Nano structured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 4

Lecture - 35

Magnetic Properties – II

Welcome back to this course on nanostructured materials synthesis, properties, self assembly and applications. We are in module 4 lecture 7 and we are discussing magnetic properties of nanostructured materials. This is the second lecture of 3 lectures will be discussing on magnetic properties of nanostructured materials. In the previous lecture on magnetic properties, we looked at basic magnetic properties like what is ferromagnetism, what is diamagnetism, what is that magnetic moment, what are the units of these magnetic quantities? And how magnetic domains are formed what are the energy involved in a domain formation and what is the technique to look at magnetic domains in a solid? And that technique is the magneto optical Kerr effect using which you can identify different stripe like structures or a circular structures which give you the shape of the magnetic domains present in the magnetic material.

Now, these properties what we discussed in the previous lecture are generally applicable to any magnetic material. They need not be nanostructured materials they can be bulk materials as with micron size particles or larger particles. And now, we will discuss how these properties these magnetic properties will change when these materials are in the nanodimensions. So, when you have a particles of small size say 20 30 nanometers. Or even smaller how does the magnetic properties of those materials compare with their bulk materials that is those materials having micron size particles. So we will be discussing mainly the magnetic properties of nanosize materials in this lecture and the subsequent lecture to complete our 3 lectures on magnetic properties of nanostructured materials, so the lecture 7 of module 4.

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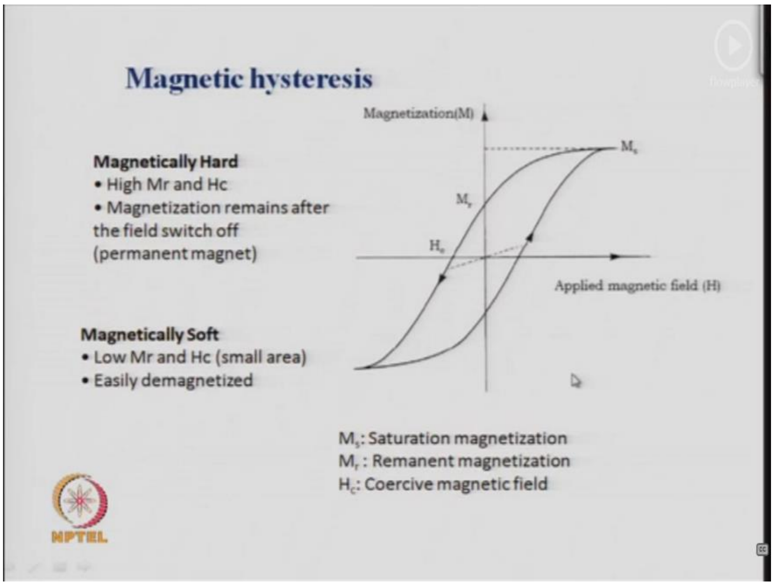

Magnetic hysteresis

Magnetically Hard
- High Mr and Hc
- Magnetization remains after the field switch off (permanent magnet)

Magnetically Soft
- Low Mr and Hc (small area)
- Easily demagnetized

M_s: Saturation magnetization
M_r : Remanent magnetization
H_c: Coercive magnetic field

So, another quantity one has to understand when one wants to differentiate between the magnetism of bulk ferromagnets. And how the magnetization changes as a function of field and how this will depend on the size of the particle is of interest was. So, magnetic hysteresis plots can be obtained if you measure the magnetization M of any material as a function of the applied magnetic field H. So, imagine that you are having zero magnetic field then the magnetization is 0. So, you are here and if you increase the magnetic field the magnetization will increase. So, initially it will increase from the origin it will go like that. And then it will reach saturation which is called the M s or saturation magnetization. That is given by extrapolating this line to the y axis and this value of magnetization is the saturation magnetization.

Now, ideally in a normal ferromagnet you will see this kind of a hysteresis loop. And as you change the magnetic field it increases go reaches a maximum then you decrease the magnetic field. The magnetization will start decreasing however it will not come to 0 from where you started. But will intercept the y axis at some position and this point where the magnetization cuts the y axis is called the remanent magnetization. Now, the field applied at this point is 0. So you are having a net magnetization which is remaining even in the absence of a magnetic field and hence it is called a remanent magnetization.

And this is a property of anything which is ferromagnetic or ferromagnetic. And it is because of the magnetic domains present in the magnetic material and the alignment of the magnetic vectors within those domains. Now, if you change the magnetic field in the opposite direction, so you are increasing the magnetic field in the negative direction. Then the magnetization will further decrease till it hits the x axis at a particular field. So, you are making the field negative or which means the field has a direction which is opposite to the original direction of the magnetic field. So, this field which you are now applying is in the opposite direction and has a magnitude H c when the net magnetization goes to 0. That field at which the magnetization is really zero is called the H c or the coercive field.

So, what we learn from this hysteresis loop typical for ferromagnetic materials say that you will get a saturation magnetization. You will get a remanent magnetization when the field goes to 0. When you are doing this cyclic loop and when you take the field further in the other direction you will get a net magnetization is equal to 0 only at a field. Which is H c and is opposite in direction to the original field applied. And then you further increase the field in the direction in the negative direction and the magnetization changes signs. So, it goes in the negative direction and reaches a saturation which will be equivalent to the magnetic saturation magnetization in the opposite direction. So, here whatever will be the value you get a negative value that means a magnetization in the opposite direction with the similar magnitude.

And then if you again retrace the path you increase field you will again see an increase in the magnetization. So this particular loop of magnetization as a function of magnetic field is called a hysteresis loop. And is typical for ferromagnetic or ferrimagnetic systems. And the area under the loop tells you about the material about how hard is the magnet or how soft is the magnet. Something which we say is magnetically hard what does it mean something to be magnetically hard means it is difficult to magnetize that sample. That means you have to give a very high magnetic field to reach saturation magnetization. So, if you have high M r and high critical field that means is very difficult for the magnet to lose its magnetization. So, high H c means you have to go to very high magnetic fields before the magnetization goes down to 0.

So, basically the area of the loop will increase when something is magnetically very hard and not only that this breadth of this loop will be very high. Because H c will be very high means the breadth of the loop will be very high. So, typically a permanent magnet has ferromagnetic substance will have will be magnetically very hard it will have a high remanent magnetic field. And it will also have a high coercive field something which is magnetically soft will have a low remanent magnetization. And a low coercive field and this area under the loop will be very small. So, such a material can be easily demagnetized a hard material cannot be easily demagnetized whereas, a soft material can be easily demagnetized.

