Concepts of Chemistry for Engineering
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Lecture No. 31
Crystal Field Theory: Tetrahedral Complex

If you have understood octahedral splitting, you should be able to understand tetrahedral. But of course, the problem being it is tetrahedral, the angles are different. Octahedral good thing it was on dz square you have one orbital clearly and the ligands are coming from there, dxy, x and y direction ligands are coming directly.

But in tetrahedral, you see the orbitals inside somewhere, the ligands are coming from somewhere. It is not like head on coalition. It is not exactly direct approach of the ligand, I mean, direct overlap of the ligand and orbital are not happening. That is where, of course, you should be able to understand that destabilization will not be that much.

So, the splitting, of course, there will be splitting also in the d orbital, splitting extend to which the splitting will occur will not be too much, because in octahedral it is a head on collision. Bang. In tetrahedral, it is going to be side on, just touching and going, almost kissing and running away. So, that is where you will see, in tetrahedral, you will never have any low spin configuration, means the extent of separation between t and e or in this case we do not say t2g and eg, we say t2 and e, same dxy, dyz, dxz is t2, e not eg, e is dx2y2, dz2. We will come.

Since octahedral we are saying that of course six of the ligands are approaching. In tetrahedral only 4 of them are approaching. In octahedral it is a head on collision. In tetrahedral it is just sidewise you can say or very little collision, very little good evolver. The repulsion from the ligand, or ligand electron will not be able to repeal the metal electron that efficiently as you see in the octahedral case.

So, the splitting, the repulsion is this, that splitting is nothing but difference between e and t2, whatever we are saying, this three orbital versus two orbital splitting the distance. So, that is never going to be too high. If it is not too high, if it is always like this at let us say room temperature, the electron can access all of them. So, it is always going to be high spin. We do not have to worry about low spin in tetrahedral case.

Only in octahedral case we have to think about low spin and high spin. The reason is very simple number of ligands are less, so repulsion is less, 4 versus 6, four ligands versus 6 ligand, tetrahedral means 4 ligands and also the approach of the login with respect to the orbital is not going to be direct. It is almost a side approach.

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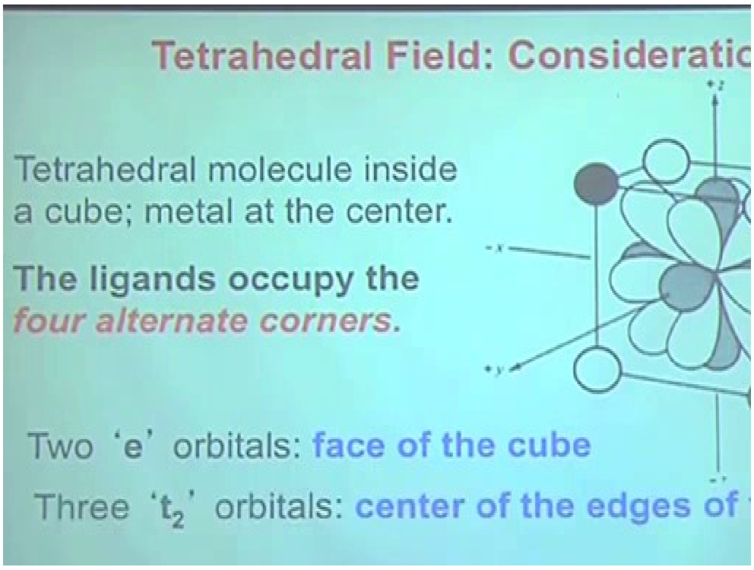

Tetrahedral Field: Consideratio

Tetrahedral molecule inside a cube; metal at the center.

The ligands occupy the *four alternate corners.*

Two 'e' orbitals: face of the cube

Three 't_2' orbitals: center of the edges of

Now, so the ligands, as you can see, occupying alternate orbital over here, alternate, occupy alternate corner 1, 2, 3 and one in the back, 4 ligands. You imagine just methane, CH4, how the hydrogens are with respect to carbon. Imagine carbon is your metal center and four hydrogens are your four ligand. That is how it is. It is not octahedral, it is tetrahedral. So, e orbitals we will be calling e orbitals and t2 orbitals.

