Magnetic materials: from the search of new phases to nanoscale engineering

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From soft to hard magnetic materials

There is a category of materials, of which the magnetisation is used as a source of a magnetic field or of a magnetic flux. All these materials are Fe, Co or Ni based (transition metal elements, M) and their spontaneous magnetisation, $M_s$, have similar typical values. Yet, they may exhibit extremely different applicative properties. This is due to differences in the strength of their coercivity, i.e. their ability to resist an applied magnetic field, $\mu_0 H_{app}$, which tends to change the orientation of the magnetisation. From extremely soft to extremely hard materials, the coercive field, $\mu_0 H_c$, at which the magnetisation finally follows the applied field, increases by more than 6 orders of magnitude (see Figure 1). Soft materials are used in magnetic circuits, transformers or sensors; hard materials are used to make motors, actuators or generators; materials with medium coercivity are used as storage media [1]. Coercivity depends on material intrinsic magnetic properties (temperature below which ferromagnetism is stable, magnetisation and anisotropy energy (see below)). It depends also on extrinsic properties (grain size, grain orientation, grain separation, etc...), which define the material microstructure.

During the last 50 years, an impressive development has occurred in the field of magnetic materials, stimulated by the better understanding of the characteristic behaviours of the different types of magnetic elements. More recently, the discovery of behaviours which are specific to nanomaterials, has open a new period. At the nanoscale, the distinction between intrinsic properties, characteristic of a given magnetic phase, and extrinsic properties, related to the detail of the microstructure, disappears.

Interactions involved and fundamental processes

The typical equilibrium magnetization configuration of a ferromagnetic material is made of micron-size domains. Within a given domain, the moments are parallel as required by exchange interactions and they are aligned along a particular direction, the easy magnetisation direction, as required by magnetocrystalline anisotropy. From one domain to the next, the magnetisation direction alternates. Globally, the magnetisation is zero; exchange and anisotropy energies are minimized, as they are in the single domain state, except within small regions, the domain walls, which constitute the transition regions between two magnetic...
domains. Additionally, magnetic domain formation allows the weaker long-range dipolar interactions to be strongly reduced with respect to their value in the single-domain state.

Under an applied field, a bulk magnetisation tends to develop to minimize Zeeman energy. In an ideally homogeneous material, the domain wall energy does not depend on the wall position. The magnetisation increases by free domain wall motion, such that the domains in which the magnetisation is along the applied field grow at the expenses of the others. Such materials are magnetically soft (Figure 2). The induced magnetisation is in turn the source of a magnetic field or of a magnetic flux. When the applied field is time dependent, the magnetisation is time-dependent as well. A voltage results, which constitutes the signal exploited in transformers or sensors.

When the applied field is further increased, one reaches ultimately a state in which only one domain remains. The magnetisation is saturated. Assuming that a field is applied again, but of reversed sign, magnetisation reversal requires that a domain of reversed magnetisation is nucleated. The value of the nucleation field is closely linked to that of the anisotropy energy. This can be understood by considering that a moment that participates in the magnetisation processes necessarily assumes an intermediate transitory position in which it is perpendicular to the easy magnetisation direction. In this unfavoured orientation, the magnetocrystalline anisotropy energy is at a maximum. Permanent magnets are based on high anisotropy materials (Figure 2). A potential energy can be stored in a field, which is antiparallel to the magnetisation. Motors or actuators transform this potential energy into mechanical energy.

The two states of saturated magnetisation, up and down, may constitute the two elementary bits of information, 0 and 1. Materials used for information storage have medium coercivity: the magnetisation-saturated states must be stable enough for the information not to be lost; at the same time, the writing process must be realised in a not too high magnetic field. Exchange decoupling between the constituent grains is a specific feature of these materials. It allows each bit of information to be written independently of the others (Figure 2).

Which Materials?
Ferromagnetism above room temperature is a unique property of the 3d transition metals (M= Fe, Co or Ni), their alloys or compounds [1]. It results from large exchange interactions existing between the magnetic 3d electrons. In general, alloys and metallic compounds have higher magnetisation than insulating compounds. At room temperature, pure Fe metal has the largest magnetisation of all known elements (\(\mu_0M_s = 2.2\ T\)).

Materials where 3d magnetism only is involved tend to have low magnetic anisotropy and often show soft magnetic behaviour. In the best of these materials, the permeability, which represents the ratio between the induced magnetisation and \(\mu_0H_{app}\), may be as high as 10^5. Most of these materials have been known for many years. This is in particular the case of the Fe-Si alloys in which 3-5 % Si is substituted for Fe [1]. The magnetisation is approximately 10 % less than that of pure Fe metal. Other properties (mechanical properties, resistivity, corrosion resistance, etc...) are decisively improved with respect to those of the pure metal. Fe-Si sheets constitute the core of all transformers used for energy transportation. Soft magnetic materials are mostly used under AC exciting fields. At high frequency, eddy-current losses develop in metallic systems. Insulating ferrites are used in electronics (AC-DC converters, inductances, etc...) at frequencies from typically 1 kHz to 1 GHz. At even higher frequencies, rare-earth garnets are used in non-reciprocal devices, for telecommunication applications.

