HIGHLIGHTS

2018

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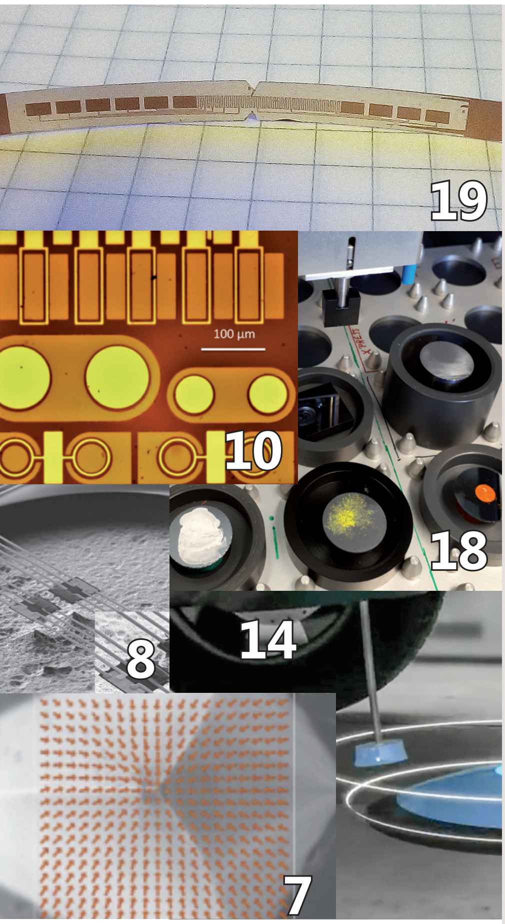


Editorial

Thank you for browsing (or more) through this year's issue of the Institut NÉEL's Highlights magazine!

Besides the traditional selection of striking technical and scientific achievements expected in any report from a lab doing mainly basic research in condensed matter, you are in for a few surprises. For one, central in this year's magazine we express our pride in practical applications of our research in the three fields of thermal properties of microstructures, wide bandgap semiconductors, and graphene, as illustrated by three start-up companies preparing to be launched in 2019. Other articles highlight our more traditional partnerships with private sector companies. The start-up projects, which are located on our site at present, are to be followed by more projects entering the incubation stage, and later by still others now in the maturation stages.

If you compare the focus on the start-ups to the descriptions of scientific research in the pages of this year's magazine, you will recognise how basic research work can lead, often indirectly, to applications. We see that work on heat transport at the nanometric scale (the level where quantum effects dominate), as well as interdisciplinary or more device-oriented studies concerning advanced materials, provide opportunities to address specific socio-economic market issues. Of course, spectacular calculations and experiments and materials research such as are reported here will lead rather to new fundamental questions, depending on the unpredictable flow of ideas across the scientific planet!

Another editorial choice of ours this year was to illustrate how both in-house and commercial methodological or instrumental developments have dramatically improved the throughput and flexibility of data processing, sample characterisation and microfabrication steps in our research work. We hope that these quite diverse and somewhat down-to-earth aspects of our activity, and their application to interdisciplinary projects, will stimulate your curiosity.

We trust that reading this issue of our magazine has brought you to conclude that cutting-edge fundamental condensed-matter experiments rely on elaborate tools and concepts which may trigger crucial advances in fields of other sciences and technologies.

I would like to thank all the authors and indirect contributors to the present 2018 Highlights, and especially the editors and designers, who have once again done a marvellous job!

Étienne Bustarret,

Director of Institut NÉEL (CNRS/UGA)

Grenoble, France

Contents

Running a nano-engine just by looking at it

In quantum physics, measuring a quantum system can strongly perturb its state, which also affects the system's energy. We have recently proposed a new kind of engine that, in theory, can extract work from such energetic fluctuations of purely quantum nature, induced by the measurement. This "nano-engine" adapts James Clerk Maxwell's thought experiment (the "Maxwell's daemon") to the quantum domain.

In classical thermodynamics, engines are devices that convert heat (*i.e.* the disorganized energy present in hot bodies) into work, *i.e.* controllable, useful energy. Stroke engines (*e.g.* an internal-combustion piston engine) are typical examples and operate cyclically: 1. The engine is coupled to a hot source. Its entropy increases while work is extracted from the source. 2. The engine is coupled to a cold source. Work is performed on the engine to decrease its entropy and reset it into its initial state. The "reset" step is essential to abide by the second law of thermodynamics, which forbids extracting work from a single hot source.

In the 19th century, however, Maxwell suggested a way to apparently overcome the second law. In his famous paradox, a daemon could decrease entropy by manipulating a shutter between two chambers of gas initially at equal temperature. Observing the gas molecules, the daemon lets only fast molecules through in one direction and only slow molecules in the other direction, decreasing the total system's disorder. Thus the daemon decreases the entropy of the engine by extracting information from it, resetting it at no cost in work.

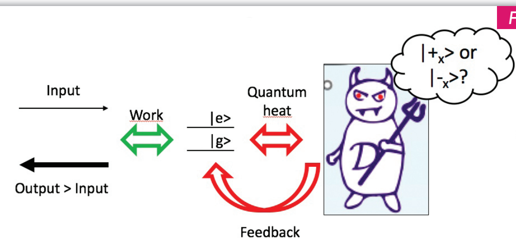
The classical paradox was solved (a century after Maxwell) by acknowledging that "information is physical". In particular, information is encoded on memories corresponding to physical properties, and its amount is also quantified by entropy. Resetting memories by encoding information thus costs energy, which solves the paradox.

Owing to the progress of quantum technologies, experimental investigations of quantum versions of the Maxwell's daemon devices have become possible. Such nano-engines are typically made of single, two-level quantum systems called quantum bits ("qubits"). One possible technical realization could be a superconducting circuit having two quantized states, with energy separation $(h/2\pi)\omega$ that can be driven resonantly by a microwave field of frequency ω. This gives rise to coherent oscillations of the occupation of the two levels, the "Rabi oscillations" (Fig. 1). These oscillations correspond to reversible exchanges of energy (work) between the qubit and the microwave field, in the form of microwave photons. Work extraction from the qubit would be successful if the microwave power output to the field from the qubit is larger than the input power.

In a typical experiment, the qubit is coupled initially to a hot source that prepares it in its ground state |g> or in its excited state |e> with equal probabilities. If no information on the qubit energy state is recorded, coupling it to an electromagnetic driving field does not lead to any net work extraction. On the other hand, a daemon can choose to measure the energy state of the qubit, and then couple it to the field only if it is excited. In that case, the qubit is forced to release its energy to the microwave field, giving rise to some net extraction of work.

In all previous experiments of this type reported so far, energy was provided by "hot sources", *i.e.* thermal noise. However, quantum systems can experience a much larger variety of noise. For instance, measuring the state of a quantum system modifies its state, so quantum measurements themselves are noise sources that perturb quantum states. Such measurement-induced perturbations can also increase the qubit energy, just as a hot source does. These energy fluctuations of genuinely quantum nature have been dubbed "quantum heat".

Fig. 2

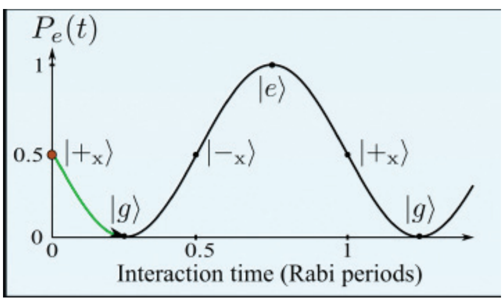


Schema of a quantum Maxwell's-daemon experiment. The qubit states (|g>, |e>) and a driving field exchange work with each other, while it is being periodically measured by the daemon in the {$|+_x>$, $|-_x>$} basis. Each time the daemon measures $|-_x>$, it performs a feedback on the qubit to bring it into the state $|+_x>$, the state which is favorable for extracting work from the qubit.

We have recently suggested a mechanism to convert this quantum heat into work within a new kind of Maxwell daemon engine (Fig. 2). This daemon performs measurements at a given point in the Rabi cycle of Fig. 1. Depending on the result, it either does nothing or does a (zero-energy cost) feedback action, that stabilizes the qubit in the state (labelled $|+_x>$ in Fig. 1) which is a particular quantum superposition of equal parts of the qubit's energy states |g> and |e>. In the Rabi oscillation, this state corresponds to a maximum slope (see Fig. 1), giving a maximum output of power into the microwave field. Here the engine performs in the absence of any hot source, extracting energy from a quantum measurement alone.

Our proposal is feasible with state-of-the-art superconducting circuits, and the idea has already been extended to other experimental setups. It would provide a first step towards evidencing the energy footprint of quantum noise, and towards assessing the energy cost of quantum information technologies.

Fig. 1



Rabi oscillations: A qubit is being driven between its ground state |g> and its excited state |e> by a microwave field. P_e (t) is the probability to find the qubit in the excited state at time (t). The superposition state $|+_x>$ transfers maximum work into the microwave field, whereas the state $|-_x>$ extracts maximum work from the field.

CONTACT

Alexia Auffèves
alexia.auffeves@neel.cnrs.fr

PhD student:
Cyril Elouard

FURTHER READING...

"Extracting Work from Quantum Measurement in Maxwell's Demon Engines"
C. Elouard, D. Herrera-Marti, B. Huard and A. Auffèves
Phys. Rev. Lett. 118, 260603 (2017).

"The role of quantum measurement in stochastic thermodynamics"
C. Elouard, D. Herrera-Marti, M. Clusel and A. Auffèves
npj Quantum Inf. 3, 9 (2017).

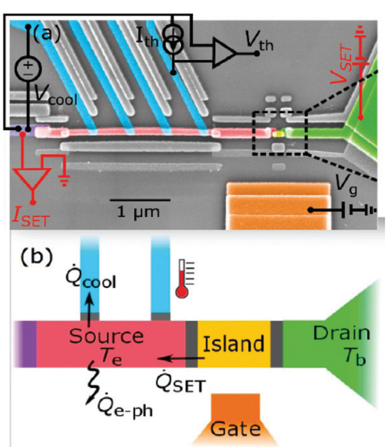
A Single-Electron Transistor **breaks the law of thermal conductivity**

Good conductors of heat are usually also good conductors of electricity. The celebrated Wiedemann-Franz law states that, at a given temperature, the thermal conductivity of a metal is proportional to its electrical conductivity. Yet, a joint group of researchers of the Institut NÉEL and Aalto University (Finland) has led an experiment revealing that this law is violated in a specific quantum electronic device, a single-electron transistor.

The Wiedemann-Franz law's interpretation is simple: every electron in a conductor carries a charge *e* and a quantity of heat of about the thermal energy k_BT, where *T* is the temperature and k_B the Boltzmann constant. This law holds in the vast majority of metallic materials and devices. But, a single-electron transistor (SET), a device so small that it transmits electrons one at a time, appeared as a candidate possibly violating the established law.

A SET consists of a nanometre scale metallic island connected to two electrodes (source and drain) through tunnelling barriers. A third electrode (gate) connects to the island through a capacitor. Due to its small capacitance, the island's electrostatic energy is relatively large and it varies significantly under the influence of the gate. At low temperature, of order 0.1 K, the tunnelling of single electrons from source to drain via the island can be energetically unfavourable in a specific range of gate voltage, so that charge transport is blocked. Thus, this so-called "Coulomb blockade" of the electron-tunnelling modulates the electrical conductance of the transistor as a function of the gate voltage.

Fig. 1



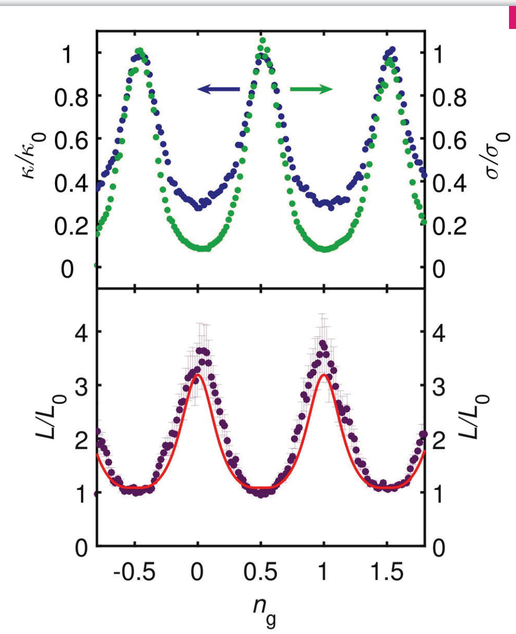
A single-electron transistor (SET) and the setup for the heat transport measurement: (a) False-coloured Scanning Electron-Microscope image of the full device. The red circuit-drawing represents the charge-transport measurement setup, while the black circuit-drawing is the heat-transport setup. (b) Schematic of the device, with the different elements coloured the same as in (a).

We designed and fabricated a single-electron transistor specifically for this study (Fig. 1). Here the source electrode is well isolated from the thermal bath and equipped with a series of superconducting tunnel junctions that could be used both as an electronic thermometer and as a heater/cooler. The electron population at the source could thus be heated or cooled and its (electronic) temperature measured at the same time.

In our experiment, we measured the charge conductance and the heat conductance of the device as a function of the voltage V_g applied to the gate. We found that their ratio obeyed the Wiedemann-Franz law at the so-called "degeneracy points". These are gate-voltage points where two subsequent values of the island charge, *Ne* and (*N*+1)*e*, are equally probable, *i.e.* points where the charging energy barrier vanishes. However, in between these points, this ratio violated the law: It was higher by a factor of up to 4 (see Fig. 2).

The results of Fig. 2 are in excellent agreement with theoretical studies. The physical understanding is based on the energy-selectivity of electron tunnelling, due to the Coulomb blockade.

