MAGNETIC NANOPARTICLES

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. For that reason nowadays, a number of companies are offering magnetic particles with a rather large range of sizes and magnetic properties. The main applications of magnetic particles 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). Magnetic nanoparticles are very useful both as the media for storage as well as part of nanoscale reading heads.
- In particular, Fe-based oxides are largely used for MNP preparation. 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 phenomenon of ***giant magnetic resistance*** arises due to the spin of the electrons and is observed in a stack of alternating, nanometer thick, magnetic and nonmagnetic layers. ***The ability to control and manipulate the spins of electrons, has given rise to a whole new field of spin-based electronics or spintronics*** where the *electron carries not only the charge but also information in the form of its spin*.

- 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.

NANOSCALE SIZE EFFECTS ON THE MAGNETIC PROPERTIES

- In addition to electronic conductivity, *magnetism is another unique property*.
- When the size of a magnetic material is reduced, the number of surface atoms becomes an important fraction of the total number of atoms, surface effects become important, and quantum effects starts to prevail. When the size of these domains reaches the nanoscale, these materials show new properties.
- 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

- In general, the ***magnetic behavior of a material depends*** on the ***structure*** of the material and on its ***temperature***. However, the two ***key issues*** *dominate the* ***magnetic properties of nanoparticles*** *are*: **finite-size effects and surface effects**, which give rise to various special features.
- 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.
- One of the important (size) effects that is observed as a result of this is the phenomenon of ***superparamagnetism*** in nanometer-sized ferromagnetic crystals.
- *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.

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*. One of the important effects that is observed as a result of this is the phenomenon of ***superparamagnetism*** in nanometer sized ferromagnetic crystals.
- 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.

Single-domain Particles

- The *typical size of classically expected domain is around* 1 μm.

❖ ***Formation of single-domain particles is only the onset of size effects in the nanoworld.***

- 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.*** Figure 7.1 shows evolution of the magnetic state of nanoparticles as function of size.
- 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.

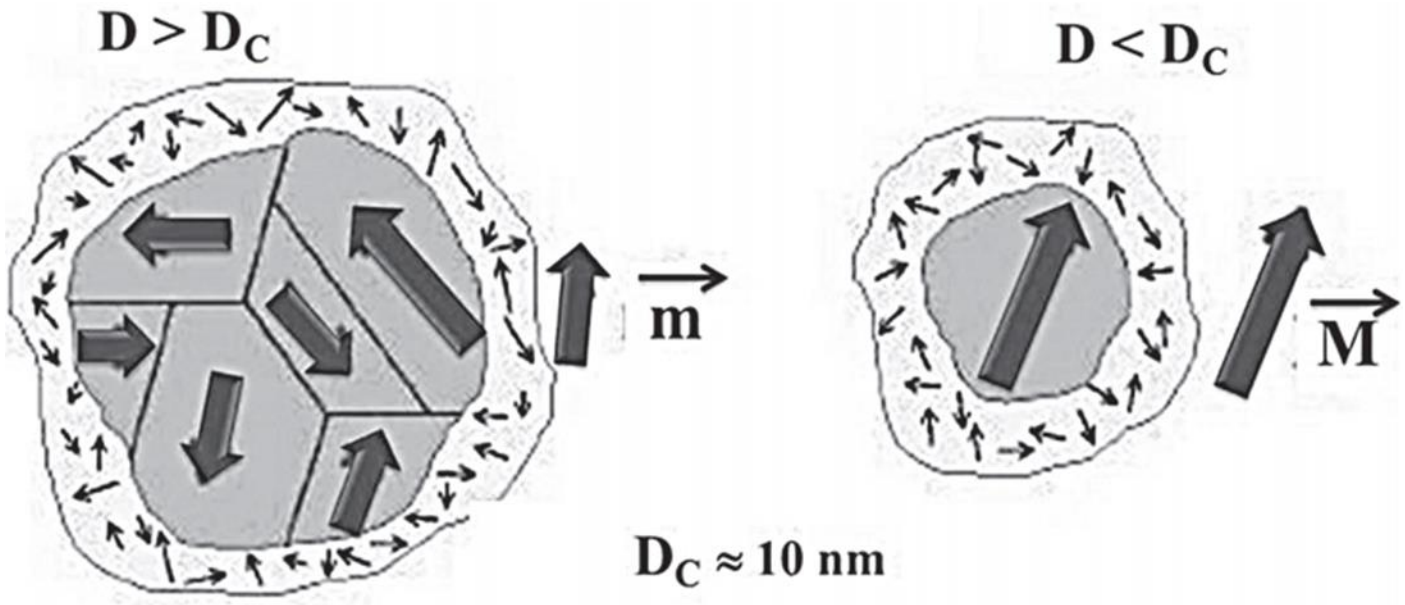


FIGURE 4.7 Multiple magnetic domains for bulk materials and single-domains for nanomaterials.

- 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*.

Critical size, or single domain size D_s: $\gamma D_s^2 \sim M_s^2 D_s^3$ to yield: $D_s \sim \gamma / M_s^2$

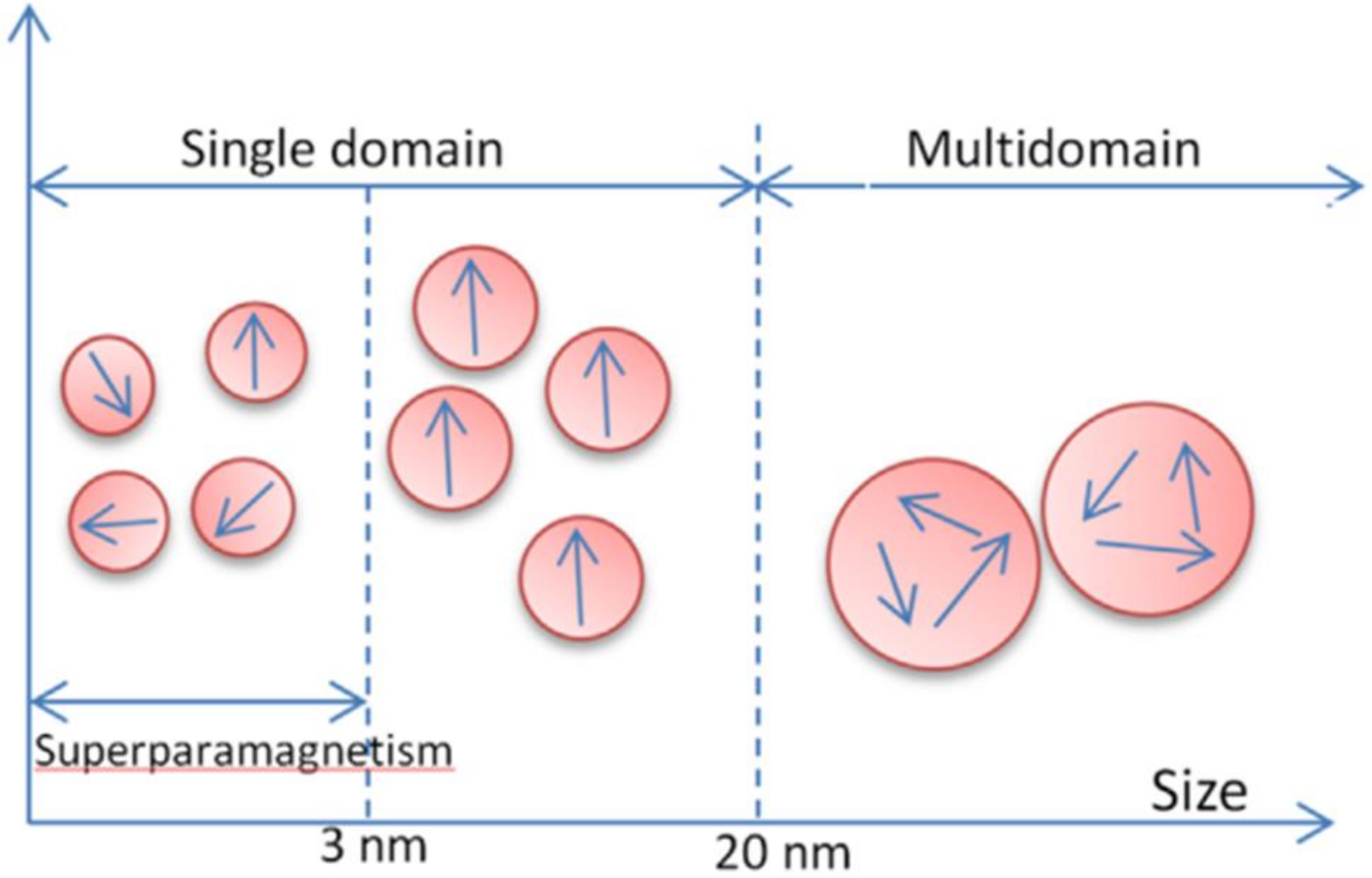


Figure 7.1 Evolution of the magnetic state of magnetic nanoparticles as function of size. The transitions are indicative and depend on the material and size.

- Domain formation requires creation of walls, which are an area. Hence if γ is the domain wall energy per unit area, we expect a $\boldsymbol{\gamma D^2}$ functionality for the total **domain wall energy**.
- Now *consider large D, then 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 **critical size, or single domain size $\boldsymbol{D_s}$,** *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: $\boldsymbol{D_s \sim \gamma / M_s^2}$
- 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*.

- ***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***.

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

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.

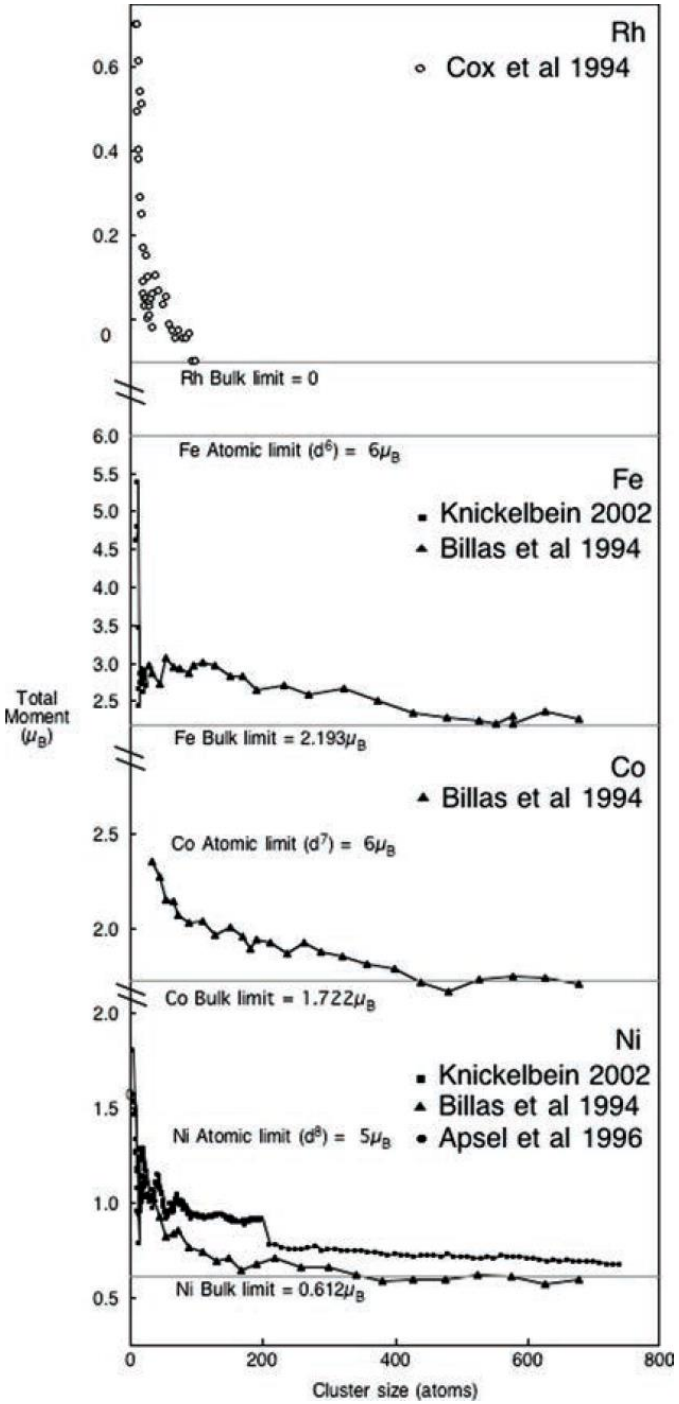
Figure 1.8 shows measurements of the magnetic moment per atom in nanoparticles of the above four metals as a function of the number of atoms in the particle. In the case of iron, cobalt, and nickel, a significant increase in the magnetic moment per atom over the bulk value is observed for particles containing 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

- Magnetic nanoparticles are made of *ferromagnetic or ferrimagnetic materials*. Hence, *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.
- If the size of the particle is small, all the magnetic moments of the MNPs are aligned along a single direction.
- *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.*
- **Because of this, single-domain particles have a larger coercivity compared to multidomain systems.** Generally speaking, *it is harder to rotate the spin magnetization than to move a domain wall.* This is the reason for the very **high coercivity** (H_c) *observed* ***in small nanoparticles***.

