Non - Metallic Materials
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Module - 05
Electrical, magnetic and thermal properties of non - metallic materials
Lecture - 26
Ceramic magnets and their applications

Welcome to my course Non-Metallic Materials. And today we are in module number 5 Electrical, magnetic and thermal properties of non-metallic materials. And this is lecture number 26 Ceramic magnets and their applications.

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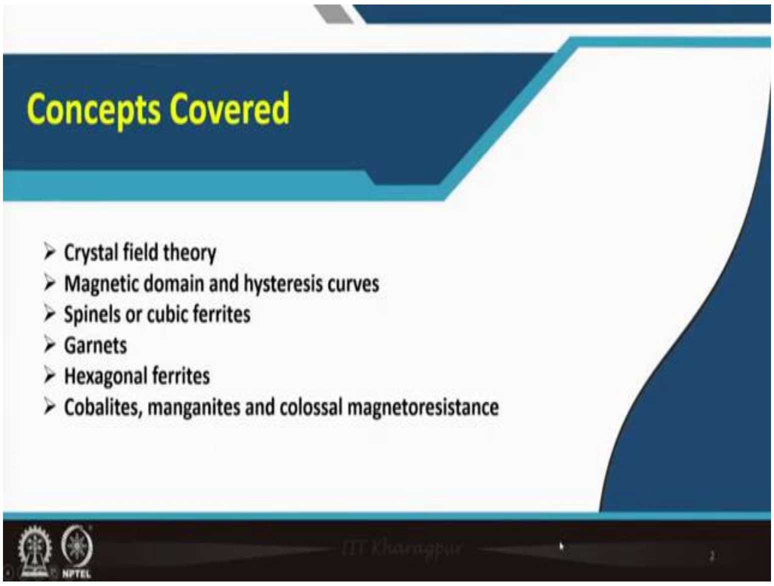

Concepts Covered

- Crystal field theory
- Magnetic domain and hysteresis curves
- Spinels or cubic ferrites
- Garnets
- Hexagonal ferrites
- Cobalites, manganites and colossal magnetoresistance

So, in the last lecture, I covered the fundamentals of magnetism, origin of magnetism and the basic magnetic materials. So, in this lecture, I will introduce the crystal field theory which is important for not only magnetic material. But, subsequently we will see when we will talk about the power source, the battery material energy storage materials, and then the concept of the crystal field theory will be useful.

And also for certain magnetic material it will be important for you to understand the crystal field theory. Then, the concept of magnetic domain and hysteresis loop will be covered, some kind of similarities are there with the ferroelectric materials. And, especially spinel type of material will be talking about and their subsequent applications.

Garnets we will be talking about hexagonal ferrite and finally, cobaltites and manganites this type of materials will be talked about and colossal magnetoresistance material with colossal magnetoresistance will be introduced.

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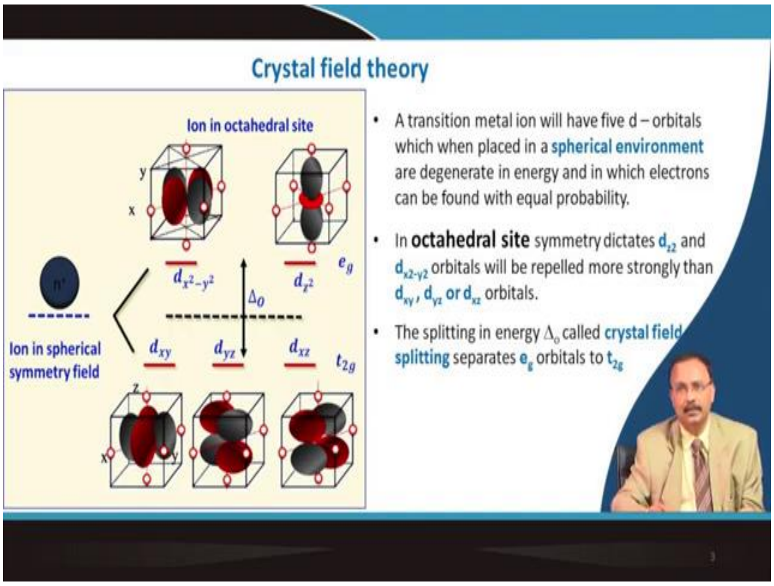

Crystal field theory

- A transition metal ion will have five d – orbitals which when placed in a **spherical environment** are degenerate in energy and in which electrons can be found with equal probability.
- In **octahedral site** symmetry dictates d_{z2} and d_{x2-y2} orbitals will be repelled more strongly than d_{xy}, d_{yz} or d_{xz} orbitals.
- The splitting in energy Δ_o called **crystal field splitting** separates e_g orbitals to t_{2g}

So, since I have not talked about the crystal structure as such in details. So, wherever necessary I will introduce the concept of the spatial crystal structures to make you understand the fundamental principles of these materials. So, a transition metal cation as you can understand that unfilled transition metal cations, with unfilled d shell and f shell will give rise to magnetic moment.

So, if you consider the d orbital so, there are five of them.

And, when it is in a spherical environment then this is having in a spherical symmetry, they are degenerate in energy state and here the electrons can be found anywhere with equal probability; but, when you place this kind of transition metal cation with unfilled d orbital in a say for example, octahedral sites, then the symmetry will dictate that especially this d z square and d x square y square orbitals will be repelled more strongly, than the d xy, dyz and d xz kind of orbitals as you can see.

So, this will be repelled and this energy is called crystal field energy, this delta in octahedral environment. And due to historic reason this is called as e g and this three orbital is called t 2g. So, in octahedral crystal environment this d orbital splits.

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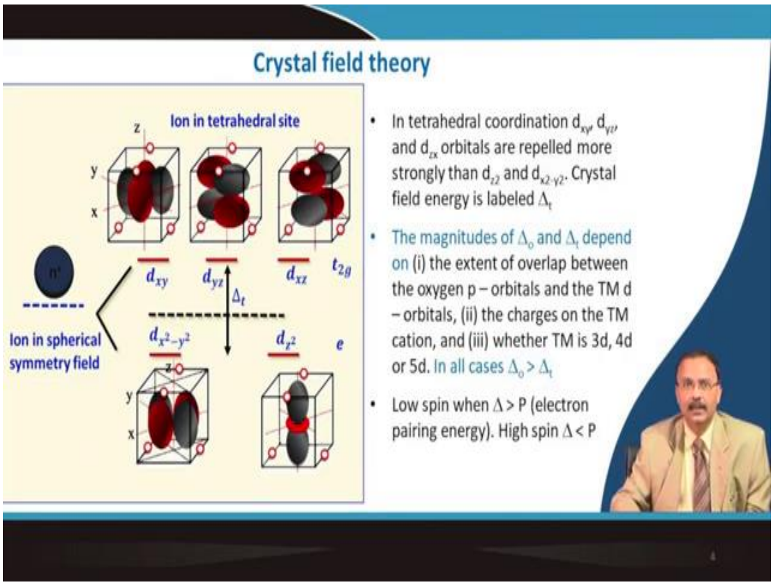

Crystal field theory

- In tetrahedral coordination d_{xy}, d_{yz}, and d_{zx} orbitals are repelled more strongly than d_{z2} and d_{x2-y2}. Crystal field energy is labeled Δ_t
- The magnitudes of Δ_o and Δ_t depend on (i) the extent of overlap between the oxygen p – orbitals and the TM d – orbitals, (ii) the charges on the TM cation, and (iii) whether TM is 3d, 4d or 5d. In all cases $\Delta_o > \Delta_t$
- Low spin when $\Delta > P$ (electron pairing energy). High spin $\Delta < P$

Similarly, in tetrahedral site also it will get splitted, but it is exactly in a opposite manner as you can see that this t 2g. So, called dz square and dx square y square is at the lower level and xy, yz and d zx orbital are repelled more strongly as compared to the other two. So, this energy is termed as delta t, the magnitude of this octahedral crystal field energy and tetrahedral crystal field energy they are basically dependent on three factor.

