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Lecture - 22 Electrical, Magnetic and Optical Properties of Nanomaterials (C4)

(Refer Slide Time: 00:14)



To summarize the story on magnetism so far, we noted that magnetism is virtually universal. It is found at the cosmic scale, the scale of the earth the scale of the plates, and also in the scale of money birds and bacteria wherein it is the nano scale actually. We said that there are two origins of magnetism. One is macroscopic flowing currents and the other is the atomic origin, which is primarily, because of the spin of the electrons and the orbital motion of the electrons.

Additionally, we noted that, because of the orbital motion lattice coupling often which is a strong coupling, often the orbital motion is quenched and the scenario might change when you go to nano particles and lower dimensional systems. We have to understand two important effects when we talk about magnetism. One is the effect of external fields, the other is the effect of temperature, and we also noted that often when we talk about magnetism we also have to worry about the band structure of materials without which the picture of magnetism would not be complete. And we had noted that there is a one kind of magnetism, which is universal, which is diamagnetism in materials and we said that we could actually use a quantity like the susceptibility to differentiate what you might call paramagnetic and anti ferromagnetic and also diamagnetic materials. The effect of temperature is typically given by what you might call the Curie law and the Curie-Weiss law, which tells you that there is something called a molecular field or an exchange, which gives a positive value of theta.

That means there are ferromagnetic materials, which become paramagnetic and these kind of materials have to be differentiated from materials which are paramagnetic always like oxygen. We also noted by mere arrangement of this atomic magnetic movements we can have collective definitions of spins which we call ferromagnetic, anti ferromagnetic and free magnetic ordering.

(Refer Slide Time: 02:22)



We also noted that in a simple metal like iron, if you want to understand magnetism. And we note that it is actually the localized electrons which a dominating in the system, which is a large number comparable to the number of like 8 valence electrons out of which 7.05 of them occupy a so called localized d band. And only 0.95 of them are free and these 0.95 cannot contribute to the magnetic movement of iron.

(Refer Slide Time: 02:40)

(especially in 3d metals which electrons (4s) do not contribut electrons in transition metals of Band theory is able to explain the values may often not match	are elemental magnets e to the ferromagnetic l are neither fully localiz the non-integral values h exactly.) are rather localized and the 'free' behaviour. Truly speaking the 3d ed nor fully free. of magnetic moment per atom; though,
The density of states varies in	a complicated manner.	
 In Fe the 3d electrons are all n character and these electrons n Using the observed magnetic n spin occupancy can be calcular 	ot fully localized and a nediate the exchange or noment per atom (μ_B) ted as:	bout 5-8% have some itinerant supling between the localized moments. of Fe to be $2.2\mu_{B}$ the up-spin and down- \Rightarrow
$N_d^{\uparrow} + N_d^{\downarrow} = 7.05$	$N_d^{\uparrow} - N_d^{\downarrow} = 2.2$	$N_d^{\dagger} = 4.62, N_d^{\downarrow} = 2.42$

Additionally, we noted that the magnetic movement of bulk iron is about 2.2 bore magnetrons and to understand this we actually have to talk about you might call the spin dependency of states that mean the up spin and down spin electron density of states are shifted with respect to each other. And this is what the way they fill gives you what you might call the non integral magnetic movements in a material like iron.

(Refer Slide Time: 03:08)



We also pointed out the task of actually going from atomic magnetic movements to magnetic movement of entire solids and hybrid is actually an adverse task. And therefore, we use certain techniques to actually make the shortcut possible. We also noted what are the thumb rules for instance for ferromagnetism based on the band picture wherein we said vacant levels, high density of state closed of Fermi level and the appropriate inter atomic distance are responsible for giving rise to magnetism in 3 d metals like iron, cobalt and nickel.

(Refer Slide Time: 03:40)



Having talked about the effect of temperature into some extent, we will now take up the effect of an external magnetic field. On the right hand side, is the very familiar diagram and which is called the B H or M H loop for an ferromagnetic material. So, we are focusing our attention on a ferromagnetic material below the curie temperature and we also said that often either B or M is constitute or B or H is constitute of what you might call fundamental quantity, but here we will focus on the M H loops.

So, we have H is the external field and M is a magnetization produced on the material and the M H loop is the one which is below. So, the cure which is the M H loop or the M H curve goes like this. In another words, when you increase the field initially you have a material in which you have 0 magnetization and we said it is actually the breaking up of domains which is responsible for the 0 magnetization. As you increase the field you notice that the magnetization increase and later on reaches a saturation value which is called M s. If you are plotting a B H loop then you would notice that even on saturation the curve continues to increase, because B is also a function of the applied field H.

That means, since H is increasing the B will continue to increase when you plot a B H loop. And therefore, there is saturation at the material level, but there is no saturation of the curve. Now, in this curve lot of important quantities can be marked the, what you might call the coercivity. And this coercivity is an important quantity, because this coercivity depends on what you might call the microstructure.

In other words, initially suppose I am plotting a B H loop and the curve initially increases then when you reduce the magnetic field it does not follow the same curve that is why it is called the hysteresis. It goes down and even at 0 field you find there is a net magnetization of the material and you actually have to put an opposite field to actually bring down the magnetization to 0 which is called coercivity. The field strength at that level is called coercivity, and further of course we can go ahead and complete the entire loop.

