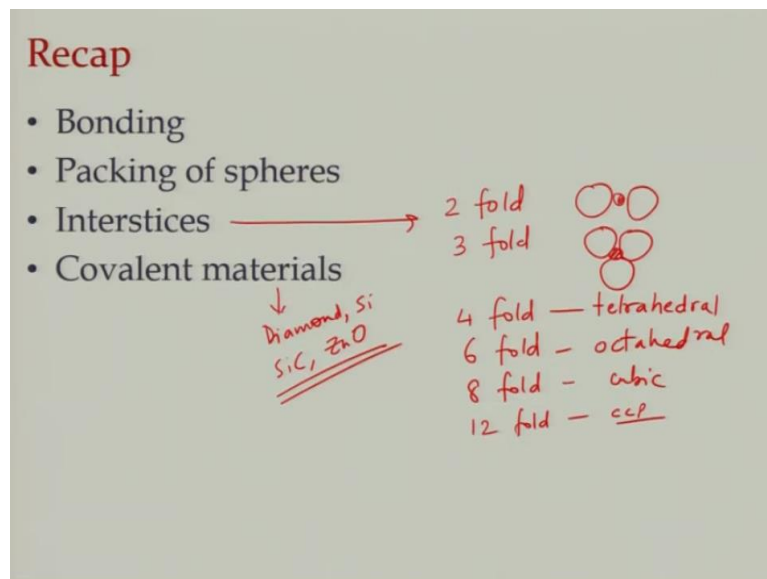**Fundamentals and Applications of Dielectric Ceramics**
Prof. Ashish Garg
Department of Material Science and Engineering
Indian Institute of Technology Kanpur

Lecture No 05
Structure Formation: Ionic Solids

Welcome again to this new lecture for the course, Fundamentals and Applications of Dielectric Ceramics. So, let us just do a brief recap of previous lecture.

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So in the previous lecture we talked about bonding in materials, ceramic materials. So, basically materials are having metallic covalent and ionic bonding and ceramics are typically ionically bonded, although there could be a fraction of some of them having partially covalent bonding. Now, some of the ceramics such as silicon carbide or diamond, they are predominantly covalently bonded though. And then we looked at packing of spheres, the way considering spherical model for atoms, how atoms pack in the space.
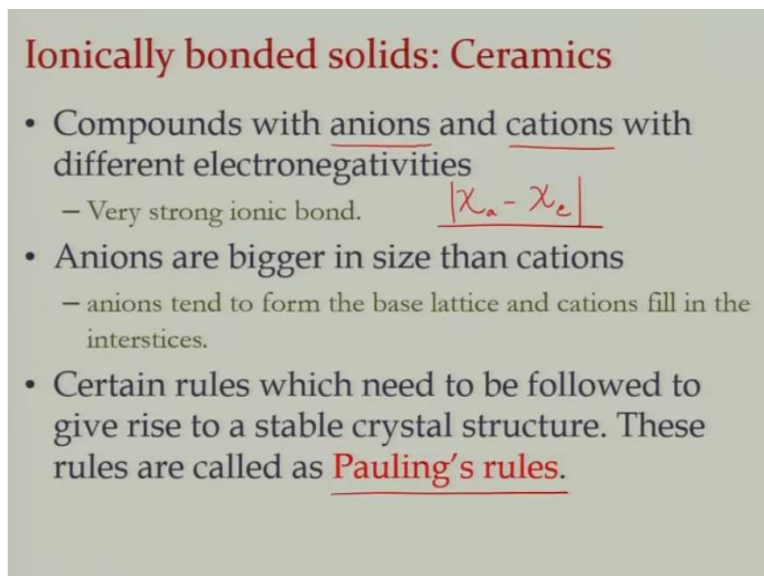
So, generally in terms of simple structures, atoms make simple cubic lattices or body centered cubic lattices or closed pack structures such as face centered cubic or cubic close packing or hexagonal close pack, packing of spheres. And, the way they these atoms pack in the space, they also leave voids between them and these voids are called as interstices and these voids are useful for hosting lot of impurity atoms especially in case of ceramics, they host cations, because the base lattice is made by anions.