The first one the extent of overlap between the oxygen, because these are all oxide material oxygen p orbitals and transition metal d orbitals. Number 2 is the charge on the transition metal cation, whether it is 3 valence or 4 valence or 5 valence. And, also whether these transition metals are having 3d, 4d or 5d it will depend on that. But, irrespective of the fact always the octahedral crystal field energy is more than the tetrahedral crystal field energy.

So, I can define now a low spin and high spin state, in case of low spin state the pairing energy of the electron in this orbital that is less than the crystal field energy. So, delta is more than P and in high spins case it is just the reverse, where delta is less than the pairing energy. So, this we will use subsequently when we will talk about the colossal magnetoresistive materials.

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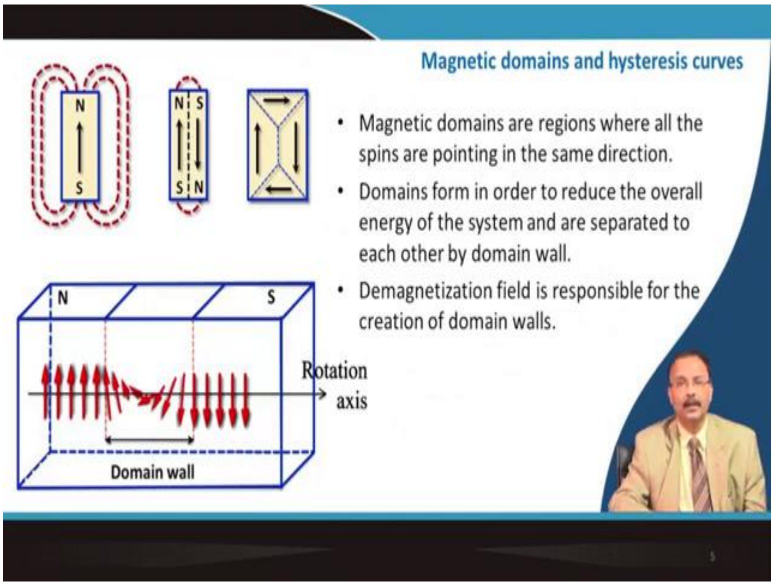

Magnetic domains and hysteresis curves

- Magnetic domains are regions where all the spins are pointing in the same direction.
- Domains form in order to reduce the overall energy of the system and are separated to each other by domain wall.
- Demagnetization field is responsible for the creation of domain walls.

So, magnetic domains are the region something similar to the polarization domain for ferroelectric material. So, in this case remember the mechanisms are entirely different that is related to cation shifting from the minimum energy position, due to the displacive phase transition. And for magnetic material, it is entirely dependent on unpaired electron spin it is related to the spin.

So, in the domain structure magnetic domains all the spins are pointing towards the same direction. So, these domains usually form to reduce the overall energy, as you can see here if it is a single domain thing, due to the depolarization or demagnetization field it will be splitted, so that this kind of configuration will be there. So, the domains form in order to reduce the overall energy of the system and they are separated by a domain wall.

So, demagnetization field is responsible for the creation of the domain wall. Now, if you compare the domain wall of a ferroelectric material and a ferromagnetic material, there is a difference in case of ferroelectric material domains wall are very thin; where the direction of the polarization is abruptly change, across the domain wall.

But, in case of your ferromagnetic material you see that the domain wall is having a finite thickness. And, where the change of the magnetization direction this is quite gradual across the domain wall. Sometimes this domain wall is also called block wall. So, this is having a finite width.

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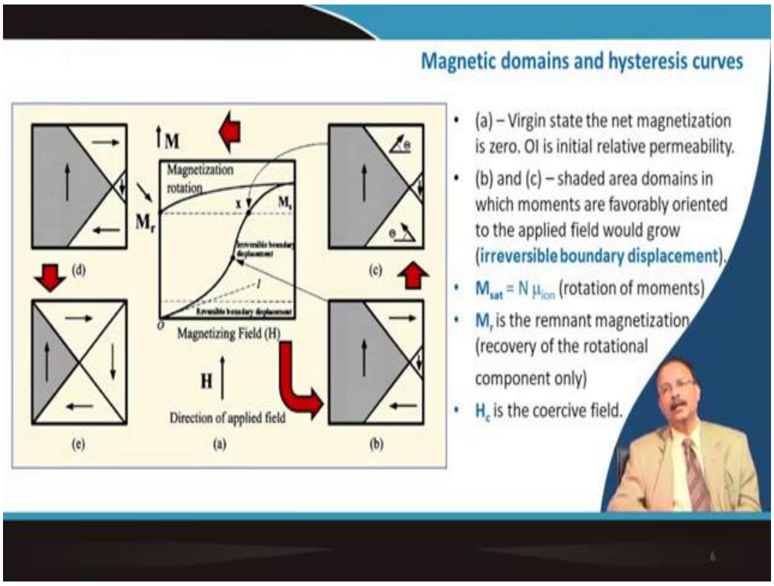

Magnetic domains and hysteresis curves

- (a) – Virgin state the net magnetization is zero. OI is initial relative permeability.
- (b) and (c) – shaded area domains in which moments are favorably oriented to the applied field would grow (**irreversible boundary displacement**).
- $M_{sat} = N\,\mu_{ion}$ (rotation of moments)
- M_r is the remnant magnetization (recovery of the rotational component only)
- H_c is the coercive field.

Now, based on this you can understand the dynamics of the domain, when a magnetic material particularly ferromagnetic material we are applying a variable magnetic field. So, from zero state you see that these domains the magnetization is oriented in all possible directions so, the net magnetization is 0.

So, once you apply the field this is almost linear. So, this is a linear region you can first see. So, initially the magnetization was 0. So, if you draw a tangent here this OI that is will give you the initial permeability of this material, but the slope will keep changing when you increase the magnetic field intensity.

Now, the b and c the shaded area domains in which the moments are favorably oriented. So, in b this area and in c as you can see that the domain is favorably oriented with the direction of the magnetic field; so, here once you apply the field then there will be irreversible boundary displacement of these domains.

So, it will in fact grow along with the field direction. So, this is irreversible it will never come back. So, finally, it will reach to a saturation level and the saturation magnetization as I have already mentioned, it is N into the individual magnetic moment. So, saturation magnetization will be achieved.

So, when you start to reduce the magnetic field intensity, then certain domain direction, they will start to rotate there is no domain boundary moment. But, there is a rotational component which was operative say from this region. So, the domain the boundary moment seized, but the rotational moment of the domain along with the magnetic field was operative.

