The physics of magnetic nano-objects and nano-systems

Material scientists and physicists are very much interested by nano-objects, such as nano-particles, quantum wires and, ultra-thin layers. Because of their small size and reduced dimensions, these systems possess unexpected properties that could be exploited for clever applications. This set of articles is devoted to magnetic nano-objects and their physical properties.

Magnetic nano-objects and nano-systems have been the subject of intense research over the last 20 years. This has been possible thanks to recent experimental advances that have provided modern and efficient tools to physicists and chemists. These tools have been important in three important fields, which are:

1. The synthesis of nanometre-sized objects: we are now able to control the size and the shape of these systems with great precision. The spatial organization in a group of several nanoparticles has also been studied, as well as the functionalization of nanoparticles.

2. The development of new methods, for analyzing atomic structure (with electron and near-field microscopes) and physical properties of nanometre-size systems. Novel methods have, in particular, been developed, which give access to the magnetic properties of individual nanoparticles and to the magnetic interaction between several particles.

3. Calculating numerical solutions of equations that govern the properties of systems containing several hundreds of atoms. Supercomputers have been used to calculate the modification of the wave functions and of the magnetic moments induced by reduced dimensions and by the presence of surfaces and interfaces. The development of magnetic nanomaterials has also been motivated by the important industrial applications offered by these materials. Applications include devices for magnetic recording, high-density magnetic media, ultra-thin magnetic layers for spintronics, magnetic sensors, and high performance permanent magnets. Magnetic particles are also studied for their application in the biomedical field, in particular for the treatment of cancer.

Dynamic research

Approximately 200-300 physicists and chemists work on magnetic nano-objects and nanomaterials in French labs. They usually meet up at the “colloque Louis Néel”, which takes place every 18 months. Teams from Toulouse organized this meeting in 2008. In Toulouse, the magnetic nano-objects and nano-systems are mainly synthesized and studied at the “Laboratoire de chimie de coordination” (LCC, CNRS lab) where spin transitions are studied in molecular compounds; at the “Laboratoire de physique et chimie des nano-objets” (LPCNO joint UPS/CNRS/INSA lab) where magnetic nanoparticles are synthesized and studied by magnetometry, micromagnetic simulations, magnetotransport measurements and hyperthermia; and at the “Centre d’élaboration des matériaux et d’études structurales” (CEMES CNRS lab) where ultrathin magnetic layers are made and characterized by transmission electron microscopy and by ab-initio calculations; and at the “Laboratoire de nanomagnétisme pour l’hyperfréquence” (LNMH joint CNRS/ONERA lab) where the microwave properties of magnetic nanomaterials are studied. These labs are involved in several European projects, including SA-NANO and NAMDIATREAM and in several projects funded by the French agency for scientific research ANR (the projects MAGAFIL, BATMAG, SPINCHAT, DICROMET).

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A device to characterize nano-magnets: the nanoSQUID

Nanomagnetism could not develop without a tool to measure magneto-transport properties of single nano-objects. It is now done thanks to a smart device based on a single carbon nanotube.

Many nano-magnets have been synthesized over the last few years. One can cite, for instance, magnetic nanoparticles or high-spin molecules. However, only their average, bulk properties could be measured due to the lack of a suitably scaled down device that can measure nanosized magnetic fluxes. The SQUID (Superconducting Quantum Interference Device), which is actually a very sensitive magnetometer commonly used in various fields, cannot characterize materials other than at the macroscopic level. To tentatively overcome this limitation, a miniaturized version of it was proposed few years ago by Wolfgang Wernsdorfer of the Institut Néel, Grenoble, which remarkably improved the sensitivity of the measurement. However, it still did not allow to access magnetisation levels below 1700 µB.

