HIGHLIGHTS

2017

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NÉEL institut

EDITORIAL

Welcome to this year's edition of the Institut NÉEL's Highlights magazine.

Among many other achievements in physics, chemistry and technology, this issue features a trampoline, some bubbles, and lots of ice! You are in for what we hope will be a pleasant and inspiring scientific tour of some of the many surprises electrons have in store for us when condensed matter is studied at the quantum level.

Using growth reactors under conditions ranging from ultra-high vacuum to high temperatures combined with high pressures or, quite often, exploiting nanofabrication processes, samples of various dimensionalities have been produced : single molecules, quantum dots, 1-Dimensional nanowires and nanotubes, 2D atomically-thin membranes, 3D thin-films, and bulk materials (crystalline or not).

These samples were then studied, frequently under extreme conditions, by advanced optical or electronic probes. Most of these instruments have been designed, assembled or adapted in-house by the Institute's scientific or technological groups. With the help of impressive and original conceptual and numerical tools, our research groups have then predicted or explained, triggered or observed, exotic magnetic orderings, unusual plasmonic and optical behaviours, elusive or optimized charge and spin transport regimes, subgap responses of superconducting resonators… These and other subjects, chosen as representative of the Institut NÉEL's recent achievements, are detailed in the following pages.

I hope you will enjoy the tour…

Like the top of an iceberg, research reports are only the smaller emerging part of greater (ad)ventures: the outcome of any scientific or technological project depends very much on the human relationships it draws on. As concerns the work described here, it is a pleasure to acknowledge the contributions made by the many colleagues with whom technical and scientific ideas were exchanged, and by those who contributed in many other ways to these projects: technicians, engineers, and researchers alike, as well as the administrative and financial staff of the Institut NÉEL. Last but not least, we thank the authors, editors and designers of this issue of our magazine.

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A nano-trampoline to probe quantum behaviour

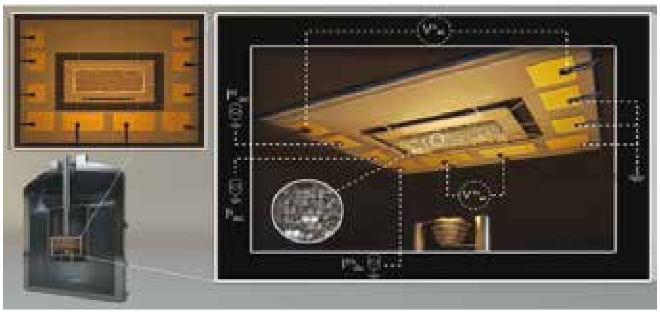
A phase transition is a general term for physical phenomena wherein a system transits from one state to another as a result of changing the temperature. Everyday examples are the transition from ice to water (solid to liquid) at zero degrees centigrade, and from water to vapour (liquid to gas) at 100 degrees. The temperature at which the transition takes place is called the critical point. In recent years the scientific community has shown growing interest in "quantum phase transitions" in which a system transits between two states at or very near absolute zero temperature (-273 degrees) as a result of varying a physical parameter such as magnetic field, pressure or chemical composition instead of temperature. In such systems, a special phenomenon takes place at the critical point, the so-called "quantum criticality". This has now been evidenced for the first time, through specific heat measurements done at temperatures near absolute zero at the Institut NÉEL.

Near a classical critical point, interesting physical phenomena occur. For example, as water is heated, small gas regions start forming and the water bubbles. As the temperature of the liquid is raised towards the critical point the size of the gas bubbles grows. As the size of the bubble becomes comparable to the wavelength of light, the light is scattered and causes the normally transparent liquid to appear "milky" – a phenomenon known as *critical opalescence*.

Something similar occurs in quantum phase transitions near a critical point. Here the change occurs not due to the thermal energy provided to the system by heating but rather by quantum fluctuations. Although absolute zero is not physically attainable, characteristics of the transition can be detected in the system's very low-temperature behaviour near the quantum critical point. Such characteristics include "quantum bubbles" of one phase in the other. The size and lifetime of these quantum bubbles increase as the system is tuned towards the critical point, giving rise to a quantum equivalent of critical opalescence.

The theoretical prediction of such quantum criticality was provided a few decades ago, but how to measure this experimentally has remained a mystery. An answer was recently provided by Institut NÉEL workers, together with Aviad Frydman, visiting from the Bar Ilan University, Israel.

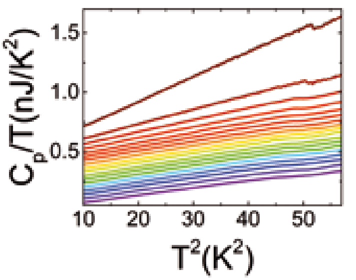
In normal phase transitions there is a unique measurable quantity which is used to detect a critical point. This is the *specific heat* which, well away from any phase transition, measures the amount of heat energy that should be supplied to a system in order to raise its temperature by one degree. Normally, increasing the temperature of a system by two degrees requires twice the energy that is needed for increasing it by one degree. However, close to a phase transition this is no longer the case. Much of the energy is invested in creating the bubbles (or fluctuations) and, therefore, more energy must be invested to generate a similar change in temperature. As a result, the specific heat rises near a critical point and its measurement provides information on the fluctuations.



1 / At top left: *the sample, a thin-film of lead on a silicon membrane, with heater and thermometer stripes.*

At bottom left: *the high-vacuum experimental chamber inside the liquid helium cryostat. The zoom at right shows how the Pb thin-films are deposited onto the membrane, by evaporation from the crucible below it. The additional zoom onto the Pb film shows its granular structure. The film's thickness is increased in-situ between each set of specific-heat measurements.*

Measuring the specific heat of a system close to a *quantum critical point* poses a much greater challenge. Firstly, the measurements must be carried out at very low temperatures. Secondly, the systems under study are very thin layers, in this case, 5 nm to 30 nm thick layers of lead, which require extremely sensitive measurements. The experiment developed at the Institut NÉEL overcame these obstacles by proposing a unique experimental design based on depositing the lead layers on a very thin silicon membrane suspended in vacuum by very narrow bridges, thereby forming a "nano-trampoline". Oscillations of the temperature of the membrane were used to measure the specific heat of the Pb thin-films through a quantum phase transition from a superconducting state to an electrically insulating state at close to absolute zero temperature.



2 / *Specific heat Cp/T vs absolute temperature T squared, for 18 Pb-film thicknesses from 9 nm (at bottom) to 29 nm (at top). Subtraction of very strong phonon contributions to this data revealed the thickness dependence of the electronic specific heat of the Pb films, evidencing the signature of quantum fluctuations at T below the superconducting critical T of bulk lead* $T_c = 7.2$ *K.*

Specific heat measurements were made for 18 different film thicknesses. In this experiment, the parameter driving the quantum phase transition is the film thickness.

The measurement performed here is the first of its kind. The results demonstrate that just as in the case of a thermal phase transition, the specific heat increases similarly in the vicinity of a quantum critical point, and can be used as a probe for quantum criticality. This work is expected to be a milestone in the understanding of physical processes that govern the behaviour of phase transitions in ultrathin systems at low temperatures.

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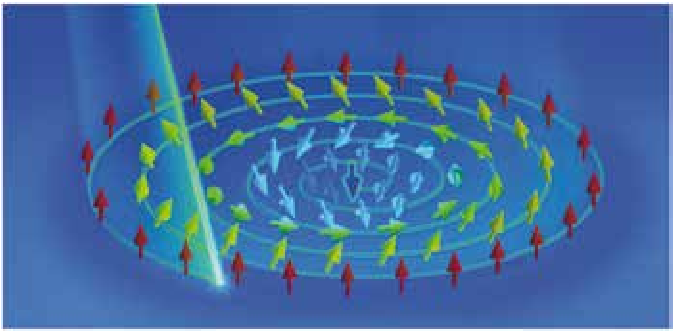
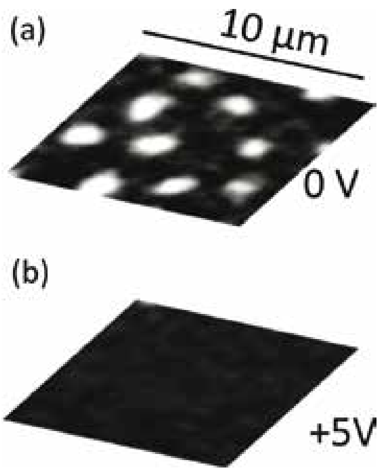
Switching magnetic **skyrmion bubbles** on and off

Skyrmions were at first a theoretical concept formulated by Tony Skyrme in 1962 in the context of nuclear physics, as a model for nucleons. Technically, they are "topological solitons" localized in space and with particle-like properties: they have quantized "topological charges", interact via attractive and repulsive forces, and can condense into ordered phases. The concept of skyrmions has spread over various branches of physics, including especially condensed matter (for example the cases of liquid crystals, quantum Hall magnets and Bose-Einstein condensates). At the Institut NÉEL, we have been studying skyrmion effects in ultrathin-film ferromagnetic metals, *i.e.* systems where the magnetic moments (the spins of the atoms) normally align parallel to each other. In these materials, a skyrmion is an anomaly, a "defect", that can arise spontaneously. It is a swirling spin "texture", a circular region where the spins tilt progressively from "up" at the periphery to "down" at the centre, as illustrated in Fig. 1 below. The compact size and potential stability of such skyrmions make them promising candidates to serve as information carriers in future technologies. But such applications will require creating, deleting, and moving skyrmions, and that at room temperature.



1 / Representation of the spin texture of a magnetic skyrmion. The arrows represent the magnetization direction.

As concerns moving the skyrmions, a recent observation of displacement of skyrmion bubbles (a type of skyrmion with larger dimensions) at room temperature, using relatively low current densities, was very promising. Creation and annihilation of skyrmions has been addressed by different techniques such as spin transfer torque, heat and strain. However, those techniques are either energy-consuming or difficult to integrate in functional devices. The use of electric field gating to manipulate skyrmions offers several advantages: low power consumption, possibility to act locally and an easy integration with conventional electronics. However, the only previous experiments attempting electrical switching of skyrmions were done at low temperature.



2 / (a) *Magneto-optical image of skyrmion-bubbles (white spots) that have formed spontaneously at room temperature in the ultrathin cobalt layer.*

(b) *The skyrmions have annihilated under an applied electric field of +5V.*

In our work, done in collaboration with Spintec Laboratory, Grenoble, we have achieved the room temperature electrical switching of skyrmion bubbles. Our experiments were carried out on an ultra-thin film structure deposited on a silicon wafer, a trilayer consisting of 3 nm of the non-magnetic metal platinum, 0.6 nm of the ferromagnetic metal cobalt and an aluminium oxide layer. This Pt/Co/oxide trilayer was imaged under an electric field applied by a transparent Indium Tin Oxide (ITO) electrode, using magneto-optical Kerr-effect microscopy, which gives grey contrast images where bright regions correspond to magnetization directed down and dark regions to magnetization directed up.

Spontaneous nucleation of skyrmion bubbles by thermal activation is observed, see Fig. 2a. We have used an analytical model to describe quantitatively the thermal nucleation and the stability of the observed skyrmion bubbles. This model gives detailed skyrmion bubble stability diagrams which compare quantitatively with experiment and demonstrates that a very particular interaction, the "Dzyaloshinskii-Moriya" interaction, which favors the tilting of spins that would otherwise be parallel, is at the origin of the stabilization of the skyrmion bubbles in our system.

Most importantly, we observed efficient and reproducible electric field "writing" and "deleting" (*i.e.* creating and annihilating) of skyrmion bubbles, via a skyrmion switch effect, see Fig. 2 (a & b). This is described very well by our analytical isolated skyrmion bubble model. These results constitute an important milestone towards the use of skyrmions for memory or logic devices.

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"Seeing" electrochemical growth of ultra-thin metal films

Ultra-thin metallic films have attracted considerable interest in many scientific fields, including physics, chemistry and biology. They have numerous industrial applications, in catalysis, nano-electronics, coatings in metallurgy, surfaces of implants in medicine... The technique of grazing incidence X-Ray diffraction is well adapted for elucidating the surface structure and morphology of such films at the atomic scale. However, "seeing" the growth of a thin film in real time requires the high brilliance of synchrotron radiation. This has motivated diffraction experiments on a synchrotron beamline to study *in situ* the electrochemical growth of ultra-thin metal films, while the electric potential is applied.

Electrochemical deposition is a relatively cheap way to grow reproducible, nanometer-thin metal films of good quality. It is performed by putting a substrate in contact with a liquid solution (an electrolyte) and applying an electric potential. Layers with well-ordered crystal structure can be obtained by deposition on a single crystal substrate. The chemical nature, structure and orientation of the substrate, along with the type of anions present in the solution, can have a huge influence on the structure and morphology of the deposited films and consequently on their macroscopic properties. Detailed crystallographic information is hence of primary importance for both scientific and technological reasons.