The hard ferrites are the first magnets that exploited the link existing between coercivity and magnetocrystalline anisotropy [2]. These materials are used in the fabrication of small motors used in the automotive industry and for home appliances. In the 1960's, extremely large anisotropies were discovered in the rare-earth metals (R = rare-earth), the second series of magnetic elements in the periodic table. The R elements are heavy elements, and the magnetic 4 f electrons are characterised by large spin-orbit coupling. By this mechanism the moment orientation is tightly linked to the crystal structure, i.e. the magnetocrystalline anisotropy is large. The interatomic 4f-4f exchange interactions are weak and magnetism in the R metals is only stable at low temperature. In the R-M compounds, strong 4f-3d interactions exist, mediated by the rare-earth 5d electrons. Rare-earth magnetism is preserved above room temperature and, with it, compounds with very large anisotropies may be obtained. Magnets based on the SmCo5 phase, with typical composition Sm(Fe,Co,Cu,Zr)2, are of particular interest for high-temperature applications [2]. The fabrication of magnets based on the Nd2Fe14B phase constituted a decisive breakthrough in the development of rare-earth based magnets [3]. These magnets associate outstanding magnetic properties (\(\mu_0M_s = 1.2-1.4\ T\), \(\mu_0H_c = 1-2\ T\)) with much lower cost than the SmCo5 magnets. They are used in particular in compact high performance motors, such as the voice coil motors of all hard-disk drives.

Pd or Pt, alloyed with M metals, may also be the source of high anisotropy. In these heavy elements, the magnetic electrons are the 4d or the 5d ones. The equiatomic L12 Fe-Pt phase has extremely large anisotropy. High performance materials have been prepared in thin film forms. Magnets inserted in microsystems could find application, despite the high cost of Pt.

The coercive field required in materials for magnetic storage is approximately an order of magnitude smaller than the coercive field of hard magnets, \(\mu_0H_c = 0.05 - 0.4\ T\). Such coercive field values can be obtained in materials, which show shape anisotropy: the moments tend to align along the long dimension of elongated particles. The \(\gamma\)-Fe2O3 particles, which constitute the most common material used in magnetic tapes, exploit this property. More recently, elongated Fe metallic particles, which have higher magnetisation and coercivity, have been developed for the same purpose.

The materials used in Hard Disk Drives (HDD) are Co-based alloys, which contain additive elements such as Cr, Pt and B [4]. The magnetic grains are coated with a non-magnetic Cr-rich layer, which ensures exchange-decoupling. Their coercivity is related to

![Fig.1: Magnetic materials according to their coercivity.](image)
magnetocrystalline anisotropy. The grains being very small, a significant fraction of the atoms are surface atoms. These are known to potentially show larger anisotropy than bulk atoms.

Amorphous alloys, which associate R elements (Gd, Tb) to M elements (Fe, Co) have been developed for perpendicular magnetic optical recording [5]. The R and M moments are coupled antiparallel and the chemical composition is such that, at room temperature, the global magnetisation is almost zero. This allows the magnetisation to lie perpendicular to the substrate surface. To first order, the rare-earth elements do not contribute to the magnetic-optical reading signal, which is approximately proportional to the transition metal magnetisation.

To the nanoscale

The understanding of the magnetism of matter is such that it appears unlikely that new alloys and compounds with significantly improved intrinsic properties may be discovered. Tailoring the magnetic properties at the nanoscale offers much more perspective. At this scale, new properties emerge because the dimensions are below the characteristic length-scales of magnetic interactions or magnetic phenomena [6].

Let us consider an assembly of exchange-coupled randomly-oriented nanocrystals. At small scale, the dipolar interactions need not to be considered. Exchange favours parallel coupling of the moments over the whole sample. Anisotropy favours moment alignment along the local easy magnetisation direction of each nanocrystal. One expects in general that exchange energy is much higher than anisotropy energy. However, the nanocrystals are coupled through their surface and thus the exchange energy intervenes as a surface term, whereas anisotropy energy is a volume term as usual. Due to the interplay between these 2 terms, a certain correlation volume must exist over which the moments can be considered as fully aligned. This volume may be expressed as $V = A/V^3$, where $A = 10^{-12} \text{J/m}$ is the exchange constant between nanocrystals, $K$ is the nanocrystal anisotropy constant and $v$ is the nanocrystal volume [7]. The number of crystallite in $V$ is not infinite and a resultant anisotropy energy exists at the scale of $V$, determined by statistics. This energy, normalised to one nanocrystal, is expected to be proportional to $1/N$, where $N$ is the number of nanocrystals within the correlation volume.

Fe-based ultra-soft nanomaterials (such as FeSiB, NbC or FeZrB) are formed of $\alpha$-Fe nanocrystals (10-15 nm in diameter) embedded into an amorphous magnetic matrix (Figure 3) [8]. For these systems, $K = 10^{-4} \text{J/m}^3$, the correlation volume thus derived is of macroscopic size. The moments being aligned over macroscopic dimensions, the global magnetic anisotropy is averaged over a very large number of grains and it is vanishingly small. This explains the ultra-soft behaviour obtained. These nanomaterials are used to make transformers for electronic applications.

