Advanced Ceramics for Strategic Applications
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Lecture - 36
Magnetic Ceramics

In this lecture also, we will continue our discussion on magnetic ceramics. Earlier we have considered general properties of magnetic phenomena, many different types of the magnetic materials. We have also discussed briefly about the ferromagnetic ordering, anti ferromagnetic ordering, as well as ferri magnetic ordering. Today, we will start with our discussion on hysteresis loop, which we have discussed briefly in the previous lecture.

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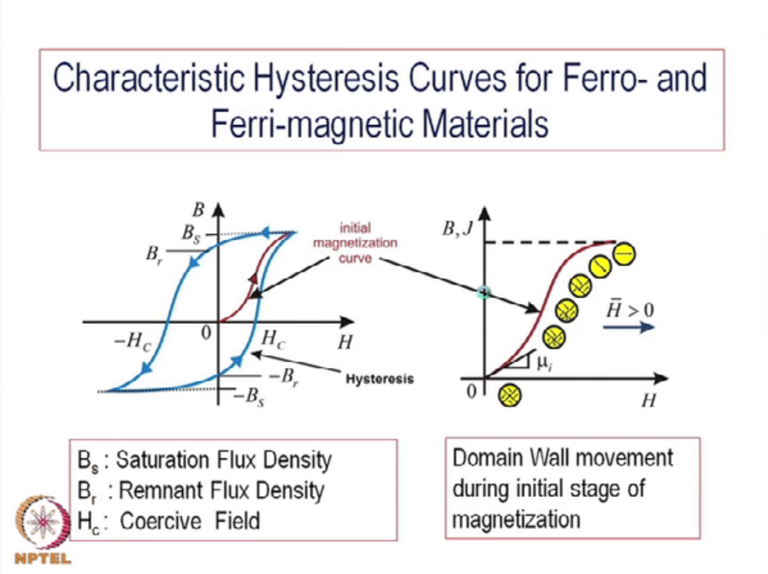

Characteristic Hysteresis Curves for Ferro- and Ferri-magnetic Materials

B_s : Saturation Flux Density
B_r : Remnant Flux Density
H_c : Coercive Field

Domain Wall movement during initial stage of magnetization

This was already shown unpresented, so we have hysteresis loop, both in ferri magnetic as well as ferromagnetic materials, and the details are the basic reason is that we have a spontaneous polarization, both in ferromagnetic and ferri magnetic ordering, and the in absence of external magnetic field H, the magnetic induction or polarization is 0, and as we increase the magnetic field, it increases non-linearly with increasing field. The initial permittivity a per permeability here, that is the slope of the initial curve, and that is the mu i the initial permeability, then of course it follows a non-linear behavior and finally, it reaches saturation, saturation concentration, or the maximum polarization.

And as we know, as we have seen in case of dielectric material, ferroelectric material in particular, this behavior comes from the domain structure, we have a large number of spontaneous magnetic moment, and there order forming domain structure will discuss, what is exact the domain? have briefly it has been shown here, these are the four domains having in the orientation of the magnetic moments in different directions.

So, statistically you have a 0 magnetic polarization, even though in the microscopic scale we have some net magnetic polarization, and as we applied the electric magnetic field the domains starts moving, the domain wall starts migrating, in such a way that all the magnetic moments slowly and slowly try to align themselves, with the direction of the magnetic field, that is in this direction.

So, more and more domains follow this particular orientation, or in other words the domains with with favor all orientation trys to grow, at the expense of unfavorable, fabily oriented domains. So, at the end saturation magnetization or saturation pollination corresponds to a kind of single domain, with the orientation of the magnetic moment in parallel with the magnetic field. So, that is how the microstructure change from a large number of domains, then one or few domains grow at the expense of the other and finally, you have only a kind of a single domain.

And you have explained earlier, once we reduced the magnetic field here, then this domains structure more or less continues stay there until now, unless we apply a negative bias or negative field, so that neutralize this structural change or domain structure change. So, that is why you do not the reverse curve, do not follow the same curve as in the forward direction. But, the reverse curve is different and you have remanent magnetization, as well as courses field which we have discussed earlier. So, primarily the domain wall movement which is responsible for the ferroelectric, sorry ferromagnetic, or the anti-ferromagnetic hysteresis curve.

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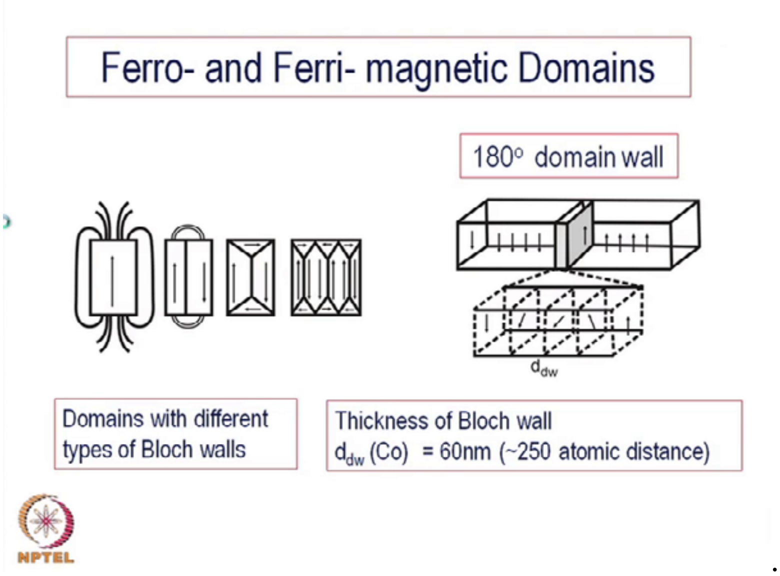

Ferro- and Ferri- magnetic Domains

180° domain wall

Domains with different types of Bloch walls

Thickness of Bloch wall
d_{dw} (Co) = 60nm (~250 atomic distance)

With this we go to the, what is exactly a domain structure? what we how much details we know about the domain structure, this is a the kind of domain structure we have for example, this is a single domain. The whole material, this is the material in which only one magnetic direction is there, that only one reduction all the moments or align in the particular direction. So, single domain material and as the magnetic lines of force goes outside the, outside the following of the sample or the volume of the solid, so ultimately it emanate from the north pole goes to the south polar, and this way since there is the magnetic lines force cannot go or cannot neutralized here, it goes outside.

Next one is the two domain structure in which on the left we have one domain, on the right another domain, and one can see their left one is the magnetic moment is pointing upwards whereas, the right one the magnetic domain or magnetic moment, the result in magnetic moment of that particular domain is pointing downwards. So there is a 180 degree rotation, and there is some lines of force outsides, solid outside the sample, but number of lines of forces certainly reduce, because they neutralize each other, part of it has been neutralize each other.

So, this is a what we called is a glown wall is a boundary between the two domains, and that is called the domain and also known as the bloch walls, this bloch walls, ok. So, this since across their boundary, there is 180 degree change in the orientation of the magnetic field, or not the magnetic magnetic magnetization, or the magnetic moment of this material, then this becomes your 180 degree domain, that is how it is like in 180 degree domain wall.

In the next structure, we have four domains and that is a very typical domain wall structure, where you have two domains side-by-side, and then there are two other domains comes in one of the top, one of the bottom. And one can see the orientation of the magnetic moment, here is a horizontal or perpendicular to the two domains we had earlier. So, this is perpendicular in this direction from left-to-right and here, it is a right-to-left.

So, this is one-domain and this another domains, so in all about four domains having orthogonal orientation between each other, and that is a very typical domains structure in a rectangular piece of magnet, or magnetic material. This boundary is however, different this is 90 degree or domain wall, because across this the orientation is at 90 degree, to each other orientation of the dipoles or orientation of magnetization is 90 degree to each other.

So, these four walls one, two, three, and four, all these are 90 degree domains walls whereas, the middle one the vertical line is actually 180 degree wall, this is also possible more and more domain walls can be formed depending on, the it want release the internal stress and internal energy. So, depending on that is single domain can be subdivided into large number of domains, and there are more number of 180 domains now, and you have more number of both 180 and 90 degree are possible.

So, this is how the domains multiply depending on the structure, depending on the situation, depending on the field, and its history. Now, this domains walls although we are talking about a changeover from one direction, one orientation to the another orientation. But, this domain wall is a finite thickness, like this is a particular wall 100 degree domain wall on this side, right-side you have magnetic moments oriented upwards whereas, on the left the magnetic moments are oriented downwards.

So, there is a changeover from upper trend to the downward trend, and so one it is a 180 degree domain wall but, if you look at the cross-section or the width of this domain, there is a finite with this domain walls as a finite width, and this d w is the width of this domain wall, and particularly for cobalt a ferromagnetic material, the width is about 60 nanometers surround 600 hang storms. So, one can see that, there is a about 250 atomic distances or inter spacing, so there are more number of there is a gradual changeover, one can see here, this is completely downwards, then there is some amount of change and then, it is almost horizontal here, then it rotates still further and finally, on this plane it is perfectly parallel or opposite each other.

So, there is a gradual changeover of the domain of the magnetic moments across the stomen, or within this thickness of the domain. So, it is certainly it is not a sudden change, buts gradual change and the thickness depends on many different parameters, many extensive parameters, and also the crystal structures the lattice parameters and of course, the kind of magnetizing ions it has.

