Coordination Chemistry
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Lecture - 29
Magnetochemistry

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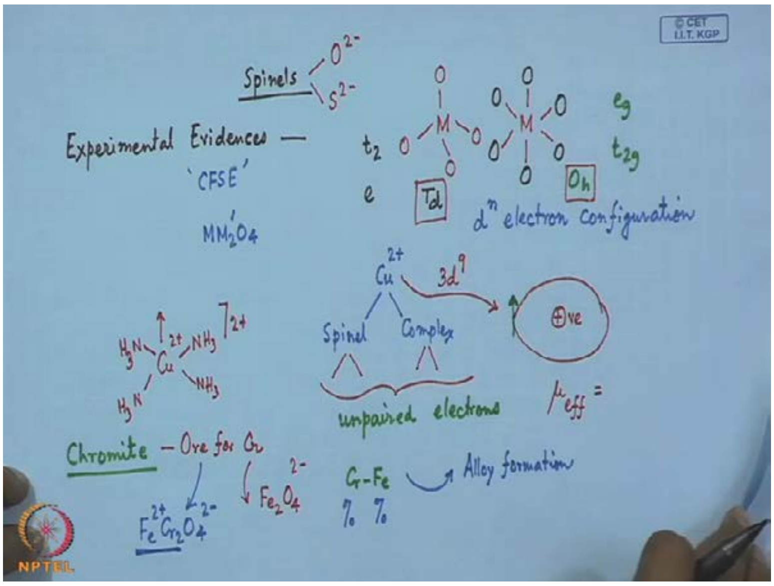

Good evening everybody. Today we will just go for some more examples of the those solid states compounds what we are talking about that means the Spinels, some remaining examples of this Spinels and what are the experimental evidences we can have. So, experimental evidences for basically the typical crystal field splitting; that means whenever a metal center is present and if it can have some immediate environments either tetrahedral or octahedral and when we talk about this spinels, we can have this oxide anions. Today, we will see also the sulphide anions.

So, these are the corresponding ligands, either oxide or sulphide, surrounding the metal ion in a typical tetrahedral geometry or an octahedral geometry. So, whether we can have the corresponding crystal field stabilization and as a result whether we can calculate out the corresponding CFSE values for these systems depending upon the different d n electron configuration. So, they can have different d n electron configurations, and based on that we can have the preferential occupation of the different levels. In case of T d, we can have e level as well as the t 2 level, and in case of the corresponding octahedral geometry, we can have the t 2 g level and the e g level.

So, when we calculate out the corresponding stabilization energy, we find that the preferential site occupancy for some of these metal ions in different electronic configurations are there for a typical spinel structure, where we have M M 2 O 4 type of formula, where M is the corresponding bivalent metal ion and M prime is the trivalent metal ion.

So, when we put this bivalent and trivalent metal ions what we know already, depending upon their different electronic configurations, we can have the corresponding CFSE for these electron configurations in these two geometrical forms. So, when we find that how many number of electron, unpaired electrons are present, as we know that if it is a copper base spinel, copper 2 plus based, it can be a spinel or it can be a corresponding simple complex, such as copper tetramine complex or copper hexaco complex.

So, when it is spinel, we can have the configurations for these two geometries, T d and O a geometries. So, we can have the corresponding number of unpaired electrons. Similarly, in case of complexes also, it can be a corresponding square planer complexes or it can be a corresponding octahedral complex. So, all these cases, we will have altogether different number of unpaired electrons. So, we have different numbers of unpaired electrons to the system.

So, if we have the unpaired electron, we will see that it can rotate around the positively charged nucleus, which is positively recharged. So, this electron can rotate around this positively charged nucleus and due to it is spin contribution as well as its orbital contribution, it can give rise to the corresponding magnetic moment.

So, depending upon the number of unpaired electron present in all the system, we should be able to calculate out theoretically as well as we can experiment it to determine the corresponding effective magnetic moment of the system. When we are talking about the system, where the individual unpaired electrons, if it is copper 2 plus, we know that is a 3 d 9 system. So, we have one unpaired electron and that unpaired electron is responsible for giving rise to the corresponding mu effective value.

So, in a magnetically dilute system, where this unpaired electron is getting filled because this unpaired electron belongs to one particular metal center. If the copper 2 plus center is there and we can have either the different oxide ions, sulphide ions or the simple ligands like ammonia.

So, this is the corresponding geometry around the copper 2 ion in a particular complex, where the individual copper centers bearing one unpaired electrons are separated. That means, this molecule is separated off to the second molecule or the third molecule and so on. So, this particular unpaired electron residing on the single copper center can give rise to a typical paramagnetic center, and it can give rise to the corresponding magnetic moment value due to the presence of one unpaired electron. If they are close enough and they are nearby, then one particular unpaired electron having some moment values can interfere with that of the second electron and they are basically coupled together. We are able to see the corresponding magnetic interaction and there are different types of such magnetic interactions, which can control the overall magnetic moment of the system due to some other type of interactions. That we will slowly discuss one after another.

So, regarding this spinels what we have seen, that we have earlier discussed about the typical aluminum spinels and the iron spinels, where the basic structure is made up of aluminum, within the aluminum spinel, we have the magnesium. In case if iron also, the Fe 2 O 4 system we can have and there, we have the other metal centers. Similarly, in case of this chromium spinels and there are three or four examples. The first one is very well known due to the presence of it as a minal system.

So chromite, we all know that this chromite is a typical ore for chromium. So, not only it can be processed for chromium extraction, but at the same time, it is present within a complex matrix of iron. So, this iron matrix is present, which is spinel matrix and this can also be processed for iron as well. So, if the system has asked that, we can have this chromium iron system and if the corresponding physical technique is available, such that the corresponding percentages of chromium as well as iron can be carbureted in some solid solution, which can be our chromium based alloy. So, that particular physical technique can also be available, where if the corresponding percentages of chromium as well as iron present in the chromium or matches to that of the corresponding alloy formation. Then that procedure can be utilized as the chromite or as the starting material or the raw material for the corresponding alloy formation.

So, like that our typical spinel structure bearing aluminum, in this particular case also, if we can have this chromite structure with that of our iron is present with Cr 2 O 4. So, if this is present, so when the chromite is present, so this is Cr 2 O 4 2 minus and iron is present as Fe 2 plus. So, this also we can have both iron and chromium and this iron and chromium can be utilized for in a similar fashion for the corresponding alloy formation.