- **Shape anisotropy is another source for the high coercivity in a system of small particles**.

- ✓ 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.***

Superparamagnetism

- The second important phenomenon that takes place in nanoscale 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

- When the size of the magnetic nanoparticle (MNP) decreases, the magnetic energy becomes of the order or smaller than the thermal energy ($k_B T$). 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.
- The transition between the superparamagnetic state and the blocked state depends on the local anisotropies of the particles and of the strength of the local magnetization.
- 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.
- **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.
- *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.* **Because of this, single-domain particles have a larger coercivity compared to multidomain systems.**

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

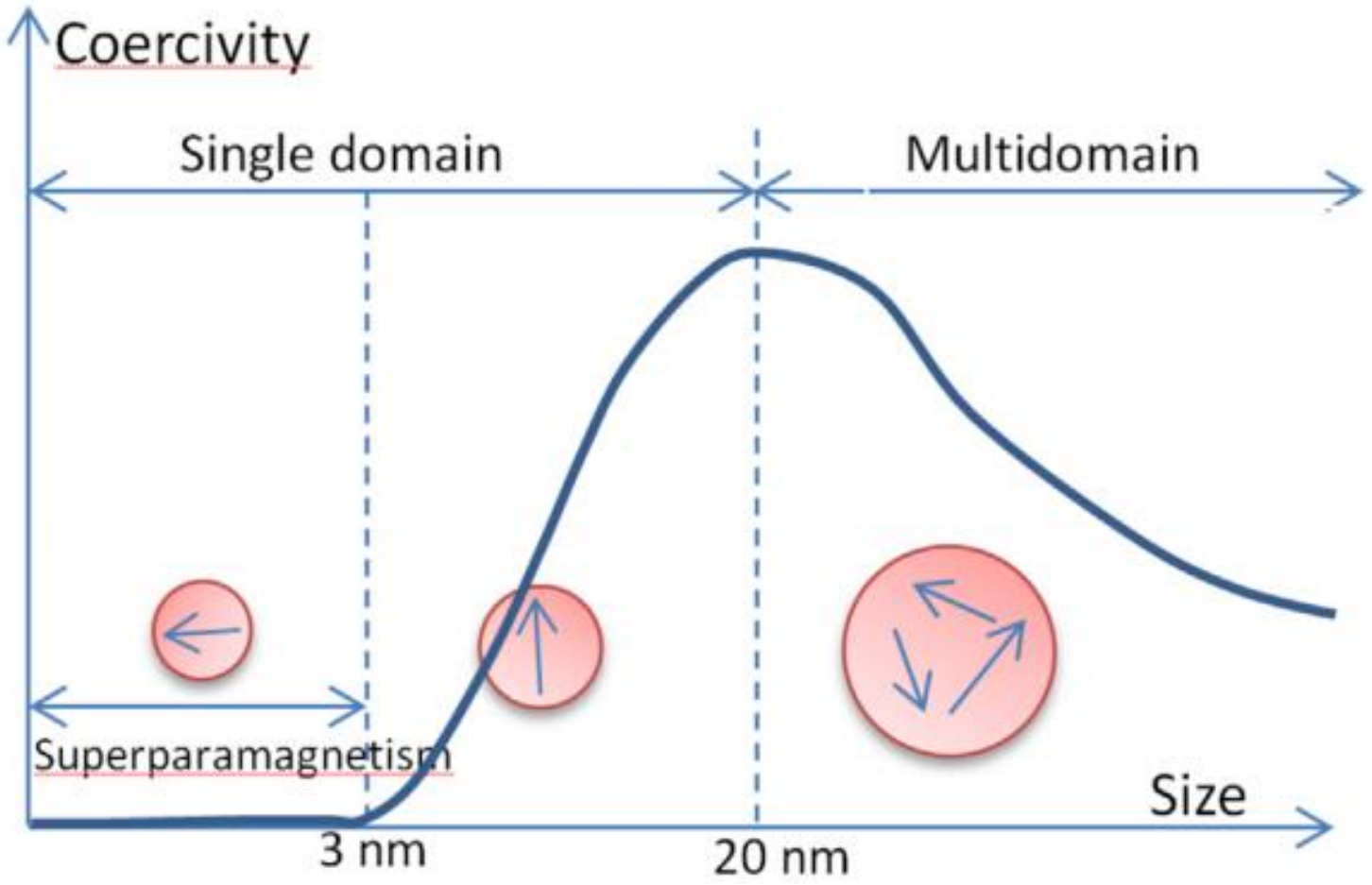


Figure 7.2 Evolution of coercivity as function of size.

- **As the particle size is reduced**, a stage is reached when the particle consists of a single domain. *In a single-domain particle, the rotation of the magnetization is the only mechanism available for the change in the magnetization.* Such rotation has to act *against magnetic anisotropy*. This ***leads to a very high coercivity*** in the single-domain particles. **At this size, the coercivity increases sharply and stays at a maximum as the particle size is decreased.**
- ***Below the Curie temperature* of a ferromagnet or ferrimagnet, *all the spins are coupled together and so cooperate to yield a large total moment*.** This moment is bound rigidly to the particle by one or more of the variety of anisotropies that we have discussed (the unit of the anisotropy constant K is Jm^{-3}). The total energy due to anisotropy is therefore KV where V is the volume of the particle.
- If the size of single domain particle is reduced, the quantity KV may become small enough to be comparable to the thermal energy kT at some size depending on the temperature. ***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. The temperature at which this happens* is called the ***blocking temperature, T_B*.**

- *Thus,* ***for a given particle size, there is a temperature that marks the transition from a permanent static moment to one that is fluctuating in a nanoparticle.***
- **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.
- 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.

The phenomenon of superparamagnetism is, in fact, *timescale-dependent* due to the stochastic nature of the thermal energy. We have seen earlier that ***KV represents an energy barrier to the total spin reorientation***. Considering that the rotation or flipping from one easy direction to another of the magnetization vector in a single domain particle is a thermally activated process with an energy barrier equal to *KV*, the *probability for jumping this barrier is proportional to the Boltzmann factor*, exp*(–KV/kT)* where *k* is the Boltzmann constant. This can be made quantitative by introducing an attempt timescale τ_0, which describes the timescale over which μ_p attempts to jump the *KV* barrier. Its frequency can then be written as

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

Here f_0 is a proportionality constant. It is usually assigned a value of ~10^9 sec^{-1}. The time τ_0 is called the ***relaxation time***. The attempt timescale τ_0 is about 10^{-9} sec. Then the timescale for a successful jump (the average time it takes for the magnetization to change from one easy direction to another) is then given by $f = \frac{1}{\tau} = \frac{1}{\tau_0}\exp(-KV/kT)$. ***If the time taken for measurement 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 is ferromagnetic**.

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***).

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.

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.

- 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.

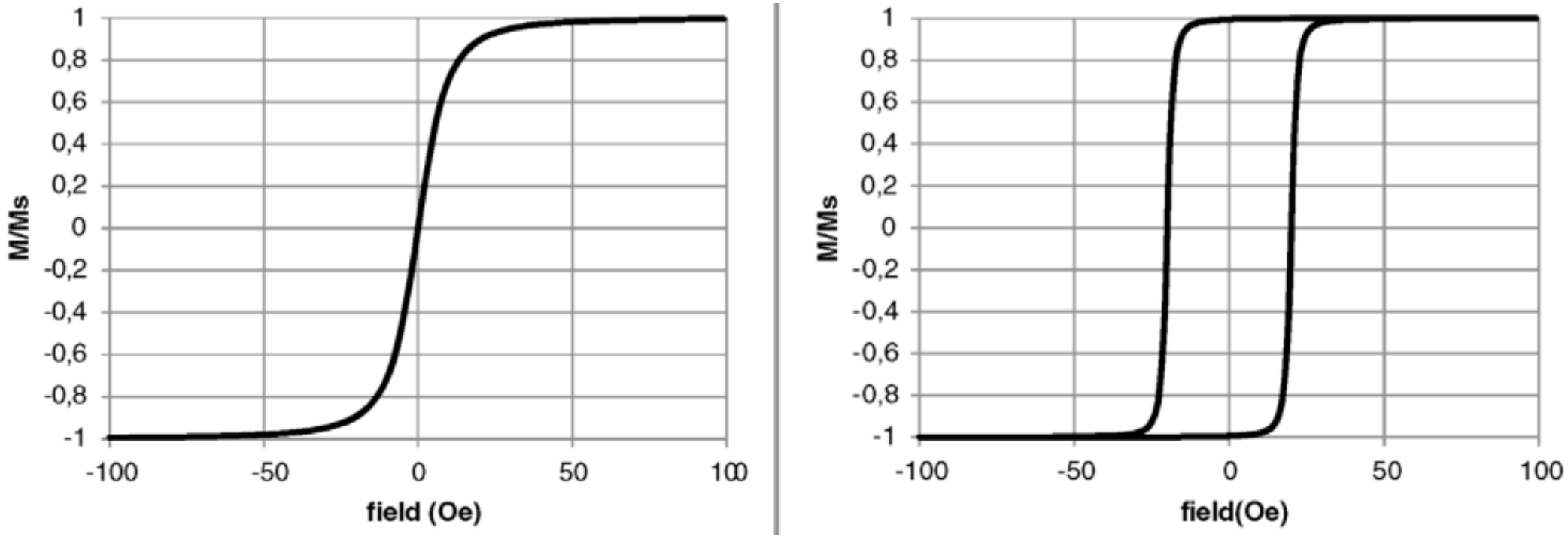


Figure 7.3 Magnetization as function of the applied external field for different nanoparticles. (a) Superparamagnetic particles; (b) single-domain particles.

- Note that *for nanoscale ferromagnetic or ferrimagnetic materials, below a critical size, their magnetization becomes thermally fluctuated*. When ***the time between two magnetization fluctuations (Néel relaxation time) 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*.
- 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.
- **Superparmagnetic 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.