So, these are the two things one must understand that, we have domains in a ferromagnetic or same thing happens in ferri magnetic also, and there is a domain wall, they can be designated as 180 degree and 90 degree, or 45 degree angles, and the domain wall there is a concept of domain wall, so that there is finite thickness with in which, this changeover takes place in a gradual manner, so that solve about the domain wall.

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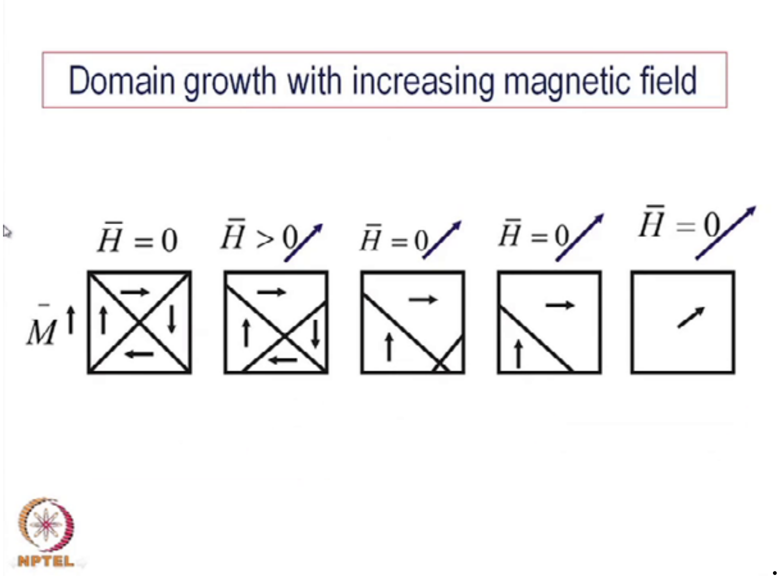

Domain growth with increasing magnetic field

We have also seen that, while you are plotting the hysteresis loop or hysteresis curve by applying electric field a applying a magnetic field slowly, the domain movement domain wall moves. For example, if we are starting with this a combination of four domain, its changing, taking into consideration that the applied field in this direction. So, whichever is preferred orient orientation? So, that will grow.

So, you can see this has grown, this has further grown whereas, the other three are slowly disappearing, or the size of those domains area of the domains are the reducing whereas, the other area is increasing. So, it is not that a completely new domains are generally created, but the existing domains some of them grow at the expense of the others depending on the their original orientation. So, that is how so it is a kind of nutrition and growth phenomena, so whichever is preferred orientation will grow, and which were not's preferably oriented, they will slowly deserve or disappear. So, this the concept of a domain growth with increasing magnetic field.

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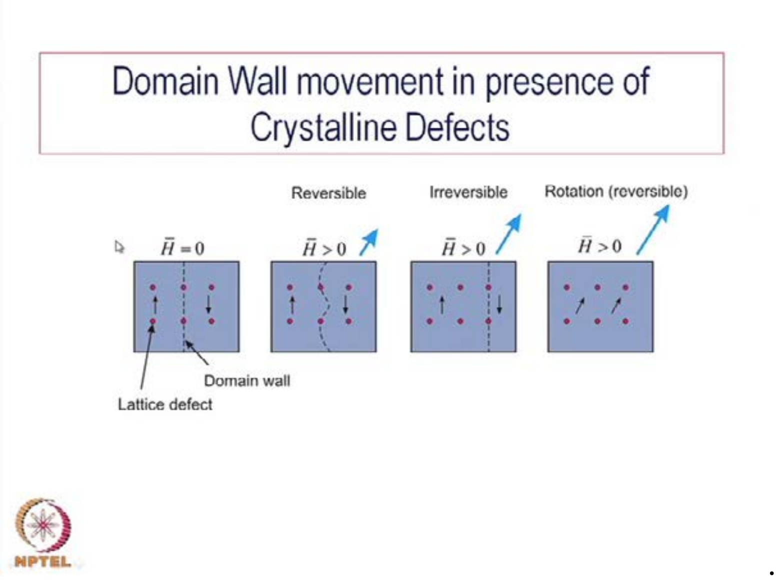

Domain Wall movement in presence of Crystalline Defects

Now, while the domains are moving in their path of the movement, they may encounter different kind of defects, the domains are moving basically, with there is a changeover of the atoms, atoms are changing their orientation, and particularly the the magnetic moment of those atoms or ions. But, in the process as if a wall is moving from one end the other, and it may encounter in addition to the normal structure of the normal lattice points of the lattice ions, it may encounter certain point defects which we have discussed earlier, there are point defects, there are line defects, there are surface defects, and so on.

So, when such kind of defects are encountered in the path of the movement of the domain wall, they get hindered or they acts as an obstacles, so any presence of lattice defects either vacancy interstitial, or solute atom of a different type. All of them acts as a hindrance to the movement of the domain wall, and domain wall movement is restricted as as long as the domain wall movement is restricted, which is means that the magnetization is restricted.

So, the magnetization restricted means you need more and more energy to magnetize it, and the reverse manner when you are demagnetize it, the presence of this defects also hindered, the reverse movement of the domain wall and therefore, once they get magnetize, it becomes difficult to demagnetize, or in other words you need higher quarts field to bring the magnetization, and the to the level of 0. So, presence of this lattice defects of different types, whether it is grain boundary, whether it is point defects vacancy interstitial, substitution alliance. All of them have some role to play.

So, far as the domain wall movement is concerned, and this is getting reflected, this gets reflected in the area, in the area of the hysteresis curve, so if you are talking about a very thin hysteresis curve, or some applications, if you are looking for a very thin hysteresis curve, or a low-energy magnetization, or demagnetization process, one must have a defect free, defect free material, large grain size material, and so on. If you have fine-grained material, and are or a large number of defects already present, because of condition, because of chemical combination, and so on. Then, there is a possibility that the energy required for magnetization, and the magnetization becomes large, so you have a fatter or larger hysteresis curve.

So, if you talking about a permanent magnet, these are very important parameters, one is to consider what should be the total energy content in the material? in terms of the b h curve. So, the area under the b h curve is actually, actually measures is a measure of a energy required for magnetization and demagnetization, and how easily one can magnetize it? or how quickly one can magnetize it? or demagnetize it. So, the presence of the defects including the grain boundaries has a very important role to play, while were to preparing the material for a particular application.

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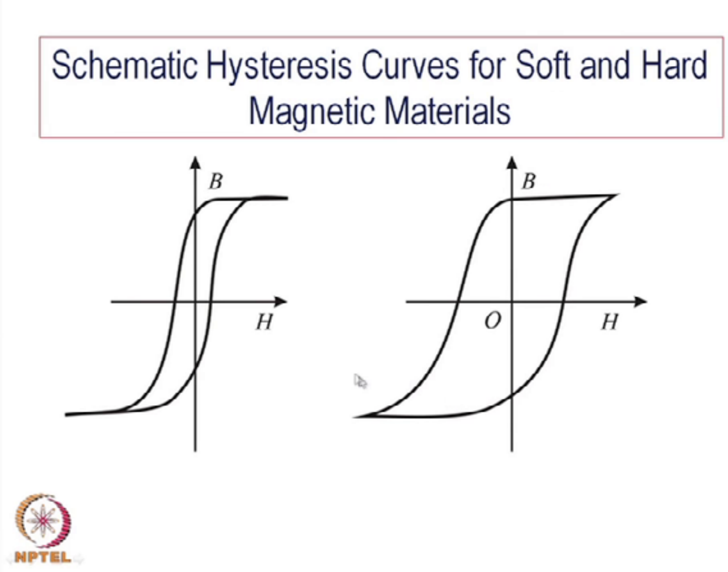

Schematic Hysteresis Curves for Soft and Hard Magnetic Materials

This is what I have shown you earlier, this also this a thinner hysteresis curve, is a thicker hysteresis curve, or a wide hysteresis curve, which means higher energy needed for magnetization as well as demagnetization, and this needs a very low field as well as low-energy. And the energy content of material is also low, so with very small fields, very small magnetic field generated, one can magnetize it, or saturated, or completely de saturated, like this.

So, this kind of curve is very important for soft ferrite or soft sock magnetic materials, and these are actually hard magnetic material, so basically there are two types magnetic material, one is designated as soft magnetic materials, like this had been hysteresis curve on this nature whereas, the hard magnetic materials should have a hysteresis curve of this, this type.