In collaboration with Eric Sibert of LEPMI (Lab for Electrochemistry & Physicochemistry of Materials & Interfaces, Grenoble), we have investigated the electrochemical growth of supported ultra-thin films of palladium. Pd films constitute a model system for fundamental studies of important reactions such as oxidation of CO, oxygen reduction, or hydrogen storage processes. Our study used dedicated cells adapted both to synchrotron experiments (minimisation of the beam absorbance by the electrolyte, no obstruction of the beam on its trajectory) and to electrochemistry (continuous presence of electrolyte in front of the crystal, easily cleanable components in a strong acid environment).

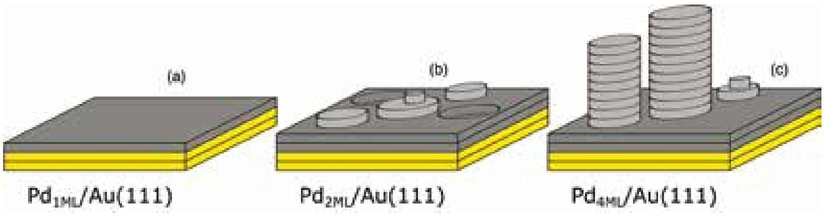
The Pd films were deposited onto the (111) surface of a gold single crystal from a $PdCl_2$ salt solution (10^{-4} M $PdCl_2$ + $3 \cdot 10^{-3}$ M HCl + 0.1 M H_2SO_4). We used Surface X-Ray Diffraction to study their growth at the French Cooperative Research Group D2AM Beamline at the European Synchrotron Radiation Facility, Grenoble. We used two types of "home-made" electrochemical cells, allowing different amounts of electrolytic solution in front of the crystal, from a few millimeters (to follow the growth mechanisms) down to less than 100 microns (to investigate the film structure).

Measuring the reflected beam intensity at an "anti-Bragg" position of the reciprocal space during the film deposition, we observed oscillating intensity for the first two atomic monolayers. This is characteristic of a layer-by-layer growth, *i.e.* one monolayer is entirely completed before the deposition of the following one begins, see Fig. 1. The film's structure at this thickness was obtained by analyzing position and intensity of the diffraction pattern in several regions of the reciprocal space. We found that the underlying Au(111) lattice determines the position of Pd atoms: they are in exactly the same sites where gold atoms would have been (this is called "pseudomorphic" growth).

For thicker deposits, palladium "islands" are formed, covering only about 20% of the surface on top of the first two Pd layers, see Fig. 1c. They can be up to 70 atomic layers thick and their crystallographic structure relaxes towards that of bulk Pd.

Contrary to what some researchers have claimed previously, we found that chloride anions play no role in enhancing the layer-by-layer growth of Pd on gold. This behavior is completely different to what we observed for deposition of palladium onto the (111) surface of platinum. Platinum has the same face centered cubic structure as gold, but a smaller lattice misfit with palladium. Unlike for Pd/Au(111), the chloride anions in the deposition solution have a major effect on the metallic Pd film structure, inducing a quite flat surface, where up to 10 complete and pseudomorphic palladium atomic layers are formed.

This work shows that *in situ* Surface X-Ray Diffraction is an excellent tool to describe the growth, the structure and the morphology of electro-deposited metallic films, and to highlight the influence of the chemical nature, structure and orientation of the substrate. A new type of electrochemical cell, developed with the "Service Études et Réalisation d'Appareillages Scientifiques" (SERAS) of the Institut NÉEL, is now being tested. It will allow simultaneous time-resolved X-ray and electrochemical measurements during transient experiments.



1 / Schematic representation of the morphology of palladium films electrochemically deposited onto a gold (111) single crystal. Pd "nML" means that the quantity of palladium deposited is equivalent to n atomic monolayers:

(a) *Pd_{1ML}: One complete Pd monolayer (dark grey) has formed on the gold substrate (yellow): it is "pseudomorphic" (i.e. strained to the same lattice constant as Au).*

(b) *Pd_{2ML}: A second pseudomorphic layer is almost completed (dark grey). Some small "relaxed" islands (i.e. with bulk Pd lattice constant) have formed (light grey).*

(c) *Pd_{4ML}: Tall, lattice-relaxed, Pd islands, some up to 20 atomic layers high, have grown on top of the two pseudomorphic Pd layers, covering only about 20% of the surface (rounded shape for islands is illustrative only, with no real correspondence). This behavior continues up to 10 equivalent ML's deposited, when islands can reach 70 atomic layers height.*

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Y. Soldo-Olivier, M. De Santis, W. Liang and E. Sibert, **"Growth mechanisms of Pd nanofilms electrodeposited onto Au(111): an *in situ* grazing incidence X-ray diffraction study"**, *Phys. Chem. Chem. Phys.* 18, 2830 (2016).

Tales **from the Ices**

When William Giauque developed cryogenics in the early 1930's, he aimed at testing the third principle of thermodynamics, one formulation of it being: "The entropy of a perfect crystal at absolute zero is exactly equal to zero". As nearly a century of work has shown, this statement is not precise enough, and there are nowadays experimental systems which, even very close to absolute zero, still fluctuate greatly, *i.e.* retain finite entropy. William Giauque's work was a milestone, highlighting water ice as a fascinating candidate to challenge the conventional statement of the third law. Since the 1990's, there are even more exotic examples, which, surprisingly, mimic water ice, but with magnetic degrees of freedom that emulate the degenerate configurations of the hydrogen bonds in water ice. These so called "spin ices", which originally appeared in certain magnetic compounds, have now been created artificially: They are designed on demand using "lab-on-chip" approaches and electron-beam lithography techniques.

When we learn thermodynamics, we soon hear about the three laws: conservation of energy, increase of entropy (arrow of time), and the third one, dealing with the states of matter at absolute zero. In recent years, new systems have appeared which have a residual entropy, *i.e.*, which seem not to order, down to the lowest temperatures reached so far. These systems are described by the so-called "spin models" in general, but also fall into another class of theoretical approaches, "vertex models". This whole area of statistical physics has proved very useful in the last fifty years. In particular, while being an abstract view of reality, they provide us with exact solutions. Our recent experimental contribution has been to realize an artificial system which shares the properties of all these aspects: it corresponds to a magnetic equivalent of water ice, it is a two dimensional version which itself maps onto a famous vertex model, and its low energy excitations reveal that it violates the simplistic version of the third law (*i.e.* zero entropy at absolute zero temperature).

In order to fabricate this artificial magnet, we used nano-lithograpy techniques. The most important innovation was to work not just in the two dimensional plane, but to shift a set of magnetic "nano-islands" vertically with respect to another set, as pictured in Fig. 1. For geometrical reasons, such a shift allows us to tune, at will, the interactions between the magnetic degrees of freedom *i.e.* the magnetization directions of each island.

Our sample was an array of 840 nickel-iron alloy magnets, each 650 nm long. Of course, even for islands this small, the magnetization directions cannot spontaneously fluctuate. In order to overcome this issue, we implemented a kinetic protocol whose purpose was to emulate an effective temperature. It consists in applying a dynamical magnetic field (a series of finely controlled demagnetizations) which brings our sample to a very low effective "temperature". Once this protocol is performed, the halted final states are imaged in real space by Magnetic Force Microscopy techniques.

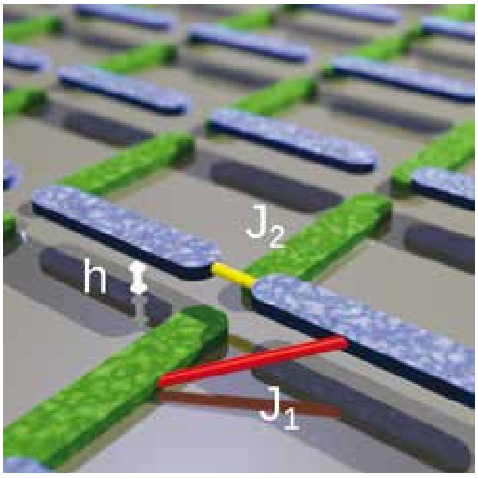
The magnetic configurations are then analyzed and compared to numerical simulations of their expected statistical-physics properties. In the simulation, each nanomagnet is represented by an Ising spin, *i.e.* an extremely anisotropic classical needle-magnet, and each Ising spin is coupled to its nearest neighbors only (the red and yellow links in Fig. 1).

The key property is that at each "vertex", *i.e.* for each set of nanomagnets forming a blue and green (staggered height) square lattice in Fig. 1, the ground state manifold (the set of states that have the lowest energy), is defined by one and only one constraint. This is that two Ising variables have to point to the centre of the vertex, the two other Ising variables have to point outward. This quite simple rule may be shown to drive the whole physics of this system and the model that describes it. And the theoretical result is that the model is degenerate at zero temperature: it has a residual entropy.

Experimentally, we do observe this degeneracy (each demagnetization scenario leads to a different configuration), a huge number of possible "two in - two out" configurations, and even more: We can probe the excitations that are built upon this degenerate manifold, that are known to behave as point-like, magnetic defects, which interact through a Coulomb-like potential. In other words, they behave like a classical magnetic monopole in reference to the hypothetical Dirac monopoles of high energy physics!

The realization of such an exotic state of matter demonstrates that it is nowadays possible to design systems that bridge different aspects of contemporary physics, here: water ice, vertex models, condensed matter spin ices, nanomagnetism.

1 / *Square array of nanomagnets. The nanomagnets are composed of a ferromagnetic alloy ($Fe_{20}Ni_{80}$) and have dimensions of the order of 500 x 100 x 30 nm^3. The blue sublattice is shifted vertically with respect to the green one to modify the magnetic interactions. When the shift is appropriately chosen, the physics of the sample maps onto the square equivalent of water ice, the famous 6-vertex model of statistical mechanics, and hosts all the properties of the class of magnetic materials called "spin ices".*



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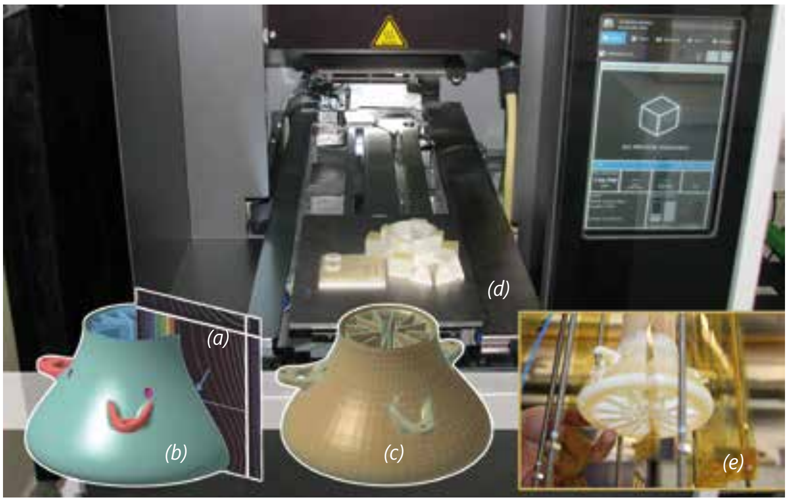
3D printing, a powerful new tool for manufacturing **prototypes for science**

"3 Dimensional printing", also called Additive Manufacturing, has been developing fast in recent years, especially with the marketing of turnkey professional machines which have much higher quality and reliability than their counterparts designed for the general public. Today a wide range of 3D printing processes can be used to make high precision parts, in many materials. These new tools are perfectly adapted to the steps involved in manufacturing experimental prototypes for scientific research. In January 2017, in order to benefit from these developments, the Institut NÉEL acquired a "ProJet MJP 3600" 3D printer, open to all the laboratory.

Emerging in the 1980's, 3D printing has increased spectacularly recently, popularized by the marketing of inexpensive consumer units (in 2016, the symbolic threshold of half a million 3D printers sold was reached). The most advanced professional uses of 3D printing have been in the medical sector and the aeronautical and space industries. Professional machines can create parts and assemblies that would be impossible to realize with other processes, with better than 0.1 mm precision, in polymers but also in metals such as 316L grade stainless steel, Inconel super-alloys or TA6V titanium alloy. To meet an increasing demand from researchers, and to propose a tool complementary to conventional fabrication methods, the Scientific Apparatus Service of the Institut NÉEL has acquired an additive manufacturing machine (Fig. 1).