Fig. 2



(a) Thermal conductance κ (blue dots) and charge conductance σ (green dots) (in units of their values κ_0 and σ_0 for no Coulomb blockade) versus induced charge $n_g = C_gV_g/e$. (b) Ratio L/L_0 between the thermal and charge conductances (purple dots), where L_0 is the Lorenz constant (the Wiedemann-Franz ratio). The grey error bars are related to the temperature measurement uncertainty. The red curve is the theoretical prediction for a single-electron transistor.

At the degeneracy gate-voltages, the electrostatic energies of two successive island charge states (*N* and *N*+1 electrons in the island) are equal and the Coulomb blockade is ineffective. The electron transport is essentially unaffected by the charging effect, and the electron population flowing through the device has a normal thermal distribution. In between these points, the Coulomb blockade "selects" (that is, it lets through) only the electrons with a large kinetic energy compared to the average. As a consequence, the electrons carry an energy larger than k_BT, while of course still carrying a charge *e*. So, the heat conductance is not as much reduced as the charge conductance, and the ratio of the two conductances increases.

Single-electron transistors can form the basis of a future quantum electronic circuitry, so our finding could be useful for managing heat in such circuitry, including circuits operating at higher temperature.

CONTACT
Hervé Courtois
herve.courtois@neel.cnrs.fr
Clemens Winkelmann
clemens.winkelmann@neel.cnrs.fr
PhD student:
Bivas Dutta

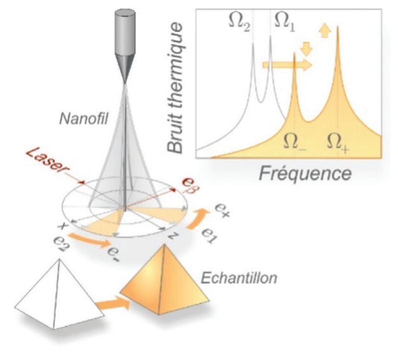
FURTHER READING...
"Thermal Conductance of a Single-Electron Transistor"
B. Dutta, J. T. Peltonen, D. S. Antonenko, M. Meschke, M. A. Skvortsov, B. Kubala, J. König, C. B. Winkelmann, H. Courtois and J. P. Pekola
Phys. Rev. Lett. 119, 077701 (2017).

Ultrasensitive and universal vectorial force-field sensor

Due to their ultralow mass, nanometre-scale mechanical oscillators can be used to convert a very weak force into a measurable displacement. By measuring the vibrations of a long, cylindrical, nanowire oscillator, and recording their modifications as the nanowire is scanned through a force field (*e.g.* an electrostatic field), one can measure and map the variations of the magnitude and direction of the force field with attonewton (10^{-18} N) precision. Lateral force-field gradients couple the nanowire's two transverse eigenmodes, *i.e.* the transverse modes of oscillation in two perpendicular directions, causing frequency shifts and rotation of the eigenmode basis. Also, rotational force fields can break the orthogonality between these two eigenmodes. The nanowire dynamics is strongly altered, thus modifying the fundamental relation which connects the mechanical susceptibility and the noise correlations of the system, and giving rise to a new fluctuation-dissipation relation.

At the Institut NÉEL, we have developed an experiment aiming at measuring the vectorial structure of force fields exerted on the vibrating extremity of a 70 micron long silicon carbide nanowire, of 200 nm diameter. This nanowire oscillates at a frequency around 70 kHz. Its two fundamental transverse eigenmodes vibrate along perpendicular orientations with quasi identical eigenfrequencies (within 1%). These lateral vibrations are read out optically using a tightly focused laser beam, allowing in particular to resolve the thermal noise or Brownian motion of both eigenmodes.

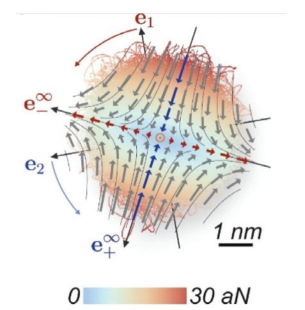
Fig. 1



The nanomechanical force-probe is a suspended silicon carbide nanowire oscillating along two transverse directions at quasi-identical frequencies Ω_1 and Ω_2. Its vibrations modulate the reflected light of a focused laser beam allowing us to detect its thermal motion. When we bring a sample (here a voltage-biased, sharp metallic tip applying an electrostatic force) up to the the nanowire extremity, its force field causes frequency shifts and rotation of the vibration modes whose analysis allows us to map the force-field gradients.

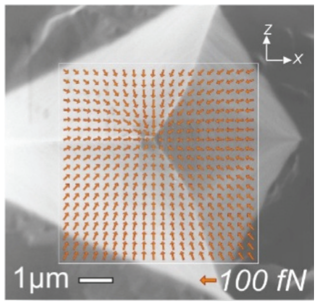
The eigenmodes of the nanomechanical oscillator are modified when it is immersed in an external force field presenting spatial variations (Fig. 1). Divergence-like force fields generate frequency shifts, while shear or rotational force fields cross-couple both eigenmodes and cause a rotation of the eigenmodes' orientations. By measuring those modifications of the nanowire's vibration properties, we can determine the local lateral force-field gradients exerted on the nanowire. Thus, the nanowire acts as a "nano-compass" (Fig. 2). It tends to orientate the axes of its eigenmodes along the eigendirections of the force field under investigation, which can subsequently be reconstructed and mapped spatially. The sensitivity demonstrated is impressive: Force gradients of a few nN/m could be observed, corresponding to force variations of a few attonewtons over the nanometer-sized spatial spreading of the nanowire's random thermal motion.

Fig. 2



The nanowire acts as a "nano-compass", i.e. its eigenmodes tend to align with the eigendirections of the local (attoNewton magnitude) force field, as inferred from thermal noise analysis.

Fig. 3



Measurements at various locations 100 nm above a sample can make a map of the (1V bias) electrostatic force-field "landscape" superposed here on a Scanning Electron Microscope image of the sharp tip employed.

Our measurement technique allows us to identify the shear components of the force field, which cannot be resolved with standard uniaxial force probes. In particular, we can explore the rotational optical force fields produced in sharply focused laser beams. Such non-conservative force fields cause a non-reciprocal coupling between the two eigenmodes and are responsible for a breaking of their orthogonality: Their orientations tend to move towards each other. By combining response measurements and thermal noise analysis, we could demonstrate a violation of the fluctuation-dissipation relation which connects the thermal noise spectrum to the imaginary part of the nanowire mechanical susceptibility. The origin of the deviation arises from the out of equilibrium state of the system induced by rotational force fields.

The theoretical model we developed explains all observed signatures, including the observed excess of thermal noise and enhanced mechanical response of the system, and has allowed us to formulate a patch to the fluctuation-dissipation relation that remains valid in the presence of non-conservative force fields.

Further developments will consist in speeding up the measurement process by analyzing trajectories driven by calibrated forces instead of by random thermal motion. This novel, universal, ultra-high sensitivity measurement-apparatus provides vectorial information about the forces exerted on a nanometric probe, providing a new way for exploring proximity, magnetic, or optical force-landscapes.

CONTACT

Benjamin Pigeau
benjamin.pigeau@neel.cnrs.fr

Olivier Arcizet
olivier.arcizet@neel.cnrs.fr

PhD student:
Laure Mercier de Lépinay

FURTHER READING...

"A universal and ultrasensitive vectorial nanomechanical sensor for imaging 2D force fields"
L. Mercier de Lépinay, B. Pigeau, B. Besga, P. Vincent, P. Poncharal and O. Arcizet
Nature Nanotech. 12, 156 (2016).

"Eigenmode orthogonality breaking and anomalous dynamics in multimode nano-optomechanical systems under non-reciprocal coupling"
L. Mercier de Lépinay, B. Pigeau, B. Besga and O. Arcizet
Nature Communications 9, 1401 (2018).

Heat transport in the quantum regime **has its own limits!**

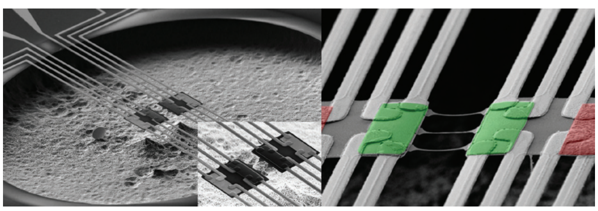
At extremely low temperature, the transport of matter, charge or energy through a very narrow "quasi one-dimensional" channel can be quantized. This has been demonstrated for a long time, for example for a current of electrical charges. Indeed, electrical conductance across a quantum dot takes values that are an integer multiple of the quantum of electrical conductance $2e^2/h$, where e is the charge of the electron and h is the Planck constant. We expect to observe the same quantization phenomenon for heat currents, a regime that would no longer follow Fourier's law, the classical law of heat conduction. As this quantization has been shown clearly for electrons and photons, it remains a mystery for phonons, the quanta of vibration of the crystal lattice.

For a quasi 1-D conductor, one expects that, regardless of the material or precise geometry of the conductor, the thermal conductance will take a universal value given by $G_q = \pi^2 k_B^2 T/3h$, a quantum composed of the Boltzmann and the Planck constants only. To get to within this limit, we have studied the thermal conductance of silicon nitride nanowires, of length a few microns and of cross-section smaller than 100 nm, connecting a heat reservoir to a colder reservoir. These dimensions are smaller than the mean free path of the phonons and smaller than their wavelength. In this regime of conduction, the phonon transport can be considered to be ballistic (*i.e.* no scattering) in the 1D waveguide. Ballistic transport means that phonons are exchanged freely without loss of energy between the two thermodynamic reservoirs. The confirmation of the existence of this limit of heat transport is essential, as it has implications for the physical limit of energy transport or information transport, and therefore consequences on information management at the quantum level.

The purpose of our experiments was to observe the quantum limit in heat transfer by phonons. We have developed a new type of ultra-sensitive device dedicated to thermal conductance measurement of suspended nanowires operating down to 50 millikelvin, close to the absolute zero. This device (Fig. 1) consists of two ultra-light suspended membranes connected by nanowires. Each membrane is equipped with a thermometer and a heater. A temperature gradient is established between these two experiment "platforms" and we measure the heat passing through the nanowires.

Our heat transport experiments (Fig. 2) go very far down into the ballistic, quantum regime. The thermal conductance K_{NW} measured for a single nanowire and for two nanowires falls with temperature but, below a few K, contrary to expectations, the thermal conductance keeps decreasing as the temperature decreases. The measured values of conductance do not flatten out at the expected universal heat conductance-quantum value of $K/G_q = 1$. Instead, they decrease by nearly two orders of magnitude at very low temperatures (Fig. 1).

Fig. 1



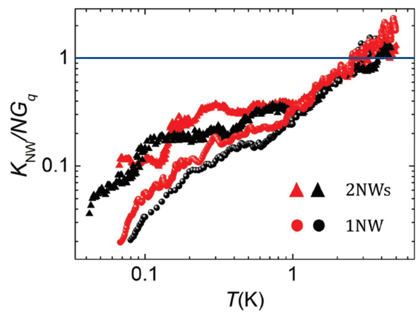
At left: Scanning Electron Microscope image (and zoom) for our device used for measuring the thermal conduction of silicon nitride nanowires. The nanowires are suspended between two platforms (extremely light membranes), which are in turn suspended on the 8 electrical heating and measurement leads. To measure the thermal conduction, we heat one platform and measure the respective temperatures of the two membranes.

At right: Zoom view showing 3 nanowires connecting two platforms. The red colour labels the heaters and green labels the thermometer elements. This sensor can operate down to 50 milliKelvin, close to absolute zero, to study conduction regimes that go well beyond Fourier's law.

This indicates that the heat transfer is limited not by the quantum of thermal conductance of the 1D nanowire but by the transmission coefficients between the 1D conductor and the reservoirs. In other words, the thermal contact between the nanowire and the reservoir is the limiting point of heat transfer.

From these experiments, it is clear that to get the maximum information about energy transport, including quantum effects, between two reservoirs, a special effort has to be made to optimize even further the connections between the 1D channels and the world outside them. Maximizing transmission coefficients will be the next experimental challenge in order to address exciting issues like phonon thermal rectification or phonon coherent effects.

Fig. 2



The thermal conductance K_{NW}/NG_q of nanowires normalized to the universal value G_q, with N being the number of heat channels. Data "1NW" is for a single nanowire, and data "2NWs" is for two nanowires in parallel. If the phonon heat transport were quantized, the curves should level out at the limit $K_{NW}/NG_q = 1$ as temperature decreases. Red/black symbols are the two opposite directions of heat transfer.

In these experiments, we have demonstrated an unprecedented power sensitivity, measuring powers as low as a few attoWatts, a world record of sensitivity! Indeed, an attowatt represents the billionth of a billionth of the power of a button cell battery.

The nano-technology developed at the Institut NÉEL for these low-temperature physics studies has been adapted for thermal applications at room temperatures, leading to the creation of the startup company MOIZ, see the article on page 11 in this magazine.

CONTACT

Olivier Bourgeois
olivier.bourgeois@neel.cnrs.fr

PhD student:
Adib Tavakoli

FURTHER READING...

"Heat conduction in a ballistic 1D phonon waveguide indicates breakdown of the thermal conductance quantization"
A. Tavakoli, K. Lulla, T. Crozes, E. Collin and O. Bourgeois
Nature Comm. 9, 4287 (2018).

"Universality of thermal transport in amorphous nanowires at low temperature"
A. Tavakoli, C. Blanc, H. Ftouni, A.D. Fefferman, K.J. Lulla, E. Collin and O. Bourgeois
Phys. Rev. B 95, 165411 (2017).

