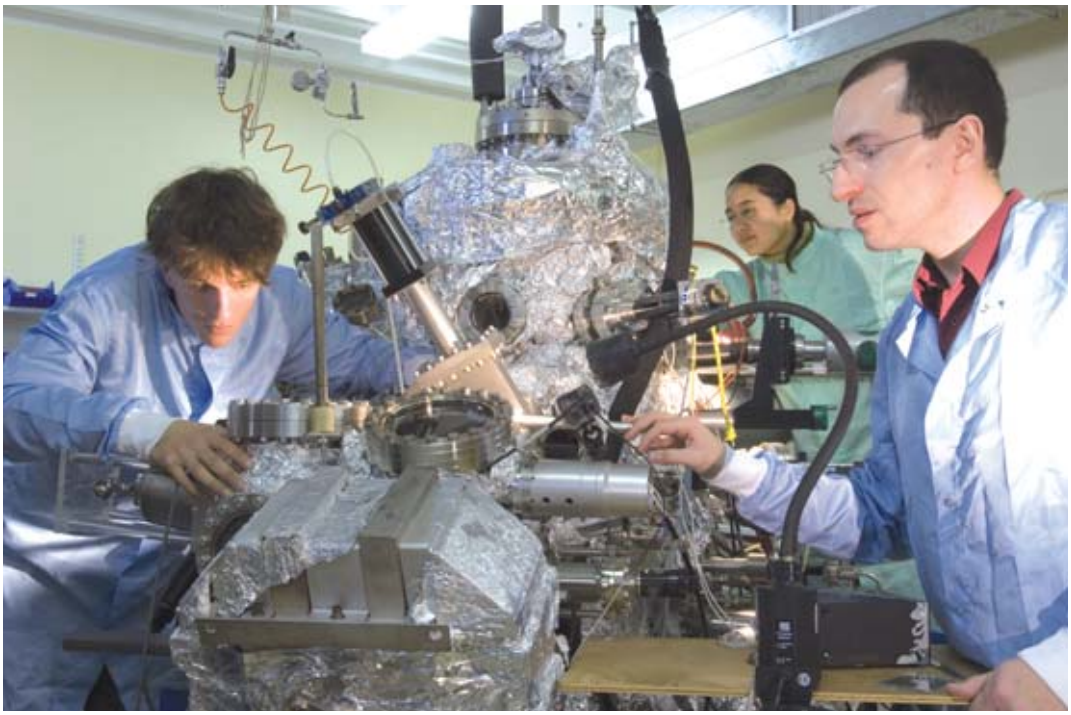
Nanoparticles: nanoprobes and magnetic grains of the future

When the size of a 'magnetic grain' is reduced to a dozen nanometres, new problems arise. New opportunities too.

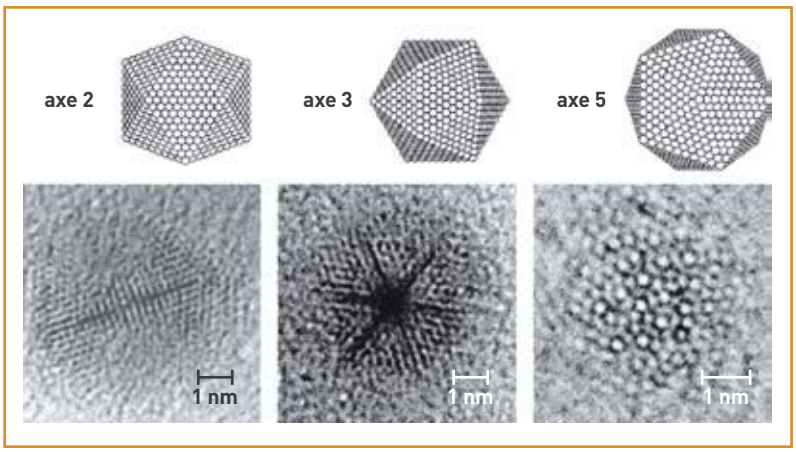


F. Vigouroux/CEA

Deposition of magnetic thin layers in a molecular beam epitaxy chamber at the Nanostructure and Magnetism Laboratory, CEA Grenoble.

Magnetic nanoparticles are small particles only **nanometres** in diameter, made up of a few thousand **atoms**. They are both the prototypes of the magnetic grains of the future, and probes with which magnetic phenomena can be studied at the nanometre scale (Figure 1). An original experimental method pioneered in recent years has made it possible to detect the reversal of the **magnetisation** of a single nanoparticle of a thousand atoms. This reversal is triggered when the energy of the cluster in the **magnetic field** succeeds in overcoming the energy barrier due to its **anisotropy**. This is the micro-**SQUID** technique developed at the **CNRS** Grenoble(1). The energy is measured by the local transition from the superconducting state to the normal state of a microloop of niobium covering the nanoparticle.

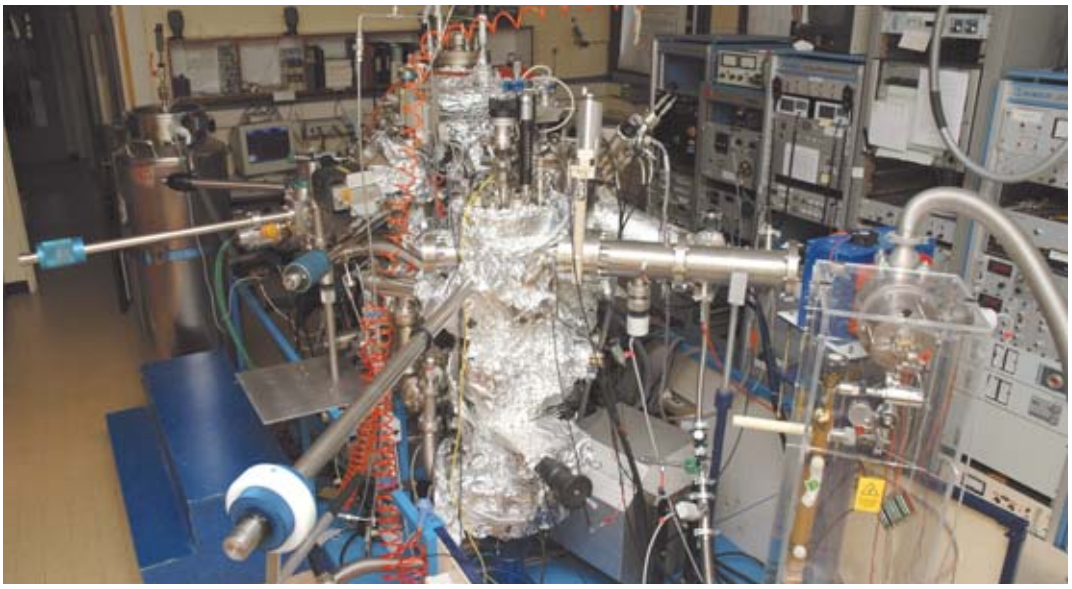
When a nanoparticle is coupled magnetically to a substrate by the exchange phenomenon, the interaction is located at the interface, at the two layers of atoms in contact. For a nanometric cluster on an antiferromagnetic substrate or enclosed in an **antiferromagnetic** shell, the contact surface – and therefore the total number of atoms involved – amounts to several hundred atoms. The joint work currently underway with the CNRS has already made it possible to observe the influence of these atoms on the reversal field of the nanoparticle. The choice of system first focused on the cobalt nanoparticle / cobalt oxide pair. One is **ferromagnetic**, the other antiferromagnetic, i.e. composed of layers of magnetic atoms with compensating **spins**. The antiferromagnetic substrate or shell is thus not magnetised, and plays the role of a **'hard' magnetic material**, with firmly set spins. These 'harden' the magnetisation of the first layer of atoms in the cluster and thereby the whole of the nanoparticle. On the macroscopic scale, a layer of nanoparticles does not behave very differently from a thin layer. When the antiferromagnetic material is cooled in a magnetic field in a state oriented in a given direction the nanoparticles are preferentially magnetised in that direction. The magnetisation cycle is



