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Highlights 2013

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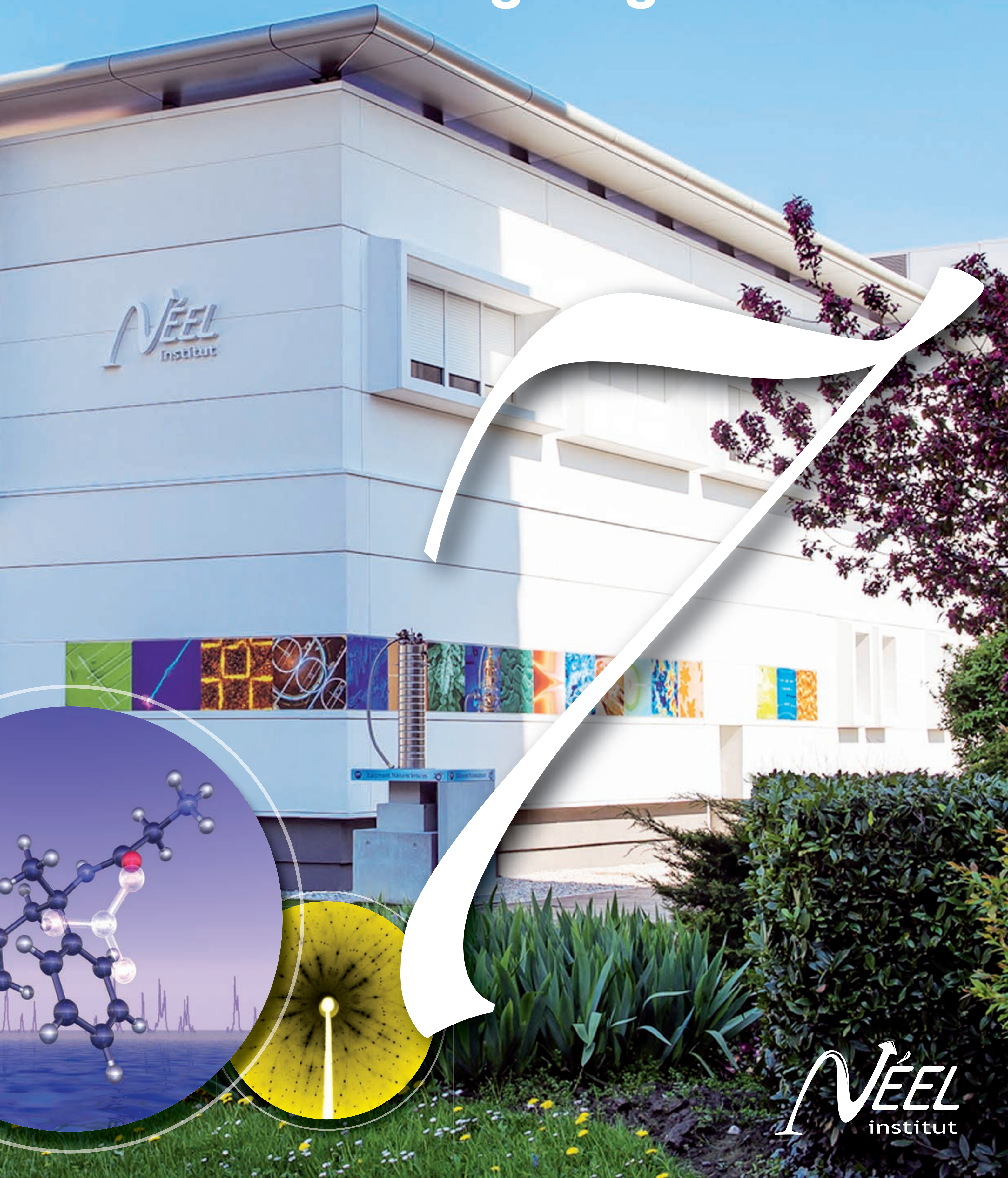

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EDITORIAL

For the Institut NEEL, the year 2013 was marked by the inauguration of a new building, designed to provide an environment where the most sensitive experiments will benefit from a very low level of fluctuations of all kinds: mechanical, magnetic, thermal... We are proud of this new research facility. With exceptional characteristics unique in Europe, it will enable our research teams to remain at the forefront in fields as varied as quantum information, crystal growth, microscopy, optics and nanofabrication. I should like to thank the many people who have contributed to the success of this project. Our new building would not have existed without the pioneering work of those who conceived the project beginning in 2005, nor without the financiers who provided the means to start construction. The building would not have had its remarkable specifications without the excellent cooperation between the CNRS-Alps Technical Services, the architect Philippe Jamet, and the representatives of the Institut NEEL's researchers, Serge Tatarenko and Philippe Gandit. Over six years, Philippe Gandit worked intensively on liasing with the building operation and on its continuous adaptation to users' wishes.

The research results presented in these pages do not come as yet from experiments done in the new building. For that, we need to wait for the next edition of *Highlights*. The present collection of 17 articles represents a selection of particularly important technical or scientific advances made over the last one or two years. In no way is this an exhaustive list. Obviously, it would be impossible to cover in just a few pages all the results obtained by a laboratory of 300 university and CNRS researchers, 130 technical staff and some 150 Ph.D. students and postdocs. The Institut NEEL is a laboratory for research in Condensed Matter Physics, with a considerable multidisciplinary component (chemistry, life sciences, engineering...) and many interdisciplinary activities. This is our strength. In spite of the great diversity of our scientific themes, our research teams cooperate effectively, sharing expertise and means and equipment throughout the Institute. They also benefit from the support provided on Grenoble's open technological "platforms", where expertise developed for each individual researcher's work becomes available to everyone.

To mark the centenary of the award of the Nobel Physics Prize to Max von Laue for his discovery of the diffraction of X-Rays by crystals, UNESCO has declared 2014 as the International Year of Crystallography. The 1913 work by William Henry Bragg and William Lawrence Bragg, co-laureates of the Nobel Physics Prize for 1915, will be similarly honoured. They broke the secret of the way atoms are arranged in crystals and so initiated the arrival of modern crystallography and materials science. Given our research themes, our many diffraction instruments, and our involvement in the large diffraction facilities (the ESRF and SOLEIL synchrotrons and the ILL neutron reactor) this year-long commemoration has special significance for us. The personnel of Institut NEEL have been working for some months already, to prepare the events which will be held in Grenoble, in France and in the world, in particular to disseminate knowledge of crystallography and related science to the public.

Alain SCHUHL
Director of Institut NEEL
Grenoble, France

CONTENTS

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DATE OF PUBLICATION: 2013

Twisting two graphene layers tunes their electronic properties

Graphene is a single layer of carbon atoms arranged in a hexagonal honeycomb structure. This fascinating material is known to host very peculiar charge carriers (electrons or holes), called "Dirac massless fermions", which generate outstanding and promising transport properties. When two graphene layers are stacked together, the system differs drastically from monolayer graphene. By introducing a rotation (twist) angle of several degrees between the two graphene layers, scientists are now unravelling additional and intriguing electronic properties.

Twisted graphene bilayers have emerged recently as a promising graphene-based material whose properties can be controlled by a single geometrical parameter: the interlayer rotation angle. As shown in Fig. 1 below, a small rotation angle introduces areas having very different stacking between the layers. This leads to an additional periodic modulation of the electric potential seen by a electron or hole moving in the carbon planes.

Electronic structure calculations show that decreasing the interlayer twist angle to a few degrees reduces the velocity of the charge carriers (compared to their velocity in monolayer graphene). Additionally, the calculated density of electronic states $\rho(E)$ of the charge-neutral system exhibits two pronounced peaks at energies $E_F \pm \Delta E/2$, where the energy separation ΔE between the peaks is roughly proportional to the twist angle (E_F is the Fermi level).

The origin of these two peaks lies in the peculiar electronic interlayer-interaction in this system, which is periodically modulated according to the arrangement of the AA and AB/BA regions (Fig. 1). This generates saddle points in the electronic band structure (i.e. points of k-space where the electron bands curve up in one direction of the wavevector and down in a different direction). In two-dimensional systems, such saddle points lead to peaks in the density of states called van Hove singularities.

The present work results from a collaboration between scientists of Institut NEEL, University Autonoma de Madrid, and Université de Cergy-Pontoise. We did a low-temperature Scanning Tunneling Microscopy (STM) study, coupled with an extensive theoretical analysis, of graphene layers grown on the Carbon face of Silicon Carbide (SiC) wafers. This growth method produces a stack of a few layers of graphene, with various interlayer twist angles, changing from one surface domain to another. We used the "spectroscopic mode" of the STM to measure the surface local density of states $\rho_s(E)$ in such domains. Fig. 2 shows an experimental $\rho_s(E)$ graph measured in a domain having twist angle 3.3°. This angle is deduced from the 4.3 nm periodicity of the moiré pattern in the STM image displayed as the background to Fig. 2. We find that van Hove singularities in the surface density of states are ubiquitously present over a broad range of twist angles (1° to 10°). The dependence of their energy position on twist-angle agrees very nicely with our theoretical calculations.

In summary, our work ascertains the mechanism of interlayer interaction in twisted graphene bilayers, i.e. the coupling of the electronic states of the individual graphene layers by a periodic potential induced by the twist.

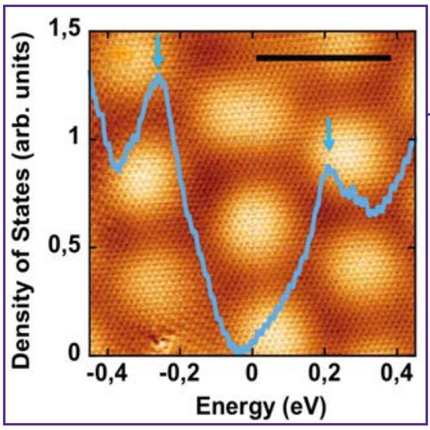

Fig. 2: Low Temperature Scanning Tunneling Microscopy performed on twisted graphene layers on SiC, in a domain with a 3.3° twist angle between the surface and subsurface graphene layers. Blue trace is a plot of the surface density of electronic states as a function of energy. The two arrows point to the van Hove singularities arising from the twist angle.

Behind the plot, we display an STM image of the corresponding area. This image with atomic-resolution (the tiny dots) shows a superstructure (moiré pattern) with 4.3 nm periodicity which reflects the alternating local AA (bright regions) and AB/BA stacking regions of Fig. 1. Scale bar: 5 nm.

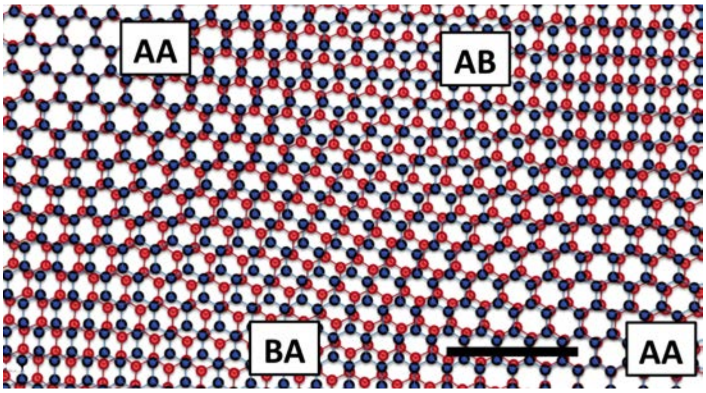

Fig. 1: A double layer of graphene with a 3 degree twist between the layers. In zones AA each carbon atom of the top layer (blue atoms) lies directly above a carbon atom of the lower layer (red atoms). In zones AB and BA, every second blue atom lies centred above a hexagon of red atoms. As a result, electrons moving through the material see a periodically varying potential, which strongly modifies the electronic structure of the system. Scale bar: 1 nm.

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FURTHER READING

UNRAVELING THE INTRINSIC AND ROBUST NATURE OF VAN HOVE SINGULARITIES IN TWISTED BILAYER GRAPHENE BY SCANNING TUNNELING MICROSCOPY AND THEORETICAL ANALYSIS
I. Brihuega, P. Mallet, H. González-Herrero, G. Trambly de Laissardière, M. Ugeda, L. Magaud, J. Gómez-Rodríguez, F. Ynduráin, and J. Y. Veuillen
Phys. Rev. Lett., 109,196802 (2012)

NUMERICAL STUDIES OF CONFINED STATES IN ROTATED BILAYERS OF GRAPHENE
G. Trambly de Laissardière, D. Mayou and L. Magaud
Phys. Rev. B 86, 125413 (2012)

Electric field trapping of a magnetic domain wall

In spintronics applications such as magnetic memories, information is written to and read from magnetic metals using electric currents. In contrast, electric fields, used extensively to control the state of semiconductor transistors, have not yet been exploited in spintronics despite the lower power consumption expected as compared to current-based devices. We have made an important step in this direction with the demonstration of electric-field control of magnetization.

