Nanomaterials and their Properties
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Lecture - 25
Magnetic Properties of Nanomaterials (II)

So, we are going to start the lecture number 25, which will be an extension of the last lecture 24. And this will be on Magnetic Properties of Nanomaterials. As you know, we have discussed about electrical properties, thermal properties. Magnetic properties are very important for nanomaterial, because many of these materials are actually in applications due to very outstanding properties they show or exhibit.

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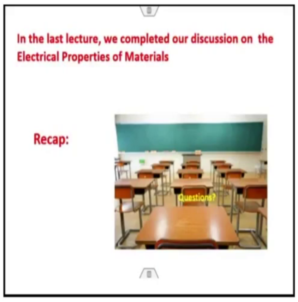

In the last lecture, we completed our discussion on the Electrical Properties of Materials

Recap:

Questions?

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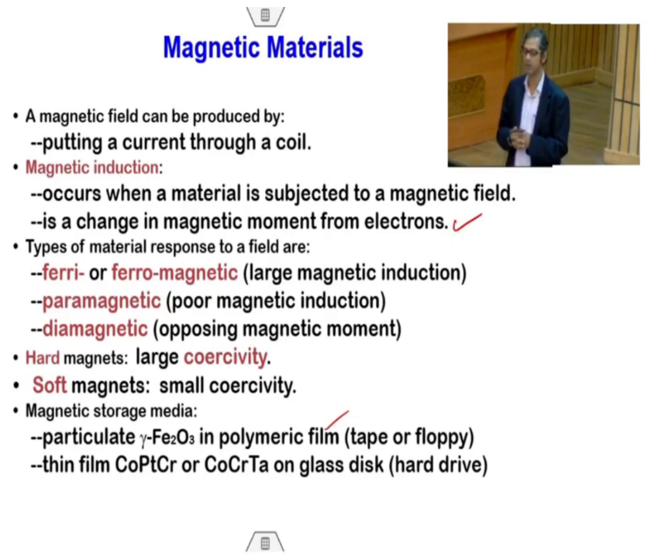

Magnetic Materials

- A magnetic field can be produced by:
  --putting a current through a coil.
- Magnetic induction:
  --occurs when a material is subjected to a magnetic field.
  --is a change in magnetic moment from electrons.
- Types of material response to a field are:
  --ferri- or ferro-magnetic (large magnetic induction)
  --paramagnetic (poor magnetic induction)
  --diamagnetic (opposing magnetic moment)
- Hard magnets: large coercivity.
- Soft magnets: small coercivity.
- Magnetic storage media:
  --particulate γ-Fe_2O_3 in polymeric film (tape or floppy)
  --thin film CoPtCr or CoCrTa on glass disk (hard drive)

So, in the last lecture, we have discussed about mostly magnetic properties of materials, not in details of magnetic properties of nanomaterials. And today, we are going to talk about some aspects of the effect of size on the magnetic properties. But before that let me just have some recap. I will always try to say this question to you that please when watching a lecture video on your computer or a mobile or tab, do write your questions. It is not possible that you will understand everything in this lecture.

So, better write it down and whenever I am going to discuss with you these lectures then it is easy for you to ask questions. Otherwise, you have to formulate the questions at the time. So, please keep in mind that these lectures are very specific. So, this will not be a complete in sense of starting from magnetic material and then talking about what is the effect of size. So, we are actually having limited number of lectures for each of these topics. So, we have to be very careful about what we are speaking.

So, as such magnetic materials are basically affected by the magnetic field, right. So, magnetic field can be produced simply by passing current through a coil, we know that. And you know if you pass current through the coil it produces a magnetic field. Now, if I keep a material inside the magnetic field, this will lead to induction of magnetic effects, ok. So, that means, there will be change in terms of magnetic moments from the electrons. That is what happens.

So, depending on that as such all the materials in the world can be divide into several categories of magnetic materials, like you can have diamagnetic materials which oppose the magnetic moments. In fact, you know this all the materials in the world inherently shows some diamagnetic properties.

So, therefore, origin of diamagnetic is basically, diamagnetism is basically found in the orbital motion of electrons of the atoms acting like a tiny electrical current loop and that can produce the magnetic fields. So, it in an external magnetic field the current loops will align in a way to oppose the applied magnetic field. So, therefore, diamagnetic materials are exposed to a force pushing them out of the magnetic field. That is why they oppose the magnetic movement, ok. These are not important for our discussions, but for the complete, sake of completeness we need to talk about it.

Then, the next category material is paramagnetic materials. They are significantly stronger than a diamagnetic and it produces magnetization in the direction of the applied field. So, in a paramagnetic material, the atoms can act as a tiny magnets or dipoles basically, that may be oriented by an external magnetic field.

So, situation paramagnetic material in absence of electromagnetic field is what I have discussed in the earlier lecture. Important materials are basically ferro and ferrimagnetic materials, and they show large magnetic induction effects. And paramagnetic materials basically, they have unpaired electron spins of the atoms and that can interact with each other and this can lead to long nudge phenomenon called the lining update of the dipoles in the material and therefore, there is a pretty strong magnetic moments.

So, depending on that you can have hard or soft magnets. Hard magnets will have a high coercivity, soft magnets will have small coercivity. And then we can also we have also discussed about in the last lecture about the storage of magnetic, storage media like you know the magnetite or thin films of cobalt platinum chromium or cobalt chromium tantalum, just which is used in the glassy on a hard drive actually. So, that is something which is very important.

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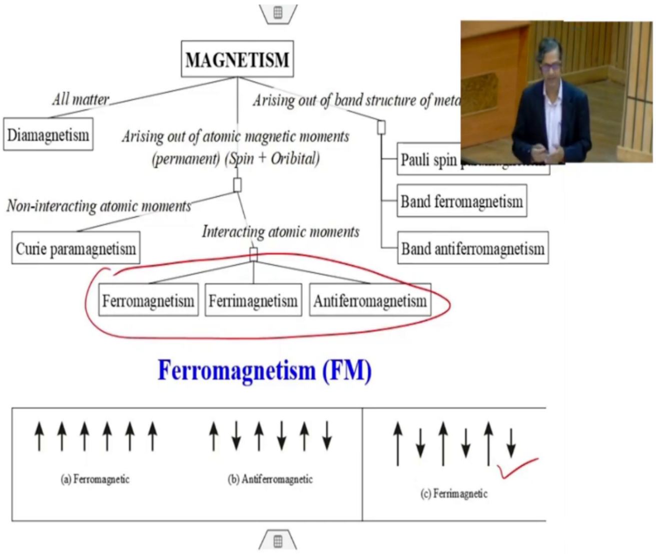

MAGNETISM

All matter

Diamagnetism

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

Arising out of band structure of meta

Pauli spin

Band ferromagnetism

Band antiferromagnetism

Non-interacting atomic moments

Curie paramagnetism

Interacting atomic moments

Ferromagnetism

Ferrimagnetism

Antiferromagnetism

Ferromagnetism (FM)

So, in a nutshell, this slide shows you everything all the material in the world shows diamagnetic behavior. And, but some of them show you know paramagnetic behavior which are much stronger. The important for us for this consider is the ferromagnetic or ferrimagnetic or antiferromagnetic materials.

