NÉEL institut

HIGHLIGHTS

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EDITORIAL

Welcome to this new issue of Institut Néel Highlights. Going through the different items will provide you an overview of our main achievements of 2021. Of course giving an exhaustive overview of NEEL activities in a few pages is not possible and you can get more information browsing our new website https://neel.cnrs.fr.

Institut Néel is a CNRS laboratory (Unité Propre de Recherche) with strong links with Université Grenoble Alpes. Our main stream research focusses on fundamental science in condensed matter physics and chemistry to push forward the frontiers of knowledge and seek out new properties or systems. Beyond this and since physics is a foundation to many social issues and technologies, the laboratory also develops top level activities and engineering at different interfaces.

In 2021, the Covid pandemy put heavy strain on Institut Néel activities. As you will see browsing these 17 articles it anyway remains at top level thanks to the involvement of our staff both on site and remote. Challenges have even been faced like the installation of a new instrument for spatial observation in Chile, at more than 5000 meters high and during lockdown (6).

These 17 articles illustrate the variety of Institut Néel theoretical (11) and experimental research. One first important characteristic is the control of complete chains from materials to applications and the strong expertise in the associated technologies – synthesis, (nano) patterning, electronics, instrumentation - even in extreme conditions – cryogeny, Ultra High Vacuum, magnetic fields, high pressure, high temperature. Another one is the large diversity of the thematics from our main stream subjects - materials science (8, 14, 18), magnetism and magnets (9), extreme physical properties (12), quantum materials and technologies (9, 11, 13, 17, 19, 21) to social issues in link with energy (15, 20), cultural heritage (16), health and biophysics (10).

Valuing results is an important issue for an ever-increasing number of researchers. The innovation medal of CNRS awarded to N. Dempsey in 2021 for her work on magnets is one illustration of the growing interest for a coupled fundamental and more applied research. The 5 startups now hosted by the laboratory are another exemple. One of them MagREEsource (7) is presented here. Beyond the necessity to add value to our results, the subject, recycling, illustrates the common will to act for a sustainable future through our research thematics and in every day way of working.

Finally, I would like to thank all the authors and J. Vogel who edited these few pages. I especially thank R. Cox who has been putting a lot of time and effort in editing and improving the articles over the passed 15 years.

Have a pleasant reading!

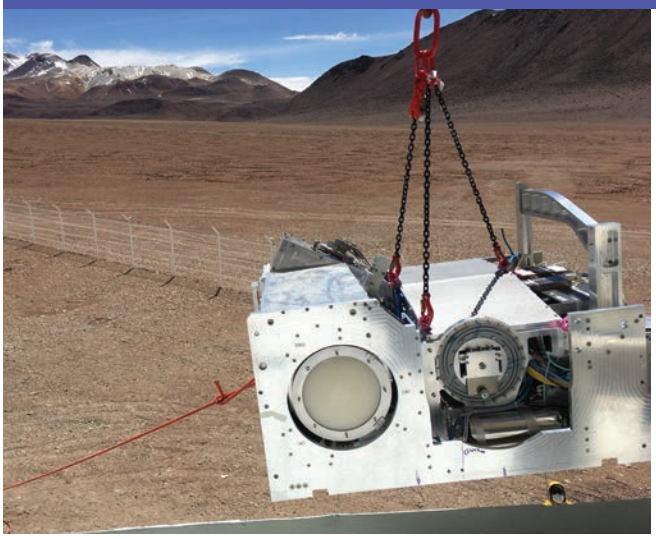
Laurence Magaud
Director

April 2022
Grenoble, France

CONTENTS

TRIPLE JUMP ON THE CHAJNANTOR PLATEAU

For astronomical observations in the portion of the electromagnetic spectrum between the infrared and radio waves, where the wavelengths are measured in millimetres, developing the instrumentation of a telescope can surely be defined as "challenging". This is because the most sensitive detectors, needed to measure tiny amounts of energy, must be operated at temperatures approaching absolute zero (i.e. -273.15°C). The CONCERTO detector instrument, constructed at the Institut Néel and installed on a radio telescope at 5100 metres altitude in Chile, pioneers wide field-of-view imaging spectrometers operating at millimetre and sub-millimetre wavelengths.



The CONCERTO chassis «flying» to APEX. The chassis, including the sub-Kelvin camera (left) and the MP-Interferometer's motors (right), being lifted to the platform of the APEX telescope in preparation for its installation in the Cassegrain cabin.

CONCERTO (an acronym for "CarbON CII line in the post-rEionisation and ReionisaTiOn epoch") was installed in April 2021 on the 12 metre radio telescope of the Atacama Pathfinder EXperiment (APEX). Covering the frequency range 100-300 GHz, CONCERTO inaugurates a new class of instruments. It combines the widest instantaneous field-of-view of the sky (20 arc-minutes), diffraction-limited angular resolution (30 arc-seconds), and tunable spectral resolution R = $\Delta\lambda/\lambda$ = 1 - 300).
In order to achieve this "triple jump", without sacrificing the optimal sensitivity, a 4.3 kilopixel cryogenic camera is coupled to a sophisticated optics system including a Martin-Puplett interferometer. A fast-moving (2.5 Hz) mirror allows separating the spectral components of the incoming radiation in the Fourier domain, for each individual pixel of the camera. When CONCERTO is observing, more than 20,000 full interferograms, converted into spectra by powerful "data crunchers", are generated every second.

The camera is contained inside a dilution refrigerator to achieve a base temperature of 0.06 Kelvin. The incoming quanta of millimetre radiation, despite their very small energy, can perturb the superconductivity of the aluminium detector pixels and thus generate a detectable signal in the CONCERTO instrument's Kinetic Inductance Detectors (KIDs).

The project, funded by a European Reseach Council grant, started in April 2018 with our first visit to APEX. This observatory combines an optimal performance telescope and optimal location (the Chajnantor plateau, 5100 metres above sea level). After the Critical Design Review, fabrication of the instrument started in February 2019. Weighing more than 1000 kg, CONCERTO is composed of thousands of mechanical pieces, several mirrors, valves, actuators, cables, pumps etc., and the detector array.

A pre-installation was carried out in February 2020. The hydraulic, electrical and network cables, linking the instrument sub-systems in the APEX telescope's tower, were prepared. But a virus was already arriving in Europe and the consequent lockdowns strongly affected the subsequent fabrication and testing plan. However, thanks to an admirable team effort and using all remote communications technologies, we managed to fully integrate the instrument in our laboratory by the end of 2020. The qualification tests occurred in January/February 2021.

The CONCERTO instrument was shipped to Chile in March, 2021. The two installation teams, and supporting collaborators, had to dribble and slalom between closed borders, special authorizations, COVID tests, quarantines, lockdowns and strict, changing rules. On the 10th of April 2021, after five days of intense work at high altitude in an atmosphere of only 550 mbars, the first cooldown of the camera at the high site was launched. Its base temperature of 0.06 K was achieved forty hours later. CONCERTO was immediately driven into the commissioning phase, with the first detection of the Moon, then the planets (as primary calibrators) with decreasing brightness from Jupiter all the way down to Neptune, and finally galactic and extragalactic sources.

In July 2021, CONCERTO, operated remotely, started its ambitious, primary science program which consists in studying the birth of the very first generation of stars in the early universe via CII-Line Intensity Mapping. This involves detecting the 158 micron emission from carbon ions in those very remote stars, which is "red-shifted" to millimetre wavelengths by the expansion of the universe. Among other targets are galaxy clusters (the largest gravitational-bound structures in the Universe) and star-forming regions in our own Galaxy.

CONTACTS

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MagREEsource: NdFeB MAGNETS MANUFACTURING WITH A CIRCULAR ECONOMY APPROACH

The energy transition challenge is leading us towards an electric future. It's pushing all countries around the planet to deploy more renewable energies and to adopt green mobility massively. However, this situation creates significant supply chain tensions on raw materials such as Rare Earth based magnets that are the heart of any electric motor.

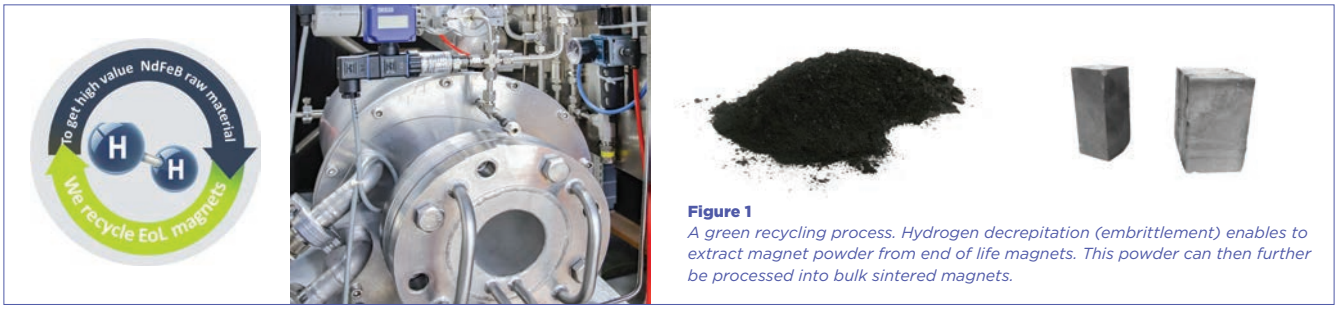

Figure 1
A green recycling process. Hydrogen decrepitation (embrittlement) enables to extract magnet powder from end of life magnets. This powder can then further be processed into bulk sintered magnets.

There are three major issues with magnets :

> First, 98% of Rare Earths based products are mined or transformed in China, the absolute magnet manufacturing leader. This raises sovereignty issues and that's why rare earth elements are classified as critical materials by the EU,

> Second, the number of electric cars, wind turbines, robots is booming. The future is electric but mining extraction cannot meet the demand increase and shortages are expected till 2030.

> Third, Chinese manufacturers have made magnets a "commodity" and standardized magnets are limiting the capacity of our European end use industries to innovate on their own core business.

Therefore, there is an urgent need for a sustainable and sovereign magnet manufacturing value chain in Europe. At MagREEsource, we want to overcome these issues with a disruptive and short loop "Magnet-to-Magnet" business model. This breakthrough is based on two main innovations :

> First, a state-of-the-art and patented hydrogen recycling technology, based on 30 years of development at CNRS/ Institut Néel in Grenoble. Magnet scraps are processed with Hydrogen to obtain an advanced magnet powder that is used directly as new raw material for our own magnet manufacturing process. This physical recycling process is green ; it doesn't have any environmental impact contrary to chemical recycling methods, involving solvent extraction and acids. Thanks to a short transformation process from the source (end of life magnets or scraps) to the newly formed magnet, it is very cost effective.

> Second, we are developing patented technologies such as additive manufacturing or sintering to produce customized magnets with optimized magnetic performances.

