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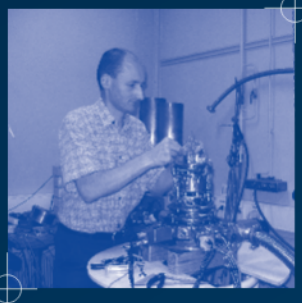
highlights 1



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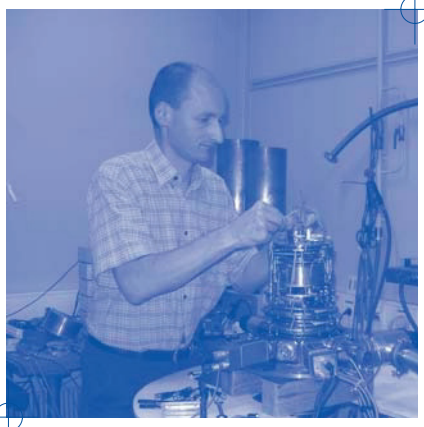
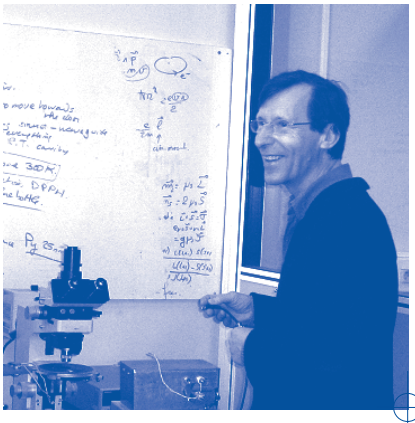
Wolfgang WERNSDORFER



Prix Olivier Khan 2006

Dominique GIVORD



Grand Prix Louis Néel 2006

UNIVERSITE JOSEPH FOURIER SCIENCES. TECHNOLOGIE. SANTÉ

Highlights - *Number 1*

The Néel Institute came into existence on 1st January 2007. It was officially inaugurated on the 27th April 2007 by the Director-General of the CNRS and the President of Joseph Fourier University in the presence of representatives of the Rhone-Alpes Region and the City of Grenoble. On that occasion, a collection of research Highlights was printed, illustrating work done in the year 2006 by the foundation personnel of the Institute. That first booklet was labelled No. 0 of a series which is to be edited twice yearly from now on. We are pleased to present here our issue No. 1, which contains summary descriptions of ten research results published in the first half of 2007.

These ten Highlights illustrate two essential pillars of the scientific strength of our Institute :

** Mastery of the samples (their making, their properties) was the key factor in demonstrating the following new concepts :*

- *superconductivity perturbed by charge density waves, and co-existence of two "superconductors in the same material",*
- *control of the coercive field in a magnetic metal by applying an electric field,*
- *creation of a new type of spin qu-bit, using rare earth ions,*
- *creation of a new state of light, the "photon triplet".*

** Expertise in high-level instrumentation, developed in particular by the Institute's technical poles and services, yielded four of the Highlights :*

- *extreme cryogenics without a cryogenic fluids supply (in collaboration with Air Liquide)*
- *pico-calorimetry,*
- *"intrication" of AFM and STM at very low temperature for imaging nanocircuits,*
- *combined X-Ray microanalysis and Scanning Electron Microscopy.*

Undeniably, the main vocation of our laboratory is fundamental research. However, we are also constantly involved in the creation of intellectual property and in the transfer of our know-how to industry. This is illustrated in these Highlights by the energy programme with storage of hydrogen in magnesium metal (two patents and technology transfer to the MCP Company of Romans-Drôme).

The first Grand Prix Louis Néel (2006) was awarded to the Institute's Dominique Givord in Lyon on 7 February 2007. This prize was established by the Groupe d'action pour la Physique (G2P) federation of nine French learned societies. It rewards "outstanding research work in the physical sciences and an exemplary career associated with technological developments directly linked to industry".

Our principal resource is our personnel. This year, twelve new permanent scientists (seven university staff and five CNRS researchers) along with three technical and administrative staff will reinforce our numbers. This is to be compared to the number of publishing scientists, 150 in 2006 (70% CNRS, 30% Joseph Fourier University, one Grenoble Institute of Technology).

We emphasize again that originality and excellence are the keys to our Institute's future. And they are essential assets for attracting Ph.D. students and post-docs and training them for careers to be driven by their own creativity and scientific skills.

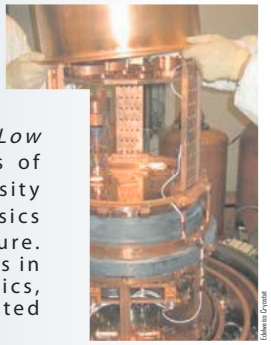
Alain FONTAINE
Director

DÉPARTEMENT

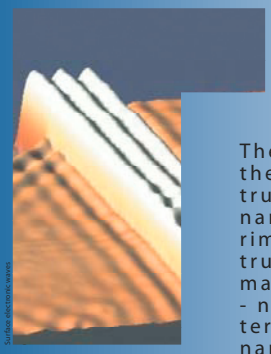
MCBT

MATIÈRE CONDENSÉE ET BASSES TEMPÉRATURES

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 µK and room temperature. The department develops transverse activities in cryogenic electrotechnology, fluid mechanics, astronomy, the life sciences and associated applications (cryogenics, aero-space).



Eddiwatax Cryostat



Surface electronic waves

DÉPARTEMENT

NANO

NANOSCIENCES

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 semi-conductors, metals, magnetic materials and molecules... Their fabrication at the nanometer scale - molecular films, nanowires, nanotubes, quantum wells and dots - leads to novel functions resulting from the most fundamental aspects of quantum physics.