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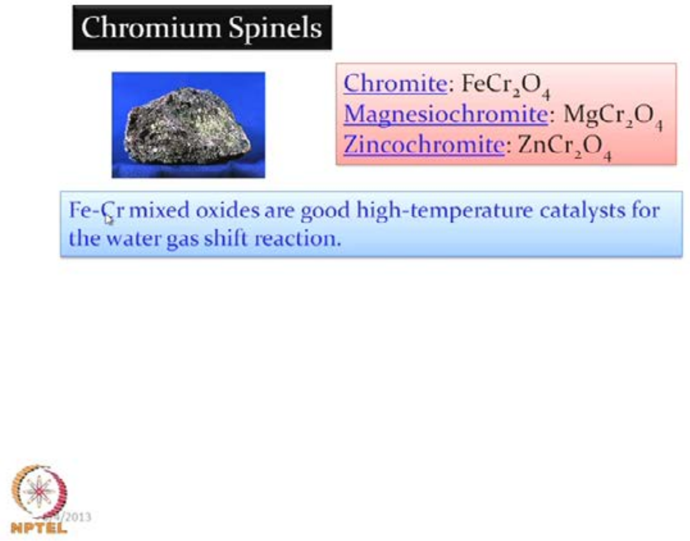

Chromium Spinels

Chromite: $FeCr_2O_4$
Magnesiochromite: $MgCr_2O_4$
Zincochromite: $ZnCr_2O_4$

Fe-Cr mixed oxides are good high-temperature catalysts for the water gas shift reaction.

So, next we see that how within this all chromium base spinel, we can have other metal ions such as magnesium or zinc. So, when magnesium is present, we get the magnesiochromite, because the basic infrastructure for this network is based on chromium and oxygen. So, the network bonding is formed with chromium and oxygen; that means, we have the corresponding oxide lattice. Depending upon its normal or inverse spinel structure, we can have the entire or the all chromium atom sitting comfortably within the octahedral sides or in the inverse structure. Some of them go to the tetrahedral sides.

Similarly, in case of zincochromite, the zinc is present along with the chromium network chromium oxygen network and also we can have the copper present in that particular spinel structure. We have the corresponding compound as copper Cr 2 O 4. Thus, we know that depending upon the nature of the spinels, the network is forming either from aluminum to giving aluminum spinel, and then for iron for iron spinel and for chromium, we get the corresponding chromium spinels.

This is one such thing; that means, this is the figure typical for the chromite ore what we can get from underground for due to its cavitations for the chromite ore. So, this can be processed furthered for utilizing it as mineral. So, this looks like a signee mineral like structure. So, when iron and chromium mixed oxides, we can have, it can be utilized for some catalytic reactions.

So, at high temperature, this particular compound, this raw material, which can also be synthesized artificially in the laboratory, we can prepare this chromite type of material having different texture, different physical morphology and different network. Or, the corresponding order structures at different. Compared to that, we get from the native environment as the ore and this can be utilized for a catalyst and the catalytic reaction is only operating at high temperature.

So, one such important example of chromite, use of chromite for water gastric reaction, where carbon monoxide is reacting with water vapor. So, how carbon monoxide could be utilized to react with water vapor for giving us the corresponding carbon dioxide and hydrogen, which is basically the mixture what we get is known as water gas. So, the corresponding water gas shift reaction can show some catalytic activity due to the presence of either chromite or some synthetically prepared, which we can prepare in the laboratory for this sought of material for its catalytic behavior. So, when carbon monoxide is coming, it can quickly interact with the chromium center.

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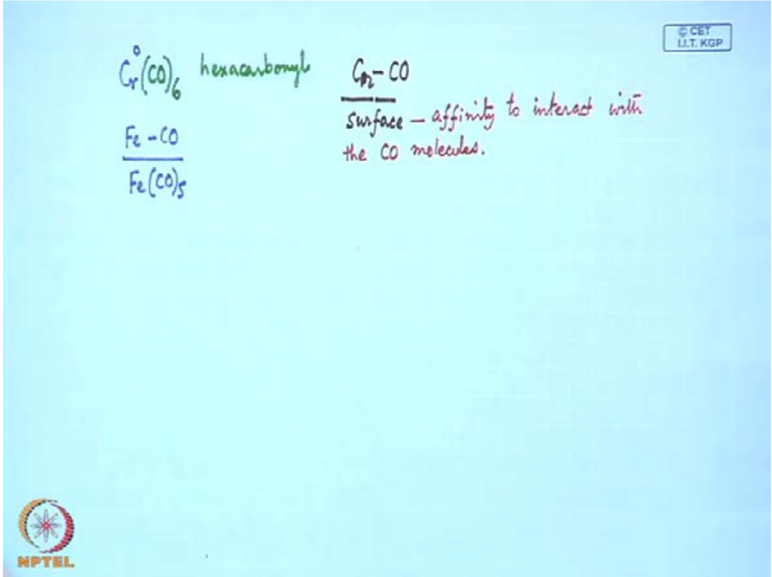

$\overset{0}{Cr}(CO)_6$ hexacarbonyl

$\frac{Fe-CO}{Fe(CO)_5}$

$\frac{Cr-CO}{\text{surface}}$ – affinity to interact with the CO molecules.

Because we all know that chromium; obviously, in its native form; that means, in its elemental state; that means, in the 0 oxidation state can react with several such carbon monoxide molecule and when it is reacting in the 0 oxidation state, it is giving chromium hexacarbonyl. So, this hexacarbonyl formation gives us some important clue that this chromium center, whether it is in the plus 2 or plus 3 oxidation state or the 0 oxidation state, can show some interaction with the carbon monoxide molecule.

So, the surface of this chromium, so this chromium surface can show some affinity for its interaction to the carbon monoxide molecule. So, surface shows some affinity to interact with the carbon monoxide molecules. So, they are showing some kind of interaction and this interaction is taking place and we can see that the corresponding water gas shift reaction we can have. So, if this carbon monoxide molecule can react with the chromium center giving rise to some kind of interaction on the chromium surface because this iron present, if it is present in the surface, this iron can also show some interaction with the carbon monoxide molecule, because this iron pentacarbonium is a type of molecules are also very much stable and well known. So, apart from these interactions for the formation of the hexacarbonyl or the iron pentacarbonyl, we see that carbon monoxide has some good affinity to react with any of these two metal centers.