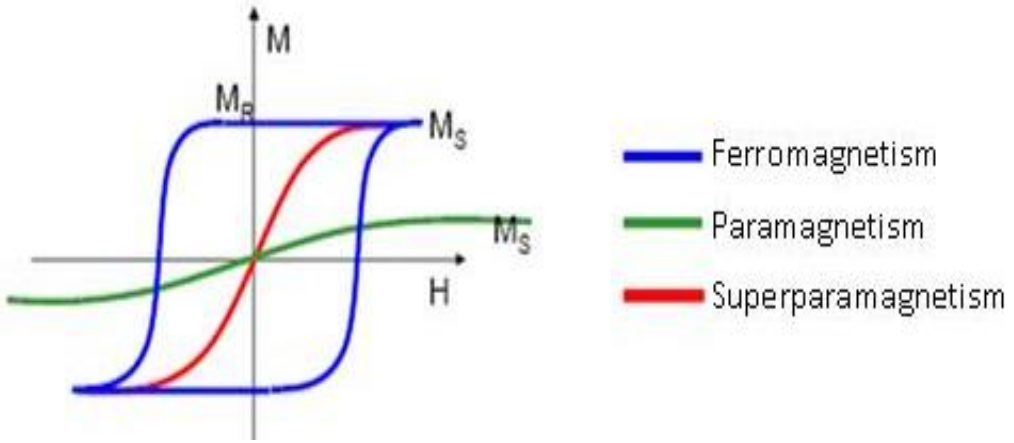


Fig. 7.4 Magnetization hysteresis loops of different magnetic materials at room temperature.

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.
- Figure 7.4 shows an example of the evolution of MRI images of rabbit hindquarters after injection of a Gd-based contrast agent.

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).

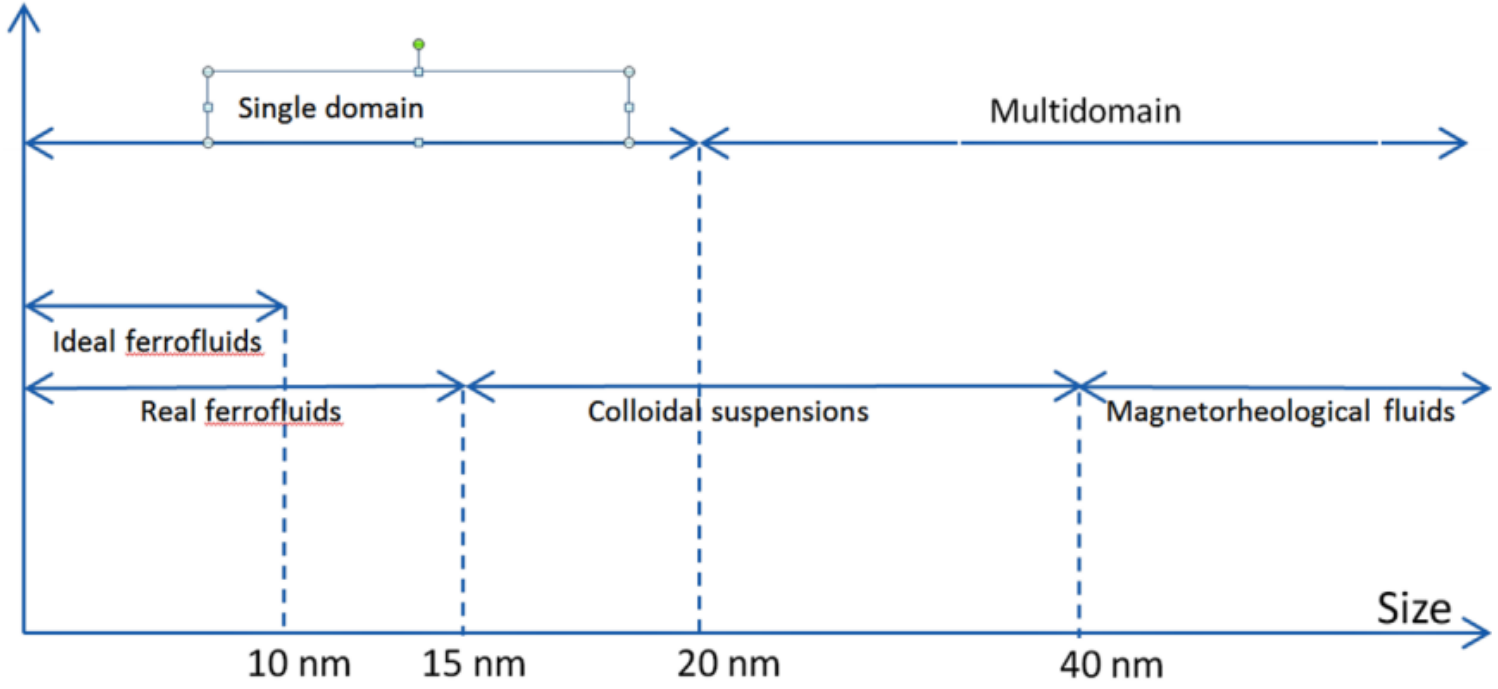


Figure 7.5 Size range of magnetic particles constituting different types of magnetic fluids.

- 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).

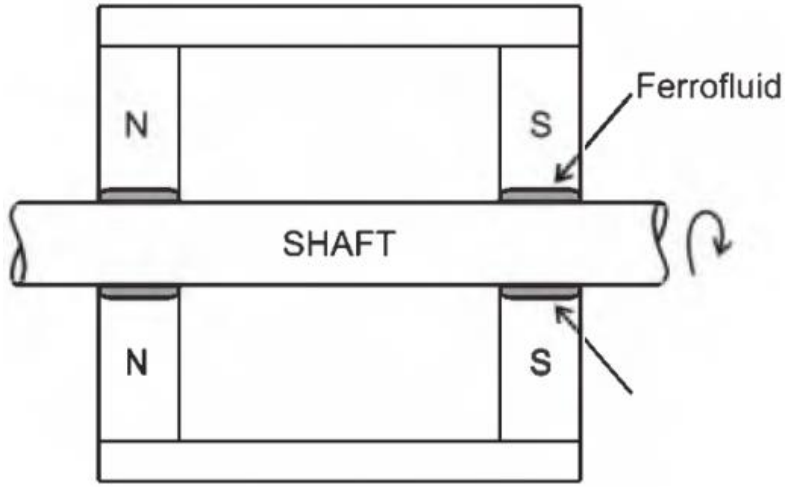


Fig. 6.14. Ferrofluid as bearing for a rotating shaft.

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.

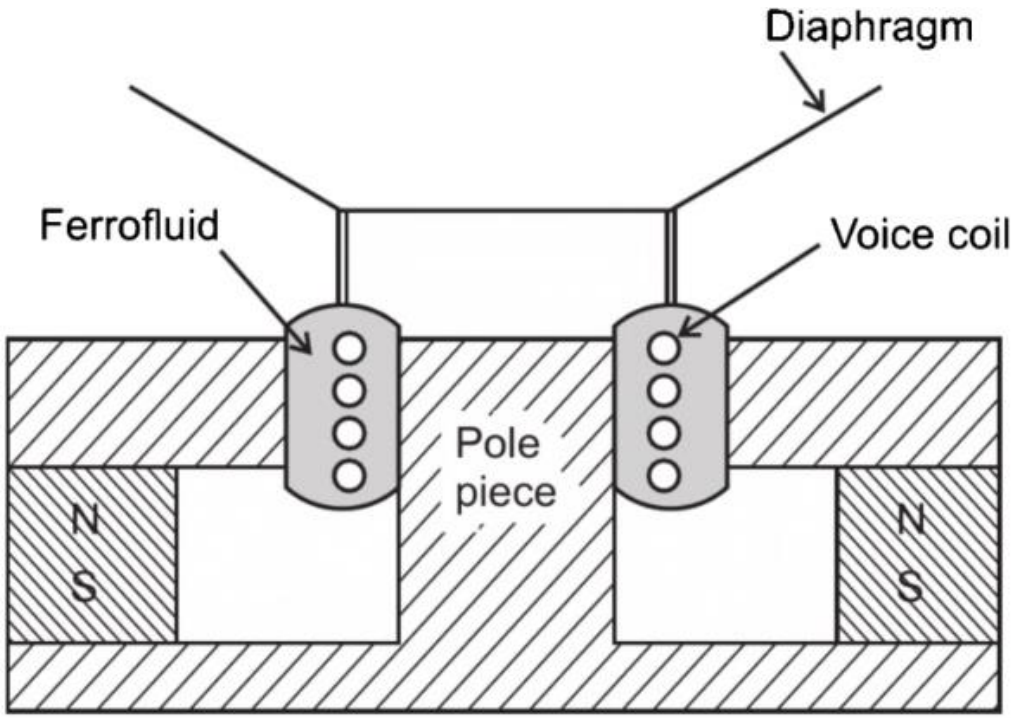
Analogous properties are observed in liquid crystals, which consist of long molecules having large electric dipole moments, which can be oriented by the application of an electric field in the fluid phase. Electric field-modulated birefringence property of liquid crystals is widely used in optical devices, 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.



Magnetic Particle Imaging

MPI is a new clinical imaging modality proposed by Gleich and Weizenecker. The principle is to inject in blood a large number of MNPs. The magnetic response to an AC magnetic field of the particles is then detected by coils. The signal detected is proportional to the number of MNPs. A 3D gradient field is applied in a way that only a single small volume sees a zero external field, the particles inside this volume can react to the AC field as the particles outside this volume are blocked. Hence, an image is obtained by scanning the zero-field volume over all the volume of interest. The main issue related to MPI is the need for very high varying field gradients that have an impact on the health of the subjects with peripheral nerve excitation and heating. A combination of MPI and MRI is also being investigated to give an accurate localization of MNPs in the anatomy. In this respect, spin electronics sensors may be a good alternative for that application.

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).*

- 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 magnetoresistan**ce (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***.

❖ Introduction to Spin Electronics

➢ Spin electronics is based on the fact that electrons have not only a charge but also a magnetic moment, called spin, which is quantified. The aim is to use this magnetic moment to filter electrons, to manipulate macroscopic magnetization, and in some cases to transport information.

➢ 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.

❖ 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***.

➢ To incorporate spins into existing semiconductor technology, one has to resolve technical issues such as ***efficient spin injection***, ***transport control and manipulation***, and ***detection of spin polarization*** as well as ***spin-polarized currents***.

➢ 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 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

- 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.
- *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 causes the electrons 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.
- ➢ 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)***.
- ➢ It originates from anisotropic spin-orbit interaction and causes the resistance to depend on the relative orientation of electric current and magnetization. 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.***

- 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* in the low temperature near the Curie temperature and *requires magnetic fields of the order of several Tesla*. *The latter property makes the applicability of CMR materials limited.*

- *The GMR effect, on the other hand, 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*.

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.