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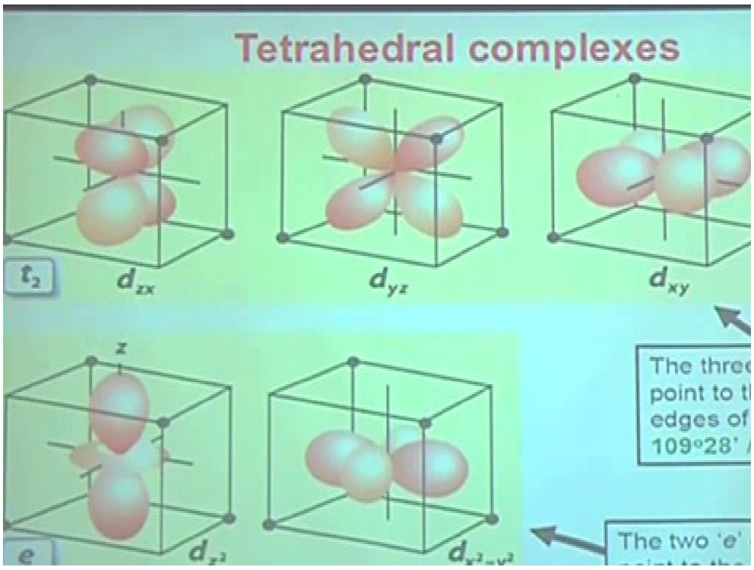

Tetrahedral complexes

The three
point to t
edges of
109°28'

The two 'e'

So, here they are. In this case, actually, I will say you why it will be. In this case, it is the reverse of octahedral. These are going to be stabilized dz2 and dx2y2 are going to be stabilize, because these orbitals are the ones which will be facing this ligand list. So, ligand is here, ligand is there, ligand is there and ligand is here. Can you see the 4 ligands, 4 black dots, strong dots, 1, 2, 3, 4. See the dz square orbital and dx2 orbital, y2 orbital these two orbitals are facing the ligand least. They are farthest from the ligand that means that repulsion will be less or they are the one which is going to be stabilized.

If you think about the octahedral, of course, from the three metal ion everything destabilize and from there further stabilized and further destabilized. Over here the pattern is just opposite. 3, 2 was for octahedral, it will be 2, 3, e will be the stabilized one, t2, not t2g mind you, not eg again, e and t2, these are coming from symmetry elements, which will not be taught. So, it is like this. So, these two orbitals are stabilized. These three are destabilized, relatively destabilized.

See, once again, these are the four ligands 1, 2, 3, 4. These four ligands are with respect to this it is more closed to the orbitals. These ligands are close to these orbitals more compared to these. You just see. Look at the angle how far they are. You will be able to see it. It is going to be little bit twisted from octahedral, because octahedral it was clear cut. Tetrahedral, you have to see that 109 angle. That is the angle between the two ligands going to be.

Now, these are the one, these d orbitals are the one which is going to be destabilized compared to these two that is because they are facing the ligand more efficiently or their ligand electrons and metal electrons are going to repel each other more strongly because they are coming too close to each other compared to that we seen here. You see it. It should be fine.

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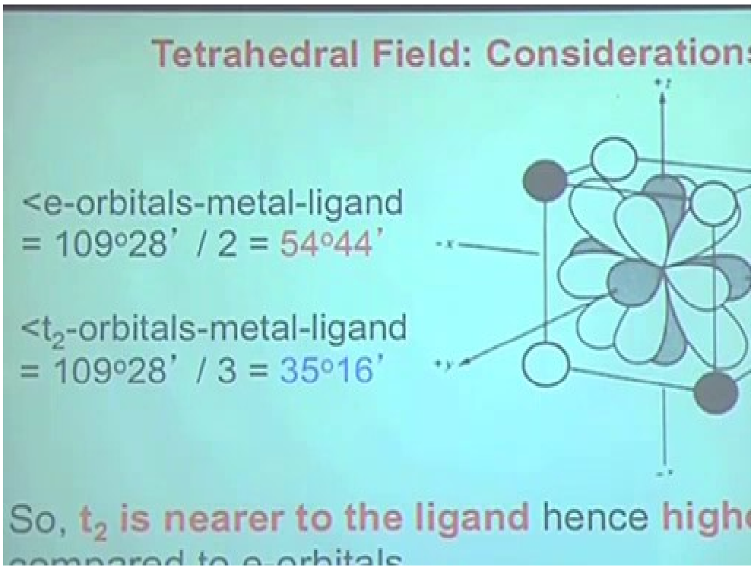

