Electroceramics
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Lecture - 37

So, we will again start a new lecture today and what we will do is that, we will first review the contents of last lecture and then we will end up, we will go on discussing this new lecture.

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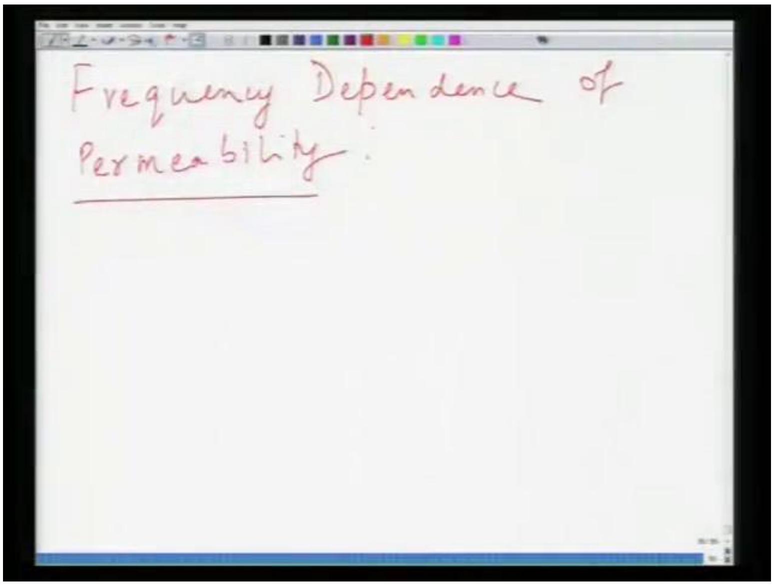

Frequency Dependence of Permeability.

So, in the last lecture we finished our discussion on ferromagnetic materials, with some thoughts on what was postulated as molecular field, which was later explained in terms of exchange interaction and exchange energy, which gives rise to magnetic ordering, whether it is an, whether in the form of ferromagnetic materials or in the form of anti ferromagnetic ordering. So, parallel or ant parallel, but in both the cases exchange interaction is dominant and then then anti ferromagnetic materials of course they have anti parallel arrangement of a spins with equal and opposite as spin magnitudes.

So, as a result there is no magnetisation and this is found to occur in some metallic elements, as well as in some oxides, where typically spins on one site are spin up and another another kind of site are spin down. So, for instance in case of nickel oxide, if you look at 1 1 0 planes, the 1 1, the nickel atoms in 1 1 0 planes, one of the 1 1 0 parallel planes are spin up and the next 1 1 0 plane are spin down. As a result they cancel completely and resulting in no magnetisation and then another variant of this anti ferromagnetic ordering was ferrimagnetic materials.

Now, there also you have this anti parallel alignment of spins, but spins or magnetic moment of these spins are of unequal magnitude. So, this is very interesting scenario and this is what we will discuss today as well, because this gives rise to a net magnetic moment, and this magnetic moment can be quite large, and as a result many times ferrimagnetic materials come in the category of or explain in just like they are ferromagnetic materials. The materials which belong to this category typically are ferrites like iron ferrite, nickel ferrite, nickel nickel iron ferrite, cobalt ferrite, so we look at those applications today, those examples today.

Then we went on discussing a comparison of all these different kind of magnetic materials and finally, we looked at what is the power loss in a magnetic material, with hysteresis curve. So, today what we will do is that, we will first have a look at the frequency dependence of magnetic permeability.

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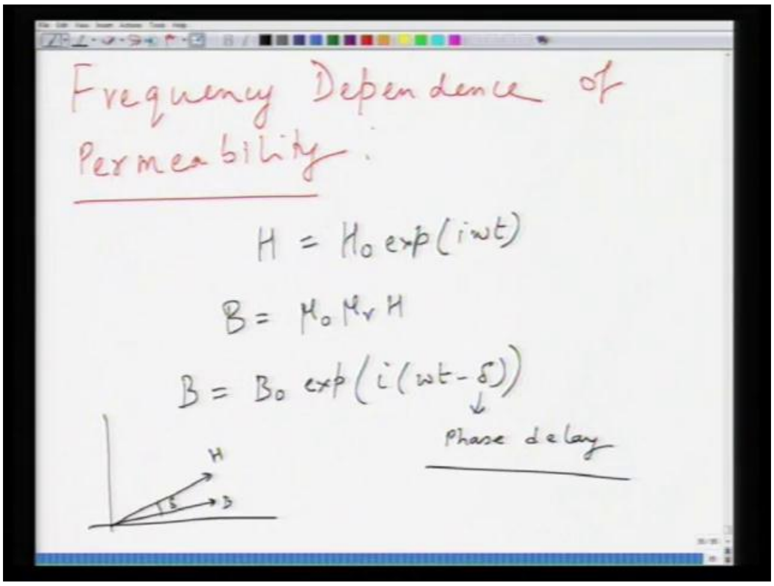

Frequency Dependence of Permeability:

$$H = H_0 \exp(i\omega t)$$

$$B = \mu_0 \mu_r H$$

$$B = B_0 \exp(i(\omega t - \underset{\substack{\downarrow \\ \text{Phase delay}}}{\delta}))$$

So, we said that just just like you have in case of electric field, you have simultaneously sinusoidally varying a c electric field, you have a magnetic field, which is also similar in the form H is equal to H naught exponential of i omega t and this since, now you know that if I, if H is of this form and you know that in a linear magnetic material B is equal to mu naught mu r into H. Now, at high frequencies these two parameters B and H are related with some lag time. So, if you can, if you write in the form of Phasors then B can be written in the form, if H is written in the form of H naught exponential, i omega t then B is written in the form of B naught exponential of i into omega t minus delta.

So, with this minus delta is suggestive of the fact that B lags to H by an angle delta. So, this delta is nothing but your phase delay between B and H. So, if you if you plot it on a on a on a on a imaginaries on a real imaginary plot, then if this is your H, then B would be somewhere here. So, this would be your delta. So, if you, now, what is magnetic permeability?

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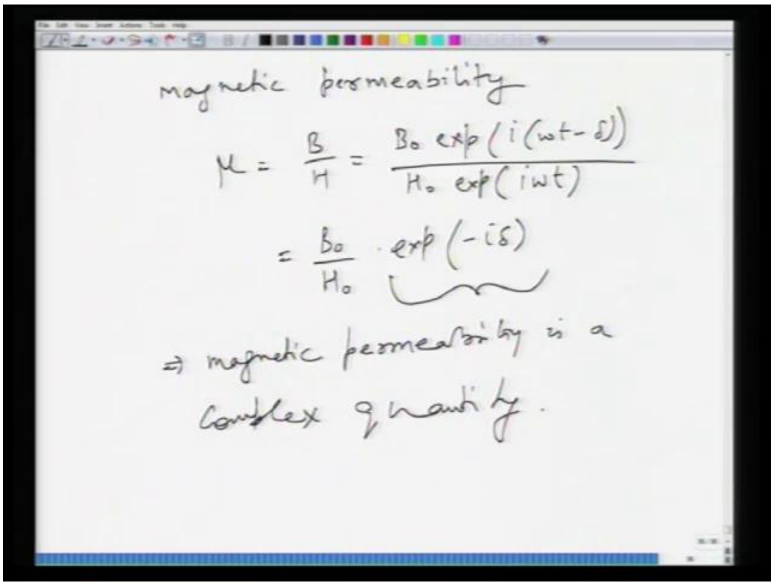

magnetic permeability

$$\mu = \frac{B}{H} = \frac{B_0 \exp(i(\omega t - \delta))}{H_0 \exp(i\omega t)}$$

$$= \frac{B_0}{H_0} \cdot \underbrace{\exp(-i\delta)}$$

⇒ magnetic permeability is a complex quantity.

Magnetic, which is mu is nothing but B divided by H and if you now replace the substitute the values, this is B naught exponential of i into omega t minus delta divided by H naught exponential i omega t. If you just substitute it rearrange the terms, what you get is B naught divided by H naught into exponential of minus i delta. This term being a complex quantity suggests that mu is also a complex quantity. So, as a result magnetic permeability is the complex quantity and this is similar to what we saw in dielectric materials, where we ended up establishing the same conclusion and by taking the a c electric field.

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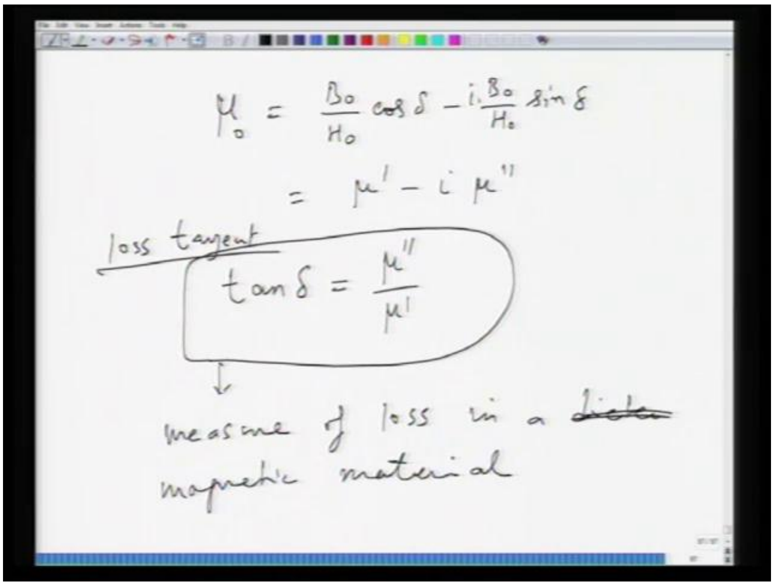

$$\mu_0 = \frac{B_0}{H_0}\cos\delta - i\frac{B_0}{H_0}\sin\delta$$

$$= \mu' - i\mu''$$

loss tangent

$$\boxed{\tan\delta = \frac{\mu''}{\mu'}}$$

↓

measure of loss in a ~~dielec~~

magnetic material

So, this B can be simply written as B naught H naught into cos delta minus of B naught H naught i multiplied by B naught H naught sine delta. This can be written as mu prime minus i mu (( )) double prime and this is what... And similarly, loss tangent and here mu prime is the real part of magnetic permeability and and mu double prime is the complex part of permeability. Similarly, just like dielectric materials, you can define a loss tangent. Tan delta as mu double prime, as mu double prime divided by mu prime, which is again representative of measure of loss in in a in a sorry magnetic material, okay?

