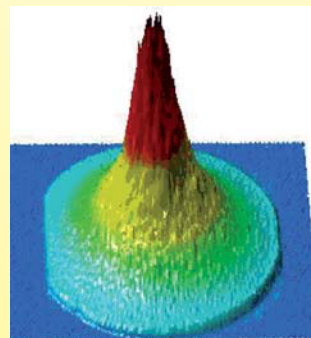
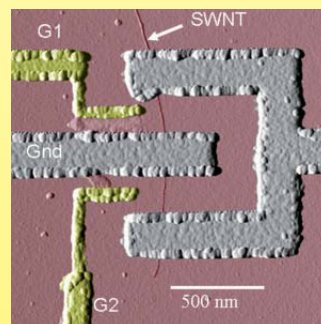


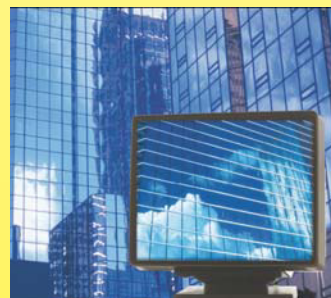
*Bose-Einstein Condensation
in a Solid*



*A superconducting interferometer
using carbon nanotubes*



*When silicon turns into
a superconductor*



**Institut Néel
Highlights
2006**

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The first highlights...

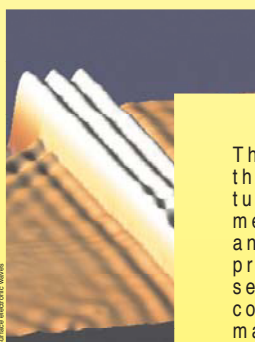
On the occasion of the inauguration of the Néel Institute by Arnold Migus, Director-General of the CNRS, we are pleased to present our first booklet of "Highlights", which will appear twice a year from now on. This first issue shows our Institute's three Departments all involved in a scientific approach flavoured "nano" but anchored in their own core disciplines. It shows too how originality and excellence in research rest on visionary scientific-instrument building and on the making of the "dream-sample".

- *Our physics of the 21st century opens with control of the phase of the electron wavefunction, and of its interferences. The single spin and the single charge make their mark on new phenomena. Photons and schools of electrons unite in the new land of "plasmonics." In the solid state, the Bose Einstein condensate - mythical object of quantum mechanics - comes in from the cold to 20 degrees K, and generates a fruitful international collaboration. Carbon - in the shape of a conducting nanotube joined onto a superconducting loop - makes an interferometric probe so sensitive it should soon measure a single spin.*
- *A single spin is indeed seen in a CdTe quantum dot - identified by six peaks of light intensity - a magnificent fundamental experiment illustrating atomic physics. Carbon again, now unfurls in single sheets felicitously named «graphene», which host a cloud of electrons that are highly mobile in their plane, and move all with one velocity whatever their energy.*
- *Instrumentation at the nano-scale for the world of low temperatures yields nanosquids to map vortices, and attojoule heat sensors to chase them : the magnetic singularities of the superconducting state. At 0.1 degrees above absolute zero, there is still electromagnetic radiation (light) to transport heat between two small islands connected by a superconducting wire.*
- *Our Very Low Temperatures are installed at the heart of Edelweiss (six French labs, two German labs, one Russian lab), a patient hunt for elusive WIMPs (Weakly Interacting Massive Particles) - which must be there in the 23% Dark Matter of the standard cosmological model.*
- *To attach organic nanocrystals to a protein is to flag it with an identity, thanks to the art of the chemist (patent 2007). Magnesium, the photographer's metal of a hundred years ago, now virtuously stores hydrogen, energy source for thermal motors (two patents and tech-transfer to MCP of Romans on Isère).*
- *Frustration, imposed on an array of spins, prevents them pairing up as each pair alone would wish. Theoreticians and experimentalists meet harmoniously around concepts like this, where creating new materials and new devices guides development of a theme.*

Alain FONTAINE
Director



The Department of *Condensed Matter and Low Temperatures* conducts fundamental studies of new states of matter (magnetism, charge density waves, superconductivity, etc.) and of the physics of helium between 100 μ K and room temperature. The department develops transverse activities in cryogenic electro-technology, fluid mechanics, astronomy, the life sciences and associated applications (cryogenics, aero-space).



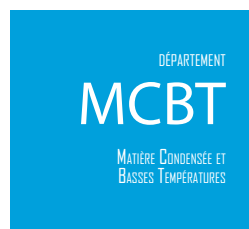
The Department of *Nanosciences* is engaged in the study of the physical properties of nanostructures : electronic transport, magnetism, nanomechanics, spectroscopy... at both experimental and theoretical levels. These nanostructures are prepared from various types of materials chosen for their specific properties - novel semiconductors, superconductors, metals, magnetic materials and molecules... Their fabrication at the nanometre scale - molecular films, nanowires, nanotubes, quantum wells and dots - leads to novel functions resulting from the most fundamental aspects of quantum physics.



The Department of *Condensed Matter, Materials & Functions* fosters fundamental research of materials and their applications. It has wide range experimental and theoretical expertises in material preparation, crystallography, electronic structure, magnetism, lasers, non-linear optics, catalysis and energy. The Department is distinguished by a strong interplay between physics and chemistry. It manages national projects at the ESRF and ILL and coordinates two thematic networks of the CNRS.



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Local imaging of the magnetization can be a very useful tool for understanding the physics of superconductors at the micron scale. A magnetic field can penetrate into a superconductor in the form of vortices, which are microscopic tubes of magnetic flux each carrying one flux quantum $\Phi = h/2e$. The vortex core is not superconducting, so vortices constitute defects in the superconductor whose behaviour gives information about the material's superconducting mechanisms.

We have developed a unique instrument : a magnetic microscope working at very low temperature ($0.1 \text{ K} < T < 10 \text{ K}$) which can draw a map of magnetic field at the micron scale. The detector is a one micron diameter superconducting loop (a microSQUID) which we move over the sample surface to map the surface magnetic field.

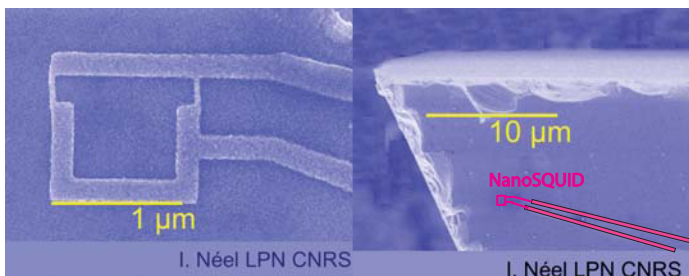


Figure 1. (a) Magnetic probe (μ SQUID) made in aluminium. (b) The silicon beam used for imaging, with the μ SQUID (magenta colour) near its end.

We have demonstrated the power of this “microSQUID microscopy” technique in studies of magnetic flux structures at the surface of the superconductor Sr_2RuO_4 ($T_c \sim 1.5 \text{ K}$). The monocrystal was grown in our institute by a molten zone method in an imaging furnace. Sr_2RuO_4 is a material with an “unconventional” superconducting state. We use a μ SQUID to probe this material under a magnetic field. We expect to find domains where the Cooper pairs have antiparallel orbital moments (opposite chirality); the presence of fractional vortices on the domain walls is predicted, and also preferential nucleation of vortices in one of the two kinds of domains.

We have indeed observed vortices in this material, for the first time. Individual vortices, each carrying a quantum of flux, appear in very weak field ($H < 10^{-4}$ Tesla). At higher fields, the vortices merge together to form magnetic domains. We deduce that there is a mechanism in this compound that alters the usual repulsion between vortices.

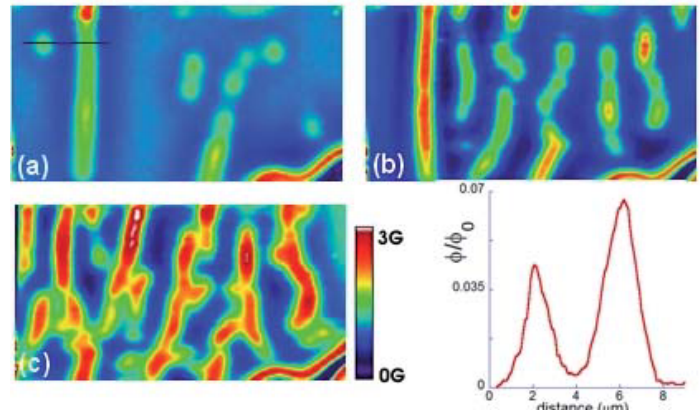


Figure 2. Microsquid microscopy image ($17 \times 31 \mu\text{m}^2$) of magnetic flux distribution on Sr_2RuO_4 at $T = 0.38 \text{ K}$ after “field cooling” in $H = 10$ Gauss at angles (a) 70° , (b) 60° and (c) 50° to the c axis. Graph (d) shows the flux profile through both a vortex and a “vortex line”, along the black trace shown in (a).

We also observe the anisotropy of this lamellar superconductor, which coexists with the fusion of the vortices. The vortex domains are stretched out and lengthened when the magnetic field is tilted towards the crystal planes.

Our novel μ SQUID-based instrument has thus enabled us to probe the nature of the superconductivity of Sr_2RuO_4 via the behaviour and interactions of vortices in the material. This technique could be applicable to many other magnetic materials.

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- “Observation of Vortex Coalescence in the Anisotropic Spin-Triplet Superconductor Sr_2RuO_4 ,” V. O. Dolocan, C. Veauvy, F. Servant, P. Lejay, K. Hasselbach, Y. Liu, and D. Mailly, Phys. Rev. Lett. 95, 097004 (2005).

The thermal response of a nanosystem to a heat pulse may be astonishingly irregular. We are performing research on the thermal and thermodynamic behaviour of matter structured at the nanoscale. Anomalous behaviour as compared to the bulk may be observed in thermal transport in one dimensional phonon waveguides, as well as in the specific heat properties of nanostructured materials.

We have found such behaviour by measuring the heat capacity of mesoscopic superconducting rings and disks placed in an external magnetic field, using an ultra-sensitive sensor. The energy sensitivity corresponds to a few tens of an attojoule (10^{-18} Joule, see reference). As one increases the magnetic field, the heat capacity starts to oscillate showing a discontinuous behaviour associated with the penetration of giant vortices in the rings. The entry of each vortex is accompanied by a phase transition; our experiment has shown that such transitions arise in a cascade as the magnetic field is swept (see Figure 2). This demonstrates that when the size of matter is reduced down to the submicron scale, the temperature rise produced by external heating is highly non-monotonous.

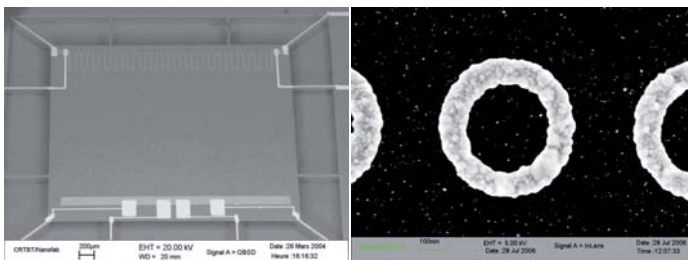


Fig. 1: Attojoule sensor and nano-objects studied by the "Thermodynamics of Small Systems" Team

Such surprising behaviour is very different from what happens in macroscopic system where only a single phase transition is observed between the superconducting and the normal state at a critical value of the magnetic field. Our results show that the thermal properties of patterned objects at the nanoscale may

be strongly modified by their small size. This may have dramatic implications for the conception of future nanoelectronics devices.

