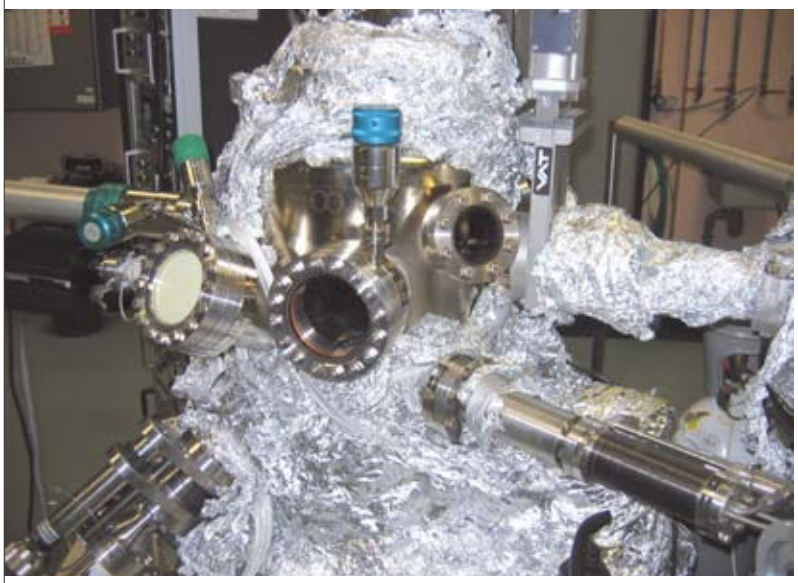
Oxides in spintronics

Magnetic oxides display novel properties that may be exploited by spintronics in applications involving spin-polarised currents.



CEA

Set-up for growth by molecular beam epitaxy (MBE) at the SPCSI (Department of Physics and Chemistry of Surfaces and Interfaces), CEA Saclay.

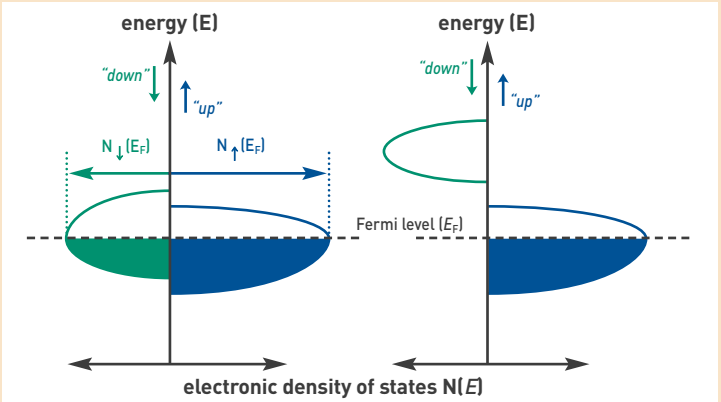
Spintronics technology began with the discovery in 1988 by Albert Fert's team at Orsay of **giant magnetoresistance** (**GMR**) in multilayers alternating a **ferromagnetic** metal with a non-magnetic metal (*e.g.* Fe/Cr or Co/Cu). In 1991, such GMR effects were also highlighted in more sophisticated multilayers or **spin valves**. These discoveries prompted an intense research activity, and in 1995 **tunneling magnetoresistance** (TMR) effects were observed in another device, called a *magnetic tunnel junction* (*MTJ*). This device is made up of two ferromagnetic metal layers separated by a non-magnetic tunnel barrier. Concomitant with these discoveries, technological advances in the growth of oxide thin films have spurred research into magnetic oxides. Here we describe the main approaches that have been explored to use the novel properties of some of these oxides in spintronics. The first approach consists in obtaining strong **magnetoresistive** effects (GMR, TMR) at high temperature which can be used in **spin** electronic devices (e.g., magnetoresistive hard disk read heads and magnetic random access memory). Obtaining these effects involves the spin **polarisation** of the transported electrons (Box). One present challenge is to find systems with a stronger spin polarisation than that of common ferromagnetic metals (iron, cobalt, nickel, etc.). Magnetic oxides form an interesting class of candidate materials.

What is a 'half-metallic' material?

A magnetic material is a material which presents a different electronic density of states* at the Fermi level (E_F)(1) for **spin** 'up' and spin 'down' electrons (Figure). To measure this spin asymmetry we define the spin polarisation (P) of the material by the equation:

$$P = \frac{N_\uparrow(E_F) - N_\downarrow(E_F)}{N_\uparrow(E_F) + N_\downarrow(E_F)}$$

The material is said to be 'half-metallic', *i.e.* metallic for one spin direction and insulating for the other, when it presents one type of electrons ('up' or 'down') at the Fermi level (on the right in the figure). In this case, the polarisation is total and equal to 100%.