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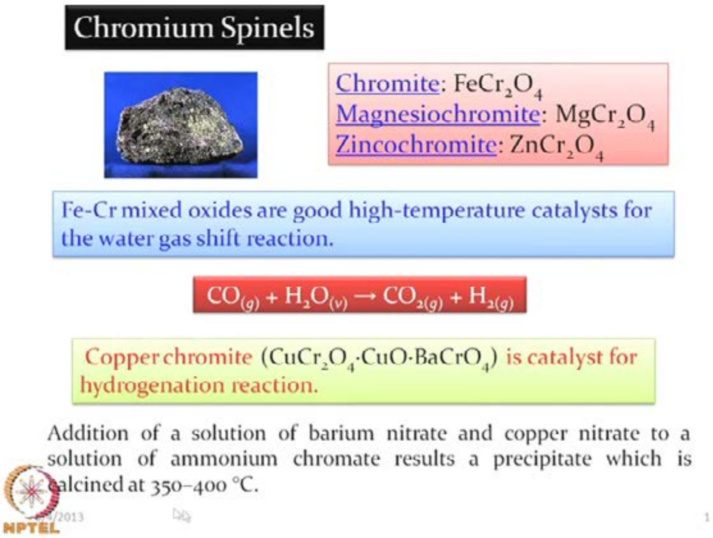

Chromium Spinels

Chromite: $FeCr_2O_4$
Magnesiochromite: $MgCr_2O_4$
Zincochromite: $ZnCr_2O_4$

Fe-Cr mixed oxides are good high-temperature catalysts for the water gas shift reaction.

$CO_{(g)} + H_2O_{(v)} \rightarrow CO_{2(g)} + H_{2(g)}$

Copper chromite ($CuCr_2O_4 \cdot CuO \cdot BaCrO_4$) is catalyst for hydrogenation reaction.

Addition of a solution of barium nitrate and copper nitrate to a solution of ammonium chromate results a precipitate which is calcined at 350–400 °C.

So, as a result, we get a mixture of these two gases when the vapor of water molecules is reacting with carbon monoxide gas giving rise to the carbon dioxide as well as the hydrogen gas. This is one of the useful techniques for utilizing this water gas shift reaction to eliminate the carbon monoxide burden in our atmosphere from automobile exhaust. Or, in some other cases for environmental point of view, we can take care of these carbon monoxide molecules and we have plenty of these water vapors available. We can produce in the laboratory also, such that we are able to produce a good fuel gas, which is our hydrogen gas. So, hydrogen gas production can be a very useful technique utilizing this spinel base catalyst. There are some other type of this catalyst can also be utilized for different types of organic transformation at the same time.

So, how we can increase the corresponding catalytic function or the catalytic behavior of this spinel type of molecules, if we go for simply changing this metal center. That means, this iron center by some other catalytically more active or catalytically efficient metal center like that of copper. So, one such example is that, is not typically a corresponding copper chromite formulation like Cu Cr 2 O 4, but it has something more.

So, is a mixed oxides structure, where we can copper chromite, copper oxide and barium chromite. So, both chromate chromite form is present over there and this chromate chromite form is coexisting together in the solid state. So, in the solid structure, we have the corresponding formulations for copper chromite, copper oxide and barium chromate. In organic chemistry, for typical organic chemistry synthesis, we find that this catalyst is very useful for hydrogenation reactions. So, there are some more of this type of spinel molecules, which are available for such hydrogenation reactions including the corresponding hydrogenation reactions followed by the ring opening reactions. Such reactions are very much useful in organic synthesis and people are still working on it to develop new and newer type of such catalyst based on the spinel structures.

So, how we can make this copper chromite formulation? If it is not available in the native form in nature, as a mineral or as some ore, we can prepare this particular material for a solution state synthesis in the laboratory or in some point to get some beautiful crystal ion form or particular size or particular sub nano particular type of molecules we can have, we get this as a typical precaution, and then corresponding treatment, the heat treatment or something else utilized for the corresponding hydrothermal synthesis.

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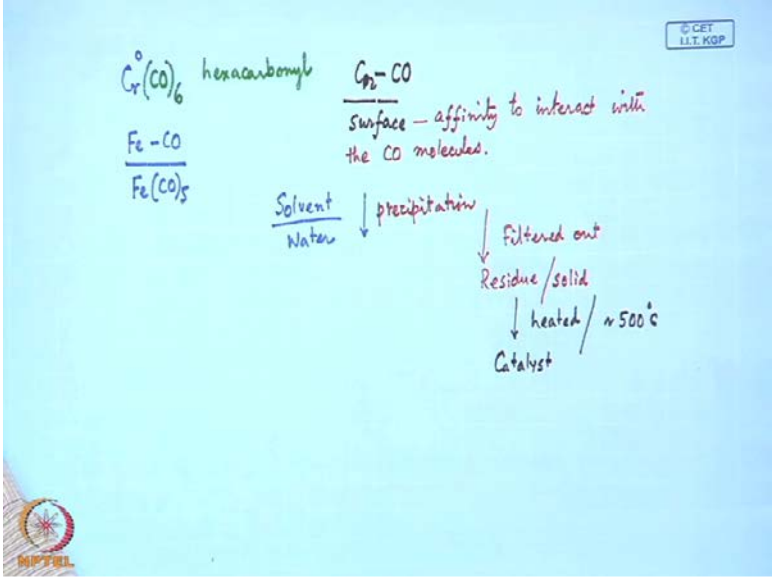

$\overset{0}{Cr}(CO)_6$ hexacarbonyl

$Fe-CO$

$Fe(CO)_5$

$Cr-CO$

surface – affinity to interact with the CO molecules.

Solvent / Water ↓ precipitation

↓ filtered out

Residue / solid

↓ heated / ~ 500°C

Catalyst

So, in solvent, if the solvent is typical water, we mix of the individual ingredients, that means the corresponding salts, which we require for the syntheses of this copper chromite including the barium; that means, some amount of barium salts, some amount of copper salt or some amount of chromite salt can be utilized. So, we have the precipitation, which can be filtered out and we get the residue as a solid product. We dry it and then we heat it at a particular temperature, heated at say about 400 or 500 degree centigrade giving the useful catalyst. So, these are the very simple techniques for solution process for the preparation of new and other type of catalyst.

So, in this particular case, how we make this barium chromate based copper chromite catalyst is that, if we take the solutions of barium nitrate and copper nitrate and a mixture of these two can be added to another solution of ammonium chromate that results in a precipitate, which is of different formulation. Say, barium nitrate can react to give with ammonium chromate giving rise barium chromate and copper nitrate is also reacting with ammonium cremate giving rise to some copper chromate formulation and ammonium ion is there and ammonium nitrate is there basically.