MagREEsource's ambition is to create the first European sustainable and competitive magnet production unit. Thanks to Circular Economy and advanced technologies, European magnet users will be able to diversify and secure their supply chain with a sustainable, reactive, cost-competitive and environment-friendly alternative.

MagREEsource's development is highly supported by public authorities through the French Recovery Fund and BPI tools and is targeting a first fund raising at the beginning of 2022. This will enable to cover the high investments needed to set up the first pilot production line in a dedicated factory, and to support the R&D efforts needed to develop customised products.
After a first pilot line with a capacity of 80 tons of magnet powder, our ambition is to set up a 500 tons sintered magnet production unit within 5 years with a turnover of 25 M€ and 35 jobs created, to start addressing premium markets like Defense and Aeronautics or robotics.

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MagREEsource
THE GREEN RARE EARTH MAGNET COMPANY

PROPERTIES FROM A LACK OF SYMMETRY: THE CAGE CRYSTAL FIELD IN CeB_6

Physicists are aware of the importance of considering symmetries for solving problems. Sometimes, the symmetry is the problem and its fault the solution ... the Crystalline Electric Field in rare-earth cage compounds is such an example, as illustrated in the paramagnetic range of CeB_6.

The degeneracy of the energy levels of a partially filled atomic shell can be lifted by magnetic or electric fields. In a crystal, the anisotropic charge distribution around a magnetic ion yields the Crystalline Electric Field (CEF). The CEF splits the degenerate atomic levels, resulting in the CEF energy scheme. The knowledge of this scheme is essential for any quantitative description of the properties of a magnetic material.
One historical success of group theory is its application to the CEF problem. From the point symmetry of the magnetic site, one can exactly determine the splitting and wave functions originating from an electronic multiplet. This success of group theory relies on an idealized picture: the crystal is perfectly organized and symmetrical. How can this agree with the fuzziness arising from quantum fluctuations and thermal disorder?

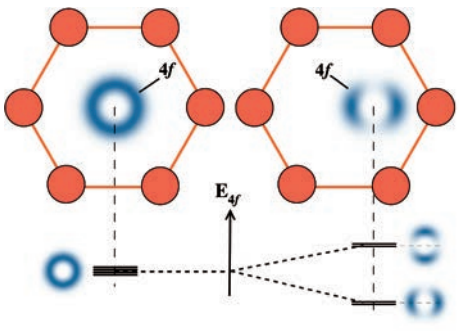

Figure 1
Schematic showing the effect, on a central degenerate rare-earth energy level, and associated 4f distribution, of an off-center position inside a cage.

The point is that, most often and over a large temperature range, atoms only slightly deviate from their equilibrium positions: the perfect symmetry is usually a sound approximation. However, some special cases must be considered. One example is a crystallographic structure where rare-earth ions sit inside oversized cages, with an unusually large amplitude of displacement. Taking the deviation of the rare-earth from the highly symmetrical cage centre into account, it can be predicted that:
> an energy level of the rare-earth 4f electrons, degenerate when the 4*f* atom is at the centre, is split when it is not (Figure 1). The 4*f* level thus acquires an energy width reflecting the fluctuating rare-earth position.
> for such an energy width of the rare-earth CEF ground state, one expects, upon decreasing the temperature in the paramagnetic range:
- a progressive reduction of the magnetic entropy.
- a Jahn-Teller effect yielding anomalous thermal expansion and a softening of some phonons.

Despite in-depth investigations, many phenomena in the rare-earth hexaboride series remain unexplained. Most analyses neglect one key feature: they are archetypal cage compounds. The models that consider a perfectly cubic rare-earth site fail already in the paramagnetic range, even in case of an unambiguous CEF scheme. For instance, the reported variation of CeB_6's magnetic entropy does not show a plateau at *R*lnN (with *R* the universal gas constant and N = 4 for a 4-fold degenerate state), as would be expected for the quadruplet CEF ground state of Ce in cubic symmetry.

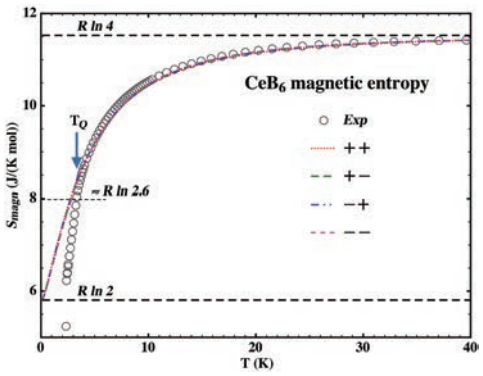

Figure 2
Experimental (circles) and computed (lines) temperature variations of CeB_6 magnetic entropy. The calculations account for the movement of the Ce^{3+} ion inside the cage.

At the Institut Néel, we addressed this issue with new specific heat measurements and an improved description, in the cage context, of the phonon contributions to the specific heat. Once corrected for these contributions and latent heats, the magnetic entropy displays the expected *R ln4* plateau (Figure 2), but at temperatures above 30 K. Below 30 K, as the ordering temperature T_Q is approached, the magnetic entropy is substantially reduced. This anomalous temperature dependence is well described (Figure 2) considering that, inside the cage, the quadruplet ground state is dynamically split by the rare-earth motion. The cage CEF interpretation is corroborated by the anomalous thermal expansion observed in the same temperature range, which materializes the so-called centrifugal Jahn-Teller effect: expanding the rare-earth distribution inside the cage lowers the 4*f* electrostatic energy.

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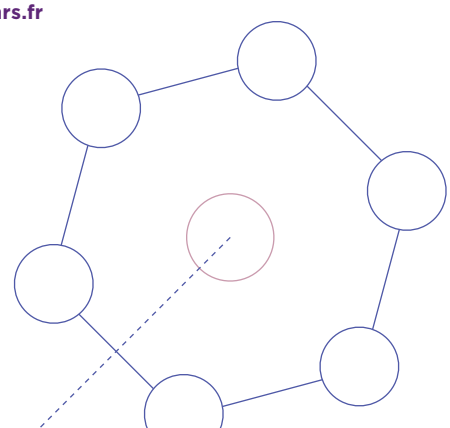

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HOLE-Cr^+ NANOMAGNET IN A SEMICONDUCTOR QUANTUM DOT

Point defects in solid-state materials have emerged as an important platform for quantum technology applications. Individual localized spins in semiconductors already find some applications in defect-based quantum systems. Many point defects exist in semiconductors and a detailed understanding of their properties and their interaction with the host material will permit discovering new relevant systems for specific quantum applications. Magnetic transition metal atoms incorporated in conventional semiconductors are of particular interest as they offer a large choice of localized electronic spins, nuclear spins as well as orbital momentum. The spin of such magnetic atoms can be probed and controlled through their interaction with confined carriers in a quantum dot.

We demonstrate here that the use of semiconductor nanostructures allows engineering the spin properties of individual defects. We illustrate this with Chromium (Cr) that incorporates naturally in II-VI semiconductors as the isoelectronic impurity Cr^{2+}: electronic configuration $3d^4$ with a spin S=2. However, Cr^{2+} is also an electron acceptor in these materials, which can capture an electron and adopt the Cr^+ electronic configuration ($3d^5$) with a localized electronic spin S=5/2.

We show that the Cr^+ ion, an unstable excited state of Cr in bulk II-VI semiconductors, is stabilized when inserted in a quantum dot. In our experiment, the quantum dot is an island of CdTe embedded in ZnTe. The negatively charged Cr^+ can attract a heavy-hole (a valence band state in semiconductors with a quantized spin $J_z=\pm3/2$) in the quantum dot, leading to a hole-Cr^+ complex. Absorption of a photon creates an electron-hole pair in the dot. Inversely, a photon is created by the annihilation of an electron and a hole. In the presence of a hole-Cr^+ complex in the dot, the energy and polarization of the emitted or absorbed photons depend on the spin state of the complex.

Magneto-optic measurements reveal that the hole and the Cr^+ spin are coupled by a ferromagnetic exchange interaction which comes from the hybridization of the 3d orbitals of the magnetic atom with the p orbitals of the host semiconductor. At low temperature, the thermalization on the ground state of the hole-Cr^+ system with parallel spins prevents the optical recombination of the excess electron on the 3d shell of the atom with the confined hole. A stable ferromagnetic hole-Cr^+ complex is formed with two degenerated ground states of total angular momentum $M_z=\pm4$ (Fig.1).

The spin of the hole-Cr^+ complex can be probed and controlled optically. We used resonant optical excitation to initialize and read out the spin states. We show that excitation with a laser beam resonant with the high energy optical transition can be used to address the ferromagnetic ground states $M_z=\pm4$. These states can be controlled by resonant optical spin pumping. A spin relaxation time in the 20 μs range is obtained at zero magnetic field and at T=4.2 K. The hole-Cr^+ complex behaves like an optically addressable, long-lived nanomagnet. Its spin memory, limited by the interaction with phonons, would be significantly enhanced at sub-Kelvin temperature.

In future work, the optical probing of this nanomagnet will be combined with modulation doping and electrical gating to demonstrate an electrical control of the oxidation state of the atom allowing a tuning of its spin and orbital momentum.

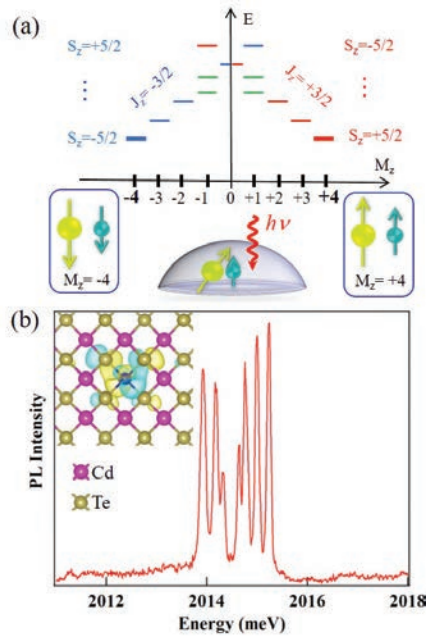

Figure 1
(a) *Energy levels of the nano-magnet formed by the ferromagnetic coupling of the spin S=5/2 of a Cr^+ ion and the spin $J_z=\pm3/2$ of a heavy-hole confined in a CdTe/ZnTe quantum dot.*
(b) *Photoluminescence spectra of a quantum dot containing a hole-Cr+ nano-magnet. A circularly polarized resonant optical excitation on the high energy line permits to address either the ground states with $M_z=+4$ or $M_z=-4$. The inset presents the calculated orbital of one of the d states of a substitutional Cr^+ ion showing the hybridization of the Cr and Te orbitals responsible of the exchange interaction with the hole spin of the host semiconductor.*

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FURTHER READING

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IS FOURIER'S LAW STILL VALID AT THE MICROMETER SCALE IN BIOLOGICAL MATTER?