Untill recently, the influence of an electric field on magnetic properties was considered negligible in ferromagnetic metals. Indeed, an electric field cannot penetrate into a metal as it is screened at the surface by charges that accumulate on the topmost few atomic layers. However, in the case of an ultra-thin film of 1 nm thickness or less, this surface charge can influence the properties of the whole film.

At Institut NEEL, in collaboration with Spintec Laboratory (Grenoble), we have realized an ultra-thin, 0.6 nm film of the magnetic metal cobalt, which is sandwiched between a layer of the nonmagnetic metal platinum and a dielectric layer of alumina (Al_2O_3). The ultra-thin magnetic film, only a few atoms thick, posseses a strong magnetic anisotropy: it is energetically more favorable for the magnetization to align perpendicular to the plane than in the plane.

We have carried out the following experiment: the magnetization of the sample is visualized with a microscope in polarized light (Kerr microscopy). We obtain grey-contrast images where bright regions correspond to magnetization directed down and dark regions to magnetization directed up. We apply an electric field using a patterned electrode made of a transparent material (Indium Tin Oxide ITO), see (Fig.1(a)), which allows us to vizualize the magnetization under the electrode. Reversal of the magnetization is investigated thus: Initially we apply a magnetic field to magnetize the sample in one direction, then we reverse the magnetic field and record images of the magnetization reversal as a function of time. The following reversal process is observed in the cobalt layer.

A small region with opposite magnetization is first created near a defect (nucleation) and this region then grows. Our sample can therefore present a region with "up" magnetization and another with "down" magnetization. The frontier between those two regions is called a magnetic domain wall and within the wall the magnetisation rotates progressively to minimize the energy Fig. (1a). We have demonstrated that when the electric field is switched on, the domain wall is pinned when it reaches the edge of the electrode leaving the magnetization unreversed below the electrode while the rest of the sample is reversed, see Fig. 1(a), and Fig. 1(b) at times t_1-t_4. When the electrode voltage is switched off the domain wall is released and the magnetization reverses everywhere (Fig. 1(b) t_5-t_6).

What is the origin of this domain wall trapping? The magnetization is the sum of the cobalt atom spins, aligned parallel to each other. Below the ITO electrode, the electron clouds of the interfacial cobalt atoms are deformed by the electric field. This deformation affects the magnetic properties: the magnetic anisotropy (the energy barrier to reversal of the magnetization) is enhanced. The movement of domain walls becomes more difficult in the high anisotropy region below the electrode and a domain wall arriving from outside the electrode is blocked at the edge of the electrode.

This demonstration opens the way to controlled domain-wall propagation, which is required for the development of domain-wall based magnetic logic or magnetic memory components, such as domain wall based Magnetic Random Access Memories.

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FURTHER READING

ELECTRIC-FIELD CONTROL OF DOMAIN WALL NUCLEATION AND PINNING IN A METALLIC FERROMAGNET
A. Bernand-Mantel et al.
Appl. Phys. Lett. 102, 122406 (2013)

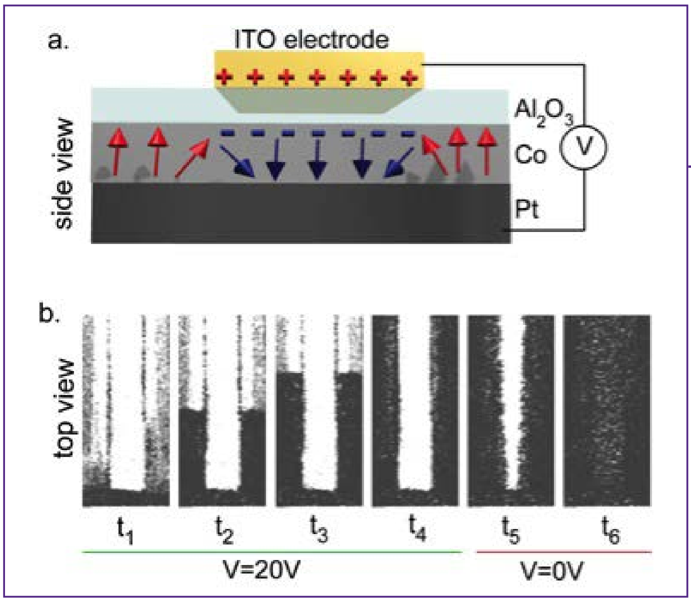


Fig. 1(a): Side view of the Platinum/ 0.6 nm Cobalt/ Al_2O_3 layer structure under a transparent Indium Tin Oxide electrode.

Fig. 1(b): Top view of the structure : Kerr reflection microscopy images recorded as a function of time in an applied magnetic field which is reversing the magnetization in the cobalt layer from "down" (white) to "up" (black). While the electric field is held on (times t_1 to t_4), the region below the electrode stays magnetized "down" (white) because the electric field blocks the domain-wall propagation. When the electric field is switched off the domain wall is released and the magnetization is reversed over the whole area (times t_5 to t_6).

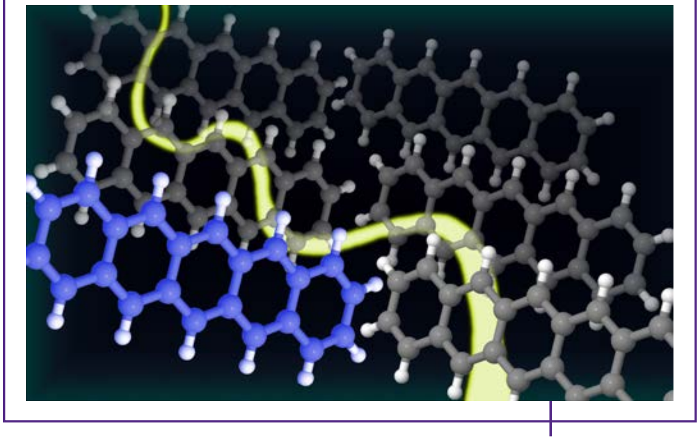
Electrons go green: Exploring organic semiconductors

Smartphones, large-size TV screens or bendable lamps: applications of OLEDs - Organic Light Emitting Diodes – are proliferating rapidly and demonstrate strikingly how fundamental research bears fruit in everyday life. These are prominent examples of the developing class of organic semiconductor devices. The latter consist of polymers or organic molecules, i.e. they are based on carbon and hydrogen instead of traditional materials like silicon. This brings convincing advantages: the end products -ranging from OLEDs to organic electronic devices- are light, flexible and environment-friendly.

Combining two worlds: Besides these promising applications, organic semiconductors are also highly interesting from a fundamental point of view. On the one hand, standard inorganic semiconductor materials are well understood and solid state physics theory provides precise models to predict their properties. On the other hand, theoretical chemistry describes the features of isolated molecules very well. Organic semiconductors lie in between these two worlds and the exact microscopic mechanisms governing their electronic properties are still open questions. These materials form crystals where, instead of atoms held together by strong covalent bonds, we have weakly connected molecules. When only the standard methods of either physics or chemistry are applied, experimental results cannot be reproduced theoretically. This limits our current understanding of organic compounds and new approaches have to be found, combining the insights of both sciences. This was the aim of recent work carried out by Institut NEEL researchers working with colleagues based in Italy, Denmark and the USA.

The experimental challenge : In this work, the electronic band structure of pentacene crystals was measured accurately using Angular-Resolved Photoemission Spectroscopy (ARPES). Pentacene is a small and rather simple molecule, and the pentacene crystal (Fig. 1) constitutes a typical case-study for organic semiconductors in general. We focused on the band structure, because it is an indispensable feature, directly related to fundamental material properties such as the conductivity and optical absorption. The band structure is like a map, indicating which values of energy and momentum an electron can possess within the crystal. The ARPES technique has been much used to measure the band structure of inorganic materials, but precise measurements for organics have only become possible during the last five years. One reason is the weak binding of the molecules, which easily evaporate under ultraviolet radiation. Moreover, it is extremely difficult to grow a perfectly periodic organic crystal – a necessary condition to obtain satisfying ARPES signals. Our collaborators succeeded in drastically improving the experimental resolution, and also reduced the molecular disorder by optimizing the sample preparation.

A challenge for theory: Determining the band structure from theory is even more challenging. Since the molecules are held together by rather weak forces- in contrast to atoms in a crystal- they mostly retain their molecular identity, but available standard band structure theories have been developed for atomic crystals. In those theories, the electrons move freely in the crystal instead of belonging to a specific atom. This is a valid description for inorganic atomic crystals, but the molecular aspect is completely missing. We demonstrated this by using one of the most accurate band structure theories and comparing the results to the measured high-resolution pentacene band structure. The disagreement between experiment and theory was obvious. The question then was: Which molecular properties are missing in the standard theoretical approach?



Artist's view of electronic transport (the green curve) in an organic crystal. The building blocks of the crystal are pentacene molecules (formula $C_{22}H_{14}$) consisting of five benzene rings linked together (e.g. the blue group in foreground). The molecules stack together in a loose, complex geometry to form the crystal.

From molecules to crystals: A hint could be found in past Photoemission Spectroscopy experiments performed on free organic molecules in the gas phase, which showed that the molecular vibrations, i.e. the periodic oscillations of their constituent atoms, completely reshuffle the available electronic energies in the molecules: a characteristic "shakeoff" spectrum appears, which is a hallmark of the strong interconnection between the electrons and vibrations. We therefore calculated the strength of this effect, the so-called electron - molecular vibration (EMV) coupling, for a single molecule and combined it with a crystal band structure calculation, to describe simultaneously the molecular (vibrational) and crystalline nature (band structure) of these materials. The resulting modified band structure shows coexisting features of the shakeoff spectra of individual molecules and of the usual bands of the crystalline solid, and is in extremely good agreement with the experimental measurements. Inclusion of the molecular ingredient was therefore crucial to explain the puzzling features observed in experiments.

Pentacene, more than a study case: Our combined experimental and theoretical study on pentacene has demonstrated unambiguously that fingerprints of the molecular constituents are clearly visible in the electronic energy spectrum. These features are now systematically being observed in experiments on several other organic molecular compounds, which suggests that the relevance of the present findings could extend well beyond the pentacene study-case presented here.

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FURTHER READING

MOLECULAR FINGERPRINTS IN THE ELECTRONIC PROPERTIES OF CRYSTALLINE ORGANIC SEMICONDUCTORS: FROM EXPERIMENT TO THEORY
S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase and S. Fratini
Phys. Rev. Lett. 108, 256401 (2012)

New density waves uncovered in fermion liquids

In spite of their exotic name, fermion liquids are common in nature: metals, atomic nuclei and neutron stars are made out of strongly interacting particles named fermions, a group that includes quarks, electrons, protons and neutrons. Fermion particles obey the Pauli Exclusion Principle, which states that two identical fermions cannot occupy the same quantum state. The other class of quantum liquids, composed of bosons like gluons and photons, is well understood, but fermion liquids remain mysterious.

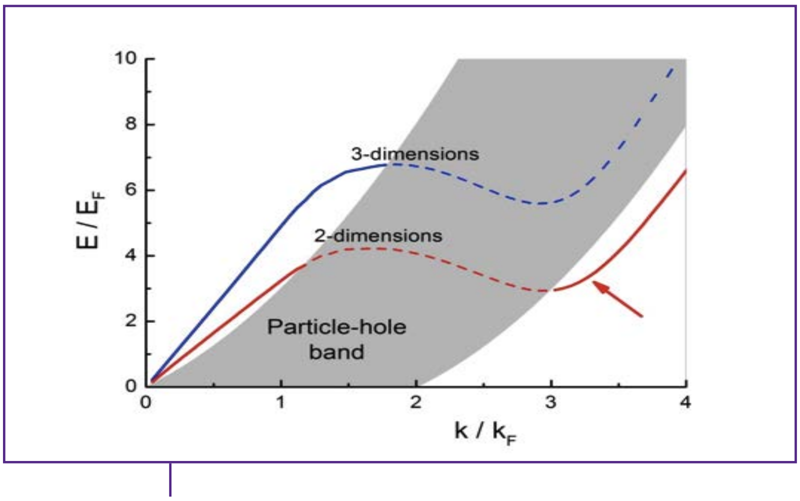

Fig. 1: Collective excitations in matter, where many particles oscillate together, are characterized by the dependence of their energy on the wave-vector k (=2π/wave-length). The linear behaviour seen at low wave-vectors is similar to what is observed for usual sound waves; in liquid ^{3}He, it corresponds to "collision-less sound", also called "zero-sound". At higher wave-vectors k, within the grey area shown in the figure, the sound waves are strongly damped, because they can create other excitations characteristic of a Fermi liquid, named "particle-hole excitations". In 3-dimensional Fermi liquids like bulk liquid ^{3}He, the zero-sound mode (blue curve) is always damped at high wave-vectors, and disappears. Here we show that in two-dimensional Fermi liquids, like a liquid Helium-3 film of atomic thickness, zero-sound (red curve) may, surprisingly, reappear beyond the particle-hole band as a well-defined collective mode (indicated by the red arrow). The mode displays a minimum in energy similar to the "roton" of liquid Helium-4.