So, that is why the concept of interstices were important. So, we looked at two major kinds of interstices such as tetrahedral and octahedral, but there could be other interstices as well depending upon the coordination. So, you can have interstices, theoretically speaking, you can have interstices is a 2-fold coordination, so, you can have something like this. So, this is an impurity atom, you can have 3-fold coordination, which is a triangular kind of lattice.

So, you may have something sitting here, 4-fold we saw tetrahedral, 6-fold we saw octahedral, so this is tetrahedral, this is octahedral, and then there is also possibility of 8-fold which is cubic coordination and then we can have 12-fold, which is basically you can say, CCP kind of coordination, okay. So, we will see that how these co-ordinations are obeyed in case of ceramic structures in subsequent slides. And then we looked at some examples of covalent materials such as diamond, silicon.

And then of course, examples are silicon carbide, zinc oxide. So, all these cubic structured materials they follow diamond structure.

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So, in this lecture, now, we will move on to ionically bonded materials, which are basically ceramics and lot of dielectrics are basically ionically bonded. So, essentially in this class of materials, these are generally compounds made of anions and cations. So, you have negatively charged atoms as anions, which are generally oxygen atoms, but it could be other atoms as well. And then cations are present as well to make the compound.

And in general, these anions and cations have large difference in the electronegativity and this

large difference in the electronegativity is the driving force behind forming a strong ionic bond. So, the difference between electronegativity of anion minus electronegativity of cation, more of this is basically related to bond strength, and higher this is, higher the bond strength is. Generally, anions are bigger than cations, as a result, anions tend to form the base lattice and cations fill in the interstices.

And since, we have ions of different valances; positive and negative, there are certain rules which have to be followed to give rise to structures, which are stable in nature and these rules are called us Pauling's rules. So, as we will see in subsequent slides, what these rules are.

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So, first of all I mean when you put these atoms together, like atom cations, anions together, the question is why should they form a stable structure rather than just remaining as a molecule? So, we need to consider the energetics to reach a conclusion about this. So, cations are defined by ionization energy and anions are generally defined by their electron affinity. This is something that you must know from 12th Standard and then energy of an ionic bond is basically, when you consider the energy of ionic bond, you consider a variety of forces.

So, one is the Van der walls interaction, which is basically attraction which is generally very weak. Then we have Pauli's repulsion to obey Pauli's exclusion principle because you cannot violate Pauli's exclusion principle. And then there is coulombic attraction because you have positive and negative ions which is very strong. And the contribution to this bonding is mainly electrostatic in nature and it is generally defined as the energy which is called as Madelung energy.
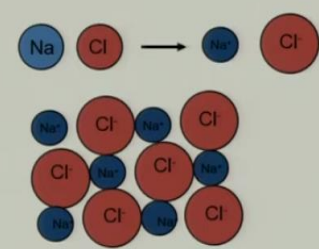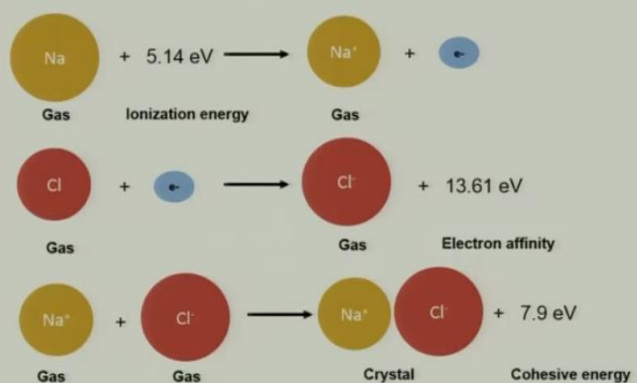
So, how this energy is arrived at, so in ionic solids, so, you would you take this for example sodium and chlorine together. So, instead of sodium chlorine remaining separately in the space or remaining isolated as sodium chlorine molecules, they form an ensemble, which looks something like this. And the reason for that is there is much stronger binding between these sodium and chlorine atoms than just the Van der walls attractive energy which goes as 1/R.

So, there are two kinds of energy, which one has to consider; first is you have to spend energy to ions. So, basically, you have ionization energy of sodium, which is the electron affinity of chlorine and then you have to gain energy to bring these atoms together and this gain in energy is called as cohesive energy.

