

**Materials Chemistry**  
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**Module - 4**  
**Lecture - 4**  
**Magnetic Materials III and Related Phenomena**

In the previous lecture, we have looked at some of the broad classifications on magnetic materials. And we also looked at a clear divide between two sets of magnetic materials; one is soft and other one is hard magnetic materials. And we looked at some example of soft magnetic materials like perm alloy, alnico and samarium cobalt and also some ferrites which shows soft magnetic properties.

And we also looked at a broad classification on permanent magnets, and what are the criteria for a permanent magnet and broad classification. And we also looked at some of the alloys which are used, mostly alloys and borides show this permanent magnet property. And also we looked at some of the ceramics materials which show this permanent magnet property. In today's lecture I am going to deal further on some of the examples of magnetic materials, specifically related to magnetic recording media.

And lastly I am going to touch on some magnetic phenomena, which always comes out when we specially deal with ferromagnetic materials, when we think of paramagnetic diamagnetic materials we do not see, so much of a manifestation as much as we deal with ferromagnetism. So, in ferromagnetic materials there are certain issues that we need to have in mind specially when we deal at low temperature; therefore, those issues which are specifically important for ferromagnetic materials, I would like to discuss in the later part of the lecture.

So, let us quickly go through some of the examples that we saw in the previous lecture on magnetic materials, we looked at the properties of permanent magnets. The classification based on metal alloys or intermetallic compounds, especially those with borides, and then a ceramic ferrite which is called barium hexaferrite. Now, the numbers that we usually look for in permanent magnets in those of coercivity and the energy product.

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TABLE W17.3 Properties of Permanent-Magnet Materials

Material	$(BH)_{max}$ (kJ/m <sup>3</sup> ) <sup>a</sup>	$B_r$ (T)	$H_c^b$ (kA/m)	$T_C$ (K)
<u>Transition Metal Alloys</u>				
Alnico 5 <sup>c</sup> : (51Fe, 14Ni, BAL, 24Co, 3Cu)	35.8	1.25	43.8	1120
<u>Steels<sup>d</sup></u>				
Cobalt steel (35Co, 0.7C, 4Cr, 5W, bal. Fe)	7.7	0.95	19.1	
Tungsten steel (5W, 0.3Mn, 0.7C, bal. Fe)	2.5	1.03	5.6	
<u>Rare Earth-Transition Metal Intermetallic Compounds</u>				
Nd-Fe-B <sup>e</sup>	200-380	1.0-1.4	700-1000	580
SmCo <sup>f</sup>	130-180	0.8-0.9	600-670	990
SmCo <sub>2</sub> Fe <sub>2</sub> Cu <sub>2</sub> Zr <sub>2</sub> <sup>g</sup>	200-240	0.95-1.15	600-900	1070
<u>Ceramics</u>				
BaO·6Fe <sub>2</sub> O <sub>3</sub> <sup>h</sup>	28	0.4	250	720

The Physics and chemistry of materials by J. J. Gordon and F. W. Smith

Energy product is defined as BH max and this is expressed in kilojoules or in mega oersted. And the more the energy product better is the behavior has a permanent magnet, and as you would see here the intermetallics usually have a larger proportion of energy product compared to alloys. And we also have a substantial, degree of contribution from a ferrite which is a ceramic compound, a ceramic compounds although they show this property, but the fabrication is a intricate issue because, it is often brittle.

Therefore, you cannot sinter it, but this particular compound barium hexaferrite you can achieve up to 95 percent theoretical density. Therefore, it is possible to use this as a permanent magnet, not only it is use as a permanent magnet is reported, but barium hexaferrite is also used in, thin film recording media we will see that shortly. So, when we look at the permanent magnet applications, we needs to bear in mind these two parameters and the more the energy product better it is application.

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TABLE W11.2 Technologically Important Magnetic Materials

Material	Magnetically Hard or Soft	Applications
<b>Metals</b>		
Steels (alloyed with W, Cr, etc.)	Hard	Permanent magnets
Fe particles (oxide-coated)	Hard	Magnetic recording media
Fe, Ni, ... alloys:	Soft	Electromagnetic devices,
78 Permalloy, Fe <sub>80</sub> Ni <sub>20</sub>		magnetic recording heads,
Supermalloy,		precision instruments
Fe <sub>80</sub> Ni <sub>20</sub> Mn <sub>10</sub>		
Invar, Fe <sub>65</sub> Ni <sub>35</sub>		
Mumetal: Fe <sub>75</sub> Ni <sub>20</sub> Co <sub>5</sub>	Soft	Magnetic shielding,
		transformer cores
Co alloys (CoCr, etc.)	Hard	Magnetic recording media
Fe <sub>3</sub> -Si <sub>2</sub>	Soft	Transformer cores
Fe-Si-Al alloys: Sendust, <sup>®</sup>	Soft	Magnetic recording heads
85Fe10Si5Al		
Alnico alloys: Alnico 5, <sup>®</sup>	Hard	Permanent magnets
51Fe14Ni8Al2Co3Cu		
Amorphous rare-earth-transition metal alloys	Soft	Magneto-optical recording media
Amorphous Fe-B-Si-C alloys	Soft	Magnetostrictive elements
<b>Intermetallic compounds</b>		
SmCo <sub>5</sub> and Sm <sub>2</sub> Co <sub>17</sub>	Hard	Permanent magnets
Nd <sub>2</sub> Fe <sub>14</sub> B	Hard	Permanent magnets
ThFe <sub>3</sub> and (Th <sub>1-x</sub> Dy <sub>x</sub> ) <sub>3</sub> Fe <sub>3</sub> (Terfenol-D)	Soft	Magnetostrictive elements
<b>Ceramic compounds</b>		
γ-Fe <sub>2</sub> O <sub>3</sub>	Hard	Magnetic recording media
CrO <sub>2</sub>	Hard	Magnetic recording media
Mn <sub>0.8</sub> Zn <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	Soft	Magnetic recording heads
Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub> (YIG)	Soft	Microwave technology
BaO·6Fe <sub>2</sub> O <sub>3</sub> or SrO·6Fe <sub>2</sub> O <sub>3</sub>	Hard	Permanent magnets
(BaFe <sub>12</sub> O <sub>22</sub> , SrFe <sub>12</sub> O <sub>22</sub> )	Hard	magnetic recording media

Composition given in weight percent.

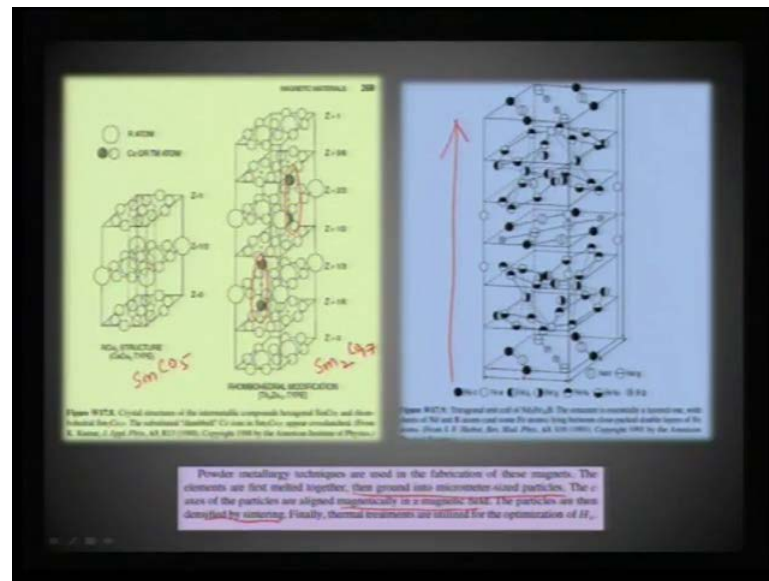
We will quickly go back to all the compounds that we have seen, and the range of applications that these magnetic materials hold, these are a wide variety of alloys that we can see. And alloy processing itself it is the challenge and therefore, there are a lot of chemistry routes, material chemistry route that is adopted to prepare magnetic materials. Specially, those of amorphous alloys because, amorphous alloys is very difficult to prepare by conventional metallurgical means because when you make alloy using conventional melting technique, you usually crystallize that alloy or they are crystalline in nature.

But, amorphous alloys have to be suddenly quenched. Therefore, the bottom up approach is usually favored for making this material, one of the most important route is sonochemistry which we have seen in one of the lectures in module one. And then we need to understand in perspective that ceramic compounds mainly those, which are iron based compounds, find use in applications as you would see here, gamma Fe<sub>2</sub>O<sub>3</sub> and CrO<sub>2</sub> both are simple oxides, but they actually hold the magnetic recording media. And even now this hold the market, although we have several other candidates there.

But, when we think of tape material, still gamma Fe<sub>2</sub>O<sub>3</sub> and CrO<sub>2</sub> hold potential and this is multibillion dollar industry, which can never be compromised or substituted by any other material. Therefore, we will study little bit about these two oxides in this lecture. And then we have seen yesterday, how by changing the zinc ferrite either

substituting with manganese or nickel, you can change the resistivity by orders, and this is also a soft material which is used in magnetic recording. Today, I will also mention little bit about Y i g which is a garnet, and hexaferrite which is used in several other applications, like microwave technology, permanent magnets and magnetic recording media.

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If you look at this samarium cobalt, which is a very popular alloy you see this is a very tricky or a very complex structure. Although they crystallize in hexagonal symmetry, this your samarium cobalt compound and this is samarium to cobalt 17, and these are very highly ordered alloys. And if you look at this samarium cobalt 5, it is exactly the base material for this samarium cobalt 17, except for some of the samarium atoms are replaced by this sort of dumbbell shaped copper cobalt, cobalt dimer.