Technological exploit

Collaboration between CEMES and the Institut Néel (Grenoble, France), combining their expertises in making carbon nanotube-based devices and magnetism respectively, has resulted in the development of a nanoSQUID. The idea was to use a single carbon nanotube as the active component of the sensor to allow optimized coupling with the nano-magnet to study, thanks to their similar size ranges. The device mimics regular SQUID geometry, that is, a superconducting loop, restricted in two places by tiny junctions that are magneto-sensitive (the so-called Josephson junctions).

Incoming electrons separate and pass through both junctions and then interfere when recombining at the exiting contact of the loop. The features of the resulting interference current are extremely sensitive to the magnetic flux inside the loop, and hence to the presence of a nanosized magnetic material. The technological exploit involves using a single single-wall carbon nanotube (~1.4 nm in diameter) contacted by three superconducting, nanosized, bimetallic pads to play the role of the Josephson junctions. One example of such a device, fabricated thanks to the nanolithography facilities at the RTB Centre hosted by LAAS (Laboratoire d’Analyse et d’Architecture des Systèmes, Toulouse) is shown in figure b.

Very low temperature measurements (35 mK) have revealed a strong, periodic modulation of the critical current when a magnetic field is applied perpendicular to the loop, with the periodicity corresponding to a quantum of flux (figure c). This is a typical feature of a SQUID. However, it is different in that the sensitivity is increased by a factor of 10E12 with respect to a regular SQUID. Hence, the nanoSQUID performances were calculated to be high enough to detect the reversal of the magnetization direction for a single high-spin molecule previously deposited onto the nanotube.

Molecular magnets

This result opens the way to advanced studies in the field of molecular magnetism. Indeed, molecular magnets are likely to be used for fabricating a spin qubit for quantum information or for storing information at the scale of a single spin. Such studies require operation at very low temperatures. Using the nanoSQUID to systematically investigate various nano-magnets also means developing methods to deposit nanosized objects at the right place on the device, which is another challenge.

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Cobalt: a ferromagnetic polymorph metal

Cobalt is a metal of many virtues. Easily magnetized, it can be synthesized as nanoparticles with varying shapes. It can have applications in medicine as well as in electronics.

Magnetic nano-objects have become very popular in recent years and can be used in domains as diverse as medicine and magnetic recording devices. However, various applications need nanoparticles with well-controlled size and shape, since their magnetic properties strongly depend on these characteristics. Cobalt is ideal in this respect because it is a ferromagnetic metal with a high magnetization and can crystallize in two phases, with a cubic and hexagonal structures that are very close in energy but which have very different magnetocrystalline anisotropies. The Nanostructures and Organometallic Chemistry groups of the Laboratoire de physique et chimie de nano-objets (LPCNO) and the Laboratoire de chimie de coordination (LCC) specializes in the liquid-phase synthesis of magnetic nanoparticles using two complementary methods: organometallic chemistry and reduction in liquid polyol.

Diabolos and dumbbells

When applied to cobalt, these two methods have allowed, by modulating the rate of metal formation and/or by using surfactants in the reaction medium, the synthesis of nanoparticles with various shapes: cubic spheres or platelets; and hexagonal nanorods and wires. The polymorphism of cobalt offers an additional degree of freedom to the liquid-phase growth and also permits the formation of particles with complex forms: diabolos and dumbbells, which result from two successive growth steps of the hexagonal phase; multipods and “sea urchins” obtained by the growth of several “arms” of hexagonal structure from a cubic structure seed.

All these originally shaped objects correspond to unprecedented magnetic configurations that can be imaged by electronic holography. Concerning applications during the last few years, the emphasis has been put on the synthesis of cobalt nanorods with a diameter inferior than 10 nm and an aspect ratio superior to 10. These anisotropic nanoparticles exhibit remarkable properties as permanent nano-magnets with coercive fields of several thousand Oersted at room temperature, as a result of their elongated form and their nanosize. They open the way to new perspectives in the domain of “hard” magnetic materials. These nanorods could be part of permanent magnets fabricated by oriented densification of these anisotropic nanoparticles and show good performance at high temperatures (one objective of the MAGAFIL ANR project). Another application is the realization of ultra-high density magnetic recording devices in the form of a dense network of nanoparticles. The project BATMAG involving the LPCNO and CEMES aims to develop “hard discs” consisting of cobalt nanorods perpendicularly organized on a flat substrate. For these two applications, cobalt with a hexagonal structure has the advantage of possessing a high magnetocrystalline anisotropy, which reinforces the shape anisotropy.