In R-M intermetallics, the anisotropy constant $K = 10^{-7} \text{J/m}^3$. The correlation volume deduced is of the order of $10^3 \text{nm}^3$, i.e. of the order of or smaller than the nanocrystal size. To first approximation, the moments are aligned along the local easy magnetisation direction. In this configuration, the anisotropy is not averaged out. This is in agreement with the existence of large coercivity in NdFeB nanostructured alloys [9]. In order to minimise exchange, the moments close to the interface between two nanocrystals, tend to orientate along some intermediate direction between the 2 local easy magnetisation directions. It results that the magnetisation is higher than the value $M_s/2$ expected for perfect alignment along the individual easy magnetisation directions of an assembly of uniaxial randomly-oriented nanocrystals. This is the phenomenon of remanence-enhancement [10].

Hard nanocomposites include soft and hard exchange-coupled nanocrystals, in which the soft nanocrystals show coercivity (Figure 3) [11]. To explain this, let us assume that the applied field is weaker than the hard nanocrystal coercive field, so that the corresponding magnetization is frozen. Due to exchange coupling at the interface, soft phase magnetisation reversal requires the formation of a moment configuration within the soft phase, which is very reminiscent of a domain wall. However, this wall is constrained to the size of the soft nanocrystals. It is much narrower than it would be in the bulk and its energy is $1-2$ orders of magnitude higher. Thus, the soft phase resists reversal [12]. The most common of these materials associate hard Nd$_2$Fe$_14$B nanocrystals and soft $\alpha$-Fe or Fe$_3$B ones; $\mu_0H_c$ values up to 0.7 T are obtained. When these materials were discovered [11], it was hoped that new high performance materials could be produced by associating a
coercive hard magnetic phase with large magnetisation soft phases. To date, the properties obtained do not merit large industrial development. The recent successful preparation of anisotropic nanocomposites may open new perspectives [13].

Storage media consist of exchange-decoupled randomly-oriented grains. The transition region from one bit to the next must be sharp. This implies that each bit is made of a large number of grains, typically 1000-5000. The recording density envisaged with magnetic tapes is of the order of 5 Gbts/in². The corresponding particle volume is around \(10^2 \text{nm}^3\). In modern HDD, the recording density approaches 100 Gbts/in². At this density, the bit size is 0.2 \(\mu\text{m} \times 0.1 \mu\text{m}\) and the particle volume is around 100 \(\text{nm}^3\). Thus, magnetic storage necessarily involves nanomaterials (Figure 3) [4].

At such small particle sizes, the phenomenon of superparamagnetism must be considered [1]. The total anisotropy energy of one nanoparticle, \(K_\text{v}\), must be compared to the energy brought by thermal activation at the temperature \(T\), of the order of 25\(k_B\)T. Setting \(K_\text{v} = 25k_B\)T, gives \(K = 10^6 \text{J/m}^3\) which represents a very significant anisotropy. In materials with lower anisotropy value, the magnetisation will fluctuate spontaneously under the effect of thermal activation. This effect is thought to set a limit for magnetic recording density and this limit will be reached before the year 2005. Various approaches are being examined to push superparamagnetism to higher temperature values. These include the growth of pillars, such that the particle volume is increased but the storage density is not affected [14]. In other approaches, the ferromagnetic film, in which the information is stored, is antiferromagnetically coupled to another ferromagnetic layer [15] or the ferromagnetic particles are embedded within an antiferromagnetic matrix [16].

The above discussion concerned longitudinal recording. The particle magnetisation lies in the plane of the substrate. Perpendicular recording is an alternative, which will allow the recording density to be pushed forward by a factor of 4 approximately. Even more promising, is the development of "quantum bits" in which each bit of information is a unique magnetic object. Approaches towards this include film deposition on structured substrates or the direct self-organisation of magnetic nanoparticles prepared by chemistry. Spectacular results in this field have been obtained with FePt nanoparticles [17].

### References


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### Imaging of micro- and nanomagnetic structures

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There is a great interest in understanding the micromagnetic behavior of thin ferromagnetic layers, driven by their technological exploitation in magnetic field sensors and magnetic random access memory devices (MRAM). As a high storage density is a key goal in the design of such memory devices, recent research has been concentrating on the investigation of ferromagnetic elements with submicrometer lateral dimensions. For a magnetic storage cell to define a bit (0 or 1), it must have two stable remanent magnetization states that are uniformly magnetized, i.e. form a single magnetic domain, independent of its magnetic history.

Apart from other powerful magnetic imaging techniques, we focus on two particular techniques to investigate the magnetic domain configurations of micro- and nanomagnetic structures: Magnetic Force Microscopy (MFM) [1,2] and Scanning Near-Field Optical Microscopy (SNOM) [3,4].

**MFM**

The MFM detects the magnetic stray fields (blue arrows in Figure 1) which are generated at the edges of magnetic elements.