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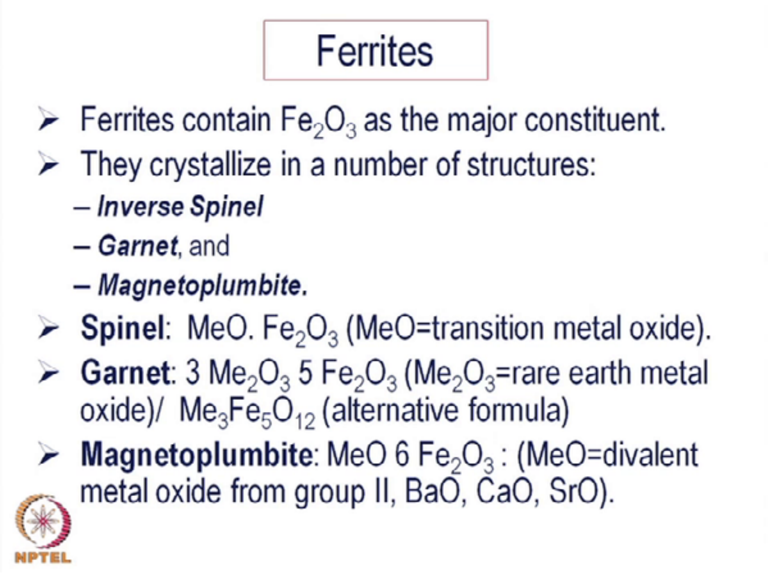

Ferrites

- Ferrites contain Fe_2O_3 as the major constituent.
- They crystallize in a number of structures:
  - ***Inverse Spinel***
  - ***Garnet***, and
  - ***Magnetoplumbite.***
- **Spinel**: MeO. Fe_2O_3 (MeO=transition metal oxide).
- **Garnet**: 3 Me_2O_3 5 Fe_2O_3 (Me_2O_3=rare earth metal oxide)/ $Me_3Fe_5O_{12}$ (alternative formula)
- **Magnetoplumbite**: MeO 6 Fe_2O_3 : (MeO=divalent metal oxide from group II, BaO, CaO, SrO).

Well with this background, we come to a group of ceramic materials, which are actually very important through the industrial point of view, at the technical application point of view. And these are known as ferrites, these are anti ferromagnetic, ferromagnetic materials, so they are not metals that compounds, and they are all regarded ceramic materials, they have all the other properties like ceramics, because they are basically mixed oxides.

There are three different thy type of ferrites basically, ceramic magnetic materials, and the characteristics are all of them content F e 2 O 3 that is the, that is why the name given as ferrites, so F e 2 O 3 is one of the major components, or the constituents of all the compounds of ceramic magnets, most of them, most of them, 90 percent of them contents F e 2 O 3. There will be some other, but most of them have F e 2 O 3.

They crystallize in in a number of structures, if you talk about ferrites, there are three major structures, structure types in which these ferrites are present, are present, are available. These are inverse spinel first of all inverse spinel, spinel is the most common of the ferrites structures, and earlier we have seen, while discussing with the crystal structure, we had two different spinel forms, we will discuss little bit more about that, just now in a few minutes.

One is the normal spinel, another is inverse spinel, the normal spinel structure or this particular name has been given from the, from the mineral large, the name of the mineral that is M g A l 2 O 4 magnesium aluminate, which is whose minarizical name is spinel, and it become it forms a structure types. So, any material any mixed oxide which crystallized in this particular form is called spinel, and there are normal spinel, sorry the magnesia magnesium alumina it has actually normal spinel whereas, all the ferrid's all the ferrid's are actually inverse spinel will tell you, what exactly it means.

Then, the second group is Garnets, these also another compound, again mixed oxide, I will tell you what is that, and then magnetoplumbite, so there are three different crystal type, crystal types in which the ferrites are available, all of them have the very important, or strong magnetic property, or magnetic magnetization. Spinel the general formula is M e o F e 2 O 3, M e o F e 2 O 3, sometimes it is also called you a o b 2 o 3, a o b 2 o 3. But, the ferrites when you are talking about ferrites b 2 O 3 is in variably F e 2 O 3, so it is M e O F e 2 O 3, M e a transition metal oxide. Normally, a transition another transition metal oxide, iron is one transition metal oxide, and M e is also another on transition metal oxide, so the combination of two transition metal oxides, one divalent, another trivalent forms the spinel structure.

Garnet, it is also very important group of magnetic ceramics, this general formula is 3 M e 2 O 3 a trivalent oxide, and also another trivalent oxide, but F e 2 O 3 is again common. This is also F e 2 O 3 in spinel, where spinel ferrites and garnet ferrites also has F e 2 O 3, but the ratio is different, it is 3 is to 5. So, M e 2 O 3 in this case, this trivalent oxide M e is not a transition metal, its a rare earth another group of compounds which has a some sermons similarity with the transition metal, so far as the electronic structures is concerned.

So, M e is actually a rare earth metal, or M e 2 O 3 is a rare metal oxide, so the alternate formula one sometimes right M e 3 F e 5 O 12, M e 3 F e 5 O 12, it is the same thing which is been written here. Only thing its here is total oxygen is 9 into 15 24 here, its only 12, so half of the molecular, molecular formula here, so this is the two ways of expression. The garnet structure will discuss little bit more about that.

And the third group of the ferrite, which is also very important from the practical point of view, or industrial point of view, is magnetoplumbite. The general formula here is M e O 6 F e 2 O 3, so the formulas are different, the ratio of F e 2 O 3 to other oxides are different. Here, it is 1 is to 1 here, it is 3 is to 5 and here is to 1 is to 6, so M e O in this case is not either not a transition metal or rare earth is actually, a divalent metal, divalent metal from the group to and like barium oxide, calcium oxide, copper oxide, strontium oxide, so either b a o c a o or s r o. So, this is what will call the magnetoplumbite structure, and because of this ratio 1 is to 6, sometimes it is also designated as hexa ferrites, ferrites of course, there is an another reason also, because a it has a hexagonal structure, these two have a cubic structure, these two have a cubic structure, and this is also as a hexagonal structure.

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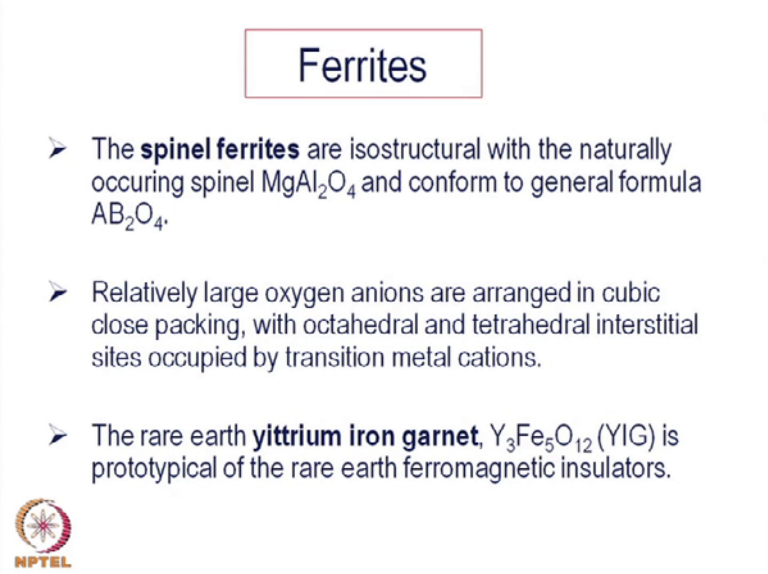

Ferrites

- The **spinel ferrites** are isostructural with the naturally occuring spinel $MgAl_2O_4$ and conform to general formula AB_2O_4.
- Relatively large oxygen anions are arranged in cubic close packing, with octahedral and tetrahedral interstitial sites occupied by transition metal cations.
- The rare earth **yittrium iron garnet**, $Y_3Fe_5O_{12}$ (YIG) is prototypical of the rare earth ferromagnetic insulators.

Well, to give you more little more information about the ferrites, the spinel ferrites are iso structural with the naturally occurring spinel, which I have mentioned just now, M g A spinel which is the M g A A l 2 O 4, and confirm to general formula F e 2 O 4 relatively large oxygen anions are the for this spinel ferrites are arranged in cubic close packing, with octahedral and tetrahedral interstitial sites occupied by the transition metal anions. So, the divalent tranisation metal anions occupies some of the sites, will look at the structure little more closely.

And the garnet structure, there are in the rare earth yttrium iron one of the major of the important components are the members is garnet family is yttrium iron garnet, where rare earth is yttrium iron is any way there F e 2 O 3. And then it is called yttrium iron garnet, or YIG is proportion a is prototypical of the rare earth ferromagnetic insulators. So, it is a rare earth ferromagnetic insulators not ferromagnetic insulators, and yttrium is the rare earth cation, and it can also replaced by other cations like one of the another members is gadolinium g d gadolinium iron garnet.