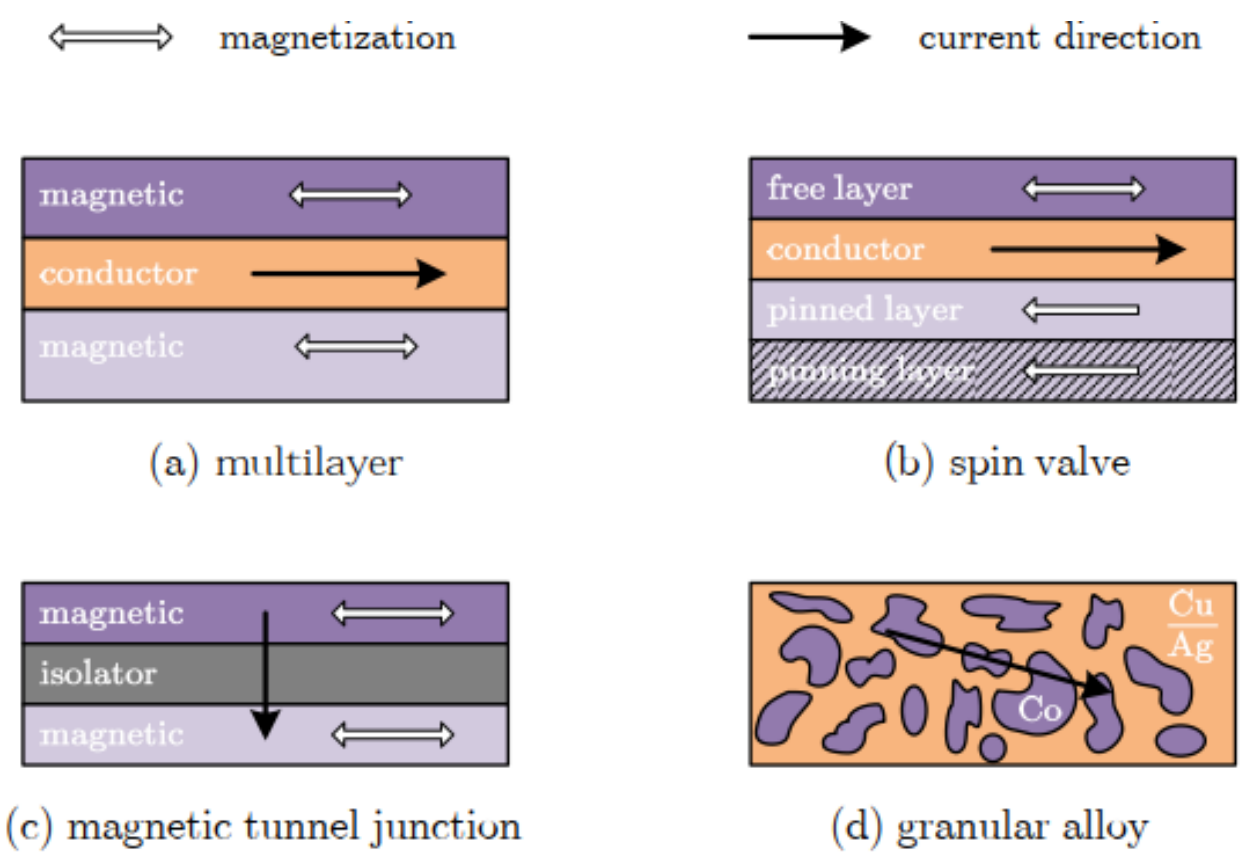


Figure 1. Basic GMR structures.

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.

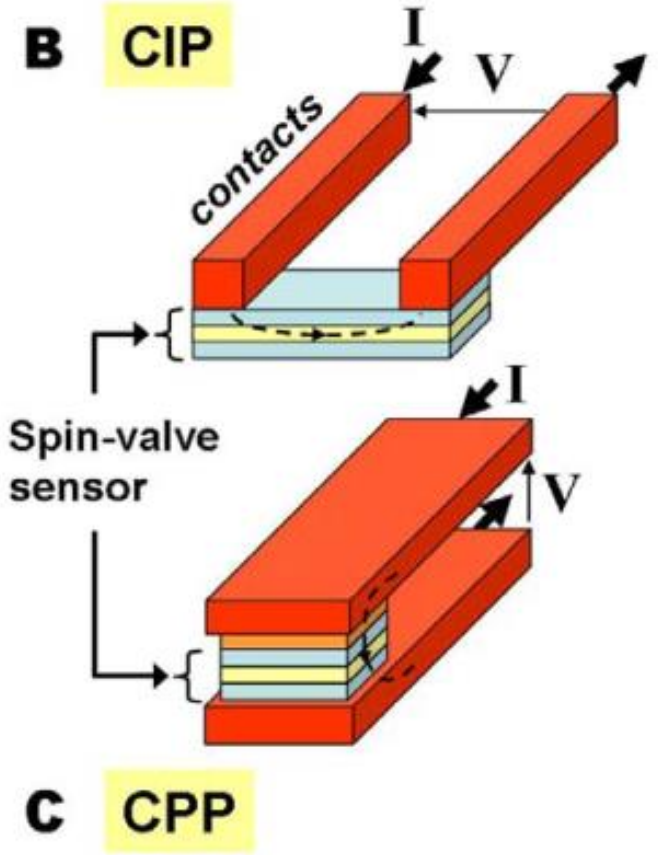
The magnetization of the free ferromagnetic layer can be changed easily by a magnetic field giving rise to a *resistance change of 5–10%* in a relatively small magnetic field. *The rotation of the "free" layer magnetization "opens" in parallel (to "pinned" orientation) configuration or "closes" in antiparallel 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 spin valve can be of "current in plane" (CIP) type where the arrangement is such that the current passes along the multilayered structure or of "current perpendicular to plane" (CPP) spin valve where the current passes across (perpendicular to) the multilayered structure (Fig. 2).

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.



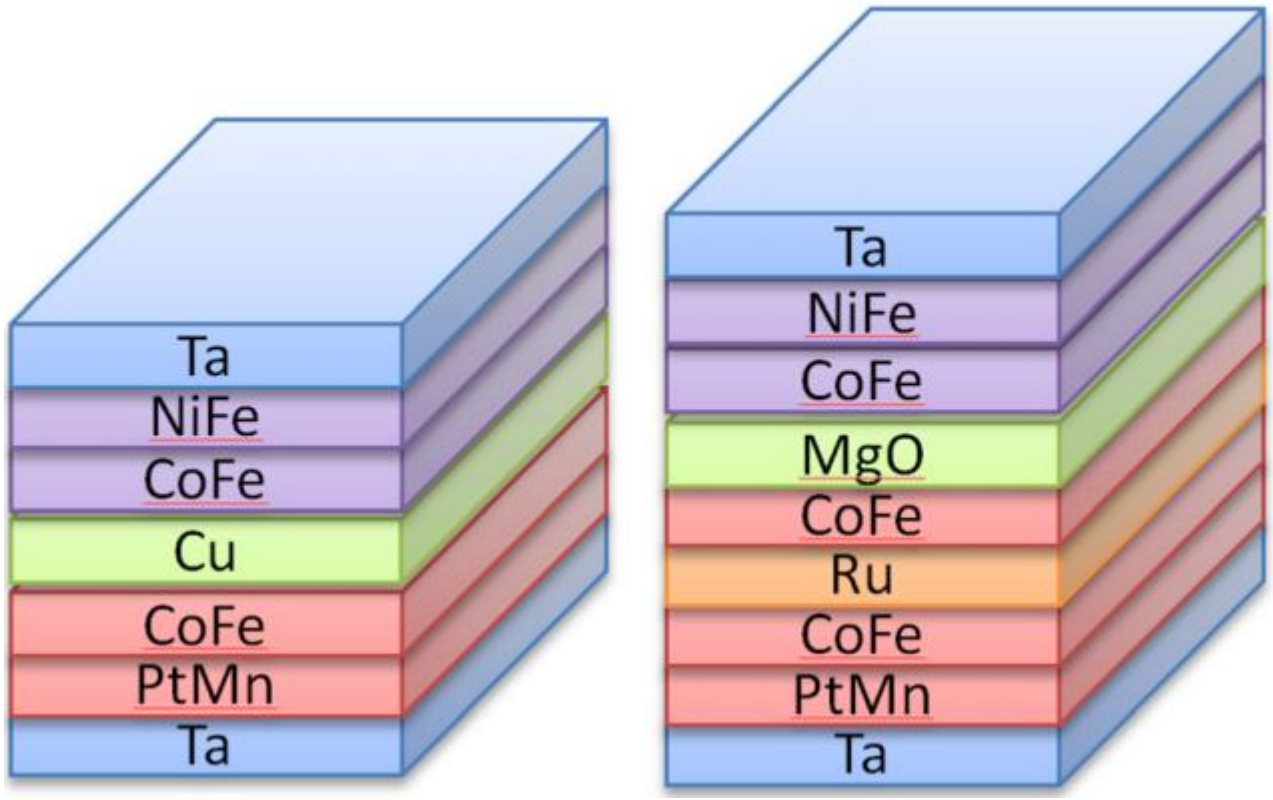


Figure 1.4 GMR simple spin valve (a). TMR spin valve with an SAF configuration (b).

3. Magnetic tunneling junction (MTJ)

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.

TMR (tunnel magnetoresistance), also called MTJ (magnetic tunnel junctions), 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.

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.

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%.

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 nanometer scale***. The thin-film technology and micronanofabrication techniques have hence played an essential role in the development of spin electronics.

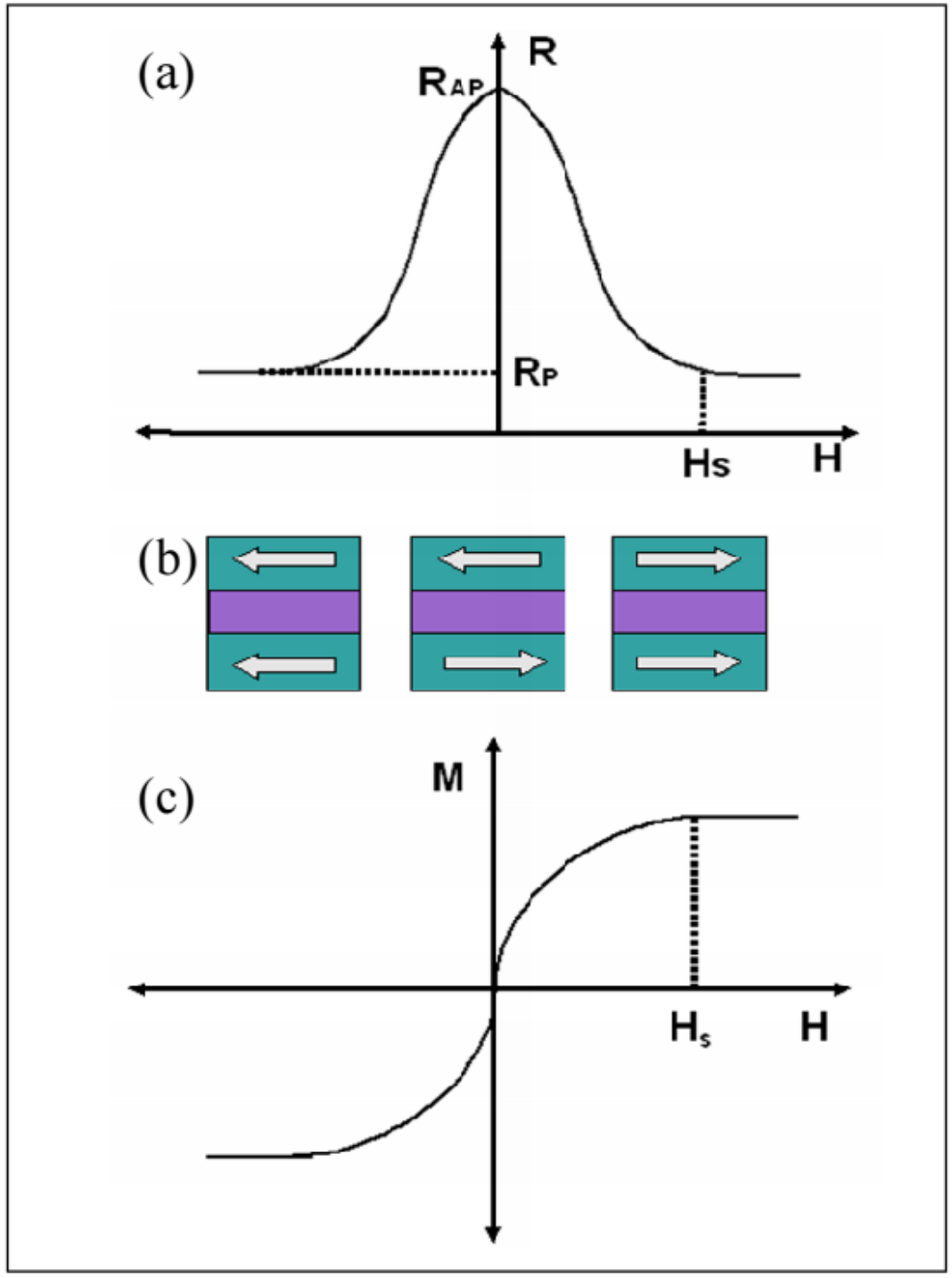
Like the other magnetoresistances (OMR, AMR), GMR is also a change in electrical resistance in response to an externally applied magnetic field, and is a quantum mechanical effect which is based on spin-dependent scattering phenomena in magnetic multilayers.