DÉPARTEMENT

MCMF

MATIÈRE CONDENSÉE MATÉRIAUX & FONCTIONS

The Department of *Condensed Matter, Materials & Functions* fosters fundamental research of materials and their applications. It has wide range experimental and theoretical expertises inmaterial 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 thematics networks of the CNRS.

Image furnace for crystal growth

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How does a two gap superconductor react to a magnetic field?

The discovery in 2001 of a superconducting transition at 40 K in MgB_2 generated excitement beyond the observation of an "abnormally" high critical temperature.

In fact, calculations of the electronic structure showed very quickly that the presence of Mg^{2+} ions between the boron sheets leads to a doping of their valence bonds (σ bonds, of type sp^2) and that the holes so formed are especially well coupled to the phonons, thus giving rise to a high critical temperature. The origin of the superconductivity was thus quickly understood, but the same calculations also showed that the Fermi level intersects *a second band* (the boron $\neq$ bonds) whose electron-phonon coupling is much less efficient; for the first time, a system had been discovered where *two superconductors coexist in the same material*. These two superconducting bands are nevertheless weakly coupled with each other, and superconductivity can be induced in the $\neq$ band up to 40K (the critical temperature for this band would not exceed 10 K in the absence of coupling).

The question then was to understand the effect of a magnetic field on the two superconductors. By combining measurements of ac- specific heat (C_p) and local magnetization, we have determined in detail the variation of the Sommerfeld coefficient ($\gamma = \lim(C_p/T)$ as T goes to zero), as a function of the magnetic field B present in the material (see Fig.1), as well as the dependence of this coefficient on the field orientation (insert in Fig. 1).

We have shown that the coupling between the bands also allows superconductivity to be induced in the $\neq$ band for values of B much greater than its "intrinsic" critical field. But this cannot occur unless the coherence length (ξ_π) associated with this band decreases with B. Nevertheless, contrary to the σ band, which anisotropy constant is of the order of 5 to 6, the $\neq$ band is practically isotropic. So this decrease stops when ξ_π reaches the largest of the values of ξ_σ (i.e. for B parallel to the c axis). Beyond this value of B ($=B_{c2}^{c}$), superconductivity is totally destroyed in the π band for all field orientations, and then survives in the σ band only .

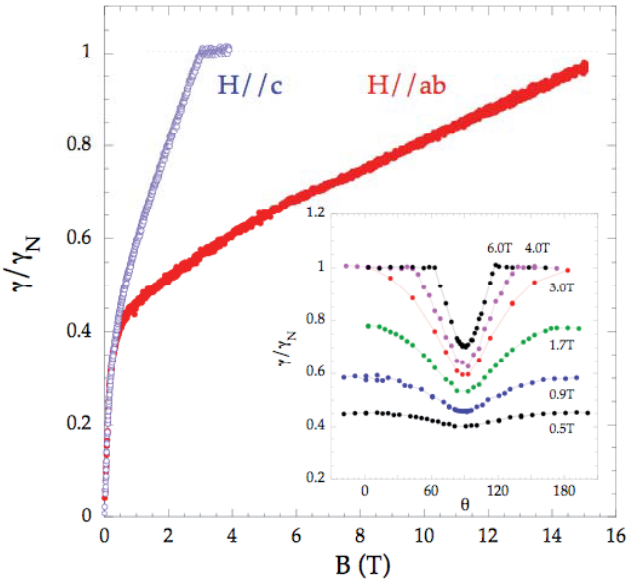

Fig. 1 : Magnetic field dependence of the Sommerfeld coefficient (γ) for an MgB_2 monocrystal along the two principal crystallographic directions. The insert shows the angular dependence of γ for different values of the applied field (θ=0 corresponds to B parallel to c), γ_N being the value of γ in the normal state

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Further reading :

• "Influence of Al doping on the critical fields and gap values in Magnetesium diboride single crystals", T. Klein et al. Phys. Rev. Lett. (April 2007)

Micro-calorimetric sensor for nano-material specific heat measurement

Starting a few decades ago, there has been a need to carry out thermal and micro-calorimetric measurements on very small samples in various scientific fields such as nano-sciences, biophysics or condensed matter.

Specifically, the study of high or low T_c superconductors defined a characteristic mass of about a few μg. By using microelectronics technologies, the miniaturization of the sensors attained this typical mass for thermal measurements. But now, the miniaturization race in microelectronics has opened up the perspective of reducing this mass-scale by another three decades. At the nanometric scale, new physical, meso-physical or quantum phenomena appear which are very interesting for fundamental research. The experience of the Néel Institute's "Capteurs Thermométriques et Calorimétrie" technology pool in design and realisation of low mass micro-calorimetric sensors has led to a new micro-sensor perfectly adapted for the detection of nano-joule to pico-joule thermal effects in thin films. The photo depicts a parylene suspended micro-sensor dedicated to specific heat measurements of magnetic thin film nano-materials. The sensitive central area is of the order of $1mm^2$. The thickness of the membrane is less than 1 μm. The addenda (heater, thermometer, membrane) have a heat capacity contribution of about 1 μJ/K at 100 K. With an easily available specific heat resolution of $\Delta C/C = 10^{-5}$, detection of heat capacity variations of about 0,1 pJ/K becomes possible. The central area on which the sample is deposited is connected to the heat bath via four arms of 50 μm width and of 1 mm length. The thermal time constant of this sensor is about 1s, which makes it easily possible to do adiabatic measurements. The possibilities of this sensor already have been tested. This first prototype, parylene membrane suspended thermal micro-sensor opens up a very large field of investigation from low temperature to room temperature physics.

