

Physics of Functional Materials and Devices
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Lecture – 29, Week 7
Magnetism at nanoscale

Welcome to the final lecture of week 7. Till now we have been talking about magnetic materials in this Welcome to the week. We have seen that you have materials which are in bulk. So, we are talking about large size materials. But if you see the previous lectures in the previous weeks, we have also talked about that you can have transformations from bulk materials to small materials that is you can go from bulk to nanostructured materials. Now, a very logical question which can be asked is will the magnetic response of a material which had bulk structure be the same if it is reduced to nano sized.

We must therefore, try to see what is the magnetism in nanostructured materials. You will find that it is quite different and new concepts need to be formulated to explain the observation of magnetic behavior tuning when you go from bulk to nanostructures. Concepts like elongated grains. You also have to formulate new theoretical models to explain the observations.

The first model which was used to explain the observation of magnetic property variations in nanostructure materials was Stoner-Wohlfarth model. That is what we will see today and then we will see how you observe the phenomena of superparamagnetism in nanostructured materials and how these properties are then used in various applications. Now, for example, let us take an example of a strongest known permanent magnet. That is an alloy $\text{Nd}_2\text{Fe}_{14}\text{B}$. So, Neodim 2, Iron 14, Boron.

This is what we have seen which has a remnant magnetization of the order of 1.3 Tesla and coercive fields of the order of 1.2 T. And you will find that these properties can be tuned by tuning the size of the alloy particles. It has been seen that the coercive field decreases significantly when you take the particles below 40 nanometers whereas, the remnant magnetization increases.

So, remnant increases, coercive field decreases when you take the size of the particles below 40 nanometers. So, let us first see how can you fabricate these alloys. Let us take an example of a soft chemistry method to synthesize this alloy. It involves two steps. Why am I talking about synthesis protocol in today's lecture? Because you can then immediately get an idea how can you tune the size of the particles of this alloy.

You can change the reaction temperatures, you can change the parameters that is synthesis parameters and you can obtain various sizes of particles in this alloy. And then we will plot

two curves which will indicate to you why that statement was made that remnant and coercive fields change when you take the particles below 40 nanometers. So, we must understand the synthesis protocols very carefully. This is what is being stressed right from the beginning of this course. You will once again understand that if you really want to do good physics get the chemistry of materials right.

So, the step one which is there to obtain the final alloy is the preparation of the Nd iron boron oxide powder. Whereas, the second step involves the reductive annealing process of the synthesized oxide powders. So, then you remove the oxygen and you have the final alloy. So, you take the initial reactants the raw materials neodymium acetyl acetonates and iron acetyl acetonate and you mix it you mix them. Then degas at 120 degrees for 1 hour in vacuum.

So, you remove all the solvents or any kind of VOCs. Then you inject $(C_2H_5)_3 .nBH_3$ into the solution. Again you have taking the temperature to 300 degrees for 1 hour under argon gas. You will find that a precipitate can be obtained if you add hexane and ethanol mixture.

This precipitate can then be separated using centrifuge. What you will get is an oxide powder containing Nd iron boron. Next step would be what? Then you anneal it. Anneal means you heat the material at higher temperatures. If you talk in terms of metallurgy or materials engineering or ceramic engineering, then there are three terms.

One is calcination, second is sintering, third is annealing. Calcination is the temperature at which the reaction gets completed. Sintering is a process which is the densification of ceramics or you have densification of the material which is being prepared at high temperatures. So, sintering temperatures are higher than calcination temperatures. And annealing process is are the ones where you remove the water components in addition you also remove any preferred growth directions and then you get the final material.

In these if you say directive annealing process, this is basically what you are doing. You are having a reduction temperature of 800 degrees for 2 hours under argon and hydrogen gas leading to the production of alpha iron, neodymium oxide, iron 3 boron and neodymium boron oxide. Now, what you do? You mix it in a glove box and then heat it again at a higher temperatures for 2 hours. What you will get? You will get the removal of oxygen from the powders. You will have the powders, but some impurities also.

You wash it. So, you can wash it and then dry it. Finally, these two impurities will be removed and what you will get is the nanoparticles of neodymium iron boron alloy. Then you measure the hysteresis loop. Take the hysteresis loop. Just measure the hysteresis loop for alloys which have different size particles.

So, you make series of alloys of Nd-Fe-B and what you do? You may tune the temperature conditions so that you get different sized particles. So, you have different size particles.