This apparatus implements the MJP (Multi-Jet Printing) process: Printing nozzles deposit fine droplets of a photosensitive resin, which are then polymerized by exposure to ultraviolet light. The part is built up layer by layer. Inside the maximum volume of 298 x 185 x 203 mm, the printer works with a precision of 32 µm (down to 16 µm in a smaller volume). The machine manages "undercuts" (areas of enlarging profile, hollows...) by depositing layers of a "support" material, removed later by heating.

The printer of the Institut NÉEL has produced over a hundred parts so far, for varied practical applications, such as replacing a broken component, small or large-scale demonstration models, supports for crystals... As an example, Fig. 2 shows a flow conditioner to be placed inside a channel of liquid helium at 4 K. To reduce turbulence, the part is shaped to fit the helium flow lines very closely. It also has radial wings that limit vortex formation, as well as 3 mounting brackets. After the CAD (Computer Aided Design) step, this part was printed at small scale to validate the shape. The final full-scale version was then manufactured and integrated successfully into the low temperature experiment. Its cost was estimated at 280 €, for a 35-hour 3D printing time.



2 / The digital development chain for the helium-flow conditioner. Computer screen images: **(a)** *Input data (flow profile),* **(b)** *CAD model,* **(c)** *The design converted to a Stereo Lithography file for the 3D printer.* **(d)** *shows 1/3 scale printing.* **(e)** *Assembly of the final part (largest diameter 12.4 cm).*

1 / The 3D printing room. At the back, the "ProJet MJP 3600" printer. On the bench, the control computer and the post-processing unit.

Additive manufacturing cannot claim to replace classical workshop machining totally for certain tasks and materials. But it represents a major leap forward in mechanical manufacturing and for the "digital chain" of product development, as well as improving response times.

3D printing significantly impacts design activity. New ways to design parts emerge, designers need to shake off traditional methodological reflexes... Through exploiting this machine, the Institut NÉEL wishes to develop related competence, particularly in the engineering method of "topological optimization". Linked with numerical simulation, the goal is to put "the right material at the right place", to meet the mechanical requirements, liberating ourselves (or almost) from classical manufacturing constraints.

With several 3D printing requests satisfied every week, the 3D printer is a real success, a powerful tool for both relatively simple parts and for precise and complex shapes. Many areas remain to be explored, particularly in the cutting-edge context of scientific prototypes: resistance to low temperatures, vacuum, radiation... The Institut NÉEL is strongly involved in promoting this machine's potential to fully meet researchers' expectations.

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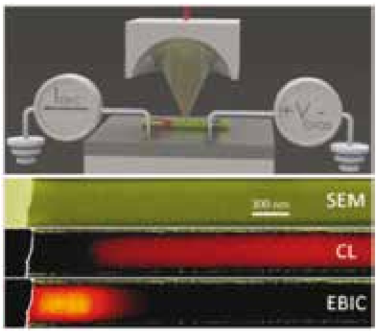
Electron beam techniques to probe semiconductor nanowires

Semiconductor “nanowires“ are long and narrow, submicron-diameter crystals of semiconducting materials. Grown from the vapour, densely packed onto a substrate, they have been under intense investigation for the last two decades, especially for their use in light emitting diodes (LEDs), photovoltaics and energy harvesting devices. Complete characterization of these materials requires measurements not only on the nanowire ensembles but also on individual single nanowires. The Scanning Electron Microscope (SEM) is an ideal tool for this. With its high resolution, it can image nanoscale objects very clearly. But it can do much more than just providing topographic images: It can be adapted to do many different in-situ experiments on single, isolated nanowires. For this purpose, at the Institut NÉEL, we have developed state of the art systems for electron beam induced current (EBIC), electron beam induced luminescence (“Cathodoluminescence“ CL), and time-resolved electron beam experiments.

The Scanning Electron Microscope works by focussing an electron beam down to a 1 nm diameter spot. It scans the beam over the sample’s surface in x,y with high accuracy while detecting the signal of back-scattered or secondary electrons. Moreover the beam energy is tunable from a few hundreds of eV to a few tens of keV, making a SEM a powerful probing tool to excite electron-hole pairs locally at different depths in a semiconductor material. This is valuable because, compared to bulk material, the electrical and optical properties of nanowires depend strongly on the state of their surface, due to their large surface to volume ratio.

Optimization of electronic devices such as LEDs or photovoltaic systems requires precise values of the important semiconductor parameters: donor or acceptor doping levels, diffusion lengths of the charge carriers, carrier lifetimes... We have equipped a scanning electron microscope with specific apparatus that enables us to record complementary topographical and electrical and optical signals (luminescence) at the same time on the same nanowire. Fig. 1 shows typical images obtained in this way for a Zinc Oxide nanowire.



1 / *Electron Beam Induced Current (EBIC) and Cathodoluminescence (CL) measurements on a single ZnO nanowire Schottky diode.*

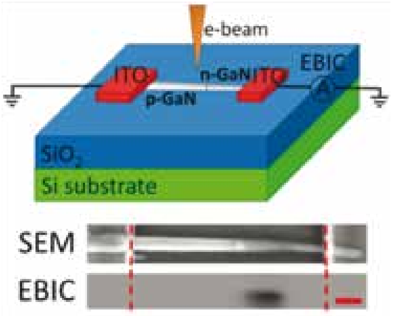
Upper part: *Electrical circuit on a nanowire under electron beam. The Schottky contact to the nanowire is at left and the ohmic contact at right.*

Lower part: *Images of the nanowire in the vicinity of the Schottky contact, for a 10 V reverse bias. The microscope’s topographic image is in green. Image of the ZnO’s ultra-violet CL is in red, EBIC signal in orange. The depletion region is revealed as a region of gradated intensity with both CL and EBIC techniques.*

The electrical measurements required electrical contacts to the nanowires. This can be done easily on an ensemble of as-grown nanowires but that will give only averaged values, so we need to work at the single wire level. We have developed several techniques for making contacts to a single nanowire in-situ in the microscope: direct connection of leads using nanomanipulators, or electron beam induced deposition of metal electrodes either directly or through a mask made of resist (previously patterned by electron beam lithography).

Via these contacts, we can do basic measurements such as current versus voltage (I-V) or field effect transistor characteristics on single nanowires. Further, and especially interesting, we can acquire electrical signals induced by the electron beam as a function of both bias and position along the length of the wire. As an example, Fig. 2 shows how, for a single Gallium Nitride nanowire containing an axial p-n junction, the electron beam induced current (EBIC) technique images the junction’s position as a dark region, allowing us to obtain its significant parameters: the depletion width and the diffusion lengths of electron and hole carriers.

By doing time-resolved luminescence experiments in-situ in the SEM, we can get the lifetimes of charge carriers or excitons (bound electron-hole pairs) generated in nanowires by a brief excitation pulse. Because the nanowires are so narrow, we can perform time-resolved experiments with a temporal resolution down to 50 ps simply by scanning the electron beam ultra-fast and periodically across the wire axis. This is done by a “beam-blanking“ system, custom-developed at the Institut NÉEL. A periodic voltage applied between two plates, 100 mm apart, inserted in the microscope column, deviates the electron beam. We record the decay of the excited carriers during the blank intervals. Combining high temporal resolution and high spatial resolution measurements, we can directly determine the lifetimes and the diffusion coefficient of excitons or charge carriers in a nanowire sample.



2 / Upper part: *Setup for EBIC measurements on an axial p-n junction in a GaN nanowire.*

Lower part: *SEM and EBIC images (without external bias voltage). The dark contrast is induced by the internal electric field in the depletion region at the p-n junction. The red scale bar is 200 nm.*

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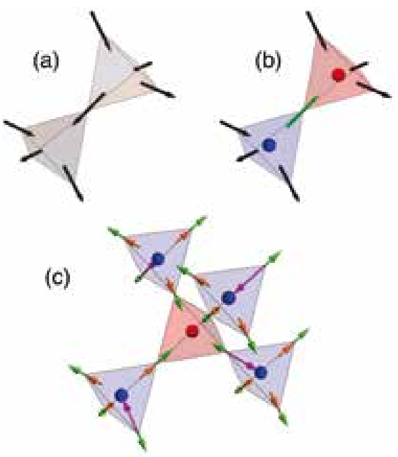
Magnetic fragmentation **in spin ice**

In the presence of competing energies, matter tries to adapt by stabilizing novel states. In magnetism, the competition between magnetic interactions can create magnetic states different from conventional ferromagnetic or antiferromagnetic ordered states, and which remain disordered down to the limit of absolute zero of temperature. Recently, the stabilization of a new state of matter, which is ordered and disordered at the same time, was predicted. It is called a "magnetic fragmented state".

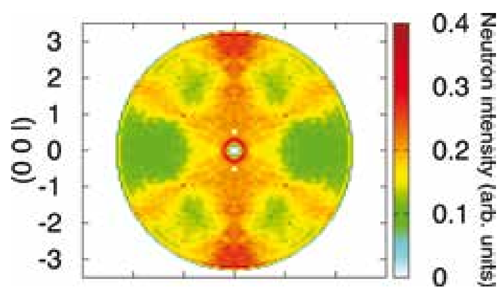
Our work concerns the "spin-ice" phase observed in certain magnetic materials of formula $R_2M_2O_7$ (R a rare earth, M a transition metal) having the "pyrochlore" lattice structure. The magnetic ions R reside on corner-sharing tetrahedra. Their magnetic moments are correlated, but the spin-ice state is a disordered phase, characterized by a massive degeneracy. The degenerate magnetic configurations obey a local rule in each tetrahedron, the "ice-rule", (so-called by an analogy with the rules for the O-H bonds in water ice) with two rare earth spins pointing towards the tetrahedron's centre and two pointing outwards ("2 in - 2 out"), as shown in Fig. 1a.

When the ice-rule is obeyed, the magnetic field at the centre of a tetrahedron is divergence free, and thus, in an electromagnetism description, there is no magnetic charge. When a spin, shared by two tetrahedra, flips its orientation, and produces "3 in - 1 out" and "1 out - 3 in" configurations, this is not true anymore: the resultant field has a non zero divergence, so that a magnetic charge, called a monopole, can be defined. Depending on the spin configuration, the resulting charge is positive or negative (Fig. 1b). If one could create a large density of such charges, an ordered "charge crystal" might be stabilized, where each tetrahedron carries a charge whose sign alternates from tetrahedron to tetrahedron (Fig. 1c).



1 / **(a)** *The spin-ice "two-in two-out" configuration of the rare earth magnetic moments (black arrows).* **(b)** *A spin flip (green arrow) creates two "magnetic charges" of opposite sign (red and blue dots) in the tetrahedron centres.*
(c) *The "fragmented" magnetic moments superimposed on the lattice. They are composed of "4 in" or "4 out" ordered moments (green arrows) from the crystallized charges, and the fluctuating spins (orange and purple arrows) from the spin-ice like phase.*

In 2014, it was predicted theoretically that there would nevertheless remain a degeneracy for the spin configurations in this ordered charge crystal. The spin system could be describable as a "fragmented" state: it minimizes its energy by condensing into a partially ordered state but maximizes its entropy by retaining some spin fluctuations. What is unique in this fragmented state is that a single degree of freedom, the spin, would have at the same time an ordered part and a fluctuating part. This fragmentation should de detectable in neutron scattering experiments as a coexistence of magnetic Bragg peaks (characteristic of the magnetic ordering) with diffuse scattering (characteristic of the correlations of the fluctuating part) exhibiting spin-ice features.



2 / *Magnetic scattering function characteristic of ice-like correlations observed by inelastic neutron scattering at E=50 µeV and T=60 mK in $Nd_2Zr_2O_7$. It is associated with the fluctuating fragment.*

We have now found this phenomenon in studies of two pyrochlore oxide materials at millikelvin temperatures. Our research combined magnetization measurements at the Institut NÉEL and neutron scattering experiments at the Laboratoire Léon Brillouin (CEA Saclay) and the Institut Laue Langevin (Grenoble). First, in Holmium Iridate $Ho_2Ir_2O_7$, where the magnetic Holmium ions are expected to stabilize a spin ice state, we have shown that the iridium ion, which is also magnetic, creates an alternating magnetic field on the Ho sublattice. This "injects" magnetic charges into the Ho tetrahedra, resulting in stabilization of a charge crystal. As predicted, the magnetic ground state then naturally fragments: half of the total Ho magnetic moment orders while the other half of the Ho spins correlate in a spin-ice-like state (Fig. 1c).

In Neodymium Zirconate $Nd_2Zr_2O_7$, where Nd is the magnetic ion, and Zr is non-magnetic, the picture is more complex and does not follow exactly the predictions of the fragmentation theory. Only one third of the magnetic moment is ordered. In addition, the diffuse scattering characteristic of spin ice observed by neutron scattering is now shifted at non-zero energy, which means that creating spin-ice like correlations costs energy. These features are the signature of a new type of fragmentation, in which the quantum properties of the Nd spins are expected to play an important role.