(*) density of states: function of energy N(E) such that N(E)dE is equal to the number of electronic states of a system whose energy lies in the interval between E and E+dE, where dE is a very small energy increment.

Half-metallic oxides

A first approach consists in using fully spin-polarised oxides as **ferro**- or **ferri-magnetic** electrodes in magnetic tunnel junctions , also called '*half-metallic*' oxides, i.e., materials having electronic states of only one spin direction (*up* or *down*)(1) at the Fermi level. Strong tunnel magnetoresistance effects at low temperatures have been obtained using the conducting ferromagnetic oxide $La_{2/3}Sr_{1/3}MnO_3$ (manganite) (Figure 1). The use of this oxide as an electrode in a magnetic tunnel junction has also provided insight into the mechanisms responsible for tunnel transport (role of the **tunnel barrier**, interface effect, etc.). However, the **Curie temperature** (T_c) of this oxide barely exceeds room temperature, and the TMR effect disappears around 300 **K**, which makes this material unsuitable for applications. Other half-metallic oxides with higher Curie temperatures have been considered, among which are the double **perovskites** Sr_2FeMoO_6 (T_c= 420 K) and chromium oxide CrO_2 (T_c = 395 K). So far the TMR effects measured at room temperature have been disappointing, mainly due to the high sensitivity of the oxide's half-metallic character to its structure and stoichiometry(2). These properties are difficult to stabilise in thin layers, especially at interfaces.
Iron oxide: Fe_3O_4 (T_c= 858 K), or magnetite, is another oxide predicted to be half-metallic at room tem-

(1) Fermi level: for a metal, the highest energy level occupied by the electrons of the system at the temperature of zero kelvin.

(2) Stoichiometry: study of the proportions in which reagents combine and products are formed in a chemical reaction. A reaction is said to be stoichiometric when the molar proportions of the reagents are the same as those in the chemical equation.