Gold tips

Cobalt particles can also serve as a base for other more complex nanoparticles combining several different materials. For example, cobalt nanorods with gold tips and nanorods of cadmium selenide (CdSe) with cobalt tips, either spherical or elongated, have been synthesized in the LPCNO in the framework of the European project SA-NANO. These multifunctional nanoparticles are novel in that they combine the individual magnetic properties of cobalt and the optical properties of gold or CdSe nanoparticles. They might be used in medical applications. In the framework of the European project NAMDIATREAM we are synthesizing cobalt nanoparticles covered by a gold layer with the objective of using these optically active nanometric compasses for detecting cancer cells in vitro. The growth of a second metal on the cobalt nanoparticles is a challenge for chemists. Understanding topologically controlled growth, as an alloy, as a core-shell or even a hybrid dimer is the focus of the French-Spanish project INTERREG METNANO.

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Because of their small size, nanoparticles are able to selectively act at the scale of molecules, proteins, or cells. This advantage could be crucial in medicine. Indeed, once correctly functionalized, nanoparticles can be used to sort or detect biomolecules, transport active molecules to a targeted area, act as contrast agents for magnetic resonance imaging (MRI) or as a local heat source in hyperthermia treatment.

**Hyperthermia**

In oncology, hyperthermia consists of increasing the temperature of tumour cells to above 42°C to make them more sensitive to chemo- or radiotherapy. Magnetic nanoparticles are already used in such techniques, but they were usually directly injected inside the tumour since a high concentration is required for sufficient heating. The patient is then placed into a safe high-frequency magnetic field (100kHz, 20 mT) that increases the temperature of the nanoparticles. Surgeons at the Charity Hospital, Berlin, treat some prostate and brain cancers in this way and have achieved good results. The nanoparticles they use are composed of iron oxides with a large size distribution. As a consequence, the heating properties of these particles are not optimized.

One of the issues in this field is to succeed in efficiently guiding nanoparticles toward the cancer cells in blood rather than by injections into the tumour itself. This would avoid metastasis and would also allow treatment of deep, small or non-detected tumours. However, for such a method to work, scientists need to compensate for the eventual loss of nanoparticles when they are strongly heated. This requires high magnetization materials. The magnetic properties of the nanoparticles also needs to be finely tuned by controlling their size, shape and surface state.

**Nano-oncology**

The “Nano-Oncology” project is funded by the Midi-Pyrénées region and the InNaBioSanté Foundation and involves physicists (LPCNO), chemists (LCC, CIRIMAT and LPCNO) and biophysicists from the “Imagerie cérébrale et handicaps neurologiques” (INSERM) laboratory, biologists from the “Oncogénèse, Signaletisation et Innovation thérapeutique” group (U563, INSERM) and radiotherapists from the “Claudius Régau Institute”. All these scientists work together to evaluate and optimize hyperthermia efficiency of nano-objects composed of a non-oxidized iron core. The objective was to demonstrate the technique on mice undergoing a coupled radiotherapy-hyperthermia treatment.

**Heating power**

During this project, LPCNO chemists succeeded in synthesizing iron nanoparticles with various shapes and diameters – for example, spherical or cubic particles with diameters ranging from 1.5 to 90 nm. They display a magnetization that is more than two times higher than that of particles composed of iron oxides. Heating power measurements on such objects confirm the expected good properties. However, there are still many challenges to overcome before such objects could eventually be used in oncology treatments. Indeed, they first need to be protected from oxidation by a biocompatible organic or inorganic shell. Then, they need to be dispersed and form a stable colloidal solution in a physiological medium. Finally, once bio-functionalized, their toxicity needs to be evaluated. These different steps will make up the future of the Nano-Oncology project. In any case, by pursuing this goal, chemists and physicists are working together to better understand the synthesis and dynamic magnetic properties of complex magnetic nano-objects.

