MAGNETIC NANOMATERIALS

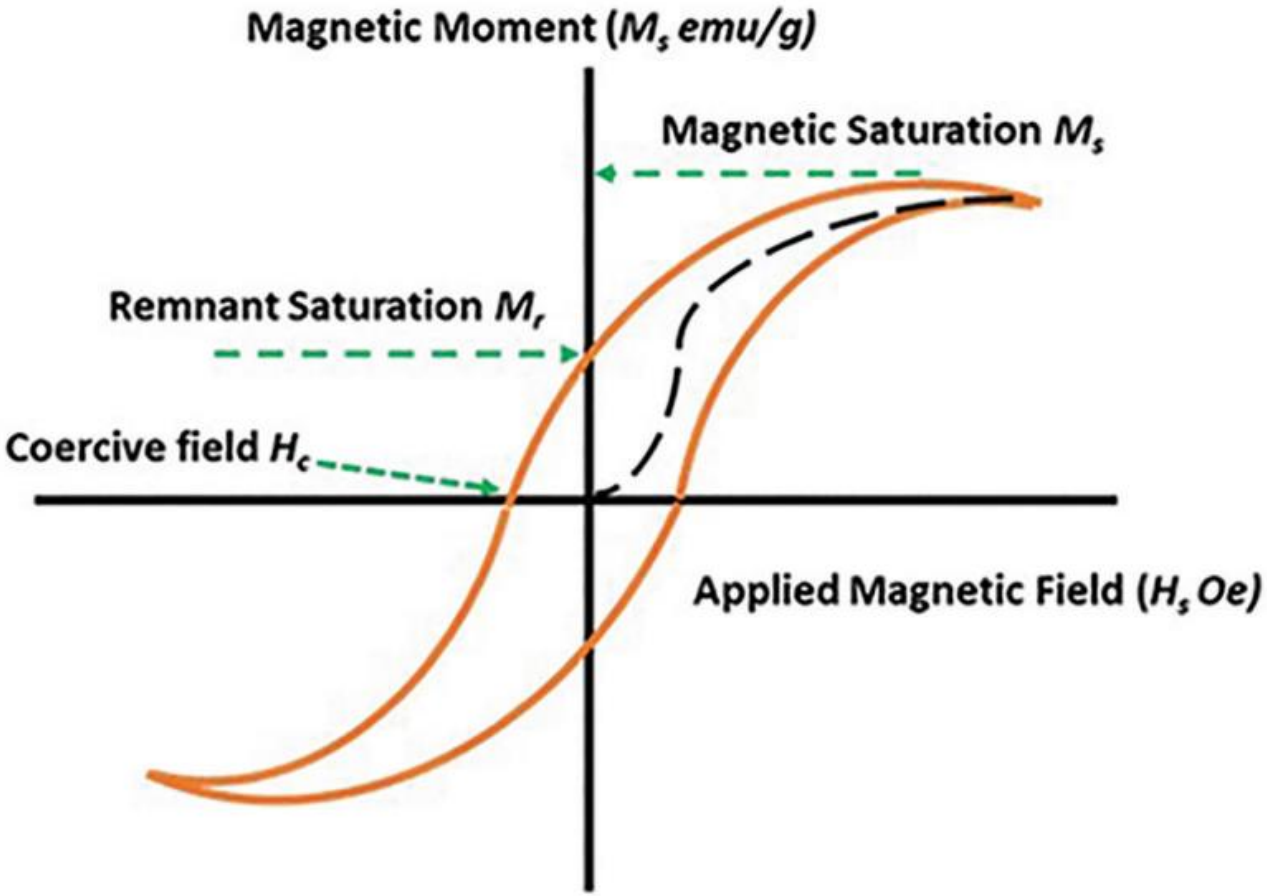
Composition and Size

- Different magnetic nanocrystals were prepared from metals, Fe, Co, Ni, FePt, etc. and metal oxides Fe_3O_4, Fe_2O_3, MnO, CoO, $MnFe_2O_4$, and $CoFe_2O_4$.
- At present, magnetic nanoparticles are of immense interest for applications.
- ✓ Magnetic nanomaterials are used as the media for information storage as well as part of nanoscale reading heads.
- ✓ Other major applications of magnetic nanoparticles (MNPs) are ferrofluids used for bearing, labeled nanoparticles for biological objects detection and manipulation, contrast agents for magnetic resonance imaging (MRI), cancer treatment by hyperthermia, and more recently magnetic particle imaging (MPI).
- Iron oxide nanoparticles such as magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3) are the most commonly employed nanoparticles for biomedical applications.
- Gd-based molecules are mainly used as contrast agents for magnetic resonance imaging owing to the large relaxation impact of surrounding nuclei.

- The size of MNPs is typically between ~2 and ~20 nm. Furthermore, recent studies have demonstrated the ability to form a *single crystalline 30 nm* magnetite (Fe_3O_4) nanotube.
- In order to obtain larger particles, these nanoparticles may be included in a larger matrix to form nanoparticles up to several microns in diameter. These matrices are polymers such as dextran (a polysaccharide made of many glucose molecules), polystyrene, or inorganic materials such as silica. Sometimes, aggregates of iron oxide particles are also available. A number of commercial MNPs either plain or labeled with various molecules targeting proteins, viruses, or cells are available.

Magnetic-Hysteresis Loop

- The magnetic-hysteresis (M-H) loop is a graphical representation that displays the magnetization and demagnetization characteristics of a material, as shown in Figure 2.4.



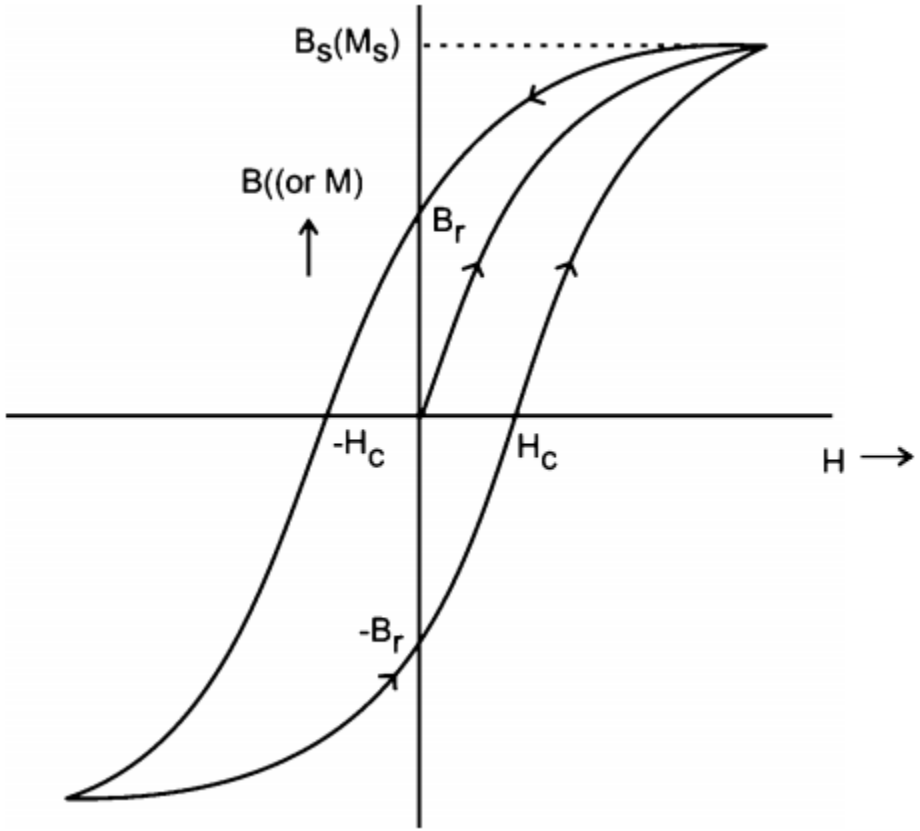


FIGURE 2.4 M-H loop of a ferromagnetic material.

- The hysteresis loop of a ferromagnet is shown above, initially in an unmagnetized, virgin state.
- Magnetization appears as an imposed magnetic field H, modifies and eventually eliminates the microstructure of ferromagnetic domains magnetized in different directions, to reveal the spontaneous saturation magnetization M_s . The remanence M_r which remains when the applied field is restored to zero, and the coercivity H_c, which is the reverse field needed to reduce the magnetization to zero, are marked on the loop.
- Hard magnetic materials have broad, square M-H loops. Soft magnetic materials have very narrow loops.
- This mechanism is similar to the electrical hysteresis loop.

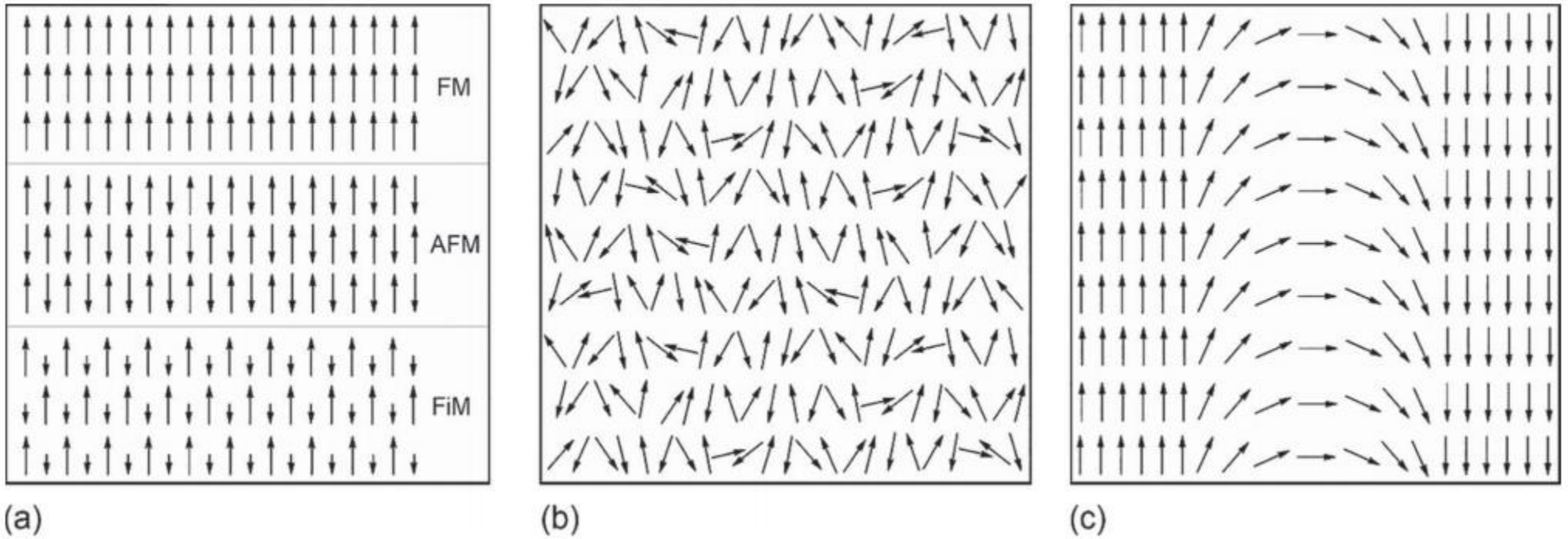


FIGURE 18.2 Some basic spin structures: (a) collinear spin structures at zero temperature (FM= Ferromagnetic; AFM=Antiferromagnetic; FiM=Ferrimagnetic), (b) noncollinear spin structure, and (c) micromagnetic spin structure (**domain wall**). Each arrow represents one atomic spin, and both (a) and (b) have zero net magnetization.

NANOSCALE SIZE EFFECTS ON THE MAGNETIC PROPERTIES

- Like the electronic conductivity, *magnetism* is another *unique property*.
- In general, the ***magnetic behavior of a material depends*** on the ***structure*** of the material and on its ***temperature***. However, when the size of a magnetic material is reduced, two ***key issues*** *dominate the* ***magnetic properties of nanoparticles*** *are*: **finite-size effects and surface effects**, which give rise to various special features and new properties.
- Finite-size effects result, for example, from the quantum confinement of the electrons, whereas typical surface effects are related to the symmetry breaking of the crystal structure at the boundary of each particle.
- With the decrease in size, *the* ***number of surface atoms*** *becomes an important fraction of the total number of atoms*, surface effects starts to prevail.
- The ***large surface-to-volume ratio results in a substantial proportion of atoms*** having ***different magnetic coupling*** with neighboring atoms leading to differing magnetic properties.
- *We know that the* ***bulk gold and platinum are nonmagnetic****, but they act as* ***magnetic particles at the nanosize***. **Au nanoclusters** become **ferromagnetic** *when they are capped with the appropriate molecules such as thiols*.

NANOSCALE SIZE EFFECTS ON THE MAGNETIC PROPERTIES

- *Several characteristic length scales in the nanometer range exist in magnetism*. These include the exchange length, the domain wall width, maximum equilibrium single domain particle size, etc.
- Some new effects should, therefore, be expected when the object size approaches any of these characteristic lengths.

Magnetic Domains

- The concept of a magnetic domain refers to a region within a magnetic material where the magnetization is uniform and aligned in the same direction. This creates a single domain with magnetic moments pointing in the same direction. However, when the material is cooled below the T_c it becomes divided into smaller regions, known as multi-domains. These multi-domains are separated by domain walls, where the magnetization in one domain may be parallel or in a different direction to another domain. The behavior of the material is determined by the structure of the magnetic domain, and the magnetization in each domain can be categorized into different angles, such as single-, 180°, and 90° wall domains. Figure 2.3 displays these categories. A domain wall consists of a spin chain that progressively tilts across the domain wall linking the magnetization in one domain to the magnetization in the next.

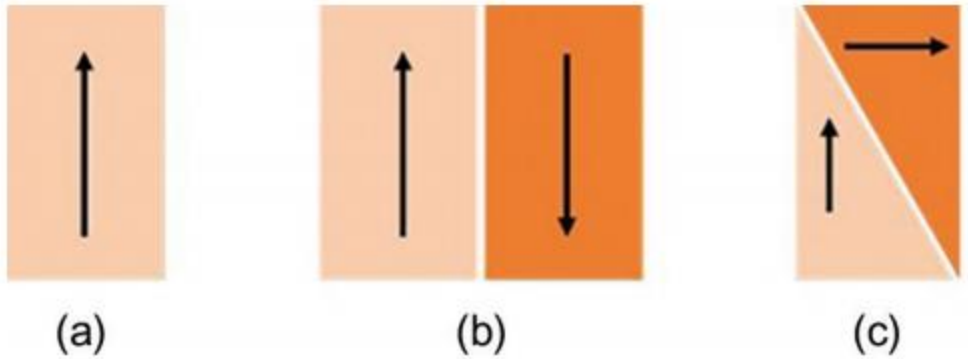
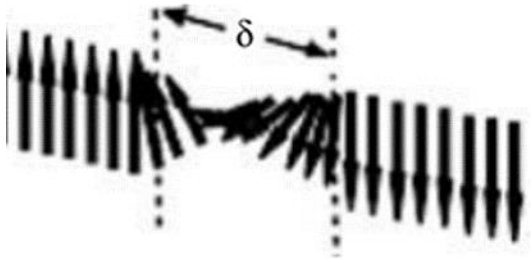


FIGURE 2.3 (a) Single-wall domain.
(b) 180° wall domain.
(c) 90° wall domain.

- In ***bulk magnetic particles***, it is well known that there is a ***multidomain structure***, *where regions of uniform magnetization are separated* ***by domain walls***.
- The *formation of the* ***domain walls*** is a process driven by the balance between the **magnetostatic energy** (ΔE_{MS}), which increases proportionally to the *volume of the materials*, and **the domain-wall energy** (E_{dw}), which increases proportionally to the *interfacial area between domains*.
- *If the sample size is reduced, there is a* ***critical volume*** *below which it* ***costs more energy to create a domain wall*** *than to support the external magnetostatic energy (stray field of the single-domain state). This further implies that* ***a single particle of size comparable to the minimum domain size would not break up into domains.*** This ***critical diameter*** *typically lies in the range of a few tens of nanometers* and *depends on the material*. It is influenced by the *contribution from various anisotropy energy terms*.

- **The critical diameter of a spherical particle (D_s), below which it exists in a single-domain state, is reached when $\Delta E_{MS} = E_{dw}$.**
- For a particle of size D (diameter) the **magnetostatic energy** is proportional to $M_s^2 D^3$ because (i) the energy density in the field goes as B^2 hence M_s^2, and (ii) the total energy is the energy density times a volume, hence the D^3 proportionality.
- Domain formation requires creation of walls, which are an area. Hence if γ is the domain wall energy per unit area, we expect a γD^2 functionality for the total **domain wall energy**.



A domain wall

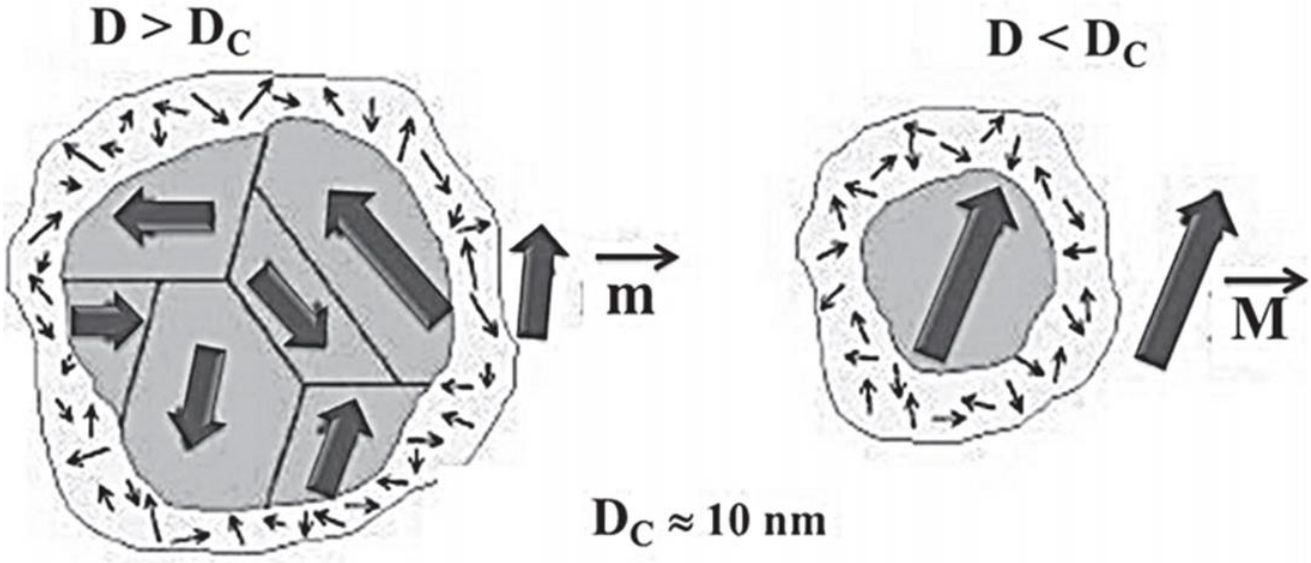


FIGURE 4.7 Multiple magnetic domains for bulk materials and single-domains for nanomaterials.

- *For large D, the D^3 term of the magnetostatic energy dominates*, so to alleviate this the smaller D^2 term of wall formation concedes and domains form.

- However, ***at small D**, the **D^2 term will dominate**, and **wall formation will be too costly***, and the particle will **not break** into domains.

- The *formation of the* ***domain walls*** is a process driven by the balance between the **magnetostatic energy** ($\Delta E_{MS} \sim M_s^2 D^3$), which increases proportionally to the *volume of the materials*, and **the domain-wall energy** ($E_{dw} \sim \gamma D^2$), which increases proportionally to the *interfacial area between domains*.

- The **critical size, or single domain size D_s,** *below which a particle will not form domains*, is *where these two energies are equal*. If we ignore proportionality constants, this implies $\gamma D_s^2 \sim M_s^2 D_s^3$ to yield: **Critical size, or single domain size D_s:** $\gamma D_s^2 \sim M_s^2 D_s^3$ to yield: $\boldsymbol{D_s \sim \gamma / M_s^2}$

- This result (essentially a dimensional analysis) is surprisingly accurate (good to an order of magnitude). Typical values for D_s range from 10 to 100 nm, *with elongated particles tending to have large D_s*. It must be noted that the estimation of the critical diameter holds only for spherical and noninteracting particles. *Particles with large shape anisotropy lead to larger critical diameters*.

TABLE 6.8 Estimated single-domain size for spherical particles

Material	D_s (nm)
Fe	14
Co	70
Ni	55
Fe_3O_4	128
γ-Fe_2O_3	166

NANOSCALE SIZE EFFECTS ON THE MAGNETIC PROPERTIES

- **An important length scale** for magnetic phenomena at nanoscale is the **domain size** in ferromagnetic crystals. Typically, the ***domain size is in the range 10-200 nm***. The two most studied finite-size effects in nanoparticles are the **single-domain limit** and the **superparamagnetic limit**. These two key features are represented by two key sizes (or length scales), **the single domain size** and **the superparamagnetic size**, each of which is described below. ***Formation of single-domain particles is only the onset of size effects in the nanoworld***.

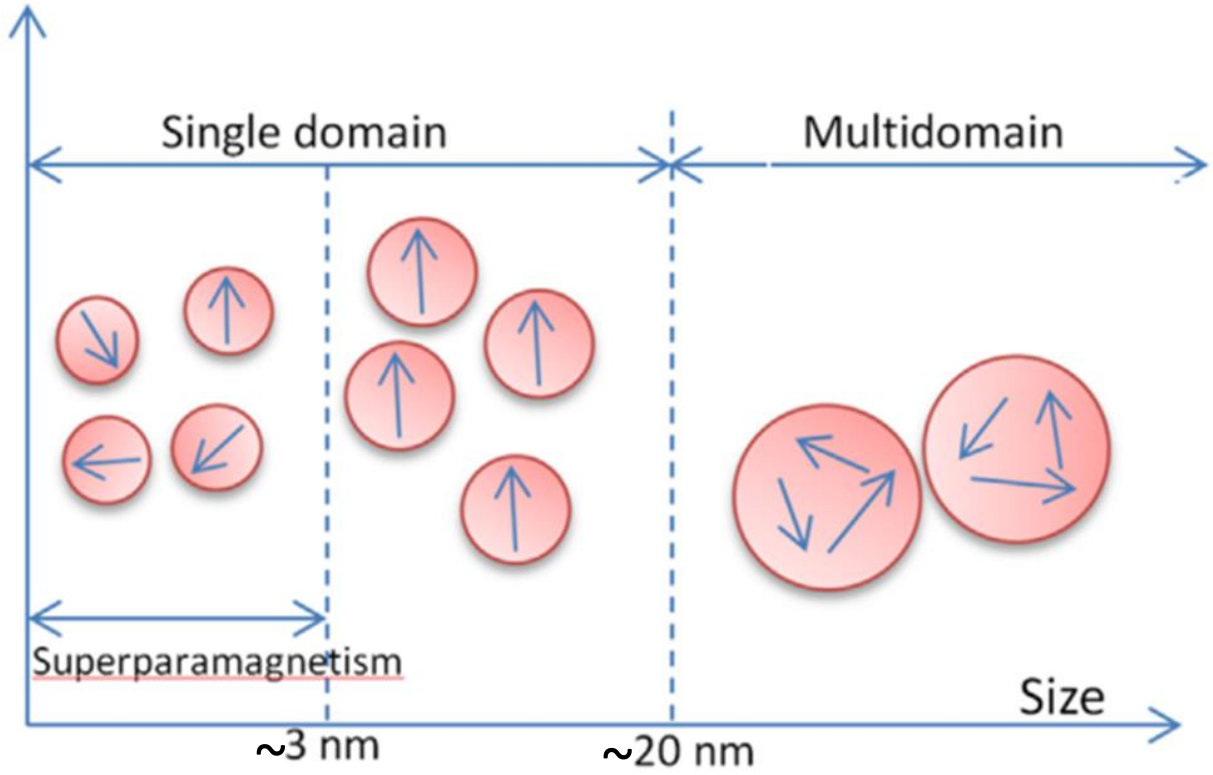


Figure 7.1 Evolution of the magnetic state of magnetic nanoparticles as function of size. The transitions are indicative and depend on the material and size.

- ***A well-known effect*** *in sufficiently small particles is that not only are* they **single domains** but also the ***strength of their magnetism per atom is enhanced***.
- ***Below about 3 nm the strength of magnetism per atom starts to increase***.
- A method for measuring the strength of magnetism (or the magnetic moment) in small free particles is to form a beam of them and pass them through a nonuniform magnetic field. The amount the beam is deflected from its original path is a measure of the nanoparticle magnetic moment; and if the number of atoms in the particles is known, then one obtains the magnetic moment per atom.
- Magnetic moments of atoms are measured in units called ***Bohr magnetons*** or μ_B (after the Nobel laureate Neils Bohr), and the number of Bohr magnetons specifies the strength of the magnetism of a particular type of atom. For example, the magnetic moments of iron, cobalt, nickel, and rhodium atoms within their bulk materials are $2.2\mu_B$, $1.7\mu_B$, $0.6\mu_B$, and $\mathbf{0\mu_B}$ **(bulk rhodium is a *nonmagnetic* metal)**, respectively.

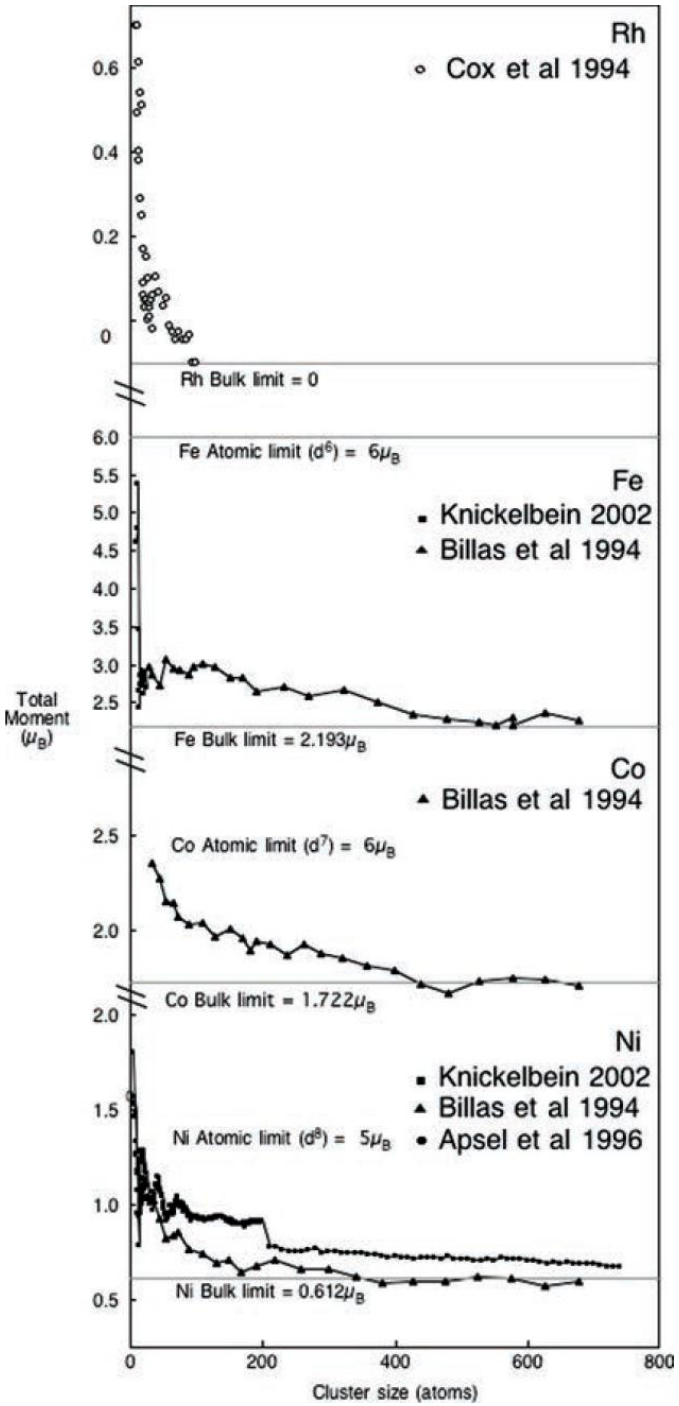
Figure 1.8 shows measurements of the magnetic moment per atom in nanoparticles of the above four metals as a function of the number of atoms in the particle. In the case of iron, cobalt, and nickel, a significant increase in the magnetic moment per atom over the bulk value is observed for particles containing less than about 600 atoms. ***Perhaps most surprisingly*, sufficiently small particles (containing less than about 100 atoms) of the metal rhodium becomes *magnetic*.** Throughout the whole size range in Fig. 1.8, *the fundamental magnetic behavior of the particles is size-dependent*. Note that for Fe (iron) when we go from a 13-atom cluster and to a 12-atom cluster, the magnetic moment per atom would jump from $2.5\mu_B$ to a staggering $5.5\mu_B$ – very close to the single-atom limit of $6\mu_B$. Do not lose sight of how strange a property this is and how it runs counter to our experience in the macroscopic world. It is as strange as a piece of metal changing color if we cut it in half (something else that happens in nanoparticles). This highlights one of the most exciting aspects of nanoparticle research. If one considers a nanoparticle as a building block and can assemble large numbers of them to make a material, then it is possible to tailor the fundamental properties of the building block just by changing its size.

