Basics in Inorganic Chemistry
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Lecture - 09
CFT for Tetrahedral Complex

If you have understood octahedral you know 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 will as on dz square you have one orbital clearly and the ligands are coming from there d xy, x and y direction ligands are coming directly.

But, in tetrahedral you see the orbitals is somewhere the ligands are coming from somewhere. It is not like head on collision, 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 the destabilization will not be that much.

So, the splitting of course, there will be splitting also in the d orbital, splitting extent to which the splitting will occur will not be too much. Because, in octahedral it is a head on collision than in tetrahedral it is going to be side on just touching and going almost kissing and running away, right.

So, that is where; that is where you will see in tetrahedral you will never have any low spin configuration. Means, the extend of separation between t and e or in this case we do not say t 2 g and e g, we say t 2 and e same d xy, d yz, d xz is t 2 e not eg; e is dx 2 y 2 dz 2 ok, will come.

Since, octahedral we are saying that of course, 6 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 you know just sidewise you can say or very little collision very little good overlap. 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 t 2 whatever we are saying; these 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 all 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 ok, clear. The reason is very simple, number of ligands are less; so, repulsion is less 4 verses 6; 4 ligands verses 6 ligand tetrahedral; means, 4 ligands and also the approach of the ligand with respect to the orbital is not going to be direct it is almost aside approach, ok.

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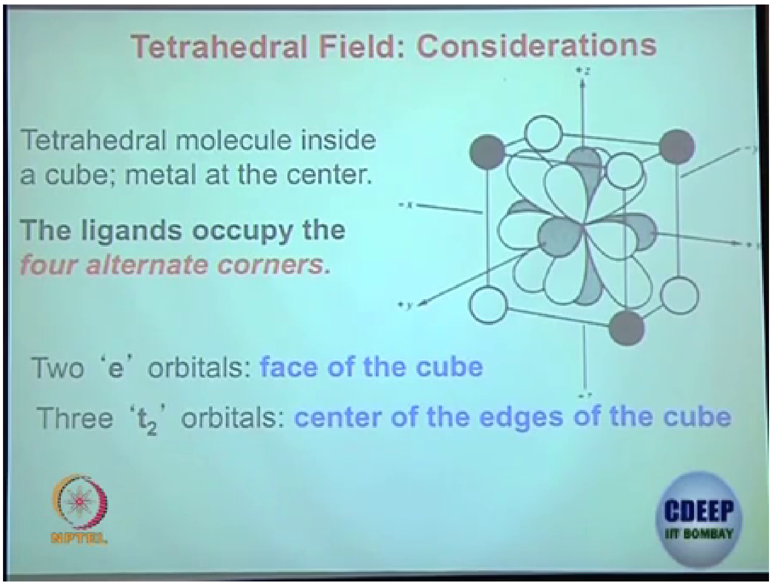

Tetrahedral Field: Considerations

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 the cube

NPTEL

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Now so, the ligands as you can see alter occupying alternate orbital over here alter alternate sorry occupy alternate corner 1, 2, 3 and one in the back; 4 ligands, right. You imagine just methane CH 4, how the hydrogens are with respect to carbon. Imagine carbon is your metal center and 4 hydrogens are your 4 ligand that is how it is right; it is not octahedral, it is tetrahedral. So, e orbitals will be calling e orbitals and t 2 orbitals, ok.

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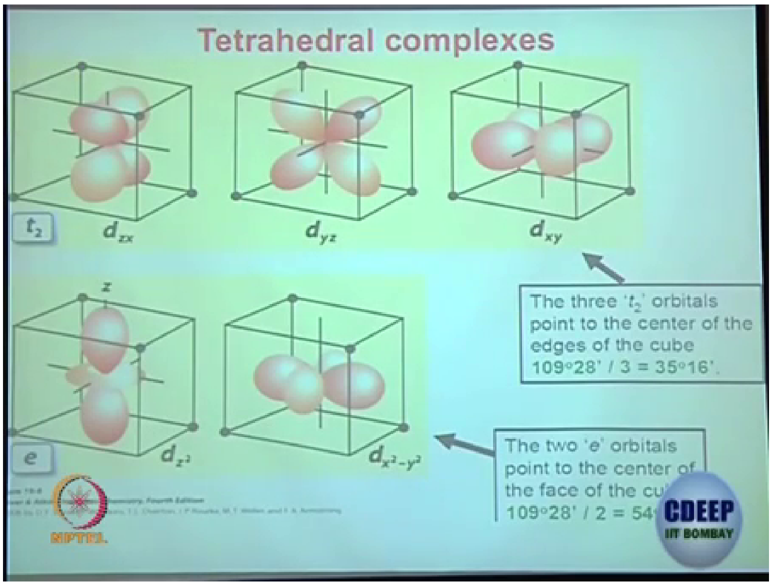

Tetrahedral complexes

The three 't_2' orbitals point to the center of the edges of the cube 109°28' / 3 = 35°16'.