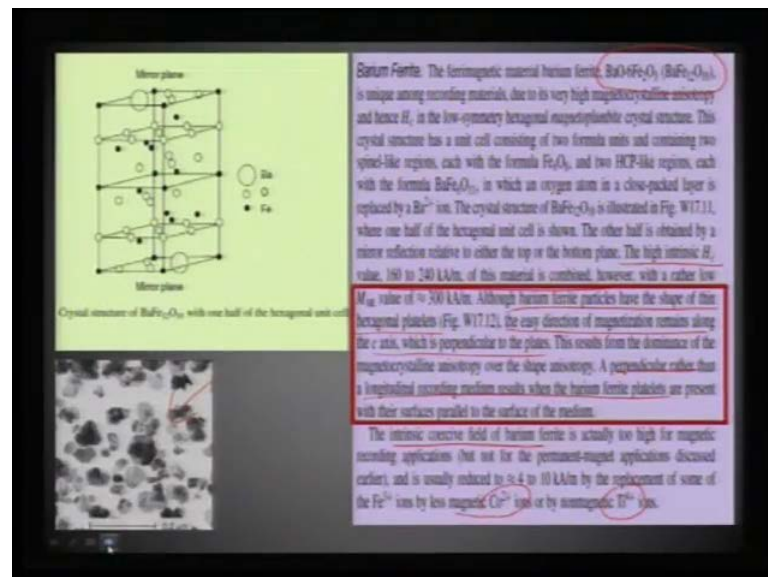
So, this is a very intricate alloy that one has to engineer to prepare it carefully. So, it is the case for neodymium iron boride where you can see, the structure is quite complex one with the tetragonal unit cell. Now, preparing these compounds is a materials challenge and that is where materials chemistry is also a valued component, most of these compounds are usually prepared by powder metallurgy. And they are melted, and when they are melted they are ground into micrometer size particles.

And once you get the preferred dimension, then these are actually oriented magnetically by a external magnetic field. And then they are densified by further sintering. So, this is a

very intricate procedure to get these permanent magnets, it is not a simple grinding and heating, but it involves a careful orientation of these grains along a particular axis, mainly the magnetic field is applied along the c axis.

So, that these are elongated particles along a preferred axis, and as you would see from the magnetic behavior, they have in all these magnets they have a preferred easy access of magnetization, meaning it cannot be randomly magnetized only in a preferred direction you can magnetize it. Therefore, preparation of these materials becomes very, very important and challenging.

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This is a ceramic ferrite or a ceramic magnet, which is called barium hexaferrite. Barium hexaferrite is named such way because, it is solid solution of barium oxide and six formula units of  $Fe_2O_3$ , you can take this and grind it to get a single phase like this. But, normally to prepare a single phase material of barium hexaferrite is very, very difficult therefore, soft chemistry routes have been adopted, very much to engineer this compound. What makes this particular compound interesting is that it has a very high intrinsic coercivity, of the order of 160 to 240 kilo amps per meter.

So, because, of this very high coercivity this is a very preferred compound for permanent magnetic materials. However, when we try to look at the morphology if you look at the morphology of this barium hexaferrite, these are hexagonal platelet and not necessarily the desired shape for recording media. But, what happens is the easy access of

magnetization actually remains along the, perpendicular direction to the plane of the surface.

As a result they usually exhibit a perpendicular anisotropy, particles may be platelet type, but the orientation of the magnetization will be perpendicular to the platelet morphology. As a result this is usually used in perpendicular recording media, not only that one hassle is there in using this for recording media, as a memory storage material, but the intrinsic coercivity is a problem because, such a high magnitude is not decide for magnetic recording.

So, if you want to use this for permanent magnet you look for high coercivity, when you want to use the same material for recording, you need to tailor down the coercivity. How do you do that, usually we substitute the iron atoms with little bit of cobalt or titanium, immediately the coercivity comes down. So, with that you can still use this for a recoding purpose or for making a thin film recording media, and the point that we need to bear in mind is because, of the perpendicular anisotropy this is one of the most preferred material, which is not exhibited in any of the other soft ferrites, although they are used for course, in several electrical applications. This is the only compound which is used for magnetic recording, because of it is perpendicular anisotropy, so that why this stands off as a most preferred material compared to some of the alloys.

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**MAGNETIC STORAGE**

- Information is stored by magnetizing material.
- **Head can...**
  - apply magnetic field  $H$  & align domains (i.e., magnetize the medium).
  - detect a change in the magnetization of the medium.
- **Two media types:**
  - **Particulate:** needle-shaped  $\text{Fe}_2\text{O}_3$   $\uparrow$  mag. moment along axis. (tape, floppy)
  - **Thin film:**  $\text{CoPtCr}$  or  $\text{CoCrTa}$  alloy. Domains are  $\sim 10\text{-}30\text{nm}$ ! (hard drive)

*Handwritten notes:* "Head - write" with an arrow pointing to the recording head diagram; "CoO<sub>2</sub>" written next to the particulate media diagram.

*Adapted from Fig. 20.19, Callister 6e. (Fig. 20.19 courtesy P. Rayner and R.L. Head, IBM Corporation.)*

*Adapted from Fig. 20.20(a), Callister 6e. (Fig. 20.20(a) from M.E. Kim, S. Choudhury, and K.E. Johnson, J. Appl. Phys., Vol. 74 (7), p. 4646, 1993.)*

Chapter 20-9

We will little bit more into discussion on magnetic storage, when we think about magnetic storage and applications of these magnetic materials, we need to understand in perceptive there are two things. One is the material that is used for storing the memory magnetic memory, and the other one is the material that is used for reading the magnetic information both are important. And to read the material that is stored, you need a magnetic material and to store you need a magnetic material.

So, in this the materials chemistry again plays a very important role and as you see, one of the important component in magnetic storage is the read head. There are several ways that you can do that, one is in one configuration the same material can write, in another configuration the material can read or it can do only one job. But, today the new generation computers are storage devices, usually have a head which is capable of writing as well as reading. So, these are popularly known as a read and write heads.

So, read write heads are also specially designed based on new generation magnetic materials. So, this is to do with the read head, which is currently used in most of our recording applications, and the other one is the material that is used for storage, if you look at the storage media there are two things that are prevalent now, we are in the age where we are using pen drives. And few years back, we were using CD and we were using floppy disk.

The floppy disk actually has a tape material compared to the CD, so that was the transformation between a particulate magnetic media, and thin film magnetic media. So, that was a clear device between this floppy disk and the CD ROMS, once the CD's came then the next question was, how much I can condense this CD's into a smaller devices that is how the iPod came, and the pen derives came. So, when we think about magnetic materials in all these applications, you have two sets of two generations of material which are used.

But, nevertheless when we think about the entertainment industry, it is all actually stored in tapes in high quality tapes. So, the material that is used for recording media is usually alpha or sorry gamma  $\text{Fe}_2\text{O}_3$ , which is a low temperature form of iron oxide, this has a very particular specific manifestation or it has a very preferred orientation, where it can prove effective for magnetic media. And if you are thinking about a thin film magnetic

recording media, then we look for alloys and the most preferred one is cobalt platinum chromium alloy or cobalt chromium tantalum alloy.

So, what do you see as a hard disk is nothing, but it is material that is made out of alloy what do you see, as a tape material is nothing. But, one which is made either of gamma Fe<sub>2</sub>O<sub>3</sub> or another popular one is CrO<sub>2</sub> which is also a good tape material. So, a particulate type and thin film type are the two generation storage materials.

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This is a cassette which I fondly like to remember because, if you have got exposed to any of the tape recorder, which is no more available now in market. Tape recorders usually had a option, to say whether it is CrO<sub>2</sub> tape because, for CrO<sub>2</sub> tape the way the read head will read or scan the tape will have a different sensitivity compared to gamma Fe<sub>2</sub>O<sub>3</sub> based tape materials. So, this is a cassette which is a CrO<sub>2</sub> cassette it is called CrO<sub>2</sub> 90 minute version cassette.

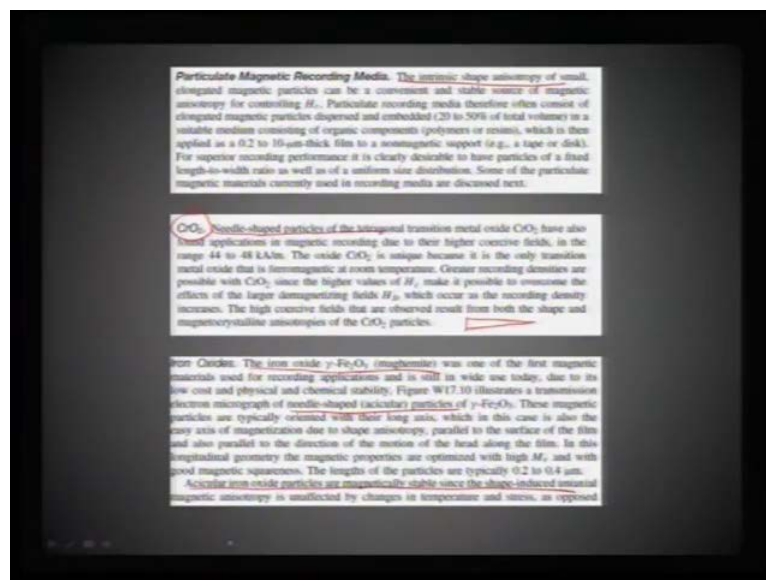
As you can see, this is a very expensive one sold those days, but we have lot of advances in this storage media. So, a typical cassette tape has a material which is made of chromium dioxide, chromium dioxide originally know as a chromium dioxide tape it is good high frequency sensitivity, actually helps in minimizing on the tape noise, because when you play the tapes, you usually have a noise the background coming and that is because, of the sensitivity.