Fig. 1.8 Measured magnetic moments per atom in magnetic nanoparticles. Experimental measurements of the magnetic moment per atom in iron, cobalt, nickel and rhodium (a non-magnetic metal in the bulk) nanoparticles as a function of the number of atoms in the particle.

For **iron, cobalt and nickel, there is a significant increase in the magnetic moment per atom over the bulk** value for particles containing less than about 600 atoms.

Rhodium becomes magnetic in particles containing less than about* 100 *atoms.

Note the very dramatic change in the magnetic moment of iron particles in going from a 12-atom particle to a 13-atom particle. (Reproduced with the permission of the American Association for the Advancement of Science (AAAS) from I. M. L. Billas et al., permission of the American Physical Society from A. J. Cox et al. and S. Apset et al., Copyright 1994 and 1996 and permission of Elsevier Science from M. B. Knickelbein.)

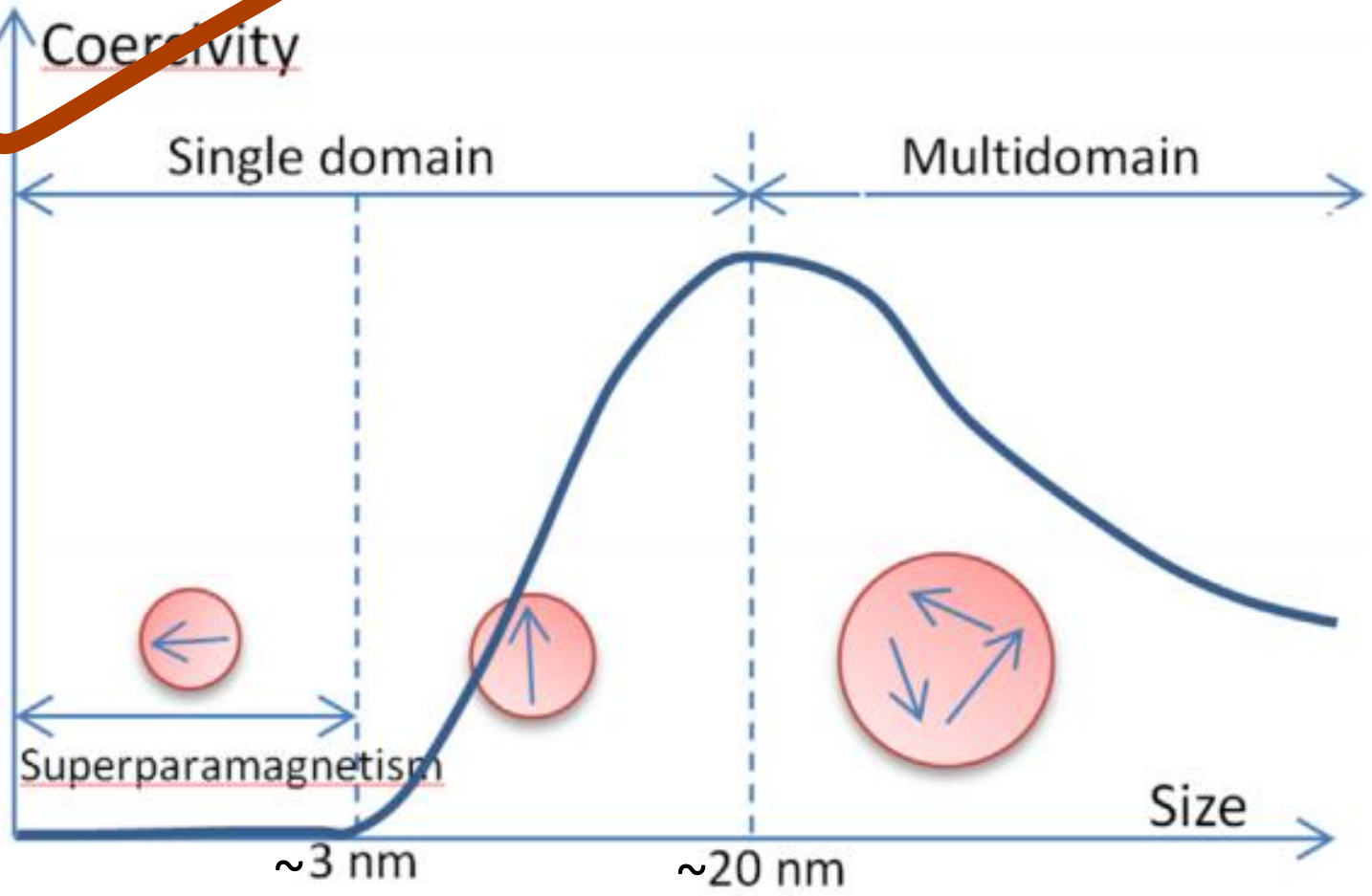


Coercivity of Single-domain Particles

- We have seen earlier that in *ferromagnetic or ferrimagnetic* nanoparticles, *there is a magnetic ordering at room temperature* that tends to *align magnetization in a single direction*. When the particle size is larger, the minimization of dipolar energy induces the creation of magnetic domains inside the particle.
- **At large sizes**, the particle consists of several domains, and the *remnance* and the *coercivity* are ***independent of the particle size***. Here *the magnetization changes by the movement of the domain walls* followed by the rotation of the magnetization at high fields.
- **As the particle size is reduced**, a stage is reached when the particle consists of a single domain. *A single-domain particle is uniformly magnetized with* ***all the spins aligned in the same direction***. **The magnetization reversal** in single-domain particles must occur via **the spin rotation** *since there are* ***no domain walls to move***. Such rotation has to act *against magnetic anisotropy*. Generally speaking, ***it is harder to rotate the spin magnetization*** *than to move a domain wall.* **Shape anisotropy (non-sphericity)** in small magnetic particles is often another source of **high coercivity** (H_c) *observed* ***in small nanoparticles***. The departure from sphericity for single-domain particles is significant and has an influence on the coercivity.

- ***For example,*** *the H_c of Fe nanoparticles increases from ~800 Oe for an aspect ratio of 1 to >10,000 Oe for an aspect ratio of 10.*
- These factors ***lead to a very high coercivity*** *in the single-domain particles* compared to multidomain systems. **At this size, the coercivity increases sharply and stays at a maximum as the particle size is decreased.**
- When ***the size*** *of the magnetic nanoparticle (MNP)* ***decreases further***, *the* ***magnetic energy becomes of the order*** *or* ***smaller than the thermal energy (k_BT)***. Then, the magnetization direction can fluctuate. This state is called **superparamagnetism** by analogy of classical paramagnetism that corresponds to the disordered state of magnetic atoms.

➢ Figure Figure 7.2 shows schematically the *change in coercivity of a single ferromagnetic particle with the change in size*.



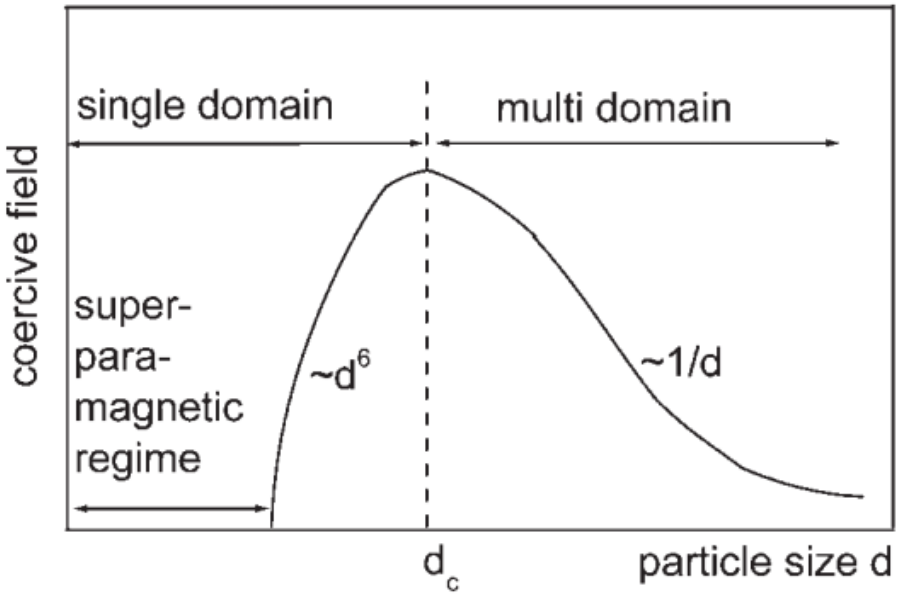


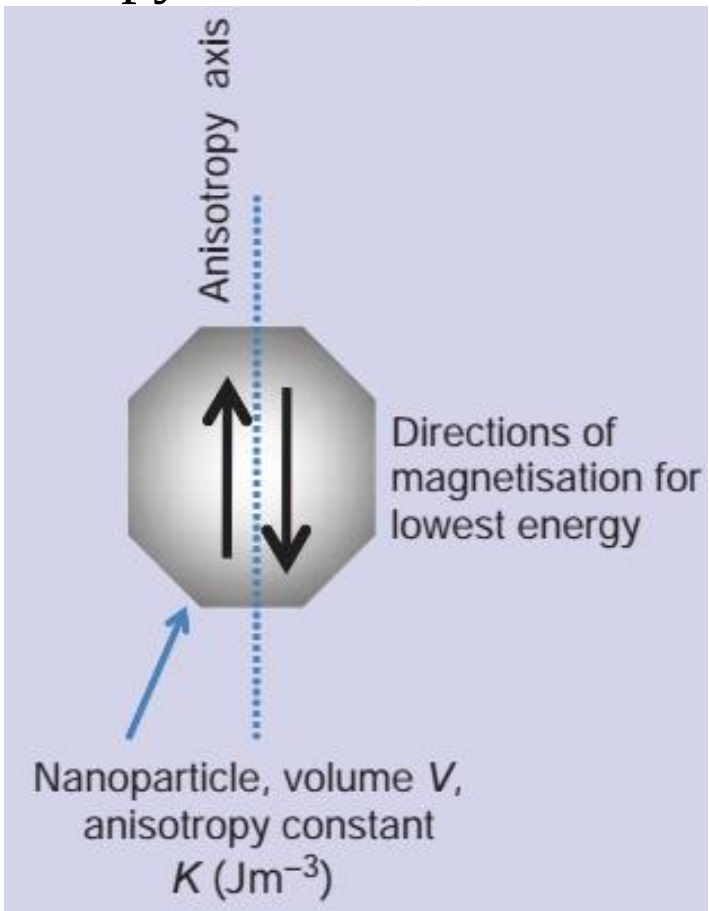
Figure 7.2 Evolution of coercivity as function of size.

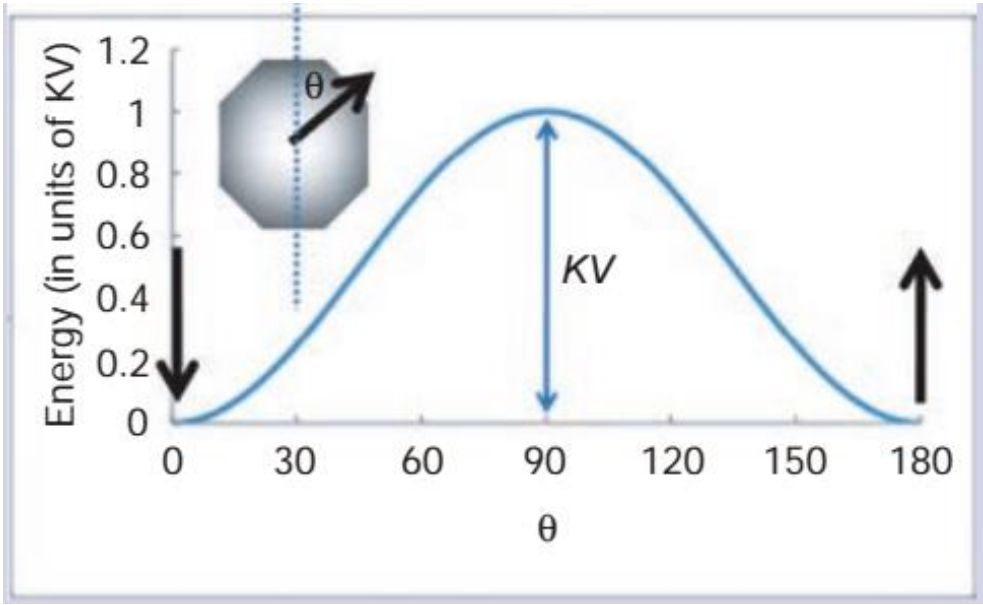
❖ Superparamagnetism

- The second important phenomenon that takes place in nanoscale single-domain magnetic particles is the **superparamagnetic** limit.
- ***Superparamagnetism*** *is the name given to the phenomenon observed in ferromagnetic nanoparticles in which the particles behave in many respects like the particles of a paramagnetic material but with high magnetic moments.*
- Superparamagnetism is a size effect of ferromagnetism.
- Superparamagnetism particles are found to have many technological applications in the field of drug delivery, hyperthermic therapy for treatment of cancer cells, etc.
- The magnetization increases as the volume of the particle increases so as to the power 3 of the size. Figure 7.1 shows evolution of the magnetic state of nanoparticles as *function of size*.

Superparamagnetism

- The magnetic moments flipping in ***superparamagnetism*** can be understood by considering the ***behavior of a well-isolated single-domain particle***.
- The ***magnetic anisotropy energy per particle*** that *is responsible for holding the magnetic moments* along a certain direction can be expressed as follows: $E(\theta) = KV\sin^2\theta$, where V is the particle volume, K is the anisotropy constant, and θ is the angle between the magnetization and the easy axis.





- In general, magnetic nanoparticles can be assumed to have a uniaxial anisotropy; that is, the magnetic energy is lowest when the particle magnetization points in either direction along a single "anisotropy axis" as indicated on the left of the above figure.
- Plotted as a function of the angle between the direction of magnetization and the anisotropy axis, θ, the extra energy arising from the anisotropy, ΔE, is zero when the magnetization points along the anisotropy axis in either direction and is maximum, at a value KV, when it is perpendicular.
- Thus, there is an **energy barrier of height *KV*** to surmount in order to reverse the magnetization. This is the anisotropy barrier. The energy barrier KV separates the two energetically equivalent easy directions of magnetization.
- As the particle gets smaller, so does KV; and for a sufficiently small particle the anisotropy barrier will be comparable to the thermal energy kT. This means that ***thermal fluctuations are sufficient to drive the particle magnetization from one state to the other***, and the particle will ***not stay magnetized***.
- ***The thermal energy can then cause the magnetization vector in the nanoparticle to flip*** *from one easy direction to another* i.e. **no external field is required to change the magnetization direction and *the coercivity becomes zero***.

- This moment is free to move and *respond to an applied field independent of the particle size. Thus,* ***for a given particle size, there is a temperature that marks the transition from a permanent static moment*** (on some defined timescale) ***to one that is fluctuating in a nanoparticle.*** *The temperature at which this happens* is called the ***blocking temperature,*** T_B.

- T_B is called the **blocking temperature**; below T_B the free movement of $\mu_p = M_s V$ is blocked by the anisotropy; above T_B, kT kicks the moment loose so that the system appears superparamagnetic.

- The **temperature below which the particle magnetization is stuck** *in one direction or the other* is known as the ***blocking temperature*** and is calculated below.

- For $kT > KV$, the system behaves as a paramagnet, instead of atomic magnetic moments, there is now a giant (super)moment inside each particle. This system is named a ***superparamagnet***. Such a system has ***no hysteresis*** *(above* T_B*)*, and the data of different temperatures superimpose onto a universal curve of M versus H/T.

- The mean time, τ , that a particle spends in one of the two minimum energy directions (the 'lifetime') is given by the Neel–Brown expression: $\tau = \tau_0 \exp(KV/kT)$
- Preexponential factor (τ_0) is a constant and is known as the Néel relaxation time. Its value was estimated to be 10^{-9} second by Néel, only in more recent years it has become customary to take it as 10^{10} s. Since Néel, more advanced theories have been introduced, but because of its simplicity, the above Equation is still used very often for a first approximation.
- The above relation can be written in the following forms:

Or, $\frac{1}{\tau} = \frac{1}{\tau_0}\exp(-KV/kT)$ Or, $f = f_0\, exp(-KV/kT)$

Here f_0 is a proportionality constant. It is usually assigned a value of ~10^9 sec^{-1}.

- Here τ_0 is the natural lifetime, that is, the lifetime at the high temperature limit. This has been measured to be about 1 nsec for nanoparticles, but its magnitude does not significantly affect the blocking temperature ***(T_B)***.
- ***The lifetime (τ) is only infinite at T = 0,*** so ***to specify a blocking temperature***, *we must decide* ***on what timescale the moment is stuck***.

- For example, we could use the **recording industry norm that the magnetization is stable for 40 years** = 1.26×10^9 sec; then the blocking temperature is

$$T_B = \frac{KV}{k(\log \tau - \log \tau_0)} = \frac{KV}{k(\log(1.26 \times 10^9) - \log(10^{-9}))}$$

- So putting in some numbers, let's say we have a 2-nm-diameter Fe nanoparticle with an anisotropy constant of 2×10^5 J/m^3 (a value measured for 2-nm Fe particles), the blocking temperature is 15 K.
- If we wanted to reliably store data on Fe nanoparticles ***at room temperature*** (say, 300 Kelvin), they would have to have ***a diameter of at least 6 nm***.
- In order to ***store data on yet smaller particles*** we need to **find ways of increasing anisotropy constant *K***. This can be done by using high anisotropy alloys such as FePt or core-shell particles.
- One of the key quantities in particular in the context of **magnetic recording** is the **magnetic anisotropy energy (*KV*)** which determines the stability of the magnetization direction against thermal fluctuations.

- The phenomenon of superparamagnetism is ***timescale-dependent*** due to the stochastic nature of the thermal energy.
- The particle ***appears*** **static** when the moment flipping time (τ) is greater than the measurement time; i.e., if τ_m is the characteristic measurement time, $\tau >> \tau_m$. ***If the time taken for measurement τ_m is smaller than τ, then the superparamagnetic behavior will not be observed because the magnetic moments will not be able to flip within the measurement time***. In this case, **the particle will appear ferromagnetic**. We define the blocking temperature T_B for a particle of volume V as the temperature at which $\tau = \tau_m$.
- The typical experiment with a magnetometer takes 10 to 100 sec. *For a given measurement time, the minimum temperature for the particle to be paramagnetic can be calculated for a given particle size* (i.e. given V). This is the blocking temperature, T_B, for that particle. Thus, for a measurement time of 100 s, and taking f_0 to be 10^9, one gets

$$\frac{1}{100} = 10^9 \exp\left(-\frac{KV}{kT_B}\right) \quad \text{or } KV \approx 25\, kT_B$$

and so, the superparamagnetism will be observed only above a temperature $T_B = KV/25k$ (note: it is **true for** the **100 second *experimental timescale***).

- Similarly, the above relationship can be rearranged to yield the ***critical volume***, $V_{sp} = 25kT_B/K$. A particle with volume smaller than this acts superparamagnetically *on the* 100 second *experimental timescale*. Typical superparamagnetic sizes for spherical (magneto-crystalline anisotropy only) iron and cobalt particles are 16 and 7.6 nm, respectively, for T = 300 K.

- The blocking temperature, above which the thermal energy can cause flipping of the magnetic moment vector, *depends on the particle size*, the *effective anisotropy constant*, the *applied magnetic field* and the *experimental measuring time*.

- In theory, the applied field can decrease the crystal-field anisotropy. *The higher applied field, the less thermal energy is needed to overcome the barrier between the two easy axis orientation and achieve the particles' magnetization*. Thus, the ***blocking temperature decreased* with the increase of the applied field**.

- **The blocking temperature of large particles is higher than small particles**. For small particles, they have *small volume* and thus lower energy barrier (*KV*) and lower blocking temperature.

- **Now consider *an assembly of single domain particles at a temperature $T > T_B$*.**
- Each particle has its magnetic moment oriented along one of the easy directions at any given instant. As this direction can be changed by thermal energy, the magnetization points in different directions in different particles **with the assembly as a whole having no net magnetic moment**.
- *An external magnetic field, if now applied, will tend to align the magnetization in all the particles along the field direction while the thermal energy will tend to redistribute them amongst the different easy directions.*
- *This is similar to the case for a paramagnetic material with atoms replaced by the nanoparticles.* This moment is the moment of the particle and is equal to $\boldsymbol{\mu_p = M_s V}$**.** It **can be quite large, thousands of Bohr magnetons**.
- Taking the example of iron where each atom has a magnetic moment of 2.2 μ_B, a 2 nm diameter particle will have 356 atoms and so $\mu_p = 356 \times 2.2 = 783\ \mu_B$.
- ***This large magnetic moment per particle together with the paramagnetic like behavior led to coin the term* "superparamagnetism"** to describe this phenomenon.

❑ Magnetization Hysteresis Loops Of Superparamagnetic Materials

- A superparamagnet is defined as an assembly of ***giant magnetic moments***, which are not interacting, and which can fluctuate when the thermal energy, kT, is larger than the anisotropy energy. When ***the time between two magnetization fluctuations is shorter than the time used to measure the magnetization of the nanoparticles, without external magnetic field the magnetization appears to be average zero for the nanoparticles***. This is when we see *superparamagnetism*.

- **Thus, superparamagnetic materials have *a high saturation magnetization*** and **zero coercivity and remanence** (***above blocking temperature***), making it to be distinguished from ferromagnetism and paramagnetism, as shown in the following Fig. 7.4.

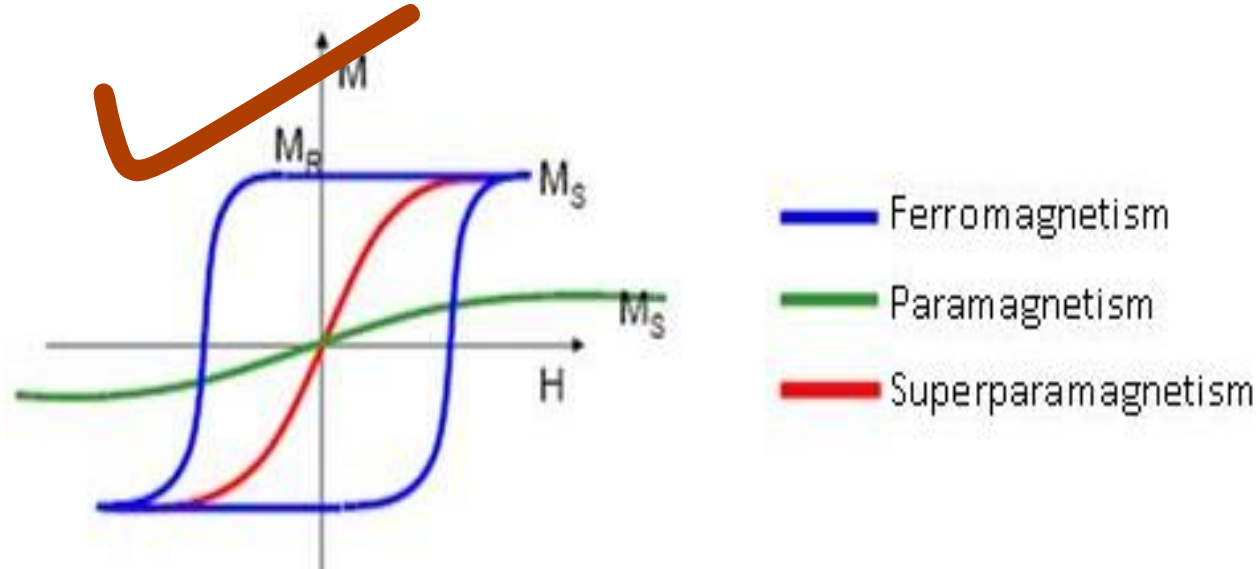


Fig. 7.4 Magnetization hysteresis loops of different magnetic materials at room temperature.

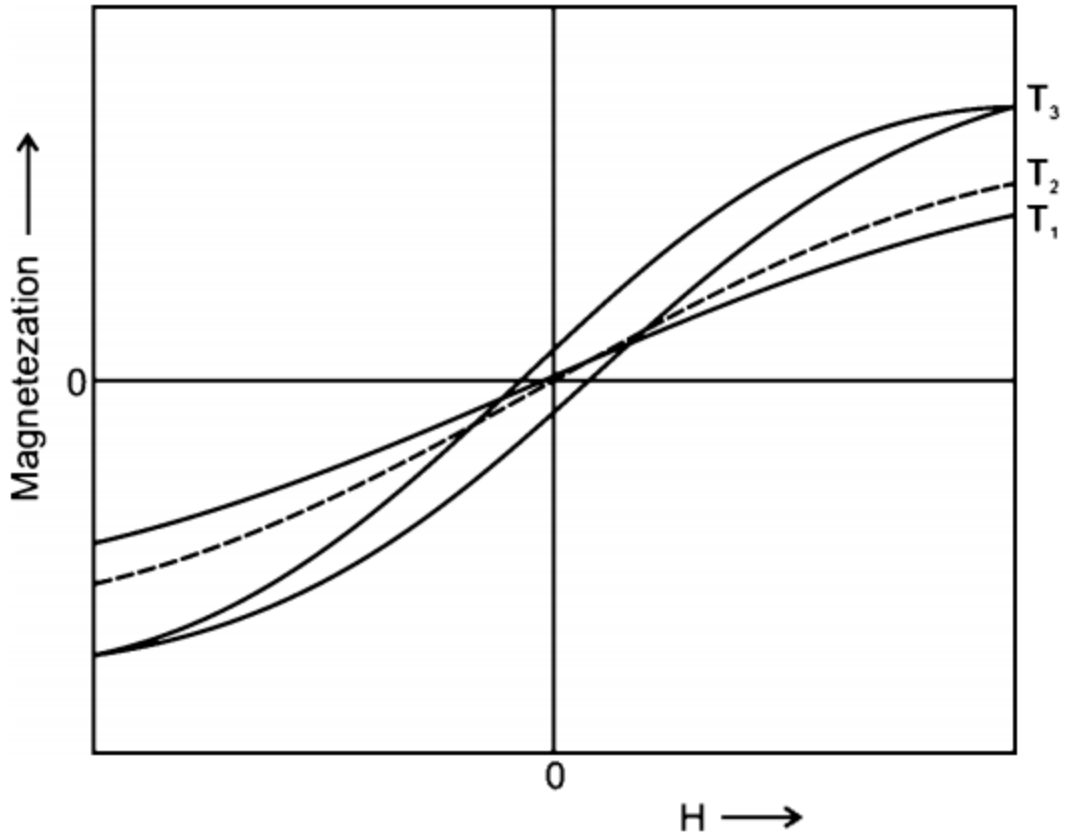


Fig. 6.11. Magnetization curves for an assembly of ferromagnetic particles at temperatures spanning the blocking temperature T_b. Temperatures T_1 and T_2 are above T_b while T_3 is below Tb.

- Figure 7.3 compares the magnetic response for different nanoparticles.
- The response of a superparamagnetic particle follows a Langevin function.
- For larger single-domain particles, the magnetization is blocked if the particle is not in a fluidic environment.
- For multidomain particles, the response is strongly related to the domain creation and destruction.