A team of researchers from the Institut NEEL and the Institut Laue-Langevin (ILL) in Grenoble, Aalto University in Finland, Oak Ridge National Laboratory and SUNY University at Buffalo in the US, and Johannes Kepler University in Linz, Austria has carried out the first direct investigation of very short wave-length elementary excitations in a two-dimensional fermion liquid. The fluid under investigation consisted of Helium-3 atoms (the He^3 nucleus, a rare isotope of helium made up of two protons and one neutron, is a fermion). The atoms were deposited onto a graphite substrate, where they remain confined at very low temperatures, forming a remarkable two-dimensional Fermi liquid.

Since fermions cannot exist in the same state as each other, the quantum ground state (the minimum energy state, at the absolute zero of temperature) of a Fermi liquid is obtained by placing the particles in successive states of increasing energy, up to the "Fermi energy". Matter can be "excited" above its ground state; the corresponding quanta of energy are named "elementary excitations". The density excitations of a Fermi liquid, analogous to sound waves, are called plasmons (for charged particles) or "zero-sound" (for neutral particles).

The excitations can be created by a beam of neutrons, which also provides us with a privileged tool (neutron diffraction) to determine the excitations' energy and velocity. However, observing these excitations on just a one-atom-thick layer of helium-3 atoms is particularly difficult. For this reason, the experiment was done in the very high neutron fluxes available at the ILL reactor. Extremely low temperatures, less than a tenth of a degree above the absolute zero of temperature, are needed in order to clearly detect the elementary excitations of the liquid.

Much to our surprise, contrarily to the broad signal we had previously observed in bulk liquid helium-3, the two-dimensional liquid displayed sharp modes of oscillation. These unexpected experimental results lie beyond the scope of the standard theory, Landau's 1957 theory of Fermi liquids. They agree very well however with a new, Dynamical Many-Body theory developed by our co-workers in Linz and show that, in two-dimensions, zero-sound waves reappear at large momentum (short wave-lengths) beyond the "particle-hole band", the range in energy and momentum where they are strongly damped, see Fig. 1.

The discovery of short wave-length collective oscillations in Helium-3 is particularly interesting, as it is thought that they should be observable in other fermion liquids. For instance, short wave-length plasmons (or magnons, the corresponding magnetic density wave) could provide a mechanism for high temperature superconductivity. Understanding these properties is a challenge for modern physics.

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FURTHER READING

OBSERVATION OF A ROTON COLLECTIVE MODE IN A TWO-DIMENSIONAL FERMI LIQUID
H. Godfrin, M. Meschke, H-J. Lauter, A. Sultan, H. M. Böhm, E. Krotscheck and M. Panholzer
Nature 483, 576 (2012)

Birefringence of X-rays

Polarization phenomena in photon scattering, from optics to X-rays, provide information on electronic degrees of freedom not available with any other technique in materials science. In the past decade, striking progress has been made with the analysis of linear and circular polarization data obtained using the highly collimated and tunable X-Ray beams available at synchrotron sources. This is especially the case in resonant Bragg diffraction, where the intensities of weak or forbidden Bragg diffraction spots are greatly enhanced when the energy of the X-ray photon is tuned to a resonance of a selected atom. Unique and valuable information can then be obtained about the spin and orbital properties of the electrons that participate in, for example, magnetism, superconductivity, and multiferroic behaviour. However, a proper interpretation of polarization data requires an accurate theory of the radiation-matter interaction near an X-Ray resonance. This theory must include, in particular, the effects of birefringence.

Below 213 K, Copper Oxide CuO is an antiferromagnet. In a recently reported experiment (V. Scagnoli et al. *Science*, 332, 696 (2011)), the magnetic reflection (i.e. a scattering by the electron spins) was recorded at 100 K for various states of the incoming polarization and with analysis of the outgoing polarization. This was done for photon energies around the Cu L2 and L3 edges at 932 and 953 keV (which correspond to excitations of a 2p core electron to the 3d outer orbitals of the Cu atom). Conventional magnetic diffraction rotates a linear polarized incident beam 90 degrees. Detection of a non-rotated component in the outgoing polarization as well, guided the above authors to the exciting possibility of a scattering from an orbital or "toroidal" electronic current around the copper atoms. This supported a recent suggestion that such multipoles play an important role in High Temperature Superconductivity in copper oxide compounds.

However, since birefringence is permitted in a CuO crystal because of its low symmetry (monoclinic), calculations of the radiation-matter interaction from first principles are required to get a reliable quantitative description of the X-Ray scattering signals, and determine what the dominant physics is. We have done such calculations and, comparing them with the diffraction data kindly supplied by the above authors, we have demonstrated that a better explanation for these experimental results is to be found in birefringence.

We indeed confirmed that the atomic magnetic scattering gives only a 90 degree rotation of the polarization. But we found that, as the beam propagates through the crystal the polarisation rotates significantly (see Fig. 1). This leads to an apparently unrotated polarization component in the finally emerging wave. We have been able to reproduce quantitatively all the experimental results purely in terms of birefringeance: the spectrum shape, its polarization dependence and its azimuthal variation (i.e. the variation with rotation of the sample around the normal to the diffracting plane). To complete our analysis, we have also performed simulations that include the scattering process related to the hypothetical toroidal current in the material. We always found its contribution to be extremely small.

This may not necessarily mean that the orbital current idea is a false trail in the quest to understand High Temperature Superconductivity, other techniques are required to elucidate that. Nevertheless, this case has demonstrated how birefringence can play a major role in X-Ray resonant diffraction experiments and that precise simulations are essential to correctly interpret energy spectra and azimuthal and polarization dependences in such experiments.

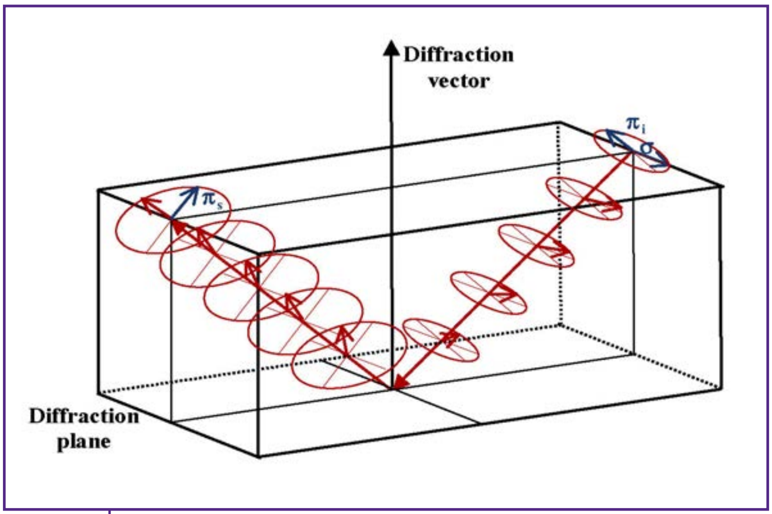

Fig.1: As the electromagnetic wave propagates in the birefringeant material, its polarization rotates progressively. When magnetic scattering occurs from a specific diffraction plane at some depth in the material, the polarization rotates by 90°. The outgoing wave then continues its slight rotation up to exit from the crystal. Because of the birefringeance, the observer measures an unexpected polarization state, a rotation different from 90 degrees.

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FURTHER READING

BIREFRINGENCE AND POLARIZATION ROTATION IN RESONANT X-RAY DIFFRACTION
Y. Joly, S. P. Collins, S. Grenier,
H. C. N. Tolentino and M. De Santis
Phys. Rev. B 86, 220101(R) (2012)

A new building

The Institut NEEL's new building dedicated to research in the nanosciences was inaugurated in April 2013. It represents the culmination of seven years of projects, planning and construction. The 17 million euro project was financed in the framework of a contract between the French State and the Rhone-Alps region. The two floor, 2600 square metre building (Fig. 1) has exceptional characteristics, unique in Europe, that will allow the Institute's research teams to remain at the forefront in areas as varied as quantum computing, crystal growth, microscopy, optics and nanofabrication.

Fig. 1: The Institut NEEL's new, 2600 square metre, Nanosciences building. Its two floors are accessed by bridges from the Institute's main building, at the right in the photo.

Financement

Coût total : 17.05 M€

Bâtiment : 13,74 M€

- Etat : 7.7 M€
- CNRS : 5.64 M€
- Région : 0.4 M€

Equipement :

- Etat : 0.2 M€
- CNRS :0.51 M€
- Région : 1.6 M€
- Communauté de communes : 0.5 M€
- Ville de Grenoble : 0.5 M€

Most of the Institut NEEL's existing laboratory buildings date from the 1960s. Inevitably, certain classes of scientific apparatus can no longer reach their ultimate performance when operated in buildings from that era. This had become an acute problem for researchers making observations and fabricating devices at or near the atomic scale.

Thus there was a clear need for an entirely new building, purpose-built to satisfy the needs of present-day and future projects that require an extremely stable environment for research samples. This means a building structure that greatly limits mechanical and acoustic vibrations, precisely controls air temperature and hygrometry, and eliminates electromagnetic perturbations.

The project was defined first of all by consulting the research teams involved. Visits were then made to recent realizations such as Minatec (Grenoble), the Lyon Centre for Microscopy, the joint CNRS/Thales physics laboratory (Paris region) and the Hamburg Institute of Nanosciences, to study the different techniques deployed there. Based on these observations, a novel solution was proposed.

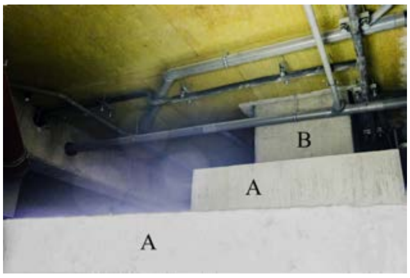

Fig. 2: A support pillar (B) resting on one of the massive concrete blocks (A) in the basement area. The pillar projects up through an aperture into the ground floor area. It remains completely independent of the building proper.

For working at the atomic scale, the primary requirement is mechanical stability of the scientific instruments, uncompromised either by any activity of the site or of the researchers themselves. Our design solution begins in the building's basement (see Fig. 2) with a foundation consisting of five massive concrete blocks of complex shape, ranging in size from 500 to 1500 tons. From these blocks, 33 individual pillars (one such pillar is seen in Fig. 2) emerge at the ground floor of the building to support the most sensitive experiments (see Figs 3, 4). The pillars are synthetic-fiber reinforced concrete, since conventional steel reinforcing would perturb experiments sensitive to magnetic fields.

This part of the structure is completely independent of the walls and floors of the enclosing building. Vibrations are reduced by a factor of 100 compared to the levels in a classic building.

One special pillar was destined for an Atomic Force Microscope which will operate at very low temperatures under high magnetic field. This pillar weighs 30 tons and rests on pneumatic dampers. Its reinforcement armature was realized in a composite material. The tubing carrying gas and fluids for the future cryostat has been buried in the concrete for optimum reduction of vibrations. All this constitutes three levels of vibration filtering, each having a different self-resonance frequency: the base block (1000 tons), the support pillar (30 tons) and a 2 tons marble table for the experiment.

for research in the nanosciences

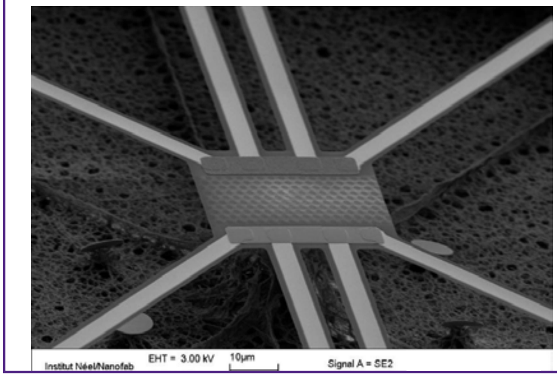

Fig. 4: Nanofab microfabricated auto-supported nanocalorimeter : ebeam and laser lithography

On the first floor of the building, 27 floating slabs mounted on springs are provided for experiments that demand a somewhat lesser level of mechanical stability.