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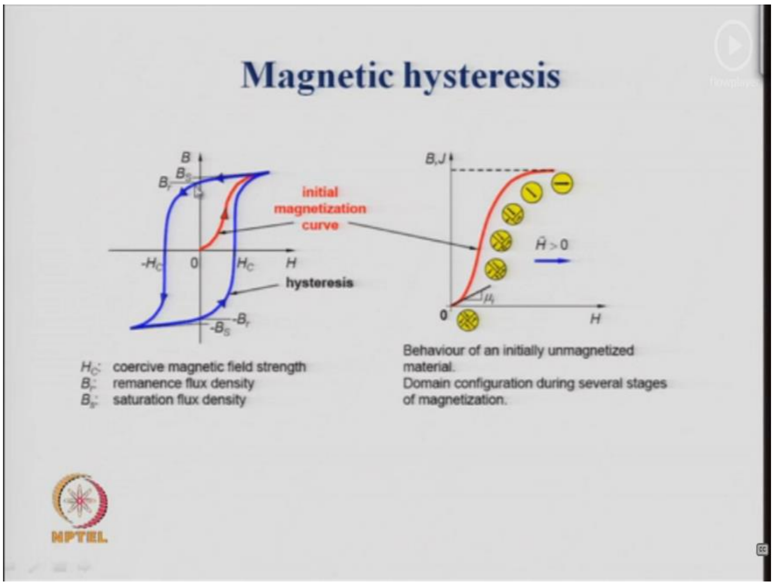

Magnetic hysteresis

H_C: coercive magnetic field strength
B_r: remanence flux density
B_S: saturation flux density

Behaviour of an initially unmagnetized material.
Domain configuration during several stages of magnetization.

So, if you look at the hysteresis loop again carefully the red line shows that initially you started with zero you reached the maximum which is possible magnetization. And here we are calling it in plotting in terms of the flux density which is related to the magnetization so you can plot the flux density also. And so you have a remanent flux density B R and then you have a coercive field and this kind of plot is shows you a ferromagnetic substance. And these if you look at this plot what is what is the type of magnetic dipoles that you have what is the orientation of the dipoles at different stages of this plot can be seen here. Especially, the red plot the initial magnetization when you started from zero magnetization the material was not polled earlier.

So, first time when you magnetically poll the material you apply a magnetic field you go through these steps. So you see initially at zero field there is zero magnetization, because all these vectors are in different orientations. Now, when you increase the magnetic field then some of these dipoles become gain in strength. You see this region is becoming larger here there are 4 quadrants all the 4 quadrants are equal. The vectors are pointing in different directions the net magnetization is zero or the net magnetic flux density is 0. When you are here then you see some of the quadrants being higher in energy and hence you have a net magnetization or a net magnetic field flux density.

And that region grows in area and so this region is increasing till you come here. And all out of 4 domains you had 4 domains here, you had 4 domains here also you had 4 domains but, very small domains some of them. And one large domain here now you have again only 3 domains and 1 large domain out of the 3 finally, you have only one domain only one vector you have you can see very large vector in one direction. But the magnetic field is in this direction. So, this vector is yet not aligned with this direction but, all the vectors within different domains have now become one and you have 1 magnetic domain. So, this is a single domain particle though the magnetic vector is not align with the magnetic field.

Now, if you increase the field further then this direction of this vector also becomes aligned with the magnetic field. So, that is the maximum that is the final stage that is when all the small domains had converted to 1 domain. And the vector in that domain has aligned with the applied magnetic field and that is the maximum magnetization you get. If you increase the field further there will be no further change because this moment cannot grow any further there are no new domains to be added to it. And so the net magnetization becomes constant and this is the explanation of this red curve here. So, you can see different stages how the magnetic dipole vectors are changing and the domains are changing as a function of the applied magnetic field.

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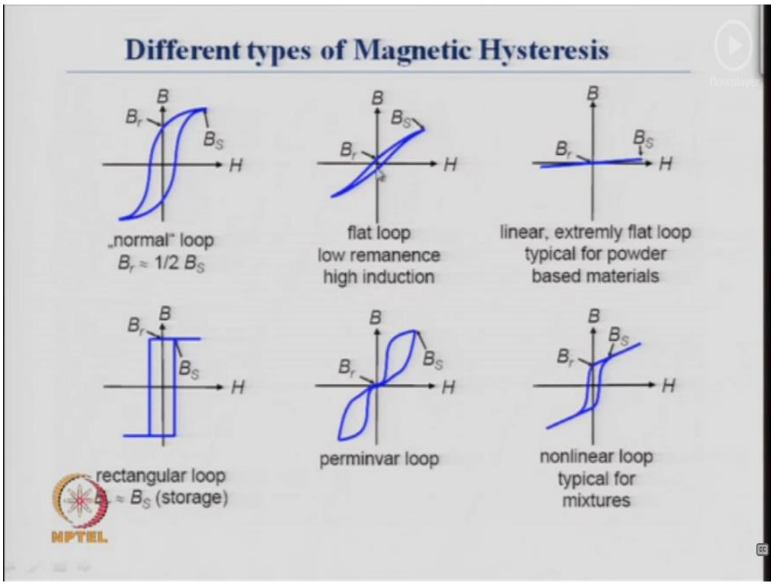

Different types of Magnetic Hysteresis

„normal" loop
$B_r \approx 1/2\ B_S$

flat loop
low remanence
high induction

linear, extremly flat loop
typical for powder
based materials

rectangular loop
$B_r \approx B_S$ (storage)

perminvar loop

nonlinear loop
typical for
mixtures

Now, you can have different types of hysteresis. So, you see you can have a hysteresis loop which is very small area here the area is large. Then you can have a hysteresis loop where you can have nearly very sharp change in the magnetization or magnetic flux density. And or you can have a smooth change in the magnetic flux density. So, there are different types of magnetization as shown by these three here the remanence is very low here the remanence is very high this also has a very high remanence. But you reach saturation very fast the moment you cross this field you immediately reach saturation. So, this is a rectangular type of loop this is normal loop and this is very good for storage. You can apply a particular field immediately all the dipoles are align you apply a field in the opposite direction all the dipoles will get misaligned and you will get a resultant flux density to be 0.

So, quick switching can occur in this kind of system. Here it is slightly slow, because it varies with the magnetic field it does not change suddenly. In this case there is very low remanence although the induction or the magnetic magnetization is high. Now, in this case there is zero remanence so this is not a particular ferromagnetic material because the remanence is nearly 0. And this is a linear type flat loop and this is typical for powder based material there is hardly any remanence its nearly zero remanence. And this is a non-linear loop for mixtures you can see that you have a ferromagnetic component shown by the hysteresis loop. But the component it it reaches saturation it never reaches saturation it never becomes flat you see it is continuing to increase with increase in field strength. So, it is a kind of a non-linear loop, because there is the change in the magnetic field is not directly proportional to the field.