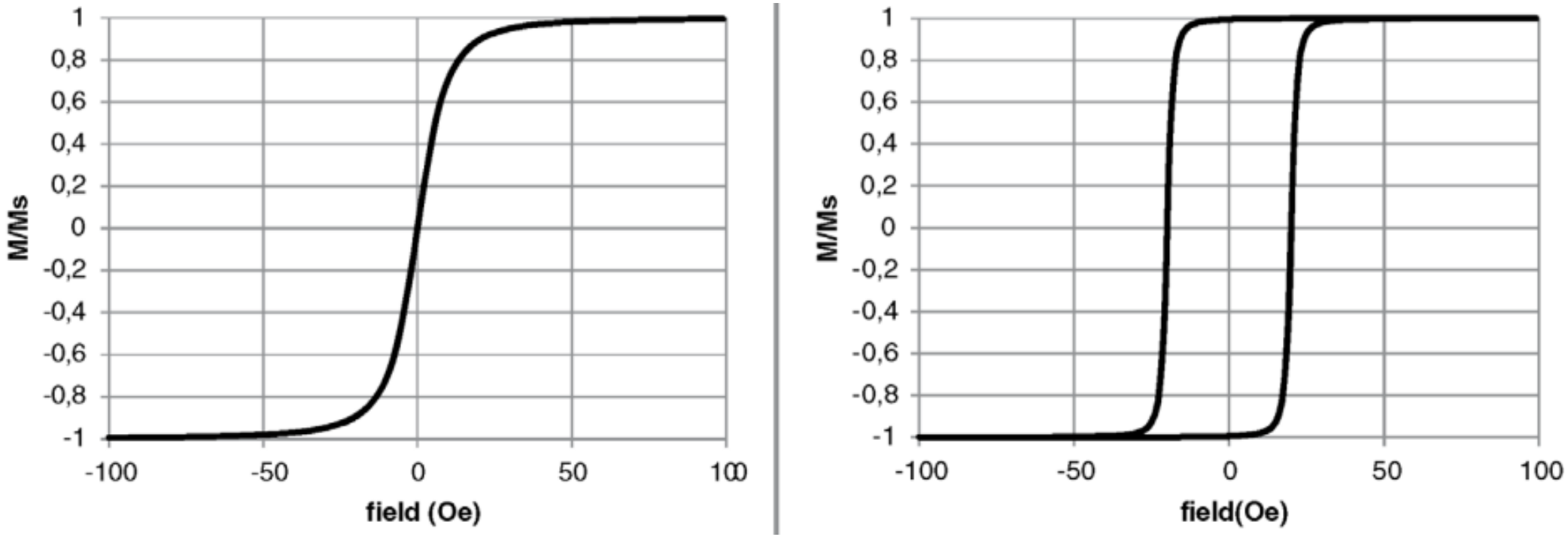


Figure 7.3 Magnetization as function of the applied external field for different nanoparticles. (a) ***Superparamagnetic particles***; (b) ***single-domain particles***.

Synthesis of Magnetic Nanoparticles

In the past decade, a lot of publications described efficient ways to produce shape-controlled, very stable, and reasonably narrow-size distribution particles.

Various chemical and physical methods are applied including coprecipitation, microemulsion, and thermal decomposition, solvothermal, sonochemical, and microwave-assisted chemical vapor deposition and combustion synthesis, carbon arc, and laser pyrolysis synthesis.

Toxicity

At present, magnetic nanoparticles are not incorporated in cosmetics or food items, but they are used as contrast agents in particular for MRI. Magnetic particle imaging has been developed as a new clinical tool and requires the injection of a nonnegligible quantity of MNPs. For these reasons, a number of studies have been done on toxicity and, in particular, on cytotoxicity of these nanoparticles.

Main Classes of Applications of Magnetic Nanoparticles

Contrast Agents for MRI

- This application is the first real medical use of magnetic nanoparticles. Contrast agents have been introduced since nearly 30 years. At the beginning, mainly ***Gd oxide-based particles were used, and more recently ferrite-based particles have been introduced***.
- MRI introduced is based on the detection of the magnetic signal produced by hydrogen atoms. As the density of protons is very high everywhere in the body except in bones, just a density image does not give a good contrast of different tissues.
- For that reason, MRI consists in doing an image of relaxation times that are very different depending on the tissues. *When a superparamagnetic magnetic particle is introduced somewhere, its fluctuations are a very strong relaxation source for the hydrogens in the vicinity and hence it is possible to detect where the nanoparticle is or to highlight a specific tissue* and, in particular, blood. For that reason, depending on the pathology, contrast agents are injected prior to the MRI examination. Today, contrast agents are not only used for angiography but may also be used for tracking cell concentration.

Labeled Nanoparticles for Cell Manipulation and Counting

- This is probably the main use of MNPs. Magnetic nanoparticles are used to label cells or other biological objects such as proteins. When labeled, the targeted object can then be detected and manipulated. The detection is made with magnetic sensors. Different types of approaches are possible: labeled surfaces that capture the targeted object, DNA or protein, with an underneath array of small magnetic sensors or flowing devices where the magnetic particle is dynamically detected.
- The manipulation is made differently: when an MNP is attached to a cell, for example, it is possible to apply a force to the magnetic particle and hence to guide it in a specific direction. A constant magnetic field orientates the particle but does not create a force able to move them. The principle is to have a field gradient. Then, the particle tends to go to where the field is the highest. The use of current lines is an easy way to create field gradients.
- Permanent magnets can also be used, and some devices use mobile permanent magnets to attract labeled cells. The force strength applied on the MNPs varies as function of their magnetic moment and thus of their volume. This explains why large MNPs are preferred for cell manipulation.

Hyperthermia for Cancer Treatment

- One possible use of magnetic nanoparticles is to specifically target tumors and use magnetic nanoparticles to locally heat and destroy cells.
- The way of heating is to apply an AC field and to reverse the particles. The energy transformed to heat is the magnetic energy, which is proportional to the hysteresis area of the particle.
- Hence, particles with largest hysteresis and highest magnetic moment are the most interesting ones.
- For that reason, particles that are just above the single-domain critical size are used. Some groups are also trying to use nanoparticles with specific shapes to increase the crystalline anisotropy.
- The main issue today with these approaches is to properly target the cancer cells.

Ferrofluids

- Ferrofluids (FFs), which are colloidal suspensions, are MNPs dispersed in a liquid carrier that do not settle even after long exposure to gravitation or to a magnetic field. Ferrofluids do not exist in nature and the first ones were produced in the early nineteenth century by Michael Faraday. Stable ferrofluids required, then, a lot of work.
- ***Carrier liquids are water, alcohols or ethers, oils, or organic solvents***. They also contain stabilizers such as surfactants or polymers that are absorbed on the surface with a physical or chemical bonding. ***Conventional ferrofluids use small-sized MNPs, below 15 nm***, but larger particles can also be used for other applications (Figure 7.5).

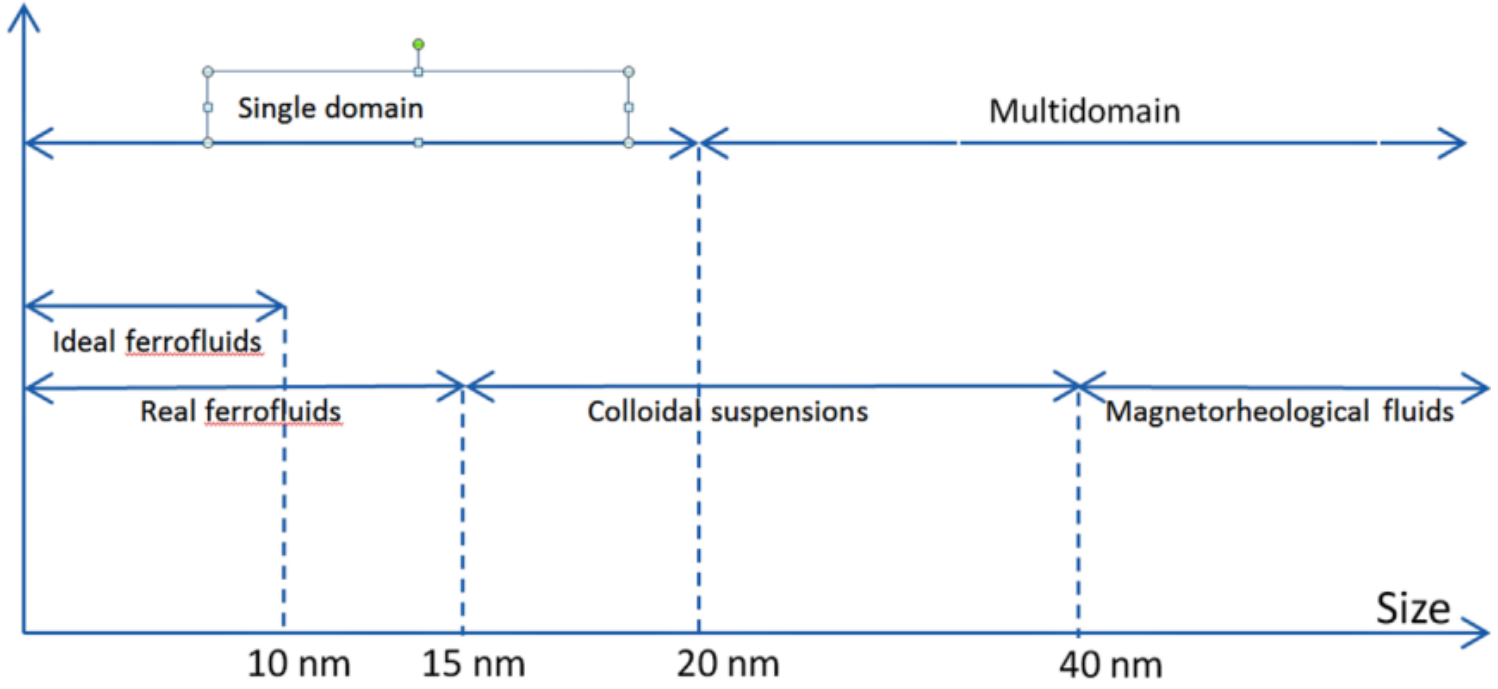


Figure 7.5 Size range of magnetic particles constituting different types of magnetic fluids.

- Apart from the interest in them for fundamental research in understanding hydrodynamics, ferrofluids have various applications.
- These applications are related to **two properties:**
- ✓ The **first** one is the ***possibility to apply a force on the liquid inducing a motion of the liquid*** and the **second** is related to ***their viscosity properties*** *that are* ***modified by the application of a magnetic field***.
- Ferrofluids can be first used to image magnetic domain structures on magnetic objects using a technique developed by Francis Bitter. In nondestructive evaluation, they may be used to image defects.
- Their viscosity properties are useful for making liquid seals. In particular, they are used in hard disks around the spinning drive shafts where the fluid of magnetic particles forms a barrier that prevents debris from entering the interior of the hard drive.
- Ferrofluids can also be used in active dampers for high-end automotive and aerospace applications, because the viscosity can be controlled by an external magnetic field.
- Thermomagnetic properties of ferrofluids are also useful for heat transfer.
- In some loudspeakers, they are used to remove heat from the coils and to control the damping. More recently, ferrofluids are being applied in microfluidic devices for mixing pumping and sorting.

Superparamagnetic materials: Ferrofluids

A well-established application of ferromagnetic nanoparticles is in ***ferrofluids***. **A *ferrofluid*, also called *magnetofiuid*, is a stable dispersion of ferromagnetic particles (e.g. γ-Fe_2O_3, Fe_3O_4) in a liquid.** The liquid is usually oil (such as transformer oil or kerosene) or water. A typical ferrofluid usually contains 3 to 8 vol. % nanoparticles and about 10 % surfactant. The particles in the ferrofluid remain suspended due to the Brownian motion and are prevented from coagulation by the surfactant coating on their surfaces. The ***nanoparticles are single-domain magnets***, and in zero magnetic field (in the absence of a magnetic field), the net magnetic moment of the assembly is zero because their moments point in random directions. ***In a magnetic field gradient, the whole fluid moves to the regions of the highest flux***. *A magnetic field can therefore be used to position and hold the ferrofluid at a desired location*. Therefore, they are employed as contaminant exclusion seals on hard drives of personal computers, and vacuum for high-speed high vacuum motorized spindles. In this latter application, ferrofluid is used to seal the gap between the rotating shaft and the pole piece support structure, as bearings for a rotating shaft (Fig. 6.14).

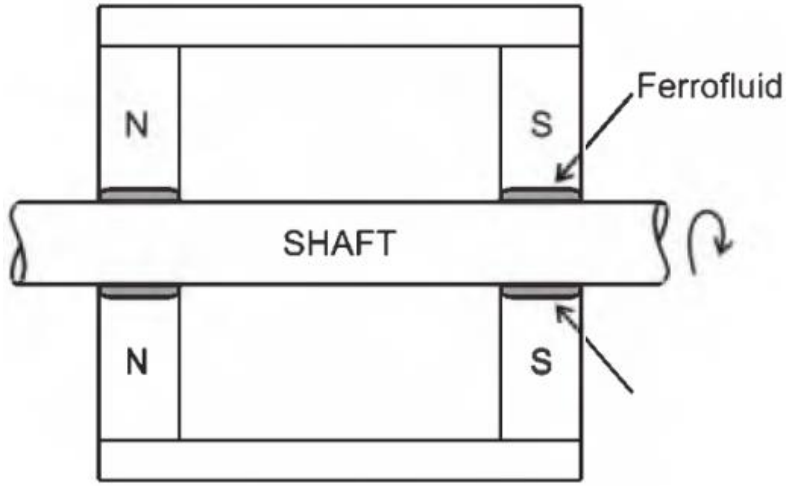


Fig. 6.14. Ferrofluid as bearing for a rotating shaft.

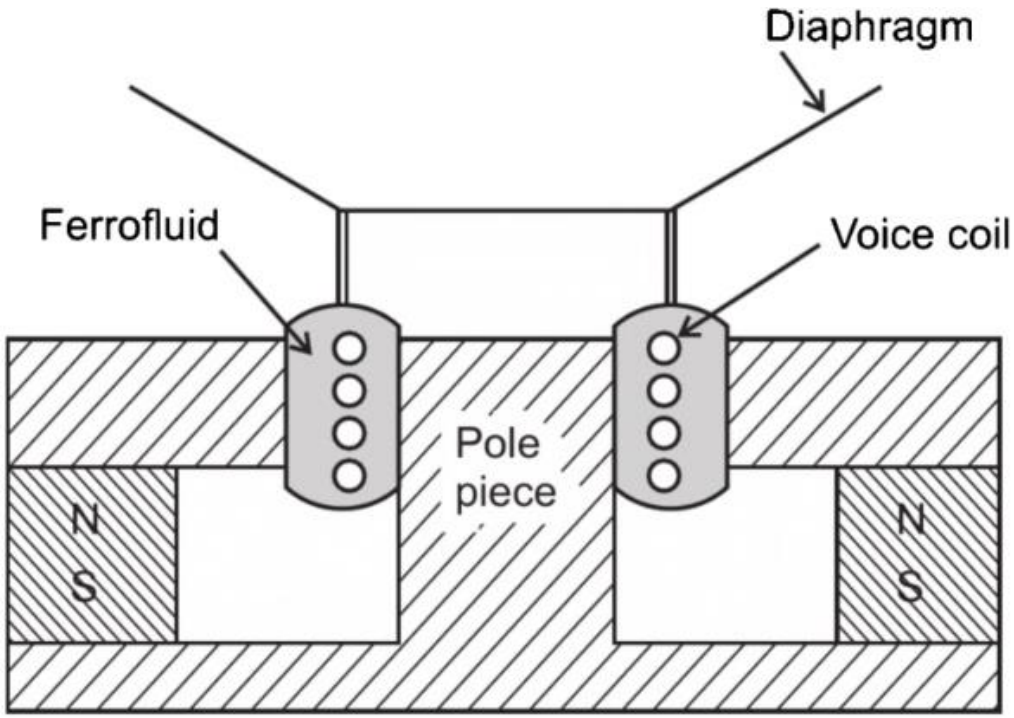
Application of a DC magnetic field to this fluid causes the fluid to congeal into a solid mass, and in the magnetic scale material is not a liquid. A prerequisite for a ferrofluid is that the magnetic particles have nanometer sizes. Ferrofluids have a number of interesting properties, such magnetic-field-dependent anisotropic optical properties. Ferrofluids have some more present commercial uses. Analogous properties are observed in liquid crystals, which consist of long molecules having large electric dipole moments, which can be oriented by the application of an electric field in the fluid phase. Electric field-modulated birefringence property of liquid crystals is widely used in optical devices, such as liquid crystal displays in digital watches, and screens of portable computers. This suggests similar potential applications of ferrofluids employing magnetic field induced birefringence.

Another important property of the ferrofluids is a significant increase in viscosity in the presence of a magnetic field. As the liquid is sheared, the particles tend to keep their moments aligned in the field direction and offer resistance to the shear force. This property is used for damping applications in the shock absorbers of automobiles and in CD and DVD player systems.

A commercially successful application of ferrofluids is in loudspeakers. By placing the voice coil of the loudspeaker inside the ferrofluid surrounded by the field of a permanent magnet, three effects are achieved simultaneously: (a) positioning of the coil in the center position (b) damping of the membrane and (c) conducting away of the heat generated by the coil (Fig. 6.15)

The ferrofluids have found several applications in addition to those indicated above e.g. for forming ***seals between regions of different pressures, magnetic ink printing, electromagnetic drug delivery,*** etc.

Fig. 6.15. Use of a ferrofluid in a loudspeaker.



Giant Magnetoresistance (GMR): Spin-dependent electron scattering in nanomaterials

"GMR can be considered one of the first real applications of the promising field of nanotechnology." —Nobel Prize Committee, October 2007

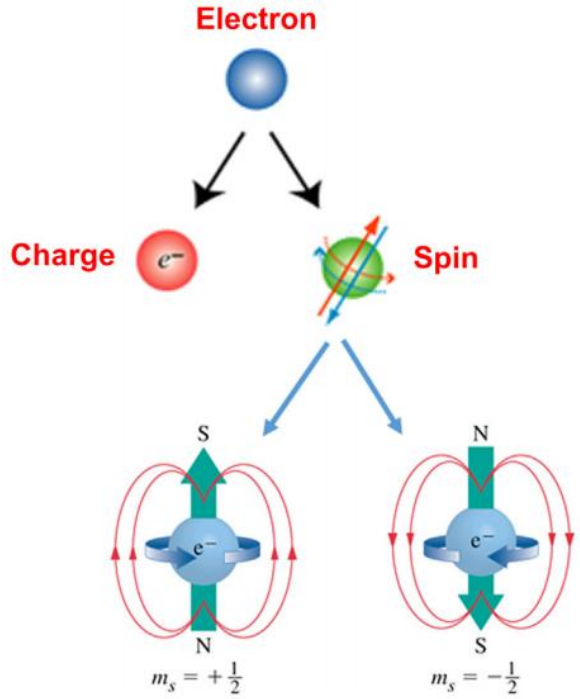
- The discovery of giant magnetoresistance (GMR) in nanostructured artificial materials in 1988 by French scientist, Albert Fert, and German scientist Peter Grünberg has been dramatically improving our digital lives. A. Fert and P. Grünberg were awarded the 2007 Nobel prize in physics for this discovery.
- *The GMR is an outstanding example of how* ***structuring materials at the nanoscale can bring to light fundamental effects, providing new functionalities to applications.***
- GMR's application to ***the read head of hard discs*** *greatly contributed to the fast* ***rise in the density of stored information*** *and led to the extension of the hard disk technology to consumer's electronics.*

- The giant magnetoresistance (GMR) effect represents the first type of this new technology and is *used in the new-generation memory devices such as the Magnetic Random-Access Memory or MRAM* used, for example, in the Apple iPod.
- *Nanoscale magnetic materials are used in magnetoresistive random access memory (MRAM).*
- ***GMR involves*** a change in electrical resistance in response to an externally applied magnetic field and is a quantum mechanical effect which is based on ***spin-dependent scattering*** phenomena in magnetic multilayers.

❖ Introduction to Spin Electronics

- Historically, ***the first spin electronic effect, called the GMR effect***, was discovered by P. Grunberg and A. Fert, who were awarded the Nobel Prize in 2007. The TMR (tunneling magnetoresistance) effect was proposed earlier by Julière in 1975 and observed later. Spin electronics applications are today mainly magnetic sensing with GMR and TMR sensors and magnetic storage with MRAMs and magnetic logics. Both are now in their commercial phase and are still being improved in terms of their performance.

❖ ***Spin electronics is based on the fact*** that electrons have not only **a charge** but also a magnetic moment, called ***spin***, which is quantified.



❖ Electrons have *a charge* and *a spin*, but ***conventionally*** *charges and spins have been considered* ***separately***.

❖ In classical electronics, *charges are moved by electric fields to transmit information* and *are stored in a capacitor to save it* (but the **spins are ignored**).

❖ Other classical technologies, *magnetic recording*, for example, are using *spin but only through its macroscopic manifestation, the magnetization of a ferromagnet*.

- This picture started to change when the discovery of the **giant magnetoresistance** (GMR) of magnetic multilayers *opened the way to an efficient control of the motion of electrons by acting on their spin through the orientation of the magnetization*. This is ***a new type of technology*** that ***exploits the spin of the electron (rather than only its charge) to store and process information***.

- To employ this spin degree of freedom – i.e., that the *spin can assume two different values* – for *faster switching of electronic components with reduced energy consumption* could lead to the next step in electronics and initiate the age of ***spin electronics*** or ***spintronics***.

- The progress toward understanding and implementing spintronics in metallic multilayers and in semiconductors is gaining momentum and ***spintronic read head sensors are already impacting a multibillion-dollar industry***.

  - There are visions that the ***merging of electronics, photonics, and magnetics*** will ultimately lead *to spin-based multifunctional devices, optical switches operating at terahertz frequencies, or quantum bits (qubits) for quantum computation and communication*.

Magnetoresistance

- The phenomenon of ***magnetoresistance (MR)*** is defined as the *change in electrical resistance (R) of a material in response to an externally applied magnetic field (H).*
- Mathematically, it is written as $\boldsymbol{MR = [R(H) - R(0)]/R(0)}$, where $R(H)$ and $R(0)$ are the resistances of the material in the presence of applied magnetic field and zero field, respectively.
- The electrical resistance in a material arises due to the processes of scattering (collision) of electrons such as electron–phonon scattering, electron–electron scattering, electron–impurity scattering, etc.
- In a real crystal, the atoms are not fixed at the perfect lattice position, but always vibrate around their equilibrium position due to thermal energy. When electrons pass by these vibrating atoms, they get scattered (electron-phonon interaction) and contribute to electrical resistance.
- In a real world, it is impossible to get a crystal completely devoid of defects or impurities. So, during the flow, the electrons get scattered by these impurities or defects as well as other electrons.

Family of Magnetoresistance

- There are many magnetoresistance contributions, and a comprehensive description of these contribution goes far beyond our scope.
- ***(i) Bulk MR** is the property of all metals and refers to **the increase in the resistance of metals in the presence of an external magnetic field**.* When a normal material is subjected to an external magnetic field (**B**), the trajectories of the electrons inside the material get affected and follow a helical motion due to the Lorentz force [q(**v** x **B**)], where q is charge and **v** is velocity.
- ✓ In this case, the magnetic field a magnetic field H curves the path of conduction electrons in nonmagnetic metals to move in a helical trajectory with the magnetic field direction as the helix axis. This increases the path length and, so, the number of scattering events. However, the field must be strong enough to curve the helix to have a pitch smaller than the mean free path of the electrons. This process usually gives a small positive ordinary magnetoresistance (OMR) of 1% in the field of order of 1 Tesla and varies as B^2 in low field regime. It also *does **not saturate*** with increasing field. *All metals show magnetoresistance, but the effect is quite small, except for the ferromagnetic metals.* In ferromagnetic metals, the change in resistance can be up to 2% when saturation fields are used.

- **(ii)** In the year 1857, W Thomson (Lord Kelvin) discovered a new phenomenon when he was measuring the resistance of iron and nickel in the presence of a magnetic field. He found a 0.2% increase in the resistance of Fe when the magnetic field was applied longitudinally and a 0.4% decrease in resistance when the field was applied in transverse direction. This phenomenon is known as ***anisotropic magnetoresistance (AMR)***.

- ✓ Anisotropic magnetoresistance (AMR) occurs in magnetic materials and reflects spin–orbit coupling. The spin perturbs the surrounding electron cloud and makes the scattering dependent on the spin direction. It ***originates from anisotropic spin-orbit interaction*** and causes the resistance to depend on the relative orientation of electric current and magnetization. For example, the resistivity depends on whether the electrons move in the x- or z-direction. However, it was subsequently found that at room temperature, the AMR in bulk alloys of Ni-Fe and Ni-Co could be of the order of 3–5%.

- ✓ AMR thin films were used for the magnetoresistive effects in connection with read out heads for magnetic disks and as magnetic field sensors.

- ✓ ***The early 'read heads' for the magnetically stored data were based on the magnetoresistance of the Ni-Fe (perm)alloy thin films.***

- ***(iii)*** The term *Giant Magneto-Resistance (GMR)* refers to a ***large change in the resistance*** of certain **ferromagnetic thin film structures** *on* ***changing the applied magnetic field***.
- The phenomenon of GMR is *quite different* from the *ordinary* magneto-resistance effects such as regular *bulk magnetoresistance (MR)* and *anisotropic magnetoresistance (AMR)* which are also exhibited in layered systems.
- Giant magnetoresistance (GMR) and grain-boundary magnetoresistance are due to rapid magnetization variations, which act as scattering centers.
- *The GMR effect is a quantum mechanical effect observed in layered magnetic thin film structures that are composed of alternating layers of ferromagnetic and non-magnetic metallic films* (Fig. 1). GMR is based on the spin-dependent scattering of the electrons *from the interface of a normal (nonmagnetic) and a ferromagnetic metal*.
- Tunnel magnetoresistance (TMR) means ***spin-dependent electron tunneling*** through a thin insulating layer.

- ***(iv)*** In addition to *ordinary (bulk)*, *anisotropic*, and *giant magnetoresistance*, there also exists *"colossal" magnetoresistance (CMR)* which was found in *doped manganite perovskites* such as $La_{3-x}Ca_xMnO_3$. ***The CMR effect can be extremely large resulting in a resistance change of a few orders in magnitude.*** **CMR originates from a *metal-insulator transition* where** the antiferromagnetic insulator $LaMnO_3$ ($La^{3+}Mn^{3+}O^{2-}{}_3$) becomes a ferromagnetic conductor in an external magnetic field H in the low temperature near the Curie temperature.

- It *requires magnetic fields of the order of several Tesla. The latter property makes the applicability of CMR materials limited.*

- ***The 151-year-old AMR remained as the main source of magnetoresistance in ferromagnets till 1988***, and there was hardly any improvement in the performance of magnetoresistive material with time. The general consensus in 1980s was that it was not possible to significantly improve the performance of magnetic sensors based on magnetoresistive effect.

- In 1988, there was an upsurge in the field of magnetoresistance as Fert's group discovered that the application of magnetic field to a Fe/Cr multilayer results in a huge reduction of electrical resistance, which was found to be *much higher than OMR and AMR* and ***named it as giant magnetoresistance (GMR)***.

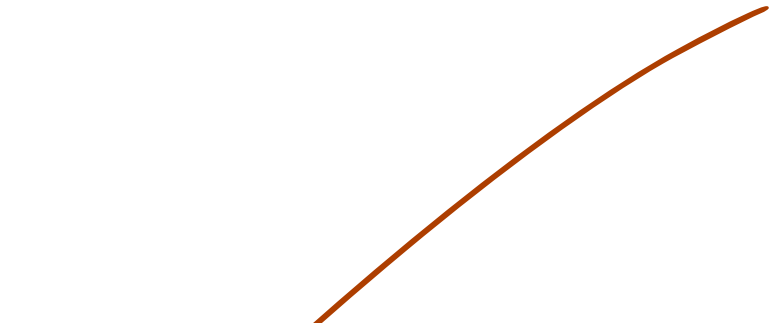
- A similar effect in Fe/Cr/Fe trilayer structure was simultaneously discovered by Grünberg's group. Both the above-mentioned structures were grown by Molecular Beam Epitaxy (MBE) technique. Therefore, the discovery of GMR was solely possible due to the development in thin film deposition techniques such as MBE, sputtering, etc., and surprisingly it was found that the layered system grown by these techniques were completely different in their properties from their constitutive bulk material. Albert Fert and Peter Grünberg were awarded the Nobel Prize in 2007 for their independent discovery of GMR .

Basic GMR structures

1. Multilayer

A multilayered structure consists of *two or more magnetic layers* of a Fe–Co–Ni alloy, as can be permalloy, *separated by a very thin* ***nonmagnetic conductive*** *layer*, as can be Cu. A general scheme is shown in Figure 1(a). With ***magnetic films of about 4–6 nm*** width and ***a conductor layer of about 3–5 nm***, the magnetic coupling between layers is slightly small. With these configurations, *MR levels of about 4%–9% are achieved*, with linear ranges of about 50 Oe. The *figures of merit* of these devices *can be improved by continuously repeating* the basic structure.

Successful applications of multilayered structures in magnetic field sensing include bioelectronics and angle detectors.



