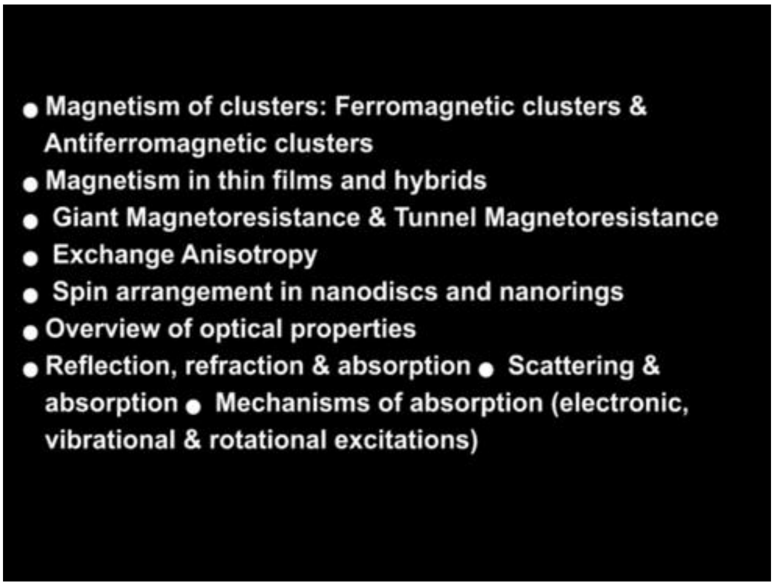
Nanostructures and Nanomaterials: Characterization and Properties

Prof. Anandh Subramaniam, Prof. Kantesh Balani
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 23

Electrical Magnetic
Optical Properties of Nanomaterials (C4)

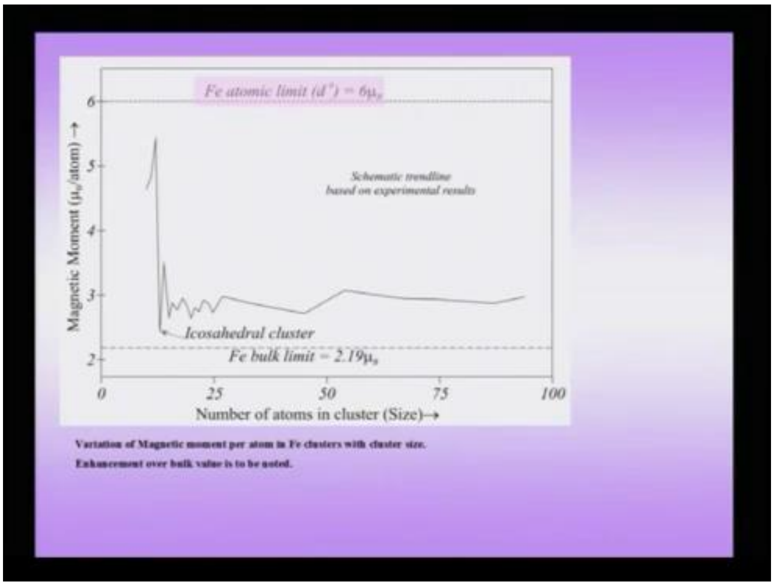
(Refer Slide Time: 00:17)



- Magnetism of clusters: Ferromagnetic clusters & Antiferromagnetic clusters
- Magnetism in thin films and hybrids
- Giant Magnetoresistance & Tunnel Magnetoresistance
- Exchange Anisotropy
- Spin arrangement in nanodiscs and nanorings
- Overview of optical properties
- Reflection, refraction & absorption ● Scattering & absorption ● Mechanisms of absorption (electronic, vibrational & rotational excitations)

After talking about magnetism in nanostructures, let us take up the topic of magnetism in clusters early on we had said that we could actually divide into materials into three size regimes. One is what we call small clusters, one we call large clusters and one we call nanocrystals and this divisions of properties was based on a variation of a property.

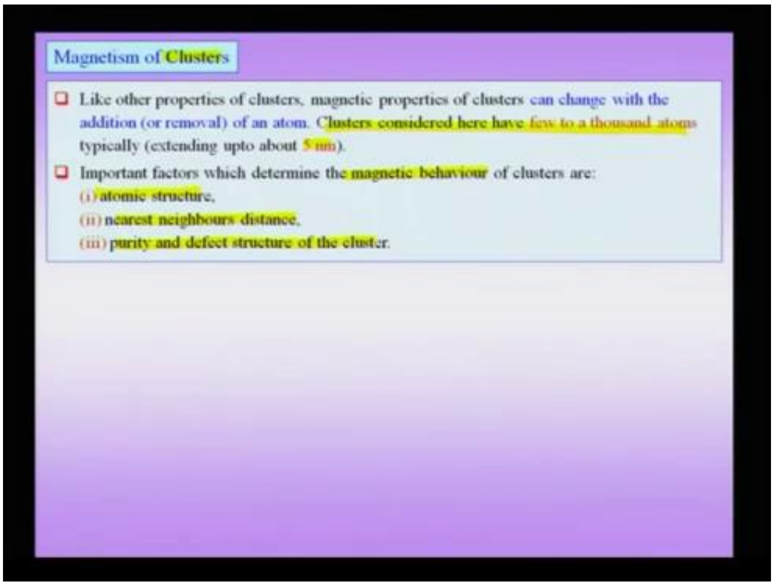
(Refer Slide Time: 00:52)



Variation of Magnetic moment per atom in Fe clusters with cluster size.
Enhancement over bulk value is to be noted.

With what you call addition of removal of more number of atoms and in fact magnetism in some sense is an ideal property to make this kind of a distinction.

(Refer Slide Time: 01:05)



Magnetism of **Clusters**

- ☐ Like other properties of clusters, magnetic properties of clusters can change with the addition (or removal) of an atom. Clusters considered here have few to a thousand atoms typically (extending upto about 5 nm).
- ☐ Important factors which determine the magnetic behaviour of clusters are:
  (i) atomic structure,
  (ii) nearest neighbours distance,
  (iii) purity and defect structure of the cluster.

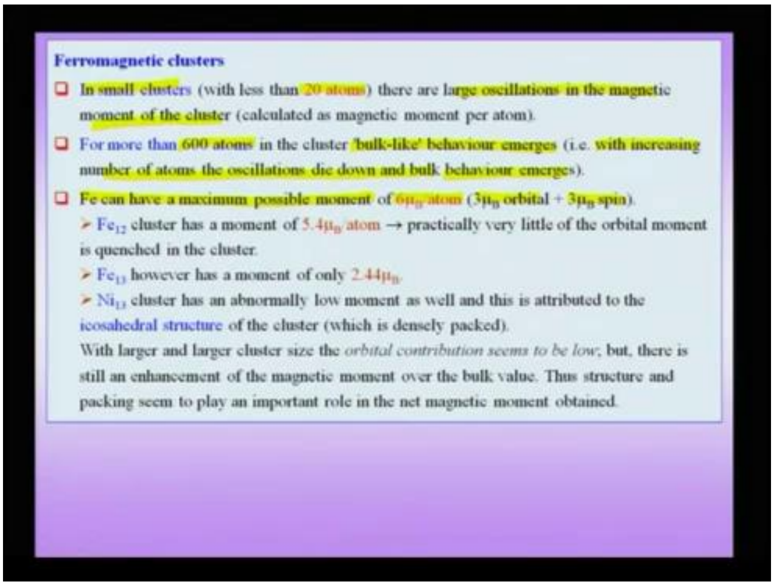
What you might call a small cluster a large cluster and a nanocrystal, we said that clusters are small clusters are that size regime wherein the addition or removal of a mere atom can cause a large variation in the property. Here, of course we are talking about a property like a ferromagnetic property of a cluster of atoms; this is important note because even you have heard in the nano crystal size regime. Mere addition of or removal of atoms does not cause a serious change in the properties, in other words there is a small change, but that is not significant with respect to the already existing value of the property.

So, these clusters are size regimes which are usually small and less than about 5 nanometres, typically we want to consider clusters wherein we can actually count the number of atoms like a 13 atom cluster or a 25 atom cluster or a 50 atom cluster. So, these are the real size regimes of clusters wherein we are really interested and in the limit what you might call the large sized limit what we obtain is called the bulk limit wherein you consider a large nanocrystal. Now, when you are talking about magnetic behaviour or ferromagnetic behaviour of clusters a few important points have to be kept in mind.

This is of course, the atomic structure and here we may note that this atomic structure need not be crystalline. In other words, this could just be a cluster which has its own structure and this is not necessarily a crystalline kind of a structure we have to worry about the nearest neighbour atom distance in the cluster. Of course, there could be more than one nearest neighbour distance depending on the size of the cluster or of course there could be one nearest neighbour there could be one other distance which is very close to a neighbour’s distance.

Then, of course, the purity and the defect structure of the cluster is also very important because manufacturing some of this clusters is very difficult and getting a right number of atoms. Of course, separating those clusters sizes based on mass spectroscopy and studying their properties is the indeed a important challenge.

(Refer Slide Time: 02:58)



Ferromagnetic clusters

- In small clusters (with less than 20 atoms) there are large oscillations in the magnetic moment of the cluster (calculated as magnetic moment per atom).
- For more than 600 atoms in the cluster 'bulk-like' behaviour emerges (i.e. with increasing number of atoms the oscillations die down and bulk behaviour emerges).
- Fe can have a maximum possible moment of $6\mu_B$/atom ($3\mu_B$ orbital + $3\mu_B$ spin).
  - Fe_{12} cluster has a moment of $5.4\mu_B$/atom → practically very little of the orbital moment is quenched in the cluster.
  - Fe_{13} however has a moment of only $2.44\mu_B$.
  - Ni_{13} cluster has an abnormally low moment as well and this is attributed to the icosahedral structure of the cluster (which is densely packed).

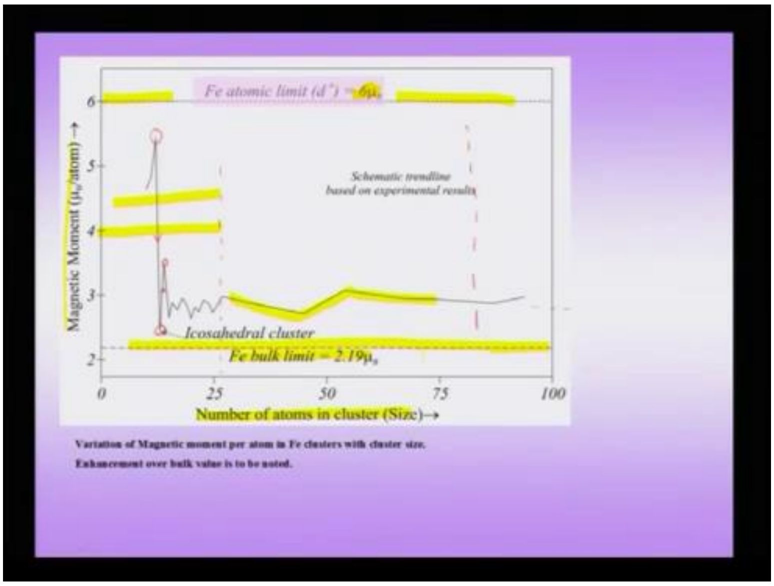
  With larger and larger cluster size the *orbital contribution seems to be low*, but, there is still an enhancement of the magnetic moment over the bulk value. Thus structure and packing seem to play an important role in the net magnetic moment obtained.

When you are talking about ferromagnetic clusters we identify the regime of small clusters with about less than about 20 atoms and here there is large oscillations in the magnetic moments of the clusters. Of course, we are talking about the magnetic moment per atom, we already noted before that when you are talking about a property like magnetic moment, you decrease the size or the scale of the system. The magnetic moment increases above the bulk value, now we would be noting that how this behaviour becomes really drastic when you are talking about small clusters,

When you are talking about a large group of atoms like more than 6 in an atom, you typically notice that bulk like behaviour emerges. That means with increasing number of atoms the oscillations in the property here, of course magnetic moment dies down and therefore there is no sharp variations with change in number of atoms. Actually, the bulk behaviour emerges, so we have two or three size regimes, which means small clusters having typically less than about 50 or 20 atoms. The big clusters from 50 atoms to say 600 atoms and finally, of course the bulk behaviour wherein you can think of what you might call the magnetic moment approaching that of the bulk value of iron.

Now, we already noted that iron can have a maximum possible magnetic moment of about 6 mu b per atom three arising from orbital and three from spin. We would also note that typically in bulk kind most of the orbital motion, orbital magnetic contribution is quenched because of the strong interaction with the lattice.

(Refer Slide Time: 04:33)



Variation of Magnetic moment per atom in Fe clusters with cluster size.
Enhancement over bulk value is to be noted.

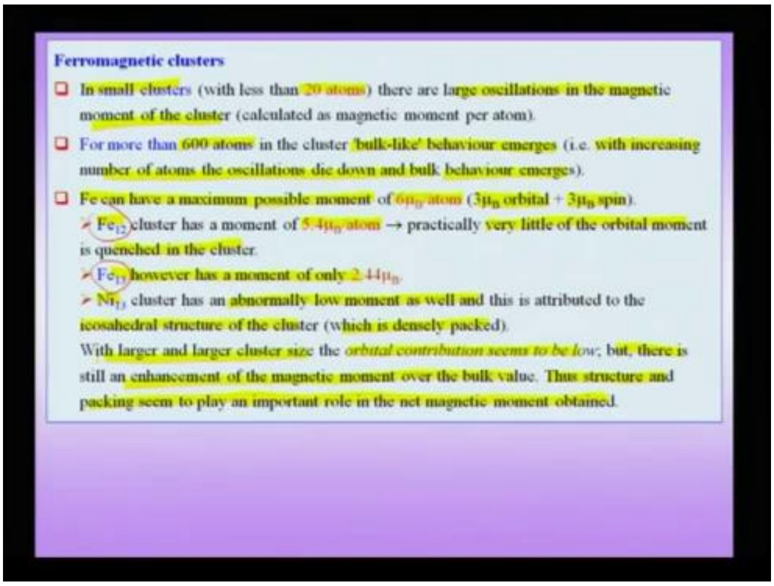
Now, if you take up individual clusters to highlight how the property changes and this is schematically shown here in this graph. Here, you are studying the number of atoms in this cluster, this is no longer a dimension like nanometre, but it is purely a number because we are really in the small cluster regime and you are studying the magnetic moment per atom on the y axis. Therefore, we can see that clearly there are three regimes what you might call the small cluster regime, which you can see wherein there are the small cluster regime where you can see there are sharp variations in the property.

Then, there is the medium cluster regime, wherein you have oscillations, but they are smaller oscillations they are oscillations spread over a large number of atoms. That means over a large collection of atoms you see these oscillations are taking place, but when you add many number of atoms not a one or two atoms, so you have this regime which is of interest.

Now, you notice that merely by adding one atom and going from this value you can see that this is the Fe 12 cluster and you go to the Fe 13 cluster. That means by just adding one atom you notice that the magnetic moment changes drastically there is serious severe precipitous fall in the magnetic moment. This is what is we will call the small cluster regime a signature of the small cluster regime and further when you add one more atom there is again a sharp increase in the magnetic moment of the cluster. These oscillations continue in what you might call in a sharp fashion till you reach about 25 atoms and after that of course, we said that cluster variation with cluster size gets a little more smoother.

Finally, of course in the bulk regime you will notice that the variation becomes even smoother and you have the bulk of behaviour emerging. In other words, the and in the large crystal regime actually approaches a magnetic moment of about 2.2 mu b per atom. In this graph, of course the lower limit is the bulk limit and the upper limit is what you might call the atomic limit, which is possible which we said is about 6 mu b because an iron atom cannot have more than or an iron cluster cannot have more than 6 mu b.

(Refer Slide Time: 06:46)



Ferromagnetic clusters

- ☐ In small clusters (with less than 20 atoms) there are large oscillations in the magnetic moment of the cluster (calculated as magnetic moment per atom).
- ☐ For more than 600 atoms in the cluster 'bulk-like' behaviour emerges (i.e. with increasing number of atoms the oscillations die down and bulk behaviour emerges).
- ☐ Fe can have a maximum possible moment of $6\mu_B$/atom ($3\mu_B$ orbital + $3\mu_B$ spin).
  - ➢ Fe_{12} cluster has a moment of $5.4\mu_B$/atom → practically very little of the orbital moment is quenched in the cluster.
  - ➢ Fe_{13} however has a moment of only $2.44\mu_B$.
  - ➢ Ni_{13} cluster has an abnormally low moment as well and this is attributed to the icosahedral structure of the cluster (which is densely packed).

  With larger and larger cluster size the *orbital contribution seems to be low*; but, there is still an enhancement of the magnetic moment over the bulk value. Thus structure and packing seem to play an important role in the net magnetic moment obtained.