We are now extending this work by applying external magnetic fields to these two materials, to probe the way the two fragments recombine and to search for new magnetic phases and topological transitions.

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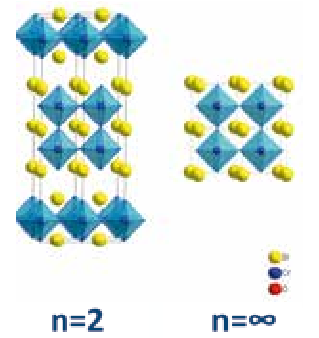
Orbital singlets indeed exist: the case of $Sr_3Cr_2O_7$

Below some transition temperature, the magnetic moments of atoms in a solid can arrange themselves in different structures. Namely, the moments can point in the same direction, rendering a rigid "ferromagnetic" order. Or (as first proposed by Louis Néel in 1936) neighbouring moments can point in alternating directions, rendering a rigid "antiferromagnetic" ordering. In certain cases, however, when we have only two values of the magnetic moment, *i.e.* up and down, neighbouring magnetic moments can fluctuate up and down while always coupled into a state with zero total magnetic moment, a "singlet state". Such states have particular and interesting properties. More generally, it has been predicted that any type of degenerate pair, *e.g.* an electron fluctuating between two degenerate atomic orbitals, can be assimilated to a pair of "pseudo-moments", developing an analogous type of behaviour. While rigid ferromagnetic or antiferromagnetic orderings of such "orbital pseudo-moments" have often been observed, up to now singlet orbital pairs of fluctuating components were just an academic hypothesis.

The oxides of chromium with perovskite-related structures potentially have very interesting properties, such as high antiferromagnetic-transition temperatures and low spins. Unfortunately they are extremely difficult to synthesize, as very high pressures (P~50000 atm) and temperatures (T~1000°C) are required to stabilize them, and so they have not been much studied. At the Institut NÉEL, we set out to study the family $Sr_{n+1}Cr_nO_{3n+1}$. These oxides contain magnetic Cr^{4+} ions, each situated within an octahedron of six oxygens, in a rectangular cage of non-magnetic strontiums.

Parameter Index $n = \infty$ gives strontium chromate $SrCrO_3$ (with the simple cubic perovskite crystal structure, see Fig. 1). With $n = 1$, Sr_2CrO_4, the compound has a structure of chromium dioxide (CrO_2) planes (which in the case of copper instead of chromium yields high temperature superconductivity). For n=2, $Sr_3Cr_2O_7$, the structure consists of bi-layers each with two parallel CrO_2 planes (Fig. 1). Thanks to the large high volume presses installed at the Institut NÉEL, we succeeded in synthesizing polycrystalline samples of all these materials, and we began by studying the previously unknown properties of $Sr_3Cr_2O_7$.



1 / *Vertical sections through the (room temperature) crystal structures of $Sr_{n+1}Cr_nO_{3n+1}$ for two values of* n. *The pale-blue octahedra represent the O_6 octahedra, each containing one chromium (dark blue atoms). For* n=2, *$Sr_3Cr_2O_7$, we have bilayers of chromium dioxide planes separated by strontium oxide layers; n= infinity is the cubic perovskite $SrCrO_3$.*

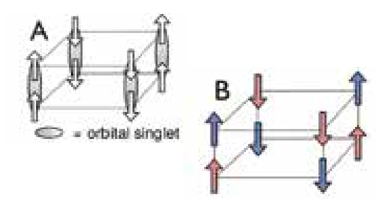
First, measuring its magnetization while lowering the temperature, we found that $Sr_3Cr_2O_7$ undergoes a transition to an overall antiferromagnetic state at a critical temperature (Néel temperature) T_N = 210 K. We then measured the fine structure of this magnetic ordering by neutron diffraction at the Institut Laue Langevin (Grenoble). We found that the chromium ion spins order antiferromagnetically in a given lattice plane, but that between the two planes of each bilayer, the pairs of Cr spins had ferromagnetic ordering, which was in agreement with predictions from band structure calculations we had done.

The neutron diffraction measurements also showed an unexpected increase of the separation between the two layers of a bilayer below the T_N of 210 K. We proceeded to determine the compound's specific heat C as a function of temperature, and observed a large anomaly in the C vs T graph around T_N. From standard thermodynamics, the area A under a C-T anomaly is determined by the number N of degrees of freedom that freeze at the transition: $Area = R \ln(N)$, where R is the universal gas constant. The magnetic moments of the chromium ions of $Sr_3Cr_2O_7$ have three degenerate components (the spins S=1/2 of their two 3d electrons are coupled in the triplet state S=1), so we expected an area $A= R \ln(3)$. Actually, we found that $A= R \ln(6)$, implying an additional ordering that freezes three other degrees of freedom.

We suspected immediately an "orbital ordering" as, according to our band structure calculations, above T_c chromium 4+ ions should have one electron occupying a 3d orbital that has threefold *orbital* degeneracy (L= 1), three degrees of freedom which could be removed by a lattice distortion occuring at T_N.

So, we performed theoretical calculations, both analytical and numerical, to try to understand this ordering of "orbital pseudo-moments". The analytical calculations predicted a rigid pseudo"antiferromagnetic" order ("B" in Fig. 2) of these moments, while the numerical (Lanczos) calculations preferred a state with the fluctuating orbital singlets ("A" in Fig. 2), favoured by the observed plane separation.

High precision X-Ray Diffraction measurements done at the European Synchrotron Radiation Facility failed to show additional small distortions necessary for an "AF" type orbital ordering, thus solidly demonstrating the existence of the long sought orbital singlets ("A" in Fig. 2).



2 / *Two different orderings obtained by numerical Lanczos calculations* **(A)** *and analytical calculations* **(B)**. *The arrows show the magnetic ordering of the 3d electron spins, while the colours indicate the two possible orbital orderings, "antiferromagnetic" for B, and "fluctuating singlet" for A.*

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Quantum plasmonics in a 2-Dimensional chiral world

Chirality, that is the lack of any mirror symmetry of a system (for example a helix) is of great importance in many fields of science especially biology and chemistry. In optics, since the pioneering work of Arago and Fresnel, it is generally linked to "optical activity", *i.e.* the remarkable capability of some optical media to induce a circular birefringence and thus a difference in propagation for left and right handed circularly polarized light. Optical activity, which has many applications for molecular detection and sensing, is usually associated with a 3-Dimensional chirality, as exists for example in sugar molecules with helical shapes. However, in recent years, it has been shown that planar systems such as the Archimedean spiral, having genuine 2-D chirality, can reveal a new form of optical chirality, which is distinct from optical activity. This kind of chirality can have impact on the field of quantum photonics with "surface plasmons", *i.e.* with waves that propagate along a dielectric-conductor interface.

With the recent development of "metamaterials" (artificial materials) in nanophotonics, planar chirality has attracted much attention for its potential for developing new integrated optical devices exploiting coupling with circularly polarized light. In plasmonics, the photonics of surface plasmons, *i.e.* charge density oscillations propagating over the interface between a metal and air, new methodologies are available for probing planar chirality using Near-field Scanning Optical Microscopy (NSOM). Importantly, the NSOM methods we have developed at the Institut NÉEL use both classical and quantum sources of light.

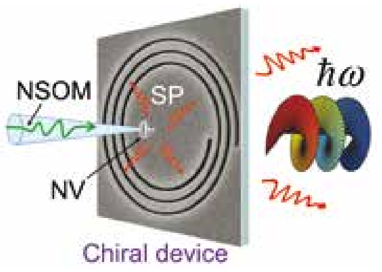
In the standard, classical regime we guide red laser light into the apex of a metalized optical-fibre tip. A sub-wavelength aperture acts as a scannable nanometre-scale source of light. The tip is coupled to piezo motors and its distance from the sample is constantly monitored and controlled. In the quantum regime, instead of using an aperture, we graft a single diamond nano-crystal at the tip's apex. This crystal hosts one or a few "NV" colour centres (Nitrogen impurity atom - carbon vacancy pairs). The NV centres act as quantum emitters of single photons and thus we can work in the "quantum plasmonic" regime. Both kinds of NSOM are of great utility for studying the local coupling of a point-like source to a chiral plasmonic environment.

In our work we studied the coupling of a scanning tip to a 2D optical grating cut through a perfectly flat gold film. Our grating has the spiral form defined by Archimedes (radius = $a + b\ \theta$). This spiral has the particularity that the inter-groove spacing is constant, thus optimising its interaction with a surface wave. The electromagnetic near-field of the tip launches surface plasmons that propagate along the air/metal interface of the planar structure. The plasmons subsequently leak through the semi-transparent thin film of gold and decouple from the rear surface into the optical far-field (the radiative electromagnetic field) as pure photons, which we detect by conventional (digital) optical microscopy, see Fig. 1.

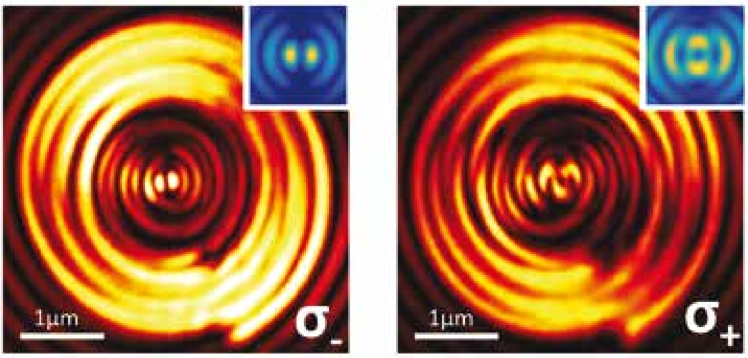
These propagative photons carry a fingerprint of the surface plasmons' interaction with the chiral environment. Specifically, this interaction leads to the generation of "optical vortices", *i.e.*, to the propagation of singular optical fields with quantized orbital angular momentum and well-defined helicity, which one can call "spin". The gold film medium is thus acting as a plasmonic "topological" material where the helicity and orbital angular momentum of a photon are coupled to the "topological charge", *i.e.* the twist, of the Archimedean spiral. We can speak therefore of "spin-orbit" coupling between photons and surface plasmons.

For probing this signature of the planar chiral device, we developed a polarization tomography approach. By scanning the tips over the spiral and mapping the Stokes vectors describing the polarization state of surface plasmons and photons respectively, we were able to characterize the point-by-point capability of the scanning tip source (either classical or quantum) to couple to surface plasmons and to induce a well-controlled spin-orbit coupling for photons emitted from the rear surface. The methods actually record the local "Purcell enhancement factor" (the local density of optical states) associated with the spin-orbit interaction.

Using quantum NSOM tips, this research could ultimately lead to the development of integrated quantum devices able to emit single photons having a specific "spin" and well defined "orbital angular momentum".



1 / *Principle of the Scanning Near Field Optical Microscope source launching surface plasmons in a chiral, planar structure. The transmitted photons, propagating out from the rear surface, carry a well-defined spin and orbital angular momentum.*



2 / *Two reconstructed images obtained by scanning the tip of a near-field optical microscope over the Archimedean spiral. A circular-polarization analyser is used to distinguish left-handed (σ-) and right-handed (σ+) polarisations.*

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Pinning and unpinning of **charge-density waves**

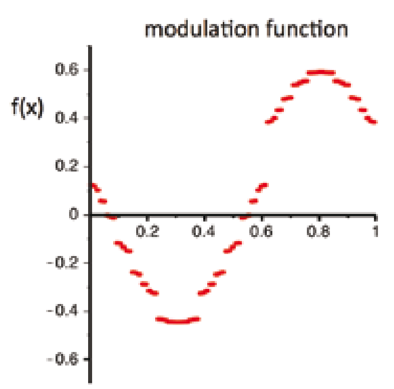
A charge-density wave (CDW) is a modulation of the electron density in a low-dimensional conducting solid. It appears below a critical temperature called the Peierls temperature, concomitantly with a periodic lattice distortion. Low-dimensional materials such as certain sulphides and selenides of niobium and tantalum have long been famous examples showing one-dimensional charge density waves. These waves are "pinned" in place until liberated by a strong enough electric field, when their coherent movement produces a large increase of the conductivity. Recently, CDWs have been identified in a two dimensional family, the Rare Earth tri-tellurides (RE-Te_3). Their properties in this new family have upset long-held ideas about CDWs, requiring a new theory about how the waves get "pinned" in place, and how they get "unpinned" by the electric field.

Compounds like $NbSe_3$ have a crystal structure consisting of parallel chains of atoms, hence their 1-D properties. A chain of equidistant atoms is a metallic conductor when the electronic band is partly filled. When the ratio of the wavelength λ of the mobile electrons at the Fermi level to the interatomic distance a is close to an irrational number, the coupling between these electrons and the positively charged atomic cores leads to a CDW state incommensurate with the lattice.