Then you have a hysteresis loop. Plot the remnant magnetization as a function of the size of the particles in nanometers. You can clearly see that around 40 nanometers there is a clear change in the response characteristic of the material.

You can also plot the coercive field and what you will see that up to 40 nanometers there is a simple behavior, but beyond 40 nanometers the behavior is quite different and you have distinct change in the slope and the magnitude of the coercive fields and the remnant magnetization. This is simply because of size effect, but why should the size of the particles which are constituting an alloy impact the magnetic response? What have we seen till now? We have seen that if you have unfilled energy levels or the orbitals then you have the magnetic movement. It nowhere were we talking about the size of the domains as such. For example, we have seen Rn 26, what it had? It had 4 d levels which were unpaired and therefore, you had strong magnetic moment appearing in that. Were we talking about the particle size? No, but here you see particle size of the same material having the same electronic configuration for different elements is having a significant change in the response under a magnetic field.

And, you saw that in these some of these materials you could also get behaviors such as Superparamagnetism. Superparamagnetism means that in small size particles the total magnetic moment of the particles can be regarded as one giant magnetic moment composed of all individual magnetic moments of the atoms which form the nanoparticle. So, you had an M-H loop and a hysteresis loop was just like this. It was not like a paramagnetic material that it had a linear variation. It had the shape of a ferromagnetic material, but the hysteresis loop was not opening.

No opening of the hysteresis loop. Why is that happening? This was basically observed and you could see that in these kind of materials, the nanoparticles were reacting similar to a paramagnet, but with a one exception that the magnetic susceptibility was much larger and that led to the coining of the word super inferred front of para magnetism. So, you had a hysteresis loop which behave like a paramagnetic material in certain region, but you also had tendency which was similar to ferromagnetic material leading to much higher susceptibility and therefore, the convoluted graph was called as super para. Therefore, the convoluted graph was called as a graph or loop being denoted by a super para magnetic material. This is what you can understand much more by looking at the three curves.

The brown one shows the super para magnetic curve, the blue shows the ferromagnetic curve and the green one shows the para magnetic nature. So, you can clearly see that super para magnetism is associated with high saturation magnetization, no remnant magnetization and zero coercivity. What is happening then? If you compare these things that means super para magnet would have under zero magnetic field domain moments that would couple as a ferromagnet does, but it does not because of the small size known as the Poultry effect. Under magnetic field, the domains find each other and now it generates a

moment comparable to a magnetic moment. So, this is the schematic representation of the super paramagnetic material which has different alignment of the domains.

So, if there are no applied magnetic field, the nanoparticles are randomly aligned. If you have an applied magnetic field, then the small domains all align in the same direction simulating a condition similar to the FM material. And once you switch off the magnetic field, these domains again randomize. Why? Because these are small domains you have thermal agitation associated with them. So, they have $k_{\beta}T$, they are small in size and therefore, the magnitude of $k_{\beta}T$ becomes larger and then they can again randomize.

Whereas, in a ferromagnetic material the FM material what you see that even if you switch off the magnetic field, the randomization is much lower and you still get a net magnetic moment. Using these materials property, they are being used in large number of applications such as targeted drug delivery, magnetic data storage, you have gene delivery, you have the magnetic resonance imaging and even biosensing. To explain this phenomena, a concept is required and that is called elongated grains. For example, let us try to see. So, let us start with bulk material.

If you have a bulk material, what do you see? You have domains not of same size, but there is a net magnetic moment in one of the directions in this, it would be probably in this direction. Now, I reduce the size of the particles. Now, if I reduce this size, you obviously will have smaller size grains. Now, if there are these are smaller size grains, if I zoom this picture, so these are smaller size grains. What will happen? The exchange interaction or the impact of the neighbour would be much higher because the size of the two is much smaller.

So, they will interact much more and one of them will supersede over the other. For example, let us say this domain supersedes over the other two. So, what will you get? You will get an alignment, these two will flip and you will get the flipping in this direction. Now, you have three small domains which have flipped in one direction. What is happening to this one? You see they are it was in the upward direction.

Now, the net magnetic moment which would be acting on the particle which is nearer to this group of particles will make it flip once again in this direction. And slowly what you will get? You will get if I zoom it further, you will have in this small particle all these small grains all aligned in one direction. Now, can you differentiate between this alignment and this alignment? No, you cannot. If they are all magnetic moments coming in because of particles which are of similar type. So, if you have alignment which are in the same direction, you call it as a grain or a you have a domain.