Ferromagnetism can be of the 3 different types. In case of ferromagnetism, as I already told the unpaired electrons or what is called the unpaired electron spins of an atom can align by application of the magnetic field, and they can interact. And if they align equal strength of magnetic spins aligned, then you call a ferromagnetic.

And sometimes it may happen that you can have equal and opposite spins aligned and so, therefore, net magnetism is 0, but the material has spins available. You can also have a situation in which you have uneven values of the spins, opposite spins, that is what is shown in case of ferrimagnetism. And so, therefore, this leads to a certain kind of a finite magnetic moments.

So, most important things are basically ferromagnetic which shows the strong magnetic coupling effects, ok. So, that is what will be our discussion in case of nanomaterials.

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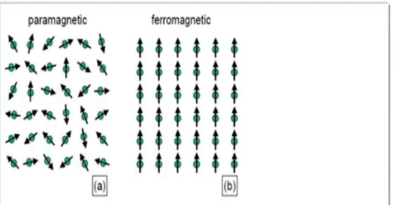

Figure 8.1 Distribution of molecular magnetic moments in different materials. (a) Paramagnetic material: the elementary magnetic moments are distributed arbitrarily. (b) Ferromagnetic material: the elementary magnetic dipoles are coupled and aligned in parallel.

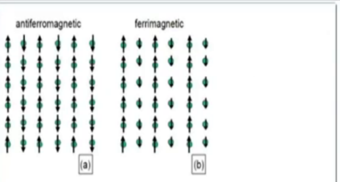

Figure 8.4 Magnetic materials exhibiting two antiparallel spin lattices. (a) Antiferromagnetic material. Here, the magnetic moments of the two antiparallel spin lattices cancel out such that the net magnetic moment of the material is nil. (b) Ferrimagnetic material. Here, the magnetic moments of the two antiparallel sublattices do not [illegible]ut, such that a net magnetic moment remains.

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So, these are the electronics spins are shown here. The parametric materials you see here the distribution of the magnetic moments are you know randomly or arbitrarily. But in case of ferromagnetic material, they are actually coupled and they aligned in a parallel with a respect to the magnetic field, ok. And in case of anti-ferromagnetism, they are having as we just discussed you have a spins which are parallel, but opposite. So, they cancel out.

And in case of ferrimagnetic material, the values of the spins, ok magnetic moments of the two antiparallel (Refer Time: 06:58) do not match. So, there is a resultant magnetic moment present and it can be useful for various applications. So, there are 3 types of this ferromagnetic material. Diamagnetic material I have not shown because they their moments will be very weak and completely random.

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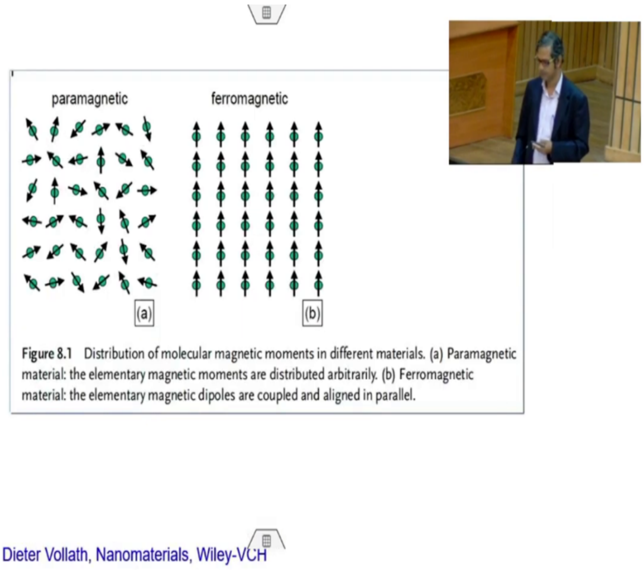

Figure 8.1 Distribution of molecular magnetic moments in different materials. (a) Paramagnetic material: the elementary magnetic moments are distributed arbitrarily. (b) Ferromagnetic material: the elementary magnetic dipoles are coupled and aligned in parallel.

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So, this is again same picture shown in a broader sense so, that you can see very clearly how the molecular magnetic moments exist in a paramagnetic and ferromagnetic materials.

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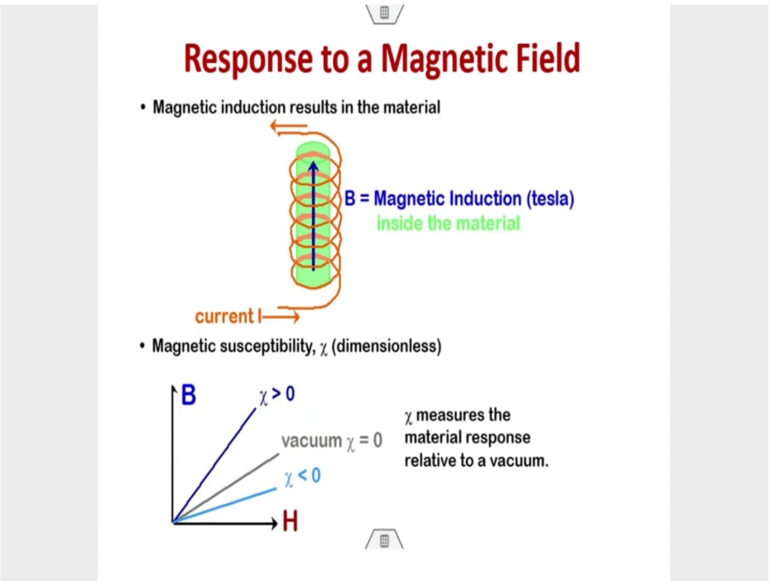

Response to a Magnetic Field

- Magnetic induction results in the material

- Magnetic susceptibility, χ (dimensionless)

χ measures the material response relative to a vacuum.

Well, this is something which I have shown you. So, this can be quantized in terms of magnetic susceptibility. What is that, thing can be quantized? The magnetic induction. The moment you pass current through a coil it produces a magnetic field. Then, if I put a material inside this, the magnetic field effect will be filled in terms of induction.

So, that can be quantizing using a quantity called magnetic susceptibility or χ. So, normally χ can be 3 types, 0, more than 1, or more than 0, or less than 0. So, χ actually measures the material response related to the vacuum. For the vacuum value of chi is 0. So, for greater than 0, that means, the magnetic induction is very strong like in case of ferromagnetic ferrimagnetic materials, less than 0 like in paramagnetic materials, the effect will be very weak not seen much.