Complex organisms have developed an evolutionary advantage by maintaining a constant body temperature that allows them to remain active in a wide range of environmental temperatures. This advantage is gained at the cost of a high basal metabolic rate (the rate of energy expenditure per unit time at rest) that produces heat and the need for food resources. Mitochondria, micrometer sized organelle inherited from the mother egg, have long been identified as the powerhouse of the cell and provide a major contribution to body heat production. Since mitochondria are considered as universal cellular radiators, a key question is whether (and to what extent) the radiator could be warmer than its surroundings.

Measuring temperature or heat generation at the subcellular scale is a considerable challenge since it requires sensitive thermometers that need to be smaller than the typical volume to be probed. Using molecular probes, temperatures within mitochondria or in their vicinity have been measured to be a few Kelvin higher than the ambient temperature and in some cases as high as 50°C.

We investigated if such a temperature elevation was possible from the point of view of heat transfer at the nanoscale. Our main goal was to evaluate nanoscale effects resulting from the complex nano architecture of mitochondrion that could reduce heat transport and explain the measured temperature elevations. In ordered crystals, heat is transported by quantum quasiparticles called phonons. Phonons diffuse from higher to lower temperatures by undergoing scattering on defects, such as impurities in the lattice, surfaces or other phonons. If the size of the system approaches the mean free path, the average path between two successive inelastic scattering events, the heat transport may be modified and Fourier's law may be not valid anymore. This has been suggested as a possible explanation for the measurement of a very high temperature gradient.

In disordered material such as glasses, polymers, liquids and by extension biological matter, the concept of phonons does not exist and should be replaced by molecular motion that propagates through the materials. Although the coherence of these vibrations is not as well defined as in ideal crystals, the behaviour is not expected to differ qualitatively. We show that at room temperature the mean free path is at the order of the molecular size and heat transport should be diffusive in accordance with Fourier's law. Hence, the thermal conductivity of these materials is in principle well defined and cannot be smaller than in insulating materials and rarefied gas, i.e. of the order of 0.1 to 0.01 $WK^{-1}m^{-1}$, ruling out the possibility to measure temperature gradients above 10^{-5} K considering the power dissipated in a single mitochondrion.

To solve this experimental discrepancy, more measurements with various thermal micro or nano-sensors should be performed. The heat dissipation in biological systems should be examined as well as the thermal transport in biological matter starting with purified molecules and going to tissues. These have concrete applications in various therapeutic strategies and will nourish the scientific debate on the heat transport at the nanoscale in biological materials.

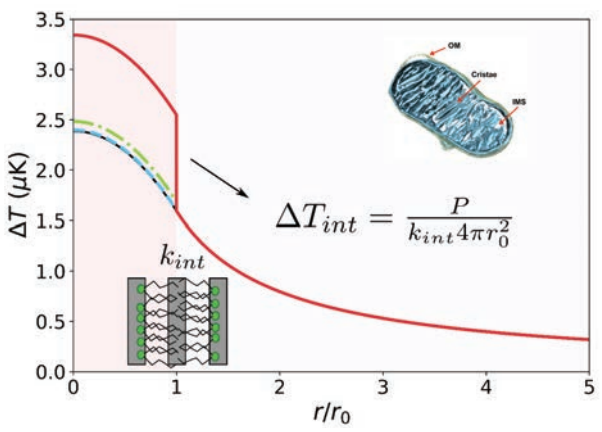

Figure
Temperature field in mitochondrion. The inset shows the 3D volume of a mouse mitochondrion reconstituted from cryogenic electron microscopy. The power dissipation generated by irreversible processes taking place in the densely folded inner membrane is approximated as a homogeneous power source while the complex elongated shape of the mitochondrion is approximated as a sphere. Various liberal or conservative assumptions including the effect of interfaces lead to a very low temperature elevation at the center of the mitochondrion.

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QUANTUM ELECTRONIC TRANSPORT IN FLAT-BANDS

Over the past years, we have been witnessing a rapidly growing interest for the physics in flat-band (FB) systems. FBs are dispersionless (crystal momentum independent) parts in the electronic spectrum that are due to destructive quantum interferences. FBs are at the origin of a plethora of exotic and unexpected physical phenomena, such as topological states, unconventional superconductivity, Wigner crystals, ferromagnetism as well as unusual quantum electronic transport (QET).

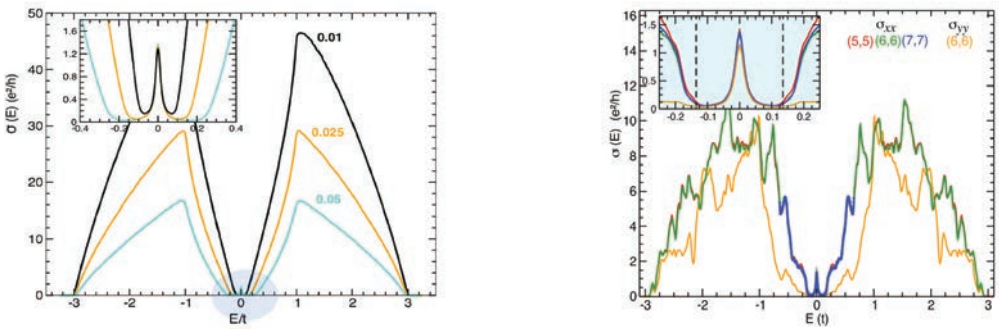

Figure 1
(left) *Conductivity (in units of e^2/h) as a function of the Fermi energy in fully compensated graphene (see text). We consider 3 different concentrations of C vacancies (x = 0.01, 0.025 and 0.05).*
(right) *Effects of nanostructuring in graphene. Nanostructuring consists in dividing a square piece of graphene into 9 congruent subsquares in a 3-by-3 grid, and the central subsquare is then removed (step1). This procedure is then repeated recursively to the remaining 8 subsquares, and so on (the Sierpinski carpet). (5,5), (6,6) and (7,7) mean respectively that the nanostructured structure has been obtained after 5, 6 and 7 recursive steps. Additionally, σ_{xx} (resp. σ_{yy}) means that the conductivity is calculated along the x-direction (resp. y-direction). In both figures, the insets magnify the neutrality point region (the FB energy is E=0).*

Here, we report an unconventional form of QET in two-dimensional (2D) systems possessing FBs. We recall that conventional QET is well apprehended semi-classically. It is of intra-band nature (Drude), controlled by the square of the Fermi velocity and extremely sensitive to the disorder which leads to the elastic and inelastic multiple scattering of the electrons. In contrast, and because of a vanishing group velocity, the FB transport is Drudeless (i.e. the intra-band contribution vanishes). It is purely of quantum nature, and controlled by the off-diagonal matrix elements of the current operator between the FB and the dispersive bands. It is robust against disorder, nanostructuring and almost unsensitive to the amplitude of the inelastic scattering processes. The presence of a gap between the FB and the dispersive bands has only a minor impact (often negligible) when the Fermi energy coincides with that of the FB. Thus, even when the FB is reduced to an impurity band the system is "super-metallic", contrasting with the insulating phase of conventional QET. The term "super-metallicity" has been introduced to characterize this unusual type of electronic transport.

To illustrate these findings, we present the calculated conductivity for two different types of graphene-based systems, the disordered fully compensated graphene (FUG) and the nanostructured graphene (NG) (Fig. 1). In the FUG, vacancies are randomly distributed on the same sublattice. This leads to (i) a E=0 flat-band and (ii) the opening of a gap between the FB and the dispersive bands. The gap scales almost as the square root of the vacancy concentration. Notice that no gap opens up when vacancies are distributed fully randomly, ignoring the sublattice index. If we focus on the FB region, we notice a peak in the conductivity that is insensitive to the concentration of vacancies, thus to the gap amplitude. The width of this peak is controlled by the inelastic scattering rate only, but the conductivity at the FB energy is independent of it. In the NG case, we find quasi-identical values of the conductivity at E=0 as well, it is insensitive to the level of nanostructuring.

To demonstrate the universal nature of FB transport, we are currently investigating other systems and lattices such as the disordered Lieb lattice, the dice lattice and the Kagomé lattice. it's very likely that the flat bands have not finished surprising us.

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G. Bouzerar and D. Mayou I Phys. Rev. B, 103, 075415 (2021)

EXCITING SUPERFLUID HELIUM!

Helium remains fluid at low temperatures, an exceptional behaviour, due to quantum mechanics. At about 2.17 degrees above the absolute zero of temperature, it undergoes Bose-Einstein Condensation (BEC), which provided in 1938 the first experimental observation of BEC. It also becomes superfluid, a new state of matter where fluid flow occurs without viscosity. The elegant ideas proposed by Lev Landau to describe a strongly interacting quantum system in terms of quantized sound waves (phonon and roton "quasi-particles") are tested here by doing a high accuracy neutron scattering measurement of the phonon-roton spectrum.

Landau predicted in 1947 the phonon-roton spectrum of the excitations in superfluid ^{4}He. His phenomenological theory introduced the fruitful concept of "quasi-particles": A complex system of interacting particles was described by a simple effective theory focusing on the quantum "excitations" of the system. In superfluid ^{4}He, a way to "excite" the fluid is to create density waves, called phonons. In the long wavelength limit, phonons are ordinary sound waves. At very short wavelengths, comparable to interatomic distances, Landau suggested the existence of a minimum in the dispersion relation (the curve described in Fig. 1). The excitations around this minimum correspond to a sophisticated vibration mode, named "roton" because it was initially believed to be a microscopic vortex. This is not the case, but the name was there to stay.

Landau's intuition was confirmed by Feynman's microscopic theory (1954). Cohen and Feynman also suggested using neutron scattering to try to observe the dispersion curve: Neutrons can create excitations in the superfluid, and determine the energy and wavelength of these excitations. The proof of the existence of a phonon-roton curve was finally brought in 1957 by Palevski et al. Although this work was followed by many neutron scattering experiments, many discrepancies remained between ultrasonic and neutron data collected in different wavelength ranges.

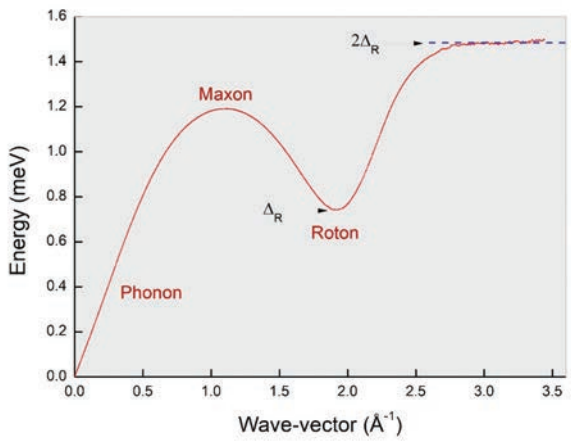

Figure 1
The measured dispersion relation of the excitations of ^{4}He. The energy of the sound waves (the "phonons") in ^{4}He is shown as a function of their wave-vector k= 2π/λ, where λ is their wavelength. At small wave-vectors, the energy of the phonons is proportional to k. At high values of k the curve displays a "roton" minimum of energy Δ_R.