And greatly that has been improvised by application of  $\text{CrO}_2$ , and the company which really marketed or made billions of dollars out of this  $\text{CrO}_2$  tape is the TDK company. And even now, the video tapes that are available those are made out of a black compound, if you have time and just take a look at the tape that is running in those video tapes you would see, it is a dark one, whereas the audio tapes that were sold will be brown in color.

So, the brown ones are usually  $\gamma\text{-Fe}_2\text{O}_3$  and the black ones are usually, those made of  $\text{CrO}_2$ . And the main contrast between these two is  $\gamma\text{-Fe}_2\text{O}_3$  is easily made compared to  $\text{CrO}_2$  therefore,  $\text{CrO}_2$  is used for very specific applications because, to make  $\text{CrO}_2$  in a preferred geometry is very important.

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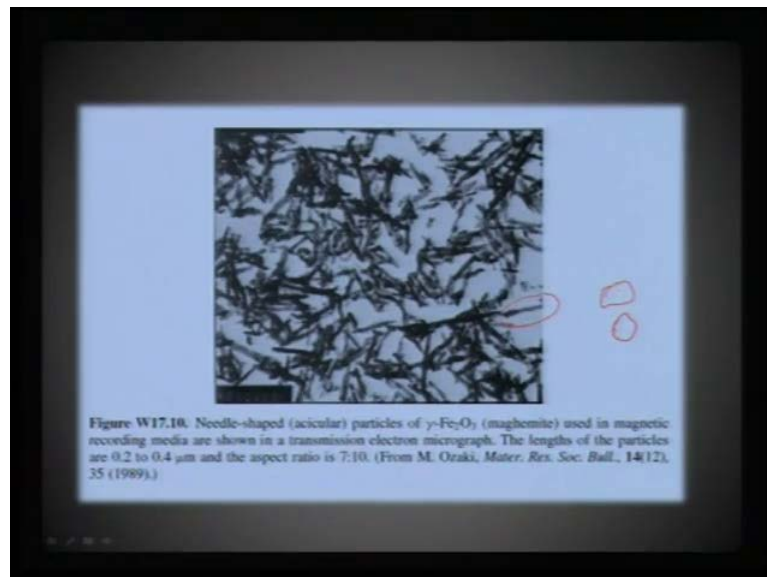
So, what are the numbers that we need to remember, regarding particulate magnetic recording media. The most important thing is the shape anisotropy of small elongated magnetic particles, which will actually give you the required coercivity that is needed for superior recording performance. So, we need to know that when we talk about particulate magnetic recording, the most governing principle there is the shape anisotropy.

And  $\text{CrO}_2$  therefore, can be successfully made using hydrothermal process, I have already dealt in one of my lectures in module 1. Where, hydrothermal conditions are the only preferred way to get  $\text{CrO}_2$  in a needle or acicular shape. So, actually this is the way you have the aspect ratio of these particles, and that is exactly needed for the

magnetic recording in a preferred direction, and mainly because, you need to smear these  $\text{CrO}_2$  particles on a tape material.

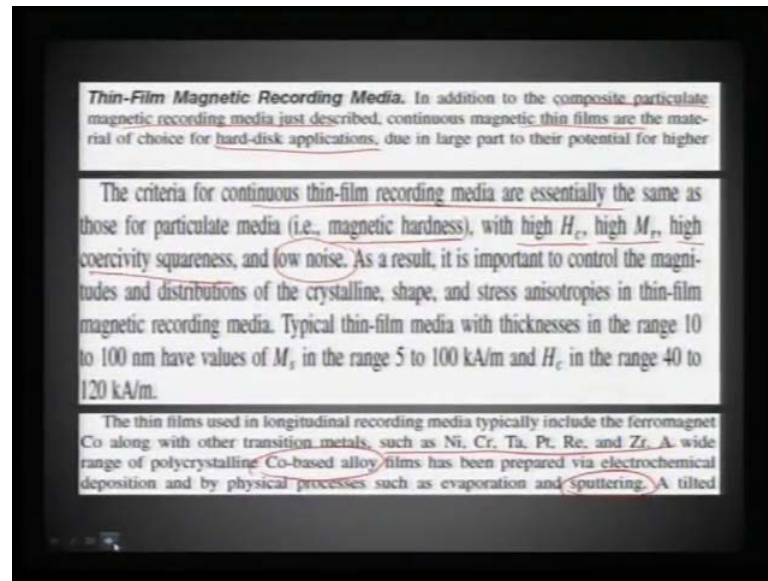
And they need to have a particular access of orientation, it cannot be random therefore, for particulate medium which is usually a tape material, which has a polymer base you prefer needle shaped  $\text{CrO}_2$  particles. So, this is one of the criteria for tape applications, the other one is iron oxide that is used and iron oxide again has a acicular or needle shaped geometry. And acicular iron oxide particles are magnetically stable, since the shape induced uniaxial magnetic anisotropy is actually dominating the magnetocrystalline anisotropy. Therefore this is of particular advantage over other materials.

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This is viewgraph to tell you what exactly I was talking about the shape anisotropy; this is the desired form of  $\gamma\text{-Fe}_2\text{O}_3$  if you want to use it for tape. Because, there are several chemical routes by which  $\gamma\text{-Fe}_2\text{O}_3$  can be made, but those usually end up with this sort of irregular shaped or spherical shaped particles. But, those are not preferred for the tape applications, so this is made specially out of a particular chemical process. So, if we really need to win over in terms of applications we need to control the morphology. And whenever we think about controlling the size, we usually resort to a particular chemical process. And hydrothermal condition usually comes as a aid, mainly because, you use the high pressure to force the morphology.

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The next point that I want to drive home is the use of these magnetic materials, for thin film media. So, thin film magnetic recording media usually is used for CD's and also for making the read heads, read heads are never tape materials those are some iron cores which is coated with the particular magnetic material. So, in addition to the composite particulate magnetic recording media, we have this magnetic thin film media which actually has taken over the hard disk applications.

So, the criteria for thin film recording media is again similar to the tape material that we mentioned, it should have magnetic hardness in terms of high coercivity, high remanence magnetization and high coercivity squareness and also the energy product. Also we need to have a low noise, this would ensure good application for thin film media, the candidates that are usually used are mostly metals or alloys. The most preferred one is the cobalt based alloys, and several processes have been developed not just the physical vapor deposition.

But, if you want to make this in a larger scale, the most convenient and inexpensive route is sputtering where you do not really look for a very high quality of epitaxy. But, just a particular orientation that is possible using sputtering because, you can really make a large area deposition for this and mainly this has to be on a reel, reel to reel basis. So, this is achieved using vacuum technology.

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TABLE W17.1 Estimates Predicted for the Upper Limit of the Coercive Fields  $H_c$  of Small Magnetic Particles

Type of Anisotropy	$H_c^a$	Typical Value <sup>b</sup> (kA/m)
Magnetocrystalline		
Single particle	$\frac{2K_1(\text{or } K_u)}{\mu_0 M_s}$	39
Randomly oriented	$\frac{0.64K_1(\text{or } K_u)}{\mu_0 M_s}$	25
Particles ( $K_1 > 0$ )		
Particle shape		
Single particle	$(N_z - N_x)M_s$	855
Randomly oriented particles	$0.48(N_z - N_x)M_s$	410
Applied stress	$\frac{3\lambda\sigma}{\mu_0 M_s}$	3.6

<sup>a</sup> $K_1$  and  $K_u$  are the magnetocrystalline anisotropy coefficients for cubic and uniaxial ferromagnets, respectively.

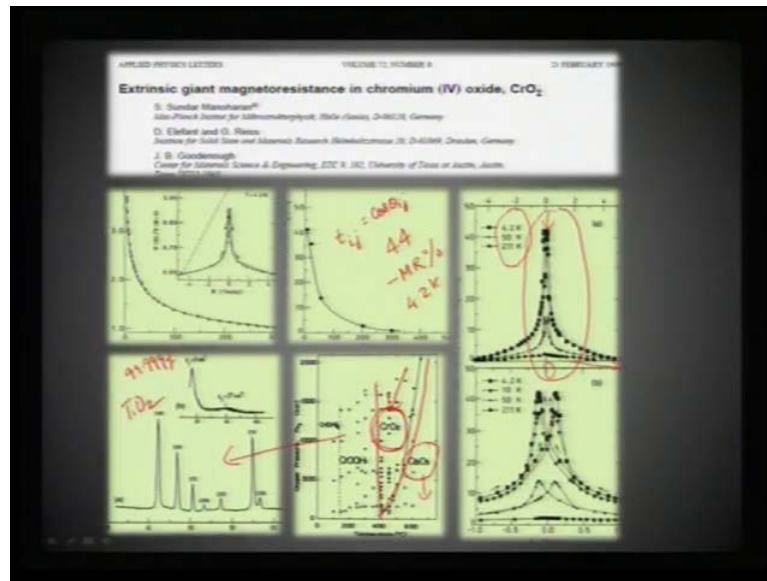
<sup>b</sup>The parameters used are those appropriate for Fe at  $T = 300$  K:  $K_1 = 4.2 \times 10^6$  J/m<sup>3</sup>,  $M_s = 1710$  kA/m, magnetostriction  $\lambda = 2 \times 10^{-5}$ , yield strength  $\sigma_y = 1.3 \times 10^8$  N/m<sup>2</sup>. For the case of shape anisotropy, the particle shape corresponds to a long needle with  $N_z = \frac{1}{2}$  and  $N_x = 0$ .

<sup>c</sup>C. Kittel, *Rev. Mod. Phys.*, 21, 541 (1949).