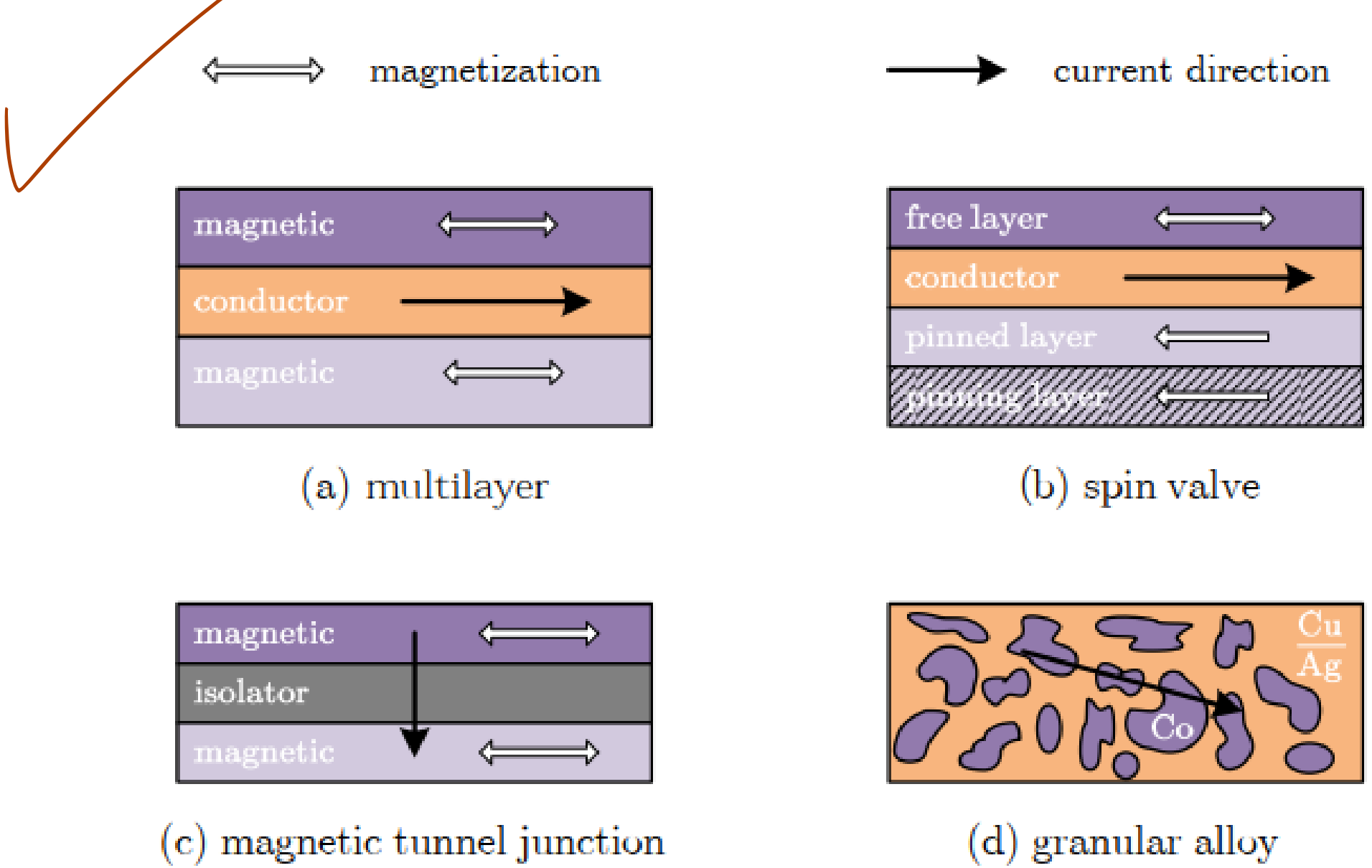


Figure 1. Basic GMR structures.

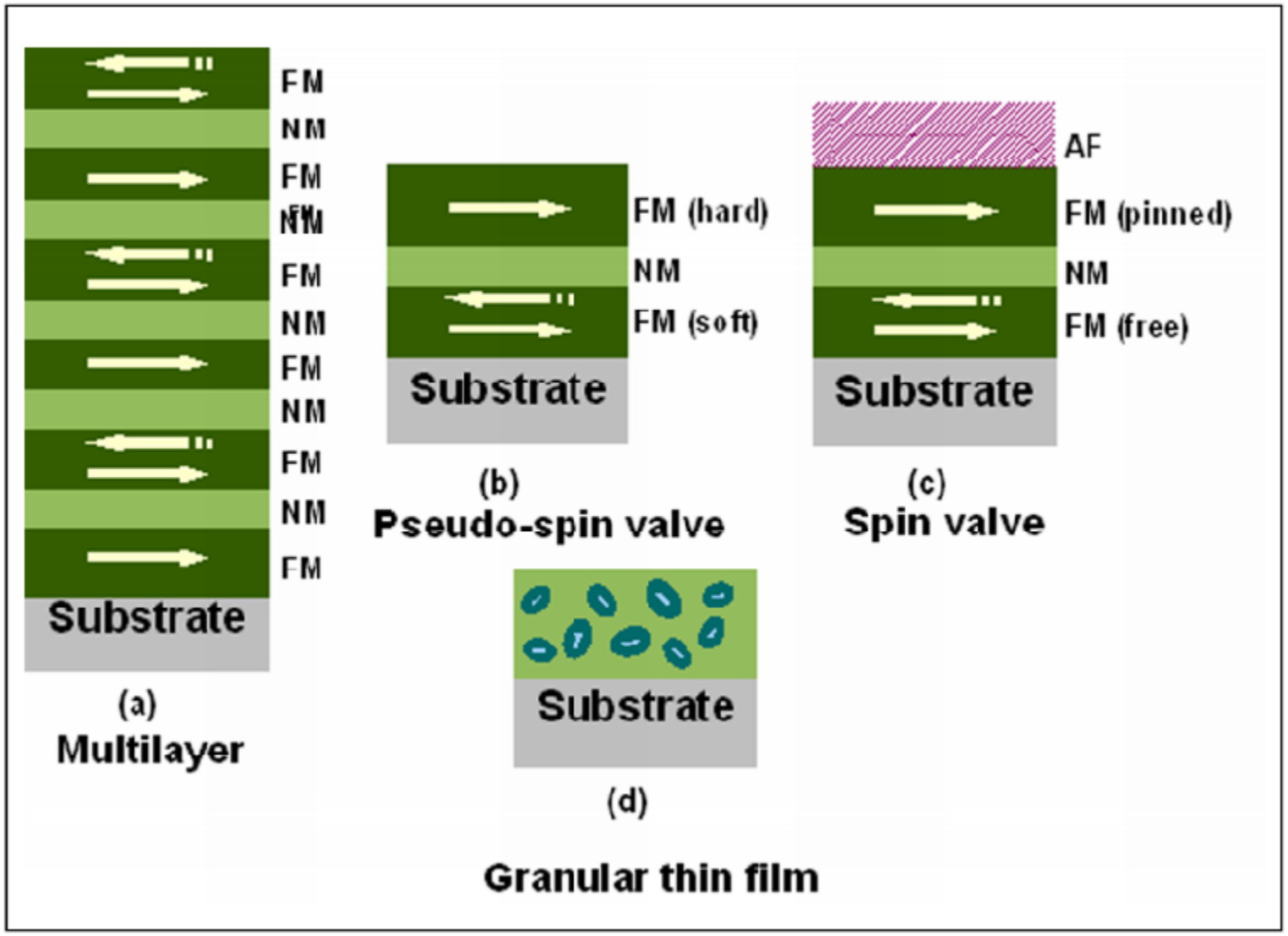
Figure 2.Different GMR structures (a) multilayer (b) pseudo spin valve (c) spin valve (d) granular thin film.

(a) In the multilayer the ferromagnetic layers (FM) are separated by nonmagnetic (NM) spacer layers. At zero field, ferromagnets are aligned antiparallel as indicated by full and partial solid arrows. At saturation field the magnetic moments are aligned parallel (the solid arrows).

(b) In the pseudo-spin valve, the magnetic structure combines a hard and soft magnetic layer; the switching of ferromagnetic layers occur at different magnetic fields providing a change in the relative orientation of magnetization.

(c) In the spin valve, the top FM is pinned by the attached antiferromagnetic (AF) layer. The bottom FM layer is free to rotate by applied magnetic field.

(d)In the granular material, magnetic precipitates are embedded in the non-magnetic metallic material. The application of magnetic field aligns the magnetic moments of randomly oriented granules.



2. Spin Valve

A spin valve (Fig. 1b) is a GMR-based device with two **ferromagnetic layers** (e.g., Fe, Ni, Co) separated by a thin **non-magnetic conductor** layer (e.g., Cu, Cr) where ***one of the ferromagnetic layers*** is "***pinned***" to *an antiferromagnetic layer*, i.e., its magnetization cannot be changed by *moderate* magnetic fields. The blocking is obtained by using an antiferromagnet, typically PtMn or IrMn, coupled with a CoFe layer. The antiferromagnet has the property of being insensitive to the external magnetic field. Furthermore, it has typically a blocking temperature below its ordering temperature. Below the blocking temperature, it is very hard to move it and above this temperature it becomes easy to move it with a field. The blocking temperature for IrMn is typically 240 °C and for PtMn about 340 °C. For that reason, PtMn is more interesting for high-temperature applications such as in automotive. Often an extra synthetic antiferromagnet (SAF) is added to increase the field stability.

The ***second magnetic layer is usually a free layer***, that is, able to rotate easily in external magnetic fields. It is in general composed of a bilayer of NiFe and CoFe. NiFe, called permalloy, is a very soft material, whereas CoFe ensures a high spin polarization.

The GMR spacer is generally a Cu thin layer. The typical **Cu thickness is about 2 nm**, and ***this insures a magnetic decoupling*** of the two magnetic layers and *a low enough spin depolarization*.

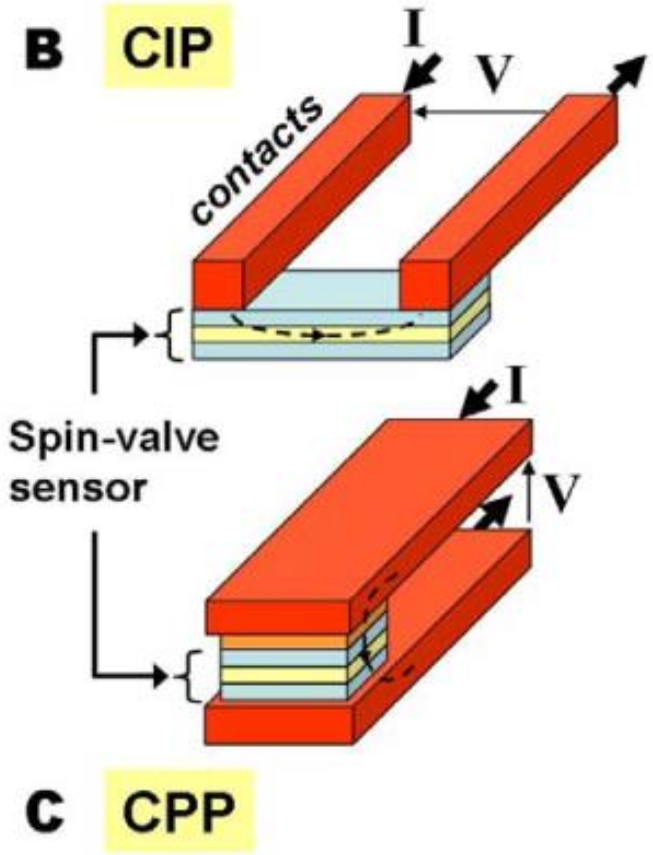
The magnetization of the free ferromagnetic layer can be changed easily by a magnetic field giving rise to a *resistance change of* ***5–10%*** in a relatively small magnetic field. *The rotation of the "free" layer magnetization "opens" in parallel (to "pinned" orientation) configuration or "closes" in antiparallel configuration the flow of electrons, acting somehow as a* ***valve***.

- ***Commercial GMR read heads use the spin-valve format for hard drives*** and magnetic field sensors.

The trilayers in the spin valve can be arranged in either CPP (current perpendicular to plane) or CIP (current in plane) configurations as shown in Fig. 6.5. In the "current in plane" (CIP) type, the arrangement is such that the current passes along the multilayered structure whereas in "current perpendicular to plane" (CPP) spin valve, the current passes across (perpendicular to) the multilayered structure (Fig. 2). It is usually CPP configuration, which gives a better performance and hence is the most commonly used. The thickness of NM layer is usually a few nanometers to reduce spin flip scattering. Historically, Cu is used for the NM layer, whereas Fe, Co, and permalloy (an alloy of nickel and iron) are the preferred choices for the FM layers.

Figure 2: The spin valve. (B) Schematic arrangement of the "current in plane" (CIP) spin valve sensor in a read head.

(C). Schematic arrangement of the "current perpendicular to plane" (CPP) spin valve sensor in a read head.



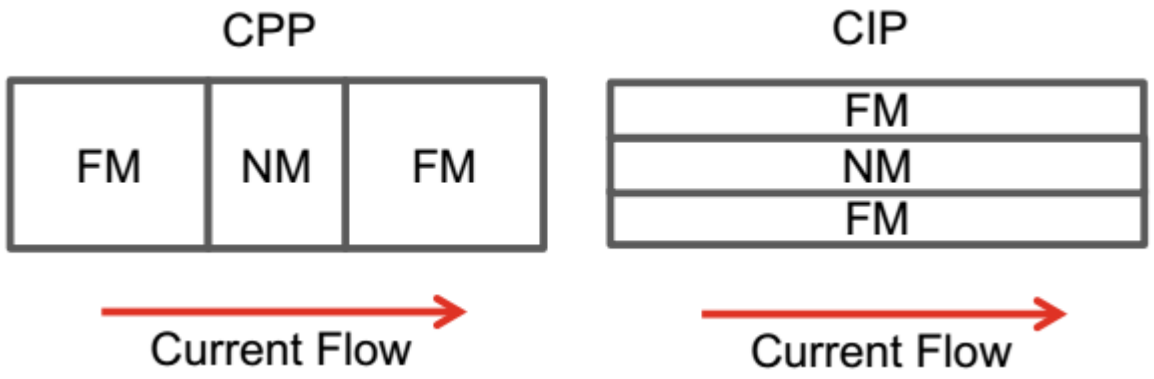


Fig. 6.5 GMR devices. CPP and CIP configurations

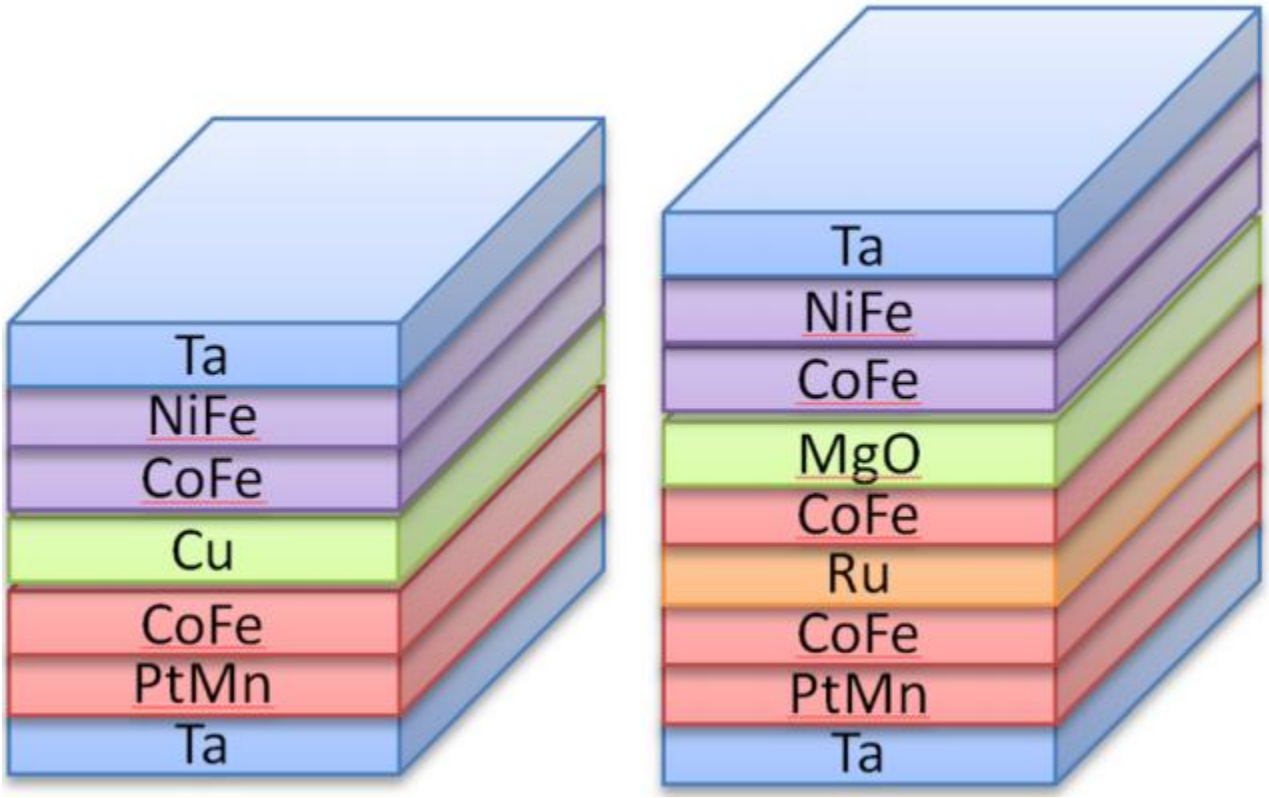


Figure 1.4 GMR simple spin valve (a). TMR spin valve with an SAF configuration (b).

3. Magnetic tunneling junction (MTJ) or ***TMR (tunnel magnetoresistance)***

A magnetic tunneling junction (MTJ) is a device (Fig. 1c) in which a ***pinned*** *ferromagnetic layer and a* ***free*** *ferromagnetic layer are* ***separated*** *by a very thin* ***insulating layer*** (e.g., Al_2O_3, MgO). The **electron tunneling phenomenon** *arises from the wave nature* of the electrons while the resulting junction electrical conductance is determined by the evanescent state of the electron wave function within the tunneling barrier. The *tunneling magnetoresistance (TMR)* arises from the difference in the electronic density of states (DOS) at the Fermi level, E_F, between the spin-up $N\uparrow(E_F)$ and spin-down $N\downarrow(E_F)$ electrons. Since ***electrons preserve their spin orientation during the tunneling process, electrons can only tunnel into the sub-bands of the same spin orientation***, thus, in the case of the same spin orientation of the two electrodes, *the tunneling conductance is proportional to the product of the Fermi level DOS values of the two electrodes*. A change from a parallel magnetization to an antiparallel magnetization of the two electrodes will result in an exchange between the two spin sub-bands of one of the electrodes for the tunneling process with a decrease of the conductance, provided that the Fermi level DOS values are different for the two spin sub-bands. *Typical* ***MR levels of MTJ are above 40%***, with Al_2O_3 as an isolating layer. More recently, high TMR values of about 200% have been reported for Co(001)/MgO(001)/Co(001) tunneling junctions. Saturation fields are in the order of 1-100 Oe.

MTJ (magnetic tunnel junctions), also called TMR (tunnel magnetoresistance), has the same structure as GMR's, but the spacer is a very thin insulating layer called barrier. The transport through this spacer is no longer a diffusive path but requires a tunnel transport, and the TMR ratio mainly depends on the electrode spin polarization at the interface. This has several consequences. The first consequence is that the resistance of the device increases exponentially as the thickness of the barrier increases and hence has to be very well controlled; the second is that the effect can be much higher than the GMR effect; the third is that for practical devices, resistance and size are partly decoupled; and finally the current has to flow through the barrier, so it requires top and down contacts. MgO insulating barriers create a symmetry filtering that increases the TMR ratios and thus are generally used.

TMR is also the basis of magnetic RAM (MRAM), a nonvolatile memory that uses magnetic moments to retain data instead of electrical charges.

4. Granular alloys

Granular films of Co–Cu and Co–Ag also exhibit a *giant magnetoresistance effect*. In this case, the giant magnetoresistance effect is due to the spin-dependent scattering taking place at the boundaries of Co clusters embedded in the host lattice, as depicted in Figure 1(d). Because of these binary systems are not miscible, the characteristics of the devices are highly conditioned by the growth conditions and the post-deposition treatments. In fact, the amount of magnetoresistance is accepted to be associated with the size of the Co clusters.

- In order to observe GMR in a magnetic multilayer, one must be able to orient the magnetic moments of the fereromagnetic layers in the parallel direction by applying a magnetic field, and in zero field they should have antiparallel magnetization arrangement.
- This antiparallel magnetization arrangement in multilayer is achieved due to interlayer exchange coupling which is antiferromagnetic (AF) in nature. The interlayer exchange coupling is mediated by the mobile electrons in the non-magnetic spacer layer like Cr.
- The interlayer exchange coupling oscillates between ferromagnetic and antiferromagnetic as a function of the non-magnetic spacer layer thickness. By suitably and judiciously tuning the non-magnetic spacer layer thickness, one can have antiparallel magnetization alignment in zero field.
- It is not that the antiferromagnetic interlayer exchange coupling is the only way to achieve GMR, there are other ways to achieve it. Antiparallel magnetization alignment can also be achieved by introducing ferromagnetic layers of different coercivities (pseudo-spin valve structure), i.e., by a combination of soft and hard ferromagnetic layers. In this case, the magnetic moments of the soft and hard ferromagnetic layers switch at different values of applied magnetic field providing a window of field values in which the layers remain in an antiparallel state with respect to each other, and thus leading to high resistance.

- Once the applied magnetic field crosses the coercive field (H_c) of hard ferromagnetic layer, both the layers align in parallel state leading to low resistance. Another way to change the alignment of the ferromagnetic layers is to tune the coercivity of one ferromagnetic layer to a higher value. This is possible when one ferromagnetic layer is pinned by the exchange coupling with an adjacent antiferromagnetic layer (spin valve structure). The other unpinned ferromagnetic layer is free to rotate with the applied magnetic field, thus providing a parallel or an antiparallel state. Though the GMR value in magnetic multilayer is higher, spin valves are more attractive because of the small magnetic field required to change the resistance of this structure. Magnetic granular systems are also ideal candidates from the GMR point of view. In these materials ferromagnetic precipitates are embedded in a non-magnetic host metal film. The randomly oriented ferromagnetic precipitates tend to align with which the application of magnetic field leads to a drop in the resistance. The different types of systems described above which exhibit GMR behavior are shown in Figure 2.

❑ **Underlying mechanism of GMR:** For the findings of both Fert and Grünberg in connection with GMR, the underlying mechanism was ***discussed in terms of spin dependent scattering*** for which, the **spin polarization** in the material plays the major role in determining the GMR. They also found that the ***interlayer exchange coupling*** plays a crucial role for getting the right multilayer structure which can show GMR effect.

❖ Spin Polarization

➢ **The base of spin electronics** is the fact that ***conduction electrons*** *in magnetic materials* ***are polarized***, that is, *the* ***direction of the spin is not arbitrary*** but ***has a preferred direction imposed*** by ***the magnetization*** *of the material*. That polarization strongly depends on the nature of the material and on its crystalline structure. CoFe is the 3D alloy mainly used in devices as it is easy to deposit and presents a large spin polarization, around 70%. See more about it later.

❖ Spin Diffusion Length

➢ When a polarized electron is sent inside a material, it experiences collisions. A lot of collisions are elastic, and the spin is conserved, while some are inelastic and may conduct to a change in its spin orientation. The ***typical length on which the memory of the spin is lost is few nanometers at room temperature***. This implies that in *a* ***nonmagnetic material***, *a spin polarization cannot be maintained beyond that distance*. The impact is that all ***spin electronics devices have to be engineered with at least one dimension at few nanometer scale***. The thin-film technology and micro-nanofabrication techniques have hence played an essential role in the development of spin electronics.

❖ Spin Polarization

Spin-polarized transport will occur naturally in any material for which there is an ***imbalance of the spin populations at the Fermi level***. This imbalance commonly occurs in ferromagnetic materials (FMs) because the ***density of states available to spin-up and spin-down electrons*** is often nearly identical, but the states are ***shifted in energy*** with respect to each other (Fig.1.2). This shift results in an unequal filling of the bands, which is the source of the net magnetic moment for the materials, but it can also cause the spin-up and spin-down carriers at the Fermi level to be unequal in number, character, and mobility. This inequality can produce a net spin polarization in a transport measurement.

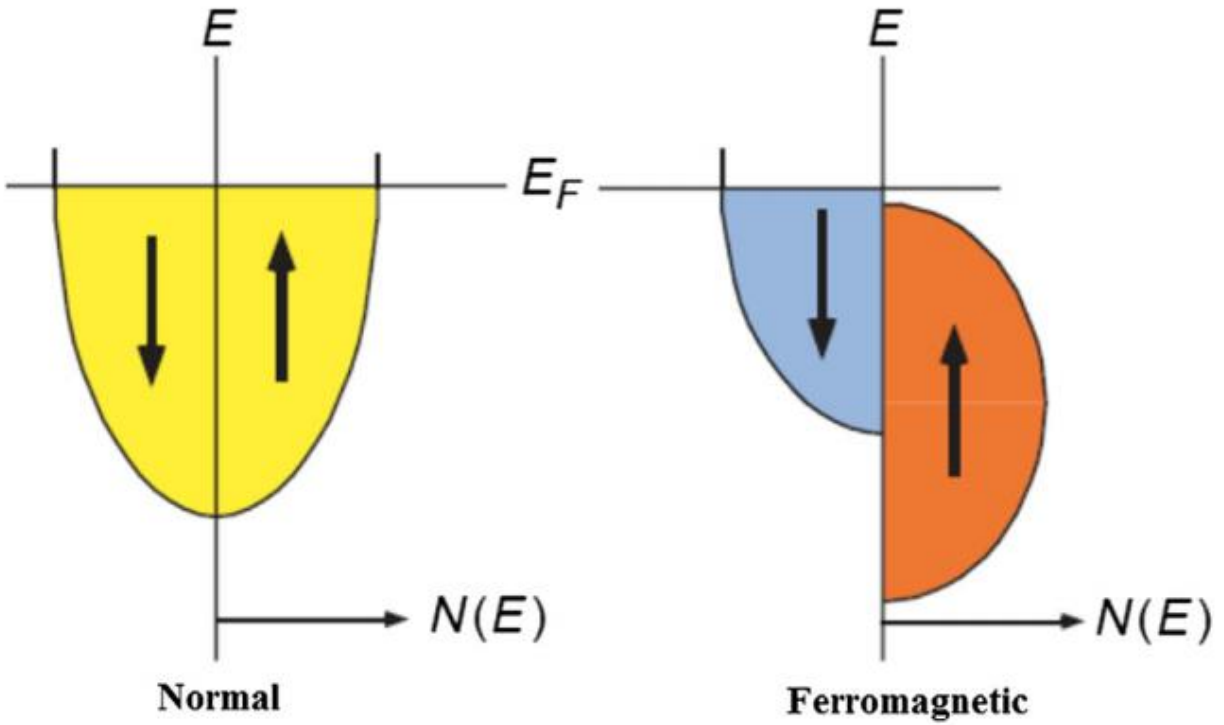


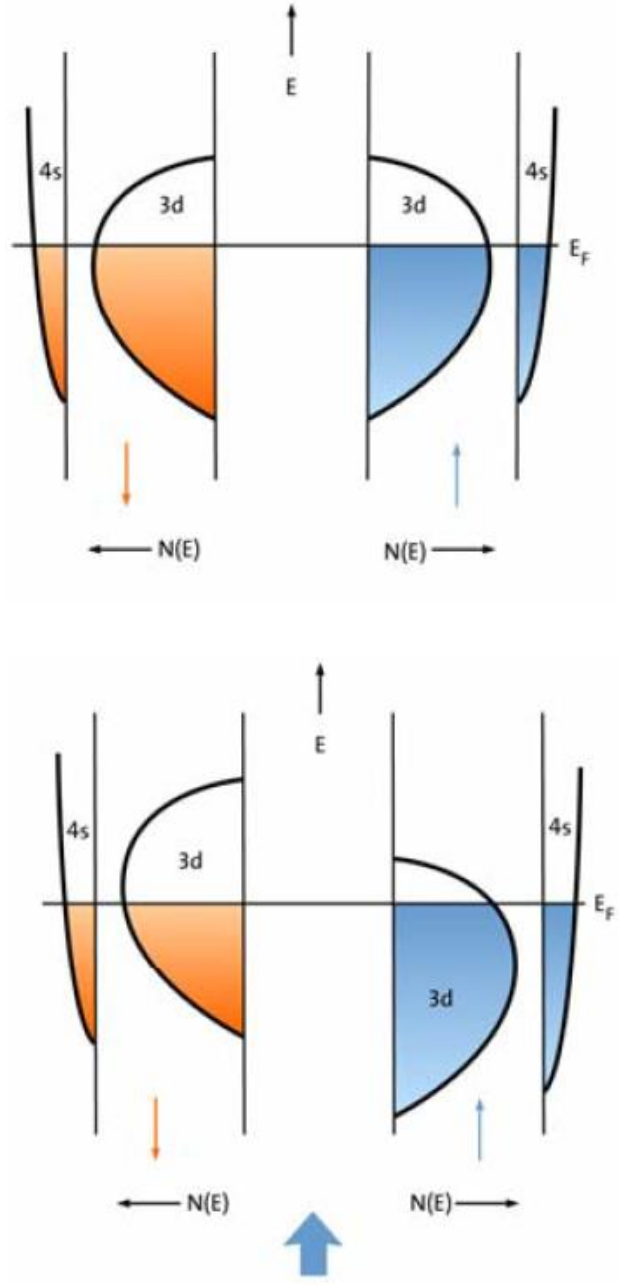
FIGURE 1.2 A schematic representation of the density of electronic states that are available to electrons in a normal metal and in a ferromagnetic metal whose majority-spin states are completely filled. *E*, the electron energy; E_F, the Fermi level; *N*(*E*), density of states. Courtesy from Prinz, G.A., 1998. Magneto-electronics. Science 282, 16601663.