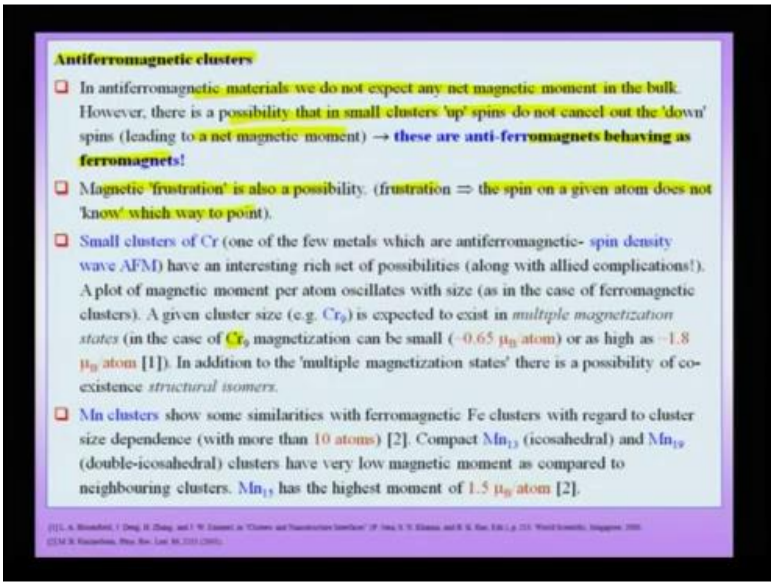
Each atom only contributes about 3 mu b from the orbital motion and three from the spin contribution, therefore, the maximum limit is 6, but all, but never the less it is important to note that all these magnetic moments which we are noting in the graph here. They are above that of the bulk limit that means there is an enhancement in the magnetic moment in the of course the nano crystalline regime in the regime of the large cluster and also in the Regime of the small cluster. So, the Fe 12 cluster has a magnetic moment about 5.4 mu b per atom that means very little of the orbital motion is quenched in this cluster. So, this is would be like approaching the atomic limit when you have a iron 12 cluster, on the other hand of which adding just one more atom making it fe 13, we notice that the it has a much lower magnetic moment of only about 2.4 mu b.

Now, if you compare this Fe 13 cluster with for instance nickel 13 cluster, it also has an abnormally low moment and this can be attributed to the icosahedral structure. In other words the cluster is densely packed that may lead to atomic separation is reduced in this cluster. We had noted earlier that three factors coming into play while deciding the magnetic moment of the cluster is the nearest neighboured distance in the cluster. Therefore, if the nearest neighboured distance is coming down when you have a reduction in that means there is an overlap of the atomic orbital. Therefore, there is a reduction in the magnetic moment with larger and larger cluster size.

The orbital contribution seems to be low, but there is still an enhancement of the magnetic moment over the bulk value. If we had noticed before, because this is purely coming from the reduction in this size the structure and packing fraction seem to play. Packing method seems to play an important role in the net magnetic moment when we are talking about these clusters of magnetic atoms. So, to summarize this story of the ferromagnetic clusters we can divide the ferromagnetic clusters into nano crystalline regime, where the oscillations are small, and the small cluster big large cluster regime.

Here, there are oscillation, but this spread over large number of atoms and this small cluster regime typically less than about 20 atoms wherein there are serious variations of sharp variations when you add or remove an atom. You can see that the cluster actually goes very close to the what you might call the theoretical possible limit for an which is close to the atomic magnetic moment of iron. On the other hands, there can be clusters like Fe 13 cluster which are closed packed cluster having icosahedral configuration which give you actually low magnetic moment.

(Refer Slide Time: 09:21)



Antiferromagnetic clusters

- ☐ In antiferromagnetic materials we do not expect any net magnetic moment in the bulk. However, there is a possibility that in small clusters 'up' spins do not cancel out the 'down' spins (leading to a net magnetic moment) → **these are anti-ferromagnets behaving as ferromagnets!**
- ☐ Magnetic 'frustration' is also a possibility. (frustration ⇒ the spin on a given atom does not 'know' which way to point).
- ☐ Small clusters of Cr (one of the few metals which are antiferromagnetic- spin density wave AFM) have an interesting rich set of possibilities (along with allied complications!). A plot of magnetic moment per atom oscillates with size (as in the case of ferromagnetic clusters). A given cluster size (e.g. Cr_9) is expected to exist in *multiple magnetization states* (in the case of Cr_9 magnetization can be small (~0.65 μ_B/atom) or as high as ~1.8 μ_B/atom [1]). In addition to the 'multiple magnetization states' there is a possibility of co-existence *structural isomers*.
- ☐ Mn clusters show some similarities with ferromagnetic Fe clusters with regard to cluster size dependence (with more than 10 atoms) [2]. Compact Mn_{13} (icosahedral) and Mn_{19} (double-icosahedral) clusters have very low magnetic moment as compared to neighbouring clusters. Mn_{15} has the highest moment of 1.5 μ_B/atom [2].

After talking about the ferromagnetic material like kind let us talk about what you might call the ferromagnetic clusters. Now, when you are talking about anti ferromagnetic clusters, these are actually not anti ferromagnetic in the cluster zone they are actually what are anti ferromagnetic in bulk. So, for instance we know that chromium is one of the few elements which are anti ferromagnetic like manganese and therefore, in the bulk form chromium or manganese is expected to be anti ferromagnetic. Here, we are talking about anti ferromagnetic materials in the bulk which are behaving like ferromagnets in the cluster zone.

That means when we are making the small clusters out of these anti ferromagnetic in bulk, then you are actually getting ferromagnetic property again very interesting observation that because we have these materials do not behave like ferromagnets. In the bulk, in anti ferromagnetic materials, we do not expect any net magnetic moment in the bulk because the up spins and down spins cancel themselves out. However, there is a possibility that a small cluster in a small cluster there are up spins and down spins do not cancel out leading to a net magnetic moment. Of course, this magnetic moment is not because this is now a small residual long cancellation and this is not expected to be as high as that you see in a ferromagnetic cluster.

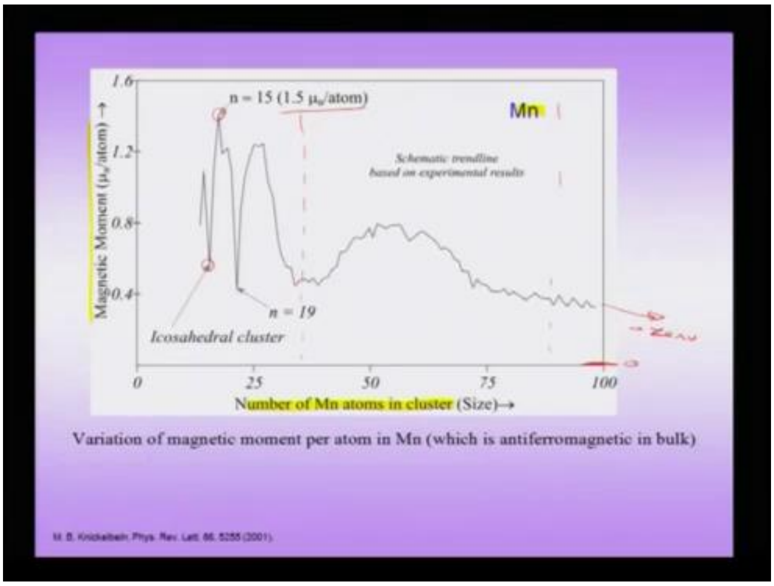
Never the less, this is an interesting possibilities in this magnets small magnetic cluster Ferro frustration is also an issue, this frustration leads to the fact that the spin on a given atom does not know which way to point.

(Refer Slide Time: 10:59)

In other words, if I had a large system, then I know in an anti-ferromagnetic material if I had spin arrangements ups and downs, they will go like this, but in a small crystal there could so happen that there is one spin which is introduced here. There could be an atom here, which does not know that this spin has to be up or down and this automatically implies that it is not following the anti-ferromagnetic order.

Therefore, there could be a net residual spin up or spin down coming from the fact that that atomic position has been frustrated with respect to the meaning of the lattice. We will take up two an examples to understand anti ferromagnetic clusters one is the example of chromium and one is the example of manganese because these are elemental. Having said that, if there elemental it does not mean that overall magnetization states are easy to understand.

(Refer Slide Time: 11:46)



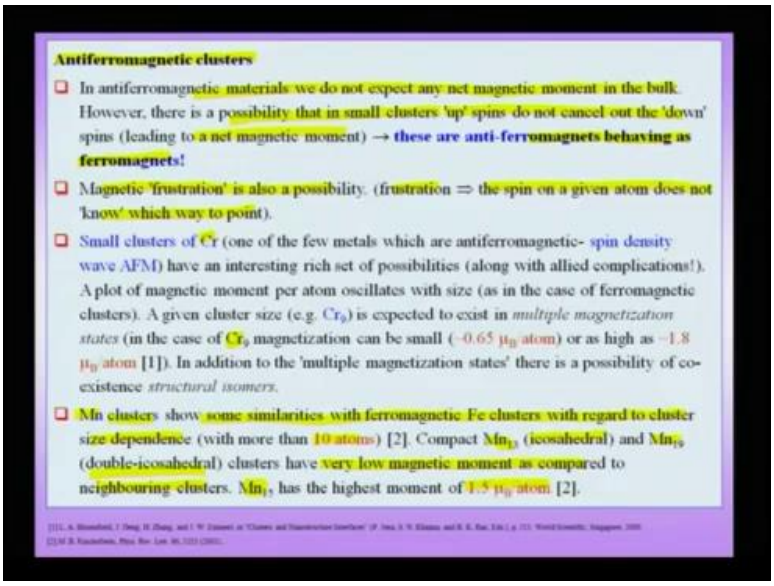
Variation of magnetic moment per atom in Mn (which is antiferromagnetic in bulk)

M. B. Knickelbein Phys. Rev. Lett. 86, 5255 (2001).

Now, if you take up the example of manganese and study now like before the number of manganese atoms in the cluster on the x axis and the magnetic moment along the y axis. Again, you do see what you might call three regime one regime which we might call the small cluster regime one you might call the large cluster regime and then the of course, is the nanocrystal regime. Finally, you have the bulk limit the bulk limit in this case is clearly the case where there is 0, net magnetic moment because you know this is an anti-ferromagnetic material. Therefore, you do not expect any magnetic moment in the bulk form, so ultimately this curve as to go down to 0 in this small cluster regime, again you notice that there are sharp variations in the magnetic moments.

You can observe that these sharp variations again can be at understood in terms of certain geometry that for instance the icosahedral cluster gives you a very small magnetic moment net residual magnetic moment. Then, by adding just of atoms you get the n equal to 50 in clusters which is have being a very high magnetic moment, but having noted that this very high is only about 1.5 mu b per atom. Unlike the case of a very high in the case of the ferromagnetic cluster, here we went up to a value of 5.4 mu b per atom because these are not inherently ferromagnetic material.

(Refer Slide Time: 13:09)



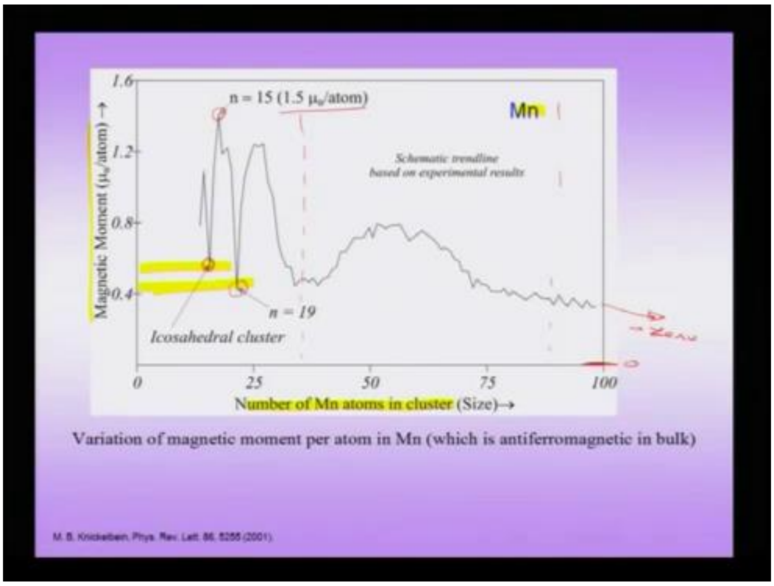
Antiferromagnetic clusters

- ☐ In antiferromagnetic materials we do not expect any net magnetic moment in the bulk. However, there is a possibility that in small clusters 'up' spins do not cancel out the 'down' spins (leading to a net magnetic moment) → **these are anti-ferromagnets behaving as ferromagnets!**
- ☐ Magnetic 'frustration' is also a possibility. (frustration ⇒ the spin on a given atom does not 'know' which way to point).
- ☐ Small clusters of Cr (one of the few metals which are antiferromagnetic- spin density wave AFM) have an interesting rich set of possibilities (along with allied complications!). A plot of magnetic moment per atom oscillates with size (as in the case of ferromagnetic clusters). A given cluster size (e.g. Cr_9) is expected to exist in *multiple magnetization states* (in the case of Cr_9 magnetization can be small (~0.65 μ_B/atom) or as high as ~1.8 μ_B/atom [1]). In addition to the 'multiple magnetization states' there is a possibility of co-existence *structural isomers*.
- ☐ Mn clusters show some similarities with ferromagnetic Fe clusters with regard to cluster size dependence (with more than 10 atoms) [2]. Compact Mn_{13} (icosahedral) and Mn_{19} (double-icosahedral) clusters have very low magnetic moment as compared to neighbouring clusters. Mn_{15} has the highest moment of 1.5 μ_B/atom [2].

These are anti ferromagnetic materials, which are behaving like ferromagnetic materials in the small scale regime. Therefore, again you see that in these cases there are what you might call minimum corresponding to the icosahedral cluster and the n equal to 19 cluster and we will talk about this in the in a few moments. These oscillations tend to die down when you have large approach large cluster regime and then of course you obtained bulk limit. Now, what you might be aware is of course you ultimately get a 0 magnetic moment, now therefore in manganese cluster show some similarities with ferromagnetic kind clusters with regard to the cluster size dependence.

This is in the regime of more than about 10 atoms compact this 13 atom clusters, which is the isosahederal configuration and the Mn 19, which is actually a double icosahedral cluster. That means there is one icosahedral shell and above that there is a second icosahedral shell which is called a double icosahedral construction. This gives very low magnetic moments compared to the neighbouring clusters like Mn 15, which has a high magnetic moment of about 1.5 mu b per atom.

(Refer Slide Time: 14:17)

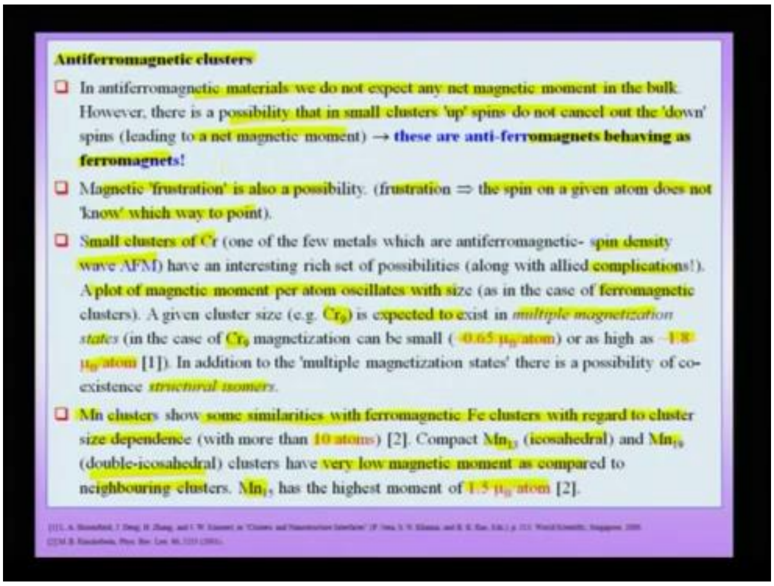


Variation of magnetic moment per atom in Mn (which is antiferromagnetic in bulk)

M. B. Knickelbein, Phys. Rev. Lett. 86, 5255 (2001).

So, the low magnetic moments are about 0.4 mu b per atom in this is in this range 0.4 to 0.5 mu b per atom while the high one correspond about 1.5 mu b per atom.

