Nano Structures and Nano Martials: Characterization and Properties
Prof. Anandh Subramaniam and Prof. Kantesh Balani
Department of Material Science and Engineering
Indian Institution of Technology, Kanpur

Lecture - 21
Electrical Magnetic and Optical Properties of Nano Materials (C4)

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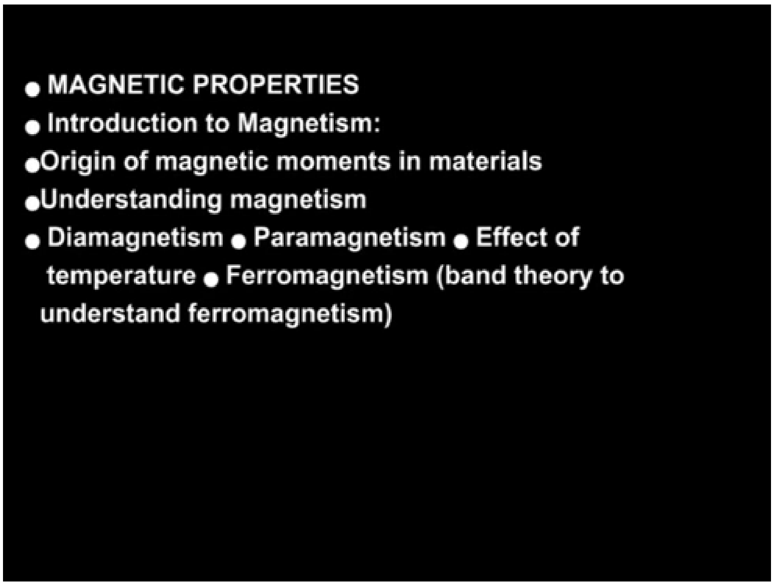

- MAGNETIC PROPERTIES
- Introduction to Magnetism:
- Origin of magnetic moments in materials
- Understanding magnetism
- Diamagnetism ● Paramagnetism ● Effect of temperature ● Ferromagnetism (band theory to understand ferromagnetism)

The next topic we take up is magnetism and nano materials.

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Magnetism in Nanomaterials

AdvancedReading

Principles of Nanomagnetism
A.P. Guimarães
Springer-Verlag, Berlin, 2009.

And students are very interested in learning more advanced topic in the area can consider the principle of nano magnetism. And this is very compact books gives you lot of detail information about magnetism in nano materials.

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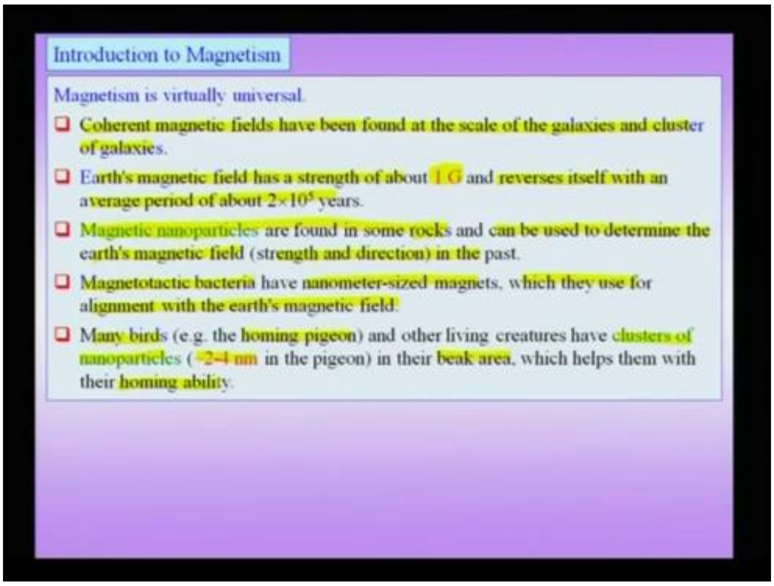

Introduction to Magnetism

Magnetism is virtually universal.

- ☐ Coherent magnetic fields have been found at the scale of the galaxies and cluster of galaxies.
- ☐ Earth's magnetic field has a strength of about 1 G and reverses itself with an average period of about 2×10^5 years.
- ☐ Magnetic nanoparticles are found in some rocks and can be used to determine the earth's magnetic field (strength and direction) in the past.
- ☐ Magnetotactic bacteria have nanometer-sized magnets, which they use for alignment with the earth's magnetic field.
- ☐ Many birds (e.g. the homing pigeon) and other living creatures have clusters of nanoparticles (~2-4 nm in the pigeon) in their beak area, which helps them with their homing ability.

As before we will take up some basics of magnetism first, followed by the changes, which occur when we go the nano scale. And we will discover very interesting and what you might call, properties which do not have an analog in the bulk scale, like super para magnetism, joint ferro magnetism, etcetera. We will also see that, the spin arrangement in certain nano magnetic nano structure can be very, very different from that of the bulk structures. If I use a phrase that magnetism is universal then, this would not be an understatement. It is been found that coherent magnetic field at the scale of galaxies and cluster of galaxies.

The origin of this is fully not understood yet, and there is still lot of work been done in this area, but even at the scale of galaxies in cluster of galaxies, you find coherent magnetic fields. Earth itself is a magnet, and earth’s magnetic field has a, it is not a very strong magnetic field, and has a strength of about 1 G, and interestingly it reverses itself with an average period of about a million years. Of course, this is an average period and there could be a smaller time period before reversal, and certain time period could be larger. And as we know today, perhaps the magnetic field as we talk now itself undergoing reversal.

Therefore, the strength of earth’s magnetic field is falling and this is perhaps signifies, the earth’s magnetic field direction is actually reversing that means, the north is going to south and south is going to north field. Magnetic nano particles are found in rocks and can actually be used to determine the earth’s magnetic field. So, how do we know that the magnetic field has been reversing? These are, because of magnetic nano particles, which are found in some special rocks, and from this we actually find out the earth’s magnetic field in strength and direction in the past.

Such kind of magnetic nano particles are also been used in what you might call plate tectonics wherein, actually see how the plates move, how they rotate, etcetera. Magnetotactic bacteria have again nano meter size magnet, which they use for alignment of the earth’s magnetic field. Another words, magnetic nano particles are also found in the biological world and there are two examples we cite here, one is the magnetotactic bacteria, the other what you might call homing pigeon.

Homing pigeon and many other birds also have clusters of nano particles and these have magnetic nano particles, and the size of these nano particles in the range of about 2 to 4 nano meter, and typically it is found in the beak area. And this is suppose to play important role in the homing ability or the ability to find direction and travel long distances without any other guidance. In other words, their guidance system is this magnetic nano particles, and this magnetic nano particle in conjunction with earth’s magnetic field gives in the direction, using which they can travel long distances, and actually even use it for migration.

So, we see that, magnetism is practically universal, it is found in the cosmic scale, it has found at the earth scale, it is also found in the biological world. Now, what is the origins of magnetism? So, anybody who has played around with magnets at the small age, knows that when you having current carrying conductor typically in the form of solenoid then, you actually have magnetic field.

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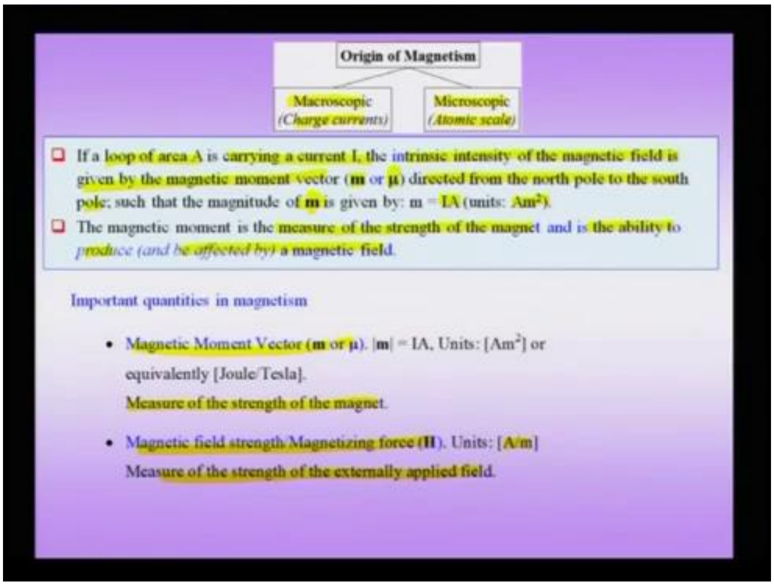

Origin of Magnetism

Macroscopic (*Charge currents*)

Microscopic (*Atomic scale*)

- ☐ If a loop of area A is carrying a current I, the intrinsic intensity of the magnetic field is given by the magnetic moment vector (**m** or **μ**) directed from the north pole to the south pole; such that the magnitude of **m** is given by: m = IA (units: Am^2).
- ☐ The magnetic moment is the measure of the strength of the magnet and is the ability to *produce (and be affected by)* a magnetic field.

Important quantities in magnetism

- Magnetic Moment Vector (**m** or **μ**). |**m**| = IA, Units: [Am^2] or equivalently [Joule/Tesla].
  Measure of the strength of the magnet.
- Magnetic field strength/Magnetizing force (**H**). Units: [A/m]
  Measure of the strength of the externally applied field.

So, there these macroscopic origins of magnetism, which comes from charge currents. The other magnetism, which we will focus about in this course, is the macro score origin which is coming from atomic scale. So, if you have a loop of area a, carrying a current I, the intrinsic intensity of the magnetic field is given by the magnetic movement vector, which is typically given as symbol m or mu and directed from the north pole to south pole such that, the magnitude of m is given by I into a.

Therefore, if you have a current carrying loop I of with an area a then, the magnitude of the magnetic movement is given by I into a and has units of ampere squares. This magnetic movement is a fundamental quantity in magnetism and is a measure of the strength of the magnet, and its ability to produce and be affected by a magnetic field. So, it is a inherit strength of a magnet, and if have an external magnetic field.

Then, how is this magnetic movement respond, this magnetic material going to respond the external magnetic field, and how much magnetic field will this material produce, is given by the strength m. We will also consider what you might call volume version of this, that is magnetic movement per unit volume in the next slide. We will also take up now certain other important quantities in magnetism, apart from this magnetic movement vector m or mu which we already seen, which is the measure of the strength of the magnet.

The other important quantity is the magnetic field strength or otherwise known as the magnetizing force, which is units of ampere per meter, and it is the measure of strength of an externally applied field. Typically when I do magnetization experiment, I apply the external magnetic field and this field can be measure in units of h.

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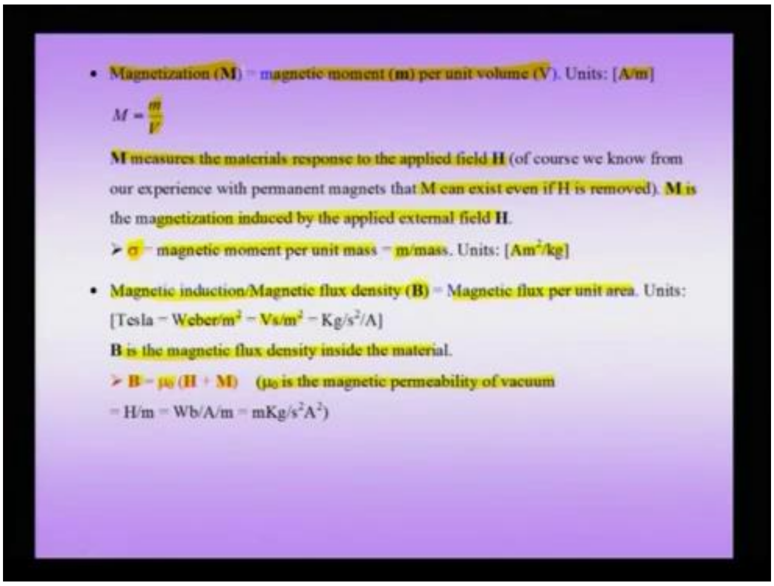

- **Magnetization (M)** = **magnetic moment (m) per unit volume (V)**. Units: [A/m]

  $M = \frac{m}{V}$

  M measures the materials response to the applied field H (of course we know from our experience with permanent magnets that **M can exist even if H is removed**). **M is** the magnetization induced by the applied external field **H**.