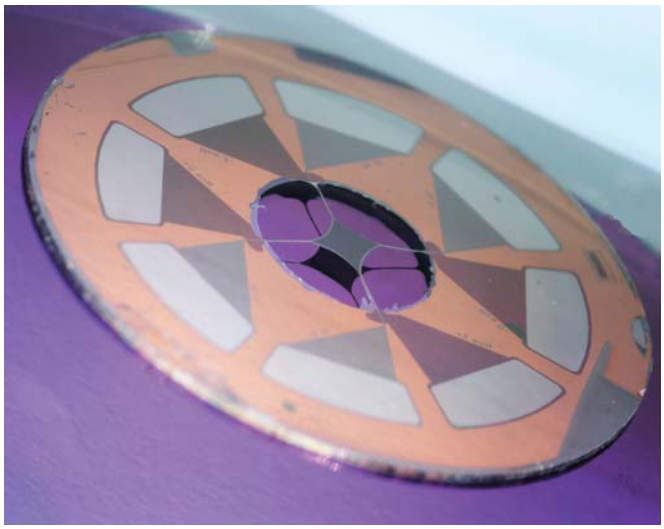

Fig. : Parylene suspended micro-calorimetric sensor for magnetic nano-material specific heat measurements. The sensitive central area on which the magnetic nano-materials are deposited is only $1mm^2$. This central part already contains the thermometer and the heater necessary for the measurement. It is thermally isolated from the copper "sample-holder" (thermal bath) via four parylene arms which carry the sensor element wires.

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Further reading :

• " A new sensor for thermodynamic measurements of magnetization reversal in magnetic nanomaterials", O. Bourgeois, C. Macovei, E. André, J.-L. Garden, J. Chaussy, D. Givord, Journal of Magnetism and Magnetic Materials 316 (2007), e94-e96

Autonomous dilution refrigerator

Following the Grenoble tradition of flirting with the Absolute Zero of temperature and facilitating access to these extreme conditions, a new type of dilution refrigerator has been realised, in the framework of a strong collaboration between the CNRS and the Air Liquide company.

Classical dilution refrigerators require a substantial infrastructure, in particular a systematic supply and transfer of cryogenic fluids (liquid nitrogen and helium). This new refrigerator is totally autonomous, thanks to the use of a pulse-tube cooler. The association of the refrigerator and the cooler required a thorough analysis of the thermal properties of the overall system, thus allowing its overall optimisation. The results are outstanding : these new systems reach temperatures as low as a few thousandths of a degree., and this is achieved much faster than with traditional systems.

The fact that these ranges operate without cryogenic fluids opens up a wide range of applications. Laboratories not equipped with liquefaction plants can now perform experiments at the lowest temperatures. The physical properties of materials, for instance, can be investigated by heat capacity or magnetisation measurements as a function of the temperature, providing valuable information on the atomic vibrations, electronic properties, defects, etc. The nanosciences also call on very low temperature studies, because the quantum phenomena ruling the electronic behaviour are most clearly observed in these extreme conditions. Let us also mention ultra-sensitive cryogenic electronics, where electrical noise is strongly reduced by the cold, and the low temperature detectors of cosmic particles which are presently looking for the mysterious Dark Matter that surrounds us, according to the astrophysicists !

Fig. 1 : This autonomous dilution refrigerator, free from cryogenic fluids, has a base temperature of less than one-hundredth of a degree above absolute zero.

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Further reading :

• "Pulse-tube dilution refrigeration below 10 millikelvins", Th. Prouvé, H. Godfrin, C. Gianèse, S. Triqueneaux, A. Ravex, J. of Low Temp. Phys. 148, sept 2007.

A superconductor in the electron waves

At low temperatures, the electrons in metals can become organised in a manner that is periodic at long distance : they concentrate at certain places and the electronic density then forms waves. This well known phenomenon is observed in certain metallic materials called "charge density wave" materials. In another class of metal, the electrons become superconducting when they are cooled below a critical temperature. Microscopically, this state results from the formation of pairs of electrons called Cooper pairs. The two electrons of a Cooper pair are bound by an attractive force that is transmitted via the lattice vibrations (the phonons). When the electrons condense into pairs in the superconducting state, their energy is lowered by a quantity Δ (the superconducting gap) which is closely related to the critical temperature T_C.

We have studied the coexistence of these two types of state in the compound Niobium Selenide $NbSe_2$ in order to learn how superconductivity is affected by charge density waves. $NbSe_2$ is a layered material and the electrons from the Niobium atoms move within the layers whereas the electrons from the selenium atoms move in between the layers. Below 33 K, certain electrons moving in the plane of the layers form a charge density wave. At lower temperature, below its critical temperature of 7 K, $NbSe_2$ becomes superconducting, but with a smaller gap than other superconductors having similar critical temperatures. Is the small size of the gap due to coexistence with the charge density wave, or does it come from a weaker electron-phonon coupling in certain electronic energy bands?
We have done high resolution measurements of the temperature dependence of the penetration length of a magnetic field inside the superconductor (Δλ in Fig. 1). This length is directly related to the supercurrents formed by the condensate of Cooper pairs flowing in a specific crystallographic direction. The width of the superconducting gap can be obtained directly by fitting calculated curves to the experimental data points (Fig. 1), and this for different electron bands. We have demonstrated that the superconducting gap is reduced in at least one of the bands where the electron-phonon coupling is strong. Amongst these bands, one band also carries the charge density wave. From these results, a new mechanism for the origin of multi-band superconductivity might be invoked.