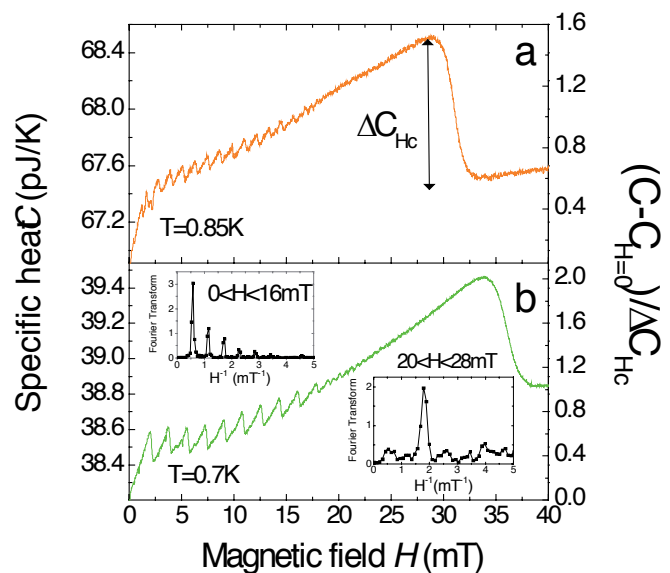


Fig. 2: The specific heat curves obtained at low temperature illustrate the oscillating behaviour specific to matter structured at the nanoscale.

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Further reading :

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- "Attojoule calorimetry of mesoscopic superconducting loops", O. Bourgeois, S. Skipetrov, F. Ong and J. Chaussy, Phys. Rev. Lett. 94, 057007 (2005) (Virtual Journal of Nanoscale Science and Technology, 11, 7, 2005).

Organic field effect transistors (OFETs) are providing exciting prospects for potential applications in electronics. The active elements of these devices use "plastic" semiconductors, based on carbon and hydrogen. Among the advantages compared to classical silicon transistors, this new generation of components should combine flexibility, low weight, transparency and low cost.

However, before they can be used in commercial applications, much work needs to be done to improve the performance of these devices. In this respect, enormous progress has been made through optimising the synthesis processes, drastically reducing the concentration of impurities present. At this point, a more fundamental understanding of the microscopic mechanisms governing electron transport in the organic materials becomes necessary.

Systematic studies of transport properties in organic transistors based on rubrene have been done by A.F. Morpurgo's team at the Institute of Nanosciences of Delft Technical University (Netherlands). In order to increase the capacitance, that is the maximum density of charge carriers, they use semiconductors having higher and higher dielectric constants for the grid material (Figure 1a).

We have noticed that the electronic conduction, instead of increasing proportionally to the number of charge carriers, has a tendency to saturate, and even to decrease. Measurements as a function of temperature showed that this phenomenon is associated with a regime where the carrier mobility becomes thermally activated : to travel from one electrode to the other, the electrons must jump from molecule to molecule, crossing a finite energy barrier at each jump. The microscopic origin of this phenomenon is to be found in the interaction of the charge carriers with the ions constituting the dielectric material of the grid. The combined effects of this "electron-phonon" interaction and the small bandwidths observed for molecular crystals (of order 0.5 eV) lead to the formation of new quasi-particles : the polarons (see Figs 1b and 1c). Polaron formation traps the carriers' wave functions on individual molecules, and their motion is then by jumps, which explains the experimentally measured energy barriers.

Further studies are being done to analyse the effects of the Coulomb interactions between the electrons. These interactions could be the origin of mysterious behaviour observed for very high grid voltages.

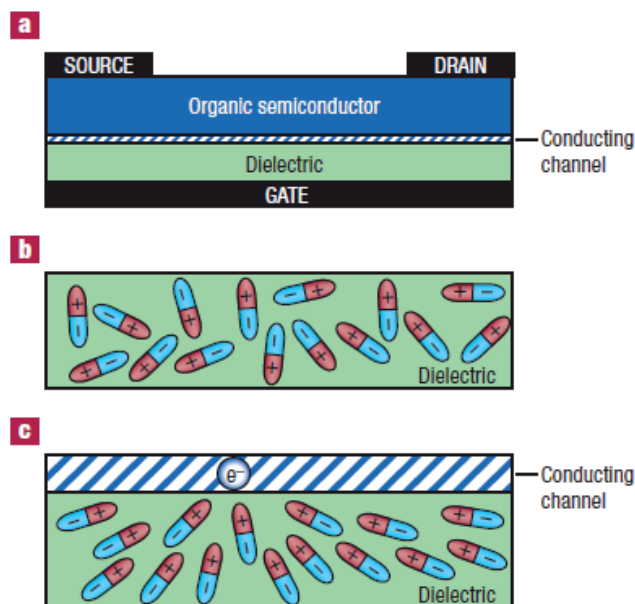


Fig. 1 (a) Field effect transistor; (b) In equilibrium, the ions of the grid semiconductor are in a disordered configuration; (c) The ions polarise and trap the electrons, giving rise to polarons. (Figure is from the second reference below).

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- "Tunable Fröhlich Polarons in Organic Single-Crystal Transistors" I. N. Hulea, S. Fratini, H. Xie, C.L. Mulder, N.N. Iossad, G. Rastelli, S. Ciuchi, and A. F. Morpurgo, *Nature Materials* 5, 982 (2006)
- "Organic transistors: a polarized response", V. Coropceanu, J.-L. Brédas, « *News and Views* », *Nature Materials* 5, 929 (2006).

Ferromagnetism may appear in materials which do not contain any magnetic ions, as in irradiated graphite (Esquinazi, PRL 2003), $\text{La}_x\text{Ca}_{1-x}\text{B}_6$ (Young, Nature 1999) and more recently in HfO_2 (Venkatesan, Nature 2004). This is indeed puzzling since d and f orbitals of both anions and cations are either completely filled or empty. This form of ferromagnetism (d⁰ ferromagnetism) which presumably results from intrinsic defects is still very controversial. Indeed, (i) it is often difficult to reproduce the experimental results and (ii) the appearance of magnetism depends strongly on the preparation conditions. It is also observed that the defects responsible for ferromagnetism are located at the interface between material and substrate.

From ab-initio calculations it was shown that cation vacancies in both CaO (Elfimov, PRL 2002) and HfO_2 (Pemmaraju, PRL 2005) lead to a ferromagnetic ground-state. In contrast, the ground state remains paramagnetic with oxygen vacancies. In the presence of cation vacancies, a localized moment on the first oxygen shell neighbouring the defects was obtained. Unfortunately, a recent study has also concluded that ferromagnetism in CaO is unlikely (Osorio-Guillén, PRL 2006). In CaO, the magnetic couplings are very short ranged and beyond a very small concentration the formation of cation vacancies is energetically unfavorable. Although, the ab-initio approach is a powerful tool that requires no adjustable parameters, it remains material specific and does not allow a simple determination of the relevant physical parameters that would control d⁰ ferromagnetism.

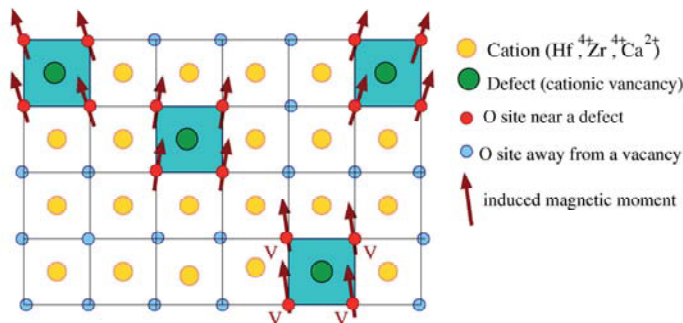


Fig. 1: Illustration of the Hubbard model in the presence of correlated disorder. A perturbation (on-site potential V) is introduced on the oxygen orbitals neighbouring the defect. On the oxygen sites the Hubbard parameter U prevents the double occupancy.

Recently (see Fig.1) a model that treats on equal footing the competition between short range correlated disorder and electron-electron correlations has shed some light on the origin of d⁰ ferromagnetism (Bouzerar, PRL 2006). The disorder is due to the non magnetic defects/ vacancies. It has been shown that ferromagnetism even beyond room

temperature is possible in a restricted region of the parameter space (strength of electron-electron interaction, disorder amplitude, and density of carriers). In this region the magnetic couplings are rather extended (beyond the percolation threshold). It was also shown that the ferromagnetism is essentially controlled by two parameters: (1) the impurity band position and (2) the density of carriers per defect.

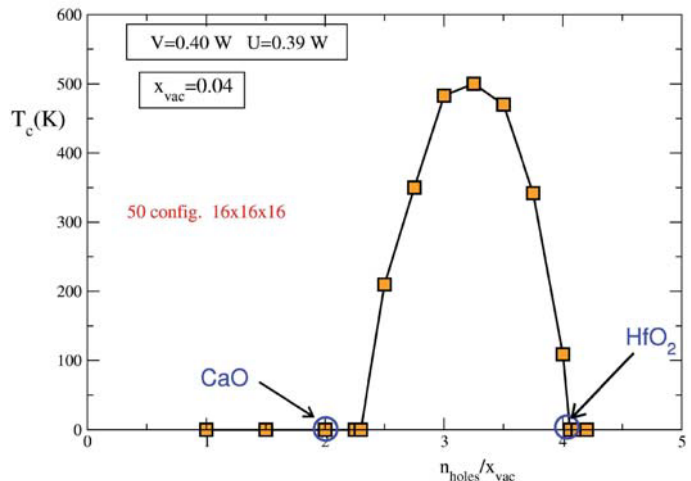


Fig.2: Curie temperature in Kelvin as a function of the carrier density per defect. The density of defects is set to $x=0.04$, the disorder potential amplitude $V=0.4$ W (W is the bandwidth) and the electron-electron correlation parameter $U=0.39$ W.

Figure 2 shows the Curie temperature as a function of hole density per defect. The parameter V which controls the disorder strength was chosen to reproduce the position of the defect band in the density of states of HfO_2 and CaO in the presence of cation vacancies as obtained from ab-initio. We observe that ferromagnetism is possible in a small window of the hole concentration. At low density, the magnetic couplings are dominated by the anti-ferromagnetic superexchange and at high density they exhibit an RKKY tail. In both cases, the system is magnetically frustrated (spin glass). We observe that both HfO_2 and CaO appear to be close to the zone boundary of the stability region of the ferromagnetic phase. This could explain the difficulty of reproducing the experiments in the case of HfO_2 . Fig.2 also shows that the optimal situation requires 3 holes/ defect. From this, one concludes that $\text{A}_{1-x}\text{A}'_x\text{O}_2$ where $\text{A}=\text{Zr}, \text{Ti}$ or Hf and $\text{A}'=\text{Na}, \text{K}, \text{Rb}$ could be good candidates for High TC d⁰ ferromagnetism. From the model study, the additional condition is that the induced impurity band be close enough to the top of the valence band. The spin-resolved density of states could be calculated within ab-initio. This study opens a new and promising path to high T_c controlled d⁰ ferromagnetism.

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Further reading :

• "Model for vacancy-induced d⁰ ferromagnetism in oxide compounds", Georges Bouzerar, and Timothy Ziman Phys. Rev. Lett. 96, 207602 (2006)

In recent years, studies in the field of molecular magnetism have been mainly concerned with the quantum properties of "molecular magnets", typically made up of a dozen atoms. At present, attention is being given to a greater diversity of systems. In particular, compounds presenting the remarkable properties of quasi-one dimensional magnetism can be obtained by the techniques of organic chemistry. Amongst the most studied compounds are certain chiral chain compounds (the chiral character is expressed as two types of chains, having right handed and left handed nature). These compounds contain two different magnetic species - transition metals and organic free radicals - alternating along the length of a chain.