So, once you take out the field and reverse the field, then this rotation again they will come back to their original position. So, actually the magnetization will start to reduce. But, even at zero magnetic field it will not be completely misaligned. So, you have a remnant polarization sorry, remnant magnetization for this ferromagnetic material.

And the field that is required to switch the magnetization from one direction to other. So, that is known as square shift field something very similar to the ferroelectric loop although the mechanism is entirely different in both these two cases.

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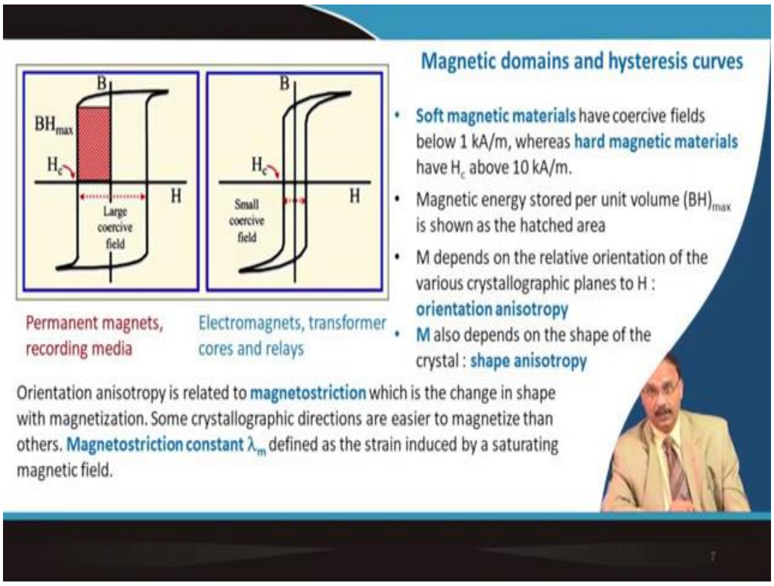

Permanent magnets, recording media

Electromagnets, transformer cores and relays

Magnetic domains and hysteresis curves

- **Soft magnetic materials** have coercive fields below 1 kA/m, whereas **hard magnetic materials** have H_c above 10 kA/m.
- Magnetic energy stored per unit volume $(BH)_{max}$ is shown as the hatched area
- M depends on the relative orientation of the various crystallographic planes to H : **orientation anisotropy**
- M also depends on the shape of the crystal : **shape anisotropy**

Orientation anisotropy is related to **magnetostriction** which is the change in shape with magnetization. Some crystallographic directions are easier to magnetize than others. **Magnetostriction constant** λ_m defined as the strain induced by a saturating magnetic field.

So, based on the nature of this ferromagnetic loop, I can define a soft magnetic material that have coercive field which is typically below 1 kilo ampere per meter. In case of hard magnetic field, it is fatter it is more nicely saturated. But, the coercive field is also quite high above 10 kilo ampere per meter the magnetic energy that is stored per unit volume is given by this value B into BH max will give you that magnetization, and the magnetic field. This value will give you the magnetic energy stored per unit volume.

Now, this magnetization that depends on the relative orientation of various crystallographic plane so, the way your magnetic moment movement is taking place that is related to various crystallographic plane. So, in that way it depends on the orientation anisotropy not all the plane will be favorably oriented towards the magnetic field direction.

Sometimes it depends on the shape of the sample as well for example, if you take a needle life sample it is very easy to magnetize along with its long axis rather than is short axis. So, this is called shape anisotropy. So, in case of a soft magnetic material electromagnets, transformer cores, relays, etceteras are usually made by it.

Because, of the simple reason it can be magnetized very easily and demagnetize also is equally possible, in case of the hard magnetic material they are usually used for permanent magnets or recording media. Another phenomena which is important is called magnetostriction, which is the change in the shape of the sample with magnetization. So, some crystallographic directions are easy to magnetize than others that is related to this orientation anisotropy.

And, we can define magnetostriction constant that is the strain which is induced by a saturating magnetic field. So, this magnetostriction is important for multipheroic composite synthesis which is a material, which exhibits both polarization ordering as well as magnetic ordering. This is beyond the scope of this lecture, but for this those type of material, it is magnetostriction is playing a very major role.

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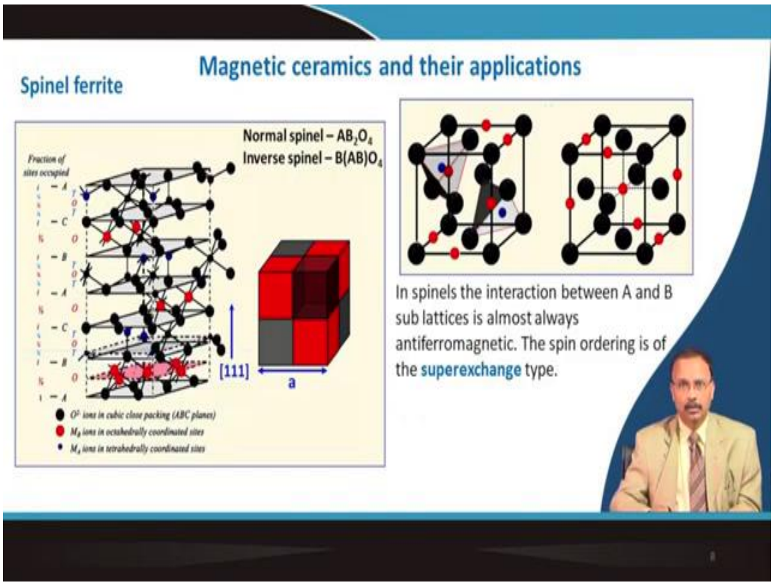

Magnetic ceramics and their applications

Spinel ferrite

Normal spinel – AB_2O_4
Inverse spinel – $B(AB)O_4$

In spinels the interaction between A and B sub lattices is almost always antiferromagnetic. The spin ordering is of the **superexchange** type.

Now, we can talk about the spinel ferrite material although exclusively, I have not talked about the crystal structure, but to give you some idea. That the normal spinel structure is having a general formula $AB_2 O_4$, A is tetrahedrally coordinated just something like this, and B cations they stay in octahedral coordinated regions.

So, there are total 64 tetrahedral position, and 32 octahedral position in a single unit cell like this, you can have 1 2 3 4 5 6 7 8 tetrahedral position along with the body diagonal. So, there are 8 such unit cells so, there are 64 tetrahedral voids. And similarly you have along with the a center you have 12 each of them are one fourth shear. So, 3 plus 1 is in the middle so, total is 4 and you have total 8 such unit cell so, 32 octahedral positions are there.

In case of inverse spinel half of this octahedral cation goes to the tetrahedral site. And all the tetrahedral cations, which are divalent goes to the octahedral sites to form the inverse spinal structure. So, in the spinel the interaction between the so, called A sub lattice which is tetrahedral cation is having in tetrahedral void, and B sub lattice is almost always antiferromagnetic in nature.

So, these two spins are in reverse direction. So, the spin ordering is the super exchange type. So, we will talk about the spin ordering in this type of material is the super exchange type.