The electron-lattice coupling may be weak or strong. The standard theory assumes a weak coupling for all 1-D systems. The modulation function $f(x)$ describing the changes δx of the interatomic distances and the associated charge-density variations has the form of a sine wave, *i.e.* $f(x)$ is periodic and continuous. Owing to this continuity and the incommensurability, the CDW's energy does not depend on its position relative to the lattice. It should be totally free to move. Under any finite electric field, this would allow a collective mode of transport, giving an extra contribution to the current and a nonlinear conductivity.

But, in reality, this conductivity enhancement occurs only above an electric threshold field of about 1eV/cm. In the weak coupling theory, it has always been supposed that impurities, randomly distributed in the medium, pin the CDW phase, with an energy scale of about 10^{-7} eV per atom, thus requiring a significant electric field to unpin the charge-density wave.

S. Aubry and coworkers have shown theoretically that a strong coupling regime would qualitatively modify the properties of a charge density wave. The modulation function becomes *discontinuous* above a certain, critical, electron-lattice coupling, corresponding to the formation of strong distortions of some of the atomic bonds, see Fig. 1. The incommensurate CDW could then be pinned naturally by the lattice distortion, without invoking impurities. But this seemed unrealistic, as the energy scale involved was 10^{-2} – 10^{-4} eV, many orders of magnitude larger than that due to impurities.



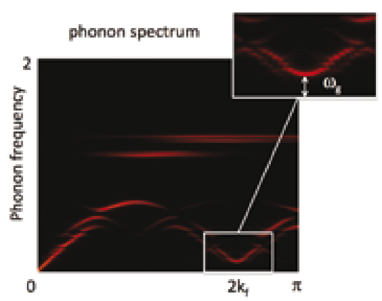
1 / *The CDW modulation function* f(x) *describing the atomic displacements at positions x (in reduced units) along a linear chain of atoms. Sinusoidal for weak coupling,* f(x) *is shown here for strong coupling, where it is discontinuous. Under applied electric field, the gaps in* f(x) *close up progressively, finally depinning the CDW at a critical field.*

A major reappraisal has become essential following recent observations of CDW depinning by electric fields in Rare Earth tri-tellurides. Many parallel experimental results had left no doubt that this system is in the strong coupling regime. The surprise came from the value of the observed depinning threshold, which is of the same order as in the supposedly weak-coupling 1-D systems (~1eV/cm). To resolve this puzzling situation, one could assume that *all* CDW compounds, old and new ones, are in the strong coupling regime. So far, a depinning mechanism in this regime had not been proposed. Our work has filled in this theoretical gap.

In all the work done on "impurity pinning", theoreticians assumed that the electrons in the CDW were submitted to the *macroscopic* applied electric field *E*. This is the "original sin" of these theories. Indeed, all CDW compounds behave as dielectrics at low temperature in a DC electric field (and in AC fields up to several hundred MHz). Amazingly, they exhibit gigantic static dielectric constants (ε~10^6 to 10^9). As is known, charge-carriers in dielectrics are not submitted to the macroscopic field, but to the local field, given roughly by E_{local}~ εE, *i.e.* >10^6 V/cm here, instead of 1V/cm.

In the strong coupling regime, when an external electric field is applied, each local bond in the chains acquires a small dipole moment. The sum of all the dipoles in all the chains and their mutual interactions are responsible for the giant dielectric constant and for the intense local electric field. Owing to the dependence of the bond-polarisability on the atomic distances, the CDW distorts and contracts under an electric field, as in a piezoelectric effect. The gaps of the modulation function of Fig. 1 close up progressively as the electric field increases. Above a certain applied field, the charge density wave is free to move: It has been unpinned.

The theory predicts that significant changes in the phonon spectrum will occur under electric field (Fig. 2). Synchrotron X-Ray diffraction experiments are being undertaken to provide a test of the theory.



2 / *The new theory predicts important changes in the phonon spectrum during depinning: The phonon gap* ω_G *seen here at* $2k_f$ *should vanish above the critical electric field.*

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Pinching off **electron edge-channels** in graphene

Recent progress in techniques for microfabrication of 2-Dimensional layered materials have led to the emergence of "van der Waals" (vdW) heterostructures. The disruptive aspect of the new assembly processes, which exploit the Van der Waals forces between atomic layers, is that the experimentalist can simply pick up 2-D crystals, put them into contact and stack them layer-by-layer, using relatively inexpensive micro-manipulation equipment. In such vdW heterostructures, materials with varied electronic properties, notably graphene, boron nitride, and transition metal dichalcogenides, can be assembled as the base for experimental electronic devices with greatly improved properties or new functionalities. With graphene vdW heterostructures in particular, the very high device quality now attainable allows state-of-the-art experiments in controlling the current-carrying "edge channels" of the quantum Hall regime.

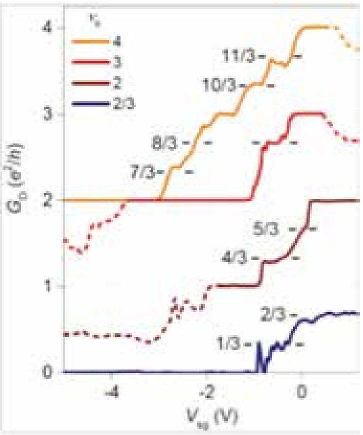
Graphene is a monolayer of carbon atoms on a 2-D hexagonal ("honeycomb") lattice, where the type of charge carrier can be changed from electrons to holes by the voltage on an electrostatic gate placed on its surface. Encapsulating this very delicate monolayer between two insulating layers of hexagonal boron nitride (BN) has boosted graphene's electronic properties to a level competitive with the classic 2-D electron gases in GaAs heterostructures. Mean free paths of tens of microns for charge carriers, electronic mobilities reaching 10^6 $cm^2V^{-1}s^{-1}$, and purely ballistic electronic transport can now be achieved at low temperature with these hBN/graphene/hBN devices.

At the Institut NÉEL, we have fabricated ballistic graphene devices and studied electronic transport through "quantum point contacts" (QPC's), electrostatic constrictions in the 2-D graphene layer. They are created by a voltage-tunable "split-gate", a pair of metal electrodes deposited on the BN insulator (see Fig. 1). The gate voltage can change the local carrier type from electron to hole, forming a repulsive "saddle-point" potential in the gap of the split-gate. But, due to the absence of an energy gap in graphene, this potential does not confine the electron flow in the split-gate gap, as opposed to what happens with QPC's in semiconductors.

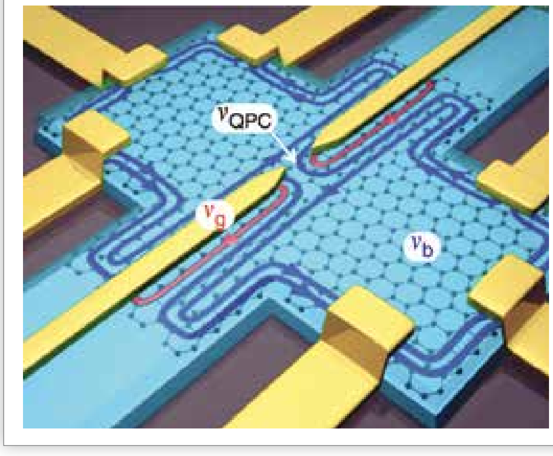
To solve this issue, we operated our devices in the quantum Hall regime, *i.e.* under large perpendicular magnetic field B that quantizes the energies of electrons and holes into discrete Landau levels. A peculiar feature of this very special regime is that the electrons flow through one-dimensional channels that propagate along the edges of the sample. Depleting the electron density beneath the split-gate electrodes diverts the quantum Hall edge channels towards and into the constriction (see Fig. 1). By pinching off the point contact with a large enough negative voltage, the transmission of the inner edge channel can even be totally blocked. Thus one can have voltage-tunable transmission or back-scattering of electrons at the point contact.

In fact, until now for graphene, this kind of control over edge-channel transmission had proved difficult to achieve due to an accumulation of positive holes localized beneath the gates, which can short-circuit the point contact. But, due to the very high carrier-mobility of our BN-encapsulated graphene samples, a large energy gap opens up between the graphene's electron and hole Landau levels. This energy gap is the key, as it spatially separates electron channels passing through the constriction and hole states localized beneath the gates, suppressing mixing between them and precluding short-circuits.

We have demonstrated gate-voltage tunable transmission of quantum-Hall edge channels in both the integer and fractional quantum-Hall regimes. It shows up as a quantized, step-like decrease of the conductance as we progressively pinch off the constriction (Fig. 2). This opens up a wealth of quantum coherence experiments based on these edge channels. New van der Waals graphene devices with more complex gate configurations can be envisioned, for quantum-Hall interferometry and electron quantum-optics experiments in the integer and fractional quantum Hall regimes of graphene.



2 / *Conductance, G_D, of the quantum point contact versus split-gate voltage V_{sg}. As V_{sg} becomes more negative, the conductance drops through a series of both integer and fractional quantum Hall plateaux, indexed ν_B, as the number of edge channels transmitted through the contact decreases by one for each plateau.*



1 / *Artist's representation of the BN/graphene/BN heterostructure device. A hexagonal network of carbon atoms is encapsulated by BN (shown semi-transparent blue). Six electrodes contact the graphene for quantum-Hall measurements. A split-gate forms a quantum point contact (QPC). Edge channels created by high magnetic field B are shown as blue lines for electrons and red lines for holes.*

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Switching **nanotube-molecule hybrids** with light

Carbon nanotubes are one or more graphene sheets (monolayers of carbon atoms) rolled into the form of a hollow, cylindrical tube. They are 1-Dimensional electrical conductors and, by their size, they bridge the gap between small-molecule electronics and conventional semiconductor technology. They offer the opportunity to realize new functions, ranging from accurate sensors to optoelectronic and quantum devices, while being promising for implementing flexible electronics. However, the peculiar nature of the 1-D density of electronic states limits their useful range of optical wavelengths. Coupling carbon nanotubes with optically-active organic molecules couples the nanotube's electrical sensitivity to the molecule's specific optical properties. This can yield efficient "hybrid" devices for transducing light to electrical current.

Most previous research into the use of nanotube-molecule hybrids for sensors or photovoltaics has been done on macroscopic assemblies of nanotubes. At the Institut NÉEL we have worked at the single-nanotube level, in order to study the conversion of light into an electrical signal at the nanometre scale. We disperse carbon nanotubes on an insulating substrate and locate suitable, isolated nanotubes (1 or 2 microns long, typical diameter 2 nm) by Scanning Electron Microscopy. We then make two electrical contacts (source and drain) onto a single nanotube by electron-beam lithography. Then we "decorate" the nanotube with optically-active organo-metallic molecules by dropping the molecules ("drop-casting") onto it.

These molecules are chromophores, specifically the porphyrins "TPPZn" with a zinc core, that can switch to an electrically-charged excited state upon exposure to light. They are synthesized by G. Royal and S. Cobo at the Département de Chimie Moléculaire of the Université Grenoble Alpes and can be tailored to provide a variety of optical-transition energies covering the visible wavelength range. Decorated with such a molecule, the nanotube's conductance is sensitive to a light-induced electrical charge on the molecule. That is, the molecule acts like the gate of a field-effect transistor (FET) and we can realize optical gating of this transistor at a desired wavelength.

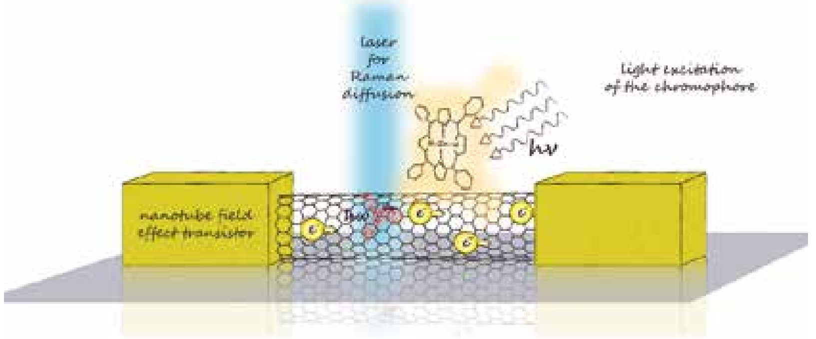
To get a more complete picture of our hybrid FET devices, we have used two complementary techniques: (i) electrical transport measurements (sensitive to the molecule's charge and to doping of carriers into the nanotube from the molecule) and (ii) Raman-scattering spectroscopy. The latter technique gives further insight into the doping effects, and information about the carbon nanotube phonons, and the optical excited states of the molecule.