So, basically it tells you an idea about, how much how much energy in the material is lost? So, this is the complex dependence of magnetic permeability in the, or complex representation of magnetic permeability in a magnetic material. Now, what we will do is that, we will take now, we will get back to what is called as more pertinent topic, which is magnetic ceramics.

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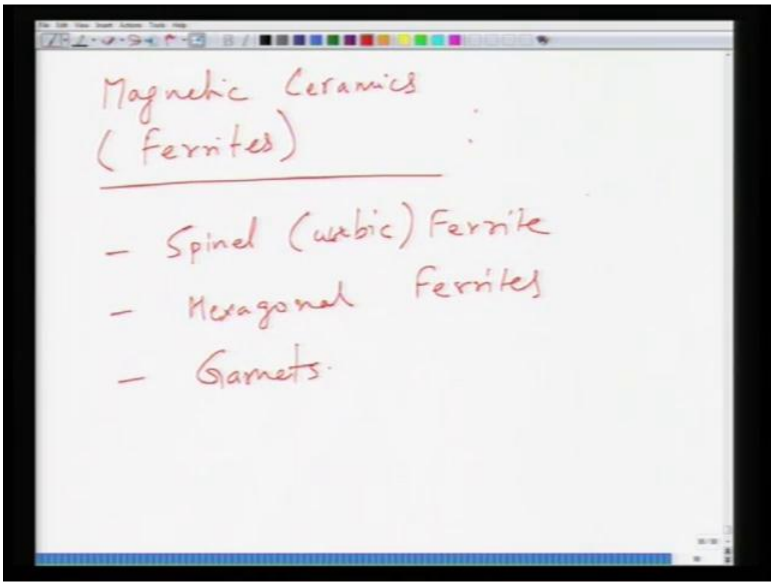

Magnetic Ceramics
(ferrites)

- Spinel (cubic) Ferrite
- Hexagonal Ferrites
- Garnets.

In this context, what we are looking going to look at basically is ferrites. So, these ferrites essentially as the name itself suggest, these are iron containing materials. So, we can have spinel, basically cubic structured ferrites. We can have hexagonal ferrites, we can have garnets. Garnets are essentially based on mineral form. So, all these are the strongly magnetic material, they are reasonably resistive in nature as well as a result, they are used in applications where losses are important thing. So, you do not want to have high losses, you can use these materials. Moreover, some of these materials can have tunable, curie temperature.

So, as a result you can change the composition of the material to change the curie temperature and hence make it more useful for your application. Composition can also lead to changes in the magnetic characteristics as well, which is what makes these... So, tunability of magnetic behaviour as well as curie temperature makes these materials extremely useful for and for variety of applications. Moreover, they are most of these are oxides in forms, their stability environmental stability is far better, there is nothing to oxidise further. So, as a result they are very useful materials. Now, we will go through each of these one by one, with the little discussion.

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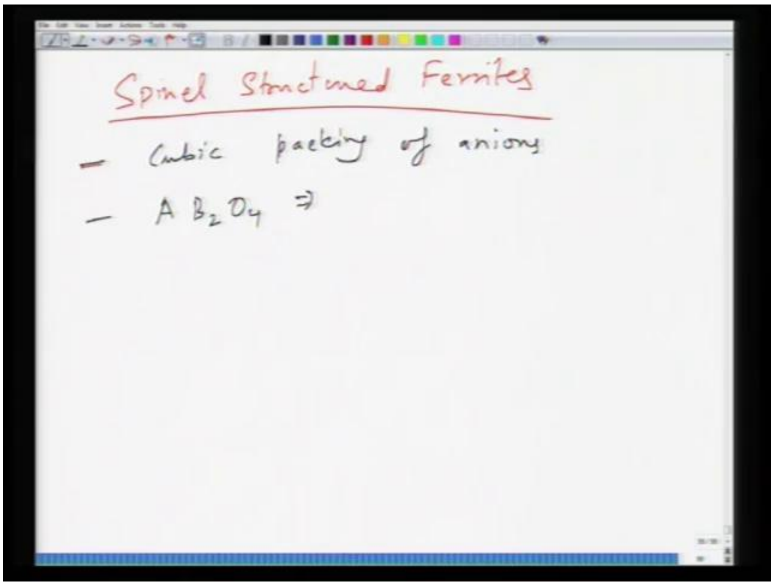

Spinel Structured Ferrites

- Cubic packing of anions
- $A B_2 O_4 \Rightarrow$

So, first we will take up, what is our spinel structured ferrites? So, essentially a spinel structured ferrites are nothing but cubic packing of based on cubic packing of anions and general formula by which they are determined is A B 2 O 4. So, here or rather you can, you can now this this formula A B 2 O 4 can be represented differently. Now, to know about these spinel ferrites, we will, we will we will go back to module 1, a little bit because that is where we discussed these materials. So, I will take you to the slides of module 1, which are...

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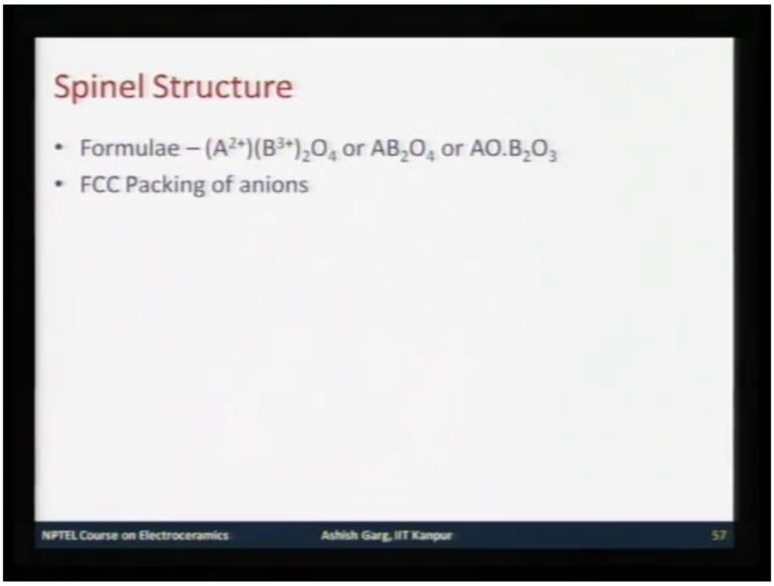

Spinel Structure

- Formulae – $(A^{2+})(B^{3+})_2O_4$ or AB_2O_4 or $AO.B_2O_3$
- FCC Packing of anions

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So, this is something which we discussed in module 1, so a spinel structure essentially spinel structure materials have formula of A 2 plus B 3 plus 2 O 4 or they are written as A B 2 O 4 or A O dot B 2 O 3. So, you have essentially it is a mixture of 2 oxides, A O and B B 2 O 3. Now, interestingly the way cations arrange these, themselves in various interstices, defines whether you have, you have a inverse spinel structure or normal spinel structure. Depending upon whether you are structure is normal or spinel, the magnetic characteristics vary accordingly.

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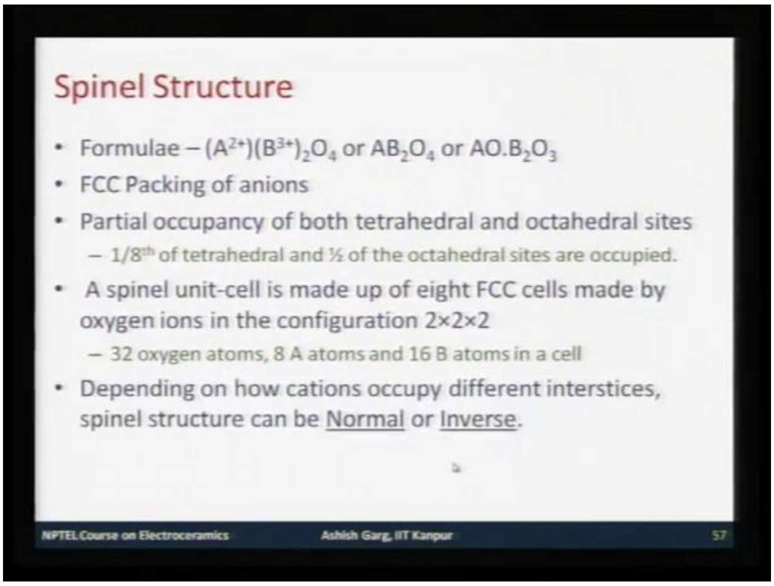

Spinel Structure

- Formulae – $(A^{2+})(B^{3+})_2O_4$ or AB_2O_4 or $AO.B_2O_3$
- FCC Packing of anions
- Partial occupancy of both tetrahedral and octahedral sites
  - 1/8th of tetrahedral and ½ of the octahedral sites are occupied.
- A spinel unit-cell is made up of eight FCC cells made by oxygen ions in the configuration 2×2×2
  - 32 oxygen atoms, 8 A atoms and 16 B atoms in a cell
- Depending on how cations occupy different interstices, spinel structure can be Normal or Inverse.

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So, as a result, so essentially what you have is a FCC packing of anions and here since you have FCC packing of anions, you will have tetrahedral octahedral site. For per formula unit, for 4 oxygen atoms you will have 4 octahedral and 8 tetrahedral sites and the whole unit cell is made up by 8 formula units. So, as a result you have essentially 32 oxygen atoms, 8 into 4, so which means you have 32 octahedral sites in a unit cell and 64 tetrahedral sites. Now, what happens is that, in these materials, in these materials these sites are not completely occupied, as you can see because cations are only 3 and and interstices are 4 plus 8, 12 per formula unit.