  - σ = magnetic moment per unit mass = m/mass. Units: [Am^2/kg]

- **Magnetic induction/Magnetic flux density (B)** = Magnetic flux per unit area. Units: [Tesla = Weber/m^2 = Vs/m^2 = Kg/s^2/A]

  B is the magnetic flux density inside the material.

  - **B = μ_0 (H + M)** (μ_0 is the magnetic permeability of vacuum = H/m = Wb/A/m = mKg/s^2A^2)

The other important quantity I have mentioned, typically it is not the magnetic movement, but the magnetic movement per unit volume, which is units ampere per meter. And this is given a symbol magnetization. So, magnetization is nothing but magnetic movement per unit volume, and deliberately we are avoiding the use of the symbol mu though sometimes we will use symbol mu for magnetize a magnetic movement, but as far as possible we will use try to use small m to confuse with the equivalent quantity which we will encounter shortly. m measures the material response to an external magnetic field, another magnetization is a measure of the response of a material to external magnetic fields, but we also have to know that m can exist even if h is removed.

In other words, magnetization can exist in permanent magnet even when there is no external field. So, this well known to us, that is why the origin of permanent magnetism. And m is the magnetization induced by an external field h. Often, we may use m or an equivalent quantity called the magnetic movement per unit mass which is given a symbol sigma, and it has units of m per mass which is ampere meter per square per k g.

Apart from magnetization, often an equivalent kind of quantity is the magnetic induction or a magnetic flux density b, which is defined as magnetic flux per unit area and has units of Weber per meter square or volt second per meter square in more fundamental terms. And B is the magnetic flux density inside the material. B is related to the previous two quantity which we defined h and m. By B is equal to mu 0, h plus m where mu 0 is magnetic permeability of vacuum.

Often a very fundamental question is asked, which is the more fundamental quantity, is it m? the magnetization or B which is the magnetic flux density. Though, there are two school of thought, in one school of thought m is concerned about the more fundamental quantity and B suppose to product of that, but in certain another school of thought B is concern the fundamental quantity and all the other quantities are derived from that. In this set of lectures, we will assume most of the time restrict our discussions to m that means, you will assume that m is the more fundamental quantity and work around it.

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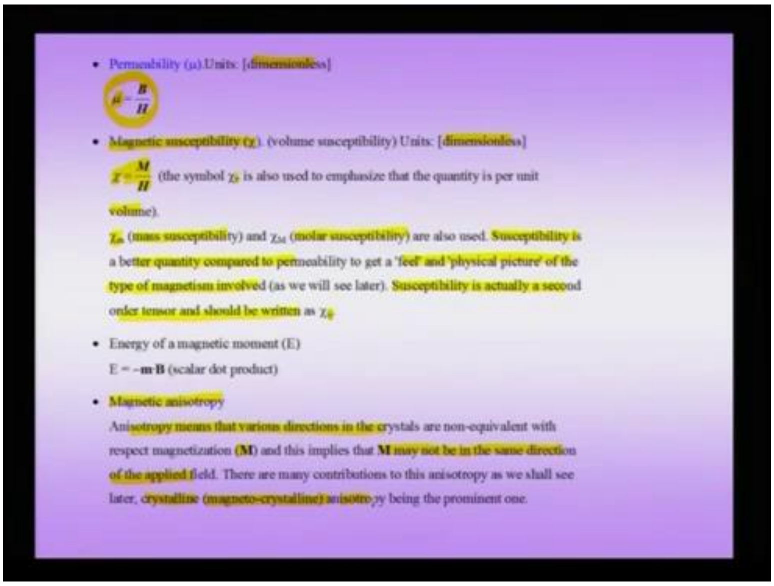

- Permeability (μ).Units: [dimensionless]

  $\mu = \frac{B}{H}$

- Magnetic susceptibility (χ). (volume susceptibility) Units: [dimensionless]

  $\chi = \frac{M}{H}$ (the symbol χ_V is also used to emphasize that the quantity is per unit volume).

  χ_m (mass susceptibility) and χ_M (molar susceptibility) are also used. Susceptibility is a better quantity compared to permeability to get a 'feel' and 'physical picture' of the type of magnetism involved (as we will see later). Susceptibility is actually a second order tensor and should be written as χ_{ij}

- Energy of a magnetic moment (E)

  E = −**m**·**B** (scalar dot product)

- Magnetic anisotropy

  Anisotropy means that various directions in the crystals are non-equivalent with respect magnetization (**M**) and this implies that **M** may not be in the same direction of the applied field. There are many contributions to this anisotropy as we shall see later, crystalline (magneto-crystalline) anisotropy being the prominent one.

So, another important quantity which is known as magnetic susceptibility chi and it is dimensionless kind of a number, and the ratio of m to h. In another words, if you have an external magnetic field h, what is the magnetism it produces m, there it responses of material to an externally magnetic, externally applied field, it response in terms of the magnetization. Sometimes subscript B is also added to be the susceptibility, because we are just to emphasis that the quantity we are talking about is what is known as the volume susceptibility.

And the reason we need to that is, that sometime x subscript m which is measure of, which is also called measure susceptibility and molar susceptibility are also used literature. If I want to compare 2 or 3 different kind of magmatic phenomena and want to understand the response of a material, susceptibility perhaps is a very good quantity, and it helps to get a feel and physical picture of the type of magnetism.

We will see lot of details of about this later, but typically if I have a paramagnetic material, the magnitude and the sign of the susceptibility will tell me that it is a paramagnetic material. If I am taking about a phenomena like diamagnetism, again that the sign and the magnitude will tell me of susceptibility will tell me that I am actually dealing phenomena like diamagnetism. In of course, technically susceptibility is a second order tensor and should be written with subscript i comma j.

As a equivalent quantity m by h for the case of B by the is called permeability, and it is again a dimensionless quantity. So, as I said, in this lecturer of lectures we will focus on m and h and chi and we will play lesser important to mu and B. Another important quantity we will deal with, is the quantity known as magnetic anisotropy. Anisotropy implies that the property in question is not equivalent in all the directions in. For suppose, I am talking about magnetization, this implies that the magnetism may not be same in all directions and the magnetization may not be in the direction of the applied field, so these are the two important things.

That means, even though I am applying a filed in certain direction, magnetization may appear in a certain different direction, which means there is an anisotropy. This also implies if you take an normal single crystal, there are easy and hard direction for magnetization and this of course, depends on kind of magnetic crystal you are talking about. For iron for instance the 001 direction is the easy direction of magnetization which changes to 110 and 111, for all other materials like cobalt and nickel.

And therefore, typically magnetic materials are anisotropic and the term used for this is called magneto crystalline anisotropy or sometime more casually as the crystalline anisotropy. There are other sources to magnetic anisotropy like the shape anisotropy, like the stress anisotropy etcetera. But without of course, adjective if this quantity magnetic anisotropic is used, we have to remember that this is arising, because of what you might call the magneto crystalline anisotropy or the anisotropy coming from the crystal scale.

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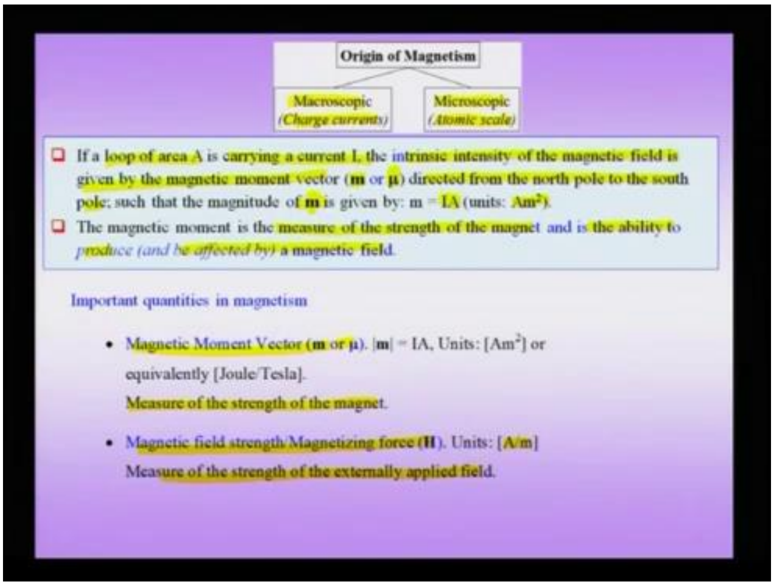

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So, let us summarize some of the important things we have talked so far number 1 is the magnetism can come from two important sources, from macroscopic currents or charge currents or from microscopic origins. The macroscopic currents is the more familiar one we are customize to, whenever we have a conductor especially in the form of loop then, if I multiply the current into the area of the loop then, the I get the quantity called magnetization. In other words, this current carrying loop is a magnet having north pole and a south pole. This magnetization, which we have defined so far is the measure of the strength of the magnet. So, if you want to say, how strong a magnet is, I will use this quantity called magnetization.

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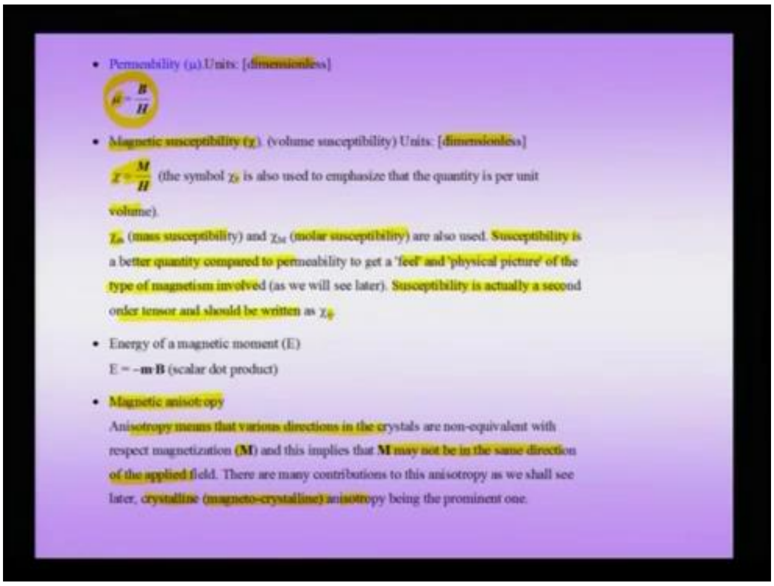

- Permeability (μ).Units: [dimensionless]

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The other important quantity in the field of magnetism are the magnetic field strength h, the magnetization m, the magnetic flux density B, the susceptibly chi which we said the very important material parameter which will discusses in detail later, and the permeability mu. And apart from this, we also talk about the magnetic anisotropy. So, these are the important quantities in magnetism.