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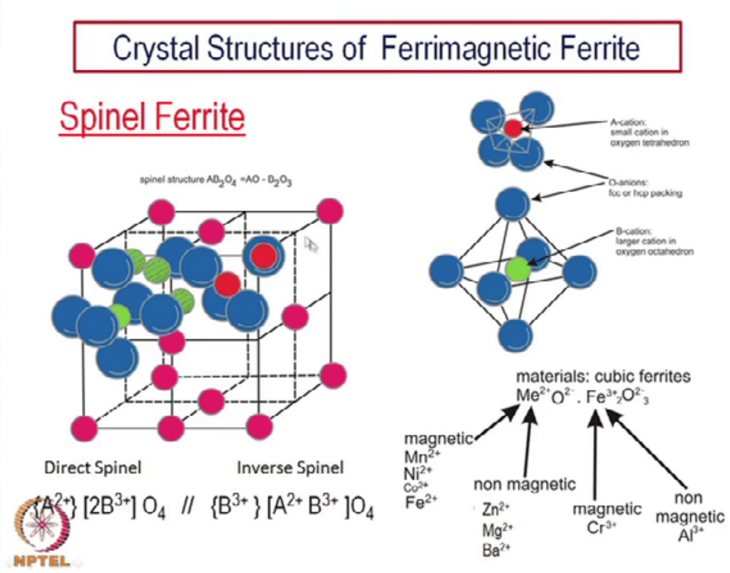

Crystal Structures of Ferrimagnetic Ferrite

Spinel Ferrite

Direct Spinel

Inverse Spinel

$\{A^{2+}\}[2B^{3+}]O_4$ // $\{B^{3+}\}[A^{2+}B^{3+}]O_4$

materials: cubic ferrites

$Me^{2+}O^{2-}.Fe^{3+}_2O^{2-}_3$

magnetic Mn^{2+} Ni^{2+} Co^{2+} Fe^{2+}

non magnetic Zn^{2+} Mg^{2+} Ba^{2+}

magnetic Cr^{3+}

non magnetic Al^{3+}

Looking at the structure of ferrites, this is the representation of the structure of the ferrites, spinel particularly the spinel structure the spinel as a as mentioned, it is F e 2 O 3, A B 2 O 4, A B 2 O 4 structure, and in which oxygen forms the close pack cubic structure, close pack cubic structure. In any close pack, cubic structure you have two different interstitial sites, one is the tetrahedral site like this having four four coordination, and other is the six four corination the octahedral site, so here also you have octahedral sites as well as tetrahedral sites.

And the two cations A and B have their preference of going to one of the particular interstitial sites, so in a direct spinel structure, in direct spinel structure all the A cations goes tetrahedral sites, so A A plus A 2 plus goes to the tetrahedral sites shown here as A second bracket, and the square bracket here represents the octahedral sites, so this represents the tetrahedral site, and this represent the octahedral site. So, the F e 2 F e 2 sorry F e 3 anions F e 3 plus anions in a ferrites of course, ferrites as increased inverse spinel.

If you are talking about normal spinel like M g l 2 O 4, so A l, A l has octahedral corination, so it goes to the octahedral, and M g 2 plus goes to the tetrahedral sites, thats the or that is the description of the spinel, in directs spinel. And in a inverse spinel, it changes out of the 2 B 3 plus cations, one goes to the tetrahedral site and another remains in the octahedral site, where as all the A sites sorry all the A cations or 2 plus cations comes to the octahedral sites. So, that is the redistribution happens, and that is the typical of what we call the inverse spinel incidentally, all ferrites F e containing F e 2 O 3 which we have discuss just now.

Crystallization the inverse spinel structure, so ferrites means inverse spinel structure not the direct spinel structure, so this is the octahedral distribution of the blue one of the oxygen, and this is B cations, B cation in case of directs spinel, and both A and B cations, in case of inverse spinel whereas, in the tetra tetrahedral site we have only either A cation or B cation, both are depending on whether it is direct or inverse.

Now, since we have talked about that the, it is a general formula A B 2 O 4 type A sites is here or in ferrits structure, if you are talking about ferrites cubic ferrites you have M e O and F e 2 O 3, so both F e and M e in principle can be substituted by other cations. So, if you are talking about the A site, M e, M e site, it is 2 plus physically, they can be substituted by large number of different divalent cations, some of them are non-magnetic they do not have a magnetic moment.

Whereas, it been depending on the on paid electrons, there is no unpaid electron, so no magnetic moment, so these are some of these cations like zinc 2 plus magnesium 2 plus or barrium 2 plus, they can go in into this sustain, but they do not, they do not have a magnetic moment whereas, other magnetic cations like M n 2 plus N i 2 plus C O 2 plus or even F e 2 plus, the other site is F e 3 plus. But this site is can also have F e 2 plus has in a as for example, in F e 3 O 4, so F e 3 O 4 is basically a combination of F e 2 F e O and F e 2 O 3; so that way this site A site can have F e 2 plus as well. So, these are magnetic substitution by magnetic cations, and these are substitution by non-magnetic cations.

Similarly, in the B site F e 3 plus site, you have one chromium, chromium has magnetic and aluminum is non-magnetic, so these are possibilities, so there are iso structure, what we called the iso structural substitution, there extensive iso structural substitution is possible in case of spinel ferrites. And correspondingly, you have different properties, different compounds both Magnetic properties, and as well as other physical properties.

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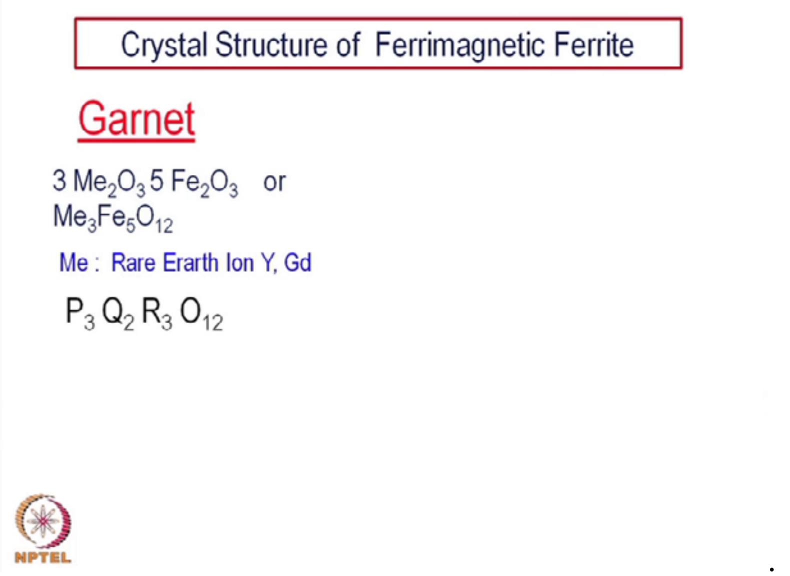

Crystal Structure of Ferrimagnetic Ferrite

Garnet

$3\,Me_2O_3\,5\,Fe_2O_3$ or

$Me_3Fe_5O_{12}$

Me : Rare Erarth Ion Y, Gd

$P_3\,Q_2\,R_3\,O_{12}$

Now, let us look at two other structures which we have just mentioned, garnet structure 3 M e 2 O 3 5 F e 2 O 3 or in other words one can write F e M e 3 F e 5 O 12 M e. As, I mention a rares time which maybe yttrium or sometimes gadolinium both are normally used. Now, the way the structure is represented here, the structure sites, structural sites, can be called by P, Q, and R. So, these are three different interstitial sites, in this in, in this case also there are large number of oxygen ions compared to four oxygen ions. There, we have 12 oxygen ions here in the formula, and you have again it forms a cubic close pack structure, and there are it is not exactly a close pack structure, but cubic symmetry.

So, there are three different kind of interstitial sites, earlier we have seen there are two interstitial sites, one is tetrahedral and octahedron here, there is an additional interstitial sites which has a eightfold coordination, it is called a dodecahedral coordination. And particularly, the rarer time goes and sits in that, so in addition to the other transition metal cations F e 2 F e 3 plus particularly, the rarer time as a different coordination. So, it is not a four fold coordination, it is not a six fold coordination is actually a eight fold coordination of the oxygen ions.

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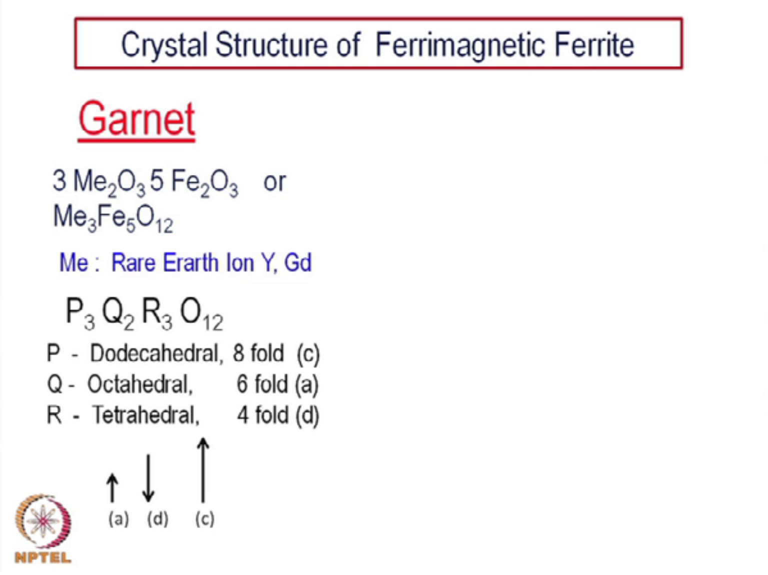

Crystal Structure of Ferrimagnetic Ferrite

Garnet

$3\,Me_2O_3\,5\,Fe_2O_3$ or
$Me_3Fe_5O_{12}$

Me : Rare Erarth Ion Y, Gd

$P_3\,Q_2\,R_3\,O_{12}$

P - Dodecahedral, 8 fold (c)
Q - Octahedral, 6 fold (a)
R - Tetrahedral, 4 fold (d)

So, we have an additional interstitial sites here. And they are sometimes, there sometimes also designated as c site, a site, and d site. P P cations that is primarily the yttrium or the rare earths goes and have not eight fold coordination, and is called sometimes c site. Q is an octahedral coordination, and the iron ions go an six sits, there six fold coordination and are is the tetrahedral coordination or with four fold, so these are also the designated as sites.

