 0.155, which means when the cation is very small as compared to anions. In that case coordination number which is preferred, so I can write this as CN let me also modified this little bit this is R R. So, in this case cord number coordination number two that is preferred this is called as linear coordination ok.

And here basically what you have you have anion and you have a tiny cation and then you have a anion. So, if I just choose a different color, this could be cation. And these would be anion. So, this is called as linear coordination second guideline is between 0.155 to 0.225.

So, when the cation ratio anion to cation cation to anion radiation ratio is between 0.155 to 0.225, then you tend to have a threefold or a triangular coordination. In this manner what you will have is first make a cation. So, this is the cation I have and the anion would be one anion would be here another anion would be here and third anion would be here.

So, the radius ratio is between not a very pretty picture I will draw it again something like that. They should be sufficient enough separation; they are not exactly touching each other, but small enough right small separation. This is your cation; this is triangular coordination. So, basically they make a triangle and between that you have this cation.

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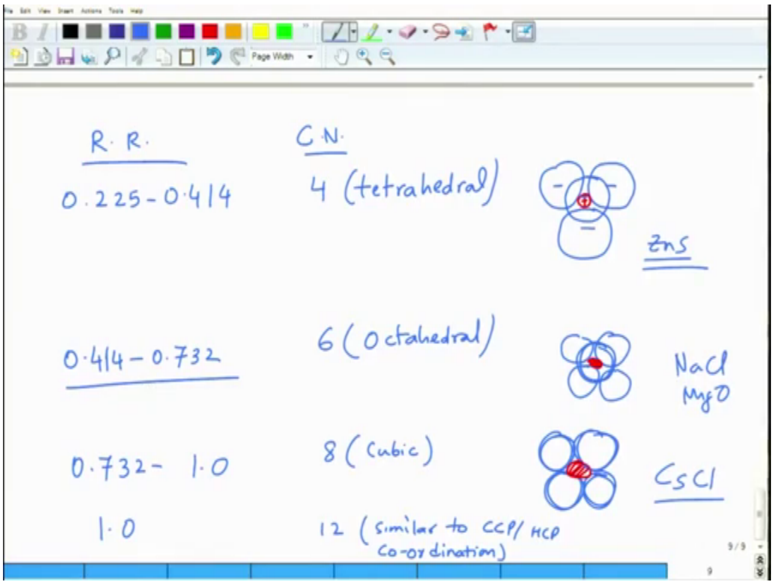

R. R.	C. N.	
0.225-0.414	4 (tetrahedral)	ZnS
0.414 – 0.732	6 (Octahedral)	NaCl MgO
0.732- 1.0	8 (Cubic)	CsCl
1.0	12 (similar to CCP/ HCP co-ordination)	

Third one is say when R R is between 0.225 to 0.414. So, if you recall 0.225 was the size of tetrahedral atom that could fit into a tetrahedral void of a closed packed structure and 0.414 was the size of octahedral. So, here the cation is smaller enough, so that it can fit into tetrahedral void, but not into octahedral. In such a situation, the coordination number tends to be 4 and this is called as tetrahedral coordination.

So, basically what you will have is you will have these anions and you will have a cation sitting here which is touching them and there will be another ion sitting on top of it. So, this will make a tetrahedral coordination. And this is followed in materials like as we will see later on for example, zinc sulfide.

Fifth one is called 0.4142 0.732. So, this is bigger than octahedral bigger than octahedral, this is called as six-fold or octahedral. So, the radius ratio is larger than 0.414, but lower than 0.732 then this is going to follow six fold coordination. So, here basically what you are going to have you are going to have an octahedron. So, this is your octahedron basically.

So, if I draw the top view of octahedron, there is the first atom. So, second atom we will have a one at the base, you will have one on the top ok; your central atom is going to sit somewhere here, this is going to be a here this is going to be cation. So, this is octahedral. And this is followed by material such as sodium chloride and all that. So, sodium chloride has octahedral coordination, Mg O has octahedral coordination and so on and so forth.

And when a when your radius ratio is between 0.732 to 1, then the materials tends to follow eightfold coordination which is cubic coordination. So, essentially what you are going to have here is you have the first layer of atoms like this. You have are the second layer of atoms like this; and between these two layers you will have a cation sitting; obviously, anions not exactly touching each other. So, this is followed by things like cesium chloride.

And then when you have 1 anions are generally bigger than cations. So, but in some cases they can be some exceptions. In that case you tend to follow a twelve fold coordination which is the close pack ordination that you have ok. Twelve fold has actually I think octahedron like that similar to CCP slat slash HCP coordination ok. So, these are the guidelines for radius ratio which give you certain configurations which make energetically stable configurations.

So, you can see that in these all of these what it tells you basically is that if you if you look at the guidelines, guidelines tell you that anions and cations touch each other; anions do not touch, but generally should be close enough and you should have maximum ligancy to minimize the electrostatic energy. So, but all of this cannot be possible without following these rules because of the cation is very small, anion is very large then obviously, anions and cations will not touch each other, if you have too many anions surrounding a cation. So, depending upon the size, there is a certain limitation on the maximum number of neighbors that 1 atom can have. As a result these structures follow these rules.