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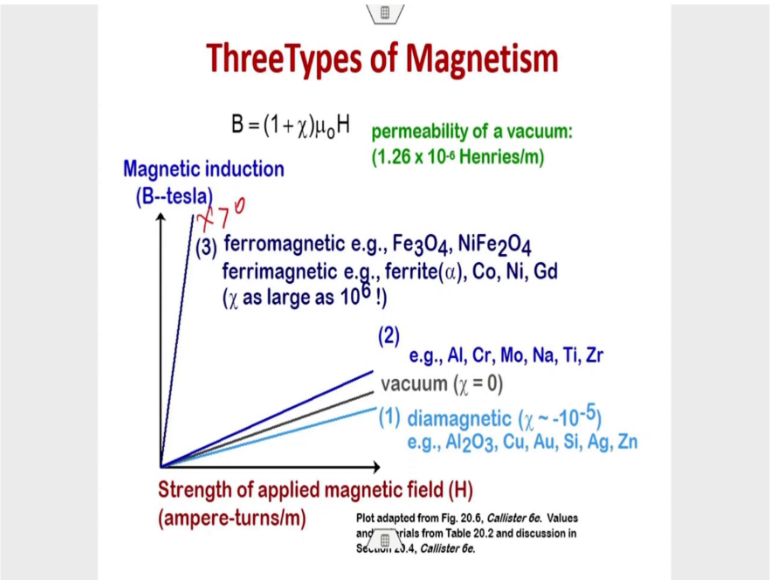

ThreeTypes of Magnetism

$B = (1+\chi)\mu_0 H$

permeability of a vacuum: (1.26 x 10^{-6} Henries/m)

Plot adapted from Fig. 20.6, *Callister 6e.* Values and [illegible]rials from Table 20.2 and discussion in Se[illegible].4, *Callister 6e.*

So, therefore, we can actually calculate we can actually write an equation of induction in terms of applied field and the permeability. So, that is equal to $(1 + \chi)\mu_0 H$, μ_0 is the permeability of the vacuum that is nothing but 1.26×10^{-6} henrys per meter.

So, if you plot the magnetic induction versus magnetic field B versus H, then you have a value of chi which is very large and more than 0 for ferromagnetic material like magnetite nickel ferrite, or ferrimagnetic material like ferrite, cobalt, nickel, gadolinium, and value can be as high as 10^6. Then, you can also have situations, where the χ is 0 that is nothing effect on that; if χ is 0, then $B = \mu_0 H$, ok.

What I will be applying, magnetic field that will multiply to the permeability of the vacuum, and then you know my induction is very small, because permeability of vacuum is already 10^{-6}, right. So, you need to apply a huge magnetic field to induce certain kind of a magnetization or magnetic induction in the material. So, aluminum, chromium, moly, sodium, titanium, zirconium and a vacuum all of them, so, chi will be 0 there is not much induction possible in this material.

And lastly, for diamagnetic materials, the χ is negative and very small. So, therefore, even if you apply huge magnetic field nothing is going to happen because spins are not cannot be aligned. This is very easily available. You can read from book of Callister.

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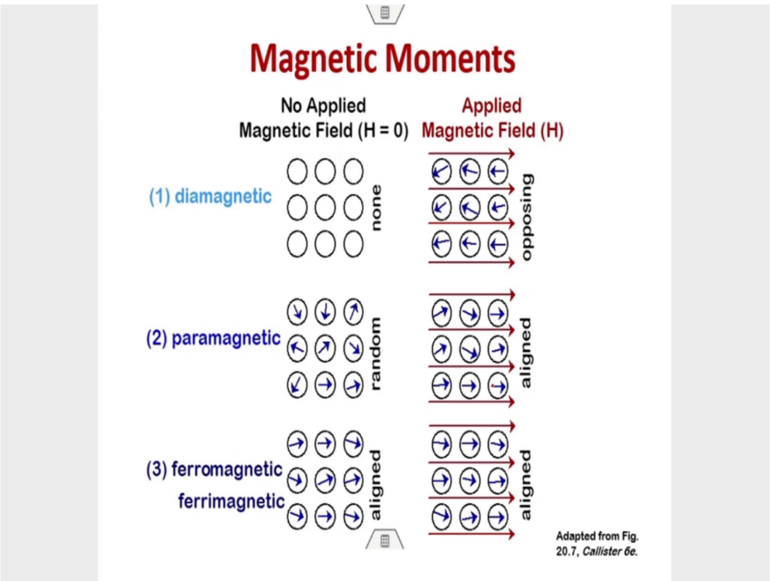

Magnetic Moments

No Applied Magnetic Field (H = 0)

Applied Magnetic Field (H)

(1) diamagnetic

none

opposing

(2) paramagnetic

random

aligned

(3) ferromagnetic ferrimagnetic

aligned

aligned

Adapted from Fig. 20.7, *Callister 6e.*

So, in terms of magnetic moments diamagnetic materials, you see when you do not have no magnetic field there is no effect. And when you apply magnetic field there is opposing effects, ok. Opposing effects of the magnetic field comes, that is why these you know the most of these materials which show diamagnetic behavior they oppose magnetic lines of forces.

And the best example is the magnets, which shows such a kind of behavior where this is the magnetic lines of forces and the spins are aligned opposite to these lines of forces. So, therefore, they cancel out, ok. But paramagnetic without any magnetic fields, there is some random arrangements. So, net magnetic moment is 0. But the moment you have applied magnetic field there is some management possible, ok for the spins or the magnetization moments, and these will align, but not properly with respect to the field.

So, therefore, effect will not be strong. For the ferro paramagnetic material applied magnetic field will make sure that these spins are aligned to the field directions. So, that the magnetization effect is strong, ok. Not only that there is a long range you know effect on the alignment of the spins also.

What I mean to say by that is that if you apply magnetic field the spins will interact with themselves, there is exchange coupling happens between these spins, and they will allow them to align in a particular direction and then strengthen the induction effects. That is something which is very common.

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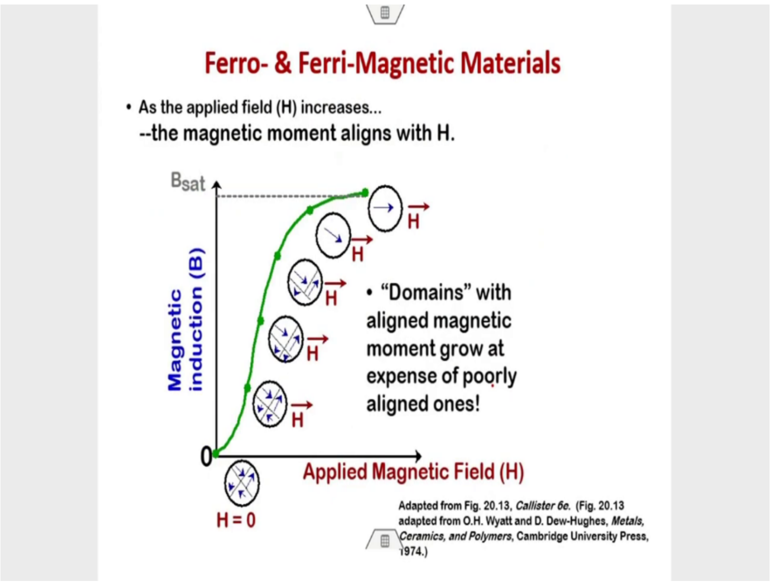

Ferro- & Ferri-Magnetic Materials

- As the applied field (H) increases...
  --the magnetic moment aligns with H.

- "Domains" with aligned magnetic moment grow at expense of poorly aligned ones!

Adapted from Fig. 20.13, *Callister 6e.* (Fig. 20.13 adapted from O.H. Wyatt and D. Dew-Hughes, *Metals, Ceramics, and Polymers*, Cambridge University Press, 1974.)

So, that is all. So, therefore, if I want to look at a detailed manner, the ferro and ferrimagnetic materials effect of magnetic field, so this is something which is all of you have studied, and nothing need to be told again and again. And then, instead of saying that, if I apply magnetic field and slowly the magnetic induction increases and then it reaches a maximum value while it saturates.

So, that is something which is mainly because of the alignments of the domains in the materials, ok. Domains are what? Domains are actually magnetic you know regions where the magnetic spins are aligned in a particular direction. So, in a material with a multigrain structure you can have domains aligned in different directions.