One of the reason, we have discussed earlier in a ferromagnetic, in a ferrimagnetic magnetic ordering there is anti-parallel ordering, the atoms the magnetic moments of the neighboring atoms as been anti-parallel ordering, but as cause that the magnitude of the magnetic moments are different. So, we still have a they do not cancel each other, unlike in a anti-ferromagnetic material where the because of the anti-parallel ordering, and the magnitudes may becoming same, the net magnetic moment is 0. Well whereas, in ferromagnetic material the spinel structure either in spinel or in garnet, or as also in ferrite hexaferrites or magnetopumbites, you have a ironical, ionical magnetic movements, which have anti-parallel orientation. And because of this anti-parallel orientation we have always a net magnetic movement in a particular structure, or in particular formula that’s what it is also happens in case of magnetic garnets.

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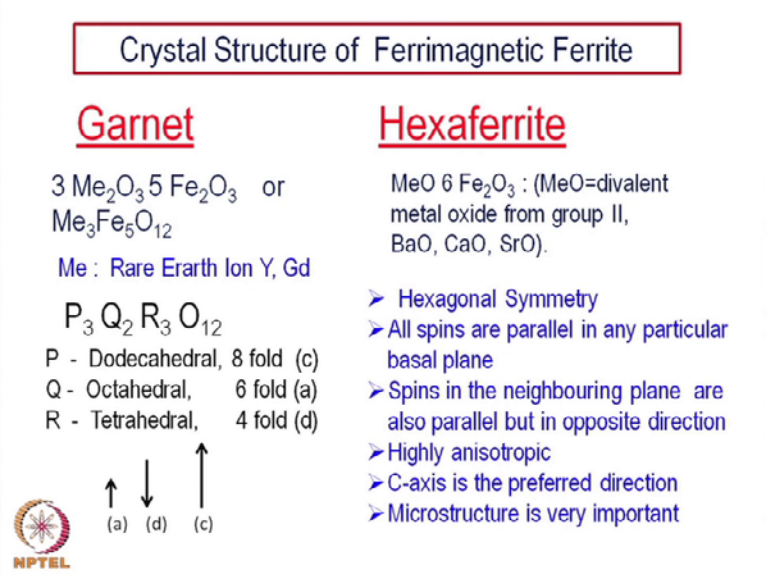

Crystal Structure of Ferrimagnetic Ferrite

Garnet

$3\,Me_2O_3\,5\,Fe_2O_3$ or
$Me_3Fe_5O_{12}$

Me : Rare Erarth Ion Y, Gd

$P_3\,Q_2\,R_3\,O_{12}$

P - Dodecahedral, 8 fold (c)
Q - Octahedral, 6 fold (a)
R - Tetrahedral, 4 fold (d)

↑ ↓ ↑
(a) (d) (c)

Hexaferrite

$MeO\ 6\ Fe_2O_3$: (MeO=divalent metal oxide from group II, BaO, CaO, SrO).

- Hexagonal Symmetry
- All spins are parallel in any particular basal plane
- Spins in the neighbouring plane are also parallel but in opposite direction
- Highly anisotropic
- C-axis is the preferred direction
- Microstructure is very important

Instead of two sites you have three sites a d and c sites, so there magnetic movements are different, so a and c are parallely oriented, whether both of them are anti-parallely oriented with d, d is the tetrahedral site, so thats the origin and the net moment. There is a net finite moment or finite magnetic moment, which comes and so it becomes a magnetic material as such, so just like any other ferromagnetic; so garnet structure is also very, very important from the point of view of ceramic magnets.

The other one is in hexaferrite well the details is in, hexaferrite well the details are not fully there, except that they have a hexagonal symmetry, and the formula we have already discussed, the compounds either the barium hexaferrite, calcium hexaferrite, or strong same hexaferrite. So all of them more or less have an identical property, all of them has hexagonal symmetry, unlike spinel and garnet, which as cubic symmetry, there in hexagonal symmetry, and all spine are parallel in any particular basal plane. So, when you are talking about a hexa hexagonal structure is basically a kind of layer, structure a b a b packing, and you have basal planes which are actually perpendicular to c axis, actually a b or a b plane, so a b plane are not normally called the basal planes.

So, in all these planes basal planes, the magnetic moments are parellel oriented, however neighbouring basal planes will have different cations, and they have a different magnetic moments, and also anti-parallel oriented. So, unlike in in spinel and garnets, the each individual ions are anti-parallel oriented, here it is planes or anti-parallel oriented, so one particular plane is having a parallel orientation, all of them are directed in the same direction or the magnetic moments of all the atoms, all the ions are directed in the same direction whereas, the neighboring planes have a different orientation, so it is a anti-parallel orientation but, of a slightly different nature.

All thats what it has been mentioned, all spins are parallel basal plane this spins in the neighboring plane are also parallel, but in opposite direction, so the anti-parallel are ordering is of a slightly different nature. And because of the hexagonal symmetry, in this case is not a cubic symmetry, so it is highly anisotropic, the properties are highly anisotropic, and c axis is the preferred direction of orientation. So, if all the magnetic moments oriented along the c axis of the crystal, it becomes very difficult to realign it to other directions.

And because of the this anisotropic properties this material, these hexaferrites or magnetopumites have a high or very large hysteresis loop and therefore, mostly there used as permanent magnets. There not soft magnets or soft ferrites, there are primarily permament magnets or hard ferrites. So, all hard ferrites are permanent whenever we talk about permanent magnets of the ceramics, permanent ceramics magnets we in very talk about the hexaferrites or magnetoplumbites structure. So, since they have a very preferred orientation or anisotropic properties, the microstructure is also very important, so microstructure is another very important property to be controlled to have the desire property, so this materials well with this.

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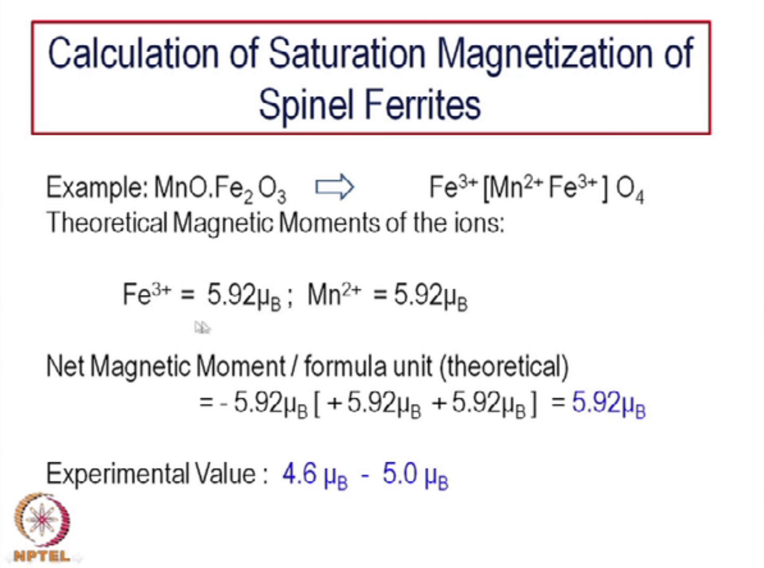

Calculation of Saturation Magnetization of Spinel Ferrites

Example: $MnO.Fe_2O_3$ ⇨ $Fe^{3+}[Mn^{2+}Fe^{3+}]O_4$

Theoretical Magnetic Moments of the ions:

$Fe^{3+} = 5.92\mu_B$; $Mn^{2+} = 5.92\mu_B$

Net Magnetic Moment / formula unit (theoretical)

$= -5.92\mu_B\,[+5.92\mu_B + 5.92\mu_B] = 5.92\mu_B$

Experimental Value : $4.6\ \mu_B - 5.0\ \mu_B$

Well, this discussion let me go through look at, there is simple way to calculate what should be the saturated magnetization of the spinel ferrites, particularly for spinel ferrites I am taking only one example here, how to calculate the magnet saturation magnet? what will be the maximum when all of them all the domains are oriented in the particular direction? what will be the maximum polarization? we expect magnetic flux density, one can expect that depends on the individual magni individual magnetic moments. So, this what one can find out.

M n O let say, we are taking an example M n O F e 2 O 3 we can write the formula in this passion, considering the sites, sites square this particular ions whether it is a tetrahedral or octahedral, so outside this square bracket this means, it is the tetrahedral site, and inside the square bracket means the octahedral sites. So, the octahedral site and keeping in mind that it is a inverse spinel, keeping in mind that inverse spinel, so there is a redistribution half of the F e 2, the b site half of the F e 2 O is the octahedral half of the other half the tetrahedral site, and all the a a atoms are in the octahedral site. So, that is the description of how this ions are distributed between the two different interstitial sites, then one can write theoretical magnetic moments of this ions, is this has already been discussed earlier.