Look at it this way, so you have this sodium in the gas form, you add to it the ionization energy of let us say 5.14 eV, you make sodium plus ions plus electrons right, it is still in the gas form. Then you have chlorine ions, chlorine atoms gain this electron they become chlorine ions are still in the gaseous form and you release energy of electron affinity which is 13.61eV, okay, which is electron affinity of chlorine.

And when you put these ions together in the gaseous form, sodium and chlorine together, they form the crystal sodium chloride and the release energy of 7.9 eV, which is basically the cohesive energy. So, unless and until the formation of a structure is energetically possible, you cannot make structure, that is why gases are like gases but solids generally are present in the form of crystalline solids or ensemble of atoms, molecules making a solid.

So, basically this is the energy which is which you are gaining to form the sodium chloride solid when you put these sodium and chlorine atoms, which ionize and then based on the differences in the ionization and then so you can see that this energy basically is the difference between the electron affinity and the ionization energy, and this is what you gain in terms of what is called as cohesive energy.

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So, you can also make a general expression about the energetics. So, you consider ion as a reference ion, which is the ion i and then you have all other ions, which are j ions, okay. So, if you consider the interaction energy of this ion i with respect to all other j ions, then I can write this

$$E_{ij} = \sum_{j \neq i} E_{ij}$$

If 1 is the reference ion, then it is going to be E_{12} + E_{13} and E_{14} and so on and so forth. So, this

is how you sum over all the energy. So, this energy turns out to be sum of repulsive energy and the attractive energy. So, there are two terms we have taken we don't take exactly the same form as Lennard-Jones potential, but Eij is approximately represented as the first part, which is,

$$\lambda exp\left(-r_{ij}/\rho\right) \pm \frac{q^2}{4\pi\varepsilon_0 r_{ij}}$$

So, this is the repulsive term and then you have this electrostatic energy, which is

$$\pm \frac{q^2}{4\pi\varepsilon_0 r_{ij}}$$

and r$_{ij}$ is the distance between the iron. So, plus or minus will be determined by whether you have like charges or unlike charges. So, suppose your reference ion is sodium ion. So, the first ion would be the chlorine ion, which means it is a negative ion, so it is a plus minus right? So, minus will be therefore for unlike charges, because plus and minus product will give you minus.

But if you have sodium ion, you will have plus value. So the way the series is going to go is you are going to have plus, then you are going to have minus, then you are going to have plus and so on and so forth. This is how you are going to, so, the first neighbor will be minus second neighbor will be positive, third neighbor will be again negative and the fourth neighbor, so this is first, second, third, fourth, and so on and so forth. That is how the series is going to go forward. And that is how the signs are going to vary.

So as I have said that here, for the repulsive component, we have used this exponential form, rather than R^{-12}, which is using in Lennard-Jones potential, but this term the exponential term, gives a better representation of the repulsive interaction in solids than, whereas -12 form is more useful for gases. So this is the term that we use, so considering that repulsive interaction is a short range interaction.

That is why considering that repulsive interaction exists only among the nearest neighbors, which means it is short range, we can write this

$$E_{ij} = \begin{cases} \lambda exp\left(-R/\rho\right) - \frac{q^2}{4\pi\varepsilon_0 R} \ (for\ nearest\ neighbours) \\ \pm \frac{1}{p_{ij}}\frac{q^2}{R} \ (otherwise) \frac{1}{p_{ij}} = \frac{R}{r_{ij}} \end{cases}$$

So, this is the first one. Or otherwise, if it is I can define a quantity R with respect to r$_{ij}$. So,

R is the distance between the nearest neighbors, but r_{ij} could be longer than R.

It could be 1R, 2R, 3R, 4R so on and so forth. So, basically, the ratio of R with respect to r_{ij} is taken as $1/p_{ij}$ or you can write this p_{ij} is nothing but r_{ij} divided by R. So, basically it is multiples of R, alright. So for the other neighbors, if this term will vanish, because it is short range so repulsive term will be nearly equal to 0 and then we can write just electrostatic term, which is

$$\pm \frac{1}{p_{ij}}\frac{q^2}{R} \quad (otherwise)\frac{1}{p_{ij}} = \frac{R}{r_{ij}}$$

So basically essentially it is nothing but q square divided by, so p_{ij} if you just replace, then it becomes r_{ij}, right? It is nothing but q square divided by r_{ij}. But it is just that p_{ij} is the multiple or sort of integer that you have.