So, the presence of ammonium nitrate in the medium basically responsible for the reduction of the precipitated copper chromate at high temperature, say not at 500 degree centigrade, but less than that, which is in the range of 350 to 400 degree centigrade. So, at this particular temperature, the ammonium nitrate which is present over there will be responsible for the reduction of copper chromate to copper chromite. So, is basically is some mixed oxides are formed like that of our typical examples what we know for different super conducting oxides, which are also different mixed oxides of say powers kite or any other type of solid state structure. So, these mixed oxides of super conducting type can be formed and it can only result at a particular calcination temperature, because the precipitate, the dried precipitate can be heated at 350 to 400 degree centigrade for the typical calcination reaction.

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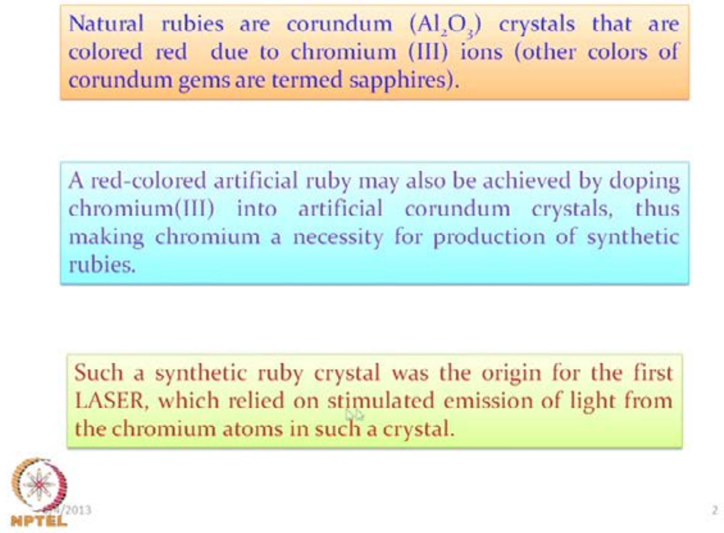

Natural rubies are corundum (Al_2O_3) crystals that are colored red due to chromium (III) ions (other colors of corundum gems are termed sapphires).

A red-colored artificial ruby may also be achieved by doping chromium(III) into artificial corundum crystals, thus making chromium a necessity for production of synthetic rubies.

Such a synthetic ruby crystal was the origin for the first LASER, which relied on stimulated emission of light from the chromium atoms in such a crystal.

So, this can also give us some other example of the ruby. So, the naturally occurring ruby material is nothing but is a corundum crystal alumina based on alpha alumina. Sometimes, that is begin doffed with some chromium 3 ions and when chromium 3 ion is doped within the alumina crystal lattice, we see that chromium is occupying some of the holes or the equivalent sides in this particular alumina structure. The chromium oxygen bond are getting lengthened and the chromium in some octahedral environment giving rise to the corresponding cathartics coloration due to the corresponding, say if which is determined by the corresponding structure of the corundum. So, that basically gives us whether we have some elongated chromium oxygen bond or compressed chromium oxygen bond and that is responsible for the corresponding d d transitions based on the chromium in plus 3 oxidation state.

This particular color is not always available. The red color, which is not available all the time, but due to this particular presence of this chromium, we can have some other colors also and this corundum based gems can also be termed as sapphires, if the colors are different from the red color of the ruby.

So, a red colored artificial ruby may also be achieved by doping chromium 3 into artificial corundum crystals. So, in the laboratory, if the available corundum is not naturally occurring, we can dope artificially chromium 3 into the artificially prepared corundum crystals and thus, we are able to make the corresponding ruby, which can be prepared in the laboratory in a synthetic way. We call them as the typical procedure for the production of synthetic rubies, because synthetic rubies are very much useful for different optical instruments and for optical properties.

So, one such synthetic ruby crystal can be utilized for the generation of laser, which is nothing but light amplification by simulated emission of radiation. So, this laser is basically dependent on the ruby crystals and these are known as ruby lasers. It is basically dependent on the stimulated emission. This s is stimulated; s is the stimulated emission of light from the chromium atoms in such a crystal when chromium is trapped within the corundum lattice. This chromium is responsible for its red coloration due to the typical crystal field, which is begin exerted on the chromium center in its plus 3 oxidation states. So, we get the corresponding ruby lasers. So ruby lasers, its red color is due to the corresponding crystal field stabilization energy within the corresponding crystal lattices of the corundum system.

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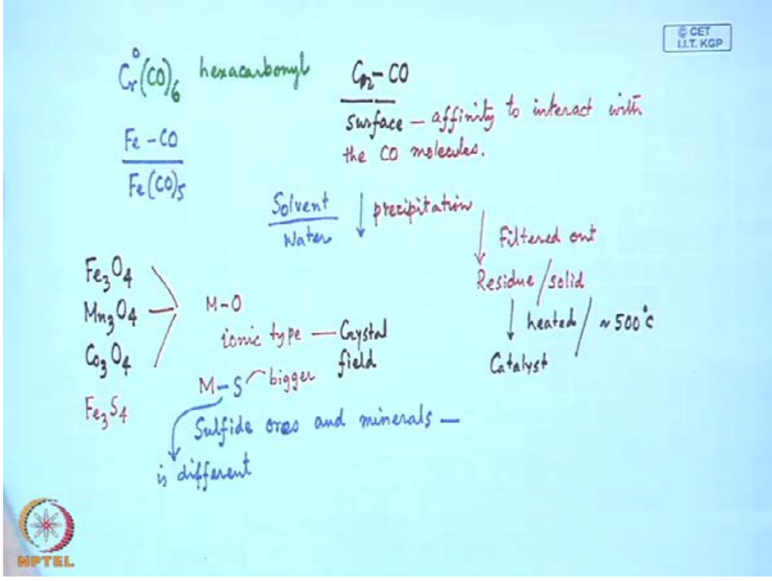

Next, we will see some molecules which belong to the Thiospinel group. So, whenever we see that the corresponding magnetite or hematite molecules, we see that there are several such spinel molecules are available, where 3 manganese, 3 cobalt or 3 iron centers are there within the O 4 oxides lattice structures. So, these structures are there and all this molecules or systems can have a very strong M O bond and the nature of this M O bond is it is ionic type.

So, all the color and all other things can be very well explained in terms of the corresponding crystal field, which we can have, which we can exalt on the corresponding metal center due to the presence of this oxides. Now, if we move from this oxide anions to some sulfide anions, because we know that large number of sulfide based ores and minerals are available in nature. Sulfide ores and minerals are there in nature. So, we can have the corresponding sulfur groups and if we substitute all the oxides spheres by these sulfides, we will have the corresponding formula of this as Fe 3 S 4, Mn 3 S 4 or Cl 3 s 4, where we can have the metal sulfur bond, and where the sulfur is little bit bigger in size compared to the oxygen atom present it the spinel.