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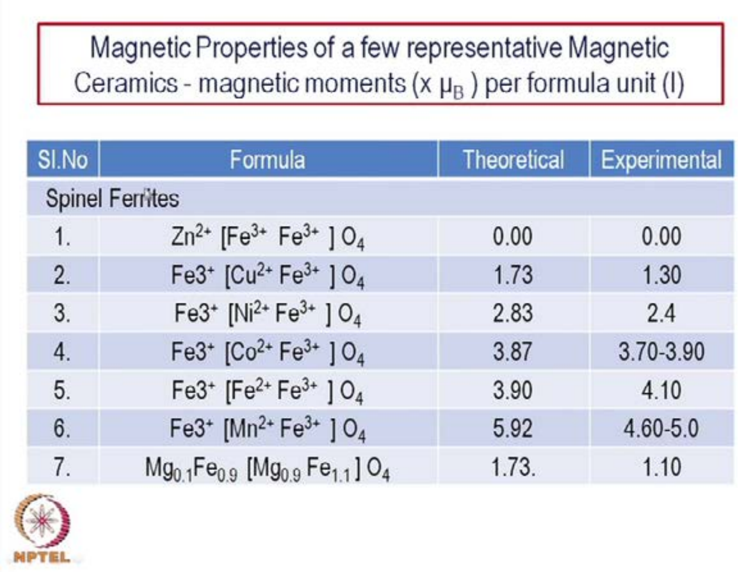

Magnetic Properties of a few representative Magnetic Ceramics - magnetic moments (x μ_B) per formula unit (I)

Sl.No	Formula	Theoretical	Experimental
Spinel Ferrites			
1.	Zn^{2+} [Fe^{3+} Fe^{3+}] O_4	0.00	0.00
2.	$Fe3^{+}$ [Cu^{2+} Fe^{3+}] O_4	1.73	1.30
3.	$Fe3^{+}$ [Ni^{2+} Fe^{3+}] O_4	2.83	2.4
4.	$Fe3^{+}$ [Co^{2+} Fe^{3+}] O_4	3.87	3.70-3.90
5.	$Fe3^{+}$ [Fe^{2+} Fe^{3+}] O_4	3.90	4.10
6.	$Fe3^{+}$ [Mn^{2+} Fe^{3+}] O_4	5.92	4.60-5.0
7.	$Mg_{0.1}Fe_{0.9}$ [$Mg_{0.9}$ $Fe_{1.1}$] O_4	1.73.	1.10

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And there is a list here, you can see from the homes rule, from the homes rule one can find out not this one sorry.

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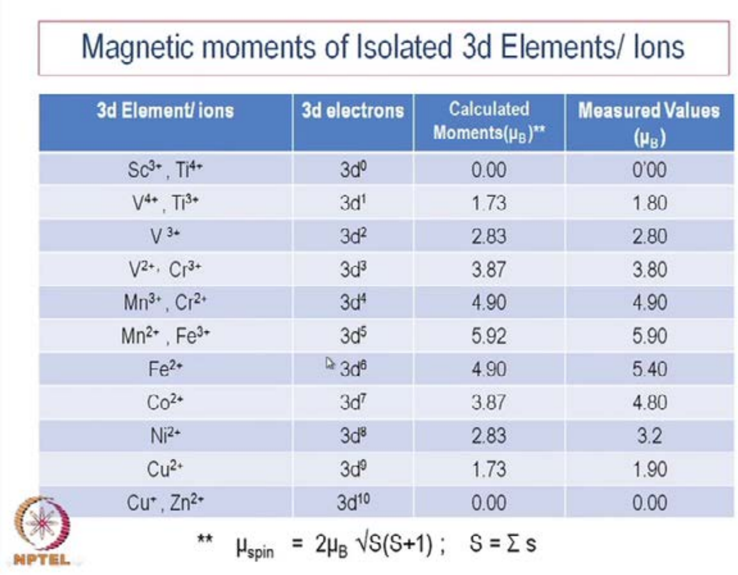

Magnetic moments of Isolated 3d Elements/ Ions

3d Element/ ions	3d electrons	Calculated Moments(μ_B)**	Measured Values (μ_B)
Sc^{3+} , Ti^{4+}	$3d^0$	0.00	0'00
V^{4+} , Ti^{3+}	$3d^1$	1.73	1.80
V^{3+}	$3d^2$	2.83	2.80
V^{2+}, Cr^{3+}	$3d^3$	3.87	3.80
Mn^{3+} , Cr^{2+}	$3d^4$	4.90	4.90
Mn^{2+} , Fe^{3+}	$3d^5$	5.92	5.90
Fe^{2+}	$3d^6$	4.90	5.40
Co^{2+}	$3d^7$	3.87	4.80
Ni^{2+}	$3d^8$	2.83	3.2
Cu^{2+}	$3d^9$	1.73	1.90
Cu^{+} , Zn^{2+}	$3d^{10}$	0.00	0.00

** $\mu_{spin} = 2\mu_B \sqrt{S(S+1)}$; $S = \Sigma s$

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This one yeah, so different cations, different cations have different number of d electrons on unpaired d electron 3d electrons and accordingly, homes rule there are number of unpaired electrons, actually give rise to the magnetic moments. So, one has to find out where will be the unpaired electrons here, up to 5 this will be the same as the total number of electrons whereas, from this site 166 its actually becomes 4 the unpaired electron becomes 4. So, accordingly you have a list of calculated magnetic moments in terms of the bohr magnet, how many bohr magnet on will be there? this expression also have been introduced to you earlier.

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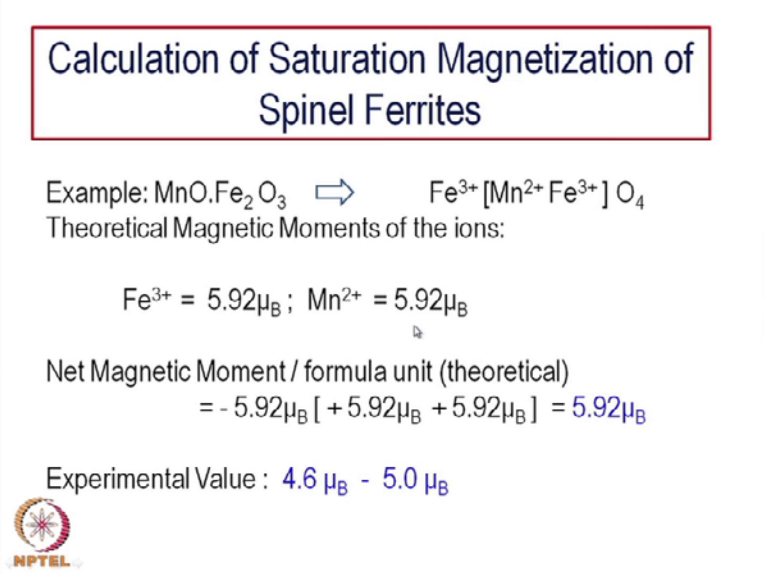

Calculation of Saturation Magnetization of Spinel Ferrites

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Net Magnetic Moment / formula unit (theoretical)

$= -5.92\mu_B [+5.92\mu_B + 5.92\mu_B] = 5.92\mu_B$

Experimental Value : $4.6\ \mu_B - 5.0\ \mu_B$

.

So, with this, with this F e 3 plus 5.92 bohr magneton F e 3 plus a 5. this is actually d 51 there are 5 unpaired electrons, so the sensitivity d 5 is a 5 high unpaired electrons, and this manganese 2 plus also has 5 un paired electrons.

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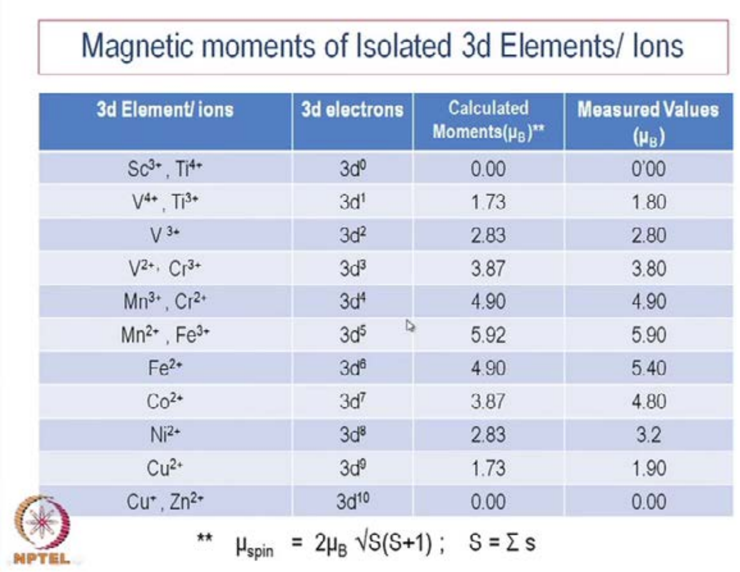

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Mn^{2+}, Fe^{3+}	$3d^5$	5.92	5.90
Fe^{2+}	$3d^6$	4.90	5.40
Co^{2+}	$3d^7$	3.87	4.80
Ni^{2+}	$3d^8$	2.83	3.2
Cu^{2+}	$3d^9$	1.73	1.90
Cu^{+}, Zn^{2+}	$3d^{10}$	0.00	0.00

** $\mu_{spin} = 2\mu_B \sqrt{S(S+1)}$; $S = \Sigma s$

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Here, it is manganese 2 plus and F e 2 F e 3 plus both of them are d 5 d 5 electrons, and since d 5 according to homes rule, that will be 5 unpaired Electron, all of them are actually unpaired.