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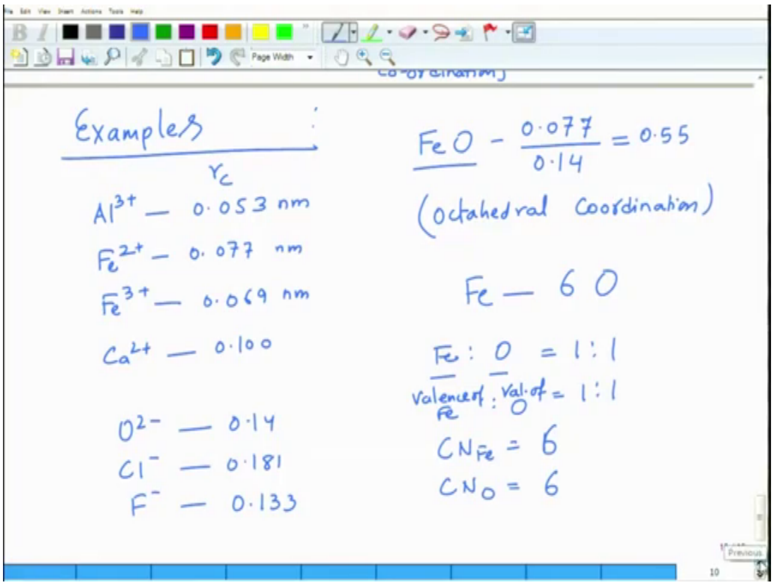

Examples

r_c

Al^{3+} — 0.053 nm

Fe^{2+} — 0.077 nm

Fe^{3+} — 0.069 nm

Ca^{2+} — 0.100

O^{2-} — 0.14

Cl^- — 0.181

F^- — 0.133

FeO – $\frac{0.077}{0.14} = 0.55$

(octahedral Coordination)

Fe — 6 O

Fe : O = 1 : 1

Valence of Fe : Val. of O = 1 : 1

$CN_{Fe} = 6$

$CN_O = 6$

So, for example, if you look at example Fe O, so if you can various cations like Al 3 plus sorry Al 3 plus has a radius of 0.053 nanometer and this is R c. Then Fe 2 plus has a radius of 0.077 nanometer; Fe 3 plus has a radius of 0.069 nanometer; Ca 2 plus has a ratio of 0.100 and so on and so forth. If you look at not just a few example, just few examples. So, and then anions various anions will oxygen has a radius of 0.14, chlorine has a radius of 0.181, and florin has a radius of 0.133.

So, let us say first we want to say take example of a Fe O ok, if you take example of a Fe O, Fe has a radius of 0.077, and oxygen has radius of 0.14. And the radius ratio that you obtain is nearly 0.55. So, if you go back to previous table where does 0.55 fit in, it fits in here. So, which means Fe O should have octahedral coordination of cations coordination octahedral coordination.

But if let us say oxygen if Fe is surrounded by if Fe is surrounded by 6 O. And based on stoichiometry what do you obtain for oxygen, how many oxygen is going to be surrounded by how many oxygen irons, how many irons round one oxygen? What is the stoichiometry? For each Fe you have one is to one the charges are 1 is to 1. What is the coordination you expect coordination number of Fe is equal to 6, coordination number of oxygen for oxygen will also be 6, they will have to maintain. So, this is for charges the valence electrons. The valency basically plus 2 to plus 2 electrons, you have which had give two electrons it can take right. So, valences are may be N is not the right letter for this I can write valance of Fe with respect to valance of valency of oxygen that is also one is to one. So, coordination number should also be equal.

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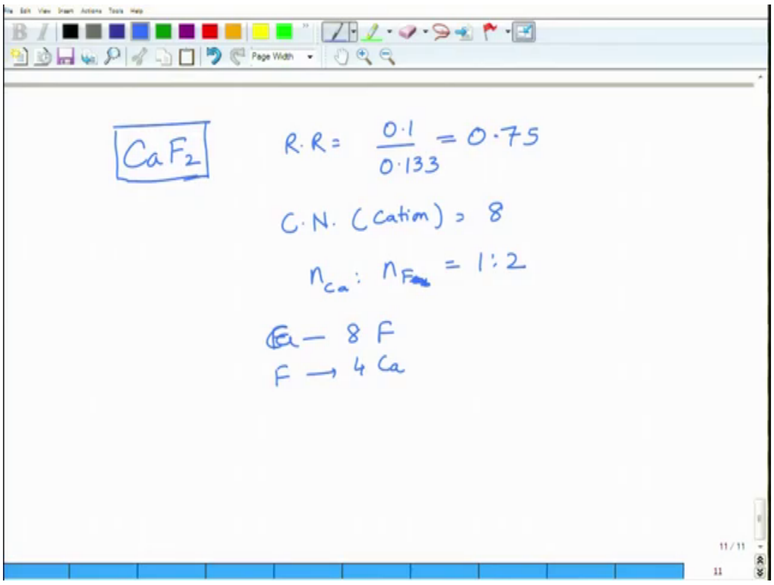

$\boxed{CaF_2}$

$R.R = \frac{0.1}{0.133} = 0.75$

$C.N.$ (Cation) $= 8$

$n_{Ca} : n_{F} = 1:2$

$Ca - 8\ F$

$F \rightarrow 4\ Ca$

You will see (Refer Time: 26:28) case of c Ca F 2, calcium has a radius of 0.1, chlorine has radius of 0.133. And this will make nearly if I just take a little bit of calculation its 0.75. If you look at 0.75 this is here. So, it tends to follow eight-fold coordination. So, you have coordination number of cation is 8, but Ca F 2 has a number of Ca 2 number of F 2 is equal to Fe is equal Fe is equal to per 1 calcium there are 2 florins valence wise calcium S plus 2 florin has minus 1. So, number of atoms and were number of valences are allow uneven then coordination number is also going to be uneven.

So, each calcium is surrounded by 8 fluorine, but each fluorine is going to be surrounded by 4 calcium ok, then only it will it is going to be electrically neutral. So, this is required for electrical neutrality to maintain the; we will see some of these examples in the coming slides. So, we will finish here. We will start on next lecture with structure of other ionic solids ok.