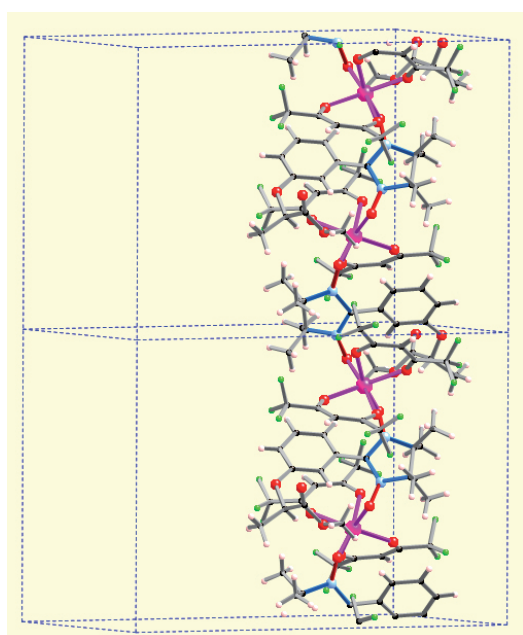


Fig. 1: Structure of a chain of the compound $Mn(hfac)_2(R)-3MLNN$

We have studied a compound where the chains incorporate the ion manganese and the radical nitronyl nitroxide. In the temperature range considered, the chains themselves are ferrimagnetic. At $T > 3$ K, there is no magnetic coupling between chains. Initial measurements of the magnetisation suggested that a ferromagnetic coupling was established between the chains at a temperature of 3 K. However, neutron diffraction

experiments at the Laue Langevin Institute gave a different conclusion : below 3 K, the order between the chains is actually anti-ferromagnetic in zero field. A very weak field is required to induce ferromagnetic ordering.

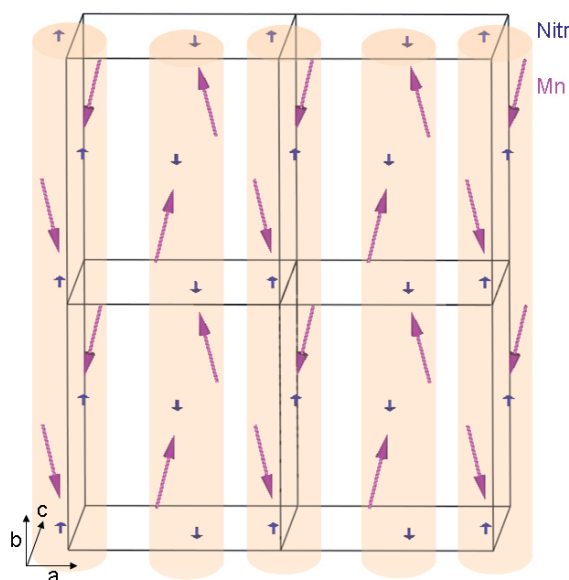


Fig. 2: Magnetic order in zero field: the chains are represented by the pink cylinders, the spins 1/2 of the radicals by the blue arrows, and the spins 5/2 of Mn^{2+} by the magenta arrows.

These apparently contradictory results have been interpreted by considering the competition between two types of weak magnetic interaction (each of the order of a milliKelvin). One is the dipolar interaction, responsible for the antiferromagnetic ordering at 3 K. The other is the exchange interaction, whose sign is revealed by ferromagnetic fluctuations seen in the regime where the chains are decoupled ($T > 3$ K). The equilibrium between the two interactions is controlled by the strong correlations within the chains, as proved by both exact calculations and mean field methods.

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Further reading :

- M. Minguet, et al., Angew. Chem. Int. Ed. 41, 586 (2002)
- "Subtle competition between ferromagnetic and antiferromagnetic order in a Mn(II) free radical chain" E. Lhotel, et al., Phys. Rev. B 75, 104429 (2007).

The most recent measurements of the diffuse cosmic background and the velocity of recession of very distant supernovae, interpreted in the framework of the standard cosmological model, place us in a Universe dominated by Dark Matter (23%) and Dark Energy (70%). First proposed in 1930, the necessity for the existence of Dark Matter in the Universe has not diminished, and the hypothesis that it is made up mostly of weakly interactive massive particles (WIMPs) has only been reinforced since.

Coming from the cosmos and capable of traversing large thicknesses of rock, this new type of particle could be detectable by the underground installations of the "Edelweiss" project. Their observation would make a large contribution to models that unify the fundamental forces of nature.

The Edelweiss consortium consists of six French laboratories, two German laboratories and one Russian laboratory (the CEA/DSM's DAPNIA and DRECAM, the CNRS/IN2P3's IPNL and CSNSM, the CNRS/MPPU's Institut Néel, the CNRS/INSU's IAP and IAS, the FZ Karlsruhe, the University of Karlsruhe, and DUBNA/DLNP). It brings together specialists from very varied disciplines : particle physics, materials physics, astrophysics, cryogenics. These teams have been working together since the early 1990s, developing and using ultra-sensitive detectors : germanium bolometers of several hundred grams mass operating at 20 thousandths of a degree Kelvin.

The consortium demonstrated its excellence at the world level in 2002 by obtaining the highest sensitivity for WIMPs detection with the three detectors of the installation "Edelweiss I". Though WIMPs were not detected, it was thus able to conduct the first exploration of the parameter ranges related to these particles and their interactions as permitted by supersymmetric models. Since, WIMPs particles are so discreet in order to discriminate their extremely rare signals, 28 new detectors are being installed in a new, ultra low radioactivity cryostat. Equipped with its shielding and its anti-cosmic ray protection, the apparatus is installed at the Modane underground laboratory of the CNRS and CEA. To have available the world's most sensitive instrument for WIMPs detection in the years 2007-2011, the Edelweiss team will build and install 90

additional bolometric detectors, making up 30 kg of germanium detector material. The new "Edelweiss II" tool will have 100 times higher sensitivity for the search for WIMPs and for testing a great variety of models coming from super-symmetry theories.



Fig. 1: In the Modane underground Laboratory (LSM), the Edelweiss II experiment has successfully accomplished the first cooldown of its cryostat and recorded the first background pulses from its detectors. This experiment is dedicated to the search for the Dark Matter of our galaxies.

In the Modane underground laboratory situated at the halfway point of the Fréjus road tunnel, Edelweiss's ultra-sensitive detectors are protected from cosmic rays by 1700 metres of rock. The installation is unique in the world by the size of the cryostat (100 litres), capable of cooling thirty kilograms of germanium detectors to a temperature close to absolute zero. For the French, German and Russian teams, it constitutes a decisive tool in the race to find WIMPs.

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Further reading :

- The Edelweiss II experiment : <http://edelweiss.in2p3.fr/pub/fichiers/demarrage-edw2/index-com.html>
- "Final results of the EDELWEISS-I dark matter search with cryogenic heat and ionization Ge detectors", V. Sanglard et al., Phys. Rev. D 71, 122002 (2005).
- "Sensitivity of the EDELWEISS WIMP search to spin-dependent interactions", A. Benoit et al. Phys. Lett. B 616 (2005).

Bose-Einstein condensates are almost mythical objects of Quantum Mechanics. Particles in this peculiar state of matter lose their individual identities, coalescing into a single quantum state and displaying macroscopic coherence effects. The ingredients required to undergo condensation are two-fold. First, particles should be bosons (particles with integer spins obeying the Bose statistics). Next, their thermal de Broglie wavelength should exceed the average inter-particle distance, which could be achieved by increasing the particle density and/or lowering their temperature.

Consider a gas of bosons of mass m , thermalized at temperature T . Since their average De Broglie wavelength scales as the inverse square root of m and T , the criterion for Bose-Einstein condensation (BEC) is most easily satisfied with particles of small mass. This is why excitons in semiconductors have been proposed for BEC since the early 60's. Excitons are quasi-particles which can be created by optical excitation of electrons from the valence band into the conduction band, leaving behind unoccupied states in the valence band or electron "holes". Holes behave as positively charged particles, and thus can be bound to electrons by Coulomb interaction, forming positronium-like particles called excitons. Although electrons and holes are fermions, excitons are (composite) bosons. Moreover their light mass, of the order of the electron mass, should permit BEC at temperatures of a few Kelvin. However, in spite of intense research efforts over the past three decades, no convincing evidence of exciton condensation has ever been firmly established.

In fact, BEC was demonstrated for the first time in a dilute gas of rubidium atoms in 1995. Because of the heavy atom mass (about five orders of magnitude larger than the electron mass), sophisticated cooling techniques were needed to lower the atomic gas temperature down to the micro-Kelvin range to achieve condensation (Nobel prize in 2001).

In this work, we show that BEC can be achieved at around 20 K (-253°C) by using microcavity polaritons. These quasi-particles result from the strong interaction between excitons confined in quantum wells and photons confined in the microcavity embedding the quantum well (Figure 1). Due to their 50% photon nature, polaritons have an ultra light mass, one billion times smaller than the rubidium atom mass, thus favouring BEC at high temperature. Figure 2 shows the distribution of polaritons in momentum space (k_x, k_y) (upper panels) and in energy-momentum space (E, k_x, k_y) (lower panels), for three optical excitation powers 0.55, 1, and 1.14 P_{thr} where P_{thr} is the threshold power for condensation. For excitation above P_{thr} , one clearly sees a conden-

sation into the ground state, out of a polariton population in thermal equilibrium at around 20 K. A similar phase transition can also be obtained by keeping the excitation power constant and lowering the temperature. These findings are promising for development of the so-called "polariton laser" and Bose condensation at elevated temperatures with wider bandgap semiconductors such as ZnO or GaN.

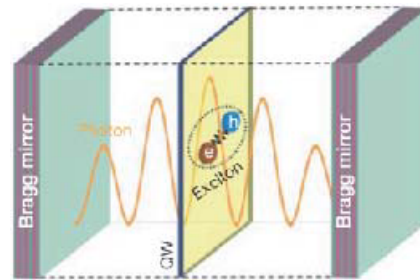


Fig. 1: Microcavity diagram. A microcavity is a planar Fabry-Pérot resonator with two Bragg mirrors at resonance with excitons in quantum wells (QW).

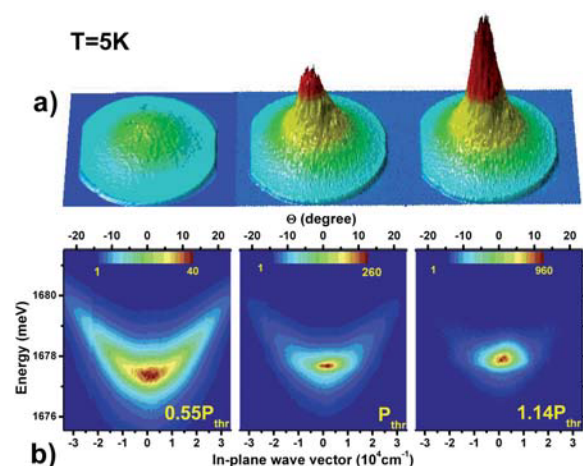


Fig. 2: Appearance of a Bose condensate of polaritons in momentum space beyond the critical density of polaritons. This density is reached above a critical excitation power (P_{thr}) for the photo-creation of electron-hole pairs.

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Further reading :

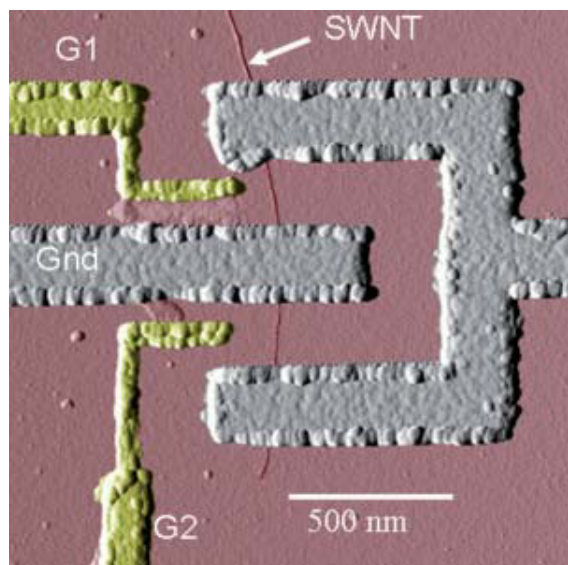
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A superconducting interferometer using carbon nanotubes : towards detection of a single spin

NANO

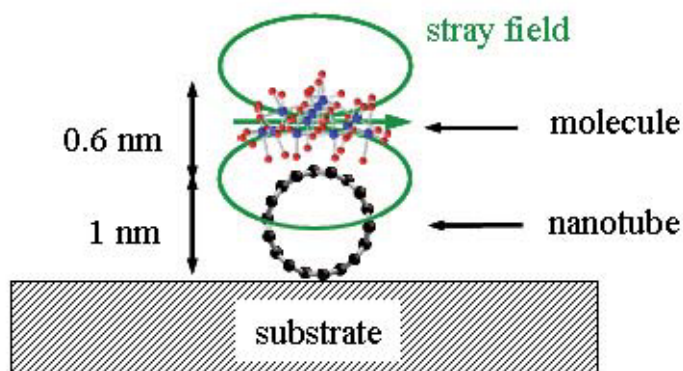
A superconducting quantum interferometer SQUID consists of a superconducting loop interrupted at two different places by two "Josephson junctions". These interferometers are used to measure very weak magnetic fields or currents. In the present device, the junctions are carbon nanotubes. They are so small that the charge induced by a nearby grid changes their energy appreciably. Thus, the interferometer can be adjusted by two grids, which change the energies of the two junctions just as the magnetic induction through the loop does. This gives the interferometer exceptional properties, revealed in this work. The device is so sensitive that detection of the spin of a single molecule may be possible.