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So for a system with let us say, 2 anions, where you have NaCl for example, so N number of chlorine, N number of sodium ions, I can write the total energy as $N*E_i$. And this is because for one of them I have already considered, so Ns are remaining. So basically, total number of N molecules. So for N molecules, you have

$$E_{total} = NE_i = N\left(Z\lambda exp\left(-R/\rho\right) - \frac{\alpha q^2}{4\pi\varepsilon_0 R}\right)$$

And here we define a term called as, so if you just follow from the previous expression. It turns out you will have this α term here and this α term is nothing but

$$\alpha = \sum_j \frac{(\pm)}{p_{ij}} = Madelung\ Constant$$

and this term is called is Madelung Constant. So, basically summed over all the neighbors.

So, for the first one it will be 1, then it will be 2, it will be 3, 4, and so on and so forth and science will vary depending upon whether you have a like ion or unlike ion. And that is how Madelung Constant, it is a series that should eventually converge. If it does not converge, then you have a problem.

So, this is the general form of this expression, where α is the Madelung Constant, and N is the number of molecules that you have in the system. And if you consider, so this is the total energy. Now, total energy must be minimum at certain point and what is that certain point? You basically differentiate, so at R = R_0, because total energy if you look at it, the way total energy goes is, a total energy must become minimum at certain point right? And this is R = R_0, right? So, which means there is a minima there. So, if we differentiate it with respect to R and then make it equal to 0 at R = R_0, I should get a, so, you just differentiate the above equation,

$$\frac{dE_{total}}{dR} = N\frac{dE_i}{dR} = -N\left(\frac{Z\lambda}{\rho}exp\left(-R/\rho\right) + \frac{\alpha q^2}{4\pi\varepsilon_0 R}\right) = 0$$

$$R_0^2 exp\left(-R_0/\rho\right) = \frac{\rho\alpha q^2}{Z\lambda 4\pi\varepsilon_0}$$

And what you get after this is, for a total lattice energy for a system consisting of 2N ions that is N of chlorine and N of sodium, which means N molecules of sodium chloride.

So, what it means is that 2N ions or N of NaCl molecules. So,

$$E_{total} = -\frac{N\alpha q^2}{4\pi\varepsilon_0 R_0}\left(1 - \frac{\rho}{R_0}\right)$$

$$-\frac{N\alpha q^2}{4\pi\varepsilon_0 R_0} : Madelung\ Energy$$

and this is what is basically a signature of upon strength in a system. So, you can see that it depends upon Madelung Constant.

So, higher the Madelung Constant is, more negative the Madelung energy is and higher the value of q is, more negative the basically energy is, bond strength is, more higher the bond strength is, more negative the bond energy is, higher the bond strength is. So, essentially this is what the differences between for example, something like sodium chloride and magnesium oxide. So, if you look for sodium chloride, sodium chloride has q = 1, q = 1, so which means q^2 will be equal to 1.

But if you take for MgO, so for sodium chloride q square will be equal to 1, if you look for MgO, what will it be? 4 because it is 2*2, right? So, that is why, if you plot this now, energy, so for sodium chloride, the plot will be something like this, but for MgO, it could be something like that, right, it is much more narrower, and also much more deeper. So for MgO, the bond energy is higher, for sodium chloride bond energy is lower. And that is reflected in the properties, MgO has higher melting point as compared to NaCl.

MgO also has lower coefficient of thermal expansion, the width of the well tells you the, it is a signature of the coefficient of thermal expansion. So coefficient of thermal expansion is basically, the change in the ΔA and change in ΔA is more in case of NaCl than in case of MgO. And that is because of change in the bond energy for that unit length and change in the bond energy with respect to the length and change in the length is more in case of NaCl than in case of MgO.

So higher the Madelung Constant, so alpha increases, you can say that bond energy decreases and then q^2 increase, E again decreases. And both of these will mean that material will have higher bond strength. So anything you know similar to you can have zirconium oxide, you can atrium oxide, you can have, so anything with higher q, generally will have high value of melting point and other properties as compared to something with lower value of, so lithium fluoride, sodium chloride they are generally low melting point.

But if you look at magnesium oxide, nickel oxide, iron oxide they are higher melting point. If you look at Y_2O_3, ZrO_2, TrO_2 even higher, Al_2O_3 higher. So, because of higher q and as a result, more negative.