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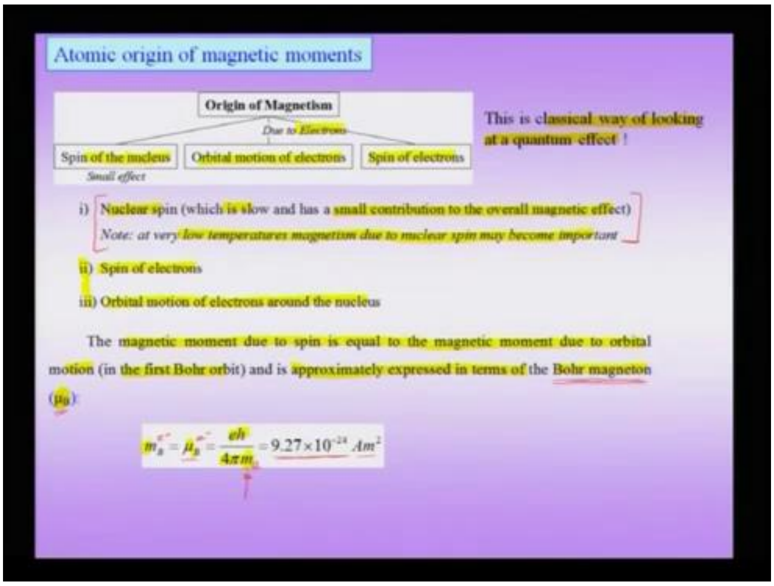

Atomic origin of magnetic moments

This is classical way of looking at a quantum effect !

i) Nuclear spin (which is slow and has a small contribution to the overall magnetic effect)
Note: at very low temperatures magnetism due to nuclear spin may become important

ii) Spin of electrons

iii) Orbital motion of electrons around the nucleus

The magnetic moment due to spin is equal to the magnetic moment due to orbital motion (in the first Bohr orbit) and is approximately expressed in terms of the Bohr magneton (μ_B):

$$m_s^{e^-} = \mu_B^{e^-} = \frac{eh}{4\pi m_e} = 9.27\times10^{-24}\ Am^2$$

Next we take up the atomic origins of magnetic movements, and we will note that there are three atomic origins of magnetic movements one due to nucleus, the other two due to the electrons. The one due to nucleus is, because of the, what you might call spin nucleus, the one due to electrons can either due to the spin of the electrons or can be, because of the orbital motion of the electrons. Now, we have to be a little careful here, because the spin is not like a rotating top, this is the intrinsic spin of an electron. And in some sense this is a classical way of looking at quantum phenomena like spin or angular motion of electron around the nucleus.

Now, typically, the nuclear spin and which is slow has a small contribution to the overall magnetic effect, and this is typically ignored in most of our discussions in this set of lectures. But we have to note that the very low temperature magnetization due to nuclear spin may become important and cannot be ignored. But in the set of lectures, we will accentually focus our attention on the magnetization appearing, because of the spin of the electron and that, because the orbital motion of the electron around the nucleus. Noting again that these are the actually what you might call not the regular spin, but the, what you might call the quantum mechanical origin of a spin.

Now, the magnetic movement due to a spin is equal to the magnetic movement due to orbital motion of course, here in the first Bohr orbit and is approximately expressed in terms of what is known as Bohr magnate or new subscript p. Of course, as I said, the mu is also has the symbol m, mu B or m B is given by e h by 4 pie m, and m is a of course, mass of electron here and it has a value of about 9.27 into 10 to the power minus 24 ampere meter square. This quantity the Bohr magneton is actually the fundamentally a very fundamental quantity, it is one of the fundamental constants of nature. And this is equivalent to what you might call for charge in the case of an electron. So, the charge is one aspect of an electron.

The other aspect of an electron is, because of its spin or angular momentum it is got and the associated magnetic movement with that spin has this value of the Bohr magneton, therefore, one of the fundamental constants of nature. Now, we looking at the this equation it must become clear since, the mass sits in the denominator and if I suppose I replace and I said that this, what you might call this magnetization is basically, because of an electron.

And instead of, instead of having defining the magnetization for an electron, if I replaces this mass with mass of an for instance, nucleus then I would know since the nucleus is much-much more massive than the given for an hydrogen atom then, an electron. And since, this quantity mass sits in the denominator, the magnetic movement arising, because of the nucleus is going to be small quantity. And therefore, because of this reason that, we can actually safely ignore nucleus spin effect in most of effect in most of the effect we will be talking about.

Now, just to summarize this important slide that, there are only three fundamental origins of magnetism and nay kind of phenomena we describe later has to come the basically from these three origins of magnetic movements. That means, the orbital motion of electron or the spin motion of electron or, because of the spin of the nucleus. So, all are the magnetism if we are going to be taking later likes ferro magnetism, anti ferro magnetism, etcetera, etcetera, will have to arise from these fundamental origins of magnetic movement.

And additionally, we have noted that there is a fundamental magnetic movement in nature which is called the Bohr magneton, which is given by e h by 4 pie m susceptive, which is the mass of the electron and it has the value of 9.27 into 10 power minus 24 ampere meter square.

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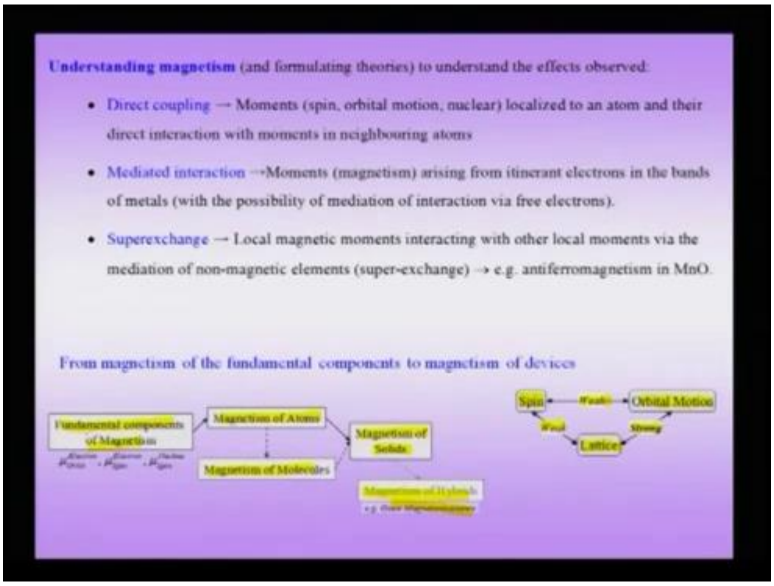

Understanding magnetism (and formulating theories) to understand the effects observed:

- Direct coupling → Moments (spin, orbital motion, nuclear) localized to an atom and their direct interaction with moments in neighbouring atoms
- Mediated interaction →Moments (magnetism) arising from itinerant electrons in the bands of metals (with the possibility of mediation of interaction via free electrons).
- Superexchange → Local magnetic moments interacting with other local moments via the mediation of non-magnetic elements (super-exchange) → e.g. antiferromagnetism in MnO.

From magnetism of the fundamental components to magnetism of devices

Now, how to do I start with this atomic magnetic movements, and understand magnetism in bulk material like a, what you might call a ploy crystalline specimen of iron. In fact, the material I could be described means could be more complicated material like, what you might call an hybrid. So, I could actually be describing magnetism of hybrids and later on we will see that certain important phenomena in the nano scale like giant magnetor assistance are phenomena which are found in hybrids.

Before I want to start with fundamental components of magnetism like, the orbital motion and spin motion of electron then, I want to travel the certain higher length scale and understand the magnetism of an atoms. Then, I want to be perhaps understand magnetism of molecule then, I want to understand magnetism of solids and finally, of course, I want to understand the magnetism of hybrids.

This is of course, an very hard work task it is very difficult task, and perhaps there are many-many steps which will not be able to pause for us to take up in this course. But there is one important step we need to note that, suppose I take this individual atomic magnetic movements and make an atom out of it that means, an atom now was many electrons therefore, there are many electrons orbiting around the nucleus, there are going to multiple spin involved. Never the less, all this finally, is going to give rise to the magnetic movement of atom, and this magnetic movement could be 0 or it could have certain positive value.

And more importantly when I take these atoms and make a crystalline solid out of it, for now we restrict ourselves to crystalline solid, then what happens to these magnetic movements? What happen is that, these spin motion can couple with the lattice, and this spin motion can couple with orbital motion in other words, the orbital magnetic movement may couple with this spin magnetic movement. And finally, there could be coupling between the orbital motion and the lattice. Because now I am talking the individual components of the magnetic movements in the form of spins and orbital motion making an atom, then I am putting together atoms in the form of lattice.

And therefore, all these couplings are possible. It is to be noted that most of the time, this spin lattice coupling is weak, this spin the orbital motion coupling is weak, but typically the orbital motion lattice coupling is strong. This is the a very important to note that implies most of the time, the orbital, the contribution to the orbital motion to the magnetic movement of a crystalline solid is going to be small.

Most of the time this coupling means that, when I apply an, as we said the magnetization is an ability to be affected by an external magnetic field, and this will be only affected if the spin is able to responds to the external magnetic field. And if these this orbital motion lattice coupling is very strong, the response is not going to be that good, it is going to be sort of frozen. And therefore, typically the orbital contribution to the magnetic movement to the solid is going to be small.

Now, this strong coupling when we go down to nano particle sizes, is going to get little weaker and we will notice, because of this reason, because now the lattice is very small, it is a small crystal. We will actually see that when you reduce the dimension of the crystal, the magnetic movement will actually increase. Even through, the fundamental contribution of magnetic movement is not changing, this coupling is actually reducing.

And therefore, we will see that the magnetic movement of nano particle etcetera reduce dimension system is going to be larger than there bulk counterpart, purely coming from the fact that now these kind of couplings operate. Now, another question we can ask is that, how can I understand magnetism? And I am talking about the magnetism means, I am talking about various phenomena of magnetism like, ferro magnetism, anti ferro magnetism etcetera.

Now, here we some, what you might call a broad overview or what you might call a simplified picture where we try to understand the magnetism in three language, of three terms. One is that there is actually direct coupling that means, that the movements, which are present in, which are localize to an atom, and the movements present in an neighboring atom talk directly to each other. And these kind of coupling typically leads to what you might call a ferro magnetic effect or there could be in other words an exchange coupling which leads to a parallel alignment of spins.

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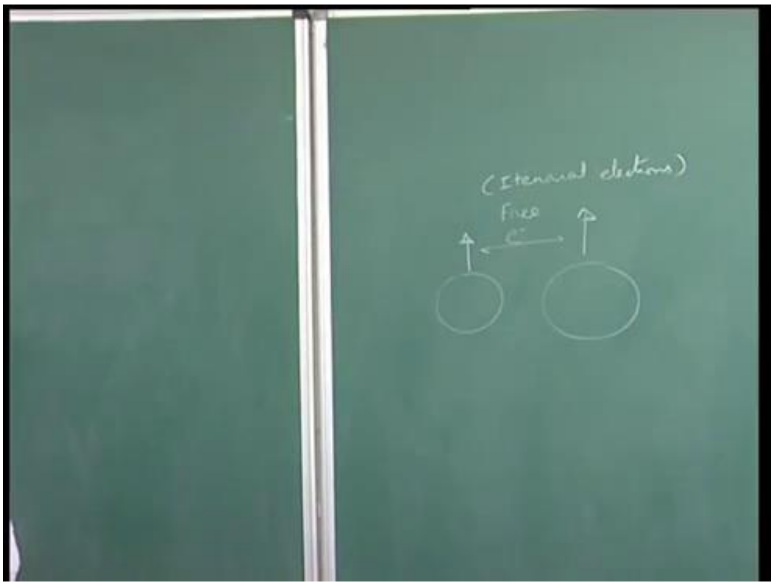

Now, I have net movement for an atom and now this is an atom and there is net magnetic movement associates with this atom. And there is another atom in the lattice and there is a net magnetic motion sector that and these two of course, in reality these way function of these two electrons actually overlap. But I am just drawing separate if I am actually talk to each other directly.

And therefore, you may have an special alignment of these kind of magnetic movement and this can we thought of an origin of instances of ferro magnetism. But sometimes even in this same material like iron there are more than one way of visualizing origin of this magnetism or the fact that it is the ferro magnetic. And this is called mediator interaction, wherein movements of magnetism arising from itinerant electrons in the bands of metals, they actually mediate the interaction of magnetic movements between the frozen electrons.