So, as you apply magnetic field, so this field strength will make the magnetic domains to be aligned along with the direction of the field, ok and finally, when all the magnetic moments align to the directional field, the magnetization gets or magnetic interaction gets saturated. So, there is no further increase in magnetic induction possible.

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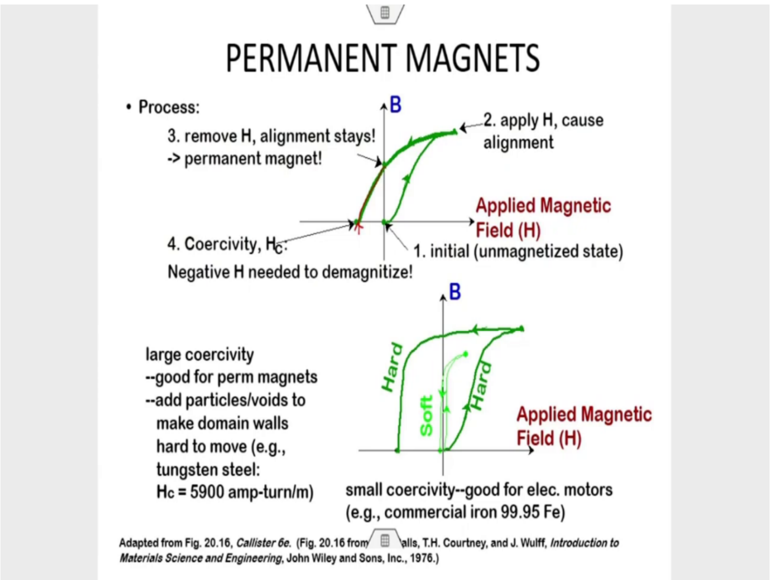

PERMANENT MAGNETS

- Process:

3. remove H, alignment stays!
-> permanent magnet!

2. apply H, cause alignment

4. Coercivity, H_C:
Negative H needed to demagnitize!

1. initial (unmagnetized state)

large coercivity
--good for perm magnets
--add particles/voids to make domain walls hard to move (e.g., tungsten steel: H_c = 5900 amp-turn/m)

small coercivity--good for elec. motors (e.g., commercial iron 99.95 Fe)

Adapted from Fig. 20.16, *Callister 6e.* (Fig. 20.16 from alls, T.H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, John Wiley and Sons, Inc., 1976.)

So, then if you reverse the magnetic field or reduce the magnetic field rather or decrease the magnetic field, so what will happen is that at a certain value of magnetic field, ok, there will be some amount of when you have 0 magnetic field. That means, when you remove the magnetic field completely, still there will be some amount of magnetic induction or magnetization will remain in the material, so, that means, magnetic memory will become not only completely lost, ok.

So, that is what is known as a remanent magnetism or remanence. Now if you keep on doing the same thing, again you go to negative directions like this way, ok it become negative. So, you need to have a certain value of negative magnetic field to make the magnetization 0, ok B

= 0. So, B is 0 with certain value of Hc. So, that is what is known as a coercivity. So, negative H is needed to demagnetize, ok.

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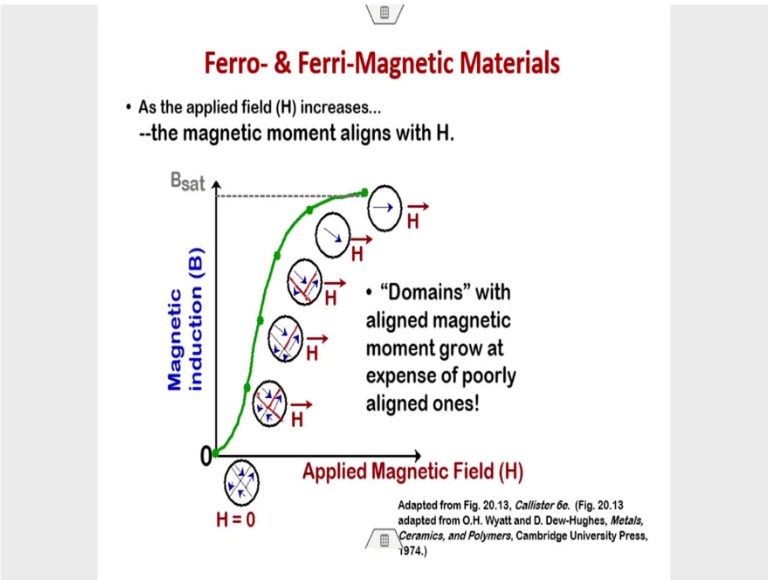

Ferro- & Ferri-Magnetic Materials

- As the applied field (H) increases...
  --the magnetic moment aligns with H.

- "Domains" with aligned magnetic moment grow at expense of poorly aligned ones!

Adapted from Fig. 20.13, *Callister 6e.* (Fig. 20.13 adapted from O.H. Wyatt and D. Dew-Hughes, *Metals, Ceramics, and Polymers*, Cambridge University Press, 1974.)

So, you understand, first thing you are doing is you are magnetizing, by applying magnetic field to the ferromagnetic or ferrimagnetic material. So, this way a magnetic moment aligns with a H, ok or the applied magnetic field. So, in a multi-grain material the magnetic moments will be aligned in different directions. So, the field strength makes sure that these magnetic moments align in only in the direction of the field. So, then you have a high magnetization.

But when all the magnetic moments align in the direction of the field, no further increase of magnetic induction is possible so, then magnetic induction reaches a saturation point. Followed by if I decrease this magnetic field, so I could see for a, you know when I remove the magnetic field completely still the magnetic moments or magnetization does not go to 0. This is remanent magnetism remains in the material, like a memory effect, and that is what is called as remanence.

Then, you can further do that keep on going down in the negative directions, so you will reach a value of Hc for which the B will become 0. So, there is a negative H required to demagnetize the material. Demagnetization means you apply the magnetic field in such way that all the spins align in opposite directions to the magnetic field. So, then there is no magnetic induction.

Well, so, therefore, there are two important parameters you learned, one is the remanence, other one is the coercivity. These two you should remember. So, for a soft magnetic material or a hard magnetic material, important aspect of this loop which is getting complete, ok.

So, if you magnetize and demagnetize, you are going to have a hysteresis loop, right. So, I am not going to discuss. This is taught in class two or may be with the first year of physics. So, if you magnetize and demagnetize you are going to have a hysteresis loop because the paths will not follow the same. So, therefore, there will be a magnetic loop or the hysteresis loop created.

So, this loop will be different for a soft and hard magnetic material. For a soft magnetic material this loop will be thin and small. For the hard magnetic material loop will be thick and big. So, what does the loop tells? The loop tells you the product, ok, B into H that is nothing but magnetic energy.

So, in a hard magnetic material the product will be very high, that is what you need. If you want to use a permanent magnet you need to have a very high value of B and H multiplication. For a soft magnetic material like a switching operation, you need a very small value of $B \times H$, $B \times H$, ok.

So, for small coercivity is good for electric motors you understand that, right, because you are switching on and switching off. So, every time you switching on and switching off if the area is large, you are losing lot of energy. So, this energy will comes in terms of heat. So, that you do not want. You do not want motor to be heated, right. You want motor to run or rotate. So, this is the things you should know very well.