CEA/ P. Bayle-Guillemaud

Figure 1.
High-resolution microscopy images showing the icosahedral structure of cobalt nanoparticles 6 nm in diameter.

(1) M. Jamet *et al.*, Phys. Rev. Lett. **86**, 4676 (2001).



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Set-up for the epitaxy of magnetic layers with perpendicular anisotropy at CEA Grenoble.

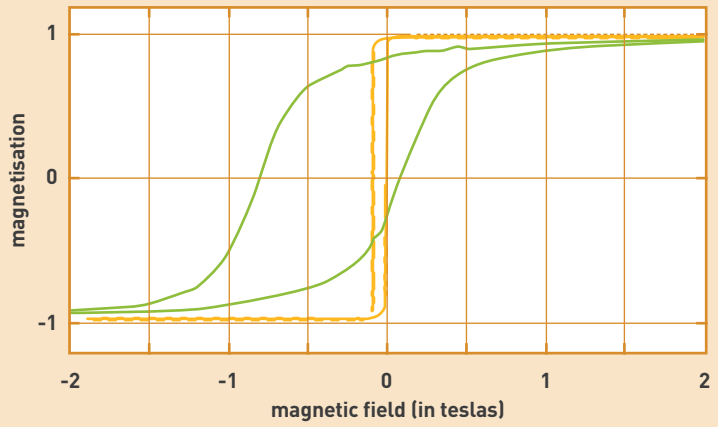
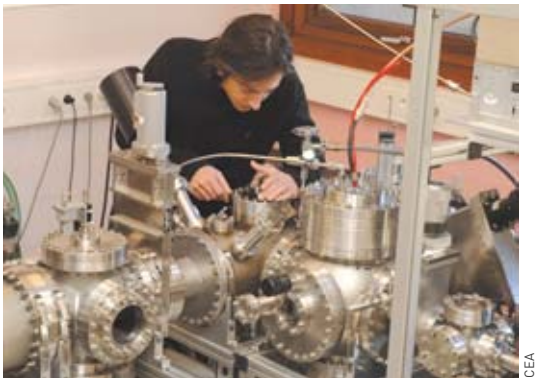


Figure 2. Magnetisation cycles shifted by exchange interaction between ferromagnetic cobalt and its antiferromagnetic oxide. Orange curve: thin layer of 18 nm-thick cobalt oxidised through 2 nm (Gruyters, Phys. Rev. B 63, 052401 (2000)). Green curve: layer of 6 nm cobalt nanoparticles oxidised through 1 nm (CEA Grenoble).

shifted (Figure 2). If the antiferromagnetic material is cooled with no magnetic field the average effect is nil, and the cycle is centred. Using micro-SQUID, it is possible to 'zoom' onto a single nanoparticle and determine whether it is still preferentially oriented. When the antiferromagnetic material is not prepared, the orientation is random: the magnetisation is thus nil on average and the cycle is centred. However, if the antiferromagnetic material is prepared, this orientation is set on average by the direction of the cooling field, and a shift in the magnetisation cycle is observed. Clearly, macroscopic measurements alone do not provide an understanding of the physics of the interaction: the direction of magnetisation is governed locally by the arrangement of atoms and spins at the interface.



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Work on the nanometric nanoparticle deposition experiment at the Nanostructure and Magnetism Laboratory, CEA Grenoble.

Theoretically, the exchange interaction should generate a much more intense magnetic coupling than that measured on current magnetic layers. Several phenomena can account for this discrepancy: rough layer surfaces, point defects, **domain walls**, uncompensated spins at the interface or even within the antiferromagnetic material, etc. To understand the situation better, the interface has to be studied close up. Using single nanoparticles, the study of the interaction can be focused on areas with nanometric dimensions and thus gain a command of these effects. The single nanoparticle associated with the micro-SQUID technique forms a nanoprobe for the interaction that offers a better understanding of exchange coupling at the local level.

Chemical synthesis of magnetic nanoparticles: towards applications

The alloy of iron and platinum (FePt) exhibits a very strong magnetic anisotropy, owing to its **crystalline** structure, but only if it is presented in an ordered phase, namely alternately stacked iron and platinum atoms. The use of nanoparticles of this phase is thus of great interest for building **discrete** magnetic media. The sizes of the magnetic grains can be considerably reduced, and storage density correspondingly increased, up to 1 **terabit** per square inch (6.45 cm^2). The high anisotropy gives the magnetisation thermal stability above ambient temperature.

The first synthesis of nanoparticles of FePt alloy was published in 2000 by researchers at IBM[(2)]. This type of particle, which averages 4 nm in size, has a metal core of a few thousand atoms, covered with a layer of organic molecules (**ligands**) that prevent the **coalescence** of the nanoparticles. The synthesis is based on the **reduction** of a platinum

(2) S. Sun *et al.*, Science **287**, 1989 (2000).