So, just want to make some sum up on these two range of materials for magnetic recording, the numbers that we are looking for is the coercive field. And this coercive field is actually controlled by two parameters, one is the magnetocrystalline anisotropy where your  $K_1$  or  $K_u$  dominates.  $K_1$  or  $K_u$  is nothing, but the magnetocrystalline anisotropy coefficients, which are specific for either a cubic or a uniaxial ferromagnet. And then, your shape anisotropy also comes into picture. So, shape anisotropy and magnetocrystalline anisotropy they determine, the value that you can generate out of it, so the values that you generate for shape anisotropy is roughly of the order of 800 kilo amps per meter. So, these are the estimates specifically mentioned for small magnetic particles.

The fascinating magnetic material, which not only shows the room temperature metallic property because, this is the only oxide which is both ferromagnetic, as well as it is metallic at room temperature. So, this is a very important oxide in magnetic recording not only that in the recent past, we have observed another unique feature of these CrO<sub>2</sub> particles, specially when you talk about small particles not as a thin film.

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If you look at the small particle you can see, the resistivity of this metal seems to be raising at low temperature. When they raise at low temperature; that means, the exchange coupling between the particles are affected because, of the random orientation of these ferromagnetic domains. So, as a result if you try to look at the influence of magnetic field on CrO<sub>2</sub>, you can see here there is a substantially increase in the magneto resistance ratio. In other words CrO<sub>2</sub> can be used not only for magnetic tape material, but it can also be used for read head application.

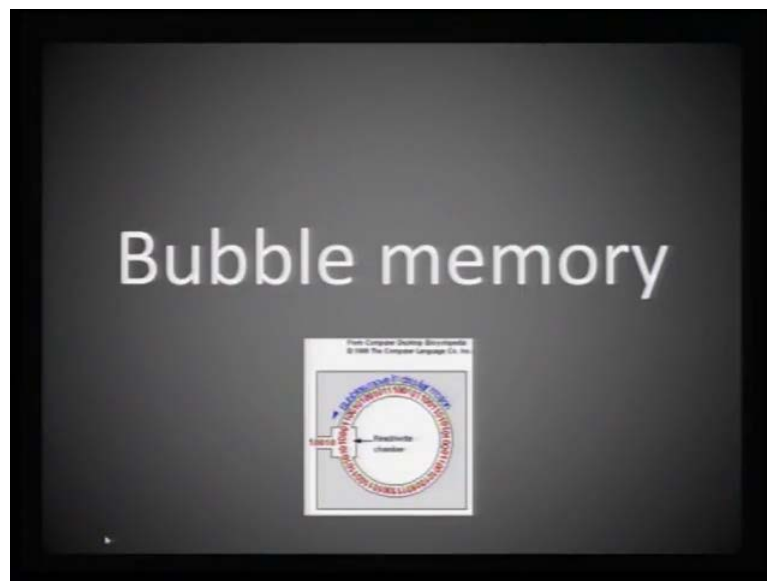
Mainly because, it is responding to a field and it varies the resistance, how it varies a resistance at 0 field, you see the resistance is at it is maximum. And at higher field the resistance almost drops down, and this is the case with change in temperature. As you would see here, nearly 44 percent of negative magneto resistance ratio is achieved at 4.2 Kelvin for these CrO<sub>2</sub> particles. And that is mainly happening because, your transfer integral of one spin to the other spin is actually governed by  $\cos \theta_{ij}$ , which is the angle that is made between two spins.

So, when you apply higher field and at low temperature you can actually bring about a collinear exchange, between two CrO<sub>2</sub> particles. So, as a result you see a large drop in resistance, even at a very fairly low field. So, this is one of a very important breakthrough in the recent passed on CrO<sub>2</sub> technology, where CrO<sub>2</sub> cannot just be used for as a tape material. But, it can also be used for magnetic sensor applications, but the challenge in CrO<sub>2</sub> is that, it has to be prepared under extremely difficult conditions.

Because, if you take  $\text{CrO}_3$  which is a lab reagent and then, you heat it all you would get is  $\text{Cr}_2\text{O}_3$  which is chromium trioxide, and this is a green compound which is thermodynamically stable. So, your  $\text{CrO}_3$  hexavalent compound comes to a trivalent compound, and it is very difficult to promote this  $\text{Cr}^{3+}$  here, to  $\text{Cr}^{4+}$  that is why it has to be stabilized under high pressure condition. So, one of the most important way by which we can stabilize  $\text{CrO}_2$  is by hydrothermal process, where you apply very high pressure to a starting compound.

So, that you can stabilize this phase, so this is a very narrow range where you can stabilize  $\text{CrO}_2$ , and the production of the  $\text{CrO}_2$  has actually crippled the massive use of this in the recording medium. And this is actually crystallizing in a  $\text{TiO}_2$  rutile phase and you can see, this is a typical x-ray pattern that you should get, but what you would see is bit of  $\text{Cr}_2\text{O}_3$  coming as a impurity which is not a desired. So, to get 99.999 percent pure  $\text{CrO}_2$  is a challenge, which is the challenge for the materials chemist.

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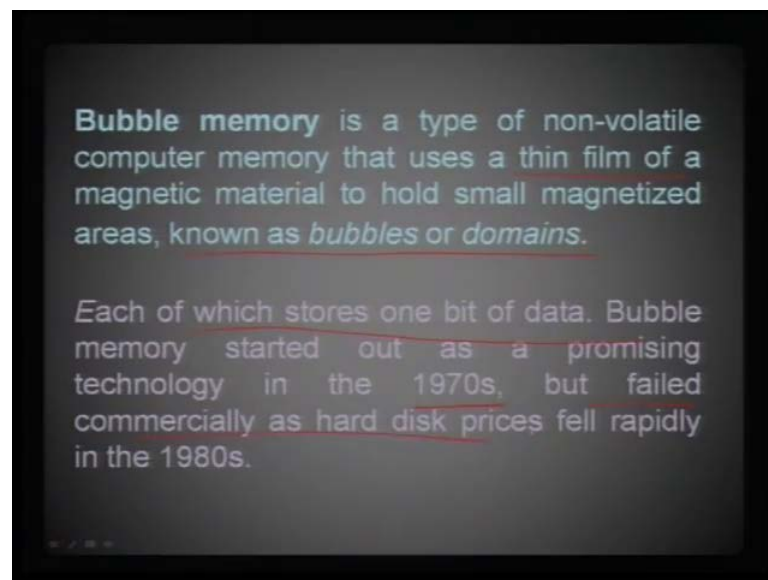


Now, the other important application in magnetic memory is bubble memory. What is this bubble memory there are some compounds, which actually in the presence of an external field, will not show a systematic orientation of domains. Rather the domains will coalesce into a bubble, and this bubble can actually move and in this bubble you can try to store the memory. And this is a cartoon which tells, what is this bubble memory about

it forms a bubble where the read write chamber is placed, and you can send this magnetic information as a 0, 1 bit.

And this is confined more in a circular motion, not in a linear fashion that is why it is called bubble memory. But, this bubble memory actually has a one critical disadvantage because, it takes more time to read the information, as a result what was predicated to be a breakthrough in the early seventies later faded out, because lot of new compounds started coming which was pleasant replacement for this bubble memory devices.

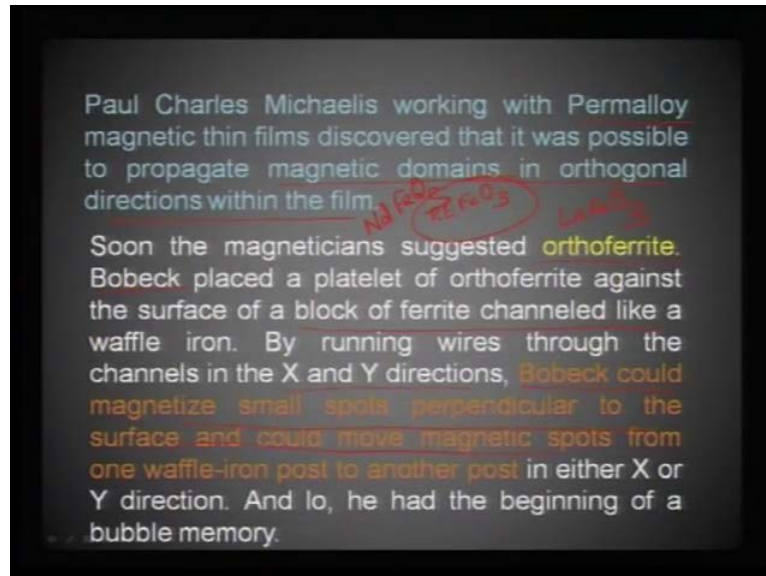
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Some of the notable materials which are used as bubble memory devices are permalloy, the first discovery was actually on permalloy and later ferrites were used. So, just run through some of the definition for what this bubble memory is about, it is a type of nonvolatile computer memory. That means, it is nonvolatile because, even after you remove the magnetic field, the magnetic information will still be there it whereas, in non-volatile memory devices, with the moment you remove the magnetic field, the memory information is lost, whereas in this magnetic bubble memory devices, it is a nonvolatile computer memory. And this actually uses a thin film magnetic material, and this thin film magnetic material can be magnetized into a small, small bits or small bubbles and therefore, you can actually hold the memory in each bubble, and you can treat each of this bubble as a bit. So, that is why you call this as a bubbles and not

domains, each of this stores one bit of data. So, bubble memory started out in 1970's, but it failed because, of the commercial disadvantage.