Nano-Neuroelectronics: **sensing the activity of neurons**

The brain is one of the most important systems of the body, activating and controlling its every function. However, it is still barely understood, in health nor in disease. The coding processes and the connections of the nervous system, are highly complex as is their relation to behaviour. It is still not attainable to follow the electrical activity of such dense and intricate networks (billions of connected neurons) without damaging them. Novel approaches and technologies are required to examine neurons and neural circuits by various means and at different scales. Especially, in order to understand how neural circuits operate, one needs to access the activity of large numbers of neurons individually and simultaneously and to identify the inter-connections, the morphology, and the type of neurons which are addressed. As a contribution to this vast subject, small neural networks can be cultured onto advanced electronics, allowing study of simple but physiologically-relevant systems, and modelling of neural processes.

Mapping the electrical activity of many cells simultaneously, and with sub-cellular scale resolution, is one of the most challenging goals of to-day. It could unveil the neural coding process by identifying the activity patterns and the wiring of neural networks. For that purpose, we need to be able to track neural spikes (sharp electrical activity events) propagating over mesoscale (mm scale) networks. As well, we need to monitor the sub-cellular activity of the synapses, ion channels and dendrites. Through their activity and plasticity, the structure and function of a neural circuit can change, eventually leading to the repair of disabled nodes of the neural network or, on the contrary, to pathological behaviour.

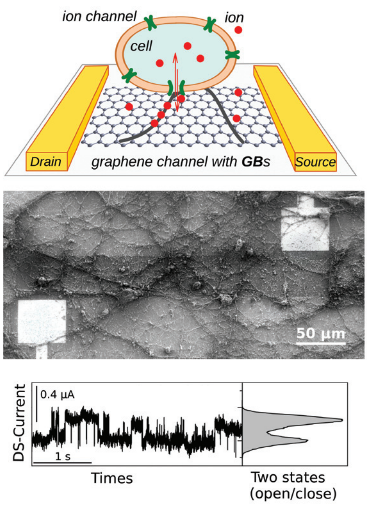


Fig. 1

At top: A single neuron interfaced with a graphene Field Effect Transistor via grain boundaries (GBs) in the graphene.

Middle: Scanning Electron Microscope image of neurons cultured above the graphene FET.

Below: Typical time-trace of the transistor drain to source current modulated by the ion flow through membrane channels. The histogram illustrates two conductance levels which are associated with the opened and closed state of the membrane ion channel.

In collaboration with workers from medical research centres (Grenoble Institute of Neurosciences, the Laboratoire Hypoxie & Physiopathologies (Grenoble), and the Ecole Polytechnique Fédérale de Lausanne), our contribution to this challenge is the implementation of versatile tools based on the Institut NÉEL's expertise in nanoelectronics and material sciences. We interface neuron assemblies with highly biocompatible and multifunctional sensing devices. Our novel "neuroelectronics" provides access to the microscopic mechanisms sustaining the electrical activity of neurons, such as ion channel activity, and enables us to follow the spiking activity of individual cells within neural networks.

In particular we are developing a neuroelectronics which is based on graphene, a single layer of carbon atoms arranged in a hexagonal lattice. Graphene shows many suitable properties for interfacing neurons, such as an exceptional biocompatibility, and high optical transparency, high bendability, and chemical inertness. Its electronic properties enable us to achieve sensitivity which largely exceeds the threshold performance of conventional semiconductors, while allowing similarly high integration and high frequency operation. This unique combination of bio-suitable properties gathered in a single material has motivated us to develop graphene Field Effect Transistors for recording neurons.

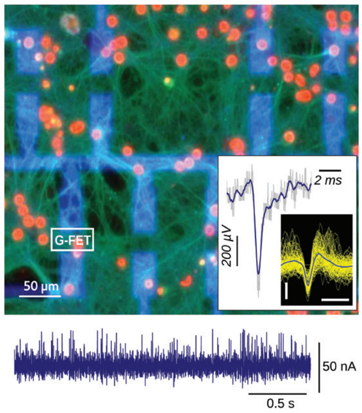


Fig. 2

Recording a single unit (neural spike) with a graphene-FET array. Neurons were grown directly on the transistor array. The soma (cell body) is labelled in red and the neurites (projections from cell bodies) in green. The metallic leads connecting to the transparent graphene transistor channel appear in blue.

Inset: Extracellular potential induced by a single, millisecond duration neural spike, derived from the modulation of the FET current's time-trace (bottom of Figure). The small inset (yellow on black) shows the superposition of all detected single spikes.

We have interfaced polycrystalline graphene FETs ("G-FETs") to mouse-embryo neurons by culturing the neural cells on top of a graphene transistor during several weeks. We were then able to demonstrate ultra-high sensitivity field-effect detection of the activity of ion channels via their crossings with graphene grain boundaries (Fig. 1), and to record spikes from individual neurons, with this transparent and flexible electronics (Fig. 2).

Beside the sensing considerations, graphene addresses another critical issue concerning the poor integration into soft matter and living matter of previous neural probes, which causes loss of signals after few weeks. Our novel materials and innovative ways of integration can now be used to overcome these limitations, ensuring the long time stability of the sensors' performances and enabling long-lasting addressing of the nervous system.

This ultimate sensitivity would be useful for fundamental investigations within in-vitro or ex-vivo preparations, as well as for the next generation of neuro-prostheses, with strong impact in electrophysiology and pharmacology.

CONTACT

Cécile Delacour
cecile.delacour@neel.cnrs.fr

PhD students:
Farida Veliev
Antoine Bourrier

FURTHER READING...

"Sensing ion channel in neuron networks with graphene field effect transistors"
F. Veliev, A. Cresti, D. Kalita, A. Bourrier, T. Belloir, A. Briançon-Marjollet and C. Delacour
2D Materials 5, 045020 (2018).

"Recording spikes activity in cultured hippocampal neurons using flexible or transparent graphene transistors"
F. Veliev, Z. Han, D. Kalita, A. Briançon-Marjollet, V. Bouchiat and C. Delacour
Frontiers in neuroscience 11, 466 (2017).

Deep depletion transistor: a new concept for **diamond power-electronics**

Silicon is the ubiquitous semiconductor for most digital and analog electronics. And silicon has been extremely useful even for the power-electronics industry. However, the performance of silicon-based devices is near their maximum capability for certain high current and high voltage applications. Materials where the gap between valence and conduction bands is much larger than the silicon bandgap of 1.1 eV are now emerging to complement or replace silicon in, for example, electric vehicle, railway traction, and electrical-power grid applications. Synthetic diamond, with bandgap 5.5 eV, is widely recognized as the ideal wide bandgap semiconductor, owing to its superior physical properties, which allow devices to operate at much higher temperatures, voltages and frequencies, and with reduced semiconductor losses. A main challenge, however, is the fabrication of a key device, a diamond Metal Oxide Semiconductor Field-Effect transistor (MOSFET).

High quality epitaxial layers of diamond can now be readily grown by chemical vapour deposition (CVD) onto synthetic-diamond substrates. Pure diamond is an insulator, but it can be made into a p-type semiconductor by doping it with the acceptor-impurity boron during the growth process. In collaboration with several other laboratories (including G2ELab in Grenoble and the LAPLACE lab at Toulouse), the Institut NÉEL has been developing a new device concept specific to wide band gap materials: a "deep depletion" MOSFET.

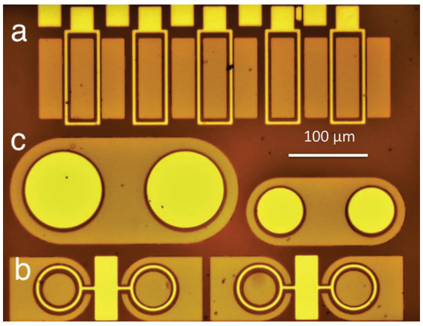


Fig. 1 *Optical microscope image of (a, b) two different geometries of our diamond Deep Depletion MOSFETs ("D2MOSFETs") and (c) diamond MOSCAPs (Metal Oxide Semiconductor Capacitors made for electrical testing).*

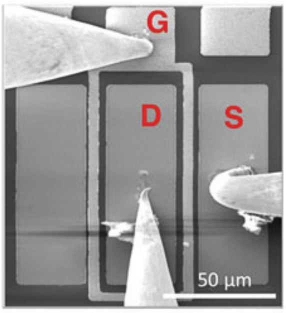
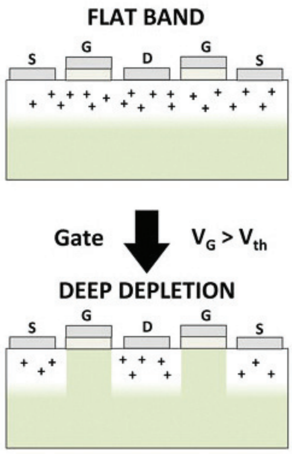


Fig. 2 *Scanning Electron Microscope image of a diamond D2MOSFET under electrical investigation with probe points. Labels S, G and D are Source, Gate and Drain electrodes.*

In this device, the conduction channel can be completely depleted of mobile charge carriers (positively charged holes in the case of diamond) by applying a strong electric field with the gate electrode. In a silicon device, this deep-depletion regime is unstable and cannot be exploited, due to silicon's smaller bandgap (as carriers of one charge type are depleted, an "inversion layer" of carriers of opposite type is created).

Our MOSFETS (Figs 1-3) are fabricated on stacks of boron-doped diamond epilayers deposited on a diamond substrate, with source and drain electrodes on the epilayer, and with a metal gate on an Al_2O_3 insulator layer over the conducting channel. In our deep depletion MOSFET, in the absence of applied gate bias, the ON state is achieved by the conduction through the p-type diamond epitaxial layer between source and drain (Fig. 3, top). When a voltage V_G is applied to the gate, the channel is depleted of holes and becomes insulating and we achieve the OFF state of the transistor (Fig. 3, bottom).

Fig. 3 *The Deep Depletion MOSFET concept for a diamond device with source (S), gate (G) and drain (D) electrodes.*



Top: In the "accumulation" or "flatband" regime, the transistor is in the "on" state. A high-mobility channel exists for positive holes in the boron-doped diamond epilayer (white) above the undoped insulating diamond (green).

Below: The "off" state is achieved thanks to the deep depletion regime under the gate. This regime is stable only for wide bandgap semiconductors. For a gate voltage V_G larger than a threshold value V_{th}, the layer underneath the gates is fully depleted of holes, so the channel is totally closed off.

Our structure has the advantage of exploiting the excellent bulk carrier mobility of boron-doped diamond. Additionally, this new type of device structure can potentially be implemented for other wide bandgap semiconductors, opening new opportunities for power electronics applications.

These diamond devices are a product that could be produced commercially by the new startup DiamFab, see the article page 12 in this issue of *Highlights* magazine.

CONTACT

Julien Pernot
julien.pernot@neel.cnrs.fr

PhD students:
Cédric Masante
Toan Than Pham

FURTHER READING...

American Institute of Physics Highlights: https://publishing.aip.org/publishing/journal-highlights/deep-depletion-new-concept-mosfets

"Deep depletion concept for diamond MOSFET"
T. T. Pham, N. Rouger, C. Masante, G. Chicot, F. Udrea, D. Eon, E. Gheeraert and J. Pernot
Appl. Phys. Lett. 111, 173503 (2017).

"Deep-Depletion Mode Boron-Doped Monocrystalline Diamond Metal Oxide Semiconductor Field Effect Transistor"
T. T. Pham, J. Pernot, G. Perez, D. Eon, E. Gheeraert and N. Rouger
IEEE Electron Device Letters 38, 1571 (2017).

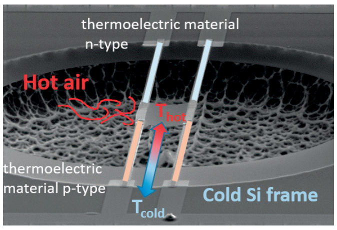
Thermal energy harvesting on a chip: **toward autonomous sensors**

The measurement of very tiny quantities of heat is essential for a deep understanding of thermal transfer in nanostructures. Fundamental research on "nanothermal" physics, carried out over ten years at the Institut NÉEL has now given rise to a disruptive technology for harvesting thermal energy at the nanometre scale. During 2015-18, our laboratory has registered three patents in this area. The patents will be exploited by the start-up company MOÏZ, winner of a "Grand Prix I-lab", a French call for funding "deeptech" (*i.e.* disruptive & proprietary technology) start-ups.

With 50 billion wireless devices forecasted for 2020, there will be a real demand for autonomous micro-sources of energy to deliver power of order 100 microwatts to many of these objects. Regular batteries or connection to the electricity grid will not satisfy all needs, particularly for the case of isolated, scattered or inaccessible devices. Many of these objects are sensors that are used to probe fluctuations in their environment. For those surrounded by heat sources (*e.g.* temperature sensors), it becomes logical to try to feed them by harvesting thermal energy from their environment.

The direct conversion of heat into electricity is possible thanks to the Seebeck thermoelectric effect: a pair of thermocouples joined back to back produces a net voltage proportional to the temperature difference at their ends. The Seebeck effect is exploited already in bulk Thermo-Electric Generators (TEGs) to provide electrical power, *e.g.* in inaccessible or remote locations... But these generators must usually be coupled to a voluminous heat sink to keep one side cool. The technology developed at the Institut NÉEL (see page 8 in this magazine) has led to breakthrough innovation in the design of devices that need no heat sink. As compared to standard 3D devices, we use a 2D technology based on a new concept where the temperature gradient occurs within the plane of a silicon wafer.

Fig. 1



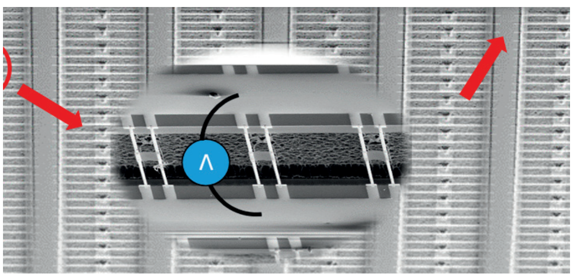
Scanning Electron Microscope image of part of an array of thousands of nanoThermoelectric Generators (nanoTEGs), each producing 0.3 nanowatts. For a 10 cm^2 array, 100 microwatts is envisageable for a temperature gradient of 10 K. The nanoTEGs are assembled in series to increase the voltage and in parallel to reduce their resistance. The central zoom shows structural details.