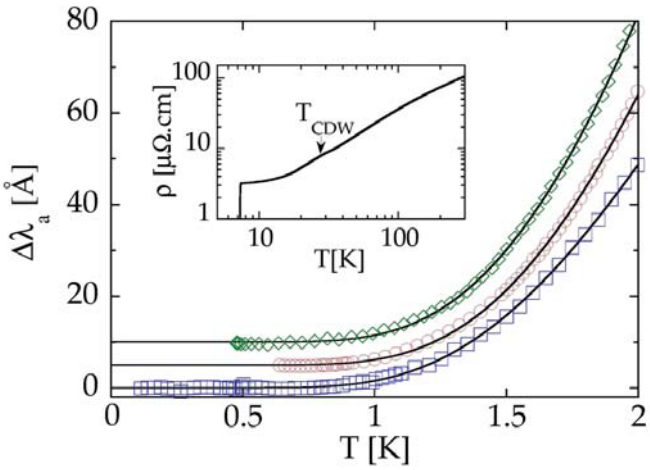

Fig. 1: Data points are temperature dependence, down to very low temperature, of the length of penetration of magnetic field for three samples from different sources. The exponential variation (fitted curves) yields a precise value of the superconducting gap, which is very small for NbSe2. The insert shows a resistivity anomaly at the temperature where the charge density wave (CDW) appears.

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Further reading :

• "Penetration depth study of superconducting gap structure of 2H-$NbSe_2$ ", J.D. Fletcher, A. Carrington, P. Diener, P. Rodière, J.-P. Brison, R. Prozorov, T. Olheiser, et R.W. Giannetta, Phys. Rev. Lett. 98, 057003(2007).

Imaging a nanocircuit by combining Force Microscopy and Tunneling Spectroscopy

Scanning Tunneling Microscopy (STM) provides very highly resolved images of surfaces, making the details of the individual atoms visible. It can also provide a local spectroscopy of the electronic properties of nano-objects with atomic scale resolution. However, requiring a metallic surface, this technique is not well adapted for mesoscopic or nanoscopic structures built on insulating substrates. On the other hand, Atomic Force Microscopy (AFM) can image any kind of surface, but gives no information about electronic properties.

The Néel Institute's «Near Field» research group has developed a new kind of near field microscopy which combines force microscopy with tunneling spectroscopy, working at very low temperatures. This instrument can be used for near field studies of nanostructures with partly insulating surfaces. To achieve this, we use a piezo-electric tuning fork on which we make electrical contact with a tunnelling point. The quartz tuning fork provides its natural rigidity to this hybrid probe, providing excellent stability for the tunnelling point in spectroscopic mode. The very low working temperatures achieved for this microscope (50 mK) guarantee very good energy resolution.

We have studied the local superconducting properties for a sub-micron epitaxial wire of Niobium on sapphire (see Fig. 1). The AFM image enabled us to localize the 8 nm high wire on the insulating sapphire surface. Once the point is positioned on the metal wire, the microscope is switched over to tunnelling mode to do local spectroscopy, measuring the variation of the density of electronic states with position. The results showed an excellent homogeneity of the surface properties.

This new experimental approach opens new perspectives for the measurement of non-equilibrium effects in superconducting nanostructures. We have started up a European (NanoSci-ERA) project working with the universities of Helsinki, Pisa and Delft to study nano-refrigeration in superconducting tunnel junctions.

The samples studied were produced on the "Nanofab" platform of the CNRS-Grenoble. Work with P. Joyez and colleagues was supported by the 2003 AC Nanosciences "AFM-STM-NME".

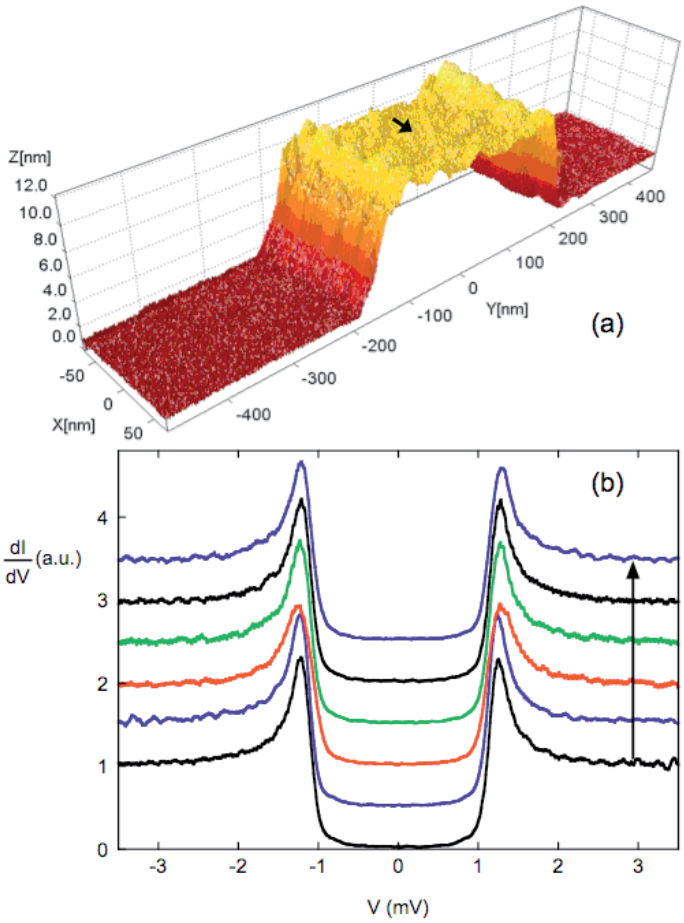

Fig. 1 (a) Atomic Force Microscopy image of a submicron Nb wire grown epitaxially on sapphire (b). Tunneling spectra give the electronic density of states at different points in the nanostructure, in the direction of the arrow drawn in (a).

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Further reading :

• "Combined scanning force microscopy and scanning tunneling spectroscopy of an electronic nano-circuit at very low temperature", Julien Senzier, Pengshun S. Luo and H. Courtois, Applied Physics Letters 90, 043114 (2007).

