

Basics in Inorganic Chemistry
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Lecture - 16

Magnetic States of Matter: Paramagnetic, Ferro and Antiferromagnetic

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Magnetism

Magnetic States of Matter

Diamagnet - A diamagnetic compound has all of its electron spins paired giving a net spin of zero. Diamagnetic compounds are weakly repelled by a magnet.

Paramagnet - A paramagnetic compound will have some electrons with unpaired spins. Paramagnetic compounds are attracted by a magnet. Paramagnetism derives from the spin and orbital angular momenta of electrons. This type of magnetism occurs only in compounds containing unpaired electrons, as the spin and orbital angular momenta is cancelled out when the electrons exist in pairs.

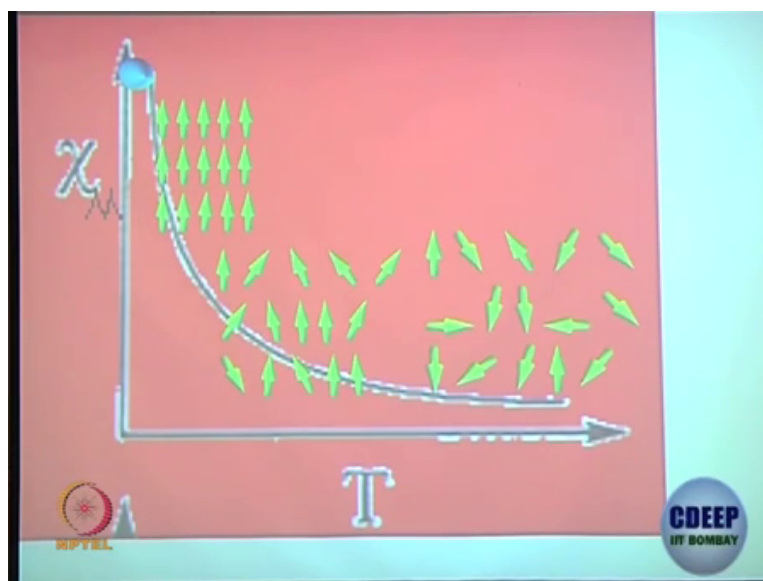
Compounds in which the paramagnetic centres are separated by diamagnetic atoms within the sample are said to be magnetically dilute.

Now, I will I will move from there to simple temperature dependence of magnetism. So, you have a material, let us say f electrons you have or b electrons you have whatever you have. You know at room temperature magnetic moment value is whatever $\times 2$ let us say 2 bore magneton whatever it is, you know there is value. The moment you are cooling it down for room temperature or from a high temperature to room temperature whatever it is the moment you are cooling it down do not spin previously you are having, now will get an opportunity to realign.

Usually, molecules means you can have different spin organized in a different fashion. Let us say you have 10 different domain, 10 different metal centers. Those 10 different metal centers are having spin 1 up another down another up and shown. It is a mixture of up and down.

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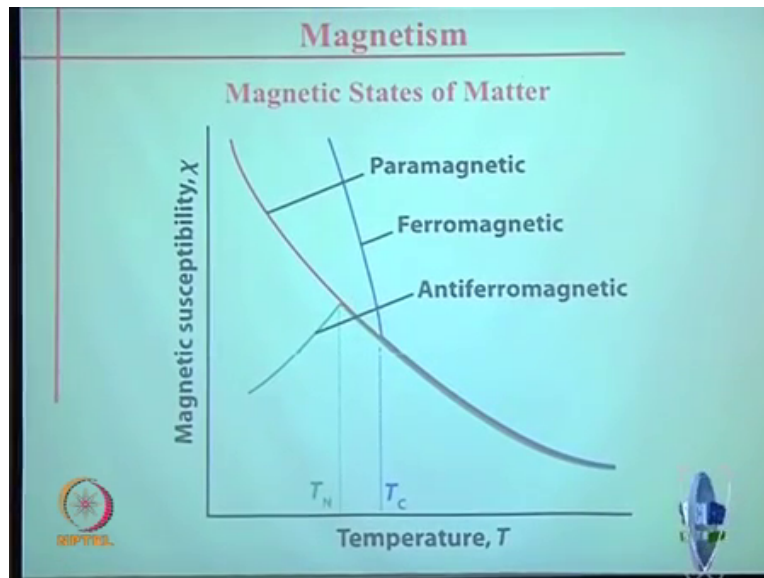


Let us say it is a mixture of up and down. This is the particular temperature, let us say this is room temperature or whatever temperature you want. Now, you cool it down you cool down the sample; what will happen? This you know randomly oriented spin will get some particular orientation.