At room temperature, when we shine light on our hybrid device, we see a strong dependence of the transistor characteristics and the graphene's Raman spectra on the light's wavelength. This wavelength dependence matches closely the molecule's optical absorption spectrum showing that the observed effects correspond to charge transfer and/or energy transfer between the molecule and the nanotube.

In our experiments, an unusual increase of the intensity of the graphene's Raman scattering and of the width of the Raman mode is observed when the light stimulus is on. These changes disappear after switching the light off, even though the molecule remains charged. The Raman intensity enhancement is a signature of a new resonance specific to the hybrid, revealing a strong coupling between a molecular excitonic state and the nanotube's electron states.

Furthermore, the molecules act as charge traps which behave as "Coulomb islands" at low temperature. At 10 K, electrons can tunnel one by one between the nanotube and the traps. This is seen as regular plateaux in the transistor's transfer characteristics. It is the equivalent of the phenomenon used to realize single-electron memories in semiconductors. Here, the molecular traps are optically active: Exposure to light modifies the features in the I-V (current vs voltage) graphs characteristic of single electron tunnelling. They change from plateaux in darkness to sharp peaks under blue light illumination, a consequence of a better coupling between excited traps and nanotube. This allows us to tune the tunneling efficiency in the hybrid device with light.

The two unconventional responses observed for our hybrid transistors, in the Raman spectra and in the low temperature I-V characteristics, are fully reversible. They are related to a modification in the alignment of the energy levels within the hybrid, which is due to the light-induced switching of the chromophore into an excited state. This opens the possibility to control the optical and electrical response of the hybrid devices with light.



1 / *A carbon nanotube is decorated with porphyrins. Stimulus with light hν excites the molecule, inducing a change of its redox state, which modifies the electronic and vibrational properties of the nanotube.*

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Nanoscale **nonlinear plasmonics**

Integrating quantum-optics devices is one of the main challenges for the next decade especially in view of microprocessor-scale quantum computing. This requires taking experiments that are done today on an optical table and downsizing them to a few hundred nanometres, the equivalent to what was done in the past century for transistors. Quantum optics makes extensive use of crystals with non-linear optical properties. But here, a major concern is that the efficiency of these components drops off on reducing their size below the optical wavelength. One potential way to overcome this issue is to compensate the intrinsic weakness of the resulting non-linear response by exploiting the optical properties of "plasmonic nanostructures", which behave as optical resonators.

Reducing a nonlinear medium from mm^3 down to a thousandth of a µm^3 for practical applications sounds like the squaring of the circle: 10^{12} times fewer atoms are interacting with light, so 24 orders of magnitude are lost in terms of efficiency due to the volume-squared dependency! How can one compete with such a vanishing contribution? Tightly focusing the light beam and using pulsed lasers are part of the answer, but the electric field experienced by the non-linear material has still to be enhanced. There are not dozens of options: either you take a very small non-linear crystal, a "nanocrystal", and enhance its properties by placing it in an optical cavity, or you use nanoscale, metallic optical resonators located in the vicinity of this nanocrystal.

We have started investigating the latter option, fabricating and characterizing plasmonic "antennas", and studying their non-linear properties at visible and near-infrared wavelengths.The most appealing property of plasmonic resonances (collective oscillations of a metal's conduction electrons) is to trap, in some sense, the photons in the vicinity of the metal surface, leading to both enhancement and localization of the electric field at a scale below the diffraction limit set by the wavelength of light.

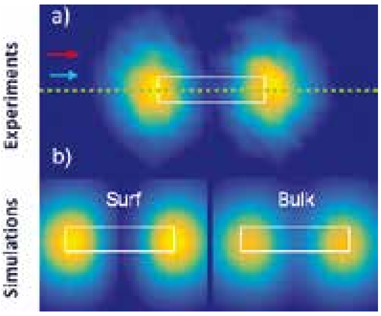
1 / *Fully computer-controlled experimental setup developed since 2014. The dense set of optical elements allows multiple physics investigations on the same single nanostructure by using various optical paths. The blue box is the optical parametric oscillator, pumped by a femtosecond laser, providing versatile wavelength tunability.*

We have used these original properties, combined with the shape-dependence of the antenna resonance frequency, to boost the nonlinear response at the nanometric scale. Having a strong intrinsic light-matter interaction and being resonant at both the excitation and the emission wavelengths are the two specifications of the best antenna one can dream of. Both of them are accessible with the aluminium antennas fabricated at NanoFab, a technical platform housed at the Institut NÉEL. They are 35 nm thick, rectangular aluminium plates, 100 nm wide and 100-500 nm long. They can be tuned to be doubly resonant nanostructures, *i.e.* resonant with both the incoming and outgoing light wave, at for example 850 nm and 425 nm respectively in a second harmonic generation experiment. Investigating quantitatively the nonlinear response of such antennas is a challenge for which we have developed two tools unique in the world.

Over three years, we have built from scratch an optical setup (Fig. 1) allowing multiple physics investigations on the same single nanostructure including linear, nonlinear, pump-probe, near-field, and even photon-correlation experiments for quantum optics purposes. Our apparatus achieves low noise (a few counts/s), long-term stability (provided by tracking algorithms to maintain the nanostructure in the focal planes), wavelength tunability (from near-UV to near-IR in order to map the plasmonic resonances), and finally full computer control with a Labview interface created in-house to automatically optimize the setup.

Advanced theoretical support is also essential for designing the proper nanostructure shape but also for an in-depth understanding of the signals collected experimentally. To this end, we have coupled analytical and numerical simulations on the Institut NÉEL's computer-cluster, taking into account the actual experimental setup (focusing, collection efficiencies, influence of substrates, etc.). With the software package we developed, theory and experiments can be compared quantitatively in terms of calculated and measured photons per second, without adjustable parameters. As a first outcome, the origin of the nonlinear optical response in aluminum plasmonic nanostructures has been firmly established (Fig. 2).

Perspectives of this work are numerous, especially as we have now reached a stage where fully classical simulations have been coupled to quantum approaches, a significant breakthrough in the theoretical support for experiment in the field of entangled photon-pair generation in plasmonics-based, nanometric-scale optical sources.



2 / *Colour-coded intensity maps of the second harmonic generation response of a 100 x 225 x 35 nm^3 aluminum antenna (schematized by white rectangles). Quantitative comparison between* **(a)**, *experiment and* **(b)**, *analytical/numerical simulations for surface ("Surf") and bulk nonlinear currents rules out the latter as generating the observed second harmonic signal.*

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A world map of organic semiconductors

An attractive feature of organic materials is the possibility of tailoring compounds with specific electronic properties by tuning the chemical structure of the component molecules. While this flexibility is real, new materials have traditionally been discovered through trial-and-error approaches, with no clear principle on how to predict and optimize the required characteristics. This has left physicists and chemists with no clue on how to systematically improve the charge mobility, the property that is key to most electronics applications, ranging from organic transistors to organic solar cells. An understanding of quantum localization effects, *i.e.* the localization of the electronic wavefunction due to scattering effects, could help to discover more efficient molecular semiconductors for organic electronics, paving the way for a new generation of organic compounds with unprecedented charge mobilities.

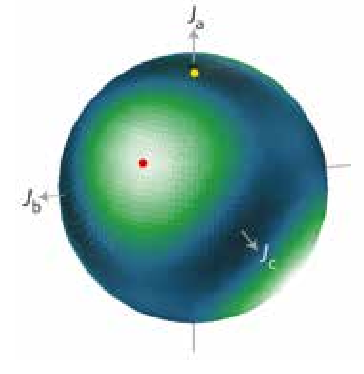
The factors that allow a charge carrier (an electron or a hole) to travel long distances within a crystalline organic semiconductor have eluded proper understanding until very recently. As a result, organic materials with mobilities exceeding 10 cm^2/Volt sec – a threshold for many device applications (cf. 1500 cm^2/ Vs for silicon) – remain extremely rare.

Molecular semiconductors transport the electrical charge in a way that is fundamentally different from prototypical semiconductors like silicon. The main reason is that the Van der Waals forces that bind an organic crystal together are much weaker than the covalent forces in atomic solids. In this soft environment, the thermal molecular motions are so large that they scatter the charge carriers far beyond the limit where the electrons can still be described as semi-classical particles. These scattering events happen so frequently that they lead to an initial localization of the electronic wavefunction, which must be overcome for the carriers to attain long distance diffusive motion.

The discovery of this genuinely quantum phenomenon, called "transient localization" (Troisi *et al.* 2006, Ciuchi *et al.* 2011), has allowed us to solve a number of open puzzles in the physics of organic semiconductors, resulting in a single, consistent model of charge transport. Specifically, our theoretical study has unveiled the mechanisms that govern this wavefunction localization.

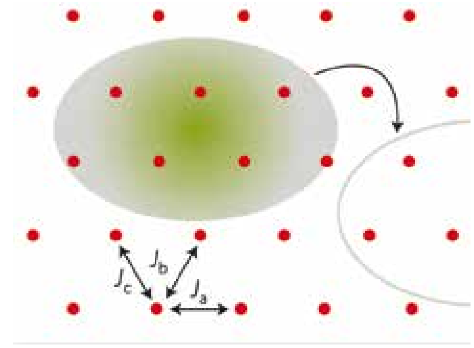
Virtually all molecular semiconductors pack into crystal structures where one can identify a relatively high-mobility plane. Fig. 1 illustrates localization of a charge-carrier moving on a two-dimensional lattice of organic molecules. The localization length L, and hence the carrier mobility, depends on the inter-molecular transfer integrals (the electronic interactions) J_a, J_b and J_c, for the three nearest-neighbour distances (Fig. 1). These vary with time, due to thermal molecular motions, localizing the carrier wavefunction into a state with size L (area ~ L^2) that spans several molecules. These localized states can diffuse across the lattice on a timescale similar to that of the molecular vibrations. For small L^2, *i.e.* strong localization, this diffusion is difficult, for large L^2, *i.e.* weaker localization, it is easier.

We have calculated L^2 as a function of J_a, J_b and J_c for a large number of molecules. Our findings are summarized in a comprehensive *world map* (Fig. 2) which can represent all of the high-mobility molecular semiconductors discovered so far and, we suggest, many structures that could be realized in the future. This "map" can be used in practice to devise a new design principle, beyond reducing intrinsic and extrinsic disorder. For achieving high mobility, the top molecular semiconductors should be located close to one of the "hot spots" on the map: the intermolecular transfer integrals should all be similar in magnitude and *identical in sign*, making the electronic structure more isotropic and therefore less sensitive to the intrinsic molecular motions. On the other hand, and contrary to what was previously believed, increasing the absolute values of these integrals as is usually attempted will lead to little or no improvement of the transport characteristics.



2 / The square L^2 of the transient localization length L is the key parameter that predicts the mobility. Here, L^2 is colour-mapped onto the surface of a sphere, as a function of the relative values of the integrals J_a, J_b and J_c. The paler areas correspond to molecules close to having J_a = J_b = J_c, (the red spot) and all with the same signs. These "hot spots" are optimal for charge transport.

Starting from these new results, it will be possible to analyse databases of known molecular crystals in search of compounds with the desirable electronic characteristics: with the help of electronic structure calculations, it would take just a few minutes per compound to calculate the inter-molecular exchange integrals and establish their positions on the map. Since the vast majority of known compounds have not been purified and grown as large crystals to the point where one can measure their intrinsic mobility, this protocol will enable a more systematic and rational process of material selection for organic electronics.



1 / The transient localization of a charge-carrier on a two-dimensional lattice of organic molecules (red dots) depends on the three, principal, intermolecular transfer integrals J_a, J_b and J_c. Their time variation, due to molecular vibrations, localizes the carrier wavefunction into a state of size L (green shadowed region). The carrier diffuses via a succession of localized states (curved arrow).

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New SKID-detectors:
a world below the superconducting gap

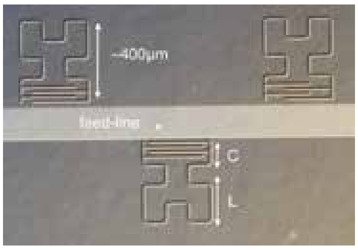
Superconductivity is a fascinating state of matter that corresponds to zero electrical resistance. It occurs in certain materials when cooled below a characteristic critical temperature T_c. From the microscopic point of view, superconductivity consists of a condensate of pairs of electrons ("Cooper pairs") flowing without any energy dissipation. The energy spectrum of this superfluid condensate possesses a gap 2Δ that is the minimum energy required to excite the superfluid. Incident electromagnetic radiation with energy $h\nu > 2\Delta$ can break Cooper pairs, and this property has been used extensively to make ultra-sensitive radiation detectors. Surprisingly, it has been found recently that superconducting thin films of an appropriate material and design can detect photons having an energy lying well below the superconducting gap.