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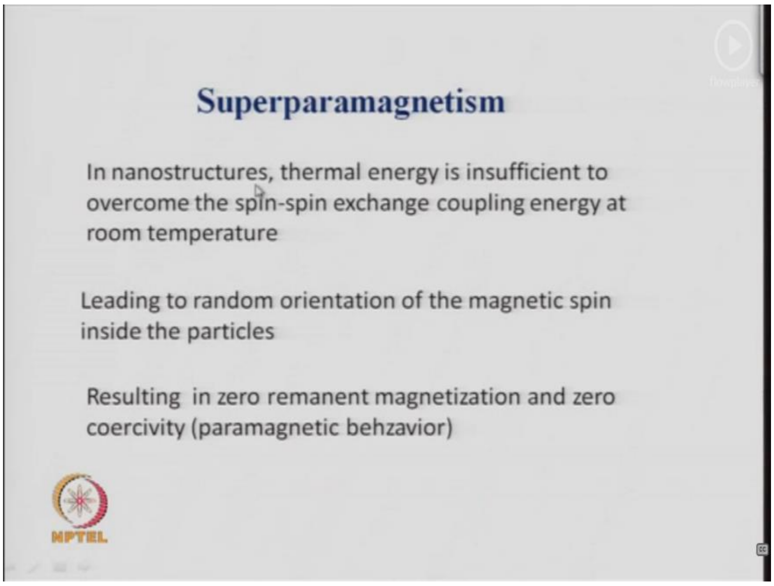

Superparamagnetism

In nanostructures, thermal energy is insufficient to overcome the spin-spin exchange coupling energy at room temperature

Leading to random orientation of the magnetic spin inside the particles

Resulting in zero remanent magnetization and zero coercivity (paramagnetic behzavior)

Now, we come to the exact problem of magnetism in nanomaterials. What is superparamagnetism? Many of these magnets when you decrease the size of the particle to the nanodimension you will get superparamagnetism. So in nanostructures the thermal energy is insufficient to overcome the spin-spin coupling energy which exists between the magnetic dipoles at room temperature. So, they are unable to change their position, so you would not have that kind of energy to overcome the spin-spin exchange coupling energy at room temperature.

And if you cannot overcome that then you will have a random distribution of the magnetic vectors. And that is what happens in superparamagnets where you have a random orientation of the magnetic spin inside the particles. And this kind of a random spin leads to zero remanent magnetization and zero coercivity which is like a paramagnetic behavior. So, not like a ferromagnetic behavior in a ferromagnetic behavior you must you will have a remanence and you will also have a coercive field. That means the plot will not go through zero whereas, whenever you have a zero remanence and zero coercive field the line will go through the origin.

That means they you need no energy to bring back the sample from its magnetize form to the zero form where there is no magnetization. So, that kind of result where you have a net remanent magnetization is zero and zero coercive field that is kind of a paramagnetic behavior. Since it is a particle and not a ion or a molecule hence will call a superparamagnet. That means several molecules are ions together form 1 magnetic vector which is disoriented or has random oriented inside the particle.

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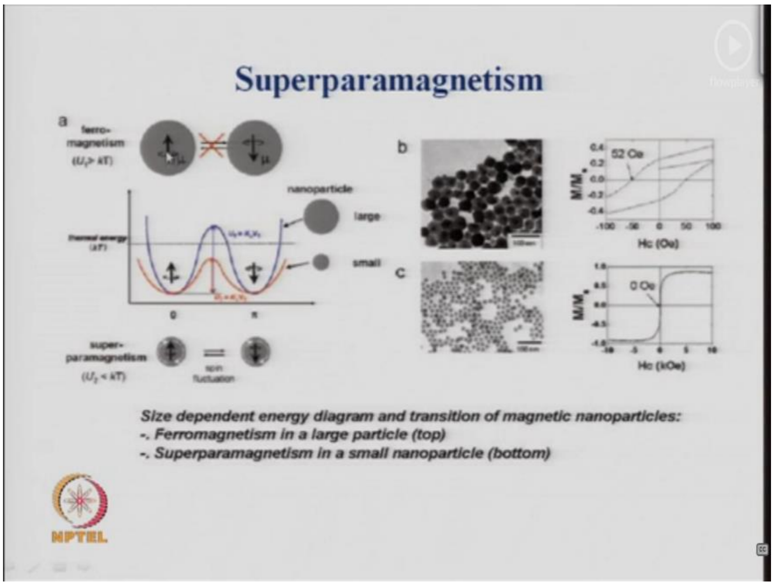

Superparamagnetism

Size dependent energy diagram and transition of magnetic nanoparticles:
-. Ferromagnetism in a large particle (top)
-. Superparamagnetism in a small nanoparticle (bottom)

So, that you can see here in this plot the difference between a large particle and a small particle what happens is if you have 2 position 2 vectorial directions. Suppose this one indicated by mu has a vector which is pointing upwards. And here it is pointing downwards and if you cannot go from here to there. Then that means you will have some net magnetization and this is ferromagnetization when the energy exchange energy is greater than k T. Now you have if you have a plot energy plots here is a thermal energy as a function of say orientation of the spins here you can consider this to be a magnetic moment. And if you are in this stability zone that means the energy is minimum here and for 1 direction.

And the energy is minimum here for the other direction of the magnetic vector. You want to go from this direction to this direction you have to overcome this energy barrier. Now, this energy barrier for a large particle is large. So, this is the total energy barrier you have to give this energy. If you want to change your spin from this direction to this direction in a small particle in a nanoparticle this energy difference is much smaller. And so it is easy for the moment to change it is this magnetic vector to change its direction by giving this kind of energy. Now, if at room temperature the thermal energy has a value of this nature which is less than the value required by the large particle. But, this energy is sufficiently more than the energy required to change the magnetic vector in a small particle. Then you will automatically have this change in the spins.

So, you can do this spin flipping by the normal temperature at normal temperature and you will have both possibilities in your system. And so this spin fluctuation then leads to superparamagnetism. So, whenever the energy required this value is called U and this value whenever it is less than k T where k T is the energy that is the thermal energy the then you can have spin fluctuation and then it will result in superparamagnetism. So, what will it look like in a when you plot the magnetization? How will the hysteresis loop look like?