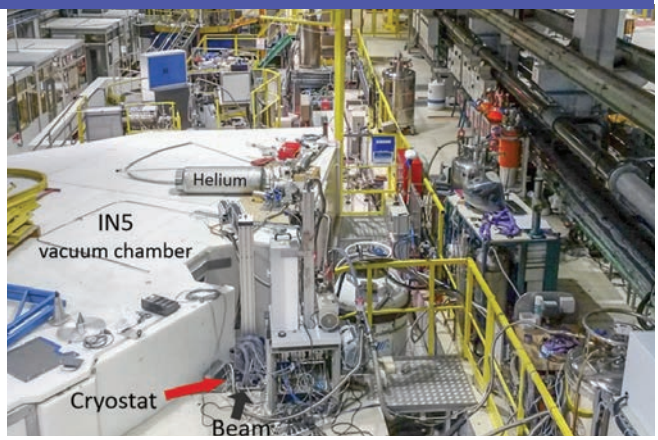

Figure 2
The dilution refrigerator and helium gas handling system on the instrument IN5 at the Institut Laue-Langevin.

Progress in neutron scattering has allowed us to bridge this gap. We measured the excitations of superfluid ^{4}He at very low temperatures, in a neutron beam on the IN5 time-of-flight instrument at the Institut Laue-Langevin, Grenoble, using a highly pixelized detector bank (10^5 pixels) to cover the energy-wavelength range of interest. Each pixel was treated as an individual detector, and a detailed analysis of systematic errors was made.

The unprecedented accuracy of the results shown in Fig. 1 allows a direct calculation of the thermodynamical properties of ^{4}He in the temperature range 0 to 1.3 K. Developing Landau's model, we could determine the specific heat, to compare with thermodynamic measurements. The neutron data are more accurate than thermodynamic measurements, in particular at very low temperatures where thermometry is difficult.

The present results offer a textbook example of the use of "effective theories" in general physics. They also have applications in experimental physics: The properties of phonons and rotons are exploited in modern detectors for particle physics and in quantum measurements on nanoscale devices, among other applications.

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FURTHER READING

Dispersion relation of Landau elementary excitations and thermodynamic properties of superfluid ^{4}He.
H. Godfrin, K. Beauvois, A. Sultan, E. Krotscheck, J. Dawidowski, B. Fåk, and J. Ollivier I Phys. Rev. B 103, 104516 (2021)

SUPERCONDUCTING $PdTe_2$ VISUALIZED BY SCANNING SQUID MICROSCOPY

Finding superconductors with new properties is an important challenge of today's condensed matter research. A promising family of materials are the transition metal dichalcogenides, to which $PdTe_2$ belongs. Angle-resolved photoemission spectroscopy has identified $PdTe_2$ as a Dirac semimetal, with a tilted Dirac cone below the Fermi energy. $PdTe_2$ is also a superconductor below T_c= 1.6 K.

Superconductors come in two types that differ in the way they react when submitted to magnetic fields: Type-I superconductors, mostly elemental (Al, Pb, IN...), are admitting magnetic flux in large bundles, while type-II superconductors admit magnetic flux in single quantized individual flux tubes. The nature of the superconducting state of $PdTe_2$ has been subject of debate. Scanning Tunneling Microscopy and point contact spectroscopies proposed mixed type-I and type-II superconductivity but DC-magnetization and AC-susceptibility measurements showed fingerprints of type-I superconductivity.

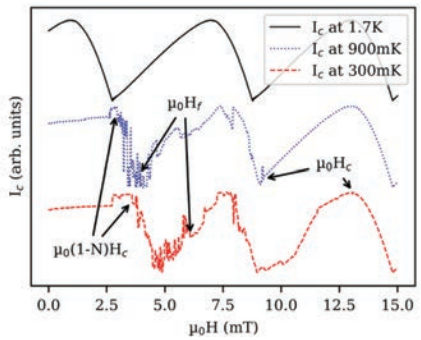

Figure 1
The SQUID response after Zero Field Cooling at three temperatures. In the normal phase (black solid line) the SQUID response is smooth and periodic. In the superconducting phase we distinguish three different behaviors: (i) flat response, i.e. screening for $H < (1-N)H_c$, (ii) high density of I_c jumps, i.e. penetration of magnetic flux tubes for $(1-N)H_c < H < H_f$, and (iii) smoother jumps, i.e. when flux tubes fuse into laminar structures $H_f < H < H_c$. The fields $(1-N)H_c$, H_f and H_c are indicated by arrows.

We undertook magnetic microscopy measurements to image the magnetic state of superconducting $PdTe_2$. Our measurements were made with a high-resolution scanning μ-SQUID microscope working in a dilution refrigerator. The microscope scanned the surface of a $PdTe_2$ single crystal having the shape of a flat rectangular prism. With the SQUID (Superconducting Quantum Interference Device) at a fixed position we measured the magnetic flux penetration upon increasing the magnetic field in the superconducting state as well as in the normal state of $PdTe_2$, see Figure 1. In the normal state (T=1.7 K) the sample is magnetically transparent, consequently the SQUID's critical current arches appear smooth and regular. In the superconducting state (T=0.9K and 0.3 K and $H<H_c$) the magnetic field is screened by supercurrents. Above a certain magnetic field, magnetic flux bundles penetrate into the sample forming regular structures, revealed by the irregular variation of the critical current of the SQUID and this up to H_c, the magnetic field where superconductivity is destroyed and the SQUID response becomes regular. In order to explore these flux structures, we imaged the magnetic field configuration at a fixed magnetic field after zero field cooling. We show in figure 2 that flux structures form a triangular array of flux

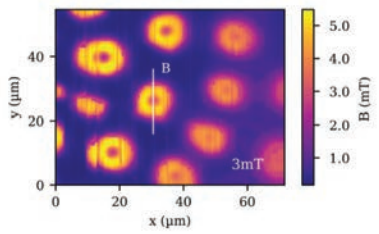

Figure 2
ZFC scanning SQUID images taken at a temperature of 900 mK (H_c = 9.1 mT) at an applied field of 3 mT (0.33 of H_c).

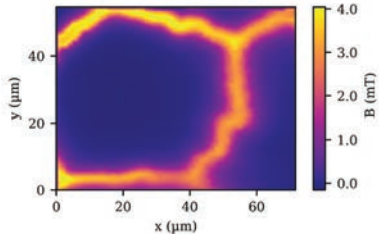

Figure 3
Scanning SQUID image taken after field cooling under 1 mT. Dark regions are superconducting and orange normal.

tubes. The applied magnetic flux funnels into the tubes bending the interface with the superconducting region. The flux tubes harbour a superconducting region in their center. The regular pattern is the result of an energy balance between the energy of the magnetic field in the superconductor and the energy of the interface between magnetic and superconducting regions. The transition from tubular to laminar patterns and the bending of the interface between the superconducting and the normal regions of the sample were predicted by the greatest theoreticians of superconductivity, and here we could demonstrate all the proposed aspects in one experiment.

Our images show the strong history dependence of type I superconductivity and the absence of single quantized vortices. When the sample is cooled in zero field the magnetic flux arranges in tube arrays as presented in Figure 2. However, when the sample is field-cooled the magnetic flux forms laminae that cross the sample from edge to edge as shown in Fig. 3. In this figure, the magnetic laminae form a honeycomb structure. The meandering of the normal region becomes more pronounced for fields close to the critical field. The intermediate state observed in $PdTe_2$ evidences type-I superconductivity.
The quantitative correspondence between theory and experiment designates $PdTe_2$ as the ideal material for exploring the intricate interplay of the energy scales relevant for the intermediate state in type-I superconductors.

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FURTHER READING

Visualization by scanning SQUID microscopy of the intermediate state in the superconducting Dirac semimetal $PdTe_2$
P. Garcia-Campos, Y. K. Huang, A. de Visser, K. Hasselbach I Phys. Rev. B 103, 104510 (2021)

DOPING AT THE NANOSCALE: WHAT CAPACITY MEASUREMENTS TELL US

The promising optoelectronic properties of gallium nitride (GaN) and its alloys have driven research activities worldwide since the first GaN-based light-emitting diodes (LEDs) were demonstrated in the early 1990s. After 30 years of development, the maturity of GaN-based LEDs for lighting applications makes these devices a potential candidate for the next generation of µLED displays in smartphones, smartwatches and for augmented reality applications.

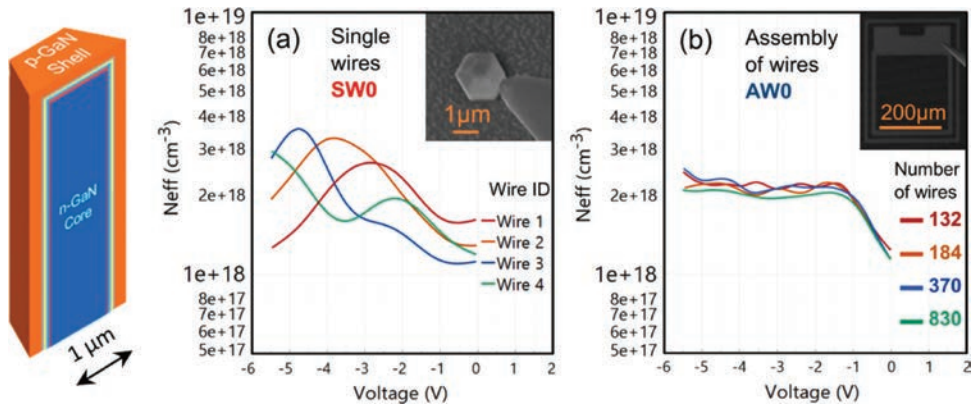

Figure
Illustration of a three-dimensional cleaved GaN core-shell wire on the left. Effective doping profile N_{eff} versus bias voltage of a single (a) and assembly (b) of core-shell wires and scanning electron microscopy picture of wires electrically connected.

Over the last decades, core-shell wire-based LEDs (see Figure) have emerged as an attractive alternative to two-dimensional (2D) LEDs for photonic device applications. The high aspect ratio due to the three-dimensional (3D) geometry increases the active region area. Moreover, the core-shell wire-based LEDs do not suffer from the efficiency reduction with downscaling. Indeed, the active region is protected from adverse surface effects thanks to a protective shell. These advantages make them very promising for future *µ*LED displays.