The two 'e' orbitals point to the center of the face of the cu
109°28' / 2 = 54

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 d z 2 and d x 2 y 2 are going to be stabilized, because these orbitals are the ones which will be facing this ligand least.

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 d z square orbital and d x 2 orbital y 2 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 pre metal ion everything destabilized and from there further stabilize and further destabilized, right. Over here the pattern is just opposite 3 2 was for octahedral, it will be 2 3; sorry, e will be the stabilized one t 2 not t 2 g mind you, not e g. Again, e and t 2 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 4 ligands 1 2 3 4. These 4 ligands are with respect to these it is more close 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, ok. It is going to be a little bit twisted from octahedral, because octahedral it was clear cut tetrahedral you have to see that 1 0 9 angle 109 angle right, that is the angle between the 2 you know 2 ligands going to be, right.

Now, these are the one t; 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 they are ligand electrons. And, metal electrons are going to repeal each other more strongly, because they are coming too close to each other compared to that we see in here, clear; see it, it should be fine.

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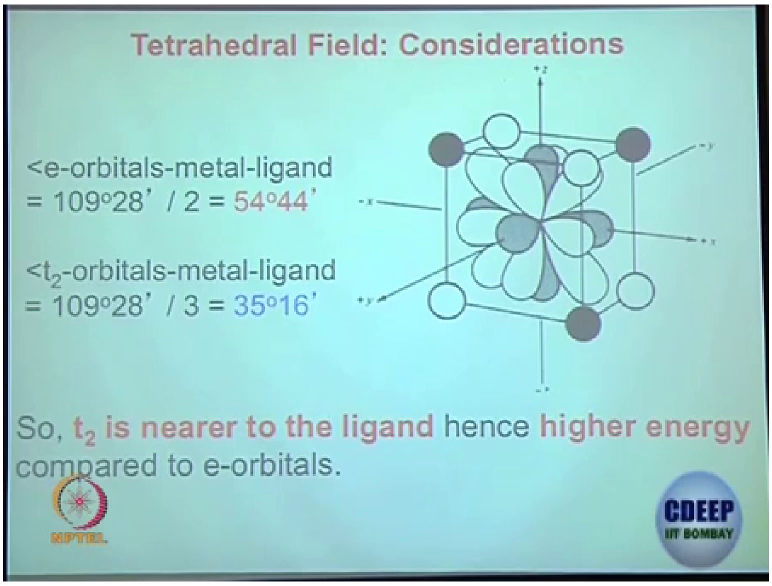

Tetrahedral Field: Considerations

<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 higher energy 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 2 of them. So, it is 54 degree with respect to the center you can come look at if it is not clear you can come back I will just. T 2 is nearer to the ligand hence higher energy e is further for ligand then 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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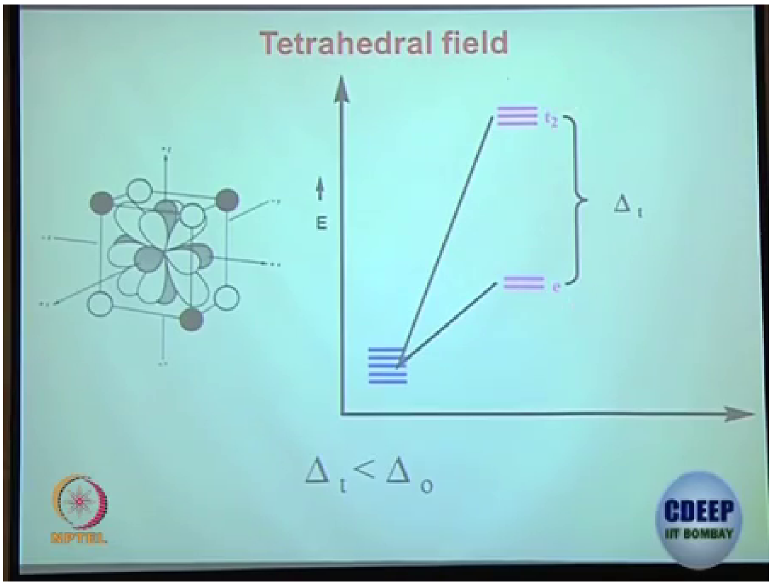