So, as a result there is a partial occupancy of these interstitial sites. So, in, so what you have is essentially 1 eighth of tetrahedral and half of the octahedral sites are occupied. So, per unit cell out of 32 octahedral only 16 are occupied and only 8 of the tetrahedral out of 64 are occupied. So, essentially the unit cell is like eight FCC cells made by oxygen atoms, in the configuration 2 by 2 by 2. So, it is a 2 by 2 by 2 cube consisting of 32 oxygen atoms and as I said depending upon how cations occupy different interstices, this structure can either be normal or inverse.

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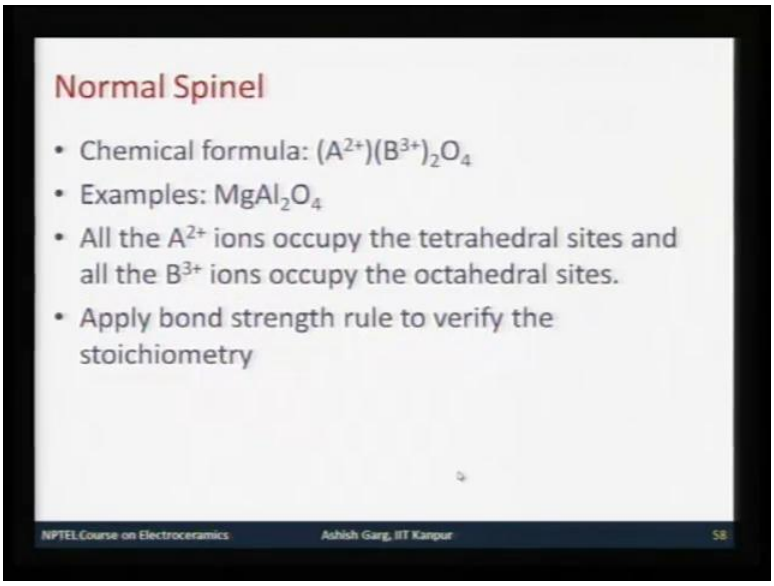

Normal Spinel

- Chemical formula: $(A^{2+})(B^{3+})_2O_4$
- Examples: $MgAl_2O_4$
- All the A^{2+} ions occupy the tetrahedral sites and all the B^{3+} ions occupy the octahedral sites.
- Apply bond strength rule to verify the stoichiometry

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So, essentially normal spinel has a formula, which is A 2 plus B 3 plus twice O 4 similar to that, now what it means is that, at the all the a atoms occupy tetrahedral sites, which means out of, so out of 4 cells you have 8 formula units, you will have 8 A atoms. So, these A atom, 8 A atoms will occupy all the 8 tetrahedral sites out of 64 and all the B atoms which is 2 per formula unit or 16 per unit cell, occupy the half of the octahedral sites, which means 16 octahedral sites occupied. You can do, you the bond, balance bond bond strength rule as I told you earlier, to satisfy yourself with the stoichiometry.

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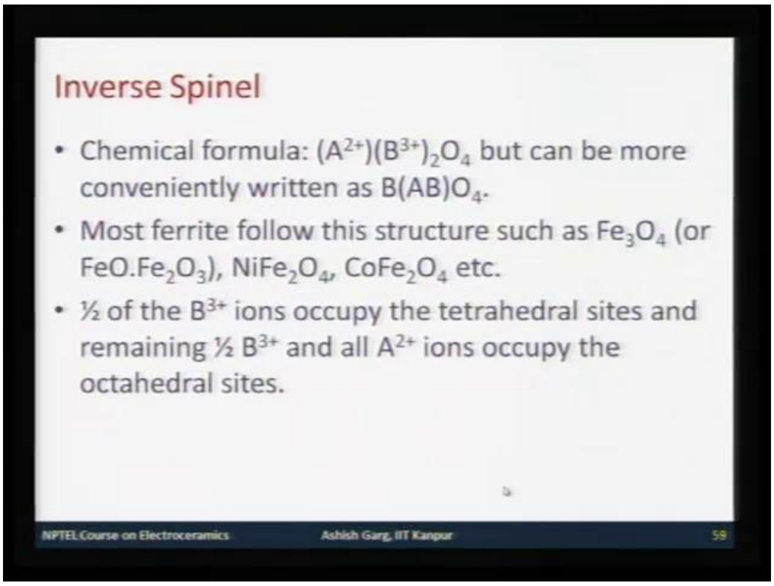

Inverse Spinel

- Chemical formula: $(A^{2+})(B^{3+})_2O_4$ but can be more conveniently written as $B(AB)O_4$.
- Most ferrite follow this structure such as Fe_3O_4 (or $FeO.Fe_2O_3$), $NiFe_2O_4$, $CoFe_2O_4$ etc.
- ½ of the B^{3+} ions occupy the tetrahedral sites and remaining ½ B^{3+} and all A^{2+} ions occupy the octahedral sites.

In case of inverse spinel what you have is, essentially a chemical formula is same, but conveniently for the, for illustrating how these atoms occupy the interstitial sites, you can say like this, half of the B atom, which means one out of two B atom or in a in a formula unit or 8 out of 16 in an unit cell occupy the tetrahedral sites. And remaining B atoms and all the A atoms occupy the occupy the octahedral sites. So, the examples of this structure are materials like Fe 3 o 4, most of the useful ferrites happen to be inverse in structure. So, you have Fe or Ni Fe 2 O 4, Co Fe 2 O 4 etcetera. Here as I said earlier, half of the B ions occupy tetrahedral sites and remaining half B ions and all the A ions occupy octahedral sites. So, this is what is the spinel structure? And this is how it looks like.

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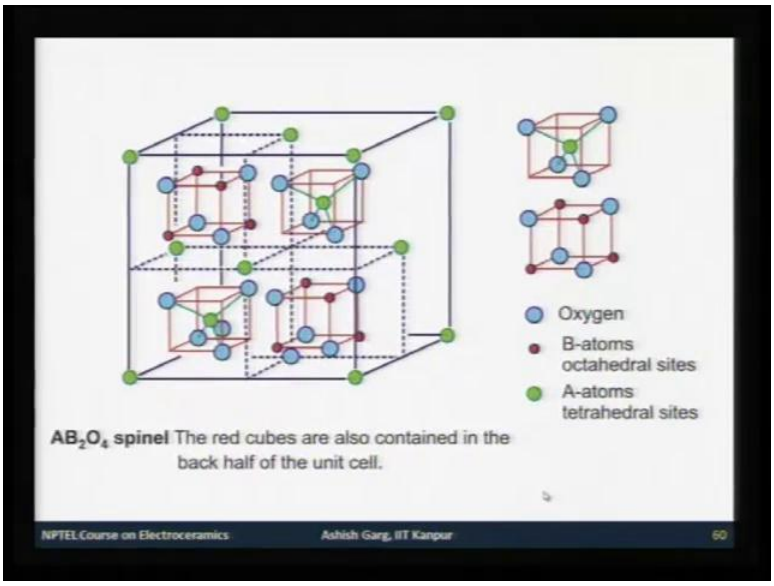

● Oxygen
● B-atoms octahedral sites
● A-atoms tetrahedral sites

AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell.

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So, you have this A B 2 O 3 spinel and the red cubes are the... So, essentially which one is the back? Yes, so essentially these are the, this is the kind of configuration you have. So, this is the configuration of essentially one type of atom, this is the configuration of... So, you can you can go through configuration yourself. So, what you have here is here is the A atom at a tetrahedral site and red one will be at the octahedral site. So, structure is little bit complex, I advice you to go through the books a little bit, to understand the structure well. So, let us go back to what we were discussing earlier, so what we were discussing earlier was this.

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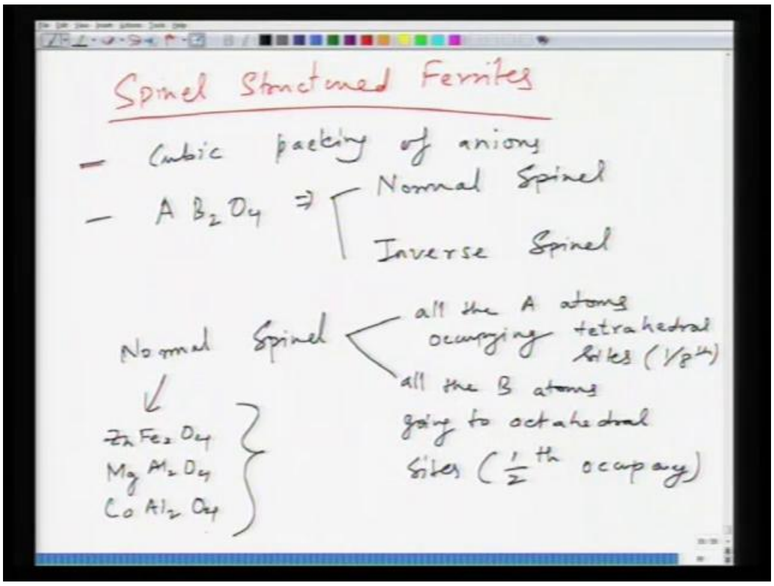

Spinel Structured Ferrites

- Cubic packing of anions
- $AB_2O_4 \Rightarrow$ Normal Spinel / Inverse Spinel

Normal Spinel — all the A atoms occupying tetrahedral sites ($1/8^{th}$); all the B atoms going to octahedral sites ($\frac{1}{2}^{th}$ occupancy)

Normal ↓ $ZnFe_2O_4$, $MgAl_2O_4$, $CoAl_2O_4$

So, essentially what you have is A B A B 2 O 4 structure. So, you can have normal, you can have inverse spinel. In case of normal spinel, you have, which means one-eighth occupancy and all the B atoms going to occupancy. The example of normal spinel structures could be your zinc ferrite, magnesium aluminate, cobalt aluminate etcetera and inverse spinel.