Now, the other point to note from this curve is that the slope of this M H curve is called the is an important quantity and this slope varies from point to point and the similar quantity if you note from the B H curve is actually called the permeability. And similarly, the permeability also varies from point to point in the curve and the permeability is not the instant slope of at any point, but is actually the slope of the tangent from the origin.

So, this is now my, what you might call the initial permeability and this is what you might call the maximum permeability this curve. In other words, permeability is not defined as instant slope at any point in the B H curve, but is actually defined as a slope of the line drawn from the origin. Now, another important point to be noted in this curve is that the field required to bring a ferromagnetic to saturation at room temperature is actually small. So, it is about the order of 80 kilo ampere per meter. But suppose that is to this point, the point till B s, but suppose I want to increase a coercivity even at the magnetization even further then the fields required are very large.

And this kind of magnetization is called force magnetization and in this lectures we will worry we will only talk about a material magnetized till only the saturation. And the coercivity in the B H loop is called the normal coercivity. On the other hand, the coercivity plotted in a M H loop is called the intrinsic coercivity and usually is added an additional i in front or in back which is, therefore it is called M i c or M c i which implies that I am now referring to an M H plot in which I am describing the coercivity. And we will be repeatedly referring to this coercivity, because as I pointed out this coercivity is a structure or what you might call a microstructure dependent property.

Therefore, to summarize this curve the magnetization in a ferromagnetic material shows hysteresis that means the magnetization curve and demagnetization curves are not what you might call a we will start with that completely demagnetized material and you for instance. If you had heated the material above the curie temperature and cooled it down and then you start magnetizing the material.

Then you would notice that such a material when during magnetization follows a path which goes from say for instance the origin to a point x to a B s. Then, while demagnetizing, it follows the curve from B s to a point y to a point z to finally, to the H c or H c i. So, it is in other words it shows a distinct hysteresis, which is what you might call usually you use such when number of materials shows a hysteresis like that you odd add a prefix to the term called Ferro.

(Refer Slide Time: 08:40)



So, let me go down to the board and write down a few of these ferro quantities like, you can have substances like which show hysteresis like ferro and you can have ferro electric. You can have ferro magnetic, you can have ferro elastic and so for and here the word ferro originally of course, originating from the term implying that there is iron in the case of magnetization, but here the word ferro in common sense actually implies that

there is actually hysteresis behind the behaviour. Now, how does this magnetization come over. In other words, I have a material which is as initially a zero magnetization and later on as you magnetize the material you see that actually you see that there is an increase in magnetization how does this come about?

(Refer Slide Time: 09:26)



This comes about at the microscopic level by preferential alignment of domains, and this is brought about by the external magnetic field. During magnetization the domains oriented favourably along the field direction grow at the expense of unfavourably oriented domains.

(Refer Slide Time: 09:43)



And to give us schematic picture of how these domains may look for instance suppose I have a picture like this here wherein suppose I am applying a magnetic field in the z direction. Then you would note that these domains are all oriented favourably, these domains are not oriented favourably. And therefore, the domains pointing with a north south up will actually grow at the expense of the ones which are pointing north south down for this is a schematic diagram and real domain structure is actually much more complicated.

(Refer Slide Time: 10:11)



But the essential point to noted that the domains oriented favourably grow at the expense of domains oriented unfavourably. And this can occur by two important mechanisms what you might call domain wall motion and the second is by rotation of magnetization of the domains.

Now, which of these two mechanisms is operative is actually a detailed you need a detailed picture of the material, you need a detailed picture of the microstructure is a poly crystalline etcetera. But crudely speaking, if you look at the M H curve then you can sort of differentiate that initially the magnetization takes place, the initial portion the magnetization actually takes place by domain wall motion. This is of course as I pointed out is some kind of over simplification and later on close to saturation it actually takes place by domain wall rotation.

So, both these mechanisms are possible and for the domain wall rotation itself, there are many sub mechanisms like coherent rotation. In coherent rotation there is there are you will come across terms like fanning, curling, etcetera. So, there are lot of detail things which do take place, but in the end what happens is that the favourably oriented domains grow at the expense of the unfavourably oriented domains.

In other words, you are obtaining magnetization. Now, even this domain wall motion has lot of details in it like it can be smooth or jerky. And this domain wall motion is happening, because now what is happening is this external magnetic field tends to align miss oriented spins in the domain wall. We will have a detailed look at the domain wall picture very soon, but domain wall is a region where the spins are not aligned along any one of the domains. It is mis-oriented with respect to both the domains.

And therefore, it is the region between the two domains. It is like a some kind of an analogous term you can you the grain boundary and this means that if spins oriented favourably are going to grow at the expense of spins, which are orient unfavourably, in other words the domain wall is going to move and this is going to lead to the displacement of the domains. And as I pointed out during quite a bit of the magnetization process some regions or some sample may actually be experiencing domain wall motion while other regions the sample may actually be undergoing domain wall rotation also this is also possible. And therefore, the actual picture little more complicated.

Now, the rotation of spin is opposed by the increase in anisotropy energy and we went back to an early slide where we define anisotropy is by the fact that now my magnetization is going to be direction dependent. We even pointed out like for instance material like iron the 0, 0, 1 direction is a favourable or the easy direction of magnetization and the 1, 1, 1 direction for instance is the unfavourable direction. That means that it is an inherent magneto crystalline anisotropy in a material, which means that when spins try to rotate there will be an opposition to it.