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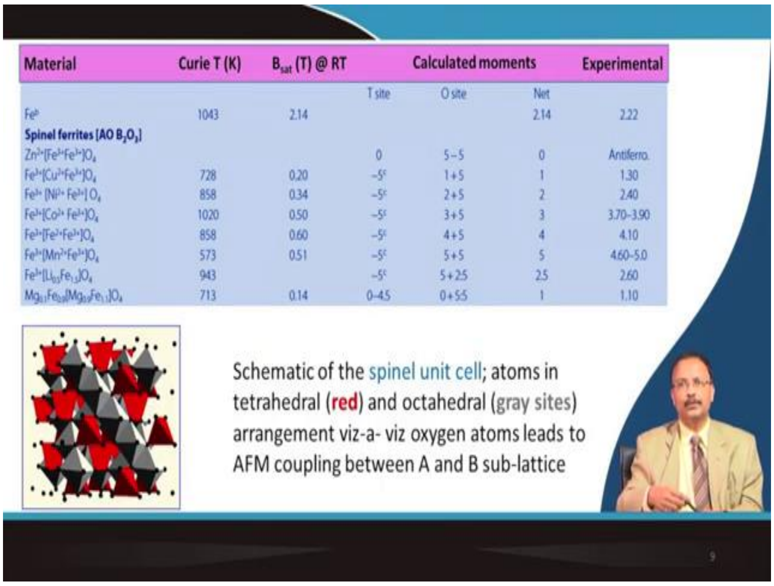

Material	Curie T (K)	B_{sat} (T) @ RT	Calculated moments			Experimental
			T site	O site	Net	
Fe^{a}	1043	2.14			2.14	2.22
Spinel ferrites [AO B_2O_3]						
$Zn^{2+}[Fe^{3+}Fe^{3+}]O_4$			0	5−5	0	Antiferro.
$Fe^{3+}[Cu^{2+}Fe^{3+}]O_4$	728	0.20	−5	1+5	1	1.30
$Fe^{3+}[Ni^{2+}Fe^{3+}]O_4$	858	0.34	−5	2+5	2	2.40
$Fe^{3+}[Co^{2+}Fe^{3+}]O_4$	1020	0.50	−5	3+5	3	3.70-3.90
$Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$	858	0.60	−5	4+5	4	4.10
$Fe^{3+}[Mn^{2+}Fe^{3+}]O_4$	573	0.51	−5	5+5	5	4.60-5.0
$Fe^{3+}[Li_{0.5}Fe_{1.5}]O_4$	943		−5	5+2.5	2.5	2.60
$Mg_{0.1}Fe_{0.9}[Mg_{0.9}Fe_{1.1}]O_4$	713	0.14	0-4.5	0+5.5	1	1.10

Schematic of the spinel unit cell; atoms in tetrahedral (red) and octahedral (gray sites) arrangement viz-a- viz oxygen atoms leads to AFM coupling between A and B sub-lattice

So, here I have shown the different types of spinel structure. So, you can identify easily 8 type A cations and B cations here. So, A and B these two spins are different early oriented. So, many of them you will see that they give the ferrimagnetic nature depending on the magnetic moment into different sites.

So, the schematic shows a typical spinel unit cell. So, atom which are there in tetrahedral voids are red and octahedral are these gray sites. And they are connected via oxygen atoms and this actually gives to antiferromagnetic coupling, because as I said the spin in this sub lattice and this sub lattice they are reversed to each other.

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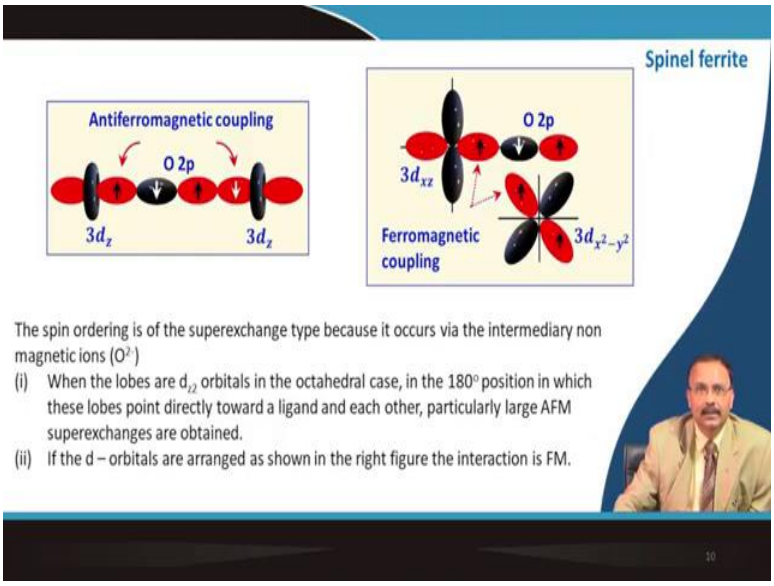

Spinel ferrite

The spin ordering is of the superexchange type because it occurs via the intermediary non magnetic ions (O^{2-})

(i) When the lobes are d_{z^2} orbitals in the octahedral case, in the 180° position in which these lobes point directly toward a ligand and each other, particularly large AFM superexchanges are obtained.

(ii) If the d – orbitals are arranged as shown in the right figure the interaction is FM.

So, the antiferromagnetic coupling that can be understood from the spin ordering, and as I told it is super exchange type because it occurs where the intermediate oxygen which are non magnetic in nature. So, when the lobes of for example, dz square or vitals in the octahedral case in the 180 degree position in which this lobes point directly towards a ligand and each other, particularly large antiferromagnetic super exchange is obtained.

But on the other hand if the d orbitals are arranged something similar to this in between oxygen is here, then the interaction is ferromagnetic type. So, depending on which type of interaction is operative on the spinel will behave either like anti ferromagnetic or ferrimagnetic or typical ferromagnetic behavior will be observed.

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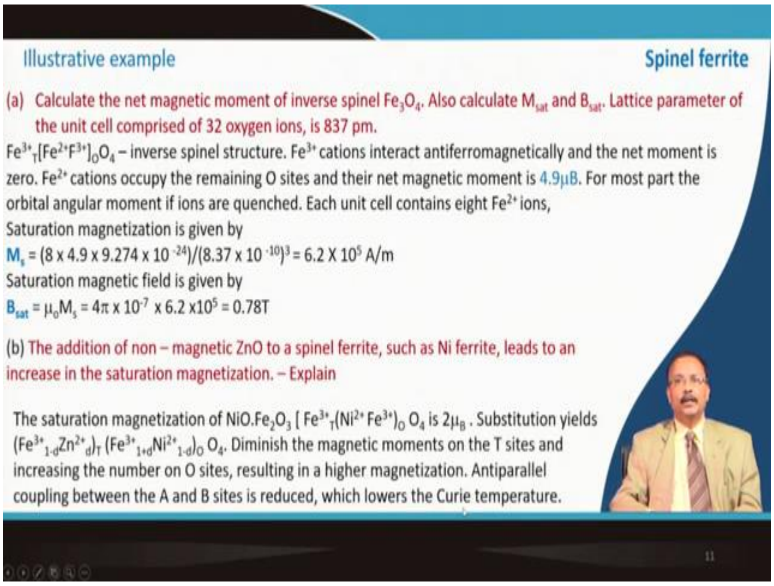

Illustrative example

Spinel ferrite

(a) Calculate the net magnetic moment of inverse spinel Fe_3O_4. Also calculate M_{sat} and B_{sat}. Lattice parameter of the unit cell comprised of 32 oxygen ions, is 837 pm.