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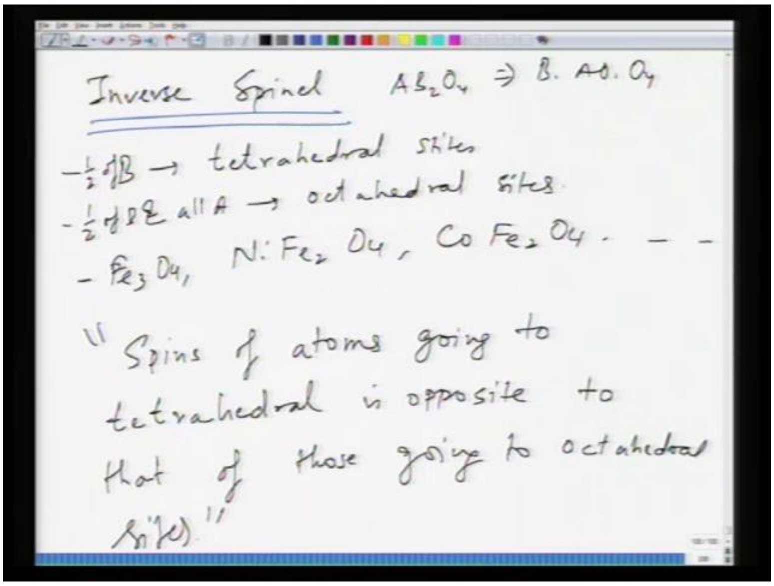

Inverse Spinel $AB_2O_4 \Rightarrow B.AO.O_4$

- $\frac{1}{2}$ of B → tetrahedral sites
- $\frac{1}{2}$ of B & all A → octahedral sites.
- Fe_3O_4, $NiFe_2O_4$, $CoFe_2O_4$. – –

"Spins of atoms going to tetrahedral is opposite to that of those going to octahedral sites"

So, you have, so you can say A B 2 O 4 as B dot A O dot O 4. So, B goes to tetrahedral sites, half of B. And half of B and all A go to octahedral sites. In the examples of such materials are Fe 3 O 4, Ni Fe 2 O 4, Co Fe 2 O 4 etcetera. Now, from the magnetic, from the magnetism point of view the the the spin of atoms going to tetrahedral site is opposite, to that of those going to octahedral sites. Now, this is something, which is ferrimagnetic material itself. So, what you have essentially a anti ferromagnetic ordering, what what you are going to have is a different picture.

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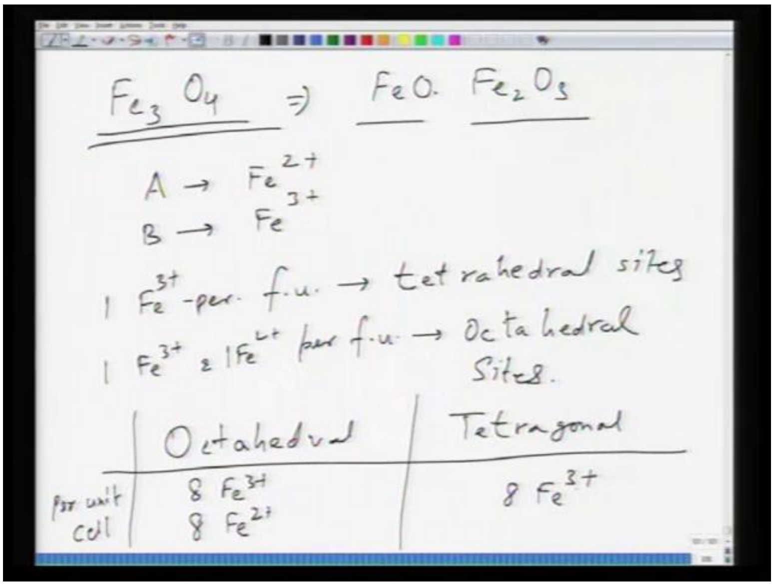

$Fe_3O_4 \Rightarrow FeO \cdot Fe_2O_3$

A → Fe^{2+}

B → Fe^{3+}

1 Fe^{3+} -per. f.u. → tetrahedral sites

1 Fe^{3+} & 1 Fe^{2+} per f.u. → Octahedral Sites.

	Octahedral	Tetragonal
Per unit cell	8 Fe^{3+} 8 Fe^{2+}	8 Fe^{3+}

So, if this was true then let us take example of, let us take example of Fe 3 O 4, so Fe 3 O 4 can also be represented as Fe O dot Fe 2 O 3. It is a solid solution of essentially Fe O and Fe 2 O 3 and what happens here is, you have two of... So, your essentially you have your A ion is Fe 2 plus and B ion is Fe 3 plus. So, you have 1 Fe per formula unit per formula unit going to tetrahedral site and you have 1. So, we can write 1 Fe 3 plus 1 Fe 3 plus and 1 Fe 2 plus per formula unit going to octahedral site. So, if this was your octahedral site and this was your tetrahedral site, if I just make two columns, so what you have is per unit cell. You have how many Fe ions going? So, you have octahedral site will have 8 of Fe 3 plus and 8 of Fe 2 plus ions and this will have 8 of Fe 3 plus ions.

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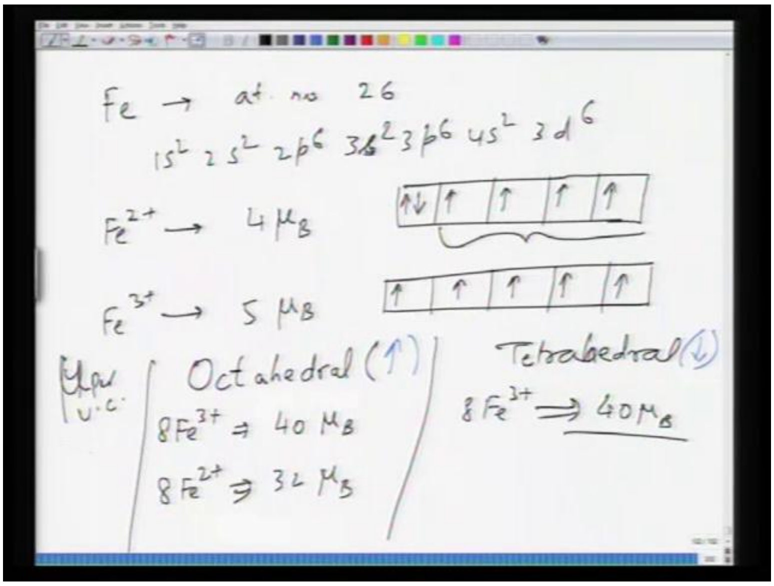

$Fe \rightarrow$ at. no 26

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

$Fe^{2+} \rightarrow 4\mu_B$

$Fe^{3+} \rightarrow 5\mu_B$

μ per u.c.

Octahedral (↑)

$8Fe^{3+} \Rightarrow 40\mu_B$

$8Fe^{2+} \Rightarrow 32\mu_B$

Tetrahedral (↓)

$8Fe^{3+} \Rightarrow 40\mu_B$

Now, what is configuration of Fe? Atomic number is 26. So, it is 1 s 2, 2 s 2, 2 p 6, 3 s 2, 3 p 6, 4 s 2, so that makes it 10 and then 3 d 6, so depending upon whether you have Fe 2 plus or Fe 3 plus. So, Fe 2 plus according to Hund's rule, will have 4 mu B of magnetisation because 1, 2, 3, 4, 5, so for Fe 2 plus all the s s electrons will be taken off. So, you need to rearrange d, so 5 of them go to 5 intercept shells and then 1 goes here. So, what you have here is, 4 mu B and Fe 3 plus likewise, will give you 5 mu B, 1, 2, 3, 4, 5 because now you will take off 2 s electrons and 1 d electrons, left with 5 d electrons.

Now, doing the math, octahedral, tetrahedral and we are going to calculate mu per unit cell. So, we had 8 of Fe 3 plus... Let us say octahedral side is spin up and tetrahedral side is spin down. So, we are saying that they are opposite to a spin up and the spin down, you can take it the way you want it, by essentially it is going to give rise to net magnetic moment. So, if 8 Fe 3 plus will give rise to 40 mu B and 8 Fe 2 plus will give rise to 32 mu B and here 8 Fe 3 plus will give rise to 40 mu B.

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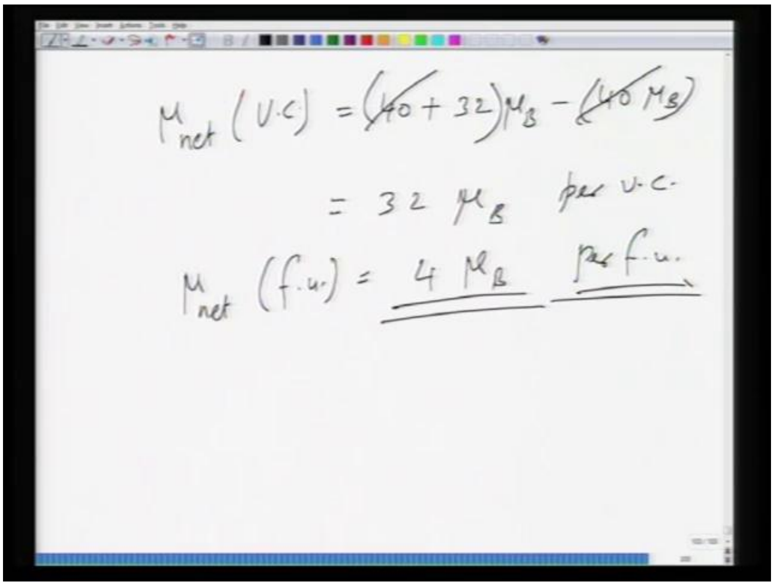

$$\mu_{net}\,(U.C) = (\cancel{40} + 32)\mu_B - (\cancel{40}\,\mu_B)$$

$$= 32\,\mu_B \text{ per u.c.}$$

$$\mu_{net}\,(f.u.) = \underline{4\,\mu_B} \ \underline{\text{per f.u.}}$$

So, essentially what you will have is, net will be, so mu net per unit cell will be equal to 40 plus 32 mu B minus 40 mu B. This 40, 40 cancel each other, what you will have is 32 mu B per unit cell. And if you want to calculate mu net per formula unit, it will be 4 Bohr magneton per formula unit, which is a very large magnetization considering magnetic materials into account. This is essentially the way you work out magnetic moments, in in a in a for a for a ferrite material. It is a very simple way of doing it, remember that the spins of octahedral and tetrahedral are equal to opposite to each other, they may or may not be equal, but they are opposite to each other.