Tetrahedral Field: Consideration

<e-orbitals-metal-ligand
= 109°28' / 2 = 54°44'

<t_2-orbitals-metal-ligand
= 109°28' / 3 = 35°16'

So, t_2 is nearer to the ligand hence high

compared to e-orbitals

Now, also just numerically speaking, you can see that the e orbitals are, of course, 109 angle total if you see the geometry and it is two of them show it is 54 degree with respect to the center, you can look at, if it is not clear, you can come back. I will just. T2 is nearer to the ligand, hence higher energy. E is further from ligand thereby lesser energy. I think this picture gives you the clear idea where the ligands are and where the orbitals are. It is a 3D view. No, amount of explanation will not be good enough. You have to look at. I cannot explain perfectly. You have to look at.

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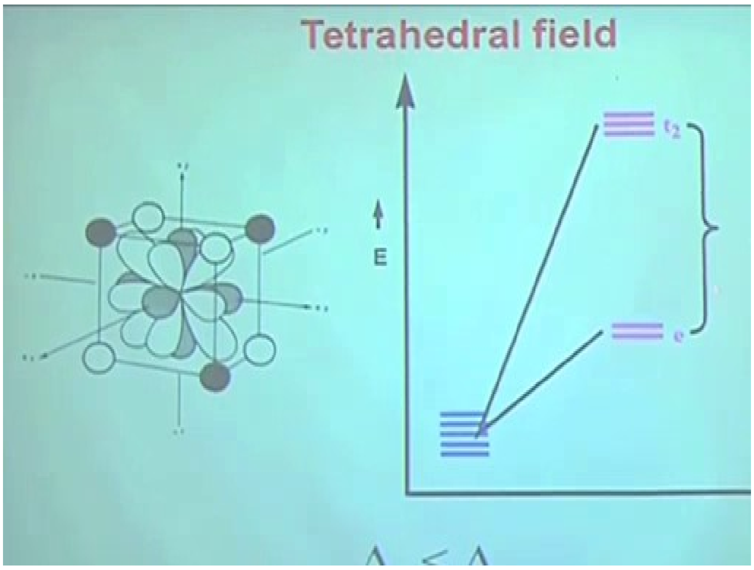

Tetrahedral field

Now, so, if you look at delta g and delta t, in delta 0, delta 0, I meant actually delta octahedral, delta t means delta tetrahedral. This is the splitting. Now, this splitting, delta 0 will be very high, that is what we are saying, compared to delta t. What is the reason? Once again 4 ligand versus 6 ligands, you have 6 ligands for octahedral, you have four ligands for tetrahedral. Thereby, the delta t will be less. Delta 0 or delta octahedral is always going to be more. Now, what is the extent, and also you have seen e below t2 up.

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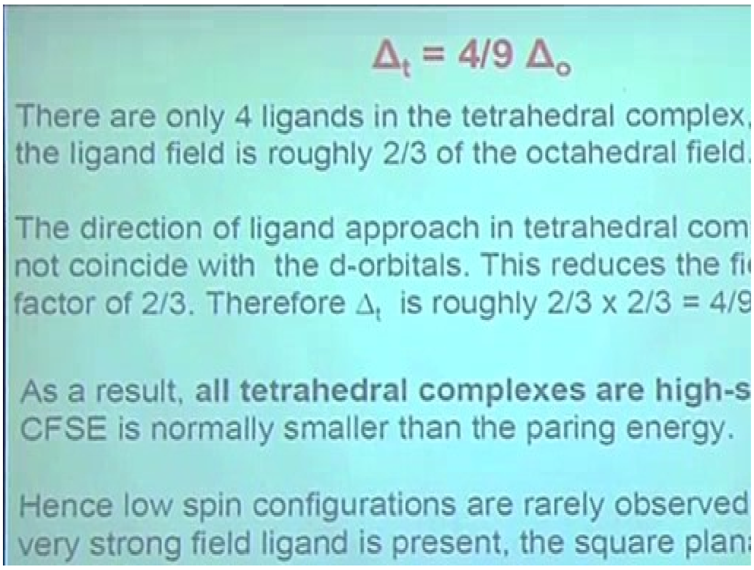