So, for a large particle where you have plot magnetization on the y axis and the applied magnetic field in o a state in the x axis you see that there is a loop although the loop is not closed here. If you go to higher fields this loop may close, but you can see that there is an area under the curve when you plot magnetization versus magnetic field. This is for large particles. Now, for same material if you decrease the size of the particle. So, suppose these particles are around 50 nanometers and these particles are around 10 to 12 nanometers. These small particles do not show this hysteresis loop, but they show a plot which goes through the 0. Which is like there is no remanence and the coercive field is 0 and this is typical for a superparamagnet.

So, it behaves like a paramagnet although it is a particle with several moments. But, the moments are flipping among themselves and so resultant is a behavior like a paramagnet. So, this particular plot shows you how a superparamagnet behaves in a magnetic field. And these two plots clearly differentiate the change in the magnetic property of a magnetic material when you decrease the size of the particle. So, this is one of the most important aspects of the magnetic properties of nanostructures. The property of superparamagnetism when you decrease the size of a magnetic material which shows a hysteresis loop when the particle size is large. But the same material when you lower the size of the particle to nanodimensions then it does not show the hysteresis loop.

But the magnetization plot versus field goes through the origin showing no remanence and no coercive field. So, this way and when will this happen? This will happen whenever the energy required to flip the 2 vectors is lower than the thermal energy. So, that is the key point that the energy to change from one vectorial direction to another vectorial direction is much smaller than the available thermal energy. Then you will see this kind of superparamagnet superparamagnetism, which is highly prevalent in magnetic materials and is a function of the size of the particle.

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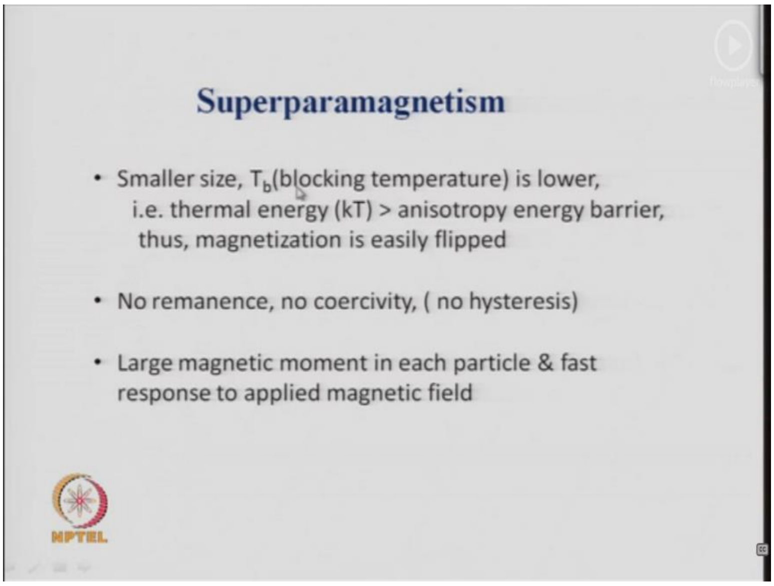

Superparamagnetism

- Smaller size, T_b(blocking temperature) is lower, i.e. thermal energy (kT) > anisotropy energy barrier, thus, magnetization is easily flipped
- No remanence, no coercivity, (no hysteresis)
- Large magnetic moment in each particle & fast response to applied magnetic field

Now, in superparamagnetism, the smaller the size then you has a temperature which is called a blocking temperature. That means that as it is behaving as your lowering the magnetization should increase in a paramagnet like in a any ferromagnet also the magnetization increases as your lowering the temperature. But, in a superparamagnet below a certain temperature the magnetization will start decreasing. Now, that temperature is called the blocking temperature. So, the blocking temperature changes as a function of size smaller the size of the particle smaller will be the blocking temperature. So, the temperature at which the of the paramagnet instead of going to a ferromagnet where it the magnetization should increase further instead of that it starts decreasing that temperature is called the blocking temperature. And the blocking temperature will change according to the size of the particle.

So, the smaller the size smaller is the blocking temperature. And this actually is due to the fact that the thermal energy is much larger than the anisotropic energy barrier that is u we discussed. And smaller the size of the particle this U will become even smaller and thus magnetization will be easily flipped. So the blocking temperature gets lowered with the size of the particle apart from that there will be no hysteresis in superparamagnets. There will be no remanence or no remanent magnetization there will be no coercivity or no coercive field. The H c will be zero the M r which is the remanent magnetization will be 0. And the large magnetic moment in each particle will be there.

So, the magnetic moment of each particle will be like the collection of the magnetic magnetic moments of the dipoles are which are present in the particle so it will have a larger magnetic moment. So, if you see the plot here which we mentioned initially you see you have these the length of the arrows may be taken as the magnitude of the moment. Now, these are very small as you the as your changing the changing the field you see this arrow is growing and it is becoming larger and larger. So, here the length of the arrow is much higher; that means the magnitude of the magnetic vector is higher. And so that is that will always be found in this kind of materials superparamagnets where you will have a large magnetic moment in each particle.

And also there will be a fast response to the applied field that means if you apply a field the moment will be there. And if you remove the field the moment will not be there it will be having a large response quick response to the applied magnetic field. And the magnitude of the magnetic moment will be larger in this each particle. And that is why it is called superparamagnet, because normal paramagnet will have some magnetic moment But when you have a particle with several of these moments aligned together to act as a single moment. Then this single moment will have a much larger value and that is why this property is called superparamagnetism.

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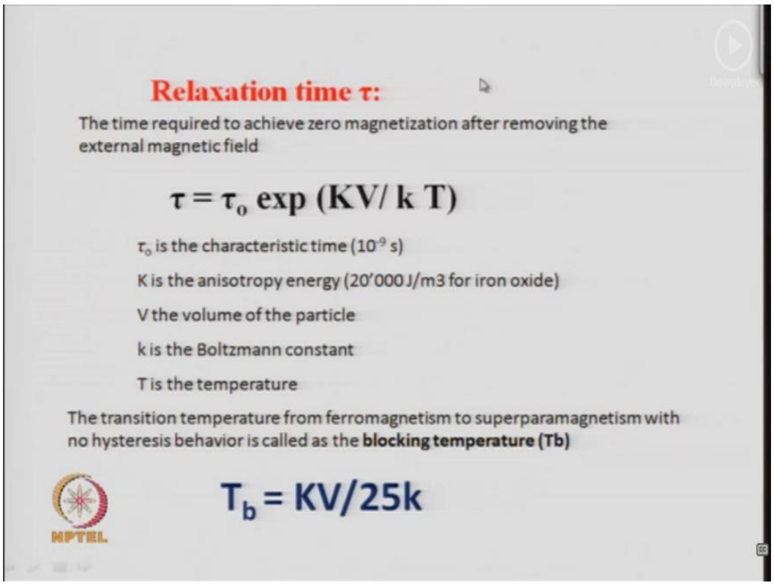