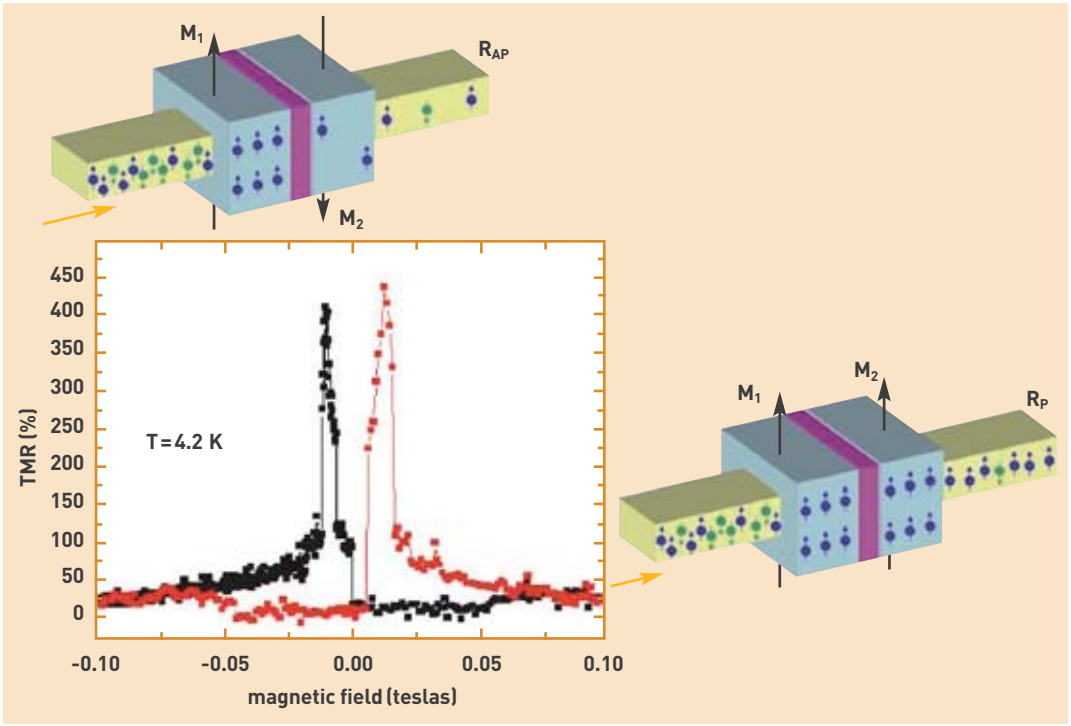


Figure 1.
A magnetic tunnel junction is made up of two ferromagnetic electrodes with magnetisations M_1 and M_2 separated by a thin non-magnetic insulating layer that the current can cross by the tunnel effect. The first magnetic electrode acts as a polariser for the conducting electrons. According to the magnetic configuration of the second electrode relative to the first, the tunnel current through the barrier is high or low. The tunnel magnetoresistance (TMR) is therefore defined by the ratio of the resistances in the parallel alignment (P) and the antiparallel alignment (AP) of the two magnetisations. According to Julliere's phenomenological model, the TMR can be linked to the spin polarisation of the two ferromagnetic electrodes by the equation:

$$TMR = \frac{R_{AP} - R_P}{R_P} = \frac{2P_1P_2}{1 - P_1P_2}$$

The figure opposite shows a tunnel magnetoresistance (TMR) curve obtained at very low temperature (T = 4.2 K) in the magnetic tunnel junction $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$ (in M. Viret *et al.*, *EuroPhys. Lett.*, 39, 545 [1997]). In 2003 record amplitudes of the order of 1850% were obtained in these magnetic tunnel junctions, though still at low temperature (M. Bowen *et al.*, *Appl. Phys. Lett.*, 82, 233 [2003]).

perature. However, when synthesised in thin layers, it displays physical properties (magnetic and electric) different from those measured in the bulk. These anomalies, which have been linked mainly to the presence of structural defects (or *antiphase boundaries*), probably explain the weak TMR effects measured.

Diluted magnetic oxides

A second approach in order to obtain materials with a high spin polarisation at room temperature consists in synthesising new ferromagnetic oxides with high Curie temperatures by doping non-magnetic **semi-conducting** oxides with magnetic **ions**. The resulting materials form the family of *diluted magnetic oxides*. Various oxides in thin layers seem to exhibit a ferromagnetic behaviour at high temperature such as titanium dioxide (TiO_2) or zinc oxide (ZnO) doped with cobalt. However, uncertainties still persist concerning the nature of the ferromagnetism in these oxides. It is very hard to demonstrate unequivocally that the observed ferromagnetic behaviour is an *intrinsic* characteristic of the material and not an extrinsic effect linked to the presence of parasitic magnetic phases.

Oxides for spin filtering

A third, less explored, approach to obtain a strong spin polarisation is to use a tunnel barrier of a ferro- or ferrimagnetic oxide: this is the spin filter concept. In an insulating ferro- or ferrimagnetic oxide, the exchange splitting of the conduction bands(3) for the two spin directions results in a different barrier height for spin 'up' and spin 'down' electrons, which induces a different transmission for these two spin directions and thus a strongly spin polarised current (Figure 2). The combination of a non-magnetic metallic electrode, which acts as an electrons source, with a magnetic oxide barrier also makes it possible to artificially reproduce a half-metal. One of the first difficulties encountered in doing this is synthesising a very thin oxide layer with the right electrical and magnetic properties. This spin filtering effect then has to be measured. One method is to redeposit a magnetic layer on the oxide barrier and make a TMR measurement in the magnetic tunnel junction thus formed. The first experiments validating this filtering concept were carried out by an **MIT** team using europium chalcogenide (EuS) barriers. However, the low Curie temperature of this material (T_c= 16 K) excludes it from applications. For this reason certain insulating oxides with higher Curie temperatures are currently being studied. Among these are barriers of europium oxide EuO (T_c= 69 K) for which a spin polarisation of conduction electrons of 29% at very low temperature (T = 0.4 K) has been measured. TMR effects have also been obtained with ferromagnetic barriers of $BiMnO_3$ (T_c= 105 K) and $La_{0.1}Bi_{0.9}MnO_3$ by the **CNRS**/Thalès joint research unit, who found spin polarisations of conduction electrons of respectively 22% and 35%, but still at very low temperature (a few kelvins).
Another family of oxides is currently offering new perspectives for the measurement of TMR effects at room temperature. These are insulating **ferrites** with spinel structures(4), of chemical formula AFe_2O_4, where A is a divalent(5) ion of a **transition**

(3) Conduction band: the electrons in a solid are localised in available energy ranges, or permitted energy bands separated by forbidden energy bands. In a conducting material the Fermi level falls inside a permitted band called the conduction band.

(4) Spinel: crystalline structure of general formula AB_2O_4 in which the oxygen anions form a face-centred cubic lattice in which cations A and B are located at tetrahedral and octahedral sites. We refer to 'normal' or 'inverse' spinel structures according to whether the two cations B occupy two octahedra or one octahedron and one tetrahedron (cation A occupying the site left vacant by cation B) respectively.