We fabricate nanoscale devices using standard MEMS (Micro-Electro Mechanical System) clean-room processes, scalable to very large numbers of interconnected nano-Thermoelectric Generators (nanoTEGs). These nanoTEGs, comprising suspended membranes, avoid the need for a voluminous heat sink. This leads to a significant size reduction, making their integration easier in many objects. This is the vision of the MOÏZ company, which will commercialize devices dedicated to powering many types of delocalized industrial sensors, paving the way to autonomous and wireless devices needing no power supply or battery.

The path from basic science to start-up creation was facilitated by two technology-transfer incentives: the CNRS's "prematuration" programme in 2016, and the Linksium "maturation" programme in 2017 (Linksium is a SATT – Société d'Accélération du Transfert de Technologies – for the Grenoble-Alps area). In parallel with assisting technical developments and Intellectual Property consolidation (patents, etc.) these programmes have funded promotional actions, including participation at specialist fairs, industrial interviews, etc., which have helped to identify relevant cases of use for these devices, and future customers. Several demonstrators have been built with the help of three industrial companies interested in the technology.

With support from the I-Lab funding won this Spring, the team leading the incubation project is planning the start-up of the company MOÏZ for early in 2019.

Fig. 2



View onto a single membrane-based nanoTEG. It consists of a silicon nitride membrane (grey) suspended between two narrow bridges of thermoelectric material. One thermoelectric junction is located at the membrane and the other junction is on the bulk silicon frame. Due to its very small weight (10^{-9} grams), the membrane's temperature can vary freely under an external source of heat such as air flow or radiation. The membrane is so highly insulated from the silicon chip that a temperature gradient as large as 10 K can be obtained without the help of a reservoir or dissipating heat-sink!

MOÏZ
Powering Autonomy
moiz-eh.com

O Bourgeois, D. Tainoff, D. Bourgault
Thermoelectric Device
https://patents.google.com/patent/WO2017140975A1/en

CONTACT
Olivier Bourgeois
olivier.bourgeois@neel.cnrs.fr
Dimitri Tainoff
dimitri.tainoff@neel.cnrs.fr
contact@moiz-eh.com

FURTHER READING...

"Themoelectric nanogenerator networks: a viable source of power for autonomous wireless sensors"
D. Tainoff, A. Proudhom, C. Tur, T. Crozes, S. Dufresnes, S. Dumont, D. Bourgault and O. Bourgeois
J. Phys. Conf. Series 1052, 012138 (2018).

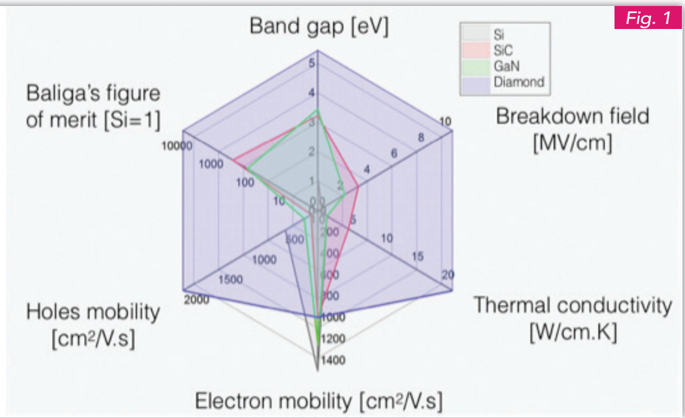
Diamond Epitaxy for future power electronics: **DiamFab**

DiamFab is a future company currently in the incubation step before its full creation in 2019. The original idea came from a small group of Institut NÉEL researchers who are participating in DiamFab. A large volume of research work done at the Institut NÉEL over the last 20 years is enabling the company to acquire skills and know-how related to the homoepitaxial growth of diamond layers on synthetic diamond substrates. During the pre-incubation phase, the Linksium SATT (Société d'Accélération du Transfert de Technologies) for the Grenoble-Alps area is helping the inventors to construct their project and prepare the establishment of the company. DiamFab's business model is focused on the epitaxial growth of diamond layers and development of diamond electronics device components for high power applications.

Diamond is a "wide bandgap" semiconductor. Its bandgap, 5.4 eV, is five times larger than that of silicon. It is the next-generation semiconductor material for high power electronics applications. This is due to its unique electrical and thermal properties, namely high charge-carrier mobility, high breakdown field and high thermal conductivity (Fig. 1).

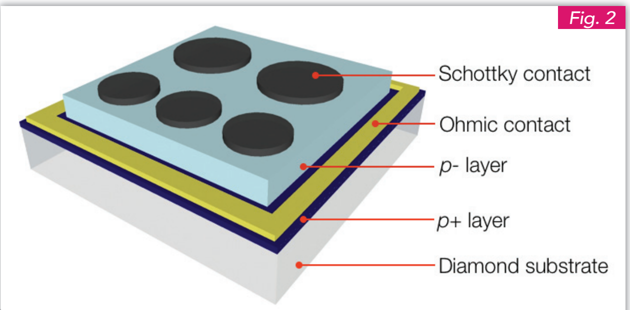
Research on growth of diamond epilayers for electronic applications was pioneered by Alain Deneuville in the Grenoble CNRS laboratories at the end of the 80s. The Institut NÉEL has continued this research intensively, working on crucial topics such as boron doping for p-type conductivity and methods for minimizing the detrimental effects of lattice defects and unwanted impurities on the hole mobility. This enabled development of Schottky diodes and Field Effect Transistors in epitaxial diamond films grown on bulk diamond crystals (see the article page 10 in this issue of *Highlights*).

Fig. 1



Significant properties of diamond (violet) compared to other wide-gap semiconductors (gallium nitride GaN and silicon carbide SiC) as well as silicon (grey). The "Figure of merit" (Baliga 1989) is a criterion for estimating power losses in high frequency high power operations. Note that diamond is ~20000 times better than Si on this criterion.

Fig. 2



Diamond substrate with epitaxial layers grown by DiamFab, supplied ready for processing into a Schottky diode.

Based on this large body of expertise, DiamFab will produce "device-ready" diamond, *i.e* a diamond substrate carrying appropriate doped layers, for making into a device. The layers will be grown on best quality synthetic diamond substrates, which are now fabricated industrially by high pressure and high temperature techniques. These diamond substrates are insulating as-grown, and both a p+ (*i.e.* highly p doped) layer and a p- (lightly p doped) layer are required in order to fabricate a "semi-vertical" diamond electronic device. Fig. 2 shows a typical stack of layers. A p+ layer lowers the access resistance for an ohmic contact while a p- layer receives the Schottky contact and withstands the voltage in the off state. Reaching the p+ layer from the top can be done either by etching the p- layer or using a selective growth technique.

DiamFab has developed a unique process to grow such layer stacks with good control of doping and thickness while minimizing the number of crystalline defects. The epitaxial layer stack fabricated by DiamFab is the key part of the electronic component since its properties and its quality will directly determine the performance of devices fabricated with it.

DiamFab, in its incubating phase, is already able to provide electronic grade diamond epilayers and is working towards proposing diamond power electronic devices in the coming years.

www.diamfab.eu

CONTACT
Gauthier Chicot
gauthier.chicot@neel.cnrs.fr
David Eon
david.eon@neel.cnrs.fr

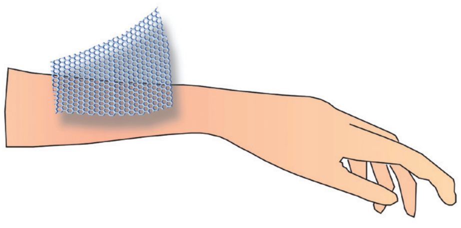
FURTHER READING...
"Optimal drift region for diamond power devices"
G. Chicot, D. Eon and N. Rouger
Diamond Relat. Mater. 69, 68 (2016).

Grapheal: Therapeutics and diagnostics of chronic wounds

Grapheal is a spin-off project of the Institut NÉEL. This startup company, currently in the creation phase, aims to develop innovative solutions for treating people with chronic wounds. Typically, chronic wounds are deep skin injuries that do not heal after 4-6 weeks. Large populations are at risk, including diabetics (whose numbers are rapidly rising around the world) as well as the elderly. The recent epidemic of chronic wounds is a major concern, as they are the leading source of necrosis, which can unfortunately lead to amputations. Such wounds are the cause of more than half a million amputations each year worldwide.

The Grapheal company aims at reducing this number by introducing a series of innovative approaches based on the introduction of a novel material. The company's mission is to put on the market a range of "smart" dressings that will allow patients and health-care providers to better monitor and manage chronic wounds. The envisioned benefits are considerable: gains in wellness, reduced pain, increased efficiency for medical and nursing staff, and lower hospitalization costs.

Fig. 1



Principle of a graphene bandage placed directly on a wound.

Our innovation involves a composite system, a "dressing" (also called a "bandage") incorporating a flexible electronic film of graphene, a novel material that has been developed at the Institut NÉEL over the past ten years. The dressing consists of a homogeneous monolayer of medical-grade graphene that is transferred and stabilized on a biocompatible polymer film.

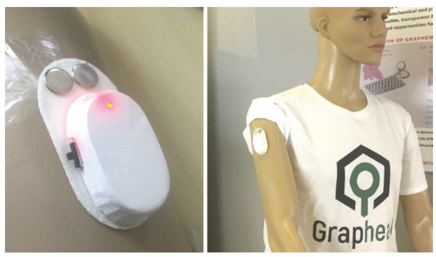
Graphene is a single atomic layer of graphite, pure carbon with the thickness of a single atom, *i.e.* a fraction of a nanometer. First isolated 15 years ago, graphene has shown significant potential for application in many fields, including nanoelectronics, mechanics, optics and more recently nanomedicine. In our process, graphene is produced by Chemical Vapor Deposition, a technique deriving from growth methods used in nanoelectronics technologies, involving natural gas (methane) as the source of carbon.

The originality of the technology to be developed by the startup lies in the integration of minute amounts of graphitic (*i.e.* sp^2-hybridized) carbon in the form of a continuous single-atom-thick layer directly integrated on the surface of a plastic film, which in turn is integrated directly on the surface of the dressing. Thus, the graphene layer is applied directly to the open wound.

Graphene combines in the one material many properties that are desirable for wound healing: It is ultra-flexible, optically transparent, conducting and, best of all, bio-stimulating. It concentrates, in the one hybrid system, promotion of healing and electronics functions, offering a bio-electronic interface platform. Our studies have shown that it offers for the first time, in a single dressing, therapeutic functions to promote rapid and complete healing as well as diagnostic functions that can inform the patient or medical staff of progress or problems.

Therapeutic action: Graphene functions as a growth matrix, a pure carbon scaffold beneficial for skin cell regeneration, thus promoting healing, but it also functions as an active electrode in direct contact with the wound enabling direct electrical stimulation of the wound. In-vitro studies conducted at the Institut NÉEL and at the Institut de Biologie et Chimie des Protéines (Lyon) have shown improvement in cellular growth. Furthermore, double-blind in-vivo tests conducted at the Grenoble and Montpellier University hospitals have shown improved wound-healing times.

Fig. 2



At left, a Grapheal graphene-based active dressing.
At right, the dressing in place on a shoulder wound.

Diagnostic action: The ultimate single-atom thickness makes the electrical resistivity of graphene highly sensitive to the physicochemical environment. As a result, the graphene film plays the role of an "on-board" detector platform via a transistor-like electric field effect. This makes it possible to measure parameters specific to the wound, allowing remote monitoring of important physiological parameters.

Our products are intended for hospital use in the first instance, but later will concern home-hospitalization and may ultimately be sold in pharmacies.

This Startup project benefits from transfer of technology from the Institut NÉEL's academic research. The project was supported by a three-year maturation program of LINKSIUM, the Grenoble-Alpes SATT (Société d'Accélération du Transfert de Technologies). This support has allowed us to protect our Intellectual Property and to validate the technology, to develop prototypes, to carry out first in-vitro tests and animal in-vivo trials, and to create a proof of concept product. The project is backed by three patents which protect specifically the concept and the technology of graphene dressings.

Grapheal has been nominated for the I-Lab 2018 Innovative Technology Companies Competition and it won the Audience Award for the Most Innovative Startup at the 2017 MEDFIT Congress for medical technologies.

Grapheal
www.grapheal.fr

CONTACT
Vincent Bouchiat
vincent.bouchiat@neel.cnrs.fr

PhD student:
Antoine Bourrier

FURTHER READING...

Patent applications WO2016142400 and WO2016142401

An electrical power plug that connects by magnetism

Connecting and disconnecting electrical-power plugs, to and from their sockets, has become a routine action for everyone, especially with the increasing numbers of electrical, electronic and computing devices. The Institut NÉEL is a partner in the project PRIMA ("PRIse MAgnétique") which is developing a novel, quick-action magnetic connector. This connector exploits a strong magnetic field to guide the plug to its socket and to attach it firmly while, at the same time, providing complete security for both the user and the power or signal. In certain applications, it will also provide a "smart" connection with inbuilt intelligence for supervision and management of the electrical power transmission. The Institut NÉEL's role is to provide its expertise in magnetic materials for the development of the powerful magnets to be integrated in these connectors.

Fig. 1

The two core elements of a simple, monophase magnetic plug (at left) and socket. More complex designs, can have up to 13 contacts. (Credit: Gulplug, https://www.gulplug.fr/).