Tetrahedral field

$\Delta_t < \Delta_0$

Now so, if you look at delta g and delta t. In delta 0, delta 0 it I meant actually delta octahedral, delta t means delta tetrahedral this is the splitting, ok. Now, this splitting delta 0 will be very high that is what we are saying compared to delta t. What is the reason, one second 4 ligand versus 6 ligands; you have 6 ligands for octahedral, you have 4 ligands for tetrahedral. There by the delta t will be less delta 0 or delta octahedral is always going to be more, ok.

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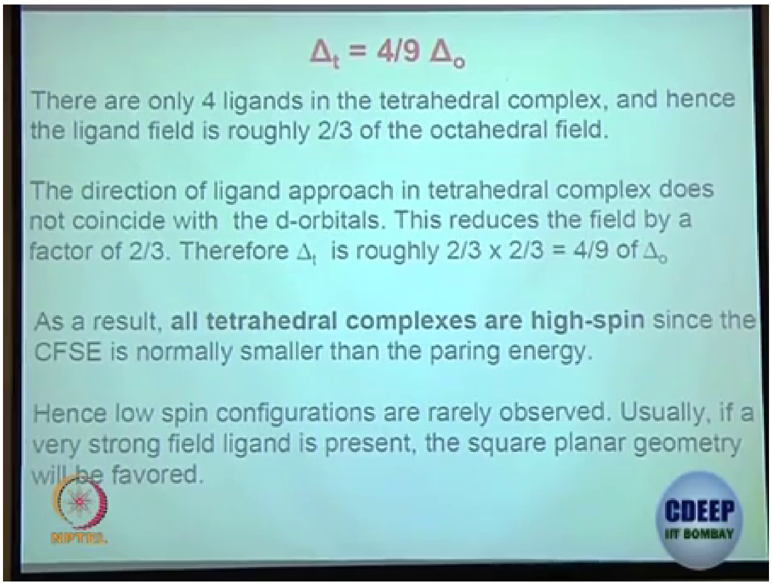

$\Delta_t = 4/9\ \Delta_o$

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

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly 2/3 x 2/3 = 4/9 of Δ_o

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

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

Now, what is the extent and also you have seen E below t 2 up. 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, four-nine. Where is that coming from, so, 4 ligands verses 6 ligands. 6 times two-third is going to be 4 ligands; 6 ligands was for octahedral, 4 ligands is for tetrahedral.

So, two-third number of ligands two-third time 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 extent to which tetrahedral is interacting. Overall that is going to be four-nine of delta 0.

Delta octahedral is always going to be higher compared to delta tetrahedral for let us say given metal complex. You have ml 4, ml 6 same metal, same ligand everything else oxidation states say same. So, tetrahedral that destabilization or the splitting is always going to be less; how less? It is four-nine times delta 0. Where the four-nine is coming from two-third times two-third; 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 anyway that is what I was trying to tell.

All tetrahedral complexes are high spin, because the splitting is less, understood; octahedral and tetrahedral completely different scenario t 2 g lower, eg up. Here, e not eg ok, e lower t 2 up that is all you need to do; now let us go.

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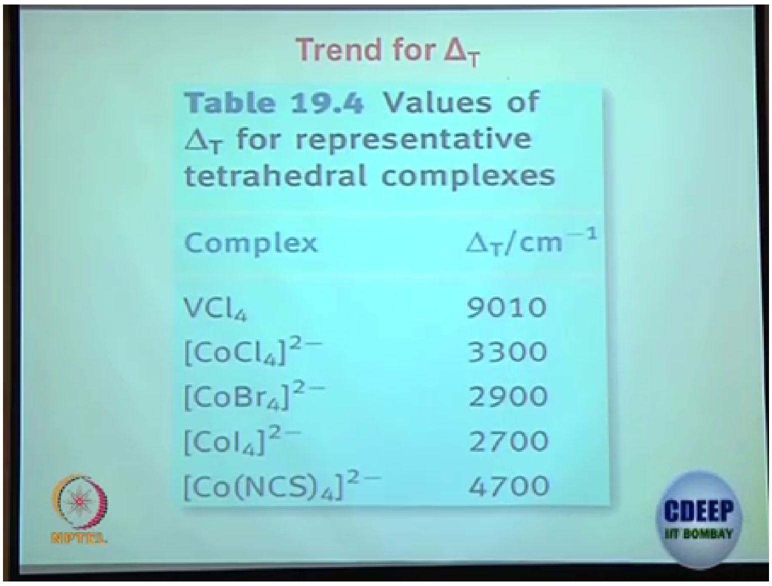