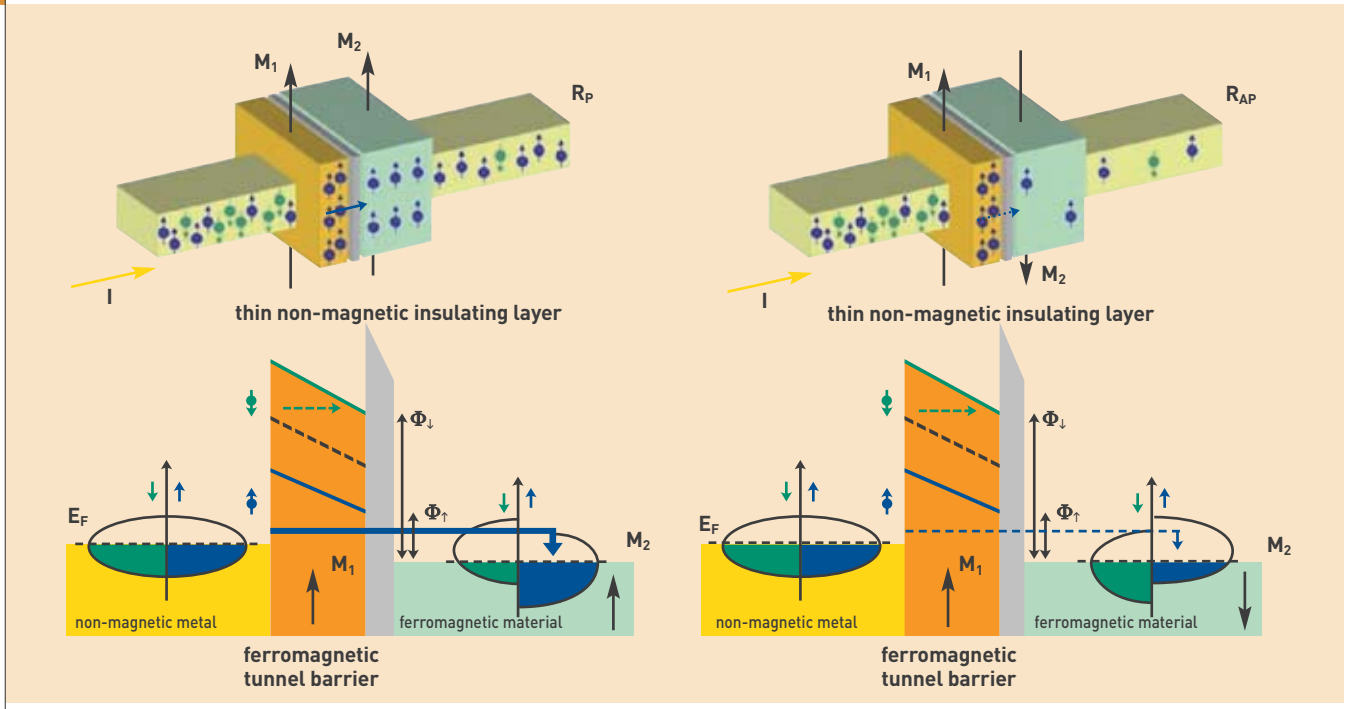


Figure 2.
Schematic diagram of electron transport in a magnetic tunnel junction based on spin filtering. The splitting of the conduction bands in the ferro- or ferri-magnetic tunnel barrier for the two spin directions introduces two barrier heights ($\phi_\uparrow$ and $\phi_\downarrow$ with here $\phi_\uparrow < \phi_\downarrow$), which generates a current (J): $J_{\uparrow(\downarrow)} \propto \exp(-\phi^{1/2}_{\uparrow(\downarrow)} d)$ where d is the thickness of the barrier.
Left: High tunnel current (blue), *i.e.* state of low resistance for parallel alignment of the magnetisations of the magnetic tunnel barrier (M_1) and the ferromagnetic counter-electrode (M_2).
Right: low tunnel current, *i.e.* s tate of high resistance for antiparallel alignment of magnetisations M_1 and M_2.
The spin filtering efficiency (P_{ef}): $P_{ef} = \frac{J_\uparrow - J_\downarrow}{J_\uparrow + J_\downarrow}$ is determined by TMR measurements using Jullière's formula.
In some structures, a very thin non-magnetic insulating layer has to be inserted between the magnetic tunnel barrier and the ferromagnetic counter-electrode to prevent magnetic coupling at the interfaces.