(Refer Slide Time: 14:28)



Antiferromagnetic clusters

- ☐ In antiferromagnetic materials we do not expect any net magnetic moment in the bulk. However, there is a possibility that in small clusters 'up' spins do not cancel out the 'down' spins (leading to a net magnetic moment) → **these are anti-ferromagnets behaving as ferromagnets!**
- ☐ Magnetic 'frustration' is also a possibility. (frustration ⇒ the spin on a given atom does not 'know' which way to point).
- ☐ Small clusters of Cr (one of the few metals which are antiferromagnetic- spin density wave AFM) have an interesting rich set of possibilities (along with allied complications!). A plot of magnetic moment per atom oscillates with size (as in the case of ferromagnetic clusters). A given cluster size (e.g. Cr_9) is expected to exist in *multiple magnetization states* (in the case of Cr_9 magnetization can be small (~0.65 μ_B/atom) or as high as ~1.8 μ_B/atom [1]). In addition to the 'multiple magnetization states' there is a possibility of co-existence *structural isomers*.
- ☐ Mn clusters show some similarities with ferromagnetic Fe clusters with regard to cluster size dependence (with more than 10 atoms) [2]. Compact Mn_{13} (icosahedral) and Mn_{19} (double-icosahedral) clusters have very low magnetic moment as compared to neighbouring clusters. Mn_{15} has the highest moment of 1.5 μ_B/atom [2].

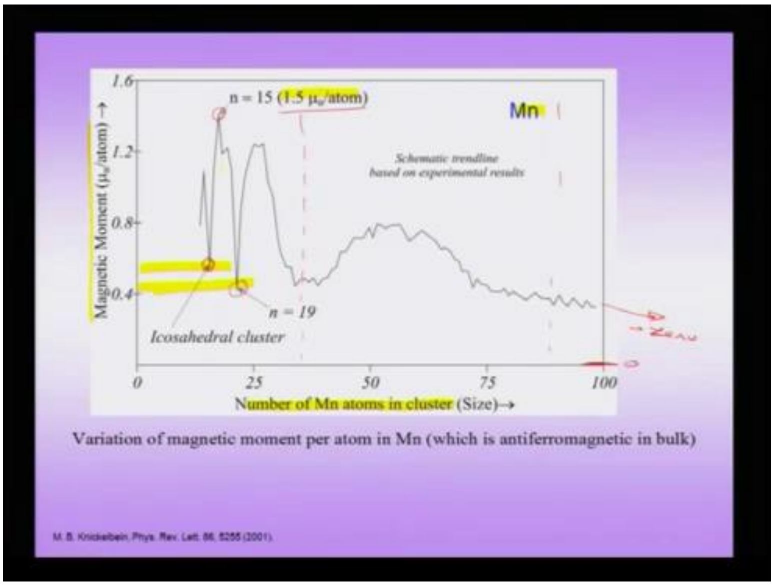
So, in the case of manganese, you notice that there is a variation about 0.4 and about 1.5 mu b per atom based on the cluster size. Again, like before in the case of iron we can understand this in case of geometrical cluster that if there is a closed packed cluster having in some kind of a single shell or double shell icosahedral configuration. Then, the magnetic moment is more the case of chromium is slightly more complicated, in fact it is significantly more complicated and it happens to be that the anti ferromagnetism in chromium is suppose to arise as what is known as a spin density wave. So, often the phrase used is that it is an incommensurate spin density wave anti ferro magnet.

That means that this is not a simple kind of an anti ferro magnet, which can be drawn like a picture using this one we saw before. This is the underlying spins have a spin density wave and this spin density wave as I pointed out can actually be incommensurate with respect to the underlying lattice. Therefore, you can have an incommensurate spin density where which can which is actually giving rise to this anti ferromagnetism in chromium and therefore this is a very rich system. This also means that there are lot of complications in understanding such a very rich system like chromium though we said that it is a elemental anti ferro magnet this is not make it a simple anti ferro magnet.

Though it is elemental, this is a king to the example of manganese in crystal structures though manganese elemental crystal. Often you know that alpha manganese and beta manganese have actually a very complicated crystal structure having many number of atoms the plot of magnetic moments oscillates with size like in the case of the manganese. The case of the ferromagnetic cluster a cluster size of Cr 9 is expected to exist in multiple magnetization states and this multiple magnetization states. Actually, it makes the analysis very difficult for us to understand that what is really giving rise to this effect. In addition to this multiple magnetization states, the issue is of there are many structural isomers also possible that means that Cr 9 cluster not only exist in a single structural form, it exist in many other structural isomers.

Therefore, these structural isomers each one of them will have a different magnetization and the net effect of on magnetization. You are seeing is actually when you do an experiment is actually an average over all these structural isomers and all these multiple magnetization states the Cr 9 magnetization can actually be small for about 0.65 mu b per atom. It can be 1.8 mu b per atom. That means a single cluster I do not mean a single structure, structurally a single number of atoms 9 atoms in the Cr 9 cluster can exist can give you a net magnetization of something like 0.6 mu b or 1.8 mu b which means a large variation.

(Refer Slide Time: 17:13)



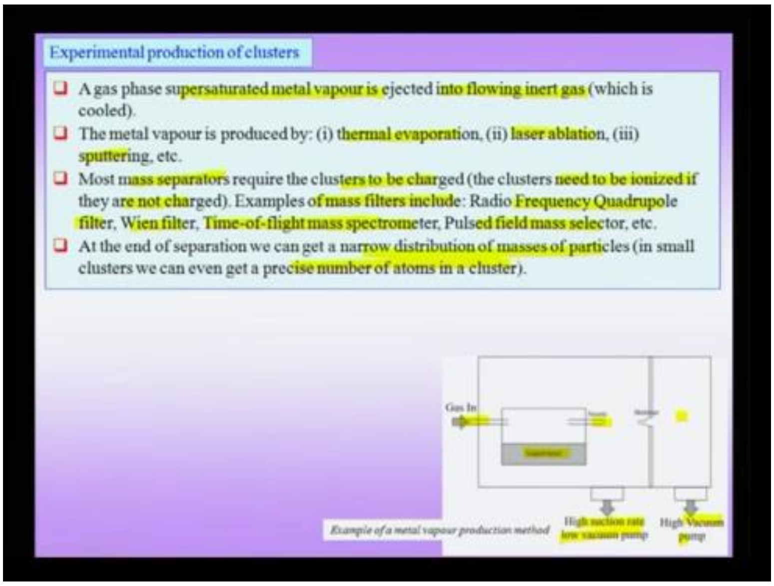
Variation of magnetic moment per atom in Mn (which is antiferromagnetic in bulk)

M. B. Knickelbein, Phys. Rev. Lett. 86, 5255 (2001).

We earlier saw that the maxima minima is between the almost the maxima and minima in such a plot. So, such large variations can it is actually difficult to understand it and the underlying mechanisms are supposed to be as I pointed out the existence of multiple magnetization states and also existence of structural isomers. So, the essential message of studying anti ferromagnetic clusters is that there can be materials which are anti ferromagnetic with zero magnetization in bulk, but which behave like ferro magnets in this small cluster regime.

In the small cluster regime like in the case of ferro magnets, ferromagnetic clusters there are larger oscillations and this oscillations finally die down and you obtain what is called the large cluster regime. Finally, the nanocluster regime additionally we noted that to understand the variation and magnetization in the small clusters. We can invoke the principles we used in the case of the iron clusters in other words the icosahedral are close packing in this crystals is expected to give us these large variations in the magnetization. So, this is a very interesting possibility that actually you are seeing ferromagnetism in small clusters of an anti ferromagnetic material.

(Refer Slide Time: 18:32)



Experimental production of clusters

- A gas phase supersaturated metal vapour is ejected into flowing inert gas (which is cooled).
- The metal vapour is produced by: (i) thermal evaporation, (ii) laser ablation, (iii) sputtering, etc.
- Most mass separators require the clusters to be charged (the clusters need to be ionized if they are not charged). Examples of mass filters include: Radio Frequency Quadrupole filter, Wien filter, Time-of-flight mass spectrometer, Pulsed field mass selector, etc.
- At the end of separation we can get a narrow distribution of masses of particles (in small clusters we can even get a precise number of atoms in a cluster).

Example of a metal vapour production method

We had seen that the magnetic properties of clusters is a very sensitive functions of the number of atoms in the cluster before we go on to other interesting magnetic properties about the nanostructures and hybrids. Let us consider briefly here the experimental production of cluster and how we can measure the magnetic moment of these clusters. Typically, a gas phase super saturated in metal vapour is ejected into a flowing inert gas, which is cooled and at the heart of or the schematic of this kind of a production technique is shown in the figure below.

Here, you see that there is a liquid metal bath, there is a gas which is flowing into the chamber this chamber is at a high suction rate, but in the low vacuum, further this liquid metal which is in the vapour state is atomized through a nozzle. It passes through a skimmer and goes into a chamber where there is a high vacuum pump which of course have a low suction rate, but it is a high vacuum pump. So, essentially we have a super saturated metal vapour which is ejected into a flowing inert gas, the metal vapour itself could be produced by thermal evaporation laser ablation sputtering or many of the other techniques. This can produce this metal vapour, further we know that now this metal vapour consists of clusters of different diverse sizes.

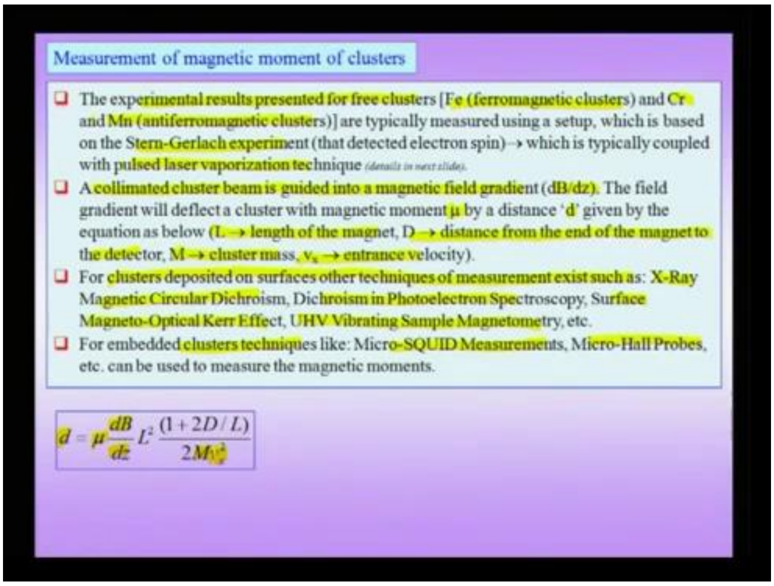
That means they may have a right from a few atoms to a few thousand atoms and we require mass separators which can actually separate out clusters of various sizes and for this the cluster typically needs to be charged. If the clusters needs to be ionized, they are not charged prior y, so this is a very important point because the mass separators will not work most of the mass separators will not work on non charged particles. Here, we list the name of some of these mass filters though we will not go into the detail of their operation or there physics behind them. These mass filters include radio frequency quadrupole filters Wien filters time of flight mass spectrometers pulse field mass selector etcetera.

As we pointed out, all these techniques typically depend on the clusters to be charged and if they are not charged as we shall see in a coming slides that we will charge the clusters before they are sent into a spectrometer. For instance, time of flight mass spectrometer at the end of the separation our goal is that we have a narrow distribution of the masses of this particles or this clusters. If you are talking about small clusters, we would even like to get a précised number of atoms in these clusters. As we had noted before that in small cluster addition or removal of a single atom can lead to very steep changes in terms of their property magnetic properties like we saw that for the case of the ferromagnetic clusters.

Here, you have noted that if you have an icosahedral cluster typically has a low magnetic moment, but if you had an atom to it, then the magnetic moment increases steeply. Similarly, for anti ferromagnetic clusters that we saw that in the small cluster regime, actually we have severe oscillations in terms of the magnetic moment of the particles. Therefore, in small clusters, we would like to isolate a précised number of atoms and as I pointed out some of these techniques like radio frequency quadrupole filters wean filters etcetera help you in separation of these different mass particles.

These also imply different number of atoms in these clusters, we shall also briefly take up here the measurement of the magnetic moments of clusters that is we had already noted that these plots which we have seen are actually experimental plots. That means people have actually produced clusters of atoms consisting magnetic material and further have gone on to measure the magnetic moments.

(Refer Slide Time: 22:26)



Measurement of magnetic moment of clusters

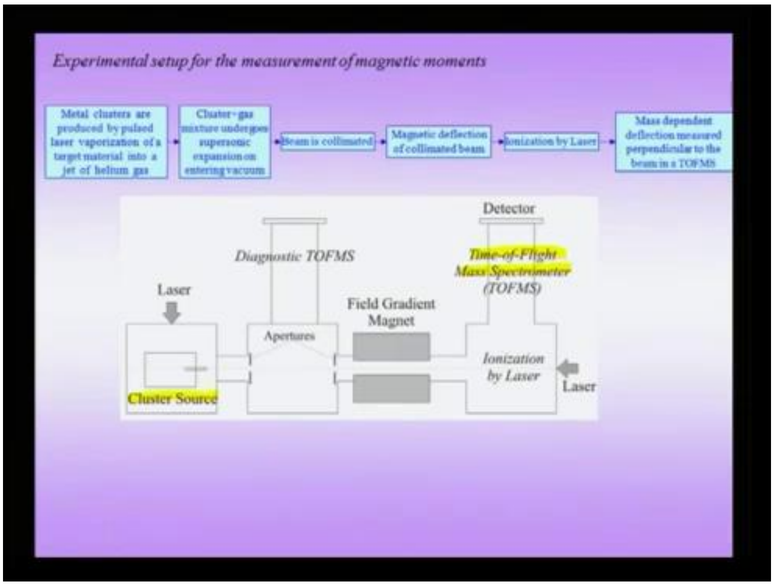
- The experimental results presented for free clusters [Fe (ferromagnetic clusters) and Cr and Mn (antiferromagnetic clusters)] are typically measured using a setup, which is based on the Stern-Gerlach experiment (that detected electron spin) → which is typically coupled with pulsed laser vaporization technique (details in next slide).
- A collimated cluster beam is guided into a magnetic field gradient (dB/dz). The field gradient will deflect a cluster with magnetic moment μ by a distance 'd' given by the equation as below (L → length of the magnet, D → distance from the end of the magnet to the detector, M → cluster mass, v_x → entrance velocity).
- For clusters deposited on surfaces other techniques of measurement exist such as: X-Ray Magnetic Circular Dichroism, Dichroism in Photoelectron Spectroscopy, Surface Magneto-Optical Kerr Effect, UHV Vibrating Sample Magnetometry, etc.
- For embedded clusters techniques like: Micro-SQUID Measurements, Micro-Hall Probes, etc. can be used to measure the magnetic moments.

$$d = \mu \frac{dB}{dz} L^2 \frac{(1+2D/L)}{2Mv_x^2}$$

So, these are experimental results and therefore we need to know how we can actually measure the magnetic moment of these clusters though our lecture. Here, it would be limited to a brief outline and students interested in these techniques may consult extensive texts on this aspect further. Now, first we shall talk about experimental results presented for free clusters, clusters can be of three types they can be free clusters, they can be clusters which are deposited on a substrate. That means they are on the substrate surface of a substrate or they can actually be embedded within a material, but here we first take up what we will present in a little detail how can we measure the magnetism or a magnetic moment of a free cluster.

For instance, this could be iron ferromagnetic clusters or it could be chromium and manganese anti ferromagnetic clusters and the typical experimental setup is based on the classic Stern-Gerlach experiment which was first used to detect the electron spin now typically this Stern-Gerlach kind of n experiment is coupled with a pulsed laser vaporization techniques and we shall consider some more these details in the next slide for instance.

(Refer Slide Time: 23:36)



Experimental setup for the measurement of magnetic moments

Metal clusters are produced by pulsed laser vaporization of a target material into a jet of helium gas → Cluster-gas mixture undergoes supersonic expansion on entering vacuum → Beam is collimated → Magnetic deflection of collimated beam → Ionization by Laser → Mass dependent deflection measured perpendicular to the beam in a TOFMS

So, typically such an experimental setup is what is used for the detection of the magnetic moment the heart of such an instrument is what you might call the time of flight mass spectrometer and the whole setup starts with the clusters source. So, before we take up this setup in detail let us go with go ahead with the further points that typically a collimated cluster beam is guided into a magnetic field gradient. That means we do not have a constant magnetic field, but field gradients which is quantified as db by dz, the magnetic field gradient will deflect a cluster with a magnetic moment mu by a distance d. This is given by the equation as here, so if you have the distance of deflection d under the influence of a magnetic gradient db by dz, then if the particle has mass m.