The high potential of GaN core-shell wires devices relies on a nanoscale spatially resolved understanding of their promising properties. In LED devices, when we apply an electrical bias, an electron (negatively charged) and hole (positively charged) can annihilate each other while producing a photon. It is thus necessary to connect two types of materials: one that conducts negatively charged electrons (*n*-doping) and one that conducts positively charged holes (*p*-doping). Such an interface is called a *pn* junction. The underlying doping profiles that rule the carriers' behaviour in 3D radial structures like our GaN wires with an *n*-doped core and a *p*-doped shell are still not fully understood. Developing electrical characterization techniques at the nanoscale, adapted to three-dimensional geometry, is essential to optimize the epitaxial structure and doping process of nano- and micro-wires.

In this context, in collaboration with the start-up company ALEDIA, we adapted a non-destructive doping profiling technique based on the measurement of the capacitance (C) as a function of the applied voltage (V) at the single nanowire level.

The measurement principle relies on the physics of LEDs. If both the *p*-doped and *n*-doped parts are conductive, the *pn* junction between them can become depleted of charge-carriers and hence non-conductive. In that case, the LED behaves as a capacitor where the depleted region plays the role of the insulator and the neutral *p* and *n* regions act as the electrodes. By measuring the thickness of the depleted region, thus C, and its extension as a function of the applied voltage V, it is possible to determine the effective doping profile N_{eff} in the *pn* junction by capacitance-voltage (C-V) measurements (see Figure).

If C-V measurements are now routinely used in the industry for macroscopic LEDs, applying such a technique to a single GaN nanowire is particularly challenging. Indeed, the junction capacitance of a single wire could be as low as 0.2 pF. Thus, we took special care to reduce the contribution of other parasitic capacitances.

Thanks to these efforts, we were able, for the first time, to measure C-V on individual core shell wires. This allowed us to study wire-to-wire homogeneity. A statistical study showed consistency between an assembly of wires and a single wire dopant profiling. This type of measurements was then applied to samples with different epitaxial growth conditions to assess the impact on doping profiles from one sample to another.

This result is a significant breakthrough with the state of the art and paves the way for the optimization of doping profiles for highly efficient *µ*LEDs based on nanowires.

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FURTHER READING

Nanoscale Dopant Profiling of Individual Semiconductor Wires by Capacitance–Voltage Measurement.
T. Lassiaz, P. Tchoulfian, F. Donatini, J. Brochet, R. Parize, G. Jacopin, and J. Pernot I Nano Letters 21, 3372 (2021).

COMBINING ELECTRONS AND X-RAYS TO SOLVE THE STRUCTURE OF A NEW BATTERY MATERIAL

Transition metal phosphates are the subject of intensive research for their application in metal-ion batteries. In this context the new sodium vanadyl hydrogen-phosphate $Na_2VO(HPO_4)_2$ has been synthesized for its potential use as cathode material. To understand and improve the properties of this material, it is crucial to have an accurate knowledge of its crystal structure, which requires to solve it from diffraction data, using model calculations and structure refinement. Due to the complexity of its diffraction diagram, the structure of $Na_2VO(HPO_4)_2$ was actually impossible to solve from powder X-ray diffraction data alone. We therefore used electron diffraction, which is a method of choice for such a study thanks to the possibility to work on individual crystallites constituting the powder.

Until 2005, the interest of electron diffraction (ED) for obtaining the crystallographic structure of unknown materials was considered limited. It actually provided only information about the unit cell through the periodicity/position of the spots. Their intensities, needed to determine the atomic positions within the unit cell, were unexploitable due to dynamical effects. Indeed, the strong electron-matter interaction allows working on a very small amount of matter, but makes also diffracted intensities unreliable (contrary to X-ray or neutron diffraction). New developments in ED over the past decade allowed to overcome this issue, using precession in electron diffraction, which significantly reduces the dynamical effects, in particular in 3-dimensions (3D). 3D Precession Electron Diffraction (3D PED) is now considered as a routine method in ab initio (i.e. from the basic physical laws) crystal structure determination. The method consists of tilting the crystallite in steps around the goniometer axis and recording an ED pattern, representing a section of the reciprocal space, at each step position. The patterns are then processed by specific ED crystallography software in order to reconstruct the 3D reciprocal space, measure the diffracted intensities and finally calculate a structure model from them.

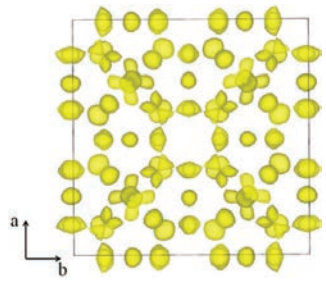

Figure 1
Electron density map of the structure of $Na_2VO(HPO_4)_2$ in a tetragonal unit cell reconstructed from calculations from a 3D-ED dataset.

However, $Na_2VO(HPO_4)_2$ is an electron beam sensitive material, which tends to get amorphous progressively under electron exposure. The 3D data collection thus needs to be performed fast enough to prevent the material from degradation. To do so, the dataset was collected by recording a video in the reciprocal space during the continuous sample holder tilt, which led to an experiment time around one to two minutes. Such a short experiment time, combined with a very spread electron beam, allowed the studied particle to remain crystallized. Thereafter, the individual ED patterns constituting the video were extracted and processed as those from conventional 3D PED. *Ab initio* structure calculations led to the 3D electron density map displayed on Fig. 1 in a tetragonal unit cell (a = b = 14.3 Å, c = 7.7 Å).

In order to confirm the tetragonal structure, a conventional powder X-ray diffraction (PXRD) refinement was performed. On the PXRD diagram, some peaks appear to be slightly doubled around specific Bragg reflexions (Fig. 2-a for example on the 200 peak), revealing an orthorhombic distortion (lattice parameters a ≠ b) which was too small to be detected from ED data. The whole structure was then successfully refined in an orthorhombic unit cell with the parameters a = 13.86852(19), b = 13.7985(2), c = 7.47677(9) Angstrom, and is depicted on Fig. 2-b.

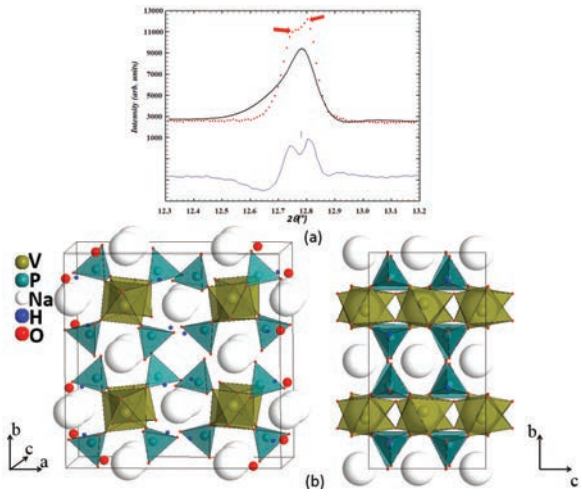

Figure 2
(a) *Structure refinement from powder X-ray diffraction diagrams: the black curve is calculated from the tetragonal unit cell, the red curve is the experimental one and shows a peak which is slightly split consistent with an orthorhombic distortion, and the blue curve is the difference.*
(b) *Refined structure in the orthorhombic system of $Na_2VO(HPO_4)_2$*

In conclusion, the combination of state-of-the art complementary diffraction techniques allowed us to determine with a very high precision the atomic structure of a new material, potential candidate to be used in future batteries.

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FURTHER READING

$Na_2VO(HPO_4)_2$: an Original Phase solved by Continuous 3D Electron Diffraction and Powder X-Ray Diffraction
C. Lepoittevin, O. Leynaud, A. Neveu, T. Barbier, M. Gnanavel, V. Gopal and V. Pralong I Dalton Trans., 2021, 50, 9725

REVEALING THE TECHNIQUES OF MEDIEVAL ARTISTS BY X-RAY ANALYSES

Cultural Heritage Sciences are developing a strong interest in understanding the skills and techniques used by early craftsmen and artists. A rapidly growing number of scientific investigations are now yielding a wealth of information on the history of art and techniques. These investigations also benefit the fields of restoration and conservation by providing detailed knowledge of the materials used and their degradation over time.

As part of the "PATRIMALP" project (a Cross Disciplinary Programme of the IDEX Université Grenoble-Alpes) several teams covering art history, physico-chemistry, numerical sciences and art restoration are involved in the study of painted works bearing specific decorations called "applied brocades" produced in the Duchy of Savoy at the end of the Middle Ages. These artefacts are of scientific interest for each of the disciplines involved, thus promoting interdisciplinarity.

The applied brocades are decorations in light relief which aimed at imitating, on a painted or sculpted support, the silks embroidered with gold or silver threads worn by the nobility during medieval times. Originating in northern Europe, this complex polychrome decoration technique quickly spread to works produced in the rest of Europe during the 15th and 16th centuries. Analyzing these decorations which consist of a complex stacking of materials of different natures (organic, inorganic, metallic...) and different crystalline states and thicknesses, often covered by late overpainting, pose a real materials-science challenge (Fig. 1).

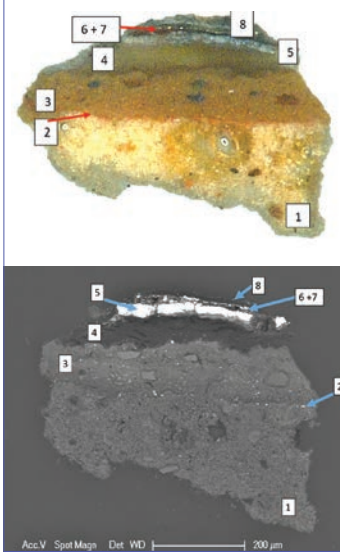

Figure 1
Typical stratigraphy of a half-mm size brocade sample (at top: optical microscopy: below: electron microscopy), from the 15th century Pietà of Montrottier castle, Lovagny, France. Layer compositions from combined analyses are:
1) gypsum
2) vermillion
3) second filling layer: saponified oil and pigments
4) first filling layer: beeswax
5) tin oxides
6) organic glue
7) gold foil and silver chloride
8) highlighting, organic layer

Our strategy was to perform systematic non-invasive investigation of a large corpus of 17 statues from the Savoy Duchy, using a portable instrument combining X-ray fluorescence and X-ray diffraction. Based on these analyses, selected micro-samples could then be taken and submitted to non-destructive synchrotron tomographic measurements, providing more precise and detailed information. These data were complemented with optical and Scanning Electron Microscopy observations and infrared and Raman spectroscopy on sacrificed micro-samples.

Our first X-ray measurements were made on a portable instrument from the Laboratoire d'Archéologie Moléculaire et Structurale (Paris). We then developed our own instrument, called "MobiDiff", which is now used in several collaborative research projects within PATRIMALP (Fig. 2).

Figure 2
Analysis of the polychromy of a medieval sculpture (Saint Jean Baptiste, early 16th century, Musée Savoisien, Chambéry) using our X-Ray instrument "MobiDiff".