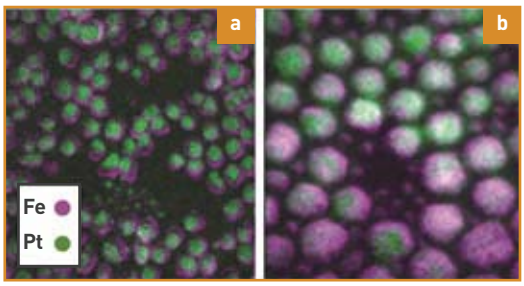

Figure 3.
Chemical mapping of FePt nanoparticles by energy-filtered transmission electron microscopy (EFTEM):
(a) 'core/shell' particles obtained by literature synthesis [M. Delalande et al., J. Mater. Chem. 17, 1579 (2007)],
(b) particles with homogeneous composition by a new process developed at the CEA (DRFMC/SPrAM).

salt and the decomposition of an iron precursor in an organic solvent at high temperature. This reaction takes place in the presence of a mixture of oleic acid and oleylamine (ligands of iron and platinum, respectivily). However, the use of these ligands gives nanoparticles made up of an iron-depleted core enclosed in a surface-oxidised shell of iron (Figure 3a). This structure arises from the differences in the reaction kinetics of iron and platinum, controlled by their interaction with the ligands. Therefore a new ligand with a stronger interaction with platinum than oleylamine had to be found. Pentadecanenitrile was chosen as it gives nanoparticles a more homogeneous composition (Figure 3b). Varying the ligand ratio also offers a broad range of nanoparticle diameters (Figure 4). **X-ray diffraction** shows that nanoparticles first crystallise in a disordered *cubic phase*, in which the iron and platinum atoms are arranged randomly. Post-synthesis treatment of the nanoparticles, for example annealing, yields the anisotropic phase (Figure 5).

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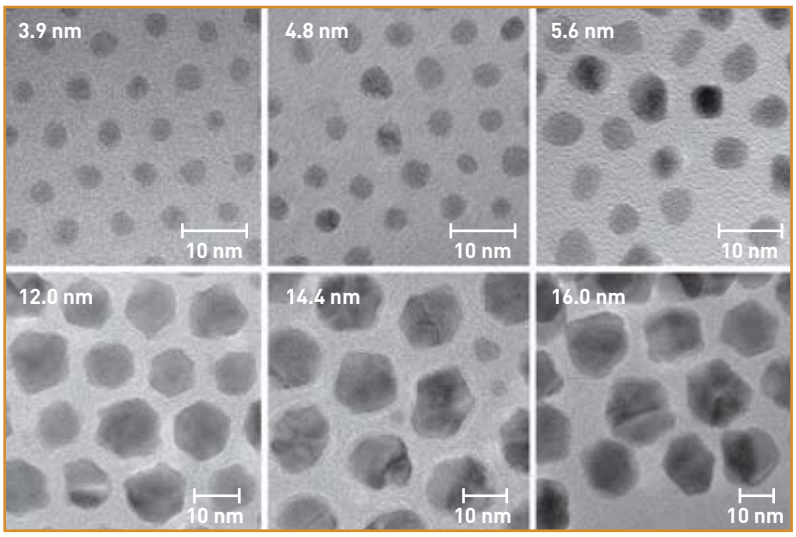

Figure 4.
Transmission electron microscopy (TEM) images illustrating the broad range of FePt nanoparticle diameters that can be obtained by the new method varying the ratio of the stabilising ligands (oleic acid and pentadecanenitrile).

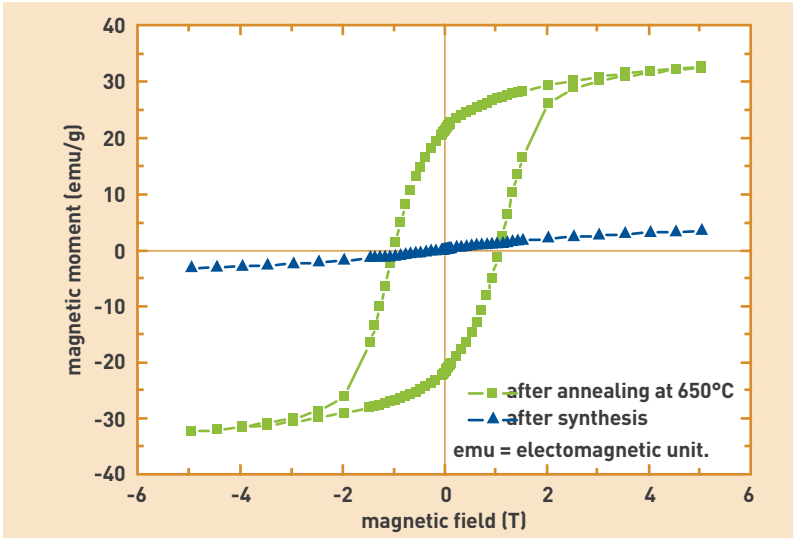

Figure 5.
Ambient-temperature hysteresis loops of nanoparticles directly after synthesis and after annealing at 650°C. The straight line indicates that the particles after synthesis are superparamagnetic (non-magnetic at ambient temperature), whereas the open cycle shows that the annealed particles are ferromagnetic.

When magnetism is all about walls

At nanometric scales, the study of magnetic domains and the walls that separate them becomes determinant for the development of ferromagnetic materials.

Ferromagnetic materials are made up of micrometer-sized **domains** within which the **magnetisation** is homogeneous and separated by magnetic walls. When a **magnetic field** is applied, the domains in which the magnetisation is favourably oriented relative to the field grow at the expense of the neighbouring domains. This causes a movement of the magnetic walls. The interactions between magnetic fields and defects thus control the properties of

Figure 1.
Magnetic force microscopy (MFM) image showing pinned magnetic domain walls (bounding black and white magnetic domains) anchored at 45°, corresponding to microtwins.

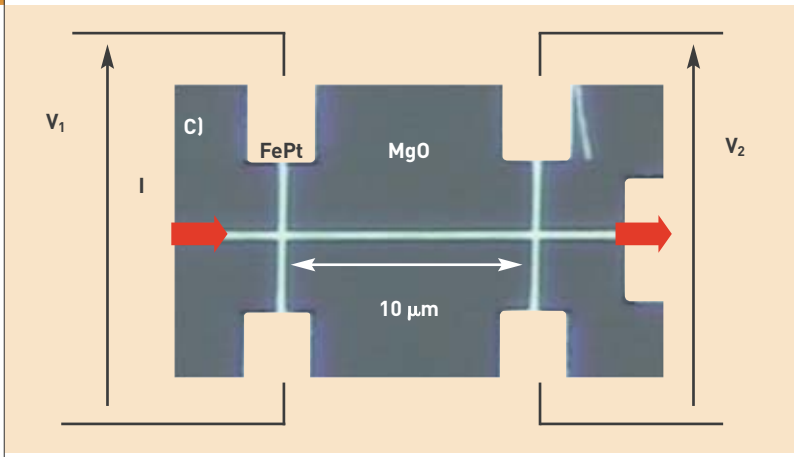

Figure 2.
Device for measuring the magnetic domain walls propagation, here in a FePt/MgO/FePt trilayer used in a magnetic tunnel junction. Red arrows indicate the direction of propagation.

hysteresis and the dynamics of magnetisation reversal, together with the geometry of the magnetic domains. It is therefore most important to gain a detailed understanding of these processes at the microscopic level.