So, the nature of these interactions, between the metal center and the sulfur is different. Due to the bigger size of sulfur, it will be easily polarized and due to its affinity for polarization and its bigger size, so we can expect that metal sulfur bonding will have some amount of covalent corrector and due to this particular type of covalence, which is been generated due to the presence of the bigger sulfur atom attached to the metal, the corresponding interaction between the metal and the sulfur center is not purely ionic and the corresponding nature of these spinels are little bit different.

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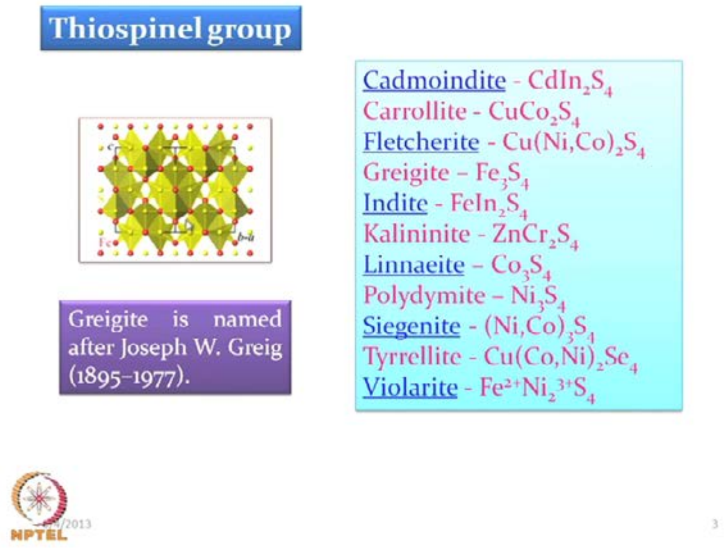

Thiospinel group

Greigite is named after Joseph W. Greig (1895–1977).

Cadmoindite - $CdIn_2S_4$
Carrollite - $CuCo_2S_4$
Fletcherite - $Cu(Ni,Co)_2S_4$
Greigite – Fe_3S_4
Indite - $FeIn_2S_4$
Kalininite - $ZnCr_2S_4$
Linnaeite – Co_3S_4
Polydymite – Ni_3S_4
Siegenite - $(Ni,Co)_3S_4$
Tyrrellite - $Cu(Co,Ni)_2Se_4$
Violarite - $Fe^{2+}Ni_2^{3+}S_4$

So, a large number of these Thiospinel molecules are available. We start from Cadmoindite from cadmium indium sulfide. So, we have Cadmium and Cadmoindite. So, we have Cadmium is there and Indium is there and that is why it is Cadmium ion 2 S 4.

So, it is like zinc and is the cadmium indium is in trivalent state. So, we have one particular arrangement for that within sulfide lattice. Then Carrollite is copper based on cobalt sulfur network. Then Fletcherite is the copper and in the octahedral sides, we can have the compositions based on nickel and cobalt. So, it is basically a three metal spinel structure. So, three metal spinel structures are also there, where this is A side and within the B side 50 percent of the B sides are occupied by 1 metal center and another 50 percent is occupied by the second metal center.

Then, Greigite, which is Fe 3 S 4. Indite is iron indium like cadmium indium. So indite; so Cadmoindite is the substitution of this. So, Indite iron is not mentioned. So, it is basically iron indium thiospinel is known as Indine and Kalininite is the zinc chromium one. Linnaeite is the cobalt sulfur, and Polydymite is the nickel sulfur. In this particular case, apart from cobalt, this nickel one, the Ni 3 S 4 is an important sulfur spinel structure, because we are now having a thiospinel with a single metal.

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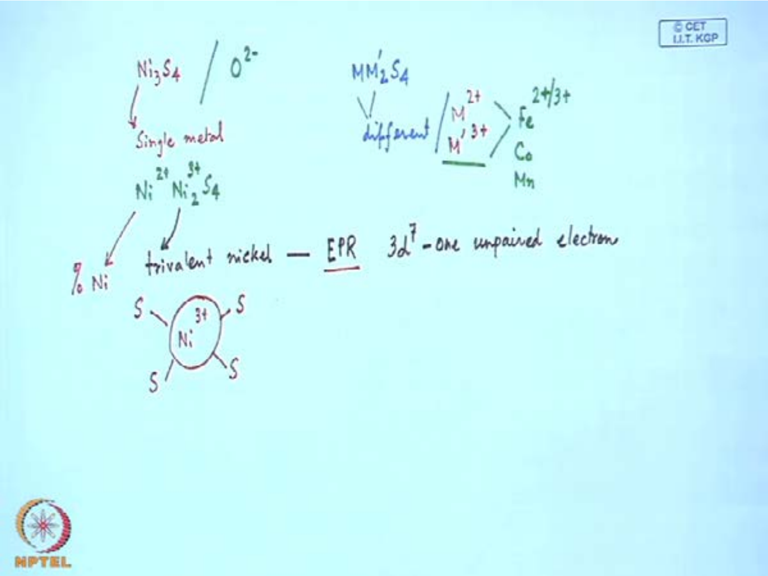

So, what we have seen earlier, that in case of M M prime system, we have M M prime 2 S 4 system. So, these two are different metal ions, because we can have M as bivalent metal ion and M prime as trivalent metal ion. This sort of spinel structure are mostly stabilized and we get large number of these spinels as examples, where the same metal ions like iron, like cobalt, like manganese can have two possible oxidations states, which are the bivalent ones and the trivalent one which are stable.

But, when we talk about the corresponding nickel spinel structure, which is polydymite, so in case of this polydymite, we have this nickel. Since, there is no such option for the trivalent metal ion, so in sulfur environment only which is not possible for the corresponding oxygen environment, so in sulfur environment, which can show some amount of polarization that this nickel center is present as both bivalent and trivalent states in Tetrasulfur environment. So, in this particular tetravalent environment, tetraoxygen environment, which gives rise to the corresponding trivalent nickel, which is not so common and the other unusual.

So, this particular trivalent nickel can be stabilized in this particular environment and spectroscopically, we can characterize the presence of this trivalent nickel, if we go for electron paramagnetic resonance spectrum. We get the corresponding signal for the trivalent nickel, which is due to the 3 d 7 with one unpaired electron and that unpaired electron can very nicely be detected in electron paramagnetic resonance spectrum.

So, if this material, if we see that it can show some interesting catalytic activity or any other thing, immediately we can characterize it first for its total nickel content . That means, we can determine the percentage of nickel and then we can find out the corresponding oxidation states. If it is EPR active for it is trivalent nature, we can safely conclude that this particular center can also be catalytically further reactive, because of this unusual oxidation state of nickel. The trivalent nickel in some biological systems also, we have seen that this particular trivalent nickel can only be stabilized for some sulfur environment. It can be a thiosulfur or it can be thiosulfur. So, in sulfur environment, this nickel can be stabilized in its trivalent state.