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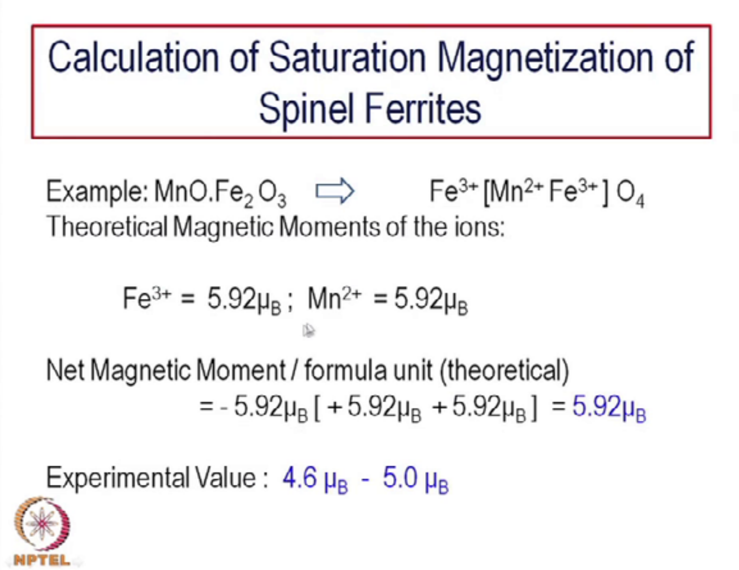

Calculation of Saturation Magnetization of Spinel Ferrites

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Net Magnetic Moment / formula unit (theoretical)

$= -5.92\mu_B[+5.92\mu_B + 5.92\mu_B] = 5.92\mu_B$

Experimental Value : $4.6\ \mu_B$ - $5.0\ \mu_B$

So, this is the magnetic movement of this ion, and this is the magnetic moments of same impact, both of them are same. So, the net magnetic moment per formula unit again theoretical is because there is a anti-parallel coupling, or anti-parallel ordering, this and this actually cancels each other. If this is pointing upwards, this should be pointing downwards, or vice versa. So, this is F e 3 plus, and this F e 3 plus actually cancel each other, so it is minus 5.92 bhor magnet, and within bracket a a this is also 5.92 from manganese, and this is also 5.92 for the iron, so ultimately the resultant is 5.92 bhor magnet.

So, these are very simple way to calculate, what is the expected theoretical value of the maximum magnetization or magnetic moment? you can expect in a structure like this, and so the experimental value in fact is close to that, but is slightly different 5, 5 instead of 5.92 its actually varies between 4.6, 5.0 of course, all these variations are there primarily because of the defense different external extraneous factors. So, this is one way, how to calculate in a very simplified form, what is the expected magnetic moment of this kind of systems.

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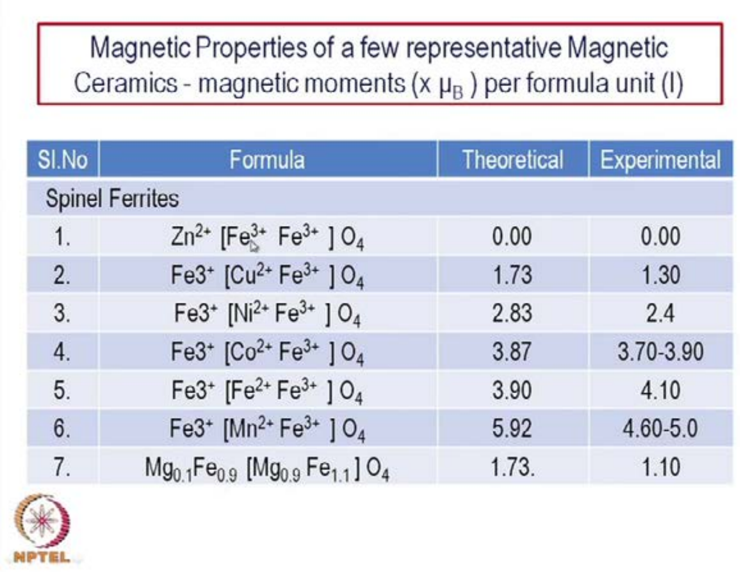

Magnetic Properties of a few representative Magnetic Ceramics - magnetic moments (x μ_B) per formula unit (I)

Sl.No	Formula	Theoretical	Experimental
Spinel Ferrites			
1.	Zn^{2+} $[Fe^{3+}$ Fe^{3+} $]$ O_4	0.00	0.00
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5.	$Fe3^{+}$ $[Fe^{2+}$ Fe^{3+} $]$ O_4	3.90	4.10
6.	$Fe3^{+}$ $[Mn^{2+}$ Fe^{3+} $]$ O_4	5.92	4.60-5.0
7.	$Mg_{0.1}Fe_{0.9}$ $[Mg_{0.9}$ $Fe_{1.1}]$ O_4	1.73.	1.10

Following that there is a list here, there is a table is been given here, for different kind of ferrites, different system of ferrites for example, this is zinc ferrite and in fact this is not a, this is not a inversely spinel, it is also although, it is called zinc ferrite. But, this is not does not have a magnetic property, because it is a inverse, is not a inverse spinel is a normal spinel, and zinc is outside and 2 F e 2 O 3 F e 3 are inside. So, there is early interaction between this site, and this site so although they have made magnetic moment, but the theoretical value is 0, they have a anti-parallel orientation.

This is the, this is F e 3 copper ferrite, this is copper ferrite and it is the copper ions, copper ions magnetization which is reflected in the overall magnetization property, or magnetic moment. So, whatever is the copper ions magnetic moment, that is the overall magnetic moment of that particular compound, same thing F e this F e 3 and this F e 3 cancel each other, and then it is 2.83 here and I get about 2.4.

F e 3 plus, here is cobalt ferrite, cobalt ferrite is actually again the same thing, it is the magnetic moment of cobalt with gets reflected here, F e 3 plus cancel each other, F e 3 plus, this is magnetite and once again that of F e 2 plus actually gets reflected here; here it is F e 3 plus and manganese ferrite. So, once again it is the manganese ions, the magnetic moments which gets reflected here, which is the maximum because the 3d 5. There are many, many solid solutions, there are many many solid solutions here, and do write please note that change, please note that change F e, this F e this F e will cancel each other, because of the anti-parallel orientation or ordering whether zinc 2 plus.

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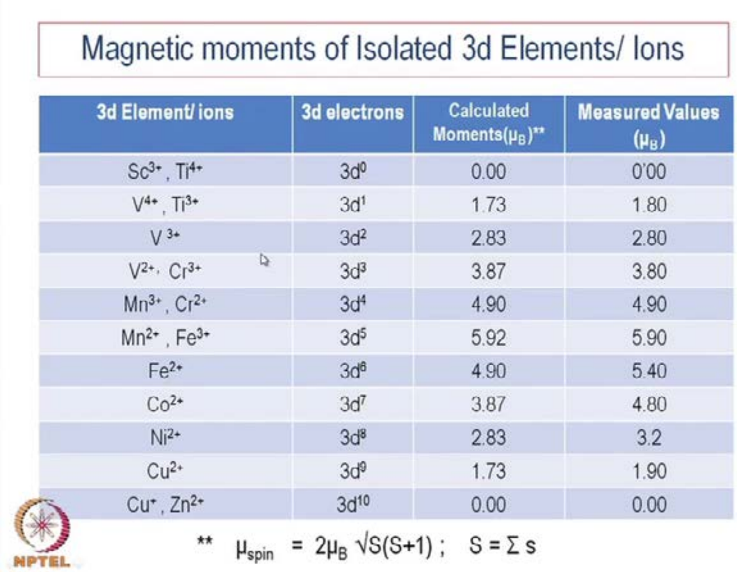

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3d Element/ ions	3d electrons	Calculated Moments(μ_B)**	Measured Values (μ_B)
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Ni^{2+}	$3d^8$	2.83	3.2
Cu^{2+}	$3d^9$	1.73	1.90
Cu^{+}, Zn^{2+}	$3d^{10}$	0.00	0.00

** $\mu_{spin} = 2\mu_B \sqrt{S(S+1)}$; $S = \Sigma s$

If we go to the table here, you can see zinc 2 plus is actually a 3 d 10, zinc 2 plus copper 2 plus all of them have to 3 d 10 aliment or ion and therefore, there is no magnetism there is no spin magnetic moment, therefore it is 0.