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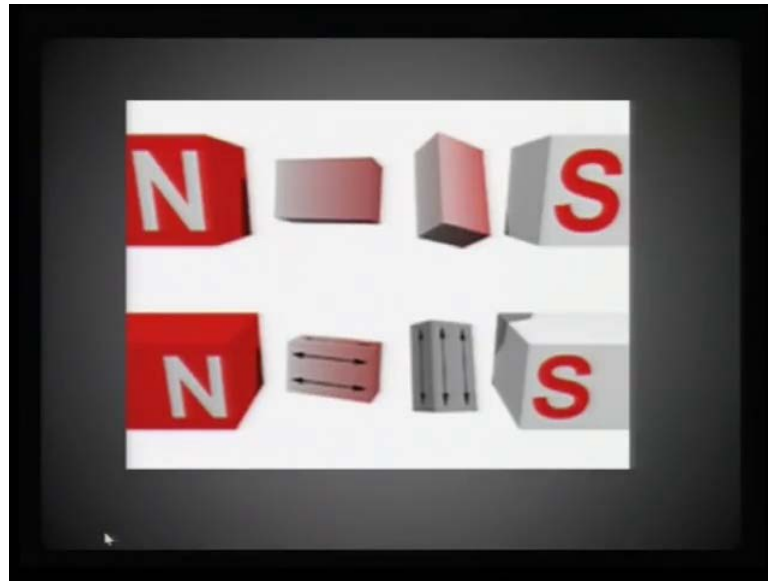


It was actually Paul Charles who worked with Permalloy, who observed that the domains can actually orient perpendicular to the plane of the film and that gives an idea about perpendicular anisotropy. So, magnetic domains are in orthogonal directions with the film, and a group of compounds which showed this property is from the ceramics ferrites. In other words oxides, and they are all called as orthoferrites, orthoferrites are usually  $REFeO_3$  where your RE is nothing, but Rare Earth.

So, we can talk about lanthanum  $FeO_3$  or we can say neodymium  $FeO_3$ , these are called orthoferrites. And one of the reasons why they are called orthoferrites is because, they show magnetization which is orthogonal to the thin film surface, and this is very peculiar because, not all the magnetic compounds can show such an orientation. And if you actually, try to channelize it by running wires on this thin film, and in X, Y direction what you can do is you can generate an array of these bubbles, and these bubbles can be used to store data's. It was later by IBM person Bobeck who could use magnetize, small spots perpendicular to the surface and could move the magnetic spots, more in whatever fashion you can design.



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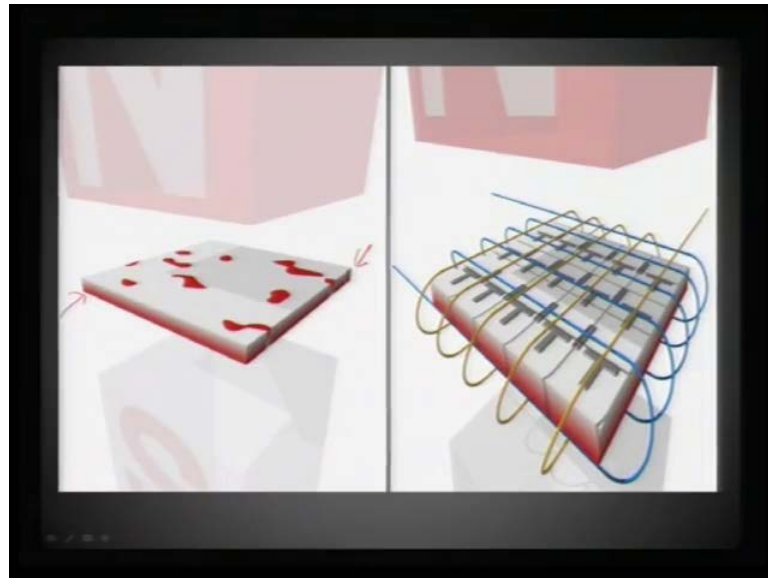
And some of the ways that you can do that, is seen in the next few slides. The difference between the orthoferrite and the normal magnetic materials is this, when you place the magnetic material between poles, usually the opposites poles attract the respective ones. So, in this case the shaded colors tells you how a typical magnet would respond, but a orthoferrite will actually respond this way, it will not align opposite, but rather it will exhibit a dipole. So, it will remain perpendicular to the pole.

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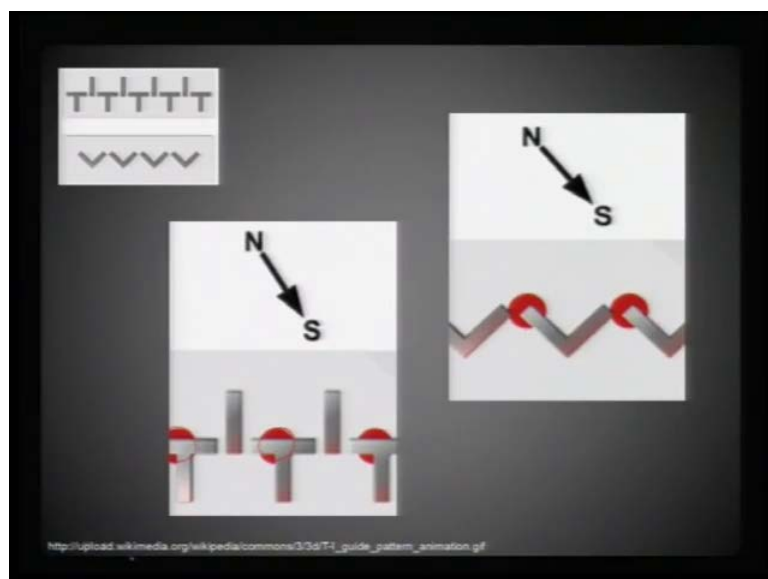
And therefore, you can get domain structure like this, a bubble memory device or material will actually show your domain in this form. And these shaded areas or colored regions are the bubbles, perpendicular to the plane of the film.

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So, now if you try to place it between a poles of a magnet, than you can see all these bubbles whatever you are seeing coalesce into small bubbles. And then, if you try to use some small magnets, then you can easily move these bubbles throughout. So, what you can do you try put some circular wires, and if you try to homogeneously apply a field, then if these are the shapes of your ferrites.

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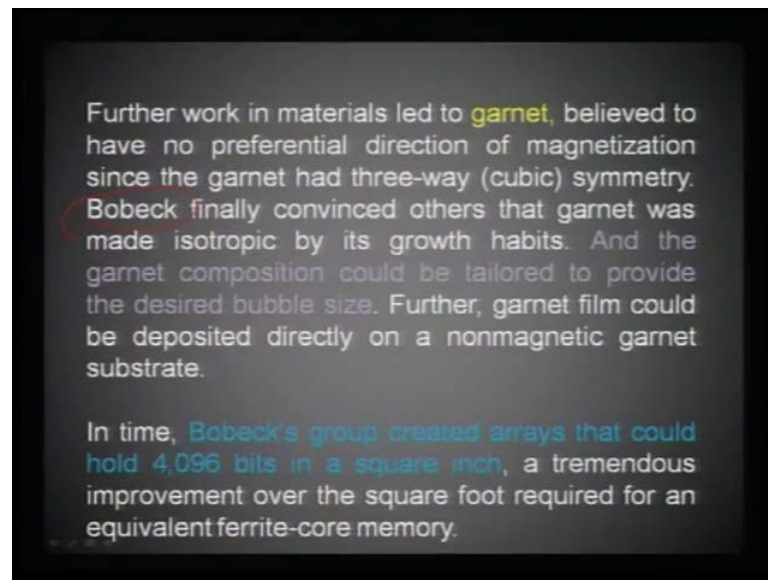
Then you can actually rotate these bubbles in any direction that you want. So, if you want this to go in a linear direction, then this is the configuration that you need to keep. So, you can generate each of these red ones what you see here is nothing, but a bubble that you can generate and you can push it along a particular direction, if you want a v shaped motion then you can design something like this. So, this is one of the very distinct features of a bubble memory device, which is used for storage applications.

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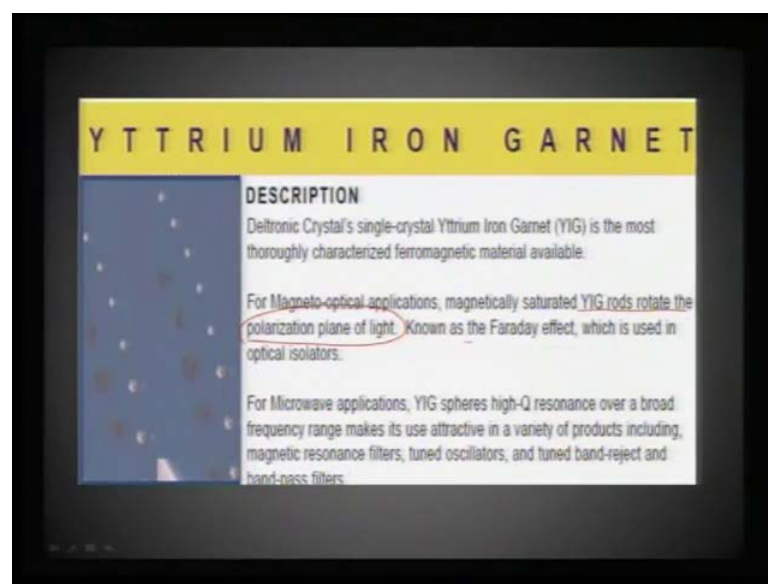


And to know whether these are really homogeneous, you can get micrographs of these orthoferrites. And you can see here this MFA mapping can clearly give you the domains which are rich in ferromagnetic component and the regions which are rich in antiferromagnetic component. So, this can be clearly studied and the phase homogeneity can be modified. Another compound which is of interest is garnet, garnet is also used in storage media this is believed to have no preferential direction of magnetization, since the garnet is cubic. So, it is not supposed to show any isotropic behavior, so this was again used by Bobeck to explore the application for a bubble memory applications.