- In ***nonmagnetic conductors***, there are equal numbers of spin-up and spin-down electrons in all energy bands.
- Let us look into the ferromagnetism of the 3*d* elements. In the free atoms, the 3*d* and 4*s* levels of the 3*d* transition elements are *hosts for the valence electrons*. In the *metallic* state, these 3*d* and 4*s* levels are broadened into *energy bands*. 4*s* orbitals overlap extensively between 4*s* orbitals of neighboring atoms and the resulting 4*s* band is spread out over a wide energy range (15 – 20 eV). On the other hand, 3*d* orbitals are much less extended in space and the associated 3*d* energy band is comparatively narrow (4 – 7 eV).
- Thus, *4s electrons are much more mobile than 3d ones* and *the conductivity of 3d transition elements is mainly determined by the 4s electrons*. However, *s*-electrons scatter into the many *d*-states which are available at the Fermi level giving rise to considerable resistance.
- As the quantum mechanical (QM) consequence of the Pauli principle, electrons with parallel spin are ***spatially separated*** by exchange interaction in order to reduce the electrostatic energy (Fig.3). In other words, the Pauli exclusion principle requires that up and down spin electrons be counted separately, and separate spin sub-bands can be formed.

Figure 3A. ***Top***: a schematic plot is shown for the energy band structure of a 3*d* transition metal. The density of states *N(E)* is shown separately for the spin up and down electrons and where a simplified separation has been made between the 4*s* and 3*d* band energies. **For the non-magnetic state, *these are identical for the two spins*.**

All energy levels below the Fermi energy are occupied states (orange and blue). The colored area (orange + blue) corresponds to the total number of valence electrons in the metal. *E is energy*.

Bottom: The above corresponding picture is illustrated ***for a ferromagnetic state***, with ***a spin-polarization chosen*** to be in the up direction (N↑ > N↓; blue area > orange area). This polarization is indicated by the thick blue arrow at the bottom figure.



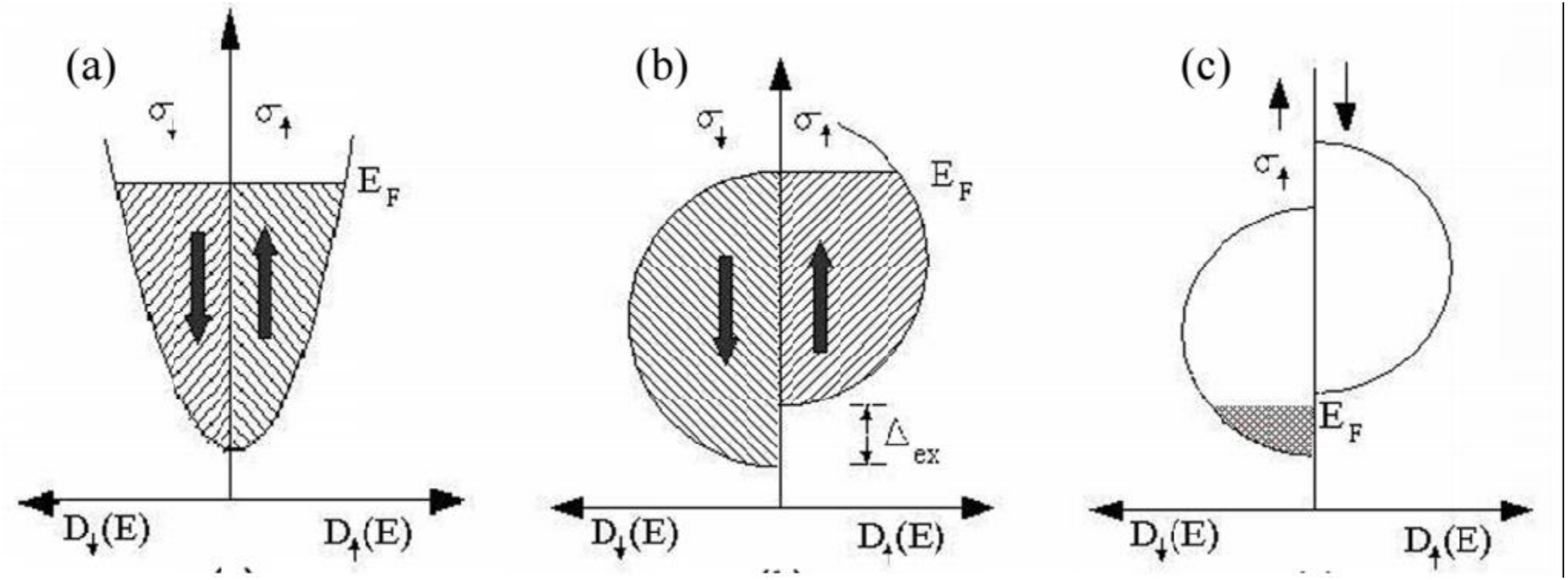


Figure 3B. Schematic diagram of density of states D(E) as a function of energy. (a) Non-magnetic metals (zero spin polarization). (b) Ferromagnetic metals (partial spin polarization). (c) Half metals (full spin polarization).

- **The origin of the magnetism behavior owes to the distribution of 3*d*/4*f* electrons in ferromagnetic metals** such as 3*d* transition metals like, Fe, Co, Ni and 4*f* lanthanides like Gd.
- Therefore, for a ferromagnetic material like Fe, Co, and Ni, the spin sub-bands are shifted with respect to each other due to exchange splitting (Δ_{ex}) as shown in Figure 3B.
- This shift results in ***an unequal filling of the bands, which is the source of magnetic moment for the ferromagnetic materials,*** and it also causes the **spin-up** and **spin-down electrons** at ***the Fermi level*** *to be* ***unequal in number,*** *and* ***mobility***.
- The ***asymmetry of density of states (D(E))*** at the Fermi level $D_{\uparrow}(E_F) \neq D_{\downarrow}(E_F)$ for ferromagnetic material leads to unequal conductivity $\sigma_{\uparrow} \neq \sigma_{\downarrow}$. **This inequality can produce a net spin polarization (P)** in the transport measurements.
- The spin polarization can be defined in terms of number of carriers (n) that have spin-up ($n_{\uparrow}$) or spin-down ($n_{\downarrow}$), as $P = [(n_{\uparrow} - n_{\downarrow})/(n_{\uparrow} + n_{\downarrow})]$. It can also be defined either in terms of conductivity ($[(\sigma_{\uparrow} - \sigma_{\downarrow})/(\sigma_{\uparrow} + \sigma_{\downarrow})]$) or $D(E_F)$ such as, $P = [(D_{\uparrow}(E_F) - D_{\downarrow}(E_F))/((D_{\uparrow}(E_F) + D_{\downarrow}(E_F))]$.

- In figure 3 (top) the density of states is illustrated schematically for a non-magnetic *3d* metal, sometimes referred to *as a paramagnet*, where there are as many electrons with spin up as with spin down, i.e., there is ***no net magnetization***. The so-called **spin polarization, *P*,**

  ***P* = (*n*↑ – *n*↓)/(*n*↑ + *n*↓),** where $n\uparrow$ ($n\downarrow$) = the number of electrons with spin up (down), is here equal to zero.

- For the ferromagnet (chosen here) $n\uparrow$ is larger than $n\downarrow$, so there is a net spin polarization, $P > 0$ (Fig. 3B(b)).

- From the definition of spin polarization, it is pretty clear that the ***non-magnetic material have zero spin polarization*** whereas ferromagnetic materials (such as Fe, Co, and Ni and their alloys) have polarization of 40–50%. Ferromagnetic materials are known to be ***partially spin polarized***.

- There exists a special class of materials (like CrO_2, $La_{0.7}Sr_{0.3}MnO_3$), which show ***100% spin polarization*** and are known to be ***half metallic***. In this case, one sub-band at the Fermi level is filled and the other sub-band is completely empty (i.e., ***one spin sub-band is metallic*** and the ***other sub-band is insulating***). Figure 3B shows the simple band picture for different spin-polarized systems.

❖ Spin transport

- ***Spin-polarized transport*** will occur naturally in any material for which there is an ***imbalance of the spin populations at the Fermi level***. This imbalance commonly occurs in ferromagnetic materials (FMs) because the ***density of states available to spin-up and spin-down electrons*** is ***shifted in energy*** with respect to each other (Fig.1.2).
- This shift results in an unequal filling of the bands, which is the source of the net magnetic moment for the materials and causes the spin-up and spin-down carriers at the Fermi level to be unequal in number, character, and mobility. This inequality can produce a net spin polarization in a transport measurement.
- The conductivity (σ) of a metal is proportional to the density of electrons at the Fermi level (E_F), and therefore proportional to the ***density of states*** at the Fermi level, $D(E_F)$, and is related by $\sigma \propto D(E_F)$.
- Electrons near the Fermi surface constantly collide, scatter and change their momentum states, but if their spin orientation remains unchanged during these processes, then a unique conductivity can be written for both up and down spin electrons such as $\sigma_{\uparrow} \propto D_{\uparrow}(E_F)$ and $\sigma \propto D_{\downarrow}(E_F)$ as shown in Figure 3.

- For non-magnetic materials like copper, silver and gold, the number of electrons in the up sub-band is equal to the number of electrons in the down sub-band and also the sub-bands are symmetric. Hence in case of non-magnetic materials, $\sigma_{\uparrow} = \sigma_{\downarrow}$.
- The asymmetry of density of states at the Fermi level $D_{\uparrow}(E_F) \neq D_{\downarrow}(E_F)$ for ferromagnetic material leads to $\sigma_{\uparrow} \neq \sigma_{\downarrow}$.
- In order to compare the energy for the ferromagnetic state with the energy for the paramagnetic state one can start from the paramagnetic state and allow for a small imbalance in the number of spin-up and spin-down electrons. Since the density of states at the Fermi surface is quite different for the two spin states for a ferromagnet it follows that there is a significant difference in resistance (conductance) for the spin-up electrons and the spin-down electrons.

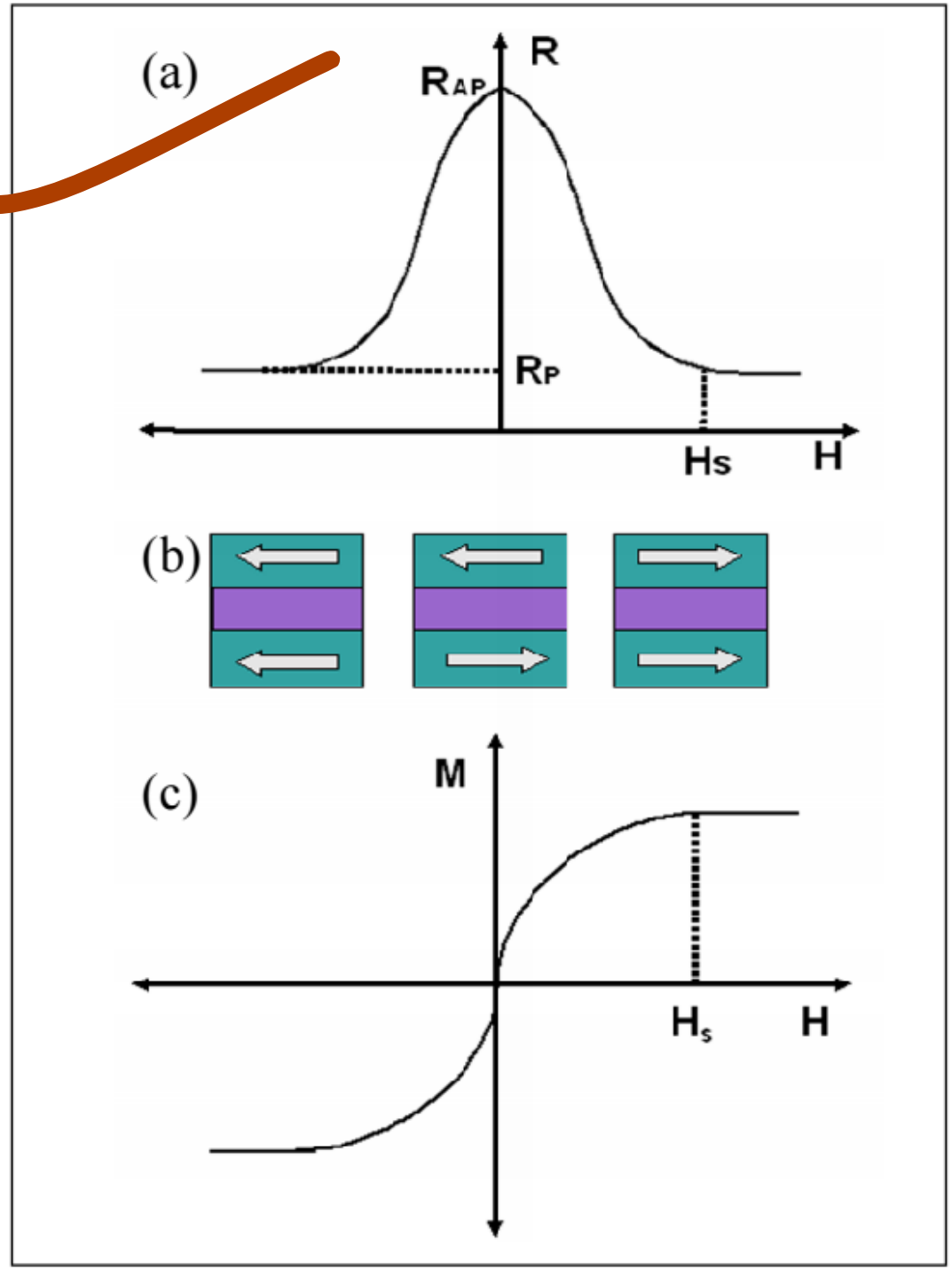
Like the other magnetoresistances (OMR, AMR), GMR is also a change in electrical resistance in response to an externally applied magnetic field, and is a quantum mechanical effect which is based on spin-dependent scattering phenomena in magnetic multilayers.

The change in resistance of the multilayer occurs when the applied magnetic field aligns the magnetic moments (magnetization) of successive ferromagnetic layers as shown in Figure 1. In the absence of applied magnetic field, the magnetic moments of magnetic layers are not aligned with respect to each other i.e., their magnetizations are antiparallel to each other and it results in higher resistance. By applying magnetic field, the magnetic moment of successive ferromagnetic layers gets aligned i.e., their magnetizations are parallel to each other and it results in a drop in resistance of the multilayer.

Mathematically, **GMR can be defined as GMR = $(R_{AP}–R_P)/R_P$, where R_P and R_{AP} are the resistances in parallel and antiparallel states**.

Unlike ordinary magnetoresistance, the GMR saturates with applied magnetic field as shown in Figure 1.

Figure 1. Schematic representation of the GMR effect.
(a)Change in the resistance of the magnetic multilayer as a function of applied magnetic field.
(b) The magnetization arrangement (indicated by the arrows) of the multilayer (trilayer) at various magnetic fields; the magnetizations are aligned antiparallel (AP) at zero field and are Aligned parallel (P) when the external magnetic field H > saturation field (H_S).
(c) M-H curve for the multilayer.



Physical Origin of GMR

The principle is to have magnetic thin layers separated by nonmagnetic layers having a large enough spin diffusion length. Electrons traveling inside the first layer have a spin polarization that depends on the magnetization direction. When they arrive inside the nonmagnetic layer, electrons conserve their polarization to a distance of the order of the spin diffusion length. If there is another magnetic material nearby, electrons enter it. But that entrance will be easier if the magnetization direction of this second magnetic layer is identical to the first one. Hence, electrical resistance of the stack will depend on the relative orientations of the magnetization of each magnetic layer.

Spin-dependent Conduction:

The origin of GMR can be understood by only considering the spin-dependent effects.

- **Mott's two-current model** forms the basis of understanding the transport in ferromagnetic material well below the Curie temperature. This model was further developed by Fert and Campbell.
- ***According to Mott***, the electrical conductivity in a metal can be described in terms of two *largely independent conducting channels* corresponding to up and down spins respectively. Total conductivity is represented by the two-current model as, $\sigma_{Total} = \sigma_{\uparrow} + \sigma_{\downarrow}$ (keeping in mind that there occurs no spin flip scattering).

- **Mott postulated** that the electric conduction takes place by the ***sp band electrons*** primarily as they have ***lower effective mass and higher mobility***.
- The electrical resistance is due to the scattering processes where the sp electrons jump from the sp-band to the d-band.
- Fermi's golden rule states that the **scattering probability** *of the conduction electrons* is ***proportional to*** density of final states, i.e. **the density of empty d states** above the Fermi level.
- As the d band is exchange split in ferromagnets, the density of states for up and down bands is different at the Fermi level.
- Resistivity of the transition metals with a partially filled d shell is thus produced by the dominant effect of itinerant **sp electrons scattering** on the **localized d hole** states.
- This ***scattering is spin selective*** where the two spin states (spin up and spin down) carry the electric ***current in parallel without much mutual interactions***, i.e. no spin flips.
- Since conduction may occur in two separate channels, the conductivities of two channels add in series.
- It is important to note that in Mott's model, the rate of spin relaxation of electronic transition is simply due to coulomb scattering of charge. At low temperature, it arises from lattice defects or impurities, and at higher temperatures, it is dominated by atomic displacements due to thermal motion (phonons).

- And since the ***coulomb interaction does not act on spin***, spin flips are forbidden, and the two spin channels are independent of each other. Hence, the itinerant **sp electrons scatter into available d-states** of the **same spin.** This spin selective scattering process is one of the reasons for spin filtering when a current traverses through a ferromagnetic layer.
- In a FM like Co and Ni, we can see from the density of states that the ***minority channel has higher number of holes available*** compared to the majority channel.
- As the ***scattering strength of itinerant sp electrons is proportional to number of d-holes available at the Fermi level***, the ***minority electrons undergo higher scattering*** in the Co (or Ni) layer, ***resulting in a preferential loss of minority spin component***. Thus, *the spin-dependent transport results in a spin filtering effect*. Since the probability of scattering for up and down sp electrons into the states near the Fermi level are different, the conductances (hence resistances) are different for the two conduction channels.
- ***Another source of spin filtering effect is spin-dependent reflection at the interface***. When current is injected at the interface, both transmission and reflection of the current occurs. The reflection and transmission probability is spin dependent on the DOSs of the FM and NM layers. Hence***, the interface plays an important role in spin filtering*** the majority and minority channels.

- Both the ***spin selective scattering*** within the **FM,** referred to as **bulk contribution**, and the *spin-dependent reflection and transmission at the interface*, referred to as the **interface contribution**, cause the spin filtering effect by a FM.

- Though most of the studies assume a transparent interface and only include the bulk contribution due to its simplicity, it has been shown that ***the interface contribution is indeed very important and is bigger than the bulk contribution***. This stresses the role played by the interface in spin injection and spin transport.

- When this spin-filtered current enters a non-magnetic layer, spin accumulation at the interface happens due to the mismatch in conductivities (for spin-up and spin-down channels) of ferromagnetic and non-magnetic layers, and it exponentially decays away from the interface. This spin accumulation results in a transient induced magnetic moment in the non-magnetic layer.

- **Calculations** based on **how electrons move through a periodic lattice give a clear picture** of the electron scattering mechanisms at the FM-NM interfaces. Figures 7 and 8 show the number of up- and down-spin electrons for each atomic layer of a system consisting of eight chromium layers embedded in iron (Fig. 7) and for a system consisting of ten copper layers embedded in cobalt (Fig. 8). Both systems show a large GMR.

- These figures give an important clue as to what is happening. For the iron-chromium layers, note that the number of down-spin electrons is about the same in the iron and chromium, but the number of up-spin electrons is very different. Conversely, the number of up-spin electrons is very similar on each layer of the copper-cobalt system, but the number of down-spin electrons changes abruptly at the interfaces.
- *The electrical resistance of a metal arises from irregularities and discontinuities in the atomic lattice potential, called defects, as seen by the electrons.* When electrons hit these defects in the atomic lattice - a process physicists call scattering, the electrons are slowed down. Therefore, scattering can generate electrical resistance.
- Let us consider the case in which the ferromagnetic layers are of cobalt and the nonmagnetic layer is copper (Figs. 8 and 9). In the Figures, the upward or downward smaller arrows indicate up-spin or down-spin electrons respectively. In Figure 9, the upward or downward medium-length arrows in the blue layers (left and right layers) show the directions of the magnetic moments in the respective layers.

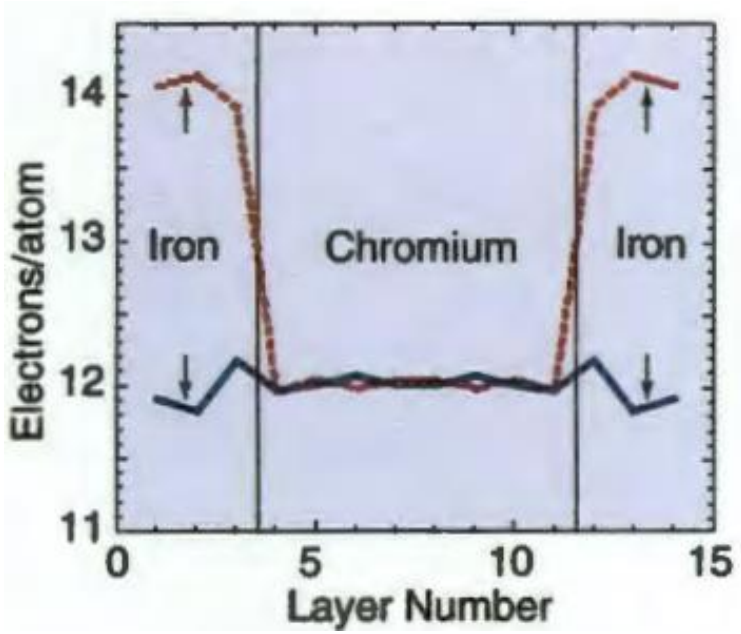


Fig. 7. The number of down-spin (blue curve) electrons per atom hardly changes between the iron and chromium layers, but the number of up-spin electrons (red curve) is higher for iron than for chromium.

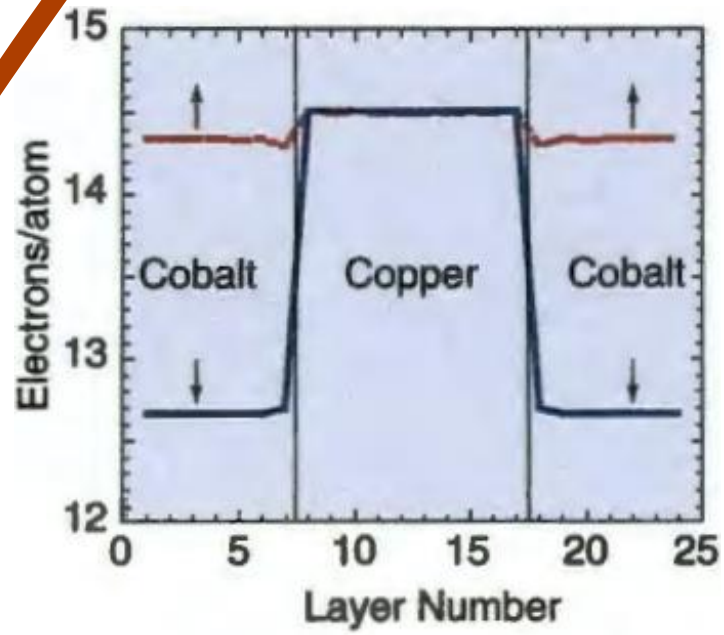


Fig. 8. The number of up-spin (red curve) electrons per atom hardly changes between the cobalt and copper layers, but the number of down-spin electrons is much lower for cobalt than for copper.

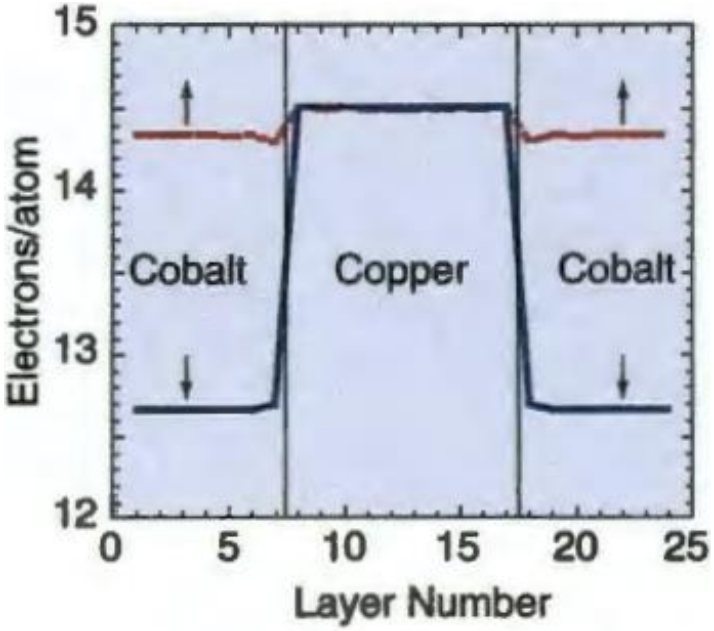
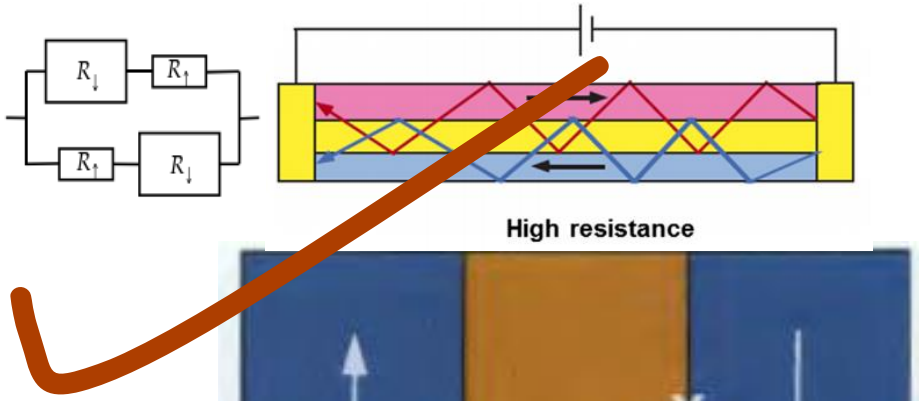
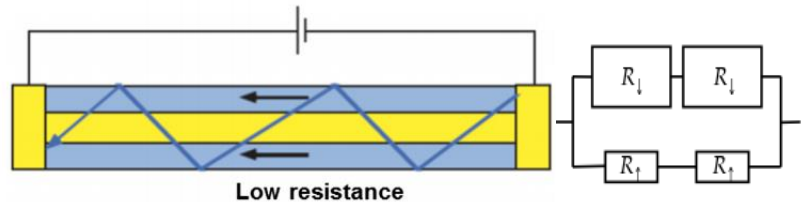
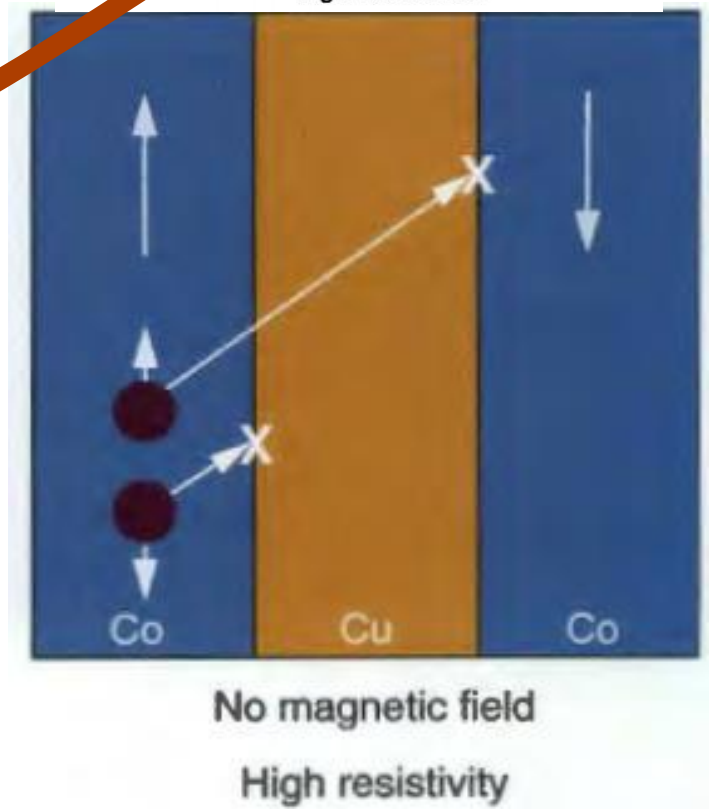


Fig. 8. The number of up-spin (red curve) electrons per atom hardly changes between the cobalt and copper layers, but the number of down-spin electrons is much lower for cobalt than for copper.