So, after Polydymite, we can have Siegenite. So, Siegenite is again nickel and cobalt present and depending upon the corresponding oxidation state, if the nickel is in the bivalent state, we have two cobalt centers. So, either 1 nickel 2 cobalt or 2 nickel 1 cobalt system, if the nickel center can also be supported its trivalent state. Then Tyrrellite is copper and cobalt nickel base selenite. So, like sulfur, we can also have the selenite, which is closely related to selnospinel group. So, like thiospinel, we can have the selnospinel also because the close similarity between sulfur and selenium.

Then Violarite. In this Violarite, we see that nickel is still present in trivalent states. So, the sulfur environment is pretty common for stabilizing the nickel in the trivalent state and iron is present in its bivalent state. So, how we get this Fe 3 S 4, which is Greigite structure? So, Greigite is the name given for the scientist known as Joseph W Greig. So, Greigite is first reported in recent years by this person who is a genealogist as well as a physical chemist who identified this Greigite structure. Within this particular case, we have the sulfur network and the iron centers are present within this particular environment. So, we have this iron, the red balls are all iron centers and sulfurs are all yellow balls.

So, we can have the typical environment for this sulfur. In some cases, we see that the sulfur is not tetra coordinate. It is penta coordinated and iron is in a tetrahedral geometry, where 1 sulfur is bound by the 4 sulfur for iron centers. So, whenever we find this particular iron, we find that we can have 4 iron centers surrounding this particular iron. If this particular iron center is there, so this particular iron always can have a tetrahedral geometry and we can have some other sides, which are available as their corresponding octahedral sides.

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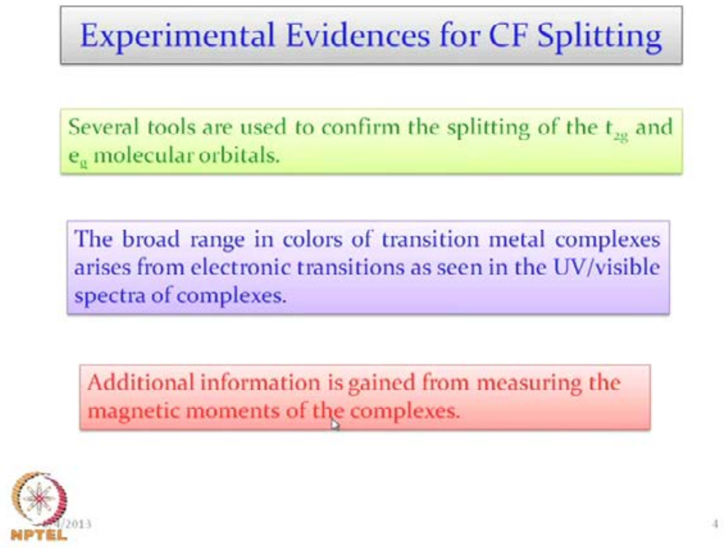

Experimental Evidences for CF Splitting

Several tools are used to confirm the splitting of the t_{2g} and e_g molecular orbitals.

The broad range in colors of transition metal complexes arises from electronic transitions as seen in the UV/visible spectra of complexes.

Additional information is gained from measuring the magnetic moments of the complexes.

So, we find that how we get all this experimental evidences for crystal field splitting. So, so far whatever we are talking about is relation to the evidences what we can have due to the corresponding crystal field stabilization.

So, if we have the splitting, we get a preferential electronic structure and that electronic structure can give rise to the corresponding crystal field stabilization due to the preferential occupancy in either the t 2 g or the e g level or e and t 2 level in tetrahedral geometry. So, what we find that several experimental tools or some theoretical mechanisms can be utilized for identifying the splitting of the 5 d orbitals of this t 2 g and e g levels.

So, several tools are used to confirm the splitting of the t 2 g and e g molecular orbitals or the corresponding orbitals which have some participation from the ligand side. That is why we are not considering this t 2 g and e g levels as pure metal d orbitals. But they are the corresponding orbitals which are formed due to the presence of the ligand orbitals at the same time.

So, what we get that the corresponding broad range in colors of these transitions metal complexes is due to the corresponding electronic transitions. That means, if we have the 1 single electron in the t 2 g level that we have discussed earlier, that the corresponding transition from the t 2 g to e g level can give rise to the corresponding electronic transition in the UV visible spectra of this complexes. So, this can also give rise to the corresponding splitting pattern and crystal field splitting is there for operating. Then only we have the corresponding d d transitions. So, the direct experimental proof for the presence of the crystal field is the observation of the corresponding d d transitions. Lastly, what we will see next that additional information we can have by measuring the corresponding magnetic moments of the complexes.

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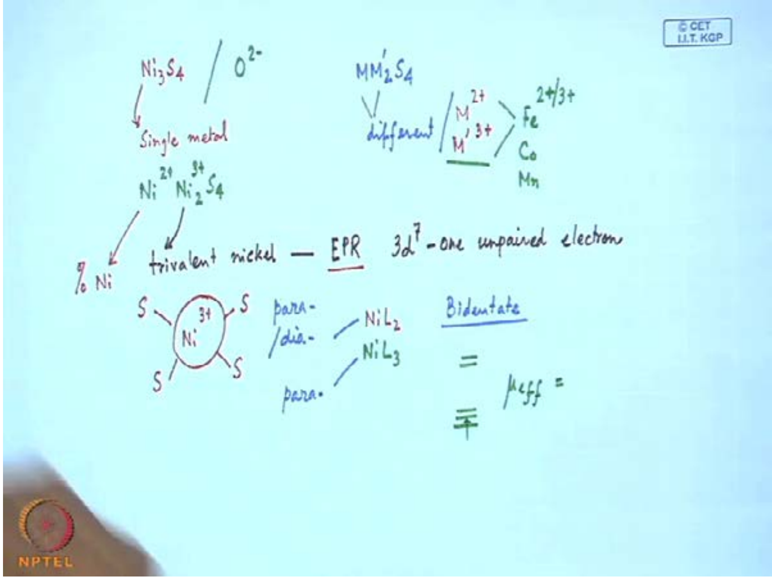

So, if we have a particular metal complex, say Ni L 2 or Ni L 3 and if L 2 and L 3 are all bidentate ligands, what we will find is that we can have two geometries due to the presence of two such ligands and another geometry due to the presence of three such ligands. We can have the different magnetic properties. Either, this Ni L 2 can be paramagnetic or diamagnetic and Ni L 3 can be paramagnetic. So, how we can get all this information because we get the corresponding crystal field splitting. Depending upon its corresponding crystal field, we can have the corresponding high spin as well as low spin electron configurations for these complexes due to the presence of several numbers of unpaired electrons on these transitions metal ions.