In other words, they are localize electrons to this, to this atom and there are localize electron to this atom and those localize electron and we will see little more details of what kind these electrons which are localized. And they may have an net magnetic movement. And what might happen this is, this mediation actually being carried out by free electrons or what you might call the itinerant electrons. So, itinerant electrons actually mediate the coupling between what you might call the localize electron, which are actually responses for what you might called ferro magnetic coupling.

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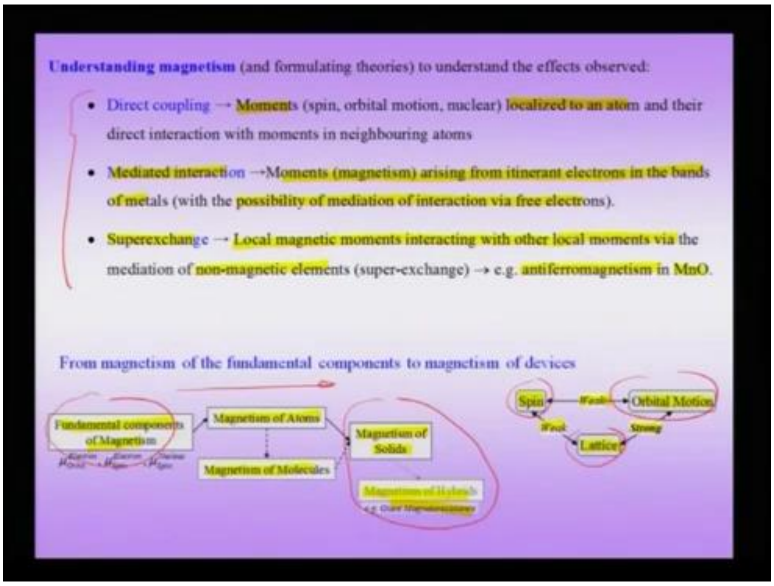

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There is another possibilities which is known as a super exchange, and this is suppose to responsible for anti ferro magnetism in materials like manganese oxide. That local magnetic movement interacting with other local magnetic movements and this mediation is done by an nonmagnetic elements, typically oxygen in these cases. This is called the super exchange phenomena and this is typically invoked when you want to understand anti ferro magnetism in oxides.

Therefore, if I want to understand magnetism there are, what you might called think interns, what you might called direct coupling that means, one magnetic movement localize in item is talking to another magnetic movement localize another atom. And when I am talking about localize magnetic movement, I imply now, it is the net resultant of all the magnetic movements coming. Some of them canceling internally like the opposite oriented spin etcetera, leaving finally, few a Bohr magnetons on magnetic movement per atom which is talking to a neighboring atom, where direct coupling.

Sometimes we may want to invoke what is the itinerant electrons in the bands which we know that the in the metal we have these bands whether they are free electrons. And these itinerant electrons may be actually be mediating, what you might call the exchange between two atoms. And finally, we have we invoked the concept of what is known as the super exchange to understand what you might called phenomena like anti ferro magnetism in manganese oxide.

So, we will have a little more to say about this spin arrangement when we talking about ferro magnetism and anti-ferro magnetism in the later slide. So, to summarize this another important aspect of this slide that, actually there is a very difficult journey involved in understanding the magnetism going from the magnetism of the fundamental component to the magnetism of solid and hybrids. And here we restrict ourselves to crystalline solid.

So, this is a difficult journey, but important cog in this journey is the fact that there is a coupling between the spins, the lattice and the orbital motion. And out of the three, the important coupling is the strong coupling between the orbital motion in the lattice, which is actually, what you might call quenching the orbital magnetic movement, which means that I am left with not the total potential magnetic movement for every atom in the crystal solid, but the actual value is actually reduce with respect to total magnetic movement.

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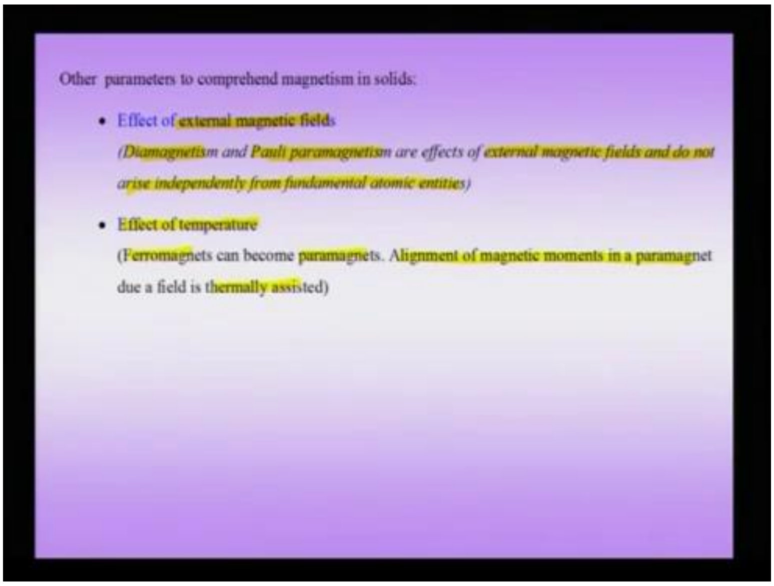

Other parameters to comprehend magnetism in solids:

- Effect of external magnetic fields

  (Diamagnetism and Pauli paramagnetism are effects of external magnetic fields and do not arise independently from fundamental atomic entities)

- Effect of temperature

  (Ferromagnets can become paramagnets. Alignment of magnetic moments in a paramagnet due a field is thermally assisted)

Two other important parameters are required when you want to understand magnetism in solids, one is the effect of external magnetic fields, another words if a material does not respond to external magnetic field then I would not call it a magnetic material. And the second important effect is the effect of temperature. And phenomenal like diamagnetism and poly para magnetism are effects of external magnetic fields and do not arise independently.

So, far we have seen this three important atomic entities contribute of magnetism, like important magnetism like ferro magnetism and anti-ferro magnetism. But there are two of them which arise purely, because the effect of external effect field, these are diamagnetism and poly para magnetism. And we will see that we discussing more about these other forms of magnetism in this course other than these two phenomena which had diamagnetism and poly para magnetism.

But never the less, we have to note that the external magnetic field can itself be a source of magnetization in a material. Though often, this is a very weak effect compare to some of these stronger effects like ferro magnetism. Effect of temperature we will see is very-very important, in another words, if I heat ferro magnetic like iron above the curic temperature, it will become a parameter.

In another words, an additionally we have to note that suppose, I have a material which is in the like iron and or if you take a paramagnetic material like oxygen and apply the external magnetic field, the effect of an external magnetic field is to apply a torque on the magnetic movement which is now randomly oriented. This torque actually will lead to, what you might call precision of the magnetic field and not alignment of the magnetic field. And therefore, if I need alignment then, this alignment itself is actually assisted by what you might call the thermal disordering effect of spins.

Therefore, effect of temperature and understanding magnetism is very, very important, so whenever I am talking about magnetism, I need to know how magnetic material is going to respond to external magnetic field and how temperature plays an important role towards understanding magnetism or magnetic state of material.

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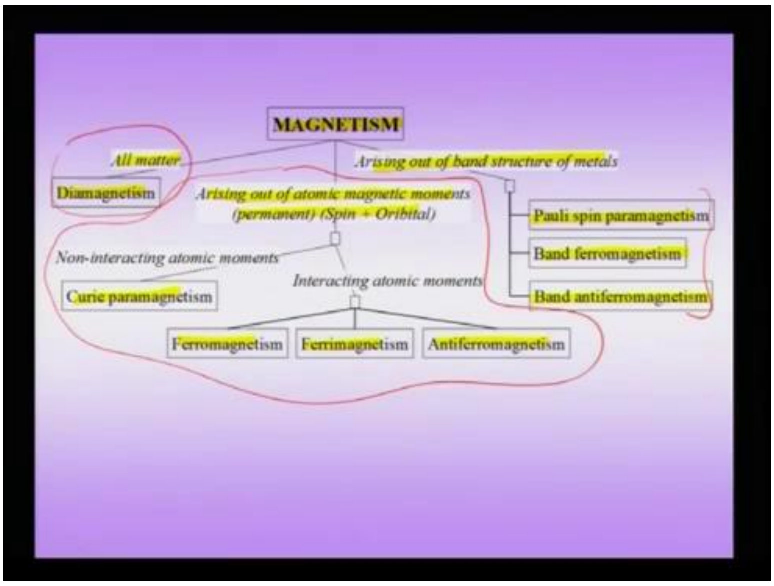

MAGNETISM

All matter

Diamagnetism

Arising out of atomic magnetic moments (permanent) (Spin + Oribital)

Non-interacting atomic moments

Curie paramagnetism

Interacting atomic moments

Ferromagnetism

Ferrimagnetism

Antiferromagnetism

Arising out of band structure of metals

Pauli spin paramagnetism

Band ferromagnetism

Band antiferromagnetism

Magnetism, can if you want to understand the branches of magnetism, there are three branches. One you may call which is now pointed out diamagnetism which is the property of all matter. The second is what you have been talking so far that arising out of magnetic movement, the spin and orbital motion of electrons.

And this is what you give rise to our familiar kinds of magnetism, like ferromagnetism, ferri magnetism, anti ferro magnetism, and Curie para magnetism. But there is a third class which is arising purely, because of band structure in materials and these include the ploy spin paramagnetism, the band ferromagnetism, and the band anti ferro magnetism.

Most of these lectures we will actually be focusing on the central branch which is this branch, and we will not spend much time on the magnetism arising out of bond structure material. But we will involve the band structure of metals, even to understand the simple phenomena like what you might call the non integral magnetic movement in very simple material like iron.

So, we have to invoke the concepts of band, but we can still understand magnetism in ferro magnetism in iron using some of the common, what you might called localize movement concept, while if the details actually involve bands. We will briefly talk about the diamagnetism though we will not take up the concept of diamagnetism in nano material in any kind of detail.

So, in this set of lectures, we will focus on the middle branch in which we will talk about those magnetic effect which can essentially can understood using what our familiar language of atomic magnetic movements. Though, some of these effects are equally important and they also have to be kept in mind when you are talking about magnetism as a global phenomena.

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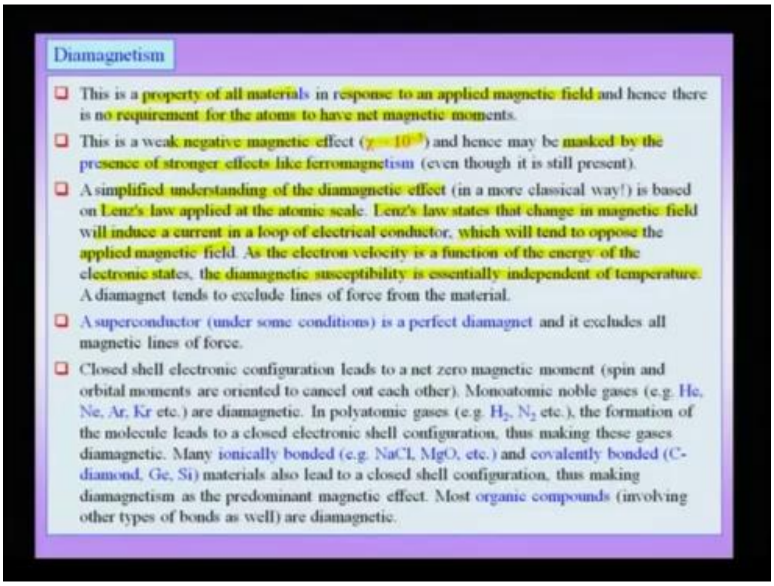

Diamagnetism

- ❑ This is a property of all materials in response to an applied magnetic field and hence there is no requirement for the atoms to have net magnetic moments.
- ❑ This is a weak negative magnetic effect ($\chi \sim 10^{-5}$) and hence may be masked by the presence of stronger effects like ferromagnetism (even though it is still present).
- ❑ A simplified understanding of the diamagnetic effect (in a more classical way!) is based on Lenz's law applied at the atomic scale. Lenz's law states that change in magnetic field will induce a current in a loop of electrical conductor, which will tend to oppose the applied magnetic field. As the electron velocity is a function of the energy of the electronic states, the diamagnetic susceptibility is essentially independent of temperature. A diamagnet tends to exclude lines of force from the material.
- ❑ A superconductor (under some conditions) is a perfect diamagnet and it excludes all magnetic lines of force.
- ❑ Closed shell electronic configuration leads to a net zero magnetic moment (spin and orbital moments are oriented to cancel out each other). Monoatomic noble gases (e.g. He, Ne, Ar, Kr etc.) are diamagnetic. In polyatomic gases (e.g. H_2, N_2 etc.), the formation of the molecule leads to a closed electronic shell configuration, thus making these gases diamagnetic. Many ionically bonded (e.g. NaCl, MgO, etc.) and covalently bonded (C-diamond, Ge, Si) materials also lead to a closed shell configuration, thus making diamagnetism as the predominant magnetic effect. Most organic compounds (involving other types of bonds as well) are diamagnetic.