Relaxation time τ:

The time required to achieve zero magnetization after removing the external magnetic field

$$\tau = \tau_o \exp (KV/ k T)$$

τ_o is the characteristic time (10^{-9} s)

K is the anisotropy energy (20’000 J/m3 for iron oxide)

V the volume of the particle

k is the Boltzmann constant

T is the temperature

The transition temperature from ferromagnetism to superparamagnetism with no hysteresis behavior is called as the **blocking temperature (Tb)**

$$T_b = KV/25k$$

Now, there are some other quantities which one relates to these kind of a superparamagnets one is of course, the blocking temperature that is the temperature where it the paramagnet should have become the a ferromagnet. But the magnetization instead of increasing starts decreasing. So, that is the temperature which is the blocking temperature. Then you have the magnitude of the magnetic moment which will be much larger and that also defines a superparamagnet. And then there are other quantities like the relaxation time, how much time it is required to achieve zero magnetization after removing the external field?

So, you apply a field and then remove the field, how much time will the moment require for it to become again zero the magnetic moment to go to zero? Because in the absence of the magnetic field any paramagnet and hence a superparamagnet should also have a zero magnetization. But it will take some time to achieve that zero magnetization that is called the relaxation time tau. And that is given by this expression tau equal to tau naught exponential capital K multiplied by v by small k T the small k is here the boltzmann constant. And capital K is something to do with the material it is called the anisotropy energy. And it changes from material to material so for example, the anisotropy energy if it is very large.

Then it will take much more time for the magnetization to decay to 0, because it is exponentially related to the capital k which is the anisotropy energy. And the anisotropy energy for iron oxide which is a good magnetic material so if you reduce the size of iron oxide particles make nanoparticles of iron oxide. Then you can observe that it will show superparamagnetism. And it will show a relaxation time tau which is related to this equation and where capital K has a value of nearly 20000 Joules per meter cube that is the value of capital K. And V is the volume of the particle. So, that means smaller the volume smaller will be the relaxation time because this is exponentially related. And of course, a higher the temperature smaller will be the time.

So, if you increase the temperature it will relax faster it is understandable, because we are increasing the thermal energy. So, k T is increasing and so k T is in the denominator of the exponential and hence higher the value of t lower will be the relaxation time it will relax faster. So, this gives you the equation between relaxation time and the material property which is the anisotropy energy which is different for different materials. And for a very good magnet like iron oxide that value is very high it is nearly 20000 and of course, this will vary whether it is F e 2 O 3, F e 3 O 4 or iron metal etcetera. Then the blocking temperature which is also very important, that is the temperature where the paramagnet becomes a superparamagnet.

That blocking temperature is also related to this anisotropy energy so larger the anisotropy energy larger is the blocking temperature. And so the blocking temperature and the relaxation time are more or less related in this manner that is if you keep other things constant. Then the material with a high anisotropy energy will have a high blocking temperature and will also have a large relaxation time. So, blocking temperature and relaxation time are that way related so this I already define that, what is this blocking temperature it is the transition temperature where you should be getting ferromagnetism. But you start getting superparamagnetism from a ferromagnetic material as it is going from a paramagnet to become a ferromagnet. But, it becomes a superparamagnet and that is the blocking temperature and it depends on different materials.

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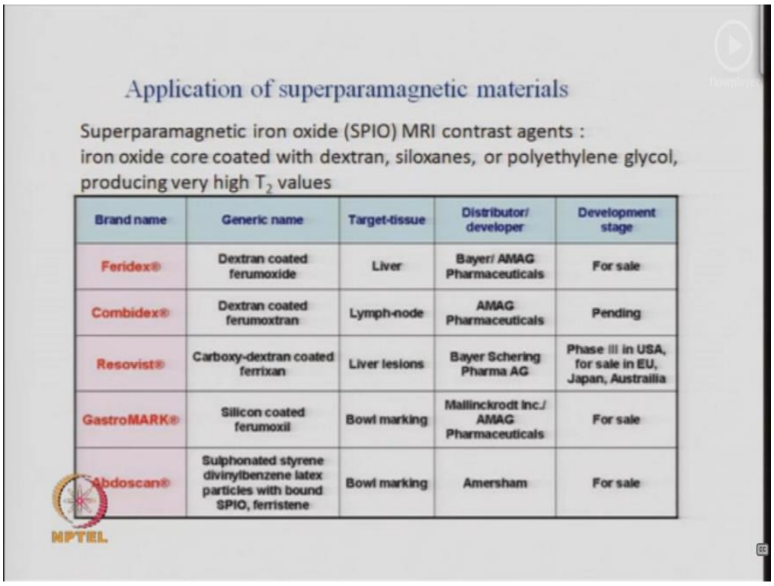

Application of superparamagnetic materials

Superparamagnetic iron oxide (SPIO) MRI contrast agents :
iron oxide core coated with dextran, siloxanes, or polyethylene glycol, producing very high T_2 values

Brand name	Generic name	Target-tissue	Distributor/ developer	Development stage
Feridex®	Dextran coated ferumoxide	Liver	Bayer/ AMAG Pharmaceuticals	For sale
Combidex®	Dextran coated ferumoxtran	Lymph-node	AMAG Pharmaceuticals	Pending
Resovist®	Carboxy-dextran coated ferrixan	Liver lesions	Bayer Schering Pharma AG	Phase III in USA, for sale in EU, Japan, Austrailia
GastroMARK®	Silicon coated ferumoxil	Bowl marking	Mallinckrodt Inc./ AMAG Pharmaceuticals	For sale
Abdoscan®	Sulphonated styrene divinylbenzene latex particles with bound SPIO, ferristene	Bowl marking	Amersham	For sale

Now, the applications of superparamagnetic materials why are they very important in nanotechnology superparamagnetic iron oxide. So, iron oxide is a ferromagnetic when we make small particles of iron oxide they become superparamagnetic. And these superparamagnetic iron oxide in short we call them SPO, they are used as MRI contrast agents. What is MRI contrast agent when you do imaging of your body like the cat scan and you can do imaging of the spinal cord. And all that using what is called magnetic resonance you do you apply a magnetic resonance principle where you have a magnetic field and you apply radio frequency. And this is known in many applications in medicine. Of course, also in chemistry and biology where you use n M r techniques this is a kind of n M r, but its imaging you are imaging some signals and this is not spectroscopy.