Due to the presence of this two different levels, which can either be the t 2 g e g or in some cases, this can be the ground state for e and this can be the excited state for t 2. If we have several such unpaired electrons, then we can determine its corresponding magnetic moment as its mu effective values. So, that gives rise to the information that the crystal field is operating on these all metal complexes.

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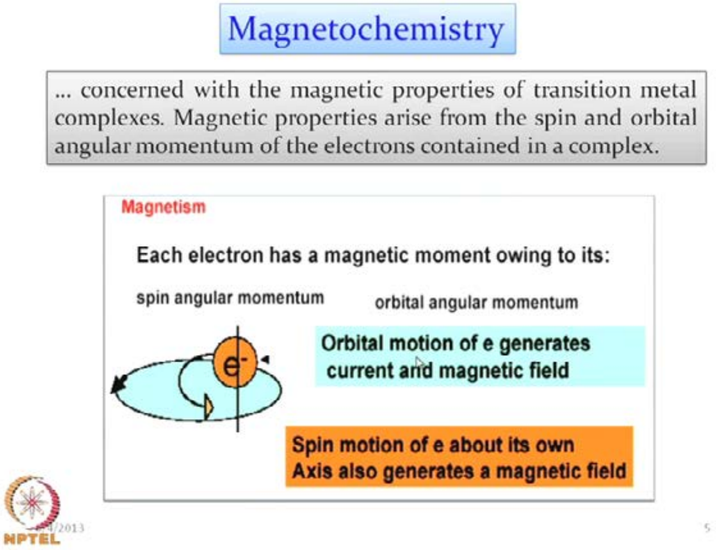

Magnetochemistry

... concerned with the magnetic properties of transition metal complexes. Magnetic properties arise from the spin and orbital angular momentum of the electrons contained in a complex.

Magnetism

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum

Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

So, next we will just talk about the corresponding magnetochemistry, that how the magnetic properties of all these coordination complexes are helpful in determining or identifying the nature of this complexes. So, this is basically a characterization technique or characterization tool, where we can determine the corresponding magnetism or magnetic properties of all these complexes.

So, it is basically concerned with the magnetic properties of transition metal complexes. So, whenever we determine the magnetic properties, whether the complex is paramagnetic or diamagnetic in a particular geometry, we will be talking in terms of its corresponding magnetochemistry. These properties arise from the spin and orbital angular momentum, because we have the spinning motion of the electrons as well as their orbital motion within the orbit which are present in the complexes and those motions can give rise to the corresponding moment. These moments can be found out in terms of its corresponding magnetic moment.

So, each electron basically has a moment owing to its two angular momentum values. One is the spin angular momentum, which is basically spinning around its own axis of this electron and the second one is the orbital angular momentum, where the spinning electron, because of its spin around its own axis, it also rotate around the central nucleus. The nucleus which is the positively charged part is present at the very center of this orbit. Due to this typical motion depending upon its different orbitals, that it can be present in 3 d orbitals, it can be present in 4 d orbitals or 5 d orbitals and sizes are also different as well as the different orientations for the different levels, we are able to generate the corresponding current and the magnetic field due to the presence of this orbital motion of this electron.

The spin motion of the electron about its own axis also generates a magnetic field. In the first transitions series, where the orbital contribution is not very much we will talk about corresponding magnetic moment values in terms of its corresponding spin only values. So, we will able to determine this magnetic moment values as its spin only values. That is why the spinning motion around the electron, around its own axis is important for developing the corresponding magnetic moment.

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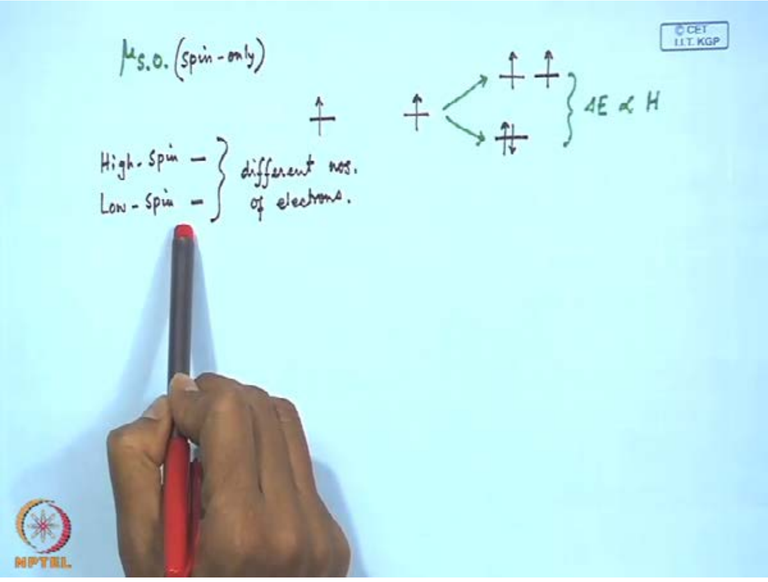

So, when a magnetic field is applied for a compound or a free ion, a first order zeeman splitting occurs. So, we can have the different orbitals or the different magnetic levels and all this magnetic levels can have different energy values depending upon the alignment of all this electrons. So, if we can have two electrons in a particular system, so one electron in one particular orbit and second electron in this two other orbit and we can have two possible levels or the magnetic levels where we can have these two electrons either paired or unpaired. So, such unpaired electron distributions in this basically gives rise to different types of unpaired electron distributions of these two forms. These two can have some energy gap, which can be considered as delta E due to the different types of these arrangements for this species, which are having different number of unpaired electron. So, these levels basically what we get can be considered as the corresponding zeeman levels.