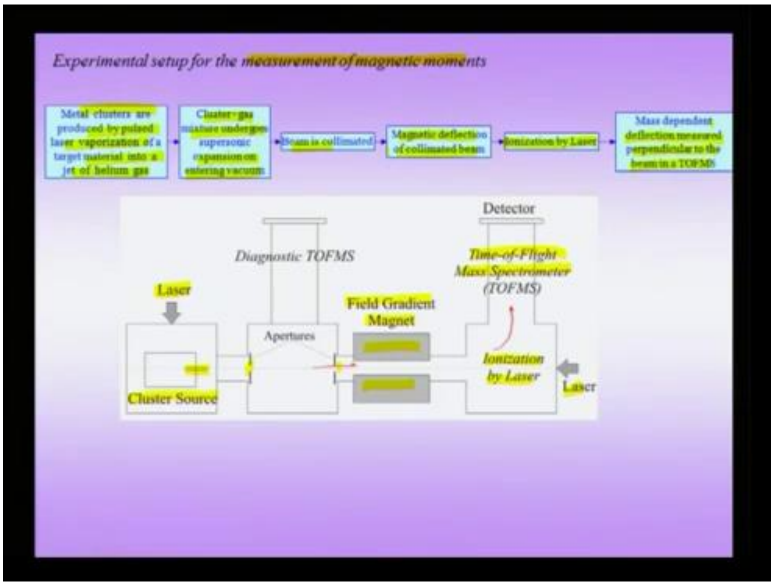
Then, this is the equation governing the deflection of the particle, now in this equation l is the length of the magnet these distance from the end of the magnet to the detector m. As I pointed out, it is the cluster mass and v x is the entrance velocity, which is assumed constant. Of course, there may be many situations in which the entrance velocity is not constant and therefore, this would be a simplifying assumptions which is used so that we can approximately find out the distance of deflection. As I had pointed out, there are other kinds of magnetic particles those which are embedded in a second phase in a metrics.

Those which are deposited on a surfaces and for clusters deposited on surface are the techniques of measurements exist that means the technique mentioned above is not suitable for that purpose. As you will see that in such a technique you need a stream of these magnetic particles and these magnetic particles will then be deflected by the magnetic field and will be put through a mass spectrometer. For particles deposited or clusters deposited on surfaces we can use techniques like extreme magnetic circular dichroism dichroism in photoelectron spectroscopy surface magneto optical Kerr effect vibrating sample magnetometry etcetera.

Here, we are just mentioning the names and interested treat obviously needs to go into text which will go into detail regarding the operation of these techniques and physics behind it. For embedded clusters techniques like micro squid measurements micro hall probes etcetera can be used for the measurement of the magnetic moments. So, a single technique is not sufficient for us to understand all kind of magnetic cluster, but here we take briefly the ones which is used one which is used for the measurement of free particle magnetic moments.

Just to summarize the slide at the heart of the experiment is the a setup which is based on a technique like this term here like experiment a class experiment which measured the electron spin. The physics behind is that you have a magnetic field gradient which deflects the particles based on the mass of the particle and its magnetic moment and based on the deflection. We can then back calculate the magnetic moment on the particle velocity assuming that the velocity of entrance of these cluster particles, cluster particles is independent of the size and it is a constant quantity.

(Refer Slide Time: 26:47)



Experimental setup for the measurement of magnetic moments

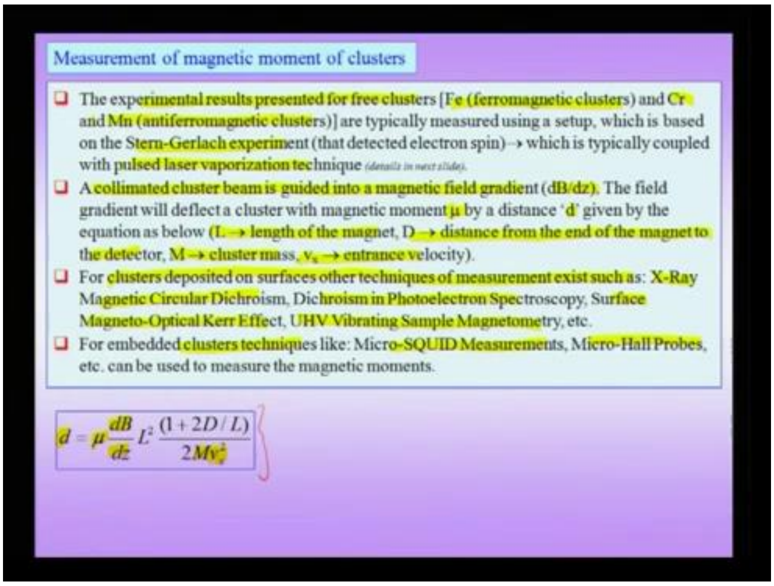
Metal clusters are produced by pulsed laser vaporization of a target material into a jet of helium gas → Cluster-gas mixture undergoes supersonic expansion on entering vacuum → Beam is collimated → Magnetic deflection of collimated beam → Ionization by Laser → Mass dependent deflection measured perpendicular to the beam in a TOFMS

So, this is the brief outline of the experimental setup for the measurement of magnetic moments first metal clusters are produced by pulse vapour deposition. Of course, other techniques may also be used for the production of these metal clusters of a target material into a jet of helium glass. Of course, helium in other words inert and therefore we will not react with the metal cluster vapour the cluster for this gas mixture is undergoes supersonic expansion on entering vacuum. So, this is the next stage after the production of these metal clusters that they undergo supersonic expansion when they enter the vacuum, then the beam produced.

So, here you have the nozzle which produces the beam the beam produces the collimated and the apertures play an important role in this collimation process. Then, further the magnetic field gradient which is produced by this field gradient magnets is used for the deflection of these collimated beam, but as I pointed out even though now you have a deflection produced unless these clusters are ionized. We will not be able to do mass spectroscopy on them, therefore, these cluster need to be ionized and the next chamber in down the line is the ionization by a laser. So, you have a laser which is specifically used to ionize this clusters and this laser is different from the laser is used initially for the production of the vaporized metal.

So, these laser has a different purpose this laser is used for the ionization of the cluster, finally after the cluster is been ionized, now there time of flight will depend on the mass and the ionization. Therefore, the mass dependent deflection is measured and is perpendicular to the beam in a time of flight mass spectrometer. That means initially the beam was arriving in this direction, but now the beam is deflected into the mass spectrometer at right angle to the original direction in which the cluster source was producing that.

(Refer Slide Time: 28:43)



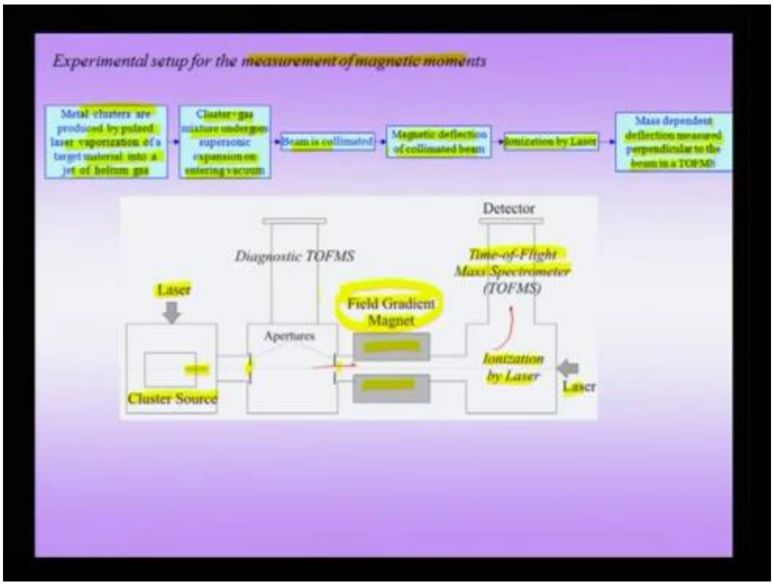
Measurement of magnetic moment of clusters

- ❑ The experimental results presented for free clusters [Fe (ferromagnetic clusters) and Cr and Mn (antiferromagnetic clusters)] are typically measured using a setup, which is based on the Stern-Gerlach experiment (that detected electron spin) → which is typically coupled with pulsed laser vaporization technique (details in next slide).
- ❑ A collimated cluster beam is guided into a magnetic field gradient (dB/dz). The field gradient will deflect a cluster with magnetic moment μ by a distance 'd' given by the equation as below (L → length of the magnet, D → distance from the end of the magnet to the detector, M → cluster mass, v_x → entrance velocity).
- ❑ For clusters deposited on surfaces other techniques of measurement exist such as: X-Ray Magnetic Circular Dichroism, Dichroism in Photoelectron Spectroscopy, Surface Magneto-Optical Kerr Effect, UHV Vibrating Sample Magnetometry, etc.
- ❑ For embedded clusters techniques like: Micro-SQUID Measurements, Micro-Hall Probes, etc. can be used to measure the magnetic moments.

$$d = \mu \frac{dB}{dz} L^2 \frac{(1 + 2D/L)}{2Mv_x^2}$$

So, to summarize this experiment we are now trying to measure the magnetic moments of free magnetic particles and for that we are using an equation like the one listed here below.

(Refer Slide Time: 28:58)

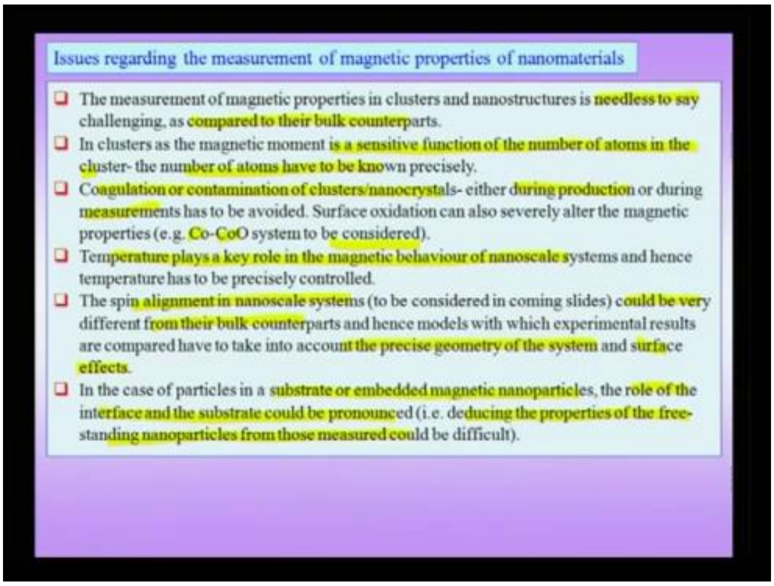


Experimental setup for the measurement of magnetic moments

Metal clusters are produced by pulsed laser vaporization of a target material into a jet of helium gas → Cluster-gas mixture undergoes supersonic expansion on entering vacuum → Beam is collimated → Magnetic deflection of collimated beam → Ionization by Laser → Mass dependent deflection measured perpendicular to the beam in a TOFMS

We are also using modified version of the stern Gerlach experiment and the flowchart for this experiment is as follows that we have a cluster source produced by a laser this cluster source is collimated and this cluster source is in mixture with a gas. Therefore, this gas and the cluster source goes through a series of apertures and then a field gradient as shown here as said goes through field gradient and this field gradient deflects the particles depending on their magnetic moment and their mass. Finally, to detect the particles, we ionize these clusters and finally, use a mass spectrometer to deflect and finally, back calculate the magnetic moments on these clusters.

(Refer Slide Time: 29:44)



Issues regarding the measurement of magnetic properties of nanomaterials

- ❑ The measurement of magnetic properties in clusters and nanostructures is needless to say challenging, as compared to their bulk counterparts.
- ❑ In clusters as the magnetic moment is a sensitive function of the number of atoms in the cluster- the number of atoms have to be known precisely.
- ❑ Coagulation or contamination of clusters/nanocrystals- either during production or during measurements has to be avoided. Surface oxidation can also severely alter the magnetic properties (e.g. Co-CoO system to be considered).
- ❑ Temperature plays a key role in the magnetic behaviour of nanoscale systems and hence temperature has to be precisely controlled.
- ❑ The spin alignment in nanoscale systems (to be considered in coming slides) could be very different from their bulk counterparts and hence models with which experimental results are compared have to take into account the precise geometry of the system and surface effects.
- ❑ In the case of particles in a substrate or embedded magnetic nanoparticles, the role of the interface and the substrate could be pronounced (i.e. deducing the properties of the free-standing nanoparticles from those measured could be difficult).

Now, obviously as we can note that there are issues regarding the measurement of magnetic particle properties of nanomaterials which are quite unique to nanomaterials and quite different from their bulk counter parts. So, needless to say that the measurement of magnetic properties of clusters and nanostructures is challenging as compared to their bulk counterparts in clusters magnetic moment is a sensitive function and number of atoms in the cluster. That means we need to know the number of atoms precisely in the case of bulk it does not matter to us that if the bulk actually is a one centimetre bulk or one point one centimetre bulk, but in the case of nanoparticles and nanocrystals.

We need to know that what are the précised number of atoms in the cluster coagulation and contamination of these clusters and nanocrystals is serious issue. This contamination may take place either during production or during measurement and has to be avoided because small amounts of contaminants can severely order the properties of these magnetic nanoparticles. Good example of this would be the surface oxidation of the cobalt magnetic particle on surface oxidation you actually form a cobalt oxide on a surface and the cobalt oxide system has a very different magnetic behaviour which we will consider shortly,

This is at the heart of the phenomena known as the exchange anisotropy, therefore we should avoid any kind of contamination or any kind of a reaction with the atmosphere during reduction or during the measurement process. As you know temperature plays a very key role in a magnetic behaviour of nanoscale systems because reduction in size is equivalent to increase in temperature. Therefore, when we assume that the temperature of the system is a particular number we have to assume which precisely measured and is constant at the level of the cluster and not merely at the average temperature of the chamber.

So, not only we precisely measure the temperature, but control it at the level of the clusters the spin alignment in nanoscale systems which we will consider in detail in the coming slides could be very different from their bulk counterparts. Hence, when you try to back calculate using a model had use a model to understand experiments, then the précised geometry of the system and the spin orientation therein has to be taken into account. That means we should know the geometry of the nanostructure, we should know the alignment of spins therein in the nanostructures and we should also take into account the surface effects else the model will not be able to satisfactorily.

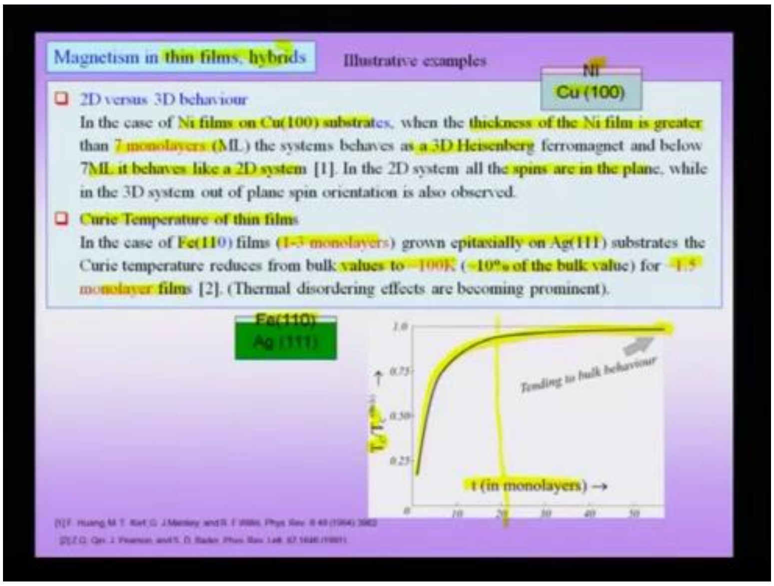
Either understand the experiment or predict properties based on the experiment in the case of particles in a substrate or embedded in embedded in magnetic nanoparticles we have to remember that this is no longer a free system. That means the properties of an particles which is in intimate contact with for instance with the substrate or a metrics is very could be very different from the free standing nanoparticle. The role of this interface of the substrate will be very pronounced and often this interface could play could alter the properties of the nanoparticle all together. Also, we should remember that if we talk about a single isolated free standing nano particle, its magnetic properties could be somewhat different from that of many clusters placed in proximity.

In other words, now the system is that nanoparticles are not free and they talk to each other and this collective behaviour could be very different from that of the single isolated nanoparticle. Either free or deposited in a substrate or embedded in a metrics and therefore did not, but also we have noted that deducing the properties of free standing nanoparticles from those measured could be very difficult.

In other words, suppose I make my measurements on a nano particle, which have been deposited in a substrate and there I try to back calculate that what could be the properties of free standing nanoparticles this could be an adverse task. Sometimes it will not give the correct results therefore, to summarise this slide issues regarding the measurements of the magnetic particles are many a few of them we have taken up in this slide. As you can see that unless some of the issues regarding for instance the purity of the nanoparticle the temperature of the system the actual knowledge regarding the number of atoms in the system.

The kind of models which have been taken into account in a underlying model like in terms of the spin alignment etcetera have to be specially constructed for these nanoclusters and nanoparticles. We cannot merely extrapolate from the their bulk counterparts and also we noted last, but not the least that isolated nanoparticles could be very different from those which are in proximity to similar kind of nano particles or nano particles of different types. Therefore, the surrounding medium is or the surrounding environment to the nano particle or the nanocluster is also of lot of importance when you try to deduce the properties.