The quantum bit or "qubit" is the basic memory element of a quantum computer. Some small quantum computers were built already in the 1990s, and progress continues. This is a rapidly expanding field, especially because of its strategic importance : certain algorithms designed for quantum logic would make it possible to do calculations unimaginable on a classical computer. The physical manufacture of the base element, the qubit, is a first necessary step. Each field has its own preferred qubit and for researchers in magnetism it is the spin, already implicated in classical magnetic memories. Two research groups, one from the CNRS and the other from the CEA, have just shown that magnetic ions of rare earths could allow implementation of a quantum computer which would benefit from a new type of spin qubit.

Unlike the classic memory element (the "bit") which has only two states such as |+1> and |-1>, a qubit can have an infinity of states going from |+1> to |-1>, as follows. When spin states |+1> and |-1> are placed in a magnetic field, their energy difference can be brought equal to the energy of an applied microwave radiation field, which will induce transitions between the states : from |+1> to |-1> with absorption of a photon and from |-1> to |+1> with emission of a photon. With an appropriate microwave pulse, one can partially invert the spins. The degree of occupation of the two spin states then oscillates at the Rabi frequency with the spin occupying, at short times, all the states included between |+1> and |-1>. These are the states |u> = a(t)|+1> + b(t)|-1>, where a(t) and b(t) are sinusoidal functions of time. A quantum computer would be made of a hundred or so such qubits capable of being "manipulated" selectively. The main factor slowing the development of such a computer is the phenomenon of loss of coherence, which attenuates the oscillations by interaction with the environment.

The rare earths are a family of magnetic elements known for their large magnetic moments, thus allowing spin manipulations in low magnetic field. Moreover, they have strong hyperfine interactions such that, at low temperature, the sum of the electronic angular momentum J and the nuclear spin I is a "good quantum number". Contrary to other spin qubits, which are either electronic or nuclear spins, rare earth qubits are "electro-nuclear". They can be manipulated just as well by electronic frequencies (Electron Paramagnetic Resonance) or by nuclear frequencies (Nuclear Magnetic Resonance), see Fig. 1. Coherence times of order 10 μs are observed at temperature 2 K, and 300 μs is expected at 1.5 K, which would allow a sufficient number of operations (~10^4) for a quantum calculation. This preliminary work has provided a roadmap for the first French project for implementation of a spin quantum computer, involving the CNRS and the CEA (Commissariat à l'Energie Atomique).

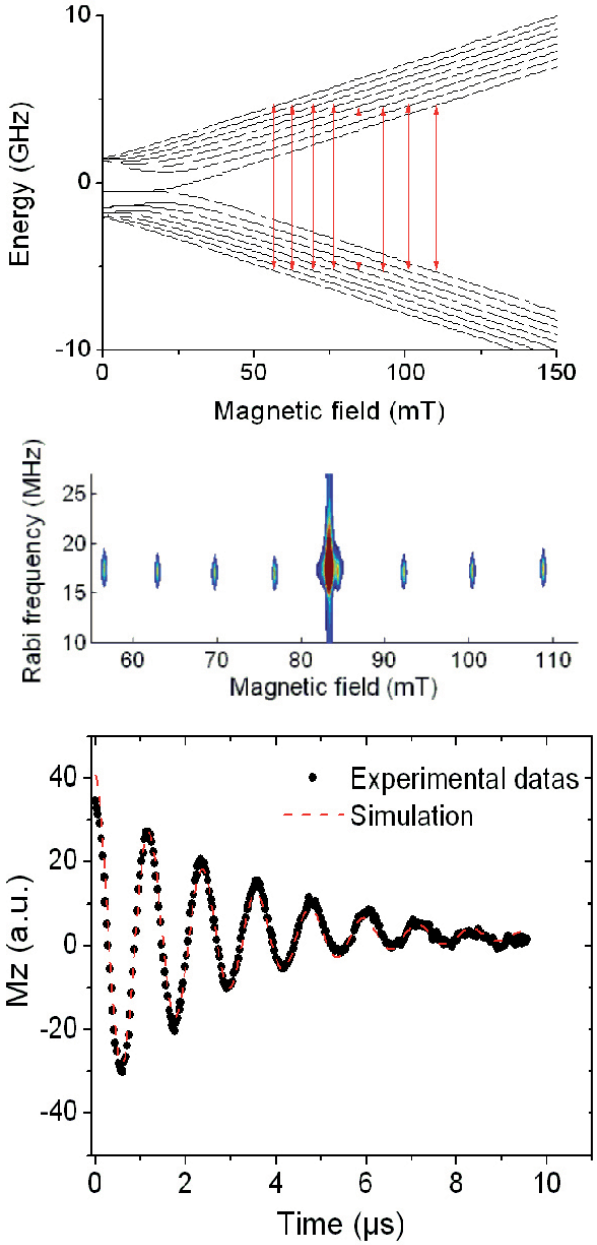

Fig. 1: Middle figure shows frequency of Rabi oscillations measured at 9.7 Ghz on a system of Er^{3+} ions diluted in a $CaWO_4$ matrix (colour scale shows number of ions with Rabi frequency at a given magnetic field). The eight peaks are due to electro-nuclear transitions involving ^{167}Er with nuclear spin I=7/2 and are expected from the calculated, field-induced level splitting shown at top. One can pass from one qubit to the next by a small field change (8 mT). At bottom, Rabi oscillations associated with one of the peaks. They represent the evolution with time of the mixture of states |+1> and |-1>. At instant t, the system is in the state a(t)|+1> + b(t)|-1>.

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Further reading:

•"Rare-earth solid-state qubits" S. Bertaina, S. Gambarelli, A. Tkachuk B. Malkin, A. Stepanov, and B. Barbara, Nature Nanotchnology 2, 39, (2007).