In the course of the last decades, the study of domain wall propagation has benefited from the development of manufacturing methods (manufacturing of appropriately-scaled **nanometre**-sized thin layers and devices) and measurement techniques (transport measurements, imaging, etc.). New techniques have opened the way for the study of single wall dynamics. In addition, research to which CEA teams have contributed has demonstrated an electrical resistance effect associated with the presence of a domain wall. It is also possible to move a domain wall by applying an electrical current perpendicular to it. A whole new technology for detecting and handling magnetic domain walls has come into being, allowing new applications to emerge and exciting new physical phenomena to be studied.

The hysteresis loops of ferromagnetic materials measured on a macroscopic scale are generally continuous. But at the **submicron** scale the presence of defects actually makes the wall movement discontinuous, and the magnetisation varies by the rapid wall jumps between defects (*Barkhausen jumps*). In solid materials they can be demonstrated by induction. However, in thin layers and nanodevices the much weaker signal requires other techniques, such as for example the measurement of the Extraordinary **Hall effect** in the crosses obtained by **lithography** and etching.

To exert greater control over the role of a defect and to make sure it is unique, some researchers have artificially created a defect using lithographic techniques in nanometric devices and studied the anchoring of a wall on this single defect. The measurement is most often made in a track between two Hall crosses, sometimes extended by magneto-optical observations to examine the wall pinning more directly. The CEA team set out to study this wall pinning on a small number of natural defects obtained during the growth of thin layers. These structural defects, called *microtwins*, on which magnetic domain walls are pinned are due to the relaxation of growth constraints, and they bound the cells, which form a chequered pattern (Figure 1).

To study the fundamental behaviour of the walls, a sub-micron-sized device was made by lithography and etching. It was composed of a central 200 nm-wide line set between two Hall crosses (Figure 2).

After measurements on the individual crosses showing Barkhausen jumps, the researchers studied wall propagation in the line between the two crosses. The sample was first saturated, and a magnetic reversal field was applied. The time interval between successive reversals of the magnetisation in the two crosses made it possible to measure the wall propagation time in the line. Numerous repeated measurements showed that this propagation time was random. The distribution of pass-through times showed a descending exponential pattern. Hence one defect (barrier) pins the wall predominantly relative to all the others. If several barriers in series with equivalent heights successively pinned the wall, there would be a lag between the reversals of the two crosses. The CEA team has shown (Figure 3) that the crossing of this barrier obeys a thermal activation law that makes it possible to estimate an activation volume and a barrier energy. The activation volume corresponds to a cube of 5 nm sides. This volume is much smaller than that of the cells bordered by the microtwins (40 nm-thick squares with 70 nm sides). It is also small relative to the volume of microtwins that make up the barrier. Hence we must consider the possibility that the barrier release occurs *via* a mechanism of localised **nucleation**.

These highly novel results[1] have made it possible to demonstrate the existence of Barkhausen jumps, study a magnetic domain wall propagation mechanism and link it to the microstructure of the material used. This work is necessary in order to define the physical framework in which the mechanisms

(1) J.-P. Attané *et al.* Phys. Rev. Lett. **96**, 147204 (2006).

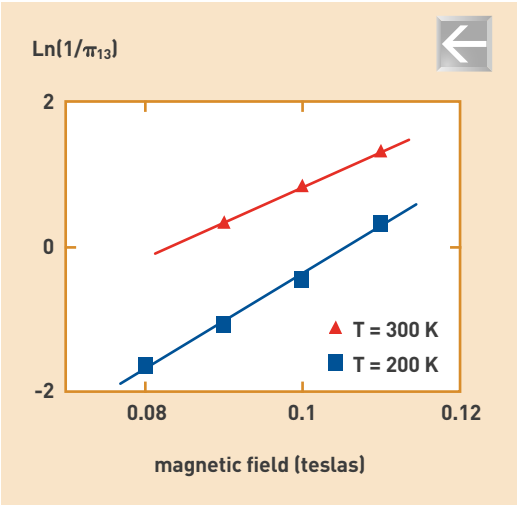

Figure 3.
Frequency against field at different temperatures (log scale). Lines are linear regressions corresponding to the thermal activation law.

of the magnetisation dynamics involve fluctuations and defects.

Numerical simulation of the interaction between magnetic domain walls and microtwins

To interpret these results, the team conducted a numerical study of the interaction of magnetic domain walls with microtwins observed experimentally. As they are atomic lattice defects, microtwins have to be described at the atomic level. A code for minimising magnetic energy based on atomic spins in the Heisenberg model(2) was developed for this purpose. This atomic description makes it possible to make a precise simulation of the interaction between crystalline structure and magnetic configuration. It is a computation of the dipole term involving all the spin pairs and so restricts the size of the systems studied to a few nanometres. To be able to address larger-sized systems, a rapid multipole method for dipolar interaction was adapted. This method, based on grouping the magnetisation in multipole developments, uses a structure that ranks the distribution of the spins to calculate the dipolar term in a linear time in relation to the number of sites (the *n*-order method).

It offers the advantage of providing an efficient description of uneven spin distributions and, in thin layers, of yielding walls separating magnetic domains that have the form of Bloch walls surface-modified by what are called *Néel caps*. Néel caps allow a better closure of the field lines. Under the action of a magnetic field, the Bloch wall is propagated in the thin layer and is pinned in the microtwin. The structure of the wall is completely modified in this defect, the rotation of the magnetisation occurring entirely in the plane of the figure (Figure 4). If a sufficiently strong magnetic field is applied, the wall is 'depinned' and recovers its Bloch structure.

The study of the energy profile according to the position of the wall pinned in the defects was conducted by maintaining the z-axis magnetisation constant during the minimisation, which sets the position of the wall. This made it possible to demonstrate a potential well asymmetry for the wall in the microtwin(3). The form of the potential well does not depend solely on the atomic structure of the defect, but is also linked to the direction of wall propagation before pinning. This asymmetry is seen in the depinning fields, whose values can differ by as much as 25%.

The role of magnetic domain walls in inter-electrode coupling

Ferromagnetic materials are used more and more for sophisticated stacking to make storage elements and sensors. The different layers can then influence each other via the **leakage flux**. In the case of materials with perpendicular magnetisation referred to above, this flux is maximal above the magnetic walls. For example, in the FePt/MgO/FePt trilayers used in magnetic tunnel junctions, the two ferromagnetic **electrodes** are separated by a few **atomic** layers. One of the electrodes, chosen as a reference, must have a set magnetisation. It is therefore designed to present a high reversal field. The second layer, called the '**soft**' layer, serves to store information. Its reversal field is weaker, because its magnetisation has to be reversed (Figure 5).