And we additionally pointed out that another anisotropy factors like shape and stress also play an important role and an additional point to be noted is that during rotation all spins need not be parallel to one another, and this makes the picture actually somewhat complicated.

So, the broad take home message from this slide is that magnetization occurs by the growth of the favourable domains at the expense of those which are unfavourably oriented. Two underlying mechanisms can be thought of for this one is called a domain wall motion, which essentially comes about. Because here magnetic field is trying to align those spins, which are miss oriented along the domain wall to a direction, which is aligned to the magnetic field and this automatically will lead to a domain wall displacement.

The second process is what you might call rotation of domains and or rotation of magnetization within the domains and which leads to a rotation of the domains and we also point out that both these process might be simultaneously occurring during the magnetization of a sample. Let us return to this topic of effect of temperature once more. We broadly pointed out that at the curie temperature a ferromagnetic material will become paramagnetic.

(Refer Slide Time: 14:13)



But actually the real complicated picture is that this demagnetization process actually occurs by a process which involves spin waves, and the quantized version of these spin waves is called magnons.

(Refer Slide Time: 14:22)



So, the reason behind is that suppose I have all spins oriented in one direction, and I suddenly say that there is one of these spins is going to be pointed in opposite direction. In other words, this spin is going to flip in other words it is not, it is randomly going to

flip, because of the thermal energy. Then, such a isolated spin flip actually cause more energy than a distributed spin flip which is what is a origin of spin based.

In other words, now my spins have a certain orientation dependence they are not just one spin flip, but there is a disturbance, which is carried across the crystal, and such a spin wave is actually carrying out the demagnetization process on heating. So, we are not going to details of magnons for now, but it this is equivalent to furnace for thermal disordering which is positional for the atoms.

(Refer Slide Time: 15:07)



Here, it is a orientation dependent disordering which we call the and the quantized version is magnons. Now, the important thing to note that at the see the susceptibility becomes infinite and the reason for the susceptibility, and of course we had already pointed out.

Though we talk about a sharp curie temperature in reality the curie temperature is not that sharp. In fact, even after the curie temperature there are localized regions in this sample where there are local magnetic clusters which are still oriented that means, the domain structure is not completely been broken down. And this means that there is some magnetization which is still remaining after the curie temperature, and since there is an inherent propensity for the material to get magnetized at curie temperature. You might say it is a critical temperature at which the thermal forces are just balanced my magnetization forces or the internal exchange forces. Now, that means that if I now apply a little extra magnetic field, the material will tend to alike. That means a susceptibility is going to be very high and in fact you might say that at the curie temperature my susceptibility is going to be infinite. And I just pointed out there are beyond T c there are local clusters or spin clusters of magnetically aligned moments. Obviously, maximum magnetization is obtained when all magnetic moments have a parallel orientation and this is corresponding to the highest magnetization state M 0 and some time you can also use the per unit mass sigma 0.

And therefore, if I plot my sigma s by sigma 0 which is s stands for saturation and T by T c where c is a curie temperature then we will expect that there will be a master curve which you can plot for demagnetization of all materials with temperature. So, in other words you can have a master curve for various materials using two normalization quantities. One is the saturation magnetization M 0 and the other have got the maximum magnetization possible M 0 and the other is your T c which is the curie temperature. So, we see that effect of temperature is very important on a material and we will return to this when you talk about magnetism in nano scale materials. Now, it is important to note a few more things regarding the domain structure and the magnetization process.

(Refer Slide Time: 17:21)



And herein we will note that even in normal bulk materials there are certain entities, which you cannot avoid which are in the nanoscale. Like we noted in a bulk material also

we had a grain boundary and the grain boundary was typically, what I call ascribed width of the order of about 0.5 nano meter to 1 nano meter, which is the nano scale.

Now, the reason that the material as a ferro magnet actually splits into domains is, because of a combination of various energies which we will see now and this in effect overall reduces the magneto static energy or the overall energy stored in the external magnetic field. Now, what I am saying is that suppose I had a material and the whole material. Now, this is a macroscopic material I am talking about and not a nano scale material.

Then, if this material where a single domain then the energy stored in the external magnetic field will be large and the material with this energy of course, is called the magneto static energy. The material will try to reduce the magneto static energy by splitting into domains as you can see few split into two domains pointing in the opposite direction then the overall external field reduces. If we split into 4 domains it further reduces and you can reduce this quantity even further by actually having what you might call domains which are the normal domains plus what are called closure domains.

And therefore, now I can form continuous loops of B. So, using these magnetic domains and closure domains I can actually reduce my magneto static energy. Now, the region separating two of these the region here is the domain wall and you can see in the domain wall you have of course, all spins oriented in the up direction on the left hand side, all spins oriented in the down direction on the right hand side. That means that the spins are switching orientation at the domain boundary or what you might call the domain wall. So, this is my domain wall. Broadly two types of domain walls can be differentiated and the one which is usually found in bulk material is called the block wall.

Additionally, there are other kind of walls which are called as neel walls and neel walls are typically found in you what you might call thin films and they are not found typically in bulk materials. Now, other walls apart from block walls and neel walls are also possible and they are given names like cross-tie walls and etcetera. And there are even more complicated configurations which can be present in a domain wall.