Electric field induced modification of magnetism in ultra-thin metallic films

Iron, cobalt and their alloys are the most common magnetic materials. These are metallic systems in which the electrons responsible for the magnetic properties participate in electrical conduction. Under a voltage V, an electric charge is produced as in a capacitor. An electric field induced modification in the material's magnetic properties is expected, directly linked to the existence of this charge. The charge is proportional to the strength of the electric field E, but also to the surface area of the considered specimen. Thus effects induced by E are expected to be significant in samples with large surface/volume ratio, i.e. nano-objects.

FePt and FePd alloys were chosen as model systems to reveal the effect of an applied electric field on the magnetism of matter. These alloys have high coercivity : after the magnetisation has been saturated along a given direction, it will reverse 180° only when the applied magnetic field reaches the value of the coercive field, $\mu_0 H_c$, which for these systems is typically between 0.1 T and 1 T. Because of the need for the surface atoms to represent a significant fraction of the total number of atoms, ultra-thin films were studied. For the experiments considered here, the samples were immersed in an electrolyte and a voltage of the order of 1 V was applied between the sample and a counter-electrode. Under such conditions, the voltage drop in the electrolyte is almost entirely confined in the Helmoltz double-layer, approximately 1 nm-thick. Under 1V, the resulting electric field amounts to typically 10^9 V/m, and the electric charge to about 0.05 electron/surface atom. For a 2 nm-thick FePt layer (Figure 1), where 10 % of the atoms are surface atoms, a -4.5 % relative change of the coercive field was found when the applied voltage was varied between -0.4 V and -1.0 V. The decrease of H_c is much less for a 4 nm-thick FePt sample (Figure 2). In FePd the coercive field variation is much less than in FePt and it is of opposite sign.

These variations of H_c cannot be directly compared to theoretical calculations since the value of H_c depends upon extrinsic physical parameters such as the crystallite size. However, considering that the magnetocrystalline anisotropy is the fundamental source of magnetic coercivity, it is legitimate to assume that, to first approximation, H_c is proportional to the anisotropy field, H_A. It turns out that the experimental variations in H_c are in agreement, both qualitatively and quantitatively, with calculations of the variations in the anisotropy field to be expected from a change in the number of unpaired d electrons in response to the applied electric field.

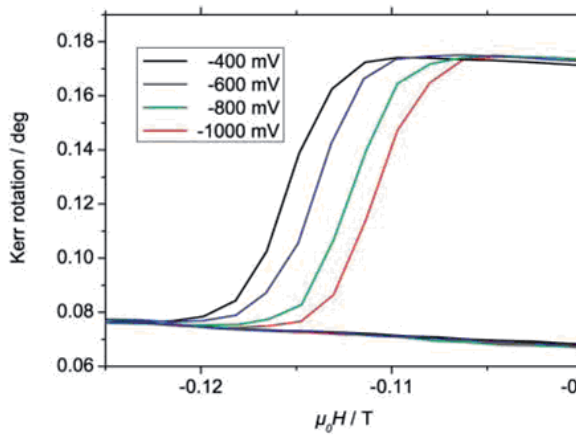

Fig. 1 : Hysteresis cycles for a 2nm thick FePt film measured at voltages between -0.4 V and -1 V.

These results constitute an experimental demonstration that the magnetic properties of metallic systems may be altered under electric field. We are now trying to identify systems where a magnetic transition (e.g. ferromagnetic to antiferromagnetic) could be induced by an electric field. By initially placing the system in a situation where it is close to the magnetic transition, enhanced electric field effects could be achieved. Magnetic nano-systems could be developed which would exploit electric field activation, associating simplicity and energy efficiency.

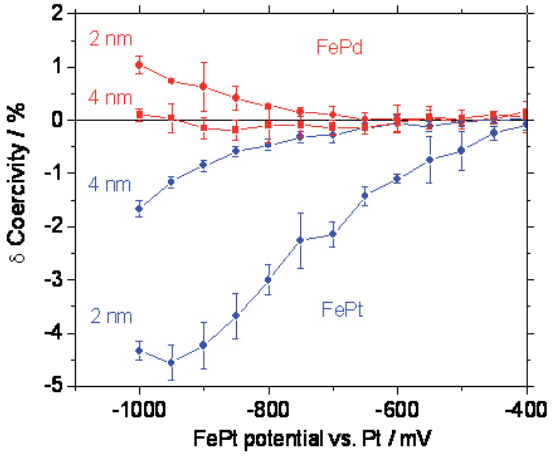

Fig. 2 : Voltage dependence of critical field H_c as a function of the applied voltage, for the two alloys and two thicknesses studied.

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Further reading :

"Electric Field-Induced Modification of Magnetism in Thin-Film Ferromagnets", M. Weisheit et al. Science 315, 349 (2007)

We have achieved the first generation of triple photons, by using a third order nonlinear optical interaction in a $KTiOPO_4$ crystal. During this process, which is governed by the third order electric susceptibility $\chi^{(3)}$, three highly correlated photons, with the energies $\hbar\omega_1$, $\hbar\omega_2$ and $\hbar\omega_3$, are created from the splitting of a photon at $\hbar\omega_0$ as shown in figure 1.

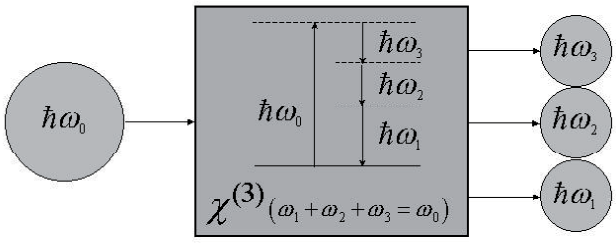

Fig. 1 : photonic diagram corresponding to triple photon generation

These triplets constitute a Greenberger-Horne-Zeilinger (GHZ) state of light that exhibits quantum correlations different from those of twin photons, with Wigner functions presenting quantum interferences and negativities as illustrated in figure 2 [2] .