So, as a result they give rise to net magnetization. Now, simple similarly, you can work it out for other ferrite materials like nickel ferrite, cobalt ferrite etcetera, they are again simple. You just need to work out, what is the net magnetic moment of each ion by applying Hund’s rule and take the oxidation state, and then work out, what is the final magnetic moment of that material. Another thing that you can do with spinels is, with the spinels you can also make mixed spinels.

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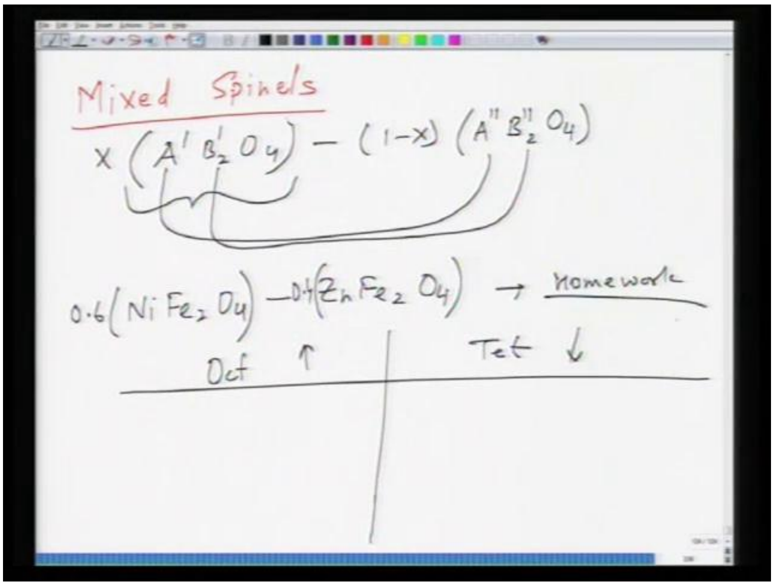

This mixed spinels is nothing but if you have one type of compound, let us say A prime B prime 2 O 4. So let us say x of this, then you can make another one, 1 minus x A double prime B double prime 2 O 4. So, this is so this is nothing but mixed spinel is nothing but solution of two different kind of spinels. So, where A and A aprime and A double prime substitute for each other and assuming that there is a random occupancy on the designated sites. Then B double prime and B prime again occupy for each other. So, as a result you have mixed occupancy of the intersites. So, for instance you can take Ni Fe 2 O 4 and Zn Fe 2 O 4.

So, let us say this is 0.6 Ni Fe 2 O 4 and you can make it 0.4 Ni Fe 2 O 4. So, here now what you need to do is that, you need to do the same exercise. So, go to octahedral tetrahedral sides, now you know that, nickel ferrite is inverse, zinc ferrite is normal, make sure you get the site distribution, the distribution of irons in the sites correctly, workout the magnetic moment. So, you take this spin up spin down, work out the magnetic moment, multiply this by x and 1 minus x for the relevant ion and then get the final moment per unit cell or per formula unit. So, you can do it the same way, it is just that, it is nothing but rule of mixtures. So, so it is a it is a simple exercise I will leave it to you, to do it at, do it as a homework.

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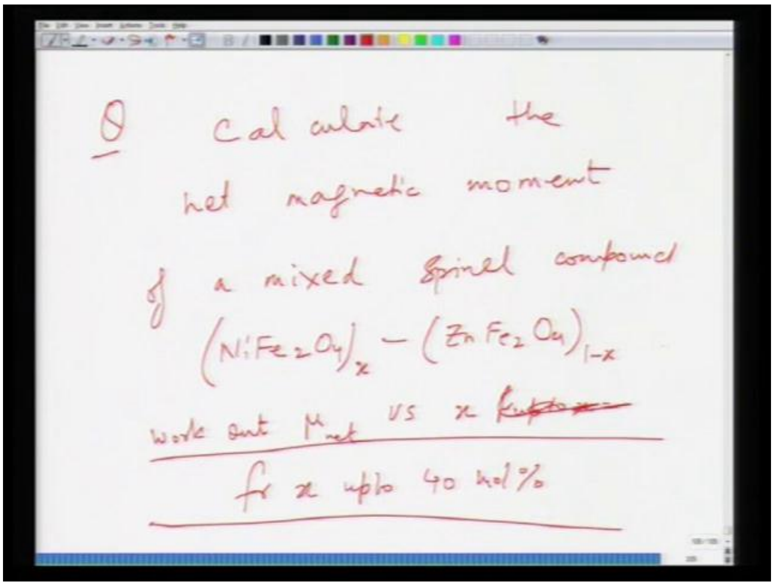

Q Calculate the net magnetic moment of a mixed spinel compound

$(NiFe_2O_4)_x - (ZnFe_2O_4)_{1-x}$

work out μ_{net} vs x ~~[illegible]~~

for x upto 40 mol%

Essentially what it, what I am going to ask you is, calculate the net magnetic moment of mixed spinel compound, which is Ni Fe 2 O 4, Zn FE 2 O 4 1 minus x, where x, you and work out mu net versus x up to x for for x up to 40 mole percent. So, this you can do it at home, okay?

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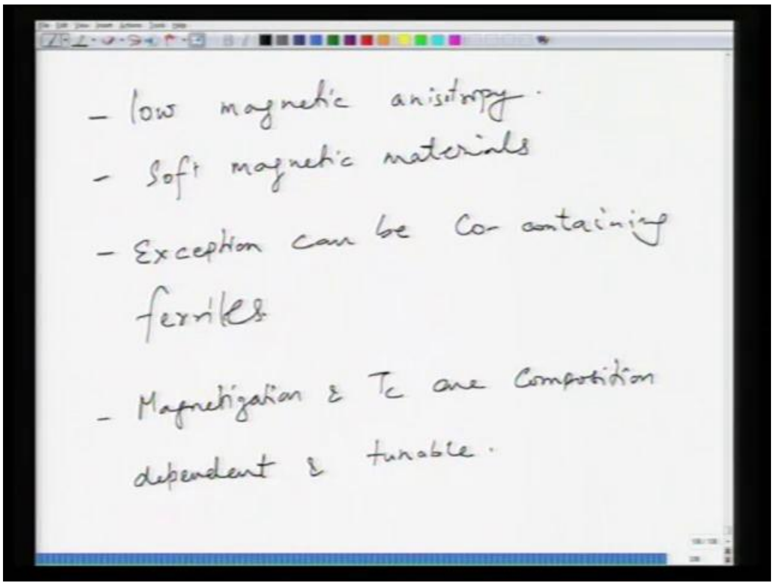

- low magnetic anisotropy.
- Soft magnetic materials
- Exception can be Co-containing ferrites
- Magnetization & T_c are composition dependent & tunable.

Another thing that you find in spinel, perovskite spinel, cubic spinel, ferrites is that that they have low magnetic anisotropy, which means they do not have a strong dependence of magnetisation on the crystallography. So, as on the crystallographic directions, so as a result they are magnetically, soft magnetic materials. So, they do not have large hysteresis losses and some of the exceptions could be cobalt containing ferrites, which tend to have large, some somewhat large magnetic anisotropy. They also have very large course of field strength, so they could be exception. So, but otherwise in but by and large these magnetic ferrites have low magnetic anisotropy, which make some useful in the polycrystalline form.

As a result the switching is easier and they have, and that is why they are called as soft magnetic materials, with low coercivity. They also, so just like a ferromagnet, ferrimagnetic these ferrites also, show a hysteresis loops, like a ferromagnet and they also tend to have reasonably large curie temperature. I will show you the, I will show you a table where curie temperature etcetera for these ferrites are given typically. If you look at ferrites, they might have curie temperatures above the room temperature, which are composition dependent as well. So, you can say magnetisation and T c are composition dependent and tunable. They can tune the properties by changing the composition.

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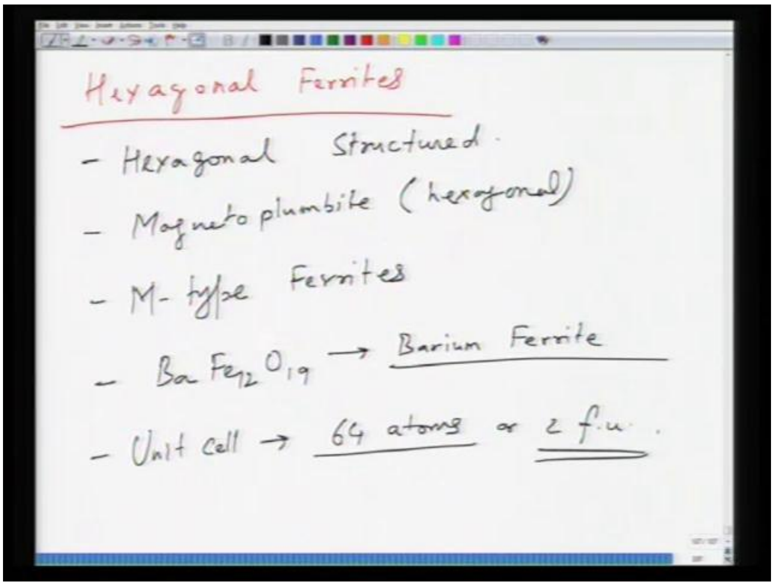

Hexagonal Ferrites

- Hexagonal Structured.
- Magneto plumbite (hexagonal)
- M- type Ferrites
- $BaFe_{12}O_{19}$ → Barium Ferrite
- Unit cell → 64 atoms or 2 f.u.