$\Delta_t = 4/9\ \Delta_o$

There are only 4 ligands in the tetrahedral complex, the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral com not coincide with the d-orbitals. This reduces the fi factor of 2/3. Therefore Δ_t is roughly 2/3 x 2/3 = 4/9

As a result, **all tetrahedral complexes are high-s** CFSE is normally smaller than the paring energy.

Hence low spin configurations are rarely observed very strong field ligand is present, the square plan

Now, overall, this is the one you have to kind of remember. It is like two third and two third. Why two-third and two-third? So, 4, 9, where is that coming from? So, 4 ligands versus 6 ligands, 6 times two-third is going to be 4 ligands. 6 ligands was for octahedral, 4 ligand is for tetrahedral. So, two-third number of ligands, two-third times 6 is 4. There is a component of two-third.

And there is this, roughly due to the angle since they were colliding head on and here it is a 109 degree angle is there and thereby how the orbitals are oriented towards the ligand that gives you another two-third. Means what I am saying is the extent to which ligand in octahedral case is interacting versus the extent to which tetrahedral is interacting. Overall, that is going to be 4, 9 of delta 0.

Delta octahedral is always going to be higher compared to delta tetrahedral for a let us say given metal complex. You have ML4, ML6, same metal, same ligand, everything else, oxidation states chase in. So, tetrahedral, that destabilization or the splitting is always going to be less. How less? It is 4, 9 times delta 0. Where the 4, 9 is coming from, two-third times two-third, two-third due to the number of ligands, 6 times two-third is 4, another two-third due to the angle of approach, how it is coming.

That is what I was trying to tell. All tetrahedral complexes are high spin, because the splitting is less. Octahedral and tetrahedral completely different scenario, t2g lower, eg up. Here, e not eg, e lower, t2 up. That is all you need to know. Now, let us go.

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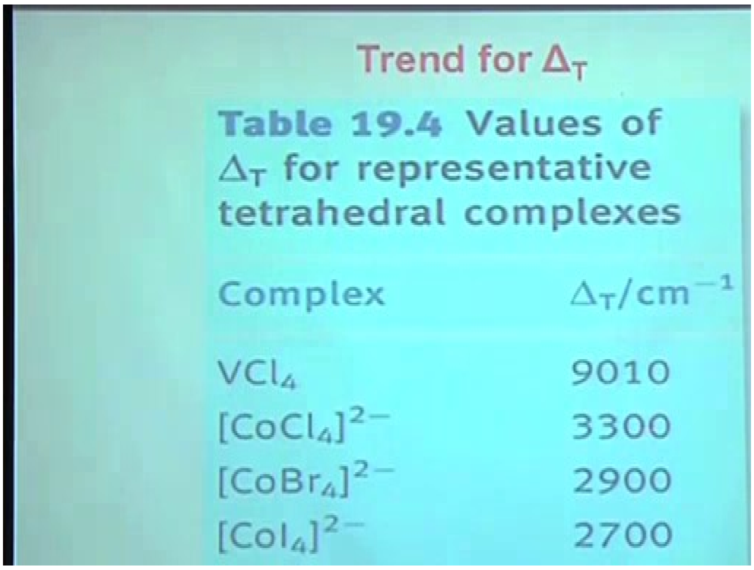

Trend for Δ_T

Table 19.4 Values of Δ_T for representative tetrahedral complexes

Complex	Δ_T/cm^{-1}
VCl_4	9010
$[CoCl_4]^{2-}$	3300
$[CoBr_4]^{2-}$	2900
$[CoI_4]^{2-}$	2700

So, as you see, now, you look at these values. We were saying 20,000, 25,000 and so on for this delta octahedral. Delta tetrahedral is always very small in number. If you now go back and look at the corresponding, let us say, octahedral complex, you will be able to see that these are lower in number 5, 10 minutes, 5 minutes.