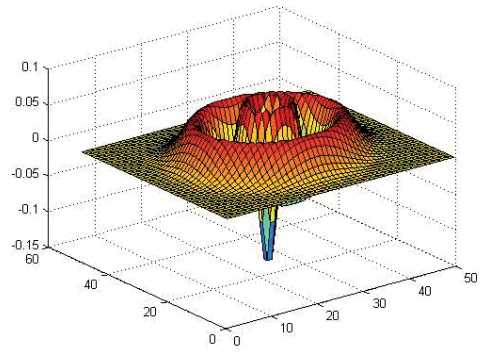

Fig. 2 : example of Wigner function of photons triplets with same frequencies and polarization states.

Triple photons are interesting from a fundamental point of view and also for new schemes of quantum cryptography using three particles. The efficiency of the spontaneous generation of photon triplets being too weak for any measurement, it was necessary to stimulate the process. We used a scheme where the stimulation is performed by two photons at ω_2 and ω_3. Thus the scission of the pump photon at ω_0 leads to a mixed state containing the triplet $\{\omega_1, \omega_2, \omega_3\}$, but also injection photons at ω_2 and ω_3. We used laser beams at $\lambda_0 = 532$ nm, and $\lambda_2 = \lambda_3 = 1665$ nm with orthogonal polarizations, with pulse durations close to 20 ps with a repetition rate of 5 Hz. We obtained as much as 4.5 μJ/pulse at $\lambda_1 = 1474$ nm, which corresponds to 3.34×10^{13} photons per pulse. That means that 3.34×10^{13} $\{\omega_1, \omega_2, \omega_3\}$ triple photons per pulse are created, the generation at ω_1 being symptomatic of triple photon generation. The photons at ω_2 and ω_3 that belong to the triple state are mixed with the injection photons, *i.e.* 4.19×10^{14} photons per pulse at ω_2 and 4.19×10^{14} photons per pulse at ω_3, the number of incident pump photons being 2.0×10^{15} photons per pulse. This is the first demonstration of triple photon generation. This significant result is a fundamental step for new quantum experiments on three-photon GHZ entanglement. Experiments to measure quantum correlations measurement are in progress.

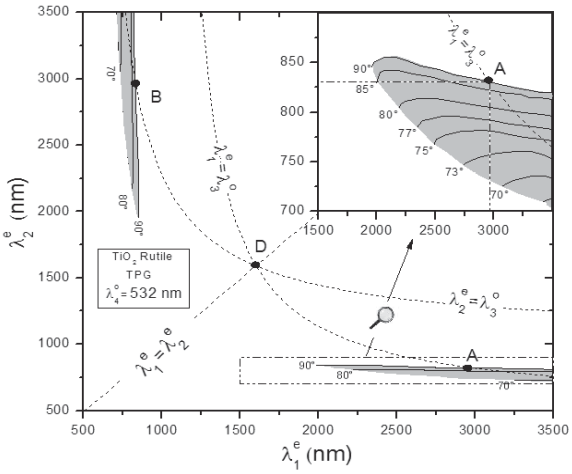

Fig. 3 : Supplementary results : calculated phase-matching curves of triple photon generation [λ^4_o -> λ^{e1} + λ^e_2 + $\lambda_3{}^0$] in TiO_2 rutile. The indices o and e refer to the ordinary and extraordinary polarizations respectively. The three dotted lines correspond to the situations where two wavelengths are equal. Point D corresponds to degeneracy in wavelength, i.e. $\lambda_1{}^e = \lambda_2{}^e = \lambda_3{}^0$. Each continuous line refers to phase-matching directions of equal θ angles.

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Hydrogen can be used in fuel cells to produce electricity via electrochemical reaction with air, without any emission of greenhouse gases. Fuel cell technology is still under development, but hydrogen fuelled thermal engines could provide a reasonable intermediate solution. Although hydrogen is sourced from fossil hydrocarbons at present, it could represent a clean alternative for storage of energy involving zero CO_2 emission if it were itself produced by renewable energy sources. Nevertheless, development of a true "hydrogen economy" requires an efficient and safe method to store hydrogen. Current proposals such as very high (700 Bars) pressure or cryogenic liquid storage are not yet satisfactory in terms of safety, volume density and the energy consumption for densification. Conversely, storage in reversible metal hydrides, from which hydrogen easily desorbs by heating or by lowering the overpressure, makes a much safer solution. The metal is loaded under a H_2 pressure of only 10 Bars, and any brutal release of hydrogen is self-interrupting because the desorption reaction is endothermic.

Magnesium Hydride MgH_2 is an excellent hydrogen storage system since Mg is an abundant, low cost, non-toxic element. Its mass storage capacity is remarkable : up to 7.6% by weight. If the kinetics of hydrogen absorption and desorption are slow for standard Mg powders, the powders can be strongly activated by aggressive ball-milling them together with transition metal elements.

We have investigated the processes occurring in energetic co-milling of poorly reacting MgH_2 with small amounts of transition metals (TMs) such as Ti, V, Nb, etc. We find that the initially micron size crystal grains are restructured at the nanometre scale and that TM nanoparticles are deposited as hydrides TMH_x. This produces a dramatic enhancement of the hydrogen sorption kinetics. The initating role of the TM hydride was seen in neutron diffraction studies at the Institut Laue-Langevin. During hydrogenation, MgH_2 appears only in a second step : the transition metal hydride TMH_x forms first and acts as catalyst for dissociation of hydrogen molecules and the diffusion of the hydrogen into the magnesium.