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.



- 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 and is analogous to Ruderman–Kittel–Kausya–Yosida (RKKY) interaction between localized magnetic moments present in a matrix of non-magnetic metal.
- 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.

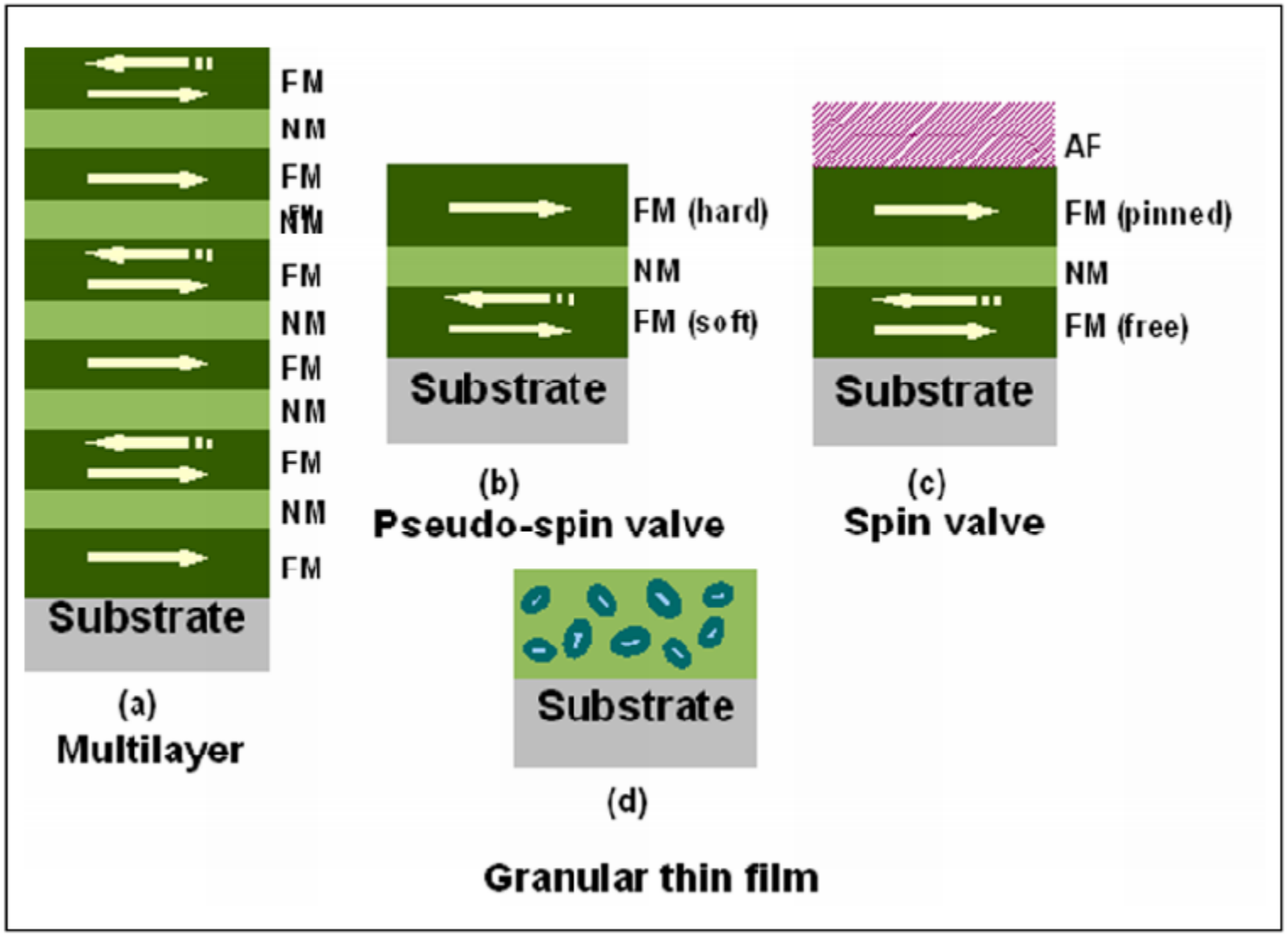
Figure 2.Different GMR structures (a) multilayer (b) pseudo spin valve (c) spin valve (d) granular thin film.

(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.



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 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 $\sigma \propto D(E_F)$.

The Pauli exclusion principle requires that up and down spin electrons be counted separately and separate spin sub-bands can be formed. 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 $\sigma_{\downarrow} \propto D_{\downarrow}(E_F)$ 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, $\sigma_{\uparrow} = \sigma_{\downarrow}$.

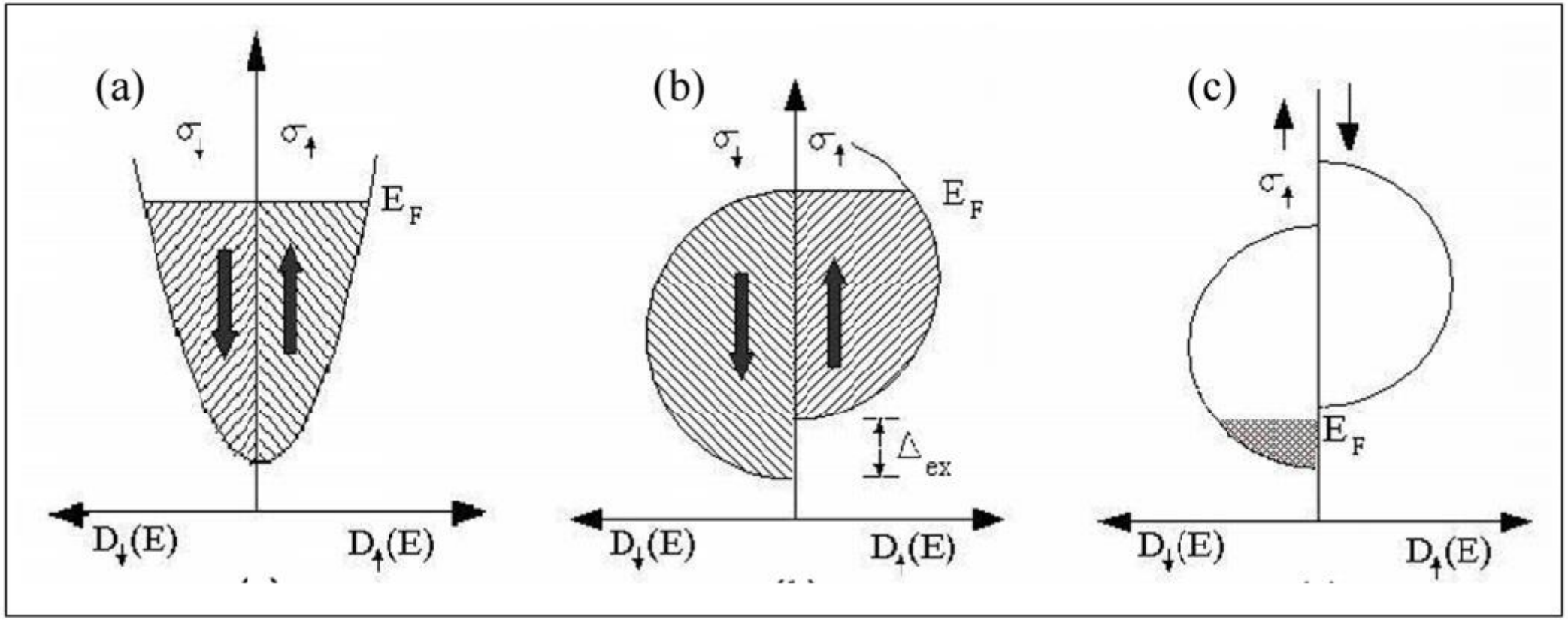


Figure 3.Schematic diagram of density of states D(E) as a function of energy. (a) Non-magnetic metals (zero spin polarization). (b) Ferromagnetic metals (partial spin polarization). (c) Half metals (full spin polarization).

But for a ferromagnetic material like Fe, Co, and Ni, the spin subbands are shifted with respect to each other due to exchange splitting (Δ_{ex}) as shown in Figure 3.

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 at the Fermi level $D_{\uparrow}(E_F) \neq D_{\downarrow}(E_F)$ for ferromagnetic material leads

to $\sigma_{\uparrow} \neq \sigma_{\downarrow}$. 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, $P = [(D_{\uparrow}(E_F) - D_{\downarrow}(E_F))/((D_{\uparrow}(E_F) + D_{\downarrow}(E_F))]$.

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%. These 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 3 shows the simple band picture for different spin-polarized systems.

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.

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). According to him, the electric conduction takes place by the sp band electrons primarily as they have lower effective mass and higher mobility.

As the d band is exchange split in ferromagnets, the density of states for up and down band is different at the Fermi level.

Therefore, the probability of scattering for up and down sp electrons into the states near the Fermi level are different. So, the conductivities are different for the two conduction channels.

Using Mott's simple argument, it is possible to understand the origin of GMR in magnetic multilayer. Let us consider a collinear magnetic configuration of two magnetic layers separated by a non-magnetic spacer layer as shown in Figure 5.

We will assume that the scattering is strong for spins antiparallel to magnetization direction and weak for parallel magnetization direction. In case of parallel configuration, the spin-up electrons are weakly scattered in all layers and leads to low resistance but, in contrast, the spin-down electrons are strongly scattered in magnetic layers so that they weakly participate to the conduction of current.

But in the case of antiparallel configuration, both up and down electrons get alternately strongly and weakly scattered, leading to higher 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.

As described above, the spin-dependent scattering in magnetic multilayer can also be understood from the band structure picture shown in Figure 5: (i) In the case of parallel magnetization alignment, the up-band electrons from one ferromagnetic layer can be transported to the other ferromagnetic layer due to the availability of density of states at the Fermi level, and this leads to low resistance. (ii) For the antiparallel case the transport of up electrons from one ferromagnetic layer to other is not allowed and it results in high resistance.

Thus depending on the direction of magnetization of a material with respect to spin polarization of the current, a material can behave either as an insulator or a conductor.

A classic analogy can be made with the phenomenon of polarized light passing through the analyzer. However, in optical case crossing the polarizer axis at 90^{o} with respect to analyzer axis prevents the transmission of light, whereas for spin-polarized electrons the magnetization of successive layers should be rotated by 180^{o} to stop the electrical conduction.