Our investigations show the variations of the materials used, and their stacking within a brocade, which could reveal the knowhow of local workshops or craftsmen and provide markers to follow the diffusion of artworks at the regional scale. For example, the material used to fill the tin foil relief and to transfer it to its support was often found to consist of two distinct layers, one being made of beeswax, the other of saponified oil and pigments. In some cases, the gilding was made of zwischgold, a mixture of gold and silver, rather than pure gold. We could also observe the effect of time to heavily degrade the original brocades: the tin metal foil is always observed as a mixture of tin oxides (romarchite and cassiterite), while the silver metal from the zwischgold gilding is transformed to silver chloride and sulfide. These observations help to reconstruct the original appearance of the decorations (which may be hardly detectable today) using computer graphics, and thus provide crucial information to the restorers.

This work was presented in the exhibition: "Pietà - Dans l'atelier des sculpteurs savoyards à la fin du Moyen Âge" at the Musée-Château, Annecy, from December 2021 to March 2022.

We dedicate this article to Alain Prat, who died in October, in appreciation of his valuable work on the design and the construction of the MobiDiff instrument.

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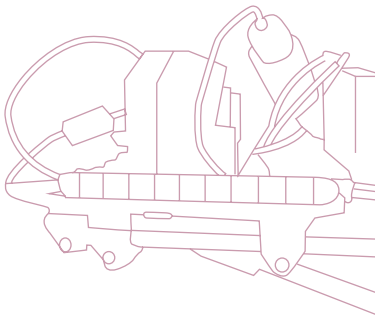

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Non-invasive X-ray investigations of medieval sculptures: New insights on "applied tin-relief brocade" technique.
P. Martinetto, N. Blanc, P. Bordet, S. Champdavoine, F. Fabre, T. Guiblain, J.-L. Hodeau, F. Lelong, O. Leynaud, A. Prat, E. Pouyet, E. Uher, Ph. Walter I J. Cultural Heritage 47, 89 (2021)

GERMANIUM ISLANDS AS TUNABLE SUPERCONDUCTING QUANTUM CIRCUITS

In collaboration with the Technical University of Vienna, we fabricate superconductor-semiconductor – superconductor junctions which are attractive for the realization of gate-tunable superconducting quantum bits. Using the substrate as a back gate, the transparency of the superconductor-semiconductor interface can be tuned by applying a voltage, going from a quantum dot regime to a supercurrent regime upon increasing voltage.

In this work, we succeeded in building aluminum (Al)-germanium (Ge)-Al junctions with high quality interfaces. A junction is fabricated from a Ge nanowire (NW) deposited onto a doped silicon substrate covered by a dielectric layer which can be used as a back gate. This NW is connected to two Al pads using electron beam lithography. Thermal annealing induces the substitution of the Ge inside the NW by the Al from the leads, giving rise to the motion of the Al-Ge interfaces along the wire as Ge diffuses into the pads and the Ge segment gets smaller. By controlling the duration of the annealing, this technique enables the fabrication of NWs with ultrashort Ge segments contacted by self-aligned quasi-1D crystalline Al leads (see the inset of the figure 1).

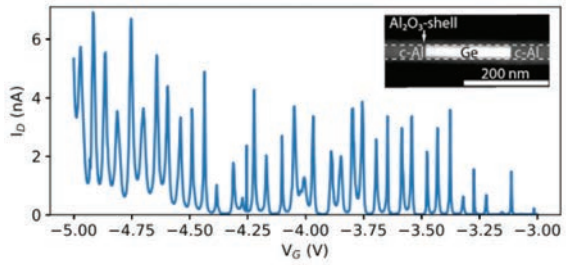

Figure 1
Coulomb oscillations of the current characteristic of the transport through a quantum dot with low tunnel coupling to the leads. Insert: Transmission electron microscopy image of an Al-Ge-Al junction with a Ge segment of 200 nm.

The transport measurements of the NWs show that a current can be measured only when a negative gate voltage is applied: this is because the carriers in the Ge are holes instead of electrons. The physical properties of the junction at low temperature are related to those of the interface. At a metal-semiconductor interface, a potential barrier called a Schottky barrier forms in order to align the Fermi energies across the interface. For a negative gate voltage close to 0V, the two barriers, combined with the inherent confinement of holes in the NW, result in the formation of a quantum dot whose characteristics are tunable. For a quantum dot, current can only propagate at specific gate voltages, which gives rise to periodic current oscillations called Coulomb oscillations, as shown in figure 1. Between two current peaks, the current is blocked and the number of holes in the dot is a well-defined integer.

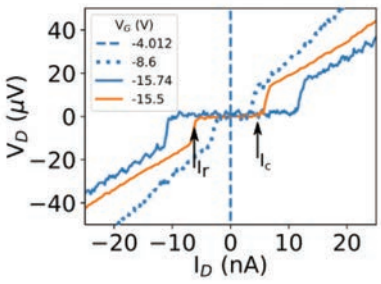

Figure 2
I-V characteristic of a junction with a Ge length around 40 nm for different gate voltages showing a zero resistance plateau related to a supercurrent through the NW.

As the gate voltage becomes more and more negative, the number of holes in the dot increases and the energy required to add a hole in the dot, called the charging energy, decreases. The strength of the barriers decreases with a more negative gate voltage, which increases the tunnel rate through the barriers, thus increasing the current maximum of the Coulomb oscillations. The range of variation of the tunnel rate and the charging energy is such that the Al-Ge-Al NW can be tuned beyond the Coulomb blockade. For a gate voltage around -10 V and for junctions with a length of Ge around 40 nm, the transparency of the barriers is high enough to allow the propagation of a supercurrent as shown in figure 2. This supercurrent, which is observed experimentally as a region of zero resistance, is tunable with the back-gate and reached a maximum of 10 nA.

Such a tunability of our hybrid device combined with the high transparency of the interface in the supercurrent regime are the most promising properties of the system. They allow fundamental studies of the influence of superconductivity on the physical properties of the semiconductor. The fabrication process is sufficiently robust and reproducible to adapt it to the fabrication of gate tunable superconducting quantum bits as well as topological superconducting systems.

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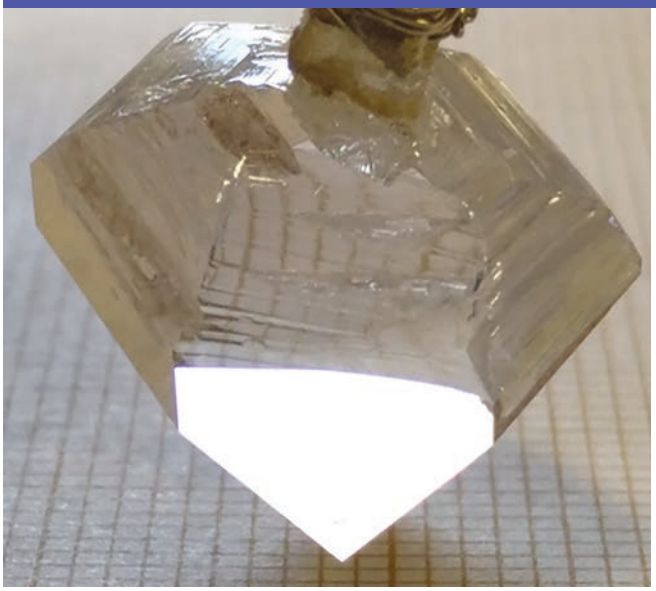
Al–Ge–Al Nanowire Heterostructure: From Single-Hole Quantum Dot to Josephson Effect.
Delaforce, J., Sistani, M., Kramer, R. B. G., Luong, M. A., Roch, N., Weber, W. M., den, M. I., Robin, E., Naud, C., Lugstein, A., Buisson, O. I Adv. Mater. 2021, 33, 2101989.
https://doi.org/10.1002/adma.202101989

A NEW NONLINEAR CRYSTAL FOR INFRARED EMISSION

α-GeO_2, which belongs to the Quartz family, is well known for its piezoelectric properties at high temperature. We have succeeded in growing several high-quality α-GeO_2 crystals using the so-called Top Seeded Solution Growth method. Our goal was to investigate these crystals for interesting nonlinear optical properties, such as sum frequency or difference frequency generation. The performed optical studies revealed that α-GeO_2 is a good candidate for generating coherent radiation in the mid-infrared wavelengths.



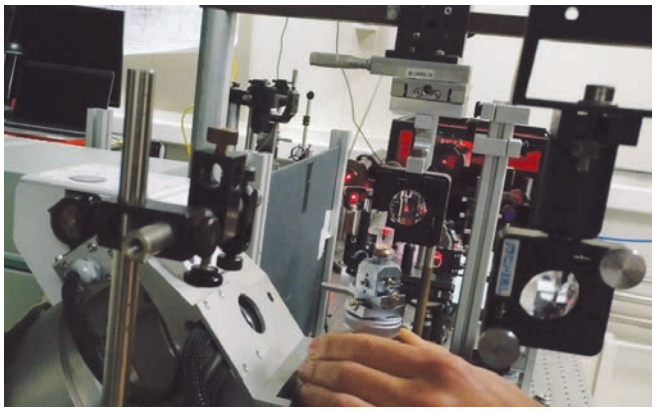
Piezoelectric materials, such as Quartz (α-SiO_2), are commonly used as sensors and actuators in applications like the measurement of mechanical strain and stress, energy conversion, and the generation and detection of ultrasonic waves. Of the many existing piezoelectric materials, only few can be used in high temperature environments, i.e. between 600 and 1000 °C, without suffering from phase transitions or chemical degradation that would affect the dielectric, piezoelectric and electromechanical properties.

At Institut Néel, we have grown α-GeO_2 crystals with volumes up to 3.5 cm^3 (Figure 1), using a high temperature solution method called Top Seeded Solution Growth. We obtained crystals that are free from OH- impurities, which is not the case when using the hydrothermal method commonly used for growing Quartz. Our α-GeO_2 crystals are thermally stable up to their melting temperature, around 1100 °C. We observed only a small evolution of the piezoelectric constant and the dielectric properties up to 600 °C, which highlights the potential of α-GeO_2 crystals for applications in harsh environments.

α-GeO_2 being an acentric crystal, it can exhibit the nonlinear coupling between three waves of different wavelengths, which can lead to the generation of infrared waves when using visible incoming radiations, corresponding to the so-called Optical Parametric Oscillation.