metal (Ni^{2+}, Co^{2+}, etc.), and whose Curie temperatures are higher than room temperature. In 2006 TMR effects were measured at very low temperatures (4 K) in MTJs with tunnel barriers of nickel ferrite $NiFe_2O_4$ corresponding to a spin filter efficiency of 22%. Despite a Curie temperature well above room temperature (T_c= 850 K), integrating this oxide in an MTJ caused spin filtering to disappear at room temperature, pointing to a need for further work. More recently, work carried out at the SPCSI with the CNRS/Thalès joint research unit demonstrated the first spin filtering effects in cobalt ferrite: $CoFe_2O_4$ (T_c= 793 K). $CoFe_2O_4$/γ-Al_2O_3/Co magnetic tunnel junctions have been made by **molecular beam epitaxy**, yielding systems of high crystal quality with controlled interfaces (Figure 3). An ultra-thin non-magnetic insulating layer of aluminium oxide (γ-Al_2O_3) had to be inserted to ensure magnetic decoupling between the $CoFe_2O_4$ magnetic tunnel barrier and the cobalt electrode. After advanced optical **lithography**, significant TMR effects were observed at low temperature in these magnetic tunnel junctions, corresponding to a spin polarisation of conduction electrons of -25%, and also at room temperature (spin filter efficiency of -4%), showing the potential of this oxide[6].

(5) Divalent ion: atom (or group of atoms) that has lost (cation) or gained (anion) two electrons.

(6) See A. V. Ramos *et al.*, *Appl. Phys. Lett.*, **91**, 122107 (2007); *Phys. Rev.* B. **75**, 1 (2007).

(7) Ferro-electric: property of a material that possesses a permanent electric dipole moment (separation between the centre of gravity of the positive charges and that of the negative charges) even in the absence of an external magnetic field.

Multiferroic oxides

Lastly, research on magnetic oxides is not restricted to generating a strongly spin-polarised current. Another class of magnetic oxides has appeared in spintronics: *multiferroic oxides*. These materials combine a magnetic order (ferromagnetic or antiferromagnetic) and an electric order (ferroelectric[7]) by magnetoelectric coupling. In these materials we can control the electric polarisation by a magnetic field, or inversely, the magnetisation by an electric field. These oxides include the antiferromagnetic and ferroelectric oxides $YMnO_3$ and $BiFeO_3$, which are being studied in particular to control electrically the magnetic exchange interaction between the oxide layer and an adjacent magnetic layer. Recent work carried out by the CNRS/Thalès joint research unit shows that the ferroelectric character of the ferromagnetic oxides $BiMnO_3$ and $La_{1-x}Bi_xMnO_3$ can also be used advantageously in spin filter tunnel junctions to obtain not just two resistance states, but four states arising from the magnetic and ferroelectric configurations of the barrier. Few materials intrinsically possess both a magnetic and an electric order. An