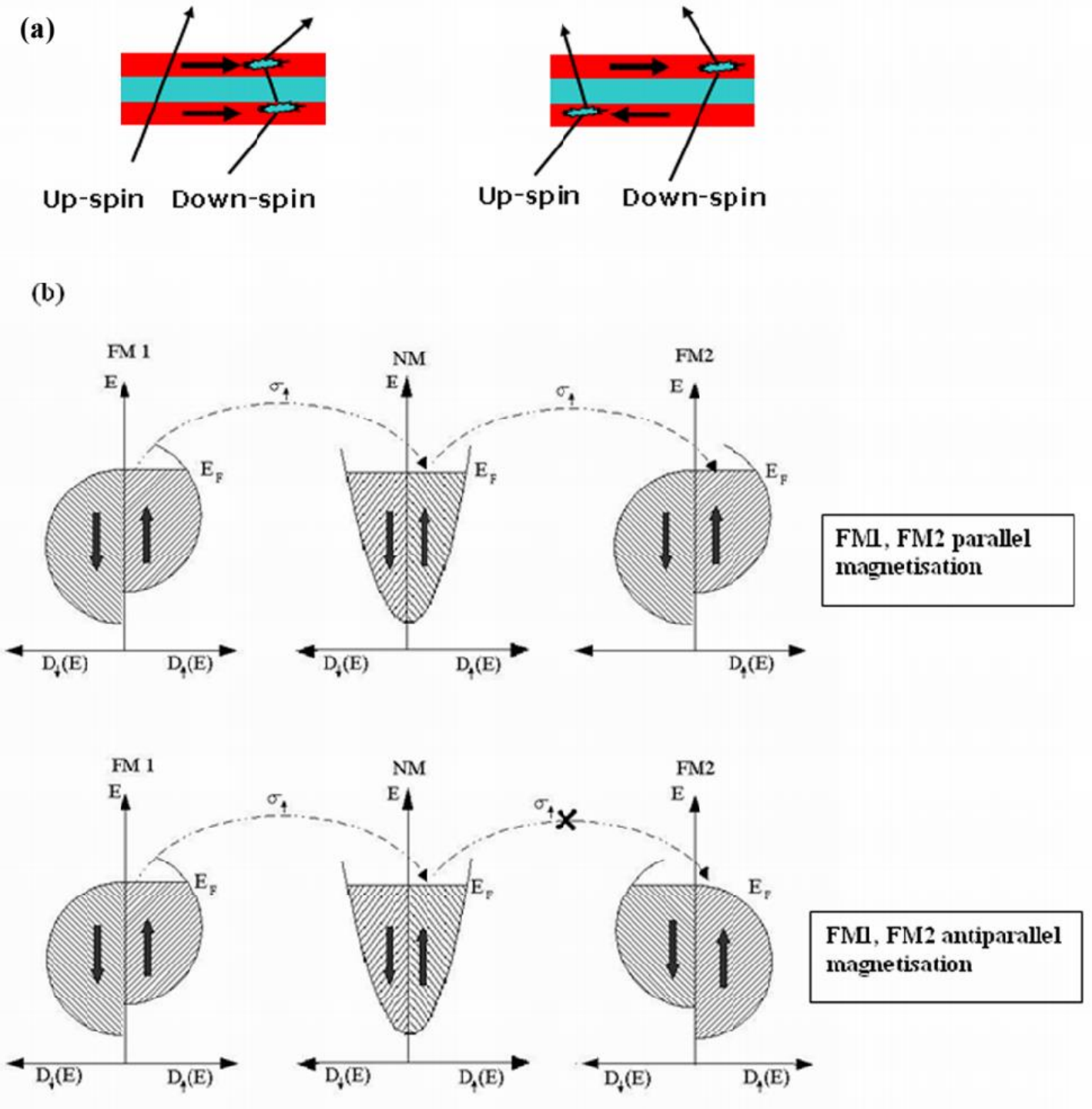
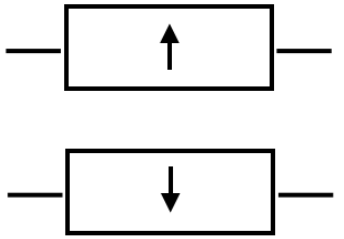


Figure 5. (a) Schematic illustration of electron transport in a multilayer for parallel and antiparallel magnetizations of the successive ferromagnetic layers. The magnetization directions are indicated by the arrows. The solid lines are individual electron trajectories within the two spin channels.
(b) Schematic representation of microscopic spin-polarized transport from a ferromagnetic metal (FM1) through a normal metal (NM) and into a second ferromagnetic metal (FM2) for parallel and antiparallel magnetizations. For antiparallel magnetizations, the transport of up-spin electrons from FM1 to FM2 is not allowed as shown by a cross (higher resistance) but for parallel case it is allowed (low resistance).

- In nonmagnetic conductors, there are equal numbers of spin-up and spin-down electrons in all energy bands.

$$R_\uparrow = R_\downarrow$$

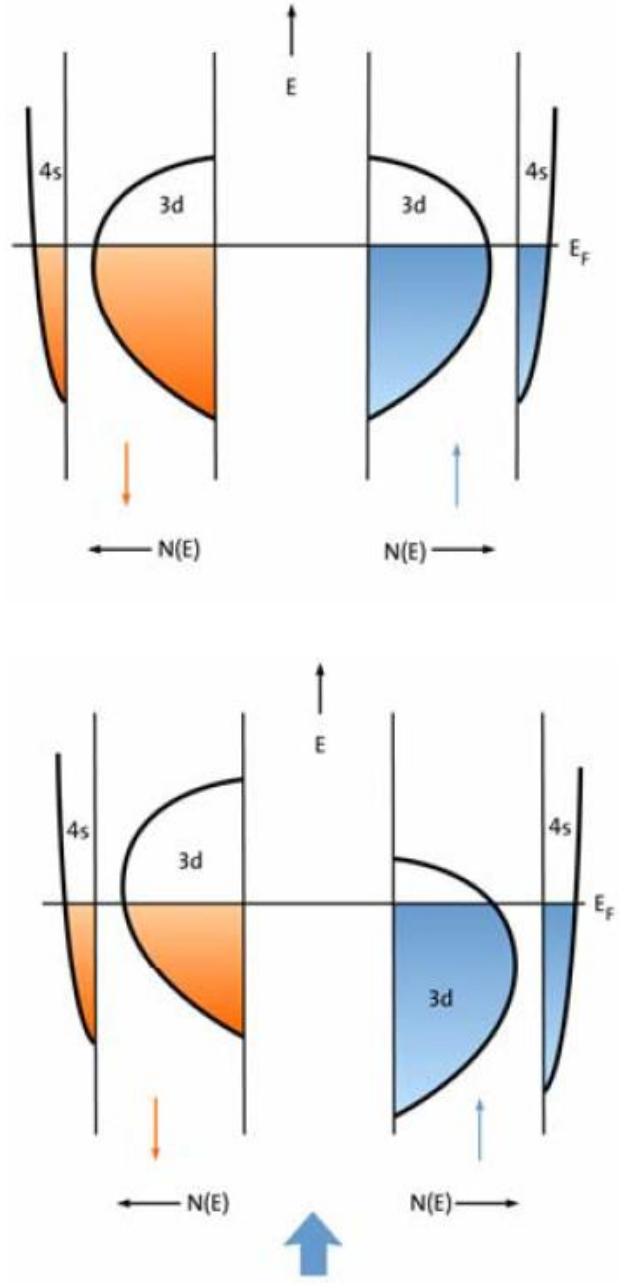


- **The origin of the magnetism behavior owes to the distribution of 3*d*/4*f* electrons in ferromagnetic metals** such as 3*d* transition metals like, Fe, Co, Ni and 4*f* lanthanides like Gd.
- Let us look into the ferromagnetism of the 3*d* elements. In the free atoms, the 3*d* and 4*s* levels of the 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).

Figure 3. ***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.



- 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*,

$P = (N\uparrow - N\downarrow)/(N\uparrow + N\downarrow)$, 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. 3, Bottom).

- 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.

- Using Mott's arguments, it is straightforward to explain GMR in magnetic multilayers. 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 accordance with Mott's second argument.

- At *zero magnetic field* ($H = 0$), *due to antiferromagnetic interlayer exchange coupling*, the *magnetization directions are aligned antiparallel* as indicated by the (fat) arrows (Figs. 4, upper panel and 5a).
- ***For the antiparallel-aligned multilayer***, ***both the up-spin and down-spin electrons are scattered strongly*** within one of the ferromagnetic layers (Fig. 5a), *because within the one of the layers the spin is antiparallel to the magnetization direction. Thus,* ***in this case the total resistivity*** *of the multilayer* ***is high***.

- For the ***parallel-aligned magnetic layers***, (Fig. 4 (lower panel) and Fig. 5b (right)), ***the up-spin electrons pass through the structure almost without scattering***, because ***their spins are parallel to the magnetization*** of the layers. On the other hand, the down-spin electrons are scattered strongly within both ferromagnetic layers, because their spin is antiparallel to the magnetization of the layers. Since *conduction occurs in parallel* for the two spin channels, the total resistivity of the multilayer is determined mainly by the highly conductive up-spin electrons and appears to be low.