Another category of magnetic ferrites is hexagonal ferrites. So, as a name itself suggests these are hexagonal structured and parent structure for these compounds is basically magneto plumbite, which is hexagonal compound and typically you call these materials, they are also called in literature as M type ferrites. M type comes from magneto plumbite, so M type ferrites and the and the moral compound the the the the the the material, which is used to represent the structure is typically barium ferrite, Ba Fe 12 O 19, very long formula unit. So, this is barium ferrite, hexagonal in structure, consists of 19 oxygen atoms, 12 iron atoms and 1 of barium atoms total of 19, 12, 31, 32 atoms per unit cell and the structure and the unit cell unit cell has 64 atoms or 2 formula units. So, which means the structure will have 2 of barium atoms 24 of iron atoms and 38 of oxygen atoms.

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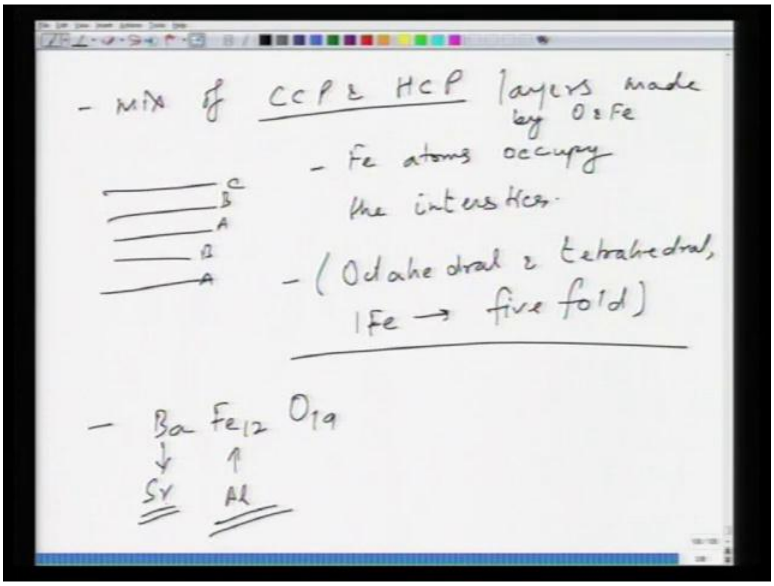

- mix of CCP & HCP layers made by O & Fe
  - Fe atoms occupy the interstices.
  - (Octahedral & tetrahedral, 1 Fe → five fold)

- $Ba\ Fe_{12}\ O_{19}$

Ba ↓ Sr, Fe_{12} ↑ Al

Essentially you can you can easily represent this structure as if it is a mixture of... Let us, it is a mix of CCP and HCP packing and these are the close packed layers, which are made by barium and oxygen ions. This can happen because CCP and HCP structure you know that you have, this is your HCP A B A B and then in between you can have A B C A B C as well. So, this is A B C A B C. So, all you need is a stacking fault essentially. So, that is where you have a stacking fault. So, mix of CCP and HCP layers giving rise to a total of, eventually giving rise to a hexagonal structure and material is bound to have stacking faults. So, essentially stacking of CCP HCP layers, with some stacking faults in between and the base structure is formed by barium and oxygen ions and iron atoms occupies the interstices.

So, and so iron atoms here they occupied interstices of the type octahedral. So, they occupy both octahedral, tetrahedral and another peculiarity of the structure is that one of the iron atoms remain one Fe atom remains 5 fold in coordination. So, this is one peculiar thing about the structure, so not only you have octahedral and tetrahedral coordination, but you also have a 5 fold coordination at certain places in the structure. The way you can change the magnetisation of this magnetic behaviour of this material is, so you have B a Fe 12 O 19, so naturally if you substitute iron by some other atom you will change the net magnetic moment. I will show you in a while, how these magnetic moments are distributed in the lattice?

But it is quite, it is it is quite straight exercise to work it out, when you replace iron, let us say by aluminium, you will work you will change the magnetic characteristics. You can also change barium by a strontium barium is a non magnetic ion, but you can change barium by a strontium, so it changes the strain environment of the material. So, basically size and valence being different gives rise to changes in... So, not only so you have changes in the size and the valence and they give rise to changes in the magnetic behaviour of the material.

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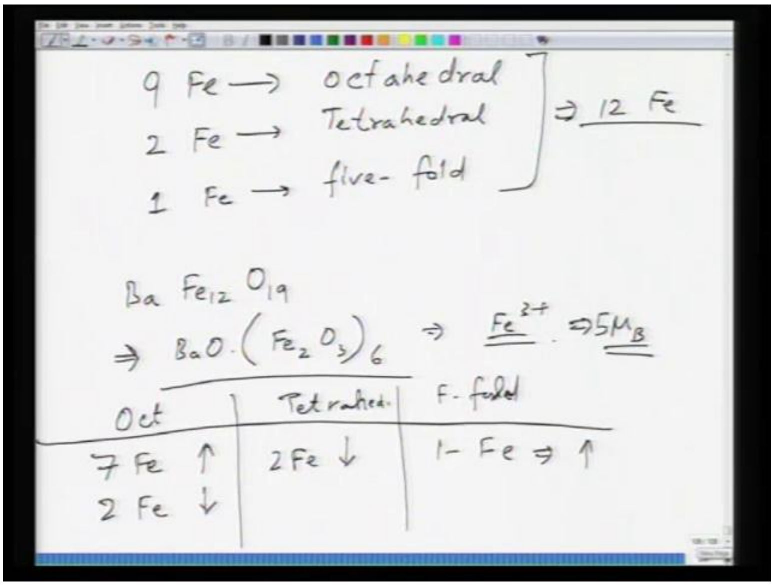

9 Fe → octahedral
2 Fe → Tetrahedral
1 Fe → five- fold

$\Rightarrow$ 12 Fe

$BaFe_{12}O_{19}$

$\Rightarrow BaO\cdot(Fe_2O_3)_6 \Rightarrow \underline{\underline{Fe^{3+}}} \Rightarrow \underline{\underline{5\mu_B}}$

Oct	Tetrahed.	F- fold
7 Fe ↑ 2 Fe ↓	2 Fe ↓	1- Fe ⇒ ↑

So, coming back to magnetic characteristic now, you have 9 iron atoms going to octahedral sites, out of 12 and 2 iron atoms going to tetrahedral sites and 1 atom remain 5 fold coordination. So, this makes up 12 Fe and the formula is B a Fe 12 O 9. So, essentially it is going to be, Ba O dot Fe 2 O 3, into 6. So, this is how the structure is essentially and now you can also see why it is like, why it is like a mixing of hexagonal and cubic layers because Fe 2 O 3 has a hexagonal structure, as we have seen from the module, as as you can see in the module 1, which is based on Al 2 O 3 type structure.

Then D a O will have rock salt structure and if you mix these rock salt and and hexagonal structures you you you result in this Ba Fe 12 O 19 kind of a structures. Of course, they are going to be more number of layers containing Fe 2 O 3 than Ba O. So, this is the structure, now here you can see that Fe 2 plus Fe is in Fe 3 plus form. So, Fe 3 plus form means, magnetic moment per atom is going to be 5 mu B. So, you have 5 mu B of this thing, so based on that, if you rearrange them in the various sites, so you have 9. So, you have octahedral, tetrahedral and 5 fold. Now, here what happens is that, in case of octahedral sites out of 9, 7 Fe are spin up and 2 Fe are spin down.

Now, up and down you can of course, choose, but if you choose 1 up you have to choose other 1 down and with reference to this, the 2 n octahedral down sites, they are spin down and 1 in 5 fold. So, 1 in 5 fold is spin up, so essentially what you have, total of 8 iron atoms is spin up and 4 iron atoms is spin down.

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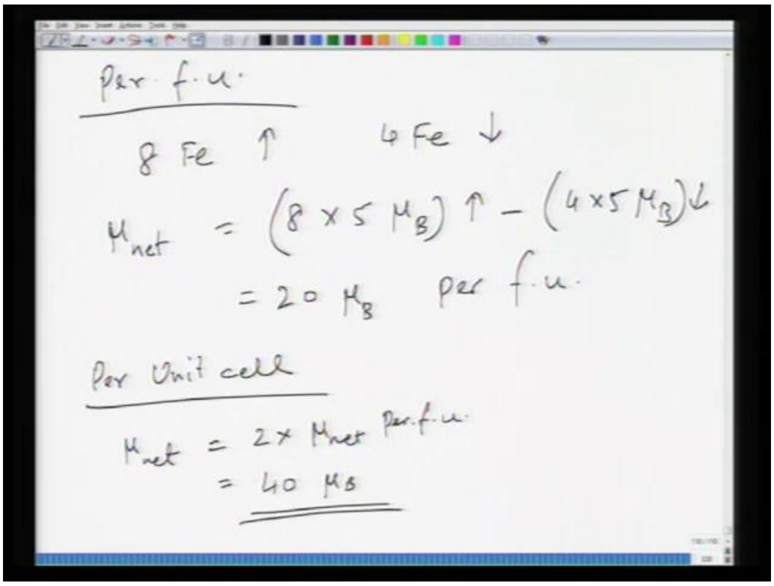

Per f.u.