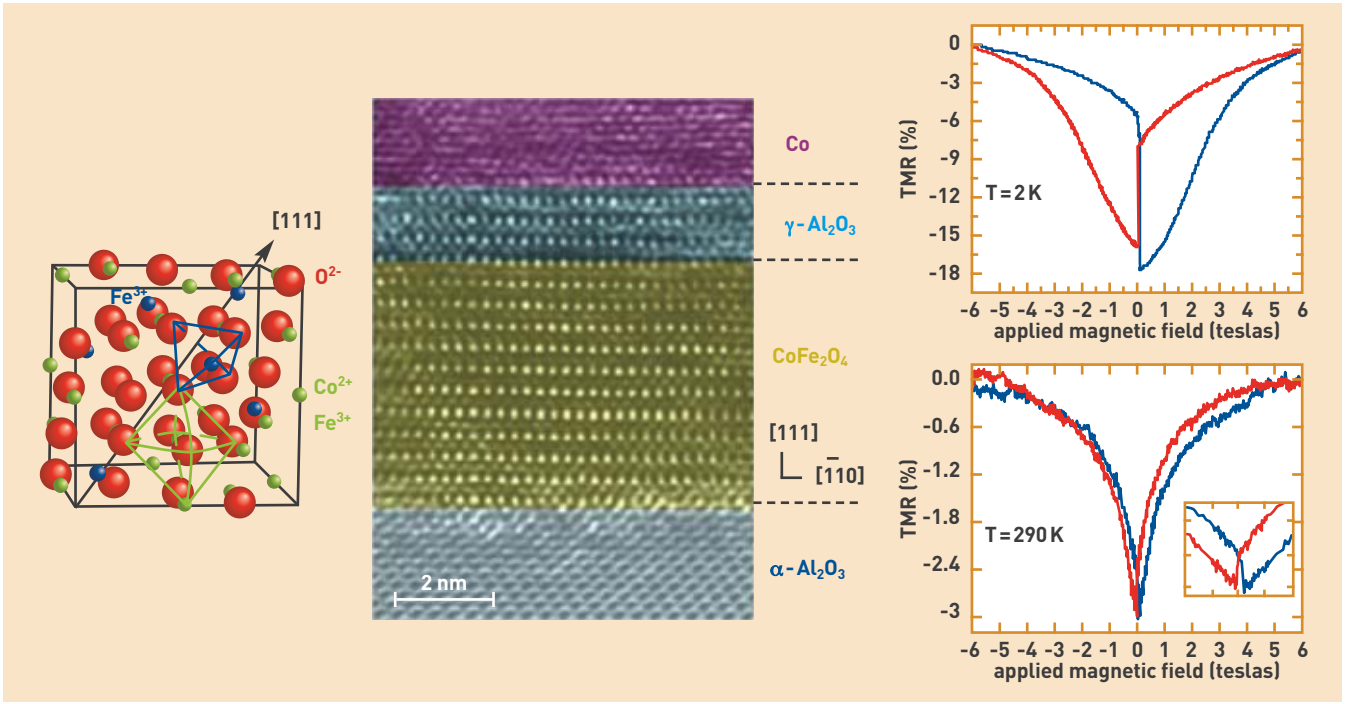


Figure 3.
Left: representation of the crystal lattice of ferrite $CoFe_2O_4$, which has an inverse spinel structure, and transmission electron microscopy image (by CEMES-CNRS and Inac/SP2M), showing the high crystalline quality of the magnetic tunnel junction $CoFe_2O_4$(5 nm)/γ-Al_2O_3(1.5 nm)/Co(10 nm) produced by molecular beam epitaxy on a sapphire substrate (α-Al_2O_3). The different layers are shown in different colours.
Right: Tunnel magnetoresistance at low temperature and at room temperature in the magnetic tunnel junction Pt(20 nm)/$CoFe_2O_4$(3 nm)/γ-Al_2O_3(1.5 nm)/Co(10 nm) demonstrating the spin filtering capacities of $CoFe_2O_4$ (by UMR CNRS/Thalès). The bias voltage is 200 mV and the junction area measured is 24 μm^2.
The negative sign of the TMR curves indicates that the magnetic barrier of $CoFe_2O_4$ and the cobalt electrode have spin polarisations of opposite sign, which is consistent with the negative polarisation of $CoFe_2O_4$ predicted by the band structure calculations and the positive polarisation measured for cobalt.

alternative consists in developing artificial multiferroic materials combining magnetic and ferroelectric layers in a same heterostructure. This will again require new expertise in growth and characterisation.
To conclude, research on magnetic oxide thin layers has seen a notable expansion in the last 20 years. New families of oxides, namely, half-metallic oxides, diluted magnetic oxides and multiferroic oxides, have emerged. Although a strong spin polarisation at room temperature has not yet been measured in an oxide, the recent observation of spin filtering effects with spinel ferrites heralds potential TMR effects and suggests numerous applications, in particular in the injection and/or detection of spin-polarised currents.

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Optical microscope examination of lithographed samples in a clean room Iramis/Spec, CEA Saclay.

The different types of magnetism

The origins of magnetism lie in the properties of electrons as explained by the laws of quantum physics. Part of an electron's magnetic properties (*spin magnetism*) results from its quantum-mechanical spin state, while another part results from the orbital motion of electrons around an atom's nucleus (*orbital magnetism*) and from the magnetism of the nucleus itself (nuclear magnetism). This is put to use, in particular, for nuclear magnetic resonance imaging in the medical field. Magnetism is therefore produced by electric charges in motion. The force acting on these charges, called the Lorentz force, demonstrates the presence of a magnetic field.

Electrons have an intrinsic magnetic dipole moment (the magnetic quantum state being the Bohr *magneton*), which can be pictured as an electron's rotational motion of spin around itself in one direction or another, oriented either upwards or downwards. The *spin quantum number* (one of the four numbers that 'quantifies' the properties of an electron) equals 1/2 (+ 1/2 or - 1/2). A pair of electrons can only occupy the same *orbital* if they have opposite magnetic dipole moments.