When it is brought near its socket, this new power-plug (Fig. 1) orients and guides itself and snaps into place. To develop this concept, it was necessary to optimise the plug and socket design from the technical point of view while respecting the rules of eco-design, *i.e.* minimising both the environmental impact of the product during manufacture and its cost. In particular, the "magnets architecture" was developed specifically to minimize the quantity of magnetic material needed without compromising the magnetic field strength.

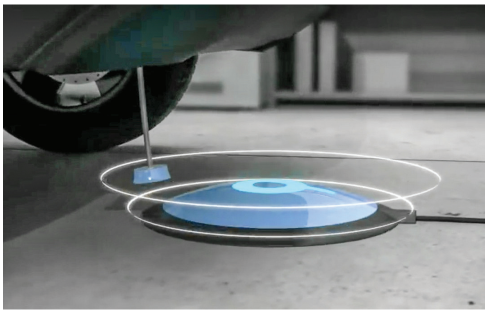
Commercial magnets are usually dense materials, mostly made by sintering *i.e.* heating a "green" compact of the magnetically-oriented powder of the magnetic material to form a solid block. This new connector will use "bonded" magnets, made by binding magnetic particles together with a polymer matrix. Bonded magnets can be manufactured using extrusion processes which produce long spaghettis that are then cut into pellets (a process called granulation). This compound (Fig. 2) can be readily formed into complex shapes, without any machining, by injecting it into a heated mould.

To select powders to meet the specifications of the PRIMA project, the Institut NÉEL participants have worked on the composite material, conducting a wide range of experiments to study the influence of multiple parameters: types of powder (isotropic or anisotropic), choice of bonding-matrix polymer, and phase fraction in the compound, process parameters, etc. Our bonded materials were injected into moulds to determine the optimum injection parameters for each type of material mixture, and to determine the process's limits, For that purpose, we characterized and tested our bonded magnets mechanically, structurally (Scanning Electron Microscopy and X-ray Diffraction), and magnetically. In particular, the magnets were tested up to 7 Tesla in the laboratory's high field superconducting magnets. The final choice of material and process, as developed at the Institut NÉEL, was then transferred to the industrial partners in charge of the magnet production.

Fig. 2

The composite magnetic material, cut into pellets of optimum size for injection into the mould which shapes a magnet (pellet lengths approximately 5 mm).

Fig. 3



A prototype charging system for the battery of an electric automobile. The car driver needs only to position the vehicle approximately, and the electrical cable & plug unit guides itself magnetically to the power socket. Recharging is initiated without the driver's intervention (Credit: Gulplug, https://www.gulplug.fr/).

This project groups eight participants, including the designers and the manufacturers of the magnetic connectors, and two final commercial users, leaders in their respective markets. The CNRS is involved as concerns both the magnetic materials development and characterization (Institut NÉEL) and the magnets architecture (Grenoble Electrical Engineering G2ELab). The project received funding from BPIfrance, the *pôles de compétitivité* (competitiveness clusters) Plastipolis and Minalogic, and the local authorities.

Some of the applications envisaged for these electrical connectors, ranging from 12 to 240 Volts, are: Rapid connectors for the automobile industry (*e.g.* see Fig. 3), robotics applications, electric wheel-chairs and other devices for the health sector, fully waterproof electrical sockets, *e.g.* for nautical applications.

CONTACT
Sophie Rivoirard
sophie.rivoirard@neel.cnrs.fr
Salvatore Miraglia
salvatore.miraglia@neel.cnrs.fr

FURTHER READING...

"Electrical Plug and Socket Assembly"
J.P. Yonnet
Patent WO/2017/001755 (Jan. 2017).

New ceramics for **domestic and cryogenic magnetic refrigeration**

A continuously growing energy demand worldwide intensifies the need for development of new, high-performance energy conversion and storage technologies. A large part of energy consumption is due to cooling in the industrial sectors such as food conservation as well as air-conditioning for housing, buildings and vehicles. Hence, refrigeration appears as a major concern for the future involving both energy consumption and impact on the environment. To date, the energy for refrigeration comes primarily from fossil fuels which produce CO_2 and it uses HFCs (hydrofluorocarbon type) gases for the classical gas-compression cycle. Both these gases pollute the environment. From this point of view, cooling based on using magnetocaloric ceramic oxides as the refrigerant material appears as a promising alternative.

The magnetocaloric phenomenon is a reversible process of heating up and cooling down magnetic materials by alternately applying and removing an external magnetic field *B*. Applying *B* orders the material's magnetic moments, whereas removing *B* allows the moments to disorder again. This gives a reversible change of the material's lattice temperature, called the adiabatic temperature change ΔT_{ad}, which is a consequence of the magnetic entropy changes (ΔS) that express the changes of the magnetic disorder.

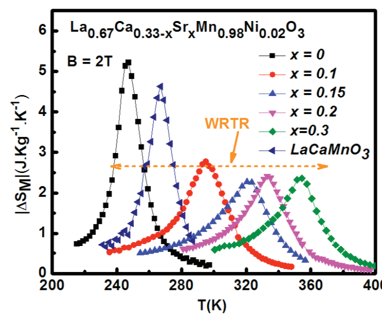
The essential parameter ΔT_{ad}, depends on the working temperature T, the field B and the specific heat capacity Cp via $\Delta T_{ad}(T,B) = -T\Delta S/Cp(T,B)$. Refrigeration is achieved by repeating the cycle (magnetization/demagnetization) and engineering appropriate transfer of heat from the material to the outside environment after each demagnetization phase of the cycle.

Noteworthy magnetocaloric materials are the ceramic oxides derived from lanthanum manganite $LaMnO_3$, the Fe_3O_4 ferrites, and the sesquioxide $Ho_{2-x}Mn_xO_3$. Using these materials, with permanent magnets for applying the magnetic field, appears as an appropriate solution for future refrigeration and cooling systems. Magnetizing and demagnetizing can be achieved by pushing the magnetocaloric material alternately into and out of the field.

In collaboration with researchers in Morocco and Tunisia, the Institut NÉEL's research activity in this field involves synthesis, characterization and physical property measurements of magnetocaloric materials, as well as theoretical studies (simulations). For the synthesis of our ceramics, solid-state reaction methods are employed for bulk oxide materials, whereas "soft" chemical reactions at low temperature such as co-precipitation, solvothermal, and sol-gel methods are used for the synthesis of nanometre-scale ceramic particles. We use X-ray diffractometry and Scanning Electron Microscopy to deduce the ceramics' crystal and grain structures. SQUID Vibrating Sample Magnetometers and PPMS (Physical Property Measurement System) instruments are used to investigate the magnetocaloric properties and the specific heat capacity, respectively.

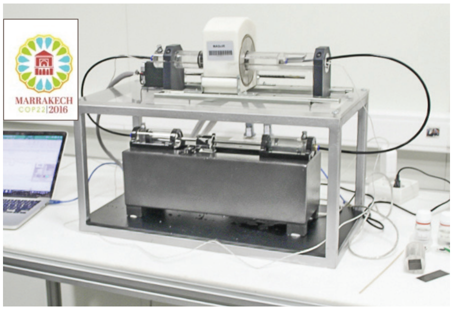
Materials optimization is a key part of our work. For this, we need to understand the correlations between crystal structure and the magnetocaloric effect. Optimization means finding the best ceramic composites with enhanced magnetocaloric performance but requiring minimum quantities of costly raw materials.

Fig. 1



Magnetic entropy changes ΔS versus temperature T for six lanthanum manganite structure samples. Field B = 2 Tesla. A Working Refrigeration Temperature Range (WRTR) as large as 135 K, obtainable by including all six lanthanum manganite compositions, has potential for domestic refrigeration and industrial cooling.

Fig. 2



Prototype magnetocaloric cooling system presented at COP22, the UN climate change conference held at Marrakech in 2016.

Evaluation of the magnetocaloric quality of the ceramics is based on measurements of Cp(*T,B*) and measuring the magnetic entropy change *ΔS*, induced by the field *B*, as a function of temperature *T* (see Fig. 1 for *B*= 2 Tesla). Since *ΔS* increases near the paramagnetic to ferromagnetic transition temperature T_c, these measurements are repeated for many temperatures around T_c.

Composites of ceramics with various chemical compositions give different variations of *ΔS* with *T* (Fig. 1). Combining the *ΔS* variations and specific heat measurements yields the "Working Refrigeration Temperature-Range" (WRTR). We have identified composites that give WRTRs extending from 370 K to 235 K, the potential application ranges for domestic and industrial refrigeration (Fig.1) and, with $Ho_{2-x}Mn_xO_3$, WRTRs from 11K to about 1K, for cryogenic cooling. Our extensive measurements of the dependence of ΔT_{ad} on *ΔS* and on Cp variations emphasizes that a material's magnetocaloric efficiency is intimately related to high *ΔS* and low Cp.

In parallel with this research into the physical properties of magnetocaloric ceramics, an actual cooling system using our best-optimized ceramics has been realized. Fig. 2 shows our prototype presented at the 22nd Conference of the Parties to the United Nations Framework Convention on Climate Change (COP22) held at Marrakech in 2016. It operates at temperatures close to room temperature.

Based on our research, we can reasonably conclude that our classes of ceramic are appropriate materials for cooling systems, providing a continuous range of cooling possibilities from room temperature with Lanthanum manganites down to cryogenic temperatures with $Ho_{2-x}Mn_xO_3$ compositions.

CONTACT

El-Kebir Hlil
el-kebir.hlil@neel.cnrs.fr

Emilio Lorenzo
emilio.lorenzo@neel.cnrs.fr

FURTHER READING...

"Large reversible magnetocaloric effect in antiferromagnetic Ho_2O_3 powders"
A. Boutahar, R. Moubah, E. K. Hlil, H. Lassri and E. Lorenzo
Sci. Rep. 7, 13904 (2017).

"Effect of (Al, Sn) doping on structural, magnetic and magnetocaloric properties of lanthanum manganites"
Khadija Dhahri, N. Dhahri, J. Dhahri, K. Taibi and E.K. Hlil
J. Alloys and Compd 699, 619 (2017).

Lithium-ion diffusion pathways within **new battery-cathode materials**

Li-ion batteries form a basic component on which our world of mobile electronics and communication is built. And they are increasingly used in high power applications such as electric vehicles and the storage of electricity from solar and other renewable power sources.

In these batteries, the cathode is a lithium-containing compound. During a battery's charging and discharging, Li^+ ions are alternately extracted from and reinserted in the cathode as they move through the electrolyte to the anode and back. The cathode material must sustain wide variations of its Li^+ ion content over many cycles. To date, the best performing cathode materials, combining good cyclability and high charging capacity ($LiCoO_2$, $LiFePO_4$…) are layered compounds. The Li^+ ions are arranged in specific 2D crystal-structure planes that allow fast ionic mobility and ensure good reversibility during cycling. Recently, a new high capacity cathode material, a lithium manganese oxide with formula $Li_4Mn_2O_5$ was reported (Freire *et al.* 2016). This material has a very different, cubic-type crystal structure, but shows record charging capacity and promising cyclability. At the Institut NÉEL, we have been investigating its local structure to understand how Li^+ ions can circulate so easily and reversibly in such a 3D atomic arrangement.

Our research was done in collaboration with this material's discoverers: CRISMAT laboratory (Caen) and the French battery company SAFT. The new $Li_4Mn_2O_5$ material is prepared by high energy milling, yielding submicron size grains and a quite defective crystal structure at the nanoscale. On average, it has been found to be of the cubic rock-salt (NaCl) type, the Li and Mn occupying the same cation site and 1/6 of the oxygen sites being vacant, leading to additional disorder.

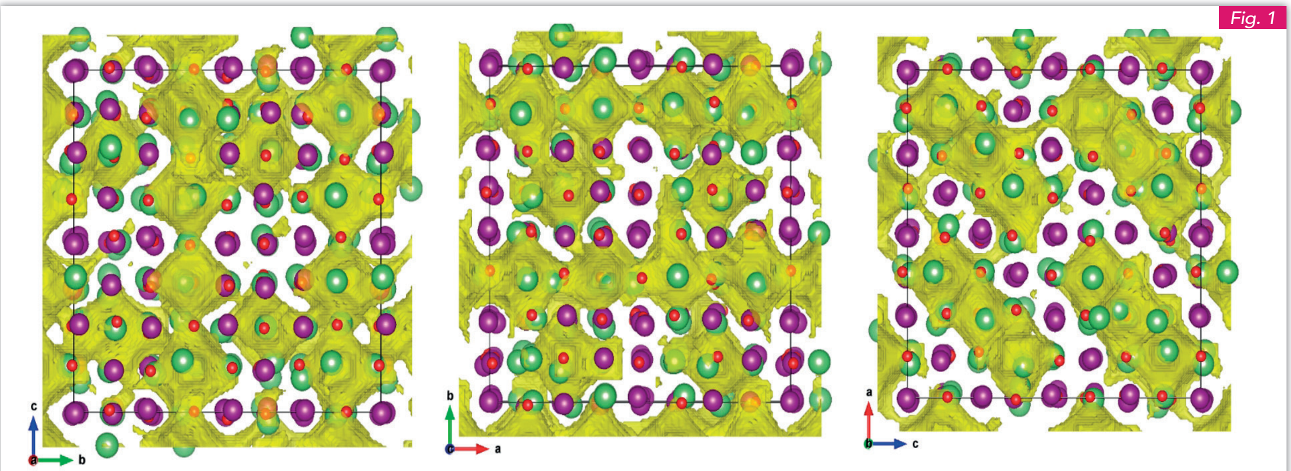
We used a combination of X-ray absorption near-edge spectroscopy (XANES) and pair distribution function (PDF) analysis of neutron and X-ray powder-diffraction data to reach a precise description of the atomic arrangement at the local scale. The measurements were carried out at the French Collaborative Research Group beamlines of the European Synchrotron Research Facility, and at the Institut Laue Langevin, Grenoble.