In a superconducting loop, a permanent current flows such that the magnetic flux threaded through the loop ($\Phi = \text{current} \times \text{surface}$) is a multiple of the flux quantum $\Phi_0 = h/2e$. When the loop is interrupted by two junctions, a constructive interference occurs between the two arms of the interferometer, such that the total current crossing the device reaches a maximum value proportional to $\cos(\pi\Phi/\Phi_0)$. Measuring this current gives the value of the flux Φ with very high precision.



In the interferometer shown in the electron micrograph image, the junctions are single wall nanotubes (SWNT) whose diameter is less than a nanometer. Given this very small size, the energy of the circuit depends not only on the flux inserted in the loop (formed

by the superconductor and the nanotubes) but also on the charge on each nanotube. The charges can be adjusted by the grids (G1 and G2) such that there is either an even or odd number of electrons on each junction. For an even number of electrons, the device behaves as an "ultra-sensitive" interferometer. For an odd number of electrons, the nanotube junctions change the electronic phase by π . Where does this phase shift come from? When the two electrons of a Cooper pair traverse a "quantum box" containing a single spin, the spin of each electron must be flipped to transit by the single spin state available. This spin reversal corresponds to changing the sign of the wavefunction, so an extra phase of π is acquired in this way.



It is the very small diameter of the nanotube junctions that makes this device useful : if one grafts a molecule carrying a spin onto the nanotube, some of the magnetic field lines induced by the molecule will be threaded by the nanotube, changing the total flux through the interferometer loop. Given the very high sensitivity of the device, it appears possible to detect the spin of a single molecule. This would have many applications in the field of molecular magnetism. Also, by functionalising the nanotube beforehand, specific molecules (pollutants, etc...) could be detected. This new interferometer is thus a powerful tool for the study of nanoparticles.

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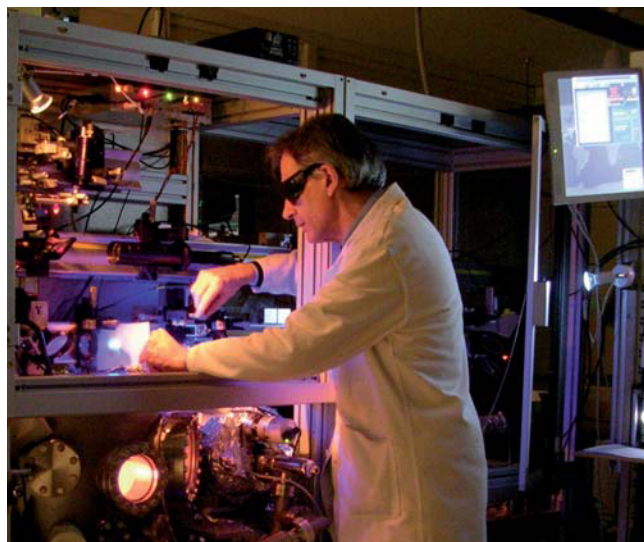
Silicon is “the” semiconductor of reference and has provided the main base material for solid state electronics and microelectronics for many years. In view of the huge amount of research that has been devoted to silicon over the last 50 years, what could possibly be news about this material's properties? It turns out that, processed in the right way, silicon becomes a superconductor. Actually, for this to happen, silicon must be “outrageously” doped with boron, and then cooled down to a temperature quite close to absolute zero ($0.3\text{ K} = -273^\circ\text{C}$). Under such conditions, the archetypal semiconductor may become a superconductor at ambient pressure.

It is something of a paradox that the very same characteristic that makes silicon so well suited to electronics has so far prevented us making it into a superconductor : it allows only very small amounts of other elements to be incorporated into its crystal lattice. This is the reason why high purity silicon can be made relatively easily. Such a pure “intrinsic” semiconductor has very few free electrons that could carry an electrical current and behaves therefore as an insulator. This feature changes as soon as one introduces into the crystal lattice a controlled amount of specific chemical impurities which have one more (phosphorus) or one less (boron) electron than silicon. This process, called doping, has matured into an art where positioning of dopants and charge carriers in a well-designed device is the basis of most of the products that the microelectronics industry launches in the market every day.

It is well known that when the concentration of dopants becomes high enough, the orbitals of the additional electrons surrounding the impurity atoms start to overlap. The electrons are then mobile over the whole crystal, which becomes a metal. This metallic conductivity persists down to low temperatures and is mainly limited by the number of available carriers, i.e. the dopant concentration, which must remain lower than the solubility limit of this element in the crystal (typically 1% for boron in silicon). A new approach, different from the usual crystal growth strategies, is thus necessary in order to obtain a superconducting alloy, where 5 to 10 at. % of silicon atoms would be replaced by boron : the trick is to use the pulsed laser-assisted localized melting of the surface region of a silicon wafer during a short time interval in the presence of a boron-containing gas. Our colleagues at the Institut d'Electronique Fondamentale have thus used 200 laser pulses of 25 ns to superface

melt silicon [see picture], in order to accumulate several at. % of boron atoms. These were trapped on crystalline bonding sites during the quench, and yielded a single crystal silicon layer with an unprecedented concentration of free carriers. This crystal became a superconductor at low temperatures. Ab initio calculations made at the LPMCN in Lyon, which have been validated by room temperature experiments at the Institut Néel, show that the results are compatible with a “conventional” origin for this superconductivity.

It is far too early to expect that one day superconducting silicon may be integrated in electronic devices for the general public. Nevertheless, if it were to become possible, it would be something of a revolution.



Picture : Adjusting the optical path of the laser beam into the gas immersion reactor at the Institut d'Electronique Fondamentale, Orsay

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In some materials systems, termed "2-dimensional", the electrons move in a plane. The best known examples are the Gallium Arsenide heterojunctions used in mobile phones and optical communications. There, the electrons are confined at the interface between two materials: Al-GaAs and GaAs. Graphene is a new 2-dimensional material. It consists of a single sheet of graphite, the most common form of carbon. In graphene, the carbon atoms form a hexagonal lattice (see Figure 1), and the conduction electrons occupy the π orbitals and move freely over the entire sheet.

If 2-dimensional materials exist already, why be interested in graphene? The answer lies in its unique electronic properties. The electrons have relativistic dynamics : they move with a velocity of 10^6 m per sec, whatever their energy; this is the velocity of light in the material. Moreover, the charges participating in electrical conduction are either negative (electrons with positive energy) or positive (holes with negative energy). Thus, whatever the energy, charge carriers are available. The carriers move freely in the plane: their motion is termed "ballistic" because it is limited only by the "edges" of the material. Finally, electrons in graphene possess, as well as their spin, a supplementary "colour". With properties so different from usual semiconductors, one can imagine an all-graphene electronics based on components providing entirely new functions.

Several methods have been proposed for producing planes of graphene. The most common method is to peel individual layers off a piece of graphite and to transfer them to a glass plate. Despite its "low tech" nature, this method has allowed researchers to demonstrate the Quantum Hall Effect (for both positive and negative charges) and to confirm the transport properties expected in this very special material. Another method has been developed by Walter de Heer's group at Georgia Tech. The surface of a silicon carbide crystal is decomposed at high temperature and the surface then "reconstructs" as one or more planes of graphene. This material is easy to etch and can be formed into different shapes (ribbons, etc..).

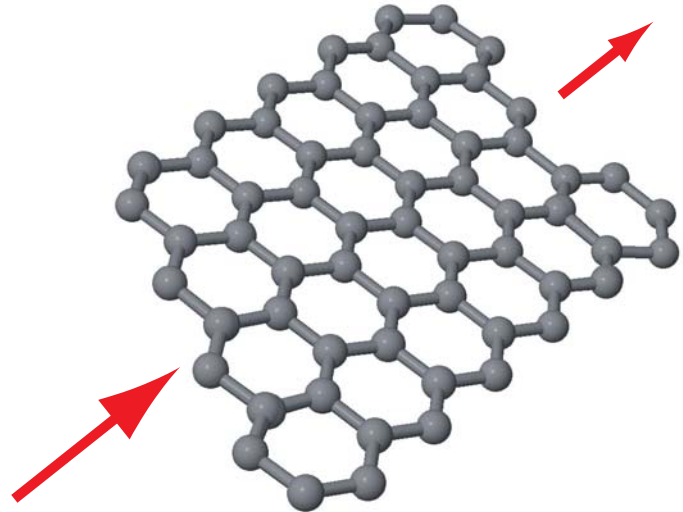


Fig. 1 A graphene plane with its carbon atoms arranged in a honeycomb structure. If the material is formed into a ribbon shape with clean zig-zag edges as shown, ideal conductance is obtained in the direction of the red arrows.

Magneto-transport experiments carried out in collaboration with Georgia Tech have shown that their synthesis procedure gives higher performance material showing most of the characteristic properties expected for graphene. A major challenge now is to demonstrate the technological potential of this material, especially given its compatibility with silicon, the present base material of the electronics industry.

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In a recent experiment, Matthias Meschke, Wiebke Guichard and Jukka Pekola studied the heat exchange between two very small pieces of metal, connected together only by superconducting wires. The results showed that, at very low temperature when phonon and other processes are frozen out, heat transfers by electromagnetic radiation. This work elucidates the heat transfer processes, at temperature only 0.1 degrees above absolute zero, for circuits having nanometre or micron sizes placed on a simple silicon chip.

Until now, experts agreed that superconductors are ideal insulators with respect to heat transport. These new experimental results show that, at low temperature, heat is transferred by electromagnetic radiation. They also show that the heat transfer rate cannot have an arbitrary value : it is limited to a value called the quantum of thermal conductance. This provides a new example of the way that the laws of physics change when quantum mechanics comes into play.

The experiments are extremely demanding because the temperature has to be measured on minute metallic islands. Any ordinary thermometer would be far too big for this task. The problem is resolved by quantum mechanics itself : the electrical probes used have cross-sections of only a hundred nanometres and use the tunnel effect, a quantum mechanical phenomenon which allows particles to penetrate into regions forbidden by classical mechanics. An electric current due to tunnelling monitors the energy distribution of the electrons in a metallic island and so measures its temperature. To separate out the noise signal from the environment, a "switch" is inserted in the superconducting wire. This alternately allows and blocks the passage of heat by electromagnetic radiation along the wire. Figure 1 shows the temperature variation of the metallic island, as a function of the magnetic field which operates the switch cyclically.

These experiments have provided a better understanding of the thermal transport mechanisms in nanometre scale structures.

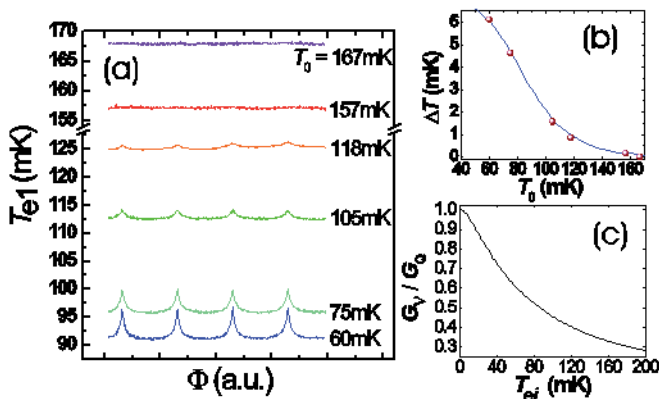


Fig. 1: a) Temperature changes of a metallic island as a function of the magnetic flux ϕ which periodically switches the device that turns electromagnetic heat transfer on and off. The temperature increases sharply when heat arrives on the island. (b) : Amplitude of the temperature oscillation for various temperatures (c) : As temperature decreases, the thermal conduction G_v saturates at a value corresponding to the quantum of thermal conductance G_Q .