As I just pointed out diamagnetism is a property of all materials. So, it is ivicutous in all materials, and it is a response to a externally applied magnetic field and that means that there is no requirement on the type of atoms or the atoms to have any net magnetic movements.

So, it is just a property of matter and therefore, they need not the, these atoms need not have net residual magnetic movement like in the requirement for the case of ferromagnetism. This is the weak negative magnetic effect, the susceptibility is negative and of the order of 10 power minus 5. So, this is the negative susceptibility, in other words diamagnetic otherwise the reason the word dia is used, because it opposes your externally applied field, and usually this is masked by presence of other stronger effect like ferro magnetism.

So, whenever we talk about ferro magnetic material, there is this underlying diamagnetic effect in this material also, this weak susceptibility which is the negative susceptibility, but since the magnitude of the susceptibility is very small, usually ignore this and we only talk about the effect which is coming from ferro magnetism. A simplified way of understanding diamagnetic effect, which is something like a classic way of using is the Lenz’s law applied at the atomic scale. Wherein, Lenz’s law states that, the change in the magnetic field will induce the current in loop of the electrical conductor, which will tend to oppose the append magnetic field.

That means, the material when you change the magnetism will oppose by putting out a magnetic field in the opposite direction. And this can be thought of as an election velocity is a function of the energy of the electronic states, the diamagnetic susceptibility in essentially independent of temperature. So, it is like schematically we have shown that of course.

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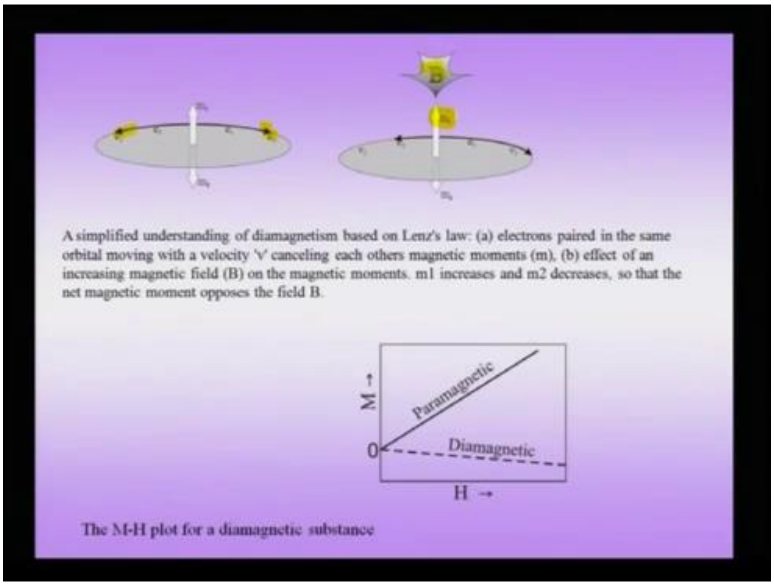

A simplified understanding of diamagnetism based on Lenz's law: (a) electrons paired in the same orbital moving with a velocity 'v' canceling each others magnetic moments (m), (b) effect of an increasing magnetic field (B) on the magnetic moments. m1 increases and m2 decreases, so that the net magnetic moment opposes the field B.

The M-H plot for a diamagnetic substance

there are electrons moving in this direction with velocity, and there is an electron moving in this direction, and these velocities are equal. But when I applied an external magnetic field, there is an imbalance created and this imbalance tend to cause, and this of course I am talking about the material which the spins are balancing out that means, orbital spin are angular momentum or the spin magnetic contributions are canceling out.

Therefore, there is no residual magnetic movement, only then this effect is nicely observed. But when you apply a change in magnetic field, you see that this m 1 becomes larger than m 2 and therefore, this material response by putting out magnetic field which is opposing your applying.

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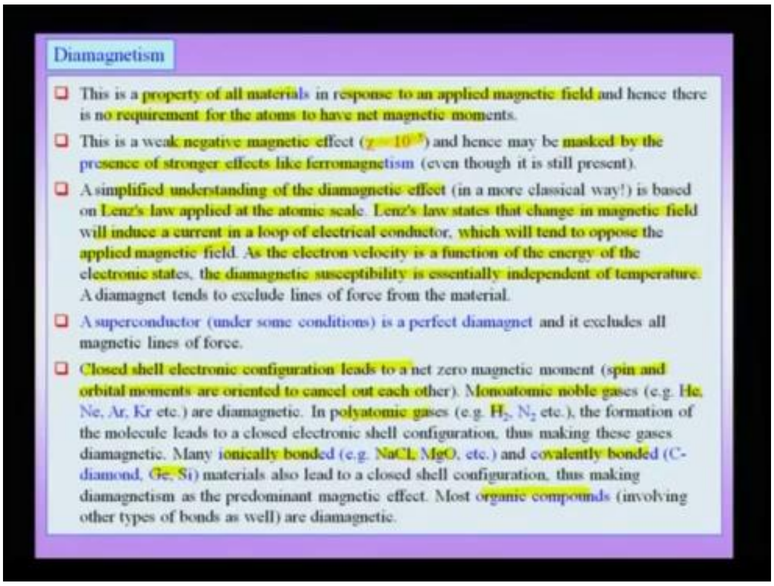

Diamagnetism

- This is a property of all materials in response to an applied magnetic field and hence there is no requirement for the atoms to have net magnetic moments.
- This is a weak negative magnetic effect ($\chi \sim 10^{-5}$) and hence may be masked by the presence of stronger effects like ferromagnetism (even though it is still present).
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Typically this kind of effect is observed in closed shell electronic configuration and that means, the spin an orbital movement cancel out each other. And there are nice example these for instance helium which are monoatomic noble gases, polyatomic gases like hydrogen. Then, there are other materials like ionically bonded material like sodium chloride, magnetism oxide, covalently bonded martial like germanium and silicon are also diamagnetic and many organic compounds also are diamagnetic.

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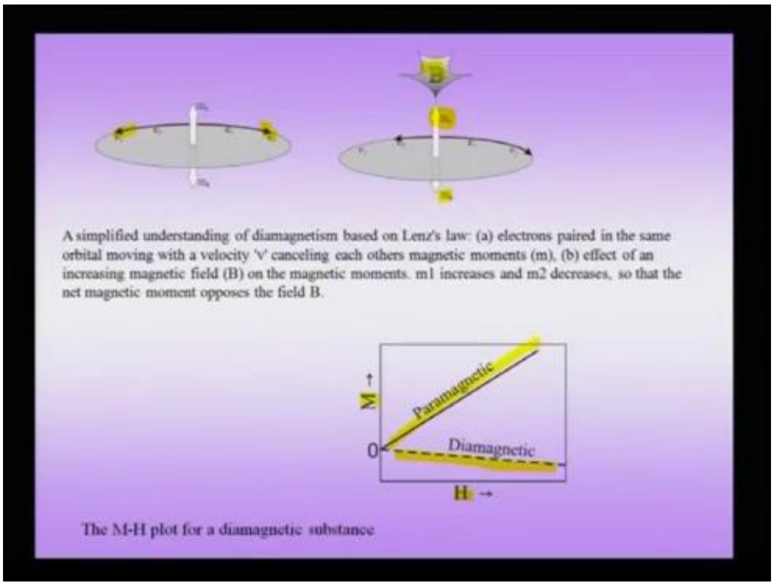

A simplified understanding of diamagnetism based on Lenz's law: (a) electrons paired in the same orbital moving with a velocity 'v' canceling each others magnetic moments (m), (b) effect of an increasing magnetic field (B) on the magnetic moments. m1 increases and m2 decreases, so that the net magnetic moment opposes the field B.

The M-H plot for a diamagnetic substance

But since, we are not going to talk too much about diamagnetic effect of nano materials, we will skip it for now, except noting that this is a ubiquitous effect found in all kind of materials and this is susceptibility in an M-H plot slope here we already noted called the susceptibility is negative and small. And later on, we will be comparing it with para magnetic susceptibility, which has got a slightly larger value and positive.

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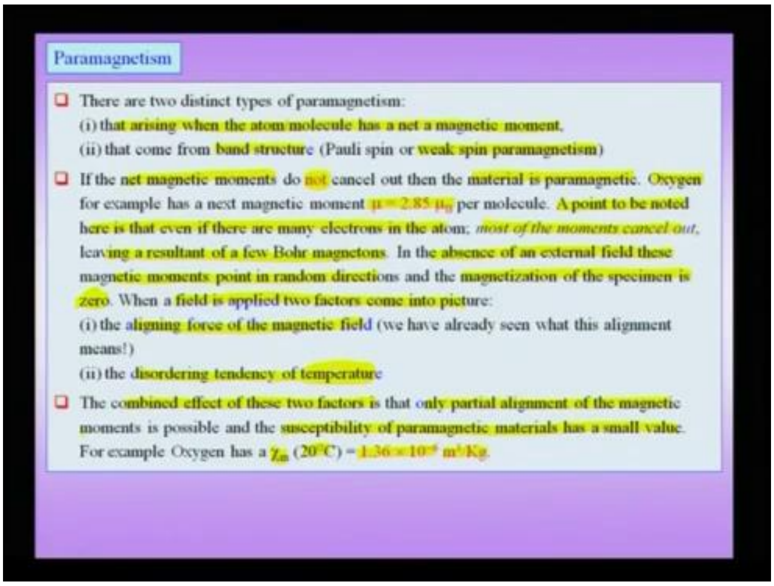

Paramagnetism

- There are two distinct types of paramagnetism:
  (i) that arising when the atom molecule has a net a magnetic moment.
  (ii) that come from band structure (Pauli spin or weak spin paramagnetism)
- If the net magnetic moments do not cancel out then the material is paramagnetic. Oxygen for example has a next magnetic moment $\mu = 2.85\ \mu_B$ per molecule. A point to be noted here is that even if there are many electrons in the atom; *most of the moments cancel out*, leaving a resultant of a few Bohr magnetons. In the absence of an external field these magnetic moments point in random directions and the magnetization of the specimen is zero. When a field is applied two factors come into picture:
  (i) the aligning force of the magnetic field (we have already seen what this alignment means!)
  (ii) the disordering tendency of temperature
- The combined effect of these two factors is that only partial alignment of the magnetic moments is possible and the susceptibility of paramagnetic materials has a small value. For example Oxygen has a χ_m (20°C) = 1.36×10^{-6} m³/Kg.

The next important magnetic phenomena is para magnetism, and this is important from two aspects, because it arises when the atom or molecule has a net magnetic movement. Additionally paramagnetic effects can come from what is might call the band structure and we had noted that before that actually when you noted that, it can either you can have para magnetism coming, which is called Curie para magnetism. Or there is an addition form which is coming from the band structure which is called the poly spin para magnetism.