(Refer Slide Time: 34:46)



Magnetism in thin films, hybrids

Illustrative examples

- 2D versus 3D behaviour

  In the case of Ni films on Cu(100) substrates, when the thickness of the Ni film is greater than 7 monolayers (ML) the systems behaves as a 3D Heisenberg ferromagnet and below 7ML it behaves like a 2D system [1]. In the 2D system all the spins are in the plane, while in the 3D system out of plane spin orientation is also observed.

- Curie Temperature of thin films

  In the case of Fe(110) films (1-3 monolayers) grown epitaxially on Ag(111) substrates the Curie temperature reduces from bulk values to ~100K (~10% of the bulk value) for ~1.5 monolayer films [2]. (Thermal disordering effects are becoming prominent).

Next, we take up magnetisms in thin films and hybrids and we have pointed out while we talked about thin films that there are couple of important things that in thin films of magnetic materials ferromagnetic materials. You actually observe what you might call Neel walls, which are not found in typically in bulk materials where you actually observe what you call domain walls which are called block walls. Interestingly, we will talk about when we talk about magnetism in hybrids we will come across very interesting phenomena later on. First let us talk about this dimensionality of this system when we talked about previously about the thin films we noted that the magnetization is in plane.

There are no components of magnetization out of plane, of course this is only true for very thin films and when the system size grows you would note that there is an out of plane component of magnetization or the orientation of the spins. This means the system starts to behave like a three d system, so when is this transition from a two d behaviour to a three d behaviour is what we are noting. So, people have studied of course these thin films cannot be free standing thin films because they would tend to war when they are difficult to study typically these thin films are grown on a substrate.

In the case of nickel films which have been studied on a copper 1 0 0 substrate, of course it is copper is chosen because copper is not a magnetic material. Often, you may also notice that in some of this systems studied the film may actually be epitaxial with respect to the substrate. Now, in the case of the nickel films on copper substrates and copper 1 0 0 single crystal substrates has been used in the experiment when the thickness of the nickel films is greater than about 7 mono layers. That means this is very thin film regime the system behaves like a 3 d Heisenberg ferromagnet, in other words it becomes a 3 d ferromagnet.

That means which spins out of plane when already this system size is only about seven mono layers on the other hands below seven mono layers it behaves like a 2 d system. In other words, all the spins are in the plane while in the 3 d systems spins can be out of plane. So, this implies that you can have a transition from 2 d to 3 d behaviour in these nickel films which are grown on copper substrates for a very thin size of films like about seven mono layers. So, below seven mono layers you actually have 2 d system, where all the spins are in plane and above seven mono layers, the system starts to behave like a 3 d ferromagnet, wherein the spins have an out of plane component also.

This means that now correspondingly then the Neel wall which we talked about wherein all the spins are rotating in plane would also have a certain out of plane component in such kind of systems. Of course, we had now that we are talking about a multi domain system in the film if you have to consider that. The next thing we talk about in this thin films is the case of the Curie temperature in thin films, we had noted earlier itself that the Curie temperature actually varies in size in the case of iron 1 0 0 films grown epitaxially on the silver 1 1 1 films. That means my substrate is now silver 1 1 1 substrate and you are actually growing a iron 1 0 film on it. Again, we are in what you might call the very thin regime wherein we had tracking the layers layer by layer.

That means it is one monolayer or 2 monolayer or 3 monolayer, now when you are talking about these thin films, we notice that the Curie temperature can actually be reduced with respect to the bulk value. We already told that decreasing the size in some sense is like increasing the temperature and when you increase the temperature what happens is that there is a ferromagnetic to paramagnetic transition, which means that actually you are crossing the curie temperature. So, this is clear, so when I plot the thickness of these mono layers with respect to t c and of course now I am normalizing this t c with respect to the t c of the bulk material, which is what we normally call the Curie temperature.

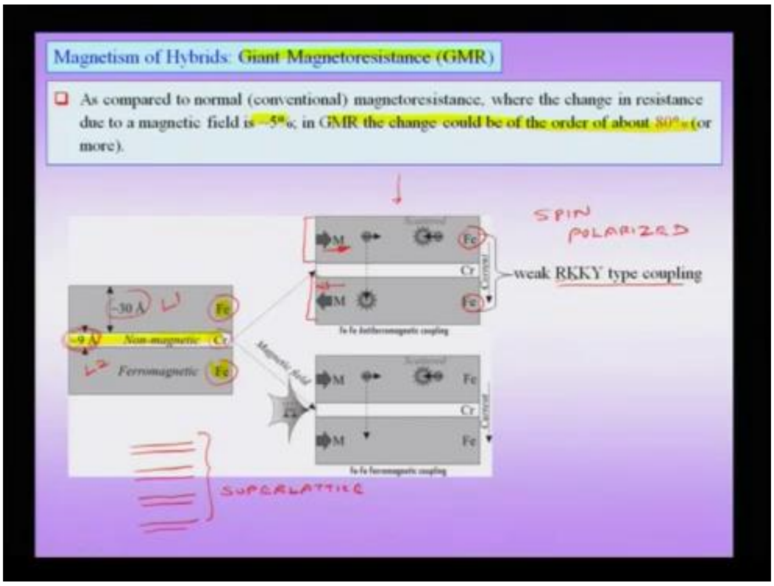
You would notice that of course for large sizes of mono layers more than about 50 mono layers, you approach the bulk limit that when t c by t c becomes 1, but as you go down to the very thin mono regime the Curie temperature actually falls. In other words, in this very thin mono layers less than about 20 mono layers, you can see that the exchange coupling is not able to fight against the thermal disordering that effectively because there are just not enough number of atoms in this layer. This implies that the curie temperature is going to be reduced in the case we are talking about here, the iron 1 1 0 film on silver 1 1 1 substrate, the curie temperature can actually be depressed by about 100 kelvin with respect to the bulk.

That means you can approach about 10 percent of the bulk value when you are in the regime of about 1.5 monolayer thick films. That means that in this thin films again like because reduced dimensionality systems the thermal disordering effects becomes very important on magnetization. Therefore, though there is this possibility we might use that in the reduced dimensionality systems there is this enhanced magnetism per atom.

We can obtain that means the number of bore magnetrons I can for an atom increases that is possibility is there, but then this is also fighting against the thermal disordering effects. Therefore, we will have to pull the system to actually obtain the value of what you call the possibility or the potential magnetization per atom before we take up what you might call magnetism in hybrids. Let us summarize this slide by saying that in very thin films, you have a 2 d kind of a behaviour and this very thin. We mean is in the order of a few mono layers and here as I pointed out we are not really studying free standing thin films because free standing thin films are difficult to study.

So, these are typically films which are grown either epitaxially or otherwise on some kind of a substrate typically the substrate used is of choice is a nonmagnetic material like copper or silver which is a single crystal. These single crystalline over layers when they are in the small size regime typically behave like 2 d system and later on they start to behave like a 3 d system for thicker sizes. Additionally, these very thin films can actually have a depression in what you might call the Curie temperature with respect to the bulk of a large value. That means it can actually reduce to about 10 percent or more for very thin films for when you are trying to find a Curie temperature of these thin films, next we take up magnetism of hybrid.

(Refer Slide Time: 41:10)



Magnetism of Hybrids: Giant Magnetoresistance (GMR)

- ☐ As compared to normal (conventional) magnetoresistance, where the change in resistance due to a magnetic field is ~5%; in GMR the change could be of the order of about 80% (or more).

In this context, we will take up the important phenomena known as giant magneto resistance or called as G M R for short it is important to note we had earlier noted a concept known as the anisotropic magneto resistance. We had noted that that magneto resistance value is typically about 5 percent that means in the presence of the magnetic fields and in the absence of the magnetic field the resistance value changes only about by 5 percent. We had also talked about an important concept; in that context that was the concept of the spin dependent scattering. That means the resistance is coming from a new kind of phenomena, which is not the usual charge scattering arising due to furnace or impurities, but what you might call in dependent scattering.

The important thing in the giant magneto resistance that the word giant implies that the change in resistance could be of the order of 80 percent or more, so this is a very important point known that is why it is called giant magneto resistance. There is also a related phenomena or a different kind of phenomena known as colossal magneto resistance, which we will not talk about in this course, but this giant magneto resistance is not the same as colossal magneto resistance. Another important point about giant magneto resistance is that it is actually found in hybrids that mean it is found only in the composite structures. There are cases where giant magneto resistance has been reported in other kinds of systems also, but the classical system is that often hybrid.

So, what is the configuration which is giving the giant magneto resistance, it is typically a nonmagnetic layer in lying in between two magnetic layers. This is of course the simplest configuration, you can think of let me talk about for instance in this case example given here you have two layers of iron which is a ferromagnetic. There is a nonmagnetic layer like chromium the thickness of this chromium layer is very important as we shall see soon and typically it is of the order of about nine angstrom. The thickness of the iron layer is about thirty Armstrong's instead of making one single sandwich structure like this you could actually repeat this structure to form a larger layer structure consisting of these irons an these chromium.

This kind of a multilayer super lattice structure can actually give you an even higher enhanced value of giant magneto resistance. The overall physics can easily be understood by considering only a three layers system consisting of two ferromagnetic materials and a non ferromagnetic interlayer between the two. Of course, it is as I told you the nonmagnetic layers, thickness is very important and of a very specific size.\

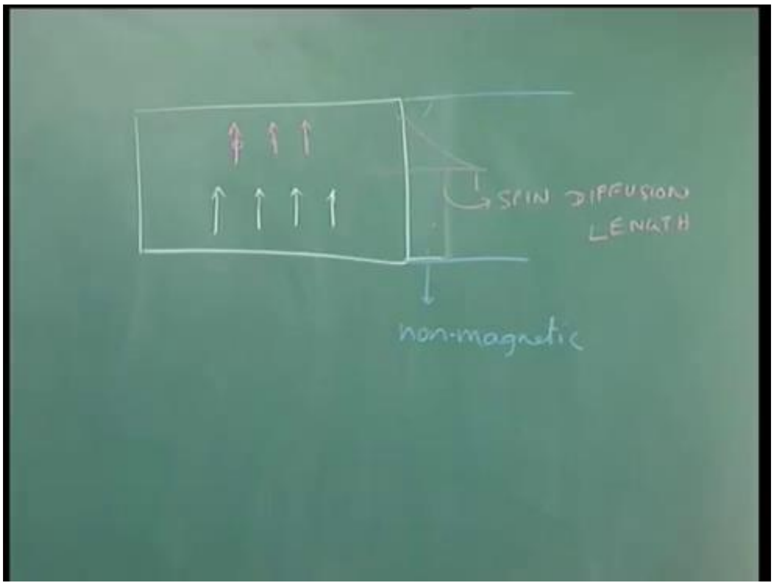
The reason is that depending on the size of the nonmagnetic layer there is an anti ferromagnetic coupling between the two layers of iron that means the two layers of iron one layer has magnetization pointing in one direction. The other layer has magnetization pointing in the other direction I have a chosen configuration known as the magnetization in plane. There is other configuration where a magnetization perpendicular to plane also is possible, but the essential physics again does not change. So, in this case you have one magnetic layer which is pointing in this direction that means all the spins in this top layer is pointing to the right while all the spins of course again we are ignoring the interface spins which could be little distorted that out.

In this layer, all are pointing towards the left this anti ferromagnetic coupling is a weak coupling coming from the phenomena known as the RKKY coupling. In the RKKY coupling depending on the distance between the two ferromagnetic layers the coupling can either be ferromagnetic or can be anti ferromagnetic. That means if I have made two layers at a certain distance if it is of course joining together, then it will be ferromagnetic coupling on a certain distance. It will become anti ferromagnetic coupling at certain larger distance, it will become ferromagnetic. Again, that means there is a oscillatory coupling between these two layers and this is called RKKY coupling coming from authors whose name start as ruder man and kittle.

So, you see that this is at the heart of the understanding of what you might call giant magneto resistance. In other words there are two layers and in the absence of any external magnetic fields the two layers of the ferromagnetic material are anti ferromagnetically coupled. I am not saying they had become anti ferromagnetic these individual layers continue to be ferromagnetic, but a coupling between these two layers which I call layer 1 and layer 2 are anti ferromagnetic. That means they point in opposite direction, now what happens when you are passing a current and when you pass a current through a ferromagnetic material then the current becomes spin polarized.

When the current that means when you are passing a current in a normal materials, the spins are pointing randomly while you pass a current through a ferromagnetic materials, the spins get polarized. Now, all these spins in the ferromagnetic materials are pointing in the same direction that means now you have a spin polarize current. That means not only is a charge being transported to the ferromagnetic materials spins are also being transferred to the ferromagnetic material.

(Refer Slide Time: 46:26)

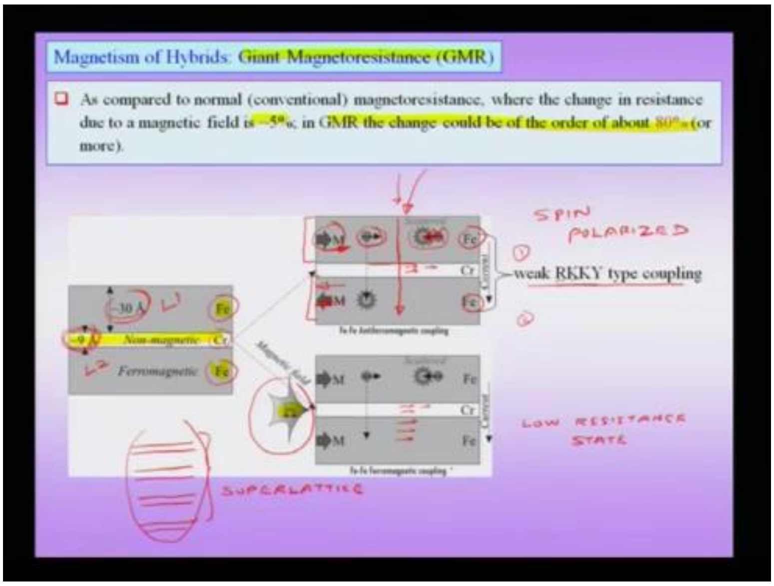


Now, let me draw this schematically like this, now you have a ferromagnetic material like this in which all the spins are pointing upward say for instance and now you have a material which is nonmagnetic. For now, I will assume that this is again a long piece of material which is nonmagnetic, so when I pass current through this material, this spin gets spin polarized; the current which is flowing this is of course the fixed charges on lattices. So this fixed magnetic moments in a material, but this is the one which is carrying the current and that thus I am drawing separately in that. Therefore, the current they charges become spin polarize and this is travelling, therefore when it crosses the interface this material is nonmagnetic.

This spin polarization would actually died down from after a certain length and this length is called the spin diffusion length. In other words in the magnetic material when the current is flowing it becomes spin polarized, but since this material is nonmagnetic there is there is no internal field or no internal spin polarization to keep the current as spin polarized and after a certain distance. When it travels in the nonmagnetic material, it loses its spin memory, in other words it becomes after the spin diffusion length it rather its spin memory is lost and it becomes the spins become randomly oriented.

Now, the important point to note is that this intermediate nonmagnetic layer as a very small thickness. That means typically its thickness is less than the spin diffusion length which implies that the material spin current flows across the nonmagnetic layer without the spin memory being lost.

(Refer Slide Time: 48:28)



Magnetism of Hybrids: Giant Magnetoresistance (GMR)

- As compared to normal (conventional) magnetoresistance, where the change in resistance due to a magnetic field is ~5%, in GMR the change could be of the order of about 80% (or more).

So, that is a very important point, so I have a spin polarized current coming from the top layer which goes down to the bottom layer. Now, what is happening initially since the magnetization of the first material is in this direction if there are any spins in the current originally pointing in the wrong direction. For instance, you might have a normal conductor actually injecting electrons into these ferromagnetic layers. Those spins will get scattered preferentially which are pointing in the wrong direction that means this kind of a spin which is pointing to the left will get scattered more preferentially as compared to the spin in other electron. This is preferentially oriented with respect to the magnetic field so spins which are wrongly pointed get scattered.

Now, this resistance with that means if they are scattered that means it is contributing to a resistance and this is purely coming from spin polarization related scattering. That means spin related scattering and not the usual photonic or impurity kind of a scattering which we had talked about before.

So, this is new kind of a phenomena and therefore, what is happening here is that you have resistance arising from that. Therefore, when the when the charges cross this interface and come to the chromium layer you have a spin polarized current in which all spins are pointing towards a right direction which is the direction of magnetization in the layer 1. This is field polarized as I pointed out this chromium layer is thin and I have said that it is smaller than the spin diffusion length. That means that when it goes to layer number two you have another magnetic layer, but unfortunately this magnetic layer, the magnetization is in the opposite direction of the respect to the first one.