It will try to freeze, you will be able to freeze these spin more and more if you decrease the temperature. You start with 1000 degree centigrade come to room temperature, magnetic

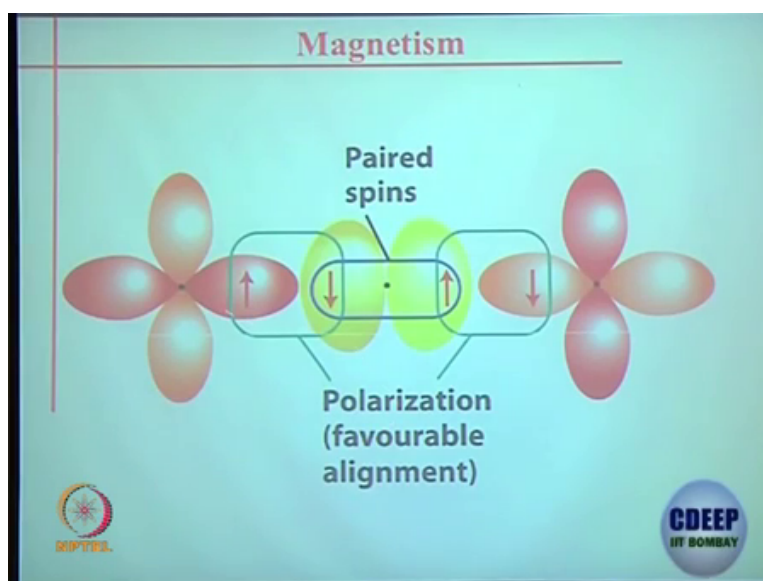
moment value will increase for the sample. This is the behavior you are expected to see for paramagnetic complex ok. So, random spin little bit organized further organized.

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Now, that is the kind of behavior you should expect for paramagnetic species. Sometime, what happens is once spin of one molecule is influencing the spin of other molecule. How it is? Let me give you an example here.

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Let us say, this is a spin this is the d orbital of 1 atom or 1 metal center, this is the d orbital of another metal center. Now, in absence of anything in between, if there is no bridging between these two metal center this is spin up, this is spin up half and half.

So, total spin should be half plus half 1, but in presence of a ligand or breathing species having 2 electrons, what will happen; this ligand will ligand spin will be down, this is up this is down that there is a bond formation. If this is down this is going to be up, that will enforce this spin to be down to start with you have up spin for this up spin for that, two centers up.

Since, they are bridged by a second ligand, something let us say oxide O^{2-} it has two unpaired electrons. Let us say you have copper 2 plus or copper 3 plus oxide copper. Copper

2 plus oxide copper 2 plus; copper 2 plus is d 9 1 unpaired electron oxide 2 unpaired electron 2 unpaired electrons and then another copper 2 plus, another unpaired electron.

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Let us say you are having copper oxide copper 2 plus 2 plus 2 minus there is net charge is going to be let us say 2 plus does not matter. Now, this is a d 9 electronic configuration; this is a d 9 electronic configuration. 1 spin up 1 spin up. 1 unpaired electron 1 unpaired electron oxide is having 2 unpaired electron.

What it is making it? Essentially since this is a coupled species, this spin or this copper is bonded with oxide, this oxide is also bonded with that; this will enforce this up spin to go down. So, this is copper spin this is your oxide 1 spin that will mean that this will go up and this spin will go down. It is spin pairing they will try to pair it up.

So, up down; up down over all although it is the d 9 electronic system, it was supposed to be paramagnetic; unpaired electron means it is paramagnetic. Net effect is due to these exchange it will become diamagnetic ok. So, what I am trying to tell you is that; knowing the whole thing is important. Just individual metal center is not good enough to tell the bulk properties of the compound or bulk properties of the material. You need to know what they are bound with, how they are bound with, are they communicating with each other ok.

So, it is a very interesting phenomenon you can see the magnetic properties can be communicated. If it can be decreased there is other orientation where it can be increased by having some interaction. So, both decrease and increase is possible right. So, this is where what actually you see kind of this anti ferromagnetic behavior you see, it is after certain temperature you can see the magnetic moment value is decreasing.

So, because they are interacting after that temperature they are interacting with other molecule in a way that will canceling some of the spin. It could also increase as you see for ferromagnetic cases. So, it is nothing but, electronic spin are varying different way with respect to temperature. It may be pairing up or it may be getting more unpaired ok.