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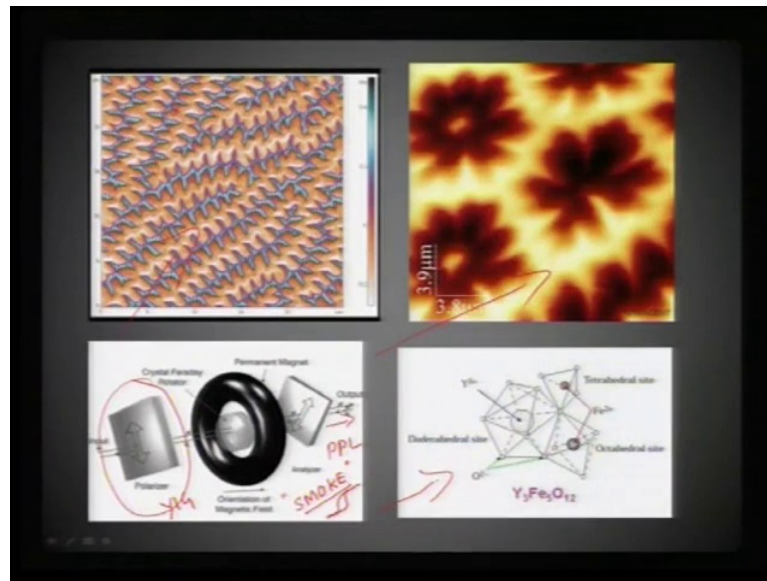


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One of the important feature of this garnet is that, it is used more in magneto optical devices. Reason they can this YIG or yttrium iron garnet, is actually capable of rotating the plane of light. So, this can be used in magneto optical application specially for faraday effect, where you can use this more as a polarizer.

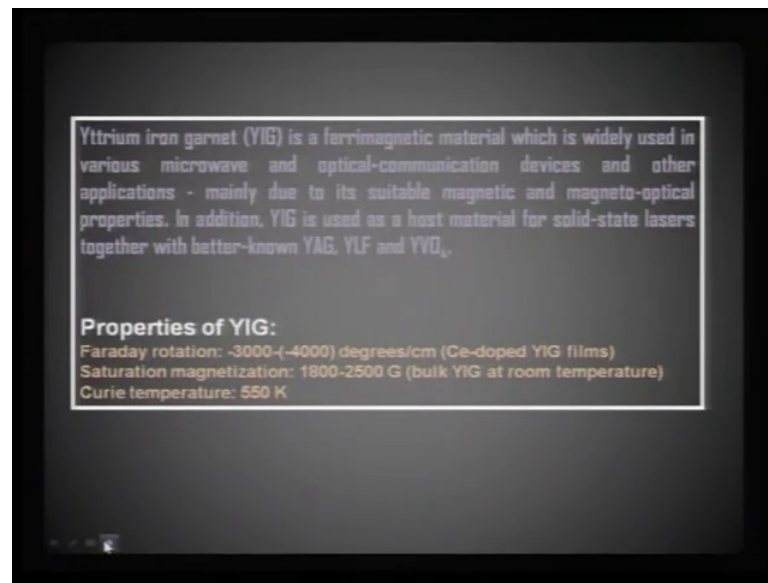
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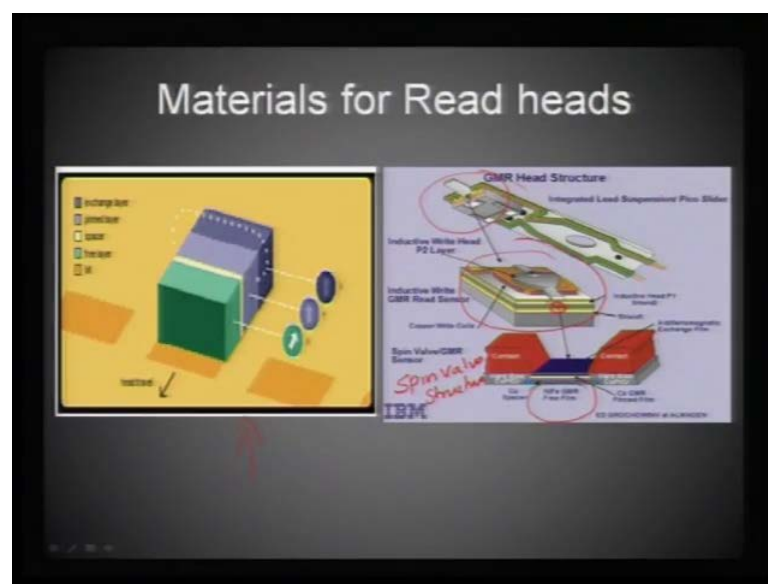
So, if you use this light you can plane polarize it when you passed through a polarizer made of YIG. And in that case, you can actually get a plane polarized light as a output therefore, you can study the ferromagnetic response of any magnetic material. So, this is one of a very important application of garnet that is used in today's device for example, notable application is in the field of smoke, smoke is nothing, but surface magneto optical kerr effect, this is a optical way of studying the kerr rotation.

So, if a magnetic material if a material is magnetic, then it will actually rotate the plane polarized light in different directions. So, you will get a hysteresis like this similar to what you get in a VSM in a Vibrating Sample Magnetometer or using squid, if you see a hysteresis the same hysteresis can be generated using a plane polarized light, and this is specifically used for recording media. These are some of the viewgraphs of YIG shows how the ferromagnetic domains are aligned. This is a mapping under magnetic imaging this is MFM image of the same thing and this is a unusual structure, which is not as simple as the spinal structure or the orthoferrite structure. So, this has it is own characteristics of crystal.

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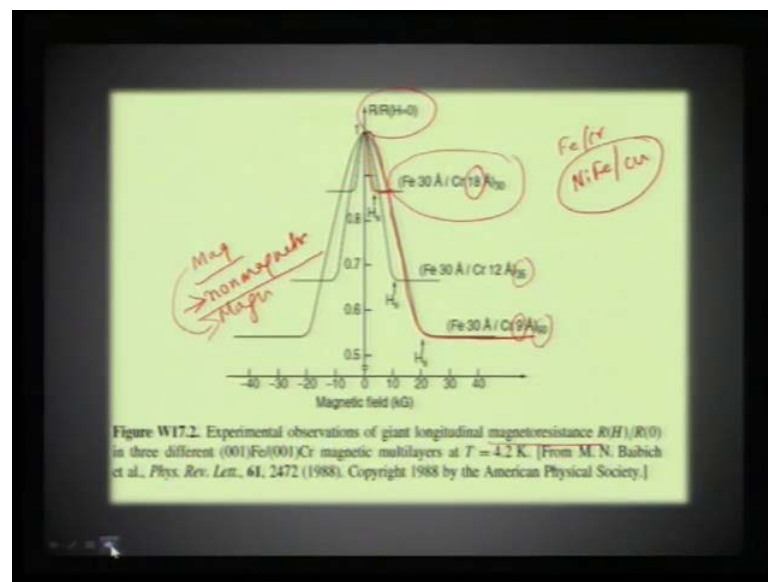
And lastly I would like to conclude on the classification of these magnetic materials with, those which are present generation materials used for read heads. This is a cartoon that you would see in a IBM website where, the current read head mechanism is very clear mentioned, and what is being used now days is permalloy based read head material. That is nothing, but a multilayer device.

So, if you look at the read head structure this is where your read head is which is a very small spot, and if you try to magnify that to see this is multilayer which is kept over

inductive coils. And the tip of this read head is nothing, but a multilayer which is of this geometry, and this is made of several structures and popularly this called as spin valve structure, because with ease it is possible for you to rotate the magnetic moment of the top layer.

So, if your layer has to read your magnetic memory or magnetic information in 0, 1 bit then this top layer magnetic moment has to rotate very freely, and that is why it is called spin valve, it can easily be flipped. So, this spin valve is the current generation one and that is one of the region why we are able to store lot of memory even in a small area. So, the field sensitivity of this spin valve is very, very important.

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And the compound that really shows, such a read head capability or the spin valve device is nothing, but bi layers of iron chromium or nickel iron, and copper sort of multilayer's. The viewgraph that we see here is nothing, but a response of resistance normalized resistance over a field and what you see is a multilayer device, which is made of iron chromium repeat of the order of 30 such bi layers or 36 or 60 such bi layers. You can make where after every 3 nanometer iron layer, you see a 0.9 nanometer thin chromium layer.

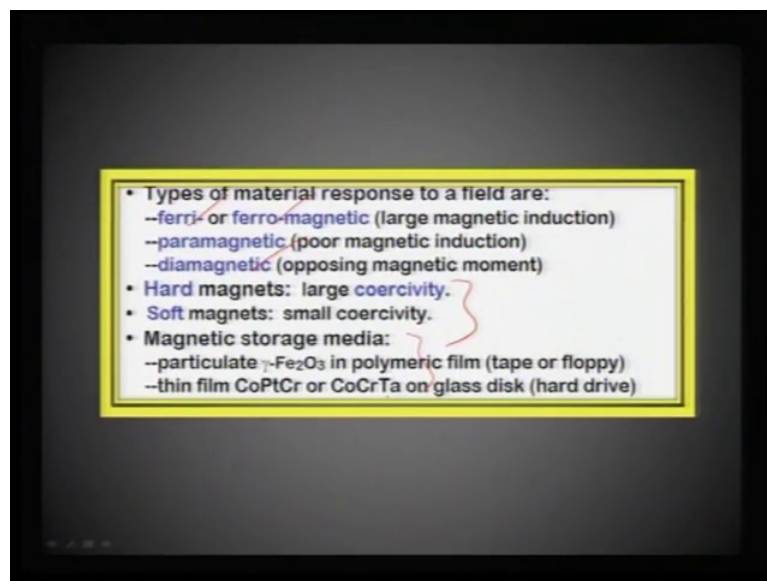
So, this is nothing, but magnetic nonmagnetic bi layers. So, if you stack such magnetic, nonmagnetic bi layers what you are effectively bringing into perspective is a ferromagnetic and a anti ferromagnetic coupling, between two magnetic layers. So, if

you have this sort of an anti ferromagnetic, ferromagnetic coupling then in the presence of the field and in the absence of the field you see a change in the response, and that is what we call it as magneto resistance.