Each atom acts like a tiny magnet carrying an intrinsic magnetic dipole moment. A nucleus (the neutron and proton individually have a half-integer spin) will have a half-integer spin if it has an odd atomic mass number; zero spin if the atomic mass number and charge are even, and an integer spin if the atomic mass number is even and the charge odd.

On a larger scale, several magnetic moments can together form magnetic domains in which all these moments are aligned in the same direction. These spatial regions are separated by domain walls. When grouped together, these domains can themselves form a macroscopic-scale magnet (Figure E1).

The type of magnetism that comes into play is determined by how these elementary constituents are ordered, and is generally associated with three main categories of material: *ferromagnetic*, *paramagnetic* and *diamagnetic*.

Any material that is not diamagnetic is by definition paramagnetic provided that its magnetic susceptibility is positive. However, ferromagnetic materials have particularly high magnetic susceptibility and therefore form a separate category.

1. Ferromagnetic materials are formed of tiny domains inside which atoms exhibiting parallel magnetisation tend to align themselves in the direction of an external magnetic field like elementary dipoles. In fact, the magnetic moments of each atom can align themselves spontaneously within these domains, even in the absence of an external magnetic field. Applying an external field triggers domain wall movement that tends to strengthen the applied field. If this field exceeds a certain value, the domain most closely oriented with the direction of the applied field will tend to grow at the expense of the other domains, eventually occupying the material's whole volume. If the field diminishes, the domain walls will move, but not symmetrically as the walls cannot fully reverse back to their original positions. This results in remanent magnetisation, which is an important feature of naturally occurring magnetite, or of magnets themselves.

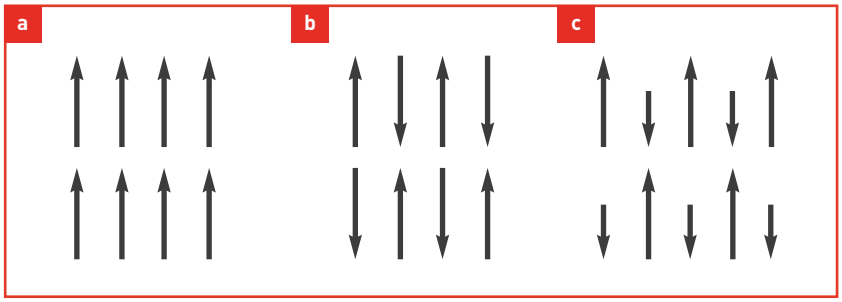

Figure E1.
Intrinsic magnetic dipole moments have parallel alignment in ferromagnetic materials (a), anti-parallel alignment but zero magnetisation in antiferromagnetic materials (b), and anti-parallel alignment with unequal moments in ferrimagnetic materials (c).

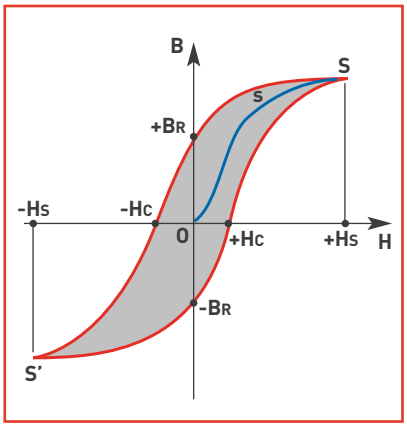

Figure E2.
The induction B of a magnetic material by a coil is not proportional to its magnetic excitation (*field H*). While the initial magnetisation forms an OsS-type curve, shown in blue in the figure, it reaches saturation at point s. Only a partial induction is retained if the field approaches zero; this remanent induction can only be cancelled out by reversing the magnetic field to a "coercive" field value. This hysteresis loop illustrates the losses due to "friction" between the magnetic domains shown on the area bounded by the magnetisation and demagnetisation curves.

The whole process forms a hysteresis loop, i.e. when the induced field is plotted against the applied field it traces out a *hysteresis curve* or *loop* where the surface area represents the amount of energy lost during the irreversible part of the process (Figure E2). In order to cancel out the induced field, a coercive field has to be applied: the materials used to make artificial permanent magnets have a high coercivity.

Ferromagnetic materials generally have a zero total magnetic moment as the domains are all oriented in different directions. This ferromagnetism disappears above a certain temperature, which is known as the Curie Temperature or Curie point.

The magnetic properties of a given material stem from the way the electrons in the metallic cores of a material or of a transition metal complex collectively couple their spins as this results in all their spin moments being aligned in the same direction.

