

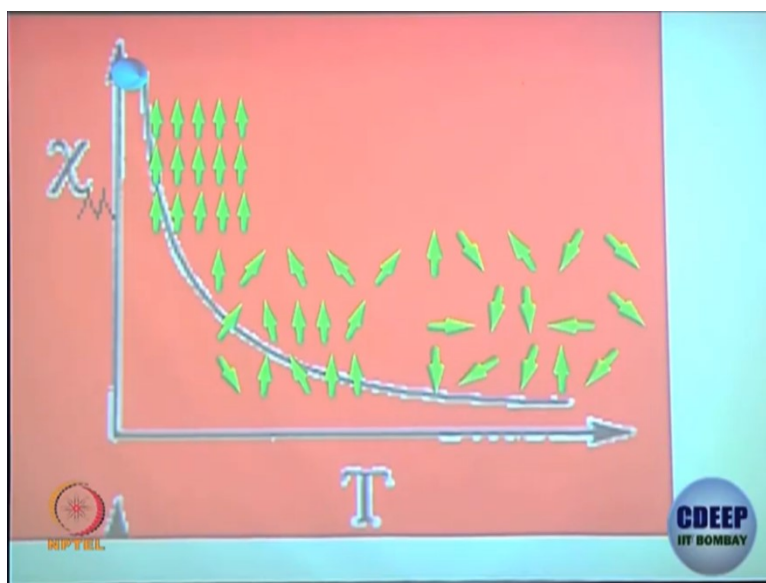
Concepts of Chemistry for Engineering
Indian Institute of Technology, Bombay
Professor Debabrata Maiti
Lecture 38

Magnetic States of Matter: Paramagnetic, Ferro and Antiferromagnetic

Now, I will move from there to simple temperature dependence of magnetism. So, you have a material let us say f electrons you have or d electrons you have whatever you have. You know at room temperature magnetic moment value is whatever χ let us say 2 Bohr 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, those spin previously you are having, now we will get an opportunity to realign, usually molecule means you can have different spin organized in a different fashion. Let us say, you have 10 different domain, 10 different metal centres, those 10 different metal centres are having spin one up, another down another up and so on its a mixture of up and down.

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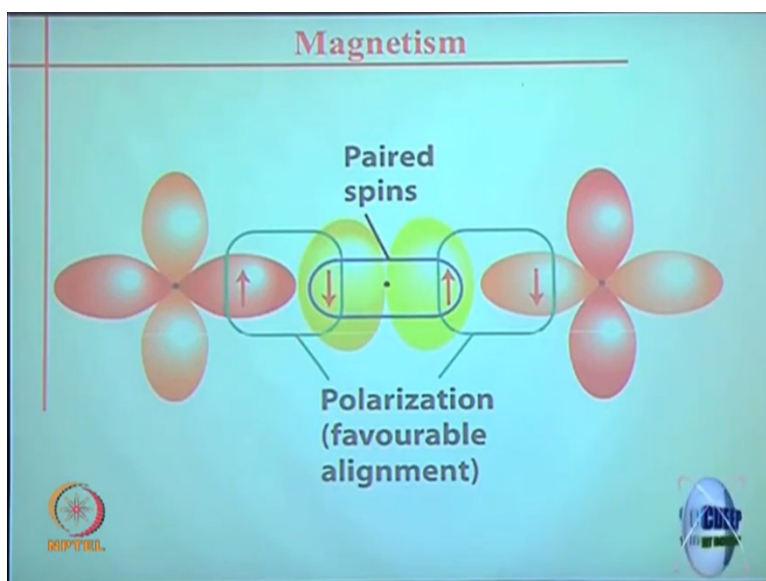
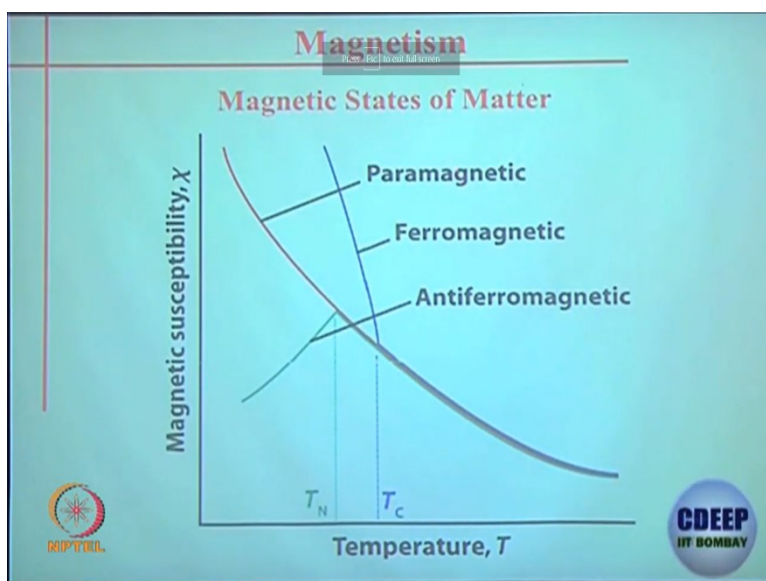