That means there will be a strong spin dependent scattering in the second layer, the layer 2 will scatter all these electrons very strongly, in other words you will have an high resistance state, so this is very interesting. Now, I am producing a high resistance state just by anti ferromagnetic coupling two layers by using a spacer layer and using spin dependent scattering as a mechanism for increase in the system. So, you have a high resistance state in the absence of any external magnetic fields, now suppose what happens when I put in an external magnetic field h. What happens now is that in the presence of an external magnetic field the magnetization vectors in the bottom layer are also pointing in the same direction.

We already noted that the spin polarized current in the middle layer when it crosses is pointing towards. So, when it comes down to the bottom layer, there is nothing which is impeding it in fact it is going to reinforce this polarized current and the current can flow unimpeded. That means we have obtained a low resistance state in the presence of a magnetic field. Of course why is this external magnetic field easily able to switch the magnetization direction because we said that this RKKY coupling is actually a weak coupling is not a very strong coupling. So, when you apply an external magnetic field this weak anti ferromagnetic coupling is overridden.

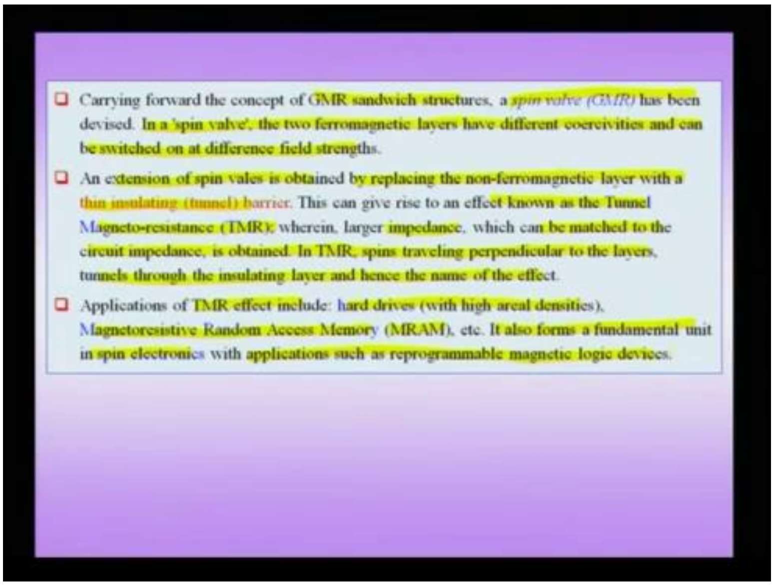
You have both the magnetization both the layers layer 1 and layer 2 pointing in the same direction. Now, we have an very interesting effect which is coming from which is definitely in the domain of nano magnetism coming from composites or hybrids made of magnetic layers. Of course, you have to do as I point out, you have to include a nonmagnetic layer which could be a conductor as in this case or it could be a resistance or a dielectric as we shall see in a next slide.

So, to summarize this slide number one, you could have very high values of magneto resistance which are called giant magneto resistance which is coming in hybrids. This exceeds a value of about 80 percent unlike the case of normal anisotropic magneto resistance where you expect a value of about 5 percent. That means the state in the presence of the magnetic field is different in the systems from the state in the absence of a magnetic field and there is this difference is of the order of 80 percent in this structure. A typical structure consists of two ferromagnetic materials which with the space arranged between with a very small thickness of about 9 Armstrong's and this plays an important role of anti ferro magnetically coupling the two layers.

They themselves are very thin this is of the order of three nanometres you can see at this layers and actually you can make a multi layer super lattice which will give you an enhanced value of this effect. The essential at the heart of it is two phenomena, one is the weak RKKY coupling reading to this anti ferromagnetic coupling, number two is the spin polarized current which is and the spin dependent scattering giving rest to resistance.

Finally, noting that in the presence of a magnetic field I have a low resistance that means now I have a control to switch this material from a ferromagnetic or a low resistance state to an high resistance state by using an external magnetic field. Therefore, I have control over the resistance of the material by using an external magnetic field; this gives us lot of interesting rich possibilities and important applications.

(Refer Slide Time: 53:21)



- ❑ Carrying forward the concept of GMR sandwich structures, a *spin valve (GMR)* has been devised. In a 'spin valve', the two ferromagnetic layers have different coercivities and can be switched on at difference field strengths.
- ❑ An extension of spin vales is obtained by replacing the non-ferromagnetic layer with a thin insulating (tunnel) barrier. This can give rise to an effect known as the Tunnel Magneto-resistance (TMR); wherein, larger impedance, which can be matched to the circuit impedance, is obtained. In TMR, spins traveling perpendicular to the layers, tunnels through the insulating layer and hence the name of the effect.
- ❑ Applications of TMR effect include: hard drives (with high areal densities), Magnetoresistive Random Access Memory (MRAM), etc. It also forms a fundamental unit in spin electronics with applications such as reprogrammable magnetic logic devices.

Now, some of these applications we will sight in this slide I had pointed out that when you are dealing with this system I can actually replace this nonmagnetic layer in between with what you might call as a dielectric material. Now, before we come to that we will talk about another interesting structure which is based on this concept which is the concept of GMR in the concept of GMR and sandwich structures a spin valve GMR also has been devised. In a spin valve, the two ferromagnetic layers have different coercivities and can be switched at different field strengths. So, we are getting additional control here in earlier we applied one magnetic field and we got the anti ferromagnetic or ferromagnetic coupling.

Here, what we are doing is that we have different coercivity for the two layers and we can actually switch one of those preferentially. So, this is what you might call the spin valve structure now and this spin valve implies that now I am able to control the spin dynamics, which means that I can enter new domain known as the spintronics. Here, I would like to manipulate charge and do electronics, I am able to control the spin of the materials and do spintronics. So, this is a very interesting domain which is of magnetism which is gaining prominence of recent times.

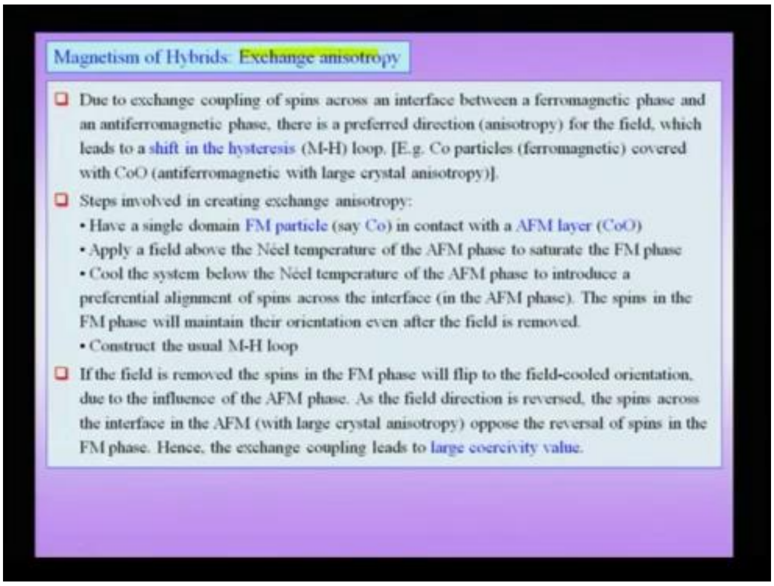
As I pointed out that an extension of spin valve can be obtained by replacing the non ferromagnetic layer by a thin insulating layer a thin insulating layer is otherwise called a tunnel barrier. In this corresponding case, the effect is known as tunnel magneto resistance the critical difference between the two is that in the previous case of giant magneto resistance the inter layer was a conductor. That means electrons could easily flow in this case, it is an insulator that means that now the electrons can have to tunnel through this barrier and we have already discussed about the concept of tunnelling that means that with the thickness of the tunnel region.

The resistance exponentially increases, but the important thing is that the overall impedance of the system is large and therefore it can be matched to the circuit impedance to obtain you know match systems in GMR. The tunnel magneto resistance phenomena spins travelling perpendicular to the layers tunnels through the insulating layer and hence is the name of the effect. So, this is very similar to the giant magneto resistance phenomena we saw before the important difference being is now the current through the insulating layer is a tunnelling current.

Therefore, is much reduced in value as compared to the GMR case wherein I had a conducting material like chromium as the inter layer the GMR effect. The other GMR effect etcetera are found in the important applications which include hard drives with the increased areal densities the magneto resistive random access memory MRAM. Other important applications, these also form fundamental units in spin electronics as I pointed out with applications such as re programmable magnetic logic devices.

So, these are important areas of research wherein lot of intensive research is going on to build better and better high density storage devices and devices which can be integrated with the current technology silicon technology. Therefore, we have seen effects, two important effects the GMR effect and the TMR effect, wherein magneto resistance is the heart of you know designing important devices, next we take up we continue with the topic of magnetism in hybrid.

(Refer Slide Time: 56:39)

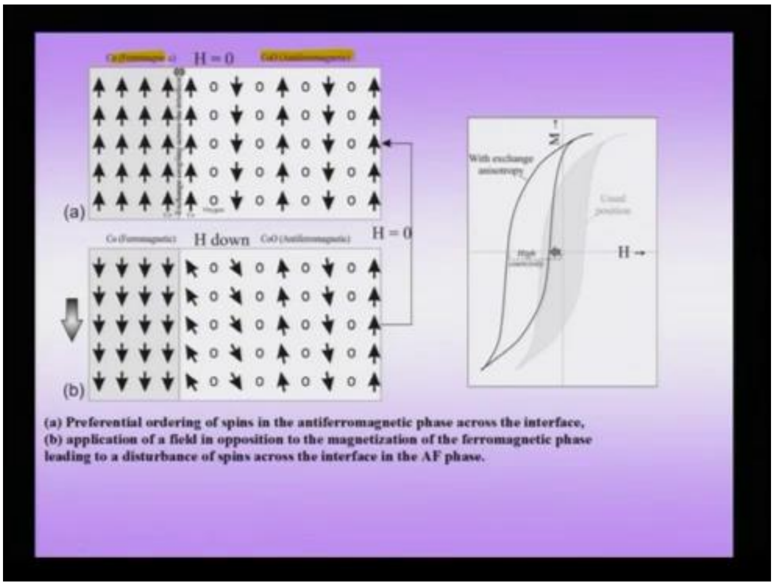


Magnetism of Hybrids: Exchange anisotropy

- Due to exchange coupling of spins across an interface between a ferromagnetic phase and an antiferromagnetic phase, there is a preferred direction (anisotropy) for the field, which leads to a shift in the hysteresis (M-H) loop. [E.g. Co particles (ferromagnetic) covered with CoO (antiferromagnetic with large crystal anisotropy)].
- Steps involved in creating exchange anisotropy:
  - Have a single domain FM particle (say Co) in contact with a AFM layer (CoO)
  - Apply a field above the Néel temperature of the AFM phase to saturate the FM phase
  - Cool the system below the Néel temperature of the AFM phase to introduce a preferential alignment of spins across the interface (in the AFM phase). The spins in the FM phase will maintain their orientation even after the field is removed.
  - Construct the usual M-H loop
- If the field is removed the spins in the FM phase will flip to the field-cooled orientation, due to the influence of the AFM phase. As the field direction is reversed, the spins across the interface in the AFM (with large crystal anisotropy) oppose the reversal of spins in the FM phase. Hence, the exchange coupling leads to large coercivity value.

We talk about phenomena known as exchange anisotropy, now in exchange anisotropy you again have a composite.

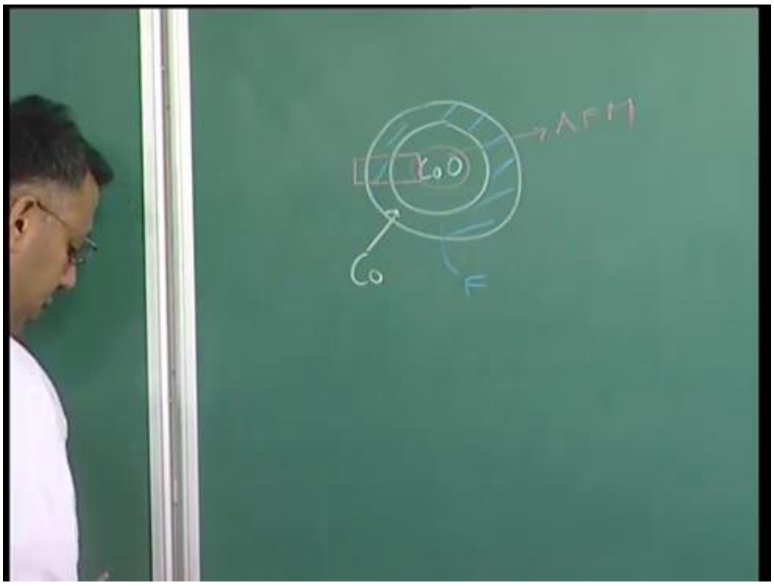
(Refer Slide Time: 56:48)



(a) Preferential ordering of spins in the antiferromagnetic phase across the interface, (b) application of a field in opposition to the magnetization of the ferromagnetic phase leading to a disturbance of spins across the interface in the AF phase.

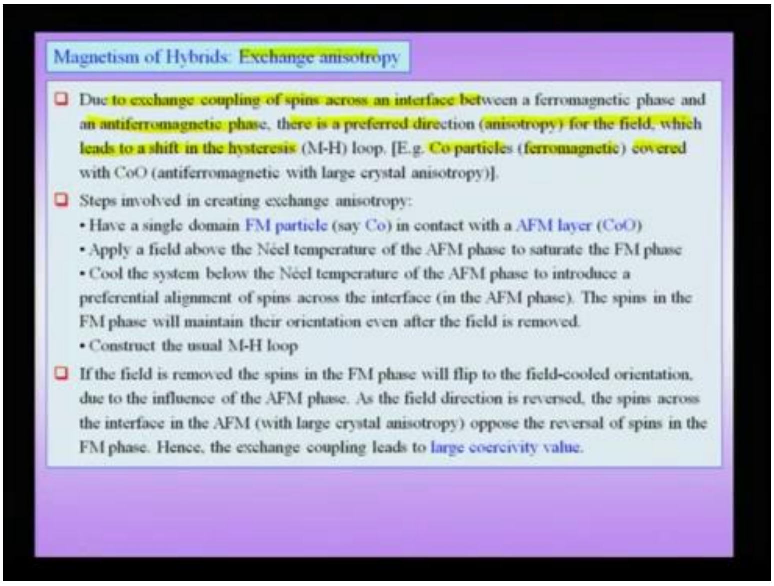
In this composite, there is a layer which is anti ferromagnetic and there is a layer which is ferromagnetic though we are showing here it has a linear configuration in reality this could be actually a particle.

(Refer Slide Time: 57:02)



What you might call a core shell kind of a structure, which we had held to it before and this could be the Co O particle and this could be the Co and this external layer is the ferromagnetic layer. So, this is a ferromagnetic layer and the inside layer the core of this structure is the anti ferromagnetic layer. So, we are actually now focusing on this interface region between the two so this is the region we are assuming in on this picture so this kind of a configuration is what we had seen, so we have an anti ferromagnetic layer and a ferromagnetic layer in adjacent to each other.

(Refer Slide Time: 57:40)



Magnetism of Hybrids: Exchange anisotropy

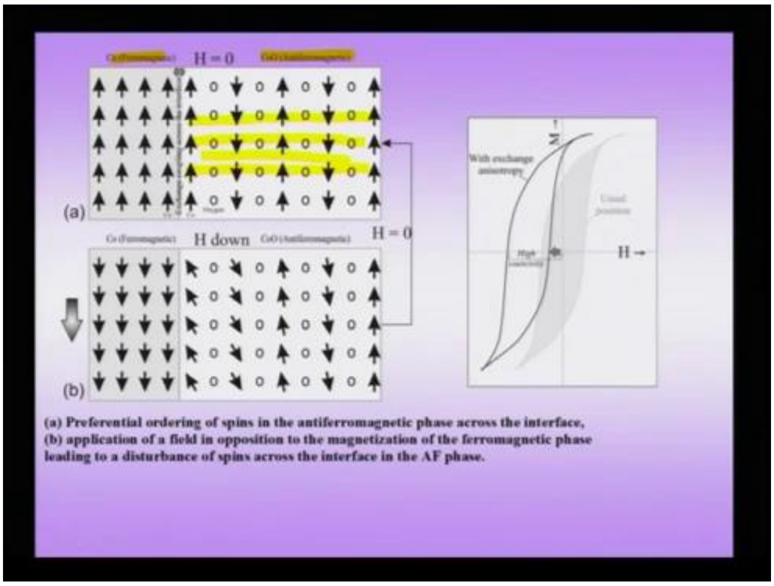
- Due to exchange coupling of spins across an interface between a ferromagnetic phase and an antiferromagnetic phase, there is a preferred direction (anisotropy) for the field, which leads to a shift in the hysteresis (M-H) loop. [E.g. Co particles (ferromagnetic) covered with CoO (antiferromagnetic with large crystal anisotropy)].
- Steps involved in creating exchange anisotropy:
  - Have a single domain FM particle (say Co) in contact with a AFM layer (CoO)
  - Apply a field above the Néel temperature of the AFM phase to saturate the FM phase
  - Cool the system below the Néel temperature of the AFM phase to introduce a preferential alignment of spins across the interface (in the AFM phase). The spins in the FM phase will maintain their orientation even after the field is removed.
  - Construct the usual M-H loop
- If the field is removed the spins in the FM phase will flip to the field-cooled orientation, due to the influence of the AFM phase. As the field direction is reversed, the spins across the interface in the AFM (with large crystal anisotropy) oppose the reversal of spins in the FM phase. Hence, the exchange coupling leads to large coercivity value.