So, n M r is a spectroscopic tool whereas, MR I is an imaging tool where you want to see some place some part of the body where the magnetic field can be mapped. So, MRI machines image places with differences in magnetic fields. And to make a good contrast you need to add some MRI contrast agents. That is which create the differences in magnetic fields locally such that you can see them better using an MRI machine. So, in that case this superparamagnetic iron oxide particle are very important. They are given to in the body it is transmitted normally coated with dextran or siloxanes or poly ethylene glycol it is coated with these materials inside the iron oxide which is of a very small size, because it has to be superparamagnetic.

So, the idea is you do not want ferromagnetic iron oxide you want superparamagnetic iron oxide that means you want nanosized iron oxide. And this nanosized iron oxide when it is coated with some of these is sold in the market as different commercial names are there. For example, you have feridex which is dextran coated ferumoxide that means iron oxide and it targets the liver and so if you want to do MRI of the liver. That means you want to see the different parts of the liver this can be used and this is already marketed by certain commercial companies.

There are other kind of drugs or MRI contrast agents to be more specific based on iron oxide all of them are based on iron oxide, because iron oxide is biocompatible. So, you cannot use any nanoparticle; you have to use nanoparticles which are biocompatible our body will not reject such particles. And so iron oxide is one such magnetic particle which the body does not reject and so iron oxide nanoparticles are being used as MRI contrast agents, because they show the property of superparamagnetism.

So, if you make iron oxide you have to make it in very small size such that they are in nanometers in dimensions. And then because you want to avoid some other reactions you coat it with certain polymers or some other chemicals as given here like dextran siloxanes etcetera. And then you introduce into the body and these particles are transported to specific places. Because of the coatings the coatings kind of functionalize these particles to take them to certain positions in the body like the liver or the lymph node etcetera. And there they create a contrast which the MRI machine can see much more easily. Without these contrast agents also you can see, but the contrast will not be good hence clarity will be less.

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Magnetic nanoalphabets

So, this MRI contrast agents can be seen we will see them. Now this is just magnetic materials these are not MRI contrast particles there is nothing coated on the magnetic particles. But, it is to show that I can agglomerate magnetic particles such that I can write alphabets out of them. So, you have written A B C etcetera with magnetic particles they have been brought close together and assembled in a fashion that they look like different letters in the of our alphabets. But they are basically nanoparticles having size of around 10 20 nanometers and which have been assembled by some technique in this fashion to write down. So, it is possible to assemble magnetic nanoparticles but, what is the application. Now, we will look at the application how do you make these assemblies like I said you can assemble them in a particular manner say I want in a linear manner like this. Or I want in a curve like that how do you plan these kind of assembly of nanoparticles which are magnetic in nature.

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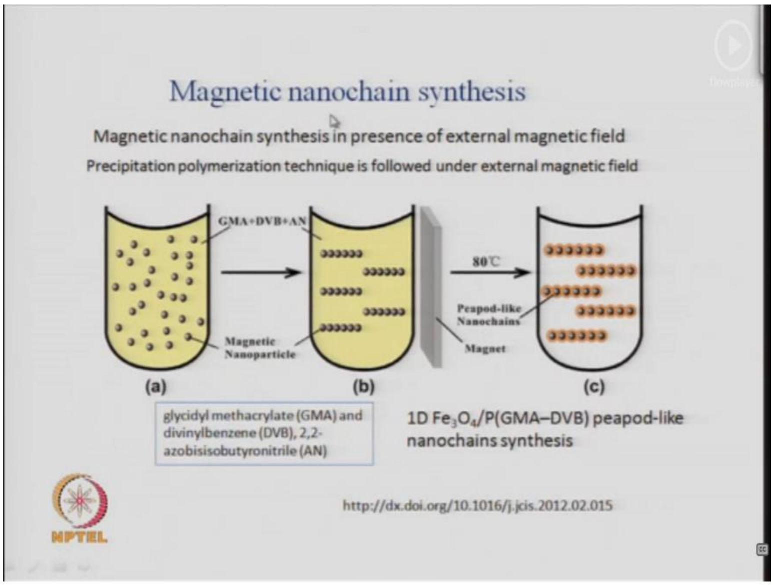

Magnetic nanochain synthesis

Magnetic nanochain synthesis in presence of external magnetic field

Precipitation polymerization technique is followed under external magnetic field

glycidyl methacrylate (GMA) and divinylbenzene (DVB), 2,2-azobisisobutyronitrile (AN)

1D Fe_3O_4/P(GMA–DVB) peapod-like nanochains synthesis

http://dx.doi.org/10.1016/j.jcis.2012.02.015

So, this is one process where you create magnetic chains so magnetic nanochain synthesis how do you do this in the laboratory that is of importance. So, what people have done they have taken submagnetic nanoparticles. So, this black spheres are taken are magnetic nanoparticles and can be iron oxide. And then it is put into a solution of a some chemicals which can be polymerized. So, you add like glycidyl methacrylate and divinylbenzene D V B. So G M A and D V B are these. And then you also add 2 azobisisobutyronitrile which is called here as A N it is normally called as A I B N a for azo and i for iso and butyronitrile so B N. So, these three reagents can be added.

So, you have this then you add them together with the magnetic nanoparticles and you apply a magnetic field. So, you bring a magnet close to it so the magnet will align these particles. And once they are aligned this mixture of these 3 the monomers of these will polymerize. So, you have a precipitation polymerization technique so you want them to polymerize. And this polymerizes at around 80 degree Celsius. So, you once in the presence of the magnet this particles are made into chains then the polymerization occurs. And when the polymerization occurs they form this kind of a peapods peapod like nanochains peapod means you have those p’s with its cover. And they form a well defined cover on top of these particles. So, this is a methodology for synthesis of nanochains. Now, this is one methodology.

There are many other methodologies by which nanochains can be created. And here the method is what is called precipitation polymerization technique. And it uses these kind of polymerizing agents and monomers to form polymers at a particular temperature. So, these are iron oxide it is 1 dimensional so it is A 1 d F e 3 O 4 because it is chains. So, it is one dimensional, so 1D F e 3 O 4 chains with a peapod like a polymer which is covering it on top. So, this is a very interesting method of making a self assembled or a chain of a magnetic nanoparticle specifically of iron oxide and can be used for several applications.