So, let us take the case of a simple bi layer like this at 0 field it has a very high resistance, and at say 10 kilo gauss you can see that the resistance has shifted. But, if you control the size of this interlayer from 1.8 nanometer, if you go down to 0.9 nanometer you can see this fall is quite steep. So, thinner the nonmagnetic layer, higher the magneto resistance response, so what essentially it means is in the absence of field and in the presence of the field I can control the resistance.

So, that is why it is called as a magnetic sensor and this is precisely sort of layer that is used in the current read head applications. So, this is actually taking over most of the attention compared to the traditional magnetic materials that are used in the read head applications.

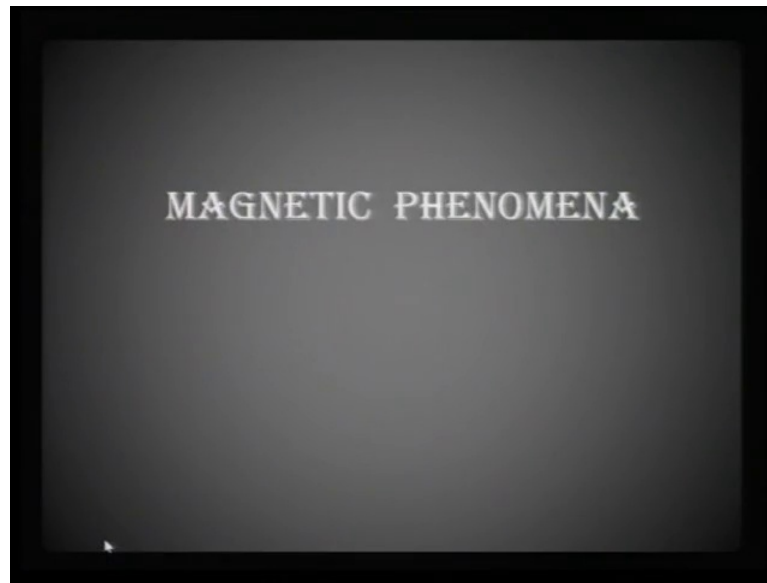
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So, what we have seen, so far is the range of the magnetic materials, from ferrimagnetic to ferromagnetic we have seen some of the examples of diamagnetic materials. And we have largely looked at, the different classification of compounds between hard and soft magnets and some of the candidates for magnetic storage media.



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In the next few minutes I am going to discuss with you about some of the problems one would encounter, when we handle a ferromagnetic compounds. Although ferromagnetic compounds are a luxury to use, in several applications the way the magnetic response happens at a wide range of temperature, say room temperature and low temperature. Actually brings about interesting physics and chemistry.

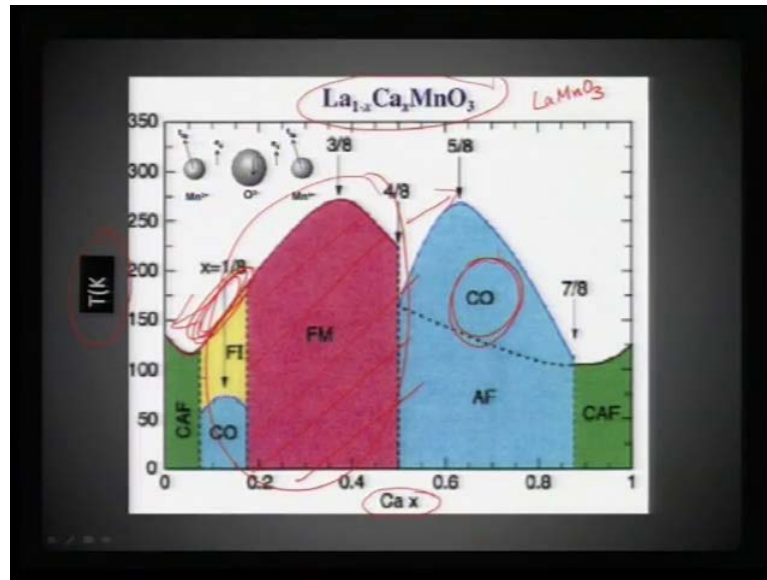
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So, I am going to show some of the magnetic phenomena's which are embedded in system, which we need to understand in perspective. Some of these examples I will be

discussing in detail in the next module, but I will show only examples to highlight the point of magnetic phenomena. For example, one issue that often we confront in ferromagnetic material is spin glass, it is not only seen in oxides, but also in other metallic compounds.

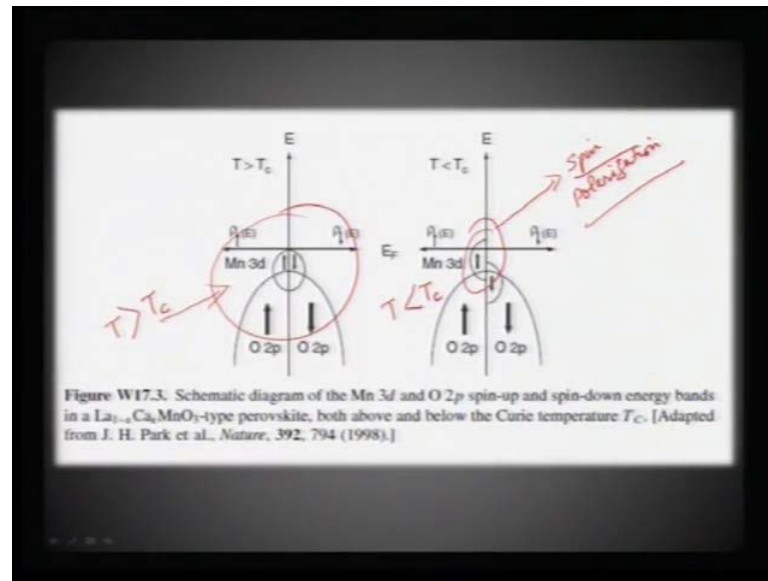
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To show what this spin glass behavior is, I take this popular example of a phase diagram of lanthanum calcium manganite. If you take lanthanum manganite, and dope it with calcium then as a function of calcium, you can see the ferromagnetic response varies, in other words the curie temperature keeps on varying. So, there is a domain where you can see, this is the domain where you get a very strong ferromagnetic response, but as you keep on substituting calcium, before and after here and here.

The ferromagnetic response vanishes completely, and you get into a sort of related phenomena. And that is exactly one of the phenomena is spin glass, which you can actually see in this domain spin glass, and what we also observe in the same ferromagnetic material is a charge ordering, these are all embedded along with the system and we can understand, how to eliminate or what the origin of these mechanisms are...

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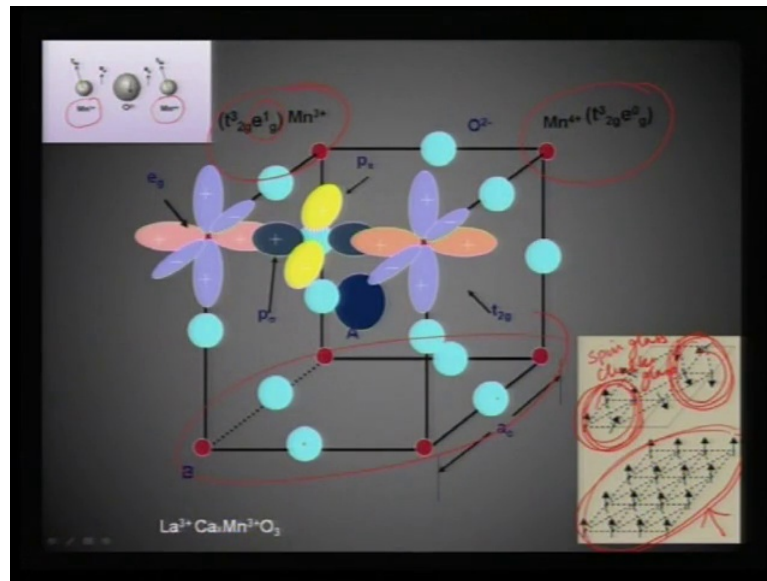


Now, what makes this lanthanum manganite more interesting is that, if you look at the band structure of this lanthanum manganite, these are the 2 p bands from oxygen and this is the three band from manganese. And you would see, that this is the situation when the material is above  $T_c$ , temperature is above the Curie temperature, this is the band structure. But, once you go to temperature below  $T_c$  when the system or the material is showing ferromagnetic nature.

You can see, that at the Fermi level the up spin electrons are the d bands dominate over the other sub band that is the low spin sub band. So, as a result this has high degree of spin polarization and this makes it a very important for magnetic application, spin polarization. But, what happens this half metallicity or 100 percent spin polarization of one particular carrier of electron, is actually distorted by several other factors which happens in the lattice.

Now, this is the cartoon which tells what is important about this lanthanum manganite, and what is the magnetic phenomena usually we confront with, what is happening here is you have a manganese 3 plus and you have a manganese 4 plus. So, this manganese 3 plus has a easy electron, which actually goes via oxygen 2 p to manganese 4 plus and then this becomes a manganese 3, and this manganese 4.