The important characteristic of a block wall is that the spin at spin vectors rotate out of plane in the wall itself. So, there is a schematic diagram here, there is a domain 1 which is on the left hand side, there is a domain 2 on the right hand side, the spins are as shown

here. Now, in the domain wall the spins rotate, but they do not rotate in plane you can see the spins. Actually rotate out of plane so this spin is slightly miss oriented, this plane is miss oriented little more, this spin is miss oriented little more and so forth finally, you obtain the new orientation of the other domain.

Now of course, you may say that why not put up an abrupt wall, because now these miss oriented spins are actually going to cost you in terms of the anisotropy energy. But an abrupt spin change would mean that I am going to pay a higher price in terms of the exchange energy, because exchange coupling is actually trying to orient two of these spins, neighbouring spins parallel to each other.

Therefore, the system actually comes to an equilibrium in a competition of these kind of various kind of energies and we will list them in the next slide soon. So, overall configuration actually consists of normally block walls where in the orientation in a block wall is or the miss orientation takes place gradually. Of course, here this is schematic and you should actually note that the domain wall is much larger, much longer and actually the miss orientation between the neighbouring spins is much smaller than that shown in this crude schematic.

The domain wall is actually much larger and typically you would note that this domain walls have a width in the nano scale and we will take up some numbers for this in coming slides. In the passing it is important to note here that neel walls which are seen in thin films and these thin films. I am talking about nano scale materials of the order of about 40 nanometres and in these the spin actually rotates in plane.

(Refer Slide Time: 21:42)



In other words, and if I have now a material which is a thin film such a system can actually if you look down from the top, if you are looking down from the top can be thought of as a 2 d system. And here suppose spins are oriented here in this left hand side, the spins are oriented downward on the right hand side the spin miss orientation the rotation actually takes place in plane.

So, now this rotation you can see is actually in plane and this kind of an in plane wall is called a neel wall and this is found in basically in thin films on nanostructure, 2 d nano structured materials. And we have to note that this domain wall is also a nanostructure in its own ride, because it has got a thickness of about few 100 atomic diameters.

So, when you are talking about domain walls two things are important. Number one, the equilibrium bit of the domain wall is determined by a competition of various energies. The reason that the materials splits into domain is to the overall reduce the magneto static energy. Number two is that the domain wall actual miss orientation between the spins is small. In normal materials, that kind of wall you find is called a block wall. In thin films which are of about forty nano meters thick you find this neel walls wherein the miss orientation or the spin rotation actually occurs in plane in about the whole system remains 2 d, because of the configuration of the thin film and the domain wall itself is a nanostructure in its own right.

(Refer Slide Time: 23:31)



Now, few more words about this domain wall and there energetic reasons behind it. The domain wall represents a region of high energy at the spin vectors are not aligned in directions of easy magnetization. Hence, thicker walls represent higher energy and materials with high magneto crystalline anisotropy like for example, the rare-earth materials the domain walls are typically thin. They are about 10 atomic diameters.

If the magneto crystalline anisotropy is small then you find thicker walls on the other hand there are other source of anisotropy as we have pointed out due to shape and residual stresses. A competition between the magneto static energy and the magneto crystalline energy essentially decides the thickness of the wall. Now, the word essentially has been used, because the other factors like magneto elastic energy, which is coming from the process of magnetostriction.

Now, in other words if somebody were exposed to an Hartman diagram this is what you might call a cross coupling term wherein, because of application of a magnetic field you are actually having a change in dimension this is called magnetostriction. And, because of this change in dimension there is actually an elastic energy associated with the process of magnetization. Now, this implies and the familiar example given for magnetostriction giving raise to sound is, in the case of magnetic course and transformers that is a hum and this hum is coming from this phenomena of magnetostriction. And this magnetostriction energy is also going to contribute to the overall energy. And now when

the optimization takes place the system tries to optimise putting together all these energies.

In other words, total energy can be given by the fundamental exchange energy between the spins the magneto crystalline anisotropy energy or have coupled with of course, the other anisotropies. The magneto elastic energy coming from these strains associated with the magnetization process and of course, the external magnetic field, which is the magneto static energy. So, the overall equilibrium width of a domain wall is determined by the competition between these energies. And therefore, the system tries to minimize this overall energy.

So, at the heart of the magnetization process we note that is the fact that there are domains. These domains want to orient themselves in the process that there is there are domain walls. These domain walls are nanostructures in their own ride and the motion and rotation of these domain walls are important and finally lead to the magnetization of this sample. Now let us take up another important topic, which is a concept of magneto resistance. Again this is like a cross coupling term. In other words, there is a change in resistance the electrical resistance as you impose some magnetic field.

Like in the previous slide, we have seen there is a change in size or there is a strain associated with the magnetization so this is a cross coupling term. Normally when we apply a magnetic field then the natural response is magnetization or not the strain right. So, this is a cross coupling term between what you might normally expect stress to be causing stains and not a magnetization to be causing strain. So, this is a cross coupling term between stress and magnetization.

(Refer Slide Time: 26:35)



Similarly, there can be a cross coupling term between magnetic magnetism and resistance which is called magneto resistance. The resistance of a conductor can change when placed in an external magnetic field this effect is called magneto resistance. In other words, in the absence of a magnetic field there is one value of resistance and in the presence of a magnetic field there is a different value of resistance and here we are talking about electrical resistance. The resistance is higher if the field is parallel to the current and lower if the field is perpendicular to the current.