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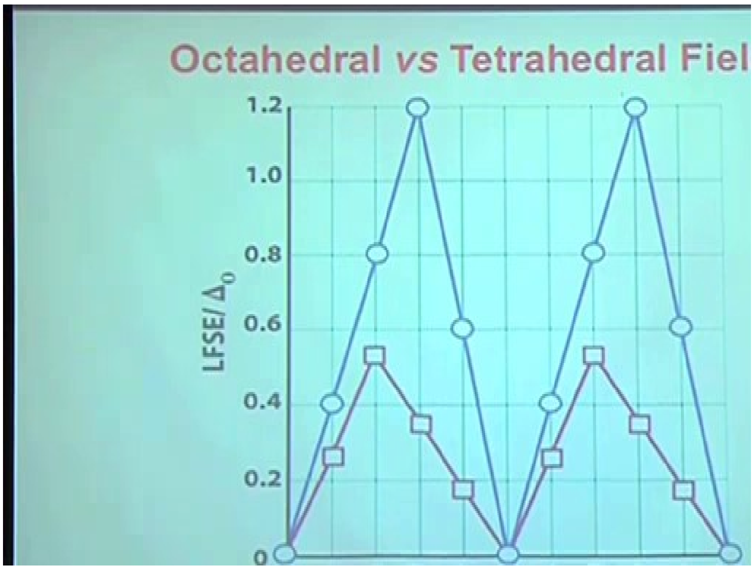
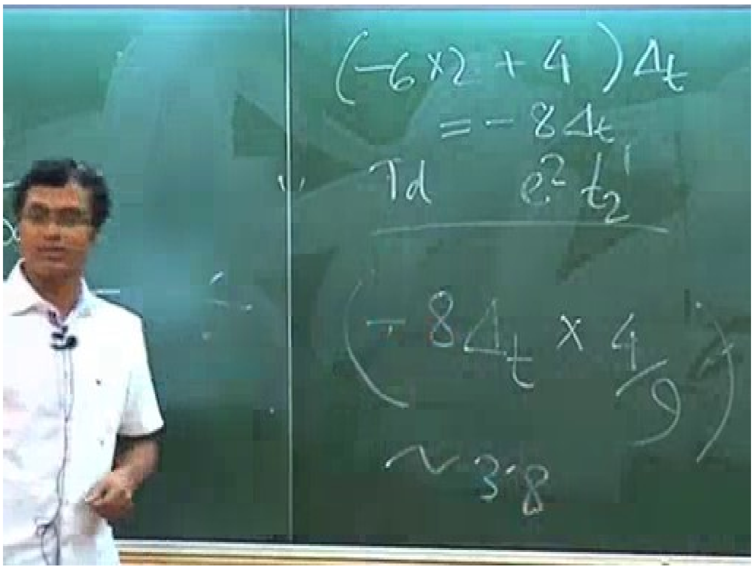


Octahedral *vs* Tetrahedral Fiel



So, if you now compare the stability or overall between octahedral and tetrahedral, if it is 0 electron no stability, let us say, we are not talking. If it is one electron in the octahedral case, the blue line is for octahedral, ligand field stabilization energy plot versus number of electrons plot. So, if you have a one electron, it is going to be in t2g1 for octahedral case. It is going to be 0.4. If you have two unpaired electron, it is going to be 0.8 or 8Dq or 0.8 delta 0. We were talking 4Dq, 8Dq. If it is three, it is 12 or 1.2 delta 0.

Similarly, you can start putting for tetrahedron. Tetrahedral, it is e1, not t, e1, e2. E1 is going to be 6 delta t. If that 6 delta t you multiply by 4, 9 of delta 0, which that 4, 9 term, you will be able to see that this is the actual difference. This plot actually makes complete sense. 5 unpaired electron. We are talking all high spin versus high spin, octahedral high spin, tetrahedral high spin we are comparing. 5 unpaired electron high spin in octahedral means t2g3eg2, 0, total 0. Three of them are in here, two of them are in here, so 0.