Materials whose atoms are widely distributed throughout their crystal structure tend to better align these elementary magnets via a coupling effect. This category of materials, which is characterised by a very high positive magnetic

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A Transrapid train using magnetic levitation arriving at the Long Yang bus station in Shanghai (China). This German-built high-speed, monorail train was commissioned in 2004 to service the rail link to Pudong international airport.

susceptibility, includes iron, cobalt and nickel and their **alloys**, steels in particular, and some of their compounds, and, to a lesser extent, some **rare earth** metals and alloys with large crystal lattices, and certain combinations of elements that do not themselves belong to this category. In **ferrimagnetic** materials, the magnetic domains group into an anti-parallel alignment but retain a non-zero magnetic moment even in the absence of an external field. Examples include magnetite, ilmenite and iron oxides. Ferrimagnetism is a feature of materials containing two types of atoms that behave as tiny magnets with magnetic moments of unequal magnitude and anti-parallel alignment. **Antiferromagnetism** occurs when the sum of a material's parallel and anti-parallel moments is zero (e.g. chromium or haematite). In fact, when atoms are in a close configuration, the most stable magnetic arrangement is an anti-parallel alignment as each magnet balances out its neighbour so to speak (Figure E1).

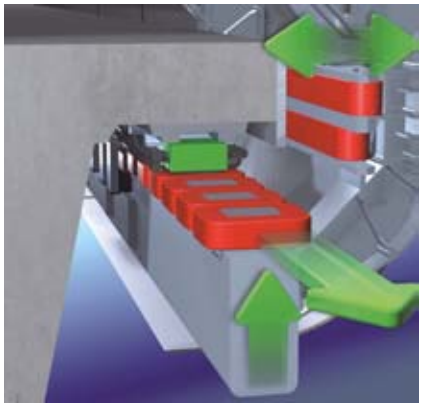
2. **Paramagnetic** materials behave in a similar way to ferromagnetic materials, although to a far lesser degree (they have a positive but very weak magnetic susceptibility of around 10^{-3}). Each atom in a paramagnetic material has a non-zero magnetic moment. In the presence of an external magnetic field, the magnetic moments align up, thus amplifying this field. However, this effect decreases as temperature rises since the thermal agitation disrupts the alignment of the elementary dipoles. Paramagnetic materials lose their magnetisation as soon as they are released from the magnetic field. Most metals, including alloys comprising ferromagnetic elements are paramagnetic, as are certain minerals such as pegmatite.

3. **Diamagnetic** materials exhibit a negative and an extremely weak magnetic susceptibility of around 10^{-5}. The magnetisation induced by a magnetic field acts in the opposite direction to this field and tends to head away from **field lines** towards areas of lower field strengths. A perfect diamagnetic material would offer maximum resistance to an external magnetic field and exhibit zero **permeability**. Metals such as silver, gold, copper, mercury or lead, plus quartz, graphite, the noble gases and the majority of organic compounds are all diamagnetic materials.

In fact, all materials exhibit diamagnetic properties to a greater or lesser extent, resulting from changes in the orbital motion of electrons around atoms in response to an external magnetic field, an effect that disappears once the external field is removed. As Michael Faraday showed all that time ago, all substances can be "magnetised" to a greater or lesser degree provided that they are placed within a sufficiently intense magnetic field.

Electromagnetism

It was the Danish physicist Hans Christian Ørsted, professor at the University of Copenhagen, who, in 1820, was first to discover the relationship between the hitherto separate fields of **electricity** and **magnetism**. Ørsted showed that a compass needle was deflected when an electric current passed through a wire, before Faraday had formulated the physical law that carries his name: the magnetic field produced is proportional to the intensity of the current. **Magnetostatics** is the study of static magnetic fields, i.e. fields which do not vary with time.



Close-up of the magnets used to guide and power the train.

Magnetic and **electric fields** together form the two components of **electromagnetism**. **Electromagnetic waves** can move freely through space, and also through most materials at pretty much every frequency band (radio waves, microwaves, infrared, visible light, ultraviolet light, X-rays and gamma rays). **Electromagnetic fields** therefore combine electric and magnetic **force fields** that may be natural (the Earth's magnetic field) or man-made (low frequencies such as electric power transmission lines and cables, or higher frequencies such as radio waves (including cell phones) or television.

Mathematically speaking, the basic laws of electromagnetism can be summarised in the four **Maxwell equations** (or **Maxwell-Lorentz equations**) which can be used to provide a coherent description of all electromagnetic phenomena from electrostatics and magnetostatics to electromagnetic wave propagation. James Clerk Maxwell set out these laws in 1873, thirty-two years before Albert Einstein incorporated the theory of electromagnetism in his *special theory of relativity*, which explained the incompatibilities with the laws of classical physics.