The building is designed to minimise variations of its interior microclimate. In particular, the laboratories housing the high resolution microscopes have thicker walls. Especially for the ground floor, recessed windows (see Fig. 1) limit the effects of direct sunlight. A thick mineral sheath on the facade of the building attenuates the effects of wind. A very high level of thermal insulation (on both the exterior and interior) gives the building high thermal stability, limiting daily and seasonal thermal variations.

Services components and equipment (stairways, toilets, heat pumps, air conditioning...) are isolated in independent areas of the building. There is no elevator, as this would be a large source of vibrations and electromagnetic perturbations. Instead, access to both floors is by bridgeways from the adjacent main building of the Institute (Fig. 1). All pipes and tubing liable to produce vibrations are supported on spring mountings (Fig. 5).

Particular care was taken with the sound-proofing between different rooms. Perturbing experiments like furnaces and magnets are placed well away from the most sensitive experiments. Inductive loops have been installed in certain rooms to compensate stray magnetic fields, which would limit especially the resolution of electron microscopes. Also, throughout the building, users can access an electric-equipotential reference that is independent of the mains network.

Air temperature and humidity are controlled by three separate air treatment systems. One system is dedicated to the clean room, a second system cools the room that houses the high temperature furnaces, while the third system maintains temperature and humidity for the building generally. A 500 kW heat pump provides heating or cooling as needed. The air is monitored by 800 measurement points distributed throughout the building

The construction of this complex building was done in two years, from May 2011 to its inauguration on 12th April 2013. Also, as part of this building operation, an extra floor (1000 square metres) was erected above a section of the Institute's main building. This provides space for new offices and meeting rooms, for an expansion of the Institute's store, as well as a convivial area for discussions next to the Institute's main seminars room.

Finally, the 1700 square metres of laboratory space liberated by transfer of experiments into the new building will be completely rehabilitated.

Fig. 3: Image furnace for crystal growth installed on the top of its square support pillar. Note the separation between the pillar and the laboratory floor: the pillar is independent of the building.

Fig. 5:Technical area underneath the clean room. All the tubing is supported on spring mountings. (All Photos: photothèque CNRS)

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Dual OPO for studying of far-infrared to terahertz nonlinear crystals

High-intensity, coherent light sources emitting two very close wavelengths are of much interest for the generation of infrared to terahertz optical frequencies via the process of Difference-Frequency Generation (DFG). By combining two mid-infrared light beams in a crystal that has a strongly non-linear optical susceptibility, one can generate a far infrared or terahertz output beam. For this purpose, we have conceived and validated a dual light source. It is a pair of independently tunable Optical Parametric Oscillators, made from crystals of the ferroelectric material Magnesium Lithium Niobate that had been periodically poled in an electric field.

Our unique, dual wavelength source (see Fig. 1) uses two Optical Parametric Oscillators (OPOs) pumped simultaneously with nanosecond pulses from a Nd:YAG (Neodymium Yttrium Aluminium Garnet) laser having wavelength λ_p= 1.064 µm. Each arm of the dual OPO uses a 5-mm-thick, 38-mm-long crystal (green slabs in Fig. 1), cut as a partial cylinder from a crystal of PP 5%MgO:$LiNbO_3$.

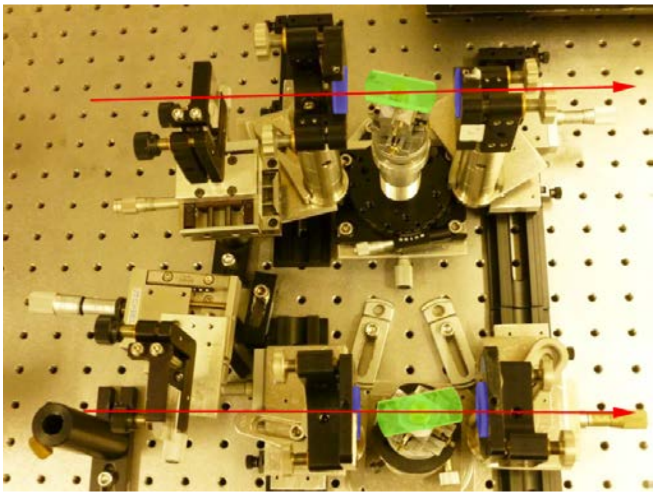

Fig. 1: Photo of the dual OPO source consisting of two independent Optical Parametric Oscillators made of Periodically Poled 5%MgO:$LiNbO_3$ crystals. The crystals, cut as partial cylinders, are tinted green on the photo. The cavity mirrors are tinted blue. Red arrows mark the input/output light paths.

"PP" means that, before cutting, the two partial cylinders had been "periodically poled" in an electric field, i.e. made into a sequence of ferroelectric domains of alternating spontaneous electric polarisation along the cylinder axis (which is the optic axis, z). This creates an optical grating. The grating period is λ_0 =28 µm. In such a grating, the sign of the crystal's nonlinear optical susceptibility coefficient inverts periodically. This allows the generation of two, coherent, output light-beams with a wavelength smaller (λ_s) and longer (λ_i) than the pump wavelength λ_p, and verifying $1/\lambda_p=1/\lambda_s - 1/\lambda_i$. The process is called "quasi-phase-matching".

Focusing the Nd:YAG beam with a cylindrical lens ensures parallel propagation of light in each partial cylinder crystal. Each crystal is inserted between two plane mirrors (see Fig.1), forming an optical cavity that sustains oscillations of a stimulated three-wave-mixing parametric process. The coatings of the mirrors are such that the beam at longer wavelength $\lambda\iota$ is amplified by oscillations of the beam at the shorter wavelength λ_s in the optical cavity, as the Nd:YAG beam makes a round-trip in the partial cylinder.

A continuous tuning of the output wavelengths of each OPO, λ_s and λ_i, is achieved by rotating each partial cylinder *independently*, by an angle Φ, which gives a continuous variation of the effective grating periodicity as $\Lambda_{eff}(\Phi)=\Lambda_0/\cos(\Phi)$. A rotation through 30° is sufficient to access the full tunability of the crystals, i.e. from 1.4 µm to 4.4 µm. The oscillation threshold of each OPO is around 1.5 mJ and the energy conversion efficiency is high, ranging from 20% to 27% for 10 mJ input Nd:YAG pulses.

With this new dual OPO we successfully generated far infrared light in the birefringent compound CdSe. A CdSe crystal was cut into a 5-mm-diameter cylinder with its optic axis z perpendicular to the cylinder axis and polished to optical quality (see insert in Fig. 2). The wavelength of one of the two incident OPO beams was kept fixed, λ_i = 2.79 µm. By tuning the wavelength of the other OPO λ_i from 3.8 to 4.2 µm, and rotating the CdSe cylinder, we successfully generated an output wave from the CdSe crystal accurately tunable in the range 8.3-10.2 µm (36-29 THz) (see Fig. 2). Alternatively, by pumping a fixed CdSe crystal slab, we could generate light in the range 8-13 µm by varying the wavelengths of the two incident OPO beams.

Such studies can be extended to other materials for the generation of wavelengths in the low THz range. Efficient light sources at these spectral ranges should be very useful in biomedical imaging or atmospheric spectroscopy for example.

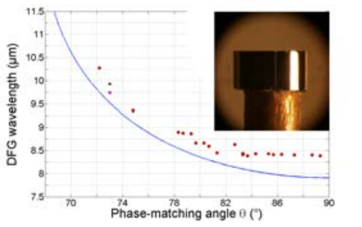

Fig. 2: Data from a Difference-Frequency Generation (DFG) experiment that used our dual OPO source. The two light beams (one was fixed at 2.79 µm, the other was varied) pumped a 5-mm-diameter, cylindrical CdSe crystal (insert photo). Output light at the difference frequency is obtained for a crystal orientation where the two input waves interfere constructively (the phase-matching condition). Red points are measurements; the blue curve is a calculation.

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FURTHER READING

Widely tunable optical parametric oscillator in a 5-mm-thick 5% MgO:PPLN partial cylinder
V. Kemlin, D. Jegouso, J. Debray, P. Segonds, B. Boulanger, B. Menaert, H. Ishizuki, and T. Taira
Optics Letters 38, 860 (2013)

Cavity quantum electrodynamics in a solid by nonlinear spectroscopy

Milestone achievements in cavity quantum electrodynamics (cQED) were honoured recently by the award of the 2012 Nobel Prize in Physics to Serge Haroche and David J. Wineland. Their explorations of the interaction between electromagnetic radiation and matter at the most fundamental quantum level were done in microwave cavities on individual atoms. Similar cQED effects can now be observed in nanostructured semiconductor objects, which will be better suited for miniaturization and commercialization. Furthermore, employing optical transitions in semiconductor nanostructures, one can operate at optical wavelengths compatible with glass fibre communications.

Individual modes for radiation and matter can be realized, on the one hand by confining photons in solid state resonant cavities and, on the other hand, by confining an electron and a hole in a semiconductor Quantum Dot (QD), so as to obtain an atom-like species called an exciton. When these two kinds of excitations are matched in frequency and space, the photon-exciton coupling is radically enhanced. The unison of light and matter is then achieved in the "strong-coupling" regime, where single portions of excitation are reversibly exchanged between the photons trapped in a cavity mode and a QD exciton.

The quantum and nonlinear character of the light-matter interaction is particularly pronounced at low photon occupation number. In this regime of strong coupling, described theoretically in 1963 by Jaynes and Cummings, the transfer of excitation from photon to exciton and back to photon – a kind of temporal "ping-pong" known as Rabi oscillation – shortens in discrete steps when increasing the number of optical excitation quanta. Going from one to two (or n) photons carried by the cavity mode, the period of the Rabi oscillation is reduced by a factor $\sqrt{2}$ (or $\sqrt{n}$). This non-intuitive "Jaynes-Cummings nonlinearity" can be pictured as if two tennis players (one player being a photon, the other an exciton, and a ball being an excitation) exchanged faster and faster, while putting more and more balls into the game.

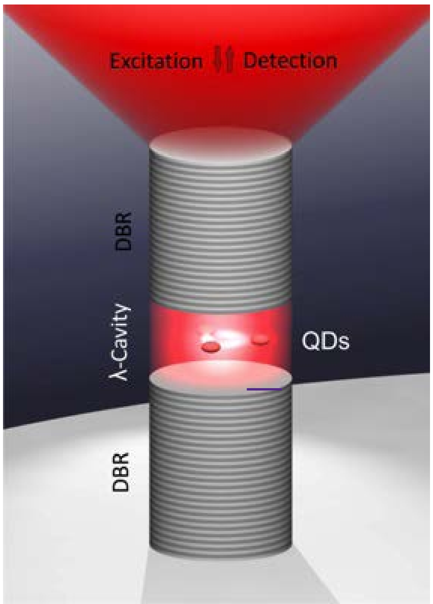

Figure 1: The semiconductor microcavity including the light coupling from the top facet. The sample, shaped into a 2 micron diameter pillar, consists of two GaAs/Aluminium Gallium Arsenide DBR's (Distributed Bragg Reflectors), and a one wavelength thickness GaAs spacer (the cavity) hosting a layer of Indium Gallium Arsenide quantum dots (QDs).

Following initial studies in 2010, we have directly demonstrated Jaynes-Cummings nonlinearity in a solid, in the framework of a collaboration between Cardiff University (UK), Würzburg University (Germany) and the Institut NEEL. We have employed a tiny cylindrical pillar, as depicted in Fig. 1, precisely sculpted in a pair of interference mirrors that sandwich a layer of Quantum Dots. The pillar provides a cavity of effective volume 0.3 microns^3 that can host near-infrared photons of wavelength 930 nm for about 10 picosec (10^{-11} sec). We inject individual photons into the pillar using a pulsed laser. During its trapping time a cavity photon can be absorbed by a Quantum Dot matched to the cavity wavelength, generating an exciton in the dot. The exciton subsequently decays emitting a photon, which feeds back into the cavity mode to once again excite the dot: the coupled exciton-photon system survives several periods of these Rabi oscillations, before the photon escapes to the outside world via leakage out of the top facet of the pillar.