In tetrahedral, it is always high spin e2 t23. So, it is once again going to be 0. That is how for, as the number of electron increases, how the high spin case ligand field stabilization energy is varying, you will be able to understand. I think we are losing the concentration. I am with you just 1 or 2 minutes. I will not take too much.

Now, so, let us look at this one. If you understand a little bit of this one, I think I will let you go today. Anything you pick up three unpaired electron, number of electrons is 3, number of 3 unpaired electrons or 3 electrons, d3 configuration. For octahedral case it is what, t2g and eg, it is going to be 1, 2, 3, t2g3 and eg0. T2g3 means each of them are having 4Dq stabilization. So, it is going to be minus 12Dq or minus 1.2 delta 0 or delta octahedral. That is the stabilization energy. That is over there.

Now, you talk about tetrahedral case, three electron, it is going to be e and t2, e2t21. E2 means, 6 plus 6; 12, 12Dq stabilization. If it is 3 electrons 1, 2, 3, it is never going to pair up, unless there is no option then it will pair up. It is never high spin, low spin situation. It is always high spin situation. 1, 2, 3 each of them are 6 delta t, not delta 0, delta t. So, two of them are 12 delta t. One of them is 4 delta t, minus 12 plus 4 minus 8 minus delta t now that is tetrahedral. How much it is in terms of octagon multiplied by 4, 9. So, apparently close to four delta 0. Most of you got it.

So, minus 6 times 2 plus 4 delta t that is going to be for e2t21 this is going to be for tetrahedral e2t21 electronic configuration. Overall, how much it is? It is going to be minus 8 delta t. Now, as you know minus 8 delta t means this is time 4 by 9 for overall this is going to be in delta 0, so it is nearly going to be let us say 3.8 or 3.9 whatever it is, 9 and 8 cancel out or whatever it is 32 divided by 9.

So, now, you look back in here 3.8 or so. So, that is how each of the electronic configuration, once again mind you this is high spin, tetrahedral is always high spin, tetrahedral high spin versus octahedral high spin we are trying to compare. You should be able to do this plot by yourself. If you think you have understood this class or if you after studying 10 minutes, 15 minutes whatever it takes you or one hour or whatever it takes you, after studying it, if you can plot this one, I think that will reflect that you have understood the delta 0 and delta t business.

Now, there is another term which is called octahedral site stabilization energy. What is that? That is nothing but the same electronic configuration or same electron number if it is given for octahedral versus it is given for tetrahedral what is the stabilization, net stabilization, let us say, net stabilization. This is two electron stabilization for octahedral. This is two electron stabilization for tetrahedral. What is the difference between the two?

You will never see that octahedral is less stable compared to the tetrahedral. It is always octahedral is more stable. How much stable that is what is usually called octahedral site stabilization energy, OSSE. It is perhaps not discussed in the class. So, you can understand the difference for the same type of electron or same electronic configuration how much stability octahedral is going to get compared to tetrahedral.

But mind you again this is the comparison between the high spin, high spin, tetrahedral high spin, tetrahedral is always high spin, octahedral high spin. But sometimes this octahedral site stabilization energy can differ, sometimes tetrahedral is more stable if octahedral stabilize, I mean, octahedral that crystal field stabilization energy becomes less that can happen if it is, let us say, I mean, scenarios will be there where you can have such thing. We will discuss those.

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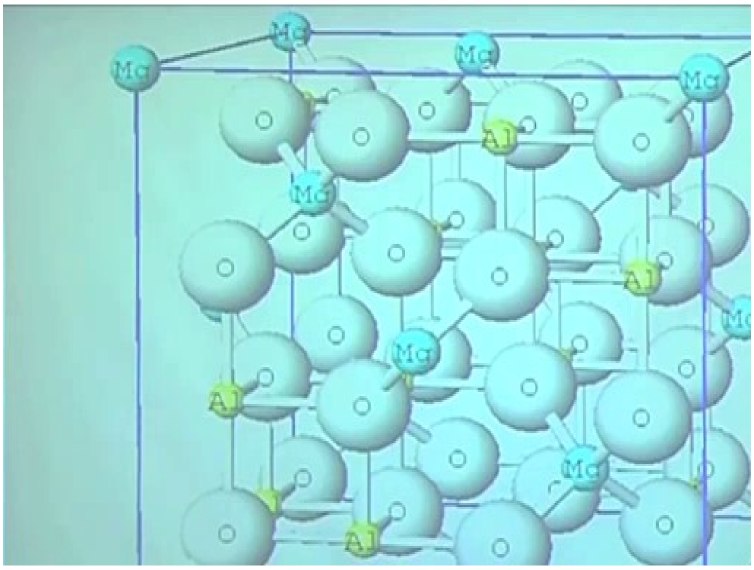