$Fe^{3+}{}_T[Fe^{2+}F^{3+}]_O O_4$ – inverse spinel structure. Fe^{3+} cations interact antiferromagnetically and the net moment is zero. Fe^{2+} cations occupy the remaining O sites and their net magnetic moment is 4.9μB. For most part the orbital angular moment if ions are quenched. Each unit cell contains eight Fe^{2+} ions,

Saturation magnetization is given by

$M_s = (8 \times 4.9 \times 9.274 \times 10^{-24})/(8.37 \times 10^{-10})^3 = 6.2 \times 10^5$ A/m

Saturation magnetic field is given by

$B_{sat} = \mu_0 M_s = 4\pi \times 10^{-7} \times 6.2 \times 10^5 = 0.78T$

(b) The addition of non – magnetic ZnO to a spinel ferrite, such as Ni ferrite, leads to an increase in the saturation magnetization. – Explain

The saturation magnetization of $NiO.Fe_2O_3$ [$Fe^{3+}{}_T(Ni^{2+}Fe^{3+})_O O_4$ is $2\mu_B$. Substitution yields $(Fe^{3+}{}_{1-d}Zn^{2+}{}_d)_T (Fe^{3+}{}_{1+d}Ni^{2+}{}_{1-d})_O O_4$. Diminish the magnetic moments on the T sites and increasing the number on O sites, resulting in a higher magnetization. Antiparallel coupling between the A and B sites is reduced, which lowers the Curie temperature.

So, I have tried to show a illustrative example to calculate the net magnetic moment of an inverse spinel. And how to calculate the saturation magnetization the saturation field, corresponding to the saturation magnetization; lattice parameter is given which is typically 37 pico meter.

So, we will write the relation here the cation in the tetrahedral site, these cations are in the octahedral sites this is having inverse spinel structure. So, Fe 3 cations interact antiferromagnetically and net moment is zero. Cations Fe 2 whatever is remaining in the octahedral sides the net, magnetic moment you can calculate the way I showed earlier slides S into S plus 1 root over 2 mu B you can calculate is 4.9 more magneton and we are assuming in the most part l is 0.

So, saturation magnetization you can calculate from this relation, this relation also I have defined earlier number of ions. You will have to get and the individual magnetic moment. Saturation magnetic field is nothing but permeability into the magnetization, which is about 0.78 Tesla. In addition to non magnetic zinc oxide to a spinel ferrite such that nickel ferrite, if you add zinc that leads to the saturation magnetization and the question is why.

So, your original material nickel ferrite the structure is something like this. Now, the substitution if you do then zinc will be substituted in Fe 3 plus site. And, corresponding charge balance we have maintained you know that how to do the charge balance in case of the non stoichiometric oxide.

So, that diminish the magnetic moments in the T sites and increase the number of O sites resulting a higher magnetization. So, this T site and O site they will cancel, but due to this charge neutrality you will get a knit magnetic moment that is larger. So, usually the antiparallel coupling between A and B site is reduced. And this actually lower the Curie temperature as well experimentally it is formed.

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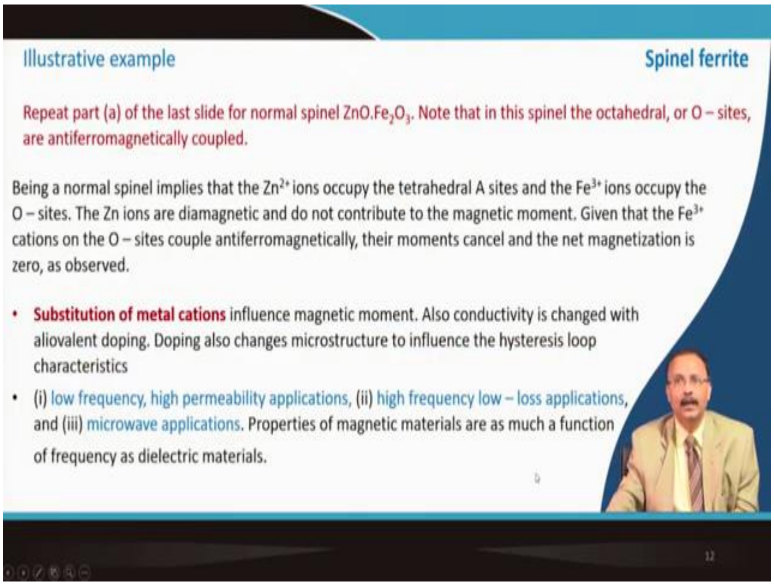

Illustrative example

Spinel ferrite

Repeat part (a) of the last slide for normal spinel ZnO.Fe_2O_3. Note that in this spinel the octahedral, or O – sites, are antiferromagnetically coupled.

Being a normal spinel implies that the Zn^{2+} ions occupy the tetrahedral A sites and the Fe^{3+} ions occupy the O – sites. The Zn ions are diamagnetic and do not contribute to the magnetic moment. Given that the Fe^{3+} cations on the O – sites couple antiferromagnetically, their moments cancel and the net magnetization is zero, as observed.

- **Substitution of metal cations** influence magnetic moment. Also conductivity is changed with aliovalent doping. Doping also changes microstructure to influence the hysteresis loop characteristics
- (i) low frequency, high permeability applications, (ii) high frequency low – loss applications, and (iii) microwave applications. Properties of magnetic materials are as much a function of frequency as dielectric materials.

So, again another illustrative example is that party of the earlier problem. The normal spinel is this one and in this spinel octahedral or O sites are antiferromagnetically coupled.

So, it is a normal spinel so, zinc plus 2 occupies the tetrahedral site and Fe 3 plus occupies the octahedral sites. So, zinc ions diamagnetic in nature they will not contribute to the magnetic moment. And Fe 3 plus cations in the O sites, they couple antiferromagnetically their moments actually cancel. So, the net magnetization for this normal spinel is 0.

So, substitution of metal cation influence the magnetic moment, also conductivity is changed with the aliovalent dopant addition dopant also change the microstructure to influence the hysteresis loop. So, low frequency high permeability application this spinel are good, sometimes high frequency and low loss application or microwave application and, properties of this magnetic material a function of frequency just same as we have found in case of dielectric material.