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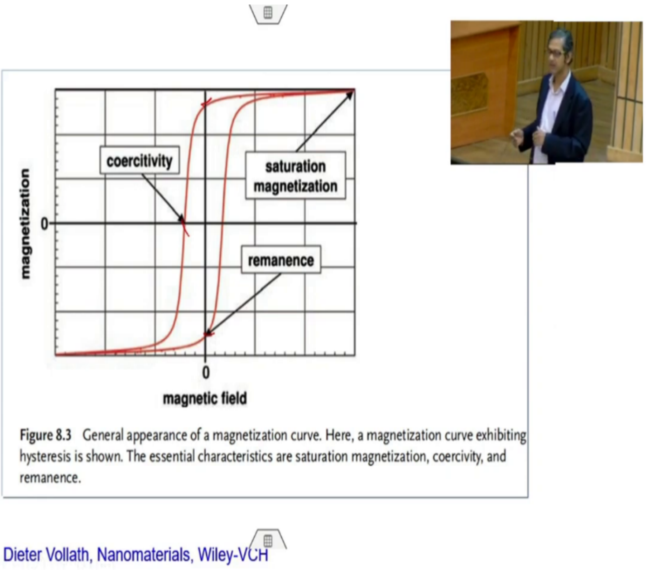

Figure 8.3 General appearance of a magnetization curve. Here, a magnetization curve exhibiting hysteresis is shown. The essential characteristics are saturation magnetization, coercivity, and remanence.

Dieter Vollath, Nanomaterials, Wiley-VCH

So, this is shown in this picture taken from Dieter Vollath's chapter number you know 8. As you can see here that this is the remanent magnetism here or here. So, when field is 0, some kind of a magnetic induction remains in the material. That is what is called remanence. Coercivity is the negative field required demagnetized, and saturation magnetization is the highest possible magnetization which can be reached upon application magnetic field, ok. So, remember these terms and how they look like.

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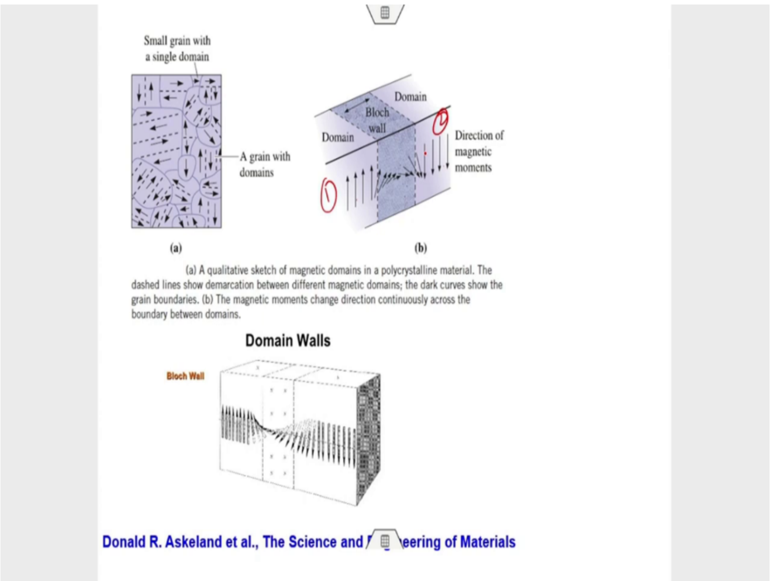

(a) A qualitative sketch of magnetic domains in a polycrystalline material. The dashed lines show demarcation between different magnetic domains; the dark curves show the grain boundaries. (b) The magnetic moments change direction continuously across the boundary between domains.

Domain Walls

Donald R. Askeland et al., The Science and eering of Materials

Well, so you know now the question is important; in the ferromagnetic material, why such a kind of things happens like this one, ok. Why such a kind of things, when field is 0 how these domain structure align? So, in a ferromagnetic material you should understand that magnetic energy because magnetic reasons, ok, further way, in ferromagnetic materials what is known as a dipole or these spin dipoles, they can be represented by unpaired electrons or rather unpaired electron spins of an atom, they interact.

They actually, that is why they have a long range you know alignment of the spin is possible. And this leads to a longing ordering of the phenomenon which can cause lineup of the dipoles parallel to the magnetic field, right. So, but for energetic reasons, you cannot have you know in a bulk material all the spin align to the field, right, directions, because that will be energetically very costly, ok.

You have many other things limited like grain boundaries, you can have you know solid atoms, you can have impurities. So, those will you know making forcing everybody all the spins align with direction of the field in a material is very expensive and costly. So, therefore, size range where this parallel magnetization occurs in ferromagnetic material is always limited, ok. That has to be limited otherwise it will lead too it will be very analytically costly.

And these ranges are actually known as magnetic domains. That means, each of these areas you see here you can see each of there is a one domain. So, you create a domain, separate from the other domain by a wall and these walls are called as a domain walls. As you see here this is domain wall here, ok. There is a domain wall. If I have a domain wall here, so they are these domains are separated by walls or domain walls, ok. The situation is something like that.

Now, I do not know whether I have a picture, yes. This is what is shown here you can see in a big grain like that there are alignment of the spins parallel in different directions, ok. And they are separated by these dotted lines. These are called walls, ok domain walls. And these walls are called Bloch walls because this was first described by Bloch, ok scientist name called Bloch.

Now the question is very simple here, so if I have a domain 1, if I have domain 2, the spins in the domain 1 and domain 2 are opposite, you can see. So, when you want to you know the changeover of spin happens through this Bloch wall a very systematic way. That is what I was telling.

So, if you want all the spins to be aligned properly and then it is analytically very costly, so, this alignment of this magnetic moments, can happen across this Bloch wall through a reorientation of the spin. So, it was like this, and slowly, slowly, slowly, the spins reorient to the Bloch wall, and at this another domain 2, this is the domain 1, suppose this is domain 1, this is domain 2, and domain 2 they are aligned in opposite directions and therefore, these walls are called Bloch walls.

So, that means, each of these domains are separate from other one by a Bloch wall. So, Bloch wall has certain amount of energy. You might be you must be asking me this question. Sir, why not align all of them in one go? Well, that will be very costly because then you have to have a very long-range effect across the whole sample, and that requires the field to be very high or extremely high which is impossible to achieve even.

And not only that because of the magnetic anisotropic effect, crystalline anisotropic effect, it is not possible, each grain has a different crystallographic orientation. So, that is also not possible. Because magnetic spins will always like to align in the direction which is easy magnetization directions like. If you think of a pure iron, and you think of 3 important directions of pure iron, ok and one is the 100 directions, other one is 110 directions, other one is 111 directions, ok. The 3 important directions, right.

Now, do you think the magnetic, magnetization, magnetization effect or you know all of them are same, on you know all the directions it will have same effect? Answer is no. In fact, 1 o is easy based magnetic magnetization direction compared to the other two directions. That means, if a grain is oriented along 1 o directions, it is easy to magnetize by applying field, then it is with oriented along 110 or 111. That is something which is very well known.

So, this is a quantitative qualitative sketch of magnetic domains in a polycrystalline material which can happen. And you know these dashed lines which is shown here, they are actually demarcation between different magnetic domains. The dark curves are basically grain boundaries. So, in a polycrystalline material, this is what will happen. Your grain boundaries, and within their grains, you will have different domain walls present.