Trend for Δ_T

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
$[Co(NCS)_4]^{2-}$	4700

So, as you see now you look at these values we were saying 20000 25000 so on for this delta; 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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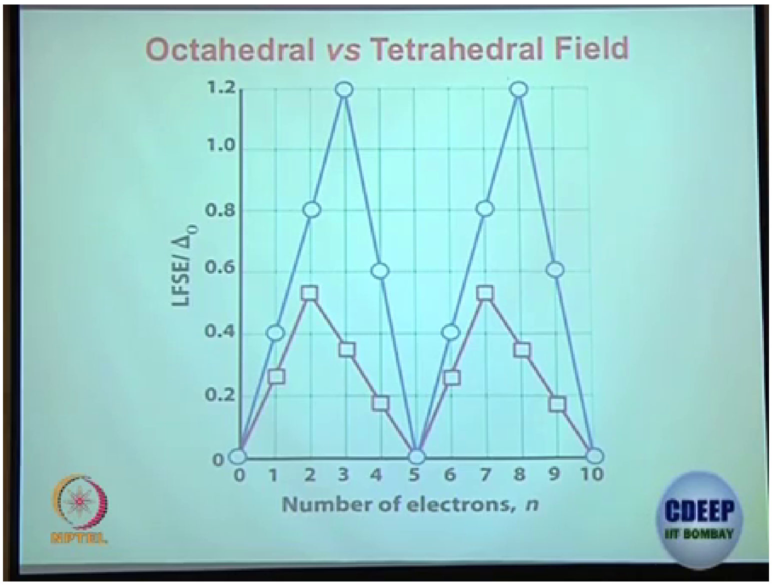
Octahedral *vs* Tetrahedral Field

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 1 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 1 electron it is going to be in t 2 g 1 for octahedral case, it is going to be 0.4.

If you have to unpaired electron it is going to be 0.8 or 8 dq or 0.8 delta 0; we are talking 4 dq, 10 8 dq, if it is 3 it is 12 or 1.2 delta 0. Similarly, you can start putting for tetrahedral,

tetrahedral it is e 1 not t, e 1 e 2. E1 is going to be 6, 6 delta t, if that 6 delta t you multiply by four-nine of delta 0 which that four-nine term. You will be able to see that this is the actual difference, this plot actually makes complete sense.

Five unpaired electron, we are talking all high spin versus high spin; octahedral high spin, tetrahedral high spin we are comparing. Five unpaired electron high spin in octahedral means t 2 g 3 eg 2 0 total 0; 3 of them are in here, 2 of them are in here so, 0. In octa in tetrahedral it is (Refer Time: 13:15) high spin e 2 t 2 3, right. So, it is once again going to be 0, ok. That is how far 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, ok.

Now so, let us look at this one if you understand little bit of this one I think I will let you go today, ok. Anything you pick up 3, 3 unpaired electron; number of electrons is 3 number of three unpaired electrons or 3 electrons d 3 configuration.

For octahedral case it is what t 2 g and eg, it is going to be 1 2 3 t 2 g 3 and eg 0; t 2 g 3 means each of them are having 4 dq stabilization. So, it is going to be minus 12 dq or minus 1.2 delta 0 or delta octahedral that is the stabilization energy ok, that is over there.

Now, you talk about tetrahedral. Tetrahedral case three electron, it is going to be e and t 2; e 2 t 2 1, e 2 t 2 1. E 2 means 6 plus 6 12, 12 dq 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 o delta t.

So, 2 of them are 12 delta t, one of them is 4 delta t minus 12 plus 4 minus 8; minus 8 delta t now that is tetrahedral how much it is in terms of octahedral? Multiplied by four-nine. So, apparent close to 4, 4 delta o right. Most of you got it.

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So, minus 6 times 2 plus 4 delta t that is going to be for e 2 t 2 1, this is going to be for tetrahedral e 2 t 2 1 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 minus 8 delta t means this is time 4 by 9 for overall this is going to be in delta 0, right. So, it is nearly going to be let us say 3.8 or 3.9 whatever it is 9 and 8 cancel out whatever it is 32 divide by 9, right.