However, on reversal, one or more magnetic domain walls propagate in this layer. After a large number of reversal cycles, the leakage flux can end up reversing the **hard** layer where its defects lower the reversal field. Thus, after a large number of cycles, the hard layer may become strongly demagnetised. This can be observed by atomic force microscopy. It is therefore important to study the defects present in this type of layer and the interaction between these defects and the leakage flux generated by wall movement.

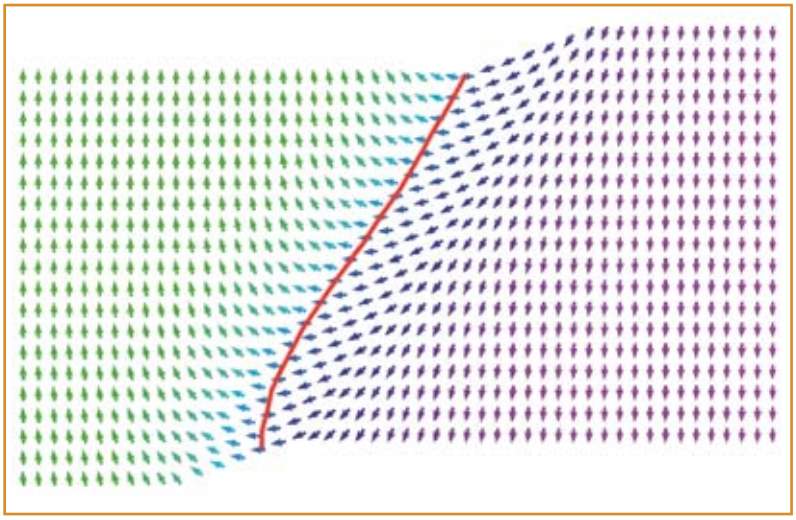

Figure 4.
Cross section of the simulated magnetic configuration of a magnetic wall pinned in the microtwin (the line indicates the centre of the wall).

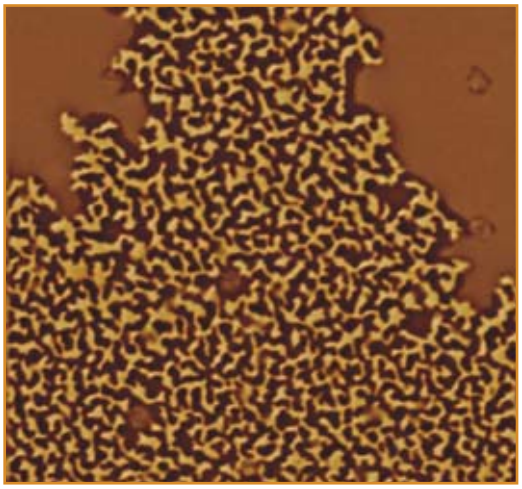

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Figure 5.
Magnetic force microscopy image (10 µm × 10 µm) of a FePt/MgO/FePt magnetic tunnel junction. The magnetic domains of the hard layer grow in a compact manner.

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(2) The Heisenberg model considers atomic spins as electrostatic and magnetic potentials that can be oriented in space with classical effective interactions between them.

(3) T. Jourdan *et al.*, Phys. Rev. B **75**, 094422 (2007).

Magnetic imaging in transmission electron microscopy

Imaging methods that enable us to approach the magnetic structure of materials at the nanometre scale are now providing researchers with fully-fledged nanolaboratories.

Ch. Morel/CEA

The Titan transmission electron microscope installed at CEA Grenoble boasts a holographic mode.

In research on magnetic materials for applications such as high density storage or **spin electronics**, the size of **magnetic domains** has reached the **nanometric** scale. Acquiring better knowledge of domain size, of how induction is distributed inside these domains and what types of **walls** separate them sets challenging aims. Accordingly, methods that make it possible to image magnetic structure and obtain quantitative information with a **spatial resolution** in the nanometre range have become of prime importance. The transmission electron microscope (TEM) has always been first-choice tool for imaging structures at the **atomic** scale and extracting chemical information(1). As a probe, this device uses a beam of **electrons** transmitted through the sample. The electrons are charged particles and so are sensitive to the **magnetic field** present. The first TEM images of magnetic domains were obtained in the sixties. The image in a conventional TEM was simply defocused, and the fringes located on the magnetic domain walls were visualised.

Origin of magnetic contrast

Classical theory can be used to obtain a simple description of magnetic contrast. A charged particle moving in a magnetic field undergoes the **Lorentz force**, which is proportional to its charge, its velocity and the field strength, in a direction perpendicular to the particle's vector and the field. The effect of this force is that the electrons are deflected as they travel through the sample by the field created by its magnetisation. This magnetic imaging technique is called *Lorentz imaging*. The angle of deflection is a few hundredths of a degree, considerably smaller than the diffraction angle of Bragg peaks(2) (at around a degree). It depends on both the field and the thickness of the zone examined. The technique is sensitive to planar magnetisation (perpendicular to the electron beam). In the case of a sample that possesses only one domain – a single axis of magnetisation – no contrast is obser-

(1) see *Clefs CEA* n° 52, The nanoworld, from the laboratory to the field.

(2) Bragg peaks: intensity peaks that appear by diffraction when electromagnetic radiation passes through a crystal.

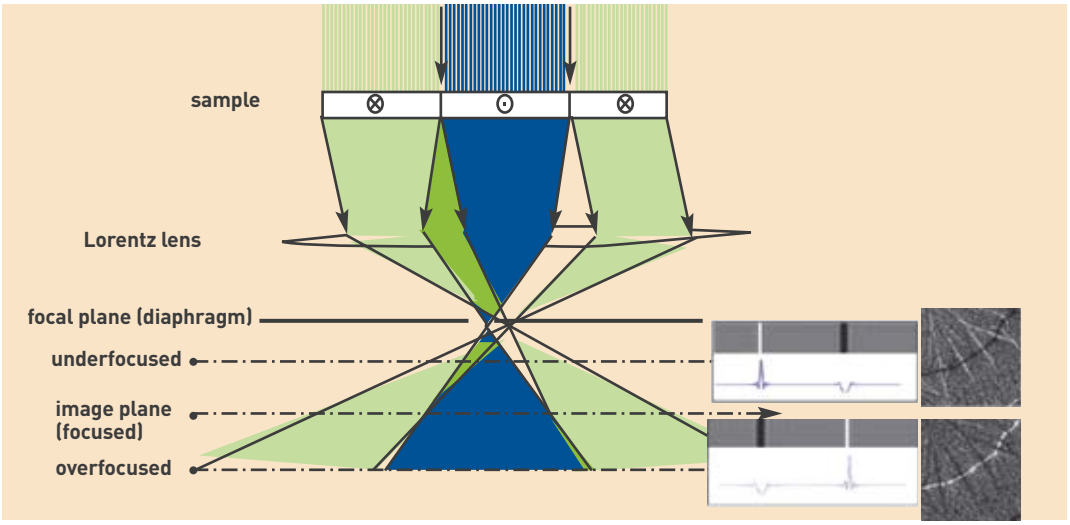

Figure 1. Deflection of electrons caused by magnetisation in planar domains. Fresnel fringes obtained by defocusing the image. Bottom right, examples of over- and underfocused Fresnel images: black and white fringes show walls between magnetic domains.