Kinetic Inductance Detectors (KIDs) are state-of-the-art detectors for millimetre wavelength radiation. These KIDs are built as small superconducting RLC resonators; the detection principle is based on monitoring variations of the resonator frequency $f=(LC)^{-1/2}$.

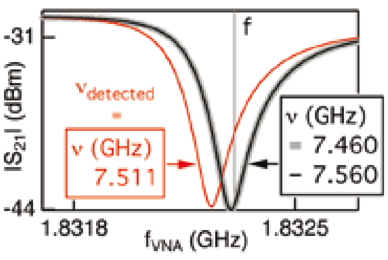
The inductance L is mainly due to the kinetic inductance of the superfluid condensate. "Kinetic" inductance, the imaginary part of the AC conductivity in the Drude theory for metals, is dominant in superconducting circuits where the carrier collision time τ goes to infinity. The kinetic inductance is inversely proportional to the superfluid density n_s (the density of cooper pairs): $L \sim 1/n_s$.

In the now classical KIDs implementation, incident electromagnetic radiation with an energy larger than the superconducting gap 2Δ, breaks down Cooper pairs of electrons, decreasing the density n_s, so increasing the kinetic inductance L and thus modifying the detector circuit's resonance frequency.

We are developing a radically new technology (Fig. 1), which we call Sub-gap Kinetic Inductance Detectors or "SKIDs". In extensive testing of resonator circuits made out of a specific superconducting material, namely amorphous indium oxide, we have established that these SKIDs can be sensitive to radiation in the range 7 to 10 GHz, well below this material's superconducting gap of about 200 GHz. And, contrary to classic KIDs which are broad-band, a SKID's sensitivity is extremely selective in frequency. We attribute this sensitivity to the incident radiation exciting harmonics 2*f*, 3*f*, 4*f*... of the detection circuit's fundamental resonance mode (see Fig. 2 which shows third-harmonic detection of 7.5 GHz microwaves). So the frequency detected can be varied by adjusting the fundamental frequency of the superconducting resonator.



1 / *Part of a 22 element array of amorphous indium oxide SKIDs on a silicon substrate, showing three RLC resonators coupled to a common feed-line. The superconducting strips are 12 microns wide and 50 nm thick. The inductor section L is identical for all resonators. The lengths of the four "interdigitated" capacitor fingers C are different for each resonator. An external measuring circuit distinguishes the 22 elements by their resonance frequencies* $f=(LC)^{-1/2}$.



2 / *Our SKIDs are tested at 100 mK with microwave radiation from an antenna outside the cryostat. We show three Vector Network Analyser (VNA) frequency scans of a resonator whose fundamental frequency is f ~1.832 GHz. First, (the grey curves) irradiation by 7.46 and 7.56 GHz microwaves hardly perturbs the detector's resonance mode. Then, 7.511 GHz microwaves (= the frequency ~4f of the detector's third harmonic) gives a measurable shift of the detector's resonance (red curve), even though 7.5 GHz lies far below the InO superconductor's 200 GHz excitation gap.*

The coupling between the resonator's fundamental and higher order modes is due to the non-linearity of the kinetic inductance with current: the electrical current induced by photons penetrating into the resonator decreases the superfluid density n_s, and thus increases $L \sim 1/n_s$. This phenomenon is expected to occur in any superconducting thin film above the "depairing" current (the current at which breaking of Cooper pairs begins). Sensitivity to a few incident photons is only achieved in superconductors with a low depairing current. Compared to a superconducting metal such as aluminium, our amorphous indium oxide, being a highly disordered material, has a lower Cooper pair density and lower depairing current.

Within the Bardeen-Cooper-Schrieffer theory of superconductivity, the critical temperature (T_c) and the superconducting gap (2Δ) are directly related by $\Delta = 1.76\, k_B T_c$. For classic KIDs, detection of lower frequencies requires superconductor materials with smaller gaps, and so it requires lowering the operating temperature. For example, to detect a 100 GHz radiation one needs an operating temperature $T \ll 1$K, and to detect a 10 GHz radiation $T \ll 100$ mK would be required.

So, the SKIDs are innovative with respect to current KIDs technology for two reasons: they can operate at higher temperatures and, secondly, they are very selective in frequency.

In the future these new Sub-gap Kinetic Inductance Detectors may be implemented to do GHz-imaging and/or on-chip spectrometry. Since molecules, H_2O among others, have vibration frequencies that lie in the low-GHz range, the SKIDs may be employed in passive cameras either for security, medical or astrophysics purposes. As concerns astrophysics in particular, SKIDs are a candidate technology for frequency-selective microwave detectors on a future satellite project.

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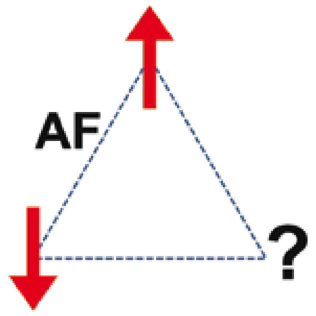
Order or disorder: How close do you look?

When magnetic atoms are positioned on a triangular lattice, strange things can happen. When the interaction of the magnetic moments favors neighboring moments to be anti-parallel (one directed up, the other down), the three magnetic moments of a triangle cannot all be in their ideal magnetic state. If the first atom on a triangle has its magnetic moment in the up direction, the second atom should have its magnetic moment pointing down. But then, the atom on the third corner of the triangle cannot satisfy the interactions with both of these atoms, it cannot be simultaneously antiparallel to the other two (see Fig. 1). This so-called "magnetic frustration" property is highly interesting from a theoretical point of view. Notably, Philip Anderson predicted in 1973 that it could give rise to a "spin liquid" state at low temperature. This has been observed only very rarely, a problem being that there are very few examples of existing materials that exhibit this triangular magnetic frustration.



1 / A triangular configuration of magnetic moments. With antiferromagnetic interactions the third magnetic moment cannot be antiparallel to both the other moments.

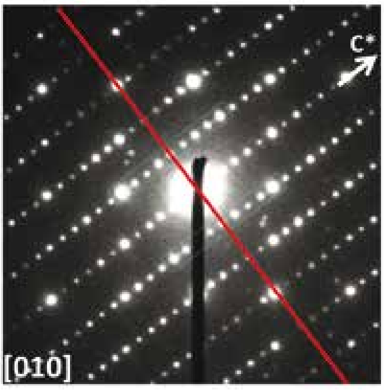
Barium nickel antimonite $Ba_3NiSb_2O_9$ could be an example of a magnetically frustrated phase with the magnetic nickel atoms positioned on a triangular lattice. Since ambient pressure syntheses of this compound did not yield a magnetic frustration, we performed a high pressure/ high temperature synthesis in order to obtain a different crystal structure with the same composition. And, indeed, the synthesis at 620°C and 2.5 GPa resulted in a powder that did not show any magnetic ordering down to 0.35 K. It could therefore be an experimental realization of a magnetically frustrated material, but in order to be sure of this, we had to prove that the magnetic Ni atoms do form a triangular lattice and that the absence of magnetic ordering is not due to structural disorder.

The most common method for structural investigations is X-ray powder diffraction (XRPD). In addition we carried out neutron powder diffraction (NPD) at the Institut Laue Langevin, Grenoble. Due to the difference in scattering contrasts between atomic species for the two radiations, combined refinements of both datasets should yield more accurate results. The resulting fits were satisfactory and the conclusion of the refinements was that the crystal structure had 6-fold symmetry, with existence of disorder between nickel and antinomy (these two atoms swapping positions). At this point, it appeared that regular triangular planes of Ni do not exist, so no magnetic frustration.

To get more detailed information about this apparent disorder, we investigated the sample by electron diffraction, which is done with a transmission electron microscope. As compared to X-Ray and neutron diffraction, electron diffraction can get single crystal diffraction data from a single particle of a powder sample. We can therefore obtain 3D diffraction information. We use especially the powerful technique of "precession" electron diffraction (PED), setting the electron beam at a small angle (2.5 degrees) from the optical axis of the microscope and precessing it continuously around a cone. This provides insight into the crystal structure at a much more local level.

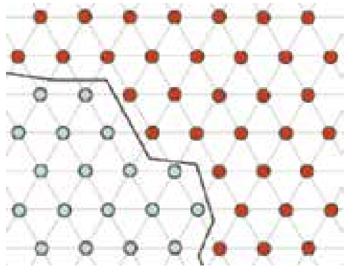
Fig. 2 shows a PED pattern obtained from a very small region of the sample. If the crystal has a 6-fold symmetry, the intensities should have a mirror symmetry with respect to the red line. Since this is not the case, only a 3-fold axis exists in the crystal.

So how can the above conflicting observations (hexagonal symmetry with Ni-Sb disorder, or trigonal symmetry with no disorder) be reconciled? If the sample contains crystal-structure domains at a small length scale, inside of which the crystal is perfectly ordered while neighboring domains have a different order, all our observations could be explained. Electron diffraction would be sensitive to the order inside one domain (size ~10 nm), whereas X-Ray and Neutron diffraction would "see" many domains and thus yield the average structure as being disordered.



2 / A precession electron diffraction pattern of a very small zone of the $Ba_3NiSb_2O_9$ sample. The intensities are not symmetric with respect to the red line, which proves that the crystal does not have a 6-fold axis, but at most a 3-fold axis.

Therefore, remembering the relevant length scales for these methods, we could derive a model reconciling the local ordered structure with an overall disordered structure (Fig. 3). Indeed, measurements of the magnetic properties of this phase are also in favor of the existence of ordered triangular Ni-lattices at least on a local scale.



3 / In each crystal domain, the Ni atoms are on a triangular lattice. But in the neighboring domain there are Sb atoms in the same plane, the Ni planes being in a plane shifted perpendicularly to the plane of the figure. The average over all domains therefore yields a mixture of Ni and Sb in the lattice, even though each individual domain is perfectly ordered.

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further reading...

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Imaging **quantum dots** with strain

One of the key elements of a quantum technology toolbox is a source of quantum light, capable of producing single photons on-demand. In the visible wavelength domain, the most advanced prototypes are semiconductor photonic nanostructures with embedded, light-emitting, quantum dots (QDs). A difficult aspect of this technology is that the fabrication method produces quantum dots located randomly in the nanostructure. Pinpointing their exact positions in the material could greatly help the characterization, engineering and scalability of these devices. But how can we map the dots' positions, non-destructively, with nanometric resolution, when they are embedded inside a dielectric nanostructure that does not allow conventional optical imaging techniques? The dependence of a quantum dots' emission wavelength on strain provides a path to resolving this problem.

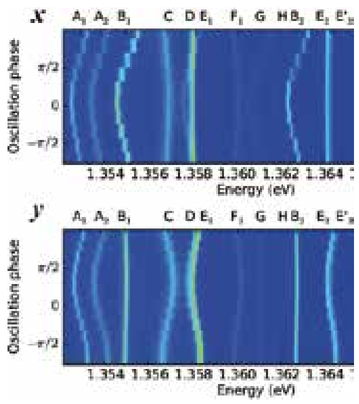
Several single-photon sources are based on quantum dots embedded in semiconductor micropillars or microwires. These dots, which are produced via spontaneous "self-assembly" processes, are randomly distributed in a single plane within the microstructure. To measure their positions in *x* and *y*, we drew inspiration from the medical imaging techniques of echography (which employs ultrasound waves) and Magnetic Resonance Imaging (which applies field gradients). Our basic idea is to use a known field-gradient that the QDs are sensitive to, in order to determine their position.

For this demonstration, we used a very efficient single photon source designed and fabricated by J. Claudon and J.-M. Gérard of the CEA's Institut Nanosciences et Cryogénie (Grenoble). This source is a gallium arsenide semiconductor "photonic-wire" antenna containing indium arsenide quantum dots. The dots are located in a horizontal plane at the base of the nanowire, see Fig. 1. Using a piezoelectric transducer, we excite the fundamental flexural mechanical vibration mode of the wire, which lies around *f*= 500 kHz. This vibration mode generates in turn a large oscillating strain gradient in the plane of the dots, as illustrated in Fig.1.

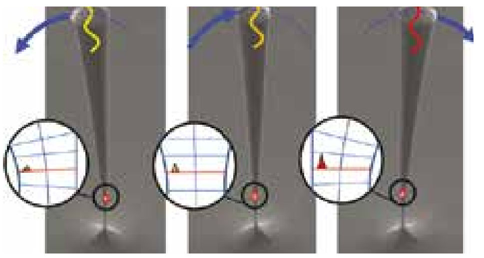
A quantum dot's energy levels are strongly coupled to local strain. As a result, the dot's emission wavelength is modulated in phase with the vibration as shown in Fig. 2.