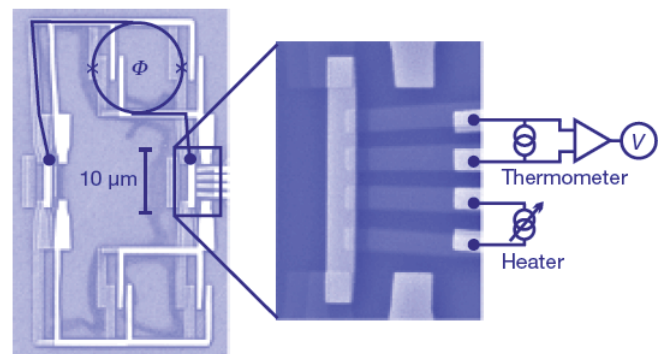


Fig. 2 : On the left, overall image (electron micrograph) of the device used. On the right, enlargement showing the resistance with four tunnel contacts and the superconducting wire.

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Classical methods for information processing in electronic devices are based on control of the charge flow in semiconductors, whereas information storage typically exploits the magnetic properties of metals. Continuing progress in miniaturization has dramatically reduced the number of atoms necessary to process and store one bit of information. In this respect, storing a single bit in a single atom would be an ultimate limit. With possible relevance to such a goal, we have managed recently to localize an individual magnetic atom in a semiconductor quantum dot. Such a quantum dot can be addressed optically and we have shown that the energy and polarization of the photon emitted during the recombination of an injected, single electron-hole pair depends on the spin state of the magnetic atom. This property is exploited to do optical probing of the spin state of an individual magnetic atom.

The quantum dots we chose for this study are based on the II-VI "Diluted Magnetic Semiconductors" Cd(Mn)Te. The photoluminescence of individual quantum dots doped with a manganese atom Mn is isolated using micro-spectroscopy techniques. The photoluminescence spectrum of a single quantum dot without any magnetic atom consists of a single sharp line, which results from the recombination of an electron having a spin $S = 1/2$ with a hole having a spin $J = 3/2$. When a Mn atom is included in the quantum dot, the spin of the optically created electron-hole pair can interact with the five outermost electrons of the 3d shell of the Mn atom. The 3d electrons are aligned so that their total spin S has a value $5/2$ and a measurement of S along any direction must yield a quantized result having one of $2S+1 = 6$ possible values: $S_z = \pm 5/2, \pm 3/2, \pm 1/2$. This leads to a splitting of the initially simple photoluminescence spectrum into six equally spaced components. The splitting comes mainly from the spin structure of the holes. In our "self-assembled" quantum dots, the strains in the quantum dot plane lift the fourfold degeneracy of the hole levels and, in the lowest energy state, the spin of the hole is quantized along the growth axis and its projection can take only the values $J_z = \pm 3/2$. The interaction between the hole and the Mn is reduced to an "Ising" term $J_z S_z$. This coupling shifts the emission energy of the quantum dot, depending on the relative projection of the Mn and hole spins. The interaction of the electron-hole pair with the Mn is then equivalent to an effective magnetic field, which splits the different Mn spin levels even without an external magnetic field.

Since the spin state of the Mn atom fluctuates during the optical measurements, the six lines are observed simultaneously in the luminescence spectra.

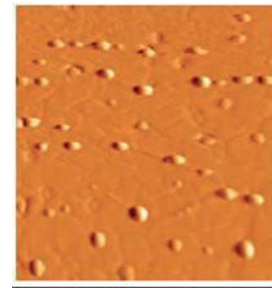


Fig. 1: Atomic Force Microscope image of CdTe quantum dots dispersed on a ZnTe surface. The image is 1 micron wide and the quantum dots have sizes of order 10 nm.

Their intensity reflects the probability for the Mn to be in one of its six spin projections and the statistics of the emitted photons reflect the dynamics of the Mn spin fluctuations. The emission from the quantum dot is then a direct probe of the spin state of the magnetic atom and could be employed as a read-out tool in an information processing protocol using a single Mn spin to store one bit of information.

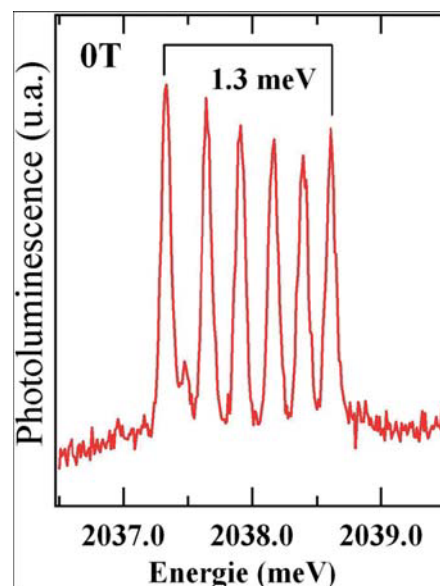


Fig. 2: Photoluminescence spectrum of an individual quantum dot containing a single Mn atom. The excitation creates a confined electron-hole pair, whose spin interacts with the spin of the Mn ($S=5/2$), splitting the atom's six spin sublevels. The emission seen when electron and hole recombine with each other then consists of six distinct lines. Each line corresponds to a given projection of the Mn spin, allowing an optical readout of the magnetic atom's spin state.

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How does a metal transport electrical current ? We have shown that a full understanding of electrical transport can only be achieved with the most modern tools of quantum mechanics and large computers.

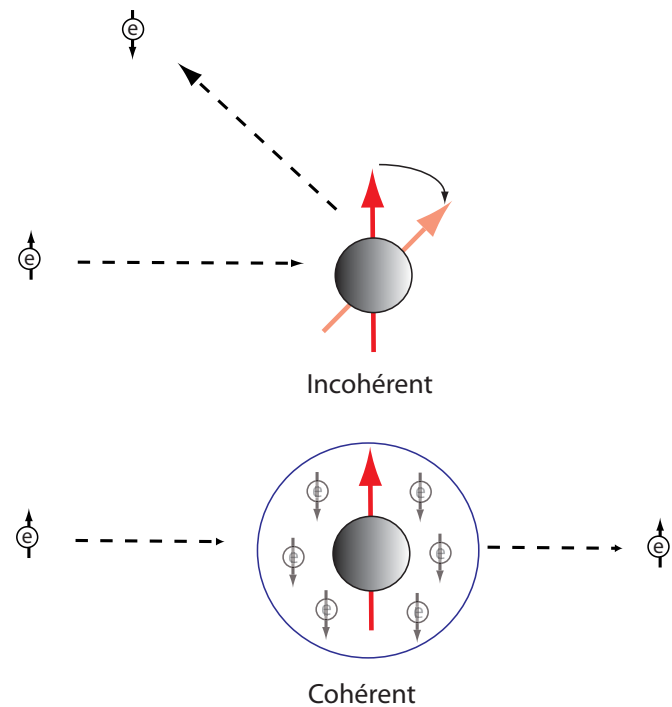
A metal can be viewed as a lattice of charged ions, through which the electrons flow freely. When an electric field is applied, by applying for example a voltage difference at the ends of a conductor, the electrons are accelerated: this is the electric current. One key question has been omitted: what limits the magnitude of the current ? The acceleration of the electron does not lead to an infinite increase of its speed and hence of the current. The basic ingredient is provided by collisions of the electrons with impurities or between themselves. First, electrons diffuse on atomic defects : this is crystallographic disorder. Second, collisions between electrons also slow down the current flow. At room temperature, the collisions between electrons are dominant, while impurities and lattice defects dominate at low temperature. Taking into account all these phenomena in transport equations, it is possible to account precisely for the resistance of metals.

But new experimental phenomena have been discovered : when a minute fraction of the lattice ions are replaced by magnetic ions (for example iron), the electrical resistance increases at low temperature, something which cannot be explained by standard diffusion processes ! Jun Kondo discovered the origin of this phenomenon which is known by his name: electrons carry not only an electric charge but also a magnetic moment. The interaction of this moment with magnetic impurities generates collisions of a novel type, which are more and more efficient as the temperature is lowered !

In our work, we investigated the influence of magnetic impurities and their coupling to conduction electrons on the quantum behaviour of the electrons and their phase coherence. This problem touches on the actual concept of the electron : since the coupling between the electrons and a magnetic impurity becomes so strong, does "a novel particle" replace the actual electron ? In fact below a temperature T_K (the Kondo temperature), the quantum state of electrons is strongly affected by collisions with magnetic impurities. This is what we have observed in a study of the quantum coherence of electrons as a function of temperature and applied magnetic field. In fact, as the temperature is

lowered, electrons form a cloud around magnetic impurities which exactly screens their magnetic moment. In this "collective effect", the magnetic moment of a large number of electrons compensates exactly the impurity's magnetic moment. One can say that the impurities are "screened" and everything behaves as if ... the impurities have disappeared ! Using powerful computing algorithms we have been able to compare our measurements with exact numerical results and have shown that this scenario, based on the Kondo effect, is correct.

The understanding of electrical transport in metals has thus reached a new level: the most modern theoretical models appear to be essential for a complete comprehension of phenomena which are as basic as the electronic transport governing the resistance of metals.



Top : electrons are diffused incoherently above the Kondo temperature, leading to an increase of the resistance. Bottom : below T_K a cloud of electron spins screens the impurity, which becomes "transparent" to electronic transport.

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Nanostructures can achieve model physical situations, where novel phenomena arise due to a fine tuning of the control parameters. One example is given by the Kondo effect : in a very small metallic island (a quantum dot) defined by electrostatic gates (Fig. 1) in a two-dimensional metal, one can fabricate an "artificial atom" by progressively filling the quantized electronic levels. Each time the highest occupied level carries a single electron with spin $\frac{1}{2}$, adding another electron is forbidden by a Coulomb barrier. In this way, an "artificial magnetic moment" has been produced.

The two states with spins $\uparrow$ and $\downarrow$ have the same energy, which gives the system very special properties. When the quantum dot is coupled to two metallic leads (or charge reservoirs) by tunnel barriers (source and drain in figure 1), the electron hopping between the quantum dot and the reservoirs is able to "screen" the spin $\frac{1}{2}$. The artificial magnetic moment disappears below a characteristic temperature called the "Kondo temperature". Then, despite the strong Coulomb interaction on the quantum dot, the system behaves as if the quantum dot was replaced by a perfectly conducting metallic grain. The conductance through the quantum dot becomes equal to the maximum value $2e^2/h$ allowed by quantum mechanics.

Recently it was discovered that the Kondo effect may also occur when the last electron added in the dot can occupy two quantum states with the same energy, described by different orbital wavefunctions. This can happen for instance by using two dots, coupled to the same leads, the added electron occupying one or the other dot (Figure 2). The *orbital Kondo effect* is obtained by strongly coupling the two dots by a capacitance.

What happens to the electron spin in this case? The two degenerate orbital states are obtained by "freezing" the spin in one of its states, using a magnetic field which decreases the energy of $\uparrow$ electrons and increases that of $\downarrow$ electrons (Zeeman effect).