8 Fe ↑ 4 Fe ↓

$$\mu_{net} = (8 \times 5\ \mu_B) \uparrow - (4 \times 5\ \mu_B) \downarrow$$

$$= 20\ \mu_B \text{ per f.u.}$$

Per Unit cell

$$\mu_{net} = 2 \times \mu_{net} \text{ per f.u.}$$

$$= \underline{\underline{40\ \mu_B}}$$

So, basically per formula unit 8 Fe spin up and 4 Fe spin down. So, mu net would be 8 into 5 mu B spin up minus 8 into sorry 4 into 5 mu B is spin down and what this gives rise to is essentially 20 mu B per formula unit. So, essentially what you have is, 20 Bohr magneton of magnetic moment per formula unit of barium ferrite. Now, for per unit cell if you want to calculate, then per unit cell mu net is going to be equal to 2 multiplied by u mu net per formula unit and this would be 40 Bohr magneton. This is a very large magnetic moment for a material and that is why make this makes this barium ferrite a very useful material.

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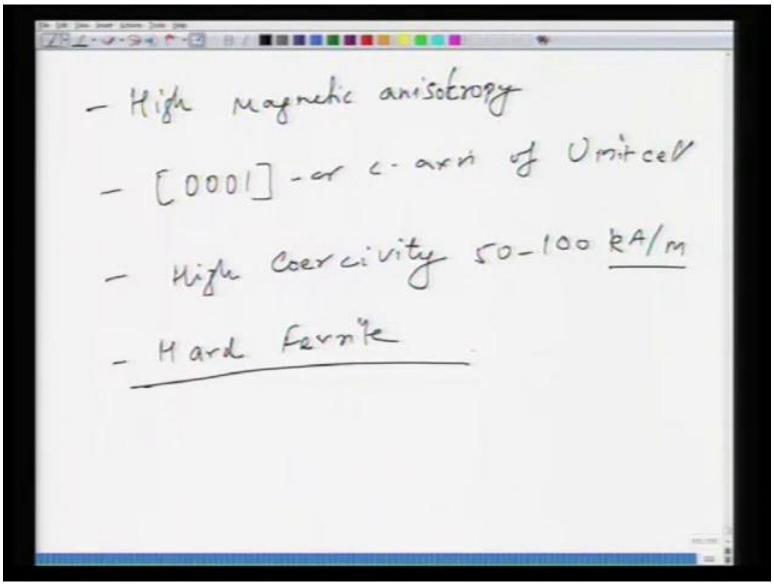

- High magnetic anisotropy
- [0001] - or c-axis of Unit cell
- High Coercivity 50-100 kA/m
- Hard Ferrite

So, another features of this material, this has high magnetic anisotropy, which is expected for a hexagonal material. It magnetises easily along 0001 or C axis of unit cell. So, C axis being the easy magnetisation direction of this material, as a result this material is... Now, since it has very large magnetic anisotropy it happens to have high co-ercivity. And this coercivity can be anywhere between 50 to 100, 1000 kilo ohm, kilo ampere 50 to 100 sorry not 1000, 50 to 100 kilo ampere per meter and this depends upon micro structure and composition etcetera. So, as a result this material is characterised as hard ferrite.

So, essentially barium ferrite is a hexagonal material with large number of atoms, 2 2 2 formula units per unit cell, making up the hexagonal unit cell, which essentially based upon iron oxide structure, Fe 2 O 3 structure hexagonal iron oxide structure. This contains ions in such a position that it gives you a very large magnetic moment per cell of the order of 40 Bohr magneton. So, this is a large number, now what we are going to next take up is essentially the case of garnets.

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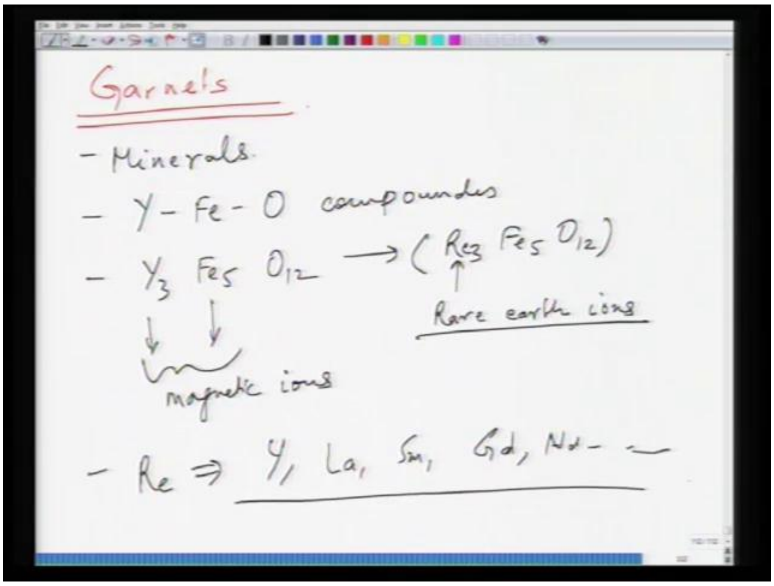

Garnets

- Minerals
- Y - Fe - O compounds
- $Y_3 Fe_5 O_{12} \longrightarrow (Re_3 Fe_5 O_{12})$

Rare earth ions

magnetic ions

- Re ⇒ Y, La, Sm, Gd, Nd - —

Now, these garnets are essentially known as minerals. So, basically and the general, but so essentially when you talk about garnets, you are talking about minerals. But the, from the point of view of magnetic magnetism, the general formula for garnets on which they are based upon, is essentially why their y Fe O compounds, yttrium iron oxygen compounds and the general formula for them is y 3 Fe 5 O 12. So, this is a general formula for the compounds and a more general formula, if you sorry yttrium is a rare earth ions. So, you can make it R 3 Fe 5 O 12, so R could be R e, let us say so R e 3 Fe 5 O 12, which is a R e is a rare earth ion.

So, essentially you have here two magnetic ions, this is magnetic and this is magnetic, both of these are magnetic ions. So, the the the the fact that you have two kinds of magnetic ions, one is the rare earth, second is the iron. The total magnetic moment of the, this material is quite modifiable, tunable by putting in different kind of elements in there and as a result you can you can play around with this material. Now, so this example of this R e 3 R R e can be you of course, you you can of course, have yttrium, you can have lanthanum, you can have samarium, you can have gadolinium, neodymium, any kind of rare earth atom can be used here, to tune the magnetic moment of this material and this material again is a is a quite complex from structure wise.

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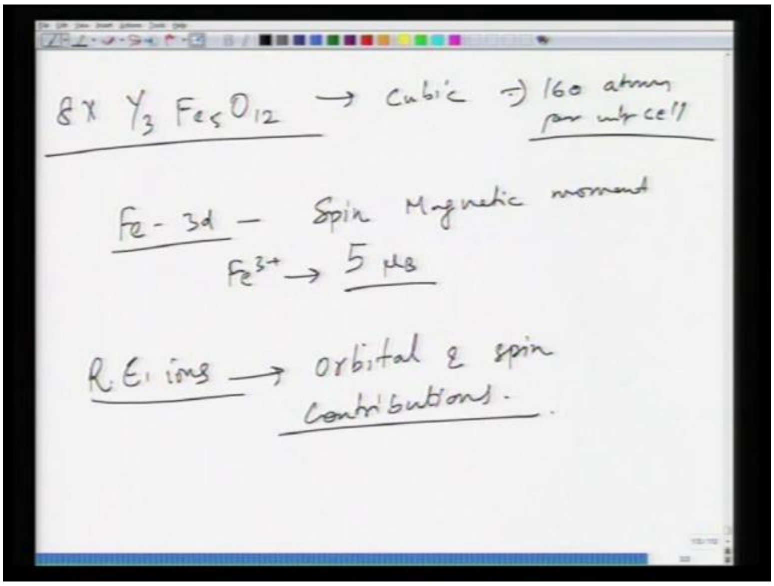

$8 \times Y_3 Fe_5 O_{12} \rightarrow$ Cubic $\rightarrow$ 160 atoms per unit cell

Fe - 3d – Spin Magnetic moment

$Fe^{3+} \rightarrow 5\ \mu_B$

R.E. ions $\rightarrow$ orbital & spin contributions.

So, you have y 3 Fe 5 O 12, the structure is cubic and the structure contains 8 formula units. So, 8 formula units multiplied by one, one of this. So, 8 formula units of y 3 Fe 5 O 12 make a cubic structure. So, this is a very large compound total of you can calculate 12 12 plus 5, 17 into 3, 7 to plus 3, 20, so that means 160 atoms per unit cell. This gives rise to very large, this give rise to very large structure which is highly tunable, magnetic structure. Now, here since iron is a 3 d ion, irons contribution mainly comes from spin spin magnetic moment because in iron, the orbital magnetic moments are quenched because of crystal field as we discussed earlier in the form of, in the case of paramagnetism. So, the only magnetic contribution to iron comes from a spin magnetic moment. So, as a result Fe 3 plus will have 3 mu B, 5 mu B. Sorry In case of in case of these rare earth ions, all lanthanides, you can say they have both, they are 4 F kind of atoms. So, as again if you recall the discussion on paramagnetism, they have both orbital and spin contributions. As a result the magnetic moment of these is quite different, from from those of iron.

So, it is, so it depends upon the strength of magnetism in these ions, which decides which is a crucial factor in governing the type of magnetism, that you get out of these compounds.