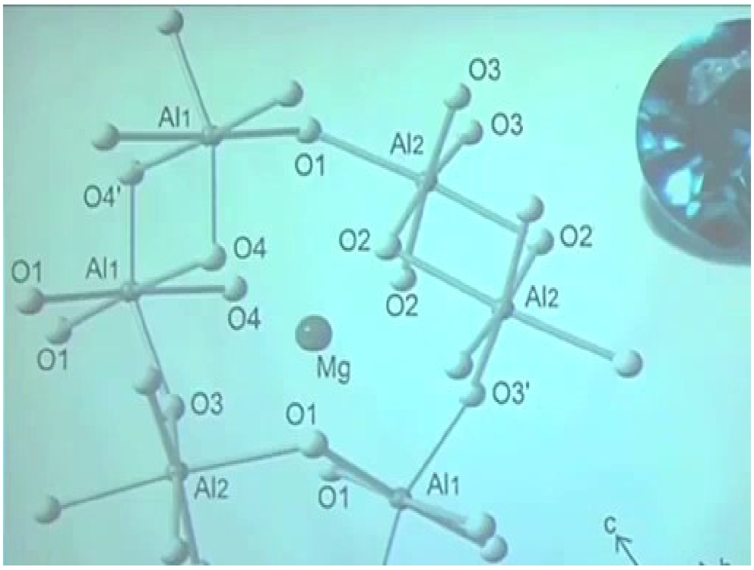

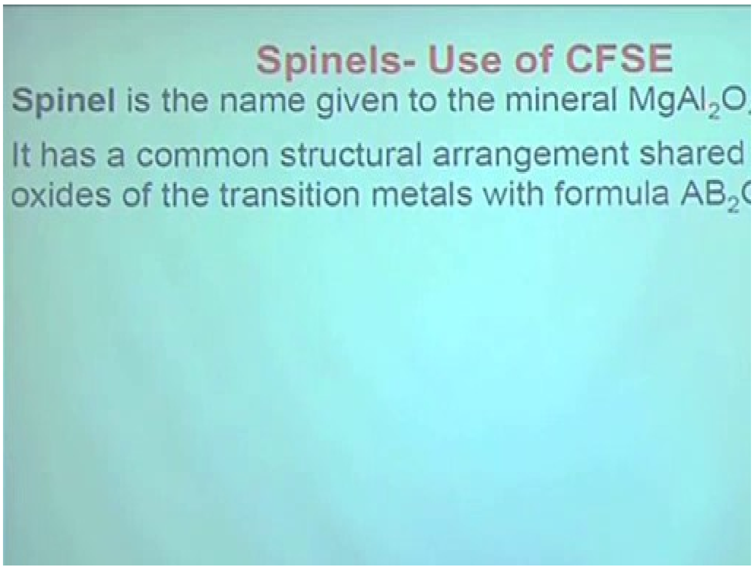

Spinels- Use of CFSE

Spinel is the name given to the mineral $MgAl_2O$

It has a common structural arrangement shared

oxides of the transition metals with formula AB_2

So, those next topic will be spinel, normal spinels. Spinels are what? Spinels are nothing but the gems what do you see. These are different metal oxides with the form AB2O4, magnesium, aluminum, one magnesium, two aluminum and four oxygen. Different of these the jewels that you see, different rocks these are nothing but spinel. Spinels are of two types, normal spinel and inverse spinel. This is the only topic that is left for this chapter coordination complex. So, the class is over.