Thereby, you see of course, Ferro this is nothing but more of a paramagnetic but the increment with respect to temperature is huge all of a sudden right. So, it is increasing as you decreasing the temperature, but at certain after certain temperature you see that there is a jump or the slope is changing right. So, something is happening in terms of electronic arrangement that is all it says ok.

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Magnetism

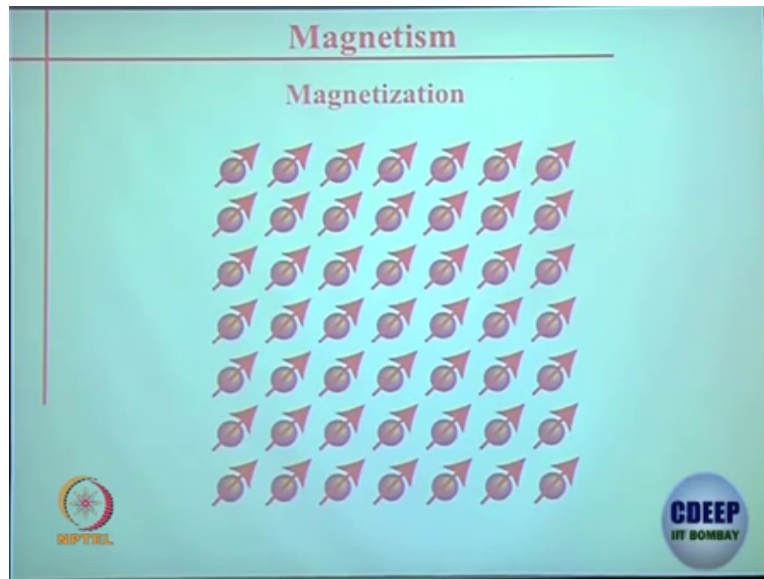
Magnetic States of Matter

- These two forms of paramagnetism show characteristic variations of the magnetic susceptibility with temperature.
- In the case of ferromagnetism, above the Curie point the material displays "normal" paramagnetic behavior. Below the Curie point the material displays strong magnetic properties. Ferromagnetism is commonly found in compounds containing iron and in alloys.
- For antiferromagnetism, above the Neel point the material displays "normal" paramagnetic behavior. Below the Neel point the material displays weak magnetic properties which at lower and lower temperatures can become essentially diamagnetic. Antiferromagnetism is more common and is found to occur in transition metal halides and oxides, such as $TiCl_3$ and VCl_2 .

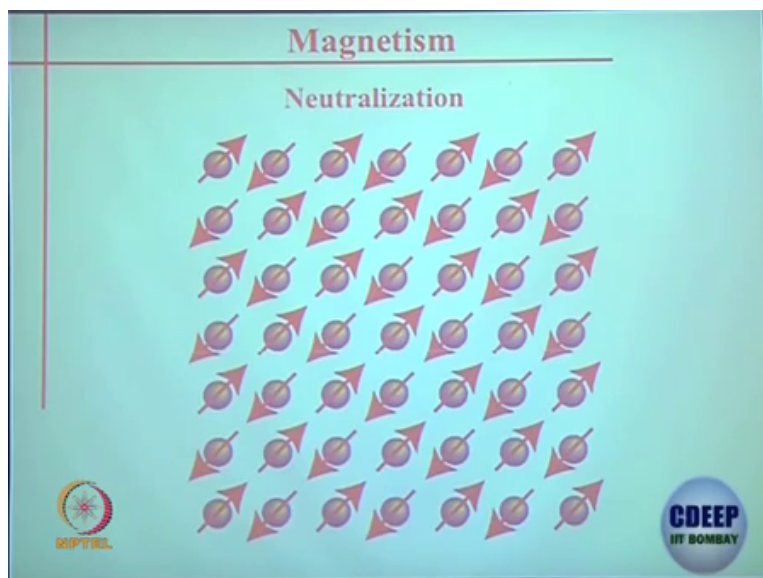
 

Now, you can see the read about these of Curie temperature and whatever this mini temperature and so on. I think you have studied it before, paramagnetic, anti ferromagnetic and ferromagnetic you study from a book.