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Example: NaCl

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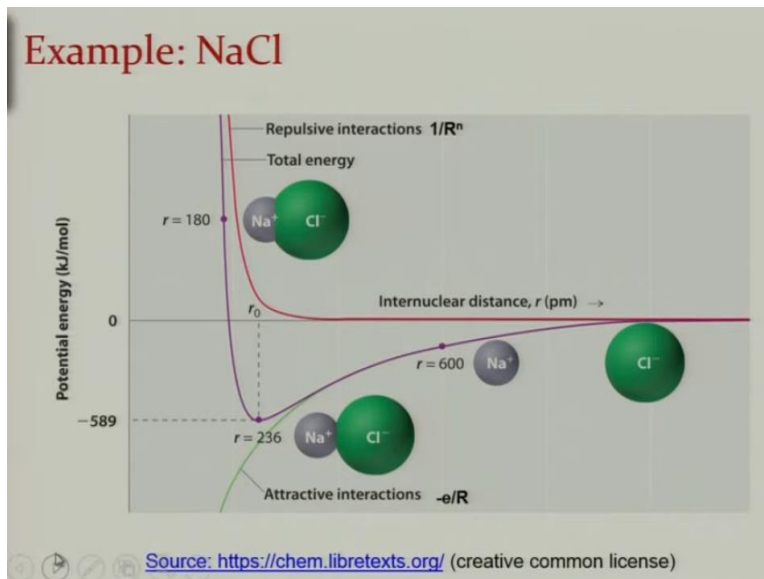
So, this is the fundamental basis of ionic solid and this is how you plot for example, for a given material, so, repulsive interaction in sodium chloride will give you this plot, the red one, the attractive interactions which go as -q/r will give you this plot and the total plot will be the sum between the two and at $r = r_0$, which is basically $r = 236$ picometer. So, basically 236 picometer is the equilibrium distance between sodium and chlorine ions in the system, inter-nuclear distance.

And the energy, potential energy at that point is -589 kilojoule per mole. So, this -589 is the value for sodium chloride, this value will be even more negative for something like MgO or Al2O3 or TiO2 because of the reasons that I explained in the previous slide, okay. And you can see that, the potential the α value will depend upon the slope of this line, okay. So, more steep the curve is, lower the α is going to be, as compared to.

Because this energy can be represented in the form of kT, alright. So, you can represent this in the form of kT and differential of A with respect to T will give you the coefficient of thermal expansion. So, more steep the line is, lower the coefficient of thermal expansion is going to be, which is the case in case of MgO as compared to NaCl, okay.

So, this is what we have to discuss in the form of bond energy and essentially basically, we have formed a basis of why electric materials with ionic bonding can be strong and weak depending upon various parameters and how do you determine the energy.

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So, ionically bonded solid structures, as I said, they consist of large and small ions. Large ions are anions and small ions are cations. And generally, what happens since anions are large and remember these are anions and cations. So, what must happen intuitively for a structure to be stable, anions cannot touch each other and cations cannot touch each other, they have to be separated from each other. But anions and cations would be as close as possible.

So, in general, the structures which are formed are formed by anions, so anions generally form the closed packed structures. In between close packed structures, you will always have polyhedra depending upon the type of voids. So, polyhedra and the closed pack structures are typically formed by anions and they follow, what we call us Pauling rules. So, let us see what these Pauling's rules are. These are sort of guidelines to form these structures.

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Pauling's rules

- Rule 1
    - Cations are coordinated by the anions.
    - Coordination determined by the radius ratio of cations (r_c) to anions (r_a) i.e. r_c/r_a

$r_{tet} = 0.225 \, r$

interstitial atom

host atom.
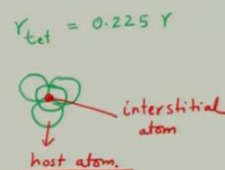
So, rule number one is cations are coordinated by anions, every cation is surrounded by anions, okay. So, it has certain coordination number, this coordination number, the number of nearest neighbors or number of nearest anion neighbors is determined by the radius ratio of cations with respect to anions, that is r_c/r_a if r_c is the radius of cations and r_a is the radius of anions.