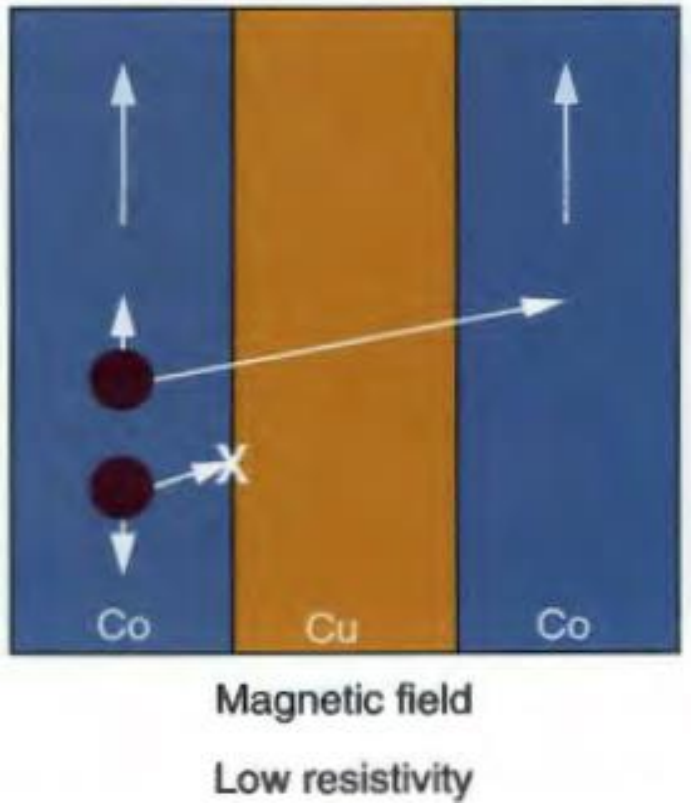


Fig. 9. When excess spins in both cobalt layers are aligned, up-spin electrons pass from layer to layer without scattering.

- See the **number of electrons per atom (DOS)** of Co and Cu. In this case, the number of Co up-spin electrons (DOS) is very similar to the DOS of copper layer, but the number of down-spin electrons changes abruptly at the interfaces. This suggests that:

  - The ***up-spin electrons hardly notice any difference*** in **the number of electrons per atom (DOS)** as they travel from the ferromagnetic layer to the nonmagnetic layer. To them the lattice potential is smooth and almost defect free. On the other hand, the **down-spin electrons** see a ***large difference*** in electron numbers between atoms of copper and cobalt. They see many bumps at the interface (because copper and cobalt atoms often mix with each other there), so they are very likely to scatter there.

- **The down-spin electron gets scattered at the Co-Cu interface** (slanted small arrow, left panel, no magnetic field Figure) **whereas the up-spin electron passes through** the Cu-Co interface (Fig. 9, left panel, no magnetic field). Under no applied magnetic field ($H = 0$), the magnetic field of the right Co layer will be coupled to the left Co layer. Thus, the up-spin and down-spin electrons (DOSs) get reversed in the right layer with respect to the left Co layer (the excess spins in the right ferromagnetic Co layer have opposite directions; downward magnetic moment). Therefore, the up-spin electrons get scattered here at the Cu-Co interface due to the mismatch of the DOS (due to reversal).

- *With no magnetic field: Antiparallel magnetic field orientation:* ***highest resistance due to scattering of both up- and down-spin electrons***.
- When a magnetic field ($H \neq 0$) is applied to make parallel magnetic moment orientation in both the left and right Co layers (Fig. 9, right panel, magnetic field), due to the matching of the DOSs, the up-spin electrons can travel freely from one ferromagnetic (cobalt) layer across the Cu interfaces to the other ferromagnetic layer (without being scattered at the interfaces). On the contrary, due to the mismatch of the down-spin DOSs, the down-spin electrons will scatter at the Co-Cu interface.
- *With magnetic field: Parallel magnetic field orientation:* ***Lowest resistance due to the scattering of only down-spin electrons***.

- Using Mott's arguments, it is straightforward to explain the GMR in magnetic multilayers where the DOS of FM excess spins matches with the DOS of the NM layer. In a **two-currents model**, the current consists of each **spin-up** and **spin-down electrons movement**. *Quantum mechanics dictates that the probability of an electron being scattered when it passes into a ferromagnetic conductor depends on the direction of its spin.* In general, **electrons with a spin aligned** with the **majority of spins** in the ferromagnets will **travel further without being scattered.** Thus, the *scattering* ***is strong for electrons with spin antiparallel to the magnetization direction*** and is weak for electrons with spin parallel to the magnetization direction. This is supposed to reflect the asymmetry in the density of states (DOS) at the Fermi level in FM layer, in accordance with Mott's second argument.

- Now consider Fe-Co-Fe trilayer in Fig. 7. The number of up-spin electrons per atom (about 13) is higher (majority) than the number of down-spin electrons per atom (about 12) of Fe layer. According to the above argument then **down-spin electrons (minority spins in Fe)** will **be more scattered** than the down-spin electrons in two Fe layers.

- Under no applied magnetic field (H = 0; when the **magnetic moments are aligned in the anti-parallel** directions in the two Fe layers), one will see the following:

(i) The down-spin electrons (minority) are scattered strongly within left Fe layer and the up-spin electrons (minority) are more scattered within the right Fe layer because their spin is antiparallel to the magnetization of the respective layers.

(ii) At the Fe-Cr (left) interface, the DOS of down-spin electrons is similar to that of the Cr layer. Therefore, at the left interface, the up-spin electrons will get scattered. On the other hand, although the down-spin electrons will cross the left Fe-Cr interface and travel up to the right Cr-Fe interface where they get scattered due to the antiparallel alignment, at the Cr-Fe (right) interface, the Cr DOS will match with that of the up-spin DOS of Fe (right layer).

- ***For the antiparallel alignment**, **both the up-spin and down-spin electrons are scattered strongly.** Thus, **in this case the total resistivity** of the multilayer **is high**.*

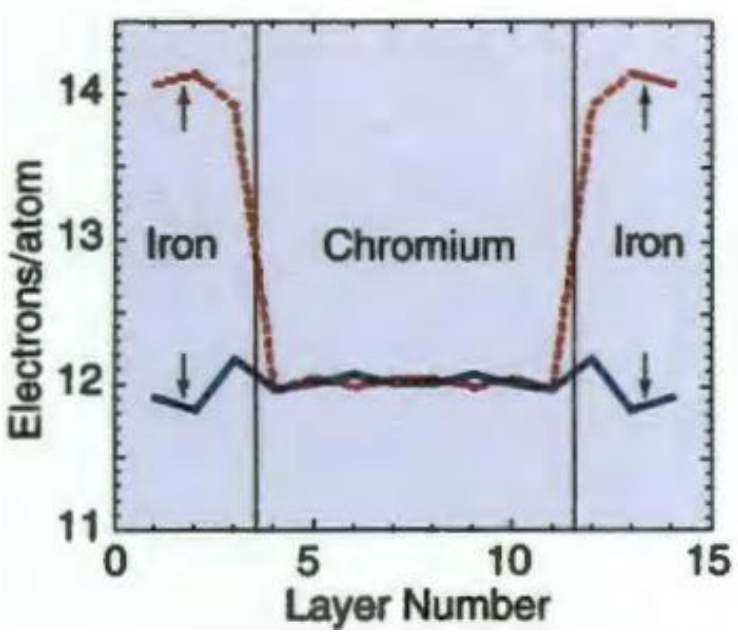


Fig. 7. The number of down-spin (blue curve) electrons per atom hardly changes between the iron and chromium layers, but the number of up-spin electrons (red curve) is higher for iron than for chromium.

➢ For the ***parallel-aligned magnetic layers*** (when a magnetic field ($H \neq 0$) is applied**):**

(i) The down-spin electrons (minority) are scattered strongly within both ferromagnetic layers, because their spin is antiparallel to the magnetization of the layers.

(ii) Under the parallel alignment condition, the down-spin electrons pass through the interfaces almost without scattering, because of ***their DOSs matching with the NM layer.*** On the other hand, the up-spin electrons are scattered at the interfaces due to the DOS mismatch. Since *conduction occurs in parallel* for the two spin channels, the total resistivity of the multilayer is determined mainly by the highly conductive down-spin electrons and leads to low resistance.

Figure 4. Schematic illustration of the spin-dependent scattering of a trilayer system with two ferromagnetic layers separated by a nonmagnetic material layer (grey). Left Panel: For the case without external magnetic field (H=0), i.e. when the two magnetic layers have opposite magnetizations (indicated by the thick arrows).

Right Panel: For the case when an external magnetic field ($H \neq 0$) has forced the two magnetizations to be parallel (two thick arrows at).

- **The resistance, therefore, changes depending on whether the moments of the magnetic layers are parallel (low resistance) or antiparallel (high resistance).**

- The ***change in the resistance of the magnetic multilayer as a function of the applied magnetic field*** is shown schematically in Fig. 6.

- Under the external magnetic field, as the applied field is increased, the magnetic moments of the ferromagnetic layers progressively rotate towards the field, leading to a decrease in the resistance of the multilayer. At the saturation magnetization field, the magnetic moments are aligned parallel and hence giving the lowest value of the resistance.

- The same argument can be used for understanding of **GMR in granular system** also. In zero field, the magnetic moments of precipitates are randomly oriented. So, up and down spins are scattered strongly resulting in high resistance. But with the application of saturating magnetic field, all the precipitates align and it results low resistance.

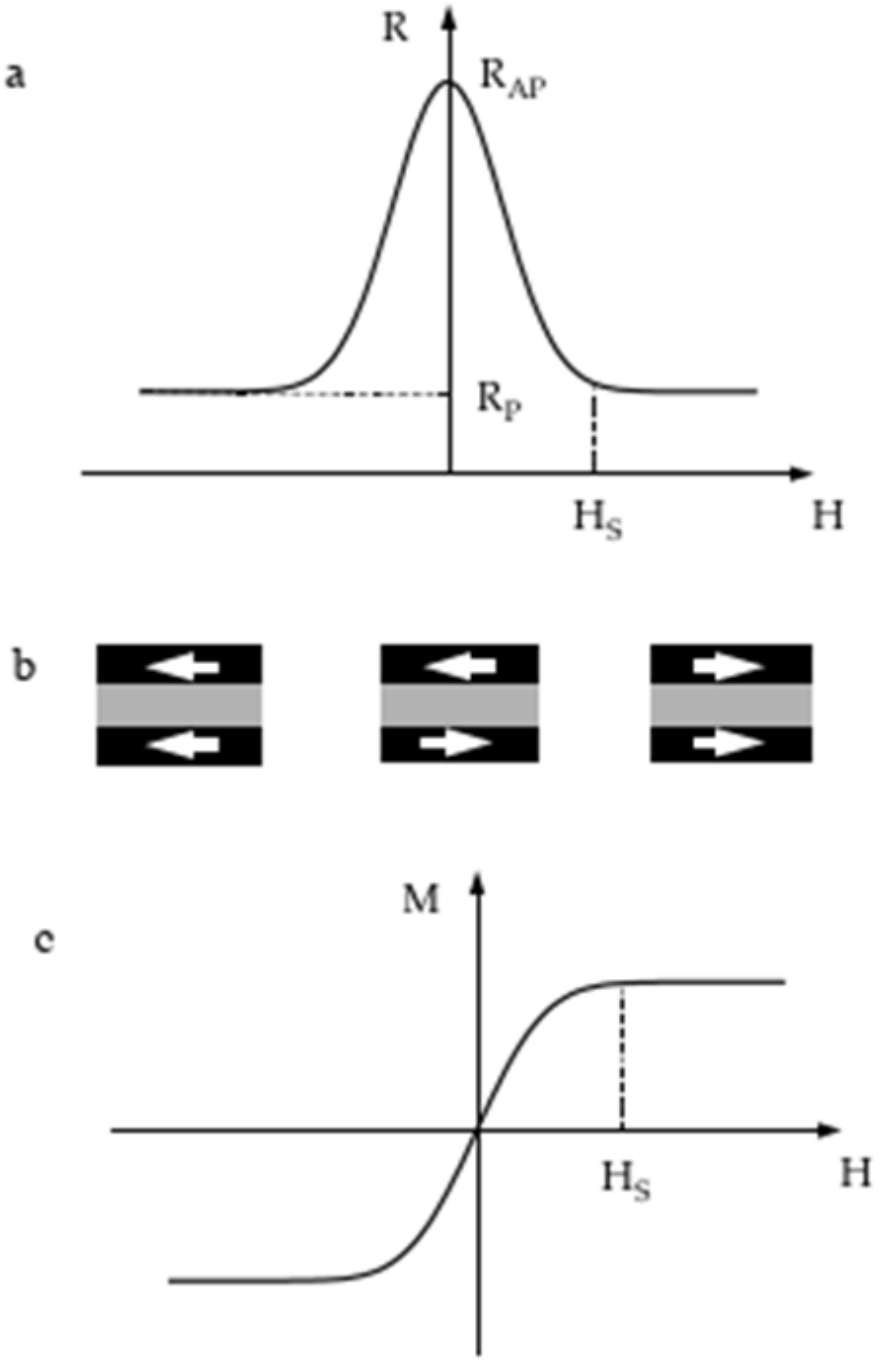
Figure 6: Schematic of the GMR effect.

(a): Change in the resistance of the magnetic multilayer as a function of applied magnetic field.

R: resistance; *AP*: antiparallel; *P*: Parallel.

(b): The magnetization configurations of the multilayer: the magnetizations are aligned antiparallel at zero field; the magnetizations are aligned parallel when the external magnetic field H is larger than the saturation field H_S.

(c): The magnetization curve for the multilayer.



With this picture, one expects that ***there would be a strong resistivity change if one could manage to change the direction of the local magnetization within the mean free path of the electrons or on an even shorter scale***.

For spin-dependent scattering to be a significant part of the total resistance, the layers must be thinner (to a magnitude of several nanometers) than the mean free path of electrons in most spintronic materials. As mean free paths are of the order of 10 nm, the 1 nm thickness by which the magnetic layers are separated in the coupled structures perfectly fulfills this condition.

A typical GMR medical sensor has a conducting layer approximately 3 nm (or one ten-millionth of an inch) thick. For reference, that is less than 10 atomic layers of copper, and less than one ten-thousandth the thickness of a piece of tissue paper.

Optimal layer thicknesses enhance magnetic-layer antiparallel coupling, which is necessary to keep the sensor in the high-resistance state when no field is applied. When an external field overcomes the antiparallel coupling, the moments in the magnetic layers align and reduce the resistance. If the layers are not the proper thickness, however, the coupling mechanism can destroy the GMR effect by causing ferromagnetic coupling between the magnetic layers.

❑ *Current and Future Applications of Nanoscale Magnets in Data Storage*

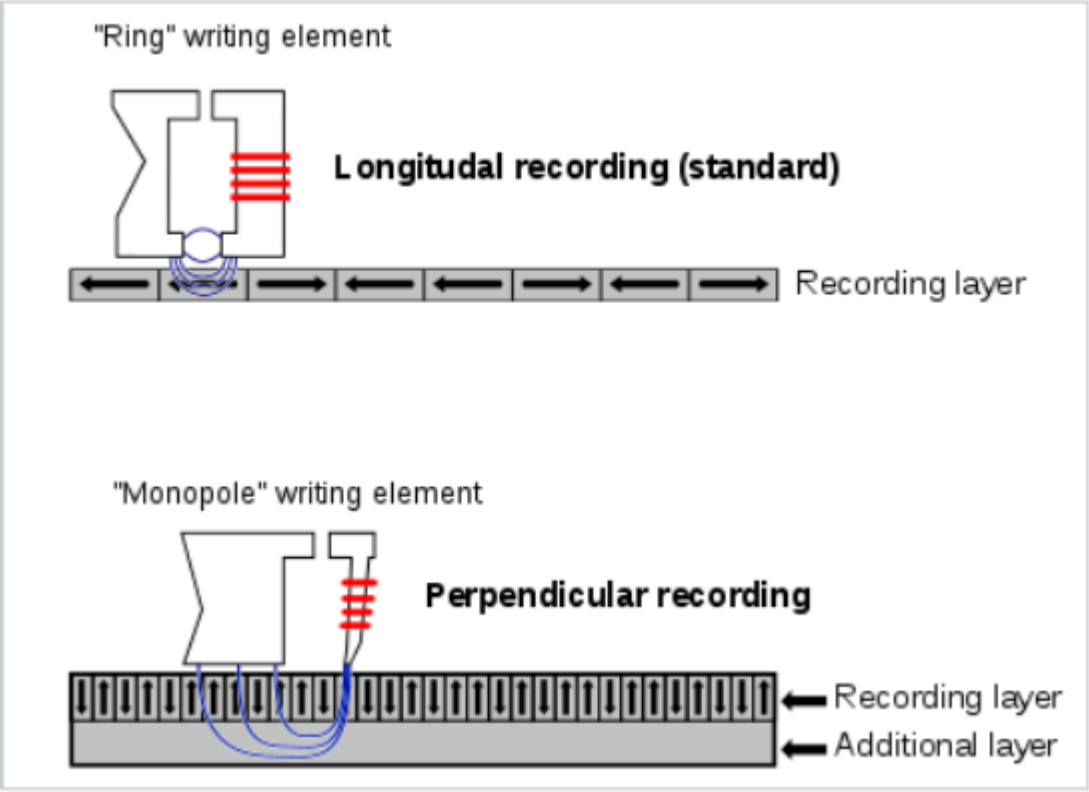
- Information on computer hard-disk drives (HDDs) is encoded using minute magnetic domains with their direction of magnetization representing the logical levels 0 and 1. Hard drives store data in well-organized patterns of ones (1's) and zeros (0's) across a thin sheet of magnetic material. This sheet of magnetic material is spread on either one side or both sides of a disk called a **substrate**. Substrates used to be made from aluminum allowing for the magnetic coating to ride on a hard surface while the light weight could spin quickly. Now glass is used as a substrate primarily due to its improved surface uniformity which increases reliability; low surface defects which reduces read/write errors; better stiffness; better resistance to shock; and ability to have the read/write mechanism ride closer to the surface allowing for better data density.

- Ferro- and ferrimagnetic materials such as iron and chromium oxide are used for digital storage of information in hard disks. The individual memory bits, which can be oriented **perpendicular** or **parallel** *to the plane of the disk* as shown at the right, store a logical "0" or "1" depending on the orientation of their magnetic dipole.

- To be useful, this information must be **non-volatile**, i.e., the magnetic bit must retain its polarization in the absence of an applied field from the read/write head.

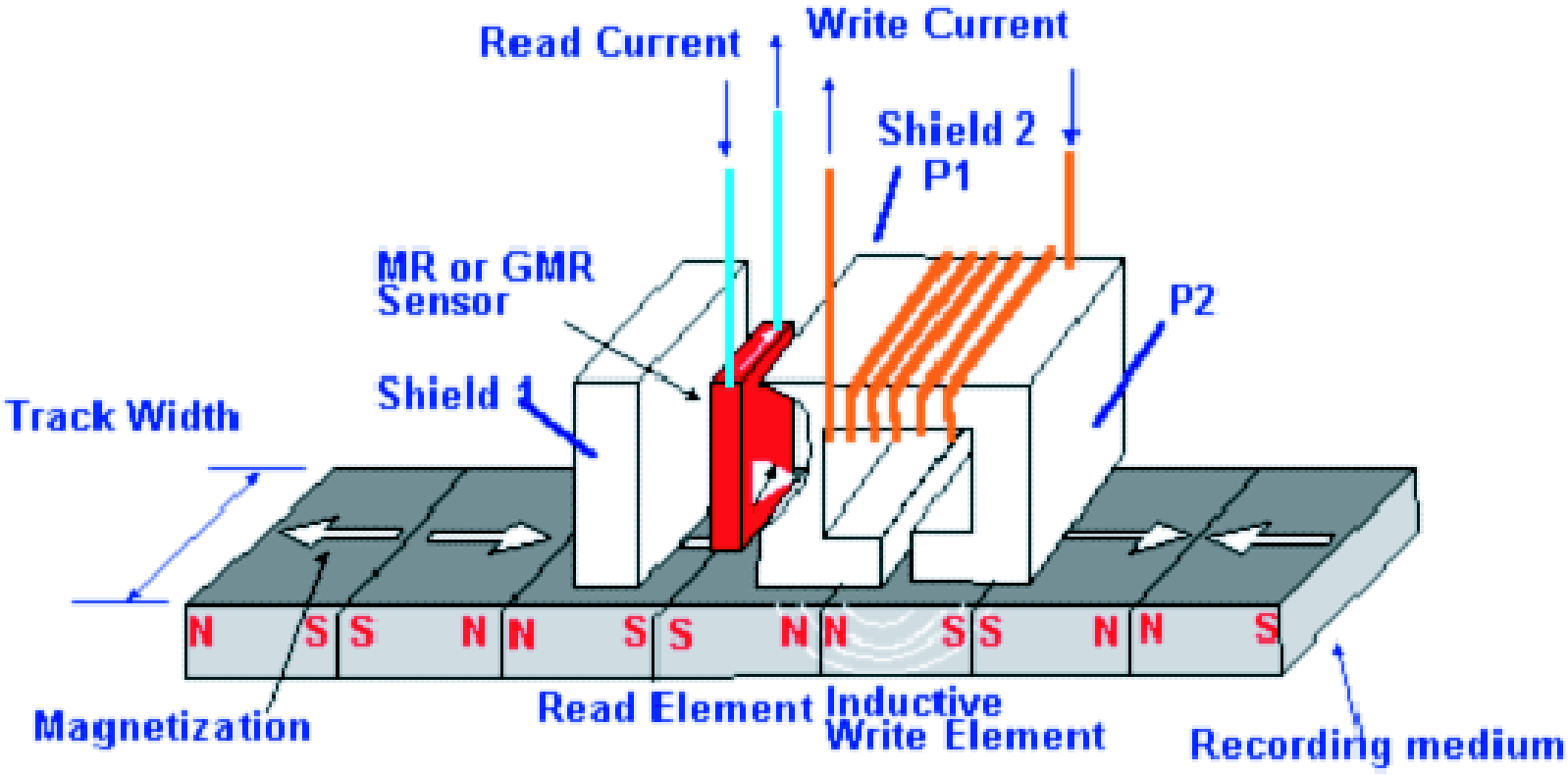
Reading and Writing to Disks

- Recording and retrieving data from the magnetic coating on the substrate is done with conductive coil(s) called a head(s). Older drives and floppy drives used a single head that performed both the read and the write operations. The head is shaped like a "C" with the small gap between the ends positioned so that it faces downward close to the magnetic material. A coil of wire was wrapped around portion of the head away from the magnetic material. The figure below shows the configuration of this type of head.



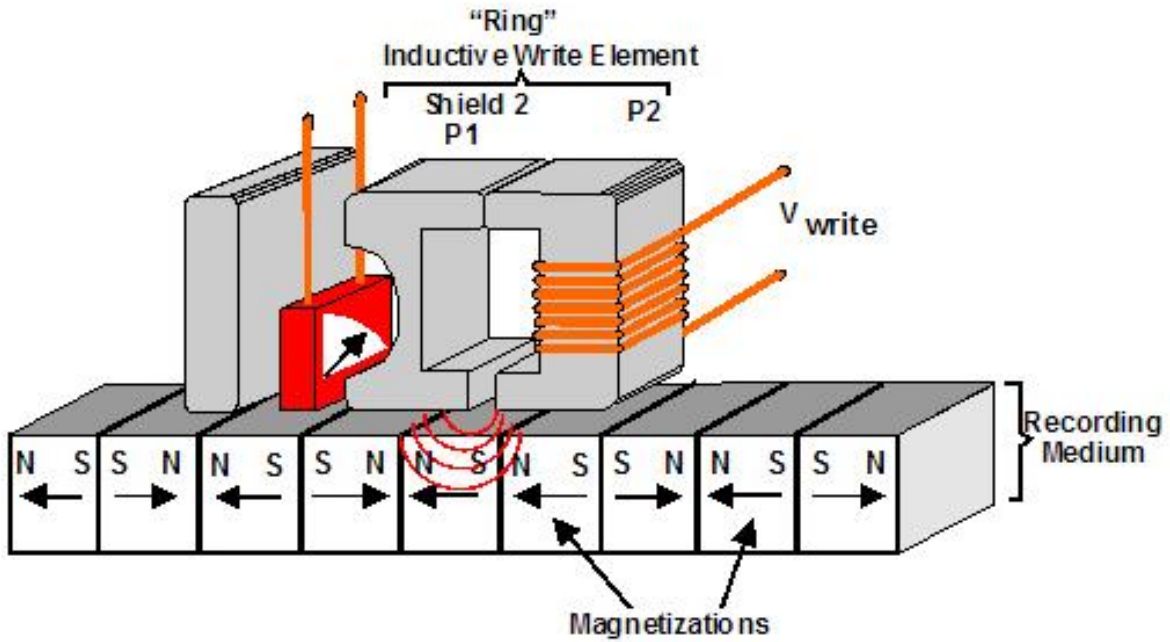
Longitudinal and perpendicular recording, two types of writing heads on a hard disk.

- In order to write data, an ***electrical current*** was passed through the wire which created a magnetic field within the gap of the head close to the disk. This field would charge the magnetic material in a specific direction. ***Reversing the current*** would charge the magnetic material in the opposite direction. ***These two directions allow for the storage of the two types of data, ones and zeros***.
- The same head was used to read the data back from the disk. If a magnetized material passes close to a coil of wire, it produces a small current. The direction of the current changes if the direction of the magnetization is changed. In this way, the same coil that is used to write the data can be used to read the ones and zeros back.
- **Newer hard drives** use **two heads**, one for ***reading*** and one for ***writing***. The read head works differently than the old heads in that it is made of a special material that changes its resistance (GMR or TMR) depending on the magnetic field that is passing under it. These changes in resistance affect a current that the hard drive controller is passing through the read head during the read operation. In this way, the hard drive controller can determine whether a one or a zero was stored to the portion of the disk that is passing under the head.
- At the time of a read or write operation head is stationary while platter rotates beneath it.


Read Current
Write Current
Shield 2
P1
MR or GMR
Sensor
P2
Shield 1
Track Width
N S S N N S S N N S S N N S
Magnetization
Read Element
Inductive
Write Element
Recording medium

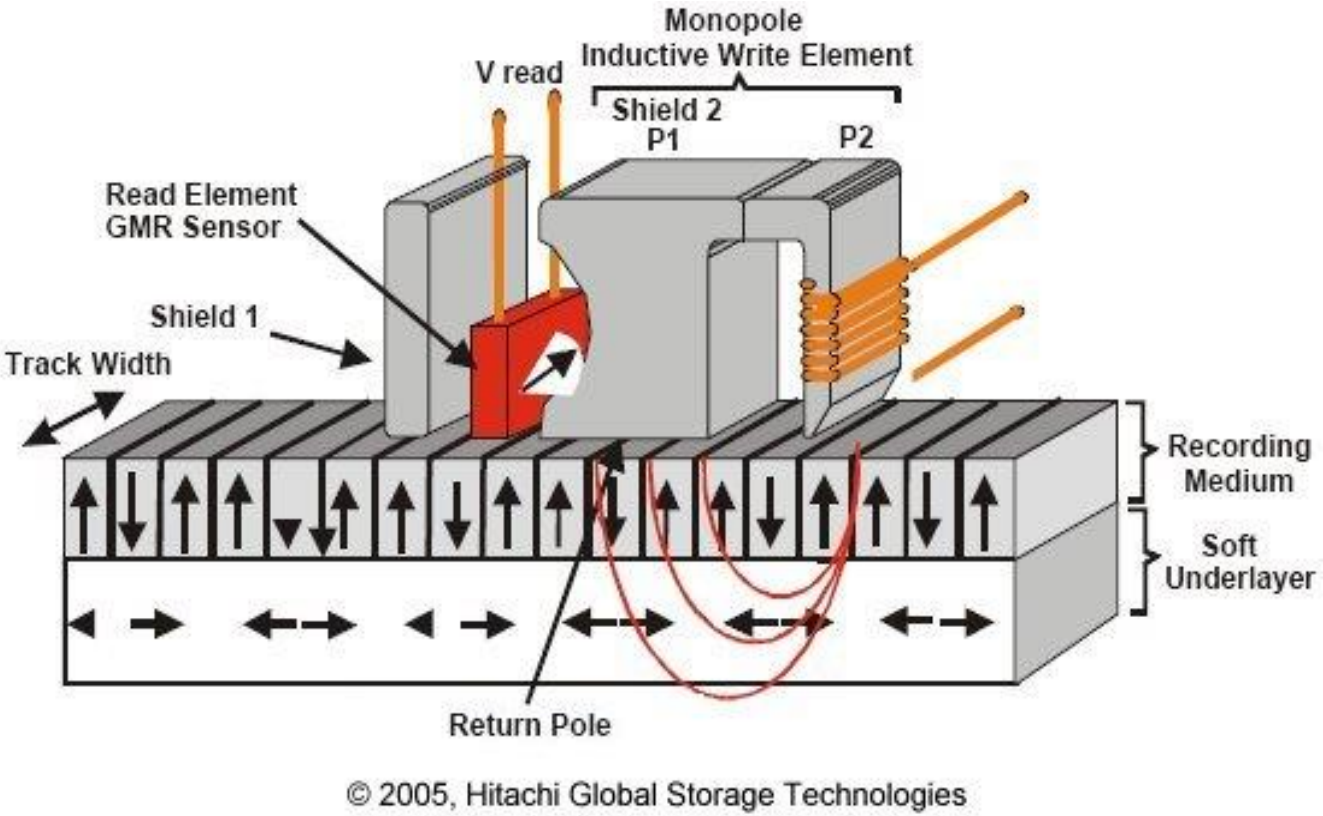
- An electromagnet in the write head writes information to the disk by magnetizing small sections of the disk, called sectors, in a one direction or another to indicate a 1 or a 0.
- The bit-coded information can be therefore stored by magnetizing pieces of the recording medium along directions 0 or 1. The size of the magnetized bit is a critical design parameter for hard disks. In addition, for the actual data rates, magnetization dynamics cannot be neglected in the writing process.
- The read head detects the orientation of these sectors when reading information from the disk.
- Previously, the ***sectors on the platters were magnetized parallel to the surface of the platter***. This style of recording was called **longitudinal recording**.
- However, ***a breakthrough*** was made by ***magnetizing*** *the platters* ***perpendicular*** *to the platter*, *allowing for more information to be stored in the same amount of physical space*. This new style, called **perpendicular recording**, ***has allowed for hard drive capacities to increase*** greatly.