Let us say it is a mixture of up and down. This is the particular temperature let us say this is room temperature or whatever temperature you want. Now, you pull it down, you pull down the sample what will happen, this you know randomly oriented spin will get some particular orientation it will try to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

You will be able to freeze the spin more and more if you decrease the temperature. You start with 1000 degrees centigrade come to room temperature, magnetic moment value will

increase for the sample. This is the behaviour you are expected to see for paramagnetic complex. Okay, so random spin a little bit organized further organized.

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Now, that is the kind of behaviour you should expect for paramagnetic species. Sometime, what happens is once spin of one molecule is influencing the spin of other molecules. How it is? Let me give you an example here let us say this is this spin. This is the d orbital of one atom or one metal centre, this is the d orbital of another metal centre. Now, in the absence of anything in between, if there is no bridging between these two metal centres, this is spin up this, this is spin up, half and half. So, total spins should be half plus half, one.

But in presence of a ligand or bridging species having two electrons what will happen, this ligand will, ligand spin will be down. This is up this is down 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 centres up-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 , one unpaired electron. Oxide, two unpaired electron, okay, two unpaired electrons and then another copper 2 plus another unpaired electron.

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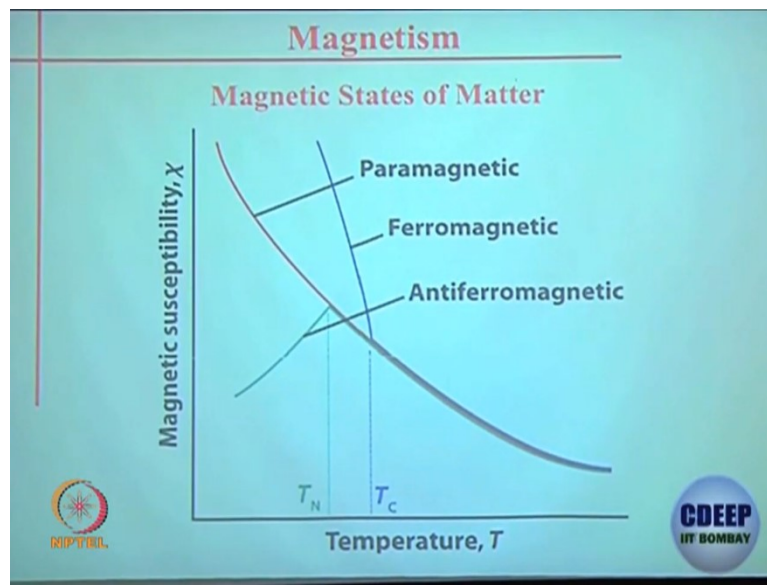


Let us say you are having copper oxide copper, 2 plus 2 plus 2 minus that is net charge is going to be let us say 2 plus does not matter. Now, this is a d^9 electronic configuration, this is a d^9 electronic configuration one spin up one spin up, one unpaired electron one unpaired electron. Oxide is having two unpaired electrons. What it is have making it essentially since this is a coupled space, 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 one on 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 overall, 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 this exchange it will become diamagnetic okay. So, what I am trying to tell you is that knowing the whole thing is important, just individual metal centre 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 to it, are they communicating with each other, okay. 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.