The X-ray spectroscopy allowed us to show that, despite the large number of vacancies on the O sites, the coordination of the Mn cation remains octahedral (that is 6 oxygens around every Mn atom). With this crucial information we could build a starting structural model which was used for a pair distribution function analysis. This technique allows one to obtain a histogram of the interatomic distances in a sample, disregarding its degree of ordering, and it can be used for liquid or amorphous as well as crystalline materials. It was the tool of choice to investigate, at the nm scale, the local structure of this highly disordered $Li_4Mn_2O_5$ material. For this investigation, we performed a joint fit to the neutron and X-ray total scattering data, both in direct and reciprocal space, by calculating a large box containing 21000 atoms while applying suitable constraints on distances and ion charges. (This used the Reverse Monte Carlo algorithm and the RMC-Profile software.) Analysis of the final calculated atomic configuration that best fitted the data revealed that the Mn cation network is almost regular cubic, while most of the structure distortion is in the Oxygen anion network.

Then by calculating the "bond-valence sums" for all points in voids inside the above structure, we could obtain a map of the 3D energy landscape (Fig. 1). This describes the regions available to the Li^+ ions with minimal energy cost. Fig. 1 shows that the accessible volumes are connected in the three directions, so the Li^+ ions can circulate within the structure, explaining the excellent electrochemical performance of $Li_4Mn_2O_5$.

This was the first time that this 3D energy landscape type of analysis was carried out for a disordered compound. We performed similar calculations on the well-known structures of the layered cathode materials having an ordered lamellar structure. The comparison shows how the 3D pathways in $Li_4Mn_2O_5$ can give Li^+ ion mobility equivalent to that of the lamellar compounds.

Fig. 1



Views of the disordered cubic $Li_4Mn_2O_5$ structure along a, c and b axes, with Mn ions in purple, Li ions in green, O ions in red. The yellow-coloured regions are a shaded-isosurface potential-map for the volumes that are accessible for the Li^+ ions to diffuse in. These yellow volumes are interconnected in the three directions of space.

CONTACT

Pierre Bordet
pierre.bordet@neel.cnrs.fr

FURTHER READING…

"Local structure and lithium diffusion pathways in $Li_4Mn_2O_5$ high capacity cathode probed by total scattering and XANES"
M. Diaz-Lopez, M. Freire, Y. Joly, C. V. Colin, H. E. Fischer, N. Blanc, N. Boudet, V. Pralong and P. Bordet
Chem. Mater. 30, 3060 (2018).

High throughput characterisation of magnetic films

The functional magnetic properties of magnetic films depend on their main constituent phase and their microstructure (grain size, grain orientation, secondary and grain-boundary phases…). These in turn depend on the film's chemical composition as well as the deposition and annealing conditions applied during film preparation. "Combinatorial" thin film studies, based on the preparation and characterisation of films having a composition gradient across their width, are being used for the high-throughput screening and optimization of a range of functional materials. With the aim to apply the combinatorial approach to the study of high performance hard magnetic materials, we have developed a high field scanning Magneto-Optic Kerr Effect (MOKE) magnetometer, for non-destructive high-throughput magnetic characterisation.

The magneto-optic Kerr effect is a change of polarization or intensity of light when it is reflected off a magnetic surface. The highly original aspect of our scanning MOKE system, developed with Marlio Bonfim from Universidade Federal do Paraná, Brazil, is the fact that it uses a compact, bi-polar, pulsed current generator which produces magnetic field pulses of duration ~15 µs and intensity up to 10 T at the surface of millimetre-sized coils. By passing the incident and reflected light beam, used to measure the magneto-optic signal, through the field-generation coil, we minimise the distance between the coil and the surface of the magnetic film, and thus we maximise the field strength experienced by the film.

To demonstrate the capabilities of our scanning MOKE system, we have prepared and characterised compositionally-graded binary material systems: Samarium Cobalt (SmCo) and Iron Platinum (FePt) which contain high anisotropy magnetic phases. The films were deposited onto 100 mm diameter silicon substrates by sputtering using a base sputtering target consisting of one element (*e.g.* Co or Fe) with asymmetrically superposed pieces of the second element (Sm or Pt). An example of a 2-D array of hysteresis loops measured on an Fe-Pt film is shown in Fig. 1, together with a map of the alloy composition measured separately using Energy Dispersive Spectroscopy.

While the MOKE measurement takes about 3 hours to perform, weeks would be required to gather the same data-set using a magnetometer, *e.g.* a VSM (Vibrating Sample Magnetometer), a SQUID (Superconducting Quantum Interference Device) or a VSM-SQUID equipped with a superconducting-magnet coil. The latter approach would also require the sample to be diced into a large number of individual samples that can fit into the magnetometer.

We used this technique to characterize a series of FePt films annealed under different conditions, so as to establish the optimum processing parameters for this material system. The scanning MOKE system is now being used to study compositionally graded films based on a range of hard magnetic phases (*e.g.* $Nd_2Fe_{14}B$, $SmFe_{11}Ti$). Such films serve as model systems to study the link between functional properties and microstructure, and this work forms part of a broader study of high performance hard magnetic materials for use in green-energy applications (hybrid electric vehicles, wind turbines). The high field scanning MOKE system could also be used in the search for new hard magnetic materials, in combination with high throughput computational methods of material screening.

The pulsed magnetic field system could also be used with other magnetic characterization techniques (*e.g.* Magnetic Force Microscopy, Magneto-Optic microscopy, magneto-transport…). Finally, it has been demonstrated that the pulsed magnetic field system can be used to increase the uptake of iron oxide nanoparticles by living cells, and its use in a range of bio-medical applications is now being explored in collaboration with a number of other laboratories.

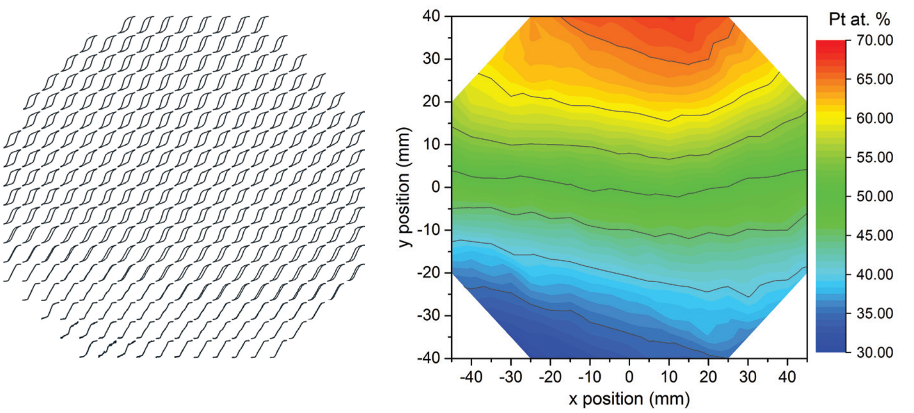


Fig. 1

Left: 2D array of hysteresis loops of a compositionally-graded FePt alloy film obtained by scanning Magneto-Optic Kerr Effect microscopy. At each point on the sample, the magnetic hysteresis loop is recorded during a 15 µs magnetic field pulse (maximum applied field = 4 T).

Right: Corresponding map of the atomic percentage of platinum in the alloy, as measured separately by Energy Dispersive Spectroscopy. This graded-compositional technique gives a very fast way of measuring magnetic properties as a function of alloy composition. (Sample preparation and characterization by Yuan Hong, visiting from South China University of Technology).

CONTACT

Nora Dempsey
nora.dempsey@neel.cnrs.fr

PhD student:
André Dias

FURTHER READING…

"Preparation and characterisation of compositionally graded SmCo films"
A. Dias, G. Gomez, D. Givord, M. Bonfim and N. M. Dempsey
AIP Advances 7, 056227 (2017).

"The use of pulsed magnetic fields to increase the uptake of iron oxide nanoparticles by living cells"
M. Uzhytchak, A. Lynnyk, V. Zablotskii, N. M. Dempsey, A. L. Dias , M. Bonfim, M. Lunova, M. Jirsa, Š. Kubinová, O. Lunov and A. Dejneka
Appl. Phys. Lett. 111, 243703 (2017).

From nanomaterials to the bulk, **one instrument to characterize them all**

In materials science, characterizing the materials goes along with synthesizing them. One of the best and fastest characterization techniques is X-ray diffraction. This technique has mostly been restricted to well crystallized, homogeneous powders or bulk materials. However, research projects at the Institut NÉEL are now focusing on more complex materials, such as nanomaterials, ultrathin films and layers, or striped alloys. These challenging cases, as well as increased demand from our researchers, have called for a dramatic evolution of our instrumentation. In that perspective, acquisition of a state-of-the-art X-ray diffractometer, together with development of new sample holders adapted for very small samples, was becoming essential.

Powder X-ray diffraction, *i.e.* measuring the diffraction of X-rays for a powder of randomly oriented crystallites, is a powerful but simple method for materials characterization. The diffraction pattern for a given material is usually unique (like DNA for humans!) so we can identify known materials with the help of databases. And, for new materials we can "solve" the material's structure, that is deduce the periodic arrangement of its atoms. However, this technique is usually restricted to well crystalized materials, meaning materials where the atoms are arranged periodically over at least microns range. Furthermore at least a few hundred milligrams of ground powder have been necessary.

But, we are now confronted with "nanomaterials" exhibiting very small crystallite sizes (<50 nm), as well as materials produced by high-pressure synthesis or spray-drying techniques that yield only microgram quantities. We have thin film materials (down to a few nm thickness) deposited on substrates. But we also have bulk samples (textured intermetallic alloys) that are difficult to grind into fine powders without altering the material. For these present-day research topics, "classical" X-ray diffractometers are obsolete: The signal acquired by the X-ray detector is too noisy, too broad, too weak. And longer acquisition times will not resolve the problem, especially as more and more researchers are requesting access.

In response to these new needs, the Institut NÉEL has acquired a state-of-the-art X-ray equipment, the Bruker company's "D8 Endeavor-Eco" diffractometer (Fig. 1). One of this unit's main features is a fast, "linear", X-ray detector, a linear array of silicon-detector pixels extending across the circular powder-diffraction pattern. It can acquire the diffraction data 30 times faster than a classical, stepping, single scintillation detector. And, this new detector can discriminate as a function of the X-ray energy, so it can filter out parasite radiation and/or scattering from the sample, thus reducing background noise.

Furthermore, the instrument has an automatic robotic arm (Fig. 2) that fetches and returns the samples, bringing much faster sample turnaround, especially for unattended functioning overnight. This equipment has reduced the waiting times for access to X-ray characterization from weeks to hours, allowing reserchers to optimize their synthesis strategy on a dramatically shorter time scale.

Fig. 1

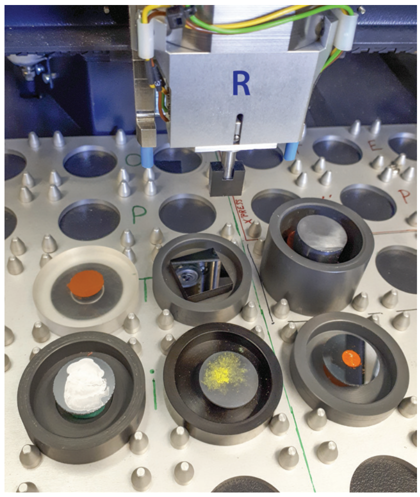
The "D8 Endeavor" is a state-of-the-art X-ray diffractometer. It possesses a fast, linear, energy-discriminating, silicon-pixels detector (not visible, behind a radiation shield). Users can insert more samples while the instrument is working and a robotic arm provides fast turnaround of the samples.

Fig. 2

The robotic arm (R) is moving to grab a sample holder to bring it into the X-ray chamber for measurement.

Top row, left to right: a traditional sample holder (white), a thin film on a substrate, and a bulk "shape-memory" metal ingot.

Bottom row, small quantities of powder samples on "zero-background" miscut silicon support plates.



Left to right: an evaporated sample of Mg carbonate (white), a deposited sample (yellow), and a sample inside a small, 0.5 mm deep recess. The orange and yellow samples are fluorescent experimental tumour-marker materials.

A major improvement has been the development in our laboratory of new sample supports (Fig. 2). Analyzing small amounts of powders was challenging as the contribution from the sample support could dominate the resulting diffractogram. In addition to bulky materials, we can now handle very small amounts of materials using a "zero-background" sample support. This is a "miscut" single crystal silicon wafer, whose crystal axes are orientated such that none of its diffraction spots fall on the detector array. Thereby, weak contributions such as from nanoparticles, can now be measured precisely.

This instrument and the specific developments of these new sample-supports provide our researchers with a versatile, high turnaround instrument fulfilling most of their needs in X-ray characterization of materials. One year after its commissioning, more than 2000 measurements have been performed on the D8 diffractometer by more than 70 research staff and students for characterizing materials ranging from nanopowders to bulk materials.

CONTACT
Olivier Leynaud
olivier.leynaud@neel.cnrs.fr

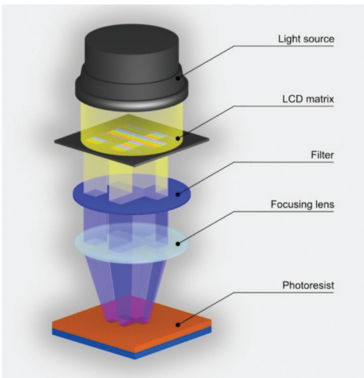
A tool for "smart" projection-photolithography

The Institut NÉEL's research work has created a vital need for fabrication "in house" of highly specialized microelectronics devices. These include silicon devices such as diodes, p-n and field-effect transistors, etc., for use in a wide variety of experiments. These devices are fabricated on demand by depositing different materials (*e.g.* metal leads, contacts, electrodes...) on the silicon wafer and performing oxidations and other processes, often in very complex geometric patterns. Photo-lithography is a key technique in this work, being used to create the masks that define the circuit patterns. Recently, new specific needs have been emerging for doing photolithography on non-planar samples, or at working distances of some millimetres instead of placing masks in contact with the wafer. In response to this demand, Nanofab, the Institut NÉEL's central technology service, whose principal mission is microfabrication, has recently acquired a "SmartPrint" unit, a versatile projection-lithography system developed by the Grenoble startup company Smart Force Technologies.