ved. Conversely, two magnetic domains magnetised in opposite directions deflect the electrons at opposite angles. In a simplified representation of the electron path (Figure 1), we obtain zones where the beams overlap (convergence, high intensity) or where there are few electrons (divergence, low intensity). The effects are localised on the walls separating the magnetic domains. To visualise these *lines*, the lens used for the imaging has to be defocused. Over- and underfocused images reveal domain walls with inverted contrast: these are called *Fresnel contrast* by analogy with interference fringes produced in optics by **photons**. In the focal plane of the lens, the deflection of the beams in two opposite directions when they leave the sample results in two spots. The insertion of a small diaphragm at this point lets us select one or the other set and thereby image the magnetic domains separately. This is the *Foucault imaging* technique.

This technique, through the interaction of the electrons with the magnetic field, provides information not only on the magnetisation in the sample, but also on the **leakage flux** outside it. In nanomagnetism, where the domain size is increasingly small, the challenge is to achieve a spatial resolution high enough to yield magnetic information. In classical TEM, the sample is held in the magnetic field of the lens used to form the image, which disturbs its magnetisation. To obtain images bearing magnetic information, another dedicated lens is needed, called a *Lorentz lens*. It is located underneath the sample and so does not disturb the magnetic configuration of the sample being examined. Only a few microscopes are equipped with this lens, which has a spatial resolution of about a nanometre. This high-performance technique is therefore not yet very widely available.

TEM, a nanolaboratory for magnetism

The information given by a single image is not sufficient to elucidate the configuration of the domains and their walls or the dynamics of these domains under the effect of an outside stimulus. In TEM, it is fortunately possible *in situ* to apply magnetic fields of the order of a **tesla** perpendicularly to the sample, and fields of a fraction of a tesla in the plane, by tilting the sample. Heated or cooled sample holders allow thermal studies, e.g. close to the **Curie temperature**. The engineering of new sample holders permits a large number of *in situ* studies, and TEM has become a nanolaboratory. Dynamic measurements can be made, but only at time scales greater than half a second, because of the limits imposed by the image acquisition rate.

Mapping magnetic distribution

The Fresnel or Foucault contrasts can be used to image domains and their walls. Improvements have been made not only to the quantification of information, to the image resolution and to the map-

Mapping magnetisation using Foucault contrast... 1

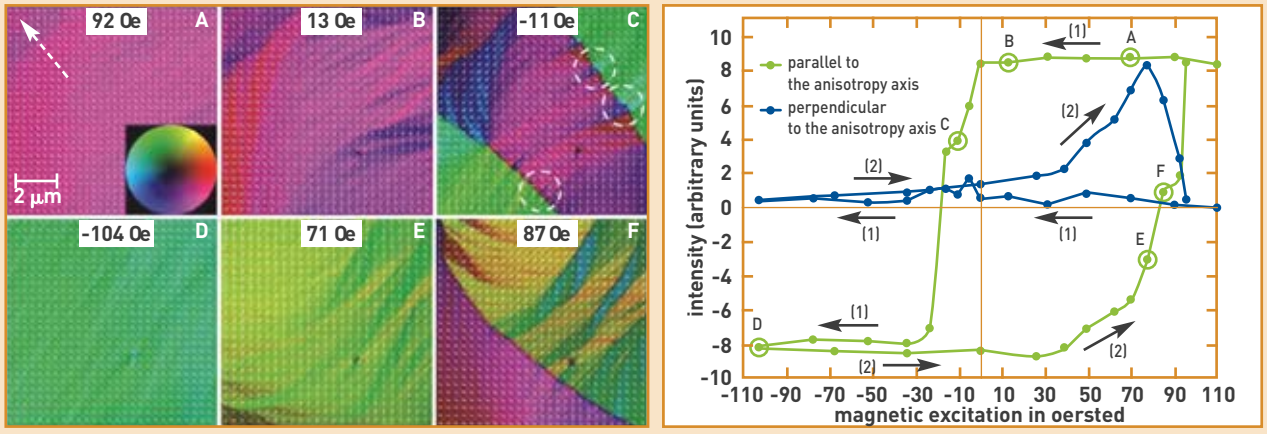

Figure.

The series of magnetic maps shown below (Figure), obtained by the reconstruction method using Foucault images on a $Co_{35}Fe_{65}$ (70 nm)/NiMn (50 nm) bilayer illustrates the reversal of **magnetisation** in a sample with planar magnetisation, an effect of exchange coupling in the CoFe/MnFe system. The **ferromagnetism** / **antiferromagnetism** coupling between these two layers creates an exchange **anisotropy** in the direction marked by the white arrow in Image A. To study the processes of ferromagnetic layer reversal with planar magnetisation, a magnetic field was applied *in situ* parallel to the direction of anisotropy. The value of this field is given for each image, starting in the first (A) from a saturation state. The colour wheel makes it possible represent the directions and amplitudes of the reconstructed magnetisation. Two **hysteresis** loops were calculated from these images by projecting the magnetisation in the directions parallel and perpendicular to the anisotropy axis. The value of the exchange field obtained was in very close agreement with the measurements made *ex situ* (30 **Oe**). This study demonstrates the existence of two magnetic reversal processes.

For a decreasing field following pathway (1) (Images A, B, C and D), the reversal occurs by **nucleation** and **wall** propagation: the perpendicular component of the magnetisation remains nil, which means there is no rotation of the magnetisation.

For an increasing field following pathway (2) (Images D, E and F), the reversal of the ferromagnetic layer occurs by coherent rotation – clearly visible on Image E, where the perpendicular component is non-nil – followed by the creation of a wall (F) and saturation.

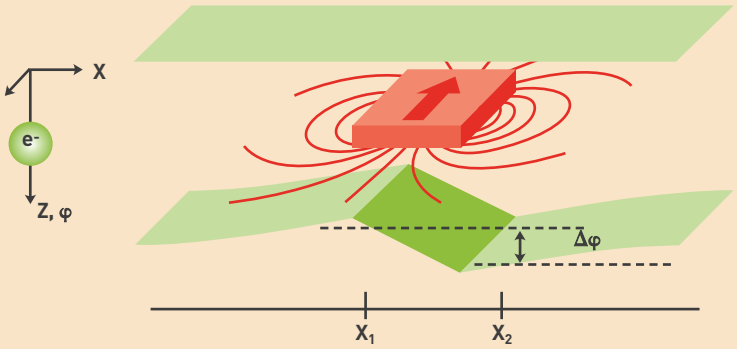

Figure 2.
Dephasing of the planar electron wave by a magnetic field (Dϕ (x)= ϕ(x1,y) - ϕ(x2,y) ~ Cste ∫x B(x) dx).

ping of the distribution of magnetic induction, but also to the functionalisation of the objects observed. The mapping can be achieved by various techniques.