And in general the resistance depends on the angle between the current and the magnetic field and this effect has a general name called the anisotropy magnetic resistance otherwise called A M R. An important point to note that this magnetic resistance arising, because of the magnetic field is typically small and most materials is does not usually exceed the value of about 5 percent. And this magneto resistance arises from a larger probability of s-d scattering of electrons. And we will take a more pictorial picture when we actually go down to nano materials and talk about this enhanced version of this magneto resistance which is called the giant magneto resistance.

But essentially we note it comes from a larger probability of scattering and this is now spin dependence scattering which is important and this arises in a direction parallel to the magnetic field. This A M R effect itself has been put to good use in magnetic field, sensing devices. And whenever you have an enhanced value of A M R which is anisotropy magneto resistance, it is beneficial in using it in the form of a sensing devices. To summarize this slide in normal materials in the presence of a magnetic field there is usually about the five percent change and in some very special compounds like uranium compound, this value can reach as large as 50 percent.

But never the less, this is usually a small value this change in resistance caused by an external magnetic field and this is coming, because of a larger probability of s-d scattering electrons parallel to the magnetic field coming from, what you might call the spin dependence scattering. And in general the value of this resistance depends on the angle between the current and the magnetic field and that is why this is called the anisotropic magnetic resistance. So, this is an important phenomena as this finds important applications like in magnetic field sensing devices. And once you have magnetic field sensing device you can put it to various kinds of good uses like you may use it like a counter, you can use it like a sensor and so many possibilities.

In other words, suppose I have a sensor here and in the presence of there is a magnet here and if this magnet comes close to this and this is going to click one, because a magnetic field resistance is resistance in this conductor is going to change. And therefore, I can keep on counting the number of times this sensor is actually passing through this region. So, we will find that there are even more applications of this effect when it comes down to nano materials.

(Refer Slide Time: 29:32)

Magnetic nanostructures in bulk materials					
Evv	n in bulk magnetic materials some structures can be in the nanoscale:				
	Domain walls in a ferromagnet (-60nm for Fe).				
•	Some domains (especially those in the vicinity of the surface or grain boundaries), could themselves be nanosized.				
	Spin clusters above paramagnetic Curie temperature (θ_p) could be nano-sized.				
w	ten we go from bulk to 'nano' only the structure sensitive magnetic properties (like				
	coercivity) is expected to change significantly.				
So	me of the possibilities when we go from bulk to nano are:				
	Ferromagnetic particles becoming single domain				
	Superparamagnetism in small ferromagnetic particles (i.e. particles which are ferromagnetic in bulk)				
	Giant Magnetoresistance effect in hybrids (layered structures)				
-	Antiferromagnetic particles (in bulk) behaving like ferromagnets etc.				

Now, let us switch from magnetism of bulk materials wherein it was we studied some of the important effects the origin of magnetism, the effect of temperature and the effect of magnetic fields to now magnetism in nano materials. When you talk about magnetic nanostructures they exist even in bulk materials as we had pointed out like the example was domain walls for instance 60 nanometre in iron. We even said that even though we are talking about domains in bulk materials, some domains like small grain boundaries could exist even in an bulk large grain size micron grain size sample. So, some domains could be very small especially so close to the surface or in a close to the grain boundary in a polycrystalline material.

That implies that even in a bulk material, some domains could actually be nano sized, because of the distribution of domain sizes. We also noted that spin clusters, above the paramagnetic temperature, close to the paramagnetic transition temperature could also be nano-sized. So, there are three entities which are clearly nano-sized even in bulk magnetic materials which are the domain walls, some domains in an overall distribution domain sizes and finally, spin clusters just above the paramagnetic transition temperatures. We have to additionally note that when you go from bulk to nano only the microstructure sensitive magnetic properties like coercivity is expected to change.

The overall the for instance the micro structure in sense to properties like saturation magnetization is not expected to change much. And we will note now that there are extremely, what you might call interesting possibilities in magnetism. When we go from the bulk to the nano and this include that the ferromagnetic particles could become single domain. That means the entire particle is a single domain. We will encounter a phenomena like super para magnetism in small ferromagnetic particles and there is no bulk analogue of super para magnetism. We will also encounter giant magneto resistance and we will note that this is a phenomena exclusively found in or mostly found in hybrids.

In other words, we can construct hybrids, synthetic hybrids wherein you will find phenomena like giant magneto resistance. Then additionally and a very equally interesting phenomena is that you will find that material which are anti ferromagnetic in bulk. That means they are they show properties which are purely anti ferromagnetic there is an equal and opposite magnetic moments aligned in a material. Therefore, all the magnetization actually cancels out, but they start to behave like ferro magnets though with us reduced amount of we do not have very high amount of bore magnetrons per atomic magnetic moment. But still never the less, they will start to behave like ferro magnets. So, we see that when you go from bulk to nano in Magnetism there are very interesting possibilities and many of these do not have any analogue in the bulk world.