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Measuring local magnetic properties with a transmission electron microscope

Do you remember the school experiment consisting of depositing iron filings on a sheet of paper placed over a magnet to observe magnetic field lines? This was proposed by Pierre Pèlerin de Maricourt around 1270 and was part of the pioneering work on magnetism that was intensively studied from the end of the 18th century. New issues arise as the object size shrinks, so how is it possible to observe magnetic field lines produced by a magnet far smaller than iron filings? How can we measure magnetic properties of devices whose size does not exceed tens of nanometres?

Holography
One technique that combines good spatial resolution and high sensitivity to magnetism is electron holography. This method relies on measuring the phase shift encountered by an electron beam when it interacts with a magnetic material. In this case, the phase shift is directly linked to the sample thickness and magnetic induction. Measuring this phase shift consists of splitting the beam into two parts, one that interacts with the object and the other acting as a reference. When these two two beams are combined, interference fringes are observed (the hologram) from which the induction is measured. Obtaining holograms in this way is simple compared to the treatments needed to isolate the magnetic contribution from the phase shift, to measure local variation in the induction and to interpret the images. It is also important to note that the magnetic contribution observed in the hologram is a two dimensional projection of a three dimensional magnetic configuration.

Iron nanocubes
In the CEMES and LPCNO labs, researchers use electron holography to study the magnetic configurations of various nanomaterials, nanoparticles or thin films. We present some holograms obtained on 30 nm iron nanocubes that could provide information on the magnetic configuration of isolated or interacting objects. The figure shows a map of the magnetic induction produced by two iron nanocubes interacting through dipolar coupling and acting like a unique magnet. Electron holography is a powerful tool to measure locally not only the magnetic induction but also the magnetic interactions between objects.

Another way of measuring local magnetic properties is being developed in the CEMES lab: the EMCD (Energy-loss Magnetic Chiral Dichroism). This method, similar to the one that uses polarized synchrotron radiation for twenty years now, uses a non-polarized electron beam to measure the magnetic moment with a spatial resolution in the 10 nm range. It is based on electron energy-loss spectroscopy (EELS) which measures the number of electrons that have lost a certain amount of energy when interacting with the sample. The EEL spectrum is the signature of the electronic structure of the observed material and several spectra need to be combined to measure the magnetic moment.

Electron holography and the EMCD techniques are able to locally measure the magnetic properties of nanomaterials and therefore to study the influence of particle size, environment or local strain on the magnetic properties. The results from this work could be important for spintronic devices or for magnetic recording applications.

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Magnetic nanomaterials for spintronic devices

Electronics will benefit from recent research on spintronics. This discipline takes advantage of an electron’s spin, with the aim of building new nanodevices.

Magnetic nano-systems have been intensively studied over the last 20 years and are now used in a variety of microelectronic devices. They can, for instance, be found in read heads for hard disk drives. Magnetic nano-objects will soon be used in magnetic random access memories (MRAM), which will allow computers to be switched on instantaneously. Other systems have been studied in laboratories during recent years, like the spin-transistors - analogous to classical transistors used in microelectronics, but in which the configuration of the device is controlled by an electron’s spin. All these systems form the family of spintronic devices.

Spintronics

Two different spintronic devices, the magnetic tunnel junction and the spin valve, are already being used. These devices use magnetic layers (the magnetic electrodes) separated by a non-magnetic spacer with a thickness of a few nanometres. We have obtained a spin valve when the spacer is metallic, and a magnetic tunnel junction when the spacer is an insulator. In both cases, the electric resistance of the stacking depends on the relative orientation of the magnetizations of the electrodes. This is the magnetoresistance effect.