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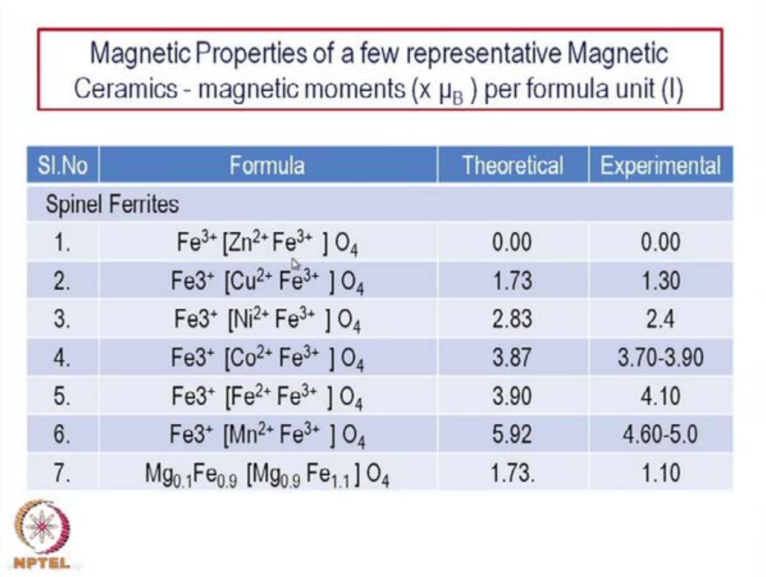

Magnetic Properties of a few representative Magnetic Ceramics - magnetic moments (x μ_B) per formula unit (I)

Sl.No	Formula	Theoretical	Experimental
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7.	$Mg_{0.1}Fe_{0.9} [Mg_{0.9} Fe_{1.1}] O_4$	1.73.	1.10

And that is the reason, that is the reason zinc ferrite will have a 0 magnetic moment, and this F e 3 plus and this F e 3 plus will cancel each other, so thats happen in all of them.

The F e 3 plus one atom or one ion one atim is inside, or at ion is inside, inside the octa octahedral site, the other is tetrahedral site, so they cancel all each other. Because, there are in anti-parallell ordering, what I was telling is magnesium? this is magnesium ferrites and we have here magnesium is in the both the sites insight as well as outside, and that makes a little different here, you can see once, you add magnesium into the… So, most of it actually goes inside, but part of it is there outside, outside in the sense in the tetrahedral site, so magnesium gets distributed between tetrahedral and octahedral sites.

And as a result iron also gets redistributed between the octahedral site and tetrahedral sites, so which was 1 is to 1 distribution. Now, it is become 0.9 and 1 so, because of the magnesium substitution, and then as a result you have a net magnetization, which is of the order of 1.73, but the actual value, experimental value is about 1.10. So, this kind of iso structural substitution and looking at the structure itself, one can calculate on, one can really predict how much magnetic moment one can expect? and what will be saturation magnetization? so for all spirited is the structure which is important, and this kind of simple concentration gives you the magnetic moment of the overall material.

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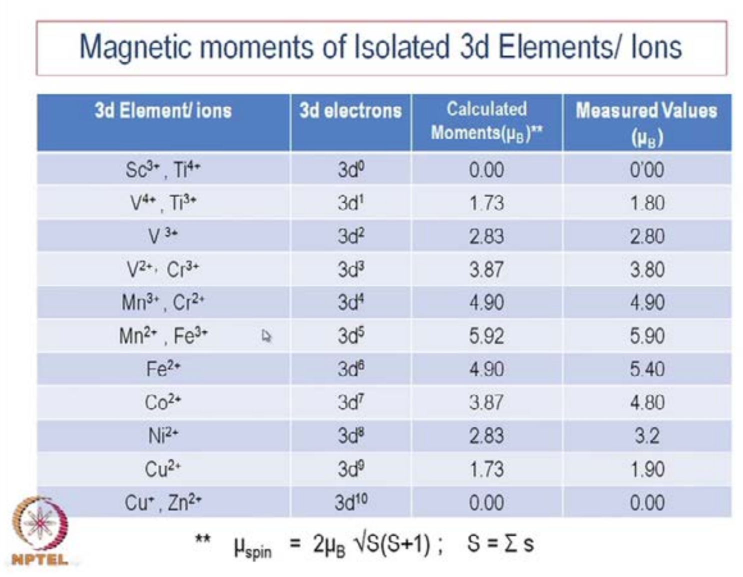

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Cu^{+} , Zn^{2+}	$3d^{10}$	0.00	0.00

** $\mu_{spin} = 2\mu_B \sqrt{S(S+1)}$; $S = \Sigma s$

.

This is just a reference, this was given earlier, and in all these cases, you have to remember this is the formula, which has been used to arrive at these figures, because there are integers only, so far as the number of electrons are concerned. But, only when you we use this formula, the integers are different integers, it is no longer integer and some fractions comes up, so this relationship must also be remember.

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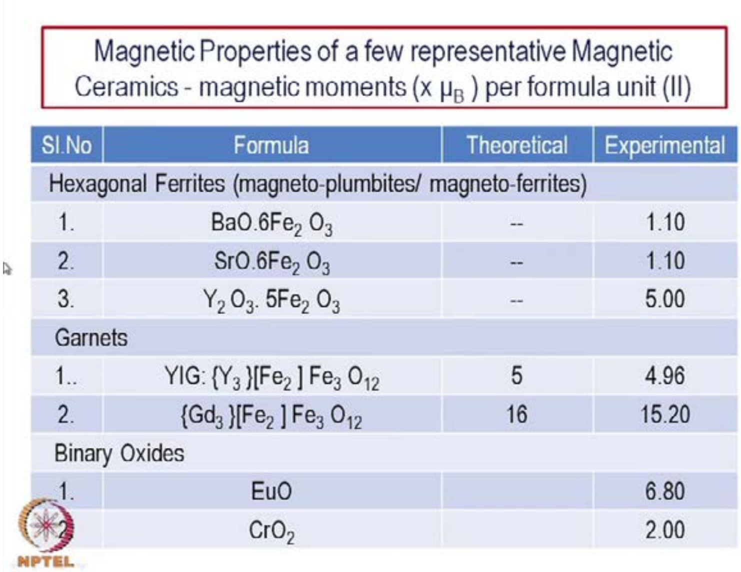

Magnetic Properties of a few representative Magnetic Ceramics - magnetic moments (x μ_B) per formula unit (II)

Sl.No	Formula	Theoretical	Experimental
Hexagonal Ferrites (magneto-plumbites/ magneto-ferrites)			
1.	$BaO.6Fe_2 O_3$	--	1.10
2.	$SrO.6Fe_2 O_3$	--	1.10
3.	$Y_2 O_3 . 5Fe_2 O_3$	--	5.00
Garnets			
1..	YIG: $\{Y_3\}[Fe_2] Fe_3 O_{12}$	5	4.96
2.	$\{Gd_3\}[Fe_2] Fe_3 O_{12}$	16	15.20
Binary Oxides			
1.	EuO		6.80
2	CrO_2		2.00

Well, we are talking about the calculation of the magnetic moment of different structures, particular the spinel structure we have already considered, here is some kind of data particularly, for the other two types of structure, hexagonal ferrites or the magnetoplumites or sometime called magneto ferrites, there called. So, barrium hexa ferrite as the experimental, it is difficult to calculate here, spinel it is not as easy in case of spinel structure, spinel structure it is relatively easy to calculate whereas, magnetoplumbite structure it is not so easy, so far the from the consideration of the crystal structure point of view. But the experimental values are here. It is B a O F e 2 O 3 and S r O 6 F e 2 O 3 is 1.1, once again there is some problem, this should be garnet I will change them.

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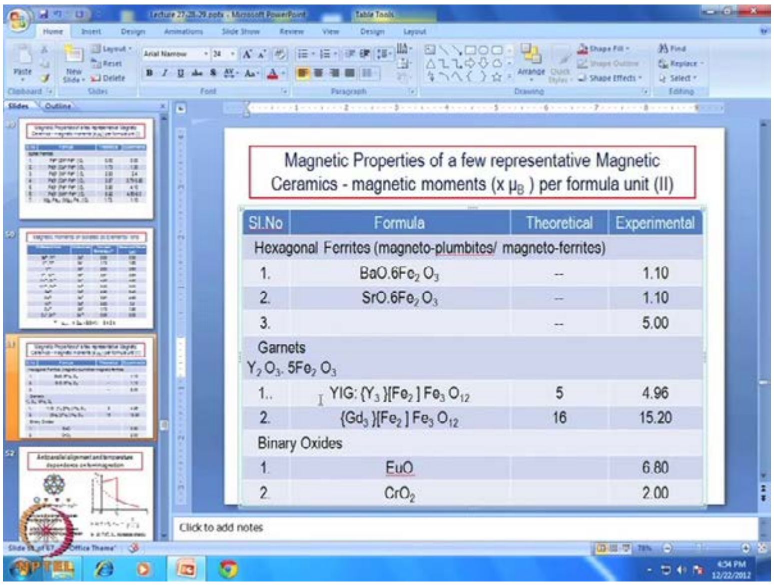

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2.	$\{Gd_3\}[Fe_2]Fe_3O_{12}$	16	15.20
Binary Oxides			
1.	EuO		6.80
2.	CrO_2		2.00

Click to add notes

These are actually garnet structures, so the distribution of heat as we have mentioned earlier, this in the, in the dodecahedron site, and this is, a, this is a a a b c kind of structures, I will, I will discuss them later on. So, the garnets, these are all garnets structure, and then we have some binary oxides some binary oxides also has some magnetic properties. Particularly, one important thing is about chromium oxide, chromium oxide is extensively used for tape-recording, and so on. So, they have also some magnetic properties, I think we will discuss them little details in the next lecture.

Thank you, thank you for your attention.