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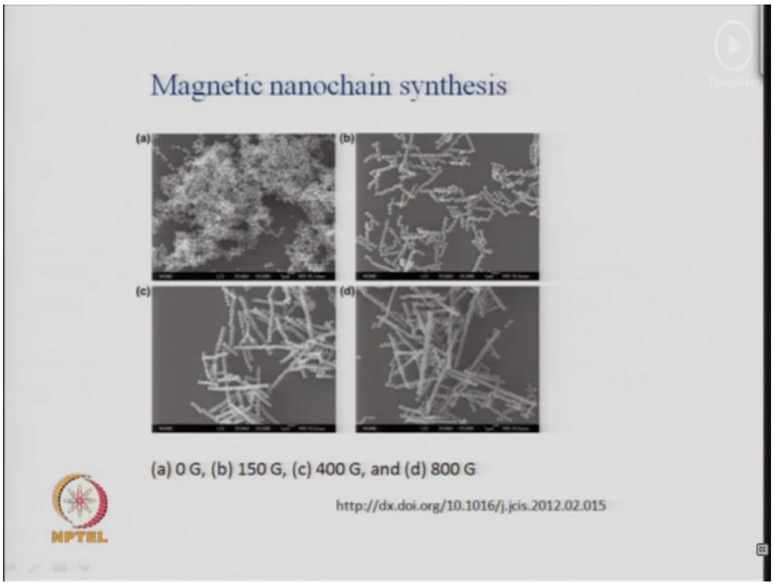

Magnetic nanochain synthesis

(a) 0 G, (b) 150 G, (c) 400 G, and (d) 800 G

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This is the real picture in the presence of a magnetic field. So, you have these particles and in the presence of zero field. So, at zero gauss all the particles are agglomerated you see there is no particular orientation that means no nanochain formation here. When you apply the magnetic field of 150 gauss then you start seeing some chains being formed here so this is like the previous plot. Here we are shown it schematically that you apply a magnetic field and this is what should happen when you have this particles. Which we can now see through our eye that means through an electron microscope you can see that when there is no magnetic field. There is no alignment when you apply a magnetic field you there is some alignment, when you increase the strength of the field then you get much longer chains. So, from 150 gauss if you are going to 400 gauss you see the number of long chains are increasing.

And henceforth you increase it further to 800 gauss you see still longer chains. So, it tells you that the methodology which we described earlier bringing a magnetic field to align this particles is working. And you can get aligned particles like long chains as a function of magnetic field. So, zero magnetic field no chains small magnetic field small chains and they increase the strength of the magnetic field you increase the length of the chains of this magnetic nanoparticles. So, this is very interesting for applications. Now, if you measure the property of these chains so depending on different amount of monomers.

So, you want to because you want to polymerize on top of this you want this polymer. So, if you add different amount of monomers the amount of polymerization will be different and so the magnetization will also be different. Because if it is uncovered you will see some magnetization if you cover it with a polymer then the effect of magnetization will decrease. So, that one can study when you do the real experiment of measuring the magnetization using either a v s m which is a vibrating sample magnetometer or a squid where you can measure magnetization in both of them. You can do magnetization as a function of field.

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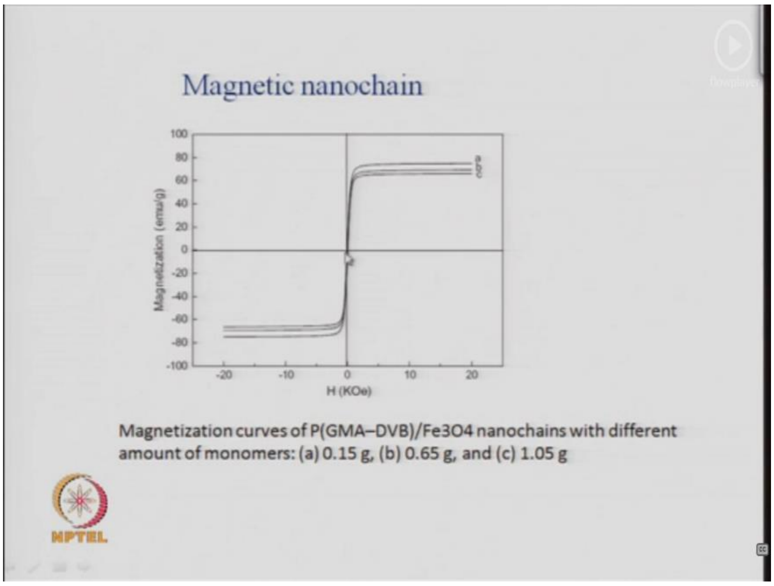

Magnetic nanochain

Magnetization curves of P(GMA–DVB)/Fe3O4 nanochains with different amount of monomers: (a) 0.15 g, (b) 0.65 g, and (c) 1.05 g

And when you do that study on these magnetic nanochains, you see this superparamagnetic behavior. This is what I described earlier that any superparamagnet will show a behavior where it will go through the origin. That means the remanent field should be zero and the coercive will field will be zero. So, all the 3 compositions made with 3 different amounts of monomers show the same superparamagnetic behavior which we explained earlier. This is a superparamagnetic behavior there is no hysteresis which one expects in a ferromagnetic material like iron F e 3 O 4, but F e 3 O 4 here is in very small size in nanosized and hence it shows a superparamagnetic behavior.

What is the difference in the 3 plots? The difference in these 3 plots is the amount of coating one has, because you have added different amount of monomers. The amount of coating has changed. So this is very small a, is very small amount of polymerization which has taken place and so you see the magnetization is higher. Because the iron oxide can feel the applied magnetic field and its magnetization is high. When you add more amount of the monomer then more of the chains are covered with the polymer. So, the magnetization decreases from a to b, and then if you add further increase of the monomer the magnetization decreases further to c.

So effectively with the change with the thickness of the polymer around the around the particles if you increase this polymer which is forming by increasing the amount of monomer you are adding you will decrease the magnetization. And that is what is happening so you can get controlled magnetization of these chains by controlling the amount of monomer that you are adding in the system, before you heat it at 80 degrees to polymerize. So, you can vary the amount of magnetization. All the 3 cases which we discussed show superparamagnetism. But the amount of magnetization changes with the amount of monomer that you are adding in the system. So, this is a good control of the superparamagnetism in this system.