(Refer Slide Time: 32:29)

J There is a mere system.	sase in magne	stic momen	t atom as	we decrea	se the dimer	isionality of the
This is indicati	ve of fundam	ental diffe	rences in i	magnetic b	ehaviour be	tween nano-
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So, next we will take up topic that how the magnetic moment and here we are talking about magnetic moment which is intrinsic to the material depends on the dimensionality of the system. It is to be noted that there is an increase in the magnetic moment per atom as we decrease the dimensionality of the system. This implies that there are fundamental differences in a magnetic behaviour between nanostructures and bulk materials. This effect is all the more noteworthy.

(Refer Slide Time: 32:59)



Because if you take a nano scale material we would notice that the spins on the interior could all be aligned parallely causing for instance in a ferromagnetic material. But then the surface spins will actually be somewhat misalign with respect to the bulk. In other words, the surface spins are actually contributing less to the magnetization of the material. And the overall saturation magnetization or the overall magnetization I get from such a particle is going to be small, because of the misalignment of the surface spins. But in spite of this effect we actually find that the nano scale materials or introduced dimensionality systems we actually find an increase in the magnetic moment per atom.

(Refer Slide Time: 33:38)



So, if you look at for instance iron and you look at the bulk iron, it has got magnetic moment of about 2.2 bore magnetrons per atoms. But if you took at a 2 d iron you see that the magnetization as already increased to 2.96. You go down 1 d system made of iron, then it goes down to about 3.3 and in a zero d system it increases even further to about 4.0. This trend line can also be noted for nickel wherein again you can see the bulk magnetization is about 0.56 bore magnetrons per atom, and this increases to 0.68 for 2 d, 1.1 for 1 d and 2 for 0 d.

In other words, there is an increase in magnetic moment per atom as you reduce the dimensionality of the system from bulk to 2 d to 1 d to 0 d. So, this could be for instance an example of a quantum dot, this would be for instance a quantum wire, this could be a quantum well like this and this is of course a bulk material. Now, the important comparison number is of course, the maximum possible magnetic moment possible for an iron atom, because you have 3 mu be arising from the orbital contribution. 3 mu b from the spin contribution and in the bulk material we had noted that most of this orbital motion is quenched.

And therefore, you land up with the small number for the overall magnetic moment which is about 2.2 only. So, bulk materials do not have very high magnetization, but if you note now for a 0 d system you can see that the value has increased this implies that in 0 d nano crystals very little of the orbital magnetic moment is quenched.

That means, that now, because of the reduced dimensionality the lattice orbit coupling which we had talked about which is a strong coupling was actually reading to this reduce magnetic moment. You are finding that that is weakening up and therefore, you have an increased magnetic moment. So, this is very interesting that purely by reducing dimension now I am changing one of the fundamental properties of magnetization which is the number of bore magnetrons I can achieve from an atom in a material. So, this is changing and this is changing progressively with a reduction in the dimension and this trend line can be seen and these are I thing calculated values.

This can progressively be seen both for a material like nickel and iron. This implies that there is a fundamental change when you go down to the nano scale and to reiterate the important point here. There is always is in influence of the surface spins which is now, what you might call disordered or not that well oriented with respect to spins in the bulk which implies now that this expect is almost startling when you go down to small sizes. So, there is there are fundamental changes fundamental differences in the magnetic behaviour between nano scale structures and bulk materials, and we will take up a few more examples as you go down to more and more systems.

(Refer Slide Time: 36:26)



One of the important effects when you reduce the size of a system is the effect of super para magnetism. To understand super para magnetism, let us talk about what you might call a change in coercivity. And here we are plotting log of intrinsic coercivity and we said that intrinsic coercivity is the quantity when you are plotting an M H loop and not the B H loop. And you typically include a subscript i for indicating that it is the intrinsic coercivity we are plotting, and we are plotting log.



(Refer Slide time: 37:01)

Because now we are talking about a variation in coercivity of 2 to 3 orders of magnitude a large variation in coercivity. It is not a small variation, but an extremely large variation in coercivity and this variation in coercivity is coming again of course, from large variation in particle diameters.

So, we are talking about 5 orders of magnitude in particle size here weigh from about a nanometre to about a micron, about 5 orders of magnitude in sizes. And this are talking about free standing particles and about 3 orders of magnitude changes which is occurring in coercivity. In other words, the coercivity of bulk materials is very different from coercivity of nano particles. This is the important thing to note. Now, what is happening to the behaviour of a material when you are reducing the size starting from a micron sized particle.

Of course, here this micron sized are bigger particles can be classified as bulk. In other words, we are tending to bulk behaviour close to the right of the diagram and as you reduce the particle size you would notice that the coercivity is increasing. It reaches a peak value and at this peak value you draw it you give it a value D s. And further to that

this coercivity decreases on further reduction of size and finally the coercivity falls to 0. And this is another critical number which is called D p.

Now, this behaviour has to be understood and this is understood in terms of the domain structure, which is changing as you are reducing the size. In very large sizes of course, you know there is a multi domain structure and domain wall motion is one of the important mechanisms by which magnetization is taking place. In very small materials very small particles the mechanism actually is a domain wall rotation, which is a mechanism and the structure actually changes from what you might call when in the bulk scale it is multi domain. And in this stage the coercivity increases with decrease in size. That is what you have seen in the trend line here. Finally, of course, you obtain a peak in coercivity, which corresponds to a single domain and so this.