So, now this is something which is available in the books of Donald Askeland and others, Science and Engineering of Materials. You can also see it internet available. So, this Bloch walls actually in reality thickness of each Bloch wall is about 100 lattice constant or even more and Bloch walls may connect magnetic domains to orientation difference of 90 or 180 degrees. And size of domain and the width of the Bloch walls are always determined by the thermodynamical aspects, which I am not discussing here.

So, direction of magnetization within the grain is changed by moving the Bloch walls. You can change them; you can move the Bloch walls then you can actually; that means what? You can actually change the problem magnetic field you can change this Bloch wall positions then you can change this directional magnetization way.

So, if you move this Bloch wall all these spins will align parallel to this domain 01. That is what happens in a real material. So, as you keep on increasing the strength of the magnetic field, that is what shown here. What is happening? Each of these spins are slowly orienting along the field by moving the Bloch walls, ok, by movement of the Bloch walls. So, that is something which is perceived to be happening in materials. Am I clear?

So, it is important to note that existence of magnetic domains and Bloch walls make it easier to change the direction of magnetization. That is why this concept is useful. So, most magnetic materials the specimen will remain magnetized to some extent after the (Refer Time: 23:28) magnetic field. And this is what is I already discussed about remanence.

And this tendency of material, remember the magnetic field magnetic history is what is known as hysteresis loop, correct. So, therefore, let me see whether I have a picture, ok no. So, therefore, upon knowing all these aspects, now we can move what is the effect of these things on the nano materials, ok. So, what do you think will happen?

So, therefore, you know the effect of size will be mostly on coercivity and the remanence and also on some saturation magnetizations, right. There will be some additional effects also which we will discuss much later, but as you understand the effect will be mostly on remanence and the coercivity. So, how does it happen?

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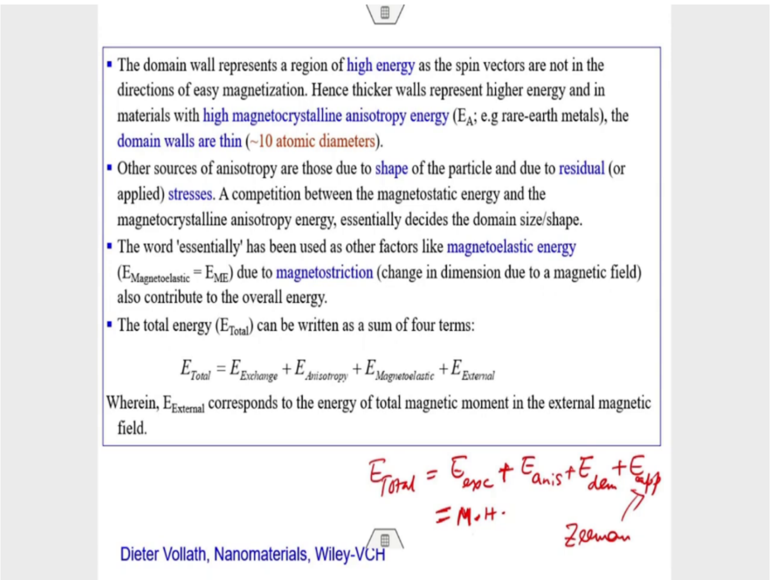

- The domain wall represents a region of high energy as the spin vectors are not in the directions of easy magnetization. Hence thicker walls represent higher energy and in materials with high magnetocrystalline anisotropy energy (E_A; e.g rare-earth metals), the domain walls are thin (~10 atomic diameters).
- Other sources of anisotropy are those due to shape of the particle and due to residual (or applied) stresses. A competition between the magnetostatic energy and the magnetocrystalline anisotropy energy, essentially decides the domain size/shape.
- The word 'essentially' has been used as other factors like magnetoelastic energy ($E_{Magnetoelastic} = E_{ME}$) due to magnetostriction (change in dimension due to a magnetic field) also contribute to the overall energy.
- The total energy (E_{Total}) can be written as a sum of four terms:

$$E_{Total} = E_{Exchange} + E_{Anisotropy} + E_{Magnetoelastic} + E_{External}$$

Wherein, $E_{External}$ corresponds to the energy of total magnetic moment in the external magnetic field.

$$E_{Total} = E_{exc} + E_{anis} + E_{dem} + E_{app}$$

$= M \cdot H \cdot$

Zeeman

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So, domains walls represent a region of high energy, right as the spin vectors are not in the direction of the easy magnetization. Hence thicker wall represent higher energy and material with high magneto crystalline anisotropy, ok has the domain walls very thin, ok. What is the meaning of magneto crystalline anisotropy? That is what I discussed already, ok.

So, every material crystal material has different directions of orientations, right. If you consider pure iron, it has 3 important directions of orientations. So, magnetization effect on each of these directions are not same. So, therefore, the crystalline orientations, dictates the magnetic induction.

If I apply magnetic field on a semi crystal of iron, which is oriented along 100 directions and another single crystal is oriented along 100 110 directions and third one along 111 directions the one which is along 10 directions will magnetize fast and easily, ok. But on the other hand, one which is oriented along 111 directions will be most difficult to magnetize although pure iron at room temperatures is ferromagnetic, right.

So, this effect of crystalline directions is what is known as a crystalline anisotropy. That means, in different direction has different values of magnetizations, ok, energy required. So, that has cost. That is what is known as a magneto crystalline anisotropic energy. And in case of rare earth material this is pretty high than hexagonal crystal structure, in fact, this is much higher therefore, domain walls are thinner.

So, as you know domain walls actually has sufficient energy, ok. So, a thicker domain walls means more energy, thinner domain walls means higher lower energy, right. So, in order to keep the domain wall energy smaller, the for rare earth materials the thin domain walls are created because otherwise you know because of high magneto crystalline anisotropy energy it will be very high.

Other source of anisotropy will be shape of the particles, ok that is something which is understandable, shape of the nanoparticle, shape of the any material, grains actually and also these residual stresses, ok. So, competition between this mangnetocrystalline and magnetostatic energy, and the magnetocrystalline anisotropy energy, essentially basically decides the domain size and shape. What is magnetostatic energy?

The energy which is making the spin align, ok. So, what essentially is you know used here because like magnetic elastic energy due to magnetostriction everything, also contribute to the overall energy. But magnetostriction is only possible for certain category materials.

So, hence important aspect for you to know is the total energy of the system can be written as a exchange energy, anisotropic energy, magnetoelastic energy and the external energy. External energy means, the total magnetic moment in the external magnetic field; that means, when you apply magnetic field, what is the external energy.

In the book of you know Michael Ashby, and other thinks they have written the same equation in terms of like this, E total is equal to E exchange plus E anisotropic plus E demagnetization plus E applied that is external, ok. So, what is exchange? Exchange energy is what? Exchange energy is the if energy is related to basically and this is equal to written as M.H, ok, M is the magnetization vector and H is the external applied magnetic field. So, if you apply magnetic field, ok then you can get effect on the material in terms of energy like this way. Please remember that.

Now, the tendency of magnetism vectors to align in one direction is what is gives the external, exchange energy and that is this quantum mechanical, ok because this tells you interaction about between atomic magnetic moments and this is what is lead to tendency for the magnetization vectors to align along the field directions, ok. That is something which is very important.