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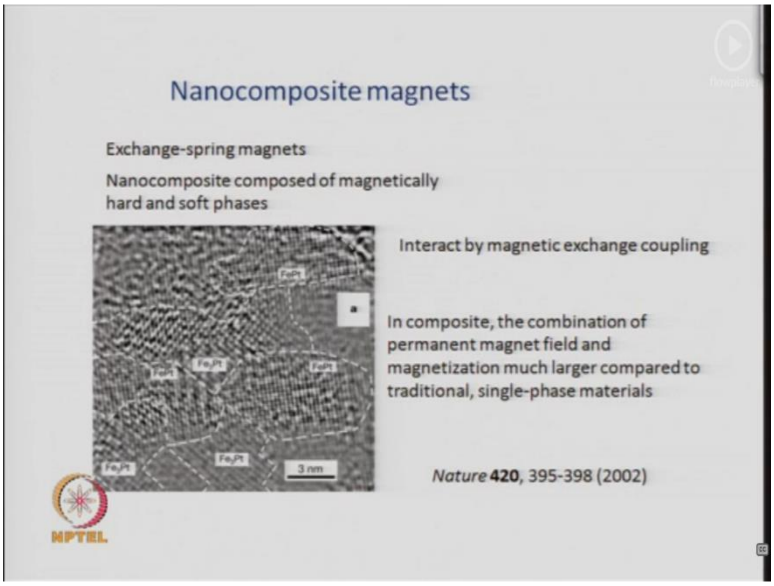

Nanocomposite magnets

Exchange-spring magnets

Nanocomposite composed of magnetically hard and soft phases

Interact by magnetic exchange coupling

In composite, the combination of permanent magnet field and magnetization much larger compared to traditional, single-phase materials

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Now, finally, one more thing probably the last point I want to discuss today is about nanocomposite magnets. How you can change the magnetization if you have materials with 2 different types of magnetization. So, suppose something is a hard magnet and something is a soft magnet. So, what is a hard magnet we discussed earlier in a hard magnet the remanent magnetization will be high, the coercive field will be high and the area under the hysteresis loop will be very high so that will be a hard magnet. And in a soft magnet all these things will be smaller the coercive field will be smaller remanent magnetization will be smaller and the area under the hysteresis loop will be smaller. So, if you have a mixture of 2 materials one is a hard magnet and one is the soft magnet then what is found is that you can alter the net magnetization effectively.

So, if you make nanocomposites of magnets take hard and soft magnets and make a composite a mixture of 2 different magnets. For example, this is a high resolution transmission electro micrograph and its quite high resolution as you see the scale is 3 nanometers. So you are seeing a very a small regions in these samples and you have a region which you can identify using energy dispersive x ray analysis in A t e m you can find out the composition. That this part of the material if this material has this part is having a formula one iron is to one platinum. So, it is an alloy particle of iron is to platinum and this is also iron platinum.

Whereas, this part you can see it has a different kind of contrast and different kind of lattice fringes. So, this different as the lines you are seeing here are called lattice fringes and they tell you about the crystal structure the play difference in the planes atomic planes in the material. So, from that we can identify that this is iron platinum one from their lattice fringes secondly by doing energy dispersive x ray analysis on this part of the sample you can find out that this is iron platinum 1 is to 1. And this part we can find out that this is iron platinum 3 is to 1 ratio and they are 2 different types of materials this is a hard magnet. Because it has a high remanent field if you take pure iron platinum particles it is a hard magnet. If you take pure iron 3 platinum it is a soft magnet. And a combination of the 2, because in this particle which is probably around 15 is around 15 to 20 nanometers in this side and 15 to 20 nanometers in this side.

So, the whole particle is around 15 by 15 nanometer has got many such small regions which are different in their properties. So, this part will have a different property because it is F e 3 p t. And this part is a different property, because it is F e p t. So this is hard magnet type this is soft magnet type and together they are existing and what is the result. The result is whenever you have a combination of this permanent magnetic field like given by a hard magnet. And magnetization due to a soft magnet then you will get much larger magnetization as compared to traditional single phase materials. And why is that why do you get much higher magnetization in such composites, because they are interacting between each other by exchange coupling. So, when you have hard and soft particles within the same material you can have this kind of a magnetic exchange. And you can have much larger magnetization then the single phase materials and how was this kind of a composite made.

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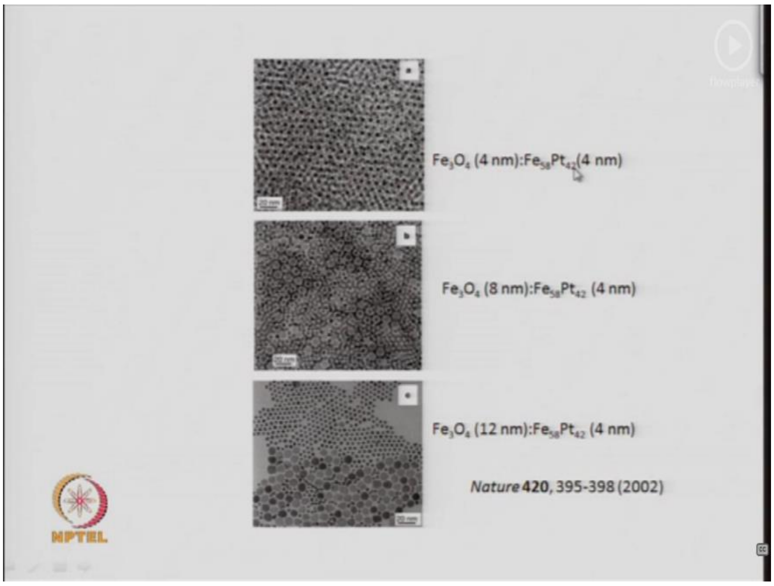

Fe_3O_4 (4 nm):$Fe_{58}Pt_{42}$(4 nm)

Fe_3O_4 (8 nm):$Fe_{58}Pt_{42}$ (4 nm)

Fe_3O_4 (12 nm):$Fe_{58}Pt_{42}$ (4 nm)

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What you do is you start with the mixture of iron oxide and iron platinum alloy so these are 4 nanometer or 8 nanometer 4 nanometer. You can mix them with different sized particles of iron platinum and iron oxide and then you anneal them. Now, you can see them differently these are particles of iron platinum alloy. The small particles 4 nanometers these large particles are iron oxide particles 12 nanometers. Of course, here you have 8 and 4. So, you can have different mixtures and once you anneal them that means you heat them. Then these form this kind of a composite having iron platinum and iron 3 platinum type of domains which are in the composite material. And this kind of nanocomposite magnets is more interesting because they are better than permanent magnets.

Because the soft and the hard components this, the hard iron platinum grain and the soft iron three platinum grain interact with through magnetic exchange and you get very good magnetization. So, these are some of the properties one can change when one talks of magnetic properties of nanomaterials. And one can do tremendous amount of applications using these nanocomposites or just nanoparticles covered with polymers in drug delivery in MRI contrast agents. And in other magnetic applications which we will do some more applications we will do in our next lecture. So, today we end the second lecture of our 3 lectures on magnetic properties of nanostructures. And this was the seventh lecture of module 4, we have 5 more lectures remaining one more lecture on magnetic properties which will be our next lecture.

Thank you very much.