Two patent applications have been made and the techniques developed here have been transferred to Metals Composites Powders Mg-Serbien, a company specialized in magnesium granulation. At present, 1 kg batches of highly reactive powders are produced at a semi-industrial scale. These powders retain very stable properties through successive absorption/desorption cycles.

A prototype tank to contain MgH_2 has also been developed. The main challenge was to measure and control the heat gradient in the bed of MgH_2, which results from the exothermic nature of the Mg-H reaction and the poor thermal conductivity of MgH_2 powder. That is, charging with hydrogen sharply increases the temperature so that Mg-MgH_2 equilibrium is quickly reached, stopping further hydrogenation. Optimizing heat exchangers has given a much reduced loading time. This first reservoir stores 170 litres gas volume of hydrogen at a volume density comparable to that of liquid hydrogen. A Proton Exchange Membrane Fuel Cell (PEMFC) was fuelled from the reservoir, lighting a halogen lamp for one week.

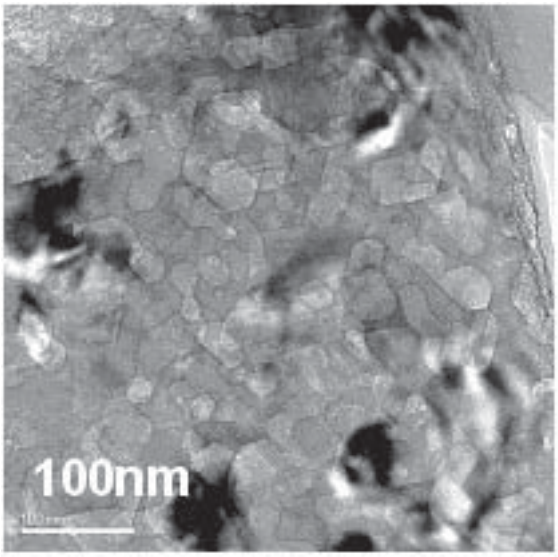

Fig. 1 : Mg nano-crystallites, as observed by HREM after co-milling with transition metals, after hydrogen desorption.

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Characterizing Thin Films by an Electron Beam Probe

The development of materials in the form of very thin films has produced an explosion in the performance of sensors and electronic devices. However, a major problem in thin film applications is the difficulty of obtaining reproducible characteristics. Film properties depend of course on their chemical composition, but also on their thickness. For evaluating these parameters, a powerful tool is provided by coupling X-Ray microanalysis with Scanning Electron Microscopy. This combination can be used both to characterize the morphology of films (deposited in our case by "soft" chemistry, from the vapour phase...) and to perform chemical analyses. The technique is most applicable to electrically conducting materials and is non-destructive. One of its strong points is that it can be used for measurements on buried films in such complex architectures as Si/Mn/Ni/W multilayers.

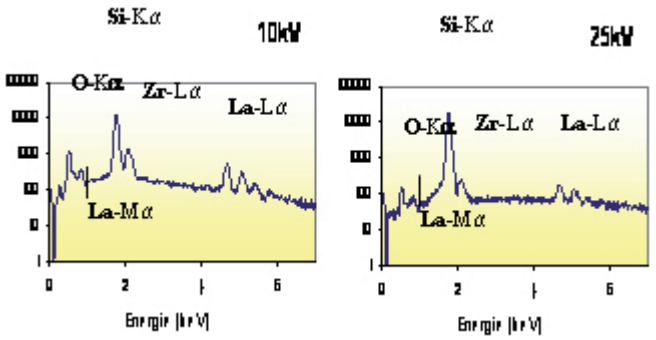

Fig. 1: 1 EDS-X analysis spectra obtained at 10 keV and at 25 keV for a 80nm thick layer of $Zr_2La_20_7$ deposited on silicon. Increasing the energy of the incident electrons increases visibility of the substrate relative to the layer.

We determine chemical composition and thickness of thin films by Energy Dispersive X-ray Spectroscopy (EDS-X) in a Scanning Electron Microscope. Changing the energy of the incident electrons varies the volume of the electron-matter interaction in the sample : at low beam voltage for example, the upper layers are favoured compared to buried layers and the substrate. A multi-layer sample is characterized by doing X-Ray analyses at different beam voltages. The results are treated by off-line calculation software packages (STgem and SAMx) which simulate the depth dependence of the ionisation events and of the emergent X ray intensities. The calculations use the nominal layer architecture as starting point, estimating fluorescence and absorption for its geometry. At the end of an iteration process, curves of predicted relative intensities corresponding to the chemical compositions and thicknesses found are drawn for each chemical element present and compared with the experimental points to validate the analysis. The substrate composition can be determined at the same time.

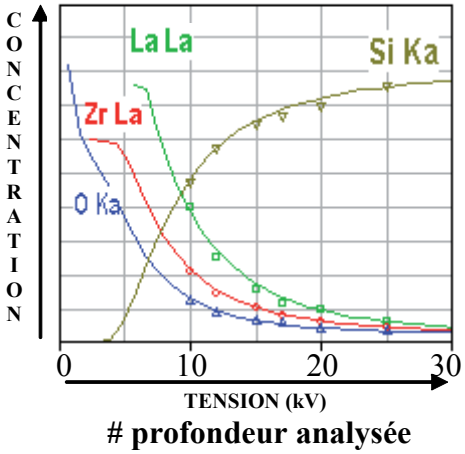

Fig. 2: Curves of the theoretical X-Ray intensities calculated for the thickness and composition found at the end of an iterative calculation: 80 nm layer of $Zr_2La_20_7$ on silicon. The points are experimental values for Si-K, O-K , La-L and Zr-L peaks measured at different beam voltages

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Date of publication : 2007-2

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