Due to exchange of spins coupling of spins have cross the interface between the ferromagnetic phase and the anti ferromagnetic phase there is a preferred direction anisotropy. That means that there is anisotropy for field which leads to a shift and the hysteresis loop. We will of course see why this is happening very soon, in other words the example layer sighted, the cobalt oxide particles of the ferromagnetic particles and they are covered with an cobalt oxide which is a anti ferromagnetic system with a large anisotropy.

So, what we see in these phenomena of exchange anisotropy is that there is a large coercively increases and this coercively increase is coming because now you have made the system highly anisotropic. That means the system the ferromagnetic system highly anisotropic by coupling it with an anti ferromagnetic layer. This is shown schematically on the right hand side, now I obtain high coercively for this ferromagnetic layer on the left hand side and this is coming because of the anisotropy introduced by the geometry. Now, this is an external enforce anisotropy by coupling it with an anti ferromagnetic material the steps involved in creating this exchange anisotropy areas follows first.

Of course, you have a single domain ferromagnetic particle like cobalt in this example in contact with an anti-ferromagnetic material like cobalt oxide.

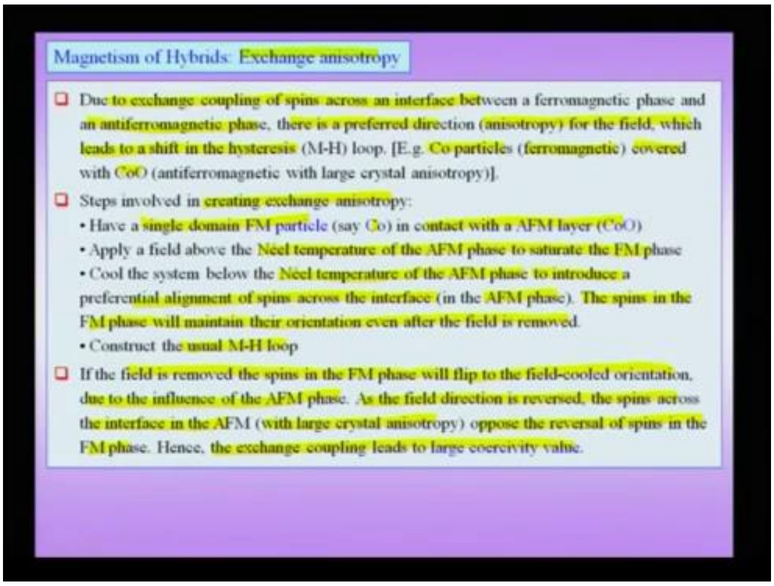
(Refer Slide Time: 59:05)



(a) Preferential ordering of spins in the antiferromagnetic phase across the interface,
(b) application of a field in opposition to the magnetization of the ferromagnetic phase leading to a disturbance of spins across the interface in the AF phase.

We had already noted that this anti ferromagnetic coupling is actually mediated by a phenomena knows super exchange by these oxygen molecules oxygen atoms. That means that this coupling between the two anti ferromagnetic coupling is mediated by a super exchange wherein oxygen plays the important role.

(Refer Slide Time: 59:21)

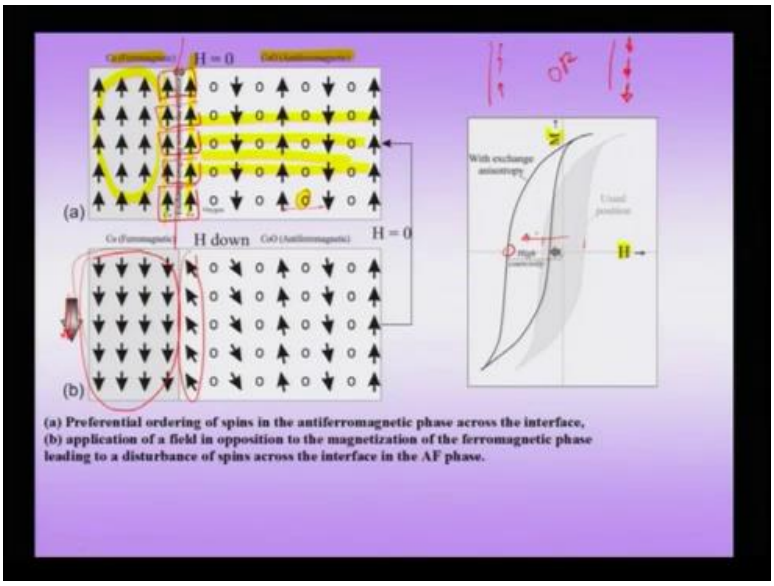


Magnetism of Hybrids: Exchange anisotropy

- ❑ Due to exchange coupling of spins across an interface between a ferromagnetic phase and an antiferromagnetic phase, there is a preferred direction (anisotropy) for the field, which leads to a shift in the hysteresis (M-H) loop. [E.g. Co particles (ferromagnetic) covered with CoO (antiferromagnetic with large crystal anisotropy)].
- ❑ Steps involved in creating exchange anisotropy:
  - Have a single domain FM particle (say Co) in contact with a AFM layer (CoO)
  - Apply a field above the Néel temperature of the AFM phase to saturate the FM phase
  - Cool the system below the Néel temperature of the AFM phase to introduce a preferential alignment of spins across the interface (in the AFM phase). The spins in the FM phase will maintain their orientation even after the field is removed.
  - Construct the usual M-H loop
- ❑ If the field is removed the spins in the FM phase will flip to the field-cooled orientation, due to the influence of the AFM phase. As the field direction is reversed, the spins across the interface in the AFM (with large crystal anisotropy) oppose the reversal of spins in the FM phase. Hence, the exchange coupling leads to large coercivity value.

Now, what we do is that we take the system above the Neel temperature of the anti ferromagnetic phase and saturate the ferromagnetic phase. That means now above the Neel temperature the anti ferromagnetic phase has become an paramagnetic phase. Above that, we saturate the ferromagnetic phase now when we cool the system below the Neel temperature of the anti ferromagnetic phase. We introduced a preferential alignment of spins across the interface in the anti ferromagnetic phase.

(Refer Slide Time: 59:52)



(a) Preferential ordering of spins in the antiferromagnetic phase across the interface,
(b) application of a field in opposition to the magnetization of the ferromagnetic phase leading to a disturbance of spins across the interface in the AF phase.

That means that originally of course if I did not have the left hand size of the picture that means we had only the right hand side and we did not have the interface. What could happen is that the anti ferromagnetic phase could have across the interface spins pointing either upwards or it could have been spins pointing downwards when you cool below the Neel temperature. So, this could be all spins pointing downwards, so these two possibilities this or this could exist, but now since there is a ferromagnetic phase which has a preferred orientation. You see that the spins are matched across the interface when you cool down below the Neel temperature of the anti-ferromagnetic phase.

Now, the spins in the ferromagnetic phase will maintain the orientation even after the field is removed because how did you get that preferential alignment towards the top originally in this ferromagnetic phase above the Neel temperature. We used an external magnetic field right now because now when you remove the external magnetic field the spins in the ferromagnetic field do not sort of lose their orientation. That is because there is this anti ferromagnetic layer which is imposing the anti Ferro magnet across imposing itself on the ferromagnetic phase on the right side. That means the ferromagnetic phase now retains its orientation which is now coupled to the anti ferromagnetic layer, now we have made the desired composite or what you might call a structure.

We can construct the usual M H loop if the field is removed the spins in a ferromagnetic phase will flip to the field cooled orientation due to the influence of the anti ferromagnetic phase. As the field directions reverses the spins across the interface in anti ferromagnetic phase with large crystal anisotropy oppose the reversal of spins in the ferromagnetic phase and this exchange coupling leads to large coercivity value. Now, have been made a structure like this I can construct what you may call an M H loop which we normally do and while this field is pointing in the direction of the ferromagnetic phase.

There is no problem the magnetization is very easy and you can easily obtain the saturation, but when you are trying to put the field in the opposite direction as in the graph below. The fact that the ferromagnetic layer is now constrained by the anti ferromagnetic layer and the spins in the anti ferromagnetic layer cannot switch to the opposite direction of the field or of the spins across the interface. Now, this is a material with high exchange anisotropy the or high anisotropy that implies that these spins sitting across the interface will somehow try to what you call tell its neighbours. The ferromagnetic phase is not to switch its spins directing towards a magnetization direction which is externally applied.

That means that there is going to be a large coercivity a large amount of field you need to a device so that all the spins will start to point in a direction of the field. This implies that you going to get an high coercivity in an M H loop, in other words what you had seen is that and of course in an M H loop, we already pointed out the coercivity called intrinsic coercivity. In other words this is as if the loop originally, which was shaded in grey here has shifted to a left and therefore, you are getting an high value of anisotropy. So, to summarize these slides, we see how we are actually obtaining new phenomena known as exchange anisotropy.

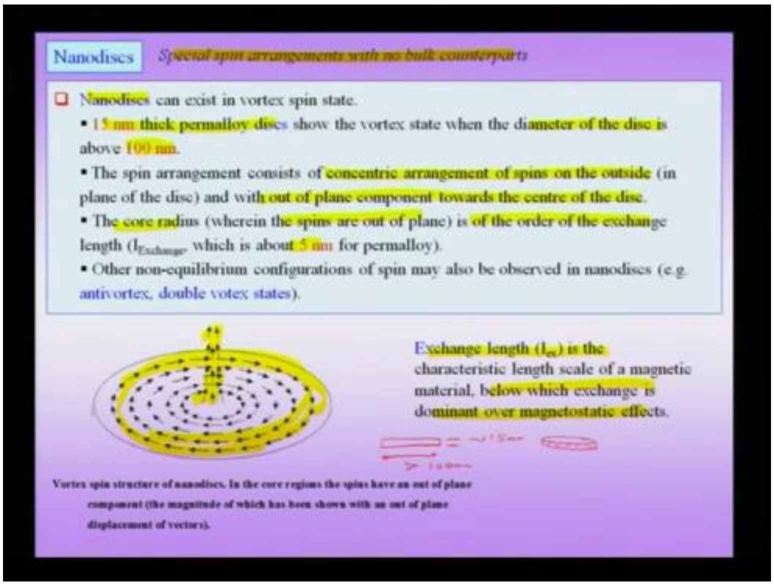
So, we had already noted that anisotropy in materials in ferromagnetic materials can come from share can come from stress or the inherent anisotropy which is called the magneto crystalline and anisotropy. Here, we are creating an anisotropy we making an hybrid and in this hybrid there is an anti ferromagnetic layer in touch with an ferromagnetic layer. An example we saw is the cobalt particles in touch with the cobalt oxide particles, in other words you leave cobalt outside, it gets oxidised and you get this combination.

Now, to get the desired high coercivtity effect or the exchange anisotropy effect, what we do is that we make a single domain cobalt oxide cobalt on anti ferromagnetic cobalt oxide layer be heat the system above the Neel temperature. Then, we apply an external magnetic field to saturate the ferromagnetic phase then we cool the system below the Neel temperature. This implies that the anti ferromagnetic order is now dictated by the ferromagnetic phase and the spins across the interface pointing in the same directions out of the two options. We said one of the options is chosen as the spin up option because these spins are up in the ferromagnetic phase.

Then, of course what we do is that we can go ahead and construct what we know as the usual M H loop while constructing the M H loop in the forward upward direction of the spins. There is no problem magnetic field pointing upward when the magnetic field points downward the ferromagnetic layer wants to switch to the down spins, but because there is an coupling across the interface and the cobalt oxide has high anisotropy. This implies that this spins in the ferromagnetic layer do not want to change their orientation across the interface, they are coupled to the spins across the interface.

Therefore, this is as if those spins are holding them in an upward direction that means I have to apply even larger field to actually causes the reversal of spins in the ferromagnetic layer. This implies that my coercivity value is going to be high, so this is the case of what you might call the exchange anisotropy. Therefore, we have seen two important effects arising in hybrids one is the giant magneto resistance and the other effect of the exchange anisotropy.

(Refer Slide Time: 01:05:26)



Nanodiscs *Special spin arrangements with no bulk counterparts*

- Nanodiscs can exist in vortex spin state.
  - 15 nm thick permalloy discs show the vortex state when the diameter of the disc is above 100 nm.
  - The spin arrangement consists of concentric arrangement of spins on the outside (in plane of the disc) and with out of plane component towards the centre of the disc.
  - The core radius (wherein the spins are out of plane) is of the order of the exchange length ($l_{Exchange}$, which is about 5 nm for permalloy).
  - Other non-equilibrium configurations of spin may also be observed in nanodiscs (e.g. antivortex, double votex states).

Exchange length (l_{ex}) is the characteristic length scale of a magnetic material, below which exchange is dominant over magnetostatic effects.

Vortex spin structure of nanodiscs. In the core regions the spins have an out of plane component (the magnitude of which has been shown with an out of plane displacement of vectors).

Now, let us take up some nanostructures or materials with actually a certain specific dimensions. Let us see the spins states of some of these it is important to consider at least few examples here because the spins states of these nano dimension objects can be very different from the bulk counterparts. We have already seen how this spins are oriented in the bulk that they are divided into domains and within domains spins are oriented parallel. Of course, in the domain wall that you obtain, a slightly more what you might complicate configuration of spins, which means that spins would actually start to rotate. So, we talk about first we take up the example of nano discs, wherein there are special spin arrangements with no bulk counterparts in 15 nanometre thick.

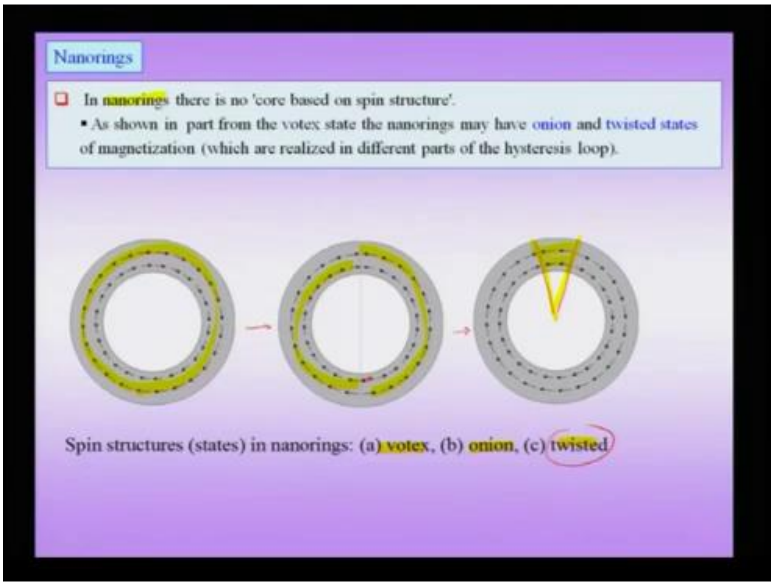
Then, perm alloy disc greater than about hundred nanometres so these are thin nano discs having a large diameters these are like thin discs like these if you look from this side. They are thin discs like this and the thickness of these discs is of the order about 15 nanometres and the diameter of these discs is about greater than about 100 nanometres. So, they are thin discs the spin arrangement in these kind of nano disc consists of concentric arrangement of the spins on the outside and with out of plane component towards the centre of the disc. Of course, this is schematically shown here like this in the case of the spins on the outer side of the disc.

They are the concentric, but in the centre they are pointing upward this z displacement does not mean the spins have come out of the disc. It just implies that the magnitude of the magnetization is large that is what we are implying by pointing the z displacement. The core radius wherein the spins are out of plane is of the order of the exchanged length and exchanged length is defined is a characteristic length of a magnetic material below which exchange forces are dominant over magneto static effects. We know that when magneto static effects are dominant then spins in a domain will be aligned and when and neighbouring domain could be misaligned and exchange below the exchanged length.

It is the exchange coupling between the spins which is dominant, which mean the spins will tend to align parallel to each other. So, you can see that the central region of the disc them, which is below the of the order of the exchange length then you see that the spins are all parallel aligned and the magnetization is very large on the outside. You see that the spins are concentric, so there is no what you might call analogue of this in bulk materials. This is a very special kind of spin arrangement and we also see that clearly in this example that in on the outside this concentric spins are like 2 d system in the centre. It is like a three transition, it is a like a three system that means there is a transition between a 2 d to a 3 d Ferro magnet right in a single discs.