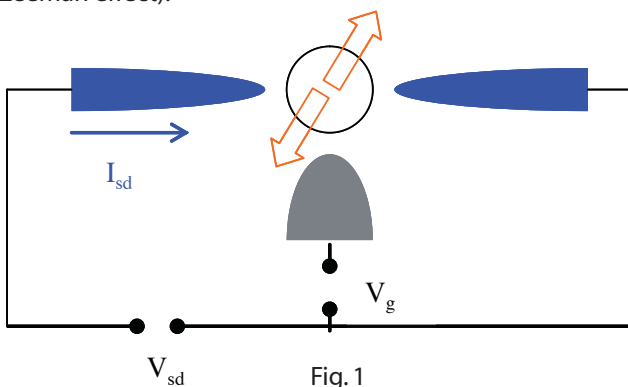


Fig. 1

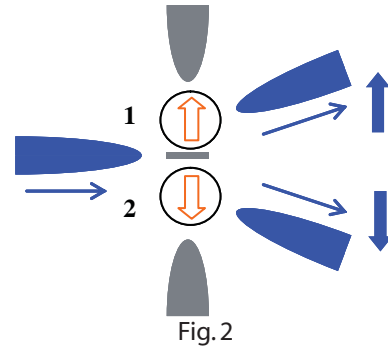


Fig. 2

One can go further and tune the electrostatic gates so that the two states with the same energy are $(1 \uparrow)$ and $(2 \downarrow)$. This requires that the gate potentials acting on dots 1 and 2 compensate the Zeeman energy splitting between $\uparrow$ and $\downarrow$ states. In the geometry of Figure 2, the Kondo effect can develop and this has striking consequences ! The total conductance between left (single source) and right (two drains) is maximal, but electrons with spin $\uparrow$ are forced to go through dot 1, while electrons with spin $\downarrow$ are forced through dot 2. This effectively splits the incoming electronic current into two spin-polarized currents, with opposite polarizations. This device could be realized with state-of-the-art techniques and would achieve an electronic equivalent of the Stern-Gerlach experiment, with high efficiency. Although it might work only at temperatures well below 1K, it would allow a number of fundamental experiments in nanoelectronic structures where it is necessary to "filter" the electronic spin.

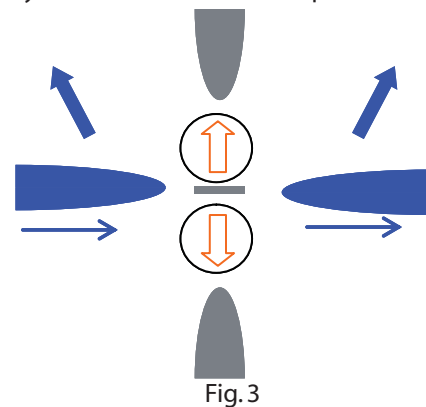


Fig. 3

The association between a spin and an orbital degree of freedom, embodied in the two states $(1 \uparrow)$ and $(2 \downarrow)$, can be coherent enough to yield a so-called "quantum entanglement". Then, using quantum interferences between two electronic paths crossing dots 1 and dot 2 (Fig.3) one can imagine other experiments where the electronic spin can be manipulated, using only static electric and magnetic fields.

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Investigations of quantum-coherent nanostructures lie at the leading edge of semiconductor research with implications ranging from fundamental issues in solid-state physics to future nanoelectronics applications. Most often, such structures and related electron transport phenomena are analysed in terms of macroscopic parameters (typically the overall conductance). In collaboration with the Université Catholique of Louvain-la-Neuve (Belgium) and the IEMN Institute in Lille, we have applied a weakly invasive scanning probe microscopy technique able to image in real space the low temperature transport properties of nanostructures patterned in a subsurface two-dimensional electron gas (2DEG). By adding the local dimension to traditional measurements, this method, called Scanning-Gate Microscopy (SGM), sheds new light on the electron transport through open buried nanostructures.

The structures we studied are ring-shaped electron interferometers, i.e., "Aharonov-Bohm" (AB) rings (Fig.1). They are patterned by electron-beam lithography from a 2DEG confined at the interface of a GaInAs-based heterostructure. The 2DEG is buried at 25 nm below the free surface, too deep to be accessible directly using Scanning Tunnelling Microscopy (STM).

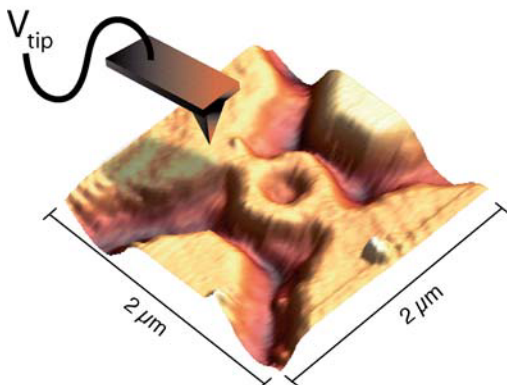


Fig. 1: AFM topographic image of a quantum ring

The Atomic Force Microscope (AFM) constructed in our laboratory works at low temperature and in a magnetic field in order to reveal coherent effects that emerge for sizes of the device smaller than the electron coherence length. SGM uses the electrically-polarized AFM tip as a flying nano-gate that can be located at any desired position above the structure. A local perturbation is generated in the potential experienced by elec-

trons within the quantum ring, which, in turn, alters their transmission through the device. By recording the ring conductance as the tip is scanned over the ring and its vicinity, we build conductance maps (Fig.2) that reflect changes in electron transmission.

The conductance image shown in Fig. 2 reveals a rich pattern of conductance fringes whose shape depends on the scanned region. Whereas fringes are predominantly radial when the tip is located directly above the ring, they become concentric when the tip moves away from the ring. The analysis of this outer fringe pattern reveals that it builds a real-space image of electron interference phenomena that take place within the coherent electron system. This pattern is interpreted as a combination of the electrostatic AB effect (the biased tip modifies the phase accumulated by electron wavefunctions propagating in each arm and, therefore, their phase detuning at the ring output) and of the magnetic AB effect. In the latter effect, the magnetic flux captured by the AB-ring applies an additional phase shift to electron wave-functions that is periodic with the applied magnetic field.

The interpretation of the inner radial fringe pattern under realistic simulations of the electron-probability density within the quantum ring reveals that it is also linked to the coherent nature of the electron system. Therefore, the SGM technique opens new perspectives in the analysis of electronic nano-devices based on the quantum transport of charge carriers. In the future, it could form a powerful tool for designing and diagnosing coherent electronic nano-devices which would exploit the electron phase in addition to the charge state.

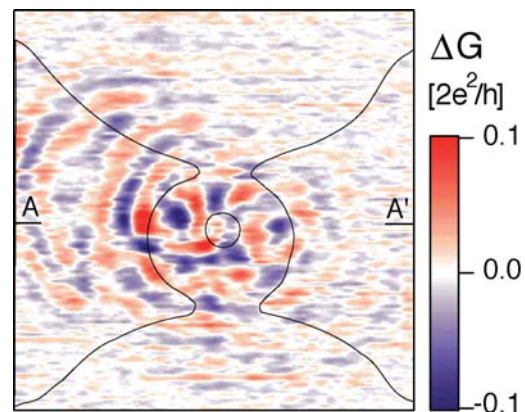


Fig. 2: Filtered conductance map taken as a function of the position of the biased-tip. The temperature is 4.2 K and the applied magnetic field strength is 2 T.

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Fundamental research on magnetic materials has led to magnets with exceptional properties and yields new applications : miniature motors and sensors, data storage in computer disks.... Further progress requires mastering the production of the materials and a better understanding of their physical properties.

Alloys between iron and platinum have been known for decades but their magnetic properties are still the subject of intense research work. Amongst them, the alloys with similar concentrations of Fe and Pt atoms can crystallize in two different phases : a disordered phase called A1 (where the Fe and Pt atoms are randomly distributed on the same crystallographic site, see Fig. 1 at left), and an ordered phase called L10. The latter can be seen as an alternating succession of planes of Fe and Pt atoms (Fig. 1 at right). This special structure gives the compound extraordinary magnetic properties, classing it in the category of the most powerful magnets. In thin film form, these materials are promising candidates for data storage at ultra high density. This might seem surprising given that in Fe-Pt only 50% of the atoms are magnetic.

The discovery of their high performance has renewed interest in research on these compounds, especially as their properties and behaviour are not well enough understood. For example, the temperature at which the magnetic moments become ordered (Curie temperature), but also the magnetic anisotropy (orientation of the magnetic moments in a privileged direction) are very sensitive to the degree of ordering of the Fe and Pt atoms; inversely, the macroscopic magnetization is generally described as being mainly independent of the degree of ordering (at fixed composition).

In a neutron diffraction study conducted in collaboration with a team from IFW Dresden (Germany), we have analyzed how the ordering of the Fe and Pt atoms and the Fe/Pt ratio influence the magnetic properties of Fe-Pt alloys. Neutrons, being neutral particles, traverse matter in depth and give information about the positions of atoms in a crystal (the ordering). But also, since neutrons have a magnetic moment themselves, neutron diffraction experiments can determine magnetic moments at the atomic scale. Whereas the magnetization (a macroscopic property) of these alloys is not very sensitive to the atomic ordering, our study at the microscopic

scale has revealed that, on the contrary, the atomic magnetic moments of iron and platinum decrease when the iron content increases. This is unusual, for the magnetic moment carried by iron atoms usually increases when the iron concentration is increased in alloys of iron and a non-magnetic element (for example aluminium).

Our experimental results have been confirmed by theoretical calculations of the electronic structure. In the compound $\text{Fe}_{59}\text{Pt}_{41}$, the considerable reduction of the magnetic moment of iron compared to the stoichiometric compound $\text{Fe}_{50}\text{Pt}_{50}$ could be attributed to the reduced volume of its unit cell.

In addition, calculations of the electronic structure have shown that atomic disorder has two opposite effects on the magnetism : on the one hand, the chemical disorder between Fe and Pt atoms leads to a decrease of the electronic density at the Fermi level, with reduction of the magnetic moment of the iron atoms. On the other hand, the atomic disorder increases the volume of the crystallographic unit cell giving a stronger localization of the 3d electrons carrying the magnetism, increasing the magnetic moment of iron atoms.

Depending on the alloy composition and the degree of ordering of the atoms, the magnetic moment can vary from $2.45\mu_B$ to $2.9\mu_B$. For an ordered $\text{Fe}_{59}\text{Pt}_{41}$ compound, the two effects mentioned above compensate and the magnetism is hardly sensitive to the Fe content. The compounds presenting the best properties are equiatomic Fe-Pt compounds well ordered in the L10 Phase : they combine strong magnetization and high Curie temperature.

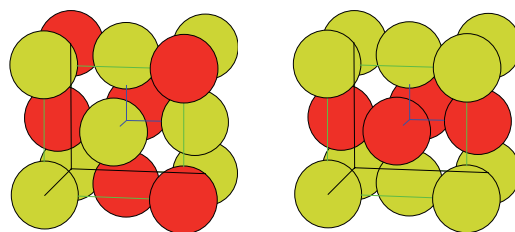


Fig. 1: Atomic arrangement of Fe-Pt alloys in the disordered state A1 (at left) and the ordered state L10 (at right). The two colours represent the two different atoms.

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Further reading :

- "Ordering of nanocrystalline Fe-Pt alloys studied by in situ powder neutron diffraction", J. Lyubina, O. Isnard, I. O. Gutfleisch, K.H. Müller, L. Schultz, J. Appl. Phys. 100 (2006) 094308
- "Influence of composition and order on the magnetism of Fe-Pt alloys : Neutron powder diffraction and theory", J. Lyubina, I. Opahle, M. Richter, O. Gutfleisch, K.H. Müller, L. Schultz, O. Isnard Appl. Phys. Letter 89 (2006) 032506.

Langasites make up a very large series of compounds (more than 100 have been identified), discovered in the 1980s in the former Soviet Union. The archetype is $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (hence the name). These materials are known mainly for their piezoelectric properties, which make them serious competitors to quartz, especially in filtering applications using surface acoustic waves in mobile phones. We are interested in the magnetism of certain compounds of this class where the rare earth ion carries a magnetic moment.

Figure 1 shows the crystal structure of langasites. The rare earth ions (coloured violet) are arranged on a lattice of triangles that share vertices, called the "kagome" lattice (Japanese name for a cane basket of the same shape). This arrangement favors the appearance of magnetic frustration phenomena when the interactions are antiferromagnetic : the magnetic moments which tend to orient anti-parallel to each other cannot do so because of the lattice topology. The "compromises" found by magnetic systems of this type lead to "exotic" highly degenerate ground states. Very strong fluctuations persist down to low temperatures, which translates the difficulty of establishing long distance magnetic order.