Until now, the photon lifetime, still rather short in state-of-the-art solid-state optical resonators of this kind, has hampered demonstration of Jaynes-Cummings nonlinearity. To tackle this issue we have applied nonlinear spectroscopy methods capable of probing phenomena occurring at the pico-second timescale. We were able to inject either just one or just two photons into the pillar and, by measuring an optical signal called Four-Wave Mixing (FWM), we observed a speed up of Rabi oscillations by $\sqrt{2}$, as predicted by the theory of Jaynes and Cummings.

Most recently, we have used this FWM technique to probe the radiative coupling between excitons in separate QDs. This type of coupling is a central issue in many research areas, ranging from biology (where it is essential for understanding photosynthesis) to quantum information science (where the "quantum bus" technology aims at constructing long-range coupling channels between distant quantum bits). We have measured subtle dynamics of radiative coupling in a trio of spatially distant Quantum Dot excitons, having nearly identical energy, mediated via the photon mode of a pillar operating in the strong coupling regime. Here, a tentative analogy from the macroscopic world could be a tennis game, where three of the players (on one side!) are excitons, while the fourth player is a cavity mode.

Experiments are being undertaken at Institut NEEL and elsewhere to exploit such radiative coupling mechanism to "wire up" distant emitters that are embedded in waveguides or networks of photonic-crystal cavities, to enable a long-range coupling, and thus to implement "quantum bus" technology in semiconductors.

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FURTHER READING

COHERENCE DYNAMICS AND QUANTUM-TO-CLASSICAL CROSSOVER IN AN EXCITON–CAVITY SYSTEM IN THE QUANTUM STRONG COUPLING REGIME
J. Kasprzak et al.
New. J. of Phys. 15, 045013 (2013)

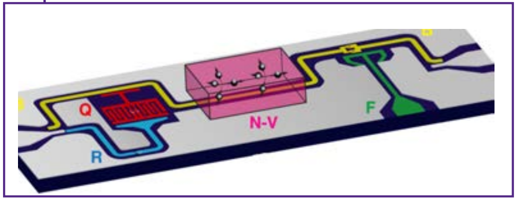
MICROCAVITY CONTROLLED COUPLING OF EXCITONIC QUBITS
F. Albert, K. Sivalertporn, J. Kasprzak et al.
Nature Commun. 4, 1747 (2013)

Strong radiation-matter coupling in hybrid circuits

Strong coupling is a key regime of quantum optics where radiation and matter exchange energy in a coherent and reversible way. Since the early eighties, this regime has been studied for ensembles of atoms and single atoms that have been strongly coupled to optical and microwave cavities. These experiments led to propositions that strongly coupled systems could constitute building blocks for quantum information processing. In the solid state, recent impressive developments in the new field of Circuit Quantum Electrodynamics hold the promise that strong interaction between radiation and matter can be exploited at the single photon level, in quantum processing and quantum memory elements that can be replicated and integrated to construct a ”quantum computer.”

In the usual picture of Cavity Quantum Electrodynamics (cavity QED) from atomic physics, radiation and matter are reduced to their simplest forms, corresponding to the mode of an electromagnetic resonator and one or more atoms, respectively. The atoms have an optical absorption/emission transition resonant with the cavity frequency. The strong coupling is characterized by a reversible and coherent exchange of energy between the cavity and the atom(s), the "Rabi oscillations" (see also the preceding article "cavity QED in a solid). To observe and exploit these oscillations, the effect of decoherence (atomic relaxation, finite resonator lifetime) should be negligible at the timescale of the radiation-matter interaction. This condition is far easier to reach for huge numbers of emitters N, since the time for energy-exchange scales as 1/(√N). Consequently, the first demonstrations of cavity QED in the 1980's were performed with large atomic ensembles.

Fig.1: A hybrid superconducting circuit involving, a microwave ”bus” resonator (B), an ensemble of N-V centres (absorbers/emitters of microwave radiation) in a crystal of diamond, and a Josephson artificial atom of the ”transmon qubit” type (Q).



Now, thanks to progress in nanotechnologies, it has become possible to integrate, on the same chip (see Fig.1): (i) a superconducting microwave resonator and (ii) an ensemble of absorbing/emitting Nitrogen-Vacancy centres "NV" (a Nitrogen impurity next to a lattice vacancy in a crystal of diamond). The device also incorporates (iii) a superconducting circuit whose energy spectrum is analogous to that of an atom, a so-called "Josephson artificial atom". Such a hybrid circuit, bringing together multiple microscopic degrees of freedom (the NV centres) and a macroscopic degree of freedom (the artificial atom), constitutes a promising building block for, respectively, storage and processing of quantum information.

That is, the relatively large superconducting artificial atom can be very strongly coupled to the electromagnetic field, making it well adapted for fast processing operations like quantum gates. However, it suffers from large decoherence (its quantum states decay rapidly). On the contrary, each tiny NV centre is poorly coupled to radiation, but is characterized by an exceptionally long coherence time. Taking advantage of their collective coupling, an ensemble of NV centres provides naturally a large, high fidelity quantum memory.

We have investigated the potential of such an ensemble of NV centres for the storage of quantum information. Because of their irreducible random interactions with the solid-state matrix hosting it, the collection of absorbers/emitters is characterized by a large "inhomogeneous" broadening of its spectrum (each centre has a different emission/absorption frequency). This is a major difference with the atomic systems where all emitters have the same transition frequency. In the solid state system under study, the spectrum width is much broader than the resonator's linewidth, so that only a very small number of NV centres is directly resonant with the resonator mode.

We have revisited the theory of the strong coupling criteria in this novel regime. We have shown that, surprisingly, the radiation-matter coupling involves all the emitters, even those that are considerably "detuned" from the resonator.

Moreover, the typical damping time of the Rabi oscillations depends dramatically on the shape of the NV centres' spectral distribution: in particular, our analysis showed that, if the distribution is Gaussian, i.e. falls off rather steeply each side of its central frequency, the lifetime of the Rabi oscillations can be increased at will by increasing the coupling to the resonator mode. Despite a huge linewidth of the spectral emitters, strong coupling can be attainable. This "cavity protection" effect is a promising tool to eliminate the effects of inhomogeneous broadening in solid-state quantum memories.

This theoretical study was the prelude to a series of experimental demonstrations. Its predictions have been confirmed by our colleagues from the Quantronics group at CEA-Saclay. The strong coupling regime has been demonstrated between an ensemble of 10^{12} NV centres and the superconducting resonator of Fig.1, as well as the storage and retrieval of a single-quantum excitation in the NV centre ensemble. This confirms the potential of circuit Quantum Electrodynamics for quantum information technologies and for further fundamental investigations.

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FURTHER READING

STRONGLY COUPLING A CAVITY TO INHOMOGENEOUS ENSEMBLES OF EMITTERS
I. Diniz, S. Portolan, R. Ferreira,
J-M. Gérard, P. Bertet, and A. Auffèves
Phys. Rev. A 84, 063810 (2011)

HYBRID QUANTUM CIRCUIT WITH A SUPERCONDUCTING QUBIT COUPLED TO A SPIN ENSEMBLE
Y. Kubo et al.
Phys. Rev. Lett. 107, 220501 (2011)

The impossible antiferroquadrupolar order of CeB_6

For three decades, the cubic rare-earth compound Cerium Hexaboride CeB_6 has been presented as the archetype of a type of ordering called "antiferroquadrupolar" (AFQ). The change in the lattice periodicity implies a symmetry lower than cubic for an AFQ state. Very accurate magnetic and magnetostriction measurements have now been done on CeB_6 at the Institut NEEL. They show that, in the supposedly antiferroquadrupolar phase, the crystal remains perfectly cubic...

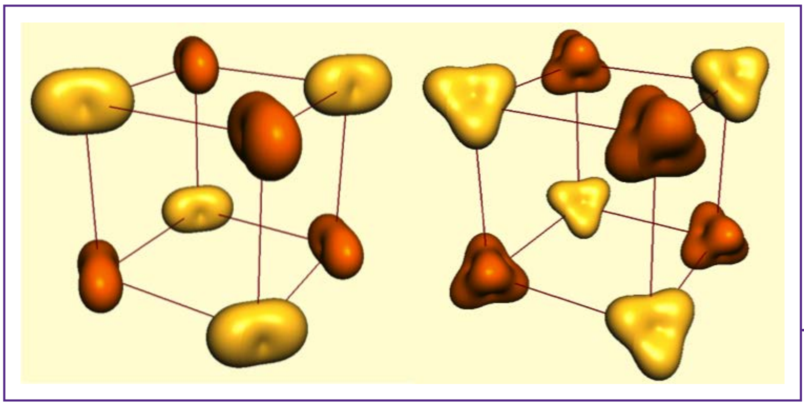

Fig.1: At left : example of an antiferroquadrupolar structure in CeB_6, as hitherto attributed to this compound, with [1/2 1/2 1/2] wave vector. The oblong shapes represent an aspherical angular distribution of the 4*f* electron of Ce^{3+}: the system is no longer cubic and the crystal must distort. At right : our proposed, octupolar structure with the same wave vector, that can be realised via a dynamical de-centering of the Ce^{3+} ions inside the boron cages. Perfectly cubic, this structure explains the absence of crystal distortions.

A quadrupolar order is of orbital nature : the atoms with unpaired electrons, in the 4f orbitals for the case of rare-earth atoms, collectively distort. This distortion of electronic charge clouds translates into the emergence of electric quadrupoles. In its antiferroquadrupolar variant, by analogy with antiferromagnetism, the distribution of the 4f electrons alternates from site to site.

In CeB_6, below a critical temperature "T_Q" = 3.3 K, macroscopic measurements (specific heat etc.) show that a new ordering develops. Neutron diffraction studies show that this order is not of magnetic nature. They also reveal an underlying difference between two kinds of Cerium sites that alternate on the cubic lattice according to the [1/2 1/2 1/2] wave vector. This has been interpreted as the consequence of an antiferroquadrupolar ordering. X-ray diffraction later confirmed that a charge distribution with *the* wave vector [1/2 1/2 1/2] develops below "T_Q".

Many subsequent experiments were systematically interpreted with a bias in favour of the antiferroquadrupolar scheme. However, there are obvious consequences of the antiferroquadrupolar hypothesis that have not been thoroughly investigated. Given the reported [1/2 1/2 1/2] wave vector, AFQ models for CeB_6 are necessarily of low symmetry (see Fig. 1, left side). Such a symmetry-lowering induced by quadrupoles is expected to result in large striction phenomena: in order to accommodate the new distribution of the 4*f* electron charge clouds, the crystal should anisotropically distort below "T_Q". Other properties of the system should reflect this anisotropy, in particular, the first-order magnetic susceptibility. Therefore, at the Institut NEEL, we undertook high accuracy measurements of the magnetic susceptibility and magnetostriction of CeB_6 below "T_Q", to check the symmetry properties of this supposed antiferroquadrupolar state.

As concerns the magnetic susceptibility, the result was surprising: Within the experimental accuracy, we found that the susceptibility is isotropic.

We then searched for distortions of the crystal using the Institut NEEL's high resolution magnetostriction apparatus, which can detect relative deformations as small as 10^{-7}. If there were a symmetry-lowering, the crystal would be expected to decompose into domains having different deformations. In which case, if the crystal is rotated in an applied magnetic field, its probed length should change abruptly as the field alternately selects different domains. No such effect could be detected. Studying as a function of temperature under magnetic field, we looked for tetragonal and trigonal distortion modes. Again, no specific effect could be observed while crossing the temperature T_Q.

This shows that the cubic symmetry of the crystal is preserved below the temperature "T_Q", which is strictly inconsistent with the antiferroquadrupolar interpretation. Furthermore, symmetry arguments show that, beyond quadrupoles, this cannot be accounted for by higher degree 4*f* electric multipoles.

In conclusion, alternative charge distributions have to be sought for, and one cannot ignore that rare-earth hexaborides realize a class of "cage-type" materials. Inside its cage of borons, a Cerium ion can dynamically move (vibrate) off-centre, thus realizing other kinds of charge distribution. At the right in Fig. 2, we propose an alternating octupolar distribution of the Cerium ion displacements that preserves the cubic symmetry of the crystal.

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FURTHER READING
CeB_6 macroscopically revisited
M. Amara and R.-M. Galéra
Phys. Rev. Lett. 108, 026402 (2012)

Decoding the fading of Prussian blue pigment

An understanding of degradation and alteration processes in painting materials is essential for preservation and for art history issues. The task is complex however because of the highly heterogeneous character of a paint layer, which consists of a mixture of pigments and a binder on a support. All the components interact and influence the ageing process of the paint layer. The work described here is focused on understanding the discoloration over time of a particular pigment, Prussian blue, a synthetic pigment discovered in 1704 in Berlin.