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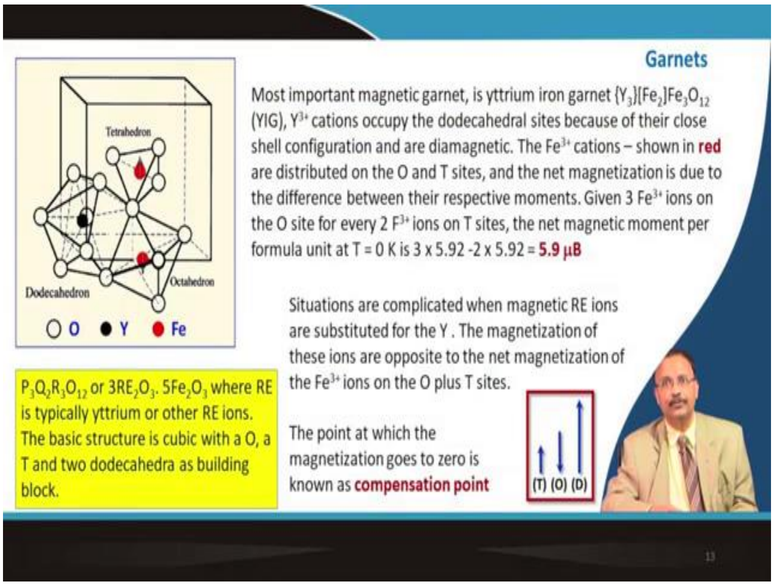

Garnets

Most important magnetic garnet, is yttrium iron garnet $\{Y_3\}[Fe_2]Fe_3O_{12}$ (YIG), Y^{3+} cations occupy the dodecahedral sites because of their close shell configuration and are diamagnetic. The Fe^{3+} cations – shown in **red** are distributed on the O and T sites, and the net magnetization is due to the difference between their respective moments. Given 3 Fe^{3+} ions on the O site for every 2 F^{3+} ions on T sites, the net magnetic moment per formula unit at T = 0 K is 3 x 5.92 -2 x 5.92 = **5.9 μB**

$P_3Q_2R_3O_{12}$ or $3RE_2O_3 . 5Fe_2O_3$ where RE is typically yttrium or other RE ions. The basic structure is cubic with a O, a T and two dodecahedra as building block.

Situations are complicated when magnetic RE ions are substituted for the Y . The magnetization of these ions are opposite to the net magnetization of the Fe^{3+} ions on the O plus T sites.

The point at which the magnetization goes to zero is known as **compensation point**

There is another type of material which is garnet type. And in garnet type material the actual formula is something similar to this, typically yttrium iron garnet is one of the examples. And the Fe 3 plus cation as you can see that it is either in the tetrahedral void, or it is in the octahedral void and your yttrium is sitting in a dodecahedral void.

So, something similar to the spinel case you can calculate the magnetic moment for this kind of material. And the good part of this garnet material is that you can change this rare earth values. And you can eventually control the magnetic moment, just we have seen in case of addition of zinc in nickel ferrite that can improve the magnetic moment here also.

It is possible you can make it zero magnetic moment material or you can make you can increase the magnetic moment for this type of material. And, basically it goes something similar to this you have different sub lattices the magnetic moment either cancels out or there are remnant magnetic movement gives you the ferrimagnetic kind of behavior.

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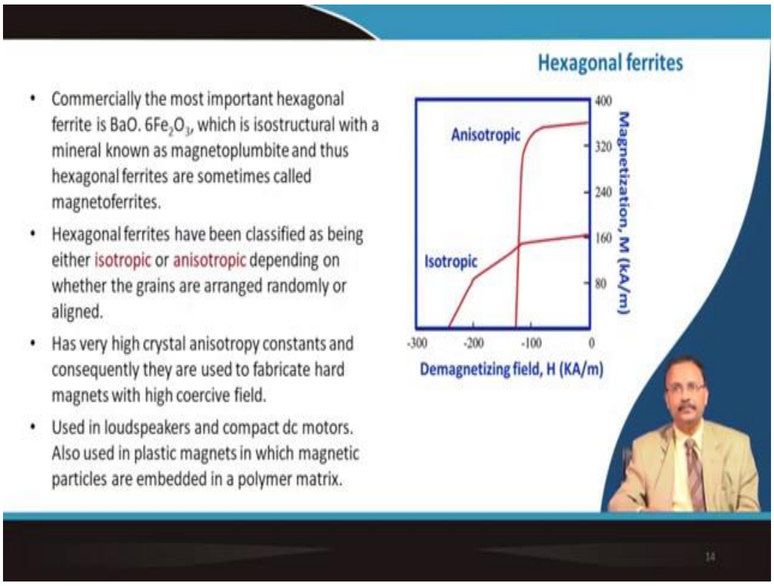

Hexagonal ferrites

- Commercially the most important hexagonal ferrite is BaO. $6Fe_2O_3$, which is isostructural with a mineral known as magnetoplumbite and thus hexagonal ferrites are sometimes called magnetoferrites.
- Hexagonal ferrites have been classified as being either isotropic or anisotropic depending on whether the grains are arranged randomly or aligned.
- Has very high crystal anisotropy constants and consequently they are used to fabricate hard magnets with high coercive field.
- Used in loudspeakers and compact dc motors. Also used in plastic magnets in which magnetic particles are embedded in a polymer matrix.

Hexagonal ferrite they are good materials for hard magnet and commercially the most important hexagonal ferrite is isostructural with magnetoplumbite, and this that is why they are called are magnetoferrites. And they have been classified either being isotropic or anisotropic in nature. So, when the grains are randomly oriented during the fabrication itself by putting a strong magnetic field you can align the grains.

And very high crystal anisotropy constants can be found in this type of material and it is good to fabricate a hard magnet. And, usually they are used in loudspeaker or compact DC motors also they are dispersed in plastic, and form a plastic magnet. These hexagonal ferrites are good for permanent magnets.

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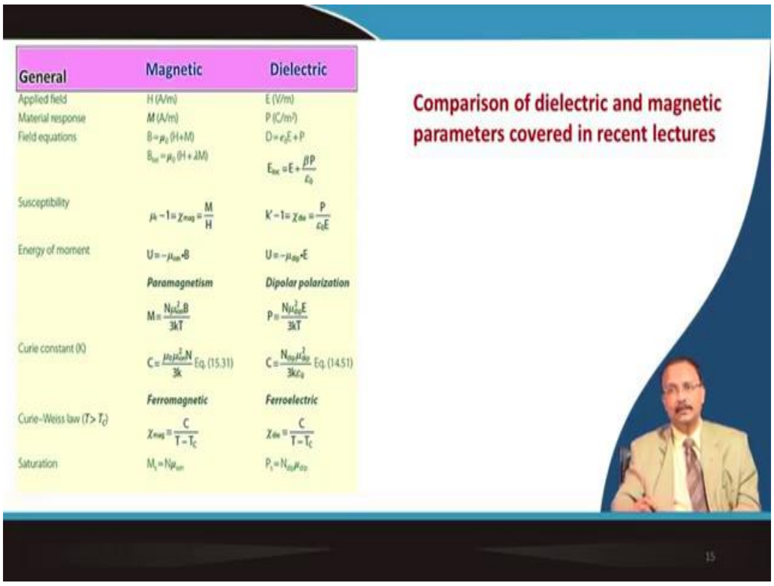