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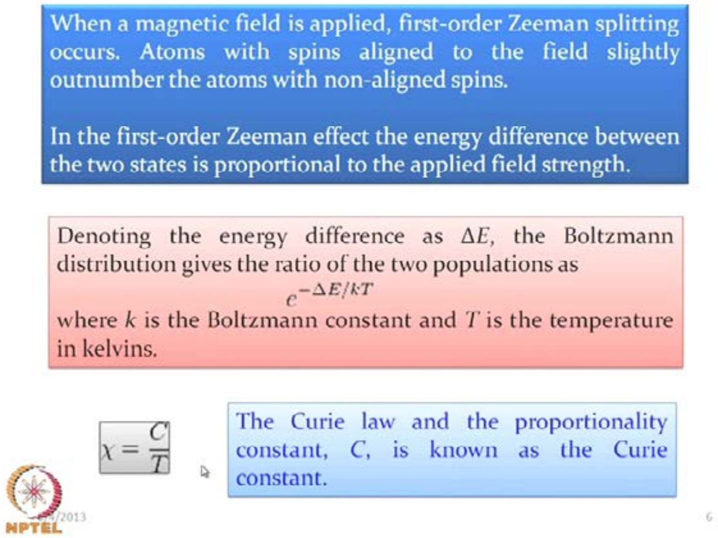

When a magnetic field is applied, first-order Zeeman splitting occurs. Atoms with spins aligned to the field slightly outnumber the atoms with non-aligned spins.

In the first-order Zeeman effect the energy difference between the two states is proportional to the applied field strength.

Denoting the energy difference as ΔE, the Boltzmann distribution gives the ratio of the two populations as

$$e^{-\Delta E/kT}$$

where k is the Boltzmann constant and T is the temperature in kelvins.

$$\chi = \frac{C}{T}$$

The Curie law and the proportionality constant, C, is known as the Curie constant.

So, atoms or molecules with spin aligned to the fields slightly outnumber the atoms with non aligned spins. So, more and more number of spins will be aligned to the applied magnetic field to the system. If we consider the first order zeeman effect only, the energy different between these two states is proportional to the applied field strength. So, like that of our crystal field, this corresponding energy gap is dependent on the corresponding fields. So, if the field is H, the delta E values for this system will be proportional to the field strength of the magnet.

So, if we have a very strong magnetic field, we should be able to generate a corresponding delta E value much more. So, it would be proportional to the applied field strength, which we are putting for the determination of the magnetic moment. So, these delta E values basically denoting the energy difference as delta E and if we can have the Boltzmann distribution, which we all know, that a thermally controlled population is dictated by Boltzmann distribution law and K is the Boltzmann constant. Then the ratio of these two states or the two populations will be given by E to the power minus delta E by k T, where k T is the thermal energy term, which is the product of Boltzmann constant and T in temperature in Kelvins at that particular point.

So, with respect to the k T value, we will have the corresponding delta magnitude of these delta E values and the magnitude of these delta E values are much less compared to this k T values because the k T values at room temperature would be close to 100 Centimeter inverse. But these delta E values are very less. It can only be 1 2 3 5 to 10 Centimeter inverse.

So, at that particular point, when the delta E values are much less compared to k T value, we can consider it as 1 minus delta E by k T value is equal to 1 minus delta E by k T. So therefore, the susceptibility term, the kai value will be inversely proportional to the temperature. As we increase the temperature, our corresponding kai value will basically decrease with a constant of proportionality. This constant proportionality is known as a Curie constant and this is nothing but the Curie law. This Curie law is useful to determine the corresponding magnetic moment of all these molecules and the C value is known as its corresponding Curie constant. If this temperature can have some correction term, we consider it as the corresponding another T th thermal term or the T term, which is due to the Weses and the Curie Weses law is also very much useful to show some proportionality with respect to the corresponding susceptibility value. If the susceptibility value is not directly proportional to the temperature, inversely proportional to the temperature, we can go for its corresponding correction term utilization the Weses law.

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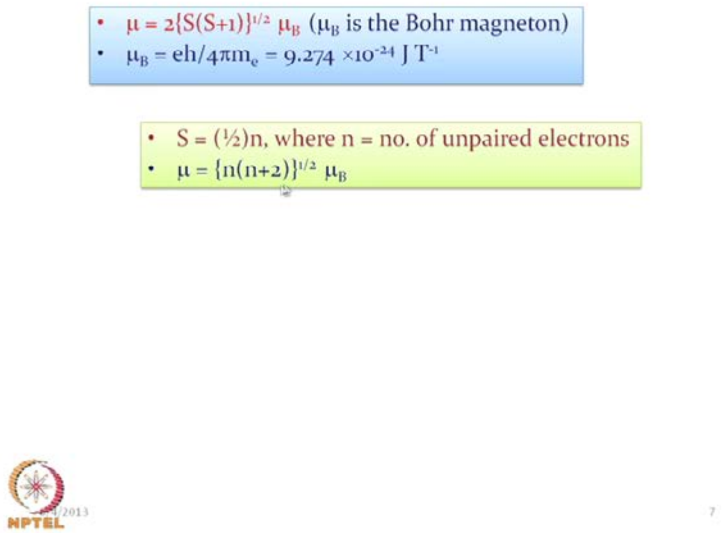

- $\mu = 2\{S(S+1)\}^{1/2}\ \mu_B$ (μ_B is the Bohr magneton)
- $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24}\ \mathrm{J\ T^{-1}}$

- $S = (\frac{1}{2})n$, where n = no. of unpaired electrons
- $\mu = \{n(n+2)\}^{1/2}\ \mu_B$

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So, what we find that, when we know the corresponding total spin values of the system; that means, S values is equal to the total number of unpaired electron, then we can correlate it to the corresponding magnetic moment as the mu value, which is nothing but twice of S into S plus 1 route mu B. mu B is nothing but its corresponding value in Bhor magneton, which is a constant term and mu B is equal to e h by 4 pi m e, m e is the mass of the electron is equal to 9.274 into 10 to the minus 24 joule per tesla.

So, this particular mu B term basically gives rise to calculation where we can calculate the typical number of this unpaired number of electrons. So, if M values are the unpaired electrons, the number of unpaired electrons and if we substitute S is equal to half of M, because the total S is we are getting due to the contribution of the individual unpaired electrons contributing a spin value equal to half. So, half multiplied by M giving rise to the total S value and this S value, when we put in this equation we get the corresponding mu value.

In the same way, instead of putting the S values in the equation, if we directly put the corresponding M values; that means, the number of unpaired electrons, which is very easy to find out; if we know the corresponding crystal field splitting pattern also, because for the two different types of compounds where we can have the high spin complexes and the low spin complexes, we can have different numbers of electrons. So, for high spin complexes and low spin complexes, which is the direct manifestation of the crystal field splitting and that splitting gives us different number of unpaired electrons for high spin compounds as well as for the low spin compounds. As a result, we can have this corresponding mu effective values or mu spin only values, because we are considering only the spin only values. The different magnitudes of mu effective values for the high spin complexes as well as low spin complexes. So, next day we will consider all these things. That means, all these values; that means, the different number of m values for determining the corresponding magnetic values for all these complexes.

Thank you very much.