The first method uses series of Foucault images acquired by moving the diaphragm in the focal plane, and so scanning the angular information in the *x* and *y* directions. Processing these images gives images proportional to B_x and B_y, and so maps the distribution of the magnetisation (box 1).

Electronic holography and focal-series reconstruction

To gain a fuller understanding of the processes observed under the microscope and simulate them more accurately, wave mechanics becomes necessary. The beam of electrons is no longer considered as a set of particles, but as an electron wave, described by an amplitude and a phase. The magnetic sample then becomes a 'phase object' - it dephases the incident electronic wave. This dephasing is linked to the **electrostatic** and magnetic vector potentials (Figure 2). In a TEM, two methods can be used to deduce this 'magnetic' dephasing information: electronic holography(3) and focal series reconstruction. Electron holography was proposed theoretically by Dennis Gabor in the fifties, initially to improve the spatial resolution of TEM. This interference technique needs a source of highly coherent electrons and a 'biprism', which splits the beam into two (a reference wave and a wave transmitted in the sample). It was not until the seventies, with improved field-emission electron guns, that the first experimental results were obtained. The second method of phase reconstruction is easier to use. It is based on the solution of a mathematical equation (the transport of intensity equation) and only requires the acquisition of three Fresnel contrast images (overfocused, focused and underfocused). It is thereby possible to map the dephasing of the electron wave and deduce the distribution of the magnetic induction (box 2).

These imaging techniques are becoming essential tools for the understanding of magnetic configurations at scales approaching a few nanometres. Recent progress in electron optics for microscopy and numerical methods of phase reconstruction make it possible to map magnetism and also to quantify the information. A TEM is now considered as a nanolaboratory where *in situ* experiments can be conducted to follow the dynamics of processes involving domain wall movement, rotation of magnetisation and coupling between layers and nanostructures.

... and focal-series reconstruction 2

An example of focal series reconstruction is given here (Figure) for an **epitaxial** bilayer presenting a magnetic **anisotropy** perpendicular to the surface. The study of this bilayer in two directions (edge view and top view) enables us to visualise and analyse the distribution of the magnetic **induction** in the **walls**. Mapping by reconstruction is achieved by solving the transport of intensity equation (TIE). The sample is composed of an iron/palladium (FePd) alloy with perpendicular anisotropy, the magnetic distribution of which has been simulated (a). It is structured in **magnetic domains** pointing up and down and separated by walls whose main component is planar. The map obtained from the top view (b) shows domains organised in interlaced ribbons in which the different zones due to the domains or walls are marked by black and white arrows, respectively. The edge view (c) shows the two types of domain for the B_x component by black and white contrasts, together with the closing domains in the lower layer (component B_y) and in vacuum (colour mapping).

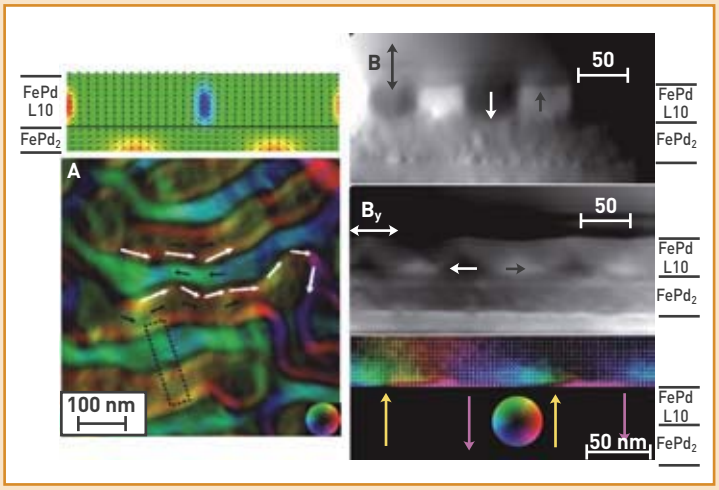

Figure. a) Side view in magnetic simulation. b) Mapping (top view) of magnetic induction. The arrows show the directions of the planar component. c) Side view with reconstruction of components B_x and B_y and highlighting leakage flux outside the sample (at the surface).

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(3) Electronic holography: technique based on the formation of an interference pattern, or hologramme, which makes it possible to determine the phase of the electron beam that has passed through a sample examined under a transmission electron microscope. This information is lost in other techniques. Since the phase is sensitive to both the component of the magnetic induction in the plane and the electrostatic potential in the material. The hologramme gives quantitative information on the spatial distribution of the magnetic and electrostatic field in the sample, with nanometric precision.

GeMn, a magnetic semiconductor

Among the magnetic semiconductors of potential use in spintronics, manganese-doped germanium offers clear advantages.

Today, microelectronics is almost entirely based on the transport of current and on the transport and storage of charges. However, **charge carriers**, *i.e.* **electrons** and **holes**, also possess **spin**. Means to control the spin of the charges carrying information would make it possible to considerably reduce their numbers and also add new functions to existing devices. This is precisely the challenge of **spintronics**, in which spins are injected and manipulated in **semiconductors** (see above). When this brand-new branch of microelectronics appeared in the nineties, the very first idea was to place a semiconductor in contact with a **ferromagnetic** metal to produce a metal/semiconductor/metal structure. Theoretically, it seemed that spin **polarisation** could be controlled simply by using two layers of ferromagnetic metal as spin injector and collector and setting the orientation of these spins by applying an electric field to the semiconductor. Unfortunately, it didn't work! The difference in **resistance** between the semiconductor and the ferromagnetic metal was such that the electrons completely lost their spin polarisation.

One possible solution was a magnetic semiconductor. Here the aim was to dope a semiconductor with **atoms** to supply localised spins and spin-polarise the charge carriers. The very first magnetic semiconductor was made by diluting tiny quantities of manganese (Mn) in indium arsenide (InAs). Today, ferromagnetic properties have been observed in many semiconductors. These are called diluted magnetic semiconductors (DMSs) and are doped with atoms of **transition metals** (*e.g.* manganese, iron, cobalt, nickel or chromium) or **rare earths** elements (europium, gadolinium or erbium). However, in almost all cases their ferromagnetic properties appear only at low temperatures.