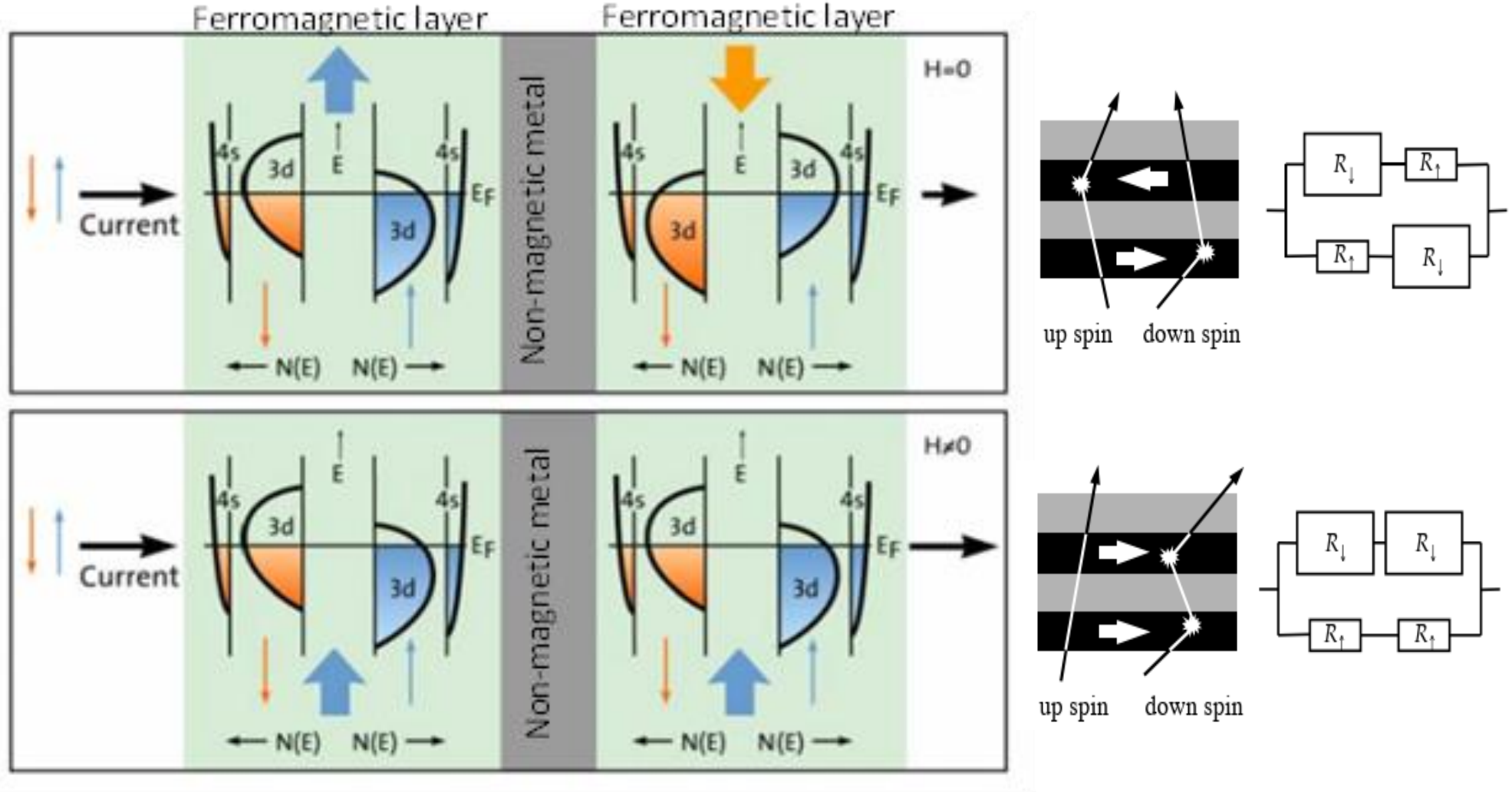


Figure 4. Schematic illustration of the ferromagnetic DOS and Spin-Dependent Scattering of a trilayer system with two ferromagnetic layers (light green) on both sides separated by a nonmagnetic material layer (grey). *E* with thin black arrow indicates the increasing energy directions. Thin orange and blue arrows indicate down-spin and up-spin electrons respectively. The top panel is for the case without external magnetic field ($H=0$), i.e. when the two magnetic layers have opposite magnetizations (indicated by the thick blue and orange arrows at the top of the top panel). The bottom panel of the figure is for the case when an external magnetic field ($H \neq 0$) has forced the two magnetizations to be parallel (two thick blue arrows at the bottom of the lower panel of the figure). The magnitude of the four magnetizations is the same.

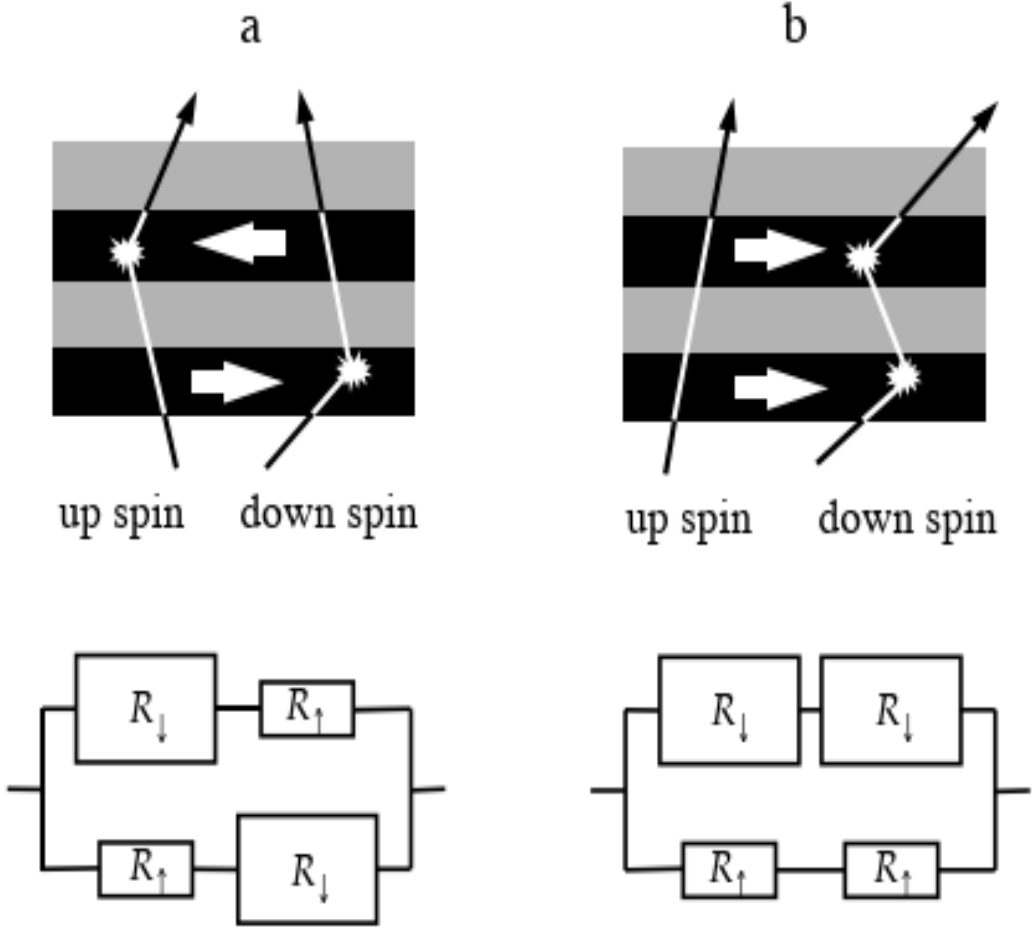


Figure 5: Schematic illustration of electron transport in a multilayer for parallel (a) and antiparallel (b) magnetizations of the successive ferromagnetic layers. The structure is made of combinations of ferromagnetic and non-magnetic metals layers simultaneously. The magnetization directions are indicated by the arrows. The solid lines are individual electron paths with the two spin channels. ***Bottom panels*** show the resistor network within the two-current series resistor model

❖ **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.

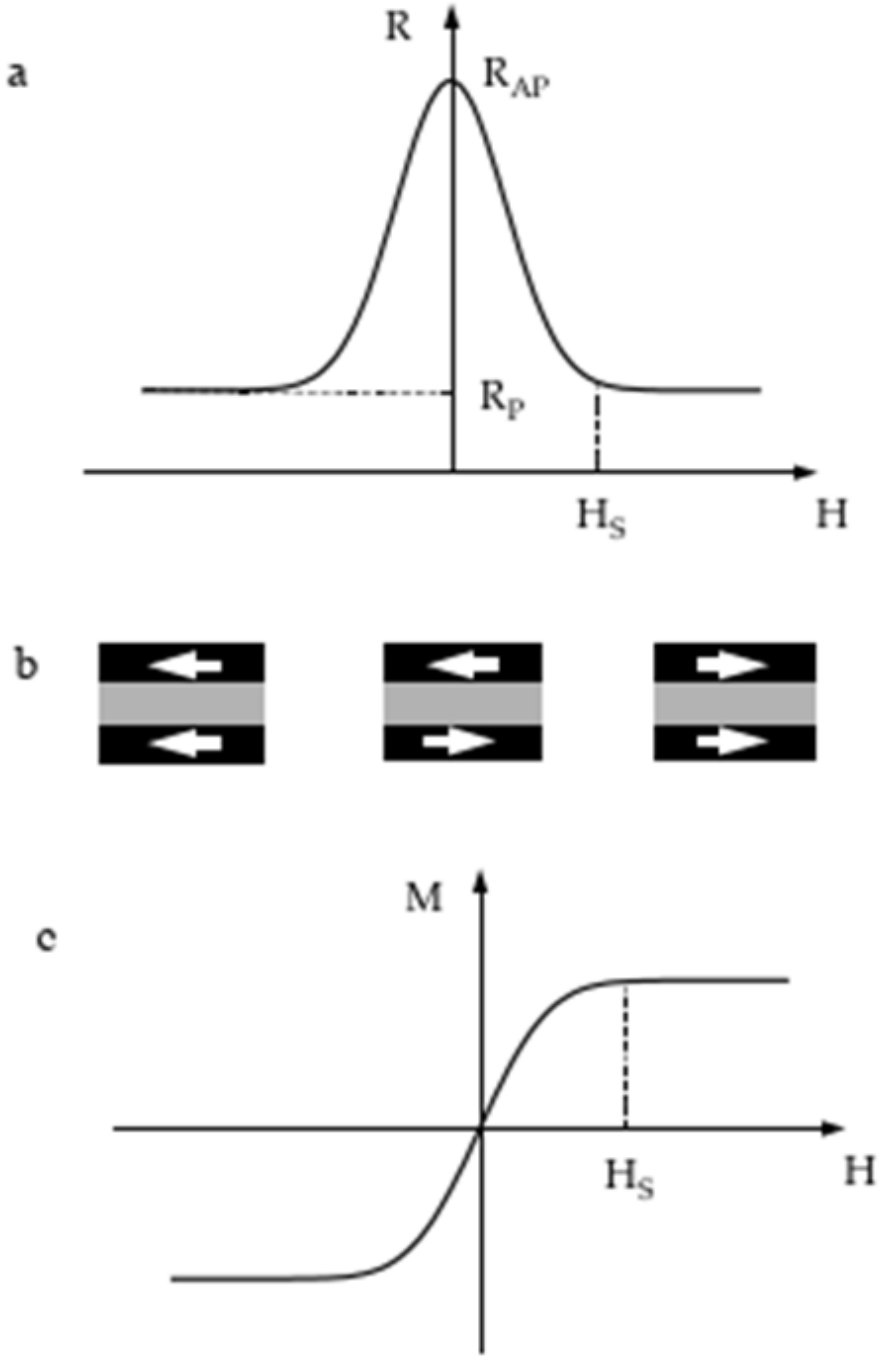
Figure 6: Schematic of the GMR effect.

(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.

Role of Non-magnetic Conducting Layer

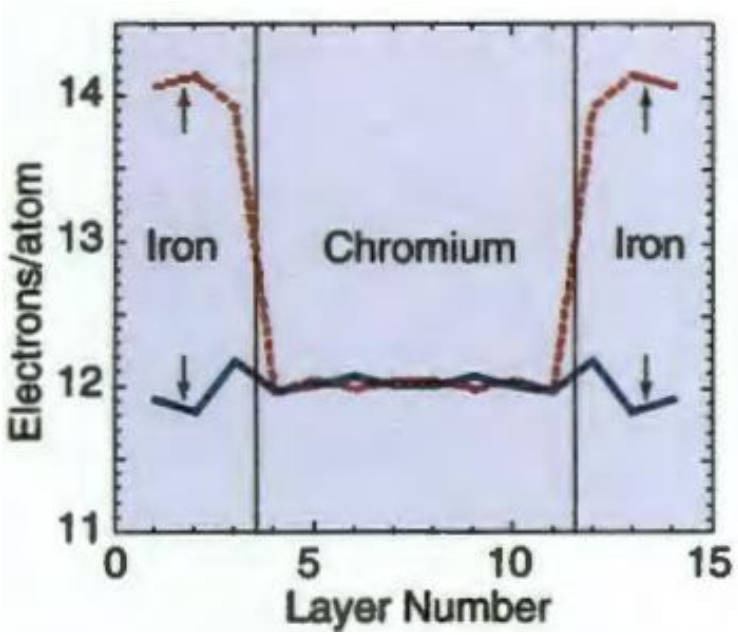


Fig. 7. The number of down-spin (blue curve) electrons per atom hardly changes between the iron and chromium layers, but the number of up-spin electrons (red curve) is higher for iron than for chromium.