If the magnetization magnetic moment is very high, very large, the resulting magnetic field can drive the nearest neighbors to align in the same directions. You got it. So, you have many many magnetic spins there in the material. So, magnetic energy or magnetic moment is very high or sufficiently large, the magnetic field can then drive the nearest neighbors to align directions.

And this is only possible when external energy is much higher than the thermal energy because you know thermal energy which is in terms of kt can always leads to destabilization of the spins, ok. But only when the external energy is much higher than this thermal energy if you have applied the magnetic field, then only you can align these spins in the particular direction to the field, correct.

Second term which is nothing, but anisotropic energy is basically tendency to align parallel to specific crystallographic axis that is what I told you. So 100, 110 or 111 in pure iron, and they are all called easy or difficult axis of magnetizations. So, therefore, some magnetic materials will exhibit low anisotropic energy, hence hard magnetic material will use so high anisotropic energy.

That is obvious some magnetic materials can be demagnetized magnetized very easily. That is why they have a very small BH loop, right. But hard magnetic material it is not easy to do that. Thus, see something which is very important. So, therefore, both exchange energy and anisotropic energy will try to order the spins to align parallel to the magnetic field, right.

But in case of third one which is nothing but a diamagnetic magnetization energy, ok related to the magnetic field dipole character or spin, and this can lead to this is what leads to magnetics domains actually. Just now we discussed few minutes ago. Thus, for a microscopic ferromagnetic material all the magnetic moments are aligned in the magnetic directions. Although magnetism vectors of different domains are not parallel.

All the magnetic spins will align in the direction of the field, but magnetization vectors of the different domains will not be parallel to each other. Each domain is magnetized to saturation with the moments and typically align in the easy directions but depending on these ratios of the anisotropic demagnetization energy, this can be open or closed structures, ok. So, that means, depending on this energy, the domain walls can be open or closed.

And the last one is the applied energy which is nothing but a Zeeman energy. This is also known as a Zeeman energy. Zeeman means, the same Zeeman who discovered many things Zeeman energy, ok Zeeman as one n not two n, am I clear one n. So, however, you know, so therefore, this is something which is you need to know and that is the effect of these on these aspects. So, let us now discuss what will affect of size on this material.

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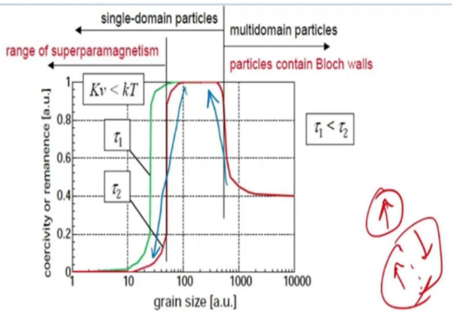

Figure 8.5 Dependency of coercivity or remanence of magnetic materials as a function of grain size. While Bloch walls subdivide the grains, coercivity and remanence are small. In single-domain particles without Bloch walls, coercivity and remanence increase dramatically; this is the particle size range for magnetic data storage. At smaller particle sizes, coercivity and remanence rapidly approach zero; this is the range of superparamagnetic materials. The grain size of this reduction depends on the time constant of the measurement.

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So, important aspect of effect of size in material is the, this coercivity or remanence as I told you. So, let us talk about effect of size as a function of coercivity or remanence. So, you can see here its grain size, that is suppose you start with you know, this is something like 100 nanometers, this is 10 nanometers, 1 nanometer, this is 1000 nanometers and this is 10000 nanometers, ok.

So, for bulk material, where grain size is more than 100 nanometers, ok, so, something like let us start from 10000, you can see the particle size has no effect on the coercivity. That is obvious because you have multi domain particles, and particles contains Bloch walls. So, therefore, if you apply magnetic field slowly the magnetic spins align to the field and then you can reach a saturation. And then, your you know field required to demagnetize the materials and its coercivity, is also remain constant.

But you know below a certain size, it seems as soon as the single domain particles; below certain size means when this particle size will become smaller then you can have a single domain particle. That means what? You can do away with this Bloch walls, ok. Particles are small, so that they can have a single wall, ok.

The single wall means, the single say single domain means only one domain. Each particle has a single domain. There is no suppose in a big particle become two domains and domain walls, that is will not be there in a single domain particle. In that case, the this, their magnetic coercivity or remanence will increase very rapidly and reach a very high value, correct. So, therefore, this is something which is very important.

So, if you consider the dependency as a function of particle size, [FL] large magnetic particles will be always subdivided by the Bloch walls into the magnetic domains. And the size of Bloch walls and magnetic domains are controlled energetically. So, therefore, remanence and coercivity will be largely independent of the size. They will not be effect on many sides. That is what you see here. There is no effect on many sides.

On the other hand, decrease the particle size, it leads to side energies when particle will consist only a single domain, there will be no Bloch walls. So, particles become smaller and smaller, so therefore, it one-part small particle become a single domain particle. So, as the Bloch walls are not there, so therefore, coercivity remanence will increase drastically. That is what you see here, coercivity and remanence increasing drastically, right.

Sorry, I should change my color of this thing, so that you can see very, you can see very easily. So, this is what happens, it increases very rapidly you can see that. And these are your particles are mostly employed in for magnetic data storage, correct. But if you further decrease the particle something else happens.

So, if you further decrease the particle remanence and coercivity start dropping. That is what you see this is dropping further drop. And in fact, it reaches a very small value, 0 almost, when particle size become very small. And these are the range of particles which are called superparamagnetic particles, ok. Paramagnetic we have seen, ok. This is called superparamagnetic particles.

So, this size critical size where it will happen will be decided by the time constant what is written as a τ_1 or τ_2 or time τ_m, basically measuring methods how we are measuring it, ok. Every method has a time constant, right whether we are measuring this VSM or we are measuring which VSM speed, that are different times constant there. So, this changeover will depend on the time constant.

So, what is the reason for this phenomenon? Let us first discuss that. Magnetic properties of isolate and domain particles or a group of such interactive particles, can be observed here like this, ok.

(Refer Slide Time: 35:32)

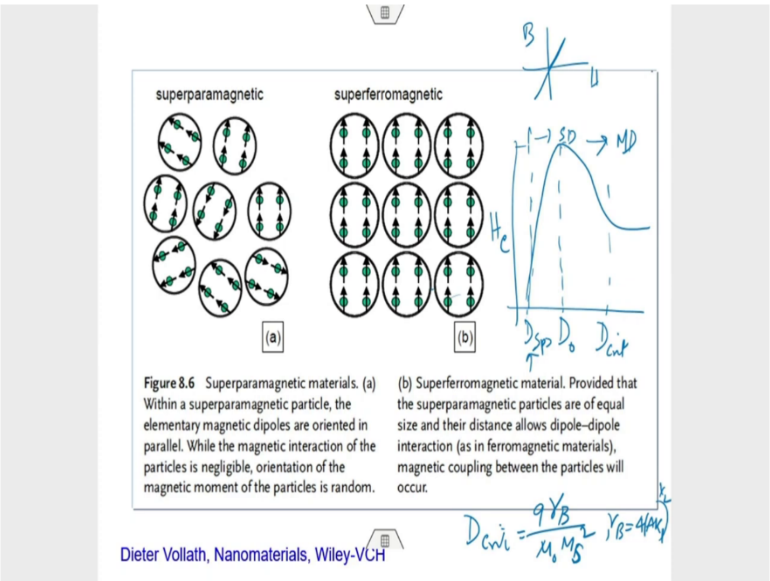

Figure 8.6 Superparamagnetic materials. (a) Within a superparamagnetic particle, the elementary magnetic dipoles are oriented in parallel. While the magnetic interaction of the particles is negligible, orientation of the magnetic moment of the particles is random. (b) Superferromagnetic material. Provided that the superparamagnetic particles are of equal size and their distance allows dipole–dipole interaction (as in ferromagnetic materials), magnetic coupling between the particles will occur.