Spin valves are used in magnetic sensors. Magnetic tunnel junctions form new magnetic memories, which can be used to store binary information. The magnetization of the electrodes can be either parallel or antiparallel. A different value of the electric resistance (high or low) is measured for these two magnetic configurations. These two different values of the resistance correspond to the bits “1” or “0” that can simply be read by measuring the resistance.

Nobel Prize

Albert Fert and Peter Grünberg won the Nobel prize in 2007 for their discovery of the magnetoresistance properties of spin valves. Most spin valves use Fe/Cr/Fe or Co/Cu/Co multilayers. Epitaxial magnetic tunnel junctions using Fe electrodes and a MgO barrier with a thickness of a few nanometres have been widely studied over the last few years. In this case, the electric current which is measured is due to electrons that cross the thin MgO barrier by the tunnelling effect. Electrons in magnetic tunnel junctions therefore behave according to the rules of quantum mechanics.

For several years now, magnetic tunnel junctions have been grown and studied at the Centre d’élaboration de matériaux et d’études structurales (CEMES). We have, for instance, recently studied tunnel junctions in which the Fe electrodes have been replaced by a magnetic alloy like Fe1−xVx. The density of structural defects is lowered at the interface between MgO in this electrode material because the lattice mismatch is smaller with this alloy. For this reason, the magnetoresistance is higher when the Fe electrode is replaced by the alloy. We have also studied magnetic tunnel junctions containing half-metallic magnetic electrodes (that is, with a 100% spin-polarization at the Fermi level). This can be achieved using magnetite Fe3O4 or some complex metallic alloys. We have calculated the electron wave functions for these interesting magnetic tunnel junctions (see figure). We have also designed tunnel junctions using an organic semiconducting material for the insulating barrier.

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Fascinating bi-stable molecules

Spin crossover molecules are fascinating because these so-called bistable molecules can be used for storing and manipulating information. Researchers at the LCC are studying this phenomenon in a pluridisciplinary approach combining chemistry with physics, nanotechnology and theory.

The molecular spin crossover phenomenon, involving thermo-, photo-, magneto- and piezo-chromic properties of a class of transition metal complexes, is of growing importance in the area of functional materials, especially for applications in sensor and display devices and as molecular switches. These complexes have a molecular bistability of high-spin and low-spin electronic configurations. Reversible switching between these two states can be achieved using various physical or chemical stimuli. In particular, we have shown that thetransition can be achieved at room temperature using a short laser pulse or an electric field (see also CNRS press release: (www2.cnrs.fr/presse/communique/695.htm).

Clean rooms
The “Switchable Molecular Materials” group at the LCC focuses its research on better understanding the molecular spin crossover phenomenon as well as on developing related technological applications. In practice, we investigate the bistability of various molecular properties, such as the magnetization, electronic polarizability or optical absorption in these molecular materials. The same methods can be used for investigating any other molecular materials exhibiting phase transitions associated with changes in the electronic structure. The molecular compounds are synthesized as bulk solids or nanomaterials (nanoparticles or thin films). The nanoscale patterning of these materials is done in the clean rooms of the LAAS in Toulouse using electron-beam lithography (www2.cnrs.fr/presse/communique/1152.htm) and emerging “soft-lithographic” methods. The nanomaterials are then studied by different solid state physics spectroscopic methods. For theoretical modelling, we are developing statistical physical approaches. In particular, two-level Ising-like dynamical models are being investigated using either the mean-field approximation or Monte-Carlo methods.

Nano-objs
The molecular origin of the spin crossover phenomenon sets a very low limit for the miniaturization of these materials. Indeed, recently we have been able to synthesize ultra-small (4 nm) spin crossover nanoparticles, which maintain their memory properties around room temperature. At present we are exploring the technological potential of these bistable nano-objects in various fields including high-density information storage, sensors, microelectronics and photonic devices as well as “general public” applications, such as thermochromic coatings and paints.

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