Photolithography consists first of all of depositing a light-sensitive resin (the "photoresist") on the wafer. Next, the resist is exposed to ultraviolet light through a patterned mask placed on its surface. A solvant then removes the photoresist where it was exposed to light, exposing the wafer surface for processing.

Lithography on an uneven or curved surface presents a new challenge. First, it can be difficult to coat the resin evenly onto such a surface, but the major problem is that the resolution and geometry of the lithography will be inhomogeneous. Precise masking is essential to guarantee transferring the exact dimensions and sharpness of the pattern, for example lines of width 2 microns with 2 micron separation, into the resin.

Fig. 1

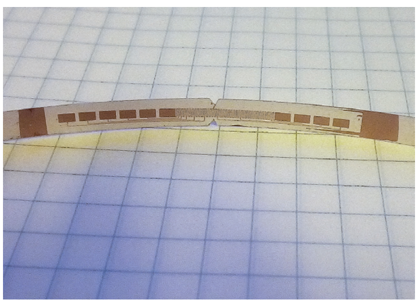


The projection component of the "SmartPrint" system. An image of the LCD matrix is projected onto the layer of photoresist covering the semi-conductor wafer. (credit: Smart Force Technologies).

Usual laboratory lithography systems employ projection through a physical mask of glass or quartz, made individually and at considerable expense for each project. Instead, the new SmartPrint system projects light through an image on a transparent liquid crystal matrix and focusses the image precisely on the photoresist (Fig. 1). The ability to vary the focus-distance, combined with a certain depth of field, enables treating non-planar surfaces.

The LCD image is fed from easily modifiable image files (format .png, .gds...) on the associated computer. This all yields a very large saving in time and expense. For example, we often have to patch a defective item on a single object, or to do lithography on very fragile samples. This new tool allows us

Fig. 2



Lithography of thermometer components on a large, non-planar surface (background blue squares are 5 x 5 mm). Length of the sample: L=5cm.

Fig. 3

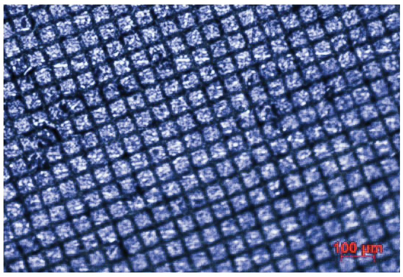
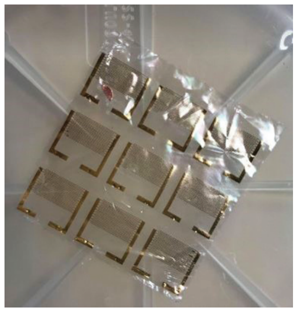


Photo of part of the anti-reflection pattern engraved on the spherical surface of a 4 inch diameter silicon lens. This component is being developed for the far-infrared optics of the Institute for Millimetre-wave Radio-Astronomy (IRAM) radiotelescope on the Pico Veleta in Spain.

to do such operations much faster and without any contact between a glass mask and the sample.

The technique is both versatile and reliable. It has precision of order 1 micron, whether for engraving a pattern or in repositioning the projected image when creating a second level of components on top of a preceding level.

Fig. 4



Lithography of electrodes on a graphene layer on a flexible surface, a film of parylene©.

Following initial testing, development of procedures and implementing upgrades, carried out with the help of our researchers and in close collaboration with the Smart Force Technologies company, we have achieved very encouraging results. We are now confident that we can satisfy the laboratory's photo-lithography needs with a wide choice of techniques. These now consist of lithography without a physical mask by the "Smartprint"system in addition to our existing Heidelberg Instruments"Direct Write Laser" system, as well as conventional lithography with physical masks.

An increasing number of the laboratory's researchers and technical personnel are adopting this new technique. They can readily learn to use it autonomously, and can test their devices in their experiments and perfect them as necessary with short turnaround times.

CONTACT
Bruno Fernandez
bruno.fernandez@neel.cnrs.fr

Sionludino: **A flexible control system** for automation of experiments

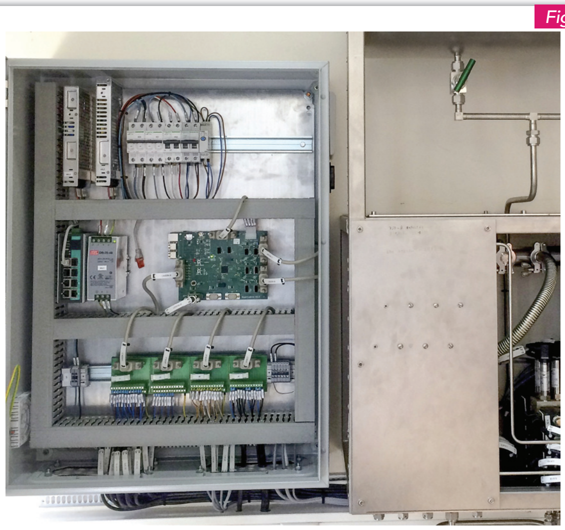
Experiments are getting more and more complex, more and more precise, more and more greedy for measurement and control systems. Requirements for these systems also include high reliability and high repeatability. In this context, various options exist. Commercial programming systems can be a solution, but they are often an expensive way to go and they do not always fit with the experiments. Thus, technology developers must develop alternative solutions for and with researchers, in a concern for both optimization and cost reduction. A recent example arises from an Institut NÉEL research team's request for the implementation of an electronics system to automatically control a "table-top" dilution refrigerator for physics experiments near zero Kelvin.

This development was a cooperative project of the Institut NÉEL technical services and the researchers requesting the new facility. It has led to the creation of a control system that we have named "Sionludino". This is based on the open-source (*i.e.* free) programming and hardware platform "Arduino", used for building electronics projects. Our Sionludino control system was developed initially for the automation of a new generation of the "Sionludi" table-top ^{3}He-^{4}He dilution refrigerator. This cryostat concept, invented at the Institut NÉEL in 1990 and upgraded progressively since then, mounts on a table and has an "upside-down" (inverted) geometry, with the cold space (temperatures down to 15 mK) at the top.

Our Sionludino control system is a cost-effective alternative to our previous solution that was based on a programmable logic controller, and it can be used for the control and automation of any experiment that involves the control of pumps, solenoid valves, mass flow controllers, pressures gauges and relays.

The system (Figs 1 and 2) consists mainly of two parts, the hardware and the software. The Sionludino hardware (Fig. 1) is placed between the experiment and a client computer, the user's interface to the experiment. It has two principal hardware components. First, a custom Printed Circuit Board (PCB) developed by us, that drives the experiment's hardware and hosts an ATmega2560 micro-controller. The second component is a Raspberry Pi (a minimalist, single-board computer) plugged underneath the PCB. It communicates with the ATmega micro-controller through a serial link, and it runs the server software.Via its Ethernet port, it acts as a server to the user's client computer (which may be situated at the experiment or connected remotely via Ethernet).

Fig. 1

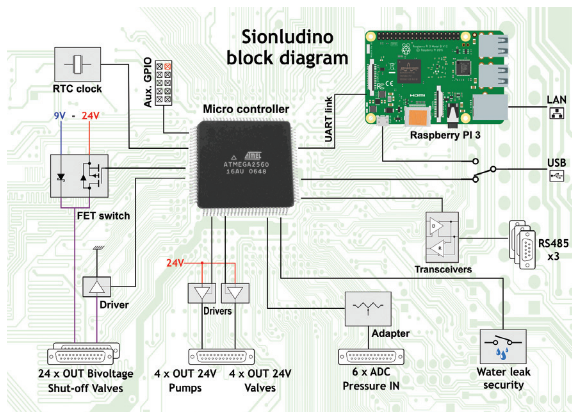


The Sionludino hardware rack integrated in an experiment. It has been designed for the automation of a table-top dilution cryostat.

The user performing the experiment can access the Raspberry server by using an ordinary web browser, which provides an interactive, web-style interface view of the experiment being controlled. Alternatively, users can write their own, optimized software on top of the web Application Programming Interface (API) provided by the server.

The software is composed of two main parts. First, a firmware component, residing in non-volatile memory on the ATmega micro-controller, built on top of the core library of programs of the Arduino software package. It handles the low-level aspects of controlling the experiment and also provides a simple command line interface at its serial port. The second software component is a server-software package, based on the open source javascript environment Node.js. It controls the high-level part of the operations and provides a simple web-based API.

Fig. 2



Schematic of the Sionludino system for controlling cryogenics experiments.

Our researchers are now programming this flexible system successfully themselves, to control their varied cryogenics experiments. It is used by two different teams at the Institut NÉEL and also at the Karlsruhe Institute of Technology. We plan to integrate it in all next generations of top-table dilution fridges, as it is a stable, flexible and low cost system for automation of experiments.

CONTACT
Maurice Grollier
maurice.grollier@neel.cnrs.fr
Edgar Bonet
edgar.bonet@neel.cnrs.fr
Eric Eyraud
eric.eyraud@neel.cnrs.fr

Scanning **Hall-Probe Microscopy**

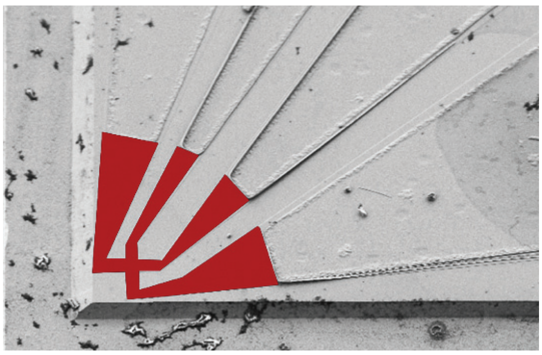
At the Institut NÉEL, we develop many highly sophisticated scanning probes to use for a large variety of experiments under extreme conditions of magnetic field, low temperature and vacuum, as well as microscopes sensitive to charge, to currents, to magnetic fields, forces, electrical potential, to name just a few. Here, we wish to highlight a microscope which does not operate under extreme conditions but has the advantage of being extremely versatile. This microscope is a "Scanning Hall-Probe Microscope" (SHPM) which allows us to do direct, quantitative measurements of the spatial variation of a magnetic field, that is to "map" the field.

Our sensor uses the Hall Effect, the transverse voltage induced when a magnetic field is applied perpendicular to the flow of an electric current. It can measure over a large magnetic field range while giving a simple, quantitative relation between the measured transverse voltage and the magnetic field deflecting the electric charges. It was developed in particular for the quantitative study of the stray magnetic fields produced by high performance micro-magnet samples but can have many other uses. The scanning probe, being sensitive to a sample's long-range stray field can survey encapsulated and somewhat rough surface states as it can maintain sufficient resolution while scanning at a moderate distance above the sample's surface.

The spatial resolution of the Hall probe microscope is determined by several factors: the size of the sensor (which is a "Hall cross"), the intrinsic electrical noise of the material used to form the Hall cross, the distance between it and the source of the stray magnetic field, and the distance between adjacent field sources. Evidently, the closer the Hall cross can be brought near the sample, the better the spatial resolution.

Our Hall probes are fabricated in a GaAs/AlGaAs semiconductor heterojunction grown on a gallium arsenide substrate. A very high mobility, two-dimensional electron gas (2DEG) lies at only 50 nm below the surface of the semiconductor chip. Using laser lithography, a photomask is structured to allow a wet chemical etch of 100 nm depth that leaves intact a "+" shaped 2DEG, the Hall cross. Four ohmic contacts are created by diffusing a metallic AuGe alloy into the ends of the bars of the cross to contact the 2 DEG. An additional deep etch, the "mesa etch" of at least 10 microns depth, is made in order to place the Hall cross exactly at the corner of the chip (see Fig. 1).

Fig. 1



Hall Cross mesa formed by etching a GaAs/AlGaAs two dimensional electron gas. The cross and its 4 contact leads are coloured red. This cross has size about 4 microns.

The sensitivity of a Hall probe is expressed by the "Hall resistance" (the ratio of the transverse voltage to the electron current). Our 2DEG has a Hall sensitivity of 200 Ω per Tesla. Hall probes of size 1 to 5 microns have been prepared. A limiting factor is the in-line resistance of the bars that form the Hall cross; the narrower the cross's bars, the higher the longitudinal resistance and thus the higher the Johnson noise.

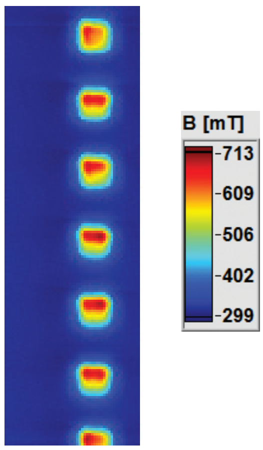
The Hall probe is inclined at a slight angle (<5 deg.) as we approach it to the sample surface. Keeping the probe as close as possible to the surface during scanning is a challenge that we tackle by coupling a sensitive force sensor with it. The probe is attached to a piezoelectric-quartz tuning fork, similar to those used in watches. The resonance frequency of the tuning fork shifts as the Hall probe comes into close proximity with the sample surface, and this frequency shift is used in a control loop to retract or approach the GaAs chip as necessary, in order to maintain the proximity force constant while scanning. The scanning-microscope uses high resolution, long-range stepper motors for its displacement. The smallest step size is of the order of 100 nm.