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So, this is where what actually you see kind of this anti-ferromagnetic behaviour 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 molecules in a way that will cancelling some of the spin.

It could also increase as you see for ferromagnetic cases. So, it is nothing but electronic spins are varying different ways okay with respect to temperature, it may be pairing up or it may be getting more unpair okay. Thereby, you see of course, this is nothing but more of a paramagnetic but the increment with respect to temperature is huge all of a sudden, right.

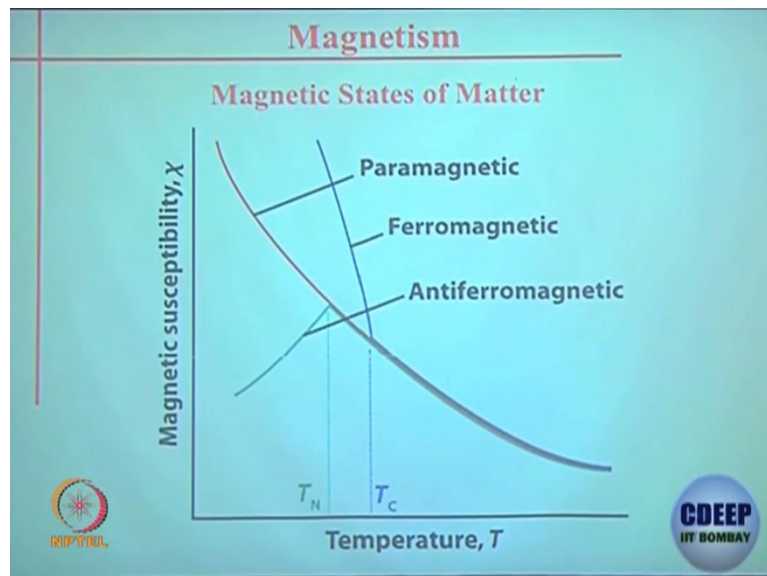
So, it is increasing-increasing as you decreasing the temperature, but at certain after certain temperature you see that there is a jump or the slope is changing, right. So, something is happening in terms of electronic arrangement, that is all it says okay.

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Magnetism

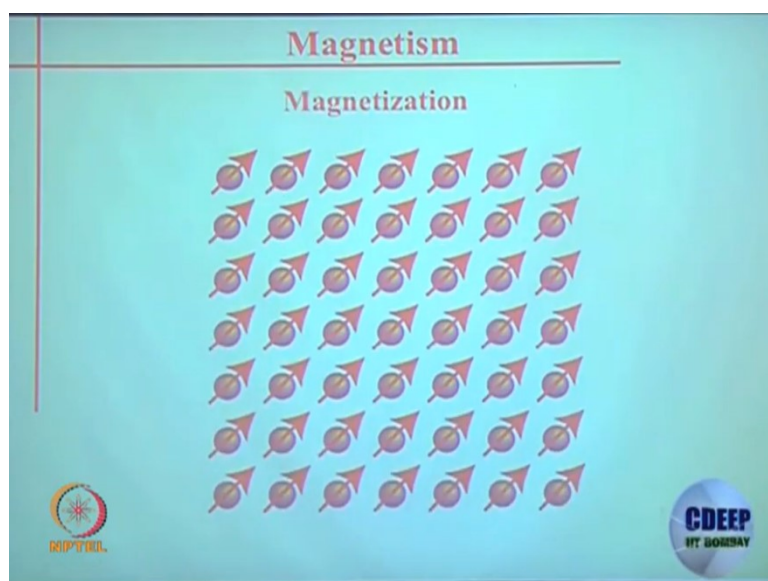
Magnetic States of Matter

- 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 Neel temperature and so on. I think you have studied before ferromagnetic, anti-ferromagnetic and paramagnetic you study from a book okay.