Comparison of dielectric and magnetic parameters covered in recent lectures

General	Magnetic	Dielectric
Applied field	H (A/m)	E (V/m)
Material response	M (A/m)	P (C/m²)
Field equations	$B = \mu_0(H+M)$ $B_{loc} = \mu_0(H + \lambda M)$	$D = \varepsilon_0 E + P$ $E_{loc} = E + \frac{\beta P}{\varepsilon_0}$
Susceptibility	$\mu_r - 1 = \chi_{mag} = \frac{M}{H}$	$K' - 1 = \chi_{die} = \frac{P}{\varepsilon_0 E}$
Energy of moment	$U = -\mu_{ion} \cdot B$	$U = -\mu_{dip} \cdot E$
	Paramagnetism	***Dipolar polarization***
	$M = \frac{N\mu_{ion}^2 B}{3kT}$	$P = \frac{N\mu_{dip}^2 E}{3kT}$
Curie constant (K)	$C = \frac{\mu_0 \mu_{ion}^2 N}{3k}$ Eq. (15.31)	$C = \frac{N_{dip}\mu_{dip}^2}{3k\varepsilon_0}$ Eq. (14.51)
	Ferromagnetic	***Ferroelectric***
Curie-Weiss law ($T > T_C$)	$\chi_{mag} = \frac{C}{T - T_C}$	$\chi_{die} = \frac{C}{T - T_C}$
Saturation	$M_s = N\mu_{ion}$	$P_s = N_{dip}\mu_{dip}$

So, here I have compared the magnetic and dielectric the equivalent terms applied field, then material response here, in one case is magnetization, other one is polarization field equations are defined susceptibility is defined what are the difference between these two. This is just to compare the relevant equations, taught in the class of dielectric material, and ferroelectric material and the magnetic material as such just for you to compare.

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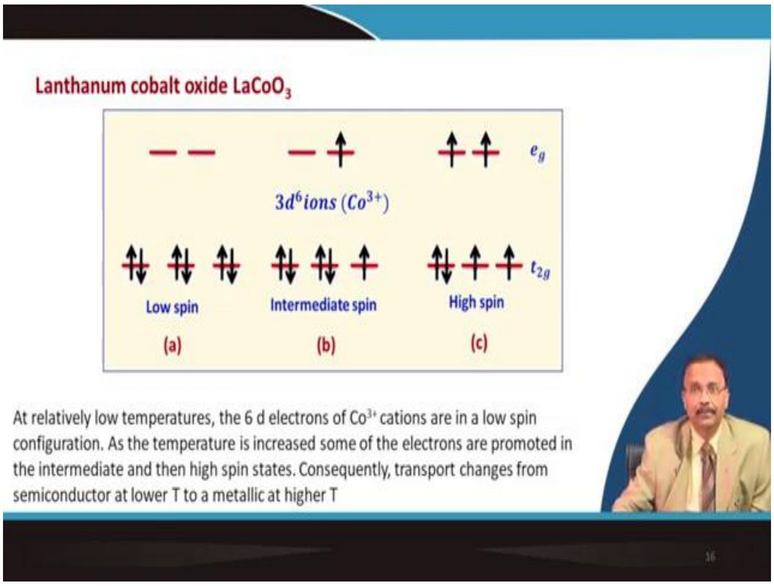

Lanthanum cobalt oxide $LaCoO_3$

At relatively low temperatures, the 6 d electrons of Co^{3+} cations are in a low spin configuration. As the temperature is increased some of the electrons are promoted in the intermediate and then high spin states. Consequently, transport changes from semiconductor at lower T to a metallic at higher T

Interesting material are lanthanum cobalt oxide which is cobaltites. And this is related to the high spin and low spin state I was talking about, at relative low temperature there are

6 d electrons for Co 3 plus you can calculate. They are in low spin configuration you see that here, the pairing is favored as compared to going to the higher crystal field energy this orbital’s.

As the temperature is increased there is a intermediate state and then finally, they go to the high spin state. So, the transport changes from low temperature which was semiconductor, it turns to be metallic at high temperature higher temperature for this type of material.

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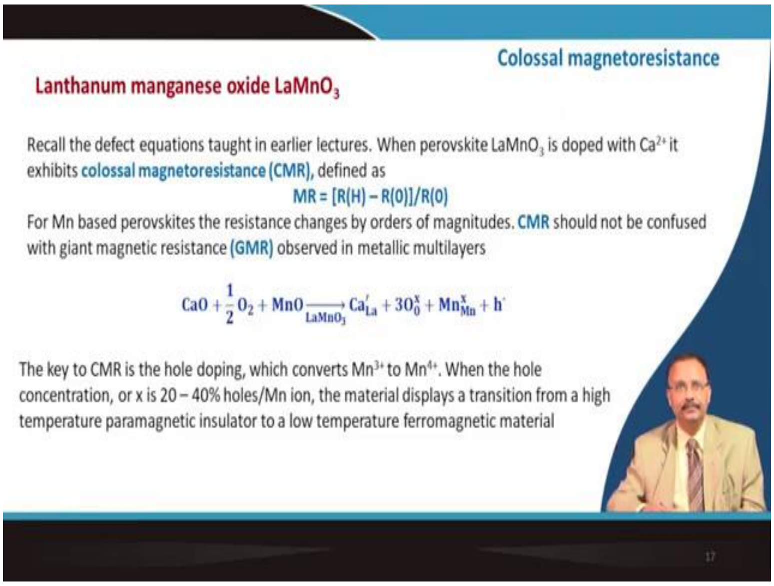

Colossal magnetoresistance

Lanthanum manganese oxide $LaMnO_3$

Recall the defect equations taught in earlier lectures. When perovskite $LaMnO_3$ is doped with Ca^{2+} it exhibits colossal magnetoresistance (CMR), defined as

MR = [R(H) – R(0)]/R(0)

For Mn based perovskites the resistance changes by orders of magnitudes. CMR should not be confused with giant magnetic resistance (GMR) observed in metallic multilayers

$$CaO + \frac{1}{2}O_2 + MnO \xrightarrow[LaMnO_3]{} Ca'_{La} + 3O_O^x + Mn_{Mn}^x + h^{\cdot}$$

The key to CMR is the hole doping, which converts Mn^{3+} to Mn^{4+}. When the hole concentration, or x is 20 – 40% holes/Mn ion, the material displays a transition from a high temperature paramagnetic insulator to a low temperature ferromagnetic material

Lanthanum manganese oxide it is perovskite structure, this is also important material. And you remember that we talked about that you can change the defect state by aliovalent doping. So, once it is doped with calcium 2 plus, when you replace lanthanum with calcium 2 plus. Then, it exhibits a colossal magnetoresistance and that is defined as resistance with the field applied, it is much larger as compared to when there is no field applied.

So, this is colossal magnetic resistance and it should not be confused with giant magnetic resistance, which is observed in multi layer metals. So, this is the relevant defect equations. And as you can see here that with this dopant, it generates hole. And this basically converts manganese 3 plus in the parent material in Li a $LaMnO_3$ to Mn 4 plus.

Now, when the hole concentration is in the range of 20 to 40 percent holes per manganese ions, the material displays a transition from high temperature paramagnetic insulated to a low temperature ferromagnetic material.