The intensity of such generated parametric light depends on several key parameters that we determined for the first time, to our knowledge, in α-GeO_2. By performing optical measurements on an α-GeO_2 crystal that we shaped as a cylinder with a diameter of 9.17 mm, its curved face being polished to optical quality, we determine the variation of the two refractive indices as a function of wavelength in the transparency range of the crystal. We also determined the magnitude and relative signs of the four nonlinear coefficients of the second-order electric susceptibility tensor of α-GeO_2. In the original experimental setup that we used (Figure 2), the cylinder is coupled to tunable laser sources, which are properly focused to ensure the beam propagation along the cylinder diameter for any orientation of the crystal. With one incoming beam on the sample, we studied Second Harmonic Generation as well as Optical Parametric Generation. With two incoming beams, we studied Sum- and Difference-Frequency Generation. By comparing thin oriented slabs of $KTiOPO_4$ (KTP, the absolute reference in nonlinear optics) and of α-GeO_2 we found that the four nonlinear coefficients of α-GeO_2 are equal, and three times smaller than the equivalent coefficient of KTP, while their optical damage thresholds are comparable.

Our experimental data indicate that α-GeO_2 can generate a super continuum light with wavelengths between 1.2 μm and 3.0 μm when pumped by a Ti:Sapphire laser emitting at 0.86 μm. All these indicators reveal α-GeO_2 as a promising new nonlinear crystal able to generate an optical parametric coherent radiation in the near- and mid-infrared range.



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FURTHER READING

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MOVING A MACROSCOPIC OBJECT THANKS TO A QUANTUM SYSTEM

We now know how to prepare atoms, or artificial atoms such as semiconductor quantum dots, in a well-defined quantum state via optical excitation using lasers. On the other hand, we cannot directly prepare a macroscopic mechanical system in a quantum state, because of its large number of degrees of freedom. Having such systems available would allow, among other new applications, the realization of force or position sensors with extraordinary precision, or the implementation of new functions in quantum information processing. One strategy explored by the community is to integrate an artificial atom into the heart of the mechanical system, prepare it in a well-defined quantum state, and then transfer this state to the macroscopic system.

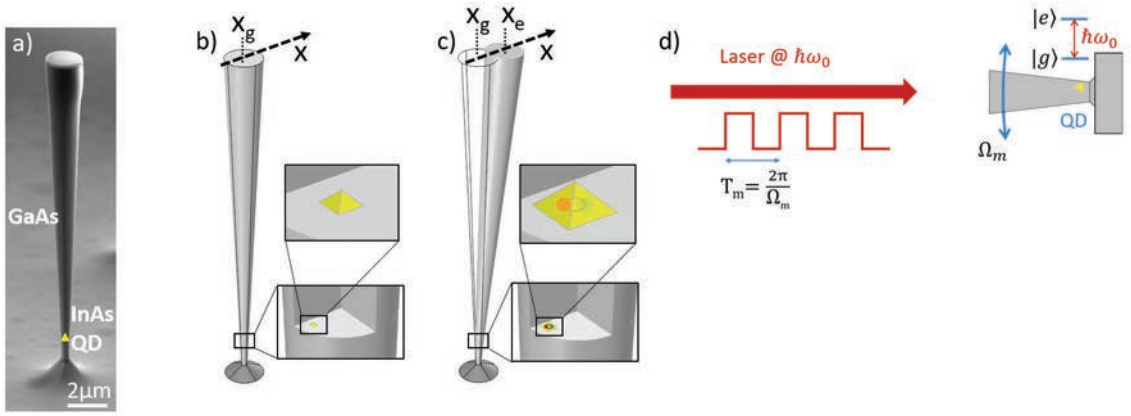

Figure 1
(a) *Image of the «hybrid» micro-wire developed by the team.* **(b - c)** *Principle of coupling between the quantum dot (QD) and the deflection of the micro-wire. The presence of an electro-hole pair modifies the effective volume of the quantum dot* **(c)**, *which leads to a deflection with respect to its equilibrium position* **(b)**. *The principle of the experiment is shown in* **(d)**: *a laser is chopped at the mechanical frequency and excites the QD in the microwire, and the induced motion is measured optically (not shown).*

Together with colleagues from CEA IRIG, ENS Lyon, University of Campinas, and University of Nottingham we have been able to set into motion a micro-wire by optically driving a single semi-conductor quantum dot (QD) thanks to a strain mediated coupling.

The device designed and fabricated by our colleagues J. Claudon and J.-M. Gérard from CEA-IRIG consists of an 18 μm long gallium arsenide semiconductor conical micro-wire, embedding at its basis an indium arsenide quantum dot (QD), offset from the axis of symmetry (see Fig. 1). The excited state of this type of quantum dot corresponds to the formation of an electron-hole pair, also called an exciton. The presence of this exciton in the QD modifies its effective volume (see Fig. 1c), which leads to an important modification of the strain field within the micro-wire. Since the QD is off axis, this strain field leads to a deflection, which is used to set the wire in motion. Experimentally, we use the pulses of a laser tuned to the transition of the QD to periodically form these excitons. The resulting vibration of the micro-wire is detected synchronously by an ultra-sensitive optical technique.

One of the major challenges to achieve these results is reducing the effects of thermal fluctuations in the position of the oscillator (50 pm rms) at the temperature of the experiment (T=20 K), as well as the photothermally induced motion caused by the periodic heating of the micro-wire (50 pm rms). Both effects tend to mask the very weak QD-induced motion of the oscillator (0.6 pm rms). Thus, the experiment had to be repeated a large number of times over 10 hours in order to average out these effects, which requires an experimental set-up of extreme stability.

While significant progress is still needed to encode quantum states from an artificial atom to a macroscopic mechanical oscillator, this proof-of-principle demonstration highlights the strong potential of all-optical manipulation of hybrid quantum dot/semiconductor microwire systems in this context.

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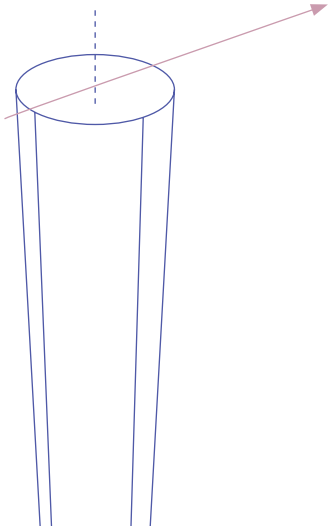

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SUNLIGHT IN THE SERVICE OF CHEMICAL REACTIONS

Solar radiation is a clean and inexhaustible source of energy. Many efforts have been made over recent decades to benefit efficiently from it, for instance producing electricity with photovoltaic cells. The conversion of sunlight into chemical energy is also a challenging issue, expected to give rise to large improvements in photochemistry or photocatalysis. Semi-conductors have been intensively studied for this, as they can absorb photons that create active electrons and holes able to initiate reduction or oxidation of chemicals. Unfortunately, the response of the most active semiconductor materials is restricted to ultra-violet (UV) wavelengths, and sunlight is only about 5% UV (cf 45% VIS, 50% infrared). Several ways have been explored in order to increase efficiency in the visible (VIS) region, such as cationic or anionic doping and organic-dye molecules. Very recently, a promising new approach has emerged, taking advantage of the ability of noble metal nanoparticles (NPs) to absorb light at specific wavelengths across the visible part of the electromagnetic spectrum.

This absorption property is due to the excitation of collective electronic oscillations, known as Localized Surface Plasmon Resonance (LSPR), see Fig. 1. It has been shown that this plasmonic effect can enhance chemical reactivity, such as in H_2 dissociation, CO oxidation or splitting of water molecules.

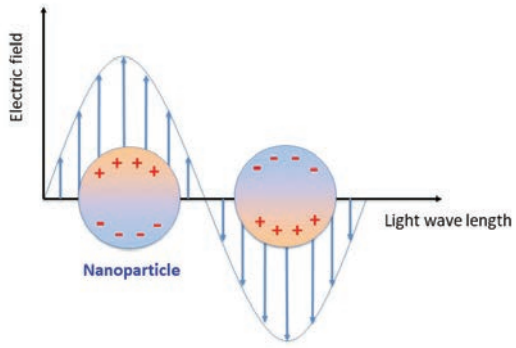

Figure 1
Localized Surface Plasmon Resonance (LSPR): The electric field of the incident light induces a collective oscillation of the free electrons in the metal nanoparticle. The resonance frequency depends on the size, shape, composition and local optical environment of the particle, and typically occurs in the visible spectrum for noble metal nanoparticles (gold, silver, copper).

For a complete understanding of the underlying mechanisms, knowledge of the relationship between structural properties and optical properties of the nano-crystals is essential. We have investigated *in situ* the structural and morphological properties of small (2 to 6 nm size) gold nanoparticles growing on the (110) surface of rutile (TiO_2), this by performing Grazing Incidence X-Ray Diffraction (GIXRD) and Grazing Incidence Small Angle X-ray Scattering (GISAXS), at the SIXS beamline of the SOLEIL synchrotron (France). The nanoparticles' optical response to visible light was simultaneously recorded by Surface Differential Reflectivity Spectroscopy (SDRS), see Fig. 2. Thanks to an experimental setup developed at the Institut Néel, we were able to separate the plasmonic vibration modes perpendicular and parallel to the surface.

We demonstrated that the surface state of the rutile substrate, flatter or rougher depending on the surface preparation procedure, has a major effect on the growth of the gold nanoparticles, and on their plasmonic response, both its frequency and its vibration modes.

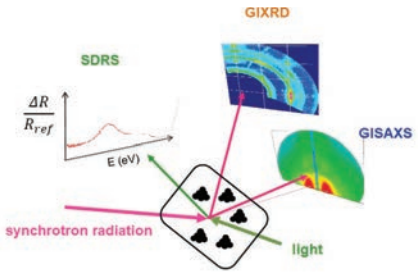

Figure 2
The set of techniques used simultaneously to characterize the morphology (GISAXS), the atomic structure (GIXRD), and the plasmonic response (SRDS) of the gold nanoparticles supported on the rutile substrate.

The GIXRD data showed that NPs grow epitaxially on the terraces of a flat (110) TiO_2 surface, while textured orientationally-disordered NPs are mostly present on the rougher substrate.

The optical response (from the SDRS data) was analyzed as a function of the size of the gold NPs (from GISAXS). We observed an overall blue shift of the frequencies of the plasmonic-peaks with decreasing NP size, for both substrates. The blue shift is weakly dependent on the NPs' environment. However, the optical responses of the two deposits are quite different. Compared to the epitaxial clusters growing on the flat TiO_2 surface, the LSPR response of the NPs on the rougher surface is observed at a lower wavelength. This is the signature of a weaker interaction between NPs and the substrate, in agreement with the structural characterization. Moreover, for the smallest deposited NPs (<4 nm size) plasmonic modes perpendicular to the crystal surface are no longer negligible.

Our results show clearly the possibility of tuning the Localized Surface-Plasmon Response as a function of the surface state of the substrate and also of the incident light polarization and of the nanoparticles' size. Indeed, tuning the LSPR resonance frequency is a key step to initiate, enhance and control chemical reactions.