The development of this new generation of mesa-etched and precision-diced Hall sensors enables close approach to the sample surface (<2 microns) resulting in images with highly resolved features (Fig. 2). The spatial resolution of the magnetic field distribution is limited by the size, ~1 micron, of the Hall probes. Depending on the acquistion time, the magnetic field resolution in our measurements is about 100 µTesla/√(Hz).

Our Scanning Hall-Probe Microscope SHPM system demonstrates the usefulness of a combination of concepts formerly used separately, namely tuning-fork feedback-based height control, scanning with stepper motors, Hall probe measurements, and customized nanofabrication. It is the tool of choice for quantifying the stray fields produced by micro-magnets, which have many applications in bio-medical studies and MEMS (micro-electromechanical systems).

Fig. 2

Scanning Hall-Probe Microscope Image demonstrating the magnetic flux concentration in a row of soft Fe pillars, spaced 30 microns apart. The millitesla colour bar gives the stray magnetic field measured above the pillars.



CONTACT

Klaus Hasselbach
klaus.hasselbach@neel.cnrs.fr

Roman Kramer
roman.kramer@neel.cnrs.fr

FURTHER READING...

"A scanning Hall probe microscope for high resolution, large area, variable height magnetic field imaging"
G. Shaw, R.B.G. Kramer, N. Dempsey and K. Hasselbach
Rev. Sci. Instrum. 87, 113702 (2016).

Dirac electrons' spins get locked **on a topological insulator's surface**

"Topological insulators" are a novel class of materials attracting great interest both theoretically and experimentally, because of the unique electronic and spin properties arising at their surfaces. Their defining characteristic is that they are insulating in their interior but they have conducting surface states. The surface electrons and hole states have a remarkable "Dirac-like" energy dispersion function, *i.e.* their kinetic energy is linear in their momentum, not quadratic. Also the surface electrons show the property of perpendicular "spin-momentum locking": the orientation of the electron spins is locked perpendicular to the direction of the electron current flow, a feature potentially useful for spintronics and quantum technologies.

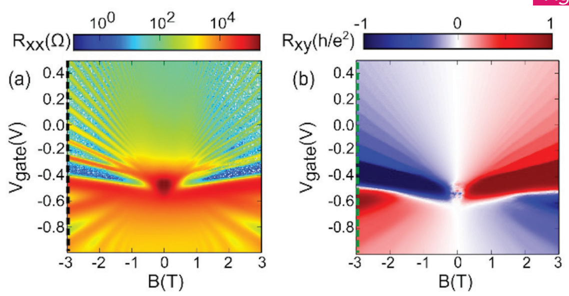
Good examples of topological insulators are small bandgap semiconductors such as strained mercury telluride (HgTe) and bismuth tellurium selenide. In collaboration with Grenoble partners at the CEA's Technology Research Institute LETI and the Institute for Nanoscience and Cryogenics, Institut NÉEL researchers have been focusing effort on mercury telluride heterostructures. Our chief experimental methods are electronic transport measurements, angle-resolved photoemission spectroscopy (ARPES) and spin-pumping techniques.

The compound mercury telluride HgTe is normally a semi-metal, with an inverted band structure (*i.e.* the conduction band crosses over the valence band). However, HgTe becomes a good topological insulator if one opens its band-gap by tensile strain (Fig. 1). This is done by growing it as a thin layer (10-80 nm), strained onto a cadmium telluride (CdTe) substrate. HgTe layers, covered with a very thin protective HgCdTe alloy barrier, were grown by Molecular Beam Epitaxy (MBE) and processed into top-gated Hall bars for low-temperature electronic transport measurements. Hall-Effect investigations revealed very large carrier mobility, in excess of 5.10^5 cm^2 /(V.s) for a carrier density of a few $10^{11}/cm^2$. This high mobility was achieved after a careful optimization of the HgTe surfaces and the nano-fabrication process.

The Dirac nature of the electrons in the surface states of the HgTe topological insulator was demonstrated by transport measurements under magnetic fields at low temperatures (Fig. 2). Because of the high quality of the heterostructure, clear signatures of the Quantum Hall Effect are observed, namely conductance plateaux corresponding to the successive filling of Landau levels, but with energy splitting characteristic of Dirac surface states. Associated with these Landau levels is the total vanishing of the longitudinal conductance, thus giving direct evidence of the absence of bulk (*i.e.* 3D) conduction within the HgTe layer.

To demonstrate the spin properties of the surface states, we used techniques borrowed from the field of spintronics in order to inject a spin current (*i.e.* a flow of spin angular momentum) in the surface states of our topological insulator. Specifically, we covered a HgTe sample with a ferromagnetic material (NiFe) by evaporation. We could then inject a spin current from the NiFe into the HgTe surface states using "spin-pumping" methods. We were able to demonstrate a very efficient conversion of spin current to charge current at room temperature in the strained HgTe. We also demonstrated that the HgCdTe barrier, used to protect the HgTe surface states from direct contact with the ferromagnetic layer, enhances the conversion efficiency.

Fig. 2

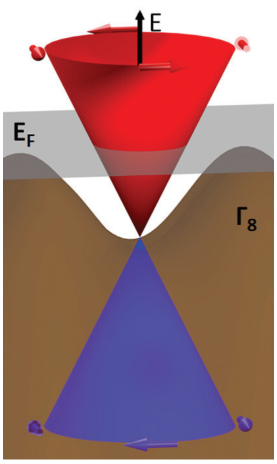


Longitudinal (a) and transverse (b) colour-coded resistance maps for a HgTe topological insulator sample in a perpendicular magnetic field B at 100 mK, showing a charge-neutrality point as the gate voltage V_g scans from valence-band hole transport to high mobility electron transport.

The dependence of the conversion efficiency on the HgTe layer thickness differs from the usual dependence observed in spin Hall materials. This, associated with the temperature dependence observed for the resistivity, suggests that the high conversion efficiency can be attributed to the phenomenon of locking between spin-and momentum at the surface states of the HgTe (Fig. 1). Our results underline the necessity to add a thin insulating interlayer between the topological insulator and the ferromagnetic metal to obtain high efficiency of the conversion of spin current to charge current.

With clear evidence of topological transport and spin-momentum locking now available in the case of mercury telluride surfaces, new developments can be envisioned to implement topological insulators into real devices. Among the numerous options, elementary building-blocks of spintronics such as filters or transistors can be developed. Also, proximity-induced superconductivity (*i.e.* inducing superconductivity in HgTe surfaces with the help of superconducting contacts) will be examined.

Fig. 1



Artist's view of the band structure for the strained-HgTe topological insulator (E versus momentum k_x, k_y). The linear dispersion of the surface states gives the two cone shapes (red= electron states, blue= hole states). The Γ_8 valence band of the bulk is in brown. E_F is the Fermi level. Red and blue arrows represent the helical configuration of the carrier spins, which are locked perpendicular to k.

CONTACT

Tristan Meunier
tristan.meunier@neel.cnrs.fr

PhD student:
Candice Thomas

FURTHER READING...

"Highly efficient spin-to-charge current conversion in strained HgTe surface states protected by a HgCdTe layer"
P. Noel, C. Thomas, Y. Fu, L. Vila, B. Haas, P-H. Jouneau, S. Gambarelli, T. Meunier, P. Ballet and J. P. Attané
Phys. Rev. Lett. 120, 167201 (2018).

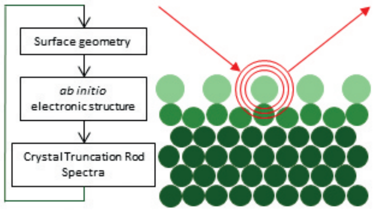
"Revealing topological Dirac fermions at the surface of strained HgTe thin films via Quantum Hall transport spectroscopy"
C. Thomas, O. Crauste, B. Haas, P-H. Jouneau, C. Bäuerle, L. P. Lévy, E. Orignac, D. Carpentier, P. Ballet and T. Meunier
Phys. Rev. B. 96, 245420 (2017).

Simulating Surface **Resonant X-Ray Diffraction**

The technique called Surface Resonant X-Ray Diffraction is a powerful tool for characterizing an ultra-thin film on a surface or an electro-chemical interface. It probes the *crystallographic structure* of such surface systems by recording 2-Dimensional diffraction peaks at fixed X-ray energy. Also, one can probe the *electronic structure* around selected atoms by recording the absorption of X-rays as a function of their energy, especially at resonance with the binding energy of the atoms' core electrons. However, the interpretation of the X-ray data requires development of sophisticated *ab initio* theoretical methods that can create simulated spectra to be compared with the experimental spectra.

Since X-rays are scattered only weakly by a surface or a thin film, Surface X-Ray diffraction ("SXRD") requires using the intense, highly focused X-ray beams available at synchrotron radiation sources. For a beam diffracting off a crystal surface or a thin film, *i.e.* a combination of 2D and 3D diffraction, the diffraction image is a pattern of short, broadened lines called "truncation rods". These "rods" give information about the arrangement of the atoms on and near the surface.

Fig. 1



Resonant scattering process for an atom at a surface (e.g. Br on Cu). An incoming X-ray photon promotes, from an atomic core state, a virtual photoelectron which probes the close surroundings. The transition back to the core occurs with the emission of a new photon with the original energy. The amplitude of the resonant scattering contains information about the local crystallographic and electronic structures around the resonating atom. At left is summarized our iterative simulation of the data.

But, as well as being scattered, X-rays are absorbed by the atoms. The absorption spectrum is sensitive to the electronic density on and around an atom, especially for X-ray energies at or near the "absorption edges". These absorption onsets, termed K, L, etc., begin where the X-ray photon energy matches the binding energy of a 1s, 2s,.., electron of the atom. The sensitivity is enhanced when recording X-ray diffraction data for X-ray energies in resonance with the absorption transition (Resonant X-Ray Diffraction, "RXRD").

Up to now no one had been able to fit surface resonant diffraction data accurately. Our work was aimed at filling this deficiency, using an *ab initio* (from first principles) theoretical method to simulate both the rod diffraction patterns and the spectra. In surface crystallography it is convenient to distinguish between the bulk contribution, (where the atomic and electronic structures are supposed to be the same as in an infinite crystal) and the surface which includes the substrate's topmost atomic layers and the possible adsorbed layers. The X-ray structure factors are the simple sum of both contributions. The aim of our work was to deduce the atoms' positions and the occupancies of the atomic orbitals, as well as the details of the surface roughness and the thermal mean square displacements, etc. These quantities are the "unknowns" to be "solved" by fitting them to the X-ray data.

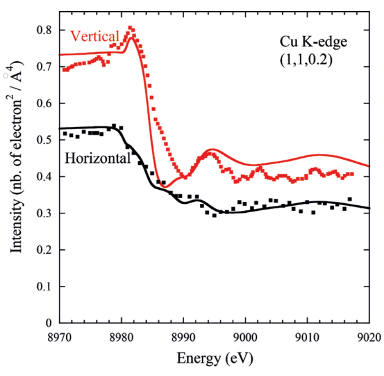
Our fitting procedure begins from a starting model of the surface geometry. We calculate this model's interaction with X-rays, compare it with the diffraction and absorption data, adjust our model, and iterate (Fig. 1) until a good match is obtained. We use the *ab initio* Density Functional theory to calculate the electronic structure around the resonant atoms. From it, one gets the charge on each atom and the bonding with the neighbor atoms but also the atoms' resonant scattering amplitudes. These amplitudes are highly dependent on both the energy and the polarization angle near the absorption edges. (The fitting procedure actually makes much use of a "virtual diffractometer" routine, which operates to simulate the geometry of the experimental setup during the measurement.)

We have demonstrated the validity of this approach by studying two very different systems. First was a thin film of magnetite (Fe_3O_4) on silver. This was related to the search for the thinnest film to undergo the metal to insulator transition (the Verwey transition), well known in bulk magnetite. We successfully interpreted the changes seen in the surface resonant X-ray diffraction across this transition.

Our second study concerned the charge transfer and nature of the chemical bonding at an electrochemical interface, specifically the interface between an adsorbed layer of bromine and a copper substrate in an electrochemical cell (experiments done *in situ* at the European Synchrotron Radiation Facility). Fig. 2 shows just the comparison of our simulated X-ray absorption spectra with the data around the copper K-edge. The agreement is good. Briefly, the energy shift of these spectra relative to a copper reference gives the oxidation state of the copper atoms, and most of the other features are signature of the bonding of copper atoms in the two topmost layers with their neighboring atoms. Similar good fits were obtained for data obtained at the Bromine K-edge.

Fig. 2

Surface Resonant X-ray Diffraction spectra at the Cu K-edge for a Br c(2x2) adsorption-layer on a (100) Cu crystal for vertical and horizontal X-ray linear polarizations. The linear dichroism is quite strong and shows the anisotropy of the local electronic structure close to the surface. There is good agreement between simulation (full line) and experiment (dotted).



The interest of this approach is that when the fit to the data is good, one has obtained the geometric structure and the electronic structure of the surface at the same time. This gives the possibility to get detailed insight into the bonding at electrochemical surfaces and at surfaces under reactive conditions, which do not allow for conventional ultrahigh-vacuum spectroscopic studies.

CONTACT
Yves Joly
yves.joly@neel.cnrs.fr

PhD student:
Antoine Abisset

FURTHER READING...
"Simulation of Surface Resonant X-ray Diffraction"
Y. Joly, A. Abisset, A. Bailly, M. De Santis, F. Fettar, S. Grenier, D. Mannix, A. Y. Ramos, M.-C. Saint-Lager, Y. Soldo Olivier, J.-M. Tonnerre, S.A. Guda and Y. Gründer
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Institut Néel - CNRS
25, rue des Martyrs - BP166
38042 Grenoble cedex 9 - France

neel.cnrs.fr