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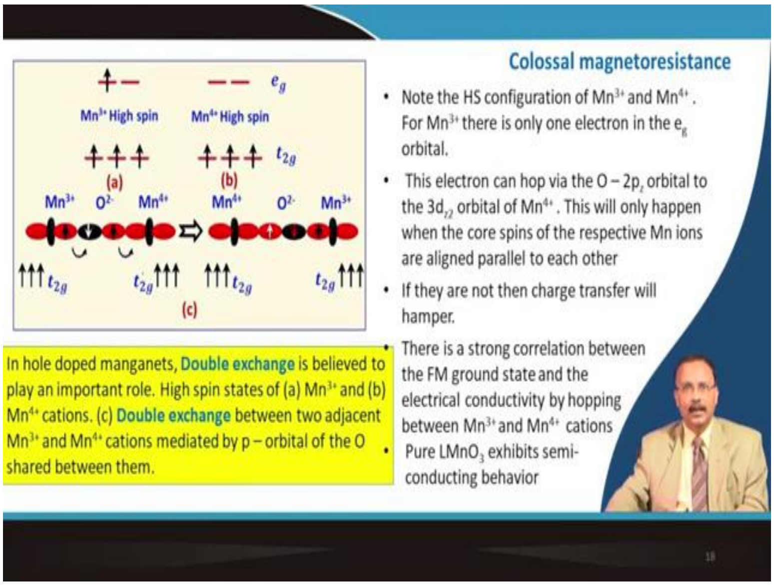

Colossal magnetoresistance

- Note the HS configuration of Mn^{3+} and Mn^{4+}. For Mn^{3+} there is only one electron in the e_g orbital.
- This electron can hop via the $O-2p_z$ orbital to the $3d_{z^2}$ orbital of Mn^{4+}. This will only happen when the core spins of the respective Mn ions are aligned parallel to each other
- If they are not then charge transfer will hamper.
- There is a strong correlation between the FM ground state and the electrical conductivity by hopping between Mn^{3+} and Mn^{4+} cations
- Pure $LMnO_3$ exhibits semi-conducting behavior

In hole doped manganets, **Double exchange** is believed to play an important role. High spin states of (a) Mn^{3+} and (b) Mn^{4+} cations. (c) **Double exchange** between two adjacent Mn^{3+} and Mn^{4+} cations mediated by p – orbital of the O shared between them.

Now, this the interaction is something similar to this that in hole doped magnates. There is a phenomena called double exchange is believed to take a role, in high spin state manganese 3 plus and manganese 4 plus cations are there. So, they undergo a double exchange between 2 adjacent Mn 3 plus and 4 plus cations, and through this mediated oxygen which is shared between them.

So, in high spin configuration Mn 3 plus Mn 4 plus is there for Mn 3 plus, there is only one electron in the e g orbital. This electron can hop via oxygen 2 p z orbital to 3 d g this z square orbital of manganese 4 plus this will happen, when the all the coarse pins of respective magnesiums are in the same direction.

And it will not happen when they are anti-parallel in nature, if there are no charge transfer then of course, its resistance will be quite high. So, there is a strong correlation between the ferromagnetic ground state, and the electrical conductivity by hopping between Mn 3 plus and Mn 4 plus cations. Pure lanthanum manganese exhibits a semiconducting behavior. So, that is the origin of colossal magnetoresistance in these materials.

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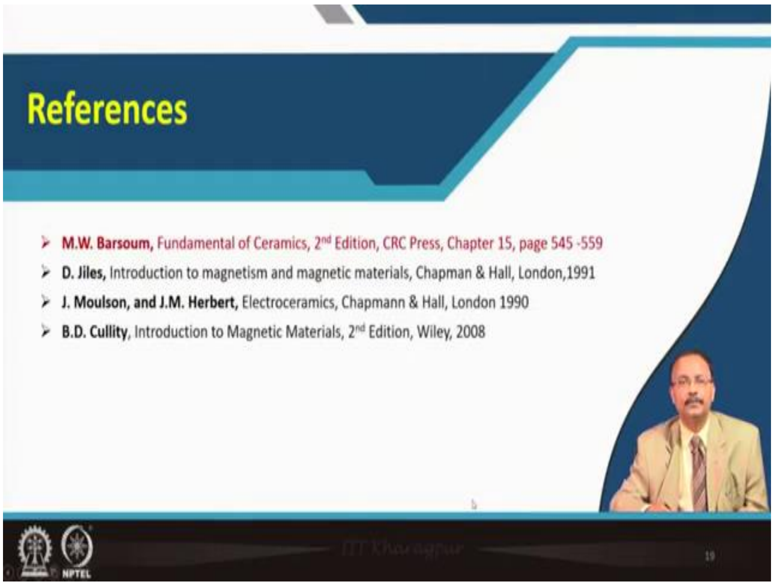

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- **D. Jiles,** Introduction to magnetism and magnetic materials, Chapman & Hall, London,1991
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- **B.D. Cullity,** Introduction to Magnetic Materials, 2nd Edition, Wiley, 2008

So, the study material for this part of the lecture is again the book by Barsoum chapter 15 and other relevant textbooks are also mentioned.

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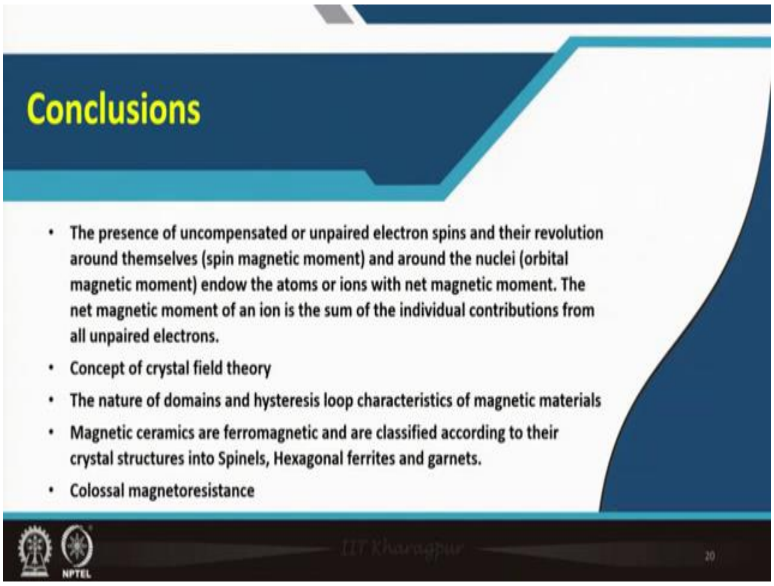

Conclusions

- The presence of uncompensated or unpaired electron spins and their revolution around themselves (spin magnetic moment) and around the nuclei (orbital magnetic moment) endow the atoms or ions with net magnetic moment. The net magnetic moment of an ion is the sum of the individual contributions from all unpaired electrons.
- Concept of crystal field theory
- The nature of domains and hysteresis loop characteristics of magnetic materials
- Magnetic ceramics are ferromagnetic and are classified according to their crystal structures into Spinels, Hexagonal ferrites and garnets.
- Colossal magnetoresistance

So, here we have shown the presence of uncompensated or unpaired electron spins and their revolutions around themselves, yielding the spin magnetic moment and around the nuclei that endorse the atoms with net magnetic moment. Concept of crystal field theory has been introduced the nature of domains and hysteresis loop characteristics of the magnetic material has been explained.

Magnetic ceramics are ferromagnetic, and are classified along with their crystal structure like spinels, hexagonal ferrites and garnets this different crystal structure how it induces magnetism that is defined. And finally, we have talked about colossal magnetoresistance.

Thank you for your attention.