So, therefore there is a peak coercivity corresponding to a single domain. Now, further when you reduce the size of this single domain particle the coercivity begins to decrease and finally, the coercivity vanishes. When you obtain particles which or are of the order of for instance tens of nanometres. And throughout this process as you pointed the whole curve can be ascribed to an important property which is now my change in the domain structure. So, here it is a multi domain structure wherein I have domain wall motion for dominating and here it is a single domain structure in the low sizes wherein I have what you might call domain wall rotation which is predominating. And this overall effect is that I have a material below D p which behaves in a way which is called super paramagnetic.

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Now, we will talk a little more about super paramagnetic materials soon, but we will take up what are the things which we need to note before we take up this concept. As the particle size is reduce, the whole particle becomes single domain as we noted below the critical size. Now, why does it become single domain? There are two ways of understanding it.

Number one is that smaller particle then the domain wall thickness itself cannot support a domain wall that is obvious. Suppose, I am talking about a domain wall width of about 40 nanometres and suppose the particle is 20 nanometres, it is obvious this particle will not support domain walls. In other words, the magneto the exchange coupling will win over this particle and therefore, you will have a single domain particle.

Now, and typically of course that we will note that the domain wall thickness may not be constant with size that is also expected to change. It is not that 40 nano metre I said is going to remain constant with size, but never the less we have to note that there is expected to be critical size below which a domain wall cannot be supported.

Secondly, we have to note that the magneto static energy is a volume term, which goes as r cube. The domain wall energy is an interfacial err a ((Refer Time: 41:15)) course scales as r square. And therefore, we expect such a system like you know in the case of nucleation, in the case of phase transformation wherein, you see a critical size you expect there will be a critical size below walls, domain walls is not going to be stable.

Look at it either from picture like one or two, we note that a domain wall is not going to be stable at small sizes. In other words, a whole particle is expected to become single domain when you reduce the particle size. And the general trend line seen is that this critical size below which it becomes and of course, we will just come to it in a moment.





So, we note that below a certain size, the material is become totally single domain structure. Now, the reason that this coercivity is increasing in this region is that, because some of the along with domain wall motion. There are other phenomena like curling, which is a way of domain orientation taking place is also occurring and this curling term is now dependent on size and that is why you where actually have an increase in coercivity. Now, why does the coercivity decrease after it becomes a single particle, single particle? This is where the thermal disordering effect start to set in. Now, implies that you have in a nano particle.

(Refer Slide Time: 42:32)



Unlike a bulk material very few a limited number of magnetic moments aligned. That means exchange overall is limited to limited number of what you might call magnetic spins. And therefore, if I employ temperature on this system, the thermal disordering effects will set in sooner and this system can actually be disordered more easily, because there are limited now. It is like smaller system effect wherein now this thermal disordering is going to lead to a slow progressive reduction in the coercivity.

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And finally, of course as we have seen at certain size, the thermal disordering effects win over and finally, you have 0 coercivity. We had earlier pointed out whenever you are talking about reduction in size, in some sense we said this can be thought of as an increase in temperature. We pointed this out. So, now instead of increasing the temperature to cause a material to become paramagnetic, we are actually reducing the size to make it paramagnetic. Because we have in a, in a different context we had noted that reduction in size can equivalently, mentally thought of as increase in temperature.

Now, though this material has become paramagnetic we use a important suffix for this material super. In other words, it is normal it is not this material is not a normal paramagnetic like paramagnet like oxygen, but this is a super paramagnet, because if you look at any temperatures slightly below this transition D p. Then, you would note that this material is now become paramagnetic either one way of thinking, by increasing the temperature we said even beyond the curie temperature there are local spin clusters. And therefore, there is some partial alignment and when you apply a magnetic field this tend to become proper aligned system.

And therefore, we said that susceptibility is going to be very high. Similar to this, in this case the material has become paramagnetic by reduction of size. That means there is this is not a normal paramagnet, this is a paramagnet wherein there is lattened tendency, because of exchange coupling to become ferromagnetic. So, there is a lattened tendency and this implies, when I apply a magnetic field quickly all the spins would align. And therefore, the susceptibility will be very high.

Therefore, now when I plot an M H loop for such a material and I plot instead of plotting an M H, I plot M H by t, because now I can scale this whole system with temperature. Then I note that such a material will show a, what you might call a magnetization curve which has no hysteresis. In other words, the magnetization follows the magnetic field. So, suppose I am having a field in this direction the magnetization will point in that direction if I rotate my field then the magnetization will rotate along with the external field. In other words, there is no hysteresis and the spin field is opposite direction.

It will align along the opposite direction such a material in other words show zero coercivity and this is reminiscent of a paramagnetic material wherein there is the magnetization will follow the if it suppose you try to magnetize iron then it will follow the direction of the field. But noting very clearly this magnetization effect is much larger in magnitude then the normal paramagnetic material, because these are in an early as i pointed out ferromagnetic materials, which have become paramagnetic purely by the change in size. Therefore, this phenomena, because of the intensity of the effect is called super paramagnetic.

And if you look at this hysteresis curve breaks down into a line. In other words, this material, this is a signature that the material has become super paramagnetic. This value of D p is I pointed out in the nano scale in, if you look at it for iron it is of the order about 16 nanometres, for cobalt it is about 8 nanometres, for nickel about 35 nanometre.