So, this is a very interesting kind of an arrangement and we are talking about the large disc because the exchanged length is of the order of 5 nanometres. Therefore, we need a the disc which is large enough in diameter to actually see this transitions, so this is a very interesting kind of an arrangements in nano discs. Similarly, when you take up a disc which does not have a core obviously, you would expect or you would have guessed that there is going to be no out of plane components in this.

(Refer Slide Time: 01:08:38)



Nanorings

- ❑ In nanorings there is no 'core based on spin structure'.
  - ▪ As shown in part from the votex state the nanorings may have onion and twisted states of magnetization (which are realized in different parts of the hysteresis loop).

Spin structures (states) in nanorings: (a) votex, (b) onion, (c) twisted

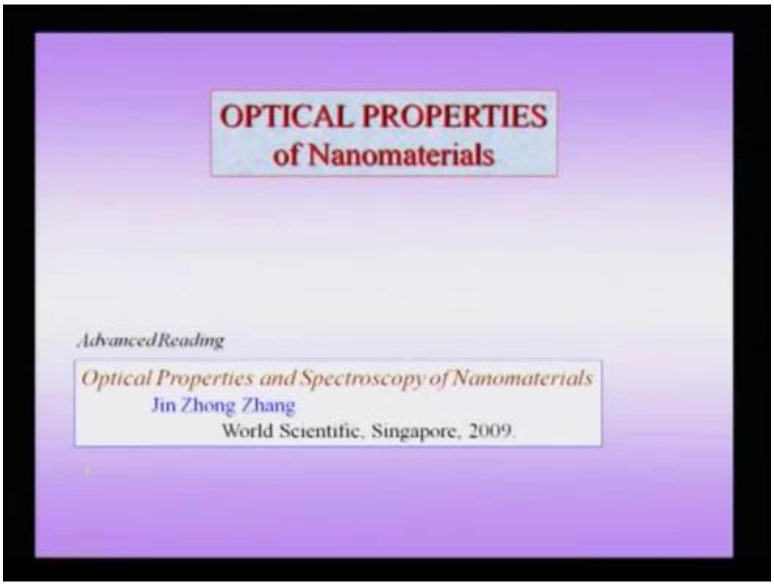
The core has been removed and in these nano rings and these kinds of structures are called the nano rings. There are more than one possible way of spin arranging itself this left structure is called the votex structure where you see that the spins are going concentric in plane. Then, there is something known as an onion structure, wherein spins on one half of the disc is pointing one direction and spins in the other half. So, you see other half are pointing in the other direction so that this kind of arrangements is possible. So, one small correction is required here so this spin has to point in this direction and of course this mis orientation of spins need not be across the entire half ring.

It could be in only in a small region defined by a sector like this, so you see that and this state is called the twisted state of this nano ring. Therefore, you see that more or more interesting and complicated arrangements of spins are possible in these nanostructures like the nano rings and nano discs. It is interesting to note that suppose I were constructing actually a M H loop or a hysteresis loop in a starting with the votex structure. Then, I would observe that I would obtain these other states like the onion and twisted structures during some part of the magnetization hysteresis loop. That means this state would change from the one from votex to an onion or to a twisted state during a magnetic magnetization process itself.

So, we had taken up two interesting examples of nano discs, wherein there are special arrangements of spins which have no what you call bulk analogues and you might can see that these are the concentric spin states. Here, in the case of the nano disc we saw that there is a small region on the core of that disc wherein actually there is spins going out of plane, in other words the system behaves like a 3 d system unlike a 2 d system, which we expect a thin disc to behave like.

So, with this we come to the topic end of the magnetization in nanostructures and nanomaterials and we have already seen that magnetization is a very rich field wherein you have very interesting effects. We have seen the effects of super para magnetism giant magneto resistance etcetera, it is important to note that many of these actually have what you might call very interesting applications the very important technologic applications.

(Refer Slide Time: 01:10:51)



OPTICAL PROPERTIES
of Nanomaterials

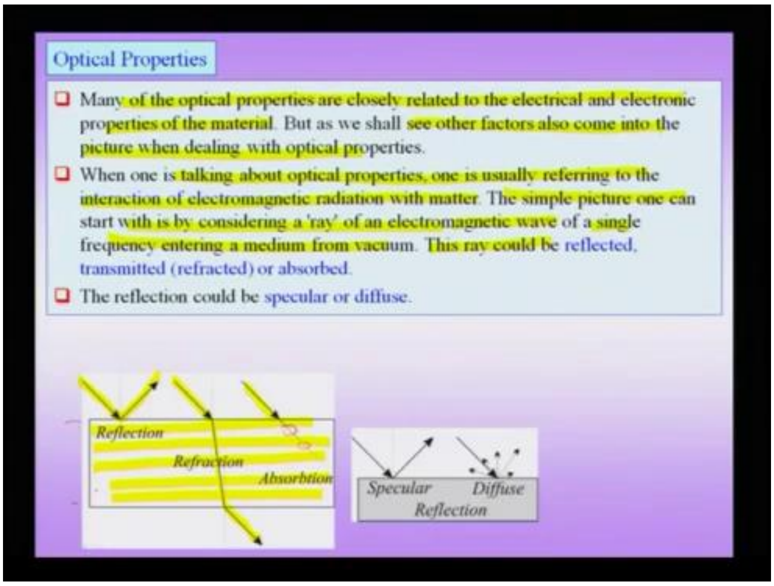
Advanced Reading

Optical Properties and Spectroscopy of Nanomaterials
Jin Zhong Zhang
World Scientific, Singapore, 2009.

Next, we take up the topic of optical properties of nano materials we had notes that earlier that optical properties essentially come from the electromagnetic structure. We had noted that some of the important concept likes band structure which plays an important role in the optical properties. We will see further aspects of optical properties of normal materials and then further proceed to optical properties of nanomaterial.

In this topic or in this chapter, people who are interested in an advanced reading regarding the optical properties of nanomaterials may consult the book by zhang. Here, he talks in detail about not only about optical properties, also spectroscopy of nano materials.

(Refer Slide Time: 01:11:32)



Optical Properties

- Many of the optical properties are closely related to the electrical and electronic properties of the material. But as we shall see other factors also come into the picture when dealing with optical properties.
- When one is talking about optical properties, one is usually referring to the interaction of electromagnetic radiation with matter. The simple picture one can start with is by considering a 'ray' of an electromagnetic wave of a single frequency entering a medium from vacuum. This ray could be reflected, transmitted (refracted) or absorbed.
- The reflection could be specular or diffuse.

First, we start as I pointed out with the broad overview of what we mean the optical properties what are the possibilities. Then, we take specific examples in nanostructure materials many of the optical properties are closely related to electrical and electronic properties of a material. So, this is a optical property a natural consequence of the electrical and electronic structure of a material this is as expected, but then other factors also come into play. When we are dealing with optical properties which include for instance the arrangement of atoms and other what you might call the spatial distribution of the scatters etcetera. This plays an important role in determining the optical properties when one is talking about optical properties.

One is usually referring to the interaction of electromagnetic radiation with matter and though the word optical would imply that we are talking about visible radiation that means which is visible to the human eye.

In general, we have to talk about electromagnetic radiation covering the entire spectrums starting from gamma rays to radio waves this all this interaction with matter can be thought of as optical properties. Though often we are restricting ourselves to only the visible part of the electromagnetic spectrum, the simple picture one can start with is by considering a ray of an electromagnetic wave. If you know that a ray is actually a geometrical construct and has no physical reality and we consider a single frequency entering a medium from vacuum. So, this is starting picture of what you might think as an interaction of electromagnetic radiation with now this ray implies that the all the wave fronts in the wave are actually perpendicular to this ray.

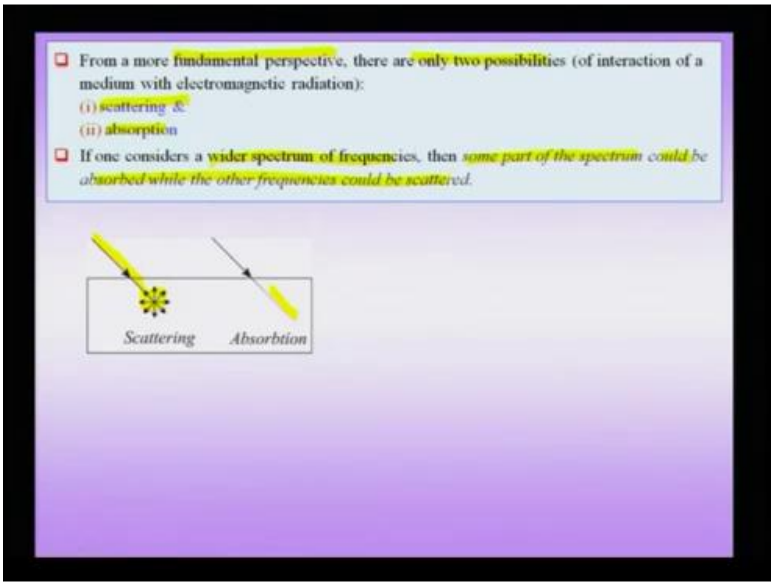
This ray could be reflected this ray could be transmitted into the medium and refracted when I am talking about the medium. This is my medium which I am shading in yellow an I imply that this medium has an higher optical density or n higher refractive index with respect to the medium surrounding it which we consider for now to be vacuum. So, this ray could be reflected it could be refracted and it could also be absorbed in other words this ray entering the medium could lose all its energy within the medium. Therefore, this does not propagate beyond what you may call even this a finite medium then it does not propagate beyond it and therefore you will notice that the way I am diced.

Now, ultimately of course all the energy in the electromagnetic radiation will have to be converted into heat. Therefore, this absorption essentially implies that the electromagnetic energy in the electromagnetic radiation is converted into heat. When you are talking about reflection, it essentially means that of course there is no system which is 100 percent reflecting or 100 percent refracting or hundred percent absorbing. So, we you typically have a combination of all these three effects and one of these may be dominated like you take up a highly polished silver mirror surface, then you would expect that such a system is strongly reflecting.

Most of the energy is actually sent back into the medium from which the original ray originated and here we have seen in the case of refraction. We have drawn a certain configuration which we consider to be what I call the material having a positive reflective index. We will have a few more things to say that how we can consider construct structures with negative refractive index has filled later. Now, this reflection itself could be specular or diffuse, so you take a case of a polished mirror.

Then, you see that there reflection would you follow something like a Snell’s law and you have a reflection, but the rough surface like any wooden surface would have typically a diffused scattering. This means that you cannot see images in a case where there is diffuse kind of a reflection and not specular reflection.

(Refer Slide Time: 01:15:22)



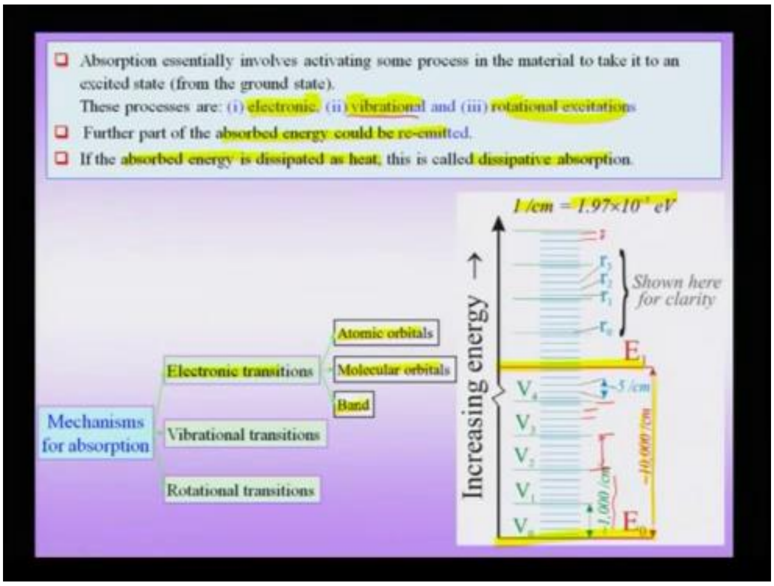
- From a more fundamental perspective, there are only two possibilities (of interaction of a medium with electromagnetic radiation):
  (i) scattering &
  (ii) absorption
- If one considers a wider spectrum of frequencies, then *some part of the spectrum could be absorbed while the other frequencies could be scattered.*

Suppose I have considered from this whole process of the interaction of the electromagnetic radiation with matter from a more fundamental perspective there are only two possibilities of interaction of a medium with electromagnetic radiation. One is scattering another is absorption and the transmission can be thought of as a forward scattering phenomena. So, you send a electromagnetic radiation into wave or a ray into wave and there could be scattering or there could be absorption. So, these are the more fundamental perspective and if you are talking of not about a single frequency entering a material, but there is a wider spectrum of frequencies.

In other words, you have what you might call a panchromatic radiation then some part of this electromagnetic spectrum could be absorbed while other frequencies could be scattered. In other words you could have a medium which absorb some frequencies which transmits other frequencies and which could actually reflect certain other frequencies.

So, these are the possibilities when you have a radiation consisting of a large variation in the frequencies. Now, when you are talking about absorption it essentially means that certain resonance in the material has been exited which means that the material now can be taken to an exited state by this electromagnetic radiation. That means that it needs to have a certain bare minimum frequency because frequency is the handle on energy we know that de equal to h mu for a radiation and this frequency is able to excite some kind of a resonance in a material.

(Refer Slide Time: 01:16:48)



- Absorption essentially involves activating some process in the material to take it to an excited state (from the ground state).
  These processes are: (i) electronic, (ii) vibrational and (iii) rotational excitations
- Further part of the absorbed energy could be re-emitted.
- If the absorbed energy is dissipated as heat, this is called dissipative absorption.

Therefore, this absorption is taking place what is the kind of excitation which this material can undergo these process include the electronic excitation the vibrational excitation or it could be the rotational excitations. A nice example for instance the rotational excitation would be the case of microwave heating in our oven wherein we note that suppose size and microwave radiation into the microwave oven then the water molecules which have a natural polar character. That means water molecules are polar and therefore they have net polarization in some direction. Now, what happens is that suppose now I send an alternating electromagnetic the electro magneto wave, which consists alternating electric and magnetic fields.

Then, this water molecules will tend to rotate this electric field will tend to follow the electric field of the incoming radiation if the frequency is too high. Then, it will not couple with it if the frequency is too low then the heating is going to be too small, but the right frequency which is of the order of about three centimetres. The wavelength of the electromagnetic radiation the three centimetre wave length, then what happens is that the frequency the water molecules are able to follow the externally applied field and which is coming of course from the radiation itself.

Since the water molecules are rubbing against each other this whole process is going to be dissipative and therefore, overall the water in the food or the water in the tumbler actually gets to heat up. So, these rotational excitations can be possible and it is a nice example of a rotational excitations if you are talking about for instance phenomena typically like an electronic excitation which can also take place if there is a critical amount of frequency available. Then, this absorbed energy cools actually be reemitted when the system relaxes to the ground state again. Finally, of course we have to note that any energy we had noted before that any absorbed energy is finally dissipated a heat and this is called dissipative absorption.

Now, the important thing to be note between these three kinds of mechanism the electronic vibrational or rotational excitation is a fact that the electronic energy levels are highly separated. So, you can see that e 1 and e 0 are separated and this corresponds to wave number of about 10,000 per centimetre, so you need lot of energy to actually excite and you can find equivalence between the wave number and the e v's. So, this is a larger wave number associated with the electronic excitations that means you need lot of energy to excite an electron from the lower energy level in an atom or a molecule to an high energy level.

Of course, this could also be a solid you could be describing, on the other hand you could notice that the vibrational levels which is a next level is actually closely spaced. That means that I require a lower amount of energy and corresponding wave number is of the order of about 1,000 per centimetre. That I multiply this 1,000 of course by this 1.97, 10 power minus 5, I can obtain the value in electron volts, but I require a lower amount of energy to excite the vibrational level. That means that if I am having an electromagnetic spectrum the electronic transitions that typically exited by the high energy radiations while the vibrational transitions are excited by a slightly lower energy radiation.

Finally, the rotational excitations have even smaller spacing which is shown here or for clarity I will show it here and that means that I have to impose a very small energy to excite a rotational excitation. So, even though there are three possible mechanisms by which I have I can excite a material which of course again this excitation may relax to the ground state again by rumination of radiation. These energies are all not the same and therefore, depending on the frequency of the electromagnetic radiation one of these might be exited.

Therefore, the absorption would be in a certain frequency regime based on what you may call the energy which is required to excite this. So, again to go into the detail little more about these excitation the electronic transitions themselves could be from atomic orbitals could be from molecular orbital or it could be to a band that means an electronic energy level lying in a band. We have already noted whenever there is a relaxation of a level from a band, then the range of frequency is usually brought because band is a semi continuous set of energy levels.