Longitudinal Recording



- **Unfavorable for Shrinking Bit Size**

Perpendicular Recording



- **Favorable for Shrinking Bit Size.**
- **More Volume for the Same Area.**
- **Favored by Shape Anisotropy**

- Check out the video from Hitachi Global Storage Technologies to learn more about new method of recording.

❑ Where are giant magnetoresistive (GMR) materials used?

- The basic idea of GMR effect is that the resistance of two ferromagnetic layers decoupled by a spacer layer (typically Cu or Au) is dependent upon their relative magnetic alignment. This structure is called a spin valve device. If both the layers are aligned parallel to each other, then the resistance is lower compared to the case when they are aligned antiparallel to each other. The difference in resistance of up to 110% has been observed between two configurations. A few years later after the discovery of GMR, every hard disk drive was using this effect to ***'read' orientation of magnetic bits*** which are used to store data. GMR effect is also used in **biosensors**, microelectromechanical systems (**MEMS**) and magnetoresistive random-access memory (**MRAM**) applications.

- Information on computer hard-disk drives (HDDs) is encoded using minute magnetic domains with their direction of magnetization representing the logical levels 0 and 1. This information can be read using a simple iron spinel magnet 'head' and coil, where passing the head over the encoded surface generates small electrical currents in the coil depending on the direction of the magnetization. However, such devices have a low sensitivity, demanding relatively large regions of magnetic material, and the amount of information that can be stored on such a device is limited.

- In the 1990s HDDs were developed that used **magnetoresistive effects, allowing much greater read sensitivity** and ***hence higher data storage densities***. A GMR-based HDD in essence consists of two ferromagnetic layers separated by a spacer layer, which results in a weak coupling between the layers; a layer of an antiferromagnetic material fixes or 'pins' the orientation of one of the ferromagnetic layers. This overall structure is known as a **spin valve**.
- The first application to produce a substantially large economic impact was that for the **read heads** in magnetic disk recorders, which are components of every computer. The ***read head senses the magnetic bits*** that are stored on the media (disks or tapes). This information is stored as magnetized regions of the media, called magnetic domains, along tracks (see Fig. 1.5).

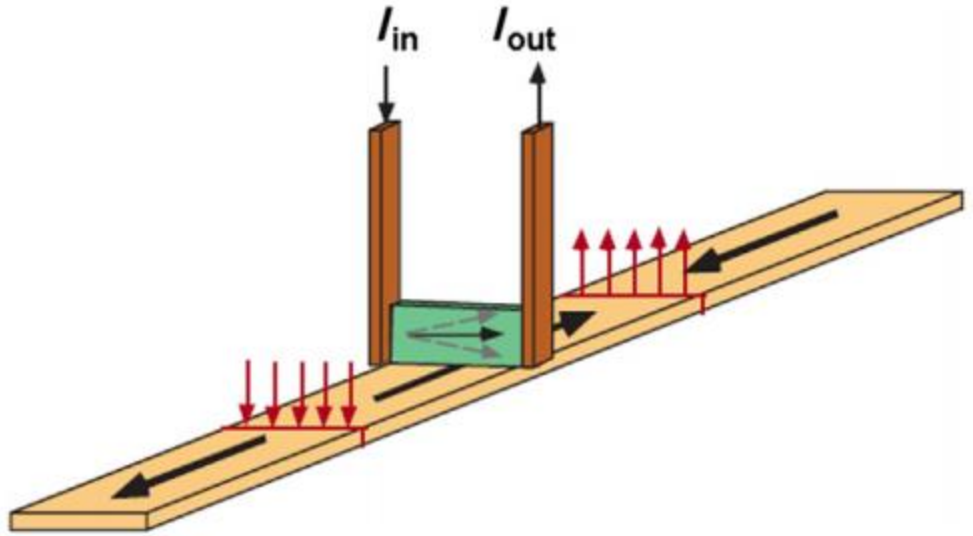
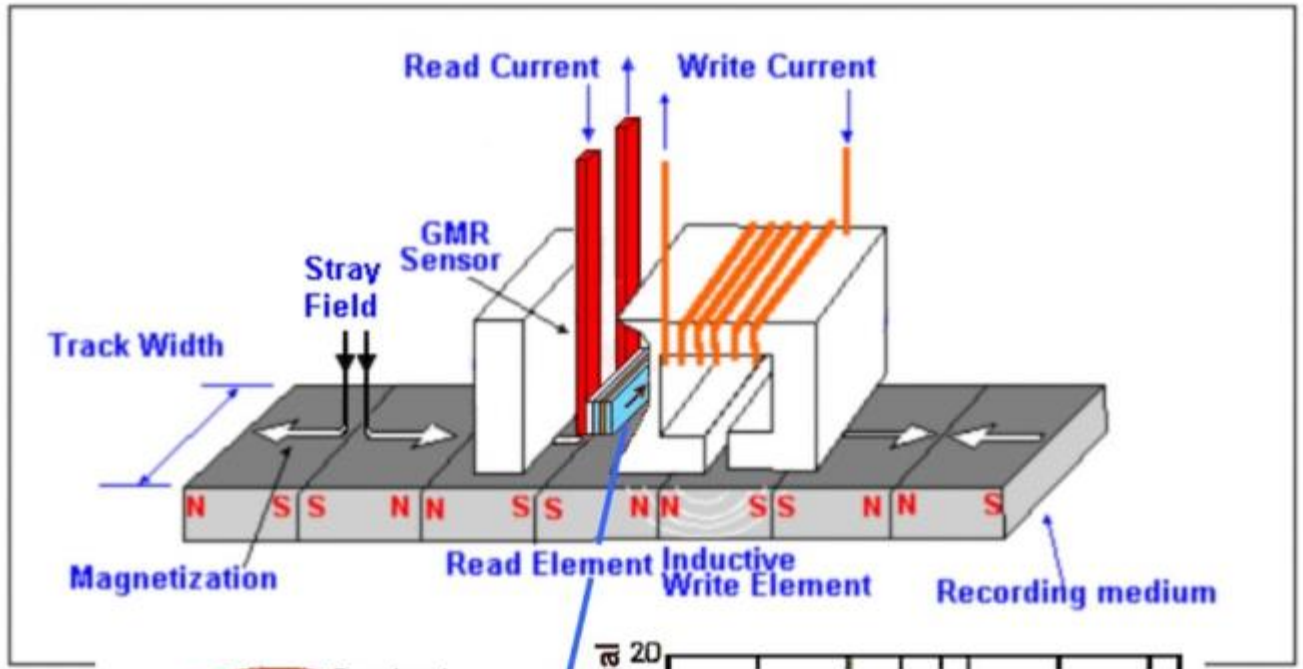
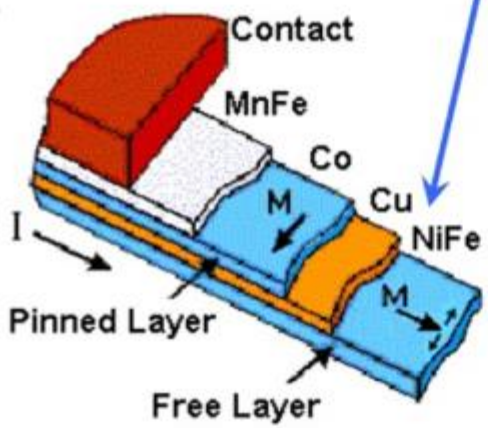
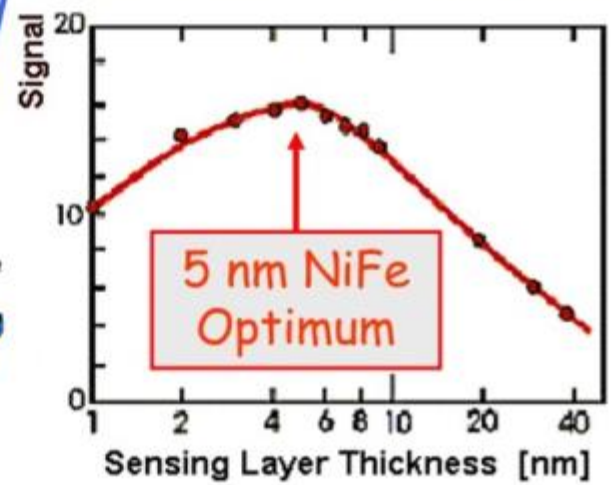


FIGURE 1.5 A schematic representation of a GMR read head (green) that passes over recording media containing magnetized regions. The magnetization direction of the soft (free) layer in the head ***responds to the fields that emanate from the media by rotating either up or down***. The resulting change in the resistance is sensed by the current, *I*, passing through the GMR element.
Courtesy from Prinz, G.A., 1998. Magneto-electronics. Science 282, 16601663.

GMR Reading Head





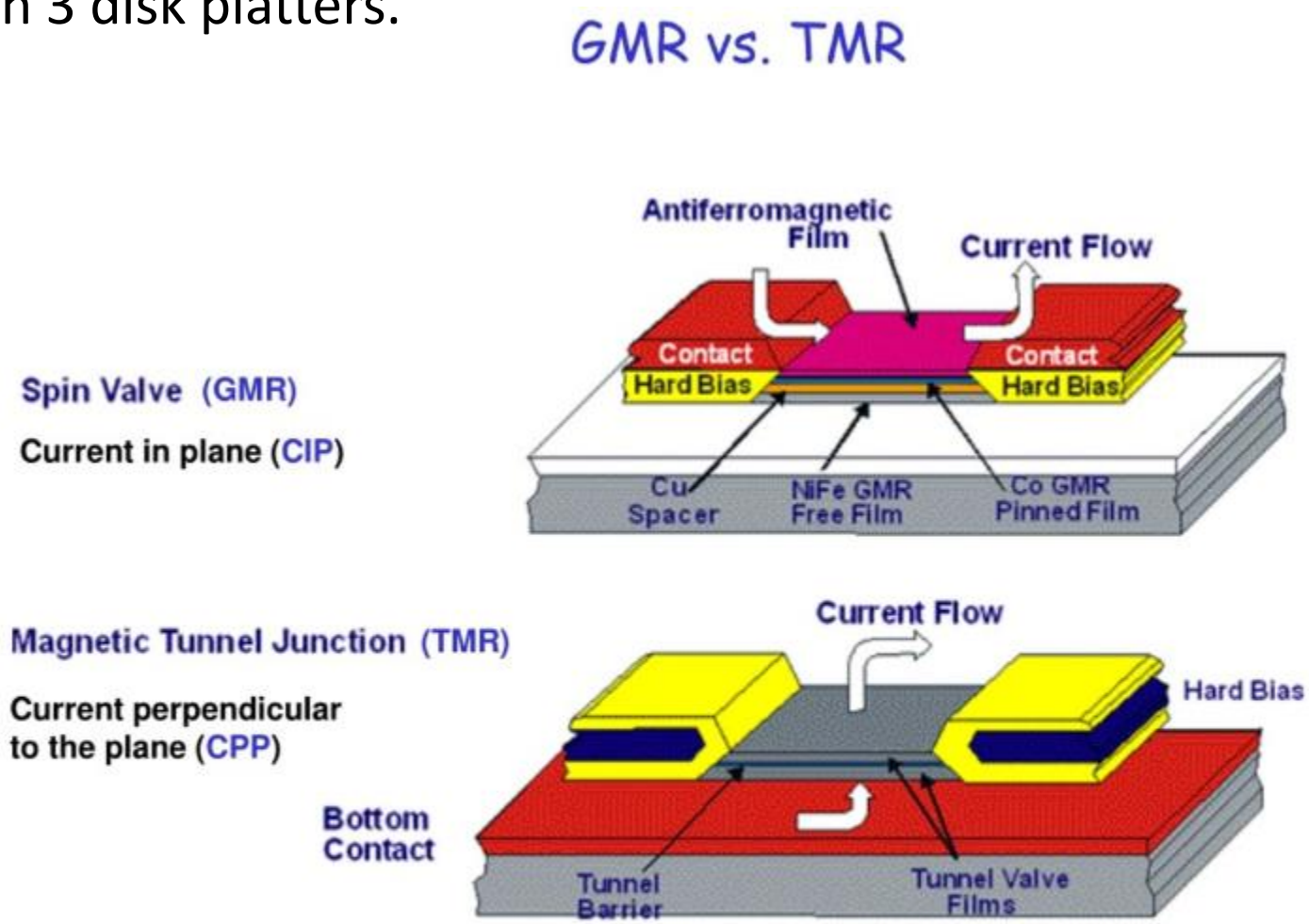


- Magnetization is stored as a “0” in one direction and as a “1” in the other. **Where two of these oppositely magnetized domains meet**, ***there exists a domain wall***, which is a microscopic region of 100-1000 Å (depending on the material used in the media).
- Although there is no magnetic field emanating from the interior of a magnetized domain itself, ***uncompensated magnetic poles in the vicinity of the domain walls generate magnetic fields*** *that extend out of the media*. There is a change in the magnetization direction between two adjacent bits on the disk. ***It is these fields that are sensed by the GMR*** element. Where **the heads of two domains meet**, uncompensated positive poles generate ***a magnetic field directed out of the media***, and where ***the tails of two domains meet, the walls contain uncompensated negative poles*** that ***generate a sink for magnetic lines of flux*** returning back into the media.
- The GMR head element is fabricated so that the ***magnetic moment in the free layer lies parallel to the plane*** of the media in the absence of any applied fields. The ***magnetic moment in the fixed magnetic layer of the GMR element is oriented perpendicular*** to the plane of the media.
- Thus, ***when the head passes over a positive domain wall, the magnetic field pushes the easily reversed magnetic moment up***, and when the head passes over a negative domain wall, the magnetic moment is pulled down. The measured resistance of the GMR element thus increases (for ***more antialigned*** layers) or decreases (for ***more aligned*** layers).

- In this way, by applying constant current to the read head, one can use the measured voltage (and thus resistance) at read head to determine the logical ‘0’ and ‘1’ depending upon the parallel or antiparallel alignment of the two ferromagnetic layers.
- This can be easily measured electronically as the readout of the encoded surface.
- The design goal for this element is to obtain a maximum rate of change in the resistance for a change in the sensed field. Typically, changes in resistance of 1% per oersted are reported.
- **Giant magnetoresistance has shown a magnetic appeal: It allows more data to be packed on computer disks.** If improvements are made in the interfaces between magnetic layers in thin-film structures, ***the number of new applications could prove irresistible***.
- The majority of materials used in HDDs are layers of simple ferro- and ferrimagnetic materials such as metals or alloys like iron, FeCr, and chromium oxide.
- In the interest of developing even ***more sensitive devices, it*** has led to research on materials exhibiting ***CMR effects***, including the manganites described earlier.

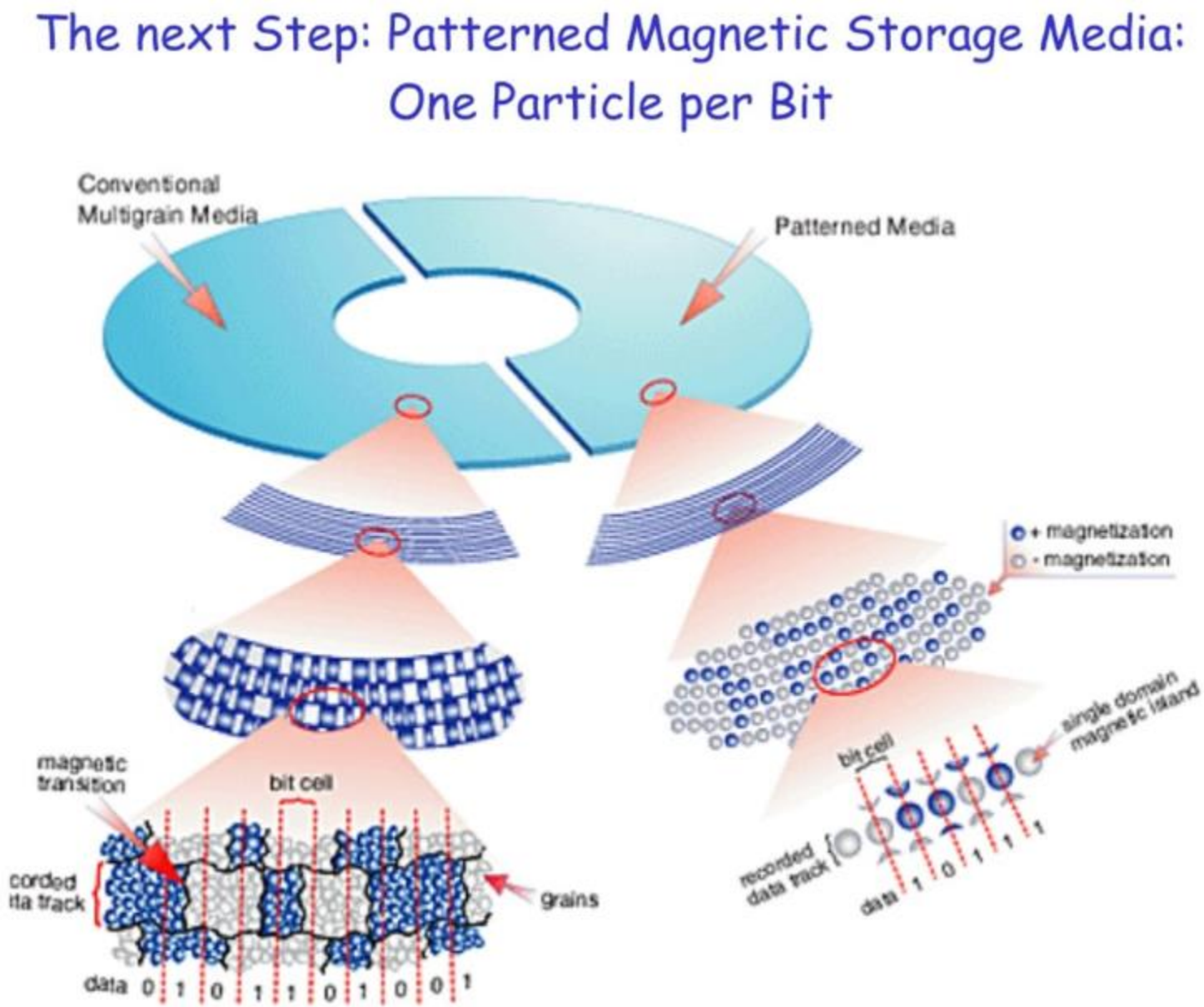
TMR heads

In 2004, the first drives to use tunneling MR (*TMR*) heads (write/read) were introduced by Seagate allowing 400 GB drives with 3 disk platters.



TMR has taken over GMR in hard disk reading heads: Larger effect with the current perpendicular to the layers, no shorting by the metal layer.

❑ DATA STORAGE ON MAGNETIC NANOPARTICLES



❑ DATA STORAGE ON MAGNETIC NANOPARTICLES

- No one can fail to be impressed by the massive increase in the density of stored data on magnetic disks achieved over the last few decades. Among many factors, development of sensitive GMR (TMR), perpendicular recording/writing approach and smaller and better nanomagnets.
- On magnetic hard disks, digital data are stored as a series of binary digits or bits ("1" or "0") patterned by reversals of magnetization in circular tracks around the surface of a rotating disk and the density is normally quoted in bits/in.^{2}. The first hard disk magnetic storage system the RAMAC produced by IBM in 1956 had a storage density of 2000 bits/in.^{2}. Fifty years later, personal computer hard disks had typical storage densities of 200 Gb/in.^{2} (2×10^{11} bits/in.^{2}), an increase by a factor of 100,000,000.
- Recently, Seagate demonstrated a disk system with a storage density of 421 Gb/in.^{2}, and existing magnetic technology is predicted to "top out" at about 1 Tb/in.^{2} (10^{12} bits/in.^{2}).
- On the RAMAC device a data bit required a storage area of side ~0.5 mm, which has shrunk to about 35 nm.
- To put the increase in perspective, if it took a football field to store a single data bit in 1956, it now takes an area the size of a lentil.

- This push to ever-higher storage densities is driven by demand because we are increasingly used to storing and transferring massive amounts of data as multimedia uses ever-higher definition pictures and movies.
- Until now the technology has kept pace with this demand, but the storage density is starting to come up against fundamental limits that require a paradigm shift in storage methodology.
- In the last few years there have appeared many different types of mass storage devices including flash drives, rewritable DVDs, and so on, whose storage density rivals magnetic recording. These will not be discussed in this section, which will focus on the fundamental limits of magnetic storage and describe how nanotechnology can overcome these. Similar limits are to be found in the other storage technologies with, again, nanotechnology offering solutions. For example, there are the prospects for miniaturizing electronics using nanoparticles and carbon nanotubes as circuit elements.
- Magnetic recording of data has some distinct advantages—for example, its extreme nonvolatility. The magnetization of a piece of magnetic material can be reversed at gigahertz frequency for geological timescales without affecting it in any way. Solid-state devices such as flash memories have a limited number of read/write cycles before storage becomes unreliable.
- The main disadvantage of hard disk drives at present is their complex mechanical structure that makes them less robust than flash drives, but in future generations of magnetic recording

devices it may be possible to dispense with the rotating disk.

- At present, data on hard disks are stored on a continuous magnetic film consisting of densely packed nanoparticles on the surface with data bits written onto small areas containing many particles (see Fig. 5.1).

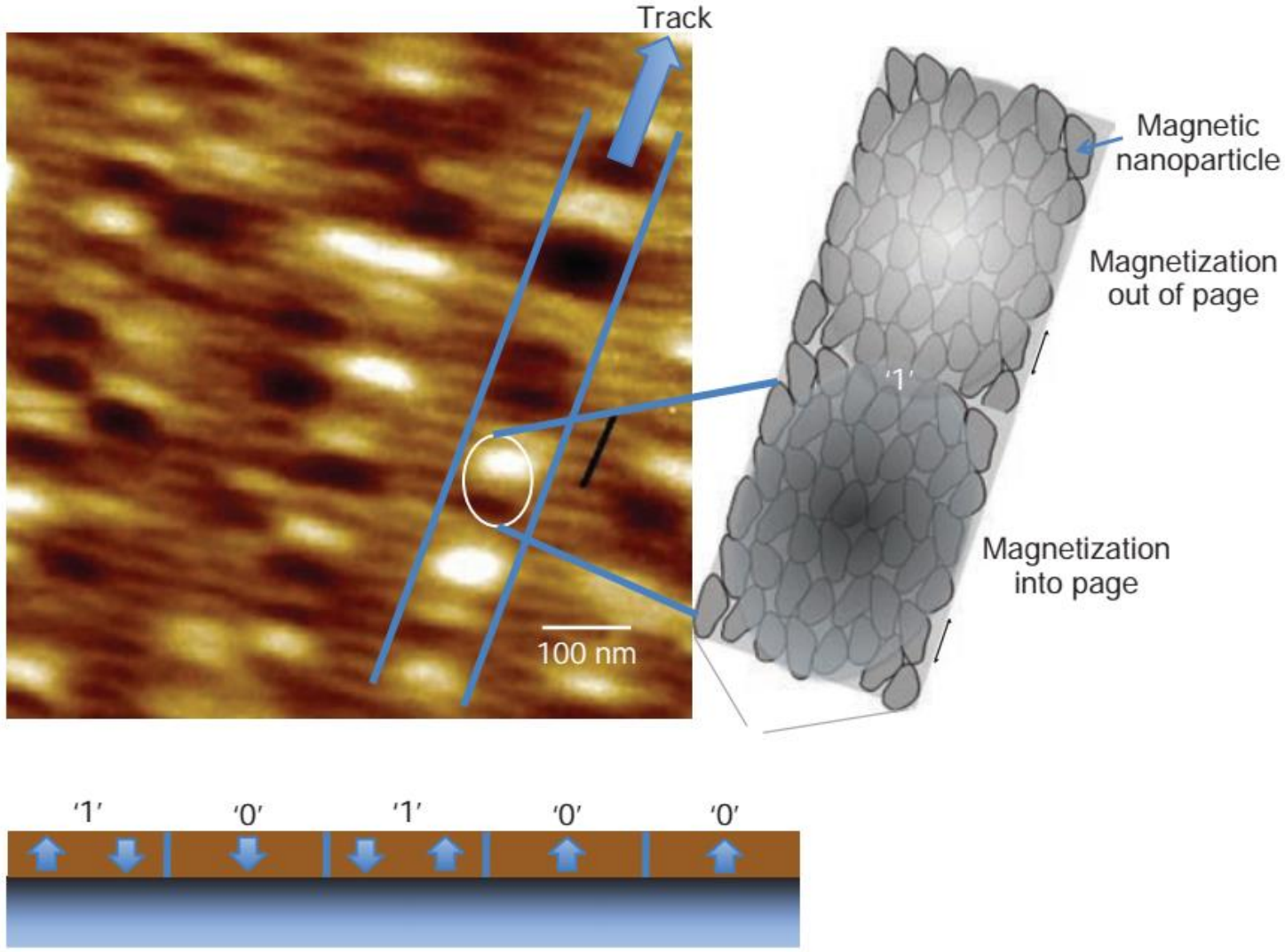


Fig. 5.1 MFM Image of 394 Gb/in^2 disk. Magnetic Force Microscope (MFM) image of the magnetization pattern on the surface of a 500 Gigabyte Seagate 5400.6 Momentus hard disk. The magnetic medium is granular and consists of nanoparticles with sizes in the range 10–20 nm. The information is stored by magnetizing the medium perpendicular to the disk surface (in and out of the page).
As illustrated in the lower diagram A magnetic reversal within the area of a data bit represents a '1' and the absence of a reversal represents a '0'.
Each data bit is written onto a number (~100) of the nanoparticles as indicated by the blow-up showing an individual '1' bit.
MFM image reproduced with permission from NanoMagnetics Instruments (www.nanomagnetics-inst.com).

- Suppose, instead, that data could be stored by magnetizing individual magnetic nanoparticles such as the Fe particles with a diameter of 3 nm shown in Fig. 1.9. If these were in an array and separated sufficiently so that changing the magnetization of one did not affect its neighbors (separation required is approximately equal to particle diameter), then, for example, “up” magnetization could represent “1” and “down” magnetization could represent “0” (see Fig. 5.2). The recording density in such as system could reach 100 Tb/in.^{2}—that is, a factor of 100 higher than the predicted limit of current technology.