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FURTHER READING

SYNTHESIS AND FADING OF EIGHTEENTH-CENTURY PRUSSIAN BLUE PIGMENTS: A COMBINED STUDY BY SPECTROSCOPIC AND DIFFRACTIVE TECHNIQUES USING LABORATORY AND SYNCHROTRON RADIATION SOURCE
L. Samain, F. Grandjean, G. J. Long, P. Martinetto, P. Bordet, J. Sanyova and D. Strivay
J. Synchrotron Rad. 20, 460 (2013)

RELATIONSHIP BETWEEN THE SYNTHESIS OF PRUSSIAN BLUE PIGMENTS, THEIR COLOR, PHYSICAL PROPERTIES, AND THEIR BEHAVIOR IN PAINT LAYERS
L. Samain, F. Grandjean, G. J. Long, P. Martinetto, P. Bordet, and D. Strivay
J. Phys. Chem. C 117, 9693 (2013)

Because of both its very intense colour and its low cost, Prussian blue was widely used as a pigment in paintings until the 1970's. However, reports of discoloration already appear in eighteenth and nineteenth century books. The early preparation methods were rapidly recognized as a contributory factor in the colour changes of the pigment.

In collaboration with the Centre Européen d'Archéométrie de Liège, Belgium, we have conducted research to identify the reasons for these alterations in early paintings. Typical eighteenth century empirical recipes were reproduced at Liège (Ph. D. thesis L. Samain, University of Liège 2012). We studied the resulting pigments using a combination of spectroscopic and X-Ray diffraction techniques.

Prussian blue is known to be a hydrated iron(III) hexacyanoferrate(II) complex, with an ideal chemical formulae $Fe_4^{III}[Fe^{II}(CN)_6]_3.xH_2O$. It is now known that only two reagents are needed to produce Prussian blue by precipitation: an iron salt and an alkali hexacyanoferrate. However, the latter product was unknown in the eighteenth century and was indirectly obtained from the calcination of animal matter (dried ox blood) and an alkali. Even though the synthesis process is expected to be better controlled under modern laboratory conditions as compared to the situation in the eighteenth century, reproducing the old empirical recipes is problematic. Thus, the Prussian blue powders synthesized according to the early methods are variable in colour and composition. They are often poorly crystallised, even showing amorphous-like diffraction patterns, revealing the presence of nanostructured compounds (see Fig. 1(b)).

A set of complementary structural methods has been used to characterize these powders. Because traditional crystallography breaks down at the nanoscale, a Pair Distribution Function analysis, a method used to study glasses, liquids and amorphous materials, was performed on high energy X-ray powder diffraction data, collected at the European Synchrotron Radiation Facility, Grenoble (beam line ID11). This analysis allowed the identification of two undesirable and until now undetected nanocrystalline reaction products in the synthesized pigments: an alumina hydrate and the ferrihydrite $Fe_{10}O_{14}(OH)_2$. The ferrihydrite is orange in colour and, mixed with blue, explains the greenish tint taken by some samples.

Additionally in order to evaluate the light fastness of the synthesized pigments, the pure pigment powders were painted from arabic gum on watercolour paper and subjected to accelerated light exposure (Fig1(a)). The samples that exhibit the highest colour changes contain a large amount of the undesirable ferrihydrite impurity. They also are the least well crystallized, compare Figs 1(a) and (b) where the samples that discolour show strongly broadened X-Ray patterns. The paint layer turns green because upon prolonged exposure to light the Prussian blue phase tends to fade and the orange tint of the ferrihydrite then becomes more apparent.

In conclusion, the results presented herein help to better understand the numerous early reports of degradation of Prussian blue and directly relate the tendency of Prussian blue to turn green to the eighteenth-century preparative methods, which easily lead to the formation of a variable but substantial amount of an undesirable iron(III) oxide. This study also demonstrates the power of combined diffraction and spectroscopic techniques to answer the highly complex questions arising due to the intrinsically heterogeneous nature of real life materials.

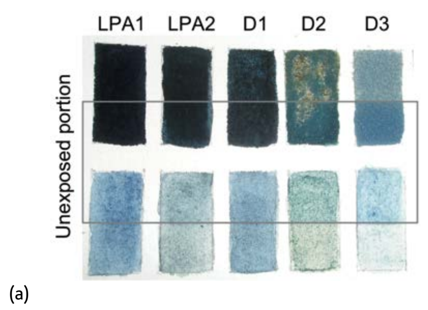

Fig. 1(a): Fading test on layers of the eighteenth-century Prussian blues, painted on watercolour paper : dark (top) and light shades (bottom). The rectangle delineates the location of the aluminium cover during the accelerated light exposure.

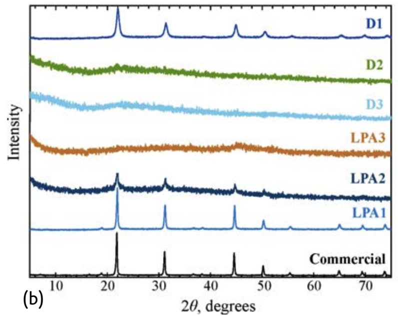

Fig. 1(b): X-ray powder diffraction pattern of some of the pigments shown in (a) with a modern commercial Prussian blue pigment given as reference (laboratory diffractometer, λ_{K_α} Fe).

Electronic read-out of a single nuclear spin

Spin is one of the intrinsic quantum properties of particles. The spin of the electrons orbiting an atom has many significant consequences, in particular it determines the magnetic properties of materials. At the present time, electronic spins have been favoured candidates as carrier of quantum information in studies of potential devices for quantum computing. However, electronic spin states are subject to strong environmental influences, resulting in very short relaxation and coherence times. In alternative concepts, atomic nuclei, which can also have spin, have been proposed as the building blocks for quantum computing, since nuclear spin states are much less strongly coupled to the environment. However, weak coupling comes at a price: it remains challenging to address and manipulate individual nuclear spins.

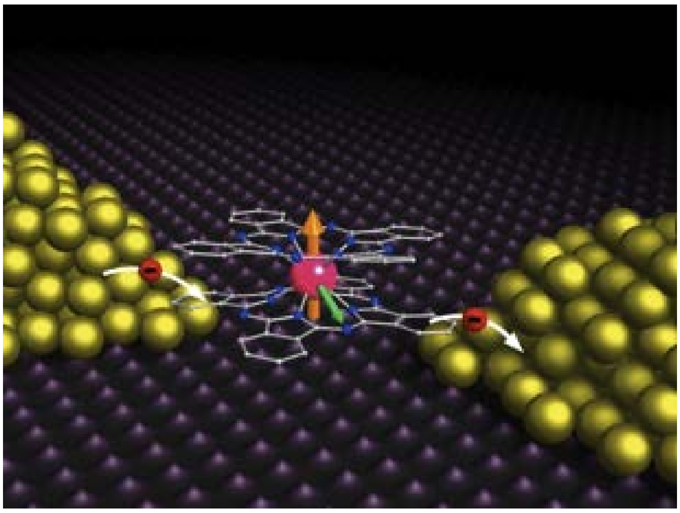

Fig. 1 : Artist's impression of a spin transistor based on a Single Molecule Magnet. The Terbium ion (red) is sandwiched between two organic molecules (grey and blue) to form the Single Molecule Magnet. The orange and green arrows represent the orientation of the electronic spin and nuclear spin carried by the Tb^{3+} ion. Yellow spheres are gold atoms: the molecular magnet is situated in a break in a gold nanowire above a gate electrode (dark background). By monitoring the current (white arrows) flowing from source to drain through the organic molecule, the four possible nuclear spin states of the Tb^{3+} ion can be detected electrically.

The magnetic moment of a nucleus is several orders of magnitude smaller than that of an electron, hence the relative difficulty of reading out the spin state of a single nucleus. To meet this challenge, there have been various proposals to measure instead the state of an electronic spin that is correlated to the nuclear spin state, in order to obtain an indirect and non-destructive measurement of the nuclear spin's state. Towards this goal, at the Institut NEEL, in collaboration with chemists of the Karlsruhe Institute of Technology, Germany, we have demonstrated the ability to perform electrical detection of the state of a single nuclear spin using a spin transistor based on a "Single-Molecule Magnet".

The advantage of molecular materials is that they can be chemically "tailored" for the active operations that process the spin quantum state, yet integrated with existing electronics technologies. Our technique involves the use of a bi-molecule of $TbPc_2$ (Terbium Pthalocyanine). As depicted in Fig. 1, The electronic spin (red in the Figure) and the nuclear spin (green) are carried by a Terbium 3+ ion sandwiched between the two complex organic molecules (the pthalocyanines). We integrate this Single-Molecule Magnet in a three-terminal transistor geometry (source, gate and drain), using an electromigration technique.

By sweeping an external magnetic field, we can find four field values where the electronic spin can switch from a "spin-up" to a "spin-down" configuration, without changing the nuclear spin state. This occurs via a process called Quantum Tunneling of Magnetization QTM (at the "anticrossing" points in the graphs of spin-state energy levels versus field). These four field values can be identified with the four possible spin states of the Terbium I = 3/2 nucleus.

While sweeping the magnetic field, we use the transistor device to monitor the flow of electrons through the two pthalocyanines in the vicinity of the Terbium. Because there is a ferromagnetic coupling between these flowing electrons and the Terbium ion, the current is sensitive to the Tb^{3+} electronic spin state. In this way, we have been able to detect the Quantum Tunneling of Magnetization for a single electronic spin, and thus perform a non-destructive electronic read-out of the state of a single nuclear spin.

These experiments have demonstrated the possibility of addressing and detecting the spin state of a single nucleus using Quantum Tunneling of Magnetization in a Single-Molecule Magnet. In combination with the long lifetimes (tens of seconds) that we measure for the nuclear spin states, this provides a pathway towards nanospintronics devices with integrated memory, logic and possibly quantum logic functions.

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FURTHER READING

ELECTRONIC READ-OUT OF A SINGLE NUCLEAR SPIN USING A MOLECULAR SPIN-TRANSISTOR
R. Vincent, S. Klyatskaya, M. Ruben,
W. Wernsdorfer & F. Balestro
Nature, 488, 357 (2012)

Coupling magnetism and mechanics on a molecular level

The magnetism of an atom or a nanometre-scale object such as a "Single-Molecule Magnet" (SMM) is governed by the laws of quantum mechanics. Various quantum effects ranging from tunnelling processes to coherent phenomena have been observed in single molecule magnets. But probing the quantum nature of these magnets remains a challenging task and requires the use of an appropriate magnetometer, preferably one with molecular dimensions itself. Encouraged by recent progress in using the quantized mechanical vibrations of carbon nanotubes to probe magnetism, we have developed a magnetometer design based on a carbon nanotube nanoelectromechanical system (a "NEMS"). Our magnetometer can measure extremely small magnetic moments.

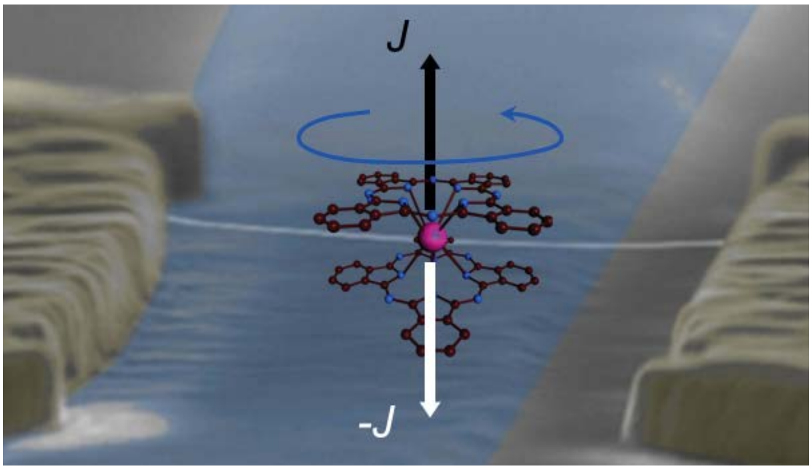

Fig. 1 :
A carbon nanotube nano-electromechanical system (NEMS) functionalized with a Single Molecule Magnet (SMM).

A Terbium Pthalocyanine molecule is grafted onto the carbon nanotube (white wire) stretched across a gap between platinum electrodes.

Due to angular momentum conservation, the magnetization reversal from *J* (black arrow) to -*J* (white arrow) in a magnetic field results in a rotation of the SMM (blue arrow). This rotation generates a quantized longitudinal phonon mode in the carbon nanotube.