And this poly spin para magnetism is also called the weak spin para magnetism. In the case of a para magnet, the net magnetic movement of atom do not cancel out and the material is then said to be para magnetic. A nice example of this is oxygen and which has net magnetic movement of 2.85 mu B, where mu B noted was the Bohr magneton, which is the fundamental quantity which measures the magnetic movement or fundamental unit of magnetic movement. A point to be noted here that even if their many electron in the atom which is the case of the oxygen atom, most of the movements cancel out leaving out of few Bohr magnetism as the net magnetic movement.

So, this is the important thing and that means, that even through there are many-many electron in any given atom, only the net magnetic response the material is only the few Bohr magnetons. In the absence of the external magnetic field, these magnetic movement points in the random direction and the magnetization of the specimen is 0. These materials are called paramagnetic, because in normal circumstances suppose, I had the region where I enclose a gas oxygen gas then, I would not find any magnetization from this. Because even through the individual atoms are carrying the magnetic movement, what does happening is there all randomly pointing, because of thermal motion of course, motion of molecules in this case.

And if we talking about a solid material even then, if it is a para magnetic material, this overall there is no, there is random orientation of the magnetic spins, and that implies that there is no net magnetization for the material. Whenever we apply a field of course, there is an aligning tendency for this magnetic movements. And there are two things which we need to note is, there is of course, aligning force of the magnetic field, but additionally the disordering tendency of temperature is constantly present.

This is very-very important, because later on we will be seeing the phenomena like super para magnetism, where the effect of temperature tends to win, when we go down to the small particle sizes. Even than that we talking about in material like ferromagnetism. In a para magnetic material, even through each atom has got some net magnetic movement, there is no tendency for neighboring atoms to align parallel, so there is that tendency is missing. Each atom has a magnetic movement, and when I apply a magnetic field only then there is a tendency for parallel alignment, so this is a paramagnetic material. But later on when we talk about ferromagnetism, there is a natural tendency for magnetic movements to actually align within this solid.

So, always there is an external magnetic field which is trying to align the magnetic movements and there is this effect of temperature which is trying to disordering. But also we have seen that, even in when we want to align in spins, actually temperature plays an important role there, because if you just apply a field on a magnetic movement then, there will be only precision and there will be no alignment.

So, this alignment actually recur help from temperature. The combined effect of this magnetic field and the disordering effect of temperature, only means that there is only partial alignment of the magnetic movements that means, there is no complete alignment in a paramagnet. A paramagnetic movement never completely get align at any reasonable positive kelvin temperature, and the susceptibility of paramagnetic materials usually small. For the oxygen at 20 degree celsius has a susceptibility of 1.36 into 10 power meter cube per kg. So, this, so it seems that in para magnetic material since, there is no inherent tendency for magnetic, adjacent magnetic coming for adjacent atoms to align.

The overall effect is that this susceptibility is very, very small, and this susceptibility is a positive quantity, because the alignment is along the magnetic field unlike the case of diamagnetism where the tendency is to oppose the external applied negative field. Now, when we are talking about the para magnetism, it is important to differentiate two kinds of paramagnetics.

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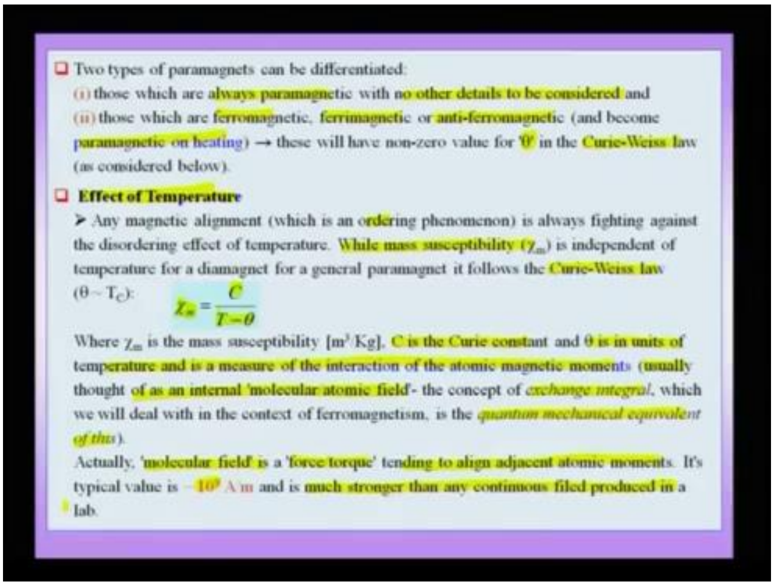

❑ Two types of paramagnets can be differentiated:

(i) those which are always paramagnetic with no other details to be considered and

(ii) those which are ferromagnetic, ferrimagnetic or anti-ferromagnetic (and become paramagnetic on heating) → these will have non-zero value for 'θ' in the Curie-Weiss law (as considered below).

❑ **Effect of Temperature**

➢ Any magnetic alignment (which is an ordering phenomenon) is always fighting against the disordering effect of temperature. While mass susceptibility (χ_m) is independent of temperature for a diamagnet for a general paramagnet it follows the Curie-Weiss law ($\theta \sim T_C$):

$$\chi_m = \frac{C}{T-\theta}$$

Where χ_m is the mass susceptibility [m^3/Kg]. C is the Curie constant and θ is in units of temperature and is a measure of the interaction of the atomic magnetic moments (usually thought of as an internal 'molecular atomic field'- the concept of *exchange integral*, which we will deal with in the context of ferromagnetism, is the *quantum mechanical equivalent of this*).

Actually, 'molecular field' is a 'force torque' tending to align adjacent atomic moments. It's typical value is $\sim 10^9$ A/m and is much stronger than any continuous filed produced in a lab.

Those which are always paramagnetic and wherein there we need not be consider any other kind of detail, and those which are ferromagnetic ferrimagnetic and anti-ferromagnetic and which become paramagnetic on heating. Like you take an iron sample at room temperature it is ferromagnetic, you heat it up then, it becomes paramagnetic.

This kind of a para magnet is different from a paramagnet which is always paramagnetic and wherein there is no ferromagnetic ability on cooling down. Because when we later on when we in the next slide, when we plot this quantities, we will note that for a material which is just paramagnetic, the theta will be having a 0 value which will define what is theta soon. And this obeys a called as Curie law while a material which is ferro magnetic which became paramagnetic will obey at slightly different law which is called as Curie Weiss law.

So, I have to wonder, if this material I am talking about which is paramagnetic was always paramagnetic even on cooling or was it a ferromagnetic which are on ferrimagnetic or anti-ferromagnet which is heated up to actually cause this para magnetism. So, the effect of temperature which we told is an effect of actually causing disordering, and the when we plot the mass susceptibility for a material like, so the effect of the temperature on paramagnet is actually different from the effect of a temperature on a diamagnetic material.

Because the masses susceptibility for a diamagnetic material does not depend on the temperature, while the mass susceptibility of paramagnet can be given by what is known as Curie Weiss law which is given as chi m, the mass susceptibility given by constant C dived by T minus theta. Where T is temperature and theta also have units of temperature, C is also called as the Curie constant, and theta we shall see the value of theta will differentiate a material like we said which is always paramagnetic from an material like we said which always paramagnetic from a material which is ferromagnetic, which is paramagnetic and also can be used to differentiate material which is anti-ferromagnetic. Theta has units of temp and it is the measure of interaction of the atomic magnetic movements.

So, in a normal paramagnet, there is no like a oxygen there is no interaction of atomic magnetic movements. And this theta can also be thought of as a internal molecular or atomic fields. So, this concept goes back to Weiss, so Weiss has made two important contributions to magnetic, the field of magnetism, one of them was the introduction of this concept of molecular field and the other concept was the concept of domains. Because we ask the question, that iron is actually magnetic, all there are atomic magnetic movement are parallelly align.

But you take any normal magnetic sample, it does not attract any other magnetic sample. The reason is that it is divided into domains and therefore, the internally all the magnetic field are cancelled and there is no net external field. So, this is one of the important concepts proposed by Weiss long time back, and this concept is very similar to the concept of an exchange integral which is a quantum mechanical equivalent of this.

So, this molecular field is older concept at the quantum mechanical equivalent is the exchange integral. This molecular filed is actually a torque then, this is not a field, but actually a force or a torque tending to align a adjacent magnetic movements. We said that there is a tendency for parallel magnetic movement to actually align or either parallelly or anti-parallelly. Then, you get the important magnetic effects like ferromagnetism and anti-ferromagnetism. Its value is very-very high of the order of 10 power 9 ampere per meter, and this is much stronger than any continues field produced in the lab.

So, this molecular fields though its a force or a torque, is much is much-much larger than anything which manners produce in the continues film. Then of course, very strong field which can be produced in the very small time frame, like you can produce the mega gauze in a fem to second. But if you want to have continuous field which are the much longer than fem to second time scale, then it becomes difficult to maintain such kind of fields.

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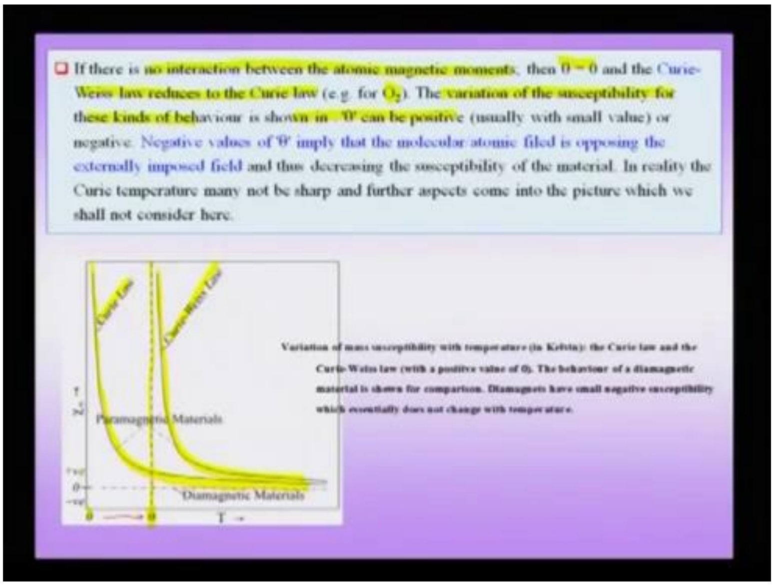

☐ If there is no interaction between the atomic magnetic moments, then θ = 0 and the Curie-Weiss law reduces to the Curie law (e.g. for O_2). The variation of the susceptibility for these kinds of behaviour is shown in . 'θ' can be positive (usually with small value) or negative. Negative values of 'θ' imply that the molecular atomic filed is opposing the externally imposed field and thus decreasing the susceptibility of the material. In reality the Curie temperature many not be sharp and further aspects come into the picture which we shall not consider here.

Variation of mass susceptibility with temperature (in Kelvin): the Curie law and the Curie-Weiss law (with a positive value of θ). The behaviour of a diamagnetic material is shown for comparison. Diamagnets have small negative susceptibility which essentially does not change with temperature.

Now, this equation chi m where T minus theta can be plotted for either, we said para magnet, which is always a paramagnet in which case you observe a law called as Curie law and this is the variation of the mass susceptibility with temperature. In other words, it false asymptotically with temperature.

On the other hand, the other material, which have a positive value of theta, and these are the materials where this concept of a molecular filed has to be invoked. And in such matetrials, again the law is very-very similar to the Curie law and this is called the Curie Weiss law, which is what we wrote wherein this theta has a positive value and not a 0 value. So, there are two possibilities here, both the possibilities have very asymptotic dependence on temperature of the mass susceptibility in other words, susceptibility falls with the temperature.