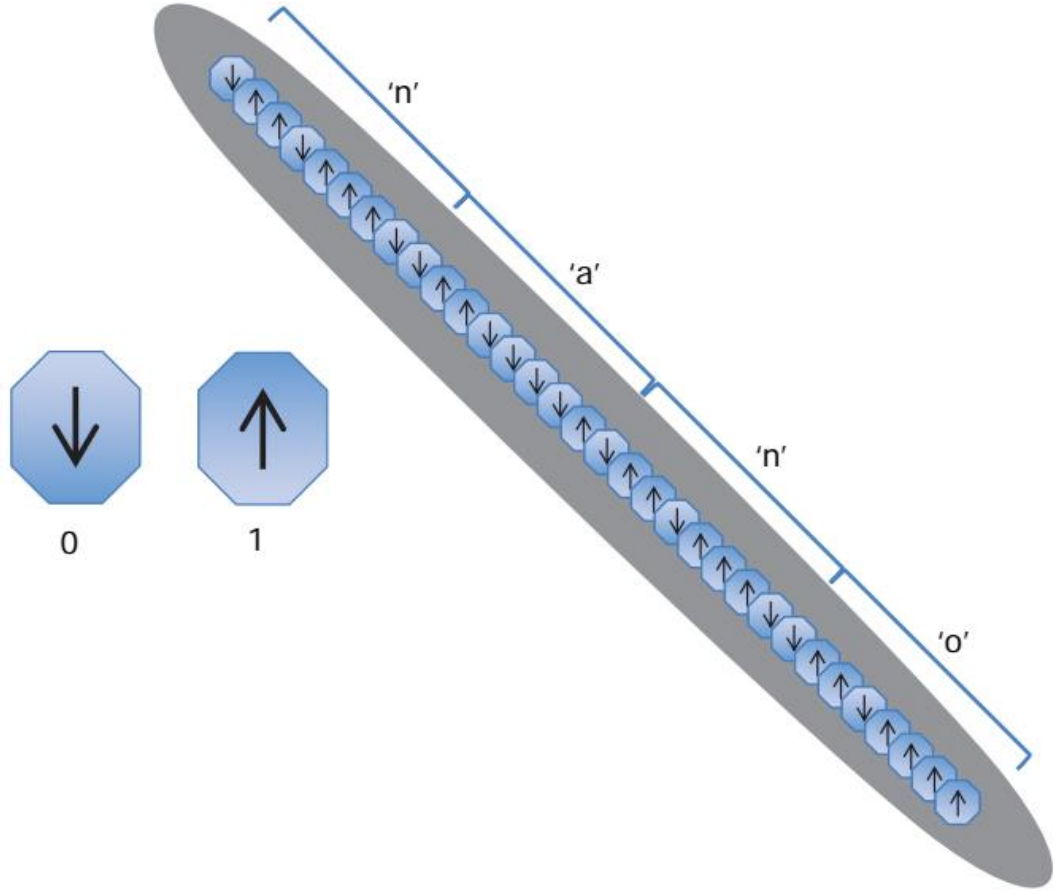


Fig. 5.2 Hypothetical data storage onto individual magnetic nanoparticles.
Schematic of a recording medium where each nanoparticle stores a data bit with, for example a ‘0’ represented by ‘down’ magnetization and a ‘1’ by ‘up’ magnetization. The image shows the word ‘nano’ stored in ASCII code along a line of particles.
If these particles were at the superparamagnetic limit the storage density would be ~100 Tb/in^2, that is, about 100 times higher than the predicted limit for existing technology.

- In our hypothetical single-particle recording system, each nanoparticle becomes a memory element and performs an individual function—that is, storing a single data bit—and the technology is thus evolutionary nanotechnology. This task requires a pair of transistors in a flash memory, for example.
- We will discuss below the fundamental limits of magnetic recording and what problems have to be overcome to enable data storage onto individual nanoparticles.
- In order to permanently store data, a piece of magnetic material has to be a single magnetic domain, which requires it to have a diameter less than about 100 nm. Thus, any particle we would be interested in down to the size of a single atom can be assumed to be a single magnetic domain. As we shrink the size down from the single-domain limit at about 100 nm toward single atoms, there is a size below which the magnetization becomes unstable due to thermal fluctuations, and the magnetization will be lost in the absence of an applied magnetic field.
- The critical size, below which the particle demagnetizes itself, depends on a number of factors including the temperature, shape, and chemical composition of the particle; but at room temperature for spherical Fe nanoparticles, for example, it is of the order of 6 nm.
- The temperature below which particles of a given size have a stable magnetization direction and can thus store data is known as the “blocking temperature.”

- This is a fundamental limit that sets the maximum data storage density at a given temperature. Particles below the critical size are “superparamagnetic”; that is, they will magnetize in an applied field along the direction of the field but will demagnetize when the field is turned off. In fact, this is normal paramagnetic behavior, and the “super” pronoun is used because the magnetic moment of the nanoparticle is derived from the individual atomic magnetic moments locked together to form a single “giant” moment.
- The limit to the data storage density set by the onset of thermal instability in the nanoparticle magnetic moment is known as the **superparamagnetic limit**. This would set the ultimate limit for magnetic storage at about 100 Tb/in.^{2} unless the temperature is reduced but cooling the storage medium is generally disregarded. This is not because it is technologically difficult but because it is pointless to store large quantities of data in a tiny space if a large cooling unit is required next to the storage device.
- The 1 Tb/in.^{2} quoted above for current technology is also a superparamagnetic limit, but present-day devices store a single data bit on an area of a disk containing about 100 nanoparticles (see Fig. 5.1); so, if they are individually superparamagnetic, information can’t be stored.

- Achieving magnetic storage at ***data densities significantly higher than 1 Tb/in.^{2} requires technology that can read from and write to individual nanoparticles***.
- This involves ***two major and presently unsolved technological challenges***.
- ✓ **One** is the ***ability to organize suitable nanoparticles*** (i.e., those that can hold a permanent magnetization at room temperature) ***in an ordered array*** such as lines of uniformly spaced nanoparticles as illustrated in Fig. 5.2.
- ✓ The **other** is a method of ***reading the magnetization*** of individual nanoparticles and *changing the magnetization of a selected particle* (***the "write" process***).
- A promising approach to producing suitable ordered arrays is to chemically prepare nanoparticles of **FePt**, a magnetic alloy which, in the correct phase, has a ***very high anisotropy and thus, for a given size, a high blocking temperature***.
- Ordered arrays of the FePt nanoparticles can be produced by dispensing a drop of the suspension on a flat surface and allowing the liquid to evaporate. With this method the spacing between the particles and ordered arrangement can be controlled by choosing the surfactant coating of the particles. Figure 5.3 shows an atomic force microscope (AFM) image of 6-nm FePt nanoparticles manufactured by chemical synthesis and formed as an ordered square array.

- These are an illustrative example of functionalized nanoparticles. The constituent alloy of the particles has been chosen to give them suitable magnetic properties, and their surface has been coated with a surfactant that enables them to self-assemble with the desired arrangement and spacing.
- It is also possible to control the magnetic anisotropy of the nanoparticle by coating each one with a thin shell a few atomic layers thick of an antiferromagnetic material such as Cr. This can be done using the gas-phase production method and adds a further layer of functionalization allowing the synthesis of complex nanoparticles with “designed” properties and function.
- The problem of producing ordered arrays of nanoparticles can therefore be solved in principle, though doing it in a reliable way with the right sort of nanoparticles over macroscopic areas remains a challenge for bottom-up methods.
- It is also possible to manufacture magnetic arrays using top-down methods such as electron beam lithography (EBL) and focused ion beam (FIB) milling. The problem with these methods is that they have not yet achieved the synthesis of sub-10-nm nanostructures possible with bottom-up methods. In addition, they are exceedingly slow at manufacturing macroscopic areas of nanoparticles and would be unsuitable for the commercial manufacture of storage media.

- Even if producing ordered magnetic nanoparticle arrays over macroscopic areas were routinely achievable, reading from and writing to the array is at present not feasible on anything like the scale shown in Fig. 5.3.
- The process of reading and writing (R/W) requires the capability of imaging the magnetic pattern on the surface with the resolution of a single nanoparticle and changing the magnetization state of a single chosen nanoparticle. At present the method for imaging magnetic patterns with the highest resolution is magnetic force microscopy (MFM); this has demonstrated a resolution of about 20 nm in ambient conditions, but this is certainly not routine. It is likely that better resolution can be obtained in vacuum; but as with cooling, this is not an option for any commercial storage device.

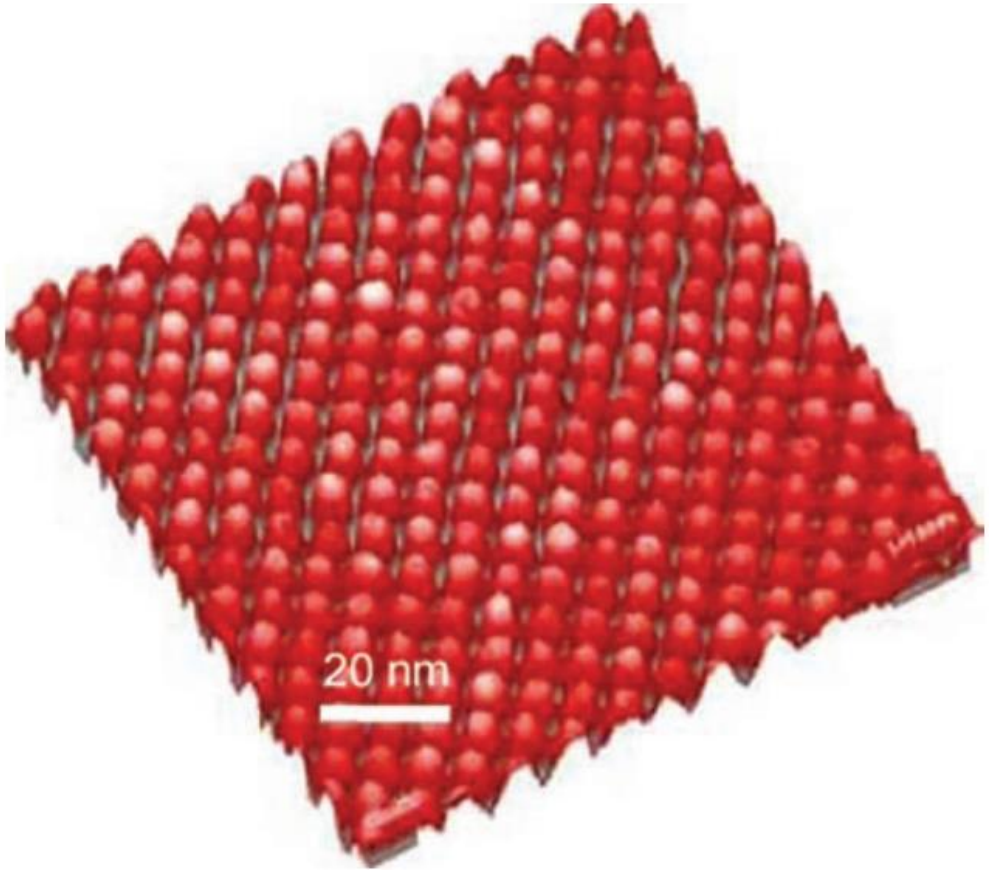


Fig. 5.3 Ordered array of FePt nanoparticles. AFM image of ordered array of 6 nm diameter FePt nanoparticles. Reproduced from the nanowerk website (http://www.nanowerk.com/spotlight/spotid=301.php) with permission from Prof. Shouheng Sun, Brown University, U.S.A.

- In summary, the state of the art in data storage on individual magnetic nanoparticles is at various stages relative to conventional magnetic storage technology, depending on which parameter is compared.
- Media of arrays of individual magnetic nanoparticles can be prepared with a density of >10 Tb/in.^{2}—that is, about a factor of 50× greater than existing hard disk drives but not reliably over macroscopic areas.
- At present there is no way to read and write (R/W) using a magnetic array at this density.
- The key point, however, is that the limitations are technical rather than fundamental and can be overcome with improvements in MFM technology and multiple-tip arrays.
- There is no reason, in principle, why it should not eventually be possible to use arrays as dense as the one shown in Fig. 5.3.
- One further benefit of MFM-based technology is that it dispenses with the rotating disk and can be built entirely into a solid-state and extremely thin platform.

- The storage density of such magnetic memories is impressive. We now have good synthetic methods for making these same materials as crystals with dimensions of only a few nanometers. **Why aren't those nanocrystals used to make even more dense memory disks?**
- The reason is that the energy needed to flip the magnetization (i.e., to turn a "0" into a "1" and vice-versa) is strongly size-dependent. For a ferro- or ferrimagnet this energy is equal to Mr, where M is the magnetic energy per unit volume and r is the characteristic dimension (e.g., the length of the edge of a cube, or the diameter of a sphere) of the magnetic grain. For typical materials such as iron, this energy becomes comparable to kT when r is about 3-5 nm. Such small particles are superparamagnetic, meaning that they still have a large magnetic moment because of the ordering of their spins, but they do not retain a permanent polarization in the absence of an applied magnetic field. Superparamagnetic particles are thus not useful for magnetic memories, but they are interesting and practical in other ways, for example in ferrofluids, magnetic resonance imaging (MRI), and some emerging medical diagnostic and therapeutic applications.
- In the illustrative examples (involving electronic conduction, magnetic behavior, and light emission), ***the transition to new properties involves a crossover in which the characteristic energy of the system is comparable to the thermal energy kT***. It just so happens that for many physical phenomena, this crossover occurs on the length scale of nanometers.

❑ Spin Transfer Torque (STT) and STT-RAM

- The understanding of methods to manipulate magnetism was transformed in 1996, when Slonczewski and Berger independently predicted that the free layer in spin valve structure can be switched by current instead of the field.
- If high-enough current density is passed through a spin valve stack as shown in Figure 17.9, the fixed FM acts as a spin polarizer/filter, and the current is spin polarized; i.e. it has a net magnetic moment. This spin-polarized current applies a torque on the free layer when it passes through the free layer. It transfers its angular momentum to the free layer and switches the magnetization of the free layer. This phenomenon is called STT, where current is used to manipulate magnetic alignment of the free layer. As current can be constrained and manipulated much easily in comparison to fields, STT is a promising candidate for future data storage and non-volatile memory applications. In 2012, Everspin Technologies successfully produced a 64 MB **STT-RAM**, based on STT effect.
- The key mechanism underlying GMR and STT effect is spin injection from ferromagnetic layer to non-magnetic layer (which then traversed through the second ferromagnetic layer). As mentioned above, the current which goes through the fixed ferromagnetic layer gets spin polarized. This spin-polarized current results in various kinds of interesting phenomena, spin accumulation at the interface where spins are injected from a FM to nonmagnet (NM) called as spin injection, switching of the other ferromagnetic layer (STT, described above) and can also excite spin waves or vortex oscillations.

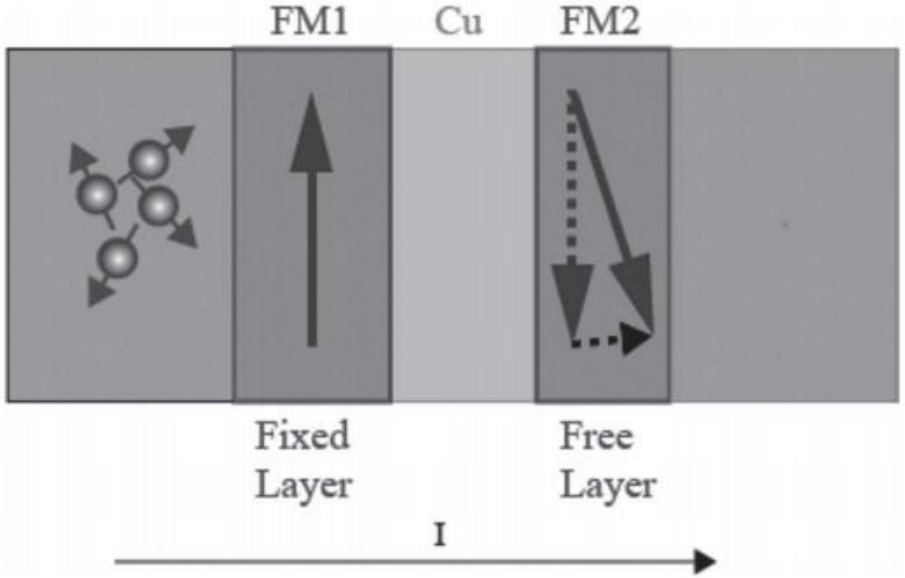


FIGURE 17.9 Spin Transfer Torque (STT): Using current to manipulate the magnetization of the free layer.

❑ MRAM (magnetoresistive random access)

- Magnetoresistive random access memory (MRAM) is a nonvolatile and nondestructive readout memory, which is based on a magnetic anisotropy energy to retain information and the principle of magnetoresistance to retrieve information (instead of using the electrical bits to store your data). It is sometimes called as “ideal memory”. As it is a non-volatile type of memory, no refresh is required to retain the data and the power consumption is very less.

- **A memory device follows at least three key requirements**: (1) the proposed device should be able to ***store information***. If the information is stored for long periods of time even without power, then it is called a **nonvolatile memory device**, (2) there should be mechanisms to ***write information*** onto the device, and (3) there should be mechanisms to ***read information*** from the device. To achieve these requirements in MRAM, researchers have designed and investigated various kinds of MRAM schemes in the past. In MRAM, these functions are performed as following: (1) The read operation is carried out by sensing the resistance difference between two states of a magnetoresistive device. (2) The storage of information relies on the magnetic retention properties, arising from the magnetic anisotropy of storage layer. (3) The write operation is performed by changing the orientation of storage layer magnetization, which can be achieved by inducing a magnetic field.

Working Principle:

- The magnetoresistive device used in MRAM is very similar to the device used for the read head of magnetic hard disk drives.

- The first storage element used in MRAM for storing information was based on **spin valve** or **MTJ** structure. Spin valve mainly consisted of two ferromagnetic layers sandwiching a nonmagnetic conductive layer. The two ferromagnetic layers are called the free/soft layer (FL) and the hard/pinned layer, respectively. An AFM (antiferromagnetic) layer is used in proximity of or in contact with the pinned layer in order to pin the magnetization direction of the layer, which ***should not be reversed during the operation of the memory device***.

- The MTJ is composed of a fixed magnetic layer, a thin dielectric tunnel barrier and a free magnetic layer. When a bias is applied to the MTJ, electrons that are spin polarized by the magnetic layers traverse the dielectric barrier through a process known as tunneling. Like the spin valve, the MTJ device has a low resistance when the magnetic moment of the free layer is parallel to the fixed layer and a high resistance when the free layer moment is oriented antiparallel to the fixed layer moment. This change in resistance with the magnetic state of the device is an effect known as magnetoresistance, hence the name "magnetoresistive" RAM.
- The reference layer is used to maintain the magnetic direction, while the free layer, can have its direction changed by using magnetic fields or by applying polarized currents.
- Unlike most other semiconductor memory technologies, the data is stored as a magnetic state rather than a charge and sensed by measuring the resistance without disturbing the magnetic state.
- Storing of a logical element (0 or 1) takes place by changing the resistance of a spin valve or an MTJ. The resistance depends on the relative spin orientations of two ferromagnetic layers, and can be of two types: high resistance (logical 1) or low resistance (logical 0).
- **Figs. 1 and 2 show** an illustration of MTJ MRAM architecture. Arrays of several MRAM cells form a memory device. A typical MRAM cell has a transistor and a magnetoresistive element, quite similar to a DRAM (dynamic RAM), which contains a transistor and a capacitor. While the charge stored in the capacitor of a DRAM defines its memory state, the resistance of the magnetoresistive element determines 1 and 0 states. A transistor for every MRAM cell is required as the absolute difference between the resistances, and hence, the voltages of two states are not high enough to function without a transistor. Moreover, the transistor also provides the current required for the write operation.

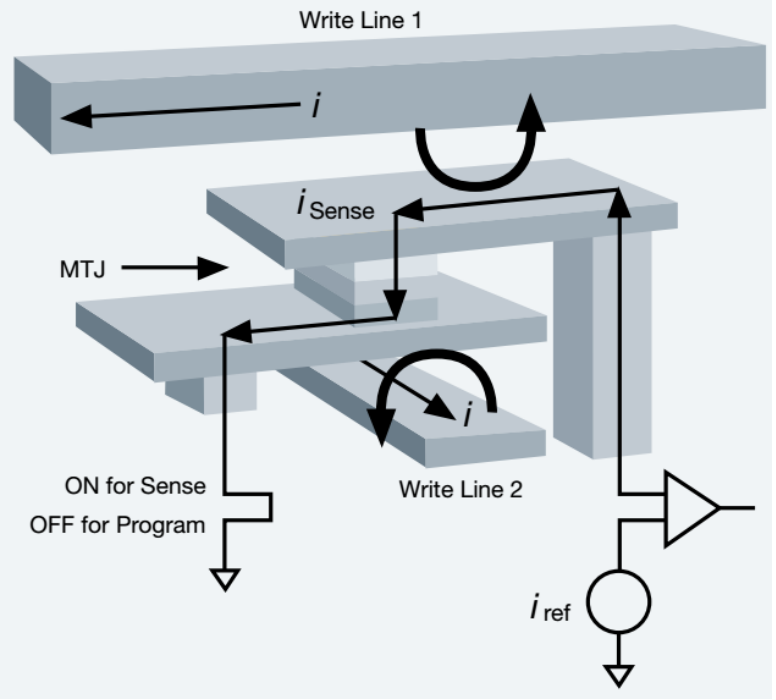


Figure 1. Schematic of a 1-transistor, 1-MTJ memory cell showing the write lines above and below the bit and the read current path.

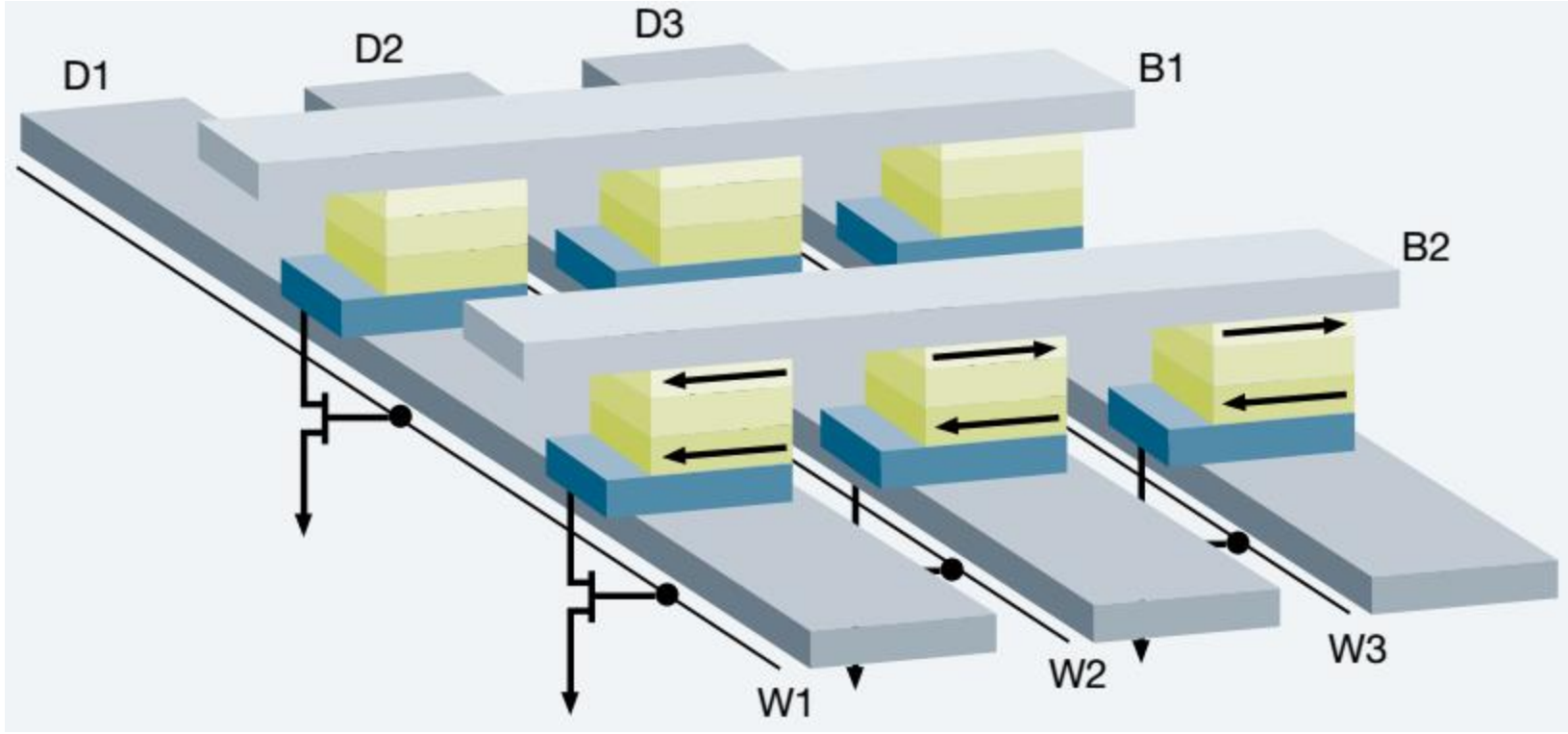


Figure 2. A memory array consisting of many MRAM cells with digit and bit lines for cross-point writing and isolation transistors controlled by word lines.

Courtesy: Freescale™ Semiconductor

freescale semiconductor

- To make a high-density memory, the MRAM cells shown in Figure 1 are arranged in a matrix with each write line spanning hundreds or thousands of bits, as shown in Figure 2. During the write operation, current pulses are passed through a digit line and a bit line, writing only the bit at the cross point of those two lines. During the read operation, the target bit's isolation transistor is turned on to bias the MTJ and the resulting current is compared to a reference to determine if the resistance state is low or high.

- Based on the storage mechanism, the MTJs may be classified into two types: (1) in-plane MTJ, which has magnetization of ferromagnetic layers in the film plane and (2) perpendicular MTJ having the magnetization perpendicular to the film plane.

- The storage principle of an MRAM is based on the energy barrier (E_B) required to switch the magnetization of a single-domain magnet from one direction to the other. The magnetization will be fixed in a particular direction if the E_B for magnetization reversal is high enough to overcome the external stray fields and the thermally assisted reversal of magnetization. This storage principle is very similar to that used in magnetic recording, although the way the materials are designed and the information is written, are different.

- In an MRAM, the magnetization direction of the reference layer or pinning layers (P_L) is fixed and only the magnetization direction of the free layer (FL) varies to store "0" and "1" states. Since the direction of the reference layer must never be changed, it is made of materials that have a huge E_B. The FL is designed with materials that have a magnetic anisotropy, just sufficiently high enough to store the magnetization for certain years (typically 10 years in the case of magnetic recording).

- The E_B that helps store the information is typically proportional to KV (where K is the magnetic anisotropy constant and V is the volume of the FL). **This energy must be much larger (60 times, for storage time longer than 10 years) than the thermal energy *kT***. In certain cases, the E_B may be different from KV and hence, the thermal stability factor is simply written as D(=E_B/kT).

- Although a high anisotropy is preferred for storing information, the ***anisotropy of these materials cannot be too high***, as their magnetization direction needs to be oriented at will, to write 0 and 1 states.

- Using a magnetic state for storage has two main benefits. First, the magnetic polarization does not leak away with time like charge does, so the information is stored even when the power is turned off. And second, switching the magnetic polarization between the two states does not involve actual movement of electrons or atoms and thus no known wear-out mechanism exists.

- **Why MRAM should be used?**

- DRAM has the advantage of being cheap, but is comparatively slow and data is lost when power is off.
- SRAM, on the other hand is faster than DRAM. But it can cost up to 4 times as much as DRAM and data is lost when power is turned off.
- FLASH memory saves data when the power is off, but the process is too slow and consumes a lot of power.
- MRAM potentially combines the density of DRAM and the high speed of SRAM and the non-volatility of FLASH memory or hard disk, and all this is done using very less power. MRAM can resist high ionizing radiation, can operate in extreme temperature conditions and thus is very suitable for aerospace applications when combined with suitable CMOS technology.

- **Advantages of M-RAM:**

MRAM can resist high radiation, can operate in extreme temperature conditions, and can be tamper resistant. This makes MRAM suitable for automotive, industrial, military and space applications, and these are important segments for MRAM developers.
M-RAM offers several advantages over traditional memory technologies like DRAM and SRAM. Firstly, M-RAM is non-volatile, which means it does not require power to retain stored data. This feature makes it ideal for use in portable devices that require long battery life. Secondly, M-RAM is extremely fast, with read and write speeds that are comparable to DRAM and SRAM. This feature makes it ideal for use in high-speed memory applications like cache memory. Finally, M-RAM is highly durable, with the ability to withstand extreme temperatures, radiation, and physical shock. This makes it ideal for use in harsh environments like outer space and military applications.

➢**Potential Applications of M-RAM:**

M-RAM has the potential to revolutionize the way we store and access data, with several potential applications in various industries. One of the most promising applications is in portable devices like smartphones and tablets, where M-RAM's non-volatile nature and fast read and write speeds can significantly improve battery life and performance. M-RAM can also be used in cache memory applications, where its fast read and write speeds can significantly improve computer performance.

Another potential application of M-RAM is in automotive electronics, where its high durability and ability to withstand extreme temperatures can significantly improve reliability and performance. M-RAM can also be used in military applications, where its high durability and ability to withstand radiation and physical shock make it ideal for use in harsh environments.

➢**Applications of M-RAM:** MRAM has a potential in all memory applications in these devices:

•Digital Cameras; Cellular Phones; MP3; HDTV; Laptops

Conclusion:

Magnetic Random Access Memory (M-RAM) is a promising technology that has the potential to revolutionize the way we store and access data. With its non-volatile nature, fast read and write speeds, and high durability, M-RAM can significantly improve the performance and reliability of various electronic devices.