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FURTHER READING

MOLECULAR SPINTRONICS USING SINGLE-MOLECULE MAGNETS
L. Bogani, W. Wernsdorfer
Nature Mat. 7, 179 (2008)

STRONG SPIN-PHONON COUPLING BETWEEN A SINGLE-MOLECULE MAGNET AND A CARBON NANOTUBE NANOELECTROMECHANICAL SYSTEM
M. Ganzhorn, S. Klyatskaya, M. Ruben, and W. Wernsdorfer
Nature Nanotech. 8, 165 (2013)

In order to achieve sensitivity at the molecular scale, the vibration of the carbon nanotube should exhibit large quality factors (*Q*) and be strongly coupled to the molecular magnet. We have indeed demonstrated strong coupling of the quantized mechanical motion of a carbon nanotube to the magnetization of a Single Molecular Magnet. This is the Terbium Pthalocyanine SMM whose properties have been introduced in the preceding article in this issue of Highlights.

The terbium molecule constitutes a rare-earth SMM where the magnetic moment is carried by a single Tb^{3+} ion. Due to the highly anisotropic 4f electron shell and the strong spin-orbit coupling of Tb^{3+}, the ground state is a well isolated magnetic ground state, a doublet $J=6$ with $J_z = \pm J = \pm 6$. This defines the magnetic behaviour of the molecule. Also, the Terbium nucleus has a spin, $I=3/2$ and each state of the ground doublet splits into four nuclear spin states by hyperfine interaction.

If the magnetization of the SMM reverses from *J* (black arrow in Fig. 1) to –*J* (white arrow), a mechanical rotation of the molecule occurs simultaneously, in order to conserve total angular momentum. This phenomenon is a quantum mechanical analogue of the classical Einstein-de Haas effect. In our experiment, we graft the molecule rigidly to a carbon nanotube (the grey wire in Fig. 1). The molecular rotation induces a strain in the nanowire and excites a quantized longitudinal phonon stretching mode in the nanotube.

It is the state of this stretching mode that we detect, using an electronic readout technique which exploits the sensitivity of a single-electron current through the nanowire to the wire's state of vibration at very low cryogenic temperatures. We perform a sensitive, indirect, non-destructive probe of the molecule's nuclear magnetic state as follows.

As we sweep an external magnetic field, the electronic spin *J* reverses via quantum tunneling at one of the four field values that identify the four possible spin states of the Terbium $I = 3/2$ nucleus. The electronic spin reversal *does not change* the nuclear spin state (see also the preceding article, page 15).

In these experiments, the electronic spin reversals are detected via the coupling to the additional mechanical degree of freedom. We find a strong coupling of the order of 1 MHz between the nanotube's mechanical degree of freedom and the molecule's electronic spin.

From an application point of view, a magneto-mechanical coupling of this magnitude should enable us to detect the magnetic state of many other SMMs. From a more fundamental point of view on the other hand, the strong coupling opens the path to coherent spin manipulation and to quantum "entanglement" between one or several electronic spins and a quantized mechanical motion.

Symmetry analysis: exploring structural subtleties of complex materials

Understanding the relationships between crystal structure and physical properties is one of the biggest challenges in functional materials, especially in view of engineering new compounds. This is very much so in the case of the "multiferroics", materials that exhibit more than one type of "ferroic" (or anti-ferroic) order *e.g.* ferromagnetism, ferroelectricity, etc. In such materials, the possibility of controlling an electric polarization by applying a magnetic field or, inversely, of controlling magnetization with an electric field could have considerable applications, for example in data storage devices. Since symmetry puts strong constraints on the existence and nature of the various ferroic orders, the use of the technique called "symmetry analysis" is a must for understanding the properties of these complex materials.

Very often, a crystal structure can be considered pseudo-symmetric with respect to some configuration of higher symmetry, denoted as its parent structure. The observed structure can then be described as the parent crystal structure plus a static, symmetry-breaking structural distortion. The distortion relating the two structures may be quite complex but can be decomposed into contributions from different modes, with symmetries given by the irreducible representations of the parent space group. Modes are collective, correlated, atomic displacements fulfilling specific symmetry properties. Depending on the amplitudes of the modes, by describing a structure in terms of symmetry modes one can discriminate between the modes which are fundamental for the stability of the low symmetry phase and those which are marginal. Such a description introduces a physical hierarchy among the structural parameters; this is the purpose of the so-called "symmetry-mode analysis" method.

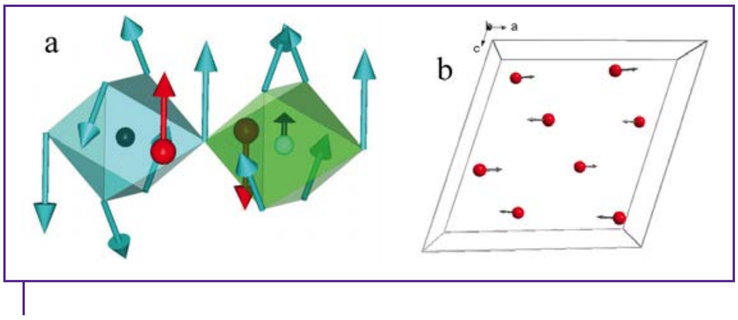

Figure 2 : (a) The distortion mode responsible for the antiferroelectricity of $BiCrO_3$: blue arrows are directions of displacements of the O^{2-} ions , red arrows are displacement directions for Bi^{3+} ions.

(b) The antiferroelectric arrangement of the eight Bismuth ions, within the unit cell (cf. Fig.1), as deduced by symmetry analysis. Arrows represent local electric dipoles resulting from the relative displacement of each Bi^{3+} ion (red spheres) within its cage of twelve O^{2-} ions (not shown).

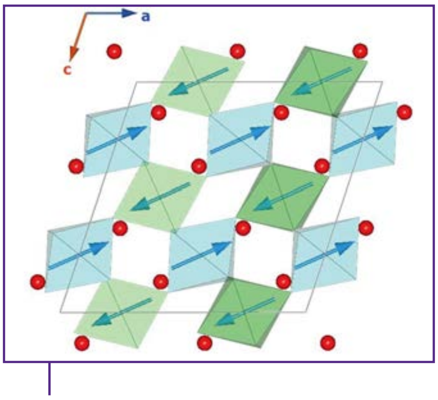

Fig.1: The highly distorted crystal structure of Bismuth Chromate $BiCrO_3$. The orientations of the Cr^{3+} spins (arrows), responsible for the compound's antiferromagnetism, are shown within their coordination octahedra (green and blue figures; the O^{2-} anions, not shown, occupy the 6 vertices). Red spheres are Bi^{3+} ions.

We have successfully applied this method of analysis to Bismuth Chromate $BiCrO_3$. The compound was synthesized under high pressure and temperature at the Institut NEEL and studied by X-Ray Diffraction (for the crystal structure) and by neutron diffraction (for the magnetic structure). The structure of $BiCrO_3$, see Fig 1, is a distorted form of the classic, cubic, "perovskite" structure. It combines the "lone-pair" ion Bi^{3+}, which favours a non-centrosymmetric structural distortion and thus can induce electric polarization, and a transition-metal ion with a partially filled 3d-electron shell, Cr^{3+}, which can generate magnetism.

Indeed $BiCrO_3$ is clearly antiferromagnetic, below a Néel temperature T_N=109 K. However, its ferroelectric properties are very controversial. Whereas dielectric measurements seem to indicate the existence of a ferroelectric polarization, the compound is found to crystallize in a centro-symmetric space group, incompatible with ferroelectricity.

Symmetry-mode analysis allowed us to decompose the highly distorted crystal structure of $BiCrO_3$ in terms of six distortion modes with respect to the ideal cubic perovskite structure. The six distinct distortion components have different importance for the material's properties. One of the two major modes is very specific to Bi-based perovskites: it involves displacements of Bi, Cr, and a complex distortion of the oxygen octahedra (Fig.2a). The respective displacement of the Bi^{3+} cation within its cage of twelve O^{2-} anions is about 0.4 Å, giving rise to a local electric dipole. But, the analysis shows that in the unit cell, the eight local electric dipoles are oriented in opposite directions (Fig. 2b). Thus, the total dipole moment is zero within the cell, as follows from the inversion centre in the space group. This mode is therefore responsible for the very complex and specific antiferroelectric arrangement in $BiCrO_3$.

In conclusion, the symmetry-mode analysis is a very powerful method that allows one to hierarchize the distortion modes and to identify those modes which stabilize the various distorted structures of a crystal. Symmetry analysis can be applied either a posteriori to analyse a given distorted structure, or a priori to parametrize a structure to be determined. This method gives very useful physical insight into the structure and can be applied to many different material systems.

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FURTHER READING

Symmetry Adapted Analysis of the Magnetic and Structural Phase Diagram of $Bi_{1-x}Y_xCrO_3$
C.V. Colin, A.G. Pérez, P. Bordet, C. Goujon, and C. Darie
Physical Review B, 224103 (2012)

When holes lose their statistics

The search for exotic quantum spin liquids is one of the challenges of modern condensed matter physics. The term quantum spin "liquid" refers to a state of interacting spins on a lattice that remains a disordered state even at low temperature. Philip Anderson proposed that the parent (insulating) state of the cuprate High-Temperature Superconductors, is in fact of this type, a special liquid made of spin singlet pairs of electrons. In his theory, once the pairs are broken, the liquid exhibits a separation of the spin and the charge degrees of freedom (and superconductivity). Each original electron fractionalizes into two emergent particles, a holon carrying the charge quantum and a spinon carrying the spin quantum. Although the original electron is a fermion, the question of the actual statistics of holons and spinons in such a "deconfinement" scenario remains an open issue.

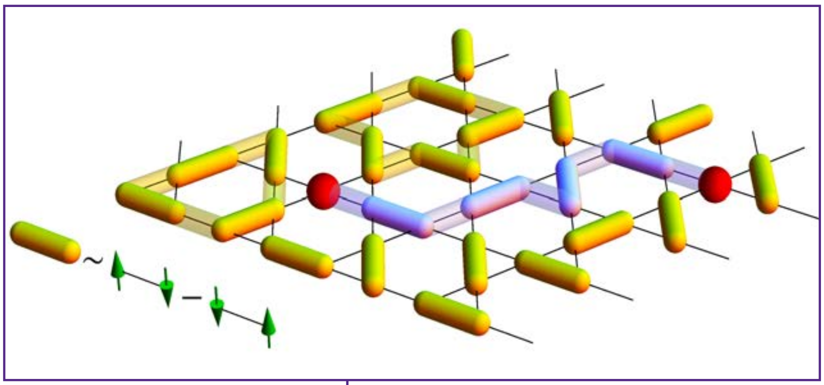

Figure 1: Schematic snapshot of a doped dimer configuration with no particular order on the kagome lattice. Each lattice site is either involved with a neighbouring site in a spin singlet dimer of electrons (the coloured rods), or else occupied by a hole (red spheres). Quantum fluctuations on dimers are represented by resonating loops (yellow transparent and opaque dimers). Holes move along a given path (blue) by switching of the electron dimers from site to site, thus changing the background of dimers.

Anderson's proposal dates from 1987. He suggested that the strange behaviour of cuprate (copper oxide) materials, at the transition between the superconducting and the magnetically ordered insulating phases, could be described by a so called resonating valence bond (RVB) state. In the RVB state, pre-existing spin singlet pairs of electrons become charged superconducting pairs when the insulator is doped with holes by removing electrons.

Just one year later appeared the first effective model to describe magnetically disordered phases in which the magnetic degrees of freedom are disregarded in favour of the more pertinent singlet degrees of freedom whose quantum dynamics are quantum resonating loops of singlet pairs of nearest neighbour electrons dubbed "dimers" (see Fig.1).This is in fact a model of the "Quantum Dimer" type. The description of a magnetic system by a quantum dimer model was performed successfully in Heisenberg antiferromagnets on "frustrated" lattices, such as the kagome lattice (a triangular lattice of triangles), as presented in Fig.1. The existence of Resonating Valence Bond spin singlet liquid phases appears to be confirmed in such quantum dimer models, as well as in certain antiferromagnets. Hence the issue of superconductivity in doped spin liquids becomes a more pressing question.

Doping of (i.e. removing electrons from) a RVB spin liquid is expected to induce a novel type of elementary excitation called a "holon", that behaves as a quasi-particle carrying electric charge e but no spin. Superconductivity may be realized if the holons "proliferate" (condense), but the nature of the superconducting phase is an open question.