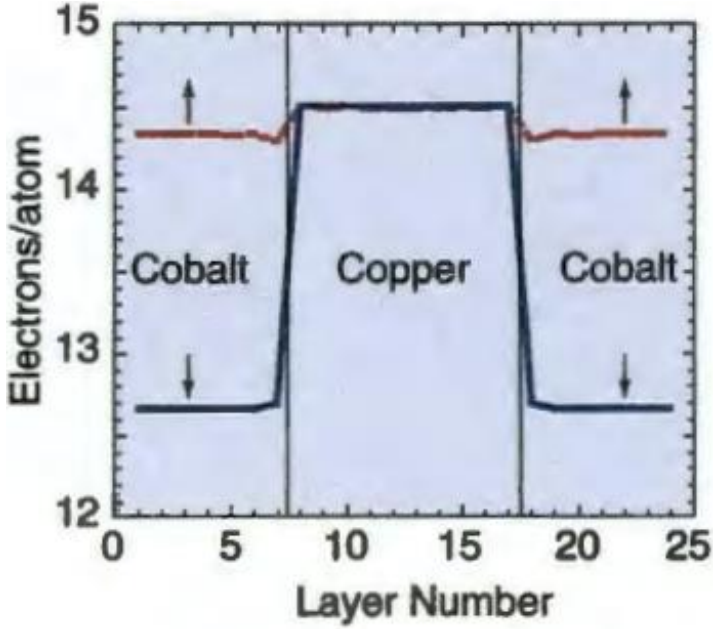


Fig. 8. The number of up-spin (red curve) electrons per atom hardly changes between the cobalt and copper layers, but the number of down-spin electrons is much lower for cobalt than for copper.

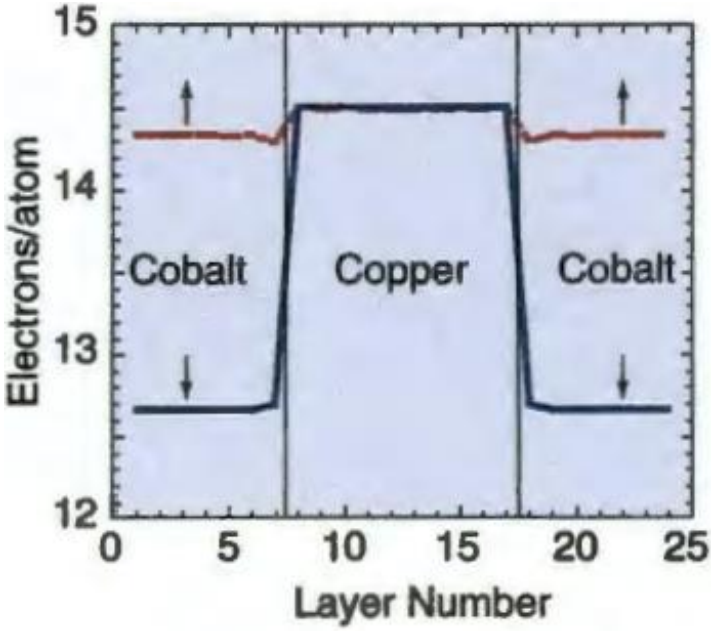


Fig. 8. The number of up-spin (red curve) electrons per atom hardly changes between the cobalt and copper layers, but the number of down-spin electrons is much lower for cobalt than for copper.

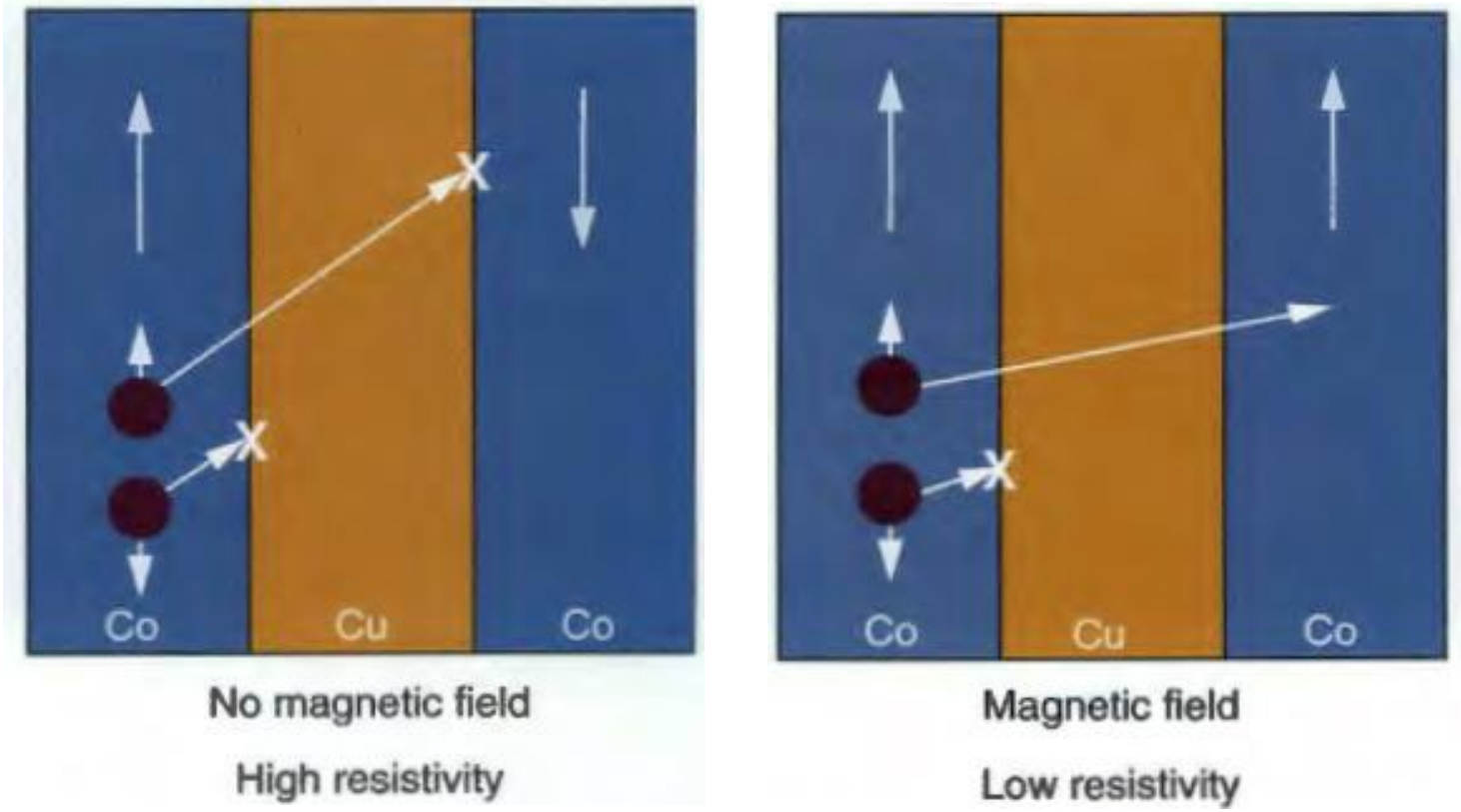


Fig. 9. When excess spins in both cobalt layers are aligned, up-spin electrons pass from layer to layer without scattering.

Current and Future Applications of Giant Magnetoresistance (GMR)

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***.

Read sensors that employ the GMR effect provide the best technology currently available for detecting the fields from these tiny regions of magnetization. These tiny sensors can be made in such a way that a very small magnetic field causes a detectable change in their resistivity; such changes in the resistivity produce electrical signals corresponding to the data on the disk which are sent to the computer (Fig. 10). It is expected that the GMR effect will allow disk drive manufacturers to continue increasing density at least until disk capacity reaches 10 gigabits per square inch. At this density, 120 billion bits could be stored on a typical 3.5-inch disk drive, or the equivalent of about a thousand 30-volume encyclopedias.

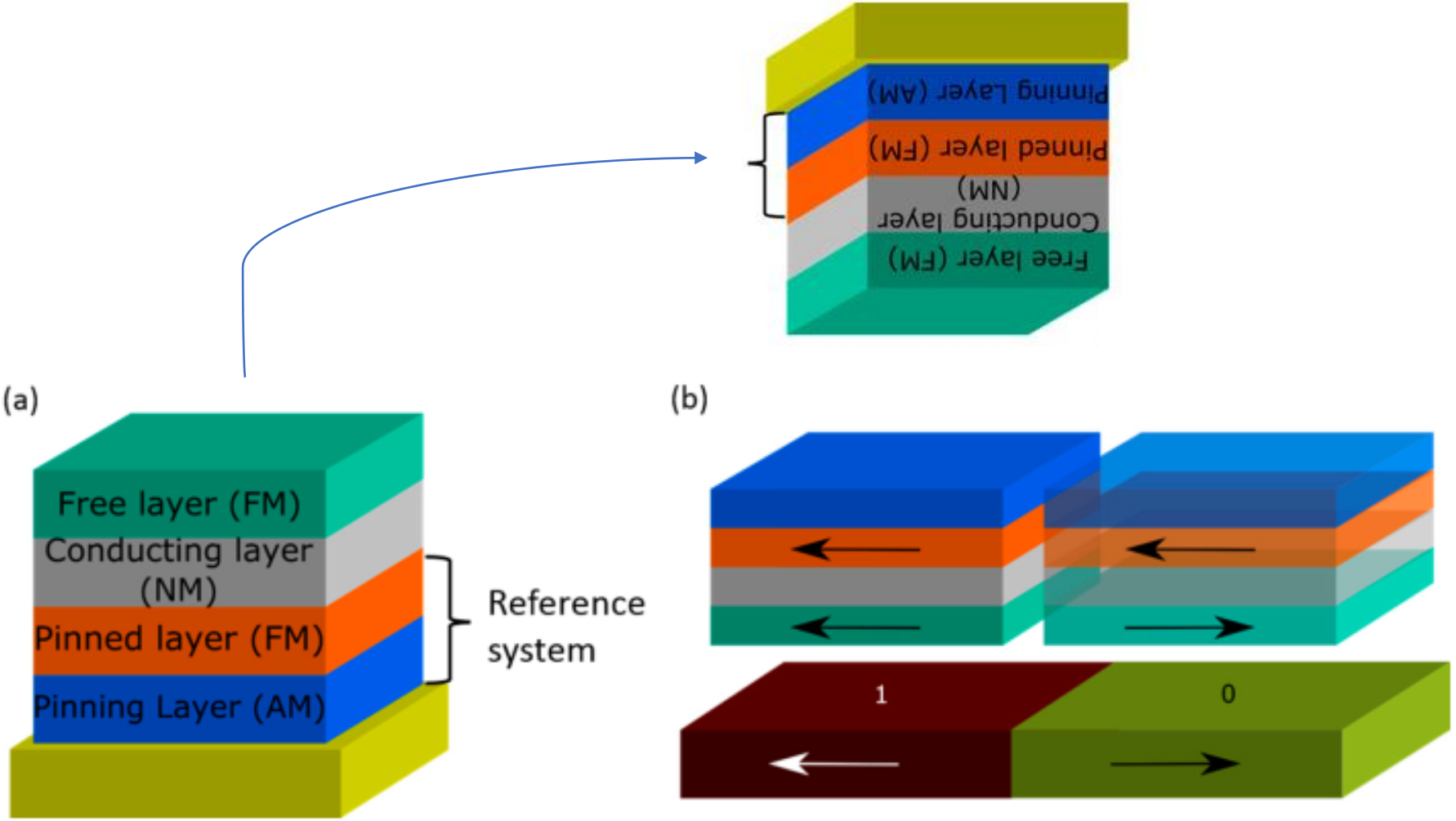


Figure 10. (a) Schematic setup of the stack configuration of a GMR spin-valve sensor; (b) Conceptual operation of a GMR read head: when a spin-valve sensor moves across an interface between two bits with magnetic moments oriented in opposite direction (marked by "1" and "0"), the magnetic moment of the free liner (green colored) is reoriented according to the orientation of the next bit.