So, this is one domain, this is the other domain or the grain. Now, if you have all the particles which are in the same direction although the particles are different, but the net

magnetic moment of all of them have been forced to flip in one of the directions because they are small in size and the impact of the neighbour was much higher and slowly it started forcing the realignment throughout the structure. And if all of them are looking at same then what is it looking at? You are seeing a grain which is much larger, but it also composes of smaller grains, but all the grains are aligned in the same direction and that is what the concept of elongated grains means. So, you have a large size grain which composes of smaller grains, but all of them have been forced to flip in the same direction and therefore, you get a large size grain and it was called as elongated grain. Using this concept of elongated grain, the Stoner Wolworth model was proposed which said that if you have such kind of smaller elongated grains then they have only two stable states in classical picture and which are both favourable.

That means, you can have up and down spins and you have nearly the same values of the potential well for these two concepts. But when you go to the quantum mechanical picture for the nanoparticles that is the elongated grain concept then you see the dotted line shows that the energy curve that is the potential energy curve gets modified and one of the alignment becomes preferable over the other and you can clearly see that this one in this case the up direction is much more stable than the down direction because the system will always like to minimize the energy and hence you can clearly see from the dotted curve that the field which is shown for the up alignment is going to be much more preferred because the energy will be lower and you will have the whole grain aligning in the up direction. So, when you go from the classical picture that is the bulk size particles to nano size particles the energy curve gets modified and you have one of the directions which is preferred and that leads to the change in the magnetic properties of the materials. If you want to see the agitation of these particles as a function of thermal activation this is given by an Arrhenius process that is given as that if you have a probability of reorientation that will be proportional to $e^{-\frac{E}{k_{\beta}T}}$ where E is the height of the energy barrier. So, you have the height of the energy barrier which the system will have to obtain to flip from this region to the other minima.

So, this is the height of the barrier $k_{\beta}T$ is the thermal energy. So, if the system has to flip what it should have it must have energy much more than $k_{\beta}T$ otherwise the moment $k_{\beta}T$ is larger it would be making the system go back to the original state. The particle can we know in quantum mechanics that particles can also flip its orientation by a much lower probability process but that will occur when you consider the quantum mechanical tunneling processes that some of the electrons can jump over the potential step function even if the energy of the incident electron is much lower. But in addition to that you can also have the flipping of the orientation if $k_{\beta}T$ is much less than the barrier height. So, if you reduce the value of $k_{\beta}T$ then you can have flipping and if a magnetic field is applied

obviously the shape would change and you can flip from up direction to the down direction because of the applied magnetic field.

But as long as these factors are not there you will find that the elongated grain will not randomize and you will start getting a behavior like a ferromagnetic material or a particle and so you will have transformation from let us say a paramagnetic material transforming its properties to a ferrimagnetic or ferromagnetic like behavior when you reduce the size and now I hope you understand why the remnant and coercive fields were changing when you reduce the size of Nd-Fe-B alloy particles. But this model has some limitations and it has been modified many times and if you go to research publications many more modifications are being proposed in this fundamental model which was initially proposed. The problem which people found out with this model that it actually overestimates the strength of the coercive field because it only allows one path of transformation that you will have one path of transformation from one minima to the other. But in reality there can be many more reasons by which transformations can take place. It also assumes that the magnetic energy of the particles depends on its volume.

But when particles are of the order of let us say 10 nanometers, 5 nanometers, 2 nanometers, 6 nanometers most of the particles are on the surface. So, this means that the property the very belief that the prop the volume would be the driving force is a claim which is not justified because now you will have the surface energy and the surface properties which will come into picture and this will become very prominent in nano materials. Therefore, the dynamical behavior of very small magnetic particles is much more complicated than directed by the S-W model. But this model can be used to at least understand the transformation in the magnetic response of materials when they are transformed from bulk to nano sized. And now you have a very clear understanding why new magnetic materials are being reported by researchers as well as industries for various applications.

What are they basically doing? They have the same material, but they are making them in different sizes and as they obtain materials with different sizes the response of the material changes and then you can choose the application of these materials depending upon the response characteristic of that material. So, very clearly I have tried to explain today the magnetism at nano scale. I have kept the description brief because this is slightly at a higher level topic, but a very interesting topic and if you are interested in the field of magnetism this is where the future lies. We have also seen the dynamical behavior of small size particles and how theoretical models have been used to explain the behavior in nano sized magnetic particles. You can use these books to understand more about these topics and this brings us to the end of lectures of week 7 and I thank you for attending lecture 4 of week 7. Thank you very much.