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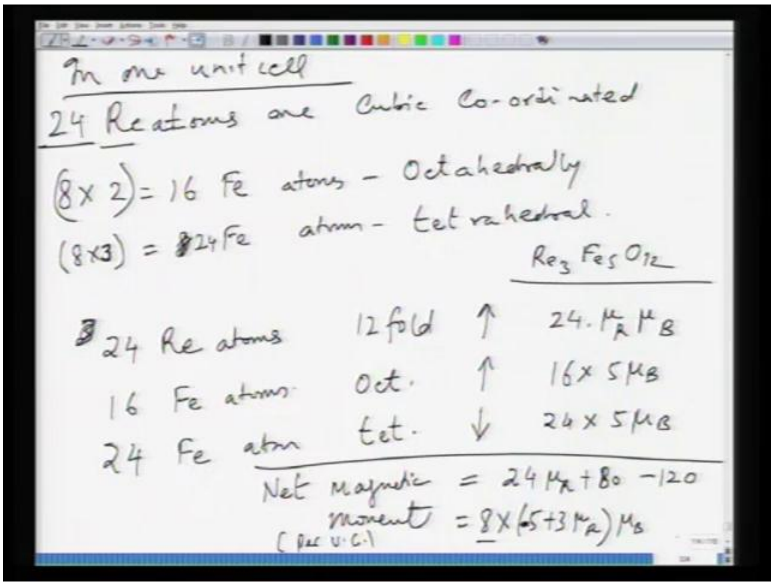

In one unit cell

24 Re atoms are Cubic Co-ordinated

$(8 \times 2) = 16$ Fe atoms - Octahedrally

$(8 \times 3) =$ ~~8~~24 Fe atom - tetrahedral.

$Re_3Fe_5O_{12}$

~~8~~24 Re atoms	12 fold	↑	$24 . \mu_R \mu_B$
16 Fe atoms	Oct.	↑	$16 \times 5 \mu_B$
24 Fe atm	tet.	↓	$24 \times 5 \mu_B$

Net magnetic moment (per u.c.) $= 24 \mu_R + 80 - 120$

$= 8 \times (-5 + 3 \mu_R) \mu_B$

So, what you have in this structure essentially is... So, here R atoms, R e atoms here, R e atoms are cubic coordinated, which means they have 12 fold coordination. Now, out of 5, so 3 R e atoms are cubic coordinated in, in so essentially, let me just put it this way. In 1 unit cell, so you have, since you have 8 formula units. So, 24 R e atoms are cubic coordinated and you have 8 into 2 is equal to 16 iron atoms octahedrally coordinated, and 8 into 1 8 iron atoms, as tetrahedral coordination. Now, here so basically 24 R e atoms you have, sorry.

Now, here you have essentially 8 into 3, so this should be 24 Fe atoms because the structure because of formula is, R e 3 Fe 5 O 12. So, as a result you have 2 iron sitting on octahedral sites and remaining 3 go on the tetrahedral. So, 24 iron atoms tetrahedral site, so please note that modification. So, you have 24 R e atoms going on 12 fold coordination, you have 16 iron atoms, which are octahedral coordination and you have 12 20, sorry you have 24 iron atoms, which are tetrahedral coordination. Let, if these 12 fold coordinated material atoms were spin up, they will give rise to some magnetic moment.

This magnetic moment would be 24 into mu R, mu R is the strength of magnetism in that lanthanide ion and this could be anything from 0 to any number higher onwards. So, mu R is the strength of moment of R ion multiplied by mu B and octahedral site you have spin down spin up again. This would be your 16 into 5 mu B, and this would be down, the tetrahedral is the one which is down, so this is 24 into 5 mu B. So, net magnetisation, so net magnetic moment to be precise, is equal to 24 mu R plus 80 minus 120. So, I can take of course, 3 out of it.

I can take 8 definitely out of it, because 8 will mean as 8 formula unit. So, it would be 8 multiplied by 5 minus 3 mu R. sorry So, you can say essentially this is minus 5 plus 3 mu R into mu B and of course, you take the mod to get the magnetisation. So, essentially you can take a spin down spin up and spin down, the way you want it. But the fact is one is a spin up, then another one will be the opposite is spin, will be spin down or vice versa.

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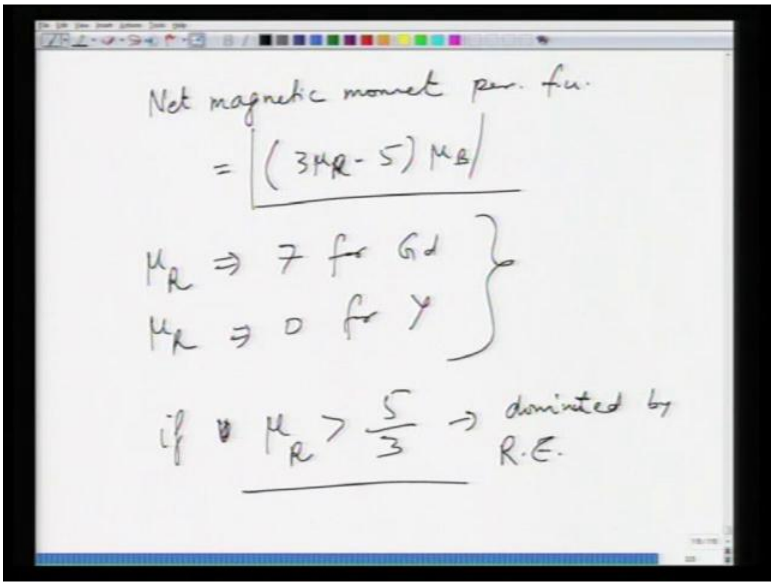

Net magnetic moment per f.u.

$$= \left| (3\mu_R - 5)\mu_B \right|$$

$\mu_R \Rightarrow 7$ for Gd

$\mu_R \Rightarrow 0$ for Y

if $\mu_R > \frac{5}{3} \rightarrow$ dominated by R.E.

So, essentially you can say the net magnetic moment is, per formula unit would be... So, we have calculated what is the magnetic moment per this is per unit cell. So, 8 unit cells multiplied by 3 mu R minus 5 into mu B will be the magnetic moment. So, per formula unit would be divided by 8. So, what you will have is essentially is, 3 mu R minus 5 into mu B, will be the net magnetic moment of a garnet, per formula unit. When you take the magnetic moment finally, you take the mod of it. So, positive or negative depending upon, how you calculate this sign will cancel each other.

And this mu R will be 7 for gadolinium and it is a 0 for yttrium. So, depending upon which ion you choose, you can tune the magnetisation of this material and then and the magnetic moment will be dominated by rare earth ions if, of course, you can see from that if mu R is greater than 5 by 3. If mu R is greater than 5 by 3, then dominated by R e ions, otherwise it is dominated by iron ions. So, this is how you work out the magnetic moment of garnet.

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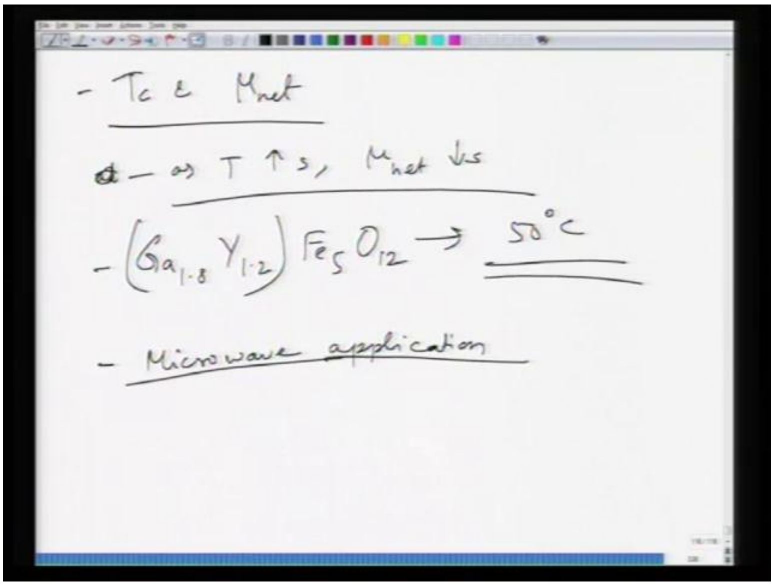

- T_c & μ_{net}
- as T ↑s, μ_{net} ↓s
- $(Ga_{1.8} Y_{1.2}) Fe_5 O_{12} \rightarrow$ 50°C
- Microwave application

Another thing which you can, which is possible to do in garnets is, both T c and mu net can be tunable by tuning the composition, and this is basically because of coupling between the rare earth ions and the iron ions. Typically as temperature increases the mu net decreases. So, as a result as a result for a strongly magnetic ions like gadolinium or terbium or diptherium, that is where the... And this is specially true for these ions basically, when you have these ions present in the system. In this in this context the gadolinium doped composition which is G d, which is G d 1.8, y 1.2 into iron 5 and oxygen 12.

As a rather stable magnetic moment and as a, and it has a temperature window of the operation of 50 degree centigrade. So, in this case, in garnets the temperature window of temperatures can be quite unstable. So, as a result you need to choose the composition, which give you rather stable window of operation and this is for garnet. Garnets are very useful for microwave applications, because they have high resistivity. So, as a result they have low process and they can be very useful for microwave frequencies. More importantly garnet can be prepared quite easily in the single crystalline poly crystalline form.

So, as a result fabrication is easier and it is very easy to tune the magnetic as well as structural characteristic of this material, by changing the composition. So, these are the three different kind of ferrites, that we have discussed today. We have discussed the iron iron containing or basically, spinel structured cubic cubic ferrites, which are essentially most more or less, most of most of them being iron containing a inverse spinels. They they have very large magnetisation, they also tend to have very large curie temperatures, which which we will see in the in the in the coming lecture. Then you have, what is called as hexagonal barium ferrite, which has which has very large magnetic moment, but it has very large magnetic anisotropy unlike cubic spinel ferrite.

Cubic spinel ferrites are not anisotropic and they are that is why soft ferrites. Whereas, barium ferrites, they are, they have large magnetic isotropy and they tend to be hard ferrites. So, they are used in applications where large co-ercivity is required. Similar, and then we had garnets, where it is a mixture of rare earth and iron containing material. As a result you have very large window of structure and magnetic tuning of the material. And they they typically are used for microwave applications, where losses are of great concern. So, we will finish today’s lecture here. In the next lecture, we will complete some of the remaining characteristics of these three different kind of ferrites, look at the properties and then finally, we focussed upon the applications in the next class.

Thank you.