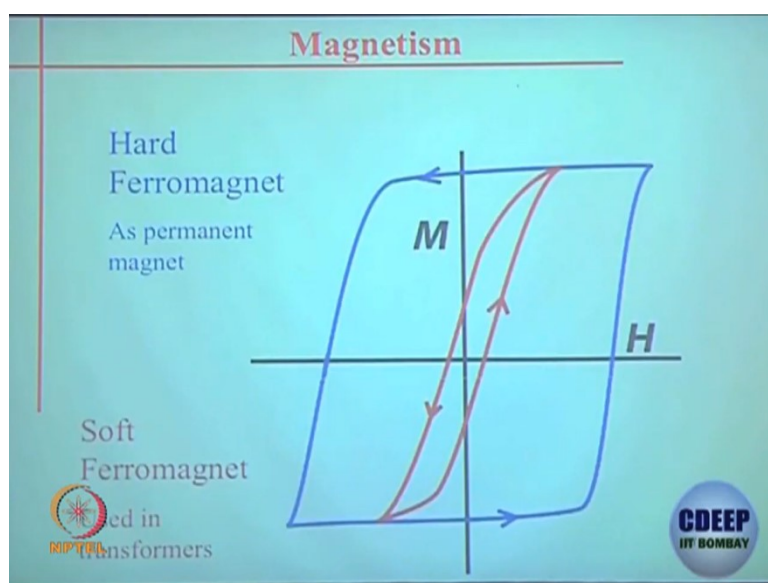
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Magnetization okay. So, if you see if you are trying to magnetize one species, let us say with a magnet you are trying to magnetize another species. What essentially happening is you are reorienting the spin of those molecules. So, for example, this is the magnetization if you want, if you can reverse the spin this is going to lead to that neutralization.

It is nothing but changing the spin, all up, all down, one up, one down, how many up how many down going to determine the magnetic properties or magnetic behaviour of a compound. 2 more minutes, maybe one minute will be good enough. Okay, you read this okay.

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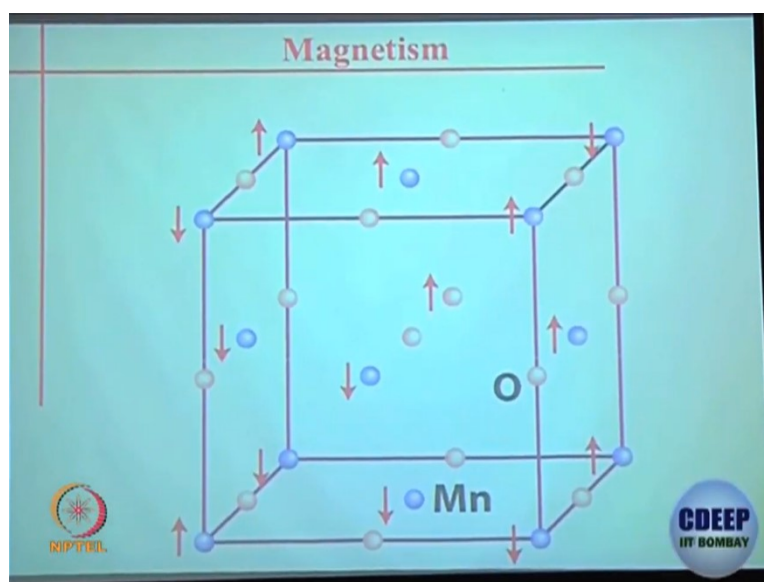


There is some material, for example, over here, if you are increasing the temperature or decreasing the temperature, you can understand how you can give low spin to high spin. You know that if you heat it up for example, you can go from low spin to high spin. Spin will increase right so, if that is happening, you are going to increase the magnetic moment.

So, you are increasing the 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 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 behaviour for some time.

Those are hard magnet, usual magnets are hard magnet, there are soft magnet, you hit it a little bit, it goes up you know magnetic values goes up, low spin to high spin configuration occur. But then again, cooling down, it comes back very quickly. These are called soft magnet. So, you can read about hard magnet and soft magnet once again from any book. Okay, almost done. I think this is done. This is one or two last slides.

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Its the same thing. So, we have learned so far hard magnet, soft magnet, anti-ferromagnetic, ferromagnetic, paramagnetic. Now, 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 a lot of spin up, lot of spin down. Theoretically, then you have to do almost a calculus and in computer to figure out the net magnetic moment of the spaces. All right. I think that is all for today.