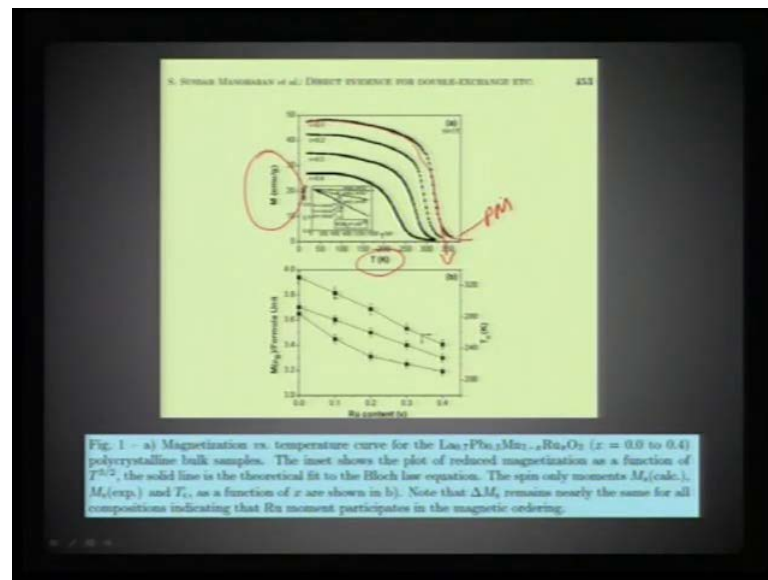
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Then the same electron can go reverse back, which is called as double exchange ferromagnetism, and when this double exchange ferromagnetism happens, if you look at the A, B plane which is nothing but manganese oxygen, manganese oxygen, manganese. So, this is you are A, B plane the ferromagnetism is actually ordered in this direction, and this is a strong ferromagnet. It is a correlated ferromagnetism, but when you go to low temperatures what happens, some of these ferromagnetic clusters can actually disalign and they can get frozen into a cluster.

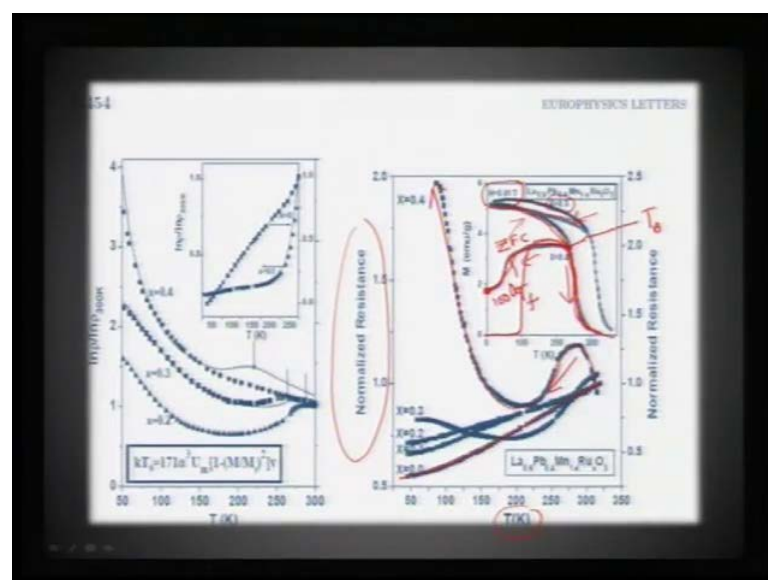
Therefore, this can freeze as it is as disordered state, but each of this can be grouped as a ferromagnetic domain. So, this is not completely it has lost ferromagnetism, but there is a competing interaction to the strongly ferromagnetic character that you would see at the  $T_c$ . So, at room temperature when it is a ferro magnet this is the situation when you go to low temperatures, you have competing interactions which we call it as spin glass or as cluster glass. What happens, this is ferromagnetic domain, this is the ferro magnet, but they are misaligned as a result you would not get a strong ferromagnetic loop, rather in the absence of a magnetic field you would see that it is almost going towards 0.

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So, how do we see that in a typical magnetic response, this is a M versus T data which shows there is a strong ferromagnetic transition. At low temperature there is now problem it is strongly ferro magnet, and as you bring it to the curie temperature it becomes a paramagnetic situation. So, this is a simple M versus T response of a typical ferromagnetic compound.

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But, what happens when you try to remove the field and cool the substance, what is happening here is the same compound, which is showing a very sharp transition here

when you do a ZFC that is 0 field cooling, it immediately shows a response like this. So, what is this response this is called as blocking temperature  $T_B$ , and this is called as  $T_f$  which is called a freezing temperature. Why because, at this place the ferro magnet domains are totally frozen into a spin glass, it is a more like a cluster glass.

And how do I know that, you if you carefully look at the relative or the complimentary response of this resistance, versus temperature. You can see corresponding to this transition you can see a very clear metal insulator transition, but as you go down the temperature, with the fields that are freezing you can see the resistance is sharply going. So, it is showing metallicity in this regime which is corresponding to this ferromagnetic ordering, when it is getting cluster glass situation or when it is frozen as a spin glass.

Then you see that the, domains are not coupling together or there is no exchange coupling between two domains as a result, you can see the resistance is going. So, when you have a complementary response between resistance and magnetization, and when you see this sort of typical behavior then you can classify this as cluster glass. Now, what is the difference between cluster glass and a anti ferro magnet.

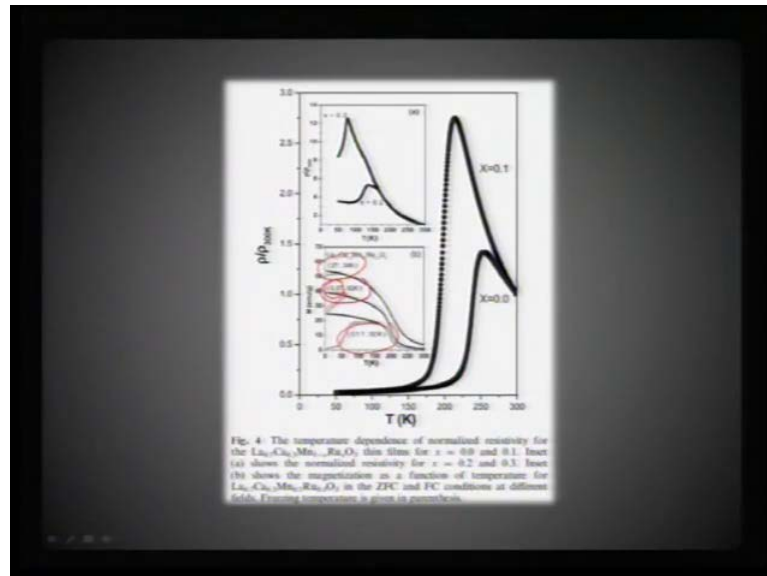
In a anti ferro magnet you would exactly see the whole thing, the moment sharply going to 0, which means even with a very little field it is it would not be possible for me to reverse the anti ferromagnetic coupling. So, if you apply a an external field say 1000 oersted or 500 oersted, it is not possible to remove this anti ferromagnetic coupling. Whereas, in spin glass or cluster glass even with very little field for example, it is mentioned here as 100 orsted, with 100 oersted if I apply somewhere if I sit here at this temperature and apply 100 oersted, then immediately this behavior comes back.

So, this is the signature of a cluster glass or a spin glass, but why we are studying this why this is important because, this can certainly bring about a candid response or influence on the electrical behavior. So, if you want your material to be a metallic material down to 100 k or 50 k, and if you want a magnetic response then there should not be any spin glass behavior. In that case, we need to modify the composition, so that we can get a strong ferromagnetic ordering.

For example, if you take another compound or a another substituted compound of ruthenium, lanthanum manganite, you can see between this and this there is a very small opening. It is not as this one, what it means is the spin glass behavior in this particular

composition is very, very less than this one therefore, the competing antiferromagnetic interactions are minimal, in this case compared to this composition.

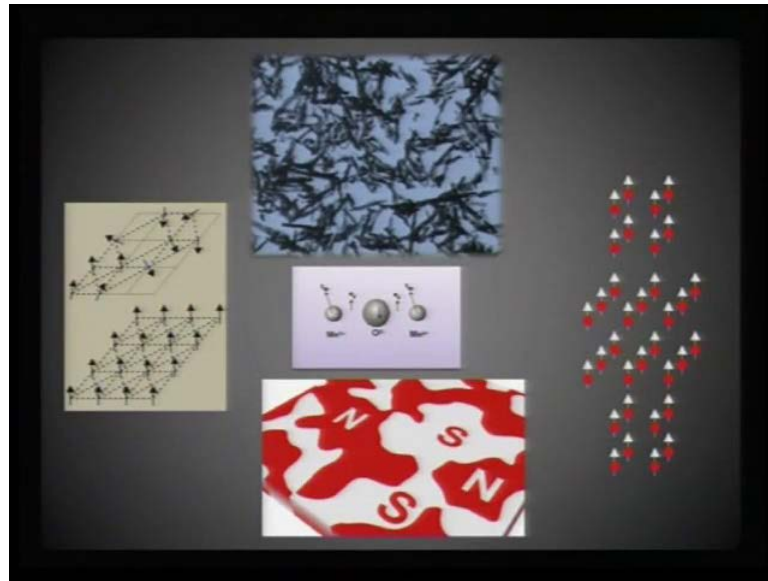
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So, this much of information we can try to understand for want of time I will not be able to discuss other issues, but I just want to sum up on this cluster glass. Here is another compound, but this compound is actually varied with different applied external field, and the ZFC and FC curves are recorded here. As you would see here if I do the ZFC, FC curve at two tesla, you hardly see any change between these two, which means the cluster glass influence is actually suppressed by a external magnetic field.

Whereas, if you lessen the external field to just 300 oersted then the opening becomes bigger, and if you go still further if you just apply very meager magnetic field, then you can see a very clear spin glass or cluster glass behavior coming. So, what it means is this antiferromagnetic interactions can be largely minimized, when you study this material under high magnetic field, with this I should be able to end because, I do not have much time to cover other examples.

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So, I would just sum up with one particular viewpoint that we have seen some of the issues related to magnetic phenomena in ferromagnets. Specially, the spin glass and I have also touched upon in this lecture on special materials, which are specific to bubble memory devices and also storage recording media.