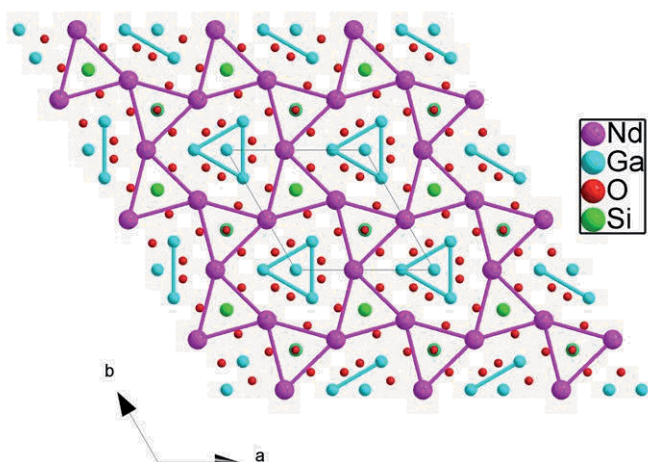


Fig. 1 : Structure of $\text{Nd}_3\text{Ga}_5\text{SiO}_{14}$ looking along the c axis. The magnetic ions Nd^{3+} (violet coloured) form a kagome lattice.

Materials showing such phenomena are extremely rare. Amongst them, rare earth langasites are

especially interesting because they can be synthesized as large, high quality monocrystals usable for the broad range of experiments (neutron spectroscopy, NMR, muons, etc..) necessary to characterize and understand the phenomena at the base of magnetic frustration.

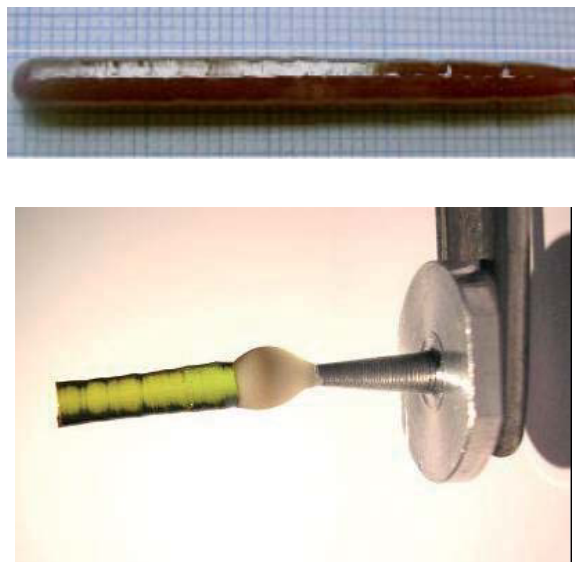


Fig. 2 : Monocrystals of $\text{Nd}_3\text{Ga}_5\text{SiO}_{14}$ (at top) and $\text{Pr}_3\text{Ga}_5\text{SiO}_{14}$ (at bottom) synthesized in an image furnace.

For this study, we were able to do the first synthesis of centimetre size monocrystals of the compounds $\text{Nd}_3\text{Ga}_5\text{SiO}_{14}$ and $\text{Pr}_3\text{Ga}_5\text{SiO}_{14}$ using the zone melting method in an image furnace (Figure 2). The magnetic measurements done on these samples have confirmed the antiferromagnetic nature of the interactions and the absence of ordering at low temperature. Inelastic neutron scattering measurements are being done to look for fluctuations down to low temperatures, typical of the frustrated magnetic state.

At present, we are extending the study of magnetic langasites to include their magneto-electric and magneto-optic (multiferroism) properties, and also their non-linear optical properties. This project has support from the Agence Nationale pour la Recherche.

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Further reading :

- "Magnetic frustration on a Kagomé lattice in $R_3\text{Ga}_5\text{SiO}_{14}$ Langasite with $R=\text{Nd}, \text{Pr}$ ", Bordet P. et al., Journal of Physics-Condensed Matter 18-22,5147 (2006).
- "Spin-liquid correlations in the Nd-Langasite anisotropic Kagomé antiferromagnet" Robert, J et al., Phys. Rev. Lett., 96,197205 (2006); Physical Review Letters, 97, 259901(E) (2006).

Protein and ADN biochips have become key tools in clinical research (for diagnostic tests, new therapies...). But their enormous potential is under used because they have only low sensitivity at present. Even if fluorescence biochips are the most used at the present time, they are less sensitive than chips using radioactive tracers and do not allow analysis of precious and rare clinical samples, or genes and proteins present in low proportions. Detection in this kind of sensor is usually achieved by reactivation of the luminescence of the "signal function" entities. In our case, the latter are organic nanocrystals presenting high luminescence intensities in the crystalline state. To develop a biochip, the nanocrystals are "functionalised" by grafting onto their surface half-strands of DNA carrying a probe molecule. The probe molecule totally inhibits the fluorescence of the nanocrystals. When half strands of DNA identical to those carried by the sensor are present in the aqueous solution being analyzed, they can hybridize with them. This will modify the state of the probe molecule (change its position, conformation, absorption spectrum....) such that it no longer inhibits fluorescence of the nanocrystal. One then gets detection of the specific DNA strands by detecting the reactivation of the fluorescence of some of the nanocrystals.

For several years, we have been growing organic nanocrystals in the pores of thin films of sol-gel silicates. In 2006, we mastered etching of the sol-gel surfaces by slow dissolution in basic aqueous solution (2-3 nm/hour). In this way, we get emergence of the organic nanocrystals while conserving the initial surface roughness, of about 0.5 nm on average, for the silicated layer. The conservation of very low roughness illustrates the perfect control of the etching procedure; operating by a process of dissolution by molecular monolayers, it is very homogeneous in thickness over the whole nanocomposite deposit (CNRS patent-March 2007). Our procedure yields nanocrystals mechanically stabilized by silicated layers. Since they are in direct contact with the environment, their direct functionalization is possible for detection of macromolecules in aqueous solution (see Figure1).

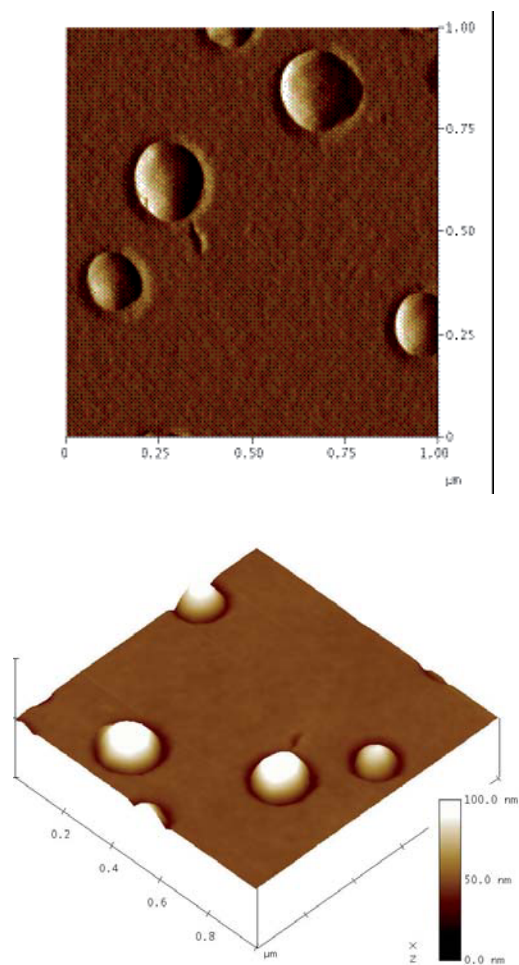


Fig. 1 : Atomic Force Microscopy images of a partially etched thin film showing emergent nanocrystals.

Moreover, these nanocrystals with size several tens of nm are made up of a very large number of fluorescent molecules (10^4 - 10^6), giving high absorption cross-sections and fluorescence intensities. So the new type of high luminosity nanosensor resulting from our dissolution procedure should lead to new fluorescence biochips 100 to 1000 times more sensitive than to-day's. Their development should give the company GENEWAVE, at Polytechnique-Palaiseau, a strong position in the market for next generation biochips (ANR "Ultra Bright Biochips" of the "Biotechnology Innovation Network").

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Further reading :

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An important issue in present developments in optics is controlling light (guiding, localisation, focussing etc) at the sub-wavelength scale. One reason for this is that electronics is now reaching an intrinsic limit related to the time for transport of numerical information from one point to another in the processor. Light, which travels much faster than electrons, could provide a solution to this problem if it becomes possible to make optical components at the scale of several tens of nanometres, that is smaller than the light wavelength.

Beyond sub-wavelength optics, control of the localisation of strong electromagnetic fields should also lead to development of ultra-sensitive optical spectroscopy techniques, in particular Surface Enhanced Raman Scattering (SERS).

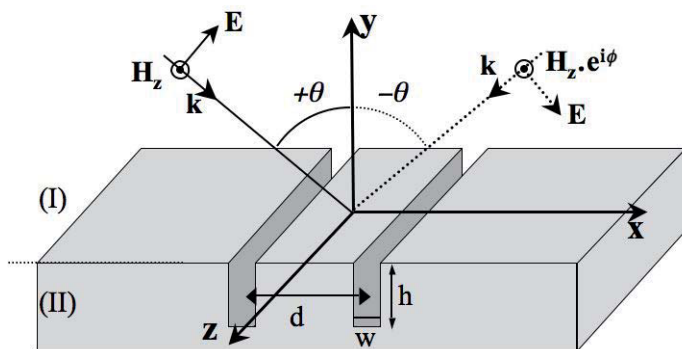


Fig.1 : The system studied, with $d=0.5 \mu\text{m}$, $h=10.5$, $w=0.2 \mu\text{m}$

In this context, we have done a theoretical study of the very simple metallic system represented in Figure 1 consisting of two deep rectangular cavities with sub-wavelength openings. When illuminated by an incident wave with its electric field in the plane of incidence, this system sustains electromagnetic resonances, the surface plasmons, which induce localisation of the electromagnetic energy at the system's surface or in its cavities. In the latter case, the field is effectively confined and concentrated in volumes inferior to that

allowed for the incident light. In addition, the electromagnetic energy localised in each cavity is about 500 times more intense than the incident energy. Last, we have shown that the localisation position is controllable by adding a second incident wave, dephased by ϕ with respect to the first wave (Figure 2).

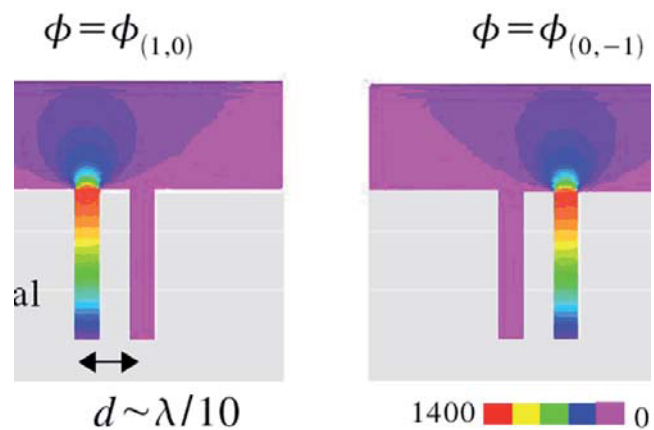


Fig.2 : Map of field intensity near the surface. The field can be localised in one or the other cavity by the choice of dephasing ϕ .

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• "Controlling strong electromagnetic fields at subwavelength scales"
J. Le Perchec, P. Quémerais, A. Barbara, T. Lopez-Rios, Phys. Rev. Lett 97, 036405 (2006)

In heterogeneous catalysis, processes involving nanometre size particles have been known for a long time. But studies at this scale have received a new impetus from the discovery that gold, in the form of nanoparticles supported on an oxide, can become a very active catalyst although normally it is quite inert. It can then catalyse the oxidation of carbon monoxide starting from room temperature. The origin of this behaviour is controversial but clearly the size and the morphology of the nanoparticles play a crucial role: active atoms on ridges, on the perimeter,... quantum effects due to the small size,... etc.