In the plots of Fig. 2, each spectral line corresponds to a different quantum dot (each dot having a slightly different size). The amplitude of oscillation of the photon energy scales as the dot's coordinate along the axis of the gradient. The gradient direction is known from a native asymmetry of the photonic wire: its cross-section is slightly diamond-shaped rather than circular (Fig. 3). This asymmetry splits the wire's mechanical vibration into two orthogonally polarized modes. Thus, we can determine the dots' coordinates *x* and *y* by exciting, in turn, the wire's two mechanical frequencies (Fig. 2).

With this dataset and an appropriate calibration, we can produce a map (Fig. 3) of the dot locations with a precision ~30 nm near the wire's edge, ~1 nm at the centre (cf. dot size 10 nm).

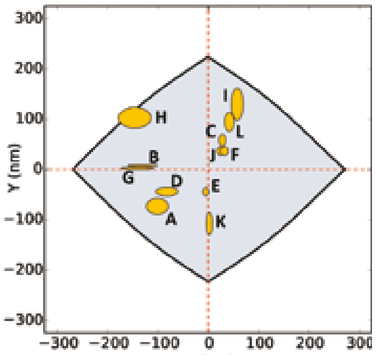


2 / *Stroboscopic measurement of the energy of the photons emitted by some of the QDs as a function of the phase of the two mechanical vibration modes, x-polarized (top panel) and y-polarized (bottom panel). Each emission line corresponds to a single dot (labelled A1, A2...). Their colours encode photons count rates.*



1 / *Scanning Electron Microscope image of the photonic-wire "antenna" embedding quantum dots. A dot (symbolized as a triangle), is shown during three different phases of the wire's vibrations. The dot emits photons upwards, of shorter wavelength under compressive strain (left panel), of longer wavelength under tensile strain (right panel).*

Our method is in principle applicable to many other kinds of embedded two-level systems such as nitrogen-vacancy (NV) centres in diamond, or rare earth ions in crystalline matrices. The only condition is the ability to apply a strain gradient across the emitters, either using a built-in mode of the nanostructure or by applying an appropriate excitation, such as a standing strain-wave.



3 / *Positions in x and y of the QDs (labelled A...) within their plane in the nanostructure, as obtained by our technique. Each ellipse represents a quantum dot, and its major and minor axes represent the location accuracy obtained by our technique.*

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P.-L. de Assis *et al.*, "**Strain-Gradient Position Mapping of Semiconductor Quantum Dots**", *Phys. Rev. Lett.* 118, 117401 (2017).

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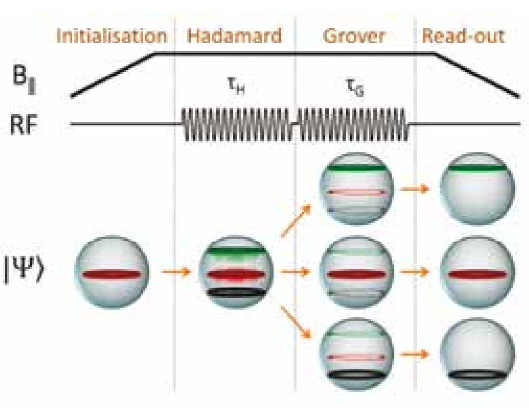
Molecular spin devices **for quantum algorithms**

Scrapbooks or social networks are collections of mostly unsorted data. The search for single elements in very large data volumes, *i.e.* for a needle in the data haystack, is extremely complex for classical computers. Classical computers switch transistors either on or off to symbolize data as ones and zeroes. In contrast, quantum computers use quantum bits, or qubits that, because of the bizarre nature of quantum physics, can be in a state of superposition where they act as both 1 and 0 *simultaneously*. In view of quantum computing, algorithms are being developed for cryptography, searching, optimization, simulation, and solving large systems of linear equations. Although a universal quantum computer is still a vision, special quantum systems that promise to solve certain tasks more quickly than a classical computer are already playing an important role in science.

Instead of creating quantum computers based on qubits that can each adopt only two possible options, some researchers make use of quantum devices possessing a number $d > 2$ quantum states. Called "qudits", they have the potential to open up a new way to create incredibly powerful quantum computers. As an example, for the task of reliably finding a certain element in unsorted data, a conventional computer has to run through, in the most unfavourable case, all N search elements successively. A qudit system implementing the search algorithm proposed in 2001 by L Grover accelerates this search quadratically.

In a recent experiment, we have implemented Grover's algorithm quantum-mechanically and executed it successfully, using a "molecular qudit". This is a "single molecular magnet" comprising a central, magnetic terbium ion (Tb^{3+}) sandwiched between two phthalocyanine molecules aligned parallel to each other. This complex is extremely robust, allowing its deposition on various substrates at high temperatures while conserving its molecular, electronic and magnetic characteristics.

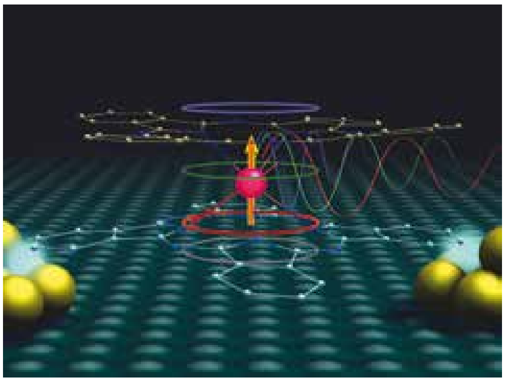
The Tb^{3+} ion carries a nuclear spin $I = 3/2$. Due to hyperfine coupling with the electronic spin, the 3/2 nuclear spin is split into $2I+1 = 4$ spin states with non-equidistant energy levels (Fig.1). The number N of spin states we decide to work with defines our database. The coherent manipulation of this multilevel quantum system (qudit) is achieved by means of electric fields only.



2 / *The Grover algorithm is implemented in four steps: (i) Initialization (application of a magnetic field B) to start the sequence from a desired initial state. (ii) Hadamard gate, a microwave pulse ("RF") to generate the database by creating a coherent superposition of three nuclear states, each having a probability 1/3. (iii) Grover gate (a different RF pulse) to "highlight" the searched-for state, i.e. to increase its probability up to approaching 1/1. (iv) Read-out of the final state by removing the field B.*

To treat the problem of the type "needle in a data haystack", we have used a database consisting of only three of the four nuclear spin states to implement the Grover algorithm, the idea being to establish a proof of concept. Thus, the haystack is the set of $N=3$ different nuclear spin states, and the needle is the nuclear spin state we are looking for.

The Grover algorithm is the succession of two quantum "gates" (Fig. 2). The first one, the "Hadamard" gate, starts from an initialised state to create a superposition of all three nuclear spin states. Then, the Grover gate amplifies the amplitude of the searched-for state, which has been labelled previously via its phase or its energy. As a result, making use of quantum amplitudes to determine the probabilities of an event, it is most probable to find the state searched for. By operating on a highly superposed system, the Grover algorithm succeeds in achieving a quadratic speedup of the search, as compared with a classical computing algorithm.



1 / *The spin based transistor on a Si substrate. A terbium "double-decker" single-molecule magnet is connected to two gold metal leads for electrical read-out of the terbium's electronic spin orientation (orange arrow), which itself "reads" the nuclear spin via the hyperfine interaction. Blue, green, red, grey rings depict the 4 nuclear spin states. The three different resonances between them can be addressed simultaneously using appropriate microwave pulses (the blue, red and green waves).*

The method presented here is of universal character and can be implemented in any multilevel quantum system with unequally spaced energy levels, opening the way to the use of other novel quantum search-algorithms.

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further reading...

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C. Godfrin *et al.*, **"Electrical read-out of a single spin using an exchange-coupled quantum dot"**, *ACS Nano* 11, 3984 (2017).

Spintronics at the **single electron level**

A single electron spin isolated in a quantum dot (a very small area in a semiconductor nanostructure) has been demonstrated to be an elementary magnetic memory useable for storing one bit of quantum information. Such a memory is very well protected from the solid state environment. Nevertheless, to use it to calculate or communicate in a more efficient way than in classical information processing, it is essential to be able to accurately transfer this electron spin and its quantum information between remote places. Institut NÉEL researchers, in collaboration with colleagues in Japan and Germany, have achieved transfer of spin information between two quantum dots separated by several microns. This was realized by an original approach: propelling the electron along a narrow channel at high speed by surface acoustic waves. Our most recent work has enabled us to quantify how the spin of the electron is affected by the displacement procedure, and thus evaluate the fidelity of the spin transfer at this single electron level.

The realization of static quantum dots relies on the deposition of thin gold gates on the surface of a thin layer of aluminium gallium arsenide (AlGaAs) deposited on a substrate of GaAs (Fig. 1). Electrons, initially free to move laterally over the interface between the two semiconductors, can be trapped electrostatically when the gates are polarized negatively. The nanofabrication procedure also allows us to produce extremely sensitive on-chip electrometers, that are used to measure the presence of electronic charges within the quantum dots but also their spin.

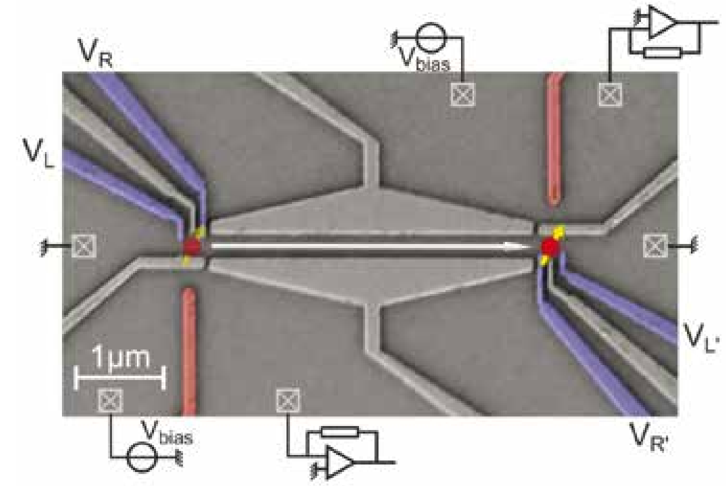
Reading the quantum state of a spin (the "read-out" process) is based on a spin-to-charge conversion, realized with the help of a spin-dependent tunnelling process in which an electron is forced to leave the quantum dot. More precisely, we apply a magnetic field to lift the degeneracy between the two spin states, and only an electron in the higher energy spin state will be energetically allowed to tunnel out of the dot.

Early pioneering work done in the field of electron control in a quantum dot of this type demonstrated the ability to preserve the spin information stored in a single electron, trapped in a quantum dot, for over several milliseconds. To transfer the electron between two quantum dots separated by 4 microns, we use electrostatic gating to define a quasi 1-Dimensional channel, depleted of electrons, between them (Fig. 1). We displace an electron in a "moving quantum dot", a moving trapping potential, which is generated in the channel by a controlled excitation of 2.6 GHz surface acoustic waves, a process that exploits the piezoelectric properties of AlGaAs/GaAs nanostructures. The electron then propagates at the speed of sound and the duration of its journey between the two static quantum dots is only 1.3 nanoseconds.

In more detail, the complete procedure to transfer the spin information carried by a single electron consists of three steps: First the information is imprinted in the spin degree of freedom of the electron trapped in the static quantum dot. Secondly, the electron is injected into a moving quantum dot which transports it to the second static quantum dot. Finally, the read-out of the transferred electron's spin is performed in this second static quantum dot. Repeating this procedure ten thousand times, we have demonstrated an overall fidelity approaching 65%. The fidelity is limited at present by depolarizing processes mainly occurring during the injection phase between the static source dot and the moving quantum dot, not during it's travel along the channel.

The depolarization of the electron appears to be due to a perturbation of its spin state by the surface acoustic wave. An appropriate redesign of the static quantum dots may permit reaching higher overall fidelities, as the accuracy of the initial loading of a spin state into the source dot is 96% and, for reading out the spin state from the destination dot, it is 92%.

We have also demonstrated the ability to transfer two entangled electron spins between the two quantum dots, a prerequisite for on-chip communication protocols. Our demonstration of spintronic experiments at the single and two-electron level on timescales much faster than the electron's typical decoherence and relaxation times paves the way to the use of individual electrons as a building block for future quantum nanoprocessors.



1 / *Scanning electron microscope image of the spin transfer device. Two quantum dots are defined at left and right by two sets of four surface gates (blue and grey). The properties of the dots can be changed at microsecond timescales by varying the voltages applied to the blue gates. The long middle gates (grey) define the channel along which the electron propagates with its spin state (yellow arrow) intact. The charge state of each dot can be monitored using an on-chip electrometer (a quantum point contact) defined by the red gate.*

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HIGHLIGHTS

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