And let us note that, if there are, there is no interaction between the atomic magnetic movements then, theta is 0, and the Curie Weiss law to reduces to what is known as the Curic law, and this is what you observe for the martial like oxygen. The variation of susceptibility for these kind of behavior, there are two behavior which you are seeing is shown in figure below and negate. So, if the theta is positive, what we are talking about is the ferro-magnetic material, which has become paramagnetic.

In other words, there is a internal molecular field which is tending to align this materials, but since, you have heated the top, the thermal disordering effects are one over. And never the less, the masses susceptibility of such paramagnet follows similar to the Curric law, but it is now shifted from the origin by a value which is theta, which is now in the units of temperature.

This theta becomes negative for anti-ferromagnetic materials; that means, that you can use this value of theta itself as a discriminator whether it is just paramagnetic material or it is an anti-ferro magnetic material which became paramagnetic or ferromagnetic material which became paramagnetic. Of course, whenever I am talking about the disordering temperature like Curie temperature, this may not actually be sharp and we have to worry about other aspects like local clusters, which may for one instance suppose a heat of ferromagnetic, it is expected to become paramagnetic above the Curie temperature. But then there may be still local clusters which are still aligned and therefore, the curve may not be sharply fall down to 0, and we have to worry about other affects.

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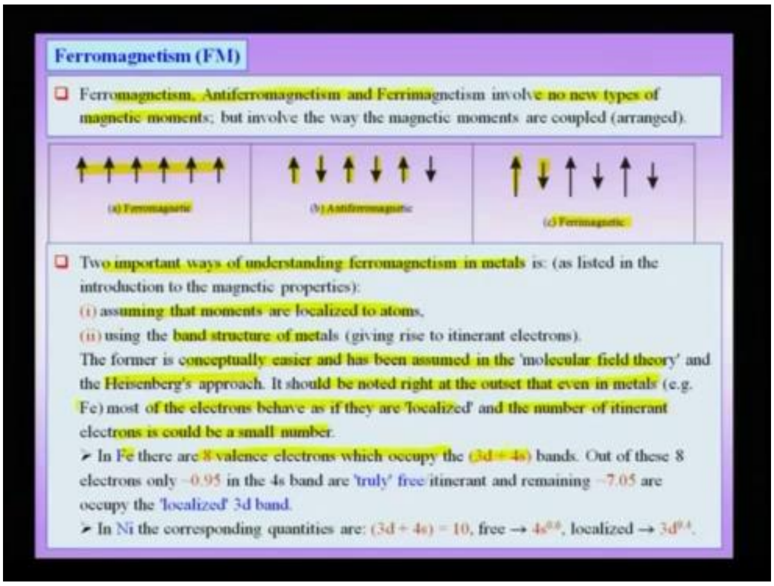

Ferromagnetism (FM)

- Ferromagnetism, Antiferromagnetism and Ferrimagnetism involve no new types of magnetic moments; but involve the way the magnetic moments are coupled (arranged).

- Two important ways of understanding ferromagnetism in metals is: (as listed in the introduction to the magnetic properties):
  (i) assuming that moments are localized to atoms.
  (ii) using the band structure of metals (giving rise to itinerant electrons).
  The former is conceptually easier and has been assumed in the 'molecular field theory' and the Heisenberg's approach. It should be noted right at the outset that even in metals (e.g. Fe) most of the electrons behave as if they are 'localized' and the number of itinerant electrons is could be a small number.
  - In Fe there are 8 valence electrons which occupy the (3d + 4s) bands. Out of these 8 electrons only ~0.95 in the 4s band are 'truly' free itinerant and remaining ~7.05 are occupy the 'localized' 3d band.
  - In Ni the corresponding quantities are: (3d + 4s) = 10, free → $4s^{0.6}$, localized → $3d^{9.4}$.

Now, we come to the most important effect, which is ferro magnetism. And we know that of course, you have pointed out that you have compass and this is align by earth magnetic field and this compass is nothing but a ferro magnet which is a permanent magnet.

The three forms starting from the atomic magnetic movement which has the tendency to align, giving rise to three forms of magnetism, one is ferromagnetism wherein all the magnetic movements have equal strength and they are align parallelly. The second is the anti-ferromagnetic wherein the magnetic movement have equal strength, but they are align in the opposite direction. The third possibilities ferrimagnetic which is similar to ferromagnetic wherein there is net magnetic movement, unlike the anti-ferromagnetic case where everything cancels out. But this net magnetic movement is smaller, because there is another anti parallel arrangement of another spin, which is not of the same magnitude.

Therefore, there is no net cancellation, because the magnitudes of the two spins are different. But never the less, you have the overall net magnetic movement which is similar that of the ferromagnetic material. And it is important to note that these effects like ferromagnetism, anti-ferromagnetism, etcetera involve no new types of magnetic movements, it is basically the atomic magnetic movement which we have been talking about before the spin and the angular motion of electron. Two important ways of understanding ferromagnetism in metals is that, one is assuming that the magnetic movement localize to atoms and they talk to each other by phenomena known as the exchange. The other is using what is the band structure of metals.

So, we said that, we will not be really going into deep in understanding the phenomena of magnetism which is arising from, purely from the band structure of metals. But it is important note even to understand simple phenomena like magnetism and iron, we may want to invoke band structure of metals, especially if you want to understand quantitatively.

Now, it is clear that, itinerant electron, or moving electrons, or free electrons cannot give rise to magnetism, so there has to be a local character to the magnetic movement, which is, which has to give rise to magnetism. The localize picture to atoms is actually conceptually easier and has been assume in the molecular filed theory of Weiss and in also in the Heisenberg approach. It should be noted right at the outside that even in metals like iron, most of the electron behave as if they are localized and the number of itinerant electron could be small number.

So, this is very, very important note, though we are talking about bands and free electrons, the character of the electron may be that, if you take an material like iron to give an example, there are 8 valance electron which occupy the 3d plus 4s bands. And we had even schematically drawn these two bands like how this 3d and 4s band look.

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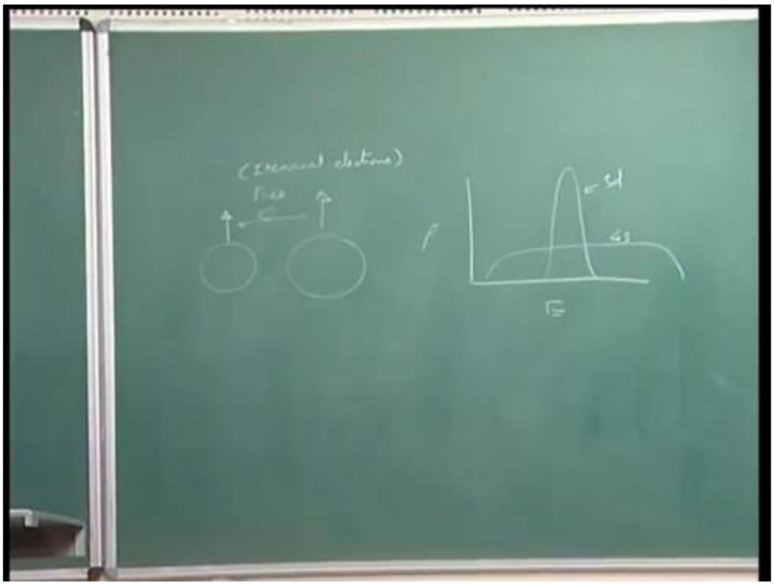

It is said that the 4s band is could be kind of a and suppose I am now plotting density of states rho and with energy, and I noted that the 4s band is more like a broad band, while the 3d band is a more localize band. And we said that these are what you might call this is my 3d band and this is my 4s band.

So, we noted that, these are simplified picture in themselves and we said that actually the 3d band has a very kind of a density of states actually has a more, much more complicated variation. But the important point to note that, these 3d and 4s bands fill parallelly. We have noted that the even when we drew the picture of how the atoms come together to form a band structure.

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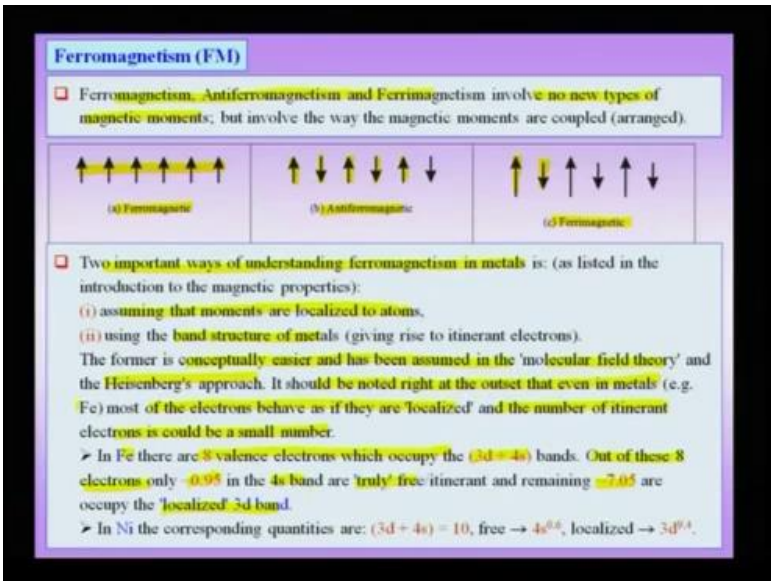

Ferromagnetism (FM)

❑ Ferromagnetism, Antiferromagnetism and Ferrimagnetism involve no new types of magnetic moments; but involve the way the magnetic moments are coupled (arranged).

❑ Two important ways of understanding ferromagnetism in metals is: (as listed in the introduction to the magnetic properties):
(i) assuming that moments are localized to atoms,
(ii) using the band structure of metals (giving rise to itinerant electrons).
The former is conceptually easier and has been assumed in the 'molecular field theory' and the Heisenberg's approach. It should be noted right at the outset that even in metals (e.g. Fe) most of the electrons behave as if they are 'localized' and the number of itinerant electrons is could be a small number.
➢ In Fe there are 8 valence electrons which occupy the (3d + 4s) bands. Out of these 8 electrons only ~0.95 in the 4s band are 'truly' free itinerant and remaining ~7.05 are occupy the 'localized' 3d band.
➢ In Ni the corresponding quantities are: (3d + 4s) = 10, free → $4s^{0.6}$, localized → $3d^{9.4}$.

Out of these 8 electrons, only about 0.95 electrons in the 4s band are truly free. So, this is very important note that, though we are talking the bands and we are talking about the itinerate electrons. The truly free character of electrons restricted about 0.95 out of these 8 electron which are now residing in the 4s and 3d bands which fill parallelly.

And most of the electron which is about 7.05 are actually localize to the 3d band, because this is 3d band has higher density of state as you can see that. And the narrow width of the 3d band implies at an electron here has more a localize character, so the width of the band itself can be used as a measure of the localize character of the electron. While the 4s electron, you can see that their density of states is widely spread in energy and this means that there are energy states available for a electron to actually we promoted they are is easily accessible.

But then the number of such electron is small which are truly itinerant. In nickel if you see again the picture does not change much, the 3d plus 4s electron is 10 in number, out of which only about 0.6 is truly free, and 9.4 of them will reside in the 3d band are almost localize. So, these localize movements are what is contributing to what you might call the magnetic movement, but without understanding the band structure and how the bands fill, we will not able to arrive at the exact magnetic movement.