$D_{cri} = \frac{9\gamma_B}{\mu_0 M_S^2}$, $\gamma_B = 4(AK_1)^{1/2}$

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So, super magnetic particles, within super magnetic particles elementary magnetic dipoles oriented parallel, ok. You can see here. They are parallel, correct. While the magnetic interaction particle, magnetic interaction of the particles seems negligible, so orientation of the particle remain random. What is the meaning of that?

Within these super magnetic particles, the magnetic dipoles are parallel to each other. But from one to other particle there is no interaction. So, therefore, the orientations from one particle to the other particle become random, ok. And this happens because of the thermal energy, ok kt terms. So, that makes this orientation random. And because of that, there is no exchange among the particles from one particle other particles.

So, all the spins in different particles do not align in one direction to show a strong magnetic effect. And that is what happens to a paramagnetic material, ok. So, that is the main reason for these as to happens. One reason for this is that materials retain the orientation of their magnetization, but because of magnetic anisotropic.

The most dramatic way this is observed when the thermal energy of the particle is greater than the anisotropic energy, correct. I am not going back again to anisotropic energy. I have already explained to you. So, therefore, you know you will have a point in which thermal instability will occur. Thermal instability means thermal energy will misalign the spin of the particles.

And however, in case of interacting super paramagnet, like on the right side, interaction super paramagnet additional phenomena will also allow absorb. So, super paramagnetic particles of equal size and the distance allows dipole-dipole interaction; that means, these dipoles will interact among the particles, and this can lead to a very high magnetic effect or the magnetization actually.

So, therefore, you understand, the difference between superparamagnetic and super ferromagnetic material. Paramagnetic means random or ferromagnetic means they are proper are aligned properly, ok. That is what is. And the word super means the effect is strong, that is what word super is used, ok. Am I clear? So, this is something which is very important for you to know. So, I will explain again, so that you do not forget.

These two books were providing a good example of that. You know, so as you know the for nanocrystalline ferromagnetic material, important thing is that interaction energy among this exchange energy, interaction among the exchange energy and super energy and magnitude energy happens.

For very small particles the exchange forces are dominant due to the strong coupling effect. So, therefore, it can lead to all the spin and (Refer Time: 38:13) against to align, superseding effect of anisotropic energy or diamagnetic energy. But you know there is a critical size, ok. That is what is shown here. This is what is plotted in the last diagram. I am plotting again a C versus this diagram.

And this will be like this, ok. And you see here this is the multi-domain particles and this is the single domain particles, S D. And this is therefore, $D_{critical}$ below which the coercivity increases rapidly, and this the single one particle itself all the spin aligned and this is what is the super Para magnetism below which this situation will happen. Figure 8.6 from Vollath, you know Dieter Vollath's book.

So, this is something which is important. And this $D_{critical}$ is can be given as 9, do not try to derive it, this is derived I am just giving you the value, ok. So, where gamma B is equal to $4\left(AK_1\right)^{1/2}$, where A is a constant, and this is basically wall energy, A is a constant, energy constant, and it is known as exchange stiffness and K_1 is an anisotropic constant, ok. (Refer Time: 39:42), so anyways its permittivity and this free space and emerges as saturation magnetization it is M_S not M_B, ok.

So, important aspect to know; it basically what does it tells you? It tells you the effect of magneto crystalline anisotropy. Magneto crystalline anisotropy will try to align the spins properly, and thermal energy will try to disturb these spins, ok. That is what happens. So, if the particles or grain size is below the critical diameter, the material is single domain and basically for cobalt this is about 70 nanometers, for iron is 50 nanometers.

The particular grain size becomes significantly smaller. There is few nanometers, then critical diameter, then magnetization is likely to become unstable, and then loss of magnetization occurs because of thermal fluctuation. That is what is these superparamagnetic what is written here. At this position that is what will happen thermal effects will superset you know the crystalline anisotropy effect.

Crystalline anisotropy effect will allow the spins to align in particular directions, ok as easy magnetic direction. Thermal energy will make them you know random. So, when these two are balanced out that is why the superparamagnetic starts. And below this value everything will be completely random, and you have a 0 value of coercivity. That is what is known as super paramagnetic behavior.

Well, other than that there are other effects like you know magnetic properties also affected by the scale, ok. What is that? Well, you know coercivity of a paramagnetic material is obviously, increase or decreases with grain size, and reaches this maximum value within a size range of critical diameter, ok. Coercivity is reaching a maximum value you can see here that value is at a certain value of D, ok or D_0, correct.

So, if the particle size is further decrease, the coercivity decreases rapidly, magnetization become unstable and within this design hysteresis can be completely gone. You will not see any hysteresis in the superparamagnetic, ok. Why? Because there is no remanence magnetism. So, why you will see hysteresis loop? You will see a single line like that. So, what you will see is very simple like this, if I plot B versus H in superparamagnetic, you will see like that. You will not see any hysteresis loop because there is no coercivity.

So, for the you know amorphous iron nickel cobalt, which having you know amorphous mostly nanocrystalline, not amorphous about 10 to 15 grain size practically shows no hysteresis loop, ok. So, technically point of view, if the idea is to fabricate a strong magnet, strong paramagnetic, permanent magnet, coercive force should be as higher as possible.

Therefore, these things are it cannot be used, but they can be used for nice switching operations because they have no hysteresis loop, so no loss of energy, right. You understand that. So, you would like to have a superparamagnetic effect to utilize in case of switches. In addition to coercivity magnetization reversible also is strongly affected by the size. Magnetization reversible means, if see if we are changing the magnetic field, the magnetization reversal will happen, the spins will align in the direction of spin field.

So, if you reverse the field, this is what should happen. So, within a specific range of this you know diameters typically greater than the super paramagnetic diameter, but lower than the critical diameter, the exchange interaction energy sufficiently strong to keep the spins aligned during the reversal process.

Above this range of diameters, but still below the critical diameter is the critical, ok. The process of magnetization reversible become very incoherent involving switching of the small volumes of material within the magneto nano particles of nano grains. The size of magnetic nano particles or the grains also has effect basically, very has strong effect on the saturation magnetization, magnetizing, magnetization basically increases below a particle size, ok. So, that is something which is also important.

So, nonetheless what you need to know is very importantly this curve, which is shown here also, the effect of particle size on the coercivity and the remanence magnetism. This is something which is very important for you to remember. So, by this we have almost done on the magnetic properties of nanomaterials. And there will be some small discussion may require which I will do in the next class.

And upon that I am going to discuss about optical properties of material that will conclude all the properties for you, because I need to spend some lectures on characterization of the material. So, therefore, I will not wind up all that, I will not take all the lectures on properties. I need to keep some lectures free. So, if you have any questions, we will discuss further.

Thank you.