To elucidate such questions, new experimental tools must be developed to control the production of model catalysts (their size, their dispersion, their interaction with the substrate...) and also to observe their evolution during the reaction itself. The apparatus we have constructed is a response to these objectives. Built to operate on the BM32 beam line at the European Synchrotron Radiation Facility (ESRF), it enables deposition of nanocatalysers under ultra high vacuum, followed by their transfer into a reaction chamber. There, their catalytic activity is monitored while doing measurements of Grazing Incidence X-Ray Diffraction (GIXD) and Grazing Incidence Small Angle X-Ray Scattering (GISAXS). These two techniques provide structural information (crystallography, interatomic distances, epitaxial relation) and the morphology (size, shape and distribution of aggregates...). The combination of these two approaches, with the added possibility of "post-mortem" Auger spectroscopy, constitutes an instrument which is unique at the present time.

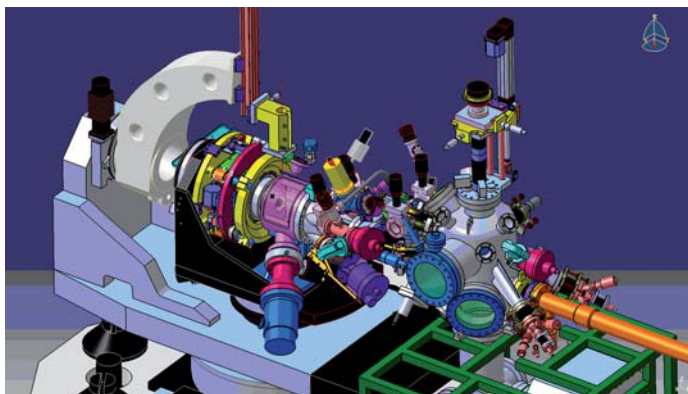


Fig. 1: Apparatus for monitoring nanoparticle reactions in real time by diffraction and scattering of X-Rays

The overall performance of our apparatus has now been validated by an in-situ study by X-Ray Diffraction and by GISAXS of gold nanoparticles deposited on (110) oriented TiO_2 under oxygen and during the oxidation of CO. This study was done for amounts of gold equivalent to various thicknesses between 0.25 and 3.0 atomic monolayers. Despite the very small quantity of reactive atoms we could detect the oxidation reaction of CO at 200°C, by mass spectrometry.

Figure 2 shows, for nanoparticles of mean size 1 and 2 nm, the variation of the diffracted intensity as a function of the rotation angle around a gold diffraction peak. Exposure to 20 mBar of oxygen induces a first change of the spectrum obtained, showing there is interaction of oxygen with the nanoparticles. Reaction occurs when CO is added (here 0.1 mBar). It gives a much more significant change of the spectrum, indicating a restructuring of the nanoparticles. Analysis of the whole set of data is being carried out in order to understand the significance of these variations.

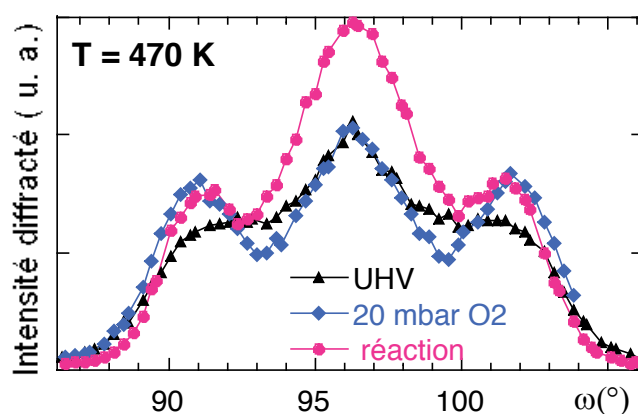


Fig. 2: Catalysis of CO_2 on gold nanoparticles, monitored in real time by X-Ray Diffraction.

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Further reading :

- "A new reactor dedicated to in operando studies of model catalysts by means of surface X-Ray Diffraction and Grazing incidence small angle X-ray scattering", M.-C. Saint-Lager, A. Bailly, P. Dolle, R. Baudouin-Savois, P. Taunier, S. Garaudée, S. Douillet, O. Geaymond, S. Cuccaro, G. Perroux, O. Tissot, J.-S. Micha, O. Ulrich, F. Rieutord, Rev. Sci. Inst. 78, 083902 (2007).
- "Size-and support-dependency in the catalysis of gold", M. Haruta, Catal Today 36 (1997) 153.

A new family of very high pressure valves, operating up to 1.5 GPa (15000 Bars) has been developed recently in the framework of the CNRS's High Pressure Network (Réseau des Hautes Pressions, <http://www.reseauhpc.org>). This work is the subject of a patent application.

The operating principle of these isolation valves is based on the elastic deformation of materials and is characterized by the absence of a stuffing box (O-ring) (Figure 1). This is a real innovation for a flexible seal between the valve body and the needle stem is a source of many problems: leaks, pollution, and above all large friction effects requiring high force for opening/closing the valve and causing large hysteresis.

In the 1.5 GPa version, the opening and closing operations are performed via a hydraulic pressure, allowing very fine adjustment of flow rates bubble by bubble at 1 GPa). The 0.2 GPa version, a less expensive construction, is operated by compressed air (5 Bars). A licensing arrangement has been concluded with Autoclave Engineers France for marketing this device. A third, 0.5 GPa version is also being developed. Based on the same principles as the 0.2 GPa version, it will allow higher flow-rates.

The novel characteristics of the 0.2 GPa valve (Figure 2) have led to development of an apparatus for regulating gas pressures 0-2000 Bars applied to a chamber of small volume (5cm³) for supercritical fluid work. It is used to automate the

changes of threshold pressure for internally heated autoclaves used on beam lines BM30 and 32 at the European Synchrotron Research Facility.

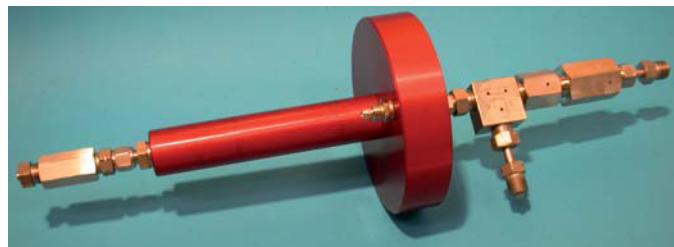


Fig. 2 : High Pressure Valve, 0.2 GPa version

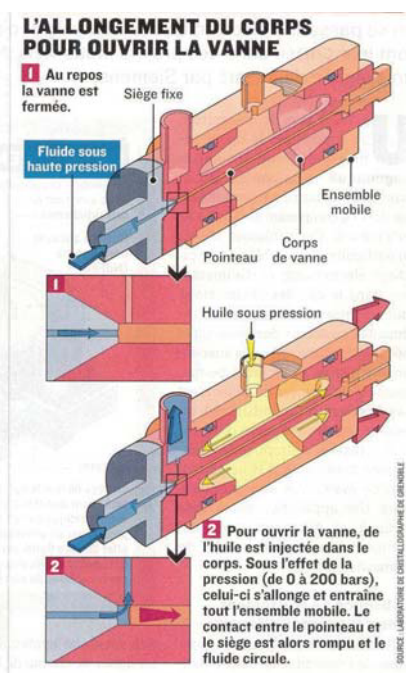


Fig. 1 : Operating principle of the high pressure valves

The system is presented as an easily transportable 19 inch rack containing a two loop programmer-regulator, which gives precise control of the pressure inside an experiment chamber via a series or ethernet link. The pressure generator is a metallic membrane compressor, which can be either pneumatic or electric. The first control loop regulates the pressure in a 50 cm³ buffer reservoir, which handles the rapid pressure variations that occur when the compressor starts up. A discharge valve, manual or automatic, is placed on the reservoir. The novel aspect of the apparatus concerns the second control loop. Two 0.2 GPa valves (one to increase the pressure and the other to decrease it) are operated by air fluxes coming from compressed air, proportional valves (5 bars), which are themselves electrically driven by the proportional analogue signal (0/10V) of the regulator. Optimisation of the PID parameters of this second loop and the absence of valve hysteresis provide extremely fine pressure control (0.1 Bars at 2000 Bars). System security is ensured electronically using the regulator's alarm relays (upper threshold or variation rate) and physically by a rupture disk installed in the pressure circuit. Since the regulator is a programmer, the system can generate varied pressure cycles including ramps (typical rates 50 Bars/minute), plateaux and jumps.

The associated technology is being transferred to industry by arrangement with Autoclave Engineers France. This work was also presented at the 5th forum on High Pressure Technology at Monthieux in November 2006.

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Further reading :

- Very high pressure valves, Patent CNRS n° 04 00 515.
- R. Bruyère, A. Prat, J.L. Hazemann Device for regulating a pressure applied to a small volume (5 cm³) operating from 0 à 200MPa of Helium, 5th forum on High Pressure Technology, Monthieux (November 2006)

Grenoble, April 26th, 2007

The Néel Institute is a laboratory of the CNRS and the Joseph Fourier University of Grenoble, with interdisciplinary research activities spanning many fields of physics and chemistry. Its creation on 1st January 2007 followed a year 2006 marked by the high scientific productivity of our constituent research teams and by the dedicated efforts of all our staff to build a bright future for the new Institute.

The remarkable creativity of our researchers in 2006 continues a longstanding tradition. It is a real pleasure to point to our recent publications in "Nature" and "Science" (ten over the last 12 months) and the many letters and articles in other highly-regarded journals.

Our future will also be shaped by our recent successes in winning funding for such initiatives as a major nanosciences partnership with the Commissariat à l'Energie Atomique (CEA), the Joseph Fourier University (UJF) and the Grenoble Institute of Technology (INPG), and for a long term research contract between the French government and the Rhône-Alpes Region.

Just as important has been our part in leadership, coordination and promotion of science, especially in condensed matter physics, at the local, regional and national levels, and our organisation of national and international conferences. Let us cite our Institute's major role in the new Rhône-Alpes Centre of Competence "C'Nano", an important component of the "NanoSci-European Research Area" project, administered by the CNRS for the European Union's ERA-NET Scheme.

The human motor of these varied activities is the quality of all our staff in the entire range of their different professions. The international reputation of the Néel Institute's research teams will continue to flourish, drawing on their strengths in four key domains :

- innovation in experimentation at the extreme limits of the technically possible*
- mastery of the manufacture of the materials, objects and devices to be studied experimentally*
- theory closely associated with experiment, but also pioneering in untouched fields*
- fostering partnerships with industry at both national and international levels.*

Situated on the CNRS-UJF campus in Grenoble's "Polygone Scientifique", the Néel Institute has deep roots in the exceptional scientific environment provided by the city's many other research centres, notably the Joseph Fourier University, the Grenoble Institute of Technology, the CEA, and the two European Large Instruments : the Institut Laue Langevin (ILL) and the European Synchrotron Radiation Facility (ESRF).

At the heart of the Néel Institute's research endeavours are 19 talented groups and 20 technology "poles" and services, with their state of the art techniques, their success in publishing in the best journals and in securing patents for their discoveries. Our Institute offers an ideal environment for young scientists and students wishing to develop their potential at the highest international level. Ph.D. training available at the Institute is an excellent springboard for a career in research, or in engineering at top world companies.

Alain Fontaine
Director

Institut NEEL is a new research centre created by the merging of four independent CNRS laboratories of Grenoble's "Polygone Scientifique" and four external research groups. Physics and chemistry are strongly linked within its three interdisciplinary departments : *Condensed Matter and Low Temperatures*, *Nanosciences and Condensed Matter*, *Materials & Functions*.

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**More than 100 invited talks per year in international conferences, 400 articles in international journals including 50 letters : PRL, APL, Europhysics Lett., Optics Letters, ... are produced by 180 researchers (CNRS scientists and university lecturers), 130 support staff (engineers, technicians and administrators) and more than 100 graduate students, post-docs and visitors.*

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