And therefore, you can see that D p which is now my transition temperature, transition size below which the material becomes super paramagnetic is of the order of few to tens of nanometres. To summarize the stories of our for reduction in size initially and now we are we have to note that the reduction size has to be a few orders of magnitude only then you obtain significance effects. Number two, we observe a large variation in coercivity and below a certain size the material cannot support below certain size like D s the material cannot support a multi domain structure. In other words, the material becomes a single domain structure and after it becomes a single domain structure thermal disordering effects play start playing a very important role.

And therefore, you reduce a size even further then you note that the coercivity falls down to 0 and below a critical size D p, which is a the material becomes super paramagnetic, and this D p has an value in the scale of few tens of nanometres. So, in other words, there is this beautiful effect called super para magnetism which comes from reduction in size.

(Refer Slide Time: 47:25)



A quick comparison between para magnetism, super para magnetism is necessary and to do this we will assume that we are applying a very strong magnetic field of the order of about 20 into 10 power 6 ampere per metre. And we are talking about magnetization of oxygen which is about 2.85 bore magnetrons per molecule and we know that in a mole of oxygen there are about 6 into 10 power 23 molecules. And if you divide by the atomic mass you get the number of or molecular mass you get the number of molecules oxygen, molecules in this kg of matter.

Now, we are asking the question what is the magnetizing effect of this strong field? We know that the susceptibility of oxygen is actually very small and this susceptibility is of the order of 10 power minus 6, it is 1.36 into 10 power minus 6. That means that if I apply a magnetic field and see how much magnetization takes place, I would notice that I can multiply kai m by H and I would get H. Of course, magnetic field which I had given before I would get a value of 27 ampere metre square per kg. But if you compare this value with the overall potential magnetization that means, I assume that all the molecules are parallely oriented then I have this mole of molecules of course, per kg divided by this 0.032. Then, I would notice that actually I will get a magnetization which is of the order of 497 ampere metre square per kg.

Therefore, only a small fraction of the molecules are actually effectively contributing to the magnetization of material. That is which what is basically reflected in this susceptibility. We know that the only about 5 percent of the molecules are effectively contributing to magnetization. In other words, even strong fields are poor in aligning magnetic moments in a para magnetic material and now we are talking about a pure paramagnetic material which is not a ferro magnet which is been heated above the curie temperature. So, it is important to note that very strong fields cannot also align a pure paramagnetic material very effectively and thermal disorder is actually what is winning in this case.

But suppose, I talk about a 9 nano particle about 50 nanometre in size and we assume that this particle is now in the regime of super paramagnetic sizes. It is below D p, I will assume and given that of course, I am here assuming a bulk value of iron, I can correct it for by using a different value iron for magnetization for a reduce system which I should do actually. But I just take some number which is the magnetization value for an iron value. I would notice that if I have calculate the volume of the particle which is about 1767 arm strong cube and volume per atom is this lattice parameter cube divided by 2, because there are 2 atoms in BCC unit cell.

Then I would note this 11.82 arm strong per atom in a BCC unit cell the number of atoms, iron atoms in the particle is about 149 atoms and I would notice that the magnetic moment under particle saturation is 329 mu B. Of course, I as pointed out this may have to be corrected for the fact that in a nano particle the effective magnetization could be higher. In other words, in a super paramagnet you can get high magnetization values, because all the particles except for the ones on the surface actually are aligned along the direction of the magnetic field.

While in the case when you apply a magnetic field and because now this is a single domain structure there is no question of domain wall motion at all. And for now I will assume that the magneto crystalline anisotropy is small so that the magnetization vectors of the spin vectors can actually rotate rather freely. In that case, I would note is that I obtain a magnetization, which is come and spread with all these spins aligning parallel to the field. While on the other hand you would notice that the effective magnetization for a normal paramagnet is going to be a small number, because thermal disordering effects are stronger.

(Refer Slide Time: 51:24)

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Now, this is an interesting example we have taken up. Earlier in the course we had talked about how we can understand various properties and performances which can arise when you reduce a size. We said that there are 4 classes, we classified them and we said that change in size can lead to a change in structure, which can lead to a change in mechanism, which can lead to a change in property. And finally, any change in property is going to perhaps lead to a change in the desired performance of the material. So now, if you look at this case of magnetization in the case of reducing sizes then reduction in size as we saw can lead to change in domain structure.

Here of course, we are talking about not change in crystal structure, but the domain structure a micro structural kind of a parameter. This we saw can lead to a change in magnetization process we said that even the, what you call the mode of magnetization changes to domain wall rotation from domain wall migration predominantly.

And we see phenomena like super para magnetism that means that properties are going to change, we are going to have a net coercivity and retaintivity equal to 0. And this means an high sensitivity of this paramagnet to an externally applied paramagnetic field and needless to say this kind of a material can be put to good performance. Because now this material shows a extreme sensitivity to a external magnetic field as compared to a normal paramagnet. So, this would be a nice example wherein you are noting that the whole gamete of possibilities which we pointed out the change in size can lead to a change in structure either crystal structure or the case may be some kind of a micro structural entity. Then, change in magnetization, which is leading to the change in coercivity. And finally, of course, a performance of any kind of a device, which will be based on super para magnetism. Therefore, magnetism is important to understand from a, what you call a mechanism perspective apart from the, what you might call the phonological perspective as well.

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The next topic we take up is magnetism of clusters.