At least naively, one could imagine that the resulting superconductor would be "exotic" with a condensation of charge-e holons, instead of the usual charge-2e Cooper pairs. A fundamental issue in this problem is the statistics of these holons; to condense without forming pairs, they must be bosons, otherwise the Pauli exclusion principle for fermions would prevent such a scenario. Interestingly, a "transmutation" of the statistics is possible in such systems: the statistics of holons as elementary excitations appearing in the low-energy limit can be different from the statistics assigned to holes in the original spin 1/2 microscopic model.

We summarise here the results of recent theoretical work on this problem carried out with collaborators at Toulouse, the University of La Plata (Argentina) and the University of Tokyo. We obtained evidence for the existence of a dynamical statistical transmutation in doped quantum dimer models. The dimer quantum dynamics experienced by the holons can transmute their original statistics, e.g. from fermions to bosons. More particularly, we have established a rigorous and general proof establishing that boson holes in a given dimer background are equivalent to fermion holes with other dimer fluctuations. This means that while dealing with fermion holons in the original spin model, holes can be transmuted from fermions to bosons dynamically, thanks to the quantum fluctuations of the singlet background.

This result opens amazing possibilities as for example the detection, via a gauge invariant holon Green's function (involving a string of dimers as illustrated in Fig. 1) similar to that of Quantum Electrodynamics, of rather strong and direct evidence for the existence of an exotic superfluid phase due to condensation of holons carrying a single charge e (a "charge-e superfluid phase"). This is a spectacular example obtained from our theory at intermediate values of the doping, where the system seems to switch from a standard Fermi liquid to a (bosonic) charge-e superfluid phase.

The above kinds of dynamical statistical transmutations have different physical signatures and can be controlled in principle via the microscopic parameters (spin coupling, electron hopping and interactions...). Our results provide motivation for investigating, in a new light, different microscopic models which may give rise to the doped Quantum Dimer Model as an effective model which captures the low energy physics of the original spin systems.

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FURTHER READING

STATISTICAL TRANSMUTATION IN DOPED QUANTUM DIMER MODELS
C. A. Lamas, A. Ralko, D. C. Cabra, D. Poilblanc & P. Pujol,
Phys. Rev. Lett. 109, 016403 (2012)

HOLE STATISTICS AND SUPERFLUID PHASES IN QUANTUM DIMER MODELS
C. A. Lamas, A. Ralko, M. Oshikawa, D. Poilblanc & P. Pujol
Phys. Rev. B 87, 104512 (2013)

New apparatus for materials studies on the French D2AM beamline

Institut NEEL has close associations with the European Synchrotron Radiation Facility (ESRF), situated on a neighbouring site in Grenoble. The Institute, in collaboration with the CEA's Institute of Nanosciences and Cryogenics, is involved in the operation of three X-Ray beamlines. This article describes our contributions made in the framework of the D2AM, a French Collaborating Research Group (CRG) financed by the CNRS and the CEA.

The D2AM group ("Diffraction et Diffusion Anomale Multilongueurs d'onde") is hosted on the BM02 beamline, which was one of the first lines to operate at startup of the ESRF in 1994. It is open to the French and European communities through national and international peer-review committees.

The D2AM's beamline delivers intense beams of X-rays with energies from 6 to 40 keV. It is dedicated to studies of the microscopic structure of materials using two principle techniques: (i) wide angle X-ray scattering, which provides information on long-range ordering at the atomic scale and (ii) small angle X-ray scattering, which provides information on the morphology of objects at the mesoscopic scale (typically 3 nm to 0.3 micron). Both of these methods can be coupled with "anomalous" X-Ray scattering, which yields additional chemical information by providing contrast between different kinds of atoms.

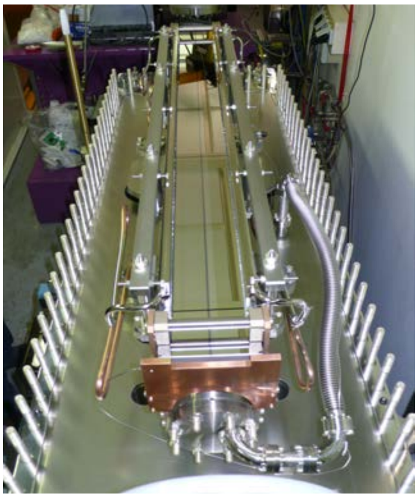
Figure 1 : The first mirror (1 metre long) in its bender and cooling system along the X-ray beam path, before closing its vacuum vessel.

It is also the beamline where the powerful technique of Diffraction Anomalous Fine Structure spectroscopy (DAFS), which measures the diffraction as a function of the X-Ray energy, has been developed. A major recent improvement is the possibility of performing multiple-wavelength Anomalous Diffraction and DAFS Spectroscopy in grazing incidence geometry, for focusing on the structural properties of thin films and nano-objects. The grazing incidence greatly reduces the contribution of scattering from the substrate.

The D2AM beamline has been used in very wide ranging fields of Materials Science: characterisation of short-range and long-range order in samples ranging from gels and amorphous materials to quasi-crystals, bulk and/or surface characterizations, nanomaterials, microelectronics, catalysts and soft condensed matter. It is the most advanced French beamline in the field of anomalous scattering, and has the most extensive users' community. It is also well recognized for its very versatile SAXS (Small Angle X-ray Scattering) experiment where a user can easily adapt various sample environments for "in situ" studies (of a sample undergoing an experiment) or "in operando" studies (on a real working device during its operation). A GISAXS (Grazing Incidence Small Angle X-ray Scattering) chamber can also be adapted on the SAXS bench.


Figure 2 : Experimental hutch with the kappa geometry goniometer on the right and, behind at the left, the SAXS instrument on its marble bench.

In 2012, the whole beamline was refurbished with new instruments and state of the art X-ray optics:

A "kappa geometry" diffractometer is now available. It allows easy switching from surface to volume diffraction and offers a much larger free space to install varied sample environments. Users can now do GISAXS experiments with the sample aligned on the goniometer and with an in-vacuum distance to the detector between 50 cm and 5.5 m. The SAXS bench is now 4 meters long to access smaller scattering angles, and thus larger objects.

The new X-Ray optic includes a 2 crystal monochromator, with a relative energy selection of 10^{-4}, placed between two cylindrically curved Pt/Ru-coated mirrors that focus the X-Ray beam to a 100x200 microns^2 spot on the sample. The new monochromator, designed for spectroscopy by Alain Prat of the Institut NEEL, yields very precise and repeatable positioning in energy. The new polished silicon mirrors have error slopes smaller than 0.3 microradians (a gain of a factor of 16 over previous mirrors), at all radii of curvature.

This large project was financed by the Nanosciences Foundation, the French National Research Agency, the CRG/F "EQUIPEX" project, the CNRS and the CEA. Users can apply for beamtime through the CRG committees via the SUNSET usergroup at http://sunset.synchrotron-soleil.fr/sun/.

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Terahertz magneto-electric excitations in a chiral material

The term "multiferroics" designates a remarkable class of solid materials where both ferromagnetism (i.e. an alignment of magnetic dipoles) and ferroelectricity (an alignment of electric dipoles) can coexist. Multiferroics are receiving much attention as a promising way to achieve electric-field control of magnetic dipoles and, conversely, magnetic-field control of electric dipoles, this for application in a number of future hybrid technologies, for instance novel electronics based on both spins and charges. These electric/magnetic cross-manipulation effects can have signatures in the THz frequency range, in the form of resonances (phonons and magnons) that are characteristic of the multiferroic order in the material.

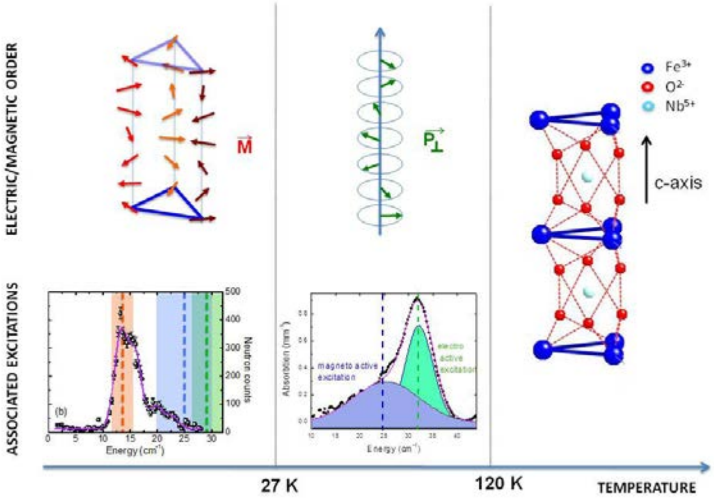

Fig. 1: At right: a simplified drawing of the chiral, tubular lattice structure of the langasite compound $Ba_3NbFe_3Si_2O_{14}$, characterized by its triangles of Fe^{3+} ions along the vertical c-axis.
At centre: below 120 K, a helical electric polarization exists (green arrows) which supports dual magneto-electric excitations. They can be induced by either the magnetic or the electric field components of incident electromagnetic radiation, with maximum efficiency at 25 cm^{-1} (blue fitted peak) and 32 cm^{-1} (green peak) respectively, as probed by polarized THz spectroscopy.
At left: Below 27 K, additionally, a helical ordering of the Fe^{3+} spins (horizontal arrows) exists along the c-axis. In this "multiferroic" phase, we also observe magnon excitations (spin waves) as shown by the peak at 13 cm^{-1} in the inelastic neutron scattering measurements.

Phonons and magnons are quantized states of two kinds of wave propagation in a solid. They correspond to coherent deviations of the atoms' positions or spins away from their equilibrium in an atomically or magnetically ordered phase. Normally, phonons and magnons couple to the electric and magnetic components of the electromagnetic field respectively. In 2006, a novel type of excitation was discovered, called the "electro-magnon", which is a magnetic excitation that can couple to the oscillatory electric field. Now, by combining several sophisticated techniques we have obtained evidence for a new kind of magneto-electric excitation, a phonon that is magnetically active.

We used terahertz spectroscopy on the synchrotron source SOLEIL (Paris), and inelastic neutron scattering at the Institut Laue Langevin, Grenoble, working in the energy range where magnons and low energy phonons might be present. Radiation of frequency 1 THz has a wavelength of 0.3 mm (energy of 5 meV). The highly sensitive polarized THz spectroscopy allows us to identify the way the observed excitations are activated by the oscillating electric and/or magnetic field of the incoming radiation. The neutron scattering measurements clearly identify magnetic excitations, which interact with the neutron's magnetic moment.

We applied these two tools to study the energy spectrum of an iron langasite ($Ba_3NbFe_3Si_2O_{14}$), a complex magnetic material first synthesized at Institut NEEL and studied for its remarkable magnetic and structural properties. It has static magneto-electric properties. Moreover, it is totally "chiral" : both its atomic structure and its magnetic order cannot be superimposed on their images in a mirror. Thus this material is a good candidate for multi-ferroic behaviour. In this langasite, we see clearly the expected ordinary magnons in the antiferromagnetic phase below the Néel temperature of 27 K (see at left in Fig.1). At somewhat higher temperature we identified a dual non-magnetic mode, a phonon mode, at frequencies around 0.8 THz (= 28 cm-1). This mode is excited by the electric field component of the electromagnetic radiation and also, more surprisingly, by its magnetic field component (see in centre of Fig. 1).

These findings demonstrate that not only magnons but also phonons, i.e. atomic vibrations, can acquire a combined magneto-electric character. From symmetry arguments, we interpret our results as rotational atomic vibrations that can be excited by an oscillating magnetic field (via the Lorentz force) if a spontaneous helical electric polarisation is present. We deduce that a complex ferroelectric phase exists below a temperature (120 K) four times higher than the temperature (27 K) where the magnetic order sets in, and that below the Néel temperature the compound is multiferroic. The microscopic polarization is formed by a helical arrangement of electric dipoles (see Fig.1 at centre) which, due to the chirality of the compound, has a definite sense of rotation.

Finally, our findings widen the type of magneto-electric excitations that could be used in "magnonics", a new information science that would use magnetic excitations to carry and process information.

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FURTHER READING

THZ MAGNETOELECTRIC ATOMIC ROTATIONS IN THE CHIRAL COMPOUND $Ba_3NbFe_3Si_2O_{14}$
L. Chaix, S. de Brion, F. Lévy-Bertrand, V. Simonet, R. Ballou, B. Canals, P. Lejay
Phys. Rev. Lett, 110, 157208 (2013)

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Highlights 2013

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