A CEA team (Institute for Nanoscience and Cryogenics/SP2M) at Grenoble has been working in this area for some years. A manganese-doped semiconductor that remains ferromagnetic beyond ambient temperature was made there for the first time in 2006(1). It was based on germanium containing 6% manganese ($Ge_{0.94}Mn_{0.06}$). Specifically, it was a very thin layer (80 nm) of germanium, doped with manganese and deposited on a germanium substrate. The technique used, **molecular-beam epitaxy**, consisted in evaporating the two materials on a substrate heated to the appropriate temperature, called the growth temperature. The ferromagnetic properties of these layers are very sensitive to both the manganese concentration and the *growth temperature*. Other teams also working on this material have reported ferromagnetic properties in germanium doped with manganese, but its ferromagnetic properties disappeared at temperatures above 200 **K**. In the GeMn layers produced in Grenoble, the manganese is not dispersed evenly. If this material is produced at the right growth temperature, very small, very manganese-rich zones are formed that are visible on cross section and in-plane electron microscope images (Figure 1). These are nanocolumns with diameters close to 3 nm, which cross the layer along its growth direction. Chemical analysis has shown that the manganese concentration in these nanocolumns is about 30%, while between them, in the germanium matrix, it is less than 1%. These nanocolumns are still ferromagnetic at 400 K (Figure 2). In addition, the CEA team has made measurements of electric transport in the plane of the layers. The charge carriers (here holes, because the manganese is an **acceptor** in the germanium) circulate in the manganese-depleted matrix and in the columns. The researchers used Extraordinary Hall effect measurements to demonstrate that the charge carriers were sensitive to the magnetisation of the nanocolumns. This means that the holes are spin-polarised in the GeMn layers. This property is extremely important for the use of this material as an injector or collector of spins in non-magnetic semiconductors. Also, if the holes are responsible for the ferromagnetic coupling between atoms of manganese, the application of an electric field should make it possible to control the magnetic properties of GeMn layers. Such control is targeted in many applications.

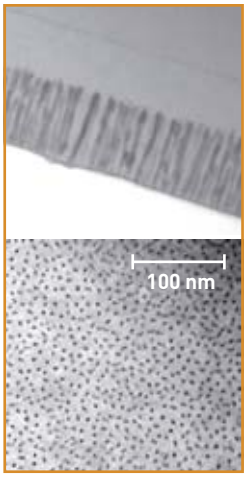

Figure 1.
Transmission electron microscopy images of a GeMn film. Left: cross section. The dark elongated regions correspond to Mn-enriched nanocolumns. Right: planar view. Dark spots correspond to nanocolumns.

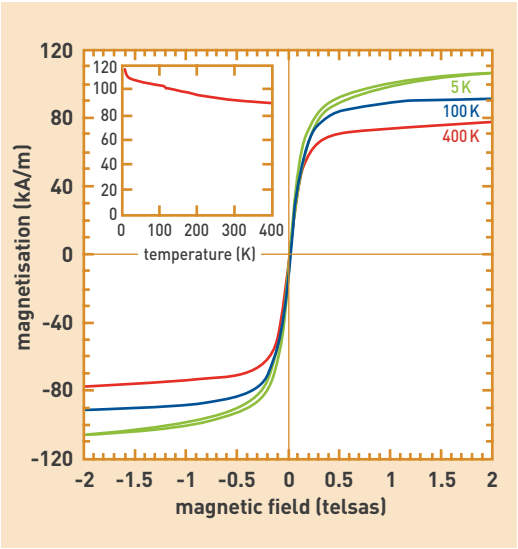

Figure 2.
Magnetisation curves for a layer of $Ge_{0.94}Mn_{0.06}$ made at 130°C measured at 5 K, 100 K and 400 K in a SQUID magnetometer. Also shown is the saturation magnetisation of the sample measured at 2 teslas. The magnetic signal is still strong at 400 K.

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(1) M. Jamet *et al.*, Nature Mater. **5**, 653 (2006)

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.

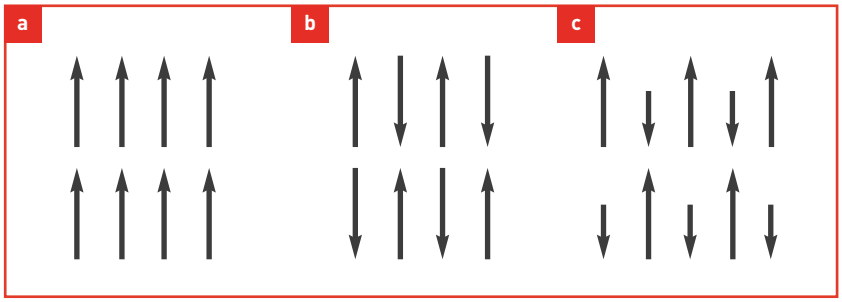


Figure E1.
Intrinsic magnetic dipole moments have parallel alignment in ferromagnetic materials (a), anti-parallel alignment but zero magnetisation in antiferromagnetic materials (b), and anti-parallel alignment with unequal moments in ferrimagnetic materials (c).

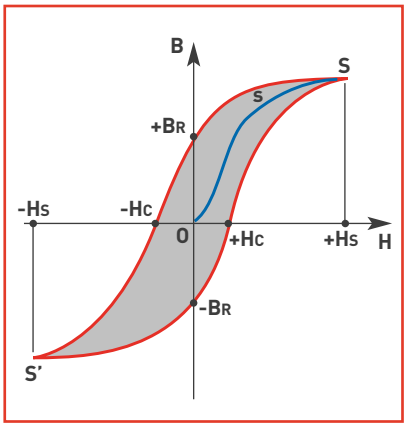


Figure E2.
The induction B of a magnetic material by a coil is not proportional to its magnetic excitation (*field H*). While the initial magnetisation forms an OsS-type curve, shown in blue in the figure, it reaches saturation at point s. Only a partial induction is retained if the field approaches 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

Stoiber Productions, München

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).

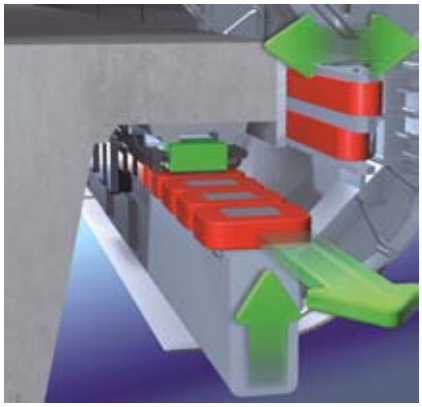
2. **Paramagnetic** materials behave in a similar way to ferromagnetic materials, although to a far lesser degree (they have a positive but very weak magnetic susceptibility of around 10^{-3}). Each atom in a paramagnetic material has a non-zero magnetic moment. In the presence of an external magnetic 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.