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, ok.

If you think you have understood this class or if you after studying 10 minutes 15 minutes whatever, it takes you or 1 hour 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 (Refer Time: 17:46), ok.

Now, there is another term which is called octahedral sight 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 electrons stabilization for octahedral, this is two electrons stabilization for tetrahedral what is the difference between that two. You will never see that octahedral is less stable compared to 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, ok.

But mind you again this is the comparison between that high spin high spin tetrahedral high spin octa tetrahedral is always high spin octahedral high spin. But, sometime this octahedral sites stabilization energy can differ, sometime tetrahedral is more stable if octahedral stabilize is 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, ok.

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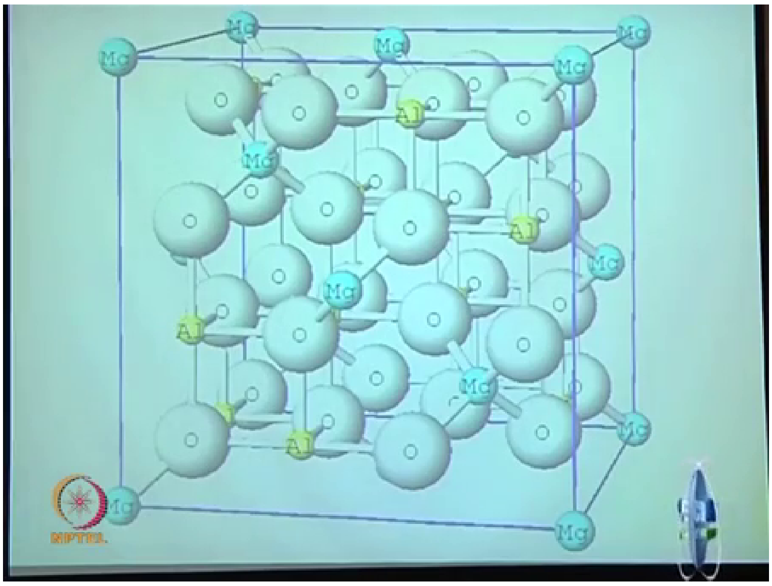

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So, those next topic will be spinal normal spinals. Spinals are what, spinners are nothing, but the gems what do you will see, ok. This these are different metal oxides with the form AB 2 O 4; magnesium aluminum that 1 magnesium, 2 aluminium and 4 oxygen.

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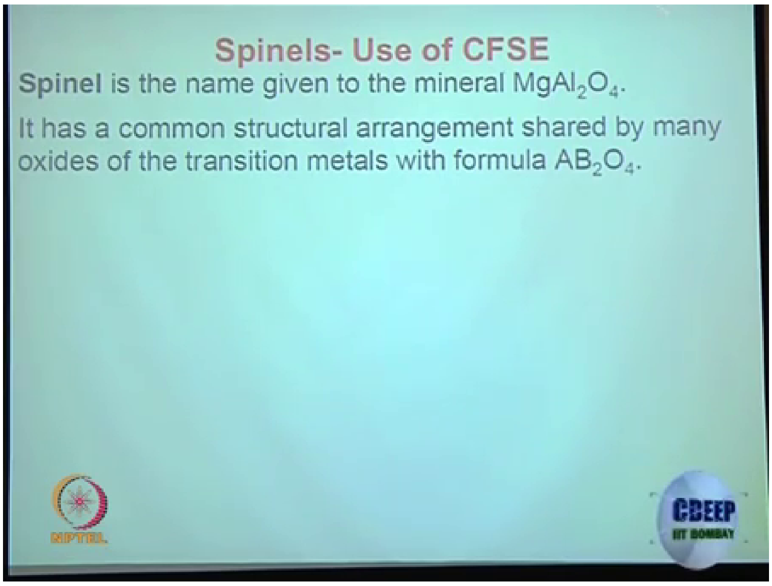

Spinels- Use of CFSE

Spinel is the name given to the mineral $MgAl_2O_4$.

It has a common structural arrangement shared by many oxides of the transition metals with formula AB_2O_4.

Different of this you know the jewels that you see different rocks, these are nothing, but spinal. Spinals are of two types normal spinal and inverse spinal. This is the only topic that is left for this chapter coordination complex. So, the class is over.