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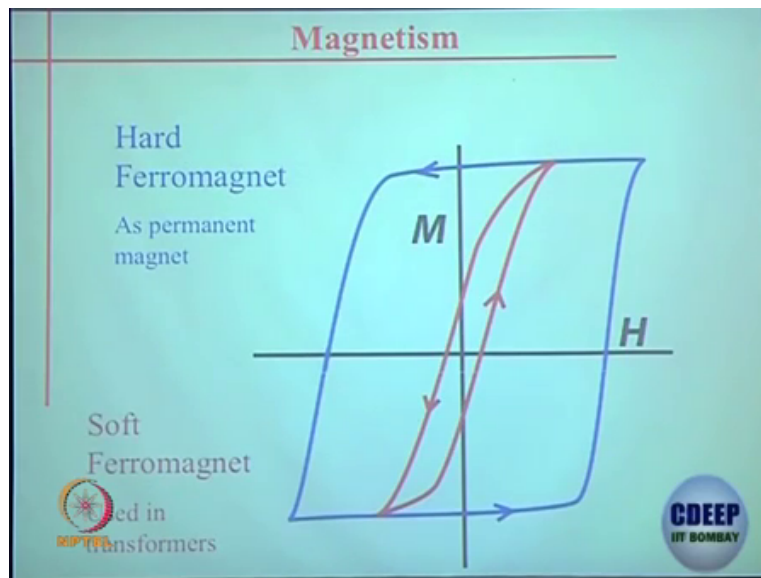
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Magnetization ok. So, if you see, if you are, if you are trying to magnetize 1 species; let us say with a magnet you are trying to magnetize another species, what essentially happening is you are reorienting the spin of those molecule ok.

So, for example, this is the magnetization. If you want if you can reverse the spin this is going to lead to that neutralization right. It is nothing but, changing the spin all up all down 1 up 1 down, how many up how many down. Going to determine the magnetic properties or magnetic behavior of a compound, 2 more minutes maybe 1 minute will be good enough you read this, ok. There is some material ok.

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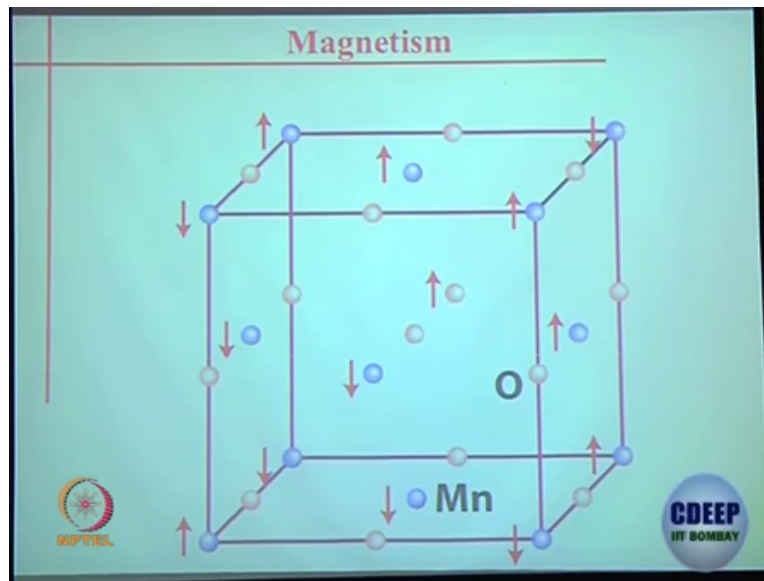
For example over here, if you are; if you are increasing the temperature or decreasing the temperature, you can understand how you can give low spin to high spin. You know that; if you heat it up for example, you can go from low spin to high spin, spin will increase right.

So, if that is happening, you are going to increase the magnetic moment right. So, you are increasing the temperature; temperature and at certain temperature high spin complex will be forming from there low spin to high spin complex is formed. Now, if that high spin species upon cooling down or bringing it to room temperature does not come back to the previous orientation that mean low spin orientation quickly those are the one are called the hard magnet.

Then you can heat it or you can change the external condition, you can keep it in a high spin state and it can hold on to that magnetic behavior for some time, though they are hard magnet

usual magnets are hard magnet. There are soft magnet; you heat it little bit it goes up speed you know magnetic values goes up high slow spin to high spin configuration occurs, but then again cooling down it comes back soft very quickly, these are called soft magnet. So, you can read about hard magnet and soft magnet once again from any book, almost done. I think this is done, this is one or two last slide it is the same thing.

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So, we have learned so far hard magnet, soft magnet, anti ferromagnetic, ferromagnetic, paramagnetic. Now, if you have a cluster; if you have a cluster for example, manganese oxo cluster. Manganese can have spin; oxo can also have spin manganese 2 plus let us say oxide, oxide 2 minus has unpaired electron. Overall you have lot of spin up lot of spin down. Theoretically, then you have to do almost a calculation in computer to figure out the net magnetic moment of the species, all right. I think that is all for today.