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FURTHER READING

Localized surface plasmon resonance of Au/TiO_2(110): substrate and size influence from in situ *optical and structural investigation.*
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A SINGLE-QUANTUM-DOT HEAT VALVE

Good electrical conductors are in general also good thermal conductors. The Wiedemann-Franz law, for instance, states that most materials show a constant ratio between the charge and heat conductances at a given temperature, with superconductors as a notable exception. As a rule of thumb, the Wiedemann-Franz law applies as long as the transport processes are energy independent over a window larger than the amplitude of thermal fluctuations, k_{BT}. This condition does not hold when the conduction processes are strongly energy dependent, like in the presence of a single, highly energy-selective transport channel. In such a narrow channel in energy space, electrons can only go back and forth at this constant energy. Consequently, the heat conductance of the channel is nil, while its charge conductance can be very high. In other words, the Wiedemann-Franz law is maximally violated.

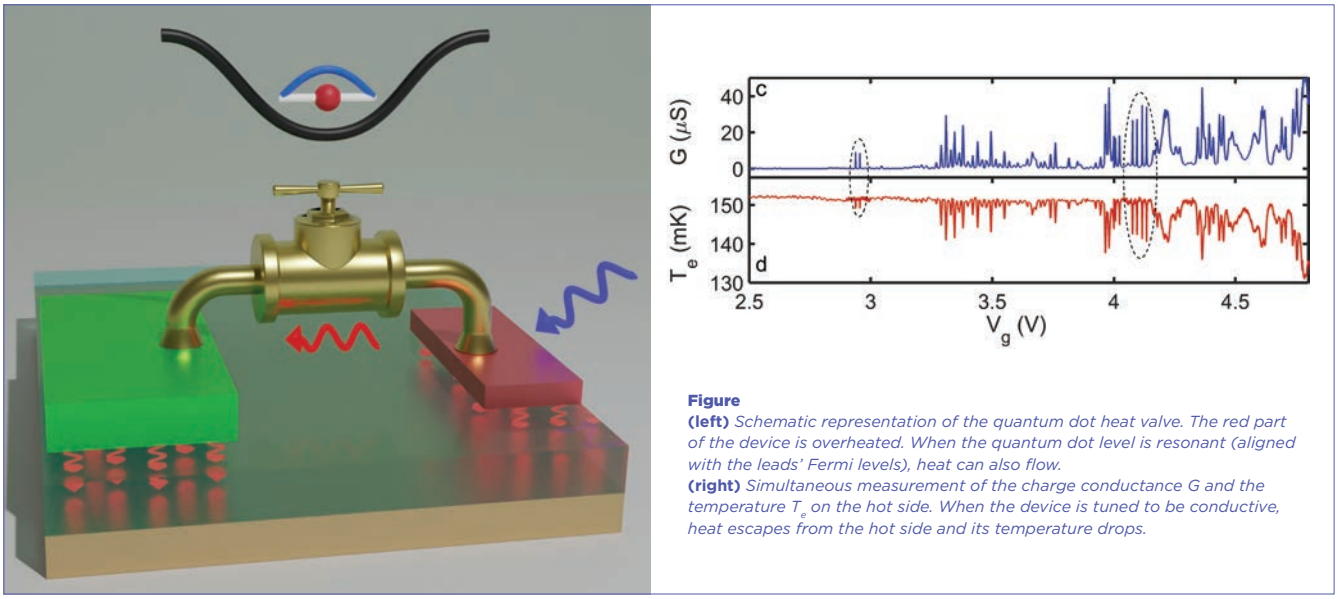

Figure
(left) *Schematic representation of the quantum dot heat valve. The red part of the device is overheated. When the quantum dot level is resonant (aligned with the leads' Fermi levels), heat can also flow.*
(right) *Simultaneous measurement of the charge conductance G and the temperature T_e on the hot side. When the device is tuned to be conductive, heat escapes from the hot side and its temperature drops.*

In order to test the above picture, we performed heat transport measurements across several gate-tunable single-quantum-dot junctions. A quantum dot is an object sufficiently small such that quantum confinement of the electrons leads to a discrete energy ladder. In our case, the quantum dot can be either a gold nanoparticle or an electrostatically delimited nanoscale region in a semiconducting InAs nanowire. When such a quantum dot is connected between two macroscopic metallic contacts, and only one of its quantum energy levels is tuned to the vicinity of the Fermi levels of the contacts, this indeed leads to sharply resonant electronic conductance features. Is it therefore, according to the above argumentation, a thermal insulator?

Our experiments show that, no, a single quantum level still conducts heat. The reason for this resides in the fact that, owing to the quantum dot's coupling to the leads, the levels acquire a finite lifetime, that is, a spectral broadening. The level is therefore not infinitely sharp. In our experiments, we focused on quantum dot junctions that present a spectral broadening comparable to the amplitude of thermal fluctuations. Consequently, we observe that the situation is qualitatively half way between a thermal insulator and a Wiedemann-Franz type heat conductor. Quantitatively, the results are in very good agreement with theory, in the frame of elaborate non-equilibrium Green's functions calculations, as well as using a simpler, non-interacting scattering transport picture.

Quantum dot junctions are ubiquitous in quantum nanoelectronics, and have recently become a central element in the quest for scalable semiconducting quantum information processing architectures. However, it appears that the ensuing dissipation and heat management in such devices is not sufficiently studied until now. Our results thus pave the way for better understanding and routing heat flows in quantum nanoelectronic devices.

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FURTHER READING

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ULTRASENSITIVE NANOMECHANICAL FORCE FIELD SENSORS OPERATED AT mK TEMPERATURE

Cooling down a nanomechanical force probe allows increasing its sensitivity by reducing its random thermal motion, which ultimately limits its force sensitivity, and by increasing its mechanical quality factors. In order to explore fundamental forces at ultralow temperatures, a dilution cryostat hosted in a quiet experimental environment compatible with ultrasensitive force sensing requirements was developed in the Institute.

Our nanomechanical force probes are suspended silicon carbide nanowires, glued at the end of a sharp metallic tip, whose vibrating extremity is used as a scanning probe force sensor: an external force modifies the mechanical properties of the nano-pendulum which are read out by optical means. When focussing a laser on their extremity, the nanowire vibrations generate a modulation of the back-scattered light flux, which can be recorded on a photodetector and allows recording its position fluctuations. Analysing this signal allows assessing the impact of the external force under investigation.

In experiments performed at room temperatures, optical readout powers in the 10-100 μW range are sufficient to probe the nanowire vibrations without inducing significant perturbations on its dynamics. This is not the case at dilution temperatures since the force sensitivity of the nanowire largely increases, but also because the heat conduction becomes extremely inefficient. The very large aspect ratios of the nanowire, required to reach extreme mechanical susceptibility (diameters in the 100-200 nm range and lengths of a few 100μm), are associated to a large thermal resistance. While the heat conduction of silicon carbide is excellent at room temperature, it is strongly reduced, as for most materials, at dilution (sub-K) temperatures.

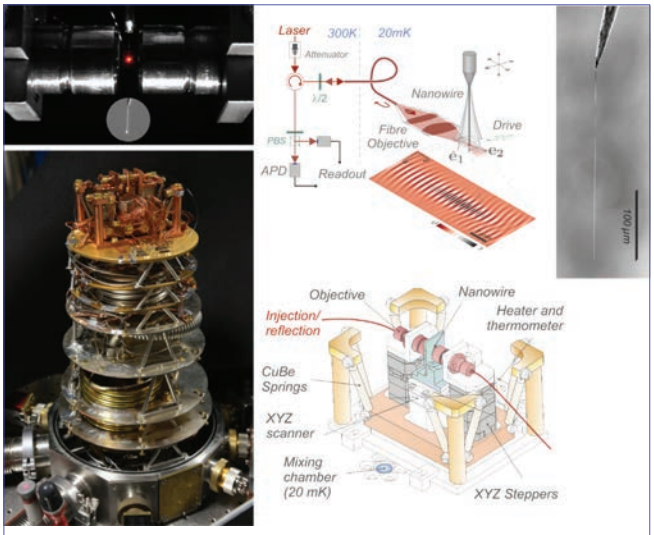

Figure
Sketch and images of the dilution cryostat, developed by Wolfgang Wernsdorfer and Eric Eyraud, and of the optical head, of the optical readout scheme and a scanning electron microscope image of a typical long aspect ratio nanowire employed in the experiment.

We developed optical readout techniques capable of operating at minimal optical fluxes, by using internally developed interferometric objectives compatible with operation at dilution temperatures, and readout protocols based on avalanche photodiodes operated in the Geiger mode (the photon counting regime) to operate in a regime where standard detectors are completely blinded by their dark noise. Mechanical vibrations are thus encoded as time modulations of the reflected photon flux, while the position sensitivity is only limited by the intrinsic quantum fluctuations of the probe laser beam.

By measuring and analysing the nanowire thermal noise spectra, one can determine its vibrational temperature after a proper calibration procedure. We could observe noise temperatures as low as 32 mK, for a cryostat temperature of 26 mK, provided that extremely faint optical fluxes are used (100 fW injected) so that the absorbed photons do not significantly heat up the nanowire. In this regime, less than a photon is detected per mechanical oscillation period. At such low temperatures, the force sensitivity of the nanowire approaches 40 zN (40 x 10^{-21} Newton) in 1 second, a magnitude which corresponds to the Coulomb force between 2 electrons 100μm apart, and represents a 3 orders of magnitude improvement over room temperature sensitivities. A sensitivity to lateral force field gradients of 1 fN/m in 10s was also demonstrated, underlining the extreme capacity of those nanomechanical force probes for future scanning probe measurements of faint forces. Achieving such numbers requires tracking and minimizing all the sources of electrical and mechanical noises and in particular to implement a mechanical suspension apparatus to isolate the experiment from the vibrations induced by the He-mixture circulation in the cryostat.

Those measurements also allowed characterising and better understanding the peculiar mechanical and heat conduction properties of the nanowires, which will help improving the force probes and will be subject of further investigations.

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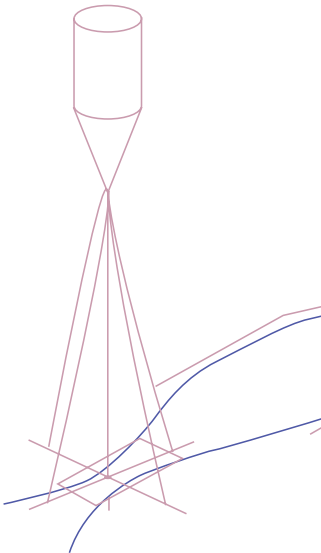

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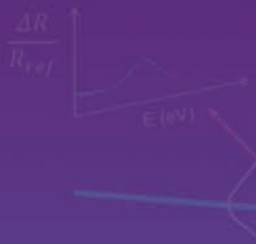

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