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Ligancy or Coordination number	Range of Radius Ratio (r_c/r_a)	Configuration
2	0.0-0.155	Linear
3	0.155-0.225	Triangular
4	0.225-0.414	Tetrahedral
6	0.414-0.732	Octahedral
8	0.732-1.0	Cubic
12	1.0 or above	FCC or HCP

So, there is a range. So, as I said, as we saw earlier, if you now look at it, the tetrahedral coordination gives you $r_{tetrahedral}$ as $0.225r$, but this is a strictly valid only when all the atoms are touching each other and in between I put a cation. So, this is the interstitial atom and these are the host atom. Now, this situation is, so, this is the radius, this is the size of an atom that can be placed inside the tetrahedral void without displacing the host atoms and the host atoms are touching each other.

But in case of ceramic materials, consisting of anions and cations, the host atoms cannot touch each other because of electrostatics. If they touch each other, the electrostatic repulsion will be very high repulsion and repulsion will be very large at close distances. So, as a result, the radius ratio is determined in such a manner so that the radius of the ion that is going to sit in a particular site is little larger than the size of the ion that can be placed inside, little larger than the size of the void.

So, that is why you will see the ratios are determined in such a manner, in case of linear obviously it is not an issue, in case of linear you will have two atoms like this and then in between you put a small atom like this. Generally, smaller atoms whose radius ratio is less than 0.155 will follow this kind of linear configuration, so, this is anion and this is cation.

Triangular void is something which is more than 0.155 and 0.155 is actually the lowest limit of triangular void.

So, which means, if you look at the ideal triangular void, is going to be something like this, right. And this is the size of atom that will fit inside, this is the size of atom that will fit inside without displacing these atoms, right. So, this is a triangular configuration and this is the void. By geometry, you can calculate the size very, this size turns out to be 0.155. So, which means any atom which goes to triangular side in a ceramic structure should be bigger than 0.155, that will ensure that all the anions are away from each other, okay.

So, essentially what is going to happen is, these are the anions, they are going to be little away from each other and the cation, which is going to be like this. So, this is little bigger the ideal size of the triangular void, okay. So, it is more than 0.155 but it is less than 0.225 because 0.225 is now the limit of tetrahedral void, okay. So, the moment it crosses 0.225, which means it is more favorable by the tetrahedral void. So, anything bigger than 0.225 will have tetrahedral coordination.

Similarly, anything, sorry this should be 0.41. Bigger than 0. 414 will be octahedral coordination and anything more than 0.732 will be cubic coordination and these sizes can be determined very easily. So, tetrahedral will basically be, you will have tetrahedral like this, okay. So, this is your host atom and somewhere in between I will put a small atom. So, this small atom will be touching these anions but touching just enough so that theliy are displaced enough because repulsive forces decay very fast they do not have to go too far, they just have to go far enough, so that repulsive forces are minimum.

So, it is just more than 0.225. Octahedral will have this kind of coordination. So, you will have octahedral like this, okay. So here, you will have, these are the atoms and somewhere in between, we will have this little octahedral void, which is less than 0.732 but more than the size of octahedral void, okay. The moment you reach 0.732, it is the boundary of cubic and what is cubic coordination, it is basically eight fold coordination, where you have these as host atoms.

And the impurity will sit inside somewhere in between eight fold coordination, okay. This is 0.732, again you can calculate very easily, if all of them are touching each other,

then,

$$4r = \sqrt{3a}$$

,okay. So, this can be calculated easily. And when you go to 1, 1 is nothing but, your FCC or HCP kind of configuration, where you have 12-fold coordination, just like you have FCC structure, right. So, that is something which we see for example, in barium titanate, okay, where barium is a very big ion.

So, basically it goes, as you go from smaller cation to large cations, the configuration changes from linear to triangular to tetrahedral to octahedral to cubic to FCC. And this is solely determined by the fact that size of the iron should be little bigger than the ideal size of the void. Ideal size represents the condition when the anions are touching each other, but we do not want to have touching situation because of repulsion, that is why the ions are slightly, so the size is slightly bigger than the ideal size.

So, that anions are displaced with respect to each other, but cations and anions always touch each other. So, this is the radius ratio concept which determines what kind of coordination a cation will have in an anion lattice. So, we will stop here. We have looked at the first rule of Pauling's rules and other four rules are basically based on electro statistics, fairly similar to each other, okay. So, we will look at them in the next lecture.