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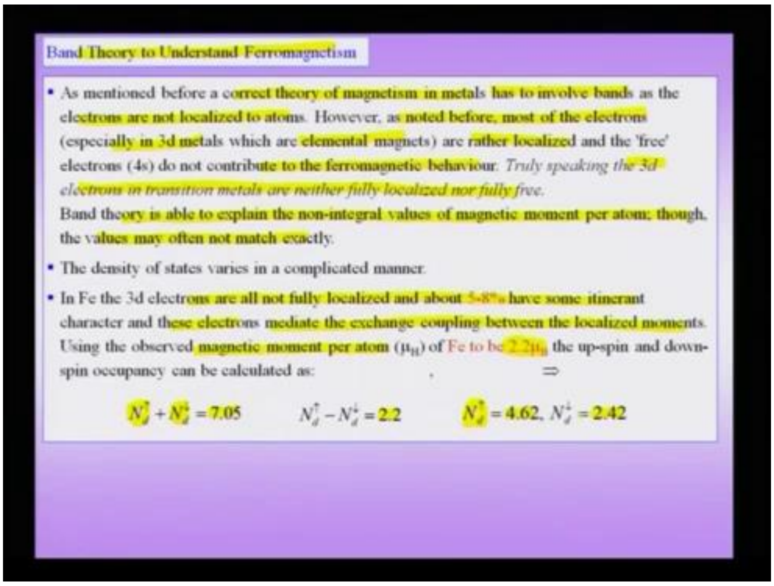

Band Theory to Understand Ferromagnetism

- As mentioned before a correct theory of magnetism in metals has to involve bands as the electrons are not localized to atoms. However, as noted before, most of the electrons (especially in 3d metals which are elemental magnets) are rather localized and the 'free' electrons (4s) do not contribute to the ferromagnetic behaviour. *Truly speaking the 3d electrons in transition metals are neither fully localized nor fully free.*
  Band theory is able to explain the non-integral values of magnetic moment per atom; though, the values may often not match exactly.
- The density of states varies in a complicated manner.
- In Fe the 3d electrons are all not fully localized and about 5-8% have some itinerant character and these electrons mediate the exchange coupling between the localized moments. Using the observed magnetic moment per atom (μ_H) of Fe to be $2.2\mu_B$ the up-spin and down-spin occupancy can be calculated as:

$$N_d^{\uparrow} + N_d^{\downarrow} = 7.05 \qquad N_d^{\uparrow} - N_d^{\downarrow} = 2.2 \qquad \Rightarrow \qquad N_d^{\uparrow} = 4.62,\ N_d^{\downarrow} = 2.42$$

So, how do we understand the band theory to understand ferromagnetism. Therefore, we need to know that the correct theory of magnetism in metals has to involve bands right, because we are talking about the outer most electron, which are which is what is contributing into this magnetic effect. And these electron are typically not localize to atoms however, as we noted before most of the electrons especially in the 3d metals which are elemental magnets, because we know that 3d like, metals like cobalt, nickel etcetera are element magnets.

These three electrons are rather localized and free electrons do not contribute the ferromagnetic behavior. So, in some sense this 3d electron in transition metals are neither fully localized or true, or fully itinerate. So, because they are in a band now, we have to talk about the being the localize, but at the same time they are not that localize as we can talk to about them as to what you might call a totally free electron.

The band theory is actually that theory which is able to explain the non integral values of magnetic movement per atom though often, we have to go beyond even the standard band theory to understand how, what is the correct values of this magnetic movements. Now, in iron the 3d electrons are not fully localized and about 5 to 8 percent has some itinerant characters as we noted before. And these electrons in some theory is actually are what mediate the exchange coupling between the localize movements.

So, we said that in a mental picture of magnetism either you can talk about magnetic movements talking to each other directly or being mediated by an by iron what you might called the free electron rightly itinerant character of electron. But in this second picture, we can think of these some, somewhat itinerant electrons or the itinerant character of the electron mediating the exchange.

Now, if you look at the observed magnetic movement per atom in iron, it is about 2.2 mu B and this can be only understood by a band structure, and a band structure which depends on spin. So, if you look at the number of electron occupying the up spin orbital, and if you look at the number of electrons occupying the down spin orbital, the total number is 7.05 and the difference between the two is 2.2. And putting them together we can see that actually you have an occupying in the up spin is about 4.62 and down spin is 4.2.

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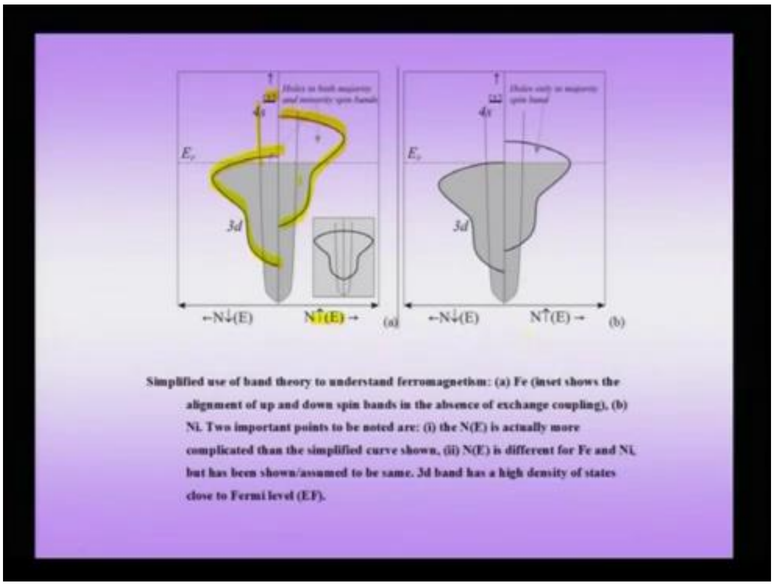

Simplified use of band theory to understand ferromagnetism: (a) Fe (inset shows the alignment of up and down spin bands in the absence of exchange coupling), (b) Ni. Two important points to be noted are: (i) the N(E) is actually more complicated than the simplified curve shown, (ii) N(E) is different for Fe and Ni, but has been shown/assumed to be same. 3d band has a high density of states close to Fermi level (EF).

So, in other words to explain a little more clearly you have now orbital, which are now depend on the spin character. In other words, if you are talking about 4s orbital here, this is the energy versus number of states, and you note that the 4s orbital is a free electron orbital and the 3d orbital is now split depending on the spin.

So, this is the spin up orbital, and this is the spin down orbital, and this is the case of iron on the right hand side the same picture is drawn for nickel. And you note that the 3d and 4s orbitals are filling parallelly and knowing this number of electron which are actually filling these two orbitals, the up spin and down spin orbitals, I can actually go ahead and calculate the iron magnetic movement, which turns out to be non-integral. Because the complicated vary way in which the magnetic orbitals are filled. So, we can use some kind of a simplified band theory to understand this, what you might call the non-integral value of magnetic movement.

Though at this point of time, we are not going to lot of details of actually how this calculation is made what is the error involved in this calculation, but the important note this fact that now we have a band structure which is depended on spin. That means, the up spin orbital fills in a different way as compared to down spin orbital, and many of the important magnetic effects come, because of this fact that, the up spin orbital and down spin orbital do not fill parallel and they are shifted with respect to each other in energy.

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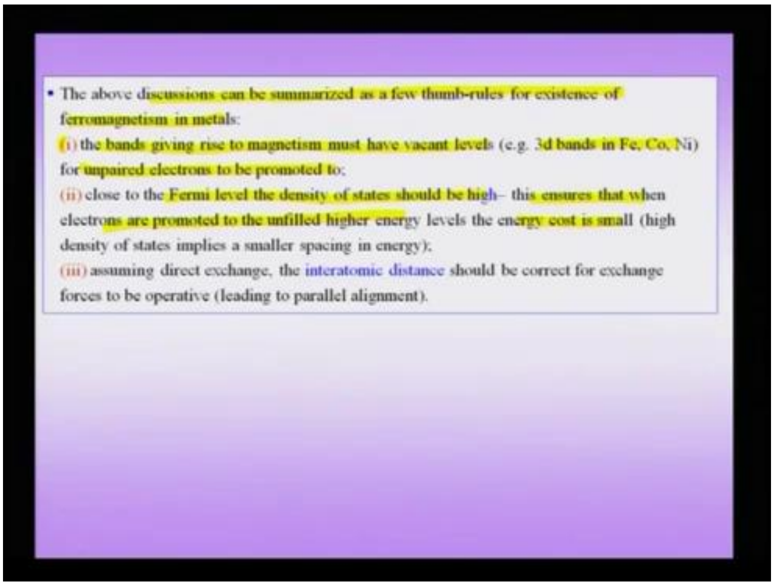

- The above discussions can be summarized as a few thumb-rules for existence of ferromagnetism in metals:

(i) the bands giving rise to magnetism must have vacant levels (e.g. 3d bands in Fe, Co, Ni) for unpaired electrons to be promoted to;

(ii) close to the Fermi level the density of states should be high– this ensures that when electrons are promoted to the unfilled higher energy levels the energy cost is small (high density of states implies a smaller spacing in energy);

(iii) assuming direct exchange, the interatomic distance should be correct for exchange forces to be operative (leading to parallel alignment).

So, the above discussion can be summarized as a few thumb rules existence of ferromagnetism in metals. Number one, the bands giving rise to magnetism must have vacant level for instance, the 3d bands in iron, cobalt and nickel. For unprepared electrons to be promoted, because you know that exchange coupling is actually promoting electrons to a higher level, while they could actually have been in lower level and paring out with the preexisting electron.

But exchange coupling is actually promoted them to a higher level, unless there are free levels available above and there is going to be no magnetism arising from the band picture of magnetism. Close to the fermi level, the density of states should be high, this ensures that when an electron are promoted to the unfilled higher level, the energy cost is small. And this is what you see the density of states in the d orbitals is the 3d orbital is high as compared to 4s orbital.

That means, that the cost of promoting an electron from a level, which is the lower level for instance, in the 3d band to the next level is actually small, and you can see that the density of state is actually high close to the fermi level, and this is the fermi level. So, number two is that the density of states should be high so that, the energy cost of the exchange in other words, for the parallel alignment of the spin is small.

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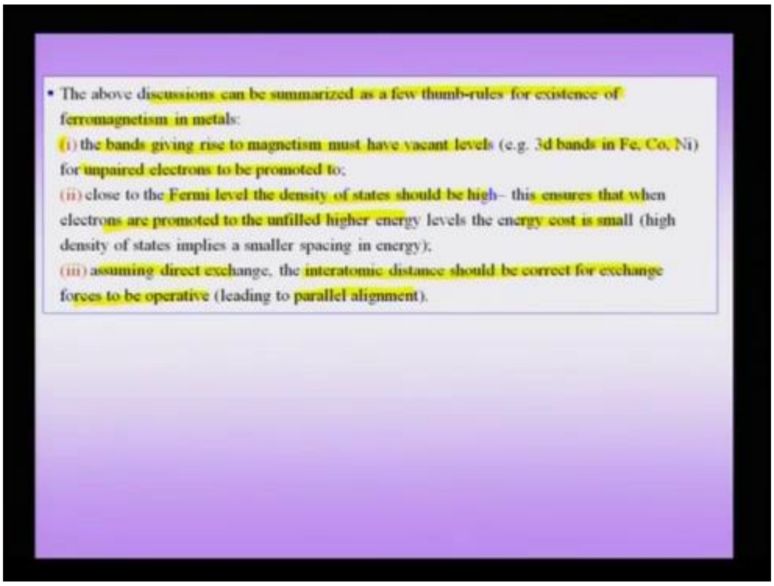

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The third thing, if we are going to assuming the picture of direct exchange then, the inter atomic distance should be correct for exchange forces to be operative, which is parallel alignment. And typically this is done using what is known as the ((Refer Time: 52:08)) plot in which actually what they do is, they plot the ratio of inter atomic separation with respect to the 3d orbital distance to actually find that which kind of element should give rise to the ferro magnetism. But never the less, the inter atomic distance is a important factor, which gives rise to magnetism, ferromagnetism.

So, to understand ferromagnetism, number 1, there should be vacant levels in the band which is giving rise to magnetism which is typically the 3d band in iron, cobalt and nickel. number 2, close to the fermi level, the density of the state should be high so that, the overall costs of this exchange coupling is not too much. Number 3, the inter atomic distance should be correct that means, too much distance or too less distance does not give you ferromagnetism.